The Infrared Band Shapes of Methyl Iodide in Solutions

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The infrared band shapes of methyl iodide in solutions were simulated by the superposition of the Lorentzian functions. The a_1-type band was well repoduced by a single Lorentzian function. Its half-width was reasonably explained by the reorientational and vibrational relaxations. The e-type band was reproduced by two Lorentzian functions; one represents the central main peak of the band, while the other is much broader and appears like a background. The half-width of the former was nearly proportional to the Q-branch line spacing in the gas spectrum, while that of the latter seems to be related to the A_1-E-type Coriolis coupling.

The infrared band shape of a molecule in the liquid phase contains information about the rotational diffusion of the molecule.[1—12] However, in order to get insight into the details, it is necessary to take into account the vibrational relaxation of the resonant-exchange[9,10] and translational-diffusion types,[11,12] and the vibration-rotation interaction[6] as well. The effect of other overlapping vibrational transition can not be neglected, either.[11]

It is well-known that the e-type bands of methyl halides in the liquid phase have considerably greater widths than the a_1-type bands. Jones and Sheppard[13] attributed this fact to a large difference between the two kinds of moments of inertia of the molecules. They also suggested that the Coriolis interaction between the degenerate vibration and the rotation about the three-fold axis was operative on the e-type band widths, since a considerable degree of rotational freedom about the three-fold axis remained in solutions. On the other hand, Glass and Pullin[14] and also Bulanin and Tonkov[15] reported that no clear correlation was observed between various half-widths of the e-type bands and the Coriolis constants. Bulanin and Tonkov proposed that the broadening of the e-type band was caused, rather, by the splitting of the degenerate level as a result of the intermolecular force field. However, the observed splittings in a crystal[16] resulting from the intermolecular force field are too small to explain the various half-widths of the e-type bands in the liquid phase. Under these circumstances, more detailed analyses of the bands are necessary in order to clear up the character of the infrared band shape. In a previous paper we reported on the ν_3 band of methyl iodide.[11] In the present work, the simulation of the observed band shape by means of analytical functions has been extended to the eight a_1-type transitions and the five e-type transitions of the same molecule in solutions.

Experimental

The infrared transmission was measured at room temperature with a JASCO DS-701G Spectrophotometer. The spectral slit widths were set at 1.0—1.5 cm^{-1} and about 2 cm^{-1} in the measurement of the a_1- and e-type bands respectively. Under these conditions, no correction is needed for the effect of the finite slit width on the observed band-widths.[17] Uncertainties in the observed band-width were estimated, in the manner described in the previous report,[11] to be ±0.3 cm^{-1} and ±1 cm^{-1} for the a_1- and e-bands respectively. The concentrations of methyl iodide in solutions were arranged between 0.4 and 2.3 mol/l. They are in the same concentration range as was employed in the previous work,[11] where the observed band shapes in the ν_3 region were almost independent of the concentrations. Therefore, the concentration-dependence of band shapes was also ignored in the present work. Carbon disulfide and carbon tetrachloride were used as solvents. The two kinds of solutions yielded almost the same band-width wherever both solvents can be used for measurements.

Decomposition of Bands

The observed intensity was obtained by means of this equation:

$$I(\nu) = \ln(\mathbf{T}_0/\mathbf{T})_\nu[\nu(1-\exp(-hc\nu/kT))]^{-1}, \qquad (1)$$

where $(\mathbf{T}/\mathbf{T}_0)_\nu$ is the transmittance at wavenumber ν and where T is the absolute temperature. The observed values are indicated by small circles in Figs. 1—5. If the random-reorientation model is adopted for the ensemble of molecules, the band-shape function (1) for a single vibrational transition centered at ν^0 is given by:[1]

$$I(\nu) \sim \sum_{i,f}\rho_i|\langle i|\boldsymbol{\varepsilon}\cdot\boldsymbol{m}^{\mathrm{v}}|f\rangle|^2\delta[(E_f-E_i)/hc-(\nu-\nu^0)] \qquad (2)$$

From this equation, one can easily derive the following relationship:

$$I(2\nu^0-\nu) = \exp(-hc(\nu-\nu^0)/kT)\cdot I(\nu) \qquad (3)$$

This is nothing but the condition of the detailed balance.[18] Such a function, $I(\nu)$, can be represented in terms of a symmetric function, $I_s(|\nu-\nu^0|)$, as follows:

$$I(\nu) = \exp(hc(\nu-\nu^0)/2kT)\cdot I_s(|\nu-\nu^0|) \qquad (4)$$

Here, $I_s(|\nu-\nu^0|)$ represents the Fourier transform of a real autocorrelation function of the transition dipole moment. It is widely accepted that the dipole correlation function should show an exponential decay at a long time in the liquid phase. It follows from this that the central part of the infrared band should be described by a Lorentzian profile. Thus, $I_s(|\nu-\nu^0|)$ was assumed to be Lorentzian. The observed intensity in a given region is, then, expressed in general by:

$$I(\nu) = \sum_i \exp(hc(\nu-\nu_i^0)/2kT)\frac{p_i(\omega_i/2)^2}{(\nu-\nu_i^0)^2+(\omega_i/2)^2}, \qquad (5)$$

where ν_i^0, ω_i, p_i denote the band center, the half band-width, and the peak height respectively for the i-th vibrational transition. The right-hand side of Eq. 5 is divergent on the high-frequency side. However, since the absorption regions in question were limited near the

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Table 1. Band parameters of the a_1-type vibrations of methyl iodide

	Solvent	Concn mol/l	ν^0 cm^{-1}	cm^{-1}
ν_1	CS_2	1.0	2952.4	10.8
	CCl_4	1.0	2958.0	10.7
$2\nu_2$	CCl_4	1.5	2841.0	20.0
$\nu_3+\nu_5+\nu_6$	CCl_4	1.5	2818.0	18.3
$2\nu_2(0\rightarrow2)$	CS_2	1.6	2464.2	9.1
$2\nu_2(1\rightarrow3)$	CS_2	1.6	2453.0	9.0
ν_2	CS_2	0.4	1239.5	7.7
$2\nu_3$[a]	CS_2	2.3	1046.7	13.2
$\nu_3(0\rightarrow1)$[a]	CS_2	1.5	526.8	8.3
	CCl_4	1.5	527.6	8.3
$\nu_3(1\rightarrow2)$[a]	CS_2	1.5	520.2	7.7
	CCl_4	1.5	521.0	8.3

a) Reproduced from Ref. 11.

band centers, no difficulty occurred in the band analysis. The parameter values fitted are summarized in Tables 1 and 2. Practically, the parameter values adjusted for bands with half-widths smaller than 30 cm^{-1} did not depend upon whether or not the exponential factor in Eq. 5 was ignored. Therefore, the values for the ν_3 band in Table 1 are taken from the previous report, in which this factor was ignored.[11]

Results and Discussion

a_1-Type Bands. The band shape of the fundamental a_1-type vibration is well reproduced by a single Lorentzian function, except for slight deviations from the Lorentzian functions in the lower-frequency wings, as may be seen in Fig. 1. A similar deviation was also found for the ν_3 fundamental band.[11] These deviations may be attributed to the vibration-rotation interaction, as was mentioned in the previous report on the ν_3 band.

The doublet in the region from 2740 to 2900 cm^{-1} was observed as parallel bands in the gas phase and was assigned to the Fermi doublet, $2\nu_5$ and $\nu_3+\nu_5+\nu_6$, by Matsuura and Shimanouchi.[19] The decomposition of the doublet was performed after subtracting the wings of the ν_1 and ν_4 bands from the total absorption. The results are shown in Fig. 2a.

In the absorption region of the $2\nu_2$ band, a small band is observed in the lower-frequency wing, as is shown in Fig. 2b. The best-fit parameter values of the two Lorentzian functions are $\nu_a{}^0=2464.2$ cm^{-1}, $\nu_b{}^0=2453.0$ cm^{-1}, $\omega_a=9.1$ cm^{-1}, and $\omega_b=9.0$ cm^{-1}, and the ratio of band areas, $p_b\omega_b/p_a\omega_a$, is 0.095, where the subscripts a and b denote the $2\nu_2$ and the small band respectively. The small band may be assigned to the hot band transition, $2\nu_2+\nu_3-\nu_3$, since its half-width is nearly equal to that of $2\nu_2$ and since the area ratio is in agreement with the theoretical values, $\exp(-hc\nu_3/kT)=0.081$, at $T=300$ K. The anharmonicity constant was estimated using the relation $x_{23}=(\nu_b{}^0-\nu_a{}^0)/2$ to be -5.6 cm^{-1}. This value is nearly equal to the value of -5 cm^{-1} obtained by using another relation, $x_{23}=(\nu_2+\nu_3)-\nu_2-\nu_3$, in a CCl_4 solution.[20] Although such a non-zero x_{23} should produce the $\nu_2+\nu_3-\nu_3$ hot band at the frequency lower than that of the ν_2 fundamental by about 5 cm^{-1}, it is impossible to resolve the observed band into the two components. However, the effect of the hot band on the parameter values obtained for the ν_2 fundamental band may be small and need not be taken into account in the following discussion.

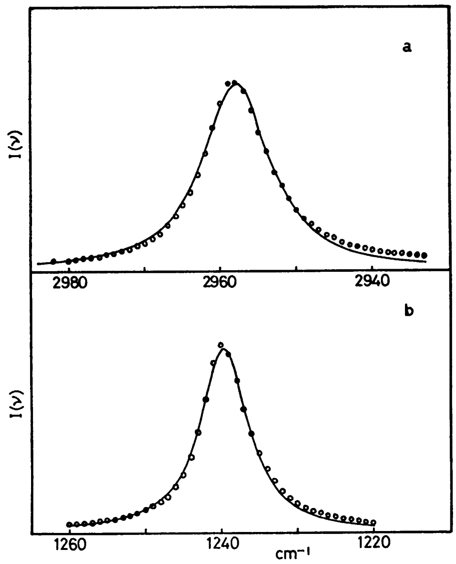

Fig. 1. The infrared bands of methyl iodide in solutions: (a) ν_1 in CCl_4, (b) ν_2 in CS_2.
●●●●●●: Observed; ——: calculated.

The band width of the overtone, $2\nu_2$, is larger than that of the fundamental, ν_2. This is probably due to the difference between contributions from the vibrational relaxation of the translational-diffusion type,[12] as was pointed out in the case of the ν_3 transition.[11] If there is no other cause of the band broadening, the width due to the vibrational relaxation is estimated to be $\omega_2(0\rightarrow2)-\omega_2(0\rightarrow1)=1.4$ cm^{-1}; accordingly the width due to the reorientational relaxation becomes $\omega_2(0\rightarrow1)-1.4$ cm^{-1}

Table 2. Band parameters of e-type vibrations of methyl iodide[a]

	Solvent	Concn mol/l	$\nu^0(L_1)$	$\omega(L_1)$	$\nu^0(L_2)$	$\omega(L_2)$	ω(ap)	ζ	$\omega(L_1)/(1\text{-}\zeta)$
ν_4	CS_2	1.5	3046	29	3029	200	76	0.060[b]	31
	CCl_4	1.5	3051	27	3042	202	76		29
$\nu_2+\nu_6$	CCl_4	2.3	2126.3	28					
ν_5	CCl_4	1.5	1430.0	31	1418	171	43	−0.016[c]	30
$\nu_3+\nu_6$	CCl_4	1.5	1400.3	30					29
ν_6	CS_2	1.5	881.3	24	882	80	30	0.210[d]	30

a) Frequencies in cm^{-1} unit. b) Taken from Ref. 27a. c) Average of $\zeta_5=-0.242$ and $\zeta_{36}=0.210$, see text.
d) Taken from Ref. 27d.

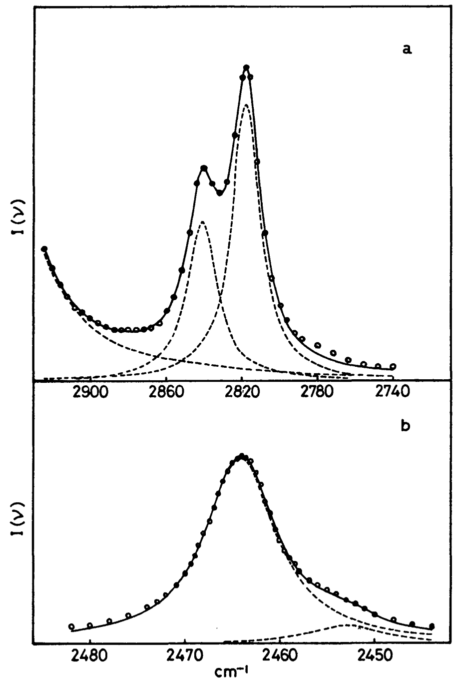

Fig. 2. The infrared bands of methyl iodide in solutions: (a) the region of the doublet $2\nu_5$ and $\nu_3+\nu_5+\nu_6$ in CCl_4, (b) the region of the $2\nu_2$ band in CS_2.
∘∘∘∘∘: Observed; ——: calculated, total; ------: calculated, components.

$=6.3$ cm^{-1}. In order to estimate the reorientational relaxation for the ν_1 band, some Raman data is available. The width of the isotropic component of the Raman ν_1 band has been found to be 3.5 cm^{-1} in CS_2 solutions (1.7 mol/l).[21] This width may be considered to be due to the vibrational relaxation and to be transferable to the infrared-band width.[11,22–25] Then, the bandwidth of the infrared ν_1 vibration due to the reorientational relaxation is estimated to be $\omega_1(0\rightarrow1)-3.5$ cm^{-1}$=7.3$ cm^{-1}. The widths of the ν_3 band due to the reorientational and vibrational relaxations have previously been estimated to be 6.3 and 2.0 cm^{-1} respectively.[11]

The vibrational species of the same symmetry have transition dipole moments in the same direction in the molecular framework. Therefore, their band-widths based upon the reorientational relaxation should be identical to one another only if the effect of the vibration-rotation interaction is negligible. This is the case for the a_1-type band of CH_3I. The estimated bandwidths due to the reorientational relaxation, 7.3, 6.3, and 6.3 cm^{-1} for the ν_1, ν_2, and ν_3 vibrations respectively, agree approximately with one another in spite of a scattering of the observed total widths, 10.8, 7.7, and 8.3 cm^{-1}.[26]

The band-widths of the Fermi doublet, $2\nu_5$ and $\nu_3+\nu_5+\nu_6$, are much larger than those of the other a_1-type bands. Matsuura and Shimanouchi[19] have pointed out that the unperturbed $(\nu_3+\nu_5+\nu_6)^0$ band behaves as a quasi-perpendicular band with an effective Coriolis constant of -0.47, whereas the unperturbed $(2\nu_5)^0$ band has the normal profile of a parallel band. The band-widths observed in solutions are intermediate between those of the a_1-type and the e-type bands. It is probable that the vibration-rotation interaction is operative in solutions and that, as a result, the broadenings of the components of this doublet are much larger than those of the other a_1-type bands.

e-Type Bands. The absorption region of the e-type vibration is, as a rule, well reproduced by two Lorentzian functions. The narrower Lorentzian, designated as $\nu(L_1)$, and the broader one, designated as $\nu(L_2)$, represent the shape near the band center and a background-like absorption of a greater width respectively.

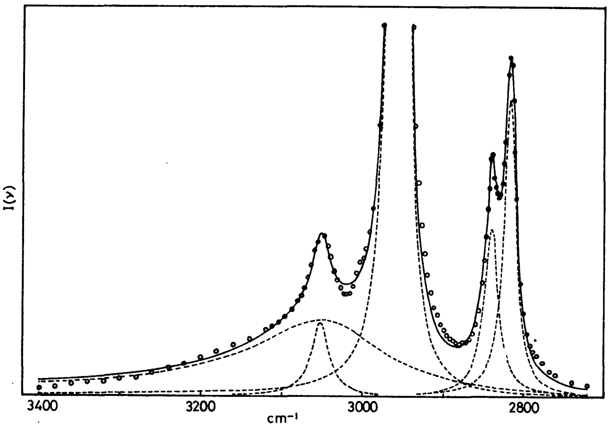

Fig. 3. The infrared absorption in the region from 2720 to 3400 cm^{-1} of methyl iodide in the carbon tetrachloride solution.
∘∘∘∘∘: Observed; ——: calculated, total; ------: calculated, components.

Figure 3 shows the absorption ranging from 2720 to 3400 cm^{-1}, of methyl iodide in carbon tetrachloride. In addition to the e-type ν_4 band, there appear three a_1-type bands, ν_1, $2\nu_5$, and $\nu_3+\nu_5+\nu_6$. The absorption in this region is well reproduced by five Lorentzian functions. It should be noted that $\nu_4(L_2)$ is much broader than the others and spreads all over the region.

In the absorption region of ν_5, the combination band $\nu_3+\nu_6$ also appears. This region is well reproduced by three Lorentzian functions, as is shown in Fig. 4. It has

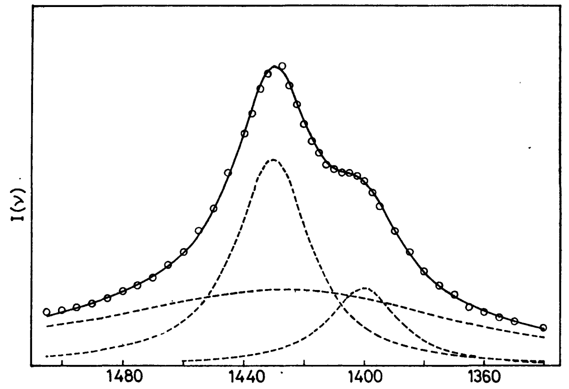

Fig. 4. The infrared absorption in the region of the Fermi doublet ν_5 and $\nu_3+\nu_6$ of methyl iodide in the carbon tetrachloride solution.
∘∘∘∘∘: Observed; ——: calculated, total; ------: calculated, components.

been established that the Fermi-resonance occurs between the ν_5 and $\nu_3+\nu_6$ bands.[27] If the value of the Fermi-resonance parameter, $W=K_{356}/\sqrt{2}$, in the solution is assumed to be equal to that in the gas phase, 10.4 cm^{-1},[27d] the unperturbed frequencies may be estimated to be 1426.5 and 1403.8 cm^{-1} for $\nu_5{}^0$ and $(\nu_3+\nu_6)^0$ respectively. The value of the anharmonicity constant, x_{36}, is, then, obtained to be as follows: $x_{36}=(\nu_3+\nu_6)^0-\nu_3-\nu_6=-4.8$ cm^{-1}. This value agrees with those obtained in the gas phase, -5.6[27d] and -5 cm^{-1}.[27b] Both the values of K_{356} and x_{36} seem to be almost unchanged on going from gas to solution.

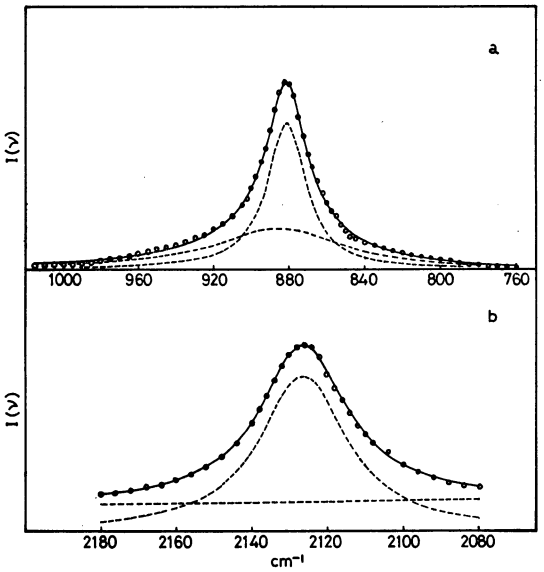

Fig. 5. The infrared bands of methyl iodide in solutions: (a) ν_6 in CS$_2$, (b) $\nu_2+\nu_6$ in CCl$_4$.
●●●●●: Observed; ——: calculated, total; ------: calculated, components.

The region of the ν_6 vibration is simply reproduced by two Lorentzian functions, as is shown in Fig. 5a. The combination band, $\nu_2+\nu_6$, is much weaker than the other e-type bands studied in the present work. The background-like absorption in Fig. 5b looks nearly constant throughout the region. This is probably because of the overlap of the wings of the neighboring bands. It is impossible to extract the $\nu(L_2)$ from the whole background.

The shapes of ν_4, ν_5, and ν_6 fundamental bands, each of which is composed of $\nu(L_1)$ and $\nu(L_2)$, are compared in Fig. 6. Their band-widths, ω(ap), are very different from each other, as is shown in Table 2. Nevertheless, the half-widths of $\nu(L_1)$, $\omega(L_1)$, are much less dispersive and in the order of $\omega_5(L_1)>\omega_4(L_1)>\omega_6(L_1)$, in accordance with that of the Q-branch line spacings in the gas phase. The Q-branch line spacing of methyl iodide in the gas phase is nearly proportional to $1-\zeta$, where ζ is the Coriolis coupling constant. The values of ζ have been reported to be 0.060,[27a] -0.242,[27d] and 0.210[27d] for ν_4, ν_5, and ν_6 respectively. If a strong Fermi resonance occurs, the Q-branch line spacing of each Fermi component may be related to the mean value of ζ for the unperturbed vibrations, at least in the region near the band center. Therefore, we tentatively adopted the value of $\zeta=(\zeta_5+\zeta_6)/2$ for the Fermi doublet, by using ζ_6 in place of ζ_{36}. The values of $\omega(L_1)$ divided by $1-\zeta$ are given in the last column in Table 2. They are constant; in other words, $\omega(L_1)$ is proportional to the Q-branch line spacing.

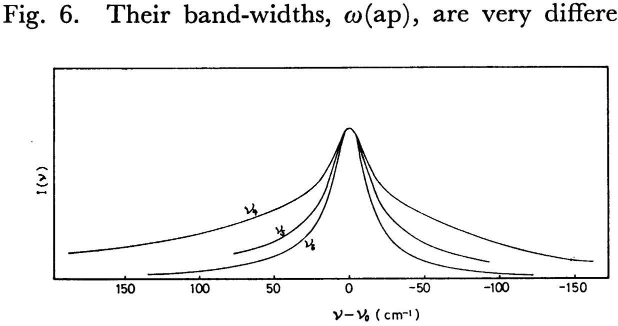

Fig. 6. Comparison of the normalized shapes of the ν_4, ν_5, and ν_6 bands, each of which is composed of $\nu(L_1)$ and $\nu(L_2)$.

The absorptions specified by $\nu(L_2)$ serve for the broadening of the observed bands; the percentage of each $\nu(L_2)$ occupying the band area and the broadening are much larger for ν_4 than ν_5 and ν_6. No definite conclusion can be drawn about their origin and precise shape at present. However, the $\nu(L_2)$ parts of the e-type bands seem to be related to the A$_1$-E-type Coriolis coupling, with the intense nondegenerate band in the neighborhood. The intensity perturbation due to the A$_1$-E-type Coriolis coupling is approximately proportional to $[J(J+1)-K(K+1)]$ in the gas phase.[28] This type of coupling probably intensifies the band-wing, even in the solutions. For methyl iodide, the separations between the degenerate bands and their nondegenerate intense neighbors are $\nu_4-\nu_1\approx 90$ cm^{-1}, $\nu_5-\nu_2\approx 170$ cm^{-1}, $\nu_2-\nu_6\approx 360$ cm^{-1}, and $\nu_6-\nu_3\approx 350$ cm^{-1}. Therefore, the A$_1$-E-type Coriolis coupling may affect the ν_4 band most strongly and the ν_6 band most weakly. This is consistent with the observed order of the magnitudes for $\omega(L_2)$.

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