

Combined analysis of the temperature dependences of the fluorescence spectra and images of single molecules in polymer films

Tatiana Anikushina^{1,2,*}, Andrei Naumov^{1,2}, and Lothar Kador³

¹Moscow State Pedagogical University, 29/7 Malaya Pirogovskaya Str., Moscow, 119991 Russia

²Institute for Spectroscopy RAS, 5 Fizicheskaya Str., Troitsk, Moscow, 108840 Russia

³Bayreuth University, 30 Universitätsstraße, Bayreuth, 95447 Germany

Abstract. In this poster talk we discuss a possibility to realize the combined analysis of the temperature dependences of the zero-phonon line widths and fluorescence images of single molecules in thin polymer films. Such analysis is aimed to obtain the local characteristics of low-temperature vibrational dynamics (individual parameters of quasi-localised low-frequency vibrational modes) in relation to the sample structure.

One of the most topical interdisciplinary scientific fields has recently become the single molecule spectromicroscopy (SMSM) in condensed matter [1]. This method opens the possibility of investigating the internal dynamics of the medium at the microscopic level and allows the diagnostics of the materials with an ultra-high spatial resolution [2, 3].

This method acquires special capabilities in the detection of electron-vibrational spectra of impurity molecules, embedded as nanoprobe into a solid medium, at low (cryogenic) temperatures [1-4]. At such temperatures (below a few or tens of degrees Kelvin, depending on the impurity/matrix system), it is possible to detect the zero-phonon spectral lines (ZPL), that correspond to purely electronic transitions in impurity molecules. Parameters of ZPL such as frequency, intensity, width, time dynamics, etc. are very sensitive to the parameters of the local environment of the corresponding chromophore molecule, which makes it possible to use OM as spectral probes to obtain data on the structure and internal dynamics of solids, as well as other local values of various characteristics of the medium.

In most cases, at the temperatures up to dozens of Kelvin, ZPL broadening due to the quadratic electron-phonon interaction is discussed. In general, this contribution can be described in terms of the theory of I.S. Osad'ko [4]:

$$\Delta\Gamma_{e-ph}n(T) = \frac{1}{4\pi} \int_0^{\infty} d\omega \cdot \ln \left[1 + \frac{4n(\omega)[n(\omega)+1]W^2 \cdot \Phi_{Ph}^2(\omega)}{[1-W \cdot \Omega(\omega)]^2 + W^2 \cdot \Phi_{Ph}^2(\omega)} \right], \quad (1)$$

where $\Omega(\omega) = \frac{2}{\pi} \int_0^{\infty} d\nu \cdot \Phi_{Ph}^2(\nu) P\left(\frac{\nu}{\omega^2 - \nu^2}\right)$; $n(\omega) = \frac{1}{\exp(\hbar\omega/kT) - 1}$ and $\Phi_{Ph}(\nu)$ is the density of vibrational states in the matrix. In the case when the long-wave approximation and the weak

* Corresponding author: anikushina@isan.troitsk.ru

coupling approximation are applicable for the impurity-matrix system under study, and also if the density of vibrational states can be described by the Lorentz function corresponding to the effective (quasi-localized) low-frequency vibrational mode (LFM), expression (1) is simplified to

$$\Delta\Gamma_{e-phon}(T) = B \frac{\exp(-h\nu/kT)}{[1 - \exp(-h\nu/kT)]^2} \quad (2)$$

For the most diverse impurity systems (glasses, polymers, molecular crystals), the temperature dependences of ZPL width demonstrated the validity of the indicated approximations for the study of bulk (macroscopic) samples. Such an analysis can also be carried out at the level of single molecules (SM) interacting with their local environment, which makes it possible to measure the value of the frequency (energy) of the LFM and the constant of quadratic electron-phonon coupling [5, 6].

Detection of fluorescent images allows to determine SM spatial coordinates with subdiffraction accuracy by computer analysis of image of single molecule taking into account the point-spread function [2, 3].

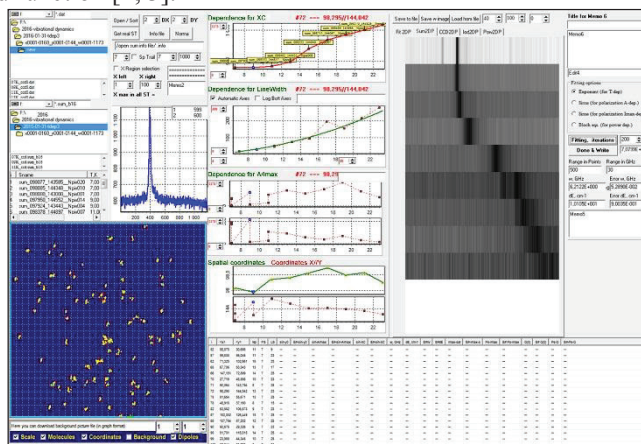


Fig. 1. Screen-shot of the special home-built computer program for combined analysis of temperature dependences of the fluorescence spectra and images of single molecules.

Thus, on the one hand, the direct experimental verification of the applicability of various approximations (leading to simplification of the Eq. (1)) on the level of a single molecule and its local environment and on the other hand was produced the mapping of LFM energy values in the sample.

T.A. acknowledges the grant of RFBR for young researchers (16-32-00841). The methods of statistical processing of SMSM data were developed under support of Russian Science Foundation (proj. No 14-12-01415).

References

- [1] M. Orrit et al., *Faraday Discussions* **184**, 275 (2015)
- [2] A.V. Naumov, *Physics-Uspexhi* **56**, 605 (2013).
- [3] A.V. Naumov, I.Y. Eremchev, A.A. Gorshelev, *Eur. Phys. J. D* **68**, 348 (2014)
- [4] I.S. Osad'ko, *Selective Spectroscopy of Single Molecules* (Springer, 2003)
- [5] A.V. Naumov, Yu.G. Vainer, L. Kador, *Phys. Rev. B* **79**, 132201 (2009)
- [6] Yu.G. Vainer, A.V. Naumov, L. Kador, *Phys. Rev. B* **77**, 224202 (2008)