A THEORETICAL STUDY ON THE IONIC STATES AND THE PHOTOELECTRON SPECTRA OF DIFLUOROMETHANE (CH_2F_2)

Kouichi TAKESHITA [1]

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

Received 18 September 1989; in final form 12 October 1989

Ab initio calculations have been performed to study the four low-lying ionic states, $^2B_2$, $^2B_1$, $^2A_1$ and $^2A_2$ of difluoromethane (CH_2F_2). The equilibrium molecular structure of these states is presented. The theoretical ionization intensity curve including the vibrational patterns is also presented and is compared with the photoelectron spectra of CH_2F_2 and CD_2F_2. A new assignment of the photoelectron spectra is proposed.

1. Introduction

The photoelectron (PE) spectra of CH_2F_2 have been observed in the energy range from 12.7 to 16.6 eV [1–4]. The spectra consist of three bands; the first ranges from 12.7 to 14.4 eV and two other bands are overlapping in the region between 14.5 and 16.6 eV. Brundle et al. [2] assigned the first band to the transition to the $^2B_2$ state with the zero–zero ionization energy (0–0 IE) at 12.72 eV. Two bands centered at 15.6 eV have been assigned as overlap of ionization to the $^2A_1$, $^2B_1$ and $^2A_2$ states. However, there has been no clear analysis on the two overlapping bands [2]. Brundle et al. have also observed the PE spectrum of CD_2F_2. The PE spectrum of CD_2F_2 is almost the same as that of CH_2F_2, except for the change of the vibrational structure of the first band. The first band of CH_2F_2 has a well resolved vibrational structure which has been assigned as the excitation of the ν_2 (H–C–H bending) mode, but the vibrational structure has disappeared completely in the PE spectrum of CD_2F_2. There has been no clear explanation for this change.

In the previous theoretical studies on CH_2F_2, the assignment of the PE spectrum has been performed mostly by considering the vertically ionized states only [5–8]. As the molecule is ionized, the equilibrium molecular structure is changed from that of the ground state. The PE spectrum reflects this change and shows structure of vibrational excitations. It is, therefore, interesting to investigate the detailed structure of these bands. In this work, we obtain an approximate theoretical intensity curve using the Franck–Condon factor (FCF) which is given by the square of the overlap integrals between the vibrational wavefunction of the ground state and that of the ionic state.

The purpose of the present work is to study the nature of the four low-lying ionic states $^2B_2$, $^2B_1$, $^2A_1$ and $^2A_2$ of CH_2F_2 by means of a theoretical method. We determine the equilibrium molecular structure of the ground and four ionic states by using the ab initio self-consistent-field (SCF) method. We calculate the harmonic force constant matrix elements over variables of totally symmetric (C_{2v}) distortion and the vibrational frequencies of the totally symmetric modes (ν_1–ν_4) using the harmonic oscillator approximation. We calculate the FCFs and the theoretical intensity curve of the ionization. Using the results of these calculations, we discuss the deuteron substitution effect in the PE spectra and the details of the two overlapping bands.

2. Method of calculation

We used the basis sets of the MIDI-3 [9] for H

[1] Present address: Faculty of Bioindustry, Tokyo University of Agriculture, Abashiri, Hokkaido 099-24, Japan.

0009-2614/90/$ 03.50

and MIDI-4 [9] for C and F augmented by polarization functions which have been proposed by Tatewaki and Huzinaga [9]. The gradient technique for the Roothaan restricted Hartree–Fock (RHF) method was used to determine the optimum molecular structure of the ground and four ionic states of CH_2F_2.

The single and double excitation configuration interaction (SD-CI) method was carried out to obtain accurate ionization energies beyond the SCF level. Using a single reference configuration of an SCF wavefunction of the respective state, singly and doubly excited configuration state functions (CSFs) were generated where the K shell electrons of C and F were kept frozen. The CSFs generated were restricted to the first-order interacting space [10]. The number of the generated CSFs of the $^1A_1$, $^2B_2$, $^2B_1$, $^2A_1$ and $^2A_2$ states are 19604, 20197, 20268, 20287 an 20178, respectively.

The harmonic force constant matrix elements were calculated from RHF wavefunctions by means of the gradient technique; the second derivative was estimated by the numerical differentiation of the analytically calculated first derivative. We calculated the FCFs of only the totally symmetric vibrational modes. In calculating FCFs, we approximated the vibrational wavefunctions by those obtained by the harmonic oscillator model. We assumed that the initial state was the zero-point vibrational level of the ground state. We took the vibrationally excited levels of the ionic states into account where the maximum quantum number was restricted to be below 30. The method of calculation of the FCF and theoretical intensity curve was the same as that used in a previous paper [11].

This work has been carried out by using the computer program system GRAMOL [12] for the gradient technique and the calculation of normal modes, and MICA3 [13] for the CI calculations.

3. Results and discussion

The optimized molecular structure of the ground and four ionic states are listed in table 1. This indicates that an appreciable distortion occurs in the $^2B_2$ and $^2B_1$ states by ionization. The equilibrium C–H and C–F bond distances and the H–C–H angle of the $^2B_2$ state have the largest change among the four ionic states. The F–C–F bond angle of the $^2B_1$ state is reduced. The change is the maximum among the four ionic states.

Table 1
Optimized geometries by the SCF calculation

State	C–H (Å)	C–F (Å)	∠H–C–H (deg)	∠F–C–F (deg)
$^1A_1$	1.087	1.335	112.45	108.47
(exp.) [a]	1.091	1.358	112.1	108.23
$^2B_2$	1.185	1.246	77.66	117.00
$^2B_1$	1.082	1.382	121.66	83.53
$^2A_1$	1.119	1.335	128.50	118.95
$^2A_2$	1.084	1.392	118.74	95.10

[a] Ref. [14].

Table 2
Ionization energies

State	Ver. IE [a]			AIE [a]	
	SCF	SD-CI	obs. [b]	SCF	SD-CI
$^2B_2$	13.56	13.25	13.27	12.37	12.52
$^2B_1$	15.15	14.98	15.3	14.19	14.14
$^2A_1$	15.61	15.31	–	15.28	15.01
$^2A_2$	16.34	15.86	15.71	15.98	15.52

[a] Ver. IE; vertical ionization energy. AIE; adiabatic ionization energy. The calculated total energies of the ground state by the SCF and SD-CI methods are −237.655549 and −238.134090 au, respectively.
[b] Ref. [2].

Table 2 contains the vertical IEs by the SCF and SD-CI methods in comparison with the experimental ones which have been estimated by Brundle et al. by analyzing the PE spectrum. The vertical IEs of the $^2B_2$ and $^2A_2$ states by the SD-CI method are in good agreement with the observed ones. Brundle et al. have proposed the vertical IE of the $^2B_1$ state as 15.3 eV. The present result shows that the vertical IE of the $^2B_1$ is situated at 15.0 eV and that of the $^2A_1$ state at 15.3 eV.

Table 2 also gives adiabatic ionization energies. Those of the $^2B_2$, $^2B_1$, $^2A_1$ and $^2A_2$ states obtained by the SD-CI method are lower than the vertical IEs by 0.73, 0.84, 0.36 and 0.35 eV, respectively. As is expected from the large geometrical change of the $^2B_2$ and $^2B_1$ states, the energy lowering of those states are larger than the other two states.

Table 3 contains the calculated vibrational frequencies of the totally symmetric modes of the ground and ionic states of CH_2F_2. A classical half amplitude of the zero-point vibration was calculated in order to characterize each normal mode. The result shows that a half amplitude of the C–H stretching in the ν_1 mode is the largest for all states. Thus, the ν_1 mode may be characterized as C–H stretching. The ν_2 and ν_4 modes may be assigned as H–C–H and F–C–F bending modes, respectively. The ν_3 mode is the C–F stretching mode accompanied by a contribution from F–C–F bending motion.

The vibrational frequencies of the deuterated substitute, CD_2F_2 and $CD_2F_2^+$, are listed in table 3. The frequencies ν_1, ν_2 and ν_3 decrease on deuteron substitution. The ν_1 and ν_4 modes are assigned as the C–D stretching and F–C–F bending modes, respectively. These assignments are the same as for CH_2F_2 and $CH_2F_2^+$. On the other hand, the ν_2 and ν_3 modes except those of the $^2B_2$ state are a mixture of the C–F stretching and the D–C–D bending motion. The phase of the linear combination of the C–F stretching and D–C–D bending is in-phase for the ν_2 mode and out-of-phase for the ν_3 mode. The ν_2 and ν_3 modes of the $^2B_2$ state are assigned as the D–C–D bending and C–F stretching, respectively.

Using the adiabatic IEs by the SD-CI calculation, we estimated the 0–0 IEs of CH_2F_2. The result is presented in table 4. The table contains the FCFs for the 0–0 transition. As is expected from large geometric changes, the FCFs of the $^2B_2$ and $^2B_1$ states are quite small. The 0–0 IEs and FCFs between CD_2F_2 and $CD_2F_2^+$ are shown in table 4. The 0–0 IEs of $CD_2F_2^+$ are almost the same as those of $CH_2F_2^+$.

Fig. 1A shows the theoretical intensity curve of the ionization of CH_2F_2. A total intensity curve was obtained by assuming the same transition probability for the electronic part. Fig. 1B is the observed PE spectrum by Brundle et al. [2]. The theoretical intensity curve is similar to the observed PE spectrum. The theoretical intensity curve of the $^2B_2$ state has larger vibrational spacing than the observed one but overall features of the vibrational structure are close to the observed PE spectrum. The present

Table 3
Vibrational frequencies (cm^{-1})

State	CH_2F_2				CD_2F_2			
	ν_1	ν_2	ν_3	ν_4	ν_1	ν_2	ν_3	ν_4
$^1A_1$	3258	1659	1224	580	2367	1295	1124	568
(obs.) [a]	2963	1508	1079	532				
$^2B_2$	2650	1288	1412	659	2023	924	1341	646
$^2B_1$	3336	1605	1192	608	2421	1236	1092	606
$^2A_1$	2835	1449	984	479	2028	1118	930	468
$^2A_2$	3318	1624	1122	544	2408	1270	1065	541

[a] Ref. [15].

Table 4
Zero–zero ionization energies

State	CH_2F_2			CD_2F_2		
	ZPVE [a] (eV)	0–0 IE [a] (eV)	FCF [a]	ZPVE (eV)	0–0 IE (eV)	FCF
$^1A_1$	0.42	–	–	0.33	–	–
$^2B_2$	0.37	12.48	0.001	0.31	12.50	0.000
$^2B_1$	0.42	14.14	0.000	0.33	14.14	0.000
$^2A_1$	0.36	14.95	0.038	0.28	14.96	0.020
$^2A_2$	0.41	15.51	0.017	0.32	15.51	0.016

[a] ZPVE; zero-point vibrational energy. 0–0 IE; zero–zero ionization energy. FCF; Franck–Condon factor.

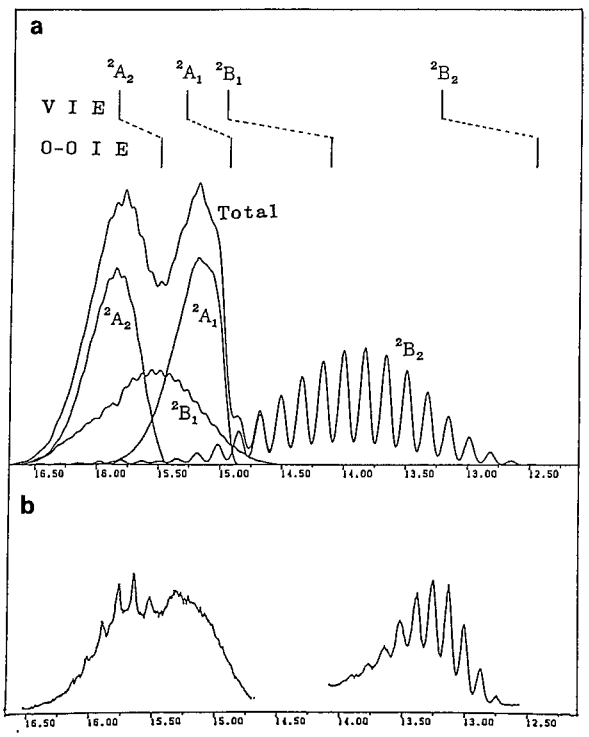

Fig. 1. Theoretical intensity curve and photoelectron spectrum of CH_2F_2. (A) Theoretical intensity curve. (B) Photoelectron spectrum of CH_2F_2 from Brundle et al. [2]. VIE; vertical ionization energy. 0–0 IE; zero–zero ionization energy.

calculation indicates that the vibrational levels of (0, 0, 1, 0)–(0, 0, 7, 0), (0, 1, 0, 0)–(0, 1, 6, 0), (0, 2, 0, 0)–(0, 2, 5, 0), (1, 1, 0, 0)–(1, 1, 4, 0), (1, 0, 1, 0)–(1, 0, 5, 0) and (2, 0, 1, 0)–(2, 0, 3, 0) contribute to the intensity below 13.57 eV. Brundle et al. have assigned these observed vibrational peaks as those of the ν_2 mode. However, from our calculations, the contribution of the higher vibrational excitation to the ν_1 and ν_3 modes is also important. Because of the reduction of the H–C–H angle and shortening of the C–F distance relative to those of the ground state, the ν_2 (H–C–H bending) and ν_3 (C–F stretching) modes are excited in the $^2B_2$ state. Although three vibrational modes of different vibrational frequencies contribute significantly, the PE spectrum has a well resolved vibrational structure. This feature can be explained by observing the following relation among the vibrational frequencies: the vibrational frequency of the ν_2 mode is very close to that of the ν_3 mode and is about half of the ν_1 mode ($\nu_2 \approx \nu_3 \approx \frac{1}{2}\nu_1$, see table 3).

Fig. 1A shows how the $^2A_1$, $^2B_1$ and $^2A_2$ states contribute to the second band of the PE spectrum; the $^2A_1$ state mainly contributes to the first peak near 15.3 eV, the $^2A_2$ state to 15.8 eV and the $^2B_1$ state to the intermediate region of the two peaks.

The vibrational structure is observed in the PE spectrum of the $^2A_2$ state. Brundle et al. have assigned these structures as the excitations of the ν_3 (C–F stretching) and ν_4 (F–C–F bending) modes. Lempka et al. [4] have assigned them as ν_2 (H–C–H bending) and ν_3 modes. The present calculation shows that the vibrational levels of (0, 0, 0, 1)– (0, 0, 0, 5), (0, 0, 1, 0)–(0, 0, 1, 6) and (0, 0, 2, 0)–(0, 0, 2, 4) have large intensity. This result supports the assignment by Brundle et al.

The positions of vertical IEs and 0–0 IEs are illustrated in fig. 1A. The 0–0 IE of the $^2B_2$ state has been assigned by Pullen et al. [1] as 12.70 eV which is the onset of the first peak. The calculated FCF of the 0–0 transition is so small that the peak of the 0–0 IE is difficult to find in the theoretical intensity curve. Fig. 1A shows that the first appreciable peak is found at 12.65 eV. This peak may correspond with the observed first peak at 12.70 eV and is due to the vibrational excitation to the (0, 1, 0, 0) and (0, 0, 1, 0) states. Thus, the 0–0 IE may be 12.5 eV from the calculation.

The theoretical intensity curves of the ionization of CD_2F_2 are illustrated in fig. 2A. They are compared with the observed PE spectrum in fig. 2B. The theoretical intensity curve is similar to the PE spectrum. It is noted that well resolved vibrational structure of the $^2B_2$ state in CH_2F_2 disappears in CD_2F_2. The reason is that the relation, $\nu_2 \approx \nu_3 \approx \frac{1}{2}\nu_1$, does not hold for CD_2F_2.

4. Conclusion

The PE band corresponding to the ionization to the $^2B_2$ state has contributions from the vibrational excitation of the ν_1 (C–H stretching), ν_2 (H–C–H bending) and ν_3 (C–F stretching) modes. A well resolved vibrational structure of the first band is ascribed to the relation $\nu_2 \approx \nu_3 \approx \frac{1}{2}\nu_1$ among the vibrational frequencies. However, this relation does not

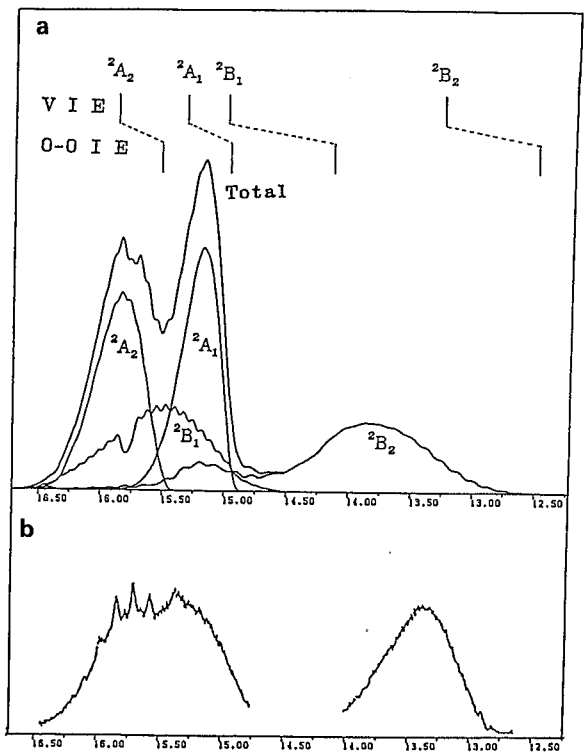

Fig. 2. Theoretical intensity curve and photoelectron spectrum of CD_2F_2. (A) Theoretical intensity curve. (B) Photoelectron spectrum of CD_2F_2. (*) A hole of the $^2B_1$ state near 15.6 eV is due to neglect of the higher vibrational levels of ν_4 mode (F–C–F bending).

hold in CD_2F_2, for which the PE spectrum has no resolved vibrational structure. The onset of the observed PE spectrum near 12.7 eV is assigned as the vibrational excitation to the (0, 1, 0, 0) and (0, 0, 1, 0) states. The 0–0 IE may be 12.5 eV from the calculation.

The first peak near 15.3 eV of the second band is due to ionization to the $^2A_1$ state and the second peak near 15.8 eV is the $^2A_2$ state. The $^2B_1$ state contributes to the intermediate region of the two peaks.

Acknowledgement

The author is grateful to Professor Kimio Ohno for reading the manuscript. He also wishes to thank Dr. Kiyoshi Tanaka for helpful discussions. Computations were carried out on HITAC M-680H systems at the Institute for Molecular Science and the Hokkaido University Computing Center.

References

[1] B.P. Pullen, T.A. Carlson, W.E. Moddeman, G.K. Schweitzer, W.E. Bull and F.A. Grimm, J. Chem. Phys. 53 (1970) 768.
[2] C.R. Brundle, M.B. Robin and H. Basch, J. Chem. Phys. 53 (1970) 2196.
[3] D.W. Turner, A.D. Baker, C. Baker and C.R. Brundle, Molecular photoelectron spectroscopy (Wiley–Interscience, New York, 1970).
[4] H.J. Lempka, D.G. Streets, A.W. Potts and W.C. Price, Phil. Trans. Roy. Soc. (London) A 268 (1970) 59.
[5] S.R. Langhoff and D.P. Chong, Chem. Phys. 55 (1981) 355.
[6] R. Cambi, G. Giullo, A. Sgamellotti, F. Tarantelli, R. Fantoni, A. Giardini-Guidoni and A. Sergio, Chem. Phys. Letters 80 (1981) 295.
[7] G. De Alti, P. Decleva and A. Lisini, Chem. Phys. 76 (1983) 185.
[8] D. Li, J.-K. Zhu, J.-G. Li and Y.-K. Pani, J. Electron Spectry. 34 (1984) 1.
[9] H. Tatewaki and S. Huzinaga, J. Comput. Chem. 1 (1980) 205.
[10] A.D. McLean and B. Liu, J. Chem. Phys. 58 (1973) 1066.
[11] K. Takeshita, J. Chem. Phys. 86 (1987) 329.
[12] K. Takeshita and F. Sasaki, 1981 Library Program at the Hokkaido University Computing Center, in Japanese;
H. Kashiwagi, T. Takada, E. Miyoshi and S. Obara, RHF Program JAMOL3, GRAMOL Program System, Library Program at the Hokkaido University Computing Center (1977), in Japanese.
[13] A. Murakami, H. Iwaki, H. Terashima, T. Shoda, T. Kawaguchi and T. Noro, 1986 Library Program at the Hokkaido University Computing Center, in Japanese.
[14] D.R. Lide Jr., J. Am. Chem. Soc. 74 (1952) 3548.
[15] E.L. Pace, J. Chem. Phys. 18 (1950) 881.

Chemical Physics 143 (1990) 239–244
North-Holland

A THEORETICAL STUDY ON THE IONIC STATES AND THE PHOTOELECTRON SPECTRUM OF DICHLOROMETHANE (CH_2Cl_2)

Kouichi TAKESHITA [1]
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan

Received 3 January 1990

Ab initio calculations are performed to study the molecular equilibrium structure and the vibrational level of the low-lying four ionic states, $^2B_2$, $^2B_1$, $^2A_1$ and $^2A_2$ of dichloromethane (CH_2Cl_2). The theoretical intensity curve obtained by the Franck–Condon factors for the ionization transitions are also reported and compared with the photoelectron spectrum of CH_2Cl_2. A number of new assignments of the photoelectron spectrum are proposed.

1. Introduction

Photoelectron (PE) spectra of CH_2Cl_2 have been reported by many workers [1–5]. In fig. 1 the PE spectrum observed by Kimura et al. [5] is presented. There are two bands below 13 eV. These probably originate from the four low-lying ionic states $^2B_2$, $^2B_1$, $^2A_1$ and $^2A_2$, and are an electron ionization from Cl lone pairs. The first band ranges from 11.32 to 12.5 eV. The vibrational progression of three peaks at 11.32, 11.40 and 11.48 eV has been observed by Potts et al. [3]. They have assigned this progression as the CCl_2 stretching mode of the $^2B_2$ state. A broad tail of the first band ranging from 11.5 to 11.8 eV has been assigned as the $^2A_2$ state. The second band around 12.2 eV has been interpreted as the $^2B_1$ state and the following tail as the transition to the $^2A_1$ state.

Theoretical approaches to the PE spectrum of CH_2Cl_2 have also been reported [1,5–10]. Katsumata and Kimura [5] have carried out the SCF MO calculation and reported the order of states as $^2B_2$, $^2B_1$, $^2A_1$ and $^2A_2$ based on Koopmans' theorem. The first band was assigned as the $^2B_2$ and $^2B_1$ states and the second one was assigned as the $^2A_1$ and $^2A_2$ states. Li et al. [10] have calculated the vertical ionization energies (IEs) by the SCF Xα method and provided the ordering of states as $^2B_1$, $^2B_2$, $^2A_1$ and $^2A_2$.

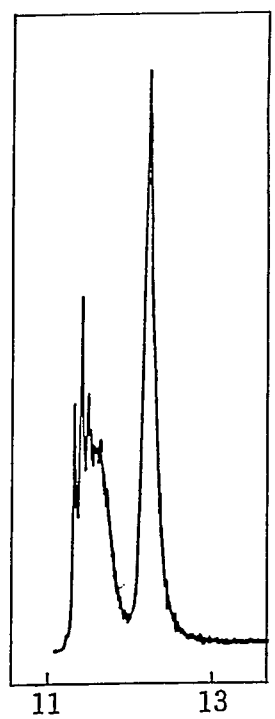

Fig. 1. Photoelectron spectrum by Kimura et al. [5].

In these theoretical studies on CH_2Cl_2 [5,10], the assignment of the PE spectrum has been made by considering only the vertical ionization energies. As the PE spectrum reflects changes in molecular equi-

[1] Present address: Faculty of Bioindustry, Tokyo University of Agriculture, Abashiri, Hokkaido 099-24, Japan.

librium structure and the distribution of vibrational levels, it is desirable to investigate the potential energy surface near equilibrium and the vibrational levels and to calculate a theoretical intensity curve of the transition.

The purpose of the present work is to study the nature of the four low-lying ionic states $^2B_2$, $^2B_1$, $^2A_2$ and $^2A_1$ of CH_2Cl_2 theoretically. An ab initio self-consistent-field (SCF) method was applied for determining the molecular equilibrium structure and the harmonic force constant matrix element of the ground and four ionic states. Using the harmonic oscillator approximation, we obtained vibrational frequencies of the totally symmetric modes (ν_1–ν_4). We also calculated Franck–Condon factors (FCFs) and the theoretical intensity curve of ionization. Based on these results, we reexamine the assignment of the PE spectrum of CH_2Cl_2.

2. Methods of calculation

We used the basis sets of the MIDI-4 type prepared by Tatewaki and Huzinaga [11,12]. These are augmented by one p-type polarization function for H and one d-type polarization function for C and Cl. The exponents of the polarization function for H, C and Cl are 0.68, 0.61 and 0.56, respectively. The gradient technique for Roothaan's restricted Hartree–Fock (RHF) method was employed to determine the optimum molecular structures of the ground and four ionic states with restriction of C_{2v} symmetry.

The single and double excitation configuration interaction (SD CI) method was employed to obtain more accurate ionization energies at the equilibrium structure. By using a single reference configuration of an SCF wavefunction of the respective state (see table 1), singly and doubly excited configuration state functions (CSFs) were generated with the inner shells (K shell of C, K and L shells of Cl) kept frozen. The generated CSFs were then restricted to the first-order interacting space [13]. The number of the generated CSFs of each state is also given in table 1.

The totally symmetric harmonic force constant matrix elements were calculated by means of the gradient technique within the framework of the RHF method. The second derivative was estimated by numerical differentiation of the first derivative. We calculated the FCFs only for the totally symmetric modes. The method of calculation of the FCF and theoretical intensity curve was the same as the one used in our previous study [14].

Table 1
Electronic configuration

State	Reference function [a]	#CSF
$^1A_1$	$...(2a_2)^2(9a_1)^2(7b_2)^2(3b_1)^2$	19604
$^2B_2$	$...(2a_2)^2(9a_1)^2(7b_2)^1(3b_1)^2$	20268
$^2B_1$	$...(2a_2)^2(9a_1)^2(7b_2)^2(3b_1)^1$	20197
$^2A_1$	$...(2a_2)^2(9a_1)^1(7b_2)^2(3b_1)^2$	20287
$^2A_2$	$...(2a_2)^1(9a_1)^2(7b_2)^2(3b_1)^2$	20178

[a] The b_1 and b_2 orbitals have a nodal surface in the Cl–C–Cl and H–C–H planes, respectively.

This work has been carried out by the use of the computer program system GRAMOL [15] for the gradient technique and the calculations of normal modes [#1]. The program MICA3 [17] was used for the CI calculations.

3. Results and discussion

The optimized molecular structure of the ground and four ionic states are listed in table 2. The differences of geometric parameters between the ionic states and the ground states are also presented in table 2. An appreciable change occurs in the $^2B_2$ and $^2B_1$ states. In the $^2B_2$ state, the change in Cl–C–Cl angle is the largest among the four ionic states. We notice that, as for the C–H and C–Cl bond distances and H–C–H angle, the change in the $^2B_1$ state is the largest among the four ionized states.

The vertical IEs (VIE) and adiabatic IEs (AIE) obtained by the SD CI method are listed in table 3. The energy lowering of AIE from the VIE is 0.51, 0.14, 0.14 and 0.07 eV for the $^2B_2$, $^2B_1$, $^2B_1$, $^2A_1$ and $^2A_2$ states, respectively. As is expected from the large distortion of the $^2B_2$ state, the energy lowering is the largest among the four ionic states.

Table 4 contains the calculated vibrational frequencies of the total symmetric mode of the ground and ionic states by the SCF method. A classical half-amplitude of the zero-point vibration was calculated

[#1] GRAMOL included the program JAMOL3 of the RHF calculation written by Kashiwagi et al. [16].

Table 2
Optimized geometries by the SCF calculation and the geometric change in the ionized state relative to the ground state

State	C–H (ΔC–H) (Å)	C–Cl (ΔC–Cl) (Å)	H–C–H (ΔH–C–H) (deg)	Cl–C–Cl (ΔCl–C–Cl) (deg)
$^1A_1$	1.082	1.775	111.74	112.55
$^2B_2$	1.083 (+0.001)	1.780 (+0.005)	117.25 (+5.51)	90.84 (−21.71)
$^2B_1$	1.113 (+0.031)	1.707 (−0.068)	102.24 (−9.50)	118.58 (+6.03)
$^2A_1$	1.092 (+0.010)	1.765 (−0.010)	119.01 (+7.27)	121.10 (+8.55)
$^2A_2$	1.083 (+0.001)	1.794 (+0.019)	114.05 (+2.31)	103.79 (−8.76)

Table 3
Ionization energies (eV). The total energies of the $^1A_1$ state by the SCF and SD CI methods are −956.968094 and −957.364785 au, respectively.

State	VIE [a]	AIE [b]	0–0 IE [c]
$^2B_2$	11.30	10.79	10.80
$^2B_1$	11.34	11.20	11.16
$^2A_1$	11.95	11.81	11.78
$^2A_2$	11.98	11.91	11.90

[a] Vertical ionization energy.
[b] Adiabatic ionization energy.
[c] 0–0 ionization energy.

Table 4
Vibrational energies (cm^{-1})

Mode	State				
	$^1A_1$	$^2B_2$	$^2B_1$	$^2A_1$	$^2A_2$
ν_1	3305	3312	2963	3171	3301
ν_2	1572	1547	1186	1458	1566
ν_3	755	807	721	640	744
ν_4	304	330	337	310	303

in order to characterize each normal mode. The results are shown in table 5. The table indicates that a half-amplitude of the C–H stretching is the largest for the ν_1 mode for each electronic state. The ν_1 mode may be characterized as the C–H stretching. The ν_2 mode is clearly the H–C–H bending mode, and the ν_4 mode is the Cl–C–Cl bending mode. The ν_3 mode is the C–Cl stretching mode accompanied with a Cl–C–Cl bending motion except for the $^2B_1$ state. The ν_3 mode of the $^2B_1$ state is a mixture of the C–Cl stretching, Cl–C–Cl bending and H–C–H bending motions.

Using the adiabatic IEs from the SD CI calculation and the zero-point vibrational energies, we estimated the zero–zero (0–0) IEs. The result is presented in table 3. The FCFs of 0–0 transition for the $^2B_2$, $^2B_1$, $^2A_1$ and $^2A_2$ states are 0.000, 0.200, 0.096 and 0.108, respectively. As is expected from the large distortion of the $^2B_2$ state, the FCF for the 0–0 transition for $^2B_2$ is negligibly small in comparison with the other 0–0 transitions. Observation of the 0–0 transition for $^2B_2$ may be impossible. The geometric changes in the C–H and C–Cl bond distances and H–C–H angle of the $^2B_1$ state are the largest among the four ionized states; nevertheless the FCF for the 0–0 transition is the largest of all states. This situation is ascribed to the large classical half-amplitude of the zero-point vibration of the C–H and C–Cl bond distances and H–C–H angle of $^2B_1$ which is compared with the amplitude of the geometric changes in the C–H and C–Cl bond distances and H–C–H angle (see tables 5 and 2).

Fig. 2 shows the theoretical intensity curve of the ionization with a half-width of 645 cm^{-1}. A total intensity curve was obtained by using the assumption that the transition probability of the electronic part is the same for each ionic state. The theoretical intensity curve agrees well with the observed PE spectrum in fig. 1. The 0–0 ionization energy of $^2B_2$ is lower than that of $^2B_1$. However, fig. 2 reveals that the maximum intensity of the first band of the PE spectrum is due to the ionization to the $^2B_1$ state. The $^2B_2$ state contributes to the tail of the first band. The $^2A_1$ and $^2A_2$ states contribute to the head and tail of the second band of the PE spectrum, respectively.

Vibrational structure is observed in the first band of the PE spectrum. Potts et al. [3] have associated this structure with the $^2B_2$ state. The present calculation shows that the vibrational structure is attributed to the $^2B_1$ state. The vibrational levels of the $^2B_1$ state are presented in table 6. The calculated 0–0 IE is 11.16 eV. The FCF of the 0–0 transition is large enough to

Table 5
Classical half-amplitude of the zero-point vibrational state

State	Bond distance /angle [a]	Vibrational mode			
		ν_1	ν_2	ν_3	ν_4
$^1A_1$	C–H	0.073	−0.003	0.001	−0.001
	C–Cl	−0.004	0.006	0.040	0.010
	H–C–H	−0.4	11.5	0.9	−0.0
	Cl–C–Cl	0.4	−0.6	−2.8	3.4
$^2B_2$	C–H	0.073	−0.001	0.002	−0.000
	C–Cl	−0.004	0.007	0.046	0.003
	H–C–H	−0.5	11.6	1.1	−0.3
	Cl–C–Cl	0.3	−0.5	−2.3	3.1
$^2B_1$	C–H	0.077	−0.009	−0.005	−0.001
	C–Cl	−0.003	−0.002	0.040	0.008
	H–C–H	0.0	12.3	4.8	−0.2
	Cl–C–Cl	0.4	−0.1	−3.1	3.5
$^2A_1$	C–H	0.074	−0.000	−0.001	0.000
	C–Cl	−0.003	0.006	0.041	0.007
	H–C–H	−0.5	11.9	0.6	0.1
	Cl–C–Cl	0.3	−0.7	−2.9	3.8
$^2A_2$	C–H	0.073	−0.002	0.001	−0.000
	C–Cl	−0.004	0.006	0.044	0.007
	H–C–H	−0.4	11.5	1.3	−0.1
	Cl–C–Cl	0.3	−0.5	−2.6	3.3

[a] Distances in Å; angles in degree.

be observed. Thus, the observed first peak at 11.32 eV should correspond to the 0–0 transition of the $^2B_1$ state. The second peak at 11.40 eV with maximum intensity is due to the (0010) state. The third peak at 11.48 eV is attributed to the (0020) state. The FCF of (0030) transition is large so that this transition is observed as the fourth peak. The result indicates that excitations to the vibrational levels of the ν_3 mode contribute to the intensity curve. Although the 0–0 ionization energy of the $^2B_2$ state is lower than that of the $^2B_1$ state, the maximum of the $^2B_2$ state is beyond that of the $^2B_1$ state. This situation is due to the large geometric change in the Cl–C–Cl angle of the $^2B_2$ state and the contribution of the higher vibrational excitation of the ν_4 mode (Cl–C–Cl bending) to intensity curve (see table 7).

No vibrational structure is found in the theoretical intensity curve and the PE spectrum of $^2A_1$ and $^2A_2$. However, the present calculation shows that higher vibrational excitations to the ν_4 (Cl–C–Cl bending) mode contribute to intensity. The band of the $^2A_1$ state is mainly due to the vibrational levels of (0000), (0001), (0002) and (0003). The band of the $^2A_2$ state is ascribed to the (0000), (0001), (0002) and (0003) transitions. Higher vibrational excitations to the ν_4 mode are connected to the geometrical change in Cl–C–Cl angle which is larger than the amplitude of the zero-point vibration of the ν_4 mode.

4. Conclusion

The molecular equilibrium structure and the vibrational frequency are calculated for the ground and lower four ionic states. By the use of the FCFs we obtain the transition intensity curve. The main results are as follows.

The 0–0 IE of the $^2B_2$ state is lower than that of the $^2B_1$ state by 0.41 eV; nevertheless the maximum intensity of the $^2B_2$ state is found beyond that of the $^2B_1$

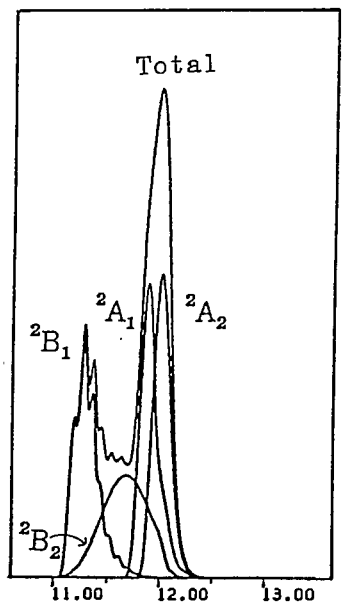

Fig. 2. Theoretical intensity curve with a half-width of 645 m^{-1}.

Table 6
Vibrational levels of the $^2B_1$ state

Quantum number ($v_1v_2v_3v_4$)	IE (eV)	FCF [a]	Obs. IE ref. [3]
(0000)	11.16	0.200	11.32
(0010)	11.25	0.309	11.40
(0020)	11.34	0.233	11.48
(0030)	11.43	0.114	
(0040)	11.52	0.041	
(0050)	11.61	0.011	

[a] Franck–Condon factor.

state. This situation is ascribed to the large geometrical change of Cl–C–Cl angle of the $^2B_2$ state.

The vibrational structure of the first band of the PE spectrum is due to the vibrational excitations of the ν_3 mode of the $^2B_1$ state. The character of the ν_3 mode of $^2B_1$ is a mixture of the C–Cl stretching, Cl–C–Cl bending and H–C–H bending motions. The four vibrational peaks of the PE spectrum are assigned as the vibrational levels of (0000), (0010), (0020) and (0030).

Table 7
Vibrational levels of the $^2B_2$ state

Quantum number ($v_1v_2v_3v_4$)	IE (eV)	FCF
(000 10)	11.21	0.006
(000 11)	11.25	0.009
(000 12)	11.29	0.014
(000 13)	11.33	0.020
(000 14)	11.37	0.026
(000 15)	11.41	0.034
(000 16)	11.45	0.041
(000 17)	11.49	0.047
(000 18)	11.54	0.053
(000 19)	11.58	0.056
(000 20)	11.62	0.058
(000 21)	11.66	0.058
(000 22)	11.70	0.056
(000 23)	11.74	0.053
(000 24)	11.78	0.048
(000 25)	11.82	0.043
(000 26)	11.86	0.037
(000 27)	11.90	0.031
(000 28)	11.95	0.026
(000 29)	11.99	0.021
(000 30)	12.03	0.017

Acknowledgement

The author is grateful to Professor Kimio Ohno for reading the manuscript. He also wishes to thank Dr. Kiyoshi Tanaka for helpful discussions. Computations were carried out on HITAC M-680H systems at the Institute for Molecular Science and the Hokkaido University Computing Center.

References

[1] R.N. Dixon, J.N. Murrell and B. Narayan, Mol. Phys. 20 (1971) 611.
[2] D.W. Turner, A.D. Baker, C. Baker and C.R. Brundle, Molecular Photoelectron Spectroscopy (Wiley, New York, 1970).
[3] A.W. Potts, H.J. Lempka, D.G. Streets and W.C. Price, Phil. Trans. Roy. Soc. London A 268 (1970) 59.
[4] F. Hopfgarten and R. Manne, J. Electron Spectry. 2 (1973) 13.
[5] K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki and S. Iwata, Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules (Halstead Press, New York, 1981).

[6] S. Katsumata and K. Kimura, Bull. Chem. Soc. Japan 46 (1973) 1342.
[7] J.C. Bunzli, D.C. Frost, F.G. Herring and C.A. McDowell, J. Electron Spectry. 9 (1976) 289.
[8] U.C. Singh, P.K. Basu and C.N.R. Rao, J. Mol. Struct. THEOCHEM 87 (1982) 19.
[9] D. Li, J.-K. Zhu, J.-G. Li and Y.-K. Pani, Chem. Phys. Letters 87 (1982) 463.
[10] D. Li, J.-K. Zhu, J.-G. Li and Y.-K. Pani, J. Electron Spectry. 34 (1984) 1.
[11] H. Tatewaki and S. Huzinaga, J. Comput. Chem. 1 (1980) 205.
[12] Y. Sakai, H. Tatewaki and S. Huzinaga, J. Comput. Chem. 2 (1981) 100.
[13] A.D. Mclean and B. Liu, J. Chem. Phys. 58 (1973) 1066.
[14] K. Takeshita, J. Chem. Phys. 86 (1987) 329.
[15] K. Takeshita and F. Sasaki, Library Program at the Hokkaido University Computing Center (1981), in Japanese.
[16] H. Kashiwagi, T. Takada, E. Miyoshi and S. Obara, Library Program at the Hokkaido University Computing Center (1977), in Japanese.
[17] A. Murakami, H. Iwaki, H. Terashima, T. Shoda, T. Kawaguchi and T. Noro, Library program at the Hokkaido University Computing Center (1986), in Japanese.