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Ultra-fast charge transfer in organic electronic materials and at hybrid interfaces studied using the core-hole clock technique

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ABSTRACT

The focus of this brief review is the use of resonant photoemission in its "core-hole clock" expression for the study of two important problems relevant for the field of organic electronics: the dynamical charge transfer across hybrid organic–inorganic interfaces, and the intermolecular charge transfer in the bulk of organic thin films. Following an outline of the technique, a discussion of its applicability and a short overview of experimental results obtained thus far, two examples are used to illustrate particular results relevant for the understanding of the charge transport in organic electronic devices. First, for Fe(II)-tetraphenylporphyrin molecules on semi-metallic molybdenum disulfide substrates, the electronic coupling to the substrate and the efficiency of charge transport across the interface different for the individual molecular electronic subsystems is discussed. And second, a discotic liquid crystalline material forming columnar assemblies is used to illustrate ultra-fast intermolecular charge transfer on the order of a few femtoseconds indicating an electronic coupling between the phthalocyanine units stronger than expected from the macroscopic charge transport characteristics of the material.

1. Introduction

Static charge transfer has been shown to control interfacial electronic properties at hybrid organic–inorganic and organic–organic interfaces in organic electronics [1–5]. Knowledge of the *dynamics* of electron and hole transfer processes between π-conjugated molecules and metal or semiconductor surfaces, however, is key to the understanding of molecular charge-injection or charge-extraction devices.

Studies of the interfacial electronic structure, as a static property, are often carried out using the rather uncomplicated technique of photoelectron spectroscopy, in particular, ultraviolet photoelectron spectroscopy, or UPS [6–9]. Charge transfer (CT) dynamics, on the other hand, are more difficult to access. Pump-and-probe techniques [10,11] that study the behavior of optically excited electrons as a function of time after the excitation allow an independent tuning of pump and probe processes. In a rather flexible way, this technique can therefore be employed to study charge transport processes occurring at different time scales. With no suitable high-energy lasers available thus far, they are, however, restricted to low-energy excitations that relate, in the case of organic materials and interfaces, to molecular valence orbitals and their hybrid interfacial states.

On the other hand, in order to obtain atomic-site specific information related to different elements and chemically distinguishable electronic environments, techniques sensitive to the chemical shift of core-levels shall be employed. These chemical shifts are discerned in X-ray photoelectron (XPS) spectra, derived from the original name "Electron Spectroscopy for Chemical Analysis", or ESCA, by Professor Kai Siegbahn and his colleagues at Uppsala University [12]. The availability of tunable X-ray light sources, namely synchrotrons, and advances in the theoretical description of scattering processes involving core-excited states [13] have lead to the development of powerful experimental techniques related to X-ray absorption and X-ray resonant scattering processes. Today, near-edge X-ray absorption fine-structure spectroscopy (NEXAFS) is a technique well established for both the study of the orientation of molecular adsorbates and of the properties of core-excited states [14]. Inclusion of the decay channels of the core-excited state leads to the development of resonant X-ray emission (XES) and resonant Auger spectroscopies, as well as of resonant photoemission (RPES), depending on which radiative or non-radiative decay channels are exploited. These different techniques and their applications have been described in excellent reviews [13,15–17]. We therefore summarize only details needed to discuss the

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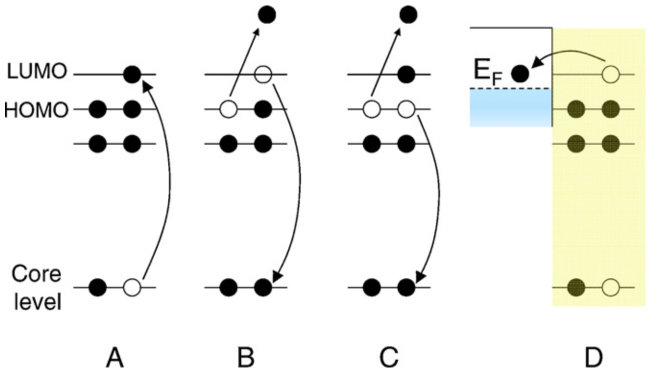

Fig. 1. Diagram illustrating (A) the X-ray absorption process leading to a core-excited state, as well as resonant (B) participator and (C) spectator decay processes. Case (D) illustrates charge transfer at an interface from the core-excited state.

RPES technique as applied to organic materials and hybrid interfaces.

Note that the application of X-ray resonant spectroscopic techniques for the study of thin solid films and surface problems related to the electrical engineering of (nanoscale) devices is not and will never be as straightforward as XPS and UPS. In this regard, while the general principle is quite intriguing and relatively easy to understand, it is always necessary to critically validate assumptions made in the interpretation of "core-hole clock" experiments.

2. Resonant photoemission

Core-excited states created upon X-ray absorption (Fig. 1, case A) decay either through radiative processes or by emitting one or even more electrons. In the non-radiative case, participator (case B) and spectator decay (case C) processes are distinguished [17–19]. Sharp features in the low-binding energy region, with strongly varying intensities as a function of the photon energy, are usually related to participator one-hole final states that are electronically similar to those reached in off-resonance, direct photoionization processes [17,20,21]. The related spectroscopy is therefore often called resonant photoemission, or resonant photoelectron spectroscopy (RPES). There are important differences between direct and resonant photoelectron emission processes: While the former is a vertical transition between the potential surfaces of the initial (ground) and final (ionized) states of the process governed by the dipole operator, the latter involves an intermediate, core-excited state, with the decay governed by the Coulomb operator [16,22].

Since direct and resonant processes involve the same electronic initial and final states, they do interfere with each other leading to either constructive or destructive interference. Observed intensities can change significantly in this way. Note, however, that for photon energies within absorption resonances, direct and resonant processes compete for a given photon flux. For this reason, direct photoionization may be already significantly suppressed, as compared to photon energies out of resonance. Such, for organic and in particular aromatic molecular materials, it is often observed [20,21] that resonant processes related to the absorption into particular π^* resonances are very strong and dominant with respect to non-resonant channels. In this case, a consideration of interference effects mentioned above may be not needed.

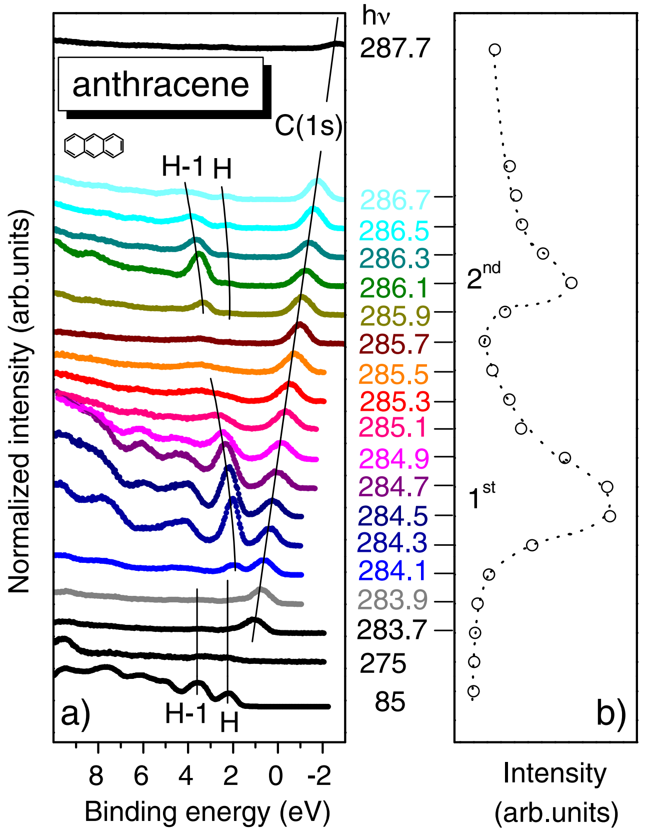

Fig. 2. (a) Photon-energy dependent electron emission spectra of a polycrystalline anthracene film prepared at 77 K *in situ* on a polycrystalline Au substrate. The non-resonant valence band spectrum obtained with $h\nu = 85$ eV is compared with resonant spectra obtained in the vicinity of the C k edge. The position of the C(1s) XPS peak obtained with 2nd order light is indicated. Features h and H-1 relate from one-hole final states derived from the HOMO and HOMO-1, respectively. (b) Partial yield C K-edge NEXAFS spectrum of the polycrystalline anthracene film. The positions of the 1st and 2nd resonances are indicated.

In order to illustrate characteristic features of RPES spectra of aromatic, organic materials, in Fig. 2a are shown photon-energy dependent electron emission spectra of a polycrystalline anthracene multilayer film prepared *in situ* at 77 K on a polycrystalline gold substrate [23]. The valence band spectrum obtained with a photon energy of $h\nu = 85$ eV is shown at the bottom. Peaks related to the occupied molecular orbitals are well recognized, those for the highest (HOMO) and second highest (HOMO-1) are denoted H and H-1 and located at about 2.2 eV and 3.5 eV, respectively. At $h\nu$ below the C(1s) X-ray absorption threshold, or C K-edge, located at about 283.9 eV, these two spectral features are barely recognizable anymore.

Tuning the photon energies above the threshold leads to absorption into distinct resonances, denoted 1st and 2nd in Fig. 2b. Note that at the onset of X-ray absorption, the C(1s) XPS line excited by second order light appears in the low binding energy region of the RPES spectra. It can be easily distinguished from features related to excitation with first order light by its linear dispersion with the photon energy. Since its line shape is invariant, it can be subtracted, if necessary, for a quantitative evaluation of resonant features.

Within the first resonance, several strong features related to resonant decay channels are observed. The first peak, denoted H, is certainly due to a one-hole final state related to the anthracene HOMO. It displays a strong dispersion with the photon energy that is caused by a vibrational progression of basically C–C stretching modes, as revealed in corresponding RPES measurements on the free anthracene molecules [23]. Note that the nature of the hole-vibrational coupling in oligoacene molecules has been studied extensively providing values for the so-called geometrical reorganization energy that is an important parameter in the description of the hopping transport in organic electronic devices [24,25].

In the case of resonant processes involving core-excited states, an analysis of vibrational progressions reveals information on the shape and displacement of potential surfaces of the initial,