Infrared Band Shape of the C–I Stretching Vibration of Methyl Iodide in Solutions

Kenji Fujiwara,* Kohji Fukushi, Shun-ichi Ikawa, and Masao Kimura**

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

(Received April 17, 1975)

The infrared band shapes of the fundamental and overtone C–I stretching vibrations of methyl iodide in solutions are well approximated by the superposition of Lorentzian functions. From a comparison of the band-widths of the $\nu_3(0\rightarrow1)$, $\nu_3(1\rightarrow2)$, and $\nu_3(0\rightarrow2)$ transitions, it is pointed out that the vibrational relaxation of the translational-diffusion type proposed by Bratos *et al.* contributes to the band-widths, in addition to reorientational relaxation. A slight deviation from the Lorentzian function was observed in the low-frequency region of the fundamental band.

The band shape of the infrared spectra of a liquid involves information about the molecular dynamics in the liquid. Shimizu[1] and Gordon[2] first showed that the band shape is given by the Fourier transformation of the time correlation function for the vibrational-transition dipole moment. They adopted a model of random reorientation of molecules in condensed phase. Since then, many studies have been carried out by means of the Fourier transformation of observed band shapes.[3–14] Meanwhile, it has been recognized that only the reorientational process is not always sufficient to provide a full account of an observed band shape. It is often necessary to take into account additional factors, such as the vibrational relaxation,[12,15] the vibration-rotation interaction,[13] the overlap of hot bands,[16] the overlap of bands of various isotopic species,[16] and the dielectric-field effect.[5,17–19]

In order to discuss band shape and molecular dynamics, it is necessary to extract the band assigned to a single transition from an observed band. Since methyl iodide is a representative of symmetric top molecules and has no isotopic species, extensive spectroscopic studies have been carried out on it. However, there are only a few studies on the band shape and on the reorientational process of this molecule in solutions.[20–22] Among the observed bands of methyl iodide, the ν_3 band of the C–I stretching vibration is appreciably deformed by the overlap of hot bands. Therefore, the half-width[23] of the ν_3 band reported in previous work must include some uncertainty. The present study has been undertaken in order to obtain the half-widths of the individual transitions, *i.e.*, the fundamental $\nu_3(0\rightarrow1)$, the hot band $\nu_3(1\rightarrow2)$, and the overtone $\nu_3(0\rightarrow2)$. For this purpose, the observed band at about 525 cm^{-1} was decomposed into the components, $\nu_3(0\rightarrow1)$ and $\nu_3(1\rightarrow2)$, by assuming a Lorentzian profile for each. A similar analysis was also applied to the overtone band, $\nu_3(0\rightarrow2)$, which appears at about 1030 cm^{-1} in the high-frequency wing of the intense ν_6 band.

Experimental

The infrared transmission was measured by a single beam method using two JASCO DS-701G Spectrophotometers at room temperature. The spectra were run at the rate of about 2.5 cm^{-1}/min. It was confirmed that no deformation of the observed band shape was induced at this scanning speed. For a band with a half-width of 10 cm^{-1} or narrower, it is very difficult to correct the observed half-width for deficiencies in the linearity of the wave number scale of the spectrophotometers. The reproducibility of the observed half-width on a spectrophotometer was good to within ±0.1 cm^{-1}, but the results from the two spectrophotometers differred from each other by about 0.3 cm^{-1}. Therefore, we estimated the error due to the uncertainty in the wave number scale to be ±0.2 cm^{-1}, although this estimate is rather arbitrary. The slit width was set to provide a resolution of about 1.5 cm^{-1}. Thus, the effect of the finite slit width on the band-width observed in the present study is insignificant.[24] Base lines were corrected for solvent absorption which exists more or less for all the solvents used. An error in the observed half-width due to uncertainties in drawing the base line and in reading the transmission on a chart was estimated to be 1%. Thus, the over-all error included in the observed half-width, ω_{obsd}, was estimated to be ±0.3 cm^{-1}.

Concentrations of methyl iodide in solutions were chosen in between 2.0 and 0.4 mol/l and the sample cells used were 0.2 to 1 mm thick. No concentration dependency of half-widths and solvent-induced frequency shifts, $\Delta\nu$, were observed for all the methyl iodide-solvent systems studied in the present work. The observed infrared absorption bands in some solutions are shown in Fig. 1.

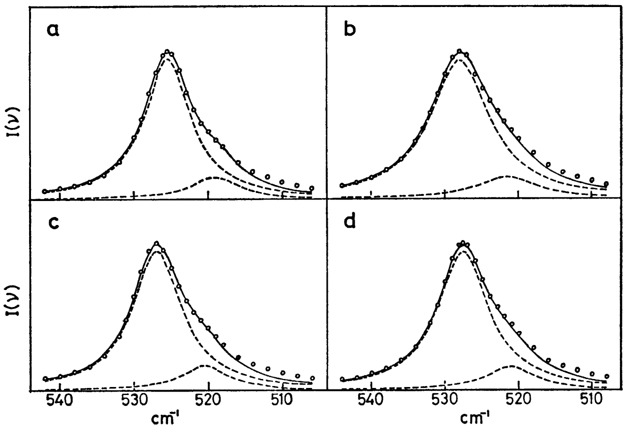

Fig. 1. The infrared ν_3 band of methyl iodide in solutions: (a) $CHCl_3$, (b) n-C_6H_{14}, (c) CS_2, and (d) CCl_4; ∘∘∘ observed band, — calculated band, --- component bands; (1) $\nu(0\rightarrow1)$ and (2) $\nu(1\rightarrow2)$.

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* Present address : Canon Inc., Ota, Tokyo.

** To whom correspondence should be addressed.

Table 1. The observed and calculated parameter values of the ν_3 band of methyl iodide[a)]

Solvent	Band center (cm^{-1})		Half-width (cm^{-1})				
	ν^0_{obsd}	$\nu^0(0\rightarrow1)$	ω_{obsd}	$\omega(0\rightarrow1)$	$\omega(1\rightarrow2)$	ω_{obsd} in Refs.	
n-C_5H_{12}	528.8	528.7	11.9	10.8	11.9		11.5[22)]
n-C_6H_{14}	528·5	528.6	11.2	10.2	10.6		10.7[22)]
CCl_4	527.4	527.6	9.1	8.3	8.3	13[20)]	9.1[22)]
CS_2	526.8	526.8	9.2	8.3	7.7	7.8[21)]	9.7[22)]
$CHCl_3$	525.5	525.6	8.8	7.9	8.4		9.1[22)]
C_6H_5Br	525.2	525.3	9.1	8.2	8.9		9.1[22)]
C_6H_5	525.0	525.0	9.3	8.2	8.1		9.3[22)]
	ν^0_{obsd}	$\nu^0(0\rightarrow2)$		$\omega(0\rightarrow2)$			
CS_2	1046.5	1046.7		13.2			

a) Uncertainties in the observed values are ±0.3 cm^{-1}, see text.

Analysis of Bands and Results

The absorption bands of the solutions were measured at sample thicknesses of 0.2 mm or larger. For such weak bands, the deformation of the band shape by the dielectric field is negligible.[19)] The observed half-widths are shown in the fourth column of Table 1. The values reported previously[20–22)] are also entered in the last two columns. The present results agree fairly well with those of Higuchi *et al.*[22)] Except for the solutions in n-pentane and n-hexane which give rise to notably broader bands, the half-widths are identical to one another within the experimental errors. It appears to be difficult to determine a simple relation between the observed half-width and any physical quantity of the solvent, such as a relation associated with the viscosity of the solvent as proposed by Higuchi *et al.*[22)]

The band was decomposed into two components corresponding to the fundamental transition, $\nu_3(0\rightarrow1)$, and the hot-band transition, $\nu_3(1\rightarrow2)$, by the least-squares method based upon the following equation

$$I(\nu)=\frac{(\omega(0\rightarrow1)/2)^2P(0\rightarrow1)}{(\nu-\nu^0(0\rightarrow1))^2+(\omega(0\rightarrow1)/2)^2}+\frac{(\omega(1\rightarrow2)/2)^2P(1\rightarrow2)}{(\nu-\nu^0(1\rightarrow2))^2+(\omega(1\rightarrow2)/2)^2}$$

where $I(\nu)$ is the observed band intensity defined by $\ln(T_0/T)_\nu/\nu(1-\exp(-hc\nu/kT))$,[2)] and $\nu^0(m\rightarrow n)$, $\omega(m\rightarrow n)$, and $P(m\rightarrow n)$ are the wave number of the band center, the half-width, and the intensity of the band center for the m to n transition, respectively. The above equation contains six parameters to be adjusted. The second term is concerned with the hot band and accordingly, it makes only a small contribution to the total intensity. Since there must be a strong correlation between the parameters for the fundamental and hot bands, it was expected that the possible minor deviation of a single-transition band from a Lorentzian profile and small errors included in the observed intensity might obscure the resulting parameter values for the hot band. Indeed, it was found by a preliminary calculation that no plausible parameter values were obtained for the hot band. In such circumstances it is desirable to adjust the parameters under reasonable constraints.

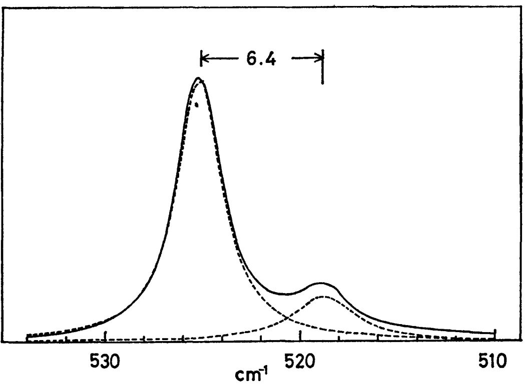

Fig. 2. The Raman ν_3 band of methyl iodide in carbon disulfide (1.8 mol/l). The band was decomposed into $\nu(0\rightarrow1)$ and $\nu(1\rightarrow2)$ using the Lorentzian functions shown by broken lines. The spectrum was recorded on a JASCO R300S Laser Raman Spectrophotometer.

The following two restrictions were then introduced into the calculations: (1) the ratio of the band areas, $[\omega(1\rightarrow2)\cdot P(1\rightarrow2)]/[\omega(0\rightarrow1)\cdot P(0\rightarrow1)]$, is equal to a theoretical value, $2\exp(-hc\nu/kT)$, which is 0.162 at $T=300$ K and $\nu=527\ cm^{-1}$, and (2), the separation between the fundamental and the first hot bands, $\nu^0(0\rightarrow1)-\nu^0(1\rightarrow2)$, is equal to the value in the gas phase, 6.6 cm^{-1}. This value was calculated from the fundamental and first overtone frequencies reported by Jones and Thompson[25)] by means of the relation $\nu^0(1\rightarrow2)-\nu^0(0\rightarrow1)=2x_{33}=\nu^0(0\rightarrow2)-2\nu^0(0\rightarrow1)$, where x_{33} is the anharmonicity constant for ν_3. This value is supported by the Raman spectrum of methyl iodide in carbon disulfide. As is shown in Fig. 2, the separation, $2x_{33}$, is almost the same as in the gas phase. The width of the highly-polarized Raman band is narrower than that of the infrared absorption band, so that the hot band is more conspicuous in the Raman spectrum.

The simulation was carried out over a range from 508 to 548 cm^{-1} for the solutions in n-pentane, n-hexane, and carbontetrachloride, and a range from 504 to 544 cm^{-1} for the solutions in carbon disulfide, chloroform, benzene, and bromobenzene. Figure 1 shows examples of the results. Good fits between the observed and calculated bands were obtained for all the solutions except for slight discrepancies in the low-frequency wing. The higher hot-bands ignored in the above calculations are too weak to indicate this discrepancy. For the other a_1-type bands, ν_1 and ν_2, of methyl iodide, slight discrepancies were also found in the low-frequency wings,[4,21,26] although the general profile of each band was well reproduced by a Lorentzian function.[21] The deviation of the observed band from a Lorentzian function is a measure of the asymmetry of the band and will be discussed later.

The parameter values obtained are summarized in Table 1. If we take into account the fact that the values of $\omega(1\rightarrow2)$ involve more uncertainty than those of $\omega(0\rightarrow1)$, it may be said that the $\omega(0\rightarrow1)$ and $\omega(1\rightarrow2)$ values are nearly equal to each other in all the solutions studied and that they are about 10% smaller than the corresponding apparent half-widths, ω_{obsd}.

The band shape of the overtone, $\nu_3(0\rightarrow2)$, was determined from the spectrum of a solution in carbon disulfide. The overtone ν_3 band overlaps on the high-frequency wing of the strong degenerate vibrational band, ν_6. As may be seen in Fig. 3, the $\nu_3(0\rightarrow2)$ peak is well-resolved and the foot of the ν_6 band forms a strong background. Since the wing of the ν_6 band has been found to be well-reproduced by a Lorentzian function,[26] the spectrum ranging from 1010 to 1080 cm^{-1} was decomposed by means of the superposition of three Lorentzian functions. The analysis was carried out under the restriction, $\omega(0\rightarrow2)=\omega(1\rightarrow3)$, which was set referring to the results obtained for the fundamental band. The best fit parameters are as follows: $\nu^0(0\rightarrow2)=1046.7\ \text{cm}^{-1}$, $(\nu^0(1\rightarrow3)-\nu^0(0\rightarrow2))/2=-6.9\ \text{cm}^{-1}$ $(=2x_{33})$, $[\omega(1\rightarrow3)\cdot P(1\rightarrow3)]/[\omega(0\rightarrow2)\cdot P(0\rightarrow2)]=0.14$, and $\omega(0\rightarrow2)=\omega(1\rightarrow3)=13.2\ \text{cm}^{-1}$. The half-width of the hot band is larger than that of the fundamental band. The value of $2x_{33}$ obtained here agrees with the value of $-6.9\ \text{cm}^{-1}$, which is derived using the relation $2x_{33}=\nu^0(0\rightarrow2)-2\nu^0(0\rightarrow1)$. The value, $-6.6\ \text{cm}^{-1}$, assumed in the decomposition of the fundamental band is also satisfactorily close to $-6.9\ \text{cm}^{-1}$. The ratio of the band area, 0.14, is nearly the same as the ratio of 0.16, which was assumed in the analysis of the fundamental band.

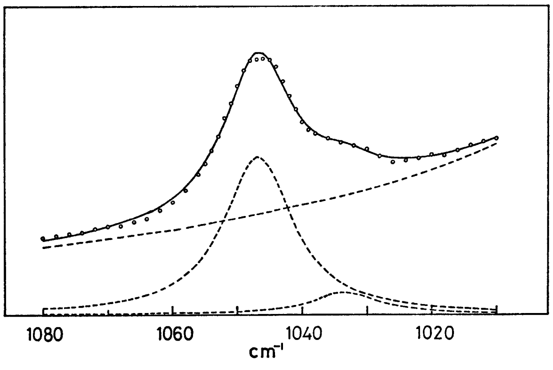

Fig. 3. The overtone $\nu_3(0\rightarrow2)$ band of methyl iodide in carbon disulfide solution (2 mol/l); ○○○ observed band, — calculated band, --- component bands; (1) $\nu_3(0\rightarrow2)$, (2) $\nu_3(1\rightarrow3)$, and (3) ν_6.

Discussion

An infrared band shape may be expressed by the convolution of spectral densities associated with the reorientational and vibrational relaxations of the transition dipole moment of a molecule.[15] If both of the relaxations are assumed to be characterized by exponential decays, the band width is given by the sum of the widths of the two spectral densities.[12]

The reorientational motion of a molecule should contribute equally to the band widths of the $\nu_3(0\rightarrow1)$, $\nu_3(1\rightarrow2)$, and $\nu_3(0\rightarrow2)$ transitions, for the vibration-rotation interaction, such as A_1-E type Coriolis interaction,[27] may be negligible in these transitions. Therefore, the observed difference in band-widths between the overtone and fundamental bands must be due to the difference in the vibrational relaxation for the two transitions.

According to Valiev,[28] the broadening of a quantum level due to the resonant exchange of vibrational energy between solute molecules is proportional to the square root of the product of its quantum number n and the concentration of the solution c. Then, the band broadening of the transition $n\rightarrow n'$ is given by the sum of the broadening of the n and n' vibrational levels as follows,

$$\omega_{\text{res}}(n\rightarrow n') = A\sqrt{c}(\sqrt{n}+\sqrt{n'}),$$

where A is a constant involving the dipole moment derivative with respect to the normal coordinate in question, the Stokes radius of the molecule, and the molecular weight. Accordingly, the half-widths for the $0\rightarrow1$, $1\rightarrow2$, and $0\rightarrow2$ transitions are given by $A\sqrt{c}$, $(1+\sqrt{2})A\sqrt{c}$, and $\sqrt{2}A\sqrt{c}$, respectively. However, the observed half-widths were independent of concentration, at least in the concentration range employed, and furthermore, $\omega(1\rightarrow2)$ and $\omega(0\rightarrow1)$ are nearly equal to each other and both are smaller than $\omega(0\rightarrow2)$. This means that the vibrational relaxation of the resonant exchange type does not contribute appreciably to the broadening of the C–I stretching band of methyl iodide in solution.

The vibrational relaxation of the translational diffusion type proposed by Bratos *et al.*[15] seems more favorable in order to interpret the present experimental results. According to their theory, the broadening of a band is related to the difference between the mean energies of the solute-solvent interaction in the two vibrational states involved in the transition. This difference is merely reflected in the solvent-induced frequency shift of the band center. The relationship between n and the frequency shift for a $0\rightarrow n$ transition, $\Delta\nu_{0n}$, was evaluated by Bratos *et al.*[15] As may be seen in Fig. 4 of Ref. 15, $\Delta\nu_{0n}$ is nearly proportional to n for a few lower vibrational states. This is obtained in the present study for the C–I stretching band of methyl iodide in carbon disulfide, *i.e.*, $\Delta\nu_{01}=6.4\ \text{cm}^{-1}$ and $\Delta\nu_{02}=13.2\ \text{cm}^{-1}$ [29]. Since $\Delta\nu_{12}=\Delta\nu_{02}-\Delta\nu_{01}$, $\Delta\nu_{12}$ is nearly equal to $\Delta\nu_{01}$. Bratos *et al.* also showed that the time scale in the decay of the vibrational relaxation function for the $n\rightarrow n'$ transition is inversely proportional to the frequency shift, $\Delta\nu_{nn'}$. Then, the band broadening caused by vibrational relaxation of this type, $\omega_{tr}(n\to n')$, is roughly proportional to $\Delta\nu_{nn'}$. It follows that the values of $\omega_{tr}(0\to1)$ and $\omega_{tr}(1\to2)$ are nearly equal to each other and the value of $\omega_{tr}(0\to2)$ is about twice as large as those values. This is consistent with the information obtained about on the half-widths of $\omega(0\to1)$, $\omega(1\to2)$, and $\omega(0\to2)$. It has been pointed out that for a symmetric top molecule, the broadening of the isotropic component of an a_1-type Raman vibrational band arises exclusively from the vibrational relaxation of the molecules.[26,30-32] For the $\nu_3(0\to1)$ band of methyl iodide in carbon disulfide (concentration, 1.7 mol/l), the width of its isotropic component was measured to be 2.0 cm^{-1}.[33] The width due to vibrational relaxation may be the same for both the Raman and infrared absorption bands. If the observed value of 2.0 cm^{-1} is attributed to vibrational relaxation, then the contribution of the reorientational relaxation to $\omega(0\to1)$ is evaluated to be 6.3 cm^{-1} by subtracting the value of 2.0 cm^{-1} from the observed $\omega(0\to1)$ value. Moreover, if the vibrational relaxation is of the translational diffusion type, the $\omega(0\to2)$ value may be estimated by adding twice the vibrational contribution 2×2.0 cm^{-1}, to the reorientational one, 6.3 cm^{-1}. The resulting value of 10.3 cm^{-1} is smaller than the observed value of 13.2 cm^{-1} and is insufficient to interpret the observed width. Further explanation seems to be required to explain the broadening of the overtone band. Since the estimation of $\omega(0\to2)$ described above is very rough, it is inappropriate to draw any definite conclusion from the present results. However, for the time being, it appears that in addition to the reorientational relaxation, the vibrational relaxation of the translational diffusion type proposed by Bratos *et al.* contributes to the width of the ν_3 band.

A slight deviation from the Lorentzian function in the low-frequency wing was recognized in the observed band. In the band envelope of the ν_3 band of methyl iodide in the gas phase, the P branch has a longer tail than the R branch, as is shown in Fig. 4. This is due to the fact that the value of $B'-B''$ is not equal to zero because of the vibration-rotation interaction, where B is the rotational constant about the axis perpendicular to the three-fold symmetry axis, and the prime and double prime denote the excited and ground states respectively. This asymmetry of the band in the gas phase seems to correspond to that in the solution, although the latter is much less marked.[34]

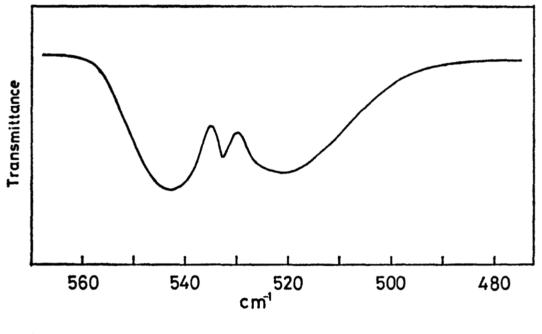

Fig. 4. The envelope of the infrared ν_3 band of methyl iodide in the gas phase.

The authors wish to thank Professors Kozo Tanabe and Osamu Yonemitsu of the Hokkaido University for permission to use the JASCO DS-701G infrared spectrophotometers. The numerical calculations were carried out on a FACOM 230—60 of the Hokkaido University Computing Center.

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34) The value of $B'-B''$ for the 0→2 transition is about two times larger than that for the 0→1 transition. Thus, the overtone $\nu_3(0\rightarrow2)$ band should be more asymmetric than the fundamental $\nu_3(0\rightarrow1)$ band. However, such detailed character of the $\nu_3(0\rightarrow2)$ band cannot be discussed because of the uncertainty due to overlap with the intense ν_6 band.