ELECTRONIC SURFACE RESONANCE ENHANCEMENT OF VIBRATIONAL LOSS

INTENSITIES

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ABSTRACT

A high resolution EELS study of the electron reflectivity lineshape and \((E, k_f)
\) dispersion relations of surface barrier resonances on \(W(100)\) is reported. Their effect on the impact energy dependence of the symmetric stretch-vibration excitation cross-section of chemisorbed hydrogen is to produce resonance enhancement. Results are presented for both the low coverage \(c(2 \times 2)H\) and high coverage \(p(1 \times 1)H\) chemisorbed layers. The energies of these resonances would appear to fit a simple Rydberg type series of levels for a smooth monotonic image potential surface barrier. However, the dispersion behaviour of the intense "ground state level" is shown to be anomalous and to deviate strongly from two-dimensional free electron behaviour. Strong resonance intensity is found only for energies corresponding to energy gaps in the surface projection of bulk states. The effect on adsorbate vibrational selection rules is discussed in terms of the degree to which the resonance electron density overlaps the short range scattering potential of the vibrating atoms.

INTRODUCTION

The overall process underlying any observation of inelastic reflection of electrons at surfaces is usually pictured as a sequence of events which include an elastic reflection either preceded or followed by inelastic scattering\(^1\). Under certain conditions, low energy electrons incident on a crystal surface can become temporarily trapped in electron surface states\(^2\). The electron-surface interaction produces a surface (electrostatic
image) barrier which refracts the incident electron beam and can cause total internal reflection of back-scattered diffracted beams. Non-specular beams emerging from the crystal substrate which have insufficient kinetic energy normal to the surface to surmount this surface potential energy barrier are scattered back into the crystal. If the beam is subsequently strongly reflected by the substrate atoms, a sustained multiple scattering can occur between the barrier and the crystal. The interference between the specularly scattered and multiply internally reflected waves produces narrow fluctuations of elastic (specular) scattering intensity with respect to variation of the incident beam energy $E_0$ and incident direction, defined in terms of the polar angle $\theta_i$. These temporary or nonstationary states are quantized with respect to the electron's momentum normal to the surface, forming a discrete Rydberg-like series of energy levels associated with the Coulombic form of the surface barrier potential $\mathcal{P}$. The lifetime of these states is relatively long and, since the electrons are confined to a region close to the surface, we expect that such conditions will lead to a resonant enhancement of inelastic losses arising from the vibrational excitation of adsorbate-induced surface modes $\text{a}$. This mechanism of "inelastic surface resonance scattering" is illustrated in Fig. 1.

An electron can scatter directly from the surface, exciting an adsorbed molecule $X$ in the process. Alternatively, providing the $(E, k'_\parallel)$ values correspond to an elastic resonance condition, the electrons can become temporarily trapped in a surface resonance state, thereby enhancing the vibrational excitation cross-sections. The inelastic reflection corresponding to excitation energy $E' = E - \Delta E_{\text{loss}}$ and parallel momentum transfer $k'_\parallel$, will exhibit resonance fluctuations for $(E, k'_\parallel)$ values displaced by $(E', k'_\parallel)$ from the elastic resonances. The ratio of the inelastic to elastic intensi-

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**Figure 1** - Schematic drawing illustrating the direct and surface resonance mechanisms of inelastic interaction with an adsorbed molecule $X$: $k_0$ and $k_1$ refer to the incident and scattered electron wavevectors respectively.