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Symmetrized Local Mode Analysis of CH_2 Stretching Mode in 1,1-Dichloroethylene

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A symmetrized local mode (SLM) model based on the two dimensional Morse oscillator was developed and applied to the analysis of the spectrum of the CH stretching modes in 1,1-dichloroethylene in the range of 3000—17000 cm^{-1}. More than twelve absorption peaks were assigned in terms of the mixed SLM states. The calculated frequencies with finally determined parameters: $\omega_e=3191.6$ cm^{-1}, $\omega_e\chi_e=57.63$ cm^{-1}, and $f_{12}=2170$ cm^{-1} agreed well with the observed ones. The kinetic coupling was found to be more responsible for the mixings between SLM states than the potential coupling. The observed intensity data were analyzed by the use of the obtained mixing coefficients and the two dimensional dipole moment function parameters: M_1, M_2, M_{12}, and θ. The finally determined dipole moment function parameters were: $M_1=-0.290$ D Å^{-1}, $M_2=-0.875$ D Å^{-2}, $M_{12}=0.386$ D Å^{-2}, and $\theta=38.4°$. Careful examination of the influence of M_{12} upon the integrated intensities clarified the validity of the one dimensional intensity analysis of our preceding work. An SLM representation was confirmed to be useful for the systematic analysis of the CH stretching spectrum through the fundamental and the high v local mode bands which include highly structured low v summation bands. An SLM representation was also found to be convenient for making a simple correlation between local mode and normal mode pictures.

Many reports on local mode (LM) spectra[1] have been published in recent years since the idea was introduced by Henry and Siebrand[2] and later developed by Albrecht.[3] Our preceding articles[4,5] on the determinations of the dipole moment functions of CH bonds in benzene, cyclohexane, and chloroform were based upon the one-dimensional LM model. A simple LM picture is not adequate, however, for an explanation of the complicated spectral structures in the fundamental band and low v overtone bands. These structured bands are usually analyzed by the conventional method[6,7] developed in a normal mode (NM) picture, although the NM picture is not so convenient either, because of the large Darling-Dennison resonance[8] in the summation band regions. In relation to the above statment, there still exist some problems which have been not solved thoroughly. One is how to express the states which are assigned in the NM picture in terms of the LM picture, or how to clarify the correlation between LM and NM quantitatively. The other is to examine the magnitude of the interactions between equivalent LM states quantitatively. The latter would be necessary to test the validity of the one-dimensional LM approximation when it is applied to various particular subjects, such as the deduction of dipole moment parameters.

In this paper, we introduce symmetrized local mode states (SLM) for the analysis of the spectrum of the CH stretching modes in 1,1-dichloroethylene. An SLM representation would be one of the most convenient pictures because some of the large interactions between equivalent LM states are automatically included in the diagonal elements in zero-th order and because it could be easily correlated to the states in a NM picture which were intrincically symmetrized at the stage of the construction of the coordinates. Two dimensional analysis of the CH_2 stretching modes in an SLM picture would also enable us to determine two-dimensional dipole moment parameters.

The vibrational spectra of 1,1-dichloroethylene and its deuterated compounds were measured by Winter *et al.*[9] and by Enomoto *et al.*[10] Yamaoka and Machida[11] have analyzed these spectra, including the overtones and the combinations, and have determined some anharmonic potential parameters. It would be interesting to compare their parameters for the CH_2 group with ours, which are determined by a completely different method.

Experimental

The absorption spectra of 1,1-dichloroethylene in the liquid phase were measured with a Fourier transform spectrometer (NICOLET 7199) in the frequency region of 2800—10000 cm^{-1} and with a UV-visible spectrometer (CARY 17) in the visible region. The sample was purchased from Tokyo Chemical Industry Co., Ltd. and used without further purification.

The observed frequencies at the absorption maxima, ν_{obsd}, and the integrated intensities, Γ_{obsd}, are listed in the first and the second columns of Table 1, respectively. The definition of Γ and the correction for the dielectric field are the same as those described in our preceding paper.[4]

Results and Discussion

NM Approach and LM Approach. In Fig. 1, two different approaches to reach the eigenstates are schematically summarized. In the NM approch, the coordinates of the oscillators are first delocalized by symmetrization and diagonarization of a GF matrix[12] prior to the quantizations and the quantum mechanical mixings caused by the anharmonic characters of the potential. On the other hand, the quantizations precede the symmetrizations and mixings in the LM approach. The differences between these two approaches may be analogized with those of the MO and VB theories for electronic structures, since orbitals are symmetrized and delocalized in MO before adding electrons whereas electronic structures in VB are constructed by making

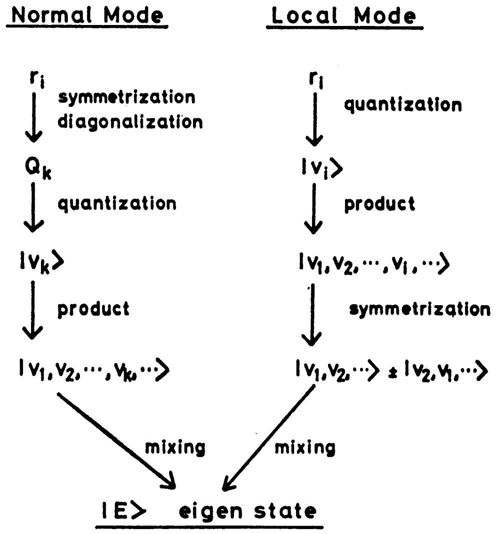

Fig. 1. Two different approaches to the eigen states.

proper pairs of the electrons which already belong to individual localized atomic orbitals.

The most different step in both approaches is the quantum mechanical mixings which may correspond to configuration interactions (CI) in the electronic theory. Therefore, the question of which method is more suitable must be answered from several points of view. One is to see which representation would cause smaller mixing or which can give closer states to the true eigenstates when the mixing process is discarded. The mixings in the NM representation are caused only by anharmonic terms in the potential, whereas any cross terms in kinetic and potential parts can cause mixings in the LM representation even in a completely harmonic system. So the NM approch would be better for fundamentals and also for low v overtones and combinations of skeletal vibrations where anharmonic characters are usually not so significant. However, hydrogen stretching motions in CH, OH, or NH are very anharmonic because of their large amplitude and high frequency. If there is a large anharmonic coupling term in the potential, and if there are more than two equivalent or nearly equivalent anharmonic oscillators, the anharmonic coupling term causes a mixing of the NM states, even if these two anharmonic oscillators are completely independent of each other in the internal coordinate system, that is,

$$v = \frac{1}{2}kq_1^2 + hq_1^3 + \frac{1}{2}kq_2^2 + hq_2^3$$

$$= \frac{1}{2}kQ_s^2 + \frac{1}{2}kQ_a^2 + \frac{h}{\sqrt{2}}Q_s^3 + \frac{3h}{\sqrt{2}}Q_sQ_a^2, \tag{1}$$

where

$$Q_s = \frac{1}{\sqrt{2}}(q_1+q_2) \text{ and } Q_a = \frac{1}{\sqrt{2}}(q_1-q_2). \tag{2}$$

Such induced anharmonic coupling causes very strong perturbations in the overtone region of CH_2 or CH_3 stretching modes, which are known by the name of Darling-Dennison resonances. The LM approach in such an anharmonic system, however, may not cause such strong mixing since all the effects of the anharmonic character can be considered at the stage of a one-dimensional oscillator problem. Although the harmonic coupling is large in this representation, the symmetrization procedure can greatly reduce the final mixings, as will be seen in the following section.

The second point of view on the choice of the LM or NM representation is to see which representation makes it easier to obtain the interaction terms related with the mixing. The third is to see which can give more physically meaningful descriptions for the finally obtained eigenstates. The answers from these points of view are obvious. Perturbation terms in the NM representation cannot be so simple because a normal coordinate itself is an already complicated linear combination of internal coordinates. By the same reason, an eigenstate expressed by a linear combination of NM states is difficult to visualize. On the other hand, an LM or SLM representation would make it much easier to obtain the perturbation terms as well as to understand the meaning of each eigenstate because of the simplicity of the basis modes. It must be emphasized that this advantage of LM or SLM is extremely important for wider application of the assigned spectra rather than for prediction of the absorption frequencies.

Hamiltonian of Coupled Morse Oscillator. The Hamiltonian of two equivalent interacting Morse oscillators may be written as

$$H = H_1 + H_2 + H_{12}, \tag{3}$$

where

$$H_i = \frac{1}{2m}p_i^2 + D_e(1-\exp(-\alpha q_i))^2, \tag{4}$$

$$H_{12} = g_{12}p_1p_2 + f_{12}q_1q_2. \tag{5}$$

H_i is the one-dimensional Hamiltonian for the i-th oscillator and H_{12} is the perturbation which couples the two oscillators. The first and second terms in Eq. 5 correspond to the kinetic and potential coupling, respectively. The higher order anharmonic coupling terms in the potential were neglected in Eq. 5. The eigenvalue of the H_i is expressed by

$$E_{v_i} = \omega_e\left(v_i+\frac{1}{2}\right) - \omega_e\chi_e\left(v_i+\frac{1}{2}\right)^2, \tag{6}$$

where

$$\omega_e = \left(\frac{\alpha}{\pi c}\right)\sqrt{\frac{D_e}{2m}}, \tag{7a}$$

$$\omega_e\chi_e = hc\omega_e^2/4D_e. \tag{7b}$$

Then the matrix elements of the two dimensional Hamiltonian, H, can be written as

$$\begin{aligned}\langle v_1,v_2|H|v_1,v_2\rangle = E_{v_1} + E_{v_2} + g_{12}\langle v_1|p|v_1\rangle\langle v_2|p|v_2\rangle \\ + f_{12}\langle v_1|q|v_1\rangle\langle v_2|q|v_2\rangle,\end{aligned} \tag{8}$$

$$\begin{aligned}\langle v_1,v_2|H|v_1',v_2'\rangle = g_{12}\langle v_1|p|v_1'\rangle\langle v_2|p|v_2'\rangle \\ + f_{12}\langle v_1|q|v_1'\rangle\langle v_2|q|v_2'\rangle,\end{aligned} \tag{9}$$

where $|v\rangle$ is an eigenstate of a one-dimensional Hamiltonian H_i, and

$$|v_1,v_2\rangle = |v_1\rangle|v_2\rangle. \tag{10}$$

Harmonic approximation for the matrix elements of H_{12} may be convenient for a preliminary analysis or for qualitative understanding of the mixing effects, although the exact matrix elements based on the Morse oscillator wavefunctions are not so difficult to obtain. Some values used for 1,1-dichloroethylene are tabulated in the Appendix. The off-diagonal elements other than $v_1'=v_1\pm1$ and $v_2'=v_2\pm1$ are all zero in harmonic approximation or small even in exact solution.

Introducing the symmetrized local mode (SLM) states as

$$(u_1,v_2)^{\pm}=\begin{cases}\dfrac{1}{\sqrt{2}}(|v_1,v_2>\pm|v_2,v_1>) & \text{for } v_1>v_2\\ |v_1,v_2> & \text{for } v_1=v_2 \\ & \text{and } (+) \text{ state}\end{cases}, \tag{11}$$

the Hamiltonian matrix is reduced to

$$\begin{aligned}<v_1,v_2,\pm\,|H|v_1',v_2',\pm> &= <v_1,v_2|H|v_1',v_2'>\\ &\quad\pm<v_1,v_2|H|v_2',v_1'>\\ &\qquad \text{for } v_1>v_2 \text{ and } v_1'>v_2',\end{aligned} \tag{12}$$

$$<v,v,+|H|v,v,+>=<v,v|H|v,v>, \tag{13}$$

$$<v,v,+|H|v_1,v_2,+>=\sqrt{2}<v,v|H|v_1,v_2>. \tag{14}$$

Since the states which have the same value of v_1+v_2 form a nearly degenerate group, and since the off-diagonal elements are very small compared to the energy difference between the different groups, the mixing of the states may essentially occur between these states belonging to the same group.

The degenerate pair states in LM, (v_1,v_2) and (v_2,v_1), split into doublets, $(v_1,v_2)^+$ and $(v_1,v_2)^-$, in SLM. The magnitude of the splitting, however, is large only when $v_2=v_1-1$, as easily seen in harmonic approximation. For other states, splitting is mainly caused by small differences of mixings between (+) and (−) states through higher order perturbations, although the anharmonic character of the off-diagonal matrix elements may be also responsible to some extent. The splitting of $(v,0)^{\pm}$ decreases rapidly with the increase of v and the states behave as a pure local mode state. Figure 2 shows a schematical energy diagram which correlates NM states to LM states from the above considerations.

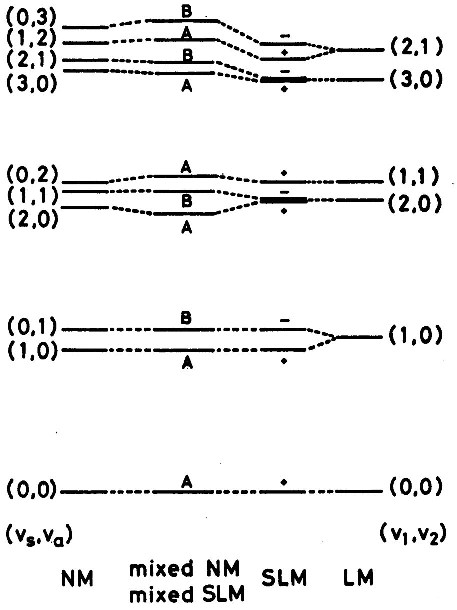

Fig. 2. Schematical energy diagram wich correlates NM states to LM states. The structure in NM was drawn using the tentative values for the parameters, $(\omega_e\chi_e)_s$ and $(\omega_e\chi_e)_a$, the effects of $\chi_{s,a}$ were taken in mixed NM. A and B denote the symmetric stretching and antisymmetric stretching states for the C_2 operation around the molecular axis. (+) and (−) states were defined by Eq. 11.

Frequency Analysis and Potential Parameters. Prior to the two dimensional analysis of the spectrum, ω_e and $\omega_e\chi_e$ were estimated to be 3194 cm^{-1} and 58 cm^{-1} respectively by the use of the Birge-Sponner relation[13] for the overtone series, assuming a one dimensional oscillator model. There were two more parameters, f_{12} and g_{12}, necessary for the two dimensional calculation. It was, however, very difficult to determine these two parameters independently because $<v_1,v_2|H|v_1+1,v_2-1>$, which is most responsible for mixing, always contains f_{12} and g_{12} in the same combined form in harmonic approximation, although such constraint is to be destroyed in $<v_1,v_2|H|v_1+1,v_2+1>$ which connects different groups and also in the anharmonic calculation. Therefore, we used the calculated value of $(1/m_C)\cos(\angle\text{HCH})=-0.04167$ amu^{-1} for g_{12} using the assumed angle of $\angle\text{HCH}=120°$. g_{12} was fixed at this value throughout the present analysis.

A preliminary calculation was done neglecting f_{12} under a harmonic approximation for the off-diagonal

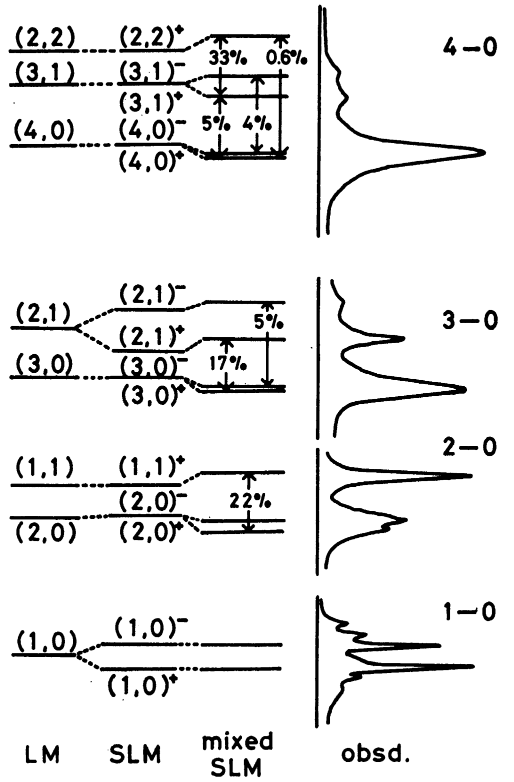

Fig. 3. Observed spectrum and their assignment. The energy diagram was shown by the diagonal elements in each representation in order to show how to approach to the eigen values. The numbers in % show the degree of the mixing between the two states which are connected by the arrows.

TABLE 1. OBSERVED PEAK FREQUENCIES (ν-obsd), OBSERVED INTENSITIES (Γ-obsd), THEIR ASSIGNMENTS, CALCULATED PEAK FREQUENCIES (ν-calcd), AND CALCULATED EIGENSTATES AS A LINEAR COMBINATIONS OF SLM

ν-obsd / cm^{-1}	Γ-obsd / cm^2 mol^{-1}	Assign.[a)]	ν-calcd / cm^{-1}	Eigenstates (mixed SLM)
3035	197	$(1, 0)^+$	3032	$(1, 0)^+$
3130	131	$(1, 0)^-$	3124	$(1, 0)^-$
5990	3.26	$(2, 0)^+$	5993	$0.882(2, 0)^+ \quad +0.471(1, 1)^+$
6025	4.3	$(2, 0)^-$	6042	$(2, 0)^-$
6210	5.2	$(1, 1)^+$	6205	$0.882(1, 1)^+ \quad -0.471(2, 0)^+$
8860	0.54	$(3, 0)^+$	8849	$0.912(3, 0)^+ \quad +0.410(2, 1)^+$
		$(3, 0)^-$	8869	$0.974(3, 0)^- \quad +0.228(2, 1)^-$
9070	0.21	$(2, 1)^+$	9076	$0.912(2, 1)^+ \quad -0.410(3, 0)^+$
9230	0.03	$(2, 1)^-$	9226	$0.974(2, 1)^- \quad -0.228(3, 0)^-$
11601	0.051	$(4, 0)^+$	11599	$0.970(4, 0)^+ \quad +0.227(3, 1)^+ \quad +0.080(2, 2)^+$
		$(4, 0)^-$	11601	$0.977(4, 0)^- \quad +0.212(3, 1)^-$
11880	0.003	$(3, 1)^+$	11897	$0.784(3, 1)^+ \quad +0.576(2, 2)^+ \quad -0.231(4, 0)^+$
11990	0.003	$(3, 1)^-$	11994	$0.977(3, 1)^- \quad -0.212(4, 0)^-$
—	0	$(2, 2)^+$	12191	$0.814(2, 2)^+ \quad -0.577(3, 1)^+ \quad +0.068(4, 0)^+$
14204	0.006	$(5, 0)^+$	14219	$0.982(5, 0)^+ \quad +0.184(4, 1)^+ \quad +0.052(3, 2)^+$
		$(5, 0)^-$	14220	$0.983(5, 0)^- \quad +0.181(4, 1)^- \quad +0.027(3, 2)^-$
14705	0.002	$(4, 1)^+$	14649	$0.821(4, 1)^+ \quad +0.542(3, 2)^+ \quad -0.182(5, 0)^+$
—	0	$(4, 1)^-$	14694	$0.946(4, 1)^- \quad +0.270(3, 2)^- \quad -0.182(5, 0)^-$
16722	0.0008	$(6, 0)^\pm$	16720	

a) Most dominant SLM state.

matrix elements. The results were good enough to assign all the peaks in the observed spectra. The three peaks at 5990 cm^{-1}, 6025 cm^{-1}, and 6210 cm^{-1} in the first overtone region were assigned to the $(2,0)^+$, $(2,0)^-$, and $(1,1)^+$ dominant states. These bands were assigned to $2\nu_1$, $\nu_1+\nu_9$, and $2\nu_9$, respectively, in the NM representation by Yamaoka and Machida.[11)] The 8860 cm^{-1} peak was assigned to the unresolved $(3,0)^+$ and $(3,0)^-$ pairs corresponding to $3\nu_1$ and $2\nu_1+\nu_9$ respectively, whereas $(2,1)^+$ and $(2,1)^-$ were assigned to the 9070 cm^{-1} peak ($\nu_1+2\nu_9$, in the NM representation) and 9230 cm^{-1} peak ($3\nu_9$, in the NM representation), respectively, which show larger splitting. Other peaks were also assigned as shown in the third column of Table 1 and in Fig. 3.

Next, f_{12} and more refined ω_e and $\omega_e\chi_e$ values were determined by the least squares methods still within the harmonic approximation. The final parameters in Table 2 were obtained using the exact matrix elements based on the Morse potential which are listed in the Appendix. The calculated frequencies were in good agreement with the observed ones, as shown in the fourth column of Table 1. The last column of Table 1 shows the calculated eigenstates as a linear combination of SLM.

TABLE 2. SPECTROSCOPIC PARAMETERS

ω_e/cm^{-1}	3191.6
$\omega_e\chi_e$/cm^{-1}	57.63
f_{12}/cm^{-1} Å^{-1}	2170 (0.043 mdyne Å^{-1})
g_{12}[a)]/amu^{-1}	−0.04167
D_e/cm^{-1}	44190
α/Å^{-1}	1.755

a) Calculated assuming ∠HCH=120°.

The changes of the spectral structures with the change of the basis representations are schematically shown in Fig. 3 together with the observed spectra. The degeneracy of the fundamental bands, (1,0) and (0,1) in LM, was easily resolved into $(1,0)^+$ and $(1,0)^-$ in the SLM representation as well as in the other $(v,v-1)$, $(v-1,v)$ pair states. However, (2,0) and (0,2) in LM were still practically degenerate in pure SLM. The splitting of these levels were caused by a second order perturbation which mixed $(2,0)^+$ and $(1,1)^+$ by 22%. The other pair states which did not show splitting in SLM were also split by mixing to a greater or lesser degree, although the splitting of $(v,0)$ states became smaller with the increase of v, as stated in the previous paragraph.

Intensity Analysis and Dipole Moment Function. The change of the dipole moment with the displacement of q_1 and q_2 could be expressed by

$$\boldsymbol{D}(q_1,q_2) = \boldsymbol{D}_1(q_1) + \boldsymbol{D}_2(q_2) + \boldsymbol{D}_{12}(q_1,q_2), \tag{15}$$

where $\boldsymbol{D}_1$ or $\boldsymbol{D}_2$ is the change induced by the change of q_1 or q_2, respectively, while the other coordinate q_2 or q_1 remains unchanged. $\boldsymbol{D}_{12}$ expresses the interacting effect which appears when q_1 and q_2 change simultaneously. Instead of Eq. 15, $\boldsymbol{D}(q_1,q_2)$ may be written in another form as

$$\boldsymbol{D}(q_1,q_2) = D_{//}(q_1,q_2)\,\boldsymbol{i} + D_{\perp}(q_1,q_2)\,\boldsymbol{j}, \tag{16}$$

where $\boldsymbol{i}$ and $\boldsymbol{j}$ are the unit vectors parallel and perpendicular to the molecular axis respectively, as shown in Fig. 4. Here, we assume that directions of $\boldsymbol{D}_1$ and $\boldsymbol{D}_2$ do not change because of the magnitude of q_1 and q_2. Let θ be the angle of $\boldsymbol{D}_1$ measured from the direction of $\boldsymbol{i}$ and let M be the scalar part of $\boldsymbol{D}_1$. Then we obtain this relations:

$$D_{//} = (M(q_1) + M(q_2))\cos\theta + M_{12}q_1q_2, \tag{17}$$

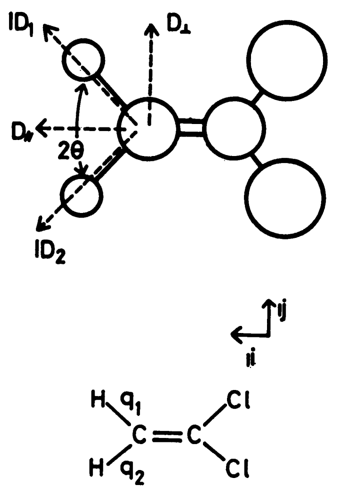

Fig. 4. The change of the dipole moment of CH_2CCl_2 and its relation to the molecular framework.

$$D_\perp = (M(q_1) - M(q_2))\sin\theta. \tag{18}$$

Here, we make a further approximation by neglecting the higher order terms in $\boldsymbol{D}_{12}(q_1,q_2)$ such as $M_{122+}(q_1q_2{}^2+q_1{}^2q_2)\,\boldsymbol{i}$ and $M_{122-}(q_1q_2{}^2-q_1{}^2q_2)\boldsymbol{j}$. $M(q)$ is a dipole moment function in one dimensional approximation as treated in our preceding paper[4)] and we can expand it in a power series of q:

$$M(q) = M_1q + M_2q^2 + \cdots. \tag{19}$$

The higher order terms in Eq. 19 were again neglected. θ is an unknown parameter because $\boldsymbol{D}_1$ will not necessarily be parallel to the direction of the displacement of q_1. So we have four parameters to be determined from the intensity analyses of the observed spectra.

The symmetry considerations show that a transition from the ground state to any (+)-state or to any (—)-state must be induced by $D_{/\!/}$ or $D_\perp$, respectively. The transition moments in the SLM representation are given by

$$\begin{aligned} \langle v,0,+|\boldsymbol{D}|0\rangle &= \sqrt{2}\cos\theta\langle v|M|0\rangle\,\boldsymbol{i} \\ &\quad + \sqrt{2}\,M_{12}\langle v|q|0\rangle\langle 0|q|0\rangle\,\boldsymbol{i}, \end{aligned} \tag{20}$$

$$\langle v,0,-|\boldsymbol{D}|0\rangle = \sqrt{2}\sin\theta\langle v|M|0\rangle\,\boldsymbol{j}, \tag{21}$$

$$\langle v_1,v_2,+|\boldsymbol{D}|0\rangle = \begin{cases} \sqrt{2}\,M_{12}\langle v_1|q|0\rangle\langle v_2|q|0\rangle\,\boldsymbol{i} & \\ & \text{for } v_1 \neq v_2 > 0 \\ M_{12}\langle v|q|0\rangle^2\,\boldsymbol{i} & \text{for } v_1 = v_2 > 0. \end{cases}$$

The second term of Eq. 20 is smaller than the first term because an anharmonic character is necessary for $\langle 0|q|0\rangle \neq 0$. Thus, we may say that M is responsible for the appearence of the fundamental and pure overtone bands whereas M_{12} is responsible for the appearence of pure combinations with (+)-symmetry. Pure combination bands with (—)-symmetry are inactive in this approximation, although they may appear in higher order approximation through the terms such as M_{122-}.

The transition moment corresponding to a mixed state, $|n\rangle = \sum C_{nv}|v\rangle$, is written as

$$\langle n|D|0\rangle = \sum C_{nv}\langle v|D|0\rangle \tag{24}$$

where $|v\rangle$ is a representative of a pure SLM state $|v_1,v_2\rangle$ and C_{nv} is a linear combination coefficient as listed in Table 1.

Deduction of the Dipole Moment Parameters. The appearence of the combination bands would be totally attributed to the degree of mixing with allowed pure overtones in the absence of M_{12}. The 6210 cm^{-1} peak assigned to the $(1,1)^+$ dominant state, however, was stronger than the 5990 cm^{-1} assigned to the $(2,0)^+$ dominant state, although the calculation showed only 22% of mixing between the two SLM's. This fact indicated considerable contribution of M_{12} to the spectrum.

Analyzing the observed intensities of the five peaks in the fundamental and the first overtones using Eqs. 20—24 and the matrix elements of the Appendix, we obtain:

$$\begin{aligned} |\langle 1|M|0\rangle| &= 2.56\times10^{-2}\,\mathrm{D}, \\ |\langle 2|M|0\rangle| &= 4.76\times10^{-2}\,\mathrm{D}, \\ |M_{12}| &= 0.386\,\mathrm{D}\,\mathrm{\AA}^{-1}, \\ \theta &= 38.4^\circ \pm 0.2^\circ. \end{aligned}$$

Here, the sign of M_{12} depends on M. It must be chosen so that it can be constructive with M in the $(1,1)^+$ dominant band but destructive in the $(2,0)^+$ dominant band.[14)] From these values, the contribution of M_{12} to the total integrated intensity over the second overtone region was estimated to be less than a few per cent, and much less for the higher overtones. Thus we could use the one-dimensional approximation for the other $|\langle v|\boldsymbol{D}|0\rangle|$'s with $v>2$. In the determination of M_1 and M_2 in M, the procedure described in our preceding papers[4,5)] was employed. The intensity values were converted to those of the one-dimensional model by subtracting small contributions from M_{12}. These corrected values showed a slight dip in the $2\leftarrow0$ transition (see Fig. 5) as seen in benzene and cyclohexane.[4)] Therefore, the relation, $M_1M_2>0$, could be obtained.[4)] It would be reasonable to choose $M_1<0$ and $M_2<0$, according to the *ab initio* calculation for ethylene and also

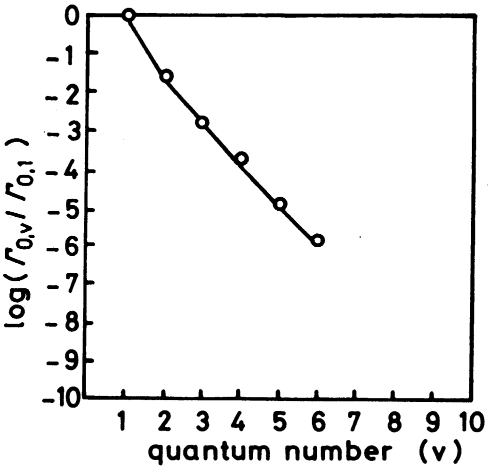

Fig. 5. The logarithmic relative intensity, $\Gamma_{0,v}/\Gamma_{0,1}$, for liquid 1,1-dichloroethylene plotted against a vibrational quantum number, v. Open circles represent the observed values, while the solid line connects these values calculated from the best-fit parameter, $M_2/M_1 = 3.03$ Å^{-1}.

TABLE 3. DIPOLE MOMENT PARAMETERS

	This work	Ethylene (*Ab initio*)
M_1/D Å^{-1}	−0.29	−0.64
M_2/D Å^{-2}	−0.88	−1.23
M_{12}/D Å^{-2}	0.39	0.57
θ/°	38.4	52.3

considering the results of benzene and cyclohexane. This choice of the sign for M enforced $M_{12}>0$. The finally obtained parameters are listed in Table 3.

Comments on the Final Results. There are two causes which mix the states in the SLM representation, namely, kinetic coupling and potential coupling. We ignored the anharmonic coupling in the potentials. The excellent agreement between the calculated and observed frequencies seems to confirm this approximation. The contributions from these two types of coupling were evaluated numerically to see which is more effective in the 1,1-dichloroethylene system. One off-diagonal elements, shown as

$$\begin{aligned}\langle 2,0,+|0|1,1,+\rangle &= \sqrt{2}\,(q_{12}\langle 2|p|1\rangle\langle 0|p|1\rangle \\ &\quad + f_{12}\langle 2|x|1\rangle\langle 0|x|1\rangle) \\ &= -111.5\,\mathrm{cm^{-1}} + 26\,\mathrm{cm^{-1}}\end{aligned}$$

indicated that f_{12} was less effective in the mixing. This might be one of the reasons why the preliminary calculation with $f_{12}=0$ led to the frequencies which are satisfactory enough to allow assignment of the observed spectrum.

The f_{12} value determined in this work was positive, unlike that of Yamaoka and Machida.[11] Our value is close to f_{12} of ethylene, 0.0185 mdyne/Å, including its sign, which was obtained by the same authors.[15] D_e and the Morse parameter, α, were deduced from ω_e and $\omega_e\chi_e$ and are listed in Table 2. The α-value of 1.75 Å^{-1} was 10% larger than Machida's value.

Our approach has the advantage of giving more physically meaningful assignments for the spectrum as well as some simplicity of the analysis. The assignments in the NM representation, such as $2\nu_1$ or $\nu_1+2\nu_9$, may not have much physical meaning except for the symmetry because of the strong mixing due to the Darling-Dennison reasonance in the CH overtone regions. Although the mixing can never be neglected in SLM, the meaning of the mixing is still clear. We found the $(v,0)^{\pm}$ dominant states tended to be more isolated and tended to degenerate rapidly for $v>3$. This corresponds to the formation of pure local modes in spectra. The other states, however, did not show these tendencies even in the highest states examined. So we may say that the LM representation is surely preferable in the cases of the optically allowed high v states. But we should remember that there are many other excited states which neither LM nor NM can describe in a simple form, although they are almost forbidden in absorption spectra.

The intensities calculated from the parameters in Table 3 are listed in the fourth column of Table 4. The numbers in the parentheses are the intrinsic intensities of the pure SLM bands in the absence of mixing. The contributions of M and M_{12} to each transition moment are separately listed in the sixth and seventh columns respectively. The last column shows the percent contribution of M_{12} to the total integrated band intensities, f_{M12}. It can be seen that f_{M12} is not very large. It is only 13.6% even in the largest case, for the 2←0 band. The second largest is 3.4% for the 3←0 band. If the effects of M_{12} in other molecules are the same order in magnitude, the one-dimensional analysis in the preceding paper[4] would be

TABLE 4. CALCULATED INTENSITIES AND THE CONTRIBUTION OF M_{12}

ν_0 / cm^{-1}	Assign.	Γ-obsd / cm^2 mol^{-1}	Γ-calcd / cm^2 mol^{-1}	Γ-intrinsic / cm^2 mol^{-1}	$\langle n\|M\|0\rangle$ / 10^{-3} D	$\langle n\|M_{12}q_1q_2\|0\rangle$ / 10^{-3} D	$f_{M_{12}}$ / %
3035	$(1, 0)^+$	197	198	(198)	−28.7	0.61	0.03
3130	$(1, 0)^-$	131	129	(129)	−22.7	0	
5990	$(2, 0)^+$	3.26	3.25	(7.2)	−4.62	1.65	13.6
6025	$(2, 0)^-$	4.3	4.39	(4.39)	−4.18	0	
6210	$(1, 1)^+$	5.2	5.28	(1.33)	2.50	2.03	
8860	$(3, 0)^+$	0.54	0.38	(0.57)	1.36	−0.135	3.4
	$(3, 0)^-$		0.33	(0.34)	1.14	0	
9070	$(2, 1)^+$	0.27	0.20	(0.025)	0.69	0.33	
9230	$(2, 1)^-$	0.03	0.016	(0)	0.25	0	
11601	$(4, 0)^+$	0.051	0.036	(0.038)	−0.39	0.01	0.7
	$(4, 0)^-$		0.024	(0.024)	−0.31	0	
11880	$(3, 1)^+$	0.003	0.004	(0.0006)	0.097	0.040	
11990	$(3, 1)^-$	0.003	0.004	(0)	0.075	0	
—	$(2, 2)^+$	0	0.0003	(0.0001)	−0.027	−0.010	
14204	$(5, 0)^{\pm}$	0.006	0.0036	(0.0036)	0.12	−0.002	0.0
			0.0025	(0.0025)	0.10	0	
14705	$(4, 1)^+$	0.0002	0.0002	(0.0000)	−0.022	−0.009	
16722	$(6, 0)^{\pm}$	0.0008	0.0006	(0.0006)			0.0

Intensities and matrix elements are connected by the following relation:

$$\Gamma = \frac{8\pi^3 N}{3hc}|\langle 0|M|v\rangle|^2 = 2.508\times 10^5|\langle 0|M|v\rangle|^2 \quad \text{(see Ref. 4).}$$

practically assured.

M_{12}, however, shows a great deal of perturbations on the intensity distributions in the overtones. This is due to interferring interactions with M which happened to contribute to the same transition moment through mixing of the states. From columns 6 and 7, we see that M alone and M_{12} alone explained only 31% and 20% of the total intensity of the $(1,1)^+$ dominant transition. The remaining 49% must be attributed to the constructive property[14] of M and M_{12} in the transition moment. In contrast to this transition, $(2,0)^+$ dominant states were 40% smaller in intensity than what M alone could induce. This was attributed to the destructive[14] contribution of M_{12}.

The obtained dipole moment parameters were compared with the *ab initio* values of ethylene, since we failed to find the corresponding experimental parameters in the literature. The *ab initio* calculation was the one described in the preceding paper.[4] The sign of M_{12} was found to be positive, as shown in Table 3. However, θ was smaller than expected. The direction of the change of the dipole moment induced by a displacement of one CH bond deviates more than 20° from the direction of the displacement, whereas the *ab initio* value of θ in ethylene was very close to what we expected from the direction of the displacement. We believe the experimental error in θ is not so large, since it is strongly correlated to the ratio of the intensities of $(1,0)^-$ and $(1,0)^+$ bands. Polarization of the electrons in chlorine atoms induced by the stretching of CH bonds might be responsible for such small values of θ.

Appendix

MATRIX ELEMENTS FOR MORSE OSCILLATOR WITH THE PARAMETERS IN TABLE 2

$\langle v|q|v'\rangle/10^{-2}$ Å

	0	1	2	3	4	5	6
0	1.57						
1	7.71	4.80					
2	−0.748	11.00	8.18				
3	0.120	−1.32	13.60	11.7			
4	−0.025	0.25	−1.91	15.90	15.47		
5	0.0064	−0.059	0.40	−2.52	17.96	19.40	
6	−0.0019	0.016	−0.105	0.59	−3.14	19.87	23.53

$\langle v|q^2|v'\rangle/10^{-4}$ Å^{-2}

	0	1	2	3	4	5	6
0	62.41						
1	40.64	205.2					
2	79.15	118.5	377.2				
3	−19.19	132.8	224.6	582.2			
4	4.90	−38.2	181.0	357.0	825		
5	−1.414	11.19	−60.1	224.0	517	1109	
6	0.453	−3.53	19.5	−84.23	260	699	1428

$\langle v|p|v'\rangle/i(\mathrm{cm}^{-1}\,\mathrm{amu})^{1/2}$

	0	1	2	3	4	5
0	0.668					
1	−37.457	1.925				
2	6.274	−51.665	3.082			
3	1.294	10.748	−61.629	4.190		
4	0.314	−2.600	15.005	−69.211	5.099	
5	−0.082	0.714	−4.124	19.127	−75.139	5.958
6	0.028	−0.212	1.257	−5.842	23.077	−79.778

i: The unit pure imaginary number.

In the final stage of preparing this paper, we received a preprint of a new work on local mode spectra of dihalomentanes from B. R. Henry. We should point out an accidental similarity in the way of approach between their work and this work.

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14) The absorption intensity, I, is expressed in terms of M and M_{12} as,

$$I \propto (\langle M\rangle + \langle M_{12}\rangle)^2 = \langle M\rangle^2 + \langle M_{12}\rangle^2 + 2\langle M\rangle\langle M_{12}\rangle.$$

The effect of M_{12} is said to be "constructive" or "destructive" with M according to whether the sign of the $\langle M\rangle\langle M_{12}\rangle$ term is "positive" or "negative," respectively.

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