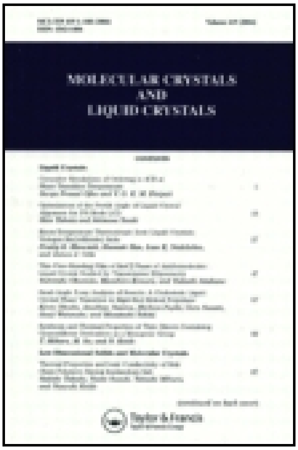

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ANALYTICAL DESCRIPTION OF EXTERNAL-FIELD EFFECTS ON PERSISTENT-HOLE SPECTRA IN DISORDERED MATERIALS

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Abstract External-field effects on persistent-hole spectra in disordered solids can be described with a stochastic theory of dye–matrix interaction. For obtaining analytical results, usually two approximations are performed in the calculation, the continuum approximation which is valid for sufficiently low matrix densities, and the Gaussian approximation which is valid for high densities. Hence, the validity range of the results is not clear *a priori*. The paper shows for the special case of pressure tuning that both approximations must be relaxed in a proper description of the physical situation. Especially the continuum approximation which consists in neglecting any correlations between the matrix molecules, leads to quantitatively incorrect results.

Keywords: hole-burning, pressure tuning, continuum approximation, Gaussian approximation

INTRODUCTION

Site-selective spectroscopic experiments such as persistent hole burning yield an improved spectral resolution in the optical wavelength region. Especially in amorphous solids which are characterized by large inhomogeneous-broadening effects, the gain in resolution often amounts to several orders of magnitude and sensitive measurements can be performed which are not feasible otherwise. This can be utilized for the investigation of the effects of small external perturbations such as electric fields or hydrostatic pressure.

An external perturbation usually gives rise to a shift and a concomitant broadening of a hole spectrum. The broadening is an inhomogeneous phenomenon; it arises from the fact that an ensemble of molecular absorption lines which are accidentally degenerate before the application of the perturbation, is spread out to a distribution of non-zero width when the perturbation is turned on. Hence, the total inhomogeneous absorption band of the sample and the kernel determining the hole broadening in an external field are closely related and can be described within the same theoretical framework.

A powerful means to do this is the stochastic theory of dye–matrix interaction which, in its original form, was devised by Markoff in the beginning of this century.[1] A review of this theory was published lateron by Stoneham.[2] Kikas and Rätsep,[3] and independently Laird and Skinner[4] extended the theory to a two-dimensional form to describe the effects of an external perturbation on a microscopic level. The theory leads to an expression which is very general but is difficult to treat mathematically. Therefore, usually two approximations are performed to obtain simple analytical results, the continuum approximation which is valid for sufficiently low matrix densities and the Gaussian approximation which is valid for high densities. The error introduced by the Gaussian approximation was investigated by numerical calculations under the assumption that the continuum approximation is still valid.[5,6] On the other hand, the error of the continuum approximation was determined within the framework of the Gaussian approximation for theoretical liquid systems.[7,8] In the present paper, we show for the special case of hydrostatic-pressure effects that the Gaussian approximation can be extended in an analytical fashion[9] to describe all the experimental findings on hole-burning systems and that correlation effects between the matrix molecules, which are neglected in the continuum approximation, can be incorporated in this form.[10] Moreover, we evaluate the expressions of Refs. 8 and 10 for two real polymeric hole-burning systems. It turns out that neglecting the matrix correlations leads to quantitatively incorrect results for the molecular parameters although the experimental data are well reproduced.[4]

GENERAL FORMULATION OF THE THEORY

We consider an ensemble of dye molecules embedded in a disordered solid matrix at a concentration low enough such that no interaction between the dye molecules occurs and only the interactions with the matrix units are important. We assume these interactions to be pairwise additive. Hence, the probability distribution that a dye molecule experiences the solvent shift ν with respect to its absoption frequency in vacuum can be expressed as[4]

$$I(\nu) = \frac{1}{V^N} \int_{(V)} d\underline{R}_1 \cdots \int_{(V)} d\underline{R}_N \, P(\underline{R}_1, \ldots, \underline{R}_N) \, \delta \left[\nu - \sum_{n=1}^{N} \tilde{\nu}(\underline{R}_n) \right] \qquad (1)$$

where V denotes the volume of the sample, N the total number of matrix (solvent) molecules, and $P(\underline{R}_1, \ldots, \underline{R}_N)$ the spatial $(N+1)$ particle distribution function describing the probability that the matrix unit with index n is located at position $\underline{R}_n$ $(n = 1, \ldots, N)$ provided that a dye molecule is in the coordinate origin. $\tilde{\nu}(\underline{R}_n)$ is the contribution of a matrix molecule at position $\underline{R}_n$ to the total solvent shift of the impurity.

In analogy to the inhomogeneous distribution, also the pressure kernel, *i. e.* the distribution of the probability that a dye molecule with the original solvent shift ν experiences an additional line shift of magnitude $\Delta\nu_p$ upon a pressure change Δp, can be written in the form[4]

$$\begin{aligned} f\left(\frac{\Delta\nu_p}{\Delta p}\middle|\,\nu\right) &= \frac{1}{I(\nu)\,V^N}\int\limits_{(V)} d\underline{R}_1 \cdots \int\limits_{(V)} d\underline{R}_N\, P(\underline{R}_1,\ldots,\underline{R}_N) \\ &\quad \times\delta\left[\nu - \sum_{n=1}^{N}\tilde{\nu}(\underline{R}_n)\right]\,\delta\left[\frac{\Delta\nu_p}{\Delta p} - \sum_{n=1}^{N}\tilde{\alpha}(\underline{R}_n)\right] \end{aligned} \tag{2}$$

where $\tilde{\alpha}(\underline{R}_n)$ denotes the contribution of a matrix unit at $\underline{R}_n$ to the molecular pressure shift. Note that the distributions $I(\nu)$ and $f(\Delta\nu_p/\Delta p|\nu)$ are normalized to unity when integrated over the total range of their respective argument (ν or $\Delta\nu_p/\Delta p$).

APPROXIMATIONS

Eqs. (1) and (2) contain the most general description of inhomogeneous distributions of absorption frequencies (or absorption frequency shifts) within the framework of the stochastic theory. However, these expressions are difficult to handle, since they contain a large number of spatial integrations over an $(N+1)$ particle distribution function which is not known in general. Hence, usually two important (and, as we will see, often contradictory) approximations are applied. The first one is the so-called continuum approximation. It consists in factorizing the complicated $(N+1)$ particle distribution function $P(\underline{R}_1,\ldots,\underline{R}_N)$ into a product of N equal two-particle solute–solvent distribution functions $g(\underline{R}_n)$,

$$P(\underline{R}_1,\ldots,\underline{R}_N) = \prod_{n=1}^{N} g(\underline{R}_n). \tag{3}$$

While Eq. (3) drastically simplifies the mathematical problem in evaluating Eqs. (1) and (2), it imposes the restriction that any correlations between the matrix units are neglected. As we will see, this is a very crude approximation even in totally disordered materials, because in this way the finite size of the molecules and the fact that two molecules cannot be located at the same position, is not taken into account. Only for dilute, for instance gaseous, systems, Eq. (3) seems to be justified.

If we nevertheless apply the above approximation, we can express the delta functions by their Fourier representations and cast Eqs. (1) and (2) in the form[4]

$$I(\nu) = \frac{1}{2\pi}\int\limits_{-\infty}^{+\infty} dx\, e^{i\nu x}\, e^{-J(x)} \tag{4}$$

$$f\left(\frac{\Delta\nu_p}{\Delta p}\middle|\,\nu\right) = \frac{1}{4\pi^2 I(\nu)}\int\limits_{-\infty}^{+\infty} dx \int\limits_{-\infty}^{+\infty} dy\, e^{i\nu x}\, e^{i\frac{\Delta\nu_p}{\Delta p}y}\, e^{-j(x,y)} \tag{5}$$

with

$$j(x,y) = \rho \int_{(V)} d\underline{R}\,[1 - e^{-i\tilde{\nu}(\underline{R})x}\, e^{-i\tilde{\alpha}(\underline{R})y}] \tag{6}$$

$$J(x) = j(x,0). \tag{7}$$

At this point the second approximation can be performed which finally yields analytical results. It is valid in the limit that the matrix density $\rho = N/V$ is sufficiently high, and it consists in expanding the functions $J(x)$ and $j(x,y)$ into their respective Taylor series, for instance[4,9,10]

$$j(x,y) \approx iAx + iA'y + \frac{1}{2}Bx^2 + \frac{1}{2}B'y^2 + Cxy - \frac{1}{2}iE'xy^2. \tag{8}$$

This approximation is called the (extended) Gaussian approximation since it leads to Gaussian profiles of $I(\nu)$ and $f(\Delta\nu_p/\Delta p|\nu)$. The coefficients $A, A', \ldots, E'$ are given by spatial integrals over powers of $\tilde{\nu}(\underline{R})$ and $\tilde{\alpha}(\underline{R})$, multiplied by the two-particle distribution $g(\underline{R})$

$$A = \rho \int_{(V)} d\underline{R}\, g(\underline{R})\, \tilde{\nu}(\underline{R}) \tag{9}$$

$$A' = \rho \int_{(V)} d\underline{R}\, g(\underline{R})\, \tilde{\alpha}(\underline{R}) \tag{10}$$

$$B = \rho \int_{(V)} d\underline{R}\, g(\underline{R})\, [\tilde{\nu}(\underline{R})]^2 \tag{11}$$

$$B' = \rho \int_{(V)} d\underline{R}\, g(\underline{R})\, [\tilde{\alpha}(\underline{R})]^2 \tag{12}$$

$$C = \rho \int_{(V)} d\underline{R}\, g(\underline{R})\, \tilde{\nu}(\underline{R})\, \tilde{\alpha}(\underline{R}) \tag{13}$$

$$E' = \rho \int_{(V)} d\underline{R}\, g(\underline{R})\, \tilde{\nu}(\underline{R})\, [\tilde{\alpha}(\underline{R})]^2. \tag{14}$$

The difference between the "regular" and the "extended" Gaussian approximation is that in the latter one the third-order term with the parameter E' is included which in lowest order describes the variation of the pressure broadening with the frequency position in the inhomogeneous band (see below). The maximum position ν_s and the width (FWHM) Γ_s of $I(\nu)$ are calculated as[4]

$$\nu_s = A \tag{15}$$

$$\Gamma_s = 2\sqrt{2\ln 2}\,\sqrt{B}. \tag{16}$$

The expressions for the maximum $M_p(\nu)$ and the width $\Gamma_p(\nu)$ of the distribution $f(\Delta\nu_p/\Delta p|\nu)$ read[4,9,10]

$$M_p(\nu) = A' + \frac{C}{B}(\nu - A) \tag{17}$$

$$\Gamma_p(\nu) = 2\sqrt{2\ln 2}\left[B' - \frac{C^2}{B} + \frac{E'}{B}(\nu - A)\right]^{1/2} . \tag{18}$$

TEST OF THE APPRPOXIMATIONS FOR TWO POLYMERIC SYSTEMS

In the following we will check whether or not the two approximations discussed above are valid for two real polymeric hole-burning systems, namely, polyethylene and polystyrene doped with free-base phthalocyanine. To this end, we must first specify the molecular interaction potentials $\tilde{\nu}(\underline{R})$ and $\tilde{\alpha}(\underline{R})$. We use the forms[4]

$$\tilde{\nu}(\underline{R}) = 4\epsilon\left[\left(\frac{\sigma}{R-R_0}\right)^{12} - \left(\frac{\sigma}{R-R_0}\right)^{6}\right] \tag{19}$$

$$\tilde{\alpha}(\underline{R}) = -\kappa\frac{R}{3}\frac{\partial\tilde{\nu}(\underline{R})}{\partial R} \tag{20}$$

with κ the isothermal compressibility of the matrix material. For $g(\underline{R})$ we insert a step function which is equal to one outside a sphere of radius $R_0 + R_c$ and zero inside. We start by using the same molecular parameters which were derived before for the two hole-burning systems;[4,5] they are summarized in Table I (upper part).

We first check the validity of the extended Gaussian approximation as given in Eq. (8) under the assumption that the continuum approximation can be applied. We calculate the pressure shift distribution $f(\Delta\nu_p/\Delta p|\nu)$ as a Gaussian with the maximum position and width given by Eqs. (17) and (18), respectively, and compare the result with an exact numerical calculation according to Eqs. (4) - (7). The profiles obtained for the polystyrene system at different solvent shift values ν are plotted in Fig. 1. The frequency dependences of both the maximum position and the width of the distribution are very well approximated by the analytical calculation [part (b)] as compared to the numerical results [part (a)]. The only minor difference is that the exact profiles are slightly asymmetric, falling off more rapidly for large pressure shift values, whereas the Gaussian approximation yields symmetric Gaussian shapes. The slight asymmetry of the exact distribution can be understood in terms of simple statistical arguments, as was discussed in an earlier paper.[5] For phthalocyanine in polyethylene, the coincidence between the exact pressure shift distributions and the results of the Gaussian approximation is similar as for the polystyrene matrix.

Figure 1 shows that in condensed matter the number density ρ of the matrix molecules is high enough such that the Gaussian approximation works well. On the other hand, this raises the question as to whether or not the continuum approximation is applicable. In the literature[7,8] a mathematical method is described which allows one to calculate Eqs. (1) and (2) for sufficiently high matrix densities ρ without applying the continuum approximation. It yields an analytical result which is formally identical to the Gaussian approximation [Eqs. (4), (5), and (8)],

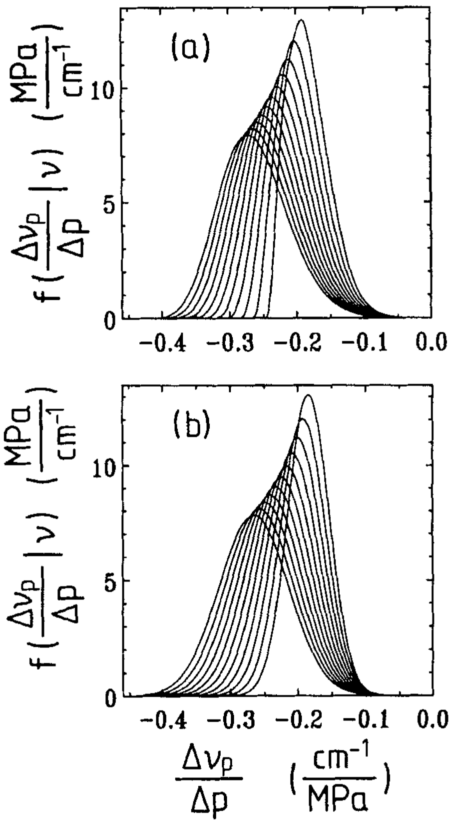

FIGURE 1 Theoretical profiles of the pressure shift distribution $f(\Delta\nu_p/\Delta p|\nu)$, calculated for the system free-base phthalocyanine in polystyrene. The curves in part (a) are exact within the continuum approximation, those in part (b) were obtained with the extended Gaussian approximation applied in addition. The profiles in both parts correspond to the same solvent shift values ν which vary between -534.4 cm^{-1} (rightmost curves) and -1003.1 cm^{-1} (leftmost curves).

yet, with different expressions for the coefficients. The basic difference is that a cumulant expansion is applied directly to Eqs. (1) and (2) so that the parameters $A, \ldots, E'$ are cumulants rather than coefficients of a simple Taylor series. Hence, the first-order parameters A and A' are identical as above, but additional terms appear in the higher orders. For instance, the new expressions for B, B', and C read

$$\begin{aligned} B &= \rho \int_{(V)} d\underline{R}\, g(\underline{R})\, [\tilde{\nu}(\underline{R})]^2 \\ &\quad + \rho^2 \int_{(V)} d\underline{R} \int_{(V)} d\underline{R}'\, g(\underline{R})\, g(\underline{R}')\, \tilde{\nu}(\underline{R})\, \tilde{\nu}(\underline{R}')\, [g_s(|\underline{R} - \underline{R}'|) - 1] \end{aligned} \tag{21}$$

$$\begin{aligned} B' &= \rho \int_{(V)} d\underline{R}\, g(\underline{R})\, [\tilde{\alpha}(\underline{R})]^2 \\ &\quad + \rho^2 \int_{(V)} d\underline{R} \int_{(V)} d\underline{R}'\, g(\underline{R})\, g(\underline{R}')\, \tilde{\alpha}(\underline{R})\, \tilde{\alpha}(\underline{R}')\, [g_s(|\underline{R} - \underline{R}'|) - 1] \end{aligned} \tag{22}$$

$$\begin{aligned} C &= \rho \int_{(V)} d\underline{R}\, g(\underline{R})\, \tilde{\nu}(\underline{R})\, \tilde{\alpha}(\underline{R}) \\ &\quad + \rho^2 \int_{(V)} d\underline{R} \int_{(V)} d\underline{R}'\, g(\underline{R})\, g(\underline{R}')\, \tilde{\nu}(\underline{R})\, \tilde{\alpha}(\underline{R}')\, [g_s(|\underline{R} - \underline{R}'|) - 1]. \end{aligned} \tag{23}$$

The integrals over R' have the form of three-dimensional convolutions and can thus be evaluated most easily with the Fourier technique.[7,8] For the solvent–solvent correlation function $g_s(\underline{R})$ we insert a step distribution similar to $g(\underline{R})$, yet, with a different cutoff radius R_s which is given by the size of the matrix units. Note that for $R_s \to 0$ or, equivalently, for $g_s(\underline{R}) \equiv 1$, the correction terms in Eqs. (21) – (23) vanish and we obtain the original results again. This limit corresponds to the continuum approximation.

If we insert the original molecular parameters as given in the upper part of Table I (and set $R_s = \sqrt[6]{2}\,\sigma$ corresponding to the equilibrium position of the solvent–solvent Lennard–Jones interaction potential) to calculate the coefficients B, B', and C according to Eqs. (21) – (23), we obtain dramatically different results. In fact the parameter B becomes even negative for both systems, which

TABLE I Molecular parameters for the systems polyethylene (PE) and polystyrene (PS) doped with free-base phthalocyanine.

Matrix correlations neglected

	$\rho[\text{Å}^{-3}]$	$\kappa[\text{GPa}^{-1}]$	$\epsilon[\text{cm}^{-1}]$	$\sigma[\text{Å}]$	$R_c[\text{Å}]$	$R_0[\text{Å}]$	$R_s[\text{Å}]$
PE	0.0368	0.141	6.35	3.82	3.93	6.61	—
PS	0.00602	0.179	35.5	5.27	5.51	3.69	—

Matrix correlations taken into account

	$\rho[\text{Å}^{-3}]$	$\kappa[\text{GPa}^{-1}]$	$\epsilon[\text{cm}^{-1}]$	$\sigma[\text{Å}]$	$R_c[\text{Å}]$	$R_0[\text{Å}]$	$R_s[\text{Å}]$
PE	0.00604	0.141	39.2	3.8	3.9	6.6	4.265
PS	0.00181	0.179	116.2	5.3	5.5	3.7	5.949

corresponds to the unphysical situation of an imaginary value of the inhomogeneous band width Γ_s. In order to correct this problem we have to change the parameters to the values given in the lower part of Table I. Especially the matrix density ρ must be decreased by factors of 6.1 (polyethylene) and 3.3 (polystyrene), and the amplitude ϵ of the interaction potential must be increased by the same factors to obtain the correct solvent shift values ν_s again. We can make an independent estimation of the density ρ by assuming that the matrix molecules are of spherical shape and that they occupy about 64% of the total space (typical for disordered solids). Then we obtain density values of 0.016 $Å^{-3}$ (polyethylene) and 0.0058 $Å^{-3}$ (polystyrene), which are in between the values in the upper and in the lower part of Table I. It seems reasonable that the actual density around the big bulky dye molecules is even somewhat lower. The above calculation shows that the continuum approximation is inappropriate for describing the situation of the two polymeric dye–matrix systems in a quantitatively correct way, although all the salient features of the experimental data are reproduced quite well.[4,9,10] Further implications of this finding are to be investigated in the future.

CONCLUSIONS

The stochastic theory of dye–matrix interaction is a powerful tool for describing inhomogeneous distributions in spectroscopic experiments. In order to apply the theory to real systems and to obtain quantitative results, usually two approximations are applied in the calculation, the continuum approximation which is valid for low matrix densities and the Gaussian approximation which is valid for high densities. In the present paper we showed for two polymeric hole-burning systems that the (extended) Gaussian approximation yields very good results but that the continuum approximation is inappropriate. Hence, also in the case of other solid dye–matrix systems it seems to be necessary to take the correlations between the matrix molecules into account.

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