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Atom addition reactions in interstellar ice : new pathways towards molecular complexity in space -

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III

Surface NO Hydrogenation: A Solid Pathway to NH₂OH Formation in Space

Icy dust grains in space act as catalytic surfaces on which complex molecules form. These molecules are synthesized through exothermic reactions from precursor radicals and, mostly, hydrogen atom additions. Among the resulting products are species of biological relevance, such as hydroxylamine - NH₂OH - a precursor molecule in the formation of amino acids. In this Letter, laboratory experiments are described that demonstrate NH₂OH formation in interstellar ice analogs for astronomically relevant temperatures via successive hydrogenation reactions of solid nitric oxide (NO). Inclusion of the experimental results in an astrochemical gas–grain model proves the importance of a solid-state NO + H reaction channel as a starting point for prebiotic species in dark interstellar clouds and adds a new perspective to the way molecules of biological importance may form in space.

E. Congiu, G. Fedoseev, S. Ioppolo, F. Dulieu, H. Chaabouni, S. Baouche, J. L. Lemaire, C. Laffon, P. Parent, T. Lamberts, H. M. Cuppen, H. Linnartz, 2012, APJL, 750, L12

3.1 Introduction

Molecular astrophysicists explain the chemical diversity and complexity in space as the cumulative outcome of gas, grain, and gas–grain interactions in dense interstellar clouds, the birth sites of stars and planets (Wakelam *et al.* 2010; Herbst & van Dishoeck 2009). More than 180 species have been unambiguously identified so far, and icy dust grains are the template where stable species like acetonitrile, a precursor molecule for the simplest amino-acid glycine, are formed (Codella *et al.* 2009, Hudson *et al.* 2008). In quiescent dark clouds, cold grains indeed provide micrometer-sized surfaces onto which gas-phase species accrete, meet, and react (van Dishoeck 2004, Öberg *et al.* 2011). Particularly, hydrogenation of interstellar ices, *i.e.*, H-atom additions, can induce the formation of species in the solid phase and, therefore, it has been the topic of recent laboratory-based studies. The efficient surface formation of the bulk of interstellar ices, *i.e.*, water, methanol, carbon dioxide, formaldehyde, and formic acid has been demonstrated through H-atom additions of CO- and/or O₂-ices under interstellar relevant conditions (Watanabe *et al.* 2006, Fuchs *et al.* 2009, Cuppen *et al.* 2010, Noble *et al.* 2011). In space, thermal atom-addition induced chemistry occurs mostly at low temperatures (~ 10 K), *i.e.*, in the innermost part of the clouds where newly formed species are protected from radiation to a great extent by dust particles. These regions are part of collapsing envelopes that feed young stellar objects and that provide the original material from which comets and ultimately planets are made (Sandford *et al.* 2006). The solid-state formation of organic material is therefore of considerable interest, as efficient surface reaction routes provide a general recipe to form prebiotic species in star and planet-forming regions (Charnley *et al.* 2001). The focus in this Letter is on hydroxylamine, NH₂OH, that has been proposed as an important precursor species in the formation of amino acids (Blagojevic *et al.* 2003, Barrientos *et al.* 2012). Inter- and circumstellar nitrogen chemistry is rather poorly understood as well as the mechanisms leading to the inclusion of interstellar nitrogen into a refractory aminated species. Charnley *et al.* (2001) suggested that hydroxylamine can be formed through hydrogenation of NO ice under quiescent cloud conditions:



However, to date there has been no experimental evidence that this reaction indeed proceeds. Here, we present a successful attempt to form hydroxylamine under fully controlled laboratory conditions via the non-energetic route NO + H on crystalline H₂O ice and on amorphous silicate, two very realistic analogs of grain surface materials in the interstellar medium, and on a bare gold substrate through subsequent hydrogenation reactions.

3.2 Experimental

The experiments are performed using two different setups: FORMOLISM located at the University of Cergy-Pontoise (FR; Accolla *et al.* 2011) and SURFRESIDE at the Sackler Laboratory for Astrophysics in Leiden (NL; Ioppolo *et al.* 2010). Both setups comprise a central ultrahigh vacuum chamber with a base pressure of $\sim 10^{-10}$ mbar in which a sample holder is mounted in thermal contact with the cold finger of a closed-cycle He cryostat. We have studied the reaction $\text{NO} + \text{H}$ ($\text{NO} + \text{D}$) at low temperatures (10–15 K) by exposing the substrate surface to a molecular beam of NO and H- (D-) atoms generated in state-of-the-art atom beam lines. Atoms are cooled and instantaneously thermalized upon surface impact. In Cergy, NO hydrogenation is studied with sequential deposition of NO and H- (D-) atoms in the low surface coverage regime not exceeding one monolayer of NO on the 10 K silicate or water-ice substrate. In Leiden, co-depositions of NO and H- or D-atoms are studied for lower ($\sim 7 \cdot 10^{12}$ atoms cm^{-2} s^{-1}) and higher ($\sim 3 \cdot 10^{13}$ atoms cm^{-2} s^{-1}) H- and D-atom fluxes in the high surface coverage regime (>50 monolayers) on the 15 K cold gold substrate. Newly formed species upon H- or D-atom addition are monitored in the solid phase by means of Fourier transform Reflection-Absorption Infrared Spectroscopy (RAIRS; Greenler 1966) using vibrational fingerprint spectra in the 4000–700 cm^{-1} region and in the gas phase by means of Quadrupole Mass Spectrometry (QMS) upon temperature programmed desorption (TPD) by steadily heating the ice and monitoring evaporated species. Special efforts have been made to exclude contaminants in the ultrahigh vacuum chambers and on the ice surface, the actual reaction site. A series of control experiments is performed to assure that the final key product is indeed only due to successive hydrogenation of solid NO (Equation (3.1)).

3.3 Results

In the two setups, hydroxylamine is produced at comparable rates on all surfaces regardless of the hydrogen isotope used, H or D. Moreover, the NO ice is almost completely consumed by an equivalent amount of hydrogen atoms, suggesting a $\text{NO} + \text{H}$ ($\text{NO} + \text{D}$) reaction with an efficiency close to one and able to proceed with no appreciable barrier even at 10 K. Figure 3.1 displays RAIR spectra at 15 K after simultaneous deposition of NO during low- and high-hydrogen atom flux (Figure 3.1(a) with $\text{H}/\text{NO} = 0.2$ and Figure 3.1(b) with $\text{H}/\text{NO} = 4$, respectively). Spectral features appearing upon solid NO hydrogenation are assigned to bulk NH_2OH (3317, 3261, 3194, 2899, 2716, 1608, 1514, 1203, 919 cm^{-1}), isolated NH_2OH (1175, 1359, 1144 cm^{-1}), HNO (1561, 1507 cm^{-1}), and N_2O (2235, 1286 cm^{-1} ; Nightingale & Wagner 1954, Jacox & Milligan 1973, Sivaraman *et al.* 2008). The simultaneous detection of NH_2OH and HNO is consistent with the reaction

scheme given in Equation (3.1).

At lower H-atom flux the NO is not completely consumed by hydrogen atoms, and the strongest bands (1865, 1776 cm^{-1}) correspond to NO-dimer transitions (Fateley *et al.* 1959). However, also under these conditions HNO is formed, and isolated bands of NH_2OH molecules are visible. This indicates that even at the lower H-atom flux the addition process proceeds fast. In the higher H-atom flux experiment NO-dimer bands are barely visible.

In both the low- and high-hydrogen atom flux experiments nitrous oxide (N_2O) is found, likely formed via



Figure 3.2 shows TPD spectra of NH_2OH ($m/z = 33$, peak at ~ 188 K) produced after six cycles of H-atom exposure of one monolayer coverage (10^{15} molecules cm^{-2}) of NO on a silicate surface. This procedure ensures that the reaction $\text{NO} + \text{H}$ occurs for each cycle on the surface of the ice, until all NO molecules have been consumed. The repetition of several cycles enhances the signal-to-noise ratio of the QMS ion count upon ice sublimation. In the figure, signals are recorded at $m/z = 33$ (NH_2OH) as well as 30 (NO), 17 (OH), and 16 (NH_2), reflecting partial fragmentation upon NH_2OH ionization in the QMS head (Kutina *et al.* 1982).

All signals have a common peak at $T \sim 188$ K, confirming NH_2OH fragmentation upon ionization. The 150 K temperature peaks for $m/z = 30$ and 17, included here for the sake of completeness, are due to co-desorption of NO molecules and OH fragments from thermal desorption at $T \sim 150$ K of the newly formed water ice through reaction of $\text{H} + \text{OH}$ (Dulieu *et al.* 2010).

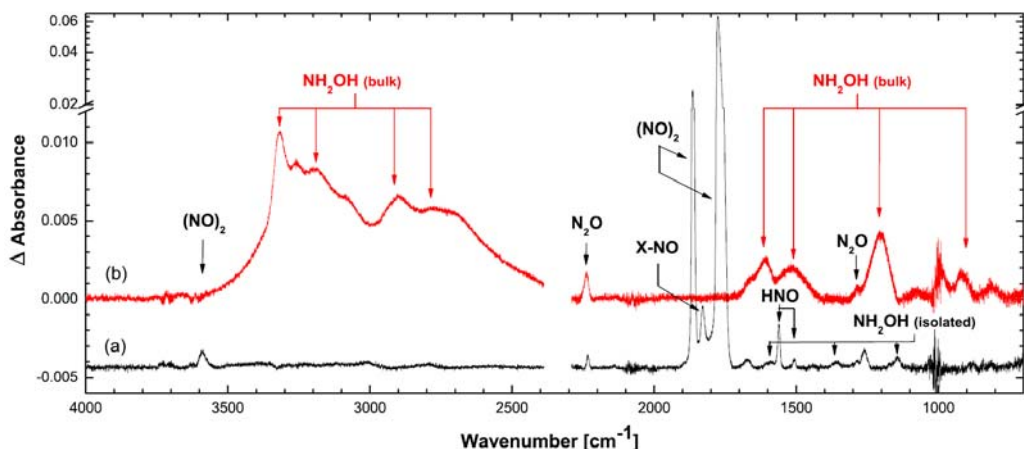


Figure 3.1. RAIR spectra of solid NO deposited on the gold substrate at 15 K upon H-atom exposure. Diagram (a) shows the resulting spectrum for a co-deposition experiment during 60 minutes and H-atom flux of $7 \cdot 10^{12}$ atoms $\text{cm}^{-2} \text{s}^{-1}$ ($\text{H}/\text{NO} = 0.2$). Diagram (b) shows the spectrum for a deposition time of 120 minutes and an H-atom flux of $3 \cdot 10^{13}$ atoms $\text{cm}^{-2} \text{s}^{-1}$ ($\text{H}/\text{NO} = 4$). Spectra are offset for clarity.

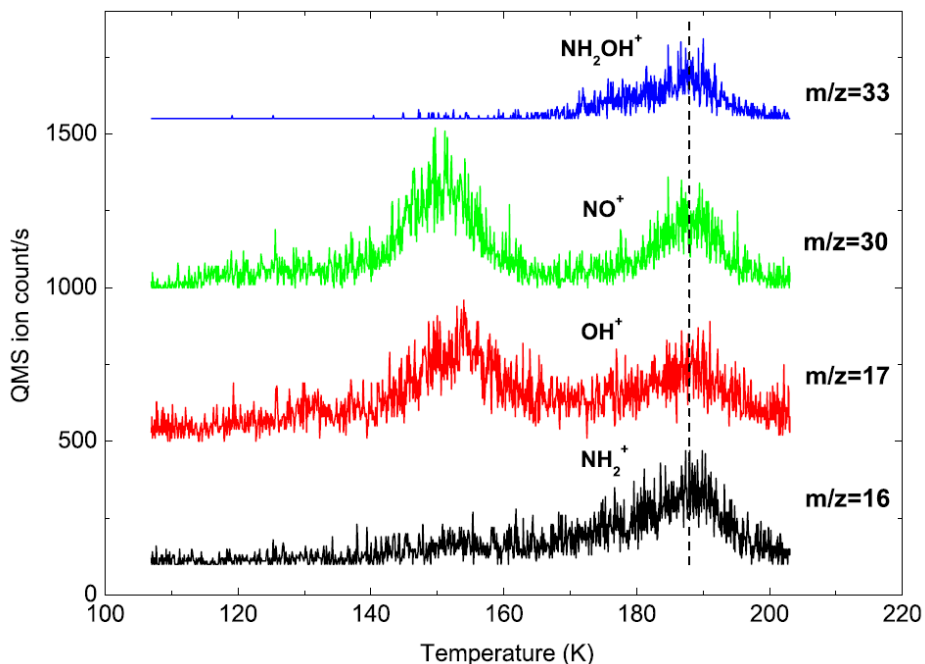


Figure 3.2. Quadrupole mass spectrometer signal as a function of temperature during a TPD experiment after six sequential depositions of ~ 1 ML of NO and H-atoms on a bare silicate surface at 10 K. The peak at $T \sim 188$ K indicates desorption of hydroxylamine (NH_2OH , mass = 33 amu). NH_2OH fragmentation is induced in the mass spectrometer head upon ionization, resulting in NO^+ , OH^+ , and NH_2^+ fragments. Low temperature peaks for mass = 30 and 17 amu are due to co-desorption of NO molecules and OH fragments with water at $T \sim 150$ K. The traces are offset for clarity.

3.4 Discussion

The present study proves NH_2OH formation upon NO hydrogenation at low temperatures and without external energetic input. It therefore provides a likely pathway for an efficient formation in quiescent cold dense clouds where energetic processing is not likely to be efficient. Two previous experimental studies showed the formation of NH_2OH by irradiating a mixture of NH_3 and H_2O ices with UV photons (Nishi *et al.* 1984) and electrons (Zheng & Kaiser 2010). The experimental conditions used there are not fully representative for quiescent cold dense clouds, regions where NH_2OH is assumed to be already present in the ice as indicated by our results. The astronomical relevance of $\text{NO} + \text{H}$ is discussed below. Interstellar temperatures and substrates can be rather well reproduced in the laboratory, but experiments are not fully representative of dark cloud conditions, especially in terms of timescale and ice inhomogeneity. To prove that the presented reaction scheme facilitates NH_2OH formation in dense cores, a gas–grain model (Hasegawa *et al.* 1992, Hassel *et al.* 2008) is used that comprises a full gas and grain chemical network. Conditions are chosen as in the prototypical dense cloud “TMC 1” (Semenov *et al.* 2010). The resulting predictions are shown in Figure 3.3. The reaction between H and HNO in the current chemical networks (dashed lines in Figure 3.3) leads to H_2 and NO and NH_2OH is usually formed through $\text{NH}_2 + \text{OH}$. Along this reaction pathway, no NH_2OH is formed under dark cloud conditions and NO is mostly converted into HNO or N_2O . This is in agreement with Garrod *et al.* (2008) who performed chemical models of star formation and found that NH_2OH is only abundantly formed in the “hot core” phase when the grain is lukewarm and NH_2 and OH become mobile. On the other hand, with a model including the NO hydrogenation reactions experimentally proven in this paper (the solid lines in Figure 3.3), NH_2OH is found to be abundantly present in both the solid and the gas phase. The hydroxylamine abundance peaks at 10^5 years, with relative values with respect to gas phase H_2 of at least $7 \cdot 10^{-9}$ on the grain surface and $3 \cdot 10^{-11}$ in the gas phase at the end of the lifetime of a dense cold cloud (1–10 Myr), *i.e.*, before the core collapse. This finding is particularly relevant for a better understanding of the molecular evolution of the universe. This work indeed shows that the hydroxylamine locked up on the grains at the beginning of the core collapse becomes available for further reactions at later stages, when a protostar forms and UV irradiation and thermal processing start. So far, positive identifications of NH_2OH in molecular clouds have not yet been reported, but upper limits have been derived for a number of sources (Pulliam *et al.* 2012). These correspond to fractional abundances of $<10^{-11}$. This is around the same order of magnitude as the gas-phase model predictions for dense clouds, concluded here. Gas-phase abundances in the model are upper limits since destruction routes that lead to the formation of more complex species are not included.

Snow *et al.* (2007) showed that gas phase NH_2OH can react with CH_5^+ to form NH_3OH^+ that in turn reacts with different carboxylic acids to form protonated amino acids. These reactions are not included in the available chemical networks and therefore can not be traced. The left panel of Figure 3.3, however, shows that CH_5^+ and H_3^+ - both able to protonate hydroxylamine - are available in the gas phase. The present work and a previous study (Zheng & Kaiser 2010) show that NH_2OH desorbs at relatively high temperatures (>175 K under laboratory conditions) from the ice. Therefore, abundances may be high enough for gas-phase detection only in those parts of the cloud that experienced a dramatic heating phase. In fact, NH_2OH provides a solid-state nitrogen reservoir along the whole evolutionary process of interstellar ices from dark clouds to planets. We expect that in the nearby future the faint radio hum from NH_2OH molecules will be recorded by the receivers of ALMA that will investigate the inner parts of protoplanetary disks and hot cores with high temperatures (Herbst 2008). ALMA will also come with a hugely improved sensitivity that, added to a high angular resolution, will allow perhaps detection of NH_2OH in cold starless cores and pre-stellar cores as well. The present laboratory study illustrating that possible precursor molecules of amino acids are efficiently formed on the surface of dust grains along with an astronomical detection of NH_2OH in space will confirm that the building blocks of life are omnipresent in the universe.

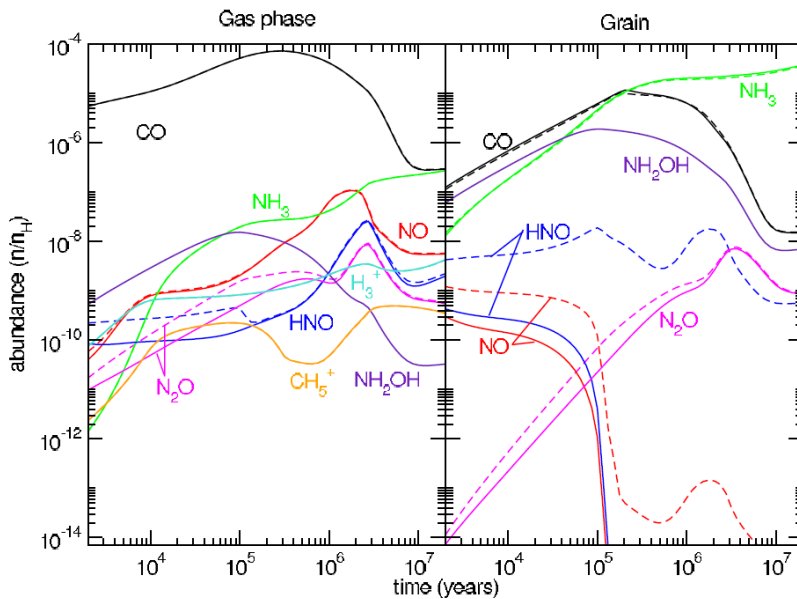


Figure 3.3. Fractional abundance of species involved in nitrogen chemistry for an astrochemical model in which the effect of an NO hydrogenation channel is shown. Solid lines are with NO + H and dashed lines do not take this surface reaction into account. The left panel indicates gas-phase species; the right panel shows the grain-surface abundance with respect to the gas-phase density of H nuclei ($n_{\text{H}} = n(\text{H}) + 2n(\text{H}_2)$).

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