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## Absorption and refraction of radiation by liquids

### II. Solvent effects on the absorption intensity

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**Abstract.** Absorption intensities are given in terms of the vapour phase solute transition dipole moment, and the dielectric properties of the solvent. The Chako factor is derived from perturbation theory and shown to be due to off-resonance excitation exchange between the solute and the solvent. A complete first-order perturbation correction is made to the transition dipole moment and applied to the calculation of the intensification factor. The calculated and observed solvent intensifications are compared for strongly and weakly absorbing systems.

#### 1. Introduction

Molecular properties such as polarizability, transition and permanent dipole moments are often obtained from measurements of the dielectric and spectroscopic properties in condensed phases rather than from the isolated molecules in the gas. Also the values of molecular properties obtained in one condensed state are often used in the determination of the properties in others. It is therefore important to have valid relationships between molecular properties and the measurable bulk quantities.

The transition dipole moment is of central importance. It is obtained by equating the transition probability per unit time with the theoretical Einstein  $B$  coefficient. For isolated molecules the relation (1) holds, giving the square of the transition dipole moment ( $q$ ) in terms of the extinction coefficient  $\epsilon$ :

$$q^2 = \frac{3hc}{8\pi^3 N e^2} \int \epsilon \frac{d\omega}{\omega} \quad (1)$$

$\omega$  being the circular frequency of the transition and  $N$  Avogadro's number. Various modifications have been proposed in which the medium effects are taken into account. Mulliken and Rieke (1941) allowed for a changed velocity of light in a medium of refractive index  $n(\omega)$  to obtain (2):

$$q^2 = \frac{3hc}{8\pi^3 N e^2} \int \frac{\epsilon}{n(\omega)} \frac{d\omega}{\omega} \quad (2)$$

Chako (1934) considered the solute molecule at the centre of a small spherical cavity within a uniform dielectric. The polarization on the inside of the cavity then gives an electric field to be added to the medium electric field acting on the solute molecule, making up the effective local field (Lorentz cavity field) and changing the effective magnitude of the dipole to expression (3). If the effective field at the dipole does not include the local field, expression (4) is obtained.

$$q^2 = \frac{3hc}{8\pi^3 N e^2} \int \frac{9n(\omega)}{\{n^2(\omega) + 2\}^2} \epsilon \frac{d\omega}{\omega} \quad (3)$$

$$q^2 = \frac{3hc}{8\pi^3 Ne^2} \int \epsilon n(\omega) \frac{d\omega}{\omega}. \quad (4)$$

These treatments are classical, and other expressions based on electrostatic corrections have been proposed, as for example that of Weigang (1965) but none is entirely satisfactory in interpreting the experimental observations.

All these methods have been based directly or indirectly upon an electrostatic derivation of the effective electric field at the position of the molecule. This effective electric field is the sum of the incident electric field and the internal field due to polarization of the surrounding molecules. The internal field can be obtained from a quantum electrodynamic treatment of the complete system of radiation field plus molecular array, the approximations required to produce the electrostatic results being explicitly demonstrated.

In an earlier paper (Dissado 1970 a) the operator (5) was derived for interactions between solute molecules and the medium radiation field, valid in the dipole approximation, formally similar to that of Power and Zienau (1957).

$$H_{\text{int}} = -\mathbf{q}_m^s(\mathbf{r}) \cdot \boldsymbol{\epsilon}^\perp(\mathbf{r}). \quad (5)$$

The effective solute transition dipole moment  $\mathbf{q}_m^s(\mathbf{r})$  is given by

$$\mathbf{q}_m^s(\mathbf{r}) = \mathbf{q}^s(\mathbf{r})/n_m. \quad (6)$$

The operator (5) gives the interaction between the effective electric field within the medium and a transition dipole moment equivalent to the complete set of possible transitions in its interaction with the field. The transition dipole moment  $\mathbf{q}^s(\mathbf{r})$  is the exact expectation value for the transition  $s$  of the molecule at  $\mathbf{r}$  in the presence of all other molecules. It is to be obtained by an application of perturbation theory to the solvent-solute liquid system, the operator (5) then being used to derive its interaction with the radiation field, giving the absorption probability.

## 2. Determination of the relationship of measured intensity of absorption to the transition dipole moment

### 2.1. Transition dipole uncorrected for intermolecular interaction

The method of correcting the transition dipole of a state, which was introduced in Part I (Dissado 1970 b—to be referred to as I), will be applied here to the determination of the medium correction to the solute transition dipole. The solution is taken to be very dilute. Such corrections as previously discussed will alter the form of the expression used in estimating the transition dipole from the experimentally obtained absorption intensities.

We must first relate the theoretically obtained absorption probability to the experimental extinction coefficient  $\epsilon$ . This has been carried out using operator (5) (Dissado 1970 a) for transition dipoles uncorrected for non-resonance interactions. The resulting expression

$$(\mathbf{q}^y)^2 = \frac{3hc}{8\pi^3 Ne^2} n_m(\omega) \int \epsilon \frac{d\omega}{\omega}$$

is identical to Chako's alternative expression (4) if his refractive index is taken to be that of the medium. If we had used  $\mathbf{q}^y$  instead of  $\mathbf{q}_m^y$  as the dipole moment operator,

Mulliken's expression (2) is obtained. As in I, the use of the operator (5) involves a reduction of the zero-order coupling matrix. We must again allow for intermolecular interactions prior to this reduction. Expression (4) is thus obeyed for the corrected solute dipole  $q_s^{yc}$ .

$$(q_s^{yc}) = \frac{3hc}{8\pi^3 e^2 N} n_m(\omega) \int \epsilon \frac{d\omega}{\omega}. \quad (7)$$

A similar model to that of I is advanced. The solute molecule ( $s$ ) is assumed to be surrounded by solvent molecules ( $m$ ) only. No solute-solute interaction will be assumed to occur. All states of the system are taken to possess an average transition dipole of magnitude  $\bar{q}$  lying along the polarization vector. The solvent states are taken as fully corrected for solvent-solvent interactions, it being these solvent states which are removed from explicit consideration by use of the operator (5).

### 2.2. Complete first-order correction to the transition dipoles

Before considering a full first-order correction of the transition dipole, it is worthwhile examining the result obtained when only intermolecular excitation exchange is considered. In this approximation the solute dipole is given by

$$\overline{q_s^{yc}} = \left( \frac{n_m^2 + 2}{3} \right) \overline{q_s^y} \quad (8)$$

the analogue to the previously obtained expression for the pure liquid (I—equation (31)). Here  $n_m$  is measured at the frequency of the transition. Substituting into (7) we obtain Chako's formula (3).

As shown in I, the Lorentz factor arises from correction of the excited state wave function to include non-resonance interactions for a many-body system of which only one molecule is excited at a time. Since the exact wave function for the state  $y$  is required for the use of operator (5), further corrections to the wave function from liquid states which may interact with  $y$  at any order of perturbation theory can be expected. The Lorentz correction is thus only the first of a sum of corrections, but it has generally been used to modify the dipole after quantum mechanical correction of the wave function (Weigang 1965). It is therefore necessary to recalculate the complete first-order correction isolating the Lorentz correction as one of a set of factors rather than as an overall multiplier.

Both the ground and excited state wave functions must be corrected for coupling to states possessing one and two excitations. The wave functions for these states are taken to be

$$\psi_{y\alpha}(K, K) = \frac{1}{(N_s N_p)^{1/2}} \sum_p \exp(i\mathbf{K} \cdot \mathbf{p}) \sum_s \exp(i\mathbf{K}_1 \cdot \mathbf{s}) \phi_{y(s)\alpha(p)}. \quad (9)$$

Here we have  $N_s$  solute molecules and  $N_p$  solvent molecules situated at sites  $r, s$  and  $p, l$  respectively. The solvent excited states are labelled  $a$ , and  $b$ , while those of the solute are labelled  $x$  and  $y$ .  $\phi_{y(s)\alpha(p)}$  is therefore a product wave function for all molecules in their ground state except the  $s$ th solute molecule in its  $y$ th state and the  $p$ th solvent molecule in its  $a$ th state. The wave function (9) is taken to represent a Fourier component of the polarization wave produced by the excitation of the system by two photons of different frequencies. When the sum over wave vectors involved in the correction (10) is evaluated, only states for which  $\mathbf{K}_1$  is equal to  $\mathbf{K}$  contribute. As

discussed in I, the only polarization state which may couple to the exciting wave is that for which  $\mathbf{K}$  is equal to  $\mathbf{Q}$ . Under these restrictions (9) is seen to represent the polarization wave. First-order (in intermolecular interactions) perturbation theory gives the corrected wave functions as

$$\begin{aligned} \psi_y^c(K) = & \psi_y(K) + \sum_{x \neq y} \frac{H_{yK,xK}}{E_y - E_x} \psi_x(K) + \sum_a \sum_{K_1} \frac{H_{aK_1yK,yK}}{E_y - E_{ay}} \psi_{ay}(K, K_1) \\ & + \sum_a \sum_{x \neq y} \sum_{K_1} \frac{H_{aK_1xK,yK}}{E_y - E_{ax}} \psi_{ax}(K, K_1) \end{aligned} \quad (10)$$

for the solute state  $y$ , and

$$\begin{aligned} \Phi_G^c = & \Phi_G + \sum_x \sum_K \frac{H_{xK,G}}{-E_x} \psi_x(K) + \sum_a \sum_{K_1} \frac{H_{aK_1,G}}{-E_a} \psi_a(K_1) \\ & + \sum_a \sum_x \sum_{K_1} \sum_K \frac{H_{aK_1xK,G}}{-E_{ax}} \psi_{ax}(K_1, K) \end{aligned} \quad (11)$$

for the ground state  $G$ .

$E_a$ ,  $E_{ax}$  and  $E_x$  are energies for transition from the ground state to the excited state indicated. Since we are correcting for interaction between all states the unmodified Coulomb operator must be used to find the matrix elements  $H$ . For the static form of perturbation theory giving (10) and (11), the denominator containing the sum of transition energies does not appear. This extra term is replaced when the transition dipole is obtained from a complete treatment including the field and molecules (Philpott 1966). In the static form the polarizability becomes

$$\alpha_m(\omega_y) = \sum_a \frac{(\bar{q}^{ac})^2}{\omega_a - \omega_y} \quad (12)$$

and the dielectric constant is given by

$$d = n^2 = 1 + \sum_a \frac{(\bar{q}^{ac})^2 4\pi}{(\omega_a - \omega)V_a} \quad (13)$$

This form will be used in place of the more general form of I (equation (24)) to identify the correction factors.

In obtaining the transition dipole moment from (10) and (11) it must be remembered that the matrix elements also contain interactions of the solute and solvent permanent dipoles with the transition dipoles. These permanent dipoles are taken to be randomly oriented at the frequency of absorption, thus all matrix elements in which these appear as a single power average to zero. This does not apply to solvents of high dielectric constant whose permanent dipoles may be self oriented. The results obtained for the model advanced will be used to determine its applicability to such solvents. The polarizability of the medium will again be taken to be isotropic as in I.

The only cross-term remaining after averaging is that for the first term of (11) with the fourth term of (10) for  $x$  as the ground state. This term is the correction due to excitation interchange and gives the Lorentz factor as has been shown in I.

When the permanent dipole appears as a square the average value over all angles is  $\frac{2}{3}$  of the matrix element (Margenau 1939).

$$\begin{aligned} \overline{q^{yc}} = & \left\{ \frac{n_m^2(\omega_y) + 2}{3} \sum_p \sum_a \frac{(\overline{q_i^{ac}} \overline{q_i^y})^2 \beta_{ii}}{(E_a^2 - E_y^2) R_{ps}^6} \right. \\ & \left. + \frac{2}{3} \sum_p \sum_a \sum_r \frac{(\overline{q^{ac}})^2 \mu_0^2(r)}{E_a^2 R_{pr}^6} - \frac{2}{3} \sum_p \frac{\mu_0(p)^2 (\overline{q^y})^2}{E_y^2 R_{ps}^6} \right\} \overline{q^y}. \end{aligned} \quad (14)$$

$\mu_0(r)$  and  $\mu_0(p)$  are the permanent dipoles of the solute and solvent ground states respectively. A thorough discussion of this derivation has been given by Weigang (1965). Only differences arising from different identification of the matrix elements will be described. Since the transition dipoles are taken to be parallel no average over angles has been carried out for the second term of (14). The sum over molecules is again carried out by integration to give

$$\begin{aligned} \sum_p (\overline{q^{ac}})^2 (\overline{q^y})^2 \frac{\beta_{ii}}{R_{ps}^6} &= \frac{(\overline{q_i^{ac}})^2 (\overline{q_i^y})^2}{V_m} \int_a^\infty \frac{1}{R^6} d^3R \\ &= \frac{16\pi}{5V_m} \frac{(\overline{q_i^{ac}})^2 (\overline{q_i^y})^2}{3a^3} \end{aligned} \quad (15)$$

where  $V_m$  is the average molecular volume of the medium, which for a dilute solution becomes that of the solvent molecules.  $a$  is the effective radius of the solute molecule, and is taken to be the mean molecular radius.

Using (13) the contribution of this term is given as

$$\frac{(\overline{q^y})^2 \{n_m^2(\omega_y) - 1\} 4}{\langle E_a \rangle 3a^3 5}. \quad (16)$$

Similarly the third correction term becomes

$$\frac{N_s - 1}{3a^3 \langle E_a \rangle} \mu_0^2(r) \{n_m^2(0) - 1\} \quad (17)$$

where the factor  $N_s - 1$  appears because there are only  $N_s - 1$  ground-state solute molecules when one solute molecule is excited. In both these terms the expression  $\langle E_a \rangle$  refers to the mean transition energy for the solvent, weighted by the contribution of each transition to the dielectric constant.

The fourth term gives

$$\frac{4\pi \mu_0^2(p) (\overline{q^y})^2}{V_m (E_y)^2 3a^3}. \quad (18)$$

Here  $\mu_0(p)$  is the uncorrected permanent dipole and should be obtained from I (equation (39)) giving

$$\frac{4\pi}{3V_m} \mu_0^2(p) = \left\{ \frac{d-1}{d+2} - \frac{n_m^2(0) - 1}{n_m^2(0) + 2} \right\} \left\{ \frac{d+2}{n_m^2(0) + 2} \right\} 3kT \quad (19)$$

where  $d$  is the solvent dielectric constant.

The transition dipole moment  $\overline{q}^{yc}$  obtained using these expressions must be normalized. In accordance with Weigang (1965) we take the normalizer to be

$$\left[ \int (\Phi_G^c)^2 d\tau \int \{\psi_y^c(K)\}^2 d\tau \right]^{1/2}.$$

The matrix elements involved are evaluated in a similar way to (15). The denominator is then expanded by the binomial theorem and only the first terms retained to give

$$\begin{aligned} \overline{q}^{yc} = & \left\{ \frac{n^2(\omega_y) + 2}{3} \right\} \left[ 1 + 3A \left\{ \frac{n_m^2(\omega_y) - 1}{n_m^2(\omega_y) + 2} \right\} + 3B \left\{ \frac{n_m^2(0) - 1}{n_m^2(\omega_y) + 2} \right\} \right. \\ & \left. - 3C \left\{ \frac{d-1}{d+2} - \frac{n_m^2(0) - 1}{n_m^2(0) + 2} \right\} \frac{(d+2)}{\{n_m^2(0) + 2\}\{n_m^2(\omega_y) + 2\}} \right] \overline{q}^y. \end{aligned} \quad (20)$$

Here the first correction term has been removed as a factor for comparison purposes. The coefficients  $A$ ,  $B$  and  $C$  are given by

$$\begin{aligned} A = & \frac{4}{15} \frac{\overline{q}_y^2}{\langle E_a \rangle a^3} - \frac{2}{15a^3} \left\{ \frac{\langle E_a \rangle - \langle E_y \rangle}{\langle E_a \rangle (\langle E_a \rangle + \langle E_y \rangle)} \right\} \left( \sum_{x \neq y} q_{xy}^2 + \sum_x \mu_x^2 \right) \\ B = & \frac{2N_s - 1}{9a^3 \langle E_a \rangle} \mu_0^2(r) - \frac{1}{9a^3 \langle E_a \rangle} \{N_s \mu_0^2(r) + (N_s - 1) \mu_0^2(r)\} = - \frac{\mu_0^2(r)}{9a^3 \langle E_a \rangle} \\ C = & \frac{2kT \overline{q}_y^2}{a^3 E_y^2} + \frac{kT}{3a^3 \langle E_y \rangle} \{\alpha_s(0) + \alpha_s(E_y)\} \end{aligned} \quad (21)$$

where  $\alpha_s$  is the polarizability of the solute.

The expression obtained by Weigang given in (22) to be compared with (20).

$$\begin{aligned} \overline{q}^{yc} = & \frac{\{n_m^2(\omega_y) + 2\}}{3} \left[ 1 + A' \left\{ \frac{n_m^2(\omega_y) - 1}{2n_m^2(\omega_y) + 1} \right\} + B' \left\{ \frac{n_m^2(0) - 1}{2n_m^2(0) + 1} \right\} \right. \\ & \left. - C' \left\{ \frac{d-1}{d+2} - \frac{n_m^2(0) - 1}{n_m^2(0) + 2} \right\} \right] \overline{q}^y. \end{aligned} \quad (22)$$

### 2.3. A comparison with experimental values

The constants  $A$  and  $A'$ ,  $C$  and  $C'$  are similar in form and magnitude and need not be further discussed. The refractive index factors for  $A$  and  $A'$ , though different in form, show only slight differences in the region of experimental values. A major difference occurs in the estimation of  $B$  and  $B'$ . Weigang finds  $B'$  to be zero in the limits taken for the binomial expansion of the normalizer, whereas  $B$  is shown to be of the same order of magnitude as  $A'$  and  $C'$  for dipolar solutes.

The presence of a contribution depending upon the permanent dipole of the solute molecule should be most significant for weak systems in which  $A'$  and  $C'$  are very small. A typical example of this type of system is the  $36\,000\text{ cm}^{-1}$  transition of acetone, whose permanent dipole is  $2.71 D$ . The intensification values calculated from (20) are shown in table 1. An almost negligible change from the Chako factors is found. Thus the observed deviations from the Chako values are not due to interactions with doubly excited states of the solute-solvent system (the source of corrections  $A'$ ,  $B'$  and  $C'$ ).

**Table 1. Ratio of observed oscillator strengths in solution to that of the vapour for the acetone 36 100 cm<sup>-1</sup> system**

Solvent	Chako factor	Expression 20	Experimental†
Carbon tetrachloride	1.35	1.35	1.32
Chloroform	1.34	1.33	1.31
Dichloromethane	1.31	1.31	1.20
Benzene	1.56	1.55	1.06
Iso-octane	1.27	1.27	1.13
Cyclo-hexane	1.34	1.33	1.02
Ethyl alcohol	1.24	1.24	1.29
Methyl alcohol	1.21	1.20	1.31
Water	1.22	1.20	2.12
Diethyl ether	1.24	1.24	1.29

† Values given by Bayliss and Wills-Johnson 1968.

A possible source of error is due to the consideration of the solvent as continuous, required to evaluate the dipole sums by integration. This approximation can be removed by including an extra term in  $A$ , the magnitude of which is the ratio of the difference between the real and integrated dipole sums to the integrated value. In this way allowance may be made for a local arrangement in which the solvent transition dipoles are not assumed to be aligned along the electric field vector.

This term gives a 10% alteration of the intensification factor  $\frac{1}{3}(n_m^2 - 1)$  when its own magnitude is approximately 0.1, which, for the solvents discussed, requires a difference between real and integrated dipole sums of 200 cm<sup>-1</sup>/(unit dipole length)<sup>2</sup>. If the local order of the solvent is taken to be a cubic lattice of touching spherical molecules with permanent point dipoles situated at the molecular centre aligned parallel to the electric field vector, the correction gives an increase of approximately 1% which is negligible. However, this model is unrealistic when considering the short-range order, since most molecules are far from spherical, and a correction of 10% would not be excessive especially in the case of benzene.

In the case of water and the alcohols some hydrogen bonding would also be expected to occur. These solvents also possess very high dielectric constants and may be thought of as having some local molecular alignment, which will result in a local field due to permanent dipoles. A dipolar solute or one capable of hydrogen bonding will have a fixed orientation due to the local arrangement. Under these conditions the solute molecule no longer possesses a random orientation and an average over transition dipole orientations need not give the  $\frac{1}{3}$  factor used. Since the dipole interactions between excited states should contain the factor  $1/d$  (Dissado 1970 a), contributions from solute-solvent interaction will be drastically reduced. If the dielectric constant is very large the maximum intensification becomes  $3/n$  (considering  $\bar{q} = q$ ). In the case of water this gives 2.2, close to the observed value for acetone. This agreement is only superficial however since much higher values are obtained for the nitroparaffins, but it serves to illustrate the change in magnitude brought about when the averaging factor  $\frac{1}{3}$  does not apply.

The experimental results obtained for nitroparaffins in the same solvents all show an increase compared with Chako's factor, that (20) is unable to interpret. However, corrections of the transition dipole for solute-solute interactions via the medium introduces extra corrections which can to some extent reproduce these



results (Bayliss and Wills-Johnson 1968). Remembering that all solute molecules are to be taken as isolated from each other, this term can be found from second-order perturbation theory, in a similar way to the previous corrections, and is given by

$$- \sum_{x \neq y} \frac{4}{5a^3} \frac{\{n_m^2(\omega_y) - 1\}}{3} \left( \frac{\overline{q^x} \overline{q^y}}{E_y - E_x} \right) \overline{q^x}. \quad (23)$$

This term may be positive or negative according to the difference in energies  $E_y - E_x$ . If the state observed is a weak transition lying just below a strong transition, the term (23) is positive and will increase the intensification factor. Thus increases of the intensification factor as compared with the Chako factor can be accounted for. It should be noted here that this term contains a factor

$$\frac{1}{3}\{n_m^2(\omega_y) - 1\}$$

and not the generally used Chako factor; it may be included in (20) to contribute extra terms to  $A$ .

For the case of a strong transition the factors  $A$  and  $C$  can be large, and the term (23) will generally be small unless the neighbouring transition is also strong.

As an example of strong transition we take the 39 000  $\text{cm}^{-1}$  state of anthracene. Here there are no reliable vapour values for the oscillator strength, hence equations (20) and (22) have been solved iteratively from the solution values. Of the results given in table 2, the third value is generally taken to be high and can be neglected. Successive

Table 2. Oscillator strengths for anthracene 39 100  $\text{cm}^{-1}$  level

Observed value of $f$	Expression 20			Expression 22	
	1	2	3	1	2
(a) 1.56	1.25	1.25	1.24	1.22	1.23
(b) 1.70	1.25	1.26	1.25	1.21	1.23
(c) 2.28	1.79	1.80	1.78	1.72	1.74

† 1 and 2 stand for first and second iteration, 3 for inclusion of correction (23). Experiment values (a), (b) and (c) are given by Jones and Keir 1956, Morris 1959, and Klevens and Platt 1949.

iteration brings the other two results to agreement. Inclusion of the solute-solute interactions (23) decreases the intensification factor here, since the closest interacting transition lies below the observed state. This transition is weak and has little contribution. We have a check on the magnitude of the oscillator strength in this case, from a comparison with the crystal spectrum. In the crystal this state is split into two

Table 3. Davydov splitting of 39 000  $\text{cm}^{-1}$  anthracene system, for varying oscillator strengths. Observed value  $\approx 15\,000\ \text{cm}^{-1}$

Splitting ( $\text{cm}^{-1}$ )	Oscillator strength
28 200	2.3
20 900	1.7
17 200	1.4
15 300	1.25
12 300	1.0

widely separated levels, the magnitude of the separation being dependent upon the oscillator strength of the free molecule. Using a value of  $-2661$  for the inequivalent dipole sums (obtained by computation), the magnitude of the splitting is given in table 3 for various oscillator strengths. Because the state is intense, other crystal parameters will have only a minor effect on the calculations. The estimated oscillator strength of  $1.25$  using (20) is seen to agree very well with the observed splitting which is in the region of  $15\,000\text{ cm}^{-1}$ .

### 3. Conclusions

It has been shown that the correction to transition dipoles following from an application of the Lorentz-cavity field is only the first of a series of corrections, and cannot be used as an overall factor. It has thus to be used with care when estimating medium intensification. Since this factor arises from non-resonance intermolecular interactions leading to a correction of the wave function, its use is limited to cases in which perturbation theory applies. The presence of medium states lying close enough for quasi-resonance with the representative state requires a different approach. For these states a simple perturbation theory is no longer applicable and allowance must be made for the overlapping of the bands of the two states. The remaining states being treated as characterizing the medium, the simple Lorentz field factor will be added to a more complicated factor obtained from explicit consideration of interaction between the overlapping states. It is useful to state the approximations involved in obtaining the Lorentz field factor. They are:

- (i) That there is no short-range order about the molecule absorbing the radiation.
- (ii) That the orientation of the transition dipoles can be replaced by an average component along the electric field vector.
- (iii) That the dielectric constant  $d$  of the solvent is approximately equal to the square of its refractive index.

These approximations are necessary if the interaction sum is to be evaluated by integration and the result identified with the medium refractive index.

Such approximations should hold best for the non-polar pure liquid, for which each molecule is in a typical position and any short-range order effect will be included in the medium refractive index  $n'$ . The approximations will be least correct for solution and liquid mixtures for which one or all components are dipolar, any short-range order of orientation about the absorbing molecules will not be that of the medium and will not be compensated for by use of the medium refractive index. It is just these systems for which the deduced expressions are in worst agreement with experiment. If the short-range order and orientation is known the interaction energy given by the shell of ordered molecules may be added to the integral result, which is valid for a lower limit of intermolecular separation of  $40\text{ \AA}$  and less (in the optical region). An extra contribution will thus be added to the Lorentz field factor in correcting the transition dipole whose magnitude will be determined by the short-range order. Inclusion of this contribution would allow for any effects due to molecular anisotropy.

The method detailed allows calculations to be made for such large molecules as globular proteins, in which absorption may be essentially confined to a particular region of the molecule. A direct calculation enables local structure to be accounted for, whilst the surrounding medium may be allowed for in the way we have shown. It is also possible to make sample calculations for various local arrangements for comparison with experiment. It must be remembered that the Lorentz correction is then an additive factor. Such calculations could also be made for solid solutions in glasses

where the local order could be obtained from neutron or electron diffraction in principle. The most probable local arrangement in liquids should vary with temperature, and the experimental investigation of this point should lead to a better understanding of the spectral solvent effect.

In the case of crystals where the local order is known, good results for the oscillator strength have been obtained when interactions with only one intense medium state have been considered, due regard being given to the crystal structure (Thirunamachandran 1968). The system investigated was that of a tetracene solution in anthracene, the strong anthracene transition which contributes most to the results lies  $13\,000\text{ cm}^{-1}$  above the tetracene state. Though this gap will be reduced in the crystal it seems that such intense states do not need to be very close to have a large effect. It must be remembered that such intense solvent states will also be shifted, and the energy gap is not necessarily that of the free molecules. Thus it seems that solvents of strongly anisotropic molecules or possessing low-lying intense transitions are better treated by assuming some short-range order, and estimating the molecular sums of equation (27) (see I) directly. The result is to be added to the integrated value of the matrix element, the sum over medium states being evaluated in terms of  $(n_m^2 - 1)$  multiplied by a constant dependent upon the local arrangement. For low-lying solvent transitions the sum over medium states may be evaluated directly. When estimating interaction between such solvent states and the solute it should be noted that both transition energies and dipoles of the solvent must be fully corrected for solvent-solvent interaction, if possible the values used should be obtained from the pure solvent spectra.

The success demonstrated in obtaining the classical electrostatic expressions, by a simple quantum-mechanical approach, points to the applicability of quantum mechanics as a route to the determination of bulk properties. Thus a basis has been provided for a more sophisticated quantum-mechanical approach to the theory of condensed systems.

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