

LETTER TO THE EDITOR

# Detection of anhydrous hydrochloric acid, HCl, in IRC +10216 with the *Herschel* SPIRE and PACS spectrometers<sup>★</sup>

## Detection of HCl in IRC +10216

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### ABSTRACT

We report on the detection of anhydrous hydrochloric acid (hydrogen chlorine, HCl) in the carbon-rich star IRC +10216 using the spectroscopic facilities onboard the *Herschel* satellite. Lines from  $J = 1-0$  up to  $J = 7-6$  have been detected. From the observed intensities, we conclude that HCl is produced in the innermost layers of the circumstellar envelope with an abundance relative to  $H_2$  of  $5 \times 10^{-8}$  and extends until the molecules reach its photodissociation zone. Upper limits to the column densities of AlH, MgH, CaH, CuH, KH, NaH, FeH, and other diatomic hydrides have also been obtained.

**Key words.** stars: individual: IRC +10216 – stars: carbon – astrochemistry – line: identification – stars: AGB and post-AGB

## 1. Introduction

The chemistry of chlorine (Cl) in the interstellar medium (ISM) is particularly poorly known, mainly because of the relatively small number of Cl-containing molecules detected to date (see Neufeld & Wolfire 2009). This element has two stable isotopes ( $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ ) and has a relatively low solar abundance of  $3 \times 10^{-7}$ , relative to H (Asplund et al. 2009). Anhydrous hydrochloric acid (HCl; also known as hydrogen chloride) remains the only chlorine-bearing molecule observed to date in the interstellar medium, and is believed to be one of the major reservoirs of chlorine in the ISM. It has been observed in both the dense and diffuse interstellar medium (Blake et al. 1985; Federman et al. 1995). The three metal chlorides AlCl, NaCl, and KCl have also been observed in space (Cernicharo & Guélin 1987), but solely in circumstellar envelopes (CSEs) around evolved stars, where they are formed in the hot and dense stellar atmospheres under thermochemical equilibrium. Although it has not yet been observed in such environments HCl is also expected to be a major chlorine species in circumstellar envelopes. Being a light hydride, its rotational transitions lie in the submillimeter and far-infrared domain, which is difficult to observe from the ground because of severe atmospheric absorption. Other light species, mostly metal-bearing hydrides such as AlH, FeH, MgH, and CaH, are detected in sunspots and M-type stars (Gizis 1997;

Wallace et al. 2001) and are also potentially present in the innermost zones of carbon-rich circumstellar envelopes.

The infrared source IRC +10216 (CW Leo) is one of the brightest in the sky, making it an ideal target to be observed with the *Herschel* Space Observatory (Pilbratt et al. 2010). Around 50% of the molecules observed in space have been detected towards this object. Most of those molecules are heavy carbon chain radicals (Cernicharo & Guélin 1996a), metal-bearing species (Cernicharo & Guélin 1987), and both diatomic and triatomic molecules (Cernicharo et al. 2000). Its far-infrared spectrum, obtained with low spectral resolution with the Infrared Space Observatory (ISO), was analyzed by Cernicharo et al. (1996b) with ISO with limited spectral resolution. The spectrometers on board *Herschel* (Pilbratt et al. 2010) offer the possibility to search for light diatomic hydrides with high sensitivity, thanks to the telescope's large collecting area and the performances of the instruments, and with high spectral resolution compared to ISO. In this Letter, we report on the first detection of HCl toward the circumstellar envelope of the carbon-rich star IRC +10216, and discuss the implications for the chemistry of chlorine in these astronomical regions. We also present upper limits to the abundance of metal hydrides.

## 2. Observations and data reduction

The three instruments on board the *Herschel* satellite (Pilbratt et al. 2010) have medium to high spectral resolution spectrometers. PACS and SPIRE spectroscopic observations

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

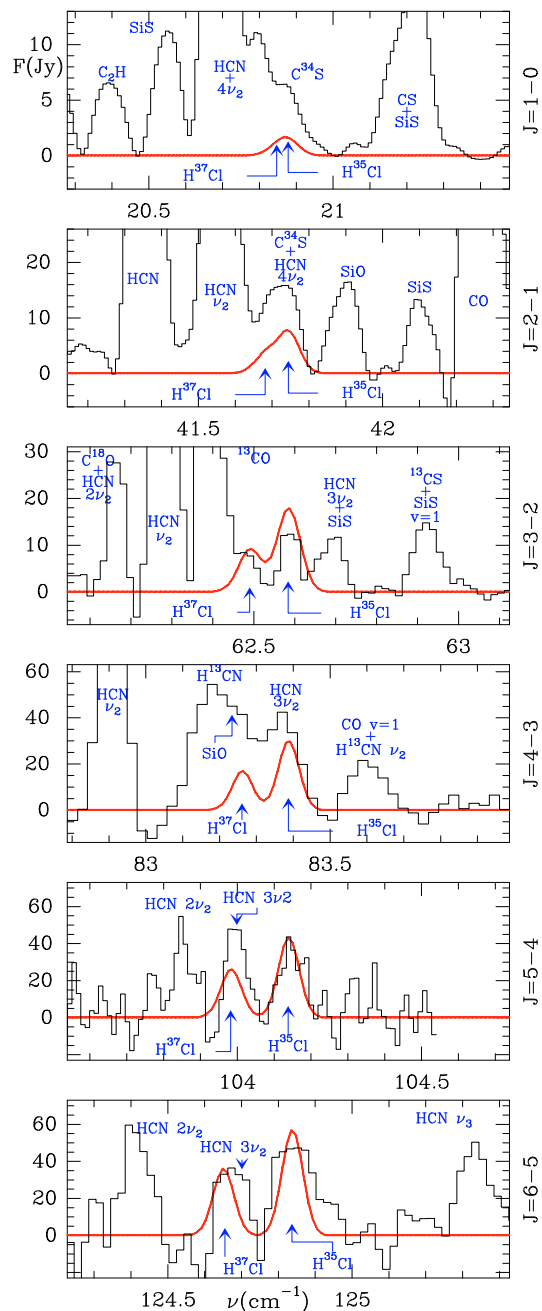
were obtained in the context of the guaranteed time key programme Mass-loss of Evolved StarS (Groenewegen et al., in prep.). The PACS instrument, its in-orbit performance and calibration, and its scientific capabilities are described in Poglitsch et al. (2010). The PACS spectroscopic observations of IRC +10216 consist of full SED scans between 52 and 210  $\mu\text{m}$  obtained in a  $3 \times 1$  raster, i.e., a pointing on the central object, and two additional ones located  $30''$  on each side of it. The observations were performed on Nov. 12 2009 (OD 182). The position angle was 110 degrees. The instrument mode was a non-standard version of the chop-nod PACS-SED AOT, used with a large chopper throw ( $6'$ ). A description of that mode and of the data reduction process can be found in Royer et al. (2010). The estimated global uncertainty in the line fluxes is 50%. However, the relative calibration is much better, hence it is possible to estimate the contribution of the most abundant species to the lines of HCl by using adjacent lines of these species. PACS and SPIRE photometry observations are presented in Ladjal et al. (2010).

The SPIRE FTS measures the Fourier transform of the source spectrum across short (SSW, 194–313  $\mu\text{m}$ ) and long (SLW, 303–671  $\mu\text{m}$ ) wavelength bands simultaneously. The *FWHM* beamwidths of the central SSW and SLW pixels vary between 17–19'' and 29–42'', respectively. The source spectrum, including the continuum, is restored by taking the inverse transform of the observed interferogram. For more details about the SPIRE FTS and its calibration, we refer to Griffin et al. (2010) and Swinyard et al. (2010). We made use of two observations of IRC +10216 with the high-resolution mode of the SPIRE FTS on the 19 November 2009 (OD 189). For each observation, ten repetitions were carried out, each of which consisted of one forward and one reverse scan of the FTS, each scan taking 66.6 s. The total on-source integration time for each FTS spectrum of IRC +10216 was 1332 s. In the end, both FTS spectra were averaged. The unapodized spectral resolution is 1.2 GHz ( $0.04 \text{ cm}^{-1}$ ), which after apodization (using extended Norton-Beer function 1.5; Naylor & Tahic 2007) became 2.1 GHz ( $0.07 \text{ cm}^{-1}$ ). The sensitivity of the SPIRE/FTS spectrometer allows us to detect lines as weak as 1–2 Jy. The whole PACS+SPIRE spectrum of IRC +10216 has been shown by Decin et al. (2010).

### 3. Results

In addition to lines arising from vibrational levels up to 10 000 K (Cernicharo et al. 1996b, 2010), HCN is the main contributor to the spectral features detected with the SPIRE and PACS spectrometers. The frequencies of these lines were calculated by Cernicharo et al. (2010) from the rotational constants provided by Maki et al. (1996, 2000). These frequencies were used to identify most features shown in Fig. 1. The other strong features arise from CO, SiS, SiO, and CS. These lines were analyzed by Decin et al. (2010), and the data used to estimate the contribution of these species to the lines of HCl shown in Fig. 1. HCl has two stable isotopologs,  $\text{H}^{35}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$ , the former being 3.1 times more abundant than the latter in IRC +10216, according to the  $^{35}\text{Cl}/^{37}\text{Cl}$  abundance ratio derived from observations of NaCl, KCl, and AlCl (Cernicharo et al. 2000). Frequencies for  $\text{H}^{35}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$  were computed from the rotational constants derived by Cazzoli & Puzzarini (2004). The laboratory measurements have an accuracy better than 0.5 MHz for lines up to  $J_{\text{upper}} = 14$ .

The first two rotational transitions of HCl are covered within the spectral range of SPIRE, and are detected as emission lines in the spectral data obtained towards IRC +10216 (see Fig. 1). The low spectral resolution of SPIRE (2.1 GHz) prevents us



**Fig. 1.** Continuum-removed spectra of IRC +10216 observed with SPIRE and PACS showing the first 6 rotational lines of HCl (black histograms) and the line profiles resulting from the LVG model (continuous red lines). The contribution of the isotopes of CS and the vibrationally excited states of HCN to some of the HCl and  $\text{H}^{37}\text{Cl}$  lines has been estimated from adjacent lines of these species (see text).

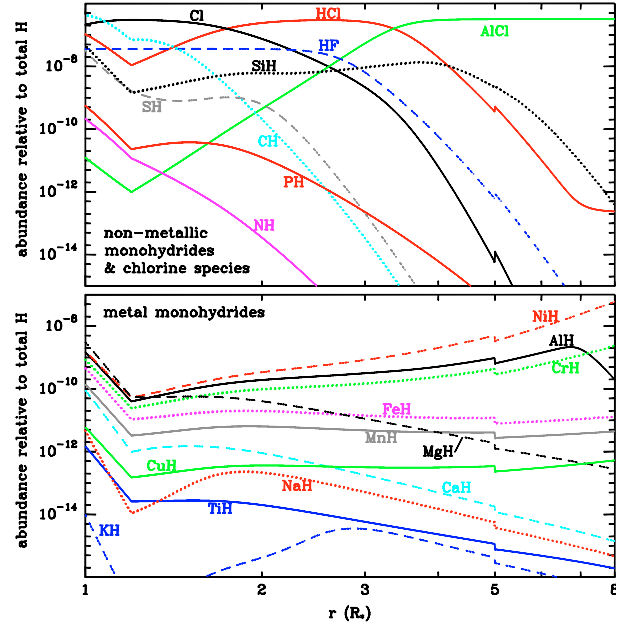
from resolving the individual emission components related to  $\text{H}^{35}\text{Cl}$  and  $\text{H}^{37}\text{Cl}$ , which are separated by 940 and 1879 MHz for the  $J = 1-0$  and  $J = 2-1$  transitions, respectively. The  $J = 1-0$  emission is blended with the  $J = 13-12$  transition of  $\text{C}^{34}\text{S}$ . Together, they appear as a shoulder at the high frequency side of a stronger emission feature, which is a composite of several rotational lines of HCN in different vibrational states (we estimate a flux of 3 Jy for the  $J = 1-0$  line of HCl). The  $J = 2-1$  transition is less severely blended with stronger features, although it does overlap with the  $J = 26-25$  transition of  $\text{C}^{34}\text{S}$  and with some  $\ell$ -doubling components of the  $J = 14-13$  transition of HCN in its  $\nu_2 = 4$  vibrational state. Inspection of the line

intensities of these species ( $C^{34}S$  and  $HCN \nu_2 = 4$ ) in the nearby spectral region (see Decin et al. 2010), indicates that they contribute at most half of the intensity of the detected emission feature. Hence, the measured flux for the  $J = 2-1$  transition of HCl is 9 Jy.

The spectral range of PACS covers the  $J = 3-2$  up to the  $J = 9-8$  rotational transitions of HCl. The data acquired toward IRC +10216 allow one to clearly identify the  $J = 3-2$  to  $J = 7-6$  transitions (see Fig. 1), the components related to  $H^{35}Cl$  and  $H^{37}Cl$  being spectrally resolved. The lines are clearly seen without the contamination of stronger lines with derived fluxes, after removing the contribution from other species, of 12, 26, 40, 45, and 60 Jy for the  $J = 3-2$  to  $J = 7-6$  lines, respectively. Among them, only the  $J = 4-3$  rotational transition appears appreciably contaminated, mostly by the  $J = 29-28$  transition of  $H^{13}CN$ , which severely hampers the visualization of the  $H^{37}Cl$  line, and to a lesser extent by the  $J = 28-27$  transition of HCN in its  $\nu_2 = 3 \ell = 1$  vibrational level, which still leaves the  $H^{35}Cl$  line visible. The  $H^{35}Cl$  component of the  $J = 7-6$  transition is observed as an emission feature at the correct frequency and with an intensity compatible with the lower  $J$  transitions. However, the signal-to-noise ratio is only 5, providing only upper limits to the intensity of the  $H^{37}Cl$  isotopomer. Higher  $J$  lines are not detected because of the limited sensitivity at these frequencies. In spite of the low spectral resolution and the, in some cases quite severe, contamination of the observed HCl lines, the large number of transitions covered by the SPIRE and PACS data makes the identification of HCl in the circumstellar gas of IRC +10216 quite certain.

The observed HCl lines have been interpreted with the aid of an excitation and radiative transfer model based on the Large Velocity Gradient (LVG) formalism. The  $H^{35}Cl/H^{37}Cl$  abundance ratio is poorly constrained from the observations and was fixed to be 3.1, as derived for the  $^{35}Cl/^{37}Cl$  abundance ratio from previous observations of NaCl, KCl, and AlCl in IRC +10216 (Cernicharo & Guélin 1987; Cernicharo et al. 2000). We included the first 20 rotational levels within the ground vibrational state of both  $H^{35}Cl$  and  $H^{37}Cl$ . The adopted dipole moment is 1.109 D (De Leeuw & Dymanus 1971). The rate coefficients for collisional de-excitation from HCl levels up to  $J = 7$ , through collisions with  $H_2$  and He, were taken from Neufeld & Green (1994), and the Infinite Order Sudden (IOS) approximation was applied for higher  $J$  levels. The circumstellar envelope is simulated as a spherically distributed gas expanding at a constant velocity of  $14.5 \text{ km s}^{-1}$ . The gas density and temperature radial profiles were taken from Agúndez (2009) and Fonfría et al. (2008). The adopted distance to IRC +10216 is 120 pc (Schöier & Olofsson 2001).

Molecules in IRC +10216 are either concentrated around the central star (e.g., HCN) or distributed in a hollow shell of radius  $10''-20''$  (e.g. CN). The lack of information about the HCl line profiles prevents one from deciding which of these two distributions HCl follows. Several radial distributions for HCl were tested, but the LVG model indicates that the observed relative intensities of the HCl lines can only be reproduced if HCl is concentrated around the central star. We thus adopted an abundance radial profile in which the abundance of HCl relative to  $H_2$  is constant from the stellar photosphere out to the radius where it is photodissociated by the ambient interstellar UV field. The adopted photodissociation rate for HCl is  $1.1 \times 10^{-9} \exp(-1.8 A_V) \text{ s}^{-1}$  (Roberge et al. 1991), where  $A_V$  is the visual extinction against interstellar light at each radial position in the envelope. The derived abundance of  $H^{35}Cl$ , relative to  $H_2$ , is  $5 \times 10^{-8}$ , which produces line profiles that are



**Fig. 2.** Abundances of several hydrides computed by thermochemical equilibrium for the stellar atmosphere and inner envelope of IRC +10216. Abundances are relative to total H and are shown as a function of the distance to the center of the star.

in reasonable agreement with the observed ones, as shown in Fig. 1.

### 3.1. Chlorine chemistry in IRC +10216

To verify whether the above conclusion is compatible with chemical arguments, we calculated the composition of the gas in the surroundings of the stellar atmosphere of IRC +10216 under thermochemical equilibrium (TE). The utilized code is described in Tejero & Cernicharo (1991). We included 24 chemical elements with solar abundances (Asplund et al. 2009), and assumed a higher carbon abundance so that  $[C]/[O] = 1.5$ . The thermochemical data of the included molecules were taken from Chase (1998), with updates for various species being taken from the recent literature. In particular, the thermochemical data of TiH were updated according to Burrows et al. (2005). The adopted parameters for IRC +10216 are presented in Agúndez & Cernicharo (2006). In Fig. 2, we show the calculated abundances of several hydrides in the stellar atmosphere and inner envelope of IRC +10216. We see that HCl reaches a maximum abundance of  $6 \times 10^{-7}$  relative to  $H_2$  (i.e., half that value if expressed relative to H) in the  $2-3 R_*$  region, where TE still holds. According to the results shown in Fig. 2 the species that lock most of the chlorine in the inner envelope of IRC +10216 are atomic Cl (in the region inner to  $2 R_*$ ), HCl (in the  $2-3 R_*$  region), and AlCl (at radii larger than  $3 R_*$ ). The HCl abundance derived from the SPIRE and PACS data is lower than the calculated thermochemical value by a factor of  $\sim 10$ , which is acceptable given the uncertainties associated with the observations and with both the LVG and the thermochemical equilibrium models. Other Cl-bearing molecules observed in IRC +10216 are AlCl, NaCl, and KCl (Cernicharo & Guélin 1987), for which the abundances relative to  $H_2$  derived from the IRAM 30-m data are  $3.5 \times 10^{-8}$ ,  $1.0 \times 10^{-9}$ , and  $2.5 \times 10^{-10}$ , respectively (Agúndez 2009). Hence, HCl and AlCl are the most abundant chlorine-bearing molecules in the inner envelope of IRC +10216, HCl being slightly more abundant. As the circumstellar gas expands, molecules become exposed to the ambient UV field and are then photodissociated.

The chlorine carried by HCl will then be liberated to the gas phase as atomic Cl, which in the outer molecular shells (at  $10''$ – $20''$ ) is just slowly ionized by interstellar UV photons (the ionization potential of Cl is 13.0 eV, i.e., lower than, but very close to, that of hydrogen). Therefore, it can participate in rapid chemical reactions to form new Cl-bearing molecules. Which are the most likely such molecules is difficult to predict because of the lack of chemical kinetics data for reactions between atomic Cl and abundant molecules in the outer envelope of IRC +10216. The literature on the chemical kinetics of chlorine is vast, but focuses mainly on species such as chlorofluorocarbons (CFCs), which are of interest as important pollutants of the terrestrial atmosphere. Some reactions of atomic Cl with unsaturated hydrocarbons such as  $C_2H_2$  have been also studied, although the derived rate constant is normally for the three body process, which is not of interest in the outer envelope of IRC +10216. The UMIST Database for Astrochemistry (Woodall et al. 2007) contains several reactions involving chlorine species, but is mostly oriented toward the formation of HCl in interstellar clouds. Since atomic Cl is relatively reactive, it is expected to react with abundant carbon-bearing molecules, such as the radicals  $C_2H$  or  $C_4H$ , forming chlorine-carbon molecules. The detection of these species (e.g., CCl, HCl,  $C_2Cl$ , etc.) would certainly aid in understanding the chemistry of chlorine in the outer layers of circumstellar envelopes, which until to now has been a mystery.

### 3.2. Other hydrides in IRC +10216

As stated above, several metal hydrides have their rotational transitions in the submillimeter and far-infrared domains. These species are known to be abundant in the photosphere of AGB stars (Gizis 1997), and we expect to detect them if they are not condensed onto dust grains. We checked the rotational transitions of several of these hydrides and we found no clear detection at the sensitivity limit of the data (3 Jy for SPIRE and 10–20 Jy for PACS, depending on the degree of blending, at the  $3\sigma$  level). Moreover, many of their transitions are located in frequency domains in which the line confusion limit is reached. This is mainly the case for the ranges associated with the HCN lines. As an example, the  $J = 5-4$  and  $10-9$  lines of AlH lie at 62.825 and 124.562  $cm^{-1}$ , respectively. Neither line is detected (see Fig. 1). Assuming that the emitting region for metal hydrides has an average kinetic temperature of 300 K, then the  $3\sigma$  upper limits to their abundance (relative to  $H_2$ ) are  $3 \times 10^{-9}$  (NaH),  $9 \times 10^{-9}$  (CuH),  $1.6 \times 10^{-6}$  (AlH),  $4 \times 10^{-8}$  (MgH),  $3 \times 10^{-7}$  (CaH),  $2 \times 10^{-9}$  (LiH),  $3 \times 10^{-9}$  (KH), and  $10^{-9}$  (FeH). We assumed that CaH and FeH have a dipole moment of one Debye. In addition, SiH has its rotational transitions in the SPIRE and PACS frequency domains. However, its dipole moment is rather low and the upper limit to its abundance relative to  $H_2$  is  $6 \times 10^{-6}$ . Another interesting species is HF for which our chemical models predict an abundance  $\sim 10$  times below that of HCl. Unfortunately, its  $J = 1-0$  and  $J = 2-1$  lines are strongly blended with HCN vibrationally excited lines and those of other species. The data used to estimate these upper limits are shown in Fig. 1 of Decin et al. (2010).

## 4. Conclusions

The detection of HCl in IRC +10216 indicates the active role of chlorine in the chemistry of the warm innermost region of

the circumstellar envelope. Together with AlCl, HCl is the most abundant chlorine-bearing species in this circumstellar envelope, in contrast NaCl and KCl having abundances 10 and 30 times lower, respectively. HIFI observations are needed to spectroscopically resolve the rotational lines of light species and to distinguish them from those of more abundant molecules. These observations will provide more precise upper limits and might perhaps hold some detections of light species.

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