The Electrostatic Effect of the Solvents on the Frequency Shifts and the Intensity Changes of the Infrared Absorption Spectra

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Recently a theory was presented by the author[1] on the frequency shifts of the infrared absorption bands in the liquid state in terms of the intermolecular potential by Onsager's theory of dielectrics. The treatment given there, however, was essentially classical, so that it may be desirable to reconsider it in quantum mechanics.

For simplicity let us take a heteronuclear diatomic molecule with one degree of freedom of vibration which may be expressed approximately by a harmonic oscillation. As was stated in the preceding paper[1] the molecules in the liquid are stabilized by the interaction with the surrounding molecules and the energy to be added is given by[2]

$$\Delta H=-\frac{\epsilon-1}{2\epsilon+1}\,\frac{C}{a^3}\,[\mu+e'Q]^2 \quad \text{......(1)}$$

It is easily shown that the first order perturbation energy due to the operator, Eq. (1), gives rise to

$$\int\psi_0\Delta H\psi_0 d\tau=-\frac{\epsilon-1}{2\epsilon+1}\,\frac{C}{a^3}\left[\mu^2+\frac{e^2h}{8\pi^2m\nu}\right] \quad \text{......(1a)}$$

for the ground state and

$$\int\psi_1\Delta H\psi_1 d\tau=-\frac{\epsilon-1}{2\epsilon+1}\,\frac{C}{a^3}\left[\mu^2+\frac{3e^2h}{8\pi^2m\nu}\right] \quad \text{......(1b)}$$

for the first excited state, respectively. There ψ_0 and ψ_1 denote the wave functions of the ground and the first excited states of the harmonic oscillator. Then the energy absorbed in the transition, 0→1, is given by

$$h\nu'=h\nu-\left[\int\psi_0\Delta H\psi_0 d\tau-\int\psi_1\Delta H\psi_1 d\tau\right]$$
$$=h\nu\left[1-\frac{\epsilon-1}{2\epsilon+1}\,\frac{C}{a^3}\,\frac{e^2}{4\pi^2m\nu^2}\right] \quad \text{...(2)}$$

Thus the decrease in frequency observed at the transfer from the gas to the liquid state becomes

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

where

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

This is exactly the same expression as that obtained by the classical consideration in the preceding paper.

The intensity of this absorption band depends upon the squared value of the (0, 1) element of the electric moment, while the latter in the liquid state is increased by the factor C referred to that in *vacuo*;

$$m=C\,[\mu+e'Q] \quad \text{......(4)}$$

Therefore the absorption intensity in the liquid state, I_l, is obtained from that in the gaseous state, I_g, by the relation

$$I_l=C^2\,I_g \quad \text{......(5)}$$

To test the above conclusions the recent measurement by Barrow[3] is quoted here. The absorption of the stretching frequency of C=O group of various compounds were measured in the solutions of chloroform and carbon tetrachloride as well as in the vapor. Here are selected the following four examples: acetone, methyl and ethyl acetate, and methyl carbonate. In order to compute the frequency shifts by Eq. (2′), it is necessary to know the values of a's, the effective radii of the molecules. They are usually estimated from the density of the liquid, but in this paper they are treated as adjustable parameters so as to give the best fit with the observed ones in $CHCl_3$ and CCl_4 solutions. In Table I the calculated $\Delta\tilde{\nu}$'s are given to be compared with the observed values. In this table are listed the values a's assumed, together with the frequencies in *vacuo* $\tilde{\nu}$'s (in the unit of cm^{-1}), and the intensities in *vacuo* A's quoted from the paper by Barrow. It is noted that, since $A=N\pi\left(\frac{\partial\mu}{\partial Q}\right)^2/3c^2\ 1000$ given in the unit of mole^{-1} litre cm^{-1} is used, Eq. (2′) becomes

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[1] E. Hirota, This Bulletin, **26**, 397 (1953).

[2] Eq. (4*b*) in reference 1, in which the energy necessary to polarize the molecule, $\alpha R^2\,2$, was omitted. (Cf. C. J. F. Böttcher, "Theory of Electric Polarization", Elsevier Publishing Co., Amsterdam, 1952, pp. 138—139.) This correction being included, the factor C^2 in Eq. (4*b*) in reference 1 should be replaced by C, but it does not essentially alter the conclusion obtained there. C^2 in Eqs. (6*b*), (7*b*), (8*b*) and (8*b*′), should also be corrected to C. About notations used in this paper one should consult with referrence 1.

[3] G. M. Barrow, *J. Chem. Phys.*, **21**, 2008 (1953).

TABLE I
FREQUENCY SHIFT

Compound				$CHCl_3$ soln. $(\epsilon-1)C/(2\epsilon+1)=0.444$		CCl_4 soln. $=0.253$	
	$a\ (A)$	$\tilde{\nu}(\mathrm{cm}^{-1})$	A*)	calc.	obs.	calc.	obs.
Acetone	1.48	1747	$1.2\ 10^4$	$(38._0)$	38	$21._6$	—
Methyl acetate	1.68	1776	1.9	$40._3$	38	$23._0$	25
Ethyl acetate	1.73	1772	2.1	$41._7$	38	$23._2$	27
Methyl carbonate	2.20	1781	2.9	$27._2$	25	$15._5$	18

*) $A=N\pi\left(\frac{\partial\mu}{\partial Q}\right)^2/3c^2\ 1000$, given in the unit of mole^{-1} litre cm^{-1}.

$$\Delta\tilde{\nu}=\frac{\epsilon-1}{2\epsilon+1}C\frac{3}{4\pi a^3}\frac{10^3}{N\pi^2}\frac{A}{\tilde{\nu}}\quad\ldots(2'')$$

The values of dielectric constants are taken to be 5.0 for $CHCl_3$ and 2.23 for CCl_4, while $n^2=2$ is assumed through out. It follows that $(\epsilon-1)C/(2\epsilon+1)=0.444$ for $CHCl_3$ and 0.253 for CCl_4 solutions. For the last three compounds in Table I. the calculated values of $\Delta\tilde{\nu}$'s for $CHCl_3$ solutions are larger than the experimental values, whereas the contrary is the case for CCl_4 solutions.

The values assumed above for a's are found to be far smaller than the molecular radius $a_0=(3M/4\pi Nd)^{1/3}$, which is the radius of the spheres just filling the entire liquid. The bond moments of C=O and C−O are considered to be greater than those of C−C and C−H, so that the interactions of the bonds C=O and C−O with other molecules may play the main role in this case. The radius of a sphere encircling just this group of oxygen and carbon atoms is taken to be the rough estimate for a. The atomic radii and the bond angles of acetate and carbonate groups are taken from Pauling's book[4], where the two end oxygen atoms in acetate groups are assumed to have radii $0.605=(0.66+0.55)/2$ and the three in carbonate group to have radii $0.623=(2\times0.66+0.55)/3$. The values obtained thus are 1.28A for acetone, 1.75A for two acetates and 2.25A for carbonate. It may be interesting to note that a's used for the calculation of $\Delta\tilde{\nu}$ 1.48A, 1,68A, 1.73A and 2.20A run roughly parallel to these rough estimates.

Another comparison is carried out for the intensity change. As evident from Eq. (5), the intensity ratio I_l/I_g is given by C^2, which depends on ϵ and n, but is free from the value of a. Inserting the values of dielectric constants for $CHCl_3$ and CCl_4 as quoted above and using the intensities *in vacuo* I_g measured by Barrow, one can obtain I_l, the intensities in solutions, which are listed in Table II. It will be seen that the agreement with the observed I_l is very satisfactory.

TABLE II
INTENSITY CHANGE (1)

Compound		A_1*) $C^2=1.49$ $CHCl_3$ soln.		$C^2=1.265$ CCl_4 soln.	
	A_g*)	calc.	obs.	calc.	obs.
Acetone	$1.2\ 10^4$	$1.7_9\ 10^4$	$1.9\ 10^4$	$1.5_2\ 10^4$	…
Methyl acetate	1.9	2.8_3	2.8	2.4_0	$2.2\ 10^4$
Ethyl acetate	2.1	3.1_3	3.2	2.6_6	2.6
Methyl carbonate	2.9	4.3_3	4.2	2.6_7	3.8

*) See the footnote of Table I.

Further it is also possible to compare the intensities in different solutions; the ratio of the intensities in two solutions is given by

$$I_{li}/I_{lj}=C_i^2/C_j^2\quad\ldots\ldots(6)$$

where C_i and C_j denote respectively the constants for both solutions. Thus the intensity ratio is a definite constant, determined by the solvents, and common to any absorption bands of any melecules. In Table III. a comparison is made of the intensity ratios $\rho=A\ (CHCl_3)/A(CCl_4)$ of C=O bands of various compounds in chloroform and carbon tetrachloride. It will be clearly seen that the intensity ratios are obtained in the deviations less than 10% from the calculated ratio $\rho_{\mathrm{calc.}}=C^2(_{CHCl_3})/C^2(_{CCl_4})=1.18$, except in the cases of propionaldehyde (14.7%) and ethyl benzoate (10.1%). According to Barrow, the accuracy of the intensity measurement is about 2% in solutions and about 5% in the gaseous phase. The discrepancies between the

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[4] L. Pauling, "The Nature of the Chemical Bond" Cornell Univ. Press, 1940, pp. 164, 203, 208 and 209.

TABLE III
INTENSITY CHANGE (2)

	$A_{obs.}$ *)			$\frac{\rho_{obs.}-\rho_{calc.}}{\rho_{calc.}}$
Compound	$CHCl_3$ soln.	CCl_4 soln.	$\rho_{obs.}=A(CHCl_3)/A(CCl_4)$	Deviation in ρ (%)
Diethyl ketone	1.9 10^4	1.55 10^4	1.2_2	3.7
Propionaldehyde	2.1	1.55	1.3_5	14.7
Benzaldehyde	2.6	2.1	1.2_4	5.1
Benzophenone	2.4	2.2	1.0_9	−7.4
Acetophenone	2.7	2.1	1.2_8	9.0
Ethyl propionate	3.2	2.8	1.1_4	−3.1
Methyl crotonate	3.4	3.1	1.1_0	−6.9
Ethyl benzoate	3.6	3.4	1.0_6	−10.1
Ethyl carbonate	4.7	4.1	1.1_4	−2.9
Acetyl chloride	3.1	2.5	1.2_3	5.3
Phenyl acetate	3.1	2.9	1.0_7	−9.2
Acetanilide	3.6	3.1	1.1_6	−1.4

$\rho_{calc.}=C^2(CHCl_3)/C^2(CCl_4)=1.49/1.265=1.18$

*) See the footnote of Table I.

calculated and the observed values are of this order of magnitude.

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