

Reply to "Dynamics of core-hole decay in adsorbates"

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First, arguments are given that, at least in the case of strongly coupled adsorbates, a fast electronic rearrangement occurs *between* the primary excitation step (resonant x-ray absorption or x-ray-photoemission process) and core-hole decay such that the decay starts from a fully relaxed neutral core-hole state, independently of the primary excitation process. Second, the highest-kinetic-energy peak of the Auger spectrum of weakly coupled CO on Cu is still believed to belong to a $5\sigma^{-1}\pi^{-1}$ final state resulting from a weakly screened initial state, rather than to a π_M^{-2} final state as has been suggested by Ohno.

The preceding interesting Comment¹ deals with a not yet fully resolved issue. However, we think that some of the points made are not well taken. In the following we shall thus try to clarify why we disagree with the major conclusions drawn. We shall also use very recent results as corroboration of our arguments.

Basically, two main questions are addressed in the Comment.¹ First, the relationship between x-ray-absorption resonances and x-ray-photoemission energies is discussed for strongly adsorbed molecules; based on the conclusions drawn, a tentative explanation for the similarity between resonantly and off-resonantly excited Auger spectra is given. Second, the nature of a distinct double-peak structure in the Auger spectra of a specific weakly bound system, namely CO on Cu, is addressed.

The main conclusion of the first part is that the experimentally observed equivalence of Auger decay spectra following resonant and off-resonant excitation, respectively, is purely accidental despite the experimental fact² that these two excitation processes require different energies and hence should lead to different Auger initial states.¹ The reason for their striking similarity is believed to be due to a cancellation of the various effective Coulomb interaction integrals.¹ It is hard to understand why the presence of the π^* -spectator electron should not lead to a significantly different Coulomb interaction causing, for instance, a rearrangement of the valence orbitals. It seems even more unlikely that these terms should cancel each other for such different adsorbate systems as CO/Ni(111),³ CO/Ru(001),⁴ CO+K/Ni(111),³ CO+K/Ru(001),⁴ and NO/Ni(111) (Ref. 5) for which the equivalence of resonantly and off-resonantly excited Auger decay spectra has been observed experimentally.

Quite on the contrary, there are strong arguments for a fast charge rearrangement *between* the primary excitation step and core-hole decay which leads to the result that decay starts from a fully relaxed neutral core-hole state, independently of the primary excitation process. In addition

to the arguments given in Refs. 2, 3, and 6 we present two additional, very recent results.

First, we have recently compared CO on Pt(111),⁷ a strongly coupled system showing no difference between resonant and off-resonant Auger decay, and physisorbed CO on a monatomic Xe spacer layer on Pt(111), for which participant (one-hole) final states and a large (~ 7 eV) spectator shift are observed after resonant excitation. The absorption spectra show that the linewidths of the π^* -resonances for the two systems differ by about a factor of 10, similar to the case of CO/Ni(111) and condensed CO reported earlier.⁸ This is a clear indication that a fast relaxation process is highly likely for strongly coupled adsorbates, fast on the time scale of the core-hole decay which mainly governs the linewidth of the resonance for the physisorbed species. We note that the origin of the energy difference between the energetically lower (adiabatic) x-ray-photoemission final state and the x-ray-absorption final state is not yet fully understood. We believe, however, that a cluster model with a single metal atom¹ is inadequate for a solution of this question, especially when fast relaxation processes and the correspondingly large bandwidths of the participating states are involved.

Second, for very weakly adsorbed SF₆ on various substrates we observed additional (high-energy) Auger structures with intensities that increase proportional to the strength of adsorbate-substrate coupling.⁹ These features arise because of charge-transfer screening of the core-hole state, which is the more likely the stronger the coupling. Note, however, that this charge-transfer must occur *between* the x-ray-photoemission process and Auger decay since no charge transfer screening is observed in the x-ray-photoemission spectra in all cases.⁹

We now turn to the second major issue of the Comment: the assignment of the [high-kinetic-energy (KE)] double-peak structure in the Auger spectra of CO on Cu. We would like to point out why we think that the peak

with highest kinetic energy cannot be attributed to a double hole in the bonding π_M orbital. First, Ohno completely neglects the difference in initial occupancy of the bonding π_M orbital which in turn should give a higher intensity for this peak the more *strongly* bound the molecule is. The opposite is found experimentally.^{2-4,6} Second, considering the carbonyl case,¹⁰ this peak has indeed very small intensity in both resonantly ($1s \rightarrow \pi^*$) and off-resonantly excited Auger spectra. While in the former case Ohno assigns this peak to a 5σ autoionization (participant) state (i.e., $5\sigma^{-1}\pi^{*-1}$), he postulates that in the latter case it should be due to a π_M^{-2} final state. However, there is no indication for a significant π_M participant (i.e., $\pi_M^{-1}\pi^{*-1}$) contribution in the resonantly excited spectra (see also Ref. 1), which should be observable if the second-highest KE peak is due to a spectator-shifted $5\sigma^{-1}\pi_M^{-1}$ state with a minor contribution from a 4σ participant ($4\sigma^{-1}\pi^{*-1}$) decay. Thus we conclude that the carbonyl example does not corroborate the interpretation given by Ohno for the CO/Cu case.

On the contrary, the absence of a double-peak structure in the off-resonantly excited carbonyl spectra implies

that it is related to two different states involving the 5σ electron, namely $5\sigma^{-1}\pi^{*-1}$ (i.e., 5σ participant peak), and $5\sigma^{-1}\pi_M^{-1}$ (i.e., spectator-shifted peak). The involvement of the 5σ and π orbitals is also the reason why the double-peak structure is smaller in the oxygen decay spectra but nevertheless still visible.

In summary, we find a two-peak structure for CO/Cu which does not depend on the primary excitation process, in contrast to the case of carbonyls, and which appears with almost equal intensity ratio and angular dependence for C and O Auger spectra.^{3,4} These observations make it very unlikely that the two peaks belong to two different types of final states with different symmetry and local overlap, such as $5\sigma^{-1}\pi^{*-1}$ and π_M^{-2} , as has been suggested by Ohno.¹ Rather, we still believe that they belong to the same type of final state ($5\sigma^{-1}\pi^{-1}$) but arise from two different Auger initial states.

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