

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

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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.

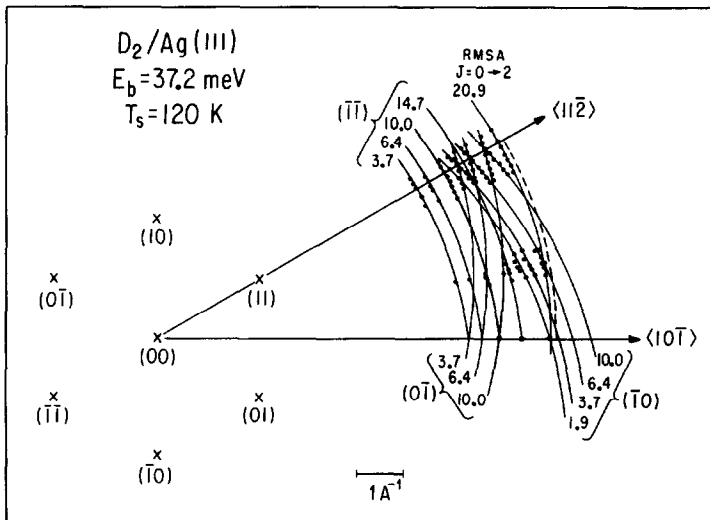


Fig. 1 Selective adsorption loci for $D_2/Ag(111)$ plotted in the momentum plane parallel to the crystal surface. The dashed line denotes the limit of accessible energies probed in this experiment.

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