Experimental Evidence of the Local Character of Vibrations Constituting the Boson Peak in Amorphous Solids

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We report the first measurement of the density of states of low-energy vibrational excitations in a disordered solid via single-molecule (SM) spectroscopy. Optical spectra of many single *tetra-tert-butylterrylene* (TBT) molecules embedded to amorphous *polyisobutylene* (PIB) as spectral probes were recorded at low temperatures. The T dependences of SM spectral linewidths showed the broad distribution of local frequencies of vibrations under study. The obtained distribution was compared with the ''Boson peak'' in pure PIB measured in [R. Inoue *et al.*, J. Chem. Phys. **95**, 5332 (1991)] by neutron scattering. We found that embedding of a small amount of TBT into PIB does not influence markedly on the observed vibrational dynamics. These results prove the local character of low-energy vibrational excitations in glasses and the existence of relationship between these excitations and the Boson peak.

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A wide variety of solid objects ranging from glasses and polymers to nanoparticles and biological media are characterized by the presence of lattice disorder on a microscopic level. The vibrational dynamics of disordered solid media and its relationship to the properties of these materials has been a topic of extensive long-term scientific research [1–5]. One of the intriguing and ubiquitous features of such media, which seems to be one of the universal fingerprints of complex disordered solids, is the so-called ''Boson peak'' [6–9]. This is an anomalous enhanced vibrational density of states in the low-frequency spectral range over that predicted by Debye, which was observed in all complex disordered solids, including random crystalline systems.

The Boson peak was observed in inelastic light [8,10], neutron [4,11,12], and x-ray [13] scattering experiments, as well as in absorption spectra in the THz region [14] and in calorimetric measurements [1]. In spite of the numerous studies, the physical origin of the Boson peak has remained unclear and is still a matter of discussion.

Many theories have been formulated to explain the microscopic origin of this peak [15–20]. They attribute it to different types of vibrational excitations. Some of them ascribe the Boson peak to strongly localized excitations induced by the intrinsic disorder [15,16], whereas others attribute it to collective propagating modes [17,18]. In the soft-potential model [21,22] quasilocalized low-frequency vibrational modes, which have their origin in localized soft potentials in a disordered matrix, are considered to be the reason of the excess vibrational density. Other theories explain the Boson peak by systems of coupled harmonic oscillators and predict a crossover from propagating to nonpropagating modes at a characteristic frequency [17]. These approaches are extreme positions, and it is possible that the reality is best described by elements of all of them.

A key question in understanding the microscopic nature of the Boson peak is whether this peak is associated with localized excitations or with propagating modes. Previous experiments do not provide unambiguous information about the origin of these vibrations. Some investigations conclude that they are mainly of collective character [7,23], whereas others attribute them to localized vibrational modes [24]. There are also studies, which describe the data by the coexistence of excitations of both types [25]. Moreover, the authors of some studies come to opposite conclusions when analyzing identical experimental data. For example, in Ref. [23] the Boson peak in silicate glass was attributed to transverse acoustic modes, whereas in Ref. [26] it was ascribed to localized excitations.

In perfect crystals, in which numerous acoustic, optical, and pseudolocal phonon modes with identical parameters exist, the knowledge of individual parameters of these modes is not very interesting: the averaged parameters of vibrational modes are sufficient for a correct description of the observed dynamics. The situation is quite different, however, in the case of more complex disordered solids, which are characterized by local inhomogeneity. The dynamical properties of these solids show essential differences as compared to perfect crystals.

The anomalous dynamics of disordered solids at temperatures below 1–2 K is usually described with the concept of ''tunneling two-level systems'' (TLSs) [27,28]. At higher temperatures, the properties of glasses cannot be explained in the framework of this concept. In most studies it is assumed that their anomalous behavior at intermediate temperatures (a few—several 10 K) arises from the existence of low-frequency vibrational modes (LFMs) in addition to the phonons predicted by Debye [29] and TLSs. So far, most of the principal questions regarding vibrational excitations in glasses are still open. The microscopic nature of these excitations remains unclear. In particular, it is

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unknown whether or not these excitations are characterized by broad distributions of their individual parameters and what is the spectrum of these excitations. It is not clear whether it coincides with the Boson peak as measured by ensemble averaging methods.

All conventional experimental techniques used for study the Boson peak yield data averaged over a large ensemble of vibrational excitations. This averaging leads to a considerable loss of information about the glass dynamics. Hence techniques used so far cannot distinguish unambiguously whether the observed excess vibrational density in glasses is associated with localized or with collective modes.

As studies of complex solid systems find more and more interest, the possibility to measure directly the local characteristics of vibrational modes and their distributions is very topical. This makes it principally important to obtain information about the local or even individual parameters of LFMs in a disordered solid.

Here we use single-molecule spectroscopy (SMS) for the direct observation of the local parameters of low-frequency vibrational modes in disordered solids. SMS is a powerful method which does not suffer from the problem of ensemble averaging [30]. The optical spectra of chromophore molecules embedded in transparent solid matrices as spectral probes are very sensitive to the parameters of their environment. Individual dopant molecules provide direct information about the local parameters of LFMs in their respective environment. If these excitations are strongly localized, they comprise a small number of atoms; hence, broad distributions of their individual parameters can be expected. If they are mainly delocalized, on the other hand, the observed parameters should all be very similar. Therefore, SMS makes it possible to discriminate between the two opposite cases.

We have studied the line broadening in the spectra of individual chromophore tetra-tert-butylterrylene (TBT) molecules doped into an amorphous polyisobutylene (PIB) at very low concentration. We measured the optical spectra of a large number of single TBT molecules at different locations in the sample. The measurements were performed in the temperature region up to a few tens of Kelvin, where the LFM dynamics dominates the spectral broadening behavior. The analysis of the data allowed us to determine the local frequencies of the LFMs in the sample and to find their energy spectrum.

The optical spectra of SMs in disordered matrices at low temperatures can be very different [31,32]. Slow flips of nearby TLSs cause line splitting and frequency jumps, whereas fast flips of nearby TLSs as well as transitions of numerous distant TLSs and the interaction with nearby LFMs give rise to line broadening. As a result, the individual spectra of chromophores in glasses have complex shapes, differ from molecule to molecule, and vary with time. Depending on the parameters of the local environment, the spectrum of a given chromophore can consist of one or more peaks. One has to address the question of how to extract information about the vibrational excitations from these complicated spectra [33]. Our analysis is based on the fact that the interaction of a chromophore with a LFM contributes to the broadening (rather than the splitting) of the peaks in its spectrum. Hence, we determined the LFM frequencies by measuring the individual temperature dependences of the spectral widths of SMs.

We prepared a sample of about 300 nm thickness by spin coating a toluene solution of TBT in PIB onto a microscope slide. The slide was mounted in the focus of a microscope objective inside a ^{4}He cryostat. Measurements were performed in the temperature region 1.6–40 K. The fluorescence emission was excited by a frequency-stabilized single-mode dye laser (Coherent CR599-21), whose total spectral width (including jitter) was smaller than 2 MHz. The excitation wavelength was in the range between 575 and 581 nm. To record a large number of SMs simultaneously we used a sensitive thermoelectrically cooled CCD camera (PCO Sensicam QE). The widths of the most intense peaks in the SM spectra were determined by fits with a Lorentzian profile. (For a description of setup and measurement procedure, see Ref. [34].)

The temperature dependence of the spectral widths of SMs has a random character and varies from molecule to molecule. At $T < 2$–3 K the TLS contribution to the spectral widths predominates, whereas at higher temperatures the line broadening caused by the LFMs prevails. The temperature dependences of these two contributions differ markedly: the TLS contribution varies close to a power law, whereas the broadening caused by LFMs shows a much faster quasiexponential variation with temperature. This makes a separation of the two contributions possible. Figure 1 shows an example of the spectral broadening of an individual SM line with temperature. The crossover between the two contributions is clearly visible. Around the crossover point, the description of the broadening is somewhat dependent on the details of the linewidth model, but in the limits of low and high temperatures it is clearly dominated by either of the two contributions. Quantitative analysis of the linewidth data shows that at $T > 8$–10 K the contribution of TLSs can be neglected. Hence, we determined the LFM frequencies in the local environment of the 281 single chromophores by analyzing the high-temperature part of individual T dependences of their linewidths (see details in Ref. [35]).

To determine the LFM frequencies we fitted the high-temperature part of the measured T dependences with the well-established equation [36]

$$\Delta\Gamma^{i}_{\mathrm{LFM}}(T) = w^{i,j}\frac{\exp(-h\nu^{j}/kT)}{[1-\exp(-h\nu^{j}/kT)]^{2}}, \qquad (1)$$

which describes the contribution to the line broadening, $\Delta\Gamma^{i}_{\mathrm{LFM}}(T)$, caused by the interaction of the ith chromophore with the jth vibrational mode of frequency $\nu^{j} = \Delta E^{j}/h$. Here $w^{i,j}$ is the coupling constant for this pair, and k is the Boltzmann's constant. According to this equa-

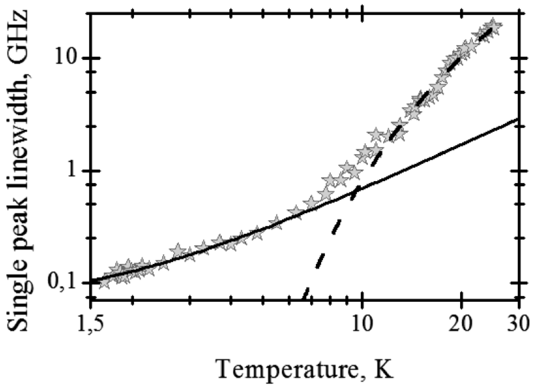

FIG. 1. Example of the T dependence of the spectral width as measured for a single TBT molecule in amorphous PIB in a broad temperature range (☆) in the double-logarithmic data representation. The lines show the TLS contribution to line broadening, approximated by a power law (solid line) and the contribution of a nearby LFM, fitted with Eq. (1) (dashed line).

tion, the spectral width of a SM varies close to a monoexponential law if the chromophore interacts with only one single nearby LFM. In the case of coupling to two LFMs, the T dependence is expected to have roughly a biexponential form. If the number of LFMs, which interact with the chromophore, is large, the T dependence will be closer to a monoexponential behavior again, and the corresponding vibrational frequency will be an effective, averaged value. Moreover, in this case the individual T dependences of different SM spectra are expected to be characterized by roughly the same effective LFM frequency due to the averaging. Our experimental data clearly support the picture which is expected for the first case. Most of the measured T dependences show a monoexponential behavior, and the corresponding values of the local LFM frequencies are subject to a broad distribution between 3 and 70 cm^{-1}. This means that different single chromophore molecules in various places of the sample sense different vibrations of matrix. We observed this effect already in our first measurements [35], but the data obtained only for 9 single molecules do not allow to find the energy spectrum of LFMs and to conclude about the relation between vibrations observed via SMS and the Boson peak.

In this work we measured frequencies of LFMs in surroundings of 281 molecules and found the energy spectrum of LFMs. This spectrum is presented on the Fig. 2 as a histogram together with the Boson peak in pure PIB as measured by inelastic neutron scattering in Ref. [12].

Thus, the existence of a broad distribution of vibrational frequencies and the measured monoexponential temperature laws clearly demonstrate the local character of these vibrations. It yields strong support for those theories which predict a nonpropagative and temporally stable character of LFMs in disordered solids.

One of the principal questions of our study was whether the spectra of LFMs measured in a pure material, which do not contain probe molecules, and in a doped sample are the same. Note that ensemble averaging techniques showed that an incorporation of impurity molecules with low dipole moment does not change markedly the average (effective) value of LFM frequencies (e.g., [37]). SMS allows to look this question more deeply and to find the energy spectrum of LFMs.

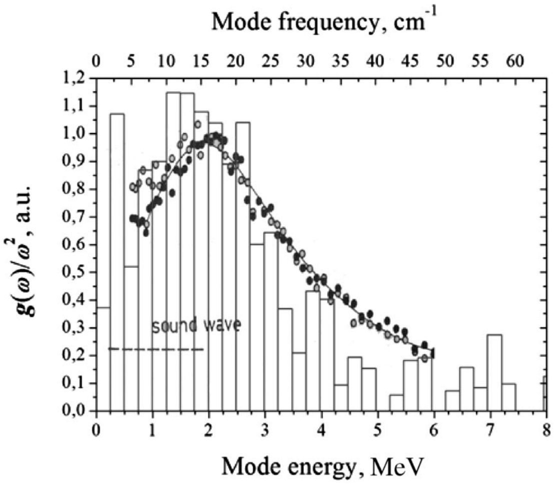

FIG. 2. Spectrum of the LFMs in doped PIB and the Boson peak for pure PIB, as measured by two different methods: (1) by SMS (*histogram*), which yields the individual values of LFM frequencies in the local environment of 281 single chromophore molecules, and (2) by inelastic neutron scattering (circles), which provides the data averaged over the whole monochromatic ensemble of vibrational excitations (from Ref. [12]). Both spectra were modified to take the Bose factor into account. In order to highlight the vibrational excitations exceeding the Debye spectrum, the SMS and neutron scattering data have been plotted as $g(\omega)/\omega^2$, where $g(\omega)$ is the density of states. The dashed line indicates the contribution of the sound waves in the case of the neutron scattering data.

The comparison of our measured by SMS frequency spectrum of the LFMs with the Boson peak as determined in pure PIB by neutron scattering shows an additional interesting and nonobvious result: both distributions are very similar.

It seems improbable that this coincidence is accidental. It is more likely that this result has important physical reasons. (1) The microscopic origin of the vibrations, which cause the observed line broadening in the spectra of single TBT molecules in PIB, and of the vibrations, which constitute the Boson peak in pure PIB, is the same. (2) The incorporation of a small amount of TBT molecules into amorphous PIB as required for single-molecule spectroscopy does not change the observed vibrational dynamics of this material markedly.

It is difficult to imagine some mechanism which makes so that untruth of the first conclusion compensates exactly the untruth of the second one and as result makes the observed LFM spectrum equal to Boson peak. The first conclusion, together with the local character of the vibrational modes, generally opens up new possibilities for answering questions regarding the microscopic nature of vibrational excitations in amorphous solids. The second conclusion is of utmost importance for the optical spectroscopy of impurity centers. In these experiments it is highly desirable that adding a small amount of a selected chromophore to an amorphous matrix does not give rise *greatly* to new vibrational excitations in this matrix (as it occurs in crystals) and does not affect the parameters of the observed dynamics.

Thus, for the first time the density of states of elementary low-energy vibrational excitations in a doped amorphous solid has been measured via single-molecule spectroscopy. The results obtained clearly demonstrate that SMS yields new microscopic information about the intrinsic vibrational excitations in disordered solids.

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