

Thermal effects on zero-phonon holes in the optical spectra of molecular probes in polymer glasses

Indrek Renge*

Institute of Physics, University of Tartu, Riia Street 142, EE51014 Tartu, Estonia

(Received 14 April 2003; published 25 August 2003)

Purely electronic zero-phonon transitions in impurity molecules are of interest as highly sensitive local probes of solids. Spectral holes were created at different positions in the inhomogeneous optical-absorption bands of tetrapyrrolic chromophores in polymer glasses, and the thermal shift and broadening were investigated between 5 and 50 K. In addition, hole shifts were determined under He gas pressure up to 200 bars with the aim to separate the phonon-induced line shift from the “trivial” component caused by thermal expansion of the matrix. A prominent frequency dependence of a pure thermal, phonon-induced shift was discovered. The shift becomes progressively more negative (bathochromic) with increasing transition energy in the inhomogeneous ensemble of chromophores. In theory the corresponding negative quadratic electron-phonon coupling constant W reflects phonon mode softening in the excited state. In several cases the holes burned on the low-frequency edge show practically no thermal shift. The line broadening that depends on the square of W remains almost constant over the inhomogeneous contour. The role of intermolecular repulsive and attractive potentials on local phonon frequencies is elucidated.

DOI: 10.1103/PhysRevB.68.064205

PACS number(s): 71.55.Jv, 33.20.Kf, 78.40.Me

I. INTRODUCTION

Temperature studies of optical transitions in impurity ions or molecules doped in crystalline^{1–5} or glassy host matrices^{6–8} have been a classical field of research for several decades. In recent years thermal line-shift and broadening experiments have been done with ultimate sensitivity and spectral selectivity using single fluorophores.^{9–11} Theories of quadratic electron-phonon coupling (QEPC) responsible for the shift and broadening of purely electronic lines have undergone considerable progress^{12–15} and reached a general consistent form in nonperturbative approaches developed by Osad'ko¹⁶ and Skinner and Hsu.¹⁷

Organic dye molecules consisting of tens of π -electronically conjugated C atoms can possess strong purely electronic transitions that couple to matrix phonons surprisingly weakly.^{18,19} In noncrystalline host matrices the 0-0 transition is smeared out over a considerable interval of about 1% of the S_1 - S_0 energy gap.^{20–22} Inhomogeneous broadening is particularly large in polymer host matrices.²² Spectral hole burning can be the most useful method to investigate (quasi-)homogeneous properties of zero-phonon lines, provided the system is subject to photoinduced bleaching at low temperatures.²³ At the same time, optical hole burning is a promising strategy for creating ultrahigh-density optical memories.^{23,24} The optimization of potential optical recording materials requires better understanding of line broadening and vibronic coupling mechanisms in polymer glasses at low temperature.

Until now preference has been given to hole-broadening studies.^{7,23–26} Thermal line shifts have been rarely considered,^{1,2,5,8,10,26–28} since additional knowledge of pressure data is needed for separating the phonon-induced and matrix dilatation effects.^{8,28} The shifts are by no means less interesting, because the sign of QEPC constant W can be determined from the shift measurements.^{16,17} Line shifts provide information about softening or stiffening of phonon

modes as a result of optical excitation, in contrast to broadening that depends on W^2 .^{16,17}

The transfer of a chromophore from vacuum (e.g., a cold supersonic molecular beam) (Refs. 29–31) to a solid matrix has several fundamental consequences. First, spectroscopic energies (and oscillator strengths) will change and second, the transition will be coupled to matrix dynamics. The solvent shift of the transition equals the difference in stabilization energies of the ground (S_0) and excited (S_1) levels. On the other hand, the thermal shift and (quasi-)homogeneous broadening of purely electronic lines in the matrix depend on phonon frequencies in the S_0 and S_1 states. It is particularly obvious for pseudolocal phonons that both the phonon frequencies and solvent shifts should be correlated with intermolecular force constants in the solute-solvent system. Therefore, general relationships between the vacuum-to-matrix shifts and the phonon coupling processes have been predicted earlier.³²

We report here the temperature effects on spectral holes as a function of burning frequency over the inhomogeneous bands. This allows one to specify the interconnection between the two aspects of guest-host interaction: the solvent shifts and the phonon-induced shift and broadening. Several optical probes with greatly varying vacuum-to-matrix optical energy shifts and inhomogeneous bandwidths were investigated in two polymers of different polarities. A prominent and universal frequency dependence of phonon-induced line shifts is discussed. The detailed mechanisms of microscopic solvent shifts of $S_1 \leftarrow S_0$ energies in a disordered environment are treated in terms of repulsive, dispersive, and electrostatic interactions between the molecules. The reasons for mode softening/stiffening for (pseudo-)local phonons in glassy polymers are assessed.

II. EXPERIMENT

The pigments (for structural formulas see Fig. 1) and low-density polyethylene (density 0.915 g cm⁻³, melting tem-

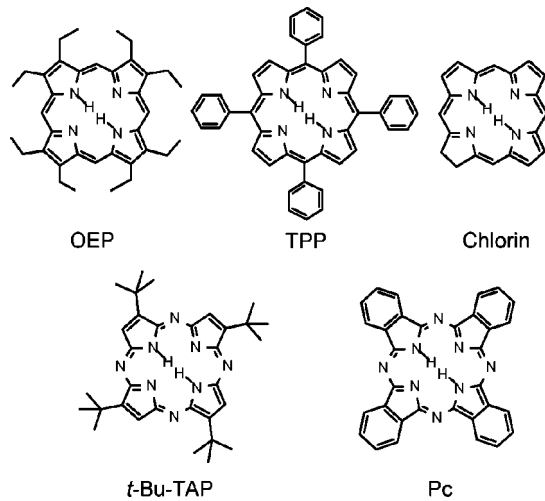


FIG. 1. Chemical structures of probe molecules.

perature 115 °C) were purchased from Aldrich. As a high molecular weight poly-(methyl methacrylate) (PMMA) commercial Plexiglass was used. The 0.1–0.5-mm thick polymer films were cast from the solution as described in Ref. 26, where the details of measurements and data treatment can also be found. In short, the samples were fixed in a continuous flow optical cryostat CF1204, and the temperature was maintained to within 1° with the ITC-4 temperature controller (both Oxford). Optical holes were burned with a LPD 3002E dye laser, pumped with 308-nm light from a LPX 100 excimer laser (both Lambda Physik). Holes were detected in transmission by scanning the dye laser with attenuated energy and a 40-Hz pulse frequency. The recording was accomplished with a two-channel setup using a Molecron JD2000 joulemeter/ratiometer with a sensitive J3S-10 (10^9 V/J) probe in the sample channel and a less sensitive one, J3-09 (10^3 V/J), as a reference. The holewidths were corrected for the laser linewidth by subtracting its double magnitude, 5 GHz, from the value obtained by Lorentzian fitting of the measured hole shapes. Pressure studies were carried out in a

simple cell made of stainless steel and supplied with two sapphire windows. The sample volume of $2 \times 4 \times 4$ mm³ was filled with gaseous He at 200 bars, cooled down to 5 K, and the holes were burned. Then the pressure was released step by step (for details see Ref. 33). Spectral positions ν , hole shifts $\Delta\nu$, and broadening $\Delta\Gamma$ are expressed in frequency, energy, or wave-number units as the context requires, without indicating the conversion factors.

III. RESULTS

Inhomogeneously broadened $S_1 \leftarrow S_0$ absorption spectra of octaethylporphyrin (OEP) and tetraphenylporphyrin (TPP) in PMMA and chlorin (Chl), tetra-*tert*-butylporphyrazine (*t*-Bu-TAP) and phthalocyanine (Pc) in polyethylene (PE) host matrices at 6 K are shown in Fig. 2. The peak maxima and the double half widths at half maxima for the long-wavelength slope of the band in both polymers are summarized in Table I together with pressure shift data.

Temperature effects were investigated on deep holes burned at different positions over the inhomogeneous band at 7 K. Relatively high light doses were applied, and as a result, the width of initial holes exceeds the quasihomogeneous value by a factor of 2 to 4 (Fig. 3). Thermal hole shifts (Figs. 2 to 6) display a pronounced dependence on burning position, in contrast to broadening (Figs. 2 and 7).

The observed thermal shift $\Delta\nu_{\text{obs}}$ of optical transitions consists of a density-dependent solvent shift and a pure thermal, phonon-induced contribution.^{8,28} The shift component caused by thermal expansion can be estimated on the basis of pressure shifts $d\nu/dP$, the isobaric thermal-expansion coefficient of the matrix α_P [$\alpha_P = (dV/dT)_P/V$], and the isothermal volume compressibility β_T [$\beta_T = -(dV/dP)_T/V$], where T , V , and P stand for temperature, volume, and pressure, as usual. The pure thermal shift ($\Delta\nu$) is calculated as follows:^{8,28}

$$\Delta\nu = \Delta\nu_{\text{obs}} - (d\nu/dP)(1/\beta_T) \int_0^T \alpha_P dT. \quad (1)$$

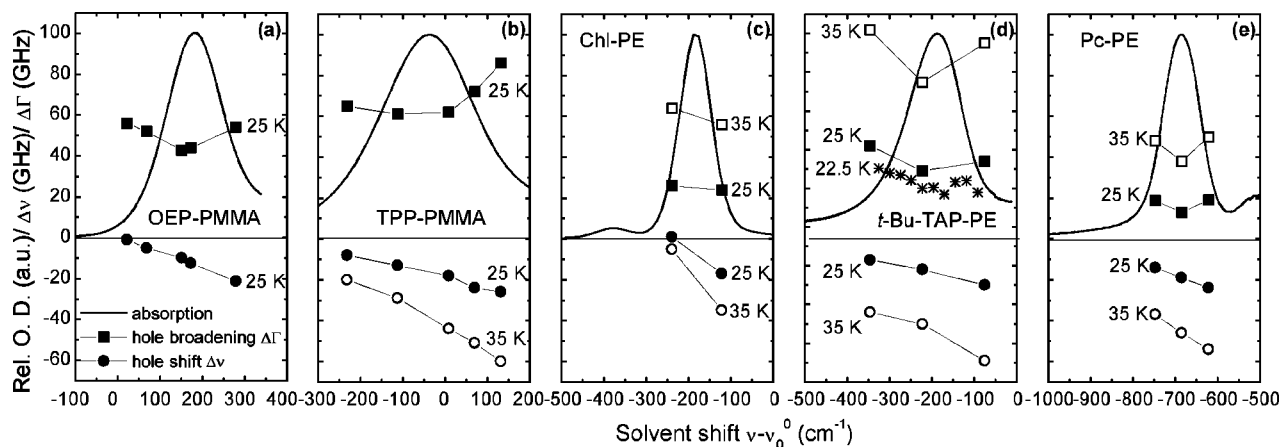


FIG. 2. Normalized absorption spectra of dyes in PMMA [(a) and (b)] and polyethylene [(c) to (e)] at 6 K, plotted relative to the 0-0 origin of free chromophore in vacuum. The phonon-induced shifts of spectral holes burned at 7 K and measured at 25 K (●) and 35 K (○) are shown in the lower portion. Similarly, the extent of thermal hole broadening ($\Delta\Gamma$) between 7 and 25 K (■) or 35 K (□) is indicated. For *t*-Bu-TAP in high-density polyethylene the frequency dependence of quasihomogeneous holewidths (Γ_{qh}) at 22.5 K (*) is shown in (d).

TABLE I. Spectroscopic properties of pigments in polymers at 6 K.

Pigment	ν_0^0 (cm^{-1}) ^a	$\nu_{\text{max}} - \nu_0^0$ (cm^{-1}) ^b		Γ_{ih} (cm^{-1}) ^c		$(d\nu/dP)_{\text{max}}$ (GHz/bar) ^d		a (10^{-5} bar^{-1}) ^e	
		PE	PMMA	PE	PMMA	PE	PMMA	PE	PMMA
OEP	16 056(s)	64	182	84	160		0.055		3.37
TPP	15 617	-105	-38	232	276		-0.118		3.59
Chlorin	15 912	-180	-97	87	230	-0.173	-0.121	4.38	2.25
<i>t</i> -Bu-TAP	16 326(s)	-190	-87	155	328	-0.279	-0.263	3.62	2.42
Pc	15 132	-687	-566 ^f	103	276 ^f	-0.451		4.36	

^aTransition frequency of the free dye in vacuum, measured in a cold supersonic jet (Refs. 29–31), error $\pm 1 \text{ cm}^{-1}$, or extrapolated from the solvent shift (s) (Ref. 34), error $\pm 20 \text{ cm}^{-1}$.

^bAbsolute shift of the band maximum, error $\pm 5 \text{ cm}^{-1}$.

^cInhomogeneous bandwidth, equal to the double value of the half width at half maximum on the red side of the band, error $\pm 5 \text{ cm}^{-1}$.

^dPressure shift coefficient at the band maximum (Ref. 33), error $\pm 0.01 \text{ GHz/bar}$.

^eSlope of the plot of pressure shift coefficients $d\nu/dP$ vs the hole frequency (Ref. 33), error $\pm 0.2 \times 10^{-5} \text{ bar}^{-1}$.

^fReference 8.

Strongly T -dependent α_P values of PMMA and low-density PE of 42% crystallinity were taken from Refs. 35 and 36, respectively (the tabulated linear-expansion coefficients were multiplied by a factor of 3). The β_T values are equal to $1.30 \times 10^{-5} \text{ bars}^{-1}$ for PMMA and $1.41 \times 10^{-5} \text{ bars}^{-1}$ for PE, and nearly independent of T between 5 and 77 K.³⁷ For convenience, the isochores of PMMA and PE (in bar units) were approximated to the following power laws:³⁸

$$(1/\beta_T) \int_0^{32} \alpha_P dT = -1.15 + 0.0189T^{2.317} \quad (5 < T < 32 \text{ K}) \quad (\text{PMMA}), \quad (2)$$

$$(1/\beta_T) \int_0^{47} \alpha_P dT = -0.68 + 0.00864T^{2.571} \quad (3 < T < 47 \text{ K}) \quad (\text{PE}). \quad (3)$$

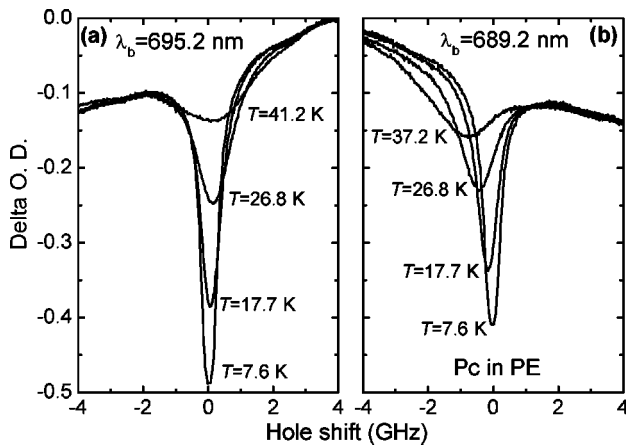


FIG. 3. Temperature-induced changes of spectral holes burned at 7.6 K on the red (695.2 nm) (a) and blue (689.2 nm) (b) edges of the absorption band of phthalocyanine in polyethylene. The initial deep holes are broadened by an excessive dose of exposure (0.03 J cm^{-2}).

Frequency-dependent pressure shifts $d\nu/dP$ were available from our previous work.³³ They can be found from the values at band maxima $(d\nu/dP)_{\text{max}}$ and the slope factors a (Table I).

The frequency dependence of calculated pure thermal shifts between the burning T (6–8 K) and 25 or 35 K are plotted in the lower parts of Fig. 2. The T dependence of both $\Delta\nu_{\text{obs}}$ and $\Delta\nu$ for OEP-PMMA at several hole positions is shown in Fig. 4. Relative contributions of the solvent shift and $\Delta\nu$ to the observed shift $\Delta\nu_{\text{obs}}$ are illustrated separately for Chl (Fig. 5) and Pc (Fig. 6) in the PE host matrix. The pure thermal shift $\Delta\nu$ is predominately negative and shows less spread with respect to the burning position than $\Delta\nu_{\text{obs}}$. The T dependence of most pure thermal shifts can be fitted perfectly well to power laws with coefficients lying between 2.0 and 2.8, as indicated in Figs. 4 to 6. Remarkably, small absolute values of $\Delta\nu$, recorded at 622 nm in OEP-PMMA (Fig. 4) or at 638 nm in Chl-PE (Fig. 5), exhibit a clear

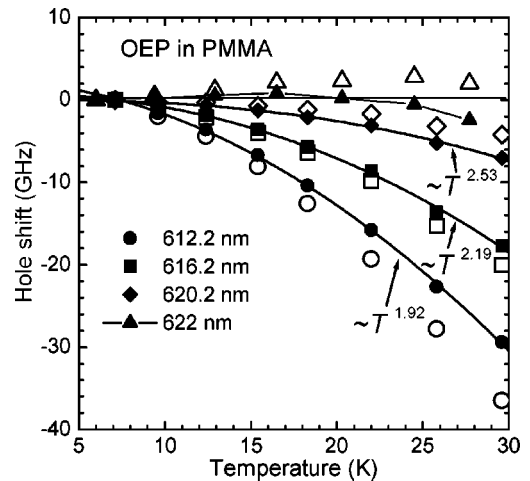


FIG. 4. Thermal shifts of spectral holes burned between 612.2 and 622 nm in the absorption band of OEP in PMMA at 7 K. The phonon-induced shift ($\Delta\nu$) (filled symbols) is calculated from the observed shift (open symbols) [Eq. (1)]. The T dependence of $\Delta\nu$ obeys power laws (thick lines; the T coefficients are indicated).

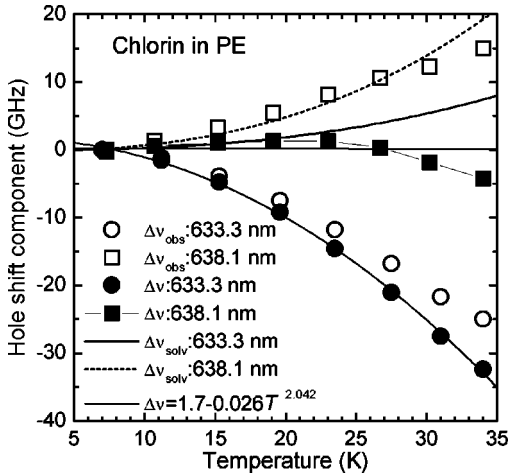


FIG. 5. Temperature-induced shifts of spectral holes burned at 7 K on the red (638.1 nm) (□,■) and blue (633.3 nm) (○,●) edges of the absorption band of chlorin in the polyethylene host matrix. The phonon-induced shift $\Delta\nu$ (●,■) is calculated from the observed shift (○,□) by subtracting the solvent shift due to the matrix expansion (dotted and thick lines) [Eq. (1)]. The T dependence of $\Delta\nu$ at 633.3 nm obeys a power law (thin line).

switching from the initial blueshift to a bathochromic behavior at 20 and 27 K, respectively.

As a rule, truly homogeneous, dephasing rate-dependent linewidths cannot be obtained from holewidths in glasses. The widths of shallow persistent holes created and measured at the same T have mainly been reported earlier.^{7,23–27} These widths are referred to as quasihomogeneous (Γ_{qh}), since spectral diffusion broadening may occur during the experiment, in addition to pure dephasing.^{7,39–41} In these experiments the hole depth should not exceed 5% of zero-phonon optical density in order to avoid the broadening by the absorbed light dose. Note that the optical linewidth amounts to one-half the holewidth Γ_{qh} .

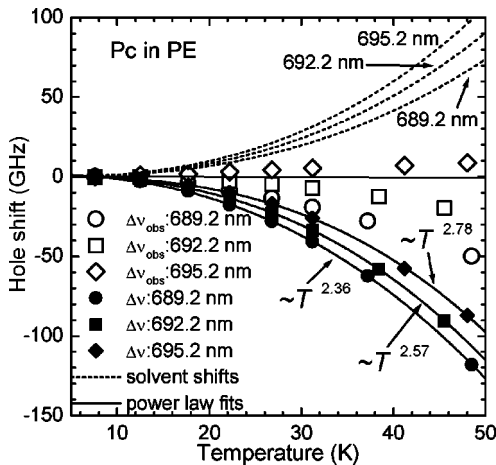


FIG. 6. Thermal shifts of spectral holes burned at different positions in the absorption band of phthalocyanine in polyethylene at 7.6 K. The phonon-induced shift $\Delta\nu$ (filled symbols) is calculated from the observed shift (open symbols) by subtracting the solvent shift due to the matrix expansion (dotted lines) [Eq. (1)]. The T dependence of $\Delta\nu$ obeys power laws (thick lines; the T coefficients are indicated).

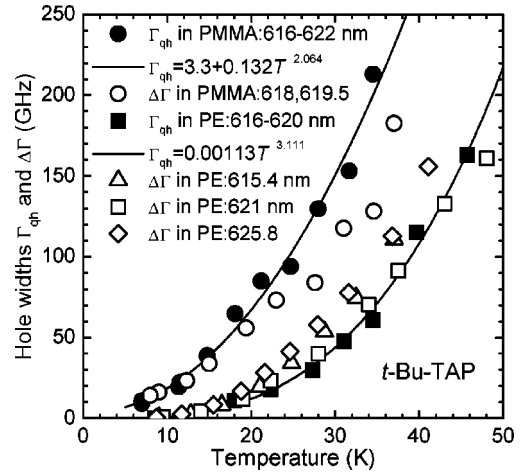


FIG. 7. Temperature dependence of quasihomogeneous holewidths Γ_{qh} of t -Bu-TAP in PMMA (●) and polyethylene (■) host matrices. The burning interval is from 616 to 622 nm for PMMA and from 616 to 620 nm for PE. Owing to nanoscopic strains in the matrix the broadening of single holes $\Delta\Gamma$ burned at 7 K at 621 nm in PMMA (○), or at 615.4 (△), 621 (□), and 628.8 nm (◇) in PE is much larger than the expected value of $\frac{1}{2}\Gamma_{qh}$.

As compared to Γ_{qh} the broadening of a single hole ($\Delta\Gamma$) burned at low T is further enhanced by nanoscopic strains caused by a T change, and has therefore been rarely considered.³⁸ Both Γ_{qh} and $\Delta\Gamma$ are displayed in Fig. 7 for t -Bu-TAP imbedded in PMMA and PE matrices. In partially crystalline PE the strain-induced component is larger than that in PMMA. Both the magnitude and the T dependence of Γ_{qh} and $\Delta\Gamma$ are rather similar. Only about 50% of $\Delta\Gamma$ is of dynamic origin, since in the absence of strains the hole broadening $\Delta\Gamma$ would amount to $\frac{1}{2}\Gamma_{qh}$.³⁸ Nevertheless, single deep holes were given preference here, because of the better signal-to-noise ratio, in particular, on the far wings of spectra. Unlike the shift, the broadening is weakly dependent on burning position.

Large burning doses can bleach excessive amounts of centers as a result of excitation via the low-frequency sidebands, and give rise to a phonon pseudoband. If the burning is performed at the flat maximum of a broad contour, the difference spectrum is quite close to the phonon wing.²⁶ On the band edges an approximate correction for sloped inhomogeneous site distribution function was done by dividing the hole burning difference spectrum by the initial absorption curve. Phonon sideband maxima show a small but significant down shift from $17.5 \pm 1.5 \text{ cm}^{-1}$ at 612 nm to $15 \pm 1 \text{ cm}^{-1}$ at 616 (band maximum) and 620 nm in OEP-PMMA, and from $17.7 \pm 0.6 \text{ cm}^{-1}$ at 689 and 692 nm (band maximum) to $14.8 \pm 1 \text{ cm}^{-1}$ at 695 nm in Pc-PE (data not shown).

IV. DISCUSSION

A. Inhomogeneous broadening and solvent shifts: Microscopic models

The frequency dependence of the T -induced line shift implies that dynamic phenomena must be correlated with static parameters that cause microscopic spectral solvent shifts,

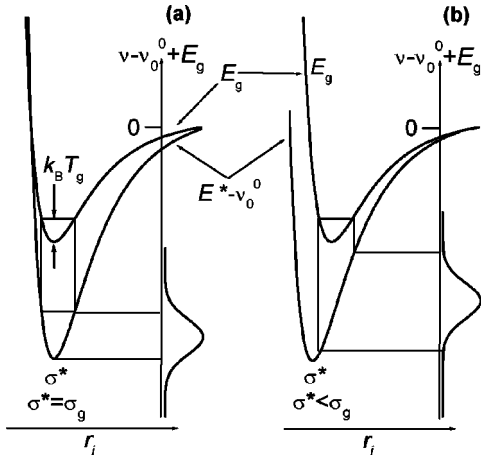


FIG. 8. Distance dependence of Lennard-Jones energy for guest-host pairs in the ground state E_g [Eq. (4)] (upper curves). It is assumed that the potential well is deeper if the guest molecule is electronically excited [lower curves, Eq. (5)]. In the S_1 state the equilibrium distance σ^* remains either unchanged (a) or decreases (b). The distribution of intermolecular distances becomes frozen at the glass transition temperature (T_g) of the matrix and cannot relax upon further cooling. The formation of inhomogeneous spectral bands results from the projection of the Boltzmann distribution of intermolecular distances r_i of the ground-state manifold onto the excited-state potential function, as illustrated. Note that the spectral curves shown on the right-hand side of each figure deviate from the inhomogeneous distribution of solvent shifts $\nu - \nu_0^0$ by ground-state energy E_g .

such as the spatial distribution of matrix particles and the intermolecular forces. The ground-state energy (E_g) of an impurity molecule surrounded by solvent particles, each at a distance r_i , can be expressed as a sum of short-range repulsive and long-range attractive interactions characterized by power laws with coefficients m and n ($m \gg n$), respectively. In the Lennard-Jones potential the exchange repulsion is represented by $m=12$ and the dispersive stabilization by $n=6$:⁴²

$$E_g = \varepsilon_g \sum_i [(\sigma_g/r_i)^{12} - 2(\sigma_g/r_i)^6], \quad (4)$$

where ε_g is the depth of the potential well and σ_g is the distance between the solute and solvent particles in the ground-state equilibrium. The potential curve of the excited state is up-shifted by transition energy in vacuum ν_0^0 , and the well depth and the minimum position may change:

$$E^* = \varepsilon^* \sum_i [(\sigma^*/r_i)^{12} - 2(\sigma^*/r_i)^6] + \nu_0^0. \quad (5)$$

The absolute microscopic solvent shift $\nu - \nu_0^0$ (in energy units) is the difference between the potential curves in the excited (E^*) and the ground states minus the transition energy in vacuum (Fig. 8):

$$\nu - \nu_0^0 = E^* - E_g - \nu_0^0. \quad (6)$$

The solvent shift mainly depends on matrix molecules in the closest coordination layer surrounding the chromophore. The solute-solvent interactions are obviously degenerate in the sense that the same energy corresponds to a certain loosely and a tightly packed guest-host configuration, even in the case if a single host particle with $r_i \neq \sigma_g$ is considered. The particle distribution becomes fixed at a T close to the glass transition temperature of the matrix T_g , so the characteristic variation range of the ground-state solvation, or stabilization energy E_g , is $\sim k_B T_g$.

It has been assumed that in the excited state only the depth of the potential well changes, i.e., $m = m^*$, $n = n^*$, and $\sigma_g = \sigma^*$.⁴² In this case, degeneracy remains also in transition energies [Fig. 8(a)]. This fact has important consequences as far as frequency-dependent behavior of spectral holes is concerned. For the centers absorbing on the red edge the solvent particles are placed at a distance close to σ_g , whereas both appressed ($r_i < \sigma_g$) and loosely packed ($r_i > \sigma_g$) impurity molecules contribute simultaneously to the high-frequency edge. As a result, a prominent frequency dependence of hole broadening under elastic compression is expected.⁴² In the blue edge enormous broadening is expected, since both up and down shifts of resonance frequencies are large, and occur with comparable probabilities when the accidental degeneracy is removed by pressure. By contrary, on the red edge the pressure broadening should be small. However, in our dye-polymer systems such an effect is not observed: the extent of hole broadening under the He gas pressure remains constant to within 10%–20%, and usually shows a small minimum in the middle of the band (data not shown). Therefore, the assumption that the equilibrium positions remain the same in both the ground and excited states⁴² is clearly not justified.

Alternatively, it is assumed in Fig. 8(b) that the solvent shell would tend to be tighter in the excited state, i.e., $\sigma^* < \sigma_g$. Now the centers with smaller average r_i values absorb at lower frequencies, and vice versa. An (anti-)correlation between the attractive and repulsive forces can be established in the sense that at a spectral position on the red edge large dispersive stabilization is accompanied with large repulsive destabilization, and vice versa. This anticorrelation has been introduced by us earlier to explain steep frequency dependencies of pressure-induced hole shifts.⁴³

In both cases (Fig. 8) a correlation between the change of the potential well depth (or the average solvent shift, $\nu_{\max} - \nu_0^0$) and the inhomogeneous bandwidth Γ_{ih} is expected. A rough proportionality between $\nu_{\max} - \nu_0^0$ and Γ_{ih} has indeed been ascertained for polycyclic hydrocarbons in nonpolar solvent glasses.²⁰ OEP, Chl, and Pc have similar bandwidths in PE ($\Gamma_{\text{ih}} \sim 100 \text{ cm}^{-1}$), in spite of considerable variation of absolute solvent shifts between 64 and -687 cm^{-1} (Table I). The unusually narrow band of Pc in PE (103 cm^{-1}) results from the large size disparity between the guest and host particles, allowing the large pigment molecule to be uniformly solvated with small methylene (CH_2) units.⁴²

B. Inhomogeneous broadening and solvent shifts: Continuous dielectric models

Van der Waals forces depend on polarizabilities and dipole moments of interacting molecules.⁴⁴ The polarizability of a bulk solvent is characterized by the Lorentz-Lorenz

function $\varphi(n^2)$ of a refractive index at optical frequencies (n): $\varphi(n^2) = (n^2 - 1)/(n^2 + 2)$. The polarity of solvents is described with a similar function of static dielectric constant (ϵ), $(\epsilon - 1)/(\epsilon + 2)$, minus electronic polarizability $\varphi(n^2)$. The optical spectra are subject to solvent shifts as a result of changes in polarizability and the dipole moment between the ground and excited states. As a single distance parameter, the spherical Osager cavity radius is usually applied.^{20,34,44}

The probe molecules of this study are centrosymmetric, and thus devoid of a dipole moment (Chl has a small dipole moment). Aliphatic hydrocarbon solvents, including PE, are nondipolar, since ϵ is equal to n^2 .⁴⁵ The shift of band maxima $\nu_{\max} - \nu_0^0$ in PE ranges from -687 cm^{-1} in Pc to 64 cm^{-1} in OEP (Table I). Besides dispersive stabilization of the excited state by London forces, the shift can include a contribution of repulsive interactions. It follows from the Lennard-Jones model potential [Eq. (4)] that the average repulsive shift is $-\frac{1}{2}$ of the attractive stabilization (if $\sigma_g = \sigma^*$), or in other words, equal to the observed shift taken with a reversed sign. The analysis of the frequency dependence of pressure-induced hole shifts has shown that the hypsochromism resulting from exchange repulsion may actually be smaller than predicted by the 6-12 potential.⁴³

Another matrix, PMMA, contains C-O groups having large dipole moments, and belongs to highly polar polymers, with $\epsilon \gg n^2$ in a (hypothetic) liquid state. The polarizability of PMMA is slightly less [$\varphi(n^2) = 0.30$] than that of PE (0.329) at 5 K.^{35,36,45} In PMMA a rather uniform, $\sim 100 \text{ cm}^{-1}$, shift of all band maxima to the blue is observed as compared to PE (Table I). This hypsochromic solvent shift of S_1 bands of freebase porphyrins in polar media is mainly caused by electrostatic interactions that modulate the distance between the two protons in the center of the macrocycle.³⁴

The bandwidth is more than doubled in PMMA as a result of polarity (Table I). The electrostatic interactions always cause strong broadening, since both redshifts and blueshifts are possible, depending on the mutual orientation of multipolar moments. The microscopic shifts caused by electrostatic interactions may not shift the center of gravity of the whole band if the reaction field is negligible. A rule of thumb connecting Γ_{ih} with $\nu_{\max} - \nu_0^0$ has been established for aromatic compounds in frozen solvent glasses.²⁰ First, the extent of broadening in nonpolar glasses is about 10% of the dispersive band shift. This Γ_{ih} to $\nu_{\max} - \nu_0^0$ ratio is in accordance with the fact that a dye molecule can accommodate approximately ten solvent particles in its closest coordination layer, and there is about 10% free volume in glasses. Second, the electrostatic mechanisms, such as Stark effects of the cavity or reaction fields, lead to shifts and broadening of comparable magnitude. Finally, there is a residual broadening of $70\text{--}100 \text{ cm}^{-1}$ that has been ascribed to repulsive and multipolar effects.^{20-22,33,43}

In PMMA the hypsochromic band shift and the additional broadening are indeed of similar magnitude, about 100 cm^{-1} , as compared to PE (Table I). The absolute band shift of OEP is perhaps negligible in PE, but the width still amounts to 84 cm^{-1} (the ν_0^0 of OEP has been obtained by extrapolation of

solvent shifts at room temperature and may contain a large error of $\pm 50 \text{ cm}^{-1}$).³⁴ The chemical structure of chromophores can have a strong influence on Γ_{ih} . There is an extra broadening as large as 150 cm^{-1} in TPP, because the $S_1 - S_0$ energy is modulated by angle-dependent conjugation of phenyl substituents with a porphyrin macrocycle. The bulky *tert*-butyl groups attached to tetraazaporphine in order to ensure better solubility of *t*-Bu-TAP seem to create additional disorder in the polymer matrix and enhance the Γ_{ih} by 50 cm^{-1} .

C. Thermal line-shift and broadening theory

The line broadening and shift at temperatures above 0 K are of dynamic origin, in contrast to inhomogeneous broadening that is a consequence of static, microscopic solvent shifts. Broadening depends on dynamic modulation of electronic levels by matrix fluctuations, whereas the shift arises as a result of a phonon frequency change accompanying optical excitation. In the following the shift and broadening will be rationalized with the aid of nonperturbative quadratic electron-phonon coupling theory after Osad'ko¹⁶ and Skinner and Hsu.¹⁷

The difference between Born-Oppenheimer potential surfaces in the ground (E_g) and excited (E^*) states can be expanded in terms of a single collective coordinate of the matrix and impurity (ϕ):¹⁷

$$E^* - E_g = \nu + a\phi + \frac{1}{2}W\phi^2, \quad (7)$$

where ν is the 0-0 transition energy that includes the solvent shift, and a and W are the linear and quadratic electron-phonon coupling (QEPC) constants, respectively.

The experimental dependence of thermal hole shifts on burning frequency, or in other words, on the solvent shift means that the collective normal-mode coordinate ϕ should include intermolecular guest-host distances r_i [Eq. (4)]. In a regular array of particles the phonon wavelength cannot be shorter than the lattice constant, defining the so-called Debye cutoff limit. The Debye limit corresponds to the intermolecular displacement modes. These modes cannot propagate in glasses, and coincide with pseudolocal vibrations. Moreover, disorder can reduce the effective Debye temperature of organic solids from $\sim 100 \text{ K}$ to $20\text{--}30 \text{ K}$, i.e., down to the boson peak region.⁴⁶ The intermolecular modes have the largest coupling constant W , since the latter increases sharply with increasing (acoustic) phonon frequency.¹

In the case of weak interaction of an electronic transition with a single harmonic pseudolocal mode the nonperturbative theory yields the following expressions for line shift ($\Delta\nu$) and broadening ($\Delta\Gamma$) (in frequency units):¹⁷

$$\Delta\nu = \frac{1}{2}W\omega_0 n(\omega_0); \quad (8)$$

$$\Delta\Gamma = \frac{1}{4}W^2\omega_0^2\tau_0 n(\omega_0)[n(\omega_0) + 1], \quad (9)$$

where ω_0 is the phonon frequency, if the impurity is in the ground state; τ_0 is the lifetime of phonon level; and $n(\omega_0)$ is the Bose population factor $\{n(\omega_0) = [\exp(h\omega_0/k_B T) - 1]^{-1}\}$.

The QEPC constant W characterizes the difference of curvatures of potential-energy surfaces for a (pseudo-)local vi-

bration between the ground and excited electronic states of the chromophore. It depends on the respective harmonic frequencies as

$$W = (\omega_1 / \omega_0)^2 - 1. \quad (10)$$

For the low-temperature limit ($k_B T \ll h\omega_0$) one obtains from Eqs. (7) to (9) that both the shift and broadening obey the Arrhenius law with activation energy $h\omega_0$. In the high-temperature limit ($k_B T \gg h\omega_0$) the Bose factors reduce to linear and quadratic laws, respectively:

$$\Delta\nu = \frac{1}{2} \omega_0^{-1} (\omega_1^2 - \omega_0^2) T; \quad (11)$$

$$\Delta\Gamma = \frac{1}{4} \omega_0^{-2} (\omega_1^2 - \omega_0^2)^2 \tau_0 T^2. \quad (12)$$

A comparison of phonon wing maxima (15–18 cm^{-1}) with $k_B T$ in the T range under investigation (6–50 K) reveals that we are actually in the intermediate regime. The experimental shift (Figs. 4 to 6) and broadening (Fig. 7) data can be fitted reasonably well to power laws with coefficients varying between 2 and 3. The experimental T dependencies are steeper than predicted for a single mode model [Eqs. (11) and (12)] because the high- T approximation is not valid over the whole T range. Exponential contributions to the initial portions of the shift and broadening curves are masked by an inhomogeneous spread of phonon frequencies and uncertainties of the measurement. The broadening in PE obeys a nearly cubic T dependence (Fig. 7), whereas the shift curves (Figs. 5 and 6) are usually by 0.5 units less steep, in qualitative accordance with the theory. For a given guest-host combination the variation of T coefficients over the spectral band for both $\Delta\nu$ and $\Delta\Gamma$ curves is also about 0.5 units.

D. Frequency dispersion of thermal line shifts

For all dye-polymer combinations the pure thermal, phonon-induced line shifts reach the largest negative magnitudes on the high-frequency absorption edge (Fig. 2). On the opposite (red) edge of the band the shift is less negative, or even negligible, as in the case of OEP-PMMA (Fig. 4) and Chl-PE (Fig. 5).

In a single harmonic mode approximation the shift depends on phonon occupation numbers and the difference in phonon frequencies ω_0 and ω_1 [Eqs. (8) and (11)]. If the coupling is weak, ω_0 and ω_1 are similar, and the Bose factor could be expressed in terms of just one of them, ω_0 . The phonon pseudowings in hole burning spectra yield excited-state frequencies ω_1 . Since the pseudowing peak maxima tend to be $\sim 10\%$ higher for hypsochromically displaced centers, a slightly higher activation energy is predicted for thermal shifts on the blue side of the absorption contour, in contradiction with the observed trend of larger (negative) shifts. Therefore, the difference between ω_0 and ω_1 , and not the activation energy, must be the leading term.

The molecules at the absorption band center (ν_{max}) are the most stabilized as far as the ground state is concerned [Fig. 8(b)]. The chromophores at resonance with band edges have higher ground-state energies. Whether the electronic transition is redshifted or blueshifted with respect to ν_{max} depends

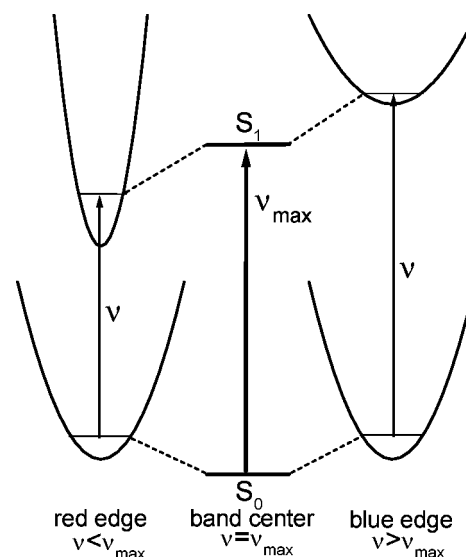


FIG. 9. The change of potential-energy surfaces for a (pseudo-)local phonon on electronic excitation of the impurity molecule. The molecules absorbing at the blue edge of the inhomogeneous band have their excited state destabilized with respect to those in resonance at the band maximum. This leads to softening of phonon modes that in turn will be responsible for bathochromic thermal shifts. The situation is reversed on the low-frequency absorption edge where a thermal blueshift is predicted. The centers absorbing at the band edges correspond to appressed or loosely packed host-guest configurations and have their ground states at higher energies relative to the bulk of centers contributing to the peak maximum.

on the position of the excited level. Figure 9 shows the adiabatic potentials for two centers selected from the opposite edges of the inhomogeneous manifold. The potential functions are rendered steeper in the case of stabilization of the excited state. Thus, mode stiffening should accompany spectral redshifts, whereas the blueshift results in softening of pseudolocal phonons. In QEPC theory the latter means negative W values for the holes probing the blue edge of the band, in accordance with experiment (Fig. 2).

However, the holes burned close to the peak maxima at 6 K shift to the red in all cases. At 25 K the shift varies between -8 GHz (Chl-PE) and -23 GHz (*t*-Bu-TAP) (Fig. 2) and shows no clear dependence on neither the absolute solvent shift $\nu_{\text{max}} - \nu_0^0$ (Table I) nor polarity of the matrix. The prevalence of redshifts is difficult to account for in terms of local phonons, bearing in mind that bathochromic solvent shifts indicate the stabilization of the excited state. It seems that in the T range under investigation the frequency-dependent shifts appear on the background of a general thermal redshift. A review of published thermal shift data in many systems,^{18,26,47,48} including the d and f ions^{1,2} and defect centers⁴⁹ in inorganic crystals, reveals that in many cases redshifts predominate over large T intervals. Concerning the scattering of bulk phonons on localized optical excitations, the probability for a delocalized, propagating phonon to gain energy at the expense of electronic energy could be higher than to lose it to the impurity center. As a result this Raman-type mechanism⁵⁰ could produce mainly redshifts.

E. Thermal hole broadening

Thermal broadening of spectral holes is only marginally affected by burning position (Fig. 2, upper parts; Fig. 7). A slight decrease at the band center of both the quasihomogeneous holewidth Γ_{qh} [Fig. 2(d)] and the thermal broadening of single holes $\Delta\Gamma$ [Figs. 2(a), 2(d) and 2(e)] renders the dependence of Γ_{qh} or $\Delta\Gamma$ on burning position a characteristic V shape. It is particularly remarkable that broadening can be relatively large on the low-frequency edge where the shift is nearly negligible: at 622 nm in OEP-PMMA (Fig. 4) and at 638 nm in Chl-PE (Fig. 5).

According to QEPC theory, the pseudolocal phonons whose frequency is identical in both the ground and excited states ($\omega_0 = \omega_1$) can cause neither shift [Eq. (11)] nor broadening [Eq. (12)], since the QEPC constant is equal to zero.^{16,17} As a result of disorder not only the solvent shifts, but also the phonon frequencies, phonon lifetimes, etc., are subject to statistical spreads in glassy polymers. A small thermal shift can occur as a result of adding up the contributions from centers with positive and negative values of QEPC constants W . In fact, on the red absorption edge a reversal of the sign of phonon-induced shifts from positive to negative can be detected at 20 K in OEP-PMMA (Fig. 4) and at 27 K in Chl-PE (Fig. 5). Therefore, the phonons operating at higher T are subject to some softening, while the opposite is true at lower T . Unlike the shift, the dynamic broadening is not reduced by this compensation phenomenon, since it depends on the square of electron-phonon coupling constant W^2 .

A slight depression at the band maximum that gives the width dependence a curved V shape means that the phonon frequency shifts between the S_1 and S_0 states appear to be smaller at the peak maximum. The centers absorbing in the vicinity of ν_{max} are surrounded by matrix molecules at average distances close to the equilibrium value σ_g [Fig. 8(b)]. As a result, at ν_{max} the difference $|\omega_1 - \omega_0|$ seems to be smaller and less fluctuating than at the extreme edges of the $S_1 - S_0$ energy distribution function.

In the dye-polymer systems under consideration the broadening varies from 13 GHz in Pc-PE to 62 GHz in TPP-PMMA (between 7 and 25 K). The variation of $\Delta\nu$ has a smaller range, from -8 to -23 GHz. The absolute magnitudes of $\Delta\Gamma$ are larger than that of $\Delta\nu$, with the exception of Pc-PE (13 GHz vs the shift of -18 GHz) (Fig. 2). $\Delta\Gamma$ runs parallel to the inhomogeneous bandwidth Γ_{ih} (Table I), including the strong effect of matrix polarity on both parameters.

Line-broadening phenomena are of crucial importance in practical applications of spectral hole burning. The results of this study reveal that depending on the local environment of the impurity center the QEPC constant can have different signs. The guest-host configurations with vanishing QEPC

constants could be of special interest. If identified, such structures may be designed by means of molecular engineering and used for creation of organic optical memory materials with higher working temperatures.

V. SUMMARY

Spectral holes are extremely sensitive with respect to the changes of temperature and the external pressure or electric field. The frequency dependence of hole properties is of particular interest, since it monitors directly the responses of probe molecules in structurally different local environments. Pseudolocal modes, nuclear two-level systems, structural relaxation dynamics, local compressibility, electric field in the cavity, etc. can be explored by means of hole burning. However, extracting the wealth of information hidden in hole properties is not a straightforward task. The derivation of characteristics of the neat, undoped material requires a proper calibration with respect to the sensitivity of the probe. Fortunately, the perturbation introduced by doping of van der Waals glasses appears to be minor, in contrast to crystals, where the mismatch in molecular mass and particle size introduces severe distortions to the phonon spectrum. Thus, the shape of phonon pseudowings bears more similarity to the inelastic neutron-scattering spectrum than to the far-infrared or Raman profiles in the boson peak region ($5-100 \text{ cm}^{-1}$).⁵¹ This similarity of the first-order coupling constants means that optical hole burning could perhaps be developed into a "poor man's neutron spectrometry" for disordered solids.

Temperature-induced line shift and broadening reported here depend on quadratic electron-phonon coupling. A comparison of several chromophores embedded in polymers with very different polarities, polyethylene and PMMA, has revealed a qualitatively uniform dependence on burning frequency for inhomogeneous ensembles of molecules. Thermal shift is always bathochromic, and becomes less negative with decreasing frequency. It can be negligible on the low-frequency edge of the band (in OEP-PMMA and Chl-PE), where the broadening remains large. Thus, the energy-selected centers may have QEPC constants W of different signs. In polar PMMA the electrostatic interactions enhance the fluctuation amplitudes of W . As a result, the broadening that depends on W^2 increases, while the shift remains small.

ACKNOWLEDGMENTS

This work was supported by the Estonian Science Foundation Grant No. 4511. I would like to thank Professor Urs P. Wild for kind hospitality during my stay in the Physical Chemistry Laboratory, Swiss Federal Institute of Technology in Zurich, where this study was started.

*FAX: +3727-383033. Email address: renga@fi.tartu.ee

¹G. F. Imbusch, W. M. Yen, A. L. Schawlow, D. E. McCumber, and M. D. Sturge, *Phys. Rev.* **133**, A1029 (1964).

²W. M. Yen, W. C. Scott, and A. L. Schawlow, *Phys. Rev.* **136**, A271 (1964).

³F. P. Burke and G. J. Small, *J. Chem. Phys.* **61**, 4588 (1974).

⁴H. W. H. Lee, C. A. Walsh, and M. D. Fayer, *J. Chem. Phys.* **82**, 3948 (1985).

⁵W. H. Hesselink and D. A. Wiersma, *J. Chem. Phys.* **73**, 648 (1980).

- ⁶W. M. Yen and R. T. Brundage, *J. Lumin.* **36**, 209 (1987).
- ⁷P. J. van der Zaag, J. P. Galaup, and S. Völker, *Chem. Phys. Lett.* **166**, 263 (1990).
- ⁸Th. Sesselmann, W. Richter, D. Haarer, and H. Morawitz, *Phys. Rev. B* **36**, 7601 (1987).
- ⁹W. P. Ambrose, Th. Basché, and W. E. Moerner, *J. Chem. Phys.* **95**, 7150 (1991).
- ¹⁰D. Walser, G. Zumofen, A. Renn, and T. Plakhotnik, *J. Phys. Chem. A* **105**, 3022 (2001).
- ¹¹M. Vacha, Y. Liu, H. Nakatsuka, and T. Tani, *J. Chem. Phys.* **106**, 8324 (1997).
- ¹²C. B. Harris, *J. Chem. Phys.* **67**, 5607 (1977).
- ¹³P. de Bree and D. A. Wiersma, *J. Chem. Phys.* **70**, 790 (1979).
- ¹⁴R. Silbey and K. Kassner, *J. Lumin.* **36**, 283 (1987).
- ¹⁵V. Hizhnyakov, *J. Phys. C* **20**, 6073 (1987).
- ¹⁶I. S. Osad'ko, *Phys. Rep.* **206**, 43 (1991).
- ¹⁷J. L. Skinner and D. Hsu, *Adv. Chem. Phys.* **65**, 1 (1986).
- ¹⁸*Shpol'skii Spectroscopy and Other Site Selection Methods: Application in Environmental Analysis, Bioanalytical Chemistry, and Chemical Physics*, edited by F. Ariese, C. Gooijer, and H. Hofstraat, Wiley Series on Chemical Analysis (Wiley, New York, 2000), Vol. 156, pp. 19–71.
- ¹⁹I. Renge, *J. Lumin.* **98**, 213 (2002).
- ²⁰I. Renge and U. P. Wild, *J. Lumin.* **66&67**, 305 (1996).
- ²¹I. Renge, *J. Phys. Chem. A* **104**, 7452 (2000).
- ²²I. Renge and U. P. Wild, *J. Lumin.* **86**, 241 (2000).
- ²³*Persistent Spectral Hole-Burning: Science and Applications*, edited by W. E. Moerner (Springer, Berlin, 1988).
- ²⁴*Zero Phonon Lines and Spectral Hole Burning in Spectroscopy and Photochemistry*, edited by O. Sild and K. Haller (Springer, Berlin, 1988).
- ²⁵S. Völker, in *Relaxation Processes in Molecular Excited States*, edited by J. Fünfschilling (Kluwer, Dordrecht, 1989), pp. 113–242.
- ²⁶I. Renge, *J. Chem. Phys.* **106**, 5835 (1997).
- ²⁷S. Voelker, R. M. Macfarlane, and J. H. van der Waals, *Chem. Phys. Lett.* **53**, 8 (1978).
- ²⁸A. I. Laisaar, A. K.-I. Mugra, and M. N. Sapozhnikov, *Fiz. Tverd. Tela (Leningrad)* **16**, 1155 (1974) [*Sov. Phys. Solid State* **16**, 741 (1974)].
- ²⁹U. Even, J. Magen, J. Jortner, J. Friedman, and H. J. Levanon, *J. Chem. Phys.* **77**, 4374 (1982).
- ³⁰U. Even and J. Jortner, *J. Chem. Phys.* **77**, 4391 (1982).
- ³¹P. S. H. Fitch, L. Wharton, and D. H. Levy, *J. Chem. Phys.* **70**, 2018 (1979).
- ³²I. Renge, *J. Opt. Soc. Am. B* **9**, 719 (1992).
- ³³I. Renge, *J. Phys. Chem. A* **104**, 3869 (2000).
- ³⁴I. Renge, *J. Phys. Chem.* **97**, 6582 (1993).
- ³⁵K. G. Lyon, G. L. Salinger, and C. A. Swenson, *Phys. Rev. B* **19**, 4231 (1979).
- ³⁶G. K. White and C. L. Choi, *J. Polym. Sci., Polym. Phys. Ed.* **22**, 835 (1984).
- ³⁷I. I. Perepechko, *Low Temperature Properties of Polymers* (Mir, Moscow, 1980), p. 272.
- ³⁸I. Renge, *Chem. Phys. Lett.* **357**, 409 (2002).
- ³⁹G. Schulte, W. Grond, D. Haarer, and R. Silbey, *J. Chem. Phys.* **88**, 679 (1988).
- ⁴⁰R. Jankowiak and G. J. Small, *Phys. Rev. B* **47**, 14 805 (1993).
- ⁴¹Y. S. Bai and M. D. Fayer, *Phys. Rev. B* **39**, 11 066 (1989).
- ⁴²B. B. Laird and J. L. Skinner, *J. Chem. Phys.* **90**, 3274 (1989).
- ⁴³I. Renge, *J. Phys. Chem. A* **105**, 9094 (2001).
- ⁴⁴N. Mataga and T. Kubota, *Molecular Interactions and Electronic Spectra* (Marcel Dekker, New York, 1970).
- ⁴⁵*Polymer Handbook*, 3rd ed., edited by J. Brandrup and E. H. Immergut (Wiley, New York, 1989).
- ⁴⁶A. J. García and J. Fernández, *Phys. Rev. B* **56**, 579 (1997).
- ⁴⁷I. Renge, R. van Grondelle, and J. P. Dekker, *J. Photochem. Photobiol., A* **96**, 109 (1996).
- ⁴⁸I. Renge and U. P. Wild, *J. Phys. Chem. A* **101**, 7977 (1997).
- ⁴⁹A. Halperin and O. Nawi, *J. Phys. Chem. Solids* **28**, 2175 (1967).
- ⁵⁰B. di Bartolo, *Optical Interactions in Solids* (Wiley, New York, 1968), Chaps. 15 and 18.
- ⁵¹I. Renge, *Phys. Rev. B* **58**, 14 117 (1998).