

Structural and time-domain peculiarities of the fluorescence excitation spectra of single Mg-TAP in a polymer at low temperatures

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Abstract. The results of low-temperature measurements of spectral trails (temporal evolutions of individual fluorescence excitation spectra) of single molecules Mg-tetraazaporphyrin embedded in polyisobutylene are presented. Spectral trails were recorded in a broad spectral range (up to 4000 GHz) at a temperature 6K. Spectral diffusion in a broad spectral range has been found. Individual spectra of single molecules with a broad peak shifted with respect to zero-phonon line at $\sim 14 - 15 \text{ cm}^{-1}$ were recorded. These broad peaks can be interpreted as the phonon sidebands.

Single molecule spectromicroscopy is a quite novel but well-established experimental technique. The method is especially powerful at cryogenic temperatures when bright and narrow zero-phonon lines (ZPL) are reachable for the observation in the single molecules (SM) spectra [1,2]. Ultra-high sensitivity of the ZPLs to the SM local (nanometer-scale) environment reveals the possibility to probe solid-state media at the microscopic level [2,3]. It is well known that stochastic spectral jumps of ZPL position in spectra corresponds mainly to the coupling of impurity chromophores with tunnelling two-level systems (TLS), in turn, the electron-phonon interaction leads to the appearance of homogeneous broadening and shifts of ZPLs and gives rise to the phonon sidebands (PSB).

One of the very intriguing questions is how impurity molecules interact with so-called quasilocalized low-frequency vibrational modes (LFM). The way to study this interaction is a direct measurement of a PSB by the technique of fluorescence excitation SM spectroscopy. The PSB contains the information about LFM's energy spectra and in some cases theoretically can disclose even the individual parameters of LFM's.

Mg-tetraazaporphyrin (Mg-TAP) molecules play an important role in the photosynthesis processes and are of particular interest for studying the processes of energy storage and conversion in biological objects. Moreover, from the hole-burning experiments Mg-TAP molecules are known to be photochemically stable luminophores with narrow ZPL. In general, metal-organic molecules are very promising for nanophotonics applications [4].

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In the present research at cryogenic temperatures (6 K) the individual spectra of single Mg-TAP molecules embedded in polyisobutylene were detected. The measurements of spectral trails in a broad spectral range up to 4000 GHz ($\sim 130 \text{ cm}^{-1}$) were also performed. SM fluorescence was excited by a Coherent CR-599 tunable dye laser with an effective linewidth of 10 GHz ($\sim 0.33 \text{ cm}^{-1}$), the scan step was 5 GHz ($\sim 0.16 \text{ cm}^{-1}$). The spectra were recorded in a spectral range (570 – 595 nm) corresponding to the Q-band absorption maximum of Mg-TAP molecules. The Stokes component of single-molecule luminescence was recorded in the wavelength range from 612 to 644 nm using high-sensitive EM-CCD camera (Andor iXON Ultra) [5].

The measured zero-phonon luminescence manifests different temporal dynamic and exhibits wide distribution of the values of spectral shifts in a broad range from 10 to 950 GHz ($\sim 0.33 - 31 \text{ cm}^{-1}$) that considerably exceeds the characteristic values observed earlier [6]. In the dipole-dipole approximation of the interaction between SM and TLS [7], the value of 950 GHz corresponds to the distance in the order of 1 nm between them. Another possible explanation of such anomalous behavior is switching between conformational substates in Mg-TAP molecules.

One of the recorded spectral trails consists not only from ZPL but also from the broad peak shifted with respect to ZPL by $\sim 15 \text{ cm}^{-1}$ and performing synchronous spectral jumps with ZPL. This corresponds to the peak in LFMs energy spectra – «bozon peak» that had been measured earlier in different independent experiments (see [8] and references therein). This peak can be interpreted as PSB. In another individual spectrum a quite broad peak ($\sim 4.1 \text{ cm}^{-1}$) shifted with respect to ZPL at 13.9 cm^{-1} was observed. This peak possibly corresponds to the interaction of a SM with a single LFM [9].

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