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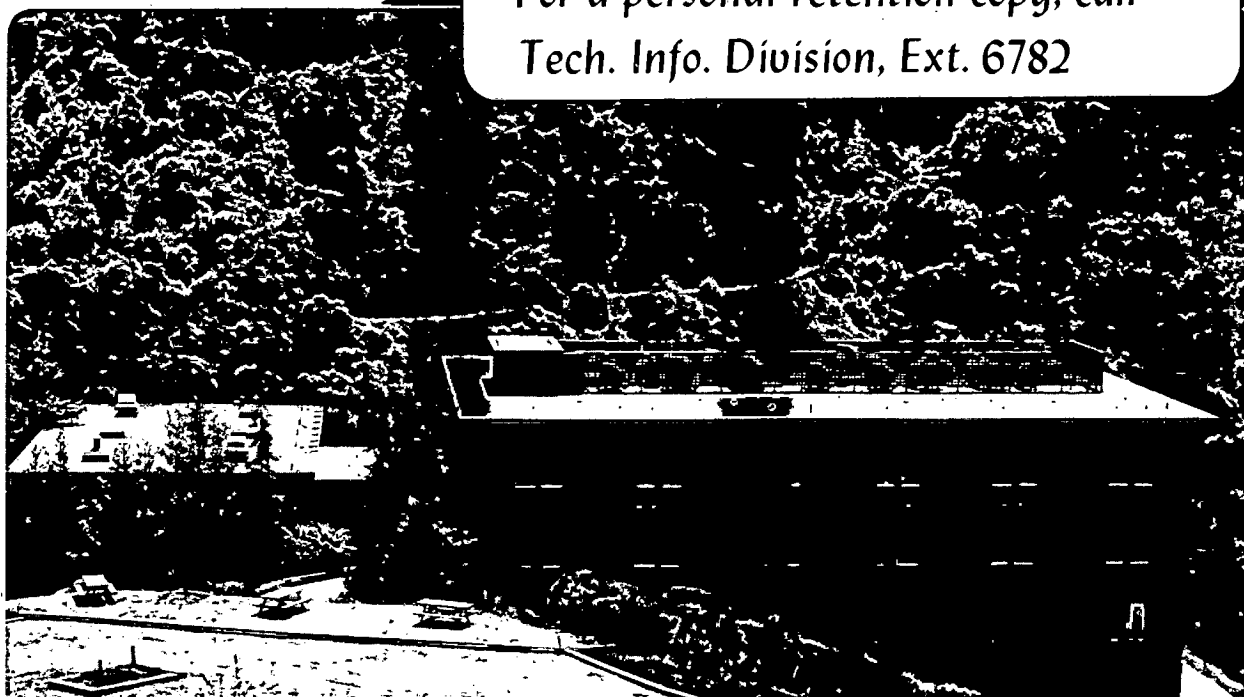
MULTIPHOTON IONIZATION PHOTOELECTRON SPECTROSCOPY
OF CCl_2F_2 AND CCl_3F

J. W. Hepburn, D.J. Trevor, J.E. Pollard,
D.A. Shirley and Y.T. Lee

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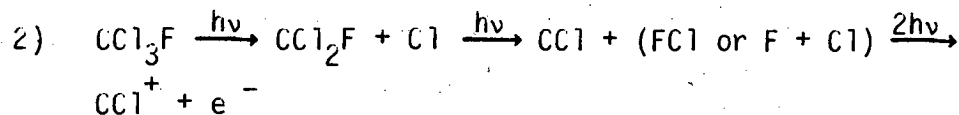
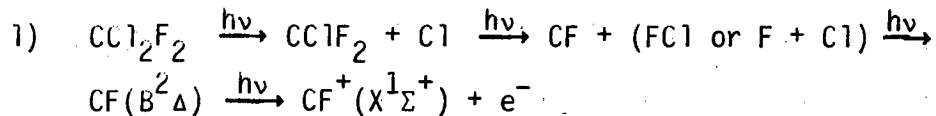
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In the past few years, there has been great interest in elucidating the detailed mechanism for the fragmentation that occurs during multiphoton ionization (MPI) of polyatomic molecules. This efficient and extensive fragmentation was quite surprising when it was first seen,¹ and only recently has the mechanism for fragmentation of benzene been made clear.²⁻⁵ The mechanism for benzene is a sequential one, in which initial absorption ionizes benzene to give C_6H_6^+ , and subsequent absorption of photons by this ion results in fragmentation.

In other molecules, radiationless processes in the neutral molecule can dramatically alter the nature of the multiphoton ionization process.⁶⁻⁸ In this Communication, we discuss a multiphoton ionization study of CCl_2F_2 and CCl_3F in which an ArF laser was used as the ionizing laser and the resulting photoelectrons were energy analyzed. Our data show that extensive and sequential fragmentation of the parent molecules to smaller neutral radicals precedes ionization, resulting in the formation of small fragment ions such as CF^+ and CCl^+ from the corresponding radicals, via such processes as:

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The experiments were performed with a molecular beam photoelectron spectrometer described in detail elsewhere.⁹ Briefly, CCl_2F_2 or CCl_3F molecules in a collimated supersonic beam were ionized with focused radiation from an ArF laser (Lumonics TE-861). The resulting ions could be mass analyzed by a quadrupole mass spectrometer, or the resulting photoelectrons could be energy-analyzed by an electrostatic energy analyzer equipped with a multichannel detector. The instrumental energy resolution used for these experiments was 20 meV (FWHM), as measured from the 584 Å photoelectron spectrum of Ar.

The laser was spatially filtered to less than 5 mJ/pulse and then loosely focused by a 50 cm focal length lens to a spot of $\sim 0.02 \text{ cm}^2$, resulting in power densities of less than 25 MW/cm^2 . The linewidth of the laser was measured to be 7 Å (FWHM), or about 25 meV, centered at 1933 Å (6.41 eV).

The electron energy spectra resulting from MPI of CCl_2F_2 and CCl_3F are shown in Fig. 1. No electrons were detected at energies above 4 eV in either case, and for both molecules the energy spectra below 2 eV were featureless continua. The regions of the measured spectra showing recognizable structure are shown in Fig. 1.

To minimize the effects of laser power fluctuations, each spectrum was recorded as a series of ten or more individual scans, which were then added. In each case the scan was from high to low kinetic energy, and the data as shown are uncorrected for the 20%-30% drop in laser power that occurred during each scan. The count rate for the 3.6 eV peak in the CCl_2F_2 spectrum was found to be proportional to the laser power to the 3.5 ± 0.5 power, implying that in order to form those electrons the system absorbs more than three photons.

The mass spectra of the ions formed by multiphoton ionization showed CF^+ to be the major ion formed in both cases. For CCl_2F_2 , the ions seen and their intensities relative to CF^+ were: CF^+ (1.0), CF_2Cl^+ (0.35), CCl^+ (0.15), C^+ (0.05). For CCl_3F , the ions seen and their relative intensities were: CF^+ (1.0), Cl_2^+ (0.8), CCl^+ (0.7), CFCl_2^+ (0.6), C^+ (0.2). In neither case was the parent molecular ion seen (CCl_2F_2^+ or CCl_3F^+).

Thus, CCl_2F_2 and CCl_3F are very similar to other molecules ionized by the ArF laser¹⁰ in that extensive fragmentation is seen. However, unlike benzene¹ and several other large molecules,¹¹ the parent ions are not observed, and in fact a small fragment, CF^+ , is the major product.

The fact that the parent ions are not observed is not surprising in light of the known photochemistry of these freons.^{12,13} The absorption spectra around 1933 Å are both structureless continua, and both molecules photodissociate with a unit quantum yield, the major channel being Cl atom elimination. Thus, as was seen in the case of $\text{C}_6\text{H}_5\text{I}$,⁷ the

photodissociation following the absorption of the first photon is too rapid to allow absorption of additional photons by the parent molecule which would result in parent ion formation.

The photoelectron spectra shown in Fig. 1 have several well resolved features, as well as underlying continua. In both cases, but especially with CCl_2F_2 , a vibrational progression with a large spacing can be seen. This sort of energy spectrum is typical of photoelectron spectra of diatomics,¹⁴ and can be assigned to be the result of two photon ionization of CF to give CF^+ , as shown in Fig. 1. Although the CF^+ vibrational spacing has not been previously measured, an estimate can be obtained from known Rydberg states in CF.¹⁵ The vibrational spacing expected is about $1800\text{--}1900\text{ cm}^{-1}$, and from the peaks observed the measured spectral constants for CF^+ are: $\omega_e = 1800 \pm 40\text{ cm}^{-1}$ ($223 \pm 5\text{ meV}$) and $\omega_e x_e = 10 \pm 10\text{ cm}^{-1}$ ($2 \pm 2\text{ meV}$). Although the ionization energy of CF has not been measured directly, it has been estimated from spectral data to be 8.9 eV ¹⁶ and derived from appearance potential data to be 9.23 ± 0.08 .¹⁷ Thus our measured value of $9.0 \pm 0.2\text{ eV}$ is what one would expect for CF. The major cause of uncertainty in this ionization potential is the difficulty of determining the absolute energy calibration of the electron energy analyzer for these experiments. It should be noted that despite this uncertainty in absolute electron energy, relative energies in a spectrum can be determined with high accuracy, about $\pm 10\text{ meV}$ in these experiments.

The fact that CF^+ is seen with high yield is a result of coincidence of the ArF wavelength with an absorption in CF .¹⁸ The band origin for the $X^2\Pi(v''=0) \rightarrow B^2\Delta(v'=2)$ absorption is at 1936 Å, which overlaps with the ArF laser spectral distribution. The intensities of the various vibrational states of CF^+ are determined by the intermediate state, which is a non-Rydberg state of CF .¹⁹ When reasonable corrections are made to account for overlapping bands in the energy spectrum, and laser power drift, the observed intensities agree with Franck-Condon factors calculated for transitions from $v=2$ of $B^2\Delta$ in CF to the final vibrational states in the $X^1\Sigma^+$ state²⁰ of CF^+ (for the $B^2\Delta$ state $B_e = 1.321 \text{ cm}^{-1}$,¹⁹ for the CF^+ X state B_e was estimated to be 1.725 cm^{-1} , based on the $A^2\Sigma^+$ and $D^2\Pi$ Rydberg states).

In CCl_3F , the energy spectrum due to two-photon ionization of CCl_3F is observed, as shown in Fig. 1. The 3.8 eV peak of CCl_2F_2 overlaps with a peak at higher energy assigned to CCl ionization. From the mass spectra, CCl_3F MPI results in about five times more CCl^+ than MPI of CCl_2F_2 (relative to CF^+ yield) which explains the observed difference in intensities for CCl^+ in the energy spectra. No information on ω_e and $\omega_e x_e$ can be obtained from these data, but the ionization potential for CCl can be determined to be $8.9 \pm 0.2 \text{ eV}$ (0.1 eV lower than CF). The only previous determination of the IP of CCl is by the reaction threshold technique²¹ which gives an upper limit of 10.6 eV, and on the basis of chemical intuition, a value less than or equal to that for CF would be expected.

The other features in the spectrum which are not given assignments are most likely due to two photon ionization of larger fragments of the parent molecules. The conclusion that can be drawn from the data presented here is that the mechanism of CCl_2F_2 and CCl_3F is photofragmentation of the parent molecule into neutral fragments, followed by two-photon ionization of these fragments. Data on other halocarbons, to be discussed in a future paper, would indicate that this is generally the case in MPI of freons with the ArF laser.

ACKNOWLEDGMENTS

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract Number W-7405-Eng-48. The laser used in these experiments was borrowed from the San Francisco Laser Center. This material is based on work supported by the National Science Foundation under Grant Number CHE79-16250 awarded to the University of California at Berkeley in collaboration with Stanford University. We would like to thank C. W. Matthews for useful discussions about the CF spectrum.

REFERENCES

1. a) L. Zandee, R. B. Bernstein and D. A. Lichtin, J. Chem. Phys. 69, 3427 (1978). b) L. Zandee and R. B. Bernstein, J. Chem. Phys. 70, 2574 (1979). c) L. Zandee and R. B. Bernstein, J. Chem. Phys. 71, 1359 (1979).
2. a) S. Rockwood, J. P. Reilly, K. Hohla and K. L. Kompa, Optics Commun. 28, 175 (1979). b) U. Boesl, H. J. Neusser and E. W. Schlag, J. Chem. Phys. 72, 4327 (1980).
3. John T. Meek, Robert K. Jones and James P. Reilly, J. Chem. Phys. 73, 3503 (1980).
4. R. S. Pangolphi, D. A. Gobel and M. A. El-Sayed, J. Phys. Chem. 85, 1779 (1981).
5. Y. Achiba, K. Sato, K. Shobatake and K. Kimura, J. Photochem. 17, 53 (1981).
6. J. D. Reilly and K. L. Kompa, Adv. Mass. Spec. 8, 1800 (1979).
7. T. G. Dietz, M. A. Duncan, M. G. Liverman and R. E. Smalley, J. Chem. Phys. 73, 4816 (1980).
8. R. J. S. Morrison, B. H. Rockney and E. R. Grant, J. Chem. Phys. 75, 2643 (1981).
9. J. E. Pollard, D. J. Trevor, Y. T. Lee and D. A. Shirley, Rev. Sci. Instrum. 52, xxxx (1981).
10. M. Seaver, J. W. Hudgens and J. J. Decorpo, Int. J. Mass Spectr. Ion. Phys. 34, 159 (1980).

11. a) D. M. Lubman, R. Naaman and R. N. Zare, J. Chem. Phys. 72, 3034 (1980). b) D. H. Parker, R. B. Bernstein and D. A. Lichtin, J. Chem. Phys. 75, 2577 (1981). c) T. E. Carney and T. Baer, J. Chem. Phys. 75, 4422 (1981).
12. R. Milstein and F. S. Rowland, J. Phys. Chem. 79, 669 (1975).
13. R. E. Rebbert and P. Ausloos, J. Photochem. 4, 419 (1975).
14. J. Berkowitz, Photoabsorption, Photoionization and Photoelectron Spectroscopy (Academic Press, 1979), p.186 ff.
15. W. P. White, R. M. Pitzer, C. W. Matthews and T. H. Dunning Jr., J. Molec. Spectr. 75, 318 (1979).
16. P. K. Carroll and T. P. Grennan, J. Phys. B: Atom. Molec. Phys. 3, 865 (1970).
17. T. A. Walter, C. Lifshitz, W. A. Chupka and J. Berkowitz, J. Chem. Phys. 51, 3531 (1969).
18. W. P. White Jr., Ph.D. Thesis, Ohio State University, 1971.
19. T. H. Dunning Jr., W. P. White, R. M. Pitzer and C. W. Matthews, J. Molec. Spectr. 75, 297 (1979).
20. The Franck-Condon factors calculated for $CF\ B^2\Delta(v'' = 2) \rightarrow CF^+\ X^1+$ ($v' = 0,1,2,3,4,5,6$) are (normalized to $v' = 0$): 1.00, 1.48, 0.22, 0.45, 1.24, 0.16, 0.67. The intensities (corrected for laser power drift) measured for CF^+ formed in MPI of CCl_2F_2 are: 1.00, 1.3 ± 0.3 , 0.2 ± 0.1 , <1.5 , 1.6 ± 0.4 , <0.5 , 0.7 ± 0.3 . The peaks corresponding to CF^+ formed in $v' = 3$ or $v' = 5$ are obscured by peaks due to other ions.

21. L. C. Frees, P. L. Pearl, and W. S. Koski, Chem. Phys. Lett. 63, 108 (1979).
22. K. P. Huber, and G. Herzberg, Constants of Diatomic Molecules (Van Nostrand Reinhold, 1979) p.126.

FIGURE CAPTIONS

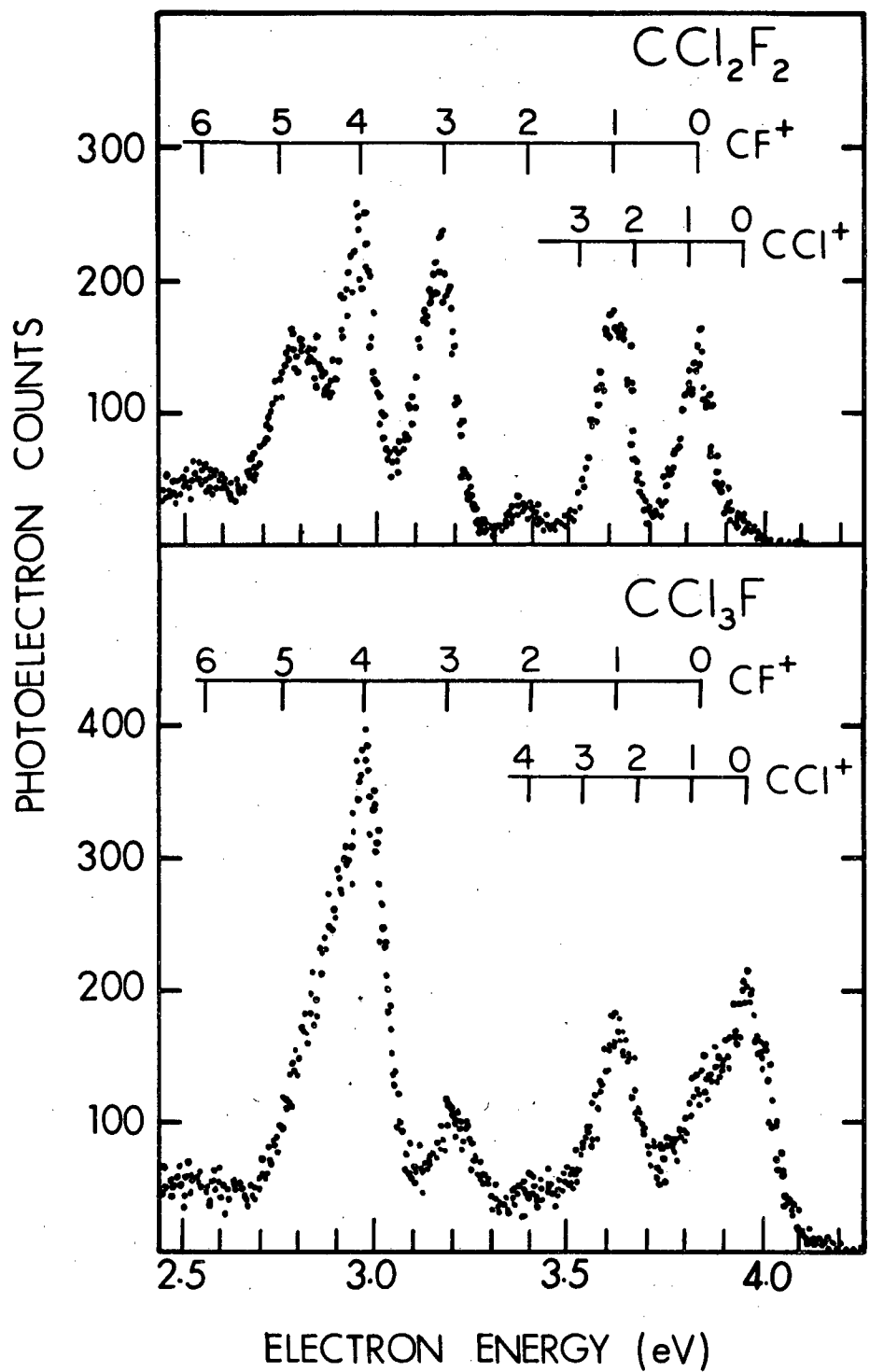
Fig. 1. Photoelectron kinetic energy spectra for electrons formed by ArF laser multiphoton ionization of CCl_2F_2 and CCl_3F .

Assignments are indicated for two-photon ionization of CF and CCl to give CF^+ and CCl^+ in various vibrational states.

Positions for CF^+ peaks were calculated using constants given in text. (I.P. = 9.0 eV, $\omega_e = 0.223$ eV, $\omega_e x_e = 0.002$

eV.) Positions shown for CCl^+ were calculated using an I.P.

of 8.9 eV, and $\omega_e = 0.146$ eV, $\omega_e x_e = 0.001$ eV.²²



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Fig. 1

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