

Ji, Lu, and Gao Reply: In the preceding Comment [1], the key issue that Schreiber *et al.* raise is in regards to the photoemission process and its time scale, which were not discussed in detail in our Letter [2] due to the page limit, and now we clarify as follows. In our Letter [2], we emphasized that the effect of core-hole induced structural relaxations must be considered in normal incidence x-ray standing wave experiments. Specifically there are two aspects of the core-hole induced relaxation: i.e., the rapid electronic one and the subsequent slow ionic one. When a core hole is created on perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) adsorbed on Ag(111), the valence electrons will relax, and a portion of the substrate electrons will transfer onto unoccupied antibonding orbitals to screen the core hole, keeping the system neutral. This brings out the chemical environment changes, resulting in the changes of core level chemical shift that we described between the electronic initial state and the ionic initial state (IIS), and further induces the ionic structure relaxed to a new one in response to the changes of the electronic structure that we described between the IIS and the ionic final state. On the time scale, electronic relaxation is quickly done in femtoseconds while ionic relaxation takes about 100 fs. Because of misunderstanding and confusion regarding the two different time-scale processes, Schreiber *et al.* raised the second question of an inherent inconsistency with our Letter.

Basically, there are two kinds of associated processes to eliminate the core hole [3]. The first one is the Auger process, which results in two outer shell holes left. As mentioned by Schreiber *et al.*, this process is rapid, usually thought to be at the time scale of a few femtoseconds. The other process is the x-ray fluorescence process, in which a valence electron combines with the core hole, giving off a fluorescence of $h\nu$. Its time scale is almost 3 orders of magnitude larger than that of the Auger process, i.e., a few picoseconds [4]. The transition matrix elements of a nonradiative Auger process are determined by the Coulomb interactions between the initial and final states, formulated by several two-center integrals. In PTCDA on Ag(111), the $2s$ and $2p$ electrons of C and O are highly hybridized and delocalized. What happens here is the KVV Auger process, the outer shell holes being the valence holes. This makes the integrated transition rates different from, and very likely much smaller than, localized systems like free molecules. Thus the core hole's lifetime derived from simple molecules may not be appropriate to the system like PTCDA on Ag(111). Actually a recent study shows an 88 fs lifetime for S $2p$ core hole [4]. This suggests that a long-lived core hole indeed exists in certain circumstances, which is up to the time scale of ionic motions (~ 100 fs). On the other hand, for a KVV Auger process, even in the case that the core hole's lifetime is very short, the resulting two valence holes would hold a few ps [5], which still keeps the system away from equilibrium.

As a matter of fact, ionic structure relaxation induced by core excitation was observed [6] a decade ago and investigated in recent years [7]. One further proposed a new method to synthesize diamond from graphite by core excitations [5]. The idea is similar to the one we used in studying the 16FCuPc case [2].

Schreiber *et al.* asked the third question of whether or not the density-functional theory (DFT) method we used is proper, whereas they claim that the PTCDA-Ag(111) interactions are all based on dispersion effects. This would be true if the dispersion effects could (1) generate charge transfers, (2) hybridize electronic states, or (3) shorten the C/O-Ag distances so that they are over 0.5 Å shorter than the sum of the VdW radius, all of them happening in PTCDA on Ag(111). Clearly the dispersion effects can do none of the above. In addition, the measured adsorption energy of PTCDA on Ag(111) by the authors is over 1 eV [8]. It is very clear that the PTCDA-Ag(111) interaction is of an electronic (chemical) nature, which can be well described by DFT. Actually, Ref. [2] in the Comment shows that the authors regard the PTCDA-Ag interaction as a chemical one as well. The state at 0.3 eV is the antibonding state hybridized by PTCDA's lowest unoccupied molecular orbital (LUMO) and Ag $s(p)$ state. What the UV-PES experiment observed is the LUMO-Ag hybrid bonding state, being 0.5 eV below the Fermi level in our calculation. The authors failed to understand our data.

Finally, there is a technical misunderstanding. In our Letter, a chemical bond forms between *carboxylic* O atoms and the Ag atoms underneath, which the authors question from the fact that there is no chemical interaction between *anhydride* O atoms and Ag atoms.

Wei Ji,¹ Zhong-Yi Lu,² and Hongjun Gao¹

¹Beijing National Laboratory for Condensed Matter Physics
Institute of Physics
Chinese Academy of Sciences
P.O. Box 603, Beijing 100080, China

²Department of Physics
Renmin University of China
Beijing 100872, China

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