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Hot-electron dynamics in thin films of sodium-doped perylene-3,4,9,10-tetracarboxylic dianhydride

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Time-resolved two-photon photoemission of the doping process of perylene-tetracarboxylicdianhydride (PTCDA) thin films with sodium gives insight into the dynamics of hot electrons in this system. Interaction with Na results in a charge transfer from Na to PTCDA and increases the lifetime of optically excited electrons. A similar increase in lifetime can be observed for ultrathin PTCDA layers on Ag(111). Both results are discussed in the one-electron picture, treated in "classical" photoemission theory, and in the many-electron picture as commonly considered for strongly correlated systems.

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I. INTRODUCTION

Today, the transport properties of electrons in molecular semiconductors as function of different doping processes are rather well understood. However, little is known about the excited-state dynamics of hot electrons with excess energy much larger than kT, which becomes important at any metal-polymer junction, in particular in the case of a Schottky barrier. It can be expected that both electron-phonon and electron-electron interactions play important roles in determining the nature of fundamental electronic energy dissipation processes in π-conjugated molecules.

Perylene-tetracarboxylicdianhydride (PTCDA) as an archetypical molecular organic semiconductor is a well-investigated system and has become a prototype for studying electron transport in such materials. Due to its high electron affinity it can easily be n doped, whereas common organic semiconductors show hole rather than electron conduction. The interaction of alkali metals as electron donors with organic semiconductors is hence well studied,[1–6] and the growth of PTCDA on standard surfaces used in photoelectron spectroscopy [highly oriented pyrolytic graphite (HOPG), Ag(111), etc.] is reported in detail.[7,8]

In this work time-resolved two-photon photoemission (TR-2PPE) of two systems—bulk PTCDA stepwise doped with sodium and ultrathin PTCDA films on Ag(111)—was carried out. The work combines the recently gained knowledge of real-time experiments in the fs-time scale with the accumulated knowledge of the static electronic picture of organic semiconductors. The measurements show that in Na_2PTCDA, the lifetime of hot electrons can be modified quite drastically with respect to the lifetime values obtained in pristine PTCDA. These findings are important for a fundamental understanding of transport properties of any hybrid electronic and spintronic devices, where barriers at the metal-semiconductor interface will increase the excess energy of the carriers.

II. EXPERIMENTAL

TR-2PPE has proven to be a powerful method for observing fast relaxation processes at surfaces in real time.[9] This technique involves excitation of electrons by a first ultrashort laser pulse into an intermediate state followed by a second—suitably delayed—probe-laser pulse which leads to photoemission of the electrons. By measuring the amount of photoelectrons as a function of the delay between pump and probe pulse, one is able to determine the lifetime of hot electrons as a function of their excitation energy.

The experimental setup for TR-2PPE used in this investigation is similar to that reported in Ref. 10. Briefly, the laser system consists of a Ti:sapphire laser pumped by 7.5 W from a cw Nd:YVO4 diode laser. The system delivers sech^2 temporally shaped pulses of up to 10 nJ/pulse with duration of 35 fs at a repetition rate of 76 MHz and at 790 nm wavelength. The linearly polarized laser output is frequency doubled in a 0.2-mm-thick beta-barium-borate (BBO) crystal to produce UV pulses at $h\nu \approx 3.1$ eV. The laser radiation is focused on an *in situ* prepared PTCDA sample in ultrahigh vacuum (UHV); the photoemitted electrons are analyzed by use of a cylindrical sector analyzer (CSA). The presented TR-2PPE spectra were measured with a pair of cross-polarized laser pulses in order to avoid coherence effects.

To interpret the results of these investigations within the context of occupied and unoccupied electronic states on one hand and within the context of excited states on the other hand, ultraviolet (UPS) and inverse photoemission (IPE) spectroscopies and ultraviolet absorption spectroscopy (UV-Vis) were carried out. IPE was performed in bremsstrahlung isochromate mode; UPS by use of a standard discharge laboratory UV-Source [(UVS) 35/10, Leyboldt design)] and a hemispherical analyzer (Phoibos 150 MCD-9, Specs). Density-functional theory (DFT) calculations as well as time-dependent DFT calculations (TDDFT) (B3LYP, 6-31G*) for the ground and excited electronic states were performed (Gaussian03) to assist the interpretation.

PTCDA was deposited *in situ* (base pressure $<2 \times 10^{-9}$ mbar). The evaporation temperature was in the range of 550 K while the substrate was held at room temperature. As substrate for the photoemission experiments, a Ag(111) single crystal was chosen. PTCDA is known to grow on Ag(111) in Stransky-Krastanov mode lying flat, i.e., with the molecular plane parallel to the (111) surface. The nominal layer thickness of the Na-doped PTCDA layers was 120 nm. For UV-Vis spectroscopy an UV transparent mica substrate was used. Subsequent Na doping was performed by use of standard dispenser sources (SAES, Milano). As alkali metals are known to perform a diffusion process from the surface into the bulk, after each doping step a delay of at least 10

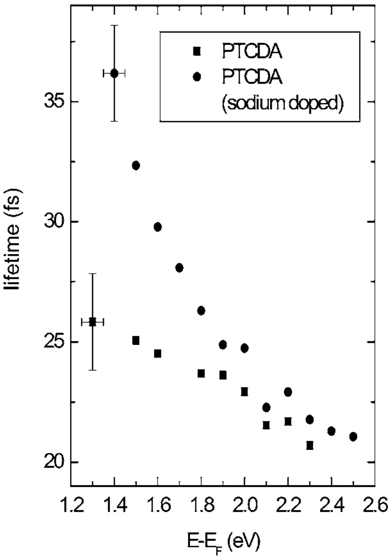

FIG. 1. Lifetime of hot electrons in pristine and Na-doped PTCDA as a function of their excited-state energy above E_F.

min was taken in order to complete amalgamation. An accumulation of Na at the interface between PTCDA and the silver substrate was not found in secondary-ion mass spectrometry depth profiles.[4]

III. RESULTS AND DISCUSSION

A. PTCDA vs Na-doped PTCDA

TR-2PPE measurements of hot electrons in pristine and Na-doped PTCDA show two central results (Fig. 1). On one hand, for both systems the lifetime τ of electrons excited to unoccupied states decreases with increasing energetic distance of the probed states from the Fermi level E_F. On the other hand, subsequent Na doping leads to an increase in τ for probed states in the energy range of 1.2–1.8 eV above E_F.

The measurements presented in this contribution can be discussed from two physical viewpoints. On one hand classical UPS, IPE, and 2PPE experiments at metallic surfaces are commonly treated as one-electron process (Koopmans' theorem). On the other hand organic semiconducting molecules are known to represent a class of systems that show strong electron correlation and electron-phonon coupling. In these systems, absorption of photons with an energy smaller than the thin-film work function is able to produce excited states of bound electron-hole pairs, so-called excitons, which have to be treated within terms of many-electron wave functions. As the energy of the first laser pulse (3.1 eV) in the 2PPE experiment is smaller than the PTCDA work function (4.6 eV), the occurrence of excitonic states is probable.

First the situation within the one-electron picture will be considered. It is known that Na doping of PTCDA shows a charge transfer (CT) from Na to PTCDA.[4] UPS and infrared (IR) absorption spectroscopies corroborated by DFT calculations point to a coordination of two Na atoms with one PTCDA molecule in a C_{2v} symmetry. For the formation of only singly doped PTCDA molecules, no experimental hints have been found. The formation of Na$_3$PTCDA is energetically not preferred.[11] As quantitative x-ray photoemission spectroscopy shows, in a PTCDA thin film an average of about 1.4 Na atoms is able to coordinate with one molecule, i.e., only about two of three molecules have reacted with two Na atoms; the others remain undoped.

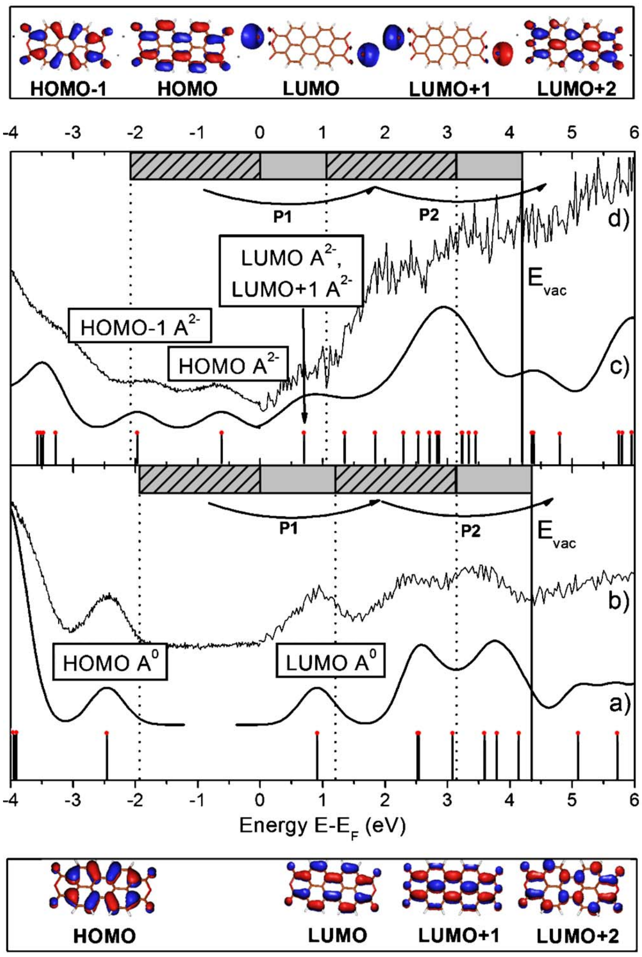

FIG. 2. (Color online) Evolution of occupied (UPS) and unoccupied (IPE) electronic states of pristine (b) and Na-doped PTCDA (d). (a) and (c) show simulations based on DFT calculations (B3LYP, 6-31G*) for (a) a single pristine PTCDA molecule and (c) a molecule coordinated with two Na atoms in an asymmetric configuration. The marked regions are accessible by the 2PPE experiment. Additionally, sketches of the molecular orbitals of pristine (bottom) and Na-doped (top) PTCDA are included.

The reaction of PTCDA with Na occurs under the transfer of the two Na atoms outer 3*s* electrons to the PTCDA molecule. Electronically, these two electrons fill up the lowest unoccupied molecular orbitals of the pristine PTCDA (LUMO A^0), which is thereby energetically lowered and shows up in UPS as new electronic state (HOMO A^{2-}) at -0.7 eV in the former PTCDA transport gap (Fig. 2). Additionally the highest occupied molecular orbital of the pristine molecule (HOMO A^0) is destabilized and appears as second new state at -1.8 eV in the former transport gap (HOMO$-$1 A^{2-}). In the IPE spectra the lowest unoccupied states of the Na-doped molecule A^{2-} cannot clearly be observed. This may be caused by a reduced transition matrix element for the IPE process from these orbitals. However, compared to the pristine PTCDA, the density of states in the energetic region of the higher unoccupied orbitals ($E-E_F>1$ eV) rises under Na doping, both absolutely and with respect to the LUMO A^0, respectively, LUMO and LUMO+1 A^{2-} density of states.

Within the one-electron picture, the energetically lowest electrons which are able to leave the pristine PTCDA layer by use of two laser pulses have their origin in the raising tail of the HOMO and are excited to the LUMO [see Fig. 2, curves (a) and (b)], both broadened either by $\vec{k}$ dispersion in highly ordered regions [bandwidth about 300 meV (Ref. 12)], by different vibronic substates, by oligomerization, or by slightly different chemical surroundings of the single molecules in amorphous regions. The higher intermediate electronic states probed by 2PPE (>1.2 eV for PTCDA) cannot be reached by an electronic excitation starting from a PTCDA molecular orbital. For these electronic levels, it is more probable that an excitation of electrons from impurity bands situated within the transport gap as described in Ref. 6 occurs. The decreasing lifetime of electrons excited into higher intermediate states in both pristine and Na-doped PTCDA is caused by the rising number of relaxation channels for these states.[13] The second effect, the raised lifetime of electrons excited into unoccupied states between 1.2 and 1.8 eV in Na_2PTCDA in this interpretation, is related to a completely different electron probability distribution if compared to the unoccupied states below 1.2 eV (Fig. 2) as predicted by the DFT calculations. While the lower ones are mainly localized in the region of the Na atoms, the higher ones are concentrated on the PTCDA core. This leads to a small overlap between the wave functions of states that are temporarily occupied by the photoexcited electrons and the wave function of the unoccupied states that serve as decay channels. For undoped PTCDA, DFT shows for all relevant unoccupied states a probability distribution that is delocalized over the whole molecule. Thus if compared with pristine PTCDA, the number of states reachable by electronic decay is reduced in Na_2PTCDA and relaxation is suppressed.

Within the many-electron picture the situation becomes more complicated. Assuming that the first 3.1 eV laser pulse in 2PPE produces an excited state of the Na_2PTCDA molecule, a situation comparable to UV-Vis absorption spectroscopy is realized. UV-Vis absorption spectra of pristine PTCDA (Fig. 3) show the well-known[7,14] CT excitations between 2.1 and 2.3 eV and excitations from the S_0 ground state to different vibronic "substates" of the first-excited state S_1, which appear as broadened band between 2.2 and 3 eV.

Our TDDFT calculations of the $S_0 \rightarrow S_1$ transition come to the result that within a many-electron picture, the transition to the S_1 state is dominated by an excitation from HOMO to LUMO and a smaller contribution from HOMO−6 to LUMO+1 (see Table I). Under subsequent Na doping the UV-Vis spectra become broadened on the lower energetic part, where our TDDFT calculations show the occurrence of a $S_0 \rightarrow S_3$ transition, which is an excitation from HOMO to LUMO+2, while the main contribution is held by the $S_0 \rightarrow S_6$ transition, i.e., an excitation of an electron from HOMO to LUMO+3. The $S_0 \rightarrow S_1$ (HOMO→LUMO) and the $S_0 \rightarrow S_2$ (HOMO→LUMO+1) transitions are predicted to have no oscillator strength. For an occurrence of a charge-transfer exciton in doped PTCDA no evidence can be found.

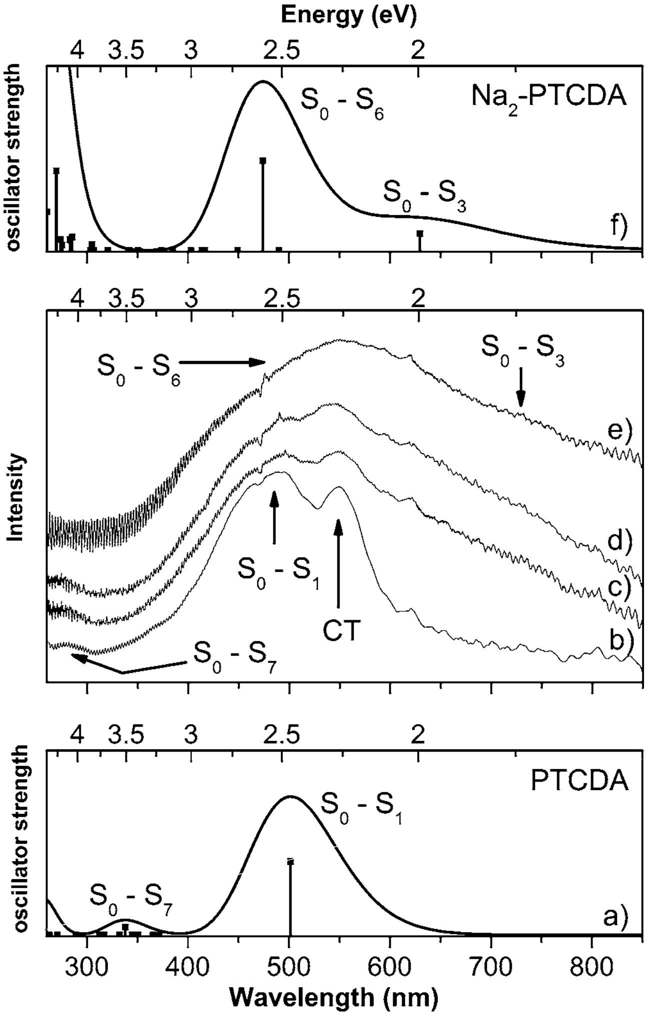

FIG. 3. (b) UV-Vis spectra of pristine PTCDA and (c)–(e) under stepwise Na doping, and TDDFT calculations of the excited states of (a) pristine and (f) Na-doped PTCDA.

Within this context, the performed measurements can be interpreted as follows. As the laser energy in the 2PPE experiment is 3.1 eV, the first laser pulse excites a PTCDA molecule to a higher state in the vibronic manifold of S_1 or CT. The remaining excitation energy is stored in the vibronic system. In the case of Na_2PTCDA, the two excited states reachable by a 3.1 eV laser pulse are higher vibronic levels of S_3 and S_6.

On the considered time-scale energy relaxation can either occur by internal conversion (IC) or in highly ordered systems by bandlike relaxation within excitonic bands.[15] In terms of exclusive IC the observed raise of lifetime in the doped system cannot be explained satisfactorily. Compared to pristine PTCDA, the doped system shows more excited states energetically below the ones produced by the first laser pulse. These states may serve as channels for population decay and one would expect a decrease in lifetime, in contradiction to the experimental results. One hint that not all reachable states are really accessible by electrons from higher excited states and therefore cannot serve as depopulation channels comes from the probability distribution in

TABLE I. Contribution of the particular molecular orbitals to the relevant excitonic transitions in PTCDA and Na_2PTCDA as predicted by TDDFT. The other transitions in the investigated energy range show almost no oscillator strength.

$S_0 \rightarrow S_n$	Energy (eV)	Oscillator strength	Molecular orbitals
		PTCDA	
1	2.47	0.5987	HOMO→LUMO (0.61) HOMO−6→LUMO+1 (−0.12)
7	3.67	0.0657	HOMO−5→LUMO+3 (−0.11) HOMO−4→LUMO (0.64) HOMO→LUMO+4 (−0.25)
		Na_2PTCDA	
1	1.17	0.0000	HOMO→LUMO
2	1.17	0.0004	HOMO→LUMO+1
3	1.97	0.1363	HOMO→LUMO+2
6	2.61	0.7283	HOMO→LUMO+3

Na_2PTCDA, as discussed in the one-electron picture. An access to these molecular orbitals by IC of electrons excited to unoccupied orbitals with a probability density mainly located on the former PTCDA molecule may show only a small transition probability due to the mismatch of the density distributions. The DFT calculations show that these two orbitals participate on the excited states S_1, S_2, S_4, and S_5, i.e., for S_3, IC into lower excited states is not probable and for S_6 only S_3 can serve as decay channel on the considered time scale. Compared to pristine PTCDA where the excitation mainly occurs from the HOMO to the LUMO (S_1) and no further depopulation channel below S_1 exists, in Na_2PTCDA the excitation probably occurs to S_6 (LUMO+3) and internal conversion to S_3 (LUMO+2) is possible, which should result in shorter not longer lifetimes.

An alternative interpretation might be given assuming relaxation within excitonic bands in well-ordered PTCDA layers that vanishes in Na_2PTCDA. A hint that this may be the case comes from angle-resolved UPS that shows strong angle-dependent variations in the spectral shapes in pristine PTCDA but not anymore after Na doping: an indication that the ordered surface region of pristine PTCDA layers becomes more amorphous under Na doping. Under these circumstances the formation of CT-exciton bands[15–17] is more probable in pristine PTCDA layers and disappears under Na doping. As a result bandlike relaxation cannot further serve as decay channel and the lifetime of hot electrons in Na_2PTCDA raises. This interpretation implies that relaxation in excitonic bands is a dominant process in the investigated system.

B. PTCDA on Ag(111) and HOPG

Interestingly, a result similar to the situation in Na_2PTCDA can be observed for low PTCDA coverages on Ag(111). Figure 4 shows the lifetime τ at an intermediate-state energy $E-E_F$ of 1.3 eV as a function of the PTCDA overlayer thickness on Ag(111). At submonolayer to monolayer coverage, τ exceeds the value of clean Ag(111) as well as the lifetime at higher PTCDA coverages up to a factor of 1.5.

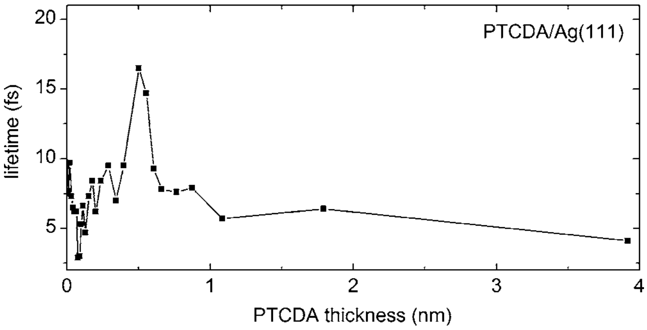

FIG. 4. Evolution of the lifetime of hot electrons in PTCDA thin films on Ag(111) ($E-E_F=1.3$ eV).

A preliminary interpretation of this result may be given as follows. It is known that PTCDA on Ag(111) forms chemical bonds[18–20] by a charge transfer from the Ag(111) surface to the PTCDA molecules. DFT studies of 1 ML PTCDA on Ag(111) have shown that the formed LUMO-Ag hybrid orbital is 1.4 eV broad and located about −0.1 eV below the Fermi level. It has accepted ≈0.6 of an electron from the metal, resulting in a metallic characteristic of the PTCDA/Ag(111) interface. The electron dynamics in metals is known to be (much) faster than in semiconductors; but unlike the electron transport in a solid, it is not just the density of states around E_F that counts for the excited-state dynamics of hot electrons. In fact the integrated unoccupied DOS in the whole energy range between E_F and the energy E of the excited electron has to be taken into account. Therefore, due to the downshift and even partial filling of the LUMO state, the overall density of unoccupied states between E_F and E is reduced resulting in a decreased scattering rate in the excited electrons. For thicker films the PTCDA-LUMO opens new reachable unoccupied states, i.e., decay channels. By this, the lifetime of intermediate states decreases. No similar effect is expected, e.g., at a PTCDA/HOPG interface, because no charge transfer between HOPG and PTCDA has been reported. Indeed the lifetime just increases monotonically at higher coverage up to the bulk value (not shown here).

IV. CONCLUSIONS

In summary time-resolved 2PPE studies of the Na doping process of PTCDA thin films are reported. They give insight into the dynamics of hot electrons in organic semiconductors. It could be shown that within a one-electron picture, an increase in the lifetime of hot electrons in Na_2PTCDA compared to the one in pristine PTCDA can be explained. It is a result of the different numbers of states that is reachable by electronic decay of the electrons excited into higher unoccupied states in the two considered systems. In Na_2PTCDA this number is reduced by a mismatch of the probability densities of the higher unoccupied states and the LUMO and LUMO +1 that therefore cannot serve as channels for population decay. The one-electron picture can also explain the observation of a raised lifetime of hot electrons in thin PTCDA layers on Ag(111). Treated within a many-electron picture that has to be taken into account if one considers the absorption of the first 2PPE pulse by a molecule as creation of an excited molecular state, the observed raise of lifetime in Na_2PTCDA can only be explained if additional effects, e.g., CT-exciton bands in well-ordered layers are taken into account.

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