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Spectroscopic studies of impurity-host interactions in dye-doped polymers: Hydrostatic-pressure effects versus temperature effects

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The method of photochemical hole burning is an excellent means for investigating small pressure shifts of the optical transitions of dye molecules embedded in polymeric host matrices. We have investigated both pressure- and temperature-induced line shifts and line broadenings and have been able to separate volume and temperature effects, which cannot be distinguished by only considering temperature-cycling experiments. On the basis of a concept, originally developed for vibrational dephasing in liquids, which separates the impurity-host interaction potential into two parts, we are able to determine quasistatic and dynamic contributions of the considered molecular interaction potentials in a quantitative fashion. These two contributions are opposite in sign and partially compensate each other in a temperature-cycling experiment. The "static" linewidth and line-shift parameters are governed by the van der Waals–like part of the impurity-host interaction potential and yield matrix parameters like the polymer compressibility κ by solely evaluating spectroscopic experimental data. The more complex "dynamic" contributions require the assumption of a steep short-range repulsive part of the interaction potential which is mainly responsible for the scattering (T_2) processes leading to a phase loss in ground and excited states of the dye molecule. For our experimental studies we used the polymer glasses polymethylmethacrylate, polystyrene, and polyethylene doped with the dye molecule free-base phthalocyanine (H_2Pc).

I. INTRODUCTION

The temperature and pressure tuning of homogeneous optical lines is closely related to the theory of line shifts and shapes. We shall, therefore, begin this paper by briefly summarizing the basic ideas of the different line-shape theories developed up to now. There are, as for instance outlined in Ref. 1, basically two approaches for the interpretation of spectral line shapes in terms of the underlying mechanisms of the interaction between excited states and their local environment: stochastic models on the one hand and various microscopic Hamiltonian models on the other.

In the stochastic models the use of density-matrix methods for the calculation of a large variety of correlation functions characteristic of the various fields like NMR, ESR, vibrational and electronic absorption, and Raman scattering experiments has become standard since the pioneering studies of Anderson[2] and Kubo and Tomita[3] in the early 1950s. Of particular interest are the experimental parameters such as the homogeneous and inhomogeneous linewidths of the involved transitions, which contain—in principle—information about the specific interactions of the excitations which are studied (e.g., nuclear or electron spins or vibrational or electronic transition dipole operators) with their matrix environment which may consist of other (different) electron spins, of nuclear spins, or of lattice excitations (phonons). This latter part is, in general, treated only in terms of its average properties characterized by an "equilibrium" temperature and thus can serve as a heat bath. The connection between the excitation of a given physical quantity and its subsequent time evolution is made by calculating the corresponding time or ensemble average. This automatically takes care of the dynamics of the bath system. In the reciprocal-wave-vector and frequency space, the modification of the original energy eigenvalue is expressed by a complex self-energy leading to both a shift and a broadening of the originally sharp transition energy. It is this quantity, which can be directly compared with the experimental values of the corresponding energy shifts and homogeneous line widths. The application of density-matrix techniques to infrared absorption and Raman scattering in liquids was first made by Gordon[4] in a series of seminal papers. Extensions to deal with the irreversible aspects of this description were subsequently made by several authors,[5–11] and it is, in particular, the approach of Schweizer and Chandler (SC) (Ref. 5) which we intend to apply to the problem of optical linewidths and shifts of photochemically generated holes in polymers. The SC approach belongs to the class of theories which extract a phase-dependent part from the normalized correlation function, which describes the loss of coherence in the excited state due to a random, cumulative modulation of the phase by collisions with the bath system, e.g., for liquids with the constituents of the solvent. The standard statistical assumption about the random (stochastic) nature of this modulation implies that the bath correlation times are short compared to the experimental time of interest. The cumulative loss of phase memory due to the random modulation of the frequency then directly leads to a decay of the appropriate correlation function, and corresponds in a NMR or ESR description to a T_2 process.

The pioneering work on microscopic theories has been done by McCumber and Sturge.[12] Their perturbation approach has been extended by various authors[13–18] in the past years who consider the influence of quadratic electron-phonon coupling using perturbation theory of infinite order. The calculations have been performed by cumulant expansion (Osad'ko[13] and Hsu and Skinner[14–17]) or by optical Redfield theory (de Bree and Wiersma[18]). All theories consider the influence of Debye, optical, and pseudolocal phonons on optical transitions and can therefore describe, to a certain extent, transitions in both crystalline and amorphous materials.

Since amorphous materials show, at low temperatures, evidence for additional low-lying excitations usually referred to as two-level systems (TLS's),[19,20] linewidth theories for transitions in amorphous host systems have to take the influence of the TLS's into account.[21–25] Various coupling mechanisms for the TLS to the transition and the phonon bath have been proposed by different authors. Most of the theories can explain the observed temperature dependencies of the linewidths. In a recent paper by Osad'ko[26] the various contributions to the homogeneous linewidth are discussed. It is shown that both TLS's and phonon processes must be simultaneously considered. The TLS's contribute in a twofold fashion: by a "static" and by a "dynamic" line shift and broadening process. The static part represents a "slow" (compared to T_2) relaxation by a single-barrier crossing leading to a shift of the center frequency of the optical excitation considered. This process is usually referred to as spectral diffusion and is, although it can lead to Lorentzian line shapes, inhomogeneous in nature. The dynamic TLS contribution takes into account repeated barrier crossings induced, for example, by phonon scattering processes with the TLS. The method of separating the influence of the TLS into a static and a dynamic part has, to our knowledge, been proposed for the first time by Morgan *et al.*[27] some years ago. The authors argue that dynamic contributions cause homogeneous line shifts and broadenings whereas static contributions cause inhomogeneous shifts and broadenings. Our own arguments will, in the following, be partially based on similar considerations.

Osad'ko shows that beside these TLS processes, phonon processes both of acoustic phonons and, especially in amorphous systems, of localized phonons contribute to the homogeneous linewidth. In his work the temperature dependences of the various contributions are examined and it is evident that the TLS's are dominant only at very low temperatures. At higher temperatures the local phonons will dominate because of their activated temperature dependence. It therefore seems reasonable to us to restrict ourselves to phonon processes as the origin of the homogeneous dephasing at our experimental temperatures of $T \geqq 1.6$ K.

As we have outlined above, the microscopic theories explain only homogeneous linewidths and shift contributions due to the dynamic nature of the phonon bath. Inhomogeneous contributions have to be accounted for in the microscopic model by considering the influence of a quasistatic environment. Microscopic solvent-shift theories have been developed by Buckingham[28] for vibrational transitions in liquids and by a number of authors for the optical case.[29,31] In a recent paper of Henke *et al.*[31] the existing theories have been reviewed and extended. A detailed theory is presented which accounts for various kinds of dipole-dipole interactions, i.e., permanent dipoles in both solute and solvent, permanent dipoles only in solute or solvent exclusively, and for purely dispersive interaction. We will use similar arguments in the case of a dye molecule embedded in solid host matrices.

In the present work we will try to establish a semiempirical link between stochastic and microscopic theories. Some steps in this direction have recently been made by Skinner and Hsu.[32] They show in a theoretical paper the equivalence of stochastic and microscopic theories in certain limiting cases. We believe that our experiments can give experimental support for some of their results. In the following we will apply the basic assumptions of the SC theory for vibrational transitions in liquids to the electronic transitions of a dye molecule embedded in a solid host system. The SC approach relates the short-range repulsive part of the molecule-environment interaction potential to the homogeneous contributions to the line shifts and broadenings and the long-range attractive part to the inhomogeneous linewidth and line-shift parameters. Typical experiments on vibrational transitions are subpicosecond experiments[6,10,33] like transient Raman scattering experiments which reveal the shape of the homogeneous line in an inhomogeneously broadened band. The corresponding optical experiments are the high-resolution techniques of photochemical and photophysical hole burning,[25,34] fluorescence line narrowing, and photon-echo experiments.[35] These techniques also allow the "labeling" of a homogeneous line in an inhomogeneously broadened band. In analogy to the SC theory we relate the homogeneous linewidth and its temperature dependence to dynamical processes governed by the interaction potential between the dye molecule and its matrix environment (dye-matrix interaction potential) and therefore mainly to its short-range repulsive part. The shifts and broadenings of the holes with variable pressure as investigated in our pressure-tuning experiments can be related to the solvent shift and the width of the inhomogeneous band as it is shown below. We will make a connection between the pressure shifts and broadenings and the solvent shifts and widths of the inhomogeneous bands, and the static part of the dye-matrix interaction potentials, i.e., the long-range attractive part of the interaction as discussed in detail in Sec. III. Since the pressure tuning of spectral holes can be looked upon as a perturbation of the solvent shift, we are able to determine the compressibility of the dye in its environment by solely considering the static part of the dye-matrix interaction. It should be noted, that the influence of electric fields on photochemically burned holes as investigated in Refs. 36–38 is also an inhomogeneous process and thus can also be described in terms of solvent-shift theories. In Sec. II of this contribution we will present our hydrostatic-pressure-tuning experiments. The magnitudes of the line shifts and broadenings are reported and compared with the shift parameters obtained by independent temperature-cycling experiments.[39,40] The independent determination of the pressure-dependent terms allows a separation of the temperature shifts into a purely "homogeneous" contribution and a purely "inhomogeneous" one which is caused by the thermal contraction or expansion of the host lattice. A separation in pressure- and temperature-dependent terms is well known from Sapozhnikov's work on zero-phonon lines of optical spectra in molecular crystals.[41] In Sec. III we will show that the stochastic models originally developed for vibrational dephasing in liquids can be successfully applied to the case of optical dephasing of dye molecules in amorphous solids. We argue that we are able to distinguish explicitly in our experiments between homogeneous and inhomogeneous contributions to optical line shifts. Moreover, this separation allows us to determine "mechanical" matrix parameters like the hydrostatic compressibility by optical experiments.

For completeness it should be noted that our first pressure-tuning experiments[42] have been performed with a uniaxial-pressure apparatus. In this particular case, however, the sensitivity of our method is so large that small irreversible sample deformations lead to irreversible line broadenings. The reason is that it is close to impossible to exert uniaxial pressure in a completely homogeneous fashion. Therefore, a slightly wedge-shaped sample arrangement will lead to irreversible strains which will prevent the sample from returning to its original state after a pressure cycle has been performed. A detailed comparison of uniaxial and hydrostatic experiments has been given in Ref. 43. The present work reports hydrostatic-pressure experiments which turned out to be completely reversible and which therefore are the appropriate experiments for use in connection with the high-resolution techniques of spectral hole burning.

II. EXPERIMENTS AND RESULTS

A. Sample preparation and method of hole burning

In our experiments, we examined the polymers polymethylmethacrylate (PMMA), polystyrene (PS), and polyethylene (PE) doped with the dye molecule free-base phthalocyanine (H_2Pc). The doping concentrations were on the order of 10^{-4} mole of dye per mole of the monomer. Details of the photochemical hole-burning method are reviewed in Ref. 25. Since the photochemistry is only stable at low temperatures, the temperature region of our experiments was between 1.6 and 20 K. The holes were burned and recorded with a highly stabilized tunable dye laser with a spectral resolution of about 3 MHz. Our experimental setup is shown in Fig. 1.

Only the zero-phonon part of the hole burned into the inhomogeneously broadened $S_1 \leftarrow S_0$ transition of the dye molecules was investigated. Figure 2 shows the solvent shift, i.e., the difference between the absorption energy of the dye molecule in the gas phase and in solid solution at low temperatures. For determining the magnitude of the shift we take the center of the inhomogeneous band. The spectroscopic features on top of the inhomogeneous band are the extremely narrow (a few hundreds of MHz) zero-phonon line and the broader structure of the pseudophonon wing (e.g., Ref. 25).

B. Pressure-tuning experiments

The hydrostatic-pressure experiments were performed at $T = 1.6$ K in a pressure cell with liquid He as the pressure-transmitting medium (see Fig. 3). The cell was inserted in a He-bath cryostat below the level of the liquid He. Pressure was exerted from a gas chamber outside the cryostat onto the surface of the liquid He inside the closed cell. Thus hydrostatic pressures up to 20 MPa could be created with an accuracy of better than 10 hPa. Due to the high resolution of the hole-burning method pressure variations of several tens of hPa are sufficient to produce measurable changes in the hole spectra. The measured pressure shifts of the holes of up to 10 GHz allow one to perform a very accurate analysis of the line shifts. In our hydrostatic low-pressure regime, all measured shifts and changes in the line shapes turned out to be completely reversible. Due to the low pressures the measured hole widths do not depend on the pre-pressure, i.e., the pressure under which the hole has been produced via site-selective photochemistry.

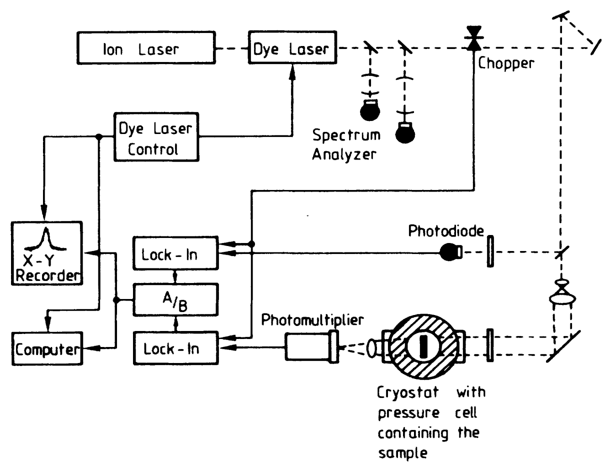

FIG. 1. Experimental setup for the high-resolution hole-burning experiments. The holes were burned and detected (via transmission) with a highly stabilized tunable dye laser (recording intensity attenuated). The hydrostatic pressure cell (see Fig. 3) is inserted in the liquid-He–bath cryostat.

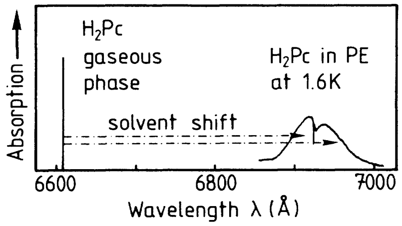

FIG. 2. Optical absorption of the dye molecule free-base phthalocyanine in the gas phase as compared to its absorption in solid polyethylene at low temperatures. The narrow pattern on top of the inhomogeneously broadened $S_1 \leftarrow S_0$ transition is the zero-phonon hole, the broader one the pseudophonon wing.

Therefore, the pressure difference Δp applied after the burning is the only parameter of our experiments. The influence of "negative pressure" ($\Delta p < 0$) can also be investigated by burning the holes at a high pre-pressure and then reducing the external pressure. Increasing pressure produces a red shift of the hole (Fig. 4) whereas decreasing pressure causes a blue shift (Fig. 5). These shifts are accompanied by a superimposed broadening for both increasing and decreasing pressure. Depending on the nature of the matrix, the holes were smeared out completely with pressure variations of 1–3 MPa. Even for large pressure variations, the holes change widths and positions in a completely reversible fashion. It should be noted that the dominantly linear shifts reflect the magnitude of the dye-matrix interactions, whereas the observed broadenings give some insight into the local degree of order around the dye molecules. Both the shifts and broadenings will be discussed in detail below. Figure 6 shows the measured red shift ($\Delta\bar{\nu} < 0$) of the hole spectra for H_2Pc in PMMA, PE, and PS. As we will explain below, the larger shifts in PS can be partially correlated with the higher low-temperature compressibility of this particular matrix. Since the method of photochemical hole burning can detect even small pressure variations, it is especially well suited for determining the linear shift parameters. These parameters are given in Table I for the three matrices. For the sake of completeness it should be noted that in the case of PMMA the molecular masses have been varied from 30×10^3 to 5×10^6 g/mole. No dependence of the linewidths and shifts on the chain lengths could be observed. This seems to be reasonable because the dye-matrix interaction should be dominated by intermolecular forces rather than intramolecular ones. Nevertheless, the polymeric nature of the material is important, because it determines the amorphous or at least partially amorphous structure of the matrix.

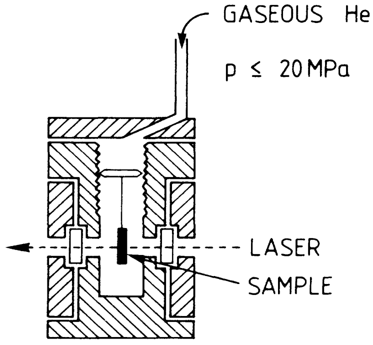

FIG. 3. Hydrostatic pressure cell with liquid He as pressure-transmitting medium. The cell was inserted in a He-bath cryostat. The pressure was exerted from a He gas chamber outside the cryostat. Pressures up to 20 MPa could be adjusted with an accuracy of less than 10 hPa.

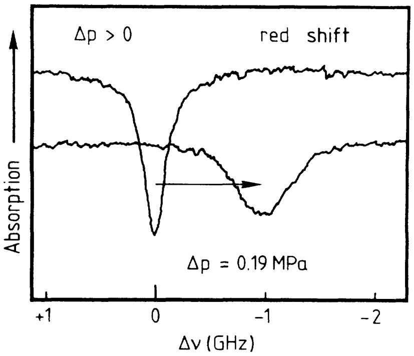

FIG. 4. Red shift of a hole with increasing pressure. The shift is accompanied by an additional broadening (sample: H_2Pc in PE, $T = 1.6$ K).

Our experimental results in the low-pressure regime have to be compared with typical pressure data required to shift "broad line spectra" which are of the order of several tens of GPa.[44–46] These large external pressures must be considered as sizeable perturbations on the equilibrium interaction potentials. They are almost comparable to the "internal pressure" which we define as the pressure one would have to apply in order to achieve a line shift comparable to the solvent shift. Since photochemical hole burning allows a gain in the spectral resolution of the order of 10^4, we can operate with our low-pressure experiments close to the equilibrium position of the involved intermolecular potentials and, hence, obtain

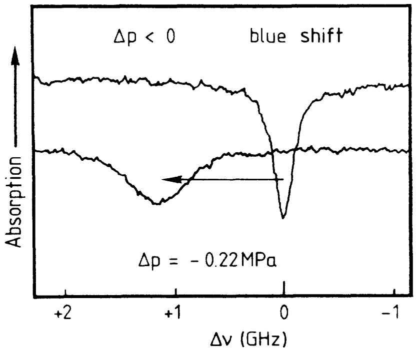

FIG. 5. Blue shift of a hole with decreasing pressure. The shift is accompanied by an additional broadening (sample: H_2Pc in PE, $T = 1.6$ K).

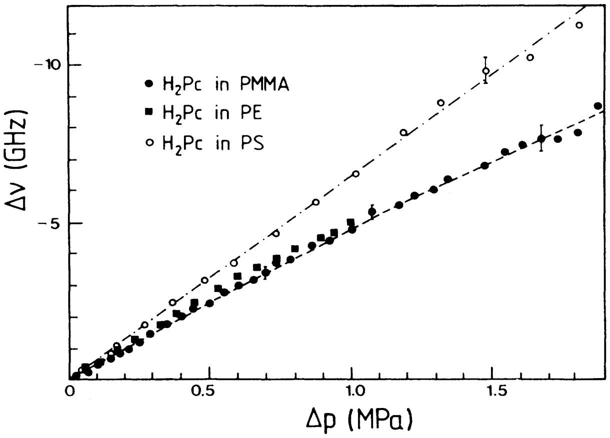

FIG. 6. Spectral shifts with increasing pressure for H_2Pc in three different matrices at $T=1.6$ K.

"unperturbed" parameters (for instance, compressibilities).

C. Temperature-versus-pressure effects

In the following we connect line shifts caused by temperature and pressure variation. Temperature-cycling experiments used to obtain temperature-broadening and shift data have been reported elsewhere.[39] The different mechanisms leading to the observed temperature phenomena are well investigated[40] and in a recent paper also discussed theoretically.[26]

The correlation between temperature and pressure shift data can be clarified by a crucial and simple experiment which shows that a naive model of the observed optical line shifts leads to erroneous conclusions: We have seen that an increase in pressure, and thus a decrease in volume, leads to a red shift of the optical transition energies (Figs. 4 and 6). A seemingly reasonable conclusion that a temperature-induced volume reduction by cooling the sample under isobaric conditions would also lead to a red shift is, however, in contradiction with the experimental data. Figure 7 show that an isobaric decrease in temperature ($\Delta T<0$) corresponding to a volume reduction leads to a blue shift of the observed transitions quite in contrast to the findings in case of the pressure-induced volume reductions.

TABLE I. Normalized pressure shifts $\Delta\bar{\nu}(p)/\Delta p$ and pressure broadenings $\Delta\gamma(p)/\Delta p$ of the holes with increasing pressure for the different matrices PE, PS, and PMMA.

	$\frac{\Delta\bar{\nu}(p)}{\Delta p}\left[\frac{\text{cm}^{-1}}{\text{MPa}}\right]$	$\frac{\Delta\gamma(p)}{\Delta p}\left[\frac{\text{cm}^{-1}}{\text{MPa}}\right]$
PMMA	-0.17 ± 0.01	0.09 ± 0.01
PE	-0.18 ± 0.01	0.06 ± 0.01
PS	-0.22 ± 0.01	0.12 ± 0.01

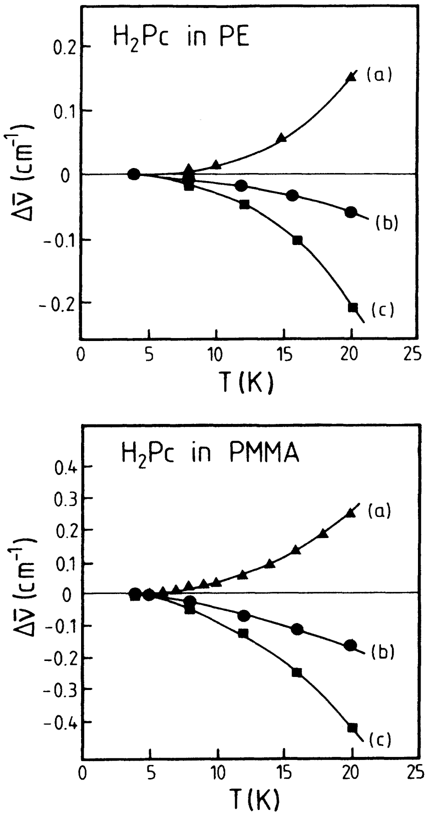

FIG. 7. Various line-shift contributions as separated by the two terms of Eq. (3) for H_2Pc in PE and PMMA, respectively. (a) Shift due to the thermal expansion of the polymer lattice [calculated from the isothermal pressure shifts $(\partial\bar{\nu}/\partial p)_T$, the thermal expansion coefficient, and the hydrostatic compressibility]. (b) Overall shift as experimentally observed by temperature-cycling experiments. (c) Homogeneous shift due to the dynamics in the dye-matrix interaction potential [difference (b) − (a)].

The total frequency change $d\bar{\nu}/dT$ can be generalized as

$$\frac{d\bar{\nu}}{dT}=\left(\frac{\partial\bar{\nu}}{\partial T}\right)_V+\left(\frac{\partial\bar{\nu}}{\partial V}\right)_T\frac{\partial V}{\partial T}\,, \tag{1}$$

where the second term can be written as

$$\left(\frac{\partial\bar{\nu}}{\partial V}\right)_T\frac{\partial V}{\partial T}=\left[\left(\frac{\partial\bar{\nu}}{\partial p}\right)\left(\frac{\partial p}{\partial V}\right)\right]_T\frac{\partial V}{\partial T}=-\frac{3\alpha_{\text{lin}}}{\kappa}\left(\frac{\partial\bar{\nu}}{\partial p}\right)_T .$$

κ is the hydrostatic compressibility and α_{lin} the linear thermal expansion coefficient. The above derivation neglects the temperature dependence of the compressibility. This is reasonable for our temperature interval of $1.6\leq T\leq 20$ K. In fact the compressibilities vary less than 5% between 4.2 and 77 K and still less than 50% between 4.2 and 293 K.[47] Therefore, we can rewrite Eq. 1 in a way showing that the variables V and p scale with a constant factor and one gets

$$\frac{d\bar{v}}{dT}=\left[\frac{\partial\bar{v}}{\partial T}\right]_V-\left[\frac{\partial\bar{v}}{\partial p}\right]_T\frac{1}{\kappa}3\alpha_{\text{lin}} . \tag{2}$$

In the above equation the experimentally observable value is $d\bar{v}/dT$ as shown in Fig. 7. From our pressure-tuning experiments we get the parameter $(\partial\bar{v}/\partial p)_T$, and thus the whole temperature dependence of the second term of Eq. (2) is given through the temperature dependence of the thermal expansion coefficient α_{lin}. This allows us to write Eq. (2) in an integrated form as

$$\Delta\bar{v}(T)=\int_{T_1}^{T_2}\left[\frac{\partial\bar{v}}{\partial T}\right]_V dT-\frac{3}{\kappa}\left[\frac{\partial\bar{v}}{\partial p}\right]_T\int_{T_1}^{T_2}\alpha_{\text{lin}}dT . \tag{3}$$

As we found no temperature dependence of the quantity $\partial\bar{v}/\partial p$ in the whole temperature regime, we take it as a constant for the following calculations. Using the tabulated α_{lin} values of the polymer matrices PE and PMMA (Refs. 48 and 49) and the measured $\Delta\bar{v}(T)$ values of our experiments, we can calculate the contribution of $(\partial\bar{v}/\partial T)_V$. Figure 7 show graphically the various contributions to the line shifts in PE and PMMA matrices. [For PS a complete set of reliable $\alpha_{\text{lin}}(T)$ data was not available.]

It had been shown in a previous publication that the compressibility κ and the $(\partial\bar{v}/\partial p)_T$ parameter can be successfully correlated by using long-range dispersive forces with a $1/r^6$ behavior.[50] We can therefore follow an argument put forward by Schweizer and Chandler and separate the various molecule-matrix interaction terms into quasistatic contributions (inhomogeneous) and into dynamic (homogeneous) contributions. The upper curves (a) of Fig. 7 contain the completely quasistatic strain shifts as determined by our hydrostatic experiments together with the temperature-dependent α term. The $(\partial\bar{v}/\partial T)_V$ term [curves (c)] describes exclusively dynamical contributions, predominantly determined by the steeply repulsive part of the potential and has opposite sign with respect to the second term in Eq. (1) containing the $(\partial\bar{v}/\partial p)_T$ contributions. Due to the direct connection between line shifts and line broadenings, the dynamic term describes the strongly temperature-dependent phase loss in the excited state and can be accounted for by the various dephasing theories. The above outlined separation is a straightforward method to extract the contributions due to dephasing processes from the temperature-shift data, which contain both dynamical dephasing and statical strain contributions. It is interesting to note that the two contributions almost compensate each other, leading to a rather small $d\bar{v}/dT$ contribution as is measured in a nonisochoric experiment.

III. THEORETICAL MODELS AND DISCUSSION

A. Basic ideas

In the past, theories dealing with the linewidths and line shifts of molecular absorbers could be subdivided into two categories: dynamical theories on the one hand, taking into account the various processes modulating the molecular energy levels and thus leading to a dephasing in ground and excited states (homogeneous T_2 processes),[12–18] and, on the other hand, theories describing the quasistatic solvent shifts of molecular absorbers. The latter are mostly based on perturbative approaches taking into account the various long-range interactions (dipolar interactions or interactions based on induced dipoles).[28–31] Our experimental data [see Eq. (2)] can clearly discriminate between temperature effects $(\partial\bar{v}/\partial T)_V$ and pressure effects $(\partial\bar{v}/\partial p)_T$. Taking into consideration the quantitative description of the pressure dependences enables us to focus on the strongly temperature-dependent terms of Eqs. (2) and (3) and thus to correlate these contributions with the purely homogeneous dynamical line-shift and linewidth parameters, as has been suggested by SC. The underlying conceptual assumption in our approach, which can be justified by our experiments, is that both homogeneous and inhomogeneous processes can be considered in the same model. Static molecular interactions cause an inhomogeneous solvent shift and are appropriate to explain the pressure effects, whereas dynamical motions of the dye molecule in the same interaction potential[51–53] (librations and/or other impurity-induced localized modes) together with phonon-scattering processes from the bulk material are the microscopic origin of the dephasing, i.e., are the reason for the homogeneous linewidth and shift contributions.

Considering the specific interaction-potential surface, we follow in our analysis of the dye-matrix interaction the rather elegant partitioning of the interaction potential used in liquid-state perturbation theory[54,55] into a purely repulsive potential (see Fig. 8)

$$V_R(r)=\begin{cases}V_R e^{-\delta(r-r_0)}, & r\leqq r_0\\ 0, & r>r_0 ,\end{cases} \tag{4a}$$

where δ defines the range of the repulsive potential and a

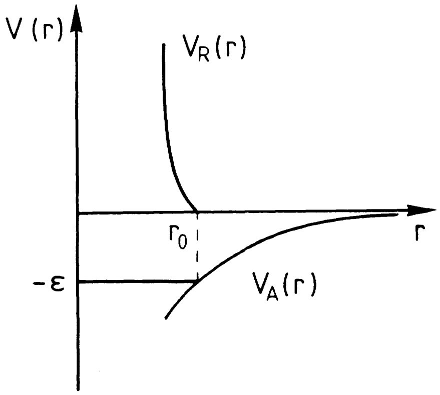

FIG. 8. Decomposition of interaction potential for impurity-polymer host system into attractive $(r\geqq r_0)$ and repulsive regions. A change in pressure $p_0\rightarrow p_0+\Delta p$ leads to a change in equilibrium distance $r_0\rightarrow r_0+\Delta r$.

long-range attractive part

$$V_A(r)=\begin{cases} -\dfrac{A}{r^6}, & r>r_0 \\ -\dfrac{A}{r_0^6}:=-\varepsilon, & r\leq r_0 \, . \end{cases} \tag{4b}$$

The total potential $V(r)$ is then simply the sum of both terms, namely

$$V(r)=V_R(r)+V_A(r) \, . \tag{5}$$

In the above equations the first part [Eq. (4a)] represents the steeply repulsive interaction, which plays an important role in the dephasing phenomena of excited states via modulation through librations or other impurity-induced local modes together with phonon scattering processes from the bulk material. In the second term [Eq. (4b)] the dipolar interaction terms are parametrized. In our case of a nonpolar molecule in a nonpolar matrix we can assume that the dispersive interaction term (induced-dipole–induced-dipole) is the dominating contribution, giving rise to the $1/r^6$ dependency.

The assumption of spherical symmetry is an oversimplification of the real molecular impurity-host problem. Nevertheless, we proceed with this assumption, noting that the generalization from spherical to ellipsoidal shape is analytically striaghtforward, but complicated in detail. Also, this treatment would only be warranted if experiments on single-crystalline matrices with defined solvent cages would become available. In the latter case, however, the characteristic elastic material parameters would be given by tensors. In the case of amorphous host materials, however, the local anisotropies have to be averaged, and thus one can deal with quasi-isotropic material parameters as is done in the following.

Having discussed the general impurity-host interaction potential in the ground state, one has to consider the corresponding excited-state interaction potentials, since our optical experiment depends on the pertinent energy differences:

$$h\nu_0=E_e(r_0)-E_g(r_0) \, . \tag{6}$$

In the above expression r_0 stands for the equilibrium value of a multidimensional configuration coordinate representing, in general, the complex host-impurity geometry. As has been mentioned above, we will only deal with a one-dimensional problem, reflecting a spherical geometry. As far as the explicit interaction potentials are concerned, we will consider the attractive part of the interaction potential as being appropriate for describing the solvent shift.[30,31] A calculation of the spectroscopic shifts based on perturbation theory yields for the solvent shift of a nonpolar molecule in a nonpolar host[31]

$$\Delta\bar{\nu}_s=\sum_{\substack{i,j\\(i\neq j)}}\sum_{k(>0)}\frac{|\langle\Phi_i\Psi_0|\hat{H}'|\Phi_j\Psi_k\rangle|^2}{E_j+F_k-E_i}-\sum_{j(>l)}\sum_{l(>0)}\frac{|\langle\Phi_0\Psi_0|\hat{H}'|\Phi_l\Psi_k\rangle|^2}{E_j+F_k}\, , \tag{7}$$

where Φ_i,E_i and Ψ_k,F_k are the eigenfunctions and eigenvalues of the impurity and host molecules, respectively, and

$$\hat{H}'=\sum_\beta\frac{\mathbf{m}\cdot\mathbf{n}^\beta}{r_\beta^3}-\frac{3(\mathbf{r}_\beta\cdot\mathbf{m})(\mathbf{r}_\beta\cdot\mathbf{n}^\beta)}{r_\beta^5}\, . \tag{8}$$

$\hat{H}'$ is the electrostatic dipole-dipole interaction between a host (solvent) molecule β with dipole-moment operator $\mathbf{n}^\beta$ and the impurity (solute) molecule with dipole operator $\mathbf{m}$ at distance $\mathbf{r}_\beta$ from molecule β. Using standard resuls for van der Waals interaction,[30] these expressions can be brought into the form corresponding to a single pair of impurity and host molecules:

$$\Delta\bar{\nu}_s=\frac{\alpha_I\alpha_H}{r^6}f(E_I,E_H)\, , \tag{9}$$

where $\Delta\bar{\nu}_s$ gives the solvent shift in wave numbers, α_I and α_H are the polarizabilities of the impurity and host molecules at a center-of-mass distance r. $f(E_I,E_H)$ is a function depending on the characteristic excitation energies of impurity and host, respectively.[31] The physical picture of the origin of dispersive forces as described by Eq. (9) is that of nonvanishing fluctuations of the electronic position operators

$$\sum_i\langle 0|\hat{r}_i^2|0\rangle_I\sim\alpha_I \quad\text{and}\quad \sum_j\langle 0|\hat{r}_j^2|0\rangle_H\sim\alpha_H \tag{10}$$

in both impurity and host molecules interacting via unretarded dipole-dipole interactions. Of course, the origin of this force is purely quantum mechanical and arises from the inevitable ground-state fluctuations of the electronic position operators.

The standard approach in gas- and liquid-state phenomena related to solvent shifts is to consider the pairwise dispersion interaction [Eq. (9)] only for molecules of the host nearest-neighbor coordination shell at distance $\bar{R}_{\mathrm{NN}}$ leading after summing over the number of nearest neighbors to a factor of $\bar{z}$ ($\bar{z}$ is the average number of nearest neighbors),

$$\Delta\bar{\nu}_s^{nn}=-\frac{\alpha_I\alpha_H}{\bar{R}_{\mathrm{NN}}^6}\bar{z}f(E_I,E_H)\, . \tag{11}$$

B. Pressure effects

Such a dependence has recently been used for the explanation of high-pressure effects on the entire inhomogeneous band.[56] Starting with Eq. (11), we have shown[43,50] that a quantitative relation can be obtained for the pressure shifts of the holes only considering first-neighbor shells:

$$\Delta\bar{\nu}(p)=\Delta\bar{\nu}_s(1+2\kappa_{\mathrm{loc}}\Delta p)\, , \tag{12}$$

where $\Delta\bar{\nu}_s$ is the solvent shift and $\kappa_{\rm loc}$ is the local compressibility of the solvent cage.

In the above derivation a pairwise summation over van der Waals terms was made, considering only the first nearest-neighbor shell.[57] On the other hand, it is well known from the treatment of dispersion forces for similar systems (e.g., a physisorbed molecule on a semi-infinite solid) that the inclusion of *all* pairwise interactions over the entire half-space seems appropriate.[58–60] Therefore we have to discuss the two different approaches in more detail.

We replace the spatially inhomogeneous density distribution of the polymer host by an average density $\rho_H(p)$ of polarizable material, filling the space from a solvent cavity radius R_c to infinity. $\rho_H(p)$ contains the polarizabilities of impurity and host molecules and depends explicitly on pressure. Within this model one can express the solvent shift as

$$\Delta\bar{\nu}_s(p_0) = -\int_{R_c(p_0)}^{\infty} \rho_H(p_0)\frac{4\pi r^2}{r^6}\,dr \ . \tag{13}$$

For evaluating our experimental data we have to calculate the solvent shift after applying a pressure change Δp and get

$$\Delta\bar{\nu}_s(p_0+\Delta p) = -\int_{R_c(p_0+\Delta p)}^{\infty} \rho_H(p_0+\Delta p)\frac{4\pi r^2}{r^6}\,dr \ . \tag{14}$$

By expanding $\rho_H(p)$ in the vicinity of p_0 into a power series and carrying only linear terms we get

$$\begin{aligned}\rho_H(p_0+\Delta p) &= \rho_H(p_0) + \left.\frac{\partial\rho}{\partial p}\right|_{p_0}\Delta p\\ &= \rho_H(p_0)(1+\kappa_{\rm bulk}\Delta p)\ ,\end{aligned} \tag{15}$$

where $\kappa_{\rm bulk}$ is the hydrostatic compressibility of the bulk material.

Using this procedure, one can rewrite Eq. (14) and get

$$\Delta\bar{\nu}_s(p_0+\Delta p) = -\rho(p_0)(1+\kappa_{\rm bulk})\frac{4\pi}{3}\left[\frac{1}{R_c(p_0+\Delta p)}\right]^3 . \tag{16}$$

Equation (16) represents a detailed expression for the solvent shift; it considers the interaction between the dye molecule and the whole bulk material. It corresponds to Eq. (11) written in terms of bulk parameters.

The distinction between bulk parameters and molecular cage parameters can be formally made by correlating the cavity radius R_c with a local compressibility $\kappa_{\rm loc}$ which can, in principle, be different from the bulk compressibility. An expansion of R_c including only linear terms yields

$$\left[\frac{1}{R_c(p_0+\Delta p)}\right]^3 = \left[\frac{1}{R_c(p_0)}\right]^3(1+\kappa_{\rm loc}\Delta p)\ . \tag{17}$$

Inserting Eq. (17) into Eq. (16), one gets

$$\Delta\bar{\nu}_s(p_0+\Delta p) = \Delta\bar{\nu}_s(p_0)[1+(\kappa_{\rm bulk}+\kappa_{\rm loc})\Delta p + O(\Delta p^2)]\ . \tag{18}$$

The above equation is more rigorous than Eq. (12), since it includes local and bulk effects. Taking identical values for $\kappa_{\rm loc}$ and $\kappa_{\rm bulk}$ transforms Eq. (18) into Eq. (12). Up to now, the difference between $\kappa_{\rm loc}$ and $\kappa_{\rm bulk}$ could only be discussed on a qualitative level.[50] Our experimental results seem to indicate, however, that Eq. (12) is valid for the polymers investigated within an error margin of about 20%. Table II gives the compilation of our optically determined compressibilities (for $\kappa_{\rm loc} = \kappa_{\rm bulk}$) compared with "mechanically" determined low-temperature compressibilities.[47] The necessary solvent-shift data were obtained by comparing our low-temperature spectra with the optical data of molecular-beam experiments.[61,62] Considering the fact that our model does not contain any adjustable parameters, the agreement between the different data of Table II is remarkable ($\leq 20\%$). It will be an intriguing question whether future experiments on less-homogeneous polymers (e.g., block copolymers, etc.) will allow a separation between local parameters and bulk parameters as given in Eq. (18).

Finally we have to compare our own work with previous theories on high-pressure shifts of molecular absorptions in various host polymers (see Refs. 63–65 and references therein). The available parametrized theories had been worked out, and yield for small Δp values

$$\Delta\bar{\nu}(p) = \Delta\bar{\nu}_s + C(p-p_0) = \Delta\bar{\nu}_s + C\Delta p\ , \tag{19}$$

where C is a constant characterizing the coupling between the dye molecule and its matrix environment (C contains matrix elements with ground- and excited-state wave functions; see Ref. 65). By comparing Eqs. (18) and (19) we get

$$C = 2\Delta\bar{\nu}_s\ . \tag{20}$$

Figure 9 shows the solvent shifts for the three polymers used in this work. From our discussion it is clear that the magnitude of the solvent shift reflects the magnitude of the impurity-host interaction predominantly via dispersion interactions (polarizability) and the cavity size parameter R_c. On the other hand, we notice in Fig. 9 and Table III considerable variations in the inhomogeneous widths Γ_0 of the studied transition in the three different polymer hosts. Turning to our studies of the effect of hydrostatic pressure on the hole width (see Table I) we argue that the variation of the environment, which accounts for the width of the inhomogeneous line, should also be reflected in the pressure broadening of photochemical holes $\Delta\gamma$ (i.e., in the dispersion of the op-

TABLE II. Solvent shifts $\Delta\bar{\nu}_s$, compressibilities $\kappa_{\rm loc}$ as obtained by our optical experiments, and mechanically measured low-temperature compressibilities as taken from the literature, $\kappa_{\rm lit}$ (Ref. 47).

	$\Delta\bar{\nu}_s$ (cm^{-1})	$\kappa_{\rm loc}$ (GPa^{-1})	$\kappa_{\rm lit}$ (GPa^{-1})
PMMA	-566 ± 10	0.150 ± 0.028	0.130
PE	-690 ± 10	0.130 ± 0.020	0.141
PS	-742 ± 10	0.148 ± 0.021	0.179

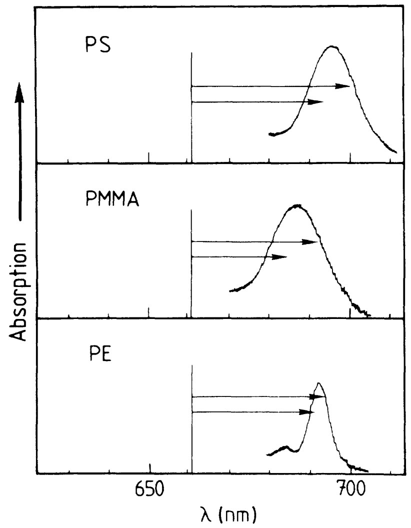

FIG. 9. Inhomogeneously shifted and broadened $S_1 \leftarrow S_0$ transition of H_2Pc in the three different matrices at $T = 4.2$ K as compared to its absorption line in the gas phase (vertical bar).

tical shift parameters as shown in Figs. 4 and 5).

To eliminate the effect of different compressibilities in different matrices we form the following ratios for which Eq. (21) should hold:

$$\frac{\Gamma_0}{\Delta\bar{\nu}_s} = \frac{\Delta\gamma(p)}{\Delta p}\left[\frac{\Delta p}{\Delta\bar{\nu}(p)}\right] = \frac{\Delta\gamma(p)}{\Delta\bar{\nu}(p)} , \tag{21}$$

where Γ_0 is the width of the inhomogeneous band (see Table III), $\Delta\bar{\nu}_s$ is the experimental solvent shift (see Table III) and $\Delta\gamma(p)/\Delta p$ and $\Delta\bar{\nu}(p)/\Delta p$ are the normalized pressure broadening and shift, respectively (see Table I). Since the two quantities in Eq. (21) both reflect the dispersion in the solvent shift which is a measure for the electronic and geometric degree of order in the neighborhood of the dye molecules, the correlation seems to be reasonable. Table III gives a tabulation of the parameters used in Eq. (21). There is a reasonable agreement between the various parameters considering the crude assumptions we have made in describing both the solvent shift (or width) of the inhomogeneous band and the pressure shifts (or broadenings) only in terms of the long-range attractive part of the dye-matrix interaction potential. In addition, it should be noted that the broadenings and shifts in PE and PMMA are of the same magnitude, whereas the ones in PS are larger due to the higher compressibility of PS (see Table I). In Table III, on the other hand, the value for PE is the smallest. This shows, that Eq. (21) in fact characterizes the degree of order as reflected in the widths of the inhomogeneous band. The inhomogeneous band for PE is considerably narrower than the ones measured for PS and PMMA (see Fig. 9).

TABLE III. Widths of the inhomogeneous bands Γ_0, widths divided by the solvent shifts, $\Gamma_0/\Delta\bar{\nu}_s$, and pressure broadenings divided by the pressure shifts, $\Delta\gamma(p)/\Delta\bar{\nu}(p)$.

	Γ_0 (cm^{-1})	$\Gamma_0/\Delta\bar{\nu}_s$	$\Delta\gamma(p)/\Delta\bar{\nu}(p)$
PMMA	276 ± 10	-0.53 ± 0.04	-0.53 ± 0.07
PE	116 ± 10	-0.18 ± 0.03	-0.31 ± 0.06
PS	276 ± 10	-0.41 ± 0.03	-0.55 ± 0.05

At first sight, one could attribute this narrower inhomogeneous line to the partially crystalline structure of PE. However, this argument is not very stringent in view of the fact that the dye molecules are most likely incorporated into the amorphous phase of the matrix. For a further clarification of this aspect, experiments on polymeric materials of variable crystallinity are required.

In this context we would like to make a final remark, concerning the "local cavity," surrounding the dye molecule in a complex polymer matrix. It is known, that the properties of amorphous (glassy) polymers reflect the existence of a fairly large fraction of "free volume." It is conceivable that guest molecules are preferentially incorporated into these free-volume-like cavities. At the present time the experimental data are not conclusive enough to warrant the introduction of a distribution of R_c values characterizing the various host environments.

C. Temperature effects

So far we have extensively discussed the static interaction between a dye molecule and its matrix environment with special consideration of pressure effects. However, our optical data also contain the temperature as an experimental parameter [see Eq. (2)]. Since the effects of external pressure can be adequately described by using the long-range potential, the temperature effects are, to first approximation, contained in the $(\partial\bar{\nu}/\partial T)_V$ term and in the temperature variation of the linear expansion coefficient α_{lin} [see Eq. (3)]. Both terms of Eq. (1) must therefore also include parameters which are characteristic of the short-range repulsive part of the interaction potential. With this argument we follow the basic ideas of the SC theory.[5] In their work on vibrational dephasing, SC also report shifts with opposite sign, resulting from the repulsive and attractive part of the interaction potential, respectively. The authors examined the different parts of the interaction by independent pressure and temperature variations. As in our experiments, both contributions partially compensate each other. The idea seems to be intriguing that an expression equivalent to Eq. (1) (see Ref. 41) could discriminate between homogeneous and inhomogeneous line-shift and linewidth contributions. Arguing along those lines, it seems interesting to us that only the dynamical contributions show strong temperature variations, whereas the static contributions show very little temperature dependence. This is reflected by the almost temperature-independent κ value (5% change in the interval $4.2 \leqq T \leqq 77$ K).

IV. CONCLUSION AND OUTLOOK

We have shown that a stochastic line-shape model[5] originally developed for vibrational transitions in liquids can be successfully applied to the case of dye molecules embedded in a polymeric environment. We have used semiempirical arguments to link both homogeneous and inhomogeneous aspects of the linewidth to a single qualitative model[5] of the guest-host interaction. In particular, the separation between the various long-range and short-range contributions to the molecular interaction potentials in liquids, which had been introduced by SC (Ref. 5), is an interesting aspect, which could be further pursued by performing model experiments in the solid state, in which pressure and temperature effects are separated. It seems to us, that experiments of the above kind will be important for verifying quite recent theoretical work on linewidths and line shifts done by Skinner and Hsu.[32]

An explanation of the pressure shifts and broadenings of spectral holes in terms of the long-range attractive part of the potential, i.e., the dipolar attraction, allows for our small pressure variations a rather good correlation between optical data and macroscopic matrix parameters. Thus matrix compressibilities can be determined in a purely optical experiment and evaluated without any fit parameter. An aspect which has been discussed in this paper but needs more-detailed experimental treatment is the question of local versus bulk parameters of the matrix. To pursue this goal, polymeric systems with special impurity-host geometries must be synthesized.

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