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The Far-infrared Absorption Intensities and the Dipole Moments of Acetone and Dimethyl Sulfoxide in Solutions

Yusei Ohkubo* and Masao Kimura

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

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Synopsis. The effective dipole moments of acetone and dimethyl sulfoxide in nonpolar solutions were obtained from the far-infrared absorption intensities on the basis of an extended Onsager model with an eccentric point dipole.

Dipolar molecules in the liquid phase have absorptions in the far-infrared region[1–5] due to the rotational motion of the molecules and the temporary dipole moments induced by collision. However, the collision-induced absorption is generally much weaker than the dipolar absorption.[6] If the far-infrared absorption is attributed solely to the rotational motion of the molecule, the effective dipole moment can be obtained using Gordon's sum rule[7] after correcting for the internal-field effect.[8,9] In a previous study of CH_3I, $CHCl_3$, CH_2Cl_2, and CH_3CN in solutions,[5] the far-infrared absorption intensities were explained successfully by taking into account the internal-field effect and the internal moment[10] based upon Onsager's model. In the present study, far-infrared absorption intensities were measured for acetone and dimethyl sulfoxide (DMSO) in dilute C_6H_6, CCl_4, C_2Cl_4, and n-C_6H_{14} solutions. The observed intensities, however, cannot be interpreted by the same model as was employed in the previous study. Therefore, the model for the reaction field has been extended to a model with an eccentric dipole-location.

Experimental

The far-infrared spectra were measured at room temperature by means of an apparatus described previously.[5] Solutions were prepared from spectroscopic-grade reagents except for the deuterated compounds, which were already more than 99.6% pure when obtained from CEA and Merck. The concentration range was 0.06—0.17 M.

Results and Discussion

The absorption coefficients, $\sigma(\nu)$, of the solutes in nonpolar solvents are given by:

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

where ρ is the concentration (molecules cm^{-3}); l, the sample thickness (cm), and T_0 and T, the transmittances of the solvent and the solution respectively. The observed results are shown in Fig. 1, where the fine broken lines indicate the spectra profiles assumed in order to obtain the intensities, $A=\int\sigma(\nu)d\nu$. The value of A for each solution was determined by measurements at four concentrations. The results obeyed Beer's law. The A values were estimated, from the fluctuation of the four measurements, to be within ±3%. The systematic errors are due mainly to uncertainties in the assumed curves. The area of the assumed portion is 3—4% of the total area. Thus, the total experimental errors in A were estimated to be ±5% at most.

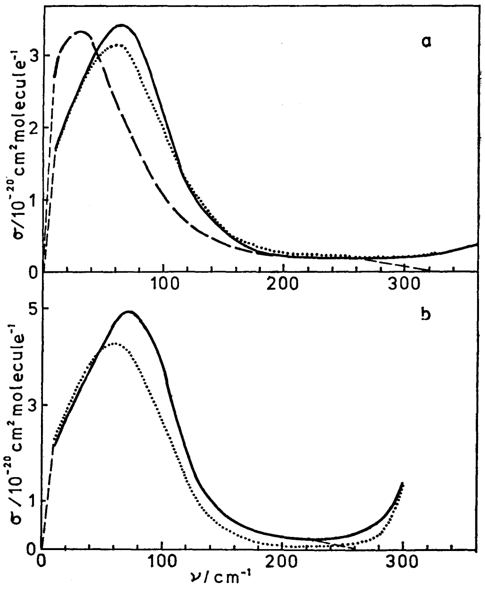

Fig. 1. a) Far-infrared absorption bands of $(CH_3)_2CO$ dissolved in CCl_4(——), in C_6H_6(······), and n-C_6H_{14} (----). b) Far-infrared absorption bands of $(CH_3)_2SO$ dissolved in CCl_4(——), and in C_6H_6(······).

The intensities, as corrected for the internal field effect, A_c, are given as:[8,9]

$$A_c = xA, \quad x = n_s\{[(n/n_s)^2+2]/(n^2+2)\}^2, \qquad (2)$$

where n and n_s are the refractive indices of the solute and the solvent respectively. For C_{2v} symmetric molecules, Gordon's sum rule is expressed by:[7]

$$A_c = (\pi\mu^2/3c^2)(1/I_x+1/I_y), \qquad (3)$$

where c is the velocity of light; μ, the effective dipole moment taken along the z axis, and I_x and I_y, the moments of inertia about the x and y axes respectively. The μ values, μ_I, obtained from Eq. 3 are shown in the fourth column of Table 1, together with the values of the moments of inertia and the permanent dipole moments in the gas phase, μ_0. The μ_I values for the H-compounds are in good agreement with those for the D-compounds, which have different moments of inertia. Furthermore, the μ_I values are about 10—30% larger than the μ_0 values for all the solutions.

In Onsager's model, the internal moment, μ^*_I, is expressed as:[10,11]

$$\mu^*_I = \mu_0(n^2+2)(2\varepsilon+1)/3(2\varepsilon+n^2), \qquad (4)$$

where ε is the dielectric constant of the uniform medium and can be replaced by n_s^2 to a good approximation. The μ^*_I values calculated from μ_0 are listed in the fifth column of Table 1. However, the μ_I

Table 1. Observed intensities and dipole moments[a)]

Solute	Solvent	A	μ_{I}	μ^*_{I}	μ_{II}	μ^*_{II}	μ_0	I[b)]
		10^{-19} cm mol^{-1}	D					10^{-40} g cm^2
$(CH_3)_2CO$	C_6H_6	34.6	3.6_5	3.2_6	3.4_8	3.4_2	2.93[c)]	$I_x=82.56$, $I_y=170.9$
	CCl_4	35.8	3.7_2	3.2_4	3.5_6	3.3_8		
	C_2Cl_4	33.1	3.5_7	3.2_6	3.4_0	3.4_2		
	n-C_6H_{14}	29.5	3.4_1	3.1_9	3.2_8	3.3_1		
$(CD_3)_2CO$	CCl_4	30.0	3.7_5	3.2_4	3.5_8	3.3_8		$I_x=99.09$, $I_y=209.2$
$(CH_3)_2SO$	C_6H_6	40.6	4.4_3	4.5_5	4.1_6	4.8_5	3.96[c)]	$I_x=119.3$, $I_y=198.9$
	CCl_4	51.1	5.0_0	4.5_1	4.7_1	4.7_9		
$(CD_3)_2SO$	C_6H_6	35.6	4.5_1	4.5_5	4.2_3	4.8_5		$I_x=139.2$, $I_y=241.0$
	CCl_4	43.4	5.0_1	4.5_1	4.7_2	4.7_9		

a) I: The simple Onsager model; II: The eccentric dipole model. b) Calculated from the rotational constants taken from Ref. 12. c) Ref. 13.

values are larger by about 10% or more than the μ^*_{I} values except for that of DMSO in the C_6H_6 solutions. Onsager's model was extended to a model with an ellipsoidal cavity and an eccentric point dipole.[11)] It turned out that, in nonpolar solvents, the magnitude of the reaction-field effect was almost independent of the cavity shape, but was significantly dependent on the position of the dipole in the cavity. For a molecule with an eccentric point dipole in a spherical cavity, the internal-field correction factor, x, and the internal moment, μ^*, are given by:[11)]

$$x = n_S[3\varepsilon/(2\varepsilon+1)(1-f\cdot\alpha)]^{-2}, \tag{5}$$

$$\mu^* = \mu_0/(1-f\cdot\alpha), \tag{6}$$

where:

$$f = (1/a^3)\sum_{m=1}^{\infty}[m^2(m+1)(\varepsilon-1)/(m+m\varepsilon+\varepsilon)](s/a)^{2m-2}, \tag{7}$$

and where α is the average polarizability of the molecule, a is the radius of the cavity, and s is the distance from the center of the cavity to the point dipole. The parameter, s/a, is a measure of the eccentricity of the position of the dipole. α and a are related in a good approximation by:[10)]

$$\alpha = a^3(n^2-1)/(n^2+2). \tag{8}$$

If $s=0$, Eqs. 5 and 6 reduce to Eqs. 2 and 4. The μ and μ^* values thus calculated with $s/a=0.3$, μ_{II} and μ^*_{II}, are shown in Table 1. There is no other means to confirm the propriety of the s/a value. However, a good agreement between μ_{II} and μ^*_{II} is obtained except for the C_6H_6 solutions of DMSO. For acetone, the internal moments are the least in the hexane solutions and almost the same in the other solutions, reflecting the dielectric constants of the solvents. Unlike as in the results for acetone, the μ_{II} value in the C_6H_6 solutions of DMSO is distinctly smaller not only than that in the CCl_4 solutions, but also than the μ^*_{II} value. There seems to exist a short-range ordering of C_6H_6 molecules around a DMSO molecule, such as the alignment of benzene rings perpendicular to the direction of the dipole moment of DMSO. The reaction field becomes weak because the axial polarizability of benzene molecules is smaller than the average polarizability, and so a μ_{II} value smaller than the μ^*_{II} value is obtained.

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References

1) P. Datta and G. M. Barrow, *J. Chem. Phys.*, **43**, 2137 (1965).

2) M. Davies, G. W. F. Pardoe, J. Chamberlain, and H. A. Gebbie, *Trans. Faraday Soc.*, **66**, 273 (1970).

3) M. W. Evans, *Spectrochim. Acta, Part A*, **30**, 79 (1974).

4) Y. Ohkubo, S. Ikawa, and M. Kimura, *Chem. Phys. Lett.*, **43**, 138 (1976).

5) K. Sato, Y. Ohkubo, T. Moritsu, S. Ikawa, and M. Kimura, *Bull. Chem. Soc. Jpn.*, **51**, 2493 (1978).

6) K. Fujiwara, S. Ikawa, and M. Kimura, *Bull. Chem. Soc. Jpn.*, **52**, 227 (1979).

7) R. G. Gordon, *J. Chem. Phys.*, **38**, 1724 (1963).

8) W. C. Mallard and J. W. Straley, *J. Chem. Phys.*, **27**, 877 (1957).

9) W. B. Person, *J. Chem. Phys.*, **28**, 319 (1958).

10) H. Fröhlich, "Theory of Dielectrics," 2nd ed, Oxford University Press, London (1960).

11) C. J. F. Böttcher, "Theory of Electoric Polarization," 2nd ed, Elsevier, Amsterdam (1973).

12) Landort-Börnstein, "Numerical Data and Functional Relationships," New Series, II/4, Springer, Berlin (1967).

13) A. L. McClellan, "Tables of Experimental Dipole Moments," Rahara Enterprises, El Cerrito, Cal. (1974), Vol. 2.