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Vibrational properties of organic donor-acceptor molecular crystals: Anthracene-pyromellitic-dianhydride (PMDA) as a case study

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We establish a reliable quantum-mechanical approach to evaluate the vibrational properties of donor-acceptor molecular crystals. The anthracene-PMDA (PMDA = pyromellitic dianhydride) crystal, where anthracene acts as the electron donor and PMDA as the electron acceptor, is taken as a representative system for which experimental non-resonance Raman spectra are also reported. We first investigate the impact that the amount of nonlocal Hartree-Fock exchange (HFE) included in a hybrid density functional has on the geometry, normal vibrational modes, electronic coupling, and electron-vibrational (phonon) couplings. The comparison between experimental and theoretical Raman spectra indicates that the results based on the α PBE functional with 25%-35% HFE are in better agreement with the experimental results compared to those obtained with the pure PBE functional. Then, taking α PBE with 25% HFE, we assign the vibrational modes and examine their contributions to the relaxation energy related to the nonlocal electron-vibration interactions. The results show that the largest contribution (about 90%) is due to electron interactions with low-frequency vibrational modes. The relaxation energy in anthracene-PMDA is found to be about five times smaller than the electronic coupling. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4936965>]

INTRODUCTION

Bimolecular charge-transfer (CT) organic molecular semiconductors are systems in which one type of molecule acts as an electron donor (D) and the other as an acceptor (A). There is currently an increasing interest in these systems due to their potential applications in opto-electronic devices.¹⁻¹⁶ For example, several groups have recently reported the fabrication of ambipolar field-effect transistors using CT compounds as active elements.^{3,9,10,13,17} Electrodes based on highly conductive CT systems have also been shown to yield superior organic thin-film transistor characteristics, compared to conventional electrodes.^{18,19} In order to design new, highly performing CT systems, a deeper understanding of the microscopic parameters that define the electrical and electronic properties of these systems is desirable. In most of the recent studies, the emphasis has been placed on the electronic couplings,^{5,9,16,20} while the electron-phonon interactions and vibrational properties of these systems have been much less investigated.

From a theoretical standpoint, the availability of reliable quantum-mechanical approaches to evaluate and predict the electronic and electron-vibration (phonon) couplings is of high importance. Over recent years, density functional

theory (DFT) has been extensively used for the evaluation of the charge-transport microscopic parameters in organic semiconductors.²¹ However, it was demonstrated that in one-component crystals, such as pentacene, the DFT estimates for both electronic coupling (transfer integrals)²² and electron-vibration couplings²³ are very sensitive to the choice of the DFT functional and especially to the amount of nonlocal Hartree-Fock exchange (HFE) included in the functional. In a very recent work, we studied the dependence of the transfer integrals, band gaps, bandwidths, and effective masses on the HFE amount in dibenzotetrathiafulvalene (DBTTF)-7,7,8,8-tetracyanoquinodimethane (TCNQ), a high-mobility mixed-stack CT system. We found that, whereas in the pentacene crystal, the electronic coupling increases linearly with an increase in HFE, in DBTTF-TCNQ, the electronic couplings for holes and electrons, due to their super-exchange nature, depend only slightly on the HFE amount.²⁰ Here, we extend this approach to the investigation of the vibrational properties and electron-vibration couplings in CT crystals. The anthracene-PMDA (PMDA = pyromellitic dianhydride) crystal, where anthracene acts as an electron donor (D) and PMDA as an electron acceptor (A), is taken as a representative system (Fig. 1). We also report the infra-red (IR) and Raman spectra of this crystal. Our choice of anthracene-PMDA is motivated by the high quality non-resonance Raman spectra we could obtain for this system, which allow a direct comparison between the theoretical and experimental results.

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FIG. 1. Chemical and crystal structure²⁴ of anthracene-PMDA. The long, short, and *z* (perpendicular to the plane) molecular axes are shown in red, with the origin defined at the center of mass. The green arrow indicates the donor-acceptor pair with the largest direct electronic coupling (t_{DA}).

COMPUTATIONAL METHODOLOGY

The electronic-structure calculations on anthracene-PMDA were performed on the basis of both experimental²⁴ and optimized crystal structures. During the optimization, the positions of the atoms in the unit cell were relaxed, while the cell parameters were kept fixed at the experimental values. Following our earlier study,²⁰ the impact of HFE has been investigated by using the α PBE functional, based on the original PBE functional,^{25,26} following the simple hybrid scheme proposed by Adamo and Barone,²⁷

$$E_{\alpha\text{PBE}} = \alpha E_X^{\text{HF}} + (1 - \alpha) E_X^{\text{PBE}} + E_C^{\text{PBE}}, \quad (1)$$

where $\alpha = 0.25$ corresponds to the PBE0 functional.

For the electronic-structure calculations on the crystal, the Brillouin zone was sampled using a Γ -centered uniform k -point $8 \times 6 \times 8$ grid. The Γ -point phonons (lattice vibrations), macroscopic dielectric tensors, and IR and Raman intensities were obtained via a coupled perturbed Hartree-Fock (CPHF) approach.^{28,29} All calculations were performed using the α PBE functional and the 6-31G basis with the CRYSTAL14 package.³⁰ The effective masses and their orientations were calculated by diagonalizing the inverse of the effective mass tensor ($1/m_{ij}$); the latter was obtained from the valence band maximum or conduction band minimum using a finite-difference method on a five-point stencil with a 0.01 1/bohr step (1 bohr = 0.529 Å). G_0W_0 calculations^{31,32} were performed on the basis of PBE-derived wavefunctions and energies using the BerkeleyGW code.³³ The PBE wavefunctions and energies were computed with a wavefunction kinetic energy cutoff of 1225 eV using norm-conserving Troullier-Martins pseudopotentials (core radii: 1.5 au for C, 1.3 au for H, and 1.3 au for O),³⁴ as implemented in Quantum-ESPRESSO.³⁵ The direct electronic couplings (t_{DA}) between anthracene and PMDA molecules along the stacking direction were obtained using the fragment orbital approach.³⁶

FIG. 2. Valence and conduction bands of the anthracene-PMDA crystal at the experimental geometry obtained using the α PBE functional with different HFE amounts (solid lines) and G_0W_0 (crosses). The points of high symmetry in the first Brillouin zone are labeled as follows: $\Gamma = (0, 0, 0)$, $X = (0.5, 0, 0)$, $Y = (0, 0.5, 0)$, $B = (0, 0, 0.5)$, $C = (0.5, 0.5, 0)$, $A = (0.5, 0, 0.5)$, $E = (0.5, 0.5, 0.5)$, and $D = (0, 0.5, 0.5)$, all in crystallographic coordinates.

The effective electron [hole] electronic couplings (t_{eff}) were evaluated using the energy-splitting approach by considering the frontier levels of an A-D-A [D-A-D] triad.⁵ All electronic couplings were calculated at the α PBE/6-31G level with the Gaussian package.³⁷

Experimental

To grow anthracene-PMDA CT crystals,³⁸ the donor and acceptor were each dissolved in 2-butanone. The two solutions were mixed and the formation of the complex was noted immediately by the red hue of the resulting solution. This mixture was then heated to evaporate enough solvent to induce super-saturation. Slow cooling resulted in the formation of single crystals that could be tuned in size by adjusting the cooling rate.

Polarized Raman spectra in the range 20–2000 cm^{-1} were obtained in the backscattering geometry with a DilorXY triple-grating spectrometer, manufactured by Jobin-Yvon, outfitted with a liquid nitrogen cooled CCD detector. The spectrometer was equipped with a 32X microscope objective of numerical aperture 0.3 to focus the incident light on the sample to a spatial resolution of approximately 5 μm ; it was operated in subtractive mode with a resolution of $\sim 0.3 \text{ cm}^{-1}$ and accuracy of $\sim 1 \text{ cm}^{-1}$. A Spectra-Physics 375b dye laser with Kiton red dye was used to produce a 631 nm excitation wavelength. Low-temperature measurements at 80 K were made under vacuum ($\sim 10^{-6}$ Torr) using a Joule-Thomson refrigerator manufactured by MMR Technologies. The sample was placed on the fridge mount such that the polarization of the incident light was parallel to the *c*-axis of the crystal. Due to their small relative size, the crystals were electrostatically attracted to the fridge mount and did not necessarily require any added

adhesive; however, a speck of vacuum grease was attached to one corner of each crystal.

RESULTS AND DISCUSSION

Electronic structure

We first discuss the impact that the degree of HFE has on the band structure of anthracene-PMDA, based on the experimental crystal geometry (Fig. 2).²⁴ We note that calculations using a HFE amount larger than 35% did not converge; therefore, we only discuss here the results obtained within the 0%–35% range of HFE. We recall that (semi)local DFT functionals³⁹ underestimated the band gaps. As a result, calculations based on functionals with a low HFE amount predict a vanishing band gap for many CT crystals, as was shown, for instance, in the case of DBTTF-TCNQ²⁰ and tetrathiafulvalene-*p*-chloranil (TTF-CA).⁴⁰ For anthracene-PMDA, a non-zero gap is obtained even with the pure PBE ($\alpha = 0$) functional. In agreement with findings for other CT crystals,²⁰ the band gap for the investigated HFE range shows a linear increase from 0.94 eV to 2.68 eV, i.e., it increases by a factor of almost three ($R^2 = 0.999$) with the increase in HFE. In contrast, there occurs only a very slight increase by about 0.044 eV [0.031 eV] for the valence bandwidth (from 0.328 to 0.372 eV) [conduction bandwidth (from 0.209 to 0.240 eV)]. As a result, the observed decrease in the smallest component of the hole [electron] effective mass calculated at the Γ [Y] point is also very small, varying from 1.156 to 1.093 m_0 [from 1.123 to 1.084 m_0] (Table I). The small variations in the bandwidths and effective masses with respect to the HFE amount are the result of the super-exchange nature of the effective electronic couplings for holes and electrons in CT crystals.^{5,20} Indeed, while the direct donor-acceptor couplings within the investigated HFE range show a 50% increase from 0.300 eV to 0.452 eV, both effective hole and electron transfer integrals increase only slightly from 0.048 to 0.053 eV and 0.046 to 0.053 eV, respectively.

As a result of the weak dependence of the bandwidths on the HFE amount, good agreement with the G_0W_0 results is obtained for the valence and conduction bandwidths even using the pure PBE ($\alpha = 0$) functional. A linear extrapolation of the α PBE results suggests that a HFE amount of

TABLE I. DFT- α PBE estimates of the fundamental gap, valence bandwidth (VBW), conduction bandwidth (CBW), effective electronic couplings, and smallest hole and electron effective masses (m_{Hole} , m_{El}) of the anthracene-PMDA crystal based on the experimental geometry.²⁴

	0% HFE	25% HFE	35% HFE	G_0W_0
E_{gap} , eV	0.941	2.143	2.682	3.240
VBW, eV	0.328	0.365	0.372	0.351
CBW, eV	0.209	0.233	0.240	0.212
$t_{\text{hole}}^{\text{eff}}$, eV	0.048	0.052	0.053	...
$t_{\text{el}}^{\text{eff}}$, eV	0.046	0.051	0.053	...
t_{DA} , eV	0.300	0.445	0.452	...
m_{Hole} , m_0	1.156	1.110	1.093	...
m_{El} , m_0	1.123	1.097	1.084	...

TABLE II. Fundamental gap, valence bandwidth (VBW), conduction bandwidth (CBW), direct and effective electronic couplings, as calculated at the α PBE level with 25% HFE, based on anthracene-PMDA crystal geometries optimized with different HFE amounts.

% HFE	E_{gap}	VBW	CBW	$t_{\text{hole}}^{\text{eff}}$	$t_{\text{el}}^{\text{eff}}$	t_{DA}
0	1.705	0.426	0.294	0.062	0.061	0.471
25	1.909	0.382	0.268	0.055	0.055	0.455
35	1.971	0.372	0.252	0.053	0.053	0.450

approximately 45% would be needed to reproduce the G_0W_0 band gap value. This value is much larger than the values of 32% and 33% we have previously found for pentacene and DBTTF-TCNQ crystals.²⁰

We now turn our attention to the comparison of optimized geometries obtained using different HFE amounts in the α PBE functional (Tables S1–S4⁴¹). Table S1⁴¹ lists the deviations of the individual atoms in an optimized structure from the experimental geometry as well as the weighted root-mean-square deviations (RMSDs) for all atoms in the unit cell. The largest deviation (not exceeding 0.1 Å) is obtained for the C=O groups. Weighted root-mean-square deviations obtained for the calculations using different HFE amounts do not exceed 0.04 Å, which suggests that given the constraint of keeping the experimental unit-cell parameters, the α PBE functional captures well the intermolecular interactions for this crystal for all α values investigated here. In order to assess the effect that the geometry has on the electronic properties, we have computed the electronic parameters using α PBE with 25% HFE for all optimized geometries (see Table II). As seen from Table II, the variations in geometry lead to changes of about 10% in the values of the effective hole [electron] coupling, valence [conduction] bandwidth, and band gap, and of only about 4% in the donor-acceptor electronic coupling. The comparison of the results based on the calculations with 25% HFE shown in Tables I and II indicates that the bandwidths and electronic couplings computed at the optimized geometry are only slightly larger than the corresponding values obtained using the experimental geometry.

Γ - point vibrational modes

The DFT estimates for the low-energy (0–300 cm^{-1}) Raman-active and IR-active vibrational modes of the anthracene-PMDA crystal are given in Tables III and IV, respectively. A complete listing of all Γ -point phonons is given in Table S5 of the supplementary material.⁴¹

Our experimental Raman data (Figure 3, Table III) agree very well with the previously reported spectrum measured at 2 K (Table III).⁴² The Raman-active frequencies calculated using the α PBE functionals with α equal to 0.25 and 0.35 agree slightly better with the experimentally determined frequencies than the results based on the pure PBE functional ($\alpha = 0$), see Table III. Root-mean-square deviations in this frequency region do not exceed 6 wavenumbers for any α value. The Raman intensities calculated using the α PBE functionals with $\alpha = 0.25$ and $\alpha = 0.35$ outperform the results based on the PBE functional. This is related to the fact that Raman

TABLE III. α PBE calculated and experimental low-frequency Raman-active phonons (cm^{-1}) in the anthracene-PMDA crystal. L—libration, A—anthracene, and P—PMDA.

Expt. ^a	Expt. ^b	0% HFE	25% HFE	35% HFE	Assignment
43	45	49	44	42	(L) A/P: Out-of-phase in-plane rotation around the z-axis
47	49	49	46	43	(L) A/P: In-phase in-plane rotation around the z-axis
57	58	65	62	61	(L) P: Rotation around short axis
83	86	77	76	74	(L) P: Rotation around long axis
113	115	117	113	110	(L) A: Rotation around long axis
127	130	130	124	120	(L) A: Rotation around long axis
178	...	184	184	184	P: C=O/C—O—C out-of-plane bend
208	...	216	212	211	P: Ring stretch/C=O out-of-plane bend
253	...	263	258	257	P: Ring stretch/C=O out-of-plane bend
254	...	263	260	259	A: Out-of-plane skeletal bend
273	...	273	271	270	P: Ring breath/C=O out-of-plane bend
279	...	282	284	283	A/P: Skeletal bend
280	...	285	286	285	A/P: Skeletal bend
RMSD		6	5	5	

^aThis work.^bLow-energy Raman vibrations of the anthracene-PMDA crystal measured with a 630 nm excitation wavelength at 2 K.⁴²

intensities correspond to derivatives of the macroscopic dielectric tensor,⁴³ which has been shown to depend strongly on the HFE amount included in the functional.^{44,45}

Based on the results derived with $\alpha = 0.25$, we turn now to the assignment of the vibrational modes. From their normal-mode patterns (Figure 4), the first six Raman-active phonons in the 0–130 cm^{-1} region can be assigned as pure librations (rigid-body rotations).⁴² In particular, the two lowest-energy librations (experimentally at 43 and 47 cm^{-1} ; these are labeled as 44 and 47 cm^{-1} in Figure 4) are related to in-phase and out-of-phase in-plane rotations of both anthracene and PMDA around the axis perpendicular to the molecular plane. The next two librations (57 and 83 cm^{-1} ; 62 and 76 cm^{-1} in Figure 4) correspond to PMDA rotations around the short and long molecular axes. The two higher-frequency librational modes at 113 and 127 cm^{-1} (124 cm^{-1} in Figure 4) involve a large rotational motion of the anthracene molecule approximately around the long molecular axis as well as weak rotations of PMDA. Our assignments of the librational modes are in qualitative agreement with previous reports⁴² based on the molecular moments of inertia. Higher-frequency vibrations in the 140–300 cm^{-1} region are mostly related to the intramolecular motions. In particular, the experimental modes at 178, 208, 253, and 273 cm^{-1} are related to the bending of

the C=O/C—O—C groups and central ring of PMDA; the vibrational mode at 254 cm^{-1} corresponds to a skeletal bend of anthracene; and the modes at 279 and 280 cm^{-1} are related to a combination of skeletal bends of anthracene and PMDA. The results for the high-energy Raman modes are given in Figure S2.⁴¹

We now turn to the discussion of the IR spectra. The DFT results and the assignment of the IR-active modes in the 0–300 cm^{-1} region are listed in Table IV. Since the displacement patterns of the modes obtained at the α PBE level with 0%, 25%, and 35% HFE are similar, we only discuss the results using 25% HFE. In the case of the IR-active low-frequency modes, only the two lowest-energy modes can be described as purely intermolecular (Fig. 5). These modes correspond to out-of-phase translations of anthracene and PMDA along the short molecular axis (54 cm^{-1}) and out-of-phase translations along the stacking direction (74 cm^{-1}); thus, these modes significantly modulate the intra-stack distances. The next two modes at 89 cm^{-1} and 103 cm^{-1} are described by different combinations of anthracene translation along the stacking direction and bending of the C=O group in the PMDA molecule. Higher-frequency modes possess a very small intermolecular character. The 125 cm^{-1} and 145 cm^{-1} modes represent in-phase and out-of-phase combinations,

TABLE IV. α PBE calculated low-frequency IR-active phonons (cm^{-1}) of the anthracene-PMDA crystal.

0%HF	25%HF	35%HF	Assignment
60	54	51	(L) A/P: Out-of-phase translation along short axis
82	74	70	(L) A/P: Out-of-phase translation along z-axis
92	89	88	A: Out-of-phase translation along z-axis/P: C=O out-of-plane bend
107	103	101	A: In-phase translation along z-axis/P: C=O out-of-plane bend
124	125	124	A/P: In-phase out-of-plane skeletal bend
146	145	144	A/P: Out-of-phase out-of-plane skeletal bend
166	164	162	A/P: In-phase out-of-plane skeletal twist
175	172	170	A/P: Out-of-phase out-of-plane skeletal twist
184	184	184	P: C=O/C—O—C out-of-plane bend
239	235	233	A: In-plane ring bend

FIG. 3. Low-frequency α PBE calculated (red bars) and experimental (blue lines) Raman spectra.

respectively, of skeletal bending of both anthracene and PMDA. Similarly, the next two modes are associated with in-phase (164 cm^{-1}) and out-of-phase (172 cm^{-1}) combinations of the skeletal twists of the donor and acceptor molecules.

In the high-frequency region ($300\text{--}2000\text{ cm}^{-1}$), the crystal vibrations are intramolecular in nature. As in the low-frequency region, the RMSDs of the α PBE functionals with α equal to 0.25 and 0.35 are lower than for α equal to 0.

FIG. 4. Eigenvectors of the intermolecular lattice vibrations in the anthracene-PMDA crystal. Only one donor-acceptor pair is shown for clarity. The calculated vibrational frequencies are for α PBE with 25% HFE.

The RMSDs for this frequency region do not exceed 60 wavenumbers for different α values.

It is a common practice to scale the calculated frequencies in order to better match the experimental values. We calculated the optimal scaling factors (λ^α) using the least-square method,⁴⁶

$$\lambda^\alpha = \sum_i^{\text{all}} \omega_{i,\text{calc}}^\alpha \omega_{\text{exp}} / \sum_i^{\text{all}} (\omega_{i,\text{calc}}^\alpha)^2, \quad (2)$$

where $\omega_{i,\text{calc}}^\alpha$ and ω_{exp} are the calculated and experimental Raman frequencies, respectively. The derived scaling factors for the α PBE functionals with 0, 25, and 35% HFE are equal to 1.0056, 0.9602, and 0.9449, respectively. A similar inverse relation between the HFE amount and the scaling factor values has been previously reported in several studies.^{46–49}

Electron-phonon coupling

In order to quantify the effect of lattice vibrations on the donor-acceptor electronic couplings along the molecular stacks (t_{DA} , see Fig. 1), we evaluated the nonlocal electron-phonon (e-ph) coupling constants (v) and the related nonlocal e-ph relaxation energies (L_{DA}), which are defined as⁵⁰

$$v_i = \frac{dt_{\text{DA}}}{dQ_i}, \quad (3)$$

$$L_{\text{DA}} = \sum_i \frac{v_i^2}{2\hbar\omega_i}. \quad (4)$$

Here, Q_i is the normal-mode coordinate of mode i with frequency ω_i . The nonlocal relaxation energies and coupling constants for the low-frequency vibrations ($0\text{--}300\text{ cm}^{-1}$) are listed in Table V. In general, both t_{DA} and L_{DA} increase with an increase in the HFE amount. However, the values of both t_{DA} and L computed with 25% HFE and 35% HFE differ by only 3%. A direct account of the effect of the HFE amount on the individual coupling constants is not possible since calculations with different HFE amounts yield slightly different crystal geometries and normal modes. However, when the calculations with various HFE amounts are performed on the basis of the same set of normal modes

FIG. 5. Eigenvectors of the IR-active low-frequency vibrations in the anthracene-PMDA crystal as obtained at the α PBE level using 25% HF exchange. A single donor-acceptor pair is shown for clarity.

(see Table S6⁴¹), the coupling constants for the majority of modes show a close-to-linear dependence on the HFE amount. We focus next on the contribution of each individual vibration mode to the relaxation energy, and we only discuss the results based on 25% HFE. As seen from Table V, the contribution of the low-frequency vibrations (0–300 cm^{-1})

accounts for about 90% of the relaxation energy L . This is in agreement with previous studies on both single-component (oligoacenes,⁵¹ rubrene⁵²) and binary CT crystals.⁵ Both IR and Raman-active modes contribute to the nonlocal electron-phonon interaction. The IR-active 74 and 125 cm^{-1} vibrations have the largest coupling constants. Both modes can be

TABLE V. Dependence of the nonlocal coupling constants (ν), relaxation energies (L), and transfer integrals (t_{DA}) on the HFE amount based on calculations of the crystal geometries, normal modes, and electronic parameters at the same level of theory. Parameters ν , L , and t_{DA} are given in meV.

Active	0% HFE		25% HFE		35% HFE	
	Frequency, cm^{-1}	ν	Frequency, cm^{-1}	ν	Frequency, cm^{-1}	ν
Raman	49	2.71	44	1.00	42	4.93
Raman	49	−1.93	46	−8.79	43	1.50
IR	60	7.57	54	5.50	51	6.14
Raman	65	6.36	62	−10.43	61	−10.93
IR	77 (R)	−8.00	74	−27.36	70	−29.00
Raman	82 (IR)	17.50	76	9.64	74	8.36
IR	92	−6.14	89	−8.86	88	−3.00
IR	107	9.14	103	12.57	101	12.00
Raman	117	6.21	113	10.57	110	12.43
Raman	124 (IR)	20.21	124	−1.57	120	−2.71
IR	130 (R)	−3.50	125	−20.29	124	−14.79
IR	146	4.00	145	1.64	144	7.50
IR	166	−2.79	164	−3.21	162	−2.43
IR	175	−0.43	172	4.64	170	0.50
Raman	184	1.43	184	8.07	184	13.21
IR	184	4.43	184	−5.71	184	−5.36
Raman	216	2.21	212	4.36	211	5.07
IR	239	−3.43	235	−4.14	233	−4.36
Raman	263	−1.57	258	2.43	257	5.71
Raman	263	−1.79	260	0.29	259	0.79
Raman	273	−1.00	271	−0.79	270	−1.21
Raman	282	2.86	284	−1.36	283	−0.14
Raman	285	−0.93	286	−2.07	285	−2.79
L_{DA}	51		100		103	
L_{DA} (0–300 cm^{-1})	47		90		88	
t_{DA}	259		455		468	
L/t_{DA}	0.20		0.22		0.22	

described as modulating the π -stacking distance. The Raman-active modes at 46 and 62 cm^{-1} also contribute significantly to the nonlocal coupling.

The description of the nonlocal interactions related to the modulation of the effective transfer integrals $t_{\text{el}}^{\text{eff}}$ and $t_{\text{hole}}^{\text{eff}}$ represents a very complex problem due to the super-exchange nature of the transfer integrals; a complete discussion of this mechanism will be provided elsewhere. In order to estimate the electron-vibration couplings along the molecular stacks, we have used here a simplified approach based on a treatment of the super-exchange mechanism in the perturbation limit. In this limit, the effective transfer integrals for holes and electrons along the stacking directions are equal and are given by⁵

$$t_{\text{hole}}^{\text{eff}} = t_{\text{el}}^{\text{eff}} = \frac{t_{\text{DA}}^2}{\Delta E_{\text{DA}}}. \quad (5)$$

Here, ΔE_{DA} represents the energy of the charge-transfer state of the DA pair. From Eq. (5), the effective electron-phonon coupling and the related relaxation energy ($L_{\text{el(hole)}}^{\text{eff}}$) are given by $\frac{dt_{\text{eff}}}{dQ_i} = 2 \left(\frac{t_{\text{DA}}}{\Delta E} \right) \left(\frac{t_{\text{DA}}}{dQ_i} \right)$ and $L_{\text{el(hole)}}^{\text{eff}} = 4L_{\text{DA}} \left(\frac{t_{\text{DA}}}{\Delta E} \right)^2$, respectively. Based on the latter formula, Eq. (5), and the t_{DA} and t_{eff} values from Table II, we estimate ΔE_{DA} to be 3.8 eV and $L_{\text{el(hole)}}^{\text{eff}}$ to be 6 meV. The value derived for $L_{\text{el(hole)}}^{\text{eff}}$ is similar to that estimated for holes and electrons in pentacene.⁴ Finally, we note that the $L_{\text{DA}}/t_{\text{DA}}$ and $L^{\text{eff}}/t^{\text{eff}}$ ratios in anthracene-PMDA are about 0.2 and 0.1, respectively, which underlines that the electron-phonon interactions are much smaller than the electronic interactions. This result indicates that the nonlocal electron-phonon interactions in this system can be treated in the perturbation limit.⁵¹

CONCLUSIONS

We have investigated the vibrational and electron-vibration properties of the anthracene-PMDA crystal. Our results underline that the calculations based on the α PBE functional with HFE amounts in the range of 0%–35% yield comparable geometries and normal vibrational modes (crystal phonons). In contrast, the nonlocal electron-vibration coupling constants are found to strongly depend on the HFE amount included in the functional. A similar trend is obtained for the electronic couplings, in agreement with the conclusions of our earlier work. Our results indicate that the DFT-derived Raman spectra based on the α PBE functional with $\alpha = 0.25$ and $\alpha = 0.35$ are in better agreement with the experimental results compared to those based on the pure PBE functional ($\alpha = 0$). This finding is in line with our previous result on the DBTTF-TCNQ crystal, which pointed to an optimal α value of about 0.33; therefore, the use of density functionals containing an amount of ca. 30% HFE is recommended for the description of the electronic properties of these systems. However, further investigations along these lines and, in particular, the application of range-separated hybrid functionals on such periodic donor-acceptor systems are desirable.

The DFT results indicate that the largest contribution (about 90%) to the nonlocal relaxation energy is due to

electron interactions with low-frequency vibrational modes in the range of 0–300 cm^{-1} . Both IR and Raman-active modes contribute to the nonlocal electron-phonon interaction. The $L_{\text{DA}}/t_{\text{DA}}$ and $L^{\text{eff}}/t^{\text{eff}}$ ratios in anthracene-PMDA are about 0.2 and 0.1, respectively, which means that the nonlocal electron-phonon interaction in this system can be treated in the perturbation (weak coupling) limit.

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