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Temperature Dependences of Single Dye-Molecules Zero-Phonon Line Widths in a Broad Range of Low Temperatures

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Abstract. In the present work the individual temperature dependences of zero-phonon spectral line widths of single tetra-tert-butylterrylene dye-molecules in polyisobutylene were measured in a broad range of low temperatures (from 20 K up to 67 K). The obtained data show the broad distribution of single molecule zero-phonon spectral line widths measured at the different points of the polymer matrix at the same temperature. It proves that the dynamical processes resulting in spectral lines broadening in this temperature range have the localized character. In particular, it proves the existence and considerable contribution of the localized low-frequency vibration modes to the matrix dynamics along with the phonons.

Keywords: single-molecule spectroscopy, zero-phonon lines, low frequency vibrational modes

Ultra narrow spectral lines of chromophore molecules in solid matrixes (polymers, glasses etc.) at cryogenic temperatures originate due to purely electronic transitions in the molecules without changes in the density of phonon states of the host matrix (see [1-3] and references therein). These narrow zero-phonon lines (ZPL) are extremely sensitive to the dynamical processes in host media. At the level of single molecules (SM) the ZPL parameters contain valuable information on the matrix nanometre-scale dynamical processes. The temperature range where SM ZPLs are usually observable is limited to several Kelvin degrees, very rarely to 10-25 K. (At the same time in laser selective spectroscopy experiments for ensembles of impurity molecules ZPL measurements were performed in a large temperature range for a big number of impurity molecule/host matrix systems). [4] This is due to a dramatic decrease of the Debay-Waller factor and a strong ZPL broadening with temperature growth. The former leads to a dramatic decrease in the signal-to-noise ratio, the latter leads to the necessity of scanning the laser in the broad spectral range (from several to tens inverse centimeters). However, the temperature interval extension is important for the investigation of the electron-phonon interaction (for example, to improve the accuracy of determining the values of the electron-phonon interaction constants and the individual frequencies of the localized vibrational modes), for the study of the thermally activated processes in glasses and polymeric matrices, and is perspective for multicolour super-resolution microscopy. [5]

ZPLs of tetra-tert-butylterrylene SMs in polyisobutylene matrix (molecular weight 420.000 g/mol) were registered via measuring the SM luminescence excitation spectra near 0-0 electronic transition

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frequencies. The measurements were performed in the optical helium (RTI) cryostat at temperatures from 20 K to 67 K (see description of the setup in [5]). Scanning of the excitation light frequency in a broad spectral range was performed by the tunable dye-laser Coherent CR599 with the laser linewidth 0.3 cm^{-1}. Continuous tuning of the laser frequency in the diapason from 565 nm to 630 nm was done via driving the birefringent filter (modification of the Lyot filter) by the motorized linear actuator under Arduino control. The excitation luminescence spectra and the luminescence images of SMs were captured by ultrasensitive CCD cameras: Andor Ixon Ultra and PCO Sensicam EM. The employment of the matrix detector allowed simultaneous measurements of a large number of SM ZPLs in the field of view of the cryogenic microscope and the determination of SM lateral coordinates with sub-diffraction accuracy [5].

In this work the temperature dependences and distributions of ZPL widths of single tetra-tert-butylterrylene dye-molecules in polyisobutylene were measured for the first time in a broad range of low temperatures (from 20 K to 67 K). The experimental data show the broad distribution of SM ZPL line widths measured at the different points of the polymer matrix at the same temperature. The data also reveal the differences in the individual ZPL widths temperature dependencies. It proves [6] that the dynamical processes in matrix resulting in spectral lines broadening in this temperature range have the localized character, and has not be distorted markedly by impurity dye-molecules.

Figure 1 shows the example of SM ZPL measured at 45 K and its approximation by the Voigt function (a) as well as four individual SM ZPL linewidth temperature dependencies measured in the different sample points in the temperature range from 45 K to 67 K (b).

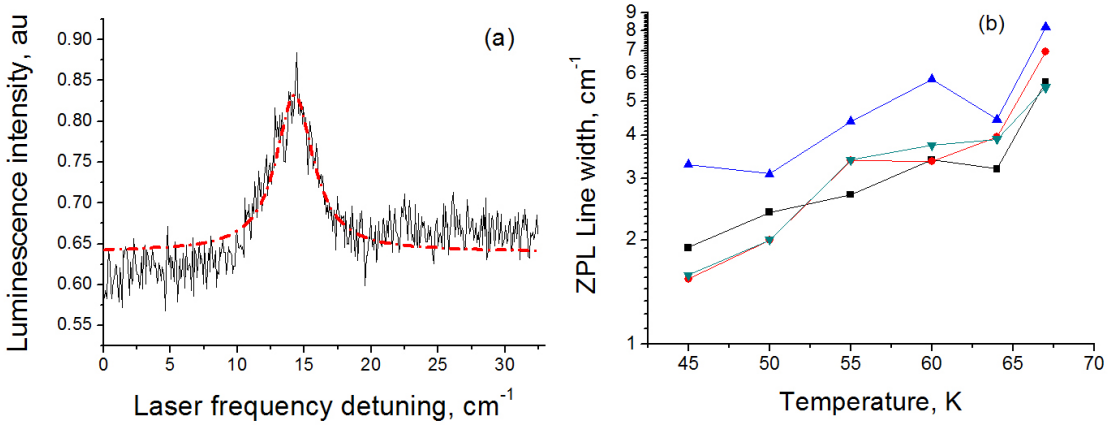

Figure 1. a) Zero-phonon line of tetra-tert-butylterrylene single molecule (the excitation luminescence spectrum near the 0-0 transition frequency) measured at 45 K and its approximation by the Voigt function; b) Four individual SM linewidth temperature dependencies measured in the different sample points in the temperature range from 45 K to 67 K.

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