

Supporting Information

Formation of Carbonisocyanatidic Amide in Interstellar Ice Analogs as a Candidate Precursor to Prebiotic Pyrimidines

Xilin Bai,¹ Jinghui Lu,⁴ Baoyu Song,⁴ Jiuzhong Yang,⁴ Yang Pan,⁴ Zhibiao Li,^{6,7} Cheng Zhu,^{3,6,7} Zhubin Hu,^{1*} Haitao Sun,¹ Zhenrong Sun,¹ Ralf I. Kaiser,^{5*} Tao Yang^{1,2,3*}

¹ *State Key Laboratory of Precision Spectroscopy, East China Normal University, Shanghai 200062, China*

² *Collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan, Shanxi 030006, China*

³ *State Key Laboratory of Radio Astronomy and Technology, Xinjiang Astronomical Observatory, Chinese Academy of Sciences, Urumqi, Xinjiang 830011, China*

⁴ *National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, China*

⁵ *Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI 96822, USA*

⁶ *Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China*

⁷ *University of Chinese Academy of Sciences, Beijing 100049, China*

*Corresponding Authors:

Zhubin Hu, zbhu@lps.ecnu.edu.cn

Ralf I. Kaiser, ralfk@hawaii.edu

Tao Yang, tyang@lps.ecnu.edu.cn

Methods

Experimental. The surface reaction experiments were performed at the Shanghai-Hawaii-Hefei Advanced Research Center (SHHARC), utilizing tunable vacuum ultraviolet (VUV) synchrotron radiation at the Combustion and Flame Beamline (BL03U) of the National Synchrotron Radiation Laboratory (NSRL).^{1, 2, 3, 4} The experimental setup features an ultra-high vacuum (UHV) chamber constructed from hydrogen-free stainless steel, with a base pressure of 10^{-11} Torr. The ice analogs were deposited onto a mirror-polished silver substrate ($13.0 \times 15.0 \text{ mm}^2$), which was thermally anchored to an oxygen-free high-conductivity (OFHC) copper coldfinger maintained at 4.8 ± 0.1 K. Isocyanic acid (HNCO) was synthesized in the gas phase via thermal decomposition of commercially available cyanuric acid (HNCO)₃ (Sigma-Aldrich, 98%) at 600 °C under primary vacuum.⁵ Minor byproducts such as CO₂ and CO were removed by fractional distillation prior to deposition. The purified HNCO was introduced through a leak valve and evenly deposited onto the cryogenic substrate using a glass capillary array (10 mm diameter) at a controlled deposition pressure of $(2 \pm 0.1) \times 10^{-8}$ Torr. The thickness of the amorphous ices ($706 \pm 40 \text{ nm}$) was determined by He–Ne laser ($\lambda = 632.8 \text{ nm}$) interferometry (Thorlabs, HNL008L), based on fringe pattern analysis and a refractive index of 1.344 ± 0.005 for the HNCO ices (Figure S4).⁶

After deposition, mid-infrared (4000 to 600 cm^{-1}) spectra of the ices were recorded utilizing a Bruker Vertex 70 Fourier transform infrared (FTIR) spectrometer, equipped with a Mid-band MCT detector with a ZnSe window, at 1 cm^{-1} spectral resolution. The FTIR spectrum of the pristine ice is shown in Figure S1, and the corresponding band positions and assignments are summarized in Table S1. The silver substrate was then repositioned and subjected to isothermal irradiation with 5 keV electrons (SPECS GmbH, EQ 22/35 electron source) (Table S5). During the irradiation, *in situ* mid-infrared spectra of the ices were recorded every 2 minutes without interrupting the electron beam, and each spectrum was averaged over 120 co-added scans. Blank and irradiated experiments were performed; pristine and irradiated spectra are compared in Figure S1. Monte Carlo simulations with CASINO 2.42 software⁷ estimated the electron penetration depth to be $434 \pm 40 \text{ nm}$ on average, while the maximum electron range remained below approximately 750 nm (Figure S5). Because the transmitted electron fraction was negligible in the simulation, substrate effects are expected to be minimal. The average irradiation dose was $9.41 \pm 1.41 \text{ eV}$ per HNCO molecule (Table S5). Here, the irradiation dose represents the average energy deposited per HNCO molecule within the electron penetration region during the irradiation period. It was calculated

from the effective energy deposited by the incident electrons and the total number of HNCO molecules within the electron penetration depth. Specifically, the effective energy deposition was obtained from CASINO simulations using the experimental ice thickness, density, electron energy, and incident angle, while the number of HNCO molecules in the irradiated volume was estimated from the ice density, irradiation area (approximately 0.9 cm²), penetration depth, and molar mass. The total number of incident electrons was determined from the measured beam current and irradiation time. Thus, 9.41 ± 1.41 eV per HNCO molecule is an average cumulative energy-deposition value over the irradiated ice, rather than the energy delivered to an individual HNCO molecule in a single excitation event.

The blank and irradiated ices were also subjected to temperature-programmed desorption (TPD), ramping from 5 K to 330 K at a constant rate of 1 K min⁻¹, regulated by a precision temperature controller (Lakeshore, Model 336; ± 0.1 K). Desorbing species were monitored in real time via synchrotron vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry (SVUV-PI-ReToF-MS).^{1, 2, 3, 8} Ions generated at defined photon energies were extracted using a pulsed voltage (-140 V, 2.5 μ s) and subsequently detected by a 40 mm dual multichannel plate detector (Jordan TOF Products, C-726). Signals were processed by preamplification (Ortec 9306, AMETEK Inc.), discrimination and amplification (Advanced Research Instruments Corp., F-100TD), and data acquisition (FAST ComTec, MCS8) with a 3.2 ns time resolution. Mass spectra were recorded with a 10 kHz repetition rate over 60 s intervals synchronized with the TPD ramp. To construct photoionization efficiency (PIE) curves for individual desorbing species, the VUV photon energy was scanned over two ranges: 9.50–11.00 eV in 0.10 eV steps and 11.40–12.60 eV in 0.05 eV steps during selected TPD windows. Ion intensities were normalized to the 11.00 eV spectrum for the lower-energy scan and to the 12.20 eV spectrum for the higher-energy scan, and corrected for the corresponding photon flux. For complementary identification, electron ionization quadrupole mass spectrometry (EI-QMS) was also employed in residual gas analysis mode throughout the desorption (Figure S6). No distinct desorption features assignable to molecular oxygen or carbon dioxide were resolved under the present EI-QMS conditions; carbon dioxide was instead identified independently by FTIR.

Computational. To identify the global minimum and low-lying C₂H₂N₂O₂ isomers, a comprehensive conformational search was conducted using the Molclus 1.12 program.⁹ Geometry

optimizations and vibrational frequency analyses for all structures were executed using Head-Gordon's long-range corrected hybrid density functional ω B97XD¹⁰ in conjunction with Dunning's augmented correlation-consistent polarized valence triple-zeta basis set, aug-cc-pVTZ.¹¹ The nature of the stationary points was confirmed by frequency calculations: local minima exhibited no imaginary frequency, while transition states were characterized by exactly one imaginary frequency. Zero-point vibrational energy (ZPVE) corrections were scaled by a factor of 0.9740.¹² To obtain more accurate electronic energies (Table S6), single-point calculations were carried out using the coupled cluster method explicitly including single, double, and perturbative triple excitations method CCSD(T)¹³ with the aug-cc-pVTZ and aug-cc-pVQZ basis sets, followed by extrapolation to the complete basis set (CBS) limit using the built-in routine in the ORCA 6.0.1 program.¹⁴ Adiabatic ionization energies (AIEs) and relative energies along the dissociation potential energy surfaces (PES) were determined using CCSD(T)/CBS electronic energies inclusive of ZPVE corrections. Furthermore, the vibrationally resolved photoionization spectrum for the global minimum was simulated within the Franck–Condon (FC) approximation at the ω B97XD/aug-cc-pVTZ level (Table S7). Crucially, the electronic origin (the 0–0 transition) of the simulated spectrum was refined using the adiabatic ionization energy obtained at the CCSD(T)/CBS level to provide a more reliable energy scale. All density functional theory (DFT) calculations were performed using the Gaussian 16 package (Revision C.02).¹⁵

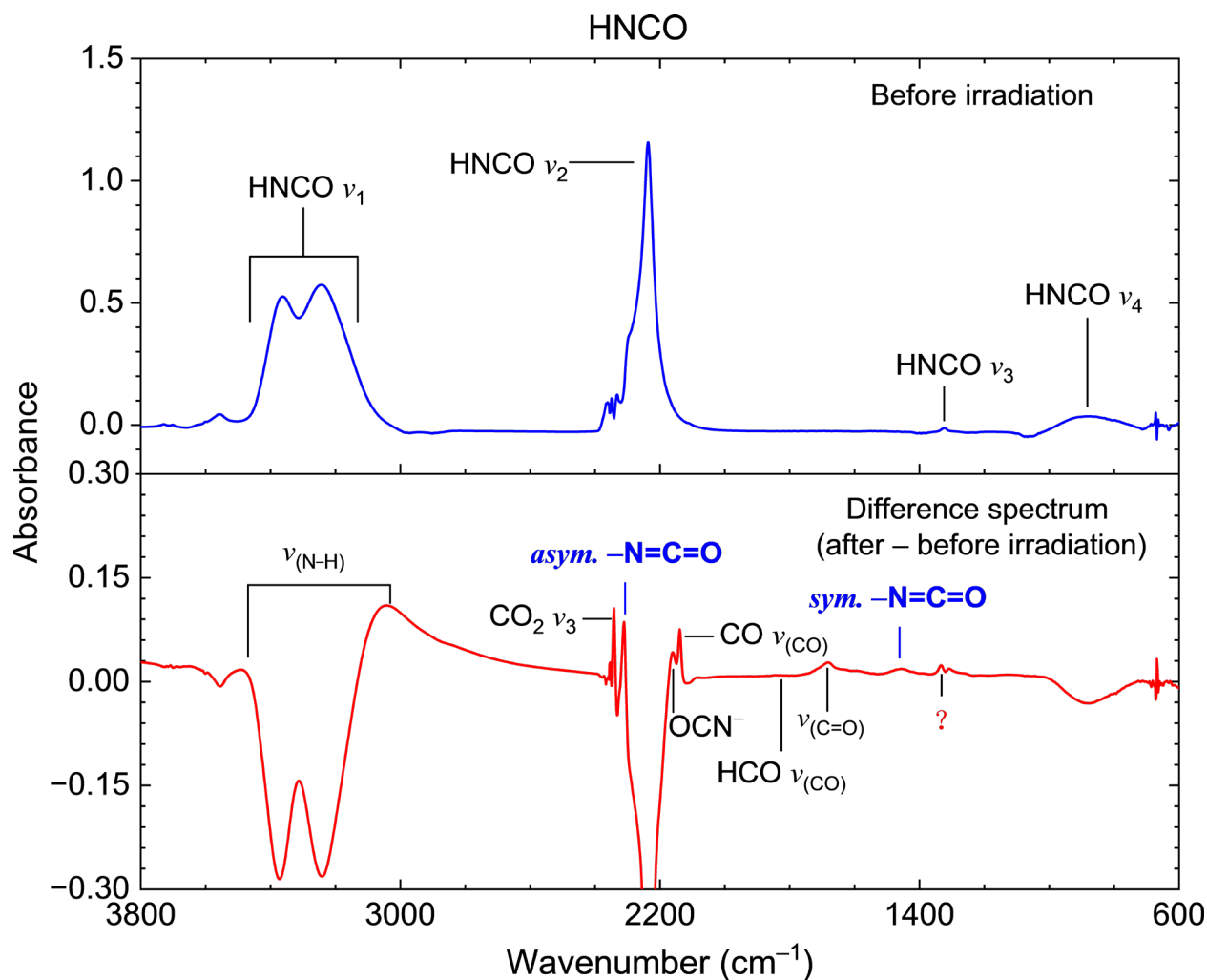


Figure S1. FTIR spectra of HNCO ice at 5 K before irradiation (upper panel) and the after-minus-before (after – before) difference spectrum following electron irradiation (lower panel). Positive and negative features indicate product formation and HNCO depletion or line-shape changes, respectively.

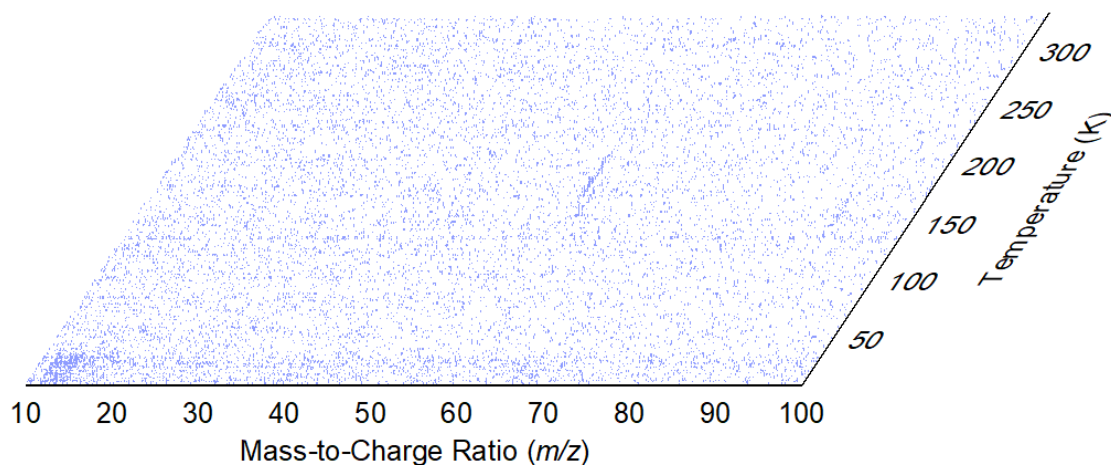


Figure S2. Synchrotron vacuum ultraviolet photoionization reflectron time-of-flight mass spectrometry (SVUV-PI-ReToF-MS) data were recorded during the temperature-programmed desorption (TPD) phase of non-irradiated HNCO ices at a photon energy of 11.00 eV.

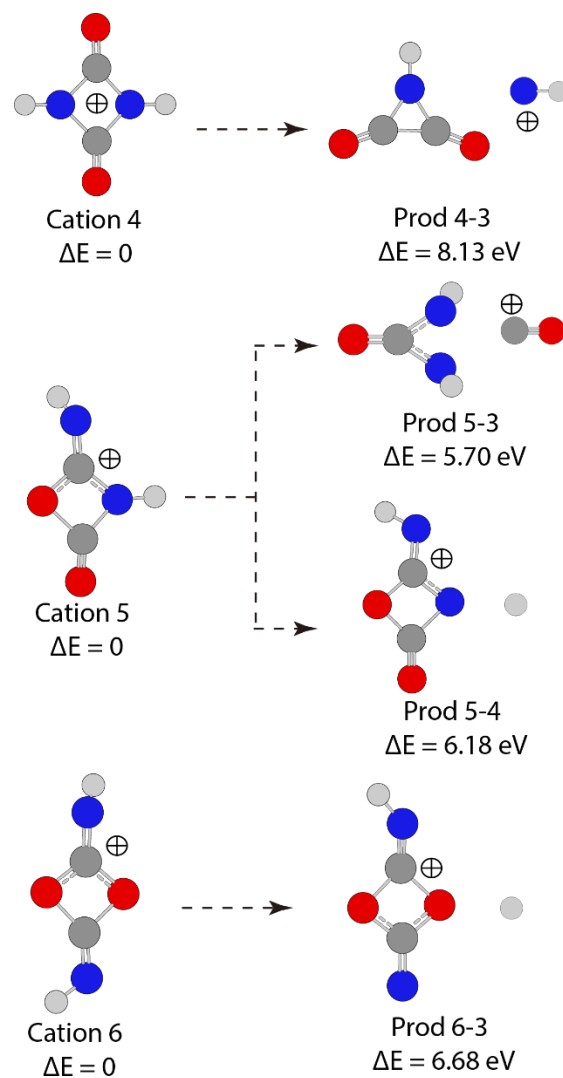


Figure S3. Calculated potential dissociation channels and corresponding dissociation energies (ΔE) for the parent cations of isomers 4–6. All energies are calculated in eV relative to the respective parent cation (set to $\Delta E = 0$).

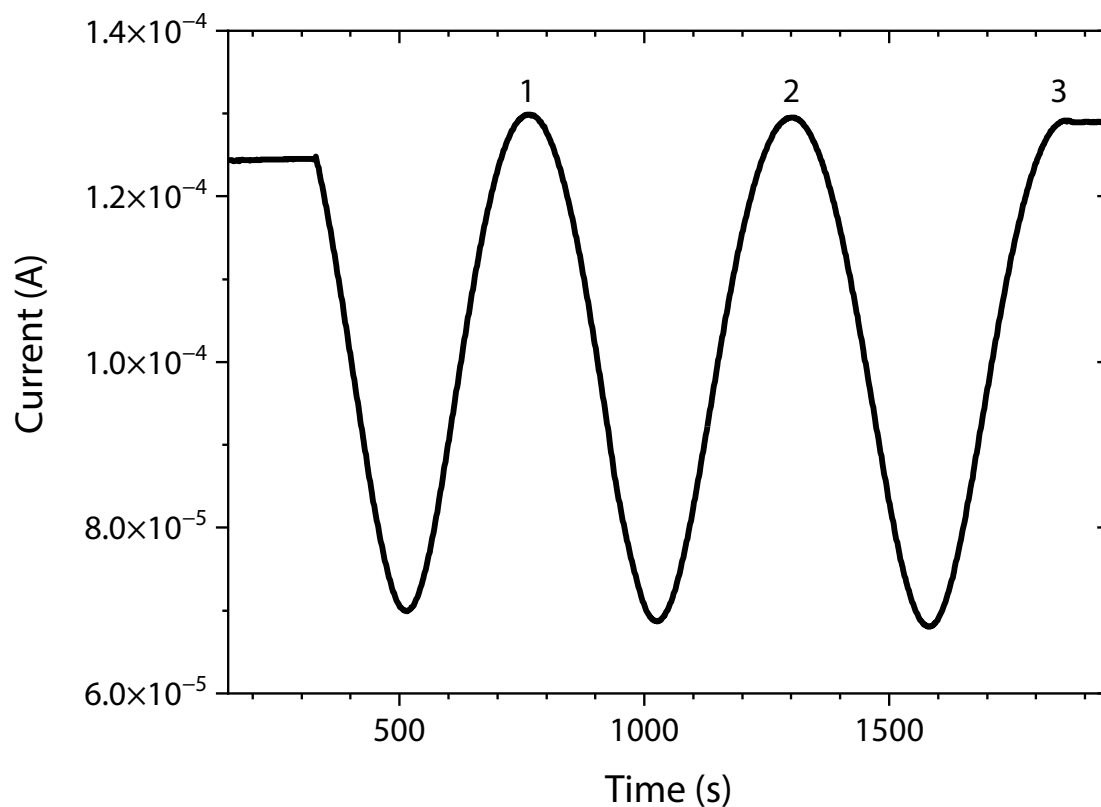


Figure S4. Interference pattern observed during the deposition of HNCO ices. The pattern was obtained by a 632.8 nm He–Ne laser at an incidence angle of 0° with respect to the surface normal. Integer numbers of fringes are indicated above signal maxima, and at the end of the deposition process, three fringes had accumulated.

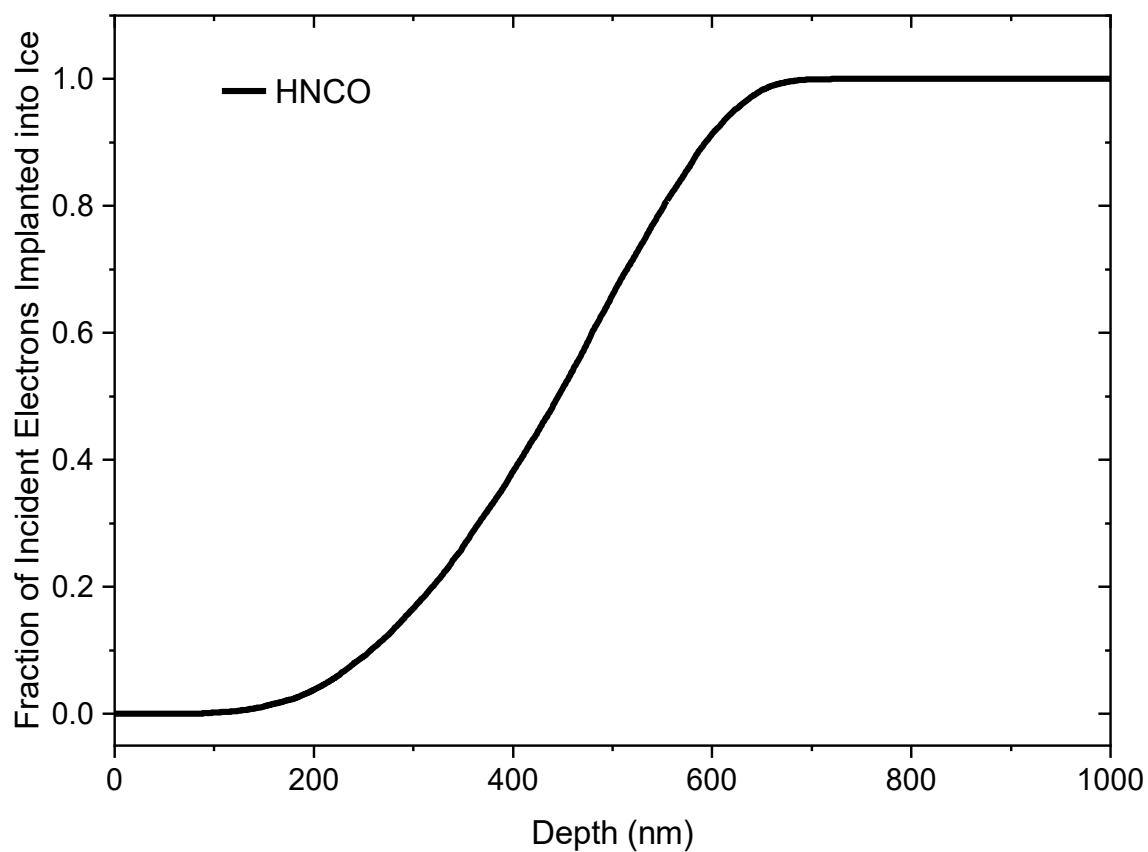


Figure S5. CASINO simulation of 5 keV electron penetration into HNCO ice. The maximum penetration depth of 5 keV electrons in the HNCO ice is less than 750 nm.

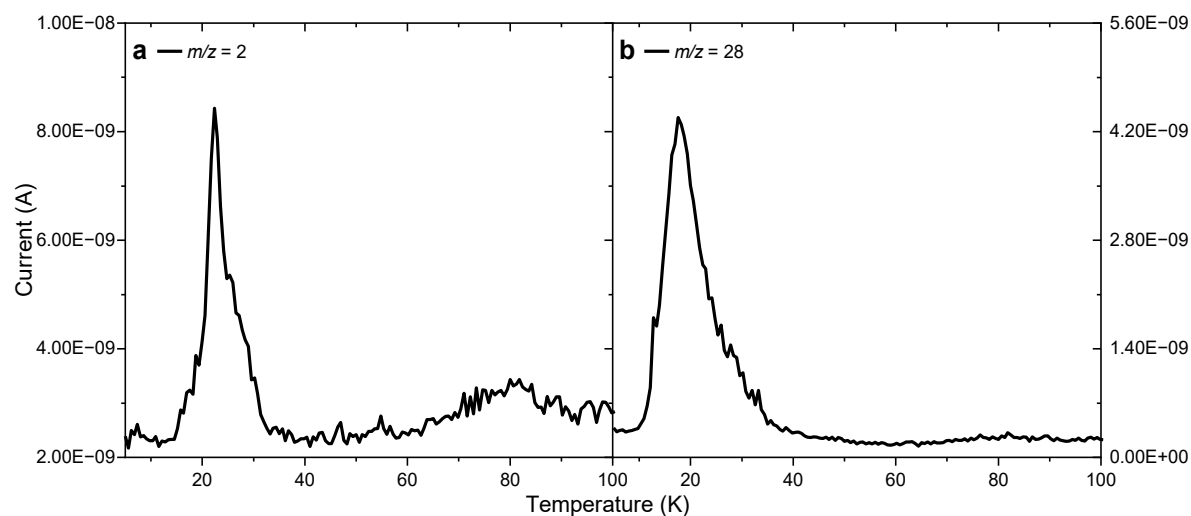


Figure S6. EI-QMS ion-current traces at (a) $m/z = 2$ and (b) $m/z = 28$ during TPD of irradiated HNCO ice. The observed features are tentatively consistent with H_2 and CO , respectively; the $m/z = 28$ assignment is additionally supported by the FTIR band of CO , although residual-gas and electron-ionization fragmentation contributions cannot be excluded.

Table S1. Infrared bands of pristine and electron-irradiated HNCO ice at 5 K. Assignments of the weak irradiation-induced bands are tentative; the 1333 cm^{-1} feature remains unassigned because of its overlap with HNCO ν_3 . Wavenumbers are given in cm^{-1} .

Peak Position	Assignment	Interpretation	Reference
Pristine ice (before irradiation, 5 K)			
3496–2971	HNCO $\nu_1, \nu_{(\text{N-H})}$	Broad hydrogen-bonded N–H stretching envelope of solid HNCO	16
2237	HNCO ν_2	Asymmetric stretching of the NCO skeleton	16
1323	HNCO ν_3	Symmetric stretching of the NCO skeleton	16
886	HNCO ν_4	HNC bending vibration	16
Processed ice (after irradiation, 5 K)			
3470–3030	Decrease of the HNCO ν_1 band and formation of a new N–H bonding	Assigned as a newly formed N–H-containing product	16
2341	CO ₂ ν_3	Irradiation product	17
2310	Asymmetric stretching of –N=C=O	Tentative functional-group assignment of an isocyanate-bearing irradiation product	18
2160	OCN [–]	Cyanate-ion formation	19
2139	CO $\nu_{(\text{CO})}$	Fundamental stretching vibration of CO	20
1844	$\nu_{(\text{CO})}$ of the formyl radical, HCO	HCO has been identified near 1842–1860 cm^{-1} in irradiated molecular ices	21
1682	$\nu_{(\text{C=O})}$ of carbonyl bearing irradiation product(s)	Compatible with an amide-I-type carbonyl vibration, may tentatively be assigned to carbonisocyanatidic amide	18
1457	Symmetric stretching of –N=C=O	Tentative functional-group assignment of an isocyanate-bearing irradiation product	18
1333	Overlap with the HNCO ν_3 region; unassigned	May reflect HNCO depletion, a small frequency shift, or a subtraction residual; should not be used as evidence for carbonisocyanatidic amide	16

Table S2. Calculated relative energies (ΔE) and adiabatic ionization energies (AIEs) using the CCSD(T) method with aug-cc-pVTZ (AVTZ), aug-cc-pVQZ (AVQZ) and extrapolated CBS basis sets for the six constitutional isomers and two conformers of isomer 2. The computed Cartesian coordinates and vibrational frequencies of neutral and ionic species are listed in Table S6. The AIE ranges were corrected for the Stark effect by -0.02 eV.⁸

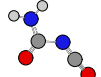
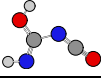
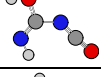
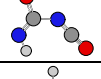
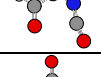
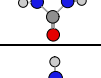
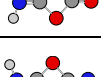
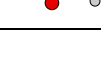
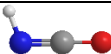
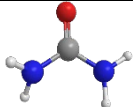
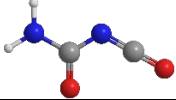
	Structure	ΔE (kJ/mol)			AIE (eV)			AIE range after error analysis (eV)
		AVTZ	AVQZ	CBS	AVTZ	AVQZ	CBS	
Isomer 1		0	0	0	10.27	10.34	10.39	10.345 – 10.395
Isomer 2		72	73	73	9.84	9.89	9.94	9.895 – 9.945
Isomer 2-1		74	75	75	9.89	9.95	9.99	9.945 – 9.995
Isomer 2-2		87	88	88	9.68	9.74	9.78	9.735 – 9.785
Isomer 3		172	172	172	9.26	9.31	9.35	9.305 – 9.355
Isomer 4		49	49	49	10.69	10.75	10.79	10.745 – 10.795
Isomer 5		102	103	103	10.44	10.50	10.55	10.505 – 10.555
Isomer 6		175	178	179	10.65	10.71	10.75	10.705 – 10.755

Table S3. Mass-to-charge ratios (m/z), molecular formulas, and proposed assignments of ion signals detected during temperature-programmed desorption (TPD) of irradiated HNCO ices.

m/z	Formula	Structure
17	NH ₃	
30	H ₂ CO	
43	HNCO	
45	H ₂ NCHO	
60	H ₂ NC(O)NH ₂	
86	H ₂ NC(O)NCO	
88	C ₂ H ₄ N ₂ O ₂	[a]
101	C ₂ H ₃ N ₃ O ₂	[a]
103	C ₂ H ₅ N ₃ O ₂	[a]
129	C ₃ H ₃ N ₃ O ₃	[a]

^[a] Tentatively assigned based on nominal masses; structures could not be assigned under current experimental conditions due to low ion counts.

Table S4. Experimental conditions of isocyanic acid (HNCO) ices including ice thickness, irradiation parameters, and vacuum ultraviolet (VUV) photon energy.

Exp.	Thickness (nm)	Current (nA)	Irradiation time (s)	Dose (eV/HNCO)	Photon energy (eV)
1	706 ± 40	-	-	-	11.00
2	706 ± 40	104 ± 5	1800 ± 10	9.3 ± 1.4	12.20
3	706 ± 40	106 ± 5	1800 ± 10	9.5 ± 1.4	11.00
4	706 ± 40	107 ± 5	1800 ± 10	9.6 ± 1.4	10.50
5	706 ± 40	105 ± 5	1800 ± 10	9.4 ± 1.4	10.20
6	706 ± 40	107 ± 5	1800 ± 10	9.6 ± 1.4	PIE

Table S5. Parameters used to calculate the average dose per molecule.

Initial kinetic energy of the electrons, E_{init}	5 keV
Irradiation current, I	105 ± 5 nA
Irradiation time, t	1800 s
Total number of electrons	$(1.1 \pm 0.1) \times 10^{15}$
Average kinetic energy of backscattered electrons, E_{bs}^*	2.8 ± 0.3 keV
Fraction of backscattered electrons, f_{bs}^*	0.07 ± 0.01
Average kinetic energy of transmitted electrons, E_{trans}^*	0 keV
Fraction of transmitted electrons, f_{trans}^*	0
Average penetration depth, L^*	434 ± 40 nm
Density of the ice, ρ	1.102 ± 0.005 g cm ⁻³
Dose per molecule	9.41 ± 1.41 eV per HNCO molecule

* Values obtained from CASINO simulations.⁷

Table S6. Calculated Cartesian coordinates (Å), electronic energies (hartree), zero-point vibrational energies (hartree), vibrational frequencies (cm⁻¹) used to construct the potential energy surface for C₂H₂N₂O₂ isomers relevant to the neutral ground states, cationic states, and potential dissociative channels (if calculated).

Isomer 1			
C	0.89130600	0.14787400	-0.00002200
C	-1.44367200	-0.21724700	-0.00001500
N	1.97785900	-0.65312800	0.00002100
N	-0.30019100	-0.62282000	-0.00002100
O	0.91557400	1.35088100	0.00000100
H	1.88510200	-1.65002000	0.00000300
H	2.88417400	-0.22633100	0.00003200
O	-2.56541800	0.05214700	0.00002200
E[CCSD(T)/aug-cc-pVTZ] = -336.91641			
E[CCSD(T)/aug-cc-pVQZ] = -337.00311			
E[CCSD(T)/CBS] = -337.05532			
ZPVE = 0.04916			
Frequency			
87.02			
123.46			
220.33			
450.03			
560.97			
578.04			
638.86			
697.93			
768.12			
846.39			
1117.95			
1328.57			
1487.81			
1624.35			
1825.91			
2359.67			
3651.67			
3789.64			

Cation 1

C	0.89838600	0.06037500	0.00011000
C	-1.43908500	-0.21651400	-0.00001500
N	2.04217300	-0.55590000	-0.00003800
N	-0.26437300	-0.61895800	0.00004200
O	0.77553700	1.33169500	-0.00001500
H	2.06295000	-1.56595100	-0.00008400
H	2.91235200	-0.04375300	-0.00014900
O	-2.54750000	0.01462300	-0.00002900

E[CCSD(T)/aug-cc-pVTZ] = -336.53847

E[CCSD(T)/aug-cc-pVQZ] = -336.62269

E[CCSD(T)/CBS] = -336.67310

ZPVE = 0.04867

Frequency

80.25

142.51

437.31

449.61

523.10

585.78

613.65

647.93

710.94

892.15

1060.49

1294.12

1505.35

1608.88

1733.27

2398.05

3564.35

3685.60

TS			
C	1.03456100	0.27710000	0.05054000
C	-1.75135700	-0.41330200	0.01819800
N	1.86354800	-0.70464100	-0.07318900
N	-0.60452500	-0.68490400	0.39302900
O	0.82323500	1.40081500	0.07344800
H	1.57564200	-1.65830800	0.07851400
H	2.83742100	-0.48784600	-0.24608400
O	-2.83469500	-0.19767800	-0.29472100

E[CCSD(T)/aug-cc-pVTZ] = -336.50737
 E[CCSD(T)/aug-cc-pVQZ] = -336.59128
 E[CCSD(T)/CBS] = -336.64148
 ZPVE = 0.04507
 Frequency
-272.88
 62.42
 94.73
 254.25
 427.99
 452.42
 489.25
 518.14
 618.61
 651.88
 1126.76
 1205.15
 1310.65
 1606.65
 2021.12
 2227.65
 3554.88
 3688.87

INT

C	-2.33050300	-0.00999900	-0.00003600
C	2.39711100	-0.08486000	0.00012500
N	-1.43156800	0.87086500	-0.00002900
N	1.19491100	0.12253100	0.00008500
O	-3.11772800	-0.81493500	0.00000300
H	-0.40665100	0.59172000	0.00002500
H	-1.69295100	1.85203000	-0.00005200
O	3.53729600	-0.28861100	-0.00011600

E[CCSD(T)/aug-cc-pVTZ] = -336.52057

E[CCSD(T)/aug-cc-pVQZ] = -336.60408

E[CCSD(T)/CBS] = -336.65429

ZPVE = 0.04426

Frequency

40.65

81.45

82.45

230.20

325.49

525.24

545.30

598.89

600.67

831.93

1140.73

1260.68

1359.31

1578.70

1997.02

2431.16

2751.74

3563.11

Prod 1⁺-1**H₂NCO⁺**

C	0.15008900	-0.00014000	-0.00001800
N	-1.11688000	0.00004100	-0.00005600
O	1.27182000	0.00004800	0.00001500
H	-1.62860100	-0.87911800	0.00015800
H	-1.62833400	0.87929000	0.00021700

E[CCSD(T)/aug-cc-pVTZ] = -168.73195

E[CCSD(T)/aug-cc-pVQZ] = -168.77485

E[CCSD(T)/CBS] = -168.80045

ZPVE = 0.03336

Frequency

476.63

479.43

594.83

1123.43

1240.39

1578.71

2457.61

3488.48

3592.72

NCO

C	0.00000000	0.05235100	0.00000000
N	0.83661100	0.91894500	0.00000000
O	-0.73203500	-0.84334000	0.00000000

E[CCSD(T)/aug-cc-pVTZ] = -167.75948

E[CCSD(T)/aug-cc-pVQZ] = -167.80103

E[CCSD(T)/CBS] = -167.82589

ZPVE = 0.00891

Frequency

467.76

1387.30

2161.73

Prod 1⁺-2**HN₂C₂O₂⁺**

C	-0.77556900	-0.12719000	-0.01219900
C	1.52326300	-0.11564400	0.00377300
N	-2.07653700	-0.44889600	-0.12315200
N	0.39393300	-0.65845600	-0.00209600
O	-1.36436700	0.98825200	0.00812800
H	-2.52732200	-0.61861700	0.78561700
O	2.59179000	0.24013400	0.00958100

E[CCSD(T)/aug-cc-pVTZ] = -335.85915

E[CCSD(T)/aug-cc-pVQZ] = -335.94219

E[CCSD(T)/CBS] = -335.99202

ZPVE = 0.03717

Frequency

131.20

133.31

483.33

531.64

576.68

629.29

676.81

915.63

1049.35

1098.37

1328.76

1427.48

1926.31

2421.22

3419.65

H

H	0.00000000	0.00000000	0.00000000
---	------------	------------	------------

E[CCSD(T)/aug-cc-pVTZ] = -0.49982

E[CCSD(T)/aug-cc-pVQZ] = -0.49995

E[CCSD(T)/CBS] = -0.49998

ZPVE = 0

Isomer 2

C	0.89110800	0.10840900	-0.00001500
C	-1.43485700	-0.19376200	0.00000300
N	-0.29962900	-0.62886900	0.00000100
N	0.91538300	1.36417900	0.00000300
O	-2.54965100	0.09493400	0.00000000
H	1.87044700	1.70582700	0.00001300
H	1.69464700	-1.60575100	0.00000500
O	1.97304100	-0.68682500	0.00000300

E[CCSD(T)/aug-cc-pVTZ] = -336.88919

E[CCSD(T)/aug-cc-pVQZ] = -336.97557

E[CCSD(T)/CBS] = -337.02762

ZPVE = 0.04935

Frequency

91.83

124.25

439.49

478.16

546.21

631.52

683.07

711.87

856.26

891.83

1111.18

1228.53

1356.58

1509.02

1779.17

2363.20

3562.83

3873.32

Cation 2

C	0.87421000	0.02019100	0.01530100
C	-1.43875800	-0.19123900	0.01854000
N	-0.27733900	-0.63595600	0.09464100
N	0.91339700	1.35706700	-0.10016100
O	-2.53414700	0.08157400	-0.04164400
H	1.48396100	1.87468300	0.57392300
H	1.86503300	-1.58299000	-0.09556600
O	1.98238200	-0.62072100	-0.03870100

E[CCSD(T)/aug-cc-pVTZ] = -336.52556

E[CCSD(T)/aug-cc-pVQZ] = -336.60990

E[CCSD(T)/CBS] = -336.66041

ZPVE = 0.04729

Frequency

125.33

138.26

308.86

475.55

496.47

603.48

627.28

663.09

686.55

909.91

944.51

1153.82

1355.19

1575.18

1632.86

2398.86

3484.02

3732.05

Isomer 2-1

C	-1.47393100	-0.17960100	-0.00013300
C	0.91956900	0.08187300	-0.00024900
N	1.19650200	1.31178000	0.00004300
N	-0.32555700	-0.54000600	-0.00097000
O	-2.60703700	0.05753900	0.00056600
H	0.37988900	1.90775300	-0.00043100
H	2.71380900	-0.37987700	0.00098900
O	1.87402000	-0.85053000	0.00046200

E[CCSD(T)/aug-cc-pVTZ] = -336.88864

E[CCSD(T)/aug-cc-pVQZ] = -336.97510

E[CCSD(T)/CBS] = -337.02719

ZPVE = 0.04956

Frequency

56.20

116.77

490.08

550.33

560.12

621.18

662.55

732.29

806.54

849.68

1104.38

1254.40

1395.62

1551.53

1749.51

2387.26

3597.56

3846.94

Cation 2-1

C	-1.45624700	-0.18501000	0.00984000
C	0.88199400	0.00079300	0.01860900
N	1.00681800	1.33056600	-0.12216100
N	-0.29205800	-0.60446500	0.06988600
O	-2.55881200	0.06930600	-0.03920000
H	0.90751600	1.92353100	0.70559600
H	2.75099200	-0.29838700	-0.09036700
O	1.90677400	-0.76962500	-0.01329900

E[CCSD(T)/aug-cc-pVTZ] = -336.52241

E[CCSD(T)/aug-cc-pVQZ] = -336.60676

E[CCSD(T)/CBS] = -336.65729

ZPVE = 0.04693

Frequency

108.22

130.97

222.83

452.69

514.52

606.27

627.28

651.48

651.76

885.05

924.75

1166.40

1361.04

1535.73

1661.26

2407.13

3489.24

3752.11

Isomer 2-2

C	-0.94343400	0.12510600	0.00000300
C	1.45085800	-0.19125400	0.00003600
N	-1.16693000	1.35937900	-0.00000300
N	0.29758500	-0.54719600	0.00010200
O	-1.96031100	-0.74178700	-0.00005300
H	-0.32118400	1.91320500	0.00006500
H	-1.61551100	-1.63679000	-0.00002700
O	2.58250700	0.04618600	-0.00006700

E[CCSD(T)/aug-cc-pVTZ] = -336.88327

E[CCSD(T)/aug-cc-pVQZ] = -336.96972

E[CCSD(T)/CBS] = -337.02181

ZPVE = 0.04921

Frequency

56.17

119.42

430.77

485.81

549.16

620.46

677.14

714.41

813.95

848.69

1092.16

1241.82

1362.83

1512.48

1784.14

2374.93

3598.56

3894.32

Cation 2-2

C	-0.87418900	0.02017300	-0.01527800
C	1.43873000	-0.19125700	-0.01855900
N	-0.91331500	1.35711000	0.10015800
N	0.27731600	-0.63598200	-0.09481000
O	-1.98238900	-0.62066600	0.03879100
H	-1.48386400	1.87442800	-0.57418900
H	-1.86514600	-1.58295000	0.09561100
O	2.53410800	0.08155800	0.04172900

E[CCSD(T)/aug-cc-pVTZ] = -336.52556

E[CCSD(T)/aug-cc-pVQZ] = -336.60990

E[CCSD(T)/CBS] = -336.66041

ZPVE = 0.04729

Frequency

125.35

138.26

308.91

475.55

496.46

603.52

627.28

663.11

686.56

909.95

944.78

1153.77

1355.18

1575.12

1632.92

2398.87

3483.86

3732.06

Isomer 3

C -1.18592900 -0.18259400 -0.00001700

C 1.51762200 0.34064200 -0.00027100

N 0.98819000 -0.90083400 -0.00005800

N -0.36668000 -1.09817500 0.00014500

O -2.14077100 0.47046400 -0.00008000

H 2.61502300 0.33856700 0.00008800

H 1.53714500 -1.73915200 0.00021700

O 0.82915900 1.33520500 0.00018100

E[CCSD(T)/aug-cc-pVTZ] = -336.85057

E[CCSD(T)/aug-cc-pVQZ] = -336.93712

E[CCSD(T)/CBS] = -336.98922

ZPVE = 0.04865

Frequency

143.66

145.34

251.91

355.80

521.40

570.04

641.31

891.67

961.74

1010.99

1174.10

1393.50

1483.08

1527.18

1778.09

2319.93

3044.39

3711.89

Cation 3

C	-1.10498700	-0.17295000	-0.00005000
C	1.47057600	0.47140200	-0.00000600
N	1.01660600	-0.88799900	0.00005200
N	-0.25237500	-1.14138700	-0.00005500
O	-2.09257100	0.37892400	0.00012900
H	2.55399500	0.60212900	0.00016100
H	1.62893200	-1.69840300	0.00017700
O	0.62681200	1.30998500	-0.00012800

E[CCSD(T)/aug-cc-pVTZ] = -336.51021

E[CCSD(T)/aug-cc-pVQZ] = -336.59487

E[CCSD(T)/CBS] = -336.64551

ZPVE = 0.04862

Frequency

144.41

193.72

369.89

401.04

542.80

604.74

674.35

880.54

921.88

1001.43

1004.05

1348.88

1473.08

1544.62

1820.51

2279.35

3143.10

3561.93

Isomer 4

C	-0.99228100	0.00000000	-0.00000200
C	0.99228100	0.00000000	-0.00000200
N	0.00000000	-1.00295200	0.08345800
N	0.00000000	1.00295500	-0.08347600
O	-2.17578500	0.00000000	0.00000600
O	2.17578500	0.00000000	0.00000700
H	0.00000000	1.93094600	0.30349400
H	0.00000000	-1.93096700	-0.30345300

E[CCSD(T)/aug-cc-pVTZ] = -336.89858

E[CCSD(T)/aug-cc-pVQZ] = -336.98522

E[CCSD(T)/CBS] = -337.03751

ZPVE = 0.04985

Frequency

163.69

376.70

449.55

515.72

600.74

696.62

740.25

831.75

866.03

868.21

1163.80

1258.19

1291.85

1353.22

1909.48

2026.73

3675.29

3675.90

Cation 4

C	0.00000300	0.02207800	1.04365800
C	0.00000300	0.02207800	-1.04365800
N	-0.00019200	-1.01392000	0.00000000
N	0.00017300	0.97214600	0.00000000
O	0.00000300	0.00473800	2.20320200
O	0.00000300	0.00473800	-2.20320200
H	0.00038100	1.98910500	0.00000000
H	-0.00034000	-2.03741900	0.00000000

E[CCSD(T)/aug-cc-pVTZ] = -336.50249

E[CCSD(T)/aug-cc-pVQZ] = -336.58696

E[CCSD(T)/CBS] = -336.63763

ZPVE = 0.04665

Frequency

153.77

253.96

342.54

516.44

553.97

591.95

694.04

705.22

707.42

762.44

905.88

1147.47

1187.17

1319.12

2026.61

2113.52

3485.97

3553.83

Prod 4⁺-1**HN₂C₂O₂⁺**

C	-1.60719600	0.00711600	-0.09852500
C	1.59272500	-0.07328300	0.07520100
N	0.54126800	0.35195200	0.60685600
N	-0.53252000	0.67855000	-0.23556500
O	-2.54487700	-0.60191500	0.01532500
O	2.61869400	-0.44839200	-0.23529100
H	-0.56494900	1.58593100	-0.69936400

E[CCSD(T)/aug-cc-pVTZ] = -335.90006

E[CCSD(T)/aug-cc-pVQZ] = -335.98437

E[CCSD(T)/CBS] = -336.03473

ZPVE = 0.03720

Frequency

52.91

209.61

247.62

469.97

553.75

607.31

637.27

723.62

919.59

1220.73

1389.84

1466.38

2346.57

2424.82

3494.13

H

H	0.00000000	0.00000000	0.00000000
---	------------	------------	------------

E[CCSD(T)/aug-cc-pVTZ] = -0.49982

E[CCSD(T)/aug-cc-pVQZ] = -0.49995

E[CCSD(T)/CBS] = -0.49998

ZPVE = 0

Prod 4⁺-2**HNC₂O₂⁺**

C	-1.16022600	-0.44075000	0.00003200
C	1.20324400	0.10969100	0.00003200
N	-0.00093000	0.52075800	-0.00002700
O	-2.25555400	-0.09972100	-0.00001700
O	2.24791300	-0.29836300	-0.00001600
H	-0.19045900	1.52571600	0.00007300

E[CCSD(T)/aug-cc-pVTZ] = -281.21405

E[CCSD(T)/aug-cc-pVQZ] = -281.28427

E[CCSD(T)/CBS] = -281.32607

ZPVE = 0.03040

Frequency

152.28

184.37

426.65

480.01

542.68

596.50

859.33

1203.49

1336.93

2022.78

2429.74

3464.86

NH

N	0.00000000	0.00000000	0.12957400
H	0.00000000	0.00000000	-0.90701600

E[CCSD(T)/aug-cc-pVTZ] = -55.12933

E[CCSD(T)/aug-cc-pVQZ] = -55.14018

E[CCSD(T)/CBS] = -55.14654

ZPVE = 0.00741

Frequency

3338.30

Prod 4⁺-3**HNC₂O₂**

C	0.00000700	-0.10863000	0.74131300
C	0.00000700	-0.10863000	-0.74131300
N	-0.00003500	1.06529900	0.00000000
O	0.00000700	-0.51465200	1.84955000
O	0.00000700	-0.51465200	-1.84955000
H	0.00005200	2.08089500	0.00000000

E[CCSD(T)/aug-cc-pVTZ] = -281.54740

E[CCSD(T)/aug-cc-pVQZ] = -281.61925

E[CCSD(T)/CBS] = -281.66253

ZPVE = 0.03062

Frequency

229.06

325.03

587.04

608.35

677.57

691.06

840.15

1143.49

1234.69

1899.60

2047.57

3513.72

NH⁺

N	0.00000000	0.00000000	0.13433000
H	0.00000000	0.00000000	-0.94031300

E[CCSD(T)/aug-cc-pVTZ] = -54.65112

E[CCSD(T)/aug-cc-pVQZ] = -54.66109

E[CCSD(T)/CBS] = -54.66679

ZPVE = 0.00668

Frequency

3009.44

Isomer 5

C 0.94961700 0.03169700 -0.01044500
C -0.99080200 -0.00117700 -0.00625500
N -0.04171500 1.00543200 -0.06494300
O -2.16157900 -0.09384300 0.03955000
H -0.05800400 1.98364700 0.15536400
O -0.00038300 -0.99657400 -0.02795200
N 2.18617600 0.05595600 0.03465900
H 2.58958200 -0.87314800 0.06403100
E[CCSD(T)/aug-cc-pVTZ] = -336.87797
E[CCSD(T)/aug-cc-pVQZ] = -336.96418
E[CCSD(T)/CBS] = -337.01629
ZPVE = 0.04950
Frequency
114.11
331.62
384.41
601.16
664.23
743.40
795.10
806.43
837.81
927.68
1085.47
1139.31
1297.96
1376.31
1868.00
2039.29
3585.30
3709.35

Cation 5

C	0.87902900	0.01897900	0.01386300
C	-1.03331600	0.01590600	0.00220200
N	-0.02351900	1.00749100	0.02100000
O	-2.17367500	-0.10043500	-0.00010900
H	-0.00358100	2.01867700	0.01301200
O	0.05336000	-1.00822400	-0.00766400
N	2.17971600	-0.00140700	-0.11288400
H	2.79843700	-0.40130700	0.59597600

E[CCSD(T)/aug-cc-pVTZ] = -336.49137

E[CCSD(T)/aug-cc-pVQZ] = -336.57534

E[CCSD(T)/CBS] = -336.62579

ZPVE = 0.04663

Frequency

161.87

294.96

349.10

456.00

532.47

590.64

599.76

716.02

759.09

854.14

907.57

1172.17

1290.82

1390.69

1662.76

2158.06

3501.89

3615.64

Prod 5⁺-1**H₂N₂CO⁺**

C	-0.39418100	0.00000900	-0.00000800
N	0.83804800	-0.67041100	-0.07709500
H	1.48642200	-1.38801400	0.26072200
O	-1.54252400	-0.00000700	0.00001300
N	0.83800800	0.67039800	0.07703700
H	1.48646300	1.38811100	-0.26037600

E[CCSD(T)/aug-cc-pVTZ] = -223.26199

E[CCSD(T)/aug-cc-pVQZ] = -223.31774

E[CCSD(T)/CBS] = -223.35110

ZPVE = 0.03553

Frequency

147.43

392.75

587.52

595.48

597.62

896.56

1122.93

1207.80

1363.17

2195.11

3441.69

3462.68

CO

C	0.00000000	0.00000000	-0.64212300
O	0.00000000	0.00000000	0.48159200

E[CCSD(T)/aug-cc-pVTZ] = -113.16186

E[CCSD(T)/aug-cc-pVQZ] = -113.19023

E[CCSD(T)/CBS] = -113.20703

ZPVE = 0.00497

Frequency

2240.65

Prod 5⁺-2**HN₂C₂O₂⁺**

C	-0.95547300	0.02400400	-0.00008400
C	0.95797400	0.02224600	-0.00009700
N	-0.03653200	1.02057800	0.00005400
O	2.09660500	-0.10194500	0.00019000
H	-0.05325100	2.03334600	-0.00080200
O	-0.11662800	-1.01568100	-0.00018800
N	-2.22083500	-0.07341200	0.00021300

E[CCSD(T)/aug-cc-pVTZ] = -335.78107

E[CCSD(T)/aug-cc-pVQZ] = -335.86368

E[CCSD(T)/CBS] = -335.91327

ZPVE = 0.03495

Frequency

134.20

235.83

351.58

459.69

590.52

614.11

723.61

769.28

896.98

1142.39

1215.38

1296.17

1569.92

2150.62

3600.48

H

H	0.00000000	0.00000000	0.00000000
---	------------	------------	------------

E[CCSD(T)/aug-cc-pVTZ] = -0.49982

E[CCSD(T)/aug-cc-pVQZ] = -0.49995

E[CCSD(T)/CBS] = -0.49998

ZPVE = 0

Prod 5⁺-3**H₂N₂CO**

C	-0.31176000	0.00011000	-0.00001200
N	0.82623600	0.76112900	0.15978900
H	1.11916900	1.23627500	-0.68873800
O	-1.49182400	0.00000200	-0.00000600
N	0.82624000	-0.76131000	-0.15985200
H	1.11865800	-1.23567900	0.68929900

E[CCSD(T)/aug-cc-pVTZ] = -223.63767

E[CCSD(T)/aug-cc-pVQZ] = -223.69433

E[CCSD(T)/CBS] = -223.72855

ZPVE = 0.03871

Frequency

500.27

577.17

717.01

880.74

996.65

1097.63

1116.33

1174.14

1291.57

2039.05

3526.29

3530.05

CO⁺

C	0.00000000	0.00000000	-0.63247100
O	0.00000000	0.00000000	0.47435400

E[CCSD(T)/aug-cc-pVTZ] = -112.64856

E[CCSD(T)/aug-cc-pVQZ] = -112.67542

E[CCSD(T)/CBS] = -112.69096

ZPVE = 0.00517

Frequency

2329.29

Prod 5⁺-4**HN₂C₂O₂⁺**

C	0.88577300	0.01671800	-0.05962600
C	-1.00440800	0.00277000	0.01557100
N	0.06727000	1.09169000	-0.04149000
O	-2.15742300	0.02889000	0.05644000
O	-0.03680000	-0.99829700	-0.05986300
N	2.16394600	0.11006100	0.04560400
H	2.64708800	-0.77393000	0.26291700

E[CCSD(T)/aug-cc-pVTZ] = -335.76162

E[CCSD(T)/aug-cc-pVQZ] = -335.84347

E[CCSD(T)/CBS] = -335.89267

ZPVE = 0.03443

Frequency

73.69

294.75

366.59

545.10

655.77

683.02

756.62

786.39

843.42

1048.88

1117.42

1381.52

1534.46

2012.91

3417.67

H

H	0.00000000	0.00000000	0.00000000
---	------------	------------	------------

E[CCSD(T)/aug-cc-pVTZ] = -0.49982

E[CCSD(T)/aug-cc-pVQZ] = -0.49995

E[CCSD(T)/CBS] = -0.49998

ZPVE = 0

Isomer 6

C	0.01899200	0.94312400	0.00000000
C	-0.01899200	-0.94312400	0.00000000
H	0.90086100	2.59605300	0.00000000
O	-1.00673100	0.02626400	0.00000000
O	1.00673100	-0.02626400	0.00000000
N	0.01899200	-2.17273900	0.00000000
N	-0.01899200	2.17273900	0.00000000
H	-0.90086100	-2.59605300	0.00000000

E[CCSD(T)/aug-cc-pVTZ] = -336.85012

E[CCSD(T)/aug-cc-pVQZ] = -336.93582

E[CCSD(T)/CBS] = -336.98769

ZPVE = 0.04955

Frequency

173.24

372.69

575.94

637.26

751.52

790.12

796.15

823.61

861.80

927.63

1001.24

1089.29

1129.87

1379.56

1830.37

1988.74

3599.74

3601.04

Cation 6

C	0.98806200	0.01319500	-0.00297300
C	-0.87360200	-0.01552900	-0.01586100
H	2.82038500	-0.66131200	-0.00773200
O	-0.05007800	1.00155900	-0.00008600
O	-0.03877600	-1.01885400	-0.01655900
N	-2.17155200	-0.03115500	0.12295700
N	2.17660600	0.12090800	0.00290700
H	-2.83169000	0.18541000	-0.62715100

E[CCSD(T)/aug-cc-pVTZ] = -336.45498

E[CCSD(T)/aug-cc-pVQZ] = -336.53851

E[CCSD(T)/CBS] = -336.58879

ZPVE = 0.04567

Frequency

136.63

176.83

339.96

532.04

562.11

647.69

680.35

728.74

792.11

827.28

856.16

914.61

1155.32

1416.32

1651.37

2048.09

3501.24

3613.03

Prod 6⁺-1**HNCO₂⁺**

C	-0.62682100	0.13524200	0.00006100
O	-1.68917900	-0.20975300	-0.00001500
O	1.48335200	-0.48965800	0.00002000
N	0.63946100	0.47500500	-0.00008600
H	0.93131400	1.45880700	0.00019900

E[CCSD(T)/aug-cc-pVTZ] = -243.11795

E[CCSD(T)/aug-cc-pVQZ] = -243.17863

E[CCSD(T)/CBS] = -243.21471

ZPVE = 0.02578

Frequency

238.76

495.57

584.02

690.59

1103.52

1215.59

1468.85

2404.83

3417.34

CNH

C	0.00000000	0.00000000	-0.73545700
H	0.00000000	0.00000000	1.42245300
N	0.00000000	0.00000000	0.42718400

E[CCSD(T)/aug-cc-pVTZ] = -93.25716

E[CCSD(T)/aug-cc-pVQZ] = -93.27971

E[CCSD(T)/CBS] = -93.29326

ZPVE = 0.01544

Frequency

493.84

493.84

2124.64

3844.89

Prod 6⁺-2**HNCO₂**

C	0.28400500	-0.01822300	-0.01441000
O	1.45573500	-0.08527700	0.01689700
O	-0.70741700	0.83833700	0.01716800
N	-0.92212400	-0.70191900	-0.13893600
H	-1.23570400	-1.00170900	0.78649500

E[CCSD(T)/aug-cc-pVTZ] = -243.48758

E[CCSD(T)/aug-cc-pVQZ] = -243.54957

E[CCSD(T)/CBS] = -243.58693

ZPVE = 0.02644

Frequency

563.18

589.74

720.94

969.70

1107.30

1161.50

1265.80

2073.64

3462.30

CNH⁺

C	0.00004900	0.71789100	0.00000000
H	-0.00063200	-1.42885900	0.00000000
N	0.00004900	-0.41121300	0.00000000

E[CCSD(T)/aug-cc-pVTZ] = -92.81712

E[CCSD(T)/aug-cc-pVQZ] = -92.83854

E[CCSD(T)/CBS] = -92.85114

ZPVE = 0.01460

Frequency

638.31

2338.13

3601.38

Prod 6⁺-3**HN₂C₂O₂⁺**

C	-0.91524100	-0.00523400	-0.00008000
C	0.95014700	-0.00734600	-0.00002200
H	-2.88380000	0.54427200	0.00034200
O	0.10044000	-1.02129200	-0.00006300
O	0.11986500	1.02325300	-0.00008200
N	2.22273300	0.01351900	0.00012500
N	-2.09245800	-0.08273100	0.00007800

E[CCSD(T)/aug-cc-pVTZ] = -335.74212

E[CCSD(T)/aug-cc-pVQZ] = -335.82428

E[CCSD(T)/CBS] = -335.87369

ZPVE = 0.03380

Frequency

175.19

256.18

460.47

516.54

564.08

626.13

670.58

715.94

762.23

801.62

1124.10

1258.21

1542.31

2099.39

3658.06

H

H	0.00000000	0.00000000	0.00000000
---	------------	------------	------------

E[CCSD(T)/aug-cc-pVTZ] = -0.49982

E[CCSD(T)/aug-cc-pVQZ] = -0.49995

E[CCSD(T)/CBS] = -0.49998

ZPVE = 0

Table S7. Calculated transition energies and Franck–Condon factors (FCFs) for vibronic transitions from the vibrational ground state of neutral carbonisocyanatidic amide to vibrational levels of its ground-state cation. The FCFs are dimensionless; only transitions with an FCF of at least 0.0010 are listed.

Index	Energy/eV	FCFs	Index	Energy/eV	FCFs	Index	Energy/eV	FCFs
1	10.391	0.0190	51	10.712	0.0013	101	10.892	0.0014
2	10.408	0.0078	52	10.717	0.0046	102	10.893	0.0019
3	10.426	0.0021	53	10.717	0.0018	103	10.903	0.0015
4	10.445	0.0016	54	10.718	0.0030	104	10.904	0.0039
5	10.446	0.0242	55	10.735	0.0012	105	10.904	0.0017
6	10.464	0.0087	56	10.736	0.0010	106	10.904	0.0026
7	10.482	0.0021	57	10.738	0.0061	107	10.905	0.0026
8	10.501	0.0013	58	10.744	0.0040	108	10.921	0.0010
9	10.501	0.0032	59	10.744	0.0051	109	10.922	0.0012
10	10.502	0.0143	60	10.745	0.0047	110	10.924	0.0023
11	10.519	0.0011	61	10.755	0.0034	111	10.930	0.0020
12	10.520	0.0044	62	10.761	0.0013	112	10.930	0.0042
13	10.551	0.0078	63	10.761	0.0018	113	10.931	0.0022
14	10.557	0.0038	64	10.762	0.0013	114	10.942	0.0014
15	10.558	0.0051	65	10.764	0.0068	115	10.948	0.0016
16	10.569	0.0041	66	10.766	0.0022	116	10.951	0.0019
17	10.575	0.0012	67	10.767	0.0022	117	10.953	0.0016
18	10.576	0.0013	68	10.772	0.0011	118	10.954	0.0016
19	10.577	0.0163	69	10.773	0.0016	119	10.959	0.0011
20	10.578	0.0015	70	10.773	0.0011	120	10.959	0.0018
21	10.586	0.0013	71	10.773	0.0011	121	10.959	0.0014
22	10.595	0.0070	72	10.782	0.0031	122	10.960	0.0011
23	10.605	0.0011	73	10.785	0.0013	123	10.960	0.0017
24	10.606	0.0068	74	10.792	0.0011	124	10.972	0.0010
25	10.607	0.0112	75	10.792	0.0055	125	10.979	0.0022
26	10.613	0.0019	76	10.793	0.0090	126	10.980	0.0036
27	10.613	0.0021	77	10.799	0.0023	127	10.986	0.0012
28	10.614	0.0013	78	10.799	0.0029	128	10.986	0.0024
29	10.623	0.0024	79	10.800	0.0012	129	10.998	0.0018
30	10.625	0.0052	80	10.810	0.0020	130	11.006	0.0026
31	10.632	0.0018	81	10.811	0.0044	131	11.007	0.0012
32	10.633	0.0212	82	10.820	0.0091	132	11.008	0.0023
33	10.634	0.0011	83	10.820	0.0015	133	11.010	0.0012
34	10.642	0.0015	84	10.822	0.0030	134	11.024	0.0011
35	10.646	0.0011	85	10.823	0.0016	135	11.035	0.0028
36	10.651	0.0080	86	10.829	0.0013	136	11.035	0.0014
37	10.661	0.0011	87	10.837	0.0036	137	11.036	0.0025
38	10.661	0.0083	88	10.839	0.0012	138	11.054	0.0011
39	10.662	0.0013	89	10.848	0.0012	139	11.061	0.0013
40	10.663	0.0074	90	10.848	0.0068	140	11.062	0.0016

41	10.668	0.0020	91	10.848	0.0012	141	11.063	0.0014
42	10.679	0.0025	92	10.848	0.0019	142	11.064	0.0015
43	10.680	0.0030	93	10.849	0.0062	143	11.090	0.0011
44	10.687	0.0016	94	10.866	0.0021	144	11.090	0.0016
45	10.688	0.0032	95	10.867	0.0026	145	11.091	0.0020
46	10.688	0.0041	96	10.875	0.0016	146	11.092	0.0011
47	10.689	0.0128	97	10.875	0.0033	147	11.117	0.0017
48	10.706	0.0012	98	10.875	0.0057	148	11.145	0.0014
49	10.706	0.0017	99	10.876	0.0018	149	11.147	0.0013
50	10.706	0.0042	100	10.877	0.0019			

References

- (1) Bai, X.; Li, C.; Luo, Y.; Gong, Q. a.; Lu, J.; Yang, J.; Pan, Y.; Sun, Z.; Eckhardt, A. K.; Sun, R.; Kaiser, Ralf I.; Yang, T. Formation of hydrogen trioxide (HOOH) in extraterrestrial ice analogs and its role as an oxidizer in prebiotic chemistry. *Sci. Adv.* **2025**, *11*, eadw5720.
- (2) Marks, J. H.; Bai, X.; Nikolayev, A. A.; Gong, Q. a.; McAnally, M.; Wang, J.; Pan, Y.; Fortenberry, R. C.; Mebel, A. M.; Yang, T.; Kaiser, Ralf I. Methanetetrol and the final frontier in ortho acids. *Nat. Commun.* **2025**, *16*, 6468.
- (3) Gong, Q.; Bai, X.; Lu, J.; Yang, J.; Pan, Y.; Sun, Z.; Kaiser, R. I.; Yang, T. Formation of Polyoxymethylenes in Extraterrestrial Ice Analogs of Formaldehyde Exposed to Ionizing Radiation. *Astrophys. J.* **2025**, *994*, 70.
- (4) Bai, X.; Gong, Q.; Lu, J.; Yang, J.; Pan, Y.; Sun, Z.; Kaiser, R. I.; Yang, T. Non-Equilibrium Growth Processes to Glyceraldehyde and Glycerol as Building Blocks of Interstellar Sugars and Phospholipids. *J. Am. Chem. Soc.* **2026**, *148*, 22979-22989.
- (5) Raunier, S.; Chiavassa, T.; Duvernay, F.; Borget, F.; Aycard, J.-P.; Dartois, E.; d'Hendecourt, L. Tentative identification of urea and formamide in ISO-SWS infrared spectra of interstellar ices. *Astron. Astrophys.* **2004**, *416*, 165-169.
- (6) Hudson, R. L.; Yarnall, Y. Y.; Gerakines, P. A. Infrared Band Strengths and Other Properties of Three Interstellar Compounds—Amorphous Isocyanic Acid, Formaldehyde, and Formic Acid. *Astrophys. J.* **2024**, *977*, 130.
- (7) Drouin, D.; Couture, A. R.; Joly, D.; Tastet, X.; Aimez, V.; Gauvin, R. CASINO V2.42 - A fast and easy-to-use modeling tool for scanning electron microscopy and microanalysis users. *Scanning* **2007**, *29*, 92-101.
- (8) Zhu, C.; Wang, H.; Medvedkov, I.; Marks, J.; Xu, M.; Yang, J.; Yang, T.; Pan, Y.; Kaiser, R. I. Exploitation of synchrotron radiation photoionization mass spectrometry in the analysis of complex organics in interstellar model ices. *J. Phys. Chem. Lett.* **2022**, *13*, 6875-6882.
- (9) T. Lu, *Molclus program, version 1.12*, Beijing Kein/Kejian Research Center for Natural Science, Beijing, China, **2023**.
- (10) Chai, J.-D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615-6620.
- (11) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. Electron affinities of the first - row atoms revisited. Systematic basis sets and wave functions. *J. Chem. Phys.* **1992**, *96*, 6796-6806.
- (12) Alecu, I. M.; Zheng, J.; Zhao, Y.; Truhlar, D. G. Computational Thermochemistry: Scale Factor Databases and Scale Factors for Vibrational Frequencies Obtained from Electronic Model Chemistries. *J. Chem. Theory Comput.* **2010**, *6*, 2872-2887.
- (13) Purvis, G. D.; Bartlett, R. J. A full coupled - cluster singles and doubles model: The inclusion of disconnected triples. *J. Chem. Phys.* **1982**, *76*, 1910-1918.
- (14) Neese, F. Software Update: The ORCA Program System—Version 6.0. *WIREs. Comput. Mol. Sci.* **2025**, *15*, e70019.
- (15) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd,

E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian Inc., Wallingford, CT*, **2016**.

(16) Lowenthal, M. S.; Khanna, R. K.; Moore, M. H. Infrared spectrum of solid isocyanic acid (HNCO): vibrational assignments and integrated band intensities. *Spectrochim. Acta A* **2002**, *58*, 73-78.

(17) Bouilloud, M.; Fray, N.; Bénilan, Y.; Cottin, H.; Gazeau, M.-C.; Jolly, A. Bibliographic review and new measurements of the infrared band strengths of pure molecules at 25 K: H₂O, CO₂, CO, CH₄, NH₃, CH₃OH, HCOOH and H₂CO. *MNRAS* **2015**, *451*, 2145-2160.

(18) Socrates, G. *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*; John Wiley & Sons, New York, **2004**.

(19) Gerakines, P. A.; Materese, C. K.; Hudson, R. L. Establishing an accurate infrared band strength for the cyanate ion in interstellar ices. *MNRAS* **2025**, *537*, 2918-2924.

(20) Pettersson, M.; Khriachtchev, L.; Jolkkonen, S.; Räsänen, M. Photochemistry of HNCO in Solid Xe: Channels of UV Photolysis and Creation of H₂NCO Radicals. *J. Phys. Chem. A* **1999**, *103*, 9154-9162.

(21) Kaiser, R. I.; Maity, S.; Jones, B. M. Infrared and reflectron time-of-flight mass spectroscopic analysis of methane (CH₄)–carbon monoxide (CO) ices exposed to ionization radiation–toward the formation of carbonyl-bearing molecules in extraterrestrial ices. *Phys. Chem. Chem. Phys.* **2014**, *16*, 3399-3424.