

*THE EFFECT OF THE SOLVENT ON THE POSITIONS AND INTENSITIES
OF BANDS IN INFRARED MOLECULAR SPECTRA*

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INTRODUCTION

THE effect of the solvent on the spectral characteristics of solute molecules is of primary significance in molecular physics, since in most cases we have to investigate the optical and other physical properties of the molecules in solution. The investigated molecule is then influenced by the surrounding molecules of the medium, an influence which can change its properties appreciably. The experimentally observed spectra characterize then not the molecule itself, but a system comprising "the investigated molecule plus the medium." It is quite obvious that a study of this problem is quite vital from both the theoretical and practical points of view.

Two aspects of this question can be distinguished. The first is to explain the nature of the effect of the solvent on the spectra, and establish the main laws governing it, and the second is to use these laws to determine various physical parameters of the isolated molecule whenever this determination cannot be effected by direct means.

In spite of the importance of the problem and the exceptionally large amount of literature devoted to it, the problem is far from completely solved^[1-5]. Moreover, great differences exist even in the approach used by various authors to investigate the solvent effect.

The present paper, without claiming complete coverage of the material, will try to review critically a number of basic papers pertaining to several recently developing trends. Principal attention will be paid here to papers whose authors have attempted to unify the aggregate of experimental facts from some definite point of view.

We note also that we do not concern ourselves here with the large group of investigations of the solvent effect on the electronic spectra of molecules, since these investigations have their own specific nature^[7-12].

We must emphasize from the very outset that the problem of the solvent effect is essentially a problem of intermolecular interactions. Even a cursory examination of the material accumulated to date shows that the uncertainty in the conclusions pertaining to the solvent effect in spectra is due to the variety of types of interactions between solute and solvent molecules. These may include various types of classical van der Waals interactions (orientational,

induction, or dispersion interactions), and physical-chemical interactions of various types (complex formation, hydrogen bond, etc.). An investigation of the spectra of the interacting molecules is in principle a powerful means for studying the nature of these interactions. However, the information gained from the spectra is in code and must be decoded. Here the main problem is distinguishing the various types of effects and the establishment, in the final analysis, of quantitative relations between these effects.

Intermolecular interactions manifest themselves in the spectra of solutions in various manners, leading, as is well known, to the following most characteristic phenomena: a) band shifts; b) changes in the absorption intensity; c) changes in shape (half-width, asymmetry) of the bands.

The band shift on going from vapors to solutions or from one solvent to another is generally a first-order effect, since it results principally from a change in the relative position of the molecular energy levels between which the quantum transition takes place. The other phenomena, determined to a considerable degree by the influence of the medium on the transition probabilities and by the properties of the corresponding excited states, are more subtle effects which are very difficult to describe. Nonetheless, as will be shown below, the authors of most papers trying to encompass all the fundamental aspects of the phenomenon, consider this phenomenon as a rule from a single point of view, which predetermines the course of the arguments advanced in all cases. In the present paper, owing to lack of space, we shall touch upon only two of the questions indicated above, those of greatest interest, namely the effect of the solvent on the positions and the intensities of the absorption bands.

It is impossible to speak at present of any clear-cut development of a theory explaining the effect of the solvent on infrared spectra. Several schools exist, headed by outstanding scientists and adhering each to their own opinion on this question. Nevertheless, with some simplification, one can classify the existing papers on the subject as belonging to two trends. The first involves the examination of the collective effect of the particles of the medium on the spectra of the solute molecule and the description of this effect by introduction of macroscopic characteristics of the solvent (the dielectric constant, the refractive index, etc.). The papers belonging to the second trend aim

to establish a connection between the effect of the solvent on the spectra of the dissolved substance and the microscopic characteristics (physical, physico-chemical, and chemical) of the solvent and solute molecules. The effect of the medium is considered here to result from the interaction between the dissolved molecule and one or several of the particles surrounding it. Each of these points of view has its advantages and shortcomings, and the possibilities latent in both approaches have in our opinion not yet been fully exhausted by far. Moreover, we propose that a sufficiently complete description of real systems can be obtained only by taking into account both the collective and the individual actions.

1. EFFECT OF THE SOLVENT ON THE BAND POSITIONS

It is clear even from general considerations that the conditions under which the investigated molecule in solution interacts with a light wave differ from the conditions for an isolated molecule. In particular, this conclusion follows directly from the general premises of classical electrodynamics and involves the need for introducing generalized parameters (dielectric constant, refractive index) to account for the effect of the aggregate of surrounding particles as a physical medium on the given molecule. It is therefore natural that the first papers on the effect of the solvent on the spectra of a solute tried to relate the changes in frequency with the macroscopic physical characteristics of the solvent.

A very fruitful concept was introduced in this connection by Onsager^[13] in 1936, that of the reactive field exerted on a given molecule by its surrounding neighbors, which are polarized by this molecule. In 1937, Kirkwood^[14,15] used the Onsager model to develop a simple theory relating the relative band shift $\Delta\nu/\nu$ in the spectrum of the solute molecule with the dielectric constant of the medium; here the solute molecule was approximated by a point dipole at the center of a spherical cavity. This problem was considered later also by Bauer and Magat^[16], who took into account the anharmonicity of the oscillation. The final expression obtained in^[14-16] is

$$\frac{\Delta\nu}{\nu} = \frac{\nu - \nu_0}{\nu_0} = -C \frac{\epsilon - 1}{2\epsilon + 1}, \quad (1.1)$$

where C is a constant that depends only on the properties of the investigated molecule and ν_0 is the oscillation frequency of the isolated molecule. The simplicity of this relation and the ease with which it can be tested experimentally has attracted the attention of experimenters to this very day. It is sufficient to state that in almost every study, the authors have considered somehow the question of whether relation (1.1), which has been named the Kirkwood-Bauer-Magat (KBM) formula, is obeyed. We note that in formula (1.1) the constant C is in principle a positive

quantity, that is, the band shift on going from the gas to the solution should always be to longer wavelengths.

An extensive testing of formula (1.1) (see, for example, ^[5,17-28]) shows that in most cases it does not agree with the experimental data. This manifests itself above all in the fact that besides the frequently-observed long-wave shifts (the red shifts), there are also short-wave band shifts (blue shifts). Thus, for example, whereas the 3282 cm^{-1} frequency of the antisymmetric stretching vibration of acetylene undergoes a red shift upon solution, the 729 cm^{-1} frequency of the deformation vibration of the same molecule shifts toward the blue^[27]. A blue shift is observed also for the 671 cm^{-1} band of benzene, the 829 cm^{-1} band of furfural^[29], and in many other cases.

Along with the foregoing examples wherein formula (1.1) is not qualitatively fulfilled, it is likewise not confirmed, as a rule, by the quantitative data. Thus, de Maine and his co-workers^[5] who investigated the infrared spectra of five alcohols, four ethers, acetone, benzene, nitromethane, p-xylene, and hexane, both in pure form and dissolved in CCl_4 , observed no frequency shifts, in spite of the fact that the concentrations of the solutions varied over a very wide range: from 0.19 to 24.75 mole/liter, while the dielectric constant ranged from 2 to 34.1.

An approximate linear relation between the value of the relative shift and a function of ϵ is sometimes observed in nonpolar solvents (for example CS_2 , CCl_4 , etc.)^[30-33]. By way of illustration Fig. 1 shows the results of a test of formula (1.1), taken from^[26]. Yet in individual cases formula (1.1) describes the experimental results^[21] fairly well (Fig. 2). We point out in this connection that debates are continuing to this very date in the literature concerning the need or advisability of replacing ϵ in formula (1.1) by n_0^2 , where n_0 is the refractive index of the solvent (see, for example, ^[25,29,30]).

The poor agreement between the KBM relation and experiment is not unexpected, generally speaking, since the initial physical premises used in its derivation are quite crude. Indeed, they do not take any account whatever, in particular, of the individual prop-

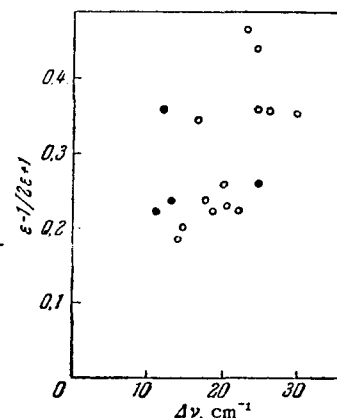


FIG. 1. A plot of the shift of the fundamental frequencies of C=O in acetone (○) and C-H in chloroform (●) against the function $(\epsilon - 1)/(2\epsilon + 1)$ (from ^[26]).

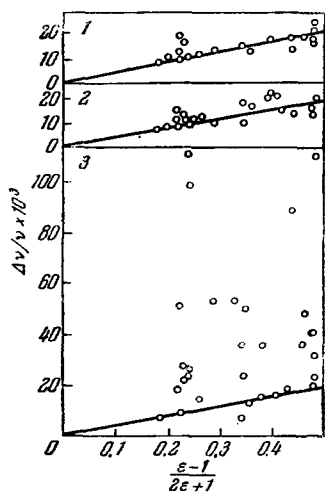


FIG. 2. A plot of the relative shift of the C-Cl frequencies in (asymmetric) cis-dichloroethylene (1), C=O in acetophenone (2), and pyrrole (3) against $(\epsilon - 1)/(2\epsilon + 1)$ (from [21]).

erties of the molecules of the solvent and solute, nor many other factors, which experiment shows to play an appreciable role in this phenomenon. It would therefore be natural to attempt to improve the theory of the dielectric influence of the medium, as has been done many times. Thus, in a series of papers by Galatry and co-workers [34-36] more precise expressions were derived for the reactive field of the dissolved molecule, taking into account the changes in the positions of the solvent particles, due to the additional interaction between the constant and induced moments of the molecules, and also the temperature.

The final expression for the relative frequency shift of a polar molecule in a polar solvent derived by Galatry [36] has the form

$$\frac{\Delta\nu}{\nu} = -\frac{e'}{2q'} \left\{ (e' + \gamma p) \left[\frac{2}{a^3} \frac{n_0^2 - 1}{2n_0^2 + 1} + \frac{3}{5\pi} \frac{1}{a^3} \frac{p^2}{kT} \left(\frac{n_0^2 - 1}{2n_0^2 + 1} \right)^2 \frac{1}{d} \right] + \frac{4\pi}{3} \gamma d \frac{n_0^2 + 1}{2n_0^2 + 1} \frac{f p q^2}{kT} \right\} \quad (1.2)$$

where e' , q' , p , and γ are respectively the charge, force constant, constant dipole moment, and anharmonicity constant of the oscillator used to approximate the investigated molecules; a is the Onsager radius of this molecule, q the constant dipole moment of the solvent molecules, and d the number of molecules of the solvent per unit volume of the solution. Relation (1.2) was used by these authors to calculate the value of a of the HCl molecule from measured values of $\Delta\nu/\nu$ in different solvents. It was found that the solvents used can be subdivided into two groups: in some (CCl_4 , CHCl_3 , $\text{C}_6\text{H}_5\text{Cl}$ etc.) the values of a are close to the Lennard-Jones radius of HCl (1.65 Å), while in others (aromatic hydrocarbons capable of associating with HCl) the molecular radius turns out to be smaller ($a \approx 1.54$ Å).

Expression (1.2) has not been subjected to an extensive experimental check, which, generally speaking, is too complicated to be readily performed. However, even a preliminary analysis shows that formula (1.2)

can likewise not explain the blue shifts of the absorption bands observed in many cases.

From among the latest papers whose authors have developed a dielectric theory of the effect of the solvent on infrared spectra, we should take up the investigations of Pullin [37-40], who attempted to examine the problem from a general phenomenological point of view.

Starting from the expression for the reactive field derived by Kirkwood, Pullin proposed that the frequency shift depends in general on the dielectric constant ϵ and the refractive index n_0 of the solvent, and also on the molar volumes V of the solvent and solute, which are implicitly contained into the Onsager expression for the radius of the cavity [13, 41]. Pullin subdivided the solvent effect into the following three parts.

1) The "distortion effect" due to the static change in the configuration of the investigated molecule when placed in the dielectric medium, owing to the action of the reactive field on this molecule. This effect, as shown in [7], should depend on ϵ and can in general (depending on the properties of the dissolved molecule) lead to either an increase or a decrease in the frequencies upon dissolution.

2) The "intensity effect," connected with the polarization of the medium by the dipole moment of the transition (that is, manifesting itself only upon application of the light field), and proportional to the intensity of the band. This effect, determined by the square of the refractive index of the medium, always leads to a lowering of the frequency and has been termed the general red shift in the world literature [42].

3) The "overtone effect," due to the need for taking into account the anharmonicity of the oscillation, an effect depending on n_0^2 and capable of leading (like the "distortion effect") either to a decrease or to an increase in the frequency. This effect is as a rule relatively small.

Thus, on the whole the frequency shift on going from vapors to solutions is given by the expression

$$\Delta\nu = Bf(n_0^2, V) + C \{f(\epsilon, V) - f(n_0^2, V)\}, \quad (1.3)$$

where B and C are constants that depend on the properties of the solute molecules, and the form of the universal function $f(x, V)$ is unknown.

On the basis of Onsager's model, Pullin proposes the following form of the function $f(x, V)$:

$$f(x, V) = \left(\frac{x-1}{2x+1} \right) \frac{1}{V}, \quad (1.4)$$

where $x = \epsilon$ or n_0^2 , while V characterizes the dimensions of the Onsager cavity [13, 41, 43].

Pullin [40] compared Eq. (1.3) with the experimental data on the frequency shifts of the stretching vibrations of the carbonyl group and the asymmetric c-c-c vibrations of the acetone molecule in thirty-four dif-

ferent solvents. Here he tried to find the best fit of theory with experiment by ascribing in turn the following values to V : the molar volume of the solvent, the arithmetic mean of the molar volumes of the solvent and solute, their geometric mean, etc. The best agreement between (1.3) and experiment was obtained when $V = R$, where R is numerically equal to the radius of a sphere of volume equal to the molar volume of the solvent.

Further attempts to improve the agreement between theory and experiment have led Pullin to the need for varying also the ratio of the constants B/C over a wide range. The final results of such a comparison for the acetone band indicated above are shown in Fig. 3, which is taken from [40]. We see that the numerous and quite artificial constructions have enabled the author only to describe the phenomenon by means of some monotonic curve. In view of the arbitrary variation of the values of the constants contained in (1.3), this expression is rather lacking in physical meaning.

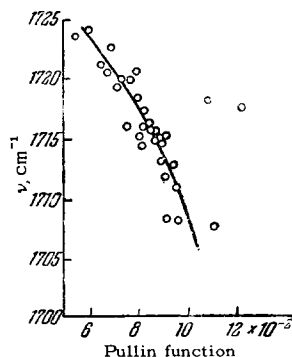


FIG. 3. A plot of the frequency of the C=O stretching vibration of acetone against the Pullin function (from [40]).

Hirota [45] has attempted to apply general quantum-mechanical concepts to study the effect of the solvent on spectra. Using the Onsager model, he obtained expressions for the operator of the energy of interaction between the dissolved molecule and the medium, and found by perturbation theory that the relative decrease in frequency on going from the gas to the solution can be expressed by the formula

$$\frac{\Delta\nu}{\nu} = -\frac{\epsilon-1}{2\epsilon+1} \frac{C}{a^3} \frac{e^2}{4\pi m \nu^2}, \quad (1.5)$$

where

$$C = \frac{(n^2+2)(2\epsilon+1)}{3(2\epsilon+n^2)}, \quad (1.6)$$

and the meaning of the other quantities contained in (1.5) is clear from the foregoing. An analogous expression had been derived by Hirota earlier by the classical method [44]. In the interpretation of the experimental data, the value of a was chosen to improve the agreement between theory and experiment. It was found that the values of a obtained thus are considerably smaller than the radii of the molecules

determined from the liquid density by the formula

$$a_0 = \left(\frac{3M}{4\pi N d} \right)^{1/3}$$

The studies of Buckingham [46-48] have shown a more general and consistent approach to the solvent effect on the infrared spectra of molecules. In our opinion, these provide the connecting link between the two aforementioned approaches, since the results of these investigations, as will become clear later on, can be used to explain the phenomenon from the point of view of both universal and specific interactions.

Buckingham treats the influence of the solvent molecules on the solute molecules by using the most general quantum-mechanical model. The theory was developed for a diatomic molecule (oscillator), but, as shown in [47], can be generalized also to include the case of a polyatomic molecule. Let us dwell briefly on the main physical premises of this theory and on the method of analysis.

The Hamiltonian of a diatomic molecule in the gaseous state can be represented in the form

$$H = H_0 + H_a, \quad (1.7)$$

where H_0 is the operator for a harmonic oscillator, while the operator H_a takes into account the anharmonicity of the oscillations. When the molecule is put in solution, it begins to interact with the surrounding particles, and the interaction energy u depends on the configuration of the surrounding molecules. If we assume that the value of u can be represented by a power series in the displacement of the nuclei of the investigated molecule from their equilibrium positions, then after averaging over all the configurations of the solvent molecules we get

$$u = u(\xi) = u_0 + u'\xi + \frac{1}{2}u''\xi^2 + \dots,$$

where

$$\xi = \frac{r-r_e}{r_e}.$$

Thus, for a solution we have

$$H = H_0 + H_a + u. \quad (1.7a)$$

The last two terms can be regarded as a perturbation, in agreement with the results of most experiments. Using the first- and second-order perturbation theory formulas, it is easy to find the shifts in the energy levels of the dissolving molecule, and consequently also the frequency shift. The corresponding expression derived by Buckingham [46], has the form

$$\frac{\Delta\omega_{m,n}}{\omega_{m,n}} = \frac{B_e}{\hbar c \omega_e^2} \left(\bar{u}'' - 3 \frac{1}{\omega_e} \bar{u}' \right), \quad (1.8)$$

where \bar{u}' and \bar{u}'' are the values of the derivatives of u with respect to ξ , averaged over all the solvent-molecule configurations, A/ω_e is the anharmonicity constant, and B_e is the rotational constant. Even this expression, derived without any special assumptions

concerning the nature of the light-absorbing center and the character of its interaction with the medium, leads to several definite conclusions. In particular, the value of the relative shift should be the same for both the fundamental frequency and the overtones.*

In addition, inasmuch as the values of the parameters B_e/ω_e^2 , \bar{u}'' , \bar{u}' , and A/ω_e do not depend on the masses of the atoms, the quantity $\Delta\omega/\omega$ should remain constant upon isotopic substitution. It should be noted that both foregoing conclusions have been confirmed by experiment (in particular, with the HC and DC bands as examples, and also OH and OD^[46,48,15,51,52]).

To obtain specific expressions relating the relative shift $\Delta\omega/\omega$ with the physical characteristics of the solvent and the solute molecules, we obviously must determine the form of u as a function of the configuration of the surrounding particles and the parameters of the investigated molecule. It is natural here to use various models capable of describing intermolecular interactions of both the universal and specific types.

Let us consider for example the influence exerted on spectra by the universal effects, which manifest themselves in a dependence of the band positions on the bulk physical characteristics of the solvent. In the general case the reactive field R acting on the given molecule in solution and due to the influence of the molecule on itself via the surrounding medium, is proportional to its dipole moment μ , that is,

$$R = g\mu, \quad (1.9)$$

where the proportionality coefficient g , which depends on the properties of the medium and the dissolved particle, is determined by the chosen model. If the energy u is represented as the potential energy of a dipole in the field R , that is, in the field of a set of other dipoles polarized by the given dipole, then the corresponding expression for u' assumes (after averaging over all the configurations) the following form:

$$u' = u'_0 \frac{g}{2(1-g\alpha_e)} \left[2\mu_e \mu' + \frac{g\alpha'}{1-g\alpha_e} \mu_e^2 \right], \quad (1.10)$$

where α is the polarizability, α' its derivative, and μ' the derivative of the dipole moment. We can derive analogously an expression for u'' . It is easy to see that in the general case the magnitude of the relative shift should depend both on the properties of the solvent and on the specific microscopic characteristics of the solute molecules (dipole moment, polarizability, etc.).

Substituting the values of u' and u'' into (1.8) and grouping terms of different powers of g , we obtain

$$\frac{\Delta\omega}{\omega} = C_0 + C_1g + C_2g^2 + \dots \quad (1.11)$$

If we use the Onsager model (see^[43]), according to which

$$g = \frac{2(\epsilon-1)}{a^3(2\epsilon+1)},$$

then

$$\frac{\Delta\omega}{\omega} = B_0 + B_1 \frac{\epsilon-1}{2\epsilon+1} + B_2 \left(\frac{\epsilon-1}{2\epsilon+1} \right)^2 + \dots \quad (1.12)$$

For polar solvents we must introduce two values of g , namely g_e and g_n , corresponding to the constant and oscillating (induced by the light wave) dipole moments of the molecule. Then

$$R = g_e\mu_e + g_n\mu_n, \quad (1.13)$$

where the first and second terms correspond to the static and dynamic effects (n is the refractive index of the solvent)^[8,9,12,42]. In this case expression (1.12) assumes the form

$$\begin{aligned} \frac{\Delta\omega}{\omega} = & B_{00} + B_{10} \left(\frac{\epsilon-1}{2\epsilon+1} \right) + B_{20} \left(\frac{\epsilon-1}{2\epsilon+1} \right)^2 \\ & + B_{01} \left(\frac{n_0^2-1}{2n_0^2+1} \right) + B_{11} \frac{(\epsilon-1)(n_0^2-1)}{(2\epsilon+1)(2n_0^2+1)} + \dots \end{aligned} \quad (1.14)$$

Evidently it is much easier to describe experimental data with formulas (1.12) and (1.14) than with expressions (1.1) and (1.3), if the constants B are arbitrary. However, it is precisely in formulas (1.12) and (1.14) that these constants are related in definite fashion with the specific microscopic characteristics of the dissolved molecule, thus eliminating the arbitrariness in their interpretation and at the same time permitting several important and interesting physically-founded conclusions to be drawn from the analysis of the experimental results.

Quite analogously, we can start from relation (1.8) to investigate the problem of the effect of the specific interactions on the spectra. Thus, in examining the interaction between a diatomic molecule and a solvent molecule via formation of a hydrogen bond, Buckingham has shown that the magnitudes and signs of the parameters u' and u'' change with the conditions, and this can in turn manifest itself either in a red or in a blue band shift. These deductions have been confirmed by the results of^[53,54].

Another very interesting general result was obtained by Buckingham^[47], wherein definite relations between the magnitudes and the directions of the band shifts corresponding to different types of oscillations, should be satisfied in the case of linear symmetric triatomic molecules in any solvent. Thus, for example, in the case of the CO_2 molecule, the bands corresponding to the stretching vibrations should shift to longer wavelengths, whereas the deformation-vibration band should shift to shorter wavelengths.

Thus, a distinguishing feature of the Buckingham method, as compared with the method considered above, is the shift in the emphasis of the problem toward a determination of the form of the potential

*We note that an analogous conclusion was reached earlier by Chulanovskaya^[49], who considered the interaction between two diatomic molecules.

function u , characterizing the interaction between the investigated molecule and its surroundings. Naturally, the more correctly the function u is approximated, that is, the better the chosen physical model reflects the real picture (regardless of the type of interaction, universal or specific, described by it), the more accurately should the obtained theoretical relations satisfy the experimental data. It must be noted that Buckingham's approach is of particular interest precisely for the problem of the specific interactions, which unlike the universal interactions do not lend themselves (at least at the present) to a description in general form, but for which it is easier to construct a concrete model, valid for a given case.

Let us turn now to an examination of the investigations following the other trend. Here, the authors, in studying the effect of intermolecular interactions on the spectra, assume that this problem cannot be solved in principle by merely accounting for the universal effects. In their opinion it is necessary to approach separately each specific case, analyzing the microscopic effects of different types (association, complex formation, hydrogen bonds, etc.) between the given molecule and its nearest neighbors. However, inasmuch as the overall dielectric effect always occurs to some degree or another, the question arises of the need for distinguishing the universal effects from the specific ones.

In this connection, interest is attached to a series of papers by Bellamy and his co-workers [3,55-64], who proposed a method for processing the experimental data in such a way as to solve this problem to a certain degree. The gist of the method is as follows. The values of the relative shifts $\Delta\nu/\nu$ of any vibrational frequency (for example X-H) of the investigated molecule in an extensive set of solvents are represented as functions of the relative frequency shifts of the analogous chromophore (Y-H) of some other molecule, chosen as a standard, in the same series of solvents. The next problem is to analyze the relationships obtained, which permit in principle rather general conclusions concerning the nature of the influence of the solvent on the molecule. In Bellamy's opinion, if the relative shift is determined exclusively by the bulk properties of the solvent (for example, the dielectric constant), then the stated function should be a straight line passing through the origin and making an angle 45° with the axes. If there is a common mechanism whereby the solvent acts on the investigated and standard molecules, but the shift depends on the properties of the solute molecule, the resultant straight lines may have different slopes. Finally, if the dependence is not linear, then the influences of the medium on the properties of the standard and investigated molecules will differ in nature. The dependence of the magnitude of the shift on the properties of the investigated molecule serves, from

Bellamy's point of view, as a symptom of specific interactions.

The method presented above was used by Bellamy to analyze a large quantity of experimental data pertaining to the solvent-dependence of the characteristic frequencies of various molecules. The choice of the characteristic frequencies for the investigation was governed by the aim to obtain as simple a physical description of the phenomenon as possible, for in this case (as for diatomic molecules) the action of the solvent on the chromophore group can be represented quite justly, in particular, as an interaction between dipoles. By way of an example, Figs. 4 and 5 show characteristic plots obtained in [3] by the described method for the X-H and C=O stretching vibrations. It is easy to see, first, that the relations are linear, and second, that they have different slopes. The order of the solvents in increasing strength of their effect on the X-H vibration bands may differ appreciably from the corresponding order for the X=O vibrations. For example, whereas ether exerts a very strong influence on the vibration frequencies of the X-H groups, it affects little the frequencies of the X=O groups. The situation with chloroform is reversed.

It was concluded on the basis of the obtained data that the specific interactions, rather than the dielectric constant, play the predominant role in the influence of the solvent on the infrared frequencies of the dissolved molecules. In Bellamy's opinion, these specific interactions are manifest in various types of association of the solute molecule with the solvent molecules. Thus, in the interaction of the X-H chromophore groups with nonpolar solvent molecules (CS_2 , CCl_4 , etc.), the association results from the

FIG. 4. Results of processing of the experimental data on the relative frequency shift of stretching vibrations of the X-H group in the molecules $\text{B}_{10}\text{H}_{14}$ (1), H_2O (2), and HBr (3) after Bellamy. [3] Standard substance - pyrrole.

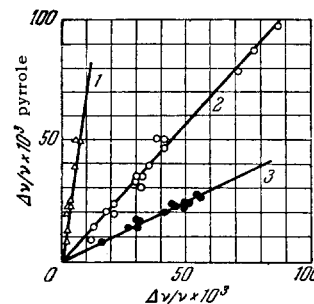
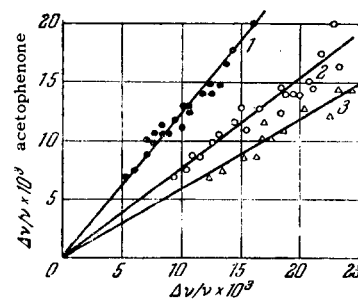


FIG. 5. Results of processing of the experimental data on the relative frequency shift of the C=O stretching vibration in molecules of benzophenone (1), cyclohexanone (2), and dimethylformamide (3) after Bellamy. [3] Standard substance - acetophenone.



action of dipole forces, while if polar media are used (alcohols or water) the association is due to the formation of hydrogen bonds.

Experiment also indicates a pronounced parallelism between the polarity of the bond and the sensitivity of the corresponding bands to the solvent effect. In other words, the higher the polarity of the bond, the greater the relative shift (see Fig. 3).

Bellamy's theories can find many practical applications^[63,65]. They were used, in particular, in^[63] to identify the carbonyl absorption frequencies in pyridones. 4-pyridone exhibits, among others, two frequencies, 1650 and 1590 cm^{-1} , which were previously attributed to C=O and C=C vibrations, respectively. Upon investigating the variation of these frequencies in sixteen different solvents, Bellamy observed that the 1650 cm^{-1} frequency shifts very little, whereas the 1590 cm^{-1} frequency undergoes radical changes. He therefore concluded that the 1590 cm^{-1} frequency belongs to the C=O bond vibrations, since the latter has a greater polarity than the C=C bond.

We must note nevertheless that we find Bellamy's point of view quite biased, so that his conclusions are not sufficiently justified in several cases. Thus, for example, he regards the differing slopes of the lines (see Figs. 3 and 4) as a sign of association. That is, he attributes this fact to the appearance of specific interactions and not to the bulk dielectric effects. At the same time it follows even from the simple KBM formula (1.1) that one should expect lines of differing slopes for different molecules in the general case (when processing the experimental data by the Bellamy method), since the values of the parameter C depend on the properties of the solute molecule. Moreover, it follows from the same formula (1.1) that, when Bellamy's method is used, the plots on Figs. 3 and 4 should be straight lines in any case. That is, the linearity can be due to the pure dielectric effect of the medium.

Let us turn now to examine the work done by Thompson and his co-workers^[1,66,69], whose unique treatment of the interaction between solute molecules and solvent molecules is of appreciable interest. Thompson investigated the solvent effect for pseudo-diatomic molecules having chromophore groups (for example HCN, DCN, etc.). The choice of such molecules as research objects was determined by an interest in discovering the micromechanism of the interaction between the particles in solution, for in this case it is much simpler to obtain a model for the investigated system and to interpret the obtained results. The displacements of the frequencies ν_{HC} and ν_{DC} were investigated in^[69] in a wide range of solvents, greatly differing in their physical and chemical properties. Even a preliminary analysis of the experimental results showed that they cannot be explained from the standpoint of dielectric effects alone,

and that local specific interactions must be taken into consideration.

According to Thompson, in examining the specific interactions between the investigated molecule and the solvent molecule, it is necessary to distinguish the groups of atoms (bonds) in the molecules which exert the most active interaction in the given specific case. Hence, naturally, in interpreting the experimental data from this point of view, it is logical to classify the solvents by grouping them as having in common the stated active centers. As a measure of the magnitude of the directional activity of a center, Thompson proposed to use Taft's concept^[70] of the so-called inductive and resonance factors σ , which characterize for the solvent molecule R-A the degree and sign of the influence of the residue R of the molecule on the electron density in the active center A.

Figures 6–9 show the results of the processing of the experimental data on the shifts of the ν_{HC} and ν_{DC} bands, and also $\nu_{\text{C=O}}$, in accordance with the notions presented above. It follows from Fig. 6 that the plot of $\nu_{\text{HC}} = f(\sigma)$ for unhalogenated aromatic solvents is linear (line 1). It must be noted that this line is obtained under the assumption that the interaction center here is the center of the benzene ring (see Fig. 7a). On going over to halogenated aromatic solvents, the resultant linear dependence has a different slope (see Fig. 6, line 2), and the points of line 2 do not lie on the continuation of line 1. In Thompson's opinion, this may result from the fact that here the dissolved molecules interact also with another active center, namely the halogen atom. To check this assumption, the same substances were investigated in a set of halogenated aliphatic solvents. The results of this investigation are shown in Fig. 8. It is easy to see that here, too, good linear relations are observed. This indicates that in the cases under consideration the active center is the halogen atom, through which the interaction is effected (see Fig. 7b). The relative

FIG. 6. A plot of the H-C vibration frequency of the HCN molecule against σ for aromatic solvents (after^[69]). 1—Hydrocarbons, 2—Chlorinated compounds.

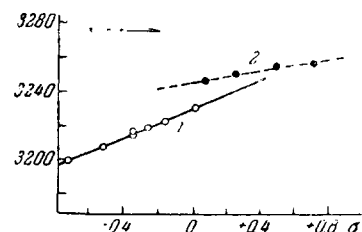
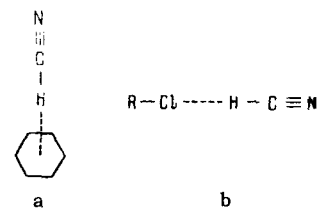


FIG. 7. Diagrams of the interaction between the molecules of the solute and solvent (after^[69]).



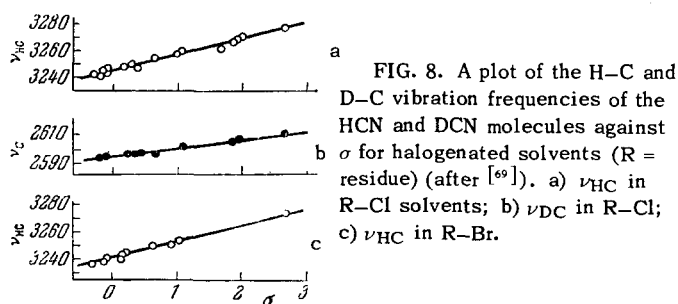


FIG. 8. A plot of the H-C and D-C vibration frequencies of the HCN and DCN molecules against σ for halogenated solvents (R = residue) (after [69]). a) ν_{HC} in R-Cl solvents; b) ν_{DC} in R-Cl; c) ν_{HC} in R-Br.

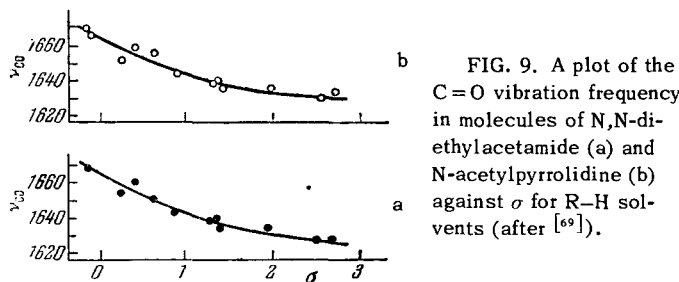


FIG. 9. A plot of the C=O vibration frequency in molecules of N,N-diethylacetamide (a) and N-acetylpyrrolidine (b) against σ for R-H solvents (after [69]).

strength of the effect of the halogen atoms on the spectra decreases in the order I, Br, Cl, F.

On the whole, on the basis of the data obtained, it was concluded that if the solvent molecules contain several active centers, the interaction between these molecules and the dissolved particle can occur in different manners. Thus, for example, for other nitriles ($\text{R}'\text{-CN}$), the interaction with a hydrogen atom of a solvent molecule can involve the nitrogen atom of the dissolved molecule, that is, in accordance with the scheme $\text{R}'\text{-CN} \dots \text{H-R}''$.

Thompson^[62] used the method described above to process the literature data on the solvent-dependence of the frequencies of another chromophore—the C=O group) in the molecules of N,N-diethylacetamide and N-acetylpyrrolidine. The results are shown in Fig. 9 under the assumption that the active center of interaction is the H atom. It is easy to see that the function is represented not by a straight line but by a monotonic curve having maximum curvature in the region containing the points corresponding to the solvents with high dielectric constant. This result offers evidence, in Thompson's opinion, that in this case the frequency shift is determined both by specific interactions and by the bulk dielectric effect. For a quantitative separation of these effects, Thompson used Buckingham's theory, writing the expression for the relative frequency shift in the form

$$\frac{\Delta\nu}{\nu} = C_1 + C_2 \left(\frac{\epsilon - 1}{2\epsilon + 1} \right) + C_3 \left(\frac{n_0^2 - 1}{2n_0^2 + 1} \right), \quad (1.15)$$

Here he assumed that (1.15) does not take any account whatever of specific interactions. Thompson proposed to take account of these interactions by adding to the three-term formula (1.15) a term of the form $C_4\sigma$. It is obvious that then the size of the coefficients C_2

and C_3 compared with C_4 will serve as a measure of the relative role of interactions of different types in the overall experimentally-observed effect. By way of illustration he considered the variations of the frequency $\nu_{\text{C=O}}$ of N-acetylpyrrolidine and acetone, and also of the frequency ν_{HC} of the HCN molecule in different media, and showed that the relative role of the specific interactions and the bulk dielectric effects depends appreciably both on the properties of the solute molecule and on the solvent. In compounds containing the carbonyl group, the second type of interaction is apparently predominant, in contradiction with Bellamy's conclusions. The situation is reversed for the frequency ν_{HC} of the HCN molecule in different halogenated solvents, in which the specific interactions play the principal role.

In connection with the foregoing, it must be noted that the notions developed by Thompson also have certain shortcomings. In particular, it is not clear a priori why the linearity of the functions $\nu = f(\sigma)$ is due to the effect of only the specific interactions, and cannot result from superposition of some other effect. In addition, the description of the experimental data in terms of a polynomial formula with arbitrarily chosen coefficients again does not help to solve the main problem, namely the elucidation of the nature of intermolecular interactions, since such a description is in general equivocal.

On the whole, on the basis of the aggregate of the results obtained, Thompson concludes that the interactions between the solvent and solute molecules depend on the nature of the molecules. One must not forget here that the region of applicability of relations such as Buckingham's equation is limited, for in the general case the objects of study are not diatomic molecules.

In conclusion, mention should be made of the work of Norrish^[50], who attempted to relate the observed frequency shift to the thermodynamically-computed energy E_S of interaction between the solvent and solute molecules. Using as an example the C=O frequency of acetone, he showed that $\Delta\nu/\nu$ depends linearly on E_S .

An analysis of the points of view presented above concerning the effect of the solvent on the position of infrared-spectrum bands indicates that neither the general theory, which attempts to explain the observed facts only on the basis of the dielectric influence of the solvent, nor the theories that take into account only the specific interactions, disclose the physical nature of the intermolecular interactions, and are capable only of describing the phenomenon in some cases. However, independently of the nature of these interactions, a study of the effect of the solvent on the position of the spectra and the establishment of various empirical relations make it possible to solve many practical problems (see, for example, [71-75]).

2. THE EFFECT OF THE SOLVENT ON THE BAND INTENSITIES

While some progress has been made with respect to the effect of the solvent on the position of the bands in infrared spectra, the problem of the effect of the intermolecular forces on the intensity of the spectra has hardly been developed. The reason for it is both the scarcity of the experimental material accumulated thus far, which to a considerable degree involves experimental difficulties, and also the great complexity of the interpretation of the results obtained [1,2,76-82]. It must be noted in this connection that, as has been mentioned above, on the one hand, the intensities of the bands are more subject as a rule to the solvent effect than their positions, and on the other hand, in a theoretical analysis of this problem one has to resort to higher degrees of approximation.

As is known, a measure of the total probability of a transition involving light absorption between energy levels of an isolated quantum system is the integrated absorption [83-87], defined experimentally as the area, expressed in appropriate units, between the spectral absorption curve and the frequency axis*, that is,

$$A_{\text{gas}} = \int \epsilon_{\nu}^{\text{gas}} d\nu = \frac{1}{N_{\text{gas}}} \int K_{\nu}^{\text{gas}} d\nu, \quad (2.1)$$

where K_{ν} is the Bouguer-Lambert law coefficient characterizing the attenuation of the radiation flux as it passes through the absorbing object, while N is the number of absorbing particles per unit volume. The form of the band, that is, its half-width and the peak value of the absorption coefficient, is related to a first approximation to the overall probability, taking into account also the transitions between levels not entailing absorption or emission of light.

Analogously, in the case of solutions, a measure of the intensity of the band is the quantity A_{sol} , defined as

$$A_{\text{sol}} = \int \epsilon_{\nu}^{\text{sol}} d\nu = \frac{1}{N_{\text{sol}}} \int K_{\nu}^{\text{sol}} d\nu. \quad (2.2)$$

We note that the quantity $\epsilon_{\nu}^{\text{sol}}$ is no longer uniquely related to the internal properties of the molecule (the Einstein coefficients), but is an experimental characteristic.

Indeed, the total amount of energy absorbed in a volume $dV = q dx$ of a gas or solution per unit time is determined by the following expressions:

$$dW_{\text{gas}} = E_{\text{gas}} u_{\text{gas}} h \nu_{\text{gas}} N_{\text{gas}} dV, \quad (2.3)$$

$$dW_{\text{sol}} = B_{\text{sol}} u_{\text{sol}} h \nu_{\text{sol}} N_{\text{sol}} dV, \quad (2.4)$$

where $B = (8\pi^3/3h^2) |D|^2$ is the Einstein coefficient for absorption at frequency ν ($|D|$ is the matrix element of the dipole-moment operator), u is the volume energy density at the site of the molecule, and

N is the number of absorbing molecules per unit volume.

On the other hand, the same amount of absorbed energy can be expressed in terms of the experimentally-measured quantities A_{gas} and A_{sol} :

$$dW_{\text{gas}} = -A_{\text{gas}} F dx N_{\text{gas}}, \quad (2.5)$$

$$dW_{\text{sol}} = -A_{\text{sol}} F dx N_{\text{sol}}, \quad (2.6)$$

where $F = Sq$ is the flux incident on the absorbing object and is the same, in accordance with the experimental conditions, for the gas as for the solution* (S is the Poynting vector and q is the cross-section of the beam), while dx is the thickness of the absorbing layer.

From (2.3)–(2.6) it follows that

$$\frac{A_{\text{sol}}}{A_{\text{gas}}} = \frac{(\int \epsilon_{\nu} d\nu)_{\text{sol}}}{(\int \epsilon_{\nu} d\nu)_{\text{gas}}} = \frac{B_{\text{sol}} \nu_{\text{sol}} u_{\text{sol}}}{B_{\text{gas}} \nu_{\text{gas}} u_{\text{gas}}}, \quad (2.7)$$

that is, the ratio of the experimentally-measured intensities of the infrared bands depends not only on the intrinsic properties of the molecule in the gas and in the solution (B_{gas} and B_{sol}), but also on the ratio $u_{\text{sol}}/u_{\text{gas}}$.

It follows from (2.7) that the actions of the solvent on the intensity of infrared bands can be arbitrarily subdivided into two types. The first involves the fact that when the molecule goes over from the gaseous state into solution the value of the light field acting on the molecule changes.

Indeed, assuming that the frequency ν , as has been noted, changes little on going from the gas to the solution, we rewrite (2.7), expressing u_{gas} and u_{sol} in terms of the corresponding field intensities:

$$\frac{A_{\text{sol}}}{A_{\text{gas}}} = \frac{B_{\text{sol}} E_{\text{eff}}^2}{B_{\text{gas}} E_0^2}, \quad (2.8)$$

where E_0 is the intensity of the light field in vacuo and E_{eff} is the effective (internal) microscopic field acting in the medium on the given molecule. E_{eff} consists of the sum of the macroscopic average field E_{av} of the light wave in the dielectric, and the field of the surrounding polarized molecules of the solvent. The field intensity E_{av} is connected with the magnitude of the in-vacuo field E_0 by a general relation that follows from the condition of continuity of the Poynting vector [88]:

$$E_0^2 = n_0 E_{\text{av}}^2, \quad (2.9)$$

where n_0 is the refractive index of the solvent. It follows from (2.8) and (2.9) that the ratio of the integrated intensities of the given band for the solution and gas cases is determined by the expression

$$\frac{A_{\text{sol}}}{A_{\text{gas}}} = \frac{B_{\text{sol}} E_{\text{eff}}^2}{B_{\text{gas}} n_0 E_{\text{av}}^2} = \frac{\gamma B_{\text{sol}}}{n_0 B_{\text{gas}}}, \quad (2.10)$$

*Going over to the solution entails changes in the volume energy density and the effective field acting on the molecule, but these changes are not registered at all by the radiation receiver, which responds only to the magnitude of the flux (compare with [10]).

*Accordingly we shall henceforth take the term "intensity of a band" to mean the value of the integrated absorption.

The second type of action of the solvent on the intensity of the infrared bands can arise from a change in the properties of the molecules themselves, a change due to the intermolecular interactions. This manifests itself in the fact that in general $B_{\text{gas}} \neq B_{\text{sol}}$, that is, perturbation of the molecule by the solvent leads to a change in the matrix element of the transition dipole moment^[89].

It is natural to attribute the effects of the first type to the general dielectric effect (the universal effect) and the second type to both the dielectric effect and to the specific actions of the surrounding molecules, in analogy with the two approaches referred to in the first chapter. It is obvious that interactions of the dielectric type can be more easily described mathematically than the specific actions. Therefore most papers published to date have tried to consider the effect of the solvent on the intensity of the bands precisely from the point of view of taking into account the dielectric effects.

Let us dwell in greater detail on this group of papers. If we take into account the variation of only the field of the light wave in the medium, we obviously presuppose the constancy of the internal characteristics of the investigated molecule on going from the gas to the solution, that is, conformance to the condition $B_{\text{gas}} = B_{\text{sol}}$. In this case

$$\frac{A_{\text{sol}}}{A_{\text{gas}}} = \frac{\gamma}{n_0} \quad (2.11)$$

To determine the value of γ , one must provide a model for the system, drawing for this purpose on the theory of molecular structure of liquids. Thus, taking into account the effect of the solvent on the intensity of the absorption bands reduces in this case to finding the value of γ , that is, in the final analysis, to establishing the correct relationship between the fields E_{av} and E_{eff} .

The first attempt to relate the form of the function γ with the macroscopic characteristics of the solvent on the basis of the Lorentz theory was undertaken by Voigt^[90] in 1901. The expression he obtained has the form

$$\gamma = \frac{(n_0^2 + 2)^2}{9} \quad (2.12)$$

so that in accordance with (2.11)

$$\frac{A_{\text{sol}}}{A_{\text{gas}}} = \frac{(n_0^2 + 2)^2}{9n_0} \quad (2.13)$$

The same relation has been obtained later by many authors: Debye^[91], Chako^[92], Kühn^[93], Kortüm^[94], Ferguson^[95], Polo and Wilson^[96], van Kranendonk^[97], and others. According to (2.13), on going from a gas to a solution the integrated absorption should increase, and the higher the refractive index n_0 of the solvent the greater the increase. We note that qualitatively this deduction agrees with most experimental results. Individual particular cases show a quantitative agreement as well (for example, the band corresponding to

the antisymmetric stretching vibration of the CS_2 molecule^[95]). At the same time, it follows from (2.13) that the relative increase in the integral absorption of any substance dissolved in a given solvent should be the same. This conclusion sharply disagrees with experiment; this may involve the shortcomings of the Lorentz model, which does not take into account the properties of the solute molecule.

A better model, which takes into account not only the properties of the solvent but also certain characteristics of the solute molecules, is the model based on the Onsager-Böttcher theory^[13,14]. According to Onsager, the internal field E_{ff} consists of two parts:

$$E_{\text{eff}} = G + R, \quad (2.14)$$

where G is the so-called cavity field, independent of the properties of the solute molecule, and R is the reactive field, which, as has been noted, is a function of such parameters of the given molecule as the dipole moment, the polarizability, the dimensions, etc.

Recently quite a few papers have appeared, attempting to determine the form of the function γ , starting with the Onsager model. Thus, Mecke^[98] derived an expression for the ratio $A_{\text{sol}}/A_{\text{gas}}$ in the form

$$\frac{A_{\text{sol}}}{A_{\text{gas}}} = \frac{1}{n_0} \left(\frac{3n_0^2}{2n_0^2 + 1} \right)^2 \quad (2.15)$$

He disregarded, however, the reactive field R , so that expression (2.15) still did not reflect the properties of the solute molecule. It follows from (2.15) that for ordinary values of the refractive index n_0 for liquids ($n_0 \approx 1.4-1.5$), the solvent effect should be very small, which, as a rule, contradicts the experimental results. Later on Polo and Wilson^[96], on analyzing the expression for the internal field, reached the conclusion that the theories of Lorentz and Onsager lead to the same form of correction for the solvent effect. They started, however, from an unfounded and essentially incorrect premise that the induced dipole moment of the molecule is determined not by the Onsager internal field but by the Lorentz internal field. Thus, naturally the expression obtained in^[96] for $A_{\text{sol}}/A_{\text{gas}}$ is in the form (2.13).

Later on la Lau^[29], analyzing the expression for the Onsager reactive field R , obtained a more rigorous relation

$$\frac{A_{\text{sol}}}{A_{\text{gas}}} = \frac{n_0^3 [n^4 (1+k^2)^2 + 4n^2 (1-k^2) + 4]^2}{\{n^4 (1+k^2)^2 + 2(n_0^2 + 1)n^2 (1-k^2) + 4n_0^2\}^2 + 16\{(n_0^2 - 1)n^2 k\}^2} \quad (2.16)$$

where n and k are respectively the real and imaginary parts of the complex "internal refractive index" of the investigated molecule^[13,43]. This relation is too cumbersome to be amenable to analysis. For the case of a nonabsorbing pure liquid ($k = 0$, $n = n_0$) expression (2.16) reduces to (2.13). It must be noted that formula (2.16), which la Lau derived only by comparing the fields acting on the molecule in the gaseous phase and in solution, reflects the intrinsic

properties of the investigated molecule, which enter into the formula via the reactive field R .

The first attempt to take into account the effect of the intermolecular interactions on the intensity of the infrared band via their influence on the intrinsic properties of the molecule, that is, on the magnitude of the Einstein coefficients, was made by Hirota in the already mentioned paper [45]. He assumed that the ratio $A_{\text{sol}}/A_{\text{gas}}$ is determined only by the value of $B_{\text{sol}}/B_{\text{gas}}$, without taking account of the variation of the light field acting on the molecule in the gas and in the solution or liquid, that is, actually putting

$$\frac{A_{\text{sol}}}{A_{\text{gas}}} = \frac{B_{\text{sol}}}{B_{\text{gas}}} = \frac{|D_{\text{sol}}|^2}{|D_{\text{gas}}|^2}. \quad (2.17)$$

To take into account the change in D_{sol} with respect to D_{gas} , Hirota used the relation between the constant dipole moments of the molecule in vacuo μ_{GAS} and in the liquid μ_{liq} , which follows from the Onsager theory (the so-called "internal dipole moment", [43])

$$\mu_{\text{liq}} = \left(\frac{2\epsilon + 1}{2\epsilon + n^2} \frac{n^2 + 2}{3} \right) \mu_{\text{gas}}, \quad (2.18)$$

where ϵ and n are the dielectric constant and the refractive index of the liquid. Inasmuch as $|D| \approx \partial\mu/\partial Q$, where Q is the vibrational coordinate [80], it follows from (2.17) and (2.18) that

$$\frac{A_{\text{liq}}}{A_{\text{gas}}} = \left(\frac{2\epsilon + 1}{2\epsilon + n^2} \frac{n^2 + 3}{3} \right)^2 = C^2, \quad (2.19)$$

where C characterizes the effect of the medium simultaneously on the positions and intensities of the bands [see formulas (1.5) and (1.6)]. Without touching at present on the question of experimental verification of (2.19), let us emphasize that it is rigorously applicable only for a pure liquid, that is, a medium consisting of molecules of the same sort.

Later on Mallard and Straley [99], Brown [100], and Person [101] attempted to take into account the variation of $|D|$ of a molecule on changing from a gas to a solution, using the well known Onsager relation [43]

$$\mu'_{\text{liq}} = \frac{\epsilon(n^2 + 2)}{2\epsilon + n^2} \mu_{\text{gas}} \quad (2.20)$$

which connects the dipole moment μ_{gas} with the so-called "external moment" of the molecule μ'_{liq} in the liquid* [43]. Assuming that this formula is valid also for solutions and replacing ϵ in it by n_0^2 (n_0 is the refractive index of the solvent) and taking account of the difference between E_0 and E_{av} [which is equivalent to the condition $\gamma = 1$ in formula (2.10)], the authors of [99-101] arrived at the expression

$$\frac{A_{\text{sol}}}{A_{\text{gas}}} = n_0^3 \left(\frac{n^2 + 2}{2n_0^2 + n^2} \right)^2. \quad (2.21)$$

It is interesting to note that expression (2.21) can

*The external moment μ'_{liq} is the moment of a point dipole μ_{liq} placed in a small sphere having the "internal refractive index" n of the investigated molecule.

be obtained from (2.16) under the condition $k = 0$, $n = n_0$ (nonabsorbing pure liquid).

Brown proposed also to take into account the effect of the solvent on the value of $|D|$ by using the semi-empirical expression relating μ_{sol} with μ_{gas} , as derived in certain papers [102, 103]. Thus, for example, in [102] the following relation is given:

$$\mu_{\text{sol}} = \left(1 + C - \frac{C}{n_0^2} \right) \mu_{\text{gas}},$$

where the sign and magnitude of the constant C are determined by the geometry of the solute molecule.

As was already noted above, no extensive comparison has been made between experiment and expressions (2.13), (2.15), (2.16), (2.19), and (2.21), in view of the patent lack of the appropriate sufficiently reliable experimental data. However, the attempts contained in the literature at comparing theory with experiment enable us to draw certain conclusions concerning the applicability of these expressions. First of all, an examination of the available papers [22, 29, 77-79, 95, 99-101, 106-115] shows that none of the formulas given above is capable of describing a sufficiently broad group of objects, although in individual cases [95, 107] a certain, more frequently qualitative, agreement between theory and experiment is observed. By way of an example, Tables I and II list data taken from [29, 100] and illustrating the non-fulfillment of relations (2.13) and (2.15). On the other hand, from the data of [99], expression (2.21) agrees satisfactorily with experiment for a whole series of bands of the CH_2Cl_2 molecule, while expression (2.15) describes fairly well the experimental data on the intensity of the band of methyl formate near 1200 cm^{-1} [107] (Fig. 10).

We note that the difficulty in estimating how well these formulas describe the experimental data involves also the fact that frequently their use has not been sufficiently well founded. Thus, for example, in [22] formula (2.19) which is applicable, as was noted, only to pure liquids, was used to process the experimental data on spectra of solutions.

The more general approach used by Buckingham in the theoretical investigation of the effect of the solvent on band shifts (see Sec. 1) was also used by him to analyze the dependence of the intensities on the intermolecular interactions [46, 48]. According to [46, 116], the integrated intensity of an infrared absorption band of a gas is

$$(A_{\text{gas}})_{k, n} = \frac{8\pi^3}{3h} (N_k - N_n) \omega_{k, n} (k | \mu' | n)^2, \quad (2.22)$$

where N_k and N_n are the numbers of molecules in these vibrational levels, and $(k | \mu' | n) = \int \psi_k^* \mu \psi_n d\tau$ is the matrix element of the dipole moment of the transition.

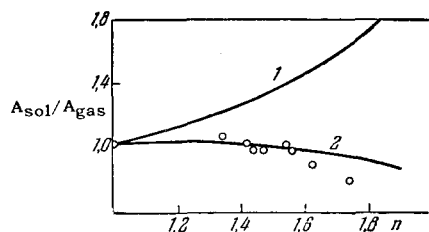
For vibrational bands of diatomic molecules, under assumptions analogous to those used above (see Sec. 1), we obtain from (2.22) for the transitions $n \rightarrow n + 1$ and $n \rightarrow n + 2$

Table I. Integrated intensity of certain infrared bands of propargyl alcohol in nonpolar solvents (from [100]).

	A, mole ⁻¹ liter-cm ²	ν_{\max} , cm ⁻¹	Solvent		A, mole ⁻¹ liter-cm ²	ν_{\max} , cm ⁻¹	Solvent
$\nu_{\text{O-H}}$	3900	3629	C ₆ H ₁₄	$\nu_{\text{C-H}}$	6600	3321	C ₆ H ₁₄
	6000	3619	CCl ₄		6800	3318	CCl ₄
	5900	3617	C ₂ Cl ₄		6600	3316	C ₂ Cl ₄
	6800	3608	CS ₂		6400	3312	CS ₂

Table II. Integrated intensity of the 780 cm⁻¹ band of naphthalene (from [29]).

Solvent	A _{exp} , mole-liter × cm ⁻²	$\frac{1}{n} \left(\frac{n^2+2}{3} \right)^2$	A _{exp}	$\frac{1}{n} \left(\frac{3n^2}{2n^2+1} \right)^2$	A _{exp}
Acetonitrile	6180	1.19	5200	1.03	6000
Nitromethane	6600	1.23	5350	1.02	6500
Cyclopentane	6200	1.25	4950	1.02	6100
Benzene	5880	1.34	4400	1.00	5900
Carbon disulfide	6680	1.47	4550	0.98	6800
Methylene iodide	6650	1.61	4150	0.95	7000

**FIG. 10.** Results of comparison of the experimental values of $A_{\text{sol}}/A_{\text{gas}}$ for the 1200 cm⁻¹ band of the methyl formate molecule (points) with theory (solid lines): 1—formula (2.13), 2—formula (2.15) (after [107]).

$$(A_{\text{gas}})_{n, n+1} = \frac{8\pi^3 N_n}{3h} \left[1 - \exp\left(-\frac{hc\omega_e}{kT}\right) \right] (n+1) B_e (\mu')^2, \quad (2.23)$$

$$(A_{\text{gas}})_{n, n+2} = \frac{4\pi^3 N_n}{3h} \left[1 - \exp\left(-\frac{2hc\omega_e}{kT}\right) \right] \times (n+1)(n+2) \frac{B_e^2}{\omega_e} \left(\mu'' + \frac{A}{\omega_e} \mu' \right)^2. \quad (2.24)$$

Buckingham derived a similar relation also for the transition $n \rightarrow n+3$. To obtain an expression for the intensity of the absorption bands of a molecule in solution, Buckingham used the results of Kirkwood's theory [117-119]. He obtained the expression

$$(A_{\text{sol}})_{k, n} = \frac{8\pi^3}{3h} (N_k - N_n) \omega_{k, n} (k|M|n)^2. \quad (2.25)$$

Here M is the moment of a small macroscopic sphere with radius much smaller than the wavelength of light, but considerably larger than the dimensions of the individual molecule, such that

$$M = Dm = \frac{9n_0^2}{(n_0^2+2)(2n_0^2+1)} m, \quad (2.26)$$

where m is the dipole moment of a microscopic

sphere containing the absorbing molecule and several of the nearest solvent molecules. It must be emphasized that in this case an account of the dielectric influence of the medium is made by considering its effect on the value of the coefficient B [see formula (2.10) above]. Thus, formula (2.25) would be valid if the moment M were the effective moment of the dissolved molecule, reduced to vacuum conditions.

Actually, the macroscopic sphere with moment M is situated in a medium represented as a continuous structureless dielectric, that is, it is subject to the action of the Lorentz field (see above), rather than the field E_0 . This circumstance was taken into account by Buckingham in a later paper [47]. The final expression giving intensity of the absorption band in solution, according to [48], has the form

$$(A_{\text{sol}})_{k, n} = \frac{9n_0^2}{(2n_0^2+1)} \frac{8\pi^3}{3h} (N_k - N_n) \omega_{k, n} (k|m|n)^2. \quad (2.27)$$

We note that an advantage of formula (2.27) is the possibility in principle, as follows from Kirkwood's theory, of taking into account the effect of the specific interactions on the intensity of the bands by constructing a suitable model relating the moments m and μ .

Assuming that the moment m can be represented in the form of a power series in the vibrational coordinate ξ , using the Hamiltonian of (1.7a), and employing first- and second-order perturbation theory, we can obtain from (2.25)–(2.27) expressions for the intensities of different absorption bands of the molecule in solution. In particular, for the transitions $n \rightarrow n+1$ and $n \rightarrow n+2$ the corresponding expressions have the form

$$(A_{\text{sol}})_{n, n+1} = \frac{9n_0^3}{(2n_0^2+1)^2} \frac{8\pi^2 N_n}{3h} \left[1 - \exp\left(-\frac{hc\omega_e}{kT}\right) \right] (n+1) B_e (m')^2, \quad (2.28)$$

$$(A_{\text{sol}})_{n, n+2} = \frac{9n_0^3}{(2n_0^2+1)^2} \frac{4\pi^2 N_n}{3h} \left[1 - \exp\left(-\frac{2hc\omega_e}{kT}\right) \right] \times (n+1)(n+2) \frac{B_e^2}{\omega_e} \left(m'' + \frac{A}{\omega_e} m' \right)^2, \quad (2.29)$$

from which, taking into account formulas (2.23) and (2.24), we obtain for the fundamental band

$$\left(\frac{A_{\text{sol}}}{A_{\text{gas}}} \right)_{0,1} = \frac{9n_0^3}{(2n_0^2+1)^2} \left(\frac{m'}{\mu'} \right)^2, \quad (2.30)$$

and for the overtone band

$$\left(\frac{A_{\text{sol}}}{A_{\text{gas}}} \right)_{0,2} = \frac{9n_0^3}{(2n_0^2+1)^2} \left(\frac{m'' + \frac{A}{\omega_e} m'}{\mu'' + \frac{A}{\omega_e} \mu'} \right)^2. \quad (2.31)$$

As has been noted above, the value of the general expressions (2.28) and (2.29) lies in the possibility of using them within the framework of any model that describes either universal or specific effects of the solvent. We can draw directly some conclusions, amenable to qualitative or even quantitative experimental verification, from an analysis of these expressions. Thus, for example, (2.28) and (2.29) imply that if $\exp(-hc\omega_e/kT) \ll 1$, the ratios $(A_{\text{sol}})_{0,1}/\omega_e^2$ and $(A_{\text{sol}})_{0,2}/\omega_e^3$ for a diatomic molecule do not depend on the masses of the atoms forming the molecule. This result is confirmed by the experimental data for the solutions of CHCl_3 and CDCl_3 in CCl_4 (bands for to the C-H and C-D stretching vibrations) [22,109]. It must be noted, however, that according to [115], the H-C and D-C frequencies of the HCN and DCN molecules do not obey these relations.

To establish a relation between the moments μ and m , Buckingham used the Onsager model, according to which [13,43]

$$m = \mu + aR, \quad (2.32)$$

where the field

$$R = mg_e + \Delta mg_n \quad (2.33)$$

is represented as the sum of two terms, determined by the constant (m) and oscillating (Δm) moments of the molecule; g_e and g_n are the constants of the corresponding reactive fields. In place of (2.30) we have here in a first approximation, keeping only the terms containing the first powers of g_e and g_n ,

$$\frac{2n_0^2+1}{3n_0\sqrt{n_0}} \left(\frac{A_{\text{sol}}}{A_{\text{gas}}} \right)^{1/2} = 1 + 0,6 \left(\frac{n_0^2-1}{2n_0^2+1} \right) + \frac{2\mu_e\alpha'}{\mu'a^3} \frac{e-1}{2e+1}. \quad (2.34)$$

Buckingham's ideas, described above, have been tested experimentally in one of the investigations of Thompson and his coworkers [115]. If we write (2.34) in the form

$$\frac{2\mu_e\alpha'}{\mu'a^3} \frac{e-1}{2e+1} = F, \quad (2.35)$$

where

$$F = \frac{2n_0^2+1}{3n_0\sqrt{n_0}} \left(\frac{A_{\text{sol}}}{A_{\text{gas}}} \right)^{1/2} - 1 - 0,6 \left(\frac{n_0^2-1}{2n_0^2+1} \right) \quad (2.36)$$

depends only on the refractive index n_0 of the solvent and on the experimentally-measured intensity ratio $A_{\text{sol}}/A_{\text{gas}}$, then, upon plotting F as a function of $(e-1)/(2e+1)$, we should expect to obtain a straight line with a slope $2\mu_e\alpha'/\mu'a^3$. However, Fig. 11, taken from [115], which shows data on the ν_{HC} and ν_{CN} frequencies of the HCN molecule in different solvents, indicates that this relation is not obeyed.

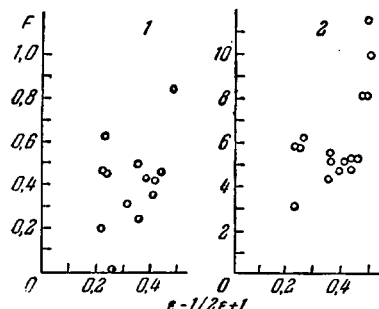


FIG. 11. A plot of Buckingham's function F for the H-C (1) and C \equiv N (2) vibration frequencies of the HCN molecule against the value of $(e-1)/(2e+1)$ (from [115]).

Thompson attributed the observed discrepancy to the presence in this case of strong specific interactions, not accounted for by formula (2.34). This conclusion agrees with the analysis of the band shifts of this molecule presented in Sec. 1.

The authors of [115] have attempted to establish, on the basis of data on the intensities of infrared bands, a correlation between the nature of the chromophores and the properties of the solvent. Thus, they have shown that the relative effect of different solvents on the ratio $A_{\text{sol}}/A_{\text{gas}}$ for bands corresponding to the vibrations of the chromophores HC and HD in the molecules HCN, DCN, and $\text{HC} \equiv \text{C}-\text{CH}_2\text{Cl}$ is the same. Further, a clear-cut parallelism is observed in the effect of solvents on the bands of the C \equiv N and C=O chromophores. This manifests itself not only in identical types of solvent-dependence of the band shift, which was demonstrated earlier [69], but also in the existence of a definite connection between the C=O band shift and the intensities of the C \equiv N oscillation bands (Fig. 12). It was also shown that the intensity of the H-C and C \equiv N bands of HCN molecules in halogenated solvents varies linearly with the Taft inductive factor σ of the residue R (see Sec. 1 and Fig. 13). The last result confirms the conclusions derived earlier from the study of the band shift, concerning the directionality of the interaction of the molecules, which takes place in accordance with the scheme R - Cl . . . HCN.

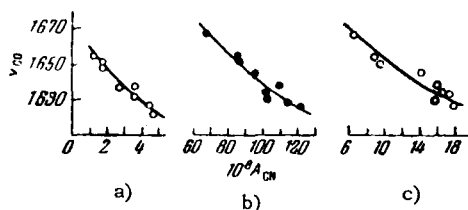


FIG. 12. Correlation between the frequency of the C=O vibration of acetylpyrrolidine and the intensity of the C≡N bands of the molecules ICN (a), $(\text{CH}_3)_2\text{N-CN}$ (b), and $\text{C}_6\text{H}_5\text{CN}$ (c) (from [115]).

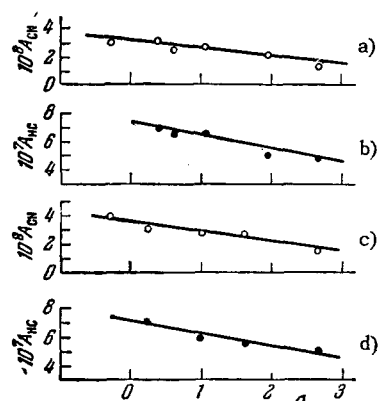


FIG. 13. A plot of the intensity of the H-C and C≡N bands of the HCN molecule against the value of σ for halogenated solvents (R = residue) (from [115]). a) A_{CN} in R-Cl solvents; b) A_{HC} in R-Cl; c) A_{CN} in R-Br; d) A_{HC} in R-Br.

Unlike the HCN and DCN molecules, the general dielectric effect plays a relatively more important role in the solvent effect in the other nitriles (CH_3CN , CCl_3CN , $\text{N}(\text{CH}_3)_2\text{CN}$, and $\text{C}_6\text{H}_5\text{CN}$), and the specific interaction can not only weaken but also change in direction (for example, the interaction goes over to a pattern: $\text{R}'\text{CN}$ -solvent molecule). In this case the plot of the function $F = f(\epsilon - 1/2\epsilon + 1)$ is closer to linear, as illustrated in Fig. 14. The authors of [115] assume that the deviations of the experimental points from the theoretical line can be eliminated by introducing into Buckingham's equation (2.34) an additional

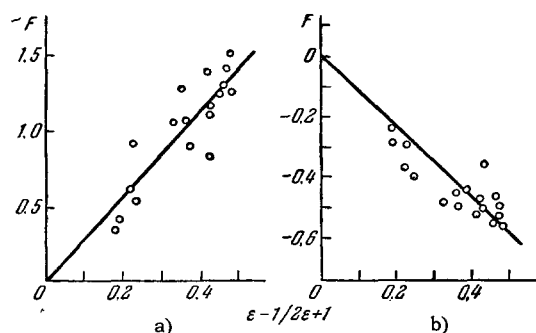


FIG. 14. A plot of the Buckingham function F for the C≡N vibration frequencies of the molecules CH_3CN (a) and CCl_3CN (b) against the value of $(\epsilon - 1)/(2\epsilon + 1)$ (from [115]).

σ -dependent term, but the functional form of this correction remains uncertain.

Thus, in the question of the effect of the solvent on the band intensities, Thompson again adheres to the opinion that the appreciable role that the specific interactions can play in many cases make it hardly possible to establish a general low fitting a large set of media.

In conclusion let us dwell briefly on one interesting consequence that follows from the results of Buckingham's way of processing of the experimental data. As has been indicated, the slope of the lines on Figs. 11 and 14 is determined by the quantity $2\mu_e\alpha'/\mu'a^3$. Figure 14 indicates that the CCl_3CN molecule shows a negative sign of the quantity $2\mu_e\alpha'/\mu'a^3$. This means that in going over from CH_3CN to CCl_3CN the sign of μ_e , or more probably of μ' , of the C≡N bond is reversed. This result confirms the hypothesis previously advanced by Jesson and Thompson in [67].

It follows from the foregoing that in spite of the major and important information which can be gained on the basis of a correct interpretation of the experimental data on the intensities of infrared spectra of solutions, the difficulties encountered in obtaining and analyzing these data are quite large. This has brought about a situation wherein the existing theories have hardly been subjected to an extensive experimental verification.

CONCLUSION

As shown by an examination of the material given above, the possibility of taking into account the effect of the solvent on the positions and intensities of the infrared spectra of molecules is in general quite limited. Essentially, in most works where the authors start from the concept of the influence of the solvent as a dielectric medium, the matter reduces to a tendency to describe the phenomenon by establishing a monotonic connection between the experimentally observed effects and the macroscopic characteristics of the medium. Agreement with experiment is reached here frequently by introducing into the formulas several indeterminate parameters, which naturally, makes it difficult and in some cases simply impossible to explain the nature of the intermolecular interactions.

The impossibility of describing the solvent effect with the aid of theories that consider only effects of the dielectric type is not accidental. First of all, this involves the existence in the solution of specific interactions which these theories do not take into account. In addition, it seems to us that the method of analysis from the standpoint of the general dielectric influence of the medium can be greatly improved. Favoring this assumption is the fact that models of this type are much more widely applicable to real systems that is customarily assumed.

In particular, Dekker^[120] has shown that Onsager's formula for the internal field is valid also for a model of a spherical cavity containing an eccentrically-located mathematical dipole having a radial orientation. Later Frod and Dekker^[121] have shown without any additional assumptions that Onsager's formula for the dielectric constants of liquids, derived under the assumption of a spherical molecule with a mathematical dipole at its center, is perfectly applicable also to the case of a spherical particle with an extended dipole of arbitrary position and direction. Finally, Scholte^[122] has stated that the conclusion of Frod and Dekker is a particular case of the more general problem of the reactive field of a particle containing an arbitrary distribution of electric charges. In addition, we shall point out that recently a number of more refined theories have appeared, in which account is taken of the short-range interaction between molecules in a liquid^[43,123,124].

On the other hand, attempts to solve the problem by reducing the interactions between molecules of the solute and solvent to specific interactions alone (hydrogen bonds, association, etc.) that is, revealing one aspect of the mechanism of the phenomenon, can also hardly prove successful. Investigations belonging to this trend are too one-sided in their approach to the problem; in the final analysis, this leads again to a tendency more to describe the phenomenon rather than to explain it. Obviously, in the general case the specific interactions appear always and unavoidably against a background of the universal effect of the medium, and therefore one of the most urgent problems is that of separating the universal and specific effects and establishing quantitative relations between them. We note that investigations of this kind are already being reported (for example, the series of papers by Thompson and his co-workers). The possibility of such a separation will permit a more justified and deeper quantitative analysis of the specific interactions. Thus, the separation of the general dielectric effect from the overall effect observed in experiment is of particular importance particularly from the standpoint of the problem of specific interactions.

The question of a quantitative analysis of the specific interactions aimed at clarifying their nature is undoubtedly much more complicated and calls for the creation of a specific model for each case, such as to take into account the individual features of the interacting particles. Some successful attempts at such an analysis can already be found in the literature. Thus, LaLau^[29] has constructed a very simple physical model, based on taking into account the localized electrostatic interaction of the atoms belonging to the solute and solvent molecules, and has thus succeeded in giving a semi-quantitative explanation of the blue shifts of the benzene bands belonging to the γ -CH deformation vibration, upon interaction with

polar molecules like acetone and acetonitrile.

Generally speaking, the subdivision of the intermolecular interactions into universal and specific is quite arbitrary. It is natural to take the former to be the classical van der Waals interactions (orientational, induction, dispersion^[6,125]), which after averaging over the configurations and the volume lead to the action of the solvent as a physical dielectric medium (bulk dielectric effect).

Interactions of the second type, which are characterized by their directionality, are now of a physico-chemical character and lead actually to the formation of more or less strong bonds between the molecules, the energies of which are still much smaller than the energies of chemical bonds. Obviously, this type of interaction depends to a greater degree than the first interaction on the individual properties and the nature of the molecules of the solute and solvent. One can conceive of systems in which specific interactions of one type or another do not occur, whereas van der Waal's interactions occur in all cases.

At the present stage, when, as already noted, there is no rigorous and consistent theory of the effect of intermolecular interactions on the infrared spectra of molecules, the subdivision of the interactions into universal and specific is justified. One must bear in mind, however, that there are already sufficient grounds for attempting to create a molecular theory of the phenomenon such as to permit us to regard the interactions from a unified point of view, whether they be universal or specific. The need for developing such a theory, and the need for further extensive experimental research in order to obtain reliable quantitative data, are insistently dictated by the demands of science and practice.

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