CONFERENCES AND SYMPOSIA

Joint scientific session of the Physical Sciences Division of the Russian Academy of Sciences and the Joint Physical Society of the Russian Federation
(35th anniversary of the Institute of Spectroscopy)
(28 November 2003)

A joint scientific session of the Division of General Physics, Russian Academy of Sciences, and the United Physical Society of the Russian Federation was held in the conference hall of the Institute of Spectroscopy, RAS, Troitsk, Moscow Region, on 28 November 2003 to commemorate the 35th anniversary of the Institute of Spectroscopy (ISAN). The following reports were presented at the session.

1. **Vinogradov E A** (Institute of Spectroscopy, RAS, Troitsk) "Opening address";

1. **Mishin V I** (Institute of Spectroscopy, RAS, Troitsk) "Resonance-ionization laser ion source of short-lived isotopes";

3. **Vaĭner Yu G** (Institute of Spectroscopy, RAS, Troitsk) "Single-molecule spectroscopy and disordered solid dynamics";

4. **Agranovich V M** (Institute of Spectroscopy, RAS, Troitsk) "Negative refraction in the optical domain and nonlinear wave propagation";

5. **Ryabov E A** (Institute of Spectroscopy, RAS, Troitsk) "Laser isotope separation by IR multiphoton dissociation of molecules";

6. **Koshelev K N** (Institute of Spectroscopy, RAS, Troitsk) "Short-wave plasma radiation at high currents";

7. **Kompanets O N** (Institute of Spectroscopy, RAS, Troitsk) "Portable optical biosensors for the determination of biologically active and toxic compounds".

Brief presentations of reports 3, 4, 5, and 7 are given below.

Single-molecule spectroscopy and disordered solid dynamics

Yu G Vaĭner

Recently, a large number of studies have been devoted to the properties of disordered doped solids using selective spectroscopic techniques. Many of them have been concerned with a fundamental problem in condensed state physics — the low-temperature dynamics of solid media with a disordered microstructure. For all that, the majority of basic questions important for the understanding of dynamic low-temperature phenomena remain to be clarified. Specifically, a microscopic theory for low-temperature dynamics of disordered media is lacking and the microscopic nature of elementary excitations underlying these processes is unknown; also, mechanisms of interaction between these excitations and an absorbing center remain unknown. One of the main reasons for this situation is the serious drawback inherent in selective spectroscopic techniques: these methods provide information averaged over a large ensemble of absorbing centers, and in the case of disordered media, this leads to the loss of a substantial portion of the information contained in individual spectra.

Single-molecule spectroscopy (SMS) is a recently developed method for the study of solid media [1, 2] that allows recording individual spectra of single chromophore molecules (SMs) used as spectral microprobes. The new method totally eliminates effects of averaging over a large number of absorbing centers intrinsic in traditional techniques and yields information about the media at the level of a single dopant molecule and its microenvironment. Soon after the advent of the new method, it was employed in a number of works to study low-temperature dynamics of doped amorphous systems. But the method has never found extensive application in these investigations. The main cause for the restricted use of SMS appears to be the difficulties encountered in interpreting the detected spectra. Detailed consideration of the principal concepts of low-temperature dynamics of disordered solids and its manifestations in the spectra of absorbing centers may contribute to a better understanding of the subject in question.

The very first studies on the properties of disordered solid media related to their internal dynamics (dependence of the thermal capacity and conductivity on temperature, ultrasonic attenuation, and other effects) date to the early 1970s. They demonstrated that all substances having a disordered microstructure display a number of universal properties that are altogether different from those of ordered materials and virtually independent of the specific structure of the substance under investigation. It became clear that these properties stem from the locally disordered distribution of atoms and molecules in such substances. Therefore, investigations of the anomalous properties shared by disordered solids and manifest in their low-temperature dynamics are conducive to the understanding of the fundamental characteristics of solid bodies related to the chaotic spatial arrangement of their constituent atoms and molecules.

According to the currently accepted concept, the dynamics of amorphous media at $T < 8 - 10$ K are governed by the following elementary low-energy excitations:

a) two-level systems (TLSs) associated with local tunneling transitions of atomic and molecular groups between levels in double-well potentials formed at the potential surface of disordered bodies

b) acoustic phonons with a wavelength longer than characteristic interatomic distances, which makes them independent of the chaotic dispersion of such distances

c) quasilocal low-frequency vibrational modes (LFMs) that can be arbitrarily regarded as residual short-wave phonons localized because of the translational symmetry breaking of the medium.

The interaction of dopant atoms and molecules with acoustic phonons and LFMs accounts for the broadening of spectral lines, and their interaction with TLSs leads to a drift of line frequencies. If the frequency shifts induced experimentally by transitions in TLSs are smaller than the spectral line width, their combined effect is apparent at its broadening. If the shifts are larger than the line width, they cause the frequency to jump or split the line. Large frequency shifts can produce only TLSs located close to a given center, and there are normally few of them (as a rule, fewer than $3 - 5$) as shown in experiments. Whenever spectrum splitting is caused by a single TLS, it results in a doublet. If the number of such TLSs is n, the spectrum consists of 2^n components. When the TLS jumps with a frequency higher than the frequency shift, it causes the spectral line of the absorbing center to broaden rather than split. Because characteristic parameters of TLSs (shift repetition rate, asymmetry of energy levels) and their location relative to absorbing centers vary considerably, individual spectral lines of the absorbing centers in low-temperature glasses can have a different number of peaks, whose number and parameters can have different time-dependent patterns.

Complicated and in many respects random patterns of SM spectra account for serious difficulties encountered in their identification and analysis. How can a spectrum displaying a few peaks be attributed to a single molecule rather than to several? How can such spectra be adequately characterized? Evidently, the notion of line width is insufficient to fully describe them. What is the way to retrieve general information about properties of the medium being investigated from the spectra that largely reflect random parameters of their immediate environment? We believe these problems to be the main reason for a small number of studies on the low-temperature dynamics of glasses using SMS. Indeed, averaging over SM spectra is needed if general information about their environment is to be obtained from them. Therefore, it seems possible to use the aforementioned traditional methods of selective spectroscopy of absorbing centers in which such averaging is inherent. But it should be taken into consideration that averaging algorithms are dictated by the very nature of these methods and cannot be modified, and hence some information contained in the spectra is irretrievably lost. For example, such averaging results in the loss of information about the shape and asymmetry of individual spectral lines containing important data on the interaction between an absorbing center and elementary excitations of the medium.

In our work, we used a new approach that eliminates many of the above problems associated with the application of SMS techniques for the study of doped system dynamics.

The essence of this approach consists in recording a large number of SMS spectra and their subsequent statistical treatment. The difficulty of identification of the observed spectra was overcome by repeated registration and subsequent analysis of their evolution over time. A detailed description of the measuring method and procedure for the treatment of experimental data can be found in Refs [3 – 5]. The present communication is confined to the concise characteristic of major aspects of our approach.

In the overwhelming majority of SMS studies, including our experiments, SM spectra were measured by detecting fluorescence excitation spectra of the molecules being investigated. For this purpose, spectra are usually measured by means of single slow retuning of the laser frequency within a chosen range. A relatively large duration of the whole measuring process (dozens of seconds or more) is used in order to obtain an acceptable signal-to-noise ratio. In our experiments, the possibility of observing time-dependent changes in SM spectra was assured by repeated (hundreds of times) and rapid (less than $1 - 8$ s) scanning of the frequency of a narrow-band laser (generation line width approximately $2 - 3$ MHz) in a given part of the spectrum. The spectra thus detected were represented as a two-dimensional figure (2D plot) in which the horizontal coordinate corresponds to the laser frequency and the vertical one to the spectrum number (hence, to the time from the beginning of the measurement). Density of black points on the plot corresponds to the spectrum intensity that is proportional to the fluorescence signal. Figure 1a gives an example of such data presentation obtained by recording spectra of one of the molecules. Figure 1b shows an integrated spectrum obtained by summation of individual spectra detected within a 120 s interval. The interval is indicated by two dashed horizontal lines. The summation was done to enhance the signal-to-noise ratio. We regarded the integrated spectra as those measured for 120 s. It follows from the figures that the analysis of such spectra containing a few peaks each fails to identify the number of molecules that could possibly produce it. But this identification can easily be achieved by analyzing the time
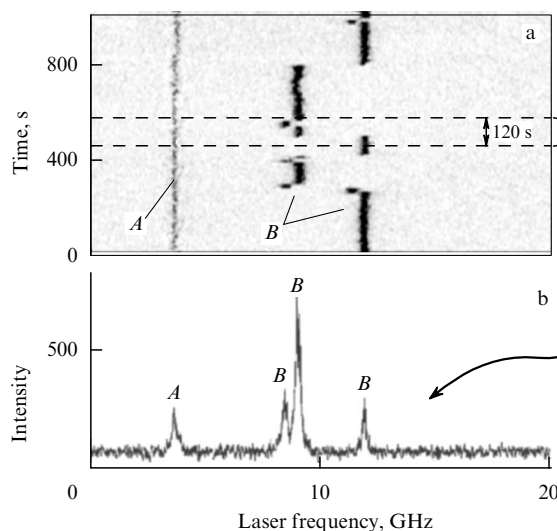

Figure 1. (a) An example of representation of the recorded single-molecule spectra as a two-dimensional picture; (b) an integrated spectrum obtained by summation of the spectra measured during a time interval shown by the horizontal dashed lines in (a). Letters in circles denote spectral peaks of two molecules *A* and *B*.

evolution of the constituents of a given spectrum. The explanation lies in the fact that a transition in one of the TLSs that interacts with the given molecule sufficiently strongly is manifest as a similar and simultaneous jump in all peaks of its spectrum. At the same time, there is practically no such transition in the spectra of other molecules because they are, as a rule, remote. In very rare cases, the transition can be apparent as shifts differing from the one above in terms of magnitude.

To quantitatively describe SM spectra of a complex configuration, we used the distribution moment concept frequently employed in the statistical analysis of complex distributions. In addition, we described the spectra under investigation using the cumulant concept, which is also applied to the statistical analysis for the description of distributions. Cumulants are expressed through the moments, and their use for the description of low-temperature SM spectra gives certain advantages, as was demonstrated in [6].

Based on the proposed approach, we studied spectra of 244, 381, and 187 molecules of tetra-tert-butylterrylene immersed in amorphous polyisobutylene, and performed statistical analysis on the results obtained. The spectra were measured at $T = 2$, 4.5, and 7 K.

Figure 2 shows distribution histograms of the first three moments for the SM spectra measured at $T = 2$ K. To compare the theoretical and measured SM spectra, we performed model calculations of the SM spectra for the system of interest and calculated the distributions of their moments. The calculated distributions are depicted in the figure as solid and dotted curves. The first moment (Fig. 2a) that characterizes the position of the center of gravity of a distribution reflects, in our case, the position and the shift of the effective frequency of the spectrum being observed. The figure shows a symmetric and rather narrow shift distribution
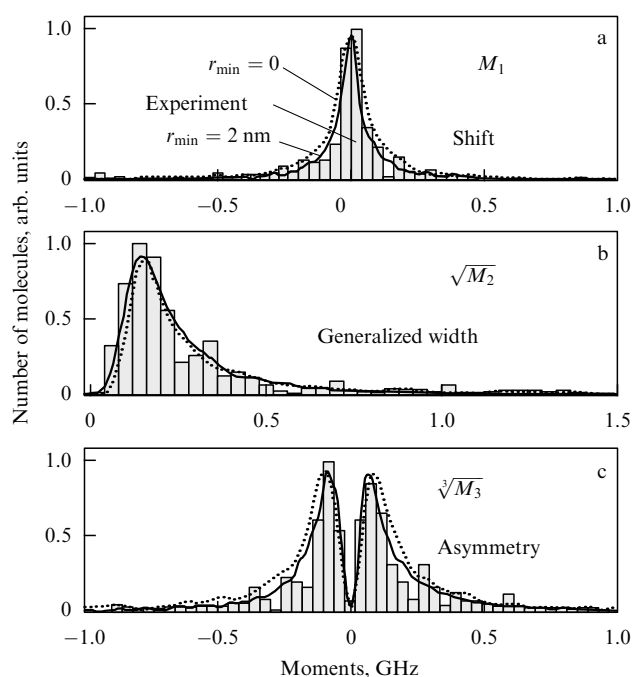
of the measured spectra. The second moment (Fig. 2b) that determines the root-mean-square deviation of the distributed values characterizes the generalized width of the spectra of interest, taking both the broadening and the splitting of spectral peaks into account. In this case, the splitting is manifest as a long tail in the distribution. The third moment (Fig. 2c) is known to be responsible for the distribution asymmetry. The result of measurement is quite intriguing because it reveals a deep gap in the center of the distribution. The presence of such a gap indicates that there are practically no symmetric SM spectra in the system under consideration. This result seems to be of a general character. It can be explained in the framework of the standard model of low-temperature glasses by the fact that transitions in symmetric TLSs cause no shifts of spectral lines from the absorbing centers, whereas transitions in asymmetric TLSs induce such shifts; therefore, the latter transitions are responsible for the asymmetry of the observed spectra. The best agreement between theoretical and experimental curves was obtained by taking into consideration that there exists a minimal distance r_{min} between a chromophore molecule and the TLS. The estimate $r_{min} = 2$ nm appears realistic because this value is comparable with the dimensions of tetra-tert-butylterrylene molecules (~ 2 nm in diameter) and the expected minimal size of the TLS that is supposed to be a function of the minimal size of the TLS constituent molecules.

An important problem encountered in the studies of SM spectra in disordered media pertains to statistical laws that govern the behavior of such spectra. A theoretical study in [7] has demonstrated that if the assumptions of the standard low-temperature glass model and certain additional assumptions (e.g., that of the dipole–dipole nature of interactions between dopant molecules and TLSs) are satisfied, the complicated and largely random nature of SM spectra in low-temperature amorphous matrices can be described in terms of the Levy statistics. For this purpose, such spectra must be characterized by cumulants. The Levy statistics is used for the analysis of distributions of random values when their deviation from the average is not limited. It can be regarded as a generalization of the Gaussian statistics [8].

Figure 3 shows distributions of the first and second cumulants calculated for the SM spectra measured in our study at $T = 2$ K [6, 9]. The same figure illustrates approximation of these distributions by the Lorentz and Smirnov dependences that must describe distributions of the first and second cumulants in the framework of the Levy statistics. It can be seen from the figure that the experimental distributions are actually well described by these dependences. This suggests that the assumptions in Ref. [7] are quite well satisfied in the case under consideration. Specifically, it is safe to say that properties of the doped system studied are adequately described under the assumption of the dipole–dipole nature of the interaction between the TLS and the chromophore molecule. Such an assumption appears to be applicable to all similar systems.

An interesting result was obtained by the comparative analysis of spectra measured at three different temperatures ($T = 2$, 4.5, and 7 K) [10, 11]. In this case, our purpose was to obtain information about the contribution made by LFMs to the broadening of doped molecule lines in the system under study. For this, we analyzed peak width distributions in the measured SM spectra because the LFM contribution must primarily manifest itself as peak broadening. The peaks were characterized by their half-height width.
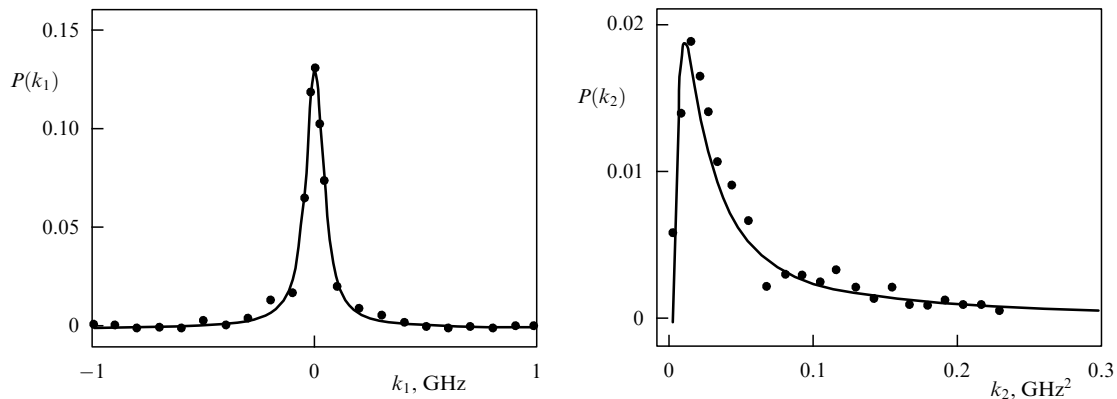

Figure 2. Distributions of the first three moments deduced from the measured (histograms) and model (solid and dotted curves) single-molecule spectra.

Figure 3. Distributions of the first and second cumulants obtained from the measured single-molecule spectra (dots) and their approximation by Lorentz and Smirnov functions (solid curves) predicted by the Levy statistics.
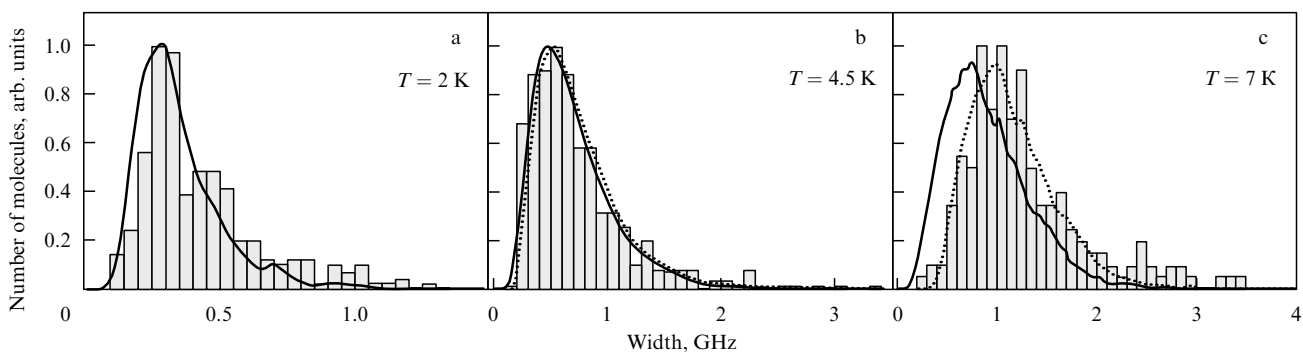

Figure 4. Experimental (histograms) and calculated (solid curves) peak width distributions in the spectra of single tetra-tert-butylterrylene molecules immersed into amorphous polyisobutylene. Dotted lines show model computation results in case of broadening caused by low-frequency modes of the matrix.

The distributions thus obtained are represented in Fig. 4 in the form of histograms. To compare the theoretical and measured SM spectra, we performed model calculations of SM spectra for the system under study and calculated their peak width distributions. The calculated distributions are depicted in the figure as solid and dotted curves. The solid curves were computed in the framework of the standard low-temperature glass model without accounting for the LFM contribution. The dotted curves represent the same distributions shifted toward larger width values to obtain better agreement with the experimental findings. It was assumed that the contribution of LFM to the line broadening is the same for all spectra and that it can be disregarded at $T = 2$ K. In this case, the magnitude of the shift determines the LFM contribution to the line broadening at a given temperature. Thus estimated, the LFM contributions are $\Gamma_{\mathrm{LFM}} = 0.04$ GHz at $T = 4.5$ and $\Gamma_{\mathrm{LFM}} = 0.24$ GHz at $T = 7$.

References

1. Moerner W E, Kador L *Phys. Rev. Lett.* **62** 2535 (1989)
2. Orrit M, Bernard J *Phys. Rev. Lett.* **65** 2716 (1990)
3. Vainer Yu G et al. *Opt. Spektrosk.* **94** 926 (2003) [*Opt. Spectrosc.* **94** 864 (2003)]
4. Vainer Yu G et al. *Opt. Spektrosk.* **94** 936 (2003) [*Opt. Spectrosc.* **94** 873 (2003)]
5. Naumov A V et al. *Phys. Rev. B* **63** 212302 (2001)
6. Barkai E et al. *J. Lumin.* **107** 21 (2004)
7. Barkai E, Silbey R, Zumofen G *Phys. Rev. Lett.* **84** 5339 (2000)
8. Feller W *An Introduction to Probability Theory and Its Applications* Vol. 2 (New York: Wiley, 1970)
9. Barkai E et al. *Phys. Rev. Lett.* **91** 075502 (2003)
10. Naumov A V et al. *J. Chem. Phys.* **119** 6296 (2003)
11. Naumov A V et al. *J. Lumin.* **107** 287 (2004)

Negative refraction in the optical domain and nonlinear wave propagation

V M Agranovich

Over 30 years ago, V Veselago noted very unusual properties of electromagnetic wave propagation in an isotropic medium with negative values of the dielectric permittivity and magnetic permeability, $\varepsilon < 0$, $\mu < 0$. Because the wave vector **K**, the electric field **E**, and the magnetic field **H** form a left-handed orthogonal set in such media, as opposed to the right-handed one formed in ordinary media, the former media are called left-handed materials (LHMs) in the English literature, to distinguish them from the normal right-handed materials (RHMs). An interesting and unusual property of wave propagation in these media is the antiparallel directions of the wave vector **K** and the Poynting vector **S**. Moreover, a