UV Photolysis of C_4N_2 in Water Ices: New Possible Route of Synthesis of Ammonium Bicarbonate and Ammonium Formate

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Laboratory experiments involving ultraviolet (UV) irradiation of dicyanoacetylene (C_4N_2) trapped in water ice at 10 K have been conducted and monitored by infrared spectroscopy (FTIR). By the support of isotopic experiments and theoretical calculations, the irradiation of a DCA/H_2O ice mixture at $\lambda > 230$ nm has been found to be a possible source of $NH_4^+HCO_3^-$ (ammonium bicarbonate) and $NH_4^+HCOO^-$ (ammonium formate). These latter compounds can arise from a proton-transfer reaction between H_2O and the CN radical, which is issued from photolyzed C_4N_2.

1. Introduction

One of the major questions in the formation and evolution of condensed-phase molecules in interstellar environments is their production, which may proceed either via grain-surface chemistry or by accretion of simple molecules with subsequent processing by cosmic rays, UV photons or a combination of both. In the interstellar medium, under UV irradiation field originating from hot stars, the ices are subject to photochemical processes. This can lead to the formation of many complex organic molecules.[1] The knowledge of the composition of the icy grain mantles, essentially constituted by H_2O,[2] is assumed to be a key in the understanding of the interstellar chemistry.

In the past few years, our laboratory experiments have focused on the processing of irradiations of mixed ices to study the infrared spectra of key molecules and to identify new species formed during the photolysis processing.[3] Among the interstellar molecules we have studied, the dicyanoacetylene C_4N_2 has increased our interest. Indeed, this CN-bonded species compound, detected in condensed phase in Titan's atmosphere,[4] is suspected to be abundant in other astrophysical objects.[5] This molecule has particularly attracted the interest of many scientists since it is one of the most exotic molecules in regard to its unusual structure and its rich photochemistry.[6]

Furthermore, the nitrile compounds have astrobiological significance since some of them, such as HCN[7] and HC_3N,[8] are known to be the essential precursors in the synthesis of amino acid building blocks. Indeed, it has been shown theoretically[9−11] that the combination of nitrogen compounds with molecules, such as formic acid (HCOOH) and the formate anion ($HCOO^-$), could induce the formation of key compounds such as glycine.

According to previous works,[12] upon UV irradiation at $\lambda > 230$ nm, the dicyanoacetylene molecule photodissociates by the opening of one C−C single bond, leading to the formation of C_3N and CN radicals. Therefore, the $^{\bullet}CN$ species combined with H_2O, also detected on Titan,[13] could lead to the formation of complex organic molecules. Indeed, water ice can play a role in the photochemistry of species trapped in its lattice, acting as a reactive cage.[3b,14]

We report here the UV irradiation experiments of dicyanoacetylene trapped in water ice at $\lambda > 230$ nm, monitored by means of in-situ infrared spectroscopy, as a new possible route of synthesis of the following compounds:

- Ammonium bicarbonate, $NH_4^+HCO_3^-$.
- Ammonium formate, $NH_4^+HCOO^-$.

2. Experimental Setup

The apparatus used in these experiments is an evacuated sample chamber (10^{-7} mbar) containing a rotation gold-plated mirror kept at 10 K, coupled with Fourier Transform Infrared spectrometer (Nicolet series II Magna system 750) equipped with a liquid N_2 cooled detector, a germanium-coated KBr beam splitter and a globar source.

Pure dicyanoacetylene C_4N_2 (DCA) was synthesized using slightly modified methods of Moureu and Bongrand.[15] The dicyanoacetylene was distilled before each deposition. H_2O was doubly distilled before use. D_2O (99.8%) was supplied by SDS and used without further purification. Water and D_2O were degassed by successive freeze−thaw cycles under vacuum before each use.

The gas mixtures were prepared using the standard manometric techniques described elsewhere in the literature.[16] The relative concentrations of DCA/H_2O(D_2O) 1/5 were performed and sprayed by codeposition onto a golden copper plate cooled to 10 K. This vapor deposition technique produces intimately mixed ices with the H_2O in a high density amorphous form only observed at low temperatures and pressures. This is a representative form of the H_2O-rich ices in interstellar objects.[17]

Then, these mixed ices were irradiated using an Osram 200 W high-pressure Hg−Xe lamp equipped with a quartz envelope. This lamp produces light with an intense line spectrum between 230 and 620 nm, followed by a continuous spectrum up to 2600 nm, and contains some additional xenon lines between 750 and 1000 nm.

The samples'spectra were recorded in transmission mode between 4000 and 650 cm^{-1} before and after irradiation processing at various times. This facilitates the identification of the molecules produced during the photolysis because it

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allows a correlation of the different bands that appear. After irradiations, the samples were warmed at a rate of 1 K·min^{-1}. The warm-up was halted at regular intervals and infrared spectra were recorded to monitor the chemical evolution of the sample. The resolution was set to 1 cm^{-1} and 150-scan accumulations were recorded for each spectrum.

To identify and to verify the nature of the products obtained during the DCA/H_2O mixed ice photolysis, the following work was performed:

•We carried out isotopic experiments irradiating a DCA/D_2O mixed ice

•We deposited on the substrate the pure ammonium formate ($NH_4^+HCOO^-$, Aldrich 99%) at 10 K after purification by vacuum distillation. The ammonium bicarbonate, $NH_4^+HCO_3^-$, breaking down in the gas phase, we based on works reported in the literature for its identification

•We performed calculations, using the DFT method, to model the vibrational spectra of the reaction products. The Gaussian 03[18] program package, using the B3LYP[19] procedure with a 6-31G** basis set, was used for these calculations.

3. Previous Works

The UV absorption spectrum of DCA was measured for the first time by Miller et al.[20] in the 200−400 nm range. They reported two singlet band systems, the first one at 280 nm and the second one at 268 nm. Another absorption band, observed at 235 nm, corresponds to the strong progression of an electronic transition mode vibrationally allowed by ν_6 or ν_7 vibrations. The vacuum UV spectrum[21] presents two bands at 161 nm (very strong) and 172 nm (medium).

The matrix isolation spectroscopic technique has been shown to constitute a very successful approach for studying photochemical processes because it permits the trapping of reactive and unstable compounds. Indeed, the very low working temperature (10 K) does not allow further evolution of these species.[22] Thus, to make easier the analysis of the results of the photolysis of DCA trapped in water ice, we first carried out the UV irradiation of the 1:1 DCA:H_2O complexes in cryogenic matrices at 10 K.

The DCA:H_2O complexes were first irradiated at $\lambda > 230$ nm and the results were presented in a previous paper.[23] In summary, two final products were observed and characterized with FTIR spectroscopy. The former corresponds to the isonitrile NC_3NC, one of the isomers of DCA,[24] complexed with water. The latter has been assigned to the cyanoketene:HCN complex, which is produced by addition of water to the C_3N and CN radicals, issued from the DCA photolysis. Though the UV photolysis of these complexes were performed at other wavelengths ($\lambda > 120$ nm and $\lambda > 180$ nm) in argon matrix, the most interesting results (formation of cyanoketene and HCN) were obtained at $\lambda > 230$ nm. Therefore, the irradiation experiments of DCA trapped in water ice were carried out at the same wavelengths.

4. Results and Discussion

4.1. Experimental Results. In the 2420−1300 cm^{-1} region, the infrared spectrum of the DCA/H_2O mixture at 10 K shows three DCA vibrational modes[4,24a] and the characteristic bending mode of water ice (Figure 1a). In this region, the DCA is characterized by a strong vibrational band at 2248 cm^{-1}, which is attributed to the ν_{as}(C≡N) stretching mode, and two other weak features at 2339 and 2277 cm^{-1}, assigned to a Fermi resonance between the ν_1 (ν_s(C≡C)) and $2\nu_5$ modes.

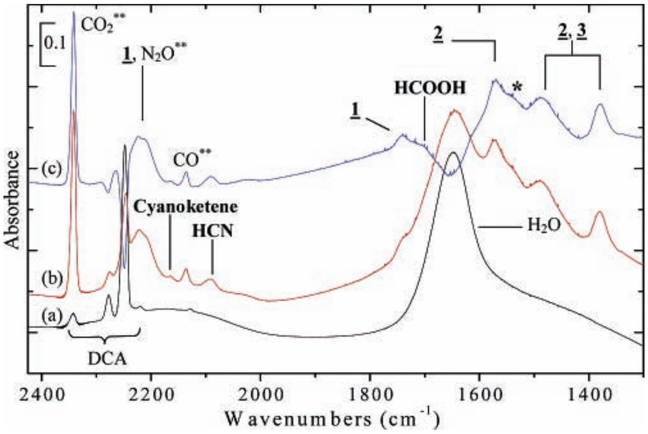


Figure 1. Infrared spectra of a DCA/H_2O mixed ice at 10 K before and after UV irradiation at $\lambda > 230$ nm. (a) DCA/H_2O (1/5) reference spectrum, (b) DCA/H_2O (1/5) after 39 h of irradiation, (c) Subtraction spectrum (b − a). The starred band remained unassigned. The compounds noted with two asterisks probably arise from impurities present in the sample. Their formation does not interfere with that of the new identified products since the latter are formed at the early stages of the experiment.

During the irradiation, we observed a decrease in intensity of the DCA and H_2O absorption bands and the growth of several other bands. We noted the formation of two features at 2164 and 2091 cm^{-1}, easily assigned to cyanoketene and cyanhydric acid with respect to the results of the photolysis of the DCA:H_2O complexes.[23] These two bands are assigned to the ν(CCO) stretching mode of cyanoketene[25] and the ν(C≡N) stretching mode of cyanhydric acid[26] respectively. Moreover, the evolution of the cyanoketene and HCN absorption bands, trapped in water ice, shows that they are reaction intermediates, though they behave as final products during the irradiation of the DCA:H_2O complexes in argon matrix.[23] In regard to these results, we hypothesized that the cyanoketene and HCN products could react during the experiment.

To confirm our results, we performed the photolysis of the DCA−D_2O mixed ice. We observed that the feature assigned to the cyanoketene at 2164 cm^{-1} is shifted in the DCA/D_2O irradiation toward the lower wavenumbers and observed at 2158 cm^{-1}. The good agreement between this shift value (6 cm^{-1}) and that reported in the literature[25a] between cyanoketene and D-cyanoketene (7 cm^{-1}) validated our assignment. At last, the non-observation of the ν(C≡N) stretching mode of DCN,[27] expected around 1920 cm^{-1}, is probably due to the weakness of this band.

Besides the primary products formation, we observed the build-up of several large bands (Figure 1, spectra b and c). These latter are located at 2218, 1743, 1576, 1490, and 1384 cm^{-1}. The evolution of the integrated absorbances vs time shows that these bands are associated with final reaction products. In addition, the analysis of the evolution of these absorption bands during the annealing experiment performed after irradiation, from 10 to 260 K, shows the formation of several products.

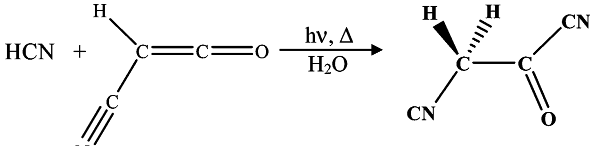
4.2. Identification of the Photoproducts. *4.2.1. Identification of the Keto−Nitrile Compound.* The bands formed at 2218 and 1743 cm^{-1} are characteristic of the ν(C≡N) and ν(C=O) stretching modes of nitrile and carbonyl groups respectively, which suggests the probable formation of a keto−nitrile compound **1**: the 2-oxo-succinonitrile (Scheme 1). This last product could be produced by the reaction between cyanoketene and HCN. Indeed, these latter compounds, which arise from the same reaction process,[23] are in close vicinity in the ice bulk allowing their reaction.

TABLE 1: Experimental and Theoretical (B3LYP/6-31G) Frequencies (cm^{-1}) of 2-oxo-succinonitrile and the D_2−2-Oxo-succinonitrile**

experimental			theoretical[c]		
DCA/H_2O[b]	DCA/D_2O[b]	$\Delta\nu$(exptl)[a]	2-oxosuccinonitrile (I)[d]	D_2−2-oxosuccinonitrile (I)[d]	$\Delta\nu$(calcd)[a]
			2959 (1)	2191 (<1)	768
			2924 (5)	2128 (4)	796
			2294 (2)	2294 (<1)	0
2218	**2217**	**1**	**2253 (24)**	**2253 (27)**	**0**
1743	**1741**	**2**	**1749 (100)**	**1747 (100)**	**2**
			1382 (13)	1373 (55)	9
			1302 (28)	1280 (40)	22
			1174 (<1)	1142 (76)	32
			1039 (10)	976 (<1)	63
			924 (22)	909 (27)	15
			903 (3)	883 (2)	20
			805 (4)	796 (1)	9

[a] $\Delta\nu$(exptl or calcd) = ν(H) − ν(D). [b] The experimental intensities were not calculated due to the overlapping of the absorption bands in the ν(C≡N) and ν(C=O) stretching region. [c] The frequencies are scaled with a factor of 0.96.[19] [d] The theoretical integrated intensities given between brackets are expressed as a percentage of the strongest band.

SCHEME 1: Formation of the 2-oxo-succinonitrile by Photolysis of a DCA/H_2O Mixed Ice at λ > 230 nm



2-oxo-succinonitrile
1

In addition, upon UV irradiation of the DCA/D_2O mixed ice, both features are slightly shifted to lower wavenumbers (2217 and 1741 cm^{-1}), suggesting a very weak influence of the deuterium atoms on the C≡N and C=O stretching modes of the suspected 2-oxo-succinonitrile. In Table 1, we report the calculated vibrational frequencies for both 2-oxosuccinonitrile and D_2−2-oxosuccinonitrile compounds. The analysis of these data shows a fair agreement between the experimental (2/1 cm^{-1}) and theoretical (2/0 cm^{-1}) frequency shifts for the C≡N and C=O stretching modes, respectively. The fact that the detectable <u>**1**</u> and <u>**1D**</u> spectra were reduced only to two bands found the explanation in the DFT results. Indeed, the bands are either predicted to be too weak to be observable or masked by strong bands of other products, especially by the H_2O or D_2O infrared features.

4.2.2. Identification of the Carboxylate Compounds. In view of the previous results, only the absorption bands at 1576, 1490, and 1384 cm^{-1}, produced during the irradiation of the DCA/H_2O mixed ice, have to be assigned.

4.2.2.a. Isotopic Substitution. Parts a and b of Figure 2 show, for a better comparison, the subtraction spectra before and after the irradiation of the DCA/H_2O and DCA/D_2O ices, respectively. During the DCA/D_2O photolysis, we observed in the 1800−1250 cm^{-1} region the increase of four bands at 1572, 1489, 1382, and 1329 cm^{-1}. We can note that the three former bands are scarcely shifted with respect to those obtained at 1576, 1490, and 1384 cm^{-1} in the DCA/H_2O irradiation experiment. The slight shifts observed between the two experiments suggest that either the products formed are not hydrogen-containing compounds or the presence of the H (D) atom in these products does not greatly influence the vibrational modes.

Finally, all these infrared bands increased until the end of irradiation but their correlation was not possible. Thus, an annealing experiment was performed.

4.2.2.b. Temperature Effects. Upon annealing of photolyzed DCA/H_2O from 10 to 260 K (Figure 3), we noticed the decrease in intensity of the features formed during the irradiation, due to the desorption of the products. Their desorption occurs at

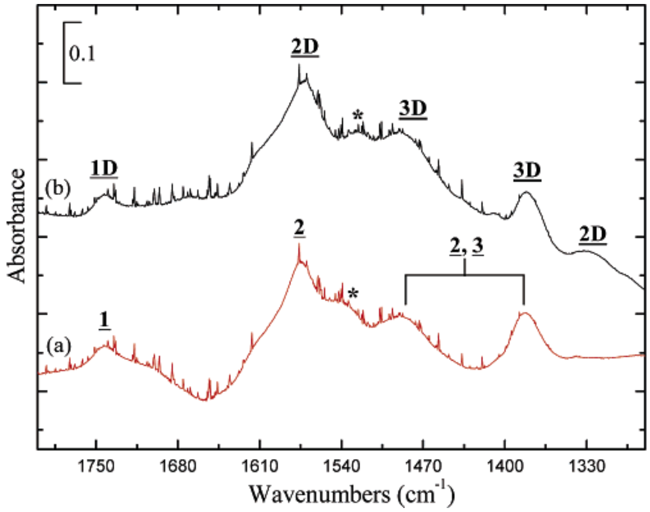


Figure 2. Comparison of the subtraction spectra after and before irradiation at 10 K of a) DCA/H_2O mixed ice with b) DCA/D_2O mixed ice at λ > 230 nm. The starred band remained unassigned.

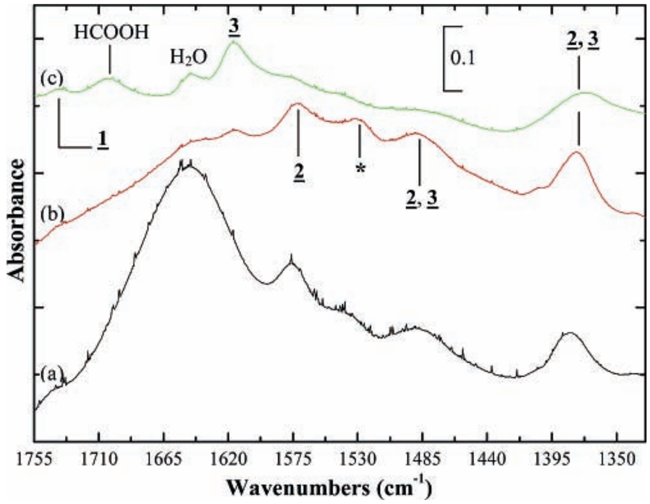


Figure 3. Infrared spectra of photolyzed DCA/H_2O mixed ice in the 1800−1350 cm^{-1} region after the annealing at (a) 10, (b) 170, and (c) 200 K. The starred band remained unidentified. The band at 1648 cm^{-1}, present at 200 K, likely corresponds to a small quantity of H_2O embedded in the more refractory material.

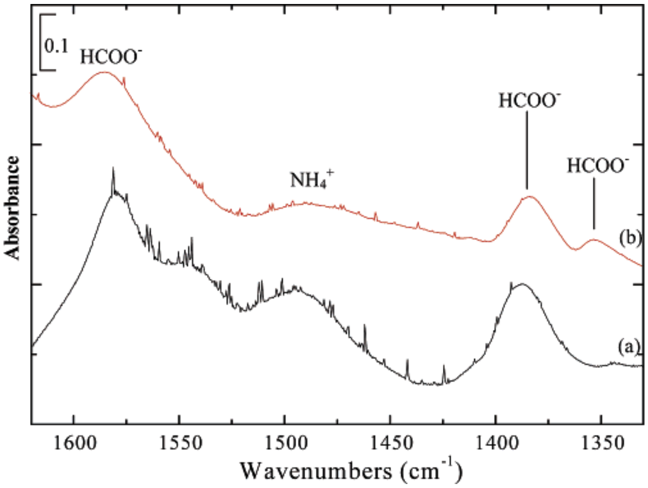


Figure 4. Comparison of (a) the subtraction spectrum after and before irradiation of the DCA/H_2O mixed ice at 10 K with (b) the infrared spectrum of $NH_4^+HCOO^-$ deposited on the substrate at 10 K.

different temperatures, which indicates the formation of several compounds during the irradiation.

In addition, during the warm-up which causes the water ice to sublime, two other bands can be seen at 1700 and 1616 cm^{-1}. These features are shifted to lower wavenumbers at 1671 and 1600 cm^{-1} respectively during the photolysis of the DCA/D_2O sample.

At last, the evolution of the absorption bands at 1490 and 1384 cm^{-1} indicates the presence of at least two components in these features.

4.2.2.c. Spectral Assignments. In the literature, it has been shown that most of the carboxylate compounds as formate[28] and bicarbonate[29,30] species exhibit two prominent infrared absorption bands, the former between 1630 and 1420 cm^{-1}, and the latter between 1390 and 1330 cm^{-1}. These features correspond respectively to the asymmetric $\nu_{as}(COO^-)$ and symmetric $\nu_s(COO^-)$ stretching vibrations of the COO^- groups (hereafter referred to as ν_{as} and ν_s, respectively).

Hudson et al.[31] have recently studied the radiation chemistry of water−methanol ices near 16 K, which led to the formation of the formate ion $HCOO^-$. This last species has been found to be characterized by three bands located at 1589, 1384, and 1353 cm^{-1}. Similar results were obtained in the literature[28] assigning these absorption bands to the ν_{as}, $\delta(CH)$ and ν_s modes, respectively. Therefore, these latter features appear to be in good agreement with those obtained at 1576 and 1384 cm^{-1} in the irradiated DCA/H_2O experiment.

To verify our hypothesis, we deposited the pure (solid) ammonium formate on the substrate at 10 K. The infrared spectrum of this compound, as shown in Figure 4, is characterized by absorption bands at 1585, 1384, and 1353 cm^{-1}, attributed to the formate ion, and by a weak band at 1486 cm^{-1}, due to the ammonium ion. The analysis of Figure 4 shows a good correlation between the $NH_4^+HCOO^-$ infrared spectrum and that obtained in our irradiated sample. However, during the irradiation we do not observe the $HCOO^-$ band at 1353 cm^{-1}, which is the least intense band of this anion. This could be explained by the fact that the formate ion is not produced in sufficient amount.

Moreover, isotopic substitution experiments performed by Collins et al.[28a] showed that the ν_{as} and ν_s stretching modes of the $DCOO^-$ species are shifted to lower frequencies by 5 and 30 cm^{-1} respectively (Table 2). Though the formate species are formed in a different way by Collins et al.[28a] (hydrogenation of carbonates at 473 K), the frequency shifts they obtained are of the same order of magnitude than those observed in our experiment: 4 and 55 cm^{-1}.

TABLE 2: Comparison between the Experimental Frequency Shifts $\Delta\nu$ (= ν(H) − ν(D), cm^{-1}) of the Frequencies of Ammonium Formate and Its Deuterated Species Obtained in Our Experiment and Those Reported in the Literature by Collins et al.[28a]

	frequencies (cm^{-1})					
	literature[28a]			our work		
assignments	$HCOO^-$	$DCOO^-$	$\Delta\nu$	DCA/H_2O	DCA/D_2O	$\Delta\nu$
$\nu_{as}(CO_2)$	**1580**	**1575**	**5**	**1576**	**1572**	**4**
$\delta_{CH(D)}$	1386	1029	357			
$\nu_s(CO_2)$	**1372**	**1342**	**30**	**1384**	**1329**	**55**

Therefore, all these results indicate that the ammonium formate **2** is a good candidate for the bands observed at 1576, 1490, and 1384 cm^{-1}. Nevertheless, the annealing experiment results suggest that other products contribute to these absorption bands. Indeed, at 200 K, the ammonium formate desorbs while the bands situated at 1490 and 1384 cm^{-1} remain (Figure 3).

Khanna et al.[32] demonstrated that the radiation chemistry of $NH_3/(H_2O + CO_2)$ mixture gave rise to strong features at 1597, 1498, 1480, 1441, and 1375 cm^{-1} which are all ascribed to the ammonium bicarbonate $NH_4^+HCO_3^-$. Karmali et al.[33] studied the infrared spectrum of $NaHCO_3$ and showed that the HCO_3^- species is characterized by absorption bands at 1625, 1455, and 1365 cm^{-1} assigned to the carbonate stretching vibration modes. The analysis of these data shows that $NH_4^+HCO_3^-$ can be a viable candidate for the features obtained at 1616, 1490, and 1384 cm^{-1} during the irradiation of the DCA/H_2O sample. Probably overlapped by the 1490 cm^{-1} large absorption band, the 1498 and 1480 cm^{-1} bands obtained by Khanna et al.[32] are not distinctly observed in our experiment.

Furthermore, calculations of the harmonic frequencies show that the ν_{as} and ν_s modes of $NH_4^+HCO_3^-$, the most intense vibrational bands, are shifted to lower wavenumbers by 13 and 2 cm^{-1} respectively with respect to the $ND_4^+DCO_3^-$ features (Table 3). These frequency shifts, which are close to those obtained in our experiments, 16 and 2 cm^{-1}, are consistent with the formation of ammonium bicarbonate $NH_4^+HCO_3^-$ **3** by the irradiation of the C_4N_2 molecule trapped in water ice.

Finally, by comparing the spectra of Figure 5, a good match is obtained between the band at 1700 cm^{-1}, which increases during the annealing of the photolyzed DCA/H_2O, and that at 1699 cm^{-1}, observed in the formic acid infrared spectrum at 170 K. Furthermore, it is worthwhile noting that HCOOH is also characterized by weak bands at 1609, 1388, and 1369 cm^{-1}, which can therefore contribute to the bands observed in our experiments. In addition, the experimental frequency shift (24 cm^{-1}) obtained between the bands observed at 1700 cm^{-1} (DCA/H_2O) and 1676 cm^{-1} (DCA/D_2O) is consistent with the result reported in the literature[34] ($\nu(C{=}O_{(HCOOH)}) - \nu(C{=}O_{(DCOOD)})$): 17 cm^{-1}. Thus, with respect to these data, we can assume that the formic acid is formed during the irradiation of the DCA/H_2O mixture.

It must also be noted that during the warm-up several bands are formed in the 3200−2600 cm^{-1} region after the water ice sublimation. Nevertheless, the presence in this area of both harmonic and combination bands of NH_4^+, HCO_3^-, and $HCOO^-$ does not allow us to conclusively assign these absorption bands.

With respect to these results, we can make the following assumptions:

TABLE 3: Experimental and Theoretical (B3LYP/6-31G) Frequencies (cm^{-1}) of Ammonium Bicarbonate and Its Deuterated Species**

experimental			theoretical		
DCA/H_2O^b	DCA/D_2O^b	$\Delta\nu$(exptl)[a]	$\nu(HCO_3^-)$ $(I)^c$	$\nu(DCO_3^-)$ $(I)^c$	$\Delta\nu$(calcd)[a]
			3813 (1)	2774 (1)	1039
1616	**1600**	**16**	**1766 (100)**	**1753 (100)**	**13**
1384	**1382**	**2**	**1291**[d] **(48)**	**1289**[d] **(42)**	**2**
			1197 (10)	940 (11)	257
			839 (35)	837 (31)	2
			815 (4)	814 (3)	1
			620 (1)	612 (2)	8

[a] $\Delta\nu$(exptl or calcd) = ν(H) − ν(D). [b]The experimental intensities were not calculated due to the overlapping of the absorption bands in the 1800−1350 cm^{-1} region. [c] Theoretical integrated intensities given in parentheses are expressed as a percentage of the strongest band. [d] The strength of this infrared absorption band is always underestimated by the calculations.[41]

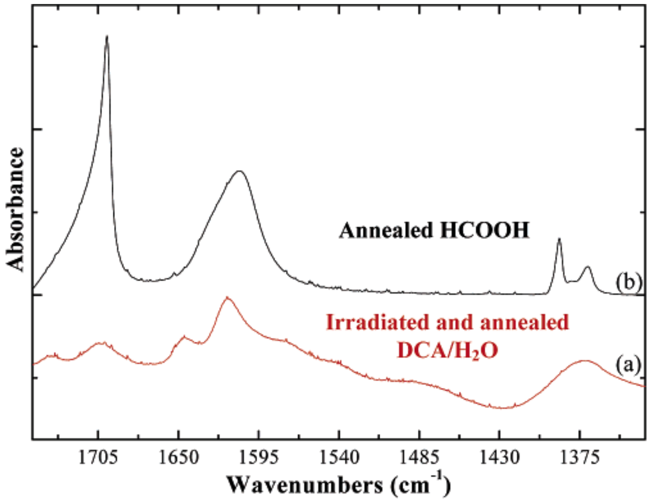


Figure 5. Comparison of the infrared spectra in the 1760−1320 cm^{-1} region of (a) photolyzed DCA/H_2O mixed ice after the annealing at 200 K with (b) solid HCOOH at 170 K.

TABLE 4: Summary of the Photoproducts Obtained by Irradiation of DCA Trapped in Water Ice at λ > 230 nm

frequencies (cm^{-1})	attribution
1700	HCOOH
1616	HCO_3^-, HCOOH
1576	$HCOO^-$
1490	NH_4^+, HCO_3^-, HCOOH
1384	$HCOO^-$, HCO_3^-, HCOOH

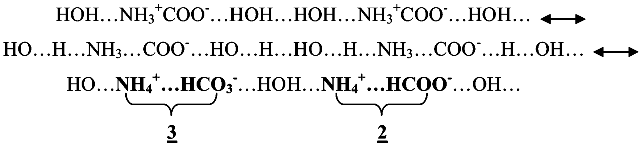
•The bands observed at the end of the irradiation and annealing experiments are the result of the contribution of several products, summarized in Table 4

•The irradiation of a DCA/H_2O mixed ice at λ > 230 nm can lead to the formation of the carboxylate species $HCOO^-$ and HCO_3^-, both associated with the ammonium ion NH_4^+.

4.3. Discussion. Previous experiments[12,23] showed that irradiations of DCA at λ >230 nm induced photodissociation by the cleavage of one CC single bond, leading to the formation of the C_3N and CN radicals. Furthermore, by performing irradiations at these wavelengths only the DCA molecule photodissociates, water absorbing essentially at λ < 200 nm.

The photolysis of a DCA/H_2O mixed ice shows that water can play an active role in the irradiating processes and thus in the production of new species. Indeed, cyanoketene and cyanhydric acid arise from addition of water to the CN and C_3N radicals, produced by the C−C opening of DCA. Thus, these two components, issued from the same reaction process, are in close vicinity in the water ice, allowing their reaction, which leads to the 2-oxo-succinonitrile.

SCHEME 2: Possible Mechanism of the Formation of Ammonium Bicarbonate ($NH_4^+HCO_3-$) and Ammonium Formate (NH_4^+HCOO-) by Proton Transfer Reaction



It is noteworthy that we do not observe the isomerization of DCA during the irradiation experiments. This result, already observed in the literature,[3b,35] could be explained by the fact that the radicals $CN^\bullet$ and $C_3N^\bullet$, coming from the photolysis of DCA, react with water as soon as they are formed, making the observation of the isomers impossible.

One of the new and interesting results from our irradiation experiments, described in the previous sections, is the formation of ammonium bicarbonate and ammonium formate. The mechanism of their formation is quite unclear, but it could be assumed, however, that the production of both compounds is initiated from reaction between water and the CN radical, through the formation of a possible intermediate: NH_2COOH, carbamic acid. As reported in the literature,[32] this last species could exist in a zwitterionic form in solid phase: $NH_3^+COO^-$, stabilized by formation of hydrogen bonding in the solid state.

Furthermore, it has been reported[36] that the polar environment can induce proton transfer at cryogenic temperatures from the acid to the base in the condensed phase, even for weak acids and bases. Water molecules are known to be strongly efficient in forming hydrogen bonds, and there exist a very extended number of hydrogen bonds in the ice mixture. This could promote the proton transfer[37] as shown in Scheme 2.

In addition, the experimental results have shown that the absorption bands of the $NH_4^+HCO_3^-$ and $NH_4^+HCOO^-$ salts strengthen during the warm-up, indicating that these ions could also be formed by thermal processes. Indeed, the temperature increasing enhances the interactions in the mixed ice and thus the proton transfer between the molecules.[38]

In conclusion, we can assume that ammonium bicarbonate and ammonium formate can arise from acid−base reactions through the carbamic acid, a possible intermediate not observed during our experiments.

5. Conclusion

In this paper, we showed that the experiments involving UV irradiation of DCA/H_2O mixed ice at λ > 230 nm can produce ammonium bicarbonate and ammonium formate, respectively characterized by absorption bands at 1616, 1490, and 1384 cm^{-1}, and 1576, 1490, and 1384 cm^{-1}. Therefore, we proposed here a new possible route of ammonium bicarbonate and ammonium formate synthesis. Indeed, both compounds are probably obtained by a proton-transfer reaction between H_2O molecules and the CN radical, this last species being initiated by the photolysis of the dicyanoacetylene molecule.

Finally, these results have important implications because they can be used to find traces of these molecules inside other interstellar objects such as in cometary nuclei, essentially constituted of water[39] and where the CN radical is supposed to be abundant.[40]

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References and Notes

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