

# High resolution photoelectron spectroscopy of $\text{CH}_2\text{F}_2$ , $\text{CH}_2\text{Cl}_2$ and $\text{CF}_2\text{Cl}_2$ using supersonic molecular beams<sup>1</sup>

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## Abstract

Molecular beam photoelectron spectroscopy using He I radiation (584 Å) has been used to study the electronic structures of  $\text{CH}_2\text{F}_2$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CF}_2\text{Cl}_2$ . The spectra obtained at a resolution of 13 meV show a number of new features, in addition to those reported earlier in the literature. Accurate values of the ionization potentials were obtained, and many new vibrational progressions were resolved and assigned. The first four ionic states are discussed in more detail on the basis of reported configuration interaction calculations and photoionization measurements. Ambiguities regarding the ordering of these states have been resolved. Although the agreement between theory and experiment is good in  $\text{CF}_2\text{Cl}_2$ , there are significant differences in  $\text{CH}_2\text{F}_2$  and  $\text{CH}_2\text{Cl}_2$ .

## Introduction

Since the discovery of the ozone depleting nature of chlorofluorocarbons [1] in the stratosphere, the photochemistry and photophysics of these systems have received renewed attention. There is a wealth of data on the photoabsorption and photofragmentation of these molecules (see, for example, Ref. 2) from the ultraviolet to soft X-ray regions. Studies using (e,e), (e,e+ion) and (e,2e) spectroscopies [3,4] have been reported. The basic electronic structure of chlorofluorocarbons is quite well understood. Systematics in the electronic structure of simple hydrocarbons on fluorination

and chlorination are also well known. Photoelectron (PE) spectroscopy using He I, He II and synchrotron radiations [5–15] have been used to unravel the experimental electronic structure. There are a number of electronic structure calculations [16–26] available, based on a variety of approximations. However, some details of the electronic structure in the valence region are still not clear. This study addresses those issues.

The present investigation is limited to three molecules;  $\text{CH}_2\text{F}_2$ ,  $\text{CH}_2\text{Cl}_2$  and  $\text{CF}_2\text{Cl}_2$ . These systems were chosen primarily because of the availability of detailed experimental (photoionization [27,28] and photoelectron [5–15]) data and theoretical calculations [11,12,16–26]. One other interest was to compare the recently published theoretical photoelectron spectra [19,24,26] with the experimental data. In these molecules, there are seven molecular orbitals in the He I energy region. They fall into two groups, four in the lower ionization energy region and three in the higher energy region, separated by a few electron volts. Self-consistent

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field calculations and the corresponding Koopmans' ordering are in general agreement with the experimental spectra. However, configuration interaction calculations give a different ordering for the first four ionic states.

In  $\text{CH}_2\text{F}_2$ , the SCF ordering [6] of the first four ionic states is  $1^2\text{B}_2$ ,  $1^2\text{A}_1$ ,  $1^2\text{B}_1$  and  $1^2\text{A}_2$  and the configuration interaction (CI) calculation [20] finds it to be  $1^2\text{B}_2$ ,  $1^2\text{B}_1$ ,  $1^2\text{A}_1$  and  $1^2\text{A}_2$ , in the order of increasing ionization energy. The theoretical photoelectron spectrum is in poor agreement with the available experimental data. The 0–0 ionization energy (IE) calculated by theory is in poor agreement with appearance potential [29] and photoelectron [5–8] measurements. The Franck–Condon (FC) envelope of the first band calculated by Takeshita [20] is quite different from the PE spectrum. The PE spectrum of the ground ionic state shows only one progression attributed to the  $\nu_2$  mode although there are two possible vibrations of nearly the same frequency,  $\nu_2$  and  $\nu_3$ . These nearly degenerate vibrations in  $\text{CH}_2\text{F}_2$  may not be so in  $\text{CD}_2\text{F}_2$  [6], and this was used to explain the absence of any vibrational structure in the PE spectrum of the latter. Theoretical calculation predicts appreciable distortions in the structure on ionization in  $\text{CH}_2\text{F}_2$ : this should result in changes in the frequencies of the  $\nu_2$  and  $\nu_3$  modes which should make them distinct at high resolution although they are nearly degenerate in the ground state [30]. The FC envelope of the theoretical PE spectrum extends further than the experimental spectrum, showing the calculation to be unreliable. As far as the published experimental spectrum is concerned, there existed significant scope for improvement. It was in this context that we decided to reinvestigate the PE spectrum.

The PE spectrum of  $\text{CH}_2\text{Cl}_2$  has been reported by five different groups [7–11]. The ordering of the four low-lying states was thought to be  $1^2\text{B}_2$ ,  $1^2\text{B}_1$ ,  $1^2\text{A}_1$  and  $1^2\text{A}_2$ . An  $X\alpha$  calculation [23] predicts the ordering to be  $1^2\text{B}_1$ ,  $1^2\text{B}_2$ ,  $1^2\text{A}_1$  and  $1^2\text{A}_2$ . Theoretical calculations by Takeshita [24] give an ordering consistent with the PE spectrum. The theoretical spectrum was artificially broadened to

fit the available experimental data and consequently the true features of ionization were not evident. We felt that some of the finer details got lost in the process of artificial broadening. The PE spectrum shows only two bands in the 12–14 eV region, where four bands are expected. Another important aspect was the re-examination of the adiabatic IE: the calculation [24] finds it to be considerably lower than the PE value.

In the case of  $\text{CF}_2\text{Cl}_2$ , the SCF calculations predict an ordering  $1^2\text{B}_2$ ,  $1^2\text{B}_1$ ,  $1^2\text{A}_2$  and  $1^2\text{A}_1$  for the four states [13]. The CI calculations [25,26], however, show a different ordering,  $1^2\text{B}_2$ ,  $1^2\text{A}_2$ ,  $1^2\text{B}_1$  and  $1^2\text{A}_1$ . The photoionization study [28] gives an appearance potential of 11.99 eV for the  $\text{CF}_2\text{Cl}^+$  and the process was attributed to  $\text{CF}_2\text{Cl}_2 \rightarrow \text{CF}_2\text{Cl}^+ + \text{Cl}^- + e^-$ . The PE spectrum [13] reflects a Cl–C–Cl vibration, extending to the dissociation limit, suggesting that the dissociation is taking place via the  $\nu_4$  mode. However, the resolution was not adequate to observe other calculated progressions. In the PE spectrum of Jadry et al. [15], vibrational structure was observed in the  $1^2\text{B}_2$  and  $1^2\text{A}_2$  states. A vibrational progression with a spacing of 70 meV was suggested on the  $1^2\text{B}_1$  band.

We have investigated the PE spectra of these three molecules using a supersonic molecular beam photoelectron spectrometer at an operating resolution of 13 meV. The rotational cooling due to supersonic expansion and the high resolution made it possible to observe new features in the PE spectra. Ionization energies of the valence states are given to a much better precision.

## Experimental

The molecular beam photoelectron spectrometer used in the present investigation is fully described elsewhere [31] and only a brief description is provided here. Supersonic beams of the unseeded gases under investigation were crossed by a He I beam emerging from a windowless discharge lamp at 90°. The photoelectrons were sampled at 90° with respect to both the molecular and photon beams

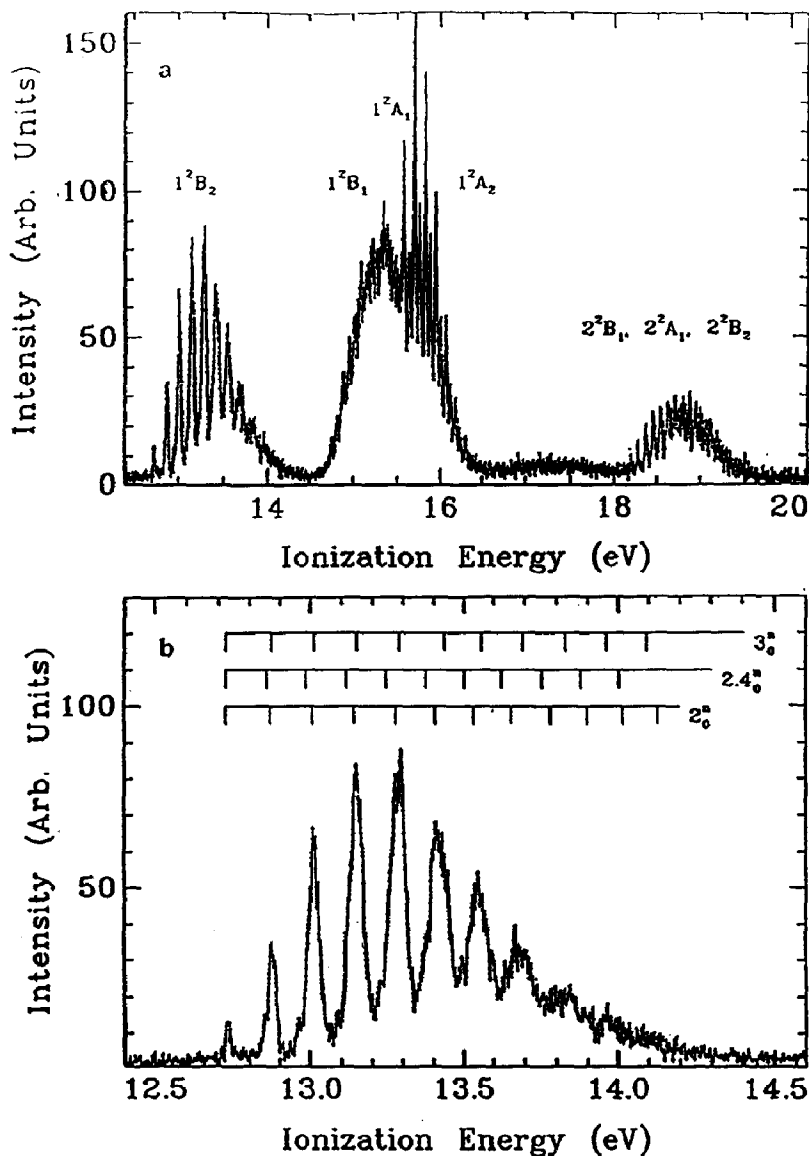


Fig. 1. (a) He I photoelectron spectrum of CH<sub>2</sub>F<sub>2</sub> in the 12.5–20 eV region. The band assignments are based on C<sub>2v</sub> symmetry. (b) The ground ionic state of CH<sub>2</sub>F<sub>2</sub>. The notation, 2<sub>0</sub><sup>+</sup> stands for M(ν<sub>2</sub> = 0) → M<sup>+</sup>(ν<sub>2</sub> = n) + e<sup>-</sup>. Spectra presented in this paper have been smoothed using a seven point-smoothing function.

and were subsequently analyzed by a hemispherical electrostatic sector at a pass energy of 1 eV. The resolution observed was 12–13 meV on Ar<sup>2</sup>P<sub>3/2</sub> and deteriorated to 14 meV during the day-long runs. The spectra were measured at a stagnation pressure of 360 Torr at room temperature. Prior

to each run, a calibration run by argon under identical conditions was carried out to fix the energy position. Commercially available samples were used without further purification. Quoted purity of the samples was better than 99% and no impurities were detected in the PE spectra.

## Results and discussion

### CH<sub>2</sub>F<sub>2</sub>

The PE spectrum of CH<sub>2</sub>F<sub>2</sub> has been measured by a number of workers [5–8]. In the HeI region the spectrum exhibits four bands. The first two are due to four electronic states and the last due to the three remaining states. Brundle et al. [6] found the 0–0 IE of the first band to be 12.72 eV. The highest occupied molecular orbital (HOMO), 2b<sub>2</sub> in CH<sub>2</sub>F<sub>2</sub> is C–H bonding and C–F antibonding. Vibrational structure of the first band, spaced at 1010 cm<sup>-1</sup>, is assigned to the  $\nu_2$  mode. This structure is completely absent in CD<sub>2</sub>F<sub>2</sub>. There are two alternative interpretations for this. (1) More than one vibrational mode is excited in CH<sub>2</sub>F<sub>2</sub> and there is an accidental degeneracy among these modes in CH<sub>2</sub>F<sub>2</sub> but not in CD<sub>2</sub>F<sub>2</sub>. (2) In CD<sub>2</sub>F<sub>2</sub>, predissociation becomes important, imposing lifetime limitation and concomitant peak broadening. There are vibrational structures observed for other states as well, but they have not been resolved well nor assigned precisely.

The total PE spectrum of CH<sub>2</sub>F<sub>2</sub> in the energy range 12.5–20 eV is presented in Fig. 1(a). The spectrum shows the previously reported bands at a much better resolution. The bands are labeled with their assignments. The spectroscopic quantities derived from the PE spectrum are presented in Table 1. There are four totally symmetric vibrational modes in CH<sub>2</sub>F<sub>2</sub> [20]. The  $\nu_1$  mode is charac-

terized as due to the C–H stretching mode. The  $\nu_2$  and  $\nu_4$  modes are H–C–H and F–C–F bending modes, respectively. The  $\nu_3$  mode is a C–F stretching mode accompanied by an F–C–F bending motion. The experimental ground state frequencies of  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  and  $\nu_4$  modes are 2949, 1262, 1116 and 528 cm<sup>-1</sup> respectively [30,32]. Figure 1(b) shows the PE spectrum of the 1<sup>2</sup>B<sub>2</sub> band in more detail. The 0–0 IE observed correlates well with the appearance potential measurements [29] and the previous PE spectroscopic study [5–8]. The appearance potential measured by the electron impact technique [29] (12.6 eV) is significantly lower, but the measurement itself has a large error bar. In the absence of any precise determination of the adiabatic IE by photoionization, we believe 12.729 ± 0.001 eV to be the IE of CH<sub>2</sub>F<sub>2</sub>. The band exhibits intense vibrational structure which Brundle et al. [6] assigned to the  $\nu_2$  mode. Potts et al. [8] also assigned the vibrational excitations as due to  $\nu_2$ . According to the theoretical calculations [20], the most drastic change in the structural parameters accompanying ionization is the reduction in the H–C–H angle: it changes from 112.45° in the ground state to 77.66° in the 1<sup>2</sup>B<sub>2</sub> state. The C–H, C–F distances and the F–C–F angle are also different, but the changes are not as large as in the H–C–H angle. Examination shows that the progression cannot be assigned as due to one mode alone. There is a significant increase in the linewidth as the vibrational quantum number is increased. It may be worth mentioning that a

Table 1  
Ionization potentials and vibrational frequencies of the ionic states of CH<sub>2</sub>F<sub>2</sub> in the HeI region<sup>a</sup>

Ionic state	Adiabatic IE <sup>b</sup> /eV	$\nu_1, \omega_e x_e^c$	$\nu_2, \omega_e x_e^c$	$\nu_3, \omega_e x_e^c$	$\nu_4, \omega_e x_e^c$
1 <sup>2</sup> B <sub>2</sub>	12.729		1173, 11.8	1176, 6.9	1058, 2.7 <sup>d</sup>
1 <sup>2</sup> B <sub>1</sub>	14.611				
1 <sup>2</sup> A <sub>1</sub>	15.572			1075, 10.6	
1 <sup>2</sup> A <sub>2</sub>	15.624			1072, 11.1	
2 <sup>2</sup> B <sub>1</sub>	18.208			724, 6.7	
2 <sup>2</sup> A <sub>1</sub>	18.236			673, 2.5	
2 <sup>2</sup> B <sub>2</sub>	18.270			727, 9.7	

<sup>a</sup> Labelling of the states are based on C<sub>2v</sub> symmetry. The F and H atoms lie on the XZ and YZ planes, respectively. <sup>b</sup> The IEs are accurate to 0.003 eV. <sup>c</sup> Using the relation,  $E_\nu = E_0 + \omega_e(\nu + 1/2) - \omega_e x_e(\nu + 1/2)^2$ , in cm<sup>-1</sup>. Vibrational frequencies refer to the  $\omega_e$  values. <sup>d</sup> For the 2 $\nu_4$  overtone.

Table 2  
Ionization energies and assignments of the  $1^2B_2$  band of  $CH_2F_2$

IE/eV	Assignment	$\Delta G(\nu + 1/2)/cm^{-1}$	IE/eV	Assignment	$\Delta G(\nu + 1/2)/cm^{-1}$
<b>Progression 1</b>			13.289	(00 40)	1104
12.729	(0 000)		13.435	(00 50)	1177
12.872	(0 100)	1153	13.560	(00 60)	1108
13.010	(0 200)	1112	13.694	(00 70)	1081
13.195	(0 300)	1088	13.827	(00 80)	1073
13.278	(0 400)	1072	13.959	(00 90)	1065
13.407	(0 500)	1040	14.090	(00 100)	1057
13.535	(0 600)	1032	<b>Progression 3</b>		
13.660	(0 700)	1008	12.729	(000 0)	
13.780	(0 800)	967	12.859	(000 2)	1048
13.898	(0 900)	951	12.989	(000 4)	1048
14.013	(01000)	927	13.118	(000 6)	1040
14.127	(01100)	919	13.247	(000 8)	1040
<b>Progression 2</b>			13.375	(000 10)	1032
12.729	(000 0)		13.502	(000 12)	1024
12.874	(001 0)	1169	13.628	(000 14)	1016
13.014	(002 0)	1129	13.753	(000 16)	1008
13.152	(003 0)	1112	13.877	(000 18)	1000
			14.001	(000 20)	1000

doubling of the vibrational bands is seen for the  $80856\text{ cm}^{-1}$  band of  $CH_2F_2$  in the vacuum UV absorption spectrum [33] although it was attributed to the associated rotational structure. There are two nearly degenerate vibrations in  $CH_2F_2$  ( $\nu_2$  and  $\nu_3$ ). The calculated frequencies [20] of these two modes in the  $1^2B_2$  state are  $1288$  and  $1412\text{ cm}^{-1}$  respectively. In addition to these vibrations, the spectrum exhibits yet another mode, attributed to a combination band. This combination band,  $2\nu_4$ , is observed in the ground state [30] with a frequency of  $1054\text{ cm}^{-1}$  and strong intensity. Table 2 gives all the ionization energies of the  $1^2B_2$  band and their assignments.

The appearance potential of  $CF_2H^+$  measured by electron impact [29] is  $13.11\text{ eV}$ , within the envelope of the ground ionic state, implying a dissociation channel  $CH_2F_2 \rightarrow CF_2H^+ + H + e^-$ . This dissociation does not seem to take place via the  $\nu_2$  mode (H–C–H bend) since the spectrum does not show any discontinuity. The PE spectrum shows the beginning of an unstructured background at this energy, and the data suggest that another channel (other than  $\nu_2$ ) may be involved. From  $14.4$  to  $14.6\text{ eV}$  there is no PE intensity at all:

however, the theoretical spectrum [20] extends all the way to  $16\text{ eV}$ .

The second band in the PE spectrum corresponds to the  $1^2B_1$  state (Fig. 2(a)). According to the theoretical calculation [20], this ionization would produce significant change in the F–C–F angle from  $108.47^\circ$  (in the neutral state) to  $83.53^\circ$  and correspondingly the spectrum exhibits an extended  $\nu_4$  stretch. The vibrational frequency observed is  $583\text{ cm}^{-1}$ , very close to the neutral state value, in agreement with theory. The appearance potential [29] observed for  $CH_2F^+$  is  $15.28\text{ eV}$ , suggesting that the dissociation may be proceeding via the  $\nu_4$  mode. Although we have assigned only one progression, it may be noted that one or more progressions are involved since the bandwidth cannot be explained by the  $\nu_4$  mode alone.

The remaining portion of the band is assigned to the  $1^2A_1$  and  $1^2A_2$  states. Both these states produce similar PE bands in the theoretical spectrum [20]. The orbitals from which photoemission takes place are essentially nonbonding, with  $a_1$  slightly C–H bonding [6]. The  $a_2$  orbital, however, has only F–F overlap. This would mean

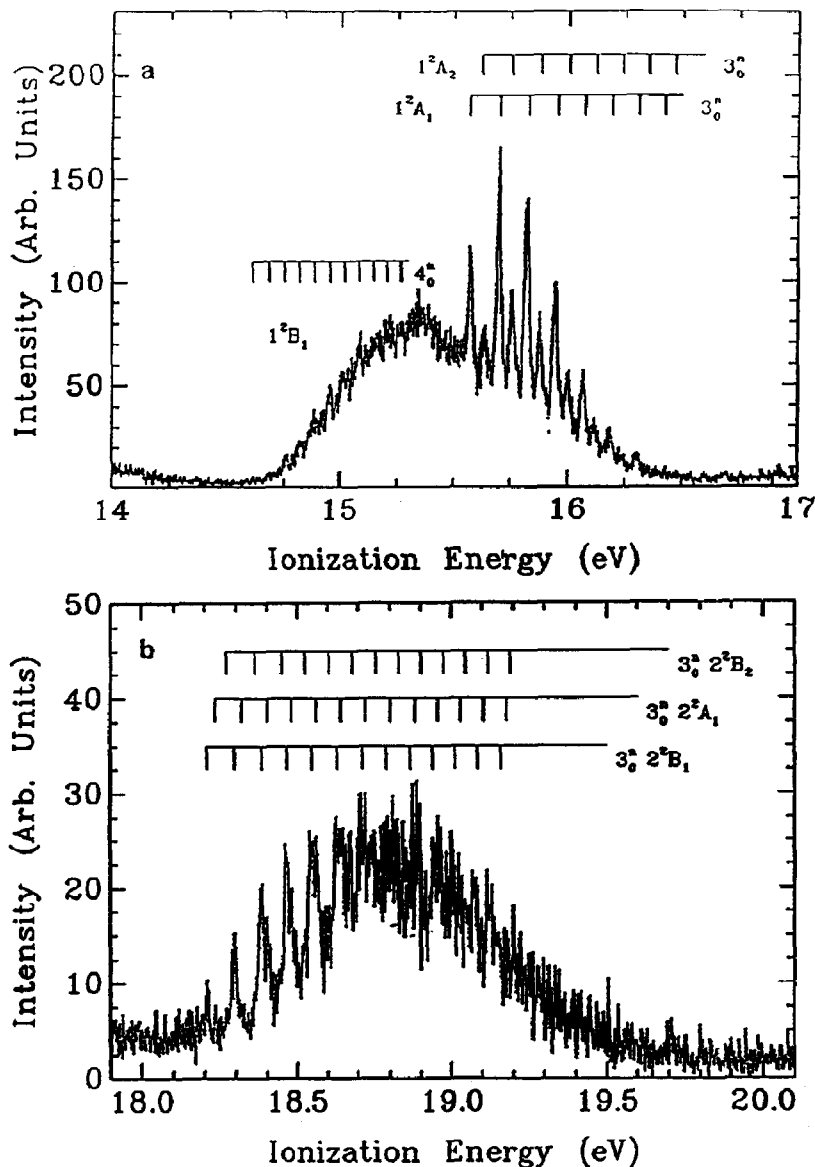


Fig. 2. (a) The  $1^2B_1$ ,  $1^2A_1$  and  $1^2A_2$  bands of  $CH_2F_2$ . (b) The  $2^2B_1$ ,  $2^2A_1$  and  $2^2B_2$  states of  $CH_2F_2$ . Low intensity as a result of poor transmission is the reason for the high noise levels.

that the vibrational excitation will most probably be  $\nu_3$ . We find the vibrational frequency to be about  $1070\text{ cm}^{-1}$ , very close to the theoretical estimate of  $984\text{ cm}^{-1}$  (for  $1^2A_1$ ) and  $1122\text{ cm}^{-1}$  (for  $1^2A_2$ ). The calculated frequencies for the  $\nu_2$  mode are  $1449\text{ cm}^{-1}$  (for  $1^2A_1$ ) and  $1624\text{ cm}^{-1}$  (for  $1^2A_2$ ). The calculation also shows that the most important structural change in these two electronic states is the change in the F–C–F angle. It is

unlikely that the differences in the calculated and experimental values are widely different. Therefore, we assign the progressions to be due to  $\nu_3$ . Brundle et al. [6] assigned the vibrational excitations in this energy region as due to  $\nu_3$  and  $\nu_4$ . Potts et al. [8] assigned them as due to  $\nu_2$  and  $\nu_4$ .

Figure 2(b) shows the last band in the PE spectrum of  $CH_2F_2$ . This band is due to the  $2^2B_1$ ,  $2^2A_1$  and  $2^2B_2$  states. All these orbitals are

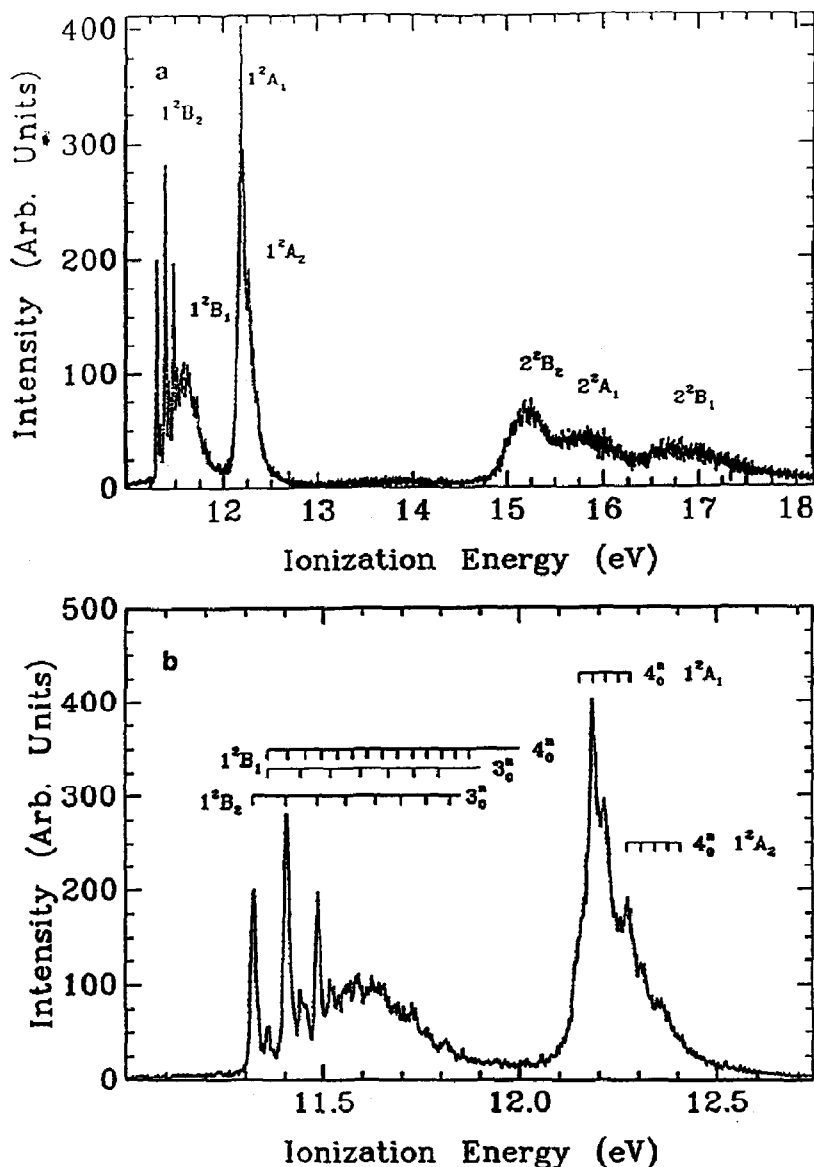


Fig. 3. (a) The total PE spectrum of  $\text{CH}_2\text{Cl}_2$ . (b) The first four ionic states of  $\text{CH}_2\text{Cl}_2$ .

C–F bonding and contributions from other atomic orbitals are negligible. According to the SCF calculations these orbitals are nearly degenerate [6]. The observed vibrational progression is assigned to the  $\nu_3$  (C–F stretch) mode. Brundle et al. [6] also assigned the vibrations to  $\nu_3$ . The vibrational frequencies are much smaller than the ground-state values, consistent with ionization from bonding orbitals. The appearance potential

of  $\text{CF}^+$  is well within the band envelope and this dissociation channel may be responsible for the band broadening.

Our assignment of the electronic states differs considerably from the literature for the first four states. Brundle et al. [6] gave the ordering as  $1^2\text{B}_2$ ,  $1^2\text{A}_1$ ,  $1^2\text{B}_1$  and  $1^2\text{A}_2$  and our assignment shows the ordering to be  $1^2\text{B}_2$ ,  $1^2\text{B}_1$ ,  $1^2\text{A}_1$  and  $1^2\text{A}_2$ . Our assignment is in general agreement with the

Table 3  
Ionization potentials and vibrational frequencies of some of the ionic states of  $\text{CH}_2\text{Cl}_2$  in the He I region<sup>a,b</sup>

Ionic state	Adiabatic IE/eV	$\nu_1, \omega_e x_e$	$\nu_2, \omega_e x_e$	$\nu_3, \omega_e x_e$	$\nu_4, \omega_e x_e$
$1^2\text{B}_2$	11.320			716, 1.7	
$1^2\text{B}_1$	11.357			712, 17.5	418, 9.2
$1^2\text{A}_1$	12.152				286, 4.8
$1^2\text{A}_2$	12.271				308, 5.7
$2^2\text{B}_2$	14.856			553, 5.9	

<sup>a</sup> Labelling of the electronic states is based on  $C_{2v}$  symmetry. The Cl and H atoms are assumed to lie on the  $YZ$  and  $XZ$  planes respectively. <sup>b</sup> See footnotes b, c and d of Table 1.

theoretical photoelectron spectrum [20]: however, there are differences in the observed vibrational progressions. We find the vibrational excitations in the  $1^2\text{B}_2$  band to be due to  $\nu_2, \nu_3$  and  $2\nu_4$  modes and the calculation finds only  $\nu_2$  and  $\nu_3$  excitations. We find distinct bands in the photoelectron spectrum due to  $1^2\text{B}_1, 1^2\text{A}_1$  and  $1^2\text{A}_2$  electronic states, with well-resolved vibrational excitations. The spectrum is in general similar to that reported by Brundle et al. [6], but the assignments vary. Based on our study, we propose that the absence of vibrational structure on the  $1^2\text{B}_2$  state in  $\text{CD}_2\text{F}_2$  is due to the excitation of multiple vibrational modes and that the nearly degenerate  $\nu_2, \nu_3$  and  $2\nu_4$  modes are not so in  $\text{CD}_2\text{F}_2$ .

### $\text{CH}_2\text{Cl}_2$

Photoelectron spectroscopy of methylene chloride has been carried out by a number of groups [7–11]. There are two band systems below an ionization energy of 13 eV, and these are attributed to four electronic states. The ordering of the electronic states differs according to different workers. Potts et al. [8] found three vibrational features in the 11.32–12.5 eV region and attributed them to the  $\text{CCl}_2$  stretching mode of the  $1^2\text{B}_2$  state. The rest of the electronic states were in the order,  $1^2\text{A}_2, 1^2\text{B}_1$  and  $1^2\text{A}_1$ . According to Kimura et al. [11], the electronic states are in the order,  $1^2\text{B}_2, 1^2\text{B}_1, 1^2\text{A}_1$  and  $1^2\text{A}_2$ . Using the SCF  $X\alpha$  method, Li et al. [23] found the ordering to be  $1^2\text{B}_1, 1^2\text{B}_2, 1^2\text{A}_1$  and  $1^2\text{A}_2$ . The CI calculations of Takeshita [24] predict the ordering to be  $1^2\text{B}_2,$

$1^2\text{B}_1, 1^2\text{A}_1$  and  $1^2\text{A}_2$ . No CI calculations exist on the remaining states in the He I region. SCF calculations [7] predict the ordering to be  $2^2\text{B}_2, 2^2\text{A}_1$  and  $2^2\text{B}_1$ . The first four orbitals are essentially non-bonding orbitals of chlorine. The next two are C–Cl bonding and the last one is C–H bonding.

The CI calculations of Takeshita [24] show that, out of the four totally symmetric modes in the molecule,  $\nu_1$  is largely C–H stretching,  $\nu_2$  is H–C–H bending and  $\nu_4$  is Cl–C–Cl bending. The  $\nu_3$  mode is a combination of C–Cl stretching and Cl–C–Cl bending except in the  $1^2\text{B}_1$  state where it is a combination of C–Cl stretching and H–C–H and Cl–C–Cl bending modes. The calculations pertain to only the first four ionic states.

Figure 3(a) shows the total PE spectrum of  $\text{CH}_2\text{Cl}_2$ . The band assignments are indicated on the figure. The ionization energies and vibrational frequencies are listed in Table 3. Figure 3(b) shows the first four electronic states in greater detail. It can be seen that all four electronic states are resolved along with their associated vibrational structures. The first feature, extending from 11.32 to 12 eV, has three distinct progressions. The calculations of Takeshita [24] predict appreciable change in the structure of  $\text{CH}_2\text{Cl}_2$  ion in the first two electronic states. In the  $1^2\text{B}_2$  state, Cl–C–Cl angle changes drastically. In the  $1^2\text{B}_1$  state, however, the C–H and C–Cl distances and H–C–H angle change appreciably. From these results, it is clear that the most probable vibrational excitation in the  $1^2\text{B}_2$  state is  $\nu_3$ . In the  $1^2\text{B}_1$  state, however, there are two vibrational modes which are likely to



Table 4  
Ionization energies and assignments of the  $1^2B_2$  and  $1^2B_1$  bands of  $CH_2Cl_2$

IE/eV	Assignment	$\Delta G(\nu + 1/2)/cm^{-1}$	IE/eV	Assignment	$\Delta G(\nu + 1/2)/cm^{-1}$
$1^2B_2$			$1^2B_1$ Progression 2		
11.320	(00 0 0)		11.357	(000 0)	
11.404	(00 1 0)	677	11.407	(000 1)	403
11.485	(00 2 0)	653	11.454	(000 2)	379
11.560	(00 3 0)	604	11.497	(000 3)	347
11.635	(00 4 0)	604	11.538	(000 4)	331
11.700	(00 5 0)	524	11.577	(000 5)	315
11.765	(00 6 0)	524	11.614	(000 6)	298
11.825	(00 7 0)	484	11.652	(000 7)	306
$1^2B_1$ Progression 1			11.690	(000 8)	306
11.357	(00 0 0)		11.729	(000 9)	315
11.441	(00 1 0)	677	11.767	(000 10)	306
11.520	(00 2 0)	637	11.804	(000 11)	298
11.596	(00 3 0)	613	11.839	(000 12)	282
11.666	(00 4 0)	565	11.873	(000 13)	274
11.731	(00 5 0)	524			
11.795	(00 6 0)	516			

get excited, namely  $\nu_3$  and  $\nu_4$ . It may be noted that Potts et al. [8] assigned the vibrational excitations in this region as due to  $CCl_2$  stretching.

An examination of the band shows three distinct progressions, two with an approximate spacing of  $700\text{ cm}^{-1}$  and one with a spacing of  $410\text{ cm}^{-1}$ . We assign the first progression to the  $\nu_3$  mode of the  $1^2B_2$  state and the other two to the  $\nu_3$  and  $\nu_4$  modes of the  $1^2B_1$  state. The vibrational frequencies observed are comparable to the theoretical predictions. Takeshita [24] predicts that the FC factor of the (0–0) transition of the  $1^2B_2$  state is too small to be observed experimentally. However, the observed transition at 11.320 eV cannot be assigned as due to the  $1^2B_1$  state because the geometric change discussed above would excite a  $\nu_4$  mode along with  $\nu_3$ . The most recent photoionization measurement [27] gives a value of  $11.32 \pm 0.01\text{ eV}$  for the ionization potential of  $CH_2Cl_2$ , and we assign the 11.320 eV peak as due to the 0–0 transition of the  $1^2B_2$  state. Table 4 lists all the IEs and assignments.

The  $a_1$  and  $a_2$  orbitals are Cl–Cl bonding and antibonding respectively. Consequently, the most important geometrical change accompanying ionization from these orbitals is the change in the Cl–C–Cl angle and the vibrational modes asso-

ciated with the ionizations should be  $\nu_4$ . Theoretical calculations of Takeshita [24] predict that the intensity of the  $1^2A_1$  state is mainly due to (0000), (0001), (0002) and (0003) vibrations. The  $1^2A_2$  state also has four similar vibrations contributing to the intensity. We find five vibrational quanta of the  $\nu_4$  mode are getting excited in these two states.

The photoionization study [27] finds that the appearance potential of  $CH_2Cl^+$  to be  $12.14 \pm 0.02\text{ eV}$ . The adiabatic IE observed for the  $1^2A_1$  state is  $12.152 \pm 0.003\text{ eV}$ , which means that the dissociation is not arising from this state. However, the dissociation limits of the  $1^2B_2$  and  $1^2B_1$  states work out to be 12.277 and 12.255 eV along the  $\nu_3$  mode. We believe that the dissociation might be occurring much below the reported appearance potential, since the PE band shape (of the  $1^2B_2$ ,  $1^2B_1$  band) could not be fully described by the vibrational excitations alone. The vibrational fine structure is overlapped with an unstructured background. The dissociation might be occurring via fast energy transfer from excited vibrational modes to another one whose dissociation limit seems to be lower than that along the  $\nu_3$  mode and this vibrational mode may not be accessible by direct ionization due to poor FC factors.

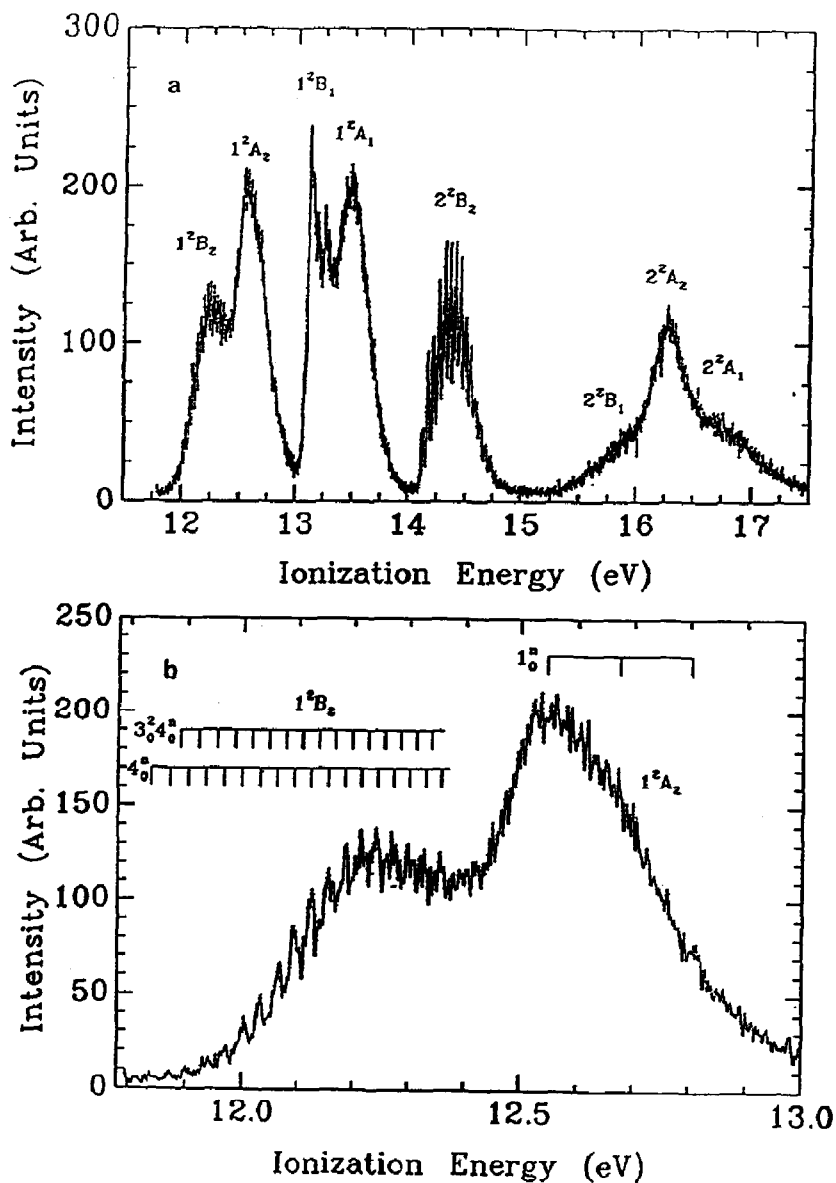


Fig. 4. (a) The total PE spectrum of  $\text{CF}_2\text{Cl}_2$ . (b) The  $1^2\text{B}_2$  and  $1^2\text{A}_2$  bands of  $\text{CF}_2\text{Cl}_2$ .

The remaining three bands in the PE spectrum are assigned to  $2^2\text{B}_2$ ,  $2^2\text{A}_1$  and  $2^2\text{B}_1$  states respectively. Our PE spectrum reproduces the features of the spectrum of Kimura et al. [11]. Only one state,  $2^2\text{B}_2$ , exhibits vibrational structure. This progression is assigned to the  $\nu_3$  mode.

The present study has established that the first four ionic states of  $\text{CH}_2\text{Cl}_2$  are  $1^2\text{B}_2$ ,  $1^2\text{B}_1$ ,  $1^2\text{A}_1$  and  $1^2\text{A}_2$  in the order of increasing IE. Vibrational

progression of the  $1^2\text{B}_2$  state is due solely to  $\nu_3$ , and in the  $1^2\text{B}_1$  state both  $\nu_3$  and  $\nu_4$  get excited. In the  $1^2\text{A}_1$  and  $1^2\text{A}_2$  states only the  $\nu_4$  mode contributes to the intensity. Our assignment differs from that of Takeshita [24] but agrees with that of Kimura et al. [11].

#### $\text{CF}_2\text{Cl}_2$

The photoelectron spectrum of  $\text{CF}_2\text{Cl}_2$  has been

Table 5  
Ionization energies and assignments of the first five ionic states of  $\text{CF}_2\text{Cl}_2^a$

State	Adiabatic IE/eV	$\nu_1, \omega_e x_e$	$\nu_2, \omega_e x_e$	$\nu_3, \omega_e x_e$	$\nu_4, \omega_e x_e$
$1^2\text{B}_2$	11.734 <sup>b</sup>				481, 12.1
$1^2\text{A}_2$		1072, 8.1			
$1^2\text{B}_1$	13.078				306, 2.5
$1^2\text{A}_1$					
$2^2\text{B}_2$	14.126			375, 0.27	

<sup>a</sup> See the footnotes of Table 1; the coordinate system adopted is as in  $\text{CH}_2\text{Cl}_2$  (see Table 3, footnote a). <sup>b</sup> Estimated value, from the relation,  $E_\nu = E_0 + \omega_e(\nu + 1/2) - \omega_e x_e(\nu + 1/2)^2$ .

investigated by a number of workers [12–15]. The low-lying ionic states up to an IE of 14 eV are due to chlorine lone-pair orbitals. According to Cvitas et al. [13] and Jadrny et al. [15], the first four states are in the order  $1^2\text{B}_2$ ,  $1^2\text{B}_1$ ,  $1^2\text{A}_2$  and  $1^2\text{A}_1$ . Lewerenz et al. [25] calculated the ionic states by the MRD-CI method and the ordering of the states was found to be  $1^2\text{B}_2$ ,  $1^2\text{A}_2$ ,  $1^2\text{B}_1$  and  $1^2\text{A}_1$  in the order of increasing IE. The high-resolution PE spectrum of Cvitas et al. [13] shows a progression on the first band with a spacing of  $280\text{ cm}^{-1}$ , and no vibrational structure was observed on any of the other states discussed above. Jadrny et al. [15] also found the same progression on the  $1^2\text{B}_2$

band. In addition,  $\nu_1$  (C–F stretch),  $\nu_2$  (C–Cl stretch) and  $\nu_4$  (C–Cl deformation) vibrational modes were observed in the  $1^2\text{A}_2$  band. The  $2^2\text{B}_2$  state showed a well-resolved progression due to the  $\nu_3$  mode.

Figure 4(a) shows the complete PE spectrum of  $\text{CF}_2\text{Cl}_2$ . All the band assignments are indicated in the figure. The IEs, state assignments and spectroscopic quantities are listed in Table 5. Figure 4(b) shows the first two bands in more detail. The first band is due to the  $1^2\text{B}_2$  state, in agreement with Takeshita [26], Cvitas et al. [13] and Jadrny et al. [15]. As a result of ionization, the geometry undergoes appreciable distortion. The most significant

Table 6  
Ionization energies and assignments of the ground ionic state ( $1^2\text{B}_2$ ) of  $\text{CF}_2\text{Cl}_2$

IE/eV	Assignment	$\Delta G(\nu + 1/2)/\text{cm}^{-1}$	IE/eV	Assignment	$\Delta G(\nu + 1/2)/\text{cm}^{-1}$
Progression 1			Progression 2		
11.837	(000 2)		11.888	(002 2)	
11.870	(000 3)	266	11.921	(002 3)	266
11.903	(000 4)	266	11.954	(002 4)	266
11.934	(000 5)	250	11.984	(002 5)	242
11.966	(000 6)	258	12.016	(002 6)	258
11.996	(000 7)	242	12.047	(002 7)	250
12.030	(000 8)	274	12.078	(002 8)	250
12.062	(000 9)	258	12.108	(002 9)	242
12.093	(000 10)	250	12.138	(002 10)	242
12.124	(000 11)	250	12.168	(002 11)	242
12.155	(000 12)	250	12.198	(002 12)	242
12.186	(000 13)	250	12.227	(002 13)	234
12.215	(000 14)	234	12.256	(002 14)	234
12.244	(000 15)	234	12.285	(002 15)	234
12.273	(000 16)	234	12.314	(002 16)	234
12.302	(000 17)	234	12.340	(002 17)	210
12.331	(000 18)	234			
12.358	(000 19)	218			

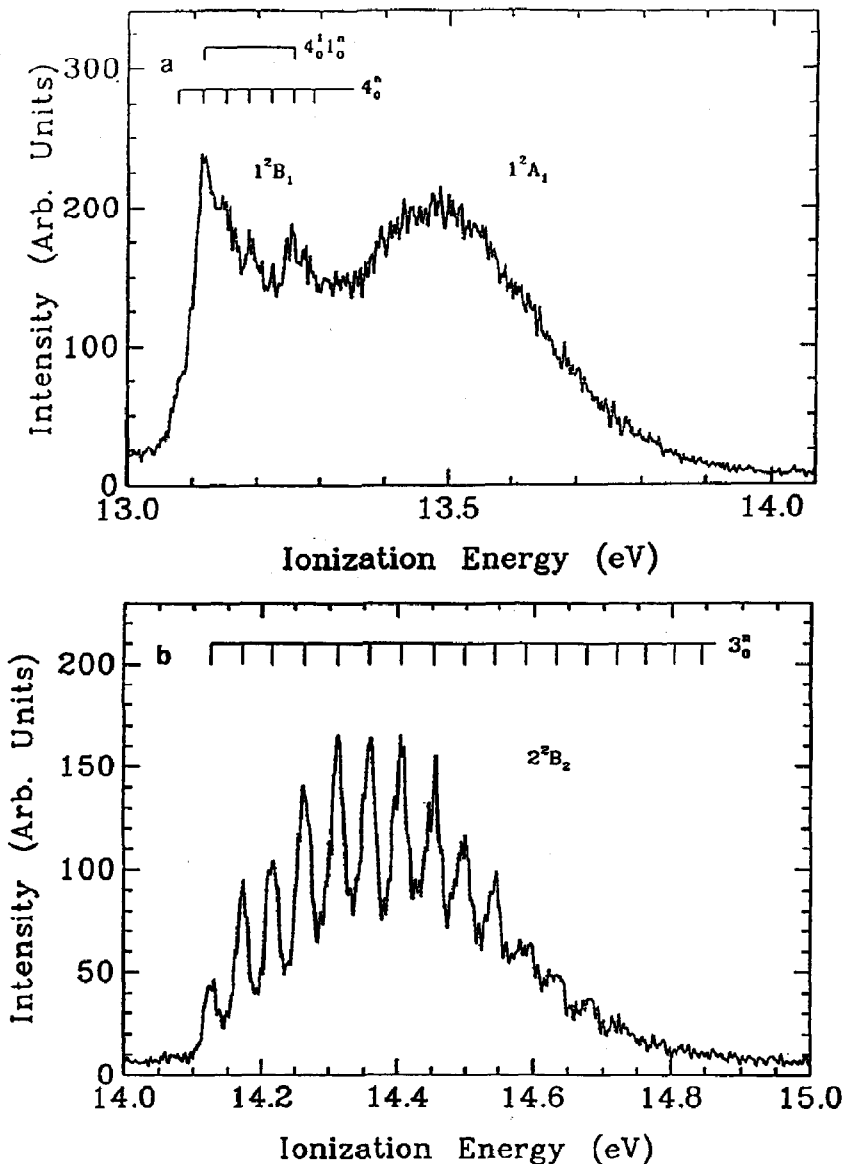


Fig. 5. (a) The  $1^2B_1$  and  $1^2A_1$  states of  $CF_2Cl_2$ . In the  $1^2B_2$  state, the values of  $n$  are 2, 3, 4, etc. (b) The  $2^2B_2$  state of  $CF_2Cl_2$ .

change is in the Cl-C-Cl angle; the calculation shows a reduction of  $20.37^\circ$  in this angle [26]. As a result of this change in geometry, the FC factor for the 0-0 transition is very small. The theoretical estimate of the FC factor for the 0-0 transition is 0.000, and consequently we believe the transition is not observed in the PE spectrum. Appearance potential measurements by Ajello et al. [28] give an IE of  $11.75 \pm 0.037$  eV for  $CF_2Cl_2$ . By extrap-

olating the observed vibrational excitations in the PE spectrum, we get an IE of  $11.734 \pm 0.003$  eV.

As mentioned above, the most important structural change occurring as a result of ionization is the reduction in the Cl-C-Cl angle. The  $\nu_4$  mode of this molecule can be characterized as the Cl-C-Cl bending mode. The other four symmetric modes cannot be classified by simple descriptions. Strong coupling is found among

C–Cl stretching, F–C–F bending and Cl–C–Cl bending for these modes [26]. The spectrum shown in Fig. 4(b) closely resembles the theoretical spectrum of Takeshita [26] with a half-width of  $121 \text{ cm}^{-1}$ . The spectrum consists of two progressions. The  $\nu_4$  mode contributes to both progressions. The IEs and the assignments are listed in Table 6. Although the calculation finds that the  $\nu_1$ ,  $\nu_3$  and  $\nu_4$  modes contribute to the intensity, we have been able to observe only the  $\nu_3$  and  $\nu_4$  modes.

Calculation [26] shows that two distinct vibrations contribute to intensity in the next band ( $1^2A_2$ ). They are  $\nu_1$  and  $\nu_4$ . The experimental spectrum shows no resolved structure, however; the band profile is attributed to three excitations of the  $\nu_1$  mode.

Theory [26] predicts three modes ( $\nu_1$ ,  $\nu_3$  and  $\nu_4$ ) accompanying ionization leading to the  $1^2B_1$  state (Fig. 5(a)). We find evidence for only the  $\nu_1$  and  $\nu_4$  modes. As predicted by theory, the  $1^2A_1$  state does not show any vibrational excitations. The next band,  $2^2B_2$  (Fig. 5(b)) shows a well resolved progression of the  $\nu_3$  mode, which has been observed before [13,15]. Our spectrum closely resembles the published spectra in the higher IE region.

## Conclusions

The PE spectra of the three molecules discussed above are similar. However, there are significant differences in detail. Theoretical PE spectra are generally in agreement with the experiment. In the case of  $\text{CF}_2\text{Cl}_2$  the agreement is very good in that the PE spectrum does not show the adiabatic IE, as predicted by theory. In the cases of  $\text{CH}_2\text{F}_2$  and  $\text{CH}_2\text{Cl}_2$ , the theory overestimates structural changes and fails to reproduce the PE spectrum completely. Calculated FC factors for the 0-0 transitions are close to zero for the ground ionic states, but the experiment shows the adiabatic IEs. The present study has established that the four low-lying ionic states of  $\text{CH}_2\text{F}_2$  and  $\text{CH}_2\text{Cl}_2$  are in the order,  $1^2B_2$ ,  $1^2B_1$ ,  $1^2A_1$  and  $1^2A_2$ . The ordering of the states in  $\text{CF}_2\text{Cl}_2$  is  $1^2B_2$ ,  $1^2A_2$ ,  $1^2B_1$  and  $1^2A_1$ . In  $\text{CH}_2\text{F}_2$  and  $\text{CH}_2\text{Cl}_2$ , the experimental spectrum

shows more vibrational modes than predicted by theory. The study has established the adiabatic IEs of  $\text{CF}_2\text{Cl}_2$  and  $\text{CH}_2\text{Cl}_2$ . The 0–0 IE is not observed in  $\text{CF}_2\text{Cl}_2$  but is estimated to be  $11.734 \pm 0.003 \text{ eV}$ .

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