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Spectroscopy of Intermolecular Field Interactions in Solutions

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Methods of interpreting data on the effect of the solvent on the spectral characteristics of molecules are critically compared. It is shown that the effect of field-induced intermolecular interaction in solutions on molecular spectra can be calculated in terms of the London-Debye-Keesom pair potential. 145 references.

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I. INTRODUCTION

Condensed media, in which the distance between molecules is smaller than in gases, invariably show substantial interaction between molecules with saturated chemical bonds (intermolecular interaction, IMI). The features of the IMI determine the thermodynamic properties of liquids and the kinetics and mechanisms of the elementary chemical acts: the IMI also control the formation of donor–acceptor complexes, and are responsible for the formation of colloidal systems. In biological systems intermolecular forces control the stability of all the compounds which are essential to life.

Intermolecular interactions can be studied experimentally by a variety of methods[1], mostly spectroscopic[2]. The interactions reveal themselves in the spectra of molecules in different ways (shifts in the absorption and in the emission bands, changes in intensity and shape of the bands, appearance of new bands). Information on the nature of the IMI can be obtained also from measurements of the polarisation and dipole moments of molecules[3,4].

All the different types of IMI can be classified into two main groups. Terenin[5] subdivides intermolecular forces into physical (determined by the physical characteristics of the interacting molecules) and chemical (responsible for the formation of directional chemical or quasi-chemical bonds between molecules). Other workers[6,7] classify the IMI into volume interactions (in which each molecule is bound to surrounding molecules by a force inversely related to distance) and local interactions (in which two or more molecules are held together fairly strongly but the bonds between these groups of molecules have only secondary importance). Others[8-10] distinguish between short-range and long-range order when classifying intermolecular forces. The former involves interactions described in terms of the physical parameters of the molecules, whereas the latter involves valency or chemical forces arising from overlap of the electron clouds of the interacting molecules. Bakhshiev[2] suggests classifying the IMI not according to their forces or radii of action, but according to the "generality of their occurrence". He classifies all types of IMI as universal or specific. The former operate between molecules in all systems, without exceptions, and are determined by the physical parameters of the molecules: they describe the collective influence of the surrounding molecules on the properties of one particular molecule. The specific IMI do not occur in all systems: they are individual manifestations, confined to a particular pair of interacting molecules. They have a quasi-chemical (exchange) origin and a high degree of selectivity towards certain molecules, leading to the formation of a definite bond which can be strong or weak[2].

In spite of these differences in terminology, and in the light of the physical meaning of the term IMI, we shall use the following classification of the IMI into two groups: the first group includes the van der Waals interactions, which are additive and non-directional (attractive forces due to orientation, induction, and dispersion effects, and repulsive forces arising from the mutual impenetrability of molecules), and the second group includes all forms of interaction of donor–acceptor origin and showing the typical attributes of a chemical bond (saturability and directionality).

The interaction energy of two molecules can be expressed as the sum $U_{tot} = U_{or} + U_{ind} + U_{dis}$, where the terms in the right-hand side denote the energies arising from the orientation, induction, and dispersion interaction of the molecules, given by the London–Debye–Keesom formulae[11] as

$$U_{or} = -\frac{2\mu_1^2\mu_2^2}{3kT\bar{R}^6},$$

$$U_{ind.} = -(\alpha_1\mu_2^2 + \alpha_2\mu_1^2)/\bar{R}^6, \quad U_{dis} = -\frac{3}{2}\frac{I_1 I_2}{(I_1 + I_2)}\frac{\alpha_1\alpha_2}{\bar{R}^6}.$$

In these expressions $\bar{R}$ is the average distance between the molecules, μ_1 and μ_2 are the (constant) dipole moments, α_1 and α_2 are the isotropic polarisabilities, and I_1 and I_2 are the first ionisation potentials of the molecules.

A strict solution of the intermolecular interaction problem (and an exact calculation of U_{tot}) are possible by using quantum mechanics. This calculation (so far attempted only for the simplest molecules) yields the interaction energy of the molecules as a function of the intermolecular distance $\bar{R}$. For more complex molecules the quantum-mechanical calculation becomes unacceptably laborious, and empirical models of the intermolecular potential are used to calculate the IMI energy. Depending on the properties of the system, the Lennard-Jones, Morse, Kihara, Stockmaier, Buckingham, and other potentials have all been widely used. For example, the well-known Lennard-Jones potential

$$U(r) = E\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$

(where E is the minimum potential energy of the pair of molecules, σ is the distance for which U is a minimum, and r is the Onsager radius of the molecule) ignores many-particle interactions and does not explicitly allow for the parameters I, α, and μ, which (together with the structural parameters $\bar{R}$ and $\bar{Z}$, the number of nearest neighbours) determine the value of U.

In this review we shall attempt to generalise the large amount of published data on the determination of the IMI energy by using the theoretically well-justified London–Debye–Keesom potential for the pair interactions between

molecules in a liquid in order to study the spectral characteristics of molecules in solutions.

II. EFFECT OF THE MEDIUM ON THE I.R. SPECTRA OF MOLECULES AND COMPLEXES

1. Methods of Calculating the Effect of the Medium on the I.R. Spectra

Two types of relationship between the spectral characteristics and the properties of the solvent are generally used to allow for the IMI effects of a universal type on the characteristics of the vibrational spectra of molecules in solutions: those involving macroscopic parameters such as the dielectric constant ε and the refractive index n, and those involving molecular parameters such as the dipole moment μ, the polarisability α, and the ionisation potential I. The first group includes relationships based on potentials for the collective interation between solvent and solute molecules. Kirkwood[12], and Bauer and Magat[13], used the Onsager reactive field model[14] to derive the widely used expression (KBM formula)

$$\frac{\Delta\nu}{\nu_s} = \frac{\nu_s - \nu_{gas}}{\nu_{gas}} = -C\,\frac{\varepsilon - 1}{2\varepsilon + 1} \ .$$

Buckingham[15] replaced ε by n^2 in this formula, converting the KBM formula into

$$\frac{\Delta\nu}{\nu_s} = \frac{\nu_s - \nu_{gas}}{\nu_{gas}} = -C\,\frac{n^2 - 1}{2n^2 + 1}$$

where ν_{gas} is the stretching vibration frequency of the isolated molecule, ν_S is the vibration frequency in the medium, $\Delta\nu$ is the frequency shift, C is a constant depending on the properties of the solute molecule, and ε and n are the dielectric constant and the refractive index of the solvent respectively.

However, these expressions have had only limited success with both polar[16,17] and non-polar solvents[18], and they cannot be applied to systems in which $\nu_S > \nu_{gas}$ to calculate the vibration frequency of groups able to form H-bonded complexes[2].

The KBM theory was further developed by Pullin[19], who examined the effect of the solvent on the spectrum of the solute in terms of ε, n, the molar volume of the solvent, and the molar volume of the solute. However, in Pullin's expression

$$\frac{\Delta\nu}{\nu_0} = C + \frac{A}{R}\,\frac{n^2 - 1}{n^2 + 2} + B\,\frac{\varepsilon - 1}{2\varepsilon + 1}$$

(where A and B are constants, and R is the radius of a sphere circumscribing the molecule) the physical significance of the constants is not clear, and the ratio A/R is found to depend on the nature of the medium.

The work of Buckingham, based on quantum-mechanical considerations, is especially interesting[20]. By using first- and second-order perturbation theory he obtained an expression for the relative frequency shift of the absorption corresponding to the transition between levels with vibrational quantum numbers m and n,

$$\frac{\Delta W_{m,n}}{W_{m,n}} = \frac{B_e}{hcW_e^2}\left[\bar{U}'' - 3\,\frac{A}{W_e}\,\bar{U}'\right] \ ,$$

where B_e is the rotational constant, A/W_e is the anharmonicity constant of the vibration, and U' and U'' are the first and the second differential of U (the interaction energy of the solute molecule with the solvent molecules) with respect to the vibration coordinate.

By applying the Onsager reactive field theory Buckingham[20] arrived at the following expressions for the relative frequency shifts in non-polar solvents,

$$\frac{\Delta\nu}{\nu} = C_1 + \frac{1}{2}\,C_2\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) + \frac{1}{2}\,C_3\,\frac{n^2 - 1}{2n^2 + 2} \ ,$$

and in polar solvents,

$$\frac{\Delta\nu}{\nu} = C_1 + C_2\,\frac{\varepsilon - 1}{2\varepsilon + 1} + C_3\,\frac{n^2 - 1}{2n^2 + 2} \ ,$$

where C_i are constants determined by the microscopic characteristics of the molecules in solution (polarisability, dipole moment, etc.).

The most important attribute of these expressions is the fact that the physical meaning of their constants is relatively clear, though their application is limited to diatomic molecules. Attempts to apply them to polyatomic molecules[21] by calculating all the C_i values from experimental $\Delta\nu$ values are physically meaningless. This is especially true of the expressions which include a fourth term ($C_4\sigma^*$) to allow for the specific interactions of the molecules in solution[18,22].

From the Onsager model Bakhshiev obtained[2] the following expression for the shift in vibration frequency:

$$H\Delta\nu = -\Delta R\left[\frac{\mu_0\left(\frac{\partial\mu_0}{\partial R}\right)_{R_{s,d}}(F_1 + F_2)}{1 - \alpha_0(F_1 + F_2)}\left(\frac{\partial\alpha}{\partial R}\right)_{R\,equil} F_3\right];$$

$$F_1 = \frac{2}{a^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{\varepsilon_\infty - 1}{2\varepsilon_\infty + 1}\right); \quad F_2 = \frac{1}{a^3}\left(\frac{\varepsilon_\infty - 1}{2\varepsilon_\infty + 1}\right);$$

$$F_3 = \frac{3}{2a^3}\,\frac{I_s I_d}{I_s + I_d}\left(\frac{n^2 - 1}{n^2 + 2}\right) \ ,$$

where H_ν is the energy, and the subscripts 0, s, and d denote the gas phase, the solvent, and the dissolved substance (throughout this paper). This expression includes, in addition to macroscopic properties of the medium, also parameters which characterise the properties of the solute molecules. However, the relationship is difficult to apply, even to diatomic molecules[2,23,24]. In the case of more complex molecules the difficulties in determining the molecular parameters and in defining rationally the Onsager radius of the mole (a) become almost insuperable. Furthermore, the presence of macroscopic parameters of the solvent in the expression destroys the clarity of the presentation of the dependence of $\Delta\nu$ on the molecular properties of the solvent and makes it impossible to correlate $\Delta\nu$ with the basic characteristics of the molecular structure of the liquid.

The limited possibilities of all expressions which include generalised parameters of the solvent led to the belief that the universal IMI are always accompanied by specific interactions, or even that their effect is negligible and limited to the formation of low-stability complexes. The former point of view is implicit in the Caldow and Thompson expression[22]

$$\Delta\nu = C_1 + C_2\,\frac{\varepsilon - 1}{2\varepsilon + 1} + C_3\,\frac{n^2 - 1}{n^2 + 2} + C_4\sigma^* \ ,$$

where σ^* allows for the inductive or resonance effect of the substituents in the solvent molecule. The latter point of view is expressed in the work of Bellamy[25-27], who studied the correlation of the $\Delta\nu/\nu$ values for different vibrators in the same series of solvents. These workers assumed[22,25-27] that specific interactions can occur in non-polar as well as in polar solvents.

These views were further developed[28,29] in the cell theory of liquids. Using the terminology of that theory, strong specific interaction can be related mainly to the formation of donor–acceptor complexes in systems of the "polar solute–polar solvent" type, and weak non-specific interaction to the formation of collision complexes in systems of the "polar solute–non-polar (or weakly polar) solvent" type. This treatment excludes from the start any possibility of revealing characteristic dependences of the solvent effect on the composition and structure of the molecules for different types of IMI.

Another group of expressions for calculating the effect of IMI on $\Delta\nu$ relies on the pair interaction potential concept. The first expression of this type was proposed by Vol'kenshtein[30], who calculated the potential energy of the van der Waals interaction between solvent–solute pairs of molecules in the approximation of the London–Debye–Keesom potential:

$$U = \frac{1}{\bar{R}^6}\left(\frac{2}{3kT}\mu_s^2\mu_u^2 + \mu_s^2\alpha_d + \mu_d^2\alpha_s + \frac{3}{4}I\alpha_s\alpha_d\right).$$

Solution of the equations of motion leads to the following expression for the normal vibration frequency of the system:

$$\Delta W = WW_0 = -\frac{1}{2}\frac{B}{mW_0} \pm \frac{A}{mW_0},$$

where m is the reduced mass, and A and B are the sums of coefficients describing the orientation (o), dispersion (α), and induction contribution (i) to the pair interaction:

$$A = A_o + A_i + A_\alpha;\ B = B_o + B_i + B_\alpha .$$

The frequency shift is given by the factor B/mW_0, the line broadening by A/mW_0, with

$$B_0 = \frac{4}{3kT\bar{R}^6}\left[\mu^2\left(\frac{\partial\mu}{\partial q}\right)^2 + \mu^3\frac{\partial^2\mu}{\partial q^2}\right];\ B_\alpha = \frac{3}{4}\frac{I}{\bar{R}^6}\alpha\frac{\partial^2\alpha}{\partial q^2};$$

$$B_i = \frac{2}{\bar{R}^6}\left[\alpha\left(\frac{\partial\mu}{\partial q}\right)^2 + \alpha\mu\frac{\partial^2\mu}{\partial q^2} + \mu^2\frac{\partial^2\alpha}{\partial q^2}\right].$$

In these expressions $\bar{R}$ is the distance between dipoles, q is the relative displacement from the equilibrium position, μ is the dipole moment of the molecule, $\partial\mu/\partial q$ is the effective charge on the dipole, and $\partial^2_\mu/\partial q^2$ is the electrical non-linearity of the dipole.

Vol'kenshtein and coworkers[31] included not only the dipole–dipole inductive and dispersion interaction energy in their calculation of the IMI in terms of pair interaction energies, but also the repulsive energy of the molecules. The energy of the interaction between two molecules was identified with the sum of the pair interactions between bonds[32]. In this way, ignoring the second differential with respect to the vibration coordinate, we can arrive at the following expression for $\Delta\nu$ in the case of solutions of a polar substance in a non-polar solvent:

$$\Delta\nu = -\frac{3K_{11}}{8\pi^2c^2M_2V}\left[\frac{\alpha'_d}{\alpha_d} - 6\frac{R'_{s,d}}{R_{s,d}} + \frac{I'_d}{I_d} - \frac{I'_d}{I_d + I_s}\right]E_{disp} \qquad (1)$$

and for a polar solute in a polar solvent

$$\Delta\nu = -\frac{3K_{11}}{8\pi^2c^2M_2V}\left\{\left[\frac{\alpha'_d}{\alpha_d} - 6\frac{R'_{s,d}}{R_{s,d}} + \frac{I'_d}{I_d} - \frac{I'_d}{I_d + I_s}\right]E_{disp} + \right.$$

$$\left. + \frac{2\mu'_d}{\mu_d}E_{disp} + \left[\frac{\mu'_d}{\mu_d} - 3\frac{R'_{s,d}}{R_{s,d}} + \frac{I'}{I}\right]E_{or} - \left[\frac{a'}{a} - b'R_{s,d}\right]E_{rep}\right\}, \qquad (2)$$

where α', I', and μ' are the differentials with respect to the vibration coordinate of the polarisability, the ionisation potential, and the dipole moment respectively, $R_{s,d}$ is an orientation factor, a' and b' are the constants in the exponential expression for the repulsive energy, c is the velocity of light, M is the reduced mass of the molecule, ν is the frequency, and K is the force constant.

Acceptably precise calculations of $\Delta\nu = \nu_s - \nu_{gas}$ for quite simple molecules present almost insuperable difficulties in the evaluation of the pair interaction potential (as in the case of the potentials based on the collective interaction of molecules in solution). This explains the growing practice of correlating $\Delta\nu$ with various empirical parameters of the solvent[16,33]. However, the main advantage of using the pair interaction potential is the explicit presence in this type of expression for E_{in} of the molecular properties of the solvent (μ_s, α_s, I_s) as well as those of the solute, and also the explicit presence of characteristics of the molecular structure of the solution (Z and $R_{s,d}$). Unlike the expressions relying on collective interactions, the pair interaction relationships make it possible to study the dependence of $\Delta\nu$ on various specific properties of both the solvent and the solute molecule, and also its dependence on $\bar{Z}$ and $\bar{R}_{s,d}$. Thus, by using Eqns.(1) and (2) we can calculate E_{or} from the Keesom expression for the orientation interaction averaged over all configurations ($E_{or} \cong \mu_s^2\mu_d^2/\bar{R}^6$) instead of the expression for the local interaction, which makes it unnecessary to calculate I. Since α'_d is negligibly small, and α_d is almost independent of the nature of the solvent, but μ'_d varies with μ_d, we can expect that for a given solute in a series of solvents with similar values of I_s and $\bar{R}_s$ (and therefore similar values of $\bar{R}_{s,d}$) the combined contribution to $|\Delta\nu|$ from all the effects associated with the change of solvent will be quite small [Eqns.(1) and (2)] in comparison with the contribution from the energy of the pair interactions. For such a series of solutions with $\mu_s = \mu_d = 0$ we can expect $|\Delta\nu| \propto E_{disp} - E_{rep}$, whereas with $\mu_s \neq 0$ and $\mu_d = 0$ we have $|\Delta\nu| \propto E_{disp} + E_{ind} - E_{rep}$, and with $\mu_s \neq 0$ and $\mu_d \neq 0$ we have $|\Delta\nu| \propto E_{IMI} = E_{disp} + E_{ind} + E_{or} - E_{rep}$.

Since at ordinary temperatures and pressures the $\bar{R}_{d,s}$ values averaged over the whole volume vary between 5 and 8 Å, the contribution from E_{rep} to the IMI energy is negligible in comparison to that from E_{attr}, as confirmed by the small values of $\Delta\nu$ for many vibrators even at relatively high pressures[31]. If $E_{rep} \ll E_{attr}$ we can expect that in a series of solutions of a non-polar substance in non-polar solvents of the same type

$$|\Delta\nu| \propto E_{disp}. \qquad (3)$$

In the case of solutions of a polar substance in a series of non-polar solvents

$$|\Delta\nu| \propto E_{attr} = E_{disp} + E_{ind}. \qquad (4)$$

On the other hand, for solutions of polar substances in a series of polar solvents of the same type we have

$$|\Delta\nu| \propto E_{attr} = E_{disp} + E_{ind} + E_{or}. \qquad (5)$$

2. Effect of Intermolecular Interactions in Solutions on the Vibration Frequency of Functional Groups in Molecules

Expressions of the type of (3)–(5) have been used[34] to interpret data on ν_{max} for the stretching vibrations of different groups of polar or non-polar molecules. In that work the E_{attr} value (as a function of the molecular properties and of characteristics of the molecular structure

of the solution such as $\bar{Z}$ and $\bar{R}_{s,d}$) was fitted to a London–Debye–Keesom potential for condensed media[35,36]:

$$E_{attr} = \overline{const} \cdot \sum_k \left(\frac{\bar{Z}}{\bar{R}^6_{s,d}}\right)_k \left[\frac{3}{2}\frac{I_s I_d}{I_s + I_d}\alpha_s\alpha_d + \mu_s^2\alpha_d + \mu_s^2\alpha_s + \frac{2\mu_s^2\mu_d^2}{3kT}\right].$$

In studies of the behaviour of a single vibrator in a series of solvents of the same type we can write

$$|\Delta\nu| \propto \sum_k \left(\frac{\bar{Z}}{\bar{R}^6_{s,d}}\right)_k \left[\frac{3}{2}\frac{I_s I_d}{I_s + I_d}\alpha_s\alpha_d + \mu_s^2\alpha_d + \mu_d^2\alpha_s + \frac{2\mu_s^2\mu_d^2}{3kT}\right]. \quad (6)$$

By using Eqn.(6) we can recognise special features in the dependence of $\Delta\nu$ on the characteristics of the solution ($\bar{Z}$ and $\bar{R}_{s,d}$) and on the properties of the vibrator molecule and of the solvent molecule (μ, α, I). It follows from Eqn.(6) that for a given non-polar substance ($\mu_d = 0$) dissolved in a series of non-polar solvents ($\mu_s = 0$) having similar values of I_s we can write

$$\Delta\nu_s \propto C_1 \sum_k \left(\frac{\bar{Z}}{\bar{R}^6_{s,d}}\right)_k \alpha_s \qquad \left(C_1 = \frac{3}{2}\frac{I_s I_d}{I_s + I_d}\right)\alpha_d. \quad (7)$$

For a polar solute ($\mu_d \neq 0$)

$$\Delta\nu_s \propto C_2 \sum_k \left(\frac{\bar{Z}}{\bar{R}_{s,d}}\right)_k \alpha_s \quad (C_2 = C_1 + \mu_d^2). \quad (8)$$

In a series of non-polar solvents with similar values of I_s and α_s and T = const. containing a single non-polar solute ($\mu_d = 0$) we have

$$\Delta\nu_s \propto C_1 \sum_k \left(\frac{\bar{Z}}{\bar{R}^6_{s,d}}\right)_k \alpha_s + C_3 \sum_k \left(\frac{\bar{Z}}{\bar{R}^6_{s,d}}\right)_k \mu_s^2 \quad (C_3 = \alpha_d). \quad (9)$$

For a polar solute

$$\Delta\nu_s \propto C_2 \sum_k \left(\frac{\bar{Z}}{\bar{R}^6_{s,d}}\right)_k \alpha_s + C_4 \sum_k \left(\frac{\bar{Z}}{\bar{R}^6_{s,d}}\right)_k \mu_s^2 \quad \left(C_4 = \alpha_d + \frac{2}{3kT}\mu_d^2\right). \quad (10)$$

In these expressions C_i are quantities whose variation in a series is slight in comparison to that of the quantities under the summation sign.

We have tested[37] Eqns.(7)–(10) by measuring the ν(C–Cl) absorption for CCl_4 and $\nu(OH)_{free}$ for ethanol in polar and in non-polar solvents. Our results (Fig.1) show that, as required by Eqns.(7)–(10), the ν(C–Cl) and $\nu(OH)_{free}$ values decrease almost linearly with the parameter

$Y \equiv \bar{Z}\dfrac{I_s I_d}{I_s + I_d}\dfrac{\alpha_s}{\bar{R}^6_{s,d}}$ (i.e. that $\Delta\nu = \nu_s - \nu_{vap}$ increases with Y). This is confirmed by a large amount of published work. For many non-polar solvents of this type the ratios $\bar{Z}I_s/(I_s + I_d)$ and $\alpha_s/\bar{R}^6_{s,d}$ vary in the same sense: this also explains the often reported correlation between $\Delta\nu$ (or ν) and the $\alpha_s/\bar{R}^6_{s,d}$ value in a series of solvents[29,39,40]. The existence of this correlation is confirmed by the large deviation from the straight-line plot of ν or $\Delta\nu$ observed (point 6 in Fig.1) when H-bonded complexes or charge transfer complexes can be formed between the solute molecules and those of the non-polar solvent[41].

Dispersion and inductive interaction can cause a large decrease in ν_s, often of the same order as in polar solvents, which cannot form complexes with solute molecules[40,41]. A large contribution from inductive interactions in the case of polar vibrators in non-polar solvents can be recognised by comparing the $\Delta\nu$ values of the same vibrator for compounds of different polarity in the same non-polar solvents[22,31]. In the case of solvents which cause large deviations from Eqns.(7) and (8) we can calculate the contribution from complex formation or $\pi-\pi$ interaction of the solute and solvent molecules. On the other hand, a study of the contributions from dispersion and inductive IMI has shown that CCl_4 and CS_2 molecules do not take part in complex formation with molecules containing A–H groups[42,43].

The validity of these expressions for intermediate values of α_s, $\bar{Z}_s$, and $\bar{R}_{s,d}$ suggests a volume (as opposed to a local) mechanism for the interaction between molecules in solutions of this type. A volume mechanism can also explain the fact that the $\Delta\nu$ values in non-polar solvents having different but relatively small molecules all lie approximately on the same straight line. Similarly, the strong temperature and pressure dependence of the dispersion and inductive interactions is also consistent with a volume mechanism. An increase in temperature produces a large increase in $R_{s,d}$, and therefore a decrease in $\Delta\nu$.[44] An increase in pressure has the opposite effect on $\Delta\nu$.[31]

In a series of polar solvents with similar values of I_s and α_s (Fig.2) the $|\Delta\nu_s|$ values increase almost linearly with $\bar{Z}\mu_s^2/\bar{R}^6_{s,d}$, as required by Eqns.(9) and (10).

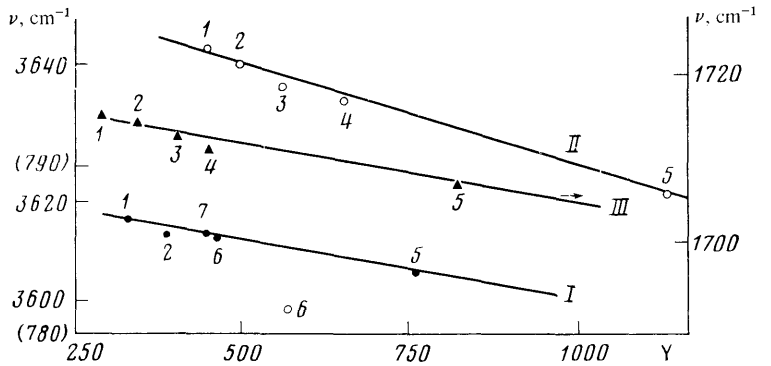


Figure 1. Dependence of ν(C–Cl) on $Y = \bar{Z}\dfrac{I_s I_d}{I_s + I_d}\dfrac{\alpha_s}{\bar{R}^6_{s,d}}$ for CCl_4 (*I*), and dependence of ν(O–H) for ethanol[37] (*II*) and of ν(C=O) for benzaldehyde[44] (*III*) in non-polar solvents: *1*) hexane, *2*) cyclohexane, *3*) CCl_4, *4*) C_2Cl_4, *5*) carbon disulphide, *6*) benzene, *7*) dioxan.

An analysis of the above expressions has revealed the following features of the field-induced (dipole–dipole and inductive) interaction of molecules in solutions (in comparison to the specific interactions accompanying the formation of complexes by the same molecules):

a) $|\Delta\nu_S|$ is usually smaller than the usual values for specific interaction between a vibrator molecule and a solvent;

b) the dipole–dipole interaction effect can take place even when the access of the solvent molecules to the proton-donor A–H group is blocked by steric hindrance;

c) the dependence of $|\Delta\nu_S|$ on the chemical composition and structure of the solvent molecules is different from (and almost opposite to) the effects observed during the specific interaction of a vibrator with a solvent[45]. For example, dipole–dipole interaction causes a decrease in $|\Delta\nu_S|$ rather than the increase expected from the decreasing *s*-character of the orbitals of the heteroatom in the solvent molecule [$CH_3CN > C_5H_5N > (C_2H_5)_3N$; $(CH_3)_2C{=}O > (C_2H_5)_2O$]. For solvents which include elements from the same period as heteroatoms, $|\Delta\nu_S|$ decreases in the following sequence: $RCN > RNO_2 > R_2CO > R_2O > R_3N$, which is the inverse of the series describing the tendency of solvents to form H-bonded complexes;

d) in the case of large differences in the size and nature of the solvent molecules (from both the aromatic and the aliphatic series) the $|\Delta\nu_S|$ values for a given vibrator lie on different straight lines if the interaction is of the dipole–dipole type;

e) if the solvent molecules are complex (with several polar functional groups) the $|\Delta\nu_S|$ values are determined by the molecule as a whole rather than by individual dipole moments or by the moment of the most polar group.

3. Effect of the Medium on the Vibrational Spectra of Molecules with Intramolecular and Intermolecular Hydrogen Bonds

In ternary systems [solvent, RAH, and BR', including the RAH...BR' complexes (K)] the vibrational spectra of the A–H group (which forms intermolecular hydrogen bonds) are affected both by changing the solvent and by changing the $c_{BR'}/c_{RAH}$ ratio[16,17,35]. The type of change is not very different from that of a vibrator not involved in hydrogen bond formation. The calculation of these solvent effects merely in terms of macroscopic characteristics such as ε and n,[47–49], or by using empirical relationships[16,46], has been criticised by several workers[2,47,50,51]. One of us[38] has examined the possibility of calculating the effect of the medium on the properties of the A–H group (involved in complex formation) by assuming proportionality (in the case of solvents of the BR' type with similar values of I_S and α_S) between $\Delta\nu_S$ and the parameter $\bar{Z}\mu^2_{BR}/\bar{R}^6_{K,BR'}$, which reflects the change in dipole–dipole interaction of the complex K with the excess of BR' molecules[37,45,52]. The proton-acceptor solvents BR' are chosen so that the changes in $\bar{Z}\alpha_S/\bar{R}^6_{S,d}$ are much smaller than those in $\bar{Z}\mu^2_S/\bar{R}^6_{S,d}$.

An analysis of the absorption spectra revealed the following features in the influence of the medium on the properties of the A–H group in H-bonded complexes. In relation to ν_{max} and $\Delta\nu_{1/2}$ the effect of the medium is relatively unimportant (as compared with the formation of the hydrogen bond itself). On changing from low-polarity ($\mu_{BR'} \leq 1.2$ D) to high-polarity solvents ($\mu_{BR'} > 1.2$ D) the sign of $\Delta\nu_{max}$ changes from positive to negative, and that of $\Delta\nu_{1/2}$ changes in the opposite sense[37]. We should note that when $\mu_{BR'} > 1.2$ D the effect of the medium on all the absorption characteristics is the same as the effect of complex formation. Under these conditions $\Delta\nu_S$(OH) for the complex is always much greater than $\Delta\nu_S$ for the free molecule.

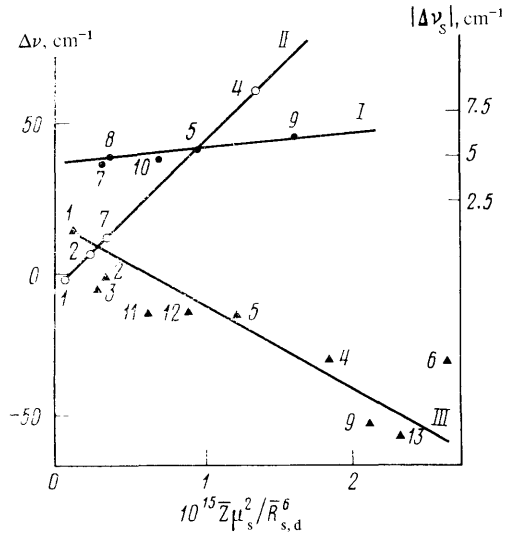


Figure 2. Plots of $\Delta\nu = \nu_{CCl_4} - \nu_{BR'}$ for CCl_4 (*I*), $\Delta\nu$(OH) for *o*-nitrophenol (*II*), and $\Delta\nu = \nu_{BR'} - \nu_{CCl_4+BR'}$ for ethanol (*III*) against $\bar{Z}\mu^2_S/\bar{R}^6_{S,d}$ in polar solvents[37]: *1*) $(C_2H_5)_2O$, *2*) C_4H_9Cl, *3*) $CH_3COOC_2H_5$, *4*) CH_3NO_2, *5*) $(CH_3)_2CO$, *6*) CH_3CN, *7*) CH_3COOCH_3, *8*) $HCOOC_2H_5$, *9*) $HCON(CH_3)_2$, *10*) CH_3COCl, *11*) $HCOOCH_3$, *12*) $CH_3COC_2H_5$, *13*) $(CH_3)_2SO$.

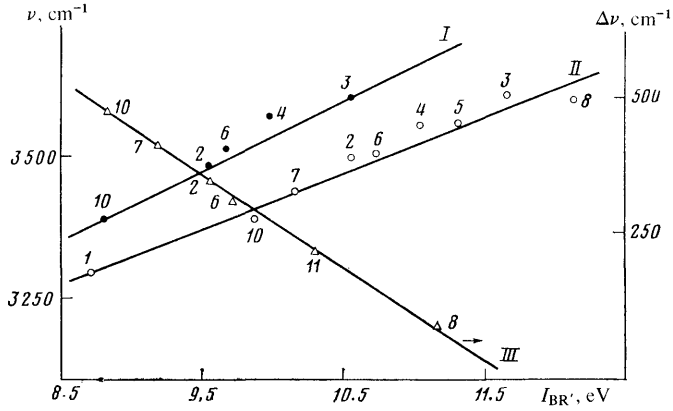


Figure 3. Plots (against the ionisation potential) of the ν(OH) values for ethanol in the ternary ($C_2H_5OH + CCl_4 +$ BR') system (*I*) and in the binary (C_2H_5OH + BR') system (*II*), and of $\Delta\nu_S(OH) = \nu_{CCl_4} - \nu_{BR'}$ for *p*-nitrophenol (*III*),[37] where BR' is: *1*) $(C_2H_5)_3N$, *2*) $(C_2H_5)_2O$, *3*) n-C_4H_9Cl, *4*) $HCOOCH_3$, *5*) $CH_3COOC_2H_5$, *6*) $(CH_3)_2CO$, *7*) $HCON(CH_3)_2$, *8*) CH_3NO_2, *9*) CH_3CN, *10*) $(CH_3)_2SO$.

The ν_{max} (or $\Delta\nu_{max} = \nu(OH)_{free} - \nu(OH)_{h.b.}$] values for the ν(OH) band in the complexes of ethanol and *p*-nitrophenol with BR′ are inversely proportional to $I_{BR'}$ (Fig. 3), as required by the electronic model of the hydrogen bond[38]. The only exceptions are molecules with a proton-accepting power much lower than that of ethanol and a large dipole moment (for example, CH_3NO_2 and CH_3CN). On the other hand, the $\Delta\nu(OH) = \nu(OH)_{bin} - \nu(OH)_{tern}$ values are almost linearly related to $\overline{Z}\mu^2_{BR'}/\overline{R}^6_{RAH,BR'}$, a parameter which characterises the dipole–dipole interaction between the BR′ molecules and the complex (Fig. 2). This justifies the assumption that the main contribution to the change in vibrational frequency caused (for high values of $c_{BR'}/c_{RAH}$) by the displacement of surrounding molecules of non-polar CCl_4 by molecules of polar BR′ comes from the increased dipole–dipole interaction between the complex and the medium.

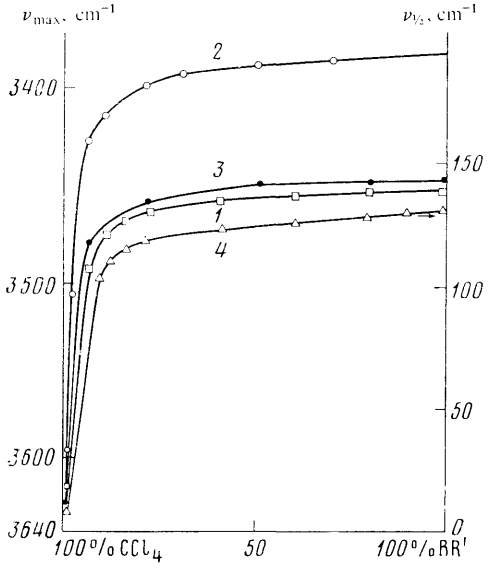
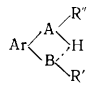


Figure 4. Spectral characteristic ν_{max} of the ν(OH) band against the solvent concentration ratio[37] for *1*) ethanol [BR′ = HCON$(CH_3)_2$]; *2*) ethanol [BR′ = $(CH_3)_2$SO]; *3*) *p*-nitrophenol (BR′ = CH_3NO_2); *4*) is the $\nu_{1/2}$ value of the ν(OH) band of phenol (BR′ = CH_3CN).

In ternary systems the dependence of ν_{max} on $\overline{Z}\mu^2_{BR'}/\overline{R}^6_{RAH,BR'}$ (and hence, for a given value of $\mu_{BR'}$, on $\overline{Z}$ and on $\overline{R}_{RAH,BR'}$) follows from the nature of the change in the spectral characteristics with $c_{BR'}/c_{CCl_4}$.[53–55] The steep increase of ν_{max} (Fig. 4, from Ref. 38) at low values of the ratio $c_{BR'}/c_{CCl_4}$ is due to the formation of a complex with BR′. The more gradual change in ν_{max} is due to the increase in Z caused by the replacement of molecules of non-polar solvent from the first coordination sphere of the complex by excess molecules of the polar compound BR′. The subsequent, even slower, change in ν_{max} is ascribed to the interaction of the complex with BR′ molecules from the outer coordination spheres, for which the interaction energy is very low (because of the large increase in $\overline{R}_{s,d}$).

The spectra due to the formation of intramolecular hydrogen bonds in compounds such as



(where Ar is an aryl group, and R′ and R″ are other parts of the molecule, attached to the atoms A and B) differ in several ways in the ν_s(A–H) absorption region from the spectra corresponding to the formation of an intermolecular hydrogen bond by the *para*-isomer[56,57]. For *o*-nitrophenol[58] and *o*-nitroacetanilide[54] these features are observed also in the effect of the medium on ν_{max} for ν_s(A–H) band of the intramolecular hydrogen bond. In different polar solvents of the BR′ type the ν_{max} value for this band increases in the opposite sense to the normal sequence for the ν_s(A–H) band of the intermolecular hydrogen bond. In solvents having a high proton-accepting power we find an additional band whose maximum usually lies at frequencies higher than the maximum of the ν_s(A–H) band for the intermolecular hydrogen bond[54,58–60].

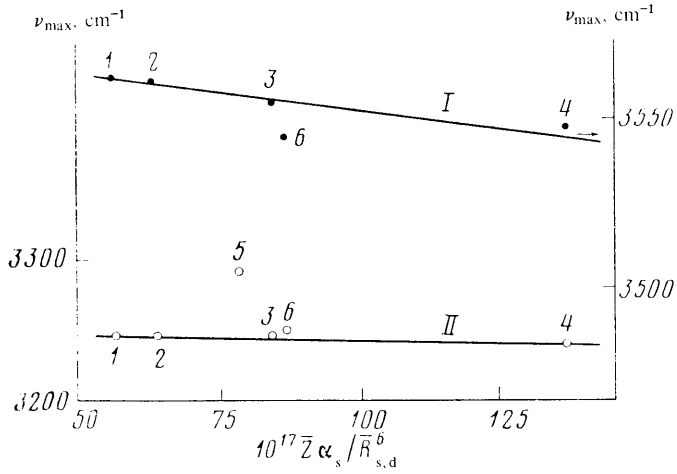


Figure 5. Plots against $\overline{Z}\alpha_S/\overline{R}^6_{S,d}$ of ν_{max} for the ν(OH) bands of guaiacol (*I*) and of *o*-nitrophenol (*II*) in non-polar solvents; *1*) hexane, *2*) cyclohexane, *3*) CCl_4, *4*) hydrogen sulphide, *5*) dioxan, *6*) benzene[58].

These effects of the medium have not yet been fully explained. Some workers[59,60] ascribe them to the breaking of an intramolecular hydrogen bond, with formation of complexes with molecules of the solvent, while others[61] postulate a three-particle complex with a forked hydrogen bond. Some published papers[62,63] explain the increase in ν_{max} in compounds with intramolecular hydrogen bonds in terms of dipole–dipole interactions, which lift the BR′ group from the plane of the aryl ring or displace the bridging proton. In an attempt to solve the problem more strictly[38], the spectral behaviour of molecules with intramolecular or intermolecular hydrogen bonds, and of molecules with a strong or a weak intramolecular hydrogen bond, has been compared as a function of $c_{BR'}/c_{CCl_4}$. The difference $\Delta\nu_{max} = \nu_{CCl_4} - \nu_{BR'}$ was found to increase with the

dispersion interaction energy[64]. This is confirmed by the fact that ν_{max} has about the same dependence on $\overline{Z}\alpha_s/\overline{R}^6_{s,d}$ as $\nu(OH)_{free}$ (see Fig.5, from Ref.38). In ternary systems containing *o*-nitrophenol only the $\nu_s(OH)$ intramolecular hydrogen bond band is observed. The high stability of this bond in *o*-nitrophenol is shown by the slight increase in $\nu_{max}(OH)$ caused by small additions of strong proton acceptors, followed by a steep fall, whereas additions of weak proton acceptors produce a continuous increase in ν_{max} towards the value for the pure BR′ compound (Fig.6),[38] i.e. the strong proton acceptors can break the intramolecular hydrogen bond and displace the equilibrium towards the formation of complexes involving intermolecular hydrogen bonds. On the other hand the increase in ν_{max} for the (A–H) band of the intramolecular hydrogen bond is probably due to non-specific interactions between molecules which contain intramolecular hydrogen bonds and the surrounding medium[65].

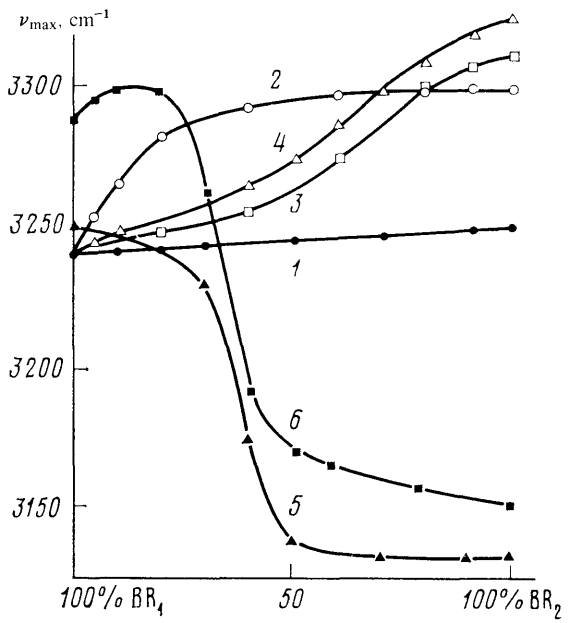


Figure 6. Plots of ν_{max} of the ν(OH) band for *o*-nitrophenol against the solvent concentration ratio (c_{BR_1}/c_{BR_2}) in ternary systems of the *o*-nitrophenol + BR_1 + BR_2 type. The BR_1 + BR_2 combinations are: *1*) CCl_4 + n-C_4H_9Cl, *2*) CCl_4 + CH_3NO_2, *3*) CCl_4 + CH_3CN, *4*) CCl_4 + $CH_3COC_2H_5$, *5*) n-C_4H_9Cl + $(CH_3)_2SO$, *6*) CH_3NO_2 + $(CH_3)_2SO$.[63]

III. INTERMOLECULAR FIELD INTERACTION AND THE CHEMICAL SHIFT OF PROTON SIGNALS

Ever since the first report of its use in studies of the hydrogen bond[66] the proton magnetic resonance (PMR) method has been one of the most useful and successful means of identifying and characterising intermolecular interactions. This is because the PMR spectra reflect both the nature and the extent of the participation of a proton in various interactions. The quantity δ_H (the chemical shift of the signal from hydrogen nuclei) in the PMR spectrum is determined to a first approximation by three independent factors[67]: the state of the electron shell surrounding a particular H atom (i.e. its shape and size), the effect of the surrounding atoms and functional groups in the molecule, and the effect of different kinds of IMI. Thus the quantity δ_H is defined by the structure of the molecule, by the interaction between atoms and functional groups within the molecule, and by the interaction with neighbouring molecules in a pure liquid or in a solution.

The change from the gaseous to the condensed state causes large changes in δ_H(A–H), where A = O, H, C, S. etc. The increment $\Delta\delta_H$(A–H) caused by the medium can be divided into five independent contributions[68–71]:

$$\Delta\delta_H(A\cdots H) = \delta_{vol} + \delta_{an} + \delta_{disp} + \delta_{pol} + \delta_{sp}. \qquad (11)$$

where δ_{vol} is the contribution from the volume susceptibility of the sample, δ_{an} is that due to the non-zero average anisotropy of the magnetic susceptibility of the solvent molecules, δ_{disp} is due to the dispersion interactions between solute molecules and solvent molecules, δ_{pol} is due to polarisation interaction between the molecules, and δ_{sp} is the contribution from specific interactions between molecules of the solvent and of the solute.

Most of the PMR studies of intermolecular interaction published so far are aimed at the contribution δ_{sp}, for two reasons: 1) this contribution is by far the largest, and 2) it can potentially give information on the genesis of intermolecular complexes involving a redistribution of electron density, which are currently of great interest. Since in most cases δ_{sp} is greater than the combined contribution from the other terms in Eqn.(11) it is not unusual to find the whole of the shift $\Delta\delta_H$ caused by the solvent ascribed to intermolecular association effects, the non-specific (field) interaction between solute and solvent molecules being completely ignored.

It is difficult to isolate one of the terms in Eqn.(11) for special study, even with carefully chosen series of solutes and solvents. If the change in volume susceptibility (and hence in δ_{vol}) is allowed for, and the contributions δ_{an} and δ_{sp} can be ignored, the observed increment $\Delta\delta_H$(A–H) should be determined only by field interactions of the molecules (dispersion effects, δ_{disp}, and polarisation effects, δ_{pol}).[67]

The quantity δ_{disp} is determined by two effects[67]: a) the interaction between molecules of the solute and of the solvent causes a loosening of the electron cloud surrounding the nuclei of the solute molecules, leading to a decrease in the diamagnetic screening effect (long-range interaction), and b) the interaction can perturb the symmetry of the electron clouds in the solute molecule (in the *s*-state), giving rise to a paramagnetic contribution in the screening constant (short-range interaction, temperature-dependent).

A quantum-mechanical calculation of the effect of dispersion interaction on the screening constant of the hydrogen atom has shown[72] that van der Waals forces lower the screening and shift the signals towards lower fields. Experimental measurements of the contribution δ_{disp} involve some serious difficulties. The direct method of isolating the contribution δ_{disp} involves comparing the δ_H values for a series of structurally similar non-polar compounds in the gas state and dissolved in non-polar isotropic solvents[82,83]. However, in practice the NMR spectroscopy of gaseous samples is far from straightforward.

To calculate the contribution of dispersion interaction to the magnetic screening of protons in solutions several models have been proposed: the "continuous" dielectric model, the lattice model, and the statistical model. Theoretical calculations of the contribution of the constant G_{disp} to δ_{disp} are also very difficult. The "excess" chemical shifts in the spectra of liquid systems consisting of magnetically isotropic molecules were first explained[74] in terms of dispersion forces. The model developed in that work[74] gives

$$G_{disp} = -\frac{3B\alpha_2 I_2}{2R^6} \qquad (12)$$

where B is the bond parameter ($B = 0.74 \times 10^{-18}$ for the hydrogen atom[75]), and α_2 and I_2 are the polarisability and the ionisation potential of the perturbing solvent molecule.

The "continuous dielectric" model, proposed earlier by Linder[77] for determining the potential energy of the dispersion interaction in pure liquids, has also been used in these calculations[76]. Starting from experimental values of the shift caused by the interaction in a solution of the solute 1 in the solvent 2 (at infinite dilution) Howard and coworkers[76] arrived at the expression

$$G_{disp} = -\frac{3B(2n^2-2)h\nu_1\nu_2}{4(2n^2+1)a^3(\nu_1+\nu_2)} \qquad (13)$$

where n is the refractive index of the solvent, a is the radius of the solute molecule, and $h\nu$ is the excitation energy. A similar model was used in Ref.73. The "continuous" dielectric model led to the conclusion[76] that the contribution of G_{disp} can be described by the expression

$$G_{disp} = -6\left[\frac{(n_2^2-1)^2}{(2n_2^2+1)(n_2^2+2)}\right]_{soln.} \cdot \left[\frac{K_1 B \Delta E_1}{\alpha_1}\right]_{solute}$$

where ΔE_1 is the energy of formation of the transition complex, which can be equated to twice the ionisation potential of this complex, and K_1 is a factor determined by the location of the proton and depending on the geometry of the solute molecule. However, in experimental tests of the expressions for δ_{disp} based on collective interaction concepts[73,74,76] the theoretical values of G_{disp} were inconsistent with measured values.

Calculations of G_{disp} by the "continuous" dielectric model rely on measurements of the characteristic frequencies of the solvent and of the solute (ν_1 and ν_2). These frequencies can be obtained by the formula $\nu = I/h$, which follows from the London approximation[78], where I is the ionisation potential of the molecules. Another formula for calculating the characteristic frequency[77,79] is

$$\nu = -4m_e c^2 \chi_m / hN\alpha \qquad (14)$$

where m_e is the mass of the electron, c is the velocity of light, N is Avogadro's number, α is the polarisability, and χ is the molar susceptibility of the molecules. Lastly, the characteristic frequencies have been calculated[80] by the Lorentz–Lorenz formula for the refractive index.

A calculation of G_{disp} for a large number of systems[81] has given very different results for given systems, depending on the method used to determine ν. A rational choice of the preferred method of calculation among those used in Ref.81 cannot yet be made. It has been suggested[82] that the influence of the medium on the chemical bond arises from the interaction of a solute molecule with the nearest molecules of the solvent "lattice", i.e. that $G_{disp} = Z \cdot G_{disp}(pair)$, where Z is the number of nearest solvent molecules in the "lattice" and $G_{disp}(pair) = -3B\alpha_2 I_2/R^6$ (by analogy with the formula given in Ref.74). The parameter Z was obtained[82] by dividing the area of a sphere passing through the centres of the molecules in the first coordination sphere $[4\pi(r_1+r_2)^2]$ by the effective cross-sectional area of the solvent molecules $(2r_2)^2$. Putting $R = r_1 + r_2$ we find

$$G_{disp} = -\frac{3\pi B\alpha_2 I_2}{(r_1+r_2)^4 r_2^2} \qquad (15)$$

where r_1 and r_2 are the radii of the solute and solvent molecules respectively.

With a suitable choice of series of compounds this model gives δ_{disp} values in good agreement with experiment: however, the results are less reliable when the same approach is used for molecules differing in size, shape, or chemical composition. Better agreement with experiment was obtained[86] by introducing into the formula the factor S_6^g, determined by the location of the resonating proton, and the additional empirical factor K_6^c, depending on the temperature and on the configuration of the solvent and solute molecules:

$$G_{disp} = -K_6^c \frac{3\pi B\alpha_2 I_2}{(r_1+r_2)^4 r_2^3} S_6^g .$$

An alternative approach was developed[83] by studying the effect of the medium in gaseous systems. The contribution from G_{disp} was calculated[83] in terms of binary collisions between the molecules only. The average contribution to the chemical shift from dispersion interactions was determined by using the Lennard-Jones intermolecular potential, and the following formula was obtained:

$$G_{disp} = -\frac{\pi NB\alpha_2 I_2 H_6(X)}{V_2 r_0^3 X^4} \qquad (16)$$

where V_2 is the molar volume of the solvent, $H_6(X)$ is a function tabulated in Ref.84 [$X = 2(\varepsilon/kT)^{1/2}$], ε/kT and r_0 are the force constants in the Lennard-Jones potential, and N is Avogadro's number.

The method[83] is essentially a semi-empirical statistical method, which has proved successful when applied to gases and gas solutions. Other workers[85,86] applied it to liquids, and obtained an expression not very different from (16). However, the model is relatively crude. Firstly, the calculated G_{disp} values are in qualitative rather than quantitative agreement with experiment, even when empirical coefficients are added to the formula. Secondly, the model cannot distinguish between the solvent effects on chemically non-equivalent protons in complex solvent molecules. The theory of pair collisions in gases was later modified[86] in order to apply it to liquids. The van der Waals interaction field $\langle\overline{E}^2\rangle$ near the peripheral protons of the solute molecule was shown to be different from the $\langle\overline{E}^2\rangle$ value at the centre of the molecule, and a correction to allow for the position of the proton in the molecule was added to the formula. The possibility of introducing a term for the repulsive effects into the expression for G_{disp} was examined, but the correction was found to be negligible. The formula finally proposed to describe quantitatively the contribution of dispersion interaction to the chemical shift also includes a temperature factor, to allow for the temperature dependence of G_{disp}:

$$G_{disp} = -(1.46 \pm 0.0064t) \cdot 1.36 \cdot 10^6 \frac{\alpha_2 I_2 H_6(X)}{V_2 r_0^3 X^4} S_6^g . \qquad (17)$$

The parameters S_6^g and $H_6(X)/X^4$ are tabulated in Ref.86. The physical nature of the temperature factor is not stated. Experimental tests of Eqn.(17) were on the whole satisfactory.

In a study[87–90] of various contributions from the medium to the chemical shift a linear combination of terms (including one due to dispersion interaction) was used to express the

chemical shift. The dispersion term was written as a product of contributions from the solvent and the solute respectively. By using this method the authors were able to determine experimentally the G_{disp} contribution for a number of systems. The experimental results were compared with theoretical calculations by the formulae of the collective interaction model[76,77], or by a formula obtained[85,86] from the statistical theory of pair collisions. The agreement in both cases was surprisingly good, and a critical analysis of the two methods of calculating G_{disp} was thought unnecessary.

The two sets of calculations (Refs.76, 77 and 85, 86), though differing in detail, have a great deal in common. First of all they both rely on generalised collective parameters, and therefore they cannot be used to study the dependence of δ_{disp} on the microscopic parameters of the interacting molecules. In spite of its relative success in calculations of G_{disp}, formula (17) (which was obtained from the theory of pair collisions in gases) has a number of shortcomings. The model is not applicable to large molecules, which require replacement of the one-centre Lennard-Jones potential by a many-centre potential force field. This is a serious limitation of all the models discussed above, especially in the case of aromatic solvents. The reliance on physical constants which are not always available creates further obstacles to the use of this working formula. Thus, though G_{disp} values have been successfully calculated, the method is not suitable for day-to-day use in the laboratory.

Allowance for polarisation effects is needed when one of the components of the solution is polar. This contribution is usually small[113], and can be described by the formula

$$\delta_{pol} = \delta_{disp} \frac{2\mu_2^2}{3\alpha_2 I_2}$$

where μ_2 is the (constant) dipole moment, α_2 is the polarisability, and I_2 is the ionisation potential of the solvent molecule. However, for small solvent molecules with large dipole moments the contribution from δ_{pol} becomes comparable to δ_{disp}.[103] An approximate calculation[60] has shown that for a proton of the A–H group the screening component associated with the external electric field is $\sigma_E = -AE_z - BE^2$, where A and B are constants and E_z is the component of the electric field E in a direction parallel to the A–H bond. The shift of the proton signal caused by the electric field is explained by the repulsion experienced by the excess charge on the proton, which lowers the electron density on the 1s orbital of the hydrogen and the screening constant[91]. Furthermore, the presence of an electric field hinders the diamagnetic current circulation within the hydrogen atom, which again lowers the screening constant and shifts the proton signal towards lower fields[92].

A polar molecule added to a solution polarises the surrounding medium, and its nuclei experience the reactive field of the medium. Starting from the Onsager model[14], and identifying E_z with the reaction field, Linder[77] obtained the following formula for δ_{pol}:

$$\delta_{pol} = -\text{const} \cdot \left(\frac{\varepsilon - 1}{2\varepsilon + n^2}\right) \frac{\mu \cos\varphi}{2} \qquad (18)$$

where ϕ is the angle between $\vec{\mu}$ and the C–H bond.

According to formula (18), in a binary solution the solute is characterised by the refractive index n, the dipole moment μ, and the polarisability α, and the solvent is characterised only by one macroscopic property: the dielectric constant ε.

Diehl and Freeman[93] made some improvements in Buckingham's theory to allow for the polar contribution, and proposed a slightly different model, which takes account of the shape of the solute molecule. They arrived at a modified formula for the reaction field, which reduces to the formula given by the Onsager model in the case of spherically symmetrical molecules. However, the expression obtained in Ref.93 is not very different from Eqn.(18). Better correlations have been obtained[94] by using formula (18) for the internal (or relative) shift between two non-equivalent protons in a molecule rather than for the chemical shift of any one proton. This should allow all effects to be excluded except the reaction field effects. This assertion was tested[95] with a series of methyl-substituted nitrobenzenes in 13 different solvents. It was found that only by limiting the choice of solvents to those having carefully chosen properties could good correlations be obtained with experimental data on the internal chemical shift, calculated by the reaction field theory based on the Onsager model.

If the polar component is the solvent, the influence of the electrostatic field created by its dipoles on the solute molecule is almost equivalent to the reaction field calculated by Buckingham[68], whose linear effect causes a change in the polarity of the A–H bond. It is clear from formula (18) that solutions of a polar solute in a series of solvents having different ε values should be described by the expression

$$\Delta\delta_H(\text{A}-\text{H}) \sim \frac{\varepsilon - 1}{2\varepsilon + n^2} \cdot \qquad (19)$$

However, expressions for the polar contribution to the chemical shift of protons in a solute molecule in terms of the macroscopic properties of the solution[68,96,97] are not precise enough for use in PMR.

In many polar (and in some non-polar) solvents the chemical shifts are very different from those calculated by formulae such as (19). Thus, according to Buckingham[68] solvents like n-hexane, nitromethane, acetonitrile, and acetaldehyde do not follow the correlation (19); carbon tetrachloride, acetone, acetonitrile, etc.[97], and dimethylsulphoxide, *N*,*N*-dimethylformamide, etc.[98,99] are also found to behave abnormally. On the other hand, as a result of the use of generalised properties of the components in these correlations it is impossible to study directly the dependence of the chemical shift $\Delta\delta_H$(A–H) on the physical properties and on the structure of the solute and solvent molecules and on the different types of intermolecular interaction. This led to various attempts to relate the $\Delta\delta_H$(A–H) values to other properties of the components, such as the polarity constant of the solvents[96], the dipole moment of the solute molecules μ_d,[98–100] the ratio of the dipole moment to the molar volume μ_d/V,[69] etc.

The calculation of the effect of dispersion and polarisation field interactions on the chemical shift of protons in the interacting molecules has also been examined from a different aspect[101]. A physically more justifiable set of equations was obtained[101] by assuming proportionality between the chemical shift due to field interactions and the energy of the pair interactions between the solute and the solvent molecules ($\Delta\delta_{field} \propto |U_{s,d}|_{pair}$). The parameter $|U_{s,d}|$ was calculated in the dipole approximation[8]: $|U_{s,d}|_{pair} = |E_{s,d}|_{disp} + |E_{s,d}|_{pol} + |E_{s,d}|_{el.st.}$, using the London, Debye, and Keesom potentials respectively for the additive contributions to the energy. In the case of dilute solutions, when the solute molecules are surrounded by solvent molecules only and no local interactions take place through the overlap of electron clouds, we can write[8]

$$\Delta(\delta_{disp} + \delta_{pol}) \propto |U_{s,d}|_{pair} = \frac{1}{\bar{R}^6_{s,d}} \left\{ \frac{3}{2} \frac{I_s I_d}{I_s + I_d} \alpha_s \alpha_d + \mu_s^2 \alpha_d + \mu_d^2 \alpha_s + \frac{2}{3} \frac{\mu_s^2 \mu_d^2}{kT} \right\}. \qquad (20)$$

Formula (20) has a number of advantages over those given above. It shows explicitly the relationship between the chemical shift due to field interactions and the microscopic properties of the interacting molecules. The expression contains one of the most important parameters of IMI: the distance between the interacting molecules, which does not appear in formulae based on Onsager concepts. Furthermore formula (20) suggests a suitable methodology for studying the dependence of $\Delta\delta_{H,field}$ on molecular properties: by the strict selection of series of compounds related by particular characteristics. Thus, it follows from Eqn.(20) that the expression

$$\Delta(\delta_{11})_{disp} \sim \alpha_s/\bar{R}^3_{s,d} \qquad (21)$$

can be applied to solutions of a given non-polar substance ($\mu_d = 0$) in a series of non-polar solvents ($\mu_S = 0$) with similar values of I_S (i.e. in the presence of dispersion interaction only between molecules of the components).

Similar relationships apply to the chemical shifts of solutions of a given polar substance in a series of non-polar solvents with similar values of I_S, and also to solutions in a given non-polar solvent of a series of polar substances for which μ_d = const but with widely different values of α_S. For solutions of a given non-polar or polar substance in a series of polar solvents with similar values of I_S, α_S, and $\bar{R}_S$ (a condition easily satisfied by isoperiodic solvents with molecules of similar shape) we find the correlation[101,102]

$$\Delta\delta_{11}(A-H) \sim \mu_1^2/\bar{R}^6_{s,d} \qquad (22)$$

or, for a series of solvents selected more critically in respect of molar volume and molecular shape, we find the expression

$$\Delta\delta_{11}(A-H) \sim \mu_s^2 \ . \qquad (23)$$

These expressions have been tested[102] against a large amount of experimental information from different laboratories. Many data for δ_H(A–H) are quoted[102], but only for A=C (ring protons, protons in CH_3 groups, etc.) does comparison between calculation and result confirm the validity of Eqns.(21)–(23) when applied to different series of binary solutions of aromatic or aliphatic compounds. Calculation of δ_{disp} and δ_{pol} by Eqn.(20) shows that δ_H(C–H) is determined by interactions between solute and solvent molecules which are not local in character but are averaged over all possible orientations of the interacting molecules. Under these conditions the proton can become unscreened either as a result of proton withdrawal effects due to the electric field or as a result of the displacement towards the carbon atom of the electrons in the C–H σ-bond, also due to the electric field[83]. The change in the charge on the carbon atom[104] due to the redistribution of the electron density in the remainder of the molecule (other than the C–H group) under the influence of the field may also have a part to play.

A field interaction (of the volume type) with the surrounding molecules may also explain the change in the spectra of complexes in solution[102]. As Fig.7 (taken from Ref.102) shows, the change in the chemical shift of the bridging proton signal in the spectra of phenol and chloroform complexes with the proton acceptor BR′ caused by interaction with the medium is linearly related to the parameter $\bar{Z}_S\mu_S^2/\bar{R}^6_{S,d}$ (except in the case of very weak proton acceptors). This relationship also accounts for the change in chemical shift caused by varying the ratio of the concentrations of the proton acceptor solvent (BR′) and of the non-polar solvent in ternary systems (Fig.8, from Ref.102).

Thus the London, Debye, and Keesom potentials for pair interactions of the field type between component molecules can be used to calculate the effect of the solvent on the magnitude and direction of the chemical shift of the proton signal in solutions where complex formation cannot take place.

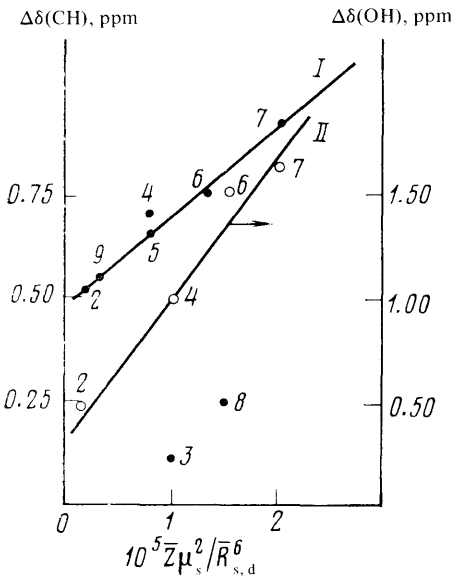


Figure 7. Plots of $\Delta\delta_H = (\delta_H)_{BR'} - (\delta_H)_{CCl_4+BR'}$ against $\bar{Z}\mu_S^2/\bar{R}^6_{S,d}$ for δ(CH) of chloroform (*I*) and δ(OH) of phenol (*II*) and different BR′: *1*) CCl_4, *2*) $(C_2H_5)_2O$, *3*) n-C_4H_9Cl, *4*) $(CD_3)_2CO$, *5*) $CH_3COC_2H_5$, *6*) $HCON(CH_3)_2$, *7*) $(CD_3)_2SO$, *8*) CH_3NO_2, *9*) $CH_3COOC_2H_5$.[102]

IV. EFFECT OF THE SOLVENT ON THE BASIC CHARACTERISTICS OF THE ELECTRONIC SPECTRA OF MOLECULES

1. Comparison of Methods of Calculating the Effect of the Medium on the Electronic Spectra of Molecules

Several studies of the influence of solvents on the basic characteristics (ν_{max} and the oscillator strength *f*) of the electronic spectra of molecules have been reported[105–109]. The parameter ν_{max} is usually obtained from universal expressions in terms of the generalised properties of the solvent *n* and ε.[2,108].

Bayliss[110] proposed the concept of a "general red shift", determined by the interaction with the medium of the dipole moment associated with the transition of the molecule. The shift $\Delta\nu$ is given by the formula

$$\Delta\nu = -cf\frac{n^2-1}{2n^2+1} \ , \qquad (24)$$

where *f* is the oscillator strength of the band, *c* is a constant, and *n* is the refractive index of the solvent.

Bayliss and Rae[111], using the Franck–Condon principle, arrived at a general scheme describing the effect of the solvent on electronic absorption spectra which allows

(qualitatively) for the main types of IMI. According to this treatment the displacement of the absorption band of a compound in solution relative to the spectrum of the same compound in the vapour phase is due to the difference between the energy of the interaction with the surroundings of the molecule in the ground and in the excited electronic state. Under these conditions the stabilisation energy for different electronic levels should be determined in each particular case in terms of the nature of the interaction between the molecule under study and the solvent molecules.

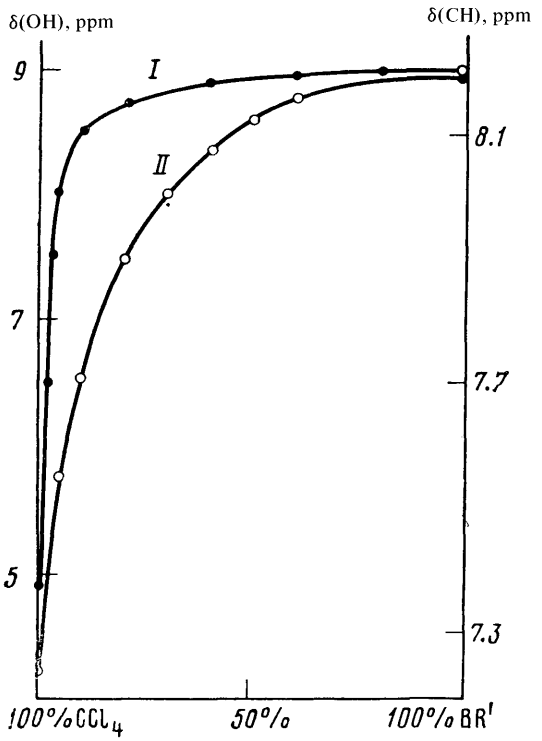


Figure 8. Plots of δ_H for the δ(OH) band of phenol (*I*) and of δ(CH) for chloroform (*II*) against the concentration ratio of CCl_4 and BR' [BR' = $(CD_3)_2CO$ for (*I*) and $HCON(CH_3)_2$ for (*II*)].[102]

An attempt has been made[112] to calculate the stabilisation energy of the electronic levels of molecules in solutions by assuming IMI of the dipolar type only. The stabilisation energies of the various levels were calculated from the basic characteristics of the interacting molecules, allowing for the changes in some of these characteristics caused by the absorption of a light quantum. The shift in the spectrum is treated essentially as due to the statistical averaging of the set of interactions between the solute molecule and the nearest-neighbour solvent molecules, and quantitative expressions are obtained by using the Onsager model.

A theoretical discussion[113] of the effect of the solvent on fluorescence spectra has shown that in general the shifts in the absorption and the emission band of any molecule undergoing a phase transition should be different. Two explanations are suggested: firstly, that the configuration of the solvent molecules around the solute molecule is different for solute molecules in the ground and in the excited state, and secondly that this configuration is not changed by the electronic transition (as required by the Franck–Condon principle).

A theoretical analysis of the effect of dipole–dipole interactions on the frequency of bands in the electronic spectra of solutions is given in Ref. 114. A simple electrostatic model yields expressions relating the frequency shifts in absorption and emission spectra to the parameters n and ε of the solvent. A theory of the effect of van der Waals interactions on the electronic spectra of molecules has been developed[115] from both semi-classical and quantum-mechanical foundations: the two approaches give qualitatively consistent results.

Important advances have been made in the application of computers to the analysis of experimental results[113–119]. The use of Kosower's Z parameter[119], an empirical characteristic of the polarity of the medium or (according to Kosower[119]) a microscopic measure of the type and strength of the interaction between solute and solvent molecules, has given interesting results in the analysis of experimental data on band shifts in electronic spectra. The same author has developed a method of determining the H-bond energy and the dipole moment in the excited state from absorption spectra by using the Z parameters.

The current state of spectroscopic research on intermolecular interactions has been systematically reviewed by Bakhshiev[2], who also showed[120] that intermolecular interactions in condensed media can affect, in general, not only all the physicochemical properties of the molecule of interest but also the field strength associated with a light wave acting on the molecule and inducing transitions between energy levels. He derived a general expression for the change in integral intensity of a band caused by the transfer of the molecule from the gas to the condensed state, which includes the correction factor $\bar{\theta}_\uparrow$ to allow for all the effects of the difference in field strength of the light wave between the condensed medium and a vacuum.

The first attempt to determine the form of the factor $\bar{\theta}_\uparrow$ by using the Lorentz model gave an expression[121] (applicable to dilute solutions) of the form

$$\bar{\theta}_\uparrow = 9n/(n^2+2)^2 \,. \qquad (25)$$

On the other hand, by using the Onsager model the following expression was obtained[131] for $\bar{\theta}_\uparrow$:

$$\bar{\theta}_\uparrow = n\left(\frac{2n^2-1}{3n^2}\right)^2 . \qquad (26)$$

The following formula was also obtained[123]:

$$\bar{\theta}_\uparrow = \frac{(2n^2+1)^2}{9n^3}\left(1-\frac{\bar{\alpha}}{a}\frac{2n^2-2}{2n^2+2}\right)^2 , \qquad (27)$$

where $\bar{\alpha}$ is the mean value of the real part of the complex polarisability of the molecule of interest, and a is the Onsager radius of the molecule.

A quantitative theory of the shift in electronic bands produced by universal intermolecular interactions is developed in Bakhshiev's papers, with full allowance for the different types of IMI. According to Bakhshiev the contribution from universal IMI is given by the formula $\Delta\nu^0 = C_1^a F(\varepsilon,n)$, where C_1^a is a characteristic of the properties of the solute molecule, and the universal interaction function $F(\varepsilon,n)$ characterises mainly the properties of the solvent. The function

$$F(\varepsilon,n) = \left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n_D^2-1}{n_D^2+2}\right)\frac{2n^2+1}{n^2+2} + P\frac{n^2-1}{n^2+2} \equiv A+PB \qquad (28)$$

is determined by the dielectric constant ε and the refractive index of the solvent (n_D for the visible region of the spectrum and n for the spectral region which includes the band of interest). The parameter P depends mainly on the change in polarisability of the solute molecule caused by the electronic excitation.

This method has been used[124,125] to separate the contributions ($\Delta\nu^0$) of the universal IMI from those ($\Delta\nu$) due to the formation of intermolecular hydrogen bonds (the $n \to \pi^*$ absorption bands of some aliphatic ketones). Though the Onsager model yields relatively simple expressions, readily tested experimentally[2,108], in both the quantum-mechanical and the classical approach, its application has been shown[126] to be severely limited. In addition to the well-known approximations implicit in the Onsager model, the Stark effect is ignored in the universal functions, and the parameter which characterises the size of the hole in the liquid structure is not expressed with adequate precision. Therefore the universal functions $f(\varepsilon)$, $f(n)$ and $f(\varepsilon,n)$, which rely on the generalised properties of the solvent, depend also on a number of features of both the solution structure and the various types of IMI.

Because of this, the effect of solvents on the ν_{00} value of absorption bands has been studied[126] by the model of pair interactions between molecules. The resulting expression explicitly includes the role of one of the most important factors in IMI: the distance between solvent and solute molecules. The expression is

$$\Delta\nu = \nu_s - \nu_{vap} = \frac{\bar{Z}\bar{\varphi}}{\bar{R}^6_{s,d}}\left\{\frac{3}{2}\left(\frac{I_d^{FC}\alpha_d^{FC}}{I_s^{gr}+I_d^{FC}} - \frac{\alpha_d^{gr}I_d^{gr}}{I_s^{gr}+I_d^{gr}}\right)I_s^{gr}\alpha_s^{gr} + [(\mu_d^{FC})^2 - \right.$$
$$\left. -(\mu_d^{gr})^2]\alpha_s^{gr} + [\mu_s^2(\alpha_d^{FC}-\alpha_d^{gr})] + \frac{2}{3kT}[\mu_d^{gr}\mu_d^{FC}\cos\beta - (\mu_d^{gr})^2]\mu_s^2\right\}, \quad (29)$$

where $\bar{\varphi}$ is a correction for non-additivity of the pair interactions and for the inaccuracy of the expressions for the various contributions to the potential, the superscripts "gr" and "FC" denote parameters of the ground state and the Franck–Condon state respectively, and β is the angle between the vectors $\vec{\mu}^{gr}$ and $\vec{\mu}^{FC}$.

For a given non-polar or polar solute undergoing a given electronic transition in a series of non-polar solvents the following expression was obtained[126]:

$$\Delta\nu = \bar{Z}\bar{\varphi}\left\{\left[\left(\frac{A}{I_s^{gr}+I_d^{FC}} - \frac{B}{I_s^{gr}+I_d^{gr}}\right)+C\right]\frac{\alpha_s}{\bar{R}^6_{s,d}}\right\}, \quad (30)$$

and for a series of polar solvents

$$\Delta\nu = \bar{Z}\bar{\varphi}\left\{\left[\left(\frac{A}{I_s^{gr}+I_d^{FC}} - \frac{B}{I_s^{gr}+I_d^{gr}}\right)-C\right]\frac{\alpha_s}{\bar{R}^6_{s,d}} + D\frac{\mu_s^2}{\bar{R}^6_{s,d}}\right\}, \quad (31)$$

where A, B, C, and D are constants. If the I_s^{gr} values are similar, if the product $\bar{Z}\bar{\varphi}$ is constant, and if no complexes are formed between molecules of the components, we find $\Delta\nu \propto \alpha_s/\bar{R}^6_{s,d}$ in the case of non-polar solvents, whereas in polar solvents with similar values of $\bar{R}_{s,d}$ and α_s but relatively large differences in μ_s we find $\Delta\nu \propto \mu_s^2/\bar{R}^6_{s,d}$ (or even $\Delta\nu \propto \mu_s^2$).

Many workers have tried to establish a relationship between the intensity of the absorption band and the solvent effect[126–130]. Thus, Chako proposed a formula[127] based on the classical theory of dispersion interaction which sets out the relation between f_s and f_{vap} but does not take account of the properties of the solute molecule:

$$\frac{f_s}{f_{vap}} = \frac{(n^2+2)^2}{9n^2}. \quad (32)$$

The changes in the field of the light wave in the dielectric have also been studied in detail by the Onsager model by Schleyer[128], who proposed a method of calculating the ratio of the molar extinction coefficients for the solution and the gaseous state. Abe[130] obtained the following expression:

$$\frac{f_s}{f_{vap}} = \frac{(n^2+2)^2}{9n^2}\frac{E_s}{E_{vap}}, \quad (33)$$

(where E is the energy of the transition), based on the Onsager model, which takes account of not only the effect of the solvent but also the properties of the solute molecule.

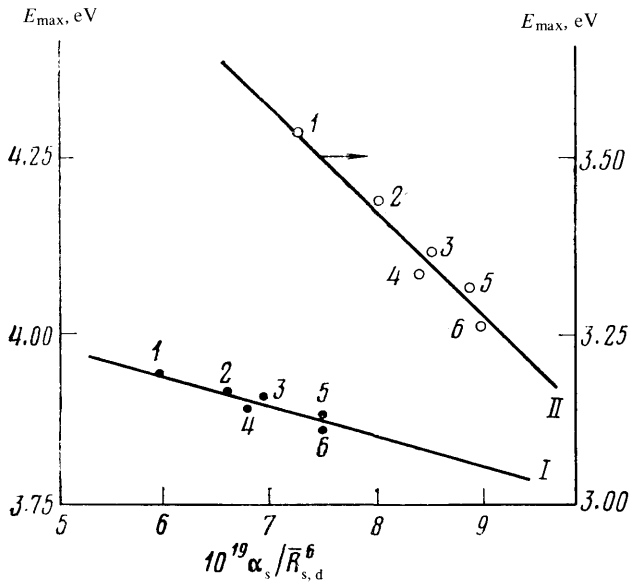


Figure 9. Plots against $\alpha_S/\bar{R}^6_{S,d}$ of the E_{max} values of the bands for the $\pi^* \leftarrow \pi$ transition in azobenzene (*I*) and the $\pi^*_{NO_2} \leftarrow n_{N(CH_3)_2}$ transition in *p*-nitrodimethylaniline (*II*). Solvents: *1*) hexane, *2*) cyclohexane, *3*) CCl_4, *4*) *p*-xylene, *5*) mesitylene, *6*) benzene[132].

2. Effect of Field Interactions on the Characteristic Absorption Bands of Substituted Benzenes

The effect of field interactions between solvent and solute molecules has been studied[131,132] in order to test the expressions (28)–(31). Fig.9 (from Ref.132) shows the dependence of E_{max} on $\alpha_S/\bar{R}^6_{S,d}$ for a number of substances. In the series of non-polar solvents the variation (increase) of E_{max} with $\alpha_S/\bar{R}^6_{S,d}$ is almost linear, both for the $\pi^* \leftarrow \pi$ band of the transition in azobenzene and for the $\pi^* \leftarrow n$ charge transfer bands of the other aromatic compounds. Fig.10 (from Ref.133) shows plots of E_{max} against $\mu_S^2/\bar{R}^6_{S,d}$ for two solutes in a series of polar solvents having the same (or similar) numbers of atoms of elements from the same period. In this case E_{max} decreases linearly with $\mu_S^2/\bar{R}^6_{S,d}$.

Thus we may conclude that the interaction between solute and solvent molecules is of the field type, i.e. that dispersion, dipole–dipole, and inductive interactions take place between the molecules. The contribution from inductive interaction in non-polar solvents depends on the difference in dipole moments, and in the case of polar solvents it depends also on the difference in polarisability of the solute molecules in the Franck–Condon and in the ground state.

Some special features of the effect of solvents on the oscillator strength f of the absorption bands of a range of compounds have been pointed out[132]. Starting from the formula (given in Ref.130) $f_S/f_{vap} = \frac{(n^2+2)^2}{9n^2}\frac{E_S}{E_{vap}}$ we find that for a given electronic transition in a solute molecule in a non-polar solvent $f = \text{const}\,\frac{(n^2+2)^2}{9n^2}E_{S,max}$. Fig.11 shows that this expression is reasonably well-obeyed. In Fig.12 (from Ref.132) we note that the parameter f decreases almost linearly with increase in $\alpha_S/\bar{R}^6_{S,d}$ in non-polar solvents.

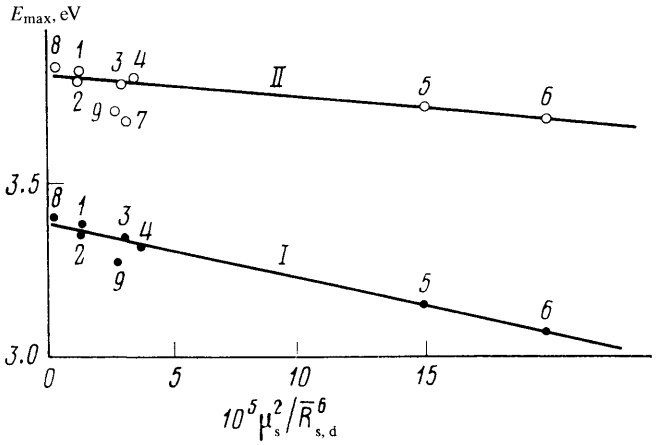


Figure 10. Plots against $\mu_S^2/\bar{R}^6_{S,d}$ of the E_{max} values of the bands for the $\pi^*_{NO_2} \leftarrow n_{N(CH_3)_2}$ transition in *p*-nitrodimethylaniline (*I*) and the $\pi^*_{CHO} \leftarrow n_{N(CH_3)_2}$ transition in *p*-dimethylaminobenzaldehyde (*II*). Solvents: *1*) $(C_2H_5)_2O$, *2*) $(C_2H_5)_2NH$, *3*) $n\text{-}C_4H_9Cl$, *4*) CH_3COOCH_3, *5*) $HCON(CH_3)_2$, *6*) $(CH_3)_2SO$, *7*) $iso\text{-}C_3H_7OH$, *8*) $N(C_2H_5)_3$, *9*) $n\text{-}C_3H_7OH$.[132]

3. Intermolecular Interaction with Hydrogen Bond Formation

The electronic spectra of H-bonded complexes are discussed in several papers, but the type and extent of the influence of complex formation on the electronic spectra (or, more exactly, on the E_{max} and f values) are not yet fully understood. From the fact that ΔE_{max} (and $\Delta\nu_{max}$) are described by the universal functions $f(\varepsilon)$ and $f(\varepsilon,n)$ [134,135] some workers conclude that specific interactions are weak, or absent, in the electronic spectra of compounds forming complexes with a solvent[2]. The main contribution to ΔE_{max} during complex formation has been ascribed[136–139] to the difference in energy of the hydrogen bond in the ground and the excited state. However, a more widely held view[140,141] is that E_{max} under these conditions is equal to the sum of two contributions: the van der Waals interaction and the ΔE_2 value for the formation of the hydrogen bond, and either of these contributions can be predominant under suitable conditions. Attempted calculations of these contributions in terms of universal functions[124,125] yielded functions which proved both cumbersome and inaccurate. Because of the approximations implicit in the derivation of universal functions based on the Onsager model, and because the interaction with solvent molecules affects the complex as a whole (and not the separate molecule of solute[64]), the influence of the solvent on hydrogen-bonded complexes has been studied[133] in terms of the potentials of pair interactions between the molecules[126].

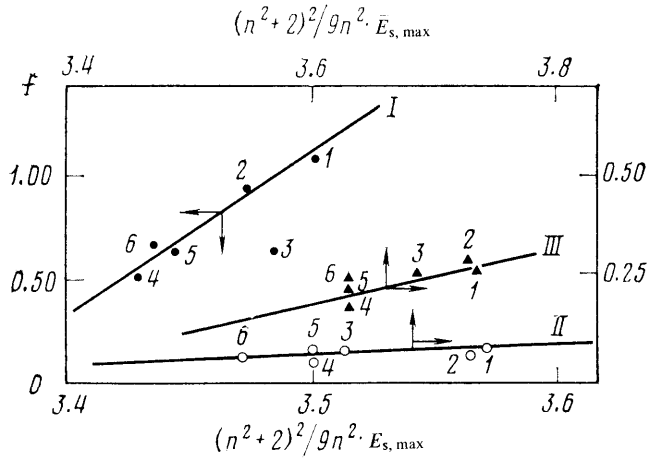


Figure 11. Plots of f against $(n^2+2)^2/9n^2\cdot E_{max}$ for the absorption bands of azobenzene (*I*), *o*-nitroanisole (*II*), and *p*-nitroanisole (*III*). Solvents: *1*) n-hexane, *2*) cyclohexane, *3*) CCl_4, *4*) *p*-xylene, *5*) mesitylene, *6*) benzene[132].

Both in compounds which contain no proton-donor groups and in compounds able to form hydrogen-bonded complexes the E_{max} value decreases linearly with $\alpha_S/\bar{R}^6_{S,d}$ in non-polar solvents, and with $\mu_S^2/\bar{R}^6_{S,d}$ in polar solvents. This suggests that the predominant contribution to the solvent effect in the formation of the intermolecular hydrogen bond comes from ΔE_1 rather than from ΔE_2. Methods of calculating the separate contributions to ΔE_{max} from ΔE_1 and ΔE_2 have been suggested[132].

4. Effect of Solvents on the Electronic Spectra of Molecules with Conjugated Chains of Different Length

The optical absorption of these compounds has been studied in a large number of solvents[142,143]. Kuhn and Schweig[144] have calculated the shifts in the absorption and fluorescence bands of polar molecules of organic dyes under the influence of solvents. We have examined[145] the dependence of E_{max} (for the absorption bands) on $\alpha_S/\bar{R}^6_{S,d}$ and $\mu_S^2/\bar{R}^6_{S,d}$ in a series of compounds with conjugated chains of different length of the NO_2ZNR_2 type (where Z is an aryl group containing different numbers of π bonds).

The E_{max} value of the long-wave band with appreciable charge transfer, of the $\pi^*_{NO_2} \leftarrow n_{NR_2}$ type, was exactly described by the proposed expression[145] in every case, whatever the size of the solute molecule: it decreases linearly as the parameter $\alpha_S/\bar{R}^6_{S,d}$ increased. In polar

solvents also the E_{max} value of both absorption bands decreases as $\mu_S^2/\bar{R}_{S,d}^6$ increases. As the number of π bonds in the aromatic ring increases, the E_{max} value decreases almost linearly, and the slope of the linear plots increases slightly. For all the NO_2ZNR_2 compounds examined in polar solvents the dependence of f on $\mu_S^2/\bar{R}_{S,d}^6$ (produced by varying the size of the group Z) was accurately linear.

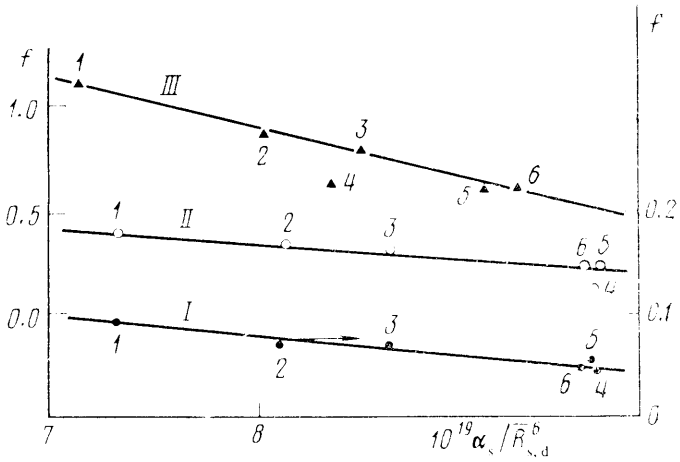


Figure 12. Plots against $\alpha_S/\bar{R}_{S,d}^6$ of the parameter f for the absorption bands of *o*-nitroanisole (*I*), *p*-nitroanisole (*II*), and *p*-dimethylaminobenzaldehyde (*III*). Solvents: *1*) n-hexane, *2*) cyclohexane, *3*) CCl_4, *4*) *p*-xylene, *5*) mesitylene, *6*) benzene[132].

Thus in a series of non-polar solvents with similar values of the ionisation potential the difference in the effect of the solvent on ν_{max} is due to $\alpha_S/\bar{R}_{S,d}^6$, whereas in polar solvents with similar values of $\bar{R}_{S,d}$ and α_S it is due to the parameter $\mu_S^2/\bar{R}_{S,d}^6$.

We have shown that the effect of intermolecular interactions in solutions on the spectral characteristics of molecules can be calculated by using the London–Debye–Keesom pair interaction potential for condensed media. The main advantage of this method is that it leads to expressions for the interaction energy containing in an explicit form the molecular properties of both the solute and the solvent (dipole moment, ionisation potential, polarisability) as well as parameters which characterise the molecular structure of the solution (Z and $\bar{R}_{S,d}$).

The expressions apply both to compounds which do not form hydrogen bonds and experience only intermolecular interactions of the field type and to compounds able to form hydrogen bonds with the solvent.

We have also shown that the relative contributions to the intermolecular interaction energy from field interaction effects and from complex formation by hydrogen bonds can be calculated approximately.

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