

## 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%  $\text{CHF}_3/\text{He}$  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  $\text{CF}^+$  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  $\cong 0.10 \text{ cm}^{-1}$ ).  $I_2$  spectra are recorded simultaneously for linearization and absolute frequency calibration.

For the  $(v', v'') = (0, 9)$ ,  $(0, 10)$ ,  $(1, 11)$ , 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 ( $A''$  ranges from 77 to  $70 \text{ cm}^{-1}$  for  $v'' = 0$  to 12 (6)). The observed line positions are listed in Table 1.

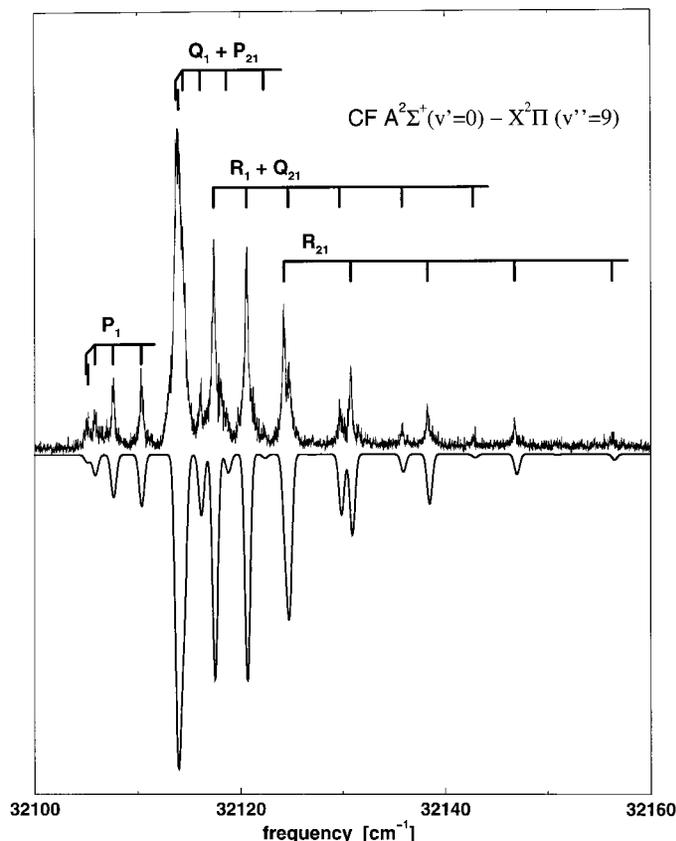
The  $(1, 13)$  and  $(1, 14)$  bands were observed with band origins around  $29\,465$  and  $28\,425 \text{ cm}^{-1}$ , respectively, but S/N ratios are approximately 20 times smaller than observed for the bands given in Table 1. This prohibits an unambiguous assignment. The poor signal strength, even 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  $\text{CF}^+ (X^1\Sigma^+) \leftarrow \text{CF} (X^2\Pi)$  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  $\text{CF}^+$  (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  $\text{CF}^+ (v' = 1)$  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  $\sim 32\,220$

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  $0.055 \text{ cm}^{-1}$  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  $-0.5 \text{ cm}^{-1}$ , 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  $(v', v'') = (0, 9)$  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  $\sim 10(3) \text{ K}$ .

**TABLE 1**  
**Observed Line Positions [cm<sup>-1</sup>] of the A<sup>2</sup>Σ<sup>+</sup> ← X<sup>2</sup>Π<sub>1/2</sub> Electronic System of CF**  
**for 9 ≤ v' ≤ 12 and v'' = 0 or 1**

(v',v'')	J <sup>m</sup>	P <sub>1</sub>	o-d <sup>a</sup>	Q <sub>1</sub> /P <sub>21</sub>	o-d <sup>a</sup>	R <sub>1</sub> /Q <sub>21</sub>	o-d <sup>a</sup>	R <sub>21</sub>	o-d <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		
6.5					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			
(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<sup>-1</sup>] for A<sup>2</sup>Σ<sup>+</sup> ← X<sup>2</sup>Π**

(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 ≤ v' ≤ 12.

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