

# Supplementary Information: Constraining the atomic and molecular nitrogen abundances in a cold dark cloud

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## Supplementary Discussion

**Chemical modeling** Our chemical model is a gas grain network<sup>1</sup> including the effects of molecular freeze-out onto grain surfaces and desorption by photo-desorption and cosmic rays impacts. The network focuses onto the formation of simple molecules, and includes the effects of isotopic fractionation. Time dependent chemical equations are solved using a stiff ODE solver. For example,  $\text{N}_2\text{H}^+$  is mainly formed by the following reaction:



and is destroyed mainly by the following reactions:



and:



In addition,  $\text{N}_2\text{H}^+$  can be destroyed by recombination on polycyclic aromatic hydrocarbons (PAHs) or other small particles<sup>2</sup>. However, this destruction route can probably be neglected in dense molecular clouds, since PAHs may have frozen out on the larger dust grains.

The time dependent equation for these species is:

$$\frac{d [N_2H^+]}{dt} = [H_3^+][N_2]k_1 - ([e^-] (k_2 + k_3) + [CO]k_4) [N_2H^+] \quad (5)$$

where  $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$  are the rates of the above reactions and  $[N_2H^+]$ ,  $[H_3^+]$ ,  $[N_2]$ ,  $[e^-]$  and  $[CO]$  are the concentrations (*i.e.* the number of a given specie per  $\text{cm}^3$ ) of  $N_2H^+$ ,  $H_3^+$ ,  $N_2$ ,  $e^-$  and  $CO$  respectively. In the above equations, we have neglected other formation and destructions routes. However, our model include them.

**Time dependence in our chemical modeling** In our chemical modeling, the cloud is assumed to have initially the following composition (with respect to H nuclei):  $X(\text{He}) = 0.14$ ,  $X(\text{CO}) = 8.5 \times 10^{-5}$ ,  $X(^{13}\text{CO}) = 9.5 \times 10^{-7}$ ,  $X(\text{C}^{18}\text{O}) = 1.7 \times 10^{-7}$ . The metal abundance is a free parameter of the study. N and  $N_2$  initial abundances are also free parameters, but the total nitrogen abundance is fixed ( $2 \times 10^{-5}$ ). Water is assumed to be frozen on grains, with an abundance of  $2.2 \times 10^{-4}$ . We have assumed that the density and temperature profiles do not change with time. The abundances are computed as a function of time, as the cloud chemically evolves, until a time of  $10^5$  years is reached. This time corresponds to the chemical age of B68, as determined from observations and modeling of CO and isotopologues<sup>3</sup>. The chemical age is different from the physical age of the cloud, since we have assumed that CO is pre-existing (*i.e.* the time to form CO is not included).

**Oxygen abundance and the elemental deficiency of nitrogen in comets** The formation of molecular nitrogen from atomic nitrogen depends on the amount of atomic oxygen present in the gas phase. Atomic oxygen forms OH after a series of fast ion neutral reactions and dissociative re-

combination. OH reacts with atomic nitrogen to form NO, which itself reacts with N to form N<sub>2</sub>:



As a consequence, if no atomic oxygen is present in the gas phase, the chain of reactions that leads to the formation of N<sub>2</sub> is blocked. In our model, oxygen is assumed to be initially fully molecular, either in CO or H<sub>2</sub>O ices. Because of the high binding energy of H<sub>2</sub>O on the grain surface, water ices can not be evaporated in cold dense clouds. Thus the only source of atomic oxygen is the dissociation of CO by He<sup>+</sup> ions. In the inner part of the core (where the N<sub>2</sub> formation is the most effective because of the high density), the CO abundance is mainly controlled by the cosmic ray desorption from the grain surfaces. Because the efficiency of this process is very uncertain, the CO abundance, and in turn the atomic oxygen abundance, could be much lower than expected from present chemical models. Consequently, a larger fraction of nitrogen could be present in atomic form in the gas phase, with respect to our model predictions. Because atomic nitrogen does not freeze on the grains, only a small fraction of the elemental nitrogen would be incorporated in the grains mantles, which would explain the nitrogen deficiency in comets. Note that in this scenario, less ammonia formation is required on the grain surfaces.

**Comparison with earlier studies** In an earlier paper<sup>4</sup> Charnley & Rodgers first suggested that the low N<sub>2</sub> abundance in comets, as well as the nitrogen fractionation anomalies observed in meteorites and IDPs, could be a result of a high interstellar N / N<sub>2</sub> ratio. They showed how a core in which

the gas had undergone almost complete N to N<sub>2</sub> conversion could then evolve large N / N<sub>2</sub> ratio. Such high N / N<sub>2</sub> ratios are reached provided that N<sub>2</sub> stays in the gas phase while other molecules containing carbon and oxygen (mostly CO) deplete. They argue that this would happen if the binding energy of N<sub>2</sub> is lower than CO. However recent measurements of the N<sub>2</sub> binding energy seem to rule out this scenario<sup>5</sup>.

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