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Interaction of molecular hydrogen ions with the LiF(100) surface

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Scattering of H_2^+ molecules from a LiF(100) surface at grazing incidence is studied in the energy range from 600 to 4000 eV. The scattered particle yield measured in an azimuthal scan at various temperatures showed peaking at the $[\bar{1}00]$ direction. A W-shaped peaked yield was observed near the $[\bar{1}00]$ direction above a temperature of about 200 °C, which shows that there is no charging up of the LiF crystal at this temperature. About 70% molecular survival was obtained at a very low primary energy of about 600 eV and this dropped to about 20% around 1300 keV. At low H_2^+ energies a very low charge state fraction H^+ and H^- ions were observed and it reached a maximum to about 15%, and 10%, respectively, around $2-2.5$ keV and decreased at higher energies. The molecular survival fraction and the charge state fractions stabilize above 250 °C. The molecular survival fraction was found to be higher at a random condition when compared to the yield at the $[\bar{1}00]$ axis. The mean energy loss of the neutral atoms is found to increase linearly with energy.

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I. INTRODUCTION

Interaction of atomic and molecular projectiles with insulating surfaces of ionic crystals have gained a lot of attention in recent years.[1–6] An efficient mechanism prevailing in such insulator projectile systems in the production of negative ions finds application in the design of low-flux negative-ion beam sources and also in the construction of neutral particle detectors in space research. The understanding of electron exchange processes[7] that control the majority of chemical reactions on surfaces is very much relevant in surface chemistry. So it becomes important to study such interactions. LiF is an insulator with a large band gap of 14 eV. This large band gap affects the resonant electron capture and loss but does not play an active role in the energy-loss and electron emission processes.

There are reports showing a very high negative-ion formation when neutral projectiles (like H, O, and F) interact with alkali-halide surfaces.[2,8] Neutralization of the ions via resonant tunneling and the consequent negative-ion formation via local electron-promotion mechanism have been reported in the case of proton impact on ionic compounds.[9] There are few reports on the H_2^+-LiF interaction at various energies above 1 keV, but not many reports are found below 1 keV region. In this paper, we report the azimuthal scans for molecular hydrogen ion scattered from a LiF(100) surface at various target temperatures. Molecular survival fractions and ion charge state fractions at various temperatures measured along a random and an axial position with respect to the LiF(100) surface will also be presented.

II. EXPERIMENTAL PROCEDURE

The details of the experimental apparatus has been described elsewhere.[10] The experimental setup consists of an UHV chamber coupled to a low-energy accelerator system. The accelerator consists of a plasma ion source where any gaseous ions can be produced. The charged gaseous ions are then energy and mass selected by a magnet and the beam is directed onto the sample placed in a UHV system. A gas cell present between the analyzing magnet and target chamber is used to produce neutral beams. The energy of the scattered particles are measured using a time-of-flight (TOF) system. The TOF beamline is fixed at an angle of 10° with respect to the primary beam direction and all measurements are performed under specular reflection, i.e., a glancing angle of 5° is used. Particle detection is acheived by using a multichannel plate detector with an aperture of 1.2° (full width). By using an appropriate acceleration, voltage separation of different charged particles could be achieved. The detection probability of the TOF detector for H_2^+ molecular ions is measured by deflecting the primary beam into the TOF tube and measuring the yield in the TOF detector for various energies of the molecular ions. H_2^+ ion energy could be varied by raising or lowering the accelerating voltage.

LiF(001) surface was sputtered slightly with 1 keV Ar^+ at angles of incidence between 15° . . . 5° and then annealed. A TOF spectrum taken after this showed no detectable level impurites. Estel *et al.* showed long back that LiF surface is very stable. At room temperature they showed no adsorption on LiF when they tried to adsorb water.[11] During all the measurements, the temperature of the sample was kept at 330 ° C to avoid a pileup of surface charges that otherwise will deflect the incident ion trajectory.

III. RESULTS

Figure 1(a) shows the azimuthal scan yield at various target temperatures. The sample was azimuthally rotated from 0° to 70°. The azmimuthal rotation was performed with a fine stepper motor controlled system. In our case, the sample was rotated from $-25°$ to $+47.5°$ with respect to the [100] direction. Azimuthal scans were taken from about 40 to 300 °C. At low temperatures, the incident primary beam was

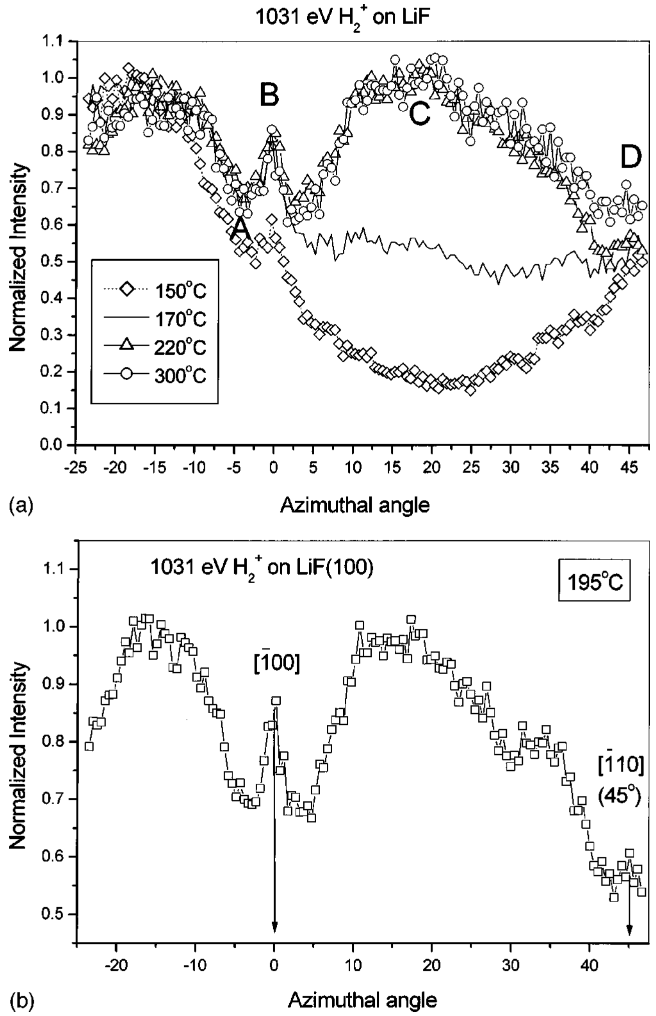

FIG. 1. An azimuthal scan yield for 1031 eV H_2^+ incident on LiF(100) surface at various temperatures. At 150 °C the peak begins to appear at the [100] direction (marked *B*). Symmetrical yield is not observed at 150 °C and 170 °C due to the deflection of the incident beam because of charging. At about 220 °C, the sample becomes conducting thus averting charging. The position *C* corresponds to the random case. (b) An azimuthal scan yield for 1031 eV H_2^+ incident on LiF(100) surface at 195 °C. [100] and [110] directions are marked in the figure.

deflected directly into the TOF tube due to the surface charge pileup. This charge pileup was confirmed by the observation of the primary beam in the scattered TOF spectrum. The appearance of a primary beam occured till about 190 °C. At about 200 °C, this primary beam completely vanished indicating that at this sample temperature, there is no charge pileup. In the figure, we show the azimuthal scan yields taken at 150, 170, 220, and 330 °C. A W-shaped spectrum appearing between $-15°$ and $+15°$ with a peak around 0° is from the [100] direction. The maximum intensity observed comes from the region far outside the low indexed orientations. It is clear from the spectra that the shape of the spectrum does not change from about 220 °C. Even at 195 °C [Fig. 1(b)], the spectrum shows a W-shaped peaking at [100] direction. This indicates that even at 195 °C, there is no charge pile-up and ionic conductivity is thus evident at this temperature.

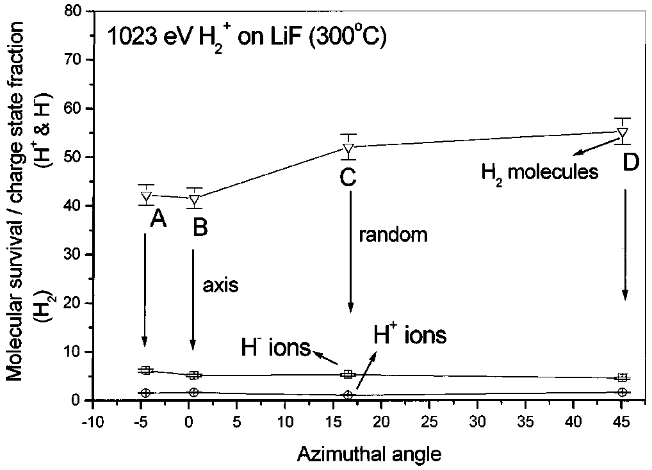

FIG. 2. Molecular survival fraction and charge state fraction for 1023 eV H_2^+ on LiF(100) surface measured at various crystallographic configurations *A*, *B*, *C*, *D* as marked in Fig. 1 showing the azimuthal scan. The measurements were taken at a sample temperature of 300 °C. The solid lines are just to guide the eye.

Figure 2 shows the molecular survival and charge state fraction for 1023 eV H_2^+ ions with a grazing incidence on LiF(100) surface held at 300 °C. Spectra were taken at different crystallographic orientations of the sample with respect to the incident beam trajectory. At four different configurations marked *A*, *B*, *C*, and *D* [in Fig. 1(a)] the spectra were taken. Positions *B* and *D* corresponds to two crystallographic orientations i.e., [100] (0°) and [110] (45°) directions. Analysis of these spectra as described in Refs. 12 and 13 revealed marginal difference in the molecular survival yield and charge state fractions. The molecular survival yield ranges from about 42%–55%. A higher molecular survival yield (~55%) was observed in the random case and along the [110] direction when compared to the [100] case (~42%). Negative ion (H^-) formation is dominant (~5%) when compared to the positive ion (H^+) formation (~1%). There is no change in the observed charge state fractions at various positions.

Figure 3 shows the molecular survival and charge state fraction of 1018 eV H_2^+ ions incident under grazing conditions on LiF(100) crystal oriented at constant random conditions taken at various temperatures. It is seen from the figure that the molecular survival stabilizes beyond 250 °C (about 45–50%). The charge state fraction of H^+ ions and H^- ions also stabilize beyond about 250 °C. Stabilization of the yield/charge state fraction suggest that beyond this temperature LiF becomes a good ionic conductor.

Figures 4(a), 4(b), and 4(c) show typical TOF spectra of H_2^+ ions at different energies scattered off a LiF(100) surface at a grazing incidence. For each energy, two TOF spectra were taken at negative and positive bias applied to the accelerating stage. In the case of applied negative bias, positive molecular and atomic hydrogen ions were detected along with neutral atoms and molecules. In the case of positive bias, negative hydrogen ions along with neutral atoms and

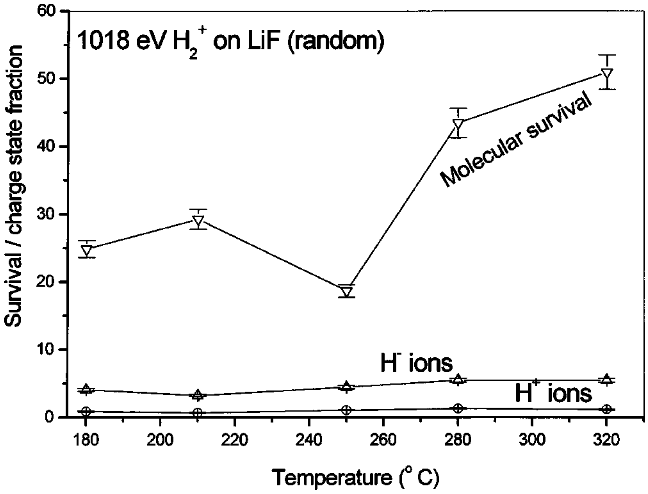

FIG. 3. Molecular survival fraction and charge state fraction for 1018 eV H_2^+ on LiF(100) surface measured at position *C* (random case) as marked in Fig. 1 showing the azimuthal scan. The yield gets stabilized above 250 °C.

molecules were detected. In Fig. 4(a) for 602 eV primary H_2^+ ions, distinct atomic (H^+) and molecular (H_2^+) hydrogen ion peaks are seen in the high energy side of the TOF spectra with negative bias voltage. In the low-energy side, a nice hatlike neutral molecular peak is seen riding over a broad neutral atomic peak. Similarly, in the positive bias case, a broad negative hydrogen ion peak is seen. In Fig. 4(b) (993 eV) the hatlike neutral molecular peak is not as sharp as seen in the low-energy case (602 eV) indicating a reduction in the surviving neutral molecules. At still higher energies [Fig. 4(c) (2889 eV)], there is no visible surviving molecules that are reflected in the absence of a hatlike neutral molecular peak.

Figure 5 shows the molecular survival fraction as a function of primary energies of H_2^+ particles scattered off a LiF(100) surface. The survival fraction decreases with increasing primary energy. At about a primary molecular ion energy of about 1400 eV, no more molecules survive in the scattering process. At higher energies, vibrational excitation dominates the molecule surface interaction,[14] and the probability of the breaking up of the molecules increases. A closer look at the shape of the curve reveals a region (from 700 eV to about 1000 eV in Fig. 5) where the molecular survival shows an increased scatter of the data and a plateau-like region. At present, we have no explanation for this reproducible feature.

Figure 6 shows the charge state fraction as a function of primary energy. It is clear from the figure that at low-incident primary energies, both negative and positive hydrogen ion productions are low and increase gradually with energy and reaches a maximum at about say 2500 eV and falls off at higher incident primary energies.

Figure 7 shows the plot of mean-energy loss of neutral atoms as a function of primary energy/atom. The mean energy loss increases with incident energy of the particle. This is very consistent with observed results reported earlier.[5,15] Winter *et al.*[16] recently have reported the energy loss of H° atoms at various energies. In their case, they show almost a constant energy loss below 1.0 keV. In our case, we observe a fairly constant value only below 400 eV (energy/atom). This difference could be due to the higher grazing incidence in our case (5°) when compared to theirs (0.18°). At low energies within the experimental error, their values match with our measurements.

IV. DISCUSSION

We report here evidence for surface axial channeling effects of LiF [Figs. 1(a) and 1(b)]. These channeling patterns have been reported frequently from metal surfaces but mainly in the backscattered ion yield.[17,18] The observed structures in the case here, forward scattering, are due to the particular combination of the crystal structure and the shadow cone produced by the ions. For metals, He on Ni(110), similar azimuthal yields have been observed[19] and reproduced by classical trajectory simulations.[20] Here the axial channeling effect serves two purposes: (i) establishing the temperature range where no surface charging occurs and (ii) where the surface is properly annealed and has an ordered structure. The ion yields, or rather, the charge state fractions, i.e., $H^+/(\Sigma \text{ all particles})$ and, i.e., $H^-/(\Sigma \text{ all particles})$ respectively, are approximately independent of the azimuthal orientation (Fig. 2). For the molecular survival fraction $H_2/(\Sigma \text{ all particles})$, there is a shallow minimum for scattering along the $[\bar{1}00]$. Slightly off the axis is orientation *B* in Fig. 1(b), where the molecular survival is slightly higher, and approximately 20% higher for orientations *C* (random) and *D* $[1\bar{1}0]$. Qualitatively, by comparing with the classical trajectory calculation of a metal,[14] this is due to the increased probability of rotational excitation of the H_2 molecules in the $[\bar{1}00]$ channels. The molecular survival is also strongly affected by the temperature (Fig. 3), which is due to the lack of a well-annealed surface structure. Below 280 °C the LiF surface is obviously rough, thus causing more dissociation. The qualitative behavior of both the ion yields and the molecular survival as a function of the beam energy can be read from the ‘‘raw data’’ (Fig. 4). These figures show original energy spectra as converted from the TOF spectra and described in Sec. II. The respective fractions are plotted in Figs. 5 and 6. Beside the plateaulike region below 1000 eV the molecular survival fraction shows the same qualitative behavior as in the case of metal surfaces.[14] However, the molecular survival at low energies is appreciably higher, a factor of 2 than for, e.g., H_2^+ scattering of Pd(110).[21] The higher dissociation on the metal surface is caused by electron capture into the H_2 antibonding triplet state, which is comparably unlikely on a wide band-gap insulator. Similar differences have been observed for O_2^+ scattering of Pd(110) and a diamond surface.[22] For N_2 no such difference is found, because N_2 has no such triplet state as O_2. Neverthless, charge transfer of one and two electrons is happening into H_2^+ on LiF, as seen from the high yields of neutral H_2 and H and H^-, respectively. The charge capture from LiF is understood in terms of an atom-molecule or atom-atom charge exchange process between the anionic

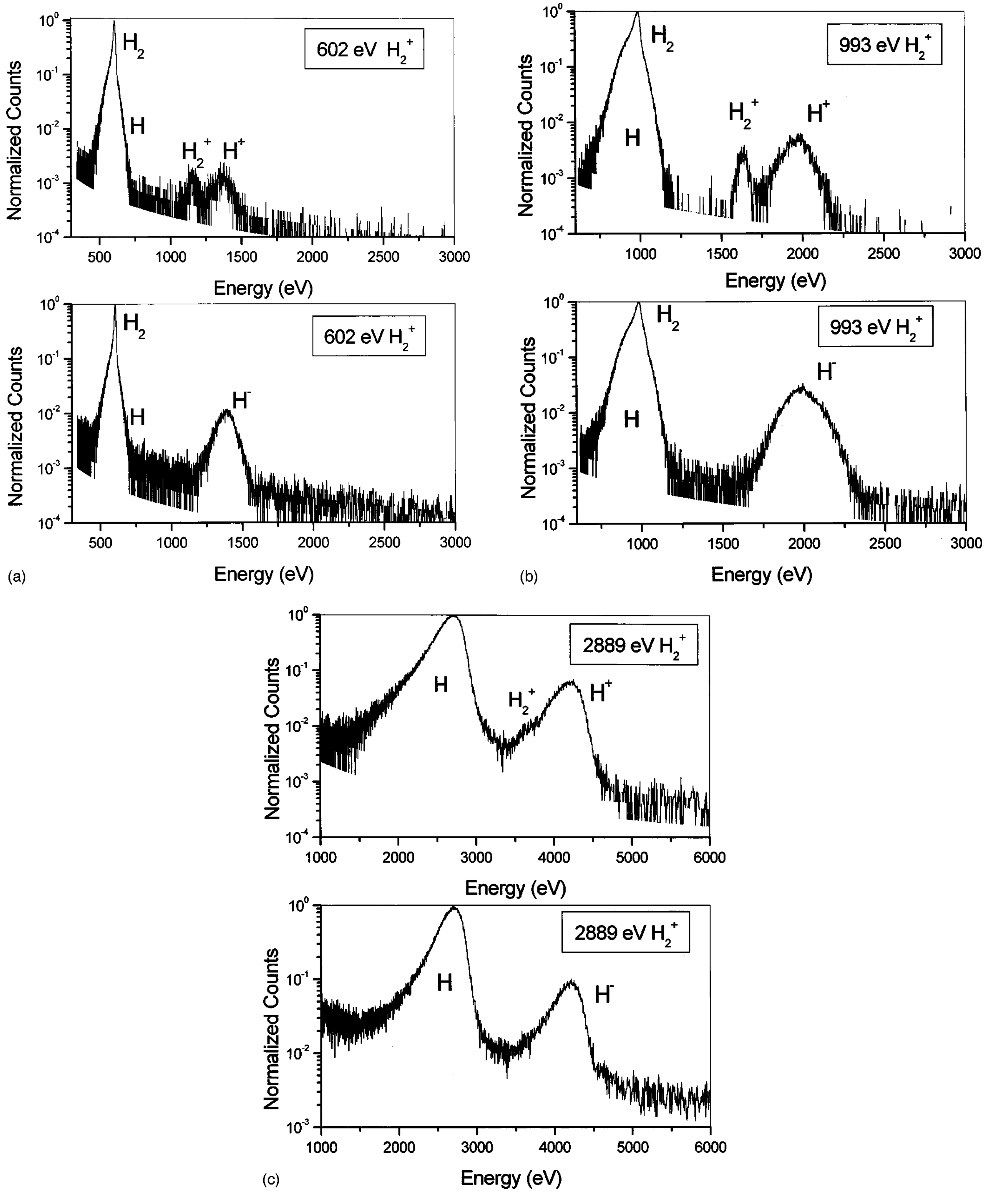

FIG. 4. Energy spectra H_2^+ scattered from a clean LiF(100) surface at an angle of incidence of 5° and a scattering angle of 10°. A narrow peak riding over the broad neutrals peak at low-energy side is from H_2 neutrals. At higher energies, H_2^+ and H^+ peaks are seen. These positions depend on the acceleration voltage applied. H_2^+ particles are (a) 602, (b) 993, and (c) 2889 eV.

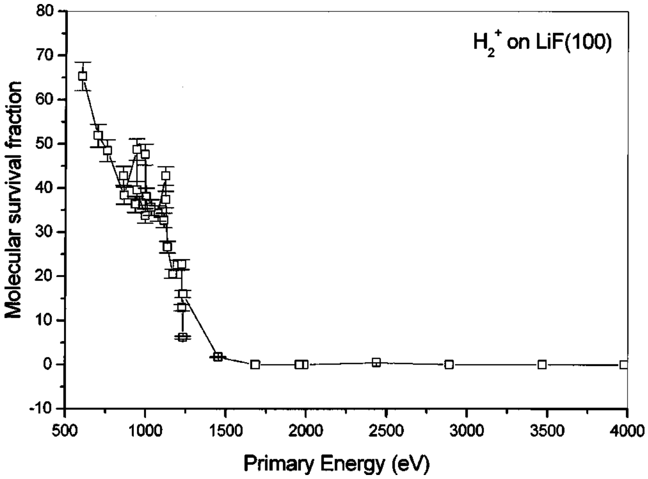

FIG. 5. Molecular survival fraction of H_2 scattered from a LiF(100) surface at 5° incidence angle and 10° scattering angle. The solid line is just to guide the eyes.

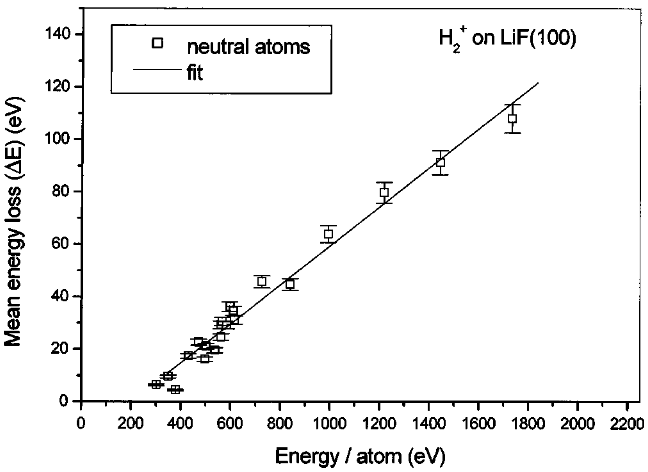

FIG. 7. Energy loss of neutral hydrogen atoms at various primary energies per nucleon. The energy loss increases linearly with incident energy.

site, F^-, and the H_2^+ or H to form H_2 or H^-, respectively.[23] Alternatively it has been argued that, albeit the F^- delivers the electron, the process is induced by the broadening of the F^- levels due to the parallel velocity component of the ions,[24] hence, the process is resonantlike as on a metal surface. Unfortunately, both theoretical approaches give charge fraction-energy dependences, bellshaped, as in Fig. 6.

In Fig. 8 we give a schematic energy-level diagram of LiF and the important energy levels of the hydrogen system. The H_2 2 $s\sigma(\uparrow\downarrow)$ ground state will be shifted up by image potential effect and, hence, be in perfect resonance with the F 2 *p* valence band of LiF. There is no competition with Auger capture effects as in the case of metals like Al where, due to the wide bandwidth, both resonant and Auger capture is possible.[25] In LiF, there are no electrons available for an Auger-type process. The H_2^- level is also in resonance and, hence, capture into this state may occur and lead to dissociation with some H^- as the final product. In the gas-phase terminology[6] this would be called a resonant ion pair production:

$$AB^{+}+2e\rightarrow AB^{-\star}\rightarrow A^{(+)}+B^{-}+electrons. \qquad (1)$$

The other possibility is that the H_2^- is not formed by a double electron capture but, rather, in a second independent step as discussed for the H^- formation,[23,24] i.e., by electron capture in an atom (F^- site)-molecule (H_2) collision. Vibrationally and rotationally induced dissociation produces H atoms. These H atoms collide with F^- sites producing H^- ions. This is the case over most of the energy range studied. Figure 8 gives, from the point of view of existing theories,[14,23,25,26] a consistent, qualitative interpretation of the dissociation and ionization processes observed here. In the most recent theoretical approach,[26] an ''electron promotion'' model is used to

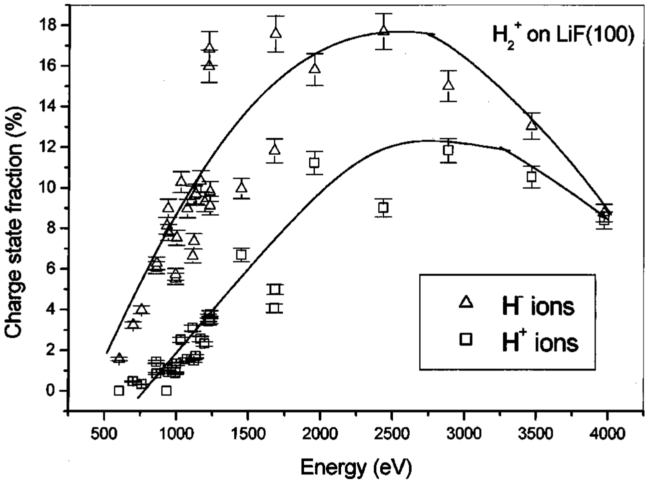

FIG. 6. Charge state fraction for H^+ and H^- ions at various H_2^+ primary energies scattered off a LiF(100) surface. The charge state fractions increases with energy and falls slightly at higher energies. The solid lines are to guide the eyes.

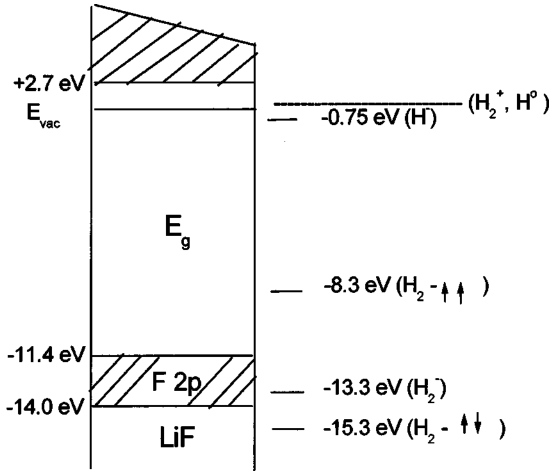

FIG. 8. Energy-level diagram of LiF and the important energy levels of H_2 and H. Note: The H_2 $Z_{p\sigma}(11)$ state is antibonding, so the value of −8.3 eV is valid only for a Franck-Condon transition from the H_2^+ ground state. The vacuum energy of the H_2 energy levels is the H_2^+ ground state and H° for the H^-, respectively.

calculate H-induced secondary electron spectra of LiF. Due to the promotion, doubly excited F^{-**} is formed at the surface from which electrons are emitted by autoionization. Here, we would suggest that H atoms capture electrons from these F^{-**} sites to form H^-.

V. CONCLUSION

Scattering of H_2^+ molecules from a LiF(100) surface at grazing incidence has been studied in the energy range from 600 to 4000 eV. The azimuthal scan measuring the scattered particle yield showed a peak at the [100] direction with a good symmetry around it only at about 195 °C (not shown in the figure) and above. No such symmetry is observed below this temperature. This clearly demonstrates that the charging of the LiF crystal persists till about 195 °C. A symmetrical peak appearing at the axis shows that scattering measurements on LiF should only be done at temperatures above 250 °C where complete ionic conductivity is present. At this temperature, the molecular survival fraction and the charge state fractions got stabilized. A higher molecular survival fraction for low incident primary H_2^+ ions is observed that is very high when compared to the case of metals. At low H_2^+ energies a very low charge state fraction H^+ and H^- ions are observed and it reached a maximum of about 15% and 10%, respectively, roughly around $2-2.5$ keV and decreased by a factor of 2 at higher energies. The molecular survival fraction was found to be higher at a random condition when compared to the yield at the [100] direction due to the penetration and scattering of incident particles in the latter case. The mean energy loss of the neutral atoms is found to increase linearly with energy, which agrees well with the existing theories.

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