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Far-infrared Absorption Intensities and the Dipole Moments of Some Molecules in Solutions

Kimihiro SATO, Yusei OHKUBO, Tadaharu MORITSU, Shun-ichi IKAWA,
and Masao KIMURA*

Department of Chemistry, Faculty of Science,
Hokkaido University, Sapporo 060

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The integrated intensities of the far-infrared absorptions of CH_3I, $CHCl_3$, CH_2Cl_2, CH_3CN, and their deuterated compounds in dilute solutions have been measured. They can be well explained by the rotational motion of the molecules with the dipole moments enlarged by Onsager's reaction field.

It is well known that the broad far-infrared absorption of a dipolar molecule in the liquid phase contains valuable information about the molecular rotational motion in the liquid. If the absorption is attributed solely to the rotational motion of the molecule, its band shape is reducible to the reorientational correlation function by the Fourier transformation[1)] and its integrated intensity after correcting for the internal field effect[2—4)] is related through Gordon's sum rule[5)] to the dipole moment and the moments of inertia of the molecule. But all the integrated intensities so far observed,[6—15)] except for the previous result for HCl dissolved in CCl_4,[16)] are appreciably larger than the values estimated on the basis of the permanent dipole moments in the gas phase. Hitherto the excess absorptions have simply been ascribed to the temporary dipole moments induced by collision with neighboring molecules. However, even in the simple form of Gordon's sum rule, which was widely used,[6—16)] the dipole moment involved is considered to be a gross dipole moment consisting of the permanent dipole moment in the free state and the statistical average of the induced dipole moment. In this case, the dipole moment may conveniently be interpreted in the macroscopic point of view. In the theory of dielectrics,[17,18)] the actual dipole moment of a molecule in the liquid phase differs from the gas-phase value owing to the reaction field. Since the actual dipole moment which was referred to as the *internal moment* by Fröhlich,[17)] simply follows the rotation of the molecular framework, it takes part in the far-infrared absorption. Then, the actual dipole moments estimated by the theory of dielectrics are worth comparing with the dipole moments obtained by Gordon's sum rule from the far-infrared absorption intensities.

In the present study, we have measured the far-infrared absorption intensities of CH_3I, $CHCl_3$, CH_2Cl_2, CH_3CN, and their deuterated compounds dissolved in non-polar solvents and adopted Onsager's reaction field for estimating the internal moments of the molecules.

Experimental

The far-infrared spectra were measured at room temperature on a HITACHI FIS-21 single beam spectrophotometer equipped with a germanium-bolometer detector which was operated at pumped liquid-helium temperature, 1.8 K. The resolution was higher than 2 cm^{-1} over the observed region, 10—360 cm^{-1}. Two cells of equal thickness with low-density polyethylene windows were set in a closed compartment placed between the monochromator and the detector. Atmospheric water vapor in the compartment was purged by a steady flow of dried nitrogen gas, while the monochromator was evacuated by a rotary pump. The two cells filled with the solution and the solvent were alternately introduced into the light path by manipulating from outside. The transmitted intensities were determined by observing for 5 min at every fixed wave number with intervals of 5—10 cm^{-1}. In this way, the S/N ratio was improved and the influences of the long-time fluctuations of the light source (high-pressure mercury lamp) and the bolometer sensitivity were effectively eliminated from the results. Spectroscopic grade reagents were used for C_6H_6, CCl_4, CS_2, n-C_6H_{14}, CH_2Cl_2, and CH_3CN. For CH_3I and $CHCl_3$, the commercially available samples were used after purification[19)] to eliminate a slight amount of polar impurities, such as H_2O and C_2H_5OH. The deuterated compounds were purchased from CEA and used without further purification. The concentration ranges employed were 0.20—1.1 M, 0.25—1.1 M, 0.13—0.48 M, and 0.03—0.16 M for the solutions of CH_3I, $CHCl_3$, CH_2Cl_2, and CH_3CN respectively.

Results and Discussion

The observed absorption coefficients, $\sigma(\nu)$, of CH_3I dissolved in the non-polar solvents are shown in Fig. 1 as examples. The band shapes for all the solutions studied do not depend on concentration, but they depend appreciably on the solvents. By extrapolating the observed spectra to the origin, as shown by the fine broken lines in Fig. 1, the integrated intensities

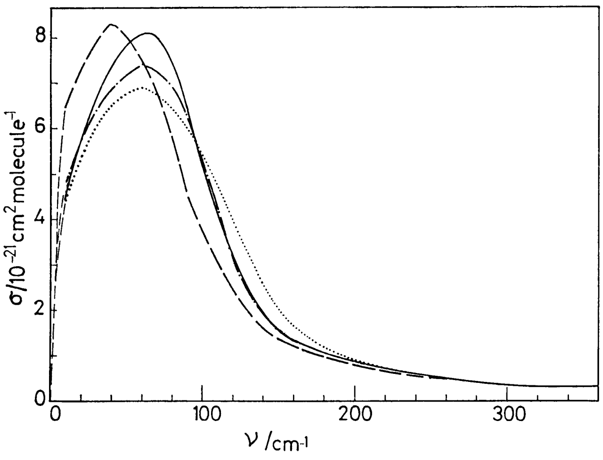

Fig. 1. Far-infrared absorption bands of CH_3I dissolved in C_6H_6(······), CCl_4(——), CS_2(—·—), and n-C_6H_{14} (— — —).

were obtained by

$$A = \int_0^{360} \sigma(\nu)\mathrm{d}\nu, \tag{1}$$

where

$$\sigma(\nu) = \frac{1}{\rho l}\ln(T_0/T)_\nu ,$$

and ρ denotes the concentration of the dipolar molecule (molecules·cm^{-3}), l the sample thickness (cm), and T_0 and T the transmittance of the solvent and the solution, respectively. The most probable values of A were evaluated from the slopes of the Beer's law plots shown in Fig. 2, and are listed in Table 1. The internal-field correction was applied to A. The corrected intensities, A_c, were obtained by the equation[3,4]

$$A_c = n_s\left[\frac{(n/n_s)^2+2}{n^2+2}\right]^2 A, \tag{2}$$

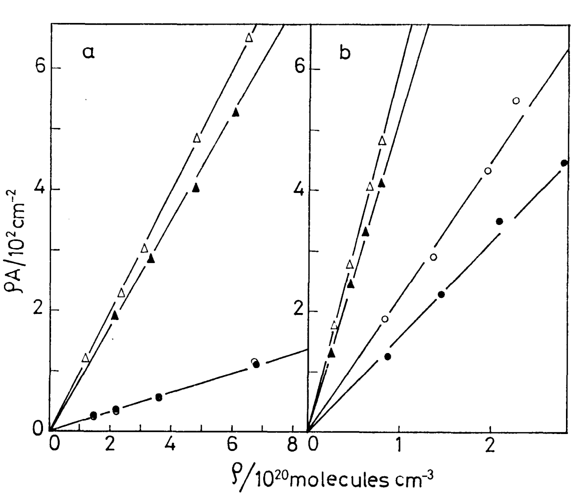

Fig. 2. Beer's law plots for CH_3I(a- △), CD_3I(a- ▲), $CHCl_3$(a- ○), $CDCl_3$(a- ●), CH_3CN(b- △), CD_3CN-(b- ▲), CH_2Cl_2(b- ○), and CD_2Cl_2(b- ●) dissolved in CCl_4.

where n and n_s denote the refractive indices of the solute and the solvent respectively. In the present study, they were replaced by the values for the Na_D-line. This replacement introduces only a few percent uncertainty in the A_c values.

Since the dipole moment of the C_{2v} or C_{3v} symmetric molecule lies along one of the principal axes of the moment of inertia, say the z axis, Gordon's sum rule is reduced to[5]

$$A_c = \frac{\pi\mu^2}{3c^2}\left(\frac{1}{I_x}+\frac{1}{I_y}\right), \tag{3}$$

where c is the velocity of light, μ the dipole moment, and I_x and I_y the principal moments of inertia about the x and y axes. The μ values calculated from A_c by Eq. 3 are shown in Table 1, together with the values of the moments of inertia and the permanent dipole moments in the gas phase, μ_0, taken from the literature. The μ values are about 10—20% larger than the μ_0 values for all the compounds studied. Moreover, almost the same μ values were obtained for the H- and D- compounds, which have different moments of inertia. These facts can be explained by regarding μ as the internal moments in the solutions. According to the concept of the reaction field in the theory of the dielectrics,[17,18] the internal moment, μ^*, is larger than the dipole moment in vacuum or in the gas phase, μ_0.

In Onsager's model, the internal moment μ^* is expressed as[17,18]

$$\mu^* = \frac{1}{1-f\alpha}\mu_0, \tag{4}$$

where

$$f = \frac{1}{a^3}\cdot\frac{2\varepsilon-2}{2\varepsilon+1}, \tag{5}$$

and α is the average polarizability of the molecule, ε the dielectric constant of a continuous medium, and $a^3=3/4\pi N$ (N: the number of the molecules per cm^3). Introducing Eq. 5 into Eq. 4 and rewriting by the use

Table 1. Observed integrated intensities and dipole moments

Solute	Solvent	A	A_c	μ	μ^*	μ_0	I[a]
		10^{-20} cm·mol^{-1}		D			10^{-40} g·cm^2
CH_3I	C_6H_6	102	74.1	1.8_8	1.9_2	1.65[b]	$I_x=I_y=111.9$
	CCl_4	99.7	74.0	1.8_8	1.9_0		
	CS_2	99.4	71.2	1.8_4	1.9_7		
	n-C_6H_{14}	94.3	72.0	1.8_5	1.8_6		
CD_3I	CCl_4	86.2	64.0	1.9_4	1.9_0		$I_x=I_y=138.9$
$CHCl_3$	CCl_4	16.1	12.5	1.1_7	1.1_6	1.02[c]	$I_x=I_y=254.2$
$CDCl_3$	CCl_4	16.4	12.7	1.1_9	1.1_6		$I_x=I_y=258.3$
CH_2Cl_2	C_6H_6	230	179	1.9_1	1.8_3	1.62[b]	$I_x=26.22,\ I_y=273.8$
	CCl_4	227	178	1.9_0	1.8_2		
	n-C_6H_{14}	202	162	1.8_3	1.7_9		
CD_2Cl_2	CCl_4	157	123	1.8_2	1.8_2		$I_x=35.44,\ I_y=280.3$
CH_3CN	C_6H_6	662	538	4.6_1	4.3_4	3.92[b]	$I_x=I_y=91.22$
	CCl_4	615	502	4.4_0	4.3_2		
	CS_2	668	539	4.6_1	4.4_1		
	n-C_6H_{14}	569	473	4.3_2	4.2_5		
CD_3CN	CCl_4	535	437	4.4_7	4.3_2		$I_x=I_y=106.8$

a) Calculated from the rotational constants taken from Ref. 20. b) Ref. 20. c) Ref. 21.

of the Lorenz-Lorentz relation, $\alpha/a^3=(n^2-1)/(n^2+2)$, we have[17,18]

$$\mu^* = \frac{(n^2+2)(2\varepsilon+1)}{3(2\varepsilon+n^2)}\mu_0. \qquad (6)$$

Since ε can be replaced by n_s^2 to a good approximation, Eq. 6 is also written as

$$\mu^* = \frac{(n^2+2)(2n_s^2+1)}{3(2n_s^2+n^2)}\mu_0. \qquad (7)$$

Since $\boldsymbol{\mu}^*$ will always be in the same direction as $\boldsymbol{\mu}_0$, it follows the rotation of the molecular framework as $\boldsymbol{\mu}_0$ does. Then the molecule in the solution absorbs the far-infrared radiation through the dipole moment of μ^*.

The μ^* values calculated from μ_0 using Eq. 7 are listed in Table 1. They are in good agreement with the observed μ values. Thus, the far-infrared absorptions observed in the present study can be explained almost wholly by the rotational motion of the $\boldsymbol{\mu}^*$ vector. It follows that the observed band shape corresponds directly to the Fourier transform of the reorientational correlation function of the molecule.

The observed μ value of HCl dissolved in CCl_4 was nearly equal to the μ_0 value,[16] in contrast with the cases in the present study. Since the molar volume of CCl_4 is considerably larger than that of HCl, the cavity radius in Onsager's model must be larger than that estimated from the actual molar volume of HCl. In this case the $f\cdot\alpha$ value becomes small, or n^2 approaches to unity, so that the μ^* value may be nearly equal to the μ_0 value.

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