Photoexcitation energy loss in molecular semiconductors

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Abstract

Energy relaxation of electron-vibrational excitations through the emission of ground-state phonons is investigated in single sexithiophene crystals. In the experiment, short laser pulses excite vibron states, i.e. excitons bound to intramolecular vibrations. A fraction of the excess vibrational energy is released to the electronic ground state through a vibron fission process in which a non-equilibrium population of C–C stretching vibrations is created. This basic phenomenon was predicted in the 1960s by Davydov and Rasbhe, but, as far as we know, never observed. The hot ground-state intramolecular phonons are probed by a delayed laser beam which stimulates transitions from these vibrational modes to the lowest exciton bands. Hot vibrational states up to the third quantum level are observed.
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1. Introduction

In molecular organic semiconductors, the exciton and intramolecular phonons produced upon absorption of a quantum of light interact each other via the vibronic interaction. This coupling can give rise to bound states, named molecular *vibrons* [1]. These particles are the "solid-state" counterpart of the electron-vibrational excitations in a single molecule. Vibronic relaxation following photoexcitation is a very fast process, which typically occurs in the subpicosecond time-scale. In large molecules, the excess vibrational energy is very quickly redistributed, due to anharmonic coupling, among the large number of vibrational modes, which behave like a thermal bath [2]. Similar *intramolecular* spectral relaxation mechanisms are expected to be also active in polymers and organic crystals. Solid-state interactions, however, can change the nature of the electronic states and their decay processes. Specifically, electronic coupling can open new *intermolecular* energy relaxation channels, which have no analogous in the single molecule. One of these processes has been anticipated by Davydov and co-workers in the 1960s [1], when the bases of the theory of molecular excitons were outlined. In this theoretical framework, vibrons are described as unstable quasiparticles, which can split into unbound excitons and vibrations. The fission process is schematically shown in Fig. 1. In the initial vibron state, the nuclei oscillate in the excited state potential surface. In the final states, the outgoing exciton states move away, leaving the hot vibrations to oscillate in the potential energy surface of the electronic ground-state configuration, creating, in this way, an intramolecular phonon. As the process transfers a fraction of the initial excess energy to the electronic ground state, vibron fission represents a peculiar mechanism of photoexcitation energy *loss* in organic semiconductors.

We report here direct experimental evidence of intermolecular energy relaxation, i.e. vibron splitting. Experiments are made in sexithiophene crystals. The choice of this system has been dictated by the fact that (a) very high quality sexithiophene crystals are now available, and (b) the basic electronic and optical properties of sexithiophene are known. Specimens are photoexcited by short laser pulses, 1 eV above the excitonic gap. High energy vibrons are generated, followed by a fast energy relaxation. The ensuing non-equilibrium population of ground-state modes is interrogated by a delayed laser beam, which stimulates transitions from these vibrational levels to the lowest exciton bands. The optical process is exemplified in Fig. 2. Hot vibrational states of the carbon–carbon stretching modes are observed. The ground-state vibrations decay in a few picoseconds.

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2. Experimental

Single sexithiophene crystals were excited by the second harmonic of a regenerative amplifier laser, delivering
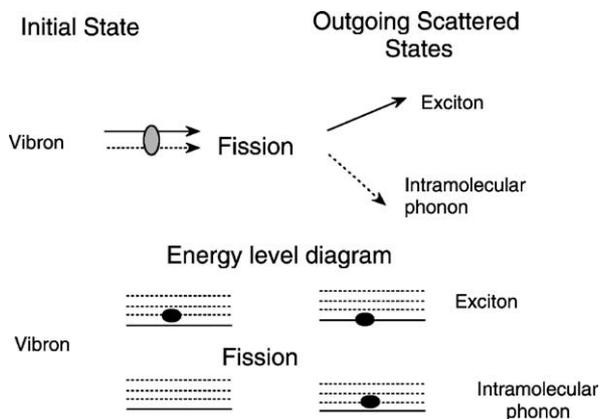
Fig. 1. Fission of molecular vibrons. Initial state: a vibron made up by an exciton bound to an intramolecular phonon. Outgoing scattered states: a ground-state intramolecular vibration plus a pure exciton state.

1 kHz-train of 150 fs-long pulses at 1.61 eV. The excess photon energy, ΔE, with respect to the optical gap was $\sim$1 eV. Excitation intensity was kept between 40 and 150 nJ per pulse, focused on a spot diameter of 80 μm. Samples were held in nitrogen atmosphere to reduce photodegradation effects. A small fraction of the IR pump laser was focused with a suitable time delay on a 1 mm-thick sapphire plate to generate a single filament of a stable white-light continuum. The white-light beam was split into two parts. One beam was focused onto the sample by means of a pair of off-axis mirrors; the second one was used as reference to account for intensity fluctuations. The delay between the 1.8 and 2.4 eV spectral components of the probe beam was estimated in $\approx$200 fs at the sample surface. Both white beams were focused, vertically shifted, by means of a cylindrical lens onto the input
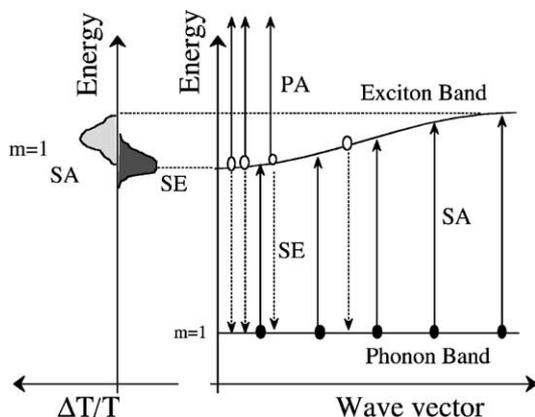
Fig. 2. Survey of the optical processes stimulated by a weak probe beam with photon energy just below the optical gap. Due to the highly localized nature of intramolecular phonons, these excitations show a very flat energy dispersion. Vibron fission gives rise to hot phonons with wavevectors *k* over all the Brillouin zone. Conversely, excitons quickly thermalize towards the lowest energy band states. SE: exciton-to-phonon stimulated emission; SA: hot-phonon-to-exciton stimulated absorption, SA is blue shifted with respect to SE because of the different *k*-distribution of the hot phonons and excitons; PA: photoinduced absorption from the lowest exciton band to higher exciton states; $\Delta T/T$: differential transmission.

slit of a polychromator. The spectrum intensity of the probe and reference train pulses was measured, respectively, by the upper and lower part of a charge coupled device at the output of the polychromator. Typically, the noise on the differential transmission spectrum, $\Delta T/T$, was 10^{-3}. For probe energies below 1.8 eV, instabilities were too large to allow for reliable differential transmission signals. Time-resolved photoluminescence (PL) experiments were also performed using up-conversion techniques [4]. The comparison between PL and $\Delta T/T$ data allows us to univocally distinguish between stimulated emission (SE) and stimulated absorption (SA) signals in the $\Delta T/T$ spectra. Time-resolved experiments were performed at room temperature. In the following, $\Delta T/T$ is defined such that a decrease of the signal is caused by SE or by bleaching of the optical transitions, while an increase arises from an induced absorption.

3. Results and discussion

The unit cell, the absorbance and PL spectra of the sexithiophene crystals are reported in Fig. 3. Single crystals have the shape of thin plates with the *b* and *c* axis in the basal plane [5]. The lowest molecular optical transition gives rise in the crystal to several bands between 2.28 and $\approx$3.5 eV [6]. The lowest energy exciton transition at 2.28 eV is quite weak and strictly *b*-polarized [6]. The linewidth of this resonance at low temperature is a few meV, revealing a negligible disorder-induced inhomogeneous broadening. The high crystal quality is fully confirmed by the absence of any significant Stokes shift between the intrinsic *b*-polarized pure excitonic emission and absorption [7,9]. In our samples, we can therefore reasonably exclude the observation of kinetics of exciton spectral diffusion within an inhomogeneously broadened density of states [9], which could make difficult the observation of SA transients from hot phonons.
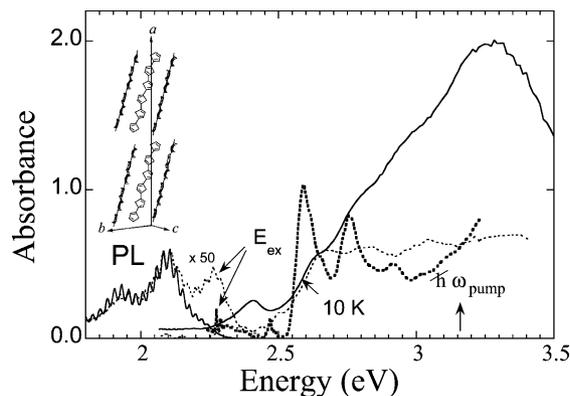
Fig. 3. Inset: unit cell of sexithiophene crystal. cw-absorbance and photoluminescence (PL) spectra at 300 K. Spectra recorded with *c*-polarized (*b*-polarized) light are reported as a continuous (dashed) line. The *b*-polarized absorbance spectrum is also shown at $T = 10$ K to display the narrow spectral structures. E_{ex} is the lowest exciton transition. The sample thickness for *b*- and *c*-polarized absorbance spectra are 2.8 and $\ll$1 μm, respectively.
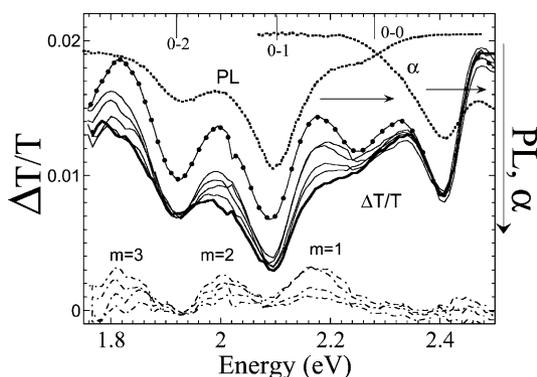
Fig. 4. Dashed curves: photoluminescence (PL) and absorbance spectra for *c*-polarized light. Continuous lines: differential transmission spectra ($\Delta T/T$) for different pump–probe delays. Pump and probe beams are polarized parallel to the *b*- and *c*-axis, respectively. The time delays, Δt, from the bottom to the top, are: 5.5 (thick line), 2.5, 1.5, 1.0, 0.5 and 0.25 (curves with dots) ps. Dotted-dashed lines: net transient hot-phonon-to-exciton induced absorption bands, as explained in the text.

The major contribution to the *b*-polarized absorption spectrum is provided by the vibron progression with origin at 2.6 eV [6]. This polarization geometry is particularly suitable for the creation of high energy vibrons, as the pump photon energy, $h\nu = 3.22$ eV, is just below the fourth vibronic replica. In the following, we thus discuss $\Delta T/T$ experiments in which pump pulses were polarized along the *b* crystal axis. We note, however, that the *c*-polarized PL is as much as 50 times more intense than the *b*-polarized one [8]. As a similar polarization behavior is expected for hot-phonon-to-exciton transitions, the differential transmission experiments have been done with *c*-polarized probe beam.

The *c*-polarized PL and absorption (α) spectra for energies below 2.5 eV are reported in Fig. 4. These spectroscopic data are discussed in details as they allow us to identify the exciton and vibronic transitions probed in the differential transmission experiments. The low energy part of the absorption spectrum is dominated by transitions to a set of vibron states, yielding the composite structure at 2.4 eV [6]. PL consists of a vibronic progression in which a free exciton is annihilated and $m \neq 0$ quanta of the C–C stretching mode, $h\nu_{CC} = 0.18$ eV, are created. It is worth stressing that for *c*-polarized light the pure excitonic transition is forbidden, but not the vibronic replica [8]. The weak shoulder at ~2.25 eV is omnipresent in photoluminescence spectra of crystalline sexithiophene [7], and is due to the emission of a low energy vibration.

$\Delta T/T$ spectra are reported in Fig. 4 for various delays, Δt, between the pump and probe beams. The $\Delta T/T$ curves are suitably renormalized to account for a small reduction, ~20%, of the exciton population, as described later on. A few picoseconds after excitation, the spectral shape of the non-linear transmission, shown through a thick line in Fig. 4, becomes independent of delay. The observed structures match very well those in the luminescence and absorp-

tion spectra. We thus correlate the peak at 2.4 eV with the bleaching of the vibronic transitions [10]. The structures at energies lower than the forbidden pure excitonic transition at 2.28 eV are assigned to SE from the bottom of the exciton band to the *m*-vibrational levels of the electronic ground state. A net optical gain is not observed, owing to the simultaneous presence of an intense photoinduced absorption (PA). This signal has been attributed to transitions from the lowest exciton level to higher excited states [11]. Yet, the very alike shape of the SE and PL spectra indicates that the PA response in the spectral range 1.8–2.4 eV is smooth.

We now discuss in more detail the $\Delta T/T$ data processing. The amplitude of the SE, bleaching and PA signals decrease of ~20% for increasing Δt ($0 < \Delta t < 5$ ps). To facilitate the comparative spectral analysis at different delays, the $\Delta T/T$ curves in Fig. 4 represent the original experimental spectra vertically shifted and divided by a factor, n_{ex}, in order to get the same bleaching response observed for $\Delta t = 0.25$ ps at 2.4 eV. The $\Delta T/T$ spectrum at $\Delta t = 0.25$ ps is reported without any renormalization. As both bleaching and SE are proportional to the photoexcitation population, the scaling procedure counterbalances the effect of exciton decay on $\Delta T/T$ response [12]. In Fig. 5, the values of n_{ex}, which result from the $\Delta T/T$ renormalization at different delays, are compared with the PL transients. The latter directly monitor the exciton population dynamics. The good agreement between PL and n_{ex} decays provides an independent experimental support to the validity of the $\Delta T/T$ scaling procedure.

The early dynamics of the $\Delta T/T$ spectra monitors the fast relaxation of the exciton population towards the lowest exciton band. SE and PL signals reach the maximum value after a delay $\tau_r = 0.3$–0.4 ps. This estimate of the relaxation time is consistent with other recent results in sexithiophene [3,11]. For $\Delta t > \tau_r$, $\Delta T/T$ still shows pronounced SA bands at the high-energy side of each of the vibronic emission lines, which last a few picoseconds. To isolate this contribution, the spectrum taken at a long delay, $\Delta t = 5.5$ ps, when
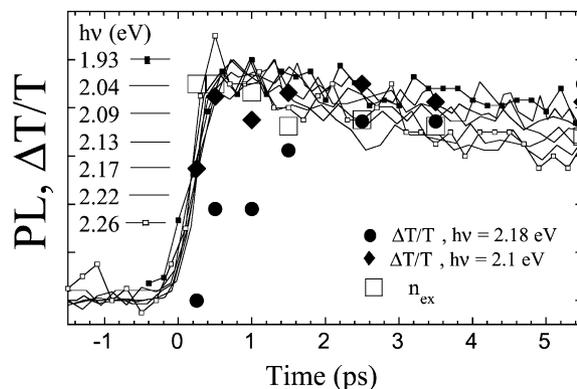
Fig. 5. Continuous curves: PL transients measured at different emission energies $h\nu$. Diamonds and circles are the transients of $-\Delta T/T$, reported in Fig. 4, at 2.1 and 2.18 eV, calculated using an offset value of 0.014. Squares represent the renormalization factor, n_{ex}, proportional to the exciton density.

SA is negligible, has been subtracted to all the differential transmission curves. The resulting curves are shown in the bottom part of Fig. 4; they feature peaks at 2.18, 2.00 and 1.82 eV. These structures can not be ascribed to PA from the exciton band to an higher exciton manifold, as these transitions yield a peak at about 1.3 eV and show quite a different temporal dynamics [11]. We assign these structures to transitions from the hot $m = 1, 2$ and 3 quantum vibrations of the ground state C–C stretching mode to the lowest exciton band. Transitions from the $m = 4$ vibrational levels might also be active, but their frequency is too close to the IR pump energy to be detected. The rationalization of these transient signals to hot-phonon-to-exciton transitions is backed by the following arguments:

(i) The energy spacing between the SA vibronic peaks equates the energy of the CC-stretching vibration energy;

(ii) The energy position of the SA vibronic peaks is consistent with the nature of the hot-phonon-to-exciton transition, as discussed in the following. Since hot intramolecular phonons are excitations localized on the molecular scale with a very flat energy dispersion, we are expected that vibron fission process creates phonons with wavevectors k over all the Brillouin zone. Consequently, as shown in Fig. 2, the SA process creates excitons with both small and large k. In the limit of a negligible dependence of the oscillator strength on the phonon quasi-momentum, the SA bands should monitor the exciton density of state, which is peaked at higher energy with respect to the exciton–phonon transition at $k = 0$. As thermalized excitons mainly occupy states with low wavevector, the SE band is redshifted with respect to SA. Such a correlation between SE and SA spectra has been verified in oligoacene crystals [1], where SA from thermally excited low frequency vibrations has been observed.

(iii) The observation of hot $m = 1, 2$ and 3 quantum vibrational levels of the ground state C–C stretching mode is consistent with the energy level scheme of sexithiophene, as shown in the following. In the $\Delta T/T$ experiments, the pump photon energy is just below the fourth vibronic replica. This vibron state is made up by an exciton bound to $m = 4$ C–C stretching internal phonons. The fission decay pathways are several: the vibron can dissociate into m ground-state vibrational quanta, with m between 1 and 4, plus one molecular vibron, formed by an exciton bound to four-m intramolecular phonons. The rate of the m-SA transition scales as $n_m I(m)$, where n_m is the density of molecules in the m-vibrational quantum level, and $I(m)$ is the Franck–Condom factor. In *contrast* with the SE vibronic progression, all the SA bands exhibit a similar intensity, which yields $n_m \propto 1/I(m)$. As $I(m)$ decreases

for increasing m, we conclude that vibron fission preferentially yields hot ground-state vibrations with high m values.

In the following, we discuss if a slow thermalization towards the low energy exciton states can provide an alternative explanation to the $\Delta T/T$ behavior for $\Delta t > \tau_r$. The delayed filling of the bottom exciton states must give rise to slowly rising SE contributions at the low energy side of each SE band [9]. The slow relaxation of hot excitons may then explain the retarded vibronic transients at 2.18, 2.00 and 1.82 eV. However, any delayed SE onset must also be observed as delayed spontaneous emission onset in PL experiments. Fig. 3b shows the transient PL emissions for energies spanning the vibronic bands. The rise time of the PL is found independent of the emission energy and essentially limited by the time-resolution of our experimental apparatus. The absence of any delayed emission conclusively implies that the $\Delta T/T$ response is not due to a slowly rising SE, i.e. to a slow thermalization towards the low energy exciton states, but to a slowly decaying SA signal from hot ground state C–C stretching modes.

In conclusion, in the present contribution we have investigated the energy relaxation processes of photoexcited exciton-vibrational states in molecular crystals. We have found experimental evidences for intermolecular energy relaxation, which lead to the emission of hot phonons in the electronic ground state. This process, which has no counterpart in isolated molecules, represents a basic mechanism of excited state relaxation in molecular crystals.

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