

Vibrational dynamics of glasses at low temperatures: Investigation by single-molecule spectroscopy

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Abstract

The paper summarized the recent results in vibrational dynamics of disordered solids obtained in joint research of Bayreuth University and Institute of Spectroscopy RAS groups via single molecule spectroscopy (SMS). New information about microscopic parameters of the low-frequency vibrational modes (LFMs) in low-temperature glasses was obtained. Studies were based on observations of the line-broadening processes in spectra of single chromophore molecules (SMs) incorporated to disordered matrix as a local spectral probe. Solid organic system, amorphous polymer—*polyisobutylene*, doped with *tetra-tert-butylterrylene* molecules, on temperature region 1.6–40 K have been studied. The values of LFM frequencies and SM-LFM coupling constants for the LFMs in the local environment of dopant chromophores were determined. Pronounced distributions of the observed local parameters of LFMs were found. The obtained results demonstrate that SMS is an efficient tool in the study of vibrational dynamics in solid disordered systems on microscopic level. © 2006 Elsevier B.V. All rights reserved.

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1. Introduction

Amorphous solids (organic and inorganic glasses, polymers, rosins etc.) are currently the subject of great interest in solid-state physics and chemistry. This is associated with their remarkable properties which made them important materials for advanced applications. At low-temperatures dynamical properties of amorphous solids—independent of their structure and chemical composition—dramatically differ from the corresponding properties of highly ordered crystals [1,2]. Moreover, idem anomalous phenomena are observed in most of complex solid systems: in different kinds of nanoobjects and clusters, in frozen biological media and even in crystals (e.g. in defective or mixed crystals). It clearly demonstrates

that the physical origin of the above anomalies is intimately related to the internal disorder and local inhomogeneities of a solid medium. In the present article, for simplicity, we will call all solid disordered materials by “glasses”.

The dynamical behavior of glasses at T below 2–3 K one usually explains with the standard model of low-temperature glasses. This is very popular phenomenological model based upon the concept of “*tunneling two-level systems*” (TLSs)—elementary low-energy localized excitations, intrinsic to all disordered solids [3,4]. According to the standard TLS-model, at low T the density of TLSs in glasses prevails the density of acoustic phonons and contribution of TLSs to observed dynamics predominates.

At higher T the dynamical phenomena in glasses became more intricate and cannot be described in the framework of the standard TLS-model. It is widely accepted that anomalous properties of glasses in the region of the so-called intermediate temperatures (from 2–3 K to a few dozen K) are related to the another type of the specific to glasses low-energy excitations—*low-frequency vibrational*

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modes (LFMs), which exist in disordered solids in addition to TLSs and acoustical phonons (for review see Ref. [5] and references therein). Not many details are known about the origin and properties of these modes. The hypotheses proposed for explanation of the dynamical properties of glasses at intermediate temperatures are based on different concepts. In the part of them one assume that dynamical properties of glasses are determined by propagating modes of collective character (see, for example, Refs. [6,7]). Other hypotheses attribute the observed anomalous dynamics of glasses to the localization of the vibrational modes induced by internal disorder [8,9]. The above approaches can be considered as extreme positions and studies which explain the real nature of vibrational excitations in glasses in between or in a more complex manner were also developed (see, for example, Refs. [10–13]).

An intriguing and ubiquitous feature, which seems to be one of the universal fingerprints of solid disordered objects, is the so-called “Boson peak”—an anomalous enhancement of vibrational density of states at low frequencies. The Boson peak was observed in low-frequency light [14], inelastic neutron [15] and X-ray scattering experiments [16] and in calorimetric measurements [1]. It is widely accepted that the Boson peak has a close relation to unusual dynamical properties of glasses at intermediate T and is caused by LFMs.

In spite of numerous studies, most of the principal questions concerning the physical origin of the LFMs and Boson peak in glasses are still open. The scopes of validity of the models, developed for description of the dynamics of glasses at intermediate temperatures, when LFMs play the main role, are also not yet clear.

Until recently, information about the nature and properties of LFMs in glasses were mainly obtained by three different classes of experiments. The *first* one comprises calorimetric and sound propagation measurements, which yield information about processes of energy conversion in glassy (T -dependence of thermal capacity and conductivity, ultrasonic absorption and other effects). The *second* group is based on the low-frequency light and inelastic neutron scattering and gives the data about the spectrum of LFMs. The *third* group consists of line-narrowing spectroscopy methods—fluorescence line narrowing and hole burning in the frequency domain, and photon echo in the time domain (see, for reviews [17–19]), they yield data about the interaction of LFMs with impurity centers.

All the techniques mentioned above have in common that they yield data which are the average of a large ensemble of LFMs. In disordered solids, however, the parameters of individual LFMs are expected to be different and could be characterized by broad distributions. Averaging over such distributions, which is inherent to all conventional experimental methods, leads to a considerable loss of information about the glass dynamics. One should take into account also that the above-mentioned methods are characterized by different ways of averaging over ensemble of LFMs, sample volume, time intervals and

other parameters. Hence, ensemble average techniques yield only some “effective” values of LFM parameters and cannot provide unambiguous data about the local characteristics and the microscopic origin of LFMs in glasses. This makes it interesting and principally important to obtain direct information about the local parameters of LFMs in disordered solids.

In the last years experimental advances have made feasible to measure the optical spectra of single molecules (SMs) isolated in a transparent matrix [20,21]. Optical spectra of chromophore molecules embedded to transparent disordered matrix as a spectral probe are very sensitive to parameters of local environment and contain a valuable information about dynamics of matrix. In this way SMs serve as a microscopic instrument, which reports us about the dynamical processes in their immediate neighborhood. One of the major advantages of single-molecule spectroscopy (SMS) is the ability to remove completely any kind of ensemble averaging over a large number of chromophores, which is inherent to all methods of conventional spectroscopy. It is important that SMS allows to measure the local parameters of excitations in different points of the sample. It opens up possibilities to obtain direct information about the individual parameters of LFMs. Nevertheless the studies of LFM-dynamics in low-temperature glasses using SMS were very limited. One of the main reasons of this fact, for our opinion, is related to complicated shape of SM spectra in low-temperature glasses. The interaction of dopand molecules with TLSs and LFMs leads to line splitting and line broadening in SM spectra and made them continuously varying with time. Interpretation and analysis of such spectra cause serious problems.

In the present work, a new approach for study of LFM-dynamics in glasses via SMS which eliminates most of the above problems is discussed. The essence of this approach is based on recording a large number of SM spectra and their subsequent statistical treatment. This publication is aimed on review of the recent results on LFMs dynamics in organic disordered system—polyisobutylene (PIB) weakly doped with *tetra-tert-butylterrylene* (TBT) molecules obtained using the above approach. PIB was chose as a matrix because it is known to be completely amorphous [22]. The studies under discussion were published in Refs. [23–25]. The article focuses on the concise consideration of major aspects of the proposed approach and brief characteristic of the obtained results.

2. LFMs in glasses and spectra of single impurity molecules

At present, a generally accepted theory of LFMs in glasses is still absent. Many theoretical models have been proposed to explain the physical origin of these excitations (localized, propagating, extended non-propagating modes, etc) and no consensus on the main assumptions of these models has been achieved so far. One of the theories is the soft-potential model [26]. It explains most of the

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