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# DARK CLOUD CHEMISTRY OF NITROGEN HYDRIDES WITH THE HERSCHEL SPACE OBSERVATORY

R. Le Gal[1], P. Hily-Blant[1, 2] and A. Faure[1]

**Abstract.** Stars form in dark clouds. A complete knowledge of dark cloud chemical composition can be helpful to understand star- and planet-formation processes. Nitrogen is the sixth most abundant interstellar element, and also a basic component of prebiotic molecules. Yet, the reservoir of gaseous nitrogen in dark clouds is not precisely known. It is expected to be mainly N and/or $N_2$, but both are unobservable in dark gas. Their abundances therefore derive indirectly from those of other N-bearing species through chemical modelling. In this context, our work focuses on a revision of the nitrogen-hydride chemistry in dark clouds using fundamental rotational transitions of NH, $NH_2$, and $NH_3$ observed with *Herschel*/HIFI towards a sample of low-mass protostellar objects. To this purpose, we update and upgrade a chemical network containing the chemistry of the *ortho* and *para* forms of nitrogen-hydride molecules, allowing to reproduce the NH : $NH_2$ : $NH_3$ ratios observed with *Herschel*/HIFI towards IRAS 16293-2422, putting constraints on the budget of gas-phase carbon, oxygen and sulphur. Furthermore, our results explain the non-thermodynamical *ortho*-to-*para* ratio of ammonia observed in cold diffuse gas.

Keywords: gas-phase astrochemistry, interstellar molecule abundances, dark cloud conditions.

## 1 Introduction

Nowadays, a comprehensive view of the chemical content of the densest parts of the interstellar medium (ISM), where stars form, is still lacking. One such issue regards the nitrogen chemistry in dark clouds. Our strategy has been to compare recent *Herschel* observations with chemical models in order to constrain, and so try to understand, the nitrogen chemistry.

### 1.1 Nitrogen riddle

Nitrogen ($^{14}$N) is, in abundance, the sixth element in our local Universe (after the hydrogen, helium, carbon, oxygen and neon elements, see *e.g.* Nieva & Przybilla 2012) with a nuclear spin $I = 1$ playing a crucial role in nitrogeneous molecule spectroscopy by inducing an hyperfine structure. As of today, almost 70 N-bearing species have been detected through their rotational transitions in the gas-phase ISM from diatomic molecules, *e.g.* CN (McKellar 1940; Adams 1941) and NH (Meyer & Roth 1991), to complex organic molecules (COMs) with up to 13 atomes, with $HC_{11}N$ (Bell et al. 1997), in a wide range of astrophysical objects in our Galaxy and in more distant galaxies, from diffuse gas (Liszt & Lucas 2001) to prestellar cores (Bergin & Tafalla 2007) and protoplanetary disk (Dutrey et al. 2007). N-bearing molecules can thus serve as tools to probe the physico-chemistry of the ISM. For instance, CN is a probe of magnetic fields in dense regions (thanks to the Zeeman effect, see *e.g.* Crutcher 2012), $N_2H^+$ and its isotopologue $N_2D^+$ are tracers of the high density regions ($n \sim 10^5\,\mathrm{cm}^{-3}$, Pagani et al. 2007; Crapsi et al. 2007), the inversion transitions of ammonia can probe the gas temperature in molecular clouds (Walmsley & Ungerechts 1983; Maret et al. 2009). Nitrogen is also an essential component of Earth-like life-related molecules, explaining why there is a great interest in its initial form during planet formation (Geiss & Bochsler 1982; Mumma & Charnley 2011).

So, a natural question arising is : What is the nitrogen reservoir in the ISM? Is it in the form of $NH_3$, hidden in ices, or in gaseous form as N or $N_2$, or in something else? The problem is that, in dark clouds, neither of these two latter forms are observable. But, other N-bearing molecules can serve as indirect probes, for instance nitriles (HCN, HNC, CN *etc.*) and nitrogen hydrides (NH, $NH_2$, $NH_3$).

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[1] Université Grenoble Alpes/CNRS, Institut de Planétologie et d'Astrophysique de Grenoble (IPAG) UMR 5274, France
[2] Institut Universitaire de France

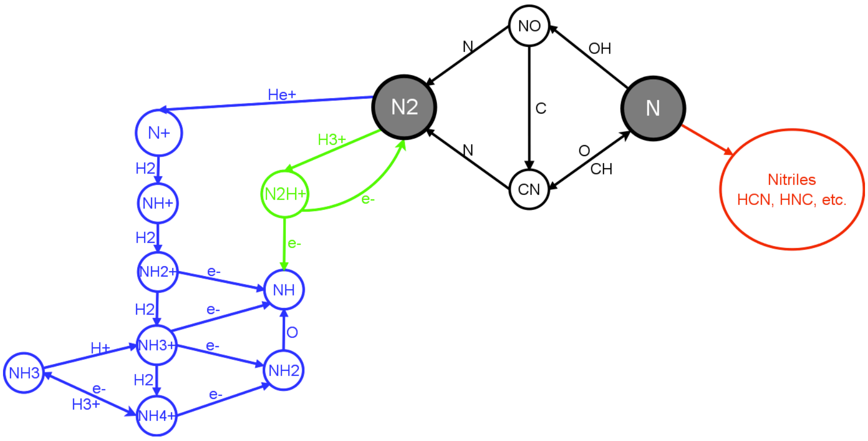

**Fig. 1.** The principal gas-phase reactions involved in the first stages of nitrogen-hydride interstellar chemistry in dark clouds. The main formation route of NH is highlighted (green). Adapted from Hily-Blant et al. (2013).

### *1.2 Interstellar nitrogen chemistry*

The reduced network presented on Figure 1, representing the first stages of nitrogen-hydride chemistry in dark gas, shows that nitriles result from atomic nitrogen and N-hydrides from molecular nitrogen. The latter point is specific to nitrogen chemistry in cold gas. As for carbon or oxygen chemistry, the ionic form of the atomic element is needed to form hydrides, but, in the case of nitrogen chemistry, the ionisation potential of nitrogen is higher (14.53 eV) than that of hydrogen. Moreover, the reaction between N and $H_3{}^+$ is endoenergetic contrary to its analogues in carbon and oxygen chemistry. $N^+$ is in fact mainly formed from the dissociative ionisation reaction between $N_2$ and $He^+$, (the direct cosmic-ray ionisation being less efficient) and can then initiate the nitrogen-hydride formation. As a consequence, the $N/N_2$ ratio could, for instance, be constrained *via* a combination of nitrile and N-hydride observations.

Our study of the interstellar nitrogen chemistry has focussed on the three nitrogen hydrides NH, $NH_2$, and $NH_3$ in cold gas, thanks to hitherto unprecedented observations performed with the HIFI instrument (Roelfsema et al. 2012) onboard the *Herschel* Space Observatory (HSO) (Pilbratt et al. 2010). Ratios of these N-hydrides have been derived in diffuse cold gas with $NH : NH_2 : NH_3 \approx 1 : 1 : 1$ (Persson et al. 2010), and, in the cold envelope of the low-mass protostar IRAS 16293-2422, with $NH : NH_2 : NH_3 \approx 3 : 1 : 20$ (Hily-Blant et al. 2010; Le Gal et al. 2014).

The reduced chemical network, Figure 1, also shows that one of the first stages of the interstellar chemistry of nitrogen hydrides is the N to $N_2$ conversion. This process has profound consequences on the kinetics of interstellar nitrogen chemistry because neutral-neutral reaction rates are typically ten to a hundred times lower than Langevin rates, characteristic of ion-neutral reactions. Therefore, the synthesis of nitrogen hydrides, under cold conditions, is considered to be a slow process compared to carbon- or oxygen-hydride formation proceeding directly through ion-neutral reactions.

### *1.3 Influence of the $H_2$ o/p*

On the reduced network presented in Figure 1, the main pathway of the NH formation is highlighted in green. We see that it differs from the synthesis of $NH_2$ and $NH_3$. NH predominantly results from the dissociative recombination (DR) of $N_2H^+$, itself deriving from the proton-exchange reaction $N_2 + H_3^+$, while $NH_2$ and $NH_3$ proceed from the DR of $NH_4^+$, which itself results from a series of $H_2$ hydrogenations from $N^+$ (product of the reaction $N_2 + He^+$, as previously discussed). Therefore, $H_2$ plays an important role in the formation of $NH_2$ and $NH_3$ but not in that of NH.

$H_2$ forms on grain surfaces in its two nuclear configurations, *ortho* ($H_2$(o)) and *para* ($H_2$(p)), in an $H_2$ o/p ratio supposed to be equal to its nuclear spin statistical value of 3 : 1. Once formed, $H_2$ undergoes proton-exchange reactions with the major protonated ions of the medium ($H^+$, $H_3^+$, and $HCO^+$) which tend to decrease the $H_2$ o/p towards the thermal value. Below 100 K, the two $H_2$ spin modifications are essentially in their fundamental states, separated by an energy of 170.5 K, $H_2$(o) lying above the $H_2$(p). The key reaction $N^+ + H_2$, initiating N-hydride formation, has a small endoenergeticity close to this energy difference ($\sim$ 200 K, according to Gerlich 2008). Dislaire et al. (2012) have revised the rate of this reaction using all available experimental data, showing that, when the temperature decreases, the impact of the $H_2$ o/p value on the reaction rate increases. So the formation of $NH_2$ and $NH_3$ depends on the $H_2$ o/p, in contrast to the NH formation. In that way, Dislaire et al. (2012) have shown that the NH : $NH_2$ ratio measurement can constrain the $H_2$ o/p in dark clouds : $H_2$ o/p $\approx 10^{-3}$. This value is consistent with the Flower et al. (2006b) prediction, who pointed out that at low temperature the $H_2$ o/p thermal value is not reached due to the competition between the $H_2$ recycling on grains and the proton-exchange reactions. Typically at 10 K, this value is by four orders of magnitude higher than the Boltzmann equilibrium value ($\approx 3 \times 10^{-7}$ at 10 K). Pagani et al. (2009) obtained a similar conclusion using the deuterium fractionation of molecules ($H_2$ o/p $\lesssim 10^{-1}$).

## 2 Modelling

### 2.1 A new *ortho-para* nitrogen chemical network

Our work has consisted in revising the *ortho-para* chemical network of nitrogen hydrides in order to understand their abundances, derived from *Herschel*/HIFI observations towards low-mass protostars, in cold gas. As mentioned above, Dislaire et al. (2012) have stressed the critical influence of the $H_2$ o/p on the N-hydride chemistry. In the continuity of this work, we undertook the update of N-chemistry with self-consistent computation of the $H_2$ o/p. To this purpose, we employed the chemical network initially developed by Flower et al. (2006a) including the *ortho* and *para* forms of $H_2$ and N-hydrides. Another advantage of this network is that it only contains a small number of reactions (1755) and species (146) compared to those commonly used (such as the OSU and UMIST networks, containing each $\sim$ 6000 reactions and $\sim$ 600 species without including *ortho* and *para* forms).

We first updated the ion-molecule hydrogen chemistry of this network using the recent data of Honvault et al. (2011, 2012), Dos Santos et al. (2007), McCall et al. (2004), and Hugo et al. (2009) for the reaction $H^+ + H_2$, $H_3^+ + H_2$ and $H_3^+ + e^-$. Then, we updated the N-hydride *ortho-para* synthesis, including nuclear spin branching ratios, as detailed in Rist et al. (2013). We also updated the N to $N_2$ conversion reactions, thanks to new theoretical calculations and experimental measurements (Jorfi & Honvault 2009; Daranlot et al. 2011, 2013), showing that the kinetic rates are lower than previously thought, implying a slowing down of the chemistry. This confirms that nitrogen-hydride synthesis is a late process. We also updated the branching ratios (BR) for the DR of nitrogen-hydride ions (see Hily-Blant et al. 2010, and reference therein), and especially the rate and BR of the $N_2H^+$ DR, with a 7% BR into NH (see Vigren et al. 2012). Some oxygen reactions such as the $H_3O^+$ DR (Jensen et al. 2000) and the $H_3^+ + O$ reaction (KIDA recommandation, Wakelam et al. 2012) were also updated.

### 2.2 Building our model

Gas-grain reactions are not considered in this work, except for the $H_2$ formation and charge-exchange reactions. Our new gas-phase chemical network contains 103 species and 907 reactions and is valid up to a temperature of $\simeq$ 50 K. The rate equations were solved with the chemical code of Flower et al. (2006a) to obtain the gas-phase abundance as function of time, until a steady-state is reached, for a temperature of 10 K, a density $n_H = 10^4\,cm^{-3}$, and an ionisation rate $\zeta = 1.3 \times 10^{-17}\,s^{-1}$. The freeze-out of gas-phase species onto grains was included through depleted initial abundances (Le Gal et al. 2014). Concerning these initial abundances, we note that the elemental oxygen abundance is uncertain by up to one order of magnitude and the elemental sulphur abundance by three orders of magnitude. As a result, we chose to vary these two parameters in our model, resulting in particular in an elemental gas-phase C/O ratio varying between 0.3 and 1.5 (*via* the oxygen abundance).

### 2.3 Results

Our new chemical model emphasizes the influence of several parameters in the nitrogen-hydride chemistry, as the gas-phase elemental C/O ratio or the elemental gas-phase amount of sulphur (Le Gal et al. 2014). The impact of the gas-phase elemental C/O ratio on N-hydride abundances results from the fact that $N_2$ involves carbon and oxygen for its formation *via* the N + CH or N + OH reactions. We identified two distinct regimes : a low C/O regime with C/O < 0.8 and a high C/O regime where C/O > 1. For these regimes $N_2$:N > 1 and the fractional abundance (with respect to hydrogen nucleus) of $NH_3$ is a few $10^{-8}$, but in the high C/O regime

NH and $NH_2$ abundances are significantly lower because atomic carbon becomes one of their main destroyer. Concerning the total gas-phase amount of sulphur $[S]_{tot}$, we showed that its enhancement drastically diminishes the efficiency of the N to $N_2$ conversion. Sulphur is indeed mostly in its ionic form $S^+$, due to its low ionisation potential (10.36 eV), making it the main carrier of positive charge when its abundance increases. It is also the main destroyer of CH and OH, essential to the N to $N_2$ conversion. Thus, a high elemental gas-phase sulphur abundance ($8.0 \times 10^{-6}$) diminishes by up to two orders of magnitude the abundances of several nitrogen species.

Finally, we obtain a *best model* for an elemental gas-phase C/O ratio of 0.8 and a total gas-phase sulphur abundance of $[S]_{tot} = 8.0 \times 10^{-8}$, reproducing the observations of NH, $NH_2$, and $NH_3$ performed by *Herschel*/HIFI in typical dark gas physical conditions, towards the Sun-like protostar IRAS 16293-2422 (Hily-Blant et al. 2010). At that time, this was not possible with any existing chemical models.

On the left panel of Figure 2 we see that our chemical model predicts $NH{:}NH_2 > 1$, as observed in the cold envelope of IRAS 16293-2422, confirming the main pathway to form NH suggested by Dislaire et al. (2012) and experimentally confirmed by Vigren et al. (2012): the $N_2H^+$ DR. Our *best model* thus leads to $NH : NH_2 : NH_3 \sim 3 : 1 : 3$, compatible with the observed ratio of $3 : 1 : 20$, within the error bar of observations. Higher values of $[S]_{tot}$ are also possible, but abundances as high as $8.0 \times 10^{-6}$ are clearly excluded by our steady state models, as well as a C/O ratio outside the range $0.7 - 0.8$. For early times ($\sim 2 - 5$ Myrs), the observations can be reproduced with similar total abundance of sulphur, (*i.e.* $[S]_{tot} < 8.0 \times 10^{-6}$) and a slightly higher C/O, in the $0.9 - 1.1$ range. We also observe (see left panel of Figure 2) that the $H_2$ o/p is $\sim 10^{-3}$, as in Dislaire et al. (2012), and it does weakly depend on C/O.

Besides, thanks to our new chemical network, we published in Faure et al. (2013) an explanation to the non-thermodynamical $NH_3$ o/p ratio ($< 1$) observed by Persson et al. (2012). The right panel of Figure 2 represents our chemical model predictions for the $NH_2$ and $NH_3$ *ortho*-to-*para* ratios which are in good agreement with the observed ratios of 2.3 (C. Persson priv. comm.) and $\sim 0.7$ (Persson et al. 2012), derived in a 30 K gas. Those ratios are thus compatible with a pure gas-phase chemistry obeying nuclear spin selection rules in an $H_2$(p) enriched gas (*i.e.* o/p $H_2 < 10$ %).

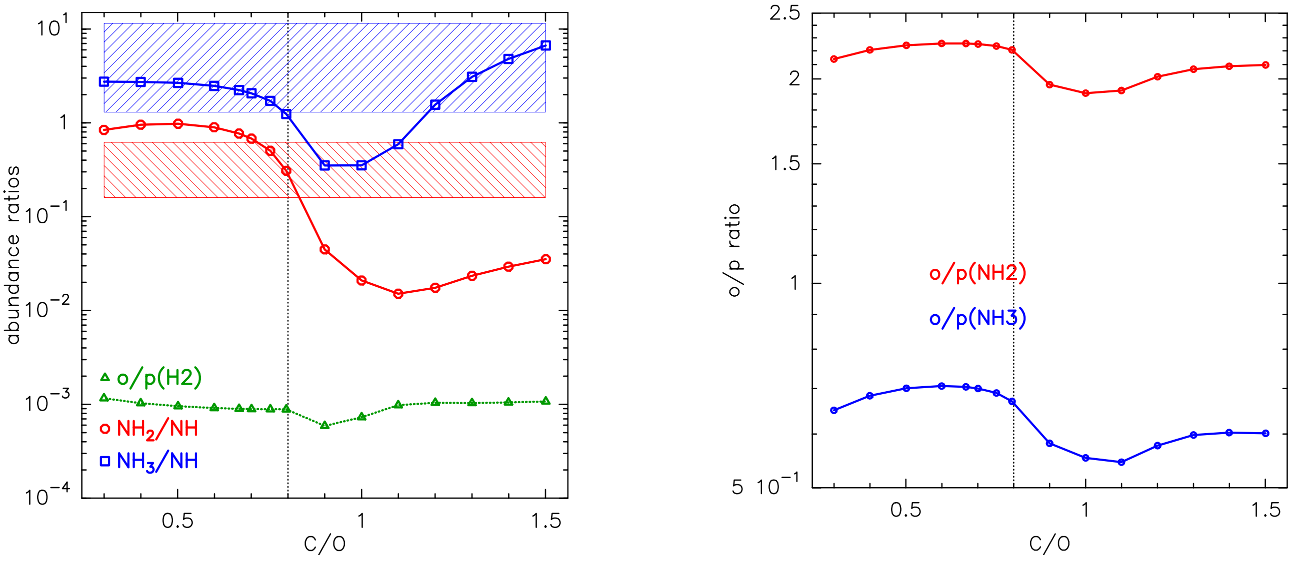

**Fig. 2. Left:** Nitrogen-hydride ratios (blue and red) derived from observations towards IRAS 16293-2422 (hatched boxes) *vs* our steady-state model predictions (solid lines) with the evolution of the $H_2$ o/p at steady-state (green), as a function of the elemental gas-phase C/O. **Right:** Evolution of our $NH_2$ and $NH_3$ o/p steady-state model predictions with C/O.

## 3 Conclusions and future works

The aim of our work was to understand in details the gas-phase processes of nitrogen chemistry in dark gas conditions, relying on cold envelope observations in foreground of different low-mass protostars, representatives of dark gas conditions. In Le Gal et al. (2014), the comparison being restricted to only one astrophysical object

(IRAS 16293-2422), one is led to question the validity and, where appropriate, to question the generalisation of these results in other cold protostellar envelopes. This is why we are now working on *Herschel*/OT1 (PI: Hily-Blant) data obtained in the cold envelope of a sample of other low-mass protostars. These data have provided detections in absorption, in the foreground of *continuum* emitted by deeply embedded protostars, of several rotational lines of ammonia and hyperfine structures of fundamental rotational transitions of amidogen ($NH_2$) and imidogen (NH), allowing a robust determination of their column densities. Overall, $NH:NH_2 \sim 2:1$ towards three other protostellar envelopes, confirming the $NH > NH_2$ result found in the cold envelope of IRAS 16293-2422 (Hily-Blant et al. 2010). Analysis of these data is still in progress.

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