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Shapes of Fundamental Bands of Liquid Carbon Disulfide. Vibrational and Reorientational Relaxations

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The shapes and intensities of the fundamental bands, ν_2 (the CSC bending) and ν_3 (the C–S antisymmetric stretching), were measured for liquid carbon disulfide and its chloroform solutions. The intensity data were corrected for the effect of the dielectric field at each frequency. The analyses of the ν_2 and ν_3 bands indicate that the band-widths of liquid carbon disulfide can not be explained only in terms of reorientational relaxation. It is also shown that the vibrational relaxation of the resonance type can well explain the concentration dependence of the observed band-widths. The magnitudes of the vibrational and reorientational relaxations obtained from the band-shape analyses are given. It is emphasized that the measurement of the absolute intensity is indispensable for the analyses of the infrared-band shapes of condensed phases.

In recent years it has been realized that the band shapes of infrared absorption spectra of liquid should yield much information about molecular motion. The descriptions of Shimizu[1] and Gordon[2] have encouraged infrared spectroscopists interested in the rotational motions of molecules in the liquid phase. However, progress has been rather disappointing because of many problems, both experimental[3–5] and theoretical. A question has arisen about the analyses of band shapes by the use of reorientational-relaxation theories, that is, it has been questioned whether or not the half band-widths of the infrared absorption spectra of liquids can be completely explained in terms of the reorientational relaxations. One of the criteria is whether or not the half-widths associated with the same symmetry species of a molecule have the same value. In fact, the fundamental bands of methyl cyanide or carbon disulfide have been found to be too strange to be explained only in terms of the reorientational relaxations.[6,7]

The present report will be concerned with observations of the band shapes for liquid carbon disulfide and with the introduction of vibrational relaxation to explanations of the band-widths. The theoretical and experimental evaluation of vibrational relaxation in liquids is under active discussion.[8–13] We will tentatively follow the idea of Valiev[13] in the present work.

Theoretical

The intensity distribution of an infrared absorption band, $I(\omega)$, has been shown to be a Fourier transform of a dipole correlation function, $\Phi(t)$:[1,2]

$$I(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}\Phi(t)e^{-i\omega t}dt \tag{1}$$

and:

$$\begin{aligned}\Phi(t)&=\int_{-\infty}^{\infty}I(\omega)e^{i\omega t}d\omega\\&=\langle\boldsymbol{M}(0)\boldsymbol{M}(t)\rangle_{av}\end{aligned} \tag{2}$$

where ω is the angular frequency displacement from a band origin, $\boldsymbol{M}(t)$ is the Heisenberg operator of the transition dipole moment of the vibration concerned, and $\langle\ \rangle_{av}$ means an ensemble average over the equilibrium distribution. If we assume that the mechanisms of the vibrational and reorientational relaxation processes are not correlated, then the ensemble average can be taken separately with respect to the two processes:[14]

$$\Phi(t)=\Phi_v(t)\Phi_r(t) \tag{3}$$

where $\Phi_v(t)$ and $\Phi_r(t)$ refer to the vibrational and reorientational correlation functions respectively.

If both $\Phi_v(t)$ and $\Phi_r(t)$ are assumed to be exponential functions, $\Phi(t)$ is expressed as:

$$\Phi(t)=e^{-|t|/\tau} \tag{4}$$

Therefore:

$$(1/\tau)=(1/\tau_v)+(1/\tau_r) \tag{5}$$

where τ_v and τ_r are the vibrational and reorientational relaxation times respectively. The intensity distribution function, $I(\omega)$, is calculated from Eqs. (1) and (4):

$$I(\omega)=\frac{1}{\pi}\frac{(1/\tau)}{(1/\tau)^2+\omega^2} \tag{6}$$

Thus, the half band-width of the absorption band, $\Delta\nu_{1/2}$, is given by:

$$\frac{1}{2}\Delta\nu_{1/2}=(1/\tau_v)+(1/\tau_r) \tag{7}$$

Equation (7) means that a total half-width of an absorption band is a sum of the vibrational and reorientational widths. In some cases the assumption of an exponential function for $\Phi_v(t)$ or $\Phi_r(t)$ may not be appropriate. This can be checked by seeing whether

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[1] H. Shimizu, *J. Chem. Phys.*, **43**, 2453 (1965).

[2] R. G. Gordon, *ibid.*, **43**, 1307 (1965).

[3] T. Fujiyama, J. Herrin, and B. L. Crawford, Jr., *Appl. Spectrosc.*, **24**, 9 (1970).

[4] B. L. Crawford, Jr., A. C. Gilby, A. A. Clifford, and T. Fujiyama, *Pure and Applied Chemistry*, **18**, 373 (1969).

[5] R. P. Young and R. N. Jones, *Chem. Rev.*, **71**, 219 (1971).

[6] C. Alliot, M. Cameo, and J. Vincent-Geisse, *C. R. Acad. Sci., Paris, Ser. B*, **266**, 391 (1968).

[7] T. Fujiyama and B. L. Crawford, Jr., The lecture presented in Gordon Conference (1969).

[8] L. Landau and E. Teller, *Physik. Z. Sowjetunion*, **10**, 34 (1938).

[9] A. Litoviz, *J. Chem. Phys.*, **26**, 469 (1957).

[10] M. Fixman, *ibid.*, **34**, 369 (1961).

[11] R. Zwanzig, *ibid.*, **34**, 1931 (1961).

[12] B. J. Berne, J. Jortner, and R. G. Gordon, *ibid.*, **52**, 439 (1970).

[13] K. A. Valiev, *Opt. Spectrosc.*, **11**, 253 (1961).

[14] S. Bratoz, J. Rios, and Y. Guissani, *J. Chem. Phys.*, **52**, 439 (1970).

or not the observed band shapes are of the Lorentzian type of Eq. (6).

If we assume that the contribution of the vibrational relaxation to a band shape is much smaller than that of the reorientational relaxation, $\Phi(t)$ may be set equal to a reorientational relaxation function, $\Phi_r(t)$. Then the observed half-width, $\Delta\nu_{1/2}$, of the band can be simply related to τ_r by:

$$\frac{1}{2}\Delta\nu_{1/2} = 1/\tau_r \tag{8}$$

If we designate the molecular fixed axes by i (where $i=x, y$, and z), the physical meaning of $(1/\tau_r)^i$ is the rate of reorientation of a molecule around the i-th axis. For example, consider the parallel and perpendicular bands of a linear or symmetric-top molecule. For a parallel band,

$$\frac{1}{2}\Delta\nu_{1/2}^{(p)} = 2(1/\tau_r)^x \tag{9a}$$

and for a perpendicular band,

$$\frac{1}{2}\Delta\nu_{1/2}^{(s)} = (1/\tau_r)^x + (1/\tau_r)^z \tag{9b}$$

If absorption-band shapes of both parallel and perpendicular types are observed, we can determine τ_r^x and τ_r^z from Eq. (9) provided that the contributions of the vibrational relaxation are negligibly small.

On the other hand, when the contribution of the vibrational relaxation is predominant, an observed half-width, $\Delta\nu_{1/2}$, is directly related to the vibrational relaxation time, τ_v. At first, let us confine ourselves to one type of vibrational relaxation—the transfer of vibrational energy from a vibrationally-excited molecule to its surroundings by resonance between oscillators of the same type. For this particular case, Valiev[13] evaluated the probability per unit time that an excited molecule undergoes a transition $n \to n-1$. Some further modification of Eq. (24) of the reference leads to, for a fundamental band:

$$W_{1-0} = \frac{c}{2\pi}\sqrt{\rho\frac{c_m}{3W_m}}S\cdot\Gamma \tag{10}$$

where c is the velocity of light (cm/sec); ρ, the density of a solute itself (g/cm^3); W_m, the molar weight of a solute (g/mol); c_m, the molar concentration of a solution (mol/cm^3), and Γ, the absolute intensity of a vibration band (cm^2/mol). It is found that n_i' of Eq. (24) of the reference should be replaced by a factor, S, defined by:

$$S = \frac{1}{2}\left(1 + \frac{1}{\tanh(\hbar\omega_i/2kT)}\right) \tag{11}$$

This arises from the fact that, in the derivation of Eq. (24) of the reference,[13] only one transition, $n'-1 \to n'$, is taken into account for the surrounding molecules. Actually, all the transitions, $0\to1$, $1\to2$, $2\to3$, ··· *etc.*, should be considered. Moreover, Valiev multiplies Eq. (10) by the probability of a molecule being in a n-th vibrational state, or by the Boltzmann factor. However, as the quantity we need is not a joint probability but a condition probability that the vibrational energy of a molecule relaxes if it is in a state n at time zero, multiplication by the Boltzmann factor is not necessary. A little observation of Eq. (10) leads to the conclusion that the vibrational width depends on both the vibrational intensity and the molar concentration of a solute. In the case of liquid carbon disulfide, where $W_m=76.14$, $\rho=1.2634$, and $c_m=\rho/W_m$, an absolute intensity of 4×10^3 cm^2/mol corresponds to 1 cm^{-1} of the W_{1-0} of Eq. (10) if S is put equal to 1.

In case where the contributions of vibrational and reorientational relaxations to the band shapes are comparable, the explanation of a half-width is not straightforward. However, it is very probable that the rate of reorientation depends little upon the molar concentration. If so, observations of half-widths for various concentrations can be useful in identifying vibrational and reorientational widths, because a vibrational width is concentration-dependent.

Experimental

The carbon disulfide and chloroform used in the present work were commercial products. Prior to each observation, samples were purified following the procedures described in a reference.[15]

The infrared spectra were recorded by the use of a Perkin-Elmer 112G single-beam infrared spectrometer and a Perkin-Elmer 12C single-beam infrared spectrometer mounted with a CsBr prism. These spectrometers had been carefully modified to eliminate the effect of stray light or thermal emission originating from the spectrometers themselves. The spectrometers were operated with a resolution of about 2 cm^{-1} and at room temperature (23°C). The thicknesses of the sample cell were determined by means of the interference fringes. The observed spectra of ν_2 (the CSC bending vibration) of liquid carbon disulfide are shown in Fig. 1. The spectra were corrected for the dielectric field using the method described in the Appendix. Measurements were also made for ν_2 of carbon disulfide in chloroform solutions (80, 60, 40, 20, and 0.6 mol%).

The spectra for the ν_3 (the C–S antisymmetric stretching) of carbon disulfide were recorded only for dilute solutions because of its very strong intensity. For higher concentrations, the ATR data observed by William Krueger of the University of Minnesota were used.[16] In Fig. 2, the observed

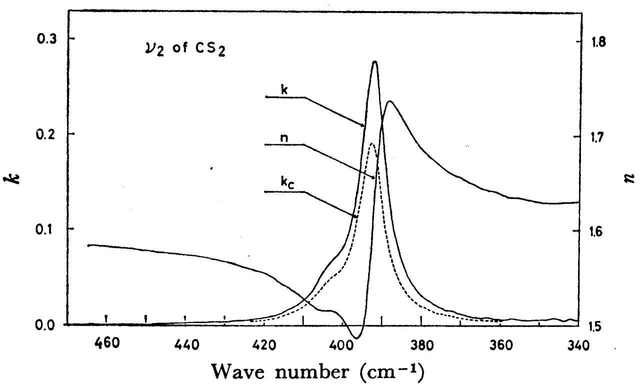

Fig. 1. Absorption and refractive indices for ν_2 band of liquid carbon disulfide. k: absorption index, n: refractive index, k_c: corrected absorption index.

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15) "Organic Solvents" Clarendon Press, Oxford, (1935).

16) W. C. Krueger, Thesis submitted to the University of Minnesota (1966).

spectra for dilute solutions are illustrated. In this case, the dielectric-field correction was rather straightforward, because the refractive indices are also available from the ATR data. The effect of the slit function on the observed band shapes was ascertained to be small for both ν_2 and ν_3.

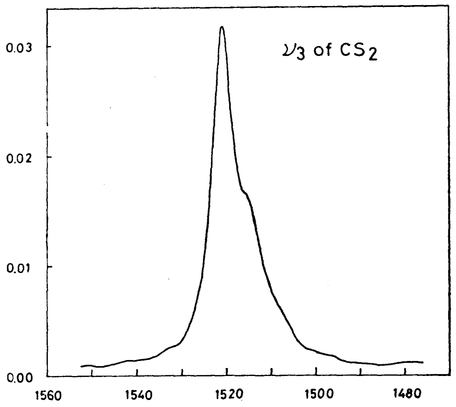

Fig. 2. Absorption index for ν_3 band of carbon disulfide in chloroform solution (0.6 mol%).

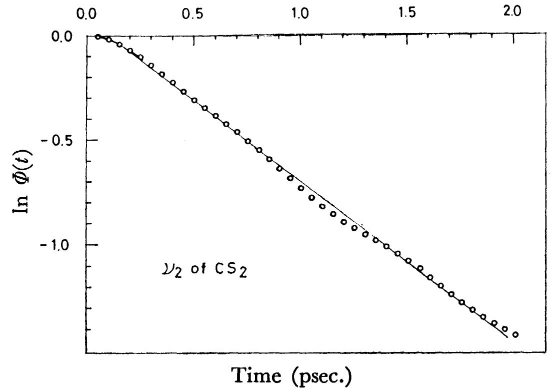

Fig. 3. Logarithmic time-correlation function for ν_2 band of liquid carbon disulfide.

Discussion

Band Shape and Evaluation of Half-band-width. As both ν_2 and ν_3 suffer considerably from the effect of overlapping with other bands, especially in chloroform solutions, too detailed discussions of the band shapes might be misleading, especially for the wing parts of the bands. It may be concluded, however, that the band shape of the ν_2 of liquid carbon disulfide follows a good Lorentzian-type function. Figure 3 shows the logarithmic time-correlation function calculated from the observed $I(\omega)$ through Eq. (2). It may be seen that the logarithmic plot of the time-correlation function of ν_2 falls beautifully on a straight line. This justifies the assumption used in the derivation of Eq. (4) and, at the same time, indicates that free rotational reorientation does not play an important role in the relaxation process of liquid carbon disulfide.

It is known that the ν_3 band of carbon disulfide is overlapped with the hot band, $\nu_2+\nu_3-\nu_2$.[17] It may be seen from Fig. 2 that the separation of these two bands is not large enough for us to evaluate the half-band-width directly from the observed spectra. The situation is even more serious for higher concentrations. Therefore, we resolved the bands into two Lorentzian-type bands by means of numerical calculations. It seems reasonable to assume that the shapes of these bands are of a Lorentzian type because of the conclusion obtained from the ν_2 band.

The evaluated half-band-widths for ν_2 and ν_3 are listed in Table 1, together with the observed absolute intensity values.

Analysis of Half-band-width. It may be seen from Table 1 that the half-width of the ν_3 band changes its magnitude approximately from 5 to 20 cm^{-1} as the concentration of the chloroform solution increases, while that of ν_2 takes a constant value of about 7 cm^{-1}.

If the band-widths are treated as being completely determined by the reorientational motions of the solute, then the reorientational relaxation times around the principal axes can be evaluated from Eqs. (8) and (9):

TABLE 1. CONCENTRATION DEPENDENCE OF BAND SHAPE PARAMETERS.
(Numbers in parentheses indicate standard errors.)

	Γ 10^3 cm^2/mol	mol%	$W_{obs}=\frac{1}{2}\Delta\nu_{1/2}$ cm^{-1}	W_v cm^{-1}	$W_{obs}-W_v$ cm^{-1}
ν_2	1.74 (0.06)	100	3.95 (0.04)	0.48 (0.00)	3.47 (0.04)
		80	3.69 (0.05)	0.42 (0.00)	3.27 (0.05)
		60	3.79 (0.04)	0.37 (0.00)	3.42 (0.04)
		40	3.58 (0.04)	0.27 (0.00)	3.31 (0.04)
		20	3.62 (0.08)	0.21 (0.00)	3.41 (0.08)
		0.6	0.42 (0.09)	0.03 (0.00)	3.39 (0.09)
ν_3	33.32 (1.37)	100	10.3 (0.5)	8.07 (0.32)	2.23 (0.82)
		80	9.67 (0.47)	7.01 (0.27)	2.66 (0.74)
		60	8.74 (0.42)	5.89 (0.21)	2.85 (0.63)
		40	7.50 (0.36)	4.67 (0.16)	2.83 (0.52)
		20	5.73 (0.28)	3.24 (0.11)	2.49 (0.39)
		0.6	3.20 (0.08)	0.35 (0.02)	2.67 (0.10)

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17) D. F. Smith, Jr. and J. Overend, *Spectrochim. Acta*, **26A**, 2269 (1970).

$$(1/\tau_r)^x = \frac{1}{4}\Delta\nu_{1/2}^{(\nu_3)}$$

and:

$$(1/\tau_r)^z = \frac{1}{4}\left(2\Delta\nu_{1/2}^{(\nu_2)} - \Delta\nu_{1/2}^{(\nu_3)}\right) \tag{12}$$

where $\Delta\nu_{1/2}^{(\nu_2)}$ and $\Delta\nu_{1/2}^{(\nu_3)}$ are the half-widths of ν_2 and ν_3 respectively. The reciprocal relaxation times thus obtained are shown in Fig. 4 (designated as "apparent $(1/\tau_r)$"). The results are peculiar in showing that:

(1) The $(1/\tau_r)^x$'s are larger than the $(1/\tau_r)^z$'s for all the concentrations, which means that carbon disulfide rotates around the molecular axis much slower than it does around the axis perpendicular to the molecular axis, and

(2) $(1/\tau_r)^z$ becomes negative for the higher concentrations. Thus, it may be concluded that the band-widths are not determined only by the reorientational relaxation.

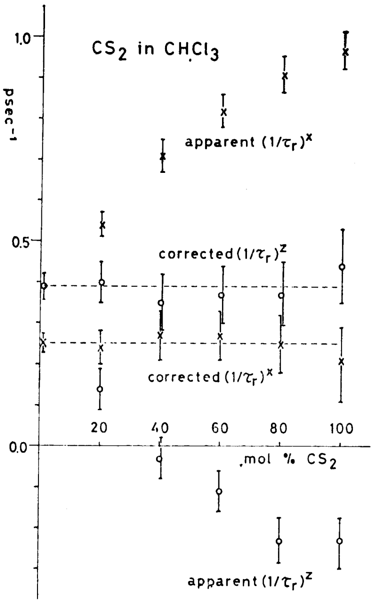

Fig. 4. Reciprocal reorientational relaxation times for carbon disulfide in chloroform solutions. Vertical lines indicate limit of experimental errors.

Let us consider next the effect of the vibrational relaxation of the resonance type. The vibrational relaxation width, W_v, is calculated from Eq. (10) and the relation:

$$W_v = (1/\tau_v) = W_{1-0} \tag{13}$$

The results thus calculated are summarized in Table 1. It may be seen from the table that the calculated W_v's are smaller than the observed half-widths. If we assume that the contributions of vibrational and reorientational relaxations to the band-widths are comparable and that the difference between the observed band-width and the calculated W_v value originates from the reorientational relaxation, then the reciprocal reorientational relaxation time can be calculated from Eq. (12). The results are visualized in Fig. 4 (designated as "corrected $(1/\tau_r)$").

Now we can see from Fig. 4 that the corrected $(1/\tau_r)$ does not vary over the entire concentration range, $(1/\tau_r)^z$ being always greater than $(1/\tau_r)^x$. The results seem reasonable in the sense that the molecule rotates around the molecular axis more rapidly than it does around the axis perpendicular to the molecular axis. We are not going to assert too strongly that the difference between the observed band-width and W_v is due to the reorientational relaxation only. However, the constancy of the reciprocal relaxation times for all the concentrations seems to support this idea, for the reorientational relaxation time is expected to be rather independent of the concentration.

TABLE 2. CONCENTRATION DEPENDENCE OF RECIPROCAL REORIENTATIONAL RELAXATION TIMES.
(Numbers in parentheses indicate standard errors.)

mol%	$(1/\tau_r)^x$ psec^{-1}	$(1/\tau_r)^z$ psec^{-1}
100	0.21 (0.08)	0.44 (0.09)
80	0.25 (0.07)	0.37 (0.08)
60	0.27 (0·06)	0.37 (0.07)
40	0.27 (0.06)	0.35 (0.07)
20	0.24 (0.04)	0.40 (0.05)
0.6	0.25 (0.01)	0.39.0.03)

Conclusion

The mechanism of reorientation is mainly governed by the diffusional reorientation, rather than by the free rotation of the carbon disulfide molecule. This can be concluded from the band shape of ν_2.

It is evident from the analyses of the ν_2 and ν_3 bands that the band-widths of liquid carbon disulfide can not be explained only in terms of the reorientational relaxation. It can also be concluded that the vibrational relaxation of the resonance type can well explain the concentration dependence of the band-widths. The differences between the observed band-widths and W_v's may be ascribed to the reorientational relaxation.

The reciprocal reorientational relaxation times are calculated to be:

$$(1/\tau_r)^x \simeq 0.25 \text{ (psec}^{-1})$$

and: $$(1/\tau_r)^z \simeq 0.39 \text{ (psec}^{-1})$$

This means that carbon disulfide rotates by these rates around the molecular axis (z-axis) and the perpendicular axis (x,y-axes) respectively.

Appendix Dielectric-field Correction for Transmittance Data

It has previously been pointed out that dielectric-field correction is indispensable for band-shape analyses of condensed phases.[4,18,19] For this correction, a formula has been presented expressing the corrected absorption index, k_c, in terms of the observed absorption index, k, and the refractive index, n, assuming the Lorentz field for the internal field.[18] When k and n are measured simultaneously (*e.g.*, by the ATR method), k can be corrected at

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18) A. A. Clifford and B. L. Crawford, *J. Phys. Chem.*, **70**, 1536 (1965).

19) T. Fujiyama and B. L. Crawford, Jr., *ibid.*, **72**, 2174 (1968).

each frequency. On the other hand, when the measurement of an absorption band is carried out by the use of the transmittance method, the correction can not be made straightforwardly. In this case, however, the following method may be conveniently used.

As is well known, n and k are related by the Kramers-Kronig dispersion formula:

$$n(\nu) = n_0 + \frac{2}{\pi}\int_0^\infty \frac{k(\nu')\nu'}{\nu'^2-\nu^2}\mathrm{d}\nu'$$

Therefore, when reliable data of $k(\nu)$ are available, $n(\nu)$ can be calculated by this formula, and then $k(\nu)$ can be corrected at each frequency. In doing so, the most difficult problem is to determine the constant n_0. Generally, n_0 is not equal to the refractive index in the visible region or to the square root of the static dielectric constant. Furthermore, n_0 may take different values for different absorption bands. There is, in fact, no general way to estimate n_0. The only way to override this difficulty is to observe $n(\nu)$ experimentally for at least one point near the absorption band. Once n_0 is determined for an absorption band, the n_0 corresponding to the next lower-frequency band can be estimated as follows: Let ν of Kramers-Kronig's formula go to infinity; then

$$n(\nu) \to n_0 \quad (\nu \to \infty)$$

and if ν goes zero,

$$n(\nu) \to n_0 + \frac{2}{\pi}\int_0^\infty \frac{k(\nu')}{\nu'}\mathrm{d}\nu' \quad (\nu \to 0)$$

$$\simeq n_0 + (c_m\Gamma/2\pi^2\nu_0)$$

where ν_0 is the resonance frequency in cm^{-1}, and Γ, the absolute intensity in cm^2/mol. Thus, the increment in n_0 by this absorption band, Δn, is $c_m\Gamma/2\pi^2\nu_0$. $n_0+\Delta n$ may be considered to be the n_0 for the next-lower-frequency band. In Fig. 1, the $n(\nu)$ curve is calculated using $n_0=1.6000\pm 0.0046$, which is estimated in this way from the $n(\nu)$ and $k(\nu)$ curves of ν_3 as observed by the ATR method.

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