On the Infrared Frequency Shift in the Liquid State and its Relation to the Atomic Polarization

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Introduction

It is a well-known fact that the infrared frequencies of molecules in the liquid states are, in general, lower than those in the gaseous states. This fact implies that the molecules are slightly deformed in condensed phase by the intramolecular field due to the surrounding molecules. The deformation of molecules in a static external field is, on the other hand, indicated as the so-called "atomic polarization." Therefore the frequency shift in the liquid state may have some relation to the atomic polarization. Kirkwood, West, and Edwards[1] studied the frequency shift of HCl, but their work was limited to a simple molecule such as HCl and not extended to the relation of the frequency shift with the atomic polarization. Here the frequency shift will be treated as a more general problem and connected with the atomic polarization.

Atomic Polarization

The atomic polarization induced by ith infrared active normal vibration is given by[2]

$$P_{Ai}=\frac{1}{3}\,\frac{4\pi N}{3}\,\alpha_{Ai}=\frac{4\pi N}{9}\,\frac{e_i^2}{4\pi^2 m_i \nu_i^2} \quad (1)$$

where N denotes Avogadro's number, e_i the effective charge, m_i the effective mass, and ν_i the frequency of the ith normal vibration. The factor 1/3 in Eq. (1) takes account of the fact that the vibration under consideration has only one degree of freedom rather than three as does the isotropic oscillator.[3] As a whole it gives rise to

$$P_A=\sum_i P_{Ai}=\frac{4\pi N}{9}\sum_i\frac{e_i^2}{4\pi^2 m_i \nu_i^2} \quad (1')$$

where the summation is extended over all the infrared active vibrations.

Frequency Shift

A) A Simple Treatment (Heteronuclear diatomic molecules, with only one normal mode).—Let us consider first a simple case in which the molecule has one vibrational degree of freedom (e.g. HCl). In view of the complexity of the intramolecular force field in the liquid phase one can not obtain a satisfactory expression for it. But Onsager[4] gave an ingeneous method of evaluating the intramolecular force by solving an electrostatic equivalence. Let us make a spherical cavity in the liquid phase with dielectric constant ε, whose radius is denoted by a, and put at its center the electric moment $\boldsymbol{m}$. Then this dipole polarizes the surrounding medium and produces a "reaction field" $\boldsymbol{R}$ at its own place, which is given by

$$\boldsymbol{R}=\frac{2(\varepsilon-1)}{2\varepsilon+1}\,\frac{\boldsymbol{m}}{a^3} \quad (2a)$$

where

$$\boldsymbol{m}=\boldsymbol{\mu}+e\boldsymbol{x} \quad (3a)^{*)}$$

and $\boldsymbol{\mu}$ denotes rigid dipole of the molecule, e the effective charge, and $\boldsymbol{x}$ the displacement of the nucleus (treated as a vector quantity; the directions of $\boldsymbol{\mu}$ and $\boldsymbol{x}$ coincide with the axis of the molecule in this case). This field stabilizes the molecule by the amount,

$$-\Delta E=\frac{1}{2}\,\boldsymbol{R}\boldsymbol{m}=\frac{\varepsilon-1}{2\varepsilon+1}\,\frac{1}{a^3}\,(\boldsymbol{\mu}+e\boldsymbol{x})^2 \quad (4a)$$

so that the force constant for the molecular vibration is decreased in the liquid phase by the amount,

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[1] W. West and R.T. Edwards, *J. Chem. Phys.*, **5**, 14 (1937): J. G. Kirkwood, ibid., **2**, 351 (1934) Cf. E. Bauer and M. Magat, *Physica*, **8**, 718 (1938).

[2] J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities", Oxford University Press, London, 1932. pp.42f. & 361t.

[3] Reference 2, p.46.

[4] Lars Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936 .

*) It may be artued that the Onsager's model is an electrostatical one and, therefore, cannot be adequately applied to the time-dependent phenomena such as vibrations of nuclei. But when the wave-length of the radiation is far greater than the size of the radiating system (the molecule in this case), one can treat this process as a "quasi-stationary" one.

$$-\Delta f=-\frac{\partial^2\Delta E}{\partial x^2}=\frac{2(\varepsilon-1)}{2\varepsilon+1}\frac{e^2}{a^3}=2ce^2 \tag{5a}$$

where

$$c=\frac{\varepsilon-1}{2\varepsilon+1}\frac{1}{a^3}$$

It follows that the fundamental frequency in the liquid phase, ν', is related to that in the free state, ν, by the relation:

$$\nu'=\left(\nu^2-2c\frac{e^2}{4\pi^2 m}\right)^{\frac{1}{2}}\cong\nu\left[1-\frac{ce^2}{4\pi^2 m\nu^2}\right] \tag{6a}$$

or

$$\frac{\Delta\nu}{\nu}=\frac{\nu-\nu'}{\nu}=c\frac{e^2}{4\pi^2 m\nu^2}=c\alpha_A \tag{7a}$$

where m is the effective mass of the harmonic oscillator composed of the diatomic molecule. Inserting this relation into Eq. (1′), we obtain

$$P_A=\frac{4\pi N}{9}\frac{1}{c}\frac{\Delta\nu}{\nu}=\frac{2\varepsilon+1}{3(\varepsilon-1)}\frac{M}{d}\frac{\Delta\nu}{\nu} \tag{8a}$$

where M and d denote molecular weight and density of the liquid respectively, which are related to a by

$$\frac{4\pi}{3}a^3=\frac{M}{N\cdot d}$$
(4)

It is necessary to compare this simple and rather straightforward derivation of $\Delta\nu$ with the result obtained by Kirkwood, whose idea was only quoted by West and Edwards and not given in details.[1] Their expression is

$$\frac{\Delta\nu}{\nu}=\frac{\varepsilon-1}{2\varepsilon+1}\frac{1}{a^3}\frac{(\boldsymbol{\mu}_1{}^2+2\boldsymbol{\mu}_0\boldsymbol{\mu}_2)}{4\pi^2 m\nu^2} \tag{7a'}$$

where

$$\boldsymbol{\mu}_1=[(\partial\boldsymbol{\mu})/(\partial\boldsymbol{x})]_{x=0},\ \boldsymbol{\mu}_2=[(\partial^2\boldsymbol{\mu})/(\partial\boldsymbol{x}^2)]_{x=0}$$

and

$$\boldsymbol{\mu}_0=[\boldsymbol{\mu}]_{x=0}$$

This differs from Eq. (7a) only in the point that Kirkwood took into account the anharmonicity of vibration by introducing the second derivative of the dipole moment with x.

B) More General Treatment (Polyatomic molecules, with more than one infrared active normal mode).—The principle of the calculation is, in general, the same as that used in A) except the introduction of the polarizability α, which is, according to Onsager, given by

$$\alpha=\frac{n^2-1}{n^2+2}a^3 \tag{8}$$

where n stands "internal refractive index". The total electric moment induced in the center of the cavity is given by

$$\boldsymbol{m}=\boldsymbol{\mu}+\alpha\boldsymbol{R}+\sum_i e_i'\boldsymbol{Q}_i \tag{5b}$$

in which $\boldsymbol{R}$ is given by the same expression as Eq. (2a) and e_i' denotes $e_i/\sqrt{m_i}$ [*] and $\boldsymbol{Q}_i$ the ith normal coordinate (treated as a vector quantity).[**]

Combination of Eqs. (2a) and (3b) affords, by means of Eq. (8),

$$\boldsymbol{R}=\frac{2(n^2+2)(\varepsilon-1)}{3(2\varepsilon+n^2)}\frac{1}{a^3}[\boldsymbol{\mu}+\sum_i e_i'\boldsymbol{Q}_i] \tag{9}$$

and

$$\boldsymbol{m}=\frac{(n^2+2)(2\varepsilon+1)}{3(2\varepsilon+n^2)}[\boldsymbol{\mu}+\sum_i e_i'\boldsymbol{Q}_i]$$

$$=C[\boldsymbol{\mu}+\sum_i e_i'\boldsymbol{Q}_i] \tag{10}$$

In this case the energy of stabilization becomes

$$-\Delta E=\frac{1}{2}\boldsymbol{R}\boldsymbol{m}=\frac{\varepsilon-1}{2\varepsilon+1}\frac{C^2}{a^3}[\boldsymbol{\mu}+\sum_i e_i'\boldsymbol{Q}_i]^2 \tag{4b}$$

which is considered as a perturbing potential. Changing the variables from $\boldsymbol{Q}_{is}'$ to ξ_{is}', i.e.,

$$\boldsymbol{Q}_i=\xi_i+\boldsymbol{Q}_{io}$$
($\boldsymbol{Q}_{io}$: a constant to be determined)

and choosing $\boldsymbol{Q}_{io}$ to satisfy the relations

$$\lambda_i Q_{io}{}^2-R'e_i'(\boldsymbol{\mu}\boldsymbol{Q}_{io})-R'\frac{e_i{}^2}{m_i}Q_{io}{}^2$$
$$-R'\sum_j e_i'e_j'(\boldsymbol{Q}_{io}\boldsymbol{Q}_{jo})=o$$

where and

$$\lambda_i=4\pi^2\nu_i{}^2 \qquad R'=\frac{2(\varepsilon-1)}{2\varepsilon+1}\frac{C^2}{a^3}$$

the perturbing potential Eq. (4b) reduces to, except constant terms,

$$-\Delta E=\frac{1}{2}R'[\sum_i\frac{e_i{}^2}{m_i}\xi_i{}^2+2\sum_i\sum_j e_i'e_j'(\xi_i\xi_j)] \tag{4b'}$$

in which the second terms depend only upon the cross products of ξ_{is}' and, therefore, may

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[*] It is to be noted that the dimension of Q_i is $[M]^{\frac{1}{2}}[L]$.

[**] See Discussion.

be neglected in the first order approximation. The change in ν_i, in this order of approximation, turns out to be

$$\nu_i' = \left[\nu_i^2 - \frac{2(\varepsilon-1)}{2\varepsilon+1}\frac{C^2}{a^3}\frac{e_i^2}{4\pi^2 m_i}\right]^{\frac{1}{2}}$$

$$\cong \nu_i\left[1 - \frac{\varepsilon-1}{2\varepsilon+1}\frac{C^2}{a^3}\frac{e_i^2}{4\pi^2 m_i \nu_i^2}\right] \quad (6b)$$

or

$$\frac{\Delta\nu_i}{\nu_i} = \frac{\nu_i - \nu_i'}{\nu_i} = \frac{\varepsilon-1}{2\varepsilon+1}\frac{C^2}{a^3}\frac{e_i^2}{4\pi^2 m_i \nu_i^2} \quad (7b)$$

Thus, similarly to Eq. (8a), the total atomic polarization is given by

$$P_A = \frac{4\pi N}{9}\frac{2\varepsilon+1}{\varepsilon-1}\frac{a^3}{C^2}\sum_i \frac{\Delta\nu_i}{\nu_i} \quad (8b)$$

$$= \frac{2\varepsilon+1}{3(\varepsilon-1)}\frac{1}{C^2}\frac{M}{d}\sum_i \frac{\Delta\nu_i}{\nu_i} \quad (8b')$$

where the summation is extended over the terms due to the infrared active vibrations and

$$C = \frac{(n^2+2)(2\varepsilon+1)}{3(2\varepsilon+n^2)} \quad (11)$$

stands for a small correction due to the polarizability, reducing to 1 in the limit $n^2=1$.

Comparison with Experiments

In order to check the relation obtained above, two quantities should have been measured : i.e., the frequency shift $\Delta\nu$ and the atomic polarization P_A. But unfortunately precise data have not been available for either of them. The following are several examples useful at present to confirm the results.

Ex. 1. Hydrogen Chloride.—West and Edwards[1] observed the fundamental frequencies of HCl in the gaseous state and in CCl_4 solution, which are 2886 cm.$^{-1}$ and 2833 cm.$^{-1}$ respectively. Inserting this date and $\varepsilon=2.23$, the dielectric constant of carbon tetrachloride, in Eq. (8a) one obtains $P_A=1.0$ cc. Using the frequency 2780 cm.$^{-1}$ in pure HCl liquid obtained by Hettner[5], $P_A=0.8$ cc. These should be compared with the value $P_A=1.25$ cc. obtained from the measurement of the dielectric constant of the gaseous HCl by Zahn[6].

Ex. 2.—Water in carbon tetrachloride solution.—The molecule H_2O has three infrared active modes, the two of which were measured by Borst, Buswell, and Rodebush[7] in its CCl_4 solution. The results are as follows: for the fundamental frequency of 3652 cm.$^{-1}$, $\Delta\nu=43$ cm.$^{-1}$ and for $\nu=3756$ cm.$^{-1}$ $\Delta\nu=44$ cm.$^{-1}$. Assuming $\Delta\nu=20$ cm.$^{-1}$ for the remaining bending vibration (1595 cm.$^{-1}$), one can calculate $P_A=0.8$ cc. (See Table 1.). Various values of P_A have been obtained experimentally, only three of which are quoted here: $P_A=3.2$ cc. was obtained by the measurement of infrared dispersion[8], $P_A=2.0$ cc. by the dielectric constant of the solid[9] and $P_A=0.1$ cc.

Table 1

Frequency Shift of H_2O[7]

ν in Gas (cm.$^{-1}$)	ν in CCl_4 solution (cm.$^{-1}$)	$\Delta\nu$ (cm.$^{-}$)	$\Delta\nu/\nu$
1595	—	(20)	(0.0125)
3652	3609	43	0.0118
3756	3712	44	0.0117
			$\sum\Delta\nu/\nu$ 0.036

Table 2

Frequency Shift of CH_3I[11]

Symmetry	ν in Gas (cm.$^{-1}$)	ν in Liquid (cm.$^{-1}$)	$\Delta\nu$ (cm.)	$\Delta\nu/\nu$
A_1	532	552	10	0.0188
E	883	887	−4	−0.0091*)
A_1	1250	1242	8	0.0064
E	1441	1429	12	0.0166
A_1	2967	2950	17	0.0057
E	3058	3050	8	0.0052
				$\sum\ \nu/\nu$ 0.0527

*) This term is neglected for the calculation of $\Delta\nu/\nu$.

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[5] G. Hettner, *Zeits. f. Physik*, **89**, 234 (1934).

[6] C. T. Zahn, *Phys. Rev.*, **24**, 400 (1927).

[7] L. B. Borst, A. M. Buswell, and W. H. Rodebush, *J. Chem. Phys.*, **6**, 61 (1938).

[8] C. H. Cartwright and J. Errera, *Proc. Roy. Soc.*, **A154**, 138 (1937).

[9] J. Errera, "Polarisation dielectrique." quoted in Reference 8.

by the dielectric constant of the gas[10].

Ex. 3. Methyl Iodide.—From the results of Fenlon, Cleveland, and Meister[11] (Table 2) with Eq. (8b) one obtains $P_A=1.6$ cc., which should be compared with 1.4 cc., the value obtained by C.P. Smyth[12].

Ex. 4. Benzene.—Using the available data for $\Delta\nu$[13,14] (Table 3), one can estimate very roughly the value of P_A for C_6H_6, resulting to 1.9 cc., which agrees fortuitously with the value of Smyth[12] 1.9 cc.

Discussion

It should be noted here that the effective charges, $e_i's$, in Eq. (3) and others are those for the vibrations of molecules in the condensed phase and may differ from $e_i's$ defined by Eq. (1) or by Eq. (1′), the coincidence of both expressions being a formal one. This discrepancy might, if it were a real one, afford apparently greater "atomic polarization". An assumption is also made about the nuclear motion; that is, the vibration of nucleus is trated here simply by assuming no electrical and no mechanical anharmonicity. Since the errors originating from this treatment are not large, this solution may be allowed for the present as an approximate one.[15]

Table 3

Frequency Shift of C^6H^6

Symmetry	ν in Gas (cm.$_-$^{1})[13]	ν in Liquid (cm.$^{-1}$)[14]	ν (cm.$^{-1}$)	$\Delta\nu/\nu$
A_{2u}	671	675	−4	−0.0024*)
E_{1u}	1037	1036	1	0.0020
E_{1u}	1485	1478	7	0.0094
E_{1u}	3099	3089	10	0.0064
				$\sum\Delta\nu/\nu$ 0.0178

*) This term is neglected for the calculation of $\Delta\nu/\nu$.

Onsager's theory assumes that the geometry of the cavity is a spherical one and the dipole of the molecule is considered to be concentrated at the center of this sphere. It has already been pointed out by Wada[16] that these two assumptions are serious, and for a special case of 1,2-dichloroethane a more precise model was proposed to give a satisfactory result. In fact, the dipole induced by the infrared active normal vibration is not obviously a point one, contradicting the assumptions of Onsager's theory. However, if we are allowed to assume Onsager's theory at least as the first approximation, the theory stated above provides the effective charge for a normal vibration of the molecule from the frequency shift of the vibration. Detailed discussions are postponed, because of deficiencies in the accuracy on the theoretical as well as the experimental sides. Nevertheless, it is very interesting to note that the atomic polarization, which is a quantity difficult to measure, can be obtained by the frequency shifts in infrared absorption bands.

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[10] P. Debye and H. Sack, "Handb. d. Radiologie", IV. Akad. Verlag., Leipzig. 1934.

[11] P. F. Fenlon, F. F. Cleveland, and A. G. Meister, *J. Chem. Phys.*, **19**, 1561 (1951).

[12] C. P. Smyth, *J. Chem. Phys.*, **1**, 247 (1933).

[13] G. Herzberg, "Molecular Spectra and Molecular Structure", Band II., D. Van Nostrand Co. New York, 1949.

[14] American Petroleum Institute Research Project 44, Serial No. 307, 498 and 499.

[15] B. L. Crawford, Jr., and H. L. Dinsmore, *J. Chem. Phys.*, **18**, 983 (1950), B. L Crawford, Jr., *J. Chem, Phys.*, **20**, 977 (1952).

[16] A. Wada, Private communication. See also D. G. Frood and A. J. Dekker, *J. Chem. Phys.*, **20**, 1030, (1952).