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CORRELATION OF THE ZERO-PHONON ELECTRONIC TRANSITION PROBABILITIES (DEBYE-WALLER FACTORS) FOR MOLECULAR IMPURITY CENTRES IN AMORPHOUS HOSTS WITH SPECTRAL MATRIX SHIFTS

(Presented by K. K. Rebane)

The relative intensities of purely electronic zero-phonon transitions (the Debye-Waller factors, DWF) for organic molecules imbedded in polymer and frozen solvent glasses have been gleaned from the literature and tabulated. Correlations were established between the DWF and the spectral matrix-shifts of the transition frequencies as well as with related parameters, such as the changes of the dipole moments ($\Delta\mu$) and polarizabilities ($\Delta\alpha$) on electronic excitation.

The spectral band-maxima of several dyes have been measured as a function of the refractive index and dielectric permittivity of the solvent. Small solvent-shift of the $S_1 - S_0$ band maximum as a function of the solvent polarizability, which corresponds to the low value of $\Delta\alpha$, can explain the weakness of the coupling to low-frequency quasi-local and matrix modes in case of porphyrins. Zero-phonon transitions are observable for the molecules with $\Delta\mu$ values not much exceeding 2 D. Useful predictions about the maximum zero-phonon hole depth at liquid helium temperatures can be made on the basis of room temperature solvent-shifts.

1. Introduction

Broad-band spectral contours can be often regarded as a convolution of the spectrum of a single center (the homogeneous spectrum) and the distribution function of the resonance frequencies in disordered environment [1]. The homogeneous spectrum is described as a superposition of a narrow zero-phonon line and a broad sideband of vibronic origin. The integral zero-phonon line to zero-phonon-line-plus-phonon-wing intensity ratio (the Debye-Waller factor, DWF) [1] critically depends on the structure of the dopant.

Despite the relevance to site-selection and hole-burning spectroscopy, the interrelation between the DWF and the parameters of the guest molecules as well as the nature of low-energy excitations forming the phonon wing have not been extensively discussed.

The absence of site-selection effect (DWF=0) in amino-substituted arenes was ascribed to strong electron-phonon coupling associated with intramolecular charge transfer on electronic excitation [2]. It was pointed out that the phonon wing is stronger for ionic dyes than for uncharged porphine [3]. Earlier, it was noticed that hydrogen bonding between cationic proflavin and ethanol may result in dense manifold of low-frequency levels and lead to the disappearance of sharp-line spectrum [49].

On the basis of accumulated experimental data it became possible at present to establish reasonable correlations between the DWF and the differences of intermolecular interaction parameters in the ground and excited states (dipole moments, polarizabilities).

According to the Franck-Condon principle, the probability of exciting low-frequency intermolecular vibrations in the course of electronic transition is higher when the minima of the intermolecular interaction potentials are displaced. In other words, in case of a large difference between the

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The dependence of Debye-Waller factors on matrix shifts of purely electronic transitions ($\nu_{\text{burn}} - \nu_0$) as well as on the difference of dipole moments ($\Delta\mu$) and polarizabilities ($\Delta\alpha$) between the S_1 and S_0 states

Dopant	Matrix	DWF	T, K	$\nu_{\text{burn}}, \text{cm}^{-1}$	$\nu_{\text{burn}} - \nu_0^a, \text{cm}^{-1}$	$\Delta\mu, \text{D}$	$\Delta\alpha, \text{Å}^3$
1	2	3	4	5	6	7	8
Porphine	2-methyltetrahydrofuran	~1	4.2	16 373 ^[9]	53 ^[10]	0.059—0.103 ^[8, 11] , c	
"	glycol	0.4—0.6	4.2	16 405 ^[12]	85 ^[10]		2.7 ± 1 ^[15] , d
Tetraphenylporphine	PMMA	0.9	4.2	15 549 ^[13]	-68 ^[14]		
Mg porphine	ethanol	0.3	80 ^[13]				
Phthalocyanine	polyethylene	0.42	3.8 ^[16]				
"	polystyrene	0.90 ± 0.1	8—20	14 454 ^[17]	-678 ^[18]	0.16—0.34 ^[11] , b	
Ru(II) phthalocyanine	ethanol-pyridine (3:1)	0.72 ± 0.1	4—16	14 362 ^[17]	-770 ^[18]		
Prochlorophyll	ether-n-butanol (5:2)	0.4	5 ^[19]				
Tetracene	ethanol-methanol (3:1)	0.66	5 ^[20]				
"	(4:1)	~0.3	4.2	20 991 ^[21]	-1 407 ^[22]		42.5 ± 3% ^[23]
"	2-methyltetrahydrofuran	0.3—0.4	4.2 ^[26]	20 986 ^[25]	-1 402 ^[22]		62 ± 6 ^[24]
Perylene	polyvinylbutyral	0.5 ± 0.1	1.2	22 647 ^[27, 28]	-1 390 ^[22]	0.51 ^[29] , b	33 ± 4 ^[30]
Anthracene-tetracene photoadduct (a naphthalene derivative)	PMMA	0.25	1.5 ^[31]				
1,3,3',3'-Hexamethyl-2,2'-indo-tricarboyanine iodide	polyvinylalcohol	0.15	5.4 ^[32]				
Cryptocyanine	ethanol	<0.1	4.2	14 164 ^[33]	-751 ^e		
Dimethyl-s-tetrazine	polyvinylcarbazol	~0.1	10	17 630 ^[34]	-130 ^[35]		
Thioindigo	paraffin oil, ethanol	0.05—0.2	4.2 ^[36]				
9-Aminoacridine	polyvinylbutyral	0.2	1.2 ^[27]				
Quinizarin	ethanol-methanol (3:1)	0.17	4.2	19 436 ^[21]	-483 ^[37]	0.83 ^[31]	
"	"	0.13	4.8	19 200 ^[38]	-719 ^[37]	1.64 ± 0.03 ^[38]	
"	silica (sol-gel made)	0.20	4.8 ^[39]				
Resorufin Na salt	PMMA	0.4—0.5	4	16 807 ^[40]	-778 ^g	0.2 ^[41]	
"	hydroxylic hosts, PMMA	0.2—0.3	4.2 ^[42]			0.42 ^[42]	
Rhodamine 640 (101)	polyvinylalcohol	0.35—0.48 ^h	2 ^[43]	17 367 ⁱ	-768 ^e	1.7 ^[44]	
Cresyl violet perchlorate	polyvinylalcohol	0.15	7	16 528 ^[45]	-1 140 ^g	2.1 ^[42]	
"	hydroxylic hosts, PMMA	0.15—0.3	4.2 ^[42]				
Oxazine 720 perchlorate	polyvinylalcohol	0.3—0.4	7 ^[45]				

1	2	3	4	5	6	7	8
Oxazine 4 perchlorate							
1-Aminoanthracene,	polyvinylbutyral	~0.3	1.7 [46]			0.66 [42]	
2-aminoanthracene,	80% (glycerol-water (5:4)) +						
1-aminopyrene	+ 20% ethanol, methylcyclo-	0	4.2 [47]	25 250 [48] ^k	-2 500 [48] ^l	6.1 [48] ^m	
Proflavine (3,6-diaminoacridi-	hexane-2-methylpentane (1:1)	0	< 10 [4]				
ne hydrochloride)	ethanol						
Laser dye DCM	polystyrene	0 [49]		21 716 [50] ⁿ	-2 300 ^o	20.2 [50] ^m	
Cresyl violet, neutral	ethanol	0 [12]		21 044 ⁱ	-3 400 ^z		
Coumarin 153	EPA		77	22 000 [51] ^p	-4 000 [51]		

^a ν_0 is the $S_1 - S_0$ transition frequency of the jet-cooled molecule, if not indicated otherwise. The citation refers to the source of the ν_0 value.

^b Matrix-induced dipole moment in polyvinylbutyral calculated from the Stark broadening of spectral holes.

^c For octaethylporphine.

^d $\text{Tr}\{\Delta\alpha\}$.

^e ν_0 was calculated according to Eq. (5), Table 2.

^f Estimated from the ratio of holewidths in the frequency and electric field dimensions, Table 1 in [7], and $\Delta\mu$ for perylene 0.51 D [27, 28].

^g ν_0 was used, Eqs. (3,5), Table 2.

^h Measured on the long-wavelength slope of the absorption band.

ⁱ Band maximum in acetonitrile at 20 °C.

^j For rhodamine B cation.

^k Band maximum in cyclohexane at 20 °C.

^l ν_0 was calculated from the band maxima in cyclohexane and benzene, Eq. (1).

^m From solvent-shift measurements.

ⁿ Band maximum in toluene.

^o ν_0 from Table 2.

^p Intersection point of normalized absorption and fluorescence bands.

van der Waals forces in the ground and excited states, small DWF values are expected, and vice versa. On the other hand, the transition energy shift is explained in terms of relative stabilization of the respective electronic levels upon transfer of the free molecule to the condensed phase [5]. For instance, the strengthening of the interaction with surrounding molecules in the S_1 state results in the downward shift of the S_1-S_0 transition frequency, and vice versa.

The highest probability of zero-phonon transitions should therefore correspond to the systems with small matrix shifts.

The DWF values were collected from the literature. In several cases the DWF have been estimated by us simply as relative saturated depth of a spectral hole (in optical density scale) burned near the band maximum. This is a crude approximation which presupposes that all centres are photoactive («burnable») and the inhomogeneous site-distribution function is considerably broader than the phonon side-band. The hole was considered to be saturated when a pseudo-wing of remarkable intensity appeared, i. e. the less efficient burning via phonon-wing absorption has been started.

The matrix shift was calculated as a difference between the resonance frequency of the free molecule seeded in the supersonic jet (ν_0) and the frequency at which the spectral hole was burned, or alternatively, between ν_0 and absorption band maximum.

The largest contributions to the spectral matrix shift arise from the dispersion interaction and the reaction field effects characterized by the variations of polarizabilities ($\Delta\alpha$) and dipole moments ($\Delta\mu$) of the guest molecules and by refractive indices (n) and dielectric permittivities (ϵ) of the host [5].

The $\Delta\mu$ and $\Delta\alpha$ values are taken mostly from spectral Stark shift studies. Centrosymmetric molecules doped into amorphous polymers show a linear Stark broadening of the spectral hole at relatively weak electric field strengths [6-8]. The average matrix-induced values of $\Delta\mu$ obtained this way are also included in Table 1.

Table 2

Solvent-induced shifts of the $S_1 \leftarrow S_0$ absorption maxima at 20°C

Compound	Solvents ^a	Argument ^b	Slope, cm ⁻¹ , c	Intercept, cm ⁻¹ , d	N^e	$ r ^f$
Tetraphenylporphine	$\epsilon = n^2$	$f(n^2)$	-639	15 613	5	0.994
Coronene	—	„	-820 ± 20 [52]			
Tetracene ^g	$\epsilon = n^2$	„	-5 137	22 512	6	0.997
Cryptocyanine iodide	$\epsilon = \text{const}$	„	-3 802	14 999	3	0.992
Quinizarin	$n = \text{const}$	$f(\epsilon)$	86	13 887	3	0.907
Resorufin Na salt	$\epsilon = n^2$	$f(n^2)$	-2 413	19 850	4	0.999
Rhodamine 640 (101)	$\epsilon = \text{const}$	„	-2 840	17 585	3	0.997
perchlorate	„	„	-1 975	17 768	3	0.980
Cresyl violet perchlorate	$n = \text{const}$	$f(\epsilon)$	-386	17 625	3	0.963
DCM	$\epsilon = \text{const}$	$f(n^2)$	-3 956	17 665	5	0.975
Cresyl violet, neutral	$\epsilon = n^2$	„	-8 145	24 050	4	0.999
	$\epsilon = \text{const}$	„	-15 000	24 481	8	0.948

^a Three sets of solvents were used: n -alkanes with $\epsilon = n^2$, and those with constant ϵ and n .

^b The peak maxima were plotted vs. $f(n^2) = (n^2 - 1)/(n^2 + 2)$ or $f(\epsilon) = (\epsilon - 1)/(\epsilon + 2)$.

^c Depending on the solvent set, the slope is equal to A , B , or C of Eqs. (2-4).

^d Depending on the solvent set, the intercept is equal to ν_0 , $\nu_{0,\epsilon}$ or $\nu_{0,n}$.

^e Number of solvents.

^f Linear regression coefficient.

^g Data from [53].

It was necessary to complement the electrochromism data with spectral solvent-shift measurements, since the $\Delta\mu$ and, particularly, the $\Delta\alpha$ data are scarce.

Within a set of structurally related solvents, e. g. *n*-alkanes, the relationship between the peak frequency (ν) of the absorption band and the solvent polarizability function $f(n^2) = (n^2 - 1)/(n^2 + 2)$ is perfectly linear (Table 2). With $f(n^2)$ approaching zero, ν extrapolates to the purely electronic resonance frequency of the free molecule (ν_0).

In case of non-polar solvents, when $n^2 = \epsilon$, the band maximum is a function of the ground and excited state dipole moments (μ_g , μ_e) and polarizabilities (α_g , α_e) [5], see also [54]:

$$\nu = \nu_0 + \left\{ \frac{1.25(\mu_g^2 - \mu_e^2)}{r^3 hc} + \frac{\alpha_g - \alpha_e}{r^3 hc} \left[\frac{3}{2} \frac{II'}{(I+I')} \right] \right\} \frac{n^2 - 1}{n^2 + 2}, \quad (1)$$

where h and c are the Planck constant and the velocity of light, r is the Onsager cavity radius of the solute, I and I' are the ionization potentials of the solute and solvent molecules, respectively. If μ is given in Debye units, α and r^3 are in \AA^3 and $I = I' \approx 10$ eV, the slope A (in cm^{-1}) of the plot of ν vs. $f(n^2)$ becomes:

$$A = [6.3 \cdot 10^3 (\mu_g^2 - \mu_e^2) + 6.0 \cdot 10^4 (\alpha_g - \alpha_e)] / r^3. \quad (2)$$

When ϵ is kept constant, e. g. within a set of solvents like acetonitrile, nitromethane, dimethylformamide, γ -butyrolactone and nitrobenzene, the slope B of the linear plot of ν vs. $f(n^2)$ is given as:

$$B = [-6.3 \cdot 10^3 (\mu_g^2 - 2\mu_g\mu_e \cos \Phi + \mu_e^2) + 6.0 \cdot 10^4 (\alpha_g - \alpha_e)] / r^3, \quad (3)$$

where Φ is the angle between dipole moments in the S_1 and S_0 states.

In a set of solvents with $n = \text{const}$, e. g. chloroform, 1,2-dichloroethane and dimethylsulfoxide, the slope C of the plot of ν vs. $f(\epsilon) = (\epsilon - 1)/(\epsilon + 2)$ reflects only the contribution of orientational reaction field [5]:

$$C = 1.25 \cdot 10^4 \mu_g (\mu_g - \mu_e \cos \Phi) / r^3. \quad (4)$$

The average ν_0 value for free ionic dyes, which do neither evaporate nor dissolve in apolar media, can be evaluated by combining the solvent shift measurements at constant ϵ and n :

$$\nu_0 = 1/2 [\nu_{0,\epsilon} + \nu_{0,n} - Bf(n^2) - Cf(\epsilon)], \quad (5)$$

where $\nu_{0,\epsilon}$ and $\nu_{0,n}$ are the intercepts for $\epsilon = \text{const}$ and $n = \text{const}$, respectively.

The polarizability difference $\Delta\alpha$ for the molecules without dipole moments in S_1 and S_0 states may be calculated from Eq. (2) or (3), provided that the cavity radius is known.

The slopes A , B and C as well as intercepts ν_0 , $\nu_{0,\epsilon}$ and $\nu_{0,n}$ are given in Table 2. The details of absorption measurements at 20 °C will be published elsewhere.

2. Debye-Waller factors for various groups of organic compounds

It is evident from Table 1 that most molecular impurities with high DWF are centrosymmetric and formally without dipole moments in both ground and excited states (porphyrins, arenes, cyanine dyes, dimethyl-s-tetrazine, thioindigo).

Tetrapyrrolic pigments (porphyrins, phthalocyanines) possess outstandingly strong zero-phonon lines. Moreover, in contrast to the other

organic impurities, zero-phonon holes have been observed even at 80 K for phthalocyanine [55] and tetraphenylporphine [13]. Well-resolved vibronic structure was observed in site-selection spectra of iron-free porphyrin cytochrome *c* and Zn-cytochrome *c* at 60–77 K [56, 57].

On the other hand, porphyrins are characterized by unusually small matrix-shifts of the $S_1 \rightarrow S_0$ transition frequency. The trace of the polarizability tensor difference between ground and excited states $\text{Tr}\{\Delta\alpha\} = 2.7 \pm 1 \text{ \AA}^3$ [15] and the slope of the plot of the absorption band maximum vs. $f(n^2)A = -639 \text{ cm}^{-1}$ (Table 2) for tetraphenylporphine are approximately, by an order of magnitude, smaller than the corresponding values for polycyclic arenes. The matrix-induced dipole moment differences in polar polyvinylbutyral host are 0.06–0.1 [11] and 0.51 D [29] for octaethylporphine and perylene, respectively, which are in accordance with their $\Delta\alpha$ values. Thus the strength of dispersion interaction between porphyrin and matrix molecules is very close in both S_0 and S_1 states.

The blue-shift of the $S_1 \leftarrow S_0$ band in polar media is caused by diminishing of the $S_2 - S_1$ splitting as a result of the screening of electrostatic repulsion between the central hydrogens. This interesting phenomenon will be discussed elsewhere.

The saturated hole-depth and the apparent DWF of the porphine magnesium complex is smaller by a factor of two [16] due to the degeneracy of lowest excited energy level in metallo-porphyrins of D_{4h} symmetry.

Polycyclic aromatic hydrocarbons (arenes) are another large group of the compounds thoroughly studied by high-resolution laser spectroscopy. The fluorescence line-narrowing spectrum of the pyrene is accompanied by weaker side-bands than that of the perylene, at vibronic excitation within the α and p transition regions, respectively [58]. Very sharp site-selection spectrum was reported for chrysene at α band excitation [26]. It is well established that weak $\alpha(^1L_b)$ bands are less solvent-sensitive than strong $p(^1L_a)$ bands [59]. Consequently, weak electron-phonon coupling is expected for $S_1 \leftarrow S_0$ transition of the coronene, because the slope A is as small as $-820 \pm 20 \text{ cm}^{-1}$ [52]. Indeed, a phosphorescence spectrum of the coronene displays hardly any phonon wings in glassy 1-bromobutane [60] (although $\Delta\alpha$ may be different for $T_1 - S_0$ and $S_1 - S_0$ transitions).

The DWF for the third group of π -electronic systems — cationic polymethine dyes (cyanines) does not exceed 0.15 [32, 33]. The quasi-line structure in their vibronically excited fluorescence spectra disappears already at 25 K [61]. Bulkier heterocyclic rings as well as the bridging and halogene substitution in the polymethine chain result in better line-to-background ratio [61]. Fairly large solvent-shift for cryptocyanine ($B = -3802 \text{ cm}^{-1}$, Table 2) reveals that the polarizability of the molecule greatly increases in S_1 state. Intramolecular torsional vibrations may also contribute to the phonon wing intensity in these flexible-chain molecules.

Tricyclic dyes with oxygen and/or nitrogen containing heterocyclic central ring and with a pair of symmetrically substituted amino or oxy groups on the side-rings (rhodamines, oxazines, etc.) are characterized by large variations in DWF (Table 1). High probabilities of zero-phonon transitions, reported for resorufin [12, 40] and rhodamine 640(101) [43], may be ascribed to small $\Delta\mu$ (0.2 [41] — 0.42 [42]) and solvent shift values ($B = -1975$, $C = -386 \text{ cm}^{-1}$) for these dyes, respectively. An angularly annelated benzoderivative of the oxazine, the cresyl violet, which is devoid of twofold symmetry, shows an appreciable dipole moment difference ($\Delta\mu = 2.1 \text{ D}$ [42]) and smaller DWF. On the contrary, for unsubstituted rhodamine 110 [62] and proflavine [4] the site-selection effect was not observed. It still remains unclear, whether the diversity in DWF-s within this group of structurally related dyes can be explained solely on the

basis of the changes in dipole moments and polarizabilities or, alternatively, the role of torsional modes of phenyl and amino substituents should be taken into account.

From Table 2 it follows that the transitions accompanied with pronounced intramolecular charge transfer ($\Delta\mu > 6$ D) display no zero-phonon component. Extensive band shifts in apolar solvents or in the solvents with constant dielectric permittivity ($A = -8145$ and $B = -15000$ cm^{-1} for DCM and neutral cresyl violet, respectively) arise as a result of summation of both dispersion and dipole-induced-dipole contributions in Eq. (2) and (3), when $\mu_e \gg \mu_g$. It is worth noticing that a great number of intramolecular low-frequency modes (> 30 cm^{-1}) becomes active in optical spectra of relatively fixed structures with large $\Delta\mu$, such as in jet-cooled coumarins with rigidized amino groups [51].

3. Some criteria for the selection of impurity systems with improved properties

Low-frequency wing accompanying purely electronic transitions in amorphous host can ruin otherwise promising spectrally highly selective photochromic materials by badly lowering the hole-to-background contrast. Desirably, the DWF ought to be close to unity. Such an impurity system must possess a small spectral matrix-shift, i.e. small dipole moment and polarizability differences between the ground and excited states.

Besides the porphyrins, the arenes with S_1 state of the α rather than the p type are weakly affected by the matrix. For instance, coronene imbedded in a polar host or carrying some substituents in order to enhance the forbidden $S_1 \rightarrow S_0$ transition probability seems to be a promising case.

An interesting possibility arises when the dipole moment diminishes or changes its direction upon excitation. In this case the weakening electrostatic dipole-dipole interaction can compensate the increase of dispersion interaction (the latter is always stronger in the excited state [5]). Thus the equilibrium distance between the solute and solvent molecules remains unchanged and, consequently, the probability of exciting quasi-local vibrations may be low. Further investigation of quinizarin derivatives and other dihydroxy- p -quinones with hydrogen-bonded six-member cycles, whose dipole moments in S_1 state are lower than in S_0 state, may be of interest for testing the validity of this reasoning.

The application of perfluorinated matrices with low polarizabilities should also lead to the improvement of DWF. However, the dependence of the DWF on matrix properties is weak, since the solvent shifts relative to the free molecule for commonly used polymers and frozen solvents are quite close. Still the DWF for resorufin and cresyl violet decreases by a factor of two in highly polar protic matrices compared to those less polar ones [3]. In line with the reasoning given above, the charge redistribution on hetero-atoms occurring on electronic excitation will bring about a displacement of equilibrium geometry of hydrogen-bonded complexes. This should inevitably promote intermolecular vibrations. In poly-hydroxylated host with stronger and more numerous hydrogen bonds a drop of DWF is expected.

In conclusion it should be noted that the coupling strength of an electronic transition to the low-energy vibrational excitations is closely related to the matrix-induced frequency-shift of this transition in non-crystalline environment. A quantitative study of this relationship may provide useful evidence about the nature of both intermolecular guest-host interactions and low-frequency modes in glassy matrices.

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AMORFSESSE KESKKONDA VIIDUD MOLEKULAARSETE LISANDITSENTRITE PUHTFONOONSETE ELEKTRONÜLEMINEKUTE TÕENÄOSUSTE (DEBYE-WALLER- LERI FAKTORITE) JA SPEKTRAALSETE MAATRIKSIHETE VAHELINE KORRELATSIOON

On koostatud ülevaade suhtelistest foononvabade elektronüleminekute tõenäosustest (Debye-Walleri faktoritest = DWF) orgaanilistes molekulides, mis on viidud amorfsetesse polümeersetesse ja külmutatud lahustimaatriksitesse. On kindlaks tehtud seos DWF-i ja spektraalnihke vahel maatriksis, aga ka dipoolmomendi ($\Delta\mu$) ja polariseeritavuse muutuste ($\Delta\alpha$) vahel.

On mõdetud mitmete värvainete neeldumismaksimumide asukoht erineva murdumisnäitaja ja dielektrilise läbitavusega lahustites. Porfüriinide $S_1 \leftarrow S_0$ ülemineku sageduse väike lahustinihe, mis vastab väikesele $\Delta\alpha$ -le, seletab ka nõrka vastastikmõju madalasaduslike kvaasilokaalsete ja maatriksi võnkumistega. Foononvabad jooned ilmnevad molekulidel, mille $\Delta\mu$ ei ületa 2D. Spektraalsälgu maksimaalse sügavuse kohta vedela He temperatuuril saab teha olulisi järeldusi toatemperatuuril ilmnevate lahustimise põhjal.

Индрек РЕНГЕ

КОРРЕЛЯЦИЯ ВЕРОЯТНОСТЕЙ БЕСФОНОННЫХ ЭЛЕКТРОННЫХ ПЕРЕХОДОВ (ФАКТОРОВ ДЕБАЯ—ВАЛЛЕРА) ДЛЯ МОЛЕКУЛЯРНЫХ ПРИМЕСНЫХ ЦЕНТРОВ В АМОРФНЫХ СРЕДАХ СО СПЕКТРАЛЬНЫМИ МАТРИЧНЫМИ СДВИГАМИ

Представлен литературный обзор относительных вероятностей бесфононных электронных переходов (факторов Дебая—Валлера, ФДВ) в органических молекулах, заключенных в аморфные матрицы, полимеров и замороженных растворителей. Установлены корреляции между ФДВ и матричным сдвигом частоты перехода, а также изменением дипольного момента ($\Delta\mu$) и поляризуемости молекулы ($\Delta\alpha$) при электронном переходе.

Для ряда красителей измерены максимумы полос поглощения в зависимости от коэффициента преломления и диэлектрической проницаемости растворителя. Небольшой сольвентный сдвиг у порфиринов, соответствующий малому $\Delta\alpha$, объясняет также слабое взаимодействие с низкочастотными квазилокальными и матричными колебаниями. Бесфононные линии могут наблюдаться только у молекул с $\Delta\mu$ не выше 2D. На основе сольвентных сдвигов при комнатной температуре можно сделать выводы о максимальной глубине спектрального провала при температуре жидкого гелия.