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High-overtone Spectra and Dipole Moment Functions for the C-H Stretching Vibration of Chloroform

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The absorption spectra of liquid chloroform were observed for the C–H stretching fundamental vibration and its overtones up to $v=\leftarrow 50$. The spectral parameters were analyzed on the basis of the one-dimensional local mode representation, which led to the determination of the mechanical and electrical anharmonicities. The solvent effects on the absorption intensities are discussed from the viewpoint of the solvent effect on the dipole moment function. The finally obtained dipole moment function was compared with that obtained by the *ab initio* calculation.

The absolute intensity of the C–H stretching fundamental band of chloroform in the gas phase has been known to be anomalously weak in comparison with the absolute intensity of its pure overtone, *i.e.*, the $v=2\leftarrow 0$ band. The reason of this anomaly has been vaguely attributed to same electric anharmonicity related with this vibrational mode.[1)] Since the intensities of overtones are influenced by both mechanical and electrical anharmonicities, however, we cannot obtain any definite conclusions about this problem without analyzing these two kinds of anharmonicities simultaneously.

Previously we have reported the intensity analysis of the C–H stretching overtones for a few molecules.[2)] In the report, we emphasized the usefulness of the one-dimensional local mode model for the analysis of intensity data. At the same time, the choice of the Morse-type potential function was found to give a satisfactory approximation for the elucidation of the mechanical anharmonicity, if we are able to define the absorption bands in terms of the local mode representation. This result indicates, at the same time, that we are now able to obtain accurate knowledge about the electrical anharmonicity for a system in which a local mode can be well defined.

A chloroform molecule has only one C–H bond. Therefore, it is the most appropriate molecule to which to apply our one-dimensional oscillator model. The intensity of the $v=1\leftarrow 0$ band of chloroform is sensitive to the change of molecular environment. Such spectral changes of the $v=1\leftarrow 0$ band have been interpreted in terms of the hydrogen bonding in the liquid or solution phase.[3)] Suzuki *et al.* have reported that the concentration dependence of the intensities and the line width of the C–H stretching vibration of chloroform in carbon tetrachloride solutions can be well explained by considering the coexistence of two different types of chloroform molecules; one is a molecule which interacts with other molecules and the other is a non-interacting molecule.[4)] The role of the carbon tetrachloride molecule is to break the interaction between chloroform molecules.

The present work has examined the absorption spectra of the C–H stretching vibration of chloroform observed for the fundamental and overtone bands. The observed spectral parameters will be analyzed on the basis of the one-dimensional local mode model to obtain the dipole moment function. Based upon these results, the remarkable solvent effect observed for the intensity of the fundamental band will be discussed in relation to the solvent effect on the dipole moment function.

Experimental

All the chemicals used in this work were commercially available reagents. Chloroform was purified by column chromatography on alumina to remove ethanol.

The absorption spectra were measured for the C–H stretching vibrations of liquid chloroform with the use of a Fourier transform infrared spectrometer (NICOLET 7199) at room temperature. For the measurement of the $v=1\leftarrow 0$ band, a water-cooled Glober source and a mercury cadmium telluride detector were used. The used beam-splitter was a Ge on KBr substrate. An NaCl window cell having a thickness of 0.0025 cm was used for the $v=1\leftarrow 0$ band intensity measurement. For the measurements of the $v=2\leftarrow 0$, $v=3\leftarrow 0$, and $v=4\leftarrow 0$ bands, a water-cooled tungsten-halogen lamp, a quartz beam-splitter, and an InAs detector were used. An NaCl window cell having a thickness of 0.0107 cm was used for the $v=2\leftarrow 0$ band, while a quartz cell having a thickness of 1 cm was used for the $v=3\leftarrow 0$ and $v=4\leftarrow 0$ bands.

The concentration dependences of the absorption spectra were observed in the carbon tetrachloride solutions at the concentrations of 80, 60, 40, and 20 mol %.

For the measurement of the $v=5\leftarrow 0$ band, a UV-visible spectrometer (CARY 17) and a quartz cell having an optical path length of 10 cm were used.

All the absorption spectra were measured with a resolution of about 1 cm^{-1}.

Results and Discussion

Analysis of Intensity Data. The absolute intensity $\Gamma_{n',n''}$ related with the $v=n''\leftarrow n'$ transition can be expressed in terms of the experimentally observable quantities as

$$\Gamma_{n',n''}=\frac{f_\mathrm{d}}{nl}\int_{\mathrm{band}}\ln\left(\frac{I_0}{I}\right)\mathrm{d}\ln\nu \qquad (1)$$

where n is the concentration of sample, l is the sample thickness, I_0 and I are the intensities of the incident and transmitted light, respectively, and ν is the frequency of light. f_d is the correction factor for the dielectric-field effect. Since the absolute intensities of the observed

TABLE 1. THE BAND PARAMETERS OBSERVED FOR THE C–H STRETCHING VIBRATION IN THE LIQUID AND CCl_4 SOLUTIONS PHASES

Molar concentration of $CHCl_3$ (%)		100	80	60	40	20	Gas[a]
ν_1	ν_0/cm^{-1}	3019.5	3019.5	3019.5	3019.5	3019.5	3032.9
	$\Gamma/cm^2\,mol^{-1}$	245	216	190	172	134	5.247
$2\nu_1$	ν_0/cm^{-1}	5912	5910	5908	5907	5906	5941.4
	$\Gamma/cm^2\,mol^{-1}$	16	17	16	17	18	17.32
$3\nu_1$	ν_0/cm^{-1}	8674	8672	8672	8670	8669	—
	$\Gamma/cm^2\,mol^{-1}$	0.61	0.63	0.61	0.59	0.55	—
$4\nu_1$	ν_0/cm^{-1}	11315	11315	11315	11315	11315	—
	$\Gamma/cm^2\,mol^{-1}$	0.0251	0.0268	0.0266	0.0268	0.0306	—
$5\nu_1$	ν_0/cm^{-1}	13850	—	—	—	—	—
	$\Gamma/cm^2\,mol^{-1}$	2.46×10^{-3}	—	—	—	—	—

[a] After Rossi *et al.* (see Ref. 1).

bands are weak, the Polo-Wilson's scheme[5] can safely be applied to the dielectric-field correction.[6] Thus, the correction factor f_d can be expressed as

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

where n_D is the refractive index of the solution. The used n_D data were found in the International Critical Tables.[7]

Concentration Dependence of Absolute Intensity. The cencentration dependence of band parameters (the peak frequency and the intensity) observed for the carbon tetrachloride solutions are summarized in Table 1. The intensities of the $v=1\leftarrow0$ and $v=2\leftarrow0$ bands observed for the gas phase by Rossi *et al.*[1] are also included in the last column of Table 1.

The absolute intensity of the $v=1\leftarrow0$ band in 20 mol% of carbon tetrachloride solution is about half of that in the pure liquid chloroform. No remarkable solvent effects on the intensities were observed for the overtone bands; this result in sharp contrast with that for the fundamental band. It has been shown in our previous report that the intensities of overtone bands are determined by both the electrical and the mechanical anharmonicities.[2] Let us consider the mechanical anharmonicity first.

Mechanical Anharmonicity and Absorption Frequency. The mechanical anharmonicity is directly related with the potential term of the Hamiltonian. Therefore, it can be determined by the frequency measurement of the absorption maximum for the fundamental and overtone bands. It has been established that the frequencies of the absorption maxima of the overtone bands are well approximated by the Birge-Sponer equation, if we can assign the overtone spectra on the basis of the local mode representation,[8–10] that is

$$\frac{E_v-E_0}{v} = A + Bv, \tag{3}$$

where A and B are constants and E_v and E_0 are the eigenvalues of the vibrational states $|v\rangle$ and $|0\rangle$ respectively. Equation 4 shows that the anharmonic character of the vibrational eigenvalues can be well explained by considering the v and v^2 dependences. We assume a one-dimensional Morse oscillator for the local mode oscillator. The Morse parameters, D_e and α, were determined from these spectral parameters: $\omega_e=3130\,cm^{-1}$ and $\omega_e\chi_e=60.0\,cm^{-1}$, which were obtained from the observed frequencies of the local mode spectra. Thus we could quantify the mechanical anharmonicity and, therefore, the wavefunction $|v\rangle$.

Electrical Anharmonicity and Intensity. Next we consider the electrical anharmonicity. Using the Morse potential, we have numerically calculated the wavefunctions and the dipole matrix elements.[11] The dipole moment function, $M(R)$, is expanded as a power series of a displacement coordinate, $R-R_e$, as

$$M(R) = M_0 + M_1(R-R_e) + M_2(R-R_e)^2 \tag{4}$$

and the effects of M_1 and M_2 on the absorption intensities are to be studied. We have already described, in our

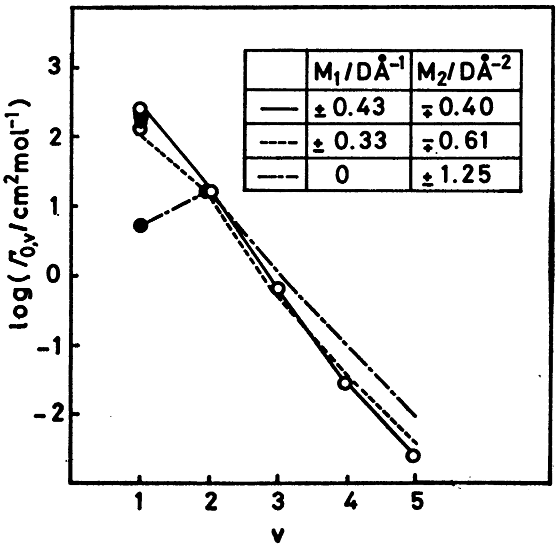

Fig. 1. The logarithmic absolute intensity plotted against the vibrational quantum number.
○: Observed values for the liquid phase, ●: observed values for the gas phase, ——: best fit curve for the pure liquid data, ----: best fit curve for the 20 mol% solution data, -·-·: best fit curve for the gas phase data. The Taylor expansion of the dipole moment function is truncated at the quadratic term, $M=M_0M_1(R-R_e)+M_2(R-R_e)^2$.

previous report,[2)] the way of determining the M_1 and M_2 values on the basis of the one-dimensional local mode model. Here again, we adopt this one-dimensional oscillator model and determine the M_1 and M_2 values for chloroform. As we did not see any remarkable solvent effects on the intensities for the $v=2\leftarrow 0$, $v=3\leftarrow 0$, and $v=4\leftarrow 0$ bands, we may regard the absolute intensity value observed at the concentration of 20 mol% as the absolute intensity value in the gas phase. In facts the intensity values for the $v=2\leftarrow 0$ band were observed to be almost identical in the gas and solution phases.

Figure 1 shows the logarithms of the observed absolute intensities plotted against the vibrational quantum number of the upper state, v. The open circles correspond to the absolute intensities in solutions, while the closed circles correspond to the absolute intensities in the gas phase reported by Rossi *et al.*[1)] The open circles arranged on the vertical line at $v=1$ correspond to the $\Gamma_{0,1}$ values associated with the pure liquid and the solutions of 80, 60, 40, and 20 mol%. The concentration dependence of the $\Gamma_{0,2}$, $\Gamma_{0,3}$, or $\Gamma_{0,4}$ values were too small to be identified in this logarithmic scale.

Using the intensity data for pure liquid chloroform, the best fit parameters were obtained to be: $M_1=\pm 0.43$ D Å^{-1} and $M_2=\mp 0.40$ D Å^{-2}. In Fig. 3 the best fit values for this case are shown by the solid line. The dotted line, on the other hand, shows the intensity values calculated for the parameter values of $M_1=\pm 0.33$ D Å^{-1} and $M_2=\mp 0.61$ D Å^{-2}, which are the best fit parameter values for the intensity observed in the 20 mol% solution. The dot-and-dash line indicates the theoretical values calculated from the M_1 and M_2 values which were determined from the gas phase intensities of the $v=1\leftarrow 0$ and $v=2\leftarrow 0$ bands, namely, $M_1=0$ D Å^{-1} and $M_2=\mp 1.25$ D Å^{-2}. Similarly, the best fit parameters, M_1 and M_2, were determined for various concentrations: these results are summerized in Table 2.

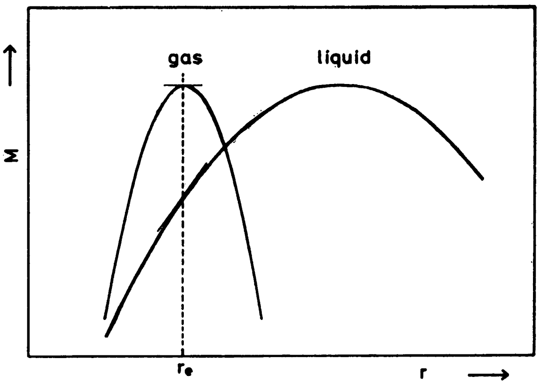

Fig. 2. The schematic drawing of the dipole moment functions for the gas and liquid phases.

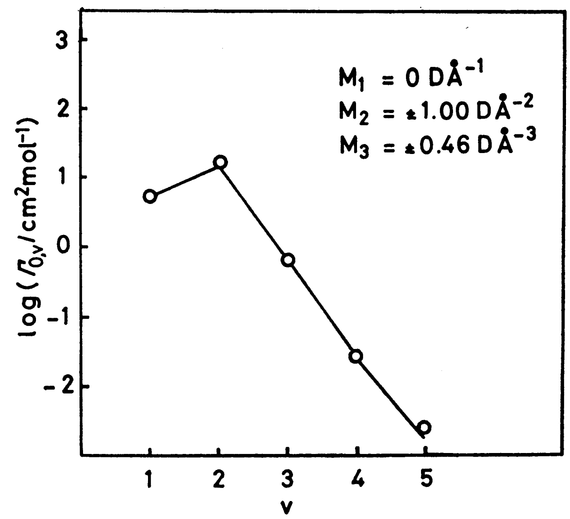

Fig. 3. The best fit curve for the gas phase intensity data. The Taylor expansion of the dipole moment function is truncated at the cubic term, $M=M_0+M_1(R-R_e)+M_2(R-R_e)^2+M_3(R-R_e)^3$.

TABLE 2. THE M_1 AND M_2 VALUES OF CHLOROFORM IN THE LIQUID, CARBON TETRACHLORIDE SOLUTION, AND GAS PHASES

Mole fraction of CHCl$_3$	M_1/D Å^{-1}	M_2/D Å^{-2}	M_3/D Å^{-3}
1.0 (Pure liquid)	±0.43	∓0.40	—
0.8	±0.41	∓0.49	—
0.6	±0.39	∓0.58	—
0.4	±0.37	∓0.58	—
0.2	±0.33	∓0.61	—
Gas a)	0	∓1.25	—
b)	0	∓1.00	∓0.46
Ab initio	−0.08	−1.00	—

a) The Taylor expansion of the dipole moment function was truncated at the quadratic term. The observed intensities for the $v=1\leftarrow 0$ and $v=2\leftarrow 0$ bands were used.
b) The Taylor expansion of the dipole moment function was truncated at the cubic term. The observed intensities for the $v=1\leftarrow 0$, $v=2\leftarrow 0$, $v=3\leftarrow 0$, $v=4\leftarrow 0$, and $v=5\leftarrow 0$ were used for the fitting.

Miyazaki and Yamamoto have calculated the M_1 and M_2 values for the C–H stretching vibration of methylchloride, methylenechloride, and chloroform by the CNDO method.[12)] The $\Gamma_{1,0}/\Gamma_{2,0}$ ratio of chloroform obtained from their calculation agrees well with the observed one, although the absolute intensities are smaller than the observed ones by about an order of magnitude. Their results agrees with the present experimental results in the sense that the M_1 value of chloroform is smaller than those of the other molecules. However, the M_2 values were calculated to be four times as small as our present results, presumably because the absolute intensity values which were calculated by the CNDO method were too small. The potential energy calculated from the CNDO method for the C–H stretching vibration does not seem appropriate, because the energy increase with the displacement from the equilibrium distance is much larger than those generally found. Therefore, we will perform the *ab initio* closed shell SCF calculation and compare the results with the experimental ones.

Ab Initio *Calculation of Dipole Moment Function.* A dipole moment function has been determined experimentally only for a very few diatomic molecules like HCl and HF. Therefore, we cannot ascertain the reliability of the dipole moment function obtained on the basis of the local mode representation. So we tried to compare the present result with the prediction of the *ab initio* closed shell SCF calculation. The programme used for the present calculation was IMSPACK GAUSSIAN 70.[13] As a basis set, the 6-31G*[14] was chosen for this calculation. The number of the inner-shell orbitals for a chlorine atom was set to be four. The 3d orbital for a chlorine atom was taken into account to improve the accuracy in the calculation of force constants or dipole matrix elements. The geometry optimization was carried out by the energy gradient technique.[15] The dipole moment derivatives were obtained by numerizal differentiations of calculated dipole moments in the Cartesian Coordinate system. The final results for M_1 and M_2 are given at the bottom of Table 2. It can be understood that the calculated M_1 and M_2 values agree well with those observed in the gas phase. It is noticeable that the M_2 values was calculated to be almost zero, which is in good agreement with the experimental result. As for the sign of these parameters, we may safely conclude that M_2 should be negative from this *ab initio* calculation. The sign of M_1, on the other hand, cannot be determined from this calculation, because the magnitude was calculated to be almost zero.

Dipole Moment Function and Solvent Effect. Let us consider now the concentration dependence of the dipole moment function observed in the carbon tetrachloride solutions. It can be seen from Table 2 that M_2 increases its magnitude and M_1 decreases its magnitude with the increase in concentration. Of course we cannot give too much quantitative meaning to the M_1 and M_2 values obtained for the liquid or solution phases, because it has been established that there exist two types of chloroform molecules in the liquid and solution phases. One is a molecule which interacts with other molecules and the other is a non-interacting molecule.[4] Therefore, the true M_1 value of the interacting molecule, for example, in pure liquid chloroform may be much larger than ± 0.43 D Å^{-1}. Thus, the M_1 and M_2 values in the liquid phase should be regarded as effective values. However, the general tendency of the concentration dependence of M_1 and M_2 is important. We remember that M_1 and M_2 values approach those of the gas phase in the infinite dilution limit.

The parameter values of $M_1 \simeq 0$ means that the dipole moment function M takes an extremum at the equilibrium distance of the C–H bond or at the distance where the C–H internuclear potential function takes a minimum value. On the other hand, the increase of M_1 with the increasing concentration corresponds to the fact that the distance at which the dipole moment function takes an extremum deviates from that of the potential minimum. This deviation may be due to the intermolecular interaction of the hydrogen bonding type between chloroform molecules. We discussed the details of this interaction in our previous reports,[4,16] where the effect of the charge transfer complex formation has been emphasized. If this charge transfer model can be applied to the present case, the sign of M_1 should be positive in the liquid and solution phases.[16] This conclusion is consistent with the fact that M_1 and M_2 should have opposite signs (see Fig. 1); the latter conclusion is drawn from the present intensity analysis.

The decrease in the absolute value $|M_2|$ with the increasing chloroform concentration corresponds to the decrease in the curvature of the dipole moment function. Taking these situations into account together with the signs of M_1 and M_2, we can draw the dipole moment functions in the gas and liquid phases schematically in Fig. 2. We cannot give any further meanings to the behavior of M_2 with the concentration change at this stage. But we can conclude that the apparent anomalous intensity behavior of the fundamental band is not due to the electrical anharmonicity M_2, but to the harmonic term M_1. The fundamental band looks quite sensitive to the change of the molecular environment, simply because the dipole moment function takes a extremum at the equilibrium distance of the C–H bond, which brings about the anomalously weak intrinsic intensity for the fundamental band. The $\Gamma_{0,1}$-value change from 5.2 cm^2/mol to 245 cm^2/mol on passing from the gas to the pure liquid phases is only a small change from the viewpoint of the hydrogen bonding. As we have proposed in our report,[16] the strength of the hydrogen bonding should be evaluated by the $(\sqrt{\Gamma_b}-\sqrt{\Gamma_f})$ value instead of the Γ_b/Γ_f value, where Γ_b and Γ_f correspond to the absorption intensities of the hydrogen-bonded and free molecules, respectively. The $(\sqrt{\Gamma_b}-\sqrt{\Gamma_f})$ value of the present case is $\sqrt{245}-\sqrt{5.2}\simeq 10$, which is equivalent to an excess enthalpy of only 200 cal/mol.

The reflection of the dipole moment function on the intensities will be understood in more detail if we watch the numerically calculated matrix elements. The absolute intensity $\Gamma_{0,v}$ corresponding to the transition from the ground state $|0\rangle$ to a vibrationally excited state $|v\rangle$ is proportional to the square of the dipole matrix element $|\langle 0|M|v\rangle|$. Therefore,

$$\begin{aligned}\Gamma_{0,v} &\propto |\langle 0|M|v\rangle|^2 \\ &= M_1^2\langle 0|R-R_e|v\rangle^2 \\ &\quad + 2M_1M_2\langle 0|R-R_e|v\rangle\langle 0|(R-R_e)^2|v\rangle \\ &\quad + M_2^2\langle 0|(R-R_e)^2|v\rangle. \end{aligned} \tag{5}$$

The numerical values for the three terms of Eq. 5 are summarized in Table 3. It can be seen from the table that the intensity of the $v=1\leftarrow 0$ band is governed by rather complicated factors. In the gas phase, the intensity is determined completely by the third term. As the concentration and, therefore, the intermolecular interaction increase, the intensity comes to be governed by the first term. The concentration dependence of the $v=1\leftarrow 0$ band is obviously governed by the magnitude of M_1. In the case of the $v=2\leftarrow 0$ band, on the other hand, the three terms can equally contribute to the intensity. It is noticeable that the second term is almost independent of the concentration. The third term decreases, while the first term increases, with the increase of the chloroform concentration. The increase and decrease of the first and third terms compensate each other, which keeps the $v=2\leftarrow 0$ band intensity almost independent of the chloroform

TABLE 3. THE NUMERICAL VALUES FOR THE DIPOLE MATRIX ELEMENTS OF CHLOROFORM

$\Gamma_{0,v}/(8\pi^3 N/3hc)=M_1^2\langle 0|\Delta r|v\rangle^2+2M_1M_2\langle 0|\Delta r|v\rangle\langle 0|\Delta r^2|v\rangle+M_2^2\langle 0|\Delta r^2|v\rangle^2$

Mole fraction of $CHCl_3$	$v=1$			$v=2$		
	1st term	2nd term	3rd term	1st term	2nd term	3rd term
1.0 (Pure liquid)	1.1065×10^{-3}	-1.1397×10^{-4}	2.9346×10^{-6}	1.1434×10^{-5}	2.1452×10^{-5}	1.0062×10^{-5}
0.8	1.0060×10^{-3}	-1.3312×10^{-4}	4.4037×10^{-6}	1.0395×10^{-5}	2.5057×10^{-5}	1.5100×10^{-5}
0.6	0.9102×10^{-3}	-1.4988×10^{-4}	6.1699×10^{-6}	0.9406×10^{-5}	2.8212×10^{-5}	2.1156×10^{-5}
0.4	0.8193×10^{-3}	-1.4219×10^{-4}	6.1699×10^{-6}	0.8466×10^{-5}	2.6766×10^{-5}	2.1156×10^{-5}
0.2	0.6517×10^{-3}	-1.3338×10^{-4}	6.8247×10^{-6}	0.6734×10^{-5}	2.5107×10^{-5}	2.3401×10^{-5}
Gas	0.0	0.0	2.8658×10^{-5}	0.0	0.0	9.8266×10^{-5}

concentration.

Higher Order Terms in Dipole Moment Function. In Fig. 1, it is seen that the dash-and-dot line deviates from the observed values at the higher vibrational quantum numbers. If we choose the parameter values which can explain the intensities of the $v=3\leftarrow0$, $v=4\leftarrow0$, and $v=5\leftarrow0$, we cannot explain the intensity of the $v=1\leftarrow0$ band. This is probably arising from the fact that the effects of the higher order term of the dipole moment function on the intensities are relatively accentuated at the higher v values, because M_1 is extremely small in chloroform. Conversely speaking, it may be possible to determine the higher term in the dipole moment function for this particular case, although the one-dimensional oscillator model may be too over-simplified to do so in general.[2] We only add here the results of the intensity analysis by taking into account the cubic term M_3 in the dipole moment function. In Fig. 3, the best fit values are shown by the solid line, while the observed values are given by the open circles. The best fit parameter values were: $M_1=0$ D Å^{-1}, $M_2=1.00$ D Å^{-2}, and $M_3=0.46$ D Å^{-3}. The sign of M_2 is probably negative, while that of M_3 can be negative because M_2 and M_3 should have the same signs.

Conclusion

The dipole moment functions of chloroform were determined from the observed intensities. The solvent effects on the absorption intensity were discussed as related to the concentration dependence of the dipole moment function. The anomalous intensity behavior of the fundamental band was clarified to arise from the accidental coincidence of the positions at which the potential function and the dipole moment function take extrema, which brings about the anomalously weak intrinsic intensity of the fundamental band. The reliability of the finally determined electrical anharmonicity parameters was confirmed by the *ab initio* calculation.

Incidentally, the one-dimensional local mode representation was shown to be useful for an intensity data analysis in the sense that a mechanical anharmonicity can be fairly easily determined for a complicated polyatomic molecule like chloroform. This, in turn, makes it possible to elucidate an electrical anharmonicity or a higher order term of a dipole moment function.

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