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The Abnormal Absorption Intensity of the C-H Stretching Vibration Band in Chloroform Vapor. I. The CNDO Calculation Involving the 3*d* Orbitals

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By the CNDO calculation involving the 3*d* orbitals, the infrared absorption intensity of the C–H stretching vibration band in chloroform vapor has been discussed in comparison with those of methyl chloride and methylene chloride. The value of the 3*d* orbital exponent of the chlorine atom was estimated on the basis of calculations using different values of the 3*d* orbital exponent on methyl chloride. The absolute intensities of the fundamental and the first overtone bands were calculated from the values of the first and the second derivatives of dipole moments with respect to the normal coordinates. From the results of these calculations, it follows that the electrical properties of the vibrating bond are the most effective factors in bringing about the abnormal absorption intensity of the C–H stretching vibration band in chloroform vapor.

The CNDO method was applied by Segal and Klein¹⁾ to the calculation of dipole-moment derivatives $\mu' = \partial\mu/\partial S_j$, where μ is the molecular dipole moment, and S_j, an appropriate symmetry coordinate. They concluded that the theory was reasonably successful in calculating both the magnitude and the sign of μ' for molecules composed of the first-row elements of the periodic table and/or hydrogen.

The CNDO method was extended to the treatment of molecules containing second-row elements by Santry and Segal.[2,3] In their papers, the importance of the 3*d* orbitals to the bonding in the molecule containing the second-row element was discussed and the CNDO parameters of the 3*d* orbitals necessary for calculation on molecules containing these elements were estimated.

The abnormal absorption intensity of the C–H stretching vibration band in chloroform vapor is particularly interesting, since the fundamental band intensity is very weak and the first overtone band intensity is much stronger than that of the former.[4–6] Robinson *et al.* interpreted this experimental result in terms of the electrical properties of the vibrating bond.[4]

In view of the above situation, it appeared of interest to investigate the abnormal intensity of the C–H stretching vibration band in chloroform vapor by the CNDO calculation involving the 3*d* orbitals of the chlorine atom. However, the values of the parameter for the 3*d* orbitals of the second-row elements are not the most desirable.[2] Therefore, in the first step of the treatment in this work, we attempted to estimate the exponent, as a parameter, for the 3*d* orbitals of the chlorine atom by fitting the calculated molecular dipole moment of methyl chloride to the experimental one. By use of the appropriate value of the 3*d* orbital exponent of the chlorine atom, the dipole-moment derivatives referring to the C–H stretching vibration of chloroform have been calculated and the abnormal intensity of this vibration band has been discussed.

Methods of Calculation

The CNDO Calculation Involving the 3d Orbitals. The molecular orbital calculation used in this work followed the CNDO method proposed by Santry and Segal[2] except for the value of the 3*d* orbital exponent. To determine the appropriate value of the 3*d* orbital exponent of the chlorine atom, we adopted the approach of examining the comparative ability of molecular orbitals, as calculated by the various values of the 3*d* orbital exponent, to predict correctly the observed dipole moment of methyl chloride.

The CNDO approximation describes the molecular orbitals, φ_i, as linear combinations of valence atomic orbitals, χ_μ:

$$\varphi_i = \sum_\mu c_{i\mu}\chi_\mu, \tag{1}$$

where the coefficient, $c_{i\mu}$, are the eigenvectors of the Hartree-Fock matrix, $F_{\mu\nu}$. An important characteristic of the calculation in this work is that the 3*d* orbitals are considered to be members of the valence atomic orbital when the atom is a second-row element in the periodic table.

The coefficient of the molecular orbital and the energy can be obtained by solving the appropriate set of secular equations and corresponding secular matrix. The elements of the SCF energy matrix are given in this method by:

$$\begin{aligned} F_{\mu\mu}(\mathrm{S,S}) = {} & -\frac{1}{2}(I_\mu + A_\mu) + \Big\{[P_{\mathrm{AA}}(S) - Z_{\mathrm{A}}] \\ & - \frac{1}{2}(P_{\mu\mu} - 1)\Big\}\gamma_{\mathrm{AA}}(\mathrm{S,S}) + P_{\mathrm{AA}}(\mathrm{D})\gamma_{\mathrm{AA}}(\mathrm{S,D}) \\ & + \sum_{\mathrm{B}\neq\mathrm{A}}\{[P_{\mathrm{BB}}(\mathrm{S}) - Z_{\mathrm{B}}]\gamma_{\mathrm{AB}}(\mathrm{S,S}), \\ & + P_{\mathrm{BB}}(\mathrm{D})\gamma_{\mathrm{AB}}(\mathrm{S,D})\}, \end{aligned} \tag{2}$$

$$\begin{aligned} F_{\mu\mu}(\mathrm{D,D}) = {} & -\frac{1}{2}(I_\mu + A_\mu) + \left\{\left[P_{\mathrm{AA}}(\mathrm{S}) - \left(Z_{\mathrm{A}} - \frac{1}{2}\right)\right]\right. \\ & \left. \times\, \gamma_{\mathrm{AA}}(\mathrm{D,S})\right\} + \left[P_{\mathrm{AA}}(\mathrm{D}) - \frac{1}{2}P_{\mu\mu}\right]\gamma_{\mathrm{AA}}(\mathrm{D,D}) \\ & + \sum_{\mathrm{B}\neq\mathrm{A}}\{[P_{\mathrm{BB}}(\mathrm{S}) - Z_{\mathrm{B}}]\gamma_{\mathrm{AB}}(\mathrm{D,S}) \\ & + P_{\mathrm{BB}}(\mathrm{D})\gamma_{\mathrm{AB}}(\mathrm{D,D})\}, \end{aligned} \tag{3}$$

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1) G. A. Segal and M. L. Klein, *J. Chem. Phys.*, **47**, 4236 (1967).

2) D. P. Santry and G. A. Segal, *ibid.*, **47**, 158 (1967).

3) D. P. Santry, *J. Amer. Chem. Soc.*, **90**, 3309 (1968).

4) C. C. Robinson, S. T. Tare, and H. W. Thompson, *Proc. Roy. Soc.*, **A269**, 492 (1962).

5) M. M. Chalaye and G. Levi, *C.R. Acad. Sci. Paris*, **t.267**, B-45 (1968).

6) I. Rossi, M. Nguyen-Van-Thanh, and C. Haeusler, *Can. J. Chem.*, **47**, 3319 (1969).

$$F_{\mu\nu}(\mathrm{S,S}) = \beta^0_{\mathrm{AB}}S_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{\mathrm{AB}}(\mathrm{S,S}), \tag{4}$$

$$F_{\mu\nu}(\mathrm{S,D}) = \beta^0_{\mathrm{AB}}S_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{\mathrm{AB}}(\mathrm{S,D}) \qquad (\mu \neq \nu), \tag{5}$$

$$F_{\mu\nu}(\mathrm{D,D}) = \beta^0_{\mathrm{AB}}S_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{\mathrm{AB}}(\mathrm{D,D}), \tag{6}$$

where the suffix S refers to *s* and *p* orbitals, where D refers to the *d* orbital, and where γ_{AB} is the electron-repulsion integral calculated as a Coulomb integral involving valence *s* functions, which are divided into two sets, such as S (involving *s* and *p* orbitals) for those with exponents defined by Slater's rules and D (involving *d* orbital) for those with smaller exponents. In this calculation, the values of the orbital exponent were taken to be 6.1 and 5.5 for the S and D of the chlorine atom respectively. The $-\frac{1}{2}(I_\mu + A_\mu)$ term is the core integral, where I_μ and A_μ are the ionization potential and the affinity of the χ_μ orbital. The P_{AA} (S) term is the total charge density of the A atom in *s*- or *p*-type orbitals:

$$P_{\mathrm{AA}}(\mathrm{S}) = \sum_{\mu \neq \mathrm{D}}^{\mathrm{A}} P_{\mu\mu}, \tag{7}$$

and P_{AA} (D) is the analogous charge density in 3*d* orbitals. The β^0_{AB} term is the resonance integral proportionality constant and is approximated as:

$$\beta^0_{\mathrm{AB}} = \frac{1}{2}K(\beta_{\mathrm{A}}{}^0 + \beta_{\mathrm{B}}{}^0), \tag{8}$$

where $\beta_{\mathrm{A}}{}^0$ depends only on the A atom and where K is 0.75 if the A atom and/or the B atom is a second-row element, and 1 otherwise. The Z_{A} term is the core charge on the A atom. The $S_{\mu\nu}$ term is the overlap integral between the χ_μ and χ_ν orbitals. The numerical values used in this calculation are listed in Table 1. The necessary overlap integrals were evaluated from the master formulas of Lofthus.[7] The electron–repulsion integrals involving *s* functions were theoretically evaluated from the master formulas, which were provided in the same way as in the derivation of Roothaan.[8]

Table 1. Parameter values (eV)

Atom	H	C		Cl		
Orbital	1*s*	2*s*	2*p*	3*s*	3*p*	3*d*
$1/2(I+A)$	7.176	14.051	5.572	21.591	8.708	0.977
$-\beta_{\mathrm{A}}{}^0$	9	21		22.33		

The Dipole Moments and their Derivatives. The molecular dipole moments were calculated as a sum of three terms, μ_{Q}, μ_{sp}, and μ_{pd}, whree μ_{Q} is the contribution from net charge densities and where μ_{sp} and μ_{pd} are terms which arise from atomic polarization due to the mixing of *s* and *p* orbitals and that of *p* and *d* orbitals respectively. They can be calculated by means of the following equations:[9]

$$\mu_{\mathrm{Q}}(\mathrm{z}) = 2.5416 \sum_{\mathrm{A}}^{\mathrm{atoms}} Q_{\mathrm{A}} z_{\mathrm{A}} \quad \text{(debyes)}, \tag{9}$$

$$Q_{\mathrm{A}} = Z_{\mathrm{A}} - P_{\mathrm{AA}},$$

where z_{A} is the appropriate Cartesian coordinate of the A atom.

$$\begin{aligned}\mu_{sp}(\mathrm{z}) = &- 2.5416 \sum_{\mathrm{A}}^{\mathrm{atoms}} \Bigg[\frac{10}{\sqrt{3}\,Z_s'(\mathrm{A})} P_{2s(\mathrm{A}),2p_z(\mathrm{A})} \\ &+ \frac{21}{\sqrt{3}\,Z_s'(\mathrm{A})} P_{3s(\mathrm{A}),3p_z(\mathrm{A})} \Bigg] \quad \text{(debyes)},\end{aligned} \tag{10}$$

where Z'_s is the appropriate orbital exponent as defined by Slater's rules.

$$\begin{aligned}\mu_{pd}(\mathrm{x}) = &-2.5416 \sum_{\mathrm{A}}^{\mathrm{atoms}} M(\mathrm{A}) \Bigg[P_{3d_{xz}(\mathrm{A}),3p_z(\mathrm{A})} \\ &+ P_{3d_{x^2-y^2}(\mathrm{A}),3p_x(\mathrm{A})} + P_{3d_{xy}(\mathrm{A}),3p_y(\mathrm{A})} \\ &- \frac{1*}{\sqrt{3}} P_{3d_{z^2}(\mathrm{A}),3p_x(\mathrm{A})} \Bigg] \quad \text{(debyes)},\end{aligned} \tag{11}$$

$$\begin{aligned}\mu_{pd}(\mathrm{y}) = &-2.5416 \sum_{\mathrm{A}}^{\mathrm{atoms}} M(\mathrm{A}) \Bigg[P_{3d_{yz}(\mathrm{A}),3p_z(\mathrm{A})} \\ &+ P_{3d_{xy}(\mathrm{A}),3p_x(\mathrm{A})} - {}^{*}P_{3d_{x^2-y^2}(\mathrm{A}),3p_y(\mathrm{A})} \\ &- \frac{1*}{\sqrt{3}} P_{3d_{z^2}(\mathrm{A}),3p_y(\mathrm{A})} \Bigg] \quad \text{(debyes)},\end{aligned} \tag{12}$$

$$\begin{aligned}\mu_{pd}(\mathrm{z}) = &-2.5416 \sum_{\mathrm{A}}^{\mathrm{atoms}} M(\mathrm{A}) \Bigg[\frac{2*}{\sqrt{3}} P_{3d_{z^2}(\mathrm{A}),3p_z(\mathrm{A})} \\ &+ P_{3d_{xz}(\mathrm{A}),3p_x(\mathrm{A})} + P_{3d_{yz}(\mathrm{A}),3p_y(\mathrm{A})} \Bigg] \\ &\text{(debyes)},\end{aligned} \tag{13}$$

$$M(\mathrm{A}) = \frac{5376[Z_s'(\mathrm{A})Z_{\mathrm{D}}'(\mathrm{A})]^{7/2}}{5^{1/2}[Z_s'(\mathrm{A}) + Z_{\mathrm{D}}'(\mathrm{A})]^8}. \tag{14}$$

The numerical values required to discuss the intensities of the fundamental and the first overtone bands related to the C–H stretching vibration bands were obtained by fitting the calculated dipole moments to a cubic function with respect to the C–H distance and by taking the first and the second derivatives at the equilibrium distance. The dipole moments were calculated for the molecule distorted in the manner dictated by the symmetry coordinate including the C–H stretching modes. All the C–H bond stretching motions were calculated at intervals of ±0.02 Å.

The Absolute Absorption Intensities of the Vibration Bands. The absolute infrared absorption intensity of the fundamental band, ($A^{*(k)}_{1\leftarrow0}$), related to the normal coordinate, Q_k, was calculated from the following equation (15), which was derived, by Wilson *et al.*,[10] from a consideration of the 0→1, 1→2, *etc.* transitions, in the harmonic oscillator approximation:

$$A^*_{1\leftarrow0} = A_{1\leftarrow0} + A_{2\leftarrow1} + A_{3\leftarrow2} + \cdots$$

$$A^{*(k)}_{1\leftarrow0} = \frac{\pi}{3C} \sum_{i=x,y,z} \left(\frac{\partial \mu_i}{\partial Q_k}\right)^2 [\mathrm{cm^2 \cdot sec^{-1} \cdot molecule^{-1}}], \tag{15}$$

where C is the velocity of light and where μ_i is the *i*-component of the dipole moment of a system.

About the absolute intensity of the overtone band, ($A^{*(k)}_{2\leftarrow0}$), in relating to the normal coordinate, Q_k, the

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[7] A. Lofthus, *Mol. Phys.*, **5**, 105 (1962).

[8] C. C. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

[9] In this calculation, we made a few corrections in Equations (2-32) of the original paper[2]; the revised coefficients are marked by small stars.

[10] E. B. Wilson, J. C. Decious, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Company, New York (1955).

equation to be used in the calculation was obtained according to the approximation employed for the calculation of the fundamental band intensity by Wilson *et al*:

$$A^{*(k)}_{2\leftarrow 0}=\frac{\Theta^2(1-\mathrm{e}^{-2U_k})}{\nu_k}\,\frac{h}{24\pi C}\sum_{i=x,y,z}\left(\frac{\partial^2\mu_i}{\partial Q_k{}^2}\right)^2 \quad [\mathrm{cm^2\cdot sec^{-1}\cdot molecule^{-1}}], \qquad (16)$$

where Θ is the partition function for the Q_k vibration: $\Theta=(1-\mathrm{e}^{-h\nu_k/kT})^{-1}$, $U_k=h\nu_k/kT$, ν_k is the normal frequency associated with the normal coordinate Q_k, k is Boltzmann's constant, h is Planck's constant, and T is the absolute temperature.

Generally, the dipole-moment derivatives related to the normal coordinates can be written as follows:

$$\frac{\partial\mu_z}{\partial Q_k}=\sum_i Ls_i^{(k)}\frac{\partial\mu_z}{\partial S_i},$$

$$\frac{\partial^2\mu_z}{\partial Q_k{}^2}=\sum_{i,j} Ls_i^{(k)}Ls_j^{(k)}\frac{\partial^2\mu_z}{\partial S_i\partial S_j}, \qquad (17)$$

where Q_k is the kth normal coordinate and where the Ls's are the elements of the $\boldsymbol{L}$ matrix which relate the symmetry cooridnates to the normal coordinates.

As for the normal coordinates considered in this work, all the Ls values are negligibly small except for the Ls(CH) related to the C–H symmetric stretching coordinate, S_{CH}. In other words, it can be assumed that the normal modes considered in this work are approximately equal to the pure C–H symmetric stretching modes. Therefore, $(Ls(\mathrm{CH}))^2$ is equal to Gs(CH), where Gs(CH) is the diagonal element of the $\boldsymbol{G}$ matrix related to the C–H symmetric stretching coordinate. Since the molecules lie along the z–axis, as is indicated in Fig. 2, the components of the dipole moments are all equal to zero except for the z–component; also, the derivatives of the x– and y–components of the dipole moments related to the C–H symmetric vibration are equal to zero.

For this reason, the absolute intensities of the fundamental and the first overtone bands of the C–H symmetric stretching vibrations in CH_3Cl, CH_2Cl_2, and $CHCl_3$ can be calculated approximately by the following equations:

$$A^{*(k)}_{1\leftarrow 0}=3.49307\times 10^{-31}(Ls(\mathrm{CH}))^2\left(\frac{\partial\mu_z}{\partial S_{\mathrm{CH}}}\right)^2 \quad [\mathrm{cm^2\cdot sec^{-1}\cdot molecule^{-1}}], \qquad (18)$$

$$A^{*(k)}_{2\leftarrow 0}=2.93118\times 10^{-43}\frac{\Theta^2(1-\mathrm{e}^{-2U_k})}{\nu_k}(Ls(\mathrm{CH}))^4\left(\frac{\partial^2\mu_z}{\partial S^2_{\mathrm{CH}}}\right)^2 \quad [\mathrm{cm^2\cdot sec^{-1}\cdot molecule^{-1}}], \qquad (19)$$

where $\partial\mu_z/\partial S_{\mathrm{CH}}$ and $\partial^2\mu_z/\partial S^2{}_{\mathrm{CH}}$ are the numerical values calculated in [Debye/Å] and [Debye/Å²] respectively. In this calculation, the Ls(CH)'s were taken to be $1.00797\times\sqrt{N_{\mathrm{A}}}$, $1.02183\times\sqrt{N_{\mathrm{A}}}$, and$1.03698\times\sqrt{N_{\mathrm{A}}}$ in $[gr^{-1/2}]$ units for CH_3Cl, CH_2Cl_2, and $CHCl_3$ respectively, where N_{A} is Avogadro's number. The value of $\Theta^2(1-\mathrm{e}^{-2U_k})$ is practically equal to unity. The observed frequencies of the fundamental bands were used for the values of ν_k's: CH_3Cl[11] $2967.8\times C\,\mathrm{sec}^{-1}$, CH_2Cl_2[4] $2989\times C\,\mathrm{sec}^{-1}$, and $CHCl_3$[4] $3033\times C\,\mathrm{sec}^{-1}$, where C is the velocity of light.

Results and Discussion

Figure 1 indicates the variation in the dipole moment of CH_3Cl in the observed geometry when the 3*d* orbital exponent of the chlorine atom is continuously changed from 0 to 6.1; here, the calculation with the zero 3*d* orbital exponent is equivalent to that without 3*d* orbitals, as has been referred to by Santry and Segal.[2] In this figure, it is obvious that the 3*d* orbitals of the chlorine atom play an important role in the molecular properties.

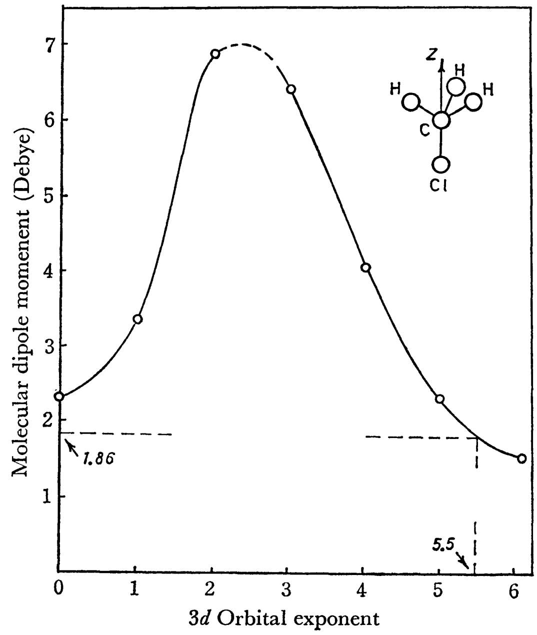

Fig. 1. The variation of dipole moment of CH_3Cl as a function of the 3*d* orbital exponent of chlorine atom.

The study of the results obtained from these calculations suggests that an optimum value of the 3*d* orbital exponent of the chlorine atom is 5.5. Table 2 records the calculated dipole moments of CH_2Cl_2 and $CHCl_3$ obtained by the use of this value. The theoretical dipole moments are in reasonable agreement with the experimental values.

From the results of the preliminary calculations, it is considered that the intensity of the vibration band in chloroform vapor can be discussed in comparison

TABLE 2. THE DIPOLE MOMENTS AND THEIR DERIVATIVES

Molecule	μ_z[Debye]		$\mu_z{}'$ [b]	$\mu_z{}''$ [c]
	Calcd	Obsd[a]	[Debye/Å]	[Debye/Å²]
CH_3Cl	1.857	1.86	−0.324	−0.325
CH_2Cl_2	2.004	1.57	−0.157	−0.473
$CHCl_3$	1.710	1.01	0.037_6	−0.650

a) G. A. Barclay and R. J. W. Le Févre, *J. Chem. Soc.*, **1950**, 556.

b) $\mu'_z=\left(\frac{\partial\mu_z}{\partial S_{\mathrm{CH}}}\right)_0$

c) $\mu_z''=\left(\frac{\partial^2\mu_z}{\partial S^2_{\mathrm{CH}}}\right)_0$

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[11] G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Company, New York (1966).

Table 3. The intensities of the C–H vibration bands in CH_3Cl, CH_2Cl_2, and $CHCl_3$

Molecule	Absolute intensity [cm^2 sec^{-1} $molecule^{-1}$] Fundamental band$^{a)}$ Calcd ($\times 10^{10}$)	Fundamental band$^{a)}$ Obsd ($\times 10^{10}$)	Overtone band Calcd ($\times 10^{10}$)	Overtone band Obsd ($\times 10^{10}$)
CH_3Cl	225 (70.5)	1006$^{b)}$ (88), 1010$^{c)}$	1.30	
CH_2Cl_2	54.1 (17.0)	334$^{b)}$ (29), 178,$^{c)}$ 176$^{d)}$	2.89	
$CHCl_3$	3.19 (1)	11.4$^{b)}$ (1), 22,$^{c)}$ 8,$^{d)}$ 15$^{e)}$	5.71	50$^{d)}$, 80$^{e)}$

a) Values in parentheses are relative intensities.
b) From Ref. 5.
c) L. A. Gribov and V. N. Smirnov, *Soviet Pnysics Uspekhi*, **4**, 919 (1962).
d) From Ref. 6.
e) From Ref. 4.

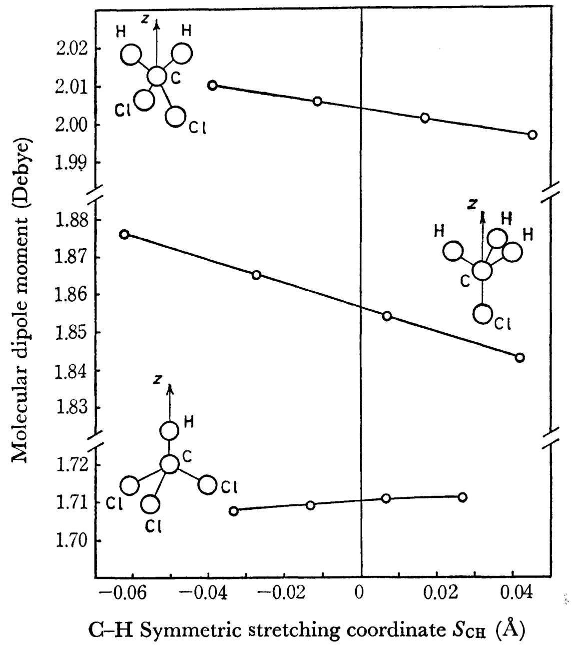

Fig. 2. Calculated variations of the dipole moments as a function of the C–H symmetric stretching coordinate $S_{CH}$$^{a)}$.
a) $S_{CH}(CH_3Cl)=(1/\sqrt{3})\ (\Delta r_1+\Delta r_2+\Delta r_3)$
$S_{CH}(CH_2Cl_2)=(1/\sqrt{2})\ (\Delta r_1+\Delta r_2)$
$S_{CH}(CHCl_3)=\Delta r$
where Δr's are displacements from the C–H equilibrium distance.

with those of methyl chloride and methylene chloride. Figure 2 indicates the variations in the dipole moments of these compounds as a function of the C–H symmetric stretching coordinate. A cursory glance at this figure will show that the fundamental band intensity of the C–H stretching vibration in chloroform is weaker than those of other compounds. The numerical values of the $\partial\mu_z/\partial S_{CH}$ are indicated in Table 2. As for the molecules considered in this work, the absolute intensities of the fundamental bands can be calculated approximately from these numerical values, $\partial\mu_z/\partial S_{CH}$, as has been stated above. The calculated absolute intensities of the fundamental bands are summarized in Table 3. The calculated values indicate that the intensity of the fundamental band of the C–H vibration in chloroform vapor is much lower than those of methyl chloride and methylene chloride. As for these vibration bands, the intensity ratio of other compounds to chloroform are in fair agreement with those obtained experimentally, although there are some questions about the experimental absolute intensities because the absorption band of the symmetric C–H vibration is difficult to distinguish from that of the antisymmetric C–H vibration, *etc.*

The second derivatives, $\partial^2\mu_z/\partial S^2_{CH}$, necessary for the estimation of the first overtone band intensities are indicated in Table 2. The intensities of the fundamental and the overtone bands cannot be discussed in terms of a direct comparison of $\partial\mu_z/\partial S_{CH}$ and $\partial^2\mu_z/\partial S^2_{CH}$. In order to compare the intensity of the first overtone band with that of the fundamental band, the absolute intensity of the first overtone band should be calculated. The absolute intensities of the first overtone bands, as calculated from Eq. 5, are summarized in Table 3. The values show that the intensity of the first overtone band is stronger than that of the fundamental band in chloroform vapor, although the calculated first overtone band intensity is much weaker than the observed one. The $A^*_{1\leftarrow0}/A^*_{2\leftarrow0}$ ratio in chloroform is indicated in Table 4, in which the ratios for other compounds are also predicted. From the results of these calculations, it was recognized that the electrical properties of the vibrating bond are the most effective factors in bringing about the abnormal absorption intensity of the C–H stretching vibration band in chloroform vapor. Since the calculated absolute intensity of the first overtone band in this work was much weaker than the observed one, the contribution of the mechanical anharmonicity to this abnormal absorption intensity should be examined, for it is a factor which cannot be overlooked.

Table 4. The relative intensity between fundamental and overtone bands

Molecule	Relative Intensity ($A_{1\leftarrow0}^*/A_{2\leftarrow0}^*$) Calcd	Obsd
CH_3Cl	173	
CH_2Cl_2	18.7	
$CHCl_3$	0.558	0.16,$^{d)}$ 0.2$^{e)}$

d) and e) References to footnotes are the same as those in Table 3.

Tables 5—7 indicated the constituent terms of the dipole moments and their derivatives. From these table, it is obvious that the relative intensity between these compounds and the abnormal intensity of the C–H stretching vibration band in chloroform cannot be ex-

TABLE 5. CONSTITUENT TERMS OF DIPOLE MOMENT (Unit in Debye)

Molecule	μ_Q	μ_{SP}^{C}	μ_{SP}^{Cl}	μ_{Pd}^{Cl}	μ[a]
CH_3Cl	1.498	−0.091	1.398	−0.949	1.857
CH_2Cl_2	1.451	−0.063	1.537	−0.921	2.004
$CHCl_3$	1.108	−0.025	1.235	−0.608	1.710

a) $\mu=\mu_Q+\mu_{SP}^{\mathrm{C}}+\mu_{SP}^{\mathrm{Cl}}+\mu_{Pd}^{\mathrm{Cl}}$

TABLE 6. CONSTITUENT TERMS OF DIPOLE–MOMENT DERIVATIVE $(\partial\mu_z/\partial S_{\mathrm{CH}})_0$ (UNIT IN Debye/Å)

Molecule	μ_Q'	$(\mu_{SP}^{\mathrm{C}})'$	$(\mu_{SP}^{\mathrm{Cl}})'$	$(\mu_{Pd}^{\mathrm{Cl}})'$	μ'[a]
CH_3Cl	-0.027_5	-0.024_7	-0.009_7	−0.262	−0.324
CH_2Cl_2	0.225	−0.105	0.032_6	−0.309	−0.157
$CHCl_3$	0.449	−0.212	0.109	−0.309	0.037_6

a) $\mu'=\mu_Q'+(\mu_{SP}^{\mathrm{C}})'+(\mu_{SP}^{\mathrm{Cl}})'+(\mu_{Pd}^{\mathrm{Cl}})'$

TABLE 7. CONSTITUENT TERMS OF DIPOLE–MOMENT DERIVATIVE $(\partial^2\mu_z/\partial S_{\mathrm{CH}}^2)_0$ (UNIT IN Debye/Å^2)

Molecule	μ_Q''	$(\mu_{SP}^{\mathrm{C}})''$	$(\mu_{SP}^{\mathrm{Cl}})''$	$(\mu_{Pd}^{\mathrm{Cl}})''$	μ''[a]
CH_3Cl	-0.038_2	−0.140	-0.021_6	−0.125	−0.325
CH_2Cl_2	−0.005	−0.353	-0.017_5	-0.097_5	−0.473
$CHCl_3$	0.091_3	−0.725	−0.109	0.092_5	−0.650

a) $\mu''=\mu_Q''+(\mu_{SP}^{\mathrm{C}})''+(\mu_{SP}^{\mathrm{Cl}})''+(\mu_{Pd}^{\mathrm{Cl}})''$

plained by the values, such as $\partial\mu_Q/\partial S_{\mathrm{CH}}$ and $\partial^2\mu_Q/\partial S^2{}_{\mathrm{CH}}$, which are contributed by net charge densities alone. Atomic polarizations and their variations with the vibrating bonds are appreciably effective in determining the molecular dipole moment and the intensity of the vibration band. This is especially the case with the mixing terms of *p* and *d* orbitals.

Conclusion

The CNDO calculation involving the 3*d* orbitals of the chlorine atom was used in discussing the abnormal absorption intensity of the C–H stretching vibration band in chloroform vapor. The results of the calculations have suggested that the 3*d* orbitals play an important role in determining the molecular properties. The appropriate value of the 3*d* orbital exponent of the chlorine atom was 5.5. The absolute absorption intensities of the fundamental and the first overtone bands of the C–H symmetric stretching vibration in methyl chloride, methylene chloride, and chloroform were calculated from the dipole-moment derivatives. From the results of the calculations, it was recognized that the electrical properties of the vibrating bond are the effective factors in bringing about the abnormal absorption intensity of the C–H stretching vibration band in chloroform vapor. The contribution of the mechanical anharmonicity to this abnormal intensity will be the subject of future study.

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