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Shapes of the ν_1 Band of Liquid Chloroform and Intermolecular Interaction

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The infrared absorption spectrum for the ν_1 fundamental of chloroform or chloroform-*d* shows strong asymmetry, with a remarkable tailing on the high-frequency side. The observed band-width of the ν_1 fundamental of chloroform-*d* is significantly narrower than that of chloroform. These asymmetric band profiles of the ν_1 bands of chloroform and chloroform-*d* can be interpreted in terms of the existence of two different types of chloroform molecules. One is a molecule which interacts with another molecule, and the other is a non-interacting molecule. The isotope effect on the band-width can be explained in terms of the difference in the reduced mass for chloroform and chloroform-*d*.

It has been well established, that the absorption maximum of the infrared absorption spectrum for the ν_1 band of chloroform decreases from 3033 to 3018 cm^{-1}, and that the intensity increases from 11 to 198 $cm^2\ mol^{-1}$, on passing from the gas to the liquid phase.[1,2] These spectral changes have been interpreted in terms of the formation of hydrogen bonding in the liquid phase.[3] However, Rothschild *et al.* have studied the band shapes of the Raman scattering spectra and the infrared absorption spectra for the ν_1 band of chloroform and have concluded that the vibrational relaxation processes for the ν_1 band of chloroform do not support the presence of hydrogen bonding in the pure liquid.[4] Thereafter, several studies of the line-shape of the ν_1 band of chloroform and chloroform-*d* in the liquid phase have been reported.[5-9] All these reports have concluded that the shape of the ν_1 band may not be affected by the existence of hydrogen bonding. In other words, the observed width of the ν_1 band has been regarded as a homogeneous width. However, as will be shown in the present report, the observed infrared absorption spectrum for the ν_1 fundamental of chloroform or chloroform-*d* shows strong asymmetry, with a remarkable tailing on the high-frequency side. Therefore, the observed band-width can not be analyzed on the basis of the homogeneous width.

It has also been established that the band-width of the ν_1 fundamental of chloroform-*d* is significantly narrower than that of chloroform. Moradi-Araghi *et al.* have considered that the increased vibrational relaxation rate in chloroform, in comparison with that in chloroform-*d*, is ascribable to the stronger coupling between the ν_1 vibration and the molecular motions in the liquid, which itself arises from the anharmonic terms in the vibrational Hamiltonian.[8]

We will show in the present report that the observed asymmetric band profiles of the infrared-absorption spectra for the ν_1 bands of chloroform and chloroform-*d* can be interpreted in terms of the existence of a hydrogen-bonding-like interaction in the liquid phase. It will also be shown that the isotope effect on the band-width can be explained in terms of the difference in the reduced mass for chloroform and chloroform-*d* instead of the anharmonicity in the vibrational Hamiltonian.

Experimental

All the chemicals used in this work were commercially available reagents. The chloroform was passed through a chromatographic column packed with alumina to remove the ethanol used as a stabilizer. The eluent was fractionally distilled. The elimination of water and ethanol from the sample solution was confirmed by observing the infrared-absorption spectra. The chloroform-*d* was purchased from E. Merck Co., Ltd., and was dried over zeorite A-3. The carbon tetrachloride was purified by fractional distillation. The solutions were prepared gravimetrically.

The absorption spectra were recorded with a Perkin-Elmer 180 infrared spectrometer at the temperature of 22± 1 °C. A sample cell with NaCl windows was used, and the thickness of a sample was determined by the interference-fringe method. The absorption spectra of the ν_1 bands of chloroform and chloroform-*d* were measured under resolutions of 0.7 cm^{-1} and 0.5 cm^{-1} respectively and at the scanning speed of 4 $cm^{-1}\ min^{-1}$.

The observed spectra were then reduced to:

$$\frac{1}{lv}\ln\left(\frac{I_0}{I}\right)$$

where v is the wave number in cm^{-1}; l, the thickness of the sample; I_0 the intensity of the incident light, and I, the intensity of the transmitted light. The relative intensities, I^c, were defined as:

$$I^c = \frac{f_d}{l}\int_{band}\frac{1}{v}\ln\left(\frac{I_0}{I}\right)dv \qquad (1)$$

where f_d is the correction factor for the dielectric-field effect. Since the intensities of the observed bands were weak, Polo-Wilson's scheme[10] was applied to the dielectric-field correction; that is, the correction factor, f_d, was expressed as:

$$f_d = \frac{9n_D}{(n_D^2+2)^2} \qquad (2)$$

where n_D is the refractive index of the solution.

Results and Discussion

Observed Spectra. The observed spectra of the ν_1 band of pure liquid chloroform are shown in Fig. 1 (see the circles). The peak frequency and the full width at the half maximum are found to be 3018 cm^{-1} and 12.8 cm^{-1} respectively. It is apparent from the figure that the part of the half-intensity band-width which falls on the high-frequency side of the

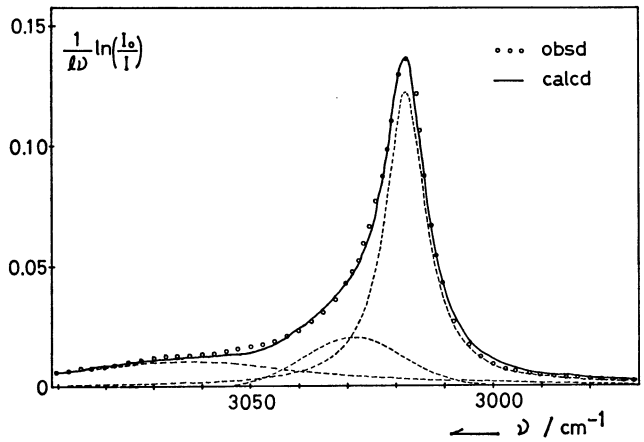

Fig. 1. Observed (circles) and calculated (real line) spectra for the ν_1 band of $CHCl_3$.

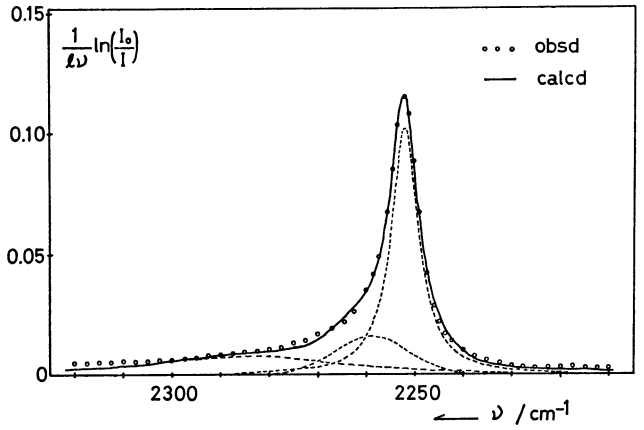

Fig. 2. Observed (circles) and calculated (real line) spectra for the ν_1 band of $CDCl_3$.

band maximum is broader than the corresponding part on the low-frequency side. The observed spectrum of the ν_1 band of pure liquid chloroform-*d* is shown in Fig. 2 (see the circles). The peak frequency and the full width at half the maximum are found to be 2252 cm^{-1} and 8.0 cm^{-1} respectively. The observed band profile of chloroform-*d* is similar to that of chloroform. However, there appears a remarkable isotope effect on the vibrational band-width.

Separation of the Observed Band into Symmetry Band Profiles. First, our attention was focused on the asymmetry of the band profile observed for the ν_1 band of chloroform. It can easily be ascertained that the asymmetry does not originate from any hot bands or any bands originating from isotopic species. Also, the asymmetry cannot be ascribed to any overlapping of summation bands, because the asymmetric band profiles are closely analogous both for pure liquid chloroform and chloroform-*d*.

An attempt was made, therefore, to resolve the observed asymmetric band profile into some symmetric intensity distribution functions in order to understand the origin of the asymmetry. First, we used two Lorentzian functions which correspond to the peaks at 3060 and 3018 cm^{-1} for pure chloroform (see Fig. 1). The agreement between the calculated and observed profiles was poor until we added another band between the 3060 and 3018 cm^{-1} bands. The best fit between the observed and calculated profiles has been obtained by considering two Lorentzian functions near 3060 and 3018 cm^{-1} and one Gaussian function near 3030 cm^{-1}. The explicit expression of the linear combination is given by:

$$F(\nu) = \frac{h_1\gamma_1^2}{(\nu-\nu_1)^2+\gamma_1^2} + h_2\exp\left\{-\frac{\ln 2}{\gamma_2^2}(\nu-\nu_2)^2\right\} + \frac{h_3\gamma_3^2}{(\nu-\nu_3)^2+\gamma_3^2}. \quad (3)$$

Table 1. Best-fit parameters of the ν_1 bands of $CHCl_3$ and $CDCl_3$

		Band 1	Band 2	Band 3
$CHCl_3$	γ/cm^{-1}	5.1	12	28
	h	0.1220	0.0204	0.0106
	ν/cm^{-1}	3017.5	3028	3062
	I^c/cm^{-1}	1.522	0.406	
$CDCl_3$	γ/cm^{-1}	3.4	9	22
	h	0.1025	0.0160	0.00799
	ν/cm^{-1}	2252	2259	2284
	I^c/cm^{-1}	0.853	0.239	

The observed and calculated spectra of the ν_1 band of chloroform are shown in Fig. 1. The best-fit parameter values of these functions are summarized in Table 1. Hereafter, we will call the broader Lorentzian at the highest frequency "the band 3," the narrower Lorentzian at the lowest frequency "the band 1," and the Gaussian "the band 2."

For chloroform-*d*, the observed intensity distribution was also expressed by a linear combination of two Lorentzian functions and one Gaussian function, as is shown in Fig. 2. The best-fit parameter values of the functions for chloroform-*d* are also listed in Table 1.

Assignment of the Resolved Bands. In order to assign the resolved bands, the spectra of the ν_1 band observed in the liquid phase are compared with those observed in the gas and solid phases in Table 2. The ν_1 band is observed at 3033 and 3007 cm^{-1} in the gas and solid phases respectively. The intensity of the ν_1 band, on the other hand, increases from 11 to 400 $cm^2\ mol^{-1}$ on passing from the gas to the solid phase. As is seen in Table 2, the frequency and intensity observed in the liquid phase take values intermediate between those of the gas and solid phases. These spectral changes have been interpreted in terms of the hydrogen-bond formation between chloroform molecules.[3] Therefore, it is reasonable to expect the existence of the two kinds of chloroform molecules in the liquid phase. One is a molecule which forms a hydrogen bonding with another chloroform molecule; the other is a molecule which behaves rather like a free molecule. We call these two kind of chloroform molecules a "strongly interacting molecule" and a "weakly interacting molecule" respectively.

Based upon these ideas, we assign the band 1 at the lowest frequency to the ν_1 vibration of the strongly

Table 2. Observed intensities and frequencies for the ν_1 bands of $CHCl_3$ and $CDCl_3$ in the gas, liquid, and solid phases

	Frequency, ν_0/cm^{-1}			Intensity, $\Gamma/cm^2\,mol^{-1}$		
	Gas	Liquid	Solid[d]	Gas[a]	Liquid[c]	Solid[d]
$CHCl_3(\nu_1)$	3032.9[b]	3018	3007	11	198	400
$CDCl_3(\nu_1)$	2265[a]	2252	2250	3	127	133

a) See Ref. 1. b) See Ref. 2. c) The direct integration of the unresolved band. d) See Ref. 16.

Table 3. Concentration dependence of band parameters and intensities

	mol % ($CHCl_3$)	100	80	50	40	20
Band 1	ν_0/cm^{-1}	3017.5	3017.5	3017.5	3017.5	3017.5
	$\Delta\nu_{1/2}/cm^{-1}$	10.2	10.2	10.2	10.2	10.2
	I^c/cm^{-1}	1.552	1.078	0.758	0.495	0.216
	I^*/cm^{-1}	1.552	1.347	1.264	1.238	1.081
Band 2	ν_0/cm^{-1}	3028	3027	3027	3027	3026
	$\Delta\nu_{1/2}/cm^{-1}$	24	24	24	24	24
	I^c/cm^{-1}	0.406	0.336	0.270	0.186	0.0972
	I^*/cm^{-1}	0.406	0.421	0.450	0.466	0.486

interacting molecule. The band 2, on the other hand, is assigned to the ν_1 vibration related to the weakly interacting molecule.

The assignment of the band 3 has not yet been established. Its band maximum is observed 40 cm^{-1} higher than that of the band 1 and its half-width is much broader than that of the band 1. Therefore, we can safely conclude that the band 3 is not related to any fundamental vibrations. As no absorption band is observed in this wavenumber region for the gas sample,[2] it may arise from the combination tone of the ν_1 fundamental and the pseudo-lattice vibrations.[11]

If the assignments of the bands 1 and 2 are correct, the relative intensities, I_2/I_1, of the bands 1 and 2 should be equal for liquid chloroform and chloroform-*d*. It may be seen from Table 1 that the relative intensity, I_2^c/I_1^c, was observed to be 0.27 in chloroform and 0.28 in chloroform-*d*. These results partially support the validity of the present assignment of the bands 1 and 2.

Concentration Dependence of the Relative Intensities of the Band 1 and the Band 2. In order to confirm the validity of the assignment of the band 1 and the band 2, the concentration dependence of the intensities of the band 1 and the band 2 were observed in the binary solutions of chloroform–carbon tetrachloride. Since excess enthalpy is positive in a chloroform–carbon tetrachloride mixture,[12] the existence of a hydrogen-bonding-like interaction can be expected between chloroform molecules. This interaction is assumed to be broken down in the carbon tetrachloride solution. With the increase in the carbon tetrachloride concentration, therefore, it is expected that the number of the strongly interacting molecules will decrease while the number of the weakly interacting molecules will increase. In other words, the intensity of the band 1 is expected to decrease, while that of the band 2 is expected to increase.

The intensity change due to dilution is listed in Table 3. The quantities, I_1^* and I_2^*, of the table are defined as:

$$I_1^* \equiv \frac{c_0 f_d}{cl}\int_{\text{band 1}} \frac{1}{\nu}\ln\left(\frac{I_0}{I}\right)d\nu \simeq \frac{c_0 f_d}{cl}\int \frac{h_1\gamma_1^2}{(\nu-\nu_1)^2+\gamma_1^2}d\nu \quad (4)$$

$$I_2^* \equiv \frac{c_0 f_d}{cl}\int_{\text{band 2}} \frac{1}{\nu}\ln\left(\frac{I_0}{I}\right)d\nu \simeq \frac{c_0 f_d}{cl}\int h_2 \exp\left\{-\frac{\ln 2}{\gamma_2^2}(\nu-\nu_2)^2\right\}d\nu, \quad (5)$$

in cm^{-1}, where c_0 is the molar concentration of chloroform in pure liquid and c, the molar concentration of chloroform in solution. Table 3 shows that, as the concentration of carbon tetrachloride increases, I_1^* decreases, while I_2^* increases. These results support the validity of the assignments for the band 1 and the band 2.

Based upon these results, an attempt was made to obtain the absolute intensities of the band 1 and the band 2. The absolute intensities, Γ_1 and Γ_2, are given by:

$$I_1^* = c_0\frac{c_1}{c}\Gamma_1 \quad (6)$$

$$I_2^* = c_0\frac{c_2}{c}\Gamma_2 \quad (7)$$

where c_1 and c_2 are the molar concentrations of the chloroform molecules corresponding to the band 1 and the band 2 respectively. The $c=c_1+c_2$ relation and Eqs. 6 and 7 give the relation:

$$\frac{I_1^*}{\Gamma_1}+\frac{I_2^*}{\Gamma_2} = c_0$$

or:

$$I_1^* = -(\Gamma_1/\Gamma_2)I_2^* + \Gamma_1 c_0. \quad (8)$$

By plotting I_1^* against I_2^* at a series of concentrations, a straight line with a slope of $-(\Gamma_1/\Gamma_2)$ is generated so long as the absolute intensities, Γ_1 and Γ_2, are independent of the concentration. The values of Γ_1 and Γ_2 are obtained from the extrapolated I_1^* value at $I_2^*=0$ and the (Γ_1/Γ_2) value.[13]

Table 4. Intensities and frequencies of the Band 1 and Band 2, and the ν_1 bands in the gas and solid phases

	Gas	Liquid		Solid[c]
		Band 1	Band 2	
Γ/cm² mol⁻¹	11[b]	250—300	45—60	400
ν_0/cm⁻¹	3032.9[a]	3017.5	3028	3007

a) See Ref. 2. b) See Ref. 1. c) See Ref. 16.

The values of the peak frequencies and the absolute intensities for the band 1 and the band 2 are listed in Table 4, together with those values for pure chloroform in the gas and solid phases. It may be seen from the table that the peak frequency and the absolute intensity of the band 1 are rather close to those values for the solid chloroform. On the other hand, the peak frequency and the absolute intensity of the band 2 are closer to those values for the gas chloroform. These results are consistent with the idea that there exist two kinds for chloroform molecules in the liquid phase. One is a strongly interacting molecule which causes the band 1 to appear, while the other is a rather weakly interacting molecule which causes the band 2 to appear.

Incidentally, the relative population of the strongly interacting molecules to the weakly interacting molecules in liquid chloroform was estimated to be 44% using the values of Γ_1 and Γ_2 and also Eqs. 6 and 7.

Isotope Effect on the Band-width. It is of much interest to consider the isotope effect on the band-width of the ν_1 fundamental. The band-widths of the ν_1 fundamentals are observed to be quite different for liquid chloroform and chloroform-*d* (see Table 1). This result is rather strange because of the following reason.

If the coupling between the vibrational and rotational motions of a molecule is negligible, the observed band-width, $\Delta\nu_{1/2}$, of an infrared spectrum may be expressed as:

$$\Delta\nu_{1/2} = \delta_v + \delta_r \tag{9}$$

where δ_v is the width originating from the vibrational relaxation and δ_r, the width originating from the reorientational relaxation. Since the moments of inertia and viscosity are almost equal for chloroform and chloroform-*d*, the values of δ_r for chloroform and chloroform-*d* should be almost equal also. It is ascertained that the effect of the vibrational relaxation of the resonace type is negligibly small for the ν_1 band because of the weak absorption intensity.[14] Therefore, we tried to explain the isotope effect on the band-width by considering the random modulation of vibration frequencies due to the surrounding molecules.

In order to elucidate the isotope effect on the vibrational relaxation due to the random-frequency modulation, we consider a harmonic oscillator whose vibrational frequency is modulated by a stochastic potential, $V(t)$, arising from the neighbouring molecules. In the present case, it can reasonably be assumed that the dissipation process of the vibrational energy is negligible, because the correlation time of $V(t)$ is much longer than the inverse of the harmonic frequency of the unperturbed oscillator. The vibrational relaxation function is, then, characterized by two parameters: the mean-square magnitude of the frequency shift, Δ, and the correlation time of the stochastic potential, τ_c, which are defined as:

$$\Delta^2 \equiv \langle(\Delta\omega)^2\rangle \tag{10}$$

$$\tau_c \equiv \frac{1}{\Delta^2}\int_0^\infty \langle\Delta\omega(0)\Delta\omega(t')\rangle dt' \tag{11}$$

where $\Delta\omega$ is the vibrational frequency shift due to the stochastic potential and where $<\ >$ indicates an average over the ensemble.[15]

If the condition

$$\Delta\cdot\tau_c \gg 1 \tag{12}$$

is fulfilled, the frequency modulation is very slow. Therefore, a line shape is a direct reflection of the random distribution of $\Delta\omega$. If the random distribution of $\Delta\omega$ is Gaussian, the vibrational relaxation function, $\psi_v(t)$, is also Gaussian, as is expressed by:

$$\psi_v(t) = \exp(i\omega_0 t)\exp\left(-\frac{\Delta^2}{2}t^2\right) \tag{13}$$

where ω_0 is the harmonic frequency of the unperturbed oscillator. Therefore, the corresponding line shape function, $I(\omega)$, is:

$$I(\omega) = \frac{1}{\sqrt{2\pi}\Delta}\exp\left\{-\frac{(\omega-\omega_0)^2}{2\Delta^2}\right\} \tag{14}$$

and the half-width due to the vibrational relaxation, δ_v, becomes:

$$\delta_v = 2\sqrt{2\ln 2}\,\Delta. \tag{15}$$

On the other hand, if the condition

$$\Delta\cdot\tau_c \ll 1 \tag{16}$$

is fulfilled, the frequency modulation is fast and the spectrum shows the phenomenon of motional narrowing. The vibrational relaxation function, $\psi_v(t)$, is expressed as:

$$\psi_v(t) = \exp(i\omega_0 t)\exp(-\Delta^2\tau_c|t|). \tag{17}$$

The line-shape function, $I(\omega)$, is expressed as:

$$I(\omega) = \frac{1}{\pi}\frac{\Delta^2\tau_c}{(\omega-\omega_0)^2+(\Delta^2\tau_c)^2}. \tag{18}$$

Therefore, the half-band width is:

$$\delta_v = 2\Delta^2\tau_c. \tag{19}$$

Since the correlation time, τ_c, of $V(t)$ is rather similar for the two isotope species, the isotope effect on the band-width may be ascribed to the mean-square magnitude, Δ, of the frequency shift. For the fundamental band, the frequency shift, $\Delta\omega$, originating from the intermolecular potential, V, is given by:

$$\Delta\omega = \frac{1}{2\omega_0}\left(\frac{\partial^2 V}{\partial Q^2}\right)_0 \tag{20}$$

where Q is the normal coordinate corresponding to the harmonic vibration. As Q is expressed as:

$$Q = \sqrt{\mu}\,\Delta r \tag{21}$$

where μ is the reduced mass of the oscillator, and Δr, the displacement from equilibrium, $(\partial^2 V/\partial Q^2)_0$ is given by:

Table 5. Calculated values of δ_r and δ_v

Modulation		Band 1		Band 2	
		δ_v/cm^{-1}	δ_r/cm^{-1}	δ_v/cm^{-1}	δ_r/cm^{-1}
Slow	$CHCl_3$	13.4	−3.2	23.6	0.4
	$CDCl_3$	10.0	−3.2	17.6	0.4
Fast	$CHCl_3$	7.7	2.5	13.5	10.5
	$CDCl_3$	4.3	2.5	7.5	10.5

$$\left(\frac{\partial^2 V}{\partial Q^2}\right)_0 = \frac{1}{\mu}\left(\frac{\partial^2 V}{\partial(\Delta r)^2}\right)_0. \tag{22}$$

A straightforward calculation using Eqs. 10, 20, and 22 leads to:

$$\Delta = \frac{1}{2\omega_0\mu}\sqrt{\left\langle\left(\frac{\partial^2 V}{\partial(\Delta r)^2}\right)_0^2\right\rangle}. \tag{23}$$

Since $\langle(\partial^2 V/\partial(\Delta r)^2)_0^2\rangle$ seems to be unchangeable on isotope substitution, Δ_H/Δ_D may be expressed by:

$$\Delta_H/\Delta_D = (\omega_{0D}\mu_D)/(\omega_{0H}\mu_H). \tag{24}$$

In Eq. 24, all the symbols suffixed by H and D correspond to chloroform and chloroform-*d* respectively. The force constant also seems to be unchageable on isotope substitution.

Therefore, the ratio of μ_H and μ_D is:

$$\mu_D/\mu_H = (\omega_{0H}/\omega_{0D})^2. \tag{25}$$

Equations 24 and 25 give this relation:

$$\Delta_H/\Delta_D = \omega_{0H}/\omega_{0D}. \tag{26}$$

Consequently, in the case of a slow modulation, the ratio of the half-widths for chloroform and chloroform-*d* is:

$$\delta_{vH}/\delta_{vD} = \omega_{0H}/\omega_{0D}. \tag{27}$$

In the case of a fast modulation, on the other hand, δ_{vH}/δ_{vD} is given by:

$$\delta_{vH}/\delta_{vD} = (\omega_{0H}/\omega_{0D})^2. \tag{28}$$

Since the δ_r value is considered to be almost equal for the two isotope species, the δ_r and δ_v values can be calculated from Eqs. 9, 27, and 28; the results are summarized in Table 5.

It may be concluded from the results shown in Table 5, first of all, that the present experimental results do not correspond to the case of a slow modulation, because the δ_r is calculated to be negative for the band 1 if we apply the slow-modulation limit to the present system.

In the fast-modulation limit, however, the δ_r values are calculated to be positive for both the band 1 and the band 2. Moreover, the δ_r of the band 2 is much larger than that of the band 1. This seems quite reasonable if we consider that the rotational motion of the molecule corresponding to the band 1 is hindered by the interaction from the surrounding molecules much more strongly than that of the molecule corresponding to the band 2. It is interesting to add that the δ_r for chloroform is calculated to be about 22.4 cm^{-1} if we apply the free-rotation model. This δ_r value of 22.4 cm^{-1} is closer to the δ_r value of the band 2 than to that of the band 1. These results support the idea that the fast-modulation limit is a more appropriate model to explain the observed isotope effect on the band-width than is the slow modulation limit. It has also been concluded that the isotope effect on the band-width of the ν_1 fundamental of chloroform arises mainly from the difference in the vibrational relaxation width. These conclusions are quite consistent with the assignment of the bands 1 and 2 to the two different types of chemical species existing in the liquid phase of chloroform, *i.e.*, the existence of the strongly and the weakly interacting molecules.

Concluding Discussion. The main results of the present work may be summarized as follows:

(1) There exist two different types of chloroform molecules in pure liquid chloroform. One is a molecule which interacts with another molecule, and the other is a non-interacting molecule.

(2) Although the infrared absorption spectrum for the ν_1 band of chloroform shows a single peak, the observed spectrum consists of two bands, which correspond to the two different types of chloroform molecules in the pure liquid. Both the peak frequency and the absorption intensity are different for these two bands in liquid chloroform; the observed band profile for the ν_1 vibration is asymmetric.

(3) The isotope effect on the width of the ν_1 band can be explained in terms of the difference in the reduced mass.

(4) Incidentally, the present results reveal the real difficulty of the intensity study of condensed phases. The intensities of the vibration spectra observed for the condensed systems have been used mainly for the study of intermolecular interactions. This can be done by comparing the intensities observed for the gas and condensed phases. It has been shown in the present work that a vibration spectrum of a condensed phase is, in principle, composed of many different bands with different band maxima and intensities. These different bands should correspond to different chemical species or different types of intermolecular interactions. In order to override this difficulty, the detailed study of the band shapes of the vibration spectra should be strongly pushed forward, together with the intensity measurements of condensed systems.

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