

Formation pathways of proteins in space

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1 **Formation pathways of proteins in space**

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10 The Netherlands.

11 **Until now, experiments demonstrated the possible formation of relatively small prebiotic**
12 **molecules under typical space conditions. We demonstrated experimentally that**
13 **condensation of atomic carbon on the surface of cold solid particles (cosmic dust) leads to**
14 **the formation of monomeric fragments of polyglycine. These fragments polymerize**
15 **effectively producing polypeptides. The chemistry involves three of the most common**
16 **species (CO, C, and NH₃) present in star-forming molecular clouds. It proceeds via a novel**
17 **pathway that skips the stage of amino acids formation in protein synthesis and is effective**
18 **even at low temperatures without irradiation or presence of water. Therefore, the amount**
19 **of proteins formed in space through this process could be quite substantial. The delivery of**
20 **proteins to rocky planets in the habitable zone might be an important element for the**
21 **origin of life.**

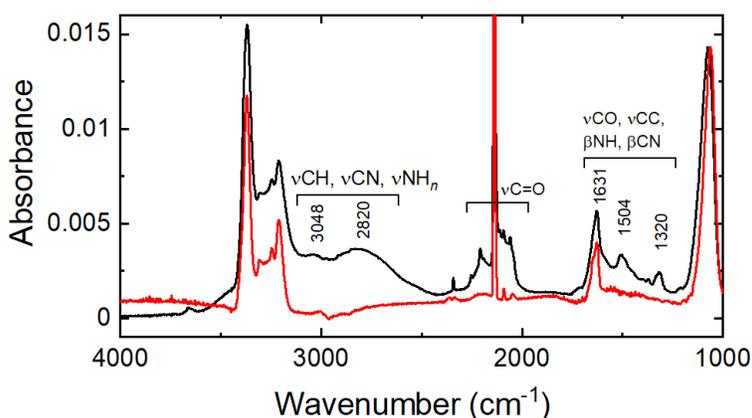
22 The origin of life has always been one of the most intriguing questions throughout human
23 history. Biomolecules delivered to early Earth by asteroids or comets during the period of heavy
24 bombardment about four billion years ago have been proposed to play a role in the origin of life
25 ^{1,2}. Similar processes may apply to rocky exoplanets. Analysis of meteoritic materials led to the
26 identification of amino acids, sugars, and nucleobases, among other complex organic molecules
27 of extraterrestrial origin ³. The amino acid glycine has been discovered in comets ⁴. The widely
28 accepted hypothesis of the formation of organic molecules in space assumes their synthesis in ice
29 mantels covering the refractory dust grains present in space ⁵. At later stages when asteroids are
30 formed from this dust, the chemistry in liquid water may also enhance the molecular complexity
31 ⁶. Experimentally, the formation of a variety of amino acids, and even their dimers as well as
32 other organic molecules, was detected after energetic processing of different molecular ices ^{7,8}.
33 These experiments are comparable to Urey-Miller-type experiments performed at elevated
34 temperatures ⁹. The non-energetic pathway was also found for different small organic molecules
35 ^{10,11} and even glycine ^{12,13}. However, till now, only very small fragments of biopolymers were
36 found to be formed in these experiments.

37 The formation of peptides and proteins is usually considered as a polymerization process of
38 amino acids. This process requires the condensation of amino acids accompanied by the loss of
39 water. This is a thermodynamically unfavourable process and, therefore, it proceeds at high
40 temperatures under the assistance of catalysts or requires energetic processing of the material ¹⁴.
41 Therefore, the prebiotic synthesis of peptides is thought to occur in two steps, each of which has
42 a low probability ¹⁵. Instead of first synthesizing amino acids in order to subsequently break them
43 down for the polymerization process, we suggest a very efficient and direct formation of the
44 monomeric fragments of peptides and its further polymerization. This reaction between NH_3 , C,

45 and CO occurs on the cold dust grains, without external energy. Quantum chemical calculations
46 predict that the $\text{CO} + \text{C} + \text{NH}_3 \xrightarrow{\text{surface}} \text{NH}_2\text{CH}=\text{CO}$ reaction is barrierless¹⁶. The polymerization
47 of $\text{NH}_2\text{CH}=\text{CO}$ results in the formation of peptide chains. In contrast to the polymerization of the
48 amino acids, the polymerization of $\text{NH}_2\text{CH}=\text{CO}$ is a much simpler process.
49 To test this reaction pathway experimentally, we performed co-deposition of these species on the
50 surface of both Si and KBr substrates cooled to 10K and placed inside an ultra-high vacuum
51 (UHV) chamber. Low-energy carbon atoms were generated by a dedicated atomic carbon source
52¹⁷. The background pressure inside the vacuum chamber (1×10^{-10} mbar) and the temperature of
53 the substrate (10 K) allowed us to mimic dense molecular cloud conditions.

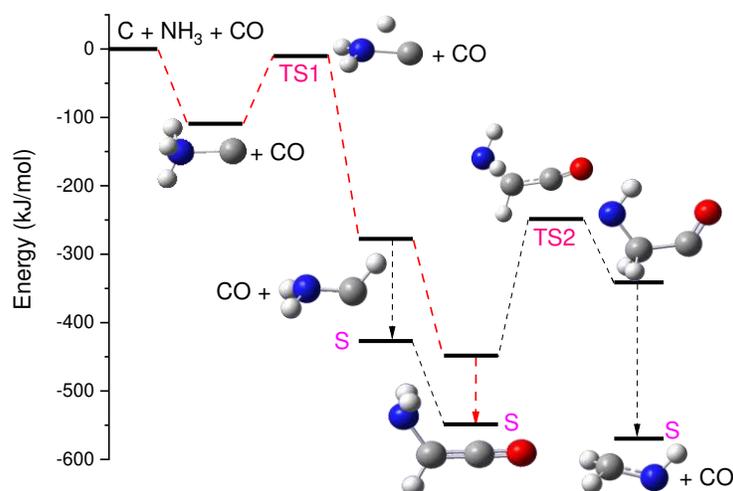
54 **Low-temperature chemistry, $T = 10$ K**

55 Infrared absorption spectra of the ice produced after the co-deposition of $\text{CO} + \text{NH}_3$ and $\text{CO} + \text{C}$
56 + NH_3 are shown in Figure 1. The addition of C atoms during the deposition leads to the
57 appearance of new absorption peaks. The control experiments involving only two reactants C +
58 CO and C + NH_3 are given in the supplementary materials (see Figures S1, S2, S3).



59
60 **Figure 1.** IR absorption spectra of the material produced by co-deposition of $\text{CO} + \text{NH}_3$ (red)
61 and $\text{CO} + \text{C} + \text{NH}_3$ (black).

62 The deposition of all three reactants (CO, C, NH₃) on the substrate at 10 K reveals new IR
63 absorption bands, which were not observed in any experiment involving only two reactants.
64 Therefore, these bands have to be assigned to a product formed by all three reactants. Moreover,
65 we observed only negligible amounts of the residue at 300 K in the experiments involving only
66 two reactants. Thus, we conclude that during the deposition at 10 K, the reaction involves all
67 three reactants, and exactly the product of this reaction is required for the formation of the non-
68 volatile products at 300 K.



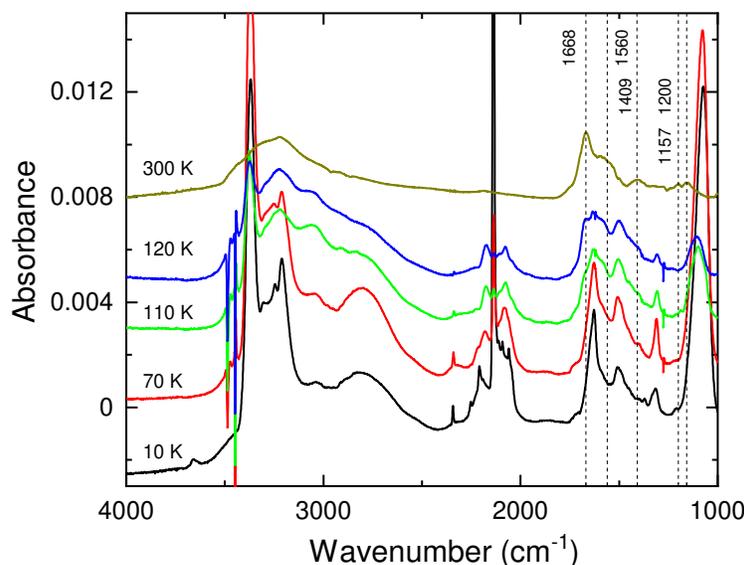
69
70 **Figure 2.** Energy level diagram for the reaction involving CO, C, and NH₃ reactants. The
71 reaction starts with the triplet state. The transition states and the singlet states are marked with
72 TS and S, respectively. The dashed lines show the possible reaction pathways and the red colour
73 marks the most probable one.

74 To better understand the chemistry of all three reactants at 10K, we performed quantum-
75 chemical calculations. Their results are shown in Figure 2. The C atom initially prefers to react
76 with the ammonia molecule. The pathway of this reaction was studied experimentally¹³ using
77 the recently developed calorimetric technique¹⁸. The overcome of the first transition state was
78 confirmed. The NH₂CH reacts barrierlessly with CO leading to the formation of NH₂CH=CO.
79 Therefore, there are two most possible products of this reaction - NH₂CH=CO and (CH₂NH +

80 CO). The last one is the same as the product of the reaction $C + NH_3$. Therefore, the reaction of
81 three reactants results in the formation of the $NH_2CH=CO$ product at 10 K. The formation of this
82 molecule is also confirmed later during the temperature-programmed desorption (TPD) by
83 monitoring the ions with the masses of 57 and 56 u (see Figure S4). At the same time, a number
84 of C atoms could react with either CO or NH_3 only. It could lead to the formation of some
85 number of CCO as well as H_2CNH and $NH_2CH_2NH_2$ molecules.

86 Chemical transformation during temperature rise

87 After the deposition, the substrate was heated with a rate of 2 K per min. The IR spectra
88 measured at important temperatures are shown in Figure 3.



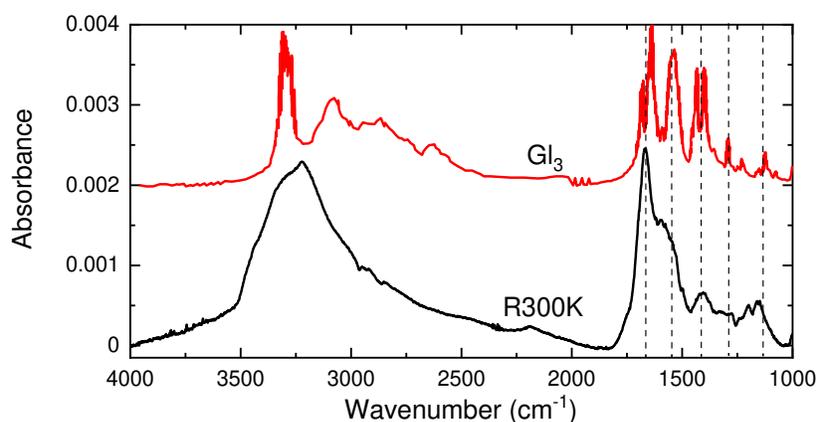
89
90 **Figure 3.** IR absorption spectra during the annealing of the material produced by co-deposition
91 of CO + C + NH_3 . Vertical numbers show the positions of the peaks appearing during heating,
92 while horizontal ones displays the temperature of the substrate.

93 The comparison of the spectra at 10 K and 70 K shows that the evaporation of carbon monoxide,
94 started at about 30 K, does not initiate a new chemistry. However, with evaporation of ammonia,
95 the products of the C atom reactions can finally meet each other and react. We observed the
96 formation and growth of new IR absorption bands 1668, 1560, while the intensity of the νNH_n

97 bands $\nu\text{C=O}$ bands decreased significantly. With the mass spectrometer we did not detect any
98 considerable desorption from the substrate besides CO and NH₃ gases. Therefore, the
99 disappearance of the IR bands is rather due to the chemical transformation than the evaporation
100 of the corresponding material. The decrease in the intensity of bands in the 2800 – 3050 cm⁻¹
101 range is a common indication of the glycine polymerization¹⁹. This takes place because the
102 NH₃⁺ or NH₂ groups of glycine are transformed into NH groups present in peptides. Additionally,
103 the C=O stretching vibration in NH₂CH=CO disappears and we observe the formation of the
104 amide I band at 1668 cm⁻¹ CO stretching and amide II at 1560 cm⁻¹, which are characteristic for
105 the peptide bond. After complete ammonia evaporation, no considerable changes in the IR
106 spectra were observed. Therefore, the material present on the substrate after warming up to
107 300 K (R300K) should have been formed at low temperature during ammonia evaporation.

108 **Characterization of the room temperature residue**

109 The characterization of R300K was performed using both in situ FTIR spectroscopy and ex situ
110 high-resolution mass spectrometry. Due to a very high resolution, the mass spectrometry
111 provides exact data on elemental compositions of molecules in the low and middle mass ranges,
112 while the IR spectroscopy shows the type of bonds present in these molecules. Analysis of these
113 experimental data in combination with the information about the molecules formed at $T = 10$ K,
114 allows us to draw the conclusions about the R300K material.

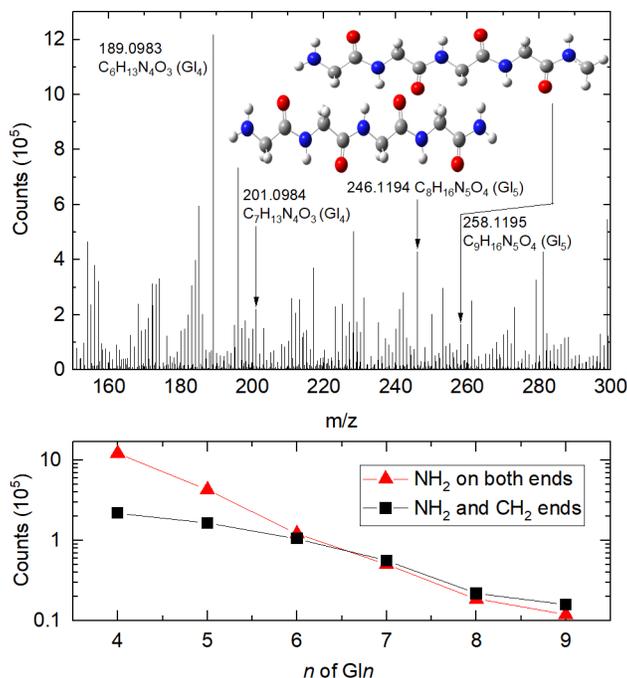


115

116 **Figure 4.** Comparison of the IR absorption spectra of R300K and triglycine (GI₃) adopted from
 117 ref 20. The vertical dashed lines are drawn to visualize the coincidences between the peaks in
 118 two spectra.

119 The IR spectrum of R300K is shown in Figure 4. It highlights the absorption features
 120 characteristic for the peptide bond. As can be seen, the spectra of R300K resemble the spectra of
 121 the glycine peptide quite closely. The main difference is a much higher width of absorption
 122 bands observed in the spectra of the R300K. This broadening is assigned to the formation of
 123 peptide chains of different lengths, which is also detected by the mass spectrometry, which we
 124 present later. It has been shown that the IR absorption band positions and intensities change
 125 notably with the number of units in the glycine oligomers²⁰. Moreover, the molecular structure
 126 of the peptide terminal groups formed in our experiments is not completely known. The
 127 polymerization of NH₂CH=CO molecules with the formation of peptide chains requires the
 128 proton transfer from nitrogen to the carbon atom of the CH group. At the same time, our DFT
 129 calculations show that NHCH₂CO as well as NH₂CHCO-NHCH₂CO molecules are not stable.
 130 They fragment by abstraction of the CO molecule. Therefore, the calculations predict that the
 131 peptide chains produced by this mechanism are terminated by NH₂ on one side, which
 132 corresponds to the classical structure of the peptide. On the other peptide side, instead of having

133 a classical COOH group, it is terminated by the CH₂ group. This should also affect the IR spectra
134 in particular in the case of short chains.



135
136 **Figure 5.** The mass spectra of the 300 K residue obtained from ex situ analysis using ESI-
137 Orbitrap mass spectrometer. The molecular structures displayed resemble the Gl₅ peptides
138 detected in the mass spectra as protonated species [analyte+H]⁺. In the lower frame, the
139 intensities of the bands from mass spectrum corresponding to the glycine peptides are plotted as
140 a function of the peptide length.

141 Ex situ mass spectrum of R300K is shown in Figure 5. We could identify a series of mass peaks,
142 which corresponds to the theoretically expected structures of the peptides terminated by NH₂ and
143 CH₂ groups starting from the glycine tetramer up to the glycine nonamer. The peaks are
144 separated by the mass of 57.0215 u. This value exactly matches the mass of the NH₂CH=CO
145 molecule, which was also detected by in situ mass spectrometry. However, the observed series is
146 not the most intense one. The most intense peak (189.0983 u) in the mass spectrum belongs to
147 the glycine tetramer terminated on both sides with NH₂ groups. We can also identify the series of
148 mass peaks corresponding to such a structure up to the glycine nonamer, and other series of mass
149 peaks separated always by 57.0215 u. For example, the series that exactly corresponds to the

150 masses of the $(\text{NH}_2\text{CHCO})_n$ molecules as well as the NH_2/NH_2 terminated peptides with addition
151 of C_2 , H_2 , and C_3H were detected. The complete list of all found series is given in the
152 supplementary materials. The formation of a variety of different peptides can be understood
153 assuming that the oligomerized NH_2CHCO molecules contain reactive sites. In the expected
154 dimer $\text{NH}_2\text{CHCO-NHCH}_2$, the C atoms in CH and CH_2 groups are not saturated and could join
155 other species. Therefore, other products formed at 10 K could be added during the polymer
156 formation. More complex chemistry could take place during the solvation. However, as most of
157 main peaks in the mass spectrum belong to the series, where peaks are separated by 57.0215 u,
158 we conclude that the polymerization of the $\text{NH}_2\text{CH=CO}$ molecule is the main chemical pathway
159 in our experiment.

160 The polymerization of $\text{NH}_2\text{CH=CO}$ requires the nucleophilic attack of the nitrogen on the
161 carbonyl carbon and an intramolecular proton transfer from NH_2 to CH. Our DFT computations
162 show a large barrier of about 240 KJ mol^{-1} for the proton transfer from NH_2 to the CH group in
163 the isolated $\text{NH}_2\text{CH=CO}$ molecule. Therefore, the polymerization is expected to take place either
164 with the action of a catalyst, which could be ammonia molecules, or by proton transfer via
165 tunnelling. The tunnelling could be quite efficient due to the quantum nature of the proton
166 motion. Even at room temperatures, the role of the tunnelling was found to be significant in a
167 variety of intramolecular proton transfer reactions²¹. The efficient polymerization of the
168 $\text{NH}_2\text{CH=CO}$ molecule at low temperatures is in line with the fact that this molecule, to the best
169 of our knowledge, has never been observed in experimental studies. As the isolated molecule is
170 predicted to be stable, their non-detection in previous experiments should be assigned to a high
171 reactivity of this molecule.

172 **Implications**

173 The reactants used in the current study are among the most abundant species present in the
174 interstellar medium (ISM). The fractional abundance of NH₃ and CO in the ice mantels covering
175 refractory dust particles amounts to up 10% and 40%, respectively²². More than 50% of all
176 carbon in the ISM exist in the form of atomic gas²³. Therefore, reactions between CO, C, and
177 NH₃ could be very common. This is a static point of view. In dynamic terms, the reactions of C
178 atoms become even more important. The carbonaceous stardust is expelled in the ISM by dying
179 stars. In the ISM, the stardust is atomized by shockwaves of supernova explosions²⁴⁻²⁶.
180 Therefore, the dust, from which planets, asteroids, and comets will be formed at later stages, has
181 to be formed in the ISM due to the accretion of gaseous species. The C atoms could be converted
182 to the molecular form before the accretion. However, this is a relatively long process²⁷.
183 Therefore, a notable portion of carbonaceous dust is expected to be formed by the accretion of C
184 atoms. This leads to the formation of organics²⁸. As revealed by the current study, a notable
185 portion of this organics could be in the form of peptides. This dust becomes building blocks of
186 comets or meteorites. Therefore, the formed organics can be delivered to early Earth during the
187 period of a heavy bombardment. An important issue is the stability of the formed organics and
188 whether it can be delivered to planets. In this matter, the spontaneous - non energetic way of the
189 peptide formation is a big advantage. If gas to solid phase transition occurs in the ISM in the
190 areas of a low UV flux, the formed proteins can survive long enough and finally be incorporated
191 into bulk solids, which would protect them. The fact that they can survive and be delivered to
192 planets is demonstrated by two very recent publications showing the presence of proteins in
193 meteorites^{29,30}. Proteins and organics can be preserved even better in most pristine and
194 unprocessed material present in comets. They might deliver intact organics produced in the ISM
195 at a rate of at least 10⁶ to 10⁷ kilograms per year². At the same time, peptides play a key role in

196 the origin of life¹⁵. Therefore, the delivery of proteins to Earth should expand the opportunities
197 for the origin of life. Thus, the conditions, under which the origin of life was commonly
198 considered to be possible, should be revised. A large variety of peptides formed in this way could
199 considerably increase a chance that the molecules required for the chemistry leading to
200 abiogenesis will be formed. Therefore, the low-temperature chemistry that happens between the
201 stars could go a long way towards the origin of life on Earth and exoplanets.

202 **Methods**

203 **In situ experiments.** The experiments were performed using the ultrahigh vacuum (UHV) setup,
204 INterStellar Ice Dust Experiment (INSIDE), described elsewhere³¹. We performed co-deposition
205 of CO, C, and NH₃ reactants on the surface of KBr substrates cooled to 10K and placed inside an
206 ultra-high vacuum (UHV) chamber. The deposition of reactants was performed for about one
207 hour. Low-energy carbon atoms were generated by an atomic carbon source¹⁷. The source
208 generates pure flux of low-energy carbon atoms in the triplet ground state C(³P_J). The
209 background pressure inside the vacuum chamber (1×10^{-10} mbar) and the temperature of the
210 substrate (10 K) allowed us to mimic dense molecular cloud conditions. We used about equal
211 amounts of CO and NH₃ molecules, while the number of C atoms was at least ten times smaller.
212 This small amount of C atoms allows to exclude their reactions with each other as well as with
213 their reaction products. The gases were introduced through two separated gas lines. The ice
214 thicknesses on substrates were monitored by infrared (IR) spectroscopy. IR spectra were
215 measured using an FTIR spectrometer (Vertex 80v, Bruker) in the transmission mode. In situ
216 mass spectra were measured by a quadrupole mass spectrometer (HXT300M, Hositrad) located
217 in the same UHV chamber. After the deposition, the substrate was heated with a rate of 2 K per
218 min. During the warming up process of the material, the IR absorption spectra of the deposit as

219 well as the mass spectra of the species released to the gas phase were measured. The TPD curves
220 were obtained by integrating the area of the corresponding bands in the IR and mass spectra.

221 **Ex situ mass spectrometry analysis.** For the mass spectrometry analysis, we used silicon
222 substrates and performed a 4-hours deposition of CO, C, and NH₃ reactants at the same
223 conditions as in the in situ experiments. We obtained very similar IR spectra on all stages of the
224 experiment, using both Si and KBr substrates. The main difference in the IR spectra of these two
225 substrates was the appearance of Si absorption features during the TPD. Therefore, they were not
226 used for in situ analysis. After warming up, the substrates were left overnight in the UHV
227 chamber, after which they were removed and analysed. The residue was extracted with a
228 water/methanol mixture (70/30) and provided for the mass spectral analysis. The mass
229 spectrometry was performed using the hybrid linear trap/Orbitrap mass spectrometer (Thermo
230 fisher QExactive plus mass spectrometer with a heated ESI source). The accuracy of the mass
231 determination is higher than 5 ppm, which, for the investigated mass range, means a possible
232 error only in the fourth decimal place. Considering the limited number of elements used in the
233 experiments (C, O, N, and H), this high resolution allows to define unambiguously the elemental
234 composition of the detected ions in the mass range shown in Figure 5. To ensure that the
235 observed mass peaks are due to the material formed in our experiment, the possible presence of
236 contaminants both on the substrate and in the mass spectrometer were checked using the same
237 procedure with clean silicon substrates.

238 **Quantum-chemical computations.** Molecular geometries of the reactants and products of
239 chemical reactions were determined at B3LYP/6-311+G (d,p) level as implemented in the
240 GAUSSIAN16³². The reaction energies were found as the difference between the sum of the
241 energies of reactants and the energy of the product molecules with vibrational zero-point energy

242 corrections. The two dimensional potential energy scan of the CO + C + NH₃ reaction was
243 performed at MP2/6-311+G (d, p) level.

244

245 **Data availability.** The data that support the plots within this paper and other findings of this
246 study are available from the corresponding author upon reasonable request.

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317 **Author contributions**

318 S.K. initiated and led the project, S.K. and K.J.C. recorded and analysed the experimental data.
319 S.K. performed the computations and wrote the manuscript. N.U. performed ex situ mass
320 spectrometry. T.H. and C.J. participated in data interpretation and discussion. All authors
321 contributed to the writing of the manuscript.

322 **Competing interests**

323 The authors declare no conflict of interest.

Figures

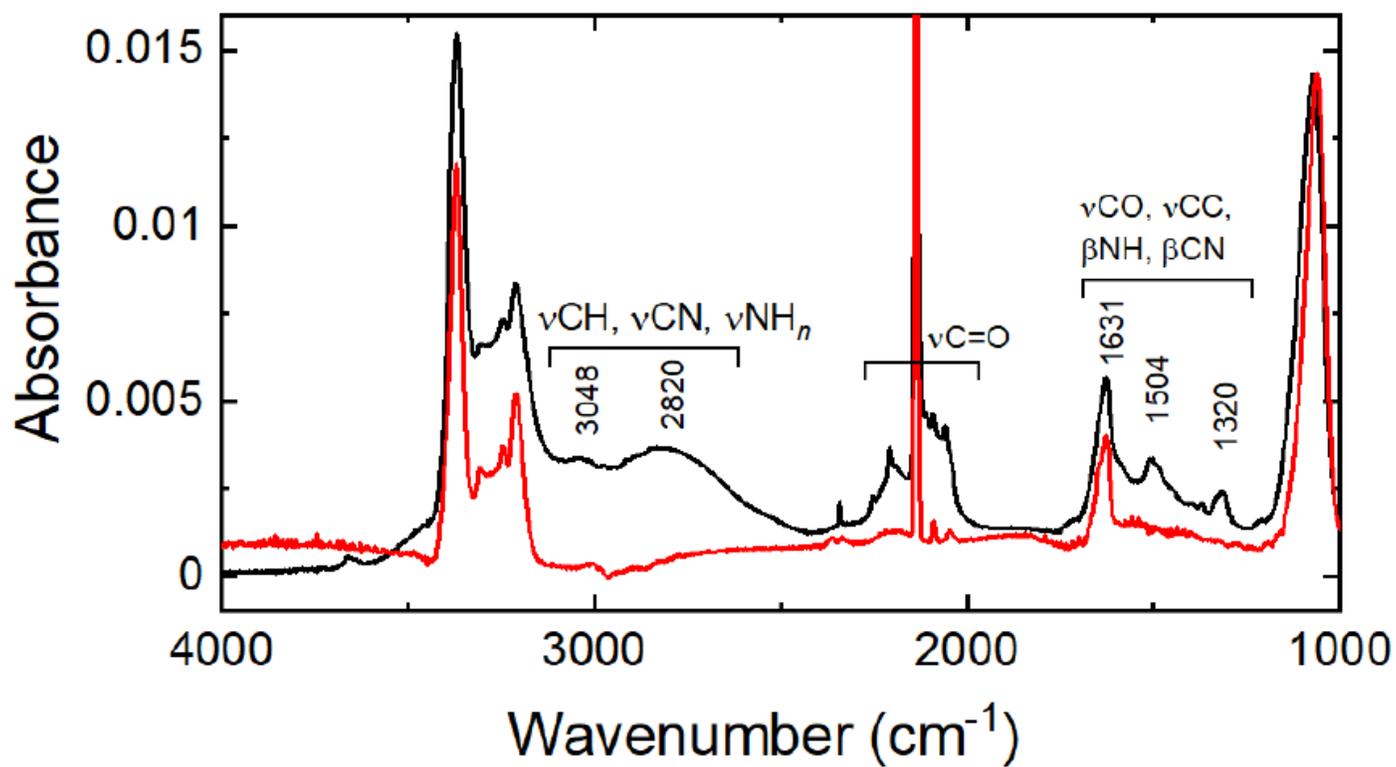


Figure 1

IR absorption spectra of the material produced by co-deposition of CO + NH₃ (red) and CO + C + NH₃ (black).

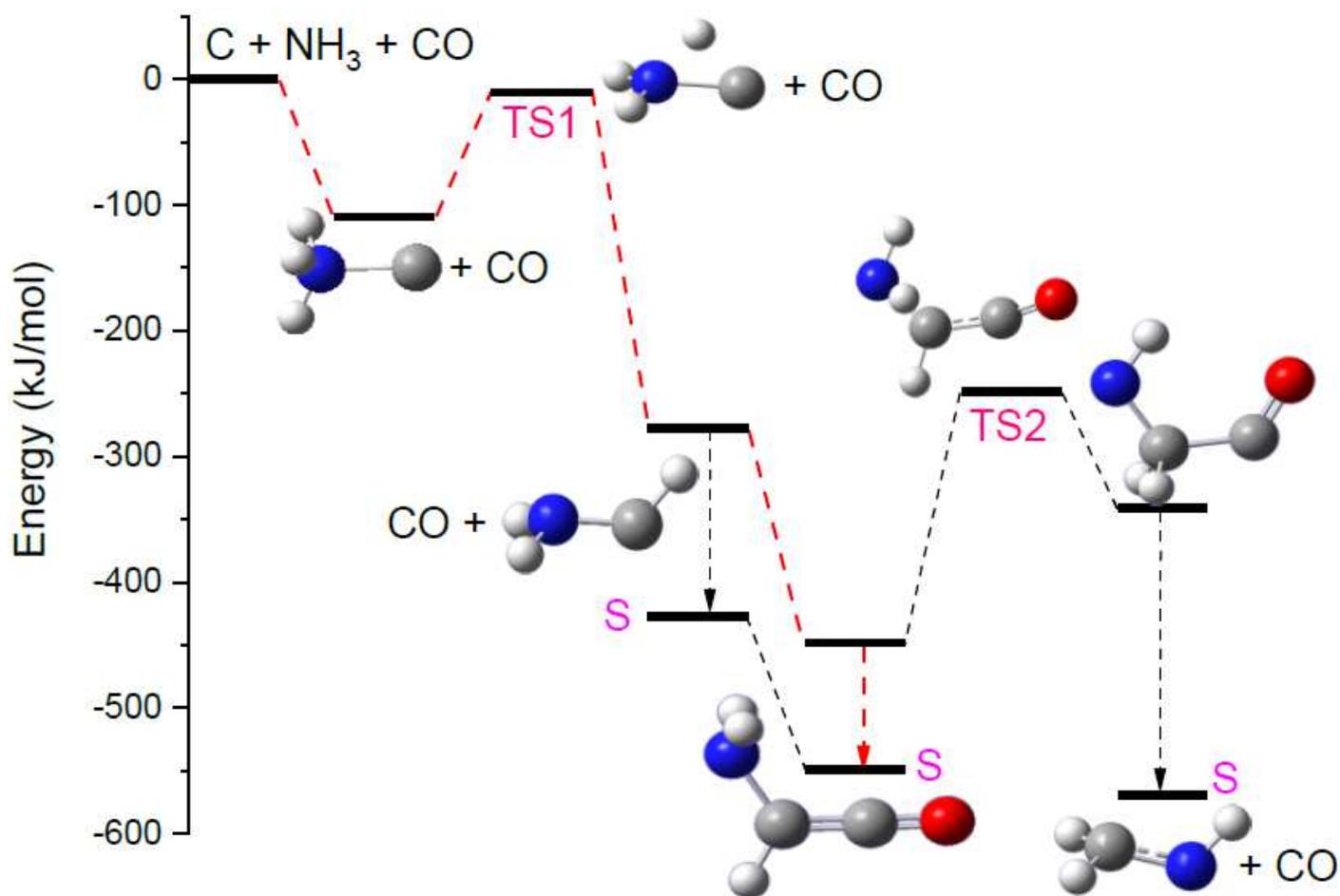


Figure 2

Energy level diagram for the reaction involving CO, C, and NH₃ reactants. The reaction starts with the triplet state. The transition states and the singlet states are marked with TS and S, respectively. The dashed lines show the possible reaction pathways and the red colour marks the most probable one.

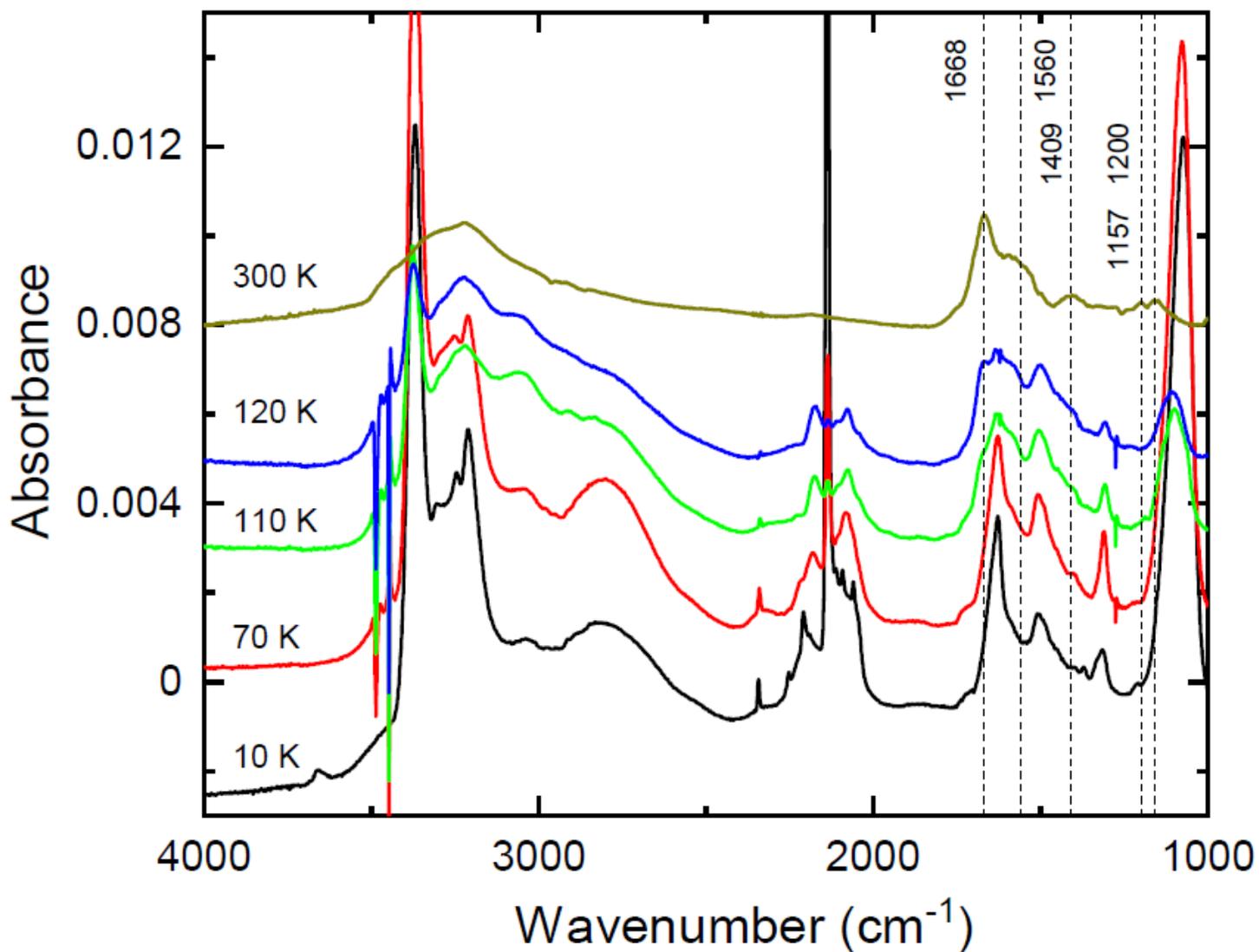


Figure 3

IR absorption spectra during the annealing of the material produced by co-deposition of CO + C + NH₃. Vertical numbers show the positions of the peaks appearing during heating, while horizontal ones displays the temperature of the substrate.

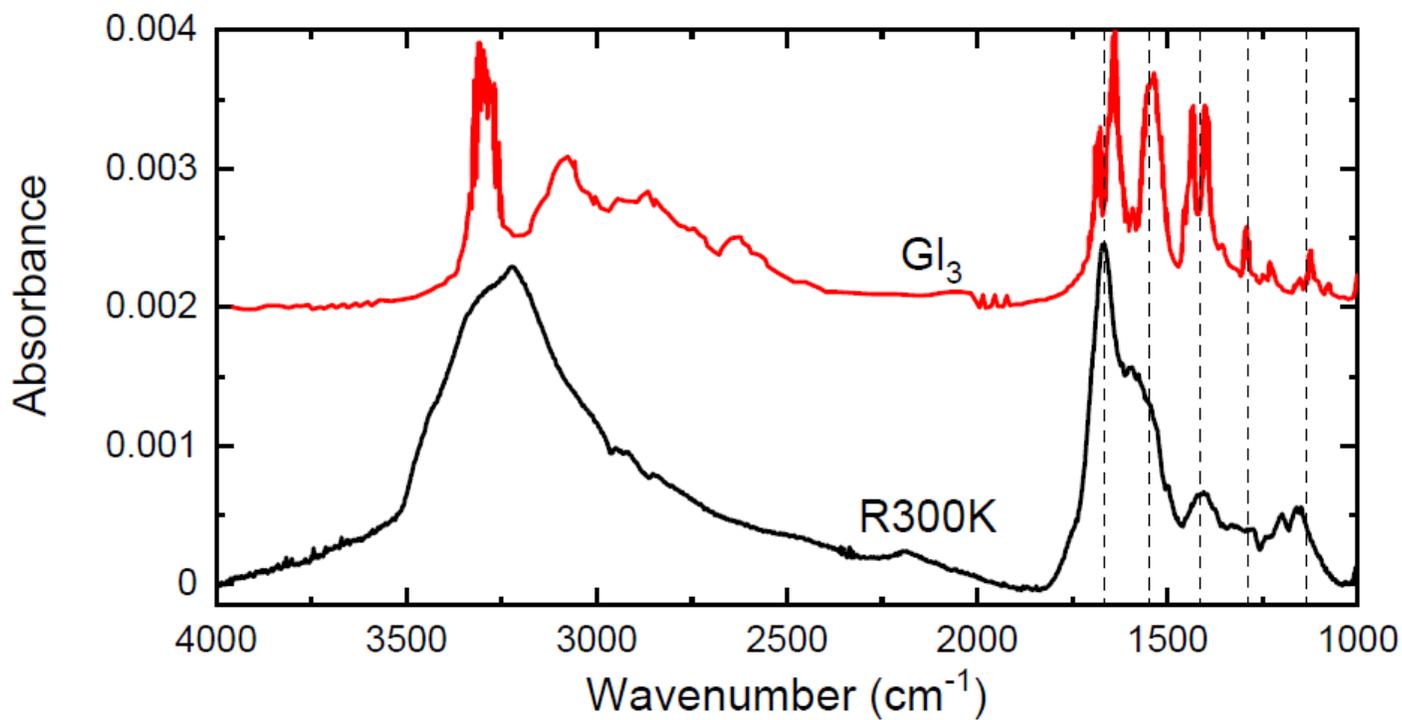


Figure 4

Comparison of the IR absorption spectra of R300K and triglycine (GI₃) adopted from ref 20. The vertical dashed lines are drawn to visualize the coincidences between the peaks in two spectra.

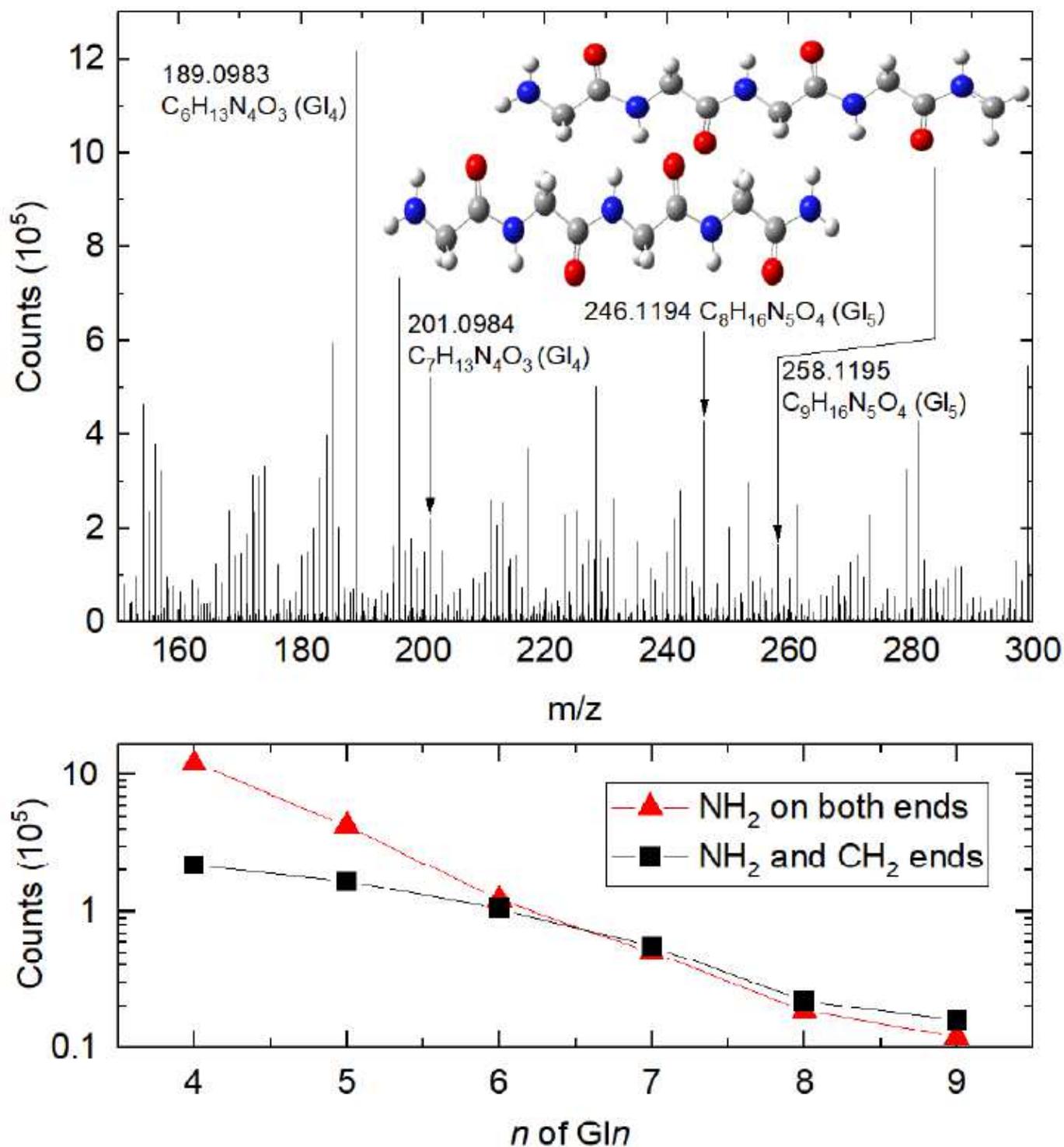


Figure 5

The mass spectra of the 300 K residue obtained from ex situ analysis using ESI-Orbitrap mass spectrometer. The molecular structures displayed resemble the GI_5 peptides 138 detected in the mass spectra as protonated species $[analyte+H]^+$. In the lower frame the intensities of the bands from mass spectrum corresponding to the glycine peptides are plotted as a function of the peptide length.

Supplementary Files

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