

Effects of Mechanical and Electrical Anharmonicities on Local Mode Spectrum

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The first and second order dipole moment parameters along the CH bond in benzene, chloroform, and cyclohexane were obtained by deducing the local mode intensities on the basis of the one-dimensional Morse oscillator model. The validity of the one-dimensional model is discussed according to a newly introduced formula which helps us to understand the nature of local mode absorptions. The relative intensities of the first overtones to the other bands were found to be crucially important in determining M_2/M_1 together with its sign, because the contributions of the mechanical and electrical anharmonicities to M_1/M_2 are often cancelled out each other accidentally. The M_2/M_1 values for benzene, cyclohexane, and chloroform were 2.3, 1.45, and -0.93 Å^{-1} respectively. These values for benzene and cyclohexane were excellently reproduced by the *ab initio* calculations for benzene and methane respectively.

The local mode idea has been recognized as a convenient representation for highly excited vibrational states, where anharmonic characters can never be neglected, since it was introduced by Henry and Siebrand¹⁾ and later developed by Albrecht *et al.*²⁾ Surprisingly simple features in high overtone spectra of many hydrocarbons were successfully explained by a virtually isolated diatomic model which represents each local CH bond. However, these facts do not immediately mean that highly excited vibrational states are always so simple. What an absorption spectrum tells us directly is change in dipole moments rather than motions of atoms. There could exist many other vibrational motions which are not responsible for an absorption spectrum line. A question is why intensities tend to concentrate into some particular transitions among many other candidates, or in other words, what restrictions on the Hamiltonian and the dipole moment operator are required for the formation of a so-called local mode spectrum. Understanding of this point is important to clarify the usefulness and the limitations of the one-dimensional oscillator model, which is used to determine dipole moment parameters from the intensities observed for both fundamental and very high overtones.

In this paper we will express the absorption spectrum in a general way using more physically meaningful basis states rather than eigenstates. Such a formulation would be convenient when the eigenstates of the Hamiltonian are severely mixed states of many physically meaningful basis states. Then we apply the formulation to deducing one-dimensional dipole moment functions of benzene, cyclohexane, and chloroform. The experimental parameters thus obtained will be compared with the theoretical values and with the results obtained by Burberry and Albrecht.³⁾ More rigorous treatment was necessary to analyze the 1st and 2nd overtones of 1,1-dichloroethylene because of the mixings between the combinations and pure overtones which have non-zero intrinsic intensities. The result will appear in a separate paper.

Theoretical Background for Intensity Analysis

An absorption intensity at a frequency ν is generally expressed by:

$$B(\nu) = C\nu |\langle 0|M|E \rangle|^2 \quad (1)$$

where $|E \rangle$ is an eigenstate of the Hamiltonian with an eigenvalue $E = h\nu$, $|0 \rangle$ is the ground state, M is the dipole moment function, and C is a constant. Inserting an identity operator,

$$I = \sum_v |v_1, v_2, \dots \rangle \langle v_1, v_2, \dots|, \quad (2)$$

into Eq. 1, we obtain the relation

$$B(\nu) = C\nu \left| \sum_v \langle 0|M|v_1, v_2, \dots \rangle \langle v_1, v_2, \dots|E \rangle \right|^2, \quad (3)$$

where $|v_1, v_2, \dots \rangle$'s are basis states which are not necessarily eigenstates as far as Eq. 2 is satisfied. Here we express the density of a basis state $|v_1, v_2, \dots \rangle$ as a function of E as

$$\rho(E) = \langle v_1, v_2, \dots|E \rangle^2. \quad (4)$$

Equation 4 represents the probability function of finding a state $|v_1, v_2, \dots \rangle$ at E or the contribution of $|v_1, v_2, \dots \rangle$ to the eigenstate $|E \rangle$. If $|v_1, v_2, \dots \rangle$ is an eigenstate, $\rho(E)$ is a delta function which has a non-zero value only when E is the eigenvalue of the Hamiltonian. In this case Eq. 3 becomes

$$B(\nu) = C\nu \sum_v \langle 0|M|v_1, v_2, \dots \rangle^2 \delta(\nu - E_v). \quad (5)$$

This is a conventional expression which uses a continuous function. If $|v_1, v_2, \dots \rangle$ is not an eigenstate but a more physically meaningful state such as local mode state or a normal mode state, on the other hand, $\rho_v(E)$ can not be so simple anymore; there appears splitting or broadening because of the mixings. Even in such a case, Eq. 3 can be reduced approximately to

$$B(\nu) = C\nu \sum_v \langle 0|M|v_1, v_2, \dots \rangle^2 \rho_v(E), \quad (6)$$

unless both of the mixing partners have non-zero intrinsic intensities at the same time. Here, the intrinsic intensity associated with a basis state, $|v_1, v_2, \dots \rangle$, is defined by

$$I'(v_1, v_2, \dots) = C\nu \langle 0|M|v_1, v_2, \dots \rangle^2. \quad (7)$$

Therefore, Eq. 6 becomes

$$B(\nu) = \sum_{\nu} I'(v_1, v_2, \dots) \rho_{\nu}(E). \quad (8)$$

Equation 8 or 6 means that an absorption band which is associated with one of the basis states, $|v_1, v_2, \dots\rangle$, must have the same structure or lineshape as $\rho_{\nu}(E)$ and that the integrated intensity over the whole band is directly related to the square of the matrix element represented by the same states used for the assignment. Any complicated interactions with other states which do not have intrinsic intensities will not affect the integrated intensity at all and the center of gravity of the band will remain unchanged, to the first order approximation, at the position which would be expected for the unperturbed state.

The above description is the theoretical basis for the intensity analysis of the present work. Equation 8 can be conveniently applied to a band which is broadened by the interactions with almost continuous background states of highly excited vibrational modes as well as external lattice mode, because such background states do not usually have their own intrinsic intensities.

Experimental

The absorption spectra of liquid benzene, cyclohexane, and chloroform were observed for the C-H stretching fundamental and its overtones. A Fourier transform spectrometer (NICOLET 7199) was used for the observation of 1,2,3 \leftarrow 0 bands, while UV-visible spectrophotometers (CARY 17 and Shimadzu D-40R) were used for the observation of 4,5,6 \leftarrow 0 bands. 6 \leftarrow 0 bands were also measured by the use of a dual-beam thermal lensing spectrometer which was designed and constructed in our laboratory. The optical path lengths of the cells used were 25 μ m, 58 μ m, and 10 mm depending upon the intensity of each absorption band. The fundamental bands of benzene and cyclohexane were so strong that the 1 : 10 diluted solutions in carbon tetrachloride were used with a 25 μ m cell instead of the pure liquid.

The observed spectra were integrated over the whole of the bands corresponding to the C-H stretching modes. The integrated intensity Γ is defined by the relation:

$$\Gamma = \frac{1}{cl} \int_{\text{band}} \ln \left(\frac{I_0}{I} \right) d \ln \nu \quad (\text{cm}^2/\text{mol}), \quad (9)$$

where c is the concentration of the sample in mol/cm³, l is the thickness of sample in cm, and I_0 and I are the intensities of the incident and transmitted light, respectively. The observed integrated intensity was corrected for the dielectric effect. The corrected integrated intensity, Γ^c , can be expressed in terms of a transition matrix element as,

$$\begin{aligned} \Gamma^c &= \frac{8\pi^3 N}{3hc} |\langle 0|M|v \rangle|^2 \\ &= 2.508 \times 10^5 M_{0v}^2 \quad (\text{cm}^2/\text{mol}), \end{aligned} \quad (10)$$

where $M_{0v} \equiv \langle 0|M|v \rangle$ is a transition moment and M is a dipole moment operator. If we express M in Debye units, Γ^c can be expressed in the units of cm²/mol.

Results and Discussion

Observed Spectra. The spectral patterns observed in the present work are essentially the same as those of the previous work.^{3,4)}

The fundamental band of benzene consists of three peaks. The $v=2\leftarrow 0$ bands are more complicated. Such complex structures were explained by Fermi resonances between the pure C-H stretching mode and overtones and/or combinations of other lower frequency modes which are probably skeletal stretching modes.⁵⁾ These overtones and combination tones do not seem to have their own intensities, because all three peaks in the C-H fundamental region of benzene disappear in deuterated benzene.⁵⁾ Then we assumed that the total integrated intensities over each $v\leftarrow 0$ band were responsible for the C-H stretching mode.

The structure of the fundamental and the overtones of cyclohexane was primarily doublet, although it contained other weak peaks or shoulders. The doublet of the fundamental vibrations can be assigned to the in-phase and out-of-phase stretching modes of the two nearly identical C-H bonds which share a common carbon atom. On the other hand, the doublet structure of the high overtones should be considered as a reflection of the difference between the axial and equatorial C-H bonds, since local mode characters are dominant in highly excited states. However, independent analyses for each bond are still very difficult. Thus, we integrated the intensity over the doublets for the determination of the effectively averaged dipole moment parameters.

In Table 1 the integrated intensities, corrected for the

TABLE 1. OBSERVED $\Gamma_{0,v}^c$ VALUES IN (cm² mol⁻¹)

v	Benzene	Cyclohexane	1,1-Dichloro-ethylene	Chloroform
1	2448	22000	328	422
2	30.8	41.5	18.8	16.4
3	3.66	11.73	0.822	0.973
4	0.237	0.770	0.0332	0.357
5	0.0189	0.0730	2.19×10^{-3}	5.97×10^{-3}
6	3.75×10^{-3}	5.93×10^{-3}	—	—

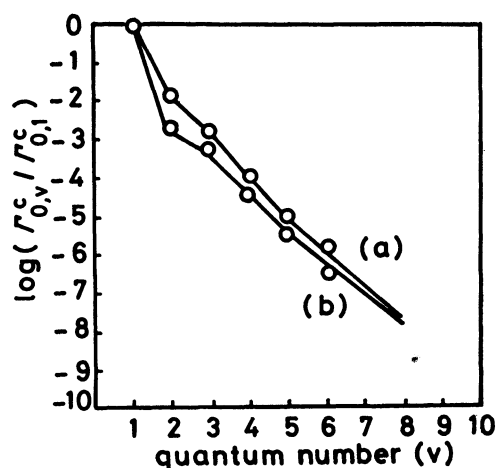


Fig. 1. The logarithmic relative intensities, $\Gamma_{0,v}^c/\Gamma_{0,1}^c$, for liquid benzene (a) and liquid cyclohexane (b) plotted against a vibrational quantum number, v . Open circles represent the observed values, while the solid line connect these values calculated from the best-fit parameter, $M_2/M_1 = 2.30 \text{ \AA}^{-1}$ for benzene and $M_2/M_1 = 1.45 \text{ \AA}^{-1}$ for cyclohexane.

local field effect, $I_{0,v}^c$, are summarized. In Fig. 1(a) the logarithmic relative intensities, $I_{0,v}^c/I_{0,1}^c$, observed for benzene are plotted against the vibrational quantum number, v . It can be seen from the figure that the intensity of the $v=2\leftarrow 0$ band is about half of that expected from the interpolation of other $I_{0,v}^c$ values. A similar plotting for cyclohexane is shown in Fig. 1(b). The decrease in the intensity of the $v=2\leftarrow 0$ band is more pronounced in cyclohexane than in benzene. In the experimental results reported by Albrecht³⁾ and Yamamoto,⁴⁾ the same tendencies are clearly observed. Unfortunately they did not pay any attention to this point, but rather emphasized the monotonous decrease in $\ln(I_{0,v}^c/I_{0,1}^c)$ with the increase of v . We will focus our attention on this singular behaviour of the $v=2\leftarrow 0$ band intensity because it is far beyond the experimental error.

Calculation of Intensity and Dipole Moment Function.

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: $\omega_e=3173\text{ cm}^{-1}$ and $\omega_e x_e=60.7\text{ cm}^{-1}$ for benzene, and $\omega_e=3020\text{ cm}^{-1}$ and $\omega_e x_e=65.94\text{ cm}^{-1}$ for cyclohexane, which were obtained from the observed frequencies of the local mode spectra. Using these Morse potentials, we have numerically calculated the wavefunctions and the dipole matrix elements.⁶⁾ The dipole moment function, $M(R)$, is expanded as a power series of a displacement coordinate, $R-R_e$, as

$$M(R) = M_0 + M_1(R-R_e) + M_2(R-R_e)^2, \quad (11)$$

and the effects of M_1 and M_2 on the absorption intensities are to be studied. After determining the M_2/M_1 value so as to reproduce the relative intensities of the overtones, the absolute values of M_1 and M_2 were determined by scaling to the absolute intensity of the fundamental band. In order to clarify the origin of the anomalous intensity behaviour observed for the $v=2\leftarrow 0$ band, the magnitude of M_2/M_1 and the signs of M_1 and M_2 were investigated in relation with the calculated intensity values. In Fig. 2 we demonstrate the depend-

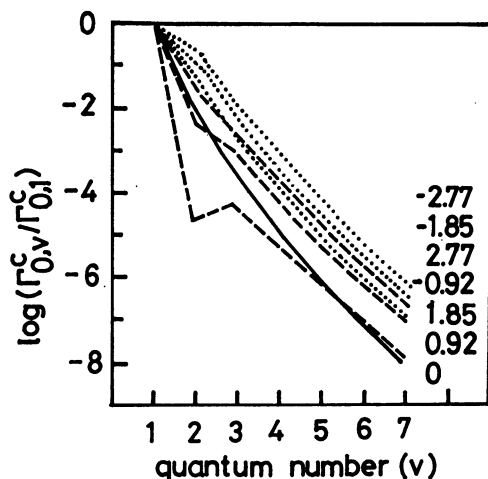


Fig. 2. The dependence of the logarithmic relative intensity, $I_{0,v}^c/I_{0,1}^c$ of liquid benzene on the parameter, M_2/M_1 . The numbers at the ends of the curves indicate the M_2/M_1 value.

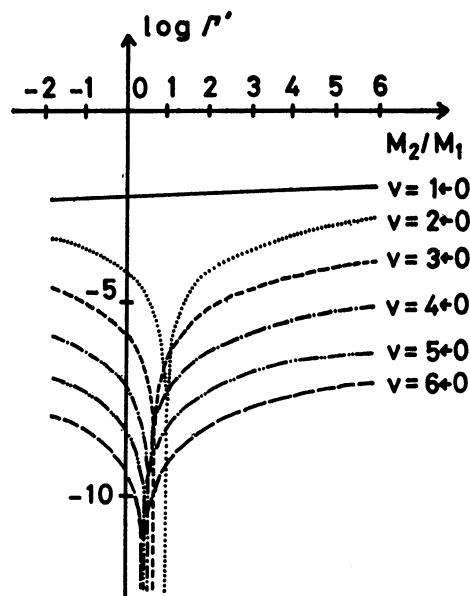


Fig. 3. The dependence of the absolute intensities of the overtones on the M_2/M_1 value in \AA^{-1} . At $(M_2/M_1) \approx 1$, the effects of the mechanical and electrical anharmonicities cancel out with each other. The absolute intensity, I' , is defined by this relation, $I' = |\langle 0 | (R-R_e) + (M_2/M_1)(R-R_e)^2 | v \rangle|^2$
$$= \frac{3hc}{8\pi^3 N} \cdot \frac{I_{0,v}^c}{M_1^2}.$$

ency of the calculated $I_{0,v}^c/I_{0,1}^c$ value of benzene on the magnitude of M_2/M_1 . The general qualitative feature which can be observed from Fig. 2 does not change much with the slight change in the Morse potential parameters. It can be seen from Fig. 2 that the relative intensity of the $v=2\leftarrow 0$ band is quite sensitive to the M_2/M_1 value: the relative intensity of the $v=2\leftarrow 0$ is diminished for a small positive M_2/M_1 value, while it is enhanced for a negative M_2/M_1 value. It is also clarified that the relative intensity of the $v=2\leftarrow 0$ band is also enhanced if M_2/M_1 takes a large positive value; this situation is illustrated in Fig. 3. So far as we know, this is the first time for anyone to recognize the fact that the overtone intensity is so sensitive to a slight change in M_2/M_1 . This anomalous behaviour of the $v=2\leftarrow 0$ band intensity is considered to arise from the accidental cancellation of the mechanical and electrical anharmonicities. The magnitudes of the matrix elements are, for benzene,

$$\begin{aligned} \langle 0 | (R-R_e) | 2 \rangle &= -0.0077064 \text{ \AA}, \\ \langle 0 | (R-R_e)^2 | 2 \rangle &= 0.0079453 \text{ \AA}^2. \end{aligned}$$

So the mechanical and electrical anharmonicities can completely cancel out each other if $M_2/M_1=0.970\text{ \AA}^{-1}$ (see Eq. 11). Of course, this accidental cancellation can occur even for the v values other than 2. The M_2/M_1 value which brings about the abnormality of the $v=2\leftarrow 0$ band intensity, however, is not likely to bring about this accidental cancellation for other v values.

The observed intensities of benzene were reproduced best for $M_2/M_1=2.3\text{ \AA}^{-1}$ (see Fig. 1(a)), while those of cyclohexane were reproduced best for $M_2/M_1=1.45$

TABLE 2. MATRIX ELEMENTS $\langle v|(R-R_e)^m|0\rangle$ FOR BENZENE

v	$(R-R_e)$	$(R-R_e)^2$	$(R-R_e)^3$	$(R-R_e)^4$
0	0.016115	6.30049×10^{-3}	3.62064×10^{-4}	1.24637×10^{-4}
1	0.077329	4.19587×10^{-3}	1.60029×10^{-3}	1.82516×10^{-4}
2	-7.70646×10^{-3}	7.94528×10^{-3}	8.03216×10^{-4}	3.71245×10^{-4}
3	1.26623×10^{-3}	-1.97764×10^{-3}	8.84528×10^{-4}	1.2578×10^{-4}
4	-2.72909×10^{-4}	5.20610×10^{-4}	-4.08416×10^{-4}	9.45319×10^{-5}
5	7.08451×10^{-5}	-1.53061×10^{-4}	1.56648×10^{-4}	-7.57525×10^{-5}
6	-2.11962×10^{-5}	4.99765×10^{-5}	-6.02466×10^{-5}	4.04809×10^{-5}
7	7.13530×10^{-6}	-1.79200×10^{-5}	2.42181×10^{-5}	-1.98537×10^{-5}

TABLE 3. THE COEFFICIENTS, M_1 AND M_2 , OF THE DIPOLE MOMENT FUNCTION, AND THE CORRESPONDING (R_m-R_e) VALUES

	$M_1/D \text{ \AA}^{-1}$	$M_2/D \text{ \AA}^{-2}$	$(R_m-R_e)/\text{\AA}$
C_6H_6	-0.48(-0.55)	-1.10(-1.40)	-0.22(-0.20)
C_6H_{12}	-0.91(-0.85)*	-1.32(-1.30)*	-0.35(-0.33)*
CH_2CCl_2	-0.36 (—)	-0.90 (—)	-0.20 (—)
$CHCl_3$	0 (-0.08)	-1.25(-1.0)	0 (-0.04)
CH_2CH_2	— (-0.64)	— (-1.24)	— (-0.26)

() : Obtained from *ab initio* calculations. ()*: Obtained from the *ab initio* calculation for methane.

\AA^{-1} (see Fig. 1(b)). The disagreement between the observed and calculated intensities for the $v=5 \leftarrow 0$ and $v=6 \leftarrow 0$ bands may be due to the neglect of these terms higher than M_2 (see Eq. 11). We did not try to add the higher order terms to get better agreement, although it is not particularly difficult, because the one-dimensional oscillator model is not accurate enough. The final results are summarized in Table 3. In addition to the absolute value, the sign of M_2/M_1 was determined to be positive. However, the signs of M_1 and M_2 could be determined separately only after the *ab initio* calculations which will be described in the next section.

A chloroform molecule has only one C-H bond. Therefore, the one-dimensional oscillator model is considered to be most appropriately applied to this molecule. Actually, the situation was not so simple, because the intensity of the ν_1 fundamental (the C-H stretching vibration) is abnormally weak and is extremely sensitive to the molecular environment. A detailed study on this problem will be described in a separate paper.¹¹⁾ We only report here the final result, that M_1 is almost zero.

For 1,1-dichloroethylene, we adopted the two-dimensional oscillator model and obtained the M_{12} value, which is the coefficient of the cross-term, $(R_1-R_e)(R_2-R_e)$, in addition to M_1 and M_2 . Although the details of this analysis will also appear in a separate paper,¹²⁾ we include the final results in Table 3. Here again $M_1M_2 > 0$.

Ab Initio Calculation of Dipole Moment Function. A dipole moment function has been determined only for a very few diatomic molecules like HCl and HF. Therefore, we cannot ascertain the validity of the dipole moment functions obtained here on the basis of the local mode representation. So we tried to compare the present results with the predictions of the *ab initio* calculation for benzene, chloroform, ethylene, and methane. Methane was chosen as a model system for cyclohexane, and ethylene was added for the con-

venience of understanding those molecules having double bonds. The program used for the present calculation was IMSPACK GAUSSIAN 70.⁷⁾ As a basis set, the 4-31G⁸⁾ was chosen for methane and ethylene, while the 6-31G*^{9,10)} was chosen for the calculations of benzene and chloroform. The calculated results are summarized in Table 3, in the brackets.

Dipole Moment Functions. From the comparison of the experimentally determined M_1 and M_2 values of Table 3, we can understand the following facts. First, M_1 and M_2 take the same sign for all the molecules except chloroform. This corresponds to the fact that the dipole moment function takes a extremum at a distance smaller than R_e . We designated this distance as R_m , and calculated the deviation from the equilibrium distance, R_e-R_m ; these results are summarized in the last column of Table 3. It can be seen from the table that chloroform is quite different from other molecules in the sense that R_m is very close to R_e .

The M_1 values are different for different molecules, while the M_2 values are rather constant for all the molecules studied: that is, $-1.3 < M_2 < -0.9$. It is of same interest to emphasize that even the M_2 value for chloroform was obtained in this range of magnitude.

The *ab initio* calculation reproduces the observed M_1 and M_2 values very well. So far, very few experimental M_2 values have been compared with the M_2 values calculated by the *ab initio* calculation, because the corresponding experimental values have been so poor. The present study shows that the agreement between the calculated and observed M_2 values are excellent for various hydrocarbons. The characteristic features of the dipole moment function of chloroform are also well reproduced by the *ab initio* calculation: M_2 is not very different from those of the other molecules, although M_1 is exceptionally small in magnitude. It may be giving too many compliments to the *ab initio* calculation to say that the slight deviations of the calculated dipole moment functions from the observed ones may be

TABLE 4. THE DIPOLE MOMENT FUNCTION FOR LIQUID BENZENE OBTAINED BY BURBERRY AND ALBRECHT.^{a)}

	Semiempirical		Theoretical	
	Morse potential	Quartic potential	CNDO	<i>Ab initio</i>
$M_1/D \text{ \AA}^{-1}$	-0.81	-0.59	-1.0	-1.78
$M_2/D \text{ \AA}^{-2}$	0.20	-1.16	-0.99	-1.48

a) See Ref. 3.

ascribed to the over-simplification of the oscillator model, *i.e.* the one-dimensional local mode model.

Burberry and Albrecht⁹⁾ determined the dipole moment function of benzene by the use of an oscillator model which is analogous to ours; their results are given in Table 4. It is puzzling to see from the table that the signs of M_1 and M_2 are different, although they use a Morse potential in their calculation. We do not see any clear reasons for this. We only emphasize the fact that Burberry and Albrecht do not seem to have paid special attention to the anomalous intensity decrease of the $\nu=2\leftarrow 0$ bands, although the anomaly can clearly be seen in their intensity data. Strange to say, their calculation has led to a dipole moment function which is very close to our present result; they used the quartic potential function in the place of the Morse potential. We are not sure at present why the quartic potential is preferable to the Morse potential for the treatment of an oscillator whose anharmonic character is very strong. Perhaps the dipole moment function is sensitive to the anomalous intensity behaviour of the $\nu=2\leftarrow 0$ band.

Mechanical and Electrical Anharmonicities. Next, we consider the contributions of mechanical and electrical anharmonicities on overtone spectra.

If a potential is completely harmonic, the dipole term related with M_2 simply allows the $\nu=2\leftarrow 0$ transition. If a potential is of a Morse type, on the other hand, all the highly excited vibrational bands can be expected to have considerable intensities even if $M_2=0$. For example, about 10% of the observed intensity for the $\nu=6\leftarrow 0$ band in liquid benzene can be ascertained to be originating from the Morse potential only ($M_2=0$). In other words, M_2 contributes only to the appearance of a $\nu=2\leftarrow 0$ band under a harmonic potential, while it can have large contributions to the appearance of the high overtones other than $\nu=2\leftarrow 0$ under the influence of a harmonic potential. Thus, we can conclude that the mechanical and electrical anharmonicities cooperatively contribute to the appearance of the high overtones. In some cases, the contribution of mechanical and electrical anharmonicities cancel out each other, as we have seen in the $\nu=2\leftarrow 0$ band. This phenomenon is most distinct in the $\nu=2\leftarrow 0$ band, simply because M_2 contributes directly to the $\nu=2\leftarrow 0$ transition. Thus, we can recognize that the present system was only a lucky case for the determination of M_2/M_1 in the sense that we could use the anomalous intensity decrease of the $\nu=2\leftarrow 0$ band. If the intensity of the $\nu=2\leftarrow 0$ band were normal, in comparison with the other high overtones, or if it were enhanced instead of diminished, we could not determine even the sign of M_2/M_1 .

Incidentally, the present theoretical treatment is quite general, provided that the dipole matrix elements related with the other modes are negligible and that the cross terms in a dipole moment function which represent the couplings between each mode in question and the other modes can be neglected. The coupling originating from the nature of the Hamiltonian does not spoil the generality of the present theory. The effects of the cross term in a dipole moment function can properly be treated by introducing a coupled oscillator model; the results of this treatment will appear in a separate paper.

Conclusion

The absolute intensities of the high overtones were observed for liquid benzene, cyclohexane, and chloroform. From these intensity values, the dipole moment functions were obtained up to quadratic terms, based upon the one-dimensional oscillator model. The corresponding parameters for benzene, methane, chloroform, and ethylene were estimated by the *ab initio* calculations. The agreement between the experimental and theoretical dipole moment functions, in turn, confirmed the validity of the one-dimensional oscillator model and the reliability of the *ab initio* calculation simultaneously.

The anomalous intensity behaviour of the $\nu=2\leftarrow 0$ band was ascertained to be arising from the accidental interaction between the mechanical and electrical anharmonicities. This effect was conveniently used for the determination of the M_2/M_1 value.

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