Selective Adsorption Resonances in the Scattering of n-H_2, p-H_2, n-D_2, and o-D_2 from Ag(111)

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Diffractive and rotationally mediated selective adsorption scattering resonances are reported for n-H_2, p-H_2, n-D_2, and o-D_2 on Ag(111). Small resonance shifts and linewidth differences are observed between n-H_2 and p-H_2, indicating a weak orientation dependence of the laterally averaged H_2/Ag(111) potential. The p-H_2 and o-D_2 levels were used to determine the isotropic component of this potential, yielding a well depth of ~32 meV.

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The phenomenon of selective adsorption has been of immense importance to the study of gas-surface interactions.[1] With few exceptions,[2,3] most of these studies have centered on highly corrugated, nonmetal surfaces where diffractive selective adsorption resonances are relatively easy to detect. These studies have been directed towards determining atom-surface potentials, or molecular-hydrogen–surface potentials with H_2 treated as a structureless particle. However, one expects that the bound-state energy levels obtained from selective adsorption measurements will be affected by the spatially anisotropic component of the molecule-surface potential.[2,4,5] Two recent low-energy electron-energy-loss (EELS) experiments dealing with the physisorption of H_2 and D_2 on Ag(111)[6] and of H_2, D_2, and HD on Cu(100)[7] of relatively low resolution [12 meV for Ag(111) and 3 meV for Cu(100)] indicate that physisorbed hydrogen behaves as a nearly free three-dimensional rotor on these surfaces. In EELS experiments the weak spatial anisotropy of the interaction should manifest itself in slight shifts of observed rotation-vibration transitions for different physisorbed $|J,m\rangle$ states and, as a consequence of this, in linewidth changes for spectra obtained as a convolution over various m substates.[7,8] Similar $|J,m\rangle$-dependent shifts should also appear in the bound-state spectrum of the physisorption well when probed by submillielectronvolt-resolution selective adsorption scattering experiments. The spectroscopy of these energy levels lies at the heart of this Letter.

We report here the first clear observation of diffractive selective adsorption (DSA) on a closest-packed (low corrugation) metallic surface,[9] Ag(111), and the first detection of rotationally mediated selective adsorption (RMSA)[2,4,5] for a homonuclear diatomic on a solid surface. Comparative DSA studies utilizing rotationally-state-selected H_2 and D_2 molecules have revealed *small level shifts* and *linewidth changes* which are the result of an average over individual J- and m-dependent level shifts. Analysis of these DSA experiments is facilitated by the extremely low corrugation of Ag(111), which virtually eliminates any complications due to band structure. These experiments were carried out with sufficient energy and angular resolution to detect energy shifts of ~0.1 meV. Extensive isotopic studies with molecular beams of pure p-H_2 and o-D_2 have also allowed us to determine the spatially isotropic component of the laterally averaged H_2/Ag(111) physisorption potential.

These experiments were carried out in an ultrahigh-vacuum beam-surface scattering apparatus described previously,[5,10] with modifications to be described elsewhere.[11] The Ag(111) crystal was cut from a 99.999% boule, and was prepared as previously described.[5] Pure p-H_2 and o-D_2 were generated by passing hydrogen (deuterium) gas through a newly constructed, liquid-hydrogen-cooled in-line catalytic converter.[11] Conventional time-of-flight measurements (0.25 μsec/channel resolution) were frequently carried out to monitor incident beam characteristics. Complete conversion to p-H_2 (o-D_2) was confirmed by comparing collision-induced $J=0\rightarrow 2$ rotationally inelastic transition probabilities with and without conversion. Experimental resolution parameters were as follows: incident beam divergence, 0.1°; detector resolution, 0.67°; $\Delta v/v=4.5\%$ (H_2) and 6.5% (D_2). Selective adsorption resonance spectra were taken by measuring the maximum intensity of the specular peak at incident polar angle increments of 0.2°.

In the general case of DSA-RMSA, the incident molecule can be coupled to a bound vibrational state on the surface through diffraction and/or rotational transitions. Neglecting phonon interactions, conservation of total energy, and crystal momentum leads to the resonance condition

$$\vec{k}_i^{\,2}=(\vec{K}_i+\vec{G})^2+(2m/\hbar^2)\Delta E_J+(2m/\hbar^2)E_v\,,$$

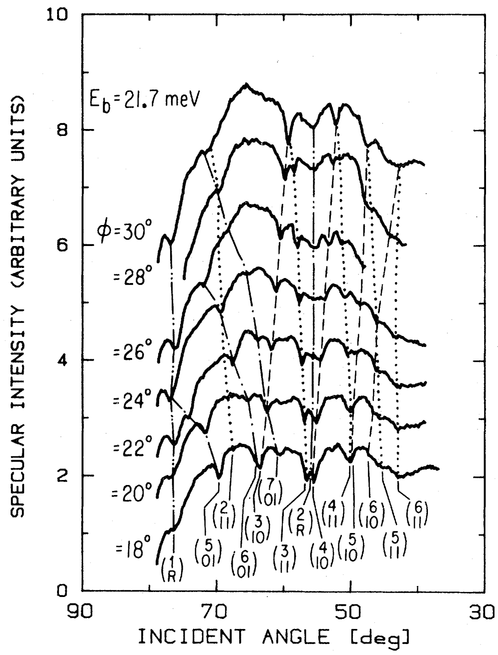

FIG. 1. Specular peak intensity of o-D_2 scattering from Ag(111) as a function of incident polar angle for seven successive azimuthal angles; $T_s = 105$ K.

with $\vec{k}_i$ the incident-wave vector, $\vec{K}_i$ the projection of $\vec{k}_i$ on the surface, $\vec{G} = (mn)$ the surface reciprocal-lattice vector of order (mn), E_v the bound-state energy of the laterally averaged potential $V_{00}(z, \theta)$, and $\Delta E_J = E(J_f) - E(J_i)$ the energy of the rotational transition. For $\Delta E_J = 0$ pure DSA occurs, while when $\vec{G} = (00)$ pure RMSA occurs.[2,4,5] In these experiments we have observed pure DSA and pure RMSA, but no mixed resonances.

Figure 1 shows several o-D_2 resonance spectra, i.e., specular peak intensities versus incident polar angles, for seven successive surface azimuthal settings. $\varphi = 0°$ is defined as the $\langle 11\bar{2}\rangle$ direction. Resonance dips are designated by $\binom{v}{mn}$ where the incident molecule is coupled to the bound level v by the reciprocal-lattice vector (mn). We observe two sets of azimuthally independent dips corresponding to two different bound levels probed by $J = 0 \rightarrow 2$ rotationally mediated selective adsorption.

In Fig. 2 the selective adsorption loci for o-D_2 are plotted in the two-dimensional reciprocal space of the surface. The resonances can be clearly grouped into three sets of concentric arcs centered about the $(0\bar{1})$, $(\bar{1}\bar{1})$, and $(\bar{1}0)$ surface reciprocal-lattice points. The two o-D_2 arcs which precess about the (00) G vector are due

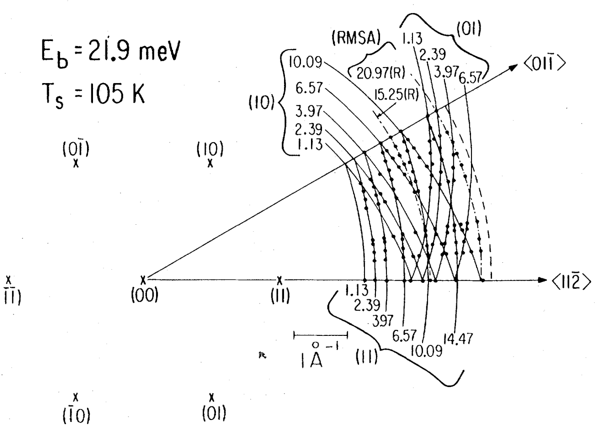

FIG. 2. Selective adsorption loci for o-D_2 plotted in the surface reciprocal-lattice plane. Arc labels denote bound levels (millielectronvolts) and coupling G vectors. Points represent dips from the resonance spectra. The dashed arc denotes the energy limit for the D_2 beam.

to RMSA associated with the $J = 0 \rightarrow 2$ inelastic transition. Note that isoenergetic arcs cross along the $\langle 11\bar{2}\rangle$ and $\langle 01\bar{1}\rangle$ symmetry directions. No discernible level splittings are seen at these crossing points, presumably because of the very small higher-order Fourier components of the potential. Similar reciprocal-space plots have also been constructed for p-H_2, n-H_2, and n-D_2. Average values of the experimental bound-level energies are listed in Table I.

Since n-H_2 contains 75% o-H_2 (primarily $J = 1$ after supersonic expansion), the n-H_2 results reflect a weighted average over $|J,m\rangle = |0,0\rangle$, $|1,0\rangle$, and $|1,\pm 1\rangle$. The p-H_2 results reflect solely $|J,m\rangle = |0,0\rangle$. The small shifts seen in Table I between the p-H_2 and n-H_2 data sets are derived from the orientationally anisotropic component of the laterally averaged potential $V_{00}(z, \theta)$. When $V_{00}(z, \theta)$ is expanded in a Legendre series, with coefficients $v_{00}^{\,l}(z)$, only even terms in l contribute for homonuclear molecules. In the simplest model we retain only the first two terms, with $v_{00}^{\,2}(z) = \beta v_{00}^{\,0}(z)$. Then shifts for molecules with $J \neq 0, m \neq 0$ in a bound state n of the isotropic potential $v_{00}^{\,0}(z)$ may be estimated by use of first-order perturbation theory as

$$\Delta E_n^{\,Jm} = \beta \langle n | v_{00}^{\,0}(z) | n \rangle \langle Jm | P_2(\cos\theta) | Jm \rangle .$$

The deviation of the n-H_2 results from the p-H_2 results reflects an average over these shifts. Although the ΔE_v's are just somewhat larger than the standard deviations, they are not artifacts due to systematic drifts. This was con-

TABLE I. Experimental bound-state energies, E_v, of H_2 and D_2 on Ag(111). σ is the standard deviation, and n the number of observations. ΔE_v is the deviation of the n-H_2 (n-D_2) levels from the p-H_2 (o-D_2) levels. The accuracy of these level determinations (limited by small uncertainties in incident beam time-of-flight analysis and azimuthal-angle setting) is ~0.2 meV, which cancels in the determination of ΔE_v. E_b =18.57, 18.09, 21.68, and 20.71 meV for p-H_2, n-H_2, o-D_2, and n-D_2, respectively.

	p-H_2		n-H_2		
v	E_v	$\sigma(n)$	E_v	$\sigma(n)$	ΔE_v
5	−1.21	0.06(11)	−1.12	0.05(5)	0.09
4	−2.61	0.13(22)	−2.52	0.07(14)	0.09
3	−5.47	0.10(45)	−5.35	0.09(30)	0.12
2	−10.11	0.09(42)	−9.91	0.09(31)	0.20
1	−16.87	0.07(28)	−16.55	0.11(14)	0.32
0	−25.74	0.07(2)	−25.53	0.21(2)	0.21
	o-D_2		n-D_2		
v	E_v	$\sigma(n)$	E_v	$\sigma(n)$	ΔE_v
7	−1.13	0.05(11)	−1.17	0.12(3)	−0.04
6	−2.39	0.10(26)	−2.36	0.06(6)	0.03
5	−3.97	0.06(21)	−3.94	0.07(9)	0.03
4	−6.57	0.10(32)	−6.52	0.07(10)	0.05
3	−10.09	0.06(25)	−10.06	0.07(7)	0.03
2	−14.47	0.20(8)	−14.40	0.05(4)	0.07
2	−15.25 [a]	0.04(5)	⋯	⋯	⋯
1	−20.97 [a]	0.04(13)	−20.98 [a]	0.02(3)	⋯

[a]RMSA dips due to $J=0\to2$.

firmed by taking data for p-H_2 and n-H_2 sequentially, without changing any other experimental conditions. n-D_2 contains only 33% p-D_2 (primarily $J=1$ after expansion), resulting in the much smaller shifts between o-D_2 and n-D_2 (Table I). Averaging over the m-dependent shifts for n-H_2 also results in linewidth broadening, as shown in Fig. 3. A preliminary Gaussian deconvolution of these line shapes, based upon three measurements for each DSA resonance, gives an energy width of 0.19± 0.04 meV for p-H_2 and 0.35± 0.01 meV for n-H_2. A full analysis will be given later.[12]

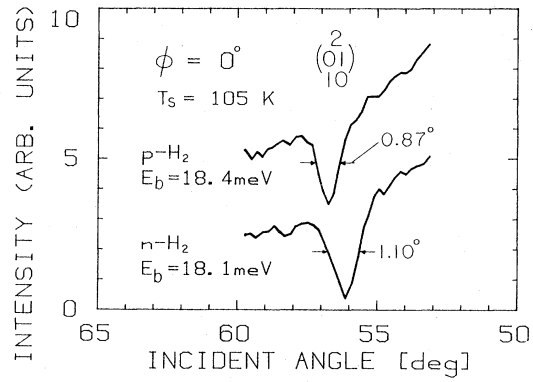

FIG. 3. Selective adsorption linewidth broadening for n-H_2 relative to p-H_2. The total shift in dip angle is due to both small $|J,m\rangle$-dependent level shifts for n-H_2 and the difference in beam energies.

Quantum numbers were assigned to the p-H_2 and o-D_2 ($J=0$) bound vibrational levels by plotting $E_v^{1/6}$ against the reduced quantum number $\eta=(v+\frac{1}{2})/\sqrt{m}$.[13] The assignment giving the best simultaneous linear fit to both isotopes is listed in Table I. This gives a well depth of ~ 32 meV, and predicts a missing level for $D_2(v=0)$ at ~ −27 meV. The only alternative assignment giving a similar quality fit predicts a well depth of 60 meV. This has been ruled out by comparing experimental rotationally inelastic HD/Ag(111) scattering cross sections with the results of close-coupled quantum scattering calculations.[11]

The experimental eigenvalues for $J=0$ H_2 and D_2 have been used to determine the shape of $v_{00}{}^0(z)$, the spatially isotropic component of $V_{00}(z,\theta)$. We find that both a variable-exponent potential (VEP),[14]

$$v_{00}(z)=D\{[1+(\lambda/p)(z-z_e)]^{-2p}-2[1+(\lambda/p)(z-z_e)]^{-p}\},$$

and an exponential-3 potential,[15]

$$v_{00}{}^0(z)=\left(\frac{\beta z_e D}{\beta z_e-3}\right)\left[\frac{3}{\beta z_e}\exp[-\beta(z-z_e)]-f(z)\left(\frac{z_e}{z}\right)^3\right],\quad f(z)=1-[2(z/a_0)(z/a_0+1)+1]\exp(-2z/a_0),$$

provide excellent fits to the experimental eigenvalues, with rms deviations of 0.13 meV (VEP) and 0.12 meV (exp-3). The parameters for the best-fit potentials are as follows: (i) VEP: D = 31.54 meV, λ = 1.065 Å^{-1}, and p = 4.293; (ii) exp-3: D = 32.46 meV, β = 2.417 Å^{-1}, and z_e = 1.988 Å. $f(z)$ is a cutoff function, which goes smoothly from $f(0)=0$ to $f(z)=1$ at large z.[16] These results are in excellent agreement with the recent predictions of Liebsch and Harris for this system.[17] We depart here from our earlier conjecture[5,18] that the well depth of the H_2/Ag(111) system is ~46 meV. This preliminary estimate was solely based on Beeby-corrected Debye-Waller analysis[19] for structureless particles. We also find that standard Debye-Waller analysis completely fails to give a consistent result for HD/Ag(111). This will be discussed in a forthcoming paper dealing with the isotropic part of the laterally averaged potential.[11]

To summarize, we have observed diffractive and rotationally mediated selective adsorption for n-H_2, p-H_2, n-D_2, and o-D_2 on Ag(111). The ability to resolve DSA dips on Ag(111), a surface of extremely low corrugation, suggests that future bound-state studies should be feasible on a much wider selection of crystalline surfaces than previously thought possible. The $J=0$ resonances have been used to determine the spatially isotropic component of the laterally averaged molecule-surface potential. This is an essential prerequisite for a full analysis of the anisotropic component of the potential. Small energy shifts and linewidth differences are observed between n-H_2 and p-H_2 bound-state resonances which are due to the weak anisotropy of the potential.

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[1]H. Hoinkes, Rev. Mod. Phys. 52, 933 (1980).

[2]J. P. Cowin, C. F. Yu, S. J. Sibener, and J. E. Hurst, J. Chem. Phys. 75, 1033 (1981).

[3]J. Perreau and J. Lapujoulade, Surf. Sci. 122, 341 (1982).

[4]K. B. Whaley, J. C. Light, J. P. Cowin, and S. J. Sibener, Chem. Phys. Lett. 89, 89 (1982).

[5]C. F. Yu, C. S. Hogg, J. P. Cowin, K. B. Whaley, J. C. Light, and S. J. Sibener, Isr. J. Chem. 22, 305 (1982).

[6]Ph. Avouris, D. Schmeisser, and J. E. Demuth, Phys. Rev. Lett. 48, 199 (1982).

[7]S. Anderson and J. Harris, Phys. Rev. Lett. 48, 545 (1982).

[8]A. J. Berlinsky, Phys. Rev. B 26, 443 (1982).

[9]Some spectral features which may be due to DSA have recently been seen for H_2, D_2/Pt(111); see J. P. Cowin, Ph.D. thesis, The University of Chicago, 1981 (unpublished).

[10]C. A. Becker, Ph.D. thesis, The University of Chicago, 1980 (unpublished); D. Auerbach, C. Becker, J. Cowin, and L. Wharton, Appl. Phys. 14, 141 (1977).

[11]C. F. Yu, K. B. Whaley, C. S. Hogg, and S. J. Sibener, to be published.

[12]C. F. Yu, K. B. Whaley, C. S. Hogg, J. C. Light, and S. J. Sibener, to be published.

[13]R. J. LeRoy, Surf. Sci. 59, 541 (1976).

[14]L. Mattera, C. Salvo, S. Terreni, and F. Tommasini, Surf. Sci. 97, 158 (1980).

[15]H. Chow, Surf. Sci. 66, 221 (1977).

[16]J. Harris, private communication.

[17]A. Liebsch and J. Harris, Surf. Sci. 130, L349 (1983).

[18]C. F. Yu, C. S. Hogg, and S. J. Sibener, J. Electron Spectrosc. Relat. Phenom. 30, 99 (1983).

[19]J. L. Beeby, J. Phys. C 4, L39 (1971).