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Optical evidence of a purely one-dimensional exciton density of states in a single conjugated polymer chain

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The excitonic luminescence of an isolated polydiacetylene polymer chain in its monomer matrix is studied by microphotoluminescence. These chains behave as one-dimensional (1D) systems with the expected $1/\sqrt{E}$ density of states between 5 and 50 K. It is also shown that the exciton coherence time is determined by interactions with LA phonons of the surrounding 3D crystal matrix, thus leading to very fast (ps) exciton thermalization within the band. The optical phonons of the chain that are involved in the vibronic transitions are found to have coherence times ranging from 300 to 600 fs.

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Excitons are the dominant optically accessible states in conjugated polymers. They are usually discussed in terms of single discrete states, as in an isolated molecule. The exciton band structure and density of states (DOS) are not considered, unlike in inorganic semiconductors for which the exciton energy dispersion and DOS are important properties. For the past decade, an important effort has been made in order to obtain a one-dimensional (1D) semiconducting system exhibiting a $1/\sqrt{E}$ DOS. Such a DOS has never been observed, neither in the quantum wires that have been realized,[1] nor in organic ''1D'' J aggregates.[2] However, a consequence of one dimensionality is a $T^{1/2}$ dependence of the exciton radiative lifetime, which has been observed by Gershoni *et al.*[3] In the present paper, we report microphotoluminescence (μ-PL) experiments on a single isolated poly-3BCMU[4] red chain and show that to properly describe excitons in this system the actual band structure must be considered. We show that the DOS is the one of perfect 1D systems with the expected $1/\sqrt{E}$ singular variation. The temperature dependence of the homogeneous width is explained by interaction with acoustic phonons,[5] and the values found for the chain optical-phonon coherence times are also presented.

Polydiacetylene (PDA) chains diluted in 3BCMU crystal monomer matrix exist in two electronic structures so-called ''red'' and ''blue'' phases. Both types of chains exhibit an excitonic resonance fluorescence.[6] Blue chain fluorescence is very weak with a quantum yield of 10^{-4}, whereas red chains have a high-fluorescence quantum yield of 0.3 at 15 K.[7] The emitting species of such chains are excitons with a large binding energy of 0.5 eV.[8] The luminescence spectrum of red chains exhibits an intense zero-phonon line and several much weaker vibronic replicas. The zero-phonon line is centered at 2.28 eV at low temperature. The two main vibronic peaks correspond to the stretching of the C═C and C≡C bounds and will now be denoted by *D* and *T* respectively. These two lines are centered at 2.09 and 2.01 eV and are due to radiative recombination with emission of a chain optical phonon with the appropriate momentum.[6] The very high dilution of red chains and their high-fluorescence yield allow the study of a single red chain by μ-PL experiments. The zero-phonon line was studied previously giving access to the homogeneous linewidth Γ_0 and its temperature dependence. It also brought evidence on long-range-energy transfer along the chain.[9] In the present paper this study is extended to the vibronic emission lines.

Macro-PL experiments on an ensemble of red chains[10] show that up to 50 K the exciton lifetime increases with temperature while the fluorescence rate decreases. This suggests that nonradiant states are populated by thermal excitation of radiant ones, a known process in exciton bands of semiconductor quantum wires. Nevertheless, in organic materials the exciton is usually considered as a single excited state. The analysis of the vibronic peaks line-shapes removes this ambiguity since they reflect the DOS in a band description.

The 3BCMU single crystals analyzed here were identical to that described in Ref. 9. The average concentration of red chains is smaller than 10^{-8} in weight, allowing the study of a single chain. The μ-PL experimental setup is the same as in Ref. 9. The excitation wavelength of the Ar^+ laser was chosen at 497 nm, nearly resonant to the *D* (Double bound stretch) absorption line. The excitation power was of the order of one μW to keep the measurement in the low-excitation regime, i.e., with at most one exciton per chain.

The D emission line at $T=43$ K is shown in Fig. 1(a). The line shape is clearly non-Lorentzian, this emission can then not be that of a single state. In such a vibronic emission, the final-state involves a 1D optical phonon of the chain so that any **k** state of the exciton band is connected to the ground state by an optically allowed transition with generation of an optical phonon with the same **k**. In Fig. 1(a), a fit barely distinguishable from the experimental data is presented as well, and the corresponding error is given in Fig. 1(b). This fit is based on three assumptions:

(i) The excitons are in thermodynamic equilibrium with the surrounding crystal, their energy then follows a Maxwell-Boltzmann distribution. As shown below, the interaction between the 1D exciton of the chain and the 3D LA phonons of the crystal is indeed strong enough to ensure this thermal equilibrium.

(ii) The energy dispersion of the optical-phonons generated in the vibronic emissions is very small compared to the

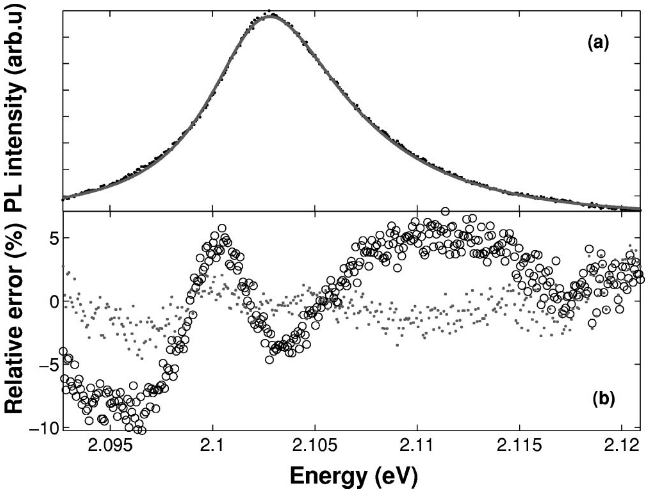

FIG. 1. (a) Data and fit using a 1D DOS of the D peak centered at 2.102 eV for $T=43$ K. (b) Comparison of the error (relative to the maximum signal value) between the fit function and the data for the 1D model (points) and for the 2D model (open circles).

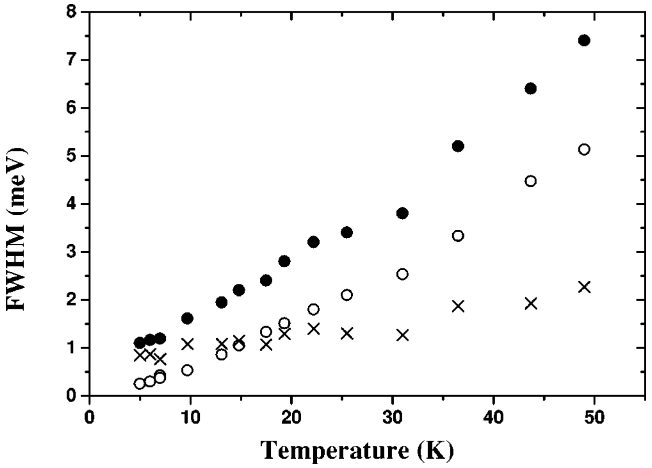

FIG. 2. Γ_D (filled circles) and Γ_0 (open circles) versus temperature. The crosses represent the difference between Γ_D and Γ_0.

one of the excitons and is neglected. Since the effective mass of the exciton is found to be $\approx 0.3m_0$[10] (m_0 is the bare mass of an electron), this hypothesis seems very reasonable.

(iii) The transition matrix elements between all the initial **k** exciton states and the final state (emission of one photon and one chain optical phonon) are equal (including the $\mathbf{k}=0$ state). The contribution of the initial **k** state to the overall homogeneous width is the same for all **k**.

The fitting function $f(E)$ is the convolution of the homogeneous Lorentzian profile and the population of emitting states (1). This population is the product of the DOS by the occupation probability. In (1) E_0 is the Lorentzian's center position and Γ_{vib} its half width. A is a constant including the amplitude of the Lorentzian and the constant parameters of the DOS. The only relevant parameter in the fitting routine is Γ_{vib} (e.g., Γ_D for the D line) which variation with temperature will be discussed.

$$f(E)=\frac{A}{(E-E_0)^2+\Gamma_{vib}^2}\left[\exp\left(-\frac{E-E_0}{k_BT}\right).DOS\right]. \qquad (1)$$

A quantitative 1D fit, i.e., with a $(E-E_0)^{-1/2}$ DOS, is obtained for all vibronic lines at all temperature studied (5–50 K). Fitting with a 2D DOS is always worse. The 2D DOS corresponds to the lowest dimensionality nonsingular density of states, and has been found to fit data on J aggregates.[2] The fitting error for the 1D and 2D models are presented in Fig. 1(b), and show the very good accuracy of our model when a 1D DOS is used.

The $1/\sqrt{E}$ DOS is that of a perfect wire, free of defects and infinite. The chain is in fact not infinite, though very long, $\geqslant 10\,\mu$m (20 000 monomers). In addition it may not be perfectly uniform and the question of the length over which the exciton is actually delocalized arises. Considering the emitting region as a quantum box (QB), two limits occur: in a short QB the excited-states energies are discrete, and a vibronic (respectively zero phonon) emission line would consist in a series of asymmetric Lorentzians (respectively Lorentzians), whereas in a long QB the vibronic emission line shape should be given by the fitting function that was considered above and the one of the zero-phonon line by a single Lorentzian. In the luminescence spectrum, peaks resulting from the emission of discrete states have never been observed neither near a vibronic emission nor near the much narrower zero-phonon line that is recorded with a dynamics of about two orders of magnitude. Thus, any extra line having an intensity of at least $\frac{1}{100}$ of the zero-phonon line would have been observed. Assuming a localization potential of the order of the experimental inhomogeneous broadening (a few meV), the D and zero-phonon emissions of the QB were simulated as a function of the box length at several temperatures, showing that for a 400 nm or longer QB the results are undistinguishable from that presented above. This is expected since a 800 monomers QB contains 800 energy levels so that a continuum description becomes valid. 400 nm is also shorter than the length of the observed emitting region of $\approx 2\,\mu$m [see Guillet *et al.*, (Ref. 9)], and much larger than the calculated[11] or experimental[8] exciton size of about 1.5 nm.

The analysis of the zero-phonon and vibronic emission linewidths and their temperature dependence, $\Gamma_0(T)$ and $\Gamma_D(T)$ (Fig. 2), allow the study of the exciton-phonon interaction process and consequently to validate our first assumption above. The model used to account for the variation with temperature of Γ_0 assumes that the dominant process is the absorption of a single acoustic phonon (LA phonon) of the crystal. It is an adaptation of the deformation potential theory to a 1D centro-symmetric system such as poly-3BCMU [see, for instance Oh and Singh (Ref. 12)]. In the expression of the Fermi golden rule, the 1D character of the excitons of the chain induces a threshold in the scattering by phonons regardless of the phonon dimension because of the energy and momentum conservation rules. LA phonons confined on the polymer chain (1D phonons) can only make exciton transitions between $\mathbf{k}=0$ and $\mathbf{k}=\mathbf{k}_{1D}$ the point where the exciton and the 1D LA phonon dispersion relations intersect as shown in Fig. 3. This is not an efficient thermalization pro-

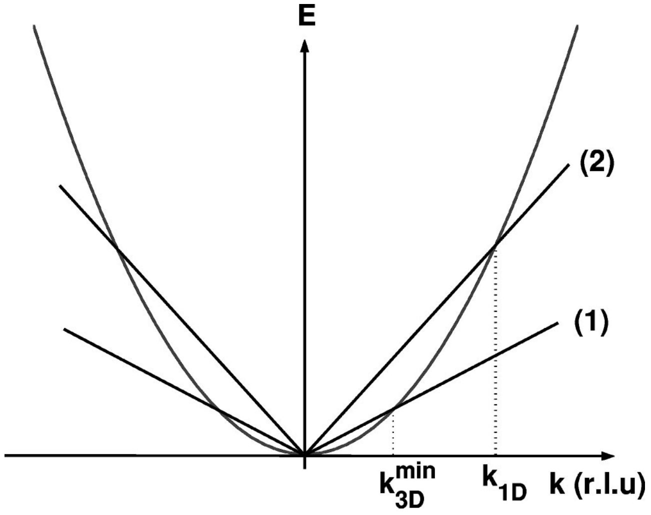

FIG. 3. Dispersion relations of the excitons and LA phonons. (1) and (2) are the dispersion curves of LA phonons of the crystal and LA phonons confined on the chain respectively. The dispersion relations correspond to m_X^* and sound velocities given in the text.

cess and does not agree with the experimental observation that all $\mathbf{k}$ states emit within an energy range $k_B T$. On the contrary, exciton scattering by 3D monomer crystal LA phonons connect $\mathbf{k}=0$ to the continuum of $\mathbf{k}$ states with $\mathbf{k} > \mathbf{k}_{3D}^{min}$ ($\mathbf{k}_{3D}^{min}$ is defined in Fig. 3) since only the component parallel to the chain of the total momentum must be conserved in the case of the 1D exciton [see, for instance Agranovitch and Dubovskii (Ref. 13)]. Further scattering processes can populate the rest of the band. Therefore, we have considered interactions with LA phonons of the crystal. This process quantitatively explains the variation of $\Gamma_0(T)$ in the range of temperature explored (see Fig. 4). The crystal sound velocity was assumed isotropic for simplicity and taken as 2.5×10^3 m s^{-1}. This value was measured in another diacetylene, pTS,[14,15] and is typical for molecular crystals. This leads to $\mathbf{k}_{3D}^{min}=1.3\times10^{-3}$ (10^{-2} r.l.u.). The slope of the 1D LA phonons dispersion curve on Fig. 3 corresponds to the sound velocity measured on poly-pTS,[14,15] and equal to 5.5×10^3 m s^{-1}. This larger value compared to the one of the monomer is related to the fact that the polymer is a chain of covalent bonds.

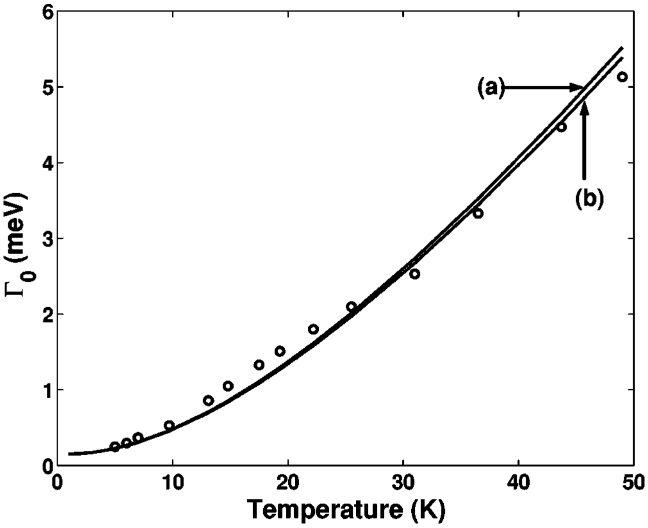

FIG. 4. Experimental data (open circles) and calculated broadening of Γ_0 with temperature for an exciton Bohr radius of 10 and 20 Å [(a) and (b), respectively] and an effective mass of 0.3 m_0. In both cases, the sum of the deformation potential for the valence and conduction band is 6 eV.

Besides the chosen sound velocity, the calculation involves three parameters: the exciton Bohr radius, its effective mass, and (D_c+D_v) the sum of the deformation potential for the conduction and valence band, respectively. Experiments and theory indicate that the Bohr radius of the exciton on PDA chains is between 10 and 20 Å.[8,11] The chosen value for this parameter is not critical as shown in Fig. 4. From the temperature dependence of radiative lifetime, an exciton effective mass m_X^* of $\approx 0.3 m_0$ is deduced.[10] To $m_X^*=0.3\pm0.1 m_0$ correspond (D_c+D_v) values equal to 6.1 ∓ 0.8 eV, which are typical deformation potentials. A smaller $\mathbf{k}_{3D}^{min}$ (smaller sound velocity) would lead to a slightly larger deformation potential to reach similar agreement with the experimental data.

Since the scattering rate of excitons by LA phonons goes to zero at zero K, a constant value corresponding to the residual linewidth at zero K has been added. Its fitted value is 150 μeV, which can only be partly due to the instrumental resolution (100 μeV). This will be the subject of further analysis. Note that the contribution of the effective lifetime of the exciton at 1 K (≈ 6 μeV)[10] is much smaller.

The inelastic processes thermalizing the excitons in their band are thus either the emission or absorption of LA phonons in the temperature range studied. The absorption is the slowest process and has a characteristic time of 2 ps or less (see the widths in Fig. 2). The excitons are then at thermodynamic equilibrium since their effective lifetime is over 100 ps in the range of temperatures studied.[10]

In Fig. 2, one notes that Γ_D is 3 times larger than Γ_0 at low temperature. Let us assume that the width of a vibronic line is the sum of the terms resulting from the initial and final state. The contribution of the initial state is Γ_0. The one from the final-state represents the coherence time of the optical-phonon emitted in the recombination that is slowly decreasing with temperature (see, for instance Fig. 2 for the *D* line). One would expect that the coherence time so obtained is not the same for all vibronic peaks. This is indeed observed; a coherence time of approximately 300 fs is found for the *D* and *T* lines, while in another vibronic line centered at 2.15 eV, distinctly narrower, a coherence time of 600 fs is found. These different values are in agreement with previous measurements made in another PDA by Chen *et al.* using a completely different method (CARS).[16,17]

Fitting the line shape of the vibronic peaks has enabled us to deduce that the excitons on the polymer chain have to be described by a band with a $1/\sqrt{E}$ DOS. Let us associate this conclusion with the analysis of the exciton decay time presented in Ref. 10. Indeed, the radiative lifetime of excitons increases as $\sqrt{T}$ for T up to 80 K at least, as it is expected for an ideal 1D wire.[18] Therefore, the finite size of the emitting regions does not affect the 1D character of the excitons unlike in inorganic semiconductor quantum wires[1].

To summarize, we have presented microfluorescence experiments performed on a single conjugated polymer chain in its crystalline matrix. The zero-phonon emission line is Lorentzian while the vibronic ones are asymmetric. Fitting the line shape of these vibronic peaks shows that the chain is a one-dimensional system that has to be described by an excitonic band with a $1/\sqrt{E}$ DOS. Furthermore, the variation of Γ_0 with temperature is explained by interactions with longitudinal acoustic phonons of the crystal in the range of temperature studied. This interaction thermalizes the excitons in their band so that they are at thermodynamic equilibrium with the surrounding medium. Finally, the chain optical-phonons generated in the vibronic emissions are found to have coherence times ranging from 300 to 600 fs at low temperature.

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