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Local vibrations in disordered solids studied via single-molecule spectroscopy: Comparison with neutron, nuclear, Raman scattering, and photon echo data

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The energy spectrum of low-frequency vibrational modes (LFMs) in three disordered organic solids—amorphous *polyisobutylene* (PIB), *toluene* and *deuterated toluene* glasses, weakly doped with fluorescent chromophore molecules of *tetra-tert-butylterrylene* (TBT) has been measured via single-molecule (SM) spectroscopy. Analysis of the individual temperature dependences of linewidths of single TBT molecules allowed us to determine the values of the vibrational mode frequencies and the SM-LFM coupling constants for vibrations in the local environment of the molecules. The measured LFM spectra were compared with the "Boson peak" as measured in pure PIB by inelastic neutron scattering, in pure toluene glass by low-frequency Raman scattering, in doped toluene glass by nuclear inelastic scattering, and with photon echo data. The comparative analysis revealed close agreement between the spectra of the local vibrations as measured in the present study and the literature data of the Boson peak in PIB and toluene. The analysis has also the important result that weak doping of the disordered matrices with nonpolar probe molecules whose chemical composition is similar to that of the matrix molecules does not influence the observed vibrational dynamics markedly. The experimental data displaying temporal stability on the time scale of a few hours of vibrational excitation parameters in local surroundings was obtained for the first time both for polymer and molecular glass.

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I. INTRODUCTION

The anomalous dynamical behavior of disordered solids at temperatures between 1–2 and 30–50 K, e.g., anomalous acoustic properties,[1–3] the existence of a plateau in the temperature dependence of the heat conductivity at the region of T about 10 K,[2,4,5] and other effects are usually ascribed to the presence of low-frequency vibrational modes (LFMs)[2,6–8] in addition to acoustic phonons and tunneling "two-level systems" (TLSs).[2,3,9–11] This view is confirmed by numerous experimental data which show that the above vibrational excitations begin to dominate the dynamical processes in amorphous solids at $T > 3-5$ K [see, e.g., Refs. 12–14]. So far, most of the principal questions regarding the main properties and the microscopic nature of these excitations are still open. In most studies it is assumed that LFMs have a local or quasilocal character and, hence, that they are associated with vibrational motion of groups of atoms or molecules within local potential minima.

One of the intriguing and universal features of disordered solids, which were observed both in organic and inorganic materials, is so-called the "Boson peak." This is an anomalous excess of the vibrational density of states in the low-frequency part of the spectrum (approximately in the range 0.03–3 THz) over that predicted by the Debye model. The Boson peak was experimentally observed in Raman[15–19] and hyper-Raman[20] light-scattering experiments, in inelastic neutron[21,22] and x-ray[23] scattering studies, as well as in calorimetric measurements[2] and in absorption spectra in the terahertz region.[24,25] In spite of significant efforts in theoretical and experimental studies of this phenomenon, the physical origin of the peak and its relationship to LFMs are still a matter of active debate. One of the central questions regarding the microscopic origin of the Boson peak is whether it is associated with vibrational excitations which are localized due to disorder or with propagating plane waves. Various theoretical models explaining the Boson peak with these two concepts have been published. The available experimental data do not provide sufficient information for an unambiguous answer to this important question. Another fundamental issue in the interpretation of the Boson peak concerns the typical spatial extension of the corresponding vibrations. So far, the experimental data could not definitely clarify this point either.

All conventional experimental techniques used in the past to study LFMs and the Boson peak in glasses yield data which are averaged over a large ensemble of excitations. In disordered systems, however, the individual parameters of LFMs at different points of the sample are expected to be different, so the LFMs in glasses should be characterized by broad distributions of their individual parameters. In this case, averaging over the whole ensemble leads to a considerable loss of information about the vibrational dynamics. As a result, the data of the Boson peak obtained via these techniques cannot distinguish unambiguously, whether the observed excess vibrational density is associated with localized or collective modes. A direct measurement of the local parameters of the LFMs and their distributions in disordered solids, therefore, appears to be highly important and interesting.

Single-molecule spectroscopy (SMS) is a powerful method which does not suffer from the problem of ensemble averaging.[26] Individual optical spectra of a given single chromophore molecule (SM) provide information about the local parameters of LFMs in the environment of the SM.[27] Here, we present the results of such measurements. We use SMS for the direct observation of the local parameters of LFMs in disordered solids. We have studied the line broadening caused by LFMs in the optical spectra of single *tetra-tert-butylterrylene* (TBT) chromophores incorporated at very low concentration in three different disordered organic matrices: (1) the amorphous polymer *polyisobutylene* (PIB) and (2) low-molecular-weight glasses - *protonated toluene* ($C_6H_5CH_3$) *and perdeuterated toluene*-D_8 ($C_6D_5CD_3$). The analysis of the individual temperature dependences of the spectral linewidths of single TBT molecules allowed us to determine the local frequencies of the LFMs in the vicinity of the SMs and to build the spectra of these excitations.

The central point of the present article is the comparison of our results with data about the vibrational dynamics obtained independently for the same amorphous solids by different experimental techniques. The LFM spectra were compared with taken with literature data of the Boson peak: (a) in pure (i.e., undoped) PIB as measured by inelastic neutron scattering,[22] (b) in pure toluene by Raman scattering,[19] and (c) in toluene doped with ferrocene molecules by nuclear inelastic scattering (i.e., resonance inelastic scattering of x rays via low-energy nuclear transitions).[28] Moreover, we compare our results with the data of optical dephasing processes as measured in the same matrices with the photon echo technique.

It is necessary to note that the main ideas of the above-mentioned experiments have one important difference. Nuclear inelastic scattering, photon echo, and our measurements have in common, that they use probe molecules incorporated in the matrix under study to obtain information about its vibrational dynamics. In Raman and inelastic neutron-scattering studies, on the other hand, pure amorphous solids are investigated and dopant molecules are not used. In this context, the important questions arise: Are the spectra of vibrations as measured by different techniques in a doped and a pure material identical? Does the incorporation of impurity molecules disturb the matrix dynamics in their vicinity? The answers to these questions, which are of utmost importance for understanding the origin of the vibrational dynamics and the Boson peak in glasses, are still unclear. A comparative analysis of the data obtained in our measurements with the literature data of the Boson peak in PIB and toluene obtained by different methods allowed us to shed some light on this problem.

In contrast to SMS, which yields information about the interaction of single chromophore molecules with LFMs in their local environment, the photon echo technique yields ensemble averaged data of the line broadening processes caused by these modes. Up to now, even principal questions concerning the above-mentioned relationship between the two types of data are still open. For example, it is not clear which parameters of the LFM spectra (the frequency of the maximum or some averaged frequency value) the data obtained by photon echo correspond to. To address this question we compare our data with the photon echo data of doped PIB and toluene published in Refs. 14 and 29.

The first step in our study of LFMs in a disordered matrix via SMS has been presented in Refs. 30 and 31, in which the local parameters of the vibrations in the environment of several single TBT molecules in a PIB matrix were derived. It was found that the local values of the LFM frequencies and the SM-LFM coupling constants are subject to broad distributions. In the following two publications,[32,33] we developed a technique which allowed us to measure the energy spectra of LFMs in doped PIB, toluene, and deuterated toluene via SMS for the first time. In the present paper, we discuss our results in more detail and present a comparative analysis of the data about the Boson peak as obtained by SMS and different other methods including the photon echo.

II. EXPERIMENT

A detailed description of our experimental setup was given previously (see Refs. 34–37). Hence, only the main points and parameters of the setup and the measurement procedure will be presented here. The samples were inserted in a temperature-regulated He-4 cryostat (Cryovac) with temperature control accuracy of ± 0.05 K. For excitation a frequency-stabilized cw single-mode Rh6G dye laser (Coherent Radiation, model 599–21) with a spectral bandwidth of about 2 MHz (including jitter) was used. The sample was illuminated from the back side by weakly focusing the laser beam to a spot with diameter ≈ 100 μm. The fluorescence images of single chromophore molecules were projected onto the photosensitive area of a sensitive Peltier-cooled charge coupled device (CCD) camera (PCO Sensicam QE) with a microscope objective (Microthek, 80×, NA 0.9) mounted inside the cryostat. The camera detection allowed for simultaneous recording of the spectra of a large number of SMs. Residual pump-laser light was suppressed by an interference band-pass filter and a Schott RG610 glass filter. The sample was immersed in superfluid helium at $T < 2.17$ K or in a stream of cold helium gas above 4.2 K, respectively. Between 2.17 and 4.2 K, the sample was placed slightly above the surface of the boiling liquid helium. At different temperatures the distance between objective and sample had to be slightly readjusted in some cases. The excitation wavelength was in the range between 575 and 582 nm. The excitation power was adjusted to a level for which the signal-to-noise ratio was best, while at the same time, no power broadening could be observed. In the investigated SM spectra, light-induced spectral diffusion was negligible at the light intensities used.

In a scan, the laser frequency was tuned over 30 GHz (500–1000 data points per scan); each scan took 120 s. At high temperatures, when the SM linewidths were comparable to the scan width, two or three laser scan ranges were combined to a broader interval (up to 70 GHz). After the end of the scan, the laser was rapidly (in about half a second) tuned back to its starting frequency, and a new scan followed. The acquisition time of one video frame varied from 120 to 240 ms. The digitized video signals from the camera were stored in a computer and used for further analysis. The individual fluorescence excitation spectra of SMs were extracted from this video database with a program which located the positions of bright sports (within a small group of camera pixels) corresponding to SMs and listed their intensity data in consecutive frames.

The polymer sample (300–500 nm thick) was prepared by spin coating a highly diluted solution of TBT in PIB onto a microscope slide; the solvent was toluene. We used the same doped polymer material (kindly provided by Professor Th. Basché, University of Mainz), which had been investigated before in SMS (Refs. 34–36) and PE (Refs. 14 and 38) experiments. To decrease the dye concentration, we added pure PIB to the solution. Liquid toluene was introduced between two thin microscope slides at room temperature and cooled quickly (during several seconds) by inserting the sample into the precooled cryostat. PIB (molecular weight $\sim 4.2 \times 10^5$), toluene (anhydrous, 99.8%), and toluene-D_8 (99.6 atom %d) were purchased from Aldrich Inc. and used without further treatment. The concentration of TBT molecules in the polymer and the glass matrix was adjusted to such a level that no more than 300–500 single molecules were detected in the whole photosensitive area of the CCD camera within the full scan range of the laser.

III. LFMs IN GLASSES AND THE BOSON PEAK

The concept of low-frequency "quasi- (or pseudo-) localized" vibrational modes is well known in the solid-state physics of crystals. According to the standard assumptions, quasilocal LFMs in crystals appear around impurities or point defects. Coupling of these excitations with low-frequency lattice modes has the consequence that they are not perfectly localized, but quasilocalized. This means that the modes are not extremely localized to the defect itself, but extend to its vicinity. In the case of a perfect crystal doped with one sort of impurity molecules, numerous quasilocal LFMs with the same (or very similar) parameters exist. Detailed information about the individual parameters of these modes is not interesting: The knowledge of their averaged values is sufficient for a correct description of the dynamics.

The situation is quite different in the case of disordered solids: Here, quasilocal vibrational modes arise from the local heterogeneities of the matrix and are inherent to all disordered materials (for a review, see Refs. 7 and 8). In this case, quasilocal LFMs can be viewed as being associated with the point "defects" which are formed by the strong local irregularities of the disordered structure. Correspondingly, broad distributions of the local parameters of the LFMs can be expected. This is confirmed by experimental data. In particular, the above-mentioned Raman and neutron-scattering studies have shown that in glasses, LFMs have broad spectra which cover the region from a few up to tens of wave numbers.

A generally accepted description of the LFMs in glasses is still missing. We do not know the microscopic nature of these modes and how they interact with other elementary excitations. One of the principal questions in our understanding of LFMs is: What is the relationship between LFMs and the Boson peak in glasses or, more precisely, is the Boson peak as observed in scattering experiments produced by "excess vibrational modes" only?

A lot of competing theoretical models have been formulated to explain the physical origin of the LFMs and the Boson peak[39–46] in disordered solids. The common view is that both LFMs and the Boson peak are inherent to glasses and originate from local disorder, but different models are based on different concepts and there is no consensus between the approaches. One of the popular theories is the soft-potential model.[9,39,47,48] It considers both the TLSs and LFMs in the framework of a unified approach. The soft-potential model explains with much success the experimental data on glass dynamics in a broad temperature range and can be regarded as a generalization of the TLS model. According to the soft-potential model, TLSs and LFMs may be viewed as collective motions of groups of atoms or molecules in the local minima of a potential-energy hypersurface: Local soft double-well potentials lead to tunneling or thermally activated TLSs, whereas single-well potentials form vibrational LFMs. The model assumes that both TLSs and LFMs are characterized by broad continuous distributions of their parameters.[49] Other theoretical studies regard a glass as a structure containing clusters (or blobs) of nanometer sizes[50–52] or as an aperiodic crystal with mosaic structure,[53] even though the medium is homogeneous on a macroscopic scale. The authors of these studies attribute the LFMs to vibrations of atoms in the clusters. It is assumed that the motions responsible for the Boson peak have the same origin as LFMs and, hence, the peak is of strongly localized character. The physical origin of the clusters remains unclear, however. Some theories are based on alternative assumptions. They explain the LFMs as arising from propagating plane-wave vibrational (phononlike) modes[54,55] and attribute the Boson peak to them. Several theories provide again a different picture. They consider the LFMs in disordered solids neither as propagating waves nor as localized modes, but as diffusive excitations. In this approach, the LFMs are described as running plane waves, the wave vector of which strongly fluctuates and moves (in momentum space) randomly in a diffusionlike manner.[56] The above approaches can be considered as extreme positions. It is also possible that in a realistic model of glasses, the LFMs and the Boson peak should be better described by elements of several of them. For example, the Arai *et al.*[57] consider the possibility of the coexistence of collective propagating and localized modes and argue that this situation could be an origin of the anomalous vibrational properties of glasses. All the theories developed so far are essentially phenomenological, and it is not clear as to which degree they describe the real processes in glasses correctly.

One of the central questions concerning the nature of LFMs in glasses is related to their spatial extension (i.e., the size of their localization if they are quasilocal modes, or the mean-free path in the case of collective plane-wave modes). Theories based on different concepts predict different values for the typical size of LFMs. In order to find an answer to this question, it is necessary to clarify the internal structure of amorphous solids. Neutron and x-ray diffraction techniques have shown that amorphous materials are not completely disordered but are characterized by short-range order on a length scale of a few nanometers. Therefore, some theories assume that the extension of the quasilocal LFMs in glasses is close to this range. Other theories suppose that the mean-free path of vibrational plane waves corresponds to several wavelengths. The exact relationship between the extension of LFMs and the above length scales is not clear, however, and is again the subject of numerous debates.

The available experimental data do not provide unambiguous information about the microscopic nature and size of LFMs and the origin of the Boson peak. For example, the authors of two different independent studies came to opposite conclusions when analyzing identical experimental data: In Ref. 58, the Boson peak in silicate glass was ascribed to localized excitations, whereas in Ref. 59, it was attributed to transverse-acoustic modes. Raman scattering yields information about the frequency spectrum of the LFMs, but the measured spectrum is weighted with the light-vibration coupling coefficient $C_i(\omega)$, the frequency dependence of which is poorly understood. Inelastic neutron scattering provides information about the vibrational density of states (VDOS) and it gives also some indications of the size of the LFM localization. The latter is not very precise, however, since the microscopic origin of the LFMs and their interaction mechanism with the neutron beam are not known.

The optical spectra of chromophore molecules embedded as spectroscopic nanoprobes in a transparent solid matrix are very sensitive to the parameters of the matrix and contain valuable information about the vibrational dynamics in their surroundings. The interaction of LFMs with the electronic transitions of a SM becomes apparent as homogeneous line broadening in the chromophore spectrum. The hole burning[60,61] and the photon echo[62] techniques allow one to completely eliminate the effect of strong inhomogeneous line broadening inherent to all disordered solids and to obtain data about the interaction of LFMs with impurity centers. However, these and other conventional spectroscopic techniques yield data averaged over large ensembles of LFMs and do not provide information about the local parameters. Significant progress in our understanding of the microscopic nature of quasilocal LFMs in disordered solids can only be achieved if information about their local parameters and the distributions thereof is obtained. SMS completely eliminates any averaging over the chromophore ensemble and measures directly the local and even individual parameters of LFMs. A general problem of spectroscopic techniques is that it is *a priori* not clear how the chromophore molecules affect the observed matrix dynamics.

IV. LFMs AND LINE BROADENING OF SPECTRA OF SINGLE CHROMOPHORES

We determined the local values of LFM frequencies and SM-LFM coupling constants in the vicinity of the observed SMs by analyzing the optical linewidths of the fluorescence excitation spectra at different temperatures. The expression describing the shape of the electronic spectrum of a chromophore located near quasilocal LFMs has been derived for crystalline systems. If the coupling between the SM and LFMs is not too strong, it has the form

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

This well-established equation describes the contribution to the linewidth $\Delta\Gamma^i(T)$ of the chromophore with index i caused by the interaction with several vibrational modes of frequency $\nu^j = \Delta E^j/h$. Here, $w^{i,j}$ are the corresponding coupling constants and k is Boltzmann's constant. In the case of a perfect crystal doped with identical chromophore molecules, Eq. (1) describes also the ensemble-averaged homogeneous linewidth, since the parameters of different SMs and LFMs are identical. Equation (1) was derived on the basis of very general assumptions; hence, we believe that it is valid also in glasses, but in this case, the averaged value of the linewidth and the individual $\Delta\Gamma^i(T)$ have to be different. This point is confirmed, in particular, by the results of photon echo (PE) and spectral hole-burning (HB) studies on doped organic amorphous systems[13,14] which have shown that Eq. (1) describes the LFM contribution to the homogeneous (or, in the case of HB, quasihomogeneous) linewidth with sufficient accuracy. The total value of the linewidth Γ_{total}, which includes both the TLS and LFM contributions, was described in the above studies by

$$\Gamma_{\text{total}}(T) = \Gamma_0 + bT^\alpha + \Delta\Gamma_{\text{LFM}}(T), \qquad (2)$$

where Γ_0 is the natural linewidth and bT^α and $\Delta\Gamma_{\text{LFM}}(T)$ are the TLS and LFM contributions, respectively. The parameters b and α are determined by the tunneling dynamics in the matrix. In the above HB and PE studies, the measured values of Γ_{total} are averaged over the ensemble of chromophores and LFMs. Therefore, the LFM parameters determined in these experiments should be considered as some effective values characterizing the amorphous system as a whole.

In our measurements, the individual SMs interact with different LFMs and different TLSs whose parameters vary from point to point. The resulting SM spectra have complex and random shapes and, in addition, can vary also with time. Such a behavior can easily be understood in terms of the random character of the local dynamics in a low-temperature glass. Slow transitions in a small number of nearby TLSs give rise to frequency jumps; fast flips of these TLSs can lead to line splitting or line broadening, whereas numerous transitions of more distant TLSs and vibrations of the surrounding LFMs cause line broadening. Depending on the parameters of the local environment, the spectrum of a given SM can consist of one or more peaks which may change their spectral positions with time. The obvious question arises as to how to extract information about the LFMs from such random and complicated spectra.

Our analysis is based on the fact that the contributions of TLSs and LFMs to the SM spectra are characterized by strongly different temperature laws. Most SM spectra exhibit a weak temperature dependence of their linewidths below 2–3 K and a much stronger broadening at higher temperatures. This allows us to clearly separate the TLS and LFM contributions in most spectra [see, for example, Fig. 1(c)]. A quantitative analysis shows that at $T > 8-10$ K, the LFM contribution to the line broadening prevails in virtually all SM spectra and the contribution of the TLSs can be neglected. Thus, the local parameters of the LFMs interacting with a given chromophore can be obtained from the high-temperature part of the individual temperature dependence of its linewidth.

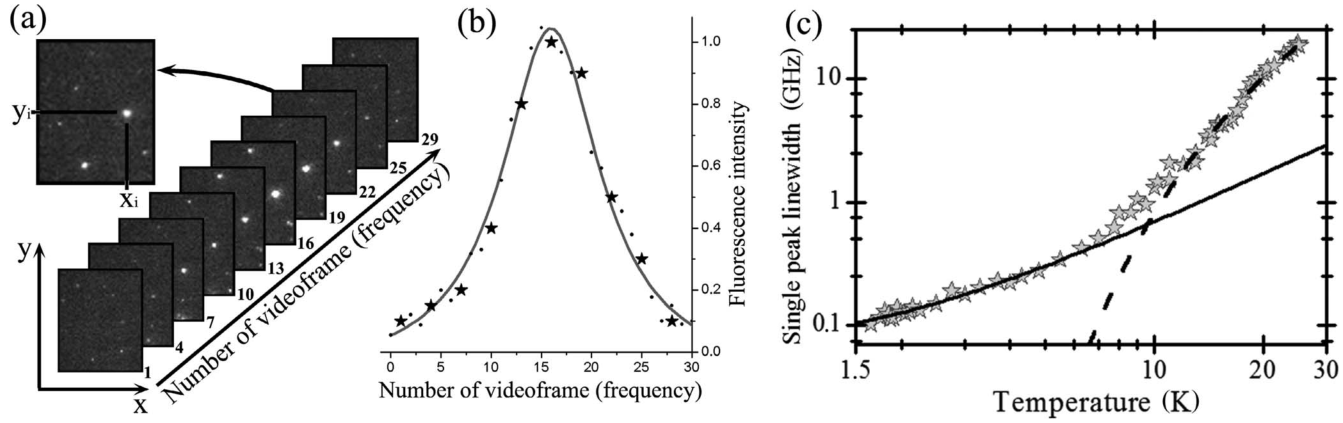

FIG. 1. Illustration of the procedure of extracting single-molecule spectra and the temperature dependence of their linewidths from a sequence of video frames. (a) Identification of luminescent images of the same single molecule upon frequency scanning of the laser at a given temperature T. (b) Fluorescence excitation spectrum of the ith molecule with coordinates x_i,y_i (*dots* and *stars*) and its fit with a Lorentz function (solid line). Stars correspond to the video frames presented in (a). (c) Temperature dependence of the linewidth of ith molecule and its fit with Eqs. (1) and (2). The lines indicate the TLS contribution to the spectral broadening, approximated by a power law (*solid line*) and the contribution of a nearby LFM, fitted with Eq. (1) (*dashed line*).

Due to the complex shapes of most experimental SM spectra, the concept of the spectral linewidth is often not well defined. Therefore, we analyzed the widths of the most intense peaks in the sum spectra. If single isolated peaks could not be identified (as happens often at high temperatures), we defined the linewidth as the width of the whole spectral signal curve. This procedure was described in more detail in our previous paper.[30] In addition to broadening, the spectra exhibit also blue and red shifts with increasing temperature, again reflecting the varying local parameters in the sample. The shifting behavior in spectra of SMs in disordered matrix was reported in Ref. 27 for single terrylenediimide molecules in polyethylene. We did not consider these effects, but restricted our analysis to the line broadening behavior.

As theories predict and experiments have shown (see, e.g., Ref. 6), the concentration of excess vibrational modes in glasses at low and intermediate temperatures is very small and the possibility that two or more LFMs exist at the same point of the sample is negligible. If the LFMs are strongly localized, the SM is expected to interact with no more than a few nearby LFMs. Equation (1) shows that if the chromophore interacts only with one single LFM, its spectral width varies roughly according to a monoexponential law. In the case of coupling to several LFMs, a "multiexponential" temperature behavior is expected. If only a small number of LFMs (two to three) interact with the chromophore and their parameters differ significantly, they can be determined from the experimental data, provided that the signal-to-noise ratio is sufficiently high. On the other hand, if the number of interacting LFMs is large, this procedure becomes impossible. In this case, the observed temperature dependence is similar to a monoexponential law again, and the LFM parameters determined with Eq. (1) can be regarded as "effective" values characterizing the whole LFM ensemble in the environment of the chromophore. Moreover, in this case the individual temperature dependences of different SMs are expected to be approximately identical due to the averaging. The question of how many LFMs influence the SM spectrum depends on the distance within which the coupling between SM and LFMs has measurable effects. Under the assumption that the coupling of the chromophore with LFMs has the same physical origin as the coupling with TLSs, we can estimate the maximum distance for TBT in PIB as the value determined in Ref. 63 which is 20–30 nm. In the case of the toluene matrices, the respective parameters are not known; hence, we cannot estimate the interaction range with the necessary accuracy.

V. EXPERIMENTAL RESULTS AND DISCUSSION

An important requirement of our measurements was that the chromophore molecules must be stable and not undergo photoinduced transformations during the experiment. We succeeded in measuring the individual temperature dependences of SM spectra in the wide temperature range 1.6–40 K. The whole range, however, could only be covered for molecules with particularly high photostability. Furthermore, for data evaluation we selected only those chromophores whose local surroundings were not subject to marked realignments (absence of major spectral jumps) which might change the local parameters of the LFMs. We easily found such molecules in any point of the sample.

Spectra of SMs were extracted from the set of two-dimensional data frames (SM images) recorded with the CCD camera at the different frequency points of the laser scan [see Fig. 1(a)]. Each laser scan comprised 500–1000 images. The program selected pixels which were attributed to SMs based on two criteria: (1) The signals in these pixels should exceed the background noise and (2) they should vary with laser frequency. After identification of the pixels containing a SM image of a given molecule, the signals of all these pixels were summed up yielding the fluorescence intensity of the respective molecule at a given frequency position. The spectra obtained in this way yielded the temperature dependence of the spectral linewidth for each molecule [see Figs. 1(b) and 1(c)]. The program eliminated shifts of

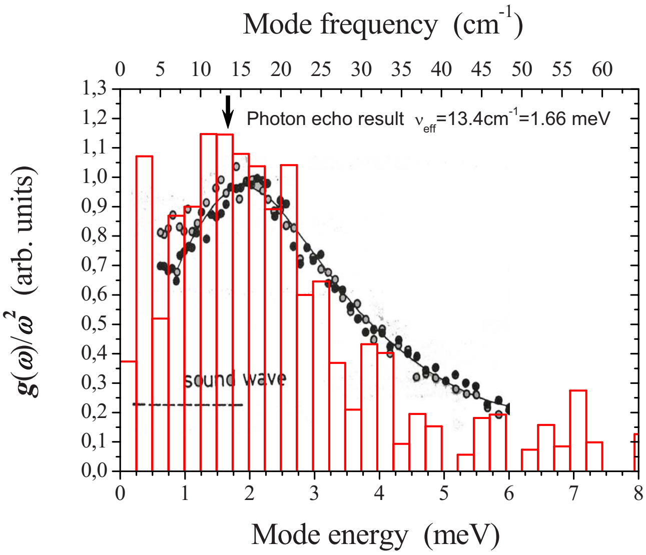

FIG. 2. (Color online) Energy spectrum of the LFMs in PIB doped with TBT and the Boson peak in pure PIB as measured by SMS and inelastic neutron scattering, respectively. *Histogram* represents LFM energies in the local environment of single TBT molecules (this study) and *circles* represent ensemble spectrum of the vibrations constituting the Boson peak as obtained by neutron scattering (Ref. 22). Both distributions were rescaled in the following way: In order to highlight the vibrational excitations exceeding the Debye spectrum, the SMS and neutron-scattering data have been plotted as $g(w)/w^2$, where $g(w)$ is the density of states. The dashed line indicates the contribution of the sound waves in the case of the neutron-scattering data. The arrow indicates the value of the effective frequency of LFMs in the same system as measured with the photon echo technique (Ref. 14). The figure adapted from Ref. 32.

the SM images on the photosensitive area of the camera which may arise after changing the temperature and which are identical for all detected SMs in a given frame.

The LFM contributions in most of the measured temperature dependences showed a monoexponential behavior. It was found that the local parameters of the LFMs (both LFM frequencies and SM-LFM coupling constants) are subject to broad distributions. The LFM frequencies ranged from 2 to 70 cm^{-1} and the coupling constants from 2 to 120 GHz. This result is expected for the case that each SM interacts only with one nearby LFM and the parameters of different LFMs differ. Experiments showed also that the obtained parameters of LFMs did not change during the measurement time. The broad distribution of the local LFM frequencies and the monoexponential temperature dependences of the individual SM linewidths together with temporal stability of the observed LFM parameters strongly support those theories which predict a local and temporally stable character of LFMs in disordered solids.

The distributions of the LFM frequencies for doped PIB, toluene, and toluene-D_8 are presented in Figs. 2 and 3, respectively (histograms). The figures show also the Boson peak as measured in undoped PIB by inelastic neutron scattering,[22] in undoped toluene by Raman scattering,[19] and in doped toluene by nuclear inelastic scattering.[28] One can see that the spectra of the local LFM frequencies obtained

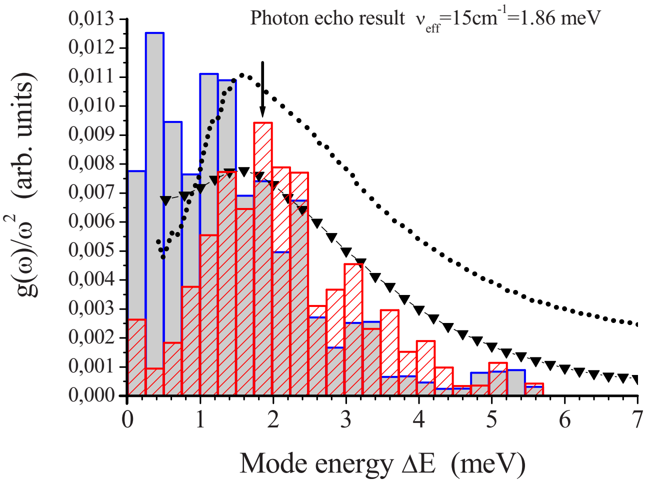

FIG. 3. (Color online) Energy spectrum of the LFMs and the Boson peak in toluene as measured by three different methods in the same representation as in Fig. 2. *Histograms with crosshatched pattern* and *gray solid pattern* represent LFM spectra in toluene and toluene-D_8, respectively, doped with TBT [as measured by SMS technique (Ref. 33)]. Triangles represent the Boson peak as measured by nuclear scattering in toluene doped with ferrocene (Ref. 28); *dotted line* is the Boson peak in pure toluene at 7 K as measured by Raman scattering (Ref. 19). The arrow indicates the effective frequency of LFMs in toluene doped with zinc-octaethylporphine as determined by photon echo (Ref. 29).

with SMS on doped matrices are very similar to the literature data of the Boson peak as measured for the same matrices (both doped and undoped) by different techniques.

Elementary consideration based on the formula $\nu \propto \sqrt{k_{\mathrm{eff}}/m_{\mathrm{eff}}}$ (where k_{eff} is an effective spring constant and m_{eff} is a reduced mass of the atoms involved in the LFM) predicts that LFM frequencies should decrease upon deuteration. The observed isotopic effect in toluene confirms this prediction: Matrix deuteration leads to a clear shift of the LFM spectrum to smaller frequencies (from ~15.5 to ~12 cm^{-1} for the frequency, which corresponds to the maximum of the vibrational spectrum). This shift is close to the value, which is expected if H/D atoms are involved in the vibrations.

When dynamical processes in solids are studied using the optical spectra of probe molecules, the principal question arises as to whether or not the processes under study are affected by the dopant molecules. In the case of crystals, it is well known that the incorporation of impurities leads to significant changes of the dynamics in the vicinity of the impurity molecules and to the appearance of quasilocal low-frequency vibrational modes around them. One may ask whether the same effect occurs also in glasses and what information about the dynamics of the matrix itself is obtained in this case. A definite answer to this question is currently missing.

Most HB and PE experiments have shown that at temperatures below 2–3 K, when the tunneling dynamics predominates, the optical spectra of the chromophore molecules yield representative information about the dynamics of the matrix itself. Yet, this was not true in all cases. For example, in Ref. 14, it was found that the power-law exponent α (see Eq. (2)), which characterizes the tunneling dynamics of the glass matrix, was virtually the same ($\alpha \cong 1.1$) for three different polymers doped with two chromophores (TBT and zinc-tetraphenylporphine), but significantly higher (about 1.9) in the case of a disordered matrix doped with ionic chromophores (resorufin). Taking into account that both TBT and zinc-tetraphenylporphine are neutral and have no dipole moment, one can assume that the above difference is related to the influence of the ionic chromophore on its environment. In particular, Pack *et al.*[64] assumed that ionic chromophores in a glassy matrix cause the so-called "shell effect" (a deviation of the TLS parameters within a spherical shell around the chromophore).

The number of experiments in which the optical spectra of probe molecules were used to investigate the vibrational dynamics of disordered solids is much smaller as compared to studies of the TLS dynamics. It was found that the incorporation of impurity molecules can indeed affect the observed vibrational dynamics of a disordered matrix. For example, in Ref. 14 the comparison of the effective LFM parameters as measured in the same glass matrix (D_6-ethanol) doped with two different chromophores (zinc-tetraphenylporphine and resorufin) revealed significant differences. This result can again be attributed to the influence of the ionic resorufin molecule. Another study found the opposite effect.[28] It was found that doping the four glass matrices toluene, ethylbenzene, dibutylphthalate, and glycerol with ferrocene molecules did not cause noticeable changes of their properties (static structure factor and calorimetric glass transition temperature) or of the parameters of their Boson peak. Also, different concentrations of ferrocene had no influence on the vibrational dynamics.

In our experiments, we used the chromophore TBT which is neutral and nonpolar. In view of the literature data, we expect that the incorporation of this dopant should not influence the vibrational dynamics of the matrix strongly, in particular, since the building blocks of the chromophore and of the matrices are very similar. This assumption is confirmed by the similar LFM and Boson peak spectra in doped and undoped PIB and toluene as measured in the present study and in Refs. 19, 22, and 28. Also, the vibrational spectra in toluene doped with two different molecules—TBT in our study and ferrocene in the case of nuclear scattering—agree very well. Hence, the incorporation of a small amount of TBT molecules into amorphous PIB and toluene glass does not seem to change the vibrational dynamics noticeably. This fact is of great general importance for the optical spectroscopy of impurity centers in glasses. For the interpretation of studies made by this technique, it is highly desirable that the incorporation of a small amount of probe molecules in a disordered matrix does not give rise to new vibrations and does not affect the parameters of the measured dynamics.

The above fact, together with two aforementioned essential results of this study, namely, (1) the coincidence of LFM spectra measured in doped PIB and toluene via SMS with Boson peak data, obtained by principally different methods and (2) the coincidence of the observed deuteration effect in toluene with the predicted one, when only one parameter is changed—the mass of H atoms in toluene matrix, allows us to make important conclusion: The SMS yields representative information about low-frequency vibrational dynamics inherent in the matrices under study. Moreover, we can conclude that the microscopic origin of the vibrations, which cause the line broadening in the spectra of single TBT molecules in PIB and toluene, and of the vibrations, which constitute the Boson peak in undoped PIB and in doped and undoped toluene, is the same. These conclusions open up new possibilities for investigating microscopic nature of vibrational excitations in amorphous solids.

At the end, we compare our results with the photon echo data of doped PIB and toluene obtained in Refs. 14, 29, and 65. The photon echo yields information about the vibrational dynamics in solids by measuring the effective optical dephasing time T_2 of the chromophores. The T_2 values obtained in this way characterize the interaction of the chromophores with the dynamical excitations in matrix, averaged over the whole ensemble of chromophores in the sample. Usually it is assumed that in the case of amorphous solids the temperature dependence of T_2 reflects the dynamics of the averaged frequency spectrum of the LFMs (see, e.g., Refs. 29 and 65).

In Refs. 14 and 29, the T_2 values of doped PIB and toluene were measured in a broad interval of low temperatures (0.35–100 K). In the case of PIB, the dopant was the same as in our experiments (TBT), whereas in the case of toluene it was zinc-octaethylporhine. From the T_2 values, the authors determined the temperature dependence of the homogeneous zero-phonon linewidth $\Gamma^{\mathrm{PE}}(T)$, according to the well-known relation: $\Gamma^{\mathrm{PE}}(T)=1/\pi T_2(T)=1/2\pi T_1+1/\pi T_2'(T)$, where T_1 is the excited-state lifetime and T_2 and T_2' are the total and pure optical dephasing times, respectively. T_2' characterizes the coupling of the chromophores with the vibrational excitations in their local environment.

As was discussed above, $\Gamma^{\mathrm{PE}}(T)$ can be described by three contributions which correspond to the natural linewidth and the contributions of the TLSs and the LFMs to the dephasing of the chromophores [cf. Eq. (2)]. Hence, the authors of the photon echo studies[14,29] described their data with the expression

$$\Gamma^{\mathrm{PE}}(T)=\Gamma_0+bT^{\alpha}+w_{\mathrm{eff}}\frac{\exp(-h\nu_{\mathrm{eff}}/kT)}{[1-\exp(-h\nu_{\mathrm{eff}}/kT)]^2}, \qquad (3)$$

where w_{eff} and ν_{eff} are averaged values of the chromophore-LFM coupling constant and LFM frequency, respectively. They could show that at $T > 4-5$ K, the observed T dependences are mainly determined by the interaction of the chromophores with the LFMs and that the TLS contribution can be neglected. Figure 4 displays the high-temperature part of the T dependences of $\Gamma^{\mathrm{PE}}(T)$ for doped PIB (a) and toluene (b), as measured in Refs. 14 and 29 and the LFM contributions as obtained by fitting the high-temperature part of Eq. (3),

$$\Delta\Gamma_{\mathrm{LFM}}(T)=w_{\mathrm{eff}}\frac{\exp(-h\nu_{\mathrm{eff}}/kT)}{[1-\exp(-h\nu_{\mathrm{eff}}/kT)]^2}, \qquad (4)$$

to the experimental data. This expression is similar to Eq. (1), but there is one principal difference. In the case of Eq.

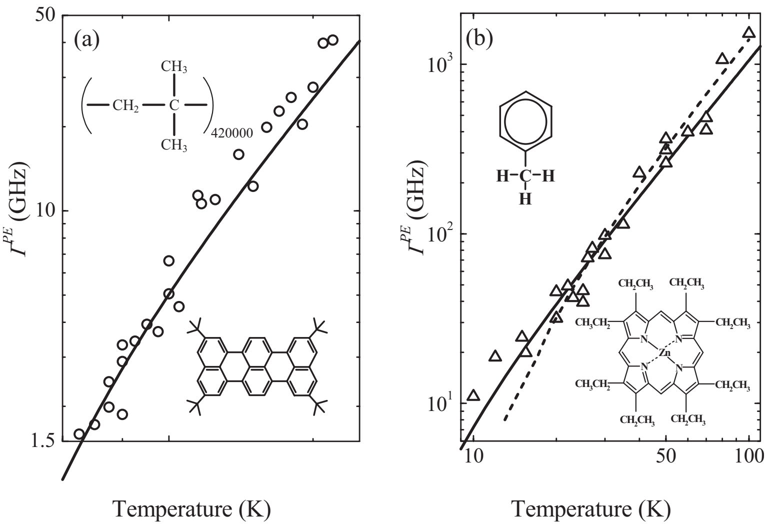

FIG. 4. Temperature dependences of the inverse optical dephasing times $\Gamma^{\mathrm{PE}}(T)=1/\pi T_2(T)$, (a) as measured via photon echo for PIB doped with TBT (*open circles*) and (b) toluene doped with zinc-octaethylporhine (*triangles*). The solid lines represent the best fits with Eq. (4). The insets show the structural formulas of probe molecules (bottom right) and matrices (top left). The dashed line in (b) presents the fit of $\Gamma^{\mathrm{PE}}(T)$ using the Boson peak data as obtained in Raman-scattering experiments (see details in Refs. 29 and 65).

(1), the linewidth $\Gamma^i(T)$ is obtained by summing over different w_i and ν_i, whereas in Eq. (4), $\Delta\Gamma_{\mathrm{LFM}}(T)$ is described by averaged values w_{eff} and ν_{eff}. We used the values of ν_{eff}, which can be considered as "effective" LFM frequencies as measured by the photon echo technique, for the comparison with the LFM spectra obtained in our experiments.

The comparison of our results with the photon echo data allows us to answer also the question: What is the relationship of the frequency spectrum of LFMs as obtained by SMS to the "effective" frequency of matrix vibrations ν_{eff} as determined via photon echo? To this end, we indicate the values of ν_{eff} for PIB and toluene in Figs. 2 and 3, respectively. In both cases, ν_{eff} is very close to the maximum of the spectrum of the local LFM frequencies. Hence, the ν_{eff} values correspond also to the maximum of the Boson peak for the two matrix materials as measured on undoped samples or samples with different chromophores. Another important conclusion can be drawn from the comparison of the PE data with the temperature dependence of the inverse optical dephasing times $1/\pi T_2(T)$, as calculated from the Boson peak data obtained in Raman-scattering experiments.[19] In Refs. 29 and 65, it was shown that the T dependence of the inverse optical dephasing time (i.e., the homogeneous zero-phonon linewidth) for toluene glass at temperatures from a few up to several tens of Kelvin can be satisfactorily described by an interaction of the chromophores with the broad continuous LFM spectrum (dashed line in Fig. 3), taken from independent Raman-scattering experiments [see dashed line in Fig. 4(b)]. Thus, the spectra of local LFM frequencies obtained in the present SMS study and the photon echo data of doped PIB and toluene yield valuable complementary information about the vibrational dynamics of amorphous solids, at least for these two materials.

VI. TEMPORAL STABILITY OF LFM PARAMETERS

One of the most important questions concerning microscopic nature of LFMs in disordered solids is the temporal stability of their characteristics. In fact, long-time stability of LFM parameters within some fixed microscopic volume of the sample would be the evidence of minor role of structure relaxation processes in system under study at a given temperature. Moreover, vice versa significant changes of LFM parameters on nanometer scale demonstrate that structure relaxation processes in system play an important role. SMS opens incomparable way to shed light on this question. As it was mentioned above, a single chromophore molecule senses dynamical processes in the nearest (not more than a few tens of nanometers) environment. Interaction of SM with fast excitations like LFM leads to SM spectral line broadening. As a result, changes in fast dynamics (i.e., changes of LFM characteristics within local environment of the SM) should look like change of SM spectral linewidth. This is a main idea of the experiment discussed below. We monitored the spectral linewidth of a selected single TBT molecule in a matrix under study during long period of time using the technique of repeated detection of fluorescence excitation spectra.

Figure 5 presents slow dynamics in surroundings of some single TBT molecule in amorphous PIB (molecular weight 420 000) as observed in spectra of this molecule during more than 4 h at $T=7$ K. On the left panel (a), the time dependence of spectral linewidth of the SM under study is shown. Right panel (b) presents spectral trajectory of this SM on the same time scale, which reveals spectral jumps caused by nearby TLSs. Short spikes on graph (a) correspond to the scans which suddenly concur with jump of the spectrum. Note that the observed linewidth dispersion for selected SM in different laser scans is within experimental error and is much smaller in comparison with linewidth distribution of big number of different SM molecules [Fig. 5(c)].

The above picture clearly demonstrates that the line broadening in the local environment of SM in PIB practically does not change during the whole time of the measurement (up to 5 h). Experiments showed that both parameters of LFMs interacting with the SM under study (LFM frequencies and coupling constants) were stable during the whole observation time.

The same measurements were performed with single TBT molecules incorporated in shock-frozen toluene (see Fig. 6). As was found in Ref. 33, slow dynamics in this glass is much more complicated than predicted by the standard tunneling

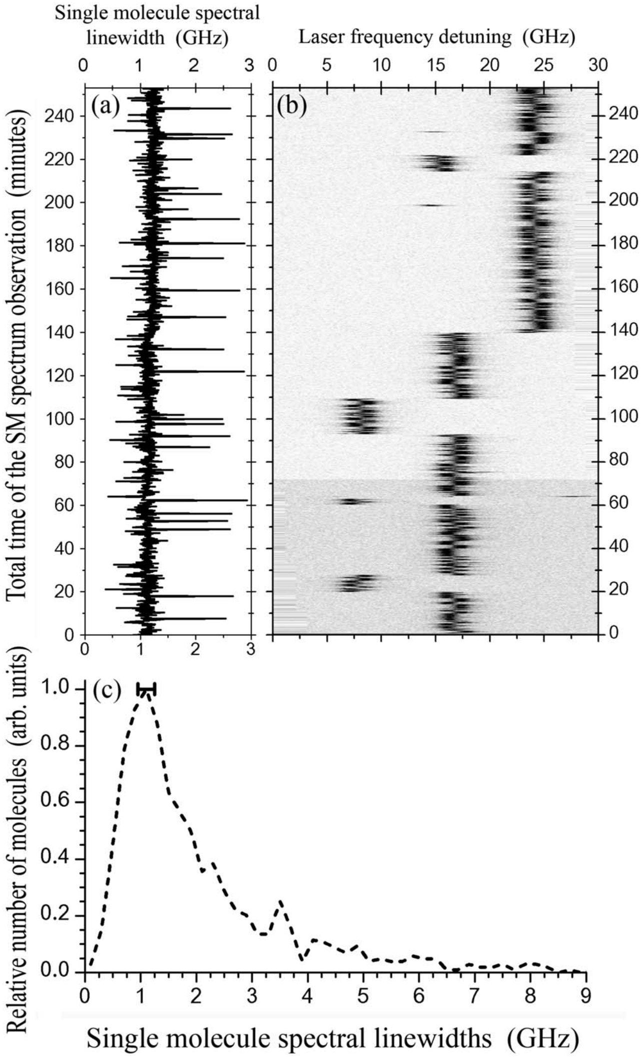

FIG. 5. Slow dynamics in nearby environment of some single TBT molecule in PIB matrix ($M=420\,000$) as observed in spectra of this molecule during more than 4 h at $T=7$ K. (a) Temporal behavior of spectral linewidth of molecule under study; (b) spectral trajectory of observed SM, which demonstrates spectral jumps, caused by nearby TLSs (total number of laser scans is 1513). (c) Distribution of linewidths of 951 single TBT molecules in $\mathrm{PIB}_{420\,000}$ at $T=7$ K (*dashed line*). Short segment on lower graph corresponds to the dispersion of linewidths for the same molecule in different scans.

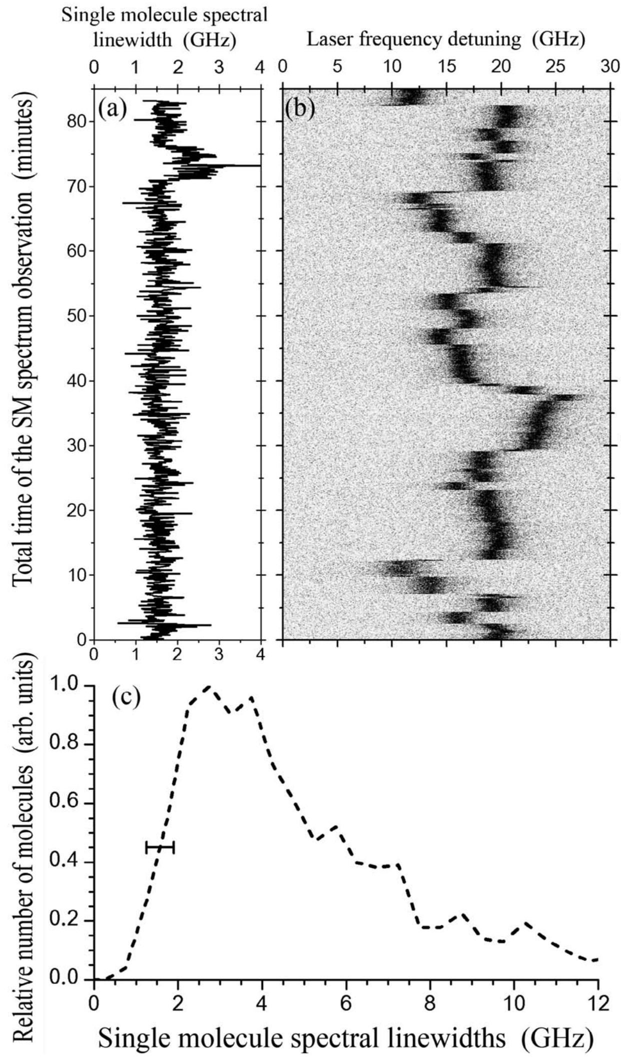

FIG. 6. The same as shown on Fig. 5, but for TBT molecules incorporated in shock-frozen toluene at $T=7$ K. Total number of scans is 996. Number of single molecules in the linewidth distribution in (c) is 1238.

TLS model. Extra contributions to the dynamics observed in this system cause drifts and irreproducible jumps of the SM spectra [Fig. 6(b)]. However, as one can see from Fig. 6(a), the line broadening processes, which determine the value of SM linewidth measured during laser scan, were very stable on the time scale of several hours. In fact, parameters of LFMs determined from spectra of single TBT molecules in shock-frozen toluene did not change during the whole time of the measurement (excluding minor increase of linewidth at 70–75 min of the measurement). The observed linewidth dispersion of the selected SM in different laser scans [Fig. 6(c)] was also within experimental error.

Thus, our experiments revealed important result: The local parameters of LFMs determined from spectra of observed SMs, both in the cases of PIB and shock-frozen toluene did not change during the experimental run (up to 5 h). This result is not obvious. It indicates that the local environment of the selected SMs in both dye-matrix systems was stable und did not undergo noticeable structural realignments in the whole temperature region. At given temperature (7 K), the main contribution to the SM spectral linewidth is coming from the interaction of a chromophore with vibrational excitations (LFMs).

VII. SUMMARY

Our results clearly demonstrate that SMS provides new experimental possibilities for studying the vibrational dynamics of disordered solids on a microscopic level. The data improve our understanding of the microscopic nature and properties of the Boson peak and its relationship to the vibrational excitations in glasses.

The optical spectra of a large number of individual probe molecules in an amorphous polymer matrix and a low-molecular-weight glass were measured over a broad temperature interval (1.6–40 K). From the individual temperature dependences of their spectral linewidths, we calculated the local vibration frequencies and the local chromophore—LFM coupling constants in the environment of the chromophores. For both parameters we found broad distributions. These results indicate the local character of the vibrational modes and support those theories which predict a local and stable character of the vibrations constituting the Boson peak.

The comparative analysis of the local LFM frequency distributions determined experimentally via SMS and the Boson peak as measured in the pure polymer by inelastic neutron scattering, in pure toluene glass by Raman scattering, and in doped toluene by nuclear inelastic scattering revealed close agreement between our data and the literature data of the Boson peak. This finding clearly demonstrates the direct relationship between the Boson peak and the local vibrations which are inherent to glasses.

The comparison of the SMS and photon echo data demonstrates that also the magnitude of the effective vibration frequencies obtained in photon echo experiments correspond to the maxima of the local LFM spectra. The temperature dependence of the inverse optical dephasing time (i.e., the homogeneous zero-phonon linewidth) can be satisfactorily described with the broad continuous LFM spectrum taken from Raman-scattering experiments up to several tens of Kelvins.

An important result is that doping the matrices with a small amount of nonpolar chromophores whose chemical composition is similar to that of the matrix molecules does not affect the observed vibrational dynamics significantly.

The new experimental results were obtained, which confirm long term (a few hours) stability of local LFM parameters both in polyisobutylene ($M=420\,000$) and frozen toluene matrices at $T=7$ K.

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