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Carbamic acid and carbamate formation in NH_3:CO_2 ices – UV irradiation versus thermal processes

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ABSTRACT

Context. We study carbamic acid [NH_2COOH] and ammonium carbamate [NH_2COO^-][$NH_4{}^+$] formation in interstellar ice analogs.
Aims. We demonstrate how carbamic acid [NH_2COOH] and ammonium carbamate [NH_2COO^-][$NH_4{}^+$] can be formed from both thermal reactions and energetic photons in an NH_3:CO_2 ice mixture.
Methods. Infrared and mass spectroscopy are used to monitor NH_3:CO_2 ice mixture evolution during both warming and VUV photon irradiation.
Results. Carbamic acid and ammonium carbamate can be produced thermally in a 1:1 ratio from NH_3 and CO_2 above 80 K. They can be also formed in a 28:1 ratio by less efficient processes such as energetic photons. Our study and its results provide fresh insight into carbamic acid formation in interstellar ices.
Conclusions. We demonstrate that care is required to separate irradiation-induced reactivity from purely thermal reactivity in ices in which ammonia and carbon dioxide are both present. From an interstellar chemistry point of view, carbamic acid and ammonium carbamate are readily produced from the ice mantle of a typical interstellar grain and should therefore be a detectable species in molecular clouds.

Key words. astrochemistry – ISM: molecules – methods: laboratory

1. Introduction

In molecular clouds, interstellar grains are responsible for the synthesis of molecules that cannot be formed in the gas phase of the interstellar medium (ISM). Observations from the InfraRed Astronomical Satellite (IRAS), Infrared Space Observatory (ISO), and Spitzer missions provide a wealth of spectral information in the mid infrared (MIR) range and enable the identification of several simple species frozen in interstellar grains (van Dishoeck 2004). More complex products can be formed by thermal processes from simpler species (Schutte et al. 1993a,b). The grain surface offers a place where two species can meet and possibly react. This surface can also have a catalytic role because it can enhance the reaction by lowering the activation barrier (Duvernay et al. 2005). These grains are also subjected to non-thermal energetic processes through different types of bombardment (cosmic rays, electrons, VUV radiation). These radiations can form radicals and ions that can react with no or little activation barrier. The complex species produced can be released into the gas phase of the ISM and in the case of star-forming regions, eventually be incorporated into comets and meteorites. A large amount of laboratory and observational data are contributing to a a more robust understanding of complex molecule formation in the solid phase of the ISM (Schutte 1995; Greenberg 2002; Elsila et al. 2007).

We focus our study on carbamic acid NH_2COOH, since it is the simplest molecule that has both an amino group and a carboxylic group, and may be an intermediate (or a deadlock) in the route toward the formation of the simplest amino acid, glycine NH_2CH_2COOH. Carbamic acid has been observed neither in the gas phase nor in the solid phase of ISM. Carbamic acid is not stable at room temperature in gas phase and spontaneously dissociates into NH_3 and CO_2 (Remko et al. 1995; Aresta et al. 2000). Therefore, there exists no gas phase spectroscopic studies of this molecule in the lab or in space. If it is present in the ISM, such as in the cold environment of outer planetary objects, including comets, carbamic acid must have be formed and be stored in a stable form such as a salt (ammonium carbamate) or a multimer, in a solid icy phase.

To produce carbamic acid, we start from a binary mixture of NH_3 and CO_2, since these two species are known to exist in interstellar grains (Whittet et al. 1996). Ammonia can be identified by its bands at 3367 cm^{-1} (2.97 μm), and at 1069.5 cm^{-1} (9.35 μm) (Dartois 2004). The ubiquitous CO_2 is identified by its bending mode band at 667 cm^{-1} (15.2 μm) and its asymmetric stretching mode at 2349 cm^{-1} (4.27 μm) (Dartois 2004). Their abundances are estimated to be less than 5–10% (Dartois 2004), (Lacy et al. 1998) and 10–23% (Gerakines et al. 1995) of the abundance of the H_2O ice, respectively.

Low temperature reactivity of thin solid films formed by condensation of the gas phase NH_3 and CO_2 was investigated by Frasco (1964). He reported that NH_3 and CO_2 react to form ammonium carbamate [NH_2COO^-][$NH_4{}^+$] under two solid forms, that he called amorphous and crystalline. On the same NH_3:CO_2 system, Hisatsune (1984) assigned the bands previously related to the crystalline form by Frasco (1964), to a prereactive complex $(NH_3)_2CO_2$. These two studies clearly demonstrated that ammonium carbamate [NH_2COO^-][$NH_4{}^+$] is formed easily in these binary NH_3:CO_2 ice mixtures, although they did not provide evidence of the formation of neutral carbamic acid NH_2COOH. However, there was controversy over the assignment of some vibrational bands to different types of amorphous ammonium carbamate solid.

Non-thermal processing of NH_3:CO_2 and NH_3:CO_2:H_2O mixtures have also been studied. (Khanna & Moore 1999) bombarded NH_3/(H_2O+CO_2) ice mixtures (a layer of NH_3 covered by a layer of a H_2O+CO_2 ice) with 1-MeV protons. After bombardment, the samples had been warmed to 250 K and were monitored by IR spectroscopy. At 250 K, the remaining organic residue was assigned to carbamic acid in its zwitterionic form $NH_3^+COO^-$. Chen et al. (2007) performed irradiation of NH_3:CO_2:H_2O ice mixtures at 15 K with UV/EUV photons of 4–20 eV (310–62 nm), and followed the reaction by IR and mass spectroscopy, while warming the ice films to 250 K. Along with the IR features HNCO, OCN^-, NH_4^+, CO and NH_2(CO)H, they identified carbamic acid in its neutral form. It is important to note that in every study, carbamic acid was identified after both irradiation and heating to 250 K. We will show that heating to 250 K after irradiation at low temperature has for effect to allow the reactants that have not been decomposed by irradiation to thermally react. Results from this study indicate that the identification in this type of ices must be considered with care to be able to separate irradiation induced reactivity from thermal induced reactivity.

In the present work, we study the thermal reactivity of NH_3:CO_2 ices. We demonstrate that NH_3:CO_2 ice mixtures react above 80 K to form both ammonium carbamate ([NH_2COO^-][NH_4^+]) and carbamic acid dimers $(NH_2COOH)_2$. In a second type of experiments, we study the photon-induced reactivity by irradiating the NH_3:CO_2 mixture with VUV photons at 10 K, followed by warming at room temperature.

2. Description of experimental methods

Carbon dioxide (CO_2) and ammonia (NH_3) are commercially available in the form of 99.9995% pure gas from Linde and Air Liquide. The NH_3:CO_2 gas mixtures were prepared into a primary vacuum pumped mixing line (10^{-3} mbar) at room temperature. They were then deposited onto a gold plated metal surface cooled down to 10 K by a Model 21 CTI cold head within a high vacuum chamber ca 10^{-7} mbar). Typical deposition times were between 5 and 10 min. The mixing line was heated by a heatgun under vacuum conditions between two different experiments to avoid contamination of our system. Pure NH_3, pure CO_2, and NH_3:CO_2 were deposited onto the cold surface. The IR spectra are recorded between 4000 cm^{-1} and 650 cm^{-1} in reflexion mode onto the gold plated surface using a NICOLET Magna 750 FTIR spectrometer. A typical spectrum has a 1 cm^{-1} resolution and is averaged over one hundred interferograms. The sample was warmed and its temperature controlled by a Lakeshore Model 320 temperature controller. The temperature ramp rate was set to 4 K min^{-1}, and the IR spectrum was monitored during the temperature ramp. Mass spectra were recorded using a MKS Microvision-IP plus RGA quadrupole mass spectrometer as the products were desorbed during the temperature ramp. The mass spectra were recorded between 1 and 80 amu (atomic mass units). The ionization source was an 70 eV impact electronic source. The IR and mass analysis were not performed simultaneously because of the limitations of our experimental configuration; as a consequence, we repeated each experiment to be able to acquire both the IR spectra and the mass spectra. The VUV radiation ($\lambda > 120$ nm) was generated by a microwave discharge hydrogen flow lamp (Opthos instruments). The flux of photons from the hydrogen lamp was estimated to be about 10^{15} cm^{-2} s^{-1}.

The true concentration ratio was obtained using two methods: standard manometric techniques and by using the IR spectra to estimate the column density of CO_2 and NH_3 according to their band strengths. However, the ratio calculated using the second method depends on the band strengths provided by the literature. The band strength for the CO_2 asymmetric stretching band at 2340 cm^{-1} was measured to be 7.6×10^{-17} cm $molecule^{-1}$ for the pure solid (Yamada & Person 1964; Gerakines et al. 1995), while in water ice a value of 1.4×10^{-16} cm $molecule^{-1}$ was found (Sandford & Allamandola 1990). The band strength for the wagging mode of NH_3 at 1070 cm^{-1} varies from 1.3×10^{-17} to 1.7×10^{-17} cm $molecule^{-1}$ (Kerkhof et al. 1999; d'Hendecourt et al. 1986) in its pure solid form. The values of the band strengths for these two molecules depend on the nature, composition, and temperature of the ice in which they are found. We therefore used the values given by Yamada & Person (1964) for CO_2 (7.6×10^{-17} cm $molecule^{-1}$) and the value given by Kerkhof et al. (1999) for the NH_3 (1.3×10^{-17} cm $molecule^{-1}$) (Kerkhof et al. 1999) with these values, we derived a ratio of 1.05 which is consistent with the value that we mesured using mamonetric techniques. The thickness of the deposited solid films, assuming densities for CO_2 of 1.60 g cm^{-3} and for NH_3 of 0.69 g cm^{-3}, are estimated to be around 0.1 μm (Bennett et al. 2004). We can also monitor the NH_3 and CO_2 IR band intensities as they are consumed during the reaction, and estimate how much of each product is formed as well as the band strength of some of their bands.

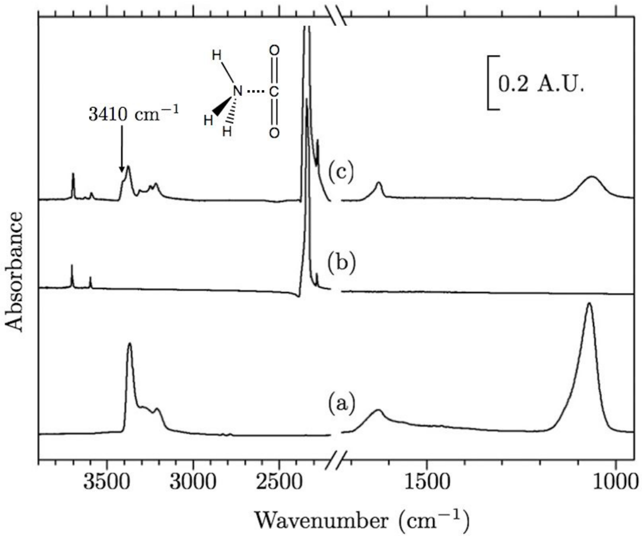

Fig. 1. Infrared spectra recorded at 10 K **a)** of pure NH_3, **b)** CO_2 ices, and **c)** a NH_3:CO_2 binary mixture in a 1:1 ratio. Arrow: NH stretching mode relative to the NH_3:CO_2 complex.

3. Results

Pure NH_3 and CO_2 solids are deposited independently at 10 K and their respective IR spectra are displayed in Fig. 1. The assignment of the bands of these species is well known and reported in Table 1 in pure solids and in the 1:1 mixture. In the pure solid, at a rate of 4 K min^{-1} CO_2 starts to sublime at 90 K, which is consistent with the results of a previous study by Sandford & Allamandola (1990). Based on the IR spectra CO_2 fully disappears at 105 K. The sublimation of pure NH_3 commences at 100 K (Sandford & Allamandola 1993) and NH_3 fully disappears at 120 K.

A binary (NH_3:CO_2) ice mixture is then deposited at 10 K within a 1:1 ratio. No reaction occurs at this temperature and the

Table 1. Infrared absorption bands and assignments of NH_3 and CO_2, in pure solids and in NH_3:CO_2 ice mixtures at 10 K.

Assignment	Wavenumbers (cm^{-1})	
NH_3 Ferraro et al. (1980)	Solid	1:1 ratio
ν_3	3375	3410; 3379
$2\nu_4$	3290	3309
ν_1	3210	3219
ν_4	1625	1626
ν_2	1075	1064
ν_5	530	
CO_2 Gerakines et al. (1995)	Solid	1:1 ratio
$(\nu_1 + \nu_3)$	3708	3700
$(2\nu_2 + \nu_3)$	3600	3594
(ν_3) ν_{as} CO_2	2337	2333
(ν_3) ν_{as} $^{13}CO_2$	2282	2278
(ν_2) δ CO_2	654	658

Vibration mode: stretching (ν), bending (δ).
Indication: asymmetric (as), symmetric (s).

IR spectrum of the mixture is mainly the superposition of the NH_3 and CO_2 spectra as seen in Fig. 1c. Nevertheless, an extra feature can be observed in the νNH stretching region in the 1:1 spectrum at 3410 cm^{-1}. This frequency is closed to the observed value in its gas phase at 3444 cm^{-1} for the νNH mode of NH_3 (Jacox et al. 1963). This mode is indeed especially sensitive to the hydrogen bonding. The gas phase frequency is lowered from 3444 cm^{-1} to 3378 cm^{-1} in crystalline NH_3, and to 3404 cm^{-1} for NH_3 dimer in a N_2 matrix (Pimentel et al. 1962). In CO_2 matrices with mole ratios CO_2:NH_3 ranging from 100 to 700, this mode was observed at 3434 cm^{-1} (Jacox et al. 1963). This new feature is consistent with the presence of a T-shaped NH_3:CO_2 molecular complex in which the nitrogen atom bonds with the carbon of CO_2. The small frequency shift that we observe between the νNH of free and complexed ammonia (30 cm^{-1}) excludes the possibility of any hydrogen bond between hydrogen of NH_3 and CO_2. This T-shaped structure has been characterized in the gas phase (Fraser et al. 1984) and by quantum calculation (Jönsson et al. 1977).

In a first series of experiments, the ice mixture were warmed to room temperature, to take into account the thermal reactivity alone. In a second series of experiments, the ice mixture are irradiated by VUV photons at 10 K followed by warming to room temperature.

3.1. Pure thermal reactivity from a binary NH_3:CO_2=1:1 ice

A binary NH_3:CO_2=1:1 ice was deposited at 10 K. The IR spectrum evolution is shown in Fig. 2. No reaction occurs at 10 K. When the sample is warmed to above 80 K, NH_3, and CO_2 are consumed, and new features are observed. After complete sublimation of the reactants around 130 K, two sets of bands can be isolated. One, labelled C decreases more rapidly than the other labelled D, as the temperature ramp continues. The two set of bands presumably correspond to two different species, the C species being the main product at 140 K. They both sublimate in the range 230–260 K. The sublimation was monitored by both FTIR and mass spectroscopy. The bands of these two species were separated by taking a difference spectrum between 230 K and 140 K as shown in Fig. 3.

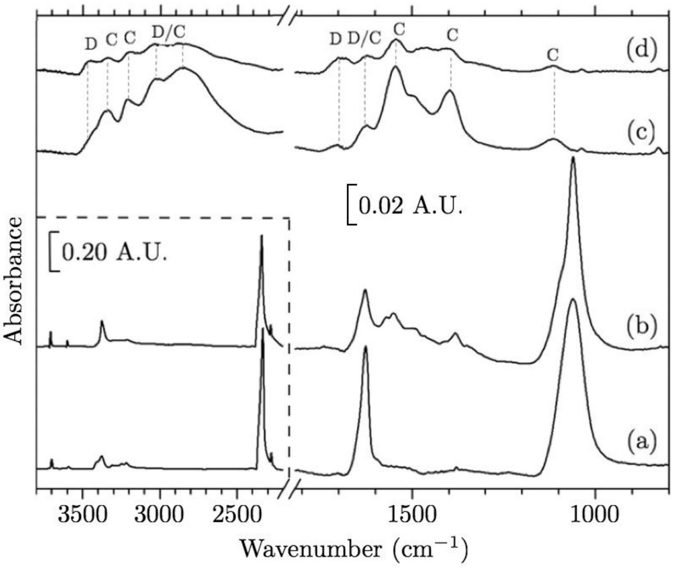

Fig. 2. Infrared spectrum of the thermal evolution of a NH_3:CO_2=1:1 binary ice mixture, **a)** at 10 K, **b)** at 90 K, **c)** at 140 K, and **d)** at 230 K.

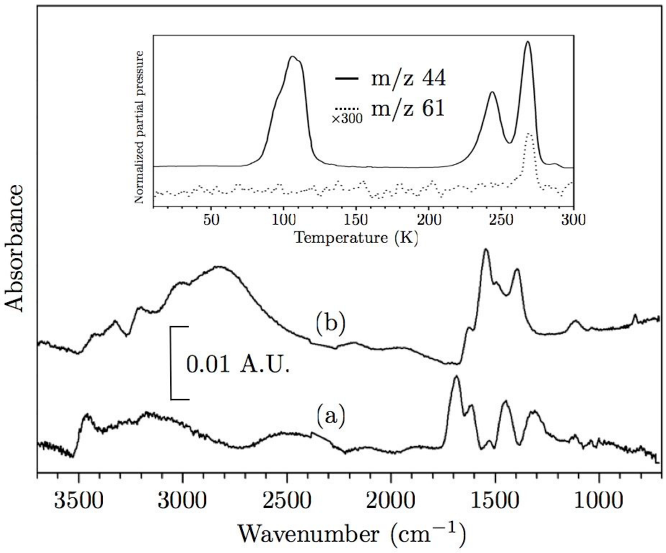

Fig. 3. Infrared spectra of **a)** carbamic acid dimer $(NH_2COOH)_2$ (labelled D in the text), obtained by substracting the spectrum of NH_3:CO_2 at 230 K and at 140 K and **b)** ammonium carbamate $[NH_2COO^-][NH_4^+]$ (labelled C in the text), obtained by substracting the spectrum of the dimer on the spectrum of NH_3:CO_2 at 230 K. *Upper panel*: the evolution of the peak at m/z = 61 and m/z = 44, relative to $NH_2COOH^{+\bullet}$ and $CO_2^{+\bullet}$, respectively during the warming from 10 K to 300 K of the NH_3:CO_2=1:1 binary ice mixture without VUV irradiation.

The C species is assigned to ammonium carbamate $[NH_2COO^-][NH_4^+]$ following the assignment given by Frasco (1964) and Hisatsune (1984). The absorption bands of the spectrum for the C species recorded at 140 K is shown in Fig. 3b, and their frequencies are reported in Table 2 along with their assignments. The IR spectrum of ammonium carbamate is dominated by ν_{as} COO^- at 1553 cm^{-1}. There is controversy about the bands at 1394 cm^{-1} and 1117 cm^{-1} attributed to νCN stretch and a symmetric COO^- stretch by Frasco and inversely by Hisatsune. Following the convention of Bossa et al. (2008) work, we assigned the bands at 1394 and 1117 cm^{-1} to $\nu_s COO^-$ and νCN, respectively. In this we also observed $\nu_s COO^-$ stretching mode of methylammonium

Table 2. Infrared absorption bands and assignments of the products formed from a binary NH_3:CO_2=1:1.

Assignment	Wavenumbers (cm^{-1})	Band Strength (cm molecule^{-1})
ν (NH_2) NH_2COOH dimer	3462	
ν (NH_2) [NH_2COO^-][NH_4^+]		
ν (NH_2) [NH_2COO^-][NH_4^+]	3325	
ν (OH) NH_2COOH dimer	(broad) 3140	
ν (C=O) NH_2COOH dimer	1691	5×10^{-18}
δ (NH_2) [NH_2COO^-][NH_4^+]	1623	2×10^{-18}
ν_{as} (COO^-) [NH_2COO^-][NH_4^+]	1553	2×10^{-17}
δ (NH_4^+) [NH_2COO^-][NH_4^+]	1495	3×10^{-18}
NH_2COOH dimer	1451	2×10^{-18}
ν_s (COO^-) [NH_2COO^-][NH_4^+]	1393	8×10^{-18}
NH_2COOH dimer	1320	2×10^{-18}
ν (CN) [NH_2COO^-][NH_4^+]	1117	4×10^{-18}
ρ (NH_2) [NH_2COO^-][NH_4^+]	1037	2×10^{-19}
δ_{oop} (OCN) [NH_2COO^-][NH_4^+]	829	6×10^{-19}
δ (COO^-) [NH_2COO^-][NH_4^+]	674	4×10^{-19}

Vibration mode: stretching (ν), bending (δ), rocking (ρ), torsion (τ). Indication: asymmetric (as), symmetric (s) and out-of-plane (oop).

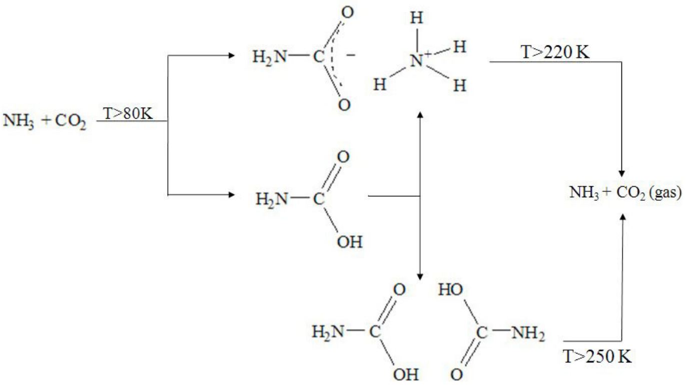

Fig. 4. Reactivity of solid NH_3 and CO_2 1:1.

methylcarbamate [CH_3NHCOO^-][$CH_3NH_3^+$] at 1409 cm^{-1} and νCN at 1141 cm^{-1}.

The D species, which produces the difference spectrum between 230 K and 140 K (Fig. 3a), is assigned to the dimer of the neutral carbamic acid NH_2COOH. This is consistent with our previous study of the thermal reaction between methylamine (CH_3NH_2) and carbon dioxide (CO_2) in which we observed the formation of the centro symmetric dimer of methylcarbamic acid (Bossa et al. 2008). Jamróz et al. (2002) calculated that the dimer of carbamic acid should be stabilized by ca 90 kJ mol^{-1}. The band at 3462 cm^{-1} is typical of a ν NH stretch and the band at 3140 cm^{-1} of the associated OH stretch. Since the OH stretch of one monomer participates in a hydrogen bond with the carbonyl of the other monomer, the OH band is broadened considerably and shifted with respect to a free OH oscillator. The ν C=O stretching mode is observed at 1691 cm^{-1}, which is also typical of dimer-like carboxylic acid. The infrared observations are correlated with mass spectrometry experiments during the warming of the sample to room temperature (Fig. 3). We observe three clear peaks for $m/z = 44$ (CO_2) at 104 K, 230 K, and 260 K, which are correlated with the observed loss of non-reacting CO_2, carbamate, and carbamic acid, respectively. For $m/z = 61$, we observed only one peak at 260 K, corresponding to the molecular ion peak of carbamic acid ($NH_2COOH^{+\bullet}$). We can therefore deduce from these results that (*i*) at 230 K, ammonium carbamate decomposes spontaneously into CO_2 and NH_3; (*ii*) at 260 K, when carbamic acid is desorbing, it partially decomposes into CO_2 and NH_3. In its gas phase, neutral carbamic acid is known to be unstable (Remko et al. 1995). The reactivity pathway for solid NH_3 and CO_2 1:1 is summarized in Fig. 4. The integrated band strength, A (cm molecule^{-1}), corresponding to the most typical bands of ammonium carbamate and dimer of carbamic acid are determined by integrating the optical depth $\tau(\nu)$ of the bands according to the equation: $N = \int \tau(\nu) d\nu / A$ and estimating the total column density of carbamate and dimer of carbamic acid molecules formed N (molecule cm^{-2}) from the amount of CO_2 molecules having reacted to produce the carbamate and carbamic acid. To evaluate the amount of CO_2 molecules, we used the C=O asymmetric stretching mode of CO_2 at 2337 cm^{-1} (7.6×10^{-17} cm molecule^{-1}) (Yamada & Person 1964; Gerakines et al. 1995). It is also clear that all the observed loss of CO_2 cannot be due only to the thermal reactivity, but can be also caused by its sublimation (Fig. 3). To evaluate the amount of non-reacting CO_2 that sublimates, we compare the relative surface area of desorbing CO_2 at 104 K and the area of both surfaces, corresponding to carbamate and carbamic acid (230 K and 260 K, Fig. 3). We estimate that 49% of the deposited CO_2 sublimates without reacting with NH_3. This implies that only 51% of the initial CO_2 is involved in the thermal reaction.

To evaluate the amount of ammonium carbamate formed, we used the band strengths of methylammonium methylcarbamate for the ν_{as} COO^- stretching mode (1.67×10^{-17} cm molecule^{-1}) (Bossa et al. 2008). Thus, given of the total amount of CO_2 molecules that reacted and the amount of ammonium carbamate formed, we can deduce easily the amount of carbamic acid formed by evaluating: $N(CO_2)_{consumed} = N$(carbamate) + N (carbamic acid). The ammonium carbamate and carbamic acid band strengths are listed in Table 2. Finally, we estimate that the warming of the 1:1 NH_3:CO_2 mixture at 140 K produces 50% of ammonium carbamate, i.e. the carbamate:carbamic acid ratio is about 1:1.

3.2. Photon induced reactivity of a binary NH_3:CO_2 1:1 ice

Binary NH_3:CO_2 = 1:1 ices were deposited at 10 K and irradiated by VUV photons. After 720 min of irradiation, newly formed species were observed (Fig. 5) and almost 50% of the reactants had been consumed. Due to the VUV light flux which used, this laboratory irradiation time was equivalent to 10^7 years in dense molecular clouds and this is consistent with the residence time of ice in dense molecular clouds (about 10^8 yrs) (Greenberg 1999). At 10 K no thermal reaction can occur, so the observed reactivity was induced only by photon irradiation. Species formed along with their characteristic bands are listed in Table 3. After 720 min of irradiation, the spectrum shows two strong bands at 2164 and 2140 cm^{-1}, assigned to OCN^- (Grim et al. 1987; Van Broekhuizen 2004) and CO (Sandford et al. 1988); (Gerakines et al. 1995), respectively. In the carbonyl region (1800–1500 cm^{-1}), we identify the dimer of carbamic acid with the band at 1691 cm^{-1}, and the ammonium carbamate with the band at 1548 cm^{-1}, which are the strongest bands for these species. The other vibrational bands for these two species are listed in Table 3. Besides carbamic acid and ammonium carbamate formation, VUV irradiation of NH_3:CO_2 ice produces an additional product: ammonium formate [$HCOO^-$][NH_4^+]. This species was identified by means of its absorbtion bands at 1590

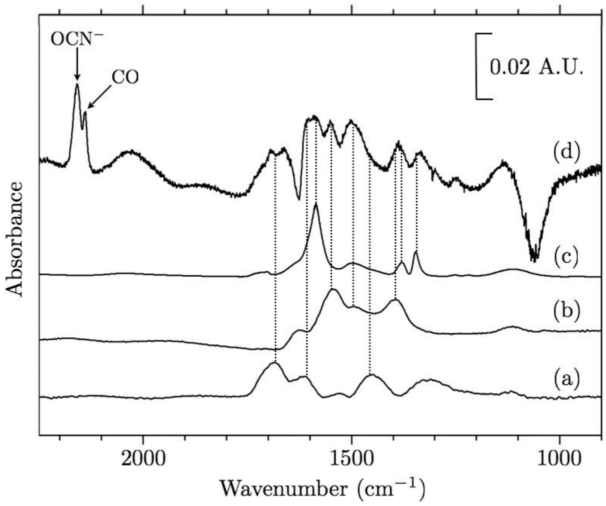

Fig. 5. Infrared spectra of **a)** carbamic acid dimer $(NH_2COOH)_2$, **b)** ammonium carbamate $[NH_2COO^-][NH_4{}^+]$, **c)** ammonium formate $[HCOO^-][NH_4{}^+]$ at 80 K, and **d)** difference spectrum between the 720 min. and 0 min. VUV irradiation times at 10 K.

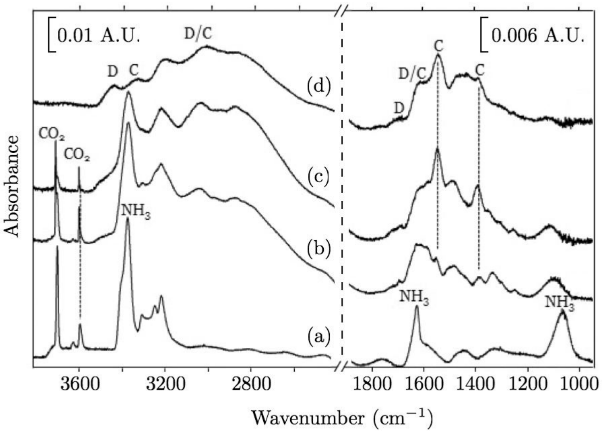

Fig. 6. Infrared spectra for the NH_3:CO_2=1:1 binary ice mixture **a)** at 10 K, **b)** after 720 min. VUV irradiation at 10 K, **c)** irradiated sample warming to 110 K, and **d)** warming to 230 K.

Table 3. Infrared absorption bands of the species formed upon VUV irradiation of a NH_3:CO_2 ice at 10 K.

Wavenumbers (cm^{-1})	Species	Assigment	Band Strength (cm $molecule^{-1}$)
2164 (w)	OCN^{-} [a]	(ν_3) ν_{as} (NCO)	1.30×10^{-16}
2140 (vs)	CO [b]	(ν_1) ν C=O	1.10×10^{-17}
1694 (vw)	NH_2COOH dimer [c]	ν C=O	5×10^{-18}
1590 (m)	$[HCOO^-][NH_4^+]$ [d,e]	$\nu_{as}(COO^-)$	1.0×10^{-16}
1548 (m)	$[NH_2COO^-][NH_4^+]$ [c]	$\nu_{as}(COO^-)$	2×10^{-17}
1501 (s)	$[HCOO^-][NH_4^+]$ [d,e]	δ_s (NH_4^+)	
1389 (w)	$[HCOO^-][NH_4^+]$ [d,e]	δ_s (CH)	8.0×10^{-18}
1330 (w)	$[HCOO^-][NH_4^+]$ [d,e]	$\nu_s(COO^-)$	1.7×10^{-17}
1319 (w)	NH_2COOH dimer [c]		
1240 (vw)	?	?	

References. [a] Raunier (2003); [b] Gerakines (1995); [c] this work;
[d] Hudson (2000); [e] Schutte (1999).
Vibration mode: stretching (ν), bending (δ).
Indication: asymmetric (as), symmetric (s).
Intensities: very strong (vs), strong (s), medium (m), weak (w) and very weak (vw).

and 1389 cm^{-1} (Schutte et al. 1999). The chemical evolution of the irradiated NH_3:CO_2 ice is assumed to proceed along the following path: direct dissociation of NH_3 and CO_2:

$$NH_3 + h\nu \rightarrow NH_2 + H \tag{1}$$

$$NH_3 + h\nu \rightarrow NH + H_2 \tag{2}$$

$$CO_2 + h\nu \rightarrow CO + O. \tag{3}$$

Reactions between primary dissociation products then lead to HCOOH and HNCO formation:

$$CO_2 + 2H \rightarrow HCOOH \tag{4}$$

$$NH_2 + CO \rightarrow HNCO + H. \tag{5}$$

Acids such as HCOOH and HNCO can react at 10 K with NH_3 to give the ammonium formate and ammonium isocyanate (Schutte et al. 1999; Raunier et al. 2004). These could explain why HCOOH and HNCO are not observed after the irradiation:

$$HCOOH + NH_3 \rightarrow NH_4^+HCOO^- \tag{6}$$

$$HNCO + NH_3 \rightarrow NH_4^+OCN^-. \tag{7}$$

Finally, the carbamic acid may be formed from the recombination of H with CO_2, followed by the addition of NH_2:

$$H + CO_2 \rightarrow COOH \tag{8}$$

$$NH_2 + COOH \rightarrow NH_2COOH. \tag{9}$$

From the band strength of the observed products (listed in Table 3, we estimate that, after 720 min of irradiation at 10 K, we formed 86% of carbamic acid dimer, 6% of $HCOO^-$, 1% of OCN^-, 4% of CO and 3% of ammonium carbamate.

We can see from Fig. 6b that NH_3 and CO_2 are still present even after 720 min of VUV irradiation. During warming the irradiated sample, the remaining NH_3 and CO_2 therefore react to produce ammonium carbamate and carbamic acid (as a dimer) as in the pure thermal reactivity case. Results from this study demonstrate that both carbamic acid and ammonium carbamate can be formed from both thermal and photochemical reaction. Nevertheless, the carbamate:carbamic acid ratio depends on the energetic process. In a pure thermal reaction, the carbamate:carbamic acid ratio is 1:1, while the VUV irradiation produces a 1:28 ratio. The interstellar detection of ammonium carbamate and carbamic acid and more specifically the ratio between them, could provide evidence of the origin of their formation in the interstellar medium.

4. Discussion

The comparison between our results and cryogenic matrix studies indicate that binary NH_3:CO_2 ice mixtures at 10 K enable molecular interactions to occur between NH_3 and CO_2 molecules such as a T-shaped complex (Jacox et al. 1963). This interaction foreshadows C–N bond formation. Warming the mixture around 80 K gives ammonium carbamate $[NH_2COO^-][NH_4^+]$ and neutral carbamic acid NH_2COOH in its dimer form D with a ratio of ~1:1. Both species desorb in the range 230–260 K. Many molecular clouds have temperatures above 80 K and carbamic acid is therefore likely to be present in the ISM, stored in its salt form, i.e. such as ammonium carbamate $[NH_2COO^-][NH_4^+]$ in the icy mantle of the interstellar grains. This straightforward reaction produces ammonium carbamate two of the most abundant species in the ice mantle, NH_3 and CO_2. However, it is unlikely that all the CO_2 and NH_3 present in interstellar grains will be converted into ammonium carbamate and carbamic acid. In genuine interstellar ices, a higher number of molecules are present in the icy mantles, resulting in sophisticated and complex chemical reaction network. The dilution in water ice should lower the reaction rate. Competitive reaction, such as the thermal reaction of formaldehyde and NH_3 (Schutte et al. 1993a,b) should significantly affect the amount of ammonium carbamate and carbamic acid formed in interstellar ices.

Nevertheless, this thermal reaction between NH_3 and CO_2 in interstellar conditions is relevant from an astrochemical point of view because it provides the peptidic prototype HN-C=O linkage without any energetic photons or particles. When the grain is heated to above 230 K, during the protostellar disk formation phase, ammonium carbamate decomposes directly into NH_3 and CO_2, and the carbamic acid then sublimes and in turn decomposes

$$[NH_4^+][NH_2CO_2^-] \rightarrow CO_2 + 2 \times NH_3 \quad (10)$$

$$NH_2COOH \rightarrow NH_3 + CO_2. \quad (11)$$

This implies that a dust grain at ca 100 K will not desorb all of its ammoniac and carbon dioxide at this temperature, but part of these molecules will be released in the gas phase much later, above 250 K when the carbamic acid and ammonium carbamate desorb. This is also well above the H_2O desorption temperature, where most of the species are released into the gas phase when water is desorbed. Carbamate acts as a reservoir for NH_3 and CO_2, in which desorption in the gas phase is delayed. This could partially explain the CO_2 depletion in hot gas around a protostar as revealed by ISO (van Dishoeck et al. 1996). Although carbamic acid is unstable at room temperature, it can be detected at 260 K by means of mass spectroscopy. If carbamic acid is therefore generated into the gas phase in hot molecular cores at temperature lower than 260 K, it could possibly be detected by radio astronomy. Below 260 K, the decomposition rate of carbamic acid should decline and its column density in the gas phase should increase. Carbamate and carbamic acid can also be incorporated into comets as interstellar matter accretes in the protoplanetary disk. A confirmation of the detection of these molecules and the ratio C/D could be provided by the Rosetta mission devoted to analyze the comet nucleus.

Our results also provide fresh insight that improves the study performed by Chen et al. (2007). In particular for the carbamic acid formation at 250 K. In this study, they irradiated at 15 K with UV/EUV photons, ice mixtures ($^{12}CO_2$:H_2O, NH_3:$^{12}CO_2$:H_2O, NH_3:$^{13}CO_2$:H_2O) followed by warming to 250 K. Chen et al. (2007) proposed that carbamic acid could be formed from a thermal reaction between H_2O and HNCO, photoproducts which were observed after irradiation. On the basis of their spectra, HNCO is formed in such low quantity (absorbance of 0.02 or less) that it is unlikely to be the origin of carbamic acid that they observed at 250 K. As demonstrated previously Raunier et al. (2003), the thermal reaction between HNCO and H_2O produces $[H_3O^+][OCN^-]$ at temperatures higher than 130 K. We propose that the products they observed at 250 K were produced mainly by thermal reaction between the residual NH_3 and CO_2.

5. Conclusion

A purely thermal reactivity occurs at low temperature, 80 K, for NH_3 and CO_2, which are abundant in interstellar ices. This implies that for molecular clouds with temperatures of around 100 K, ammonium carbamate and carbamic acid could be produced in grains, and have a contribution to the ice absorption features at 3300 cm^{-1} (3 μm) and 1500 cm^{-1} (6.6 μm). Once desorbed at 250 K, carbamate and carbamic acid can also dissociate easily into NH_3 and CO_2. This implies that ammonium carbamate and carbamic acid must be incorporated into gas-grain models as they store NH_3 and CO_2 in a stable salt form until $T > 230$ K at which they are a source of gas phase NH_3 and CO_2, after H_2O has desorbed. The amount of ammonium carbamate and carbamic acid should be affected by the composition of the ice due to competitive reactions.

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