

Carbamic acid produced by the UV/EUV irradiation of interstellar ice analogs

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Received 24 October 2006 / Accepted 14 December 2006

ABSTRACT

Context. Carbamic acid (NH_2COOH) is the smallest amino acid, smaller than the smallest proteinaceous amino acid glycine. This compound has never been observed in the interstellar medium (ISM). Previous experiments where ice mixtures containing H_2O , CO_2 and NH_3 were subjected to 1-MeV proton bombardment showed that carbamic acid is formed in a stable zwitterionic ($\text{NH}_3^+\text{COO}^-$) form.

Aims. In the present work, we have carried out irradiations of ice mixtures containing H_2O , $^{12}\text{CO}_2/^{13}\text{CO}_2$ and NH_3 with ultraviolet (UV)/extreme ultraviolet (EUV) photons provided by a synchrotron source in the 4–20 eV range, and compared the results with those obtained for energetic protons.

Methods. Infrared (IR) spectroscopy and mass spectrometry were used to identify the formed photo-products and monitor their evolution in the ices at 15 K and during the warming up to room temperature in the formed residues.

Results. We identified the IR absorption features of HNCO , OCN^- , CO , NH_4^+ and NH_2CHO at low temperature in the ices, and features assigned to carbamic acid in the residues around 250 K. Finally, we conclude that under our experimental conditions, unlike what was obtained after bombardment with energetic protons, carbamic acid may be formed in the neutral form, and propose some photochemical pathways leading to its formation.

Key words. astrochemistry – molecular processes – methods: laboratory – techniques: spectroscopic – ISM: molecules – ultraviolet: ISM

1. Introduction

Carbamic acid (NH_2COOH) is the simplest amino acid since it only contains one amino (NH_2) group and one carboxylic acid (COOH) group. Glycine ($\text{NH}_2\text{CH}_2\text{COOH}$), the smallest amino acid used to built proteins in all living beings, has one carbon atom more. Carbamic acid is an interesting compound since it may be one of the first organic species produced when interstellar ice analogs are subjected to UV photon irradiation or energetic proton bombardment. This compound is known to exist either in its neutral or zwitterionic ($\text{NH}_3^+\text{COO}^-$) form. Quantum mechanical ab initio calculations showed that the most stable geometrical structure for this molecule is the neutral form (Renko et al. 1993; Nanpeng & Brooker 1995). However, such calculations can only predict geometries for isolated molecules.

So far, carbamic acid has never been observed in the interstellar medium (ISM), neither in the gas phase nor in the solid phase. It was only characterized once in laboratory experiments by infrared (IR) spectroscopy (Khanna & Moore 1999). In those experiments, $\text{NH}_3/(\text{H}_2\text{O}+^{12}\text{CO}_2)$ and $\text{NH}_3/(\text{H}_2\text{O}+^{13}\text{CO}_2)$ ice mixtures (a layer of NH_3 covered by a layer of $\text{H}_2\text{O}+\text{CO}_2$) were bombarded with 1-MeV protons. After bombardment, each sample was warmed up to 250 K so as only an organic refractory residue remains on the substrate. The IR spectra of these residues at 250 K were compared with those of several

ammonium salts, namely NH_4HCO_3 , $(\text{NH}_4)_2\text{CO}_3$ and $\text{NH}_4\text{NH}_2\text{CO}_2$, as well as glycine ($\text{NH}_3^+\text{CH}_2\text{COO}^-$). They eventually ascribed the observed bands in the residues to vibrational modes of carbamic acid in its zwitterionic form.

The neutral form of carbamic acid, predicted to be the most stable structure by theoretical calculations, should be associated with a strong absorption band in the IR range around 1700 cm^{-1} , due to the carbonyl $\text{C}=\text{O}$ group, and two other bands due to the NH_2 stretching and bending modes around 3400 and 1600 cm^{-1} , respectively (Khanna & Moore 1999). Khanna & Moore did not observe any absorption band around 1700 cm^{-1} , but observed one at 1441 cm^{-1} , ascribed to one of the NH_3^+ bending modes, and another one at 1595 cm^{-1} , shifted to 1567 cm^{-1} when substituting $^{12}\text{CO}_2$ by $^{13}\text{CO}_2$ in the starting mixture. They ascribed this feature to the COO^- asymmetric stretching mode and therefore concluded that the compound responsible for these IR features in the residues at 250 K was carbamic acid in its zwitterionic form ($\text{NH}_3^+\text{COO}^-$).

Quantum calculations for this zwitterion predict a very long CN bond leading to the spontaneous dissociation of carbamic acid into NH_3 and CO_2 even at low temperatures (Nanpeng & Brooker 1995). However, Khanna & Moore observed that H_2CO_3 and $\text{NH}_3^+\text{COO}^-$ sublime around 250 K at about the same rate, indicating that these compounds are

probably stabilized by intermolecular hydrogen bonds in the solid phase.

In this work, we irradiated $\text{H}_2\text{O}+^{12}\text{CO}_2$, $\text{H}_2\text{O}+^{12}\text{CO}_2+\text{NH}_3$ and $\text{H}_2\text{O}+^{13}\text{CO}_2+\text{NH}_3$ ice mixtures with ultraviolet/extreme ultraviolet photons in the broad 4–20 eV range. Infrared (IR) spectroscopy and mass spectrometry were used to determine the structure of carbamic acid produced in our experiments. Our results are compared with those obtained after the bombardment of such ices with energetic protons (Khanna & Moore 1999). Finally, we also suggest some photochemical pathways leading to the formation of intermediate species and carbamic acid, and propose some candidates likely to be the precursors of carbamic acid.

2. Experimental set-up and protocol

The experiments were carried out in an ultrahigh-vacuum chamber, where the pressure is maintained below 5×10^{-10} torr. A substrate (KBr window) connected to a cold finger is mounted on a helium closed-cycle cryostat (CTI model 22), whose temperature is controlled with a ± 0.5 K accuracy between 15 and 300 K.

The gas handling system is equipped with stainless steel bottles and a Baratron gauge (MKS 122A) measuring pressures in the 0–100 torr range with a 2% accuracy. The whole system was baked out at 400 K for 12 hours and then cooled down back to room temperature before the experiments. Each component for the mixtures was kept in individual bottles: H_2O (liquid, triply distilled), $^{12}\text{CO}_2$ (gas, Sigma-Aldrich, 99.999% purity), $^{13}\text{CO}_2$ (gas, Sigma-Aldrich, 99.95% purity) and NH_3 (gas, Sigma-Aldrich, 99.5% purity). The water vapor and other gases were mixed together in another bottle, where the mixtures were kept for about 15 min. Relative proportions between the different gases in the mixtures were determined from their partial pressures in the mixing bottle, the total pressure being less than 3 torr.

The gas mixtures were injected into the vacuum chamber through a stainless steel tube (2-mm inner diameter) in order to maintain a pressure gradient between the gas handling system and the chamber. The icy films were formed by depositing the gas mixtures on the cold KBr substrate with a pressure of $\sim 1 \times 10^{-8}$ torr inside the chamber, at a temperature maintained at 15 K. The total thickness of our ice films was approximately $1 \sim 3 \mu\text{m}$, measured by monitoring the variation of interference fringes of a He-Ne laser light reflected by the KBr substrate. Optically thick ice samples prevent incident high-energy EUV photons from impinging on the KBr substrate and thus from releasing in the ices K^+ and Br^- ions and energetic electrons which may affect the experiments. Once the gas deposition was stopped, the vacuum chamber was left idling for a few hours, so all residual gases could condense on the substrate, until the chamber pressure reaches $\sim 5 \times 10^{-10}$ torr.

A Fourier-transform infrared spectrometer (Perkin-Elmer FTIR-1600) allowed us to control the deposition of the ices and their evolution during the experiments, the IR beam focusing on the substrate with a 10-mm diameter footprint. IR spectra were recorded between 4000 and 500 cm^{-1} with a 4 cm^{-1} resolution, the signal being typically averaged over 12 scans. A quadrupole mass spectrometer (QMS) (Pfeiffer Prisma-200) is also connected to the chamber in order to measure the masses of the desorbed photo-products during the irradiation and warming up steps. The mass spectra were recorded between 0 and 200 amu (atomic mass units), with a 2 amu s^{-1} scanning rate.

Three different ice mixtures were irradiated in this work, namely $\text{H}_2\text{O}+^{12}\text{CO}_2 = 4:1$, $\text{H}_2\text{O}+^{12}\text{CO}_2+\text{NH}_3 = 1:1:1$ and $\text{H}_2\text{O}+^{13}\text{CO}_2+\text{NH}_3 = 1:1:1$. NH_3 and CO_2 are known to react in the gas phase before deposition to produce $\text{NH}_4\text{NH}_2\text{CO}_2$ (Khanna & Moore 1999), but it did not occur in our experiments, since the IR spectrum of a $\text{H}_2\text{O}+\text{CO}_2+\text{NH}_3 = 1:1:1$ mixture showed no other compound besides H_2O , CO_2 and NH_3 before irradiation, and its mass spectrum displays no molecular mass higher than that of CO_2 . This clearly shows that the photo-products observed in our experiments and discussed hereafter were formed at low temperature in the solid phase (ice bulk), and not in the gas phase during the mixing step.

The ices were irradiated for about 6 hours with ultraviolet (UV)/extreme ultraviolet (EUV) photons, provided by the high-flux beamline of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. The incident photon flux was monitored by an in-line gold mesh ($\sim 90\%$ optical transmission), calibrated by a traceable photodiode (International Radiation Detectors, Inc.), forming an angle of 90° with the IR beam, so IR spectra could be recorded in situ during the whole experiment. The synchrotron beam size at the ice sample was approximately $3 \times 8 \text{ mm}^2$. The incident photon energy used was the 0th order of the white light in the broad 4–20 eV range, for a typical total integrated incident photon dose of about 3×10^{19} photons for an irradiation experiment.

EUV photons can excite the molecules to their ionization continua and break them into neutral and ionic fragments. Some molecular species may thus be synthesized after irradiation with EUV photons, but not necessarily after vacuum ultraviolet (VUV) irradiation (Wu et al. 2002). Moreover, the choice of a broad energy range for the irradiation is an interesting parameter, since radiations emitted in astrophysical environments are seldom monochromatic.

3. Results and discussion

3.1. Carbamic acid: zwitterionic or neutral form?

In order to study the production of carbamic acid, we compare the results for the three ice mixtures after UV/EUV irradiation at 15 K and warming up to 250 K at a rate of 2 K min^{-1} . Figure 1 shows the evolution of the intensities for the molecular masses 61 and 62 amu, corresponding to the total-ion masses of ^{12}C - and ^{13}C -carbamic acids, respectively, as a function of the increasing temperature during the warming up from 70 to 300 K after irradiation.

For the $\text{H}_2\text{O}+^{12}\text{CO}_2$ mixture (Fig. 1a), no signal above the noise level was observed for 61 and 62 amu over the whole temperature range. However, for the $\text{H}_2\text{O}+^{12}\text{CO}_2+\text{NH}_3$ mixture (Fig. 1b), we observed a clear peak around 250 K for 61 amu (odd molecular mass), indicating that this organic compound certainly contains an odd number of nitrogen (N) atoms. Figure 1c, where $^{13}\text{CO}_2$ was substituted to $^{12}\text{CO}_2$ in the starting mixture, shows a clear peak for 62 amu around 250 K, overlapping the peak for 61 amu of Fig. 1b. This indicates that the molecule with a mass of 61 amu only contains one carbon atom, since its mass is shifted up by 1 unit in the ^{13}C -labelled experiment. These results demonstrate that the peaks observed around 250 K to carbamic acid, indicating that this compound can be formed either after energetic proton bombardment (Khanna & Moore 1999) or UV/EUV irradiation of interstellar ice analogs.

The IR spectra of the residues obtained after UV/EUV irradiation of the $\text{H}_2\text{O}+^{12}\text{CO}_2+\text{NH}_3$ and $\text{H}_2\text{O}+^{13}\text{CO}_2+\text{NH}_3$ mixtures

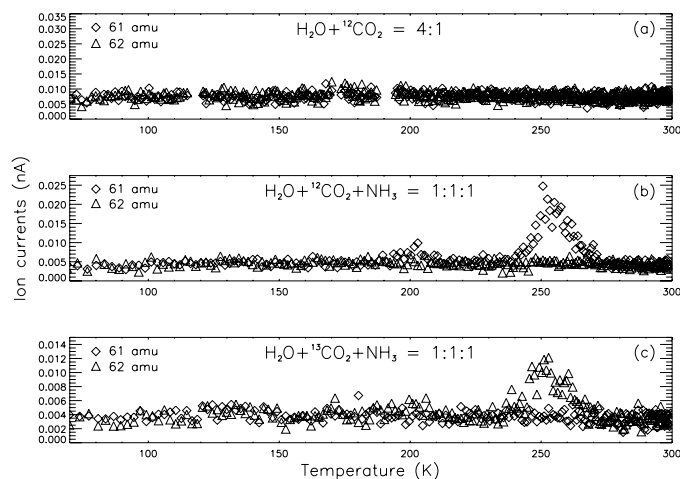


Fig. 1. Evolution of the intensities for the molecular masses 61 (diamonds) and 62 amu (triangles) during the warming up (from 70 and 300 K) for the **a)** $\text{H}_2\text{O} + {}^{12}\text{CO}_2 = 4:1$, **b)** $\text{H}_2\text{O} + {}^{12}\text{CO}_2 + \text{NH}_3 = 1:1:1$ and **c)** $\text{H}_2\text{O} + {}^{13}\text{CO}_2 + \text{NH}_3 = 1:1:1$ ice mixtures after UV/EUV irradiation.

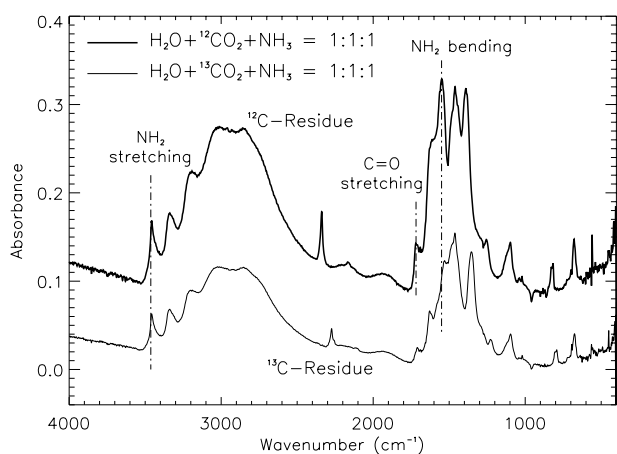


Fig. 2. IR spectra at 250 K of the ${}^{12}\text{C}$ - (thick line, offset for clarity) and ${}^{13}\text{C}$ -labelled (thin line) residues, produced after the UV/EUV irradiation of the $\text{H}_2\text{O} + {}^{12}\text{CO}_2 + \text{NH}_3 = 1:1:1$ and $\text{H}_2\text{O} + {}^{13}\text{CO}_2 + \text{NH}_3 = 1:1:1$ ice mixtures, respectively.

at 250 K are given in Fig. 2. For the ${}^{12}\text{C}$ -labelled residue, the C=O stretching absorption band at 1720 cm^{-1} and the bands of the NH_2 stretching and bending modes at 3457 and 1548 cm^{-1} , respectively, were clearly observed. In the IR spectrum of the ${}^{13}\text{C}$ -labelled residue, the absorption band for the C=O stretching was shifted to 1629 cm^{-1} . However, the bands at 3457 and 1548 cm^{-1} assigned to the NH_2 group were not shifted. This IR shift was also observed for CO_2 bands in our residues (${}^{12}\text{CO}_2$ at 2339 cm^{-1} , ${}^{13}\text{CO}_2$ at 2273 cm^{-1}) and in the samples subjected to 1-MeV proton bombardment (Khanna & Moore 1999).

The absorption band at 1720 cm^{-1} in the IR spectrum of the ${}^{12}\text{C}$ -residue is characteristic of the presence of a neutral carboxylic acid group (COOH) (Khanna & Moore 1999), different from the characteristic absorption band of carboxylates (COO^-) around 1590 cm^{-1} (Khanna & Moore 1999; Muñoz Caro & Schutte 2003). If we compare the IR spectra of our ${}^{12}\text{C}$ - and ${}^{13}\text{C}$ -residues with those obtained by Khanna & Moore (1999) after 1-MeV proton bombardment, we can see that they are very similar. The only clear difference is the absence of the 1720 cm^{-1}

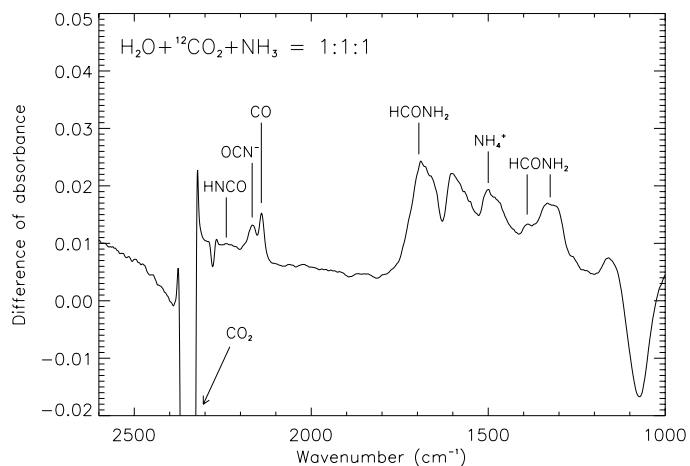


Fig. 3. IR spectrum of the $\text{H}_2\text{O} + {}^{12}\text{CO}_2 + \text{NH}_3 = 1:1:1$ ice mixture at 15 K after UV/EUV irradiation, between 2600 and 1000 cm^{-1} . The new (respectively depleted) features appear with a positive (respectively negative) difference of absorbance.

band in the IR spectrum of Khanna & Moore's ${}^{12}\text{C}$ -residue, leading to their conclusion that in their residues carbamic acid was formed in its zwitterionic ($\text{NH}_3^+\text{COO}^-$) form, stabilized by intermolecular hydrogen bonds, before evaporating around 250 K. The presence of the 1720 and 1629 cm^{-1} bands in the IR spectra of our ${}^{12}\text{C}$ - and ${}^{13}\text{C}$ -residues, respectively, tends however to favor the neutral (NH_2COOH) form for the carbamic acid under our experimental conditions.

The main reason which could explain the difference of structure of carbamic acid after proton bombardment and photon irradiation is that the secondary electrons produced by photons in the ices do not have sufficient energy to form stable negative ions, unlike protons (Gerakines et al. 2001). This result clearly suggests that the nature of the photo-products is directly correlated to the nature of the irradiation source, i.e. UV/EUV photons or energetic protons. Although unlikely, this discrepancy may be also due to a difference between the experimental protocols, since the ice components were layered in the proton bombardment experiment (Khanna & Moore 1999), whereas they were fully mixed in our UV/EUV irradiations. This experimental parameter may be studied in further experiments.

In the ISM, carbamic acid may thus exist in both neutral and zwitterionic form, since both UV/EUV photons and cosmic rays are present and likely to process gaseous and solid matter. However, in dense molecular clouds, where complex organic molecules such as amino acids are likely to be formed, the medium becomes optically thick and cosmic rays are the main source of radiation. Therefore, carbamic acid may be searched for in its zwitterionic form.

3.2. Mechanisms of formation for carbamic acid

In this section, we discuss the possible precursor(s) of carbamic acid. The IR spectrum of the $\text{H}_2\text{O} + {}^{12}\text{CO}_2 + \text{NH}_3 = 1:1:1$ ice mixture at 15 K after UV/EUV irradiation is shown in Fig. 3. Several photo-products, formed directly from the photolysis of the starting ices, could be identified thanks to their IR absorption features: HNCO (2242 cm^{-1}), OCN^- (cyanate ion, 2162 cm^{-1}), CO (2141 cm^{-1}), NH_4^+ (1499 cm^{-1}) and NH_2CHO (formamide, 1690, 1388 and 1317 cm^{-1}). The XCN absorption band at 2162 cm^{-1} , displayed more clearly in Fig. 4, is shifted

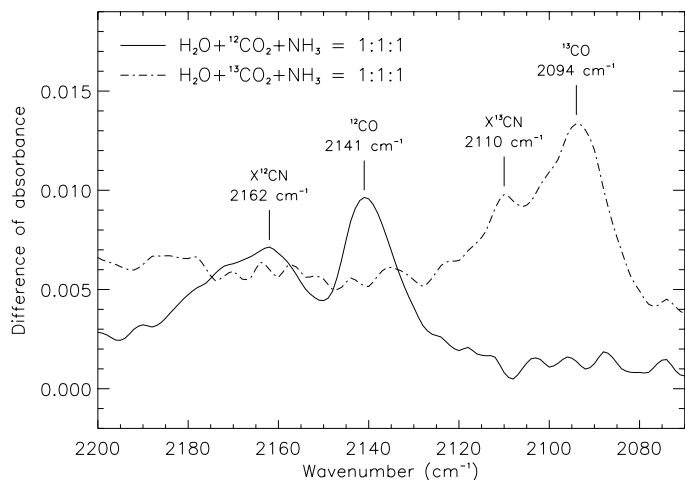
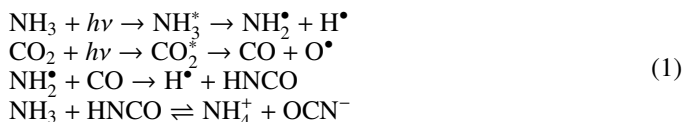


Fig. 4. IR spectra of the $\text{H}_2\text{O}+^{12}\text{CO}_2+\text{NH}_3 = 1:1:1$ (solid line) and $\text{H}_2\text{O}+^{13}\text{CO}_2+\text{NH}_3 = 1:1:1$ (dot-dashed line) ice mixtures at 15 K enlarged to the 2200–2070 cm^{-1} range.

to 2110 cm^{-1} in the ^{13}C -labelled mixture, confirming the attribution of this band to OCN^- .

Despite a clear detection and identification of its IR band around 2250 cm^{-1} in ice irradiation simulations (Moore & Hudson 2003), HNCO was only observed in the ISM in the gas phase (Snyder & Buhl 1972; Turner 1991; Zinchenko et al. 2000), but never in the solid phase. The IR band of solid OCN^- around 2165 cm^{-1} was identified in the laboratory after UV irradiation or energetic proton bombardment of ices (Hudson et al. 2001; Gerakines et al. 2004; van Broekhuizen et al. 2004), and was observed in many astrophysical environments (Lacy et al. 1984; Schutte & Greenberg 1997; Demyk et al. 1998; Chiar et al. 2002; Gibb et al. 2004; van Bruikhuizen et al. 2005). NH_4^+ was identified in the laboratory after UV irradiation of ices (Schutte & Khanna 2003) and observed in protostellar sources, thought to be associated to OCN^- to form the ammonium cyanate salt NH_4OCN (Demyk et al. 1998). Finally, formamide was detected in cold ice mixtures after UV irradiation and energetic proton bombardment (Allamandola et al. 1999; Gerakines et al. 2004), and so far observed in the ISM in the gas phase (Rubin et al. 1971; Turner 1991). It was only tentatively detected in the solid phase in the protostellar source NGC 7538 IRS9 (Raunier et al. 2004).

These species can be formed from the photolysis of NH_3 and CO_2 through the following photochemical pathway:



where HNCO appears as an intermediate species, and where the radicals are marked with dots. The characteristic IR features of HNCO , NH_4^+ and OCN^- are clearly observed in the UV/EUV-irradiated ices (Fig. 3), supporting this mechanism for their formation. The three characteristic IR bands of formamide (NH_2CHO) are also observed in our samples (Fig. 3). Formamide can be formed through the following photochemical mechanism, displaying also another possible pathway to form HNCO by radical recombination:

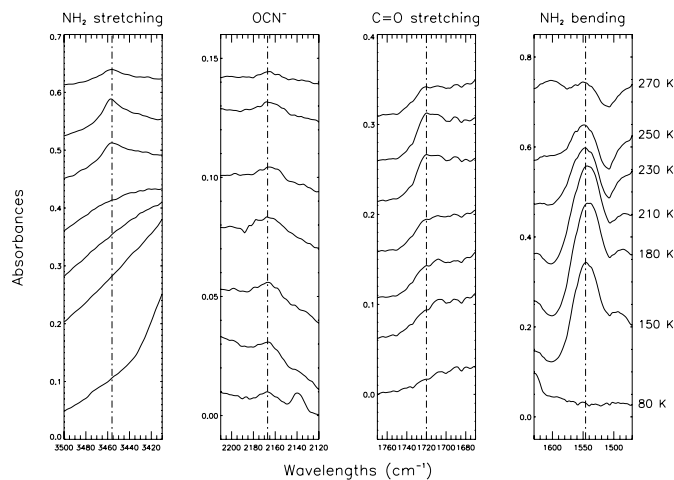
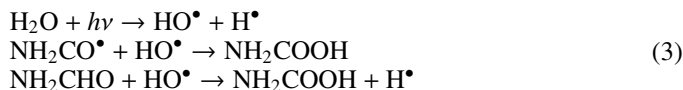
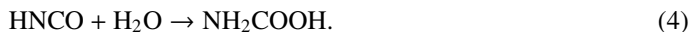


Fig. 5. Enlargements of the IR spectra around the NH_2 stretching mode, OCN^- , $\text{C}=\text{O}$ stretching and NH_2 bending mode bands (from left to right, see Fig. 3) after UV/EUV irradiation, at 80, 150, 180, 210, 230 250 and 270 K (from bottom to top). The absorbances were offset for clarity.

Carbamic acid is probably formed via a similar photochemical mechanism, with OCN^- , HNCO and NH_2CHO as its possible precursors. For instance, carbamic acid can be produced from the radical recombination of HO^{\bullet} , readily produced by the photolysis of H_2O , and $\text{NH}_2\text{CO}^{\bullet}$ or formamide, formed via Eqs. (1) and (2):



or from the direct addition of a H_2O molecule to HNCO :



Note that the addition of a HO^{\bullet} radical in the last reaction of Eq. (3) can also be rewritten as a direct addition of a H_2O molecule, leading to the formation and evaporation of molecular hydrogen (H_2).

According to the IR data, only the IR band at 2162 cm^{-1} of OCN^- could be observed on the IR spectra during the warming up of our samples till 250 K, whereas the features assigned to HNCO and NH_2CHO disappeared at lower temperatures. However, the mass spectrometry data could not allow us to confirm the presence of OCN^- at high temperatures, indicating that the 2162 cm^{-1} feature may be also due to the $\text{C}\equiv\text{N}$ stretching mode of (an)other compound(s). Therefore, many compounds including HNCO , OCN^- and NH_2CHO may be involved in the formation of carbamic acid. Figure 5 gives the evolution of the NH_2 stretching mode, OCN^- , $\text{C}=\text{O}$ stretching mode and NH_2 bending mode IR features as a function of the increasing temperature, from 80 to 270 K. It shows that the NH_2 and $\text{C}=\text{O}$ stretching mode bands display similar behaviours during the warming up, supporting a formation of carbamic acid below 250 K before its desorption (see Fig. 1). It also confirms the presence of the 2162 cm^{-1} $\text{C}\equiv\text{N}$ stretching band all over this range of temperature, but shows no clear correlation between its evolution and that of the IR features assigned to carbamic acid, confirming that OCN^- is not its unique precursor.

4. Conclusion

In the present work, we have irradiated $\text{H}_2\text{O}+\text{CO}_2+\text{NH}_3$ ice mixtures with UV/EUV photons in the 4–20 eV range at 15 K.

Several photo-products were observed at low temperature using IR spectroscopy: HNCO, OCN⁻, CO, NH₄⁺ and NH₂CHO. Carbamic acid was produced during the warming up to 250 K (mass spectrometry) in its neutral form (IR spectroscopy).

This result is different from what was observed in previous works where such ice mixtures were subjected to 1-MeV proton bombardment, and where carbamic acid was formed in its zwitterionic form, suggesting that the nature of the chemical photo-products depends mainly on the irradiation source. However, since zwitterionic and neutral forms of carbamic acid both sublime around 250 K, their structure in the ices may be mainly driven by the intermolecular hydrogen bonds. In the ISM, both neutral and zwitterionic forms may be present, since the cold solid matter is subjected to UV photons and cosmic rays.

A study of the compounds formed at low temperature after UV/EUV irradiation with IR spectroscopy allowed us to propose several photochemical pathways leading to the formation of carbamic acid and HNCO, OCN⁻, CO, NH₄⁺, NH₂CHO, which may be involved in the formation of carbamic acid. However, infrared and mass spectrometry data did not allow us to favor one or several of these compounds for being the most probable and stable precursor(s) for the formation of carbamic acid.

Acknowledgements. We are grateful for the support of the staff of the National Synchrotron Radiation Research Center, Hsinchu, Taiwan. This work was supported in part by the Ministry of Education under the Aim for the Top University Program (NCU), and based on the work supported by the NSC grant #NSC-95-2112-M008-028 (T.-S. Y. and W.-H. Ip), the NSF Planetary Astronomy Program under Grant AST-0604455 (C.-Y. R. W.), and the NASA Planetary Atmospheres Program under Grant NAG5-11960 (C.-Y. R. W.).

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