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

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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 $^2A_2$.

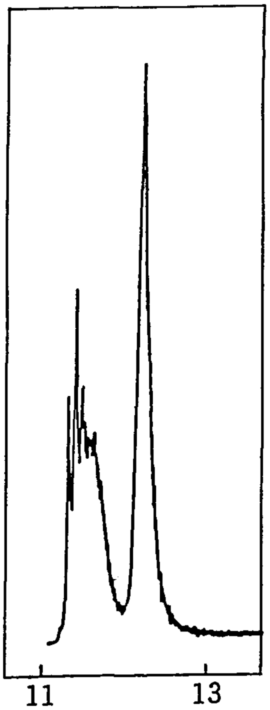

Fig. 1. Photoelectron spectrum by Kimura et al. [5].

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-

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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

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[#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 $^2B_1$

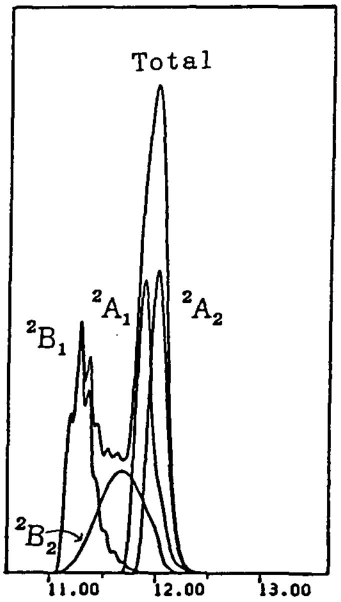

Fig. 2. Theoretical intensity curve with a half-width of 645 m^{-1}.

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

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