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Frequency dependence of the quadratic electron-phonon coupling constant in a polymer glass: Direct measurement by single-molecule spectroscopy

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The frequency dependence of the quadratic coupling constant between the electron system of the chromophores and the quasilocal vibrational modes of the matrix, $B(\omega_0)$, and its distribution was measured in a disordered system via single-molecule spectroscopy. A correlation between B and ω_0 was found which does not follow a power law. The analysis of this result allows us to suggest that, for a correct description of the broadening of optical impurity spectra in disordered solids, the applicability of the weak-coupling limit and the long-wavelength approximation should be considered separately for each single molecule interacting with its local environment. A simple formulation of the electron-phonon coupling theory for the dye-matrix system as a whole is, in general, not appropriate.

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The interaction between electronic and lattice vibrational degrees of freedom in solids plays an important role in a variety of processes, and determines such fundamental physical phenomena as superconductivity, exciton scattering, infrared light absorption, etc. One of the fields in which electron-phonon coupling plays the main role is the *optical spectroscopy of impurity centers* in solids. This method has been used for the study of *low-frequency vibrational modes* (LFMs) in crystals and amorphous solids.[1] In doped crystals, the LFMs arise around impurity centers (here we will consider only molecules) if an impurity-host-lattice local-mode frequency falls within a phonon band of the host crystal. Thus they are slightly delocalized by mixing with the matrix modes. In the case of disordered solids (for simplicity we will call all disordered solids "glasses," which, however, is not correct in general), LFMs exist even in pure materials without dopants.[2–6] It is widely accepted that their localization is caused by internal disorder. One assumes that LFMs are associated with the vibrational motions of confined groups of atoms or molecules within local potential minima and have small spatial extensions. Not many details about the nature and properties of these vibrations are known. The hypotheses proposed for the description of LFMs in glasses are based on different concepts and no consensus on the main assumptions of these models has been achieved so far.

Despite substantial efforts in studying LFMs and their coupling with optical transitions of impurity molecules, most of the principal questions concerning these phenomena both in the case of crystals and glasses are still open. All techniques used so far for the above-mentioned studies yield data averaged over a macroscopically large volume of the sample which includes numerous excitations and probe molecules. In glasses, however, the individual parameters of LFMs are expected to be subject to distributions so the above averaging leads to a considerable loss of information about the local dynamics. This makes it principally important to obtain experimental information about the origin of LFMs and their interaction with the chromophore molecules on a microscopic level. The latter can only be obtained by single-molecule spectroscopy (SMS) (see, e.g., Refs. 7–11, and references therein). It is important in the context of the present paper that SMS measures local (even individual) parameters of LFMs in polycrystalline[12,13] and disordered solids.[14–16]

In this work we present the experimental data of the frequency dependence of the quadratic electron-phonon coupling constant between the electronic transition of single chromophore molecules (SMs) and the LFMs in a doped disordered solid [amorphous *polyisobutylene* (PIB) doped with *tetra-tert-butylterrylene* (TBT) molecules] via SMS.

The individual optical spectra of isolated impurity molecules in crystals consist of a narrow zero-phonon line (ZPL) and a relatively broad phonon sideband (PSB). The ZPL results from a purely electronic transition without the creation or annihilation of matrix phonons; the PSB corresponds to a transition with accompanying emission or absorption of one or several phonons. In general, the position and shape of the ZPL is determined by the operator of electron-phonon interaction, $\hat{\Lambda}$, which depends on the nuclear coordinates q_j of the matrix atoms and can generally be expanded in a series as

$$\Lambda = \sum_j V_j q_j + \sum_{jj'} W_{jj'} q_j q_{j'} + \ \dots\ , \tag{1}$$

where the first term describes the *linear* electron-phonon interaction responsible for the relation between the integral intensities of ZPL and PSB, and the second term corresponds to the *quadratic* electron-phonon coupling, which causes the temperature-dependent homogeneous broadening and frequency shift of the ZPL; j and j' are the indices of normal coordinates.

Most of the current theories consider the interaction of electronic transitions of impurity SMs with acoustic phonons (e.g., Refs. 17–22) and pseudolocal phonons or LFMs (e.g., Refs. 21, 23, and 24) only for well-ordered *crystals* using a simple model of the LFMs. In the case of disordered solids, a comprehensive description of electron-phonon coupling is still absent.

Disordered solids differ fundamentally from crystals by

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their anomalous dynamics at low temperatures. According to numerous experiments at temperatures below several tens of kelvins, the dynamics in glasses is determined (in addition to acoustic phonons) by tunneling two-level systems[25,26] and LFMs. As a result, the shape and temporal behavior of ZPL and PSB in glasses (e.g., Refs. 21 and 27–29, and references therein) have a more complicated character than in doped crystals. Nevertheless, as was shown in numerous studies (e.g., Refs. 30–32), the concept of ZPL and PSB can be used in glasses, as well.

For the general case (at any strength of electron-phonon coupling) the following expression describing the spectral broadening (full width at half maximum) of the ZPL due to quadratic electron–local-phonon coupling was derived in Ref. 23 and later confirmed in Ref. 24:

$$\gamma = \frac{1}{4\pi}\int_0^\infty d\omega \ln\left\{1 + \frac{4n(\omega)[n(\omega)+1]W^2\Gamma_0(\omega)^2}{[1 - W\Omega_0(\omega)]^2 + W^2\Gamma_0(\omega)^2}\right\}, \quad (2)$$

where $n(\omega)=[\exp(\hbar\omega/kT)-1]^{-1}$ is the Bose factor, $\Gamma_0(\omega)$ is the dimensionless weighted density of states of the local phonons in the electronic ground state of the impurity, $\Omega_0(\omega)=\frac{2}{\pi}\int_0^\infty d\nu \Gamma_0(\nu) P[\nu/(\omega^2-\nu^2)]$ (P denoting the principal value), and W is the dimensionless quadratic coupling constant ($-1 < W < \infty$). Most theories consider W as a phenomenological constant, which hides inside it many physical details of the electron-phonon interaction. Among other points there is a question about the dependence of W on the frequency ω of a vibrational mode and its distance R from the chromophore, which is of principal importance for the development of microscopic models of electron-pseudolocal phonon coupling.

Considering the special case of a sharply peaked Lorentzian density of states $\Gamma_0(\omega)$, and introducing dimensionless variables $z=\omega/\omega_0$ and $\upsilon = 1/2\omega_0\tau_0$ (with ω_0 and τ_0 being the frequency and lifetime of the pseudolocal phonon mode, respectively), as was derived in Ref. 24, expression (2) simplifies to

$$\gamma = \frac{1}{4\pi}\int_0^\infty d\omega \ln\{1 + 4n(\omega)[n(\omega)+1]W^2\Gamma_0(\omega)\Gamma_1(\omega)\}, \quad (3)$$

where $\Gamma_0(\omega)=(\upsilon z/2)/[(z-1)^2+\upsilon^2]$, $\Gamma_1(\omega)=[\Gamma_0(\omega)]/\{[1-W\Omega_0(\omega)]^2+W^2\Gamma_0(\omega)^2\}$, and $\Omega_0(\omega)=\frac{1}{2}(\{(z-1-\upsilon^2)/[(z-1)^2+\upsilon^2]\}-[1/(z+1)])$.

In the weak-coupling limit $|W| \ll \upsilon$, expression (3) reduces further to the following simple form:

$$\gamma_{\text{weak}} = B\frac{\exp(-\hbar\omega_0/kT)}{[1-\exp(-\hbar\omega_0/kT)]^2}, \quad (4)$$

where

$$B \propto (W/\omega_0)^2 \quad (5)$$

is the constant of quadratic coupling between the electronic transition of the impurity chromophore and the pseudolocal vibrational mode of the matrix *within the weak-coupling limit*.

Numerous experimental and theoretical investigations have justified the assumption that the weak-coupling limit is valid for most mixed crystals. Moreover, it is usually believed that Eq. (4) is also applicable to low-temperature glasses. This point is confirmed, in particular, by the results of photon echo (PE) and hole-burning (HB) studies on several doped organic amorphous systems, which have shown that in these systems Eq. (4) describes the LFM contribution to the homogeneous linewidth with sufficient accuracy[21,30–34] in a broad range of low temperatures (from a few kelvins up to a few tens of kelvins). One should emphasize that it was always believed that the applicability of the weak-coupling limit is *a property of the impurity-matrix system as a whole*. Describing the electron-phonon (or electron-pseudolocal phonon) interaction, no theory has ever considered the possibility that the weak-coupling limit may be applicable only for part of the individual impurity molecules in the system, depending on the special parameters of the chromophore-LFM pair.

The reason for this approach is that all the data evaluated so far were obtained by ensemble-averaging techniques (fluorescence line narrowing, HB, PE), which lose a significant part of the information about the microscopic nature of electron-vibrational-mode interaction. The experiments confirmed only that the weak-coupling limit is justified (or not) for the selected dye-matrix system, based on the average of a huge number of impurity molecules, and it was impossible to decide whether the limit is universally true for each individual molecule. The ensemble-averaging studies obscure also the very important information about the dependence of the coupling constant on the frequency of the vibrational excitations $B(\omega_0)$ [or $W(\omega_0)$] and on their distance from the impurity molecule $B(R)$ [or $W(R)$].

In the long-wavelength approximation, since the wave vector of a mode is proportional to ω_0, the coupling constant has the dependence $W \propto \omega_0^2$ (see, e.g., Refs. 30 and 35) which, according to Eq. (5), results in

$$B \propto \omega_0^2. \quad (6)$$

This variation has never been checked experimentally, however, because of the absence of appropriate experimental techniques.

In the present work we propose and demonstrate a technique which allows us to avoid the above problems and to measure the dependence $B(\omega_0)$, even in the case of amorphous solids. Our procedure (described in Refs. 14, 16, and 36) allows us to record the spectra of a large number of SMs in the sample simultaneously over a broad temperature interval and to determine the individual temperature dependences of their optical linewidths. The sample of ~500 nm thickness was prepared by spin coating a toluene solution of PIB (M_w=420 000 g/mol, purchased from Sigma-Aldrich Co) weakly doped with TBT (kindly provided by Th. Basché, University of Mainz, Germany) onto a microscope slide. The excitation wavelength was varied in the range of 575–581 nm, with the laser having a spectral width of ~2 MHz.

We observed individual ZPLs of photostable single TBT molecules at different locations in the sample in the temperature interval of 1.6–40 K. Our analysis was based on the fact that the interaction of a SM with LFMs contributes mainly to the broadening (rather than the splitting) of the peaks in its

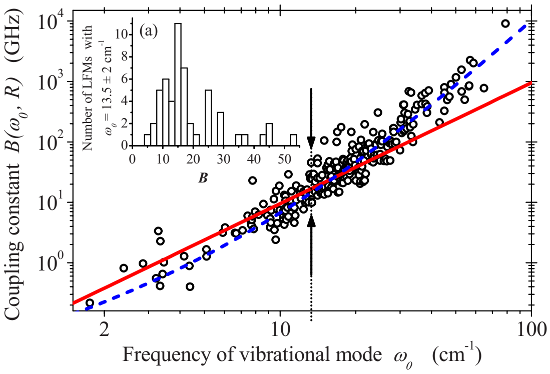

FIG. 1. (Color online) Variation in the quadratic coupling constant B between SMs and LFMs with the vibration frequency ω_0 (*circles*) for single TBT molecules in amorphous PIB. At each frequency ω_0 the values of B are subject to a distribution due to the different distances and relative orientations between probe molecules and LFMs. The *dashed line* is a guide to the eye for the data points. The *solid line* represents the fit with a quadratic dependence, $B = a\omega_0^2$. The arrows indicate the region of possible B values at the frequency $\omega_{\mathrm{BP}} \approx 13.5$ cm^{-1} which is near the maximum of the Boson peak (Refs. 16 and 37). The *histogram* in the inset (a) presents the distribution of B in a narrow frequency range $\Delta\omega_0 = \omega_{\mathrm{BP}} \pm 2$ cm^{-1}. Note the double-logarithmic representation in the main figure.

spectrum. As was shown in Refs. 14 and 15, at $T > 8-10$ K the line broadening of SM spectra in PIB is mainly determined by the interaction with LFMs. The widths of the highest peaks of the recorded SM spectra were determined by fits with a Lorentzian profile. In this way the individual temperature dependences of the spectral widths of 281 different SMs were measured. Fits of the high-temperature part of these T dependences with Eq. (4) yielded the following pairs of parameters: the characteristic frequency ω_0 of the LFM coupling most strongly to the investigated SM, and the constant B of quadratic coupling in this SM-LFM pair (within the approximation of the weak-coupling limit).

The obtained data of B are plotted in Fig. 1 as a function of ω_0. They reveal a strong correlation between the two parameters. The data also show that at a fixed frequency ω_0 the distribution of B has clear lower and upper bounds. This is the *essential result* of our study. It allows us to obtain information about the frequency dependence of B by proper statistical analysis of the data.

The reason why the B values are subject to a distribution at a given LFM frequency looks clear: for each ω_0 the SM-LFM pairs have different distances and different relative orientations. Moreover, we expect that not all the SM-LFM pairs can be described within the weak-coupling limit, in particular in those cases in which the chromophore is located inside, or very close to, a LFM. The experimental finding that the distributions of B values along the vertical axis have lower and upper bounds can also be explained. B cannot be very large because the smallest distances between SMs and LFMs are determined by their nonzero sizes (existence of a minimum distance $R_{\min}$). On the other hand, B cannot be arbitrarily small either because the maximum distance $R_{\max}$ between a SM and the surrounding LFMs is on the order of the average distance between the LFMs in the matrix (for clarity see Fig. 2). Hence, the distributions of B must be limited.

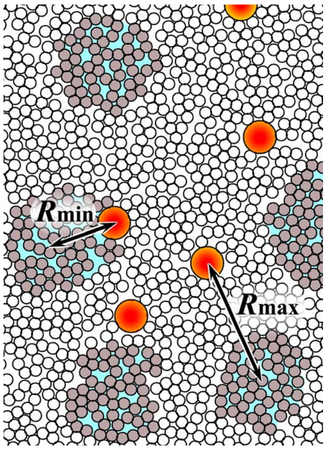

FIG. 2. (Color online) Sketch of a two-dimensional model glass consisting of round particles. Small circles represent lattice atoms (or molecules) while large circles correspond to impurity molecules. Atoms, which are involved in hypothetical LFMs, are highlighted by gray color. Arrows indicate the existence of a minimum distance $R_{\min}$ and a maximum distance $R_{\max}$ between SM and LFM, which are determined by the spatial extension of the LFMs and their average distance, respectively.

This makes it possible to determine the dependence of B on ω_0 by averaging the measured values of B at each frequency ω_0. The resulting dependence $B(\omega_0)$ is clearly nonlinear in the double-logarithmic plot of Fig. 1 (dashed line); i.e., it does not follow a power law. The best fit with a power law $B(\omega_0) \propto \omega_0^{\alpha}$ yields an exponent $a \approx 2.6$, which also differs markedly from the prediction $B \propto \omega_0^2$ of the weak-coupling theory (solid line), especially at high frequencies.

The dependence $B(\omega_0)$ and, especially, distributions of B at a fixed frequency ω_0 are insufficiently known. One can find few discussions in which the possible shape of this dependence was mentioned indirectly. For instance, the authors of Ref. 32 considered the spectral dynamics in doped polymer glasses. Taking into account that the factor B has the dimension of an energy, they assumed it to be of the form $B_j = k_j\omega_{0j}$, where k_j is a parameter and ω_{0j} the frequency of the jth local mode. The authors, however, stressed that the physical origin of this factor is unknown. We hope that the experimental single-molecule data of the frequency dependence of the quadratic electron-phonon coupling parameter in doped amorphous PIB presented in this study open up possibilities for the development of microscopic models describing the vibrational dynamics and the electron-phonon interaction in disordered solids. Moreover, it appears possible now to obtain information about the dependence of B on the distance between SM and local vibrations. In fact, the distribution of B at a fixed frequency ω_0 [Fig. 1(a)] is directly related to the dependence $W(R)$, the spatial distribution of LFMs, and probe molecules, and their relative orientations. With reasonable physical assumptions it should be possible to obtain $B(R)$ from SMS data.

We can suggest several possible explanations for the observed deviation of the experimental dependence $B(\omega_0)$ from a square law: (1) For describing the broadening of the optical spectra of chromophore molecules in disordered solids, the applicability of the weak-coupling limit in the electron-phonon interaction should be considered for each single molecule interacting with its local environment and not for the dye-matrix system as a whole. (2) The developed models which lead to the dependence $B \propto \omega_0^2$ may not be valid for all individual SM-LFM pairs in a given system, even if the weak-coupling limit applies. As a support of the second point we can refer to the circumstance that in glasses as well as in crystals, the long-wavelength approximation is valid only for low frequencies.[35] Correspondingly, the frequency dependence $W \propto \omega_0^2$ (and $B \propto \omega_0^2$) is only true for small ω_0 values. This is exactly what our experimental results suggest (see Fig. 1). (3) With increasing of temperature, the observed temperature dependence can be sensitive to more than one LFM with different frequency. (4) The general thermal expansion of matrix with temperature[38] should be perhaps taken into account. (5) The long-wavelength approximation, which considers acoustic phonon, can be broken in glasses. As a result Eq. (6) cannot be valid for LFMs in disordered solids.

The obtained results are significant for the spectroscopy of impurity centers in general. They show that a theory of electron-phonon interaction in disordered dye-matrix systems should describe each pair of molecule LFM individually using not only different parameters but different approximations for each pair. For example, weak-coupling approximation can be valid for one SM-LFM pair but not valid for another. We assure also that careful analysis of observed dependences could give data about characteristic expansion and spatial density of LFMs in disordered solids.

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