

HYDROGEN INTERACTIONS WITH Ag(111): BOUND STATE SCATTERING RESONANCES AND INTERACTION POTENTIAL DETERMINATION

Chien-fan Yu, Charles S. Hogg, and Steven J. Sibener
The James Franck Institute and Department of Chemistry
The University of Chicago, 5640 South Ellis Avenue, Chicago, Illinois 60637

The elastic and rotationally resolved inelastic scattering of H₂, D₂, and HD supersonic molecular beams from Ag(111) has been examined. These studies have been undertaken primarily for two reasons: to determine the laterally averaged isotropic and anisotropic components of the hydrogen/Ag(111) interaction potential, and to test the accuracy of different levels of quantum gas-surface scattering calculations.

Very weak minima in specularly reflected H₂ and D₂ beams have been detected as a function of incident angle and azimuthal crystal orientation for several beam energies. These minima have been found to be predominantly due to diffractive selective adsorption scattering resonances. However, a few of the scattering resonances precess in the K_x - K_y momentum plane about the (00) reciprocal lattice vector—indicating that rotationally mediated selective adsorption is also occurring (refs.1-3). In Figure 1 the selective adsorption loci for D₂/Ag(111) with E_i = 37.2 meV are plotted in the momentum plane parallel to the crystal surface. The bound levels (in meV) and coupling G-vectors are labelled for each arc. The one arc which precesses about the (00) G-vector is due to rotationally mediated selective adsorption associated with the J=0→2 inelastic transition.

The D₂/Ag(111) vibrational levels have been used to determine the shape of the potential well for this system. We find that a variable exponent potential (refs.4,5) gives an excellent fit to our experimental data. This is a three parameter potential of the form:

$$V_0(z) = D \left\{ \left[1 + \frac{\lambda}{p} (z - z_e) \right]^{-2p} - 2 \left[1 + \frac{\lambda}{p} (z - z_e) \right]^{-p} \right\}$$

The three potential parameters were determined by carrying out a non-linear least squares fit of the experimentally determined D₂/Ag(111) eigenvalues to the approximate analytical eigenvalues (ref.6) of this potential. This procedure yields: D = 43.045 meV, λ = 0.618 a₀⁻¹, and p = 4.995. The well depth found in this manner is also in good agreement with our H₂ and D₂ Debye-Waller measurements, which give a well-depth of 46 meV.

These measurements are, to our knowledge, the first diffractive selective adsorption studies ever reported for a metallic close-packed fcc surface, and have shown that measurements of this type can be used even on extremely smooth (low-corrugation) surfaces. Preliminary results with H_2 are in very close agreement with those obtained with D_2 . However, small but consistent shifts in the H_2 levels are observed from those predicted by the best fit D_2 potential. We believe that these shifts are due to J and m splittings which are a direct consequence of the anisotropic component of the laterally averaged molecule-surface potential. Experiments with ortho and para hydrogen beams are now being conducted to conclusively resolve these slight level shifts. Preliminary results indicate that the anisotropy parameter, β , of the potential: $V_0(z, \theta) = v_0(z) [1 + \beta P_2(\cos\theta)]$ has a value $-0.35 \leq \beta \leq -0.05$. Further refinement of this value is anticipated. Analysis of rotationally resolved inelastic scattering probabilities for H_2 and D_2 as a function of collision energy should also allow for another (independent) determination of this parameter.

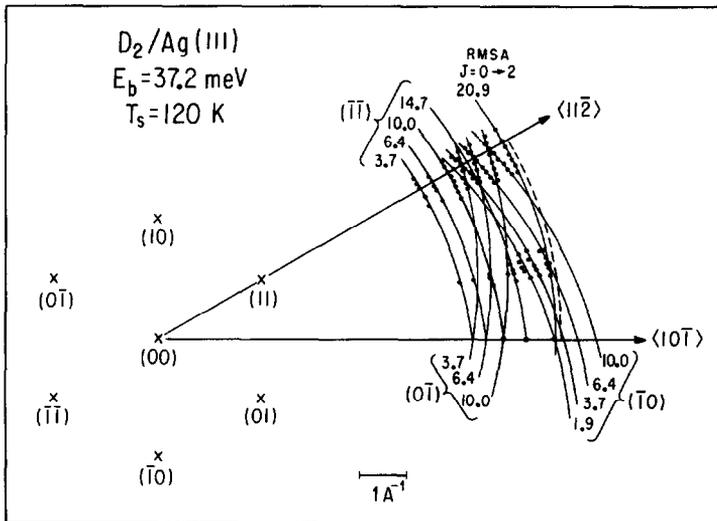


Fig. 1 Selective adsorption loci for $D_2/Ag(111)$ plotted in the momentum plane parallel to the crystal surface. The dashed line denotes the limit of accessible energies probed in this experiment.

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