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Formaldehyde chemistry in cometary ices: the case of HOCH₂OH formation[†]

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Laboratory experiments devoted to simulate the chemistry occurring in interstellar and cometary ice analogues are of paramount importance to understand the formation of complex organic molecules that are detected throughout the universe. These laboratory simulations provide relevant hints on the fundamental physical and chemical steps associated with the increase of the molecular complexity in space and moreover give benchmark results for dedicated space missions. In the present work, we study thermal-promoted reactivity of a H₂O-dominated and D₂O-dominated cometary ice analogues that contain amounts of H₂CO and NH₃ by means of Fourier transform infrared spectroscopy (FTIR), mass spectrometry and DFT calculations. Experimental measurements show that methyleneglycol (HOCH₂OH) and D₂-methyleneglycol (DOCH₂OD, the corresponding isotopologue) are formed from the H₂O- and D₂O-dominated ices, respectively, only if ammonia is present. We also reported for the first time the mass spectrum of methyleneglycol and D₂-methyleneglycol. B3LYP calculations have also been used to characterize the potential energy surface of the mechanistic steps associated with the formation of HOCH₂OH as well as to simulate the IR spectrum of this compound. The fruitful interplay between theory and experiment has allowed us to elucidate the exact role of ammonia during the warming, which essentially stands for the formation and stabilization of a NH₄⁺/OH⁻ ion pair, thus enabling the OH⁻ species to react with formaldehyde. The present results reproduce the heating of circumstellar ices in star formation regions and can be applied to the late thermal evolution of comets. In addition, the mass spectrum of methyleneglycol represents a benchmark for the analysis of the data coming from the ROSINA on-board instrument of the Rosetta mission.

1 Introduction

Comets can be considered as one of the most pristine remains of the primitive solar nebula. Thus studies devoted to analyse comet composition are crucial to understand the history of our solar system.¹ Furthermore, knowing the internal composition of the cometary nucleus also provides insights on the nature of the available organic compounds that could have been delivered on the early Earth. About twenty five gaseous species (including ions and radicals) have been observed in the cometary coma by remote sensing instruments.^{2–4} Minerals have also been detected in grains by infrared spectroscopy as well as from the analysis of the sample returned by the Stardust mission.^{5,6} Comet nuclei

consist of an agglomeration of grains which contain dirty ices made up by simple molecules such as water (the most preponderant one) as well as methanol, carbon dioxide, formaldehyde and ammonia. When comets approach the Sun, they enter into an active phase due to their exposition to energetic processes which can induce changes into their grain composition. Indeed, UV irradiation, particle bombardments and thermal heating of the cometary ices from the nearby environments of the star are able to trigger chemical reactions in or on ices, giving rise to a rich chemistry that does not occur in more quiescent environments.

The water component of dirty ices is sometimes considered as a "solvent" that induces a decrease of the overall chemical activity of the ice due to the dilution of the reactants.⁷ However, in some cases water can activate chemical reactions by lowering the energy barriers (*i.e.* water acts as a catalyst) or can participate to the reaction itself (*i.e.* water acts as a reactant).^{7–12} A good example of these possible roles of water concerns the warming of interstellar/cometary ice analogues containing H₂O, NH₃ and H₂CO. In such ice mixtures water molecules can act as "solvent", reactant or catalyst depending on the initial ice composition.^{13,14} Indeed, reactions activated at low temperature in H₂O:NH₃:H₂CO ices have been stud-

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ied by Schutte et al.^{13,14} and Bossa et al.¹⁵. In these works, three different organic compounds were distinguished by infrared spectroscopy: the polyoxymethylene (POM) formaldehyde polymer, in which water in principle acts as a "solvent"; and two ones called X and Y in the Schutte's study, which are the products for the reaction of H₂CO with NH₃ and with H₂O, respectively. The X product was identified by Bossa et al.¹⁵ to be aminomethanol (NH₂CH₂OH), in which quantum chemical calculations carried out by Rimola et al.¹⁶ identified water as a catalyst of the reaction. However, the nature of Y is still unclear. It has to be noted that the presence of ammonia in the ice mixture is required for the formation of this compound. In this work, the warming of a cometary water-dominated ices containing amounts of NH₃ and H₂CO has been studied. Based on infrared spectroscopy, isotopic labelling and mass spectrometry measurements, identification of the "Y" product in the Schutte's study as the methyleneglycol (HOCH₂OH) compound is provided. Quantum mechanical calculations based on the B3LYP density functional method (DFT) have been used to characterise the role of ammonia in this reaction as well as to simulate the IR spectrum of a model ice of this compound. The combination between theory and experiment enabled to determine that in this reaction water acts as a reactant, whereas NH₃ has been identified as the catalyst. Moreover, the mass spectrum of the methyleneglycol and its interpretation is reported for the first time, which may help the interpretation of the future data which will be reported by the ROSINA on-board instrument of the Rosetta mission. This work also provides evidences that the thermally-promoted reactions involving formaldehyde in the nuclei of comets can be an important source of complex organic compounds.

2 Methods

2.1 Experimental set-up

The experimental protocol and set-up (AHIA) have been previously described⁷. Briefly, ammonia (NH₃) is supplied by Air Liquide (99.9995% purity). Formaldehyde (H₂CO) is formed from the heating (80 °C) of paraformaldehyde (supplied by Aldrich). Water and D₂O are doubly distilled under vacuum before injection. The NH₃:H₂CO and NH₃:H₂CO:H₂O gas mixtures were prepared into a primary vacuum pumped mixing line at room temperature. They were then deposited onto a gold plated metal surface cooled down at 10 K by a Model 21 CTI cold head within a high vacuum chamber (*c.a.* 10⁻⁹ mbar). Infrared spectra were recorded at different temperatures using Fourier transform reflection absorption infrared spectroscopy (FT-RAIRS) using an tensor spectrometer with a MCT detector. A typical spectrum has a 1 cm⁻¹ resolution and is averaged over one hundred interferograms. The sample was warmed using a heating resistance and

the temperature measured by a Si diode (± 0.3 K) were controlled using a Lakeshore Model 320 temperature controller. During the warming, mass spectra of sublimating species were recorded using a MKS Microvision-IP plus RGA quadrupole mass spectrometer. The ionization source is an EI ion source (70 eV) and the mass spectra were recorded between 1 and 80 amu. The concentration ratios of the different ice mixtures were derived from the IR spectra by integrating the IR bands to estimate the column density of NH₃ and H₂CO according to their band strengths. Uncertainties when evaluating the column densities of frozen molecules were estimated to be around 30%. For NH₃, we used the value given by Kerkhof et al.¹⁷ 1.3 10⁻¹⁷ cm molecules⁻¹ for the wagging mode at 1070 cm⁻¹. For H₂CO, we used the values given by¹³ 9.6 10⁻¹⁸ cm molecules⁻¹ for the CO stretch mode at 1725.5 cm⁻¹ and 3.9 10⁻¹⁸ cm molecules⁻¹ for the CH₂ scissoring mode at 1494 cm⁻¹.

2.2 Computational details

All calculations were performed using the GAUSSIAN03 program package.¹⁸ The structure of each stationary point was fully optimized using the hybrid B3LYP^{19,20} functional with the standard 6-31+G(d,p) basis set. All structures were characterized by the analytical calculation of the harmonic frequencies as minima (reactants, intermediates and products) and saddle points (transition states). Intrinsic reaction coordinate (IRC) calculations at the same level of theory were carried out to ensure that a given transition structure connects the expected reactants and products. The free energies calculated at different temperatures were obtained by computing the thermochemical corrections to the energy values using the standard harmonic oscillator formulae computed at B3LYP/6-31+G(d,p).²¹ The vibrational frequencies of the simulated spectra have been scaled by a 0.97 factor.²²

3 Results

3.1 Warming of H₂O:NH₃:H₂CO ice mixture: infrared and mass analysis

The warming of different cometary ice analogues which contain H₂O, NH₃, and H₂CO resulted with three different organic residues that can be distinguished by infrared spectroscopy: polyoxymethylene (POM), and the two other ones called X (aminomethanol) and Y (unknown) in the Schutte's study, which are products of H₂CO reacting with NH₃ and H₂O, respectively.¹³ The nature of the products and their relative abundances depend strongly on the composition of the initial ice mixture. In the present work we focus on the formation and characterisation of the "Y" product as designated by Schutte et al.¹³

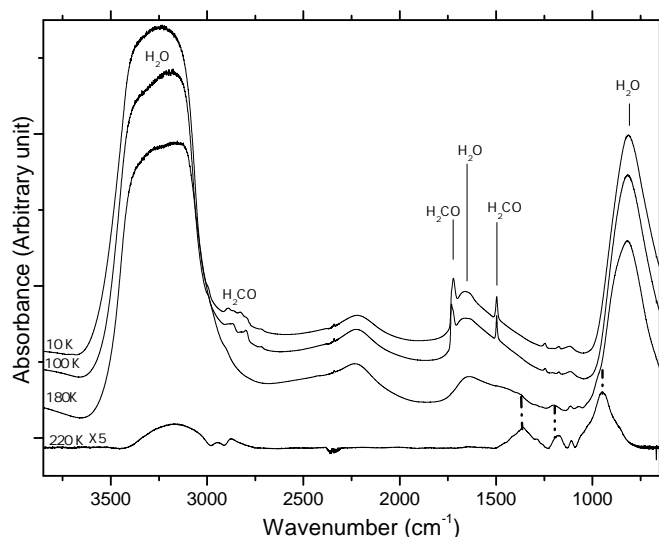


Fig. 1 FTIR spectra of a $\text{H}_2\text{O}:\text{NH}_3:\text{H}_2\text{CO}=10:0.1:0.4$ at 10 K, 100 K, 180 K, 220 K. The ice mixture is linearly warmed-up at a temperature rate of 4K/min.

This "Y" species is the dominant product when the $\text{H}_2\text{O}:\text{NH}_3:\text{H}_2\text{CO}$ ice mixtures present a $0.2 < \text{NH}_3/\text{H}_2\text{CO} < 1$ concentration ratios. In contrast, at very low $\text{NH}_3/\text{H}_2\text{CO}$ concentration ratio (i.e. $\text{NH}_3/\text{H}_2\text{CO} < 0.01$), formaldehyde polymerisation takes place leading to the formation of polyoxymethylene (POM, $\text{HO}-(\text{CH}_2\text{O})_n\text{-H}$) as the dominant product. Accordingly, the results presented along this work are based on a $\text{H}_2\text{O}:\text{NH}_3:\text{H}_2\text{CO}$ ice mixture in a 10:0.1:0.4 concentration ratio in order to form "Y" only and characterize its nature. This ice mixture has been specifically chosen according to previous studies showing that in such an ice mixture, the formation of formaldehyde hydrate ("Y" product) is the most efficient.¹³ Figure 1 shows the thermal evolution of this ice mixture. Reaction does not occur until the sample temperature reaches 100 K. At this temperature, new IR features are observed at 1374 and 984 cm^{-1} while the H_2CO IR bands decrease. At 180 K only the "Y" product and the unreacted H_2O and NH_3 remain on the metal surface. The IR spectrum of the pure product is obtained at 220 K after the complete sublimation of the residual H_2O and NH_3 . This IR spectrum reveals the presence of O-H, C-H and C-O groups, in consistency with a direct reaction between formaldehyde and water. The broad band (1085-850 cm^{-1}) centred at 956 cm^{-1} , related to the C-O stretching mode, is close to the one observed in the POM structure (Table 1).

Because the sublimation temperature of the Y product (between 210-240 K) was found to be lower than the POM sublimation temperature, Schutte *et al.* suggested "Y" to be one of the smallest members of the POM polymer series.

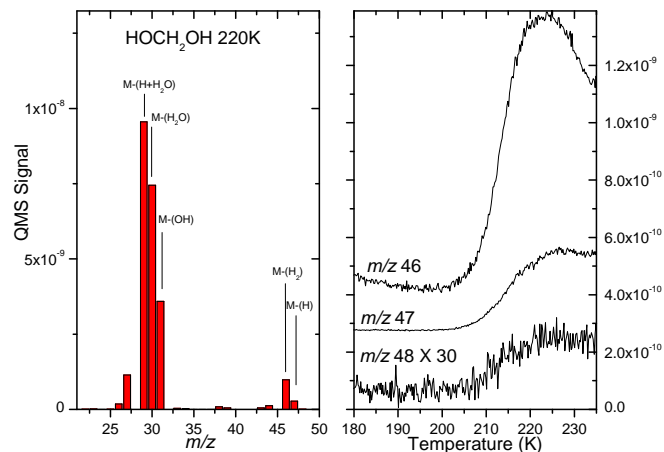


Fig. 2 Left panel: mass spectrum of HOCH_2OH recorded at 220 K. Right panel: thermal evolution of m/z 46, 47, and 48 during the warming of $\text{H}_2\text{O}:\text{NH}_3:\text{H}_2\text{CO}$ 10:0.1:0.4 ice mixture at a 4 K/min temperature ramp.

In particular, they suggested methyleneglycol (HOCH_2OH , also called methanediol), or POM oligomers of short chain lengths ($\text{HO}(\text{CH}_2\text{O})_n\text{H}$, $n < 5$). Mass spectrum measurements performed at 220 K during the temperature ramp (displayed in Fig. 2) have helped us to distinguish between these species. Indeed, in the m/z 40-50 range, POM fragmentation is characterised by a unique peak at m/z 47 assigned to the $-\text{O}-\text{CH}_2-\text{OH}^+$ ion.²³ The mass spectrum of the "Y" species, however, is characterised in this range by three peaks of m/z 46, 47 and 48, meaning that it is not a POM-like structure. The peak observed at m/z 48 can be the molecular ion of methyleneglycol, whereas the peaks at m/z 47 and 46 are due to the loss of one (M-1) and two hydrogen (M-2) from methyleneglycol, respectively (right panel of Fig. 2). Other relevant peaks are observed at m/z 30 and 31 due the loss of OH (M-17) and H_2O (M-18), which are common peaks in the fragmentation of OH-bearing molecules such as alcohols. It is worth mentioning that the low intensity of the molecular ion of methyleneglycol (m/z 48) is not surprising since these peaks are usually undetectable in HO bearing molecule such as alcohol, hemiacetal, or gem-diol²⁴. It has to be noted that lowering the electron energy from 70 to 40 eV does not significantly increase the relative intensity of the molecular ion (m/z 48). A more detailed assignment of the main fragments of HOCH_2OH will be made using isotopic substitution experiments (deuterium labelling) presented in the next section.

Table 1 Experimental IR positions (in cm^{-1}) for HOCH_2OH in water or as pure ice, integrated band strengths (A, in $\text{cm} \text{molec}^{-1}$), and B3LYP/6-31+G(d,p) IR spectrum data for HOCH_2OH , $(\text{HOCH}_2\text{OH})_4$ and $(\text{HOCH}_2\text{OH})_{10}$

mode	HOCH_2OH						
	in H_2O		Pure		B3LYP		
	Position (cm^{-1})	A	Position (cm^{-1})	A	HOCH_2OH (cm^{-1})	$(\text{HOCH}_2\text{OH})_4$ (cm^{-1})	$(\text{HOCH}_2\text{OH})_{10}$ (cm^{-1})
νOH	-	-	3191 ^a	$\times 10^{-17}$	3663	3384	3500-3367-3255-3100
νCH	-	-	2960	6×10^{-19}	2942	2949	2917
νCH	-	-	2860	2.3×10^{-18}	2847	2918	2796
δCH	1374	4.1×10^{-18}	1362	1.9×10^{-17}	1399	1416	1467
δCH	1288	-	1290	-	1316	1404	1380
$\tau\text{CH}+\delta\text{OH}$	1195	8×10^{-18}	1187	5.5×10^{-18}	1214	1172	1181
$\nu\text{C-O}$	1120	2.1×10^{-18}	1111	9.5×10^{-19}	1043	1053	1003
$\nu\text{C-O}$	984	3×10^{-17}	956	5×10^{-17}	-	1014	965

^a: broad band from 3450 to 2981 cm^{-1} centred at 3191 cm^{-1} . Vibration modes: stretching (ν), bending (δ), torsion (τ).

3.2 Warming of $\text{D}_2\text{O}:\text{NH}_3:\text{H}_2\text{CO}$ ice mixture: infrared and mass analysis

In order to strengthen the characterisation of methyleneglycol and get better assignments of its mass spectrum, we performed isotopic substitution experiments using D_2O instead of H_2O . Accordingly, the "Y" isotopologue species has been formed from the warming of $\text{D}_2\text{O}:\text{NH}_3:\text{H}_2\text{CO}$ ice mixtures in a 10:0.1:0.4 concentration ratio (the very same as that used in the H_2O -dominated experiments). Figure 3 shows the thermal evolution of this ice mixture. Similar to the H_2O -dominated ice reaction, new bands are observed around 100 K at 1375 and 985 cm^{-1} , followed by a H_2CO bands decrease. At 180 K only the "Y" isotopologue product and the unreacted D_2O and NH_3 remain on the metal surface. The corresponding infrared spectrum, recorded at 200 K after sublimation of the residual D_2O , NH_3 and H_2CO , is displayed in Figure 3. This infrared spectrum reveals the presence of C-H, O-D, and C-O groups located at 2947, 2405, and 983 cm^{-1} respectively (see Table 2). As previously observed for the H_2O -dominated ice mixture, this infrared spectrum is consistent with a direct reaction between formaldehyde and D_2O . Indeed, the presence of the broad band at 2405 cm^{-1} due to the OD stretching mode matches with a molecule containing OD-terminal groups. Mass spectrum measurements have also been performed at 220 K during the desorption of the product (displayed in Fig. 4). The mass spectrum in the m/z 40-50 range is dominated by five peaks at m/z 46, 47, 48, 49 and 50 (see Fig. 4). The m/z 50 is due to the molecular ion of DOCH_2OD , which confirms the direct reaction of D_2O with formaldehyde to yield D_2 -methyleneglycol. In addition, the presence of peaks at m/z 49 and 50 in the experiment with D_2O definitely rule out the formation (in such conditions) of $\text{HO}(\text{CH}_2\text{O})_n\text{-H}$

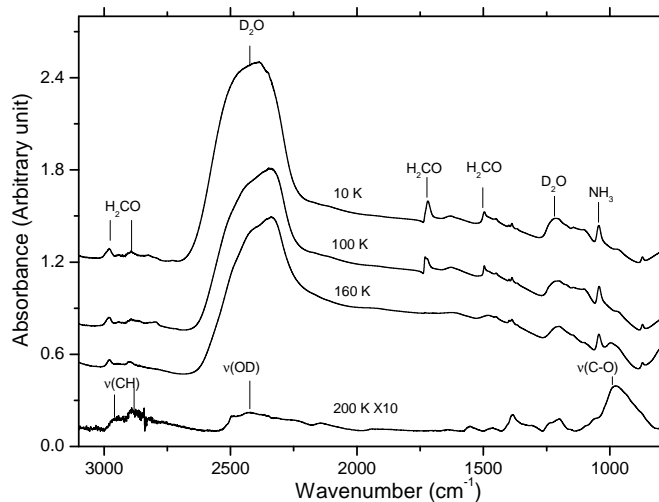


Fig. 3 FTIR spectra of a $\text{D}_2\text{O}:\text{NH}_3:\text{H}_2\text{CO}=10:0.1:0.4$ at 10 K, 100 K, 160 K, 200 K. The ice mixture is linearly warmed-up at a temperature rate of 4 K/min.

Table 2 Experimental IR positions (in cm^{-1}) for DOCH_2OH in D_2O and as pure ice, and B3LYP/6-31+G(d,p) IR spectrum data for $(\text{DOCH}_2\text{OD})_{10}$

mode	DOCH_2OD		
	in H_2O Position (cm^{-1})	Pure Position (cm^{-1})	B3LYP (DOCH_2OD) ₁₀ (cm^{-1})
νOD	-	2405 ^a	2600-2500-2416-2304
νCH	2977	2947	3027
νCH	2901	2886	2962
δCH	1375	1386	1392
$\tau\text{CH}+\delta\text{OD}$	-	1209	1207
$\nu\text{C-O}$	-	1062	1056
$\nu\text{C-O}$	985	983	987

^a: broad band from 2540 to 2184 cm^{-1} centred at 2405 cm^{-1} .
Vibration modes: stretching (ν), bending (δ), torsion (τ).

oligomer ($n>1$).

More evidences on the direct reaction between formaldehyde and D_2O are provided by fragments at m/z 46, 47, 48 and 49. By comparing the fragments from HOCH_2OH with those of DOCH_2OD , it is possible to discriminate which kind of hydrogen is removed (*i.e.* from the $-\text{OH}$ ($-\text{OD}$) groups or from the $-\text{CH}_2-$ group), since they are now discernible. The peak assignments of the mass spectrum of methyleneglycol based on the comparison between the HOCH_2OH and DOCH_2OD fragmentations are given in table 3. The most striking peak is the one observed in both experiments at m/z 46, which is assigned to the OCH_2O^+ ion where two hydrogen (deuterium) were removed from the HO- (DO-) groups. The presence of this ion in both experiments is only possible if H_2O (D_2O) does indeed react with formaldehyde. It has to be noted that in the case of the HOCH_2OH fragmentation the peak observed at m/z 46 are also due to the other ions of HOCHO^+ and HOCOH^+ . The corresponding deuterated species DOCHO^+ and DOCOD^+ are observed at m/z 47 and 48 respectively (Table 3). These results are in good agreement with the HOCH_2OH formula and strengthen the assignment of the "Y" product to methyleneglycol.

3.3 Computational analysis

Evidences for the formation of methyleneglycol during the warming of the ice mixture are also provided by quantum chemical calculations. The B3LYP-simulated IR spectra of HOCH_2OH both as a single discrete gas-phase molecule and as a cluster system made up by 4 and 10 methyleneglycol molecules are presented in Figure 5. This two latter cases consist of a way to model a pure methyleneglycol ice as

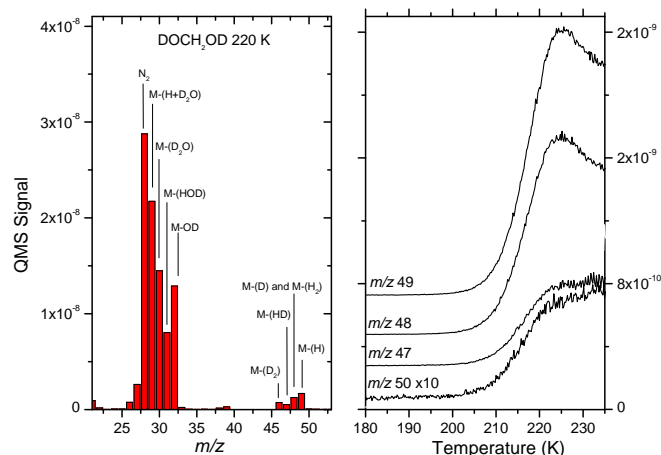


Fig. 4 Left panel: mass spectrum of DOCH_2OD recorded at 220 K. Right panel: thermal evolution of m/z 47, 48, 49, and 50 during the warming of $\text{D}_2\text{O}:\text{NH}_3:\text{H}_2\text{CO}$ 10:0.1:0.4 ice mixture at a 4 K/min temperature ramp.

Table 3 m/z characteristic values of HOCH_2OH and of DOCH_2OD isotopologue.

HOCH_2OH		DOCH_2OD	
m/z (%)	Attribution	Attribution	m/z (%)
48 (0.1)	$\text{CH}_2(\text{OH})_2^+$	$\text{CH}_2(\text{OD})_2^+$	50 (0.3)
47 (3)	HOCHOH^+	DOCHOD^+	49 (8)
47 (3)	HOCH_2O^+	DOCH_2O^+	48(6)
46 (10)	HOCOH^+	DOCOD^+	48 (6)
46 (10)	HOCHO^+	DOCHO^+	47 (2)
46 (10)	CH_2O_2^+	CH_2O_2^+	46 (3)
31 (38)	HOCH_2^+	DOCH_2^+	32 (59)
30 (78)	HOCO^+	DOCOD^+	31 (37)
30 (78)	CH_2O^+	CH_2O^+	30 (67)
29 (100)	HCO^+	HCO^+	29 (100)

recorded in the experiments. Comparison of these simulated spectra with the experimental one is reported in Figure 5. Table 1 also reports the calculated band positions. Despite its simplicity, the overall calculated IR features of the discrete molecule (spectrum *a* of Fig. 5) are in fair consistency with the experimental ones. Obviously, because the experimental IR spectrum arises from a HOCH₂OH ice, both the band positions and shape do not perfectly match one to each other, especially for those vibrations significantly affected by the H-bond interactions present in the true ice. For instance, the broad band associated with the $\nu(\text{OH})$ appears as a sharper band and at a higher wavenumber values in the simulated spectra because of the lack of H-bond interactions. The tetramer (HOCH₂OH)₄ cluster model is not large enough to reproduce the IR features of the methyleneglycol ice since the band corresponding to the $\nu(\text{OH})$ vibration is still sharp, although shifted to lower values in consistency with the H-bond interactions (spectrum *b* of Fig. 5). In contrast, the decamer (HOCH₂OH)₁₀ IR features (spectrum *c* of Fig. 5) compares reasonably well with the experiments. The upper IR region presents the two bands corresponding to the $\nu(\text{CH})$ vibrational modes and a set of bands associated with the $\nu(\text{OH})$ (between 3500-3100 cm⁻¹), which in the experimental IR spectrum are grouped in a very broad band spread over 3350-3000 cm⁻¹. It is worth pointing out that the squat shape of this signal clearly suggests the presence of sub-bands, as the simulations indicate. The lower regions are also quite similar, as they present the same bands at a reasonably similar wavenumbers, although in the simulated spectra the $\nu(\text{CO})$ band at 1111 cm⁻¹ in the experiment appears overlapped by the adjacent more intense $\nu(\text{CO})$ one (1030-965 cm⁻¹). The theoretical IR spectrum of the (DOCH₂OD)₁₀ has also been calculated and compared with the experimental spectrum (see Fig. 6). The corresponding theoretical and experimental frequencies are listed in Table 2 along with their vibrational assignments. As expected, a large bathochromic shift corresponding to the OD stretching mode at 2405 cm⁻¹ compared to the 3191 cm⁻¹ for HOCH₂OH is observed. This experimental frequency shift (786 cm⁻¹) is in good agreement with the average calculated frequency shift (850 cm⁻¹). In addition, the overall calculated IR features are in fair consistency with the experimental values (Table 2) and also support the formation of methyleneglycol from the warming of H₂O-dominated ice containing H₂CO and NH₃.

The mechanistic steps leading to the formation of HOCH₂OH from the reaction of H₂O and H₂CO in the presence of NH₃ have been explored by calculating the potential energy surface (PES) features of this reaction. The water-dominated ice model used for this purpose is shown in Figure 7a. It consists of a water cluster of 33 H₂O molecules, which adopt a disordered structure, and contains one NH₃ molecule

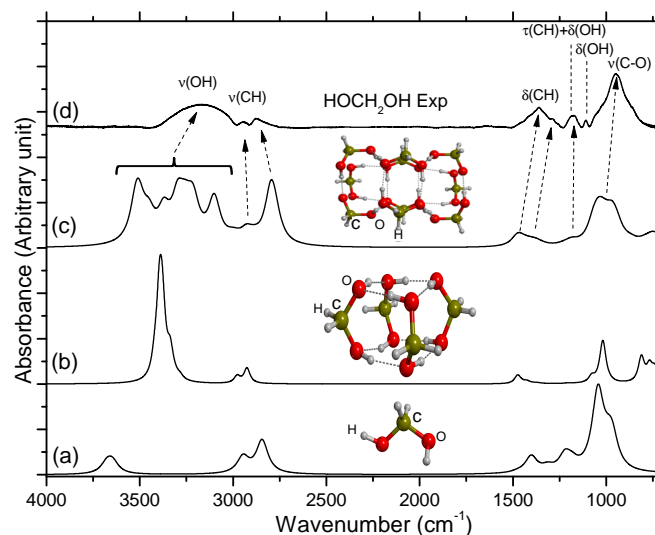


Fig. 5 B3LYP/6-31+G(d,p) IR spectra for HOCH₂OH, (HOCH₂OH)₄ and (HOCH₂OH)₁₀ (a, b and c, respectively), and experimental IR spectrum for a pure HOCH₂OH ice recorded at 200 K (d).

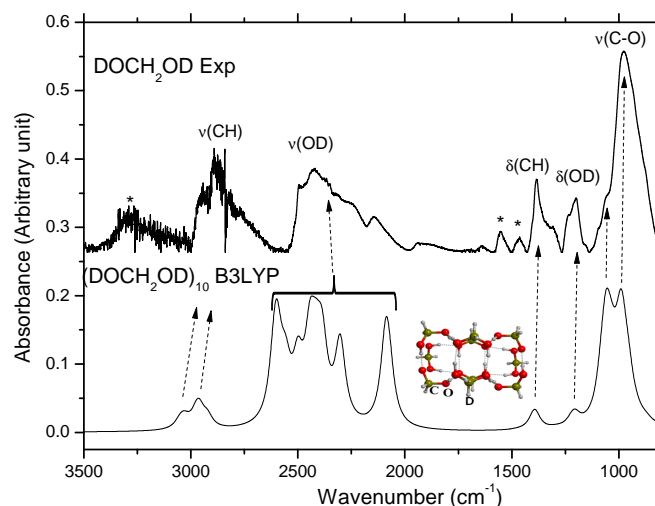


Fig. 6 B3LYP/6-31+G(d,p) IR spectrum for (DOCH₂OD)₁₀ and experimental IR spectrum for a pure DOCH₂OD ice recorded at 200 K. Stars refer to HOH and HOD contaminations.

and one H_2CO molecule, both interacting via a H-bond with the bulky water molecules. This structure is considered as the reactant state for the formation of HOCH_2OH . Obviously, other pre-reactant structures are certainly possible. However, this reactant state (manually built and subsequently optimized) maximizes the H-bond interactions between the water cluster and NH_3 and H_2CO , probably being one of the most stable pre-reactant complexes. The calculated PES is shown in Figure 7b, which also includes the structures of the localized stationary points. The first step involves a direct proton transfer from a H_2O molecule to the nearby NH_3 molecule, thus forming a $\text{NH}_4^+/\text{OH}^-$ ion pair (see TS0 and INT0 structures), which is stabilized by favorable H-bond interactions with the surrounding water molecules. The second step involves a nucleophilic attack of a water molecule towards H_2CO via a O-C coupling followed by a proton transfer of this H_2O molecule to the OH^- species (see TS1) to form HOCH_2O^- (see INT1), which is the deprotonated form of methyleneglycol. The very last step refers to the protonation of this anion to yield methyleneglycol (PROD), which takes place via proton transfer from the NH_4^+ adopting a proton relay mechanism (TS2). The calculated electronic energies for this mechanism indicate that the overall process is energetically favourable (PROD is indeed largely more stable than REACT) and that the last step is the most energetic one, while the two first steps exhibit energy barriers of moderate height.

Table 4 reports the relative free energy values computed at the different temperatures used in the experiments; *i.e.*, 10 K (initial temperature before the warming) and 100 and 180 K (temperatures at which methyleneglycol starts to form and is completely formed, respectively). Moreover, calculated rate constants using the classical Eyring equation and the corresponding half-life times (namely, the time necessary to consume the half amount of reactants) are also included. As one can see, a temperature increase does not significantly affect the stability of PROD with respect to REACT (*i.e.*, the free energy reaction is in all cases large and negative). The free energy barriers somewhat increase with temperature, the variations spanning an increment of 5–8 kJ mol^{-1} . The calculated rate constants at 10 K are for all steps very low. In contrast, the calculated rate constants at 100 K indicate that the first two steps are fast and that the third one is kinetically hampered, whereas at 180 K even the third step chemically proceeds in reasonable time scales (the $t_{1/2}$ is about 5 min). These data perfectly agree with the experimental observations. At 10 K no chemical activity in the ice is observed (the recorded bands belong to the initial ice mixture compounds) in fully agreement with the very low rate constants. At 100 K, bands related to the methyleneglycol are detected, and in particular those associated with the $\delta(\text{CH})$ and $\nu(\text{C-O})$ motions. At this temperature, although the last step does not proceed, the anionic HOCH_2O^- species is formed, which indeed contains

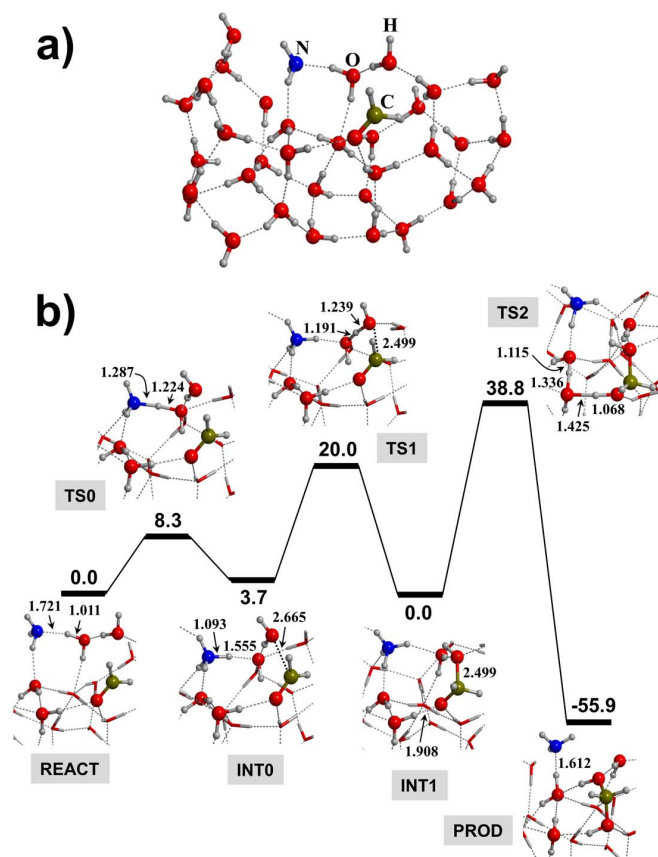


Fig. 7 (a) Cluster model employed for the simulation of the HOCH_2OH formation by reaction of H_2CO and H_2O in the presence of NH_3 . (b) B3LYP/6-31+G(d,p) potential energy profile (in kJ mol^{-1}). The chemical active sites of the localized stationary points are also included. Bond distances are in Å. REACT: reactant; TS: Transition State; INT: Intermediate; PROD: Product.

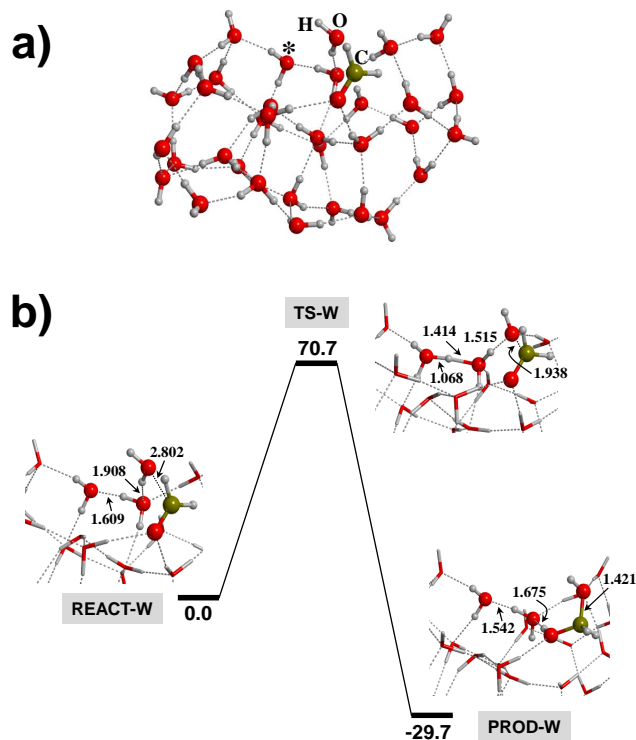


Fig. 8 (a) Cluster model employed for the simulation of the HOCH₂OH formation by reaction of H₂CO and H₂O in the absence of NH₃. The water molecule replacing NH₃ is labelled by an asterisk (see text). (b) B3LYP/6-31+G(d,p) potential energy profile (in kJ mol⁻¹). The chemical active sites of the localized stationary points are also included. Bond distances are in Å. REACT-W: reactant; TS-W: Transition State; PROD-W: Product.

both CH and CO moieties as detected by IR. Finally, at 180 K only methyleneglycol ice is present, thus indicating that the reaction is complete, in full agreement with the fast calculated reaction rates.

It is worth mentioning that, due to the size of the cluster model (107 atoms), the basis set employed is relatively small. Therefore, the calculated energy barriers, and in particular the rate constants and half-life times, are not meant to be rigorously accurate, and accordingly they must be considered as semi-quantitative values. Despite this, it is worth noting that the obtained computational results has allowed us to reproduce the trends of the experimental findings in a qualitative fashion.

It is possible, however, that the very same mechanism can take place in absence of NH₃; that is, that the water ice itself stabilizes an ion pair of the kind H₃O⁺/OH⁻ due to the hydrogen bond network (as occurs for the NH₄⁺/OH⁻ one in INT0). Thus, we performed quantum chemical calculations to have deeper insights into this point. The same water ice

Table 4 B3LYP/6-31+G(d,p) relative free energies (ΔG_{rel} , in kJ mol⁻¹) computed at 10, 100 and 180 K of the stationary points for the formation of HOCH₂OH (with respect to REACT). Calculated rate constants (in s⁻¹) and half-life times ($t_{1/2}$, in s) for the corresponding free energy barriers at these temperatures are also included.

	10 K			100 K			180 K		
	ΔG_{rel}	k	$t_{1/2}$	ΔG_{rel}	k	$t_{1/2}$	ΔG_{rel}	k	$t_{1/2}$
REACT	0.0	-	-	0.0	-	-	0.0	-	-
TS0	4.4	2.5×10^{-12}	2.8×10^{11}	6.2	1.1×10^9	6.1×10^{-10}	9.4	7.0×10^9	9.8×10^{-11}
INT0	2.2	-	-	6.3	-	-	11.1	-	-
TS1	18.6	1.8×10^{-86}	3.8×10^{85}	20.9	24.4	2.8×10^{-2}	25.4	1.5×10^5	4.4×10^{-6}
INT1	15.4	-	-	18.4	-	-	23.6	-	-
TS1	44.3	6.7×10^{-221}	1.0×10^{220}	47.0	5.7×10^{-13}	1.2×10^{12}	52.1	2.8×10^{-3}	241
PROD	-35.4	-	-	-33.6	-	-	-29.4	-	-
REACT-W	0.0	-	-	0.0	-	-	0.0	-	-
TS-W	69.8	-	-	71.6	8.0×10^{-26}	8.6×10^{24}	75.7	4.2×10^{-10}	1.7×10^9
REACT-W	-19.1	-	-	-18.3	-	-	-16.2	-	-

model was used, in which NH_3 was replaced by one H_2O water molecule (labeled by an asterisk in Fig. 8 a). Attempts to localize an intermediate species containing the $\text{H}_3\text{O}^+/\text{OH}^-$ ion pair by optimizing initial guess structures that incorporate this ion pair failed, since for all cases H_3O^+ spontaneously transfers its proton to OH^- . This also occurs even when H_3O^+ and OH^- are separated by one H_2O molecule. These results demonstrate that the formation of an OH^- species, mandatory to subsequently couple H_2CO , is only possible with the presence of NH_3 . In addition, we have also explored a reaction mechanism for the formation of methyleneglycol in absence of NH_3 , the calculated PES of which is shown in Fig. 8b. This mechanism is concerted and involves a transition structure in which one H_2O molecule couples H_2CO followed by a proton transfer from the same attacking water to an adjacent water molecule in a synchronic fashion (see TS-W). An IRC calculation in the forward direction of the transition frequency leads to the direct formation of methyleneglycol (PROD-W) through several structural rearrangements. Although the calculated reaction energy is largely exoenergetic, the electronic energy barrier was calculated to be about 70 kJ mol^{-1} . Table 4 shows the relative free energy values at different temperatures alongside the calculated rate constants and the corresponding half-life times. As one can see, the calculated free energy barriers remain high, which moreover increase with increasing temperature (e.g., 75 kJ mol^{-1} at 180 K). The calculated rate constants are very small, indicating that this reaction channel is very slow at these temperatures. These results are in good agreement with previous theoretical calculations performed by Woon,²⁵ who found that the formation of methyleneglycol via the reaction of $\text{H}_2\text{CO} + \text{H}_2\text{O}$ or via water-assisted mechanism present electronic energy barriers (including dielectric effects of the bulky water) of 165 and 99 kJ mol^{-1} , respectively. Finally, present calculations allow us to elucidate the actual role of NH_3 in this reaction. Hydration of formaldehyde to give methyleneglycol and related oligomers readily takes place at room temperature in solution with no need of catalyst.²⁶ However, *ab-initio* calculations carried out in this work and by Woon indicate that formation of HOCH_2OH via direct reaction of $\text{H}_2\text{CO} + \text{H}_2\text{O}$ or via water-assisted mechanism present electronic energy barriers which are exceedingly high to occur at the very cold temperatures of the deep-space.²⁵ In contrast, in the presence of NH_3 , our results give electronic energy barriers as large as of 40 kJ mol^{-1} . According to our results, the role of NH_3 is to activate water by accepting, in the first step, a proton from a bulky water to generate an OH^- species, which in turn participates to the O-C coupling given in the second step to form HOCH_2O^- . Water, besides being the reactant of this reaction, is also acting as a "solvent" since it allows the stabilization of the $\text{NH}_4^+/\text{OH}^-$ ion pair formed in the first step of the reaction. We have observed similar stabilizing effects on the formation of hydroxyacetonitrile (NCCH_2OH)

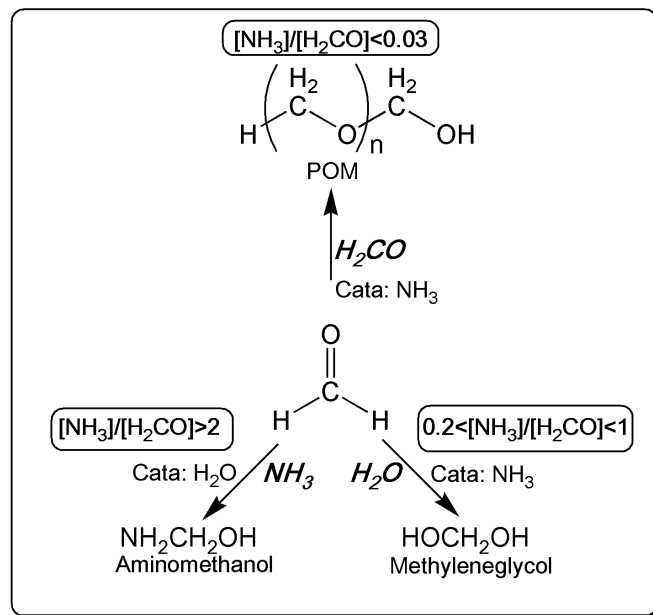


Fig. 9 Different products obtained after the warming of ice mixtures containing H_2O , NH_3 , H_2CO . The reactants are written in italic while the initial ice composition are shown in boxes. "Cata" refers to the catalyst needed for the selected reaction.

from reaction of HCN with H_2CO in water-dominated ices.⁷

4 Discussion

The chemical activity of a water-dominated $\text{H}_2\text{O}:\text{NH}_3:\text{H}_2\text{CO}$ ice mixture thermally activated results with a different branching ratio as a function of the $\text{NH}_3/\text{H}_2\text{CO}$ concentration ratio. According to the Schutte's results¹³ and the ones from this work the different domains for the existence of POM, $\text{NH}_2\text{CH}_2\text{OH}$ and HOCH_2OH can be defined. That is, with a $\text{NH}_3/\text{H}_2\text{CO} > 2$ ratios the mixture preferentially leads to the formation of $\text{NH}_2\text{CH}_2\text{OH}$, with a $0.2 < \text{NH}_3/\text{H}_2\text{CO} < 1$ ratios to the formation of HOCH_2OH , whereas $\text{HO}(\text{CH}_2\text{O})_n\text{H}$ ($n > 1$) POM oligomers are only observed as a major product for $\text{NH}_3/\text{H}_2\text{CO} < 0.03$ ratios. Fig. 9 summarizes these different branching ratios as a function of the initial ice composition. Since H_2O , NH_3 , and H_2CO are known constituents of interstellar or pre-cometary ices their formation is likely in warm environments such as star forming regions or in cometary environments. In addition, the mass spectrum of methyleneglycol, recorded for the first time in this work, can represent a benchmark in the interpretation of the mass spectrum results to be provided by the ROSINA on-board instrument of the Rosetta mission.

An underlying conclusion of the present work is the difference in branching ratios of the chemical complexity

derived from the warming of ices that only contain three basic molecules like H_2O , NH_3 and H_2CO . Such a complexity is due to the different role of H_2O and NH_3 in the reactions, which in turn is highly sensitive to the initial ice composition. Indeed, water molecules act essentially as catalysts in the formation of $\text{NH}_2\text{CH}_2\text{OH}$, while in the formation of HOCH_2OH , it has the dual role of reactant and "solvent". At its turn, NH_3 plays the role of reactant in the $\text{NH}_2\text{CH}_2\text{OH}$ formation while it is a catalyst in the formation of HOCH_2OH and POM. Remarkably, the presence of NH_3 in the initial ice composition is crucial as the warming of a water-dominated ice only containing H_2CO (i.e., in the absence of NH_3) does not show any chemical activity. The present work, alongside previous ones,^{7,13,27–30} strengthens the thesis that thermally activated reactions are chemical processes that actively participate in the increase of the molecular complexity in the universe. This work, moreover, provides robust evidences that water is also a crucial component for this molecular complexity evolution due to its direct participation in the thermally-promoted reactivity of ices of astrophysical interest. Indeed, whereas astrophysical water ices are often considered as non-thermally reactive because of the low temperature and the supposed lack of molecular diffusion in the bulk, we demonstrate that water allows the development of a highly complex chemistry through various reactive channels.¹² Finally, it is worth to remark the different chemical activity when ices are either thermally or UV photon activated. Besides the different intrinsic efficiencies when the reactions are activated by one or the other energy source, it is well-known that short wavelength (i.e. Lyman-alpha) photons cannot efficiently penetrate water ice films of deep thicknesses,³¹ limiting the UV-activated reactions to occur in the first hundreds of monolayers. In contrast thermal activated reactions can take place both on and in the ices as the whole bulk is affected by the ice warming, thus resulting with severe differences in the reaction yields. However, the formation of complex organic molecules from interstellar/cometary ice-based reactions requires the both activation energy sources in a cooperative fashion; i.e., UV photons induce the formation of activated molecules/radicals on the ice surfaces, which subsequently diffuse inside the ice bulk and finally react in the entire bulky ice during warming.³²

5 Conclusion

In this contribution, we present the thermal-induced reactivity of water-dominated cometary ice analogues that contain amounts of NH_3 and H_2CO . By means of infrared measurements and mass spectrometry experiments (including isotopic labelling), complemented by quantum chemical calculations at the B3LYP/6-31+G(d,p) level of theory, the hitherto unknown dominant reaction product which results from the

warming of these ices when the $\text{NH}_3/\text{H}_2\text{CO}$ concentration ratio spans the 0.2 - 1 range (the so-called "Y" species in the Schutte's study¹³) has been identified to be methyleneglycol (HOCH_2OH). This is indicative that warming ices with these compositions activates the reaction between H_2CO and H_2O . The mass spectrum of methyleneglycol has been recorded for the first time, which in turn represents a benchmark in the interpretation of the mass spectrum results to be provided by the ROSINA on-board instrument of the Rosetta mission. The detection of the m/z 46, 47, and 48 would validate the detection of HOCH_2OH .

B3LYP calculations based on a cluster approach to model the ice analogues have also been used to explore the potential energy surface associated with the formation of methyleneglycol. Results indicate that the process adopts a stepwise mechanism consisting of three steps: i) proton transfer from a water molecule to NH_3 to form a $\text{NH}_4^+/\text{OH}^-$ ion pair; ii) reaction of water with H_2CO in the presence of the OH^- anion to form the HOCH_2O^- species; and iii) proton transfer from NH_4^+ to HOCH_2O^- assisted by water molecules to give the final HOCH_2OH product. The obtained energetic data indicate that the overall process is exoenergetic (reaction energy of about -55 kJ mol^{-1}) and that the energy barriers are about 8, 20 and 39 kJ mol^{-1} for the first, second and third step, respectively. The free energy barriers have also been calculated at 10, 100 and 180 K and the related rate constants and half-life times derived. These estimated values indicate that at 10 K the reaction is kinetically hampered due to the very low rate constants, whereas at 100 K and specially at 180 K the reaction can proceed, in full agreement with the experimental findings, with a half-life time at 180 K of about 5 minutes.

The combination of experimental and theoretical results have enabled us to determine the catalytic role played by NH_3 , which mainly consists of allowing the formation of the $\text{NH}_4^+/\text{OH}^-$ ion pair, the presence of which is essential for the occurrence of the reaction. Moreover, it is found that the presence of water is crucial in this reaction because, besides being one of the reactants, it also acts as a "solvent" that stabilizes the $\text{NH}_4^+/\text{OH}^-$ ion pair. This work, thus, is a new proof that water is an essential component for the development of the complex chemistry in thermally activated reactions occurring in and on ices of astrophysical interest.

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