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Transmission of low-energy ($\leqslant 10$ eV) H^+ and D^+ ions through ultrathin rare-gas films

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The transmission of low-energy ($\leqslant 10$ eV) H^+ and D^+ ions through ultrathin films of Kr and Xe has been studied to address the underlying scattering and charge-transfer processes. The ions are produced by means of electron stimulated desorption (ESD) from a water-bilayer covered (H_2O or D_2O) Ru(0001) surface. Their yield as a function of overlayer film thickness is measured using a digital time-of-flight electron stimulated desorption ion angular distribution detector. Film thicknesses are determined using thermal desorption spectroscopy. The small structural difference of the H_2O compared to the D_2O film on Ru affects the shape of the rare-gas thermal-desorption spectra. About 10% of the ESD ions are transmitted through 2 ML of Kr or Xe with no significant difference in the transmissivity of H^+ and D^+. The attenuation is discussed in terms of elastic scattering and charge-transfer neutralization processes. [S0163-1829(98)01147-3]

I. INTRODUCTION

Recently a number of experiments have been performed to address the fundamental issue of the transmission behavior of low-energy ions ($\leqslant 10$ eV) through the surface layers of a solid.[1–6] The goal is to identify the underlying energy- and charge-transfer processes that affect the ion transport through these layers. To date the interactions of positive and negative ions (O^+, F^+, and F^-) with ultrathin films of condensed gases (Ar, Kr, Xe, H_2O, and NH_3) have been studied. The desorption both of neutrals (including metastables) and ions from a surface can be induced via electronic excitations by the interaction of electrons, photons, or ions with the solid;[7,8] these processes are termed desorption induced by electronic transitions (DIET). Although it is commonly assumed that most of these desorbing species originate from the top surface layer,[9,10] recent results indicate that the escape depth for ions and neutrals can be up to 10 ML deep, depending on the ion and overlayer.[1–5]

The issue of the depth of origin of ions is fundamental for investigations of DIET from adsorbates or compound surfaces. Other areas of surface and interface science where the understanding of ion transport through surface layers is important are electrochemistry, plasma processing, and surface photochemistry.

In measurements in our laboratory of ion transmission through films, the ions are generated by electron stimulated desorption (ESD) from a compound surface. This results in a low-energy ion beam with a well-defined energy and angular distribution. The thin solid films ranging from a fractional monolayer to several monolayers in thickness are condensed onto the substrate. The yield of the desorbing ions is measured after they have traveled through these layers. In the present paper, we address the transmission of H^+ and D^+ ions through ultrathin rare-gas films. Condensed rare gases represent the simplest physisorbed systems and H^+ and D^+ are the most fundamental ions. Due to their large relative mass difference a possible isotope effect should most easily be detectable compared to other ions.

II. EXPERIMENTAL SETUP AND PREPARATION OF THE SUBSTRATE

The experiments have been performed in an ultrahigh vacuum (UHV) chamber (base pressure $\approx 1.5\times 10^{-8}$ Pa) equipped with instruments for surface analysis including thermal-desorption spectroscopy (TDS), Auger-electron spectroscopy, and low-energy ion scattering. A resistive anode-based two-dimensional electron stimulated desorption ion angular distribution (ESDIAD) detector with time of flight (TOF) capability allows the mass- and angle-resolved detection of the desorption yields of the ions and also the acquisition of low-energy electron diffraction patterns. A quadrupole mass spectrometer (QMS) used for TDS can also be used for the detection of positive ions. Due to the short distance from sample to detector and the width of the kinetic energy distribution of the desorbing ions, H^+ and D^+ cannot be completely resolved in TOF. However, the ionic purity could be verified in separate measurements with the QMS.

For the experiments described here, a single crystal ruthenium sample of ~1 cm diameter with a (0001) surface was used. By means of a closed-cycle helium refrigerator the sample can be cooled to ~35 K; it can be heated to 1600 K by electron bombardment for cleaning. The experimental setup and the sample preparation and cleaning procedure have been described in detail previously.[11]

The protons desorb from the ruthenium surface that is covered with a bilayer of water molecules. This system has been well characterized and described in the literature.[12–15] In order to prepare a saturated bilayer on the Ru(0001) surface water is adsorbed at a sample temperature of ~150 K, which corresponds to the temperature of multilayer desorption. This ensures that a saturated bilayer can grow, which is confirmed using TDS. Our spectra of both H_2O and D_2O show essentially the same features as described in the literature. A striking difference in the TDS spectra of H_2O and D_2O on Ru(0001) was first reported in 1987 by Schmitz *et al.*[16] As discussed in the literature[14,15] the H_2O bilayer forms a domain structure with boundaries that have a different structure compared to the inner domain area. In contrast,

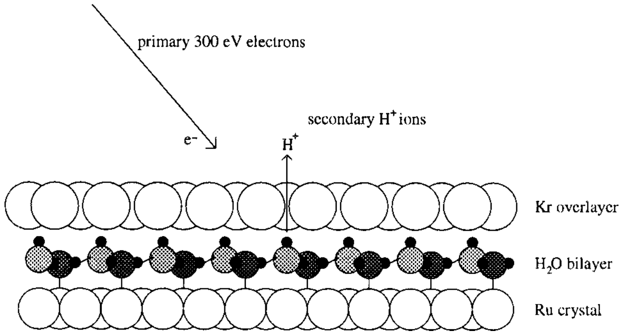

FIG. 1. Schematic of experimental approach. Protons created via electron stimulated desorption from the water covered Ru surface penetrate through a rare-gas overlayer.

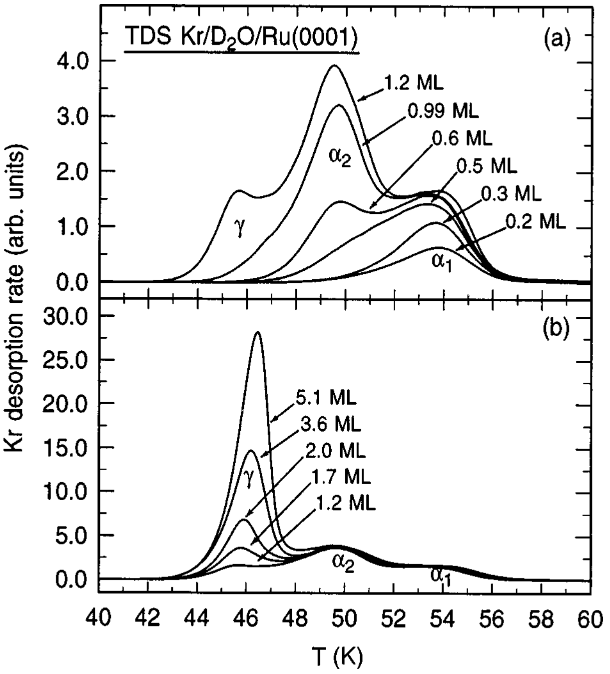

FIG. 2. Thermal desorption spectra of Kr from the D_2O-bilayer covered Ru(0001) surface: (a) low and (b) high coverage.

the D_2O bilayer covers the surface more uniformly and does not form a similar domain structure. The small difference in the structure of the H_2O compared to the D_2O bilayer has an interesting impact on the shape of the TDS curves of the rare gases desorbing from that substrate, and is described later.

Figure 1 shows schematically the essence of the experiment. The adsorption of a bilayer of water molecules leads to a hydrogen-terminated topmost layer, with O-H bonds oriented on average perpendicular to the surface.[12] The data for the H^+ and D^+ transmission experiments are recorded with the ESDIAD detector at a positive sample bias voltage of $+100$ V and a substrate temperature of ~ 35 K. A primary electron-beam energy of 300 eV with an electron flux of $\sim 2\times 10^{13}$ cm^{-2} is used. The molecules from the topmost layer produce H^+ ESD ions emitted with a symmetric angular distribution with its maximum normal to the surface (FWHM$\approx$40°) in qualitative agreement with previous results.[18] The ion kinetic-energy distribution is peaked around $\simeq 4$ eV.[17] Using the TOF capability of our system and the quadrupole mass spectrometer, H^+ ions are identified to be the only ionic species emitted by ESD of H_2O. D^+ ions are generated from the heavy-water-covered surface; the H^+ impurity in the desorbing D^+ ions is found to be approximately 10%.

III. TDS OF RARE GASES FROM THE WATER-COVERED Ru(0001) SURFACE

The rare gas is dosed reproducibly onto the water-covered crystal through a directed doser equipped with a capillary array plate. The high purity rare gases are further purified using a liquid-nitrogen-cooled trap to remove possible traces of residual water. The exposure is measured in units of Langmuir ($1\ \mathrm{L} = 1.33\times 10^{-4}$ Pa s) using an uncalibrated ion gauge that measures the background pressure.

To determine the rare-gas coverage TDS measurements are performed. As an example, Fig. 2 shows thermal-desorption spectra for various coverages of Kr from the D_2O covered Ru surface. Three desorption peaks can be resolved, of which the first (α_1) saturates at an exposure of 0.04 L and the second (α_2) at 0.1 L. In order to relate the exposure and integrated peak area with the absolute coverage in monolayers we compare these TDS spectra with those acquired from a clean Ru surface. The spectra from the clean surface are in agreement with those of Schlichting and Menzel.[19] From this we conclude that the peaks α_1 and α_2 together correspond to the desorption of one monolayer. Peak γ corresponds to the desorption of the multilayers. The rare-gas TDS measurements do not affect the water substrate since the desorption is complete at ~ 60 K, which is well below the onset of the desorption of H_2O from Ru.

The splitting of the monolayer desorption peak might be due to a transition from an incommensurate to a commensurate overlayer formation: after partial desorption of the first monolayer the remaining rare-gas atoms on the surface may relax and form a commensurate layer. The same exposures of Kr dosed onto the H_2O or D_2O bilayers, respectively, result in identical coverages.

Although the structure of the rare-gas monolayer is not measured directly, it is believed that a close-packed fcc (111) structure is formed.[4,6] The estimated number density for Kr is $\sim 7.1\times 10^{14}$ atoms/cm^2 and for Xe is $\sim 6.0\times 10^{14}$ atoms/cm^2. Based on the bulk densities of 2.17×10^{22} cm^{-3} for Kr and 1.64×10^{22} cm^{-3} for Xe,[20] we thus estimate the thickness of a rare-gas monolayer to be 3.3 Å for Kr, and 3.7 Å for Xe.

Figure 3 shows background-subtracted TDS spectra for Kr from the H_2O-covered surface; essentially the same desorption features as in the case of desorption from the D_2O surface (Fig. 2) can be identified. However, there is a small but reproducible difference between the desorption behavior of Kr from the H_2O and D_2O substrate: a small shoulder, indicated by the arrows in Fig. 3, emerges from the α_2 peak of Kr/ H_2O. We conclude that the small structural difference of the D_2O compared to the H_2O bilayer effects the structure of the rare gas overlayer. Based on the domain structure of the H_2O bilayer[14,15] one might expect more complex TDS spectra in the case of the H_2O layer. It has been demonstrated recently that the desorption of Ar can be used as a

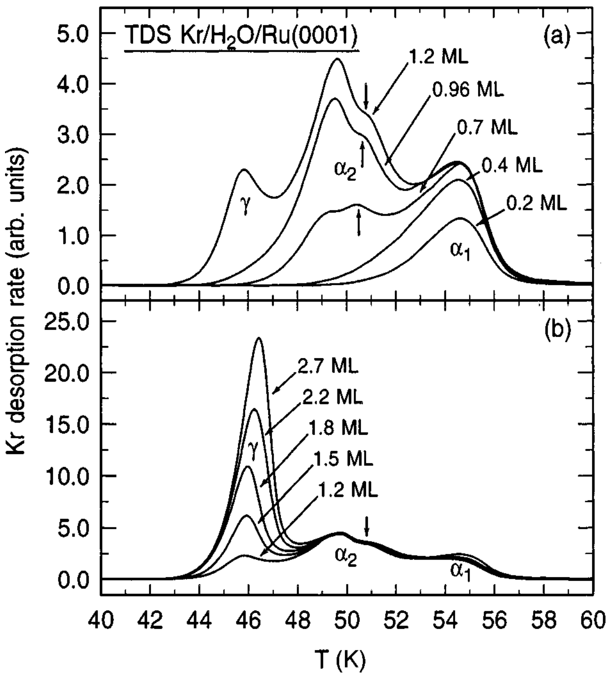

FIG. 3. Thermal desorption spectra of Kr from the H_2O-bilayer covered Ru(0001) surface (a) low and (b) high coverage. See text for discussion of small feature indicated by arrow.

nondestructive tool to investigate the structure of an underlying substrate.[21]

Similar TDS experiments to determine the rare-gas coverage were performed with Xe as an overlayer adsorbed on the water-terminated Ru surface. Just as the case of Kr/H_2O an additional feature emerging out of the α_2 peak is attributed to the structural difference between the H_2O and D_2O bilayers.

IV. RESULTS OF THE H^+ AND D^+ TRANSMISSION EXPERIMENTS THROUGH Kr AND Xe

The adsorption of a rare gas on top of the water-terminated Ru surface leads to the attenuation of the protons or deuterons produced by ESD from the underlying water bilayer. Figure 4 shows the total angle-integrated relative yield of protons and deuterons as a function of overlayer thickness expressed in ML for Kr on a log-linear plot. The errors of the measurements are estimated to be of the order of ± 0.1 ML for the coverage and ~10% for the relative ion yield. Figure 5 shows the corresponding plot for the transmission of protons and deuterons through Xe layers.

The various data points represent different measurements on different rare-gas films. In measurements from the same rare-gas overlayer, we do not observe any dependence of the transmissivity on the electron dose. This indicates that no significant electron-beam damage occurs either of the water substrate or the rare-gas overlayer. Between measurements on films of different thickness, the rare-gas overlayer was removed by heating the sample to the desorption temperature of the rare gas. The measurements are reproducible from different water bilayers. Using TDS, it was found that repeated dosing of rare gas onto the same H_2O or D_2O film, followed by desorption, leads to small changes in the water-desorption spectra, despite the large differences in desorption temperature (~100 K) between rare gas and water. Therefore, no more than five transmission experiments using different rare-gas coverages were performed using the same water bilayer. For rare-gas coverages up to ~2 ML, the data of Figs. 4 and 5 follow exponential behavior. For rare-gas coverages above 2 ML, we find that the ESD ion signal tends to an asymptotic value. We believe that this background originates from H_2O/D_2O residual gas molecules either embedded in the rare-gas layer during the dosing procedure or adsorbed on top of it. We observe the same behavior for all our transmission experiments with protons or deuterons for coverages >2 ML of rare gas.

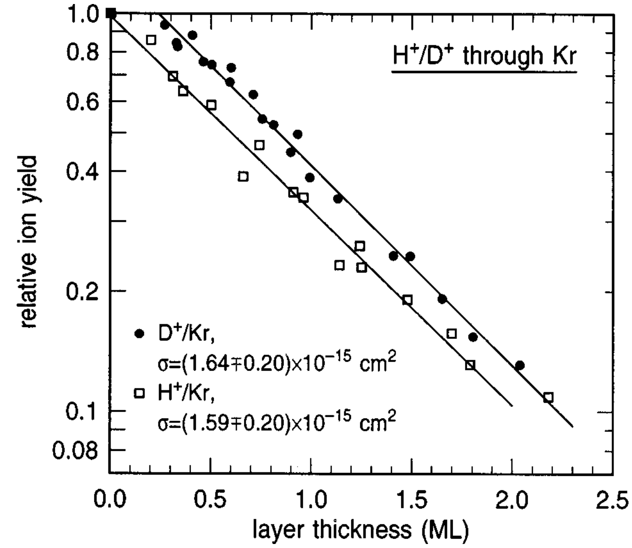

FIG. 4. Total H^+ and D^+ yield as a function of Kr layer thickness. The solid line represents the best fit according to an exponential attenuation law.

Using the mass spectrometer with its ionizer turned off we can also measure the mass and yield of the ESD ions. Compared to the attenuation data acquired with the ESDIAD detector we get essentially the same results. A disadvantage

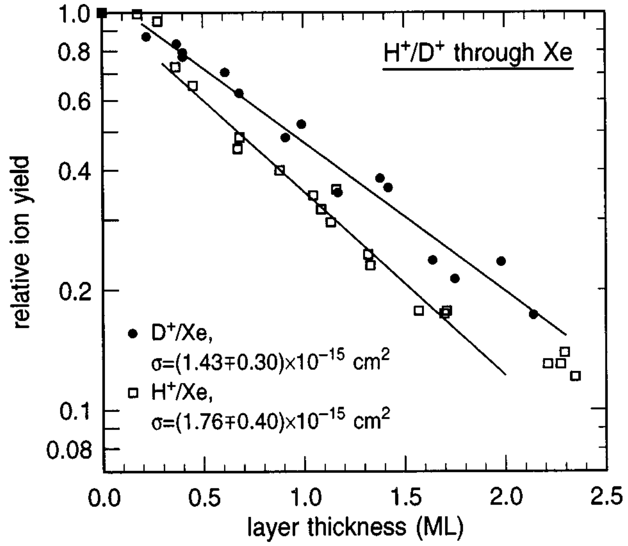

FIG. 5. Total H^+ and D^+ yield as a function of Xe layer thickness.

of this method is that it requires a higher flux of primary electrons (a factor $\sim 10\times$) due to the smaller solid angle of detection. For D^+ through Kr, the attenuation curve appears to be shifted slightly to higher coverages, which might be caused by a small depletion of the rare-gas layer via ESD of the adsorbed Kr atoms.

At this point it should be noted that the rare-gas overlayer is unlikely to cause changes in the H^+ or D^+ electron-stimulated desorption probability due to the weak interaction with the water layer. This is supported by the fact that the attenuation behavior is exponential for overlayer film thicknesses up to 2 ML. The interaction of the primary electron beam with the rare-gas film should be considered also. The cross sections for ionization of rare-gas atoms by 300-eV electrons are of the order 10^{-16} cm^2, and the electrons have not lost a major fraction of their kinetic energy on their passage through the rare-gas layer.[3,4] Since the electron-stimulated desorption process from adsorbed H_2O does not depend strongly on the primary electron energy around 300 eV, the effect of possible electron-beam energy losses on the H^+ (D^+) desorption process can be neglected.[3,4]

To analyze these data we use a continuum model resulting in an exponential attenuation law

$$\Phi = \Phi_0 \exp(-N_{\mathrm{RG}}\sigma_{\mathrm{exp}} d), \tag{1}$$

with the attenuation cross section σ_{exp}, the rare-gas film thickness d, and number density N_{RG}, and the total H^+ or D^+ flux Φ reaching the detector with Φ_0 being the flux at zero rare-gas coverage. This model is valid only if the rare-gas layer can be described by Poisson statistics meaning that the atoms are randomly distributed in the film. Layerwise growth of the rare-gas film could lead to deviations from the expected exponential attenuation. The ion transmission signal for each completed layer would still lie on an exponential curve, but within one layer the attenuation could become linear. However, if the rare gas grows layer by layer with random adsorption in one layer, Poisson-like attenuation behavior would be obtained if the effective interaction areas of the rare-gas atoms overlap. This can occur if the rare-gas atoms in the fractional layer regimes form small clusters before the layers are completed.

From Figs. 4 and 5 we observe exponential attenuation and the corresponding cross section can be obtained using

$$\sigma_{\mathrm{exp}} = -\frac{1}{N_{\mathrm{RG}}}\frac{\partial(\ln\Phi)}{\partial d}. \tag{2}$$

With N_{RG} and d given in Sec. III for Kr and Xe, we find the following values for the attenuation cross sections from the data acquired with the ESDIAD detector:

$$\sigma_{\mathrm{H^+/Kr}} = 1.6 \pm 0.2 \times 10^{-15}\ \mathrm{cm}^2,$$

$$\sigma_{\mathrm{D^+/Kr}} = 1.6 \pm 0.2 \times 10^{-15}\ \mathrm{cm}^2,$$

$$\sigma_{\mathrm{H^+/Xe}} = 1.8 \pm 0.4 \times 10^{-15}\ \mathrm{cm}^2,$$

$$\sigma_{\mathrm{D^+/Xe}} = 1.4 \pm 0.3 \times 10^{-15}\ \mathrm{cm}^2.$$

The errors associated with these values are dominated by the measurement accuracy and the limited range of the values for the ion yields. Whatever structural model is assumed for the rare-gas layer (layer-by-layer, random adsorption, etc.), the derived values for the cross sections do not differ significantly, and are within the error bars indicated above.

From the measurements using the mass spectrometer as the ion detector we derive an attenuation cross section for the transmission of D^+ through Kr:

$$\sigma_{\mathrm{D^+/Kr}} = 1.4 \pm 0.2 \times 10^{-15}\ \mathrm{cm}^2.$$

From this we conclude that within our experimental uncertainties the attenuation cross sections for protons and deuterons are essentially the same, independent of the rare-gas type. To understand these results we have to consider the various interaction mechanisms of the ions with neutral atoms.

V. ATTENUATION MODELS

In this section we discuss the various mechanisms of elastic and inelastic scattering, including charge transfer, by which the ions can be attenuated.

Elastic and inelastic interactions between the ions and the rare-gas atoms determine the transmissivity of the ions. Because the rare-gas atoms in the solid film interact only weakly via van der Waals forces, we expect that elastic scattering between projectile H^+ (D^+) and target Xe (Kr) can be described well by a series of binary collisions, and inelastic processes such as electronic excitations are less important. Large-angle elastic scattering can prevent the ion from escaping into the vacuum; it might be trapped in the film or scattered back to the interface and neutralized. Elastic scattering changes the trajectory and the kinetic energy of the ions. In the case of the transmission of O^+ through rare-gas films it was observed for Xe that the angular distribution of O^+ changes due to large-angle scattering;[4] for increasing Kr and Xe film thickness a shift in the O^+ energy distribution towards lower energies is also observed. Based on these results, elastic scattering of O^+ was considered to be the dominant attenuation mechanism. This was supported by a molecular dynamics simulation in which it was found that the attenuation behavior of the low-energy oxygen ions through thin Kr and Xe films can be successfully described by elastic collision processes, without considering neutralization.[22] A semiquantitative agreement could be obtained for ion yields and the energy and angular distributions of the transmitted ions.

Among various possible inelastic processes, charge transfer is most likely to occur. Because rare-gas films are wide band-gap insulators, charge-transfer processes are also best described by ion-atom collision models. Consider the role of charge transfer on the attenuation of the hydrogen ions in a binary collision, given schematically by

$$\mathrm{H}^+ + \mathrm{RG} \rightarrow \mathrm{H} + \mathrm{RG}^+ + \delta E,$$

where RG represents the rare gas and δE is the energy defect of the reaction. For an endoergic reaction involving a low-energy ion and a value of δE comparable to or larger than the collision energy, the reaction rate is zero. For exoergic reactions, charge transfer is possible.[23] Proton-scattering experiments with collision energies between 3 and 60 eV were performed on He, Ne, Ar, and Kr in the gas phase[24] and relative differential cross sections $\sigma(\theta)$ were measured. Calculations for the system $H^+ + Kr$ at a collision energy of 6 eV (Ref. 24) show that the experimental values can be explained on the basis of a purely elastic collision mechanism. For higher energies up to 5 keV, both experimental and theoretical evidence for charge transfer in the $H^+ + Kr$ system have been found.[25–27]

In comparing our results with the O^+ transmission experiments, we focus on the coverage regimes $\leqslant 2$ ML of rare gas. For growth of closed packed, (111)-like rare-gas layers, atomic ''channels'' exist for the first 2 ML, through which the ions can be transmitted.[4,6] As the third layer forms, the channels are blocked by additional rare-gas atoms, and the O^+ transmission probability decreases. For coverages $\leqslant 2$ ML of Kr and Xe, the attenuation cross section for O^+ was found to be $\sigma_{O^+/RG} \simeq 0.4 \times 10^{-15}$ cm^2.[3,4,28] In contrast, the cross sections for attenuation of H^+ and D^+ by $\leqslant 2$ ML of rare gas are about a factor of 4 larger than for O^+.

If elastic scattering of H^+ (D^+) is the dominant attenuation mechanism, as is believed to be the case for O^+, we would expect the H^+ (D^+) interactions with the rare-gas atoms to be somewhat comparable to O^+. The ionization energies of O^+ and H^+ are nearly the same (13.6 eV), so the scattering interactions arising from polarization of the Xe (Kr) target atoms by the projectile atoms should be very similar. Since the momentum transfer cross section can be written in terms of the center of mass energy only, the cross sections are equal for the same center-of-mass energy. This energy is $E_A M_B/(M_B + M_A)$ where A and B are the incident and target particles, and E_A the incident energy. For O^+ or H^+ on Kr or Xe, the mass factor is sufficiently close to unity so that the two ions have nearly the same center-of-mass energies and the momentum transfer/diffusion cross sections should be essentially the same. Thus, our observation that there is a significantly larger attenuation cross section for H^+ (D^+) than for O^+ does not appear consistent with a simple binary collision, elastic scattering picture. Other factors that need to be considered include multiple-scattering collisions that could exacerbate the small mass effect, or the fact that the target atoms are weakly bound to each other and are not free. Another point concerns the initial angular distribution of H^+ and O^+ ions. Whereas a quite narrow distribution (FWHM$\simeq$14°) was found for O^+ (Ref. 4) the H^+ distribution is much broader (FWHM $\simeq$40°). Since O^+ has higher momentum than H^+ at the same energy, and a narrower initial angular distribution than H^+, the O^+ may be able to penetrate through the ''channels'' in the rare-gas layers for thicknesses $\leqslant 2$ ML more easily than can H^+. This may give rise to higher measured cross section values for H^+ (D^+) attenuation than for O^+ attenuation. However, the close similarity of the values for the cross sections as determined with the angle-integrating ESDIAD detector as compared to the measurements with the mass spectrometer indicate that this interpretation is unlikely.

Whether charge transfer between the ions and the rare-gas atoms occurs depends on the difference in the ionization potentials. The gas-phase ionization energies of Kr (14.0 eV), Xe (12.1 eV), and H (13.6 eV) are relatively close, which would make charge-transfer processes possible, particularly for H^+/Xe. Note that the ionization energy of oxygen (13.6 eV) is also comparable to those of Kr and Xe, yet charge transfer is not believed to play a major role in the O^+ attenuation mechanism.[4,22] However, the exact value of the attenuation cross section depends strongly on the details of the shape of the interaction potentials.

For H^+ and D^+ ions with the same kinetic energy, the D^+ ions have an average velocity a factor of 1.4 smaller than that of the H^+ ions. If charge transfer were a dominant attenuation process then the fact that the D^+ ions spend more time traversing the rare-gas film would lead to a higher charge-transfer probability and, therefore, to a higher attenuation cross section for D^+ as compared to H^+. Within our experimental uncertainty, the opposite behavior is seen for H^+ and D^+ through Xe, and no clear effect is seen for Kr. Although we cannot eliminate one-electron charge transfer, this suggests that charge transfer is not the dominant process in the attenuation of H^+ and D^+ through rare gases. Note also that other experimental and theoretical investigations at higher H^+ and D^+ ion kinetic energies (100 eV–10 keV) have shown that the isotope effect in a charge-transfer reaction cannot be explained in a simplistic model.[29–31] Although the evidence is not conclusive, it appears that the attenuation of H^+ and D^+ in transmission through rare-gas films is dominated by elastic scattering interactions rather than by charge transfer. Large-angle elastic scattering (single or multiple scattering) may lead to H^+ (D^+) being trapped in the film, or being deflected back to the metal/H_2O interface, where effective neutralization can occur.

VI. SUMMARY

In order to develop a better understanding of the dominant processes that limit the survival probability of low energy ($\leqslant 10$ eV) ions penetrating through a condensed film of atoms or molecules, we have studied the simplest ion-overlayer system, namely, the transmission of protons through rare-gas solids. To search for a possible isotope effect, we have also studied the transmission of deuterons through the rare-gas films. The ions with known kinetic energy and angular distribution are produced by means of ESD from a water-covered (H_2O or D_2O) Ru(0001) surface. The ultrathin layers of rare gas (Kr or Xe) are condensed onto that substrate.

Within the experimental uncertainty, there appears to be a small isotope effect (H^+ attenuated more effectively than D^+) for Xe, but not for Kr. By comparison of the H^+, D^+ data with previous measurements of O^+ through Xe and Kr films, we suggest that attenuation is dominated by elastic-scattering interactions rather than charge transfer.

In order to investigate this issue further, experiments are planned using a different substrate as a proton source. The measurements may also include Ar as an overlayer film. We await the results of molecular dynamics calculations and other theoretical investigations to provide us with more insight into the nature of the dominant attenuation process.

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