October, 1987] © 1987 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 60, 3491—3497 (1987) 3491

An Ab Initio Molecular Orbital Study on Infrared Absorption Spectrum of ν_1 Vibration in Chloroform Vapor

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(Received February 25, 1987)

The infrared absorption frequency and intensity of the ν_1 vibration, referring to the C–H stretching of chloroform vapor, have been calculated from the theoretical potential energy and dipole-moment functions determined by an ab initio molecular orbital calculation. The selection effect of a Gaussian basis set in the ab initio MO method on the calculated frequency and intensity has been studied. It has been pointed out that the theoretical dipole-moment function is sensitive to a slight displacement of the chlorine in the ν_1 vibrational mode.

In two earlier papers,[1,2] the abnormal absorption intensity of the ν_1 vibration band in chloroform vapor was discussed on the basis of results calculated by the semiempirical molecular orbital (MO) method (CNDO/2).[3] From the result it was confirmed that the abnormal absorption intensity of the C–H stretching vibration band in chloroform vapor arises from the electrical properties of a vibrating bond and that the 3d orbitals on chlorine play an important role in determining the molecular properties by the CNDO/2 method.

In the previous study we assumed that the normal mode of ν_1 vibration is approximately equivalent to the pure C–H stretching mode. Since the mass of chlorine is much heavier than those of other atoms, it seemed reasonable to assume that a slight displacement of the chlorine in the ν_1 vibration is negligible. From the results of a recent preliminary investigation, however, it was found that the theoretical infrared absorption intensity is affected by a slight displacement of the chlorine in the ν_1 vibration. Then, by employing an ab initio MO calculation, the effects of this approximation for the ν_1 vibrational mode on the theoretical potential energy and dipole-moment functions are discussed in detail. Also, the infrared absorption frequencies and intensities of the fundamental and first overtone of the ν_1 vibration, calculated on the basis of these functions, are compared with the experimental values. In an effort to determine the selection effect of the basis set in the ab initio MO method on the theoretical frequency and intensity, the results calculated from five kinds of Gaussian basis sets are compared with one another.

Computational Procedure

All ab initio MO calculations were performed by employing the Gaussian 80 program provided by the QCPE, and HITAC M-680H system of the Computer Center in the University of Tokyo.

The theoretical equilibrium geometry of chloroform has been determined by the use of an energy gradient method. The basis sets employed in this work are the 4-31G, 4-31G*, 6-31G*,[4] 6-31G**[4] and Dunning contraction to [6s4p/4s2p/2s] basis[5,6] from the Huzinaga (11s7p/9s5p/4s) primitive set,[7,8] augmented by a set of d-type polarization functions on carbon and chlorine. For the exponent of the polarization function, the values recorded in the Gaussian 80 program were adopted, except for the cases described below. The exponent values of chlorine in 4-31G* (0.47) and the Huzinaga-Dunning (0.65) basis sets were evaluated on the condition of minimizing the total energy at the equilibrium structure, determined without the polarization function in question, the exponent of carbon in the latter case following the value (0.75) adopted by Kato.[11] For the exponent of the chlorine polarization function in 6-31G* and 6-31G**, the value (0.70) selected by Pople et al. was employed.[9,10]

The quadratic force constants with respect to the internal symmetry coordinates were evaluated by a numerical second differentiation of the potential energy of chloroform. By using these force constants, a normal coordinate analysis could be carried out with the Wilson's GF matrix method.[12] In the next step, the derivatives of the detailed potential energy function, $V(Q)$, with respect to the normal coordinate Q_1 were determined from the increment of total energy of the molecule distorted along the normal mode in question. The derivatives of another potential energy function, $V'(Q)$, were obtained in the same way, except that the molecule was distorted under a local-mode approximation: the normal mode ν_1 is equal to the C–H stretching mode. These two types of potential energy functions, $V(Q)$ and $V'(Q)$, have been determined by calculations with five kinds of basis sets.

From the same treatment, the derivatives of the dipole-moment functions, $\mu^z(Q)$ and $\mu^{z\prime}(Q)$, with respect to the normal coordinate Q_1 were determined from the variation of the dipole moment calculated under the two types of vibrational modes, i.e. the normal mode and the local mode. In determining these potential energy and dipole-moment functions, the cross terms between normal coordinates were neglected. By the use of these potential energy functions, the variation method has been adopted in order to obtain the vibrational energy levels in view of the mechanical anharmonicity of the vibration.13) The wave functions, ψ_i, of the molecular vibration were described as a linear combination of the harmonic oscillator wave functions, ϕ_k. By employing the vibrational wave function, ψ_i, and the dipole-moment function, $\mu^z(Q)$, the infrared absorption intensities of the fundamental and first overtone with respect to the ν_1 vibration have been determined in view of the mechanical and electrical

Table 1. Equilibrium Geometries, Dipole Moments, and Total Energies of Chloroform with Various Basis Sets

Property	Basis set					Ref.b)	Obsd	
	4-31G	4-31G*	6-31G*	6-31G**	Huz-Duna)			
Geometric Parameter								
r_{CH}/Åc)	1.06561	1.06809	1.07124	1.07247	1.07124	1.069	1.073d)	1.100e)
r_{CCl}/Å	1.83256	1.78324	1.76205	1.76185	1.76420	1.788	1.762	1.758
θ_{HCCl}/°	108.240	107.995	107.732	107.766	107.648	108.0	108.5	107.5
Dipole moment /Debyef)	1.734	1.330	1.303	1.313	1.282		1.01g)	1.20h)
Total energyi)/auj)	−0.322	−0.421	−0.502	−0.503	−1.852			

a) Dunning contractions to the [6s4p/4s2p/2s] basis from Huzinaga's (11s7p/9s5p/4s) primitive set augmented with a set of d-polarization functions on both carbon and chlorine atoms. b) From Ref. 11. c) 1 Å=10^{-10} m. d) From Ref. 14. e) From Ref. 19. f) 1 Debye=3.335641×10^{-30} C m. g) From Ref. 20. h) From Ref. 21. i) 1415 au was added to all total energies. j) 1 au=4.359814×10^{-18} J.

Table 2. Force Constants for Internal Symmetry Coordinates Calculated by Various Basis Sets

Force constantb)	Basis set			Ref.a)
	6-31G*	6-31G**	Huz-Dun	
F_{11}/mdyn Å^{-1}	6.6940	6.2358	6.4447	5.0335
F_{12}/mdyn Å^{-1}	−0.0036	0.1220	0.1027	0.1301
F_{13}/mdyn	0.1327	0.0008	−0.0132	0.0067
F_{22}/mdyn Å^{-1}	4.8734	4.9044	4.9469	4.3249
F_{23}/mdyn	−0.3196	−0.2758	−0.3174	0.2651
F_{33}/mdyn Å	1.3538	1.2692	1.3991	1.1245

a) From Ref. 15. b) 1 mdyn Å^{-1}=10^2 N m^{-1}, 1 mdyn=10^{-8} N, 1 mdyn Å=10^{-18} N m. F_{11} is the force constant for the C–H stretching, F_{22} for the symmetric C–Cl stretching and F_{33} for the symmetric H–C–Cl bending.

Table 3. Displacements of Atoms per Unit of Normal Coordinate, Q_1, referring to the C–H Stretching Mode (ΔR/Å, Q/amu$^{1/2}$ Å)b)

Atom		4-31G	6-31G*	6-31G**	Huz-Dun	Ref.c)
C	Δx	0.0	0.0	0.0	0.0	0.0
	Δy	0.0	0.0	0.0	0.0	0.0
	Δz	−0.082456	−0.080994	−0.082563	−0.082821	−0.083342
H	Δx	0.0	0.0	0.0	0.0	0.0
	Δy	0.0	0.0	0.0	0.0	0.0
	Δz	0.954496	0.955982	0.954388	0.954134	0.953590
Cl_1	Δx	0.000125	−0.000225	0.000032	−0.000045	−0.000086
	Δy	−0.000215	−0.000087	−0.000019	−0.000077	−0.000149
	Δz	0.000266	0.000390	0.000276	0.000311	0.000374
Cl_2	Δx	0.000125	−0.000225	0.000032	−0.000045	−0.000086
	Δy	0.000215	0.000087	0.000019	0.000077	0.000149
	Δz	0.000266	0.000390	0.000276	0.000311	0.000374
Cl_3	Δx	−0.000250	0.000450	−0.000064	0.000089	0.000172
	Δy	0.0	0.0	0.0	0.0	0.0
	Δz	0.000266	0.000390	0.000276	0.000311	0.000374

a) The C–H bond is placed along the Z axis. b) 1 amu=1.660565×10^{-27} kg. c) The normal coordinates analysis was carried out using the force constant set in Ref. 15 at the experimental geometry in Ref. 14.

Table 4. Derivatives of Potential Energy Function[a)]
$V(Q)=1/2\lambda Q^2+gQ^3+hQ^4+iQ^5$, ($V$/g cm^2 s^{-2}, Q/g$^{1/2}$ cm)

Derivative	4-31G	4-31G*	6-31G*	6-31G**	Huz-Dun
$1/2\lambda/10^{29}$	2.09771 (2.09482)	2.03375 (2.06325)	2.04217 (2.03701)	2.00619 (2.00478)	2.08426 (2.08345)
$g/10^{49}$	−3.34090 (−3.41561)	−3.25388 (−3.27515)	−3.20363 (−3.17872)	−3.11932 (−3.10523)	−3.22587 (−3.20956)
$h/10^{69}$	3.54013 (3.57343)	3.52320 (3.59960)	3.55615 (3.54312)	3.48373 (3.45947)	3.44164 (3.35905)
$i/10^{89}$	−2.75444 (−0.44835)	−3.09752 (−2.91560)	−3.24533 (−3.22850)	−3.22683 (−3.19301)	−3.29353 (−3.29023)

a) Values in parentheses were calculated under the local mode approximation.

anharmonicities of the vibrating bond. Details of above the treatments were reported in a previous paper.[13)]

Another series of calculations have been performed in order to consider this problem on the basis of a variation of the dipole moment in the vicinity of the experimental equilibrium geometry.[14)] The treatment in this calculation is the same as that described above except for the calculation of the force constants. We adopted the force constants[15)] determined from the experimental absorption frequencies since there is a difference between the experimental and theoretical geometries, the latter being determined by minimizing the total energy.

Results and Discussion

The theoretical equilibrium geometries, dipole moments and total energies calculated by each basis set are shown in Table 1. These values are generally in good agreement with the experimental values; in detail, the results calculated by the high-level basis set are more improved than those by other basis sets.

Table 2 indicates the force constants with respect to the internal symmetry coordinates, which are used in Wilson's GF matrix method.[12)] These theoretical force constants, F_{ii}, are slightly overestimated. This is the general tendency in the result of a Hartree-Fock level calculation.

The displacements of atoms for a unit of normal coordinate, referring to the C-H stretching mode, are summarized in Table 3. It can be seen from the table that the displacements of chlorine in the normal mode are quite small in comparison with those of other atoms. Therefore, it seems reasonable to assume that the ν_1 normal mode of chloroform can be replaced by the pure C-H stretching mode. Practically, the derivatives of $V(Q)$ and $V'(Q)$, calculated from any basis set, are in almost good agreement with each other (Table 4). As indicated in Fig. 1, the profiles of the respective potential energy functions obtained by different basis set are drawn as a thick curve together, since there has a close resemblance regarding their shapes.

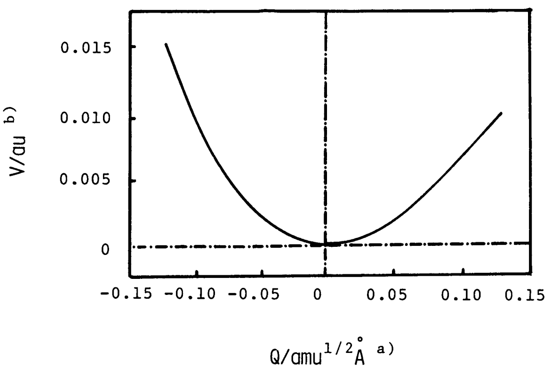

Fig. 1. Potential energy (V) vs. normal coordinate (Q). a) 1 amu=1.660565×10^{-27} kg. b) 1 au=4.359814×10^{-18} J.

The fundamental and first-overtone frequencies calculated by the variation method are indicated in Table 5. These results make clear the delicate differences between the potential energy functions. In the table, the values in parentheses are the results obtained under a local-mode approximation. The absolute deviations of the theoretical frequencies from their mean value are within 1.8%, and the frequencies calculated under the local-mode approximation coincide with those calculated under the normal-mode treatment without an approximation. This fact shows that the potential energy function with respect to the ν_1 vibration is little affected by the motion of chlorine in the normal mode and the selection of the basis set in the ab initio MO calculation.

The agreement between the theoretical and experimental frequencies is generally unsatisfactory and a calculation with a high-level basis set does not always produce a better result. However, by the variation method, the frequencies are improved by 3—4% in comparison with the harmonic results which are given in italics in Table 5. These results indicate the effect of the mechanical anharmonicity on the fundamental and first-overtone frequencies of the ν_1 vibration. Table 6 indicates an example of the energy levels and wave functions of the ν_1 vibration calculated by the variation method. From these results, the high anharmonicity of the C-H stretching mode can be obviously recognized. In this calculation, the cross terms between ν_1 and other vibrational modes in the potential energy function have been neglected.

In a previous paper, the CNDO/2 method was adopted for the molecular orbital calculation. Also, the calculated potential energy function was scaled in order to obtain the appropriate energy levels, since the force constants of stretching vibration calculated by

Table 5. Frequencies of ν_1 Vibrational Mode in view of Mechanical Anharmonicity[a)]
(Unit: cm^{-1})[b)]

Frequency	Basis set					Obsd
	4-31G	4-31G*	6-31G*	6-31G**	Huz-Dun	
Fundamental	3309.78 (3330.06)	3252.98 (3287.95)	3280.41 (3278.77)	3254.54 (3254.53)	3312.83 (3311.29)	3032.9[c)]
1st Overtone	6476.94 (6598.68)	6346.19 (6439.42)	6448.58 (6448.17)	6401.41 (6402.99)	6509.58 (6506.97)	5941.4[c)]
Harmonic frequency	*3438.64* (*3436.27*)	*3385.81* (*3410.28*)	*3392.82* (*3388.53*)	*3362.80* (*3361.61*)	*3427.61* (*3426.94*)	(3462)[d)]

a) Values in parentheses were calculated under the local mode approximation. b) $1\,\mathrm{cm}^{-1}=1.986481\times10^{-23}\,\mathrm{J}$. c) From Ref. 18. d) Theoretical value in Ref. 11.

Table 6. Coefficients of Vibrational Wave Functions, ψ, developped as a Linear Combination of Harmonic Wave Functions, ϕ[a)]

$$\psi_i(Q)=\sum_k c_{i,k}\phi_k(Q)$$

	ψ_0	ψ_1	ψ_2	ψ_3
Eigen value/10^{-20} J	*3.31707*	*9.76258*	*15.92195*	*21.64411*
Coefficient				
$c_{i,0}$	**0.99385**	−0.10603	0.00746	0.02072
$c_{i,1}$	0.10594	**0.94638**	−0.29044	−0.05767
$c_{i,2}$	0.00953	0.28896	**0.79302**	0.48191
$c_{i,3}$	0.02974	0.06092	0.47799	**−0.47065**
$c_{i,4}$	0.00697	0.06845	0.16834	−0.56723
$c_{i,5}$	0.00112	0.03171	0.13630	−0.30716
$c_{i,6}$	0.00223	0.01068	0.08840	−0.24089
$c_{i,7}$	0.00081	0.00861	0.04401	−0.19144
$c_{i,8}$	0.00023	0.00497	0.02996	−0.12611
$c_{i,9}$	0.00027	0.00231	0.02049	−0.09031
$c_{i,10}$	0.00014	0.00164	0.01230	−0.06643
$c_{i,11}$	0.00005	0.00104	0.00809	−0.04497
$c_{i,12}$	0.00005	0.00058	0.00551	−0.03098
$c_{i,13}$	0.00002	0.00030	0.00271	−0.01627

a) These results were obtained by the variation method employing the potential energy function calculated with the 6-31G** basis set under the normal mode treatment.

Table 7-1. Derivatives of Dipole-Moment Function Calculated at Theoretical Geometry[a)]
$\mu^z(Q)=\mu_0^z+M_1^zQ+M_2^zQ^2+M_3^zQ^3$,[b)] ($\mu^z$/esu cm, $Q/\mathrm{g}^{1/2}\,\mathrm{cm}$)[c)]

Derivative	4-31G	4-31G*	6-31G*	6-31G**	Huz-Dun	Ref.
$\mu_0^z/10^{-18}$	1.734	1.330	1.303	1.313	1.282	
$M_1^z/10$	1.060	−0.019	−1.633	−1.469	−2.398	
	(2.428)	(1.861)	(−0.252)	(−0.256)	(−1.169)	−0.60,[d)] 0.0[e)]
$M_2^z/10^{21}$	−7.962	−8.469	−10.033	−9.164	−7.572	
	(−7.115)	(−7.081)	(−9.022)	(−8.462)	(−6.753)	−5.60,[d)] ±5.60[e)]
$M_3^z/10^{41}$	−2.159	−2.655	−1.090	−1.874	1.317	
	(−1.441)	(−1.951)	(−0.070)	(−1.163)	(1.914)	±1.93[e)]

a) Values in parentheses were calculated under the local-mode approximation. b) The dipole-moment function has only a Z component, since the Z axis is the rotational (C_{3v}) axis and the normal mode in question is symmetric. c) $1\,\mathrm{esu\,cm}=3.33561\times10^{-12}\,\mathrm{C\,m}$. d) Values were calculated on the basis of results in Ref. 16. e) Values were calculated on the basis of experimental intensities in Ref. 17.

Table 7-2. Derivatives of Dipole-Moment Function Calculated at Experimental Geometry[a)]

Derivative	4-31G	4-31G*	6-31G*	6-31G**	Huz-Dun
$\mu_0^z/10^{-18}$	1.656	1.311	1.399	1.348	1.317
$M_1^z/10$	−0.204	−0.530	−1.407	−1.395	−2.318
	(1.203)	(0.549)	(−0.159)	(−0.145)	(−1.048)
$M_2^z/10^{21}$	−8.964	−8.795	−9.440	−8.926	−7.458
	(−8.272)	(−8.200)	(−8.711)	(−8.179)	(−6.560)
$M_3^z/10^{41}$	−1.623	−3.245	−1.623	−1.623	1.623
	(−4.196)	(−3.409)	(−1.479)	(−1.690)	(1.479)

a) Values in parentheses were calculated under the local-mode approximation.

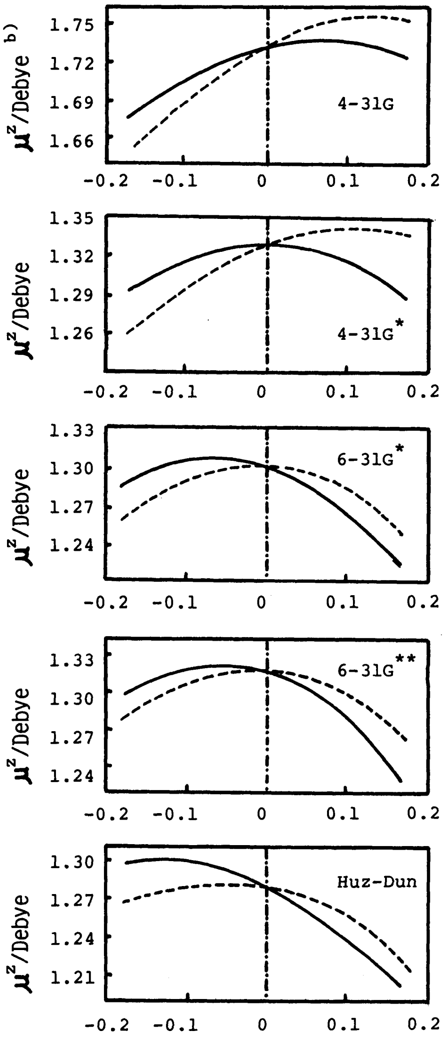

Fig. 2. Dipole moments (μ^z) vs. normal coordinate (Q). (——) normal-mode treatment, (------) local-mode treatment. a) 1 amu=1.660565×10^{-27} kg. b) 1 Debye=3.335641×10^{-30} C m.

the CNDO/2 method is much larger than those generally found. In this work, however, such a treatment has not been performed since the results from the ab initio MO calculation are much more favourable than those from the CNDO/2 calculation.

Table 7-1 records the derivatives of the dipole-moment functions calculated by each basis set with regard to a normal-mode treatment and a local-mode approximation. In the relation between $\mu^z(Q)$ and $\mu^{z\prime}(Q)$, a different tendency can be found in comparison with the case of the potential energy functions, $V(Q)$ and $V'(Q)$. The corresponding derivatives of $\mu^z(Q)$ and $\mu^{z\prime}(Q)$ are different from each other, except for the μ_0^z values.

Especially, the M_1^z values are sensitive to the type of vibrational mode as well as the basis set in the MO calculation, although they are generally small. The $\mu^z(Q)$ and $\mu^{z\prime}(Q)$ calculated from each basis set are displayed in Fig. 2. By the use of the high-level basis set, the extremum of $\mu^z(Q)$ is generally shifted to the direction of short interatomic distance. The values of M_1^z in all cases are close to zero; in other words, the dipole-moment function has an extremum in the vicinity of the equilibrium structure of chloroform.

As generally pointed out, the absorption intensities of the fundamental and first overtone mainly depend on the magnitude of the absolute values of M_1^z and M_2^z, respectively. It is noteworthy, however, that the absorption intensities are affected by the mechanical and electrical anharmonicities of vibration. Especially, these effect in the case of the ν_1 vibration cannot be neglected since the C–H stretching mode is considerably anharmonic, as shown in Table 6.

The fundamental and first-overtone intensities calculated in view of the mechanical and electrical anharmonicities are listed in Table 8-1. Also, the intensities calculated under the harmonic approximation are summarized in Table 8-2. By a comparison between the results in Table 8-1 and those in Table 8-2, the effects of the mechanical and electrical anharmonicities on the infrared absorption intensities can be easily estimated as follows: the fundamental intensity is increased and the first-overtone intensity decreased.

The infrared absorption intensities calculated by using the 6-31G* and 6-31G** basis sets under the local-mode approximation are in agreement with the experimental results. However, from a comparison between these results and those from the normal-mode

Table 8-1. Infrared Absorption Intensities in view of Mechanical and Electrical Anharmonicities[a)]
(Unit: $10^{-10}\,\mathrm{cm^2\,s^{-1}\,mol^{-1}}$)

Intensitiy (at 300 K)	Basis set					Obsd
	4-31G	4-31G*	6-31G*	6-31G**	Huz-Dun	
Fundamental	7.59 (127.75)	15.53 (61.02)	184.18 (24.09)	153.39 (23.82)	279.59 (83.08)	7.9,[b)] 15[c)]
1st Overtone	80.65 (83.92)	74.84 (77.21)	76.50 (76.65)	65.68 (68.79)	30.99 (32.43)	51.2,[b)] 80[c)]

a) Values in parentheses were calculated under the local-mode approximation. b) from Ref. 18. c) From Ref. 22.

Table 8-2. Infrared Absorption Intensities under Harmonic Approximation at Theoretical Equilibrium Geometries[a)]
(Unit: $10^{-10}\,\mathrm{cm^2\,s^{-1}\,mol^{-1}}$)

Intensitiy (at 300 K)	Basis set					Ref.[b)]
	4-31G	4-31G*	6-31G*	6-31G**	Huz-Dun	
Fundamental	39.25 (205.04)	0.01 (121.03)	93.20 (2.21)	75.35 (2.29)	200.88 (47.71)	12.7
1st Overtone	72.11 (57.61)	82.84 (57.50)	116.04 (93.95)	97.68 (83.32)	65.43 (52.04)	40.4

a) Values in parentheses were calculated under the local-mode approximation. b) Values were derived from the data in Ref. 16. The harmonic functions used here were obtained on the basis of experimental results in Refs. 14 and 15.

Table 8-3. Infrared Absorption Intensities under Harmonic Approximation at Experimental Equilibrium Geometries[a)]
(Unit: $10^{-10}\,\mathrm{cm^2\,s^{-1}\,mol^{-1}}$)

Intensity (at 300K)	Basi set				
	4-31G	4-31G*	6-31G*	6-31G**	Huz-Dun
Fundamental	2.17 (41.30)	13.40 (7.22)	73.67 (1.40)	72.41 (1.28)	180.42 (35.40)
1st Overtone	103.58 (88.19)	99.71 (86.66)	114.87 (97.80)	102.69 (86.22)	71.71 (55.46)

a) Values in parentheses were calculated under the local-mode approximation.

treatment, in which a slight displacement of chlorine in the normal mode is considered, it is found that the treatment under the local-mode approximation requires circumspection in determining the dipole-moment function.

In the present work, we did not obtain satisfactory results by employing the high-level basis set under the normal-mode treatment. However, reasonable results would be obtained if we introduced the following treatments: a configuration interaction treatment in the MO calculation, an appropriate exponent for polarization functions, and cross terms between ν_1 and other vibrational modes in the potential energy function. These are subjects for future studies.

The theoretical dipole moment is affected by the charge distribution and equilibrium geometry of a molecule. In order to investigate the effect of the charge distribution calculated by different basis sets, the dipole-moment functions have been determined by each basis set under the same equilibrium geometry. In this treatment, the experimental geometry[14)] has been adopted and the force constants determined on the basis of the experimental data[15)] have been employed. The normal coordinates of the ν_1 vibration can be determined by the use of these force constants, however, the potential energy function $V(Q)$ cannot be obtained since the experimental equilibrium geometry is not generally in agreement with the theoretical equilibrium geometry, which are determined by minimizing the total energy.

Table 7-2 indicates the derivatives of the dipole-moment functions calculated by using the experimental equilibrium geometry. These results are similar to those displayed in Fig. 2, in which the results were obtained by using the theoretical equilibrium geometry. Therefore, the graphical representation of Table 7-2 have not been provided. The fundamental and first-overtone intensities calculated from these dipole-moment functions and harmonic wave functions are listed in Table 8-3, the harmonic wave function being determined on the basis of the experimental results. These results from high-level basis sets are similar to those in Table 8-2 which are derived from the harmonic approximation at the theoretical equilibrium geometry.

The results of an ab initio MO calculation at the 6-31G* level for the dipole-moment function, referring to the ν_1 vibration of chloroform, were published by Tamagake et al.[16,17] It was reported in their papers that the first- and second-order coefficients of a dipole-moment function $\mu(R)$ were -0.08 and -1.0, respectively. For convenience, these values have been transformed to the coefficients of a function $\mu^z(Q)$. The values are -0.60 and -5.60, respectively, while the corresponding values obtained in this work are -0.252 and -9.022. They also reported that the dipole-moment function has an extremum at a distance smaller (-0.04 Å) than the theoretical equilibrium structure. Our corresponding result is -0.0109 Å. The cause of these differences between Tamagake's results and ours for the coefficients and extremum of the dipole-moment function cannot be discussed here since their report does not mention details regarding the following points: the equilibrium geometry and the exponent value of the polarization function on chlorine.

The absorption intensities based on Tamagake's results can be calculated only in the case of the harmonic approximation; however, a detailed treatment cannot be performed since a potential energy function is not published in their paper. The calculated intensities reproduce the experimental results as indicated in Table 8-2. However, if the mechanical anharmonicity is considered, it is expected that the fundamental intensity will be increased and the first-overtone intensity decreased in a similar manner (as our results indicated in Table 8-1).

Conclusion

The infrared absorption frequencies of the chloroform ν_1 vibration calculated by the ab initio MO method under the Hartree-Fock level treatment were larger than the experimental values (by about 10%). The potential energy function was insensitive to a slight displacement of the chlorine in the normal mode ν_1. Also, the selection effect of a Gaussian basis set in the ab initio MO method for the potential energy function was smaller than we have expected.

The theoretical infrared absorption intensities calculated by the 6-31G* and 6-31G** basis sets under the local-mode approximation reproduced the experimental results for the ν_1 vibration. However, satisfactory results could not be obtained by the high-level basis sets, including 6-31G* and 6-31G**, under the normal-mode treatment, which is faithful to the theoretical vibrational mode. The dipole-moment function was sensitive to a displacement of the chlorine in the normal mode ν_1 and to the selection of a Gaussian basis set in the ab initio MO method. It has been found that the local-mode treatment for ν_1 vibration requires circumspection in determining the dipole-moment function.

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