

LETTER TO THE EDITOR

Discovery of interstellar CF⁺

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ABSTRACT

We discuss the first astronomical detection of the CF⁺ (fluoromethylidyne) ion, obtained by observations of the $J = 1-0$ (102.6 GHz), $J = 2-1$ (205.2 GHz) and $J = 3-2$ (307.7 GHz) rotational transitions toward the Orion Bar region. Our search for CF⁺ – carried out using the IRAM 30 m and APEX 12 m telescopes – was motivated by recent theoretical models that predict CF⁺ abundances of few $\times 10^{-10}$ in UV-irradiated molecular regions where C⁺ is present. The CF⁺ ion is produced by exothermic reactions of C⁺ with HF. Because fluorine atoms can react exothermically with H₂, HF is predicted to be the dominant reservoir of fluorine, not only in well-shielded regions but also in the surface layers of molecular clouds where the C⁺ abundance is large. The observed CF⁺ line intensities imply the presence of CF⁺ column densities $\geq 10^{12}$ cm⁻² over a region of size $\geq 1'$, in good agreement with theoretical predictions. They provide support for our current theories of interstellar fluorine chemistry, which suggest that hydrogen fluoride should be ubiquitous in interstellar gas clouds and widely detectable in absorption by future satellite and airborne observatories.

Key words. ISM: molecules – ISM: abundances – ISM: clouds – molecular processes – submillimeter

1. Introduction

Of the ~ 120 interstellar molecules that have been detected to date¹ (e.g. Müller et al. 2005), more than 95% involve just six elements – hydrogen, carbon, nitrogen, oxygen, silicon, and sulfur – all of which have moderately high abundances ($\geq 10^{-5}$ relative to hydrogen in the Sun). Of the molecules that are formed in the interstellar medium, only four species containing other elements have been reported previously: HF (Neufeld et al. 1997), PN (Turner & Bally 1987), HCl (Blake et al. 1987) and FeO (Walmsley et al. 2002). In the case of those elements of relatively low abundance (F, Cl, and P with solar abundances of 3×10^{-8} , 3×10^{-7} and 3×10^{-7} respectively with respect to H), the detected molecules are all stable species with large dissociation energies ($D_0^0 = 5.87$, 4.43 and 7.05 eV respectively for HF, HCl and PN²). Not surprisingly, our understanding of the chemistries of interstellar fluorine-, chlorine-, phosphorus- and iron-bearing molecules is limited by the paucity of detected species that might help constrain theoretical models.

Notwithstanding this lack of observational constraints, the chemistry of fluorine-bearing molecules in the interstellar

medium has been the subject of a recent theoretical study (Neufeld et al. 2005a, hereafter NWS). The principal conclusions of that investigation were: 1) that hydrogen fluoride is formed rapidly by the exothermic reaction of F atoms with H₂ and becomes the dominant reservoir of gas-phase F nuclei over a wide range of conditions; 2) that HF is abundant even close to UV-irradiated cloud surfaces where C⁺ is the dominant reservoir of gas-phase carbon; and 3) that reaction of HF with C⁺ can lead to potentially-measurable column densities of CF⁺, a very stable molecule (dissociation energy, $D_0^0 = 7.71$ eV) that is isoelectronic with CO.

NWS showed that the chemistry of interstellar fluorine is qualitatively different from that of other elements because fluorine atoms can react exothermically with H₂, the dissociation energy of hydrogen fluoride being the largest of any neutral diatomic hydride and HF being the only such molecule more strongly bound than H₂. Fluorine is therefore unique among the elements in having a neutral atom that reacts exothermically with H₂.

Motivated by the predictions of NWS, we used the 30 m IRAM telescope and the 12 m APEX³ telescope to search for the $J = 1-0$, $J = 2-1$, and $J = 3-2$ rotational transitions of CF⁺ toward the Orion Bar, a well-studied photodissociation region (PDR) with an edge-on geometry favorable for the detection of molecular species of small abundance. The observations are described in Sect. 2 below, and the results of those observations presented in Sect. 3. A discussion follows in Sect. 4.

³ The Atacama Pathfinder Experiment (APEX) is a collaboration of the Max-Planck-Institut für Radioastronomie, the European Southern Observatory, and the Onsala Space Observatory.

¹ In addition, roughly two dozen molecules have been detected exclusively in circumstellar gas – specifically around the source IRC+10216. These molecules include species containing the elements Na, Mg, K, and Al, in addition to the elements represented by molecules formed in the interstellar medium.

² Derived from thermochemical data recommended in NIST Standard Reference Database Number 69 (a.k.a. the NIST Chemistry Web book), ed. P. J. Linstrom, & W. G. Mallard, March 2003, National Institute of Standards and Technology, Gaithersburg MD 20899; available on-line at <http://webbook.nist.gov>

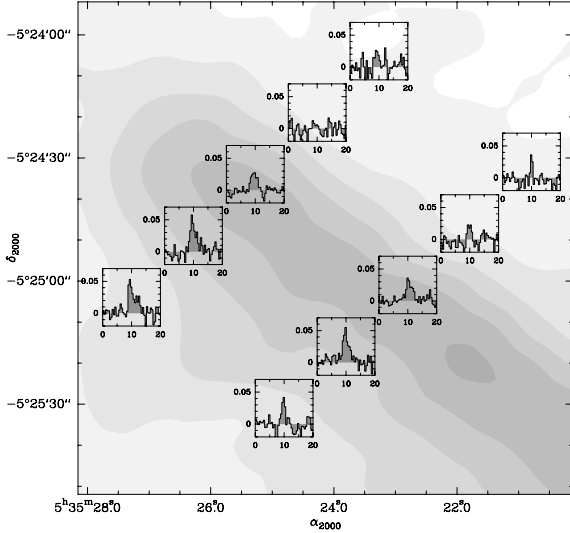


Fig. 1. CF⁺ $J = 1-0$ spectra observed at each of the positions in the Orion Bar, with the observed position for each observation indicated on a $^{13}\text{CO } J = 3-2$ map of the source (grayscale map, from Lis & Schilke 2003). For the strip centered on $(\alpha, \delta) = (05^{\text{h}}35^{\text{m}}22.8^{\text{s}}, -05^{\circ}25'01'')$ (J2000) (the “Orion Bar (CO)” position), the integrated CF⁺ $J = 1-0$ antenna temperatures are 33 ± 6 , 45 ± 8 , 86 ± 10 , 125 ± 13 and 57 ± 8 mK km s⁻¹ from NW to SE (quoted uncertainties are 1σ statistical errors); for the strip centered on $(05^{\text{h}}35^{\text{m}}25.3^{\text{s}}, -05^{\circ}24'34'')$ (J2000) (the “Orion Bar (HCN)” position), the corresponding values are <19.5 , <15.8 , 72 ± 8 , 119 ± 15 , and 140 ± 30 mK km s⁻¹.

2. Observations

The $J = 1-0$ rotational transition of CF⁺ at 102.58748 GHz (Plummer et al. 1986) was observed in two five-position strip maps in the Orion Bar, centered on the “Orion Bar (CO)” and “Orion Bar (HCN)” positions defined by Schilke et al. (2001; see our Fig. 1 caption for coordinates). The $J = 2-1$ line at 205.17445 GHz and the $J = 3-2$ line at 307.74438 GHz were observed at the central “Orion Bar (CO)” and “Orion Bar (HCN)” positions for each strip.

The observations of CF⁺ $J = 1-0$ and $J = 2-1$ were carried out at the IRAM 30 m telescope, using the A100, B100, A230 and B230 receivers in position-switching mode, with an OFF-position located 10' away in azimuth. The backend employed was the VESPA correlation spectrometer; care was taken to move the known backend defects away from the observed lines. The CF⁺ $J = 3-2$ transition was observed using the APEX 12m telescope, located at an altitude of 5100 m on the Chajnantor plateau in the Atacama desert of Chile, using the APEX-2a receiver. The observing mode was the same as at the 30 m, with the same OFF-Position. As backend, the MPIFR Fast Fourier Spectrometer was used. Calibration at both telescopes is performed using a dual load scheme and an atmospheric model. The beam sizes were 24'', 12'' and 21'' (HPBW), respectively. Since the emission is extended, in the following antenna temperature units are used.

3. Results

Figure 1 shows the CF⁺ $J = 1-0$ spectra observed at each of the positions in the Orion Bar, with the observed position for each observation indicated on a $^{13}\text{CO } J = 3-2$ map of the source. Emission in the $J = 1-0$ line is evident at 8 of the 10 observed positions. Like other optically-thin emission lines such as SiO $J = 2-1$ (Schilke et al. 2001), the CF⁺ $J = 1-0$ line peaks

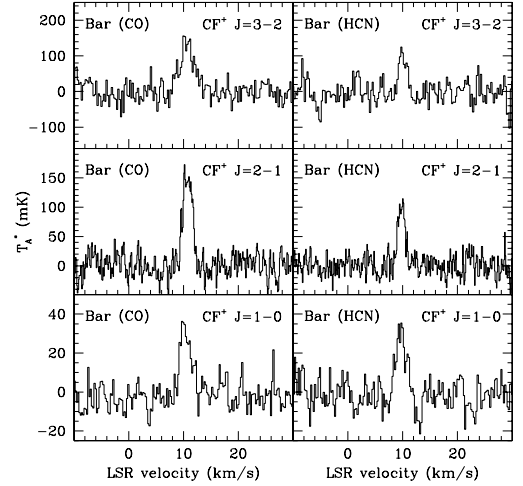


Fig. 2. CF⁺ $J = 1-0$, $J = 2-1$ (IRAM 30 m) and $J = 3-2$ (APEX 12 m) spectra obtained toward the Orion Bar (CO) and Orion Bar (HCN) positions. (Spectra of lower signal-to-noise ratio, obtained in shorter integrations toward the Orion Bar (CO) position, were published previously by Neufeld et al. 2005b.)

Table 1. Observations of the Orion Bar.

	Orion Bar (CO)	Orion Bar (HCN)
	Line strength ^a ($\int T_A^* dv$ in mK km s ⁻¹)	
$J = 1-0$	86 ± 10	72 ± 8
$J = 2-1$	337 ± 13	215 ± 13
$J = 3-2$	428 ± 34	183 ± 26
	Line centroid (km s ⁻¹ w.r.t. the LSR)	
$J = 1-0$	10.5 ± 0.15	9.6 ± 0.15
$J = 2-1$	10.7 ± 0.05	9.8 ± 0.05
$J = 3-2$	10.6 ± 0.1	10.0 ± 0.1
	Line width (km s ⁻¹ FWHM)	
$J = 1-0$	2.7 ± 0.4	2.3 ± 0.3
$J = 2-1$	2.0 ± 0.1	1.7 ± 0.1
$J = 3-2$	3.0 ± 0.3	1.5 ± 0.2
	Column density (units of 10^{11} cm ⁻²)	
$J = 1$	3.7	3.1
$J = 2$	6.0	3.8
$J = 3$	4.7	2.0
Estimated total	19	11

^a Errors given are 1 sigma statistical errors. We estimate the systematic uncertainties as $\pm 20\%$.

southeast (i.e. further from the Trapezium stars) than $^{13}\text{CO } J = 3-2$. Rather than indicating that CF⁺ and SiO are located further away from the ionization front than ^{13}CO , this behavior reflects the different sensitivity to temperature and density – and the different optical depths – of the lines from these three species. In particular, the $^{13}\text{CO } J = 3-2$ line is of moderate optical depth ($\tau > 1$), so its intensity probes the temperature at the $\tau \sim 1$ surface and is relatively insensitive to the total line-of-sight column density. Figure 2 shows the $J = 1-0$, $J = 2-1$ and $J = 3-2$ spectra obtained at the central Orion Bar (CO) and Orion Bar (HCN) positions. Table 1 lists the integrated antenna temperature, line centroid, and line width for each observed transition at these two positions.

Figure 3 shows a rotational diagram for the two positions toward which all three transitions have been observed, computed for an assumed dipole moment of 1.07 D (Peterson et al. 1990). Here, we assumed that the line emission is optically-thin, as suggested by the observed line strengths unless the covering

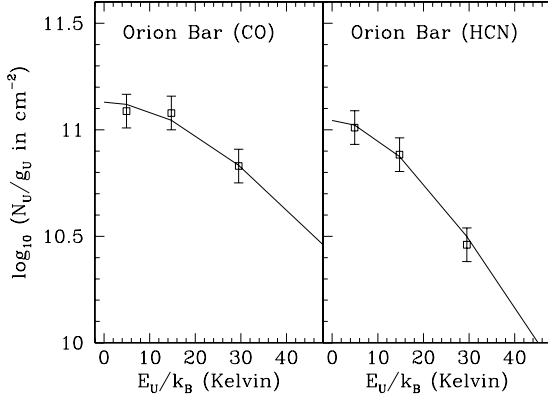


Fig. 3. Rotational diagram for CF⁺. The error bars include systematic uncertainties, which we estimate as $\pm 20\%$. The solid curves show a fit to the data, in which the critical density for each transition is assumed proportional to the radiative decay rate.

factor of the emission is implausibly small. The column densities for $J = 1, 2$ and 3 are given in Table 1. At both positions, any reasonable extrapolation of the rotational diagram implies that the $J = 1, J = 2$, and $J = 3$ states are the three most highly-populated rotational states; thus the total column density we infer is only weakly dependent upon the extrapolation procedure adopted. The solid lines show the best fits to the rotational diagrams, which imply total CF⁺ column densities of $N(\text{CF}^+) = 1.9 \times 10^{12} \text{ cm}^{-2}$ and $1.1 \times 10^{12} \text{ cm}^{-2}$ respectively for the lines-of-sight to the Orion Bar (CO) and Orion Bar (HCN) positions. Given our model predictions for the typical temperature in the CF⁺ emitting region, and as suggested by the curvature of the rotational diagrams, we assumed here that the slope is mainly controlled by the density rather than the temperature, the former being insufficient for collisional deexcitation of $J = 3$ to dominate spontaneous radiative decay.

4. Discussion

The results presented in Fig. 1 and Table 1 indicate that CF⁺ column densities $\sim 10^{12} \text{ cm}^{-2}$ are present over an extended region within the Orion Bar. Such column densities are in good agreement with theoretical predictions (NWS), which predict CF⁺ to be produced by the reaction sequence:



and destroyed primarily⁴ by dissociative recombination



Because the reaction (R1) is exothermic and moderately rapid even at low temperature (Zhu et al. 2002), HF becomes the dominant reservoir of fluorine in the gas phase, even relatively close to cloud surfaces. Beneath the surface of the UV-illuminated cloud, HF forms at precisely the point at which hydrogen becomes molecular, and long before carbon gets incorporated into CO (see NWS, Fig. 2). Thus there is a substantial area of overlap

⁴ Reaction with H₂ to form HCF⁺, considered by Morino et al. (2000) to dominate the destruction of interstellar CF⁺, is in fact substantially endothermic² (by ~ 2 eV) and therefore of negligible importance (NWS).

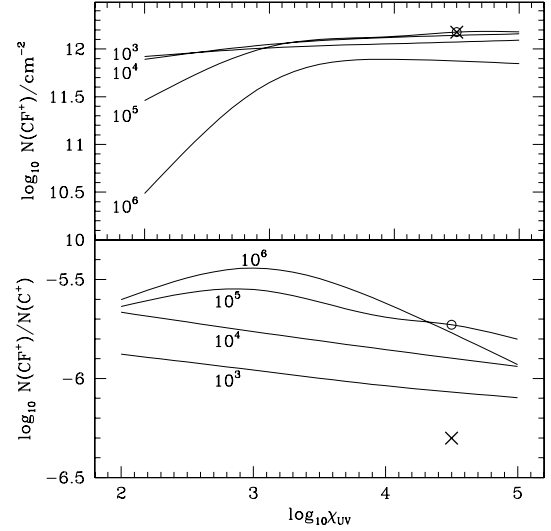


Fig. 4. **a)** Upper panel: CF⁺ column density, $N(\text{CF}^+)$, predicted by the NWS model, as a function of the normalized incident radiation field χ_{UV} . **b)** Lower panel: corresponding $N(\text{CF}^+)/N(\text{C}^+)$ ratio. Each curve is labelled with the assumed density, n_{H} . The crosses represent the mean observed values for the Orion Bar (CO) and Orion Bar (HCN) positions, along with the radiation field $\chi_{\text{UV}} = 3 \times 10^4$ estimated by Herrmann et al. (1997) for the Orion Bar, while the open circles represent the corresponding model prediction.

between C⁺ and HF where reaction (R2) can produce CF⁺ abundances $\sim \text{few} \times 10^{-10}$; here CF⁺ accounts for $\sim 1\%$ of the solar abundance of fluorine.

Figure 4a shows the CF⁺ column density predicted by the NWS model, as a function of the gas density, n_{H} , and the incident radiation field χ_{UV} (again for the case of one-sided illumination at normal incidence). The results apply to the case where fluorine depletion is estimated using the simple treatment given in NWS Sect. 3.2. The predicted and observed results are in good agreement, although the remarkable agreement suggested by Fig. 4a is undoubtedly fortuitous for several reasons: (1) Fig. 4a compares the predicted column densities for a photodissociation region (PDR) viewed face-on with the observed column densities in a nearly edge-on PDR (in which optically-thin lines are significantly limb-brightened); (2) the theoretical predictions are based upon several parameters that are substantially uncertain: e.g. the reaction rate coefficients for (R2) and (R3), and the gas-phase F abundance (see footnote 4).

The CF⁺ column densities plotted in Fig. 4a are found to track the corresponding C⁺ column densities remarkably well, with the $N(\text{CF}^+)/N(\text{C}^+)$ column density ratio (Fig. 4b) lying within a factor ~ 2 of 1.7×10^{-6} for every case represented in Fig. 4. This behavior can be understood by considering the rates of CF⁺ formation and destruction via reactions (R2) and (R3). In equilibrium, we expect a ratio

$$\frac{n(\text{CF}^+)}{n(\text{C}^+)} = \frac{k_2 n(\text{HF})}{k_3 n_e} = 4 \times 10^{-6} \left(\frac{T}{300 \text{ K}} \right)^{0.35} \frac{n(\text{HF}) n_{\text{C}}}{n_{\text{F}} n_e}$$

where k_2 and k_3 are the rate coefficients given by NWS for (R2) and (R3), and $n_{\text{F}}/n_{\text{H}} = 1.8 \times 10^{-8}$ and $n_{\text{C}}/n_{\text{H}} = 1.6 \times 10^{-4}$ are the assumed gas-phase abundances of F and C. In the region where the C⁺ and CF⁺ abundances are large, $n_e \sim n(\text{C}^+) \sim n_{\text{C}}$ and $n(\text{HF}) \sim n_{\text{F}}$.

Kuiper Airborne Observatory (KAO) observations of the C⁺ $^2P_{3/2} - ^2P_{1/2}$ (158 μm) fine-structure line carried out toward the Orion Bar (Herrmann et al. 1997) permit us to compare our theoretical prediction for $N(\text{CF}^+)/N(\text{C}^+)$ with the measured value. Since both the C⁺ and CF⁺ transitions are optically-thin, such a comparison has the merit of eliminating any limb-brightening effects, all the observed lines being enhanced by the same factor. Based upon their observations of the Orion Bar, Herrmann et al. inferred a line-of-sight C⁺ column density of $3 \times 10^{18} \text{ cm}^{-2}$, averaged over a 55'' beam. Given our estimates of $N(\text{CF}^+)$ at two separate positions along the midline of the bar, we may estimate the $N(\text{CF}^+)/N(\text{C}^+)$ ratio as $\sim 5 \times 10^{-7}$, a factor of ~ 4 smaller than the theoretical prediction. This discrepancy may suggest (weakly, in light of all the uncertainties) that the F abundance assumed by NWS is too large and/or that the reaction (R2) proceeds less rapidly than was assumed.

Despite these uncertainties, our detection of CF⁺ lends support to our theoretical model of fluorine chemistry. In particular, the observed CF⁺ column density argues strongly for a substantial region of overlap between C⁺ and HF. This, in turn, supports our contention that HF becomes abundant very close to cloud surfaces, and suggests that HF may prove a valuable tracer of molecular material in diffuse clouds. Observations of HF and CF⁺ may also provide an important tool for studying the elemental abundance and nucleosynthetic origin of fluorine⁵. As noted by NWS, absorption line observations of the 1232 GHz HF $J = 1-0$ transition will be possible with the Herschel Space Observatory and the Stratospheric Observatory for Infrared Astronomy; in addition, observations of HF at certain redshift ranges beyond $z = 0.3$ are possible at ground-based observatories and will be greatly facilitated by ALMA.

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⁵ The elemental abundance of fluorine is of particular interest because the nucleosynthetic origin of fluorine remains controversial. Fluorine is produced in stars on the asymptotic giant branch (Jorissen et al. 1992; Werner et al. 2005), but there is no consensus on the relative contributions of other sources such as Wolf-Rayet stars and type II supernovae (e.g. Renda et al. 2004; Palacios et al. 2005). Because AGB stars exhibit a large enhancement in the fluorine abundance (up to a factor ~ 250), it will be interesting to search for CF⁺ in circumstellar envelopes as well as in the wind-blown bubbles surrounding Wolf-Rayet stars (Marston et al. 1999; Marston 2001; Rizzo et al. 2003).