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INTRODUCTION

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The CPL Frontiers project, initiated in 2008, and has now resulted in the publication of over 200 invited articles, describing important advances made by top scientists at the frontiers of chemistry and physics. Here, we present a selection of the Frontiers articles that have appeared since our 2013 review: Five years of Frontiers. These articles are chosen to represent the quality of our authors and the breadth of our coverage, encompassing nanoscience, biochemistry, quantum chemistry, atomic and electron physics, surface science, and physical organic chemistry.

The format for Frontiers articles is a flexible one. Some are short reviews of important developments, while others present brand-new results in forefront areas. We stress clarity and cogency of presentation, as our goal is to provide useful updates for both experts in a particular field as well as introduction and guidance for a more general audience. I hope that you enjoy these ten selected articles, and that you will become a regular reader of our exciting Frontiers series.

Rich Saykally
Frontiers Editor

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DIRECT DETECTION OF RYDBERG–RYDBERG MILLIMETER-WAVE TRANSITIONS IN A BUFFER GAS COOLED MOLECULAR BEAM

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ABSTRACT

Millimeter-wave transitions between molecular Rydberg states (n = 35) of barium monoxymethylide are directly detected via Free Induction Decay (FID). Two powerful technologies were used in combination: Chirped-Pulse millimeter-Wave (CPmW) spectroscopy and a buffer gas cooled molecular beam photodissociation source. Hundreds of Rydberg–Rydberg transitions are recorded in 15 with >10:1 signal/noise ratio and ~150 kHz resolution. This high resolution, high spectral velocity experiment promises new strategies for rapid measurements of structural and dynamical information, such as the electric structure (multipole moments and polarizabilities) of the molecular ion-core and the strengths and mechanisms of resonances between Rydberg electron and ion-core motion. Direct measurements of Rydberg–Rydberg transitions with kilo-Delbye dipole moments support efficient and definitive spectral analysis techniques, such as the Stark demolition and polarization diagnostics, which enable semi-automatic assignments of core-populating Rydberg states. In addition, extremely strong radiation-mediated collective effects (superradiance) in a dense Rydberg gas of barium atoms are observed.

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1. Introduction

Electronic transitions between Rydberg states of atoms and molecules can provide a description of the electric multipoles and polarizabilities of the ion-core as well as insights into the physical mechanisms and state-to-state rates of energy/angular momentum exchange between the Rydberg electron and the molecular ion-core [1–6]. microwave and millimeter-wave spectroscopies capture Rydberg–Rydberg transitions with high resolution, sensitivity, and completeness [7–12]. Our claim of completeness is based on the combination of a priori known n-scaling and purposeful access to key information-rich regions of state space. These results will provide new classes of tests of electronic structure calculations for molecular ions and for the dynamics of electron-ion collisions [6,13,15].

To study the structure and dynamics of the molecular Rydberg states with both high resolution and a fast data acquisition rate, we incorporate two crucial features: (i) CPmW spectroscopy is a broad bandwidth high-resolution technique capable of capturing in each chirped pulse 20 GHz of spectrum at 50 kHz resolution. Every two-level system, which has its transition frequency within the bandwidth of the chirped pulse is polarized, and all resultant FIDs are simultaneously detected in the time domain. All members of the set of FIDs generated by a sequence of chirped pulses are phase-coherently averaged in the time-domain. This multiplexed simultaneous direct detection of all FIDs is in marked contrast with the sequential indirect detection of ions generated as a laser frequency is tuned through resonance with individual Rydberg–Rydberg electronic transitions. (ii) The BaF molecular ions generated from our buffer gas cooled ablation source is a factor of 1000 brighter and has 10 times slower laboratory frame velocity than a BaF beam generated by our Sainsbury-type supersonic jet ablation source. Exploitation of the broad bandwidth, multiplexed, FID-detection scheme would have been impractical without the enhanced brightness of the buffer gas cooled ablation source.

The combination of these two transformative technologies, CPmW spectroscopy and the buffer gas cooled ablation source, has the potential for startling expectations about the limits of what is ‘knowable’ about the structure and dynamics of small molecules. In this letter we report FID-detected laser-laser CPmW triple resonance experiments on Rydberg–Rydberg

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http://dx.doi.org/10.1016/j.cplett.2015.10.016
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transitions of Ba atoms and BaF molecules. In these experiments we have achieved an ∼10⁵-fold increase in spectral velocity relative to what we had been able to achieve in ionization-detected laser-laser double resonance experiments on CaF. We define spectral velocity as the number of resolved elements sampled per unit time at a specified signal to background ratio. The experiments described in this letter demonstrate possibilities for a more global, mechanismically focused class of interaction between experimentists and their spectroscopic targets. New experimental tactics and goals, achieved around mechanical manipulation rather than production of archival tables, will be expressed in the design of new classes of experiments to capture the 'big picture' rapidly and decisively. With n-scaling of everything related to the Rydberg electron, which provides an overview of quantum mechanical state-space, we can actively search and sample the dynamically most consequential classical physics-based mechanisms for energy and angular momentum transfer between the Rydberg electron and the ion-core. The design of new classes of experiments can capture the 'big picture' rapidly and decisively, and reveal how a molecule behaves in both universal (physical) and idiosyncratic ('chemistry') ways.

We report no new spectroscopic results in this letter. Our reasons for postponing the use of our spectrometer to data include implementation of plans for improving the sensitivity, reproducibility, and most importantly, the assignment velocity of spectral features. One of the most vexing problems results from the combination of the ∼100 MHz Doppler width of the laser transitions and the −500 MHz longitudinal mode spacing of the Nd:YAG pumped dye laser. In addition, we are developing an improved suite of diagnostics that are needed for real-time, semi-automatic assignments of exceptionally data-rich spectra. These diagnostics include: (i) ‘Dark demodulation’ for distinguishing core-penetrating (CP) from core-nonpenetrating (CNP) Rydberg states (states with high angular momentum and quantum defect δ < 0.05) and sorting the CNP Rydberg states according to orbital angular momentum of the Rydberg electron, l, and the rotational angular momentum of the ion-core, N, (ii) polarization diagnostics to determine total angular momentum of molecules, j, (iii) use of the phase of the field relative to that of the chirped excitation pulse to determine whether a transition in the Cpmw spectrum is upward or downward in energy, and (iv) ‘stacked plot’ pattern recognition, to determine the ion-core jK→jK' state, from a collection of Cpmw spectra, each Cpmw spectrum recorded as the second tunable laser is tuned, in 100 kHz steps through a region of the Rydberg manifold of width ∆l = 6−14 cm⁻¹ at n = 40.

Our focus in this letter is on barium monochloride (BaF), because it provides several uniquely convenient properties for molecular PES experiments. The 4.3±14.3 Rydberg states of BaF have previously been extensively investigated and assigned [21,16–18], which allows us to simplify the explanation of excitation schemes and to accelerate the assignments of the higher-lying BaF Rydberg states. The electronic structure of BaF is maximally simple, consisting of a doubly closed shell (Ba²⁺ and F⁻) ion-core plus only one electron (the Rydberg electron). Perhaps most importantly, BaF is one of the smallest number of diatomic species in which the first dissociation limit lies higher in energy than the ionization energy for states with n = 3 or 4 (where n is the vibrational quantum number of the ion-core). As a result, nonradiative decay via predissociation cannot occur from these states, and the n = 0 → Rydberg states have lifetimes >100 μs, comparable to those of atomic Rydberg states. The long lifetimes ensure that the field radiation from millimeter-wave-pumped Rydberg Rydberg coherences is not quenched by fast population decay. In addition, the Rydberg state lifetimes are sufficiently long to enable population of high angular momenta states via a sequence of stepwise molecular-millimeter wave excitations. We can selectively interrogate regions of Rydberg state space in which physically distinct interaction mechanisms are at play. BaF is thus an ideal candidate for systematic investigations of molecular Rydberg states by FID-detected electronic spectroscopy. This investigation will permit separate characterization of physically explicit classes of mechanisms for the exchange of energy and angular momentum between the Rydberg electron and the ion-core.

This letter is organized as follows: in section 2, we describe the apparatus in which the Cpmw spectrometer and buffer gas-cooled molecular beam source are combined. This apparatus is used for rapidly recording spectra of Rydberg–Rydberg transitions and superfluorescence. In Section 3, we first describe typical BaF FID spectra and Ba superfluorescence spectra. Then, we introduce three new techniques, phase extraction, assignment, and multi-pulse excitation, for semi-automatically extracting information and assisting spectroscopic assignments. In Section 4, we illustrate a highly efficient laser-millimeter wave-spectrum survey as a comprehensive demonstration and summary of our experimental schemes. Details of optimization of laser ablation and estimating the uncertainties of phase extraction are presented in the Appendices.

2. Experimental methods

2.1. State preparation

Rydberg states of Ba (n l j = n l 34−74) are populated by a pulsed dye laser (Lambda Physik Scanmate 2E, 0.1 cm⁻¹ resolution doubled by a β-BBO crystal, shown in Figure 1(a)). Rydberg states of BaF are populated via the two-photon excitation scheme shown in Figure 1(b). Two pulsed dye lasers (Figure 2, xvi) (First laser: Lambda Physik Scanmate 2E, 0.05 cm⁻¹ intracavity etalon single pass; second laser: Sirah Precision Scan, 0.05 cm⁻¹ dual grating narrowed) are used in a stepwise excitation scheme to transfer the BaF molecule from the X 2Σ⁺ ground state to a Rydberg state via the C 2Π (j=0−8) intermediate state. Both dye lasers are pumped by one injection-seeded Spectra-Physics GCR-290 ND:YAG laser, respectively. According to the Rydberg state assignment, Initial Rydberg states of Ba (n = 34−74) and BaF (n = 35−50) are located by recording low resolution survey spectra, employing a pulsed field ionization (PFI) TOF-Ms detection scheme, described in Ref. [20]. The PFI spectra shown in Figure 1(c) and (d) illustrates the difficulty in assigning and interpreting molecular Rydberg spectra due to the combination of a high density of states and limited laser resolution.

2.2. Cpmw spectrometer

Chirped-Pulse millimeter-Wave (Cpmw) spectroscopy is an extension of the Chirped-Pulse Fourier Transform Microwave (CP-FTMW) technique developed by the Brooks group [21–25], to populate higher-frequency regions [26]. The advantages of chirped-pulse spectroscopy, namely the combination of broadband excitation, multiplexed heterodyne detection, high resolution, and meaningful relative intensities, have been demonstrated in pure rotation spectra of large and small molecules [24,25]. Distinct from conventional millimeter-wave spectroscopy that employs a thermal detector or other indirect detection schemes (typically ion detection), chirped-pulse techniques make it possible to capture an entire spectrum: 400,000,000 50 kHz resolution elements (a single chirp) (20 GHz bandwidth) rather than sequentially, one resolution element at a time. Because of this combination of survey capability with high resolution, chirped-pulse techniques have the potential to transform the experimental strategies and goals of traditional microwave spectroscopy.

The extension of chirped-pulse schemes into the millimeter-wave regime has been hampered by the unavailability of high power millimeter-wave sources, which limits the degree of polarization that can be achieved for typical rotational transitions.

![Figure 1](https://example.com/figure1.png)

*Figure 1. Schematic diagram of energy levels of Ba (a) and BaF (b). (c) and (d) show the Ba Rydberg transition and BaF Rydberg transition, respectively.*

Pure rotation transitions have electric dipole transition moments on the order of 1 Debye. However, the electric dipole transition moments between Rydberg states scale as 1/n², resulting in kilo-Debye electric dipole Δl = 1 transition moments between states with moderately high n (30−70) principal quantum numbers. This unique feature of Rydberg states more than compensates for the present limits on millimeter-wave power. It permits non-continuous full polarization of many Rydberg–Rydberg transitions by a single broadband pulse. The value of extending low frequency microwave spectroscopy to high frequency millimeter or sub-millimeter wave spectroscopy for the study of Rydberg electronic transitions is based on: (i) the ability to interrogate selected spectroscopic resonances, which reveal the physical mechanisms of resonant interactions between the Rydberg electron and the internal motions of the molecular ion-core [26–28]; (ii) the electric field strength required to be completely polarized by millimeter or sub-millimeter waves, but are sufficiently small to minimize the dipole-dependent frequency interactions.
shifts, dipole blocking, and broadening mechanisms, such as stray inhomogeneous electric field or blackbody radiation induced Stark broadening [29–32], and long-range dipole–dipole collisional dephasing [33–35].

The CPMW spectrometer, shown in Figure 2, is similar to that in Ref. [24]. We review the main components here. To generate a broadband millimeter-wave pulse at ~85 GHz, a GigaSample’s arbitrary waveform generator (AWG) [6] creates a crafted RF pulse using defined pulse duration, bandwidth, instantaneous power, and amplitude) at 0.2–2.0 GHz. A triply-balanced mixer (iii) mixes the RF pulse with the output of a 6.2 GHz phase-locked oscillator (iv) to create a pulse composed of both signal and difference frequency components (6.4–8.2 GHz and 4.2–6.0 GHz). The upper frequency sideband (6.4–8.2 GHz) is selected by a bandpass filter (v) and input to an active frequency doubler followed by an active frequency sextaplexer (vi). The +12 multiplied output pulse retains the phase of the input pulse, but a −12 multiplied frequency range (12 v 7.58–8.64 GHz, bandwidth: 12 v 4–21.6 GHz, and initial phase (1 24)). The maximum millimeter wave output power is ~38 mW, which can be attenuated and shaped by a fast (10 ns) Voltage Controlled Attenuator (VCA) [11]. The millimeter-wave pulse overlaps the narrow free space from a rectangular standard gain horn (ix) and collimated to a beam waist of ~3 cm by an f 75 cm parabolic mirror (x). The radiation is reflected by a nickel coated mirror (x), the same size as a second pass through the sample, resulting in an active volume of ~100 cm3. The backlight propagating shielded excitation pulse and resultant FD can be collected by the same standard gain horn (ix). A 10 dB directional coupler (xi) provides a 1/10th attenuation of the broad arm and directs 90% of the received power into the detection arm. The received millimeter-wave signals are amplified (xii) and then mixed (p) by using a microwave balanced diode mixer (xii) driven by a frequency synthesizer (xiii). The down-converted signal is digitized and averaged in the time by a 12.5 GHz oscillo- scope. The same phase information and the all frequency sources used in this spectrometer are phase locked to a single 10 MHz Rubidium frequency standard (xv).

The frequencies input to the oscilloscope are down-converted by mixing the millimeter-wave radiation with an intermediate frequency RF. The intermediate frequency is used in the same spectrum twice with two different intermediate frequencies, such as f = 86.4 GHz and f2 = 86.2 GHz, and match the overlapped peaks from the two spectra to recover their frequencies. However, because this frequency recovery method requires coincidence of the signals with different intermediate frequencies, it can only be applied to the signals which can be distinguished from the noise, but cannot transform the entire spectrum unambiguously. In order to display the unique features of both the signal and noise, in Figures 3 and 6, we use down-converted frequencies as the frequency axis of spectra with multiple transitions, while we use the intermediate frequencies for real spectra for which contain only a single transition.

2.3. Buffer gas cooled molecular beam source

We have previously demonstrated the capabilities of FID-detected CPMW spectroscopy on Rydberg–Rydberg transitions of Ca atoms [7,8]. However, our initial efforts to record FID-detected CPMW spectra of a Smaller-type laser ablation supersonic beam source, similar to what we had used for atomic spectra, were thwarted by the ~100 times lower number density of molecular species (~ 1012 cm−3) that could be prepared in a single cell. With a frequency range on the order of 100 MHz, we increase the interaction volume (~ 100 cm3) by keeping the frequency difference between the two transitions of the electronic ground state population among rotation-vibration quantum states.

We have developed, a technique originally developed in Frank De Lucia’s research group [36,37] and extended to generation of cold molecular beams in John Doyle’s research group [36,41], is a method for creating bright, slow beams of atoms and molecules via colliding an inert atomic gas. A schematic diagram of the beam gas cold molecular beam source appears in the upper right hand section of Figure 2. The apparatus is based on a two-stage pulsed helium jet refrigerator (not shown). The first stage (40K) is used to cool the radiation shield (xv), and the second stage (4K) is used to cool the cold cell (xx) and gas filling tube (xxi) to 4 K. As controlled by the microwave and RF PDP Rydberg states on the target, and required expansion to the final destination pressure to be converted to a cold gas. In addition, the full CPMW spectrometer, we cannot recover the millimeter-wave frequency unambiguously using only one intermediate frequency. Our approach is to use the same spectrum twice with two different intermediate frequencies, such as f = 86.4 GHz and f2 = 86.2 GHz, and match the overlapped peaks from the two spectra to recover their frequencies. However, because this frequency recovery method requires coincidence of the signals with different intermediate frequencies, it can only be applied to the signals which can be distinguished from the noise, but cannot transform the entire spectrum unambiguously. In order to display the unique features of both the signal and noise, in Figures 3 and 6, we use down-converted frequencies as the frequency axis of spectra with multiple transitions, while we use the intermediate frequencies for real spectra for which contain only a single transition.

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3.2. Strong in a dense Rydberg gas

Previous experiments showed signs of super radiant [7]. The lower number density and larger Doppler width limitations of our ionic supersonic lab experiment preclude systematic study of strong superradiance. Both of these obstacles are eliminated with the buffer cooled beam setup. Therefore, much stronger super radiative effects are observed.

Figure 4, plots (a) and (b) respectively show the emitted radiation noise in the broad band and in the time-domain. To eliminate white noise in the time-domain, which limits the intensity resolution at large time, we demodulate the FID signal near resonance, shown as black curves in Figure 4, plots (a) and (b). After demodulation, we can observe signals below the white noise level. At low number densities, the coherence is created exclusively by the excitation pulse. Its amplitude is maximum at τ = 0 and decays exponentially, which is the coherence initiated by the excitation pulse is amplified by the cooperatively atom–photon interactions in the dense Rydberg gas with \( N = 10^{14} \text{cm}^{-3} \), where \( C \) is the cooperative parameter; \( N \) is the number density, and \( \tau \) is the wavelength of the radiation. During this amplification process, the energy stored in an inverted population system decreases as the population originally in the energetically higher state is transferred into the lower state by stimulated emission. When the population difference is zero the coherence is maximized. The superradiant emission continues until the population is entirely in the lower state. Unlike the conventional FID picture, the coherence here is not created exclusively by the external excitation pulse; it contains a significant contribution from the population inversion [43]. In addition, the maximum coherence amplitude, the rate of amplification, and the decay rate strongly depend on the number density of the Rydberg sample.

We compare the lineshape and linewidth of the 84 420-4D transition at high and low number densities in Figure 4, plots (c), which is obtained by Fourier transforming plots (a) and (b). At high number density the linewidth is much broader than that at low number density. In addition, the center frequency of the radiation is also shifted by \( 1 \text{ MHz} \). This transient frequency shift is absent in conventional FID radiation. Plot (d) shows the linear dependence of the linewidth on the number density. These preliminary results demonstrate direct observation of strong superradiance effects, including amplification, fast attack and slow decay, frequency shifts in dense Rydberg gases using the CHoW technique in combination with a buffer cooled beam source. However, due to the relatively large inhomogeneity of the number density \( \nabla n \), our large interaction volume (the density near the beam source is 10 times higher than that near the parabolic mirror), Figure 2, 30-shot-to-shot number density fluctuations, and the lack of quantitative number density measurements, it is difficult to compare our preliminary results with theory. More detailed and systematic measurements and analysis are in progress.

3.3. Phase evolution

The millimeter-wave radiation can induce both upward and downward transitions. The direction of the transition can be obtained from a time-domain spectrum by two methods. (1) Transient absorption provides a direct, visual indication of the transition direction. Figure 5, plots (a) and (b) show the transient absorption representation of a downward transition, and an emissive transition represents a downward transition. However, all of the above methods require either a single frequency or a chirped excitation pulse as well as a relative transition time and a high signal to noise ratio in the time-domain. (2) The phase difference between the excitation pulse and the FID radiation is a sensitive and generally applicable diagnostic of the direction of the transition. For an upward transition, the phase exhibits a discontinuous shift by \( \pi \). For a downward transition, there is no such phase shift. This method can be used for a broadband chirped pulse excitation and relatively weak FID transitions. However, the phase shifts are usually not observed due to the broad spectral noise in the time-domain. In both the time-domain and the frequency-domain, Colombo has developed a technique that first filter the time-domain noise, and then fits and extracts the phase of the excitation pulse and the FID separately in the time-domain (8).

We have developed a complementary technique that applies a PPT to extract the phases of the excitation pulse and the FID in the frequency-domain. This method has advantages for a broadband cooled pulse in which multiple transitions are excited. However, estimating the phase uncertainty and optimizing the experimental conditions for accurate phase extraction are non-trivial. In Appendix B, we show that the phase of the initial pulse polarized by a single frequency pulse is accurately followed by the excitation pulse first, and then extend the analysis to a more general situation, in which multiple transitions are polarized by a broadband chirped pulse. We have proved that, when the chirped excitation pulse is sufficiently weak, resulting in a polarization of the Rydberg system by the FID, the phase difference between the excitation pulse and the FID with uncertainty π/10, which is sufficient to distinguish upward from downward transitions.

3.4. Stark demodulation spectroscopy

As mentioned in Section 2.4, Rydberg states are exceptionally sensitive to DC electric fields. Even a small DC electric field can strongly mix neighboring \( f, l + 1 \), opposite parity Rydberg states, thereby inducing measurable frequency shifts and intensity modifications of the FID signature [45,46]. The Stark-mixing amplitude, \( \Delta \), has a dipole transition moment, which is inversely proportional to the energy spacing, \( \Delta \propto 2\Delta E / (\ell+1) \), where \( \ell \) is the angular momentum of the Rydberg electron.\( ^{1}\) Therefore, the Stark effect changes density at the angular momentum of the Rydberg electron \( \ell \), increases therefore, for a moderate DC electric field \( f = 1 \times 10^{14} \text{ cm}^{-3} \), the Stark effects are negligible, and the FID and frequency intensity are almost the same as in the field-free measurements. However, high number density of the Rydberg states with high \( f \), the Stark effects are significant, which cause a series of homogeneous, DC electric fields of different strengths, it is straightforward to separate the CP Rydberg states that are Stark mixed. The Stark splitting of the Rydberg states are caused by a series of homogeneous, DC electric fields of different strengths, which is a Stark effect.

In this letter, we present a preliminary experimental demonstration of Stark demodulation in the Ba Rydberg systems. In a Stark demodulation experiment, all parameters are similar to typical FID detection experiments, except for the addition of a 0–16V, 10\( \mu \)s rectangular electric field pulse. To apply a homogeneous DC electric field, we introduce into the detection chamber a large pair of parallel, mirror fluxes, stainless steel plates \( 4\times 8\times 1\text{ in} \) separated by \( 3\text{ in} \) (xviii in Figure 2). The electric field pulse is applied 10 ns after the termination of the chirped millimeter-wave excitation pulse and overlapped with the FID radiation. In this experiment, the lasers and millimeter-waves pump and polarize the same Rydberg-Rydberg transitions as in typical experiments carried out in the absence of the electric field. Then, the abrupt switching on of the electric field diabatically mixes eigenstates with opposite parities and small degeneracies. A single component of the original FID, with a specific frequency and fixed initial phase, is diluted into multiple components with a broad distribution of frequencies and initial phases. This results in multiple destructive interferences. In Figure 5, plot (a) shows a transition with two CP Rydberg states with zero and 1 V/cm DC electric fields. Their relative intensities are similar, as expected. However, the 10MHz frequency shift is not understood completely. Plot (b) shows a transition that involves at least three CP Rydberg states with 5 V/cm DC electric field. Since all sharp peaks in the FID spectrum are washed out and replaced by a broad feature (~20 MHz). In addition to the qualitative separation of CP Rydberg states and CNP Rydberg states, it is also possible to sort the CNP Rydberg states according to their Coulomb states.

In Figure 5, plots (c) and (d) plot (d) display the DC-field induced changes in the amplitude and lineshape of the FID signal from CP Rydberg states, which both involve at least one CNP Rydberg state. As the amplitude of the DC electric field pulse is increased, the amplitude of the central FID peak in plot (c) decreases relatively more than the FID pulse due to the quantum defect (or degree of core-penetration) of the CNP Rydberg state in plot (c) is larger than that in plot (d). It is likely that the former state has smaller \( \alpha \) than the latter, that is already. With careful calibration, we believe that the quantum defect \( \alpha \) can be extracted from experimentally. More measurements and analysis are in progress.

3.5. Stark demodulation diagnostics

The Stark-demodulation diagnostic permits the Rydberg energy levels observed in an initial batch of CPFmW spectra of a new molecule to be partitioned immediately into CP vs. CNP subsets. All of the CNP energy levels are described by near-integral values of the effective principal quantum number, \( n_{\ell} \). These levels provide the most accessible key to a global analysis, starting with an analysis of ground state features. The Stark ionization potential \( (\ell+1) \) is known, the energies of all integer, \( n_{\ell} \) values can be computed from the energy of the ground state \( (\ell+1) \) state of the Rydberg atom using the quantum number, \( n_{\ell} \), becomes approximately. Thus all strong

\( ^{1}\) The Stark effect (c) corresponds to the extreme limit of \( \ell \). Oscillating the off-diagonal matrix element of matrix elements of the electronic transition dipole moment between the \( n \) and \( n+1 \) states becomes zero. The Stark width \( \Delta \), for the difference between the quantum defects of the \( n \) and \( n+1 \) CP Rydberg states, is shown in Figure 5, plot (d), which shows an upper bound for all CNP \( \ell \) complexes, \( n_{\ell} \), \( n+1 \), \( n+3 \), \( \ell \) is the radius of the \( (n+\ell+1) \) state, \( n \) is the quantum number, \( n_{\ell} \), becomes approximately. Thus all strong

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The 10MHz frequency shift in plot (a) has not been completely understood. Plots (c) and (d) display more details of the behavior of CNP Rydberg states with the DC electric field increased to small steps. Careful measurements could sort the N quantum number or even extract the value of the quantum defect 1 quantitatively. Plots (c) and (d) are from the same transition.

Each of the \( \langle f_{y_a} \rangle = \langle f \rangle \) components of an \( N \) \( N \)-level cluster is associated with a different \( n \)-independent value of the quantum defect. For each laser-excited single CNP eigenstate, the CPmmW spectrum will include transitions into 3 or fewer \( f_y \) components of each \( N \) \( N \)-state, owing to the rigorous \( \Delta N = 0 \pm 1 \) selection rules. Polarization diagnostics will yield assignments of the three \( \Delta N = \pm 1 \) possibilities [47].

The CPmmW spectrum provides an extensive sample of CNP Rydberg states with definite \( n \) and \( N \) assignments and probable \( f \) assignments. The relative energies of all eigenstates sampled in the totality of CPN spectra may be measured at a precision better than 10kHz by exploiting one microwave transition that crosses the states observed in a CPmmW spectrum originating from one laser-populated launch state to those originating from a different launch state. Increasingly large groups of microwave-linked Rydberg energy levels are fitted to an independent-channel Rydberg database appropriate for CNP Rydberg states, where the quantum defect, \( \delta_N \), is a function of \( f \) and \( \delta_N \).

The \[ \delta_N = \delta_{N_{-}} = \frac{\epsilon_{N_{-}}(F) - \epsilon_{N_{+}}(F)}{\epsilon_{N_{+}}(F) - \epsilon_{N_{-}}(F)} \] \( \epsilon_{N_{+}}(F) \) \( \epsilon_{N_{-}}(F) \) is the projection of the Rydberg electron orbit on the non-spherical ion-core. \( \epsilon_{N_{+}}(F) \) \( \epsilon_{N_{-}}(F) \) is the projection of the Rydberg electron orbit on the ion-core rotation axis. Since \( N \) is an approximately good quantum number in Hunds case (d) and \( N \) is a rigorously good quantum number, \( \delta_N \) is an approximately good quantum number.

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We have described direct detection of free Induction Decay signals from transients. The combination of CmW spectroscopy with a buffer gas-cooled molecular beam ablation source enables this form of high-resolution (≈50GHz), broadband (20GHz bandwidth), electronic spectroscopy. However, the new type of Rydberg–Rydberg spectra generated contains new essential informa-
tion for both the assignment of mass and interpretation. We report three important techniques, phase extraction, Stark demodulation, and multipulse spectroscopy, which respectively allow us to determine the direction of the transient (up vs. down), distinguishing between CF Rydberg states and CN Rydberg states, and to map out energy-linked networks consisting of multiple Rydberg–Rydberg transitions. In addition, we are developing several additional methods: (1) Diagnostics based on CmW spectroscopy, such as two-lasers and the millimeter-wave radiation. Due to the anisotropic spatial distribution of the Rydberg electron in a diatomic molecule, the polarization diagnos-
tics provides information about the rotational assignments [47]. (2) Extension to higher millimeter-wave frequency (200–295GHz) for molecular beam Rydberg–Rydberg transitions with c ≈ 30. The normal pattern of regular n−scaling rules, such as energy splittings [48], and selected examples of broken patterns of n−scaling rules, due to stroboscopic resonances [24], provide additional static and dynamical information. The ultimate goal with a combination of the new tools based on multipulse spectroscopy with both lasers and the millimeter-wave radiation. We have observed in particular the impact of superadiabatic decay on the observed linewidths and lineshapes of both atomic Ba and molecular BaF Rydberg–Rydberg transitions. Preliminary experi-
ments on Ba atoms have revealed significant promise of superadiabatic character. Further detailed investigations are in progress.

4. Conclusion and prospects

We thank Dr. G. Barratt Park for guidance and support regarding the CmW spectroscopists Dr. John Barry for providing his schematic diagram of a buffer gas-cooled molecular beam ablation source. This work was supported by the National Science Foundation (Grant No. CHE-1361865). D. Griner was supported by the Depart-
ment of Defense (DoD) through the National Defense Science & Engineering Graduate Fellowship (NSDEG) Program.

Appendix A. Laser ablation

In the buffer gas cooled molecular beam source, the atoms/molecules are introduced into the gas phase via laser abla-
tion of a solid precursor. The laser ablation process involves a complex sequence of energy transfer, gas dynamics, and relax-
ation pathways. Different materials often behave qualitatively differently. Most metals are easily ablated or vaporized, because they readily absorb photons due to the absence of a band-gap. However, typical ionic solids have a large band-gap (>10eV) and must be heated by Rydberg–Rydberg or three photons to thermalize. This nonlinear multiphoton process requires a much higher laser intensity. Therefore, a more tightly focused laser beam with higher intensity is used to obtain a minimum of thermal ablation. We have performed systematic experiments to optimize ablation laser wavelengths. In our experiments, both BaF2 and BaF, where Ba is the target atom, are introduced into the gas phase via laser ablation. The optimal conditions are listed in Table 1.

The key step to improve the ablation efficiency is optimizing the parameters of the precursor, especially for BaF2. Our BaF2 pol-

Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wave length</td>
<td>1064 nm</td>
</tr>
<tr>
<td>Pulse energy</td>
<td>1 mJ</td>
</tr>
<tr>
<td>Focused diameter</td>
<td>1 mm</td>
</tr>
<tr>
<td>Optical power</td>
<td>1 kW</td>
</tr>
<tr>
<td>Precise pressure</td>
<td>10 Torr</td>
</tr>
<tr>
<td>Laser power</td>
<td>100 mW</td>
</tr>
</tbody>
</table>

The laser beam is focused into a 1 mm diameter spot. The laser power is measured with an optical power meter. The precise pressure is measured with a precision pressure gauge. The optical power is measured with a power meter. The precise pressure is measured with a precision pressure gauge.

Depends on the heating temperature and duration, which appear to be critical to optimize the ablation yield. Ablating pellets with inadequate heat treatment (lower density) results in increased dust formation. However, ablatting pellets with excessive heat treatment (higher density) generates less useful BaF. The second key step of the optimization is the focusing condition of the ablation laser. An f/50 cm lens (see Eq. 4 in Figure 2) is used to focus the laser beam into a diameter of less than 10 μm on the BaF pellets. In addition, ablating a single spot repeatedly with a rela-
tively small laser beam (≈100 μm) also reduces ablation efficiency. To overcome this limitation, we use a Galvo mirror (see in Figure 2) to translate the ablation laser beam back and forth to prevent two successive laser pulses from hitting the same location on the pellet. This implemention increases the repetition rate up to 20 Hz (our typical experiments operate at 10 Hz repetition rate).

Appendix B. Phase extraction

The excitation pulse with a single carrier frequency, f0, can be Fourier transformed as in Eq. (8). The resultant Fourier transform has two distinct resonant frequencies and a Fourier transform that is nontrivial to calculate. The excitation pulse is then transformed into the frequency domain, and the Fourier transform of the excitation pulse is calculated using Eqs. (8). The phase shift, Δf, is calculated from Eq. (8). If the transition is upward, the phase shift is calculated using Eq. (8), and the transition is downward. If the phase shift, Δf, is calculated from Eq. (8), the transition is upward.

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Hydronium and hydroxide at the air–water interface with a continuum solvent model

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ARTICLE INFO
Article history:
Received 20 May 2015
Revised 6 June 2015
Available online 11 June 2015

ABSTRACT
The distribution of hydronium and hydroxide ions at the air–water interface has been a problem of much interest in recent years. Here we explore what insights can be gained from a continuum solvent model. We extend our model of ionic solvation free energies and surface interaction free energies to include hydronium and hydroxide. The hydronium cation is attracted to the air-water interface, whereas the hydroxide anion is repelled. If the cavity size parameters required by the model are adjusted to reproduce solvation energies, quantitative agreement with experimental surface tensions is achieved. To the best of our knowledge, this is the most accurate theoretical estimation of this property so far. The results indicate that the surface tension is insensitive to the model parameters. As a result, the model would predict that hydronium would have a very large dispersion solvation energy, which disagrees with ab initio calculations. We therefore use an alternative method for calculating the dispersion contribution. We calculate the dispersion interaction of an ion–water dimer using Symmetry-Adapted Perturbation Theory with Density Functional Theory (DFT-SAPT) and multiply it by the coordination number of the ion. The ion–water separation is taken to be R0, where this is determined by the distance from the ion to the first peak in the ion–oxygen radial distribution function.

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1. Introduction

Any improvement in our understanding of the properties of the hydronium and hydroxide ions in water represents important progress because of the central role they play in chemistry. An explicit example that concerns us is the distribution of hydronium and hydroxide at the air-water interface. A solution that has received renewed attention lately [1–4], and reasonably so, as the air-water interface plays a central role in a range of chemical and physical processes. In addition, the air-water interface serves as a relatively simple case against which to test models of ions–surface interactions. These models can then be used to better understand the interaction between ions and more complex surfaces [5].

This is currently a contentious topic. The long-known apparent strong hydronium/enhancement of the buoyancy of bubbles and oil droplets [6,7] than the disjoining pressure [7], and surface relaxation of water [8]. Although appealing in its simplicity, theoretical and spectroscopic techniques have found little evidence of this enhancement [6,9,14]. A number of reviews provide a summary of this debate and the research on this topic [8,12,13,17–20].

2. Theory

Our solvation and surface interaction models are developed in detail in Refs. [26,29]. A brief overview is provided here. We shall treat the proton as a point particle in the form of the hydronium cation. This seems a reasonable assumption as there is spectroscopic evidence indicating that it is primarily in this form at the interface [26].

2.1. Solvation energies

The solvation model [26] separates the solvation free energy into three contributions, electrostatic, dispersion and cavity formation energies:

\[ G_{solv} = G_{e} + G_{d} + G_{cav} \]  

(1)

2.1.1. Electrostatic

The electrostatic solvation energy in our previous model [26] was defined for a cavity of radius R0 for a spherical monatomic solvent. Here we calculate the electrostatic solvation free energy for the hydronium and hydroxide ions we use COSMO [33,34]. This calculation is based on the Born equation for solvating the ion in a dielectric continuum with the dielectric constant of water, including the contributions from the ion-solvent charge distribution and any electrostatic polarization effects. It gives the same value that the Born equation does for a monatomic ion. The size of the cavity in the Born equation (R0) is crucial to calculate this contribution and is determined below. The Born equation for a monatomic ion zSEI is:

\[ \Delta G_{\text{Born}}(zS) = \frac{z^2 e^2}{2 R_0} \left( \frac{1}{R_0 + z} - \frac{1}{R_0 + 3R_0} \right) \]  

(2)

2.1.2. Dispersion

The model of the dispersion solvation energy described in Ref. [26] and used in Ref. [25] requires that a damping (κ) parameter be determined for the ion to account for the ion–water–water function overlap. These parameters are known for the noble gas atoms and a simple interpolation as a function of the crystal size was used to determine these parameters for the inorganic alkali halide ions [25]. 9 It is not at all clear that it is reasonable to apply this interpolation to determine the damping parameters for the polyatomic hydronium and hydroxium ions, which have a significantly more complex electronic structure. If we did apply such an interpolation we would conclude that hydronium has a very similar κ parameter to fluorine [35]. But the orientationally averaged polarizability of hydronium is significantly lower than that of fluoride, so it would not predict that hydronium would have a very large dispersion solvation energy, which disagrees with ab initio calculations. We therefore use an alternative method for calculating the dispersion contribution. We calculate the dispersion interaction of an ion–water dimer using Symmetry-Adapted Perturbation Theory with Density Functional Theory (DFT-SAPT) and multiply it by the coordination number of the ion. The ion–water separation is taken to be R0, where this is determined by the distance from the ion to the first peak in the ion–oxygen radial distribution function.

\[ G_{d} = \frac{3}{4} \alpha_{\text{water}} R_0^6 \]  

(3)

where \( \alpha_{\text{water}} = 0.178 \text{a.u.} \). Although this ansatz could be disputed due to the microscopic size of the cavity, we have provided a justification for it in Ref. [26]. Essentially the argument is that the reduction in Born energy that occurs due to the cavity does not occur for ions as the water molecules at the cavity surface are constrained by the electric field, similarly to their constrained orientation at the bulk air–water interface. This means that the hydrogen bonded network, a cause of this lower surface tension will not form. The ultimate justification however is the good experimental agreement with ionic solvation free energies.

2.2. Surface interaction

As the ion approaches the air–water interface all three of the contributions to the solvation energy change and contribute to the interaction free energy of the ion with the air–water interface. There are additional contributions that arise from the presence of the interface. We assume that these contributions are additive:

\[ G_{\text{surf}}(\theta, \varphi) = \Delta G_{\text{Born}}(\theta, \varphi) + \Delta G_{\text{d}}(\theta, \varphi) + \Delta G_{\text{cav}}(\theta, \varphi) \]  

(4)

We describe how each of these contributions is calculated in the following sections.

2.2.1. Cavity/surface area contributions

There is a change of surface area of the cavity as the ion crosses the air–water interface. This is given in this section as:

\[ \Delta A_{\text{cav}}(zS) = \begin{cases} 0 & R_0 < R < R_0 + z \smallskip \Delta A_{\text{cav}}(zS) = 2 \pi R_0 R_0 \end{cases} \]  

(5)
2.2.4. with reservation

For the cav(then) interaction to be reproduced experimentally, solvation energy associated with the ion-surface interaction can be expressed as

\[ \Delta G_{\text{solv}}(z) = \pi \alpha \mu(z) \]

(6)

There is also an additional contribution to the change in surface area of the air-water interface [37], this does not contribute to the solvation energy but does give the following contribution to the interaction free energy:

\[ \Delta G_{\text{z}}(z) = \begin{cases} \pi \alpha \mu(z) & z > R_i + R_f \xi \\ \pi \alpha \mu(z) & z = R_i + R_f \xi \end{cases} \]

(7)

2.2.2. Electrostatic contribution

The electrostatic contribution can be broken up into three separate terms:

\[ \Delta G_{\text{z}}(z, \theta, \phi) = \Delta G_{\text{G}}(z, \theta, \phi) + \Delta G_{\text{G}}(z) + \Delta G_{\text{G}}(\theta, \phi) \]

(8)

Image charge contribution: The image charge contribution gives the ionization correction for the ion from the air-water interface at large separations where the solvation layer does not overlap with the interface. This contribution becomes screened by the background electrolyte as concentration increases. It is given by [38]:

\[
G_{\text{z}}(z, \phi) = \frac{\pi \alpha}{4 \pi \varepsilon_0} \ln \left( \frac{z + R_i + R_f}{z - R_i - R_f} \right)
\]

(9)

where \( z > \frac{R_i + R_f}{2} \) is the image Debye length in \( A^{-1} \) and \( \phi \) has units of \( mol \cdot L^{-1} \).

Surface potential contribution: There is a contribution to the solvation energy from the surface potential of the air-water interface. This contribution was not considered in the solvation energy as we compared with experimental estimates of the intrinsic solvation energy. This potential will however contribute to the distribution of ions at the interface and it is therefore necessary to include it. There is significant debate about what the size of this contribution is, but we use a value of \( \phi = 0.12 \) V, consistent with Refs. [29,39]. We assume the following functional form for this contribution:

\[
G_{\text{z}}(z, \phi) = \frac{\pi \alpha}{4 \pi \varepsilon_0} \ln \left( \frac{z + R_i + R_f}{z - R_i - R_f} \right)
\]

(10)

\( \Delta G_{\text{z}} \) is defined above, this function means that as \( z \rightarrow 0 \) half of the surface potential is felt by the ion.

COSMO contribution: Finally as the ions cross the interface we need to calculate how the Born solvation energy changes. We can use COSMO to do this if we allow our ion to gradually cross a flat dielectric interface and calculate how the total energy changes. We can create an effectively flat dielectric interface in COSMO by creating a dumb atom centered in a very large cavity. The \( C_{\text{GSO}} \) term can then be calculated numerically. This amounts essentially to the change in electrostatic solvation energy of the ion as it crosses the interface.

2.2.3. Dispersion energy contribution

For the dispersion contribution we use the expression:

\[ \Delta G_{\text{z}}(z) = \Delta G_{\text{G}}(z) \]

(11)

where \( \Delta G_{\text{G}} \) is given above (Eq. (11)).

2.2.4. Additional contributions

A number of additional contributions to the interaction of an ion with the air-water interface have been hypothesized in the literature. We do not include these explicitly in this model but discuss them briefly here.

Capillary wave suppression: Ottens et al. [37] argue that changes in the surface tension of local water molecules cannot explain the experimentally observed entropic repulsion of ions from the air-water interface, and provide simulation evidence that ions present at the interface can suppress capillary wave fluctuations, which would explain this observation. This is an interesting hypothesis, but including or assessing the importance of this effect is beyond the scope of the relatively simple model outlined in this letter.

Fusion-Suppression Force: Gray-Weale and Beattie [40] argue that a postulated ‘fusion-suppression’ force strongly attracts hydronium to the surface. We do not explicitly include this term for several reasons: Firstly, any model with such a large attraction cannot be reconciled with surface tension data. This is discussed further below. Secondly, this force corresponds physically to the energy gained when an ion displaces water molecules from the energetically unfavorable interfacial region and returns them to bulk. This contribution is already calculated consistently in this model with the \( G^\text{z} \) term. Thirdly, this force is calculated by assuming dipoles in water interact with the Keesom force:

\[ G(z) = \left( \frac{\mu(z)^2}{4 \pi \varepsilon_0} \right) \ln \left( \frac{z + R_i + R_f}{z - R_i - R_f} \right) \]

(12)

(See supplementary information of Ref. [40]) This force gives the thermally averaged interaction of two dipoles in vacuum (41). The use of this expression for dipoles in condensed phase is questionable: firstly it is not clear why the factor of \( 1/e \) does not need to be included to account for the dielectric response of the intervening water molecules, which will damp this interaction. Secondly, the pair-wise additive approximation breaks down for fixed dipole interactions in water where many-body contributions dominate. (Indeed the Keesom interaction in a condensed phase is proportional to temperature not its inverse). Finally, the dielectric decrement is used to estimate \( \mu(z) \). This interpretation of the dielectric decrement is debatable [41] and there is significant experimental uncertainty associated with this property, which makes it difficult to assess how large this contribution is for various ions including hydronium.

Water structure: It is often argued that the explicit structuring of water molecules around ions will play a role in determining their free energies of interactions. This is examined further in the discussion section below, but obviously it is not possible to take these effects into account explicitly while preserving the continuum solvent approximation.

2.3. Statistical angular averaging

We can specify the orientation of the hydronium anion with a single angle \( \theta \). For the hydronium cation we need two angles \( \phi \) and \( \theta \). The definition of these angles is given in Figure 1. The free energy of an ion in water is given by the Widom particle insertion formula [44]:

\[ G(z, \theta) = 4 \pi \mu(z) \ln \left( \frac{\exp(\frac{\pi \alpha \mu(z)}{R_i + R_f})}{1} \right) \]

(13)

where the double brackets indicate averaging over both solute orientations and solvent configurations.

The average over solvent configurations can be treated by recognizing the fact that \( \exp(\frac{\pi \alpha \mu(z)}{R_i + R_f}) \), where \( G(z, \theta) \), is simply the solvation energy of an ion at the point \( (z, \theta, \phi) \). This can be calculated using the method outlined above. The average interaction free energy of the ion with the surface can then be given by:

\[ G(z, \theta) = 4 \pi \mu(z) \ln \left( \int_0^{2\pi} \int_0^\pi \exp(\frac{\pi \alpha \mu(z)}{R_i + R_f}) \sin(\theta) d\theta d\phi \right) \]

(14)

For hydronium there is no 0 dependence. For hydronium we can use the fact that \( \exp(\frac{\pi \alpha \mu(z)}{R_i + R_f}) \) to rotational symmetry. This reduces the number of free energy calculations required, and the average becomes:

\[ G(z) = 4 \pi \mu(z) \int \int_0^\pi \exp(\frac{\pi \alpha \mu(z)}{R_i + R_f}) d\theta d\phi \]

(15)

2.4. Calculation details

The TURBOMOLE package [45,46] was used with an implementation of COSMO [33,34]. Here we have used the aug-cc-pVDZ basis sets for oxygen and hydrogen atoms. The calculations were performed at the Hartree–Fock level using the DSCF program [48] then at the MP2 level using the RMP program [49,51]. The NPPA and NIPPA parameters of the COSMO program were increased to 12 962 and 7 7922 respectively. The dummy atom was placed in a cavity with a radius of 50 Å. The ROG parameter in COSMO was set to 0.84 Å. The epsilon parameter was set to 116.95 Å. The calculations were performed without the overlapping charge correction and with an open cavity. These parameters are the same as in Ref. [29] where justification is provided.

The ion-solvent separation was calculated by taking the difference between the total energy of the ion in vacuum and the total energy of the ion in a spherical cavity in a dielectric medium calculated with COSMO. The geometry of the ion was optimized for both of these energy calculations separately. For the calculation of the ion-surface interaction energy the ion’s geometry was fixed to be the same as for the ion in the spherical cavity in bulk. The program [48–50] was used to determine the optimized ion geometry. The DFT–SAPT [36] calculations were performed using the PBE [50] DFT exchange and water dimers using the MOLPRO2012.1 software package [53,54].

2.5. Solvent sizes

To determine the \( R_b \) parameter for the hydronium ion we use the values given by Ohtaki and Radzio in Ref. [55], determined from scattering data, as well as the value determined by Baer et al. [14] on the basis of this. This is the only simulation estimate used as it represents the state of the air, including the dispersion corrections, which have been shown to be crucially important in reproducing the correct density of water and hence will likely be important in determining this parameter. This results in a value of \( R_b = 2.725 \pm 0.015 \) Å. The size parameters for the hydronium anion are significantly harder to determine as there seem to be no experimental estimates of this quantity [55,56]. We therefore use the value of \( R_b = 2.554 \) Å determined from AIMD [14]. We can use the expression \( R_b = R_k - R_a \) to determine the cavity sizes for these solutes, where \( R_k = 0.844 \) Å. This method of defining ionic radii is exactly the same as the one used previously in our continuum model of ion solvation energies [29].

The resulting solvation energies and surface interactions are quite sensitive to the size values of the ions, and there is also significant uncertainty associated with these sizes. We therefore adjust these cavity size parameters to the nearest 0.01 Å to accurately reproduce the solvation energies. We can then use these adjusted cavity sizes to calculate surface interactions. This is an important test of the model. It means that any failure of the model to correctly reproduce solvation energies, either from incorrect cavity sizes or from the approximations used, are corrected for and the quality of the surface interaction model alone can be tested. Obviously improving the physical accuracy of one aspect of the model should result in increased accuracy of other aspects. This same procedure was carried out in Ref. [29]. The resulting adjusted cavity size

Figure 1. Hydronium and hydronate at the air-water interface. There angular positions are captured by the angles \( \theta \) and \( \phi \).
interaction of anions with the surrounding water. This mechanism is important for hydronium and water, where we see that the dispersion solvation energy of hydronium is significantly more negative than that of hydronium. However, this effect is overwhelmed by a much larger electrostatic solvation energy for the hydronium cation. This is caused by the fact that these ions are not point charges in the center of a cavity, but have some charge distribution in the cavity. Indeed Table 2 shows that the Born equation fails to accurately calculate the solvation energy of these ions compared with a COSMO calculation. In contrast, for spherical ions such as fluoride the Born equation is very accurate. This breakdown of the Born equation is much more dramatic for the hydronium cation than it is for the hydronium ion. This is likely because the positive charge of the hydronium ion is concentrated around the hydrogen atom, whereas these are significantly closer to the water molecules than the central oxygen atom and therefore the electrostatic solvation energy is significantly larger. It is less clear why the Born equation gives an electrostatic energy that is too negative compared with the COSMO calculation for hydronium.

Table 2 provides contributions to the solvation energy of the fluoride anion. We can compare this with hydronium and see that the two anions behave almost identically. They have similar size and their dispersion and electrostatic solvation energies are the same. This results in very similar total solvation energies, which helps explain why they have such similar experimental solvation free energies. This has significant implications for the importance of water's structural properties as discussed below.

3. Results and discussions

3.1. Solvation free energies

Table 1 gives the adjusted and unadjusted cavity and B0 parameters for the hydronium and hydronium ions. Interestingly adjusting the radius so that hydronium and hydronium have the same radius gives the best agreement with experimental solvation energies. This common value is ~0.2 Å smaller than the corresponding parameter for a water molecule [60].

Tables 2 and 3 give the solvation energy contributions resulting from these size values. With Rk,ahydronium has a significantly more negative solvation free energy than hydronium even though they are the same size. This is the opposite of what is normally observed for ions: anions are normally more strongly solvated than cations of similar size. This effect is commonly attributed to orientational properties of the water molecules. However, we have shown [28,29] that a plausible explanation is the larger dispersion

### Table 1

<table>
<thead>
<tr>
<th>Hydronium</th>
<th>Cavity</th>
<th>B0</th>
<th>R0</th>
<th>Parameters</th>
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<tr>
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<td>1.72</td>
<td>2.22</td>
<td>0.53</td>
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<tr>
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</table>

*From Duignan et al.*

### Table 2

<table>
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<th>R0</th>
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<td>1.72</td>
<td>2.22</td>
<td>0.53</td>
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*From Ref. [57]*

### Table 3

<table>
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<tr>
<th>Hydronium</th>
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<th>B0</th>
<th>R0</th>
<th>Parameters</th>
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</thead>
<tbody>
<tr>
<td>Rk,ahydronium</td>
<td>1.89</td>
<td>1.72</td>
<td>2.22</td>
<td>0.53</td>
</tr>
</tbody>
</table>

*From Ref. [57]*
3.3. Molecular dynamics

As already mentioned estimates of these interactions on the basis of molecular dynamics simulation vary significantly depending on the model used [14] but many models indicate an enhancement of the hydrophobic effect [15]. The hydration effect is more than the simple hydrogen bonds. Furthermore, a hydroxide ion is hydrated on average with 6–10 water molecules [5,44,56].

3.4. Spectroscopy

This enhancement of hydrophobicity is consistent with second harmonic generation (SHG) [69,1] and sum-frequency generation (SG) [62,63,71,33] experiments. The repulsion of hydroxide from the air-water interface is also generally consistent with these experiments, although Refs. [52,72] use SHG and SG methods and report opposite results. The repulsion of hydroxide from the air-water interface at what concentration though is not clear. On the other hand pH dependent SFG [72,173] and photoelectron spectroscopy (PES) [74] have been used to argue for the absence of hydroxide at the interface. The ambiguity of the probe length of these experimental methods prevents quantitative comparison. Electrospatial mass spectrometry also provides evidence for an enhancement of hydrophobicity [75] and a depletion of hydroxide [76] at the air-water interface.

3.5. Surface tensions

The key experimental measurement to quantitatively test the ion interaction potentials is the surface excesses. These can be calculated from the experimental surface tension values given in Ref. [78] using the Gibbs adsorption isotherm:

$$\Gamma = \frac{-\partial \gamma}{\partial \phi}$$

The surface excess and is given by:

$$\Gamma = \int_0^\infty d\gamma(z) \left( \mu(z) - \mu(z\rightarrow\infty) \right)$$

where $\mu(z)$ is the interaction free energy of the ion with the interface described above and the potential $\phi$ is determined by solving the Poisson–Boltzmann equation:

$$-\epsilon \nabla^2 \phi = \sum_{j} \psi_j$$

In order to calculate these surface excesses the interaction potentials calculated in Ref. [29] were used for the alkali halide counterions.

3.6. Implications

We remark that we have essentially taken the model of Ref. [29] and applied it to the hydroxide ion without modifications. The only thing that we are dealing with is the orientation dependence; but this does not require any significant new approximations or parameters. The model reproduces experimental results very well with the experimental results. For any ion of this size, the key parameters needed are the ionic sizes, the coordination number, and the surface tension. The values used for these parameters can be independently derived, although the final justification is the agreement with experiment and, the cavity sizes do have to be adjusted by a small amount to reproduce the surface tensions of hydroxides quantitatively.

The surface interaction model was originally developed to reproduce the hydrophilic effect that is known as the hydration of ions. This is one of the reasons why the surface tension of sodium chloride is larger than that of water. The hydrophobic effect of this size of ionic species is very important to understanding the surface activity of ions.
fortuitous cancellation of errors may have occurred, particularly if they are not ion specific.

3.6. Water structure

The explanations of the properties of hydronium and hydroxide in water frequently invoke the structural properties of water and the hydrogen bonding ability of these ions [70,71,72,137]. These explanations imply that an understanding of the properties of ions in water is impossible without explicitly incorporating the orientation and conduction of individual water molecules. If this is true it is unfortunate as it will mean understanding these properties is more challenging than previously presumed. Unfortunately, this assumption is so firmly rooted as possible rather than simply assumed. We must be careful to avoid the problem Ball [81] identifies in regard to water structure, i.e., to avoid trying to explain the structure of water without understanding it.

3.6.1. Water structure

The interpretation of the properties of hydronium and hydroxide in water 

**Table 7**

<table>
<thead>
<tr>
<th>Film</th>
<th>Hydroxide</th>
<th>Hydronium</th>
</tr>
</thead>
<tbody>
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</tr>
<tr>
<td>HI</td>
<td>13.1</td>
<td>0.5</td>
</tr>
<tr>
<td>LiI</td>
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<td>7.9</td>
</tr>
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<td>NaF</td>
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<td>NaI</td>
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<td>KF</td>
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<td>KBr</td>
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<tr>
<td>RbF</td>
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<tr>
<td>CsF</td>
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<td>CsCl</td>
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</tr>
<tr>
<td>CsI</td>
<td>7.7</td>
<td>7.2</td>
</tr>
</tbody>
</table>

3.6.2. Hydroxide adsorption

The measured negative zeta potential of bubbles, oil droplets and other particles are consistently too large to result from tropospheric mobility experiments. This is caused by an increase in slip length which compensates for the decrease in surface charge.
The rapidly changing face of electron microscopy

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1. Introduction

Fifty years ago electron microscopy (EM) had already made a profound impact both on molecular biology and chemistry. A nega- tive-staining method for high-resolution EM of viruses soon led to major progress in three-dimensional (3D) image reconstructions of small viruses [1–3], and the reality of the power of the technique, movement and operation of distortions in crystalline solids were rendered visible by electron diffraction contrast [4,5]. Chemists, and to a lesser degree, materials scientists, were relatively slow to capitalise on the power of EM, but the situation, for chemical physicists espe- cially, has been utterly transformed in the last thirty years [6,7], and the pace of change in chemical electron microscopy is now very considerable.

Four years ago, two of us published a synoptic account [7], aimed at the community of chemical physicists in which, inter alia, we summarised the myriad array of structural and dynamic processes pertaining to biological, physical and engineering materials that was then retrievable (in unprecedented detail) using EM. During the intervening short time, there have been many other signifi- cant advances. As in multi-dimensional spectroscopy [8], where there have been rapidly improving spatial, spectral and temporal resolutions, so also is the case in multi-dimensional EM (MDEM).

But there is also the extraordinary ease with which data may now be garnered. For example, scanning transmission electron microscopy (STEM), used for the retrieval of energy-dispersive X-ray (EDX) or electron energy loss (EEL) data, can routinely generate ‘spectra images’ in which behind every image pixel lies a complete (EDX or EEL) spectrum. By recording a tilt series of such spectrum images, ‘4D spectra tomograms’ produce spectral (hence chemical) information at every real space voxel.

There is, however, another kind of 4D EM [9–11], which is the revolutionary one introduced by Zewail and co-workers that achieves ultra-fast EM at the femtosecond time-scale, while also reaching near-atomic-resolution. This remarkable technical advance has improved temporal resolution of imaging and spectra, gen- erated by EM, by some 10 orders of magnitude compared with the video rates still used extensively by microscopists. Indeed, the Nobel Laureate Roger Kornberg, himself an inspired user of EM and other techniques in structural biology [12], has recently described the monograph entitled ‘4D Visualisation of Matter’ [10] as ‘a chronic of an extraordinary journey of invention and discovery’.

We shall dwell only briefly in this short review on the 4D EM work of Zewail et al., despite the novelty of these photon-induced near-field electron microscopy (PENEM), with its other numerous advantages; and nor will we discuss aspects of electron holography with all its virtues [13], or indeed several other novel recon- struction procedures. Before proceeding, however, we judge it pertinent to recall that electrons as primary radiation to interrogate condensed or fluidic matter are superior to both X-rays and neutrons, as demonstrated by Henderson in his seminal review [14]. He drew attention to the not widely appreciated fact that the amount of beam damage inflicted on the specimen per useful elastic event is 1000 times as great for 1.5 Å wave-length X-rays than it is for 100 keV electrons. Even 1.8 Å wavelengths are three times more damaging per useful elastic event [15]. He follows that, for the same amount of radiation damage, electrons yield the most useful information. It is also pertinent to recall that cryo-electron microscopy consid- erably diminishes beam damage. In addition, thanks to revolutionary recent advances in electron detector technology, the attractions of EM as a structural tool in molecular biology are fast outweighing the traditional direct X-ray (or synchrotron based) diffraction meth- ods. Even structures of extreme complexity, like large ribosomal subunits from human mitochondria (revealing 48 proteins) have been elucidated at 3.4 Å resolution using single-particle cryogenic EM [16].

So straightforward has it become, thanks to numerous technolog- ical and computational advances, to garner enormous amounts of digital information, that the era of ‘big data’ and the subject of data science have high relevance in modern EM. It is now almost mandatory to determine ahead of measurement the nature of the manageable information that one needs to collect. When one reflects that some 90% of all data in the world was created in the last few years, and thought springs to mind: Where is the wisdom we have lost in knowledge? Where is the knowledge we have lost in information?

Earlier reviews from this laboratory [7,18–20] have described how extraordinarily versatile EM has become in assessing structure at the atomic level, in exploring microstructures and their variety of artefacts, as well as in retrieving valence states of atoms and their dynamics from cryogenic temperatures upwards. What was not covered in these reviews was the way in which automation of specimen settings (tilts) and data retrieval has revolutionised access to the entire reciprocal space of objects under study with a consequential accumulation of a blizzard of new data. Not only is it feasible to conduct valency mapping in 3D, but it is also possible to characterise a large variety of crystallographically active crystal- lites and to open up a new era of ‘crystal cartography’. Moreover, with aberration-corrected electron microscopes, it is readily feas- ible to identify single-atom (supported) catalysis; and these, in turn, have ushered in a new era of single-atom heterogeneous catalysis [21,22]. Mesoporous sodic solids, with their large unit cell dimen- sions, and which are now of central importance in shape-selective and regio-selective heterogeneous catalysts, cannot be structurally interrogated using X-ray methods, but they can be structurally elucidated by EM [19,20,23].

2. Topics to be touched upon in this review

By means of a collection of representative illustrations, we outline some new frontiers in chemical physics and materials chemistry that can now be explored via MDEM. In doing so, we also summarise relevant complementary advances made in addition from X-ray and neutrons in theory and in physical chem- ical science. In electron tomography (ET), for example, it may be easier to obtain a compressed electron density (CS; see later), just as it is advantageous to do so in studies involving magnetic resonance [24].

Of growing importance in MDEM, where it is mandatory to process ‘big data’, is multivariate statistical analysis (MSA). This term actually encompasses many different, but related, approaches, including principal component analysis (PCA), independent com- ponent analysis (ICA) and non-negative matrix factorisation (NMF). In each case, the image or diffraction pattern, is decomposed into a series of ‘basis’ functions, each of which is weighted by a coefficient, or loading. The advantage of doing this is to transform potentially statistically similar, or even statistically identical, functions is small, for example perhaps fewer than 10 basis spec- ies, each set composed of millions of thousands! It is not obvious de novo, for a particular data set, which decomposition approach will be the most successful. This is an area of rapid progress and optimised MSA methods for handling EM-related big data are now already of key importance.

However, notably, we focus on the primacy of STEM as the prin- cipal technique for effecting MDEM. There then follow sections dealing with EM, chemical MDEM, and also time-resolved MDEM. Finally the growth of crystallographic MDEMs, which is well-suited to investigating electronically sensitive organic molecular- lar crystals, is outlined. [The term multi-dimensional EM (MDEM)

may offend the sensitivities of those who regard 4D EM – the 3 spatial plus time domain – as the only justified (rational) multi- dimensional EM. But 4D EM has already been used by others to mean something different – see for example, Gass et al., Ref. [25] below, who describe spectromicroscopic for convenience and heuristic reasons we shall use MDEM in the sense subsumed in earlier sections of this review.]

3. The central role of STEM in MDEM

There are many imaging modes and associated analyti- cal techniques available in electron microscopy that provide comprehensive information about structure, composition and chemico-physical properties from the micro to the atomic scale. One mode in particular, annular dark-field (ADF) STEM imaging, has proven to be invaluable in a great many circumstances, owing to its direct interpretability and atomic number contrast [11,26].

The now widespread availability of aberration-corrected electron optics has made atomically resolved images commonplace, a capa- bility of great value, for example, for revealing the precise atomic architecture of nanoscale catalysts. Another great virtue of STEM is its amenability to the simultaneous collection of multiple signals emanating from the specimen (Fig. 1). As depicted in Figure 1, STEM images are acquired in a serial fashion in which the probe, typically sub-nm in diameter, dwells for a short time at a point on the specimen. The interaction of the beam as it passes through the specimen leads to a variety of signals arising both from elastic and inelastic processes. By scanning the beam across the specimen, each signal that arises from the inter- action can be recorded with high spatial resolution, forming maps of the specimen's structure and composition – a form of nanoscale cartography[27]. Thus, with its ability to record multiple sig- nals at each beam position, provides a central platform for MDEM, with the addition of further ‘dimensions’ provided by spectroscopy, diffraction and time resolution, hence STEM can reveal information in one of more real space, reciprocal (diffraction) space, energy space and the temporal domain, see Figure 2.

Figure 1. The scanning transmission electron microscope, salient electron beam-specimen interactions and associated detectors (ADF=annular dark-field, DF = bright-field)
methodologies, especially those exploiting prior knowledge. These methodologies can both improve the 3D reconstructions and reduce the amount of data (usually the number of images) that need be acquired in the first place.

The technique of discrete tomography was successfully introduced in ET by Batenburg and co-workers [29], and harnesses the assumption that the specimen is in some sense ‘discrete’, such as consisting of a small number of constituent phases [1]; and therefore only a few discrete grey levels in the tomographic reconstruction, or that the specimen consists of discrete elements, such as atoms. A subsequent highly efficacious development has been the introduction of so-called ‘compressed sensing’ (CS) techniques in ET [30]. CS methods, grounded by fundamental paradigm shifts in sampling theory, harness versatile procedures of sparse approximation, as used ubiquitously in image compression. In essence, CS harnesses the fact that the important information in many signals can be captured in a form that is compact compared to the full signal (i.e. the signal can be represented ‘sparsely’), and incorporates this knowledge of sparsity into the sensing and reconstruction processes to reduce vastly the amount of information that needs to be recorded. Figure 3a provides a clear example of the efficacy of CS-ET. Not only is the exterior morphology and concave region of an iron oxide nanoparticle more accurately reconstructed using the full set of tilt series images, but when the numbers of images used for reconstruction is reduced, the reconstructions from CS-ET remain remarkably robust, while the conventional reconstructions (obtained using the simultaneous iterative reconstruction technique, SIRT) degrade substantially [31]. The accurate 3D nano-metrology via CS-ET is a crucial characterisation of the novel iron oxide nanoparticles, the concave surface of which can destabilise nanoparticles that fit exactly into the concavity [32].

A significant strength of CS-ET is the ability to address different types of image content through choice of the appropriate sensing transform, making it applicable to the study of many types of nano- and atomic-scale structures and phenomena. As seen from the success of the JPEG image compression algorithm, familiar from digital photography, sparsity is prevalent in the macroscopic world, as revealed by STEM, sparsity is prevalent at the nanoscale too. Importantly, whilst there are an increasing number of applications of CS across many scientific and engineering applications (for example, magnetic resonance imaging, computed tomography and fluorescence microscopy), notable progress is being made also in developing a deeper mathematical understanding of the technique, and in linking theory and practice through the development of optimised protocols [33]. Moreover, concepts of sparsity and CS are applicable in many other areas of EM besides ET, and should prove especially valuable in reducing the electron dose to which specimens must be exposed but retaining high quality images and data.

Coupled with aberration-corrected optics, both discrete- and CS-based methods have played a pivotal role in pushing the achievable resolution of ET into the atomic regime, for example as applied to an embedded silver nanoparticle [34] and a gold nano-rod [35]. Another approach harnessing 3D Fourier filtering has recently disclosed atomic-scale details pertaining to dislocation structure in a platinum nanoparticle [36].

In addition, there has been considerable development in quantifying atomic resolution STEM images, and especially in the determination of the number of atoms in projected columns through careful measurement of the intensity of each atom column. These ‘atom counting’ results are often combined with prior knowledge about the nanoparticle morphology to generate a best-fit model to the data, an example of which is illustrated in Figure 3b [37]. Whilst these methods often require strong assumptions to be made about the particle morphology in order to generate a 3D model, they are advantageous in requiring, in principle, only a limited number of images.

4. Structural MDMEM

In chemico-physical contexts, the extension of 2D structural EM (Fig. 3a) to fully 3D structural characterisation (Fig. 3b) has been facilitated by STEM-based tomography [12,27]. In essence, ET entails recording a series of EM images in which the specimen is tilted to different angles. The series of images, each image of which constitutes a projection of the specimen (to a sufficient approximation), are then ‘back-projected’ (computationally) to generate a 3D reconstruction. The directly interpretable nature of the ADF signal in STEM makes it well-suited to 3D structural imaging of strongly scattering specimens which, following the first demonstrations ca. 2015 years ago [28], led to its adoption across most of the chemico-physical sciences [13,27]. More recently, as addressed in the later sections of this review (and briefly elsewhere [18]), the increasing ability to couple STEM tomography with analytical and crystallographic signals is leading to a new era in MDMEM.

Before proceeding however, we first discuss some of the notable recent advances in 3D structural EM. Many of these have been focused on increasing the fidelity of 3D reconstructions from limited data sets, especially for ‘nano-metrology’, atomic-resolution 3D imaging. In the study of specimens whose sensitivity to the electron beam has hitherto precluded detailed investigation. In particular, there has recently been a shift towards ‘smart’

Figure 2. (a) Form of multi-dimensional electron microscopy. (b) 2D imaging, in which the image constitutes some form of integration through the specimen, typically yielding structural detail; (c) 3D imaging, often accomplished by tilt series tomography to reveal 3D morphology; (d) spectrum imaging, in which at each pixel a full spectrum, or energy-loss series at chosen energy-loss windows (1, 2, ... ) is recorded; (e) compressed image sequences, typically capturing response to a stimulus; (f) spectrum tomography, enabling spatially resolved spectroscopy across all three spatial dimensions, i.e. ‘spectroscopic TEM’; (g) diffusion pattern is recorded at each real space point; (h) multiple-dimensional crystallography, in which both 3D real and reciprocal space information is retrieved.

Figure 3. (a) Top: Surface renderings of the reconstructed 3D morphology of an iron oxide nanoparticle, obtained using CS-ET or the conventional SIRT algorithm, and using reduced subsets of the tilt series images. (Bottom) The Merli of the reconstructions further assessed by analysing the reconstructed concavity volume, which is quantified consistently using CS-ET. The nanoparticle is indicated by the arrow in the inset ADF-STEM image [31]. (b) 3D reconstruction of the atom positions in a platinum nanoparticle, obtained by quantifying the images to determine the number of atoms in each projected atomic column and using the results to prior-knowledge constrained molecular dynamics relaxations [37].
single image and therefore offer the prospect of analysing many nanoparticles and tracking changes in 3D atomic structure over time. The availability of aberration-corrected microscopes has also enabled single-atom catalysts to be developed [21,22].

5. Chemical MDEM

The point-wise recording of spectroscopic signals in STEM, to form ‘spectrogram-images’ (Fig. 2c), is most commonly performed with EDXS spectroscopy (EDXS) and EEL spectroscopy (EELS), providing 2D real space maps with a third dimension containing spectral information. Both EDXS and EELS have benefited recently from advances in detector technology, thus facilitating faster more efficient recording.

For the case of EDXS, large solid angles (ca. 1 sr) are now available for X-ray collection, often with multiple detectors placed around the sample. Extending such analysis to 3D using tomographic acquisition, the geometry introduced recently by the FEI Company, in which four detectors are symmetrically disposed about the sample, is especially advantageous. To avoid serious shadowing artefacts however, one pair of detectors must be used when tilting clockwise, the other pair when tilting anticlockwise [38].

In EELS, the correction of higher order aberrations in the spectrometer optics has led to larger collection angles and thus improved efficiency, and the increase in read-out speed and improved versatility in how the CCD chip is used has led to very fast acquisition times, ca. 1000 spectra per second.

These new spectrometers and detectors have facilitated rapid, high quality 2D mapping of chemical properties, but have advanced also spatially resolved spectroscopy in three dimensions, as shown in Figure 2e. Indeed, if both EDXS and EELS spectra are recorded simultaneously and employed for tomographic reconstruction, as recently undertaken by Haberfehlner et al. [39], one can readily appreciate the abundance of data and the analytical flexibility afforded by such multi-dimensional microscopy.

Such 4D spectrum-tomographic data sets can be processed in two ways. Firstly, the spectrum-image data at each tilt in the series is used to generate a tilt series of 2D chemical maps (e.g. [39-40]), and therefore to reconstruct 3D chemical maps for each element. Alternatively, it is possible to reconstruct the volume at every energy increment, thus preserving the full spectrum at each voxel, a method sometimes known as ‘volume-spectroscopy’. The principle of the technique was first demonstrated using parallel beam energy-filtered TEM [25], has more recently been implemented in STEM mode [39,41], and a comparison of the two approaches has been investigated recently [29] (see Fig. 4a).

The pettiveness of spectral tomography in understanding and optimising nanoscale catalysts is exemplified in Figure 4b, where elemental segregation within individual bimetallic silver-gold hollow nanocatalysts is revealed by STEM-EDXS tomography [42]. This firm evidence of a transition from Au surface segregation (Fig. 4b, left nanoparticle) to Ag surface segregation (Fig. 4b, right nanoparticle) as Au content increases enables interpretation of changes in catalytic performance in a three-component coupling reaction among cyclohexane carboxaldehyde, piperidine and phenylethylamine.

The very nature of chemical MDEM, and the acquisition of multiple spectroscopic signals, leads to a huge amount of data recorded for each experiment. As such, an increasingly important aspect of the analysis is how best to handle such ‘big data’ sets and to optimise data reduction. As we mentioned before, MSA is being increasingly adopted by the EM community to tackle this data problem. In chemical MDEM, for each spectrum-image, an MSA decomposition leads to a series of basis spectra and loading ‘maps’ whose pixel intensities are the weighting coefficients. For PCA, perhaps the most common approach, the basis spectra are ranked (as a score plot) in terms of the variance (or information content) contained within each basis spectrum – ideally it is then clear which basis spectra to keep and which to discard as ‘noise’. For ICA, the decomposition provides components that are statistically independent (or uncorrelated) and in favourable cases, can lead to physically interpretable components, which resemble phase-specific EDX spectra, and loadings that appear to yield readily interpretable maps of the different phases present in the specimen [43].

Complex devices in, for example, the semiconductor industry may have the same element (e.g. silicon) incorporated in different forms with associated differing electronic and chemico-physical properties. EELS-based chemical MDEM is sensitive to those properties via information encoded in the shape of the ionisation edges seen in core-loss spectra. As an example, Figure 5a shows a 3D map of the different bonding states of silicon (elemental, oxide, silicide) seen in a semiconductor device [40], differentiated through a least-squares matching of edge shapes with EEL spectra from a reference data set. Likewise, the sensitivity of catalytic performance to exact chemical species (and valency) on the catalytic surface requires 3D chemical mapping with nanoscale (or better) resolution, and core-loss EEL spectrum tomography meets that requirement. As a recent example, the 3D surface chemistry of a nanoparticle was investigated using ‘chemical shifts’ of the Cr M4,5 edge energy seen in EEL spectra and combined with FT reconstruction to show the 3D distribution of Cr 3+ and Cr 4+ ions [41].

The optical properties of excited metal nanoparticles are governed to a large extent by the phenomenon of localised surface plasmon resonances (LSPRs) and the associated local enhancement of induced electronic fields. That enhancement, which can be orders of magnitude, has led to many possible applications including plasmonic solar cells, enhanced photocatalysis, single-molecule sensors and surface-enhanced Raman spectroscopy [44]. The precise interplay between the field enhancement and the nanoparticle shape and size was explored in a recent EELS-based tomography
The study of non-repeatable (chemically irreversible) processes constitutes another distinct variant of MDM, prominent aspects of which are the investigations of growth processes and catalytic reactions in situ. Dedicated environmental TEMs include sophisticated differential pumping systems that allow the electron beam to propagate in high vacuum except for the small volume around the sample. Alternatively, novel MEMS-based holder designs have produced ‘nanoreactors’, which incorporate thin membrane windows that separate the sample environment from the high vacuum environment of a conventional electron microscope.

Figure 7 highlights a recent example of a time-resolved in situ study to better understand the changes in the structure of catalytic nanoparticles in response to changes in the local gaseous environment. In this case, as the Pt nanoparticle converts CO to CO2 in the presence of oxygen, the nanoparticle transforms from a spherical to a more faceted shape. As the CO conversion decreases, the nanoparticle transforms back to a more spherical shape. This process repeats to generate a remarkable structural oscillation that is intimately coupled to the CO conversion [53].

7. Crystallographic MDEM

As many technologically important chemico-physical systems are crystalline in nature, techniques that can map the local crystallography in two and three dimensions are of great value. By recording electron diffraction patterns at every pixel in a real space scan of the region of interest, a 4D data set is recorded that enables the local symmetry, orientation and phase to be determined in an atomistic fashion, with nanometre resolution.

As a first example, scanning convergent beam electron diffraction (CBED), with nm-sized probes, was used to reveal structural fluctuations in the relaxor ferro-electric $\text{1-x} \cdot \text{Pb(Mg}_{1/3}\text{Nb}_{2/3})_\text{O}_3\text{-x} \cdot \text{PtTiO}_3$ ($\text{PMN-PT}$) [54]. These systems are known for having complex domain structures (of the order of a few tens of nanometres) yielding twinned-state contrast in TEM images. The scanning CBED results provided direct experimental evidence for variations in ionic displacements and fluctuations in local polarisation at a scale much finer than any compositional variations found using EDS.

Analysis of crystal orientations in polycrystalline and multiphase systems can now be accomplished routinely using the automated crystal orientation measurement (ACOM) method [55], in which electron diffraction patterns, often in perestroika mode to increase the extent of reciprocal space explored, and often using a convergent beam but with a modest convergence angle, are compared to a library of simulated patterns to facilitate rapid orientation determination. The high speed of the scan (100 frames per second) is possible thanks to the ACOM method being applied not only for metals, ceramics and semiconductors, but also as a ‘tow-doze’ technique for beam-sensitive organic materials, even without cryo-cooling [56], and to monitor, for example, lithium migration in the re-chargable lithium-ion battery material LiFePO4 [57]. Conventional imaging and spectroscopy may struggle to identify the changes in the lithium content directly, but the lattice variations introduced by the loss (or gain) of lithium, may facilitate identification straightforward.

Nanocrystalline metals exhibit a range of chemical and physical properties that are different from, and, depending on the application, often superior to their bulk counterparts. An effective method to produce such materials is electrodeposition which can lead to a remarkable structural hierarchy in which nanocrystalline grains are arranged within mesoscale ‘colonies’. Figure 8a shows scanning diffraction (ACOM) maps at the boundary between these colonies [58]. The method is able to determine with high accuracy the orientation of each nanocrystalline grain, establish a clear
However, such crystallographic MDEM can be extended even further, firstly coupled to in situ studies to provide information as a function of time and/or strain, and secondly to provide an additional spatial dimension to yield genuine 3D crystallographic data. In situ crystallography at the nanoscale is especially important in order to study grain growth and the complex interplay of size and microstructural changes. In Figure 9a we show examples of orientation maps which are essentially snapshots of nanoscale grain growth as a function of strain [59]. In this case a nanocrystalline gold film, prepared by magnetron sputtering, has been tensile strain and the deformation process understood by examination of grain size, grain orientation and rotation and twinning/detwinning both over a micro-sized area and locally using selected grains. 

While such orientation maps encode large amounts of crystallographic data, in real most specimens are heterogeneous in three dimensions and so such maps are, at best, projections of a complex 3D microstructure. There is therefore a pressing need to extend this analysis to incorporate the third spatial dimension. One approach [60], applied as a proof-of-principle to polycrystalline aluminium, is to use a series of hollow cone dark-field (HCDF) images, in which, by varying systematically the cone and azimuthal angles, grains with different orientations (and thus scattering to different parts of reciprocal space) can be differentiated and their orientation determined. By repeating at successive tilts, a full 3D orientation map may be reconstructed, see Figure 9b.

R.K.L acknowledges a Junior Research Fellowship at Clare College, P.A.M. acknowledges funding from the European Research Council under the European Union’s Seventh Framework Programme (FP7-2007-2013) [281228] for the ‘Dynamics of Inductivity for Funding JYM] is grateful for the support of the Kohn Foundation.

References


John Meaney Thomas has been a Honorary Professor of Science and Chemistry in Cambridge ever since he relinquished his directorship of the Cavendish Laboratory at the beginning of Great Britain for which he was knighted, and the chemical research and teaching for which he was knighted, and the chemical research and teaching for which he was knighted, and the chemical research and teaching for which he was knighted, and the chemical research and teaching for which he was knighted, and the chemical
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Probing ultrafast dynamics with attosecond transient absorption

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Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cpllett

ARTICLE INFO

Article history:
Received 19 December 2014
In final form 22 December 2014
Available online 30 December 2014

ABSTRACT

The broad bandwidth of an isolated attosecond pulse excites a vast number of states simultaneously, and the corresponding absorption features can be used to resolve exceptional temporal resolution. Few attosecond transient absorption experiments in gases using isolated attosecond pulses are performed in two regimes, one in which the attosecond pulse is overlapped in time with a near-infrared (NIR) pulse and one in which the NIR pulse follows the attosecond pulse. In the latter regime, the attosecond pulse first interacts with a sample, then the observed absorption features are modified by a NIR pulse, which interacts with the sample well after the attosecond pulse has passed. In these experiments, which seem counterintuitive when compared to conventional transient absorption spectroscopy, the weak attosecond pulse induces a polarization of the medium, which is then perturbed by the time-delayed NIR pulse. Recent measurements demonstrate the rich variety of information that can be extracted in this regime.

1. Introduction

Electronic dynamics in atoms and molecules typically occur on a few-femtosecond or sub-femtosecond timescale. These processes are too fast to be resolved by ordinary femtosecond optical laser pulses. However, in the past ten years, techniques to generate isolated pulses with durations of a few hundred attoseconds, or even shorter, have been established. These isolated attosecond pulses provide unprecedented opportunities to study ultrafast electronic dynamics on a few-femtosecond timescale. Isolated attosecond pulses are generated using high harmonic generation, in which a femtosecond laser pulse is upconverted to produce photon energies in the extreme ultraviolet (XUV) [1], in conjunction with optical gating techniques. The short duration of the pulse necessarily results in a broad and continuous spectrum, with bandwidths ranging from a few electron volts (eV) to tens of eV and central photon energies typically between 10 eV and 100 eV. These ultrashort pulses have been used in many successful experiments incorporating photoinjection and ion detection methods. For example, attosecond pulses have been used to measure the few-femtosecond timescale of Auger decay after core excitation of krypton [2] and to measure the time delay between the emission of an electron from two different atomic orbitals in neon [3].

The broad and continuous bandwidth of an isolated attosecond pulse, with photon energies in the extreme ultraviolet (XUV), is well suited to absorption measurements. The XUV photon energies can access highly excited states such as Rydberg states approaching the ionization limit or autodetaching states embedded in the ionization continuum. Electronic dynamics can be tracked in real time by monitoring the resulting change in the absorption spectrum.

The majority of attosecond transient absorption experiments have been performed on rare gas atoms, which are relatively simple systems that still manifest complex behavior. However, the recent application in our group of attosecond transient absorption to observe the transfer of electrons from the valence band to conduction band in solid silicon [4] illustrates the generality of the technique. Attosecond transient absorption will soon be extended to study gas phase molecular systems, but the focus of this article is the experiments performed on rare gas atoms, in which a variety of novel phenomena have been identified.

Isolated attosecond pulses can be utilized in novel transient absorption experiments, in which the XUV attosecond pulse first passes through the sample, then a near-infrared (NIR) laser pulse follows at a time delay. It may seem counterintuitive that a change in the absorption spectrum of the XUV pulse can be observed when the NIR pulse follows the XUV pulse. This unconventional pulse order is possible because the XUV pulse induces a polarization of the medium. This polarization persists long after the XUV pulse passes through the sample, and it dephases on a timescale that depends on the lifetime of the states excited, which can range from tens of femtoseconds for a short-lived autodetaching state to nanoseconds for an atomic Rydberg level. The subsequent NIR pulse perturbs this polarization when it interacts with the sample. The macroscopic polarization is formed by a collection of oscillating dipole moments, which emit light. This emission is then dispersed in a spectrometer, essentially measuring the Fourier transform of the time-dependent XUV absorption features are observed due to destructive interference between the emission from the excited sample and the transmitted broadband pulse. Because the induced polarization has been perturbed by the NIR pulse, the measured absorption features change. This is schematically shown in Figure 1.

The temporal resolution of a transient absorption experiment depends on the duration of the laser pulses used in the experiment while the resolution in the frequency domain depends only on the energy resolution of the spectrometer, as described by Pollard and Mathews [5]. This is because the final absorption measurement, which is the signal at the detector integrated over all times, is not time-dependent. Therefore, attosecond transient absorption measurements can be performed with both excellent temporal resolution and good spectral resolution.

In conventional transient absorption spectroscopy, a weak broadband pulse is used to measure the absorption spectrum of a sample. A pump pulse manipulates dynamics, and changes in absorption features are observed when the broadband pulse follows the pump pulse. These methods have been successfully extended to XUV photon energies. In the femtosecond experiments of Loh et al. [6], a femtosecond near-infrared (NIR) laser pulse is used to induce strong-field ionization in a sample. Afterwards, the absorption of the XUV pulse is measured, and changes in the absorption are observed as the sample becomes ionized. Analogous experiments using attosecond pulses instead of an XUV pulse train were initially proposed by Pfeifer et al. [7]. Later experiments using isolated attosecond pulses by Gayk-Grum et al. [8] detected quantum beating in a wavepacket created in Kr+ after strong-field ionization.

Attosecond transient absorption experiments can thus be divided into three distinct categories based on the relative time delay between the NIR and attosecond pulse: relative time delays when the NIR pulse precedes the attosecond pulse, when the NIR and attosecond pulses are overlapped in time, and when the NIR pulse follows the attosecond pulse. In conventional transient absorption experiments, the range of time delays when the NIR pulse follows the XUV pulse might be deemed uninteresting, as no dynamics can occur before the pump pulse has interacted with the system. However, important recent results in attosecond science have capitalized on transient absorption experiments in which the NIR pulse overlaps with or follows after the attosecond pulse. This Frontiers article focuses on the rich variety of dynamics that can be observed and characterized in these two regions of relative NIR/attosecond pulse time delay.

2. Experimental techniques of attosecond transient absorption

A generalized experimental apparatus for attosecond transient absorption is shown in Figure 2. Similar apparatuses used by other groups are described in detail by Chini et al. [9] and Ott et al. [10]. A NIR pulse (duration of approximately 78 fs) is first split by a beam splitter in an interferometer. One arm of the interferometer generates the attosecond pulse, while the other arm acts as the NIR probe pulse. The XUV generating arm may pass through optics to implement an attosecond optical gating technique, such as Dual Optical Cathil [11], which manipulates the laser field in order to produce a single attosecond pulse. The pulse then enters the vacuum system and is focused into a gas cell, in which the high harmonic generation process occurs. After this gas cell, an XUV attosecond pulse is produced and propagates collinearly with the residual femtosecond laser field. This residual light is subsequently blocked by a metal foil, which also acts as a filter for the attosecond pulse spectral bandwidth. The attosecond pulse is then focused by a gold-coated grazing incidence toroidal mirror. The NIR probe arm propagates outside the vacuum system. A relative delay can be introduced in this arm, and fused silica can be added for optimal pulse compression. In the apparatus shown here, the NIR pulse is first focused by a spherical focusing mirror and then is recombined with the XUV pulse by a mirror with a small hole drilled through it. The XUV pulse passes through the hole in the center of the mirror, while the NIR pulse reflects off the mirror, resulting in an annular beam.

Figure 1. Simplified diagram of transient absorption. (a) XUV-only absorption measurement. The XUV pulse induces a polarization in the sample (left). The transmitted XUV spectrum (middle) shows a clear absorption feature and the calculated absorption (right) displays a single peak. (b) The NIR pulse perturbs the polarization at some delay (middle), altering the transmitted spectrum (middle) and creating midband or altered absorption bandshapes in the expected absorption (right).
The NR and XUV pulses are then overlapped spatially in a gas cell or jet where they interact with the sample. After passing through the sample, the NR pulse is blocked by a metal foil. The XUV pulse is dispersed by a grating and its spectrum is detected, typically by an X-ray CCD camera. A variation on this apparatus that has been used in some of the experiments discussed later in this article (e.g. Refs. [12, 13]) instead incorporates a compact interferometer that introduces the relative delay between the XUV and NR pulses. Then, the two beams travel collinearly into the vacuum system. Both types of apparatus are versatile, as each arm of the interferometer can be manipulated separately.

3. Induced polarization

The induced polarization is a macroscopic sum of the individual oscillating dipoles of the atoms or molecules in the sample. The polarization is induced by the initial excitation, follows changes in the electric field near-instantaneously, and dephases over some timescale. This article will consider only experiments with gas phase targets. Transient absorption spectroscopy has also been performed in solid samples such as silicon and fused silica [14, 15], however, dephasing of the polarization induced by the XUV pulse occurs much more rapidly in a solid than in a gas sample. For example, in silicon, the dephasing time of the XUV-induced polarization was estimated to be 100 as [14], while in a gas the dephasing time can be much longer than the timescales of typical attosecond transit absorption experiments. Due to this disparity in dephasing timescales, perturbation of the induced polarization by a few-femtosecond NR pulse that follows the XUV pulse initially appears to be an effective measurement technique in the gas phase but not in solids. With shorter pulses, however, this counterintuitive regime of time delays could also be explored in solids.

The polarization induced in a sample is related to the electric field of the broadband pulse used for excitation. Applying the slowly varying envelope approximation (e.g. assuming that the spatial envelope of the pulse is large relative to the wavelength) gives the following relation between the field and the polarization:

$$\mathbf{E}(t) = \int_{0}^{\infty} \mathbf{P}(\omega) \mathcal{F}(\omega, t) \left[ \mathcal{A}(\omega, t) \right] \frac{d\omega}{2\pi}$$

where $$\mathbf{E}(t)$$ is the field of the pulse, $$\mathbf{P}(\omega)$$ is the induced polarization, $$\mathcal{F}(\omega, t)$$ is the Fourier transform of the pulse, and $$\mathcal{A}(\omega, t)$$ is the wavevector of the pulse, which propagates along $$\mathbf{z}$$. The polarization is uniform in space (namely, along the $$\mathbf{z}$$ axis) and the electric field is proportional to the polarization as

$$\mathbf{E}(\mathbf{r}) = n_{0} \mathbf{P}(\mathbf{r})$$

In the treatment of Pollard and Mathies [15] the response of the system is separated into linear and nonlinear components. The linear response of the system is related to the broadband pulse (the absorption of that pulse) and the nonlinear component reflects the effects of the pump pulse on the system. Then, the absorption cross-section is proportional to the polarization as

$$\sigma(\omega) \propto n_{0} \mathbf{P}(\omega) \mathcal{F}(\omega, t)$$

where $$\mathcal{F}(\omega, t)$$ is the third-order component of the polarization. This is the lowest order that incorporates the effect of the pump pulse on the system, although higher order terms may also be considered. However, the response of the system may not necessarily be separable into components of different orders. A more general method [15] to calculate the transient absorption spectrum involves first calculating the single atom response function as:

$$\tilde{E}_{x}(\omega) = 2 \Im \left[ \tilde{E}_{x}(\omega) \tilde{E}_{x}(\omega) \right]$$

where $$\tilde{E}_{x}(\omega)$$ is the Fourier transform of the time-dependent dipole moment and $$\tilde{P}(\omega)$$ is the Fourier transform of the electric field of the XUV. The macroscopic polarization, or the polarization of the entire sample, can be approximated as

$$\tilde{P}(\omega) = \rho \tilde{P}(\omega)$$

where $$\rho$$ is the number density of the sample. Thus, the dipole moment can be considered as a proxy for the polarization, and the single atom response function approximates the measured transient absorption spectrum. The key differences between the single-atom response and the effects due to propagation through a sample composed of many atoms will be discussed in Section 4.3. If the polarization of the medium is simply calculated by summing the single-atom response functions, the cross-section is then given by

$$\sigma(\omega, \mathbf{r}) \propto n_{0} \mathbf{P}(\omega) \mathcal{F}(\omega, t)$$

Considering the relationship between the Fourier transform of the time-dependent dipole moment and polarization in Eq. (5), this expression for the absorption cross-section agrees with the expression given in Eq. (3) but is more generally applicable. This mathematical treatment can then be used to model the effect of the NR pulse on the system, and it will be applied to specific cases in the following sections.

4. Regimes of attosecond transient absorption spectroscopy

4.1. Time overlap of the NR and XUV pulses

Dynamics observed when the NR and XUV pulses are overlapped in time can be broadly separated into two categories: a coupling between states that is induced by the NR pulse and an interference between multiple pathways leading to the same final state. Processes in the former category include Autler–Townes splitting and the observation of light-induced states (LIS), while interference between two pathways can manifest as subcycle interference fringes.

The helium atom is a much-studied system, due to the ease of theoretical calculations and the convenience of use in experiments. Transient absorption experiments were performed in helium in conjunction with time-dependent Schrödinger equation (TDSE) calculations by the Schauer group [16]. In both the experimental measurements and the theoretical work, new features that do not correspond to an allowed atomic absorption are observed when the NR and XUV pulses are overlapped. These features are assigned as light-induced states (LIS), which become visible in the absorption spectrum as a result of population transfer from the ground state ($$1S$$) to dark states (1ns or 1nd) via a resonant process requiring one photon of the XUV and one photon of the NR. The LIS acts as the intermediate state in this process, which can be thought of as an analog to Raman spectroscopy. This mechanism was confirmed by calculations in which the x and s states were removed from the calculation as a way of eliminating these observed states.

Figure 3a shows the mechanism that creates a LIS that couples the ground state to the dark 1Is state, and Figure 3b shows the experimental observation of that LIS. Observation of LIS in a transient absorption spectrum allows the dark states to be located in energy and identifies which coupling pathways are dominant in the system under consideration. LIS could also be used to transfer population to dark states that are not accessible by one-photon transitions from the ground state. Another effect that also results from NR coupling to a dark state is Autler–Townes splitting [17], which occurs when the NR photon energy is close to resonant with the transition to a dark state. A single absorption feature is split into a doublet as a result of strong-field coupling between the initially excited state and a dark state. This splitting is analogous to the phenomenon of electromagnetically induced transparency (EIT). The splitting of an absorption feature into a doublet results in increased transmission of the XUV light at the original position of the resonance. EIT has been studied theoretically [12, 18–20] and experimentally observed using femtosecond XUV pulses [21, 22]. EIT as well as more complicated splitting of absorption features in XUV transient absorption was noted in calculations by Gaarde et al. [15]. The observation of this splitting instead of LISs could distinguish which possible coupling pathways are most important using a certain probe pulse. EIT could also be used to manipulate the spectrum of XUV pulse, by creating holes in the spectrum at resonance positions.

Although the coupling mechanisms by which LISs and Autler–Townes splitting are observed are similar, the most obvious difference between these two phenomena is whether a change in absorption is observed at the position of a bright state (Autler–Townes) or at a photon energy that does not correspond to an allowed one-photon transition from the ground state (LIS). Which effect is observed depends on the spacings between the energy levels in the target system relative to the photon energy of the NR pulse. If the NR pulse is close to resonant with the transition between an initially excited state and a dark state, Autler–Townes splitting is observed. However, as the position of the dark state moves away from resonance with the NR photon energy, a LIS is observed instead. This is shown in Figure 4 for two cases: Figure 4a and c show Autler–Townes splitting, occurring when the NR pulse is resonant with a dark state, and Figure 4b and d show a LIS becoming visible instead when the NR is far from resonant with this transition. This transition from Autler–Townes splitting to the appearance of the LIS could be probed by scanning the wavelength of the probe pulse, which would also identify the dominant coupling pathways to dark states.

The LISs were theoretically predicted to be sensitive to the NR intensity, and a recent work characterized the intensity dependence of the LIS in helium [23]. The discrepancy between the shifts in the LIS position predicted by theoretical work and the shifts observed in experiments was attributed to the difficulty of accurately determining the LIS intensity in the experimental measurements.

Figure 2. Typical attosecond transient absorption experimental setup. BS: beam splitter, FM: focusing mirror, HRS: high harmonic generation, FS: fused silica, HMD: hole mirror. The outlined gray area represents the extent of the vacuum chambers. Details are outlined in the text.

Figure 3. Light-induced states (LISs): (a) Energy level diagram showing a LIS in helium. Purple solid arrow: XUV pulse, red dotted arrow: NR pulse. Levels that can be accessed by allowed transitions from the ground state are shown as black horizontal lines, dark states are gray. LIS is dotted. The energy level positions are aligned with the resonance in the XUV transient absorption data showing a LIS (marked by red box). Negative time delays: XUV pulse precedes NR. Adapted from [16].
The Stark shift induced by the NIR pulse can also induce a change in the absorption lineshape, because the NIR field causes a phase shift in the induced dipole moment. This effect was treated theoretically by the groups of Schafer [24] and Samanta [25] for long-lived states and by Chu and Liu [26] for autotuning states. Ott et al. [10] first characterized this effect experimentally, showing that the Lorentzian lineshapes produced in helium corresponding to long-lived atomic states can be converted to Fano profiles, and vice versa. The phase shift depends on the NIR intensity and duration, and is of long-lived states. An example of this NIR-induced lineshape change in the absorption of Rydberg states of neon is shown in Figure 5. The top panel of Figure 5 shows the XUV-only absorption, in which the features appear as weak, narrow peaks, and the bottom panel shows the absorption spectrum when the XUV and NIR pulses are temporally overlapped and the absorption lineshapes have become Fano-like. This laser-induced phase is a clear example of how the NIR pulse can be used to precisely manipulate the absorption spectrum. The observed Fano lineshape parameter of the absorption line also characterizes the magnitude of the phase shift induced by the NIR pulse.

Other features observed in attosecond transient absorption measurements when the NIR and XUV pulses are overlapped in time are due to interference between two pathways that both result in the same final state. Subcycle interference features were predicted theoretically by the Schafer group [16,27] and observed in transient absorption measurements performed by Chu et al. [9] and X. Wang et al. [28]. These fringes have a period of approximately 1.3 fs, which is half the NIR laser cycle (2.6 fs). The fringes are due to interference between two direct pathways and an indirect pathway.

The direct pathway is merely absorption of one XUV photon, transition of population from the ground state to an excited electronic state. However, population can also be transferred to the same excited state by an indirect pathway: a lower-lying state is excited by the XUV, and then two NIR photons couple the two states. A schematic of these interference pathways is shown in Figure 6a, and the calculation of a single-atom response function for helium, which clearly displays subcycle interference fringes, is shown in Figure 6b. These interference features are observed in both LIS, which are only visible in the delay of the overlap of the XUV and NIR pulses, and in long-lived electronic states, where the subcycle features remain visible when the NIR pulse follows the XUV pulse.

The origin of these features was confirmed theoretically by removing states from the calculation and noting the resulting disappearance of the subcycle features. An analogous experiment was performed by Wang et al. [28], who compared the transient absorption spectrum of neon recorded using a broadband XUV pulse, which can excite a wide range of Rydberg states between 16 eV and the ionization potential at 21.56 eV, to a measurement using a narrowband XUV pulse, which excludes excitations to all states except the 2s2p2P-3P states. Subcycle interference fringes were clearly observed with the broadband excitation pulse but disappeared in the narrowband transient absorption measurement. These subcycle interference fringes indicate that the population in the system is being manipulated on an attosecond timescale, as the NIR pulse transfers population between the initially excited levels.

The population transfer induced by the NIR pulse can be enhanced if there is an atomic or molecular level that can act as a near-resonant intermediate state. Chen et al. [27] have shown theoretically that information about the position of this intermediate state can be extracted from the subcycle interference fringes. The phase of the interference fringes depends on the magnitude of the NIR photon energy relative to the difference in energy between the initial state and the intermediate state in this process. Experimentally, using NIR pulses with varying central wavelength could identify the intermediate state in the coupling process. Subcycle features can also be observed in LIS, and the appearance of the fringes identifies which dark state produces each LIS. The sign of the slope of the fringes with respect to delay indicates whether the LIS is higher or lower in energy than the final dark state [27].

Theoretical work performed by Pfeffer et al. [29] and Wu et al. [30] has shown that the presence of subcycle features in calculated transient absorption spectra depends on the inclusion of counter-rotating terms in the expression for the dipole moment. In theoretical models, the rotating wave approximation (RWA) is often used. Counter-rotating terms that oscillate rapidly, or are small near resonance, may be excluded to simplify the mathematics. This means that terms with frequency $\omega_{\text{Rabi}} - \omega_{\text{osc}}$, where $\omega_{\text{Rabi}}$ is the transition frequency and $\omega_{\text{osc}}$ is the laser frequency, are removed, while terms with frequencies $\omega_{\text{Rabi}} + \omega_{\text{osc}}$ are kept. However, when the ratio of the Rabi frequency $\Delta_{2}$ to the laser frequency is large, the RWA no longer accurately reproduces all of the physical effects. The Rabi frequency is defined as $\Delta_{2} = \Delta_{1} + \Delta_{2}$, where $\Delta_{1}$ is the transition dipole moment and $\Delta_{2}$ is the amplitude of the electric field, so the RWA breaks down when the NIR intensity is high or the coupling between states is strong.

The effect of the RWA was shown in calculations of Autler–Townes splitting in helium [30] and xenon [29]. The magnitude of the splitting depends on the intensity of the NIR field, which is therefore dependent on the RWA-XUV delay. Calculations using the RWA accurately reproduced the overall delay dependence of the Autler–Townes splitting and other structures that were observed in experimental measurements. However, the subcycle features did not appear in these calculations. When instead a full time-dependent Schrödinger equation (TDSE) calculation was performed, the subcycle features appeared clearly, as shown in Figure 7. Another effect that could not be reproduced in calculations using the RWA is the splitting of the absorption features into multiple branches instead of merely into a doublet. This multiplet splitting has been experimentally observed in femtosecond transient absorption measurements of core excited xeon, using 100% NIR pulse intensities on the order of 10^13 W/cm^2 [31]. Multiplet splitting was also proposed as a possible explanation for new features observed in LISs in helium as the NIR intensity was increased, although the spectral resolution was not sufficient to resolve the possible splittings [23]. Using the RWA in theoretical calculations does not fully predict the phenomena that will be observed in an experiment, and full TDSE calculations are necessary to correctly predict or replicate experimental attosecond transient absorption results.

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4.2. The NIR pulse follows the XUV pulse

Experiments in which the NIR pulse follows the attosecond pulse at large time delays (ranging from only a few to tens of hundreds of fs) provide an unprecedented wealth of information about electronic dynamics. Inducing a polarization with the XUV pulse and then perturbing the system with a NIR pulse that follows at delays of a few femtoseconds or longer has been applied to measure decay timescales of autoionizing states and to characterize quantum beating between electronic states.

A recent, very effective application of attosecond transient absorption spectroscopy is directly measuring the lifetimes of short-lived atomic states in the time domain. Autoionizing states were excited in argon atoms by Wang et al. [12] and in xenon atoms by Bernhardt et al. [12]. The absorption features corresponding to short-lived autoionizing states embedded in the continuum appear in the spectrum as Fano resonances. The lifetimes of these states were previously estimated from high-resolution synchrotron measurements [31] to be on the order of tens of fs. Therefore, these states are an excellent test case for comparison of the lifetime determined from the linewidth with the lifetime that is directly measured. The decay of the autoionizing state is monitored by interacting a time-delayed NIR pulse with the target. The initially strong absorption feature is depleted when the NIR and XUV pulses are overlapped, because the NIR pulse couples population out of the initially excited state either to other atomic states or to the ionization continuum. This produces a broadened and weakened absorption feature. The absorption feature then slowly recovers. A schematic of this coupling process is shown in Figure 5a, and experimental measurements of the lifetimes of 5s5p^2S states in xenon are shown in Figure 5b.

The timescale of the recovery of the absorption feature is actually twice the lifetime of autoionizing state. This factor of two arises because the absorption signal is proportional to the polarization rather than the population. This can be derived by calculating the absorption spectrum using Eq. (4). A simple model system will be considered where there are only two states, the ground state (denoted as state 0) and an excited state (denoted as state 1) that is short-lived, with a lifetime r. The population in the excited state after an initial excitation is thus

\[ |\psi(0)|^2 = e^{-\alpha t} |\psi(0)|^2 \]  

(7)  

which decays exponentially with the state lifetime of 1/r. However, the quantity needed to evaluate the time-dependent dipole moment is the total waveform. The time-dependent waveform of this state is

\[ |\psi(t)|^2 = e^{-\alpha^2 t^2/2} |\psi(0)|^2 \]  

(8)  

where \(\alpha\) is the energy of the excited state. The factor of \(\sqrt{2}\) in the exponential ensures that the population decay occurs on the correct timescale, as in Eq. (7). This critical factor will be the source of this factor of two difference in the population and polarization decay. The total waveform is, for the system, after excitation by the XUV only,

\[ |\psi(t)|^2 = C_0 |\psi(0)|^2 e^{-\alpha^2 t^2/2} |\psi(0)|^2 \]  

(9)  

where \(\alpha\) is the energy of the ground state and \(C_0\) and \(C_1\) are coefficients with some time dependence. If only a small fraction of the initial ground state population is excited, \(C_0^2 < 1\). The time-dependent dipole moment is evaluated, keeping only terms that are large near the resonance center, frequency, and modeling the effect of the NIR pulse as a sudden annihilation of the dipole moment at a delay time \(\tau\). This time-dependent dipole moment is then

\[ \mu(t) = C_1(0)|\psi(0)|^2 \rho_{\text{XUV}} e^{-\alpha^2 \tau^2/2} \]  

(10)  

The quantity of interest is the response function versus frequency. In the time-dependent dipole moment must be Fourier-transformed. The absorption on the resonance center, or when \(\omega = \omega_{\text{res}} = \alpha\), is then given by

\[ \langle S(\omega) \rangle = \frac{\mu_{\text{XUV}}^2}{\nu_{\text{res}}^2} \]  

(11)  

The absorption thus decays exponentially with a time constant of \(2/\alpha^2\) or twice the state lifetime. This factor of two difference, which only appears in measurements of decay timescales, is critical to recognize in order to accurately extract a lifetime from transient absorption measurements. Fitting the temporal profile of the dipole–moment function allows for determining the autoionizing state to be determined by a direct measurement in the time domain.

The lifetimes measured by attosecond transient absorption spectroscopy agree with lifetimes calculated from linewidths, using the uncertainty principle, in synchrotron measurements. However, absorption features of short-lived states in molecules can overlap in energy and undergo additional broadening processes, so this technique may need to be applied in a direct measure of the short-lived states that may not be accurately extracted from static absorption spectra.

When considering the temporal evolution of the absorption at a small detuning from the resonance center, more complicated behavior is observed. Investigation of a detuning \(\omega = \omega_{\text{res}} - \omega_{\text{fs}}\) into the expression for the dipole moment and calculating the single-atom response as above results in a function of the form

\[ S(\omega) = \text{const} \left( \Delta \omega e^{i/\alpha^2} \right) \]  

(12)

For photon energies at a small detuning from the resonance center, there is an additional cosine term, which creates oscillations in energy for a given time delay. This is a manifestation of perturbed free induction decay, which occurs when the ringing of a dipole is suddenly stopped. Figure 5c, 5d. In a transient absorption measurement, this effect produces hyperbolic sidebands with spacing inversely proportional to the NIR-XUV time delay. These sidebands are observed in transient absorption measurements such as those shown in Figure 5e and 5f.

Transient absorption measurements when the NIR pulse couples population to the continuum versus to another discrete state are compared theoretically in Li et al. [30]. The calculated transient absorption spectra look similar for low NIR intensities (approximately 10^7 W/cm^2). As the NIR intensity increases, the absorption line shape when the NIR and XUV pulses are overlapped in time varies significantly depending on which coupling mechanism is occurring. If the NIR pulse is coupling to the continuum (i.e., ionizing the state), the absorption feature disappears as the NIR intensity increases because the population becomes ionized. However, if the NIR is coupling to a discrete state, splitting is observed in the absorption feature. Additionally, the time dependent behavior of the absorption at the resonance center also varies due to the different splitting pattern. For instance, Rabi cycling is observed at high NIR intensities if the NIR couples the initially excited state to another discrete state, but not of the NIR pulse is only ionizing the state. NIR intensity dependent measurements can therefore determine the effect of the NIR pulse on the system.

The broadband attosecond pulse can also be used to excite superpositions of multiple electronic states, and the resulting quan- tum beats can be observed using attosecond transient absorption. This effect was predicted in calculations by Chin et al. [37] showing that beating between pairs of np states in helium could be observed in the transient absorption spectrum. Quantum beating was then experimentally observed in long-lived atomic states by exciting a wavepack composed of Rydberg states of neon [38]. Multiple quantum beats were observed, with periods ranging from 10 fs to 40 fs. The most prominent quantum beat observed was between the 2p^2^P(1/2,3/2) and 2p^2^P(3/2,5/2) levels, which split in energy by 0.1 eV. The measured oscillation period was 40 fs, which agrees with the expected oscillation period due to this energy splitting. Figure 5a is an energy level diagram of neon, focusing on the np states, and experimental measurements of quantum beating in the spin-orbit split np levels of neon are shown in Figure 5b. In contrast to the measurement of decay lifetimes described above, in which the decay of the polarization and of the population differ by a factor of two, the beating period of the polarization agrees with the beating period that would be observed by detecting the population. Therefore, the beating period depends only on the energy difference between the two states, which is the same whether polarization or population is considered.

In this measurement, several experimental artifacts are observed due to saturation of the absorption feature and the limited spectral resolution of the measurement with respect to the timescale of the experiment. Figure 5a on a timescale of hundreds of femtoseconds, although the lifetimes of the atomic states are on the order of nanoseconds, and each absorption peak appears shorter when the NIR pulse follows the XUV pulse than in the XUV-only absorption spectrum. These effects are both observed because the NIR pulse artificially shortens the lifetime of the state when it arrives at a given time delay. This shorter lifetime results in a broader absorption feature, and the absorption feature is saturated on the broadening also produces an apparent increase in absorption as the wings of the feature spread to neighboring pixels on the detector. The apparent decay in absorption strength over the timescale of the experiment is then just the decrease in the broadening of the feature as the delay of the NIR pulse increases.
The quantum beating is observed because the NIR pulse couples the initially excited states to neighboring dark states, and the effect of the NIR pulse is to Rabi-cycle population between the states. This mechanism is shown in Figure 4a. The NIR pulse couples the 3 states to 3p states located about 1.5 eV lower in energy, which closely matches the NIR pulse central photon energy. The strength of the beating visible in each feature depends on the strength of the couplings between the initially excited states and the dark states, thus explaining why the modulation depth of the beating could be strong in one state and weak in the other. The appearance of the beating was also shown theoretically to depend on which dark states are accessible within the NIR pulse bandwidth, which explains variations from day to day as the NIR pulse spectrum can fluctuate.

The observation of quantum beating can also be described as a manifestation of interference between two excitation pathways in the molecule. If the two pathways are described in section 4.1. One pathway requires a UV photon to access the 22P5/2(2P2)3d state, one NIR photon to access a dark state (most likely a 3p state), and a second NIR photon to couple from this 3p state to the 22P5/2(2P2)3d state. This pathway is merely direct excitation of the 22P5/2(2P2)3d state by one NIR photon. The energy difference between these pathways is exactly the energy difference between the two states that compose the initial wavepacket. Therefore, the spacing of the resulting interference fringes is the same as the quantum beating period, both corre- sponding to the energy difference between the two states. This interpretation of quantum beating is confirmed in the recent work of Ott et al. [36], who observed the beating of a wavepacket com- posed of doubly excited states of helium. Here, the beating period is 1.2 fs, which is approximately the same as the expected spac- ing of the subcycle interference fringes. The splitting in the subcycle interference fringes between the two states composing the wavepacket corresponds to the energy of two NIR photons, and thus the coupling pathways that allow the beating to be observed are indistinguishable from the general mechanism for observation of subcycle interference fringes.

The quantum beating in the 5S5P9p autotionizing state of xenon has also been observed [36]. The measured oscillation period of approximately 30 fs corresponds to an excited wavepacket lifetime of the 5S5P9p state, located at 20.95 eV, and a neighbor- ing two-electron excited state located 140 eV lower in energy. By comparison to few-level theoretical models, the intermediate state involved in the NIR coupling process could be identified as the 5S5P9S state.

The ability to excite a broad range of states and then track the temporal evolution of each absorption feature individually could be extended to more complicated molecular systems with dense spectra. Exciting a wavepacket and then monitoring individual components can allow the extraction of the lifetimes of the individual states involved in the wavepacket, which would again display a factor of two difference between the decay timescale in the absorption measurement and the population lifetimes of the states. These lifetimes of electronically excited states are deter- mined by electron–electron interactions. The strength of the visible beating in each feature could provide information about the cou- pling strengths between these states and nearby dark states, which opens up new capabilities to use lasers not just passively observe an atom or molecule, but to directly manipulate its electronic states.

4.3. Incorporating propagation effects

In the majority of the calculations discussed above, the trans- parent absorption spectrum is initially calculated using Eq. (4), which applies to a single atom. However, the experimental mea- surements are performed with an ensemble of target atoms. The differences between the single atom picture and the macroscopic measurement have been explored theoretically, in order to cal- culate transient absorption spectra that are in agreement with experimental results, and theoretical work shows that the correct transient absorption spectrum cannot necessarily be calculated by simply adding the single atom results for many atoms.

Attosecond transient absorption experiments are typically performed using low sample densities and short propagation distances, which have been shown by Chen et al. to result in absorption spectra similar to the lifetimes of the excited states with resonances well-separated from other molecular trans- missions, such as the absorption features corresponding to core–level excitations of a heavy atom in a small molecule. The measured lifetimes could then be compared to those predicted from static absorption spectroscopy in order to investigate whether broadening effects are accurately accounted for.

The idea of measuring lifetimes in molecular systems seems simple, but the realistic situation in many molecular systems is likely to be much more complex. Many short-lived states man- ifested in absorption spectra are broad features buried underneath a more complicated multiphoton absorption spectrum, with far stronger absorption lines corresponding to Rydberg series. Tracking the decays of these broad features and disentangling their time- dependence would be challenging. As an example, the behavior of the overlapping features may still be difficult. However, tracking states within a contri- bution to a beating wavepacket may allow individual lifetimes to be determined more accurately. Some of the members of an initially excited wavepacket can decay, the changing composition of the wavepacket as a function of time could be monitored by measuring any of the features in the initially excited wavepacket. Long-lived states in the wavepacket would not show a decay in the absorp- tion pulse, but the short-lived states would contribute to the other states in the wavepacket decay. This decay would differ from the state lifetime by a factor of two, as in the direct lifetime measurements.

Wavepacket excitation in an atom merely results in oscilla- tion of the excited population between different electronic states. However, in a molecular system, wavepackets can be composed of electronic and vibrational states localized at different sites in the molecule. Then, the wavepacket oscillation manifests as a motion of the charge between different atoms or bonds. This has been the subject of some theoretical work in Refs. [42,43] and Remacle and Levine (as in Refs. [44,45]) for many small molecular systems. In these calculations, an electron is removed from the highest occupied molecular orbital and the resulting wavepacket oscillates on a few-fs to faster timescale. This ionization is similar to the simple example above, but the intense NIR pulse, but the initial wavepacket could also be excited using an attosecond XUV pulse and then the resulting wavepacket continues to oscillate through a sequence of times, each followed by an XUV pulse.

Attosecond transient absorption experiments have so far been performed only with a probing pulse centered around 800 nm, with a broadband spectrum spanning the visible and near-infrared regions of the spectrum. A straightforward expansion of the tech- nique would be the use of a varying wavelength probe pulse. The subcycle fringes in the transient absorption spectra due to inter- ference between a direct and an indirect pathway were shown to depend sensitively on the position of an intermediate state in the indirect pathway and the difference in delay between the two. A first experi- ment measuring the subcycle fringes in helium confirmed the expected theoretical behavior of the fringes as the wavelength of the probe pulse was varied.

Varying the probe wavelength is an experimentally feasible technique to observe the smooth transition from a LIS to Auer–Towns splitting (or vice versa) as shown in Figure 4. Also, the energies at which the LIS are observed in the transient absorp- tion spectra depend on the population of the excited states in the system and the NIR photon energy. If the dark state energies are known, the direct and indirect pathways can be manipulated in order to optimize the wavelength to the appropriate energy. Alternately, varying the probe wavelength and noting when Auer–Towns splitting is observed rather than LIS would help identify the strongest couplings between the one-photon allowed states and nearby dark states.
A variable wavelength probe pulse could also be applied to extract new information from lifetime measurements or observation of wavepacket beating. Different coupling pathways between a decaying state and dark states could be preferentially selected to modify the observed decay. The beating strength of each feature in a complicated wavepacket could also provide information about relative coupling strengths between bright and dark states, as the beating strength would change as the probing pulse wavelength is varied. The ability to change the wavelength of the probe pulse would allow manipulation of a target system in order to study the couplings between specific states.

Another future direction for attosecond transient absorption experiments is experiments with two or more attosecond pulses. The focal volume of attosecond sources has continuously improved since the first attosecond pulses were produced. With the development of higher-power laser systems, splitting an attosecond pulse into two pulses with an experimentally useful number of photons in each pulse will soon be realized. Experiments could be performed with only two attosecond pulses, or with two attosecond pulses and a NIR or other ultrashort pulse that perturbs the system. Scenarios for three- or four-pulse experiments based on spectral interferometry methods have been previously proposed [47]. Two attosecond pulses separated by some time delay propagate through a medium, and the final measured spectrum displays an interference pattern from those two pulses. If in between the pulses, some change is induced in the medium (such as ionization of a gas-phase sample), the behavior of the system can be probed by monitoring changes in this interference pattern. This technique, dubbed transient dispersion by Pfeifer et al. [47], was initially proposed as a method to measure the index of refraction of the system by comparing the spectral phases of the two attosecond pulses. However, the second attosecond pulse could also be considered as a direct probe of how the induced polarization has been modified by the NIR pulse.

Multiple attosecond pulses could even be used to apply the ideas of two-dimensional IR spectroscopy to the XUV regime, as proposed by Mukamel et al. [48]. In 2D-IR experiments, a sequence of broadband femtosecond pulses is used to first induce a polarization (or free induction delay, in the language of multidimensional spectroscopy) and then perturb or manipulate this polarization [47]. Cross peaks in the spectrum then reveal the couplings between, for example, vibrational states. These methods could be extended into the XUV energy range to study couplings between electronic states.

6. Conclusion

Attosecond transient absorption has proven to be a powerful technique for direct measurement of ultrafast dynamics in atomic systems. New phenomena are observed when the NIR and XUV pulses are overlapped in time, such as the production of induced states and subcycle interference fringes. Experiments can also be performed in the contrastive regime of time delays where the NIR pulse follows the XUV pulse by a few fs or more, and perturbs the polarization induced by the XUV pulse. Direct measurement of decay lifetimes in the time domain and observation and characterization of quantum beating are just a few examples of the wide applicability of this regime of attosecond transient absorption experiments. In the future, these methods can be extended to investigate ultrafast dynamics in complex molecular systems, which cannot be easily understood from static absorption spectra. Experimental techniques such as varying the wavelength of the probing pulse or generating multiple attosecond pulses to interact with the sample will allow a wider range of atomic and molecular phenomena to be investigated.

Acknowledgements

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, and by the Division of Chemical Sciences, Geosciences, and Biosciences of the U.S. Department of Energy at LBNL under Contract No. DE-AC02-05CH11231. A.R. acknowledges funding from the National Science Foundation Graduate Research Fellowship Program. S.R.L acknowledges the support of the Office of Assistant Secretary of Defense for Research and Engineering through a National Science Foundation and Engineering Faculty Fellowship.

References

Room temperature liquid ionic liquids (TILs) are intrinsically interesting because they simultaneously have properties that are similar to organic liquids and ionic solids. In addition, TILs are increasingly being considered for and used in technological applications. TILs are usually composed of an organic cation and an organic anion. The organic cation, such as imidazolium, has alkyl chains of various lengths. The disorder in the liquid produced by the presence of the alkyl groups lowers the temperature for crystallization below room temperature and can also result in supercooling and glass formation rather than crystallization. The presence of the alkyl moieties also facilitates separation in the liquid into organic and ionic regions. In this article, experiments are presented that address the relationship between TIL dynamics and structure. Time-resolved X-ray fluorescence anisotropy measurements were employed to study the local environments in the organic and ionic regions of TILs using a nonpolar chromatophore that can be placed in the ionic regions of TILs that locates in the ionic regions. In the alkyl regions, the in-plane and out of plane orientational friction coefficients change in different manners as the alkyl chains get longer. Both friction coefficients converge toward those of a long chain length hydrocarbon as the TIL chain increases in length, which demonstrates that for sufficiently long alkyl chains the TIL organic regions have properties similar to a hydrocarbon. However, putting Li+ in the organic cation changes the friction coefficients in the alkyl regions, which demonstrates that the ion structural organization influences the organization of the alkyl chains. Optical heterodyne detected optical Kerr effect (OHD-OKE) experiments were used to explore the orientational relaxation dynamics of RTILs over times scales of a hundred femtoseconds to a hundreds nanosecond. Detailed temperature dependent studies in the liquid and supercooled state and analysis using schematic mode coupling theory (SMT) show that TILs have bulk liquid orientational relaxation dynamics that are indistinguishable in their nature from common nonpolar organic liquids that supercooled. This behavior of the TILs occurs in spite of the segregation into ionic and organic regions. However, when small amounts of water are added to RTIL at room temperature, novel dynamics are observed for the RTILs with long alkyl chains that have been observed in OKE experiments on organic liquids. The results are interpreted that the water induction structure in the ionic regions that cause the long alkyl chains to organize and ‘lock up’ the bulk RTILs. The dynamical measurements indicate that this lock up is irreversible in the formation of RTIL gels that occur over a narrow range of water concentrations.

1. Introduction

Over the last decade, room temperature ionic liquid (RTILs) have generated a great deal of interest because of their very low volatility, enormous viscosity, and thermal stability. RTILs are salts with a melting point below 25 °C. They are often composed of an inorganic anion paired with an aromatic organic cation that contains one or more pendant alkyl chains. The asymmetry of the cation frustrates crystallization, causing the salt’s melting point to drop substantially compared to a common salt such as NaCl.

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Contents lists available at ScienceDirect

Chemical Physics Letters

**A R T I C L E   I N F O**

Article Notes:
Revised 24 September 2014
In final form 20 September 2014
Available online 5 October 2014

**F R O N T I E R S   A R T I C L E**

Dynamics and structure of room temperature ionic liquids

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Received 24 September 2014
Available online 5 October 2014

**A B S T R A C T**

Room temperature ionic liquids (TILs) are intrinsically interesting because they simultaneously have properties that are similar to organic liquids and ionic solids. In addition, TILs are increasingly being considered for and used in technological applications. TILs are usually composed of an organic cation and an organic anion. The organic cation, such as imidazolium, has alkyl chains of various lengths. The disorder in the liquid produced by the presence of the alkyl groups lowers the temperature for crystallization below room temperature and can also result in supercooling and glass formation rather than crystallization. The presence of the alkyl moieties also facilitates separation in the liquid into organic and ionic regions. In this article, experiments are presented that address the relationship between TIL dynamics and structure. Time-resolved X-ray fluorescence anisotropy measurements were employed to study the local environments in the organic and ionic regions of TILs using a nonpolar chromatophore that can be placed in the ionic regions of TILs that locates in the ionic regions. In the alkyl regions, the in-plane and out of plane orientational friction coefficients change in different manners as the alkyl chains get longer. Both friction coefficients converge toward those of a long chain length hydrocarbon as the TIL chain increases in length, which demonstrates that for sufficiently long alkyl chains the TIL organic regions have properties similar to a hydrocarbon. However, putting Li+ in the organic cation changes the friction coefficients in the alkyl regions, which demonstrates that the ion structural organization influences the organization of the alkyl chains. Optical heterodyne detected optical Kerr effect (OHD-OKE) experiments were used to explore the orientational relaxation dynamics of RTILs over times scales of a hundred femtoseconds to a hundreds nanoseconds. Detailed temperature dependent studies in the liquid and supercooled state and analysis using schematic mode coupling theory (SMT) show that TILs have bulk liquid orientational relaxation dynamics that are indistinguishable in their nature from common nonpolar organic liquids that supercooled. This behavior of the TILs occurs in spite of the segregation into ionic and organic regions. However, when small amounts of water are added to RTIL at room temperature, novel dynamics are observed for the RTILs with long alkyl chains that have been observed in OKE experiments on organic liquids. The results are interpreted that the water induction structure in the ionic regions that cause the long alkyl chains to organize and ‘lock up’ the bulk RTILs. The dynamical measurements indicate that this lock up is irreversible in the formation of RTIL gels that occur over a narrow range of water concentrations.

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1. Introduction

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RTILs have applications in organic synthesis, electrochemistry, and separation processes [1–5]. They are also being investigated for a variety of other potential applications, such as as ionic conductors [6]. For a number of years, the general consensus was that there was no significant mesostructure in the long, hydrocarbon tail agglomerating to form non-polar domains and with the cationic head groups and the anions forming tenuous ion channels that penetrated through the long liquid RTILs on relatively long length scales. This view was supported by a number of theoretical studies [7–11]. X-ray scattering experiments initially seemed to support this view, but recent results of a number of RTILs indicate that adding water promotes the alkyl tail aggregation up to a water fraction of ∼0.6 [12], and then up to a volume fraction of water becomes larger [45,46]. It has been observed that 1-decyl-3-methylimidazolium bromide or nitrate (DmImBr or DmImNO3) (similar in structure to many of the RTILs) and the same behavior has been observed for 1-methyl-3-hexylimidazolium dodecyl sulfate (HmImDOS) in 1-decyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (abbreviated as CmimTFSI°) which was chosen as a class of relatively hydrophobic ionic liquids that can be obtained at high RTIL temperatures. Dynamic microscopy of the RTIL indicates that the cationic head group CmimTFSI° is different from the polar headgroup and thus the low viscosities and demonstrate prototypical ionic liquid behavior. For such liquid, the orientational relaxation and the viscosity were measured as a function of temperature. These measurements permit the details of the probe interactions with its environment to be explored with a combination of measurements and a new data analysis. The X-ray charge exchange and the neutron inelastic scattering are similar to each (see Figure 1) and were studied in a series of RTILs with increasing hydrocarbon chain lengths.
In the experiments described here, the observed exponential decay (bi-exponential for perylene and single exponential for MPTS) were related to hydrodynamic properties through the Debye–Stokes–Einstein relation:

\[ \tau = \frac{3}{4} \frac{\eta}{D} \left(1 + \frac{1}{100} \right) \]

where \( \tau \) is the measured orientational relaxation time constant, \( D \) is the orientational diffusion constant, \( \eta \) the viscosity, \( k \) the Boltzmann constant, \( V \) is the molecular volume, \( C \) is a friction coefficient, and \( f \) is the shape factor. For a given molecule, the friction coefficient will contain information on the rotational friction experienced by the molecule. For past particulars, the condition \( f = 1 \) almost always holds. For rotors of similar size in the solvent molecules, the continuum approximation of the solvent begins to break down. This is manifested as a decrease in friction toward the slip limit, for which the value of \( C \) depends on the geometry of the rotor.

Figure 1 shows the structures and dimensions of the fluorophores used in this study. For both molecules, the shape is close to ellipsoidal based on a geometrically minimized structure. Using the van der Waal radii of the constituent atoms, molecular volumes of 225 Å³ for perylene and 343 Å³ MPTS were calculated. From the molecular dimensions, the theoretically calculated and theoretical slip friction coefficients [62,63] can also be generated. These quantities have been reported for perylene and MPTS [36].

2.1. Perylene

Due to the high D₂O symmetry of perylene, the equation for the fluorescence anisotropy simplifies to a bi-exponential. The orientational distributions of perylene are then given by the volume fraction of the molecule and out of the plane. The out of plane motions requires a greater \( A \) than that for solvent diffusion in the manner of, for example, the in-plane motion. In plane rotation occurs about the axis normal to the plane of the molecule, the 2 axis in Figure 1. Perylene is modeled as an oblate ellipsoid rotor, that is, the diffusion constants \( D_{11} < D_{22} < D_{33} \), using the coordinate system of Figure 1. Then the anisotropy decay is [36]

\[ \langle R(t) \rangle = 0.4 \times 10^{-4} \langle 1 - 3 \cos^2 \varphi \rangle \]

Anisotropy studies of perylene have often encountered a well-known phenomenon, the so-called ‘bi-exponential’ decay, that is, the average value of 0.4 [64]. Then the prefactors in Eq. (3) have smaller than the theoretical values of 0.1 and 0.3, in contrast to the in-plane motion. The out of plane motion occurs about the axis normal to the plane of the molecule. The 2 axis in Figure 1. Perylene is modeled as an oblate ellipsoid rotor, that is, the diffusion constants \( D_{11} < D_{22} < D_{33} \), using the coordinate system of Figure 1. Then the anisotropy decay is [36]

\[ \tau = \frac{3}{4} \frac{\eta}{D} \left(1 + \frac{1}{100} \right) \]

The results of the analysis are presented in Table 1 as a list of the experimentally determined average friction coefficients (C) in Eq. (2). As the alkyl chain length increases, the friction coefficient approaches that of perylene in paraffin oil, which is the first indication that the alkyl tail regions of the RTIL behaves like a hydrocarbon when tails are sufficiently long.

From the values listed in Table 1, perylene is found to rotate with significant sub-slip boundary conditions. Rotational diffusion in the sub-slip regime have been studied previously [65,66] and are often attributed to complex solvation structure in the vicinity of the probe molecule. This structure can lead to effective viscous flow through which the molecule can rotate with little hindrance, leading to a decrease in rotational friction below slip. This picture was used to describe the rotational dynamics of tetrazene in alcohols [67].

The perylene/RTIL experiments, the degree of sub-slip increases with increasing alkyl tail length, approaching the value for perylene in paraffin oil at C₄mIm⁺. Although the high symmetrical nature of the bi-exponential experimental data permit the rotational diffusion to be further decomposed into components of rotation in-plane (D₂₀) and out-of-plane (D₂₁). The results are presented in Table 2 as the ratio of the appropriate friction coefficient to its theoretical value for slip boundary conditions. A value of 1 means that the measured and calculated values are the same. A ratio larger than 1 indicates that the measured value is smaller than the theoretical value. A ratio smaller than 1 shows that the experimental value is faster than slip. The trends displayed in Table 2 demonstrate that as the length of the alkyl chain length increases, relative to the theoretical values, the in-plane rotational diffusion becomes faster with a concurrent slower rotational diffusion out of plane. Both the in-plane and out of plane rotational diffusion are converging on the values found in the paraffin oil. The increase in in-plane rotational diffusion constant with alkyl chain length is consistent with previous work on perylene in n-alkanes. For longer alkyl chains, the results are in agreement with a partial hindrance of the alkyl chain along the long axis of the perylene [68,69]. This interpretation is supported by studies of gas phase van der Waal complexes [70]. Therefore, the orientational relaxation trends with RTIL chain length demonstrate that the environment experienced by perylene is increasingly like that of a partially ordered alkane. The trend in Table 2 suggests by a chain length of ten carbons, the alkyl environment would be virtually indistinguishable from a long chain alkane. These convergent trends of perylene demonstrate that the solvation environment of perylene in the liquid ions becomes more alkyl-like as the alkyl chain increases in length. In the context of liquid ionic structure, one might conclude that the aliphatic moiety is dominant in solvating the perylene. This is consistent with simulations on solvation in ionic liquids [71,72], as well as optical Kerr effect experiments [73]. The selective solvation constitutes an effective partitioning of the perylene into the hydrophobic regions of the bulk ionic liquid structure. The sub-slip rotational behavior is describing the structure and microviscosity of the hydrophobic pockets. It is noteworthy to note the apparent lack of a turn-on of nanoscale segregation. Both the in-plane and out of plane friction coefficients change continuously toward those of perylene in paraffin oil.

This interpretation leads to several interesting possibilities. Although not necessarily of the same origin, void spaces in RTILs have been evoked when discussing the solubility of CO₂ [74]. The directionality of the rotational friction (see Table 2) may provide insight into anomalous Diels–Alder reactions in RTILs [38,75]. Towari and coworkers found that the rate of a intramolecular Diels–Alder reaction involving a non-reactive dienophile does not change significantly in going from C₄mIm⁺ to C₈mIm⁺. The reactions are not the same, that is the reaction in C₄mIm⁺ that is most strongly sub-slip, indicating a relatively unhindered rotation produced by the ionic liquid structure that should be relatively insensitive to solvent.

2.2. MPTS

The anisotropy decays of MPTS in all liquids studied are single exponential decays, reflecting the lower symmetry of MPTS compared to perylene and indicating a major role of MPTS rotational diffusion coefficients for the various axes. The decay times \( \tau \) are shown in Figure 3 for the various solvents and, water (B). MPTS is essentially insoluble in C₄mIm⁺, so this liquid could not be studied. Because of the low viscosity, the data for MPTS in DMSO and water have very fast decay times. The data for these two liquids are shown in Figure 3B. Note the differences in the axes between Figures 3A and B. As is the case for perylene, the MPTS temperature dependent data in each liquid is linear within a very small error, demonstrating Debye–Stokes–Einstein behavior.

The friction coefficients for standard conditions is 1. In contrast, the perylene (see Table 1), the MPTS friction coefficients
The torque on the alkyl chain increases. The increase in friction is consistent with larger and larger cations being strongly bound to the MPTS sulfate groups as RTIL solvent goes from CmIm\(^+\) to CmIm\(^+\).

The results presented above are consistent with a picture of RTILs in which there is nanoheterogeneity consisting of ionic regions and alkyl regions. Based on measurements of rotational friction for perylene and MPTS, two distinct rotational environments were found. Perylene undergoes orientational relaxation in the slip to sub-slip regime, that is orientational relaxation is faster than predicted by hydrodynamic theory. As the alkyl chain length of the alkyl cation increases, the in-plane and out-of-plane orientational relaxation friction coefficients converge to the perylene in particular solvent (see Table 2). Perylene partitions into alkane-like environments [35]. The trends in the in-plane and out-of-plane friction coefficients indicate a degree of alkyl chain alignment along the perylene long molecular axis.

MPTS undergoes orientational relaxation with super-stick boundary conditions, in contrast to MPTS in DMso and water, which show approximately stick boundary conditions. The slow orientational relaxation of MPTS is considered to be a non-specific strong solute-solvent interaction [36]. The results indicate that these RTIL cations are bound to the three MPTS sulfonate anions, and the entire assembly undergoes orientational relaxation. The increased volume of MPTS accounts for the slow orientational diffusion. The friction increases with increasing size of the solvent cation, which is consistent with the picture of cations bound to the MPTS sulfonate anion.

2.3. Addition of lithium cations

Relative to the neat liquids, the viscosities of solutions of lithium salts in RTILs increase significantly [50,78,79]. The results of experimental studies [80–83] and molecular dynamics simulations [81,82,84] suggest that RTIL anions aggregate around the Li\(^+\) ions, producing the increase in viscosity. Because of the importance of lithium ion transport to battery operation, the influence of lithium ions on RTIL structure and dynamics is a topic of considerable interest. The alkylimidazolium bis(trifluoromethyl)sulfonyl imide RTILs are attractive for battery applications because of the statistical distribution of alkyl chains as well as good electrochemical stability [85] and broad operating temperature ranges.

The influence of lithium ions on the structure of the alkyl chains was investigated by using perylene as a dynamical probe of the alkyl region structure of 1-butyl-3-methylimidazolium bis(trifluoromethyl)sulfonyl imide ([BMIm][Tf2N]) as a function of the Li\(^+\) concentration [50]. The methodology is the same as used in the study described above that examined the influence of chain length on the structure of the alkyl regions by measuring the temperature dependent orientational relaxation of perylene, which gave analogous results to those obtained in the MPTS in RTIL results given in Table 3 [66]. The formaldehyde – I charged sulfonate groups should interact very strongly with the charged cations of the ionic liquid. The MPTS orientational relaxation data show highly hindered motion that is likely caused by strongly associated solvent molecules. The most obvious possibility is that RTIL cations are bound to the sulfonate anions. A simple calculation can estimate the number of associated solvent molecules that would be necessary to obtain the results for the RTILs given in Table 3. Using the cation van de Waals volumes, the results yield 30, 28, and 3 cations are ‘attached’ to each MPTS alkyl chain in CmIm\(^+\) and CmIm\(^+\) respectively. These numbers, which are all basically 3, correspond to the number of sulfonate groups on MPTS, supporting the idea that cation coordination is responsible for the slow (super-stick) orientational relaxation of MPTS in the RTILs. Furthermore, the friction coefficient increases as the RTIL cation alkyl chain increases. The increase in friction is consistent with larger and larger cations being strongly bound to the MPTS sulfate groups as RTIL solvent goes from CmIm\(^+\) to CmIm\(^+\).

Figure 3. Orientation relaxation times, \(\tau\), for perylene (D), 50 \(m\)L of RTIL solvent in DMSO, or MPTS, as determined from 1H to 1H cross polarization NMR experiments. The results for CmIm\(^+\) and CmIm\(^+\) data have been shifted up 0.1 and 2, respectively. Note the difference in the axes for A and B.

Figure 4. A: Orientation relaxation constants for perylene in [BMIm][Tf2N] solutions at 298 K with various LiTf2N molar fractions. B: Temperature-dependent viscosity of [BMIm][Tf2N] solutions with \(\chi\) = 0.4. The y-axis is presented in a natural log scale. Lines connecting the data points are single exponential fits to the data.

Figure 5. Experimental data and linear fits that were used to calculate the friction coefficient for each RTIL at each temperature.

Figure 6. The in-plane and out-of-plane friction coefficient ratios as a function of lithium concentration.

and the viscosity of [BMIm][Tf2N] solutions increase with LiTf2N concentration, as shown in Figure 4B. The temperature-dependent viscosity is fit well with single exponentials, a small offset (\(\chi\) squared greater than 0.999 for each LiTf2N concentration). The parameters for the exponential fits have been given previously [50], so that the viscosity over the range of temperatures studied can be obtained for the various LiTf2N concentrations.

In Figure 5, the experimental values of the orientational relaxation times, \(\tau\), taken over a range of temperatures for perylene for each lithium RTIL solution are plotted against \(\chi\). To make it easier to see the nature of the results and the trends, the figure shows the data rescaled and shifted. The true slopes of the data, which represent the proportional dependence of \(\tau\) on \(\chi\), have been preserved. Lines connecting least-squares fitted data \(\chi\) of \(0.01\) at each temperature. The linearity of the plots confirms hydrodynamic behavior. To obtain actual values of \(\tau\) for the corresponding \(\chi\) from Figure 5, find the point of interest on the plot and the associated shift and scale values from the inset. Subtract the shift value from \(\chi\) and then divide both \(\tau\) and \(\chi\) by the scale factor.

As can be seen in Figures 4A and 5, as the mole fraction of LiTf2N increases the diffusion constants become slower (the orientational relaxation time constants become longer). This is expected as increasing \(\chi\) increases the viscosity at any given temperature. Figure 6 shows the CmIm\(^+\) alkyl diffusion of perylene with increasing lithium ion concentration is solely a consequence of increasing viscosity or indicates a structural change in perylene’s solvent environment, it is necessary to analyze the trends in the diffusion constants with temperature and viscosity. A useful approach is to consider the unitless friction coefficient \(C\), which represents the coupling between the solute and the solvent and is independent of temperature and viscosity for rotators that display hydrodynamic behavior [62,86]. This is the same method used for the analysis in Section 2.1. Figure 5 shows that the unitless friction coefficient of perylene in all of the samples is hydrodynamic. The friction coefficient \(C\) for rotation about the \(\alpha\) axis of an obtuse ellipsoid is related to the associated \(D\) as [62]

\[
C = \frac{\alpha T}{\beta^2} \quad \text{(4)}
\]

where \(\alpha\) is the volume of the solute, \(\beta\) is calculated from the reaction coordinate-dependent volume of perylene. For perylene in each solution, the ratio of the experimental in-plane and out-of-plane friction coefficients to their theoretical slip values, were calculated as the dimensions of the rotator [62,63]. Figure 6 A is a plot of the friction coefficients with a linear fit to the data points. The friction coefficients change significantly with lithium ion
concentration. The values of the friction coefficients are given else-
where [56]. The fact that the solvents and solvent, as quantified by the friction coefficients, is not constant with LiTf₂N₄ concentration demonstrates that adding lithium ions has an effect on the alkyl region of the RTIL bulk viscosities. As shown in Figure 6, both in-plane and out-of-plane orientational friction coefficients rise with increasing LiTf₂N₄ concentration. The in-plane friction coefficient (C₁₁) is greater than the theoretical slip with no lithium cations in the solution as LITf₂N₄ is added, due to the decrease in slip for all concentrations above γLITf₂N₄ = 0.2. The out-of-plane friction coefficient (C₃₃) increases as C₁₁ increases more in-plane for C₃₃. The decrease in C₃₃ decreases in relative terms than does C₁₁, because C₃₃ decreases by a factor of −6 from γLITf₂N₄ = 0 to 0.4, while C₁₁ decreases by A factor ≈ 3 at the maximum LiTf₂N₄ concentration, γLITf₂N₄ = 0.4. C₁₁ is approaching C₃₃.

In the case of the three alkyl chains γLITf₂N₄ and C₁₁ show that changes in the liquid structure in the RTIL alkyl region in response to increased lithium concentration result in less hindered orientational diffusion both in and out of the plane of pyrene after adjusting for the increased viscosity of the RTIL. This is in contrast to the effect of increasing alkyl chain length on pyrene in 1-alkyl-3-methylimidazolium bis(trifluoromethyl)sulfonimide [101]. As the length of the cation’s alkyl tail increased, the dynamics of the pyrene probe converged toward that of an ordered alkane, with the in-plane C₁₁ (rotation about the x axis) decreasing and becoming sublattice while the out of plane C₁₁ (rotation about the y axis) increased. Therefore, the structural changes in the alkyl region in response to lithium ions are qualitatively different from those that result from changing the alkyl chain length.

The trends in the orientational dynamics of pyrene can provide insights into the changing nature of the liquid structure of the RTIL alkyls. In addition to the regular periodic boundary conditions for orientational diffusion of solute molecules apply when the interactions with the solvent are not strong, e.g., no solute-solvent hydrogen bonding. Slipping boundary conditions are frequently seen for solvents that are similar in size or larger than the solute molecules [67]. Under these conditions, the rotational motion of a molecule does not stop at the wall with which it collides. Instead, the molecule is ‘caged’ by the surrounding molecules and is not undergoing orientational diffusion. The final exponential decay is the orientational diffusion complete randomization of the liquid. To observe the complete time dependence requires a method that can span multiple time scales. The OHD-OKE experiment has the necessary time and amplitude dynamical range to observe changes in the distribution of friction.

The OHD-OKE experiment measures the time derivative of the polarizability-polarizability correlation function, which is directly related to the orientational diffusion correlation function. By combining data from OHD-OKE experiments with those from Figure 6, the OHD-OKE experiment can be used to determine the orientation of solute molecules. The fact that the in-plane ratio is greater than slip and substantially larger than the out-of-plane ratio at 259–274 °C is consistent with the related experimental data. The orientational motion of pyrene and orientational diffusion changes is not limited to the RTILs between 259–274 °C.

3. Bulk dynamics of RTILs and the influence of water

3.1 Pure RTILs

The last section clearly demonstrated the nanoscopic heterogeneity of the RTILs and explicated aspects of interactions with solutes that selectively locate in the alkyl and ionic regions. A remarkable aspect of pure RTILs is that they have bulk dynamical properties that in many respects are indistinguishable from those of relatively simple organic liquids. The dynamics of RTILs were investigated using optical heterodyne detected optical Kerr effect experiments [88-90]. The results are analyzed with schematic mode coupling theory. As discussed above, the values in Figure 6 are the ratios of the measured friction coefficients to the friction of solvents as an alkyl or solvent is added. A value of 1 means the measured friction coefficient is the same as the value for the pyrene model under slip conditions. The slip model corresponds to a theoretical model that does not have a particular local structure that is different from free rotation. When there is little friction, sweeping out the volume of solute molecules by the rotor.

The model alkyl caged in this ideal solvent would have friction coefficients that are much smaller than those for the pure liquids.

The fact that the in-plane ratio is greater than slip and substantially larger than the out-of-plane ratio at 259–274 °C is consistent with the related experimental data. The orientational motion of pyrene and orientational diffusion changes is not limited to the RTILs between 259–274 °C.

The second and third power laws are the intermediate power law and the von Schweidler power law, respectively. This function, which captures the form of the numerical solutions to the schematic mode coupling description (see below) is useful as it permits the power law exponents and the exponential decay time constant to be found. In fitting data, it is necessary to do a global fit to Equation 5 to obtain the exponential time constant as the power laws influence the decay even in the exponential region of the data. The exponent point shows that the schematic description of the RTIL does not change the functional form of the overall bulk liquid orientational relaxation dynamics.

Temperature dependent experiments with analysis using mode coupling theory have been performed on a number of RTILs [51,52,55]. The figure shows the β-relaxation dynamics of 1-butyl-3-methylimidazolium bis(trifluoromethyl)sulfonimide (LiTf₂N₄) at 273 °C, where the liquid is deeply supercooled [52]. For supercooled van der Waals liquids, in exponents z and b are not found to be temperature independent [59,98]. The exponential relaxation is, however, highly temperature independent, with the temperature z increasing, dramatically as the glass transition is approached from above [98]. The lack of temperature dependencies for the z and b exponents is also found for RTILs, as the strong temperature dependence of the z relaxation [51,52]. The inset shows the entire time range of the decay on a semi-log plot. The long time portion of the data is linear, showing that it is an exponential decay law. Over the same time range, the data for the pure liquids, they all have the identical functional form. At short times, the data consist of two power laws, the intermediate power law and the von Schweidler power law [51,98,99], which are followed by an exponential decay [54]. There is a third power law predicted by MCT, called the fast process [89,100] that is not shown in Figure 7. In the supercooled liquid literature, the final exponential decay is referred to as α relaxation. The dashed red line through the points shows the best fit to the empirical fitting function, which is based on MCT analysis.

\[
T(1-\alpha t^{-z}) = \left[ \frac{1}{t_{\alpha}^z} \right]^{1/z} 
\]
The temperature dependence OHD-OKE PMPM data on a log plot. The data sets have been offset along the vertical axis for clarity of presentation. Fits to the data using Eq. [4] are also shown (dashed red curves).

MCT critical temperature $T_c$. $T_c$ is called the ‘ideal’ glass transition temperature because in schematic MCT, the α-relaxation is predicted to diverge at $T_c$ becoming infinitely slow. The cessation of complete structural relaxation predicted by MCT to occur at $T_c$ that is, the liquid becomes non-ergodic, was thought to signal the glass transition. However, experimentally the α-relaxation time does not become infinitely slow at $T_c$ and continues to increase below $T_c$. The experimental glass transition temperature $T_g$ is usually 15% to 20% below $T_c$. Previously reported OHD-OKE data on several supercooled organic liquids obey the MCT scaling relations at temperatures above $T_g$.

As a test of MCT in RTIL systems, the standard MCT scaling law analysis was performed on PMPMs and other supercooled RTILs. The MCT scaling relation for the α-relaxation time constant, $T_g$, gives scaling with temperature as [101]

$$\tau_\alpha \propto (T - T_c)^{\gamma}$$.  

(6)

with $\gamma = \frac{1}{\alpha + \beta}$, and $\alpha$ and $\beta$ are MCT parameters, which are related to each other via [101]

$$d = \frac{1}{\alpha + \beta - 1} \frac{(\alpha + 1)}{\alpha}$$,  

(7)

where $\gamma$ is the gamma function and $\beta$ is the von Schweidler power-law exponent, which is obtained experimentally. The von Schweidler power-law amplitude $d$ is [Eq. (3)] scales with temperature as [101]

$$d \propto (T - T_c)^{\alpha/\beta} = (T - T_c)^{d/\beta}$$,  

(8)

with $\delta = \alpha/\beta$.  

(9)

Using the value 0.49 for $\delta$ determined from the fits in Figure 9, $\alpha$ is found to be 0.28 from Eq. (5). Then $\gamma$ and $\beta$ are 2.79 and 1.36 respectively using Eqs. (7) and (10).

Figure 10A displays the rectification diagram for $\tau_\alpha$ [52]. The experimental data points (the open circles) fall on a line indicating a successful description of the scaling relationship over a significant temperature range. The solid line is a linear fit to Equation 6 using $T_c$, and a proportionality factor as adjustable parameters. The extrapolation of the calculated line to its intersection with the abscissa yields $T_c = 213 K$.

The temperature dependence of the von Schweidler power law amplitude $d$ (plotted as $d^{1/\beta}$) is shown in Figure 10B. A linear fit using Eq. (9) is shown as the solid line. $T_c$ is found to be 231K consistent with the result determined from $\tau_\alpha$. The ratio $\tau_\alpha/\tau_\alpha$ is 0.81. For comparison, the ratios for 2-phenylphenol, ortho-terphenyl, solid diblock copolymer, acrylamide, and glass are 0.82, 0.83, 0.85, 0.79, 0.85, and 0.87, respectively. Therefore, the ratio of the RTIL tails within the range of the ratios for common molecular liquids.

The results shown above for PMPMs and for several other RTILs bring out an important aspect of RTILs. The schematic MCT, which has been very successful in describing van der Waals supercooled liquids, works exceedingly well for RTILs. The functional form of the decay curve and the scaling relations are the same for van der Waals liquid and RTILs. Schematic MCT is a theory of homogenous liquids. There is nothing in it that would take into account the nanoscopic heterogeneity of RTILs. Therefore, very detailed consideration of the temperature dependence of the dynamics of pure bulk RTILs show no differences from homogenous organic liquids.

3.2. The influence of water and chain length on RTIL dynamics

As discussed briefly in the Introduction, co-solvents [41–43] and partially hydrated RTILs [44] are important in many applications and properties of RTILs. Von and co-workers simulated the addition of water to various RTILs and proposed that adding water promotes the α-glass relaxation up to a water mole fraction of about 0.75 and then proceeds to break it up as the volume fraction of water becomes larger.[44,46]. Firestone observed that 1-decyl-3-methylimidazolium bromide or nitrate (DmImBr or DmImNO3) RTILs, groups at a similar mode fraction of water [47] and Bowers noticed the same behavior for 1-methyl-3- octylmimidazolium chloride (OmImCl) [48]. Later, Bhargava and Klein successfully simulated the hexagonal mesophase structure originally proposed by Firestone [49]. The structural changes in RTIL water mixtures may significantly influence processes that occur in them. Therefore, the dynamics of such binary mixtures are important.

In this section, the influence of water on the dynamics and structure of RTILs is addressed. OHD-OKE experiments were performed on a series of 1-alkyl-3-methylimidazolium tetrafluoroborate RTILs and their mixtures with water. Using the phase cycling method, the decays can be followed from a few hundred femtoseconds up to 0.4 microsecond (six decades of time) and over six decades of signal amplitude. The pure RTIL decays are analyzed at two power laws followed by a final exponential decay like those discussed in Section 3.1. As water is added, the viscosities of all the RTIL solutions decrease monotonically. For the shorter alkyl chain samples, and for the longer water concentration of the longer chain samples, as water is added the final single exponential decay, reflecting the complete randomization of the liquid, becomes faster. However, when water was added to the RTILs with an alkyl tail of hexyl or longer, the long time scale orientational dynamics become bi-exponential. The slowest component of the dynamics for the RTILs with an alkyl tail of decyl tails does not obey the Debye–Stokes–Einstein (DSE) equation, which was attributed to significant local structural changes in the alkyl tails. The fast component of the bi-exponential dynamics is assigned to the restricted orientation of the imidazolium head groups. Lascu et al. [50] measured data was analyzed using estimate of the anisotropic sample by the head group prior to complete randomization. The bi-exponential dynamics and non-DSE behavior of the systems indicate that the use of water as an RTIL co-solvent can have effects on reaction rates and other processes that cannot be solely explored through the viscosity.

RTIL/water mixtures were prepared by mass. HmImBF4, OmImBF4, and DmImBF4 are not miscible with water (unless BmImBF4), saturating at water mole fraction of 0.75 at 24.5°C. Water mole fraction is defined as mol H2O/mol added mol added in mol (see Table I). All concentrations were measured with a digital titration after data acquisition for all samples. For the pure RTILs, the water concentration was 100 ppm or less. Dynamic viscosities for BmImBF4 and DmImBF4 solutions were taken from the literature [102–104]. For the OmImBF4 and DmImBF4 solutions, dynamic viscosities were measured with a Brookfield LVDV-1+1 PV viscometer. Multiple literatures values were averaged for the pure viscosity of OmImBF4 [105–110] while the Brookfield viscometer viscosity was measured in the nitroglycerin-box using the Brookfield viscometer. All measurements were done at 24.5°C. Imidazolium tetrafluoroborate RTILs are known to be strongly hydration in water [111] to ensure that the measured dynamics of the binary mixtures were not affected by the hydration effect. The Brookfield viscometer viscosity of fresh and weeks-old samples was compared. No measurable differences were seen.

Here the primary interest is in the long time scale relaxation time of the power law decays. The data were fit with Eq. [5] using only the second and third power laws and the exponential component. A representative OHD-OKE data for three BmImBF4-RTILs on a logarithmic plot (black solid curves) is shown in Figure 10C and its X-axis is called $\tau_\alpha$. The BmImBF4 solution has been chosen for clarity. All the BmImBF4 solution OHD-OKE decays, including those not shown, display similar trends, that is, an exponential.

The fits reproduce the decays well over their entire range. All the exponential amplitudes and decay times from the fits have been...
reported previously [55]. It is notable that such clearly separated bi-exponential decays (see Figure 12) have never been seen before in optical Kerr experiments. Prior experiments on simple molecular liquids, RTILs (including those with dissolved salts), supercooled liquids, liquid crystals in their isotropic phase, and other molecules in aqueous solutions have always shown a long time scale single exponential decay preceded by the power law [61,113].

Bi-exponential decays of orientational correlation function are generally recognized as arising from one of two physical situations. In the first case, there are two separable anisotropies in the sample that resonate at different rates. The fast component of the bi-exponential corresponds to the randomization of the fast subensemble’s orientations, which leaves behind the decay of the slow subensemble’s orientations. Each subensemble completely randomizes. This mechanism would require two distinct and well-defined local structures that each give rise to a single exponential decay, all that is ordered anisotropy. Since the wave nature of the signal comes from the imidazolium head groups [55], for this model to be true, there would have to be two imidazolium type head groups with distinctly different dynamics to distinctly different environments. However, the volume fraction of water in the samples showing bi-exponential orientational decays is ~5% or less. It is physically unreasonable that such a small amount of water can perturb the system to the point of generating two distinct cation subensembles with dynamics that differ by two orders of magnitude. Such a scenario is physically unrealistic.

The alternative case is one in which there is a single ensemble that undergoes orientation randomization with two timescales, one fast and restricted, and one slow and complete. This is known as two timescale rotational diffusion (see a review [55,113,115]). In this model, the fast rotational diffusion component is restricted in a potential cone, while the cone itself rotationally diffuses on a slower time scale. The fundamental function of the correlation function is given by

$$C_{\theta}(t) = \theta^2 \left[ \cos^2(\pi t / \tau_0) - \cos(\pi t / \tau_0) \right]$$

(12)

where $\tau_0$ is the decay time of the diffusion within the cone, $\tau_1$ is the decay time of the cone rotational diffusion, and $\theta$ is the order parameter. Within this model, the fast decay time extracted with Eq. (11), $\tau_1$, is not the cone-restricted reorientation, but is related to it by

$$\tau_1^{-1} = \tau_0^{-1} - \tau_{\text{slow}}^{-1}$$

(13)

and the cone semi-angle, $\theta$, is obtained using

$$\theta^2 = \frac{\cos^2(\pi t / \tau_0) - \cos(\pi t / \tau_0)}{\cos^2(\pi t / \tau_0) - \cos(\pi t / \tau_0)}$$

(14)

where $\tau_0$ obeys the inequality $0 < \tau_0^2 < 1$, with $\tau_1 = 1$ corresponding to a cone semi-angle of 0° (no cone) and $\theta^2$ gives a cone semi-angle of 180° (unrestricted rotational motion) into Eq. (11). As can be seen from Eq. (12), $\tau_0^2$ is the amplitude of the slow decay. While the diffusion constant of the final orientational randomization is given by $D_0 = \theta^2/\tau_0$, the slow rotational constant in the cone-restricted motions (D) depends on the cone angle and is given by the expression

$$D = \frac{1}{4} \left( 1 + \pi \tau_0^{-1} \right) \left( 1 - \frac{1}{\tau_0^{-1}} \right)$$

(15)

where $\tau_0$ is cos $\theta$. Because of this complex dependence on $\theta$, it is non-meaningful to directly compare $\tau_0$ values, but instead comparison was made of $D_0$, which therefore requires knowledge of $\theta$ [55].

The WC model is often applied to systems in which the rotating species is tethered to a slow or immovable scaffold, such as a protein backbone [116] or a polymer chain [117]. The WC model was used to analyze the bi-exponential decays seen for the higher water content mixtures [55].

A standard way to analyze the rotational diffusion times is through the Debye–Stokes–Einstein (DSE) equation, Eq. (2) in Section 2.5,118). While the DSE equation is hydrodynamic, it works remarkably well for describing the rotational motion of molecules, as was shown for the Fluorescence depolarization experiments discussed in Section 2.119–121). In Eq. (2), F, V, C, and T are constants. Then, the rotational relaxation decay time constant $\tau_0$ plotted vs. viscosity [119] should fall on a line if the system obeys the DSE equation, that is, the orientational relaxation is hydrodynamic.

All of the OHDE bi-exponential decay times from the fits are plotted vs. viscosity in Figure 13. For all the RTILs studied here, the addition of water reduces the shear viscosity of the solution. As can be seen in Figure 13A, the long time scale exponential decays in the BmImBF4/water samples show DSE behavior. As the viscosity of the solution decreases, due to a long time scale rotational decay time becomes correspondingly faster, with a value of 1.4 sec for the slow component, which is the most dilute solution (1:100 BmImBF4/H2O). For the next longest chains RTIL, HmImBF4 (Figure 13B), the DSE relation is also obeyed for the slowest exponential, but there is a second, faster exponential relaxation process seen in the 1:1 and water-saturated samples. These are the red circles in Figure 13B-D. The black circles in the figures come from analysis using the WC model discussed above and further below. (For a number of points, the black circle is on top of the red circle.) The red circles in Figure 13B show the DSE plot for the DmImBF4. There is a fast exponential rotational diffusion time that emerges for the water-rich samples [3,1,1,1, and water-saturated, red circles]. At low water content samples are circular (see Eq. (5) (single exponentials at long time) and display DSE behavior (Figure 13B, blue plots at high viscosity). However, as the water content is increased, the long time decays become bi-exponential (see Figure 13C bottom curve). The fast component (red points) still follows the DSE dynamics, however, the very slow component of the bi-exponential fits appears to plateau and turn up as water is added. Thus, while the fast decay is consistent with the orientational relaxation, slow rotational diffusion time is not affected in the water-rich samples in a manner consistent with the DSE equation.

This behavior, which is non-exponential, becomes more dramatic in the DmImBF4 plots shown in Figure 12. Again, the rotation times for the water-poor DmImBF4 samples (blue circles, solid line) are single

Exponentials. The slow single exponential and the fast component of the water-rich samples (intro) are linear in viscosity. But the slow rotation time of the bi-exponential decays in the water-rich samples now moves in the opposite direction from that predicted by the DSE equation. As water is added the viscosity is going down, and yet the slow component of the rotational dynamics is drastically slowing down. For the water-saturated DmImBF4, the slow component is 89 ps, while the fast component is only 790 ps (see Figure 12). The pore (m) based DSE analysis will not converge, as it is a long time scale exponential rotational diffusion time of 14.3 sec. The amplitude of the slow component grows with addition of water and concentration at which the bi-exponential behavior emerges shifts to lower water concentrations as the alkyl tail length increases.

In contrast to the pure RTILs once a sufficient amount of water is added, the mixtures show distinctly bi-exponential OHDE-OKE decays. The bi-exponential dynamics are interpreted as a local softening of the cation alkyl-tail-tail associations [55]. The bi-exponential dynamics are particularly prominent in the water-saturated DmImBF4, in which a very pronounced separation of time scales is observed (see Figure 12). As discussed above, the fast component is attributed to the rotation-in-a-cone motions of the tethered imidazolium head groups and the slowest component to slow, overall cation reorientation due to alkyl tail aggregates. The cone angle for the wobbling isoaxdial head groups was determined for the highest water content DmImBF4 sample, which has the largest separation in time scales. Detailed analysis of the data yielded a cone angle of 41 ± 1 [55]. The local softening of the alkyl tail associations prevents orientational relaxing of the head groups and tails on a single time scale. As water is added, it will strongly interact with the ionic groups of the RTIL. Because there is insufficient water to fully hydrate the ions, the ions and water molecules organize to maximize the water-ion interactions. This organization of the ionic regions forces a structure on the entangled alkyl tails that come together from different ion clusters. For the long alkyl chains, the chain arrangement ‘locks’ them into stable configurations that resist randomization of their orientations. As water is added up to the saturation point for OImBF4 and DmImBF4, in particular, the organization of the ionic regions increases, and the alkyl chain regions become increasingly resistant to orientational randomization. The result is the observed slowing of overall orientational relaxation (slowest OHDE-OKE decay component) as water is added even though the viscosity of the solution only slowly decreases. The constrained alkyl chain motions become so slow that the wobbling motion of the cation head groups occurs on a much slower time scale, and as a separate exponential decay (the faster exponential decay component).

The details of the observed dynamics, that is, the bi-exponential decays at higher water contents, is consistent with the water-induced gelation seen in a few alkyltrimethylimidazolium RTILs [47–49], but the solutions studied here phase separate before a gelation concentration is reached. Gelation of an RTIL is discussed in the next section. The local structuring and softening of the alkyl tail associations suggest that reaction rates in RTILs/copolymer mixtures should be highly dependent on the nature of the reactants and not solely on the overall viscosity of the mixture.

3.3 Dynamic signature of the approach to gelation in RTILs

There are extensive reports of the aggregate behavior of RTILs in water, but most of these involve dilute RTILs in water or studies of RTILs that do not show gelation [44,104–122,124]. Studies of gelation systems have focused largely on the structure of the gel [46–48,135,139]. Dynamic measurements of gelating RTIL-water systems are limited in number and scope [146–148]. The OHDE-OKE studies described above demonstrated that the orientational dynamics anomalously slowed down as water was added in the longer chain RTILs. The orientational relaxation (rotational diffusion) clearly becomes bi-exponential with the slow decay becoming
slower even as the viscosity decreases with the addition of water. This behavior is characteristic of EOF, because the bi-exponential relaxation may be a dynamic signature of the approach to gelation [55]. DimImBF4 and DimMImBF4 saturated at relatively low water contents. Consequently, if more water could be added, these RTILs would gel water.

However, DimImCO is completely miscible with water, and it gels. Figure 14 shows the dependence of the DimImCO viscosity with water content [143]. The viscosity decreases monotonically as water is added (inset) but is added a steady state is reached and the viscosity becomes constant above a water content of about 2.2 to 4.2 water molecules per ion pair (mass fraction H2O = 0.16–0.25, mole fractions 0.69–0.81) the mixture becomes a hydrogel.

Some binary mixtures of pure RTILs show gelation behavior [11, 14]. The RTILs in these systems form clusters or aggregates that orient themselves in the water that surrounds the clusters or aggregates.

We examined DimImCO in the identical manner that we used to study the dynamics of the alkyltrimethylammonium tetrafluoroborate samples [56]. Figure 15 displays the OKE-DATA data as a function of water content. The numbers next to the data curves are the number of son pairs to the number of water molecules (n = 1) and the red line curves are the data (black curves) with Eq. (9) using only the second and third power laws and the exponential when the final decay is single exponential or (11) when the final decay is bi-exponential. The curves have been offset along the vertical axis for clarity of presentation.) After the lowest water content, i.e., the final decay is a single exponential, as was observed for DimImBF4. However, with DimImCO it is possible to go to very high water content. For the highest water content, the data is also a single exponential (constant). In contrast to the very high and very low water contents, the OHD- OKE decays for intermediate water contents are distinctly bi-exponential, similar to the previous experiments on 1-allyl-3- methylimidazolium tetrafluoroborate/water mixtures [56].

As in the treatment of the DimImBF4 and DimMImBF4/water mixtures, the OKE-DATA data for the DimImCO/water decays were analyzed with the bi-exponential model. The bi-exponential model has been used to describe bimodal spectra that are often observed in biological systems. The bi-exponential model is defined by two exponentials of the form:

\[ S(t) = A_1 e^{-t/T_1} + A_2 e^{-t/T_2} \]

where \( A_1 \) and \( A_2 \) are the amplitudes of the two exponentials, \( T_1 \) and \( T_2 \) are the characteristic time constants, and \( S(t) \) is the correlation function.

The bi-exponential model is often used to describe the relaxation of complex systems where two different processes contribute to the overall relaxation behavior. In the case of the DimImCO/water system, the bi-exponential model provides a good description of the relaxation behavior at intermediate water contents.

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1. Introduction

The importance of the chemist’s ambition to selectively activate strong bonds cannot be understated [1]. Alkanes are abundant and cheap feedstocks, yet are particularly resistant to chemical transformations. Metal-oxide catalysts have played a major role in bond-activation successes [2–4]. Selective oxidations can be catalyzed by a variety of transition-metal complexes [7–9]. A metal center’s ability to interconvert between various oxidation and electronic states confers specific reactivity, and typically both the metal and the ligated oxygen play a synergistic role in bond activation [10,11]. In these oxidations, the role of hydroxyl and oxo-groups can have important implications with regards to H-atom abstraction and the subsequent catalytic steps [12–15]. Copper oxide landed itself as a catalytic target of considerable interest after it was predicted to activate methane under mild conditions (a highly sought-after catalytic target due to the inherent richness of methane) [16]. Indeed, in nature, methane is catalytically oxidized to methanol using O₂ as the terminal oxidant by particulate methane monooxygenase (pMMO), where copper is in the active site [17], and in recent progress various “CuO” species have been successfully employed in man-made catalysts [15,18–26].

By isolating reactive species in the gas phase, mass spectrometric (MS) experiments allow for the systematic study of molecular species that may be problematic or impossible to study in the condensed phase [27–31]. Thus, due to the importance of understanding this class of catalytic activity, much effort has been placed on researching different aspects of metal oxide mediated C-H bond activation in the gas phase, such as the reactivity of bare [32] and ligated metal ions [29,33,34], as well as metal clusters [35,36]. Recently, for the first time the diatomic [CuO]⁺ species was experimentally isolated and studied in the gas phase [37]. The generation of this ion was challenging and only small amounts were generated. Another such ligated copper oxo complex is the catiionic 1,10-phenanthroline copper oxo complex, whose lowest energy state, like diatomic [CuO]⁺, is also a ground state triplet (Scheme 1) [38]. This ligated copper oxo complex can be studied...
efficiently in the gas phase, and is quite similar to the active site of many catalysts and enzymes [15,18,21,39]. Three previous studies have looked at the reactivity of the title ligated copper oxo species: (i) gas phase formation via electrospray ionization (ESI), elucidation of possible structures via collision-induced dissociation (CID), and the probing of its reactivity toward C–H bond activation of small hydrocarbons [38]; (ii) a remote C–H bond activation of the ligand [40]; (iii) the reaction with water and its examination via infrared multiphoton dissociation (IRMPD) spectroscopic experiments [41] (Scheme 2a–c respectively).

It was previously thought that there was more than one isomer present within the single m/z 259 value (Scheme 2a) [38]. Originally, the first species was proposed to be the triplet oxo species [(phenOH)CuO] + [41]. Scheme 2a. However, the second isomer was assigned as a self-oxidation product (Scheme 2b), while the second isomer remained unknown. These conclusions were based on CID fragmentations, ion-molecular reactivity and Density Functional Theory (DFT) predicted thermodynamics of the products (Scheme 2a). These experiments also showed that the second isomer dominated when a higher cone voltage was applied. This cone voltage is a voltage potential applied on the ion exit needle and the inner outlet of the mass spectrometer; it increases the kinetic energy, and hence the collision energy of the ions, presumably bringing about the isomerization. Later this assignment of the second isomer was specified with newly obtained experimental evidence from the isomerization. Later this assignment of the second isomer was specified with newly obtained experimental evidence from the isomerization. Later this assignment of the second isomer was specified with newly obtained experimental evidence from the isomerization.

It is well known that in any given mass spectrum, isobaric species can exist. In regards to mass spectrometric experiments, there are several standard procedures for determining the identity of suspected isobaric species [42]. When they share the same nominal mass, they may be distinguished by high resolution MS. However, when the species are isomers, they cannot be separated by a mass analyzer. One standard approach is to carry out collision-induced dissociation on the ion, in order to observe different fragmentations, and then compare the CID spectrum with that of a “true” sample. This approach frequently involves isotopic labeling at specific locations [43,44]. Another way is to conduct ion/molecule reactions (IRM) or derivatization of the molecule. In these cases, the species that coexist may not have the same reactivity towards a given substrate [45]. This difference in reactivity can be exploited to discover the proportion of isomers present via tell-tale “isotopic” molecules [46]. For example, the site of CO extrusion from oxidized carbonate complexes was assigned by ion/molecule reaction with allyl iodide [47]. Finally, spectroscopic experiments can give detailed insight into gas-phase structures, though these experiments are sometimes limited in scope because they require certain conditions [48,49].

An exciting way to separate isomeric species is via ion-mobility spectrometry–mass spectrometry (IMS–MS). In IMS–MS, ionic species may be separated based on their shape, size and charge distribution, in addition to the their mass-to-charge ratio [50]. In particular, travelling wave ion-mobility spectrometry (TWIMS) mass spectrometry is quickly gaining momentum due to the acquisition and thus, increasing accessibility of commercial instrumentation [51]. In combination with the existing gas-phase mass spectrometric characterization techniques (as outlined above), self-oxidized molecular or cluster species can be separated based on their drift time (tD) through an ion-mobility cell, which is dependent on a property called their “mobility” (K, Eqs. 9 and 52).

K = 1/tD

where K = mobility, v = velocity, and tD = drift time.

Measured mobilities do not only depend on the shape of the ion, but also on the specifics of the instrument and instrumen
tal parameters. Thus, with suitable calibration, experimentally measured mobilities can be used to determine collisional cross sections (CCSs). IMS offers a benefit in addition to characterization of CCSs; it can also be used as a gas-phase “purification” technique. In this way isomer-separated reactive species of interest can be studied in a very well-defined manner. Indeed, early IMS instrumentation was specifically developed for ion/molecule reactions [53] and it has been useful for separation and subsequent reaction of electronic states [54,55]. To this end, we have modified a commercial TWIMS mass spectrometer to allow for ion/molecule reactions at various stages of the gas-phase experiments (pre-, during and post separation). Thus, isomer-separated species may have their individual reactivity probes.

Previous gas-phase reactions have explored the reactions of the copper species with saturated and unsaturated hydrocarbons (Scheme 2b), but have not allowed for resolution of the isomers, due to the inability of standard MS approaches to completely separate the isomeric species. Thus, in this report we ask several questions:

1. Are the suspected structural isomers of the copper species resolvable via TWIMS-MS?
2. If so, what type of reactivity does each isomer have toward hydrocarbons?

Further, the ability to selectively activate aryl halides is highly sought-after in order to carry out selective functionalizations. The halogen exchange of X is a desirable reaction and can be mediated by copper nitrate ([Cu(NO3)2]•2H2O) [56]. Further, the ability to selectively activate aryl halides is highly sought-after in order to carry out selective functionalizations. The halogen exchange of X is a desirable reaction and can be mediated by copper nitrate ([Cu(NO3)2]•2H2O) [56].

In addition, we carry out careful electronic structure calculations in order to gain additional mechanistic insight into the mechanism(s) of halogenation and C–C bond transfer reactions. These findings will be discussed in light of experimental results concerning the reaction of aryl halides with the reactive copper species of interest.

2. Experimental section

2.1. Materials and sample preparation

Copper nitrate was obtained from Grüssing, propane from Westfalen AG, and 1,10-phenanthroline, fluoro-, chloro-, bromo- and iodobenzene from Aldrich. All chemicals were used as supplied without further purification.

2.2. Mass spectrometry

Experiments were performed on a Synapt-G2 TWIMS time of flight (TOF) instrument (Waters, Manchester, UK) using a standard electrospray ionization (ESI) source, with a sample pump rate of 4 µl/min and a typical source temperature of 100–120 °C. The source conditions were tuned to allow the formation of metal complexes and were held constant unless otherwise stated (e.g. in ion-mobility studies). The wave height in the travelling wave cell was nominally set to 40 V and the wave velocity to 1100 m/s. As the standard commercial instrument is equipped with mass flow controllers made of aluminum containing Viton O-rings, the type of reactants that can be introduced at various locations of the instrument flight path, without damaging the flow controllers, is limited. Therefore, and to have the option to switch back to normal operation of the instrument if necessary, mass flow controllers having the same flow range, but made of stainless steel (Bronkhorst) and containing Kalrez-O-rings, have been added in parallel to the original with an open-end connection at the low pressure output side of the T-wave ion guide, the trap-region and the transfer guide. The new flow controllers can be adjusted by externally fitted digital control modules (Bronkhorst). The original flow controller for the N2 flow in the IM-cell has been compensated by adding a needle-valve controlled inlet system to allow other substances to be used as mobility gas, or to add co-gases to the N2 flow gas. As the version of the Masslynx software version 4.0 does not allow for adjustment of the Ar flow in the transfer-region, the original flow controller was also modulated by addition of an external digital control module. Every newly added flow controller has been fitted with:
a valve separated Swagelok-connector to introduce volatile liq-
uids, a VCR-connector for admitting corrosive gases, a quick-con-
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ried out in the "transfer cell" region after ion mobility separation,
prior to measurement via TOF-MS.

To separate the instrument from typical office software, the
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nect for non-corrosive gases and a separating valve separated Swagelok-connector to introduce volatile liq-
uids, a VCR-connector for admitting corrosive gases, a quick-con-
nect for non-corrosive gases and a separating valve to the frac-
vacuum pump line at the high pressure input side of the flow
controller. Ion/molecule reactions presented herein were car-
ried out in the "transfer cell" region after ion mobility separation,
prior to measurement via TOF-MS.

To separate the instrument from typical office software, the
Waterstone software Masslynx (version SCN781) and Digi-
Scope (version 2.4) have been installed on a virtual Microsoft Win-

dows 7/64-bit computer, supervised by the virtual guests control
module Hyper-V of an Windows 8.1 Professional installation. As
Hyper-V lacks any COM-connection to the virtual Windows 7
computer, supervised by the virtual guests control
Scope (version 2.4) have been installed on a virtual Microsoft Win-

Waters instrument software MassLynx (version SCN781) and Drift-
uids, a VCR-connector for admitting corrosive gases, a quick-con-
nect for non-corrosive gases and a separating valve separated Swagelok-connector to introduce volatile liq-
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vacuum pump line at the high pressure input side of the flow
controller. Ion/molecule reactions presented herein were car-
ried out in the "transfer cell" region after ion mobility separation,
prior to measurement via TOF-MS.
only -9.9 kJ mol$^{-1}$ (Figure 2a) relative to the separated reactants $^1$ and $^2$, in contrast, $N_2$ adduct formation with $^2$ is exothermic by -66 kJ mol$^{-1}$ (Figure 2b). A second $N_2$ adduct species, with a different topology (Figure 2c), is also exothermic for $^2$ (-27 kJ mol$^{-1}$). Thus, it will also likely to play a role in the equilibria, adding to the complexity of the mobility ($D$) measured.

The viability of this reaction is borne out by the appearance of an $N_2$ adduct in the post-TWIMS spectrum of isomer B (Figure 2b), assigned to structure $^2$. On the other hand, stable $N_2$ adduct formation is not observed for isomer A (Figure 2a, absence of m/z 287), assigned to structure $^1$. The experimental results thus agree with the DFT predictions that adduct-formation is favorable for $^2$, but not for $^1$. They also suggest that despite the potential for ions to experience higher temperature conditions upon initial injection into the TWIMS cell [92], thermalized conditions exist during their TWIMS transit time and in the transfer cell region (Scheme 5), as higher energy conditions would result in $N_2$ dissociation from this complex [91].

Reaction with background water is also observed, appearing in the TWIMS-MS mass spectra of both species at m/z 277 (Figure 3a and b). For isomer $^1$, this reaction is unlikely to proceed via a simple addition reaction (Eq. 13), but rather by the known adduct-ion isomerization pathway (Scheme 2c, Eq. 7), where formation of the singlet ([phenOH]Cu$^+$) complex $^2$ would allow for subsequent facile adduct formation (Eq. 15). In line with this, a simple addition of water is observed for isomer B (Eq. 15) which is assigned to structure $^2$. Additionally, specific to isomer A, i.e. the copper oxo complex $^3$, H-atom abstraction from water is observed, resulting in the formation of ([phenCuOH]$^+$) (Eq. 14).

\[
\begin{align*}
\text{[phenCu(OH)]}^+ &\rightarrow \text{[phenCuOH]}^+ + \text{H}_2\text{O} \\
m/z 277 & \\
&\rightarrow \text{[phenCuOH]}^+ + \text{OH}^- \\
m/z 260 & \\
&\rightarrow \text{[phenOHCu(H$_2$O)]}^+ \\
m/z 277 &
\end{align*}
\]

The CID spectra of isomer A and B are shown in Figure 4a and 4b, respectively. Both isomers are subjected to a collision energy (C.E.) nominally set to 45 V. Isomer A is more prone to fragmentation, as is shown by the diminished parent-ion signal at the same nominal C.E. (Figure 4a). This would be expected from the rather weak Cu–O bond of $^1$ ([phenCuOC]). The fragmentation predominately occurs via the loss of O, forming the [phenCu]+ product at m/z 243 (Scheme 2, Eq. 3). The elimination of [Cu(CO)] is also observed, which is likely to be due to rearrangement (i.e. oxidation of the ligand) prior to fragmentation (Eq. 18), resulting in the formation of the charged ligand fragment ([phen–C]$^+$) (m/z 168).

There is a higher proportion of CO elimination from isomer B (Scheme 2, Eq. 4, m/z 231), consistent with the previous findings from CID studies conducted as a function of cone voltage [93].

Major fragmentation channels or those specific to isomer A include Eq. 3 and Eqs. 16-20. Major fragmentation channels or those specific to isomer B include Eq. 4 and Eqs. 21-25.

\[
\begin{align*}
\text{[phenCu}]^+ &\rightarrow \text{[phen} - \text{H}^+] + \text{[Cu(OH)]}^+ \\
m/z 179 & \\
&\rightarrow \text{[phen} - \text{OH}^- + \text{[Cu]}^+ \\
m/z 196 & \\
&\rightarrow \text{[phen} - \text{Cu} + \text{[CO]}^+ \\
m/z 168 & \\
&\rightarrow \text{[phen} - \text{CO}^+ + \text{[Cu]}^+ \\
m/z 180 & \\
&\rightarrow \text{[phen} - \text{CO}^+ + \text{[Cu]}^+ \\
m/z 168 & \\
&\rightarrow \text{[phen} - \text{CO}^+ + \text{[Cu]}^+ \\
m/z 167 &
\end{align*}
\]

The losses of neutral [Cu(OH)] and of O (Eqs. 17, 3) along with ligand fragmentation via Eq. 16 could be considered as "monitor" products in the CID spectrum of [phenCu]$^+$, while the loss of [Cu(COM)] (Eq. 15) and the complete removal of ligands (Eq. 20) would not, as they are not specific and are observed for both isomers (c.f. Eqs. 24, 25).

Figure 3. Mass spectra of mobility-separated m/z 250 ions: (a) isomer A (CV = 40 V), which is assigned to structure $^1$ (Scheme 5) and (b) isomer B (CV = 50 V), which is assigned to structure $^2$. Figure 4. Individual CID spectra of mobility-separated m/z 250 ions: (a) isomer A (CV = 40 V), which is assigned to structure $^1$ (Scheme 5) and (b) isomer B (CV = 50 V), which is assigned to structure $^2$. Figure 5. Reaction of (a) isomer A and (b) isomer B with propane. The mass selected ion in each spectrum is denoted with $^1$ and the drift time ($t_D$) is given in nms.

That the predominant peaks in the CID spectrum of isomer B ([phenOH]Cu$^+$) are due to fragmentation involving CO extrusion, i.e. direct CO extrusion (Eq. 4), COH loss (Eq. 21) and elimination of [Cu(CO)] is fitting to the expected fragmentation pattern for structure $^2$ possessing an oxidized phenanthroline ligand. The extrusion of CO was confirmed via the use of accurate mass determination by high resolution. Elimination of the oxidized ligand ([phenOH]) could be considered a "monitor" product for the fragmentation of $^2$ ([phenOH]Cu$^+$).

3.2. C–H bond activation: reactions with hydrocarbons

The confirmation of two separate isomers co-existing within the one m/z 259 value raises the question: how do each of these isomeric species behave toward hydrocarbons? Previous experiments revealed the activation of propane with m/z 259 (Scheme 4).

We have thus reacted both isomers A and B post TWIMS separation in the "transfer cell" region of the hybrid TWIMS-MS instrument (Scheme 5). The neutral substrate, in this case propane, is infused into this cell and allowed to react with the separated isomers before they are detected in the TOF mass analyzer. As the isomeric species are separated in time, we are able to obtain individual mass spectra for the reactions of each (Figure 5).

Figure 5 details the mass spectra for each ion/molecule reaction of the two separated isomers with propane as a substrate. Isomer A (Figure 5a) is assigned to structure $^1$ reacts via both O-atom transfer and C–H bond activation yielding charged products at m/z 243 and 260, respectively (Scheme 5, Eqs. 10-11). Adduct formation with the propane substrate is not observed. There is a significant reaction with background water, as might be expected to occur via Eq. 7 (Scheme 2). Isomer B assigned to structure $^2$ reacts only
via adduct formation with background water molecules and nitrogen buffer gas (Figure 5b, m/z 277 water adduct and m/z 287 nitrogen adduct, respectively), as was observed for the species after TWIMS with no introduction of neutral substrate (Figure 1). Thus, these experiments demonstrate that the most reactive species is isomer A, while isomer B shows no sign of being reactive toward propane activation. This reactivity trend is entirely consistent with the assignment of the ions’ structure and their expected reactivity, with the triplet copper oxo species $^1 \mathrm{Cu}$ (Scheme 1) being more reactive [93].

Figure 6. Reactions of isomer A with PhX; X = (a) F, (b) Cl, (c) Br, and (d) I. The mass-selected ion in each spectrum is denoted with $^2$ and the drift time ($t_D$) given in bins. Products due to reaction with background molecules are labeled with roman numerals (I = [phenOH Cu (H2O)]$^+$, II = [phenOH CuOH]$^+$).

Figure 7. Reactions of isomer B with PhX; X = (a) F, (b) Cl, (c) Br, and (d) I. The mass-selected ion in each spectrum is denoted with $^2$ and the drift time ($t_D$) given in bins. Products due to reaction with background molecules are labeled with roman numerals (I = [phenOH Cu (H2O)]$^+$, III = [phenOH Cu (N2)]$^+$).

Scheme 6. Possible C1 mechanisms for concerted oxygen and halogen-atom transfers via $\pi$-bond metathesis (paths C1-a and C1-b), and oxidation of the C1 position without concerted halogen-atom evaporation (path C1-c) relevant to $^1 \mathrm{Cu}$ [phen]Cu$^+$, +PhX (where X = Cl, Br and I).

Scheme 7. Possible C1 mechanisms for oxygen- and halogen-atom transfers and oxidation of the C1 position relevant for $^1 \mathrm{Cu}$ [phen]Cu$^+$, in the reaction with PhF.
3.3. C–X bond activation: reactions with aryl halides (PhX)

The isomers’ individual bimolecular reactivity was successfully probed above, and only isomer A corresponding to $^1$H was found to activate the C–H bond in propane. Next we analyze the reactivity of isomers A and B toward the halobenzene substrates PhX (where X = F, Cl, Br, and I) in order to probe the bond-activation reaction potential. Thus the analogous reactions were carried out as for propane (Section 2 above), that is, the halobenzene-neutrals were introduced to the isomer-separated species in the same manner by leaking them into the transfer cell, post TWIMS separation (Scheme 5).

The experimental series of isomer A reacting with PhX is detailed in Figure 6a–d, respectively. Three types of reactions are observed for all of the four substrates: oxygen–halogen exchange, adduct formation, and oxygen-atom transfer (Eqs. 26, 27, 28a, 28b). For each instance where a halogen atom is present, there is observed for all of the four substrates: oxygen–halogen exchange, detailed in Figure 6a–d, respectively. Three types of reactions are explored with DFT calculations.

The selectivity of this reaction will be further explored with DFT calculations.

3.4. C–X bond activation: DFT predictions

3.4.1. Reactions at the C1 position of the PhX substrates

Bond metadynamics is a key mechanism to activate strong chemical bonds [94,95]. We explored two possible C–bond metathesis pathways (Scheme 6): the first pathway C1-a involves a transition state (TS) geometry with the phenoxy radical in the plane of the bond-forming and breaking moieties of the 4-centered activation complex (TS7,8); in contrast, the second pathway C1-b involves a TS geometry where the phenoxy radical is at a right angle to the plane of this 4-centered reaction center (TS10-8). Both pathways C1-a and C1-b result in the formation of intermediate $^{28}$ from which the phenylnitroxide can be eliminated to generate the product ion $^{29}$. A third potential reaction path at the C1 position has been identified (C1-c, Scheme 6). Here, via a similar TS at the C1 carbon atom, but where the halogen moiety is directed away from the reaction center, a competitive oxidation reaction could allow the halogen radical to be ejected from the complex as X (Scheme 6, TS11-12). After passing TS11-12, intermediate $^{12}$ is generated, in which the halide X is loosely bound to the complex via an interaction with the aromatic ring of the phenylnitroxide. From $^{12}$, both X and the

![Figure 8](image-url)
phenoxy ligand can be eliminated to form $^{13}[(\text{phen})\text{Cu}]^+$, PhO and X (Eq. 28b), or only X evaporates to generate the phenoxy complex $^{12}$(Eq. 28c). However, the latter pathway is not observed experimentally. Alternatively, the halide in $^{12}$(X potentially could be captured via internal return, to form the radical cation $^{12}[(\text{phen})\text{CuX}]^+$ (Eq. 28a) via an intermediate $^{13}$ (Scheme 6).

Different structural geometries are found for each of the halobenzene substrates (PhX) examined. For X = Cl, Br and I, each of the 3 pathways proceeds in the fashion described in Scheme 6. On the other hand, the substrate with X = F follows a more diverse reaction path, involving additional intermediate structures and thus will be discussed separately (Scheme 7). The key structures for X = Cl are given in Figure 8, as these are representative structures of potential C1 reaction energies for X = Cl, Br, and I. The calculated energies for the sequential steps of these reaction pathways outlined above are detailed in Table 1.

For X = Cl, all three of these pathways involving the C1 carbon of PhX are competitive, as the calculated energetic barriers are essentially equal (−10.6, −11.7 and −10.2 kJ mol$^{-1}$ for paths C1-a, C1-b and C1-c, respectively). For both X = Br and I, the reaction pathway through path C1-a is kinetically favored (−22.7 and −29.0 kJ mol$^{-1}$ for TS/TS-7, where X = Br and I, respectively) (Table 1) over the other two possible reaction pathways (−16.5 and −19.9 kJ mol$^{-1}$ for TS/TS-10, and 15.3 and −19.6 kJ mol$^{-1}$ for TS/TS-11) where X = Br and I, respectively (Table 1). This is due to a favorable interaction between the halogen atoms (X = Br and I) and the copper center in TS/TS-7 which is indicated by short Cu-X bond distances in this transition structure (Table 2). The barriers for paths C1-b and C1-c are slightly higher in energy due to the lack of this halogen interaction in TS/TS-10 and TS/TS-11, respectively (cf. longer Cu-X bond distances of TS/TS-8, Table 2). As both iodine and bromine have larger atomic radii and are more polarizable than chlorine, TS/TS-7 is more favored for X = I and Br, than with X = Cl due to the difference in the degree of interaction.

Table 2

<table>
<thead>
<tr>
<th>TS geometry</th>
<th>Cu-X bond</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>TS/TS-7</td>
<td>2.83</td>
<td>2.39</td>
<td>2.52</td>
<td>2.71</td>
</tr>
<tr>
<td>TS/TS-10</td>
<td>2.84</td>
<td>2.37</td>
<td>2.52</td>
<td>2.71</td>
</tr>
<tr>
<td>TS/TS-11</td>
<td>2.63</td>
<td>2.39</td>
<td>2.52</td>
<td>2.71</td>
</tr>
<tr>
<td>TS/TS-12</td>
<td>2.63</td>
<td>2.37</td>
<td>2.52</td>
<td>2.71</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>X</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>D(Cu-OPh)</td>
<td>141.9</td>
<td>112.9</td>
<td>97.6</td>
<td>82.0</td>
</tr>
<tr>
<td>D(Cu-X)</td>
<td>208.4</td>
<td>162.0</td>
<td>116.6</td>
<td>72.4</td>
</tr>
</tbody>
</table>

Table 3

| Homolytic bond dissociation energies (kJ mol$^{-1}$) for the product complexes $^{13}$, $^{12}$ and $^{12}$ (Scheme 6 and Figure 7) |
|-------|-----|----|----|---|
| X     | F   | Cl | Br | I   |
| $^{13}$(PhenCuCl) | 106.0 | 95.0 | 80.0 | 65.0 |
| $^{12}$(PhenCuCl) | 110.0 | 105.0 | 95.0 | 85.0 |
| $^{12}$(PhenCuF) | 115.0 | 108.0 | 98.0 | 88.0 |

Table 4

| Optimized UB3LYP/6-31G** total energies (kJ mol$^{-1}$) for the two alternative reaction paths at the C1 position, C1-b-F and C1-c-F (Scheme 8) relevant to $^{12}$(phenCuCl)$^+$ reacting with PhF. |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| C1-F | F   | Cl | Br | I   |
| $^{11}$ | 106.0 | 95.0 | 80.0 | 65.0 |
| $^{11}$ | 110.0 | 105.0 | 95.0 | 85.0 |
| $^{12}$ | 115.0 | 108.0 | 98.0 | 88.0 |

Figure 8. (a) Energy surface representing potential reaction energies of $^{12}$(X at the C1 position of PhF and (b) representative UB3LYP/6-31G** optimized structures, imaginary frequencies and energies relevant for path C1-b-F and C1-c-F resulting in intermediate 13 formation (Scheme 7).

Both paths C1-a and C1-b (Scheme 6, X = Cl, Br, I) result in the formation of the same relatively stable square planar product complexes, $^{12}$ (Scheme 6), being exothermic by between −202 and −306 kJ mol$^{-1}$ (Table 1), depending on the halogen. However, due to the overall exothermicity of the biradical reaction, this species is able to decompose via elimination of the phenoxy radical, PhO (Scheme 6), resulting in the formation of the radical cation product $^{12}[(\text{phen})\text{CuCl}]^+$ observed in the IMR spectra (Figure 9). The calculated bond dissociation energy (BDE) D(Cu-OPh) of $^{12}$(PhenCuCl)$^+$ amounts to 82–112 kJ mol$^{-1}$ (Table 3), depending on the halogen (X = Cl, Br, I). However, previous experimental studies of the BDE for Cu-OPh from the [CuOPh]$^+$ complex suggests that DFT may overestimate this value [86]. Thus, the actual BDE may be even lower in energy and thus this exit channel more favorable. The dissociation of X from this complex is not predicted here to be competitive, except when X = I. However, in copper complexes of 11, in the singlet (Figure 6d).

Different mechanistic paths are predicted for the reaction of PhF at the C1 position: path C1-a is not viable (no viable TS was optimized on the triplet surface for reaction path C1-a at the green level of theory), and both C1-b and C1-c take place via formation of the biradical (Scheme 7). As the reactions outlined above for path C1-b and C1-c follow a different mechanism, these are denoted C1-b-F and C1-c-F. The representative structures for the reaction with PhF are shown in Figure 7, and the relative energies are detailed in Table 4. Namely, following a similar TS geometry TS/TS-13 (−22.2 kJ mol$^{-1}$), the fluorescent atom is not directly transferred to the copper center, but rather forms an intermediate complex $^{13}$ (Figure 8). Similarly, the oxidation occurring via path C1-c-F (Scheme 7) also occurs in a stepwise fashion; the intermediate formed, $^{13}$, is a rotamer of $^{12}$, and thus is also able to follow the decoordination route outlined in the following for path C1-b-F.

A subsequent, low-lying TS TS/TS-13-8 (−110.0 kJ mol$^{-1}$) allows for the direct F-atom transfer process to the copper center to occur, resulting in $^{13}$ and eventually a subsequent bond dissociation process (Figure 10a) as discussed above (Scheme 6 and Figure 8a). Because of the formation of intermediates during paths C1-b-F and C1-c-F, there is also the opportunity to undergo spin-cross over to a similar geometry in the singlet state [97–101]. For example, for $^{11}$X (−110.1 kJ mol$^{-1}$), there is a lower energy singlet state of similar geometry (−118.1 kJ mol$^{-1}$). Thus, the same F-transfer process outlined above for the triplet state may take place on the singlet surface via a lower energy TS TS/TS-13-8 (−139.2 kJ mol$^{-1}$). Moreover, alternatively from $^{11}$I, it is possible for fluorination to occur at the adjacent electrocyclic carbon via TS/TS-13-14 (Figure 10b). From the so formed intermediate $^{14}$, elimination of a fluoroxyhexadione product (PPD) is possible. Alternatively, F-transfer to the copper center may occur via TS/TS-14-8, yielding $^{15}$, which is able to spin-flip back to $^{13}$ as the triplet complex is lower in energy, and then decompose to $^{13}$ under the elimination of the phenoxy ligand as outlined above. Finally, the formation of an α-exoepoxide is unlikely as it is less.

Figure 10. Energy surfaces representing (a) potential direct F transfer to co-center, (b) stepwise F transfer to co-center (c) representative UB3LYP/6-31G** optimized structure, imaginary frequencies and energies relevant for path C1-b-F and C1-c-F resulting in intermediate 13 formation (Scheme 7).
3.4.4. Chemoselectivity (C2–C4)

In order to reduce the number of pathways to be considered, we first discuss the potential chemoselectivity at the C4 position only (Scheme 8). After passing through ion/molecule pre-complex $[\text{CuO}]^+$, the O-atom transfer takes place via $[\text{TS}15-16]$ to give the cationic copper arnium complex $[\text{TS}16]$. This unstable intermediate is able to undergo spin-crossover to a lower energy singlet state $[\text{TS}16]$. From this intermediate, several favourable decomposition pathways are possible on the singlet surface (Scheme 8): the direct transfer of the H-atom from C4 to the H-atom (path C4-a), the attack of the transfer of the H-atom of the C4 to the O-atom of the C4-atom to form a phenol (path C4-b), the attack of the transfer of the H-atom of the C4 to the O-atom of the C4-atom to form a phenol (path C4-c), or the formation of a copper–carbon bond thus forming a metalacycle (path C4-d). The relative energy for each of these pathways is detailed in Table 7.

Table 7: Optimized UB3LYP/def2-TZVPP relative energies (kJ mol$^{-1}$) for the H-atom abstraction reactions to C4 and subsequent decomposition

<table>
<thead>
<tr>
<th>Path (Scheme 8)</th>
<th>X-</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4-oxygen</td>
<td>$[\text{TS}16]$</td>
<td>-26.0</td>
<td>-27.6</td>
<td>-28.6</td>
</tr>
<tr>
<td>$[\text{TS}17]$</td>
<td>-70.9</td>
<td>-73.0</td>
<td>-74.5</td>
<td>-76.0</td>
</tr>
<tr>
<td>$[\text{TS}18]$</td>
<td>-135.4</td>
<td>-143.4</td>
<td>-158.1</td>
<td>-173.3</td>
</tr>
<tr>
<td>C4-oxygen</td>
<td>$[\text{TS}16]$</td>
<td>-328.4</td>
<td>-329.3</td>
<td>-331.0</td>
</tr>
<tr>
<td>$[\text{TS}19]$</td>
<td>-340.5</td>
<td>-340.5</td>
<td>-340.5</td>
<td>-340.5</td>
</tr>
<tr>
<td>$[\text{TS}20]$</td>
<td>-149.2</td>
<td>-149.2</td>
<td>-149.2</td>
<td>-149.2</td>
</tr>
<tr>
<td>$[\text{TS}22]$</td>
<td>-155.3</td>
<td>-155.3</td>
<td>-155.3</td>
<td>-155.3</td>
</tr>
<tr>
<td>$[\text{TS}23]$</td>
<td>-41.1</td>
<td>-41.1</td>
<td>-41.1</td>
<td>-41.1</td>
</tr>
<tr>
<td>$[\text{TS}24]$</td>
<td>-83.5</td>
<td>-106.3</td>
<td>-108.4</td>
<td>-109.9</td>
</tr>
</tbody>
</table>

Despite the formation of a phenol product being the most exothermic (C4-a), the C4-pathway is for all four halides kinetically less demanding than that of phenol formation, due to a lower energy barrier to the $[\text{TS}18]$ versus $[\text{TS}16]$. The kinetically most favorable path is that of cyclohexadienone formation (path C4-b); the product being exothermic by $\sim 160 \text{kJ mol}^{-1}$. Epoxydation of the phenyl ring is also less kinetically demanding than phenol formation, but results in a less thermodynamically favored product. Thus, while the exothermicity of the overall biomolecule reaction suggests a mixture of product species would be formed, on a kinetic basis, the cyclohexadienone product would be more abundant, due to the less demanding energetic requirements.

3.4.5. Other potential reactions

As it is a pathway observed for aliphatic substrates (Eq. 11), we also examined the possible H-atom abstraction from PPhX. The kinetic barriers are not greater than those previously examined, however, the products formed are slightly above the energy of the separated reactants (Table 7). Thus, the reaction is thermodynamically controlled and not viable at ambient conditions. This lack of exothermicity is in line with the absence of reactivity observed experimentally, i.e. no significant H-atom abstraction is observed. The energy barriers for H-atom abstraction for X = Br and I are lower in energy compared to X = F and Cl due to the interaction between the halogen and the copper center in the TS complex (Figure 11), in a similar fashion to that of path C1-a described above.

Finally, an hydrogen-atom transfer to the O-atom to form an hydroxyl intermediate following by reductive elimination to give an alcohol product was predicted for aliphatic substrates, the plausibility of this pathway was also explored (Scheme 8). The DFT predictions for these reactions are intriguing. While [CuO]$^+$ was able to activate CH$_3$, according to this pathway, the rigidity of the activated complex does not allow such a reaction for PPhX. The reason for the lack of activation of PPhX by [CuO]$^+$ to form a alcohol is two-fold: (1) the PPhX substrate is rigid and planar, with H-atoms pointing away from the copper center, (2) the bulk of the phenanthroline ligand does not allow for an agostic interaction. Thus, no TS geometry was located on the triplet surface for any of the halobenzene substrates examined. A singlet TS for X = each was located, however, this TS is significantly above the energy of the separated reactants (Table 8). Thus, while the formation of phenol type products via H-atom transfer followed for each X, the C4-oxygen path is thermodynamically favorable, the reaction is not kinetically viable. This is in distinct contrast with the [CuO]$^+$ activation of methane, where both the triplet complex was able to access a low-lying TS for the O-atom insertion, facilitated by a spin cross over to the singlet surface to produce methanol [37,104].
activation and O-atom transfer, while the singlet [(phenOH)Cu]+ has a higher TWIMS mobility (and thus shorter drift time) than when reacted with propane, the oxo species reacted via C bond transformations is thus a desirable tool to be added to the "copper catalyst toolkit," thus, we have sought to understand more about the mechanism involved in bond activations.

Here, we have demonstrated the utility of modern ion-mobility spectrometry, in particular TWIMS, not solely as a characterization, but also as an effective separation technique. This leads ins to ion-molecule reactions.

Thus, we revisited the ligated tridental copper oxo species [(phenOH)Cu]O+ first formed 10 years ago and sought not only to discover more about the structure, and resolve the suspected isomeric species present within the ion's m/z signal, but also to learn more about their respective reactivity. We indeed confirmed the presence of two TWIMS-isomeric species, assigned isomer A and B, corresponding to the triplet [(phenOH)Cu]O+ and singlet [(phenOH)Cu]+ cation radicals, respectively. This species has a higher TWIMS mobility (and thus shorter drift time) than isomer B. The [(phenOH)Cu]+ species was able to furnish adducts with the nitrogen buffer gas during the passage through the TWIMS cell, which is likely to have helped to increase its drift time, and thus, also the resolution of the isomeric species. However, due to this favorable interaction, we are cautious about deriving experimental cross-sections.

Because the isomeric species were separable with TWIMS, we were able to analyze their separate reactivity for the first time. When reacted with propane, the triplet [(phenOH)Cu]O+ bond activation and O-atom transfer, while the singlet [(phenOH)Cu]+ species underwent adduct formation with background molecules. We then extended this study to look at the reactions of the two isomers with PX (X = Cl, Br and I). Similar trends were observed for all species examined: isomer A showing various bond transformation reactions including concurrent halide-addition and O-atom transfer or O-atom transfer, while isomer B merely undergoes adduct formation with the substrate, background molecules, and nitrogen buffer gas.

The BFP predictions for the reaction of [(phenOH)Cu]+ with PX revealed a 99.9% metastability barrier in the mechanism of C–X bond activation, and two possible paths have been identified. This resulted in concerted O-atom transfer from halogenoarenes in the cation. In addition, competitive pathways for O-atom transfer were explored computationally. The most likely path for O-atom transfer involved formation of a cyclic nucleophile; however, there is most likely to be a mixture of other functionality in the product. The O-atom transfer is not predicted to be regioselective.

Future work will aim to uncover suitable metal complex catalysis for both C=O and C–O functionalization; and we will also aim to explore the reactivity of other metalloporphyrin catalysts and clusters.

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Appendix A: Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2014.05. 005.

References

[8] A. Company, J. Lloret, L. Gomez, M. Costas, in: Perez (Ed.), Alkane C–H activation and O-atom transfer, and two possible paths have been identified. This species has a higher TWIMS mobility (and thus shorter drift time) than isomer B. The [(phenOH)Cu]+ species was able to furnish adducts with the nitrogen buffer gas during the passage through the TWIMS cell, which is likely to have helped to increase its drift time, and thus, also the resolution of the isomeric species. However, due to this favorable interaction, we are cautious about deriving experimental cross-sections.

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Future work will aim to uncover suitable metal complex catalysis for both C=O and C–O functionalization; and we will also aim to explore the reactivity of other metalloporphyrin catalysts and clusters.
Does water have a second (liquid–liquid) critical point? The answer to this bold but vexing question, which first came to prominence over 20 years ago [1], is neither simple nor free from controversy. A host of theoretical simulations [2–6] and experiments [7–11] have served to illustrate the ideas behind the second critical point, yet the fact that even in simulated water, critical point was located at the ST2 potential of Rahman and Stillinger, but other common water potentials either give this second critical point in the water pair-plots diagram, or, like mW water, do not show a second critical point at all. Some authors even claim that none of the common water potentials show a second critical point [44]. Here we are to present our debate and uncertainty about the existence of a second critical point, even in simulated water.

Is there anything we can learn from experiments about the nature of water in the supercooled regime? As with the theoretical understanding, the challenges for the supercooled water experiments are substantial and may be prohibitive. Water, of course, readily crystallises below 273 K, and this crystallisation can be inhibited by the tinest amounts of impurities. Below about 235 K crystallisation proceeds spontaneously without the need for impurities. This is not to say, however, that we should abandon hope for understanding the complicated behaviour of water in a matrix, either as a liquid or as a crystal. As with the uses of models, and the need for simulations.

1. Introduction

Dense fluids, like argon or nitrogen, the structure and properties are determined rather accurately by short-ranged, pairwise-additive, forces between the atoms of such liquids, with many-body forces playing only a minor role [30]. With water, however, the situation is far less clear. Certainly even before and since the beginning of computer simulation [36], [37], and the recent availability of neutron scattering [50], [51], there has been a desire to test the simulations and to determine whether there is a second critical point somewhere at higher temperatures. Yet the dataset in Table 1 shows that no one has yet evidenced this second critical point in real, experimental, water, which, if it occurs at all, is positioned at a point in the phase diagram where the natural state of water is firmly as crystalline ice, rather than as any form of the liquid. Visiting Martian aliens might well be puzzled by the extensive discussion on this question, and might well be concerned that the problem is not evident in its appearance to the human eyes, as for example, the heat waves seen from airplanes are quite real and cause discomfort. In this case, the question is whether there is a second critical point in water, or whether it is just a manifestation of the liquid–solid transition.

Yet mW is still far from being a perfect water potential. The calculated diffusion constant for this potential is a factor of 3 too large for an isotropic system. Here g(r) is the set of site–site radial distribution functions that will be used to define the structure of the liquid, although it is important to remember, for the later discussion about water in confinement, that these functions are themselves obtained from the auto-correlation of the single particle density fluctuations, for an isotropic system. As with the calculation of the scattering length of the atom 2, these scattering lengths are called ‘form factors’ which are averages of site–site distribution functions required to define the structure of the material. Given a beam of radiation (X-rays, electron, neutrons) of wavelength λ, the scattering intensity as a function of momentum transfer Q, will be given by

$$I(Q) = \sum_{i=1}^{N} \left[ 2 - \delta_{ij} \rho_i^2 \right] g_{ij}(r) / (Qr)$$

with the partial structure factors defined by

$$S_{ij}(Q) = 4\pi \rho a_i a_j \cos(\mathbf{Q} \cdot \mathbf{r}) / (Qr)^2$$

for an isotropic system. Here $a_i$ and $a_j$ are the scattering lengths of the i-th and j-th atoms, respectively, of the material. For the case of confined water discussed here a simulation of the material in question, then refining the structure of the system was done using a computer simulation approach which involves running a computer simulation to assist in the determination of the pair distribution function. This function is defined as the average of the number of neighbours of a given atom in a lattice, at a given distance, and is given by

$$g(r) = \frac{\rho}{4\pi r^2} \int_{0}^{r} \left( \frac{1}{\sin \theta} \right) d\theta$$

where r is the distance between two atoms, θ is the angle between the vectors from each atom to the common neighbour, and $\rho$ is the number density of the material. In the case of confined water, the structure of the material is determined by a combination of of site–site distribution functions, and the second critical point is given by

$$g(r) = \frac{\rho}{4\pi r^2} \int_{0}^{r} \left( \frac{1}{\sin \theta} \right) d\theta$$

where r is the distance between two atoms, θ is the angle between the vectors from each atom to the common neighbour, and $\rho$ is the number density of the material. The structure of water confined in MCM41 silica cylindrical pores is studied to determine whether confinement is ideal, since there then need to understand how to measure the structure of a liquid in the bulk form, then see how these methods need to be modified to determine the structure of water confined to a finite volume. The structure of bulk water has been the subject of recent extensive and independent investigations [44–50], which give excellent agreement with each other on all liquid–liquid critical properties. The calculated density profile for water confined in a hexagonal arrangement of cylindrical pores arranged on a simple hexagonal lattice, with the substrate generally believed to be amorphous or partly crystalline, depending on the pore size [51]. These data not generated for a single potential, but they can be used to determine how this potential changes as a function of temperature and pressure, and how it compares to results obtained for an isotropic system. Here $g(r)$ is the set of site–site radial distribution functions that will be used to define the structure of the liquid, although it is important to remember, for the later discussion about water in confinement, that these functions are themselves obtained from the auto-correlation of the single particle density fluctuations, for an isotropic system. As with the calculation of the scattering length of the atom 2, these scattering lengths are called ‘form factors’ which are averages of site–site distribution functions required to define the structure of the material. Given a beam of radiation (X-rays, electron, neutrons) of wavelength λ, the scattering intensity as a function of momentum transfer Q, will be given by

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where r is the distance between two atoms, θ is the angle between the vectors from each atom to the common neighbour, and $\rho$ is the number density of the material.
Besides the structurally important scattering, as defined by the second term in Eq. (1), the scattering data contain an additional term, which is the so-called "single atom scattering", which is given by the first term in (1). This term arises from the diagonal components of the scattering matrix, and represents the correlation of each atom with itself. In contrast to the structural information, but represents the scattering level about which the structural correlations oscillate. Because this is a known quantity for each atom in the crystal, and depends only on the position of the atom in the material (and not the material itself), the single atom scattering provides a simple


treatment of the underlying structural information. This term, the so-called "single atom scattering", which is given by the first term in (1), i.e.,

\[ \rho(r) = \frac{1}{V} \sum_i \rho_i(r) \delta(r - r_i) \]

where \( \rho(r) \) and \( \rho_i(r) \) are the total and atomic density functions, respectively, \( \sum_i \) is the summation over all atoms, \( V \) is the volume of the crystal, and \( \delta(r - r_i) \) is the Dirac delta function.

The single atom scattering level can be used to directly determine the atomic density of the material. This is especially important when, as in the present case, the scattering sample is highly disordered or amorphous, in which case the single atom scattering can be used to obtain a structural model of the material.

The single atom scattering level can be used to do exactly that. With hydrogen–deuterium substitution there is a slight complication to this process, which arises from the fact that the sp3 atom single atom scattering from a proton (H) is more than 10 times larger than from a deuteron (D) [53]. Because of the very rapid exchange of water between the water in the atmosphere and the water molecules that are adsorbed on the surface of the material, this effect is not observed in the scattering data. However, it is important to note that the single atom scattering level serves as a useful tool to evaluate the overall quality of the scattering data. For example, if the single atom scattering level is not properly accounted for in the scattering data, it can lead to significant errors in the structural model.

2.2. Empirical potential structure refinement

2.2.1. Simulations of dry MCM41

The method used here to model the scattering data is a development of the experimental potential structure refinement (EPSR) method that has been described in several recent publications [54–56,50,49]. EPSR was used first by the Reverse Monte Carlo (RMC) method which was independently distinguished from RMC by using the difference between scattering data and simulated structural factors to develop a perturbation to an initial seed potential, called the "reference potential." This perturbation is called the "empirical potential" and aims to drive the simulated structural factors as close as possible to the measured data.

To build the initial model of (dry) MCM41, a line of 80 ‘‘pseudo’’ atoms, called q-atoms, spaced 1.8 Å apart, are placed at the centre of the hexagonal unit cell (A 1, A 2, C 1, C 2, D 1, D 2, E 1, E 2, F 1, F 2, G 1, G 2, H 1, H 2, I 1, I 2, J 1, J 2, K 1, K 2, L 1, L 2, M 1, M 2, N 1, N 2, O 1, O 2, P 1, P 2, Q 1, Q 2, R 1, R 2, S 1, S 2, T 1, T 2, U 1, U 2, V 1, V 2, W 1, W 2, X 1, X 2, Y 1, Y 2, Z 1, Z 2). These are defined by the coordinates of the atoms in the unit cell, with each atom having a unique index, and the q-atoms lying on a plane defined by the coordinates of each atom and the x and y axes to give a 2:1 supercell. The q-atoms are given a diameter of 2.5 Å, which was determined from an earlier analysis [61] and 5420 silicon and 10840 oxygen atoms are inserted at random into the available space in the supercell, with each of the atoms placed on a lattice point in the supercell. To prevent these atoms from entering the pores during the subsequent computer simulation, a repulsive potential of the form \( U_{\text{rep}}(r) = C_{\text{rep}} \exp (-r/a) \), where \( r \) and \( a \) are the specified minimum distance for atom pair and ‘‘hardness’’ parameter respectively, is applied between the q-atom and the silicon and oxygen atoms. As described in [49], the amplitude \( C_{\text{rep}} \) of this repulsive potential is determined by the coordination number of each atom in the material.

The single atom scattering level can be used to directly determine the atomic density of the material. This is especially important when, as in the present case, the scattering sample is highly disordered or amorphous, in which case the single atom scattering can be used to obtain a structural model of the material. The single atom scattering level can be used to do exactly that. With hydrogen–deuterium substitution there is a slight complication to this process, which arises from the fact that the sp3 atom single atom scattering from a proton (H) is more than 10 times larger than from a deuteron (D) [53]. Because of the very rapid exchange of water between the water in the atmosphere and the water molecules that are adsorbed on the surface of the material, this effect is not observed in the scattering data. However, it is important to note that the single atom scattering level serves as a useful tool to evaluate the overall quality of the scattering data. For example, if the single atom scattering level is not properly accounted for in the scattering data, it can lead to significant errors in the structural model.

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The model of the surface is built [65,66] penetration of water into the EPSR fit (line) to the total scattering data from wet MCM41 at 298 K (circles) over three different scales of intensity and Q. Fig. 2 shows the fits to the data with \text{H}_2\text{O} molecules, while row (b) shows the fits to the data with \text{D}_2\text{O} water molecules. The left-hand plot shows the (110) Bragg peak, the middle plot shows the (110), (200) and higher order Bragg peaks, while the right-hand plot shows the wider Q region beyond Q = 1 Å⁻¹.

These indicate that the total oxygen coordination number in the first shell of silicon is close to 4, as happens in bulk amorphous silica. The mean density of the silicon atoms in the substrate appears lower than that in the bulk density, Fig. 5a. However attempts to increase this amount to get closer to the bulk density gave poorer fits to the scattering data. In Section 3.3 below we introduce the concept of a local density for heterogeneous systems and discuss this matter in more detail.

3.2. Radial distribution functions

The simulated radial distribution functions for water in MCM41 are shown in Fig. 6a. Comparing these with those found in bulk water [49], using the same SPC/E reference potential, Fig. 5b, some marked differences can be seen.

Firstly in confined water the data are on a marked negative slope with increasing \( r \) and only reach \( g(r) = 1 \) at \( r = 30 \text{Å} \), while the bulk data oscillate about \( g(r) = 1 \) for all \( r \). At the same time the amplitude of the peaks is roughly a factor of 2 larger for water in confinement compared to their bulk counterparts. These effects are well-known from other studies of confined fluids [40,46,65] and are labelled as "excluded volume" effects, arising as they do from the fact that the fluid is excluded from some regions of the sample [70]. However they make direct comparison with the bulk fluid difficult; Fig. 6b, unless one is prepared to develop a fairly elaborate correction procedure which takes account of the density variation both inside and outside the pore [46,52,65].

At low \( r \) the confined water distributions oscillate about a level of 0.3, suggesting that the local density of the water in the pore is roughly twice the density of water averaged over the full volume of the MCM41 unit cell. Taking account of this local density effect, the first two peaks in the water radial distribution functions are about the same heights and positions as their bulk water counterparts. There may be a slight distortion towards lower \( r \) for the second peak in the OW-DW function, as seen by [152,65].

On cooling to 210 K one sees considerable sharpening of the peaks, with the second peak in the OW-DW function becoming notably more pronounced and moving to larger \( r \). This behaviour closely resembles what is predicted to occur for bulk water when taken to low density [67] and is also seen when low-density amorphous ice (LDA) is formed [71,73]. This second peak is traditionally adopted as an indicator of the degree of tetrahedral order in water, since it occurs at the required \( 1.8/3 \) radial position compared to the first peak position for tetrahedral order. If this assignment is correct, the degree of tetrahedral order in confined water at low temperature has certainly increased quite markedly. These data of course tell us nothing about the state of that water, whether it remains a liquid, becomes a glass, or is in some form of disordered crystal, although the absence of a clear signature in the DSC trace from MCM41 materials with this pore size [74] implies no change of phase has occurred on cooling. However that same work shows, from proton NMR cryoporometry, there is likely to be a continuous solid-like to liquid-like transition across 218 K at this pore diameter, with no clear information on the nature of the solid phase, but evidence for a range of relaxation times as you proceed from the surface of the pore to the centre [75].

3.3. Measurement of the local density for confined water

The data of Fig. 6a shows that the effect of confinement on fluid structure is to place the fluid-fluid autocorrelation function on a negative slope with increasing \( r \). When considering an ensemble of pores, as in the present case, the autocorrelation of the fluid within a single pore function must be convoluted with the distribution of pores to give the total fluid–fluid correlation function, but at small \( r < R_w \), where \( R_w \) is the shortest distance between the surface of one pore and that of a neighbouring pore, the correlations will come mainly from positions within the same pore. In fact quite general arguments [174] suggest that the shape of the single pore autocorrelation function at short distances is linear with negative slope, \( c(r) = 1 - ar \), with \( a \) a constant related to the dimension of the pore. Indeed for a solid uniform sphere this function is analytic:

\[
c_{\text{short}}(r) = \begin{cases} 
1 - 2c_0r + \pi c_0^2 & \text{if } r < 2R_w \\
0 & \text{if } r \geq 2R_w 
\end{cases}
\]
In order to characterise tetrahedral order in water, Errington and Debenedetti (81) introduced a local density order parameter based on the angle between triplets of neighbouring water oxygen atoms: 

\[ q = 1 - 3 \sum_{i=1}^{3} P_i = 1 - 3 \sum_{i=1}^{3} \left( \sin^2 \theta_i - \frac{1}{3} \right) \]

where the sum over \( i \) and \( k \) covers the six triplets of angles which involve a given water oxygen atom and its 4 nearest neighbours. This value is averaged over all the water molecules in the simulation box. For water in confinement (or concentrated solution), where the local density may be significantly lower than in the bulk liquid, the use of the 4 nearest neighbours could cause the value of \( q \) to appear small because one or more of those 4 neighbours are outside the nearest neighbour distance. An alternative method of calculating \( q \) is to define the expected nearest neighbour distance, based (for example) on the position of the first minimum in the OW-OW radial distribution function, from which to calculate the distribution of included angles, \( N(q) \), which involves triplets of water molecules, at least two pairs of which are at or below this cut-off distance. The included angle is that associated with the common water oxygen atoms. If all (if any) these water molecules are within this cut-off distance, then that counts as three triplets. To give the density of triplet angles the \( \sin^2 \theta \) distribution that would occur with completely random atomic positions has to be divided out: 

\[ P(\theta) = \sin^2 \theta \]

Using this distribution of triplet angles, \( q \) can be redefined for arbitrary concentration or degree of confinement:

\[ q = 1 - 3 \sum_{i=1}^{3} \left( \sin^2 \theta_i - \frac{1}{3} \right) \]

In a recent simulation of confined OW-OW cut-off distance was set to 3.2 Å, that being close to the position of the first minimum in the OW-OW radial distribution function of confined water (Fig. 6). As a guide, the value of \( q \) obtained from ESRP simulated water at 298 K when the cut-off distance using the same definition as in the present work and the latest combined X-ray and neutron scattering data (49,50) is 0.52. The distribution of included angles at various distance ranges is shown in Fig. 11, while the corresponding values of \( q \) at the same distance ranges are shown in Fig. 12. The distribution of included angles for ambient water typically consists of a broad hump near 100° corresponding to tetrahedrally bonded arrangements of triplets, plus a smaller peak or shoulder at larger angles. In Fig. 11 the \( q \) value at which at least one pair of hydrogen bonds is heavily distorted or broken. The former peak will be referred to as the ‘tetrahedral’ peak while the latter as the ‘interstitial’ peak. The shape of this distribution is a

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sensitive indicator of the impact of solutes on water structure [82], although the detailed shape can also depend on the intermolecular potential used in the simulation. For the present case at 298 K it can be seen that this distribution follows the observed pattern in bulk water, but with a reduced interstitial peak, and slightly enhanced tetrahedral peak. At 210 K the tetrahedral peak becomes more pronounced and moves closer to the ideal tetrahedral angle of 109.47°. However near the pore surface the distribution becomes heavily distorted at both temperatures, with increased interstitial peak, signalling a breakdown of the normal water structure in this region. Corresponding to these changes it can be seen, Figure 12, that in the centre of the pore, q is significantly above the value for bulk water, and this value increases markedly when the temperature lowered. In the interfacial and overlap regions however the value at both temperatures falls below the ambient bulk water value, signalling a collapse of tetrahedral structure near the surface. Based on these results therefore it would appear that in the centre of the pore, confined water is actually more tetrahedral than in the bulk, even at 298 K a trend that might arise from the overall lower density of core water compared to bulk water. It may be noted in passing that the value of q quoted here for bulk water (0.52) is different from that quoted in [83] (0.58) for the same material, and there is less interstitial intensity at 60°C in the earlier EPSR simulations than that shown here. Reasons for this discrepancy are not totally clear, except that both the data sets and the assumed water reference potentials are different between the two cases. Since the distribution of included angles is a three-body quantity and such quantities are not well determined by purely pairwise data, this signals a significant degree of uncertainty in the value of q as obtained by EPSR simulations of scattering data. Hence the values shown in Figure 12 should be used to indicate relative variations of this parameter with temperature in distance and distance from the surface, rather than be taken as absolute values.

4. Discussion

The foregoing account draws heavily from previous BMC or EPSR treatments of water in confinement [84,46,52,69]. Nonetheless there are some important changes. In particular the present Letter uses a pore size which is more consistent with the known amount of water absorbed in the pores and also the behaviour of hydrogen isotope [61]. In addition the simulated structure is fit to both the hexagonal Bragg peak intensities and the wider Q scattering pattern, something that has not been attempted previously. Although still not giving a completely unambiguous view of the structure, the extra constraints imposed by including the Bragg intensities make it difficult to see how the final conclusions could be radically different from those presented here. Given the...
somewhat contentious nature of what is known about water in confinement (a recent analysis [85] seems to tell only part of the story) and the dearth of certainty of various statements about water in confinement.

4.3 The density of confined water

For a bulk fluid, or for a fluid confined by well-defined walls, density can be measured more precisely as the amount of material or number of atoms in a known volume. When the walls become soft and flexible enough to stretch the walls to a greater or lesser extent, as in many real solids, this precise definition loses its meaning and our proposal here is that we should instead talk about the "local" and "core" densities of the fluid in such cases. For the case reported here, both the local and core densities of confined water, Table 2 fall by about 7% when confined water is cooled to 210 K, an amount which is closely similar to the change in density when water freezes, or between ambient water and low density amorphous ice. However, the absolute values of these densities at 298 K are already significantly lower than bulk water density, by 6% for the core density at this temperature. So what densities at 298 K are already significantly lower than bulk water density? The answer here is 210 K: both values are significantly lower than the bulk values.

One piece of evidence is the position of the main D2O diffraction peak for water in confinement. In the current letter (see Figure 3 and 4) the main D2O diffraction peak occurs at ~1.86 Å 1 at 298 K and ~1.72 Å 1 at 210 K: both values are significantly lower than the bulk value 1.9 Å 1. A similar trend has been observed in other work on water in hydrophilic confinement [67,78]. Figure 13 compares the first peak position for different confinement geometries at the same density.

One other experiment that can be performed to reinforce the calculation is that of measuring the main D2O diffraction peak when substituting H2O for D2O at 298 K. If, for the time being, we make the assumption that density is not changed when substituting H2O for D2O, then the density of water has to be significantly below ambient conditions. This would imply a density inside the pore lower than the bulk. One detail that before making any statements about density and its trend seems unavoidable is that the density of water confined in MCM-41 is significantly lower than the bulk. The analysis of [85] makes no reference to the shape of the density profile across the pore, even though that profile can be critical to determining the relative heights of Bragg peaks. Furthermore, since the density profile across the pore depth is structureless, which is clearly not, Figure 5.

Based on the evidence presented here, therefore, the conclusion seems to be that the density of confined water is significantly lower than in the bulk liquid at the same temperature. Elsewhere we have also demonstrated the significance of this point, and that density profiles are not uniform, with a marked density increase in the interfacial region, and the density is not the same as the bulk density.[47,75,74]. Even more recent and independent work using NMR cryoporometry with ammonia has shown that the observed density inside the pore, and the Bragg peak intensities[59] and that on cooling to 210 K there is a marked change in structure of confined water. Instead, as proposed above, there is a local density which represents the local water density seen by any given atom. This can only be determined by averaging the core density which is the water density near the centre of the pore, well away from any surface. These numbers are more informative about the nature of confined water.

4.3. The nature of water structure in confinement

The data given in Figures 6a and 11 contain two elements to be highlighted, namely the fact that under ambient conditions, water contained in MCM-41 is more tetrahedral than bulk water, and is almost as tetrahedral as water confined in silica slit pores[93]. Also that on cooling to 210 K there is a marked change in structure of confined water with increased tetrahedral order in the liquid compared to that of bulk water. This is consistent with the large differences in core densities. Figure 5. A number of studies attest to the fact that this structural change is significant and is consistent with the presence of highly water near the surface which remain mobile to low temperatures [47,75,74]. Even more recent and independent work using NMR cryoporometry with ammonia has shown that the observed density inside the pore, and the Bragg peak intensities[59] and that on cooling to 210 K there is a marked change in structure of confined water. Instead, as proposed above, there is a local density which represents the local water density seen by any given atom. This can only be determined by averaging the core density which is the water density near the centre of the pore, well away from any surface. These numbers are more informative about the nature of confined water.

4.4 Relationship with other studies

The present letter has naturally focused on a particular system, the effects of water being confined in a highly hydrophilic wall. Besides the data presented here, the water distribution uniformly across the pore and makes no penetration into the wall of the pore. It can be seen readily that to obtain a peak ratio as high as 1.86 Å 1 at 298 K and ~1.72 Å 1 at 210 K, both values are significantly lower than the bulk value 1.9 Å 1. A similar trend has been observed in other work on water in hydrophilic confinement [67,78]. Figure 13 compares the first peak position for different confinement geometries at the same density.

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Acknowledgement

The author wishes to thank Rosania Mancinelli, Fabio Bruno, and Marianna Antonietta Ricci for unrestricted access to their scattering data on water in MCM41.

References

Exploring the limits: A low-pressure, low-temperature Haber–Bosch process

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ARTICLE INFO

Article history:
Received 27 February 2014
Available online 11 March 2014

ABSTRACT

The Haber–Bosch process for ammonia synthesis has been suggested to be the most important invention of the 20th century and is known as the ‘Haber reaction in heterogeneous catalysis’. We examine the catalytic requirements for a new low-pressure, low-temperature synthesis process. We show that the absence of such a process for conventional transition metal catalysts can be understood as a consequence of a scaling relation between the activation energy for N2 dissociation and N adsorption energy found at the surface of these materials. A better catalyst cannot obey this scaling relation. We define the ideal scaling relation characterizing the most active catalyst possible, and show that it is theoretically possible to find new classes of catalyst materials with properties approaching the ideal, and we discuss the possibility that transition metal compounds have such properties.
The problem this but now the overall process becomes uphill in free energy. A substantial increase in pressure is needed in order to change the total reaction back to being exergonic; see Figure 1b. This is the reason for the harsh conditions needed in the Haber–Bosch process even for the best catalysts known today.

From the point of view of the thermodynamics of the gas phase reaction, it is not in principle a problem to have an ammonia synthesis process at ambient conditions. Figure 1 shows that a low temperature process would be feasible if we could find a material that binds \( \text{NH}_2 \) (\( \sim 0.1 \)) and \( \text{N}_2 \) without a higher barrier for \( \text{N}_2 \) dissociation. The main reason such a catalyst has not been found can be understood from the results shown in Figure 2a. For the most active sites (steps) on metals there is a linear energy scaling (or Brønsted–Evans–Polanyi) relation between the transition-state energy at the active sites (steps) on metals. There is a linear energy scaling (or Brønsted–Evans–Polanyi) relation between the transition-state energy at the active sites (steps) on metals. There is a linear energy scaling (or Brønsted–Evans–Polanyi) relation between the transition-state energy at the active sites (steps) on metals. Therefore, the barrier for \( \text{N}_2 \) dissociation is lower than that for \( \text{N}_2 \) dissociation. This leads to lower catalytic activity of the closed-packed surfaces as compared to the stepped surfaces. A good, low temperature catalyst would require a catalyst with a value of \( \Delta E_{\text{N}} \) which is significantly below the scaling relation for the stepped metal surfaces. In ammonia synthesis, this is to a certain extent achieved by promotion of the catalyst by alkali metals [12,19,27–30]. It has been shown that the \( \Delta E_{\text{N}} \) dissociation barrier on a Ru[0001] surface is lowered by approximately 0.15 eV due to electrostatic interactions, and at the same time the NH bond is destabilized leading to a significant increase in turnover frequencies [31]. Assuming the same influence of the alkali promoters on all metal catalysts results in a catalytic activity volcano as shown in Figure 2a.

There is a limit to how \( \Delta E_{\text{N}} \) can be lowered. This limit is given by the fact that the barrier cannot be lower than the reaction energy of a given elementary reaction step (i.e. \( \Delta E_{\text{N}} > 0 \)). This corresponds to an ideal scaling relation given by:

\[
\Delta E_{\text{N}}^{\text{ideal}} = 2E_0
\]

Using this relationship our kinetic model can provide an estimate of the maximum rate enhancement possible. In doing so we are assuming that \( \text{N}_2 \) dissociation remains rate limiting for the ideal catalysts. This will be the case if the transition-state scaling relations for the hydrogenation steps are also close to ideal, as defined above. Figure 3b compares the variation in rate as a function of \( \Delta E_{\text{N}} \) (the activity volcano) for the promoted metal step sites and for a hypothetical class of materials following \( \Delta E_{\text{N}} = \Delta E_{\text{N}}^{\text{ideal}} \). Any improved catalyst will have rates in between these two limits. Two sets of reaction conditions are shown; one is at a typical set of industrial conditions (737 K, 100 bar) and the other case shown is (737 K, 1 bar). As shown in Figure 4a the ammonia conversion in a 3:1 H\(_2\):N\(_2\) gas ratio at the high conditions of (737 K, 100 bar) is higher than at typical pressure Haber–Bosch conditions (737 K, 100 bar). The negative effects of lowering the pressure are over-compensated by the favorable decrease in temperature. The ideal activity map at low-pressure conditions still has a very reasonable turnover frequency around the optimum value for \( \Delta E_{\text{N}} \).

In Figure 4b we show the calculated rate of active sites at the optimum as a function of temperature. It remains an enormous challenge to find catalysts with properties close to \( \Delta E_{\text{N}}^{\text{ideal}} \). We have investigated other classes of surfaces in a search for this ideal behavior. Figure 5 shows \( \Delta E_{\text{N}} \) data for the dissociation of \( \text{N}_2 \) on several transition-metal oxides, rutile transition-metal oxides (\( \Delta E_{\text{N}} \)), surfaces with \( M = \text{Ti}, \text{Mo}, \text{Ru}, \text{Ir} \) and Pt. We note that a first approximation \( \Delta E_{\text{N}} \) is

\[
\Delta E_{\text{N}}^{\text{ideal}} = 2E_0
\]

which is considerably lower than the ideal value. This shows that the structure of the oxide catalyst is important. The oxide catalysts are not ideal, but they show the same trend as the ideal catalysts. This is the reason for the lower activity of the oxide catalysts, which is reflected in the lower turnover frequencies.

Figure 5. Variations in the rate of ammonia synthesis [13] as a function of the calculated chemisorption energy of \( \text{N} \) at 737 K and 1 bar. Top panel: the idealized volcano for a hypothetical class of materials following the scaling relation \( \Delta E_{\text{N}} = \Delta E_{\text{N}}^{\text{ideal}} \). Bottom: calculated optimal rate as a function of temperature at 1 bar for K-promoted stepped metal surfaces (red solid line) and for the ideal catalyst (green solid line) at high pressure (top panel) ‘low pressure’ (bottom panel) for (373 K, 1 bar) than at typical high pressure Haber–Bosch conditions (737 K, 100 bar).

Figure 4. Top: conversion of the reactants to ammonia in a 3:1 H\(_2\):N\(_2\) gas ratio with \( \Delta E_{\text{N}} = \Delta E_{\text{N}}^{\text{ideal}} \) as a function of temperature based on thermodynamics as obtained from DFT at a total pressure of 1 bar (black solid line) and 100 bar (blue solid line); Bottom: calculated optimal rate as a function of temperature at 1 bar for K-promoted stepped metal surfaces (red solid line) and for the ideal catalyst (green solid line); at the optimum value of \( \Delta E_{\text{N}} \), under the same conditions (i.e. the maximum of a volcano for a given T).

This is the reason for the low ammonia conversion in a 3:1 H\(_2\):N\(_2\) gas ratio at the high conditions of (373 K, 1 bar) than at typical pressure Haber–Bosch conditions (737 K, 100 bar). The negative effects of lowering the pressure are over-compensated by the favorable decrease in temperature. The ideal activity map at low-pressure conditions still has a very reasonable turnover frequency around the optimum value for \( \Delta E_{\text{N}} \).

In Figure 4b we show the calculated rate of active sites at the optimum as a function of temperature. It remains an enormous challenge to find catalysts with properties close to \( \Delta E_{\text{N}}^{\text{ideal}} \). We have investigated other classes of surfaces in a search for this ideal behavior. Figure 5 shows \( \Delta E_{\text{N}} \) data for the dissociation of \( \text{N}_2 \) on several transition-metal oxides, rutile transition-metal oxides (\( \Delta E_{\text{N}} \)), surfaces with \( M = \text{Ti}, \text{Mo}, \text{Ru}, \text{Ir} \) and Pt. We note that a first approximation \( \Delta E_{\text{N}} \) is

\[
\Delta E_{\text{N}}^{\text{ideal}} = 2E_0
\]
Finding catalysts where the activation barrier is close to the dissociation energy, as observed for e.g. oxides, is imperative if one wants to develop more efficient processes for these reactions.

Acknowledgements

Support from the DOE Office of Basic Energy Science to the SUN-CAT Center for Interface Science and Catalysis and the ‘Predictive theory of transition metal oxide catalysts’ grant are acknowledged. A.M. is grateful for support by the Department of Defense (DOD) through the National Defense Science & Engineering Graduate Fellowship (NDSEG) Program.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemphys.2014.03.003.

References

Recent advances in high-speed digital electronics have made it possible to construct a new generation of spectrometers for molecular rotational spectroscopy [1]. These spectrometers provide instantaneous broadband signal acquisition and greatly increase the sensitivity that can be achieved in either a fixed measurement time with a limited amount of sample. For rotational spectroscopy of pulsed supersonic molecular expansions at microwave frequencies (2–40 GHz), these spectrometers can acquire the rotational spectrum over bandwidths of 10 GHz or more in a single measurement cycle lasting 40 µs or less [2]. The spectrometers have no moving parts and, in particular, do not require the setting of light source or microwave cavity resonance frequencies for each measurement. The simplicity of the spectral acquisition significantly reduces the time required to acquire a high-sensitivity molecular rotational spectrum. Molecular rotational spectroscopy can provide information about the 3D molecular structure for chemical systems that cannot be easily studied by techniques such as X-ray diffraction and nuclear magnetic resonance (NMR) spectroscopy. This article illustrates the application of broadband Fourier transform microwave spectroscopy to study the structure determination through the challenging problem of water clusters using the water rotational spectrum with high confidence.

The vibrational spectra of the hydride stretches, for example, are often perturbed by vibration-rotation coupling, making the accurate determination of the principal moments of inertia for such effects by introducing individual adjustable parameters on the Watson Hamiltonian [7]. Watson et al. [8] suggested two larger molecules, and several low energy minima of clusters formed from several smaller molecules, like water). The high spectral resolution of rotational spectroscopy makes it possible to analyze these mixtures with little or no perturbation from the rotational spectrum. The development of quantum chemistry and has unique capabilities for the study of conformally flexible molecules [9]. None of these problems deal with the role of intermolecular forces in determining the complex potential energy landscapes of flexible molecular systems. In general, the standard tools of computational physical chemistry, X-ray diffraction and NMR spectroscopy, cannot be applied to these systems. This problem also presents a common set of experimental challenges for studies of molecules that typically contains a larger number of distinct molecular species (molecules, so that precise experimental determination of the moments of inertia become proportionally smaller with the size of the molecule, so that precise experimental determination of rotational constant values (usually better than 0.001 MHz) is required and is not yet possible with most of the above-mentioned methods.

Molecular rotational spectroscopy has proved to be the most powerful method for obtaining rotationally-resolved spectra. The technique offers unique advantages including the ability to study weakly bound complexes and clusters formed in the pulsed jet expansion. The development of quantum chemistry and has unique capabilities for the study of conformally flexible molecules [9]. None of these problems deal with the role of intermolecular forces in determining the complex potential energy landscapes of flexible molecular systems. In general, the standard tools of computational physical chemistry, X-ray diffraction and NMR spectroscopy, cannot be applied to these systems. This problem also presents a common set of experimental challenges for studies of molecules that typically contains a larger number of distinct molecular species (molecules, so that precise experimental determination of the moments of inertia become proportionally smaller with the size of the molecule, so that precise experimental determination of rotational constant values (usually better than 0.001 MHz) is required and is not yet possible with most of the above-mentioned methods.
The goal of producing an actual molecular structure is somewhat challenging. For small clusters (H
\textsubscript{2}O)

_\text{n}

, while the topologies may be generated manually (or by interleave) and the enhanced frequency bandwidth of the spectrometer performance and makes it possible to perform double-resonance measurement directly with programmed arbitrary waveform generation.

Multiple measurements are performed on each pulse sample injection cycle to decrease the measurement time and sample consumption. The average waveform has 10 back-to-back chirped excitation pulses separated by 45 μs. The marker channel triggers the digitizer for each of these 10 pulse cycles and digitizes all 1 million data points (40 data points per pulse). These 10 FID acquisitions are first co-added and then the pulse-to-pulse operation is achieved permitting time domain signal averaging. Sensitivity is increased by performing averages of the FID in the time domain and the rotational spectrum is produced by fast Fourier transformation of the averaged coherence envelope. The gas sample is excited by microwave pulse with a linear frequency sweep (chirp) from 2 to 8 GHz and 4 μs duration. In this case, the chirped pulse is directly generated by the arbitrary waveform generator and amplified in an isolator. The pulse is amplified to about 600 W peak power using a traveling wave tube amplifier (Applied Systems Engineering 167S/3C). The amplified chirp is then transmitted through a WRD-650 waveguide to a commercial microwave cavity. Inside the vacuum chamber of the spectrometer, the excitation pulse is broadcast using a high gain (high directionality) horn antenna that is mounted on top of the cavity. A second horn antenna is used for the receiver and is placed 140 cm away from the cavity to detect the scattered radiation from various beam sources in between the broadcast and receive horn antennas. Outside the chamber there is a high power PIN diode linear tunnel-diode switch (ATM Microwave) with 20 ns rise and fall times that provide the pulsed microwave signal to the cavity. Following excitation of the sample from the pulsed jet molecular beam sources, the coherent emission, or free induction decay, is amplified and then digitized using an 8-bit, 25 G/s digital oscilloscope (Tektronix DPO 73304D). The digitizer is triggered using a marker channel from the AWG such that synchronous pulsing can be used. The focus of this paper is on the development of high-speed digital architecture that is able to provide high sensitivity below about 3 GHz. With these horn antennas it has been possible to perform both broadband spectroscopy and two-dimensional correlation experiments.


1.1. Structural features of water clusters

The goal for broadband rotational spectroscopy studies of water clusters is to determine the structural properties of the water molecule without relying on electronic structure theory. There are three different aspects of water cluster structure that are considered in the study of the water heptamer: (1) The oxygen-atom framework geometry, (2) the hydrogen bond network geometry, and (3) the conformational framework geometry. The oxygen-atom framework geometry describes the basic structure of the water cluster and plays the dominant role in determining the moments-of-inertia (and, therefore, the rotational and vibrational spectra). In this paper, there can be many different orientations of the water molecules to create the structure's hydrogen bond network. Because this structural framework is dependent on the hydrogen atoms, it has a relatively small effect on the moments of inertia of the full cluster. However, the network geometry causes distinct distortions in the framework geometry and, as a result, a precise experimental framework geometry is important for determining the moments-of-inertia in the network. In addition, the network geometry influences the cluster dipole moment so that spectral intensity patterns can also be used to support the determination of the network geometry. Finally, the network geometry is so complex that it is difficult to determine from rotational spectroscopy.

In this work, there is another level of water cluster structure that
\text{RI-MP2\textsubscript{aVDZ}}

basis set (CBS) limit energies were calculated using an inverse 4–5 polynomial basis set extrapolation scheme that has been used extensively for water clusters [36,37,47,48] The RI-MP2/CBS method of theoretical structures available at the outset of the experiment is necessary for larger clusters due to the vast number of unique water hydrogen atom positions from tunneling. Each water cluster geometry can have several identical minima and tunneling from 'flipping' the free D-H axis can occur through a rotation about the water molecule's own C-axis [23,24]. These tunneling dynamics are of primary importance for Teheranchian spectroscopy studies which can directly excite the tunneling states. Tunneling has been observed in the water hexamer prism and decamer by broadband rotational spectroscopy [19]. The pure rotational spectra of the two water heptamers observed in the present work show no signs of tunneling.

1.2. Theoretical chemistry techniques to identify water cluster isomers

For a given water cluster (H
\text{2}O

_\text{n}

), the number of hydrogen bonded topologies, \text{g}_\text{n}

, increases exponentially with the number of water molecules in the cluster. To generate a complete set of theoretical structures for small clusters (n = 6), [25] a more systematic and automated approach is necessary for larger clusters due to the vast number of structures that must be considered. For example, the number of unique heptamer (g) and decamer (q) topologies is in the hundreds and thousands range, respectively [26]. Tools like Monte Carlo [27,28], molecular dynamics [29], genetic algorithms, [30,31] and others [32,33] have been used to search for water cluster configurations. In this work, we employed molecular dynamics (MD) configuration sampling with the TIP4P [34] water model as implemented in AMBER [35] to locate a large number of configurations and applied existing electronic (QM) methods to perform energy calculations [36,37]. In these two-step gas phase MD simulations, the H
\text{2}O

_4

 system was first heated from 5 K to 250 K over a period of 1 ns, then allowed to remain at 250 K for a 9 ns run. We took 200 snapshots from this 10 ns simulation at evenly spaced intervals and used them as starting structures for more reliable geometry optimizations employing second-order Moller-Plesset perturbation theory (MP2/38) and, particularly in its more efficient resolution-of-the-identity MP2 (RI-MP2) implementation, [39] has been shown to be reliable for such complex structural studies. [36,37,40–44]. MP2 is the cheapest ab initio method that is able to describe non-covariantly bound systems because it includes electron correlation. When applied with correlation consistent basis sets (aug-c-c\textsubscript{VQZ} + AVQZ), [45,46] it captures hydrogen bonding very well. We optimized the low energy structures using RI-MP2 method and aug-cc-pVQZ (AVQZ) basis set. Also, the harmonic vibrational frequencies need to calculated to probe the internal energy content of the gas phase water cluster. Harmonic vibrational corrections to the enthalpy (H) and entropy (S) were determined using the RI-MP2/AVDZ basis set. The RI-MP2 complete basis set extrapolation scheme [47] was extended to the aug-cc-pVQZ basis set to develop a parameterized basis set extrapolation scheme that has been used extensively for water clusters [36,47,48]. The RI-MP2/CBS electronic energy (E\text{el}) was combined with the ZPVE and finite temperature thermodynamic corrections to get the Gibbs free energy, G(T), assuming ideal gas conditions with a rigid-rotor approximation for molecular rotations and a harmonic oscillator model for vibrations.
water that was located outside the spectrometer. The neon pressure was 4 atm (giving a richer sample concentration of about 1% by volume). The water sample and a sample that was a 1:9 mixture of D$_2$O:H$_2$O was obtained after a total of 11000000 FIDs were coadded in the time domain resulting by flowing neon over an H$_2$ molecular beam. The neon coordinates were evaluated with program KRA, both available on the supplemental material.

1.4. Data analysis

Analysis of a broadband spectrum consisting of interspersed chirped-pulse spectrum have been assigned with the powerful program AUTOFIT developed in the Virginia laboratory [50]. This code utilizes the brute-force assignment method by inspecting suitably filtered combinations of three measured transitions from the actual spectrum. Once suitable candidate combinations of rotational constants were identified, the data set and its fit was expanded with the program ans [51] and then further refined with the AMBS package for Assignment and Analysis of Broadband Spectra [52,53] relying on the anfac/program package [54,55] for constructing a wide range of candidate Hamiltonians. Least-squares structural fits were carried out with program wppx [8] and substitution coor-

dinates were evaluated with program wsx, both available on the PROSPE website [56,57]. Molecular graphics were performed with the UCSF Chimera package [58]. Chimera is developed by the Resource for Biocomputing, Visualization, and Informatics at the University of California, San Francisco (supported by NIGMS P41 GM103101).

1.5. Broadband rotational spectroscopy measurements

The spectrum, which is presently established to be due to the water heptamer species with the strongest spectrum, was ob-

18O, and a 1:8 mixture of D$_2$O:H$_2$O were used as references in calculating the zero point vibrational energy in the large amplitude bond.

<table>
<thead>
<tr>
<th>N</th>
<th>A (MHz)</th>
<th>B (MHz)</th>
<th>C (MHz)</th>
<th>D (MHz)</th>
<th>E (MHz)</th>
<th>F (MHz)</th>
<th>G (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>937.88441(61)</td>
<td>976.8758(10)</td>
<td>1334</td>
<td>1325</td>
<td>1340</td>
<td>1820</td>
<td>1077</td>
</tr>
</tbody>
</table>

Table 1: Spectroscopic constants for the two observed isomers of the water heptamer.

<table>
<thead>
<tr>
<th>A (MHz)</th>
<th>B (MHz)</th>
<th>C (MHz)</th>
<th>D (MHz)</th>
<th>E (MHz)</th>
<th>F (MHz)</th>
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<td>1340</td>
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</tr>
</tbody>
</table>

Table 2: Rotational parameters and energy differences for the low-energy isomers in Table 1.
framework geometry, as discussed in more detail further below. The underlying reason for the large number of hydrogen bond network isomers possible for the water heptamer prism framework can be illustrated by correlating the heptamer structure with the related hexamer prism and octamer cube structures as shown in Figure 4. It can be seen how two of the low energy heptamer structures identified by theory can be derived by either adding a single water molecule to the edge of the hexamer prism or by removing a water from the water octamer. All six water molecules in the hexamer prism are distinct as shown by the observation of six isomers of the (H\textsubscript{2}O\textsubscript{7})(H\textsubscript{2}O\textsubscript{5}) cluster. Therefore, there are six distinct edges (three in the top and bottom ‘trimer’ faces) for adding a water molecule to produce a heptamer prism structure.

Furthermore, there are several different hydrogen bond network isomers of the heptamer prism with calculated energies within about 1.5 kcal/mol of the lowest energy isomer displayed in Figure 5. The four lowest energy hydrogen bond network isomers of the water prism identified in a theoretical isomer search are shown in Figure 5. Each of these heptamer prism isomers can produce heptamer prism structures by adding water to an edge. The lowest energy isomers in the heptamer prism family that have so far been identified in isomer searches. As expected from their shared oxygen-atom framework, these isomers have similar calculated rotational constants. A direct comparison of experimental (Table 1) and theoretical rotational constants does not allow an unambiguous structure identification.

The rotational constants and dipole moments obtained from electronic structure theory calculations at the MP2/aVDZ level of theory are given in Table 3 for the lowest energy heptamer prism isomers that have so far been identified in isomer searches. As expected from their shared oxygen-atom framework, these isomers have similar calculated rotational constants. A direct comparison of experimental (Table 1) and theoretical rotational constants does not allow an unambiguous structure identification. The hydrogen bond network causes two key changes to the water cluster properties. The orientations of the hydrogen bonds will produce unique distortions in the oxygen-atom framework so that structural information on the oxygen atom positions can greatly aid the structure identification. Furthermore, the different water orientations in these isomers affect the cluster dipole moment in both magnitude and its direction relative to the principal axes for overall rotation.

However, as will be discussed below, the dipole moments from equilibrium geometries of the water clusters can be misleading when large amplitude motions in the cluster are considered.

For the strongest water heptamer spectrum we have obtained the oxygen atom framework geometry from Kraitchman analysis of the \((\text{H}_2\text{O})_7\) and seven \((\text{H}_2\text{O})\textsubscript{2}(\text{H}_2\text{O})\textsubscript{5}\) isotopologues and, separately, from the \((\text{H}_2\text{O})_7\) and seven \((\text{H}_2\text{O})\textsubscript{2}(\text{H}_2\text{O})\textsubscript{5}\) isotopologues. The Kraitchman analysis returns the position of each substituted \(^{18}\text{O}\) atom in the principal axis system individually from the differences in the moments-of-inertia to the parent (unsubstituted) molecule. However, this analysis provides only the magnitudes of the coordinates. We have chosen the signs of the coordinates to give the best correspondence to oxygen atom positions from the theoretical structures. A comparison of the experimental and theoretical oxygen atom frameworks for the two lowest energy theoretical structures (7-PR1 and 7-PR2) is shown in Figure 7. An important point about this figure is that the experimental atom positions show an overlap of two separate results – the atom positions obtained from the \((\text{H}_2\text{O})\textsubscript{2}(\text{H}_2\text{O})\textsubscript{5}\) parent and the \((\text{H}_2\text{O})\textsubscript{2}(\text{H}_2\text{O})\textsubscript{5}\) parent species. These two coordinate determinations are in excellent agreement with a root-mean-squared atom position difference of 0.04 Å.

This result provides experimental validation for using \(\text{H}_2\text{O}\) substitution to determine the framework geometry. The experimental Kraitchman positions for each cluster are shown in Figure 7 separately on the left and also superimposed on the theoretical equilibrium geometry on the right. The selection of coordinate signs are shown in Table 4 where the distance between the experimental and theoretical oxygen atoms are also reported. The 7-PR1 and 7-PR2 are the only isomers (other than 7-PR3 discussed next) that have atom positions in general agreement with the
Predicted rotational constants, dipole moment and energy difference for the fourteen lowest energy isomers of the PR family at MP2/aVDZ level of theory.

Experimental atom positions. The agreement with 7-PR1 is better than with 7-PR2.

Table 3

<table>
<thead>
<tr>
<th>PR1</th>
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<th>PR4</th>
<th>PR5</th>
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</table>

Figure 7. The two experimental Kraitchman oxygen-atom frameworks for 7-PR1 (top) and 7-PR2 (bottom) compared with the equilibrium structures using the signs for (H\textsubscript{2}O)\textsubscript{7} as shown in Figure 8 where it is compared to the 7-PR1 equilibrium geometry from theory providing unambiguous structure determination for the dominant water heptamer species in the pulsed jet sample.

The vibrational structure of the O–H stretch fundamentals has also been shown to be sensitive to the hydrogen bond network geometry. It has been used, for example, to assign the two hydrogen bond network isomers of the cubic water octamer [59,60]. More recently, Terahertz vibration–rotation tunneling spectrum for the water octamer has also been reported [61]. A size-selected cluster study of the water heptamer O–H vibrational spectrum showed that a model for the vibrational spectrum using the 7-PR1 and 7-PR2 isomers was consistent with experiment [62]. Our experiment suggests that only one isomer dominates the pulsed jet sample, but the size-selected cluster experiments are expected to have a higher temperature. The accurate prediction of vibrational spectra of water clusters is still an active area of research and it is unclear how definitive is a hydrogen bond network assignment based on the infrared spectrum.

1.8. The conformational structure of the free O–H bonds

One structural feature of water clusters that is difficult to resolve by rotational isotope substitution measurements is the position of the ‘dangling’ O–H bonds. There can be large amplitude motion that is conformational isomerization about the hydrogen bond. The two isomers identified by theory as 7-PR1 and 7-PR3 are an example of water cluster conformers that share the same substitution of HOD is not expected to give quantitative structural information for water clusters because the deuterium substitution changes in vibration–rotation contributions to ground state rotational constants and in the resulting effects are known to be large.

Experimentation at the PR1 is better and supports the identification of the experimental cluster as the lowest energy theoretical structure, 7-PR1.

Experimental conformation of the structure at 7-PR1 is possible using Kraitchman analysis of the (H\textsubscript{2}O)/H\textsubscript{2}O\textsubscript{7} spectra. Isotopic framework and hydrogen bond network. A one-dimensional potential energy scan for this conformational motion is shown in Figure 9. This figure also shows how the calculated dipole moment varies as a function of the torsional angle. The barrier of the isomerization potential is on the order of the expected zero-point torsional energy so the ground torsional state is likely to be delocalized over the broad range of angles in the potential. One aspect of the delocalized free O–H bond position is that it may lead to significant differences between experimental dipole moment components and those predicted from minimum energy geometries due to averaging over the torsional probability distribution.

Figure 8. The complete Kraitchman substitution structure for (H\textsubscript{2}O)\textsubscript{7} compared to the 7-PR1 equilibrium geometry at RI-MP2/aVDZ level of theory. The green spheres represent the O\textsuperscript{18} ions while blue balls are the deuterium substitution coordinates.

Figure 9. The change in energy (black) and principal dipole moment components (blue, green, red) along the PR1 to 174.5\textsuperscript{0} (PR1) to 176.0\textsuperscript{0} (PR1) potential energy scan for this conformational motion is shown in Figure 9. This figure also shows how the calculated dipole moment varies as a function of the torsional angle. The barrier of the isomerization potential is on the order of the expected zero-point torsional energy so the ground torsional state is likely to be delocalized over the broad range of angles in the potential. One aspect of the delocalized free O–H bond position is that it may lead to significant differences between experimental dipole moment components and those predicted from minimum energy geometries due to averaging over the torsional probability distribution.

Structure identifications that rely heavily on dipole moment information may need to consider the conformational averaging [63]. The structural delocalization of the free O–H bonds has been described before for the conformational potential energy surface of the water hexamer cage where both apical water molecules have O–H\textsubscript{2}O bonds [21,64]. Even if two torsional wavefunctions with localization in the 7-PR1 and 7-PR3 wells exist, it is likely that the population would cool to the lowest energy torsional level in the pulsed jet. Therefore, we do not expect that 7-PR3 is detectable in the experiment, or probably even distinguishable from 7-PR1.
I.9. The experimental structure of the water heptamer

The HOD substitution experiments confirm that the hydrogen bond network of the observed cluster has the 7PR1 geometry. The HOD substitution measurements can now be used to determine a quantitative experimental structure for the oxygen atom framework in a more precise structure determination that combines experiment and theory. The experimental moments of inertia (MOI) available from oxygen substitution in the form of 16 different HOD—O(C1/C1/C1) isotopic species provide abundant data for determination of the least-squares molecular structure using the rHF method [7,8]. The primary parameters of fit are the complete set of 30 structural internal coordinates defining the seven oxygen atom framework—O(1)/O(2)/O(3)/O(4)/O(5)/O(6)/O(7)—noting that the H2O framework is fixed and that the parameters that are fitted are for 48 experimental observables. The internal parameters of the systems considered are water molecules, (OH) and (CH2), are fixed at the calculated 7PR1-RM2/aug-cc-pVQZ values. The angular orientations of the water units are declared in such a way as to preserve the hydrogen bond angles (OH—O). In fact the decreasing the water molecule out of the c axis and do not have a significant effect on the final fit. It is also possible to fit the effective ground state, rHF geometry in a similar least-squares manner by omitting the three c parameters, although the deviation of fit turns out to be significantly poorer.

The final water heptamer structure is shown in Figures 10 and 11, while the associated Cartesian coordinates are listed in Table 5. Figure 10 compares the rHF geometry with the substitution and theoretical structures, while Figure 11 compares the experimental and theoretical O(7) values. On the other hand the theoretical RI-MP2/aug-cc-pVQZ equilibrium geometry shows clear differences in the oxygen atom positions, as shown in the left part of Figure 10 and as already identified in Table 4. This was found to be surprising in view of the excellent agreement between experimental and computed O—O distances, until it was realized that the experimental and computed geometries can be satisfactorily aligned by a simple rotational transformation about the center of mass of the heptamer cluster. Furthermore, alternative levels of computation, such as MP2/6-311G+(d,p), deliver similar oxygen networks but at considerably different equilibrium principal coordinates. In the particular case of MP2/6-311G+(d,p), which would normally be a less preferred computational level for water clusters, the agreement of calculated principal coordinates with experiment is actually very good (supplementary information). The present working conclusion is that this results from variation in the equilibrium hydrogen positions, which tend to be more susceptible to the level of computation. On the other hand the calculated values are consistent because they are all subject to the same effective hydrogen average in the ground state. We have, therefore, one further indication that the well known anharmonicity of the one-electron basis set and n-electron correlation, while reliable, is an incomplete description of the detailed information on water clusters. The RI-MP2/aug-cc-pVDZ method, while detailed structural information on water clusters. The RI-MP2/aug-cc-pVDZ method, while detailed structural information is provoking to the considerable advances made in determining the hydrogen bond and detachment energies of individual water sites from the O(7) value, for reasons of brevity, this will be the subject of a separate report.

The comparison of the various complete 3D-frameworks for the water heptamer as made in Figure 10 reveals an intriguing discrepancy. The rHF and rMP2 (as well as the rGA) experimental Cartesian coordinates are consistent with each other at the 0.01 Å level, and the corresponding lists are included in supplementary information. The comparison of experimental, theoretical and calculated O(7) values reveals several interesting features of the heptamer cluster. The shortest O—O distance, (O5—O7) = 2.942(3) Å, is, in fact, in the interconnecting pillar directly opposite the longest distance, and a similar situation is the case in the prism heptamer. The remaining eight O—O heptamer distances group into two relatively compact regions of values, as pointed out in Figure 11. More detailed understanding of underlifying hydrogen bonding responsible for these values is possible in the complete coordinate lists included in the supplementary material. The O—O distances are consistent with each other at the 0.01 Å level, and the corresponding lists are included in supplementary information.

I.10. Structural assignment of the second water heptamer

We have identified a second spectrum in the broadband rotational spectroscopy measurement with rotational constants characteristic of the water heptamer (see Table 1). However, the current spectrometer sensitivity precludes any isotopic measurements. We propose that its structure is 7PR2, the second lowest energy isomer deduced by theory. It is, however, first necessary to consider the possibility that this spectrum might arise from an excited vibrational state of 7PR1, possibly in the 7PR1/7PR2 potential. The main evidence against this assignment is that the two spectra have different dominant dipole moment components, with the weaker spectrum being due to a species with a- and c-type transitions, while the main heptamer has a- and b-type transitions. This difference cannot be accounted for by torsional averaging. In addition, the lack of strong transitions from the parent species suggest that the second spectrum is due to excited vibrational states and the heptamer species have a factor of 2 higher signal-to-noise ratio than the main heptamer cage, prism, and book isomers that could be attributed to excited vibrational states of the oxygen framework and, of course, the hydrogen dynamics has been the dominant feature in the studies of the smaller water clusters [65].

Figure 10. Comparison between the experimental oxygen frameworks obtained from two independent Krachan analyses (centre) and of these sub-frameworks with the calculated RI-MP2/aug-cc-pVQZ equilibrium structures (left) and the final least-squares, rHF structure (right).
The top panel highlights a portion of the 2–8 GHz spectrum of water after a Fourier transform without applying a window function. The colored traces are 1.5 K (radiation temperature) simulations of the six 18O single-substituted isomers of the water hexamer. The bottom panel shows the same frequency range but after application of a Kaiser-Bessel window to increase the baseline resolution. The infrared water line (1800–1900 cm⁻¹) is at 7548.45 MHz in the middle of the millimeter-on-basement transitions belonging to isotopeologues when the water function is not applied.

significant frequency offset from the excitation frequency in the "tail" of the line shape) and these can obscure weaker transitions in the spectrum. The impulse nature of the broadband CP-TFMW measurement makes it possible to shape the HD envelope using spectral window functions that significantly improve the baseline resolution making it possible to use the full dynamic range of the spectrometer to identify low abundance (or low polarity) species; it is the presence of species that generate strong rotational transitions. This effect is shown in Figure 12 for a region of the 2–8 GHz spectrum of water.

The analysis of a broadband rotational spectrum of a complex gas sample, like water, which the expansion takes full advantage of the wide range of water clusters, poses new challenges to the data analysis. The goal is to assign all spectra to the measurement and then to attribute to them molecular structures (through comparison to predictions from computational chemistry, for example). A strength of molecular rotational spectroscopy is that the Hamiltonian is known for the most common case of an asymmetric rotor with centrifugal distortion. This model can reproduce most rotational predictions from computational chemistry, for example). A strength of molecular rotational spectroscopy is that the Hamiltonian is known for the most common case of an asymmetric rotor with centrifugal distortion. This model can reproduce most rotational predictions from computational chemistry, for example).

### 3. Conclusions

Advances in high-speed digital electronics have ushered in the era of broadband molecular rotational spectroscopy. These spectrometers provide qualitatively new levels of measurement sensitivity and are expanding the size range of molecules for structure determination. Several groups are advancing broadband rotational spectroscopy methods. Recent work has described spectrometers for pulsed jet microwave spectroscopy in the 2–20 GHz frequency range and the extension to mm-wave spectroscopy for applications to chemical dynamics. Novel molecule beam sources, including pulsed laser ablation, have been incorporated into broadband rotational spectrometers to study fragile biomolecules and to produce novel species like metal containing clusters. Both microwave and mm-wave techniques have been developed for studies of room-temperature gases and these are pushing towards real-time, broadband spectral acquisition. New experimental capabilities, like 2D-CP-TFMW spectroscopy, and advanced analysis routines have also recently been described. Some of these techniques are being used in the analysis of interstellar rotational spectra where the line shape is seen as the Jaxby Very Large Array and the Atacama Large Millimeter/Submillimeter Array are now capable of producing spatially-resolved, broadband interstellar rotational spectra for astrochemistry at data rates near 1 TByte/day. The technology advances in laboratory and observatory have opened new applications for rotational and magneto-optics and moved the field into a new area of big data science.

Aknowledgements

This work was supported by US National Science Foundation (NSF) grants CHE-0906074 and DMR-0848277, and from the Poh- ling National Science Centre, decision number DEC/2011/02/052/ 08298, and NSF grants CHE 0116453, CHE-0521063, and CHE-
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Extraordinary attributes of 2-dimensional MoS$_2$ nanosheets

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A R T I C L E  I N F O  

Article info

Received 20 May 2014
In final form 4 June 2014
Available online 12 June 2014

A B S T R A C T

The discovery of graphene, the two-dimensional network of sp$^2$ carbon atoms, has created sensation in recent years because of its amazing properties [1,2]. This discovery has given impetus to the study of other two-dimensional materials based on layered inorganic materials. In the last few years, it has been possible to synthesize two-dimensional nanosheets of a variety of inorganic layered materials such as MoS$_2$ (Figure 1) and other metal chalcogenides [3,4]. Besides atomic force microscopy and such techniques, Raman spectroscopy is specially useful in determining the number of layers and in other aspects of characterization. Amongst the various layered materials, MoS$_2$ is special, in that it exhibits a variety of properties of vital interest to physical as well as materials sciences [5,6]. Thus, single layer MoS$_2$ can be a p-type semiconductor or a metal, depending on the way it is generated. MoS$_2$ sheets exhibit unusual magnetic properties as well. Besides favorable field-effect transistor characteristics and magnetic properties, MoS$_2$ nanosheets exhibit gas sensing and photoluminescence properties as well as visible-light induced photovoltaic activity to generate hydrogen from water. Recent studies have indeed shown that MoS$_2$ nanosheets exhibit many unusual properties, some with possible applications in energy devices, spintronics and optoelectronics. In this Letter, we present the synthesis, characterization, structure and properties of single- as well as few-layer MoS$_2$. We consider MoS$_2$ and related chalcogenides to be futuristic materials of importance.

1. Introduction

The discovery of graphene, the two-dimensional network of sp$^2$ carbon atoms, has created sensation in recent years because of its amazing properties [1,2]. This discovery has given impetus to the study of other two-dimensional structures based on layered inorganic materials. In the last few years, it has been possible to synthesize two-dimensional nanosheets of a variety of inorganic layered materials such as MoS$_2$ (Figure 1) and other metal chalcogenides [3,4]. Besides atomic force microscopy and such techniques, Raman spectroscopy is specially useful in determining the number of layers and in other aspects of characterization. Amongst the various layered materials, MoS$_2$ is special, in that it exhibits a variety of properties of vital interest to physical as well as materials sciences [5,6]. Thus, single layer MoS$_2$ can be a p-type semiconductor or a metal, depending on the way it is generated. MoS$_2$ sheets exhibit unusual magnetic properties as well. Besides favorable field-effect transistor characteristics and magnetic properties, MoS$_2$ nanosheets exhibit gas sensing and photoluminescence properties as well as visible-light induced photovoltaic activity to generate hydrogen from water. Recent studies have indeed shown that MoS$_2$ nanosheets exhibit many unusual properties, some with possible applications in energy devices, spintronics and optoelectronics. In this Letter, we present the synthesis, characterization, structure and properties of single- as well as few-layer MoS$_2$. We consider MoS$_2$ and related chalcogenides to be futuristic materials of importance.

2. Synthesis

MoS$_2$ has been synthesized by reaction of molybdenum trioxide and sulfur vapor. The synthesis of MoS$_2$ nanosheets is a simple process that involves a high temperature reaction between MoO$_3$ and S$_2$ (Equation 1).

MoO$_3 + 2S = MoS_2 + O_2$

The as-prepared MoS$_2$ nanosheets were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The XRD pattern of the MoS$_2$ nanosheets showed sharp peaks at 2θ values of 12.8°, 24.3°, and 42.5°, which correspond to the (002), (100), and (102) planes, respectively. The SEM images of the MoS$_2$ nanosheets showed well-defined hexagonal shapes with a lateral size of several micrometers. The TEM images of the MoS$_2$ nanosheets showed a uniform thickness of around 2 nm, indicating the presence of single-layered sheets.

3. Electronic properties

The electronic properties of MoS$_2$ nanosheets were studied using Raman spectroscopy and photoluminescence spectroscopy. Raman spectroscopy revealed the presence of the characteristic MoS$_2$ Raman modes at 380, 408, and 505 cm$^{-1}$, which correspond to the A$_g$, E$_g$, and B$_1$ modes, respectively. Photoluminescence spectroscopy showed two peaks at 2.34 eV and 2.50 eV, corresponding to the direct and indirect bandgap transitions, respectively.

4. Conclusion

In conclusion, MoS$_2$ nanosheets exhibit a variety of properties that make them promising candidates for applications in various fields such as electronics, energy storage, and catalysis. The synthesis of MoS$_2$ nanosheets is a simple process that involves a high temperature reaction between MoO$_3$ and S$_2$. The as-prepared MoS$_2$ nanosheets were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The Raman and photoluminescence spectroscopy studies revealed the electronic properties of MoS$_2$ nanosheets, which are promising for future applications.
nanosheets do not interact with TCNE since MoS$_2$ is a p-type mate-
rial and would not accept holes. First-principles calculations show a
large decrease in the bandgap of MoS$_2$ on interaction with TTF
[38]. Electron doping has been carried out electrochemically using a
FET, the effect being monitored by Raman spectroscopy [39].

4. Raman spectroscopy

MoS$_2$ exhibits four first-order Raman active modes, $E_{2g}$, $A_{1g}$, $E_{1g}$,
and $A_{2g}$ at 32, 286, 383 and 408 cm$^{-1}$ respectively. The $E_{2g}$ mode
is the only interlayer mode arising from the vibration of the two rigid
layers against each other while all the other modes are intralayer
modes due to $5$-Mo–S vibrations, of which only the $A_{1g}$ mode is
due to an out-of-plane vibration. The frequency of the $A_{1g}$ mode
increases and that of $E_{2g}$ decreases with the increasing number of
layers as shown in Figure 4a [40]. The line-width of the $A_{1g}$ mode
becomes maximum at $n=2$ while the line-width of the $E_{2g}$ mode
does not show dependence on the number of layers. The intensity,
line-widths as well as positions of both the modes depend on the
laser power (see Figures 4b and c). An increase in the force constant
due to an extra layer is expected to stiffen both $A_{1g}$ and $E_{2g}$ modes
[41]. Softening of the $E_{2g}$ mode with the increasing number of layers
is attributed to the decrease in the lattice constant on going from 3D
to 2D [42]. The resonant Raman spectrum of MoS$_2$ collected using
a 632.8 nm laser shows bands at 160, 454, and 634 cm$^{-1}$ other than
the $E_{2g}$ and $A_{1g}$ bands owing to the resonance [34,44]. Several of
the new modes are layer dependent [44]. Most prominent among these
low frequency modes are found at $179$ (two phonon dispersion dif-
ference mode $A_{1g}(M)-LA(M))$, $230$ (first order acoustic mode),
$377$ and $409$ cm$^{-1}$ ($B_{2g}$, $454$ cm$^{-1}$). Of these, the bands at $177$ cm$^{-1}$
and $409$ cm$^{-1}$ evolve with layer thickness. Two broad second-order
modes in the region $430$ cm$^{-1}$ to $490$ cm$^{-1}$, assigned to $2A_{1g}(M)$
and $A_{2g}$ modes also show layer dependence and stiffen with increase
in $n$. In the higher frequency region, three new bands appear at
$554$ cm$^{-1}$, $588$ cm$^{-1}$ and $628$ cm$^{-1}$, the relative intensities of which
vary with $n$. The layer dependence of different modes observed in
the Resonance Raman spectra indicates that coupling between the
electronic transitions and phonons become weak in ultra-thin MoS$_2$
[44].

Single-layer MoS$_2$ and MoSe$_2$ prepared by Li-intercalation and
exfoliation (the 1T-forms) exhibit Raman spectra which are dis-
tinctly different from those of the 2H-phases. Figures 4d and e show
the Raman spectra of the 1T phases of MoS$_2$ and MoSe$_2$, in
comparison with the spectra of the 2H phases. Other than the $E_{2g}$
and $A_{1g}$ modes of MoS$_2$, new bands $J_{1}$, $J_{2}$ and $J_{3}$ arise in the 1T phase
[24].

The first order modes ($E_{2g}$ and $A_{1g}$) of micromechanically cleaved
single layer MoS$_2$ show significant temperature dependence with
temperature coefficients of $-0.0179$ and $-0.0143$ cm$^{-1}$ K$^{-1}$ for the
$E_{2g}$ and $A_{1g}$ bands respectively [47–49]. The temperature coeffi-
cients of CVD MoS$_2$ are slightly higher, $-0.0179$ and $-0.0143$ cm$^{-1}$ K$^{-1}$ for
the $E_{2g}$ and $A_{1g}$ bands, respectively [50]. The temperature coeffi-
cients are smaller for the $E_{2g}$ band of bi-layer MoS$_2$ compared to that of the single-layer while it is more negative for the $A_{1g}$ band [50]. A combined effect of the four-phonon process
and thermal expansion determines the temperature coefficients of
out-of-plane $A_{1g}$ while the four-phonon process plays a major role
in the temperature dependence of the in-plane $E_{2g}$ mode. The thick-
ess dependence of the temperature coefficient and the role of
defects on the thermal properties of MoS$_2$ have been studied
[52]. As in the case of MoS$_2$, Raman spectra of other layered metal chal-
cogenides also show strong temperature dependence. The tempera-
ture coefficient of the $A_{1g}$ mode ($-0.86 \times 10^{-3}$ cm$^{-1}$ K$^{-1}$) of MoSe$_2$
is larger than that of the $A_{1g}$ mode ($-0.54 \times 10^{-3}$ cm$^{-1}$ K$^{-1}$), the lat-
ter being much smaller than the corresponding temperature coeffi-
cients of the same mode in single-layer MoS$_2$ [51]. First-principles
calculations reveal that the difference in the temperature coeffi-
cients of the Raman frequencies of MoS$_2$ and MoSe$_2$ arises from
the difference in the strain-phonon modes. The effect of exposing few-layer MoS$_2$ to high-temperature shock
waves has been studied by recently [52]. On exposure to shock-
waves, few-layer MoS$_2$ and other transition metal dichalcogenides
undergo significant morphological changes wherein the interlayer
(002) separation decreases along with softening of the Raman $A_{1g}$
and $E_{2g}$ bands (Figure 5) [45]. A combination of shear and uniaxial com-
pressive deformation is considered to be responsible for flattening
MoS$_2$ sheets giving rise to changes in the vibrational spectra.

5. Electronic structure and coupling with phononic A

While the three-dimensional structure of MoS$_2$ is centro-sym-
metric (space group No. 194, P6$_3$/mmc, $D_{6h}$), a monolayer of MoS$_2$
lacks the inversion symmetry (space group No. 17, P 6$\bar{2}$m, $D_{6h}$)
As a result, their electronic structures are qualitatively different:
Kramer’s degeneracy of electronic states of a monolayer is lifted
due to a concomitant shift in the spin–orbit coupling [53,54].

The dependence of electronic structure on the number of layers
of MoS$_2$ is also interesting. The electronic structure of MoS$_2$ with
more than one layer exhibits an indirect band gap, in contrast to
a direct gap that is responsible for the emergence of a strong pho-
toluminescence in monolayered MoS$_2$ [27].

An indirect gap ($1.29$ eV) of bulk MoS$_2$ is between the valence
band maximum at $K$ point and the conduction band minimum at $Q$
point that lies along $F$–$K$ direction of the Brillouin zone (Fig-
ure 5a). Using first-principles calculations on a bilayer MoS$_2$
Kadantsev et al. [54] have shown that the indirect band gap increases
crly with inter-layer separation while the direct gap at the $K$ point
is nearly unchanged ($1.79$ eV). While the former is similar to a typical increase in band-gap due to quantum confine-
ment, the latter suggests that interactions between the $d$-states of
Mo are significant. Calculations of quasiparticle band structure
including excitonic effects [55] within Mott–Wannier theory sug-
gest that exact binding energies of monolayered MoS$_2$ are quite
large ($-0.9$ eV). An explanation of the observed splitting (0.15 eV)
of the excitonic peak, however, has to include effects of
spin–orbit coupling. The top-most valence band at the $K$ point
exhibits the largest spin–orbit splitting of $0.145$ eV (Figure 5b),
while the states at the bottom of the conduction band are spin-
split by just $0.003$ eV [53,54]. These estimates agree well with
the observed splittings of the excitonic peaks.

The electronic structure of MoS$_2$ is far more interesting than
what is evident in its band dispersion (Figure 6a). The valence band
maximum and the conduction band minimum occur at two
independent points (K and $K$–) at the corners of the hexagonal
Brillouin zone (Figure 5a), forming two distinct valleys of electrons
and holes. (See section 10 for further discussion of valley physics.)

The dynamics of low-energy electrons in the neighborhood of $K$
or $K$ points can be modeled using a Hamiltonian of massive Dirac
fermions [56]. While the parabolic dispersion of electronic bands

Figure 5. Variation of the (a) (002) lattice spacing of few-layer MoS$_2$ and (b) the frequency of the Raman $A_{1g}$ and $E_{2g}$ bands of MoS$_2$ with increasing number of shots of shock waves. Inset in (b) shows the variation of Raman bands of few-layer WS$_2$. (Reported from Ref. [45]).
in these valleys can also be modeled as one for non-relativistic Fermions, the topological properties of electronic states (not evident in band dispersion) require the model to be of Dirac fermions with a mass that is related to the gap, and a speed of light replaced with a Fermi velocity (which is $85\,000\,$m/s in MoS$_2$ [56], quite comparable to that in graphene). A consequence of the Dirac nature of carriers in MoS$_2$ is the anomaly of the $n = 0$ Landau level in the presence of a magnetic field. While the $n = 0$ Landau level is at the top of the valence band in one valley, it is at the bottom of the conduction band in another. This results in a difference in absorption of circularly polarized light through excitations of carriers in the two valleys [56]. We note that such interesting electronic properties should in principle be possible in other 2-dimensional materials with honeycomb lattices (e.g. BN) as well, though the specific properties of MoS$_2$ make it particularly attractive for applications and studies to probe fundamental science.

The electronic structure of monolayer MoS$_2$ is quite tunable with in-plane strain [57] that can be introduced by imposing suitable boundary conditions, such as epitaxial constraints. In contrast to the electronic structure of graphene, the electronic band gap of MoS$_2$ changes dramatically with tensile as well as shear in-plane strains, leading to direct-to-indirect and semicon-ductor to metal transitions. Among these, pure shear strain is more effective (at 18%) in driving MoS$_2$ to a metallic state with a vanishing gap [57]. In a way, this highlights again the effects of interaction between the frontier d-states of Mo that form the topmost one at the Fermi level. A recent entry by a group of authors [58] in a field-effect transistor [39]. A large generalized shear strain (shift of one sulfur sublattice with respect to the rest) transforms MoS$_2$ to the JY polytypic form, which is centrosymmetric and metallic. However, the Fermi surface of this high-symmetry JT structure is weakly nested [56], and hence it is unstable with respect to valley phonons ($K_\parallel$). Indeed, the JT structure lowers its energy by breaking its symmetry to metallic $\Delta = 3\times 1$ or semiconducting $\Delta = 3\times 3$ structures. The latter appears to be ferroelectric [58], and dipole-tron devices have been proposed based on the coupling between its electric dipoles associated with phonons or the bound charges and carriers. Strong coupling between electrons, holes and phonons is also relevant to the stability of a trion (see Section 10).

### 6. Magnetic properties

Just like graphene, single- and few-layer MoS$_2$ exhibit room-temperature ferromagnetism which has been considered to manifest from edge effects [11,59]. In Figure 7a and b, we show zig-zag edges and bends (arising from defects) in the layers. Figure 7c shows the temperature dependence of magnetization of few-layer MoS$_2$ with a divergence in the FC-ZFC curves, which disappears on application of higher fields, a behavior generally observed in magnetically frustrated systems such as spin glasses where ferromagnetic and antiferromagnetic bonds are randomly distributed. The inset in Figure 7c shows magnetic hysteresis in few-layer MoS$_2$. The value of magnetization increases with the decrease in the number of layers. A clear evidence of co-existence of both ferromagnetic and anti-ferromagnetic interactions is provided by the observation of exchange bias as shown in Figure 7d [13]. Edge states have been considered to be like conducting wires which can be observed by a scanning tunneling microscope [60]. Among the low-index edges, the 5 edge appears to be associated with magnetism [61]. Edge-oriented MoS$_2$ nanosheets exhibit magnetoresistance [62]. It is noteworthy that the MoS$_2$ nanosheets become nonmagnetic beyond a certain thickness [63]. Magnetic force microscopy has been used to characterize single and few-layer MoS$_2$ as shown in Figure 7d-63).

Zig-zag MoS$_2$ nanosheets show ferromagnetic metallic properties independent of the width and thickness of the ribbons [60]. Armchair nanoribbons are nonmagnetic and semiconducting. Spin-orbital induced spin splitting in mono-layer MoS$_2$ has been examined and the giant spin-orbit splitting suggests possible spintronics applications. Magnetotransport measurements give a spin-orbit scattering length of 430 nm suggesting the potential for few-layer MoS$_2$ in spintronics [61]. Triply resonant Raman scattering has been employed to probe the valence band spin-orbit splitting in single-layer MoS$_2$ [63]. Hydrogenation of MoS$_2$ increases the carrier density out of plane while proton irradiation gives rise to easy axis in-plane [64].

### 7. Field-effect transistors

Semiconducting MoS$_2$ and related dichalcogenides possess properties that render them suitable as channel materials in field-effect transistors (FETs). Figure 8a shows an optical microscope image of a transistor prepared on single-layer MoS$_2$ flakes, flakes with Au top-gate being separated from the MoS$_2$ layer by a 30 nm HfO$_2$. A schematic representation of the cross-section is shown in Figure 8b. Radisavljevic et al. [66] reported that a top-gated transistor used on single-layer MoS$_2$ showed an on/off current ratio of $10^6$, a room-temperature mobility of greater than 200 cm$^2$/V s and n-type conduction (Figure 8c and d). Presence of a high k dielectric in the device further enhances the mobility [66]. It must be noted that mobility of 500 cm$^2$/V s and an on/off ratio of $10^6$ with n-type conductivity had been reported earlier in a WSe$_2$ based FET [67]. Hysteresis in back-gated single-layer MoS$_2$ FET has been shown to be due to the trapping states induced by adsorbed water on the surface and also due to photomixing of the devices [68]. Figure 8e and f show hysteresis in $I_{ds}$-$V_{ds}$ curve and its evolution under ambient conditions, after heating in vacuum and under controlled humidity. Dependence of the performance of a MoS$_2$ FET on the layer thickness has been examined [69]. The mobility decreases with the increase in number of layers. A FET using 15 nm thick MoS$_2$ sheet is reported to show an on/off ratio of 200 and hole mobility of 80 cm$^2$/V s [70]. Carrier-dependent Raman study of top-gated single-layer MoS$_2$ FET has shown an on/off ratio of 10$^4$ and a mobility of 50 cm$^2$/V s $^{-1}$ [71]. The $\Delta_{FS}$ phonon modes are active in the doping range [72]. The coulomb potential from trapped charges in the substrate appears to be the dominant source of disorder in MoS$_2$ FETs [71]. This disorder leads to carrier localization. Sangwan et al. [72] have carried out a detailed study of the low-frequency noise of MoS$_2$ transistors and shown that the noise amplitude increases by an order of magnitude under ambient conditions, revealing the significant influence of atmospheric adsorbates on charge transport.

Transistors have been fabricated with MoS$_2$ nanosheets of different thickness and metal contacts. Low work function metals improve the contacts, for example Schottky barrier height has been reduced significantly in Co contact transistors by addition of thin oxide barrier or by tuning the carrier density with back gate [73]. Salvatore et al. [74] demonstrate phototransisistor fabrication of flexible few-layer MoS$_2$ thin film transistors on a PVA/PMMMA stack that could be easily transferred to any flexible substrate. The flexible transistor had an electron mobility of 19 cm$^2$/V s $^{-1}$ and an on/off ratio greater than 10$^6$, even when bent to a radius of 5 mm and after 10 consecutive cycles [74]. Flexible, transparent transistors constructed with single-layer MoS$_2$ as channel, h-BN as dielectric and graphene as the back gate on the other hand showed mobility of 45 cm$^2$/V s $^{-1}$ and operating voltage below...
Few-layer MoS$_2$ has been reported to detect infra-red radiation [78]. Chemically exfoliated few-layer MoS$_2$ can be used as nanosheets and nanoinclusions and create opportunities for applications. Tightly bound negative trions, comprising two electrons and a hole, have been recently identified in a monolayer MoS$_2$ FET [94]. These quasi-particles can be created optically with valley and spin polarized holes. The trions are associated with a fairly large binding energy of the order of 20 meV. Trions can, therefore, occur at room temperature, leading to applications.

11. Lithium and sodium batteries

Due to the reversible Li-intercalation and deintercalation properties and fast-ion conduction, MoS$_2$ can be used in Li-ion batteries. One of the first reports of a Li-ion battery with MoS$_2$ was shown by Haering et al. [95]. MoS$_2$ with an enlarged c-lattice parameter showed a charge capacity of 750 mAh/g after 20 cycles at a current density of 50 mAh/g [96]. With hydrothermally prepared MoS$_2$ nanosheets and graphene-like MoS$_2$ nanolayers, the charge capacity increased to 1000 mAh/g [97] and 1062 mAh/g [98], respectively. WS$_2$ nanosheets too show good reversible capacity of 780 mAh/g for Li-ion storage [99]. Composites of graphene with MoS$_2$ show improved reversible capacity of 1290 mAh/g at a current density of 100 mAh/g up to 50 cycles (Figure 10a) and can maintain a high specific capacity of 1040 mAh/g even at a high current density of 1000 mA/g as shown in Figure 10b [100]. Several other reports on MoS$_2/graphene composites prepared by different routes [101–104] show high reversible capacity and good cyclability for Li-ion storage. Graphene–WS$_2$ composites show better battery properties as compared to bare WS$_2$ as shown in Figure 10c and d and retain high specific capacity at high current densities of up to 4000 mA/g [105]. A-doped graphene has been used instead of...
graphene to prepare a composite with MoS 2 to obtain rising capac-
ing to the electrode [117]. For photocatalytic H 2 evolution, composites of N-doped graphene with p-type MoS 2 , thereby enhancing charge transfer from graphene to MoS 2 . N-doped graphene–MoS 2 composites act as an electron collector and enhancing the charge separation [122]. Figure 11a demonstrates the mechanism of dye-sensitized H 2 evolution over graphene–MoS 2 composites. Since graphene acts as an electron channel for transfer of electrons from the dye to MoS 2 in the dye-sensitized H 2 evolution system, use of N-doped graphene can create a p–n junction in the composites (n-type N-doped graphene with p-type MoS 2 ), thereby enhancing charge transfer from graphene to MoS 2 . N-doped graphene–MoS 2 composites show enhanced photocatalytic activity [19] and electrocatalytic activity of 2H and 1T-MoSe 2 and 1T-MoS 2 (Reproduced from Refs. [19] and [23]).

12. Hydrogen evolution reaction and catalysis

Hinnemenn et al. [108] proposed that MoS 2 nanoparticles are good catalysts for the hydrogen evolution reaction (HER) and have a moderate overpotential of 1 V–0.2 V. In some of the early studies, edge sites of MoS 2 [109] and vacancy defects [110] were found to be active for HER. Several authors have reported improved electro-
chemical and photocatalytic hydrogen evolution activity in MoS 2 samples having higher surface areas and greater density of edge sites [111–113]. Hydrothermally synthesized graphene–MoS 2 composites show better HER activity and a low onset potential com-
pared to MoS 2 [116]. Graphene providing better good electrical cou-

Figure 11. (a) Schematic representation of dye-sensitized HER activity in graphene–MoS 2 composites, (b) Comparison of photocatalytic HER activity of N-doped graphene/ MoS 2 (NRGO–MoS 2 ) and graphene/MoS 2 (RGO–MoS 2 ) analysis, (c) schematic representation of the mechanism of dye-sensitized HER in 1T-MoS 2 and 1T-MoSe 2 , (d) HER activity of 2H and 1T-MoS 2 and 1T-MoSe 2 . Reproduced from Refs. [19] and [21].
on MoS_2 nanosheets is impressive. Due to the direct bandgap, single-layer MoS_2 finds applications in flexible electronics and other areas as single-layer and few-layer species. Moreover, other metal-dichalcogenides such as WS_2 and MoSe_2 could be as valuable as materials in spintronics as well as in electronic applica-
tions. The use of MoS_2 and MoSe_2 is seen to depend on magnetic properties by splitting water deserves to be examined further. Clearly, nano-
materials of MoS_2 and related dichalcogenides are emerging as new generation materials.

Due to the d-orbital character of the bands lining the bandgap, the charge carriers in MoS_2 couple strongly with both electronic and optical phonons. As a result of the topology of these bands and a size-

spin–orbit coupling, spin and valley degrees of freedom of the optic phonons. As a result of the topology of these bands and a size-

and technological applications. Needless to say, many of the proper-

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