A theoretical study of hydrogen diffraction following photodissociation of adsorbed molecules

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(Received 25 March 1992; accepted 21 April 1992)

A new probe of surface structure is presented which is based on the photodissociation of hydrogen from an adsorbate molecule. The event creates an atomic hydrogen fragment, positioned between the adsorbate layer and the solid surface. Due to its light mass, the hydrogen dynamics is quantum mechanical in nature. A useful image is of the hydrogenic wave function behaving like a liquid able to fill all cracks. The coherent character of the hydrogenic wave function is crucial in the ability of the photodissociation experiment to act as a probe. A series of case studies has been carried out whose aim is to reveal the relation between the structure of the surface and the asymptotic energy resolved angular distribution of the hydrogen fragment. The dynamics of the hydrogen atom motion was modeled by the time dependent Schrödinger equation. The cases studied include the dissociation of a single HBr adsorbate on flat and corrugated surfaces. A broad specular peak was observed, in addition to diffraction peaks which can be correlated with the corrugation. Moreover, selective adsorption peaks, which can be correlated with the attractive part of the surface potential, have been identified. Systems in which the hydrogenic wave function scatters from several adsorbates were also investigated. It was found that the scattering is dominated by the trapping of the wave function by unstable periodic orbits. The quantization rules of these periodic orbits have been identified, creating a link between the structure of the adsorbates and the asymptotic angular distributions.

I. INTRODUCTION

The evolution of surface science from a qualitative discipline to a quantitative one is closely linked to the introduction of new surface probes. These probes have been instrumental in revealing the structure of the surface as well as dynamical processes occurring at the surface. Surface probes belong to two main categories: (a) microscopic probes in coordinate space; and (b) diffraction probes in reciprocal space, i.e., the Fourier transform of coordinate space. The information gained from these two types of probes is complementary. Probes also differ in the way they sense the surface. The scanning-tunneling microscope (STM), for example, senses the surface via the tunneling current (the manipulator gives the coordinate reading).\textsuperscript{1} Thermal energy atom scattering (TEAS) senses the surface through long- and short-range molecular potentials. The method has become one of the most powerful probes of the structure of solid surfaces, as well as of the structure of adsorbed layers on the surface.\textsuperscript{2-16}

In the present work, a new probe is studied which is similar to TEAS in that the surface is sensed by the molecular potentials, but differs significantly in many other of its aspects. The new approach has been inspired by recent studies of the photodissociation of adsorbed species.\textsuperscript{7-11} In particular, the work by the Polanyi group in which the photodissociation of H\textsubscript{2}S and HBr adsorbed on the LiF(001) surface was investigated.\textsuperscript{17} In order to compare the methods it is appropriate to examine in detail the experimental setup of a typical ideal TEAS diffraction experiment. The apparatus consists of a well-collimated molecular or atomic beam device. Ideally one can consider a monoenergetic beam with a well-defined direction which can be described quantum mechanically as a plane wave with a known initial wave vector \(\mathbf{k}\). Such an assumption, which means a long coherence length, is the reason why this probe is extremely sensitive to long-range forces.\textsuperscript{5,6} Once the beam interacts with the surface, it scatters into a superposition of plane waves. If the surface is periodic, it imposes a selection rule on \(\Delta k_{||}\) which leads to the appearance of well-defined diffraction peaks, at a detector with angular resolution. The monoenergetic property of the initial beam means that, by using a time-of-flight device with angular resolution, the final magnitude and direction of the \(\mathbf{k}\) vector is detected. This information can be used to measure inelastic processes which are not on the original energy shell. The coupling of the probe to the surface phonons is such an example.\textsuperscript{11} The main features of the TEAS method are the use of a monoenergetic probe with a large coherence length, the initiation of the wave function, and the analysis of the results in the asymptotic region.

The experimental probe modeled in this work is based on a long-range coherent wave. It therefore can classi-
fied as a diffraction probe. The difference between this method and TEAS is in the generation of the probing initial state. The basic idea is to create a coherent wave packet at a specific position on the surface. This is accomplished by the photodissociation of a hydrogen-containing molecule at a well-defined frequency; this sets the initial energy of the coherent packet. The ability to preposition the wave packet on the surface, gives some of the advantages of microscopy. The detection scheme resembles that of the TEAS experiment where a time-of-flight angularly resolved detector allows the detection of the final $k$ vector of the wave function in the asymptotic region.

On considering the example of HBr adsorbed on a LiF(001) surface, it was shown, both experimentally and theoretically, that the molecule is adsorbed on the surface with its molecular axis almost parallel to the surface, and with the hydrogen end tilted by 20° towards the surface. Following the photodissociation, the hydrogen fragment is expected to scatter from the surface and may be trapped for a number of consecutive collisions between the substrate and the adsorbate layer. Due to the coherent properties of the wave created, these scattering events can interfere and lead to an asymptotic diffraction pattern which can be correlated to the surface structure. The probe described here has not yet been experimentally employed. The purpose of this work is to derive a theoretical model aimed at gaining insight into the relation between the structure of the surface and the diffraction pattern.

II. THE MODEL

The goal of the present model is to demonstrate the qualitative features of the diffraction photodissociation probe. Complications due to realistic surface features such as surface thermal motion are not considered in this study.

The diffraction experiment can be divided into three parts:

(a) Creation of the probe wave function;
(b) interaction with the surface and other adsorbates;
(c) analysis of the asymptotic wave function. In order to elucidate the relation between the structure of the surface and the experimental data, the dynamical processes will be modeled by using a time-dependent wave packet approach.

A. Creation of the probe wave function

Consider a hydrogen-containing molecule residing on the surface. The experiment is initiated by photodissociation of the hydrogen which creates the initial hydrogenic wave function. The photodissociation can be modeled in the following way: First the ground state $\psi(0)$ of the molecule is calculated. If an infinitely short pulse is applied according to the Franck–Condon principle, there is a transition from the ground state to the excited electronic surface. Due to the repulsive forces on the excited state, the hydrogen atom gains most of the momentum in the direction of the molecular axis, $\alpha$, determines the width of the wave packet, and $N$ is a normalization constant. Recent developments in applying time-dependent wave packet methods to photodissociation processes means that the Gaussian approximation can be replaced by a more accurate wave function, provided that the ground state and excited state potentials are known.

B. Interaction with the surface and with the adsorbates

Once the initial wave function has been created, the influence of the surface and of neighboring adsorbates on the evolution of the state, can be calculated by using the time-dependent Schrödinger equation,

$$i\hbar \frac{\partial \psi(t)}{\partial t} = \hat{H} \psi(t),$$

where the Hamiltonian for the probing hydrogen atom is given by

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + \hat{V}(r, R_s) + \hat{V}(r, R_{ad}),$$

where $r$, $R_s$, and $R_{ad}$ represent the position vectors of the hydrogen atom, the surface atoms, and the adsorbate atoms (including the parent halide atom which is assumed to remain in its initial position).

In the present study the choice of the potential is schematic. It contains the main features of the hydrogen–surface interaction with enough flexibility to change parameters. This allows determination of the connection between the structure and the diffraction results. The hydrogen surface interaction was described by a Morse potential along the surface normal. The three parameters...
Two types of visualization tools were used: (a) a projection action potential was given in terms of a sum of pairwise neighbor adsorbate atoms. These pair potentials were given position along the surface. The hydrogen-adsorbate interaction potential was displayed approximately every 50 fs (1000 a.u.) in 3D. Time step for propagation $\Delta t= 1000$ a.u. in 3D $\Delta t= 5000$ a.u. in 3D

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<td>Hydrogen solid potential</td>
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<tr>
<td>Surface lattice constant</td>
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<td>Adsorbate lattice constant</td>
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<td>parameters</td>
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<td>$u_z = 0$</td>
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<tr>
<td>Grid</td>
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<td>2D grid parameters</td>
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<tr>
<td>$\Delta x = 0.085 9375$ Å</td>
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<tr>
<td>3D grid parameters</td>
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<tr>
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<tr>
<td>$\Delta y = 0.171 875$ Å</td>
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<tr>
<td>$\Delta z = 0.171 875$ Å</td>
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<tr>
<td>Chebychev time propagation</td>
<td></td>
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<tr>
<td>Convergence criteria</td>
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</tr>
<tr>
<td>Time step for propagation</td>
<td>$\Delta t = 1000$ a.u.</td>
</tr>
<tr>
<td>Total number of steps</td>
<td>$N_f = 7$</td>
</tr>
<tr>
<td>C. Analysis of the asymptotic wave function</td>
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The outcome of the scattering event is calculated by solving the time-dependent Schrödinger equation using the Hamiltonian of Eq. (1). This method of solution is based on representing the wave function on an evenly spaced multidimensional grid. The kinetic energy operator is calculated by the Fourier method. The propagation in time is carried out by a Chebychev polynomial expansion of the evolution operator. A detailed description of the method can be found in Ref. 22. This approach has been utilized successfully in the past in the study of light atom scattering from solid and adsorbate covered solid surfaces. To create the outgoing boundary conditions of scattering, an optical potential is used at the end region of the grid. The functional form of the absorbing potential is $V(z) = i\hbar A \exp [i\alpha (z - z_0)]$, where $A = 0.1$ a.u. and $\alpha = 2.0$ Å $^{-1}$. To facilitate this study the asymptotic wave function in momentum space is analyzed. The basic procedure is first to filter out from the wave function the parts of the wave function which are trapped flux and are a signature of long-lived resonances. Whirlpools represent trapped flux and are a signature of long-lived resonances.

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The analysis of the wave function is based on the fact that asymptotically the potential is constant and therefore, by analyzing the asymptotic momentum, a full energy resolution of the wave packet is achieved.26 Due to the linearity of the Schrödinger equation, propagation of a wave function starting from the Franck–Condon region containing a full band of energy components, enables the resolution of individual continuous wave (cw) photodissociation experiments. To facilitate this study the asymptotic wave function in momentum space is analyzed. The basic procedure is first to filter out from the wave function the part adsorbed onto the surface using a smooth filtering function. The functional form of the filter function was $f(z) = \frac{1}{2} + \frac{1}{2} \left[ 1 - e^{-\alpha(z - z_0)} \right]$ , where typically $\alpha = 2–5$ Å $^{-1}$ and $z_0 = 5$ Å. In the next step, the wave function is Fourier transformed into momentum space, which simulates the experiment.
space. The $p_x p_z$ representation is then changed to polar coordinates in momentum space $p_r = \sqrt{2mE}$, which describes the energy, and $\theta$ the scattering angle, $\theta = \tan^{-1}(p_x/p_z)$. A specific energy resolved experiment is described by a constant radius in $k_z$ and $k_x$ momentum plane (the origin at $k_z = 0, k_x = 0$). The asymptotic momentum or velocity picture leads to the identification of $\theta$ as the experimental scattering angle.

FIG. 1. Snapshots of the evolution of the wave function. The absolute value of the wave function is displayed superimposed on the potential. A flat surface is displayed with one adsorbed molecule. The structure at $t=2000$ a.u. is due to interference between the incoming and outgoing wave. Notice also the fast spreading of the wave.
FIG. 2. Snapshot of the flux of the wave function for the same potential as Fig. 1.
FIG. 3. Asymptotic momentum plot ($t=6000$ a.u.) of the scattering event of Fig. 1. Only the part which has escaped the surface potential was analyzed.

Time = 2000 a.u.

FIG. 4. A snapshot of the real part of the wave function impinging on a corrugated surface. Interference between constant phase fronts is clearly seen. Notice also that the wave function covers at least three periods of the potential.

FIG. 5. Asymptotic momentum plot ($t=6000$ a.u.) of the scattering event of Fig. 4. Notice the broad diffraction peaks and the resonance enhanced wide angular distribution.

J. Chem. Phys., Vol. 97, No. 3, 1 August 1992
III. RESULTS

Since the diffraction picture can become very complicated, a step-by-step approach is followed. The most simple arrangement is for one adsorbate molecule on a clean, and flat surface. Figure 1 shows a series of snapshots of the wave function in coordinate space superimposed on the hydrogen surface potential. The sequence of events becomes (a) collision of the wave function with the hard corrugated repulsive part of the potential, (b) partial trapping of the wave function by the attractive part of the potential, and (c) reflection of most of the wave function. This reflection is in a direction which is slightly less than the specular angle, because the initial wave packet is already located in the attractive part of the surface potential. The same sequence of events can be observed in the flux maps of Fig. 2. In particular notice the snapshot at $t=3000$ a.u. where the motion of the wave packet close to the surface has a parallel direction, whereas the part which escapes the surface has the specular direction. One should also notice how widely the initially concentrated wave packet spreads out after it collides with the surface. This means that a coherent packet with a correlation length of 3 to 4 Å interacts simultaneously with the surface. The creation of a spatially broad wave function is a key factor in the ability of the hydrogenic wave function to probe the surface. The spatial extent of the wave function $\delta X$ can be estimated by assuming that after the photodissociation the initially bound compact wave function moves under the influence of a constant potential leading to

$$\delta X(t) \approx \frac{\hbar t}{\Delta X_g \mu},$$

where $\Delta X_g$ is the initial width of the hydrogen wave function in the ground state prior to the photodissociation, and $\mu$ the reduced mass. From this estimate it becomes apparent why hydrogen due to its light mass is the optimal photodissociation probe and that a tightly bound molecule is the hydrogen source. For example, in HBr $\Delta X_g \approx 0.18$ a.u. which gives a spreading rate of $1.5$ Å for 1000 a.u. of time.

Turning to the asymptotic analysis, Fig. 3 is a plot of the wave function in momentum space at $t=6000$ a.u. The main feature is a broad peak, which is the expected specular scattering. Closer inspection shows a feature with a wide angular distribution and a narrow radial distribution. This feature is the result of trapping by a resonance state of the attractive part of the surface potential. Notice that the energy spread of this feature is shifted to higher energy than the mean energy of the original packet and also that the energy spread of this feature is small. This indicates that the surface resonance can be identified by the broad angular distribution obtained for a particular photodissociation frequency. The feature is sensitively dependent on the well depth of the attractive part of the surface poten-
FIG. 8. The flux map at $t=3000$ a.u. for a system composed of two adsorbates positioned such that one adsorbate serves as the target for the wave function created by the other.

FIG. 9. (a) Asymptotic momentum plot for a system composed of two adsorbates of Fig. 8. (b) A close-up view of the Fraunhofer peaks close to the main specular peak.
Deepening the well causes the specular peak to split in the z direction, a manifestation of the enhanced trapping by creating new resonance states.

The next step is to examine the effect of surface corrugation. Figure 4 shows the real part of the wave function at $t=2000$ a.u., which displays the emergence of an interference pattern that will lead eventually to the appearance of diffraction peaks (see Fig. 5). Comparing Fig. 5 to Fig. 3 broad diffraction peaks are seen to appear where surface corrugation is present. The diffraction peaks in this case are much broader than in a typical TEAS experiment due to the momentum spread in the initial wave packet. To simulate a cw radiation experiment, Fig. 6 shows an energy-resolved angular plot. The diffraction peaks are separated by approximately: $\Delta \theta = \Delta k_z/(2mE)^{1/2} \cos \theta$, where $\Delta k_z$ is the reciprocal lattice vector imposing the selection rule on momentum transfer for a periodic potential. At this step one can identify second order effects of superposition of diffraction and surface resonances. To summarize, selective adsorption induces a pattern in the z direction in momentum space, while diffraction induces a pattern in the x direction. Both features are subject to the constraint of the conservation of energy.

Once the interaction of an isolated photodissociation source with the surface is understood, the scattering of the hydrogenic wave function from several adsorbates on the surface can be considered. The simplest of such cases involves two adsorbate molecules where one acts as the source of the hydrogenic wave function and the other causes a local scattering center. It is clear that the relative position of these two adsorbed molecules will determine the results. In the case of two adjacent adsorbates, the initial motion of the wave packet is away from the source, and therefore, the influence of the adjacent molecule is small. This can be seen by comparing Fig. 7 with Fig. 3. (For the parameters used in the present study see Table I).

A very different story emerges if the second adsorbate is located at a position in which it acts as an obstacle to the outgoing wave function. Figure 8 shows the flux of the hydrogenic wave function as it collides with the second adsorbate molecule. Notice the “shadow” cast by the adsorbate downstream from the source. The flux arrows also indicate an enhancement of back scattering. Another feature is a Fraunhofer-type scattering caused by the interference of the direct wave and the part scattered from the obstacle. Figure 9 shows the asymptotic filtered momentum plot. The enhanced backscattering is clearly visible. Close examination of the main specular peak [Fig. 9(b)] shows a series of Fraunhofer peaks. They can be more clearly seen in the energy-resolved angular plots (see Fig. 10).

In trying to interpret the broad angular feature in the scattering, a clue is obtained from the single adsorbate scattering where this feature was attributed to trapping caused by the attractive part of the surface potential. When there is a second adsorbate, another mechanism for trapping the wave function is present. This trapping can be attributed to the unstable periodic orbit trapped between the surface and the adsorbate. Semiclassically, this periodic orbit can be quantized leading to a series of equally spaced peaks in the z direction of momentum spaced by approximately $\Delta k_z = \pi/L$, where $L$ is the distance between the adsorbate and the surface. Figure 11 compares two contour plots of the asymptotic momentum for a two adsorbate configuration, differing only in the distance of the adsorbate from the surface. A series of parallel peaks in the Z direction representing the quantization of the unstable periodic orbit, are clearly visible. The distance between these peaks in momentum space is inversely proportional to the distance between the adsorbed particle and the surface. Experimentally, this phenomenon can be identified in a low coverage situation where pairs of adsorbates are relatively rare. This is done by examining the backscattering direc-
Fig. 12. Snapshots of the flux map of a photodissociation event on a full adsorbed layer on a flat surface. The source of the hydrogenic wave function is from the adsorbed atom on the far right.

The next step is to consider a fully covered surface. Because the hydrogenic wave function is initially planted below the top layer of adsorbates, it becomes partially trapped and therefore the amplitude of the specular peak is reduced or even eliminated. This is demonstrated in the flux map of Fig. 12. Due to collisions with the adsorbed layer, the hydrogenic wave function fills the gap between the adsorbed layer and the surface. A useful image is that of a liquid filling all available cracks. The analogy becomes even more appropriate when it is noticed that the flux increases whenever the wave function is squeezed through a narrow passage. Figure 13 displays the absolute value of
the fully developed wave function. It seems hopeless to find any rational pattern out of such a convoluted wave function. This appearance is consistent with a classical picture where the negative curvature of the potentials leads to chaotic dynamics.27

As a start in sorting out an apparently meaningless pattern, one again resorts to identifying the unstable periodic orbits. The periodic orbit already identified which runs from the surface to the adsorbate, remains active. Examination of the asymptotic wave function in momentum space (Fig. 14) enables one to identify the quantization of this periodic orbit in the perpendicular direction similar to the quantization found in Fig. 11. It is easier to identify such a feature in the backscattering direction because the complications due to the direct scattering are eliminated (feature A in Fig. 14). Next, due to the existence of additional adsorbates, another unstable periodic orbit can be identified running parallel to the surface from one adsorbate to the other. This periodic orbit is quantized parallel to the surface, and it can be identified in the low-angle backscattering direction as it causes a checkerboard effect due to interference with the perpendicular periodic orbit (feature B in Fig. 14). Note that these two unstable periodic orbits do not exhaust the possibilities. A triangular-shaped unstable periodic orbit should also capture enough amplitude to be observed. In fact such a phenomena can be observed in Fig. 14 (feature labeled C). Further analysis can identify higher order periodic orbits, but due to their smaller $\Delta k$ quantization, it becomes more difficult to do so.

The analysis so far has neglected the periodic structure of the adsorbate overlayer. Due to the overall coherence of the hydrogenic wave function, the individual local scattering centers interfere with each other creating a modulation on the observed diffraction structure. This effect can be seen in Fig. 14 as a long-range modulation superimposed on the finer details of the individual periodic orbit scattering centers. The most prominent feature of this modulation is the hole in the angular distribution in the perpendicular scattering direction (this is even more pronounced in the upper panel of Fig. 14 or Fig. 15 where the underlying surface is corrugated). This feature is the result of destructive interference in the perpendicular direction. For the two adsorbate case a minimum in the angular distribution is found in the surface normal direction. This minimum can be traced to destructive interference coming from an amplitude running from the two sides of the adsorbate (examine Fig. 10). When a full layer of adsorbates is present (lower panel of Fig. 15) such an effect is enhanced and leads to a large hole in the angular distribution (see Fig. 16). The hole is a fingerprint of the trapping of the hydrogenic wave function and therefore can be used to differentiate the direct scattering from the resonance dominated one.

IV. DISCUSSION AND SUMMARY

In this work a new probe of solid surface structure has been considered, based on the photodissociation of
hydrogen-bearing adsorbates. The ability of the hydrogenic
wave function to probe the surface depends crucially on
the direction which the photodissociation process imposes
on the hydrogen and the fast spreading of the initial com-
pact wave function. The direct collision of the hydrogenic
wave function with the surface, leads to relatively poor
structural information because the initial wave function is
spread both in coordinate space as well as in momentum
space and eventually blurs the outcome. For example, dif-
fraction peaks resulting from the corrugation of the surface
are observed, but they are broader than the sharp peaks of
the TEAS experiment. More resolved structural informa-
tion is obtained when the hydrogenic wave function be-
comes trapped under or between the adsorbed layer. The
resonance states resulting from this trapping are strongly
influenced by fine details of the interaction potential, there-
fore yielding structural information. For example, the se-
lective absorption resonance (Figs. 3 and 5) reveals details
of the attractive part of the surface potential. The trapping
by a single adsorbate reveals details about the surface ad-
sorbate distance and also can be analyzed to obtain the size
of the adsorbate (Fig. 9). Trapping by islands of adsor-
bates or from a full overlayer can reveal the distance be-
tween them and other structural information (Figs. 14 and
16). All this information depends on the ability to interpet
or model the asymptotic angular distribution. We find that
it is much easier to interpret a full two-dimensional asymp-
totic momentum plot, than a single energy-resolved angu-
lar plot. Experimentally, such a picture can be recon-
structed from a series of angular plots where the pho-
todissociation frequency is varied.

The purpose of this work has been to supply a quali-
tative understanding of a photodissociation structural
probe. In order to derive a basis for interpretation simpli-
fied models were studied. The validity of the assumptions
on which the structural information is obtained has yet to

FIG. 15. (a) Upper panel: contour plot of the asymptotic momentum for
a full layer of adsorbed molecules on a flat surface. The size of the scat-
tering adsorbates is half the size of the ones shown in Fig. 14. Note the
emergence of a split specular peak and the very well resolved diffraction
peaks in the backscattering direction. (b) Lower panel: contour plot of
the asymptotic momentum for a full layer of adsorbed molecules on a
corrugated surface. Notice that the corrugation induces a larger fraction
of trapped wave function so that a clear diffraction picture is seen also in
the forward direction.

FIG. 14. Contour plot of the asymptotic momentum for a full layer of
adsorbed molecules on a flat surface. The lower panel is the flux map at
t=2000 a.u. superimposed on a contour map of the potential. The three
types of unstable periodic orbits are plotted and three quantization vec-
tors Δk are indicated in the momentum plot.

FIG. 16. Energy-resolved angular plot corresponding to the same scat-
tering event of the upper panel of Fig. 15. The solid curve shows the
amplitude at a photon energy of 1.5 eV, and the dashed curve corresponds
to an excess energy of 1.2 eV. Notice the minimum in the normal direc-
tion.
be critically examined from a more quantitative standpoint.

The model study raises several questions. First, would the above arguments hold if the simplified potentials employed in this study were replaced by more realistic potentials, and a more rigorous treatment of the photodissociation process which creates the initial hydrogenic wave function? Work in this direction is in progress\textsuperscript{28} and preliminary results show that many of the features described in this study are present.

Second, can the two dimensional model considered here be sustained in the real, three-dimensional world? To answer this question, three-dimensional calculations have been carried out on models similar to the ones considered above. Figure 17 display three cuts in the asymptotic momentum distribution for a case of two adsorbates similar to the 2D case shown in Fig. 8. Figure 17(a) shows the $xz$ cut in the momentum distribution the main feature is the specular peak. A lower level of contours would reveal the expected $z$ direction quantization in the backscattering. This quantization crucial for structure determination is much more pronounced in the sideways scattering [Fig. 17(b) showing the $zy$ cut]. Experimentally detection in the direction perpendicular to the initial molecular axis is preferable since this direction is well defined in relation to the polarization of the incident light. Figure 18 shows that structural information can also be obtained by identifying the quantization directions from a surface fully covered by an...
overlayer of adsorbates. A full 3D analysis is currently under investigation, but these results are enough to state that the main qualitative features which constitute the probing ability still persists or even enhanced in the 3D world.

Third, how important are inelastic processes where the hydrogen excites vibrational modes or surface phonons? By analogy with the TEAS experiment, due to its light mass, the hydrogen does not interact strongly with the vibrational modes. This means that the hydrogen-phonon interaction can be treated by a perturbation expansion, using the results presented here as the zero-order base. If the experiment is performed with a sufficiently accurate time-of-flight analyzer, inelastic effects can be measured which reveal information on the adsorbate surface vibration and surface phonons. The modeling methods described here should be modified to include the additional degrees of freedom. A time-dependent self-consistent field (TDSCF) approach seems appropriate. The treatment of such phenomena is beyond the scope of this paper, but the conclusion should be that the elastic scattering component can be analyzed independently in a manner similar to the one above.

Finally to conclude, one can compare the surface structural probe presented here to the thermal energy atom scattering TEAS probe. It has been shown that both methods strongly depend on the coherence of the initial wave function. Since in the TEAS experiment the initial momen-
turn is much better defined, it is a superior method for obtaining the global periodic structure of the solid. The advantage of the photodissociation probe is in its local application where the hydrogenic wave function is trapped in a local structure. In such a case, it yields high-quality information on the local structure itself. This means that the two methods compliment one another.

ACKNOWLEDGMENTS

We wish to thank Professor J. C. Polanyi for helpful discussions. The research was partially supported by a grant from the Israel Atomic Energy Commission. Computations were carried out on the Convex C-220 of the Hebrew University Jerusalem. The Fritz Haber Research Center for Molecular Dynamics is supported by the Minerva Gesellschaft für die Forschung, GmbH München, Federal Republic of Germany.