

Comment on “Electron Core-Hole Interaction and Its Induced Ionic Structural Relaxation in Molecular Systems under X-Ray Irradiation”

In a recent Letter [1] Ji *et al.* discuss the electron core-hole interaction and its induced structural relaxation in molecular systems under x-ray irradiation. They claim that both intramolecular electronic and subsequent structural relaxation effects have to be taken into account when explaining x-ray standing wave (XSW) data by density-functional theory (DFT). In essence, they question that XSW experiments with x-ray photoemission spectroscopy (XPS) detection [2–5] determine initial-state nuclear coordinates. They reinterpret recent experiments in a way inconsistent with established knowledge about the photoemission (PES) process, in particular, the applicability of the Born-Oppenheimer approximation. It is therefore important to comment on the shortcomings of Ref. [1].

(1) *Photoemission process and its time scale.*—The PES intensity depends on the initial and final state electron wave functions [6]. It is important to what extent this final state can be influenced by electronic and nuclear relaxation effects. For that reason time scales have to be considered, which Ji *et al.* failed to discuss. The PES process as well as the associated electronic relaxation typically take place on a (sub-)fs time scale [6]. It is terminated by the subsequent Auger decay which, e.g., for an O atom occurs 3.6×10^{-15} s after photoexcitation as derived from lifetime broadening. This is much faster than the nuclear motion, which can be estimated, e.g., for 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) by the frequency of the C=O out-of-plane bending mode (400 cm^{-1}). This motion takes $\sim 10^{-13}$ s, i.e., at least 20 times longer than the PES process. Therefore, the Born-Oppenheimer approximation holds for PES and the XSW experiment.

Since the IFS (ionic final state, after electronic and conformational relaxation) of Ji *et al.* is an inappropriate description for the PES process one may ask whether the IIS (initial ionic state, only electronic relaxation) or even the electronic initial state (EIS) model is more suited. The truth lies in between: the *intramolecular* electronic relaxation is fast compared to the PES time scale while charge transfer screening from the substrate is on the same time scale. This can be nicely observed for PTCDA on Ag(111): The monolayer XPS spectra show both an electronically fully relaxed final state after charge transfer screening (IIS) as well as a partly relaxed final state with only *intramolecular* screening (between EIS and IIS) [7]. Thus, in the context of the determination of nuclear coordinates by XSW, it is clear that the fast electronic relaxation processes proceed in the presence of unrelaxed nuclear coordinates.

(2) *Inherent inconsistency.*—The IIS values for chemical shifts are in full agreement with experiment, whereas the IFS values are significantly off, see [1]. Thus, even if the approach of Ji *et al.* were appropriate, this should have led the authors to conclude that *only* the IIS information is contained in the measured PES intensity.

(3) *Computational approach.*—It is well known that DFT calculations have difficulties to describe dispersion effects. Therefore, despite the success of DFT in other areas, absolute statements on the binding geometry of these systems [2–5] as made by Ji *et al.* are questionable, and the suggested agreement for a certain (arbitrary) mix between two scenarios (IIS/IFS) obviously does not prove that they have properly taken into account the relevant effects.

The problems of the computational approach can also be seen from two further statements of Ref. [1]. First, the claimed formation of a direct chemical bond between anhydride O and Ag atoms is clearly ruled out by published spectroscopic results, especially by x-ray absorption data [8]. Second, the result [1] that the hybridized lowest unoccupied molecular orbital (LUMO) lies 0.3 eV above the Fermi level, and hence is empty, is at variance with the experimental result of UV PES which unambiguously finds a new, mostly filled orbital *below* the Fermi level [8].

In summary, the conclusions by Ji *et al.* are misleading, since they are based on an inappropriate picture of the photoemission process and an unsuitable computational approach for the issue they are addressing. The geometries derived from XSW experiments [2–5] hence correspond to initial-state nuclear coordinates.

The authors thank G. Heimel, G. Kresse, and L. Kronik for fruitful discussions.

F. Schreiber,¹ A. Gerlach,¹ N. Koch,² E. Zojer,³
M. Sokolowski,⁴ F. S. Tautz,⁵ M. Rohlfing,⁶ and
E. Umbach⁷

¹Universität Tübingen

Auf der Morgenstelle 10, 72076 Tübingen, Germany

²Humboldt-Universität zu Berlin

Newtonstrasse 15, 12489 Berlin, Germany

³Technische Universität Graz

Petersgasse 16, 8010 Graz, Austria

⁴Universität Bonn

Wegekerstrasse 12, 53115 Bonn, Germany

⁵Jacobs University Bremen

Campus Ring 8, 28725 Bremen, Germany

⁶Universität Osnabrück, Barbarastrasse 7

49069 Osnabrück, Germany

⁷Universität Würzburg

Am Hubland, 97074 Würzburg, Germany

Received 16 February 2007; published 1 August 2007

DOI: [10.1103/PhysRevLett.99.059601](https://doi.org/10.1103/PhysRevLett.99.059601)

PACS numbers: 68.49.Uv, 68.43.Bc, 73.20.-r, 79.60.Fr

[1] Wei Ji, Zhong-Yi Lu, and Hongjun Gao, Phys. Rev. Lett. **97**, 246101 (2006).

[2] A. Hauschild *et al.*, Phys. Rev. Lett. **94**, 036106 (2005).

[3] A. Gerlach *et al.*, Phys. Rev. B **71**, 205425 (2005).

[4] J. Stanzel *et al.*, Surf. Sci. Lett. **571**, L311 (2004).

[5] A. Gerlach *et al.*, Phys. Rev. B **75**, 045401 (2007).

[6] F. J. Himpsel, Adv. Phys. **32**, 1 (1983).

[7] A. Schöll *et al.*, J. Phys. Chem. B **108**, 14741 (2004).

[8] Y. Zou *et al.*, Surf. Sci. **600**, 1240 (2006).