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Rotational excitation of physisorbed H₂ by low-energy electron scattering

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The inelastic-scattering spectrum for pure rotational transitions $(J, m) = (0, 0) \rightarrow (2, m)$ by low-energy electrons ($2 < E < 5$ eV) is calculated for H₂ molecules physisorbed on a flat surface. The anisotropic interaction with the surface is modeled by a $\cos^2\theta$ potential, and scattering is assumed to be dominated by the $^2\Sigma_u^+$ resonance. Comparison is made to the recent experimental results of Avouris, Schmeisser, and Demuth for H₂ on Ag.

Avouris, Schmeisser, and Demuth¹ have recently reported observations of the pure rotational transition $J = 0 \rightarrow 2$ of H₂ and D₂ adsorbed on an Ag surface at 10 K by low-energy (~ 3 eV) inelastic electron spectroscopy. At submonolayer coverage, the energy of the observed transition for H₂ is 49 meV which is about 10% larger than the free rotor value, $6B = 44$ meV found in gas² and solid phase³ spectroscopy. The result for D₂ is similar, but the rotational energy is only half as large, and the shift is not as well resolved.

The observed small perturbation of the $J = 0 \rightarrow 2$ transition energy implies that the rotational motion of the molecule is only weakly hindered by the anisotropic potential of the surface. Since the potential is weak, we expect it to be well approximated by the lowest nonvanishing term in its spherical harmonic expansion

$$V(\theta) = V_s(3 \cos^2\theta - 1)/2 \quad (1)$$

and its effect on the rotational splittings to be given by first-order perturbation theory. In fact, the effect of the model potential of Eq. (1) can be calculated exactly in terms of the eigenvalues and eigenfunctions of the spheroidal wave equation.⁴ One finds that the $(J, m) = (0, 0)$ level is shifted down by an amount which is quadratic in V_s/B , and that the $(J, m) = (2, m)$; $m = 0, \pm 1, \pm 2$ manifold is split into three levels with energies $6B + V_s(2 - m^2)/7$ in first-order perturbation theory.

Intuitively one expects that $V_s > 0$, i.e., that the internuclear axis prefers to lie in the plane of the surface. This implies that the $m = 0$ and ± 1 levels move up while the $m = \pm 2$ levels shift to lower energy. Since the experimentally determined transition

energy is larger than $6B$, we are led to expect that the cross section must be dominated by transitions to the $(2, 0)$ state, at least for the geometry employed by Avouris, Schmeisser, and Demuth.¹ An alternative explanation proposed by Avouris *et al.* is that B is larger for H₂ on Ag than it is for H₂ in free space because the internuclear separation r_e is reduced. This explanation seems rather implausible when one considers the fact that H₂ dissociates on most metal surfaces, corresponding to $r_e \rightarrow \infty$ and $B \rightarrow 0$.

The inelastic scattering cross section for rotational excitation is derived as follows: For the energy of interest, 3 eV, H₂-electron scattering is essentially all p wave.⁵ Taking the z axis along the incident electron beam, the amplitude for scattering into the direction Ω from a molecule oriented along the direction χ is⁶

$$f(\Omega, \chi) = \sum_{m, m'} a_{ll'm} D_{m, m'}^{(l)}(\chi) D_{0m}^{(l)}(\chi) Y_{l'm'}(\Omega) \quad (2)$$

The coefficients $a_{ll'm}$ are scattering parameters which may be obtained from a fixed-nuclei calculation. For p -wave scattering, $l = l' = 1$. $D_{m, m'}^{(1)}(\chi)$ and $Y_{l'm'}(\Omega)$ are, respectively, rotation matrices and spherical harmonics of rank 1. To simplify the calculation, let Ω be along the x direction corresponding to right-angle scattering. Then $Y_{l'm'}(\Omega) = -(3/8\pi)^{1/2} m'$.

The amplitude for scattering from the $(0, 0)$ to the (J, m'') rotational state where the projection is onto the z (incident beam) direction is

$$\langle 2, m'' | f(\Omega) | 0, 0 \rangle = a_p (\delta_{m''1} - \delta_{m'', -1}) / \sqrt{2} \quad (3)$$

where

$$a_p = 2^{-1/2} \sum_m C(211; 0, m) a_{11m} \quad (4)$$

Of course the rotational energy eigenstates are quantized with respect to the surface. If the orientation of the molecule with respect to the normal to the surface is χ_s , then

$$Y_2^m(\chi_s) = \sum_{m''} D_{m'',m}^{(2)}(0, \beta, 0) Y_2^{m''}(\chi) , \quad (5)$$

where β is the angle between the normal to the surface and the direction of the incident beam, and the scattered intensity is given by

$$I(2, m) = (|a_p|^2/2) |D_{m}^{(2)}(0, \beta, 0) - D_{-1m}^{(2)}(0, \beta, 0)|^2 \quad (6)$$

or

$$I(2, 0) = (3|a_p|^2/4) \sin^2 2\beta , \quad (7a)$$

$$I(2, 1) + I(2, -1) = |a_p|^2 \cos^2 \beta , \quad (7b)$$

$$I(2, 2) + I(2, -2) = (|a_p|^2/4) \sin^2 2\beta . \quad (7c)$$

For the experiment of Ref. 1, $\beta = 138^\circ$ and the intensities are 0.74, 0.01, and 0.25 $|a_p|^2$, respectively. Thus only transitions to the highest and lowest states should be observed, with the highest having nearly $\frac{3}{4}$ of the total intensity. In order to complete the comparison to experiment it is necessary to fit the observed line shape. If we take $V_s = 2B = 14.7$ meV, then the exact excitation energies corresponding to the model potential of Eq. (1) are $\Delta E(m) = 49.8, 46.8,$ and 40.7 meV for $|m| = 0, 1,$ and 2 , respectively. These energies and the intensities given above, combined with the experimental line shape and background of Ref. 1 are shown in Fig. 1. We note that the experiment was not capable of resolving the $m = 0$ and ± 2 features and that the only evidence that the peak contains two lines is that its width is slightly larger than the 12-meV resolution of the experiment. However, since the total splitting of the $m = 0$ and ± 2 lines is 9 meV, it would seem that a modest improvement in experimental resolution would suffice to split the two lines.

It is amusing to consider what effects might be observed at very high resolution. The analysis given above is appropriate to the dilute limit of isolated molecules. However, if the surface is smooth, then

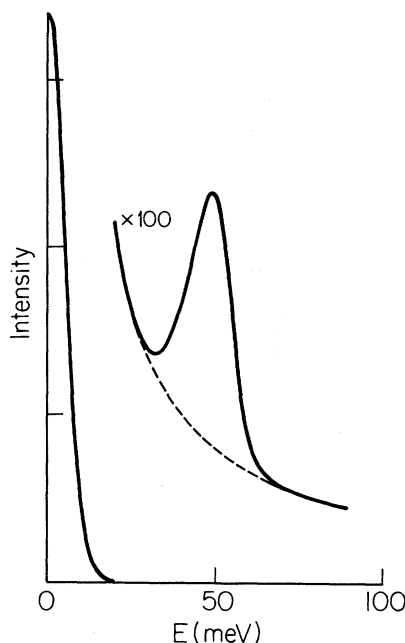


FIG. 1. Theoretical inelastic scattering spectrum for $J = 0 \rightarrow 2$ rotational excitation of H by electrons. The resolution function is assumed Gaussian with full width at half maximum = 12 meV. The inelastic peak contains features at 49.8 and 40.7 meV with intensity ratios of 3:1. The integrated area of the peak and the sloping background (dashed curve) have been chosen to fit the data of Ref. 1.

H_2 molecules in submonolayer coverages at low temperatures are likely to cluster into two-dimensional liquid or solidlike regions separated by regions of dilute gas. A $J = 2$ excitation of an H_2 molecule will act like an exciton and propagate or diffuse in the layer. Such excitations called "rotons" have been studied in solid para- H_2 and ortho- D_2 by Raman scattering.⁷ Similar high-resolution studies of rotons in para- H_2 on Ag at very low temperature could provide a useful probe of a nearly ideal two-dimensional solid.

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