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Electronic Spectra of CF$_2$Cl and CFCl$_2$ Radicals Observed by Resonance-Enhanced Multiphoton Ionization

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CFCl$_2$ and CF$_2$Cl radicals were observed between 365 and 410 nm by resonance-enhanced multiphoton ionization spectroscopy. Both spectra were generated by two-photon resonances with planar 3p Rydberg states. A third laser photon ionized the radicals. The CF$_2$Cl spectrum displayed a vibrational progression assigned to the out-of-plane bending ν_4' (b$_1$) OPLA mode ($\omega_4' = 745$ cm^{-1}), with the origin at 406.2 nm ($\nu_{0-0} = 49\,230$ cm^{-1}). Assignments for the CFCl$_2$ radical included the ν_4' (b$_1$) OPLA ($\omega_4' = 590$ (20) cm^{-1}) and the ν_3' (a$_1$) CCl$_2$ scissors ($\omega_3' = 270$ (30) cm^{-1}) modes, with the origin at 401.1 nm ($\nu_{0-0} = 49\,850$ cm^{-1}).

Introduction

Fluorine- and chlorine-substituted methyl radicals are relevant to important practical and theoretical topics. Halogenated methyl radicals play significant roles in the ozone destruction in the upper atmosphere, halocarbon-based fire suppression, and plasma etching of semiconductor surfaces during IC chip manufacture. To the development of molecular orbital theory, the halogenated methyl radicals represent an ensemble of species that are becoming accessible to the most accurate levels of computation. Thus, the paucity of experimental data pertaining to them is surprising.

In this paper we report the first observation of any electronic spectra for the CF$_2$Cl and CFCl$_2$ radicals. The spectra were observed between 365 and 415 nm by resonance-enhanced multiphoton ionization spectroscopy (REMPI). The vibrational structure of these states is analyzed, and the REMPI mechanisms that generate the spectra are assigned. The REMPI bands discussed here appear suitable for detecting these radicals in other environments.

ESR spectroscopy has established that the ground states of CF$_2$Cl and CFCl$_2$ radicals are nonplanar.[1,2] Recent molecular orbital calculations by Luke et al.[3] predict that both of these CXY$_2$ radicals possess nonplanar structures which belong to the C_s point group. According to these ab initio calculations, in CF$_2$Cl the C–Cl bond is 45.3° out of the CF$_2$ plane and in CFCl$_2$ the C–F bond is 41.2° out of the CCl$_2$ plane. The calculations also predict that the barriers to inversion through the planar structures should be $B_{inv} = 6225$ cm^{-1} and $B_{inv} = 2690$ cm^{-1} in the CF$_2$Cl and CFCl$_2$ radicals, respectively.[3]

To a large degree, the number of electrons that occupy the carbon p$_z$ orbital determines the equilibrium bond angle and the B_{inv} in each electronic state of a CXY$_2$ radical. Nonplanar structures are stabilized in their ground electronic states by one carbon p$_z$ orbital electron. Since Rydberg states associated with the first ionization potential have vacant carbon p$_z$ orbitals, their p$_z$ orbital interactions are minimal and the Rydberg states are planar. Electronic transitions to valence or Rydberg states add or remove one p$_z$ orbital electron. The change in the p$_z$ orbital population will change the form of the out-of-plane bending (OPLA) potential energy function. As a result, all electronic spectra of CXY$_2$ radicals should exhibit prominent ν_4' OPLA mode vibrational band progressions.

Since most of the bands observed in the present REMPI spectra will originate from transitions involving the ν_4 OPLA mode, general characteristics and transition selection rules of the OPLA mode are presented here. We have estimated the ground-state ν_4 OPLA potential energy levels by solving the Hamiltonian for the potential, $V = aQ^4 - bQ^2$,[4,5] and by adopting the radical geometries and B_{inv}'s reported by Luke et al.[3] According to our

calculations, the $\nu_4'' = 0$, 1 levels in both radicals are separated by <0.1 cm^{-1}. Higher $\nu_4'' = 2n$, $2n + 1$ ($n = 1, 2, 3, ...$) levels that lie below the inversion barrier energy also pair up. The energy gap that separates the $\nu_4'' = 0$, 1 levels from the $\nu_4'' = 2$, 3 levels is 260 (40) cm^{-1} for both radicals.

Although the static ground-state equilibrium geometries of CXY$_2$ radicals belong to the C_s point group, the ν_4 OPLA mode vibrational wave functions belong to the C_{2v} point group and the odd parity members are of b$_1$ symmetry.[6] Thus, transitions from the ground electronic state to nonplanar (C_s) and planar (C_{2v}) excited states are governed by the vibrational selection rule, $\Delta\nu_4 = 0, \pm2, \pm4, ...$[7,8] Electronic transitions from the ground-state $\nu_4'' = 0$ level may access only $\nu_4' =$ even levels of the upper electronic state. Similarly, electronic transitions from the ground-state $\nu_4'' = 1$ level may access only $\nu_4' =$ odd levels of the excited upper electronic state. Ironically, because the $\nu_4'' = 0$, 1 levels are nearly degenerate, the observed spectrum will appear identical with one governed by a $\Delta\nu_4 = 0, \pm1, \pm2, \pm3, ...$ selection rule.

We note that totally symmetric vibrational modes are governed by the rule $\Delta\nu = 0, \pm1, \pm2, \pm3, ...$ and that other non-totally-symmetric vibrational modes are governed by the rule $\Delta\nu = 0, \pm2, \pm4, ...$

Apparatus and Methods

The apparatus and procedures used during this study are described in detail elsewhere.[5] Briefly, the apparatus consisted of a flow reactor which produced the free radicals, an excimer pumped dye laser which ionized the radicals, a time-of-flight mass spectrometer, and a computer/data acquisition system. Radicals were produced in a flow reactor by the reactions

$$F + CHF_2Cl \rightarrow CF_2Cl + HF$$

$$F + CHFCl_2 \rightarrow CFCl_2 + HF$$
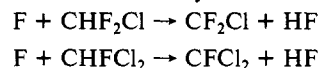
Free radicals produced in the flow reactor effused into the ion source of the time-of-flight mass spectrometer where they were ionized by a focused laser beam (energy = 10–20 mJ/pulse; bandwidth = 0.2 cm^{-1} fwhm; focal length = 250 mm). The mass spectrometer resolved the ions, and those of the appropriate mass were selected and averaged with a gated integrator. The spectra

(1) Cooper, J.; Hudson, A.; Jackson, R. A. *Mol. Phys.* **1972**, *23*, 209.
(2) Bowles, A. J.; Hudson, A.; Jackson, R. A. *Chem. Phys. Lett.* **1970**, *5*, 552.
(3) Luke, B. T.; Loew, G. H.; McLean, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 1307.
(4) Laane, J. *Appl. Spectrosc.* **1970**, *24*, 73.
(5) Johnson III, R. D.; Tsai, B. P.; Hudgens, J. W. *J. Chem. Phys.* **1988**, *89*, 4558.
(6) Herzberg, G. *Molecular Spectra and Molecular Structure*; van Norstrand Reinhold: New York, 1966; Vol. III, p 150.
(7) *Advances in Multiphoton Processes and Spectroscopy*; Lin, S. H., Ed.; World Scientific Publishing: Singapore, 1988; Vol. 4, pp 171–296.
(8) Lias, S. G.; Barmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

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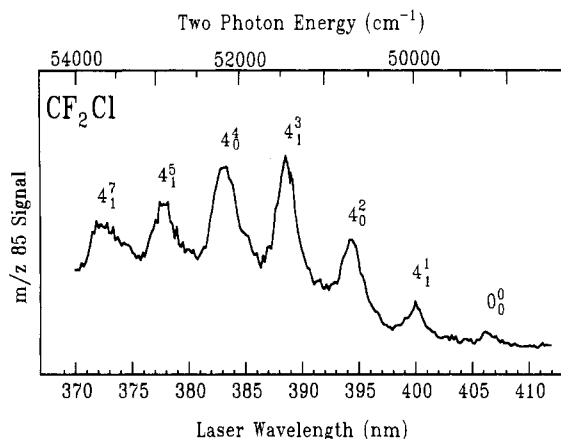‡ Formerly called the National Bureau of Standards.

Two Photon Energy (cm^{-1})

Figure 1. The composite spectrum of the CF$_2^{35}$Cl radical (m/z 85) between 365 and 412 nm.

TABLE I: Band Maxima, Assignments, and Spacings Observed in the REMPI Spectrum of the CF$_2^{35}$Cl Radical between 370 and 430 nm^a

assign	band max λ_{air}, nm	two-photon energy, cm^{-1}	$\nu - \nu_0$ interval, cm^{-1}	band interval, cm^{-1}
0_0^0	406.2	49 220	0	
				765
4_1^1	400.0	49 985	765	
				710
4_0^2	394.4	50 695	1475	
				730
4_1^3	388.8	51 425	2205	
				755
4_0^4	383.2	52 180	2960	
				730
4_1^5	377.9	52 910	3690	
				780
4_0^6	372.4	53 690	4470	

^{a} The broadness of each REMPI band limits the measurement precision to ±0.25 nm (±30 cm^{-1}).

shown here are composites of spectra taken with the laser dyes: DMQ (346–377 nm), QUI (368–405 nm), DPS (395–415 nm), and stilbene 420 (412–430 nm).

Results and Analyses

The Spectrum of CF$_2$Cl. Figure 1 displays the composite mass-resolved REMPI spectrum of the CF$_2^{35}$Cl radical (m/z 85) observed between 370 and 412 nm. All chemical and mass spectral data support the assignment of the spectrum to the CF$_2$Cl radical. An essentially identical, but weaker, m/z 87 REMPI spectrum corresponding to the CF$_2^{37}$Cl radical was also observed. The m/z 85, 87 ion signals were proportional to the reactant concentrations. Whenever the microwave discharge that generated the fluorine atoms was extinguished, the REMPI signals ceased. Laser ionization did not appear to induce fragmentation; the REMPI spectra were carried only by molecular cations.

From the heat of formation measured for the CF$_2$Cl ion[8] and radical,[9] we estimate an ionization potential of 8.23 eV. To ionize at laser wavelengths between 370 and 412 nm, CF$_2$Cl radicals must absorb three laser photons. The Rydberg formula ($h\nu =$ IP $- R/(n - \delta)^2$) predicts the 3p Rydberg state will be in the range 46 950–50 150 cm^{-1}.

Table I presents the band maxima observed in the REMPI spectrum of the CF$_2^{35}$Cl radical between 370 and 430 nm. The state energies and vibrational intervals shown in Table I assume that the spectrum arises from a two-photon absorption process. The REMPI bands between 370 and 406 nm form one progression of regularly spaced bands with two-photon intervals of 745 (25) cm^{-1}. We dismiss the possibility that the resonant excited state lies at the energy of one laser photon. The vibrational frequency implied by a one-photon assignment (373 cm^{-1} for a symmetric or 181 cm^{-1} for an antisymmetric vibration) is too small to account for any excited-state vibrational mode of CF$_2$Cl.

We have assigned the observed progression to the ν_4' out-of-plane bending (OPLA) mode. The change in the equilibrium

geometry between the ground state and the excited state gives rise to the ν_4' progression. This ν_4' mode assignment is also supported by the vacuum-UV[10] and REMPI[11] spectra of the analogous radical, CF$_3$. The spectra of the CF$_3$ radical also exhibited extensive ν_4' OPLA progressions. The average interval along these ν_4' progressions was 820 cm^{-1}.

An alternate assignment of this progression to any other vibrational mode is not supported. The REMPI band intervals lie outside those expected for valence or Rydberg state ν_1' and ν_5' C–F stretching modes (1400–1510 cm^{-1}) or for the ν_3' CF$_2$ scissors mode ($\sim$600 cm^{-1}).[12] Even though the interval $2h\nu = 745$ cm^{-1} resembles the ground-state C–Cl stretch frequency of $\omega_2'' = 761$ cm^{-1} observed in an Ar matrix,[12] a long progression in such a mode is not expected. Thus, the only reasonable assignment for the 745-cm^{-1} progression is to the ν_4' OPLA mode.

The terminus of the vibrational progression at 406.2 nm ($2h\nu = 49 220$ cm^{-1}) is the apparent electronic origin of this state. This origin falls within the range predicted for a 3p Rydberg state. Using this origin assignment and our estimated ionization potential for CF$_2$Cl to solve the Rydberg equation, we find a quantum defect of $\delta = 0.47$. CF$_2$Cl radicals in a 3p Rydberg state can ionize after absorbing one laser photon; i.e., the ion signal is generated through a 2 + 1 REMPI mechanism.

The Spectrum of CFCl$_2$. Figure 2 displays the composite mass-resolved REMPI spectrum of the CF^{35}Cl$_2$ radical (m/z 101) observed between 365 and 414 nm. Essentially identical spectra were observed at m/z 103 (CF$_2^{35}$Cl^{37}Cl) and m/z 105 (CF^{37}Cl$_2$). As expected from the $\sim$3:1 ratio of the ^{35}Cl and ^{37}Cl isotopic abundances, the intensities of the m/z 101, 103, 105 signals conformed to the ratios 10:6.5:1. The m/z 101, 103, 105 signal intensities were proportional to the reactant concentration, and the signals ceased whenever the microwave discharge was extinguished. Thus, all mass spectral and chemical data support the assignment of the spectrum to the CFCl$_2$ radical. Laser ionization did not appear to induce fragmentation; the REMPI spectra were carried only by molecular cations.

Table II presents the band maxima observed in the REMPI spectrum of the CF^{35}Cl$_2$ radical between 365 and 414 nm. The REMPI bands form two regularly spaced vibrational progressions labeled "A" and "B" in Table II. Both progressions have the same average interval of $2h\nu = 590$ (20) cm^{-1}. Using the same reasoning process described above for the CF$_2$Cl radical, we have assigned the source of the intervals along these progressions to the ν_4' OPLA mode. The regularity of the ν_4' OPLA intervals supports our assignment of the REMPI spectrum to two-photon resonances with a planar Rydberg state of the CFCl$_2$ radical.

From previous experience we expect that the double progression in Figure 2 should be comprised of a fundamental progression of 4_n^m ($n = 1, 2, 3, ...; m = 1, 0, 1, ...$) bands and a combination band progression formed from a second vibrational interval in conjunction with the $v_4' = 0, 1, 2, 3, ...$ quantum levels. The candidates for the lowest energy band of the combination band progression are (1) the 3_1^0 band, a hot band of the ground state which would indicate that ω_3'' (CCl$_2$ sciss) $= 270$ cm^{-1}; (2) the 4_1^1 band, a hot band of the ground state which would indicate that ω_4' (OPLA) $= 270$ cm^{-1}; (3) the 3_0^1 band which would indicate that ω_3' (CCl$_2$ sciss) $= 270$ cm^{-1}; and (4) the 2_0^1 band which would indicate that ω_2' (CCl$_2$ sym str) $= 860$ cm^{-1}. The candidate frequencies of 270 (30) and 860 (30) cm^{-1} originate from the combination differences between the A and B progressions. Below, we show that candidate 3 best supports the data.

Hot band assignments do not account for the nearly equal intensities of the A and B progressions. Candidates 1 and 2 propose that the combination band progression is built upon populated (or "hot") $v_3'' = 1$ or $v_4'' = 2, 3$ ground-state vibrational level(s) in combination with the ν_4' OPLA mode of the Rydberg

(9) Leyland, L. M.; Majer, J. R.; Robb, J. C. *Trans. Faraday Soc.* **1969**, *65*, 898.

(10) Basco, N.; Hathorn, F. G. M. *Chem. Phys. Lett.* **1971**, *8*, 291.
(11) Duignan, T.; Hudgens, J. W.; Wyatt, J. R. *J. Phys. Chem.* **1982**, *86*, 4156.
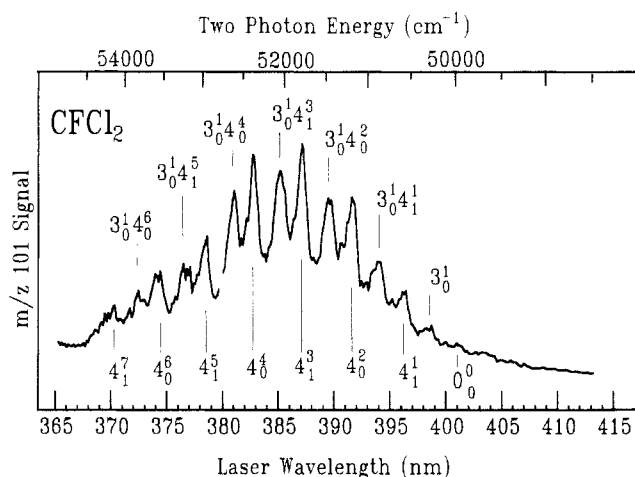(12) Jacox, M. *J. Phys. Chem. Ref. Data* **1984**, *13*, 945.
(13) Lindeman, L. P.; Wilson, M. K. *J. Chem. Phys.* **1956**, *24*, 242.
(14) Overend, J.; Evans, J. C. *Trans. Faraday Soc.* **1959**, *55*, 1817.

TABLE II: Band Maxima Observed in the REMPI Spectrum of the $CF^{35}Cl_2$ Radical between 370 and 415 nm, Their Vibrational Assignments, and Intervals[a]

assign	band max λ_{air}, nm	two-photon energy, cm^{-1}	$\nu - \nu_0$ interval, cm^{-1}	progression A, cm^{-1}	progression B, cm^{-1}
0_0^0	401.1	49850	0		
3_0^1	398.6	50160	300		
4_0^1	396.5	50430	580	580	
$3_0^1 4_0^1$	394.1	50735	885		575
4_0^2	391.8	51030	1180	600	
$3_0^1 4_0^2$	389.7	51310	1460		575
4_0^3	387.2	51640	1790	610	
$3_0^1 4_0^3$	385.2	51905	2055		595
4_0^4	382.9	52220	2370	580	
$3_0^1 4_0^4$	381.2	52450	2600		545
4_0^5	378.6	52810	2960	590	
$3_0^1 4_0^5$	376.8	53060	3210		610
4_0^6	374.4	53400	3550	590	
$3_0^1 4_0^6$	372.5	53675	3825		615
4_0^7	370.3	53995	4145	595	

[a] The measurement precision is ±0.2 nm (±25 cm^{-1}).

Figure 2. The composite spectrum of the $CF^{35}Cl_2$ radical (m/z 101) between 365 and 415 nm.

state. Since the ν_4' OPLA fundamental progression is built from the vibrationless ground state, the intensity ratio of the combination band progression and the ν_4' OPLA fundamental progression should reflect the population ratio of the hot and vibrationless levels. The temperature of our flow reactor during these studies ranged between 300 and 400 K. At these temperatures calculations predict that a ground state vibrational level which lies at 270 cm^{-1} possesses between 30% and 40% of the population that the vibrationless state possesses. This partitioning of the ground electronic state population would predict that the intensity ratio of the A and B progressions should lie between 1:3 and 2:5. Instead, both progressions exhibit nearly equal intensities. Thus, we dismiss the possibility that the combination band progression originates from hot band activity.

Candidates 3 and 4 propose that the combination band progression arises from activity along a second vibrational mode of the Rydberg state. Candidate 3 proposes that the ν_3' CCl_2 scissors mode is active and that the Rydberg 0_0^0 band lies at 401.1 nm. Candidate 4 proposes that the ν_2' CCl_2 symmetric stretch is active and also that unfavorable Franck–Condon factors between the nonplanar ground state and planar Rydberg state have caused the 0_0^0 band to be undetectable. An extrapolation of the A and B progressions would predict the origin to lie near 406 nm ($2h\nu$ = 49260 cm^{-1}).

The gas-phase vibrational frequencies of $BFCl_2$ and $COCl_2$ listed in Table III can be used to determine whether candidates 3 and 4 predict reasonable vibrational frequencies for the $CFCl_2$ Rydberg radical. This approach is reasonable because $BFCl_2$ and $COCl_2$ are isoelectronic with the $CFCl_2$ cation; the $CFCl_2$ Rydberg

TABLE III: Gas-Phase Frequencies of $ZXCl_2$ (Z = B, C; X = O, F) Species That Are Isoelectronic with the $CFCl_2^+$ Core of the Rydberg Radical and Frequencies Assigned to the $CFCl_2$ Rydberg Radical

mode description	ν, cm^{-1}		
	$BFCl_2$[a]	$COCl_2$[b]	$CFCl_2$ (Ryd)[c]
ω_1 (a$_1$) ZX str	1312	1827	
ω_2 (a$_1$) ZCl_2 sym str	554	567	
ω_3 (a$_1$) ZCl_2 sciss	260	285	270 (30)
ω_4 (b$_1$) OPLA	524	580	590 (20)
ω_5 (b$_2$) ZCl_2 antisym str		993	849
ω_6 (b$_2$) ZX rock	339	440	

[a] Reference 13. [b] Reference 14. [c] This work.

radical has nearly the same bonding as the $CFCl_2$ cation. Table III shows that ω_2 (ZCl_2 sym str) $\sim$ 560 cm^{-1} and ω_4 (OPLA) $\sim$ 270 cm^{-1}. On the basis of the frequencies presented in Table III, we have discarded candidate 4 because the proposed the frequency, ω_2' (CCl_2 sym str) = 860 (30) cm^{-1}, is too large. Table III agrees closely with the ω_3' (CCl_2 sciss) = 270 (30) cm^{-1} proposed by candidate 3. Thus, we have assigned progression A as the ν_4' OPLA fundamental progression and progression B as the combination progression formed by the ν_3' CCl_2 scissors mode with the ν_4' OPLA mode (Figure 2 and Table II).

From the measured heats of formation of the $CFCl_2$ ion[8] and radical,[15] we calculate an ionization potential of 8.17 eV for the $CFCl_2$ radical. Taking the first member of progression A as the origin at 49850 cm^{-1}, the Rydberg equation can be solved yielding a quantum defect of δ = 0.38 and a principal quantum number of n = 3. These values permit assignment of this band system to a 3p Rydberg state. Like CF_2Cl, the $CFCl_2$ radical REMPI spectrum is produced by a 2 + 1 REMPI mechanism.

Conclusion

We have assigned the REMPI spectra of CF_2Cl and $CFCl_2$ to arise from 3p Rydberg states with origins at 49220 and 49850 cm^{-1}, respectively. As expected of spectra that arise from transitions between nonplanar and planar radical structures, the REMPI band intensities diminish as the ν_4' progressions approach the origin. The origin assignments are tentative. Some uncertainty persists because they are not confirmed by the assignment of hot bands or lengthy fundamental progressions from two different normal modes. In both radicals the origins may reside a vibrational quanta lower in energy. Nevertheless, the spectra presented make possible the detection of these radicals by optical methods.

(15) Tschuikow-Roux, E.; Paddison, S. *Int. J. Chem. Kinet.* **1987**, *19*, 15.