

Dipole Active Vibrational Motion in the Physisorption Well

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We demonstrate by electron energy-loss measurements that the vibrational motion in the physisorption well is dipole active. This is a general phenomenon and data for adsorbed H₂, D₂, and HD reveal a strong nonlinear dependence of the induced dipole moments on displacement. We find that a good estimate of the dipole moment function can be obtained from a van der Waals model. [S0031-9007(97)02691-4]

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The ubiquitous van der Waals forces manifest themselves at interatomic distances larger than typical chemical bond lengths. They are of key importance for many physical, chemical, and biological systems and their frequent surface manifestations include physisorption (physical adsorption), gas-surface scattering, and atom-force microscopy. The conventional description of the physisorption interaction is in terms of a competition between a long-range van der Waals attraction and a short-range Pauli repulsion, in analogy to inert atom-atom interactions. The adsorbate-substrate electron correlations give, for example, a van der Waals potential which falls off with distance like $(z - z_0)^{-3}$, where z_0 is the well-defined van der Waals reference plane [1], but with an additional precision in the theory, an advantage that is exploited here.

The van der Waals forces also polarize the adsorbate so that the valence electrons are displaced towards the metal surface. This induced permanent dipole moment varies like $(z - z_0)^{-4}$ [2]. Density functional calculations, intended for closer distances, also reveal a rapidly varying polarization with distance [3]. Both models will, evidently, lead to the prediction that vibrational motion in the physisorption well should result in a fluctuating dipole and excitations among the well states should be dipole allowed and observable by, e.g., infrared spectroscopy. Such spectra will in principle give a direct measure of the gradients of the polarization at distances where electron-electron interactions gradually change from nonlocal to local, a challenging regime to electron structure theory.

In this Letter we present experimental evidence from high-resolution electron energy-loss measurements of dipole excited vibrational transitions among the bound levels for H₂, D₂, and HD physisorbed on the Cu(100) surface. Established potentials and fairly large excitation energies make H₂ feasible from a spectroscopic point of view, though we expect this effect to exist for physisorbed species in general. Both fundamental and overtone excitations are observed. The overtones are intense; a striking consequence of strong nonlinear variation of the dipole moment with displacement. The observed excitation energies agree very well with the

ones derived from the H₂-Cu(100) physisorption potential determined by selective adsorption measurements [4]. The data also reveal that the fundamental rotational transition of physisorbed HD is associated with a much enhanced dipole moment.

We have determined dipole strengths for the different transitions from the measured spectra using dipole scattering theory, while the permanent dipole moment was obtained from a work function measurement. We find that a van der Waals description of the H₂-Cu interaction explains our experimental observations and provides a good quantitative estimate of the dipole moment function.

The spectroscopic measurements reported here were obtained with use of a high-resolution electron-energy-loss spectrometer (EELS). The instrument, which is a modified version of a construction that has been described briefly elsewhere [5], has an optimum energy resolution of about 1 meV. Analyzer and specimen can be rotated so that angles of detection and incidence can be varied independently and angular distribution measurements were performed by rotating the analyzer at the fixed angle of incidence. The Cu(100) specimen was cleaned *in situ* by standard methods involving argon-ion bombardment and heating cycles and could be cooled, at an ambient pressure in the 10⁻¹¹ Torr range, to temperatures below 10 K using helium as a cryogen and it was heated resistively. The EEL spectra were measured for uncompressed physisorbed monolayers of H₂, D₂, and HD of approximately equal adsorbate density determined to be around 0.7 × 10¹⁵ molecules/cm² in previous desorption experiments [6]. A lower density just results in a weakening of the spectral features while a higher density causes energy shifts in the spectra.

Figure 1 shows the low-energy region of the EEL spectra from the physisorbed hydrogen monolayers. The spectra were taken for specular scattering at an incident angle of 48° and an electron energy of 3 eV. The substrate temperature was kept around 10 K during the short (≈5 min) measurements. The H₂ and D₂ spectra show two loss peaks in the region 5–20 meV corresponding to the $\nu = 0 \rightarrow 1$ and $\nu = 0 \rightarrow 2$ vibrational transitions in the physisorption well. The peaks at 7.4 and 13.6 meV

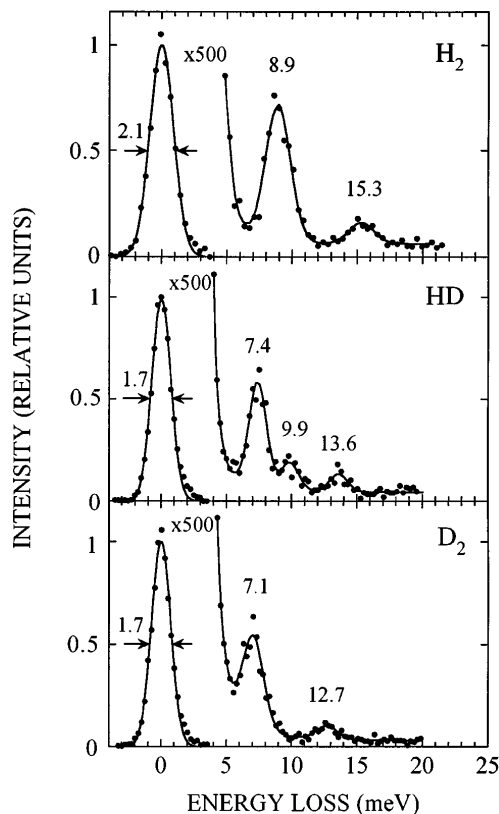


FIG. 1. Electron energy-loss spectra from monolayers of H_2 , HD, and D_2 adsorbed on Cu(100) at about 10 K. The spectra are measured in the specular direction for a 3 eV electron beam incident at 48° from the surface normal.

are the related transitions in the HD spectrum. The 9.9 meV peak in this spectrum is the $j = 0 \rightarrow 1$ rotational transition of the HD molecule. The energy is considerably lower than the free molecule value of 11.1 meV and we will discuss this observation in more detail below. We have listed the observed vibrational transition energies in Table I together with the corresponding energies derived from the H_2 -Cu(100) physisorption potential determined from selective adsorption measurements [4]. The two sets of data refer to predominantly $j = 0$ molecules and agree within the accuracy (0.1–0.2 meV) of the two methods, an observation which in fact confirms the correctness of the potential and also shows that the potential depends very weakly on the density of adsorbed molecules.

One striking feature of the spectra in Fig. 1 is the large intensity of the overtone excitations, and it is

tempting to suggest that these spectra result from resonant e - H_2 scattering. This is not the case, however. Angular distribution measurements reveal that all the excitations observed in Fig. 1 are dipole excited. Example of such distributions for H_2 ($v = 0 \rightarrow 1$, $v = 0 \rightarrow 2$) and HD ($v = 0 \rightarrow 1$, $j = 0 \rightarrow 1$) are given in Fig. 2. The elastic intensity distribution (solid curve) is symmetrical around the specular direction and has a full width at half maximum of 1.7° (H_2) and 1.4° (HD). The inelastic distributions are sharply peaked in the specular direction which is characteristic for dipole excited transitions. The inelastic electron scattering involving these excitations hence takes place via this long-range interaction. The $j = 0 \rightarrow 2$ rotation transition of H_2 at 44 meV, which is excited by resonant scattering, exhibits a broad angular distribution (see Fig. 2) which does not peak in the specular direction. The resonant scattering contribution to the intensity of the dipole active transitions is clearly small ($<10\%$).

The experimental results discussed above show that the long-range dipole interaction is the predominant mechanism contributing to the inelastic electron scattering process involving the vibrational and rotational transitions displayed in Fig. 1. The differential scattering cross section is then to a good approximation given by [7]:

$$\frac{d\sigma}{d\Omega} = n_s \left(\frac{me}{\pi \epsilon_0 \hbar} \right)^2 \mu_v^2 \frac{|k_1|}{|k_0|} \frac{1}{\cos \alpha} \frac{|k_1^\parallel - k_0^\parallel|^2}{|k_1 - k_0|^4}, \quad (1)$$

where n_s is the number of adsorbed species per unit area, μ_v is the dipole matrix element between vibrational states 0 and v , k_0 , k_1 and k_0^\parallel , k_1^\parallel are the wave vectors and their surface components of the incident and scattered electrons, respectively, and α is the angle of incidence. It is straightforward to evaluate experimental dipole matrix elements for the observed fundamental and overtone excitations μ_1 and μ_2 , respectively, from Eq. (1) by integrating over the solid angle of detection. The values obtained for H_2 , D_2 , and HD are listed in Table II.

The adsorbed molecules also acquire weak permanent dipole moments which is manifested via a reduction of the work function by about 0.1 eV at monolayer coverage. The positive end of these dipoles points away from the metal surface. This behavior is qualitatively similar to what has been observed for adsorbed rare gas layers, in which case the work function reduction can be as large as 1 eV. It has been pointed out that this permanent polarization of the adsorbate can be ascribed

TABLE I. Energies in meV of the vibrational transitions $v = 0 \rightarrow 1$ and $v = 0 \rightarrow 2$ for H_2 , HD, and D_2 measured in this work (EELS) and derived from the H_2 -Cu(100) physisorption potential determined from selective adsorption measurements (SA) [4].

	H_2		HD		D_2	
	$v = 0 \rightarrow 1$	$v = 0 \rightarrow 2$	$v = 0 \rightarrow 1$	$v = 0 \rightarrow 2$	$v = 0 \rightarrow 1$	$v = 0 \rightarrow 2$
EELS	8.9	15.3	7.4	13.6	7.1	12.7
SA	9.0	15.6	7.7	13.8	6.9	12.6

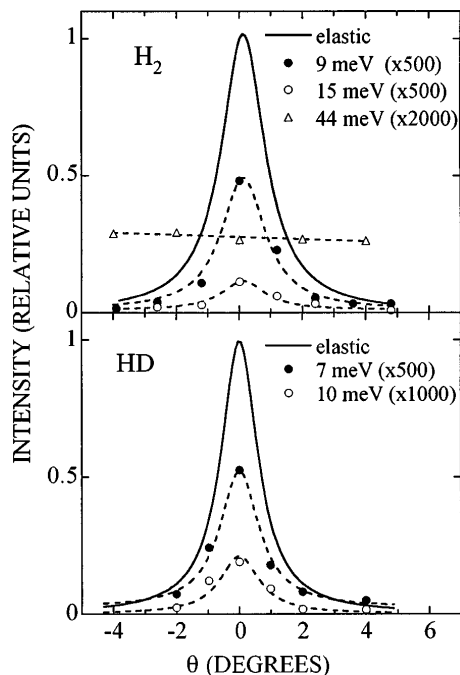


FIG. 2. Experimental elastic peak intensities (solid curves) and inelastic peak intensities vs collection angle θ ($\theta = 0$ specular, $\theta < 0$ toward surface normal) for H_2 [$\nu = 0 \rightarrow 1$ (\bullet), $\nu = 0 \rightarrow 2$ (\circ), $j = 0 \rightarrow 2$ (Δ)] and HD [$\nu = 0 \rightarrow 1$ (\bullet), $j = 0 \rightarrow 1$ (\circ)]. Conditions as in Fig. 1.

to the van der Waals forces acting between the adsorbate and the metal substrate [2]. The net effect is that the adsorbate valence electrons are attracted towards the metal surface by long-range dynamical image interaction. The van der Waals treatment yields an induced dipole moment p_z , which varies as z^{-4} with distance from the surface. Local density calculations [3], on the other hand, reveal explicitly a valence electron distribution displaced towards the metal due to short-range exchange-correlation effects. Calculations for Xe on a jellium of Al density [3] show a rapid variation of the induced dipole moment with adsorbate-substrate distance.

We are, of course, in this work, particularly interested in the dynamic dipole moment, i.e., the variation of the dipole moment with distance around the adsorbate equilibrium position. Polarization induced dipole moments seem to be a likely source of our observations. We will apply a van der Waals treatment presented by Zaremba [2]

TABLE II. Measured dipole moment μ_0 and dipole matrix elements μ_1 and μ_2 for H_2 , HD, and D_2 . The calculated values for H_2 , $\mu_{\text{calc}}^{(\text{H}_2)}$, are derived from the van der Waals treatment described in the text. The unit is Debye (D).

	$\mu_{\text{calc}}^{(\text{H}_2)}$	H_2	HD	D_2
μ_0 (D)	0.026	0.045		
μ_1 (D)	-0.016	0.020	0.018	0.017
μ_2 (D)	0.0056	0.0089	0.0083	0.0070

in order to obtain quantitative estimates of p_z . The model takes into account the retarded response of the metal electrons and defines a reference plane z_0 , from which the adsorbate position is measured when the dipole moment is evaluated. From Eqs. (14) and (15) in Ref. [2] we have

$$p_z = f/(z - z_0)^4, \quad (2)$$

$$z_0 - z_b = g(z_c - z_b), \quad (3)$$

where z_b is the position of the positive jellium background and z_c is the centroid of the induced surface charge. The quantities f and g depend on the surface plasmon energy $\hbar\omega_s$ and a common value $\hbar\omega_0$ for the spectral representation of the adsorbate electronic excitation energies. We have treated Cu as a free electron metal with one electron per atom which gives $\hbar\omega_s = 7.6$ eV and we find $z_c - z_b = 1.45a_0$ ($1a_0 = 1$ bohr) interpolating in the data of Ref. [8]. Treating the H_2 molecule as a simple oscillator with two electrons gives $\hbar\omega_0 = 16.5$ eV from the average static electronic polarizability $\bar{\alpha}_s = 5.41a_0^3$. Using these value we obtain $z_0 - z_b = 1.01a_0$ from Eq. (3).

The dipole matrix element for the $0 \rightarrow 1$ fundamental vibrational transition is given by

$$\mu_1 = p'_z \sqrt{\langle z^2 \rangle}, \quad (4)$$

where p'_z is the derivative of the dipole moment function and $\sqrt{\langle z^2 \rangle}$ is the rms. displacement of the oscillator in the ground state. The corresponding matrix element for the $0 \rightarrow 2$ overtone transition has contributions from both electrical and mechanical anharmonicity

$$\mu_2 = \frac{p''_z}{\sqrt{2}} \langle z^2 \rangle + p'_z \sqrt{\langle z^2 \rangle} \sqrt{\frac{x_e}{2}}, \quad (5)$$

where p''_z is the second derivative of the dipole moment function. The second contribution is from mechanical anharmonicity and is derived for a Morse potential [9]; the parameter x_e is a measure of the anharmonicity of the potential with an energy level spectrum $E_n = \hbar\omega_e(n + 1/2) - \hbar\omega_e x_e (n + 1/2)^2$. For this potential we also have $\langle z^2 \rangle = \hbar/2m\omega_e$ where m is the reduced mass of the oscillator [10].

We have evaluated the dipole moment and its derivatives at the equilibrium position of the H_2 molecule in the potential well which is $z_e - z_b = 4.55a_0$ outside the jellium edge [11]. The calculated values $\mu_1 = -0.016$ D and $\mu_2 = 0.0056$ D for H_2 are listed in Table II and agree remarkably well with the corresponding experimental values |0.020|D and |0.0089|D. Previously we noted that the overtones were surprisingly intense, about 0.2 of the fundamental intensity for H_2 . Mechanical anharmonicity would give only a relative contribution of $x_e/2 \approx 0.05$ [see Eq. (5)]. The two contributions to the experimental μ_2 are 0.014 D and -0.005 D from electrical and mechanical anharmonicity, respectively, adopting the signs from the model. It is clearly the strong nonlinear variation of the polarization induced dipole moment

that causes the intense overtones. The calculated permanent dipole moment $\mu_0 = p_z$ for H_2 is also included in Table II together with the experimental value deduced from the work function change $\Delta\phi = -0.12$ eV, measured for the H_2 monolayer [12]. We note that the difference between the μ_0 values is somewhat larger than between the matrix elements.

It is straightforward to derive the isotope effect for the matrix elements μ_1 and μ_2 . Assuming that the substrate mass is infinite one obtains for H_2 and D_2

$$\mu_1(D_2) = \mu_1(H_2)(1/\sqrt{2})^{1/2},$$

$$\mu_2(D_2) = \mu_2(H_2)1/\sqrt{2}$$

Using the experimental values for H_2 we get $\mu_1 = |0.017|D$ and $\mu_2 = |0.0063|D$ for D_2 which agree very well with the measured D_2 values $\mu_1 = |0.017|D$ and $\mu_2 = |0.0070|D$.

We can also apply the model to the dipole active $(j, m) = (0, 0) \rightarrow (1, 0)$ rotational transition of HD. First we note that the orientational dependence of the molecule-surface interaction is dominated by the van der Waals interaction [11] which shifts the $(1, 0)$ rotational sublevel of HD by -1.0 meV [13] from 11.1 meV to 10.1 meV in good agreement with the measured energy 9.9 meV. The orientational dependence will also influence the induced dipole moment but the magnitude of this effect is not known. The measured dipole matrix element $\mu_R = 0.0077$ D is, however, much larger than the free molecule value 0.00058 D [14]. This enhancement must in part originate from the separation $\Delta r = 0.124$ Å of the molecular mass and electronic centers. The induced polarization will oscillate when the molecule rotates around the mass center because of the motion of the electronic center with respect to the metal surface. The dipole matrix element for the rotational transition is given by $\mu_R = p'_z \Delta r \langle 10 | \cos \theta | 00 \rangle = p'_z \Delta r / \sqrt{3}$. When evaluated in the equilibrium position we get $\mu_R = -0.0039$ D which is clearly much larger than the free molecule value but smaller than the measured value. The deviation is larger than we observe for μ_1 (also $\propto p'_z$) which indicates that other effects contribute to μ_R .

In conclusion, we have shown that the vibrational motion in the physisorption well is dipole active and that the related dipole moment function can be measured in substantial detail at equilibrium distance. We find that a good estimate of this function can be obtained from a current van der Waals description of the adsorbate-metal substrate interaction. The data give explicit knowledge about the gradients of the polarization in this complex transition regime between nonlocal and local electron-electron interactions. Our observations have other interesting consequences. For example, considering the

shallow anharmonic potential well and the strongly nonlinear dipole moment function encountered in the H_2 -Cu system suggests the possibility of direct bound-free infrared photodesorption of the adsorbed molecules [15]. The rates are presumably small and we have made no attempt to study this effect in the present work.

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