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# A study of the temperature dependence of a surface catalyzed and field enhanced formation of $H_3$ and $NH_3$ on metal surfaces

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In pulsed-laser field desorption of hydrogen,  $H_3^+$  can be detected. In an  $H_2$ - $N_2$  mixed gas, the pulsed-laser field desorption mass spectrum contains  $NH_3^+$ . The formation of  $H_3^+$  and  $NH_3^+$  on about 20 metal surfaces has been studied in a pulsed-laser imaging atom probe. The signal intensity and the relative abundance of these species depend on the surface temperature, the emitter material, the laser intensity, and the applied field strength. From these dependencies we conclude that the  $H_3^+$  and  $NH_3^+$  observed are produced by field ionization above the critical distance of field ionization of the pulsed-laser, thermally desorbed  $H_3$  and  $NH_3$  molecules. These molecules are produced by surface catalyzed chemical reactions, and exist in field adsorbed states.

## I. INTRODUCTION

Surface catalyzed chemical reactions are a subject of great current interest. Information sought include how the reactivity and selectivity of a surface are related to the chemical composition and atomic structures of the surface and what are the detailed atomic steps involved in a surface catalyzed chemical reaction. The steps may consist of accommodation and adsorption of gas molecules, dissociation and diffusion, formation of a new species at specific surface sites, and desorption of the new species from some desorption sites which may or may not be the same as the sites of their formation. Surface science approaches to study these problems have been to characterize the surface in UHV and then carry out the chemical reaction at low temperatures and low gas pressures. Practical catalyses are of course mostly done at high temperatures and pressures.

There are many techniques available for studying these problems. One technique, the atom-probe field ion microscopy<sup>1</sup> seems to be well suited for such studies. An atomically well defined surface can be developed by field evaporation. Gases can be condensed on the surface, and desorption from specific surface sites can be studied by aiming the probe hole to these sites. Unfortunately, the high electric field needed in the atom-probe operation creates artifacts which often confuse with the true surface catalyzed chemical reaction one intends to study.

It is well known from early field ionization mass spectroscopic studies<sup>2</sup> that an applied high electric field can produce unusual chemical reactions on emitter surfaces. In these studies, brush like multiple emitters are used. Not only the surface conditions are poorly defined, but also most of the chemical reactions observed are field induced. With the advent of the high voltage pulse operated time-of-flight atom-probe,<sup>1</sup> surface reactions, in principle, can be studied from atomically well defined emitter surfaces developed by field evaporation. Indeed, early atom-probe studies have found formation of novel ions such as metal halides and hydrides.<sup>3</sup> Unfortunately when the high voltage pulse atom probe is employed to study adsorption-desorption of gases on metal surfaces, one invariably observes only field dissociated or associated products. For example, in CO adsorption on W surfaces, the ionic species observed are  $C^{++}$ ,  $O^+$ ,

$CO^+$ ,  $C^+$ ,  $WC^{+++}$ ,  $WO^{+++}$ ,  $WO^{+++}$ , etc. These observed ionic species do not shed any light on the adsorption state of CO on the W surface. In addition to this difficulty, it is found that some adsorbed species simply cannot be field desorbed with high voltage pulses without also field evaporating the substrate atoms. Thus the surface conditions cannot be maintained during an experimental measurement. With these serious limitations, it is not surprising that the high voltage pulse operated ToF atom probe has not been meaningfully applied to study either gas-surface interactions or catalytic reactions on solid surfaces.

These limitations of the atom probe have now been largely overcome by the introduction of the pulsed-laser technique to the ToF atom-probe operation. From a search of photon-stimulated field ion emission with laser pulses,<sup>4</sup> it was recognized that several advantages might have existed by operating the ToF atom probe with laser pulses.<sup>5</sup> One of the advantages anticipated was that field desorption could be done at a much lower field by a thermal effect, thus the disturbing effects of the high electric field could be greatly reduced. Indeed, with the development of the pulsed-laser atom probes,<sup>6</sup> gas surface interactions can now be studied.

From a measurement of the energy distribution of pulsed-laser field desorbed ions, it is now well established that the adsorbed gas atoms or molecules are first thermally desorbed from their adsorption states by laser pulse heating of the emitter surface.<sup>7</sup> When they pass across the field ionization zone, a fraction of them will be ionized. If the applied field is low enough, field dissociation and association effect can be either completely eliminated, or be greatly reduced. The detected ion species therefore reflect well the adsorbed molecular species. We are also able to desorb adsorbed species without field evaporating the substrate atoms. Thus the same surface conditions can be maintained during an experimental measurement.

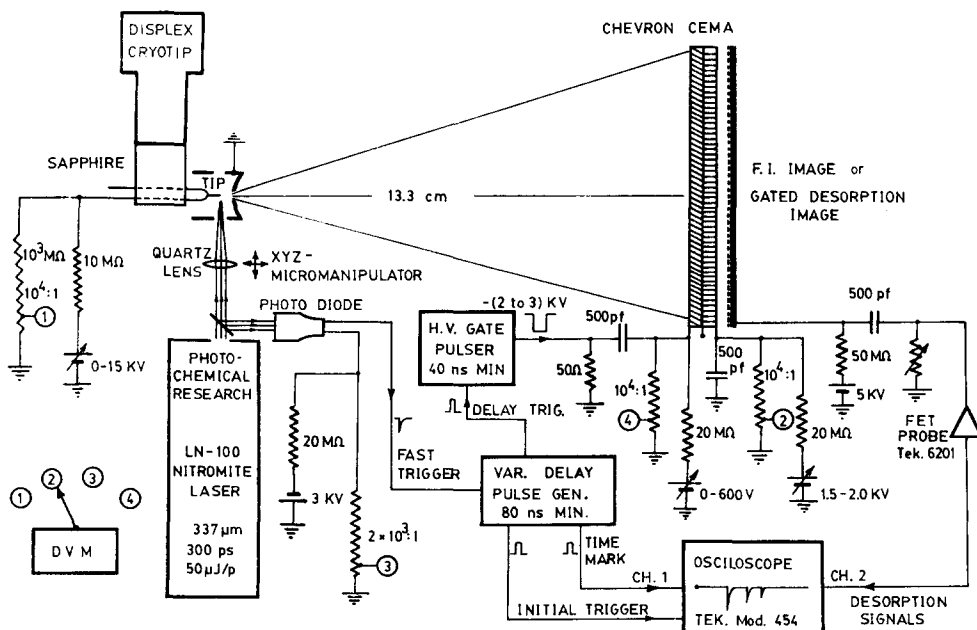
Recently we have reported a study of  $H_3$  formation using a high resolution pulsed-laser time-of-flight atom probe,<sup>8</sup> and a study of  $H_3$  formation and synthesis of  $NH_3$  from  $N_2$  and  $H_2$  using a pulsed-laser imaging atom probe.<sup>9,10</sup> In these two studies, we try to answer two questions. First, we try to find out from the field dependence of the relative abundance of the desorption species observed the conditions under

## II. EXPERIMENT

### A. Experimental methods

It is found that the signal intensity of a desorption species is related to the intensity of the laser pulse. To make sure that a laser pulse is sufficient to desorb all of the field adsorbed species, the laser power is gradually increased until the signal intensity of the species saturates. Since the laser intensity and the focusing of the laser are not completely stable, each desorption pulse signal corresponds to a slightly different laser heating of the tip. This uncertainty is about  $\pm 5\%$ . Statistical fluctuations of the signals are also considerable since each mass signal is produced by only a small

The lower the laser intensity the better the resolution of time-gated desorption images. When the laser intensity is high, the desorbed ions gain more thermal energy which causes the broadening of the image spots in the desorption image. Therefore, the resolution of the desorption pattern is much poorer than that of a He field ion image shown in Fig. 2(b). With a low enough laser intensity just sufficient to ther-



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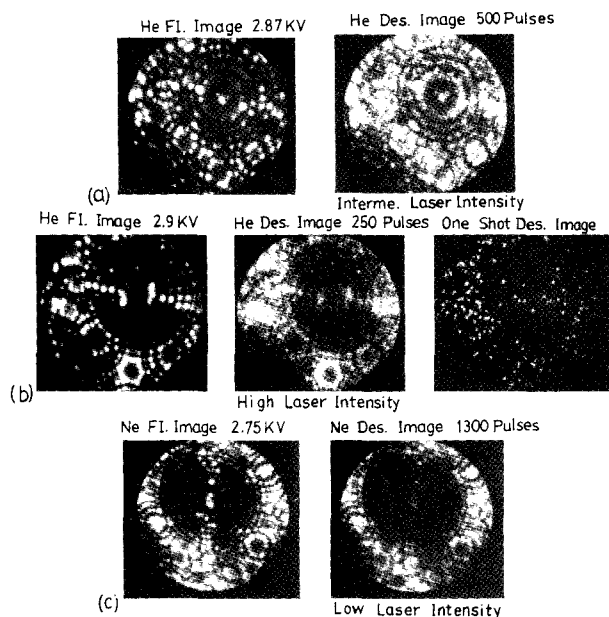


FIG. 2. Pulsed-laser promoted field desorption images of W at 80 K showing the same atomic structure of the surface as the He and Ne field ion images, with (a) intermediate, (b) high, and (c) low laser intensity.

mally desorb the field adsorbed Ne ions the resolution of the Ne desorption image is comparable to that of the Ne field ion image as also shown in Fig. 2.

For a few nonrefractory metals, such as Fe, Cu, Au, etc., surface atoms are seen to have been displaced to the terraces after irradiation of laser pulses. These displacements are mainly produced by the chemisorption of nitrogen and not by the laser heating, and cannot be avoided. The displacement of lattice atoms is especially noticeable in the study of  $NH_3$  formation as has been shown earlier in some of the  $NH_3^+$  and  $N_2^+$  time-gated images.<sup>9</sup>

### C. Experimental procedures

In our earlier studies, the emitter temperature was kept at 80 K, liquid nitrogen temperature. To carry out the temperature dependence study, a Displex Cryotip (Air Products closed-cycle liquid helium refrigerator) cold finger is used. The tip temperature can be varied from  $\sim 10$  to 300 K with an accuracy of  $\pm 0.1$  K. Usually a measurement starts from a high temperature. The temperature is then reduced step by step. It is necessary to keep not only the tip temperature constant, but also the whole cold finger at the same temperature.

In  $NH_3$  formation, the amount of  $NH_3$  formed can be greatly reduced by a small amount of contaminating gases, especially the oxygen. Therefore the system has to be carefully baked to achieve a vacuum in the  $10^{-10}$  Torr range. All the pulsed-laser field desorption is done in a reactant gas pressure of  $1 \times 10^{-7}$  to  $8 \times 10^{-8}$  Torr range. The laser pulse repetition rate is about 1 Hz. On a field ion emitter surface, the gas supply is increased by a factor of  $\sim 100$  by the polarization force. With this field enhanced gas supply it takes less than a tenth of a second to have the surface covered with a monolayer of the reactant. Thus in our experiment, the sig-

nal intensity is proportional to the equilibrium degree of coverage at the given emitter temperature.

## III. RESULTS AND DISCUSSIONS

### A. Formation of $H_3$

$H_3^+$  is known to exist since Thomson's mass spectroscopic studies. In field ion emission, Clements and Müller<sup>12</sup> observed a small amount of  $H_3^+$  in the field ionization mass spectrum of hydrogen in the field range of 2.0 to 2.5 V/Å. They also found that  $H_3^+$  originated from protruding surface atoms. Since  $H_3$  was not a stable molecule,  $H_3^+$  was considered to be a field and surface induced product. Subsequent mass spectroscopic studies confirm these conclusions.<sup>13,14</sup>

Some important questions remain. First, can  $H_3$  molecules exist on a metal surface? Second, is  $H_3^+$  just an artifact of an applied high electric field at a surface, or more specifically does formation of  $H_3^+$  depend also on the material of the emitter? If a material specificity exists then the formation of  $H_3^+$  can be considered a surface catalyzed effect. These questions have recently been addressed by Tsong *et al.*,<sup>8</sup> and Ai and Tsong<sup>9</sup> using the pulsed-laser atom-probe field ion microscope. In these studies, they focus mainly on the field dependence of the relative abundance of the desorption species  $H^+$ ,  $H_2^+$ , and  $H_3^+$ , the emitter material specificity of  $H_3^+$  formation, and the energy distributions of these ions. In this study, we have confirmed most of the earlier results. In addition we have studied how the relative abundances of the three ion species depend on the laser power, and also the emitter holding temperature. Some results and conclusions drawn from this study are listed below.

#### 1. Field dependence

In pulsed-laser field desorption of hydrogen,  $H_3^+$  is observed only in a narrow field range, from 2.0 to 3.0 V/Å. The maximum relative abundance occurs around 2.3 to 2.6 V/Å, as listed in Table I for different metals. Figures 3 and 4 give examples of this field dependence of the relative abundance of  $H^+$ ,  $H_2^+$ , and  $H_3^+$  from bcc Mo and hcp Hf surfaces. On the fcc Ir surface, no  $H_3^+$  is formed. This is shown in Fig. 5. The fact that  $H_3^+$  can be observed only in a narrow field range indicates a few possibilities. First it may indicate that  $H_3$  molecules can exist in a field adsorbed state only in this field range. Second, it may indicate that although  $H_3$  can exist in a wider field range, it cannot be field ionized below 2.0 V/Å. Thus even if it is being thermally desorbed by the heating of the laser pulses, it cannot be detected in the atom probe. The fact that  $H_3^+$  is not observed above 3.0 V/Å may indicate that it is field dissociated into  $H_2^+$  and  $H^+$ . At the present time our result is insufficient to resolve this question.

#### 2. Dependence on the atomic structure and the material of the emitter surface

Our result indicates that the maximum value of the relative abundance of  $H_3^+$  obtainable can be as high as 30%–40% for some hcp metals. For bcc metals, the maximum relative abundance of  $H_3^+$  ranges from about 12%–20%. For fcc metals, with the exception of Au, few  $H_3^+$  ions can be

TABLE I. Maximum relative abundance of  $H_3^+$  observed.

<sup>4</sup> Be hcp 40% 2.2 V/Å							
<sup>22</sup> Ti hcp 30% 2.6 V/Å	<sup>23</sup> V bcc < 1% ...	<sup>24</sup> Cr bcc ... ...	<sup>25</sup> Mn cub ... ...	<sup>26</sup> Fe bcc 12% 2.7 V/Å	<sup>27</sup> Co hcp 7% 2.6 V/Å	<sup>28</sup> Ni fcc 0% ...	<sup>29</sup> Cu fcc 0% ...
<sup>40</sup> Zr hcp 12% 2.6 V/Å	<sup>41</sup> Nb bcc 24% 2.4 V/Å	<sup>42</sup> Mo bcc 12% 2.5 V/Å	<sup>43</sup> Tc hcp ... ...	<sup>44</sup> Ru hcp ... ...	<sup>45</sup> Rh fcc < 1% ...	<sup>46</sup> Pd fcc 10% 2.6 V/Å	<sup>47</sup> Ag fcc 0% ...
<sup>72</sup> Hf hcp 30% 2.5 V/Å	<sup>73</sup> Ta bcc 20% 2.5 V/Å	<sup>74</sup> W bcc 18% 2.4 V/Å	<sup>75</sup> Re hcp 30% 2.1 V/Å	<sup>76</sup> Os hcp ... ...	<sup>77</sup> Ir fcc < 1% ...	<sup>78</sup> Pt fcc 7% 2.3 V/Å	<sup>79</sup> Au fcc 20% 2.9 V/Å

detected. In examining Table I, one notices that the values of the maximum obtainable relative abundance of  $H_3^+$  depend on the position of the emitter material in the periodic table, or on the electronic configuration of the substrate atoms. In general, metals on the left hand side of the periodic table give larger values, while metals on the right hand side of the periodic table give smaller values.

An interesting question is whether  $H_3$  can be formed on a binary alloy surface having two constituents of the same crystal structure, and also both of which do not form  $H_3^+$ . A binary alloy, Ni-5% Cu, is chosen for this investigation. Both Ni and Cu have the fcc structure, and also no  $H_3^+$  is formed on either of the surfaces. Three different surface conditions have been investigated. First we performed the experiment on low temperature field evaporated surfaces. The composition of this surface is the same as that of the bulk.<sup>15</sup>

No  $H_3^+$  is found. Second, we annealed the Ni-5% Cu tip to 600 °C for 5 min in  $10^{-9}$  Torr. According to a time-of-flight atom-probe study by Ng *et al.*<sup>13,15</sup> Cu atoms should segregate to the top surface layer of the alloy surface. The Cu concentration of the top surface layer should be 54%. When we carry out the hydrogen desorption experiment from the Cu enriched Ni-Cu alloy, we again find no formation of  $H_3^+$ . The last surface condition of this Ni-Cu alloy we investigated is an oxidized surface.<sup>16</sup> We heat the Ni-Cu tip to ~450 °C for 5 s in the atmosphere. According to a time-of-flight atom-probe analysis, the surface layers should have the composition of NiO.<sup>17</sup> When the pulsed-laser field desorption of hydrogen is performed on this surface, again we find no formation of  $H_3^+$ . This experimental result does not mean, however, that  $H_3^+$  cannot be formed on the surface of some alloys whose constituents fail to form  $H_3^+$ .

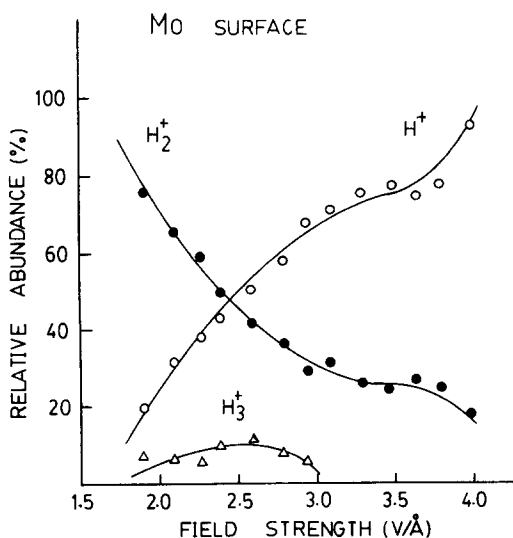


FIG. 3. Field dependence of the relative abundances of  $H^+$ ,  $H_2^+$ , and  $H_3^+$  from a bcc Mo surface.

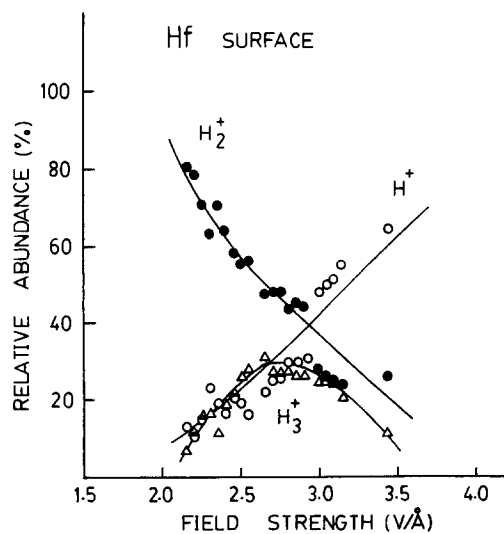


FIG. 4. Field dependence of the relative abundances of  $H^+$ ,  $H_2^+$ , and  $H_3^+$  from an hcp Hf surface.

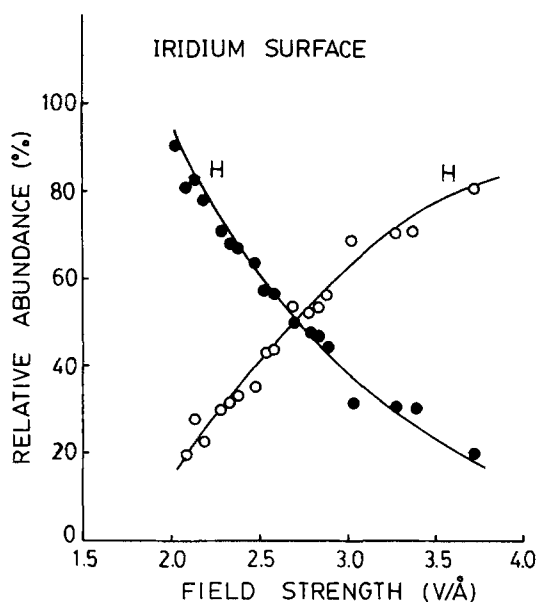


FIG. 5. Field dependence of the relative abundances of  $H^+$  and  $H_2^+$  from a fcc Ir surface. Few if any  $H_3^+$  is formed.

### 3. Dependence on the chemisorption behavior of hydrogen on the surface

This question has been investigated earlier by Tsong *et al.*<sup>8</sup> using  $H_2$ - $D_2$  mixed gases. Their conclusion is that  $H_3$  can be more readily formed on those surfaces where chemisorption of hydrogen is dissociative. Comparing the data obtained at 80 K presented in Table I and the general information available on the chemisorption behavior of hydrogen, we reach a similar conclusion. There are, however, some exceptions. Although it is known that hydrogen is nondissociatively adsorbed on Au surfaces at low temperatures, an appreciable amount of  $H_3^+$  can be observed. On the other hand, chemisorption of hydrogen is dissociative even at 80 K on Ir surfaces. Yet few  $H_3^+$  ions are detected.

### 4. Dependence on the intensity of the laser pulses

It is found that if the laser intensity is insufficient, not all field adsorbed species can be desorbed in one laser pulse; thus the signal intensity of the pulsed-laser field desorbed hydrogen depends on the laser intensity. An accurate calibration of the laser power density received by the tip surface is an impossible task because of the size of the tip,  $\sim 300$  to  $500$  Å, and the instability of the laser pulses both in power and in focusing. Fortunately, this information is not essential in our discussion. We know that the total mass signal intensity, the sum of  $H^+$ ,  $H_2^+$ , and  $H_3^+$  signals, increases monotonically with the intensity of the laser pulse. Beyond a certain laser intensity the total mass signal intensity can no longer increase since all the field adsorbed species on the surface have already been completely desorbed.

The laser intensity where the signal intensity of  $H_3^+$  saturates is found to be much lower than that where  $H^+$  and  $H_2^+$  signals saturate. The latter two species saturate at the same laser intensity. This is shown in Fig. 6(a). In Fig. 6(b) the relative abundances of  $H^+$ ,  $H_2^+$ , and  $H_3^+$  as a function of

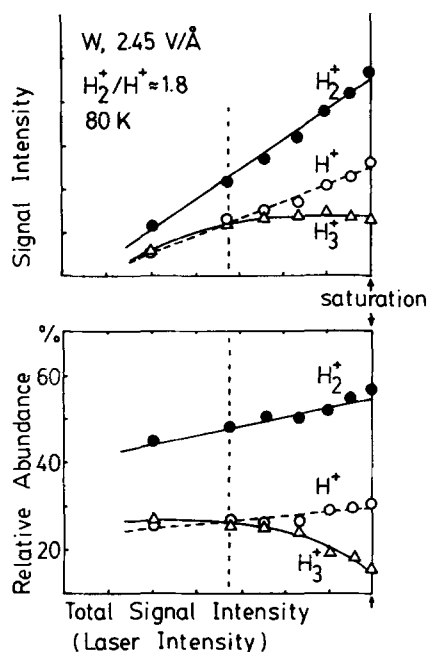


FIG. 6. (a) The signal intensities of  $H^+$ ,  $H_2^+$ , and  $H_3^+$  as a function of laser intensity; the total signal intensity of  $H^+ + H_2^+ + H_3^+$  is approximately proportional to the laser intensity before reaching a saturation value. (b) Relative abundances of  $H^+$ ,  $H_2^+$ , and  $H_3^+$  as a function of laser intensity;  $H_3^+$  saturates at a laser intensity lower than that of  $H_2^+$ ;  $H^+$  comes from field dissociation of  $H_2^+$ .

the total signal intensity is shown.

This observation indicates two significant facts. First,  $H_2^+$  and  $H^+$  are produced by the same desorbed ion species. From energy distribution measurements,<sup>7,14</sup> it has already been concluded earlier that  $H^+$  is a field dissociated product of the field desorbed  $H_2^+$ . Thus our observation further confirms this conclusion. Second,  $H_3^+$  is produced by a separate mechanism, namely by direct field ionization of thermally desorbed  $H_3$ . A  $H_3$  field adsorbed state exists which has a smaller binding energy than the  $H_2$  field adsorbed state. This mechanism has recently been suggested by us,<sup>7</sup> and this result further supports such an interpretation.

One may ask the question of whether the desorption sites, which we assumed to be the same as the field adsorption sites, of the ionic species change when the laser intensity is changed. In Fig. 7, time-gated desorption images of  $H^+$  and  $H_2^+$  taken at a low and a high laser intensity are shown. Although the signal intensity at the high laser power intensity is much higher, the gated desorption images are nearly identical to those obtained at a much lower laser intensity. Most  $H_2^+$  and  $H^+$  come from the field adsorbed  $H_2$  at protruding atomic sites. We conclude that the pulsed-laser field desorbed hydrogen comes only from the field adsorbed state, not from the chemisorbed state. In our case, the laser pulses heat the surface up to only less than  $\sim 500$  K for less than a ns, the chemisorbed hydrogen cannot be desorbed. The time-gated field desorption images of  $H_3^+$  show similar features also.

### 5. Temperature dependence

The total signal intensity, i.e.,  $H^+ + H_2^+ + H_3^+$ , as well as the  $H_3^+$  signal intensity decrease with increasing tip

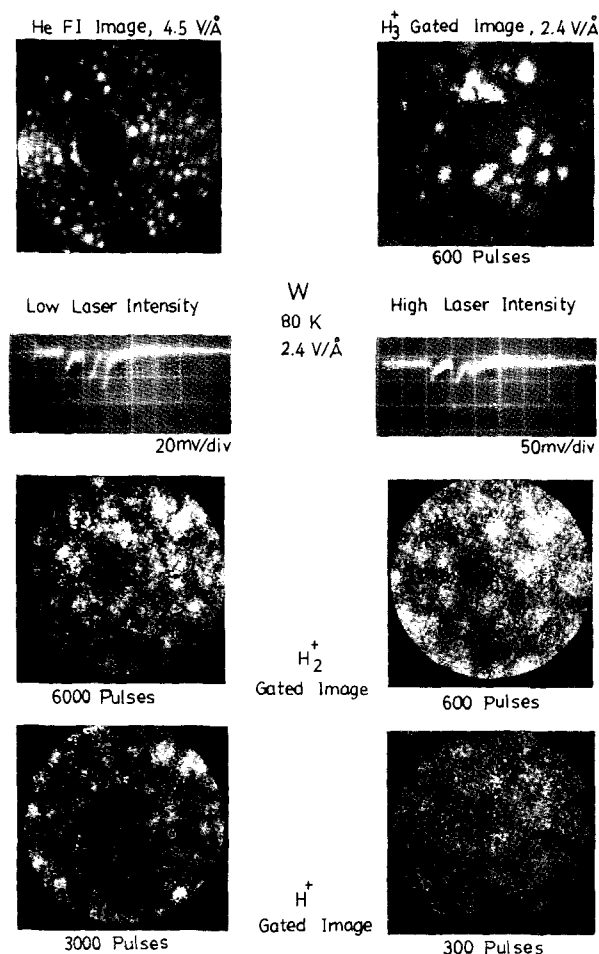


FIG. 7. Pulsed-laser promoted field desorption images of  $H^+$ ,  $H_2^+$ , and  $H_3^+$  with low and high laser intensities showing the same desorption patterns.

temperature as shown in Figs. 8(a) and 8(b). This behavior can be explained in terms of a thermal depopulation of the field adsorbed species. At a given temperature, the probability of field adsorption on each adsorption site, or equivalently the degree of coverage,<sup>8</sup> depends on the gas supply rate, the energy of field adsorption and the surface temperature. This problem has been studied earlier for field adsorption of inert gases. Our observation here is another example of this same phenomena.

In Fig. 8(b), the temperature dependence of the relative abundance of  $H_3^+$  is shown. Below  $\sim 120$  K, this quantity is almost constant. Above 120 K,  $H_3^+$  decreases more rapidly than  $H^+$  or  $H_2^+$ . This behavior again is consistent with our assertion that  $H_3^+$  comes from a different field adsorption state. On the other hand, the ratio  $H_2^+/H^+$  depends only on the applied field, not on the surface temperature, as shown in Fig. 9.  $H_2^+$  and  $H^+$  therefore originate from the same field adsorbed state. As has been pointed out in earlier sections, our conclusion is that  $H^+$  is the field dissociation product of the pulsed-laser field desorbed  $H_2^+$ .

A similar temperature dependence of the relative abundance of  $H_3^+$  persists in all fields. This is shown in Fig. 10.

## B. Synthesis of ammonia

Ammonia synthesis is one of the best known surface catalyzed chemical reactions.<sup>18</sup> Recently we found that in

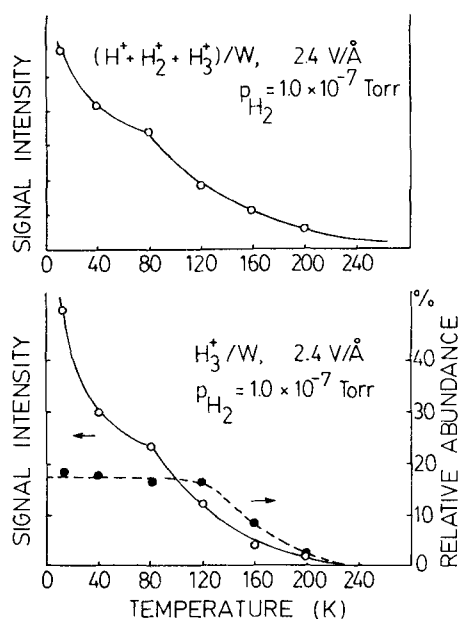


FIG. 8. (a) Total abundance of  $H^+ + H_2^+ + H_3^+$  as a function of substrate temperature. (b) Absolute abundance and relative abundance of  $H_3^+$  as a function of substrate temperature. The decrease in the signal intensity around 120 K at a field strength of 2.4 V/Å is a result of a thermal depopulation of the field adsorbed  $H_3$  molecules.

the presence of an  $H_2$ - $N_2$  mixed gas, the pulse-laser field desorption mass spectrum contains  $NH_3^+$  and  $NH_2^+$ . In the preliminary study,<sup>9</sup> we reported the formation of  $NH_3$  at 80 K from on a few transition metal surfaces such as W, Co, and Fe. We found that  $NH_3^+$  and  $NH_2^+$  can be formed on all of these metal surfaces but only on Fe and Co surfaces, a substantial amount can be detected. Fe is of course known to be an excellent catalyst in ammonia synthesis. In this study we focus on the temperature dependence of  $NH_3^+$  formation on Fe surfaces. Our results are presented below.

### 1. Material dependence

So far we have studied  $NH_3$  formation in the pulsed-laser atom probe from Fe, Co, Ni, V, Ti, Ta, and W surfaces. The amount of  $NH_3^+ + NH_2^+$  detected increases according to the sequence

$$Ni \approx W \approx V < Ti \approx Ta \ll Co < Fe.$$

This order agrees fairly well, although not completely, with the known catalytic activity in ammonia synthesis in

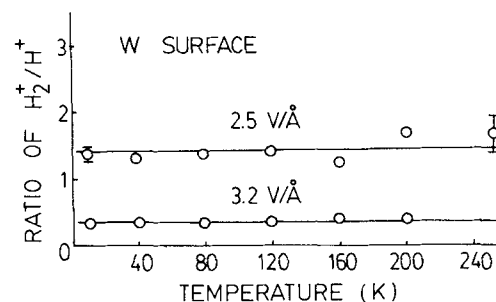


FIG. 9. Temperature independence of the ratio of  $H_2^+/H^+$  at 2.5 and 3.2 V/Å.



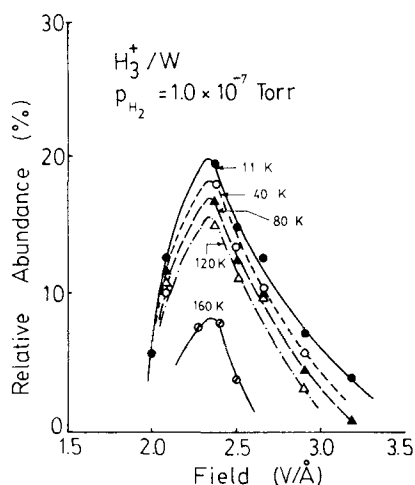


FIG. 10. Field dependence of the relative abundance of  $\text{H}_3^+$  at different substrate temperatures.

literature.<sup>19</sup> A slight discrepancy may be due to the very low temperature of our experiment, and may also be due to the effect of the applied field. In this measurement, the applied field is already considerably lower than most other field ion emission experiments.

## 2. Field dependence

In pulsed-laser field desorption,  $\text{NH}_3^+$  can be detected only in the field range from 1.2 to 2.5 V/Å. In the mass spectrum the ionic species detected are  $\text{NH}_3^+$  +  $\text{NH}_2^+$  and  $\text{N}_2^+$ . Their relative abundances depend strongly on the field strength, as shown in Fig. 11 for Fe and Co surfaces.

On Ta and Ti surfaces, in addition to the  $\text{NH}_3^+$  +  $\text{NH}_2^+$  peak, an extra ionic species of mass around 42 can be observed as shown in Figs. 12(a) and 12(b). This species is not  $\text{CO}_2^+$  since without  $\text{N}_2$  +  $\text{H}_2$  mixed gas in the system, it does not appear. This species is tentatively identified as  $\text{N}_3\text{H}_3^+$  although it may well be  $\text{N}_3^+$ ,  $\text{N}_3\text{H}^+$ ,  $\text{N}_3\text{H}_2^+$  or a mixture of these ions. This species can be observed only if the laser pulses have a sufficient intensity to raise the surface temperature to several hundred K. Thus the field adsorption energy of  $\text{N}_3\text{H}_3$  (or  $\text{N}_3$ ) is larger than that of  $\text{NH}_3$  which in turn is slightly larger than that of  $\text{N}_2$ . The field dependence of the relative abundances of  $\text{NH}_3^+$ ,  $\text{N}_2^+$ ,  $\text{N}_3\text{H}_3^+$  is shown in Figs. 13(a) and 13(b).

## 3. Dependence on the composition and the pressure of the mixed gas

At a given applied field, the amount of  $\text{NH}_3$  formed is found to be mainly limited by the gas supply of  $\text{H}_2$  to the surface. Thus to increase the amount of  $\text{NH}_3$  formed, the composition of the mixed gas has to have more  $\text{H}_2$  than that expected from the stoichiometry of  $\text{NH}_3$ , i.e., 25%  $\text{N}_2$  and 75%  $\text{H}_2$ . In fact, the amount of  $\text{NH}_3$  formed is largest when the gas contains more than 90%  $\text{H}_2$ . The signal intensity of  $\text{N}_2^+$  increases nearly linearly with the partial pressure of  $\text{N}_2$ . Therefore at a given total gas pressure, the relative abundance of  $\text{NH}_3^+$  decreases as the partial pressure of  $\text{N}_2$  increases.

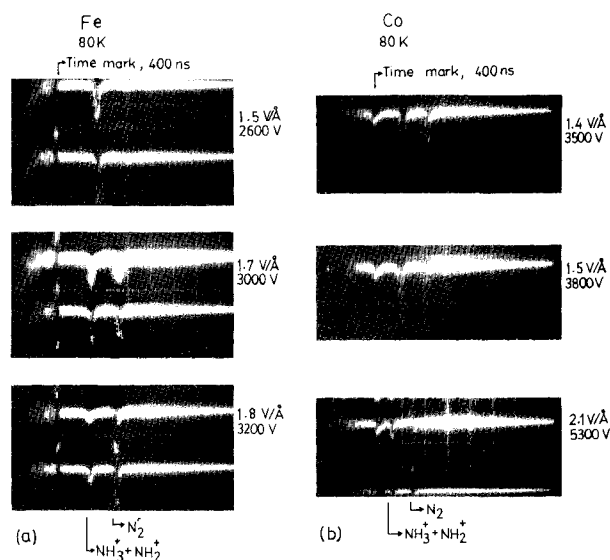


FIG. 11. The relative abundances of  $\text{NH}_3^+$  and  $\text{N}_3^+$  depend strongly on the desorption field as shown in these figures for (a) Fe and (b) Co.

We also find that at a given applied field and a given composition of the  $\text{N}_2$ - $\text{H}_2$  mixed gas, the relative abundance of  $\text{NH}_3^+$  observed decreases with increasing total gas pressure as shown in Fig. 14. This can be interpreted as the fol-

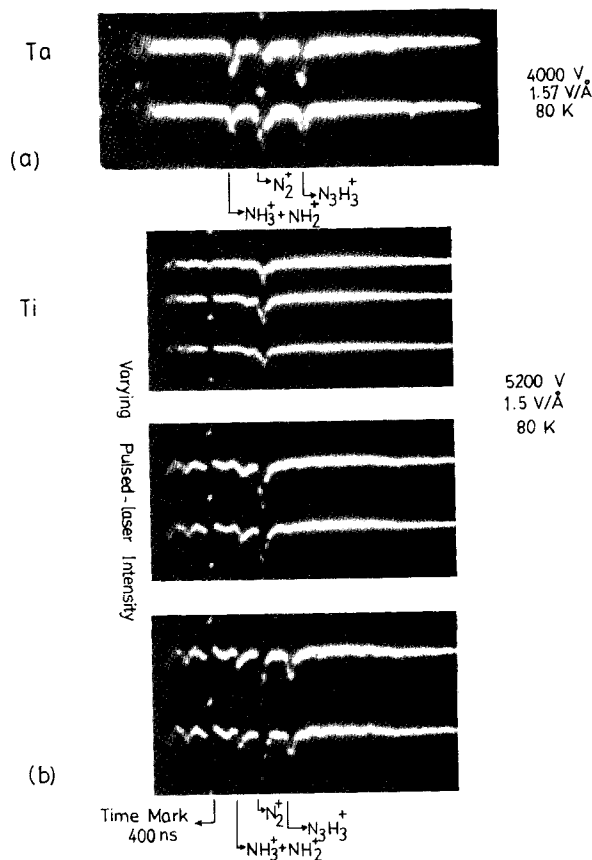


FIG. 12. (a) Single shot pulsed-laser field desorption mass spectrum showing the desorbed species of  $\text{NH}_3^+$ ,  $\text{N}_3^+$  and  $\text{N}_3\text{H}_3^+$  from a Ta surface. (b) Abundances of  $\text{NH}_3^+$ ,  $\text{N}_2^+$ , and  $\text{N}_3\text{H}_3^+$  from a Ti surface with varying laser intensity. From top to bottom, as the laser intensity increases gradually,  $\text{NH}_3^+$  starts to appear at an intermediate laser intensity, and  $\text{N}_3\text{H}_3^+$  starts to appear only at a high laser intensity.



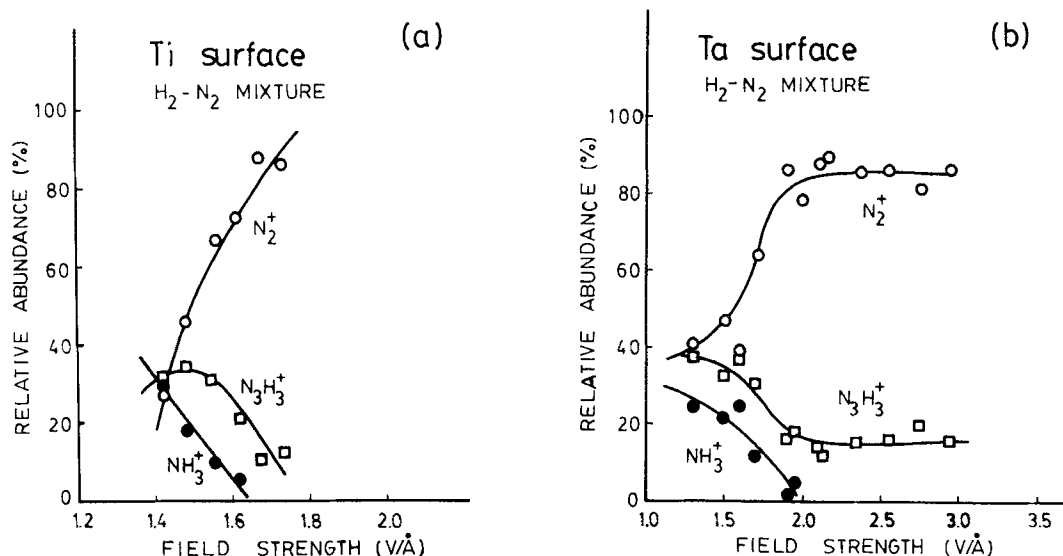


FIG. 13. Field dependence of the relative abundances of  $NH_3^+$ ,  $N_2^+$ , and  $N_3H_3^+$  from (a) a Ti surface and (b) a Ta surface.

lowing.  $NH_3$  is formed from the chemisorbed nitrogen and hydrogen atoms. The number of chemisorbed atoms already saturate at  $10^{-8}$  Torr gas pressure because of the field enhanced gas supply. The rate of formation of  $NH_3$  cannot be further increased by increasing the gas pressure. Once an  $NH_3$  molecule is formed, it is bound to a field adsorbed state at the apex site of a protruding surface atom. Thus it can be pulsed-laser field desorbed. This conclusion is drawn from the gated desorption image of  $NH_3^+$  shown in Fig. 15 of Ref. 9. On the other hand, the number of  $N_2$  in the field adsorption state will increase nearly linearly with the partial pressure of  $N_2$  in the mixed gas. Thus the relative abundance of  $NH_3^+$  observed will decrease with increasing gas pressure.

#### 4. Temperature dependence

When the surface temperature is changed, the signal intensity of each ion species changes also. On Fe surfaces, no  $NH_3^+$  is observed below 50 K. The  $H_3^+$  signal intensity increases rapidly when the surface temperature is raised above 120 K as can be seen in Fig. 15. Above this temperature,

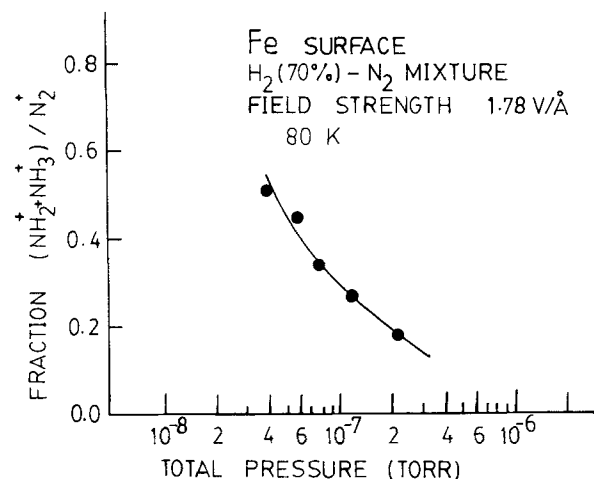


FIG. 14. The fraction,  $(NH_3^+ + NH_2^+)/N_2^+$ , as a function of total gas pressure. The relative intensities of  $NH_3^+$  and  $N_2^+$  depend strongly on the gas pressure even for a given composition of the mixed gas.

beside the  $NH_3^+ + NH_2^+$  and  $N_2^+$  mass lines, additional mass lines of masses 32, 34, 36 to 37, 42, 56, 70, and 84 appear in the pulsed-laser field desorption spectrum. The mass lines are tentatively identified to be  $(NH_2)_2^+$ ,  $(NH_3)_2^+$ ,  $Fe(NH_2)^{++}$ ,  $Fe(NH_3)^{++}$ ,  $FeN_2^{++}$  or  $N_3^+$ ,  $Fe^+$ ,  $FeN^+$ , and  $FeN_2^+$ , respectively. The compound ions, such as  $Fe(NH_n)^{++}$ , are similar to those observed by Schmidt *et al.*

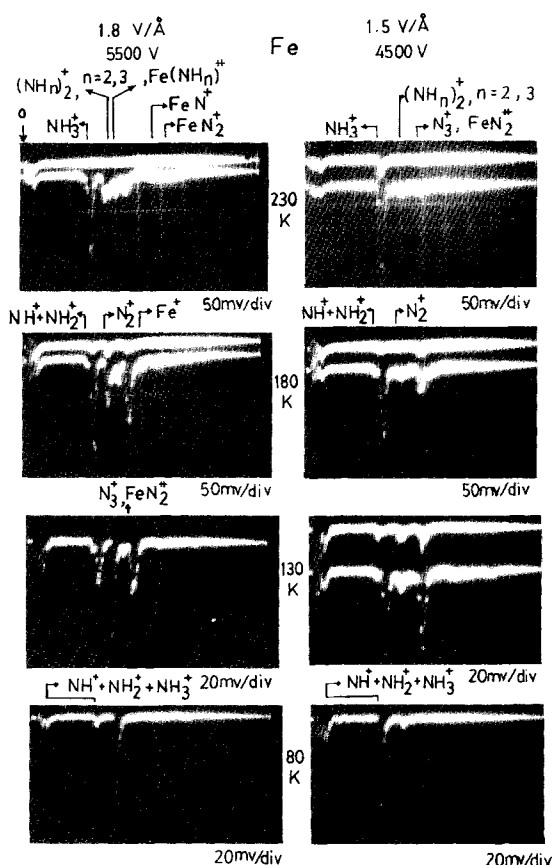


FIG. 15. Pulsed-laser field desorption mass spectra showing the desorbed species of  $NH_3^+$ ,  $N_2^+$ ,  $FeN_2^{++}$  or  $N_3^+$ ,  $Fe(NH_n)^{++}$ ,  $n = 2, 3$ , and others at field strengths of 1.5 and 1.8 V/Å with different substrate temperatures.

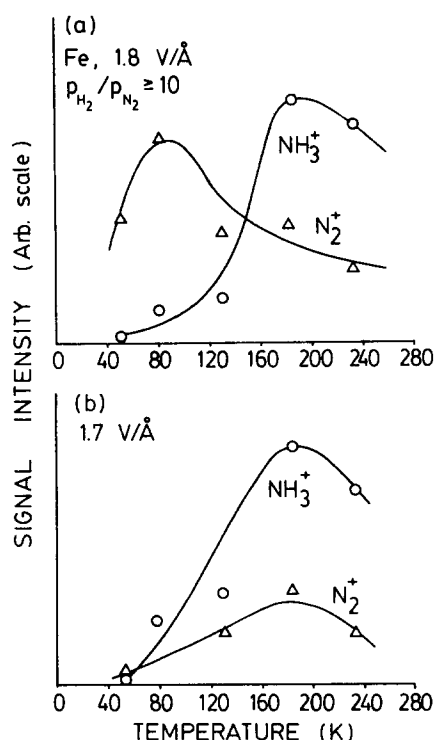


FIG. 16. Signal intensity of  $NH_3^+$  and  $N_2^+$  as a function of the substrate temperature at field strengths of (a)  $1.8 \text{ V/\AA}$ , and (b)  $1.7 \text{ V/\AA}$ .

in the field ionization mass spectroscopy of ammonia on Ag surfaces.<sup>20</sup> As these compound ions are most probably the artifacts of the high electric field, we cannot be certain of a possible formation of surface molecules. This possibility, however, cannot be ruled out entirely.

Figures 16(a) and 16(b) show the temperature dependence of signal intensities of  $NH_3^+$  and  $N_2^+$ . The temperature dependence of the  $NH_3^+$  signal intensity at an applied field of  $1.7 \text{ V/\AA}$  is nearly identical with that at  $1.8 \text{ V/\AA}$ . However, the  $N_2^+$  signal intensity at low temperatures is

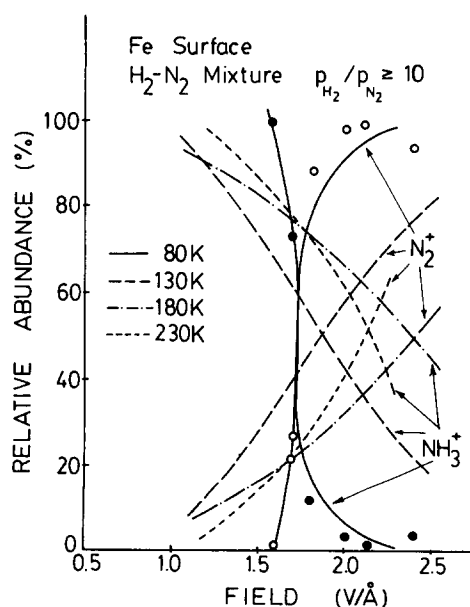


FIG. 17. Field dependence of the relative abundances of  $NH_3^+$  and  $N_2^+$  at different substrate temperatures for the Fe emitter.

very sensitive to the field strength. Although the field is changed by only  $\sim 6\%$ , the  $N_2^+$  signal intensity changes by a factor of 3 at low temperatures. As  $NH_3^+$  signal intensity is not correlated to the  $N_2^+$  signal intensity, formation of  $NH_3$  is not related to the field adsorbed  $N_2$  molecules. This result is again consistent with our earlier conclusion that  $NH_3$  is formed from the chemisorbed H and N, not the field adsorbed  $H_2$  or  $H_3$ , and  $N_2$ .<sup>9</sup>

The field dependence of the relative abundances of  $NH_3^+$  and  $N_2^+$  at different substrate temperatures is shown in Fig. 17. At a field above  $1.7 \text{ V/\AA}$  where both the thermally desorbed  $NH_3$  and  $N_2$  molecules can be effectively field ionized, the relative abundance of  $N_2^+$  decreases with increasing emitter temperature. This is in part due to an increasing amount of  $NH_3$  formed, and in part due to a decrease in the coverage of the field adsorbed  $N_2$ . The polarizability of  $N_2$  molecules,  $1.76 \text{ \AA}^3$ , is considerably lower than that of  $NH_3$ ,  $2.2 \text{ \AA}^3$ . Thus the field adsorption energy of  $NH_3$  is larger than that of  $N_2$ . A more direct evidence of this energy difference is already shown in Fig. 12(b). When the intensity of the laser pulses is too low, it is impossible to desorb  $NH_3$  from its field adsorbed state.

#### IV. SUMMARY

Formation of  $H_3$  and  $NH_3$  on about 20 transition metal surfaces has been studied with a pulsed-laser desorption technique using a pulsed-laser imaging atom probe. In both cases, the  $H_3^+$  and  $NH_3^+$  observed are attributed to a genuine surface catalyzed chemical reaction, but enhanced by the applied electric field.

In the presence of hydrogen,  $H_3^+$  is observed in the pulsed-laser field desorption mass spectrum in an applied field of  $2.0$  to  $3.0 \text{ V/\AA}$  from most transition metal surfaces. The signal intensity of  $H_3^+$  decreases with increasing surface temperature more rapidly than either  $H^+$  or  $H_2^+$ . The relative abundance of  $H_3^+$  depends both on the atomic structure of the surface and the material of the surface. From the field and temperature dependencies and the material specificity of  $H_3^+$  formation, we conclude that  $H_3$  molecules exist in a field adsorption state at protruded atomic sites of many transition metal surfaces in an applied field of  $\sim 2 \text{ V/\AA}$ . An  $H_3$  molecule is formed by bonding an H atom from its chemisorbed state and an  $H_2$  molecule from its field adsorbed state by a field induced dipole-dipole interaction.<sup>8,9</sup> In pulsed-laser field desorption,  $H_3^+$  ions are formed by field ionization of thermally desorbed  $H_3$  molecules above the critical distance of field ionization. This mechanism, which has been suggested earlier, is further supported by the temperature and laser intensity dependencies of  $H_3^+$  signal intensity observed in this study. Although in our studies we are not able to establish that  $H_3$  exist on metal surfaces in the absence of an applied field, it may in fact exist. A surface field of  $\sim 2.0 \text{ V/\AA}$  always exist near a metal surface even without an applied field as has been discussed earlier.<sup>9</sup>

In an  $H_2$ - $N_2$  mixed gas,  $NH_3^+$  ions are detected in the pulsed laser field desorption from all the metal surfaces studied. However, a substantial amount of  $NH_3^+$  can be found only from Co and Fe surfaces. The signal intensity of  $H_3^+$  as well as its relative abundance depend on the field, and the

temperature and material of the surface, similar to the formation of  $H_3^+$ . In addition, the signal intensity also depends on the composition of the mixed gas, and surprisingly also the gas pressure of the mixed gas. From these dependencies we conclude that  $NH_3$  molecules are formed by chemisorbed N and H atoms. The observed  $NH_3^+$  ions, however, come from a field adsorbed state, or a physisorbed state. This study has also demonstrated that genuine surface catalyzed chemical reactions can be meaningfully studied with a pulsed-laser field desorption technique.

## ACKNOWLEDGMENT

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