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**High Resolution Photoelectron Spectroscopy of CH_2F_2 , CH_2Cl_2 and
 CF_2Cl_2 Using Supersonic Molecular Beams**

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ABSTRACT

Molecular beam photoelectron spectroscopy using HeI radiation (584 Å) has been used to study the electronic structures of CH_2F_2 , CH_2Cl_2 and CF_2Cl_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 CF_2Cl_2 , there are significant differences in CH_2F_2 and CH_2Cl_2 .

1. Introduction

Since the discovery of the ozone depleting nature of chlorofluorocarbons¹ in the stratosphere, the photochemistry and photophysics of these systems received renewed attention. There is a wealth of data on the photoabsorption and photofragmentation of these molecules² 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 HeI, HeII and synchrotron radiations⁵⁻¹⁴ have been used to unravel the experimental electronic structure. There are a number of electronic structure calculations¹⁵⁻²⁵ 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; CH₂F₂, CH₂Cl₂ and CF₂Cl₂. These systems were chosen primarily because of the availability of detailed experimental (photoionization^{26,27} and photoelectron⁵⁻¹⁴) data and theoretical calculations^{11,12, 15-25}. One another interest was to compare the recently published theoretical photoelectron spectra^{18,23,25} with the experimental data. In these molecules, there are seven molecular orbitals in the HeI energy region. They fall into two groups, four in the lower binding energy region and three in the higher energy region, separated by a few electron volts. Self-consistent 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 are concerned.

In CH₂F₂, the SCF ordering⁶ of the first four ionic states is 1^2B_2 , 1^2A_1 , 1^2B_1 and 1^2A_2 and the configuration interaction (CI) calculation¹⁹ finds it to be 1^2B_2 , 1^2B_1 , 1^2A_1 and 1^2A_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 potential²⁸ and photoelectron⁵⁻⁸ measurements. The Franck-Condon (FC) envelope of the first band calculated by Takeshita¹⁹ is quite different from the photoelectron spectrum. The PE spectrum of the ground ionic state shows only one progression attributed to the ν_2 mode although there are two possible vibrations of nearly same frequency, ν_2 and ν_3 . These nearly degenerate vibrations in CH_2F_2 may not be so in CD_2F_2 ⁶, and this was attributed to the absence of any vibrational structure in the PE spectrum of the latter. Theoretical calculation predicts appreciable distortions in the structure on ionization in CH_2F_2 : this should result in changes in the frequencies of the ν_2 and ν_3 modes which should make them distinct at high resolution although they are nearly degenerate in the ground state²⁹. The Franck-Condon 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 photoelectron spectrum.

The photoelectron spectrum of CH_2Cl_2 has been reported by five different groups⁷⁻¹¹. The ordering of the four low-lying states was thought to be 1^2B_2 , 1^2B_1 , 1^2A_1 and 1^2A_2 . An X_α calculation²² predicts the ordering to be 1^2B_1 , 1^2B_2 , 1^2A_1 and 1^2A_2 . Theoretical calculations by Takeshita²³ give an ordering consistent with the photoelectron spectrum. The theoretical spectrum was artificially broadened to fit the available experimental data and consequently true features of ionization were not evident. We felt that some of the finer details got lost in the process of artificial broadening. The photoelectron 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 calculation²³ finds it to be considerably lower than the photoelectron value.

In the case of CF_2Cl_2 , the SCF calculations predict an ordering 1^2B_2 , 1^2B_1 , 1^2A_2 and 1^2A_1 for the four states¹³. The CI calculations,^{24,25} however, shows a different ordering, 1^2B_2 , 1^2A_2 , 1^2B_1 and 1^2A_1 . The photoionization study²⁷ gives an appearance

potential of 11.99 eV for the for CF_2Cl^+ and the process was attributed to $\text{CF}_2\text{Cl}_2 \rightarrow \text{CF}_2\text{Cl}^+ + \text{Cl} \cdot + e^-$. The PE spectrum¹³ reflects a Cl-C-Cl vibration, extending to the dissociation limit, suggesting that the dissociation is taking place via the ν_4 mode. However, the resolution was not adequate to observe other calculated progressions. None of the other three bands showed any vibrational structure.

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

2. Experimental

The molecular beam photoelectron spectrometer used in the present investigation is fully described elsewhere³⁰ and only a brief description is provided here. Supersonic beams of the unseeded gases under investigation were crossed by a HeI beam emerging from a windowless discharge lamp at 90° . The photoelectrons were sampled at 90° with respect to both the molecular and photon beams 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 $2P_{3/2}$ 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 photoelectron spectra.

3. Results and Discussion

CH₂F₂: The photoelectron spectrum of CH₂F₂ has been measured by a number of workers⁵⁻⁸. In the HeI region the spectrum exhibits four bands. The first two are due to four electronic states and the last due to three remaining states. Brundle et al⁶ found the 0-0 IE of the first band to be 12.72 eV. The highest occupied molecular orbital (HOMO), $2b_2$

in CH_2F_2 is C-H bonding and C-F antibonding. Vibrational structure of the first band, spaced at 1010 cm^{-1} , is assigned to the ν_2 mode. This structure is completely absent in CD_2F_2 . There are two alternate interpretations for this: (1). More than one vibrational mode is excited in CH_2F_2 and there is an accidental degeneracy among these modes in CH_2F_2 but not in CD_2F_2 ; (2). In CD_2F_2 , 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 not assigned precisely.

The total photoelectron spectrum of CH_2F_2 in the energy range 12.5 - 20 eV is presented in Fig. 1a. 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 photoelectron spectrum are presented in Table I. There are four totally symmetric vibrational modes in CH_2F_2 ¹⁹. The ν_1 mode is characterized as due to the C-H stretching mode. The ν_2 and ν_4 modes are H-C-H and F-C-F bending modes, respectively. The ν_3 mode is a C-F stretching mode accompanied by a F-C-F bending motion. The experimental ground state frequencies of ν_1 , ν_2 , ν_3 and ν_4 modes are 2949, 1262, 1116 and 528 cm^{-1} respectively^{29,31}. Fig 1b. shows the photoelectron spectrum of the 1^2B_2 band in more detail. The 0-0 IE observed correlates well with the appearance potential measurements²⁸ and the previous photoelectron spectroscopic study⁵⁻⁸. The appearance potential measured by the electron impact technique²⁸ (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 $12.729 \pm 0.001\text{ eV}$ to be the IE of CH_2F_2 . The band exhibits intense vibrational structure which Brundle et al⁶ assigned to the ν_2 mode. Potts et al⁸ also assigned the vibrational excitations as due to ν_2 . According to the theoretical calculations¹⁹, 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 1^2B_2 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 doubling of the vibrational bands is seen for the 80856 cm^{-1} band of CH_2F_2 in the vacuum UV absorption spectrum³² although it was attributed to the associated rotational structure. There are two nearly degenerate vibrations in CH_2F_2 (ν_2 and ν_3). The calculated frequencies¹⁹ of these two modes in the 1^2B_2 state are 1288 and 1412 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 state²⁹ with a frequency of 1054 cm^{-1} and strong intensity. Table II gives all the ionization energies of the 1^2B_2 band and their assignments.

The appearance potential of CF_2H^+ measured by electron impact²⁸ is 13.11 eV , within the envelope of the ground ionic state, implying a dissociation channel $\text{CH}_2\text{F}_2 \rightarrow \text{CF}_2\text{H}^+ + \text{H} \cdot + \text{e}^-$. This dissociation does not seem to take place via the ν_2 mode (H-C-H bend) since the spectrum does not show any discontinuity. The photoelectron spectrum shows the beginning of an unstructured background at this energy, and the data suggest that another channel (other than ν_2) may be involved. From 14.4 to 14.6 eV there is no photoelectron intensity at all; however, the theoretical spectrum¹⁹ extends all the way to 16 eV .

The second band in the photoelectron spectrum corresponds to the 1^2B_1 state (Fig. 2a). According to the theoretical calculation¹⁹, this ionization would produce significant change in the F-C-F angle from 108.47° (in the neutral state) to 83.53° and correspondingly the spectrum exhibits an extended ν_4 stretch. The vibrational frequency observed is 583 cm^{-1} , very close to the neutral state value, in agreement with theory. The appearance potential²⁸ observed for CH_2F^+ is 15.28 eV , suggesting that the dissociation may be proceeding via the ν_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 ν_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 photoelectron bands in the theoretical spectrum¹⁹. The orbitals from which photoemission takes place are essentially nonbonding, with a_1 slightly C-H bonding⁶. The a_2 orbital, however, has only F-F overlap. This would mean that the vibrational excitation will most probably be ν_3 . We find the vibrational frequency to be $\sim 1070\text{cm}^{-1}$ very close to the theoretical estimate of 984cm^{-1} (for 1^2A_1) and 1122cm^{-1} (for 1^2A_2). The calculated frequencies for the ν_2 mode are 1449cm^{-1} (for 1^2A_1) and 1624cm^{-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 difference in the calculated and experimental values are widely different. Therefore, we assign the progressions to be due to ν_3 . Brundle et al⁶ assigned the vibrational excitations in this energy region as due to ν_3 and ν_4 . Potts et al⁸ assigned them as due to ν_2 and ν_4 .

Fig. 2b 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 C-F bonding and contributions from other atomic orbitals are negligible. according to the SCF calculations these orbitals are nearly degenerate⁶. The observed vibrational progression is assigned to the ν_3 (C-F stretch) mode. Brundle et al⁶ also assigned the vibrations to ν_3 . The vibrational frequencies are much smaller than the ground-state values, consistent with ionization from bonding orbitals. The appearance potential of CF^+ is well within the band envelope and this dissociation channel may be responsible for the band broadening.

Our assignment of the electronic states differ considerably from the literature for the first four states. Brundle et al⁶ gave the ordering as 1^2B_2 , 1^2A_1 , 1^2B_1 and 1^2A_2 and our assignment shows the ordering to be 1^2B_2 , 1^2B_1 , 1^2A_1 and 1^2A_2 . Our assignment is in general agreement with the theoretical photoelectron spectrum¹⁹: however, there are differences in the observed vibrational progressions. We find the vibrational excitations in the 1^2B_2 band to be due to ν_2 , ν_3 and $2\nu_4$ modes and the calculation finds only ν_2 and ν_3 excitations. We find distinct bands in the photoelectron spectrum due to 1^2B_1 , 1^2A_1 and 1^2A_2 electronic states, with well-resolved vibrational excitations. The spectrum is in

general similar to that reported by Brundle et al⁶, but the assignments vary. Based on our study, we propose that the absence of vibrational structure on the 1^2B_2 state in CD_2F_2 is due to the excitation of multiple vibrational modes and that the nearly degenerate ν_2 , ν_3 and $2\nu_4$ modes are not so in CD_2F_2 .

CH₂Cl₂: Photoelectron spectroscopy of methylene chloride has been carried out by a number of groups⁷⁻¹¹. 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 al⁸ found three vibrational features in the 11.32 to 12.5 eV region and attributed them to the CCl₂ stretching mode of the 1^2B_2 state. The rest of the electronic states were in the order 1^2A_2 , 1^2B_1 and 1^2A_1 . According to Kimura et al⁷, the electronic states are in the order 1^2B_2 , 1^2B_1 , 1^2A_1 and 1^2A_2 . Using the SCF X_α method, Li et al²² found the ordering to be 1^2B_1 , 1^2B_2 , 1^2A_1 and 1^2A_2 . The CI calculations of Takeshita²³ predict the ordering to be 1^2B_2 , 1^2B_1 , 1^2A_1 and 1^2A_2 . No CI calculations exist on the remaining states in the HeI region. SCF calculations⁷ predict the ordering to be 2^2B_2 , 2^2A_1 and 2^2B_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 Takeshita²³ show that, out of the four totally symmetric modes in the molecule, ν_1 is largely C-H stretching, ν_2 is H-C-H bending and ν_4 is Cl-C-Cl bending. The ν_3 mode is a combination of C-Cl stretching and Cl-C-Cl bending except in the 1^2B_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.

Fig. 3a shows the total photoelectron spectrum of CH₂Cl₂. The band assignments are indicated on the figure. The ionization energies and vibrational frequencies are listed in Table III. Fig. 3b 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 Takeshita²³ predict appreciable change in the structure of CH₂Cl₂ ion in the first two electronic states. In the 1^2B_2 state, Cl-C-Cl angle changes drastically. In the 1^2B_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 1^2B_2 state is ν_3 . In the 1^2B_1 state, however, there are two vibrational modes which are likely to get excited, namely ν_3 and ν_4 . It may be noted that Potts et al⁸ 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 cm^{-1} and one with a spacing of 410 cm^{-1} . We assign the first progression to the ν_3 mode of the 1^2B_2 state and the other two to the ν_3 and ν_4 modes of the 1^2B_1 state. The vibrational frequencies observed are comparable to the theoretical predictions. Takeshita²³ predicts that the Franck-Condon 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 ν_4 mode along with ν_3 . The most recent photoionization measurement²⁶ 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 IV lists all the IEs and assignments.

The a_1 and a_2 orbitals are Cl-Cl bonding and anti-bonding 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 associated with the ionizations should be ν_4 . Theoretical calculations of Takeshita²³ predict that 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 ν_4 mode are getting excited in these two states.

The photoionization study²⁶ 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 limit of the 1^2B_2 and 1^2B_1 states work out to be 12.277 and 12.255 eV along the ν_3 mode. We believe that the dissociation might be occurring much below the reported

appearance potential, since the photoelectron 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 ν_3 mode and this vibrational mode may not be accessible by direct ionization due to poor FC factors.

The remaining three bands in the photoelectron spectrum are assigned to 2^2B_2 , 2^2A_1 and 2^2B_1 states respectively. Our photoelectron spectrum reproduces the features of the spectrum of Kimura et al¹¹. Only one state, 2^2B_2 , exhibits vibrational structure. This progression is assigned to the ν_3 mode.

The present study has established that the first four ionic states of CH_2Cl_2 are 1^2B_2 , 1^2B_1 , 1^2A_1 and 1^2A_2 in the order of increasing IE. Ordering of the electronic states is the same as in CH_2F_2 . Vibrational progression of the 1^2B_2 state is solely due to ν_3 and in the 1^2B_1 state, both ν_3 and ν_4 get excited. In the 1^2A_1 and 1^2A_2 states only the ν_4 mode contributes to the intensity. Our assignment differs from that of Takeshita but agrees with that of Kimura et al¹¹.

CF_2Cl_2 : The photoelectron spectrum of CF_2Cl_2 has been investigated by a number of workers¹²⁻¹⁴. The low-lying ionic states up to an IE of 14 eV are due to chlorine lone pair orbitals. According to Cvitas et al¹³, the first four states are in the order 1^2B_2 , 1^2B_1 , 1^2A_2 and 1^2A_1 . Apart from one vibrational progression observed for the first band, the rest of the bands did not show any resolvable structure. Lewerenz et al²⁴ calculated the ionic states by MRD-CI method and the ordering of the states was found to be 1^2B_2 , 1^2A_2 , 1^2B_1 and 1^2A_1 in the order of increasing IE. The high resolution photoelectron spectrum of Cvitas et al¹³ shows a progression on the first band with a spacing of 280 cm^{-1} and no vibrational structure was observed on any of the other states discussed above.

Fig. 4a shows the complete photoelectron spectrum of CF_2Cl_2 . All the band assignments are indicated in the figure. The IEs, state assignments and spectroscopic quantities are listed in Table V. Fig. 4b shows the first two bands in more detail. The first

band is due to the 1^2B_2 state, in agreement with Takeshita²⁵ and Cvitas et al¹³. As a result of ionization, the geometry undergoes appreciable distortion. The most significant change is in the Cl-C-Cl angle; the calculation shows a reduction of 20.37° in this angle²⁵. As a result of this change in geometry, the Franck-Condon 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 photoelectron spectrum. Appearance potential measurements by Ajello et al²⁷ give an IE of 11.75 ± 0.037 eV for CF_2Cl_2 . By extrapolating the observed vibrational excitations in the PE spectrum, we get an IE of 11.734 ± 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 ν_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 modes²⁵. The spectrum shown in Fig. 4b closely resembles the theoretical spectrum of Takeshita²⁵ with a half-width of 121 cm^{-1} . The spectrum consists of two progressions. The ν_4 mode contributes to both progressions. The IEs and the assignments are listed in Table VI. Although the calculation finds that the ν_1 , ν_3 and ν_4 modes contribute to the intensity, we have been able to observe only the ν_3 and ν_4 modes.

Calculation²⁵ shows that two distinct vibrations contribute to intensity in the next band (1^2A_2). They are ν_1 and ν_4 . The experimental spectrum shows no resolved structure, however; the band profile is attributed to three excitations of the ν_1 mode.

Theory²⁵ predicts three modes; ν_1 , ν_3 and ν_4 accompanying ionization leading to the 1^2B_1 state (Fig. 5a). We find evidence for only the ν_1 and ν_4 modes. As predicted by theory, the 1^2A_1 state does not show any vibrational excitations. The next band, 2^2B_2 (Fig. 5b) shows a well resolved progression of the ν_3 mode, which has been observed before¹³. Our spectrum closely resembles the published spectra in the higher IE region.

In summary, the photoelectron spectra of the three molecules discussed above are similar. However, there are significant differences in detail. Theoretical photoelectron spectra are generally in agreement with the experiment. In the case of CF_2Cl_2 the agreement is very good in that the photoelectron spectrum does not show the adiabatic IE, as predicted by theory. In the cases of CH_2F_2 and CH_2Cl_2 , the theory overestimates structural changes and fails to reproduce the photoelectron 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 established that the four low-lying ionic states of CH_2F_2 and CH_2Cl_2 are in the order, 1^2B_2 , 1^2B_1 , 1^2A_1 and 1^2A_2 . The ordering of the states in CF_2Cl_2 is 1^2B_2 , 1^2A_2 , 1^2B_1 and 1^2A_1 . In CH_2F_2 and CH_2Cl_2 , the experimental spectrum shows more vibrational modes than predicted by theory. The study established the adiabatic IEs of CF_2Cl_2 and CH_2Cl_2 . The 0-0 IE is not observed in CF_2Cl_2 but is estimated to be 11.734 ± 0.003 eV.

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TABLE I Ionization Potentials and vibrational frequencies of the ionic states of CH_2F_2 in the HeI region.

Ionic State	AIE ^a	$\nu_1, \omega_e x_e^b$	$\nu_2, \omega_e x_e^b$	$\nu_3, \omega_e x_e^b$	$\nu_4, \omega_e x_e^b$
1^2B_2	12.729	-	1173, 11.8	1176, 6.9	1058, 2.7 ^c
1^2B_1	14.611	-	-	-	-
1^2A_1	15.572	-	-	1075, 10.6	-
1^2A_2	15.624	-	-	1072, 11.1	-
2^2B_1	18.208	-	-	724, 6.7	-
2^2A_1	18.236	-	-	673, 2.5	-
2^2B_2	18.270	-	-	727, 9.7	-

^a Adiabatic IE, in eV. The IEs are accurate to 0.003 eV.

^b Using the relation, $E_\nu = E_0 + \omega_e (\nu + 1/2) - \omega_e x_e (\nu + 1/2)^2$, in cm^{-1} . Vibrational frequencies refer to the ω_e values.

^c For the $2\nu_4$ overtone.

TABLE II Ionization energies and assignments of the 1^2B_2 band of CH_2F_2 .

IE, eV	Assignment	$\Delta G (v + 1/2), cm^{-1}$
	Progression 1	
12.729	(0000)	-
12.872	(0 1 00)	1153
13.010	(0 2 00)	1112
13.195	(0 3 00)	1088
13.278	(0 4 00)	1072
13.407	(0 5 00)	1040
13.535	(0 6 00)	1032
13.660	(0 7 00)	1008
13.780	(0 8 00)	967
13.898	(0 9 00)	951
14.013	(0 10 00)	927
14.127	(0 11 00)	919
	Progression 2	
12.729	(0000)	-
12.874	(00 1 0)	1169
13.014	(00 2 0)	1129
13.152	(00 3 0)	1112
13.289	(00 4 0)	1104
13.435	(00 5 0)	1177
13.560	(00 6 0)	1108
13.694	(00 7 0)	1081
13.827	(00 8 0)	1073
13.959	(00 9 0)	1065

Cont....

14.090	(00 10 0)	1057
	Progression 3	
12.729	(0000)	-
12.859	(000 2)	1048
12.989	(000 4)	1048
13.118	(000 6)	1040
13.247	(000 8)	1040
13.375	(000 10)	1032
13.502	(000 12)	1024
13.628	(000 14)	1016
13.753	(000 16)	1008
13.877	(000 18)	1000
14.001	(000 20)	1000

TABLE III Ionization Potentials and vibrational frequencies of some of the ionic states of CH_2Cl_2 in the HeI region^a.

Ionic State	AIE	$\nu_1, \omega_e \times_e$	$\nu_2, \omega_e \times_e$	$\nu_3, \omega_e \times_e$	$\nu_4, \omega_e \times_e$
1^2B_2	11.320	-	-	716, 1.7	-
1^2B_1	11.357	-	-	712, 17.5	418, 9.2
1^2A_1	12.152	-	-	-	286, 4.8
1^2A_2	12.271	-	-	-	308, 5.7
2^2B_2	14.856	-	-	553, 5.9	-

^a See the footnotes of Table I.

TABLE IV Ionization energies and assignments of the 1^2B_2 and 1^2B_1 bands of CH_2Cl_2 .

State	IE, eV	Assignment	$\Delta G(v + 1/2)$, cm^{-1}
1^2B_2	11.320	(0000)	-
	11.404	(00 1 0)	677
	11.485	(00 2 0)	653
	11.560	(00 3 0)	604
	11.635	(00 4 0)	604
	11.700	(00 5 0)	524
	11.765	(00 6 0)	524
	11.825	(00 7 0)	484
1^2B_1	Progression 1		
	11.357	(0000)	-
	11.441	(00 1 0)	677
	11.520	(00 2 0)	637
	11.596	(00 3 0)	613
	11.666	(00 4 0)	565
	11.731	(00 5 0)	524
	11.795	(00 6 0)	516
	Progression 2		
	11.357	(0000)	-
	11.407	(000 1)	403
	11.454	(000 2)	379
	11.497	(000 3)	347
	11.538	(000 4)	331
11.577	(000 5)	315	
11.614	(000 6)	298	

Cont....

11.652	(000 7)	306
11.690	(000 8)	306
11.729	(000 9)	315
11.767	(000 10)	306
11.804	(000 11)	298
11.839	(000 12)	282
11.873	(000 13)	274

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

State	AIE	$v_1, \omega_e x_e$	$v_2, \omega_e x_e$	$v_3, \omega_e x_e$	$v_4, \omega_e x_e$
1^2B_2	11.734 ^b	-	-	-	481, 12.1
1^2A_2	-	1072, 8.1	-	-	-
1^2B_1	13.078	-	-	-	306, 2.5
1^2A_1	-	-	-	-	-
2^2B_2	14.126	-	-	375, 0.27	-

^a See the footnotes of Table I.

^b Estimated value, from the relation, $E_v = E_0 + \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2$.

TABLE VI Ionization energies and assignments of the ground ionic state (1^2B_2) of CF_2Cl_2 .

IE, eV	Assignment	$\Delta G (v + 1/2), cm^{-1}$
	Progression 1	
11.837	(000 2)	-
11.870	(000 3)	266
11.903	(000 4)	266
11.934	(000 5)	250
11.966	(000 6)	258
11.996	(000 7)	242
12.030	(000 8)	274
12.062	(000 9)	258
12.093	(000 10)	250
12.124	(000 11)	250
12.155	(000 12)	250
12.186	(000 13)	250
12.215	(000 14)	234
12.244	(000 15)	234
12.273	(000 16)	234
12.302	(000 17)	234
12.331	(000 18)	234
12.358	(000 19)	218
	Progression 2	
11.888	(002 2)	-
11.921	(002 3)	266
11.954	(002 4)	266

Cont....

11.984	(002 5)	242
12.016	(002 6)	258
12.047	(002 7)	250
12.078	(002 8)	250
12.108	(002 9)	242
12.138	(002 10)	242
12.168	(002 11)	242
12.198	(002 12)	242
12.227	(002 13)	234
12.256	(002 14)	234
12.285	(002 15)	234
12.314	(002 16)	234
12.340	(002 17)	210

Figure Captions

FIG. 1. a. HeI photoelectron spectrum of CH_2F_2 in the 12.5 - 20 eV region. The band assignments are based on C_{2v} symmetry. b. The ground ionic state of CH_2F_2 . The notation, 2_0^n stands for $\text{M}(\nu_2 = 0) \rightarrow \text{M}^+(\nu_2 = n) + \text{e}^-$. Spectra presented in this paper have been smoothed using a seven point smoothing function.

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.

FIG. 3. (a). The total photoelectron spectrum of CH_2Cl_2 . (b). The first four ionic states of CH_2Cl_2 .

FIG. 4. (a). The total photoelectron spectrum of CF_2Cl_2 . (b). The 1^2B_2 and 1^2A_2 bands of CF_2Cl_2 .

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 .

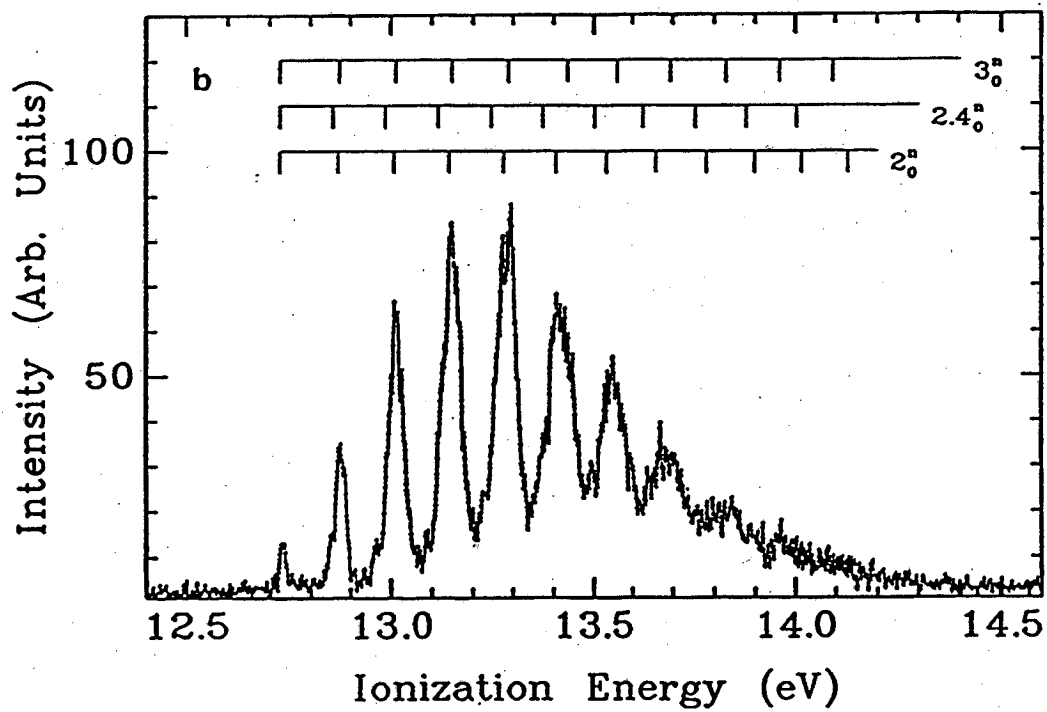
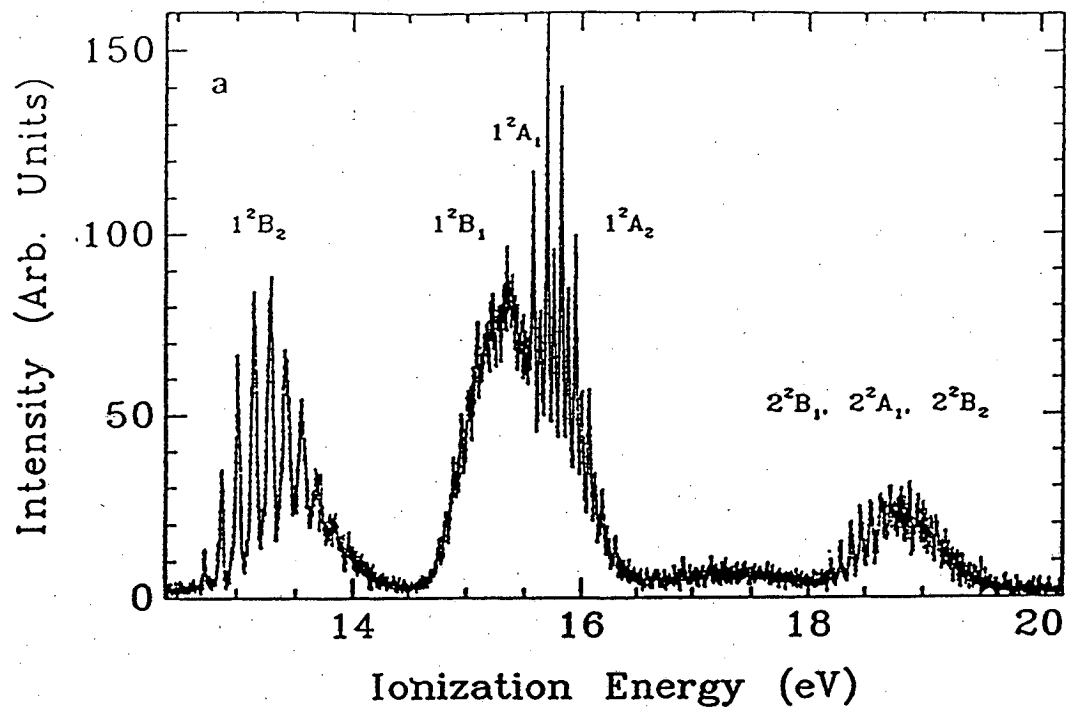


FIGURE 1

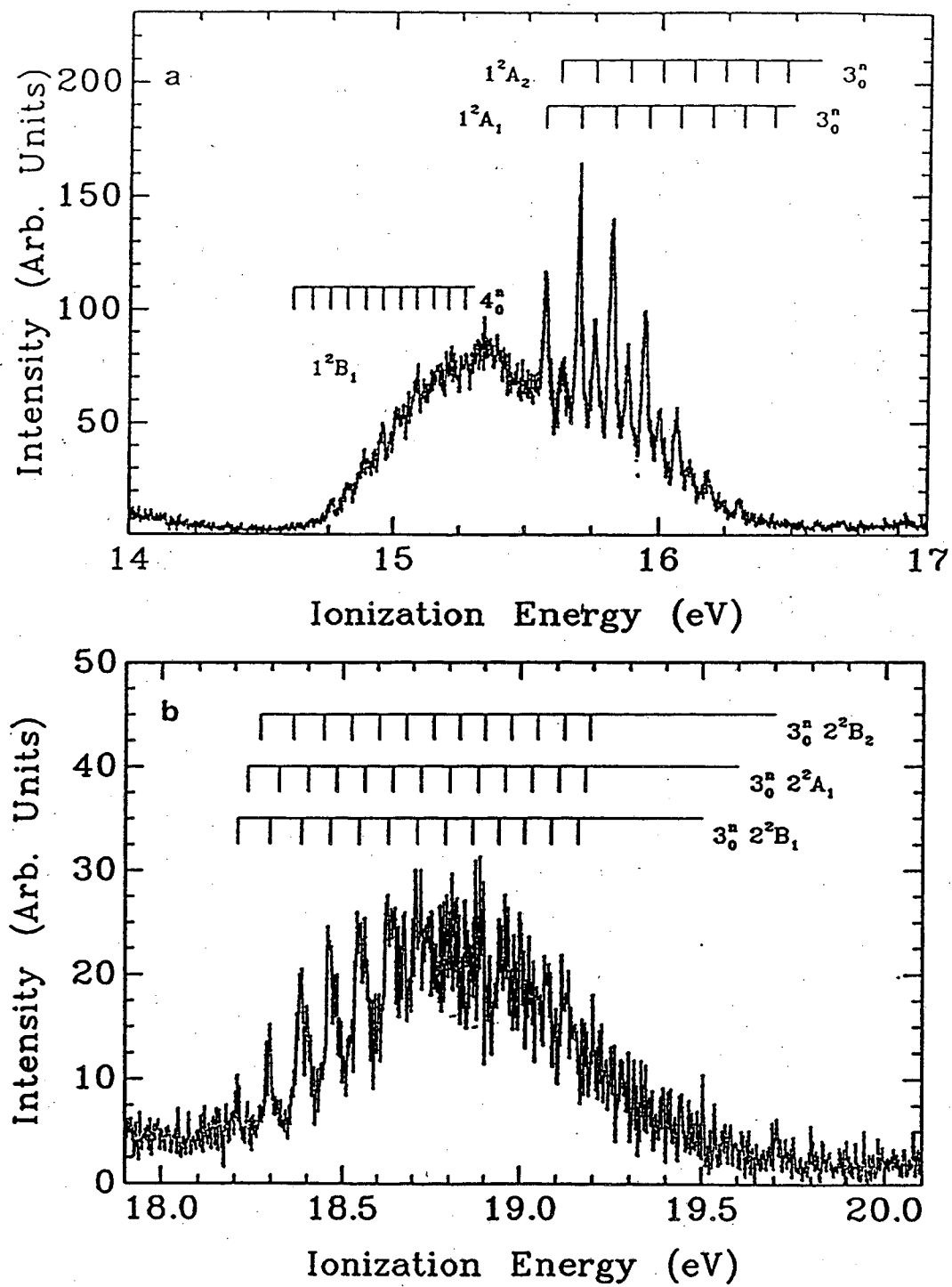


FIGURE 2

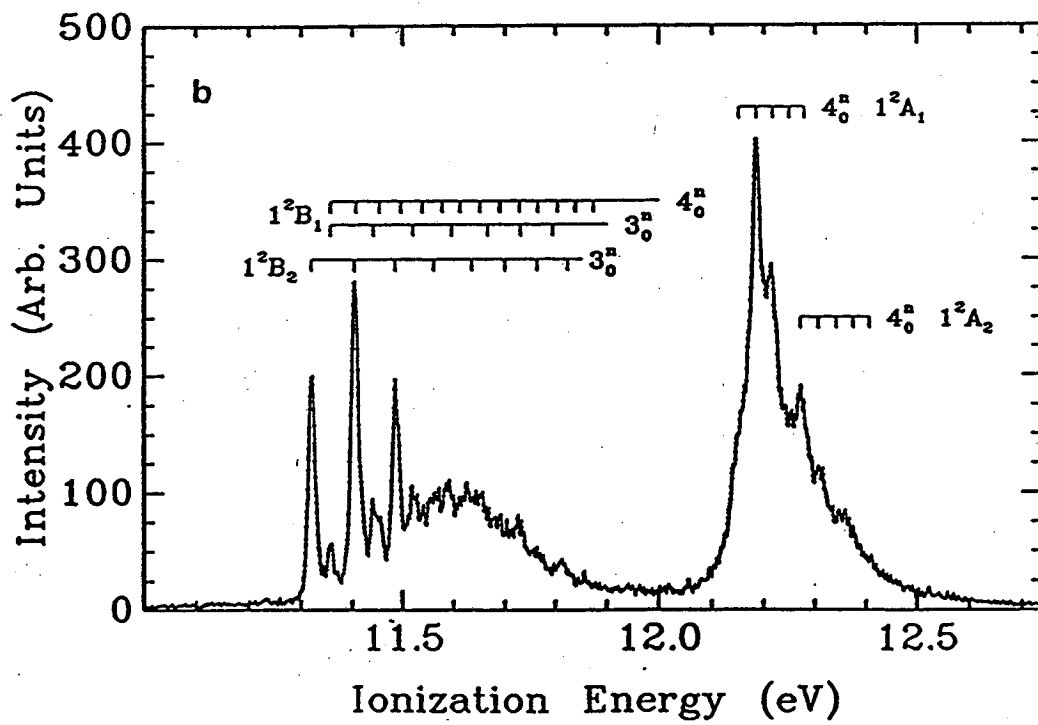
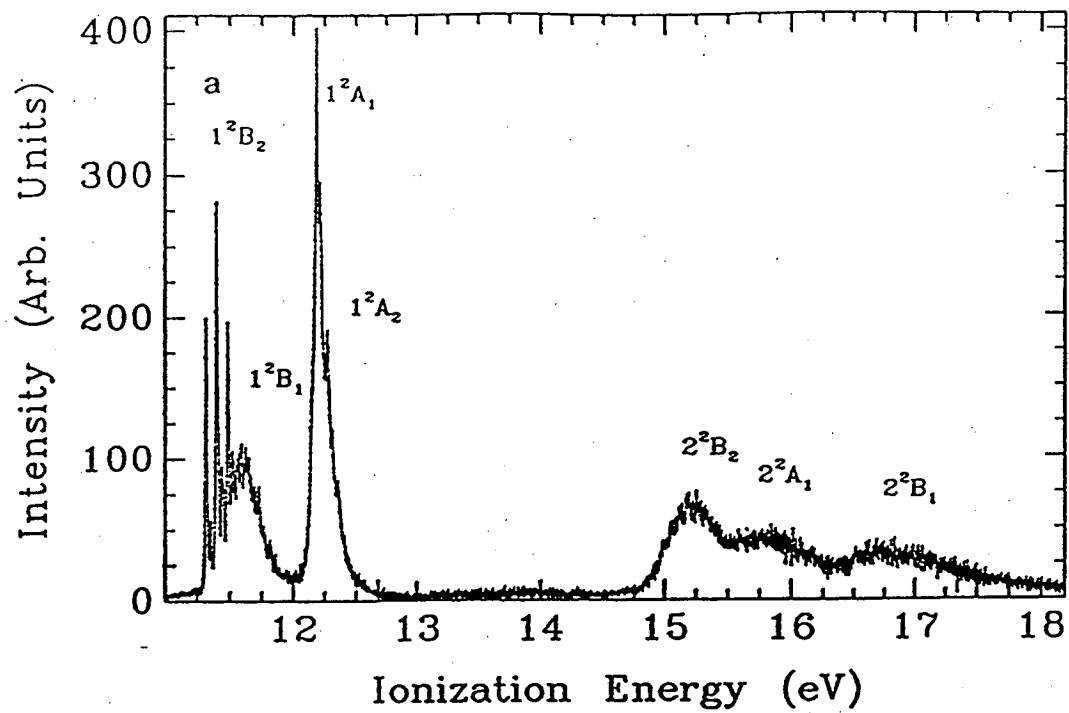


FIGURE 3

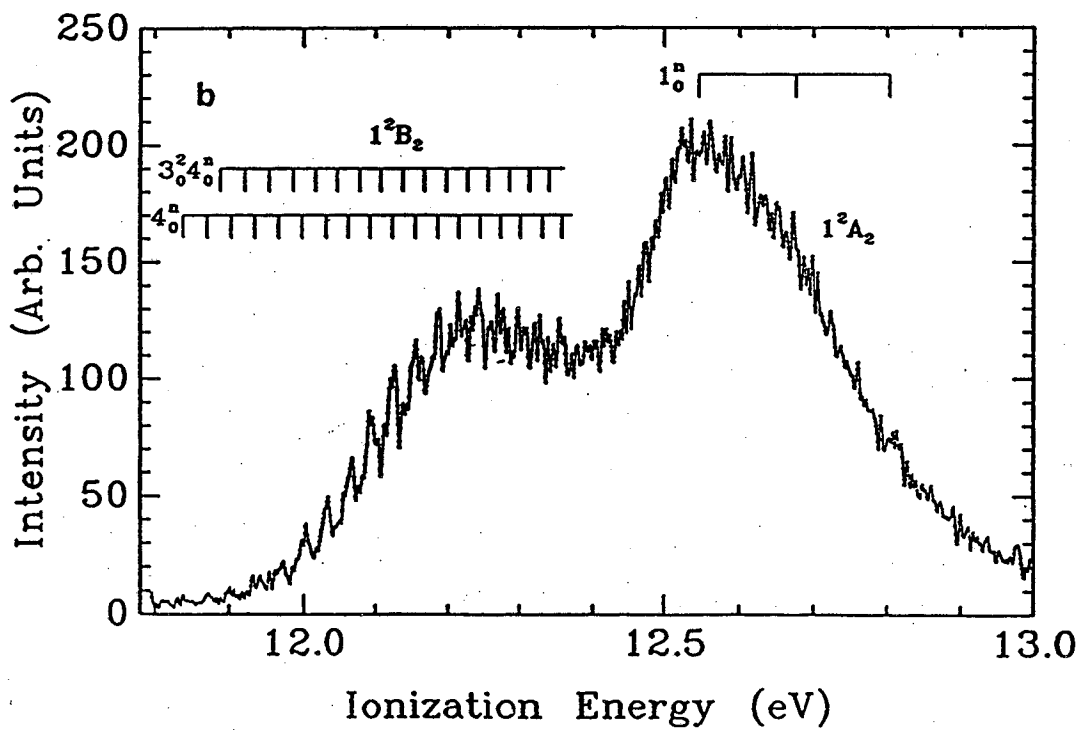
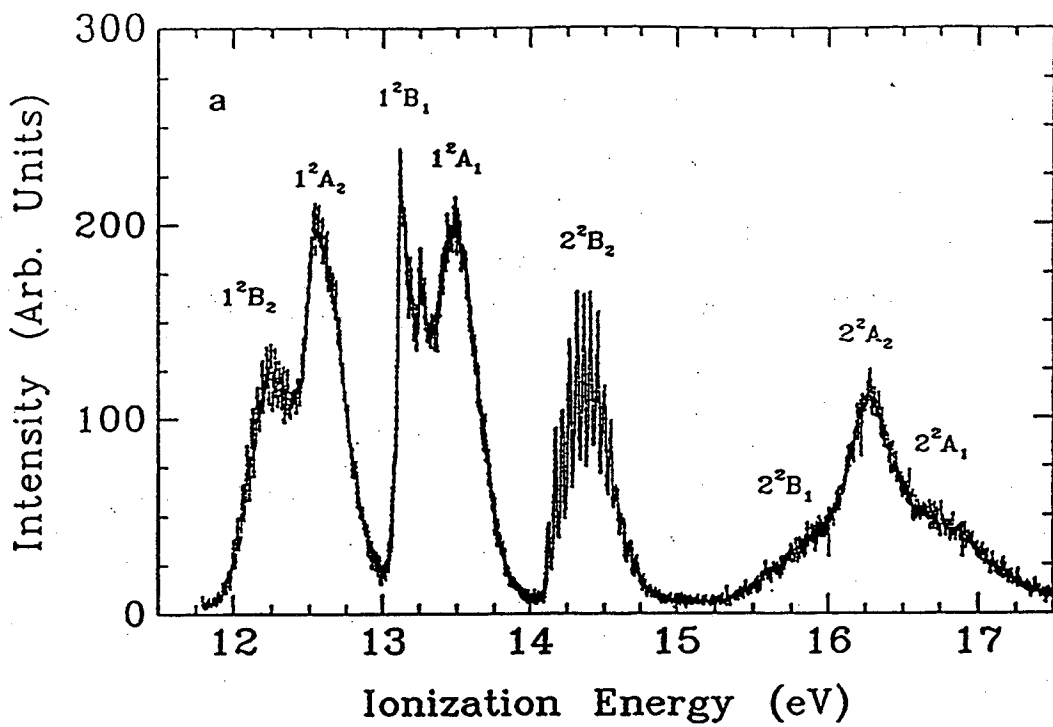


FIGURE 4

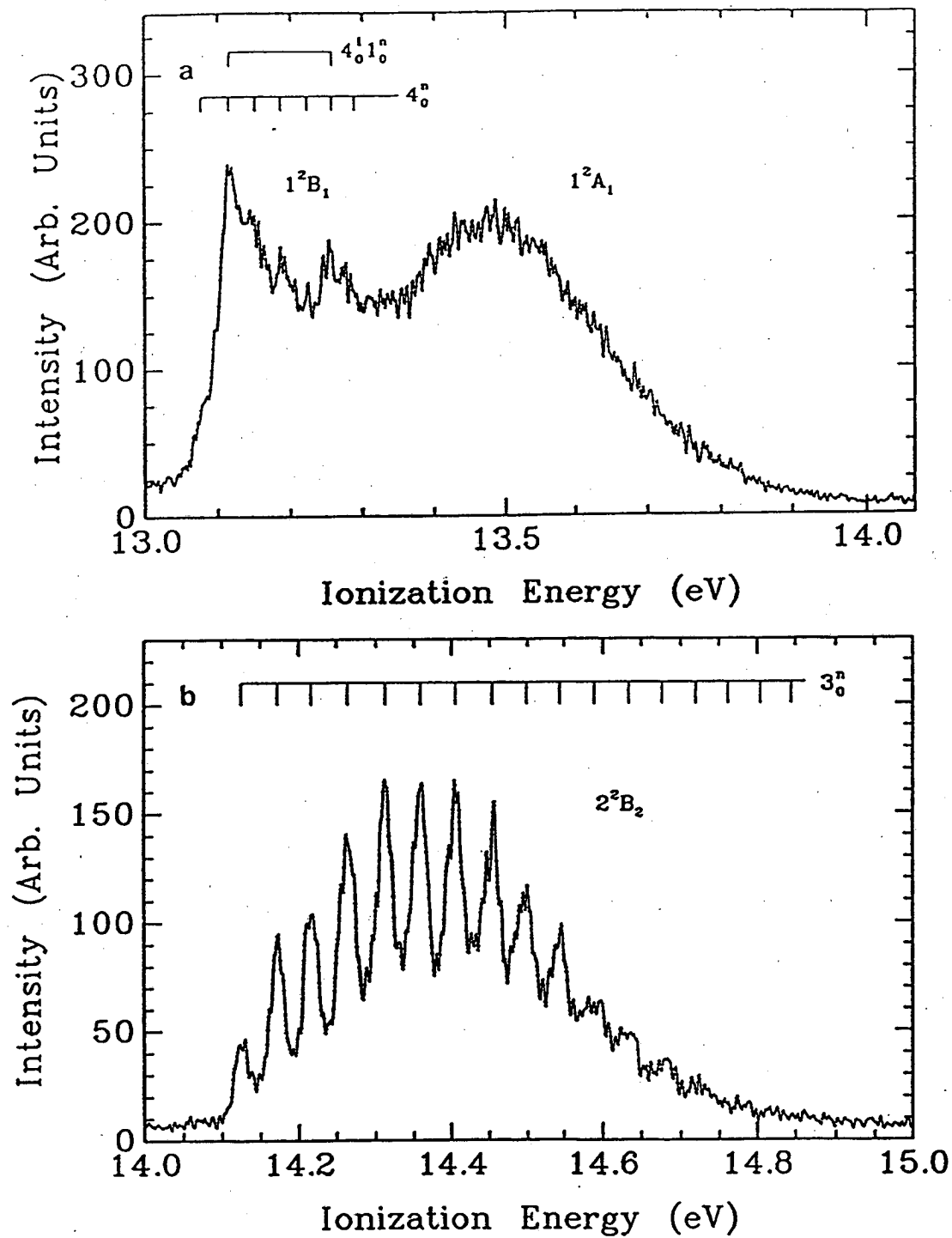


FIGURE 5

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