Bonding of Molecular Solids Probed by Low-Energy H$^+$ Scattering. Water and Oxygen on Pt(111)

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Low-energy H$^+$ ions are scattered from condensed O$_2$ and H$_2$O layers formed on the Pt(111) surface in order to investigate the nature of bonding of molecular solids on the basis of the neutralization of H$^+$. The H$^+$ yield from the H$_2$O layer is found to be less than 1/60 of that from the O$_2$ layer. This is because the 1s hole of H$^+$ tends to be localized in the physisorbed O$_2$ molecule, whereas the valence hole is rather delocalized in solid H$_2$O due to hydrogen bonds with a considerable covalent character.

The rate and lifetime of electronic excitation in atoms and molecules adsorbed on solid surfaces are the controlling factors of a variety of chemical processes on solid surfaces. An electron capture (or loss) can trigger an internal evolution in the surface species and leads to the fragmentation of a molecule, reaction at the surface, stimulated desorption, vibrational excitation, and so on. This subject also relates to various surface analysis techniques using ions, such as low-energy ion scattering (LEIS), secondary ion mass spectrometry (SIMS), and electron- and photon-stimulated desorption (ESD and PSD), but the mechanism of ion emission from solid surfaces is still a matter of controversy. In LEIS, reactive ions such as H$^+$ undergo almost complete neutralization on metal surfaces, whereas the neutralization probability is suppressed considerably on highly ionic compound surfaces.[1] This occurs because the neutralization probability of H$^+$ is determined by the lifetime of the valence holes relative to the ion−surface interaction time.[2] On the other hand, noble-gas ions such as He$^+$ survive neutralization even on metal surfaces.[3] This phenomenon has been interpreted in terms of the transient chemisorption (physisorption) of reactive ions (noble-gas ions), in which ions are neutralized mainly via the one-electron resonance process (the two-electron Auger process).[2] In this context, thin layers of physisorbed atoms or molecules on a metal surface are of interest since the surface electronic properties can be continuously changed from metallic to insulating with increasing coverage. So far, a large number of SIMS[4−7] and ESD[8−10] studies have been performed concerning the ion emission from condensed molecular solids, but very few works are done in LEIS.

In the present paper, low-energy H$^+$ ions are scattered from O$_2$ and H$_2$O layers formed on the Pt(111) surface, and the mechanism of neutralization and reionization of H$^+$ is discussed on the basis of localization/delocalization of the valence holes. These two molecules are chosen carefully in order to investigate the nature of hydrogen bonds in the condensed molecular solids. It is found that the H$^+$ yield from the H$_2$O layer is considerably smaller than that from the O$_2$ layer. The results are interpreted in terms of the delocalization of the valence holes via hydrogen bond with some covalent properties.

The experiments were carried out in an ultrahigh-vacuum chamber (base pressure of 1×10^{-10} mbar) equipped with facilities for standard surface characterization. The ion beams were extracted from a discharge and were mass analyzed using a Wien filter. In the LEIS experiment, the surface was bombarded by H$^+$ and He$^+$ ions, and the positive ions scattered from the surface were detected by means of a hemispherical electrostatic energy analyzer (ESA) operating with a constant energy resolution of 2 eV. The Pt(111) substrate was mounted on a sample holder cooled to 15 K by means of a closed cycle He refrigerator. The clean surface was obtained by Ar$^+$ sputtering and heating in oxygen. The surface cleanliness was checked in situ by LEIS using $E_0 = 1$ keV He$^+$ and SIMS under the time-of-flight mode. The surface was slightly contaminated by the residual gas during a cooling time of the sample (30 min) after flash heating (1200 K), and hence, the surface was bombarded with He$^+$ before each measurement so that the Pt surface peak intensity in He$^+$ LEIS recovered to the clean surface value. The one-monolayer (1 ML) coverage of the overlayer was determined from the decay curve of the Pt surface peak intensity in He$^+$ LEIS ($E_0 = 100$ eV) as a function of exposure time, and the film thickness was estimated on the basis of this value by assuming a constant sticking probability of unity.

Figure 1 shows the energy spectra of H$^+$ scattered from the O$_2$ adsorbed the Pt(111) surface as a function of exposure. The intensities are normalized through the ion beam current. The measurements were made using primary H$^+$ ions ($E_0 = 100$ eV) with an incidence angle of 20° (measured from the surface normal), and the ions backscattered normal to the surface were detected. The ideal elastic binary collision energies of H$^+$ on Pt and O are indicated with arrows on the abscissa. The H$^+$ spectrum from the clean Pt(111) surface exhibits a broadly humped background. With increasing O$_2$ exposure, the background increases together with the O surface peak. The background is due to the H$^+$ ions which are scattered after experiencing multiple collisions in the Pt substrate, whereas the surface peak is due to single collision with the topmost-layer oxygen atom. The 1 ML coverage of the O$_2$ molecule is achieved at an exposure of around 3 L (1 L = 1.3×10^{-4} Pa·s). The H$^+$ intensity is saturated above 10 L when the multilayer of the O$_2$ solid is formed.

The energy spectra of H$^+$ scattered from the H$_2$O condensed Pt(111) surface are shown in Figure 2, where the overlayer of 1 ML H$_2$O is formed by an exposure of around 5 L. The measurements were made under the same experimental conditions as those in Figure 1. The H$^+$ yield increases in a submonolayer coverage regime and then decreases considerably
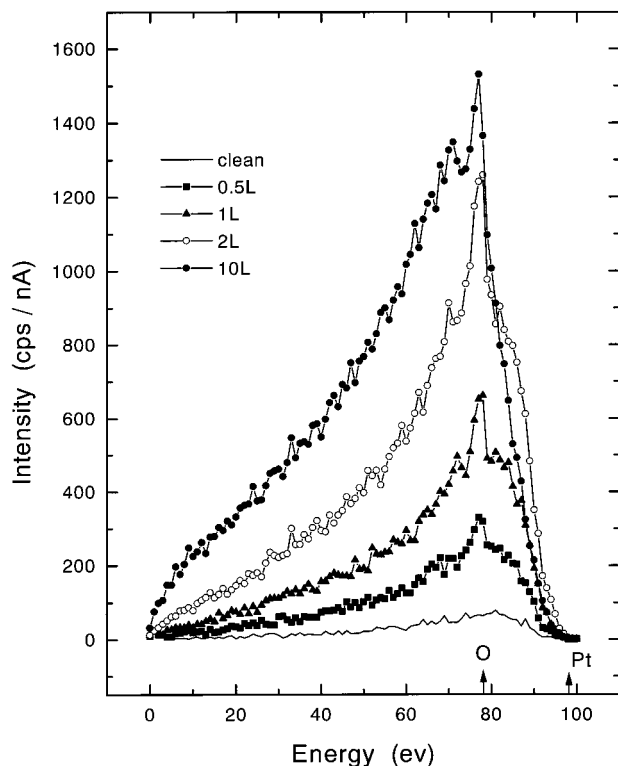
Figure 1. Energy spectra of H$^+$ scattered from the Pt(111) surface as a function of O$_2$ exposure. The surface was irradiated with an $E_0 =$ 100 eV H$^+$ beam at the incidence angle of 20°, and the ions scattered normal to the surface were analyzed. The intensities are normalized through the ion beam current. The arrows on the abscissa indicate energy positions for the elastic binary collisions of H$^+$ with Pt and O atoms.

Figure 2. Energy spectra of H$^+$ scattered from the H$_2$O adsorbed Pt-(111) surface as a function of exposure. The measurements were made under the same conditions as those in Figure 1. The intensities are normalized through the ion beam current.

when the multilayer is formed. The O surface peak is barely discernible at a higher-coverage regime after the background intensity decreases. The results contrast sharply to those of the O$_2$/Pt(111) surface. The integrated H$^+$ yield from H$_2$O/Pt(111) is only 1.6% of that from O$_2$/Pt(111) for the saturated surfaces.

It is known that the H$^+$ ion is rather unique relative to the noble-gas ions in terms of neutralization.[11,12] The He$^+$ ion survives neutralization during single collision with topmost-layer atoms and exhibits only surface peaks in the energy spectra, whereas the energy spectra of H$^+$ consist of the broad background originating from the bulk and the surface peak is usually absent completely. This is highly remarkable because the ions scattered from the solid, which interact with the valence electrons for a longer time, are thought to be neutralized more efficiently than those scattered from the topmost-layer atoms via single collision. In reality, the spectral background is due to reionized neutrals. The surface peak due to the surviving H$^+$ ions becomes dominant relative to the background in lower-energy H$^+$ scattering (<200 eV) from highly ionic compound surfaces.[1,2]

As far as the scattering cross section is concerned, the multiple scattering from a solid is much larger than the single surface scattering, and hence, the emergence of the spectral background without the surface peak such as the case for the clean Pt(111) surface is rather reasonable. The energy distribution of H$^+$ decays for lower kinetic energies despite the distribution of scattered particles increasing at lower energies as a cascade process. This is because the H$^+$ ions are caused by the reionization of H^0 due to the electron promotion mechanism during energetic collisions with the topmost layer atoms. It was revealed that the promotion of the H 1s electron occurs
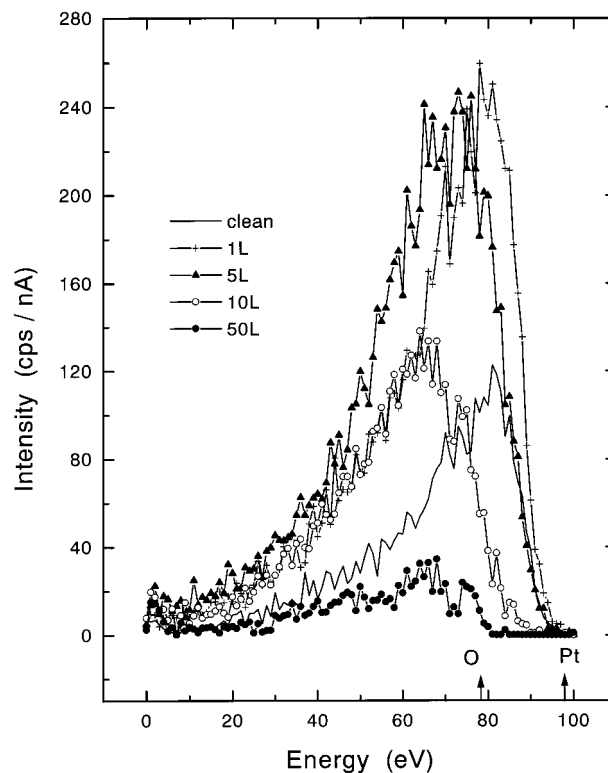
efficiently during collision with O but the symmetric H−H collision is ineffective for excitation of the H 1s electron.[13] The energetic H^0 atoms backscattered from the solid are reionized during collision with oxygen of the O$_2$ and H$_2$O molecules at the surface, and the resulting H$^+$ ions, if they survived neutralization on the outgoing trajectory, can be emitted, thereby forming the spectral background. Thus, the yield not only of the surface peak but also of the spectral background should be related to the neutralization of H$^+$. In Figure 2, the initial increase of the background intensity for the submonolayer coverage of H$_2$O is due to reionization of H^0 by the O of independently adsorbed H$_2$O molecules, but the subsequent decrease of the H$^+$ yield should be caused by the predominance of the neutralization over the reionization in the multilayer coverage regime as a consequence of the formation of solid H$_2$O. With increasing coverage, the leading edge of the energy distribution shifts toward the lower kinetic energy corresponding to O due to the ion neutralization effect and/or the blocking effect of the H$_2$O overlayer (10 ML) on the backscattered H^0 from the Pt substrate.

The underlying mechanism for determining the neutralization probability of H$^+$ is the band effect on the resonance neutralization.[14] The valence-level positions for thick O$_2$ and H$_2$O layers on Pt(111) were reported in the literature;[15] four peaks corresponding to the 3σ_g, 3σ_g + 1π_u, 1π_u, and 1π_g orbitals of the condensed O$_2$ layer are observed in the photoemission spectra at the biding energies of −12.8, −10.8, −9.2, and −4.8 eV, respectively, whereas the 1b$_2$, 3a$_1$, and 1b$_1$ orbitals of H$_2$O appear at −11.3, −7.6, and −5.4 eV, respectively. There exists no significant difference in the binding energies of the valence levels between these two molecules. Moreover, the ionization potentials of these levels with respect to the vacuum level, as estimated from the work function of about 5.5 and 5.0 eV for the O$_2$/Pt(111) and H$_2$O/Pt(111) surfaces, respectively,[15] satisfy

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the resonance or quasiresonance condition[16] (± 5 eV) with respect to the H 1s level (13.6 eV). The neutralization probability is determined by the lifetime of the H 1s hole in the transient quasimolecular states such as $(H_2O-H)^+$ and $(O_2-H)^+$ relative to the interaction time (5×10^{-15} s). If the hole is completely localized in a resonating level of these quasimolecules such as the case for the gas-phase collisions, the neutralization probability of H^+ should be at most around 0.5.[14] On metal and semiconductor surfaces, the H^+ 1s hole can readily diffuse into the valence band, since the lifetime of the valence hole, estimated by $\tau = \hbar/W$ (W, valence-bandwidth), is about 1 order of magnitude smaller than the transient chemisorption time. On the surface of molecular solids, the lifetime, related to the overlap of wave functions of the constituent molecules, should be much longer than that for the metal and semiconductor surfaces. The H^+ ion probes local electronic configurations around target atoms (or molecules) because of the small expanse of the H 1s orbital (0.5 Å). This is manifested by the H^+-scattering experiment of chemisorption systems such as alkali metals on metal and semiconductor surfaces;[17] the surface peak from the alkali adatom is observed intensively, provided that the adatom is completely ionized, but the surface peak is absent if the adatom has metallic or covalent orbital hybridization with the substrate because the H^+ 1s hole is delocalized as a consequence of diffusion into the band via such hybridizing orbitals. Thus, the neutralization probability of the H^+ ions, related to delocalization of the valence holes, should be a good measure of covalency in bonding, since it is defined as quantum mechanical sharing of the electrons (holes). According to this scheme, the emergence of the O surface peak as seen in Figure 1 indicates that the valence hole tends to be localized in the $(O_2-H)^+$ quaimolecule at least for the transient adsorption time of H^+ around 5 fs. The localization of the valence hole shows that the O_2 molecules are condensed basically via the physical bond or the van der Waals force without significant overlap of wave functions or chemical interactions.

The considerably small yields of both the surface peak and the background of H^+ scattered from solid H_2O are due to delocalization of the valence hole. It is thus concluded that a considerable covalent character exists in bonding of the water ice. The hydrogen bond is known to play an important role in condensation of the H_2O molecules and to cause many distinctive properties of water relative to the other molecules. In the core and valence level photoemission study[15,18] as well as the vibrational study,[19,20] the hydrogen bond is thought to be responsible for spectral changes from submonolayer growth to the formation of solid ice; the $3a_1$ state is largely perturbed upon solidification due to hydrogen bonding, and it substantially overlaps with the $1b_1$ state.[18] This result was ascribed to the orbital geometry effect, but the nature of the hydrogen bond itself was not clarified. It is believed that the hydrogen bonds are primarily electrostatic in nature, in which the molecules are attracted by means of separated electric charges. Since the first prediction by Pauling,[21] however, it has been suspected that the hydrogen bond has covalent properties as a consequence of the overlap of the electron wave functions between the covalent σ bonding site of the H_2O molecule and the hydrogen bonding site. Very recently, it was claimed from the experiment of Compton scattering[22] that the hydrogen bond should in part be covalent in nature, since electrons are spread out and there is an overlap of the electrons on neighboring H_2O molecules. The present result supports these works and provides another experimental evidence that the hydrogen bond in the water ice has considerable covalent properties.

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