Absorption Band Shapes and Molecular Reorientation of Liquid Methyl Cyanide

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The shapes and intensities of the fundamental bands of liquid methyl cyanide were observed by conventional transmittance method. Using the refractive indices observed by the ATR method, the observed absorption indices were corrected for the dielectric-field effect. The band shapes were analyzed from the point of view of moment analysis or correlation-function analysis. The results indicate that the shapes of a_1-type vibrations are good Lorentzian shapes, while those of the e-type can be explained as superpositions of Lorentzian and Gaussian functions. It is also found that the band-widths of the e-type vibrations were quite different from each other. Taking into account the effect of vibration-rotation interaction on the band-widths, the disagreement could be explained well. From the analyses of the band shapes of ν_7 and ν_8, the life-time function, $\phi(t)$, was obtained; it represents the decay of the fraction of freely-rotating molecules.

It has been widely accepted that an infrared absorption band shape of a liquid molecule is the Fourier transform of a dipole-correlation function, as was first pointed out theoretically by Shimizu[1] and Gordon.[2] Since a dipole-correlation function describes the time correlation of a transition-dipole moment related to the vibrational transition concerned, precise measurements of band shapes are expected to afford information about the anisotropic rotational motion of molecules in liquids. Based upon this principle, a number of experimental studies have been undertaken in order to elucidate the nature of molecular motions in liquids. Some of them have achieved fairly successful results,[3] but various difficulties have confronted spectroscopists at the same time. One of the most striking of them is seen in the spectra of liquid carbon disulfide; that is, an apparent reorientational relaxation time has a negative value if we follow the theory literally. It has been shown that this peculiarity can be resaonably explained by taking into account the contribution of vibrational relaxation to the observed band-widths.[4]

Another difficulty is found in the spectra of liquid methyl cyanide; that is, the shapes or half-widths of absorption bands belonging to the same symmetry species do not agree with each other, as was first pointed out by Vincent *et al.*[5] Vibrational transitions of particular symmetry species have their transition moments in the same direction in the molecular-fixed coordinate system; therefore, the corresponding correlation functions must be the same. No theoretical explanation of these experimental results had been found until Yamashita and Shimizu recently emphasized the effect of vibration-rotation interaction on the band-widths.[6] They calculated the change in a correlation function on varying a Coriolis constant, ζ, and showed that a correlation function decays more rapidly with an increase in $(1-\zeta)$. They also presented algebraic expressions of the second and fourth moments of vibrational bands for symmetric-top molecules, where a Coriolis coupling constant is explicitly included.

In the present work, an attempt is made to interpret the peculiarity observed for the band shapes of liquid methyl cyanide using the idea of Yamashita and Shimizu. An attempt is also made to describe the details of molecular reorientation quantitatively and to establish a general procedure for obtaining rotational diffusion constants from observed spectral information.

Experimental

The methyl cyanide used in the present work was a commercial product and was used after fractional distillation. No trace of any impurity was found in the infrared spectra covering the range of 400—4000 cm^{-1}.

All the infrared absorption spectra except for that of ν_8 were recorded by the use of a Perkin-Elmer 112G single-beam infrared spectrometer. A Perkin-Elmer 12C sinlge-beam infrared spectrometer mounted with a CsBr prism was used for the measurement of ν_8. These spectrometers had been carefully modified to eliminate the effect of stray light or thermal emission originating from the spectrometers themselves. The photometric effects and the nature of the noise spectra have also been thoroughly studied for these particular spectrometers.[7] The spectrometers were operated under a resolution of about 2 cm^{-1} and at room temperature (25°C). The effect of the finite slit-width on the observed band shapes was ascertained to be very small.

It has been recognized that an ATR method has many advantages for the precise measurements of the optical constants of liquid samples.[8] At the same time, the method is not particularly powerful for the study of absorption bands with weak intensities. Though the absorption bands of methyl cyanide were measured by the use of the transmittance method in this work, the agreement of the present data and those of the ATR method[9] was found to be excellent, probably because the absorption intensities of methyl cyanide are rather weak.

The observed light-energy distribution curve, $I(\nu)$ and $I_0(\nu)$, were reduced to the absorption index curve, $k(\nu)$, through the relation:

1) H. Shimizu, *J. Chem. Phys.*, **43**, 2453 (1965).
2) R. G. Gordon, *ibid.*, **43**, 1307 (1965).
3) C. F. Favelukes, A. A. Clifford, and B. L. Crawford, Jr., *J. Phys. Chem.*, **72**, 962 (1968); T. Fujiyama and B. L. Crawford, Jr., *ibid.*, **73**, 4040 (1969).
4) M. Kakimoto and T. Fujiyama, This Bulletin **45**, 2970 (1972).
5) C. Alliot, M. Cameo, and J. Vincent-Geisse, *C. R. Acad. Sci. Paris, Ser. B*, **266**, 391 (1968).
6) T. Yamashita and H. Shimizu, Lecture in Symposium on Molecular Structure, Tokyo (1970).
7) T. Fujiyama, Ph-D thesis submitted to the University of Tokyo (1966).
8) B. L. Crawford, Jr., A. C. Gilby, A. A. Clifford, and T. Fujiyama, *Pure Appl. Chem.*, **18**, 373 (1969).
9) T. Fujiyama and B. L. Crawford, Jr., The Lecture presented in Gordon Conference (1969).

$$k(\nu) = \frac{1}{4\pi l\nu} \ln(I_0(\nu)/I(\nu)) \quad (1)$$

where ν is the wave number in cm^{-1} and l is the thickness of the sample cell in cm. The thickness of the sample cell was determined by the interference-fringe method.

The observed $k(\nu)$ curves were corrected for the dielectric-field effect[10] using the observed $k(\nu)$ curve and the refractive index data obtained by the ATR method.[9] The observed $k(\nu)$ and/or the corrected $k_c(\nu)$ curves are shown in Figs. 1 through 4, 7, and 8. As may be seen from Fig. 1, for example, the effects of the dielectric field on the band shape are very small for these weak absorption bands. Throughout the following sections, the intensity distribution function, $I(\omega)$, should be understood as a normalized function of $k(\nu)$ and/or $k_c(\nu)$.

It is ascertained that the effects of the vibrational relaxation of the resonance type[4] are negligibly small for all the observed bands of methyl cyanide because of their weak intensities. The experimental fact that the shapes of ν_4 and ν_7 do not change essentially in a carbon tetrachloride solution (4 wt%) is another piece of evidence for this point of view.

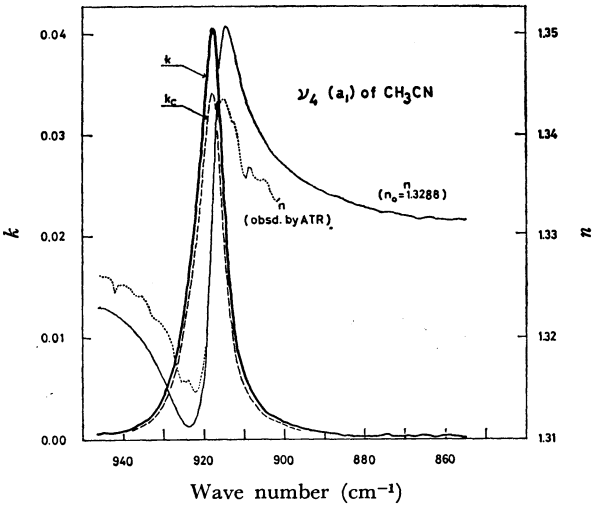

Fig. 1. $\nu_4(a_1)$ of liquid methyl cyanide. k: observed absorption index, n(solid line): refractive index calculated from k through Kramers-Kronig's formula, n(dotted line): refractive index observed by ATR method, k_c: corrected absorption index.

Discussion

Half-band-width. The half-band-widths, $\Delta\nu_{1/2}$'s, estimated from the observed $k_c(\nu)$ curves are summarized in Table 1. There is a relatively large uncertainty as to the $\Delta\nu_{1/2}$-values of ν_5 and ν_6 because they overlapped other bands considerably. It may clearly be seen from the table that the $\Delta\nu_{1/2}$'s of absorption bands

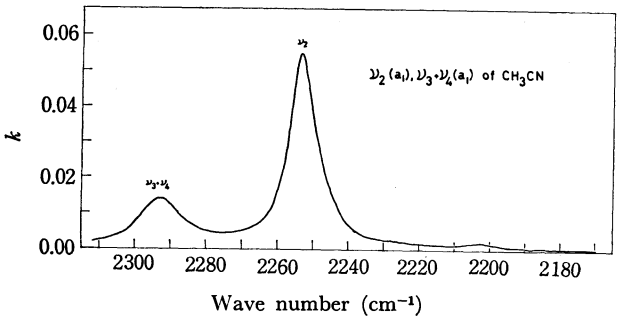

Fig. 2. Absorption index curve for $\nu_2(a_1)$ and $\nu_3+\nu_4(a_1)$ of liquid methyl cyanide.

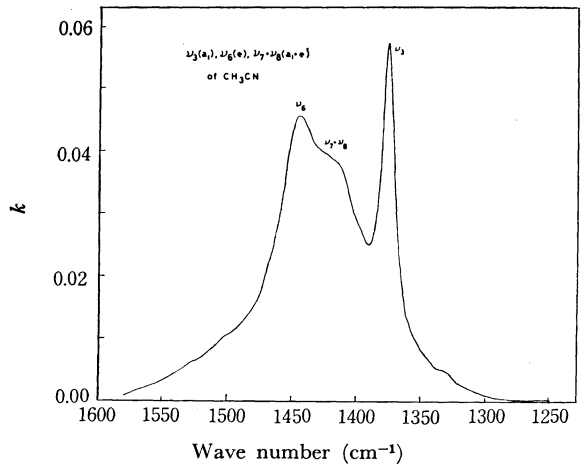

Fig. 3. Absorption index curve for $\nu_3(a_1)$ and $\nu_6(e)$ of liquid methyl cyanide.

Table 1. Spectral parameters of liquid methyl cyanide.

Γ is observed intensity. Γ_c is the intensity corrected for dielectric-field. Γ_{PW} is obtained from Γ through Polo-Wilson's formula.[19] Numbers in parentheses indicate the limits of experimental error.

	$\Delta\nu_{1/2}$ cm^{-1}	ν_0 cm^{-1}	Γ cm^2/mole	Γ_c cm^2/mole	Γ_{PW} cm^2/mole	ζ	$(1-\zeta)$
$\nu_1(a_1)$	15	2943.6	77(35)				
$\nu_2(a_1)$	8	2253.0	517(34)				
$\nu_3(a_1)$	12	1376.0	580(92)				
$\nu_4(a_1)$	8	918.4	329(24)	277(18)	277		
$\nu_2+\nu_4(a_1)$	13	3164	70(34)				
$\nu_3+\nu_4(a_1)$	14	2293.1	185(57)				
$\nu_5(e)$	40	3006	486(95)			0.062	0.938
$\nu_6(e)$	40	1443	2411(477)			−0.305	1.305
$\nu_7(e)$	23	1039.1	955(43)	806(35)	807	0.422	0.578
$\nu_8(e)$	10	379.0	699(49)	618(42)	606	0.88	0.12
$2\nu_8(a_1+e)$	18	748.8	315(13)	265(11)	266		

10) A. A. Clifford and B. L. Crawford, Jr., *J. Phys. Chem.*, **70**, 1536 (1966).

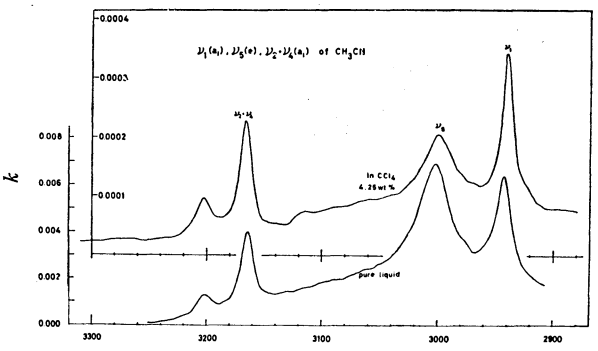

Fig. 4. Absorption index curves for $\nu_1(a_1)$ and $\nu_5(e)$ of methyl cyanide in pure liquid and carbon tetrachloride solution (4 wt%).

belonging to the same symmetry species do not agree with each other, especially for those of the *e*-type.

The observed values of Coriolis constants, ζ's, reported in the references[11,12] are also included in Table 1. It can quickly be observed in the table that there is apparent correlation between the $\Delta\nu_{1/2}$'s and the ζ's; this qualitatively coincides with the conclusion of Yamashita and Shimizu[6] that $\Delta\nu_{1/2}$ becomes larger with an increase in $(1-\zeta)$.

Moment Analysis and Mechanism of Molecular Reorientation. Corresponding to an absorption band's shape, $I(\omega)$, its n-th moment, M_n, is defined as [2,13]:

$$M_n = \int_{-\infty}^{\infty} I(\omega)\omega^n d\omega \qquad (2)$$

where ω is the angular frequency displacement from a band origin and where $I(\omega)$ is normalized to unity. Among the moments, the second moment, M_2, is the most important in the present discussion. As has been emphasized by Jones *et al.*,[14] the plotting of a second moment of an absorption band against its integration range is a useful tool in seeing if the band shape is a Lorentzian or a Gaussian function. This arises from the fact that a second moment plotted against the integration range diverges if $I(\omega)$ is a Lorentzian function, while it converges to a definite value if $I(\omega)$ is a Gaussian function. From the viewpoint of molecular rotation, a Gaussian band shape corresponds to a free-rotor model, while a Lorentzian band shape corresponds to a model of diffusional reorientation.[15]

The second-moment plottings for the bands of the a_1-type (ν_2 and ν_4) and of the *e*-type (ν_7 and ν_8) are shown in Figs. 5 and 6 respectively. It may be seen from the figures that the second moments of a_1-type bands go to infinity as the integration range increases, while those of *e*-type bands seem to converage to certain values. These facts indicate that the bands of the a_1-type have Lorentzian shapes, while those of *e*-type do not have simple Lorentzian shapes, but are presumably superpositions of Lorentzian and Gaussian curves. In other words, the molecular reorientational motion around an *x*- or *y*- axis may be described by diffusional reorientation, while molecular reorientation around a *z*-axis must be explained by a mechanism such as one in which both free and diffusional rotations take place simultaneously. The molecular symmetry axis coincides with the *z*-axis in the discussion.

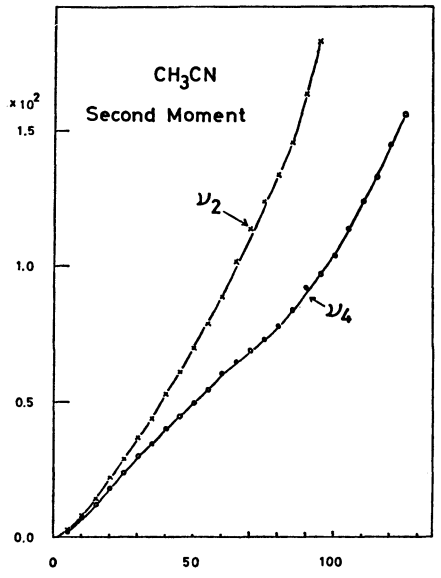

Fig. 5. Second moment plottings *vs.* integration range for ν_2 and $\nu_4(a_1)$ of liquid methyl cyanide.

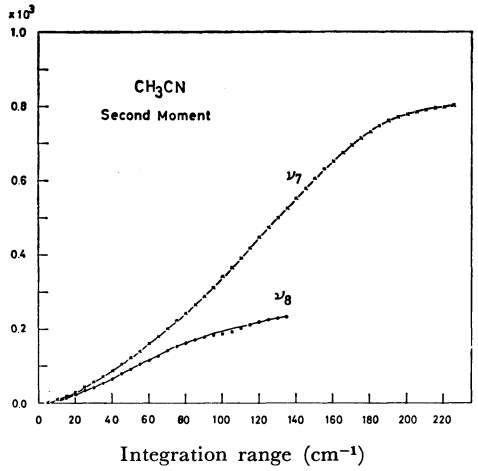

Fig. 6. Second moment plottings *vs.* integration range for ν_7 and $\nu_8(e)$ of liquid methyl cyanide.

Based upon a free-rotor model, Yamashita and Shimizu[6] proposed this algebraic expression of a second moment for a symmetric-top molecule:

$$M_2 = \begin{cases} kT\dfrac{2}{I_x}(\sec^{-2}), \text{ for } a_1\text{-type} & (3a) \\ kT\left(\dfrac{1}{I_x}+\dfrac{1}{I_z}(1-\zeta)^2\right)(\sec^{-2}), \text{ for } e\text{-type} & (3b) \end{cases}$$

where k is the Boltzmann constant; T, the absolute temperature, and I_i, the moment of inertia around the i-th axis. Equation(3) is essentially the same as the second-moment expression proposed by Gordon[13]

11) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **18**, 513 (1962).
12) H. Matsuura, This Bulletin, **44**, 2379 (1971).
13) R. G. Gordon, *J. Chem. Phys.*, **39**, 2788 (1963); **41**, 1819 (1964).
14) R. P. Young and R. N. Jones, *Chem. Rev.*, **71**, 219 (1971).
15) L. D. Favro, *Phys. Rev.*, **119**, 53 (1960).

TABLE 2. CALCULATED AND OBSERVED SECOND MOMENTS OF LIQUID METHYL CYANIDE IN 10^2 cm^{-2}

	Gordon[13]	Yamashita[6] Shimizu	Obsd
$\nu_2, \nu_4(a_1)$	2.53	2.53	diverge
$\nu_7(e)$	23.0	4.32	8.1
$\nu_8(e)$		0.80	2.5

if we put ζ equal to zero. In Table 2, the observed and the calculated M_2's are compared for a few fundamental bands of methyl cyanide. Since the calculations of Gordon and Yamashita-Shimizu are clearly based upon free-rotor models, it is rather natural that the magnitude of M_2 calculated from Eq.(3) does not agree with the observed values.

Band-shape Analysis and Life-time Function, $\psi(t)$. It was concluded in the preceding section that molecular reorientational motion around the z-axis of methyl cyanide may be interpreted as an intermediate state of free-rotation and rotational diffusion. The next problem is to analyze the observed band-shape data in a more quantitative way.

Theoretical expressions for a time-correlation function corresponding to the intermediate state may be found in the reports of Bratoz *et al.*[16] and of Shimizu.[1] Bratoz's formula is:

$$\Phi(t) = (1-\xi)\Phi_F(t) + \xi\Phi_D(t) \tag{4}$$

where $\Phi_F(t)$ and $\Phi_D(t)$ refer to time-correlation functions corresponding to free-rotation and rotational diffusion respectively, and where ξ is a constant which represents the fraction of molecules whose reorientational motion is diffusional. Shimizu expresses a time-correlation function as:

$$\Phi(t) = \psi(t)\Phi_F(t) + (1-\psi(t))\Phi_D(t) \tag{5}$$

Eqs.(4) and (5) differ only in whether the coefficients of $\Phi_F(t)$ and $\Phi_D(t)$ are time-dependent or not. In Eq.(5), $\psi(t)$ is a function of time and represents the decay of the fraction of freely-rotating molecules. We will call it a "life-time function" hereafter.

If we grant Eq.(4), then a band shape can be expressed as:

$$I(\omega) = (1-\xi)I_F(\omega) + \xi I_D(\omega) \tag{6}$$

where:

$$I_F(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\Phi_F(t)e^{-i\omega t}dt \tag{7}$$

and:

$$I_D(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\Phi_D(t)e^{-i\omega t}dt \tag{8}$$

$I_F(\omega)$ is a Gaussian function, and its half-width may be different for different vibrational transitions, while $I_D(\omega)$ is a Lorentzian function whose half-width is considered to be the same for all the bands belonging to the same symmetry species. Therefore, the decomposition of an observed band shape, $I(\omega)$, into Lorentzian and Gaussian functions can be expected to confirm the validity of the theory of Bratoz. Two e-type

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

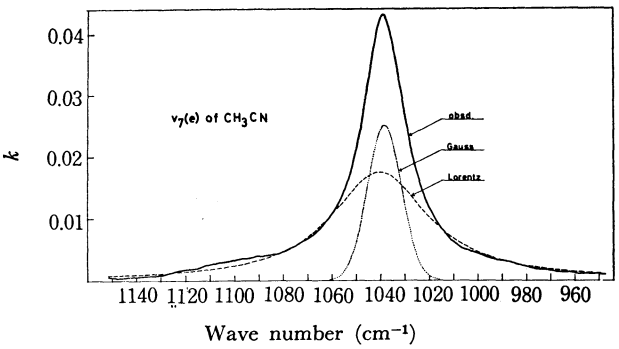

Fig. 7. Result of least-squares decomposition of $\nu_7(e)$ of liquid methyl cyanide into Lorentzian and Gaussian curves. Resultant Lorentzian and Gaussian components are shown by broken line and dotted line, respectively.

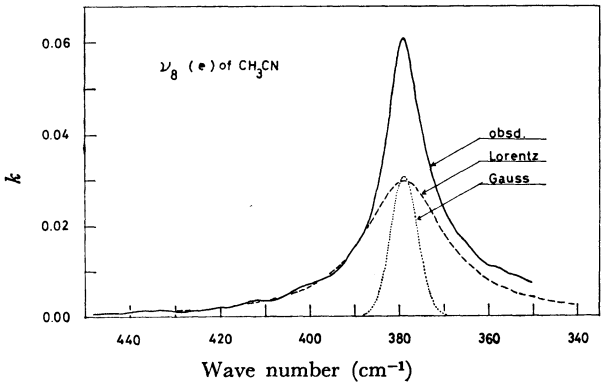

Fig. 8. Result of least-squares decomposition of $\nu_8(e)$ of liquid methyl cyanide into Lorentzian and Gaussian curves. Resultant Lorentzian and Gaussian components are shown by broken line and dotted line, respectively.

bands, ν_7 and ν_8, were decomposed into Lorentzian and Gaussian functions by the method of least-squares; the results are illustrated in Figs. 7 and 8 respectively. Unfortunately, the attempt was unsuccessful, because the shapes of the resultant Lorentzian components of ν_7 and ν_8 did not agree with each other. Therefore, Bratoz's model must be discarded.[17]

As the Fourier transform of Shimizu's formula of Eq. (5) is rather complicated to deal with, an attempt was made to analyze the correlation function obtained through the Fourier transformation of the observed band shapes of ν_7 and ν_8.

Let $\Phi_F(t)$ be a Gaussian function that will give a second moment of Yamashita and Shimizu (cf. Eq. (3b)):

$$\Phi_F(t) = \exp[-(M_2/2)t^2] \tag{9}$$

$\Phi_D(t)$ takes, as usual, an exponential form of the diffusion type:[14]

$$\Phi_D(t) = \exp[-D_e|t|] \tag{10}$$

where D_e is a rotational diffusion constant related to the e-type vibrations. Both $\Phi_D(t)$ and $\psi(t)$ are considered to be the same for all the vibrations of the e-type. Now that two sets of data, correlation functions for ν_7 and ν_8, are available, the form of $\psi(t)$ can be readily

17) The least-squares fitting did not result in a unique solution. However, the conclusion drawn here was the same for all sets of converged parameters.

estimated. A preliminary calculation showed that $\psi(t)$ is somewhat like an exponential function initiating from 1 at time zero. This fact may support the treatment of Shimizu,[1] who assumed the life-time function to be:

$$\psi(t) = \exp[-(1/\tau_L)|t|] \tag{11}$$

By employing the same form for $\psi(t)$, Eq.(5) is reduced to the form:

$$\Phi(t) = \exp[-(1/\tau_L)|t|]\cdot\exp[-(M_2/2)t^2] + (1-\exp[-(1/\tau_L)|t|])\cdot\exp[-D_e|t|] \tag{12}$$

Finally, the least-squares fitting of the correlation function of Eq.(12) to the observed correlation functions for ν_7 and ν_8 leads to the values of:

$$1/\tau_L = 1.8 \pm 0.7\ \text{psec}^{-1}$$

and:
$$D_e = 1.34 \pm 0.15\ \text{psec}^{-1} \tag{13}$$

In Figs. 9 and 10, the observed correlation functions for ν_7 and ν_8 are compared with those reproduced by Eq.(12) and the D_e and $1/\tau_L$ values thus obtained. The agreement of the two sets of correlation functions is fairly good. The standard errors attached to the parameters of Eq.(13) are estimated from the deviations between the observed and the calculated correlation functions. A rotational diffusion constant related

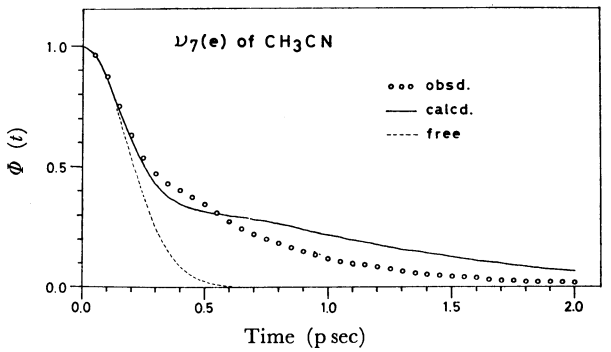

Fig. 9. Time-correlation function for $\nu_7(e)$ of liquid methyl cyanide. Open circles: Fourier transform of observed absorption index, solid line: calculated by Eq. (12), broken line: time-correlation function for a free-rotor of the form of Eq. (9).

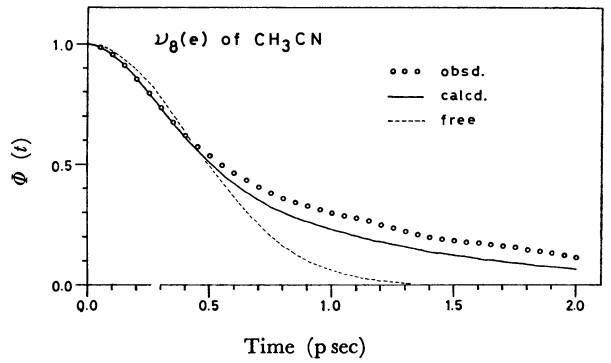

Fig. 10. Time-correlation function for $\nu_8(e)$ of liquid methyl cyanide. Open circles: Fourier transform of observed absorption index, solid line: calculated by Eq. (12), broken line: time-correlation function for a free-rotor of the form of Eq. (9).

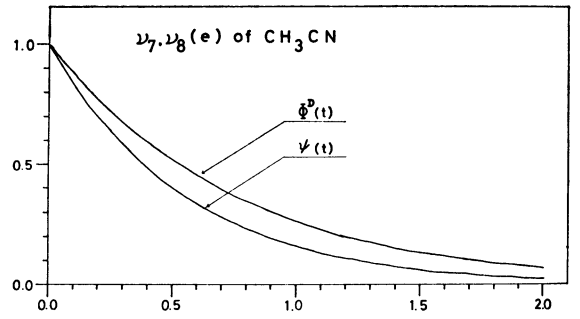

Fig. 11. Time-correlation function for diffusional reorientation, $\Phi_D(t)$, and life-time function, $\psi(t)$, obtained from time-correlation functions for ν_7 and $\nu_8(e)$ of liquid methyl cyanide.

with vibrations of the a_1-type, D_{a_1}, is directly obtained from the half-width of ν_2 or ν_4, namely:

$$D_{a_1} = 0.76 \pm 0.02\ \text{psec}^{-1} \tag{14}$$

because the shapes of a_1-type bands are good Lorentzian shapes. Using the values of D_e and D_{a_1}, the rotational diffusion constants about the x-and z-axes (D_x and D_z respectively) are calculated to be:

$$D_x = 0.38 \pm 0.01\ \text{psec}^{-1}$$

and:
$$D_z = 0.96 \pm 0.16\ \text{psec}^{-1}.$$

The correlation function related to the rotational diffusion, $\Phi_D(t)$, and life-time function, $\psi(t)$, are illustrated in Fig. 11. A comparison of Fig. 11 and Fig. 9 or 10 shows that $\Phi_D(t)$ and $\Phi(t)$ are essentially the same after about 1.0 psec; this corresponds to the situation in which $\psi(t)\Phi_F(t)$ decays very rapidly. In other words, almost all the molecules in the system follow diffusional reorientation at long times even if they behave like free-rotors at $t=0$. This result is consistent with that of a general theory of stochastic processes,[18]—that is, the finding that a correlation function of a random variable approaches a Markoffian exponential form at long times if the distribution of the variable is Gaussain.

Conclusion

The preceding discussion may be summarized as follows.

(1) The molecular reorientational motion of liquid methyl cyanide is diffusional around the x- and y-axes. The rotation around the z-axis must be understood as an intermediate state between free and diffusional ones.

(2) The vibration-rotation interaction affects the apparent correlation time.

(3) The intermediate state between free rotation and rotational diffusion may be described by the correlation function of Eq.(5).

(4) Rotational diffusion constants can safely be obtained if we can calculate a time-correlation function over a long period from the observed absorption spectra.

18) R. Kubo, *Lectures Theoret. Phys.* (Boulder), **1**, 120 (1958).
19) S. R. Polo and M. K. Wilson, *J. Chem. Phys.*, **23**, 2376 (1955).

This conclusion supports the description of a reference.[3] (5) Incidentally, a life-time function can be calculated if we have enough absorption data, which conversely describes the details of the molecular reorientation process.

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