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Bound level resonances in rotationally inelastic HD/Pt (111) surface scattering

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(Received 21 April 1981; accepted 13 May 1981)

There is currently much experimental and theoretical activity aimed at understanding the microscopic dynamics of rotationally inelastic molecule–surface scattering.[1–3] We wish to report on the HD/Pt(111) system, which we feel is an excellent prototype for comparisons between experiment and theory. HD-metal scattering is nearly ideal for study as (1) the rotational excitation probabilities are large due to the offset of the HD center-of-mass from its geometric center,[3] (2) there are typically a small number of energetically open inelastic channels, and (3) modeling can be done with only one degree of translational freedom due to the low surface corrugation.

We report on the collision induced translation-to-rotation energy transfer of HD($J=0$) scattering from Pt(111), and on the observation of sharp modulations of these $J=0\rightarrow n$ ($n=0, 1, 2$) rotational transition probabilities as a function of incident angle. The energy and azimuthal dependence of these modulations are inconsistent with elastic selective adsorption. We believe that these modulations are due to competitive scattering into bound surface state resonances of the HD/Pt(111) physisorption interaction potential, where the final HD rotational state $J=n+1$ is that of a nearly free rotor. Analysis of these resonances should determine for the first time the bound levels of a molecule on a smooth metallic surface, and hence the short range interaction potential,[4] similar to the use of elastic selective absorption to determine potentials for more highly corrugated systems.[5]

The UHV scattering apparatus, employing a rotatable mass spectrometer detector, has been previously described.[6] Scattering from a clean Pt(111) crystal was a supersonic beam of a 4 : 1 H_2–HD mixture. The HD energy was typically 109 meV, with a FWHM of 12 meV. This HD beam was predominantly in the $J=0$ rotational state. Studies were also done with beam energies of 40.8, 219, and 326 meV. The Pt surface temperature was maintained at 500 K to limit the hydrogen surface coverage to less than 1%. The incident beam was collimated to 0.1°, the detector to 1.0°.

Figure 1 shows the in-plane angular distribution for HD scattering from Pt(111) along the $\langle 10\bar{1}\rangle$ direction for a 109 meV beam incident at $\theta_i=35°$. The discrete peaks correspond to HD scattering into different final rotational states. Discrete peaks are due to coherent, dif-

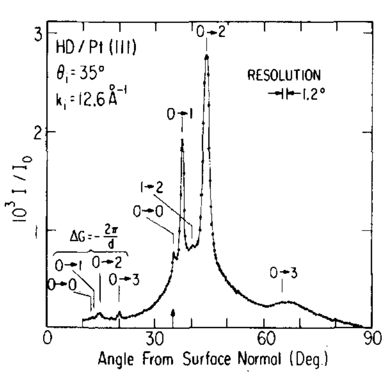

FIG. 1. Angular distribution of the reflected number density for HD scattering from Pt(111) with $\theta_i=35°$, $\phi_i=\langle 10\bar{1}\rangle$, $T_s=500$ K, $E_i=109$ meV, and periodicity $d=1.385$ Å. Vertical lines give peak positions predicted by Eq. (1).

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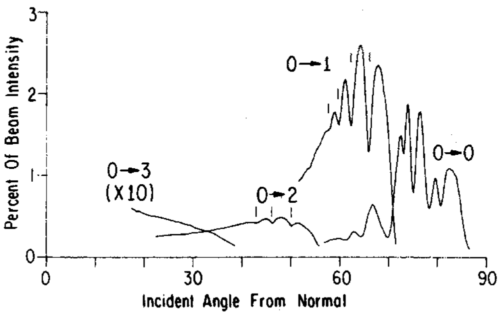

FIG. 2. Peak height versus incident angle for several rotationally inelastic transitions ($E_i = 109$ meV, $\phi_i = \langle 10\bar{1}\rangle$). Vertical lines indicate dips used to estimate bound levels in Table I.

fractive scattering from the ordered surface. Unique scattering angles are predicted from the appropriate conservation equations. Ignoring phonon interactions, they are

$$\mathbf{k}_i^2 = \mathbf{k}_f^2 + (2m/\hbar^2)[E(J_f) - E(J_i)] \; , \quad \mathbf{K}_i = \mathbf{K}_f + \mathbf{G} \; , \qquad (1)$$

where $\mathbf{k}_i$ and $\mathbf{k}_f$ are the initial and final wave vectors, m is the HD mass, $E(J_f) - E(J_i)$ is the change in rotational energy, $\mathbf{K}_i$ and $\mathbf{K}_f$ are the components of $\mathbf{k}_i$ and $\mathbf{k}_f$ parallel to the surface, and $\mathbf{G}$ is a surface reciprocal lattice vector. The presence of only weak diffraction for $\mathbf{G} \neq 0$ in Fig. 1 confirms the small corrugation of the HD/Pt(111) potential. Results using other beam energies, but with θ_i chosen to give comparable E_z values, indicate that the rotational excitation probabilities predominantly depend only on E_z, the normal component of the incident energy, and are insensitive to azimuthal orientation.[2]

In Fig. 2 the peak heights for each particular final J state are plotted versus θ_i. No subtraction of the diffuse background was made. To relate these values to probabilities, proper account of background, incident beam energy spread, angular resolution, and Debye–Waller attenuation[7] must be made. A competitive bound state resonance shows in the $J = 0 \to n$ probability when $\hbar^2 k_{fz}^2/2m$ calculated from Eq. (1) for $J = 0 \to n+1$ is negative and precisely matches a real bound level in the HD/Pt(111) potential, where k_{fz} is the component of $\mathbf{k}_f$ perpendicular to the surface. The $E(J_f)$ levels are then those of a bound hindered rotor, and will approximate free rotor levels when the degree of hindering is small. Assuming a free rotor, Eq. (1) and the dips indicated in Fig. 2 for $J = 0 \to 1$ and $0 \to 2$ are used to calculate bound levels, as listed in Table I. Also in Table I are a dip for $J = 0 \to 2$ which is not apparent in Fig. 2, but shows clearly in a Fig. 1 type plot at the appropriate incident angle, as well as $J = 0 \to 1$ data for a 40.8 meV beam. The two resonances observed for $0 \to 1$, but absent for $0 \to 2$ may have been missed due to their shallowness and

TABLE I. Bound state levels calculated from Fig. 2 and Eq. (1).

J transition	E_i (meV)	Approximate bound level energies (meV)					
0 to 1	109.9	−2.0	−5.3	−9.3	−14.8	(a)	(a)
0 to 1	40.8	−2.7	−5.8	−9.5	−15.1	(a)	(a)
0 to 2	108.3	···	···	−8.0	−14.0	−21.3	−32.9

[a]Energetically impossible to observe with this transition.

breadth. We have estimated the potential well minimum from Debye–Waller attenuation[7] to be 55 meV, suggesting that one or two bound levels may have escaped detection. The $J = 0 \to 0$ data has irregular dips which cannot be put into agreement with the levels of Table I. This may be due to the breakdown of the free rotor approximation for bound $J = 1$ states.

A careful analysis of this data including full deconvolution and time-of-flight measurements is now being carried out. Hopefully, information will be obtained on the anharmonicity of the potential well, on the rotational hindering, inelastic cross sections, and on the general nature of rotationally mediated bound state transitions in surface scattering.

We are deeply grateful to L. Wharton for his constant encouragement and advice, and to Jihwa Lee for help in the initial experiments. This work was supported in part by ONR Contract No. N00014-77-C-0240 Res. Mod. P00003, M. R. L. of the NSF at the University of Chicago, and a Camille and Henry Dreyfus Young Faculty Grant to S. J. Sibener.

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