Time Domain Investigation of the Intrachain Vibrational Dynamics of a Prototypical Light-Emitting Conjugated Polymer

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Coherent nuclear motion of the carbon backbone is monitored in real time in substituted poly(phenylene)-vinylene in both *excited* and ground electronic state using sub-10-fs light pulses. Characteristic features of the intrachain vibrational dynamics are obtained. We observe vibrational dephasing in the excited state within 1 ps (time constant $T_{2e} \approx 300$ fs). These findings are in agreement with the molecular picture for photoexcitation in conjugated polymers.

The early photophysical phenomena in π-conjugated polymer (CP) semiconductors are are not yet well understood, in spite of their growing technological impact and important opto-electronic applications. According to the molecular picture, used for describing conjugated polymers, the initial photoexcited state immediately shares electronic and vibrational energy, i.e., it involves nuclear excitation, at variance with the bandlike picture, predicting initially pure electronic excitation in a rigid lattice. Indirect evidences suggest an ultrafast time scale for vibronic relaxation in the excited state of CPs, often assumed $\ll 100$ fs [1], which is of paramount importance: in all opto-electronic devices, photovoltaic cells, photodiodes, or light emitting devices, the primary excitations are hot singlet states, not relaxed ones. A full understanding of the vibrationally coherent dynamics in solid state CPs is needed, and it may open the way towards new applications, such as coherence control by means of phase shaped pulses [2,3].

In this Letter we report on the results of real-time vibrational spectroscopy in poly[2-methoxy, 5 - (3′, 7′ - dimethyl - octyloxy)] - p - phenylene vinylene (MDMO-PPV) [4], a prototypical light emitting CP, excited by sub-10 fs visible light pulses. Coherent nuclear motion along the carbon backbone is monitored both in ground and *excited* state, providing what to our knowledge is the first information on excited state vibrational dynamics in light emitting polymers.

The sub-10 fs laser system is based on a noncollinear optical parametric amplifier, followed by chirped mirror compressor [5,6], generating nearly transform-limited pulses (7 fs, 500–700 nm), with energy of about 10 nJ. These pulses are used to excite and probe the sample, either thin film on a glass substrate or chloro-benzene solution kept into a 0.2 mm cuvette at room temperature.

The pump beam is focused at an energy density of about 0.1 mJ/cm^2 (spot size of 80 μm) avoiding sample damage. The probe beam is attenuated by about 1 order of magnitude and delayed in time with respect to the pump ($\tau_D > 0$). Time-resolved measurements of normalized transient transmission changes ($\Delta T/T$) are obtained by spectrally filtering the probe after passing through the sample and combining differential detection with lock-in amplification. The pulse bandwidth allows resonant excitation ($S_0 \rightarrow S_1$) of the conjugated polymers as well as probing of the below gap region where stimulated emission takes place ($S_1 \rightarrow S_0$). Figure 1(a) shows $\Delta T/T$ on the 1 ps time scale at 580 and 650 nm, in the stimulated emission (SE) region. Similar data are obtained for wavelengths spanning the whole SE band. The slow decay kinetics reflects S_1 deactivation, while the strong oscillating signal (zoomed out in Fig. 1(b)) indicates that vibrational coherence has been initiated in the molecular ensemble. After subtraction of the slow decay at 650 nm, Fourier transformation of the residual is shown in Fig. 2 for wave number range 1000–1700 cm^{-1} and compared to the cw resonance Raman (RR) spectrum. Prima facie there is a direct correspondence between the two spectra. The observed frequencies suggest that breathing in the oscillating amplitude, more evident at early times, be due to beating of the ≈ 1300 and 1580 cm^{-1} modes (expected with 120 fs period). It is also evident that the Raman mode at 1115 cm^{-1} appears softened in the transient spectrum (1085 cm^{-1}). The amplitude of the oscillating pattern has an initial fast decay, on the 200 fs time scale, followed by a slower damping.

A short pulse projects the ground state multidimensional vibrational wave function to the excited state [7]. If nuclear motion cannot be disregarded during the
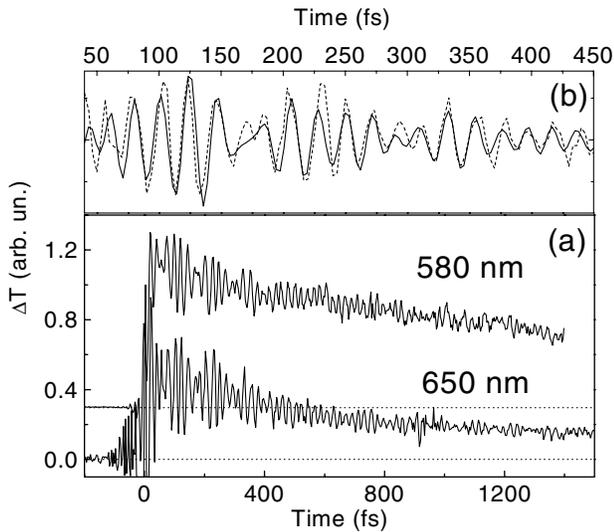
FIG. 1. (a) Transient transmission change following excitation with 7 fs optical pulses in MDMO-PPV film probed at 580 and 650 nm (stimulated emission). (b) Residual after slow background subtraction (solid) and simulated trace (dashed).

excitation pulse, a Ramanlike interaction is taking place, ending up with coherence also in the ground state [8]. As a result, both ground and excited state vibrational frequencies are going to be present in the transient signal, due to modulation of the nonstationary Frank-Condon envelope [9]. In our case, the vibrational motions coupled to the electronic excitation have periods in the $20-25$ fs range, so that significant wave packet motion takes place during the pump pulse. In order to test this scenario numerical solution of the Schrödinger equation for two dipole-coupled electronic levels with displaced harmonic potentials was performed. The experimental observation and the expected small geometric rearrangement suggest using equal ground and excited state frequencies. A test was carried out for the 1580 cm^{-1} mode, the highest observed

experimentally, and pulse duration $t_p = 8$ fs, according to our experimental condition [10]. Figure 3 shows as a contour plot the temporal evolution of the wave function in both states. The result confirms that both ground and excited state are coherently populated and indicate that ground state motion is limited to a rather small region about the equilibrium position, suggesting coherence among low quantum number vibrational states, possibly $0-1$. To single out the two contributions is not an easy task since the hot ground state contribution appears at spectral positions far away the absorption edge, practically covering the whole emission region [11]. The detection of frequencies not present in the Raman spectrum is a trivial case indicating nuclear motion in the excited state, in the presence of nonlinear electron-phonon interaction and anharmonicity [12], as recently shown [13]. In MDMO-PPV this seems undisputed only for the 1085 cm^{-1} mode [14], to be assigned to the excited state, possibly as a consequence of the longer period (about 31 fs), which reduces the ground state contribution [15]. For higher modes we find frequencies that differ by less than ± 15 cm^{-1} from those in the ground state. We have two possible interpretations: (i) ultrafast vibrational dephasing, as for instance caused by self-trapping or internal conversion (IC) [16], has washed out coherence in the excited state; (ii) both are present, with similar frequencies. Since the very existence of self-trapping in conjugated polymers has been challenged by a number of experiments [17,18] and IC does not take place in emitting systems, we favor the latter interpretation. Information on coherence loss can be extracted from a sliding window Fourier transform [19] of the oscillating signal. The analysis is done by using a super-Gaussian
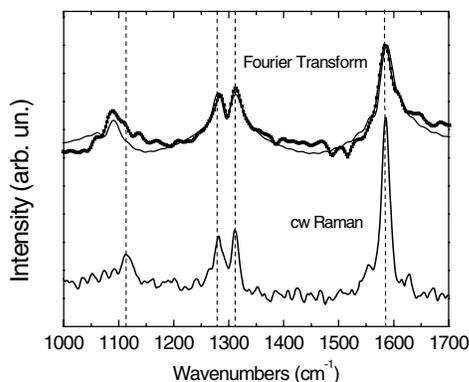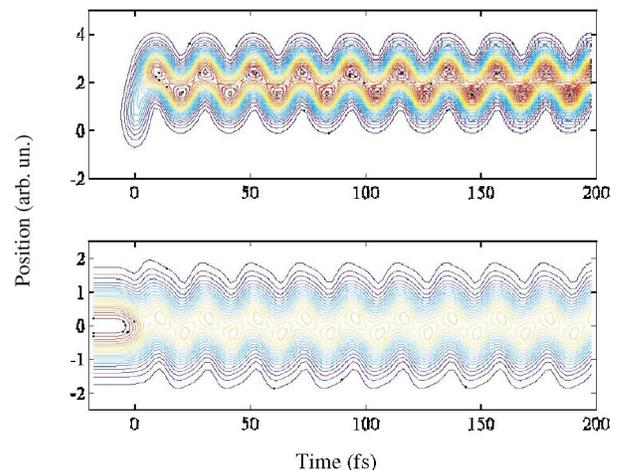

FIG. 2. Upper trace: Fourier transform of the transient trace at 650 nm (solid square), Fourier transform of the simulated data (solid line); lower trace: Raman spectrum of the same film obtained under cw excitation at 1064 nm.

FIG. 3 (color online). Contour plot of the squared wavefunction amplitude in ground (bottom) and excited (top) state. Relevant parameters are the following: mode frequency 1580 cm^{-1}, pulse duration $t_P = 8$ fs, pulse center $= 2.12$ eV, PPV gap $= 2.1$ eV, and displacement parameter (mode coupling) $B = 1.5$.

time-dependent window $g(t)$ of 70 fs HWHM. The reported quantity is $S(\omega,\tau) = \int_0^{t_{max}} s(t)g(t-\tau)\exp(-i\omega t)dt$ with $s(t)$ as the transient signal in the time domain. A faster initial decay is evident for all the modes. The complex interference pattern between at least five modes gives rise to ripples in the amplitude surface, particularly dramatic at certain wavelengths, but which do not carry any physical significance. Slices of the 3D plot give the decay of mode amplitude, as reported in Fig. 4 for the 1580 and 1310 cm^{-1} components. Note that the shape of $S(\omega,\tau)$ does not only reflect the coherence decay kinetics, but also the sliding window algorithm. Thus the initial rise time is caused by sweeping of the measuring temporal window across $\tau_D = 0$. In the case of 1310 cm^{-1}, the large dip at about 650 fs is due to interference with the nearby 1280 cm^{-1} mode (it is also seen at 1280 cm^{-1}). To fit the experimental $S(\omega,\tau)$ we build a simulating function $f(t)$, made of a series of damped sinusoids:

$$f(t) = \sum_{k=1}^n A_k(t)\cos(\omega_k t + \Phi_k), \qquad (1)$$

where $A_k(t)$ is a decaying amplitude, ω_k are the frequencies observed in the Fourier spectra and Φ_k phase constants to be determined, and work out its sliding window transform $F(\omega,\tau)$. As a first ansatz, we introduce in Eq. (1) dephasing according to the FWHM of the RR peaks ($\Delta\tilde{\nu} = 15$ cm^{-1}), corresponding to ground state dynamics (here $n = 4$). Both homogeneous (exponential, $T_{2g} = 630$ fs) and inhomogeneous (Gaussian) decay were tested without success (see dashed lines in Fig. 4). The

rise time in the simulated trace reflects the slow decay of $s(t)$ integrated by sliding $g(t)$. We can, however, extract the clear indication that exponential decay better describes the experimental dynamics, pointing to homogeneous vibrational dephasing. This can be simply rationalized by noting that strongly coupled modes in phenyl based chains show negligible dispersion with effective conjugation length, which is the main source of broadening of the optical transition [20]. As a second try we include for each mode two different exponential decay dynamics:

$$A_k(t) = A_{kg}(t)\exp(-t/T_{2g}) + A_{ke}(t)\exp(-t/T_{2e}). \qquad (2)$$

Acceptable fitting of the experimental data is obtained using the parameters reported in Tables I and II; the corresponding $f(t)$ is also plotted in Fig. 4. Good agreement is also found between $f(t)$ and the measured oscillating signal (see for instance at 650 nm in Fig. 1) and with the Fourier spectra (Fig. 2). Note that perfect matching can be obtained also with the apparent modulation of $S(\omega,\tau)$; see for instance center panels in Fig. 4, showing that those do not arise from modulation of the instantaneous frequency, but from interference of damped oscillating modes with broad frequency spectra. We can therefore reproduce our data by assuming a vibrational dephasing time $T_{2e} \approx 250–300$ fs, possibly for the excited state and $T_{2g} = 630$ fs, for ground state. We find phase difference, due to the different excitation process, between ground and excited state coherence, as it is made evident from the inset in Fig. 4 showing the sinusoid components for 1580 cm^{-1}. The same experiment on
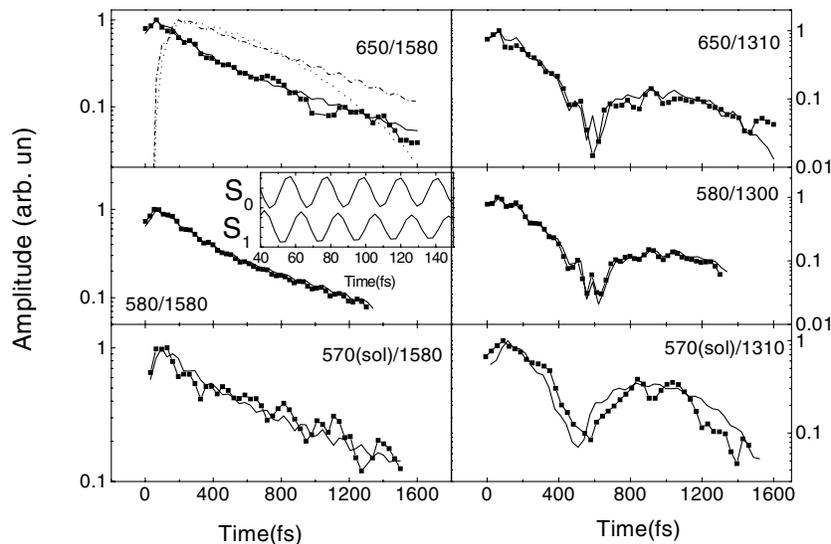

FIG. 4.   Frequency slices at 1580 and 1310 cm^{-1} of the sliding window Fourier transform at 650 nm (top), 580 nm (middle) in film, and 570 nm (bottom) in solution. Solid squares are experimental data, lines are fitting according to the procedure described in the text. Dashed and dash-dotted lines are fitting assuming only ground state dynamics. The inset shows ground and excited state Fourier component as worked out in the numerical simulation.

TABLE I. DMNO-PPV film at 650 nm (580 nm). Values in parenthesis are reported only when different. $T_{2g} = 630$ fs for all the modes.

Mode (cm^{-1})	A_e	T_{2e}(fs)	A_g	ϕ/π (rad)
1090[a]	0.45(0.1)	300	0.3(0.2)	0.65(0.7)
1280	0.4	250	0.2	0.65(0.7)
1310	0.5(0.4)	230(250)	0.2	0.65
1580	1	270	0.45(0.5)	0.65

[a]This mode is 1085 in excited state, 1115 in the ground state.

MDMO-PPV in solution produces the results shown in the lower panel of Fig. 4 and relative fitting curves. The S_1 deactivation is much slower in solution, but *vibrational dephasing is found to be comparable.*

In conclusion, we observe that carbon backbone stretching frequencies in the excited state correspond to those of the ground state within ± 15 cm^{-1}, pointing to a small geometrical rearrangement. This finding is in agreement with the molecular picture for photoexcitations in conjugated polymers. Accordingly, we note that closer lying vibrational frequencies between the ground state and the ionic, $1B_u$, excited state are typically observed in linear polyenes [21]. Homogeneous decay describes well the transient coherence, with dephasing time constant $T_{2e} = 300$ fs. The comparison film solution, showing similar damping time scales, indicates that the dephasing process is mainly intrachain. We can speculate this be rapid IVR, obtaining a lower limit for $T_{1e} > 110$–150 fs in the excited state. This value turns out to be larger than what it is usually assumed. Our results also point out that energy stored into dark modes stays available for a time exceeding 1 ps. This can be recognized by the observation that the potential energy surface of a dark mode is unchanged by the electronic excitation, thus behaving much like ground state modes (actually they are indistinguishable), with $T_{1g} > 315$ fs. Our findings provide critical information for those models assuming a role for the excess energy in the elementary process of conjugated polymers, such as dissociation of the neutral state [22] in a photoexcited chain.

TABLE II. DMNO-PPV film in ClC$_6$H$_6$ solution at 570 nm. Values in parenthesis are reported only when different. $T_{2g} = 630$ fs for all the modes.

Mode (cm^{-1})	A_e	T_{2e}(fs)	A_g	ϕ/π (rad)
1280	0.3	250	0.4	0.2
1310	0.4	230(250)	0.4	0.2
1580	1	270	0.5	0.2

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