

IR spectroscopic signatures of solid glycine and alanine in astrophysical ices

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Abstract

The conversion from solid neutral to zwitterionic glycine (or alanine) is studied using infrared spectroscopy from the point of view of the interactions of this molecule with polar (water) and non-polar (CO_2 , CH_4) surroundings. Such environments could be found on astrophysical matter. Different spectral features are suggested as suitable probes for the presence of glycine (or alanine) in astrophysical media, depending on their form (normal or zwitterionic), temperature, and composition.

1. Introduction

The identification of interstellar organic molecules is a subject of great interest, as they may provide important insights into the history of the solar system and the origin of life on Earth. Amino acids have been found in Solar System bodies and meteorites [1]. Cometary grains collected by the NASA Stardust mission have been shown to contain glycine [2] ($\text{NH}_2\text{CH}_2\text{COOH}$), the simplest of the amino acids and the most vastly studied and searched. The presence of alanine ($\text{CH}_3\text{CH}(\text{NH}_2)\text{COOH}$) in astronomical objects, which could have transported it to the Earth, is a finding directly related to the possible origin of life in our planet [3].

2. Experimental part

Our experimental setup consists on a high vacuum chamber provided with a closed cycle helium cryostat [4]. The system is coupled to a Bruker Vertex 70 FTIR spectrometer. Low temperature solid layers were prepared by deposition of sublimated vapours on a cold Si substrate. The amino acids were heated and evaporated by means of a home-made mini-oven located inside the vacuum chamber [4]. Mixed layers of glycine or alanine and the other components were prepared by introducing,

simultaneously with the amino acid, water vapour and CO_2 or CH_4 through an independent inlet. The temperature evolution of the different spectra was followed by heating the solid deposits generated at 25 K with a 5 K min^{-1} ramp up to 200 K.

3. Results and discussion

Figure 1 represents the spectra recorded at the deposit temperature of 25 K and at increasing substrate temperatures. The oven temperature was chosen to yield high proportion of neutral species. The two strongest bands associated to neutral glycine in the spectral range appear at 1730 and 1240 cm^{-1} (marked with dashed lines in the figure), whereas the zwitterionic species is the main component, but not necessarily the only one, of the other bands in this zone. For alanine the neutral bands are at 1721 , 1256 , 1084 , 978 and 821 cm^{-1} . The weakening of the main neutral bands with growing temperature reveals the transformation of the neutral to the zwitterionic species. When hot molecules hit the cold substrate their thermal energy can be used to induce proton transfer and thus convert the neutral species into the zwitterionic one, more stable in the solid phase.

In a polar environment (H_2O), the amino acids behave basically in a similar manner as the pure compound. Thus, water or zwitterionic species seem to have a similar effect on the neutral molecules in their vicinity, favouring proton transfer to generate the ionic species. On the other hand, the amino acids appear only in the neutral form at 25 K in non-polar (CO_2 and CH_4) surroundings, where the conversion to the zwitterionic structure is highly restricted. Differences in the spectra recorded at 25 K for the four systems studied here, shown in figure 2, are rationalized in terms of dipole interactions between the assigned internal motions for the selected fingerprint vibrations and the surrounding species. The analysis of the OH stretching region for the non-polar species indicates a larger interaction between

glycine or alanine and CO_2 than with CH_4 . The spectral differences must reflect the diverse interactions that the molecules feel in the vicinity of CO_2 and CH_4 .

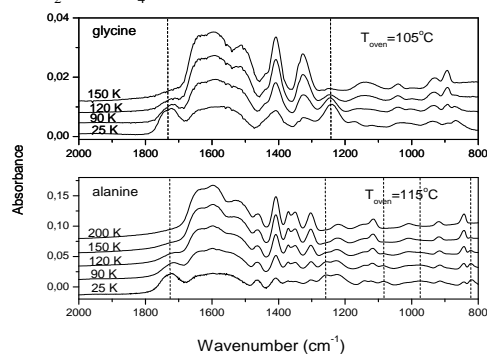


Figure 1: Spectra of vapour deposited glycine and alanine at 25 K, and warmed to the indicated temperatures. The evolution of the neutral/zwitterionic ratio in the samples can be followed by changes on the main neutral bands, marked by dashed vertical lines.

3. Summary and Conclusions

Vapour-deposited glycine or alanine contains a fraction of neutral form that depends on the generation conditions, namely temperature of the oven and of the substrate. Upon heating, the neutral form transforms completely to the zwitterionic structure. From the astrophysical point of view, the main conclusion concerns the possible structure that glycine and alanine could have in different media (H_2O , CO_2 and CH_4), where the presence of water, carbon dioxide and probably methane, accompanying glycine and alanine wherever these species could be found, can be expected.

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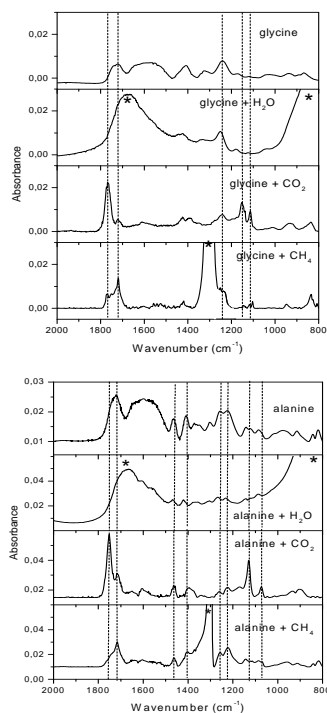


Figure 2: Spectra of pure and mixed amino acids at 25 K. The H_2O and CH_4 bands are marked with asterisks. Bands marked by dashed vertical lines emphasize the dissimilarities in the four ambients.

References

- [1] Oró J.: Amino-acid syntheses from hydrogen cyanide under possible conditions, *Nature* 190, 389-390, 1961.
- [2] Elsila J. E., Glavin D. P., Dworkin J. P.: Cometary glycine detected in samples returned by Stardust, *Meteorit. Planet. Sci.* 44, 1323-1330, 2009.
- [3] Muñoz Caro G. M., Meierhenrich U. J., Schutte W.A., Barbier B., et al.: Amino acids from ultraviolet irradiation of interstellar ice analogues, *Nature*, 416, 403-406, 2002.
- [4] Maté B., Rodríguez-Lazcano Y., Gálvez O., Tanarro I., Escribano R.: An infrared study of solid glycine in environments of astrophysical relevance, *Phys Chem Chem Phys*, 13, 12268-76 (2011).