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ORIGINAL ARTICLE

Solvent enhancement of electronic intensity in acridine and 9-aminoacridine

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Abstract The electronic absorption spectra of acridine and 9-aminoacridine have been studied in various fluid solutions at room temperature. The modified Onsager–Abe–Iweibo reaction field model for a spherical molecule was employed to determine the oscillator strength, *f*, in vapour phase. The intensity enhancements for the forbidden transition observed are ascribed to perturbation forces between the solute and solvent molecules.
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1. Introduction

Many investigations have been reported on the effects of solvent on intensity enhancement of electronically forbidden transitions in solvated molecules (Leach et al., 1961; Platt, 1962; Bayliss and Cant, 1962; Koyanagi and Kanda, 1964; Eastman and Rehfeld, 1970; Rusu et al., 2008; Reske et al., 2005; Ahmed et al., 2012a,b; Cissea et al., 2011). Second order perturbation theory had been applied to the interacting solute molecules encaged by solvent molecules to derive the expression that correlates intensity enhancement with the macroscopic solvent properties like refractive index and dielectric constant (Weigang, 1964; Liptay, 1966; Siddlingeshwar and Hanagodimath, 2010). In a similar manner, the second order perturbation theory was applied to a system of absorber (solute) and perturber (solvent) to identify the mechanism by which the solute transition can borrow intensity from other solute transitions and from transitions of the solvent (Robinson, 1967). Adopting the Louguet-Higgins and Salem mode of intermolecular forces, the intensity enhancement was correlated with the interaction between solute transition moment and transition polarizability and that of the solvent, and static electric field of the solvent (Bayliss, 1969; Ahmed et al., 2012a,b).

The expression that correlates the absorption enhancements of benzene and naphthalene with solvent polarizabilities and solute–solvent inter-molecular distance was derived (Koyanagi, 1968). An interesting example of solvent perturbations in the absorption and fluorescence spectra of pyrene and coronene in polar solvent has been demonstrated (Nakajima, 1971, 1979). It was concluded that the intensity enhancements of the origin band in the $S_0 \rightarrow S_1$ spectra of pyrene and coronene were closely correlative with solvent polarities rather than with solvent refractive indexes.

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The purpose of this paper is in part to correlate the properties of the solvated solute to that of vapour whose determination may not be experimentally feasible, and in part to identify the key terms that contribute to the intensity enhancement of the forbidden transition in solutions via the application of the first order perturbation theory using Acridine and 9-aminoacridine as case study.

2. Experimental

2.1. Materials and apparatus

Acridine and 9-aminoacridine, n-hexane, and cyclohexane were products of Tokyo Kasei (Japan), and were of spectroscopic grade. Methanol, ethanol, n-butanol, dichloromethane, chloroform, acetonitrile, tetrachloromethane were obtained from the British Drug House Ltd and were distilled several times.

Electronic absorption spectra were measured at room temperature using a Schimadzu UV-1650 double beam spectrophotometer coupled with UV-probe® 2.31 version, operated in the wavelength region of 190–500 nm. Stock solutions of each compounds dissolved in different solvents were prepared in 5 ml standard flasks and were in the concentration range of 10^{-5}–10^{-6} M. The quartz cells used were of 1.0 cm in optical path. The other experimental conditions had been described previously (Iweibo et al., 1991).

2.2. Intensity measurement

The *f*-value of the absorption spectra of the two compounds was determined using a mathematical expression that incorporates both the solvent and field correction factors as described previously (Iweibo et al., 1990).

$$f^{\exp}_{jis\rho_o} = \frac{Vmb}{N_0\pi e^2}\,(\ln 10)cv_{jis}\frac{\varepsilon(v)_s}{v}dv \tag{1}$$

where

$$\int \frac{\varepsilon(v)_s}{v}dv = \int \frac{\varepsilon(v)'_s}{v}dv + \int \frac{\varepsilon(v)''_s}{v}dv \tag{2}$$

$$v_{jiv}\int \frac{\varepsilon(v)'_s}{v}dv = \frac{1}{c'(\ln 10)l}\times \int \ln\left[\frac{(1+n)^2}{4n}\right]dv \tag{3}$$

N_0 is the Avogadro's number; V is the volume of the solution; m and e are the mass and charge of electron respectively, n is the real part of the refractive index; c is the speed of light, $\varepsilon(v)_s$ is the molar absorptivity at frequency v as defined by the Bouger-Beer-Lambert law; $\varepsilon(v)'_s$ is the experimentally determined molar absorptivity and $\varepsilon(v)''_s$ is a correction factor arising from the optics of double-beam spectrophotometers; c' is the concentration of the dissolved solute; l is the optical length; subscripts s and v denote quantities in the solution and vapour phases respectively; The values of term b depend on the unit of measurement – in the S.I. unit, $b = 4\pi\varepsilon_0$ and in the *c.g.s* units $b = 1$; ε_0 is the vacuum permittivity of free space.

Neglecting the $\varepsilon(v)''_s$ component in Eq. (2) and assuming that $v_{jiv}\int\frac{\varepsilon(v)'_s}{v}dv \approx \varepsilon(v)'_s dv$ reduces Eq. (1) to that which has been previously used (Iweibo et al., 1982). Oscillator strength in vapour phase was determined using the modified Onsager-Abe-Iweibo reaction field model as described (Iweibo et al., 1990).

2.2.1. Molecular radii and other molecular properties

The molecular radii employed were calculated using molecular weights and densities available for the liquid states, on an assumption that all the molecular are spherical (Nakashima et al., 1982). The polarizability of the solvents was computed from molar refraction as previously described (Iweibo et al., 1982; Chongwain and Iweibo, 1991; Ahmed et al., 2012a,b). Table 1 shows the polarizability data with other properties of the solvent.

3. Results and discussion

3.1. Solvent effects on transition energies

Presented in Table 2 are the transition energies (in wave number) and the maximum molar extinction coefficient values of different absorption bands for the compounds in the representative solvents. In acridine, the $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ bands are red-shifted in polar solvents relative to non-polar which suggests that the transitions are $\pi \rightarrow \pi^*$ in nature, this implies that the ground state has more charge character than the excited state. However, the $S_0 \rightarrow S_3$ bands are blue-shifted in polar

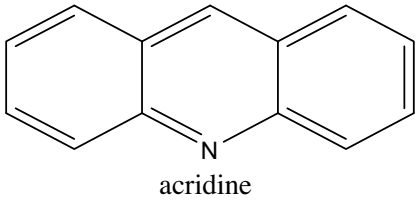
Table 1 Molecular (spherical) radii, polarizability and other solvent properties.

S/No	Solvents	Molecular radii (10^{-8} cm)[d]	Mean molecular polarizability, ($\bar{\alpha}$ (10^{-24} cm^3)[c]	Refractive index (n)[a]	Dielectric constant (D)	Density (kg dm^{-3})[b]
1	Methanol	2.13	3.26	1.3284	33.0	0.7910
2	Ethanol	2.41	5.12	1.3614	24.3	0.7890
3	Cyclohexane	2.95	10.89	1.4262	2.02	0.7791
4	Dichloromethane	2.48	6.47	1.4241	9.08	1.3266
5	*n*-Hexane	3.15	11.86	1.3749	1.89	0.6594
6	Chloroform	2.68	8.47	1.4458	4.81	1.4892
7	Acetonitrile	2.33	4.44	1.3441	37.5	0.7768
8	Tetrachlorocarbon	2.82	10.23	1.4603	2.24	1.6320
9	*n*-Butanol	2.79	8.78	1.400	17.8	0.8100

[a] Refractive index at the sodium D line.
[b] Taken from the catalog of Tokyo Kasei Co. Ltd.
[c] Calculated from refractive index and molar refraction (Iweibo et al., 1990).
[d] Computed from molecular weights and densities (Nakashima et al., 1982; Chongwain and Iweibo, 1991).

Table 2 Summary of observed absorption bands of compounds in different solvents.

Compounds and transitions	Methanol		Hexane		Dichloromethane	
	$\bar{\nu}_{max}(cm^{-1})$	ε_{max} ($\times 10^3$) M^{-1} cm^{-1}	$\bar{\nu}_{max}(cm^{-1})$	ε_{max} ($\times 10^3$) M^{-1} cm^{-1}	$\bar{\nu}_{max}(cm^{-1})$	ε_{max} ($\times 10^3$) M^{-1} cm^{-1}
Acridine						
$S_0 \rightarrow S_1$	28096	4.85	28090	4.96	27933	4.23
$S_0 \rightarrow S_2$	39992	40.45	40000	42.22	39683	27.32
$S_0 \rightarrow S_3$	47619	16.98	47170	8.93	–	–
9-Aminoacridine						
$S_0 \rightarrow S_1$	24876	5.67			24318	1.54
$S_0 \rightarrow S_2$	38168	24.13	Insoluble	Insoluble	37879	1.23
$S_0 \rightarrow S_3$	45455	11.45			–	–



acridine

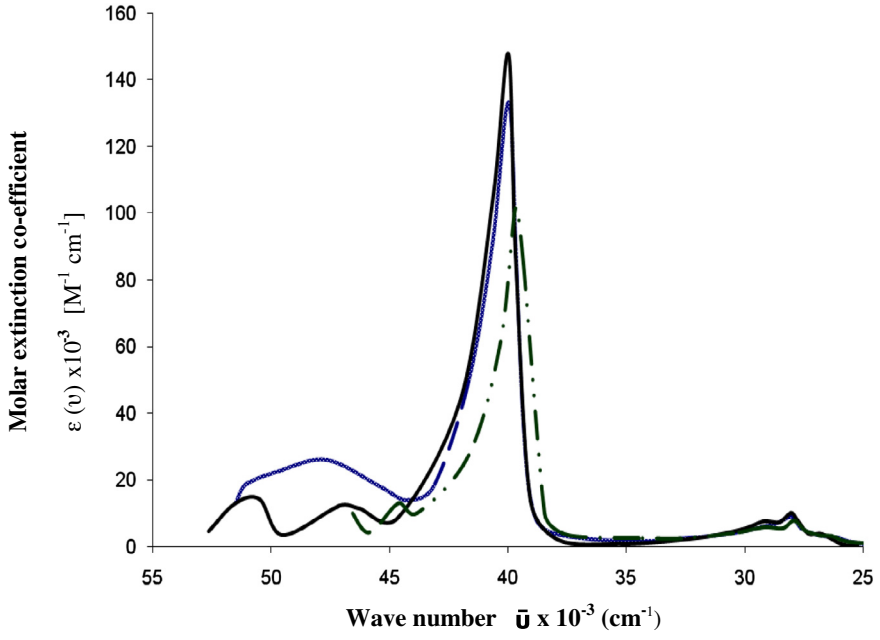


Figure 1 Electronic absorption spectra of Acridine in methanol (——), *n*-hexane (– – –) and dichloromethane (–·–·–).

relative to non-polar. A similar trend was observed in 9-aminoacridine, though it suffers solubility problem in some solvents.

Figs. 1 and 2 show the absorption spectra of acridine and 9-aminoacridine in the representative solvents. Both compounds have three major bands which are designated as $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ in the order of increasing energy. The $S_0 \rightarrow S_1$ bands in the compounds are both quantum-mechanical and overlap forbidden as reflected in their low intensity, transitions in the other two bands are intense and allowed except where the insolubility occurs. The bands show similar patterns except that vibrational fine structure of the $S_0 \rightarrow S_1$ band is much more pronounced in 9-aminoacridine. This is not unexpected because the lone-pair electron on the amino substituent is strongly delocalised. Also, 9-aminoacridine absorbs at longer wavelength compared to acridine, the shift being more pronounced for $S_0 \rightarrow S_1$ band. This displacement is due to the substituent effect which causes the perturbation of the π-electronic energy level.

3.2. Solvent effect on oscillator strength

From Table 3, the oscillator strength, *f*, obtained ranged from 10^{-2} for the forbidden electronic transition to approximately

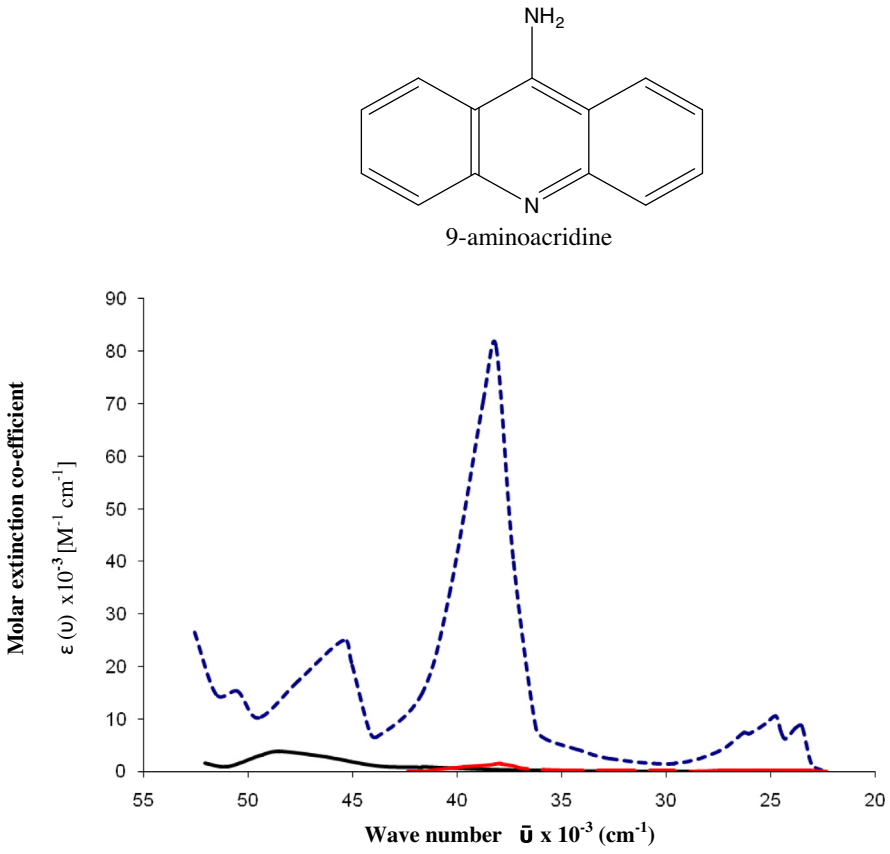


Figure 2 Electronic absorption spectra of 9-aminoacridine in methanol (——), *n*-hexane (– – –) and dichloromethane (– – –).

Table 3 Summary of oscillator strength in solution and vapour phase for the observed bands in different solvents.

Compounds and transitions	Methanol		Hexane		Dichloromethane	
	$f_{(soln)}$	$f_{(vap)}$	$f_{(soln)}$	$f_{(vap)}$	$f_{(soln)}$	$f_{(vap)}$
Acridine						
$S_0 \rightarrow S_1$	0.119	0.116	0.137	0.134	0.117	0.114
$S_0 \rightarrow S_2$	1.142	1.111	1.016	0.993	0.883	0.859
$S_0 \rightarrow S_3$	0.606	0.589	0.206	0.201	–	–
9-Aminoacridine						
$S_0 \rightarrow S_1$	0.148	0.144			0.241	0.235
$S_0 \rightarrow S_2$	0.947	0.921	Insoluble		0.052	0.051
$S_0 \rightarrow S_3$	0.409	0.398			–	–

1.0 for fully allowed transition. However, the f value of $S_0 \rightarrow S_2$ transition in acridine was found to be greater than 1.0, which suggests that more than one optical transition is contributing to the intensity of these bands (Chongwain and Iweibo, 1991).

Generally, the oscillator strength of an electronic transition of any given compound in a series of solvents increases with increase in solvent polarity. This trend is in harmony with expectation, because in polar solvents, all the van der Waal's interactions between solute and solvent (the dispersion interaction inclusive) are operative in the perturbation of the oscillator strength and are positive, additive contributions to the oscillator strength in the vapour phase whereas in non-polar solvents only the dispersion interaction terms exist.

Comparison of the oscillator strength values of these compounds in vapour phase with the corresponding ones in solution reveals that for any given transition, the vapour phase should be lower than that of the solution; this is in agreement with the Bayliss theory (Bayliss, 1969).

3.3. Solvent intensity enhancement

Applying Nakajima's treatment of environmental intensity enhancement to our study, the solvent parameter given by Nakajima (1971) is expressed as

$$f^{1} = \frac{(D-1)}{(2D+1)} - x\frac{(n^2-1)}{(2n^2+1)}$$

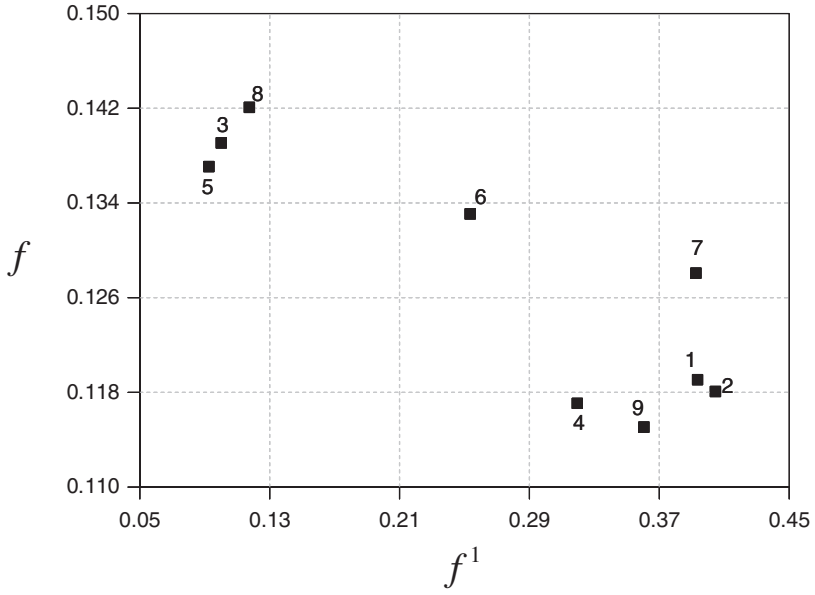


Figure 3 Plots of the oscillator strength, f of acridine against the solvent parameter given by Nakajima, The numbering of the plots is as follows: (1) methanol; (2) ethanol; (3) cyclohexane; (4) dichloromethane; (5)*n*-hexane; (6) chloroform; (7) acetonitrile; (8) tetrachlorocarbon; and (9) *n*-butanol.

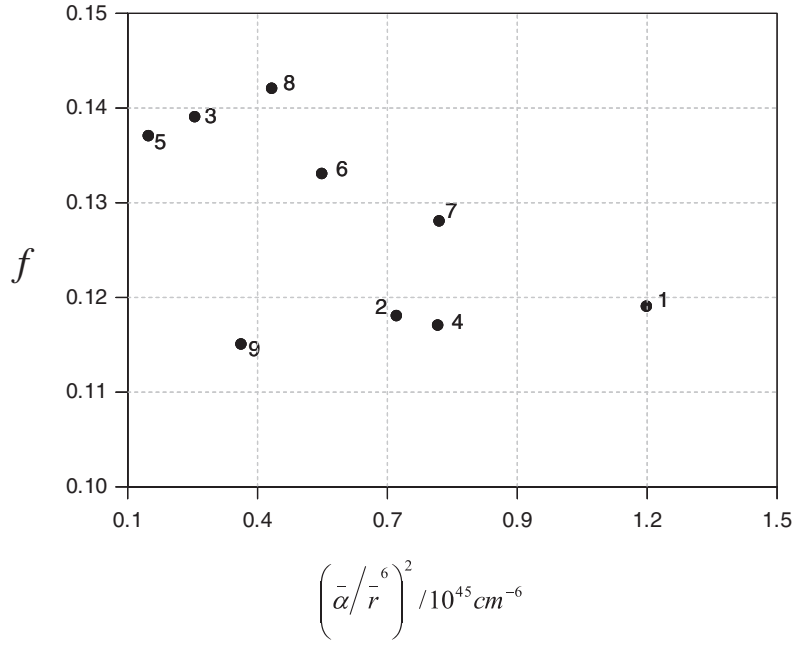


Figure 4 A correlation diagram between the oscillator strength, f, of acridine and the square of the relative dispersion energy of solvents, $(\bar{\alpha}/\bar{r}^{6})^{2}$. For the numbering of the plots, see the caption given in Fig. 3.

where D denotes the dielectric constant, n the refractive index of the solvent, and x an adjustable dimensionless parameter with arbitrary value of $x = 0.5$ and the physical meaning of f^{1} is not clear. Plots of oscillator strength f against f^{1} for acridine are shown in Fig. 3. However, we could not find any straightforward correlation between f and f^{1}. Thus, it seems that Nakajima-like treatment is not valid for the explanation of the intensity enhancement in the $S_0 \rightarrow S_1$ spectra of acridine and 9-aminoacridine. Similar plots were obtained for 9-aminoacridine despite its insolubility in some solvents.

Adopting Koyanagi's treatment of intensity enhancement by solvent properties (Koyanagi, 1968), the oscillator strength f is plotted as a function of the squared value of a relative dispersion energy between the solute and the solvent molecules; $(\bar{\alpha}/\bar{r}^{6})^{2}$. $\bar{\alpha}$ denotes the mean polarizability of the solvents and $\bar{r}$ the mean molecular distance between the solute and the

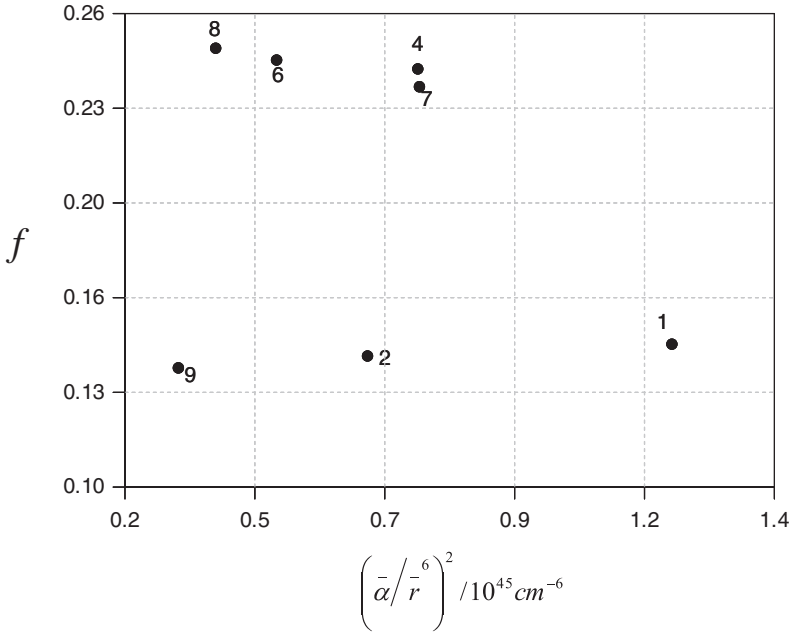


Figure 5 A correlation diagram between the oscillator strength, f, of 9-aminoacridine and the square of the relative dispersion energy of solvents, $(\bar{\alpha}/\bar{r}^6)^2$. For the numbering of the plots, see the caption given in Fig. 3.

solvent. The correlation diagram between f and $(\bar{\alpha}/\bar{r}^6)^2$ is shown in Figs. 4 and 5, respectively.

Despite the roughness in the approximation for $\bar{r}$, the observed oscillator strength of acridine and 9-aminoacridine shows an approximately linear increase with an increase in $(\bar{\alpha}/\bar{r}^6)^2$. Solvent numbers 3 and 5 (i.e. cyclohexane and *n*-hexane) are missing in Fig. 5 because of the problem of insolubility.

With the help of quantum-mechanical perturbation treatment of Bayliss model of solvent intensity enhancement, we shall here give a qualitative explanation and a comment on the environmental intensity enhancement. The wave function of solvated solute for excited state i and the ground state o is expressed (Bayliss, 1969) as the product combination of the solute and solvent wave functions and it is given as

$$(\alpha\beta)_{is} = \alpha_i\beta_o + \sum_{p\neq i,q\neq o} C_{pqio}\alpha_p\beta_q \tag{4}$$

$$(\alpha\beta)_{os} = \alpha_o\beta_o + \sum_{p,q\neq o} C_{pqoo}\alpha_p\beta_q \tag{5}$$

where α and β represent the solute and solvent wave functions, respectively, p and q denote all possible excited states in the solute and solvent, respectively.

The transition moment integral for the system gives

$$\langle(\alpha\beta)_{is}|M_s|\,(\alpha_\beta)_{os}\rangle = \langle(\alpha_i\beta_o + \sum_{p\neq i,q\neq o} C_{pqio}\alpha_p\beta_q|M|\alpha_o\beta_o + \sum_{p,q\neq o} C_{pqoo}\alpha_p\beta_q)\rangle \tag{6}$$

where $M_s = \mu_a + \mu_b$.

On expanding and neglecting terms with double summation, and imposing the orthogonality condition for the wave functions in different states, Eq. (3) gives the following non-vanishing terms:

$$\langle(\alpha\beta)_{is}|M_s|\,(\alpha_\beta)_{os}\rangle = \langle\alpha_i|\mu_a|\alpha_o\rangle + C_{iooo}\{\langle\alpha_i|\mu_a|\alpha_i\rangle - \langle\alpha_o|\mu_a|\alpha_o\rangle\} + \sum_{p\neq o} C_{pooo}\langle\alpha_i|\mu_a|\alpha_p\rangle + \sum_{q\neq o}(C_{iqoo} + C_{oqio}) \times \langle\beta_o|\mu_b|)\beta_q\rangle + \sum_{p\neq i} C_{poio}\langle\alpha_p|\mu_a|\alpha_o\rangle \tag{7}$$

The first term of Eq. (4) is the transition moment of the isolated solute and the four other terms represent modes by which the transition mode can be enhanced by solvent. The second term indicates contributions to intensity due to the difference in the permanent moment of the ground and forbidden excited state (i.e. stark term). The third term is the contribution arising from the static field of the perturber and a transition of the type $\alpha_i \rightarrow \alpha_p$ in the solute. The fourth is the dispersion term involving the forbidden transition density and that of a transition $(\beta_o \rightarrow \beta_q)$ of the perturber. The fifth term is intensity enhancement originating from $\alpha_o \rightarrow \alpha_p$ transition density and the permanent dipole moment in the solvent.

4. Conclusion

Based on the assumption that

(i) the interaction between the solute and the solvent is weak and
(ii) the distance between the solute and the solvent molecules is far apart in such a way that electron exchange does not occur between the solute and the solvent molecules.

Therefore, the intensity enhancement of the $S_0 \rightarrow S_1$ forbidden electronic absorption band of acridine and 9-aminoacridine in solutions is quantitatively interpreted in terms of dispersion interaction between the solute and the solvent.

However, a careful check is suggested for further generalization in case of other system.

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