Formation of the CF radical in comets

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Abstract. In March 2015 the European Space Agency’s Rosetta spacecraft performed a close flyby over the surface of comet 67P/Churyumov-Gerasimenko of just 15 km from the comet center. This comet belongs to the Jupiter family with an aphelion at 5.5 au and a perihelion at 1.25 au. Its orbital period is 6.5 years. The ROSINA (Rosetta Orbiter Sensor for Ion and Neutral Analysis)/DFMS (Double Focusing Mass Spectrometer) instrument on board Rosetta reported the first detection among others of glycine (C₅H₅NO₂) an amino acid, other prebiotic molecules, phosphorus atom (P), and fluoromethylidyne (CF), which is not a stable chemical species but a metastable radical [1]. In the case of phosphorus, the search for the parent (PH₃, PH, PO, PN, CP, HCP, HPO, CCP) was unsuccessful although these species have been detected mostly in the interstellar medium [2]. This work reports a study of model-dependent chemical networks, based on several databases such as UMIST and NIST among others, to explain the formation of CF radical in comets from gaseous tetrafluoromethane (CF₄).

1. Introduction

The detection of fluorine-bearing molecules in interstellar space, circumstellar shells and comets still is to some extent an enigma, and many unanswered questions remain. With a Solar System abundance of about 3×10⁻⁸ relative to hydrogen, the abundance of fluorine lies only in a factor of 6 below that of chlorine [3], and two fluorine-containing molecules – HF [4] and AlF [5; 6] – has been detected in space. Other fluorine-bearing species may be present and detectable as well, and in this work we present new information on the CF radical to aid in interstellar, circumstellar, and particularly, in comet searches.

The two simple diatomic hydrogen halides HCl and HF have been detected in interstellar clouds. Hydrogen chloride, HCl, was observed in emission by its J = 1-0 transition toward OMC-1 [7; 8] and in absorption against the dust continuum emission of the molecular cloud Sagitarius B2 [9]. An interesting feature of the halogens, lies not in HF and HCl but in another class of molecules, the metal halides NaCl, AlCl [10], KCl, and AlF, detected toward the chemically rich circumstellar envelope of the late-type carbon star IRC + 10216. The rotational spectra of all these species were first observed in emission [5]. Their tentative AlF detection has been confirmed [11], who also reported upper limits on CaF and MgF. The detection of AlF is in reasonable agreement with models that assume high-temperature thermodynamic equilibrium [12; 13] and solar abundances. Since the envelope of IRC + 10216 is carbon rich and the fluorine abundance may exceed its solar value [11], IRC + 10216 is a possible source of the
radical CF as well, although, as discussed later in a simplified thermodynamic argument, this radical may not be abundant at LTE, as compared with HF [14].

The abundance of fluorine-containing molecules other than HF in dense molecular clouds is not expected to be large, as inferred from the solar abundance of elemental fluorine [3] and from the estimated depletion value of about 50 [4].

Although C and F are abundant in the inner envelopes of carbon-rich stars and HF has been detected toward a variety of cool stars [15], it is not obvious that CF can be found in these regions in sufficient abundance for detection. The basic problem is that, unlike AlF [6], which has been detected in the inner part of the IRC + 10216 envelope, CF is not thermodynamically competitive and, if LTE prevails, its abundance will be relatively small [14].

To shed more light on the CF radical problem in space, we have extended the study to comets [1], and below we present an ion-molecule scheme that leads from gaseous CF₄ to the CF radical formation.

2. Observations and qualitative results
A sample mass spectrum measured by the ROSINA/DFMS onboard Rosetta spacecraft at 75, 45, 31 and 30 dalton in the coma of comet 67P/Churyumov-Gerasimenko is shown in Figure 1. There is a clear peak at mass 31.009 dalton, which is the exact mass of CF (carbon monofluoride) [1].

![Figure 1](https://example.com/figure1.png)

Figure 1. ROSINA DFMS mass spectra (9 July 2015) for masses 30, 31, 45, and 75 dalton. Integration time is 20s per spectrum. Error bars represent 1-σ counting statistics [1].

In this work, the possible gas-phase formation route of the CF radical in comets is studied. The Figure 2 shows the reaction network developed, starting from CF₄ (carbon tetrafluoride) and ultimately leading to CF (carbon monofluoride) in the outer coma gas, as illustrated in Figure 3.
Figure 2. Possible gas-phase formation route of the CF radical in comets.

Figure 3. Descriptive sketch of a comet.
3. Summary and conclusions

In this work, a fundamental and comprehensive chemical network was developed to explain the possible origin of the CF radical in the inner coma of comet 67P/Churyumov-Gerasimenko, detected by ROSINA/DFMS. It is shown that the neutral gaseous CF radical can be formed from CF$_4$. Chemical reaction processes with relevant photo (dissociation, ionization), photodissociative ionization, electron impact (dissociation, ionization, dissociative ionization), protonation, positive ion (+-atom interchange, charge transfer), electron dissociative recombination, 3-body (positive ion-neutral association, neutral recombination), neutral rearrangement, radiative recombination, radiation stabilized (positive ion-neutral association, neutral recombination) and neutral-neutral associative ionization reactions will be used and included as needed, in Figure 2, in the future.

Table 1. Fragmentation pattern and sensitivity used to calculate the relative abundance [16].

| Species       | Fragmentation pattern | Sensitivity |
|---------------|-----------------------|-------------|
| H$_2$O        | M                     | M           |
| CO            | NIST                  | C           |
| CO$_2$        | M                     | M           |
| CH$_4$        | M                     | M           |
| C$_2$H$_2$    | NIST                  | C           |
| C$_2$H$_6$    | M                     | M           |
| CH$_3$OH      | NIST                  | C           |
| H$_2$CO       | NIST                  | C           |
| HCOOH         | NIST                  | C           |
| CH$_2$OHCH$_2$OH | NIST              | C           |
| HCOOCH$_3$    | NIST                  | C           |
| CH$_3$CHO     | NIST                  | C           |
| NH$_3$        | M                     | M           |
| HCN           | NIST                  | C           |
| HNCO          | [17]                  | C           |
| CH$_3$CN      | NIST                  | C           |
| H$_2$S        | M                     | M           |
| OCS           | NIST                  | C           |
| SO            | estimated             | C           |
| SO$_2$        | NIST                  | C           |
| CS$_2$        | NIST                  | C           |
| S$_2$         | estimated             | C           |
| CF            | this work             | –           |

Notes. M refers to fragmentation pattern and sensitivity determined in the calibration facility. C refers to the sensitivities that were calculated from the function determined thanks to the calibration measurements.
Our next step is to use the 3-D code Suisei [18], departing from a reasonable assumed initial chemical abundance for the volatile species – due to various uncertainties and errors involved in different quantities, the species listed in Table 1 [16], should be taken as an indicator of the trend of the results rather than the actual values – in order to obtain the following:

- variation of the columnar density for the CF radical as a function of the cometocentric distance along the inner and outer coma;
- variation of the average expansion speed of the neutral gaseous CF as a function of the cometocentric distance in the inner coma;
- variation of the gaseous CF temperature as a function of the cometocentric distance in the inner coma;
- profile of the columnar density for the CF radical in the case of maximum solar flux as a function of the cometocentric distance in the inner coma;
- profile of the columnar density for the CF radical in the case of minimum solar flux as a function of the cometocentric distance in the inner coma.

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References
[1] Altwegg K, Balsiger H, Bar-Nun A et al. 2016 Science Advances 2(5) e1600285 5pp.
[2] Andreazza C M, de Almeida A A and Borin A C 2016 MNRAS 457 3096-3100
[3] Anders E and Grevesse N 1989 Geochim. Cosmochim. Acta 53 197-214
[4] Neufeld D A, Zmuidzinas J, Schilke P and Phillips T G 1997 ApJ 488 L141-L144
[5] Cernicharo J and Guélin M 1987 A&A 183 L10-L12
[6] Andreazza C M and de Almeida A A 2014 MNRAS 437 2932-2935
[7] Blake G A, Keene J and Phillips T G 1985 ApJ 295 501-506
[8] Schilke P, Phillips T G and Wang N 1995 ApJ 441 334-342
[9] Zmuidzinas J, Blake G A, Carlstrom J, Keene J and Miller D 1995 ApJ 447 L125-L128
[10] Andreazza C M, de Almeida A A and Vichietti R M 2018 MNRAS 477 548-551
[11] Ziurys L M, Apponi A J and Phillips T G 1994 ApJ 433 729-732
[12] Tsuji T 1973 A&A 23 411-431
[13] Sharp C M and Huebner W F 1990 ApJS 72 417-431
[14] Morino I, Yamada K M T, Belov S P, Winnewisser G and Herbst E 2000 ApJ 532 377-383
[15] Jorissen A, Smith V V and Lambert D L 1992 A&A 261 164-187
[16] Le Roy L, Altwegg K, Balsinger H et al. 2015 A&A 583 A1 12pp.
[17] Fischer G, Geith J, Klapotke T M and Krumm B 2002 Z. Naturforschung B 57 19-24
[18] Boice D C 2017 Journal of Applied Mathematics and Physics (JAMP) 5 311-320