## NOTE

## The $A^2\Sigma^+ \leftarrow X^2\Pi$ Transition of CF Starting from Highly Excited Vibrational States

The first detection of the fluoromethylidyne radical, CF, was reported exactly half a century ago (1) and ever since it has been topic of intense spectroscopic research. Accurate constants for the  $X^2\Pi$  ground state are available from a series of microwave, submillimeter, and infrared studies that are summarized in Ref. (2). Transitions to the electronically excited  $A^2\Sigma^+$ ,  $D^{2}\Pi$ ,  $B^{2}\Delta$ , and  $a^{4}\Sigma^{-}$  states have been reported in previous studies (3–9). The  $A^{2}\Sigma^{+} \leftarrow X^{2}\Pi$  electronic system was observed in emission (3–5), REMPI (6), and direct absorption experiments (7). Accurate information on the ground state vibrational progression (up to v'' = 12) is available from REMPI experiments on the  $D^2\Pi \leftarrow X^2\Pi$  electronic system (6, 8). The  $B^2\Delta \leftarrow X^2\Pi$  system was studied in emission (9) and the weak and spin-forbidden  $a^4\Sigma^- \leftarrow X^2\Pi$ was reported in Ref. (10). Recent studies on CF were triggered by the role of this radical in industrial plasma etching processes (7, 11), i.e., under conditions where vibrationally excited states are expected to be of interest. Here we report for the first time about the observation of transitions starting from highly excited vibrational states (9  $\leq v' \leq 14$ ) in the  $A^2\Sigma^+ \leftarrow X^2\Pi$  electronic system. The CF radicals are generated by discharging a 0.2% CHF<sub>3</sub>/He mixture in a multilayer pinhole geometry prior to the actual supersonic expansion. Such a source allows spectroscopy of vibrationally excited, but rotationally cold CF radicals (for more details see Refs. (12, 13)). The CF radicals are detected by recording the CF<sup>+</sup> mass signal in a time-of-flight setup after resonant ionization using a one-color (1 + 1) REMPI scheme. For the excitation, the light of a pulsed dye laser is used that is frequency doubled in a KDP crystal (bandwidth  $\approx 0.10 \text{ cm}^{-1}$ ). I<sub>2</sub> spectra are recorded simultaneously for linearization and absolute frequency calibration.

For the  $(\mathbf{v}', \mathbf{v}') = (0, 9)$ , (0, 10), (1, 11), and (1, 12) bands, rotationally resolved spectra of the lower spin–orbit component  $(A^2\Sigma^+ \leftarrow X^2\Pi_{1/2})$  were recorded. In Fig. 1 the rotationally resolved (0, 9) band is shown. The rotational labeling is given as well. One should note that due to the absence of a measurable spin–rotation splitting in the upper electronic state several branches coincide. The intensity profile corresponds to a rotational temperature of about 10 K. The second spin–orbit component is not populated at this low temperature because of large spin–orbit splittings in the electronic ground state  $(A'' \text{ ranges from 77 to 70 cm^{-1} for \mathbf{v}'' = 0 \text{ to 12} (6))$ . The observed line positions are listed in Table 1.

The (1, 13) and (1, 14) bands were observed with band origins around 29 465 and 28 425 cm<sup>-1</sup>, respectively, but S/N ratios are approximately 20 times smaller than observed for the bands given in Table 1. This prohibits an unambiguous assignment. The poor signal strength, even when using a focusing lens, cannot be explained by a decrease in Franck–Condon factor only and is due to a lower ionization cross section with respect to the bands given in Table 1. As the adiabatic ionization potential for CF<sup>+</sup>  $(X^1\Sigma^+) \leftarrow$  CF  $(X^2\Pi)$  amounts to 9.11 eV, the maximum excess energy for a (1 + 1) REMPI excitation from v'' = 13 or  $14 (X^2\Pi)$  through  $v' = 1 (A^2\Sigma^+)$  is not sufficient to reach the v'' = 1 level in the  $X^1\Sigma^+$  electronic ground state of CF<sup>+</sup> (14). Consequently, ionization must occur through the v'' = 0 level of the ion which is expected to be much weaker than the diagonal  $(1, 1) X^1\Sigma^+ \leftarrow A^2\Sigma^+$  ionization step. To study transitions starting from the latter or higher vibrational levels, a two-color (1 + 1') REMPI scheme will be required to surpass the energy threshold of the CF<sup>+</sup> (v'' = 1) level.

Transitions to the v' = 2 excited vibrational level in the  $A^2 \Sigma^+$  state have been observed as well. The (2, 12) and (2, 13) bands were recorded at ~32 220 and  $\sim 31\ 150\ \text{cm}^{-1}$ , respectively, and as expected from the predissociative character of the v'=2 level (7, 15), only unresolved spectra were obtained.

The transitions listed in Table 1 have been fitted, using a standard Hamiltonian for a  ${}^{2}\Sigma \leftarrow {}^{2}\Pi$  transition (16) and fixing the vibronic constants, apart from the band origin, to the available numbers for the electronic ground (6) and electronically excited state (3). This yields an rms better than 0.055 cm<sup>-1</sup> for the individual fits and accurate values for the band origin positions that are listed in Table 2. A simulated spectrum that is based on these values is shown in Fig. 1. The resulting band origin positions are compared to the values calculated from Refs. (3, 6). These are systematically off by -0.2 to -0.5 cm<sup>-1</sup>, which is probably due to the increasing anharmonicity for higher vibrational levels.

Clearly, highly excited vibrational levels of CF can be studied in a super-



**FIG. 1.** The  $(\mathbf{v}', \mathbf{v}') = (0, 9)$  band of CF in the  $A^2\Sigma^+ \leftarrow X^2\Pi$  electronic transition recorded by REMPI spectroscopy in a supersonic plasma beam (upper trace) and a simulated spectrum (lower trace). The intensity profile corresponds to a rotational temperature of ~10(3) K.

TABLE 1
Observed Line Positions $[cm^{-1}]$ of the $A^2\Sigma^+ \leftarrow X^2\Pi_{1/2}$ Electronic System of CF
for $9 \le v'' \le 12$ and $v' = 0$ or 1

(v',v'')	J۳	$\mathbf{P}_1$	0-0 <sup>a</sup>	$Q_1/P_{21}$	0-0 <sup>a</sup>	$R_1/Q_{21}$	0-0 <sup>a</sup>	R <sub>31</sub>	0-0 <sup>a</sup>
(0,9)	0.5			32113.99	0.03	32117.39	0.00	32124.23	-0.01
	1.5	32110.36	0.09	32113.77	0.07	32120.59	0.04	32130.77	-0.05
	2.5	32107.64	0.09	32114.41	0.01	32124.68	0.01	32138.29	-0.08
	3.5	32105.84	0.05	32116.10	0.04	32129.71	-0.05	32146.78	-0.10
	4.5	32105.01	0.02	32118.65	-0.04	32135.80	-0.01	32156.23	-0.13
	5.5	32105.22	0.07	32122.28	0.00	32142.75	-0.07		
(0, 10)	0.5			31003.92	0.01	31007.41	0.08	31014.18	0.00
	1.5	31000.26	0.00	31003.71	0.20	31010.59	0.05	31020.76	-0.06
	2.5	30997.57	-0.05	31004.44	-0.03	31014.79	0.04	31028.41	-0.03
	3.5	30995.98	0.01	31006.23	-0.02	31019.94	-0.01	31037.08	0.01
	4.5	30995.22	-0.10	31009.02	0.00	31026.13	-0.01	31046.64	-0.05
	5.5	30995.54	-0.13			31033.40	0.06		
	<b>6</b> .5					31041.54	0.02		
(1,11)	0.5			31630.70	0.12	31633.95	0.00	31640.66	-0.05
	1.5	31626.99	0.01	31630.46	0.10	31637.11	0.00	31647.20	-0.04
	2.5	31624.40	0.03	31631.10	-0.02	31641.31	0.06	31654.69	-0.06
	3.5	31622.71	-0.02	31632.89	0.03	31646.36	0.00	31663.19	-0.05
	4.5	31622.10	0.03	31635.61	0.03	31652.40	-0.05	31672.56	-0.14
	5.5	31622.30	-0.09	31639.26	0.00	31659.52	0.00		
	6.5					31667.52	-0.04		
4									
(1,12)	0.5			30555.56	0.01	30558.94	0.02	30565.69	0.01
	1.5	30552.01	0.01	30555.33	-0.04	30562.12	-0.01	30572.27	0.01
	2.5	30549.52	0.06	30556.20	-0.01	30566.34	0.00	30579.87	0.03
	3.5	30547.88	-0.05	30558.03	-0.03	30571.68	0.12	30588.44	-0.01
	4.5	30547.44	0.03	30560.84	-0.08	30577.80	0.01	30598.03	-0.02
	5.5	30547.84	-0.06						

<sup>a</sup> Observed minus calculated, using the constants of Refs. [3, 6].

sonic plasma with subsequent mass selective detection using REMPI spectroscopy. Even higher vibrational levels are expected to be spectroscopically accessible, when a two-color (1 + 1') REMPI scheme is employed.

TABLE 2
Experimental and Predicted (v', v') Band Origin
Positions $[cm^{-1}]$ for $A^2\Sigma^+ \leftarrow X^2\Pi$

(v',v'')	Observed band origin	Calculated band origin
(0,9)	32079.34(2)	32079.1
(0,10)	30969.71(2)	30969.2
(1, 11)	31596.49(2)	31596.0
(1,12)	30521.75(2)	30521.3

*Note.* Constants from Ref. (3) are taken for v' = 0, 1 and from Ref. (6) for  $9 \le v'' \le 12$ .

## ACKNOWLEDGMENTS

This research was made possible by financial support of Scheikundig Onderzoek Nederland and Fundamenteel Onderzoek der Materie and has been supported by the Swiss National Science Foundation, Project 20-55285.98 and the NATO science program. The authors gratefully acknowledge Tomasz Motylewski and Craig Taatjes for help and Paul Griffiths and Henning Meyer for very stimulating discussions. The experimental setup owes much to the skills of Roel Mooyman and Arjan Wiskerke.

## REFERENCES

- 1. E. B. Andrews and R. F. Barrow, Nature 165, 890-890 (1950).
- I. Morino, K. M. T. Yamada, S. P. Belov, G. Winnewisser, and E. Herbst, Astrophys. J. 532, 377–383 (2000).
- 3. T. L. Porter, D. E. Mann, and N. Acquista, J. Mol. Spectrosc. 16, 228–263 (1965).

- 4. J. P. Booth and G. Hancock, Chem. Phys. Lett. 150, 457-460 (1988).
- J. P. Booth, G. Hancock, M. J. Toogood, and K. G. McKendrick, J. Phys. Chem. 100, 47–53 (1996).
- J. Wollbrandt, M. Rossberg, W. Strube, and E. Linke, J. Mol. Spectrosc. 176, 385–396 (1996).
- J. P. Booth, G. Cunge, L. Biennier, D. Romanini, and A. Kachanov, *Chem. Phys. Lett.* **317**, 631–636 (2000).
- 8. R. D. Johnson, III and J. W. Hudgens, J. Phys. Chem. 91, 6189-6191 (1987).
- 9. P. K. Carroll and T. P. Grennan, J. Phys. B. Mol. Phys. 3, 865-877 (1969).
- F. J. Grieman, A. T. Droege, and P. C. Engelking, J. Chem. Phys. 78, 2248–2253 (1983).
- M. A. Lieberman and A. J. Lichtenberg, "Principles of Plasma Discharges and Materials Processing," Wiley, New York, 1994.
- 12. G. Bazalgette Courrèges-Lacoste, J. P. Sprengers, J. Bulthuis, S. Stolte, T. Motylewski, and H. Linnartz, in press.
- 13. J. Fleniken, Y. Kim, and H. Meyer, Chem. Phys. Lett. 318, 529-535 (2000).
- 14. J. M. Dyke, A. E. Lewis, and A. Morris, J. Chem. Phys. 80, 1382–1386 (1984).
- A. P. Rendell, C. W. Bauschlicher, and S. R. Langhoff, *Chem. Phys. Lett.* 163, 354–358 (1989).

- C. M. Western, PGOPHER v3.73, School of Chemistry, University of Bristol, UK, 1994.
  - G. Bazalgette Courrèges-Lacoste\* J. P. Sprengers\* W. Ubachs\* S. Stolte\* H. Linnartz†

\*Laser Centre and Department of Chemistry Vrije Universiteit, de Boelelaan 1083 NL-1081 HV Amsterdam The Netherlands †Institute for Physical Chemistry University of Basel, Klingelbergstrasse 80 CH-4056 Basel Switzerland

Received August 14, 2000; in revised form October 25, 2000