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Carbamic acid: molecular structure and IR spectra

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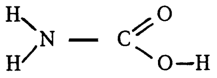
Abstract

Infrared absorption spectra of mixed H_2O, NH_3 and $^{12}CO_2/^{13}CO_2$ ices subjected to 1 MeV proton irradiation were investigated. The results of analyses of the spectra suggest formation of carbamic acid at low temperatures. The stability of this compound in the solid phase is attributed to intermolecular hydrogen bonding of the zwitter-ion ($NH_3^+COO^-$) structure.

Keywords: Carbamic acid; IR spectra; Hydrogen bonding

1. Introduction

Carbamic acid, designated in the literature as NH_2COOH has, thus far, not been characterized by any experimental technique. The structural aspect has been treated theoretically by quantum mechanical ab-initio calculations. With a 6-31G complete basis set, the most stable structure of the molecule is predicted to be [1,2]:



Since no hydrogen bonding is taken into account, this structure must correspond to the gas phase species. To our knowledge, there is no report on any identification of this species by itself in either terrestrial or extraterrestrial environment. This characteristic is shared with carbonic acid (H_2CO_3) with which it is isoelectronic. This species is also isoelectronic with acetic acid (CH_3COOH) which has been fully characterized spectroscopically. It is to be noted that the chemical constitutions of carbonic acid, carbamic acid and acetic acid correspond to 1:1 $CO_2 + H_2O$, $CO_2 + NH_3$ and $CO_2 + CH_4$, respectively.

One of the most important structural features of carbamic acid is the existence of a CN bond; in this respect, it is an amino acid which is simpler than the simplest identified amino acid, namely, amino acetic acid or glycine. Carbamic acid is an important molecule in living systems where it is thought to be produced enzymatically from urea.

In an earlier set of publications [3–6] from our group, the IR spectra of (H_2CO_3) and its isotopically (D and ^{13}C) substituted species were reported. This compound was identified with the residue obtained from a 1:1 H_2O–CO_2 ice, bombarded by 1 MeV protons at 15 K and then

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warmed to evaporate the reactant species. Subsequently, production and identification of H_2CO_3 by ion H^+ implantation in solid CO_2 [7] and by direct chemical reaction of a bicarbonate and an acid [8] were reported. Since N is an essential component of the biosphere, a study of the effects of irradiation of ices containing N species is desirable. We have investigated the effect of proton bombardment on a layer of NH_3 ice covered by a layer of $H_2O + CO_2$ ($NH_3/(H_2O + CO_2)$) ice. The IR spectroscopic studies of this ice mixture suggest the formation of solid carbamic acid by proton bombardment of this mixed ice. This phase is stable up to 250 K at which temperature it starts to sublime. Carbamic acid may be stable in the cold environments of outer planetary objects including comets which are under constant cosmic bombardment. Details of our experimental results and their analyses in support of this identification are presented in this report

2. Experimental

Experimental details of our laboratory set up, techniques for recording the IR spectra, and the proton bombardment of the samples are already in print [3]. Ice films were formed by condensing gases onto an aluminum mirror attached to the tail section of a Helium closed-cycle cryostat. The temperature of the substrate could be controlled to ± 1° between 15 and 300 K.

In this study two deposits were made. Gases were prepared in two external gas handling systems, each equipped with diaphragm manometers. NH_3 (99.99%, anhydrous, Matheson) was deposited through a small capillary tube and condensed as the first 2 μm thick layer on the aluminum mirror substrate. A gas mixture of one part H_2O (triply distilled with resistance $> 10^7$ ohm cm) and one part CO_2 (Airco, purity 99.8%) was prepared in the second gas handling system. This mixture was deposited through a second capillary tube and condensed as a 2 μm thick layer on top of NH_3. Each ice deposition rate was ~ 3 μm h^{-1}. The ice thickness was determined by measuring laser interference fringes during deposition. ^{13}C enriched carbon dioxide, used in one experiment, was 99 at.% ^{13}C (Cambridge Isotope Laboratories).

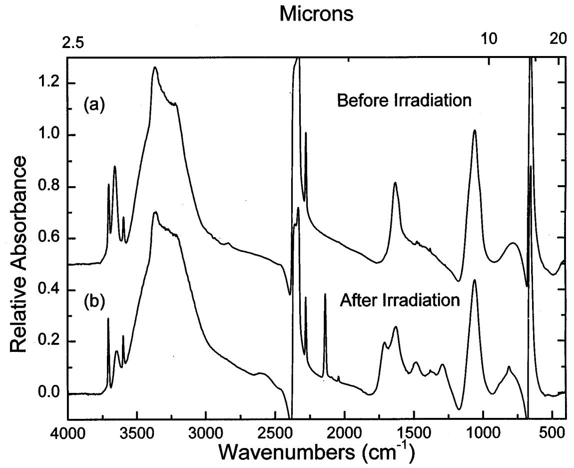


Fig. 1. IR spectrum of $NH_3/H_2O + CO_2$ ice layers at 20 K: (a) before proton irradiation, (b) after irradiation.

The composite $NH_3/(H_2O + CO_2)$ ice was bombarded with protons from a Van de Graaff accelerator with ~ 1.3 MeV of energy. Beam fluence was typically 1×10^{15} protons cm^{-2} with an average dose of ~ 9 eV $molecule^{-1}$. The energetic protons pass through the sample and come to rest in the aluminum substrate. They are the initiators of the chemical changes in the sample, but do not appear in the final products.

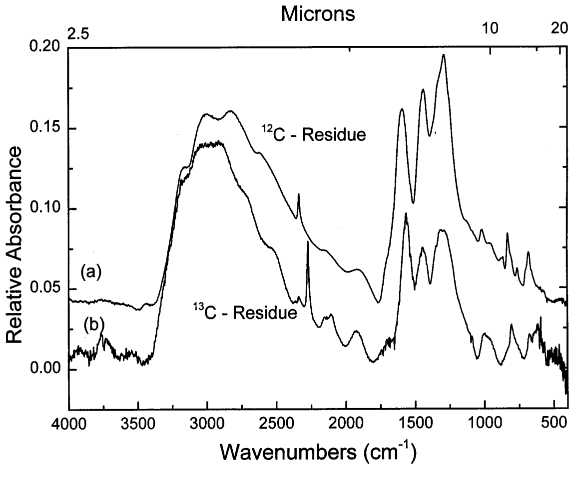


Fig. 2. IR spectrum of the residue obtained after warming the irradiated sample to 250 K (a) ^{12}C-residue, (b) ^{13}C-residue.

As a background experiment, the IR spectrum of an identical composition ice, $NH_3/(H_2O + CO_2)$ was warmed from 20 to 200 K without any irradiation. No product species were evident from the spectra. A second background experiment was the irradiation of NH_3/CO_2 (a layer of NH_3 covered by a layer of CO_2). The spectrum of the residue is identical with that of ammonium carbamate ($NH_4NH_2CO_2$). It is known that NH_3 and CO_2 react in the gas phase to produce $NH_4NH_2CO_2$. A third background experiment was the deposition of sublimed ammonium bicarbonate (NH_4HCO_3) on a cold substrate. The spectra gave distinct peaks due to NH_3, CO_2 and H_2O. On warm-up, the spectra was finally converted to $NH_4NH_2CO_2$. However, in our principal experiment (proton irradiation of $NH_3/(CO_2 + H_2O)$ ice), this does not occur. On warming, NH_3 diffuses through the top layer of irradiated $H_2O + CO_2$ mixed ice which has already formed H_2CO_3. H_2CO_3, apparently, provides ingredients for reactions resulting in a different residue which we speculate to be carbamic acid. We label the residues obtained with $^{12}CO_2$ and $^{13}CO_2$ as ^{12}C- and ^{13}C-residues, respectively.

The mid-IR spectra of the samples were recorded before and after irradiation at $T \approx 15$ K. Additional spectra were recorded during warming of the samples. The spectral resolution employed was 4 cm^{-1} on a Mattson FTIR spectrometer.

3. Discussion

The IR spectra of a 1:1:2 $^{12}CO_2$:H_2O:NH_3 film at 15 K before and after irradiation are reproduced in Fig. 1a and b, respectively. Most of the additional features on irradiation are very similar to those of irradiated $H_2O + CO_2$ ice [3]. There is no evidence of N containing molecules/radicals like NO, CN (region 1800–2200 cm^{-1}), suggesting no reaction with NH_3 which underlies the $CO_2 + H_2O$ mixed ice.

Spectra of the irradiated samples were obtained at 10–15° intervals during the sample warm-up. Between 80 and 90 K, NH_3 changes from an amorphous to a metastable phase and its vapor pressure increases. The peaks due to NH_3 (~3200, ~1130 cm^{-1}) continue to decrease in intensity until they disappear near 140 K. The amorphous to crystalline phase change of H_2O ice at 130 K possibly provides adequate energy for reorientation of the molecules resulting in intermixing and possible reactions between NH_3 and the irradiation products in the top layer. Between 140 and 230 K the spectra continue to change until they evolve into a stable spectrum corresponding to the final residues. The spectra of residues obtained with $^{12}CO_2/^{13}CO_2$, H_2O and

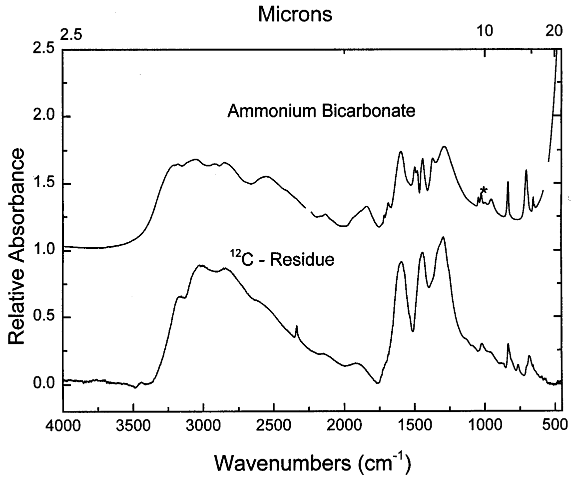


Fig. 3. (a) IR spectrum of NH_4HCO_3, (b) IR spectrum of ^{12}C-residue.

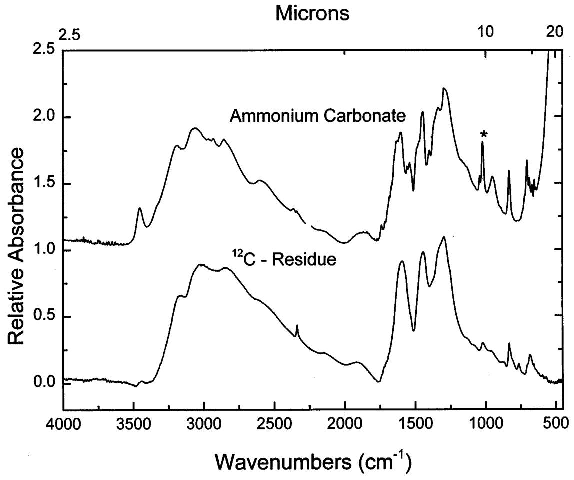


Fig. 4. (a) IR spectrum of $(NH_4)_2CO_3$, (b) IR spectrum of the ^{12}C-residue.

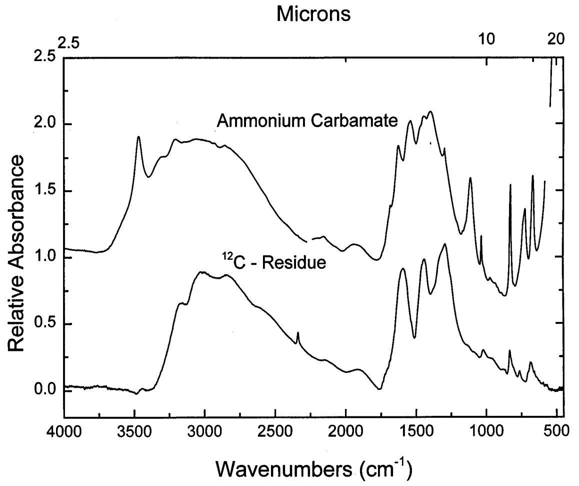


Fig. 5. (a) IR spectrum of $NH_4NH_2CO_2$, (b) IR spectrum of the ^{12}C-residue.

NH_3 are presented in Fig. 2 as ^{12}C- and ^{13}C-residues, respectively.

Among the stable and relatively small molecules expected from radiation induced chemistry of CO_2, H_2O and NH_3 are:

Formic acid (HCOOH)
Formaldehyde (H_2CO)
(H_2CO_3): Stable at low temperature
Urea ($(NH_2)_2CO$)
Ammonium carbonate ($(NH_4)_2CO_3$)
(NH_4HCO_3)
($(NH_4NH_2CO_2)$

The spectra of compounds in the above list except for $NH_4NH_2CO_2$ are readily available in the literature. For comparison of the spectra of residues obtained in the present study, the spectra of NH_4HCO_3, $(NH_4)_2CO_3$, $NH_4NH_2CO_2$ and glycine ($NH_3^+CH_2COO^-$) are presented in Figs. 3–6, respectively. The spectrum of ^{12}C-residue in included in each of these figures. The spectra in Figs. 3–6 are for the powdered samples mulled in fluorolube (4000–1350 cm^{-1}) and nujol (1350–450 cm^{-1}). The two regions were merged to obtain the composite spectrum. A weak feature at 1023 in cm^{-1} the spectra in Figs. 3–6 is due to an impurity on the NaCl substrate, possibly due to rouge used in polishing the substrate.

HCOOH, H_2CO, H_2CO_3 and $(NH_2)_2CO$ are ruled out as candidates for the residue in view of the absence of the 1700 cm^{-1} band (due to C=O) in its IR spectrum. The IR spectrum of $NH_4NH_2CO_2$ is too rich to be associated with the ^{12}C-residue; characteristic bands of NH_2 and NH_4^+ in the region 3500–2800 cm^{-1} do not match with those of the residue. Nevertheless, in the region below 1700 cm^{-1}, the spectrum of $NH_4NH_2CO_2$ exhibits features which are similar to those in the spectrum of the ^{12}C-residue.

The IR spectral features of $(NH_4)_2CO_3$ and NH_4HCO_3, reported in the literature [9,10], appear to be identical. There is a very strong resemblance of these spectra with that of the ^{12}C-residue. Many of the peak positions match within a few cm^{-1}. However, the spectra of NH_4HCO_3 and $(NH_4)_2CO_3$ have extra bands in the 1500–1350 cm^{-1} region which are not observed in the spectrum of the ^{12}C-residue (Figs. 3 and 4). The band at 1019 cm^{-1} in the spectrum of the ^{12}C-residue is shifted by ~28 cm^{-1} from the corresponding bands of NH_4HCO_3 and $(NH_4)_2CO_3$. The band at 764 cm^{-1} in the spectrum of the ^{12}C-residue is not observed in the spectra of the NH_4HCO_3 and $(NH_4)_2CO_3$.

Both NH_4HCO_3 and $NH_4NH_2CO_2$ contain carboxylate ion (COO^-) structure. Also, glycine, in the crystalline phase, has a zwitter-ion structure in

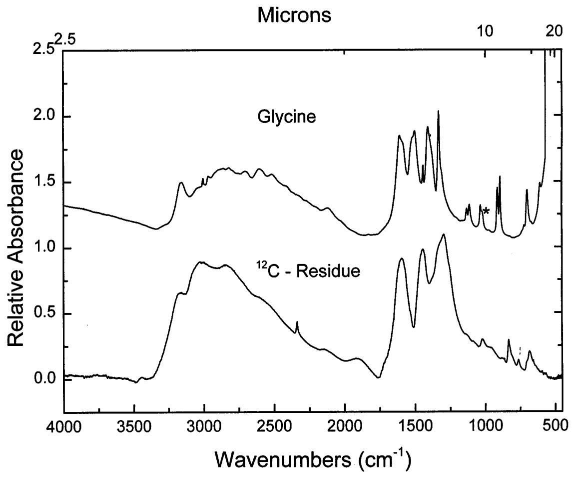


Fig. 6. (a) IR spectrum of glycine, (b) IR spectrum of the ^{12}C-residue.

Table 1
Absorption peaks (cm^{-1}) between 1700 and 500 cm^{-1} of NH_4HCO_3, $NH_4NH_2CO_2$, $(NH_4)_2CO_3$, $NH_3+CH_2COO^-$ and residue from $NH_3/^{12}CO_2+H_2O$ conjectured to be $NH_3^+COO^-$

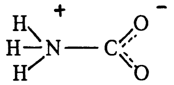
NH_4HCO_3 Ammonium bicarbonate	$NH_4NH_2CO_2$ Ammonium carbamate	$(NH_4)_2CO_3$ Ammonium carbonate	$NH_3^+CH_2COO^-$ (Glycine)	Residue ($NH_3^+COO^-$) carbamic acid
	1684 (vw)			
1597	1628	1602	1611, 1591	1595
1498	1543	1558	1520, 1504	
1480		1540		
1441	1448	1446	1444	1441
1370	1400	1397	1410	
1290	1300	1337, 1296	1332, 1300	1330, 1292
	1114		1132, 1112	
1043	1035	1043	1033	1019
1023[a]	1023[a]	1023[a]	1023[a]	
952		952	970	957
			867	
			911	
			893	883, 866
833	829	833		833
703	723	704		764
652	669	686	698	683
642				
			607	607
				580

[a] Impurity peak, possibly due to polishing powder on the substrate window.

which the NH_3^+ group is intermolecularly hydrogen bonded to the COO^-. The spectra of the ^{12}C- and ^{13}C-residues also exhibit some resemblance to that of glycine (Fig. 6). Table 1 gives a list of observed peaks in the spectra of NH_4HCO_3, $(NH_4)_2CO_3$, $NH_4NH_2CO_2$, glycine and the ^{12}C-residue. A comparison of these bands helps in the assignments of the absorption peaks in the IR spectra of the ^{12}C- and ^{13}C-residues (Table 2).

In the light of the above observations, and that the spectra of the residues have characteristics similar to those of H_2CO_3, we were led to attempt interpretation on the basis of carbamic acid. As mentioned above, the most stable structure predicted theoretically is NH_2COOH. For such a structure one would expect a strong peak around 1700 cm^{-1} due to C=O (possibly intermolecularly hydrogen bonded in the condensed phase); this is not observed. The bands due to NH_2 stretch and bend occur around 3400 and 1600 cm^{-1}, respectively. Even though bands are observed in these regions, the shift of the 1595 cm^{-1} band of ^{12}C-residue on ^{13}C isotopic substitution is inconsistent with the NH_2COOH structure. For example, if the 1595 cm^{-1} band is due to the NH_2 bend, ^{13}C substitution should not affect its frequency significantly (minor shift due to coupling with other modes is possible). In analogy with the spectral features of other carboxylate structures, this band is assigned to the COO^- asymmetric stretch. A shift of this peak to 1567 cm^{-1} on ^{13}C substitution is consistent with this assignment. The shift in the 1441 cm^{-1} peak on ^{13}C substitution is less significant (upward by ~7 cm^{-1}). This is assigned to one of the NH_3^+ bending modes. The upward frequency shift on ^{13}C substitution can occur because of coupling with other modes. The 1300 cm^{-1} band is very broad with some unresolved structure. This region displays modes due to NH_3^+ bends and COO^- symmetric stretch. In the infrared spectral data for sodium formate [11], the 1602 and 1363 cm^{-1} peaks are shifted to 1559 and 1336 cm^{-1}, respectively, and are assigned to COO^- stretches. Consequently, we assign the peak at 1292 cm^{-1} (^{12}C-residue) which is shifted to 1277 cm^{-1} on ^{13}C-substitution, to the COO^- symmetric stretch. Peaks below 1200 cm^{-1} are very similar to those in the spectra of NH_4HCO_3, $(NH_4)_2CO_3$, $NH_4NH_2CO_2$ and $NH_3^+CH_2COO^-$, and are assigned to stretching and bending modes of the $NCOO^-$ group (Table 2).

Based on the above arguments we propose that the stable structure associated with the residue is the zwitter-ion ($NH_3^+COO^-$).



Quantum calculations for the zwitter-ion predict a very long CN bond [2] which would result in spontaneous dissociation into NH_3 and CO_2 even at low temperatures. For H_2CO_3, quantum calculations predict its stability over that of H_2O+CO_2 by a 1–2 Kcal mol^{-1} [5,12]. Inclusion of H-bonding explained the stability and the temperature dependence of vapor pressure of solid H_2CO_3 [5]. It is, therefore, proposed that hydrogen bonding in the solid phase stabilizes the zwitter-ion structure $NH_3^+COO^-$ of carbamic acid. Both H_2CO_3 and $NH_3^+CO_2$ sublime by ~250 K at about the same rate, thereby indicating similar hydrogen bond strengths.

Table 2
IR Absorption peaks (cm^{-1}) in the spectra of residues assigned as $NH_3^+{}^{12}COO^-$ and $NH_3^+{}^{13}COO^-$ [a]

$NH_3^+{}^{12}COO^-$	$NH_3^+{}^{13}COO^-$	Assignment
3441		
3170	3170	
3050		
2829		
2627		NH–O stretch
2340	2276	Trapped CO_2
2153		
1920		
1595	1567	COO^- asymmetric stretch
1441	1448	NH_3^+ symmetric bend
1330 (sh)	1324	
(unresolved, vb)		NH_3^+ asymmetric bend
	1319	
1292 (vb)	1277 (sh)	COO^- symmetric stretch
1019	1007(?)	CN stretch
957 (sh)	970 (vb)	NH_3^+ coupled
883	867(?, w)	Rock and Wag
866		
833	808	$NCOO^-$ out of plane bend
764	780 (sh)	NCO^- bend
683	680	COO^- in plane bend
580	570 (?)	COO^- twist

[a] Abbreviations: sh, shoulder; vb, very broad; w, weak, ?, too weak to accurately determine its frequency.

As mentioned in the text, there is a very strong resemblance between the IR spectra (4000–450 cm^{-1}) of residues (recorded at 250 K) and those of NH_4HCO_3 and $(NH_4)_2CO_3$ (recorded at 298 K). In as much as the identification of carbamic acid (reported here for the first time) with the residue appears reasonably convincing, in order to firm up this identification, investigations of the temperature dependence of the IR spectra of these compounds are desirable. Also, far IR studies, where lattice vibrations of carbamic acid, NH_4HCO_3 and $(NH_4)_2CO_3$ are expected to be different, may provide check on this identification. Such investigations are underway in our laboratory.

Acknowledgements

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