The Abnormal Absorption Intensity of the C-H Stretching Vibration Band in Chloroform Vapor. II.

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By CNDO calculations considering the *3d* orbitals of the chlorine atom, 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 absolute intensities of the fundamental and the first-overtone bands of these compounds have been calculated in view of the mechanical and the electrical anharmoniciteis of the vibrating bond. From the results of these calculations, it was revealed that the contribution of the electrical properties of the vibrating bond to the abnormal absorption intensity of the C–H stretching vibration band in chloroform vapor is really greater than that of the mechanical anharmonicity.

In a previous paper,[1)] the abnormal infrared absorption intensity of the C–H stretching vibration band in chloroform vapor was discussed in terms of the electrical properties of the vibrating bond. By CNDO calculations involving the *3d* orbitals of the chlorine atom,[2)] the absolute intensities of the fundamental and the first-overtone bands of the C–H stretching vibrations in CH_3Cl, CH_2Cl_2, and $CHCl_3$ were calculated from the values of the first and the second derivatives of the dipole moment with respect to the normal coordinates. The calculated relative intensities of the fundamental bands of these compounds were in satisfactory agreement with the observed values. The calculated absolute intensity of the first-overtone band of the C–H stretching vibration in chloroform was stronger than that of the fundamental band, and the $A^*_{1\leftarrow 0}/A^*_{2\leftarrow 0}$ ratio was 0.558, where $A^*_{1\leftarrow 0}$ and $A^*_{2\leftarrow 0}$ are the absolute intensities of the fundamental and the first-overtone bands in a harmonic oscillator approximation respectively. From the results of the calculations, it was learned 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. However, the calculated absolute intensity of the first-overtone band in chloroform was smaller than the observed one. (The $A^*_{1\leftarrow 0}/A^*_{2\leftarrow 0}$ ratio calculated from the observed values has been reported to be 0.16—0.2.[3,4)]) Therefore, in this paper, the fundamental and the first-overtone band intensities of the C–H stretching vibrations of CH_3Cl, CH_2Cl_2, and $CHCl_3$ have been calculated in view of the mechanical anharmonicity of the vibrating bond.

Methods of Calculation

The mechanical anharmonicity of the molecular vibration can be discussed on the basis of an analysis of the potential energy expanded by the normal coordinate. The treatment of the subject in this work is simplified because the normal modes considered are approximately equal to the pure C–H symmetric stretching modes, as has been described in the previous paper.[1)]

The CNDO method, involving the *3d* orbitals of the chlorine atom, used in this work was described in detail in the previous paper of this series.[1)] From the results of the CNDO calculations for the molecules distorted in the manner dictated by the C–H symmetric coordinates (S_{CH}), the potential energy function for the C–H vibration was obtained by fitting the total energy of the molecule to a quartic function with respect to the S_{CH} coordinate. The potential energy functions thus obtained are as follows:

$$V_{CH}(CH_3Cl) = 62.1720 \times 10^4 S_{CH}^2 - 52.5935 \times 10^{12} S_{CH}^3 + 27.2339 \times 10^{20} S_{CH}^4, \tag{1}$$

$$V_{CH}(CH_2Cl_2) = 60.8290 \times 10^4 S_{CH}^2 - 61.2499 \times 10^{12} S_{CH}^3 - 1.59167 \times 10^{20} S_{CH}^4, \tag{2}$$

$$V_{CH}(CHCl_3) = 58.9394 \times 10^4 S_{CH}^2 - 83.4185 \times 10^{12} S_{CH}^3 + 31.8084 \times 10^{20} S_{CH}^4, \tag{3}$$

where the S'_{CH}s in Eqs. (1), (2), and (3) are equal to $(1/\sqrt{3})\ (\Delta r'_{CH}+\Delta r''_{CH}+\Delta r'''_{CH})$, $(1/\sqrt{2})\ (\Delta r'_{CH}+\Delta r''_{CH})$, and Δr_{CH} respectively. The units of the V_{CH} and the S_{CH} are [erg] and [cm] respectively. For our present object, the potential energy as a function of the normal coordinate (Q_k) alone will be sufficient; here the Q_k involves the C–H symmetric stretching vibration as the main constituent. Since there is a singularity about the vibration mode considered in this work, as has been described above, the energy functions can be obtained from Eqs. (1), (2), and (3) as a function of the normal coordinate, Q_k:

$$V_k(CH_3Cl) = (1/2) \times 7.60852 \times 10^{29} Q_k^2 - 2.51736 \times 10^{49} Q_k^3 + 1.01967 \times 10^{69} Q_k^4, \tag{4}$$

$$V_k(CH_2Cl_2) = (1/2) \times 7.65022 \times 10^{29} Q_k^2 - 3.05426 \times 10^{49} Q_k^3 - 0.062939 \times 10^{69} Q_k^4, \tag{5}$$

$$V_k(CHCl_3) = (1/2) \times 7.63400 \times 10^{29} Q_k^2 - 4.34747 \times 10^{49} Q_k^3 + 1.33405 \times 10^{69} Q_k^4, \tag{6}$$

where the units of the V_k and the Q_k are [erg] and [erg$^{1/2}$sec] respectively. In the above equations, the Q_ks differ from each other, but they are not distin-

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[1)] T. Miyazaki, T. Shigetani, and H. Yamamoto, This Bulletin, **45**, 678 (1972).

[2)] D. P. Santry and G. A. Segal, *J. Chem. Phys.*, **47**, 158 (1967).

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

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

guished in expression in order to avoid complexity. In rewriting the above, the Ls(CH)'s were taken to be $1.00797\times\sqrt{N_A}$, $1.02183\times\sqrt{N_A}$, and $1.03698\times\sqrt{N_A}$ in [$g^{-1/2}$] units for CH_3Cl, CH_2Cl_2, and $CHCl_3$ respectively, where the Ls(CH)'s are the elements of the $\boldsymbol{L}$ matrix which relate the symmetry coordinate to the normal coordinate, and where the N_A is Avogadro's number. Unfortunately, however, the calculated potential energy for the stretching vibration by the CNDO method is not appropriate since the energy increase with the displacement from the equilibrium distance is too much larger than that generally found. In other words, the force constant of the stretching vibration calculated by the CNDO method is too large (2—3 times). Therefore, in order to determine the appropriate potential energy of the vibration considered, we assumed that each potential energy function of Eqs. (4)—(6) can be rewritten by multiplying the coefficients by the constant (α) determined in comparison with the observed frequency of the actual vibration. To determine the constant (α), trial calculations were performed until the difference between energy levels, which were calculated by the Rayleigh-Ritz method, as will be indicated below, coincided with the observed frequency of the fundamental band. In these calculations, the wave functions, ψ_vs, involving the mechanical anharmonicity were described as linear combinations of harmonic oscillator wave functions, $\psi_i^{0\prime}$s:

$$\psi_v = \sum_{i=0}^{n} c_{vi}\psi_i{}^0. \tag{7}$$

The variational treatment of the coefficient, c_{vi}, leads to this equation:

$$\sum_j c_{vj}(H_{ij}-\varepsilon_v\delta_{ij}) = 0 \qquad i = 0, 1, 2, \cdots, n, \tag{8}$$

where:

$$\begin{aligned} H_{ij} &= T_{ij} + V_{ij}, \\ T_{ij} &= \left\langle \psi_i{}^0 \left| -\frac{\boldsymbol{h}^2}{8\pi^2}\frac{\partial^2}{\partial Q^2{}_k} \right| \psi_j{}^0 \right\rangle, \\ V_{ij} &= \left\langle \psi_i{}^0 \left| \frac{1}{2}\lambda_k Q^2{}_k + g_k Q^3{}_k + h_k Q^4{}_k \right| \psi_j{}^0 \right\rangle. \end{aligned} \tag{9}$$

In Eq. (8), ε_v is the energy for the wave function, ψ_v. H_{ij} is the matrix element of the Hamiltonian, including the kinetic (T_{ij}) and the potential (V_{ij}) energies for the vibrating system. The energies (ε_v's) are the roots of the secular equation. Practically, the n in Eq. (7) was taken to be 11, since the further addition of ψ_i^0 no longer changed the eigenvalues (ε_0, ε_1, ε_2, and ε_3) within an order of six significant figures. It should also be noted that the constant (α) is set appropriately at the first step of this calculation. The calculated energies and wave functions are listed in Table 2, in which the potential energy functions are also indicated.

Dipole Moments and Their Derivatives. The formulas used to calculate the dipole moments, in view of the atomic polarization, were given in the previous paper.[1] The dipole moments were calculated for the molecules distorted in the manner dictated by the symmetry coordinate including the C–H symmetric stretching modes. The numerical values required to calculate the absorption intensity were obtained by fitting the calculated dipole moments to a quartic function with respect to the C–H distance, and by taking the first and the second derivatives at the C–H equilibrium distance. They are listed in Table 1, in which the dipole–moment derivatives at the observed and the calculated equilibrium distances are also indicated. Although there are two distinct evaluations of the numerical values required, this problem will be dealt with in the following discussion.

Absolute Absorption Intensities. The absolute absorption intensities of the fundamental and the first-overtone bands, in view of the mechanical and the electrical anharmonicities, can be calculated by the following equation:

$$A_{v+n\leftarrow v} = \frac{8\pi^3}{3c\boldsymbol{h}}\left(\frac{N_v}{N_t}-\frac{N_{v+n}}{N_t}\right)\nu_{v+n,v}\sum_{i=x,y,z}|(\mu_i)_v{}^{v+n}|^2, \tag{10}$$

$$N_v = N_0 \exp(-(\varepsilon_v-\varepsilon_0))/\boldsymbol{k}T, \tag{11}$$

$$N_t = N_0 \sum_{v=0}^{\infty} \exp(-(\varepsilon_v-\varepsilon_0))/\boldsymbol{k}T, \tag{12}$$

$$(\mu_i)_v{}^{v+n} = \left\langle \psi_v \,\middle|\, \mu_i{}^0 + \left(\frac{\partial\mu_i}{\partial Q_k}\right)_0 Q_k + \frac{1}{2}\left(\frac{\partial^2\mu_i}{\partial Q^2{}_k}\right)_0 Q^2{}_k \,\middle|\, \psi_{v+n} \right\rangle, \tag{13}$$

where N_0 and N_v are the numbers of the molecules which are involved at the energy levels of ε_0 and ε_v respectively, and where N_t is the total number of molecules. Also, c is the velocity of light, $\boldsymbol{h}$ is Planck's constant, and $\boldsymbol{k}$ is Boltzmann's constant. In this calculation, the T was taken to be 300°K. μ_i^0 is the i–component of the dipole moment, and $\nu_{v+n,v}$ is the

TABLE 1. DIPOLE MOMENTS AND THEIR DERIVATIVES

Molecule		C–H Equilibrium distance (Å)	μ^0_z[a] (Debye)	μ'_z[a] $\left(\frac{\text{Debye}}{\text{Å}}\right)$	μ''_z[a] $\left(\frac{\text{Debye}}{\text{Å}^2}\right)$
CH_3Cl	Obsd.	1.0959[b]	1.857 (1.86)[c]	−0.3242	−0.3297
	Calcd.	1.1128	1.847	−0.3343	−0.3584
CH_2Cl_2	Obsd.	1.068[b]	2.004 (1.57)[c]	−0.1583	−0.4574
	Calcd.	1.1132	1.993	−0.1908	−0.5599
$CHCl_3$	Obsd.	1.073[b]	1.710 (1.01)[c]	0.0381	−0.6866
	Calcd.	1.1148	1.711	0.0099	−0.6802

a) $\mu^0{}_z$=dipole moment along the z-axis. $\mu'_z=\left(\frac{\partial\mu_z}{\partial S_{CH}}\right)_0$. $\mu''_z=\left(\frac{\partial^2\mu_z}{\partial S^2{}_{CH}}\right)_0$

b) "Interatomic Distances", Supplement, Special Publication No. 18, The Chemical Society (London).

c) Figures in parentheses are observed values.

transition energy in [sec^{-1}] units from the energy level (v) to the energy level ($v+n$). The summation in Eq. (12) was terminated under the condition that a further increase in the i no longer changed the absolute intensity (A), as calculated from Eq. (10), within an order of six significant figures. In the previous paper, since the vibration was approximated to be harmonic, the absolute intensity of the fundamental band, $A_{1\leftarrow 0}{}^*$, was calculated by the summation of $A_{1\leftarrow 0}$, $A_{2\leftarrow 1}$, $A_{3\leftarrow 2}$, *etc.* In this calculation, however, we cannot treat the problem in the same way in view of the mechanical anharmonicity. Fortunately, the mechod of approach to this problem was simplified, since the values of $A_{2\leftarrow 1}$ and $A_{3\leftarrow 1}$ were negligibly small in comparison with the values of $A_{1\leftarrow 0}$ and $A_{2\leftarrow 0}$ respectively.

Results and Discussion

In the treatment of this work, there are some problems which have been left unsolved. In the first place, the equilibrium distance obtained by the total energy minimization disagrees with the observed one. Consequently, the dipole moment calculated in the observed geometry differs from that at the calculated equilibrium distance. It is the same in the dipole–moment derivatives. Generally, the theoretical dipole moment has been calculated by many investigators at the observed equilibrium distance. Also, in the previous paper we discussed the absolute infrared absorption intensity of the C–H stretching vibration band in chloroform by the use of the dipole–moment derivatives at the observed equilibrium distance. In this paper, however, the dipole–moment derivatives were calculated at both the observed and the calculated equilibrium distances. Between these values, a considerable discrepancy was noted in the first derivative of the dipole moment of $CHCl_3$ as is indicated in Table 1. However, as indicated in Table 3, the absolute intensities calculated by these values were not contradictory to each other in terms of the general tendency of the problem. Second, the force constant calculated by the CNDO method is too large, as has been stated above. That is, the absorption bands calculated from the coefficients of Q^2 in Eqs. (4), (5), and (6) are by far larger than the observed values in frequency; therefore, we rewrote the potential energy by multiplying the coefficients of the function by the constant (α). The values of the constants for CH_3Cl, CH_2Cl_2, and $CHCl_3$ were 0.417, 0.435, and 0.460 respectively. In estimating the constants (α's), we made it a condition that the differences between energy levels of the vibration had to be in agreement with the observed values, where the energy levels were calculated by the variational method de-

TABLE 2-a. ENERGY LEVELS AND WAVE FUNCTIONS OF THE VIBRATION IN CH_3Cl
(ε_v, and $\psi_v=\sum_i c_{vi}\psi_i{}^0$)

v	0	1	2	3
$\varepsilon\times10^{13}$ [erg]	2.96448	8.85940	14.71216	20.52596
c_{v0}	**0.99878**	−0.04771	0.00115	−0.01216
c_{v1}	0.04767	**0.98947**	−0.13361	0.01021
c_{v2}	0.00215	0.13333	**0.96002**	−0.23982
c_{v3}	0.01298	0.01274	0.23890	**0.89868**
c_{v4}	0.00137	0.02652	0.03578	0.35187
c_{v5}	0.00005	0.00577	0.04390	0.07388
c_{v6}	0.00036	0.00069	0.01463	0.06632
c_{v7}	0.00005	0.00100	0.00280	0.02933
c_{v8}	0.00000	0.00028	0.00224	0.00768
c_{v9}	0.00001	0.00004	0.00087	0.00453
c_{v10}	0.00000_3	0.00004	0.00018	0.00211
c_{v11}	0.00000	0.00001	0.00011	0.00054

$\Delta\varepsilon_{0,1}=2968$ cm^{-1} (Obsd. 2967.8 cm^{-1}),
$\Delta\varepsilon_{0,2}=5914$ cm^{-1}.
$V_k=(1/2)\times3.17276\times10^{29}\,Q_k{}^2-1.04974\times10^{49}Q_k{}^3+0.42520\times10^{69}Q_k{}^4$, where the units of V_k and Q_k are [erg] and [erg$^{1/2}$sec] respectively.

TABLE 2-b. ENERGY LEVELS AND WAVE FUNCTIONS OF THE VIBRATION IN CH_2Cl_2
(ε_v, and $\psi_v=\sum_i c_{vi}\psi_i{}^0$)

v	0	1	2	3
$\varepsilon\times10^{13}$ [erg]	3.01564	8.95298	14.72662	20.31040
c_{v0}	**0.99811**	−0.05953	−0.00232	−0.01351
c_{v1}	0.05847	**0.98284**	−0.17228	0.00615
c_{v2}	0.00746	0.16647	**0.93088**	−0.31897
c_{v3}	0.01689	0.03271	0.29976	**0.81365**
c_{v4}	0.00350	0.03855	0.08383	0.43092
c_{v5}	0.00082	0.01341	0.07316	0.16305
c_{v6}	0.00076	0.00433	0.03508	0.12642
c_{v7}	0.00027	0.00287	0.01454	0.07497
c_{v8}	0.00009	0.00135	0.00870	0.03778
c_{v9}	0.00006	0.00057	0.00467	0.02236
c_{v10}	0.00003	0.00032	0.00229	0.01299
c_{v11}	0.00001	0.00015	0.00112	0.00620

$\Delta\varepsilon_{0,1}=2989$ cm^{-1} (Obsd. 2989 cm^{-1}),
$\Delta\varepsilon_{0,2}=5896$ cm^{-1}.
$V_k=(1/2)\times3.32785\times10^{29}Q_k{}^2-1.32860\times10^{49}Q_k{}^3-0.02738\times10^{69}Q_k{}^4$, where the units of V_k and Q_k are [erg] and [erg$^{1/2}$ sec] respectively.

TABLE 2-c. ENERGY LEVELS AND WAVE FUNCTIONS OF THE VIBRATION IN $CHCl_3$
(ε_v, and $\psi_v=\sum_i c_{vi}\psi_i{}^0$)

v	0	1	2	3
$\varepsilon\times10^{13}$ [erg]	3.08859	9.11309	14.89067	20.39499
c_{v0}	**0.99631**	−0.08323	−0.00033	−0.01669
c_{v1}	0.08160	**0.96666**	−0.23734	0.02494
c_{v2}	0.01079	0.22860	**0.86799**	−0.42178
c_{v3}	0.02364	0.05164	0.39476	**0.65778**
c_{v4}	0.00562	0.05553	0.13255	0.51959
c_{v5}	0.00132	0.02302	0.10878	0.24281
c_{v6}	0.00140	0.00809	0.06144	0.18706
c_{v7}	0.00054	0.00554	0.02854	0.12803
c_{v8}	0.00018	0.00286	0.01758	0.07258
c_{v9}	0.00013	0.00125	0.01020	0.04470
c_{v10}	0.00006	0.00073	0.00530	0.02772
c_{v11}	0.00002	0.00035	0.00257	0.01340

$\Delta\varepsilon_{0,1}=3033$ cm^{-1} (Obsd 3033 cm^{-1}),
$\Delta\varepsilon_{0,2}=5942$ cm^{-1} (Obsd 5945 cm^{-1}).
$V_k=(1/2)\times3.51164\times10^{29}Q_k{}^2-1.99984\times10^{49}Q_k{}^3+0.61367\times10^{69}Q_k{}^4$, where the units of V_k and Q_k are [erg] and [erg$^{1/2}$ sec] respectively.

TABLE 3. ABSOLUTE ABSORPTION INTENSITIES OF THE C–H VIBRATION OF CH_3Cl, CH_2Cl_2, AND $CHCl_3$ (at 300°K)

Molecule		Equilibrium distance (Å)	Absolute intensity [cm^2 sec^{-1} $molecule^{-1}$]							
			Fundamental band ($\times 10^{10}$)				1st overtone band ($\times 10^{10}$)			
			$A_{1\leftarrow 0}$	$A_{2\leftarrow 1}$	$A^*_{1\leftarrow 0}$[a)]	Obsd	$A_{2\leftarrow 0}$	$A_{3\leftarrow 1}$	$A^*_{2\leftarrow 0}$[a)]	Obsd.
CH_3Cl	Obsd.	1.0959	228.4	0.3×10^{-3}	(225)	1006[b)]	0.0346	0.7×10^{-7}	(1.30)	
	Calcd.	1.1128	243.1	0.3×10^{-3}			0.0652	0.1×10^{-6}		
CH_2Cl_2	Obsd.	1.068	58.9	0.7×10^{-4}	(54.1)	333.5[b)], 176[d)]	0.908	0.1×10^{-5}	(2.89)	
	Calcd.	1.1132	85.6	0.1×10^{-3}			1.39	0.2×10^{-5}		
$CHCl_3$	Obsd.	1.073	1.45	0.3×10^{-6}	(3.19)	11.4[b)], 8[c)], 15[d)]	6.37	0.8×10^{-5}	(5.71)	50[c)], 80[d)]
	Calcd.	1.1148	0.014	0.5×10^{-6}			5.53	0.7×10^{-5}		

a) The values were published in the previous paper[1)] where the calculation was performed with consideration of the electrical anharmonicity alone.

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

c) From Ref. 4.

d) From Ref. 3.

TABLE 4. RELATIVE INTENSITIES BETWEEN THE FUNDAMENTAL AND THE OVERTONE BANDS

Molecule	Relative intensity ($A_{1\leftarrow 0}/A_{2\leftarrow 0}$)	
	Calcd.	Obsd.
CH_3Cl	6601	
CH_2Cl_2	64.9	
$CHCl_3$	0.228	0.16–0.2[a)]

a) From Refs. 3 and 4.

scribed in the method of calculation. The potential energies used in this calculation are indicated in Table 2. The frequencies of the fundamental and the first-overtone bands calculated from the energy levels for the C–H vibration of $CHCl_3$ were in good agreement with the observed values: Calcd. 3033 cm^{-1}, Obsd. 3033 cm^{-1} for the fundamental band, and Calcd. 5942 cm^{-1}, Obsd. 5945 cm^{-1} for the first-overtone band. The calculated energy levels and wave functions are listed in Table 2. Therefore, we consider that it is reasonable to calculate the absolute infrared absorption intensity by considering the mechanical anharmonicity for the C–H stretching vibration of $CHCl_3$ by the use of the wave functions associated with these energy levels. The calculated absolute intensities of the fundamental and the first-overtone bands are summarized in Table 3. It is sufficient to consider the values of $A_{1\leftarrow 0}$ and $A_{2\leftarrow 0}$ alone in order to obtain the fundamental and the first-overtone band intensities, because the values of $A_{2\leftarrow 1}$ and $A_{3\leftarrow 1}$ were quite small. The absolute intensity of the fundamental band of the C–H stretching vibration in chloroform is much weaker than those of the symmetric C–H stretching vibration bands of CH_3Cl and CH_2Cl_2. The absolute intensity of the first-overtone band of this vibration in $CHCl_3$ is stronger than those of CH_3Cl and CH_2Cl_2. The $A_{1\leftarrow 0}/A_{2\leftarrow 0}$ ratios for these compounds are indicated in Table 4. The ratio for chloroform is in good agreement with the observed one.

In Table 5, the absolute intensities calculated from the integrals, $\langle\psi_0|\mu_i^0+(\partial\mu_i/\partial Q_k)_0 Q_k|\psi_v\rangle$ and $\langle\psi_0|\mu_i^0+(\partial\mu_i^0/\partial Q_k)_0 Q_k+1/2\,(\partial^2\mu_i/\partial Q_k^2)_0 Q_k^2|\psi_v\rangle$, are compared with the previous results,[1)] which are calculated on the basis of the electrical anharmonicity alone. This comparative table clarifies the contribu-

TABLE 5. COMPARISON BETWEEN ABSOLUTE INTENSITIES CALCULATED BY THE DIFFERENT APPROXIMATION

Molecule	Absolute intensity [$cm^2sec^{-1}molecule^{-1}$]					
	Fundamental band ($\times 10^{10}$)			1st overtone band ($\times 10^{10}$)		
	A[a)]	$A(m)$[b)]	(A)[c)]	A[a)]	$A(m)$[b)]	(A)[c)]
CH_3Cl	228.4	223.7	(225)	0.035	0.89	(1.30)
CH_2Cl_2	58.8	53.7	(54.1)	0.91	0.37	(2.89)
$CHCl_3$	1.45	3.15	(3.19)	6.39	0.042	(5.71)

a) Absorption intensity calculated with consideration of the mechanical and the electrical anharmonicities. (Calculated from the integral $\langle\psi_0|\mu^0+\left(\frac{\partial\mu}{\partial Q}\right)_0 Q+\frac{1}{2}\left(\frac{\partial^2\mu}{\partial Q^2}\right)_0 Q^2|\psi_v\rangle$.)

b) Absorption intensity calculated with consideration of the mechanical anharmonicity alone. (Calculated from the integral $\langle\psi_0|\mu^0+\left(\frac{\partial\mu}{\partial Q}\right)_0 Q|\psi_v\rangle$.)

c) The values of the previous calculation.[1)] (Calculated with consideration of the electrical anharmonicity alone.)

TABLE 6. THE NUMERICAL VALUES OF THE EFFECTIVE TERMS IN CALCULATING THE ABSOLUTE INTENSITY

Molucule	Band		$\langle\psi_0|Q|\psi_v\rangle$ $\times 10^{41/2}$ [$erg^{1/2}sec$]	$\frac{\partial\mu}{\partial Q}\langle\psi_0|Q|\psi_v\rangle$ $\times 10^{20}$ [esu cm]	$\langle\psi_0|Q^2|\psi_v\rangle$ $\times 10^{41}$ [erg sec^2]	$\frac{1}{2}\frac{\partial^2\mu}{\partial Q^2}\langle\psi_0|Q^2|\psi_v\rangle$ $\times 10^{20}$ [esu cm]
CH_3Cl	Fundamental	($v=1$)	0.3065	−2.4579	0.0253	−0.0256
	1st overtone	($v=2$)	−0.0137	0.1100	0.1305	−0.1317
CH_2Cl_2	Fundamental	($v=1$)	0.3049	−1.2105	0.0317	−0.0455
	1st overtone	($v=2$)	−0.0181	0.0719	0.1272	−0.1829
$CHCl_3$	Fundamental	($v=1$)	0.3017	0.2921	0.0433	−0.0962
	1st overtone	($v=2$)	−0.0250	−0.0242	0.1210	−0.2689

tion of the mechanical anharmonicity of the vibration to the fundamental and the first–overtone band intensities. Furthermore, in Table 6, the numerical values of the terms effective in calculating the absolute absorption intensities are indicated. Thus, it is found that the abnormal absorption intensity of the C–H stretching vibration band in chloroform vapor arises, mainly, from the electrical properties of the vibrating bond.

Conclusion

The absolute infrared absorption intensities of the fundamental and the first–overtone bands of the C–H stretching vibration in chloroform were calculated in view of the mechanical and the electrical anharmonicities of the vibrating bond. These absolute infrared absorption intensities were then compared with those of the C–H symmetric stretching vibration bands in methyl chloride and methylene chloride. The contribution of the mechanical anharmonicity of the vibrating bond to the abnormal absorption intensity of the C–H stretching vibration band in chloroform vapor was compared with that of the electrical anharmonicity. From the results of these calculations, it was confirmed that the abnormal absorption intensity of the C–H stretching vibration band in chloroform vapor arises from the electrical properties of the vibrating bond.

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