Formation of glycine on ultraviolet-irradiated interstellar ice-analogue films and implications for interstellar amino acids

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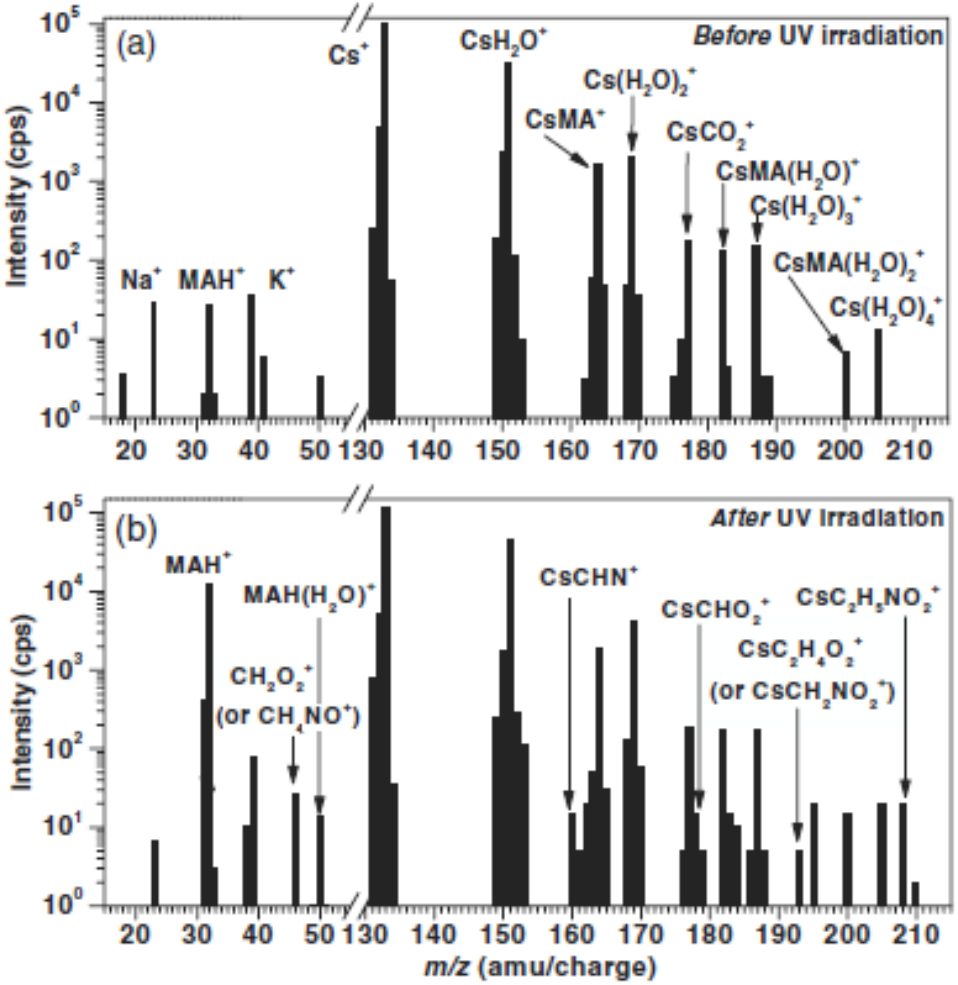
➢ Introduction

❖ Organic molecules in extraterrestrial space may have provided essential feedstock for prebiotic chemistry on Earth and played an important role in the origin and evolution of life.

❖ In the outer space meteorites are rich source of extraterrestrial amino acids.

❖ In the interstellar medium (ISM), amino acids or their precursors may form via specific gas-phase reactions or via solid-phase reactions on dust grain surfaces, stimulated by external energy sources such as ultraviolet (UV) radiation or ion bombardment.

❖ Amino acids cannot accumulate in large quantities in the gas-phase ISM under interstellar UV radiation.



Assignments of Photoproduct Signals in Figure 1(b)

m/z	Formula	Possible Structure
32	CH_6N^+	Methylammonium ion ($CH_3NH_3^+$)
46	$CH_2O_2^+$	Formic acid ion ($HCO_2H_2^+$)[a]
	CH_4NO^+	H_3NCHO^+
50	CH_8NO^+	$(CH_3NH_3^+)(H_2O)$
160	$Cs(CHN)^+$	Hydrogen cyanide, hydrogen isocyanide
178	$Cs(CHO_2)^+$	Hydrocarboxyl radical[a]
	$Cs(CH_3NO)^+$	H_2NCHO
193	$Cs(CH_2NO_2)^+$	$NHCO_2H$[a]
	$Cs(C_2H_4O_2)^+$	Acetic acid, methylformate
208	$Cs(C_2H_5NO_2)^+$	Glycine (NH_2CH_2COOH), methylcarbamic acid ($CH_3NHCOOH$), methylcarbamate (NH_2COOCH_3)

Fig. 1: LES and RIS signals appearing from an H_2O–ice film (5 ML thickness) adsorbed with CH_3NH_2 (0.3 ML) and CO_2 (0.2 ML). (a) Spectrum obtained before the irradiation with UV light. (b) Spectrum after UV irradiation for an exposure of 1 10^{17} photons cm^{-2}. The photochemical products are labeled in spectrum (*b).* The noise level in the spectrum is ~2 cps. The sample temperature was maintained at 56 K during gas adsorption, UV irradiation, and LES and RIS measurements.

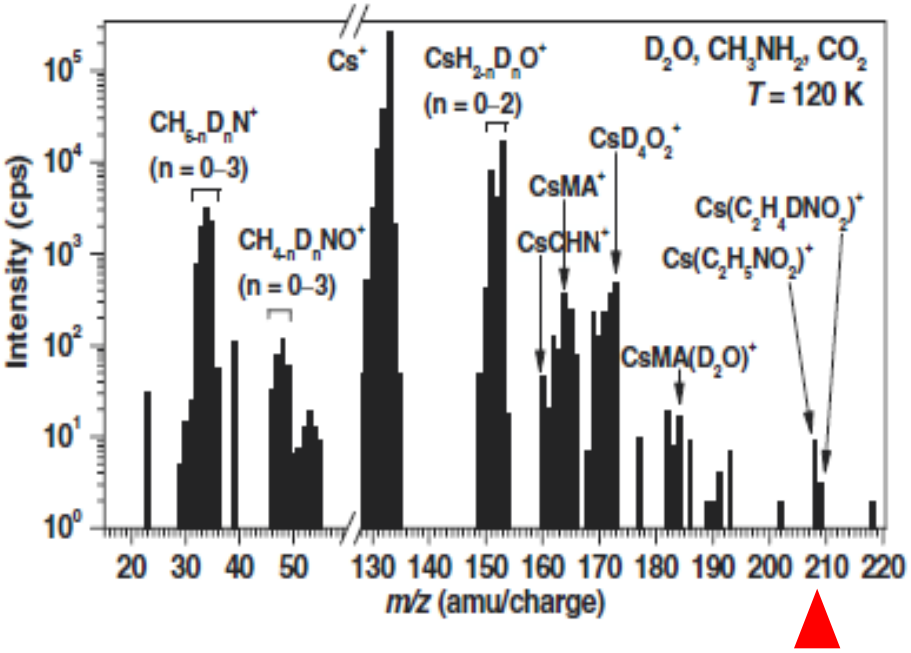


Fig. 2a: LES and RIS signals measured from a D_2O–ice film (5ML) adsorbed with CH_3NH_2 (0.3 ML) and CO_2 (0.2 ML). The sample was irradiated by
UV light at 56 K and then heated to 120 K before the measurement.

▶ m/z = 209 : d_1-glycine (NH_2CH_2COOD)
methyl-d_1-carbamic acid
($CH_3NHCOOD$)

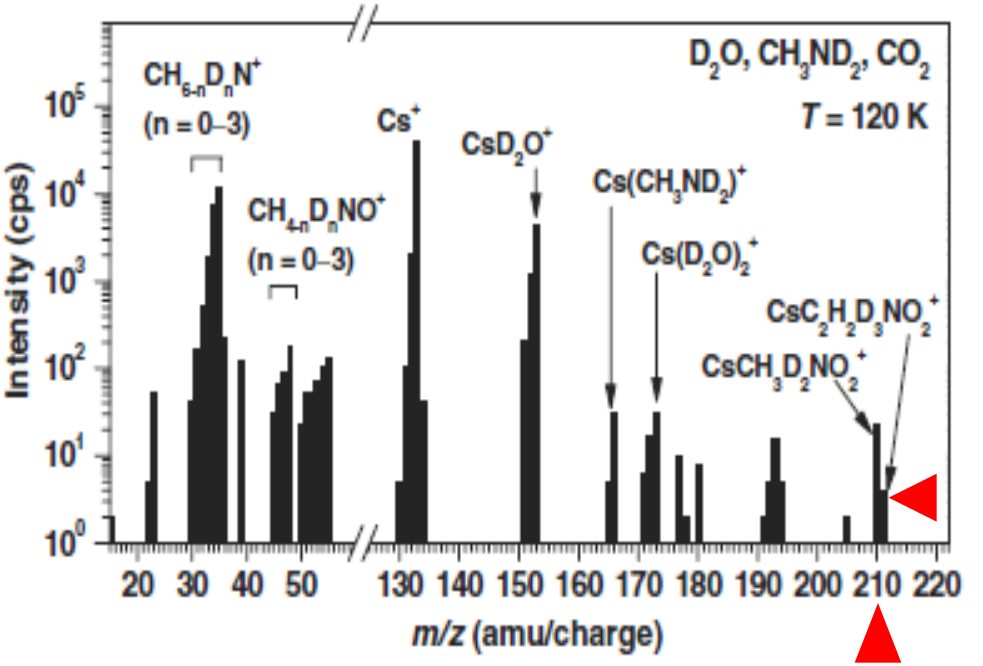
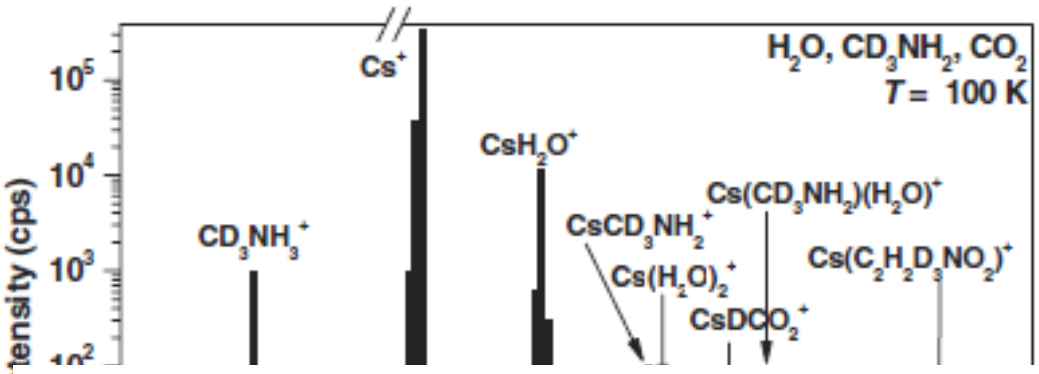
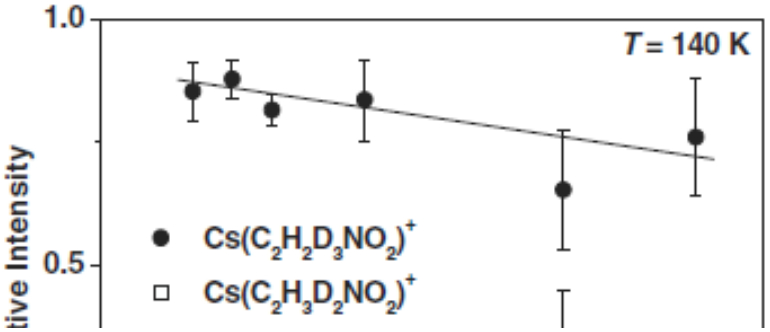


Fig. 2b: LES and RIS signals measured from a D_2O–ice film (5ML) covered with CH_3ND_2 (0.3 ML) and CO_2 (0.2 ML). The sample was irradiated with UV light at 56 K and then heated to 120 K.

▶ m/z = 210 : d_2-glycine (D_2NCH_2COOH)
methyl-d_2-carbamic acid
($CH_3NDCOOD$)
methyl-d_2-carbamte
($ND_2CO_2CH_3$)
m/z = 211 : d_3-glycine (D_2NCH_2COOD)





Samples	Observed Signals	Possible Products
(A) $CH_3NH_2 + CO_2$ on the D_2O film	$m/z = 208$	Glycine, methylcarbamic acid, methylcarbamate
	209 ($T \geqslant 120$ K)	Glycine, methylcarbamic acid
(B) $CH_3ND_2 + CO_2$ on the D_2O film	$m/z = 210$	Glycine, methylcarbamic acid, methylcarbamate
	211 ($T \geqslant 120$ K)	Glycine
(C) $CD_3NH_2 + CO_2$ on the H_2O film	$m/z = 210$ ($T \geqslant 120$ K)	Glycine
	211	Glycine, methylcarbamic acid, methylcarbamate

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ML) and CO_2 (0.2 ML). UV light was exposed with 1 10^{17} photons cm^{-2} at 56 K, and the sample was heated to 100 K before spectral acquisition. The noise level in the spectrum is ~2 cps.

a function of time at a temperature of 140 K.

▶ m/z = 211 : d_3-glycine (D_2NCH_2COOD)

➢ Proposed mechanism

1. $CH_3NH_2 + h\nu \rightarrow CH_2NH_2 + H^*$

2. $CO_2 + H^* \rightarrow HOCO$ ← m/z = 178 (slide 2)

3. $CH_2NH_2 + HOCO \rightarrow NH_2CH_2COOH$

4. $CH_3NH_2 + h\nu \rightarrow CH_3NH + H^*$

5. $CH_3NH + HOCO \rightarrow CH_3NHCOOH$

6. $CH_3NH_2 + h\nu \rightarrow CH_3 + NH_2$

7. $CO_2 + CH_3 \rightarrow CH_3OCO$

8. $NH_2 + CH_3OCO \rightarrow CH_3OCONH_2$

➢ Conclusion

1. Glycine and carbamic acid forms by UV irradiation of interstellar ice-analogue film consisting of water , methyl amine and CO_2 at low temperature.

2. Efficient photochemical synthesis of glycine occurs at ice surface.