Inhomogeneous broadening and pressure shifts of the optical spectra in organic glasses at low temperatures

2 **AUTHORS**, INCLUDING:

Urs P. Wild
ETH Zurich

343 PUBLICATIONS   **6,113** CITATIONS

Inhomogeneous broadening and pressure shifts of the optical spectra in organic glasses at low temperatures

Indrek Renge[a],*, Urs P. Wild[b]

[a]*Institute of Physics, Tartu University, Riia str. 142, EE51014 Tartu, Estonia*
[b]*Physical Chemistry Laboratory, Swiss Federal Institute of Technology (ETHZ), CH-8092 Zürich, Switzerland*

Abstract

Inhomogeneous bandwidths were measured at 6 K in glassy solutions of poly(methyl methacrylate) and ethanol for chromophores with comparatively weak electron–phonon coupling: polymethine dyes, polycyclic hydrocarbons and tetrapyrrolic compounds. The contributions of dispersive attraction, the internal electric field effects and the repulsive forces to the band broadening are considered. Spectral holes were burned in the inhomogeneous $S_1 \leftarrow S_0$ absorption bands and the pressure shift coefficients dv/dP were determined using gaseous He as pressure transmitter. Pressure shift coefficients show a linear dependence on hole-burning frequency. The slope of this dependence generally differs from the value of $2\beta_T$ (β_T is the isothermal compressibility of the matrix), predicted from the dispersive solvent shift equation. The slopes smaller than $2\beta_T$ are accounted for in terms of other solvent shift mechanisms, such as linear and quadratic Stark effects in the cavity field. The slopes larger than $2\beta_T$ are ascribed to repulsive interactions. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Essential spectroscopic properties of solid solutions, such as the solvent and pressure shifts, inhomogeneous bandwidth, the Debye–Waller factor, the dephasing rate, etc., depend on forces between the solute and solvent molecules, or more precisely, on the change of intermolecular potentials upon electronic excitation of the chromophore [1,2]. If the exact positions of the solvent molecules surrounding an impurity were known, the resulting shift of the electronic transition energy would be still extremely difficult to calculate. Therefore, the solvatochromic mechanisms are commonly expressed in terms of the theories of continuous dielectrics that use dielectric permittivities and refractive indices as parameters [3]. The attractive force of dispersive origin is responsible for energy down shifts of transitions in many molecules except for the very polar ones [4,5]. This shift is well described by the the Bakshiev formula [3]. In polar matrices, the Stark effects of both reaction and cavity fields come into play. The role of repulsive forces of electrostatic and exchange origin in organic impurity spectra has remained largely hypothetical [5].

* Corresponding author. Tel.: + 00-3727-428882, + 00-3727-304800; fax: + 00-3727-383033.
E-mail address: renge@fi.tartu.ee (I. Renge).

In low-temperature solids a relatively small pressure of He gas (< 200 bar) can produce a shift and a broadening of spectral holes that are conveniently measured by tunable lasers [6,7]. Usually, a linear relationship between the pressure (P) shift coefficient dv/dP and the burning energy holds, and the transition frequency at which the P shift vanishes ($v_{0(P)}$) may be found by extrapolation. It follows from simple model considerations, both microscopic [7,8] and macroscopic [9], that $v_{0(P)}$ can give the 0–0 frequency of the nonsolvated chromophore v_0, whereas the slope of the line is equal to the twofold value of the isothermal compressibility of medium $2\beta_T$. Recently, these predictions have been verified for a number of polymers with known low-temperature compressibilities using tetra-tert-butylporphyrazine (*t*-Bu-TAP) as a probe. Several π-electronic chromophores with available vacuum frequencies were measured in poly(methyl methacrylate) (PMMA) [9]. As a rule, a poor correspondence between v_0 and $v_{0(P)}$ as well as the respective slopes that can be considerably steeper than $2\beta_T$ were observed. Such deviations are by no means surprising, since several solvent shift mechanisms can operate simultaneously, each with a different distance dependence between solute and solvent molecules.

The problem of understanding the pressure-induced shifts of spectral holes can be split into three tasks. First, the intermolecular interactions responsible for the matrix shifts should be ascertained based on liquid-phase studies in solvents with gradually varying polarities and polarizabilities [3–5]. Second, the influence of each solvent shift mechanism on inhomogeneous bandwidth is to be established [1]. Third, the P shifts of spectral holes can be rationalized. The main objective of this paper is to explain the remarkably varying slopes of dv/dP vs. v ranging from 2.3×10^{-5} to 6×10^{-5} bar^{-1} in PMMA and 1.5×10^{-5} to 6×10^{-5} bar^{-1} in ethanol.

2. Experimental

Absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Pressure shift studies were carried out in an optical cell with two 2 mm thick sapphire windows of 4 mm diameter. The cell body consists of a stainless-steel cylinder of 20 mm diameter housing a sample volume of $2 \times 4 \times 4$ mm^3. The sample was cooled as fast as possible by plunging into liquid N_2 and loaded in a precooled CF1204 continuous flow cryostat (Oxford). A maximum He gas pressure of about 200 bar was applied, the system was allowed to thermalize during 5 min, and hole burning was performed between 5 and 8 K. Then the gas bottle valve was closed and the influence of pressure change was followed by releasing the He gas step-by-step. Holes were burned using a Lambda Physik dye laser LPD 3002E pumped with an excimer laser LPX 100. Relatively deep holes broadened by the light dose were created at 3–5 positions over the band for a single pressure run. Holes were explored in transmission with a two-channel Molectron JD2000 Joulemeter Ratiometer.

3. Results

3.1. Inhomogeneous broadening

The inhomogeneous spread of transition frequencies and the shifts of bands as a whole have the same microscopic origin: the matrix-induced changes in optical transition energies. In nonpolar solvent glasses the width of the inhomogeneous site distribution function (IDF) is about 10% of the solvent shift (plus a residual ~ 100 cm^{-1}) [1]. Because in the present case the hole-burning chromophores had small dipole moments, solvent polarization by solute dipole moments is negligible and the shift of absorption band maxima v_{max} is dispersive [1,3]. Dispersive shifts of band maxima depend linearly on the Lorentz–Lorenz function $\phi(n^2)$:

$$v_{max} = v_0 + p\phi(n^2), \quad \phi(n^2) = (n^2 - 1)/(n^2 + 2). \tag{1}$$

Both the vacuum frequency v_0 and the polarizability difference between the ground and the excited state may be estimated from the intercept and the slope (p, further on referred to as Bakshiev number) of Eq. (1), respectively [3–5].

The dispersive shifts Δv_{disp} in solid PMMA and EtOH may be calculated from the Bakhshiev
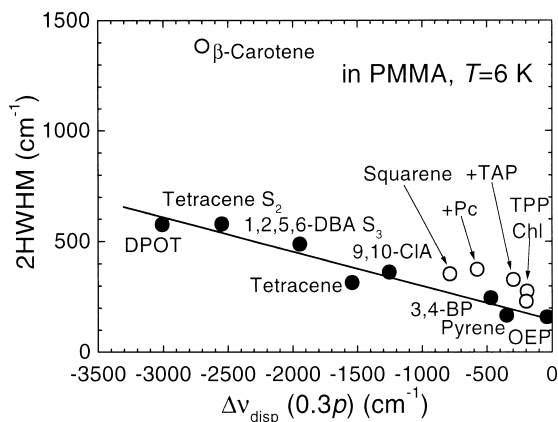
Fig. 1. Dependence of absorption bandwidth (double value of the half-width at half-maximum measured on the long wavelength slope, 2HWHM) on dispersive solvent shift Δv_{disp} in PMMA. Δv_{disp} was calculated from the solvatochromic slope factor p and the Lorentz–Lorenz function of the matrix equal to 0.3 (Eq. (1)). The regression line (Eq. (2)) was drawn for relatively rigid chromophores (filled circles): OEP, octaethylporphine; 3,4-BP, 3,4-benzopyrene; 9,10-ClA, 9,10-dichloroanthracene; 1,2,5,6-DBA, 1,2,5,6-dibenzanthracene; DPOT, 1,8-diphenyloctatetraene. The remaining compounds (open circles) are denoted as: Chl, chlorin; TPP, tetraphenylporphine; + TAP, tetra-tert-butylporphyrazine; + Pc, tetra-tert-butylphthalocyanine.

Fig. 2. Dependence of absorption bandwidth on dispersive solvent shift Δv_{disp} in ethanol glass. Δv_{disp} was calculated from the solvatochromic slope factor p and the Lorentz–Lorenz function of the matrix equal to 0.28 (Eq. (1)). The regression line (Eq. (3)) was drawn for relatively rigid chromophores (filled circles): + Terry, di-tert-butylterrylene. The remaining compounds (open circles) are denoted as: Rh 700, rhodamine 700; PIC, pseudoisocyanine; B[k]Fl, benzo[k]fluoranthene; HIDCI, 1,1′,3,3,3′,3′-hexamethylindodicarbocyanine; CV, cresyl violet.

numbers and the $\phi(n^2)$ values of these hosts at low temperatures, 0.3 [10] and 0.28, respectively. Figs. 1 and 2 show the correlation between Δv_{disp} and the bandwidths. For relatively rigid and non-polar chromophores the following linear relationships are obtained for PMMA and EtOH:

$$[2HWHM] = (147 \pm 27) - (0.154 \pm 0.016)\Delta v_{disp},$$
$$\Delta v_{disp} = 0.3p, \quad N = 8, \quad r = 0.971, \quad (PMMA),$$
(2)

$$[2HWHM] = (118 \pm 4) - (0.082 \pm 0.005)\Delta v_{disp},$$
$$\Delta v_{disp} = 0.28p, \quad N = 5, \quad r = 0.994, \quad (EtOH),$$
(3)

where N is the number of data points (compounds) and r is the linear regression coefficient.

The broadening is equal to about 10% of Δv_{disp}: 15% in PMMA and 8% in EtOH. Glasses contain ~10% of free volume that corresponds on the average to a single vacancy among ~10 solvent
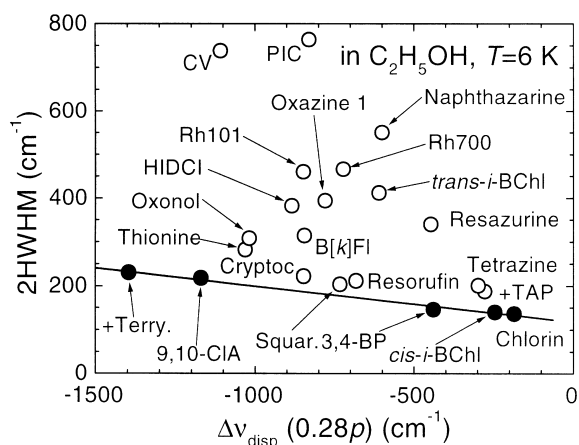
molecules in the closest coordination layer of the solute. The packing density of host molecules is much more uniform in EtOH than in PMMA. In the macromolecular host large density fluctuations are frozen in at the glass transition temperature 390 K that is by 230 K higher than that of EtOH.

The distortion of molecular backbone in the squaraine dye and β-carotene or the rotation of phenyl substituents in the meso position of tetraphenylporphine obviously produces additional broadening in PMMA. In EtOH glass a roughly linear dependence between 2HWHM and Δv_{disp} holds for polycyclic arenes (3,4-BP, 9,10-ClA, di-tert-butylterrylene), chlorin and cis-iso-bacteriochlorin (Eq. (3)). The remaining compounds have broader spectra. The excessive broadening in dipolar molecules: naphthazarine, trans-iso-bacteriochlorin, rhodamines 700 and 101, oxazine 1, benzo[k]fluoranthene and cresyl violet is caused by linear Stark shifts in solvent cavity fields of different magnitude and direction. The broadening in the oxonol dye and HIDCI as compared to cryptocyanine may stem from the conformational flexibility of the pentamethine chain in the former

structures. A presumably stiff monomethine compound, pseudoisocyanine has a 2HWHM as broad as 764 cm^{-1} (in glycerol/water) owing to a huge multiphonon side band that reduces the 0–0 transition probability to a mere 1% [10]. Strong vibronic coupling may contribute to the large bandwidth of β-carotene in PMMA as well. Specific solvation provides further inhomogeneous broadening mechanisms, i.e., the hydrogen bonding in resazurin.

Another distinctive feature of Eqs. (2) and (3) is the intercept which is as large as 147 cm^{-1} in PMMA and 118 cm^{-1} in EtOH. Such residual broadening of about 100 cm^{-1} occurs even in non-polar aliphatic hydrocarbon glasses for $\alpha(^1L_b)$ type transitions of arenes (pyrene) [1] and porphyrins (octaethylporphine, chlorin) that are accompanied by a very small polarizability change and dispersive solvent shift. We assume that either repulsive forces or bond dipole interactions are responsible for this phenomenon.

Therefore, the reasons for inhomogeneous broadening can be rather complex, and every mechanism would differently affect the hole shifts under hydrostatic pressure.

3.2. The wavelength dependence of pressure shift coefficients

The pressure shift coefficient of a spectral hole dv/dP depends linearly on the burning position in the inhomogeneous spectral contour (the so-called color effect [7,11]) (Figs. 3 and 4). The linear plots of dv/dP vs. v have attracted special interest during the last decade, since it has been hoped that a material parameter, the "local compressibility" could be extracted from their slopes $d(dv/dP)/dv$ [7,11].

The measurements were carried out in films cast of commercial Plexiglass, an amorphous high-molecular weight PMMA with isothermal compressibility β_T at 4 K equal to 1.30×10^{-5} bar^{-1} [12]. Both the pressure and solvent shifts are bathochromic, except for OEP. At a certain position the hole shows only broadening but no shift. The slopes of the linear plots of pressure shift coefficients vs. the hole-burning frequency are illustrated in Fig. 3. For t-Bu-TAP, the slope of the dependence under discussion $(d(dv/dP)/dv = 2.42 \times$
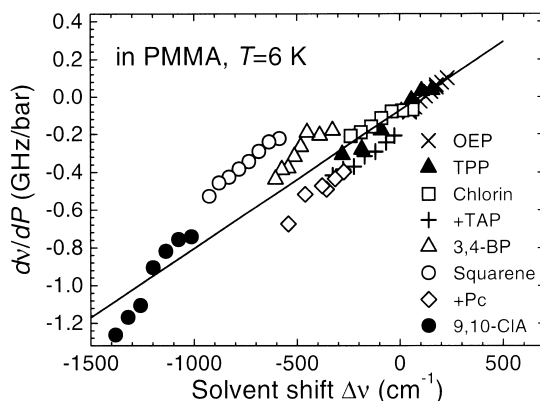
Fig. 3. Pressure shift coefficients of spectral holes burned over the inhomogeneous bands of chromophores in PMMA host matrix plotted as a function of absolute solvent shifts. Most of the linear regression lines have steeper slopes than the twofold compressibility of PMMA equal to 2.6×10^{-5} bar^{-1} at 4 K (line).

10^{-5} bar^{-1}) is very close to the twofold value of isothermal compressibility of bulk PMMA at 4 K ($2\beta_T = 2.6 \times 10^{-5}$ bar^{-1} [12]) [9]. However, the change of pressure coefficient for the remaining chromophores (except for chlorin) over the inhomogeneous band is remarkably larger.

In solid EtOH the slope factor varies between 1.5×10^{-5} and 6×10^{-5} bar^{-1} (Fig. 4). It is inversely correlated with the inhomogeneous bandwidth (Fig. 5):

$$[d(dv/dP)/dv]^{-1} = (8.8 \pm 5.8) \times 10^3$$

$$+ (98 \pm 20)[2HWHM], \quad N = 18, \quad r = 0.783. \tag{4}$$

In general, broad band spectra have shallow slopes and vice versa.

Pressure shift coefficients as a function of solvent shifts for polymethines and the other chromophores are presented in Figs. 4a and b, respectively. For comparison, a linear plot is shown for the most probable compressibility value of solid EtOH $2\beta_T = 3 \times 10^{-5}$ bar^{-1}. Almost ideal coincidence is observed for resorufin, resazurin, chlorin, t-Bu-TAP as well as red-shifted form of s-tetrazine. The data points of cryptocyanine, the squarene and oxonol dyes lie parallel with the line but are
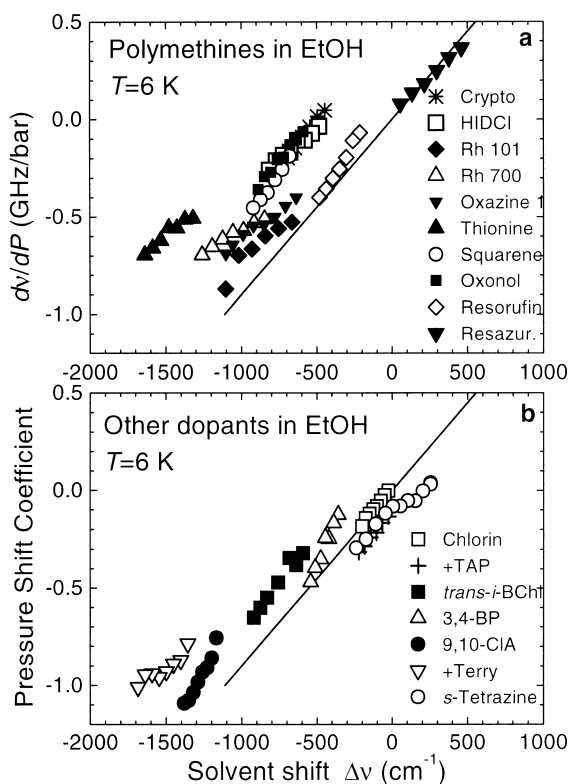
Fig. 4. Pressure shift coefficients of spectral holes plotted as a function of absolute solvent shifts. The holes are burned over the inhomogeneous bands of polymethine dyes (a) and polycyclic arenes, tetrapyrroles and s-tetrazine (b) in ethanol glass. For comparison the lines are drawn that pass zero and have a slope of 3×10^{-5} bar^{-1}, the probable twofold compressibility value of ethanol glass.
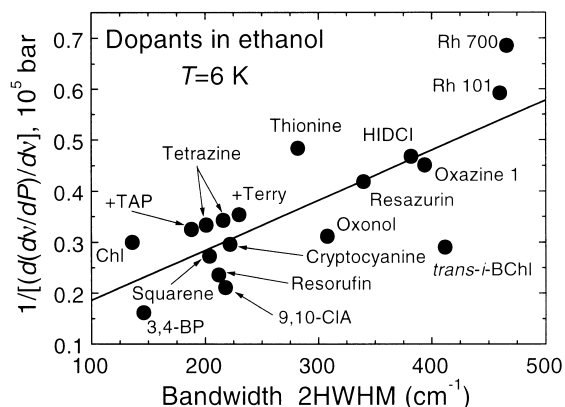

Fig. 5. Relationship between the bandwidth and the inverted slope factor of pressure shift coefficients vs. frequency in EtOH glass (Eq. (4)). The slope factor cannot be described in terms of matrix compressibility alone since it does not remain constant but decreases with increasing bandwidth.

up-shifted. The slopes are particularly shallow in HIDCI, rhodamines 101 and 700. In HIDCI the larger width (382 cm^{-1}) with respect to cryptocyanine (222 cm^{-1}) stems from the geometric distortions of π-electronic system. If the manifold of conformers with different transition energies have similar dispersive shifts, a low value of d(dv/dP)/dv would result. In rhodamines the spectra are broadened due to the linear Stark effect in the cavity field. Under external pressure the cavity field changes in proportion with linear compression $1/3\beta_{T}$ and so does the hole shift coefficient (see below). Because of the small slope, the extrapolated frequency where no hole shift occurs under the

pressure is much less than the vacuum frequency ($v_{0(P)} < v_{0}$).

Polycyclic arenes have the highest sensitivity of pressure shifts towards the hole-burning wave number and the slope factors much larger than $2\beta_{T}$. As in the case of PMMA host matrix, the involvement of repulsive potentials can be surmised in order to account for the steep slopes.

4. Discussion

The dispersion interaction is responsible for bathochromic shifts in many less-polar molecular guest–host systems [3–5]. Absorption band maxima of not very polar chromophores in apolar medium obey well the Bakhshiev equation [3–5] (Eq. (1)):

$$v_{\max} = v_{0} + p\phi(n^{2}),$$
$$p = -3II'(\alpha_{e} - \alpha_{g})/[2(I + I')a^{3}], \qquad (5)$$

where I and I' are the ionization energies of the solute and solvent molecules, $\alpha_{e} - \alpha_{g} = \Delta\alpha$ is the average static polarizability difference between the excited (e) and the ground (g) states, a is the Onsager cavity radius. The Lorentz–Lorenz function is linearly related to the density of matter

d [13]:

$$\phi(n^2) = (4\pi N_A \alpha_g / 3M)d, \qquad (6)$$

where N_A is the Avogadro's number and M is the molecular weight. Compression of the matrix under hydrostatic pressure influences both $\phi(n^2)$ and a^3, so that the solvent shift scales with respect to the volume as V^{-2}. Therefore, the pressure shift coefficient dv/dP can be expressed as a function of the absolute solvent shift $(v - v_0)$ and the isothermal compressibility of the medium $\beta_T = -(dV/dP)_T/V)$:

$$dv/dP = 2\beta_T(v - v_0). \qquad (7)$$

Strictly speaking, it follows from the above derivation that Eq. (7) applies to pressure shifts of band maxima or spectral holes burned at maximum positions of different dyes. Similarly, it should be correct for groups of molecules of the same dye selected by energy within the inhomogeneous spectral band using hole burning. Alternatively, Eq. (7) has been deduced from microscopic models [7,8].

The electric field of a cavity formed in a polar host matrix produces both linear and quadratic Stark effects on the impurity spectra. Under pressure, both the cavity and reaction field strength scale with sample volume (V) as $1/3V$. Therefore, a rather shallow dependence of pressure shift coefficients as a function of hole position is expected: $1/3\beta_T$ for the linear Stark effect in both the cavity and reaction fields and $2/3\beta_T$ for the quadratic Stark effect in the cavity field.

The role of electrostatic or exchange repulsion in impurity spectra has remained elusive. The difficulty of distinguishing the attractive and repulsive interactions is obvious, since a continuous intermolecular potential can be separated into components as far as the model curves are defined for each. The magnitude of either repulsive or attractive energy depends on the model potentials chosen. In the excited states of many nonpolar systems the minimum is deeper and, as a consequence, the attractive branch is steeper owing to the higher polarizability of the excited state that in its turn enhances the London forces. The situation with the repulsive part is less clear. Regarding the increase of molecu-

lar polarizability in terms of the volume increase of the electronic cloud one reaches the conclusion about the repulsive blue shift [5]. However, the opposite effect is also conceivable bearing in mind the possibility of partial electron transfer to the solvent and its delocalization in the excited state (the exciplex phenomenon). Thus, the repulsive branch in the upper state can be also shallower than that of the ground state.

The distance dependence of intermolecular repulsion energy in the electronic ground state is very steep, increasing as a function of r^{-12} at least. The repulsive contribution to the solvent shift is determined by the difference between the respective potentials in the ground and the excited states. It is probable that this difference has also a strong distance dependence. The pressure shift of holes in a hypothetical guest–host system with spectral disorder caused solely by repulsion might obey the $4\beta_T$ law. Therefore, the slope of the plot of dv/dP vs. v can be larger than that for the dispersive attraction $(2\beta_T)$. It seems that the exchange repulsion and its degree of correlation with the attractive forces play an important role in spectroscopic pressure effects in disordered host matrices.

5. Conclusions

In the literature, the simplest expression describing the dependence of pressure-induced shifts of zero-phonon frequency (Eq. (7)) has been used to determine the two important parameters, the matrix compressibility and the transition energy of the nonsolvated chromophore [7,11]. However, the present study in PMMA [9] and EtOH hosts doped with many dyes has revealed a more complex nature of the pressure-induced hole shifts. Because a linear relationship between the pressure shift coefficients and the hole position is observed in most cases, a question arises about the physical meaning of the slopes and intercepts of these plots as far as they fail to give $2\beta_T$ and v_0 directly. The slope factor, $d(dv/dP)/dv$ remains by no means constant in the same host matrix but decreases as the inhomogeneous bandwidth increases. In EtOH nearly a half of the dopants, including t-Bu-TAP

show the slope values clustering around $3 \times 10^{-5}\,\mathrm{bar}^{-1}$. This corresponds perhaps to the two-fold compressibility of the matrix, since a good agreement between the slope factor and $2\beta_T$ has been found for isotropic polymers doped with t-Bu-TAP [9]. The reason for smaller slopes is the band broadening in dipolar molecules such as rhodamines and oxazine in the matrix cavity fields as well as conformational flexibility of π-electronic chains (in HIDCI). The strength of a cavity field is proportional to the linear compressibility of the medium yielding slopes as small as $1/3\beta_T$.

The slope equal to $2\beta_T$ is expected for the dispersive interaction, since the polarizability of the environment increases and the Onsager volume decreases when pressure is applied. The solvent shift of the band maxima in polycyclic hydrocarbons is largely of dispersive origin. It seems puzzling that the sensitivity of P shift coefficients vs. burning wavelength can be steeper than $2\beta_T$. Also, the inhomogeneous bandwidth is rarely less than $80–100\,\mathrm{cm}^{-1}$ in solvent and polymer glasses, even in porphyrins having a very small polarizability change upon the S_1–S_0 excitation [4]. Therefore, besides the dispersive shift some other mechanism is responsible for inhomogeneous broadening. The most probable cause of these effects stems from the repulsive forces between the molecules.

References

[1] I. Renge, U.P. Wild, J. Lumin. 66&67 (1996) 305.
[2] I. Renge, J. Opt. Soc. Am. B 9 (1992) 719.
[3] N.G. Bakshiev, O.P. Girin, I.V. Piterskaya, Opt. Spektrosk. 24 (1968) 901 [Opt. Spectrosc. 24 (1968) 483].
[4] I. Renge, Chem. Phys. 167 (1992) 173.
[5] I. Renge, J. Photochem. Photobiol. A: Chem. 69 (1992) 135.
[6] Th. Sesselmann, W. Richter, D. Haarer, H. Morawitz, Phys. Rev. B. 36 (1987) 7601.
[7] G. Gradl, J. Zollfrank, W. Breinl, J. Friedrich, J. Chem. Phys. 94 (1991) 7619.
[8] B.B. Laird, J.L. Skinner, J. Chem. Phys. 90 (1989) 3274.
[9] I. Renge, J. Phys. Chem. A, accepted.
[10] I. Renge, U.P. Wild, J. Phys. Chem. 101 (1997) 7977.
[11] E. Balog, K. Kis-Petik, J. Fidy, M. Köhler, J. Friedrich, Biophys. J. 73 (1997) 397.
[12] I.I. Perepechko, Low Temperature Properties of Polymers, Mir Publishers, Moscow, 1980.
[13] C.J.F. Böttcher, Theory of Electric Polarization, Vol. 1, Elsevier, Amsterdam, 1973.