JOURNAL OF MOLECULAR SPECTROSCOPY **142**, 1–9 (1990)

A Theoretical Study on the Ionic States and the Photoelectron Spectra of Dichlorodifluoromethane (CF_2Cl_2)

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Ab initio calculations are performed to study the molecular equilibrium structure and the harmonic vibrational frequency of the low-lying four ionic states $^2B_2$, $^2A_2$, $^2B_1$, and $^2A_1$ of dichlorodifluoromethane (CF_2Cl_2). The theoretical intensity curve obtained from the Franck–Condon factors is in good agreement with the photoelectron, (PE) spectrum. The results show that the four maxima of the PE spectrum from the lower energy side correspond to the $^2B_2$, $^2A_2$, $^2B_1$, and $^2A_1$ states. Three vibrational progressions are found in the theoretical intensity curve of $^2B_2$. Higher vibrational excitations to the ν_4 (Cl–C–Cl bending) mode contribute to all progressions and vibrational excitations of the ν_1 and ν_3 modes also contribute to intensity.

1. INTRODUCTION

The photoelectron (PE) spectra of CF_2Cl_2 have been reported before (*1, 2*). In Fig. 1, the PE spectrum observed by Cvitaš *et al.* (*2*) is presented. The four low-lying maxima at 12.26, 12.53, 13.11, and 13.45 eV have been assigned as the $^2B_2$, $^2B_1$, $^2A_2$, and $^2A_1$ states, respectively. They are supposed to originate from ionization of a lone pair electron of Cl. A high resolution PE spectrum of the first ionic state has been reported by Cvitaš *et al.* They have observed a progression of 280 cm^{-1} and assigned it as the CCl_2 scissoring vibration. This progression has extended to a continuum at a higher energy region which has been interpreted as the process

$$CF_2Cl_2 \xrightarrow{h\nu} CF_2Cl^+ + Cl + e^-.$$

Lewerenz *et al.* (*3*) have carried out MRD-CI calculations on CF_2Cl_2 and discussed the photodecomposition and the dissociative electron attachment of CF_2Cl_2. They have reported the vertical ionization energies and showed the ordering of states as $^2B_2$, $^2A_2$, $^2B_1$, and $^2A_1$ from the lower energy side. Their ordering of the second and third states differs from that of Cvitaš *et al.*

In their theoretical study on CF_2Cl_2, the PE spectrum has been assigned by considering only the vertical ionization energies (IEs). As the PE spectrum reflects changes in molecular equilibrium structure and the distribution of vibrational levels, it is desirable to investigate the potential energy surfaces near the equilibrium and the vibrational levels and to calculate the theoretical intensity curve of the transitions among vibrational levels.

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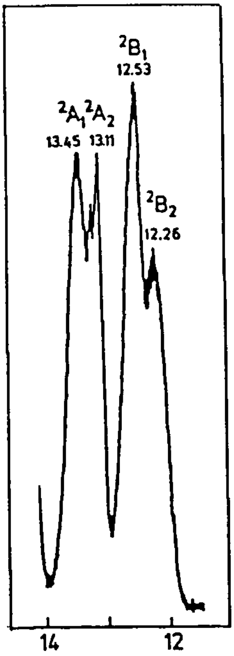

FIG. 1. PE spectrum of CF_2Cl_2 of the low-lying ionic states adopted from Cvitaš *et al.* (*2*).

The purpose of the present work is to study the nature of the four low-lying ionic states, $^2B_2$, $^2A_2$, $^2B_1$, and $^2A_1$ of CF_2Cl_2 theoretically. An ab initio self-consistent-field (SCF) method was employed to determine 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 ($\nu_1 \sim \nu_4$). We also calculated Franck–Condon Factors (FCFs) and the theoretical intensity curve of ionization. To obtain accurate ionization energies, we applied the single and double excitation configuration interaction (SD-CI) method to the molecular structure optimized by the SCF method. Based on the results of these calculations, we discuss the assignment of the PE spectrum of CF_2Cl_2.

TABLE I

Electronic Configurations

State	Reference function	#CSF	#sel.CSF
$^1A_1$	$\ldots(12a_1)^2(6b_1)^2(3a_2)^2(8b_2)^2$	77927	10963
$^2B_2$	$\ldots(12a_1)^2(6b_1)^2(3a_2)^2(8b_2)^1$	80493	11192
$^2A_2$	$\ldots(12a_1)^2(6b_1)^2(3a_2)^1(8b_2)^2$	80403	11140
$^2B_1$	$\ldots(12a_1)^2(6b_1)^1(3a_2)^2(8b_2)^2$	80493	11023
$^2A_1$	$\ldots(12a_1)^1(6b_1)^2(3a_2)^2(8b_2)^2$	80583	10939

Note. #sel.CSF: number of the selected CSF with threshold of 10 μH at the ground state's structure. The b_1 and b_2 orbitals have nodal surfaces in the Cl–C–Cl and F–C–F planes, respectively.

TABLE II

Change in the Geometry of the Ionic States Compared to the Ground State

State	C-F (ΔC-F) (Å)	C-Cl (ΔC-Cl) (Å)	F-C-F (ΔF-C-F)	Cl-C-Cl(ΔCl-C-Cl)
$^1A_1$	1.309	1.759	107.96°	111.69°
$^2B_2$	1.266(-0.043)	1.785(+0.026)	113.17°(+5.21°)	91.32°(-20.37°)
$^2A_2$	1.275(-0.034)	1.789(+0.030)	112.54°(+4.58°)	104.54°(- 7.15°)
$^2B_1$	1.277(-0.032)	1.807(+0.048)	113.32°(+5.36°)	111.37°(- 0.32°)
$^2A_1$	1.281(-0.028)	1.819(+0.060)	112.17°(+4.21°)	113.68°(+ 1.99°)

Note. Optimized geometries were obtained by the SCF calculation with the MIDI-4 basis sets augmented by one *d*-type polarization function.

2. METHOD OF CALCULATIONS

We used the basis sets of the MIDI-4 given by Tatewaki and Huzinage (*4, 5*) for C, F, and Cl, augmented by one *d*-type polarization function. The exponents of the polarization function for C, F, and Cl, are 0.61, 1.50, and 0.56, respectively. The gradient technique for Roothaan's restricted Hartree–Fock (RHF) method was employed in determining the optimum molecular structure of the ground and four ionic states with restriction of C_{2v} symmetry.

A configuration interaction (CI) method was used to obtain accurate ionization energies. In the CI, we used a SCF wavefunction as a reference function in each state (see Table I) and singly and doubly excited configuration state functions (CSFs) were generated where the inner shells (*K* shells of C and F, and *K* and *L* shells of Cl) were kept frozen. The generated CSFs were restricted to the first order interacting space (*6*). The number of the generating CSFs of each state is also shown in Table I. As the dimension of SD–CI is very large, we employed a CSF selection process by use of the second order Brillouin–Wigner perturbation theory. The threshold for the selection was taken as 10 micro-Hartree. Dimensions of the Hamiltonian matrix over selected CSFs are given in Table I. We estimated the total energy by including contribution from the rejected CSFs, where the contribution is calculated by the 2nd order perturbation theory.

The totally symmetric harmonic force constant matrix elements were calculated by use of the second derivative matrix of the potential surface, which was estimated by

TABLE III

Ionization Energies (eV) by the SD-CI Method

State	V.IE	A.IE	0-0 IE
$^2B_2$	12.06	11.66	11.67
$^2A_2$	12.55	12.47	12.47
$^2B_1$	13.08	13.00	13.00
$^2A_1$	13.44	13.31	13.31

Note. The total energies of $^1A_1$ by the SCF and SD-CI methods are −1154.471619 and −1155.156970 a.u., respectively. V.IE: vertical ionization energy; A.IE: adiabatic ionization energy; 0–0 IE: 0–0 ionization energy.

TABLE IV

Vibrational Energies (cm^{-1})

Mode	State				
	$^1A_1$	$^2B_2$	$^2A_2$	$^2B_1$	$^2A_1$
ν_1	1266	1322	1301	1271	1253
ν_2	730	753	731	712	702
ν_3	497	498	477	454	453
ν_4	285	303	268	276	282

Note. The harmonic force constant matrix elements were calculated from the SCF wave functions. The vibrational wave functions were obtained by the harmonic oscillator approximation.

the numerical differentiation of the first derivative. We calculated the FCFs only of totally symmetric vibrational modes. In calculating FCFs, we approximated the vibrational wave functions by those obtained by the harmonic oscillator model. We assumed that the initial state of the transition was restricted to the zero point vibrational state of the ground state. The method of calculation of the FCF and theoretical intensity curve was the same as that used in the previous study (*7*).

This work has been carried out by using the computer program system GRAMOL[2] for the gradient technique and the calculation of normal modes. The program MICA3[3] was used for the CI calculations.

3. RESULTS AND DISCUSSIONS

The optimized molecular geometries of the ground and four ionic states by SCF calculations are listed in Table II. The magnitudes of the geometric change by ionization are also presented in Table II. An appreciable geometric change occurs in the $^2B_2$ state by ionization. The change of the angle Cl–C–Cl is the largest in the $^2B_2$ state among the four ionic states. We also note that the C–F bond length becomes shorter and the F–C–F bond angle becomes larger in each ionic state.

The vertical IEs and adiabatic IEs by the SD-CI method are listed in Table III. The energy lowerings of the $^2B_2$, $^2A_2$, $^2B_1$, and $^2A_1$ states from the vertical IEs are 0.40, 0.08, 0.08, and 0.13 eV, respectively. Reflecting the large geometry distortion of the $^2B_2$ state, its energy lowering is the largest among the four states.

Table IV contains the calculated vibrational frequencies of the total symmetric modes of the ground and ionic states by use of the RHF method. A classical half amplitude of the zero-point vibration was calculated in order to characterize each normal mode. The results are shown in Table V. It is found that a ν_4 mode has a large half amplitude in the Cl–C–Cl bending. Thus, the ν_4 mode should be characterized as a Cl–C–Cl bending mode. The ν_1, ν_2, and ν_3 modes, however, cannot be characterized

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[2] K. Takeshita and F. Sasaki, 1981, library program at the Hokkaido University Computing Center (in Japanese). GRAMOL included the Program JAMOL3 of the RHF calculation written by H. Kashiwagi, T. Takada, E. Miyoshi, and S. Obara, 1977, for the library program at the Hokkaido University Computing Center (in Japanese).

[3] A. Murakami, H. Iwaki, H. Terashima, T. Shoda, T. Kawaguchi and T. Noro, 1986, library program at the Hokkaido University Computing Center 1986 (in Japanese).

TABLE V

Classical Half Amplitude of the Zero Point Vibrational State

		Vibrational mode			
		ν_1	ν_2	ν_3	ν_4
$^1A_1$	C-F(Å)	-0.038	0.010	0.002	-0.000
	C-Cl(Å)	0.023	0.023	-0.025	0.004
	F-C-F	3.0°	3.1°	2.3°	0.8°
	Cl-C-Cl	-2.1°	-1.5°	0.1°	3.1°
$^2B_2$	C-F(Å)	-0.036	0.008	0.002	0.001
	C-Cl(Å)	0.026	0.029	-0.025	-0.003
	F-C-F	3.0°	3.4°	2.3°	0.6°
	Cl-C-Cl	-1.7°	-1.4°	-0.1°	3.0°
$^2A_2$	C-F(Å)	-0.036	0.008	0.002	0.001
	C-Cl(Å)	0.023	0.026	-0.028	-0.000
	F-C-F	3.0°	3.6°	2.1°	0.6°
	Cl-C-Cl	-1.8°	-1.6°	0.1°	3.2°
$^2B_1$	C-F(Å)	-0.037	0.007	0.003	0.001
	C-Cl(Å)	0.021	0.025	-0.030	0.001
	F-C-F	3.0°	3.8°	1.9°	0.7°
	Cl-C-Cl	-1.9°	-1.7°	0.2°	3.2°
$^2A_1$	C-F(Å)	-0.037	0.006	0.003	0.000
	C-Cl(Å)	0.019	0.023	-0.032	0.002
	F-C-F	2.9°	3.9°	1.5°	0.8°
	Cl-C-Cl	-1.9°	-1.8°	0.4°	3.1°

Note. The harmonic oscillator approximation was used.

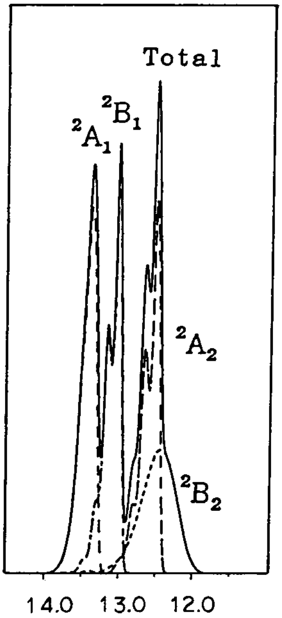

FIG. 2. Theoretical intensity curve of CF_2Cl_2 with a half width of 121 cm^{-1}.

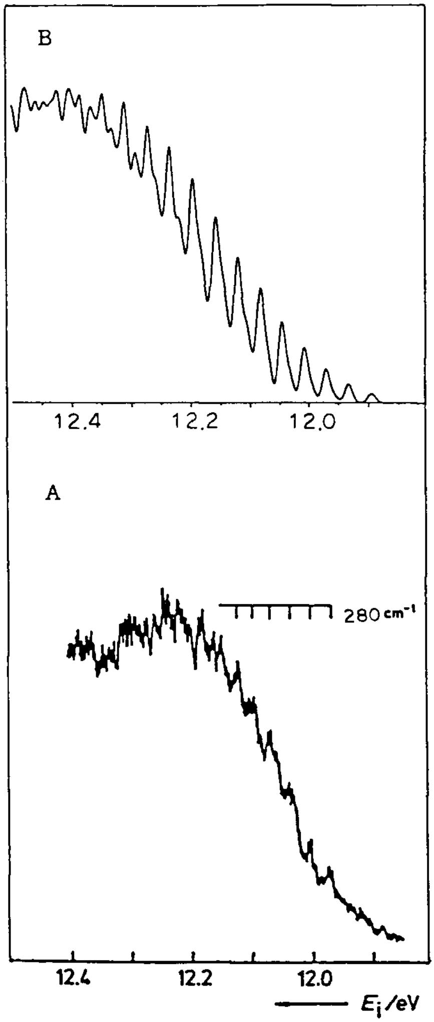

FIG. 3. Theoretical intensity curve and PE spectrum of the $^2B_2$ state. A: PE spectrum; B: theoretical intensity curve.

as simply as the ν_4 mode. We note that a strong coupling is found among the C–F stretching, C–Cl stretching, F–C–F bending, and Cl–C–Cl bending for those modes.

Using the adiabatic IEs by the SD–CI calculation and the zero point vibrational energies, we estimated the zero-zero ionization energies (0–0 IEs). They are compared with adiabatic IEs in Table III. The FCFs concerning the 0–0 transition of $^2B_2$, $^2A_2$, $^2B_1$, and $^2A_1$ are 0.000, 0.198, 0.309, and 0.120, respectively. As can be expected from the large geometric change of the $^2B_2$ state, the FCF of the 0–0 transition is negligibly small, so that observation of the 0–0 transition would be impossible.

Figure 2 shows the theoretical intensity curve of the ionization of the four low-lying ionic sates with a half width of 645 cm^{-1}. A total intensity curve was obtained by

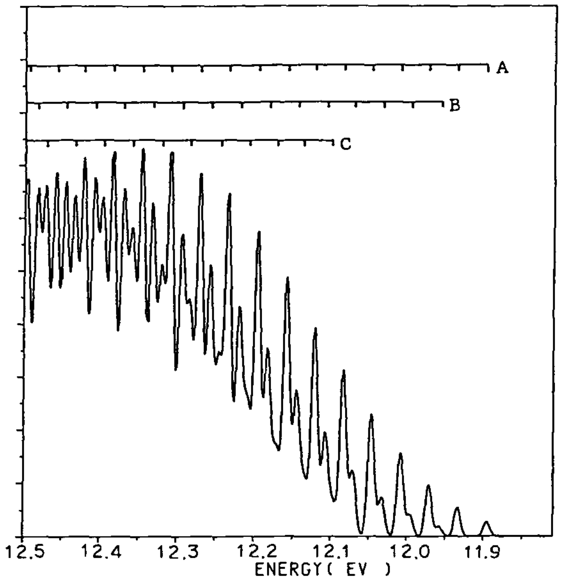

FIG. 4. Theoretical intensity curve of the $^2B_2$ state with a half width of 81 cm^{-1}.

assuming that the transition probability of the electronic part is the same for each ionic state. The feature of the theoretical intensity curve is in good agreement with the observed PE spectrum (Fig. 1) given by Cvitaš *et al.* Figure 2 indicates that the ordering of IEs is $^2B_2$, $^2A_2$, $^2B_1$, and $^2A_1$. The present assignment of the second and third peaks supports the work by Lewerenz *et al.* (*3*).

A high-resolution PE spectrum of the first ionic state has been reported by Cvitaš *et al.* Figure 3A is the observed PE spectrum ranging from 11.8 eV to 12.4 eV. The theoretical intensity curve of the ionization to the lowest $^2B_2$ state below 12.50 eV is shown in Fig. 3B, where we assumed a half width of 121 cm^{-1} for each transition. The theoretical pattern is very similar to the observed PE spectrum . In order to see a more detailed vibrational structure, we show the theoretical intensity curve with a half width of 81 cm^{-1} in Fig. 4. This figure shows that the spectrum is composed of three progressions. The first one (progression A) has strong intensity and begins at 11.89 eV. The second one (progression B) has medium intensity and starts at 11.96 eV. The third one (progression C) has weak intensity and starts near 12.25 eV. The intensity of the last two progressions becomes stronger near 12.4 eV so that the theoretical band has a complicated vibrational structure. The calculated vibrational levels and FCFs of these progressions are given in Table VI. This table indicates that the vibrational excitations to the ν_4 (Cl–C–Cl bending) mode contribute to all progressions. The calculated frequency of the ν_4 mode is 303 cm^{-1}, which should be compared with the observed value of 280 cm^{-1}. This result is consistent with the assignment of the vibrational mode by Cvitaš *et al.* The excitation to the higher vibrational states of the ν_4 mode is ascribed to the large geometric change of the Cl–C–Cl angle by ionization. The present calculation shows that vibrational excitations of the ν_1 and ν_3 modes also contribute.

TABLE VI

Vibrational Levels of the $^2B_2$ State

Quantum number (v_1 v_2 v_3 v_4)	IE (eV)	FCF	Quantum number (v_1 v_2 v_3 v_4)	IE (eV)	FCF
		Progression A			
(0 0 0 6)	11.89	0.001			
(0 0 0 7)	11.93	0.001			
(0 0 0 8)	11.97	0.003			
(0 0 0 9)	12.01	0.004			
(0 0 0 10)	12.05	0.006			
(0 0 0 11)	12.08	0.008			
(0 0 0 12)	12.12	0.010			
(0 0 0 13)	12.16	0.012	(1 0 1 7)	12.16	0.001
(0 0 0 14)	12.20	0.014	(1 0 1 8)	12.20	0.001
(0 0 0 15)	12.23	0.014	(1 0 1 9)	12.23	0.002
(0 0 0 16)	12.27	0.014	(1 0 1 10)	12.27	0.003
(0 0 0 17)	12.31	0.013	(1 0 1 11)	12.31	0.005
(0 0 0 18)	12.35	0.012	(1 0 1 12)	12.35	0.006
(0 0 0 19)	12.38	0.010	(1 0 1 13)	12.38	0.008
(0 0 0 20)	12.42	0.009	(1 0 1 14)	12.42	0.009
(0 0 0 21)	12.46	0.007	(1 0 1 15)	12.46	0.010
(0 0 0 22)	12.50	0.005	(1 0 1 16)	12.50	0.010
		Progression B			
(0 0 1 6)	11.96	0.001			
(0 0 1 7)	11.99	0.001			
(0 0 1 8)	12.03	0.002			
(0 0 1 9)	12.07	0.003			
(0 0 1 10)	12.11	0.005			
(0 0 1 11)	12.14	0.007			
(0 0 1 12)	12.18	0.009			
(0 0 1 13)	12.22	0.011			
(0 0 1 14)	12.26	0.012	(1 0 2 8)	12.26	0.001
(0 0 1 15)	12.30	0.013	(1 0 2 9)	12.30	0.001
(0 0 1 16)	12.33	0.013	(1 0 2 10)	12.33	0.001
(0 0 1 17)	12.37	0.013	(1 0 2 11)	12.37	0.002
(0 0 1 18)	12.41	0.012	(1 0 2 12)	12.41	0.003
(0 0 1 19)	12.45	0.011	(1 0 2 13)	12.45	0.004
(0 0 1 20)	12.48	0.009	(1 0 2 14)	12.48	0.004
		Progression C			
(1 0 0 7)	12.10	0.001	(0 0 2 8)	12.09	0.001
(1 0 0 8)	12.13	0.001	(0 0 2 9)	12.13	0.001
(1 0 0 9)	12.17	0.002	(0 0 2 10)	12.17	0.002
(1 0 0 10)	12.21	0.004	(0 0 2 11)	12.21	0.003
(1 0 0 11)	12.25	0.005	(0 0 2 12)	12.24	0.004
(1 0 0 12)	12.28	0.006	(0 0 2 13)	12.28	0.005
(1 0 0 13)	12.32	0.008	(0 0 2 14)	12.32	0.005
(1 0 0 14)	12.36	0.009	(0 0 2 15)	12.36	0.006
(1 0 0 15)	12.40	0.009	(0 0 2 16)	12.39	0.006
(1 0 0 16)	12.43	0.009	(0 0 2 17)	12.43	0.006
(1 0 0 17)	12.47	0.009	(0 0 2 18)	12.47	0.006

Note. FCF: Franck–Condon factor.

A vibrational structure is found in the theoretical intensity curve of the $^2B_1$ and $^2A_2$ states. According to the present calculations, the first maximum of the $^2B_1$ band is due to the vibrational transitions of the (0 0 0 0) and (0 0 0 1) states and the second peak near 13.14 eV to those of (0 1 0 0) and (1 0 0 0) states. The vibrational transitions of (0 0 0 0) and (0 0 0 1) states contribute the first maximum of the $^2A_2$ band and those of (1 0 0 0) and (1 0 0 1) states contribute the second peak.

4. CONCLUSION

The optimized molecular geometry and the calculated vibrational frequency of the ground and four ionic states are calculated. The resulting theoretical intensity curve of ionization is similar to the observed PE spectrum . The present result shows that the four maxima of the PE spectrum from the lower energy side correspond to the $^2B_2$, $^2A_2$, $^2B_1$, and $^2A_1$ states. The present assignment of the second and third peaks differs from that by Cvitaš *et al.* (*2*).

The theoretical intensity curve of the first ionic state of $^2B_2$ is in good agreement with the observed PE spectrum . This calculation shows that the 0–0 ionization energy of the $^2B_2$ state is 11.66 eV. The FCF for the 0–0 transition is negligibly small, so that observation of the 0–0 transition would be impossible. Three vibrational progressions are found in the theoretical intensity curve. Higher vibrational excitations to the ν_4 (Cl–C–Cl bending) mode contribute to all progressions. This was pointed out by Cvitaš *et al.* (*2*). However, the present calculations show that vibrational excitations of the ν_1 and ν_3 modes also contribute to intensity.

ACKNOWLEDGMENTS

The author is grateful to Professor Kimio Ohno for reading the manuscript. He also thanks Dr. Kiyoshi Tanaka for his helpful discussions. The computations were performed on the HITAC-M280H computer at the Center for Information Processing Education of Hokkaido University.

RECEIVED: January 3, 1990

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