

## INTERACTION OF $\text{NH}_3$ WITH $\text{Fe}(110)$ : IDENTIFICATION OF SURFACE SPECIES BY MEANS OF SECONDARY ION MASS SPECTROSCOPY (SIMS)

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Received 24 October 1978

The adsorption and decomposition of  $\text{NH}_3$  on a  $\text{Fe}(110)$  surface has been studied by means of secondary ion mass spectroscopy (SIMS) in the temperature range between 130 K to 800 K. Although there is some fragmentation of molecular  $\text{NH}_3$  by SIMS,  $\text{NH}_{\text{ad}}$  is unambiguously identified as an intermediate surface species by this method. Furthermore the conclusions reached in previous work on the basis of LEED, AES, UPS, work function and thermal desorption measurements on the adsorption, partial and total decomposition of  $\text{NH}_3$  on a  $\text{Fe}(110)$  surface could be fully confirmed.

### 1. Introduction

Iron forms strong hydrogen, carbon, nitrogen and oxygen bonds and because of this pronounced reactivity it is a widely used catalyst for the synthesis of hydrocarbons and ammonia. Therefore, the surface chemistry of this metal has been extensively studied in the past and some recent papers report very detailed results on the interaction of ammonia with clean low index surfaces of iron single crystals [1–3]. Grunze et al. [1] studied the adsorption and decomposition of  $\text{NH}_3$  on clean and nitrogen covered  $\text{Fe}(111)$  and  $\text{Fe}(100)$  surfaces and by UPS identified at least one intermediate surface species (presumably  $\text{NH}_{2,\text{ad}}$ ) before complete dissociation of  $\text{NH}_{3,\text{ad}}$  into  $\text{N}_{\text{ad}} + \text{H}_{\text{ad}}$  at 320 K occurs. A somewhat different behaviour was reported by Weiss et al. [2] for the interaction of  $\text{NH}_3$  with  $\text{Fe}(110)$ . On this surface  $\text{NH}_3$  adsorbs non-dissociatively below room temperature and at 350 K a stable surface intermediate, most probably  $\text{NH}_{\text{ad}}$ , is formed exhibiting a  $2 \times 2$  LEED-pattern. Above 400 K complete dissociation occurs and  $\text{H}_2$  desorbs, finally above 850 K the remaining chemisorbed N-atoms recombine and desorb as  $\text{N}_2$ . Preadsorbed N inhibits the formation of the intermediate  $\text{NH}_{\text{ad}}$ -species at 350 K.

SIMS has proven to yield detailed information on the chemical state and changes

of solid surfaces down to  $10^{-6}$  of a monolayer coverage [4] and in many cases it can even provide reliable quantitative results [5,6,7]. The present paper presents a reinvestigation of the adsorption and decomposition of NH<sub>3</sub> on Fe(110) as reported in [2], with the aim to check the SIMS-method in this kind of surface reaction system and especially to provide an unambiguous identification of the intermediate surface species.

## 2. Experimental

Experiments were performed in a stainless steel UHV-apparatus equipped with SIMS, LEED and AES as described earlier [7]. Typical operating conditions were vacuum in the low  $10^{-10}$  Torr range, primary ions: Ar<sup>+</sup> of (5–10)nA/cm<sup>2</sup> current density at 1 keV energy in the static SIMS mode and 0.2  $\mu$ A/cm<sup>2</sup> at 1.6 keV in the sputtering mode, respectively.

Ammonia was introduced through a movable capillary tube system mounted on a manipulator and ending in front of the Fe sample. As described earlier [1] this device was chosen in order to avoid contaminations and memory effects of the stainless steel chamber. It was adjusted to achieve saturation of the surface within about 10 min.

The single crystal sample exposing the (110) plane had already been used previously [2] and similar cleaning procedures were applied: (i) sputtering at 970 K with a total Ar<sup>+</sup> dose of  $5 \times 10^{14}$  ions/cm<sup>2</sup>, (ii) sputtering at room temperature up to  $10^{17}$  ions/cm<sup>2</sup> with annealing cycles up to 770 K in between, (iii) short annealing at 770 K for few minutes before every experimental run. The cleanliness of the surface was controlled by SIMS (see below) and in addition to that by AES and LEED. In the AES-spectrum (2nd derivative) the peak to peak height of carbon relatively to that of iron (651 eV) was far less than 0.1. The LEED pattern exhibited only well-developed substrate lattice spots.

## 3. Results and discussion

### 3.1. SIMS-spectra of the clean Fe(110)-surface

Main peaks in the spectrum of positive secondary ions from the cleaned Fe(110)-surface (fig. 1) are the iron ions Fe<sup>+</sup>, Fe<sub>2</sub><sup>+</sup>, Fe<sub>3</sub><sup>+</sup> and alkali contaminations (Na<sup>+</sup>, K<sup>+</sup>). The latter, however, have an extremely high detection probability with SIMS and therefore only represent surface concentrations in the range of about  $10^{-5}$  of a monolayer. In addition also spurious contaminations with carbon and oxygen are detected (FeC<sup>+</sup>, Fe<sub>2</sub>C<sup>+</sup>, FeO<sup>+</sup>, Fe<sub>2</sub>O<sup>+</sup>), the corresponding counting rates are very low, however. This represents the detection level of SIMS for C and O when in the AES-spectra practically no C and O-peaks were visible. In SIMS some hydrogen (H<sup>+</sup>)

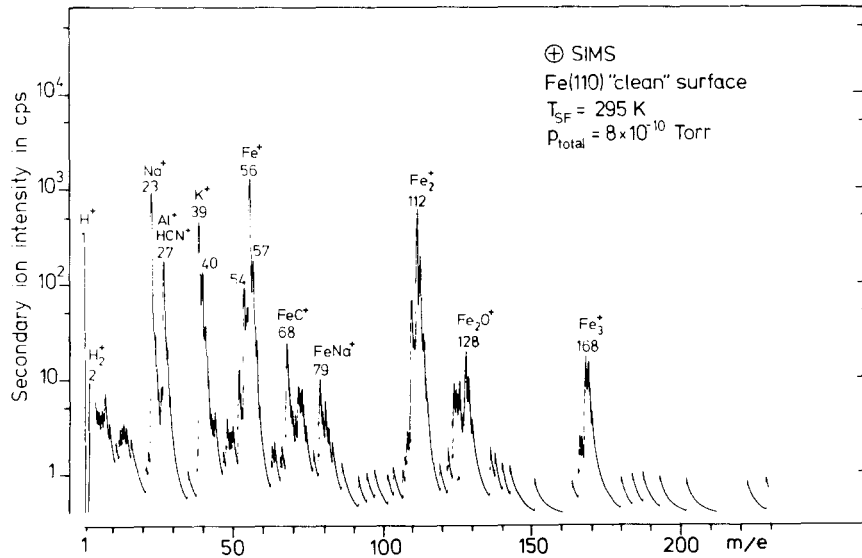


Fig. 1. Mass spectrum of positive secondary ions from a clean  $\text{Fe}(110)$  surface at room temperature. Primary ions:  $\text{Ar}^+$ ,  $E = 1 \text{ keV}$ ,  $j = 8 \text{ nA/cm}^2$ . Residual gas pressure:  $1 \times 10^{-10}$  Torr, total pressure (with argon):  $8 \times 10^{-10}$  Torr.

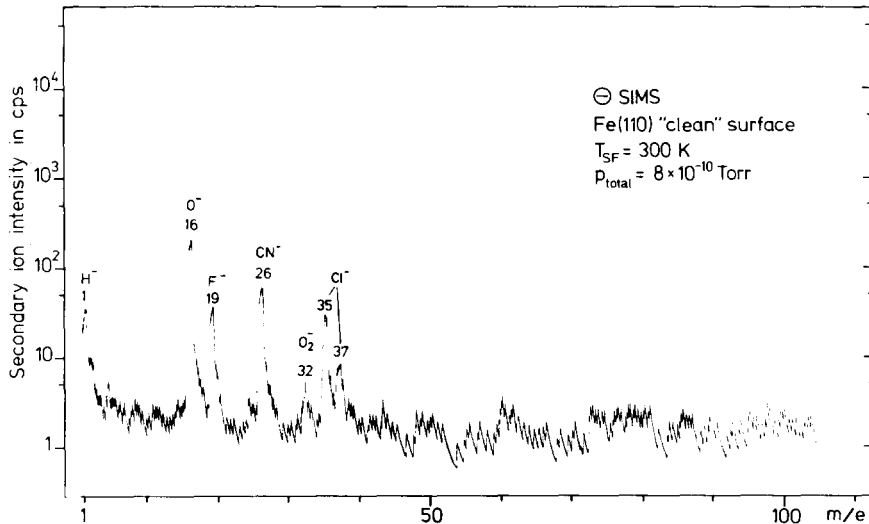


Fig. 2. Mass spectrum of negative secondary ions from a clean  $\text{Fe}(110)$  surface at room temperature. The surface is clean according to AES and LEED standards, all appearing ions are known to have high yields with SIMS.

is also seen but again this species is known to have a high detection probability. It arises probably from the ion-getter pumps of our apparatus. Correspondingly the spectrum of negative secondary ions (fig. 2) shows some impurities ( $\text{H}^-$ ,  $\text{O}^-$ ,  $\text{F}^-$ ,  $\text{CN}^-$  and  $\text{Cl}^-$ ) which again easily appear in SIMS even at very low levels of surface concentration. In summary, these spectra characterize a surface which is clean according to AES- and LEED-standards, the remaining features in SIMS being typical for this method.

### 3.2. Adsorption of $\text{NH}_3$ at low temperatures

The sample was cooled to 130 K whereby no observable changes in the SIMS-spectra occurred. Then the gas inlet valve was opened and  $\text{NH}_3$  admitted to the  $\text{Fe}(110)$  surface. During the  $\text{NH}_3$ -exposure the following changes in the mass spectrum of the positive secondary ions could be noticed (fig. 3): Ions of the compositions  $\text{Fe}_n(\text{NH}_3)_m^+$  with  $n, m = 1, 2$  and  $\text{NH}_n^+$  with  $n = 0, 1, 2, 3, 4$  appeared, simultaneously the hydrogen signals ( $\text{H}^+$ ,  $\text{H}_2^+$ ) increased and the  $\text{Fe}^+$  signals reached a saturation value with the exception of  $\text{Fe}^+$  which became constant only after 10 min. Interruption of the  $\text{NH}_3$ -exposure did not result in any changes of the signals from the saturated surface, therefore adsorption of  $\text{NH}_3$  to  $\text{Fe}(110)$  at 130 K is ob-

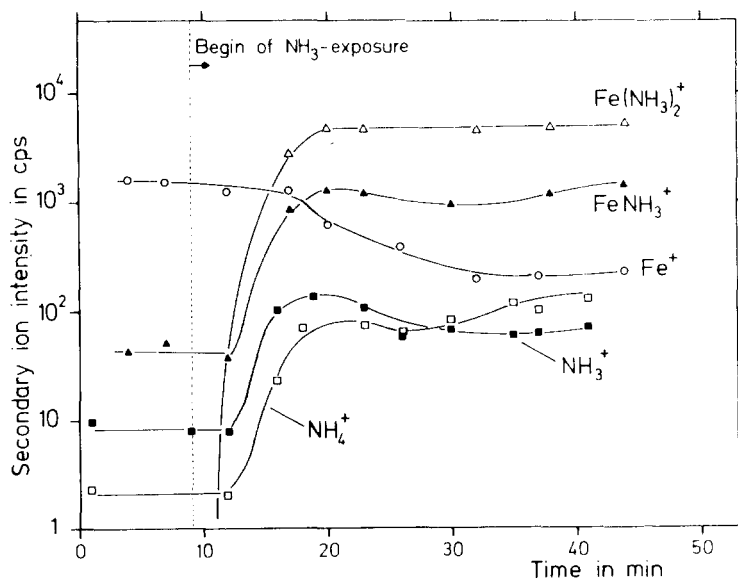


Fig. 3. Time dependence of typical SIMS signals from  $\text{Fe}(110)$  when exposed to  $\text{NH}_3$  at  $T = 135$  K beginning at  $t = 9$  min, the surface soon reaches a state of saturation. (The dashed line at  $t = 9$  min indicates the opening of the valve, subsequently there is some delay caused by the capillary system.)

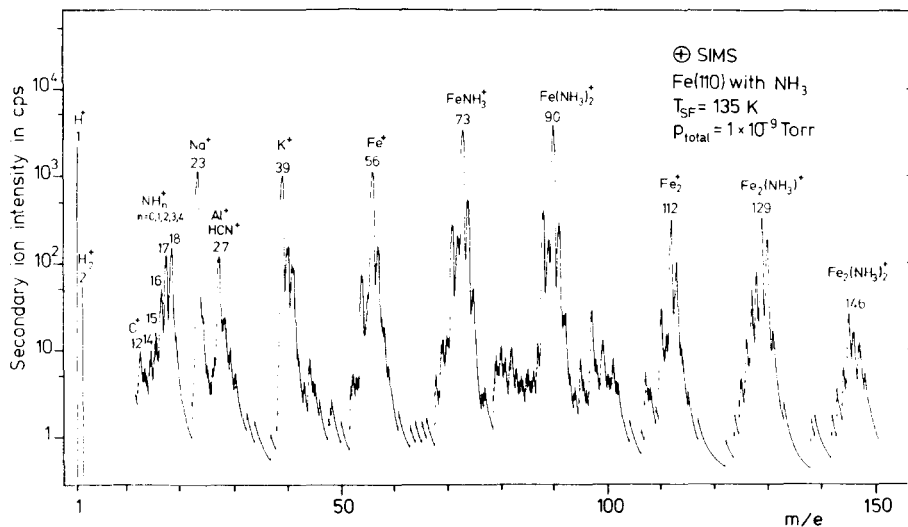


Fig. 4. Mass spectrum of positive secondary ions from a Fe(110) surface, saturated with ammonia at 135 K. The pronounced peaks of  $\text{FeNH}_3^+$ ,  $\text{Fe}(\text{NH}_3)_2^+$ ,  $\text{Fe}_2(\text{NH}_3)^+$  and  $\text{Fe}_2(\text{NH}_3)_2^+$  indicate non-dissociative adsorption of  $\text{NH}_3$ .

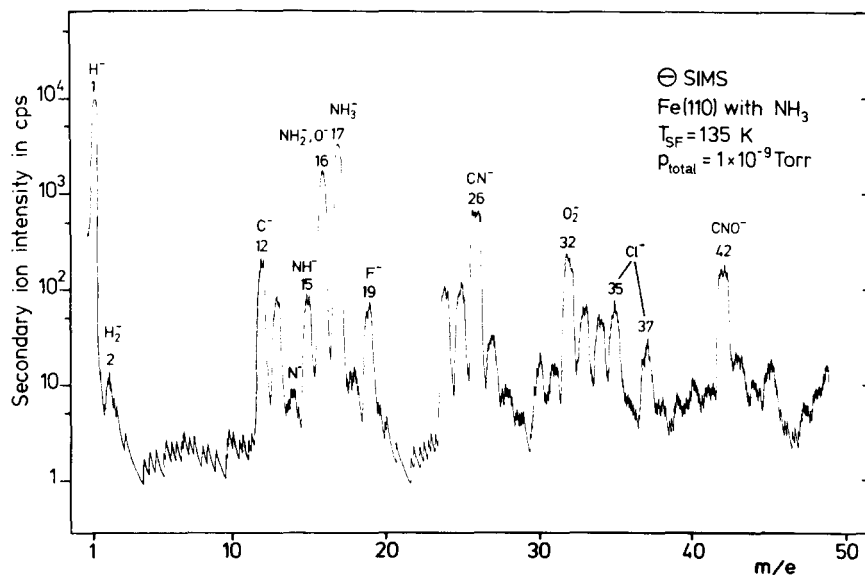


Fig. 5. Mass spectrum of negative secondary ions from a Fe(110) surface saturated with  $\text{NH}_3$  at 135 K. The most prominent feature is the  $\text{NH}_3^-$ -peak (mass 16 includes large contribution from  $\text{O}^-$ ).

viously irreversible. The pronounced appearance of Fe<sub>n</sub>(NH<sub>3</sub>)<sub>m</sub><sup>+</sup> ions clearly indicates molecular adsorption without dissociation in complete agreement with the findings of Weiss et al. [2]. In this work molecularly adsorbed ammonia was identified by UPS by the occurrence of valence ionization potentials of 6.7 and 11.2 eV below the Fermi level  $E_F$  which were attributed to the 3a<sub>1</sub> (= N lone pair) and 1e (= N–H bond) levels, respectively.

The SIMS-spectra of a NH<sub>3</sub> saturated surface are shown in figs. 4 and 5, the most prominent feature in the negative ion spectrum being NH<sub>3</sub><sup>-</sup>. The presence of signals of type NH<sub>n</sub><sup>+</sup> with  $n < 3$  will be discussed next.

### 3.3. Fragmentation of molecular NH<sub>3</sub> in the secondary ion spectra

From the occurrence of Fe<sub>n</sub>(NH<sub>3</sub>)<sub>m</sub><sup>+</sup> signals it is concluded that ammonia adsorbs non-dissociatively in Fe(110) at  $T = 130$  K. The simultaneous and non-negligible presence of ions NH<sub>n</sub><sup>+</sup> with  $n = 0, 1, 2, 3, 4$  might appear to be in disagreement with this conclusion and has therefore to be explained. One could think of the following reasons for their appearance:

(i) The corresponding neutral species NH<sub>n</sub> are indeed adsorbed on the surface. Such a conclusion would however be in clear contradiction with the UPS results which revealed evidence for the presence of only a single surface species (NH<sub>3,ad</sub>) under these conditions [2], and is therefore ruled out.

(ii) Molecularly adsorbed NH<sub>3</sub> is dissociated by primary ion impact. In this case the yield of NH<sub>n</sub><sup>+</sup> should depend on energy, current density and dose of primary ion impact. Detailed measurements however revealed no such dependence for ion energies between 0.5 and 1.8 keV at a current density  $j = 5$  nA/cm<sup>2</sup> up to 1 h. Consequently this possibility appears rather improbable.

(iii) The fragmentation of NH<sub>3</sub> occurs during the emission process, i.e. there is a certain probability for cracking molecularly adsorbed NH<sub>3</sub> during ion formation. The fragments then can be detected as H<sup>+</sup>, H<sub>2</sub><sup>+</sup>, N<sup>+</sup>, NH<sup>+</sup>, NH<sub>2</sub><sup>+</sup> and NH<sub>3</sub><sup>+</sup> and reflect electronic processes during the emission event. Experimentally we found that the secondary ion yields for the fragment masses 14–17 (i.e. N<sup>+</sup>, NH<sup>+</sup>, NH<sub>2</sub><sup>+</sup>, NH<sub>3</sub><sup>+</sup>) can be written as

$$Y(i) = c_i \cdot Y(17),$$

where  $i = 14, 15, 16$  and  $Y(i)$  = yield of mass number  $i$ . The coefficients  $c_i$  revealed to be independent of the primary ion energy and the current density as well as to be independent of NH<sub>3</sub> coverage and surface temperature in the molecular adsorption range. From a whole series of measurements below  $T = 270$  K the following coefficients were determined:

$$c_{14} = 0.12 \pm 0.02, \quad c_{15} = 0.14 \pm 0.03, \quad c_{16} = 0.41 \pm 0.04.$$

For surface temperatures above 300 K however the coefficient  $c_{15}$  (i.e. NH<sup>+</sup>) starts to behave differently as will be discussed below. It is worthwhile to notice that these

coefficients resemble very closely to those obtained by electron impact ionization of gaseous ammonia. Such a comparison was performed in the same apparatus using a conventional ionization chamber in front of the mass filter with electron energies ranging from 30 eV to 80 eV and yielded

$$c_{14} = 0.14 \pm 0.02, \quad c_{15} = 0.18 \pm 0.03, \quad c_{16} = 0.45 \pm 0.04$$

for the coefficients. (It is therefore concluded that in both ionization processes, i.e. on the surface by SIMS and in the gas phase by electron impact, similar elementary processes occur within the highly excited molecule leading to fragmentation).

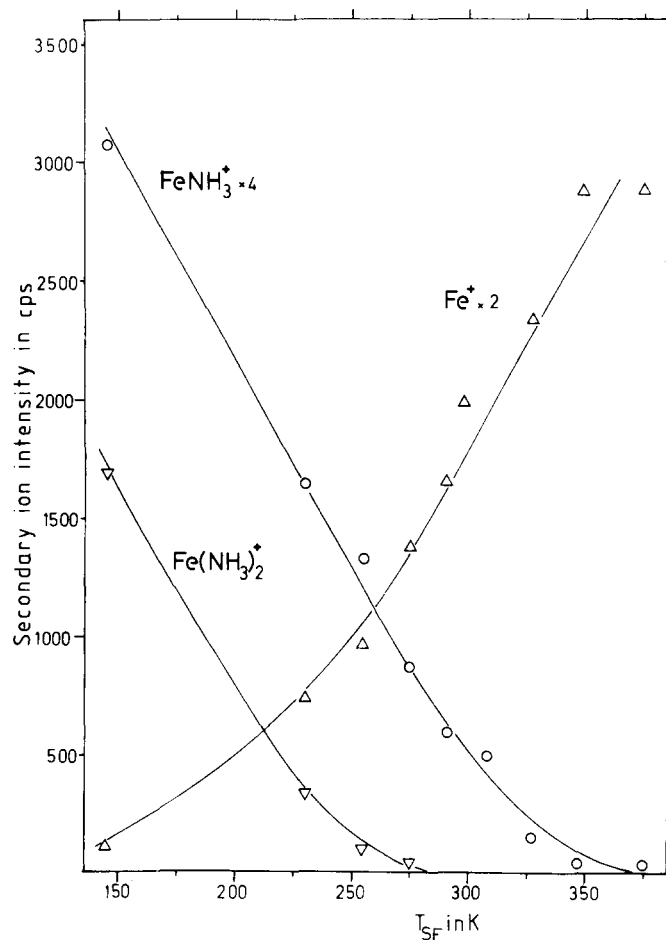


Fig. 6. Variation of some typical SIMS signals during slow heating of a Fe(110) surface previously saturated with NH<sub>3,ad</sub> at low temperature, indicating continuous desorption of NH<sub>3</sub>. (Scale factors indicate that these counting rates have been multiplied before plotting.)

### 3.4. Thermally activated chemical transformation of adsorbed ammonia

The surface was saturated with adsorbed ammonia at 135 K and then the sample temperature was continuously increased (2 K/min), while SIMS signals were measured as a function of surface temperature. Fig. 6 shows the results for the ion yields of  $\text{FeNH}_3^+$ ,  $\text{Fe}(\text{NH}_3)_2^+$ , and  $\text{Fe}^+$ , clearly demonstrating a continuous decrease of signals typical for molecularly adsorbed  $\text{NH}_3$  with a simultaneous increase in the  $\text{Fe}^+$  signal which is typical for the iron surface itself. The very same dependence on surface temperature was observed with the signals  $\text{Fe}_2\text{NH}_3^+$ ,  $\text{Fe}_2(\text{NH}_3)_2^+$ ,  $\text{H}_2^+$ ,  $\text{H}^+$  on the one hand, and  $\text{Fe}_2^+$  on the other. In the negative secondary ion spectra – again investigated during heating of a surface saturated with  $\text{NH}_3$  at low temperature – a decrease of ion yields is observed which is very similar to the temperature dependence of  $\text{FeNH}_3^+$  and  $\text{Fe}(\text{NH}_3)_2^+$  as shown in fig. 6. This statement holds for all negative ions of interest in connection with  $\text{NH}_3$ , i.e.  $\text{H}^-$ ,  $\text{H}_2^-$ ,  $\text{N}^-$ ,  $\text{NH}^-$ ,  $\text{NH}_2^-$ ,  $\text{NH}_3^-$ , and  $\text{NH}_4^-$ , thus indicating a continuous desorption of  $\text{NH}_3$  with increasing surface temperature.

A somewhat different behaviour is revealed by the signals of  $\text{NH}_3^+$  and  $\text{NH}_2^+$ : these

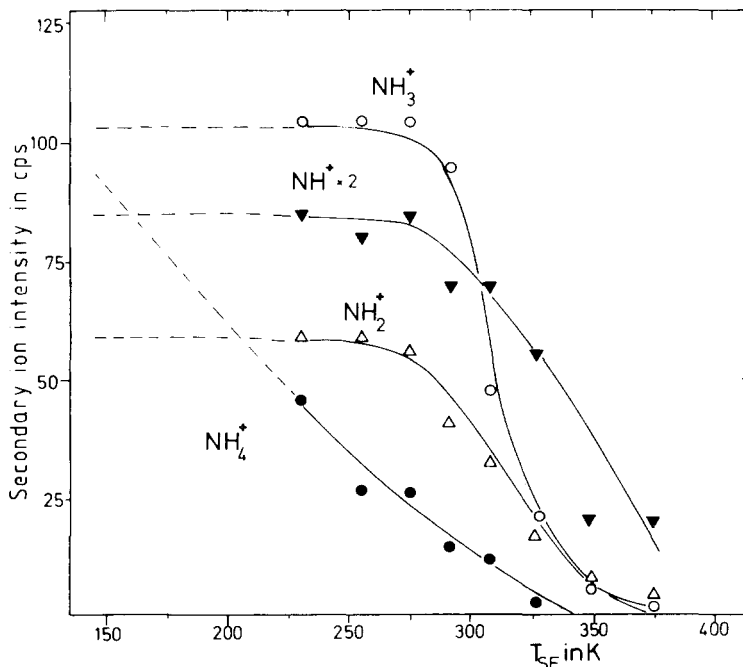


Fig. 7. Change of  $\text{NH}_3^+$  signal and related fragmentary ions during slow heating of a  $\text{Fe}(110)$  surface which was saturated with  $\text{NH}_{3,\text{ad}}$  at low temperature. The behaviour below 230 K was controlled in a different run. (For discussion see text.)

yields practically remain constant up to a surface temperature of 275 K and then drop rather rapidly to zero (at about 350 K) as can be seen from fig. 7. From these findings it is concluded that adsorbed ammonia is completely removed from the surface at 350 K. This is in complete agreement with the results of thermal desorption spectroscopy (TDS) where with a considerably higher heating rate (9 K/s) desorption of  $\text{NH}_3$  was completed at this temperature [2]. Since in the present case the temperature was increased much more slowly, however, a small fraction of the adsorbed  $\text{NH}_3$  does not desorb but is decomposed in another (intermediate) surface species. As can be seen from fig. 7, above 280 K the  $\text{NH}^+$ -yield is no longer proportional to that of  $\text{NH}_3^+$  (which would be expected if it is only an ionization fragment) but decreases much less with increasing temperature, indicating the transient build-up of a small amount of  $\text{NH}_{\text{ad}}^+$ . This conclusion will be clearly confirmed by the results described below. No simple explanation can be given for the different behaviour of  $\text{Fe}_n(\text{NH}_3)_m^+$ - and  $\text{NH}_n^+$ -yields, respectively. It is not clear at present whether this reflects different origins of the ion groups from the surface (e.g. different binding sites) or another effect on the ion yield which depends on surface temperature. Next, the freshly cleaned  $\text{Fe}(110)$  surface was exposed to  $\text{NH}_3$  at room temperature. The

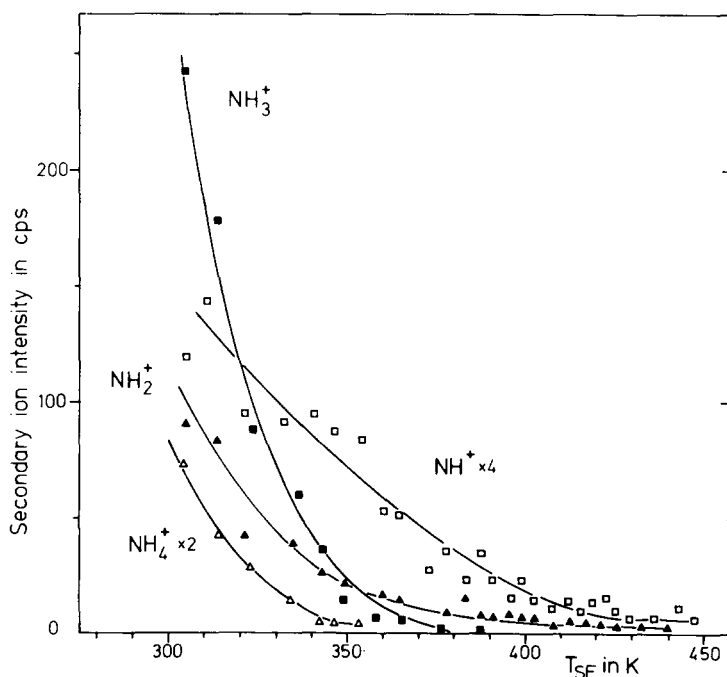


Fig. 8. Change of secondary ion yields for  $\text{NH}_3^+$  and related ions during heating of a  $\text{Fe}(110)$  surface which was covered with  $\text{NH}_3$  at room temperature. The  $\text{NH}^+$ -yield exhibits an uncorrelated behaviour.

corresponding SIMS spectra again indicated molecular adsorption. Starting from this initial state, the sample was slowly heated while simultaneously the  $\text{NH}_n^+$ -ion yields ( $n = 0, 1, 2, 3$ ) were monitored. The result is shown in fig. 8 and indicates that  $\text{NH}_3^+$  decreases with increasing surface temperature, reaching 1/10 of the initial value at  $T = 345$  K and has completely disappeared at  $T = 365$  K. The yields of  $\text{NH}_2^+$  show a similar dependence on surface temperature whereas the  $\text{NH}^+$ -yield behaves totally different. From the above discussion it is clear, that as long as molecular ammonia

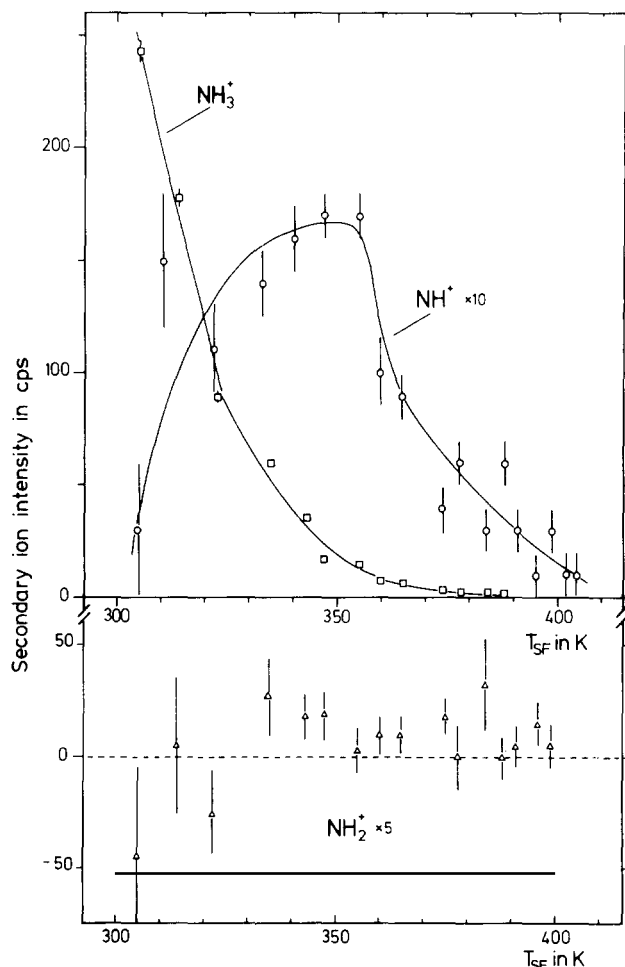


Fig. 9. Same as fig. 8, after correcting the  $\text{NH}_2^+$  and  $\text{NH}^+$ -yields for contributions of fragmentary ions from  $\text{NH}_3$ . Error bars contain statistics and uncertainty in the coefficients for fragmentation. The intermediate surface species originating from the dissociation of  $\text{NH}_3$  is  $\text{NH}_{ad}$  and exists between 300 K and 400 K.

is present at the surface, fragment ions will be formed. Therefore we subtracted from the raw data for the NH<sup>+</sup>-yields that portion which results from fragmentation. According to section 3.3 this is determined by  $Y(i) = c_i \cdot Y(17)$ , with  $c_{15} = (0.14 \pm 0.03)$  and  $c_{16} = (0.41 \pm 0.04)$  for mass numbers 15(NH<sup>+</sup>) and 16(NH<sub>2</sub><sup>+</sup>) respectively. The resulting data representing the true relative surface concentrations of NH<sub>ad</sub> and NH<sub>2,ad</sub> are reproduced in fig. 9. These data demonstrate that the surface concentration of NH<sub>2,ad</sub> is practically zero, whereas that for NH<sub>ad</sub> passes through a pronounced maximum at about 350 K. Above 400 K this species obviously decomposes. These results are in full agreement with the findings of an earlier investigation [2], where upon interaction of NH<sub>3</sub> with Fe(110) at 350 K a surface intermediate NH<sub>x</sub> ( $x = 1$  or 2) could be formed which was characterized by a  $2 \times 2$  LEED pattern and by maxima at 5.2 and 8.4 eV below  $E_F$  in the photoemission spectrum. It was, however, not possible to clearly decide on the basis of the UPS data whether this intermediate is adsorbed NH or NH<sub>2</sub>. This decision can now clearly be made from the present SIMS measurements. It was further observed [2] that this species dissociates above 400 K into N<sub>ad</sub> and H<sub>ad</sub>, followed by rapid recombination and desorption of H<sub>2</sub>. N<sub>ad</sub> was characterized by a UPS peak at about 5 eV below  $E_F$ . Recombination and desorption of N<sub>2</sub> was observed to take place around 850 K. These subsequent reaction steps were again confirmed in the present work. Interaction of NH<sub>3</sub> with the clean Fe(110) surface above 400 K showed only a continuous increase of the N<sup>+</sup> signal, caused by the build-up of N<sub>ad</sub>. This signal started to decrease in intensity only if the sample was heated to temperatures above 700 K.

Finally an experiment was performed in which a N-precovered surface was exposed to NH<sub>3</sub> at room temperature. Adsorption of ammonia was monitored by recording the corresponding NH<sub>3</sub><sup>+</sup> signal. Upon slow heating of the sample under these conditions only desorption of NH<sub>3</sub> was observed, but no intermediate formation of NH<sub>ad</sub>. This observation supports again the previous conclusions [2] whereafter preadsorbed N inhibits the dissociation of adsorbed NH<sub>3</sub>. No recombination of N<sub>ad</sub> with adsorbed hydrogen was observed under the applied low-pressure conditions which is again in agreement with previous findings [2].

#### 4. Conclusions

If a clean Fe(110) surface is exposed to ammonia below room temperature non-dissociative adsorption takes place. At 365 K desorption is on the other hand completed. Interaction with NH<sub>3</sub> above room temperature may also lead to the formation of NH<sub>ad</sub> which reaches its maximum concentration around 350 K and decomposes above this temperature into N<sub>ad</sub> + H<sub>ad</sub>. The formation of this intermediate is inhibited by the presence of preadsorbed nitrogen.

The results are in complete quantitative agreement with the conclusions reached previously for this system [2] by application of LEED, UPS, AES, work function, thermal desorption and isotope exchange methods. While these techniques were not

able to unequivocally distinguish between NH<sub>ad</sub> and NH<sub>2,ad</sub> as possible intermediate, this decision could clearly be made on the basis of the SIMS data. It is thus demonstrated that the method of static SIMS is a valuable tool for the identification of surface species and that it can reliably be used for the investigation of surface reactions, particularly if the results are compared with the data obtained with other surface sensitive techniques.

### **Acknowledgment**

Financial support of this work by the Deutsche Forschungsgemeinschaft (Wi 350/5 and SFB 128) is gratefully acknowledged.

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