Efficient surface formation route of interstellar hydroxylamine through NO hydrogenation. I. The submonolayer regime on interstellar relevant substrates

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Dust grains in the interstellar medium are known to serve as the first chemical laboratory where the rich inventory of interstellar molecules are synthesized. Here we present a study of the formation of hydroxylamine—NH$_2$OH—via the non-energetic route NO + H (D) on crystalline H$_2$O and amorphous silicate under conditions relevant to interstellar dense clouds. Formation of nitrous oxide (N$_2$O) and water (H$_2$O, D$_2$O) is also observed and the reaction network is discussed. Hydroxylamine and water results are detected in temperature-programmed desorption (TPD) experiments, while N$_2$O is detected by both reflection-absorption IR spectroscopy and TPD techniques. The solid state NO + H reaction channel proves to be a very efficient pathway to NH$_2$OH formation in space and may be a potential starting point for prebiotic species in dark interstellar clouds. The present findings are an important step forward in understanding the inclusion of interstellar nitrogen into a non-volatile aminated species since NH$_2$OH provides a solid state nitrogen reservoir along the whole evolutionary process of interstellar ices from dark clouds to planetary systems. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4738895]

I. INTRODUCTION

The chemistry of interstellar clouds can be considered the origin of the molecular diversity in the Universe. Quiescent dark clouds have been well studied through observations and modeling and are reasonably well understood. A wealth of infrared, millimeter- and microwave-wavelength observations has provided evidence that interstellar clouds exhibit a rich chemistry and are the birth sites for stars and planets. Nevertheless, models of steady-state or time-dependent gas-phase chemistry do not always match the observed molecular abundances because not all chemical processes are known and the physical conditions of interstellar regions can themselves be time dependent. Surface reactions on sub-micrometer-sized dust grains are, therefore, necessarily invoked for the formation of many organic and nitrogen-bearing species. In dense molecular clouds, the surface of dust grains becomes coated with an icy mantle (primarily water ice), and as gaseous species heavier than hydrogen and helium freeze out onto the cold grains. The chemistry occurs mostly at low temperature (∼10 K), and in the innermost part of the clouds the molecules formed are protected from radiation by the dust particles, though cosmic rays and, at a later time, UV radiation may activate processes leading to an even richer chemistry with new and larger molecules. Since dense interstellar clouds collapse to form stars and planetary systems, the molecules produced in these clouds will be eventually incorporated into solid bodies such as comets, meteors, and the early stage of planets just like the primordial Earth.

In surface reactions and solid-state chemistry, nitric oxide, NO, is thought to be the main precursor species of the N–O–bonded molecules and, together with NH$_3$, the precursor molecule of nitrogen-containing organics. NO is likely to be formed in the gas phase and is present with moderate abundances in many molecular clouds and star-forming regions. Its fractional abundance, with respect to H$_2$, is on average ∼10$^{-8}$, which means in turn a fractional abundance of ∼10$^{-5}$ with respect to H atoms. Large amounts of NO molecules (∼10% of the gas-phase abundance) are therefore likely to accrete on the extremely cold surface of dust grains at 10 K, raising the possibility that the adsorbed NO react with H atoms and be converted into other species via simple hydrogenation reactions. This assumption is also corroborated by observations of NO and HNO along the same lines of sight, which suggest that their chemistry is related and that the conversion reaction is fast. NO appears to be the cornerstone of the NO chemical network, so a possible precursor molecule for more complex N–O-containing species, such as nitrous acid (HONO), nitrogen dioxide (NO$_2$), nitrosyl hydride (HNO), nitric acid (HNO$_3$), nitrous oxide (N$_2$O), and hydroxylamine (NH$_2$OH). Hydroxylamine was suggested as a possible reactant precursor in the formation of interstellar amino acids and understanding how NH$_2$OH forms in astronomical environments would be of major interest to surface science physicists, astrochemists, and astrobiologists. Interstellar 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.\(^4\) proposed that accreted NO might be converted into HNO and NH\(_2\)OH via hydrogenation surface reactions in quiescent dense clouds. Two previous experimental studies show that formation of NH\(_2\)OH occurs after irradiation of a mixed solid system of NH\(_3\) and H\(_2\)O with UV photons\(^{15}\) and electrons.\(^{16}\) However, UV and e\(^-\) bombardment experiments do not apply, or very little, to dense cores and the formation efficiencies of these mechanisms turned out to be negligible with respect to chemical reduction and oxidation reactions occurring on grains. Joshi et al.\(^{13}\) have investigated the solid-phase reaction between NO and non-energetic OH radicals at 3 K, although they did not find NH\(_2\)OH to be a product of the NO + OH pathway. We have shown recently the first successful laboratory study to form NH\(_2\)OH via the non-energetic route NO + H in the solid phase and under conditions relevant to interstellar dark clouds.\(^{17}\)

This paper is the first in a two-article series regarding an experimental study of hydroxylamine formation via NO surface hydrogenation under astronomically relevant conditions. Here, we discuss the reactivity of NO and H (D) atoms and we present a detailed study of hydroxylamine formation on crystalline H\(_2\)O and amorphous silicate—two very realistic analogs of grain surface materials in the interstellar medium—at low temperature (10 K) and in a low-coverage regime (\(\leq 1\) monolayer). We show that the hydrogenation of NO proceeds fast and experimental results suggest that successive hydrogenation reactions proceed with no activation barrier to form NH\(_2\)OH. The formation of N\(_2\)O and H\(_2\)O is also discussed and a coherent reaction scheme is proposed. Finally, we will address the astrophysical implications of these findings. In the accompanying paper\(^{18}\) (hereafter referred to as Part II), NO hydrogenation is studied in pure NO ices as well as in more complex ice mixtures (NO:CO + H/D, NO:H\(_2\)O + H/D) in a high-coverage regime.

II. EXPERIMENTAL

The experiments were conducted using the FORMOLISM setup (FORmation of MOleculcs in the InterStellar Medium) based in the Physics Department of the Université de Cergy-Pontoise.\(^9\) The setup consists of an ultrahigh vacuum (UHV) chamber (base pressure of \(\sim 1 \times 10^{-10}\) mbar) containing a silicate-coated oxygen-free high-conductivity copper sample surface attached to the cold head of a closed-cycle He cryostat (Advanced Research Systems 4K DE-210SB cryo-cooler coupled to a ARS-10HW compressor). A schematic view of the FORMOLISM setup is illustrated in Fig. 1. The sample temperature is measured with a calibrated silicon diode clamped on the sample holder and controlled by a Lakeshore 336 controller to \(\pm 0.1\) K with an accuracy of \(\pm 2\) K in the 8–400 K range. The amorphous silicate (SiO\(_x\)) surface was recently installed in the FORMOLISM experiment,\(^{20}\) and mimics a realistic analog of bare dust grains in molecular clouds.\(^{21,22}\) The silicate sample is amorphous in nature, as evidenced by infrared spectroscopic studies, while temperature-programmed desorption (TPD) experiments reveal the surface to be non-porous on the molecular scale.\(^{23}\)

NO molecules and H (D) atoms are dosed onto the surface via two triply differentially pumped beamlines. Each beamline is equipped with a microwave frequency cavity where molecular hydrogen (D\(_2\) in beamline 1, and H\(_2\) in beamline 2) are dissociated, thermalized to 300 K upon surface impact with the source walls, and then injected into the main chamber. Dissociation efficiencies are typically
comprised between 0.5 and 0.6 and, using the King and Wells method, it has been estimated that the H (D) flux is $10^{13}$ atoms cm$^{-2}$ s$^{-1}$ within an uncertainty of 30%. In a typical experiment, the sample is kept at 10 K and is exposed to a dose of H (D) atoms expressed in exposed monolayers (EML). We use EML and not directly ML (1 ML = $10^{15}$ molecules cm$^{-2}$) because in the case of light molecules the sticking coefficient is not necessarily one. Hence, fewer molecules than those actually impinging on the surface thermalize with the substrate and are eventually physisorbed. The NO + H reactivity experiments are performed on either a nonporous amorphous water film (np-H$_2$O) of 100 monolayers or a composite ice layer of 400 ML of highly porous amorphous water ice (p-H$_2$O) grown on a np-H$_2$O sublayer. The nonporous water film is grown on the silicate by spraying water vapor from a microchannel array doser with the surface held at 120 K during water dosing. The p-H$_2$O films are grown with the surface held at 10 K on top of the np-H$_2$O substrate then annealed to 75 K to stabilize the film morphology before the subsequent heating-cooling runs between 10 and 75 K. Hydroxylamine formation experiments are performed on either bare amorphous silicate or a crystalline water ice (c-H$_2$O) film of 10 ML grown on the silicate by depositing water vapor via beamline 1. To form c-H$_2$O, the surface is held at 120 K during the deposition, then flash heated to 145 K, and finally cooled to 10 K before commencing the experiments.

A rotatable quadrupole mass spectrometer (QMS, Hiden HAL-3F) is employed for the detection of the gas-phase products in the vacuum chamber. In particular, the QMS is used to characterize the composition of the beams entering the UHV chamber and to monitor and measure the desorption of each species into the gas phase as a function of temperature. When TPD experiments are performed, the surface is heated from 10 to 200 K and the QMS is positioned 5 mm directly in front of the surface.

The current system is also equipped with a Bruker Tensor 27 Fourier transform infrared spectrometer (FTIR) used to monitor the adsorbed/formed species in situ. The FTIR is set up in a reflection-absorption infrared spectroscopy (RAIRS) configuration and the spectra are recorded at a grazing incidence angle of $83 \pm 1^\circ$. The parallel and unpolarized infrared beam is focused onto the sample using a 90° off-axis parabolic gold-plated mirror (effective FL = 250 mm), mounted in a differentially pumped housing adjacent to the UHV chamber and isolated from it with a differentially pumped KBr window. External to the UHV chamber, through a second pumped KBr window, the reflected infrared beam is collected and focused onto a liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector contained in a second pumped housing using an off-axis ellipsoidal gold-plated mirror having conjugate foci located at 250 mm and 40 mm, corresponding distances to the surface sample and the MCT detector, respectively. Infrared spectra between 4000 and 1000 cm$^{-1}$ (2.5–10 μm) are acquired with a resolution of 4 cm$^{-1}$ prior or subsequently to either deposition or TPD since the sample must be moved backward to allow for acquisition of a RAIR spectrum (in Fig. 1, the system is drawn in RAIRS mode, while the shaded sample holder indicates the sample position during H (D) exposures or TPD experiments). The number of averaged scans per saved IR spectrum is typically 500.

III. RESULTS AND DISCUSSION

A. Reactivity of NO + H/D at low temperatures

We have performed various experiments that clearly show that the efficiency of the reaction NO + H (D) is near to unity, irrespective of surface composition (water ice or silicate), its morphology, and surface temperature in the range 10–35 K.

Figure 2(a) compares the TPD profiles of 0.5 ML of NO (m/z = 30) on np-H$_2$O, and 0.5 ML of NO exposed to $\sim$1.5 EML (\sim0.5 ML) of D atoms at 10 K. Since the sticking coefficient of D atoms is estimated to be around 0.3, the number of D atoms that stick to the surface is about 1.5 EML × 0.3 = 0.45 ML, which suffices to hydrogenate 0.5 ML of NO by H (D) atoms via TPD and RAIRS spectroscopies. (a) TPD traces of NO after deposition of 0.5 ML of NO on np-H$_2$O (solid line), and after deposition of 0.5 ML of NO which is exposed to $\sim$1.5 EML (\sim0.5 ML) of D atoms at 10 K (dotted trace). (b) The solid line shows the RAIR spectrum of 1 ML of NO; the two most intense absorption bands of cis-(NO)$_2$ dimers at 1774 and 1865 cm$^{-1}$ are prominent. The dotted line shows the complete disappearance of NO from the surface after the sample has been exposed to 3 EML (\sim1 ML) of H atoms. The spectra are offset for clarity.
of adsorbed NO molecules if the reaction efficiency is actually near to unity. Figure 2(b) shows a RAIR spectrum of a similar experiment performed on amorphous silicate: about one monolayer of NO is deposited on the silicate substrate at 10 K. The lower IR spectrum (solid line) shows the two most intense absorption bands of \( \text{NO} \) at 10 K. The upper spectrum (dotted line) shows the consumption of 0.5 ML of NO deposited at 10 K. Cyan circles: NO deposited at 2 K on p-H\(_2\)O and exposed to D with the surface held at 10 K. Black squares: NO deposited at 10 K on np-H\(_2\)O and exposed to D with the surface held at 10 K. Green triangles: NO deposited at 42 K on p-H\(_2\)O and exposed to D with the surface held at 10 K. Open red square: NO deposited at 42 K on p-H\(_2\)O and exposed to D with the surface held at 35 K; this data-point is offset to allow for comparison with D exposures carried out at 10 K and to evaluate the efficiency of the NO + D reaction in a large range of temperatures (see text for details).

Deposition of NO at 42 K on p-ASW was motivated to favor the NO hydrogenation exhibits, therefore, a similar behavior observed also for \( \text{O} + \text{H} \), \( \text{O}_2 + \text{H} \), and \( \text{O}_3 + \text{H} \). More- ever, the absence of isotope differences between NO + H and NO + D indicates that, under our experimental conditions and at 10 K, tunneling does not govern this process. In Fig. 3, we show the NO surface coverage evolution as a function of D exposure time of a series of TPD experiments aimed at investigating the efficiency of the reaction between NO and D atoms on two different amorphous solid water ice substrates. The exposure to D atoms is performed at 10 K on np-H\(_2\)O and p-H\(_2\)O and, in the case of a porous ice substrate, NO was deposited either at 10 K or 42 K prior to exposure to D at 10 K. Deposition of NO at 42 K on p-ASW was motivated to favor the NO mobility both on the surface and in the pores. Figure 3 displays the consumption of 0.5 ML of NO deposited at 10 K on np-H\(_2\)O (black squares) and p-H\(_2\)O (green triangles), and 0.5 ML of NO deposited at 42 K on p-H\(_2\)O (cyan circles), as a function of increasing D exposure time at 10 K. In the first experiment performed on non-porous water ice (squares), we notice that almost 80% of the initial NO layer is consumed by an equivalent exposed dose of D atoms (1.80 EML correspond to \( \sim 0.6 \) ML). This suggests that the ratio between the number of D atoms required to consume NO and the number of NO molecules is close to 1 at the accuracy of our flux estimation (\( \sim 30\% \)), and that the reaction NO + D has a low or no energy barrier. We assume that the remaining 20% of NO on the surface is likely due to the non-perfect overlap of the two beamlines on the cold surface. The experiments related to NO deposited on p-H\(_2\)O at 10 K (green triangles) show a slower consumption rate that is caused by a reduced accessibility to NO molecules by D atoms on the more disordered and larger surface (molecules trapped in cracks, crevices, and pores). The NO consumption rate is naturally reduced further if NO is deposited at 42 K (cyan circles in Fig. 3). In fact, because of an enhanced mobility of NO molecules at a temperature close to that of desorption, the molecules are able to diffuse through the porous network and become less accessible to hydrogen atoms. D atoms, however, can still react with NO molecules because they are very mobile and able to scan the highly disordered surface even at 10 K. To test the NO + H (D) reactivity further, we did another experiment by depositing 0.5 ML of NO on porous water ice at 42 K and we exposed it to 6 EML of D-atoms at a surface temperature of 35 K. The resulting NO yield is indicated by the red open square in Fig. 3, placed near to a triangle at an abscissa value of 1.2 EML (6 EML/5). We can clearly notice that the NO + D reaction occurs at a surface temperature of 35 K as well. We set the red open square near to the data-point of the NO+D/p-ASW experiment at 10 K to emphasize that, under conditions of a high surface temperature (35 K), the NO consumption rate was only 5 times smaller than that found at 10 K. This entails a very high efficiency of the NO + D reaction because, though the NO consumption rate is found to be only 5 times smaller, the residence time of D atoms on the water ice substrate at 35 K, assuming a mean desorption energy \( E_{\text{des}} \) of 3.86 kJ mol\(^{-1}\) (40 meV), is 15 orders of magnitude smaller than residence time at 10 K. In fact, the exponential dependence on the surface temperature of the residence time \( \tau_{\text{res}} \) \( \tau_{\text{res}} = 1/\Lambda \times \exp(E_{\text{des}}/k_BT) \), with \( \Lambda = 10^{13} \) s\(^{-1}\), Ref. 25 gives a value for \( \tau_{\text{res}} \) of \( 10^{18} \) s, a lapse of time in which D atoms are able to find NO molecules within the porous network and react fast with them. This result clearly implies that the reaction NO + H (D) is fast and has an efficiency close to 1. Also, the surface morphology does not seem to affect the hydrogenation efficiency of NO owing to the high reactivity of the NO + H pathway. In other systems, however, the water substrate porosity may play an important role in the dynamics of desorption or in the energy budget of nascent species. In addition, the high-temperature experiments demonstrate that the diffusion process and hydrogenation dominate, at a certain extent, over the evaporation of hydrogen atoms even at 35 K and on a disordered surface not fully accessible to gas-phase species. These findings suggest that surface hydrogenation acts on a wide range of
temperatures and that interstellar chemistry on icy dust grains can occur in a variety of physical conditions including surface temperatures relatively far from 10 K.

B. Formation of hydroxylamine

The main finding of this study, for the implications linked to the creation of molecules of biological interest in space, is the formation of hydroxylamine—NH$_2$OH—via surface reactions leading to successive H-(D-)atom additions to NO under dense cloud conditions. In the present work, the formation of NH$_2$OH (ND$_2$OD) was confirmed via TPD spectra performed by steadily heating the surface between 10 and 200 K and monitoring evaporated hydroxylamine around 180 K. This is illustrated in Fig. 4 for all the NO + H (D) experiments carried out in this work at 10 K (Fig. 4(a): NO + H on amorphous SiO$_x$; Fig. 4(b): NO + D on amorphous SiO$_x$; Fig. 4(c): NO + D on crystalline H$_2$O) and in which hydroxylamine is produced. Figures 4(a)–4(c) show TPD spectra of NH$_2$OH, and ND$_2$OD, (peak at $\sim$188 K) produced after 6 cycles of 3 EML of H- or D-atom exposure of one monolayer coverage of NO (which totals to 18 EML of H or D atoms + 6 ML of NO per experiment) on amorphous silicate and on crystalline water ice. This procedure ensures that the reaction NO + H (D) occurs in a low-coverage regime until all NO molecules on the very surface have been consumed in each cycle. The repetition of several cycles enhances the signal-to-noise ratio of the QMS ion count upon ice sublimation. Results of the NO + H experiment on silicate are illustrated in Fig. 4(a). The signals are recorded at m/z = 33 (NH$_2$OH) as well as 30 (NO), 17 (OH), and 16 (NH$_2$), reflecting partial fragmentation upon NH$_2$OH ionization in the QMS head.42 In Figs. 4(b) and 4(c), we show the results of the NO + D/SiO$_x$ and NO + D/c-H$_2$O experiments, respectively. The signals in Fig. 4(b) are recorded at m/z = 36 (ND$_2$OD), 30 (NO), and 18 (OD and ND$_2$), and are consistent with the results of the NO + H experiment, namely, deuterated hydroxylamine is produced via D exposure of NO molecules and hence H- and D-atom additions prove to proceed at comparable rates. The TPD traces displayed in Fig. 4(c) result from the NO + D experiment performed on crystalline water ice and appear to have a different behavior from the two preceding cases. The mass spectrum at m/z = 36 shows no significant peak, which would suggest no ND$_2$OD formation. On the other hand, signals at m/z = 34 (ND$_2$O) and 30 (NO) do show a desorption peak at $\sim$188 K that we assume comes from fragmentation of ND$_2$OD molecules. We explain the non-detection of m/z = 36 peak in what follows. The TPD spectra of the NO + D experiment on water ice are complicated by the sublimation of the water substrate around 150 K and this alone eliminates the possibility of using the m/z = 18 (OD, ND$_2$, and also H$_2$O) mass spectrum as it is completely swamped with the huge signal of the water bulk. Water molecules may also be responsible for the disappearance of the peak at m/z = 36. In fact, in mixtures of water ice and molecules containing a hydroxyl group OH or OD, hydrogen/deuterium exchanges occur between the two species in the solid phase or upon sublimation.43 Newly formed fully deuterated hydroxylamine may therefore have exchanged its D atoms on the hydroxyl group with water and have desorbed in the form of ND$_2$OH (m/z = 35, not recorded). This would also explain the unusually high amount of HDO detected and not justified by H/D exchanges between H$_2$O and newly formed D$_2$O alone.

FIG. 4. TPD mass spectra as a function of temperature during a TPD experiment after six sequential depositions of (a) $\sim$1 ML of NO and 3 EML of H-atoms on amorphous silicate at 10 K, (b) $\sim$1 ML of NO and 3 EML of D-atoms on amorphous silicate at 10 K, and (c) $\sim$1 ML of NO and 3 EML of D-atoms on crystalline water ice at 10 K. The peak at T $\sim$ 188 K indicates desorption of hydroxylamine (NH$_2$OH, mass = 33 amu; ND$_2$OD, mass = 36 amu). Since NH$_2$OH (ND$_2$OD) fragmentation is induced in the mass spectrometer head upon ionization, peaks due to NO$^+$, OH$^+$ (OD$^+$), and NH$_2^+$ (ND$_2^+$) fragments are present as well at T $\sim$ 188 K. Low-temperature peaks for mass = 30, 17, and 18 amu are due to co-desorption of NO molecules and OH (OD) fragments with water at T $\sim$ 150 K. The traces are offset for clarity.
(see below). The low-temperature peaks of the TPD spectra in Fig. 4 (mainly m/z = 17, 18, and 30) are due to co-desorption of NO molecules and OH/OD fragments with water at T ∼ 150 K.

Each TPD spectrum, expressed in number of molecules coming off the surface per unit time, are known to follow the Polanyi-Wigner equation:

\[ \frac{dN}{dt} = r = -A N^n \exp\left(-\frac{E_{\text{des}}}{kT}\right), \]

where \( r \) is the rate of desorption, \( A \) is the pre-exponential factor, \( N \) is the number of molecules adsorbed, \( n \) is the order of reaction, \( E_{\text{des}} \) is the energy barrier for desorption, \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature of the surface.

Using the TPD spectrum of NH2OH and a model based on the Polanyi-Wigner equation—assuming a constant prefactor \( A \)—the desorption energy can be extracted from a fit of the desorption peak. This is illustrated in Fig. 5. Here we assumed that the desorption is a first-order process (\( n = 1 \)) and that \( A \) has a typical value of \( 10^{13} \) s\(^{-1}\). Using the best-fit values for the synthetic TPD, we calculate a desorption energy of NH2OH from amorphous silicate, which has a value of \( 54.2 ± 0.2 \) kJ mol\(^{-1}\).

Given the relatively high adsorption energy of NH2OH on silicate, it is fair to assume that this species is retained in the mantle of interstellar dust grains and that it will serve as a reservoir of interstellar solid-state nitrogen in later stages of the cloud evolution. It should also be stressed that, in the case of hydroxylamine formation on c-H2O, NH2OH desorbs after the water substrate has sublimated. This experiment clearly demonstrates that the desorption of the water ice cap from interstellar dust grains does not necessarily induce evaporation of more “refractory” species, as opposed to what commonly assumed. Implications of this finding are of great interest for chemistry, as NH2OH might also be considered one of the ingredients for water-free solid nitrogen chemistry.

C. Formation of N2O and H2O (D2O)

As stated above, we have investigated the hydrogenation of NO in a low-coverage regime (<1 ML). In order to be able to detect small amounts of new products that are below 1 ML coverage, we perform an experiment composed of 6 cycles. Each cycle consists of 5 min NO + 15 min H (D) corresponding to one monolayer of NO deposited on amorphous silicate or on crystalline water ice and exposed to ~3 EML of H (D) atoms. For each cycle, this procedure ensures that the reaction NO + H occurs on the very surface until all NO molecules have been thoroughly consumed into HNO which, in turn, is hydrogenated further due to a hydrogen-rich environment. The repetition of several identical cycles enhances the yield of new products and makes their detection easier either by RAIR spectroscopy or TPD. Figure 6 displays a series of RAIR spectra recorded during a complete 6-cycle experiment. Spectrum (a) shows the two cis-(NO)\(_2\) stretching bands (1774 and 1865 cm\(^{-1}\)) indicating the dimer assembling of 1 monolayer of NO deposited on amorphous silicate. Follows the set of IR spectra going from (b) to (g), each recorded in between two cycles of the NO + H experiment on amorphous silicate at 10 K. We can see, at 2235 cm\(^{-1}\), the \( \nu_3(N_2O) \) band mode\(^{44,45}\) of the newly formed nitrous oxide that raises clearly above the noise level of our FTIR in spectrum (d), and keeps growing as further NO + H cycles are carried out. The absence of new absorption features anywhere else in the spectrum due to radicals or product molecules (other than N2O) demonstrates that possible new products are not formed efficiently or are below the detection limit of our FTIR.

N2O formation is also confirmed by TPD mass spectra following NO + H(D) experiments performed on amorphous
silicate or on water ice at 10 K. Figure 7 shows the TPD curve for \textit{N}_2\textit{O} desorption after a complete 6-cycle \textit{NO} + \textit{H} experiment. The experimental curve exhibits a broad peak culminating around 84 K. Because we could not perform a series of TPDs of different \textit{N}_2\textit{O} coverages, we cannot determine if nitrous oxide follows a first- or zeroth-order desorption. Given the low-coverage regime, however, a first-order process appears to be the most plausible. The experimental \textit{N}_2\textit{O} TPD trace is modeled employing first-order desorption and gives a satisfactory result (solid line in Fig. 7) except for the tail of the experimental spectrum. The fit gives a heat of absorption of 23.05 ± 0.15 kJ mol\(^{-1}\). The \textit{N}_2\textit{O} TPD peak from crystalline water ice gives a very similar value of the desorption energy suggesting that \textit{N}_2\textit{O} desorption temperature is independent of the substrate composition. Therefore, at coverages of the order of the monolayer or less, \textit{N}_2\textit{O} seems to establish preferentially molecule–molecule bonds than being more strongly bound to the surface.

Figure 8 summarizes the \textit{N}_2\textit{O} yield produced after several \textit{NO} + \textit{H} cycles on amorphous silicate and on water ice. The integrated area of the \textit{N}_2\textit{O} stretching band at 2235 cm\(^{-1}\) is plotted as a function of \textit{NO} + \textit{H} (D) cycle number. It is clear that \textit{N}_2\textit{O} forms subsequently to \textit{NO} + \textit{H} (D) experiments both on \textit{SiO}\(_x\) and water ice at comparable rates (black, red, and blue traces in Fig. 8). We also performed a control experiment by exposing \textit{NO} to \textit{H}_2 molecules only (no atoms) in the same 6-cycle experiment fashion, i.e., 6 sequential cycles of 1 ML \textit{NO} + 3 EML \textit{H}_2. The result is indicated by the green line in Fig. 8. We find that the \textit{N}_2\textit{O} yield is not null in this control experiment, which shows the presence, though negligible, of condensation traces of \textit{N}_2\textit{O} coming from the \textit{NO} dosing line. The formation of \textit{N}_2\textit{O} is therefore certain during the \textit{NO} + \textit{H} (D) runs under our experimental conditions and its detection is confirmed by both TPD and RAIRS techniques. This study also shows that \textit{N}_2\textit{O} is a stable species under \textit{H}-atom exposure because apparently it is not hydrogenated at low temperatures. In fact, the \textit{N}_2\textit{O} yield is proportional to the concentration of the reactants [\textit{NO}] and [\textit{H}] ([\textit{D}]) (i.e., exposure time) and we do not observe a decrease of \textit{N}_2\textit{O} even in a regime of an excess of hydrogen atoms. This can have important consequences on the \textit{N}_2\textit{O} abundance in the interstellar medium because, whenever \textit{N}_2\textit{O} molecules are formed despite their low formation rate, they can survive on the surface of cold dust grains until a desorption process occurs and \textit{N}_2\textit{O} is released into the gas phase. This would also explain observations showing a link between the abundances of \textit{NO}, \textit{HNO}, and \textit{N}_2\textit{O} in dense molecular clouds\(^{12}\) with high abundances of \textit{NO}.

TPD spectra recorded between 100 and 200 K demonstrate that water molecules are formed in the \textit{NO} + \textit{H} (D) experiments. These results are displayed in Fig. 9: \textit{H}_2\textit{O}
(m/z = 18) is clearly formed subsequently to the NO + H experiment on amorphous SiOₓ as well as D₂O (m/z = 20) is formed in the NO + D experiments with comparable efficiency on amorphous SiOₓ. The result of the NO + H₂ control experiment is also shown and indicates that no measurable quantity of water molecules is detected in this case. D₂O is formed in the NO + D experiment performed on crystalline water ice, although the TPD results are affected by H/D substitutions with H₂O molecules of the substrate. And HD (m/z = 19) is thus the major product (about 5 times more abundant than D₂O) seen in the TPD spectrum, dotted trace in Fig. 9(d).

It is difficult to give a precise estimate of the amount of water molecules produced in this study as the stretching band of water (H₂O and D₂O) is spread over 300 cm⁻¹ and it is not detectable by RAIRS under our experimental conditions. In Part II as well, where the experiments are conducted in a high-coverage regime (>50 monolayers), a quantitative estimate of the water ice formed is not possible due to other absorption lines with which water bands blend. From TPD spectra recorded in this study, by comparison with previous experiments, we can only give a rough estimate for the water produced of ~0.5 ML. This study, together with Part II, shows that water formation subsequent to NO hydrogenation cannot be considered an efficient route to H₂O in the interstellar medium.

D. Possible reaction routes

In Fig. 10 we show a consistent reaction diagram inferred from the experimental observations of the NO hydrogenation on crystalline water ice and amorphous silicate at 10 K. Solid arrows indicate barrierless reactions while dashed arrows indicate the reactions that proceed with an activation barrier. The suggested solid-phase hydrogenation channel leading to hydroxylamine, highlighted in red, starts from NO and run horizontally via three successive H- (D-)atom additions according to the following scheme:

\[
\text{NO} + \text{H} \rightarrow \text{HNO}, \\
\text{HNO} + \text{H} \rightarrow \text{H₂NO/HNOH}, \\
\text{H₂NO} + \text{H} \rightarrow \text{NH₂OH}. 
\]

This chemical pathway to hydroxylamine formation in interstellar dark clouds was proposed by Charnely et al. and here we show experimentally that this scheme is fast at temperatures as low as 10 K in low-coverage regimes (<1 ML). As opposed to Part II, the product of reaction (2)—HNO—was below the detection limit under our experimental conditions due to the low-coverage regimes employed. In Part II, the authors show that reactions (2)–(4) proceed fast and with no apparent activation barrier in pure NO ices as well as in more complex ice mixtures (NO:CO, NO:H₂O), and that this reaction scheme is not temperature dependent.

Hydrogenation of NO or, more likely, of cis-(NO)₂ dimers on SiOₓ and c-H₂O also leads to the formation nitrous oxide. The proposed reactions leading to N₂O are as follows:

\[
\text{HNO} + \text{NO} \rightarrow \text{N₂O} + \text{OH}, \\
\text{(NO)}₂ + \text{H} \rightarrow \text{N₂O} + \text{OH}. 
\]

Experiments of sequential and concurrent deposition of 3 ML NO + 9 EML H have been performed to check whether the N₂O yield varies in the two cases and possibly infer which pathway is more likely to nitrous oxide formation. However, sequential and co-deposition experiments give comparable results, probably because the ON–NO bond is so weak (6.28–15.50 kJ mol⁻¹, Stirling et al. and references therein) that reactions (5) and (6) may be considered two alternative ways to describe the same process. An extensive discussion on the possible N₂O formation pathways is given in Part II, where their reaction (12) is thought to be the most likely formation pathway leading to N₂O via the unstable radical HONNO. Nevertheless, conditions leading to N₂O in the solid phase may be rare in space because surface coverages on interstellar grains are much lower than those in the laboratory. For this reason, we do not expect that reactions (5) and (6) are efficient pathways to nitrous oxide formation under molecular clouds conditions except in those environments where NO is abundant. The N₂O formation pathways discussed above also imply the formation of OH radicals that can react fast with H atoms and produce water molecules observed in this study, corroborating thus reactions (5) and (6) in the solid phase notwithstanding mechanisms with a high activation barrier. In fact, under our experimental conditions, formation of water molecules can only occur via reactions including OH (OD),

\[
\text{H} + \text{OH} \rightarrow \text{H₂O}, \\
\text{D} + \text{OD} \rightarrow \text{D₂O} 
\]

between hydrogen atoms from the beamline and OH radicals produced in reactions (5) and (6). The H + OH pathway was previously investigated by Dulieu et al. and this formation route for water molecules was estimated to have a 50%
efficiency. It should also be noted that recently experimental evidence was found for water formation via the following pathway:

\[
\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}
\]

(9)

or

\[
\text{OD} + \text{D}_2 \rightarrow \text{D}_2\text{O} + \text{D}
\]

(10)

at temperatures as low as 10 K.\(^{38,49}\) Given the H\(_2\) coverage expected on a surface at 10 K (1.5–2.0 \(\times\) \(10^{14}\) molecules cm\(^{-2}\)),\(^{41,50,51}\) we can assume that at least a fraction of water molecules observed in our experiments are formed through reactions (9) and (10). Again, H\(_2\)O (D\(_2\)O) can only be formed if OH (OD) radicals are present on the surface. Therefore, the formation of water molecules is an indirect validation of reactions (5) and (6) since water could not be formed otherwise.

**IV. ASTROPHYSICAL IMPLICATIONS**

This study and Part II show that hydroxylamine formation proceeds fast and is a barrierless mechanism under conditions found in interstellar dense clouds. The reaction of the neutral radicals NO and H (or D) via surface chemistry at extremely low temperature proved to be very efficient. In molecular clouds, the accretion time of NO on the surface of dust grains can be estimated by its observed abundance. According to the measurements available in the literature, NO has a rather constant column density of \(\sim 10^{16}\) cm\(^{-2}\) (Refs. 9 and 12) that, in a typical molecular cloud, means a fractional abundance of \(10^{-8}\) relative to H\(_2\), and \(10^{-5}\) relative to H. Using the H\(_2\) flux estimated by Accolla \textit{et al.},\(^{52}\) and scaling it by a factor of \(10^{-5}\), we find a NO accretion rate of \(\sim 8 \times 10^9\) molecules cm\(^{-2}\) yr\(^{-1}\), that is nearly 1/10th of monolayer in 10\(^7\) years, a lapse of time compatible with the estimated lifetime of a molecular cloud. We can fairly assume that one accreted NO molecule will always find one H atom to react with on the surface. Furthermore, since [NO]/[H] \(\sim 10^{-5}\), there will also be enough H atoms to complete the hydrogenation reactions until formation of NH\(_2\)OH and the completion of the NO hydrogenation scheme within the same time scale. Eventually, after around 10\(^7\) years, icy mantles covering dust grains in molecular clouds will contain a non-negligible fraction of a monolayer of hydroxylamine. Given that NO is likely to form on grains via accretion of other reactants as well (e.g., N+O, OH), our derived hydroxylamine abundance must be treated as a lower limit. Therefore, a considerable amount of NH\(_2\)OH will be locked up in the ices of dense clouds and will become available for further processing at later times. As soon as a protostar forms and UV radiation and thermal processing begin, energetic processes will occur and a new chemistry can take over.

Because hydroxylamine is considered a possible precursor species in the formation of amino acids,\(^{10}\) implications of NH\(_2\)OH synthesis on the surface of dust grains in the interstellar and circumstellar medium can have an enormous impact on astrobiology, Earth biochemistry, and the origin of life. In Fig. 11, we present a cartoon illustrating how NH\(_2\)OH acts as a starting point in the formation of amino acids. Once released into the gas phase, owing to its high proton affinity, hydroxylamine will react with CH\(_3\)\(^+\) or H\(_3\)\(^+\) in barrierless and exothermically favorable reactions,\(^{14}\) and eventually form glycine and \(\beta\)-alanine via reactions with acetic acid and propanoic acid, respectively. Recent calculations, however, have cast doubt on the efficiency of such processes;\(^{53}\) hence, new experimental studies at low temperatures are needed to support or disprove these findings.

Hydroxylamine has been searched for in a recent survey toward seven dense astronomical environments but its detection was not confirmed.\(^{54}\) Hence, to date, there has not been any report of positive detections of NH\(_2\)OH in molecular clouds. This is due to the high desorption energy of NH\(_2\)OH molecules as measured in this work, favoring the retention of NH\(_2\)OH in the icy mantle of dust grains. Indeed, this study and another study\(^{16}\) show that hydroxylamine desorbs at relatively high temperatures (>175 K), so it may be within detection limits only in those parts of the cloud that experienced a dramatic heating phase. Hydroxylamine proves to be a non-volatile species so, once formed, it will tend to remain adsorbed on the icy grains. For this reason, gas-phase abundances in cold regions stay below the current detection limit. Major release into the gas phase will occur as soon as a heating phase of the medium occurs, favoring NH\(_2\)OH detection via ground-based radio observations. However, only ALMA—a new and revolutionary interferometer operating at millimeter and sub-millimeter wavelengths—will be able to provide the required spacial resolution to peer at the inner parts of small-scale structures such as proto-planetary disks and small hot cores.\(^{55}\) ALMA will also come with a hugely improved sensitivity that, added to a high angular resolution, will allow perhaps detection of NH\(_2\)OH in cold starless cores and pre-stellar cores as well.

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