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Evidence for coupled rotational and phonon quantum excitation in the scattering of a nearly monoenergetic HD beam from the Ni(001) surface

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Angular distributions and time-of-flight spectra of a nearly monoenergetic ($\Delta v/v \cong 2\%$ FWHM) He seeded HD beam ($k_i = 6.80 \, \text{Å}^{-1}$, $E_i = 32 \, \text{meV}$) have been measured after scattering from a Ni(001) single-crystal surface along the $\langle 100 \rangle$ azimuth. The most intense peaks in the angular distributions are attributed to diffraction with rotational excitation while the rotationally elastic diffraction peaks are an order of magnitude smaller. All the time-of-flight distributions reveal intense peaks at $\Delta E = -11.06 \, \text{meV}$ corresponding to the HD rotational transition $j_i = 0 \rightarrow j_f = 1$. The rotational energy loss observed at angles between the diffraction peaks is attributed to incoherent inelastic scattering at defects. The other inelastic peaks in the time-of-flight spectra can be assigned to phonons which are created or annihilated in the rotationally inelastic collisions. The measured phonon dispersion curves suggest a predominant interaction with the transverse bulk edge and not with the Rayleigh mode. These results provide the first direct evidence for a coupling of rotational transitions to the phonons of a metal surface. The pronounced rotational inelasticity at step edges does not support the widely held view that nonactivated chemisorption occurs at step edges.

I. INTRODUCTION

The detailed molecular mechanism by which molecules stick on colliding with a neutral metal surface is still not well understood.[1] The hydrogen molecule, and its isotopic variants, as the simplest of all molecules, has been the subject of intensive experimental and theoretical efforts.[2] Most of the recent H_2 molecular-beam surface scattering experiments have concentrated on the low-index single-crystal surfaces of Cu (Refs. 3–6) and Ni (Refs. 7–11) although scattering experiments have also been reported for Ag,[6,12–14] Pt,[15,16] and Au.[6] One of the first scattering investigations of H_2 interactions was carried out by Balooch *et al.*,[17] who in 1974 measured the initial sticking coefficient for H_2 on Cu(001), (110), and (310) single crystals. Their results indicated an activation barrier for chemisorption which varied between 90 and 200 meV over the surface unit cell. Lapujoulade and co-workers were the first to carry out extensive experiments on the diffraction of H_2 from Cu(001), Cu(110), Cu(115), and other periodically stepped Cu surfaces.[3–5] Only a very weak additional diffraction peak for the $j = 0 \rightarrow 2$ rotational transition of H_2 was observed. The first measurements of HD angular distributions which were made by Cowin *et al.* on Pt(111) in 1981,[15] revealed intense peaks due to coherent rotational excitation. These experiments also provided the first evidence for rotationally mediated selective adsorption resonances. This has since been confirmed in several studies on Cu,[6] Ag,[12,6] and Au (Ref. 6) single-crystal surfaces. Selective adsorption resonances in the specular scattering of H_2 and D_2 have provided information on the bound states and the potential well depth of the physisorption potential in

scattering from Ag(111) (Ref. 18) and Ag(110) (Ref. 19). In an investigation of the sticking of HD on W(001), Rettner *et al.*[20] were unable to observe a correlation between rotationally mediated selective adsorption resonances and the probability of sticking. In recent years Andersson and co-workers have carried out an extensive study of the physisorption of low-energy molecular beams of H_2 and D_2 on the cold 10 K Cu(001) surface.[21,22] Their experimental results now appear to be explained by both a distorted-wave Born approximation (DWBA),[23,24] as well as by a forced harmonic-oscillator model[25,26] calculation which accounts not only for single-phonon but also multiphonon excitation. In the theory the molecular rotational degree of freedom enters in only via rotationally mediated resonances which are observed to lead to enhanced physisorption.

Sticking coefficients for H_2 on the (001), (110), and (111) faces of nickel have been measured by Robota *et al.*[7] Hamza and Madix,[8] Hayward and Taylor[9] and Rendulic, Winkler, and Karner.[10] The results, with some differences from one group to another, indicate a strong dependence on the crystal face, with the initial sticking coefficient being about 0.1 for (001),[27] even smaller for (111), and nearly 1.0 for the (110) surface. Robota *et al.*,[7] Hamza and Madix,[8] and Hayward and Taylor[11] also measured angular distributions of H_2 and D_2 from Ni surfaces. Whereas Hamza and Madix only observed a broad (FWHM = 43°) specular peak for Ni(001) at $E_i = 36 \, \text{meV}$, Robota *et al.* found a number of diffraction peaks in scattering from Ni(110) along the $\langle 100 \rangle$ direction (perpendicular to the rows of surface atoms), but were unable to observe resolved diffraction peaks from the Ni(111) surface. These were observed by Hayward and Taylor[11] for D_2 beams scattered along the $\langle 112 \rangle$ direction and were found to be an order of magnitude greater than for He scattering, in agreement with earlier observations for Ag(111).[28,29] One of the results from Robota

et al. which is of interest for our work is the observation of a greater inelastic coupling to the surface heat bath for D_2 than for H_2. This was interpreted as evidence that energy exchange with the surface is dominated by phonon rather than electron-hole-pair excitations of the solid.

More detailed and better resolved H_2 and D_2 scattering experiments are available from the alkali-halidate surfaces.[30-34] As opposed to the metals, large rotational inelastic diffraction peaks are found for the spherical molecules H_2 and D_2. This has been attributed to the shorter range of the repulsive potentials compared to the metals. Only a few time-of-flight studies have been reported. Whereas Brusdeylins and Toennies[34] were only able to observe the energy losses due to rotational transitions for n-D_2 scattered from NaF at the corresponding diffraction maxima, Allison and Feuerbacher,[33] who scattered H_2 and D_2 from LiF, observed single-phonon energy-loss peaks which were found to lie on dispersion curves for single phonons coupled with rotational transitions. For these coupled inelastic processes they observed a strong propensity for a decrease in the parallel surface wave vector for phonon creation and an increase in parallel surface wave vector for phonon annihilation [for sign conventions see Eqs. (1) and (2)]. Recent experiments on heavier molecules, where multiphonon events dominate, also reveal effects that definitely indicate the importance of dissipative interactions with phonons.[35-37]

The relative paucity of experimental scattering studies with H_2 and isotopic variants may seem surprising when compared with the vast literature on the high-resolution inelastic scattering of He from metal surfaces.[38] For one the speed ratios are less than for He nozzle beams. The highest reported speed ratio[39] for H_2 is $S = 85$,[40] while pure D_2 beams have rather broader velocity distributions corresponding to a speed ratio of about 33 ($T_0 = 80$ K, $P_0 d = 30$ Torr cm).[41] Detection of H_2 is especially difficult because of the large residual gas background in the mass spectrometer detector at the H_2 mass; this is not a problem with HD and D_2, however.

Because of their broad implications for understanding the fundamental processes of physisorption and chemisorption the results of hydrogen scattering from metals have stimulated considerable theoretical work.[42-46] In virtually all of the model calculations the surface has been assumed to be rigid, and although the number of detailed quantum-mechanical calculations is, in fact, quite limited, generally good agreement has been achieved. As far as we are aware there is only one rather early theory which attempts to account for both rotational and phonon excitation.[47] Whereas it is now well recognized that defects play a very important role in surface reactions,[2,48] there is so far only one calculation which has considered the dynamics of the scattering of molecules from single defects.[49]

In the present paper we present experimental evidence that the phonon inelastic scattering process is coupled to the process of rotational excitation and can lead to a significant additional loss in the translational energy of the scattered molecule. Moreover, the results indicate that rotational excitation also occurs with a high probability in incoherent scattering from single steps randomly distributed on the surface.

We chose the system HD/Ni(001) for the following reasons. Whereas for H_2 and D_2 additional diffraction peaks resulting from rotational excitation are very weak, they are very large for HD.[15,12,6] Moreover, HD is easier to detect with a mass spectrometer because of the much lower naturally occurring background. The (001) face was chosen since the surface phonon dispersion curves have been extensively studied by inelastic helium-atom scattering[50,51] and inelastic electron scattering electron-energy-loss spectroscopy (EELS).[52] In addition, the sticking coefficient is sufficiently low at slightly elevated temperatures that a significant scattered intensity can be expected.[7]

This article starts with a brief description of the experimental method. The measured angular distributions and time-of-flight distributions for HD scattering are presented and compared with results for He in the next section. The phonon dispersion curves measured with HD are also compared with those measured with He scattering. The paper closes with a discussion of the differences of HD and He scattering and the implications of the present experiments for mechanisms of chemisorption.

II. EXPERIMENTAL METHOD

The apparatus is the same as that described in detail elsewhere.[35,46] The molecular beam was produced in a high-pressure free-jet expansion nozzle source, then modulated by a rotating disk chopper for time-of-flight measurements before passing into a UHV scattering chamber. The Ni(001) crystal was prepared as described in Ref. 50 and analyzed *in situ* with a cylindrical mirror Auger analyzer. Most of the measurements were made with the angle between incident and scattered beams fixed at $\theta_{SD} = 90°$. For a given incident angle θ_i the final angle θ_f is given by $\theta_f = \theta_{SD} - \theta_i$, where both angles are measured with respect to the surface normal. The energy transfer is determined from the difference in incident and scattered beam energy in the time-of-flight spectra

$$\Delta E = \frac{\hbar^2}{2m_{HD}}(k_f^2 - k_i^2). \qquad (1)$$

The phonon wave vector can then be determined from conservation of momentum in the sagittal plane

$$\Delta K = k_f \sin \theta_f - k_i \sin \theta_i. \qquad (2)$$

The major experimental problem was the preparation of an intense monochromatic HD beam. A pure HD beam would not only be technically difficult to produce or expensive to buy, but would also not have a sufficient speed ratio for high-resolution energy-loss experiments. Instead, the HD was produced by passing a mixture of equal parts of H_2 and D_2 over a magnesium catalyst yielding a mixture with 50% HD.[12] To guarantee high-speed ratios the mixture was first diluted by a large excess of He, with the $H_2 + D_2$ mixture constituting between 5% and 15% of the total. With a 5% mixture at a stagnation source pressure of $P_0 = 175$ bars (nozzle diameter $= 10$ μm) and $T_0 = 150$ K the HD beam had an energy of typically 32 meV ($k_i = 6.78$ Å^{-1}) and a half width of 1.2 meV corresponding to a speed ratio of about $S = 83$. Under these conditions we expect the HD molecules to accommodate to the local translational temperature at the

freezing point of the expansion which is expected to be near-
ly the same as in a pure He beam. From the measured speed
ratio we estimate $T_{trans} = 5 \times 10^{-2}$ K ($T_0 = 150$ K). The
rotational temperature is expected to be somewhat larger. If
we assume as an upper limit $T_{rot} = 1$ K, then more than
99% of the molecules are expected to be in the $j = 0$ state.
This is consistent with the failure to see a Bragg diffraction
peak for the $j = 1 \rightarrow 0$ transition as observed previously for a
H_2, HD, D_2 mixed gas beam without He.[6] With the 5%
mixture the actual intensity of HD was about a factor of 60
smaller than for He scattering.

The Ni(001) crystal was cleaned by repeated sputter
and anneal cycles.[50,51] The main contamination carbon was
found to be less than 1% of a monolayer as measured by the
cylindrical mirror Auger analyzer. To prevent hydrogen ad-
sorption during exposure to the HD beam, the crystal was
heated to 390 K. According to the thermal desorption spec-
troscopy measurements of Christmann[27] virtually all hydro-
gen has desorbed at this temperature.

III. EXPERIMENTAL RESULTS

Figure 1 compares angular distributions along the
⟨100⟩ azimuth measured with a cold ($T_s = 150$ K) and a
warm ($T_s = 390$ K) crystal. Because of the large sticking
coefficient for H_2 and its isotopes on Ni(001) the former
surface is expected to be covered by a (1×1) H (D) over-
layer. As has been shown elsewhere the effect of the (1×1)
H layer in He scattering is to enhance the intensity of the
Bragg peaks in the ⟨110⟩ azimuth.[51,53] However, along the
⟨100⟩ direction no significant change was observed.[51] As
seen from a comparison of peaks of Figs. 1(a) and 1(b) there
is also little change with HD scattering. The diffraction
peaks in Fig. 1 were identified using Eqs. (1) and (2) and
setting ΔE equal to the known rotational energy-level differ-
ences for HD [$\Delta E(j = 0 \rightarrow 1) = 11.06$ meV; $\Delta E(j = 0 \rightarrow 2)$
$= 31.11$ meV and $\Delta E = (j = 0 \rightarrow 3) = 66.00$ meV] and ΔK
equal to the reciprocal-lattice vectors nG_{11} ($G_{11} = 3.56$
$Å^{-1}$). As observed previously for Cu(111), Ag(111),
Au(111),[6,12] and Pt(111),[15] the rotationally inelastic
$j = 0 \rightarrow 1$ specular ($n = 0$) peak is nearly an order of magni-
tude larger than the elastic specular peak. Next in intensity
are the first-order diffraction peaks ($n = 1$) for rotationally
inelastic ($j = 0 \rightarrow 1$) scattering which amount to about
1×10^{-2} of the inelastic specular peak. The ratio of the rota-
tionally elastic $n = 1$ diffraction peak intensities to the corre-
sponding specular peak is about the same. The first-order
diffraction peaks measured with He on the same clean sur-
face at a slightly higher $k_i = 9$ $Å^{-1}$ are about 2×10^{-4} as
intense as the specular peak.[51] At $k_i = 11$ $Å^{-1}$ somewhat
larger diffraction intensities have been reported[53] and ana-
lyzed in terms of a hard-wall potential with a maximum cor-
rugation amplitude of 0.015 Å. The factor 30 greater diffrac-
tion intensities, measured with HD, can be interpreted via
the Eikonal approximation[54] to indicate that the corrugation
amplitude is a factor of 5–6 larger than with He atoms. A
similar enhanced corrugation, observed previously for
Ag(111) (Refs. 28 and 29) and Ni(111),[41] has been attrib-
uted to the greater potential-well depths and resulting in-
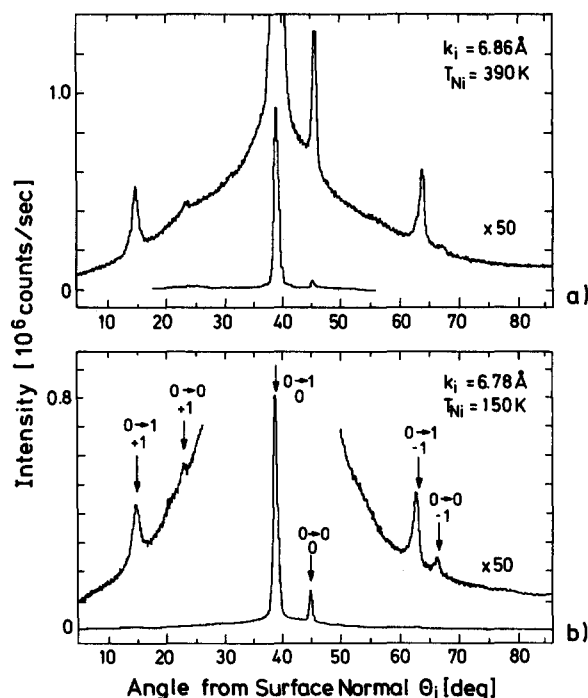creased collision energy for HD compared to He.[55] The po-

FIG. 1. Angular distributions measured for the scattering of HD ($k_i = 6.8$
$Å^{-1}$, $E_i = 32$ meV) from Ni(001) along the ⟨100⟩ direction with the sur-
face at $T_s = 390$ K (a) and at 150 K (b). In (a) the surface is clean while in
(b) it is covered with a 1×1 H adatom layer. The arrows mark the expected
locations of diffraction peaks of order n with and without rotational inelas-
tic transitions $j_i \rightarrow j_f$.

tential-well depths for He–Ni(001) and H_2–Ni(001) have
not to our knowledge been measured. The well depth for He–
Cu has been determined to be about 6 meV,[4,56] while the well
depth for H_2–Cu is now thought to be 31 meV.[57] Similar
values are expected for the potentials on Ni surfaces, and in
one recent study a value of 25 meV has been estimated from
D_2–Ni(111) diffraction intensities.[12]

Returning to Fig. 1 it is interesting to observe that the
relative size of the rotationally elastic and inelastic peaks is
about the same for the $n = -1$, 0, and $+1$ diffraction
peaks. This lack of a strong coupling between the probabili-
ties of diffraction and rotationally inelastic processes has
been predicted theoretically.[58] Moreover, in Fig. 1 it is seen
that the angular distributions for the hot and cold hydrogen-
covered surfaces are nearly the same. Previously, no signifi-
cant differences were found for the phonon dispersion curves
and intensities for the two surfaces.[50,51]

Finally, we observe that the intensity between the dif-
fraction peaks is centered with respect to the inelastic
$j = 0 \rightarrow 1$ peak and not with respect to the elastic specular
peak as is usually the case for He scattering. This shift away
from 45° to smaller angles in the incoherent elastic and co-
herent inelastic phonon intensities, which contribute to this
residual intensity, corresponds to an overall shift in the in-
elastic scattering to larger energy transfers. This is support-
ed by the time-of-flight spectra to be discussed next.

Figure 2 shows a comparison of measured time-of-flight spectra transformed to an energy-loss scale for the scattering of HD and He from Ni(001) at $T_s = 150$ K. The two sets of results were obtained with the same incident beam by simply switching the mass spectrometer from the HD mass setting to the He mass setting. Since the two components in the incident beam both have the same velocities the incident wave vector and energies of the HD beam are smaller by the ratio of the masses. The kinematic scan curves, shown in the insets of the corresponding frames which connect all possible observable events in the ΔE and ΔK spaces for a given set of incident and final scattering angles, are consequently different for the two sets of measurements. The previously measured Ni(001) Rayleigh phonon dispersion curves are also plotted in the inserts, both with respect to the usual origin $\Delta K = 0$, $\Delta E = 0$, but also with respect to the rotationally inelastic specular peak at $\Delta K = 0$ and $\Delta E = -\Delta E_{rot} (0 \to 1)$. The additional horizontal line at $-\Delta E_{rot} (0 \to 1)$ shows the dispersionless rotational energy losses expected for incoherent rotational excitation.

In both of the HD spectra in Fig. 2 the inelasticity is dominated by a loss peak at 11 ± 0.5 meV in good agreement with the energy loss expected for the $j = 0 \to 1$ transition. The elastic peaks at $\Delta E = 0$ seen in all four spectra are attributed to incoherent scattering from defects.[59] The elastic peak is considerably smaller for HD than for He, whereas the rotationally inelastic peak has nearly the same intensity as the elastic peak measured with He. On the other hand, the intensity of the additional inelastic peaks attributed to single-phonon creation are nearly the same in the corresponding He and HD spectra. The strikingly different energies of the HD phonons compared to those measured with He can be understood from the scan curves. Whereas the He phonons can be assigned to the dispersion curve originating at $\Delta K = 0$, $\Delta E = 0$, the HD phonons are explained by dispersion curves originating at $\Delta K = 0$, $\Delta E = -\Delta E_{rot} (0 \to 1)$.

To study further the origin of the HD phonon peaks a series of time-of-flight spectra were measured at $k_i = 6.80$ Å^{-1} for the clean crystal which was maintained at 390 K. The spectra shown in Fig. 3 start from $\theta_i = 60°$ and extend up to $\theta_i = 30°$. The spectra from 45° to 32° are compared with a series of He time-of-flight spectra shown on the right-hand side, taken under similar conditions. The corresponding HD kinematic scan curves for the scattering conditions of Fig. 3 are shown in Fig. 4. As in Fig. 2 the phonon peaks in both Figs. 3 and 4 are marked by solid circles and the dispersionless $\Delta E = 0$ and $\Delta E_{rot} (0 \to 1)$ peaks are designated by open circles. In all the HD spectra in Fig. 3 the rotationally inelastic peak at -11 meV is the predominant feature. The intensity of this peak has its maximum at $\theta_i = 39°$ corresponding to the rotationally inelastic specular peak in Fig. 1. From the HD spectra in Fig. 3 and the kinematic scan curves of Fig. 4 it becomes clear that almost all the other inelastic features can be attributed to the annihilation or creation of single phonons with a dispersion curve originating at the rotationally inelastic specular peak and not at the elastic specular peak. Beyond the rotationally elastic specular peak at $\theta_i > 45°$ no pronounced inelastic peaks are seen. In both of the spectra of $\theta_i = 50°$ and 48° there are broad shoulders at
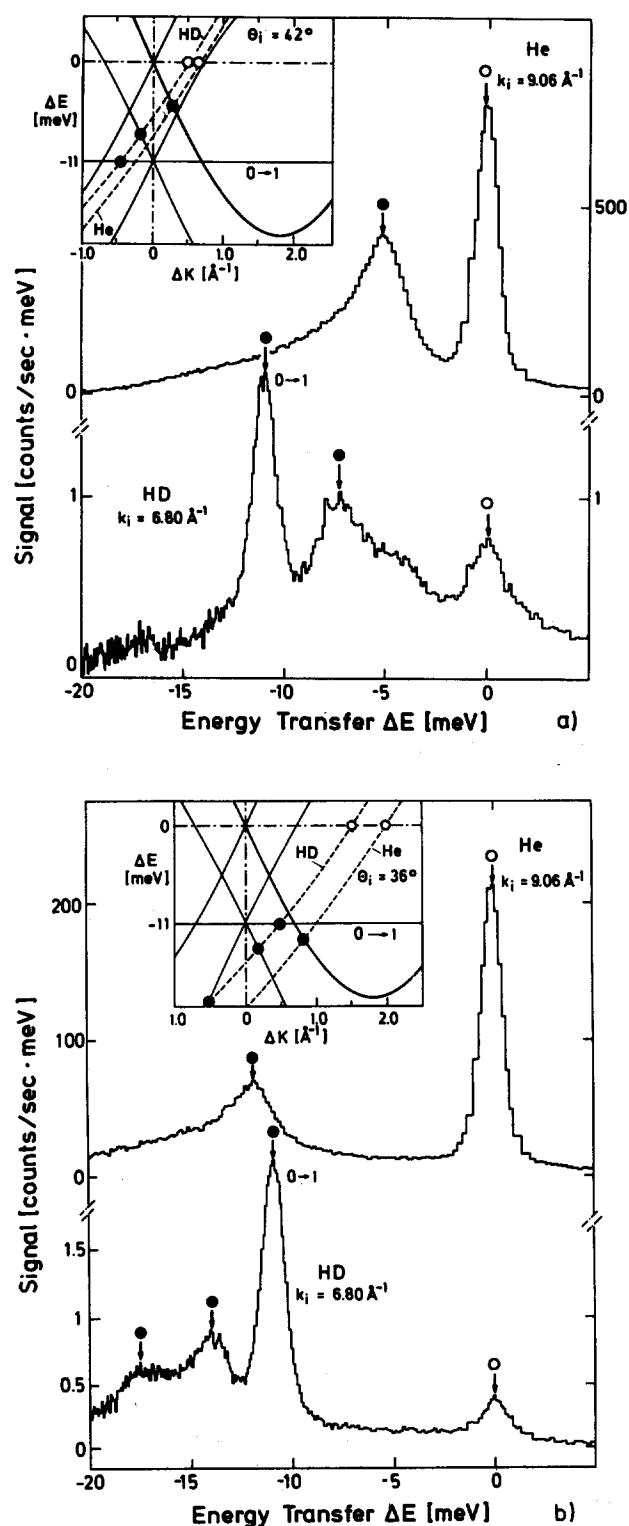

FIG. 2. Two comparisons of measured time-of-flight spectra (which have been converted to an energy-loss abscissa) measured with HD and He at $\theta_i = 42°$ (a) and at $\theta_i = 36°$ (b) along the $\langle 100 \rangle$ azimuth for the hydrogen covered surface ($T_s = 150$ K). The source conditions were the same in both sets of measurements and only the mass spectrometer was switched between the HD and He masses. Since the velocity slip in the nozzle beam expansion is expected to be negligibly small both beams have the same velocities, but because of their different masses different wave vectors of 6.80 Å^{-1} ($E_i = 32$ meV) and 9.06 Å^{-1} ($E_i = 42.9$ meV) for HD and He, respectively. The scan curves in the insets show the kinematic conditions of the measurements and provide for an assignment of the energies and wave vectors of the observed features.
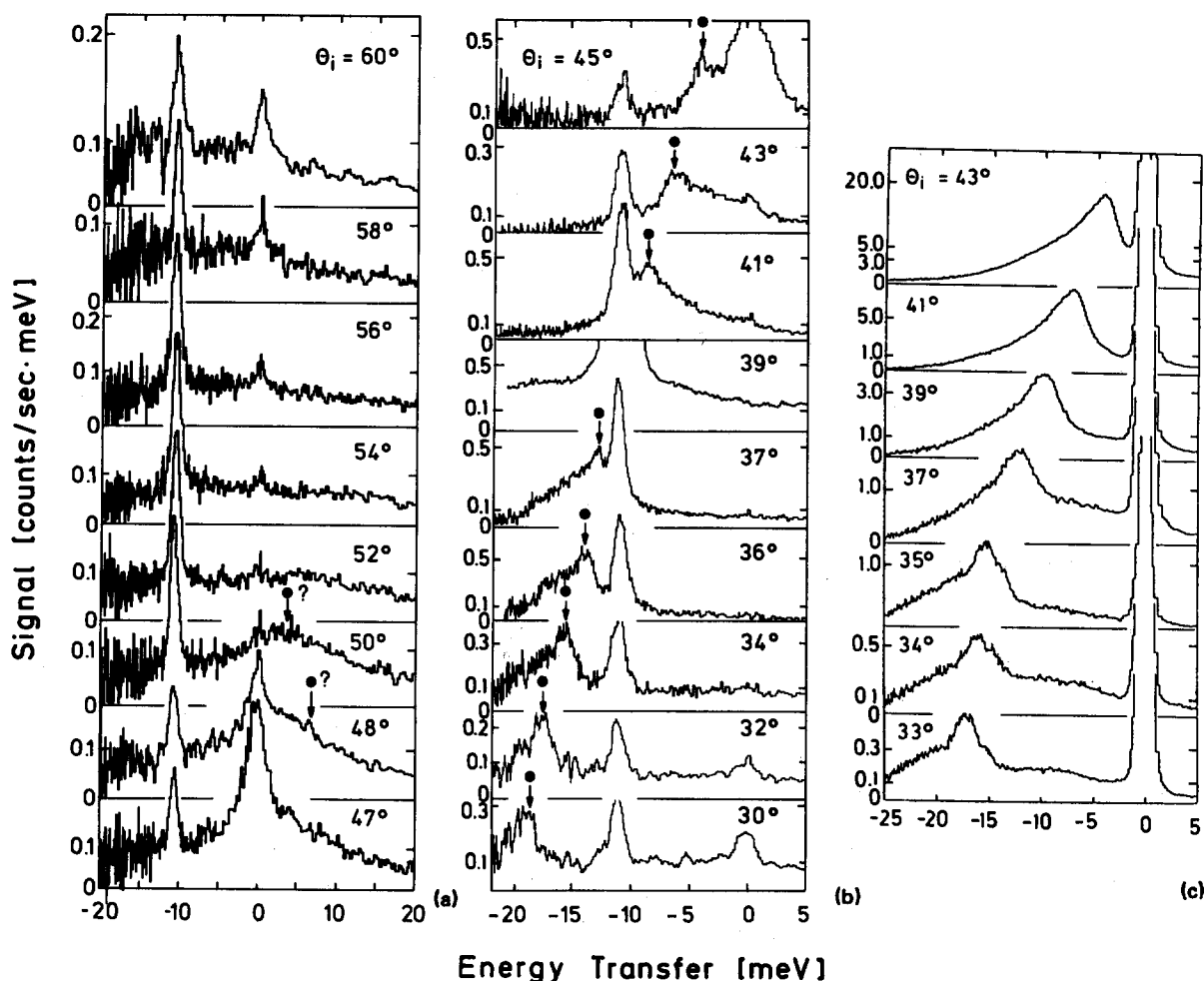
FIG. 3. Time-of-flight spectra converted to an energy transfer scale for scattering of HD from the clean surface of Ni(001) (surface temperature = 390 K) along the ⟨100⟩ azimuth for $k_i = 6.7$ Å^{-1} ($E_i = 32$ meV) and different incident angles θ_i. The final angle is given by $\theta_f = 90 - \theta_i$ in all the spectra. The major phonon peaks are marked by arrows. Note the predominance of the peak at $\Delta E = -11.0$ meV which is attributed to rotational excitation $j = 0 \rightarrow 1$. The spectra for $\theta_i = 45°$ to 32° are compared with He spectra in (c) measured also from the clean surface at $T_s = 150$ K and $k_i = 8.7$ Å^{-1} ($E_i = 39.6$ meV). In the HD spectra the phonon peaks originate from the rotationally inelastic specular peak and not from the elastic specular peak as in the He spectra. It is also interesting in observe that the defect-related incoherent elastic peaks in the HD spectra are much smaller than observed with He scattering (see also Fig. 2).

positive energy transfer which according to Fig. 4 could be due to phonons with dispersion curves originating at $\Delta K = 0$, $\Delta E = 0$ instead of at $\Delta K = 0$ and $\Delta E = -\Delta E_{rot}$. It is important to note that the widths and shapes of the HD phonon inelastic peaks at $\theta_i = 36°$ and 34° are quite similar to the He peaks at the corresponding positions on the Rayleigh dispersion curves at $\theta_i = 43°$ and 41°, respectively. Comparison with the He time-of-flight spectra also reveals again the much larger incoherent elastic peak in the He spectra.

The peaks in the time-of-flight spectra of Fig. 3 have been fitted with Gauss distributions and their positions have been used to determine the dispersion curves via Eqs. (1) and (2). The results are shown in Fig. 5 where they are compared with the Rayleigh mode dispersion curve measured by He-atom scattering[50,51] and EELS.[52] In the region close to the zone origin the Rayleigh mode dispersion curve

can be approximated by a straight line. Also shown in Fig. 5 are the bulk band edges for transverse phonons. Since He-atom scattering is not especially sensitive to the bulk phonons, the location of the bulk band edge was taken from neutron data[60] to be 22.7 meV/Å^{-1}. For a second-nearest-neighbor model with central and angular forces fitted to bulk phonon dispersion curves, Nizzoli[61] obtained a value for the ratio of the velocity of the transverse bulk band edge v_t to the Rayleigh wave velocity v_R of $v_t/v_R = 1.09$.[62] The predicted Rayleigh wave velocity of 20.86 meV/Å^{-1} agrees rather well with the experimental Rayleigh phonon slope.[50–52] The HD data points deviate significantly from the Rayleigh mode and lie closest to the estimated position of the bulk band edge. This apparent preference for the bulk band edge is completely unexpected since in all He-atom inelastic scattering experiments from metal surfaces the major peaks in the same region of small parallel
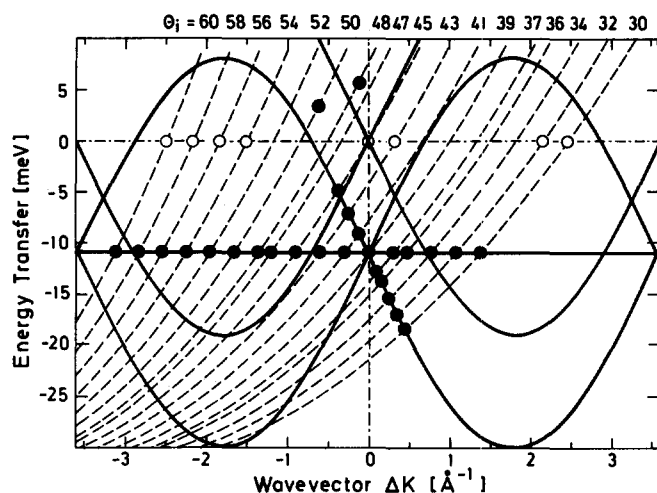
FIG. 4. The kinematic scan curves for the HD time-of-flight spectra shown in Fig. 3. The two sinusoidal curves with origin at $\Delta K = 0$, $\Delta E = 0$ and $\Delta K = 0$, $\Delta E = \Delta E_{rot}$ ($j = 0 \to 1$) show the approximate position of the measured phonon dispersion curves for Ni(001) along the $\langle 100 \rangle$ azimuth for single-phonon inelastic scattering with and without rotational excitation, respectively. The open circles mark the locations of the peaks marked by arrows in the time-of-flight spectra of Fig. 3. The solid circles mark the locations of the elastic ($\Delta E = 0$) and rotationally inelastic ΔE_{rot} ($j = 0 \to 1$) peaks.

momentum transfers can be explained by Rayleigh wave surface phonons.[63]

While the peak positions provide information on the phonon dispersion curves the peak intensities contain valuable information on the dynamics. As discussed previously[56,64] the phonon peak intensities are quite sensitive to the potential parameters of the effective two-body potential between the gas atom and an atom of the surface layer of the metal. In order to compare with phonon peak intensities measured with He atoms,[51] the ratio of the HD phonon inelastic peak to the specular coherent rotational inelastic peak at $\Delta K = 0$ is plotted together with the ratio of the helium
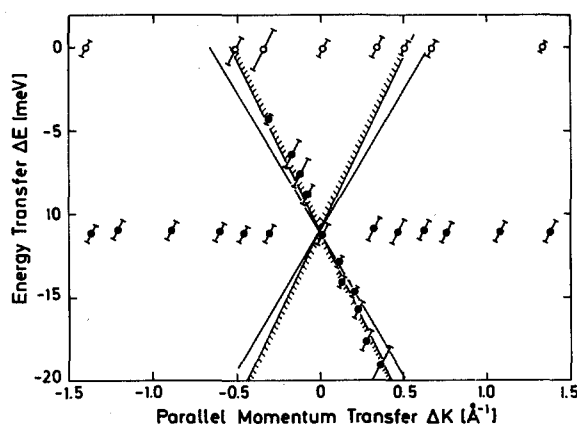

FIG. 5. Measured dispersion curve for scattering of HD from clean Ni(001) (surface temperature = 390 K) along the $\langle 100 \rangle$ azimuth for $k_i = 6.7 \text{Å}^{-1}$ ($E_i = 31$ meV). The solid line shows the Rayleigh dispersion curve measured by He-atom scattering and EELS along this direction and the hatched line shows the edge of the transverse bulk phonon band.
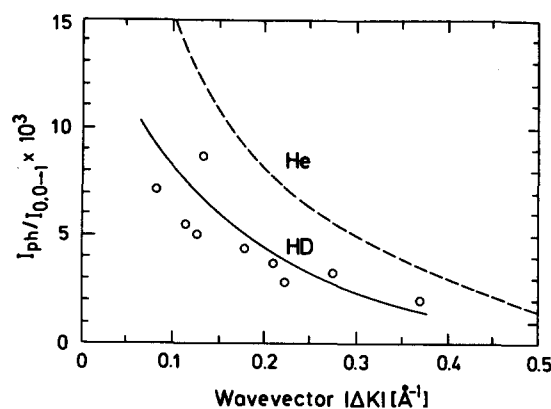

FIG. 6. Comparison of the phonon inelastic intensities for He and HD projectiles in scattering from clean Ni(001) along the $\langle 100 \rangle$ azimuth for $k_i = 6.7 \text{Å}^{-1}$. The helium inelastic intensities were normalized to the elastic specular peak intensity while the HD inelastic intensities were normalized to the specular rotationally inelastic $j = 0 \to 1$ peak. The intensities for positive and negative ΔK have been plotted together. The experimental conditions for the He experiments were $k_i = 8.7 \text{Å}^{-1}$ ($E_i = 39.5$ meV), $T_s = 150$ K (no H adsorption) and for the HD experiments $k_i = 6.7 \text{Å}^{-1}$ ($E_i = 31$ meV) $T_s = 390$ K (no H adsorption).

inelastic peaks relative to the elastic specular peak in Fig. 6. The falloff in intensities is remarkably similar in both cases and shows the expected exponential dependence. The factor of 2 difference in absolute intensities is not unreasonable in view of the differences in the measuring conditions as well as the additional energetic shift in the origin of the dispersion curves in the case of HD scattering.

As discussed in the next section the intensities of the incoherent rotationally *inelastic* $j = 0 \to 1$ peaks are also of interest. Figure 7 shows a plot of these intensities as a function of $|\Delta K|$. The peak intensities have been normalized by dividing by the specular rotationally inelastic peak. These relative HD incoherent inelastic intensities are compared to the He incoherent elastic intensities relative to the He specular peak. The two cases appear to be quite different. The HD curve shows a steeper falloff at small ΔK, which flattens off at $\Delta K > 1 \text{Å}^{-1}$, with a hint of a maximum at $\Delta K = 2.5 \text{Å}^{-1}$. Figure 7 also shows the incoherent HD *elastic* peak intensities, normalized in the same way as the inelastic intensities by dividing by the rotationally inelastic specular peak. With the exception of a few points, this signal is negligibly small and not significantly greater than the background fluctuations.

IV. DISCUSSION

The present experiments are the first detailed time-of-flight energy-loss studies of the scattering of nearly monoenergetic HD molecules from a metal surface. The major observations are as follows, (1) The rotationally inelastic $j = 0 \to 1$ diffraction peaks are larger by about an order of magnitude than the rotationally elastic diffraction peaks. (2) The diffraction intensities for both rotationally elastic and inelastic processes are larger than observed with He on the same surface by about 2 orders of magnitude. (3) The inelastic single-phonon interaction is strongly coupled to the
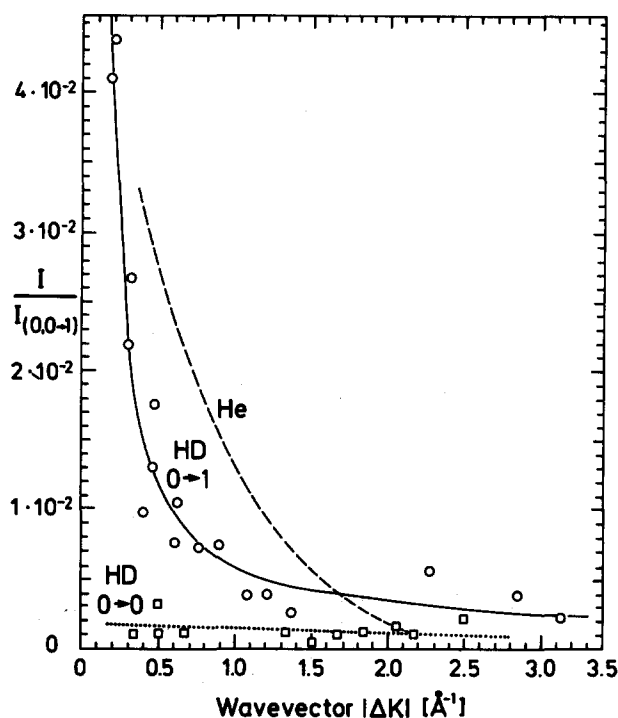
FIG. 7. Comparison of the diffuse incoherent intensities for He and HD projectiles in scattering from clean Ni(001) along the $\langle 100 \rangle$ azimuth. The experimental conditions are the same as in Fig. 6. The He intensities were normalized to the elastic specular peak intensity, while the HD intensities were normalized to the specular rotationally inelastic $j = 0 \to 1$ peak. The intensities for positive and negative ΔK have been plotted together. The HD $j = 0 \to 1$ curve ($\Delta E_{\mathrm{rot}} = -11$ meV) is for the rotationally inelastic peak and shows a similarity to the He intensity, whereas the HD $j = 0 \to 0$ ($\Delta E = 0$) peak has a negligible intensity comparable to the statistical fluctuations of the background.

rotationally inelastic process. (4) Rotational transitions have a significant probability at angles which do not fulfill the diffraction conditions. (5) The diffuse elastic intensity is greatly reduced compared to what is observed with He scattering. (6) The phonon losses appear to be due to a coupling to the transverse bulk band edge and not due to the Rayleigh surface phonons.

The first two observations agree with earlier observations for scattering of HD from Cu(111),[6] Au (111),[6,12] Au (111),[6] and Pt(111).[15] The large probability of rotational inelastic scattering is directly related to the large eccentricity resulting from the shift in the center of the mass away from the center of the charge distribution. The larger diffraction probability for HD compared to He, also observed for H_2 and D_2 on Ag(111),[18,19] Cu(001),[65] and Ni(111),[11] has been attributed to the deeper potential well resulting from the greater polarizability of HD compared to the He.[55] Thus, the molecules are accelerated shortly prior to being reflected from the hard repulsive well and at the higher collision energies experience an enhanced corrugation.

Observation (3) was also made by Allison and Feuerbacher[33] as discussed in the Introduction. In fact, this observation is not surprising and can be easily explained in the framework of the distorted-wave Born approximation,

which has been successfully used for calculating single-phonon inelastic reflection coefficients[56,64] for He. According to this approximation the inelastic intensities are proportional to the intensity of the nearest diffraction peak which is the origin of the phonon inelastic peaks. Since in the present experiments the rotationally inelastic specular peak is more intense than the elastic specular peak, the phonon dispersion curves are offset by $-\Delta E_{\mathrm{rot}}$ ($j = 0 \to 1$). In principle, we also expect a set of phonon dispersion curves originating at the elastic specular peak. Since, however, their intensities will be diminished by the ratio of the rotationally elastic to the rotationally inelastic diffraction peaks, they are, in fact, much weaker in the present experiments. If, however, we had used the more spherical molecules H_2 or D_2 instead of HD, the rotational inelasticity would be greatly suppressed and the phonon peaks would be expected to originate at the more intense rotationally elastic specular peak. Such experiments are thus expected to lead to results more similar to those found with He scattering. In the light of this explanation the conclusion of Allison and Feuerbacher[33] that "rotationally inelastic scattering ... is a dissipative rather than diffractive process" is misleading. It is more correct to state that the dissipative phonon processes are proportional to the intensity of the diffractive process. In this case the most probable diffractive process also happens to be rotationally inelastic. Finally, we note that our results do not support the selection rule of Allison and Feuerbacher connecting the direction of the change in parallel momentum transfer with the sign of the energy change. According to their rule, phonon annihilation occurs for $+\Delta K$ and phonon creation for $-\Delta K$. At first sight it would appear that our results point to just the opposite correlation. Many factors determine the relative intensities. In particular, in our arrangement the creation events with $-\Delta K$ are smeared out kinematically (see Fig. 4). A more extensive data base than presently available is needed before any generalizations can be made.

Observations (4), (5), and (6) are new and, in fact, totally unexpected, and thus more difficult explain. Observation (4) of rotational transitions at all scattering angles has not been reported in previous work. The conservation equations (1) and (2) describing coherent diffraction from a perfect ordered surface do not allow coherent rotational excitation at angles other than the diffraction angles. The previous energy-resolved inelastic experiments of H_2 and D_2 scattered from LiF(001) (Ref. 33) and NaF(001) (Ref. 34) showed no evidence for rotational excitation at ΔK values removed from the Bragg conditions. These surfaces have a large corrugation and the rotationally inelastic diffraction peaks are also larger than the rotationally elastic diffraction peaks. With respect to molecular scattering their morphology can be expected to be very similar to that of the Ni(001) surfaces.

A possible explanation is suggested by the large reduction in the incoherent elastic intensity [observation (5)]. We recall in the case of He scattering that the small amount of elastic intensity between the diffraction peaks, which is designated incoherent or diffuse scattering, can be largely attributed to defects on the surface.[59] In several helium-atom

scattering studies it has been demonstrated that most of the elastic incoherent scattering is due to scattering from steps oriented perpendicular to the scattering plane.[66,67] In these experiments weak oscillations are observed out to values of $\Delta k \approx k_i$. They have been shown to provide detailed information on the size, shape, orientation, density, and correlation function[68] of single randomly distributed steps on the surface. If in the present experiments involving HD nearly all the molecules striking the surface in the vicinity of a step undergo a rotational excitation then both observations (4) and (5) can be accounted for. From the results presented in Fig. 7 it is possible to even estimate the probability of a rotational transition at a step edge from the ratio of the HD $j = 0 \rightarrow 1$ intensity to the HD $j = 0 \rightarrow 0$ intensity. Examination of Fig. 7 indicates that this ratio drops from greater than 20 at $|\Delta K| \lesssim 0.3$ Å^{-1} to about 3–6 for $|\Delta K| > 0.1$ Å^{-1}. From the diffraction peaks shown in Fig. 1(a) we estimate the corresponding ratio for the smooth part of the surface to be about 50. Thus, for small $|\Delta K|$ the probability of rotational excitation is about the same at a step as on a terrace in support of the proposed explanation. From the He experiments we expect oscillations at larger $|\Delta K|$ resulting from quantum interferences. One point in the data at $\Delta K = 2.5$ Å^{-1} hints at a possible maximum in the same region where the first maximum in the He scattering undulations is observed. The intensity in He scattering in this region is an order of magnitude smaller and therefore not visible in Fig. 7. Possibly the relative large intensity of HD $j = 0 \rightarrow 1$ compared to that for He at $|\Delta K| > 1.7$ Å^{-1} seen in Fig. 7 is due to an especially strong positive interference in HD scattering. Obviously, additional experiments are needed to reduce the statistical fluctuations. Meanwhile, it is intriguing to speculate if the differences between HD and He intensities may be due to differences in the interactions at the step edges.

Finally, we discuss observation (6) of a preference for the excitation of bulk phonons over the surface Rayleigh mode. In He-atom scattering the greater probability for the excitation of the surface Rayleigh mode over bulk phonon band edge is explained by the greater density of states of the Rayleigh phonons at the surface.[56,64] If the effective repulsive interaction potentials are of the same type for HD as for He then, in principle, the same coupling mechanism should prevail. The most sensitive information on the z dependence of the repulsive potentials is to be found in the falloff of the inelastic phonon intensities with ΔK shown in Fig. 5. The similarities in these intensities for HD and He indicates that the two potentials are, in fact, not qualitatively different.

This similarity in repulsive potentials appears to be at variance with the work of Hamza and Madix,[8] who estimated that the activation barrier for chemisorption of H_2 on Ni(001) is about 50 meV. They arrived at this result via a simple model in which they explained the differences in sticking coefficients observed with H_2 and D_2 by the different rates of tunneling at collision energies similar to those of the present experiments. Their activation barrier is consistent with the theory of Jackson and Metui,[69] who calculated a barrier of 70 meV for the preferred on-top sites for chemisorption.

Thus, the presently available data does not point to a

straightforward self-consistent explanation of observation (6). Multiphonon effects, which are expected to be more prevalent in HD scattering because of the acceleration in the deeper attractive well, might conceivably lead to an apparent shift in the location of the energy-loss peaks to smaller values of $|\Delta K|$. Such an effect was observed in an extensive study of D_2 scattering from NaF(001),[70] but seems unlikely in the present case because of the close similarity in the shapes of the loss peaks with the He data in Fig. 3. Alternatively, the experiments may indicate an unexpected preferential coupling of the rotational excitation with the bulk phonons. By scattering H_2 and D_2 from the same surface it should be possible to distinguish between these two mechanisms. In this case the rotational phonon coupling should be suppressed and only the multiphonon effect would remain as an explanation if the inelastic intensities again show a propensity for bulk phonon excitation.

The overall mechanisms by which we have explained these results is at variance with the commonly accepted picture of sticking of H_2 on Ni(001) surfaces. In 1979, Christmann proposed that the initial sticking coefficient of 0.1 can be attributed to an enhanced adsorption at surface defect sites.[27] The assumption was made that for molecules striking defect sites the activation energy is zero and that these molecules are directly dissociated and chemisorbed. Mårtsensson, Nyberg, and Andersson interpreted their EELS data on a hydrogen saturated stepped Ni(510) surface also in terms of an nonactivated adsorption of H_2 at step sites.[71] In the most recent survey on the influence of surface defects on adsorption Rendulic presents extensive sticking coefficient data in support of enhanced sticking probabilities at steps for Maxwellian beams with temperatures less then about 400–500 K.[72,73] For our experiments this would imply that molecules striking steps would dissociate and reappear after recombination leading to a broad $\cos \theta$ angular distributed background. The intensity in both the incoherent rotationally inelastic and elastic incoherent peaks should therefore be significantly diminished, which is not observed. Another possible explanation is that the H atoms remain at the surface steps and passivate them and thereby prevent further chemisorption. This can be ruled out by the thermal-desorption spectroscopy experiments,[27] which show nearly complete desorption at the temperature of 390 K used in these experiments.

Since the incoherent intensity is the same or possibly somewhat enhanced the reason for the unexpected behavior might conceivably lie in the different conditions of the two sets of experiments. It would appear that the only major difference between the two experiments is the use of the anisotropic HD molecule in our experiments in place of H_2 and D_2. This should hardly be expected to make a difference since the strong chemisorption forces, which are proportional to the heat of adsorption (≈ 2–3 eV), should prevail over the small amount of energy in the rotations. The elevated surface temperatures in our experiments, which will have a significant effect on the sticking coefficients, will also hardly have any effect on the scattering intensities since the difference in surface temperature ΔkT is also negligible compared to the chemisorption forces.

Finally, we point out that the very different energy-loss distributions found for HD compared to He (see Fig. 5) suggest that HD should have an enhanced trapping and sticking probability compared to D_2 (and H_2). Our experiments show that for HD as a result of the highly probable rotational excitation the first moment of the energy-loss distribution is shifted downwards by -11.0 meV. Moreover, the distribution is broadened considerably with a tail extending down to $\Delta E = -22$ meV which is already 70% of the incident energy. Thus, molecules with total kinetic energies < 30 meV striking the surface at the appropriate angles corresponding to creation of a zone boundary phonon with ≈ 20 meV will have a high probability of being trapped. According to the kinematics such processes can only occur at special angles. The simple rule of normal energy scaling, which states that trapping and sticking depend only on the normal component of the incident kinetic energy, will be violated. Indeed, there are now a number of experiments with heavier molecules which suggest that this concept is not able to explain sticking probabilities.[74] As far as we are aware there is no direct evidence for a trapping mechanism involving a combined rotational and one-phonon excitation in molecule–surface collisions. The only related observation comes from recent experiments of Jacobs et al. with N_2 scattered from Ag(111).[37] They found a strong coupling of the surface heat bath to the rotations which enabled the molecules to have a higher final rotational energy than the incident kinetic energy.

In the future we hope to improve on the sensitivity of these experiments. It would be especially interesting to extend these experiments to higher collision energies close to the barriers for chemisorption. As the barrier is approached the interaction potential should become softer and large differences in the phonon excitation probabilities and the relative rotational excitation at steps and terraces should appear.

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