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Relation between Electron Scattering Resonances of Isolated NTCDA Molecules and Maxima in the Density of Unoccupied States of Condensed NTCDA Layers

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ABSTRACT: The empty-level structure of the 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) molecule is characterized by means of dissociative electron attachment (DEA) experiments in the gas phase coupled with DFT calculations. Distinct maxima in the anion currents generated by electron attachment to NTCDA, as a function of incident electron energy, are ascribed to capture of incident electrons into empty orbitals, i.e., the process referred to as shape resonance. The empty orbital energies of gas-phase NTCDA shifted to 1.2 eV

lower energy reproduce satisfactorily the maxima of the unoccupied electronic states of a multilayer NTCDA film measured by means of the very low energy electron diffraction method and the total current spectroscopy measurement scheme. The present results indicate that the empty levels of individual NTCDA molecules are stabilized in the solid state, but their relative energies remain nearly unaltered. The stabilization energy in multilayer film of NTCDA molecules is likely due to attractive polarization forces. Fragmentation of the gas-phase NTCDA temporary parent anions via the DEA mechanism, the other issue of the present investigation, leads to the rupture of the bonds between the end carbonyl groups and the naphthalene core, and occurs at incident electron energies above 2 eV. Possible chemical changes in condensed NTCDA molecules initiated by the DEA mechanism under conditions of electron transport through the film are discussed.
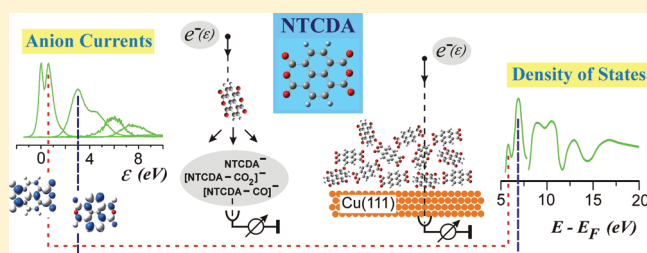
1. INTRODUCTION

Condensed-phase structures formed on a surface by deposition of large organic π-conjugated molecules like 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA, Chart 1), have received considerable interest over the last decades[1] owing to their attractive electronic and optical properties which have been intensively investigated by a variety of experimental techniques (see, for instance refs 2 and 3 and references therein). Among others, the density of unoccupied electronic states (DOUS) is an important property to be discovered in order to predict and manipulate the electron transport properties of an organic material. The individual molecules of a multilayer organic film disposed far from the interface are believed[3,4] to be weakly bound by van der Waals forces, thus probably keeping an electronic structure close to that of the isolated molecule. Therefore, the energies of the normally vacant orbitals of a single molecule are expected to be correlated with the maxima of DOUS of multilayer organic films observed by means of near-edge X-ray absorption fine structure (NEXAFS) and inverse photoemission spectroscopy (IPES)[2] and also by means of secondary electron emission spectrometry or very low energy electron diffraction (VLEED).[5] Quantum chemical calculations on the isolated molecules can thus play a significant role in the assignment of experimental findings and prediction of the electronic properties of molecules in their condensed state.[6−10]

The empty orbitals of isolated molecules are involved in the formation of gas-phase temporary molecular anions under electron-molecule scattering[11−13] at low (<15 eV) collision energies. Anions formed by the resonant electron capture mechanisms[13] can follow an accessible dissociation decay channel, so-called dissociative electron attachment (DEA), producing negatively charged and neutral fragments at suitable incident electron energies. The maxima observed in the yields of mass-selected negative ions recorded as a function of the incident electron energy by means of DEA spectroscopy[11−14] thus reflect the empty orbital structure of the target molecule. An even more suitable means to elucidate the empty-level structure of isolated molecules is electron transmission spectroscopy (ETS) in the format devised by Sanche and Schulz.[15] This technique, however, requires a relatively high sample pressure and, in spite of a lot of experiments performed with relatively small organic molecules,[16,17] encounters difficulties when the molecular system under investigation possesses a low volatility, as in the case of PTCDA. Fortunately, considerable progress has been achieved in reproducing the energies of vertical electron attachment (VAEs) measured in the ET spectra with either ab initio or density functional theory (DFT) calculations in conjunction with empirically

Chart 1

PTCDA   NTCDA

● Carbon   ● Oxygen   ● Hydrogen
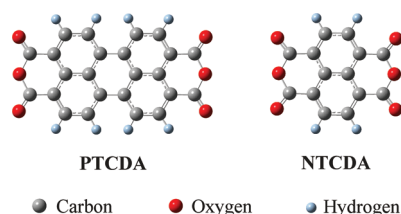
calibrated linear equations[18−20] to scale the calculated virtual orbital energies (VOEs) of the neutral molecules.

In the present work the VAEs of NTCDA are evaluated by scaling the VOEs obtained with DFT calculations. The calculated VAEs are then compared with the energies of the maxima observed in the gas-phase DEA spectra and of DOUS determined by total current spectroscopy (TCS) and derived from the literature data. The findings are discussed in relation to recent similar efforts[21] performed with PTCDA and give some more insight into the relationship between the electronic structure of organic molecule in vacuo and in the condensed state. A variety of fragment negative ions formed by DEA to gas-phase NTCDA highlights another aspect of the present investigation that is discussed in the framework of possible chemical changes[22] in condensed NTCDA under conditions of electron transport through it, i.e., under conditions of excess negative charge. The present interdisciplinary work thus provides one more attempt (see also ref 23 and recent reviews on experiment[24] and theory[25]) to link gaseous and condensed matter properties on compounds which are believed to be weakly bound in the condensed state.

2. EXPERIMENTAL METHODS

Dissociative Electron Attachment Spectroscopy. An overview of the DEAS technique may be found elsewhere.[11,12] Our apparatus coupled with a magnetic mass spectrometer was described in detail previously[26] including a schematic representation and description of specific conditions.[27] Briefly, a magnetically collimated electron beam of defined energy was passed through the collision cell containing a vapor of substance under investigation. The pressure in the main vacuum chamber was kept below 10^{-5} Pa, to ensure single-collision conditions in the collision cell (where the pressure is about 2 orders of magnitude higher). Currents of mass-selected negative ions were recorded as a function of incident electron energy in the range $0-15$ eV. The electron energy scale was calibrated with a signal of SF_6^- at zero energy generated by attachment of thermal electrons to SF_6. The full width at half-maximum (fwhm) of the electron energy distribution was estimated to be 0.4 eV, and the accuracy of determination of the peak position ± 0.1 eV. A suitable pressure of NTCDA could be achieved at 150 °C, and the walls of the collision cell were kept at 160 °C to prevent condensation. No thermal decomposition was found[28] even at significantly higher temperature (220 °C) in an ultraviolet photoemission spectroscopy study. The substance under investigation is commercially available, Sigma-Aldrich product No. N818, and was used without additional purification.

DFT calculations were carried out using the Gaussian03[29] program package. Evaluation of the empty orbital energies was performed using the B3LYP functional[30] and a standard 6-31G(d) basis set. Despite the difficulties encountered for an accurate

description of negative ion states,[31] the occurrence of good linear correlations between the neutral-state VOEs and the corresponding VAEs measured in the ET spectra has been demonstrated (see, for instance refs 18−20). The scaling parameters, determined empirically, are different for σ^* and π^* states and change with the theoretical method employed. Moreover, a more accurate correlation would be expected if the linear equation were calibrated with "training" compounds structurally close to the subject molecule. In the present study a scaling equation derived[32] with B3LYP/6-31G(d) calculations for π^* orbitals of alternating phenyl and ethynyl groups, VAE = (VOE + 1.14)/1.24, was employed to scale the π^* VOEs. Scaling of σ^* orbital energies is usually a more difficult task because a relatively small number of experimental VAEs is available, σ^* resonances being hardly visible in the ET spectra of molecules composed of the lighter elements, H, C, N, O, etc. For a rough evaluation, we employ the scaling equation (VAE = (VOE + 0.97)/0.79) found for σ^* C−Br orbitals in a series of bromoalkanes.[33]

Total Current Spectroscopy. This technique provides a convenient measurement scheme within the VLEED method.[5,34] The experiments were performed in an ultrahigh vacuum system (base pressure of 10^{-7} Pa) where Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) units were installed. An incident electron beam was normally directed onto the solid sample giving a spot of $0.2-0.4$ mm in diameter on the surface. The full width at half-maximum of electron energy distribution of the incident beam was estimated to be 0.7 eV and the typical current density used was $10^{-5}-10^{-6}$ A/cm^2. The total current $J(E)$ transmitted through the sample was monitored as a function of electron energy E in the range $0-30$ eV. The first derivative dJ/dE, referred to as the TCS spectrum, was measured using a lock-in amplifier. The energy scale was calibrated by referring to the maximum of the primary peak in TCS spectra which determines the vacuum level (VL) location. The maxima in the negative second derivative of electron current transmitted through the sample, i.e., $-d^2J/dE^2$, are found[5,34−37] to be related to maxima of DOUS and could be revealed by the present experiments starting from a few electronvolts above the VL.

Thin films of NTCDA (Aldrich) were thermally deposited in situ from the Knudsen cell onto the Cu(111) surface. The substrate was kept at ambient temperature and the evaporation temperature was set to approximately 200 °C. The actual temperature in the hottest part of the evaporation cell may differ from the temperature measured near the heated cell. Therefore, the deposition procedure was controlled by the deposition rate set approximately to 0.1 nm/min, as was monitored by the quartz microbalance. TCS measurements were carried out during the film deposition until the film thickness reached $10-13$ nm. The attenuation of the substrate spectrum also provided information on the thickness of the organic overlayer.[34,38] The AES analysis revealed a good agreement between atomic composition of the films and chemical structure of the molecules. Due to the fact that no LEED patterns from the films were observed, we conclude on formation of the disordered molecular films.

3. RESULTS

Negative Ions Produced by Electron Attachment. Currents of mass-selected negative ions formed by electron attachment to gas-phase NTCDA as a function of incident electron energy are reported in Figure 1. Likely structures of the observed fragment anions, peak energies, and relative intensities are listed in Table 1.
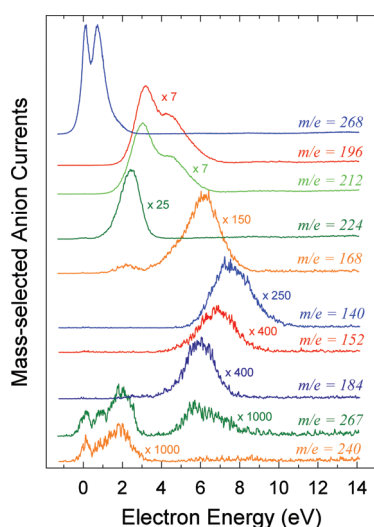
Figure 1. Currents of mass-selected negative ions formed by electron attachment to gas-phase NTCDA as a function of incident electron energy. The spectra are arranged in order of decreasing intensity.

Table 1. Negative Ions Formed by Electron Attachment to Gas-Phase NTCDA, Peak Energies, and Relative Intensities Taken from Peak Maxima

m/e	anion structure	peak energy	relative intensity
268	$[NTCDA]^-$	0.0	100
		0.7	98
		2.0 sh[a]	
267	$[NTCDA - H]^-$	2.0	0.1
		5.7	<0.1
240	$[NTCDA - CO]^-$	0.0	<0.1
		1.9	<0.1
224	$[NTCDA - CO_2]^-$	2.4	2.5
212	$[NTCDA - 2(CO)]^-$	3.0	9.3
		4.4 sh	
196	$[NTCDA - CO_2 - CO]^-$	3.2	10.4
		4.4 sh	
184	$[NTCDA - CO_2 - CCO]^-$	6.0	0.1
168	$[NTCDA - CO_2 - 2(CO)]^-$	2.2	0.1
		6.2	0.5
152	$[NTCDA - 2(CO_2) - CO]^-$	6.9	0.1
140	$[NTCDA - 2(CO_2) - CCO]^-$	7.3	0.2

[a] Note: sh. means shoulder.

Currents of parent molecular anions $[NTCDA]^-$ (m/e = 268) were clearly observed from three not completely resolved resonant states. At electron energy around 2 eV in addition to intact $[NTCDA]^-$ parent anions also fragment anions generated by DEA are observed. However, the latter are at least 2 orders of magnitude less intense. Fragmentation of NTCDA by low-energy electrons is mainly due to rupture of the bonds between the end groups and the naphthalene core and leads to elimination of various combinations of CO and CO_2 fragments. The occurrence of such complex rearrangement processes usually requires a long time.[39] A similar behavior was observed previously in the DEA spectra of a series of compounds containing anhydride or imide groups.[21,40] The only example of a single bond breaking

**Table 2. B3LYP/6-31G(d) VOEs and Their Scaled Values (See Experimental Methods) for NTCDA (Values in eV)**

orbital	VOE	scaled VOE
σ_9^*	5.395	8.06
π_9^*	5.082	5.02
σ_8^*	4.822	7.33
σ_7^*	4.669	7.14
σ_6^*	4.058	6.36
σ_5^*	3.898	6.16
σ_4^*	3.870	6.13
σ_3^*	3.160	5.23
σ_2^*	2.539	4.44
π_8^*	2.386	2.84
σ_1^*	1.954	3.70
π_7^*	1.880	2.44
π_6^*	0.101	1.00
π_5^*	−0.290	0.69
π_4^*	−1.494	−0.29
π_3^*	−1.871	−0.59
π_2^*	−2.508	−1.10
π_1^*	−4.000	−2.31

DEA process in the present case is formation of the $[NTCDA - H]^-$ fragment. It is to be noted that the very weak m/e = 267 anion current observed below 2 eV can be due to the much more intense current of the m/e = 268 $[NTCDA]^-$ molecular anion. Summarizing the data reported in Figure 1 and Table 1, we conclude that resonant bands in low-energy electron attachment to NTCDA appear at incident electron energies of 0.7−0.9, 2.0−2.4, 3.0−3.2 eV, and around 4.4, 5.7−6.2, and 7 eV; an intense signal at zero energy is also observed.

Assignment of Resonant States. The anion currents observed in the DEA spectra at incident electron energies below the threshold for electronic excitation of the target molecule can reasonably be ascribed to formation of shape resonances,[13] associated with temporary capture of an extra electron into one of the normally empty π^* molecular orbitals (MOs). The shape resonances associated with σ^* MOs of second-row derivatives (such as NTCDA) are short-lived (relative to re-emission of an extra electron) and are not expected to contribute significantly to DEA spectrum. The DEA peaks associated with short-lived resonances are usually shifted to sizably lower energies relative to the corresponding VAEs, the process being well understood in terms of the survival probability factor.[41] Calculated on B3LYP/6-31G(d) level of theory NTCDA VOEs and their scaled values are reported in Table 2.

Given that the lowest four π^* MOs lie in a bound region with negative VAEs (Table 2), the associated anions can be formed only in vibrationally excited states. This can lead to formation of molecular anions by means of the vibrational Feshbach resonance (VFR)[11−13] mechanism, giving rise to intense signals at zero incident electron energy (Figure 1). The next two, π_5^* (0.69 eV) and π_6^* (1.00 eV), MOs are likely both associated with the DEA signals at 0.7−0.9 eV. The scaled VOEs of π_7^* (2.44 eV) and π_8^* (2.84 eV) MOs nicely match the DEA negative currents observed at 2.0−2.4 and 3.0−3.2 eV, respectively. The π_9^* shape resonance contributes to DEA signals observed at higher energy. In this energy range, however, contributions could come from some σ^* state (Table 2) or, more likely, core-excited resonances.[13]

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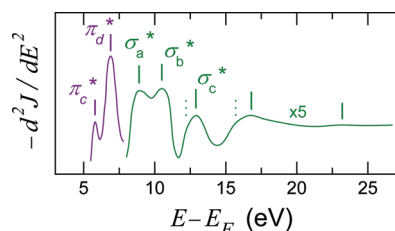
Figure 2. Negative second derivative of the total current transmitted through a 15 nm NTCDA film deposited on a Cu(111) surface. Maxima are indicated by solid vertical bars; dashed bars indicate shoulders.
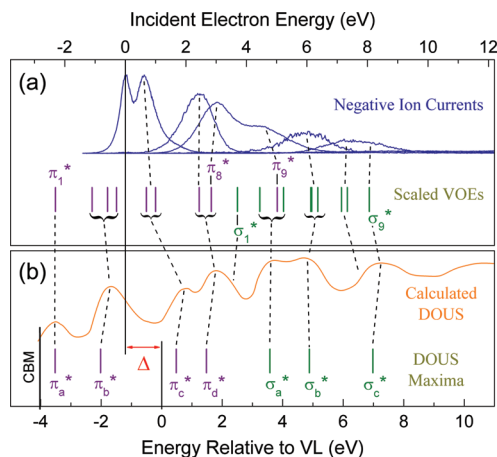
Figure 3. (a) Currents of several mass-selected negative ions (solid curves) and scaled VOEs (vertical bars) of isolated NTCDA. (b) Calculated DOUS of NTCDA film (solid curve) and DOUS maxima (vertical bars). The maxima marked with π_a^* and π_b^* are derived from refs 46−48; the others are from the present data (Figure 2). The energy scale of (a) is red-shifted relatively to that of (b) by 1.2 eV (the shift is marked with Δ).

To obtain an additional evaluation of the electron affinity (EA) of NTCDA, the vertical EA (EA_v) was calculated as the difference between the total energy of the neutral and the lowest anion state, both in the optimized geometry of the neutral state, while the adiabatic EA (EA_a) was obtained as the energy difference between the neutral and the lowest anion state, each in its optimized geometry. The EA values obtained at the B3LYP/6-311G(d) level are EA_v = 2.60 eV (not far from the negative of the first scaled VOE, 2.31 eV, see Table 2) and EA_a = 2.77 eV. The latter differs by about 0.5 eV from the experimental value of 2.28 eV reported by Chen and Wentworth,[42] being in better agreement with experiment than the value of 2.90 eV calculated[8] at the B3LYP/6-31G(d)//B3LYP/6-311++G(d,p) level. It should be noted that for such a stable anion state even basis set 6-311G(d), which does not include diffuse functions, seems to overestimate the EA.

DOUS above Vacuum Level. The negative second derivative of electron current transmitted through NTCDA film (15 nm) deposited on Cu(111) surface is shown in Figure 2. Two narrow DOUS maxima (marked as π_c^* and π_d^* in Figure 2) located at 5.8 and 6.9 eV above the Fermi level are associated with π^* orbitals of the NTCDA molecule. The signals at higher energies reveal less intense and partially superimposed bands with maxima at 8.9, 10.5, 12.9, 16.8, and 23.2 eV likely associated with σ^* DOUS states.

Two additional unoccupied states give rise to the shoulders observed at 12.2 and 15.7 eV above the Fermi level (Figure 2). The lowest DOUS maximum (π_c^* in Figure 2) disclosed by the present TCS data appears at 1.3 eV above the VL. In agreement, the data of ref 43 lead to an NTCDA film work function of 4.5 eV. Other values reported in the literature are 4.3 ± 0.1 eV[44] for a multilayer NTCDA film on a Cu(111) surface and 4.7 eV in a sandwich Au/NTCDA/PTCDA structure.[45]

4. DISCUSSION

DOUS Maxima in the Conduction Band. Figure 3b displays a plausible structure of the conduction band of an NTCDA film, as deduced from literature data. The electron affinity, measured with IPES, is equal to 4.02 eV.[46] There are four maxima of unoccupied states (labeled as $\pi_a^*−\pi_d^*$ in Figure 3) associated with π^* orbitals at energies 0.5 (assigned to the LUMO), 2.0, 4.5, and 5.5 eV above the conduction band minimum (CBM), as deduced from NEXAFS investigations of NTCDA on Cu(100) and Ag(111) surfaces.[47,48] In agreement, electron energy loss spectroscopy (EELS) of NTCDA films deposited on ZnO(0001)[49] reveals the transitions ascribed to excitations from the highest occupied molecular orbital (HOMO) to the π_a^* and π_b^* states. It can be noted that the HOMO is located 0.5 eV below the valence band maximum and the band gap is estimated to be 3.1 eV.[50,51] A maximum associated with σ^* orbitals lying 11 eV above CBM (σ_c^* in Figure 3) was found[47,48] and discussed[49] elsewhere. In addition, two more transitions (at 12.5 and 14.5 eV) were revealed by EELS.[49] Assuming they take place from the HOMO and HOMO−1 of NTCDA, two unoccupied states should exist at energies 3.58 and 4.88 eV above the VL (labeled as σ_a^* and σ_b^* in Figure 3). The DOUS plotted using the peaks positions derived from literature data[47,52,53] and a Gaussian broadening of 0.7 eV is presented in Figure 3b with a solid line. Its shape is in excellent agreement with the present TCS results shown in Figure 2 and matches the reported DOUS maxima.[†]

Correspondence between DOUS and Scaled VOEs. To match the position of the solid-phase NTCDA LUMO located at −3.51 eV (π_a^* in Figure 3) with the gas-phase LUMO (−2.31 eV, π_1^* in Table 2) the latter should be stabilized by 1.2 eV. Assuming that empty orbitals of a single NTCDA molecule are not affected by the environment in the condensed state we predict their location in the solid by shifting the scaled VOEs (reported in Table 2) to lower energy by the same amount, i.e., 1.2 eV. A probable correspondence between shifted VOEs and DOUS maxima are indicated in Figure 3 by dashed lines. Because of the uncertainty of the scaled σ^* VOEs, the indicated DOUS maxima/σ^* VOEs correlations are only tentative. On the contrary, the reliability of the π^* scaling procedure suggests that the π_9^* MO could give a considerable contribution to the DOUS maximum σ_a^*, previously associated[44] only with σ^* states. The maxima of the anion currents observed in the present DEAS investigation are in agreement with the scaled π^* VOEs (Figure 3a), thus confirming their reliability.

To match the DOUS maxima of the PTCDA film to the scaled VOEs of the isolated PTCDA molecule, the latter were stabilized by 1.4 eV,[21] this shift being ascribed to intermolecular attractive polarization forces in the condensed phase. The smaller value (1.2 eV) found here for NTCDA can be reasonably due to a smaller binding energy of the NTCDA dimer relative to the PTCDA dimer, in line with calculations[55] taking into account the van der Waals interactions. The same calculations[55] also reproduce

the different (0.5 eV[56]) adsorption energies of PTCDA and NTCDA on a gold surface.

We would like to mention that a good correlation also exists between the filled MO energies of isolated NTCDA and the occupied electronic states of the valence band of condensed NTCDA films. The energy shift between the occupied states in the gas and condensed phases was ascribed to the polarization energy.[28] At variance with the empty levels, the B3LYP/6-31G-(d) energies of the filled MOs did not require any scaling procedure. This difference can be traced back to the peculiarity of quantum-chemical calculations of anion states in comparison with cation states (see, for instance, refs 18 and 57−59).

The energy correspondence between the two close-in-energy π_5^* and π_6^* NTCDA MOs (stabilized by 1.2 eV) and the corresponding DOUS peak (π_c^*) is worse than that found for the other MOs (Figure 3). In fact, the π_5^* and π_6^* MOs seem to be more destabilized in the solid state. In PTCDA an opposite situation was observed for the π_{13}^* MO.[21] Assuming that applied scaling procedure is correct, we have no reasonable explanation for the different behavior of some orbitals on going from the gas phase to the solid state.

Solid-State LUMO Location. The unoccupied electronic levels of condensed π-conjugated molecules measured with IPES were found to correlate with the DOUS simulated using the shifted energies of vacant MOs derived from the semiempirical calculations.[6] Recent investigations[7,9] demonstrate a good correlation between the DFT LUMO energy (correlated with the negative of the vertical electron affinity of a molecule in vacuo) and the condensed-state LUMO position (that is, the solid-state electron affinity) derived from IPES measurements in a series of twenty four organic molecules.[7] For instance, in NTCDA the π_1^* VOE (-3.99 eV[7] or -4.000 eV, reported in Table 2) surprisingly coincides with the solid-state LUMO position (-4.02 eV[46]). However, this fortuitous coincidence should have no physical meaning.

Indeed, only the scaled Kohn−Sham NTCDA LUMO energy (-2.31 eV) is believed to be related to the LUMO energy of an isolated NTCDA molecule. In agreement, calculated the vertical electron affinity (2.60 eV; compare with the experimental adiabatic value of 2.28 eV[42]) of NTCDA estimated by the total energy difference between neutral NTCDA and its vertical anion correlates with -2.31 eV rather than with -3.99 eV. Then, to extend the gas-phase values into the solid state, one should take into account the intermolecular interactions in the condensed state. In this way DFT calculations coupled with the polarizable continuum model[60] utilized elsewhere[8] seems to be a more adequate approach.

Possible DEA Reactions in the Solid State. Processes in nanoscale thin films stimulated by low-energy electron irradiation have been investigated in a variety of adsorbed species (see, for instance ref 22 and references therein) and are related to resonant states observed in gas-phase experiments.[23,24] Fragmentation of gas-phase NTCDA by the DEA mechanism is significant at incident electron energies above 2 eV (Figure 1), i.e., is associated with electron attachment into π_8^* and higher-lying MOs that, in turn, correspond to π_d^* and higher-lying unoccupied states in the condensed state (Figure 3). Electron attachment to the lowest seven MOs of NTCDA generates long-lived (mass-spectrometrically observed in the microsecond time scale) undissociated parent molecular anions $[\text{NTCDA}]^-$ even in the gas phase, where a large amount of excess energy (that is, incident electron energy plus EA_a of the target molecule) is

stored inside the anion. In the condensed phase the excess energy can be quickly dissipated by interactions with neighboring molecules, thus preventing dissociation. Thus, the extent of dissociation caused by electron transport through NTCDA films is likely negligible.

5. CONCLUSIONS

The energies of resonant states associated with low-lying empty orbitals of NTCDA molecule in vacuo were revealed by means of electron attachment spectroscopy and assigned to the corresponding orbitals with DFT calculation. DOUS maxima in the conduction band of condensed NTCDA films were obtained from total current spectroscopy measurements and compared with the predicted energies of vacant orbitals of gas-phase NTCDA. To match the positions of the DOUS maxima with the vacant orbital energies, the latter must be shifted to the lower energy by 1.2 eV. This shift is attributed to polarization interactions in the condensed NTCDA film. A constant shift of the vacant orbitals implies that in the condensed state the NTCDA molecules keep their individual electronic structure, although the perturbation experienced by some orbitals is found to be somewhat different. A procedure for evaluating the solid-state LUMO position via the scaled energy of the gas-phase LUMO, corrected for polarization interactions in the film, could be proposed, whereas direct evaluation of the solid-state electron affinity from the LUMO energy supplied by DFT calculations for the isolated molecule seems to be questionable. Finally, the present results indicate that electron transport through NTCDA films should not cause chemical changes, thus fulfilling the requirement of long-term stability under these conditions.

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■ ACKNOWLEDGMENT

■ ADDITIONAL NOTE

[†] It should be noted that the DOUS curve in Figure 3b is shifted to lower energy by 0.85 eV to match the LUMO position taken from the NEXAFS data. This mismatch is probably due to the core−hole effect.[54] Nevertheless, in this section we follow the DOUS maxima whose positions are directly derived from the NEXAFS measurements to compare the present findings in NTCDA with earlier data on PTCDA.[21]

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