

RELAXATION SHIFTS AND SINGULAR BROADENING IN THE
SPECTRA OF ADSORBED SPECIES

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The interaction of adsorbed atomic or molecular species with metallic surfaces can be studied via the valence electronic structure of the adsorbates. Various spectroscopic methods for measuring changes in the adsorbate electronic spectra include photoemission, field emission, ion neutralization and others. A common feature of such spectra are shifts in energy and sometimes broadening with respect to the gas phase levels. Here we present a model which makes possible a separate treatment of the interactions leading to chemisorption bond and nonbonding image effects important in stabilizing cationic species. Here we shall confine our attention to the case of a single atom with an s-like valence orbital adsorbed on a transition metal surface and employ the Newns¹⁾-Anderson²⁾ model appropriate for neutral chemisorption. The Hamiltonian of this model reads:

$$H = \sum_{k\sigma} \epsilon_k n_{k\sigma} + \sum_{\sigma} \epsilon_a n_{a\sigma} + \sum_k (V_{ak} c_{a\sigma}^\dagger c_{k\sigma} + \text{h.c.}) + U n_{a\uparrow} n_{a\downarrow}, \quad (1)$$

where $c_{a\sigma}^\dagger$ and $c_{k\sigma}^\dagger$ are the creation operators for the adatom valence state $|a\rangle$ of energy ϵ_a and the substrate state $|k\rangle$ of energy ϵ_k , respectively, and $n = c^\dagger c$. V_{ak} is the electron hopping term due to chemisorption and U denotes the effective intra-adatom Coulomb integral. In addition to (1), we introduce the surface response function³⁾ which describes the interaction of the adatom charge with its dynamic image. For nearly spherical adatom orbitals centered at distance d outside the metal surface, this is defined as:

$$R_Q(\omega) = (2\pi e^2/Q) e^{-2ad} (1 - \epsilon_a(\omega)) / (1 + \epsilon_a(\omega)), \quad (2)$$

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where \vec{Q} is a wavevector parallel to the surface, e is the electron charge and $\epsilon_a(\omega)$ is a dielectric function of the semi-infinite medium⁴⁾. The RPA limit of (2) which comprises single-pair excitations and surface plasmons gives rise to nonbonding relaxation shifts, satellites and sometimes singular broadening in the spectra of adsorbate species.

For nonbonding long lifetime orbitals ($V_{ak} \neq 0$), the spectral density takes the form:

$$\rho_{a\sigma}^{\pm}(\omega) = \sum_{n=0}^{\infty} e^{-n\nu/\omega_S} \frac{(\nu/\omega_S)^n}{n!} F^{\pm}(\omega - \epsilon_{a\sigma} \mp n\omega_S), \quad (3)$$

where (+) and (-) refers to electrons and holes, respectively, $\nu = e^2/4d$, ω_S = surface plasmon frequency, $\epsilon_{a\sigma} = \phi - I + (U - 2\nu) \cdot \langle n_{a-} + \nu$ with ϕ = substrate work function, I = ionization potential and

$$F^{\pm}(\omega) = e^{\pm \frac{2d}{v_F} \omega} (\pm \omega)^{\gamma(d)-1} \left(\frac{2d}{v_F}\right)^{\gamma(d)} \Theta(\pm \omega) / \Gamma(\gamma(d)). \quad (4)$$

Here the singular exponent is given by:

$$\gamma(d) = (8k_F^2 d^2)^{-1} \ln(1.59k_{TF}d), \quad (5)$$

with v_F = Fermi velocity, k_F Fermi wavevector, k_{TF} Fermi-Thomas wavevector and Γ is the gamma function.

In the case of chemisorbed orbitals ($V_{ka} \neq 0$), when U is treated in the HF approximation and pair excitations are neglected in (2), a specific diagrammatic technique⁵⁾ gives

$$\pi \rho_{a\sigma}(\omega) = \frac{(1-z)\Delta}{(\omega - \epsilon_{a\sigma} - \Lambda)^2 + \Delta^2} + \frac{z(\nu/\omega_S)\Delta}{(\omega - \epsilon_{a\sigma} - \omega_S - (\nu/\omega_S)\Lambda)^2 + (\nu/\omega_S)^2 \Delta^2} \quad (6)$$

in the limit $v \ll \omega_S$ for the a-levels high above the Fermi level (e.g. alkalis). In (6) the width of the broadened a-level $\Delta(\omega) = \pi \int_k |V_{ak}|^2 \delta(\omega - \epsilon_k)$ at $\omega = \phi - I$ is assumed much smaller than $\epsilon_{a\sigma}$ and ω_S , Λ is a Hilbert transform of Δ and $z \approx \nu/\omega_S$.

References

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