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New methods of statistical processing of single-molecule spectromicroscopy data for mapping of local fields in the layer of a host matrix

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Abstract. We describe the specific algorithms for statistical processing of the data on fluorescence excitation spectra and images for large number of single dye molecules in thin solid film. Analysis of the data allowed mapping of the local fields, electron-phonon coupling parameters, and the effective refractive index in a frozen solid film. An estimation of the volume attributed to the effective local values is given.

Laser fluorescence spectromicroscopy of single probe molecules (SMSM) in transparent solids is a widely recognized area of science [1, 2]. The SMSM demonstrates its best performance at cryo-temperatures, when zero-phonon lines (ZPL) of light emitters can be detected with the use of a narrowband laser [3, 4]. The point is single molecule (SM) ZPL is very sensitive to any kind of local fields and their fluctuations [3-8]. In particular the homogeneous SM ZPL width depends on the temperature as following:

$$\Gamma_{ZPL}(T) = \Gamma_0 + \Delta\Gamma_{e-tunn}(T, t_m) + \Delta\Gamma_{e-phon}(T), \quad (1)$$

where Γ_0 is the local-field depended life-time limited ZPL linewidth, $\Delta\Gamma_{e\text{-}tunn}(T, t_m)$ is the contribution to the width of ZPL, which is determined by the interaction of SM with tunneling elementary excitations in the matrix, $\Delta\Gamma_{e\text{-}phon}(T)$ is the broadening of the ZPL caused by quadratic electron-phonon coupling. Here

$$\Gamma_0 = \Gamma_0(n) = \frac{1}{2\pi T_1} = \frac{n \cdot l(n)}{2\pi \cdot \tau_0}, \quad \Delta\Gamma_{e-phon}(T) = B\frac{\exp(-h\nu/kT)}{[1-\exp(-h\nu/kT)]^2}, \quad (2)$$

where n is effective refractive index of the matrix, τ_0 is vacuum natural excited state lifetime, ν is effective frequency of the quasi-localized low-frequency vibrational mode of a matrix, and B is electron-phonon coupling constant.

The extreme sensitivity of the ZPL parameters to the local environment of a single-molecule (SM) makes it possible to apply SMSM for the study structure and dynamics of doped solids on the nanometer-scale. In fact, the high ratio of inhomogeneous absorption band width to the very narrow ZPL homogeneous spectral width gives us the opportunity to measure fluorescence excitation spectra and determine coordinates for all sufficiently bright SMs in doped bulk solid samples (crystals, glasses, polymers) at low-temperatures [3-6]. For this purpose, we use specific algorithms and software for rapid SM spectra and images

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recognition, data processing and statistical analysis [3].

The technique for sequential-parallel detection of ZPLs and the fluorescence images of myriad probe SMs can be applied for the hyperspectral nanodiagnostics of solids [3, 4, 9, 10]. Namely, various local parameters of dye-doped systems can be.

Analyzing the Γ_0 for SMs in different places of the thin film sample one can map the local fields and corresponding effective n of matrix. For this we proceed the data about 2000 terrylene (Tr) SMs in frozen n-hexadecane film at T=1.5 K. For each Tr SM we found the XY coordinates with different accuracy as it depends on the fluorescence intensity of each SM. We calculate the effective values of the refractive index n in the locality of each SM from its excited state lifetime T_1 dependence on n. This calculation implies the use of the proper theory describing the local-field effects and the $T_1(n)$ dependence [11]. The best fits of the $T_1(n)$ dependence using different models was made and the best model is the virtual cavity model, which describe data more accurately [12]. As a result, the distribution of effective local values of the refractive index in the film was obtained.

In order to estimate the zonal volume that we can attribute to the effective local values of parameters for the h-hexadecane matrix we had to select the molecules for which the coordinate error would not exceed a certain limit. The best-positioned Tr molecules were processed in terms of looking at the distance between two SMs versus the contrast of the effective refractive index each SM indicates in the area around it. All possible combinations of best-positioned SM pairs were considered. It was shown that similar, or within the positioning error, values of the effective n are typical for SMs separated by a distance no longer than 100 nm on the XY plane. This may serve as a rough estimation of the volume size to which the concept of the effective n responsible for light emission dynamics from SM may be referred to.

Analyzing the $\Delta\Gamma_{e\text{-}phon}(T)$ contribution for each SM we can map the local vibrational dynamics and electron-phonon coupling parameters in the layer of a host matrix.

Thus, in the present paper we show the potential of ZPL-based fluorescence excitation SMSM for the characterization of complex solids on the *nm*-scale.

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