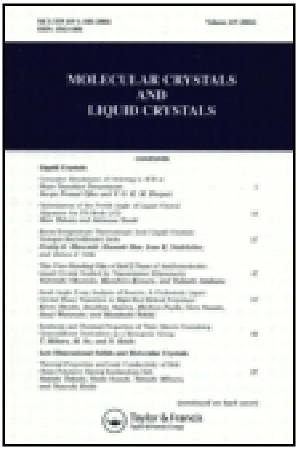

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CORRELATION BETWEEN THE PROPERTIES OF HOLE-BURNING MATERIALS AND INTERMOLECULAR INTERACTION PARAMETERS

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Abstract Relative zero-phonon electronic transition intensities (Debye-Waller factors), quasihomogeneous holewidths and inhomogeneous bandwidths of organic impurities in amorphous hosts have been correlated with the changes of molecular polarizabilities and dipole moments on electronic excitation.

INTRODUCTION

Broad-band spectral contours can be often regarded as a convolution of the spectrum of a single centre (the homogeneous spectrum) and the distribution function of the resonance frequencies in disordered environment. The homogeneous spectrum is described as a superposition of a narrow zero-phonon line and a broad side-band of vibronic origin.[1] It will be shown below that such a parameters of hole-burning materials as the inhomogeneous spectral bandwidth, the quasihomogeneous holewidth (which may be a function of the time scale of measurement) and the integral zero-phonon line to zero-phonon-line-plus-phonon-wing intensity ratio (the Debye-Waller factor, DWF) depend on the change of host-guest intermolecular interaction potentials on electronic excitation of the impurity centre ("guest").

According to the Franck-Condon principle, the probability of exciting low-frequency intermolecular vibrations in the course of an electronic transition is higher when the minima of the intermolecular interaction potentials are displaced (linear electron-phonon coupling). In other words, in case of large difference between the van der Waals forces in the ground and excited states, small DWF values are expected and vice versa.

The lifetime-limited width of a zero-phonon resonance broadens at finite temperature as a result of different frequencies of actual low-energy vibronic modes in the initial and final states. Additional broadening of spectral holes in time may occur as a result of the zero-phonon transition frequency shifts due to the flips in the two-level systems (molecules or groups having several spacial positions of close energy). Both the quadratic vibronic coupling and the sensitivity to the changes of local fields should be directly related with the polarizability and dipole moment differences between the ground-state and electronically excited dopant molecules.

ESTIMATION OF POLARIZABILITY CHANGES ($\Delta\alpha$) FROM SOLVENT-SHIFT MEASUREMENTS

The contribution of dispersion interaction (London forces) to the spectral solvent shift is described by the Bakhshiev's equation:[2]

$$\nu = \nu_0 + [3II'/2(I+I')][(\alpha_g-\alpha_e)/hcr^3][(n^2-1)/(n^2+2)], \qquad (1)$$

where ν and ν_0 are the band peak maxima in the solution and gas phase, respectively; I and I' are the ionization potentials of the solute and solvent molecules; α_g and α_e are the polarizabilities of the solute molecule in the initial and final state; h is the Planck constant; c is the velocity of light; r is the Onsager cavity radius of the solute; n is the refractive index of the solvent at a given transition wavelength.

The plots of spectral band maxima versus the solvent polarizability function $(n^2-1)/(n^2+2)$ in a series of n-alkanes from pentane to hexadecane are perfectly linear for most compounds. The extrapolation of the 0-0 band maximum to $n = 1$ yields the transition frequency, which is very close (within 100 cm^{-1}) to the purely electronic origin of a jet-cooled molecule. Absorption spectra of ionic compounds were studied in a series of highly polar aprotic solvents with different refractive indices (acetonitrile, γ-butyrolactone, nitrobenzene, etc.).

A linear relationship was established between the $\Delta\alpha = 1/3\,\mathrm{Tr}\Delta\alpha$ (in Å^3) from electrochromic measurements[3-5] and the slope y (in cm^{-1}) of the solvatochromic plot (Eq. 1) for aromatic hydrocarbons (9 values of $\Delta\alpha$):

$$\Delta\alpha = 0.3 + 1.82\cdot 10^{-5}\, y\cdot\mathrm{M.W.}, \quad R = 0.98, \qquad (2)$$

where M.W. is the molecular weight, which assumed to be proportional to the volume of solute cavity; R is the linear correlation coefficient.

Equation (2) was preferably used for calculating the $\Delta\alpha$ values, since the ionization potentials and the solute cavity radii in Eq. (1) were not available.

NON-POLAR IMPURITIES

The π-electronic systems of many porphyrins, polycyclic arenes, polymethine dyes and polyenes are centrosymmetric and formally devoid of dipole moments in both S_1 and S_0 states. Solvent-shift studies show that dispersion forces largely predominate dipole-induced-dipole interactions even in very polar environments. The change of the dispersion energy on excitation was characterized by the ratio $\Delta\alpha$/M.W. (Table 1).

Tetrapyrrolic pigments possess outstandingly strong zero-phonon lines (Table 1). Moreover, spectral holes have been observed even at 80 K for phthalocyanine[6] and tetraphenylporphine.[7] The $\Delta\alpha$ and $\Delta\alpha$/M.W. values are much smaller for porphyrins than for the other π-conjugated molecules. In case of cyanine dyes the DWFs are smaller than those for arenes since the torsional modes of the polymethine chain may contribute to the phonon wing intensity. To our knowledge, no zero-phonon lines have been detected for polyenes in amorphous hosts, in accordance with their flexibility and very high $\Delta\alpha$ values.

Quite remarkable correlation between the quasihomogeneous linewidth and $\Delta\alpha$/M.W. exists in the same matrix (Table 1). In polar PMMA matrix the pure dephasing times are much shorter than in polyethylene (1.5[11] and 53[8] ns for porphine at 1.2 K, respectively).

POLAR IMPURITIES

Molecules without the centre of symmetry have permanent dipole moments in both S_1 and S_0 states which are usually different. Small dipole moment changes ($\Delta\mu$) can be reliably calculated from the linear Stark shifts on narrow zero-phonon lines in crystalline hosts[20,25] or spectral holes in amorphous matrices[22] (see Table 2).

With increasing $\Delta\mu$ the maximum hole-to-background contrast (DWF) sharply decreases. It seems that zero-phonon transitions in glassy hosts are observable only for the molecules with $\Delta\mu$ not exceeding 2D. Besides strong coupling to low-frequency intermolecular vibrations, the large value of $\Delta\mu$ is always accompanied by a drastic increase in the intensities of the local vibrations and their overtones. Thus the 0-0

TABLE 1 Correlations between the characteristics of hole-burning systems (DWF, Debye-Waller factor; T_2^*, the dephasing time) and the molecular polarizability difference ($\Delta\alpha$) of the non-polar dopants in the S_1 and S_0 states.

Dopant	$-\Delta\alpha$, $Å^3$	$-\Delta\alpha/M.W.\cdot 10^3$	DWF	T_2^*, ns
Octaethylporphine	3.6	6.7		75[8a]
Tetraphenylporphine	8.5	13.8	0.9[7]	
Porphine	4.9	15.8	0.4 - 1[9,10]	1.5[11b], 53[8a]
Phthalocyanine	∿20	39	0.72[12]	12.5[8a]
Perylene	17.3[3]	69	0.5[13]	
Tetracene	24.7[3]	108	0.3 - 0.66[14-16]	
Pentacene	44[5c]	158		0.6[11b]
Cyanine HITCI iodide	25	61	0.15[17]	
Cryptocyanine iodide	25	71	<0.1[18]	
Tetraphenylhexatriene	70[3]	183		

[a] In polyethylene at 1.2 K. [b] In PMMA at 1.2 K. [c] Average of 3 tensor components.

TABLE 2 Correlations between the characteristics of hole-burning systems (DWF, Debye-Waller factor; Γ_0, the quasihomogeneous linewidths in PVB at 1.7 K) and the dipole moment ($\Delta\mu$) and polarizability ($\Delta\alpha$) changes for polar dopants.

Dopant	$\Delta\mu$, D	$\Delta\alpha$, $\AA^3$	DWF	Γ_0, MHz	HWHM, cm^{-1}[a]
Chlorin	0.214[19b], 0.23[20c]	4.7		160[21]	157
Resorufin Na salt	0.42[22b]	13	0.2 - 0.5[10,23]	330[22]	200
Oxazine 4 perchlorate	0.66[22b]	16	~0.3[24]	450[22]	369
Quinizarin	1.64[25d]	10.8	0.13 - 0.2[14,26]		
Cresyl violet perchlorate	2.1[22b]	19	0.15 - 0.3[10,27]	600[22]	609
2-Aminoanthracene	6.1[28e]		0[29]		1740[f]
Laser dye DCM	20.2[30e]		0[31]		

[a] Half-width at half maximum of the spectral band in acetonitrile at 20°C. [b] Stark effect on spectral holes in PVB. [c] Stark effect on spectral holes in n-hexane. [d] Stark effect on the Shpolskii line. [e] Solvatochromic value. [f] HWHM for the whole vibronic contour.

band of 2-aminoanthracene and the laser dye DCM can be distinguished as a shoulder only in non-polar alkane solvents.

Another important parameter of hole-burning materials, the quasi-homogeneous linewidth (Γ_0) turns out to be also fairly sensitive towards $\Delta\mu$ in a series of compounds: chlorin, resorufin, oxazine 4 and cresyl violet in PVB matrix at 1.7 K[22] (Table 2). In accordance with much smaller $\Delta\alpha$, the Γ_0 of chlorin is by a factor of two narrower than this of resorufin.

The ground-state dipole moment creates a reaction field in a polar liquid.[2] This reaction field produces a Stark shift of the transition frequency. In the liquid state the reaction field is perturbed by molecular movement, which gives rise to the inhomogeneous broadening. Approximate proportionality between $\Delta\mu$ and the half-width at half maximum (HWHM) of the spectral bands in polar acetonitrile at 20°C is evident (Table 2).

The reaction field strength in a solid matrix corresponds to the relatively high dielectric permittivity (ε) value at some temperature close to the glass transition point. The drastic drop of ε on matrix solidification is not accompanied by corresponding spectral effects.

Since no remarkable reduction of the spectral bandwidth takes place on cooling down a liquid to form a glass, we assume, that, at least in case of polar dyes in polar hosts, the HWHMs in the liquid and solid phase as well as the low-temperature inhomogeneous site-distribution functions are correlated with each other.

CONCLUSIONS

Both the characteristics of the hole-burning materials and the spectral matrix shifts are dependent on the changes of intermolecular interaction potentials upon electronic excitation. Both linear and quadratic electron-phonon coupling (the Debye-Waller factor and the T_2^* part of the holewidth) as well as the coupling to the two-level systems (spectral diffusion part of the holewidth) are correlated with the polarizability difference between the S_1 and S_0 states and, in particular, with the dipole moment change upon electronic excitation.

Several requirements to the hole-burning materials are contradictory. Thus, a dye with relatively large $\Delta\mu$ has such a desirable properties like broad inhomogeneous bandwidths and high sensitivity of holes to the external electric field. However, large $\Delta\mu$ unfavourably influences the limiting holedepth (DWF) and -width (Γ_0).

Still the best hole-burning systems for information storage are basing on tetrapyrrolic pigments. Because of very small $\Delta\alpha$ values the alkyl-substituted porphyrins seem to be particularly promising.

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