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LETTER TO THE EDITOR

## HIFI<sup>\*</sup> detection of hydrogen fluoride in the carbon star envelope IRC +10216

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### ABSTRACT

We report the detection of emission in the  $J = 1-0$  rotational transition of hydrogen fluoride (HF), together with observations of the  $J = 1-0$  to  $J = 3-2$  rotational lines of  $\text{H}^{35}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$ , towards the envelope of the carbon star IRC +10216. High-sensitivity, high-spectral resolution observations have been carried out with the HIFI instrument on board *Herschel*, allowing us to resolve the line profiles and providing insights into the spatial distribution of the emission. Our interpretation of the observations, with the use of radiative transfer calculations, indicates that both HF and HCl are formed in the inner regions of the envelope close to the AGB star. Thermochemical equilibrium calculations predict HF and HCl to be the major reservoirs of fluorine and chlorine in the atmospheres of AGB stars. The abundances relative to  $\text{H}_2$  derived for HF and HCl,  $8 \times 10^{-9}$  and  $10^{-7}$  respectively, are substantially lower than those predicted by thermochemical equilibrium, indicating that F and Cl are likely affected by significant depletion onto dust grains, although some chlorine may be in the form of atomic Cl. The  $\text{H}^{35}\text{Cl}/\text{H}^{37}\text{Cl}$  abundance ratio is  $3.3 \pm 0.3$ . The low abundance derived for HF in IRC +10216 makes it likely that the fluorine abundance is not enhanced over the solar value by nucleosynthesis in the AGB star, although this conclusion may not be robust because the HF abundance we derive is a lower limit to the elemental abundance of F. These observations suggest that both HF and HCl should be detectable through low  $J$  rotational transitions in other evolved stars.

**Key words.** astrochemistry – line: identification – molecular processes – stars: AGB and post-AGB – circumstellar matter – instabilities

### 1. Introduction

Light hydrides such as HF and HCl are very difficult to study in space by means of their rotational spectra, which lie in the sub-millimeter and far-infrared spectral regions that are hard if not impossible to observe from the ground owing to the opacity of the terrestrial atmosphere. Moreover, the prospects for detection are limited by the low cosmic abundance of fluorine and chlorine, although HF and HCl are expected to be the major reservoirs of each of these elements in many astrophysical environments.

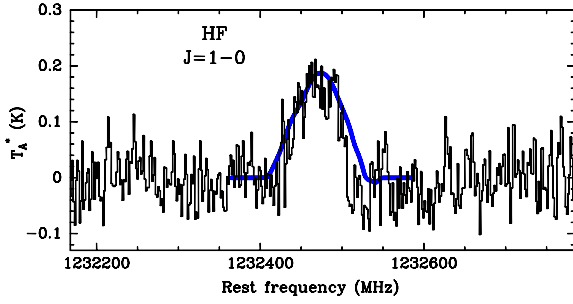
Since it is one of the lightest molecules, HF has a rotational spectrum that can only be observed from space. It was first detected with the Infrared Space Observatory in Sagittarius B2 (Neufeld et al. 1997). Observations of HCl have been conducted in molecular clouds (Blake et al. 1985; Zmuidzinas et al. 1995; Schilke et al. 1995; Salez et al. 1996) through its fundamental rotational transition, lying at 625.9 GHz and still accessible from ground, and in the diffuse cloud  $\zeta$  Ophiuchi (Federman et al. 1995) through an electronic transition at ultraviolet wavelengths

using the *Hubble* Space Telescope. That HF and HCl are very stable molecules makes them abundant in the atmospheres of cool stars and in sunspots, where they have long been observed through ro-vibrational transitions in the infrared region (Hall & Noyes 1969; Hall & Noyes 1972; Ridgway et al. 1984; Jorissen et al. 1992).

With the launch of the *Herschel* Space Observatory, it has been possible to perform very sensitive observations of the pure rotational lines of HF and HCl in different types of interstellar clouds (see Neufeld et al. 2010; Phillips et al. 2010; Sonnentrucker et al. 2010; Cernicharo et al. 2010a; Lis et al. 2010). In this Letter, we present sensitive observations of the  $J = 1-0$  rotational transition of HF and of the  $J = 1-0$  to  $J = 3-2$  transitions of  $\text{H}^{35}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$  towards the carbon star envelope IRC +10216. This is the first time that HF and three lines of the two major isotopologues of HCl are observed at high spectral resolution in IRC +10216<sup>1</sup> allowing us to resolve the line profiles and gain insight into the spatial distribution of the molecules.

<sup>1</sup> Several transitions of HCl were observed at low spectral resolution with the SPIRE and PACS instruments (Cernicharo et al. 2010b), and the  $J = 1-0$  line was observed with the CSO telescope (Peng et al. 2010).

\* *Herschel* is an ESA space observatory with science instruments provided by European-led Principal Investigator consortia and with important participation from NASA.



**Fig. 1.** HIFI spectrum of IRC +10216 showing the  $J = 1-0$  rotational line of HF (black histogram; spectral resolution is 1.5 MHz) and the line profile resulting from the radiative transfer model (blue line).

**Table 1.** HF and HCl observed line parameters in IRC +10216.

Transition	$\nu_{\text{cal}}^a$ (MHz)	$\nu_{\text{obs}}$ (MHz)	$v_{\text{exp}}^b$ (km s $^{-1}$ )	$\int T_A^* dv$ (K km s $^{-1}$ )
HF				
$J = 1-0$	1232476.3	1232467.4(80)	10.7(20)	2.4(2)
H $^{35}$ Cl				
$J = 1-0^c$	625915.2	–	–	4.2(1)
$J = 2-1$	1251450.6	1251445.3(60)	13.3(25)	4.6(6)
$J = 3-2$	1876226.6	1876216.3(80)	12.4(20)	10.5(6)
H $^{37}$ Cl				
$J = 1-0^c$	624975.1	–	–	1.5(1)
$J = 2-1$	1249571.4	1249563.3(80)	15.7(30)	3.1(5)
$J = 3-2$	1873410.7	1873402.0(80)	12.5(15)	5.4(6)

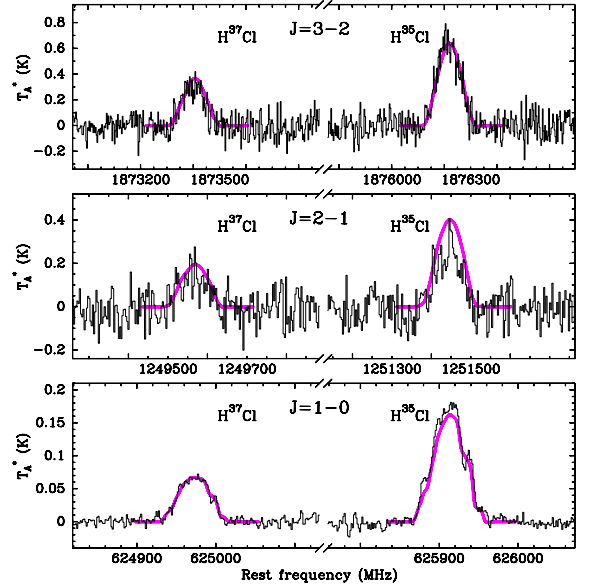
**Notes.** <sup>(a)</sup> Calculated frequencies of HF and HCl from Nolt et al. (1987) and Cazzoli & Puzzarini (2004), respectively. <sup>(b)</sup>  $v_{\text{exp}}$  is the half width at zero intensity. Numbers in parentheses are  $1\sigma$  uncertainties in units of the last digits. <sup>(c)</sup> Line fitted to three components, with the center frequencies fixed to the calculated values of the three hyperfine components and the  $v_{\text{exp}}$  parameter fixed at 14.5 km s $^{-1}$ .

## 2. Observations

Our HIFI observations of the  $J = 1-0$  line of HF and of the  $J = 1-0$  to  $J = 3-2$  lines of H $^{35}$ Cl and H $^{37}$ Cl were obtained in May and from October to December 2010, in the context of GT1 programmes to perform a line survey and to search for light hydrides in IRC +10216. Data were taken in double beam-switching mode with a spectral resolution of 1.1 MHz, and processed using the standard *Herschel* pipeline up to level 2, which provides fully calibrated spectra. The local oscillator was shifted in frequency to identify any emission from the image band. Total integration times were 43 min for the HF line, and ranged from 10 to 21 min for the HCl lines. The final spectra were smoothed to a spectral resolution of 1.5 MHz and have antenna temperature rms noise levels in the range 0.04–0.1 K. For details about the data reduction, we refer to Cernicharo et al. (2010c).

## 3. Results

The  $J = 1-0$  line of HF and the  $J = 1-0$  to  $J = 3-2$  lines of H $^{35}$ Cl and H $^{37}$ Cl are all clearly detected, free of contamination by other lines (see Figs. 1 and 2). The differences between the observed and calculated frequencies are not negligible, up to  $\sim 10$  MHz (see Table 1). They are, however, within the errors and, expressed in Doppler equivalent velocity, have values in the range 1.3–1.9 km s $^{-1}$ , thus are much smaller than the observed line widths (21–31 km s $^{-1}$ ). The detection of HF, H $^{35}$ Cl, and H $^{37}$ Cl in IRC +10216 is therefore quite secure.



**Fig. 2.** HIFI spectra of IRC +10216 showing the first three rotational lines of H $^{35}$ Cl and H $^{37}$ Cl (black histograms; spectral resolution is 1.5 MHz for the  $J = 1-0$  and 3 MHz for the  $J = 2-1$  and  $J = 3-2$  lines). Line profiles resulting from the radiative transfer model are shown in magenta. For the  $J = 1-0$  line, the calculated intensity has been divided among the three hyperfine components according to their line strengths.

The HCl hyperfine structure due to the nuclear quadrupole of the  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  nuclei can only be barely distinguished in the  $J = 1-0$  lines, but not in the higher  $J$  lines owing to the collapse of the hyperfine structure and to the line widening, expressed in frequency, with increasing  $J$ . The  $J = 1-0$  line of both isotopologues is composed of three hyperfine components but a good determination of the parameters of each component was not possible, so that we only give the total velocity integrated intensity in Table 1. The remaining lines of HCl and that of HF have roughly parabolic shapes, which indicates optically thick emission unresolved by the beam of HIFI. The  $J = 1-0$  line of HCl was observed in IRC +10216 by Peng et al. (2010) with the CSO. The smaller beam size of the CSO (13.5 $''$ ), as compared with that of HIFI (33.9 $''$ ), implies a line intensity enhancement of a factor of  $(33.9/13.5)^2 \sim 6$  for a point-like source. This is essentially the value observed for the  $J = 1-0$  line of H $^{35}\text{Cl}$  after correcting for the beam efficiency of each telescope (0.5 for the CSO and 0.75 for HIFI at 625.9 GHz). Therefore, the emission size of the HCl  $J = 1-0$  line must be substantially smaller than the 13.5 $''$  beam of the CSO. This is consistent with the source size expected for the HCl  $J = 1-0$  line based on its critical density ( $\gtrsim 10^7$  cm $^{-3}$ ), which is only exceeded in regions inside 10 $^{15}$  cm (0.5 $''$  at a distance of 130 pc).

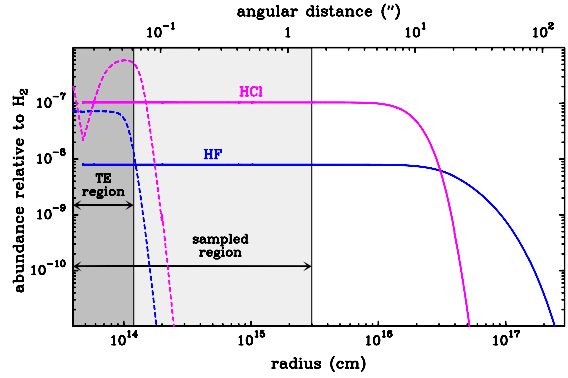
## 4. Radiative transfer modelling

To learn more about the excitation conditions and abundance of HF and HCl in IRC +10216, we performed radiative transfer calculations based on a multi-shell large velocity gradient (LVG) formalism. The physical model consists of a spherical envelope of gas and dust around an AGB star with a radius of  $4 \times 10^{13}$  cm and an effective temperature of 2330 K. The adopted mass loss rate and distance to IRC +10216 are  $2 \times 10^{-5} M_{\odot} \text{ yr}^{-1}$  and 130 pc, respectively. Further details about the physical model will be given in a forthcoming paper (Agúndez et al., in prep.).

To model the emission of the HF and HCl lines, we included the first 10 and 15 rotational states within the ground and first-excited vibrational states. The  $\nu = 1-0$  band lies at a wavelength of  $2.5 \mu\text{m}$  for HF and  $3.5 \mu\text{m}$  for HCl. Level energies were computed from the laboratory spectroscopic constants of HF (Odashima et al. 1999; Ram et al. 1996) and HCl (Cazzoli & Puzzarini 2004; De Natale et al. 1997; Le Blanc et al. 1994), neglecting the hyperfine structure for this latter species. Dipole moments used to compute the line intensities of HF are 1.826526 and 1.87368 Debye for pure rotational transitions within the  $\nu = 0$  and  $\nu = 1$  states, respectively (Muentzer & Klemperer 1970; Piecuch et al. 1998), and 0.099735 Debye for the fundamental ro-vibrational transition (Pine et al. 1985). For HCl, we used 1.109 and 1.139 Debye for the  $\nu = 0$  and  $\nu = 1$  states, respectively (De Leeuw & Dymanus 1971; Kaiser 1970), while for the  $\nu = 1-0$  vibrational band we adopted 0.072961 Debye for  $\text{H}^{35}\text{Cl}$  and 0.073049 Debye for  $\text{H}^{37}\text{Cl}$  (Pine et al. 1985). State-to-state rate constants for rotational de-excitation of HF through inelastic collisions with para and ortho  $\text{H}_2$  were taken from Guillon et al. (2011), whose calculations cover the first seven rotational levels of HF and extend up to a temperature of 200 K. An ortho-to-para ratio of 3 was adopted for  $\text{H}_2$ . For HF-He collisions, we adopted the values calculated by Reese et al. (2005), covering the first ten levels of HF up to 300 K. The use of collision rate constants with  $\text{H}_2$ , which are larger than with He by up to one order of magnitude, is critical for the excitation analysis of HF. We did not extrapolate the rate constants in temperature, based on the small variation in the collision cross sections for temperatures above 200–300 K (see Guillon et al. 2008, 2011). As rate constants for collisions of HCl and  $\text{H}_2$ , we adopted the values calculated by Neufeld & Green (1994) up to 300 K with He as collider, scaled up by a factor of 1.35 and without extrapolating in temperature. Collision rates of HCl with  $\text{H}_2$  may differ from those with He, although it is difficult to quantify these differences.

The computed line profiles are plotted in Fig. 1 for HF and in Fig. 2 for  $\text{H}^{35}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$ . The agreement between observed and calculated line profiles is very good, except for the  $J = 2-1$  transition of  $\text{H}^{35}\text{Cl}$  and of  $\text{H}^{37}\text{Cl}$ , which are predicted to be somewhat stronger than observed. The modest signal-to-noise ratio of these lines and the lack of collision rate constants for HCl and  $\text{H}_2$  could explain the discrepancies.

We derive an abundance relative to  $\text{H}_2$  in the inner regions of the envelope of  $8 \times 10^{-9}$  for HF and  $8 \times 10^{-8}$  for  $\text{H}^{35}\text{Cl}$ , with a  $\text{H}^{35}\text{Cl}/\text{H}^{37}\text{Cl}$  abundance ratio of  $3.3 \pm 0.3$ , consistent with that derived from previous observations of NaCl, KCl, and AlCl in IRC +10216 (Cernicharo et al. 1987; Cernicharo et al. 2000). The abundances of HF and HCl ( $\text{H}^{35}\text{Cl} + \text{H}^{37}\text{Cl}$ ) are plotted in Fig. 3 as a function of radius, for a model in which the initial abundances is set by the observations, but its radial dependence is a model prediction. Both HF and HCl are predicted to show a decrease in abundance in the outer layers, owing to photodissociation by interstellar ultraviolet photons. However, most of the contribution to the observed line intensities ( $\sim 80\%$ ) comes from circumstellar regions inside  $\sim 2 \times 10^{15}$  cm for HF, and  $2-4 \times 10^{15}$  cm for HCl, such that only the abundances in regions within these radii are properly sampled by the observed lines (see light shaded region in Fig. 3). The excitation of the levels involved in the observed HF and HCl lines is dominated by inelastic collisions with  $\text{H}_2$ , with the lines being subthermally excited beyond  $\sim 2 \times 10^{14}$  cm where the gas density is below  $10^9 \text{ cm}^{-3}$ . Infrared pumping via the  $\nu = 1$  vibrational state plays a non-negligible but minor role, enhancing the line intensities by 5% (HF) and 15% (HCl) with respect to the case where infrared



**Fig. 3.** Abundances relative to  $\text{H}_2$  of HF and HCl (including  $\text{H}^{35}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$ ) as a function of radius in IRC +10216. Abundances plotted as solid lines have a constant value in the inner envelope, derived from a fit to the observed lines (see Figs. 1 and 2), and decrease in the outer envelope due to photodissociation, as computed with a photochemical model. The region of the envelope sampled by the observed lines of HF and HCl (see text) extends up to  $3 \times 10^{15}$  cm (light shaded region). Dashed lines correspond to abundances computed by thermochemical equilibrium, which only holds up to  $\sim 3 R_*$  (dark shaded region).

pumping is neglected. Rotational lines within the  $\nu = 1$  state are predicted to be too weak to be detectable with HIFI, with predicted antenna temperatures of only  $\sim 0.025$  K for the  $\nu = 1$   $J = 3-2$  transition of  $\text{H}^{35}\text{Cl}$  and less than 0.005 K for all other such transitions. The abundances derived here are estimated to be uncertain by a factor of two for both HF and HCl. The error of the observations being 10–20%, 2–15% due to the noise in the spectra (see Table 1) and 10% due to the calibration of HIFI, most of the uncertainty comes from the model. For HCl, the error could be significantly larger if the collision rate constants with  $\text{H}_2$  as collider are substantially different from those with He. An increase in the collision rate constants would lower the abundance derived for HCl.

## 5. Discussion

The presence of both HF and HCl in the inner circumstellar regions of IRC +10216 is consistent with the thermochemical equilibrium (TE) calculations of the atmospheres of cool stars. In Fig. 3, we compare the abundances derived for HF and HCl with those computed under the assumption of TE, adopting solar elemental abundances (Asplund et al. 2009). The assumption of TE is only valid from the stellar photosphere out to a radius of  $\sim 3 R_*$  (dark shaded region in Fig. 3), beyond which the decrease in density and temperature causes the chemical reaction rates to drop rapidly and the molecular abundances to freeze out to the values of the TE region (Agúndez & Cernicharo 2006).

Hydrogen fluoride and AlF (whose abundance relative to  $\text{H}_2$  is  $7.5 \times 10^{-9}$ ; Agúndez 2009) are observed to be the main fluorine-bearing species in the inner envelope of IRC +10216. Thermochemical equilibrium calculations predict that HF is the major reservoir of fluorine in the TE region around both oxygen- and carbon-rich AGB stars, with the abundance of HF being essentially equal to the elemental abundance of fluorine. The abundance of HF in the atmospheres of AGB stars, derived from observations of ro-vibrational lines in the near-infrared, has been used as a proxy of the abundance of fluorine (Jorissen et al. 1992). These authors found F abundance enhancements of up to a factor of 30 over the solar value, and interpreted this as evidence of  $^{19}\text{F}$  stellar nucleosynthesis in AGB stars. The formation of fluorine remains poorly understood with three different



proposed sources: low-metallicity low-mass AGB stars, Wolf-Rayet stars, and neutrino spallation in core-collapse supernovae (see e.g. [Lucatello et al. 2011](#)). [Abia et al. \(2010\)](#) found that the analysis of the HF ro-vibrational lines made by [Jorissen et al. \(1992\)](#) was affected by line blends with C<sub>2</sub> and CN, such that the derived F abundances are only slightly enhanced (with a mean value of 0.2 dex) over the solar value, in closer agreement with theoretical predictions of low-mass AGB stellar models. In IRC +10216, we derive, through an alternative method (the observation of the HF  $J = 1-0$  rotational line), a fluorine abundance of  $3.60 \pm 0.30$  (in the usual logarithmic scale with H having a reference value of 12), which is almost one order of magnitude lower than the solar value ( $4.56 \pm 0.30$ ; [Asplund et al. 2009](#)). This seems to indicate that in IRC +10216 there is an important degree of depletion of F onto dust grains, even larger than that found in interstellar clouds where the HF abundance relative to H<sub>2</sub> is  $(1.1-1.6) \times 10^{-8}$  ([Sonnentrucker et al. 2010](#); [Monje et al. 2011](#)). Our ability to place constraints on the stellar nucleosynthesis of fluorine in IRC +10216 is hampered by the fact that the HF abundance we derive is a lower limit to the elemental abundance of fluorine. Nevertheless, the low HF abundance derived here does not point toward any F abundance enhancement over the solar value in IRC +10216, thus arguing in favour of the results of [Abia et al. \(2010\)](#). Further observations of the  $J = 1-0$  line of HF in other AGB stars will help us to understand the degree of fluorine depletion onto dust grains and any possible abundance enhancement due to stellar nucleosynthesis.

In the case of hydrogen chloride, in the inner regions of IRC +10216's envelope the derived abundance, including both isotopes, is  $1.1 \times 10^{-7}$  relative to H<sub>2</sub>, making it the major reservoir of chlorine, followed by AlCl whose abundance relative to H<sub>2</sub> is  $5 \times 10^{-8}$  ([Agúndez 2009](#)). Other chlorine-bearing species such as NaCl and KCl have lower abundances,  $1.3 \times 10^{-9}$  and  $7 \times 10^{-10}$  relative to H<sub>2</sub>, respectively ([Agúndez 2009](#)). Together, these species have a total chlorine abundance of  $8 \times 10^{-8}$  relative to the total number of H nuclei, i.e. one quarter of the solar abundance of Cl ( $3.2 \times 10^{-7}$  relative to H; [Asplund et al. 2009](#)). The abundance of chlorine should not be modified inside AGB stars as <sup>35</sup>Cl and <sup>37</sup>Cl are thought to be formed during explosive oxygen burning in supernovae ([Woosley et al. 1973](#)). Therefore, the missing chlorine in the inner envelope of IRC +10216 may be in the form of neutral atomic Cl, which together with HCl and AlCl is predicted to lock most of the chlorine according to TE calculations (see Fig. 2 of [Cernicharo et al. 2010b](#)), or alternatively may have condensed onto dust grains.

## 6. Concluding remarks

The hydrogen halides HF and HCl have been proven to be ubiquitous molecules in different types of interstellar environments. The observations presented in this Letter show that these two molecules are also important constituents of circumstellar envelopes around evolved stars. They would be formed in the inner regions close to the star under thermochemical equilibrium, which predicts that HF and HCl should be the major reservoirs of fluorine and chlorine, respectively, in the atmospheres of both O- and C-rich AGB stars. The abundances derived here for the carbon star envelope IRC +10216 are substantially lower than predicted by TE calculations, suggesting that F and Cl are likely to be severely depleted onto dust grains, by ~90% for HF and ~75% for HCl, although some chlorine may also be in the form of atomic Cl. We also find that in IRC +10216 the abundance of F is probably not enhanced over the solar value by nucleosynthesis in the AGB star, although this conclusion is weakened

somewhat because the HF abundance we derive is a lower limit to the elemental abundance of fluorine. Both HF and HCl should be detectable with HIFI through low  $J$  pure rotational transitions in other AGB stars, especially in those with high mass loss rates, which have a large amount of emitting material and are difficult to observe in the near-infrared owing to the opacity of the dusty envelope.

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