PLASMON SATELLITES AND RELAXATION SHIFTS IN ABSORPTION SPECTROSCOPY OF ADSORBED ATOMS

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Spectroscopies in which a bound electron belonging to an adsorbed atom is excited to a nonlocalized final state such as UPS and XPS, are powerful tools for investigation of adsorbate valence electronic structure. However, as the measured spectra comprise the characteristics of the intrinsic structure of the localized level and the sudden removal of the photoelectron together with the interference effects of these two processes, the deconvolution of the above contributions in the final state may be very difficult. Absorption spectroscopies in which an electron is excited from a core into an unoccupied valence level of the adatom avoid the afore-mentioned difficulties, since the initial and final states belong to the same adatom. Here we present a quantum calculation of relaxation shifts and plasmon satellites which may occur in such a transition[1]. An example might be a core → valence 6s transition in adsorbed xenon. Ignoring the spin degeneracy of the levels, the Hamiltonian of our system is:

$$H = \varepsilon_a^o n_a + \varepsilon_c^o n_c + \sum_k \varepsilon_k n_k + \sum_k (V_{ak} c_a c_k + h.c.)$$

$$+ \omega_s \sum_{\vec{Q}} a^\dagger_{\vec{Q}} a_{\vec{Q}} + (n_a + n_c) \sum_{\vec{Q}} \lambda_A (a_{\vec{Q}} + a_{-\vec{Q}}) - W^o n_a (1 - n_c) \quad , \qquad (1)$$

the notation for the a-level being the same as in the preceding article, $\varepsilon_c^o = \varepsilon_c^g + 2v$, where g denotes the corresponding gas phase level, W^o is a Coulomb integral which accounts for the intra-adatom relaxation shifts, $a^\dagger_{\vec{Q}}$ and $a_{\vec{Q}}$ create and annihilate a surface plasmon of frequency

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ω and wavevector $\vec{Q}$ and $\lambda_a=(\pi e^2\omega_s/a)^{1/2}\ e^{-ad}$ for a nearly spherical orbital centered at d outside the substrate surface.

The optical absorption is proportional to the imaginary part of the Fourier transform of the response function:

$$R(t) = -i <O|T\ X(t)\ X(O)|O> , \qquad (2)$$

where t=time, $|O>$ =ground state of the system, T=time ordering operator and $X=(c_a^\dagger c_c+c_c^\dagger c_a)$. Our method of solution first involves a unitary transformation to $H'=U^{-1}HU$, where $U=\exp\{-(n_a+n_c)\sum_Q(\lambda_a/\omega_s)a_a^\dagger+a_{-a})$ which gives:

$$H'= \varepsilon_a n_a+\varepsilon_c n_c + \sum_k \varepsilon_k n_k+\omega_s \sum_Q a_{\vec{Q}}^\dagger a_{\vec{Q}} + Wn_a n_c$$

$$+ \sum_k \{V_{ak} c_a^\dagger c_k \exp|\sum_Q(\lambda_a/\omega_s)(a_{\vec{Q}}^\dagger-a_{-\vec{Q}})| + h.c.\} . \qquad (3)$$

Here $\varepsilon_a=\varepsilon_a^o-v-W^o$, $\varepsilon_c=\varepsilon_c^o-v$, $W=W^o-2v$ and $v=e^2/4d$. For ε_a sufficiently high above the Fermi level, the term W may be neglected. Then, since $X'= X$, the response function (2) factorizes into a product of the unperturbed core level propagator G_c and a complete propagator G_a in which all V_{ka} and V_{ak} vertices are mutually connected by plasmon propagators. A Dyson expansion is obtained by using the Mayer f-like expansion to disconnect the plasmon lines. Here we present the results of the one-plasmon approximation $v<<\omega_s$ when the width $\Delta(\omega)$ of the a-level resonance is only significant about $\omega=\varepsilon_a$ and where the band width D of Δ is large compared with both ε_a and ω_s. Then the optical absorption at frequency ω_s is proportional to:

$$-\pi\ \mathrm{Im}\ R(\omega) = \frac{(1-z)\Delta}{(\omega-\omega_{ac}-\Lambda)^2+\Delta^2} + \frac{z\Delta}{(\omega-\omega_{ac}-\Lambda-\omega_s)^2+\Delta^2} , \qquad (4)$$

where $\Delta=\Delta(\varepsilon_a-v)$, $\Lambda=\Lambda(\varepsilon_a^g-W^o)+O(\Delta^2/D^2)$ and $\omega_{ac}=\varepsilon_a^g-\varepsilon_c^g$. The first term in (4) describes elastic transitions from ε_c to the valence level resonance of width Δ and the second term describes a transition accompanied by a surface plasmon loss with the probability $z \simeq (v\Delta^2/\omega_s D^2)$ which is strongly reduced with respect to the corresponding probability in XPS.[2)]

References

1) B. Gumhalter and D.M. Newns, Phys. Lett. 57A 423 (1976).
2) J. Harris, Solid State Comm. 16, 671 (1975).