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Rapid Communications

Temperature effects on the formation and the relaxation dynamics of metal-organic interface states

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Using time-resolved two-photon photoemission, we systematically study temperature effects on the Shockley-derived unoccupied interface states of perylene- and naphthalene-tetracarboxylic dianhydride (PTCDA and NTCDA) adsorbed on Ag(111). With increasing sample temperatures from 100 to 300 K, we observe a continuous decrease of the interface-state energy by 0.06 and 0.1 eV, respectively, for the two different molecule/metal systems. We relate this energy shift to a molecular lifting off the metal surface. The lifting is accompanied with an increase of the interface-state lifetime from 28 to 53 fs for PTCDA and from 60 to 110 fs for NTCDA. This is in qualitative agreement with the reduction of phase space for electron scattering associated with the thermal energy shift. The magnitude of the experimentally observed lifetime increase, however, is much stronger than would be expected from the energy shift alone.

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The interfacial electronic structure largely determines charge and energy transfer across organic/metal contacts. Besides energetic level alignment, also the presence of electronic interface states (ISs) can have a tremendous impact on the transfer efficiency at such contacts. In particular, electron transfer, mediated by a Shockley-derived unoccupied IS, has been reported for optically excited organic heterolayers on Ag(111) [1].

Shockley-derived ISs are present at many organic/metal systems [1–7]. In a simple picture, the IS derives from the occupied Shockley surface state (SS) of the clean metal, which is energetically elevated above the Fermi level due to the modified surface potential associated with the π-conjugated carbon backbone of the adsorbed molecular layer. A free-electron-like parallel dispersion is inherited from the former SS of the pristine metal surface [2,8,9]. This picture is in agreement with density-functional theory calculations, which quantitatively reproduce the experimentally observed IS energy onsets as well as the free-electron-like parallel dispersion for some showcase organic/metal systems [6,9–13]. For sufficiently small parallel momentum, the adsorbate-related lateral corrugation of the surface potential was found to have only a minor effect on the IS energy [12]. Accordingly, neglecting the actual molecular configuration and the lateral interfacial structure, the experimentally observed IS energy onset can be remarkably well reproduced using an analytical one-dimensional model potential with the carbon-metal distance, i.e., the vertical binding distance of the molecules as the only adjustable parameter [14]. More specifically, the model predicts a strong decrease of the IS energy with increasing binding distance, in agreement with experimental data by x-ray standing wave (XSW) experiments as well as scanning tunneling spectroscopy and two-photon photoemission (2PPE) [14].

Earlier studies on the interfaces of 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) and 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTCDA) with Ag(111) revealed a strong dependence of the IS energy also on the sample temperature [9,15]. In the present Rapid Communication, we relate the temperature-induced IS energy shift to an increasing molecule-metal distance. We further apply the model derived in Ref. [14] to estimate the magnitude of the molecular lifting off the metal surface. Thereby, we demonstrate the IS energy as a sensitive measure for the molecule-metal bond distance. Moreover, using time-resolved 2PPE we reveal an extraordinary increase of the IS lifetime with increasing sample temperature. Such a temperature-induced reduction of inelastic scattering has been qualitatively discussed in terms of the phase space of final states available for the scattering process [9,12]. In the present Rapid Communication, however, we show that this phase-space argument is not sufficient for a quantitative explanation of the temperature effect on the IS lifetime.

Time-resolved 2PPE experiments were performed in a pump-probe scheme with visible pump and ultraviolet (UV) probe laser pulses. For NTCDA/Ag(111), the experimental setup described in Ref. [1] was used. The laser system, based on an 80-MHz synchronously pumped optical parametric oscillator, delivered visible pump pulses with a photon energy of $\hbar\omega_{\mathrm{vis}} = 2.07$ eV and a duration of $\tau_{\mathrm{vis}} = 160$ fs. UV pulses with $\hbar\omega_{\mathrm{UV}} = 4.54$ eV and $\tau_{\mathrm{UV}} = 80$ fs were used as probe pulses. A different laser system was used for PTCDA/Ag(111): The output of an 82-MHz Ti:sapphire oscillator was frequency doubled and frequency tripled, respectively, which yields pump pulses with $\hbar\omega_{\mathrm{vis}} = 3.10$ eV

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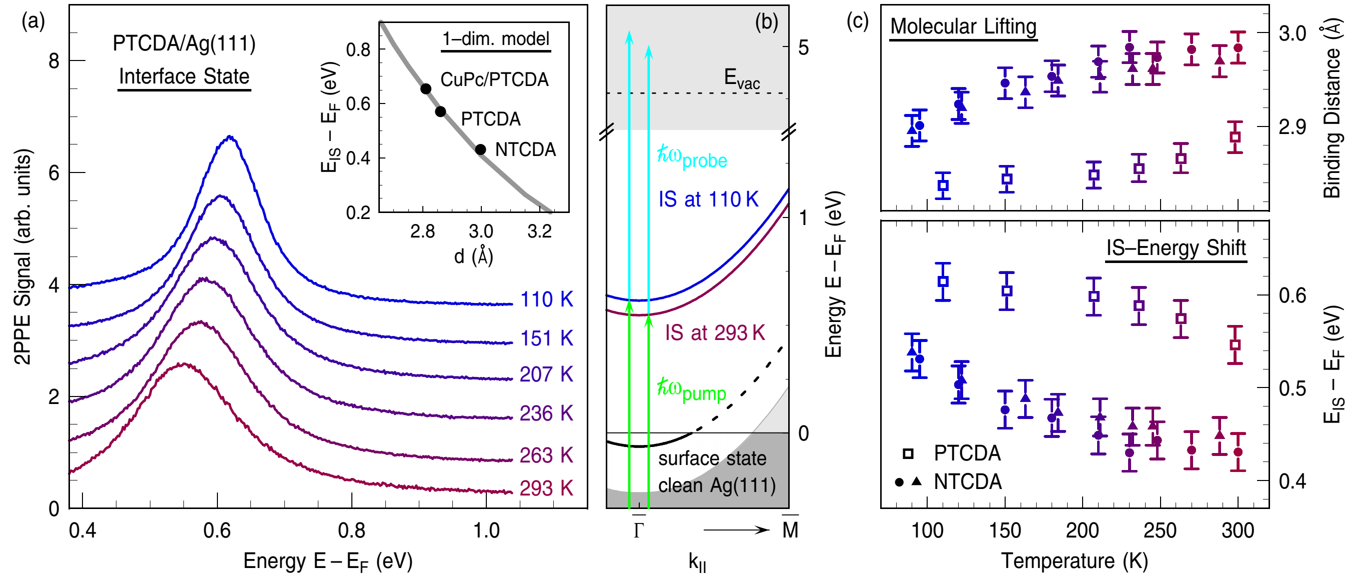

FIG. 1. (a) 2PPE spectra of PTCDA/Ag(111) in the IS region for various temperatures. The spectra are scaled and shifted along the vertical axis for clarity. Inset: Relation between IS energy and molecule-metal binding distance from a one-dimensional model calculation. (b) Schematic of the 2PPE excitation scheme illustrating momentum dispersion and the temperature-dependent energy position of the IS of PTCDA/Ag(111). (c) Bottom: Temperature-dependent IS energy determined with 2PPE. Results from two independent data sets are presented for NTCDA. Top: Temperature-dependent molecule-metal binding distances calculated from the experimental IS energies with the model curve from (a).

and $\tau_{\mathrm{vis}} = 50$ fs, as well as probe pulses with $\hbar\omega_{\mathrm{UV}} = 4.70$ eV and $\tau_{\mathrm{UV}} = 70$ fs. All 2PPE spectra were obtained in normal emission with p-polarized pump and probe laser pulses. The maximum energy resolution of the system was 65 meV with an angle resolution of 1.2°.

In Fig. 1(a) we compare the 2PPE spectra of one monolayer of PTCDA on Ag(111) in the energy region of the IS for various sample temperatures. With increasing temperature the peak position of the IS continuously shifts from 0.61 eV at 110 K to 0.55 eV at 298 K. In contrast to the high susceptibility of the IS energy to temperature variations, we found no significant temperature effect on the work function of the sample, as judged by the position of the low-energy cutoff in the 2PPE spectra. Very similar results were obtained also for the relaxed monolayer of NTCDA on Ag(111). The results for both systems are summarized at the bottom of Fig. 1(c). According to the one-dimensional model for the IS derived in Ref. [14], a shift of the IS energy towards the Fermi level would be expected for an increased vertical distance between the adsorbed molecular layer and the metal surface. In fact, molecular lifting off the metal surface would also be expected from a simple molecular dynamics argument: At finite temperatures sufficiently weakly bound molecules, or more specifically their constituting carbon atoms, oscillate in an anharmonic potential perpendicular to the metal surface. As a consequence, the average carbon-metal distance, i.e., the effective molecular adsorption height, is expected to increase with temperature.

For a more quantitative analysis, we adapt the universal model of Ref. [14] to the special case of PTCDA/Ag(111) by addition of an empirical offset of 0.25 eV. The so-modified model function does not only agree with the experimental data from 2PPE and XSW [16,17] for PTCDA/Ag(111) at 300 K, but also reproduces the experimental results for NTCDA/Ag(111) [18,19] as well as for the strongly related heterosystem CuPc/PTCDA/Ag(111) [1,20] [inset of Fig. 1(a)]. With the help of the model function we are able to translate the experimentally determined IS energies [lower panel of Fig. 1(c)] to molecule-metal distances (upper panel). Between 100 and 300 K the temperature-driven molecular lifting derived from the 2PPE results has a magnitude of 0.08 Å for NTCDA and 0.05 Å for PTCDA. As distance variations of this order of magnitude are difficult to access experimentally, especially in the light of the dynamic nature of this process, only few published experimental results are available for comparison of our results. A lifting by 0.18 Å was observed with XSW for cobalt porphine (CoP) adsorbed on monolayer hexagonal boron nitride (h-BN) on Cu(111) for temperatures between 50 and 300 K [21]. In contrast, for the related molecules CuPc and CuTPP directly adsorbed on Cu(111), no evident temperature dependence of the binding distance was found [22,23]. In the present case, the bond strength of PTCDA and NTCDA on Ag(111) lies between the strengths of the aforementioned systems, i.e., the strongly decoupled CoP/h-BN/Cu(111) and the weakly chemisorbed CuPc/Cu(111). Obviously, our estimation of the molecular binding distance based on the 2PPE data and the one-dimensional model for the IS yields realistic values for the thermal molecular lifting.

In the following we investigate how the lifting affects the electron dynamics of the IS. At similar temperatures as in Fig. 1, pump-probe experiments were performed at the respective spectral position of the IS peak. This way, the transient population of the IS was probed as a function of temperature. Exemplary 2PPE transients for PTCDA and for NTCDA are presented in Fig. 2(a). The dashed lines are the cross correla-

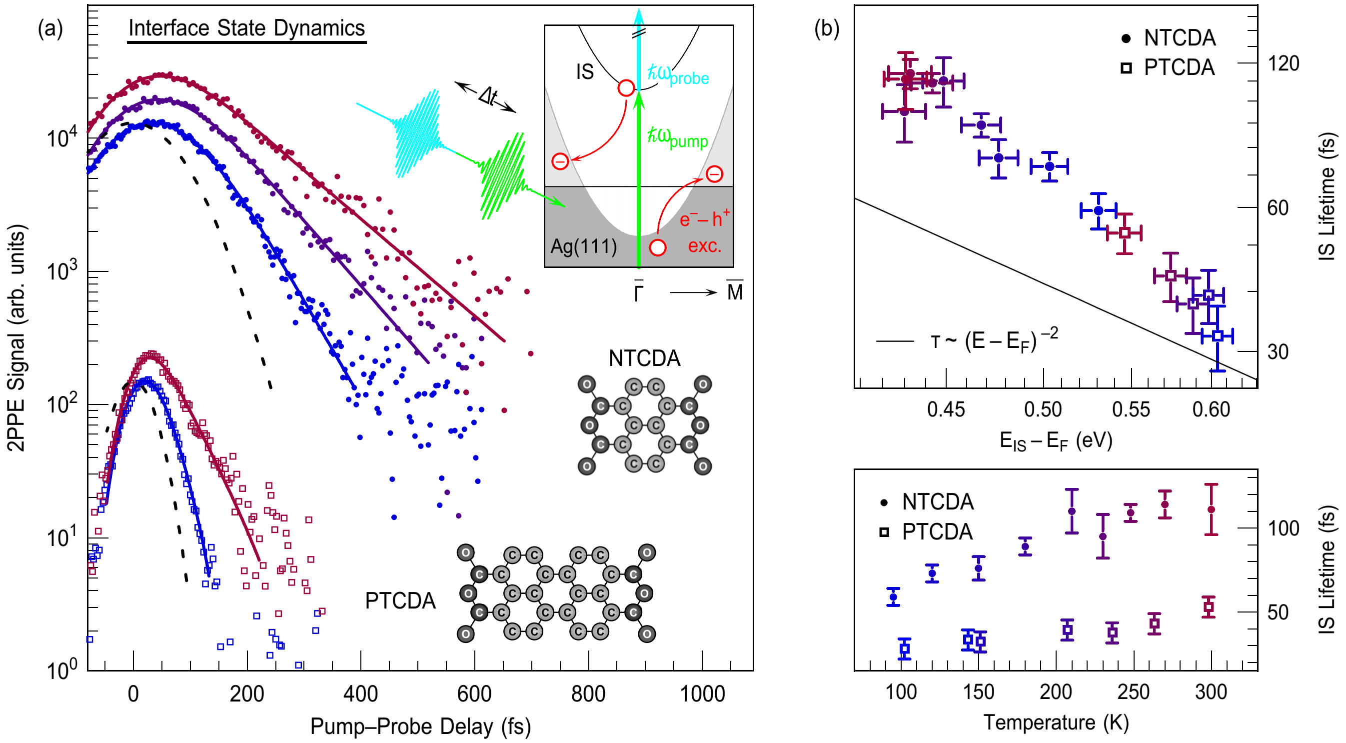

FIG. 2. (a) Exemplary time-resolved 2PPE data at the energy of the IS for PTCDA (bottom) and NTCDA (top) on Ag(111) at sample temperatures between 90 and 300 K. The dashed curve is the cross correlation of the pump and the probe laser pulses in the respective experiments. The transient 2PPE signal is scaled and shifted for clarity. (b) Bottom: Inelastic IS lifetime vs sample temperature as obtained from the 2PPE transients. Top: IS lifetime vs IS energy in a double-logarithmic plot. The colors in all subfigures correspond to the sample temperatures at which the data in Fig. 1 has been obtained.

tions of the pump and the probe laser pulses in absence of any transiently occupied intermediate states, which were obtained by time-resolved 2PPE from the occupied SS on a pristine Ag(111) sample. Note, that two different laser systems with different pulse durations were used for the experiments with PTCDA and NTCDA, respectively. The solid lines are fits to the experimental data based on a rate-equation model with a single exponential decay of the intermediate-state population. Increasing the sample temperature by approximately 200 K, for both systems the IS lifetime roughly doubles, demonstrating a severe inhibition of inelastic scattering [bottom of Fig. 2(b)].

This unusual lifetime increase has been explained qualitatively in terms of electron scattering with metal bulk states [9]: As the IS is located within the gap of projected bulk states of Ag(111), IS electrons cannot directly scatter into silver bulk states and the most important relaxation pathway is constituted by the creation of electron-hole pairs. The relaxation rate is then determined by the wave-function overlap with the metal, the dielectric screening, and the phase space available for electron-hole pair excitation in the metal. As the phase space scales quadratically with the energy, with decreasing energy at increasing temperatures (cf. Fig. 1) the IS relaxation becomes slower.

In the upper panel of Fig. 2(b) we compile the inelastic lifetimes from our 2PPE experiments as a function of the IS energy in a double-logarithmic graph. The solid line represents the expectation $\tau = \lambda\,(E - E_F)^{-2}$ from the phase-space argument outlined above. The scattering parameter λ was arbitrarily chosen to match the value of $\lambda_{Ag} = 10.4$ fs eV^2 observed for hot electrons in the SS of clean Ag(111) [24,25]. Note, that a different choice of λ would only lead to a vertical shift of the curve on the double-logarithmic scale. As can readily be recognized from Fig. 2(b), with $\tau \propto E^{-3.4}$ the energy dependence of the IS lifetime is much stronger than expected from a pure phase-space argument. Interestingly, exactly the same trend is obtained for both molecular species, suggesting the same physical principles underlying the IS relaxation in both systems.

While the comparatively long lifetimes are consistent with the position of the IS within the gap of the projected silver bulk states, the more than quadratic relation between relaxation rate and energy indicates that a simple phase-space argument is not sufficient to explain the temperature effect on the IS lifetime. If we further include the wave-function overlap with the metal in our discussion, an even weaker energy dependence would be expected: at lower temperatures, the smaller binding distance leads to a reduction of the IS wave-function overlap with the metal [9,12,14], which gives rise to enhanced lifetimes, in contrast to our experimental findings. This effect should even be enhanced due to the bending of the carboxyl groups of PTCDA and NTCDA towards the metal surface. Compared to a plane molecular geometry, the bending increases the molecular character of the IS wave function [9] and further reduces the wave-function overlap with the metal.

Obviously, the inhibition of inelastic scattering at higher temperatures is related to effects that have not been considered so far. Therefore, it would be interesting to compare our experimental results with the expected lifetimes from more realistic theoretical studies. However, full *ab initio* simulations of the lifetimes in molecule/metal systems are rather challenging due to the large computational expense of many-body calculations and the large unit cells under consideration. First calculations using the *GW* approximation and a one-dimensional pseudopotential corresponding to the clean Ag(111) surface showed that, indeed, a quadratic relation between relaxation rate and energy would be expected, if the IS was just an energetically upshifted SS [12]. A more adequate one-dimensional potential, which also accounts for the molecular layer above the metal surface, is the one used for the model in Ref. [14]. However, the smaller wave-function overlap at shorter binding distances, which is predicted with this model, would probably lead again to a weaker energy dependence of the calculated lifetimes, as outlined above.

One aspect that has not been included in our discussions so far is the lateral corrugation of the surface potential. Although it does not have a significant effect on the IS energy onset and the momentum dispersion close to the $\overline{\Gamma}$ point, the lateral molecular contribution to the IS wave function might be important for a quantitative description of the IS electron dynamics. Elastic scattering of IS electrons near the edge of the surface Brillouin zone of PTCDA/Ag(111) has already been observed as well as the opening of a small energy gap [2,26]. A much more pronounced gap was found for NTCDA/Ag(111) accompanied with a significant anisotropy of the IS dispersion [13]. Both effects provide evidence for quantum-mechanical interaction of the metal Shockley state with the adsorbed molecules [13], which certainly also affects the IS dynamics.

Also the dynamic nature of the molecular lifting might be important for the electron dynamics. At finite temperatures, molecular vibrations give rise to dynamic variations of the potential at the molecule/metal interface. One effect of these vibrations is already apparent from the 2PPE spectra in Fig. 1(a): Despite the increasing IS lifetime, the IS peak broadens with increasing temperature. With $\Gamma = \frac{\hbar}{\tau} = 24$ meV for PTCDA at 100 K, the inelastic lifetime has only little contribution to the observed peak width. Most probably, the peak broadening is connected with the high susceptibility of the IS energy to variations of the carbon-metal binding distance: With increasing temperature the molecular vibrations become stronger and give rise to a wider dynamical distribution of the carbon-metal distances. According to the model curve in the inset of Fig. 1(a), a wider molecular distance distribution leads, in turn, to a wider distribution of IS energies, i.e., to a broadening of the observed IS peak. Note also, that strong electron-phonon coupling is known, e.g., for PTCDA on Ag(111) [27]. Therefore, a quantitative description of the IS dynamics must probably also consider the molecular dynamics at the molecule/metal interface.

In conclusion, the temperature-induced energy shift of the IS of PTCDA/Ag(111) and NTCDA/Ag(111) can consistently be explained with a thermally driven molecular lifting off the metal surface. The magnitude of this lifting between 100 and 300 K is estimated to 0.05 Å for PTCDA and 0.08 Å for NTCDA. The strong temperature effect on the IS lifetimes cannot be explained with the observed energy shift and a simple phase-space argument alone. Therefore, more elaborate models are needed for an accurate description of the electron dynamics at organic/metal interfaces at finite temperatures, which probably have to incorporate not only the lateral corrugation of the surface potential but also the interaction with molecular phonons.

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