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Supplementary Material

For the article: **Synthesis of Urea in Cometary Model Ices and Implications for Comet 67P/Churyumov-Gerasimenko**

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Materials and Methods - Experimental

The ices were prepared by depositing a mixture of ammonia (NH_3) and carbon monoxide (CO) with initial partial pressures of 160 ± 20 Torr and 100 ± 20 Torr, respectively, onto a polished silver substrate at a temperature of 5.5 ± 0.1 K using a glass capillary array. The ice thickness was monitored *in situ* using He-Ne laser interferometry. The number of observed fringes is related to the ice thickness (d) according to equation (S1), where N_f depicts the number of observed fringes, λ is the wavelength of the He-Ne laser (632,8 nm), n is the refractive index of the ice and Θ is the angle of incidence (4°).

$$\text{(S1)} \qquad d = \frac{N_f \lambda}{2\sqrt{n^2 - \sin^2\theta}}$$

The refractive index was determined to be 1.3 ± 0.1 using the respective refractive indices of ammonia and carbon monoxide of 1.35[1, 2] and 1.25[3]. The mixture was deposited at a pressure of $(3.5 \pm 0.3)\times10^{-8}$ Torr for approximately 4 minutes yielding two fringes and thus a thickness of 500 ± 50 nm. The composition of the deposited ice was measured two different ways. Using known column densities of the infrared absorption features of ammonia and carbon monoxide (the CO υ_1 band at 2139 cm^{-1} with 1.1×10^{-17} cm/mol [4] and the NH_3 υ_2 band at 1092 cm^{-1} with a value of 1.7×10^{-17} cm/mol [5], the ratio of ammonia to carbon monoxide was estimated to be 4 ± 1. Additionally we compared the integrated signal of ammonia and carbon monoxide observed in the residual gas analyzer (RGA) during sublimation of the ice to the RGA signals of different gas-phase mixtures of ammonia and carbon monoxide. This method also yielded a ratio of 4 ± 1. After deposition the ices were exposed to 5 keV fast electrons with a total current of 15 nA. The total irradiation dose (D) per molecule can be estimated using equation (S2):

$$D = \frac{I\ t\ m}{e\ N_A\ \rho\ A\ l}(E_{init} - f_{trans}E_{trans} - f_{bs}E_{bs}), \tag{S2}$$

where the values f_{trans}, f_{bs}, E_{bs}, E_{trans} and l denote the fraction of electrons transmitted through the ice, the fraction of electrons which are backscattered, the average kinetic energy of the backscattered electrons, the average kinetic energy of the transmitted electrons, and the average penetration depth of the electrons. These values were determined exploiting the Monte-Carlo simulation program CASINO [6] averaging over 20,000 trajectories. Additionally, I, t, m, e, N_A, ρ, A and E_{init} are the irradiation current, irradiation time, molecular mass of the molecules, the electron charge, Avogadro's constant, the density of the ice, the irradiated area of the ice, and the initial kinetic energy of the electrons, respectively. The values are summarized in Table S1. The absorbed dose in this experiments was 2.0 ± 0.1 eV per molecule on average.

Before, during and after irradiation we recorded FTIR spectra of the ice (FTIR, Nicolet6700) from 500 to 6000 cm^{-1}. After the irradiation period, the ices were left at 5.5 K for 1 h. Then the substrate was heated with a constant rate of 0.5 K/min (TPD). During this phase we recorded the subliming molecules using a reflectron time-of-flight spectrometer coupled with a soft VUV laser ionization source. The laser beam passed the substrate surface in front of the entrance aperture of the ReTOF surface at a distance of 2.0 ± 0.2 mm. The beam diameter above the substrate was 1.0 ± 0.1 mm and the repetition rate was set to 30 Hz. Three different experiments were made. The irradiated ices were probed at 10.49 eV and 9.0 eV. Additionally we probed the unirradiated ice using 10.49 eV. The 10.49 eV laser light was produced by tripling the fundamental of an Nd:YAG (Spectra Physics, PRO-250-30) laser twice using xenon (Specialty Gases, 99.999 %) as the tripling medium in the second stage. The 9.0 eV radiation was produced using resonant sum-frequency mixing of two laser beams in xenon gas. The first beam was generated using the frequency doubled output of a dye laser (Syrah, Cobra-Stretch) pumped by the third harmonic of an Nd:YAG laser thus producing laser pulses with a wavelength of 222.56 nm. The second laser beam was generated using the direct output of a dye laser (Syrah, Precision Scan) pumped with the second harmonic of an Nd:YAG laser producing light at 579 nm. Both laser beams were focused into a pulsed valve which generates a high concentration of xenon gas in the focal point of the lasers. A lithium fluoride (LiF) lens mounted off center in the beam path of the generated and fundamental light separated lights of different wavelengths spatially. A pin hole behind this lens was then used to block the fundamental laser light from entering the interaction region. Both, the 10.49 eV and the 9.0 eV laser light had a flux of $(2 \pm 1) \times 10^{14}$ photons per pulse. A more detailed description of the light generation principles is given in references [7-12]. Ionized molecules were then accelerated into the ReTOF with an extraction electrode kept at a potential of -190V and then detected using multichannel plates. Flight times were recorded using a multichannel scaler (FAST ComTec, P7888-1 E) and time to mass conversion was performed using a set of flight times of previously measured, known masses.

The experiments described here are aimed to simulate the interaction of interstellar model ices with galactic cosmic rays (GCRs). GCRs consist mainly of helium nuclei and protons with kinetic energies in the MeV to PeV range. It is important to highlight that the GCR irradiation has to be simulated in the laboratory because no experimental device is accessible that can generate this radiation in the all required fluxes and energies. However, the physical effects of GCRs interacting with ices are well understood: GCR lose energy predominantly via ionization of molecules in the ice thus generating secondary electrons. These can further induce ionization and in this way generating electron cascades. [13, 14] The kinetic energy distribution of the electrons generated by GCRs are typically in ranges of a few eV up to the 10 keV range. Therefore, rather than exposing the samples to GCR particles, we can simulate the GCR processing by irradiating the ices with kinetic electrons. The linear energy transfer (LET) of these electrons is comparable to the LETs of protons penetrating the ices with energies in the range of 10 to 20 MeV. The energy transfer from the electrons to the ice mixture was calculated as stated above to be 2.0 ± 0.1 eV per molecule. Each second in the laboratory simulates the exposure of about 3×10^9 s in space. Therefore, the complete experiment mimics the exposure of the ices of about 2×10^6 years, which is a typical life time of a cold molecular cloud[15].

Materials and Methods - Theoretical

The optimized geometries of formamide, urea as well as cis- and trans-formohydrazine together with their cations were calculated using hybrid density functional B3LYP level of theory [16-19] with the cc-pVTZ basis set. The energies were refined using CCSD(T)/cc-pVTZ with B3LYP/cc-pVTZ zero-point energy corrections.[20-23] GAUSSIAN09 program [24] was employed in the electronic structure calculations. The adiabatic ionization energies were then obtained by taking the energy difference between the optimized ionic and the corresponding neutral species computed by CCSD(T)/cc-pVTZ with B3LYP/cc-pVTZ zero-point energy correction. Previous works at this level compared with experimentally derived ionization energies suggests that the ionization energies derived from the CCSD(T)/cc-pVTZ with B3LYP/cc-pVTZ zero-point energy correction are accurate within ± 0.1 eV (62).

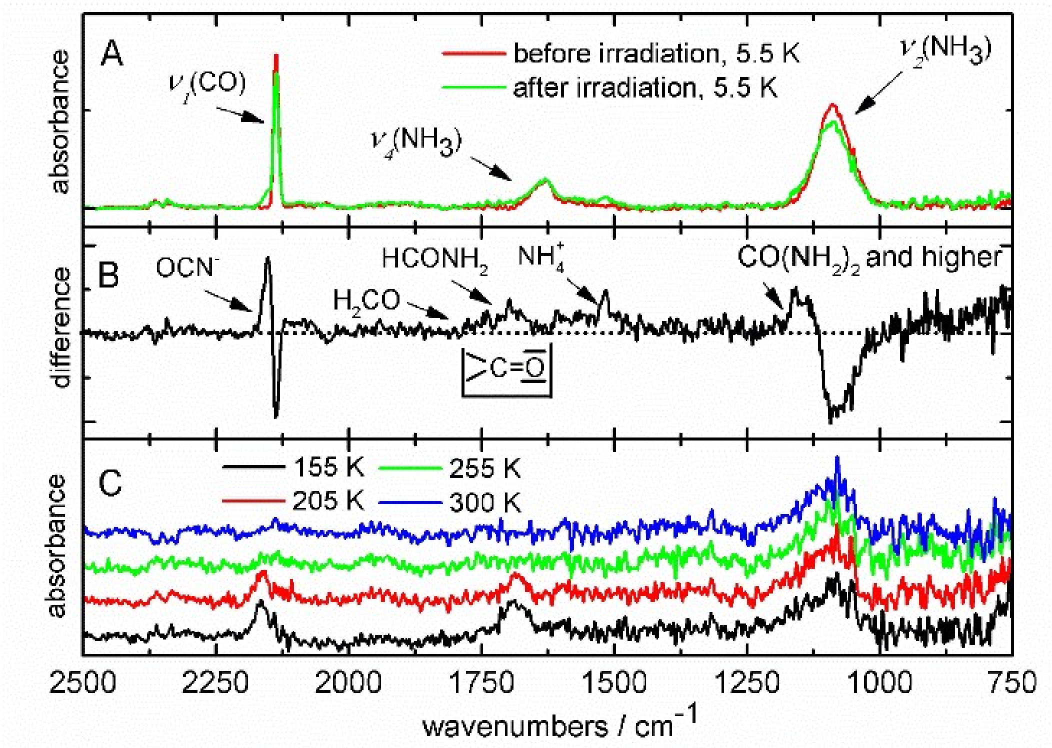

Figure S1. IR spectra of the ices before and after irradiation (A) at a temperature of 5.5 K, along with their difference spectrum (B). Panel C depicts selected IR spectra of the irradiated sample during the warmup phase.

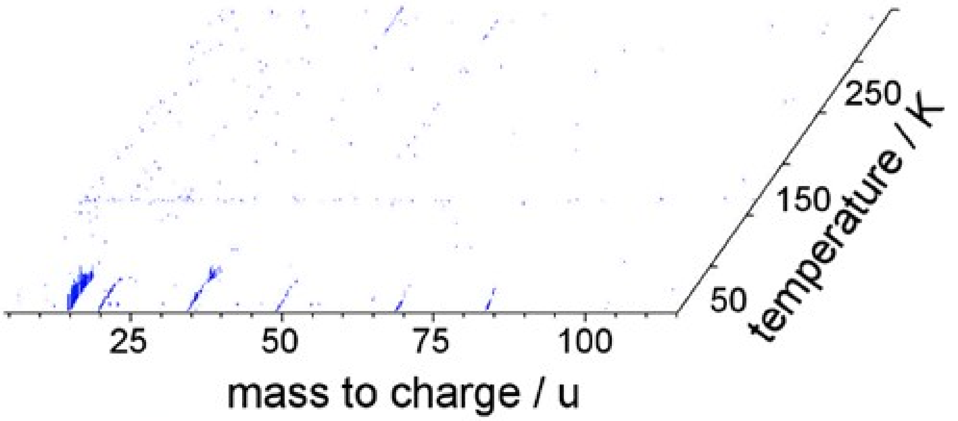

Figure S2. Temperature dependent and mass-to-charge resolved TPD profiles of molecules desorbing from irradiated ices recorded using an ionization energy of 9.0 eV.

Table S1. Values used to determine the irradiation dose per molecule

initial kinetic energy of the electrons, E_{init}	5 keV
irradiation current, I	15 ± 2 nA
total number of electrons	$(3.4 \pm 0.3)\times10^{14}$
average kinetic energy of backscattered electrons, $E_{bs}{}^{*}$	1.1 ± 0.4 keV
fraction of backscattered electrons, $f_{bs}{}^{*}$	0.3 ± 0.1
average kinetic energy of transmitted electrons, $E_{trans}{}^{*}$,	0.03 ± 0.01 keV
fraction of transmitted electrons, $f_{trans}{}^{*}$	0.03 ± 0.01
average penetration depth, l^{*}	270 ± 80 nm
density of the ice, ρ	0.95 ± 0.1 g cm^{-3}

Table S2. Infrared absorption features identified in the irradiated ices. Absorptions marked with asterisks are seen in the pristine ices. Ranges are given for wide observed bands.

absorption (cm^{-1})	literature value	reference	species[c]	feature
1087*	1092	25	NH_3	ν_2
1633*	1626	25	NH_3	ν_4
2135*	2139	4	CO	ν_1
1050 to 1150		26	NH_3, urea and higher	NNH bend and NH rocks
1150	1153	27	$CO(NH_2)_2$	ν_5
1660 to 1750		28	X-C=O	stretches
1510	1510	28-31	H_2CO	ν_3
1505	1499	28, 32	NH_4^+	ν_4
1695	1697	28, 33	$HCONH_2$	ν_2
1740	1740	28-31	H_2CO	ν_2
2150	2157	28, 29, 34	OCN^-	ν_3

Table S3. Computed energies obtained by CCSD(T)/cc-pVTZ with B3LYP/cc-pVTZ zero-point correction on B3LYP/cc-pVTZ optimized geometries of formamide, urea, cis-, trans-formylhydrazine and their cations.

	B3LYP/ cc-pVTZ[a]	E_{zpc} [b]	CCSD(T)/ cc-pVTZ	IP(eV)[c]
formamide	-169.920272	0.045253	-169.641606	0.0
formamide^{+1}	-169.552021	0.045165	-169.274443	9.99
urea	-225.300314	0.063620	-224.936903	0.0
urea^{+1}	-224.952719	0.061972	-224.581835	9.62
trans-formylhydrazine	-225.239234	0.062963	-224.873421	0.0
trans-formylhydrazine^{+1}	-224.923914	0.061296	-224.556264	8.58
cis-formylhydrazine	-225.234000	0.062569	-224.867840	0.0
cis-formylhydrazine^{+1}	-224.930734	0.062046	-224.565091	8.22

[a] B3LYP/cc-pVTZ energy with zero-point energy correction in hartree.

[b] zero-point energy by B3LYP/cc-pVTZ in hartree.

[c] relative energy by CCSD(T)/cc-pVTZ with B3LYP/cc-pVTZ zero-point energy correction in eV.

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