Suppression of Electron-Induced Positive Ion Emission by a Molecular Overlayer: Ion-Molecule Charge Exchange at a Surface

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We report suppression of electron-stimulated desorption of positive ions (O^+ and F^+) from a $TiO_2(110)$ surface caused by adsorption of a fractional monolayer of molecular NH_3. A linear decrease of O^+ and F^+ emission with NH_3 coverage is observed. This system allows us to distinguish between neutralization of desorbing ions via interaction with the substrate or adsorbed molecules. We propose a novel charge exchange mechanism where electron transfer from the occupied orbitals of the adsorbed molecules to the desorbing ions causes the decrease in detected ion yield. Charge transfer cross sections of $2.8(\pm 0.5)$ and $2.7(\pm 1)$ ($\times 10^{-15}$ cm^2) have been determined for O^+ and F^+ ions, respectively.

Charge exchange processes involving ions in close vicinity to a surface are of great fundamental and practical importance. A wide variety of surface analytical methods involve scattering or emission of ions and electron transfer processes often hamper the quantification of results. This encourages efforts to obtain a better understanding of ion-surface charge transfer processes and the parameters that influence those processes, with the goal of quantification of electron transfer probabilities [1-3]. A recent review about theoretical methods describing charge transfer processes and their application was given by Nordlander [4].

The goal of this work is to determine the influence of a fractional monolayer of adsorbed molecules on charge exchange processes in electron-stimulated desorption (ESD) of ions from a surface. Stimulated desorption processes can give important information about adsorbates on surfaces [5,6] and studies of ion emission from molecules on metal surfaces induced by electron or photon irradiation demonstrate the influence of coadsorbed species on ESD processes [7-10]. The presence of impurities on the surface may affect ESD from adsorbed molecules in different ways. The initial electronic excitation which eventually gives rise to desorption can be influenced by the presence of a neighboring adsorbate. Once a species starts to leave the surface, electron transfer between the moving species and the surface may take place, affecting the ion emission rate. The probability for reneutralization of a desorbed molecule may also be influenced by the presence of a neighboring adsorbate; the coverage dependence of desorption yields for several molecules is an example of such an interadsorbate quenching effect [11]. Usually, it is not easy to distinguish the individual contributions of initial state effects and reneutralization events to the ion emission yield. This makes the quantification of stimulated desorption processes involving ions very difficult.

In this work, we have taken a new approach to investigate the influence of a molecular adsorbate on the electron-stimulated ion emission. We have chosen a substrate which is sensitive to electron irradiation itself. By investigating the influence of overlayer adsorption on substrate emission, we are able to separate the effects of the initial desorption process from reneutralization of desorbed ions. TiO_2 is a very good candidate for such a study since ESD of TiO_2 produces O^+ ions with a relatively high probability. Knotek and Feibelman [12,13] proposed a mechanism involving interatomic Auger transitions for ion emission from a TiO_2 surface and electron- and photon-stimulated desorption processes have been studied in detail [14,15]. It should be mentioned that electron irradiation of NH_3 adsorbed on a TiO_2 surface also has interesting effects on the NH_3 molecule itself. Depending on the defect structure of the substrate, either desorption of the intact NH_3 molecule or dissociation into fragments takes place [16,17]. In this paper, the influence of ammonia on the ion emission from the substrate is addressed. We find that the O^+ yield is greatly suppressed by a fractional monolayer of NH_3, and interpret this as arising from charge transfer between desorbing O^+ ions and the occupied orbitals of adsorbed NH_3. This is the first report of charge transfer between desorbing ions and adsorbed molecules with a quantitative estimate about charge exchange cross sections.

The experimental setup is described in detail elsewhere [16]. In short, it consists of an ultrahigh vacuum chamber equipped with x-ray source, ion gun, and hemispherical energy analyzer for surface analysis. ESD measurements have been performed using a UTI quadrupole mass spectrometer as well as a LEED-ESDIAD (low electron energy diffraction and electron-stimulated desorption ion angular distribution) analyzer. Pulsing of the electron gun and the grids of the LEED-ESDIAD optics allows ESDIAD measurements in a (mass-resolved) time-of-flight (TOF) mode [18].

A rutile $TiO_2(110)$ crystal is used as the sample. For surface preparation the treatment recipes described by Pan et al. [19] are followed. In short, an initial high-temperature anneal performed with a fresh rutile single crystal induces bulk defects; this results in semiconducting properties of the crystal. A clean, stoichiometric sur-

face with almost no point defects can be achieved reproducibly by sputtering and subsequent annealing of the sample in an oxygen atmosphere. Such a surface has been used throughout the experiment; it contains almost exclusively fully oxidized cations (Ti^{4+}), and no electronic states are observed in the band gap [20]. Sample cleanliness and stoichiometry are confirmed by XPS (x-ray photoelectron spectroscopy).

Anhydrous ammonia (Matheson, purity 99.99%) purified by three freeze-thaw cycles is used for gas dosage. The sample is kept at a temperature of ~ 160 K during dosing and ESD experiments. After dosing, a N $1s$ peak with a binding energy characteristic of molecular ammonia is observed with XPS; the NH_3 coverage is determined from the XPS peak areas. No N is observed by XPS after heating a NH_3 covered sample to 473 K.

During the ESD experiments, the sample (biased at $+35$ V) faces the mass spectrometer. Electron bombardment is performed with the electron gun of the LEED-ESDIAD setup; the electrons strike the sample with an energy of 410 eV. Typically, a total electron current of 5–7 nA (measured with a Faraday cup) is used with a current density of ~ 0.8 $\mu A/cm^2$. The experimental parameters used for the mass-resolved ESDIAD measurements are described in Ref. [17].

Electron bombardment of a nominally clean TiO_2 surface induces desorption of O^+, H^+, OH^+, and F^+ [Fig. 1(a)]. Desorption of O^+ ions is expected due to decomposition of the surface by the electron beam [12,13]; the other desorption products originate from residual impurities on the surface. Electron-stimulated desorption is very sensitive to the presence of certain contaminants. In particular, small quantities of fluorine that lie well below the detection limit of most surface spectroscopies can give rise to an appreciable signal intensity in an ESD experiment [21].

Hydrogen species are always present on the surface as indicated by desorption of OH^+ and H^+. Desorption of H^+ could not be resolved in the mass spectra, but is clearly distinguished in the TOF-ESDIAD measurements with a signal whose intensity is a few percent of the O^+ signal. The hydrogen may originate either from the bulk and diffuse to the surface during the annealing treatment or from adsorption of water from residual gases [19,20].

A sharp ESDIAD pattern characteristic of emission along the surface normal is observed for O^+ ions, as was reported previously for this surface [14,17]. The time resolution of the TOF-ESDIAD setup is not sufficient to completely resolve ions with masses 16 to 19. When the time window for detection is varied in order to change the relative contribution of O^+, OH^+, and F^+ to the total signal, the ESDIAD pattern does not change significantly.

Adsorption of ammonia results in a dramatic *decrease* in the intensity of the desorbed F^+ and O^+ ions, as seen in Fig. 1(b). No change in the appearance of the ESDIAD pattern is observed upon NH_3 adsorption, only a de-

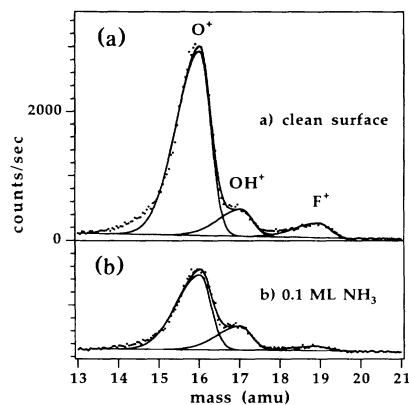
FIG. 1. Quadrupole mass spectra of positive ions desorbed from a $TiO_2(110)$ surface by electron irradiation. The electron energy is 410 eV and the sample is biased with $+35$ V. The peaks are fitted using asymmetric Gaussian functions. Spectra from (a) a nominally clean sample and (b) a sample covered with 0.1 monolayer (ML) NH_3 are shown.

crease in intensity. Peak areas normalized to the electron current are obtained from fitting asymmetric Gaussians to the data for different NH_3 coverages. Small changes in field geometry induced by a slight position change of the (biased) sample or a change in focusing of the electron gun may influence the intensities significantly $(\pm 15\%)$. For better quantification of the influence of NH_3 adsorption on the ion intensities, a reference spectrum from the uncovered (flashed to 473 K) sample is taken under exactly the same conditions as for each NH_3 coverage.

The O^+ and F^+ signal intensities normalized to the respective values from the nominally clean surface are shown in Figs. 2(a) and 2(b), respectively. The NH_3 coverages have been derived from the XPS N $1s$ peak intensities. The highest NH_3 coverage that can be obtained at 160 K was determined experimentally as 0.16 monolayer or 3.3×10^{14} molecules/cm^2 (1 ML of $TiO_2 = 2.08 \times 10^{15}$ atoms/cm^2) [16]. At this point the ESD intensities are decreased to $\sim 10\%$ of their initial value. Both the normalized O^+ and the F^+ signals decrease linearly with ammonia coverage. This linear decrease in the ion desorption yield is also observed in the raw data. Straight lines have been fitted to the data for O^+ and F^+ desorption, respectively. The scatter in the F^+ data is considerably higher due to the lower signal intensity. No such clear correlation between the intensity of desorbed OH^+ ions and the NH_3 coverage is observed.

The most striking aspect of these observations is the fact that *substrate ion emission is suppressed by adsorption of only a small fraction of a monolayer of adsorbed NH_3*. This can be envisioned with the help of the crystal model of a $TiO_2(110)$ surface with NH_3 at saturation coverage [16] depicted in the inset of Fig. 2(a).

Our experimental observations provide evidence for neutralization due to electron transfer processes from or-
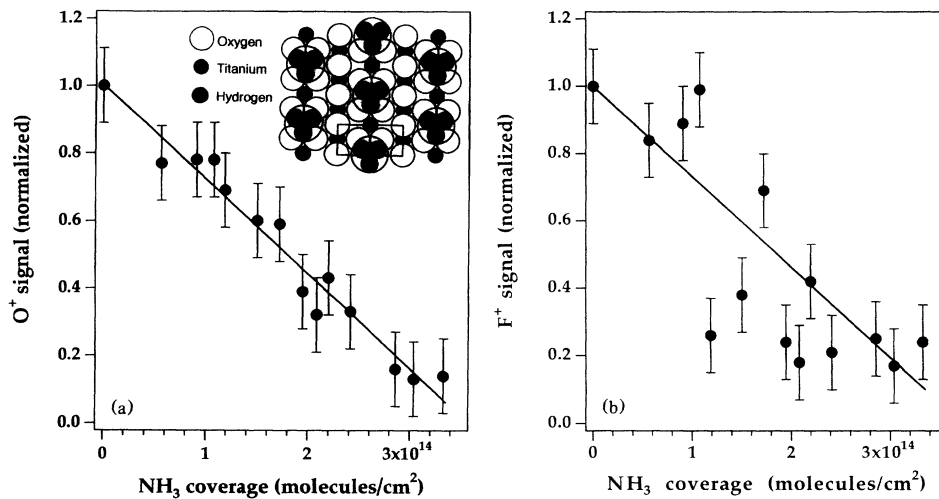
FIG. 2. Ion yields from a TiO$_2$ sample at different NH$_3$ coverages for (a) O$^+$ and (b) F$^+$, normalized to the value from a nominally clean sample. The inset in (a) shows a model of the TiO$_2$(110) surface with saturation coverage of NH$_3$ ($\frac{1}{8}$ monolayer) [16]. The white circles represent oxygen, the black circles Ti atoms, and the shaded circles the hydrogen atoms of NH$_3$. The TiO$_2$ surface unit cell is indicated; it contains one Ti atom and three O atoms, and two TiO$_2$ unit cells share one NH$_3$ molecule.

bitals of the adsorbed ammonia molecules to the desorbing ions. Before making this argument, we discuss other effects which may also be invoked for influencing a decrease in ESD ion yield.

The effect of ammonia adsorption on the incoming electron beam itself is of negligible influence on the initial excitation probability. The presence of an adsorbate increases mainly inelastic scattering of electrons and the cross section for ESD varies slowly compared to the typical energies lost in an inelastic scattering event. However, the adsorption of NH$_3$ on the surface could change the electronic excitations in TiO$_2$ that lead to ion desorption. In the picture initially proposed by Knotek and Feibelman [12,13], maximal valency was postulated as a precondition for the stimulated desorption processes. On a perfectly stoichiometric TiO$_2$(110) surface, all Ti atoms have a formal 4+ oxidation state that corresponds to maximal valency. This is apparent in very sharp Ti 2p features in the x-ray photoemission spectra. The presence of NH$_3$ on the surface does not alter the shape of these features, suggesting a largely unchanged oxidation state of the Ti cations. The charge transfer that would accompany any change in the oxidation state is expected to produce a detectable shoulder in Ti 2p photoemission, indicating the presence of Ti^{3+}. This is not observed [16]. In fact, the subtle changes in the TiO$_2$ valence band photoemission spectra that are seen upon NH$_3$ adsorption [22] can be assigned to emission from the adsorbate. Moreover, O$^+$ desorption is observed for highly oxygen deficient TiO$_2$ surfaces as well as for oxidized Ti [14,15]; the electronic structures of those systems are distinctly different from stoichiometric TiO$_2$. Thus, it is unlikely that an adsorbate-induced change in the substrate electronic structure causes the observed effects.

One could envision preferential adsorption of NH$_3$ molecules at certain sites that are especially active for ESD. For metal surfaces, it has been observed that atoms adsorbed at defects such as steps are desorbed with much higher probability. However, the linear decrease of

the O$^+$ signal with ammonia coverage [Fig. 2(a)] implies that each adsorbed NH$_3$ molecule suppresses ion emission in the same way, independent of the adsorption site. Furthermore, the presence of NH$_3$ affects O$^+$ desorption that is intrinsic to the TiO$_2$ surface in the same manner as ion emission from adsorbed fluorine; this is not expected for a "site blocking" effect.

Let us now consider neutralization due to electron transfer between occupied orbitals of NH$_3$ and the desorbing ions as the main cause for the observed ion suppression. We will base our discussion on O$^+$, but almost the same arguments hold for F$^+$ ions.

In Ref. [16], a model was proposed for the adsorption of NH$_3$ where the N atom is adsorbed at a surface cation site (Ti^{4+}) with the three attached H atoms oriented away from the surface [see inset in Fig. 2(a)]; this is similar to the configuration observed on most transition metal surfaces [23]. The desorbed O$^+$ ions that are emitted almost normal to the surface have to pass near to the H atoms of the ammonia molecules. If the emitted ion passes the molecule closer than a critical distance, electron transfer will occur with a certain probability. Each ammonia molecule thus reduces ion desorption from the surface by the same amount, the cross section σ. The value for σ is the slope of the fitted straight line in Fig. 2(a); it is $\sim -2.8(\pm 0.5) \times 10^{-15}$ cm^2 for O$^+$ and $\sim -2.7(\pm 1) \times 10^{-15}$ cm^2 for F$^+$, respectively.

The unchanged O$^+$ ESDIAD pattern supports this picture. The angular distribution of desorbing species will be changed due to scattering by the adsorbed molecules. However, if the cross section for neutralization is larger than the elastic scattering cross section, scattered particles will not survive as ions. Conversely, ions starting at a lateral distance larger than the critical distance for neutralization are traveling along trajectories that are not affected by the presence of NH$_3$.

Energy levels of an atom in the vicinity of a surface broaden and shift [4]; moreover, electron capture into excited states has to be taken into account. The ioniza-

tion potential of (atomic) O is 13.618 eV and that of F is 17.422 eV. Valence band photoemission of $NH_3/TiO_2(110)$ shows broad features peaking around 6.7 and 11.4 eV binding energy (measured with respect to the Fermi level, 5.25 eV below the vacuum level) [22]; these features have been assigned as being derived from the $3a_1$ and $1e$ orbitals of molecular ammonia, respectively. We suggest that these are the energy levels which have to be considered for charge transfer.

It is useful to compare our cross section with charge transfer cross sections between ions and atoms or molecules in the gas phase. Since the ions from the substrate have to pass by the H atoms of ammonia, let us first consider the charge transfer reaction $O^+ + H \rightarrow O + H^+$. Because of the very similar ionization potentials of O and H, the cross section for charge transfer between those atoms is very high and shows a linear decrease with the logarithm of the impact energy (accidental resonance [24]). Relatively sharp kinetic energy distributions centered around 4-5 eV have been observed for O^+ ions desorbed from TiO_2 and oxidized Ti surfaces [14,15]; the value for the charge exchange cross section between atomic H and O^+ ions is 1.6×10^{-15} cm^2 at 5 eV impact energy [24].

No data for cross section measurements of charge transfer between O^+ and NH_3 molecules in the gas phase are available in the ion kinetic energy range of interest, but flow reactor measurements where both interaction partners have thermal energies give a reaction rate for charge transfer 1.2×10^{-9} cm^3/molecule sec [25]; this can be converted into a cross section of $\sim 6 \times 10^{-15}$ cm^2. Our measured cross section value is bracketed by the two gas phase values.

The emission of H^+ increases with NH_3 coverage. H^+ may originate from molecular NH_3 or from atomic hydrogen that was created on the surface by dissociation of NH_3 under electron irradiation.

No clear correlation between the change in OH^+ desorption yield and the ammonia coverage has been observed. Small amounts of atomic hydrogen result in a big increase in the OH^+ signal as has been seen from a slightly contaminated sample. Thus it is hard to distinguish if charge exchange between OH^+ and NH_3 is less probable than for F^+ and O^+ or if increased neutralization is balanced by more OH^+ emission due to atomic hydrogen on the surface.

In summary, we have observed evidence for charge transfer between ions desorbing from a $TiO_2(110)$ surface and adsorbed molecular ammonia. A small coverage of NH_3 is sufficient to significantly suppress the detected ion yield; the measured cross section is comparable to cross sections for charge exchange in the gas phase.

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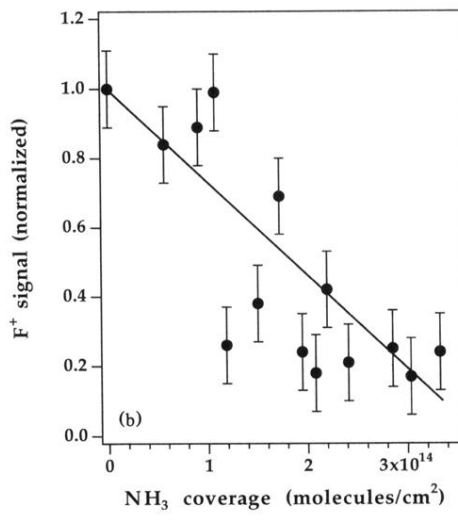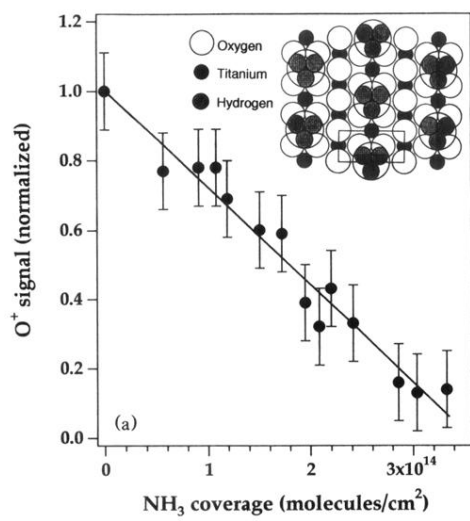[25] D. L. Albritton, At. Data Nucl. Data Tables 22, 1 (1978).

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