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Applications of Laser Techniques for the Study of Dynamics of Amorphous Solids with High Spatial Resolution: Single Molecule Spectroscopy

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Experimental advances (specifically in the field of lasers) allowed measuring the optical spectra of single molecules in transparent hosts. We demonstrate possibilities of Single Molecule Spectroscopy for the study of low-temperature properties of amorphous solids.

1. Introduction

The low-temperature properties of amorphous organic glasses and polymers differ dramatically from those of crystals. Their study is a subject of great interest of modern sciences, also in view of numerous applications of amorphous materials.

Optical spectra of impurity centers (molecules, atoms, absorbing light in the selected spectral region) incorporated in transparent solid matrix as a probe yield valuable information about internal dynamics of matrix. However, the effect of inhomogeneous broadening intrinsic to disordered solids makes difficult to study these media using traditional spectroscopic methods.

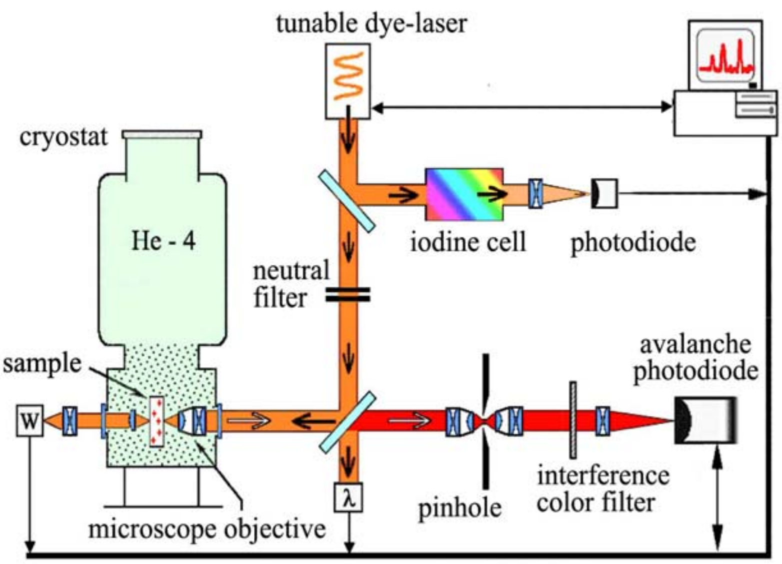
The development of *new laser selective spectroscopic techniques*, such as fluorescence line narrowing, hole-burning, different modifications of photon echo (PE) make possible to eliminate the influence of the inhomogeneous broadening on the spectra studied. In the last years experimental advances have made feasible to measure the optical spectra of single molecules (SMs) isolated in a transparent host [1,2]. In this way single chromophore molecules serve as a microscopic instrument, which reports us about the dynamical processes in their immediate neighborhood. Thus single molecule spectroscopy (SMS) allows to completely remove any kind of ensemble averaging and obtain information about glass dynamics on the level of SM environment, and furthermore, on the level of single low-energy excitation,

This work is reporting about possibilities of SMS technique for the study of low-temperature dynamical processes in disordered solids (glasses and polymers).

2. SMS experimental setup

A scheme of the experimental setup is shown in **Fig. 1**. Reducing the volume of the sample under study is an important factor in measuring the SM spectra. For this purpose, a microscope objective (Microthek, NA 0.9), placed directly inside a measuring chamber of the cryostat in our setup, was used for the illumination of the sample and light collection. This objective made it possible to illuminate a spot on the sample of about 1.2 μm in diameter (close to the diffraction limit). Additional suppression of spurious light outside this volume was performed by using a system of two microscope objectives and a pinhole.

Fluorescence spectra were excited with a *single-frequency single-mode tuned dye laser* (Coherent, CR599-21) with an effective width of the radiation line (determined by fast frequency fluctuations) of about 2-3 MHz. After the necessary attenuation, the laser beam was directed into a He-4 cryostat (Janis SVT-200) and focused on the sample by the microscope objective. A broadband interference filter cut off scattering laser radiation at the unshifted frequency and transmitted the Stokes component of fluorescence from the molecules detected. The fluorescence radiation transmitted by the pinhole was directed onto a photosensitive surface of an avalanche photodiode from an optoelectronic module (EG&G Optoelectronics, SPCM, AQR-15) operating in photon-counting mode or by CCD-camera. The sample was immersed either in superfluid helium (*T*= 2 K) or in helium vapor (*T*= 4.5, 7, or 15 K).



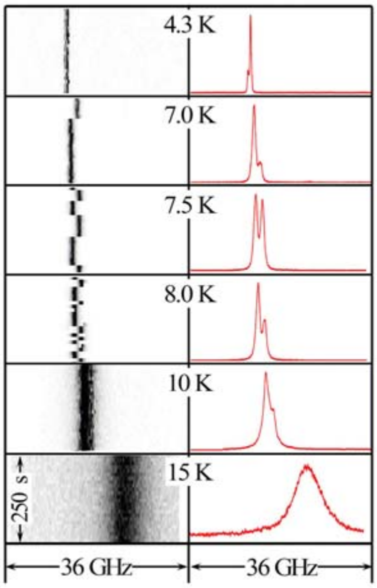


Fig. 1. Principal scheme of SMS-setup

Fig. 2. Spectral histories (left panel) and corresponding sum spectra (right panel) for the same single TBT molecule in PIB at different temperatures. The gray level of each point in the 2D-plots is proportional to the signal intensity. The horizontal axes correspond to the laser frequency detuning, the vertical axes in the 2D-plots to the number of scans.

The power of the exciting laser radiation was adjusted to a level (within 50–200 nW) at which the signal-to-noise ratio was good enough but no broadening of spectral lines and light induced spectral diffusion could occur. The wavelength of the laser radiation was varied within an inhomogeneous contour of absorption of the sample (567–577 nm). The range of continuous scanning of the spectrum of fluorescence excitation amounted to 20 GHz, with the minimal step being 10 MHz. Stability of laser system was controlled by the analysis of absorption spectrum of iodine.

In our experiments, the measurement of the SM spectra was performed by rapid multiple scanning of the frequency of the laser radiation in the selected spectral range. To visualize the measured spectra, whose number in each measurement could be as high as several hundreds or thousands, it was convenient to represent the spectra on a monitor screen as a two-dimensional image (2D plot). Analysis of spectral history on 2D-plot allows to uniquely recognize the spectral trails of different SMs.

3. Main results

SMS technique allows to realize very high spatial resolution for the study of the dynamical processes in solids, and obtain important information about elementary excitations in local environment of these impurity molecules. Namely, at temperatures $T < 2$-3 K the form of SM spectra are determine mainly by interaction of SM with tunneling **T**wo-**L**evel **S**ystems (TLS), in the temperature interval from a few Kelvins up to a dozed Kelvins a SM spectrum is formed by interaction of SM with quasi-localized **L**ow-**F**requency vibrational **M**odes (LFM). It is very remarkable that SMS allows to study the dynamics of glasses not only on the level of nearest environment of SM, but on the level of single elementary excitations. Thus the analysis of SM spectra at different temperatures (in particular, the observation of the temporal evolution of SM spectra) is very promising way to gain information about microscopic nature and individual parameters of TLSs and LFMs. Such investigations make possible to test the scope of validity of the TLS and LFM models, analyze the anomalous dynamical phenomena etc.

This work demonstrates the great possibilities of SMS for studies of solids dynamics. In particular it devotes to the investigations of temporal and temperature behaviour of spectra of single *tetra-tert-butylterrylene* molecules in pure amorphous *poly-isobutylene* matrix. Analysis of such dependences allows to clearly discriminate contributions from different kinds of excitations and obtain microscopic information both about single TLSs and single LFMs.

The results obtained can be summarised as following: (1) We demonstrate that the statistical behavior of the random line shapes of single chromophores in the doped amorphous system under study at $T < 2 - 3$ K is well described by Lévy statistics [3]. Information about the distributions of SM spectra parameters was obtained [4, 5]. (2) The T-dependences of the temporal evolution of SM spectra have been measured for the same molecules in the interval 1.6 – 40 K (**Fig. 2**). The interactions of SMs with TLSs and LFMs were clearly distinguished [6]. (3) The microscopic parameters of TLSs and LFMs were evaluated [7]. (4) Anomalous behavior of SM spectra was observed and analyzed [7, 8].

Summary

Experimental advances (specifically in the field of lasers) allowed measuring the optical spectra of single molecules in transparent hosts. We demonstrate possibilities of Single Molecule Spectroscopy for the study of low-temperature properties of amorphous solids. It is shown that this technique presents unique information about microscopical nature of different phenomena (low-energy excitations, internal dynamical processes, interaction between impurities and matrix etc.) in the systems under study.

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