

## Supporting Information

### **Nonequilibrium Formation of Pyridine (C<sub>5</sub>H<sub>5</sub>N) in Interstellar Ice Analogs: Implications for Biorelevant Nitrogen Heterocycles in Ryugu and Bennu**

Jia Wang,<sup>1,2</sup> Zesen Wang,<sup>1,2</sup> Shiori Inada,<sup>1,2†</sup> Ralf I. Kaiser<sup>1,2\*</sup>

<sup>1</sup> *W. M. Keck Research Laboratory in Astrochemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States*

<sup>2</sup> *Department of Chemistry, University of Hawaii at Manoa, Honolulu, Hawaii 96822, United States*

<sup>†</sup> *Present address: Department of Basic Science, The University of Tokyo, 3-8-1 Komaba, Tokyo 153-8902, Japan*

\*Corresponding Author:

Ralf I. Kaiser, [ralfk@hawaii.edu](mailto:ralfk@hawaii.edu)

## Methods

**Experimental.** All experiments were performed in an ultrahigh vacuum chamber operating at pressures of a few  $10^{-11}$  Torr, maintained by magnetically suspended turbomolecular pumps backed by an oil-free dry scroll pump.<sup>1,2</sup> A polished silver substrate mounted onto the cold head of a closed-cycle helium cryostat was cooled to 5 K. The cold head can be translated vertically using a bellows and rotated within the horizontal plane, allowing sequential alignment of the substrate with the deposition, irradiation, infrared, and mass spectrometric detection positions.<sup>1,2</sup> After the silver substrate was cooled to 5 K, acetylene–hydrogen cyanide ( $C_2H_2$ –HCN) ice mixtures were prepared by independently co-depositing acetylene ( $C_2H_2$ ; 99.9%, Airgas) and hydrogen cyanide (HCN, 5% in helium) onto the silver substrate through two separate glass capillary arrays. During deposition, the partial pressures of  $1.5 \times 10^{-8}$  Torr for  $C_2H_2$  and  $1.1 \times 10^{-7}$  Torr for the HCN sample were used. Acetylene- $^{13}C_2$  ( $^{13}C_2H_2$ ; >99 %  $^{13}C$ %, Cambridge Isotope Laboratories) was used in isotope-labeling experiments. During deposition, the ice thicknesses were monitored in situ by laser interferometry using a helium-neon laser operating at 632.8 nm.<sup>3</sup> The thicknesses of the  $C_2H_2$ –HCN ices were determined to be  $830 \pm 50$  nm using an average refractive index of  $1.34 \pm 0.01$ , derived from the reported refractive indices of  $C_2H_2$  ice (1.34 at 10 K)<sup>4</sup> and HCN ice (1.346 at 18 K).<sup>5</sup> Infrared spectra of the deposited ices were collected using a Fourier transform infrared (FTIR) spectrometer (Thermo Electron Nicolet 6700) over the 6000–500  $cm^{-1}$  range at a resolution of 4  $cm^{-1}$ . The  $C_2H_2$ :HCN ratio was determined to be  $(3.1 \pm 1.7)$ :1 from the integrated absorbances of the  $\nu_3$  band of  $C_2H_2$  at 3235  $cm^{-1}$  and the  $\nu_5$  band at 781 and 746  $cm^{-1}$ , using corresponding band strengths of  $2.39 \times 10^{-17}$  and  $2.42 \times 10^{-17}$   $cm$  molecule $^{-1}$ ,<sup>4</sup> respectively, together with the  $\nu_3$  band of HCN at 2100  $cm^{-1}$  and its band strength of  $1.03 \times 10^{-17}$   $cm$  molecule $^{-1}$ .<sup>5</sup> Ice densities of 0.76 g  $cm^{-3}$  for  $C_2H_2$  ice at 131 K<sup>6</sup> and 0.85 g  $cm^{-3}$  for HCN ice at 18 K<sup>5</sup> were used for the ratio calculation. The ratio of acetylene to hydrogen cyanide used in this study was chosen to enhance the formation yield of pyridine and thereby facilitate its detection.

After deposition, the acetylene–hydrogen cyanide ices were irradiated with 5 keV electrons at an incidence angle of 70° and a current of  $35 \pm 1$  nA for 45 min using an electron gun (SPECS, EQ PU-22). The 5 keV electrons were used because their linear energy transfer is comparable to that of 10–20 MeV galactic cosmic rays (GCRs) as they deposit in interstellar ices within cold molecular clouds.<sup>7,8</sup> Notably, lower-energy secondary electrons, particularly those with energies

below 20 eV, may contribute substantially to the synthesis of prebiotic molecules in interstellar ices.<sup>9-11</sup> Although the dependence of pyridine on the primary electron energy was not studied in the present study, irradiation with 5 keV electrons generates cascades of low-energy secondary electrons that may also induce pyridine formation. Future experiments utilizing a range of electron energies will be required to quantify the energy dependence of the formation yield of products such as pyridine. The energy doses deposited in the ice mixture were calculated using Monte Carlo simulations performed with the CASINO 2.42 software package.<sup>12</sup> Irradiation doses of  $2.3 \pm 0.4$  eV molecule<sup>-1</sup> for C<sub>2</sub>H<sub>2</sub> and  $2.1 \pm 0.3$  eV molecule<sup>-1</sup> for HCN were obtained, corresponding to a GCR exposure time of  $(9 \pm 2) \times 10^6$  years in a cold molecular cloud.<sup>13</sup> The incident electrons penetrated the C<sub>2</sub>H<sub>2</sub>–HCN ice to an average depth of  $360 \pm 50$  nm. Furthermore, approximately 99% of the deposited energy was confined to the upper  $600 \pm 50$  nm of the ice, well below the total ice thickness of  $830 \pm 50$  nm, thereby minimizing potential interactions between the incident electrons and the silver substrate.

After irradiation, the ices were heated from 5 to 320 K at a ramp rate of 1 K min<sup>-1</sup> for temperature-programmed desorption (TPD). After reaching 320 K, the substrate was maintained at this temperature for 10 minutes. During TPD, the desorbed molecules were photoionized in the gas phase using either pulsed (30 Hz) vacuum ultraviolet (VUV) photons at 10.49 eV and 8.17 eV or tunable ultraviolet (UV) photons spanning 220.5–244.5 nm. The 10.49 eV ( $3\omega_1$ ) photons were generated by frequency tripling the 355 nm output of an Nd:YAG laser (Spectra-Physics, Quanta Ray PRO 270-30) in a pulsed xenon gas jet.<sup>14</sup> To produce the 8.17 eV light, an Nd:YAG laser operating at 532 nm was used to pump Stilbene 420 dye, generating 425.112 nm light, which was frequency doubled to yield 212.556 nm ( $\omega_1$ ). This output subsequently generated  $\omega_{\text{VUV}} = 2\omega_1 - \omega_2$  (8.17 eV) in Kr gas by combining with 355 nm ( $\omega_2$ ). The UV photons were generated by frequency doubling the output of a dye laser pumped by the third harmonic of an Nd:YAG laser. Detailed generation parameters for the VUV and UV photons are provided in Table S3. The generated VUV or UV light was isolated from the residual laser beams using a biconvex lithium fluoride lens (Korth Kristalle,  $R_1 = R_2 = 131$  mm) in an off-axis geometry. The selected ionization beam was directed  $2.0 \pm 0.5$  mm above the ice surface to photoionize the desorbing species during TPD. The resulting ions were analyzed using a reflectron time-of-flight mass spectrometer equipped with a dual microchannel plate detector (Jordan TOF Products, Inc.). The ion signals were amplified with a preamplifier (Ortec, 9305), processed using a discriminator and amplifier (Advanced Research

Instruments Corp., F100-TD), and recorded with a multichannel scaler (FAST ComTec, MCS6A).<sup>15,16</sup> Each mass spectrum was accumulated for 2 min over 3600 sweeps, with a temporal resolution of 3.2 ns. A blank experiment using C<sub>2</sub>H<sub>2</sub>–HCN ice was also performed at 10.49 eV under otherwise identical conditions but without electron irradiation.

## Infrared Spectroscopy

Fourier-transform infrared (FTIR) spectra of acetylene–hydrogen cyanide ices were recorded in situ before, during, and after electron irradiation at 5 K (Figures S1–S2), with the assignments compiled in Tables S1–S2. The spectra of the C<sub>2</sub>H<sub>2</sub>–HCN ice were dominated by the fundamental vibrational modes of acetylene ( $\nu_3$ , 3235 cm<sup>-1</sup>;  $\nu_2$ , 1960 cm<sup>-1</sup>; and  $\nu_5$ , 781 and 746 cm<sup>-1</sup>)<sup>4,17,18</sup> and hydrogen cyanide ( $\nu_1$ , 3150 cm<sup>-1</sup>;  $\nu_3$ , 2100 cm<sup>-1</sup>; and  $\nu_2$ , 822 cm<sup>-1</sup>).<sup>5</sup> Following irradiation, multiple new absorption features emerged and were resolved by Gaussian deconvolution. The absorptions at 2957 and 1765 cm<sup>-1</sup> were assigned to C–H stretching and the –C=CH<sub>2</sub> function group, respectively, whereas the bands at 2269 and 2229 cm<sup>-1</sup> were attributed to C≡N stretching.<sup>19</sup> In the <sup>13</sup>C<sub>2</sub>H<sub>2</sub>–HCN ice, the latter features shifted to 2253 and 2228 cm<sup>-1</sup>. The band at 3279 cm<sup>-1</sup> was assigned to the  $\nu_1$  fundamental of vinylacetylene (CH<sub>2</sub>CHCCH).<sup>20</sup> The band at 2303 cm<sup>-1</sup> was attributed to the  $\nu_1$  mode of isocyanogen (CNCN),<sup>21</sup> while the features at 2159 and 2134 cm<sup>-1</sup> may arise from the C≡N asymmetric stretch ( $\nu_3$ ) of cyanogen<sup>22</sup> and/or the –N≡C function group.<sup>19</sup> The bands at 2090 and 2071 cm<sup>-1</sup> were assigned to C≡N stretching of the cyanide anion (CN<sup>-</sup>), potentially associated with ammonium cyanide.<sup>23</sup> Absorptions at 1629, 965, and 915 cm<sup>-1</sup> were assigned to the C=C stretching mode ( $\nu_2$ ) of ethylene,<sup>24</sup> the out-of-plane aromatic C–H deformation mode ( $\nu_{19}$ ) of benzene (C<sub>6</sub>H<sub>6</sub>),<sup>25</sup> and the CH<sub>2</sub> twisting mode ( $\nu_{13}$ ) of propene (C<sub>3</sub>H<sub>6</sub>),<sup>26</sup> respectively. Notably, the absorption at 2978 cm<sup>-1</sup> can be attributed to pyridine ( $\nu_{10}$ , C<sub>5</sub>H<sub>5</sub>N; **10**),<sup>27</sup> although contributions from vinylacetylene ( $\nu_6 + \nu_7$ ),<sup>20</sup> ethylene (C<sub>2</sub>H<sub>4</sub>,  $\nu_{11}$ ),<sup>28</sup> and/or ethane (C<sub>2</sub>H<sub>6</sub>,  $\nu_{10}$ ) cannot be excluded.<sup>29</sup> Therefore, extensive overlap among the infrared absorptions of the irradiation products precludes unambiguous identification of pyridine by FTIR spectroscopy alone, necessitating the need of a more sensitive, isomer-selective analytical technique.

## Possible candidates for the C<sub>5</sub>H<sub>5</sub>N isomers

The remaining  $m/z = 79$  signal is attributed to a minor contribution from singly <sup>13</sup>C-substituted benzene (Figure S3) and additional C<sub>5</sub>H<sub>5</sub>N isomers. Possible C<sub>5</sub>H<sub>5</sub>N candidates include

unsaturated nitriles and related isomers such as 2,4-pentadienenitrile ( $\text{H}_2\text{CCHCHCHCN}$ ), 2-methylene-3-butenenitrile ( $\text{H}_2\text{CCHCH}(\text{CH}_2)\text{CN}$ ), 2-isocyano-1,3-butadiene ( $\text{H}_2\text{CCHC}(\text{CH}_2)\text{NC}$ ), 2-cyclobutene-1-carbonitrile (*c*- $\text{C}_4\text{H}_5\text{CN}$ ) and 1-cyclobutene-1-carbonitrile (*c*- $\text{C}_4\text{H}_5\text{CN}$ ), 2-methylene-2*H*-pyrrole ( $\text{C}_5\text{H}_5\text{N}$ ), and/or 2,4-cyclopentadien-1-imine ( $\text{C}_5\text{H}_5\text{N}$ ). Because the ionization energy of 2-methyl-2-cyclopropene-1-carbonitrile (*c*- $\text{C}_3\text{H}_2(\text{CH}_3)(\text{CN})$ ;  $\text{IE} = 10.71 \pm 0.03 \text{ eV}$ )<sup>30</sup> exceeds the photon energy (10.49 eV) used in the experiments, the formation of this isomer can be ruled out under current experimental conditions.

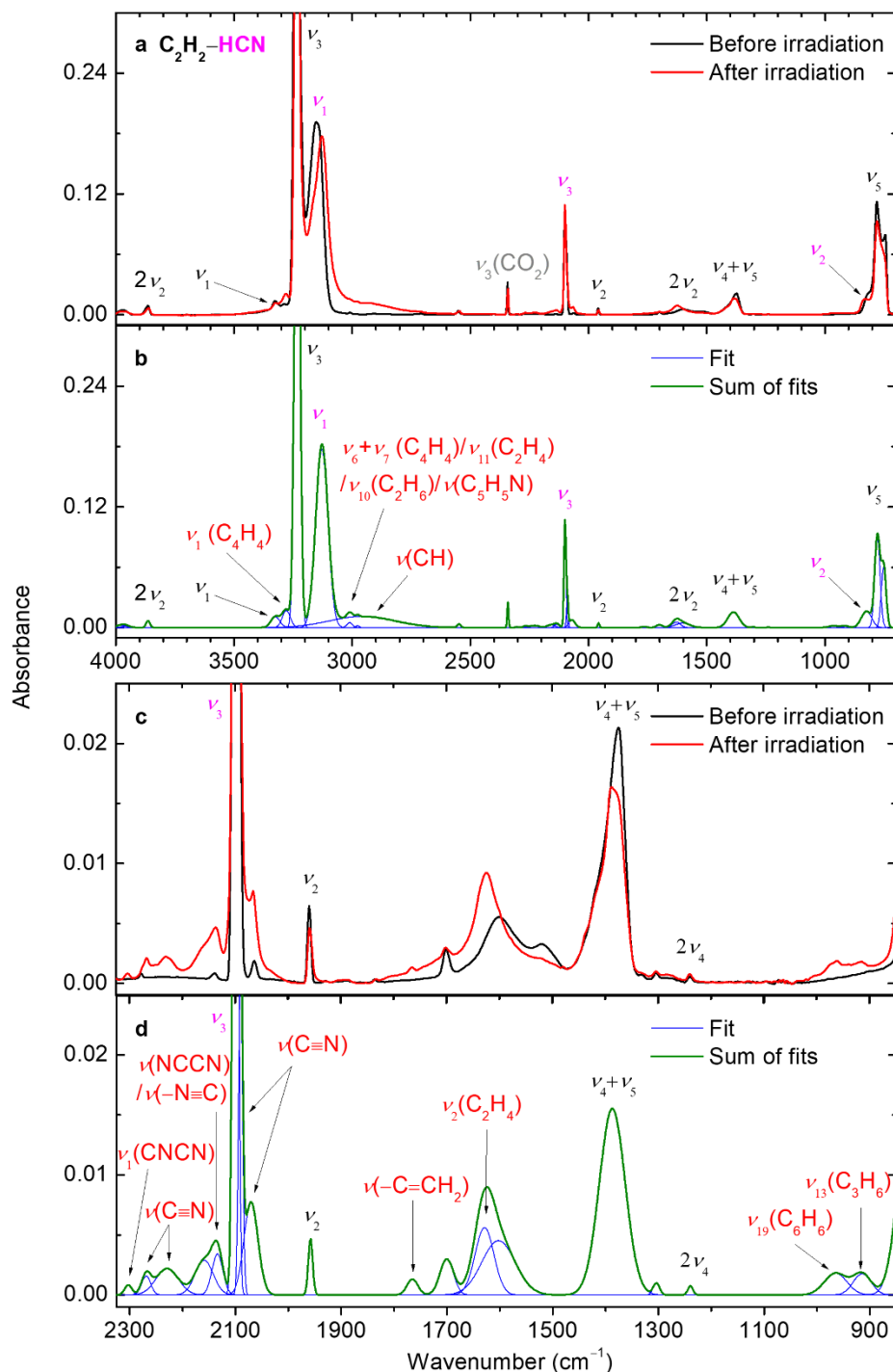


**Figure S1.** Infrared spectra of  $\text{C}_2\text{H}_2\text{-HCN}$  ice before and after electron irradiation. Baseline-corrected FTIR spectra recorded at 5 K before (black) and after (red) irradiation are shown in panels a and c. Panels b and d show magnified views of the spectra with Gaussian deconvolution of the absorption features. Bands assigned to  $\text{C}_2\text{H}_2$ , HCN, and new absorptions are indicated in black, magenta and red, respectively. Detailed assignments are provided in Table S1.

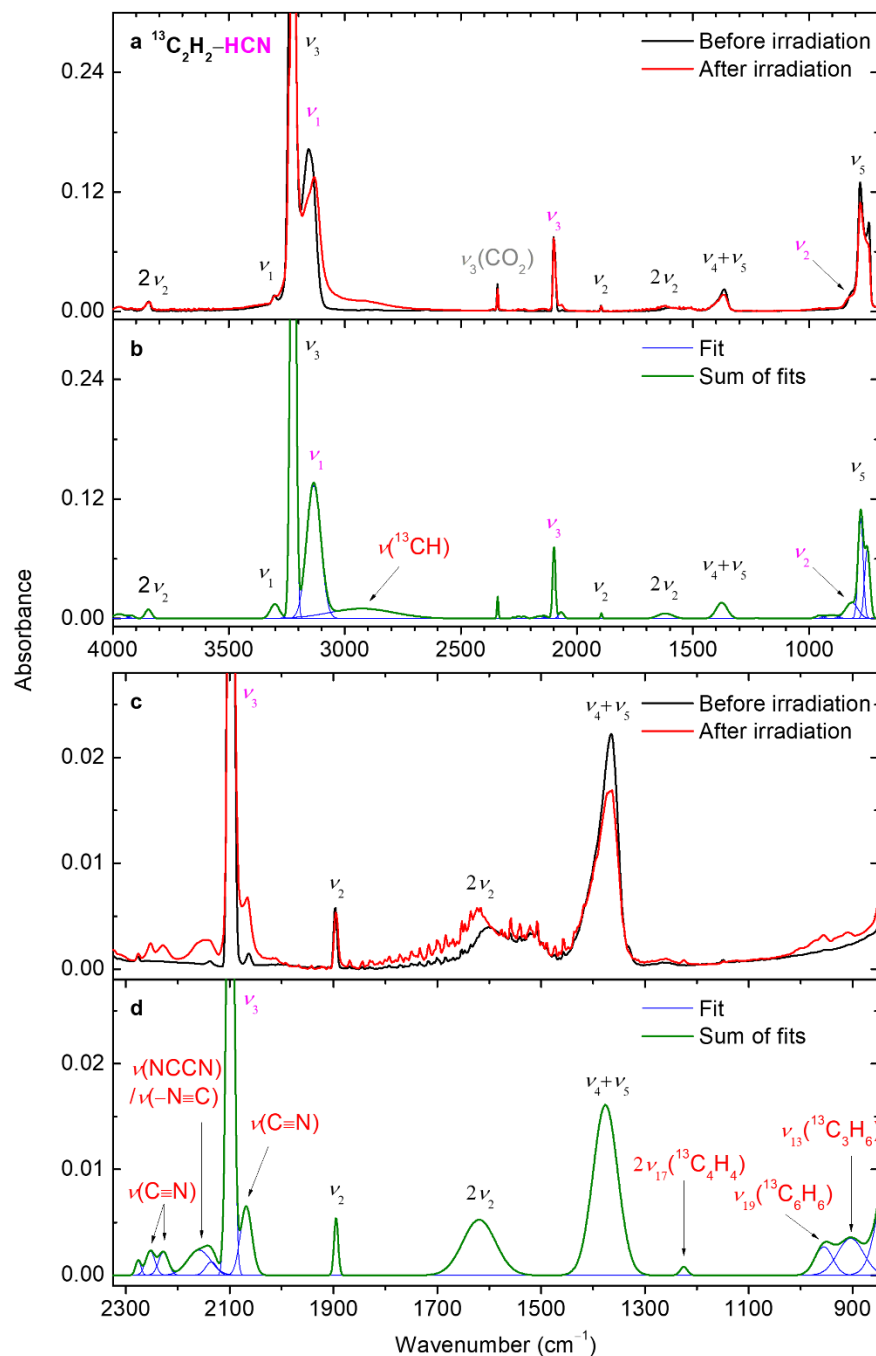


**Figure S2.** Infrared spectra of  $^{13}\text{C}_2\text{H}_2\text{-HCN}$  ice before and after electron irradiation. Baseline-corrected FTIR spectra recorded at 5 K before (black) and after (red) irradiation are shown in panels a and c. Panels b and d show magnified views of the spectra with Gaussian deconvolution of the absorption features. Bands assigned to  $^{13}\text{C}_2\text{H}_2$ , HCN, and new absorptions are indicated in black, magenta and red, respectively. Detailed assignments are provided in Table S2.

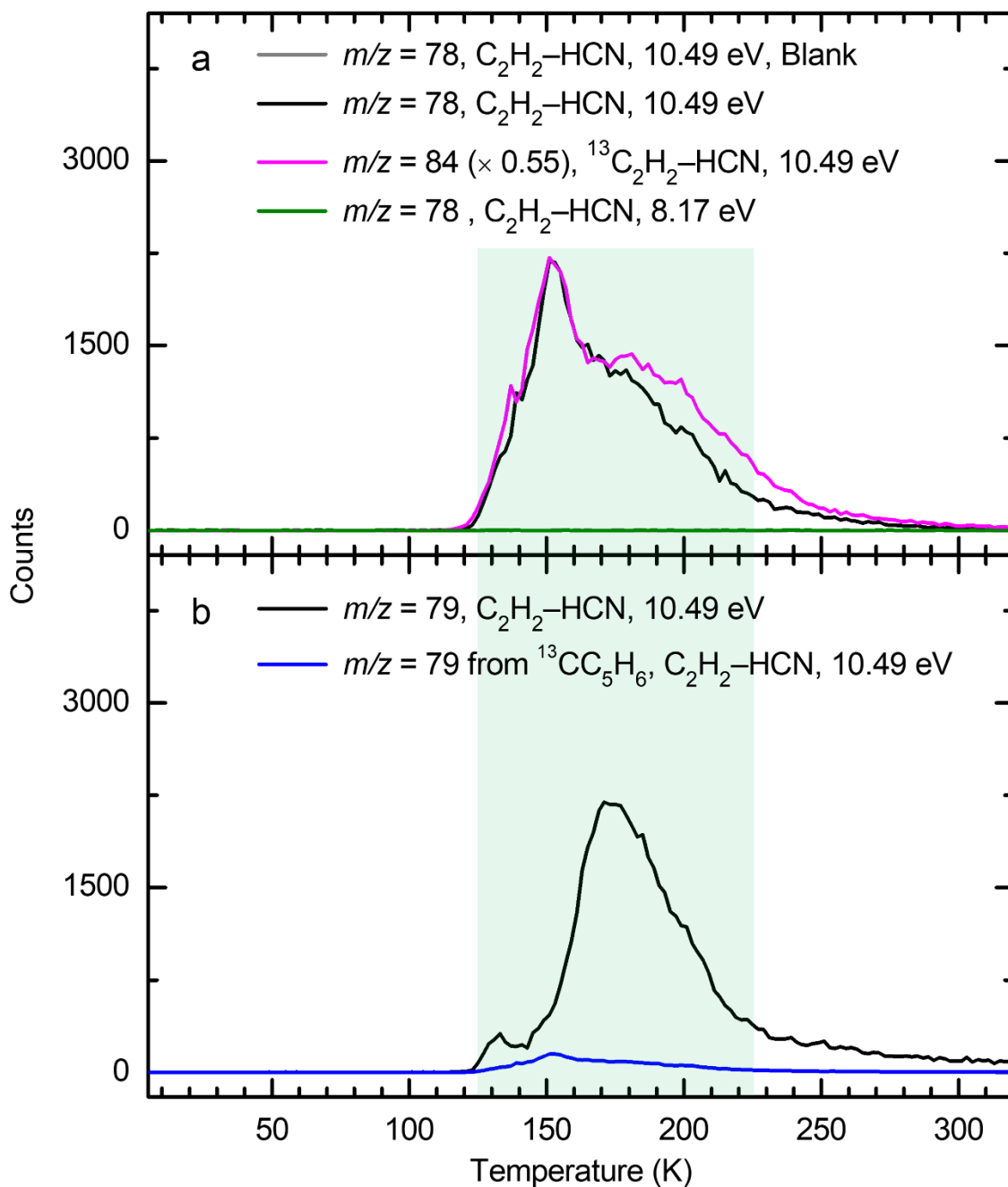


**Figure S3.** Ion signals recorded during TPD of acetylene–hydrogen cyanide ices. (a) TPD profiles were recorded at 10.49 eV for irradiated  $C_2H_2$ -HCN ( $m/z = 78$ ) and  $^{13}C_2H_2$ -HCN ( $m/z = 84$ ) ices, confirming the formula  $C_6H_6$ . The shaded region indicates the reported sublimation-temperature range of benzene ( $IE = 9.24378 \pm 0.00007$  eV)<sup>30</sup> in processed acetylene ices.<sup>31,32</sup> (b) TPD profiles of  $m/z = 79$  recorded at 10.49 eV for irradiated  $C_2H_2$ -HCN includes a contribution from singly  $^{13}C$ -substituted benzene ( $^{13}CC_5H_6$ ), accounting for  $6 \pm 1$  % of the total signal of  $m/z = 79$ .

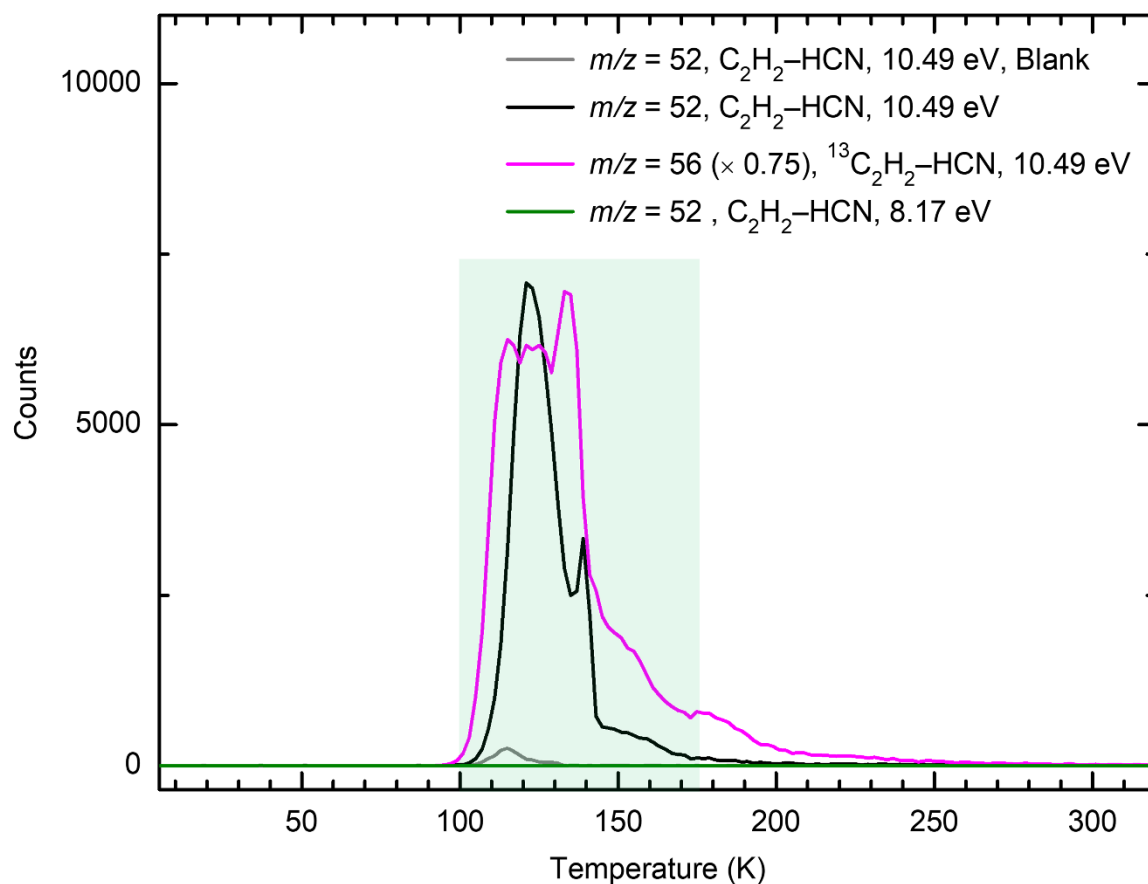


**Figure S4.** Ion signals recorded during TPD of acetylene–hydrogen cyanide ices. (a) TPD profiles were recorded at 10.49 eV for irradiated  $C_2H_2-HCN$  ( $m/z = 52$ ) and  $^{13}C_2H_2-HCN$  ( $m/z = 56$ ) ices, confirming the formula  $C_4H_4$ . The  $m/z = 52$  and 56 ion signals were saturated near their peak sublimation temperatures. The shaded region indicates the reported sublimation-temperature range of vinylacetylene ( $IE = 9.58 \pm 0.02$  eV)<sup>30</sup> in electron-irradiated acetylene ices.<sup>31</sup>

**Table S1.** Observed infrared absorption bands in C<sub>2</sub>H<sub>2</sub>–HCN ice before and after irradiation at 5 K. Vibration mode: stretching ( $\nu$ ).

| Absorptions before irradiation (cm <sup>-1</sup> )    |                                                                                                                                                                      |
|-------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| C <sub>2</sub> H <sub>2</sub>                         | Assignment <sup>4,17,18</sup>                                                                                                                                        |
| 4075                                                  | $\nu_1 + \nu_5$                                                                                                                                                      |
| 3959                                                  | $2\nu_2$                                                                                                                                                             |
| 3864                                                  | $\nu_2 + 2\nu_4 + \nu_5$                                                                                                                                             |
| 3325                                                  | $\nu_1$                                                                                                                                                              |
| 3235                                                  | $\nu_3$                                                                                                                                                              |
| 3008                                                  | $\nu_3(^{13}\text{C}_2\text{H}_2)$                                                                                                                                   |
| 2553                                                  | $\nu_2 + \nu_4$                                                                                                                                                      |
| 1960                                                  | $\nu_2$                                                                                                                                                              |
| 1374                                                  | $\nu_4 + \nu_5$                                                                                                                                                      |
| 1240                                                  | $2\nu_4$                                                                                                                                                             |
| 781, 746                                              | $\nu_5$                                                                                                                                                              |
| HCN                                                   | Assignment <sup>5</sup>                                                                                                                                              |
| 3977                                                  | $\nu_1 + \nu_2$                                                                                                                                                      |
| 3150                                                  | $\nu_1$ (CH stretch)                                                                                                                                                 |
| 2100                                                  | $\nu_3$ (CN stretch)                                                                                                                                                 |
| 2062                                                  | $\nu_3$ (H <sup>13</sup> CN)                                                                                                                                         |
| 1601                                                  | $2\nu_2$                                                                                                                                                             |
| 822                                                   | $\nu_2$ (HCN bend)                                                                                                                                                   |
| New absorptions after irradiation (cm <sup>-1</sup> ) | Assignment                                                                                                                                                           |
| 3279                                                  | $\nu_1(\text{C}_4\text{H}_4)^{20}$                                                                                                                                   |
| 2978                                                  | $\nu_6 + \nu_7(\text{C}_4\text{H}_4)^{20} / \nu_{11}(\text{C}_2\text{H}_4)^{28} / \nu_{10}(\text{C}_2\text{H}_6)^{29} / \nu_{10}(\text{C}_5\text{H}_5\text{N})^{27}$ |
| 2957                                                  | $\nu(\text{CH})^{19}$                                                                                                                                                |
| 2303                                                  | $\nu_1(\text{CNCN})^{21}$                                                                                                                                            |
| 2269, 2229                                            | $\nu(\text{C}\equiv\text{N})^{19}$                                                                                                                                   |
| 2159, 2134                                            | $\nu(\text{NCCN})^{22} / \nu(-\text{N}\equiv\text{C})^{19}$                                                                                                          |
| 2090, 2071                                            | $\nu(\text{C}\equiv\text{N})(\text{CN}^-)^{23}$                                                                                                                      |
| 1765                                                  | $\nu(-\text{C}=\text{CH}_2)^{19}$                                                                                                                                    |
| 1629                                                  | $\nu_2(\text{C}_2\text{H}_4)^{24}$                                                                                                                                   |
| 965                                                   | $\nu_{19}(\text{C}_6\text{H}_6)^{25}$                                                                                                                                |
| 915                                                   | $\nu_{13}(\text{C}_3\text{H}_6)^{26}$                                                                                                                                |

**Table S2.** Observed infrared absorption bands in  $^{13}\text{C}_2\text{H}_2\text{--HCN}$  ice before and after irradiation at 5 K. Vibration mode: stretching ( $\nu$ ).

| Absorptions before irradiation ( $\text{cm}^{-1}$ )    |                                                           |
|--------------------------------------------------------|-----------------------------------------------------------|
| $^{13}\text{C}_2\text{H}_2$                            | Assignment                                                |
| 4048                                                   | $\nu_1 + \nu_5$                                           |
| 3918                                                   | $2\nu_2$                                                  |
| 3845                                                   | $\nu_2 + 2\nu_4 + \nu_5$                                  |
| 3304                                                   | $\nu_1$                                                   |
| 3223                                                   | $\nu_3$                                                   |
| 2138                                                   | $\nu_4 + 2\nu_5$                                          |
| 1897                                                   | $\nu_2$                                                   |
| 1365                                                   | $\nu_4 + \nu_5$                                           |
| 780, 742                                               | $\nu_5$                                                   |
| HCN                                                    | Assignment <sup>5</sup>                                   |
| 3972                                                   | $\nu_1 + \nu_2$                                           |
| 3156                                                   | $\nu_1$ (CH stretch)                                      |
| 2100                                                   | $\nu_3$ (CN stretch)                                      |
| 2063                                                   | $\nu_3$ ( $\text{H}^{13}\text{CN}$ )                      |
| 1603                                                   | $2\nu_2$                                                  |
| 822                                                    | $\nu_2$ (HCN bend)                                        |
| New absorptions after irradiation ( $\text{cm}^{-1}$ ) |                                                           |
|                                                        | Assignment                                                |
| 2927                                                   | $\nu(^{13}\text{CH})^{19}$                                |
| 2253, 2228                                             | $\nu(\text{C}\equiv\text{N})^{19}$                        |
| 2159, 2135                                             | $\nu(\text{NCCN})^{22}/\nu(-\text{N}\equiv\text{C})^{19}$ |
| 2068                                                   | $\nu(\text{C}\equiv\text{N}) (\text{CN}^-)^{23}$          |
| 1225                                                   | $2\nu_{17} (^{13}\text{C}_4\text{H}_4)^{33,34}$           |
| 956                                                    | $\nu_{19} (^{13}\text{C}_6\text{H}_6)$                    |
| 904                                                    | $\nu_{13} (^{13}\text{C}_3\text{H}_6)^{26}$               |

**Table S3.** Experimental parameters used to generate vacuum ultraviolet (VUV) and ultraviolet (UV) photons. The uncertainties in the photon energies are less than 0.001 eV.

| Photon energy (eV)                 | Nonlinear medium for four-wave mixing | Wavelength for $\omega_1$ (nm) | Dye for $\omega_1$ | Wavelength for $\omega_2$ (nm) | Dye for $\omega_2$ |
|------------------------------------|---------------------------------------|--------------------------------|--------------------|--------------------------------|--------------------|
| 10.49<br>( $3\omega_1$ )           | Xenon                                 | 355                            | —                  | —                              | —                  |
| 8.17<br>( $2\omega_1 - \omega_2$ ) | Krypton                               | 212.556                        | Stilbene 420       | 355                            | —                  |
| 5.38–5.64                          | —                                     | 220.5–230.5 nm                 | Coumarin 450       | —                              | —                  |
| 5.06–5.39                          | —                                     | 230–244.5 nm                   | Coumarin 480       | —                              | —                  |
| 5.19                               | —                                     | 239 nm                         | Coumarin 480       | —                              | —                  |

**Table S4.** Proposed molecular formulae for the ion signals observed at each mass channel in irradiated acetylene–hydrogen cyanide ices. Sublimation events detected are indicated by plus signs (+). The detected fragments are indicated in italics.

| C <sub>2</sub> H <sub>2</sub> –HCN |                 |                       |                      | <sup>13</sup> C <sub>2</sub> H <sub>2</sub> –HCN |                       | Proposed formula or assignment                                     |
|------------------------------------|-----------------|-----------------------|----------------------|--------------------------------------------------|-----------------------|--------------------------------------------------------------------|
| <i>m/z</i>                         | Blank, 10.49 eV | Irradiation, 10.49 eV | Irradiation, 8.17 eV | <i>m/z</i>                                       | Irradiation, 10.49 eV |                                                                    |
| 17                                 |                 | +                     |                      | 17                                               | +                     | NH <sub>3</sub>                                                    |
| 26                                 | +               | +                     |                      | 28                                               | +                     | C <sub>2</sub> H <sub>2</sub>                                      |
| 28                                 |                 | +                     |                      | 30                                               | +                     | CH <sub>2</sub> CH <sub>2</sub>                                    |
| 30                                 |                 | +                     |                      | 30                                               | +                     | N <sub>2</sub> H <sub>2</sub>                                      |
| 31                                 |                 | +                     |                      | 31                                               | +                     | CH <sub>3</sub> NH <sub>2</sub>                                    |
| 39                                 |                 | +                     |                      | 42                                               | +                     | <i>C<sub>3</sub>H<sub>3</sub></i>                                  |
| 41                                 |                 | +                     |                      | 42                                               | +                     | <i>C<sub>2</sub>H<sub>3</sub>N</i>                                 |
| 42                                 |                 | +                     |                      | 45                                               | +                     | CH <sub>3</sub> CHCH <sub>2</sub>                                  |
| 43                                 |                 | +                     |                      | 43                                               | +                     | CH <sub>2</sub> CHNH <sub>2</sub>                                  |
| 44                                 |                 | +                     |                      | 46                                               | +                     | <i>C<sub>2</sub>H<sub>6</sub>N</i> , C <sub>3</sub> H <sub>8</sub> |
| 45                                 |                 | +                     |                      | 45                                               | +                     | CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>                    |
| 50                                 |                 | +                     |                      | 54                                               | +                     | C <sub>4</sub> H <sub>2</sub>                                      |
| 52                                 | +               | +                     |                      | 56                                               | +                     | C <sub>4</sub> H <sub>4</sub>                                      |
| 54                                 |                 | +                     |                      | 58                                               | +                     | C <sub>4</sub> H <sub>6</sub>                                      |
| 56                                 |                 | +                     |                      | 60                                               | +                     | C <sub>4</sub> H <sub>8</sub>                                      |
| 64                                 |                 | +                     |                      | 69                                               | +                     | C <sub>5</sub> H <sub>4</sub>                                      |
| 65                                 |                 | +                     |                      | 68                                               | +                     | C <sub>3</sub> H <sub>3</sub> CN                                   |
| 66                                 |                 | +                     |                      | 71                                               | +                     | C <sub>5</sub> H <sub>6</sub>                                      |
| 67                                 |                 | +                     |                      | 70                                               | +                     | C <sub>4</sub> H <sub>5</sub> N                                    |
| 68                                 |                 | +                     |                      | 73                                               | +                     | C <sub>5</sub> H <sub>8</sub>                                      |
| 70                                 |                 | +                     |                      | 75                                               | +                     | C <sub>5</sub> H <sub>10</sub>                                     |
| 74                                 |                 | +                     |                      | 80                                               | +                     | C <sub>6</sub> H <sub>2</sub>                                      |
| 76                                 |                 | +                     |                      | 82                                               | +                     | C <sub>6</sub> H <sub>4</sub>                                      |
| 77                                 |                 | +                     |                      | 82                                               | +                     | <i>C<sub>6</sub>H<sub>5</sub></i>                                  |
| 78                                 |                 | +                     |                      | 84                                               | +                     | C <sub>6</sub> H <sub>6</sub>                                      |
| 79                                 |                 | +                     |                      | 83                                               | +                     | C <sub>5</sub> H <sub>5</sub> N                                    |
| 81                                 |                 | +                     |                      | 85                                               | +                     | C <sub>4</sub> H <sub>7</sub> CN                                   |
| 82                                 |                 | +                     |                      | 88                                               | +                     | C <sub>6</sub> H <sub>10</sub>                                     |
| 84                                 |                 | +                     |                      | 90                                               | +                     | C <sub>6</sub> H <sub>12</sub>                                     |
| 89                                 |                 | +                     |                      | 94                                               | +                     | C <sub>5</sub> H <sub>3</sub> CN                                   |
| 90                                 |                 | +                     |                      | 97                                               | +                     | C <sub>7</sub> H <sub>6</sub>                                      |
| 91                                 |                 | +                     |                      | 96                                               | +                     | C <sub>5</sub> H <sub>5</sub> CN                                   |

|     |  |   |   |     |   |                                   |
|-----|--|---|---|-----|---|-----------------------------------|
| 93  |  | + |   | 99  | + | C <sub>6</sub> H <sub>7</sub> N   |
| 94  |  | + |   | 101 | + | C <sub>7</sub> H <sub>10</sub>    |
| 96  |  | + |   | 103 | + | C <sub>7</sub> H <sub>12</sub>    |
| 98  |  | + |   | 105 | + | C <sub>7</sub> H <sub>14</sub>    |
| 102 |  | + |   | 110 | + | C <sub>8</sub> H <sub>6</sub>     |
| 103 |  | + |   | 111 | + | C <sub>7</sub> H <sub>5</sub> N   |
| 104 |  | + | + | 112 | + | C <sub>8</sub> H <sub>8</sub>     |
| 105 |  | + | + | 112 | + | C <sub>7</sub> H <sub>7</sub> N   |
| 106 |  | + | + | 114 | + | C <sub>8</sub> H <sub>10</sub>    |
| 108 |  | + |   | 116 | + | C <sub>8</sub> H <sub>12</sub>    |
| 111 |  | + |   | 117 | + | C <sub>6</sub> H <sub>13</sub> CN |
| 112 |  | + |   | 120 | + | C <sub>8</sub> H <sub>16</sub>    |
| 114 |  | + |   | 121 | + | C <sub>7</sub> H <sub>3</sub> CN  |
| 115 |  | + |   | 124 | + | C <sub>9</sub> H <sub>7</sub>     |
| 116 |  | + |   | 123 | + | C <sub>7</sub> H <sub>6</sub> CN  |
| 117 |  | + |   | 124 | + | C <sub>7</sub> H <sub>7</sub> CN  |
| 118 |  | + |   | 127 | + | C <sub>9</sub> H <sub>10</sub>    |
| 120 |  | + |   | 129 | + | C <sub>9</sub> H <sub>12</sub>    |
| 122 |  | + |   | 131 | + | C <sub>9</sub> H <sub>14</sub>    |
| 124 |  | + |   | 133 | + | C <sub>9</sub> H <sub>16</sub>    |
| 126 |  | + |   | 135 | + | C <sub>9</sub> H <sub>18</sub>    |
| 128 |  | + | + | 136 | + | C <sub>8</sub> H <sub>6</sub> CN  |
| 129 |  | + | + | 137 | + | C <sub>8</sub> H <sub>7</sub> CN  |
| 130 |  | + | + | 137 | + | C <sub>10</sub> H <sub>10</sub>   |
| 131 |  | + | + | 140 | + | C <sub>9</sub> H <sub>9</sub> N   |
| 132 |  | + | + | 142 | + | C <sub>10</sub> H <sub>12</sub>   |
| 134 |  | + | + | 144 | + | C <sub>10</sub> H <sub>14</sub>   |
| 136 |  | + |   | 146 | + | C <sub>10</sub> H <sub>16</sub>   |
| 138 |  | + |   | 148 | + | C <sub>10</sub> H <sub>18</sub>   |
| 140 |  | + |   | 150 | + | C <sub>10</sub> H <sub>20</sub>   |
| 141 |  | + |   | 151 | + | C <sub>10</sub> H <sub>7</sub> N  |
| 143 |  | + |   | 152 | + | C <sub>9</sub> H <sub>9</sub> CN  |
| 144 |  | + |   | 155 | + | C <sub>11</sub> H <sub>12</sub>   |
| 146 |  | + |   | 157 | + | C <sub>11</sub> H <sub>14</sub>   |
| 148 |  | + |   | 159 | + | C <sub>11</sub> H <sub>16</sub>   |
| 150 |  | + |   | 161 | + | C <sub>11</sub> H <sub>18</sub>   |
| 152 |  | + |   | 163 | + | C <sub>11</sub> H <sub>20</sub>   |
| 154 |  | + | + | 165 | + | C <sub>11</sub> H <sub>22</sub>   |
| 158 |  | + | + | 170 | + | C <sub>12</sub> H <sub>14</sub>   |

|     |  |   |   |     |   |                                 |
|-----|--|---|---|-----|---|---------------------------------|
| 160 |  | + | + | 172 | + | C <sub>12</sub> H <sub>16</sub> |
| 162 |  | + |   | 174 | + | C <sub>12</sub> H <sub>18</sub> |
| 164 |  | + |   | 176 | + | C <sub>12</sub> H <sub>20</sub> |
| 166 |  | + |   | 178 | + | C <sub>12</sub> H <sub>22</sub> |
| 168 |  | + |   | 180 | + | C <sub>12</sub> H <sub>24</sub> |
| 172 |  | + |   | 185 | + | C <sub>13</sub> H <sub>16</sub> |
| 174 |  | + |   | 187 | + | C <sub>13</sub> H <sub>18</sub> |
| 176 |  | + |   | 189 | + | C <sub>13</sub> H <sub>20</sub> |
| 178 |  | + |   | 191 | + | C <sub>13</sub> H <sub>22</sub> |
| 180 |  | + | + | 193 | + | C <sub>13</sub> H <sub>24</sub> |
| 182 |  | + | + | 195 | + | C <sub>13</sub> H <sub>26</sub> |
| 186 |  | + | + | 200 | + | C <sub>14</sub> H <sub>18</sub> |
| 188 |  | + |   | 202 | + | C <sub>14</sub> H <sub>20</sub> |
| 190 |  | + |   | 204 | + | C <sub>14</sub> H <sub>22</sub> |
| 192 |  | + |   | 206 | + | C <sub>14</sub> H <sub>24</sub> |
| 194 |  | + |   | 208 | + | C <sub>14</sub> H <sub>26</sub> |
| 196 |  | + |   | 210 | + | C <sub>14</sub> H <sub>28</sub> |
| 200 |  | + |   | 215 | + | C <sub>15</sub> H <sub>20</sub> |
| 202 |  | + |   | 217 | + | C <sub>15</sub> H <sub>22</sub> |
| 204 |  | + |   | 219 | + | C <sub>15</sub> H <sub>24</sub> |
| 206 |  | + | + | 221 | + | C <sub>15</sub> H <sub>26</sub> |
| 208 |  | + | + | 223 | + | C <sub>15</sub> H <sub>28</sub> |
| 210 |  | + | + | 225 | + | C <sub>15</sub> H <sub>30</sub> |
| 216 |  | + |   | 234 | + | C <sub>16</sub> H <sub>26</sub> |
| 218 |  | + |   | 236 | + | C <sub>16</sub> H <sub>28</sub> |
| 222 |  | + |   | 238 | + | C <sub>16</sub> H <sub>30</sub> |
| 224 |  | + |   | 240 | + | C <sub>16</sub> H <sub>32</sub> |
| 236 |  | + |   | 251 | + | C <sub>17</sub> H <sub>32</sub> |

## References

- (1) Jones, B. M.; Kaiser, R. I. Application of reflectron time-of-flight mass spectroscopy in the analysis of astrophysically relevant ices exposed to ionization radiation: Methane ( $\text{CH}_4$ ) and D4-methane ( $\text{CD}_4$ ) as a case study. *J. Phys. Chem. Lett.* **2013**, *4*, 1965-1971.
- (2) Abplanalp, M. J.; Forstel, M.; Kaiser, R. I. Exploiting single photon vacuum ultraviolet photoionization to unravel the synthesis of complex organic molecules in interstellar ices. *Chem. Phys. Lett.* **2016**, *644*, 79-98.
- (3) Turner, A. M.; Abplanalp, M. J.; Chen, S. Y.; Chen, Y. T.; Chang, A. H. H.; Kaiser, R. I. A photoionization mass spectroscopic study on the formation of phosphanes in low temperature phosphine ices. *Phys. Chem. Chem. Phys.* **2015**, *17*, 27281-27291.
- (4) Hudson, R. L.; Ferrante, R. F.; Moore, M. H. Infrared spectra and optical constants of astronomical ices: I. Amorphous and crystalline acetylene. *Icarus* **2014**, *228*, 276-287.
- (5) Gerakines, P. A.; Yarnall, Y. Y.; Hudson, R. L. Direct measurements of infrared intensities of HCN and  $\text{H}_2\text{O} + \text{HCN}$  ices for laboratory and observational astrochemistry. *Mon. Not. R. Astron. Soc.* **2021**, *509*, 3515-3522.
- (6) McMullan, R. K.; Kvick, A.; Popelier, P. Structures of cubic and orthorhombic phases of acetylene by single-crystal neutron diffraction. *Acta Crystallogr. B* **1992**, *48*, 726-731.
- (7) Kaiser, R.; Roessler, K. Theoretical and laboratory studies on the interaction of cosmic-ray particles with interstellar ices. I. Synthesis of polycyclic aromatic hydrocarbons by a cosmic-ray-induced multicenter mechanism. *Astrophys. J.* **1997**, *475*, 144.
- (8) Ferrari, B. C.; Slavicinska, K.; Bennett, C. J. Role of suprathreshold chemistry on the evolution of carbon oxides and organics within interstellar and cometary ices. *Acc. Chem. Res.* **2021**, *54*, 1067-1079.
- (9) Mason, N. J.; Nair, B.; Jheeta, S.; Szymańska, E. Electron induced chemistry: a new frontier in astrochemistry. *Faraday Discuss.* **2014**, *168*, 235-247.
- (10) Boyer, M. C.; Rivas, N.; Tran, A. A.; Verish, C. A.; Arumainayagam, C. R. The role of low-energy ( $\leq 20\text{eV}$ ) electrons in astrochemistry. *Surf. Sci.* **2016**, *652*, 26-32.
- (11) Wu, Q. T.; Anderson, H.; Watkins, A. K.; Arora, D.; Barnes, K.; Padovani, M.; Shingledecker, C. N.; Arumainayagam, C. R.; Battat, J. B. R. Role of low-energy ( $<20\text{ eV}$ ) secondary electrons in the extraterrestrial synthesis of prebiotic molecules. *ACS Earth Space Chem.* **2024**, *8*, 79-88.
- (12) 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.
- (13) Yeghikyan, A. G. Irradiation of dust in molecular clouds. II. Doses produced by cosmic rays. *Astrophysics* **2011**, *54*, 87-99.
- (14) Wang, J.; Marks, J. H.; Turner, A. M.; Nikolayev, A. A.; Azyazov, V.; Mebel, A. M.; Kaiser, R. I. Mechanistical study on the formation of hydroxyacetone ( $\text{CH}_3\text{COCH}_2\text{OH}$ ), methyl acetate ( $\text{CH}_3\text{COOCH}_3$ ), and 3-hydroxypropanal ( $\text{HCOCH}_2\text{CH}_2\text{OH}$ ) along with their enol tautomers (prop-1-ene-1,2-diol ( $\text{CH}_3\text{C}(\text{OH})\text{CHOH}$ ), prop-2-ene-1,2-diol ( $\text{CH}_2\text{C}(\text{OH})\text{CH}_2\text{OH}$ ), 1-methoxyethen-1-ol ( $\text{CH}_3\text{OC}(\text{OH})\text{CH}_2$ ) and prop-1-ene-1,3-diol ( $\text{HOCH}_2\text{CHCHOH}$ )) in interstellar ice analogs. *Phys. Chem. Chem. Phys.* **2023**, *25*, 936-953.
- (15) Wang, J.; Zhang, C.; Eckhardt, A. K.; Kaiser, R. I. Interstellar formation of 1,2-propanediol ( $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OH}$ ) and 1,2-ethenediol ( $\text{HOCHCHOH}$ )—key precursors to sugars and sugar derivatives. *Chem. Sci.* **2025**, *16*, 21111-21120.

- (16) Wang, J.; Inada, S.; Zhang, C.; Marks, J. H.; Wang, Z.; Bergantini, A.; McAnally, M.; Eckhardt, A. K.; Kaiser, R. I. Abiotic formation of nitrile precursors to amino acids and nucleobases in interstellar ice analogues. *Chem. Sci.* **2026**, *17*, 4966–4977.
- (17) Bottger, G. L.; Jr., D. F. E. Infrared spectra of crystalline  $C_2H_2$ ,  $C_2HD$ , and  $C_2D_2$ . *J. Chem. Phys.* **1964**, *40*, 2010-2017.
- (18) Doney, K. D.; Zhao, D.; Stanton, J. F.; Linnartz, H. Theoretical investigation of the infrared spectrum of small polyynes. *Phys. Chem. Chem. Phys.* **2018**, *20*, 5501-5508.
- (19) Socrates, G. *Infrared and raman characteristic group frequencies: Tables and charts*; 3rd ed.; John Wiley & Sons, Ltd.: New York, 2004.
- (20) Tørnøng, E.; Nielsen, C. J.; Klæboe, P.; Hopf, H.; Priebe, H. The i.r., Raman and microwave spectra of 1-butene-3-yne (vinylacetylene) and 1-butene-3-yne-4d. *Spectrochim. Acta A*. **1980**, *36*, 975-987.
- (21) Stroh, F.; Winnewisser, M. Isocyanogen, CNCN: Infrared and microwave spectra and structure. *Chem. Phys. Lett.* **1989**, *155*, 21-26.
- (22) Blanch, R. J.; McCluskey, A. XCN (X = Cl, Br and I): a novel source of isocyanogen. *Chem. Phys. Lett.* **1995**, *241*, 116-120.
- (23) Gerakines, P. A.; Moore, M. H.; Hudson, R. L. Ultraviolet photolysis and proton irradiation of astrophysical ice analogs containing hydrogen cyanide. *Icarus* **2004**, *170*, 202-213.
- (24) Shimanouchi, T. *Tables of molecular vibrational frequencies Consolidated Volume I*; National Bureau of Standards, 1972.
- (25) Nna-Mvondo, D.; Anderson, C. M. Infrared spectra, optical constants, and temperature dependences of amorphous and crystalline benzene ices relevant to Titan. *Astrophys. J.* **2022**, *925*, 123.
- (26) Hudson, R. L.; Gerakines, P. A.; Yarnall, Y. Y.; Coones, R. T. Infrared spectra and optical constants of astronomical ices: III. Propane, propylene, and propyne. *Icarus* **2021**, *354*, 114033.
- (27) Hudson, R. L.; Yarnall, Y. Y. Infrared spectra and optical constants of astronomical ices: IV. Benzene and pyridine. *Icarus* **2022**, *377*, 114899.
- (28) Brock, A.; Mina-Camilde, N.; Manzanares, C. Vibrational spectroscopy of C-H bonds of  $C_2H_4$  liquid and  $C_2H_4$  in liquid argon solutions. *J. Phys. Chem.* **1994**, *98*, 4800-4808.
- (29) Comeford, J. J.; Gould, J. H. Infrared spectra of solid hydrocarbons at very low temperatures. *J. Mol. Spectrosc.* **1961**, *5*, 474-481.
- (30) P. J. Linstrom; Mallard, W. G. NIST Chemistry WebBook; NIST standard reference database number 69, 2013. <https://webbook.nist.gov/>
- (31) Abplanalp, M. J.; Kaiser, R. I. Implications for extraterrestrial hydrocarbon chemistry: Analysis of acetylene ( $C_2H_2$ ) and D2-acetylene ( $C_2D_2$ ) ices exposed to ionizing radiation via ultraviolet-visible spectroscopy, infrared spectroscopy, and reflectron time-of-flight mass spectrometry. *Astrophys. J.* **2020**, *889*, 3.
- (32) Kleimeier, N. F.; Liu, Y.; Turner, A. M.; Young, L. A.; Chin, C.-H.; Yang, T.; He, X.; Lo, J.-I.; Cheng, B.-M.; Kaiser, R. I. Excited state photochemically driven surface formation of benzene from acetylene ices on Pluto and in the outer solar system. *Phys. Chem. Chem. Phys.* **2022**, *24*, 1424-1436.
- (33) Sheppard, N. The assignment of the vibrational spectra of the  $C_4$  hydrocarbons butyne-1, butene-1, and vinyl acetylene, to the normal modes of vibration of these molecules. *J. Chem. Phys.* **1949**, *17*, 74-78.

(34) Zhou, L.; Zheng, W.; Kaiser, R. I.; Landera, A.; Mebel, A. M.; Liang, M.-C.; Yung, Y. L. Cosmic-ray-mediated formation of benzene on the surface of Saturn's moon Titan. *Astrophys. J.* **2010**, *718*, 1243.