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

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The experiments on perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride and 16FCuPc on Ag(111) surfaces by the normal incidence x-ray standing wave are poorly reproduced by first-principles ground state calculations but well reproduced by considering initial- and final-state effects, which include the response of the valence electrons to screen a core hole created by x-ray photoemission and further induced ionic structural relaxation. This study shows that the initial- and final-state effects due to screening are of great importance in characterizing molecules on metal surfaces in the normal incidence x-ray standing wave experiments.

The interaction between large aromatic molecules and metal substrates has raised considerable interest in recent years due to their novel properties, promising to be moletronics adaptable to technical applications [1]. The molecular adsorption structure and the bonding mechanism are of essential importance to understanding the interaction of molecules and substrates, which dominates the properties of the whole system [1,2]. The widely used normal incidence x-ray standing wave (NIXSW) provides a unique way to directly and precisely measure the atomic structure, especially the vertical structure to the substrate, which is essential to understanding the bonding mechanism of large aromatic molecules on metals [3]. Unfortunately, in recent practice this technique has not clarified the question of the adsorption structure and the bonding mechanism; on the contrary, it raises a new question of how to understand the NIXSW experiments with the density-functional theory (DFT) electronic structure calculations [4–7].

The story is that recently Hauschild and co-workers measured the structure of a planar molecule perylene-3,4,9,10-tetracarboxylic-3,4,9,10-dianhydride (PTCDA) on a Ag(111) surface, as schematically shown in Fig. 1(a), by using the NIXSW [4]. The measurement shows that the adsorbed PTCDA is in a vertically distorted configuration, in which the four carboxylic O atoms bonding with the Ag atoms underneath are about 0.18 Å below the plane of the perylene core, but the two anhydride O atoms are surprisingly about 0.11 Å above the plane. Moreover, this observed structure distortion received support from their own DFT calculation using the SIESTA code [4]. Shortly thereafter, another group pointed out, however, that the former calculation was not a converged result [6]. What they found is that in the fully converged calculation both carboxylic and anhydride O atoms are below the perylene core and the molecule trends to keep planar, disagreeing with the experimental measurement [6,7].

They further claimed that the present DFT calculations cannot explain the NIXSW experiment. Meanwhile, another new NIXSW measurement of 16FCuPc on a Ag(111) surface shows that the molecule 16FCuPc is again heavily distorted, with the F atom being unexpectedly 0.2 Å higher than the molecular plane [5]. All of these pose a challenge to the state of the art of DFT calculations.

In a NIXSW experiment, adsorbate atoms will have the maximum photoemission yield when they fall into the antinode planes of a standing x-ray wave field. The NIXSW experiments thus provide two types of information, i.e., the x-ray photoemission spectroscopy (XPS) data corresponding to a core electron photoemission process and the phase data of a standing x-ray wave field corresponding to an interference process of the x ray, which, respectively, give the core electron binding energy and the contact structure of a molecule on metal [3]. In a core electron photoemission process, a core hole will be generated once a core electron is excited from a core level to the vacuum level due to the absorption of a photon. It turns out that the valence electrons will relax to respond the creation of a core hole, namely, screening the core hole.
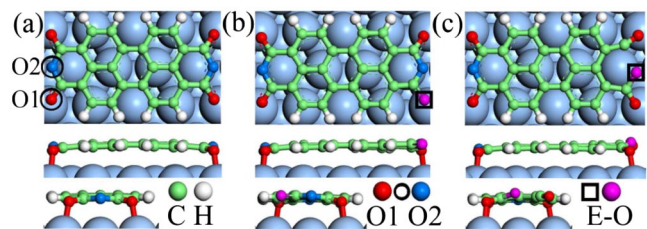

FIG. 1 (color online). Top view (top), side view (middle), and front view (bottom) of the calculated molecular geometries of PTCDA on Ag(111) in (a) the ionic initial state, (b) the ionic final state with a core hole created on carboxylic O1, and (c) on anhydride O2. E-O means the excited oxygen atom.

Subsequently, the ionic structure will relax as well due to the newly relaxed valence electronic structure. It has been known that the relaxation of the valence electrons has a significant effect on the semiconductor surface core level shift [8,9].

For a molecule PTCDA on a Ag(111) surface, currently, in both the NIXSW experiments and the DFT calculations, neither the relaxation screening of the valence electrons nor its induced ionic structural relaxation is included in experimental analysis and theoretical calculations. In this Letter, we demonstrate that it is the screening of the valence electrons to a core hole and the subsequent induced ionic structural relaxation that are responsible for the significant shift on core electron binding energies for different oxygens in PTCDA and the novel molecular distortions. With these two processes included, the DFT calculations can be in excellent agreement with the NIXSW measurements.

In order to avoid confusion, we make definitions regarding the above processes as follows. After a core hole is created due to x-ray photoemission, the electronic initial state (EIS) means that both the electronic structure and the ionic structure are kept frozen as in the neutral ground state, while the state with the electronic structure fully relaxed is defined as the ionic initial state (IIS), and the state with the ionic structure further fully relaxed is defined as the ionic final state (IFS). According to the definitions, the EIS and the IIS share the same ionic structure. We further define the core level chemical shift (CLCS) as the difference in kinetic energies of an electron emitted from the same chemical element but with different chemical environments in an adsorbate molecule. Thus, the CLCS is, in the EIS picture, simply equal to the difference between the single-particle energy eigenvalues of a core state in different chemical environments, while the CLCS is, in both the IIS picture and the IFS picture, equal to the difference in the total energies of the molecular system with a core hole generated in different chemical environments, respectively [9]. We summarize these definitions in Table I. Physically, if the relaxation of the valence electrons to screen a core hole takes place rapidly enough, the relaxation energy will be transferred to the emitted photo-

TABLE I. Definitions of initial and final states and the corresponding core level chemical shifts between oxygens O1 and O2 (shown in Fig. 1) in PTCDA on Ag(111). ESR means electronic structure relaxed, and ISR means ionic structure relaxed. E(I)I(F)S means electronic (ionic) initial (final) state. CLCS means the core level chemical shifts between oxygens O1 and O2.

	ESR?	ISR?	CLCS (eV)
EIS	No	No	1.92
IIS	Yes	No	2.33
IFS	Yes	Yes	0.50

electron. Subsequently, the ionic structure will further relax because it is no longer in equilibrium under the new relaxed electronic structure. We may thus expect that the observed XPS process will be between the EIS and the IIS, while the measured vertical atomic positions of the molecule with respect to the substrate will be between the IIS and the IFS.

We have systematically carried out theoretical DFT calculations for PTCDA and 16FCuPc on a Ag(111) surface, respectively, in which the electronic relaxation and the subsequent ionic relaxation due to the creation of a core hole were considered by the initial- and final-state pictures, respectively. The calculations were done using DFT, the local density approximation for exchange-correlation potentials [10], the projector augmented wave (PAW) method [11], and a plane wave basis set as implemented in the Vienna *ab initio* simulation package (VASP) [12]. The initial- and final-state effects were applied by a PAW-based method implemented in VASP [11]. In terms of the structure of PTCDA on Ag(111), we used a 6×7 supercell of 4-layer Ag atoms and one PTCDA to simulate the PTCDA slab. The most stable one among all possible configurations was adopted in all initial- and final-state calculations [13]. Other technical details of the calculations are described in Ref. [14].

As shown in Fig. 1, we denoted carboxylic oxygen and anhydride oxygen as O1 and O2, respectively. There are thus four O1 oxygens and two O2 oxygens for a PTCDA. Analyzing the calculations, we found that, in the ground state structure (also shared by the EIS and the IIS) shown in Fig. 1(a), each of the four O1 oxygens interacts with the substrate Ag atom underneath to form a chemical bond with a bond length of 2.45 Å. The other two O2 atoms are 0.24 Å higher than the O1 atoms with respect to the substrate but still 0.09 Å lower than the average C atoms in the perylene core. The perylene core itself is no longer planar either, with an arc of 175°. The averaged vertical distance between the perylene core and the substrate is 2.78 Å, in good agreement with the measured value of 2.86 Å. This bent aromatic core is similar to the one in the local basis DFT calculations for PTCDA on Ag(111) [6,7] and consistent with that given by the plane wave DFT calculations for NTCDA on Ag(110) [15]. Physically, a bent perylene core is more reasonable than a flat one for a PTCDA adsorbed on Ag(111) because oxygen atoms have a much stronger tendency to form chemical bonds with Ag atoms underneath than carbon atoms, as discussed in Refs. [7,15]. More importantly, the relative wide total photoemission yield curve of C indicates a vertical range of measured carbons, suggesting a bent perylene core experimentally [4]. However, we emphasize here that no ground state calculation yields that the anhydride oxygens are vertically higher than the perylene core for a PTCDA adsorbed on Ag(111), as observed in the NIXSW experiments.

The fully relaxed ionic structures of the IFS are plotted in Figs. 1(b) and 1(c), corresponding to the creation of a 1s core hole at O1 and O2, respectively. In contrast with the IIS structure [Fig. 1(a)], the excited oxygen (E-O) with a hole created and one of its adjacent oxygens lifted up by 0.3–0.4 Å (see Table II) so that the Ag-O bonds break while the others remain the same as the one in the IIS structure. Inspection of the calculations show that, when the valence electrons relax to screen a core hole, the chemical potential of the adsorbed PTCDA becomes lower and the extra charge transfers to the lowest unoccupied state. The calculations further show that the lowest unoccupied state is an antibonding π^* state at 0.3 eV above the Fermi level, which is formed through the hybridization between the bare PTCDA's lowest unoccupied molecular orbital and the Ag's d states. Therefore, that an electron transfers to this antibonding state will disfavor the hybridization and break the Ag-O bonds near the created core hole [14].

Table II lists the averaged vertical distances of O1, C, and O2 to the Ag(111) surface in the IIS and the IFS. In the experiment [4], the measured data show that the averaged vertical distances to the Ag(111) surface of O1, C, and O2 are 2.68 ± 0.03, 2.86 ± 0.01, and 2.97 ± 0.06 Å, respectively. In our calculations, the IIS structure gives the distances of 2.45, 2.78, and 2.69 Å, respectively, and 2.59, 2.82, and 3.05 Å, respectively, for that of the IFS structure. Thus, we found that the anhydride O atoms (O2) were calculated to be much higher than the perylene core (average C) in the IFS. Physically, the IIS and the IFS are two limits of the measured values. As a reference, we averaged the IIS and the IFS values in Table II (Mid-I-F). With excellent agreement of calculated values and experimental values, it turns out that the measured values are in the range between, almost in the middle of, the IIS and the IFS. It is confirmed again by subsequent 16FCuPr(Pc) calculations. This strongly suggests that the NIXSW experiment cannot be simply interpreted with a ground state structure obtained by DFT but can be well reproduced by considering the initial- and final-state effects.

The CLCSs between O1 and O2 were evaluated to be 1.92, 2.33, and 0.50 eV for the EIS, IIS, and IFS, respectively, as summarized in Table I. In comparison with the

measured CLCS of about 2.3 eV [4], the photoemission process happening in the NIXSW experiment is well described by the IIS. Thus, it can be concluded that the relaxation of the valence electrons to screen a core hole goes so fast that the relaxation energy is sufficiently transferred to a photoelectron. Very recently, Gerlach *et al.* reported the NIXSW experiment of 16FCuPc on Ag(111) and Cu(111) [5], as shown in Fig. 2(a). They found that the relative vertical position of F was 0.27 and 0.20 Å higher than that of C on Cu(111) and Ag(111) surfaces, respectively. It is further thought that this molecular distortion is possibly due to a partial transition from the hybridization sp^2 to the sp^3.

The molecule 16FCuPc is too large to simulate its adsorption on Ag(111) by the DFT calculations. Thus, we used 16FCuPr, as shown in Fig. 2(b), instead of 16FCuPc to reduce computational load, without loss of the essential physics. Subsequent discussions are thus based on 16FCuPr [14]. The calculated equilibrium structure is shown in Figs. 2(c) and 2(d), in which there are two inequivalent F atoms, denoted as F1 and F2. As we see, Fig. 2(d) indicates that the adsorption geometry of 16FCuPr on Ag(111) is almost flat. Therefore, there is no evidence that the original hybridization sp^2 in a bare molecule 16FCuPc prefers to change into the sp^3 when the 16FCuPc absorbed on Ag(111).

We then applied the IIS and IFS effects to DFT calculations. The IFS calculation shows that the bond between C and F with a core hole created is always broken while, by definition, the IIS molecular structure is the same as the equilibrium one. As analyzed before, the NIXSW measurement will be between the IIS and the IFS [9]. Accordingly, we reduced the number of excited electron from 1.0e to 0.5e (0.5 core hole created) as a numerical approximation to reduce the final-state effect, by which we attempt to quantitatively describe how a physical process underlying the NIXSW measurement happens between the IIS and the IFS. Reducing the excited electron to 0.3e or 0.7e does not change the results qualitatively. The fully relaxed structures of the IFS with 0.5 core hole created (0.5-IFS), respectively, on F1 and F2 are shown in Figs. 2(e) and 2(f). It turns out that both excited F1 and F2 atoms are substantially higher than the adjacent C atoms

TABLE II. Averaged vertical distances to the Ag(111) surface of carboxylic O (O1), C, and anhydride O (O2) in the ionic initial state (IIS), the ionic final state (IFS), the simple numeric average of the IIS and the IFS (Mid-I-F), and experiments (Exp) [4] and the averaged self-difference (Δd-I-F) on O1, C, and O2 from the IIS to the IFS.

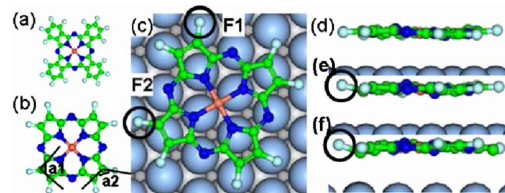|	IIS	IFS	Mid-I-F	Exp	Δd-I-F
O1	2.45	2.73	2.59	2.68(0.03)	0.28
C	2.78	2.82	2.80	2.86(0.01)	0.04
O2	2.69	3.05	2.87	2.97(0.06)	0.36

FIG. 2 (color online). Structures of (a) 16FCuPc and (b) 16FCuPr. (c) Top view and (d) side view of the fully relaxed adsorption geometry of 16FCuPr on Ag(111). The side view of the calculated geometry by 0.5e final-state approximation with a 0.5 hole created (e) on F1 and (f) on F2, respectively.

as well as the other C atoms. The F-C-N angle is only 0.8° in the equilibrium structure, but the 0.5-IFS calculation gives a value of 10.0°, which is in good agreement with the experimental value (8.5°) [5]. The F-C vertical difference in the IIS and the 0.5-IFS are 0.01 and 0.22 Å, respectively. In comparison with the experimental value 0.20 Å [5], the 0.5-IFS calculation well reproduced the experiment. This consistency strongly demonstrates the feasibility and reliability of the 0.5-IFS approximation, as well as the interpretations based on the IFS picture.

As shown in Fig. 2, in the equilibrium structure the bond angles of C-C-C ($a1$) and C-C-F ($a2$) are 108° and 126°, respectively. After relaxation with the 0.5-IFS, $a1$ and $a2$ change to 110° and 119°, respectively. Meanwhile, the C atom adjacent to the excited F atom is lower by 0.3 Å with respect to the substrate than the other C atoms. In other words, it interacts with the Ag underneath more strongly than the other C atoms. All of these evidences strongly suggest that a partial transition from the original hybridization sp^2 to the sp^3 indeed takes place here, but it is due to the IFS effect induced by the x-ray excitation rather than the adsorption as suggested by the previous study [5]. Here the underlying physics is similar to a PTCDA on Ag(111). When a core hole is created in 16FCuPr, the extra charge will transfer into the antibonding state to screen the hole. The calculation shows that the transferred charge would be mostly around the C atom adjacent to the excited F atom. If the C's π^* state is partially filled, the π bond of this C will be weakened. This means the aromaticity, which keeps the three σ bonds hybridized in a planar configuration, is dramatically reduced. Thus, the transition from the sp^2 to the sp^3 gains favor in the charge transfer to screen the core hole, which cannot be restricted by the aromaticity. Now supposing that the π^* state is fully filled, the corresponding π bond would break and a C-Ag bond would then be formed due to the charge transfer from the substrate Ag to the C atom. Subsequently, this results in the F-C bond breaking, where an F atom escapes from the molecule and the C forms three σ bonds; one is attached to the substrate Ag, and the others are contributed to the backbone of the pyrrole ring. The above analysis elucidates how the NIXSW measurement is between the IIS and the IFS.

In summary, the DFT ground state calculations for PTCDA and 16FCuPr(Pc) on Ag(111) are in conflict with those novel observations by the NIXSW, namely, the anhydride O atoms vertically over the perylene core, the large core level chemical shifts, and the F atoms higher than the pyrrole ring. We demonstrate that these novel observations result from the relaxation of the valence electrons to screen the created core holes and subsequently induced ionic structure relaxations. By including these effects, the DFT calculations can well reproduce the NIXSW experiments. The underlying physics is that the charge transfer and redistribution, due to the screening of core holes, changes the molecule-substrate or the intra-

molecular chemical bonding in PTCDA and 16FCuPr(Pc). This study not only improves our understanding on the interaction of x ray with organic molecules but also provides abundant references to protect functional molecules in the design of further molecular devices which have to work under x-ray radiation. It also reminds us that for a nanostrucutre it is very likely that the measurement tools have substantial impact on the structure itself, which requires more close interplay between theoretical calculations and experiments.

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[14] See EPAPS Document No. E-PRLTAO-97-016652 for the calculation details of PTCDA/Ag(111) and 16FCuPc/Ag(111) systems and the analysis of the lowest unoccupied state of PTCDA/Ag(111). This state would respond for the core-hole-induced charge transfer. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.

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