

INFLUENCE OF THE INTERMOLECULAR INTERACTIONS ON THE VIBRATIONAL SPECTRA INTENSITIES — II

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The effect of changes in the electronic state of a molecule of the liquid, caused by intermolecular interactions, on the intensities in vibrational spectra is analysed. A model of this phenomenon is devised, and the method of calculation is applied by way of illustration for carbon tetrachloride. The results obtained coincide well with experimental data and they enabled a new interpretation of the temperature dependence of intensities.

1. Introduction

Experiments have shown [1—7] that the integrated intensities of absorption bands in the infrared and of lines of Raman spectrum change jump-wise at the gas-to-liquid phase transition of the examined substance. Moreover, it has been found [2, 3, 5, 8] that for many substances a change in the temperature of the liquid causes a change in intensities, what cannot be explained by the temperature dependence of the population of vibrational energy levels.

It is commonly assumed that intermolecular interactions are responsible for these effects [4, 7, 9]. Two mechanisms of these interactions' effect on vibrational spectra are distinguished. The first, intermediate, consists in a modification of the field of the electromagnetic wave of radiation acting on the molecule due to polarization effects in the condensed medium. The other mechanism, direct, consists in a change of the intrinsic optical properties of the scattering or absorbing molecule due to these interactions.

This paper, like the earlier one of this series [10] (henceforth designated "paper I"), concern the latter mechanism. They contain estimates of the changes in the probabilities of vibrational transitions caused by a deformation of the electron distribution in the molecule of the liquid, under the effect of a perturbing field generated by neighbouring molecules. Considerations are limited to the fundamental infrared and Raman bands of substances in which intermolecular interaction has the character of van der Waals forces. Numerical calculations are made for carbon tetrachloride. Preliminary results of calculations have been presented in paper I. They had been obtained by using a very simple method of

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accounting for the perturbing effect of intermolecular interactions on the electron distribution of a molecule. These results, however, indicated the purposefulness of performing other, more advanced, calculations. This paper contains a fuller description of the physical model of the phenomenon and of the calculation method. The results presented here were obtained with the use of a somewhat improved model of the perturbing field and the perturbation-variational method [17] of accounting for the effect of this field on the electron distribution in a molecule. The improved method and advanced calculations made it possible to arrive at many new conclusions.

2. Model of the phenomenon and calculation method

The following physical model of the phenomenon under consideration is assumed. Molecules of the gas are taken to be isolated. In molecules of the liquid, on the other hand, the electron distribution becomes deformed under the influence of the electric field generated by surrounding molecules. This gives rise to a change in the system of energy levels and optical transition probabilities of the molecules. The emission processes are assumed to be independent in the individual molecules of the liquid, however.

The basic element of the model is the assumption that the process of absorption or scattering of radiation by a molecule of the liquid takes place at a constant perturbing field of the intermolecular forces, associated with the instantaneous configuration of the molecules. This means that the experimentally observed spectral effects of intermolecular interactions are treated as the average of effects caused by instantaneous perturbations, and not as effects of average perturbations. This approach is based on the slowness of the thermal motions of molecules in the liquid, as compared with the vibrational motions of atoms inside molecules.

Within the framework of this model and assuming the vibrations of the molecules to be harmonic [11, 12], the relative differences between the transition probabilities for a molecule perturbed by intermolecular interactions and for a free molecule may be expressed as follows: for absorption bands in the infrared,

$$\begin{aligned} (B_k^L - B_k^G)/B_k^G = & \left\{ \sum_q^d \sum_j \left[\left(\frac{\partial \mu_j}{\partial Q_{kq}} \right)_L \right]^2 - \sum_q^d \sum_j \left[\left(\frac{\partial \mu_j}{\partial Q_{kq}} \right)_G \right]^2 \right\} \times \\ & \times \left\{ \sum_q^d \sum_j \left[\left(\frac{\partial \mu_j}{\partial Q_{kq}} \right)_G \right] \right\}^{-1}; \quad j = x, y, z; \end{aligned} \quad (1)$$

for Raman lines,

$$\begin{aligned} (C_k^L - C_k^G)/C_k^G = & \left\{ \sum_q^d (\alpha'_{kq}{}^2 + 13\gamma'_{kq}{}^2)_L - \sum_q^d (5\alpha'_{kq}{}^2 + 13\gamma'_{kq}{}^2)_G \right\} \times \\ & \times \left\{ \sum_q^d (5\alpha'_{kq}{}^2 + 13\gamma'_{kq}{}^2)_G \right\}^{-1}; \quad j = x, y, z. \end{aligned} \quad (2)$$

Here, B_k denotes the vibrational transition probability associated with absorption of radiation of frequency ν_k , Q_{kq} is the normal coordinate of one of the d -fold degenerate vibrations of the molecule with the frequency ν_k , μ_j are the x , y and z components of the molecule's

dipole moment in the reference frame rigidly connected with the molecule, and C_k is the probability of Raman scattering (calculated per unit radiation density)¹. Moreover, $\alpha'_{k\varrho}$ is the trace, and $\gamma'_{k\varrho}$ the anisotropy of the derivative of the molecule's polarizability tensor with respect to the normal coordinate $Q_{k\varrho}$. The subscript L designates quantities appertaining to the perturbed molecule, G to the free molecule.

The method of calculating the right-hand sides of equations (1) and (2) is based on the fact that if the form of the parametric dependence of the molecule's electronic wave function upon the vibrational coordinates is known, it is possible to find the dependence of the molecule's dipole moment μ and the components α_{ij} of its static polarizability tensor upon these coordinates. Use is made here of well-known formulae [13, 14] according to which, for example, the μ_x component of the dipole moment is expressed as

$$\mu_x(Q_k) = e \left(\sum_{\varrho} Z_{\varrho} X_{\varrho} - \sum_i \bar{x}_i \right) \quad (3)$$

and the α_{xx} element of the polarizability tensor as

$$\alpha_{xx} = \frac{4}{a_0} \left[\sum_{ij} \overline{(x_i - \bar{x}_i)(x_j - \bar{x}_j)} \right]^2 \quad (4)$$

Here, eZ_{ϱ} denotes the charge of the ϱ -th nucleus of the molecule (e being the elementary charge), X_{ϱ} are the coordinates of this nucleus, x_i and x_j the coordinates of the respective i -th and j -th electron, and a_0 is the radius of the Bohr orbit. The bars denote averaging over the electronic wave function Ψ of the molecule, *e. g.*, $\bar{x}_j = \langle \Psi | x_j | \Psi \rangle$.

It is seen from Eqs (1) and (2) that the intensities in the vibrational spectra are expressed through the derivatives of the dipole moment and polarizability of the molecule with respect to the normal coordinates. Hence, thanks to the relations (3) and (4), the problem of the influence of intermolecular interactions on intensities is brought down to an analysis of the effect of these interactions on the electronic wave function. In practice it was found that instead of the normal vibrational coordinates it is more convenient to use the natural vibrational coordinates, *i. e.* changes of bond lengths and valence angles. Then, by applying the valence-optical theory of intensities [11, 15, 16], it is possible to express the transition probabilities by the so-called electro-optical parameters, *i. e.* the dipole moments and polarizabilities of the individual bonds and their derivatives with respect to the natural coordinates.

Therefore, the sequence of calculations is the following:

1. The derivatives of the dipole moment μ and polarizability α_{ij} of the molecule with respect to the normal coordinates Q_k are expressed in terms of electro-optical parameters, *i. e.* in symbolic fashion,

$$\left(\frac{\partial \mu}{\partial Q_k} \right) = \left(\mu_i, \frac{\partial \mu_i}{\partial q_l} \right); \quad (5)$$

$$(5\alpha_k'^2 + 13\gamma_k'^2) = F_2 \left(\alpha_{1i}, \alpha_{2i}, \frac{\partial \alpha_{1i}}{\partial q_l}, \frac{\partial \alpha_{2i}}{\partial q_l} \right) \quad (6)$$

¹ In the sense given by El'yashevich ([12], p. 496).

where μ_i is the dipole moment of the i -th bond, q_i are the natural vibrational coordinates, and α_{1i} and α_{2i} are the polarizabilities of the i -th bond in the parallel and perpendicular directions relative to its axis.

2. The electronic wave function $\Psi(r; q_i)$ of the unperturbed molecule is determined (r is the set of electron coordinates).

3. The model of the liquid structure and the approximate potential V of intermolecular interaction are introduced.

4. The wave function $\Phi(r; q_i)$ of the perturbed molecule is determined.

5. On the basis of $\Psi(r; q_i)$ and $\Phi(r; q_i)$ the electro-optical parameters of the perturbed and unperturbed molecule, and subsequently the expressions (1) and (2), are calculated.

3. Calculations for carbon tetrachloride

The results for carbon tetrachloride given in the foregoing were obtained with the use of the same description of the molecular electronic state and model of the liquid as in paper I. This means that the molecular electron state was described by means of localized molecular orbitals in the LCAO approximation, and each molecule of liquid carbon tetrachloride was treated as being placed in a "cell" formed by the twelve molecules positioned at the mid-points of the cube edges. Half of this cube's diagonal is equal to the mean intermolecular distance in liquid carbon tetrachloride. The potential V of the perturbing field inside the "cell" was calculated by making use of the point model of charge distribution in perturbing molecules. In the calculations presented here, however, assigned to each pair of free electrons is a separate point charge localized at the "centre of gravity" of the corresponding orbitals.

Formulae of the orbitals $\Phi(r; q_i)$ for a molecule in the perturbing field was found by the perturbation-variation method [17]. According to this method, for example, the perturbed orbital of a bonding electron is obtained in the form

$$\Phi = N \left[1 + \frac{\langle \Psi | V^2 | \Psi \rangle - (\langle \Psi | V | \Psi \rangle)^2}{\langle \Psi | D[V] | \Psi \rangle} V \right] \Psi \quad (7)$$

where N is a normalizing factor, Ψ is the unperturbed orbital, and

$$D[V] = \frac{1}{2} e^2 \alpha_0 \left[\left(\frac{\partial V}{\partial x} \right)^2 + \left(\frac{\partial V}{\partial y} \right)^2 + \left(\frac{\partial V}{\partial z} \right)^2 \right]$$

(x , y and z being the coordinates of the perturbed electron).

Owing to the axial symmetry of the charge density distribution of the C-Cl bond, the expression (3) for the dipole moment of this bond takes the form

$$\mu_i = e (Z_C + 7Z_{Cl} - 2 \langle \Psi | z | \Psi \rangle - 6 \langle \chi'_{Cl} | z | \chi'_{Cl} \rangle) \quad (8)$$

where Z_C , Z_{Cl} and z are the coordinates of the C nucleus, Cl nucleus and the considered electron, respectively, measured along the C-Cl bond axis, Ψ is the orbital of the bonding electron, and χ'_{Cl} is one of the free pair orbitals of the Cl atom. In turn, the static polarizabilities of the C-Cl bond, with the form of electronic wave function applied here, will be

expressed according to Eq. (4) as

$$\alpha_{1i} = \frac{8}{a_0} [\langle \Psi | z^2 | \Psi \rangle - (\langle \Psi | z | \Psi \rangle)^2]^2 + \frac{24}{a_0} [\langle \chi'_{Cl1} | z^2 | \chi'_{Cl1} \rangle - (\langle \chi'_{Cl1} | z | \chi'_{Cl1} \rangle)^2]^2; \quad (9)$$

$$\alpha_{2i} = \frac{8}{a_0} (\langle \Psi | x^2 | \Psi \rangle)^2 + \frac{8}{a_0} [\langle \chi'_{Cl1} | x^2 | \chi'_{Cl1} \rangle - (\langle \chi'_{Cl1} | x | \chi'_{Cl1} \rangle)^2]^2 + \\ + \frac{16}{a_0} [\langle \chi'_{Cl2} | x^2 | \chi'_{Cl2} \rangle - (\langle \chi'_{Cl2} | x | \chi'_{Cl2} \rangle)^2]^2. \quad (10)$$

χ'_{Cl1} and χ'_{Cl2} denote two orbitals of free pairs of the Cl atom. Equations (8) to (10) are obtained with neglect of the polarization of C and Cl atom inner shells.

Because localized orbitals are assumed, the quantities μ_i , α_{1i} and α_{2i} depend only on one natural coordinate — the change in i -th bond length. Hence, calculation of the other electro-optical parameters is reduced to differentiation of Eqs (8) to (10) with respect to the length R of this bond.

4. Results and conclusions

The orbitals used in calculations (their form is given in paper I, Eqs (4) to (7)) depend on the parameter λ designating the bond polarity and the parameter b designating the hybridization of the chlorine atom. Numerical calculations were performed with the following values of these parameters: $\lambda = 1.1136$ and $0 \leq \sqrt{1-b^2} \leq 0.3$. Considerations speaking for the values are given in paper I. Additional calculations made for $\lambda = 1.05$ and $\lambda = 1.17$ show that λ affects the final results but slightly.

As has been mentioned, the instantaneous effects of perturbations at fixed configurations of perturbing molecules and the perturbed molecule were calculated. Due to technical reasons, only several configurations distinguished by their high symmetry were considered. Some characteristic results of these calculations are presented in Tables I and II.

The relative change of the electro-optical parameters and transition probabilities (in per cent) arranged in Table I concern but one configuration of perturbing molecules (forming the "cell"), viz., one of the C-Cl bonds of these molecules being directed along the radius towards the cell center. The data arranged in the columns numbered 1, 2 and 3 concern the perturbed molecule's C-Cl bond directed towards one of the perturbing molecules (column 1), towards one of the cube walls used in constructing the cell (column 2) and towards a corner of this cube (column 3). The first six lines of this table contain the relative changes of the electro-optical parameters of the perturbed bond, the symbols of the quantities being given in the second column. The next two lines pertain to the infrared, and the following four to Raman spectrum. The relative changes in transition probabilities, collected in these six lines, were calculated as though the electro-optical parameters of all bonds changed identically under the effect of the perturbation. The subsequent lines concern vibrations of the symmetry given in the second column. The last line of the table gives the approximate value of energy W_V which the C-Cl bond gains in the perturbing field. It was calculated according to the formula

$$W_V = e \left(\sum_e Z_e V_e - \sum_i \langle \Psi_i | V | \Psi_i \rangle \right). \quad (11)$$

TABLE I

Changes in electro-optical parameters and intensities for different alignments of the perturbed molecule
(explanation in text)

		1	2	3	
Electro-optical parameter changes	μ	60	-31	-14	
	$\partial\mu/\partial R$	302	-77	-69	
	α_1	24	-10	-5.2	
	α_2	4.3	-1.5	-0.8	
	$\partial\alpha_1/\partial R$	64	-15	-13	
	$\partial\alpha_2/\partial R$	433	-10	-65	
	$\left[\left(\frac{\partial\mu}{\partial Q_k}\right)^2\right]^L$	F_q	436	-70	-51
	$\frac{\left[\left(\frac{\partial\mu}{\partial Q_k}\right)^2\right]^L}{\left[\left(\frac{\partial\mu}{\partial Q_k}\right)^2\right]^G} - 1$	F_γ	159	-53	-26
	A	182	-27	-26	
	E	92	-29	-16	
	$\frac{(5b_k'^2 + 13g_k'^2)L}{(5b_k'^2 + 13g_k'^2)G} - 1$	F_q	250	-26	-33
		F_γ	91	-29	-16
	Energy, in (atomic units)		-9.86×10^{-2}	4.46×10^{-2}	2.60×10^{-2}

TABLE II

Changes in electro-optical parameters and intensities for different alignments of the perturbing molecules
(explanation in text)

		1	2	3	
Electro-optical parameter changes	μ	23	-0.58	-20	
	$\partial\mu/\partial R$	237	-10	-189	
	α_1	14	-0.52	-10	
	α_2	2.3	-0.03	-5.5	
	$\partial\alpha_1/\partial R$	38	-2.8	-25	
	$\partial\alpha_2/\partial R$	276	-3.8	-202	
	$\left[\left(\frac{\partial\mu}{\partial Q_k}\right)^2\right]^L$	F_q	152	-4.4	-73
	$\frac{\left[\left(\frac{\partial\mu}{\partial Q_k}\right)^2\right]^L}{\left[\left(\frac{\partial\mu}{\partial Q_k}\right)^2\right]^G} - 1$	F_γ	52	-1.2	-36
	A	100	-5.5	-47	
	E	69	-2.4	-31	
	$\frac{(5b_k'^2 + 13g_k'^2)L}{(5b_k'^2 + 13g_k'^2)G} - 1$	F_q	100	-7.5	-49
		F_γ	68	-2.4	-31
	Energy in (atomic units)		-6.76×10^{-2}	8.99×10^{-4}	6.76×10^{-2}

Here, eZ_ρ denotes the charge of the ρ -th atom's core in the particular bond, V_ρ is the potential of the perturbing field at the position of the ρ -th core, and Ψ_i is the orbital of the i -th bonding electron. All results in this table were obtained with $\lambda = 1.1136$ and $\sqrt{1-b^2} = 0.1$.

Table II is an arrangement of results analogous to Table I corresponding to two different alignments of molecules forming the cell, wherein the alignment of the C-Cl bond of the perturbed molecule remains the same. This bond is directed always towards one of the perturbing molecules. The column numbered 1 concerns the alignment in which one of the perturbing molecules' C-Cl bonds is directed along the radius towards the cell center, whereas column 2 to the alignment where this bond is directed along the radius towards the cell exterior. Column 3 contains data corresponding to perturbation of a direction opposite to that in column 1. In other words, the perturbing electric field obtained in the calculation of these results was diametrically opposite to the field corresponding to column 2, but had the same absolute values of potential and intensity. The results of Table II were obtained with $\lambda = 1.1136$ and $\sqrt{1-b^2} = 0.28$. In all calculations the perturbed molecule was localized at the cell center.

The columns numbered 1 in both tables relate to the same alignment of the molecules, but different values of the parameter b . Hence, they illustrate the influence of this parameter on the perturbation effects. On the basis of these results (and others, not presented here) it may be ascertained that indeed changes of the parameter b do bring about quantitative changes in the perturbation effects, but do not alter their overall character. Moreover, if we bear in mind the aforementioned very weak dependence of results on the value of the parameter λ , the conclusion is reached that the character of the results of these calculations does not depend on details of the approximations of the molecular electronic wave function.

In all considered cases of perturbing field the trend in the change of transition probabilities for the infrared was the same as for Raman spectrum. This is in conformity with the experimentally found [3, 5, 6] parallellism of the behaviour of intensities in these two types of spectra, both in changes of the state of matter and temperature.

The data presented above are unsuitable for a direct comparison with experiment. For, as stated before, these are values of instantaneous perturbation effects, whereas in an experiment the measured effects are mean ones taken over all possible configurations of molecules of the liquid. Notwithstanding, it proved possible even on the basis of several chosen configurations to anticipate the sign of the mean perturbation effects. As illustrated by the cited data, any bond of a molecule in the liquid may be subject to the action of a perturbation leading to either an increase or a decrease in the value of its electro-optical parameters. However, a comparison of the exemplary columns 2 and 3 in Table II shows that in the case of the question the effect of the action of a perturbing field causing an increase of the electro-optical parameters and intensities is larger than that of a field of identical absolute value of potential, but oppositely sensed *e. g.* causing a drop in the quantities in mention. Moreover, it was found that in all cases considered, similarly as in Tables I and II, an increase in the electro-optical parameters and intensities always appears for the configurations where the perturbation energy W_V defined by Eq. (11) is negative, and *vice versa*. The higher efficiency of perturbations leading to an increase of intensities and the energetic preference of these per-

turbations energy allow one to conclude that for carbon tetrachloride the mean perturbation effect should be a rise in both absorption transition probabilities and those associated with Raman scattering. This conclusion is in agreement with experimental results for carbon tetrachloride. The fundamental vibrational lines in the Raman spectrum have their intensities doubled, on the average, when there is a transition from the gas to liquid phase [5, 18]. In the infrared this situation is less distinct [6, 19], for in practice only one fundamental band may be studied, and even this as a component of a resonance doublet. Nonetheless, it seems reasonable to speak here of a one-and-a-half-fold increase in intensity at the gas-to-liquid transition. It is worthwhile to add here that despite the weakness of the perturbations (*cf.* values of perturbation energy W_p) the changes in transition probabilities are relatively large and are of the same order as the observed changes in intensities. All of this indicates a sound correlation between the calculated and experimentally observed quantities.

On the basis of the results given above it is also possible to arrive at conclusions as to the temperature changes of intensities in vibrational spectra of liquids. As it is known, a rise of temperature of liquid causes among other things an increased freedom of motion of its molecules. Therefore, there is also an increased probability that molecular configurations will appear of higher (also positive) values of perturbation energy. In view of the correlation between the spectral perturbation effects and perturbation energy W_p found for carbon tetrachloride, the above conclusion leads to the drop in intensity with a rise in temperature known from experiments. This drop will be faster when the potential barriers separating alignments with minimum molecular perturbation energy are lower. Should there be correlation between perturbation changes and perturbation energy for other molecules also, then this would provide an explanation of the experimentally ascertained [5] relationship between temperature variations of intensities and the height of potential barriers of hindered rotation of the molecules in liquids.

Generalizing the above considerations one may say that the results of calculations obtained for carbon tetrachloride corroborate the following model of the influence of the gas-to-liquid transition and temperature change on intensities in vibrational spectra.

Due to intermolecular interactions in liquids, the molecules are subject to perturbations which may lead both to an increase and a decrease in the probability of vibrational transitions. Energy reasons give preference to one direction of changes. For CCl_4 calculations and experiments alike indicate the preference of intensity increase. A rise in temperature diminishes the energy preference of the single direction of perturbational changes of intensities. It therefore abolishes intensity changes which appeared due to the appearance of perturbations during the gas-to-liquid transition. Of course, apart from this mechanism of the temperature effect on intensities in vibrational spectra, a certain role may be played by changes in intermolecular distances and number of nearest neighbours due to temperature changes.

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