

Infrared and mass spectral studies of proton irradiated H₂O + CO₂ ice: evidence for carbonic acid*

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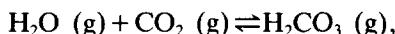
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Abstract—The effects of proton irradiation on mixed H₂O + CO₂ (1:1) ices at 20 K were investigated by infrared and mass spectroscopy. Infrared bands due to several radical (HCO, CO₃) and molecular (CO) product species were identified. In addition, several new broad and complex i.r. features were observed. On slow warming, the broad features evolved into a 215–250 K residual film whose absorptions have been tentatively assigned to carbonic acid. This identification agrees with the spectral data for irradiated H₂O + ¹³CO₂ ice and the results of an approximate normal coordinate analysis.

INTRODUCTION

CARBONIC ACID, H₂CO₃, is an elusive molecule in the sense that it has defied efforts for its detection by spectroscopic techniques. Adducts of H₂CO₃ with ethers (R₂O, R=CH₃, C₂H₅, etc.) have been prepared and these are stable below 238 K [1, 2]. At ambient temperatures the adducts decompose into H₂O, CO₂ and R₂O components.

Ab initio quantum mechanical calculations have been performed to determine the structural parameters of H₂CO₃ [3]. Similar calculations for the gas phase reaction [4];



indicate a sizable activation energy (~50 kcal mol⁻¹). This means that once synthesized, H₂CO₃ could be stabilized.

In our studies of cometary type ices we have been involved in the investigations of the effects of proton irradiation of thin films of icy mixtures including H₂O + CO₂. In several of our experiments the radiation synthesized species from H₂O + CO₂ (1:1) ice mixtures were investigated using i.r. and mass spectroscopic techniques. The original motivation for these experiments was to confirm two earlier reports of the formation of formaldehyde, H₂CO, in irradiated H₂O + CO₂ ice mixtures [5, 6]. H₂CO is of interest to astronomers since it has been identified in Halley's comet [7] and in interstellar space [8]. Although further work may be needed to clarify the mechanisms of any H₂CO synthesis in laboratory experiments, the evolution of the irradiated ice during warming resulted in a residual film whose identification is the focus of this paper. The analysis of the i.r. spectra of this residue at 215 and 250 K (after more volatile species such as H₂O, CO₂, CO and radicals have been removed by warming) suggests that the absorption features are principally due to the solid phase of H₂CO₃. A detailed discussion is presented below.

EXPERIMENTAL

Gas mixtures were prepared in an external gas handling system equipped with diaphragm manometers covering the pressure range from 0–50 torr. Water (triply distilled with resistance >10⁷ ohms cm) had dissolved gases removed by vacuum freeze–thaw cycling; ¹²CO₂ (99.5%, dry, Air Products) was used without further purification. ¹³C enriched carbon dioxide was 91.2 atom%

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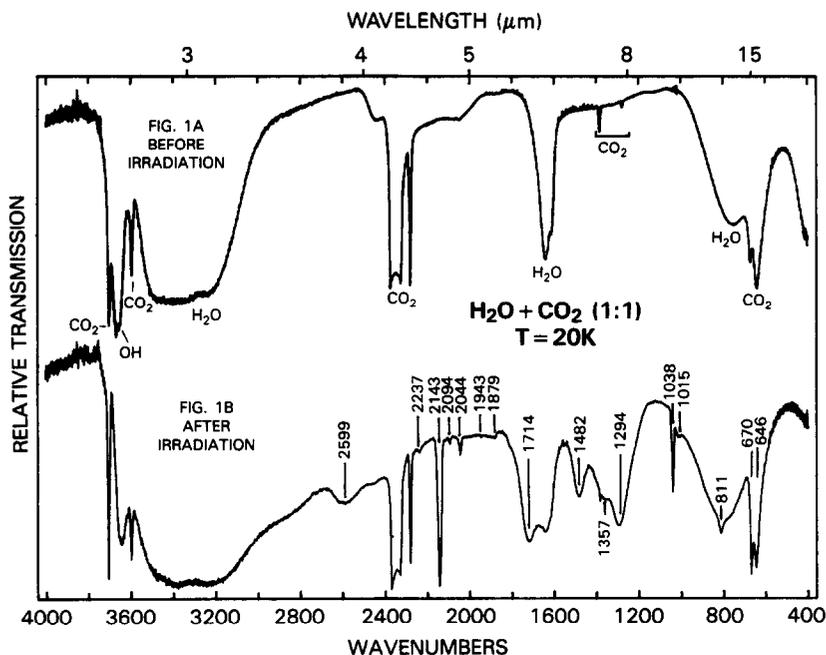


Fig. 1. (a) Infrared spectrum of $\text{H}_2\text{O} + \text{CO}_2$ (1:1) at $T = 20$ K. Physical ice thickness is estimated to be $4\ \mu\text{m}$. (b) Infrared spectrum of $\text{H}_2\text{O} + \text{CO}_2$ icy mixture after irradiation with 700 keV protons to a total incident fluence of 1.5×10^{15} protons cm^{-2} . Many new absorption features are the result of the synthesis of new molecules and radicals within the 20 K ice. Spectra have been shifted vertically for clarity.

^{13}C (Bio-Rad Lab.). H_2CO gas was obtained by slow thermal decomposition of commercial paraformaldehyde (purified, Fisher Scientific Co.) in a vacuum system.

Ice films were formed by condensing gas mixtures of $\text{H}_2\text{O} + \text{CO}_2$ (1:1) onto an aluminum mirror attached to the tail section of a closed-cycle cryostat. Similarly, thin films of solid H_2CO and $\text{H}_2\text{O} + \text{H}_2\text{CO}$ were formed by condensing H_2CO gas or a mixture of $\text{H}_2\text{O} + \text{H}_2\text{CO}$ gases and their spectra were used as references for identifications. In our optical arrangement one window of the cryostat was directed to the beam of a FTIR spectrometer, another was connected to a mass spectrometer, and a third was connected to a Van de Graaff accelerator. The sample could be rotated to face one of these ports depending on the nature of the experiment: spectroscopy, vaporization or irradiation.

Ice mixtures were irradiated with 700 keV protons to a total fluence* of the order of 10^{15} protons cm^{-2} . Mass spectra of species released from condensed films during warming were obtained with a Dycor quadrupole mass spectrometer (Model M200M).

Infrared absorption spectra of ice films were recorded using a Mattson (Polaris) Fourier transform interferometer. Using a focus projection attachment, the i.r. beam was directed at a right angle to the spectrometer bench through the cryostat window where it passed through the ice film, reflected at the ice-aluminum interface, and again passed through the ice film before traveling to the detector. Spectra were recorded from 4000 to $400\ \text{cm}^{-1}$ at $1\ \text{cm}^{-1}$ resolution.

RESULTS

The i.r. spectra of a $4\ \mu\text{m}$ thick film of $\text{H}_2\text{O} + \text{CO}_2$ (1:1 by mole) at 20 K before and after irradiation are reproduced in Fig. 1. Figure 1(a) (before irradiation) exhibits strong features due to hydrogen bonded H_2O ($\tilde{\nu}_{\text{stretch}}$ near $3200\ \text{cm}^{-1}$, $2400\ \text{cm}^{-1}$, $\tilde{\nu}_{\text{in-plane bend}}$

* Fluence (protons cm^{-2}) = $\frac{\text{proton beam current integrated over time (coulombs)}}{\text{sample area (cm}^2\text{)} \times 1.6 \times 10^{-19} \text{ (coulombs proton}^{-1}\text{)}}$

1640 cm⁻¹, and $\bar{\nu}_{\text{out-of-plane bend}}$ 750 cm⁻¹) and CO₂ ($\bar{\nu}_3$ 2343 cm⁻¹, $\bar{\nu}_2$ 655 cm⁻¹ doublet). Features due to $\bar{\nu}_3$ (¹³CO₂) at 2280 cm⁻¹ and inactive $\bar{\nu}_1$ ¹²CO₂ in Fermi resonance with 2 $\bar{\nu}_2$ at 1276 and 1383 cm⁻¹ are also observed.

After proton irradiation (total incident fluence = 1.5 × 10¹⁵ protons cm⁻²) several additional absorption features are seen [Figure 1(b)] which grow with increased fluence. Peaks at 2143 and 2094 cm⁻¹ are due to ¹²CO and ¹³CO, respectively. Weak features at 2044 and 1879 cm⁻¹ are probably due to radical species CO₃ [9] and HCO? [10], respectively, and they disappear on warming to ~90 K. Absorptions at 1714, 1482 and 1294 cm⁻¹ are similar in frequency to those measured for a condensed thin film of monomeric H₂CO or of H₂O + H₂CO (10:1), Figs 2(a) and (b). However, it has not been possible to identify H₂CO as a primary product for several reasons: (a) There is no correspondence in the relative intensities or band widths between the peaks of the irradiated H₂O + CO₂ ice and those of H₂CO; (b) the 1482 cm⁻¹ absorption is shifted 12 cm⁻¹ from the $\bar{\nu}_3$ H₂CO position and the 1294 cm⁻¹ peak is shifted by 48 cm⁻¹ from $\bar{\nu}_6$ H₂CO; (c) there is an absence [see Fig. 1(b)] of CH₂ stretch peaks from H₂CO near 2880 cm⁻¹, which are generally sharp.

Further warming of the sample results in larger changes in the i.r. spectrum as sublimation of molecular species such as H₂O, CO₂ and CO occurs. Spectra recorded at 215 K indicate that evolution of the film has resulted in a stable spectral signature (Table 1 gives the peak positions). All bands undergo approximately the same rate of sublimation suggesting that the spectrum is that of a single compound. Increasing the temperature to 250 K results in a frequency shift of the peaks by 5–15 cm⁻¹. The changes in the intensities of the bands of this residual film at 250 K with elapsed time are shown in Fig. 3. Peak positions for the 250 K residual film are also given in Table 1.

Infrared spectra of the residue at 215 and 250 K exhibit peaks in the 3200–2500 cm⁻¹ region which appear to be characteristic of the O–H . . . O system. A similar pattern is observed in the spectra of carboxylic acids [11], metallic bicarbonates [11], and other systems containing cyclic arrangements of O–H . . . O bonds [12]. Although the association of the peaks near 1700, 1500 and 1300 cm⁻¹ with H₂CO was considered, the evolved spectrum of the residue contains absorptions at 2614, 1034, 812 and 682–655 cm⁻¹

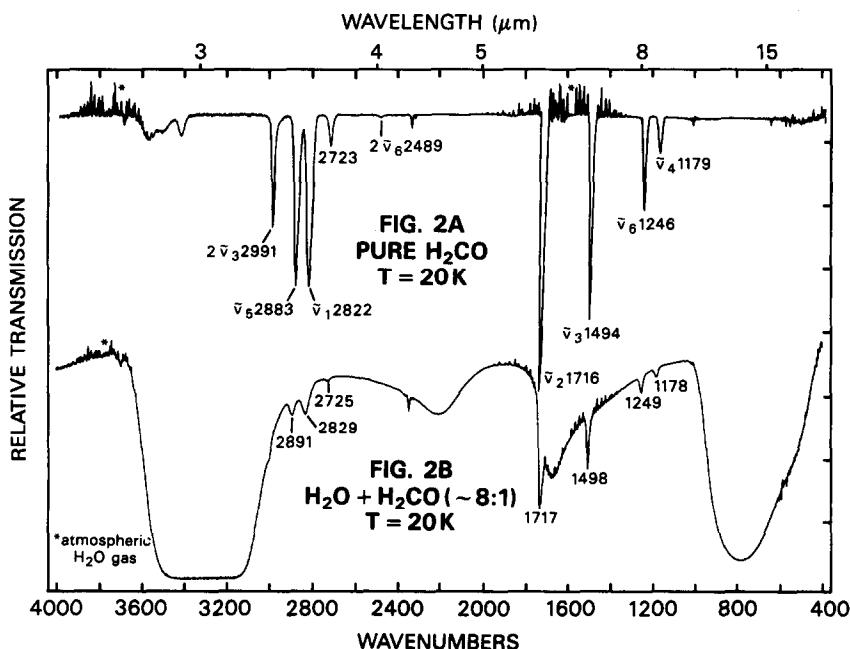


Fig. 2. (a) Infrared spectrum and identifications of condensed phase thin film of H₂CO at T = 20 K. (b) Infrared spectrum of H₂O + H₂CO (8:1) icy mixture at T = 20 K.

Table 1. Frequencies (cm^{-1}) of i.r. absorption peaks due to $\text{H}_2^{12}\text{CO}_3$ and $\text{H}_2^{13}\text{CO}_3$ and comparison with $(\text{CH}_3)_2\text{CO}_3$

$\text{H}_2^{12}\text{CO}_3$		$\text{H}_2^{13}\text{CO}_3$		$\text{H}_2^{12}\text{CO}_3$	$(\text{CH}_3)_2\text{CO}_3^\dagger$	Assignment
Obs. 215 K	Calc.	Obs. 215 K	Calc.	Obs. 250 K	300 K	
3050		3040		3030		O-H O st.
2870–2850		2850		2840		
2610		2593		2614		
1702	1702	1665	1661	1705	1756	C=O
1505		1470	(1500) [†]	1501		COH in plane bend
1308	1292	1292	1257	1296	1274	C-O* ast.
1035	1037	1034	1035	1034	1025	C-O* sst.
892		888	(888) [‡]	884		COH out-of-plane bend
806		780	(780) [‡]	812	795	CO ₃ out-of-plane bend
683		680		682	690	CO ₃ in-plane bend
656		654		655	638	

[†] Taken from Ref. [22].

[‡] Based on expected ¹³C isotopic shifts from those of $\text{H}_2^{12}\text{CO}_3$.

O* = OH or (OCH₃) groups.

(doublet) which do not exist in the spectrum of H_2CO [Fig. 2(a) and (b)]. We would not expect H_2CO to be present at 250 K because in our studies pure solid-phase monomeric H_2CO undergoes rapid sublimation in the vacuum environment (10^{-6} – 10^{-7} torr) near 95 K and $\text{H}_2\text{O} + \text{H}_2\text{CO}$ ice releases most of the H_2CO between 130–170 K. Other forms of less volatile H_2CO , e.g. trioxane (H_2CO)₃ [11], and POM (H_2CO)_n ($n \geq 4$) [13] do not explain the spectra in Fig. 3.

We notice that the spectral features in the 1500–600 cm^{-1} region of the 215–250 K residue are similar to those of the carbonate (CO_3^{2-}) ion and a bicarbonate (HCO_3^-) ion

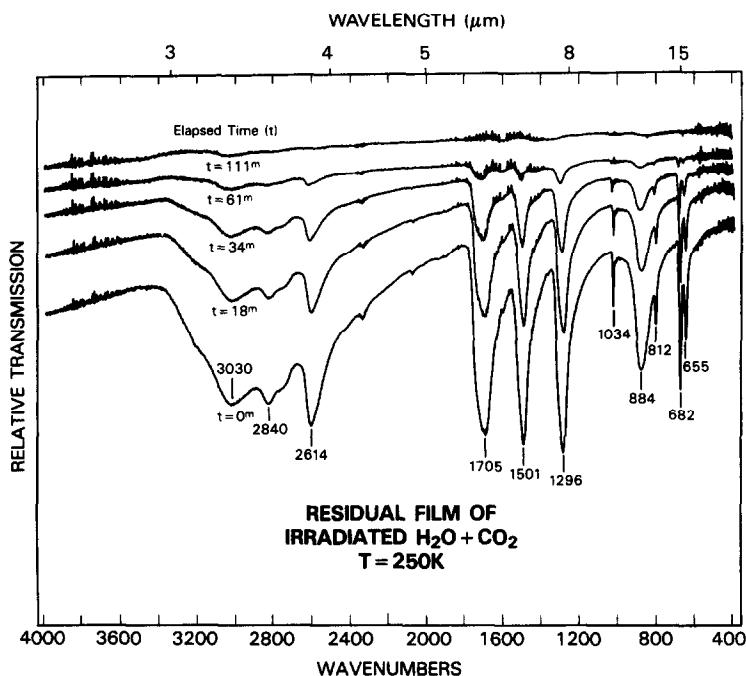


Fig. 3. Infrared spectra at 250 K vs time of a residual film tentatively identified as H_2CO_3 . This thin film remains after slow warming of an irradiated $\text{H}_2\text{O} + \text{CO}_2$ ice from 20 K. Spectra have been shifted vertically for clarity.

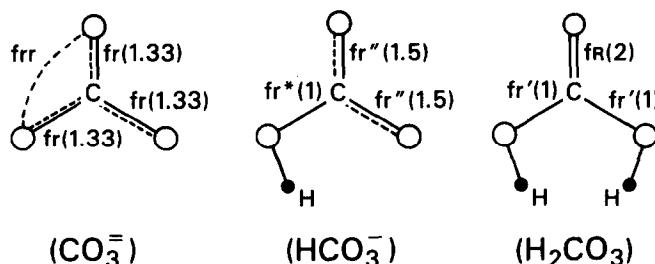


Fig. 4. Schematics of the structure, bond order and force constants for CO₃²⁻, HCO₃⁻ and H₂CO₃.

[11]. The six modes of CO₃²⁻ in calcite (symmetry group *D*_{3h}) have the following symmetry types and frequencies [14]:

$\bar{\nu}_1$ (C–O sym. st.)	$\left\{ \begin{array}{l} \text{i.r. inactive} \\ \text{R active} \end{array} \right.$	1087	(cm ⁻¹)
$\bar{\nu}_2$ (CO ₃ ²⁻ out-of-plane bend)	$\left\{ \begin{array}{l} \text{i.r. active} \\ \text{R inactive} \end{array} \right.$	879	(cm ⁻¹)
$\bar{\nu}_3$ (C–O asym. st.) (doubly degenerate)	$\left\{ \begin{array}{l} \text{i.r., R active} \end{array} \right.$	1429–1492 (i.r.) 1432 (R)	(cm ⁻¹) (cm ⁻¹)
$\bar{\nu}_4$ (CO ₃ ²⁻ in plane bend) (doubly degenerate)	$\left\{ \begin{array}{l} \text{i.r., R active} \end{array} \right.$	706 (i.r.) 714 (R)	(cm ⁻¹) (cm ⁻¹)

The stretching frequencies of the carbonate ion ($\bar{\nu}_1$: 1087 cm⁻¹, $\bar{\nu}_3$: 1450 cm⁻¹) correspond to a bond order of 4/3 for the C–O bond. For the bicarbonate ion, the observed frequencies [15] (1001, 1367 and 1618 cm⁻¹) correspond, respectively, to a CO bond order of 1 for the C–OH st., and a CO bond order of 1.5 for the COO⁻ group. Figure 4 compares the structures of CO₃²⁻, HCO₃⁻ and H₂CO₃. The spectrum of the residue at 250 K exhibits a major peak at 1705 cm⁻¹ which is typical of a C=O bond (bond order 2). Neither a carbonate nor a bicarbonate can account for this absorption. Also, if HCO₃⁻ was present in the residue, a positive ion like H₃O⁺ would be required to preserve the charge neutrality of the condensate. The vibrational frequencies of H₃O⁺ have been derived from a study of the i.r. spectra of: X–H₃O⁺, X–D₃O⁺ and X–Na⁺ where X = CH₃C₆H₄SO₃⁻ [16]. These frequencies are $\bar{\nu}_1$ 2700 cm⁻¹ (weak), $\bar{\nu}_2$ 1130 cm⁻¹ (strong), $\bar{\nu}_3$ 2600 cm⁻¹ (weak), and $\bar{\nu}_4$ 1665 cm⁻¹ (strong). A more recent study of the i.r. spectra of water adsorbed on Y-type zeolites [17] assigns absorptions at 2930, 2510 and 1690 cm⁻¹ to H₃O⁺. In any case, none of these features seem to match the absorption peaks in the spectrum of the residue shown in Fig. 3. Therefore, we believe the observed spectrum is due to solid phase H₂CO₃. We assign the peaks at 1034 and 1296 cm⁻¹ with the symmetric (in-phase) and antisymmetric (out-of-phase) stretching, respectively, of the C(OH)₂ group in H₂CO₃. The 812 cm⁻¹ is similar to the 879 cm⁻¹ peak of the CO₃²⁻ and is assigned to the out-of-plane bend. The doublet in the 660 cm⁻¹ region is due to the splitting of the in-plane bend. As mentioned above, the broad complex band in the 3200–2500 cm⁻¹ is due to O–H . . . O in the solid phase. This leaves the features at 1500 and 890 cm⁻¹ to be accounted for. These can be assigned to the in-plane and the out-of-plane C–OH bends, respectively, which are influenced by O–H . . . O hydrogen bonding. Additional confirmation of these assignments comes from an approximate normal coordinate calculation and the isotopic data on irradiated H₂O + ¹³CO₂ ice.

Based on the frequencies $\bar{\nu}_1$ and $\bar{\nu}_3$ of a CO₃²⁻ in calcite where the intermolecular coupling is negligible, the force constants, f_r (bond stretch) and f_{rr} (stretch–stretch

interaction) (see Fig. 4) are evaluated to be:

$$f_r = 7.98 \text{ mdyne } \text{\AA}^{-1} \quad f_{rr} = 1.56 \text{ mdyne } \text{\AA}^{-1}.$$

The corresponding stretching force constants for H_2CO_3 (see Fig. 4) are:

$$f_R (\text{C=O stretch}) \approx 1.5 f_r \approx 12.0 \text{ mdyne } \text{\AA}^{-1}, \text{ and} \\ f_r (\text{C-O stretch}) \approx 0.75 f_r \approx 5.98 \text{ mdyne } \text{\AA}^{-1}.$$

In the solid phase, hydrogen bonding (suggested by strong absorptions in the 3200–2600 cm^{-1} region) results in a decrease in O–H strength and, consequently, an increase in the C–O bond order. A rough estimate of this increase can be obtained by comparison with other hydrogen-bonded systems. Based on the similarity between spectra of the 250 K residue and spectra of KH_2PO_4 and carboxylic acids, the hydrogen bond strengths in our sample appear to be intermediate between those of KH_2PO_4 ($r_{\text{O-H}} \sim 1.05\text{--}1.075 \text{ \AA}$) [18] and carboxylic acids $r_{\text{O-H}} \sim 1.011 \text{ \AA}$) [19]. If we assume $r_{\text{O-H}} \sim 1.04 \text{ \AA}$ for H_2CO_3 , the corresponding theoretical estimate of the OH binding energy (110 kcal mol^{-1}) [20] is approximately 5% lower than that for a free OH. A similar magnitude increase in the binding energy and, consequently, the C–O force constant is to be expected. A 15% increase in the bond order (\sim force constant) for C–O in H_2CO_3 (solid) over that of a C–O single bond gives the best agreement between the calculated stretching frequencies of $^{12}\text{CO}_3$ and $^{13}\text{CO}_3$ groups in H_2CO_3 and the experimental data (Table 1). In these calculations the OH group is considered to be a single atom (O^*) with a mass = 17 a.m.u. and the interactions with all other modes (in-plane bends $r\text{OH}$ stretch, etc.) are ignored. The correspondence between the pattern of observed frequencies in Table 1 and the calculated value is encouraging, although, perhaps not too much importance is to be attached to the numerical agreement. The in-plane and out-of-plane bending frequencies at 682–655 cm^{-1} (doublet) and 812 cm^{-1} , respectively, occur at somewhat lower frequencies than the corresponding frequencies of a CO_3^{2-} .

After ^{13}C isotopic substitution we observe that the absorption peaks in the region 3200–2600 cm^{-1} remain practically unaltered as would be expected for O–H...O stretches. The 1505 and 892 cm^{-1} peaks assigned to the in-plane and out-of-plane COH bending modes, are shifted on ^{13}C substitution to 1470 (broad) and 888 cm^{-1} . While the shift for the out-of-plane bend ($\sim 4 \text{ cm}^{-1}$) agrees with the calculated value ($\sim 4\text{--}5 \text{ cm}^{-1}$), the shift for the in-plane bend from 1505 to 1470 cm^{-1} is larger than the predicted value ($\sim 4\text{--}5 \text{ cm}^{-1}$) and this may be due to a large coupling with the C–OH stretches. The observed ^{13}C isotope shift for the C–OH stretch is smaller than the calculated value which supports the argument for coupling between COH bending and C–OH stretching modes. Assignment of the 812 cm^{-1} peak to the out-of-plane bending mode of the CO_3 group in $\text{H}_2^{12}\text{CO}_3$ is consistent with the observed shift of 26 cm^{-1} after ^{13}C substitution (calculated value, 26 cm^{-1}). The doublet at 682–655 cm^{-1} also appears to be correctly assigned to the in-plane bend (split doubly degenerate mode). These frequencies do not shift significantly on ^{13}C isotopic substitution as has also been observed for several carbonate crystals [21].

It is interesting to note that the i.r. spectrum of the 250 K residue resembles that of dimethyl carbonate, $(\text{CH}_3)_2\text{CO}_3$ [22], which has a structure similar to that of carbonic acid; the difference being that H atoms in H_2CO_3 are replaced by CH_3 groups. The frequencies of peaks associated with the CO_3 group in $(\text{CH}_3)_2\text{CO}_3$ are also shown in Table 1. Absorption features in the spectrum not included in the Table are at 3000 (CH_3 st.), 1450 (CH_3 bend), 1100 (O– CH_3 st.), 970, 915 and 580–520 cm^{-1} (coupled rocking, wagging and twisting modes of CH_3). This comparison clearly establishes a strong case for the 250 K residue being carbonic acid.

Preliminary mass spectral data ($m/e = 4\text{--}100$) of species sublimated from $\text{H}_2^{12}\text{CO}_3$ at 250 K showed m/e peaks at 16 (O^+), 17 (OH^+), 18 (H_2O^+), 28 (CO^+), 29 (HCO^+) and 44 (CO_2^+). The mass spectral pattern (observed from $m/e = 27\text{--}65$ with background subtraction) of sublimated species from the $\text{H}_2^{13}\text{CO}_3$ sample at 250 K reveals m/e peaks

at 29(¹³CO⁺), 30(H¹³CO⁺), 31(H₂¹³CO⁺), 40(Ar⁺), 44(¹²CO₂⁺) and 45(¹³CO₂⁺). The *m/e* peak at 45 was the most intense, and the smallest peak observed was at *m/e* = 31. The detection of argon was attributed to contamination from an earlier experiment and CO⁺, OH⁺, and O⁺ were produced in the mass spectrometer ionizer from CO₂ and H₂O. This data typically had a signal-to-noise ratio of 10:1 to 20:1. Further mass spectral studies of this residual film are underway. A peak at *m/e* = 62, corresponding to H₂CO₃⁺ was not detected in our experiments. In a study by TERLOUW *et al.* [23] mass spectra of the gas phase dissociation products of NH₄HCO₃ revealed a peak at 62 (attributed to H₂CO₃⁺) with an intensity <1% that of the mass 44 peak. The signal-to-noise ratio in their experiment was better than 100:1. Thus, the mass spectral data on the subliming residue film is not inconsistent with its identification as H₂CO₃. It appears that the 50 kcal mol⁻¹ activation energy to form H₂CO₃ from H₂O and CO₂ is supplied by the proton beam and low temperature prevents its decomposition.

CONCLUSIONS

The analysis of the i.r. and mass spectral data, presented here, gives strong evidence for the formation of H₂CO₃ (carbonic acid) on irradiating a 1:1 H₂O + CO₂ ice mixture at 20 K. At least two radical (HCO and CO₃) species along with molecular CO were also identified in the i.r. spectra of the irradiated mixture at 20 K; however, on warming to 210 K the residual film appears to be principally hydrogen-bonded H₂CO₃.

One of the reviewers suggested the possibility of H₂O₂ and O₃ (chemisorbed on the substrate) being responsible for some of the i.r. features which we attributed to H₂CO₃. The mass spectral data on the residue do not reveal any peak which may be associated with O₃ (e.g. *m/e* = 48) or H₂O₂ (e.g. *m/e* = 34, 33). There is no match between the i.r. characteristics of the residue and those of the condensed O₃ and H₂O₂ films. It is likely that O₃ and H₂O₂ species are produced to a much smaller extent than HCO and CO₃. Experimental studies to understand the kinetics of the initial phases of the reactions leading to the final residue would be desirable.

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