

Combined Photon Echo and Single-Molecule Studies of Low-Temperature Dynamics in a Dye-Doped Polymer

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The photon echo (PE) and single-molecule spectroscopy (SMS) may be combined to give a very powerful tool for detailed study of low-temperature dynamics in dye-doped disordered solids such as polymers and glasses. At the same time, this type of studies are likely to reveal discrepancies when comparing characteristic times of optical dephasing T_2 and single-molecule (SM) zero-phonon spectral lines (ZPL) broadening when obtained from PE and SMS, correspondingly, namely for tetra-tert-butylterrylene in polyisobutylene in the temperature range of a few – dozen of Kelvins [1, 2]. Inexplicably, PE-experiments demonstrated T_2 -times to be much shorter than it is sufficient to cause the corresponding ZPL broadening. Here we experimentally solve this problem and show that at $T = 4.5\text{--}15\text{K}$ the incoherent PE technique gives T_2 -times which correspond the narrowest SM ZPL [3].

The PE-measurements were performed using the home-built incoherent photon echo spectrometer that was constructed originally in the mid of 1990ies. This setup was fruitfully used for the study of ultrafast low-temperature dynamics of polymers and organic glasses [1, 4], and recently reconstructed to achieve modern experimental possibilities [5, 6]. The setup consists of a resonator-less super-luminescence dye-source (ethanol solution of rhodamine-6G) cross-pumped with a solid-state pulse laser LS2131M10FF (Lotis TII, Belarus). This laser system allows generation of incoherent light with pulse duration 9 ns, repetition rate up to 10 Hz and energy up to 30 $\mu\text{J}/\text{pulse}$. Rotation of diffraction grid included into optical source scheme gives opportunity to tune the emission within the luminescence spectrum of the dye (570–610 nm). The emission spectral bandwidth of the source was selected as high as 60 cm^{-1} . Then, the beam is splitted in two pulses, one of which is passed through mechanical delay line. Thus, the delay between two pulses can be changed by variation of the optical length in one of channels (in a range of 5.6 fs to 4 ns with a step of 5.6 fs). PE signals were detected using a CCD-camera Cooke SensiCam HighSpeed (a quantum efficiency 40% at $\lambda = 580$ nm, exposure times of 100 ns to 10 ms, readout noise of 13–14 electrons, and a less than 0.1 dark count/s/pixel).

We used a thin (0.5 mm) film of polyisobutylene (PIB) doped with tetra-tert-butylterrylene (TBT) molecules. PIB ($M_w = 4.2 \times 10^6$ g $\cdot\text{mol}^{-1}$, Sigma Aldrich) was dissolved in spectrally pure toluene (Sigma Aldrich) together with TBT. The sample was prepared by disposing of the solution between two glass slides and further pumping for toluene removal. The sample was placed into the measuring chamber of an optical helium cryostat (RTI, Chernogolovka, Russia) with temperature regulation in the range of 4.5K to room temperature with accuracy of 0.1K.

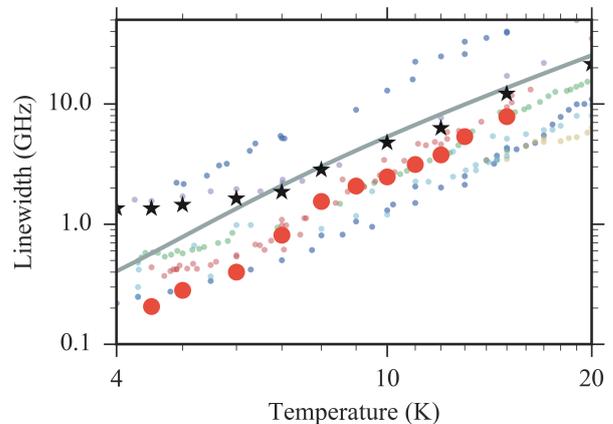


Figure 1: Temperature dependences of ZPL homogeneous width measured by means of 2IPE (big circles – new data, grey line – previous data) and SMS (small circles and stars) measured in polyisobutylene doped with tetra-tert-butylterrylene.

IPE decay curves (dependence of IPE signal intensity on the delay time between 1st and 2nd pulses) were measured by controlled moving of reflecting prism along mechanical delay-line. The typical 2-pulse Incoherent photon echo (2IPE) decay curve consists of sharp intensive peak in the region of zeros delays (which correspond to the phonon sideband in electronic-vibrational spectrum of dye-molecules) and extended tail (which correspond to ZPL of dyes). As usual [1, 4], in order to find the optical dephasing time T_2 we fit this tail with expression $I = I_0 + C \exp(-4\tau/T_2)$, where I_0 , C and T_2 are fitting parameters. The procedure was repeated in our measurements at different temperatures, thus the temperature dependence of the inverse optical dephasing time was found. This dependence is shown in Figure 1 (large red circles) together with previous 2IPE-data as measured originally in [7] (solid line); T-dependences of ZPL for several single TBT molecules in PIB (small colour dots), as measured in [8]; and T-dependence of average spectral ZPL widths for a number of single TBT molecules in PIB (black stars) as measured in [9].

Concerning the data on temperature dependences of ZPL widths for single TBT molecules in PIB, for further discussing, one needs to restate some details of experiments performed in [8,9]. In both experiments the fluorescence excitation spectra of single TBT molecules in thin (0.5–1 μm) PIB film were measured by tuning of frequency of narrowband (1–2 MHz) dye CW-laser and detection of Stokes-shifted luminescence. In [8] the confocal scheme was used with detection unit on the base of avalanche photodiode (time of measurement for one spectrum was $t_m = 250$ s), whereas in [9] the wide-field luminescence microscope scheme was used with detection by EM CCD camera (time of measurement was $t_m \sim 10$ s).

While the effective t_m for 2IPE (~ 10 ns) is much less than the effective t_m in SMS-measurements (~ 250 s), the average value of the inverse optical dephasing time measured with 2IPE should be in the region of narrowest SM ZP widths. It is exactly what was observed in the comparative SMS-/PE-studies at $T = 2\text{K}$ [7]. At higher temperatures (4–15K) the ZPL broadening (as well as optical dephasing) is mainly caused by electron-phonon coupling, although the spectral diffusion processes are also intensified with T . Again while $t_m^{2IPE} \ll t_m^{SMS}$, the value of inverse optical dephasing time should be in the region of the narrowest ZPL widths. However, this was not observed in previous studies [1,7,8]. Such discrepancy was observed in a broad range of temperatures. If we compare previous PE data (solid line) with SM (small dots) and average SM (black stars) ZPL widths, we see that inverse optical dephasing time comparable or even larger than average SM ZPL widths, that has not reasonable explanation.

In the present work we have carefully re-measured optical dephasing times for TBT in PIB in a broad range of low temperatures (4.5–15K). The high sensitivity of the updated IPE-setup allows careful measurement of power dependences, thus any saturation and light induced effects were eliminated. As one can see from the Fig. 1 the new 2IPE data are in reasonable agreement with theoretical considerations. The inverse optical dephasing times correspond to the narrow ZPLs.

As possible explanations for the question why the previous PE-data did not agree with SMS, we can suggest the following two: (1) The additional contributions into the effective dephasing processes were observed to be due to high laser excitation power. Now the modern detectors, adjustment optical scheme gives opportunity to diminish the laser pulse energy enough to obtain unsaturated values of $1/\pi T_2$. (2) Second possible reason we can suggest is difference of molecular weight of PIB used in PE- and SMS-data. As it is known now [10] when diminish the M_w , additional spectral diffusion processes are strongly activated. As information about molecular weight of PIB is absent in first original PE researches, one can assume, that it was PIB with lower Mw in comparison with SMS-experiments, that leads to larger values of $1/\pi T_2$ measured by IPE. In this case the main role play the spectral diffusion processes in nanosecond time scale.

So, in the present study the experiments were performed for careful re-measurement of optical dephasing times for polyisobutylene doped with tetra-tert-butylterrylene in a temperature range of 4.5–15K using incoherent photon echo technique. As result of our researches the unexplained discrepancy between PE- and SMS-data observed in previous studies has been eliminated. The measured inverse optical dephasing times was found in the range of narrowest SM ZPLs that is in agreement with theories which describe ZPL broadening (optical dephasing) as result of natural lifetime contribution influenced by local field effects, interaction of SM with tunnelling and localised vibrational excitation of matrix. Local disorder of polymer matrix leads to the distribution of SM ZPL widths which are in general larger than values of inverse optical dephasing times. It is because effective time of measurement in SMS-experiments on 9 orders larger than in 2IPE technique, thus the time dependent spectral diffusion processes gives the noticeable contribution in SM ZPL broadening. The possible reasons of previous discrepancy can be a lower molecular weight of PIB, and/or saturation (light induced) effects in previous PE experiments.

Acknowledgements: The financial support is acknowledged from Russian Foundation for Basic Re-

searches (proj. no 16-52-00102 – analysis of T-dependencies of ZPL-widths for study of electron-phonon coupling in dye-doped solids). K. Karimullin acknowledges support from Russian Federation President Council on Grants for governmental support for young Russian scientists (proj. no MK-342.2017.2). The authors are members of leading scientific school of Russia (proj. no. 7035.2016.2 “Spectroscopy of atoms, molecules and condensed matter”).

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