

Coherent External and Internal Phonons in Quasi-One-Dimensional Organic Molecular Crystals

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We have directly time resolved coherent phonon oscillations in quasi-one-dimensional organic crystals of MePTCDI (*N-N'*-dimethylperylene-3,4,9,10-dicarboximide), using femtosecond pump-probe experiments. We observe both higher-energy oscillations caused by intramolecular vibrations (internal phonons) and, for the first time in a quasi-one-dimensional organic system, lower-energy modulations which are related to coherent lattice phonons (external phonons). For internal A_g vibrations, the coherence decay time of about 2 ps is almost independent of the mode. In contrast, the damping time of the external phonons increases strongly with decreasing energy.

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Thin organic films with semiconducting properties have recently gained large interest due to promising device applications such as charge transport layers, organic light emitting diodes, and solar cells [1]. Particularly attractive for applications are organic molecules which form quasi-one-dimensional molecular crystals with strong orbital overlap between neighboring molecules. Here, the strong intermolecular interaction favors generation and transport of charge carriers. The optical properties, dominated by excitonic transitions, and the lattice dynamics of organic semiconducting materials are much less understood than for their inorganic counterparts. For strongly coupled quasi-1D materials, first band structure models for free excitons have only recently been proposed and compared to linear optical absorption spectra [2,3]. Even more puzzling are the fluorescence properties, with typically very low quantum yields, which prevent application in emission devices. One of the probable reasons for this low efficiency is the relaxation of free excitons into self-trapped states, a process which is not well understood [4]. Therefore, a detailed investigation of the exciton-phonon interaction is required. Although real-time phonon dynamics have been studied in great detail for inorganic semiconductors [5] and organic molecules in solution [6–8], there are only a few results in sandwich-type organic crystals [9] or polymers [10–12] and, particularly, none in quasi-1D organic molecular crystals.

In this work, we have directly time resolved the coherent motion of external and internal phonons in thin films of MePTCDI (*N-N'*-dimethylperylene-3,4,9,10-dicarboximide), employed as a model system for quasi-1D organic molecular crystals. The distance of 3.40 Å between the molecular planes within the 1D stacks is small in comparison to both the other lattice constants of the monoclinic lattice and the size of the molecules [13]. This causes strong interactions of the π -electron systems within the stacks, but a much weaker interaction in the other directions. Recently, we proposed a band structure

model for such crystals [3], where the lowest-energy excitons are described as mixed states containing the lowest Frenkel exciton with its vibronic replicas and the lowest charge-transfer exciton.

As samples, we use polycrystalline thin (approximately 15 nm) films of MePTCDI (see Fig. 1) grown by physical vapor deposition in high vacuum on a room-temperature glass substrate. The linear absorption spectrum of the sample is given in Fig. 1. The time-resolved measurements reported here are carried out using a femtosecond pump-probe technique, in which an ultrashort pump pulse excites the sample and a time-delayed probe pulse measures the resulting transmission change as a function of pump-probe delay [6]. The even parity phonon modes coupled to the excitonic transition

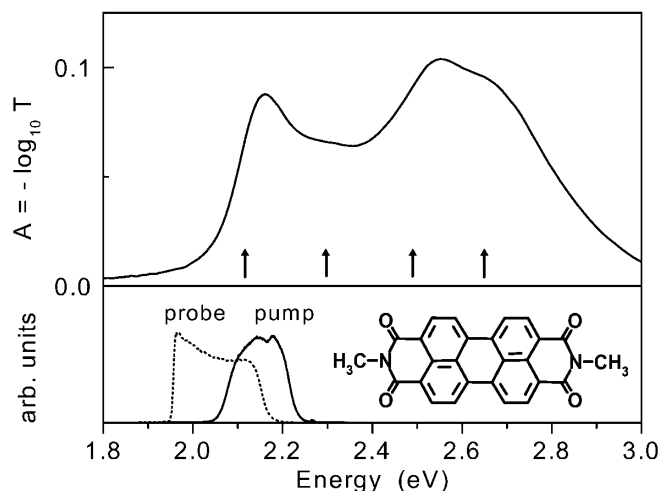


FIG. 1. Top: Room-temperature absorbance A of the MePTCDI layer, calculated from the transmission T . The arrows indicate the energies of the free exciton states at $k = 0$ as derived from Ref. [3]. Bottom: Spectral profiles of pump and probe pulses overlapping with the lowest-energy exciton band. Inset: Molecular structure of MePTCDI.

are impulsively excited, creating wave packets that are a coherent superposition of the phonon eigenstates. These nonstationary coherent superpositions, which can be formed on both the ground and the excited state potential energy surfaces, oscillate at the characteristic phonon frequencies of the material, so that they can be observed as a modulation of the differential transmission signal [14].

We use linearly polarized light pulses of about 25 fs FWHM duration, with a photon energy chosen to excite the lowest energy non-lattice-relaxed exciton band at $k = 0$. The pump pulse spectrum centered around 2.15 eV is shown at the bottom of Fig. 1. The pump pulses are generated by a noncollinear optical parametric amplifier [15]. Transient absorption measurements were carried out using collinear polarized probe pulses from a broadband femtosecond continuum. The probe spectrum was selected to monitor the dynamics at the lowest-energy exciton band (see Fig. 1). The experimental cross-correlation width, measured with a 20 μm β -barium borate crystal at the position of the sample, was ~ 35 fs over the detected energy range. For the pump-probe measurements, we use excitation densities of about 10^{18} cm^{-3} ; all measurements are performed at room temperature.

The time-resolved transmission change following impulsive excitation of the lowest-energy exciton band is given as the upper solid line in Fig. 2. The most conspicuous feature is a strong modulation due to phonon wave packet oscillations. In addition, processes like the relaxation of exciton populations and vibrational thermalization contribute to the signal [16].

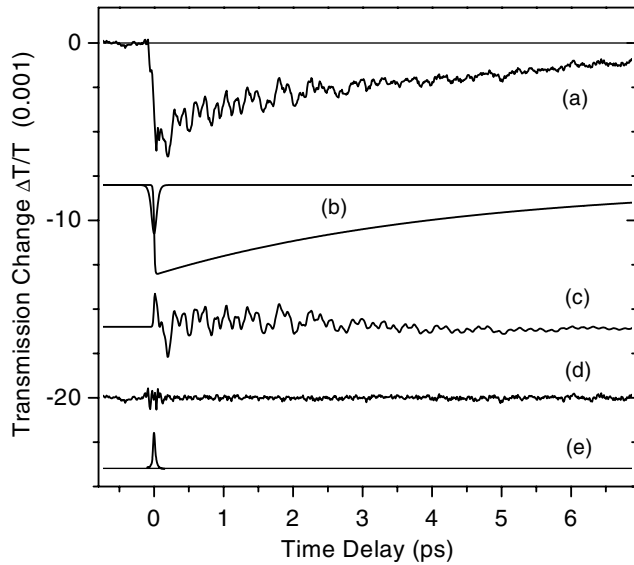


FIG. 2. Time-resolved differential transmission of the MePTCDI layer following excitation with 25 fs pump pulses. From top to bottom: Experimental signal (a), fit of the exponentially decaying contribution together with the coherent peak around zero delay (b), fit of the oscillating contribution (c), the residuum of the fit (d), and the experimental cross correlation (e). The curves are shifted for clarity.

For a reliable oscillation data analysis, we fit (using a nonlinear least-squares Marquardt-Levenberg algorithm) the entire relevant delay time t range with the following expression for the transmission change:

$$\frac{\Delta T(t)}{T_0} = aS(t/\tau)e^{-t/\tau_{\text{decay}}} + b\text{sech}^2(t/\tau_{\text{peak}}) + S(t/\tau) \sum_i c_i \cos(\omega_i t + \phi_i) e^{-t/\tau_i}, \quad (1)$$

where for simplicity we use both for the exponentially decaying contribution (corresponding to, e.g., exciton recombination) and the oscillatory part the same smoothed step function $S(t/\tau) = [1 + \tanh(t/\tau)]/2$ [17].

In Fig. 2, we display the different contributions of the fitting function and the residual of the fit. The results of the fit related to the oscillating contributions are shown in Table I. For most oscillations, the phase corresponds to a cosine started around zero delay within the duration of the rise τ . The absolute of the complex Fourier amplitude of the oscillating part is shown in Fig. 3. Both the residues in Figs. 2 and 3 demonstrate the high quality of the fit. Below we show that the three highest-energy oscillations are due to a wave packet of internal A_g vibrations, the six oscillations following towards lower energy stem from external phonons and the two lowest oscillations are interpreted as due to internal B_g vibrations.

Internal A_g vibrations.—In Table I, we compare the experimental oscillation energies with data from resonant Raman scattering (RRS) on crystalline MePTCDI films [18]. The three highest modes observed in our pump-probe experiments are in obvious one-to-one correspondence

TABLE I. Results of the fit to the oscillating part of differential transmission measurements in Fig. 2. First column: Fitted oscillation frequencies, second column: RRS data [18]; third column: mode frequencies calculated with the density-functional tight-binding (DFTB) method for a C_{2h} -symmetric isolated molecule together with the corresponding representations; fourth column: external modes of β -perylene [22] scaled down by a factor of 0.8, and their symmetries for perylene in terms of representations of the monoclinic group $P2_1/c$. The last two columns give the amplitudes and damping times. The first three rows correspond to internal A_g modes and the next six to the external phonon modes, whereas the last two are assigned to a Davydov-split phonon doublet resulting from the same internal B_g vibration.

Mode cm^{-1}	RRS cm^{-1}	DFTB cm^{-1}	Per $\times 0.8$ cm^{-1}	Ampl. 10^{-4}	Damping ps
569.2	565	577 (A_g)		1.6 ± 0.3	1.9 ± 0.4
542.0	536	537 (A_g)		0.8 ± 0.3	2.0 ± 0.9
221.1	218	219 (A_g)		6.8 ± 0.3	2.4 ± 0.2
104.9			96 (A_g)	5.0 ± 0.9	0.8 ± 0.2
89.0			81 (B_g)	7.2 ± 0.6	1.8 ± 0.2
71.2			75 (A_g)	7.2 ± 0.6	1.6 ± 0.2
56.9			67 (B_g)	4.8 ± 0.4	2.5 ± 0.3
43.0			42 (A_g)	0.7 ± 0.2	13 ± 12
33.3			32 (B_g)	0.7 ± 0.3	6 ± 4
25.3		16 (B_g)		0.5 ± 0.2	16 ± 26
4.7		16 (B_g)		6 ± 2	4.3 ± 0.7

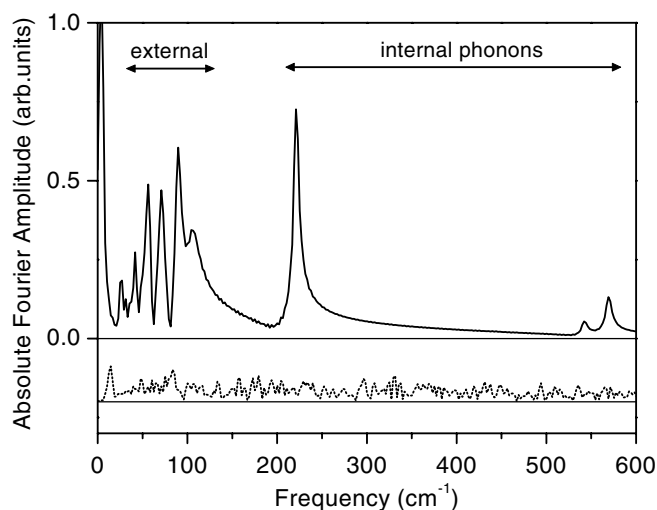


FIG. 3. Absolute Fourier amplitude spectrum of the oscillating part of the experimental data. Solid line: Fourier amplitude of the fitted oscillatory part, as derived from the fit in real time. The absolute of the complex residuum, given as a dotted line (shifted for clarity to a reference line of -0.2), shows the quality of the fit.

with the RRS data, but our frequencies show a shift of about $+1\%$, exceeding our fitting uncertainties. We assign this systematic trend to the fact that our time-resolved experiment measures an admixture of a vibronic wave packet on the excited state surface with the corresponding wave packet on the potential surface of the ground state, so that the oscillations occur with an average of the corresponding frequencies. In order to be observable separately, the difference of the frequencies would need to exceed the linewidth.

Our assignment of the three highest observed modes to the lowest internal A_g vibrations is further supported by calculations for the isolated C_{2h} -symmetric molecule in the electronic ground state (see Table I) using DFTB methods [19] already tested for the similar D_{2h} -symmetric perylene derivative PTCDA [20]. Defining x as the long axis and y as the short axis of the perylene core of MePTCDI, we found the geometry with the lowest energy has this core in the xy plane, the symmetry group of the molecule containing the operations $C_{2h}(2/m) = \{E, C_{2z}, \sigma_{xy}, I\}$.

The calculated internal A_g vibrations of the isolated molecule can be compared to the corresponding optical phonon frequencies in the crystal. Because of the commutative symmetry group C_{2h} of an isolated MePTCDI molecule, any degeneracy of vibrational frequencies would be purely accidental. However, as crystalline MePTCDI contains two molecules per unit cell, the equivalent modes of these two molecules result in a Davydov-split phonon doublet at $k \approx 0$ [21], together with an additional frequency shift due to the crystalline surrounding. Nevertheless, in molecular crystals as MePTCDI, where covalent intramolecular forces dominate over the intermolecular van der Waals forces, shifts and splittings of

internal A_g vibrational modes are expected to be small compared to their absolute values [21].

External phonons.—A monoclinic $P2_1/c$ -symmetric MePTCDI crystal with two molecules per unit cell has 12 external phonon branches: Three acoustical translational, three optical translational, and six optical rotational phonons (librational phonons). The translational optic phonons are infrared active only, whereas the librational modes with even parity (three A_g and three B_g modes in terms of representations of the group $P2_1/c$) are Raman active and could contribute to our signal. These six librational phonons are three Davydov-split phonon doublets. Based on the interpretation of the three higher energetic modulations as the lowest internal vibrations of A_g symmetry, we argue below that the six oscillations with energies between 33 and 105 cm^{-1} are due to librational external phonons, i.e., hindered rotations of the rigid molecules in the unit cell of the crystal.

Since MePTCDI has the same crystal structure as β -perylene, we compare our data with the corresponding measured and calculated perylene phonon energies [22], as outlined in Ref. [21]. As the frequency trends between different sized conjugated molecules, e.g., naphthalene and perylene, are not very pronounced [23], it can be assumed that a cancellation between mass (influencing the moment of inertia) and interaction related changes occurs. Therefore, we relate our measured external phonon modes to β -perylene with a simple scaling factor of 0.8 , giving a rough estimate of both effects; compare Table I. The good agreement with the experimental energies supports our interpretation that these six oscillations are indeed due to external phonons.

Internal B_g vibrations.—We now address the nature of the two lowest energetic modes. From group-theoretical arguments, only totally symmetric A_g vibrations of the isolated molecule can be elongated due to the dipole transitions from the electronic highest occupied molecular orbital to the lowest unoccupied molecular orbital, and the same symmetry argument applies to resonant Raman scattering [24]. However, considering now not the isolated MePTCDI molecule (symmetry group C_{2h}) but the two MePTCDI molecules in the unit cell, the symmetry is lowered from C_{2h} to the monoclinic centrosymmetric group $P2_1/c$ for crystalline MePTCDI. Thus only two symmetry operations projecting each molecule on itself remain: unity (E) and inversion (I). Hence, any vibrational mode of even parity is Raman active, including also the internal vibrations which would have B_g symmetry in the C_{2h} -symmetric isolated molecule.

Our calculation for the isolated molecule gives the lowest internal B_g vibrations at about 16 and 69 cm^{-1} . The lower is due to a rotation of the methyl groups against the perylene core including the carboxylic groups, the higher due to a rotation of the carboxylic groups against the perylene core. Assuming that a possible Raman activity of the 69 cm^{-1} mode is hidden under the rather strong

contributions of the external phonons, the existence of the 16 cm^{-1} mode can explain why we observe two further oscillatory contributions with frequencies below the expected six librational modes: We tentatively assign both the 5 cm^{-1} and the 25 cm^{-1} mode to a Davydov-split phonon doublet at $k \approx 0$ resulting from the internal B_g vibration at 16 cm^{-1} on both molecules. The splitting of about 20 cm^{-1} is comparable to the Davydov splitting of the corresponding doublets of external modes; compare Table I. The somewhat higher splitting can be related to the fact that a pair of degenerate modes is affected more by a coupling term of similar size if the mode frequency itself is low [25].

In the following, we discuss the damping times of the different modes, as obtained from the fits. Note that for some oscillations the decay time has a large uncertainty since they carry only minor amplitude. For the internal A_g phonon modes we measure similar decay times around 2 ps for all three modes. This is in close agreement with typical dephasing times for internal phonons of large organic molecules in solution on the potential surface of the electronic ground state [26,27]. In polymers, i.e., organic solids that lack the long-range order of crystals, values of 0.4–3 ps have been measured [11,12].

For the higher external modes, we obtain shorter damping times. The damping times show a clear trend with energy: They increase from 0.8 ps for the 104.9 cm^{-1} mode to 2.5 ps for the 56.9 cm^{-1} mode. For the two lowest-energy external phonons, the times increase further, although the errors become very large. The only comparable measurements have been performed for crystals of pyrene, where the molecules arrange not quasi-1D in a chain, but pairs of molecules align sandwichlike. In this case, a damping of external phonon wave packets within some picoseconds was observed [9]. To our knowledge, no microscopic theory of external phonon damping exists for organic crystals.

In summary, we reported the first observation of coherent external phonon oscillations in quasi-1D organic molecular crystals with strong orbital overlap and studied their damping behavior. We believe that our work will trigger further investigations of the exciton-phonon interaction in this technologically important material class.

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 [17] The peak in the second term accounts for coherence coupling and stimulated emission. The fit results for the pulse profile agree well with the experimentally determined FWHM of 25 fs. For the coherent peak, we find a time constant $\tau_{\text{peak}} = 51\text{ fs}$, i.e., this contribution is indeed limited around zero delay; the longer duration of this structure is interpreted in terms of a finite but small dephasing time T_2 . The transmission saturation decays exponentially on a time scale of $\tau_{\text{decay}} = 4.2 \pm 0.4\text{ ps}$.
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 [24] Vibrational modes of B_g symmetry could only contribute to the signal if nearly degenerate electronic transitions with different orientations of the transition dipoles would be available, but for the isolated MePTCDI molecule, this is not the case in our range of photon energies.
 [25] For the crystal modes, the dynamical matrix decouples into four submatrices of the same size for the four different representations occurring in $P2_1/c$, e.g., A_g , which therefore can be diagonalized separately. Each of these submatrices contains both external and internal degrees of freedom, so that after the diagonalization the eigenvectors can have a mixed character. To simplify the discussion in the main text, we have discussed the modes in terms of external and internal if we expect that the eigenvector is dominated by the corresponding contribution.
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