

Spin Polarized Metastable He^{*}(2³S, 1s2s) Stimulated Desorption of H⁺ Ions

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(Received 2 October 2000)

The yield of H⁺ in the metastable He^{*}(2³S, 1s2s) stimulated desorption (MSD) on an H₂O/Na/Fe surface has been found to depend on the spin of the incident He^{*}. By combination with the spin-resolved analysis for the surface electronic structure, it is indicated that the neutralization of the hole in the OH 3σ molecular orbital, which is created by the incident He^{*}, by Na 3s electrons plays a crucial role in the spin polarization of the H⁺ MSD intensity. The dependence of the spin polarization of H⁺ MSD on the kinetic energy of the desorbed H⁺ has been observed, and it is discussed based on the Menzel-Gomer-Readhead model.

DOI: 10.1103/PhysRevLett.86.3654

PACS numbers: 79.20.Rf, 79.90.+b

The dissociation of surface constituents followed by desorption from the surface by electronic excitation using energetic beams of electrons, photons, etc. is well known as desorption induced by electronic transitions (DIET). In the concept of DIET, the excited state on the surface caused by the primary beam lasts for a certain time, and, during this lifetime of the excited state, the conversion of the potential energy of the excited state into kinetic energy of the desorption species occurs [1–3]. In this respect, DIET is the result of the competition between the motion of the nuclei of the desorption species and the survival of this excited state. It is indicated that the lifetime of the excited state (or hole) on the surfaces differs from that in the bulk, which is generally expressed as h/W , where W represents the bandwidth [4,5]. In this context, the estimation of the lifetime of the excited state on the surfaces is quite difficult. Thus, the contributions from the surface and bulk to the DIET may have to be strictly separated.

Recently, metastable-atom stimulated desorption (MSD) of H⁺ ions by He^{*}, which has almost thermal kinetic energy, has been identified [6], although the emission of the secondary ions by the impact of fast metastable atoms had been reported by Varney much earlier [7]. Thermal metastable atoms are reflected above the surface, so that the He^{*}-surface interaction is restricted only on the outermost surface. In the present Letter, the DIET process is investigated in the MSD of H⁺ ions from a magnetized surface using spin polarized He^{*} (2³S, 1s2s). The yield of H⁺ MSD is found to depend on the spin of the incident He^{*} on the magnetized H₂O/Na/Fe surface. To the best of our knowledge, this is the first report that reveals the dependency of the desorption yield on the spin of the incident particles in the DIET phenomenon.

Based on the fact that the thermally kinetic He^{*} atoms do not penetrate into the subsurface layers, the electrons emitted via the He^{*}-solid surface interaction have been utilized to investigate the electronic structure on the outermost surface [metastable-atom deexcitation spectroscopy

(MDS) [8]]. Furthermore, the spin polarization technique for He^{*} has enabled analysis of the spin-resolved electronic structure on the topmost surface [spin polarized metastable-atom deexcitation spectroscopy (SPMDS) [9,10]]. In the present study, SPMDS measurements on the H₂O/Na/Fe surface reveal the spin polarization asymmetry of the surface bands, where asymmetry for the Na 3s, OH 1π, and OH 3σ orbitals are positive, slightly negative, and almost zero, respectively. On the other hand, the H⁺ MSD intensity obtained on the same surface by He^{*} polarized parallel to the remanence of the sample is larger than that obtained by the antiparallel He^{*}. When He^{*} polarized parallel to the remanence approaches the sample surface, only the antiparallel electrons can fill the vacancies in the He^{*} 1s inner orbital. The hole created at the sample surface by He^{*} polarized in parallel can be neutralized by electrons having antiparallel spin if He^{*} is deexcited by Auger deexcitation or autodetachment. The intensity of H⁺ MSD is related to the creation and survival probability of the hole created by He^{*}. The creation and survival probability of the hole in the surface bands depends on the electron population. The spin polarization asymmetry obtained by SPMDS reveals the dominant electrons between the parallel and the antiparallel spin configurations. In this context, the comparison between the spin polarization asymmetries of surface bands and H⁺ MSD is expected to enable revelation of the electronic transition process in MSD. In other words, the spin polarization asymmetry for each surface band obtained by SPMDS acts as a label [11], and, by the interpretation of the combination of these labels to fit the asymmetry of the H⁺ MSD, the electronic transition process may be derived. The present results are discussed with respect to this interpretation, and it is indicated that the neutralization of the hole created in the OH 3σ orbital by the Na 3s electrons plays an important role in the H⁺ MSD yield.

The experiments were performed in an ultrahigh vacuum chamber (base pressure of 5×10^{-11} Torr) which

was equipped with a cylindrical mirror analyzer (CMA), a metastable He^* atom ($2^3S, 1s2s$) beam source, and a Stern-Gerlach analyzer [12]. The He^* beam generated in the pulsed discharge source was projected onto the surface, and the ejected positive ions or electrons were detected by the CMA. The triplet-to-singlet ratio was measured by the Stern-Gerlach analyzer as 9:1. For the positive ion measurements, time-of-flight (TOF) spectrometry was performed with fixed kinetic energies. On the other hand, the energy distribution of the ejected electrons was analyzed with a time-of-flight technique using the combination with the pulsed discharge source of He^* metastable atoms. This enables separation of the contributions to the spectra between the He^* metastables and $\text{He} I$ photons which were simultaneously produced in the discharge source. The spin polarization of the incident He^* was made by optical pumping using circularly polarized radiation of 1083 nm and was confirmed by the Stern-Gerlach analyzer. Iron single crystalline films (bcc-Fe) were epitaxially grown on MgO(001) substrates with the following orientation relationship: $\text{Fe}(001)/\text{MgO}(001)$ and $\text{Fe}[110]/\text{MgO}[100]$. The iron films were pulse magnetized in the plane transverse to the primary beam, that is, along the $\text{Fe}[100]$ -easy axis of bcc-Fe. All the SPMDS data shown in the present paper were obtained in the remanent state. The deposition of Na layers and the exposure to H_2O were performed at room temperature.

Figure 1(a) shows the TOF spectra of positive ions emitted from the $\text{H}_2\text{O}[10 \text{ L} (1 \text{ L} = 10^{-6} \text{ Torr} \cdot \text{s})/\text{Na}(0.3 \text{ ML})/\text{Fe}$ surface during radiation of the spin polarized metastable He^* atoms. It is clearly observable that the intensity of the broad peaks distributed from 130 to 400 μs depends on the spin polarization of the incoming He^* while the rather sharp peak appearing on a faster time scale has no relationship with the polarization of He^* . Kurahashi and Yamauchi recently confirmed the occurrence of the MSD of H^+ ions on an $\text{H}_2\text{O}/\text{Na}/\text{Ni}$ surface [6]. The broad peak from 130 to 400 μs is also attributed to the H^+ ions by the mass analysis using the flight time of the peak. On the other hand, the peak at 10 μs is due to the H^+ ions of the photon stimulated desorption, and some peaks from 60 to 120 μs are due to the mixture of secondary ions by fast He^0 whose kinetic energy is around 100 eV, where the photon and first He^0 are unavoidably produced in the He^* discharge source [13]. As plotted in Fig. 1(a), the H^+ MSD intensity for the He^* polarized parallel to the majority spin in the target is clearly larger than that for He^* polarized antiparallel, and the asymmetry defined as $(I_p - I_a)/(I_p + I_a)$, where I_p and I_a are the H^+ MSD intensity obtained by the parallel and antiparallel spin configurations of He^* , respectively, is observed to be positive in Fig. 1(a). Shown in Fig. 1(b) is the SPMDS spectrum observed on the same surface as that in Fig. 1(a). On the surface of Na/Fe at room temperature, H_2O molecules dissociate, and subsequently adsorb in the form of hydroxyls. The SPMDS spectrum in

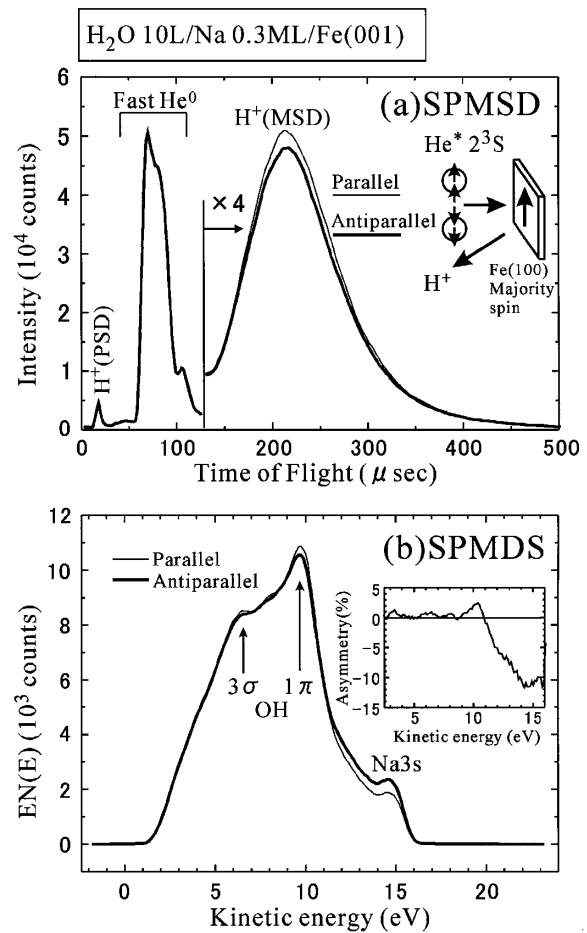


FIG. 1. (a) Time-of-flight spectra of positive ions and (b) energy spectra of electrons ejected from the $\text{H}_2\text{O}/\text{Na}/\text{Fe}$ surface. The thin (thick) curve was obtained by He^* polarized in parallel (antiparallel) with respect to the majority electrons of the magnetized Fe substrates. Inset of (b) shows the asymmetry of the SPMDS intensities.

Fig. 1(b) consists of the electron emission via the Auger deexcitation process for the Na 3s and OH peaks (OH 1π and 3σ) in the He^* -surface interaction, although an autodetachment process may also contribute to the Na 3s peak [6]. In these He^* -surface interactions, only one surface electron is involved. Therefore, the spectrum originating from these electronic transitions basically reflects the surface density-of-states (SDOS). In the spectrum, the Fermi level is at the high energy cutoff of the Na 3s peak (16 eV), and the binding energy is larger with smaller kinetic energy. According to the Pauli exclusion principle, only a minority (majority) electron can fill the vacancy of the He 1s orbital, if the incidence He^* is spin polarized parallel (antiparallel) to the majority spin of the target. Thus, the negative (positive) asymmetry in the SPMDS spectra indicates the positive (negative) spin polarization. In the inset of Fig. 1(b), negative and slightly positive asymmetries are observed at the peak position of the Na 3s and OH 1π peak positions, respectively. On the contrary, there is almost no asymmetry at the OH 3σ

peak position. The OH 3σ orbital is far below from the Fermi level ($\cong 9.5$ eV), and, consequently, the small overlapping with the Fe valence orbital is expected. On the other hand, the shallow level of Na $3s$ leads to the strong hybridization with the Fe conduction band. This contrast in the interaction with the Fe surface is interpreted to be the origin of the difference in the spin polarization between OH 3σ and Na $3s$ in Fig. 1(b). The detailed result of SPMDS on the $\text{H}_2\text{O}/\text{Na}/\text{Fe}$ surface will be described elsewhere [14].

It has been discussed that the excitation of the electrons in the OH 3σ molecular orbital which had the bonding character was responsible for the H^+ emission in MSD [6]. In this argument, the electronic excitation across the Frank-Condon gap induced by Auger deexcitation in the He^* -surface interaction, where a surface electron in the OH 3σ fills the hole at the He $1s$ orbital with the simultaneous ejection of the He $2s$ electron, and the subsequent conversion of potential energy into the motion of the H^+ causes the H^+ emission [Menzel-Gomer-Readhead (MGR) model [1–3]]. It is considered that the intensity of H^+ MSD is given by the product of the creation probability and survival probability of the hole. Note that there is no noticeable spin polarization at the OH 3σ peak [Fig. 1(b)], indicating almost equal creation probability of the hole in the OH 3σ orbital between parallel and antiparallel polarized He^* . On the other hand, the survival probability depends on the lifetime of the hole, which is determined by the bandwidth and transition probability for the case of the diffusion into the band and the transition between bands, respectively. In the present case, the OH 3σ is a semicore orbital of bonding type, and, hence, the electron in the orbital is thought to localize. This speculation is supported by the absence of asymmetry at the OH 3σ peak of the SPMDS spectrum in Fig. 1(b) which is in contrast with OH 1π , suggesting almost no hybridization for OH 3σ from the underlying magnetized Na/Fe surface. Therefore, it is reasonable to consider that the lifetime of the hole in the OH 3σ orbital depends on the transitions between bands that occur in the Auger process. It is most likely that the Na $3s$ electrons fill the hole in the OH 3σ orbitals in the present case, so that the lifetime of the hole is thought to have a relationship with the Na $3s$ electron population. The spin-resolved surface electronic structure in Fig. 1(b) indicates the difference in the population of the Na $3s$ electrons between up and down spins. The hole created by He^* , which has parallel polarization, is neutralized by the Na $3s$ electrons which have an antiparallel spin. In this respect, if the population density of the Na $3s$ electrons has a correlation with the H^+ MSD intensity, the spin polarization asymmetry at the Na $3s$ peak in SPMDS [Fig. 1(b)] and that of H^+ MSD [Fig. 1(a)] should be in reverse order. Indeed, this situation is observed in Fig. 1.

The asymmetry of H^+ MSD is shown in Fig. 2 for various kinetic energies. The sample condition was the same as that of Fig. 1. In Fig. 2, it is clear that the asymmetry of

H^+ MSD becomes greater with the increase in the kinetic energy of H^+ MSD. The inset shows the series of the H^+ MSD TOF spectra. The yield of H^+ MSD has a maximum at around 3 eV. The slight shift in the H^+ MSD peak position between Fig. 1(a) and those in the inset of Fig. 2 is due to the difference of the pulse width in the discharge for the He^* production, where the pulse widths for Fig. 1(a) and Fig. 2 were 15 and 100 μs , respectively.

In the proposed mechanism for MSD based on the MGR model [6], the kinetic energy of desorbed H^+ is the difference of the potential energy along the excited-state curve between that at the point of Frank-Condon transition and that at infinity. Shown in Fig. 3 are the potential curves obtained by the multireference double excitation configuration interaction (MRSDCI) calculations carried out for the ground state of NaOH and ${}^2\Pi$, ${}^4\Pi$ of NaOH^+ using the program ALCHEMY2 [15], where Na-O distance was fixed at 2.66 Å. The excited curves correspond to the states in which one electron is removed from the OH 3σ orbital. It is noteworthy that the potential curves of the excited state exhibit almost a repulsive form. The distribution of the kinetic energy of the H^+ MSD peak is attributed to the difference in the OH bond length caused by thermal vibration at the instant of the creation of the hole in the OH 3σ orbital. It is interpreted that H^+ MSD has a larger (smaller) kinetic energy when the electronic transitions occur between He^* and the surface on which the OH bond length becomes shorter (longer).

If the asymmetry of H^+ MSD is due to the neutralization of the hole created in the OH 3σ orbital by the Na $3s$ electrons as mentioned above, the dependence of the H^+ MSD asymmetry on the kinetic energy is discussed as follows. The velocity dependence of the survival probability P_s can be expressed by the following formula based on the semiclassical model [16]:

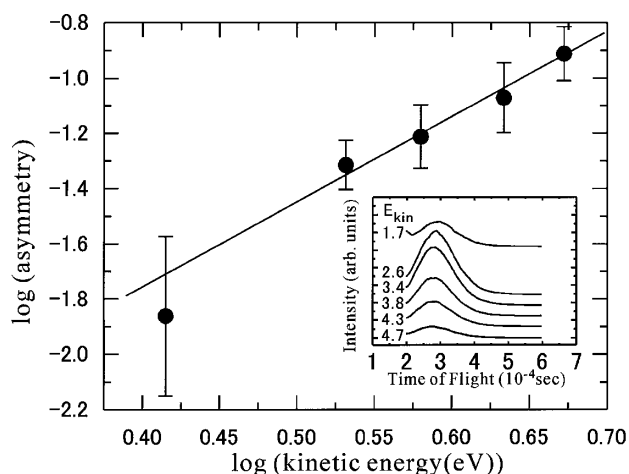


FIG. 2. The dependence of H^+ MSD asymmetry on the kinetic energy obtained on the $\text{H}_2\text{O}(10\text{ L})/\text{Na}(0.3\text{ ML})/\text{Fe}$ surface. The asymmetry is averaged at each MSD peak position from 260 to 300 μs . The inset shows the series for the H^+ MSD time-of-flight spectra.

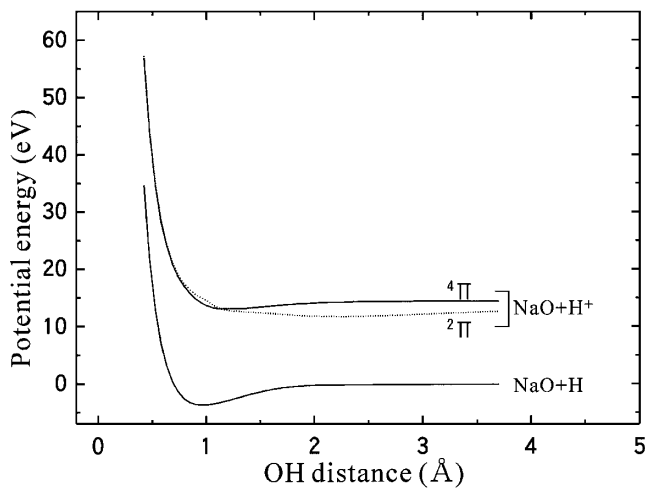


FIG. 3. The potential energy curves as a function of the internuclear separation for the NaO-H system obtained by the MRSDCI calculations, where the calculations were performed for the ground state of NaOH and NaOH⁺ in which one electron is removed from the OH 3σ orbital.

$$-\ln P_s = K\nu^{[2(a/b)-1]}. \quad (1)$$

Here, the decay rate and the potential curve of the excited state are approximated by $A \exp(-ar)$ and $B \exp(-br)$, respectively. ν is the velocity of H⁺ MSD at infinity. Briefly, as the H-surface distance at the Frank-Condon transition decreases, the chance of the neutralization of H⁺ (or the OH 3σ hole) is enhanced because of the increase of the decay rate. Thus, P_s decreases. At the same time, ν increases, which leads to a shorter H⁺-surface interaction time. This increases P_s . Equation (1) indicates that the complex variation of P_s with ν depends on the relative strength of the decay rate and the excited-state curve. K is a constant proportional to A , which is proportional to the SDOS of the Na 3s electrons neutralizing the OH 3σ hole. Thus, K has spin dependence. On the contrary, the spin dependence of a and b may be negligible because Fig. 1(b) shows no spin dependence in the energy of the Na 3s and OH 3σ bands, which determine a and b , respectively. Using Eq. (1), we obtain

$$\text{asymmetry} \equiv \frac{P_{s\uparrow} - P_{s\downarrow}}{P_{s\uparrow} + P_{s\downarrow}} \approx -\frac{K_{\uparrow} - K_{\downarrow}}{2} \nu^{[2(a/b)-1]}. \quad (2)$$

Here, $P_{s\uparrow}$ and $P_{s\downarrow}$ are the survival probability of H⁺ MSD emitted by He* polarized parallel and antiparallel, respectively. The approximation is based on the experimental fact that $P_{s\uparrow}$ and $P_{s\downarrow}$ are close to each other. Equation (2) means that log (asymmetry) has a linear relationship with

log ν [or log(kinetic energy)]. This is confirmed in Fig. 2; hence, the above interpretation for the H⁺ MSD mechanisms is supported [17].

The present study has been conducted on a low work function surface of H₂O/Na/Fe, where He* decays via the Auger deexcitation process creating one hole in the bonding state of the adsorbate. On high work function surfaces, He* is known to dissipate its excitation energy through resonance ionization followed by Auger neutralization leaving two holes in the surface valence states. The difference between a single hole and two holes initiating DIET is interesting as a future study. Furthermore, desorption of a neutral atom or molecule in addition to ion desorption should also be considered in order to completely understand the mechanism of MSD.

The authors are grateful to Professor F. B. Dunning, Professor H. Kasai, Dr. R. Souda, Dr. T. Sasaki, Dr. H. Kitazawa, and Dr. T. Takada for their valuable discussions.

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