

Studies of Proton Irradiated H₂O+CO₂ and H₂O+CO Ices and Analysis of Synthesized Molecules

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Infrared spectra of H₂O+CO₂ and H₂O+CO ices before and after proton irradiation showed that a major reaction in both mixtures was the interconversion of CO₂ ⇌ CO. Radiation synthesized organic compounds such as carbonic acid were identified in the H₂O+CO₂ ice. Different chemical pathways dominate in the H₂O+CO ice in which formaldehyde, methanol, ethanol, and methane were identified. Sublimed material was also analyzed using a mass spectrometer. Implications of these results are discussed in reference to comets.

INTRODUCTION

Formaldehyde, H₂CO, is one of the interstellar molecules with the highest relative abundance (approximately 0.3% that of H₂O [Guelin, 1984]). It may condense onto interstellar grains and become incorporated into any comets formed from these materials. Cometary H₂CO was first detected in comet Halley with a production rate a few percent of that of H₂O. Emissions were detected in the radio [Snyder *et al.*, 1989] and in the infrared spectral region [Moroz *et al.*, 1987; Combes *et al.*, 1986; Knacke *et al.*, 1986; Dankes *et al.*, 1987].

Radiation processing (photolysis and/or particle radiation) of interstellar icy materials such as H₂O, CH₄, CO, CO₂, and CH₃OH may result in the synthesis of H₂CO increasing its abundance. Therefore pathways leading to the synthesis of H₂CO have been examined in several laboratory experiments.

Results from several photolysis experiments showed the synthesis of H₂CO in icy mixtures containing H₂O and CO along with other molecules [e.g., Greenberg, 1982; d'Hendecourt *et al.*, 1986; Allamandola *et al.*, 1988]. More recently, Zhao [1990] reported the detection of H₂CO in both photolyzed H₂O+CO₂ and H₂O+CO. There have been two reports of the detection of H₂CO from ion irradiated H₂O+CO₂; one experiment used mass spectroscopy [Pirronello *et al.*, 1982] and one used infrared spectroscopy [Rocard, 1986].

We have examined the infrared spectrum of H₂O+CO₂ and H₂O+CO before and after irradiation and have identified most species synthesized in the ice. The evolution of spectra during warming was observed, along with the mass spectral detection of species released during vaporization. We compare and contrast irradiation results of these two icy mixtures.

EXPERIMENTAL PROCEDURES

Thin ice films were formed by condensing gas mixtures of H₂O+CO₂ or H₂O+CO onto an aluminum mirror ($T=20$ K) attached to the tail section of a closed-cycle cryostat. One window of the cryostat was directed to a reflection attachment on a Mattson Polaris FT-IR (Fourier Transform Infrared) spectrometer another was connected to a Dycor (model M200M) quadrupole mass spectrometer, and a third was connected to a Van de Graaff accelerator. The ice sample could be rotated to face one of these ports depending on the nature of the experiment: spectroscopy, vaporization, or irradiation. Details of this experimental setup are given by Moore *et al.* [1988].

RESULTS

The infrared spectrum from 4000 to 400 cm⁻¹ of an ~6- μ m-thick H₂O+CO₂ (~1.4:1) ice is shown in Figure 1. The absorptions of H₂O and CO₂ in the newly deposited ice are labeled in Figure 1a. After irradiation (Figure 1b) many new features appear in the spectrum. The sharp feature at 2143 cm⁻¹ is identified as ¹²CO and that at 2094 cm⁻¹ as ¹³CO. Tentative identification of carbon suboxide, C₃O₂, is at 2237 cm⁻¹ [Miller and Fateley, 1964; V.G. Anicich and M. Allen, private communication, 1991]. CO₃ radical species could be associated with the weak features at 2044 and 1878 cm⁻¹ [Jacox *et al.*, 1971]. Figure 1b "expanded" (lowest spectrum in lower box) shows a more detailed view of the irradiated sample, between 1800 and 900 cm⁻¹. There is some similarity between positions of the synthesized features at 1714, 1482 and 1294 cm⁻¹ and the positions of formaldehyde absorptions (ν_2 , ν_3 , and ν_6) in an H₂O+H₂CO ice (see Figure 2c). However, we believe this similarity is not evidence for the presence of H₂CO because there are differences between the relative intensities, positions, and bandwidths of the peaks in the irradiated ice and those of H₂CO. We observed that when irradiated H₂O+CO₂ was warmed slowly to 250 K, the ice evolved into a film whose absorptions were identified as carbonic acid, H₂CO₃ [Moore and Khanna, 1991]. There are

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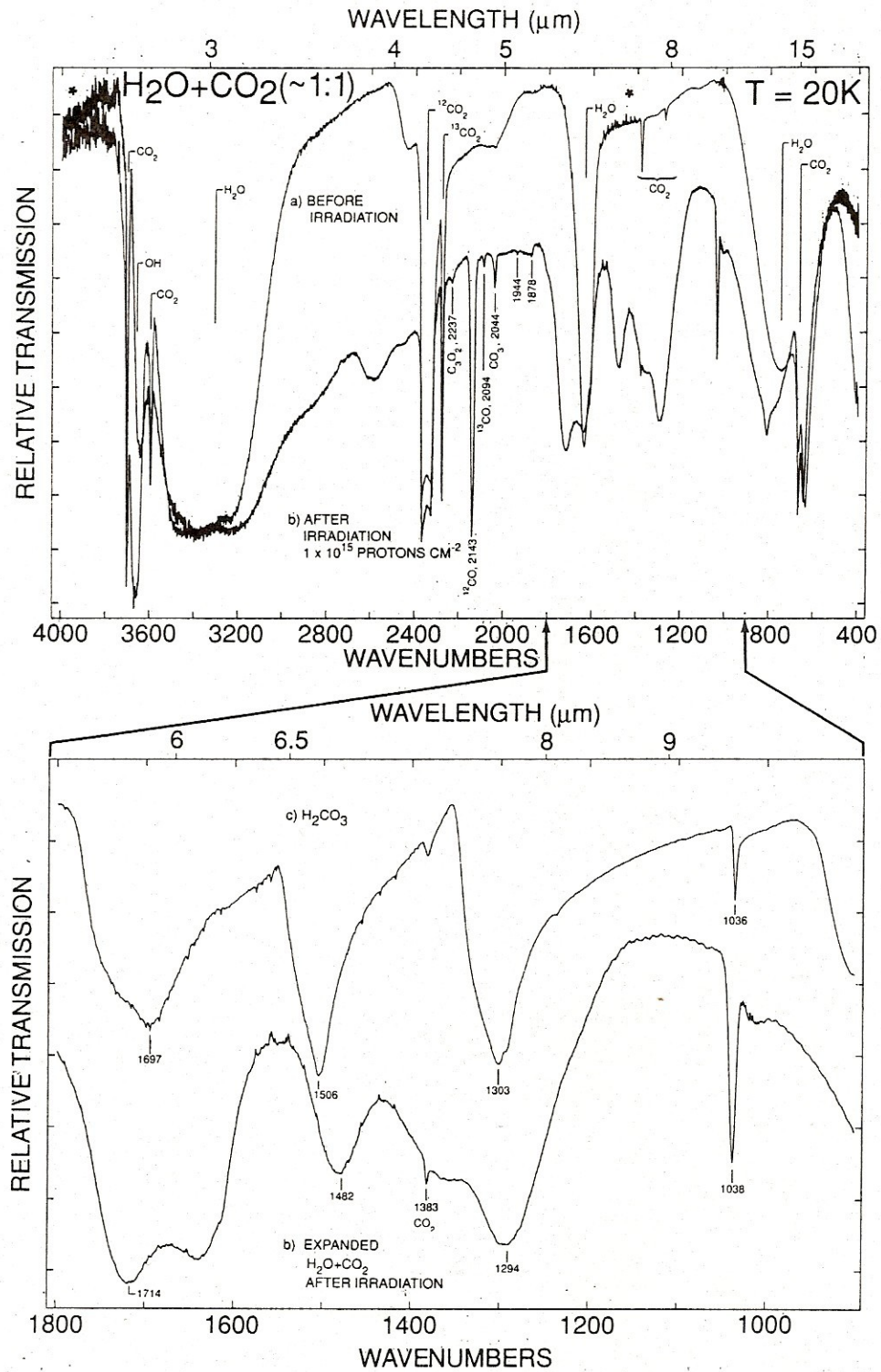


Fig. 1. The infrared spectrum from 4000 to 400cm⁻¹ of an ~6μm-thick H₂O+CO₂ (~1.4:1) ice is shown (a) before and (b) after proton irradiation. Figure 1b expanded is a detailed look at the irradiated spectrum between 1800 and 900cm⁻¹. Figure 1c is similar to the irradiated ice and resulted from freeze drying irradiated H₂O+CO₂. It was produced in our laboratory and identified [Moore and Khanna, 1991] as carbonic acid. Regions with structure due to apparent errors in ratioing are marked with an asterisk.

many similarities between the spectrum of irradiated H₂O+CO₂ at 20 K and the spectrum of H₂CO₃ recooled to 20 K (shown in Figure 1c). This correspondence suggests that H₂CO₃ forms directly during irradiation not just as a product of the thermal evolution.

Most H₂CO₃ (mass 62) dissociates into CO₂ (mass 44) and H₂O (mass 18) during vaporization and these masses, but not mass 62, were detected in the mass spectrometer during warming. Using different isotopic mixtures containing, e.g., D₂O, ¹³CO₂ we confirmed that masses 30 or 29 (attributed to

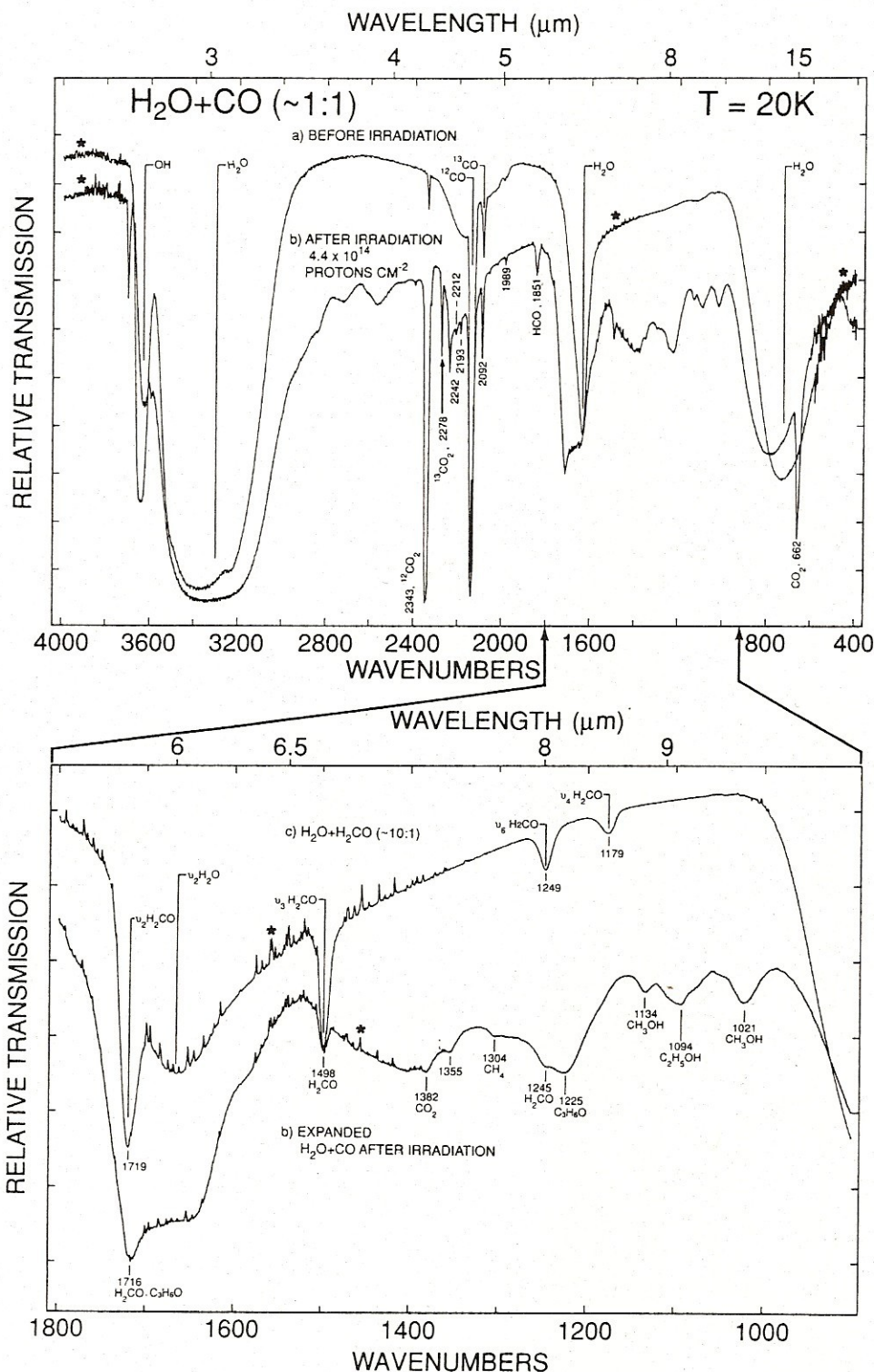


Fig. 2. The infrared spectrum from 4000 to 400cm⁻¹ of an ~3μm-thick H₂O+CO ice (~1:1) is shown (a) before and (b) after proton irradiation. Figure 2b expanded is a detailed look at the irradiated ice between 1800 and 900cm⁻¹. Absorptions of synthesized molecules are identified. The detection of H₂CO is based on similarities with Figure 2c, the spectrum of H₂O+H₂CO. Regions with structure due to apparent errors in ratioing are marked with an asterisk.

H₂CO or HCO) were also detected between 110 K and 250 K. Some H₂CO therefore exists in the ice, but its association with carbonic acid which appears to dominate the infrared spectrum is not clear.

The infrared spectrum from 4000 to 400 cm⁻¹ of an ~3μm thick H₂O+CO ice (~1:1) is shown in Figure 2. The

absorptions of H₂O and CO in the newly deposited film are labeled. After irradiation (Figure 2b) many new features appear in the spectrum. The sharp line at 2343 cm⁻¹ is due to ¹²CO₂ and that at 2278 cm⁻¹ to ¹³CO₂. The weak absorption at 1851 cm⁻¹ is attributed to HCO [Milligan and Jacox, 1964], and possible candidates for the 2242 and 1989 cm⁻¹ absorptions

are C₃O₂ and C₂O [Jacox and Milligan, 1965] respectively. At 250 K essentially no residual film remains from this irradiated ice; no formaldehyde polymer was detected. Figure 2b "expanded" (lowest spectrum in lower box) shows spectral details of the irradiated sample between 1800 and 900 cm⁻¹. The similarities between positions of the synthesized features at 1716, 1498 and 1245 cm⁻¹ and the $\bar{\nu}_2$, $\bar{\nu}_3$, and $\bar{\nu}_6$ absorptions of H₂CO in H₂O (Figure 2c) support the identification of H₂CO in this ice. The ratio of the integrated absorbance of the 1716 and 1498 cm⁻¹ peaks in the irradiated ice (bands were deconvolved using standard curve fitting programs) was larger than the corresponding ratio for the H₂O+H₂CO ice in Figure 2c. This suggests that other C=O bonded molecules are contributing to the 1716 cm⁻¹ line; a possible candidate is acetone which also has an absorption near 1225 cm⁻¹. CH₄, methanol (CH₃OH), and ethanol (C₂H₅OH) were identified by comparison with spectra of proton irradiated pure CH₃OH and CH₃OH+H₂O (new molecules synthesized were C₂H₅OH, H₂CO, CH₄, CO, CO₂ (M. H. Moore et al., manuscript in preparation, 1991)).

Mass 30 was detected with a mass spectrometer during warming from 40 K to near 200 K and was attributed to H₂CO. The detection of mass 68 at 43 K, at 54 K, and from 160 K to near 200 K was attributed to C₃O₂.

DISCUSSION

The original motivation for our proton irradiation studies of H₂O+CO₂ and H₂O+CO was to confirm earlier reports of the synthesis of H₂CO in each of these mixtures. We found that the common reaction in the spectra of both ices after irradiation was the interconversion of CO₂ ⇌ CO; in H₂O+CO₂, CO₂ → CO (the CO₂/CO ratio decreases) and in H₂O+CO, CO → CO₂ (the CO/CO₂ ratio decreases). The differences between these two ices were greatest in the 1800-900 cm⁻¹ region, suggesting that other reactions occur with different dominant chemical pathways.

We have identified H₂CO₃ in the infrared spectrum of irradiated H₂O+CO₂ but were unable to identify H₂CO. This result is consistent with the expected yield of H₂CO (calculated using mass spectral data from Pirronello et al. [1982]) which would result in intensities of H₂CO too small to be detected in our infrared spectra. Our detection of mass 30 in the mass spectrometer during warming may be due to H₂CO, consistent with the studies of Pirronello et al. [1982]. Previous identifications of H₂CO in processed H₂O+CO₂ ices relied on the 1714 cm⁻¹ line as a strong indication that H₂CO was present, but this line is also present in the carbonic acid spectrum (both molecules have a C=O stretch).

Both infrared and mass spectrometer data support the identification of H₂CO in irradiated H₂O+CO ices consistent with the photolysis results on similar ices [Greenberg, 1982; d'Hendecourt et al., 1986; Allamandola et al., 1988; Zhao, 1990]. Other spectral features in the irradiated spectrum have been identified as CH₃OH, C₂H₅OH, and CH₄ based on our preliminary studies of CH₃OH irradiation. However, neither the reaction rates nor the chemical pathways for H₂O+CO → H₂CO, CH₃OH, CH₄, and C₂H₅OH are known. In pure CH₃OH, the H₂CO/CH₃OH and CH₄/CH₃OH ratios increase with radiation processing (M. H. Moore et al.,

manuscript in preparation, 1991) but this may be different in icy mixtures or depend on whether CH₃OH is present or synthesized in the ice.

This laboratory work suggests that the abundances of CO, CO₂, CH₃OH, CH₄, and H₂CO in radiation processed ices will be different from unaltered interstellar ices. Ratios such as CO₂/CO and H₂CO/CH₃OH can be used as an indicator of processing prior to accretion into comets if the differences apply to both dynamically old and new comets. Particle radiation processing after accretion would be enhanced in the outer region of a nucleus compared to the interior. This would cause differences in molecular ratios between old and new comets. The significance of any carbonic acid in comets may lie in the possibility that icy grains could transport it into the coma where it would dissociate into H₂O and CO₂. Currently, the determination of the CO₂/CO ratio in H₂O+CO₂ and H₂O+CO ices processed until CO₂ ⇌ CO equilibrium is reached is in progress (M. H. Moore et al., manuscript in preparation, 1991). Further laboratory studies will investigate the interrelationship between H₂CO, CH₃OH and CH₄.

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