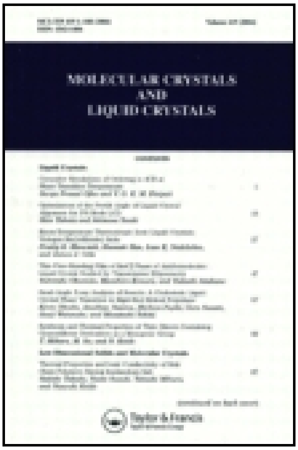

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Spectroscopic Characteristics of Dye-Matrix Interaction in Amorphous Solids

Lothar Kador [a]

[a] University of Bayreuth, Physical Institute and “Bayreuther Institut für Makromolekülforschung”, Postfach 10 12 51, W-8580, Bayreuth, Germany

Version of record first published: 04 Oct 2006.

To cite this article: Lothar Kador (1992): Spectroscopic Characteristics of Dye-Matrix Interaction in Amorphous Solids, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 217:1, 187-192

To link to this article: http://dx.doi.org/10.1080/10587259208046898

Mol. Cryst. Liq. Cryst. 1992, Vol. 217, pp. 187–192
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

SPECTROSCOPIC CHARACTERISTICS OF DYE–MATRIX INTERACTION IN AMORPHOUS SOLIDS

LOTHAR KADOR
University of Bayreuth, Physical Institute and "Bayreuther Institut für Makromolekülforschung", Postfach 10 12 51, W-8580 Bayreuth, Germany

Abstract Solvent shift and inhomogeneous broadening of optical transitions in condensed matter are direct consequences of the dye–matrix interaction. According to a stochastic theory, the ratio between the solvent shift and the width of an inhomogeneous distribution, and also its shape, depend on the average distance between the matrix units as compared to the size of the dopant molecules. In this way the nearly Gaussian shape of most absorption bands and the Lorentzian shape of spectral-diffusion kernels can be explained within the framework of the same model. By performing site-selective spectroscopic experiments at different frequencies within an absorption band it is possible to obtain more detailed information on the internal structure of the inhomogeneous distribution. Electric-field studies of persistent spectral holes, for instance, show that in weakly polar systems, the solvent shift is mainly determined by the van der Waals interaction.

INTRODUCTION

In condensed matter, the optical transition lines of organic dye molecules and inorganic ions are usually displaced from their corresponding frequency positions when the absorbing particles are in vacuum. Moreover, especially in disordered host matrices, the lines can be broader by several orders of magnitude. These phenomena which are known as "solvent shift" and "inhomogeneous broadening", respectively, originate from the interaction between the dopant molecules and their matrix environment. In the case of apolar absorbers, two physical mechanisms, namely the van der Waals interaction and the electrostatic polarization in the matrix field, can contribute to this effect. Although most spectroscopic experiments are aimed at investigating homogeneous line shapes, the inhomogeneous distribution can also yield valuable information on the dye–matrix interaction.

INHOMOGENEOUS LINE SHAPES

Inhomogeneous spectroscopic line shapes have been the subject of theoretical investigations for a long time. The fundamental ideas of a stochastic theory describing this effect were devised by Markoff in the beginning of the century[1]. A review article on inhomogeneous broadening was published by Stoneham[2]. The basic ansatz of the stochastic theory is contained in the following equation.

$$\begin{aligned} I(\nu) &= \frac{1}{V^N} \int_{(V)} d\underline{R}_1 \int_{(V)} d\underline{R}_2 \cdots \int_{(V)} d\underline{R}_N \, P(\underline{R}_1, \underline{R}_2, \ldots, \underline{R}_N) \\ &\quad \times \delta \left[\nu - \sum_{n=1}^{\infty} \tilde{\nu}(\underline{R}_n) \right] . \end{aligned} \tag{1}$$

The inhomogeneous distribution $I(\nu)$ of absorption frequencies is determined by the probability $P(\underline{R}_1, \underline{R}_2, \ldots, \underline{R}_N)$ that the N matrix units of the sample are located at the positions $\underline{R}_1$, $\underline{R}_2$, ..., $\underline{R}_N$ with respect to a dopant molecule, and by the function $\tilde{\nu}(\underline{R})$ which describes the line shift of an absorber by a matrix unit at the position $\underline{R}$. V denotes the volume of the sample. In order to simplify the expression in Eq. (1), it is usually assumed that the positions of the matrix units are statistically independent of each other so that the function $P(\underline{R}_1, \underline{R}_2, \ldots, \underline{R}_N)$ factorizes into N equal one-dimensional distributions $g(\underline{R})$. Then Eq. (1) can be cast into the form[2]

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

with

$$J(x) = \varrho \int_{(V)} d\underline{R} \, g(\underline{R}) \, \left[1 - e^{-i\tilde{\nu}(\underline{R})x} \right] . \tag{3}$$

An analytical calculation of the integrals in Eqs. (2) and (3) is in general not possible. However, there is an approximation which yields a simple analytical result: if the number density ϱ of the matrix is "sufficiently large", the function $J(x)$ can be expanded into its Taylor series up to the second-order term. With this truncation, the integral in Eq. (2) can be solved in closed form, yielding a Gaussian shape for the distribution $I(\nu)$[3,4]. Hence, the above simplification is known as "Gaussian approximation".

The validity of the Gaussian approximation depends on the number density ϱ of the matrix or, more exactly, on the product ϱR_c^3 where R_c is is the radius of the cavity containing a dopant molecule. In the limit $\varrho R_c^3 \gg 1$, the system is well described by the Gaussian approximation and the shape of the inhomogeneous distribution is Gaussian, irrespective of the form of the interaction potential $\tilde{\nu}(\underline{R})$. This is the reason why the shapes of inhomogeneous absorption (and fluorescence) bands of large organic dye molecules in compact disordered matrices are very close to Gaussian in most cases. In the opposite case $\varrho R_c^3 \ll 1$, the integrations must in general be performed numerically. The results show[5] that now the shape of $I(\nu)$ strongly depends on $\tilde{\nu}(\underline{R})$. For a van der Waals or

Lennard–Jones type potential, for instance, the distribution becomes more and more asymmetric as the parameter ϱR_c^3 decreases, with its steeper fall-off towards the vacuum transition frequency of the absorbers. Concomitantly, the quotient of band width and average solvent shift increases. Both effects can be understood in terms of basic statistics[5], since there are fewer and fewer solvent molecules in the first coordination shells when the cavity radius becomes smaller and, as a consequence, the statistical fluctuations increase. If dopant and matrix molecules interact via dipolar forces, the inhomogeneous distribution $I(\nu)$ can be calculated analytically also in the limit $\varrho R_c^3 \ll 1$. The result is a Lorentzian profile with cut-off wings; it has long been known to describe spectral-diffusion broadening in magnetic resonance[6,7] and similar effects of line-narrowed optical spectra in glasses at low temperatures[8,9]. Fig. 1 shows schematics of a dopant molecule and its surroundings in a disordered solid for the two cases of $\varrho R_c^3 \gg 1$ and $\varrho R_c^3 \ll 1$.

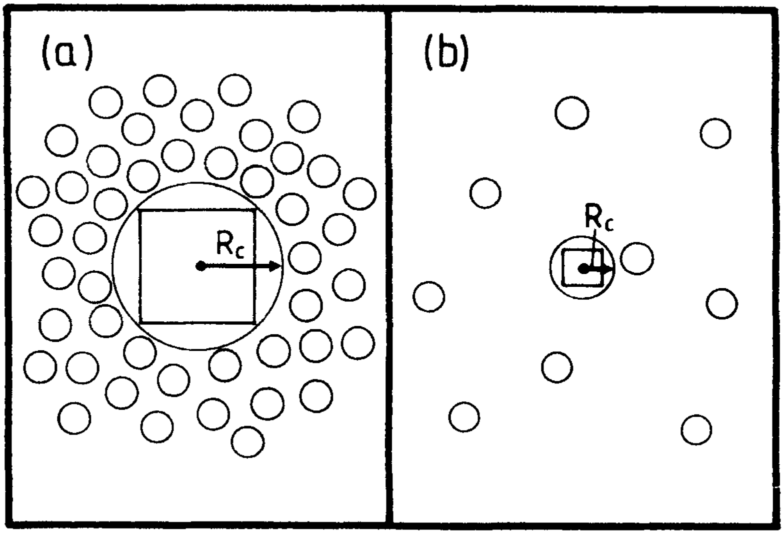

FIGURE 1 Schematic representation of a disordered matrix containing dopant molecules in "large" (a) or in "small" (b) cavities. In part (a) the situation is well described by the Gaussian approximation, in part (b) the band shapes must be calculated exactly (see text).

STARK EFFECT OF PERSISTENT SPECTRAL HOLES

The shape of an optical absorption band and its position with respect to the vacuum frequency yield information about the dye–matrix interaction, as was discussed above. Therefore, it is desirable to somehow investigate the internal structure of an absorption band. This can be done, for instance, by measuring the Stark effect of hole-burning spectra[10] at various frequency positions in the band[11]. In an external electric field, a persistent spectral hole exhibits a symmetrical broadening which, in the case of centrosymmetric dye molecules, is due to permanent matrix-induced dipole moments[12]. From the broadening, the average value of the dipole moment difference μ between the excited and the ground electronic state can be calculated. For the distribution of the square of μ, the stochastic theory[3] yields a similar expression as for the inhomogeneous band [Eqs. (2) and (3)], namely[11]

$$f(\mu^2|\nu) = \frac{1}{4\pi^2 I(\nu)} \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy\, e^{i\nu x}\, e^{i\mu^2 y}\, e^{-j(x,y)} \tag{4}$$

with

$$j(x,y) = \varrho \int_{(V)} d\underline{R}\, g(\underline{R}) \left[1 - e^{-i\tilde{\nu}(\underline{R})x}\, e^{-i\zeta(\underline{R})y}\right]. \tag{5}$$

Eq. (4) describes the conditional probability that a dye molecule is characterized by the value of μ^2 provided that its absoption line experiences the solvent shift ν. Within the Gaussian approximation, $f(\mu^2|\nu)$ is given by a Gaussian profile in μ^2 at each solvent shift ν, with the important peculiarity that the average value $\mu^2_{\max}$ varies with ν in a linear fashion.

The theoretical results can be compared to experimental data taken on the system octaethylporphin in polystyrene[11]. Fig. 2 shows the squared average values of the matrix-induced dipole moment differences as measured at different frequencies in the lowest-energy optical absorption band. $\bar{\mu}^2$ is related to the theoretical quantity $\mu^2_{\max}$ which denotes the maximum value of the distribution $f(\mu^2|\nu)$ (see above). The increase from the blue to the red wing of the band is clearly visible. It is an additional manifestation of the fact that dye molecules experiencing a larger solvent (red) shift feel a stronger interaction with their matrix environments.

From the slope $d\bar{\mu}^2/d\nu$, the polarizability difference α of the octaethylporphin molecules can be calculated, To this end, we must specify the molecular interaction potentials in our theory. We choose the forms[11]

$$\tilde{\nu}(\underline{R}) = \begin{cases} \frac{4\varepsilon}{hc}\left[\left(\frac{\sigma}{R-R_0}\right)^{12} - \left(\frac{\sigma}{R-R_0}\right)^{6}\right] - \frac{\lambda}{hc}\left(\frac{\sigma}{R-R_0}\right)^{6} & \text{if } R \geq R_0 \\ \infty & \text{if } R < R_0 \end{cases}; \tag{6}$$

$$\zeta(\underline{R}) = \begin{cases} 2\alpha\lambda\left(\frac{\sigma}{R-R_0}\right)^{6} & \text{if } R \geq R_0 \\ \infty & \text{if } R < R_0 \end{cases}. \tag{7}$$

Here ε and σ are the usual Lennard–Jones parameters, R denotes the magnitude of $\underline{R}$, and the shift of the origin by R_0 takes account of the difference in size between the dopant and the matrix molecules[3]. The parameter λ is given by

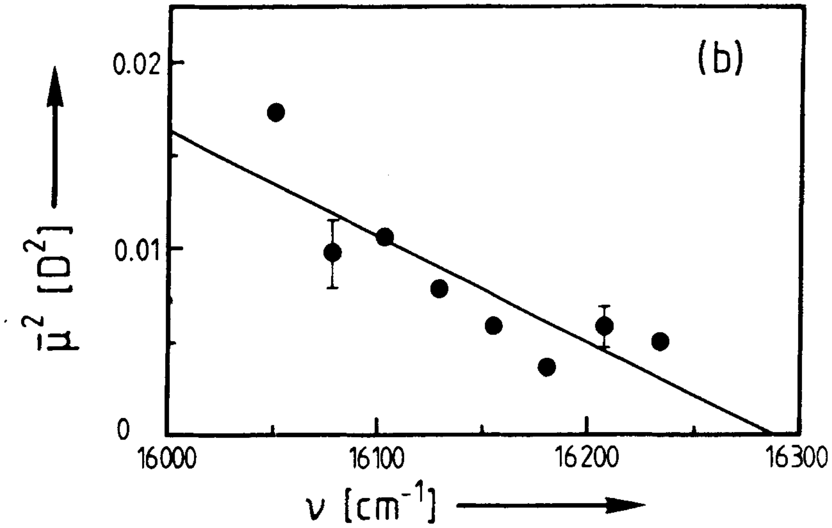

FIGURE 2 Squares of the mean matrix-induced dipole moment differences $\bar{\mu}$ of the system octaethylporphin in polystyrene, measured at various frequency position within the longest-wavelength optical absorption band. The sample was kept at a temperature of 1.5K. The straight line was obtained by a least-squares fit to the data; it has a slope of $(-5.8 \pm 1.1) \times 10^{-5} D^2/cm^{-1}$.

$$\lambda = \left(\frac{1}{4\pi\epsilon_0}\right)^2 \alpha\mu_1^2\sigma^{-6} \tag{8}$$

with μ_1 denoting the electric dipole moment of a matrix unit. The dye molecules are assumed to be isotropic so that the polarizability difference α is described by a scalar. The contributions of the van der Waals interaction and the electrostatic polarization to the solvent shift are approximately given by the parameters 4ε and λ, respectively.

The calculation shows that the expression for α becomes particularly simple in the two limiting cases that the solvent shift is mainly determined by one of the two interaction mechanisms with the other one playing only a minor role. The evaluation yields the values $\alpha/(4\pi\epsilon_0) = (0.15 \pm 0.03)\,\text{Å}^3$ if the electrostatic polarization is dominant and $\alpha/(4\pi\epsilon_0) = (20 \pm 4)\,\text{Å}^3$ if the van der Waals interaction prevails. Since the first value is far too small for an organic dye molecule whereas the second one appears to be of a reasonable order of magnitude, we can conclude that the dispersive forces are grossly determining the solvent shift in this system. The electrostatic contribution is estimated[11] to be smaller by roughly a factor of 100.

CONCLUSION

The investigation of the effects of external perturbations such as electric fields on line-narrowed optical spectra not only has the advantage of high sensitivity, but in addition it permits the experimenter to separately study the effects on different groups of dopant molecules which are characterized by different solvent shift values and, hence, different intensities of interaction with the host matrix. Conducting the measurements at various frequency positions throughout the inhomogeneous band thus leads to a sort of two-dimensional optical spectroscopy, because the sample is studied on two different axes of optical frequencies whose characteristic widths are given by the homogeneous and the inhomogeneous linewidth, respectively. Especially promising in this context are amorphous samples for which the two frequency scales are most different.

REFERENCES

1. A. A. Markoff, Wahrscheinlichkeitsrechnung (Teubner, Leipzig, 1912).
2. A. M. Stoneham, Rev. Mod. Phys., 41, 82 (1969).
3. B. B. Laird and J. L. Skinner, J. Chem. Phys., 90, 3274 (1989).
4. B. B. Laird and J. L. Skinner, J. Chem. Phys., 90, 3880 (1989).
5. L. Kador, J. Chem. Phys. (in print).
6. A. Abragam, The Principles of Nuclear Magnetism (Academic Press, Oxford, 1961).
7. J. R. Klauder and P. W. Anderson, Phys. Rev., 125, 912 (1962).
8. J. L. Black and B. I. Halperin, Phys. Rev. B, 16, 2879 (1977)
9. T. L. Reinecke, Solid State Commun., 32, 1103 (1979).
10. L. Kador, D. Haarer, and R. Personov, J. Chem. Phys., 86, 5300 (1987).
11. L. Kador, S. Jahn, D. Haarer, and R. Silbey, Phys. Rev.B, 41, 12215 (1990).
12. U. Bogner, P. Schätz, R. Seel, and M. Maier, Chem. Phys. Lett., 102, 267 (1983).