Chemical Physics 349 (2008) 244–249

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Exciton dynamics in a disordered conjugated polymer: Three-pulse photon-echo and transient grating experiments

J. Sperling [a], A. Nemeth [a], P. Baum [a,b], F. Šanda [c], E. Riedle [b], H.F. Kauffmann [a,*], S. Mukamel [d], F. Milota [a]

[a] Department of Physical Chemistry, University of Vienna, Währingerstrasse 42, 1090 Vienna, Austria
[b] Chair for BioMolecular Optics, Ludwig-Maximilians-University (LMU), Oettingenstrasse 67, 80538 Munich, Germany
[c] Institute of Physics, Faculty of Mathematics and Physics, Charles University, Ke Karlovu 5, Prague 121 16, Czech Republic
[d] Department of Chemistry, University of California, Irvine, CA 92697-2025, United States

ARTICLE INFO

Article history:
Received 22 November 2007
Accepted 24 February 2008
Available online 29 February 2008

Keywords:
Ultrafast spectroscopy
Conjugated polymer
Photon echo

ABSTRACT

We study the sub-picosecond exciton dynamics of the prototypical soluble conjugated polymer poly[2-(2′-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEH-PPV) by comparative three-pulse photon-echo peak-shift and transient grating measurements, performed under excitation energy tuning conditions. The strong sensitivity of signal decays to the chosen excitation energy is ascribed to the interplay of inter- and intra-segmental relaxation events in an ensemble of electronically coupled sites. As a result, the energetic site-to-site disorder and its contribution to the spectral lineshape is most reliably determined for excitation of the redmost part of the absorption spectrum. Comparing the data for the two solvents toluene and tetrahydrofurane, we conclude a weak sensitivity only to the specific type of solute-solvent interactions. Within our time-resolution, we surprisingly recover weak but reproducible modulations of the third-order signals that are damped out on the early picosecond timescale.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The molecular exciton model has been quite successful in explaining the main spectral features of conjugated polymers [1,2]. It rests upon the assumption of finite conjugation lengths along the polymer chain, due to a distribution of structural defects, and accordingly treats the polymer as a collection of segmental sub-units over which optical excitations are delocalized (hence the term spectroscopic units). In this picture, inter-segmental electronic couplings allow excitons to move along the chain towards sites of lower energy. The optical response is thus determined by static disorder (the spectral inhomogeneity of the site distribution), dynamic disorder (site-specific interactions with the bath), and excitation energy transfer (EET) processes. Detailed information on the interplay of these contributions remains hidden in the linear absorption spectrum of conjugated polymers, which usually consists of a single broad feature.

Time-resolved non-linear experiments are capable to provide a more detailed understanding of the lineshape of an assembly of coupled molecular chromophores [3,4]. Apart from an earlier photon-echo (PE) study on oriented films of polydiacetylene [5], Scholes et al. [6] were the first who performed PE experiments on poly[2-(2′-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEH-PPV), which serves as a typical model for ground-state non-degenerate polymers of the poly(arylenevinylene) type (cf. Fig. 1). In some analogy to the situation encountered in molecular aggregates, the structureless electronic absorption of MEH-PPV has been explained to be dominated by bath-mediated exciton scattering [6]. It was argued that, due to fluctuations of site-to-site couplings between strongly coupled units, optical excitons sample over eigenenergies within about 50 femtoseconds (fs), precluding any significant contribution from static disorder to the absorption lineshape. On the other hand, the data of more recent, closely related three-pulse photon-echo peak-shift (3-PEPS) studies [7,8], could not be explained satisfactorily without considering a residual spectral inhomogeneity arising from conformational disorder of the polymer chain.

This state of affairs motivated the present contribution, in which we report systematic 3-PEPS and transient grating (TG) measurements on MEH-PPV in the two solvents toluene and tetrahydrofurane (THF). Tuning the central energies of sub-30 fs excitation pulses across the polymer absorption band, we observe a gradual change in the shape of both nonlinear signals. This allows to differentiate between inter- and intra-segmental relaxation events, the latter observable at increasingly site-selective excitation conditions (at low excitation energies).

---

* Corresponding author.
E-mail addresses: jaroslaw.sperling@univie.ac.at (J. Sperling), harald.f.kauffmann@univie.ac.at (H.F. Kauffmann), franz.milota@univie.ac.at (F. Milota).

0301-0104/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemphys.2008.02.046

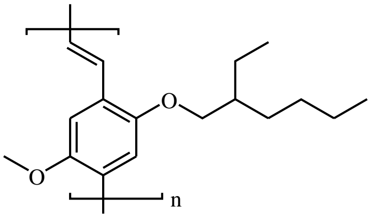

Fig. 1. Molecular structure of poly[2-(2′-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEH-PPV). Alkyloxy-chains attached to the conjugated poly(*p*-phenylenevinylene) (PPV) backbone facilitate solubility in common organic solvents.

2. Conceptual framework

In a third-order time-resolved experiment, three laser pulses (with wavevectors $\mathbf{k}_1, \mathbf{k}_2$, and $\mathbf{k}_3$) interact with the sample and create a nonlinear polarization $P^{(3)}$ that radiates the signal in a particular direction determined by phase-matching conditions. The third-order polarization $P^{(3)}$ is determined by the incoming electric fields and the third-order response function $S^{(3)}(\tau, T, t)$ of the system (we use τ and T to denote the first and second time interval between the three interactions, and t the time elapsed after the third interaction, respectively). $S^{(3)}$ can be obtained by a perturbative expansion of the system density matrix in the total electric field [3,4,9].

Since a comprehensive discussion of the underlying theory is beyond the scope of this work, we give an intuitive picture only for understanding of the main aspects to be discussed below. In a photon-echo experiment, the first pulse ($\mathbf{k}_1$) creates a coherence (i.e. a superposition) between the ground and excited state of an electronic absorber. The second pulse ($\mathbf{k}_2$, after time τ) converts the evolving coherence into population-space, creating a spatially periodic population grating of ground/excited states in the sample, which can undergo relaxation and wavepacket motion during the time interval T. The third pulse ($\mathbf{k}_3$), again, creates a superposition of states (evolving with an inverted phase), that radiates into the signal direction ($\mathbf{k}_s = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$). All signals to be discussed are measured in (time-integrated) homodyne detection mode. Assuming the impulsive limit the photon-echo signal intensity is then given by

$$I(\tau, T) \propto \int_0^\infty \mathrm{d}t |S^{(3)}(\tau, T, t)|^2. \tag{1}$$

The 3-PEPS method is based on the following scanning-scheme. In each sequence, for a particular (fixed) population time delay T, the coherence time τ is scanned and the position of the maximum of $I(\tau, T)$ is evaluated along the τ-axis. The magnitude of this peak-shift τ^* (deviation from $\tau = 0$) is recorded for a selected range of population times, to give a plot of τ^* vs. T (the peak-shift decay). The popularity of the experiment results from the fact that, at not too short population time delays, the 3-PEPS signal of a chromophore ensemble reflects the (ensemble averaged) correlation function [10–12]

$$M(t) = \frac{\langle \delta\omega_{\mathrm{eg}}(t)\delta\omega_{\mathrm{eg}}(0)\rangle}{\langle \delta\omega_{\mathrm{eg}}^2\rangle} \tag{2}$$

of the individual fluctuations $\delta\omega_{\mathrm{eg}}^i(t)$ in the electronic transition energies. Simply speaking, the 3-PEPS decay measures to what extent electronic frequencies of the system correlate on a time set by delay T. This property is particularly useful in the condensed phase, where the separation of timescales (and homogeneous and inhomogeneous contributions to the spectral lineshape) is not distinct. Thus, the method not only has been extensively used for studies of solvation dynamics on various model dyes [13,14], but also has shown to be a sensitive probe for tracing excitation energy transfer in multi-chromophore systems, like J-aggregates [15] or light-harvesting complexes [16,17].

Since the intensity of the echo signal does not enter into the 3-PEPS decay, we complement the data with transient grating measurements to gain additional information on the population dynamics during T. In TG experiments, the coherence time is fixed at $\tau = 0$ and the population time scanned through the region of interest. In the impulsive limit, the TG signal intensity is given by

$$I(T) \propto \int_{-\infty}^\infty \mathrm{d}t |S^{(3)}(\tau = 0, T, t)|^2. \tag{3}$$

3. Experimental details

MEH-PPV is purchased from American Dye Source and used as delivered. Solutions (20 mg/100 ml) in toluene and THF (both from Merck, Uvasol grade) are prepared by sonicating for several hours at elevated temperatures and subsequent filtration to remove insoluble residues. Steady-state absorption and fluorescence spectra are recorded with a miniature fiberoptic spectrometer (Ocean Optics USB 2000).

A regenerative Ti:Sapphire amplifier system (RegA 9050-system, Coherent Inc.) generates 45 fs pulses at 800 nm with a repetition rate of 200 kHz, which are used to pump a noncollinear optical parametric amplifier (NOPA) that delivers sub-30 fs pulses tunable across the visible [18]. The NOPA-output passes a sequence of fused silica prisms for pulse compression and pre-compensation of dispersive elements. Three beams of equal intensity (10 nJ/pulse at the sample position) and dispersion are prepared by broadband beamsplitters and anti-reflection coated glass substrates of the same material and thickness. Two of the beams ($\mathbf{k}_2$ and $\mathbf{k}_3$) are delayed by motorized linear stages with a resolution of 0.1 μm. All three beams are aligned in parallel as an equilateral triangle (1 cm each side) and focused onto the sample to a common spot size of 200 μm by means of a 20 cm focal-length lens. To avoid photo-degradation of the sample a total volume of 100 ml of the respective solution is circulated through a 200 μm flow-cell.

Since even small amounts of chirp can have significant effects on third-order signals (see, e.g., Ref. [19]), attention is given to eliminate any higher-order dispersion. To that end, the excitation pulses are characterized by zero-additional-phase spectral phase interferometry for direct electric-field reconstruction [20,21] (ZAP-SPIDER). With ZAP-SPIDER, the amplitude and phase of a pulse can be characterized directly at the interaction point of the experiment. By optimizing the prism compressor for lowest material insertion, shortest pulses can be generated with negligible satellites from higher-order chirp. In the present experiments, pulse durations of 28 fs with more than 95% of the energy contained in a single main pulse are routinely achieved. Pulse lengths are further cross checked by intensity autocorrelation in a 50 μm thick β-Barium-Borate (BBO) crystal placed at the sample position.

All third-order signals are spatially filtered and detected by photodiodes in combination with lock-in amplifiers. Two-pulse photon-echoes are used to determine $\tau = 0$ and $T = 0$ with high precision. Three-pulse photon-echoes and TG signals are simultaneously measured in the two directions $\mathbf{k}_s = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ and $\mathbf{k}_s' = \mathbf{k}_1 - \mathbf{k}_2 + \mathbf{k}_3$, which is done to check consistency of the TG data and to determine the peak-shift with greater precision (by Gaussian fitting of the signals and halving the temporal separation of the maxima). A typical sequence of 3-PEPS measurements is shown in Fig. 2. Testing against other fitting schemes (parabolic and higher polynomial), we observe no significant changes in the 3-PEPS decays.

Download English Version:

https://daneshyari.com/en/article/5375952

Download Persian Version:

https://daneshyari.com/article/5375952

Daneshyari.com