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M. SATTA¹ – M.H.D. VAN DER WIEL² – D.A. NAYLOR³ G. MAKIWA³ – A. ABERGEL⁴

HF molecule as a tracer of column density in interstellar diffuse gas: the adsorption on dust grain surfaces

Abstract – The HF molecule has been proposed as a sensitive tracer of diffuse interstellar gas, but at higher densities its abundance could be influenced heavily by freeze-out onto dust grains, and hence it can lead to a distortion as a mass tracer if these freeze-out effects are not properly taken into account. At this regard it is important to refer to the study of the spatial distribution of a collection of absorbing gas clouds, some associated with the dense, massive star-forming core NGC6334 I, and others with diffuse foreground clouds elsewhere along the line of sight. A far-infrared spectral imaging has been used from the Herschel SPIRE iFTS to construct a map of HF absorption at 243 mm in a region surrounding NGC6334 I and I(N). These data also imply a lack of gas-phase HF in the envelope of core I(N). Using a simple description of adsorption onto and desorption from dust grain surfaces, it can be shown that the overall lower temperature of the envelope of source I(N) is consistent with freeze-out of HF, while it remains in the gas phase in source I. The HF molecule can be used as a tracer of column density in diffuse gas ($n_H \approx 10^2 - 10^3$ cm⁻³), and it may uniquely traces a relatively lowdensity portion of the gas reservoir available for star formation that otherwise escapes detection. At higher densities prevailing in protostellar envelopes ($\geq 10^4$ cm⁻³), there are evidences of HF depletion from the gas phase under sufficiently cold conditions.

¹ CNR-ISMN, Department of Chemistry, University of Rome «Sapienza», Italy.

² Centre for Star and Planet Formation, Niels Bohr Institute & Natural History Museum of Denmark, University of Copenhagen, Denmark.

³ Institute for Space Imaging Science, Department of Physics & Astronomy, University of Lethbridge, Canada.

⁴ Institut d'Astrophysique Spatiale, CNRS, Univ. Paris-Sud, Université Paris-Saclay, France.

Introduction

Atomic fluoride is the only element in the interstellar chemistry which is mainly neutral, because of its ionization potential >13.6 eV, reacts exothermically with H, to form neutral HF, and lacks an efficient chemical pathway to produce its hydride cation HF^+ due to the strongly endothermic nature of the reaction with H^{+} . For these reasons chemical models predict that essentially all interstellar F is locked in HF molecules [1, 2], which has been confirmed by observations across a wide range of atomic and molecular ISM conditions [3]. Galactic [4] and extragalactic [5] interferometric observations show that CF⁺, the next most abundant F bearing species after HF, has an abundance roughly two orders of magnitude lower than HF. As for destruction of HF, the most efficient processes are UV photodissociation and reactions with C⁺, but both of these are unable to drive the majority of fluoride out of HF [2]. Because of the constant HF/H, abundance ratio and the high probability that HF molecules are in the rotational ground state, measurements of HF J=0 \rightarrow 1 absorption provide a straightforward proxy of H, column density. This has led to the suggestion that, at least in diffuse gas, HF absorption is a more reliable tracer of total gas column density than the widely used carbon monoxide (CO) rotational emission lines, and is more sensitive than CH or H₂O absorption [6].

Based on the above arguments, HF absorption measurements are a good tracer of overall gas column density. However, HF itself may suffer from freeze-out effects [7, 8] and the density and temperature conditions needed for HF adsorption onto dust grains have been studied in astrophysical contexts [9]. (Figure 1 is adapted from Ref. 9).

Discussion

Any freeze-out of interstellar HF will obfuscate the direct connection between HF absorption depth and H_2 column density described above. A proper analysis [9] of these freeze-out effects has been carried out by studying the filamentary, starforming cloud NGC 6334, at a distance of 1.35 kpc, which harbors a string of dense cores: specifically the region of ~ 2.4 × 1.6 pc surrounding the embedded cores NGC 6334 I and NGC 6334 I(N) (See Fig. 1). The mass of source I(N) exceeds that of sister source I by a factor of ~ 2-5, but the ratio of their bolometric luminosities is 30-140 in favour of source I because of the markedly lower temperature for source I(N).

Envelope of core I(N) is more massive than that of core I, but has a similar size, hence its total gas column density toward core I(N) should be higher. On the contrary the map of equivalent width of the HF 1 \leftarrow 0 absorption neglects this assumption. This can be explained if the the lack of HF absorption associated with the I(N) core is not due to the difference in total (H₂) column, but to the fact that HF is primarily frozen out onto dust grains in core I(N), while HF is in the gas phase in core I.



Fig. 1. Map of equivalent width of the HF 1 \leftarrow 0 absorption signature measured with Herschel SPIRE iFTS (see ref. 9).

To support the hypothesis of HF being depleted from the gas phase in core I(N), a rudimentary model has been adopted (see ref 9 and references therein). We assume that thermal desorption is the dominant mechanism that drives molecules from the grain surface back into the gas phase, where λ , and ξ , are respectively the adsorption and the desorption rate:

$$\lambda(n_{\rm H}, T_{gas}) = 4.55 \times 10^{-18} \left(\frac{T_{gas}}{m_{\rm HF}}\right)^{0.5} n_{\rm H} \ [s^{-1}] \tag{1}$$

$$\xi(T_{dust}) = v_{vib} exp\left(\frac{-E_{b,HF}}{kT_{dust}}\right) \qquad [s^{-1}]$$
(2)

Here, T_{gas} and T_{dust} are the temperatures of gas and dust, m_{HF} is the molecular weight of HF, n_{H} is the density of hydrogen nuclei, v_{vib} is the vibrational frequency of the HF molecule in its binding site, for which we adopt 10^{13} s⁻¹, k is the Boltzmann constant, and $E_{b,HF}$ is the binding energy of HF to the dust grain surface. Typical interstellar dust grains, especially those embedded in cold, star-forming regions, are covered in one or multiple layers of ice consisting of various molecules, mainly H₂O, CO, and CO₂ [10]. We collect binding energy values for several types of grain surfaces in Table 1. For CO and CO₂ ice covered grains we adopt calculated binding energies from the literature [11, 12], while for hydrogenated bare silicate grains and H₂O ice covered grains, these values result from ab initio chemical calculations 9.

To calculate the HF binding energies we carry out quantum calculations within the Kohn-Sham implementation of Density Functional Theory using the Quantum Espresso Simulation Package [13]. Perdew-Burke-Ernzerhof exchange-correlation functional ultrasoft pseudopotentials are used. KS valence states are expanded in a plane-wave basis set with a cutoff at 340 eV for the kinetic energy. The selfconsis-

Surface topology	E _b ,HF (Kcal/mol)
SiH ₂ …FH	2.23
SiH(OH)…FH	15.69
$Si(OH)_2$ FH(OH)_2Si	17.01
Si(OH) ₂ ·H ₂ O·HF	25.42
(CO) _{ICE} ···FH	2.13
$(CO_2)_{ICE}$ ···FH	2.22
$(H_2O)_{ICE}$ FH	12.68

Table 1. Binding energies for HF onto various surfaces.



Fig. 2. Schematic view of the SiH₂...FH topology.

tency of the electron density is obtained with the energy threshold set to 10^{-5} eV. Calculations are performed using the primitive unit cell containing a total number of 46 atoms for bare hydrogenated silica, and 54 atoms for hydrogenated silica covered with one layer of H₂O ice. The geometry optimization is used within the conjugate gradients scheme, with a threshold of 0.01 eV Å⁻¹ on the Hellmann-Feynman forces on all atoms; the Si atoms of the bottom layers are fixed at their bulk values.

In amorphous silica, exposed to terrestrial atmosphere, the most stable surface $[\alpha$ -Quartz(001)] is characterized by five types of terminal chemical groups: =SiH₂, =SiH, =Si-O-Si= (siloxane bridges), =SiOH (single silanol), =Si(OH)₂ (geminal silanol). =SiH₂ and =SiH groups are less probable because siloxane and silanol groups have lower energy content with respect to them. At T > 500 K silanol groups are converted in siloxane bridges, with H₂O production (dehydroxilation). The binding energy of HF with the SiH terminus of hydrogenated crystalline silica is based on calculations for the hydroxylated alpha-quartz (001) surface. The binding energy



Fig. 3. Schematic view of the SiH(OH)…FH topology.



Fig. 4. Schematic view of the Si(OH), H₂O·HF…topology.

of HF with one layer of H_2O ice on amorphous hydrogenated silicate is estimated by assuming that the most common structure in this case is the HF molecule interacting with a H_2O molecule bonded to silanol (SiOH), which is the most abundant surface group in amorphous silica [14].

The binding energies of HF with CO and CO₂ ice (Table 1) are taken from calculations for molecules in the gas phase. We consider the gas phase binding energies of HF with CO and CO₂ to be similar to those of HF with CO and CO₂ ices adsorbed on an inert surface such as that of hydroxylated amorphous silica. This approximation is based on the weak interactions of these ices with hydroxylated silica and within the CO and CO₂ molecular solids, so that the electronic density of CO and CO₂ in solid form is not significantly altered with respect to their state in the gas phase. Hence, the binding energy of the HF molecule with CO or CO₂ as calculated in the gas phase is applicable for the condensed phase. The situation is notably different for interactions with H₂O in the gas or adsorbed form, because of its stronger interaction with silica and HF. For HF interacting with H₂O ice, we use binding energies from calculations 9.

The binding energy of HF with the SiH and SiOH terminus of hydrogenated crystalline silica are shown in fig. 2 and 3. The binding energy of HF with one layer of H_2O ice on amorphous hydrogenated silicate (See fig. 4) is estimated by assuming that the the most common structure in this case is the HF molecule interacting with a H_2O molecule bonded to silanol (SiOH), which is the most abundant surface group in amorphous silica.

The analysis of the radial dependence of adsorption and desorption timescales (see eq. 1 and 2) of HF from various types of grain surfaces indicates that the grains are mainly supposed to be made of: $(CO)_{ICE}$, $(CO_2)_{ICE}$, SiH_2 ($H_2O)_{ICE}$, whereas H_2O

and OH groups seems to not play any role in the grain adsorption of HF in these ISM molecular clouds.

Summarizing, this work uses HF as a sensitive tracer for (molecular) gas at relatively low densities that may be contributing mass to star forming cores. The HF signature reveals a gas reservoir that is inconspicuous in traditional dense gas tracers such as CO. In addition, we show that gas phase HF in higher density environments $(>10^5 \text{ cm}^{-3})$ is extremely sensitive to interactions with dust grains and will be depleted significantly at low dust temperatures 9.

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