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Infrared spectra of proton irradiated ices containing methanol

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Abstract. A set of experimental results on the spectral identification of new species synthesized in irradiated CH_3OH and H_2O+CH_3OH ices is reported. Mass spectroscopy of volatile species released during slow warming gives supporting information on identifications. H_2CO is the dominant volatile species identified in the irradiated ices. CH_4, CO and CO_2 are also formed. During warming the ice evolves into a residual film near 200 K whose features are similar to those of ethylene glycol along with a C=O bonded molecular group. Irradiation simulates expected cosmic ray processing of ices in comets stored in the Oort cloud region for 4.6 billion years. Results support the idea that a comet originally containing an H_2O+CH_3OH ice component has a decreasing concentration of CH_3OH towards its outer, most heavily irradiated layers (if independent of all other sources and sinks). The CH_4/CO and CO/CO_2 ratios are calculated as a function of irradiation; after 22 eV per molecule, $CH_4/CO = 1.96$ and $CO/CO_2 = 1.45$ in an H_2O+CH_3OH ice mixture. Infrared spectra of CH_3OH at $T < 20$ K on amorphous silicate smokes show a predominantly crystalline phase ice. Irradiation of the ice/silicate composite is compared with irradiated CH_3OH on aluminum substrates. Implication for cometary type ices are discussed. Published by Elsevier Science Ltd

Introduction

Water ice and H_2O-dominated icy mixtures are important constituents of cometary nuclei (Spinrad, 1987; Mumma *et al.*, 1986; Combes *et al.*, 1988) and interstellar grains (Tielens, 1989). Icy mixtures include molecules more volatile than H_2O such as CH_3OH, H_2CO, NH_3, CO_2, CO and CH_4 (e.g. Mumma *et al.* (1993a) and references therein). Relative to H_2O, the abundance of CH_3OH is a few percent in many comets, and CH_3OH is likely to be a major component in interstellar ice (Allamandola *et al.*, 1988). The CH_3OH abundance relative to H_2O in the solid phase is near 7% based on interstellar observations of the CH stretching mode near 3.5 μm (e.g. Grim *et al.*, 1991). However, there is some variation from cloud to cloud and some controversy about the ratio. More recent results from Skinner *et al.* (1992) provide data on the 9.7 μm feature attributed to CH_3OH. This report focuses on laboratory studies of ion irradiated CH_3OH and H_2O+CH_3OH ices. The infrared (IR) spectra of these ice films are used to identify the synthesized products, and to record any differences when these ices are irradiated as ice/silicate composites. In these experiments irradiation simulates expected cosmic ray processing of ices, and smokes are used as laboratory analogs for interstellar-type silicate grains.

Several factors can affect the spectra of ices including formation and storage conditions, the exposure to a radiation environment and the incorporation of dust. The amorphous and crystalline phases of ices, whose formation and stability depend on temperature and growth rate (Kouchi *et al.*, 1994) have different spectral features. Various thermal histories of an ice can cause both reversible and irreversible changes in the IR spectrum. These effects have been discussed in some details for H_2O ice by Hobbs (1974), Hagen *et al.* (1983) and Moore and Hudson (1992, 1994). The amorphization of crystalline H_2O ice induced by ion irradiation (Baratta *et al.*, 1991; Strazzulla *et al.*, 1991; Moore and Hudson, 1992) is demonstrated by IR spectral changes; similar amorphization has been demonstrated for CH_3OH ice (Hudson and Moore, 1995). Exposure to photon and ion radiation processing also results in the synthesis of new species, which adds new features to the original spectrum (Allamandola *et al.*, 1988; Moore *et al.*, 1983; Strazzulla *et al.*, 1991). Another factor which can influence the shape of spectral features is the inclusion of grains. The presence of small grains in an ice mixture has been used to model not only the 3.1 μm band shape of H_2O ices, matching the spectra observed in interstellar molecular clouds (e.g. Greenberg,

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1991), but the 45 μm emission band of H_2O seen in circumstellar nebulae (Omont *et al.*, 1990). Recently, Moore *et al.* (1994) reported that both H_2O and CH_3OH formed crystalline phase ices, rather than the amorphous phase expected, when deposited onto silicate smoke layers at $T < 20$ K.

In the laboratory, gas, liquid and solid phase irradiations of CH_3OH result in the formation of H_2, glycol, and H_2CO, sometimes with smaller amounts of CH_4 and CO (Porter and Noyes (1959), UV photolysis of CH_3OH gas; Baxendale and Mellows (1961), γ-irradiated CH_3OH liquid; Kalyazin and Kovalev (1978), γ-irradiated CH_3OH solid). Yields of H_2, ethylene glycol ($(CH_2OH)_2$), and H_2CO for solid CH_3OH irradiated at 77 K are approximately 3.5, 3, and 1 molecules/100 eV, respectively (Kalyazin and Kovalev, 1978). These yields were determined by chemical analysis of both the gas and liquid after warming the irradiated ice. The IR spectrum of H_2O+CH_3OH ice after UV photolysis shows the formation of H_2CO, CO, CO_2, and CH_4 at $T < 20$ K (Allamandola *et al.*, 1988); they conclude that the principal product is H_2CO. Previous studies by Moore and Khanna (1991) reported the identification of H_2CO, CO, CO_2, CH_4, and ethanol (C_2H_5OH) in proton irradiated pure CH_3OH and CH_3OH+H_2O ices. Baratta *et al.* (1994) identified the formation of CO, CO_2, CH_4, and H_2O in the IR spectrum of 3 keV He^+ bombarded CH_3OH and H_2O+CH_3OH ices. They concluded that the largest yield was for a C=O bonded feature which could only partially be explained by the synthesis of H_2CO. The possible contribution of acetone ($(CH_3)_2CO$) was also discussed.

We report in this paper a set of experimental results on the spectral identification of new species synthesized in irradiated CH_3OH and H_2O+CH_3OH at $T < 20$ K. Ratios of CH_4/CO and CO/CO_2 are calculated as a function of eV molecule^{-1} and compared with data for similar ices irradiated with He^+ to higher doses. Mass spectra of gases released during warming result in supporting information about new products. Spectra of ices warmed to temperatures near 200 K are fitted with the spectrum of a possible less volatile residual product. Implications for cometary type ices are discussed.

Experimental procedures

Ices are grown on an aluminum mirror substrate cooled to $T < 20$ K in a closed-cycle cryostat. Surrounding the substrate is a six-sided chamber designed for a variety of *in situ* measurements. The chamber pressure is reduced to below 6×10^{-10} bar using an ion pump. The ice film can be rotated to face in different directions depending on the type of measurement: IR spectroscopy, mass spectroscopy, or proton irradiation.

IR absorption spectra of thin ice films are recorded with a Mattson (Polaris) FTIR. The technique used results in a transmission–reflection–transmission spectrum. Typically a spectrum is 60 scan accumulations, with a resolution of 4 cm^{-1}. Single-beam spectra are ratioed with a background spectrum recorded before any ice deposition. Ices are formed from triply distilled H_2O with a resistance greater than 10^7 ohm cm; CH_3OH was Fisher HPLC grade (99.9% pure). Both liquids had dissolved gases removed by freeze–pump–thaw cycling. Mixtures were made in glass bulbs and the relative composition of the ice was determined using the IR spectrum. An H_2O/CH_3OH abundance ratio near 2 was chosen so that our results would be comparable with other published data. Although this ratio is rich in CH_3OH compared to cosmic ices, dilution reduces the IR intensity of the products we want to identify. Thin films of ice, about 4 μm in depth, were grown at 10 μm h^{-1}. Film thickness was monitored by a laser interferometric method. A Dycor quadruple mass spectrometer is used to detect volatile species released from the ice during warming. The radiation source was a 1 MeV proton beam from a Van de Graaff accelerator. This energy proton penetrates 22 μm of H_2O ice. The experiment is designed so that the integrated beam current measured in the aluminum substrate is a direct measure of the incident fluence (p^+cm^{-2}). Details of this experimental set-up are given in Moore and Hudson (1992).

Silicate smokes are made in a separate grain condensation chamber by either evaporation of SiO solid or by combustion of SiH_4 with O_2 followed by vapor phase nucleation and growth in an H_2 atmosphere. The smokes are deposited onto the aluminum mirror substrates and then these coated substrates are attached to the tail section of the cryostat and cooled to $T < 20$ K prior to the condensation of CH_3OH or H_2O+CH_3OH gases. A discussion of the physical nature of these smokes, their 10 μm spectra, and spectra of a variety of gases deposited on these smokes is given in Moore *et al.* (1994) and references therein.

Experiments and results

The IR spectrum of pure CH_3OH deposited on an aluminum mirror substrate at $T < 20$ K is compared in Fig. 1 with the spectrum of that ice after irradiation to a total dose of 34 eV molecule^{-1}. New features in the irradiated ice are marked with an asterisk. The identification of these features and their positions are summarized in Table 1. New products easiest to identify are: the C=O stretch and C=O bend of CO_2, CO, the HCO radical, and the C—H deformation of CH_4. The feature at 1721 cm^{-1} is due in part to the C=O stretch of H_2CO. The small shoulder at 1497 cm^{-1} fits with the CH_2 scissors mode of H_2CO and the 1246 cm^{-1} feature with the CH_2 in-plane bend of H_2CO. The 1091 cm^{-1} feature is identified as the C—O stretch mode of C_2H_5OH. The relative strengths of these features vary with dose. Although, pure amorphous phase CH_3OH ice converts to a crystalline phase during warming to $T \sim 130$ K, similar phase changes are not observed for the irradiated CH_3OH ice shown in Fig. 1.

Figure 2 shows the IR spectrum of H_2O+CH_3OH (1 : 0.6) before and after irradiation to a total dose of 22 eV molecule^{-1}. All synthesized features are marked with an asterisk and their positions are included in Table 1. CO_2, CO, CH_4, and the HCO radical are identified. The 1850–600 cm^{-1} spectral region is expanded in Fig. 3a and

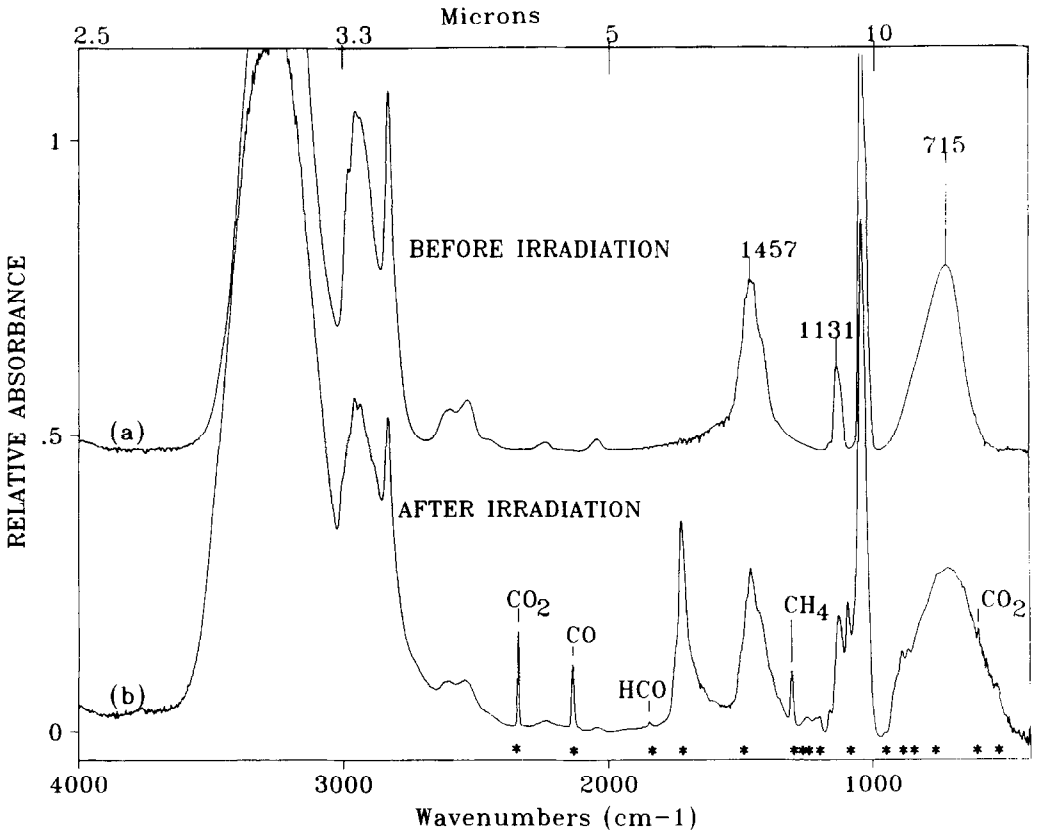

Fig. 1. (a) Infrared spectrum of a pure CH_3OH ice film deposited at $T < 20$ K. (b) Spectrum of the same ice after proton irradiation at $T < 20$ K to a dose of 34 eV molecule^{-1}. Many synthesized features are marked with asterisks; identifications and positions are listed in Table 1

Table 1. Identification and position of infrared features for synthesized products in CH_3OH and $H_2O + CH_3OH$ ices

Identification	Proton irr. CH_3OH[a] Position (cm^{-1})	Proton irr. $H_2O + CH_3OH$[a] Position (cm^{-1})	Proton irr. $H_2O + CH_3OH$[b] Position (cm^{-1})	UV photolysis[c] $H_2O + CH_3OH$ Position (cm^{-1})	Vibrational mode
ν_3 CH_4		3011		3012	C—H st
ν_3 CO_2	2339	2341	2340	2343	C=O st
ν_3 $^{13}CO_2$		2276			C=O st
CO	2134	2135		2137	C=O st
HCO	1844	1845		1850	
ν_2 H_2CO	1721	1713	1722	1720	C=O st
			1743		
ν_3 H_2CO	1497 sh	1499		1500	CH_2 scissor
		1355			
ν_4 CH_4	1302	1305	1302	1304	C—H def.
ν_6 H_2CO	1246	1250			CH_2 bend
	1211, 1198	1219, 1185, 1161 w	1263, 1213, 1196		
C_2H_5OH	1091	1089	1090		
	952, 919, 887, 864, 748		887, 865		
CO_2	650	657		657	C=O bend
$(CH_3)_2CO$[d]	532–516		523		hindered rotation

[a]Ice formed on an aluminum substrate (Figs 1–3).
[b]Ice formed on a silicate smoke (Fig. 6).
[c]Allamandola *et al.* (1988).
[d]Tentative.

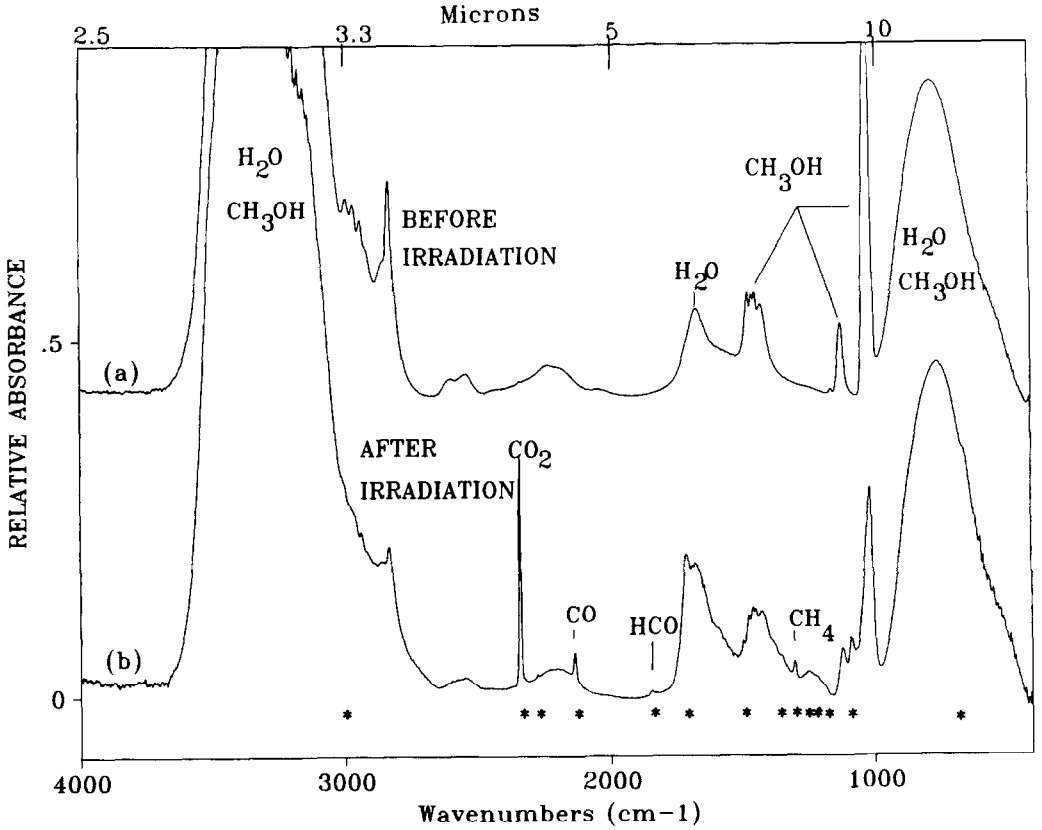

Fig. 2. (a) Infrared spectrum of an H_2O+CH_3OH ($\sim 1:0.6$) ice film deposited at $T < 20$ K. (b) The same ice after proton irradiation at 20 K to a dose of 22 eV molecule^{-1}. Many synthesized features are marked with asterisks; identifications and positions are listed in Table 1

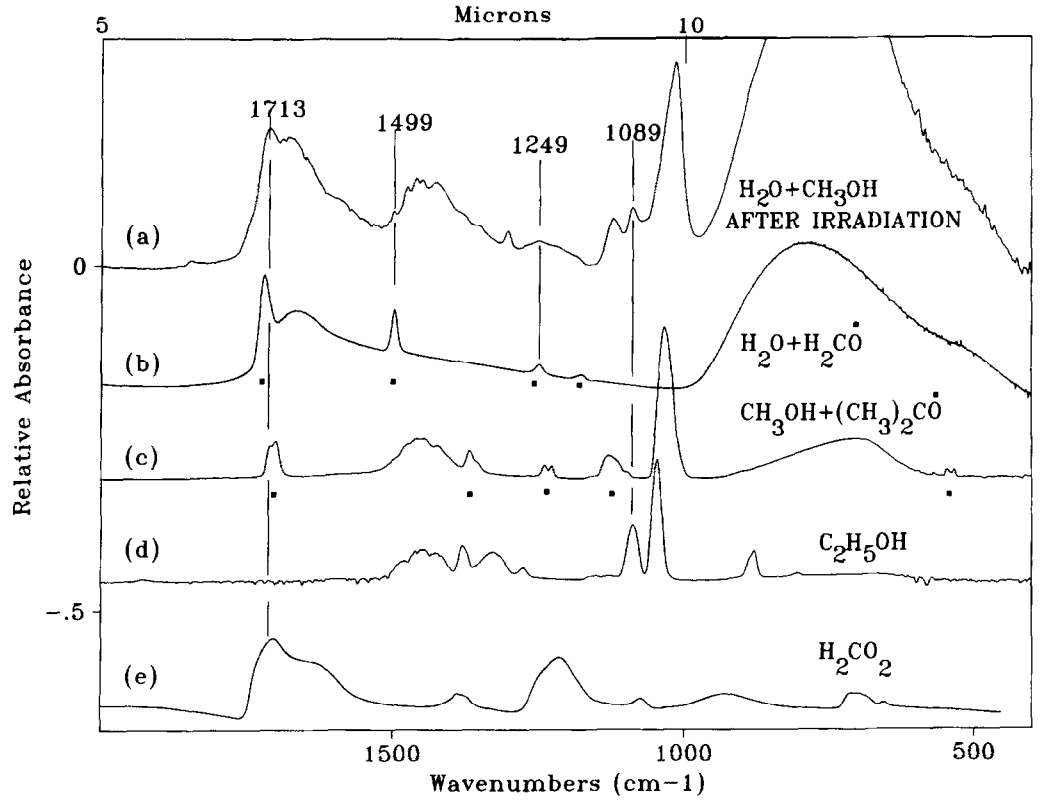

Fig. 3. The 2000–400 cm^{-1} spectral region of irradiated H_2O+CH_3OH (Fig. 2a) is compared with spectra of icy mixtures (b) H_2O+H_2CO and (c) $CH_3OH+(CH_3)_2CO$. Pure ice spectra are: (d) C_2H_5OH and (e) H_2CO_2. All spectra were measured at $T < 20$ K. Peaks marked with a "■" are identified with the component of the mixture similarly marked. Several vertical lines have been drawn to help locate the position of peaks

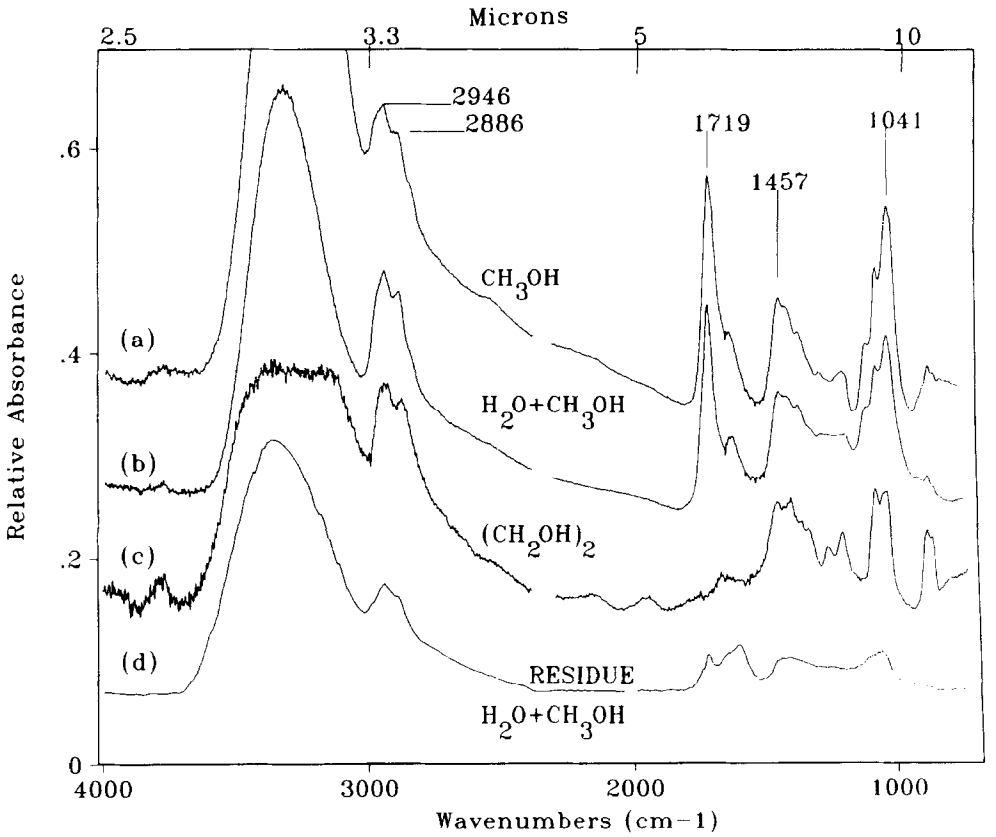

Fig. 4. The infrared spectra of residual films from irradiated (a) CH_3OH and (b) H_2O+CH_3OH ices after warming to near 200 K are compared with the spectrum of ethylene glycol, $(CH_2OH)_2$, at 170 K. Spectrum (d) shows the room temperature RESIDUE of similarly irradiated H_2O+CH_3OH ice (irradiated at 20 K)

compared with several reference spectra: (b) H_2O+H_2CO, (c) CH_3OH+acetone ($(CH_3)_2CO$), (d) C_2H_5OH, and (e) formic acid (H_2CO_2). The 1713 cm^{-1} feature in the irradiated ice is partially attributed to the C=O stretch of H_2CO (shifted by 7 cm^{-1}) combined with the O—H bend mode of H_2O. The 1499 and 1249 cm^{-1} features in spectrum (a) are fitted with H_2CO also. Spectrum (d) of ethanol at $T < 20$ K is a good match with the 1089 cm^{-1} feature in the irradiated ice. The strongest ethanol feature in spectrum (d) contributes to the broadening of the 1014 cm^{-1} CH_3OH peak in the irradiated ice. It has been suggested by Baratta *et al.* (1994) that acetone could contribute to the 1713 cm^{-1} feature (compare spectrum (c) with spectrum (a)). One argument in favor of *some* $(CH_3)_2CO$ is that it was the only simple molecule we examined that has a feature in the 530 cm^{-1} region which is similar to a weak feature measured in both pure irradiated CH_3OH and H_2O+CH_3OH. In this report, the best signal to noise ratio measured for this feature is in irradiated CH_3OH ice shown in Fig. 1b (an asterisk is near 530 cm^{-1}).

Standard curve fitting techniques were used to separate the 1713 cm^{-1} and the (OH) 1657 cm^{-1} components in Fig. 3a. The integrated absorbance of the 1713 cm^{-1} feature and the 1499 cm^{-1} feature were obtained. By comparing the relative integrated areas of these features with those in H_2O+H_2CO, we estimated that only ~25% of the 1713 cm^{-1} area in H_2O+CH_3OH was due to H_2CO. Mass spectra of gases vaporized from irradiated CH_3OH during warming near 160 K showed mass 29 and 30 peaks, and a mass 60 peak; these are consistent with HCO, H_2CO, and $(H_2CO)_2$. Also observed in this temperature range was a mass 58 peak coupled with a mass 43 peak and this observation fits a pattern for $(CH_3)_2CO$ and its fragment CH_3CO (based on mass spectra of slowly vaporized $(CH_3)_2CO$ ices in our laboratory). Similar results were observed for irradiated H_2O+CH_3OH, although detection of any masses at 58 and 43 did not occur until the temperature was near 180–190 K. These mass signals add support for the presence of some acetone, however more confidence in this assignment will require experiments with isotopically labelled components. Both CH_3OH and H_2O+CH_3OH irradiated ices evolve with warming into a residual film near 200 K. These less volatile materials are of interest since similar synthesized molecules of low volatility may be present in cometary and precometary ices.

The 1721 and 1713 cm^{-1} absorption peaks in irradiated CH_3OH and H_2O+CH_3OH ices (respectively) are part of a broad feature which remains stable on warming to room temperature, suggesting that there are contributions to this C=O stretch (st) region from molecules which are less volatile than H_2CO and $(CH_3)_2CO$. Slow warming of H_2O+H_2CO ices shows release of H_2CO before 150 K; $(CH_3)_2CO$ ice vaporizes near 150 K. Figure 4 compares the IR spectra of several residual films; trace (a) is the residual spectrum of irradiated CH_3OH ice warmed to 220 K, spectrum (b) shows the residual signature of irradiated

H_2O+CH_3OH warmed to 190 K. These two spectra are nearly indistinguishable. Spectrum (c) is ethylene glycol ($(CH_2OH)_2$) at $T = 170$ K. Ethylene glycol has similar 3.4 μm features and appears to be a good fit with several of the features in the 7–12 μm region. We calculated an integrated absorbance value for the 1084–1040 doublet of ethylene glycol at 300 K to be 6.7×10^{-18} cm molecule^{-1}. Assuming that the 12 μm signature is entirely due to synthesized ethylene glycol, we estimate that the percent of original CH_3OH in the irradiated H_2O+CH_3OH ice converted to ethylene glycol is $\sim 10\%$. Spectrum (d) is the room temperature RESIDUE of a similarly irradiated H_2O+CH_3OH ice measured in our laboratory. The 1600 cm^{-1} (6.3 μm) feature is attributed to C=O st mode of possibly carboxylic acid groups, the 1420 cm^{-1} (7 μm) to C—H vibrations, and the 1050 cm^{-1} (9.5 μm) to single bonded C—O vibrations. The RESIDUE was observed to slowly vaporize from an aluminum mirror over a period of days.

After irradiating these ices to different doses, spectra are analyzed to determine the molecular column density of synthesized species. We use the integrated absorbance values of 2×10^{-16} cm molecule^{-1} for the 2340 cm^{-1} C=O st of CO_2, 1.7×10^{-17} cm molecule^{-1} for the 2137 cm^{-1} st of CO, and 6×10^{-18} cm molecule^{-1} for the 1300 cm^{-1} C—H deformation of CH_4 (values from Allamandola *et al.* (1988) and Sandford *et al.* (1988)). The CO/CO_2 and CH_4/CO ratios are plotted in Fig. 5a and b, respectively, as a function of energy deposited per molecule in the ice. The eV molecule^{-1} is calculated by using the linear energy transfer (LET) of 1 MeV protons, the total dose (protons cm^{-2}), and the molecular density of the ice assuming a physical density of 1.0 g cm^{-3} for H_2O, CH_3OH, and H_2O ice mixtures.[1]

Figure 5a shows the calculated CO/CO_2 ratio for pure CH_3OH and H_2O+CH_3OH as a function of eV molecule^{-1}. Figure 5b is the CH_4/CO ratio for the same experiments. The CO/CO_2 ratio decreases with increasing dose and approaches a value near 1.5 for the $H_2O > CH_3OH$ mixture which is most relevant for astronomical applications. Several data points for similar mixtures irradiated with He ions from Baratta *et al.* (1994) begin at deposited energies above 20 eV molecule^{-1} and indicate a ratio near 0.5. An explanation for the difference in their CO/CO_2 ratios may be that they perform a simultaneous deposition and irradiation since the penetration depth of the ions is of the order of 100 Å. Synthesized CO (and also CH_4 which is similar in volatility to CO) may be depleted from the ice surface before it is covered. Our results show that the CH_4/CO ratio also decreases with increased proton dose and approaches a value near 2;

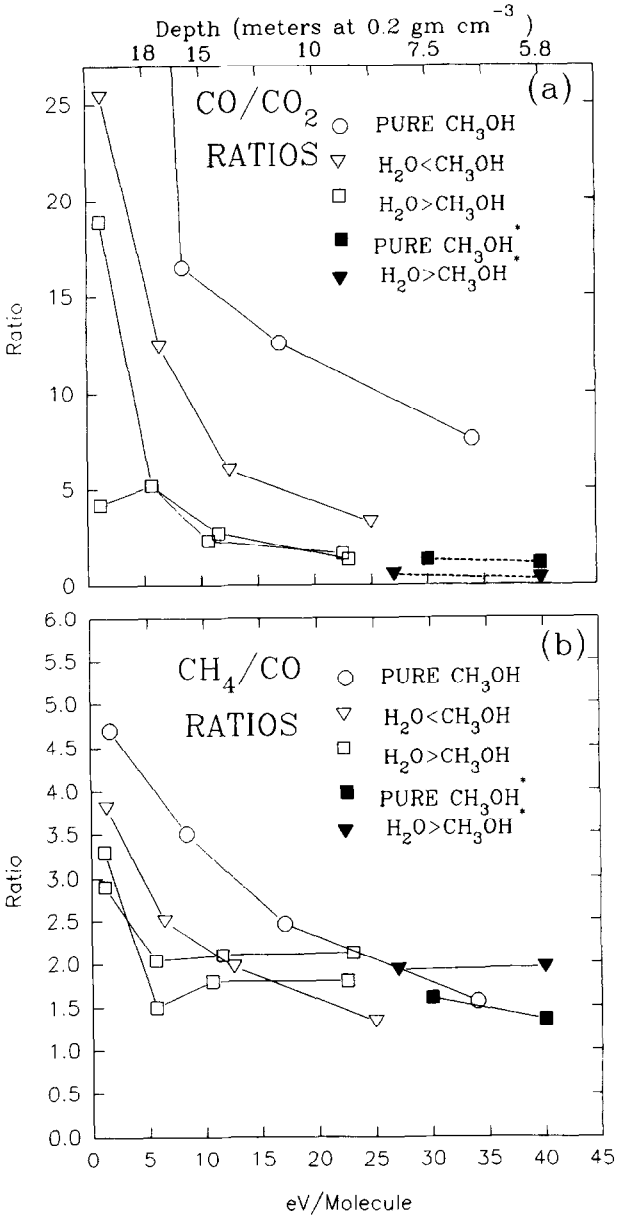

Fig. 5. Plots of the (a) CO/CO_2 and (b) CH_4/CO ratios as a function of proton dose (eV molecule^{-1}) for both pure CH_3OH and H_2O+CH_3OH ices are shown. Data from He ion irradiation (*Baratta *et al.*, 1994) are also included for comparison. The energy accumulated per molecule is related to the estimated dose accumulated by cometary ices due to cosmic ray bombardment during a 4.6 billion year storage time in the Oort cloud region (Strazzulla and Johnson, 1991). The top x-axis gives the estimate for the depth within a comet nucleus where similarly accumulated doses of energy are reached. The assumed density is 0.2 g cm^{-3}. For cometary ices with a density of 1 g cm^{-3}, multiply by 5

[1]The measured LET for 1 MeV protons in H_2O is 308 MeV cm^2 g^{-1} (Northcliffe and Shilling, 1970). Using the LET for H_2O, we calculate a LET value of 320 MeV cm^2 g^{-1} for CH_3OH using a ratioing technique based on the stopping power equation (e.g. Swallow, 1973). The LET(MIXTURE) for H_2O+CH_3OH is LET(water) + LET(methanol) weighted by the percent abundance of each molecule. The eV molecule^{-1} (MIXTURE) is calculated using LET(MIXTURE) and the molecular density (MIXTURE) which is also weighted by the percent abundance of each molecule in the mixture.

Baratta *et al.* (1994) give values near 2. We have calculated values for similar ratios from the results of Allamandola *et al.* (1988) on photolysed H_2O+CH_3OH (2:1) ices: $CO/CO_2 = 4.3$, and $CH_4/CO = 1$ after 45 min of photolysis. It is not known what the equivalent eV molecule^{-1} is for these experiments therefore we are not certain if these ratios represent the same amount of processing as our ices. Since the ratios are consistent with enhanced CO relative to the ratios in Fig. 5, one explanation could be

Table 2. Summary of ratios in p^+ irradiated H_2O+CH_3OH (1 : 0.6) ice after an accumulation of 22 eV molecule^{-1}

$CH_3OH/H_2O = 0.17$	$CH_3OH/H_2CO = 4.5$
$H_2CO/H_2O = 0.038$	
$CH_4/H_2O = 0.022$	$CH_4/CO = 1.96$
$CO/H_2O = 0.011$	
$CO_2/H_2O = 0.008$	$CO/CO_2 = 1.45$

that to a first approximation, once formed, CO is not readily photodissociated. In Fig. 5, the ratios at lower doses give valuable information that relates to possible product ratios deeper within the nucleus of a comet, as indicated by the top scale. Predicted values for the energy deposited in a comet over 4.5×10^9 years are given by Moore *et al.* (1983) and references therein, and by Johnson (1991). In general at lower doses, $CH_4 < CO$ and $CO > CO_2$.

For these experiments, the average initial ratio of CH_3OH/H_2O was 0.64 showing a typical ice spectrum in Fig. 2, and yielding typically the behavior plotted in Fig. 5a and b. The CH_3OH/H_2O ratio decreases with increasing irradiation and the synthesis of new carbon containing species. This ratio is determined using the area of the 1021 cm^{-1} line of CH_3OH, and the area of the 1657 cm^{-1} band of H_2O. Changes in this ratio are calculated assuming that the 1021 cm^{-1} feature is only due to CH_3OH (excluding contributions from any ethanol or acetone), and assuming that the area of the 1657 cm^{-1} band is unchanged with irradiation. We calculate a final ratio of $CH_3OH/H_2O = 0.17$ after 22 eV molecule^{-1}, a decrease by a factor of 3.8. A similar analysis for the H_2CO/H_2O ratio is possible by curve fitting the 1713 cm^{-1} band and assuming that 25% of its area is due to H_2CO. We estimate in this way that a final ratio of $H_2CO/H_2O \sim 0.038$ after 22 eV molecule^{-1}. Table 2 summarizes the calculated ratios of these and other products.

A study of the number of synthesized molecules formed in irradiated thin ice films deposited on aluminum mirror substrates, compared with similar ices supported on silicate smoke layers, is currently in progress. In this paper we report on the spectra of CH_3OH ice deposited at $T < 20$ K on silicate smoke layers. Instead of forming a completely amorphous phase spectrum, it appears mostly crystalline (Moore *et al.*, 1994). Spectra of CH_3OH on silicate before and after irradiation is shown in Fig. 6. A comparison of spectrum (a) with the analogous spectrum (a) from Fig. 1 shows the sharpness of several CH_3OH features along with some splitting associated with the more crystalline phase of CH_3OH on the silicate smoke. Spectra shown in Fig. 6 have been ratioed with the blank silicate smoke spectrum taken before any gas condensation. This process removes the large 10 μm silicate feature and reveals the structure of the deposited ice in that region. After irradiation, new species have been identified. A comparison of trace (b) in Figs 1 and 6 shows that there are similarities between the products. Some CO is synthesized, but its IR absorption feature is measurable only after scale expansion. Relative to the results shown in Fig. 1 for irradiated CH_3OH on aluminum substrates, for irradiated CH_3OH on silicate smoke we detect less CO and H_2CO than CH_4. A major change between spectrum (a) and spectrum (b) is the radiation-induced amorphization (phase change) of the CH_3OH. Like irradiated CH_3OH on aluminum, irradiated CH_3OH ice on silicate smoke does not convert to a crystalline phase with warming. A quantitative analysis for these results, which incorporated a meaningful analysis of the LET and eV molecule^{-1} calculations for an ice/silicate composite is underway. Problems can arise with the ratioing technique after irradiation causing some irregularities in the baseline near the edges of the wavelength region marked with the line in Fig. 6. Possibly the thickness of the silicate smoke changes and/or defect formation within the silicate occurs affecting the 10 μm feature. However, most regions of the spectrum are undisturbed.

Discussion

H_2CO is the dominant volatile species identified in irradiated H_2O+CH_3OH using IR spectra. This is consistent with the photolysis results reported by Allamandola *et al.* (1988). Other volatile species which are easily identified are, in order of abundance, CH_4, CO, and CO_2. Ethylene glycol is identified with several IR features in the irradiated mixture after warming to $T \sim 200$ K. The identification of the molecular composition of the residue will require further investigations using GC-MS analysis. The IR spectrum of the residue is consistent with the identification of some combination of polyalcohols and glycols, and with carboxyl group molecules. It is representative of one type of organic material which could exist in the outer layers of comets and contribute to the variety of organic grains detected during the Halley flyby (see review by Fomenkova *et al.* (1994) and references therein).

The data set consisting of ion irradiation (this study and Baratta *et al.* (1991)) and UV photolysis results (Allamandola *et al.*, 1988) on H_2O+CH_3OH ice is one example of only a few existing sets of data which can be compared. In the H_2O+CH_3OH case, all of the IR results are remarkably similar at $T < 20$ K. However, there are fundamental differences between photochemical mechanisms produced by UV photons and radiation–chemical mechanisms due to protons, and it is important to carry out both types of experiments.[2]

Our results show a gradual decrease in the CH_3OH/H_2O ratio with increased irradiation. The binary mixture used in the laboratory is a gross simplification for the complex icy mixture expected in comets. However, we can apply the trends to show what we would expect for CH_3OH in

[2]Only light absorbed by a molecule can be effective in producing a photochemical change, and the light is absorbed in a quantum process. Typical photons initiate reactions with a single molecule within a few hundred ångströms of the surface. Protons lose energy in discrete processes to electrons in the stopping medium and undergo a large number of interactions. The range of a 1 MeV proton is 10^{-2}–10^{-3} cm in typical organic material with densities near 1 g cm^{-3}. More energetic ions penetrate to greater depths.

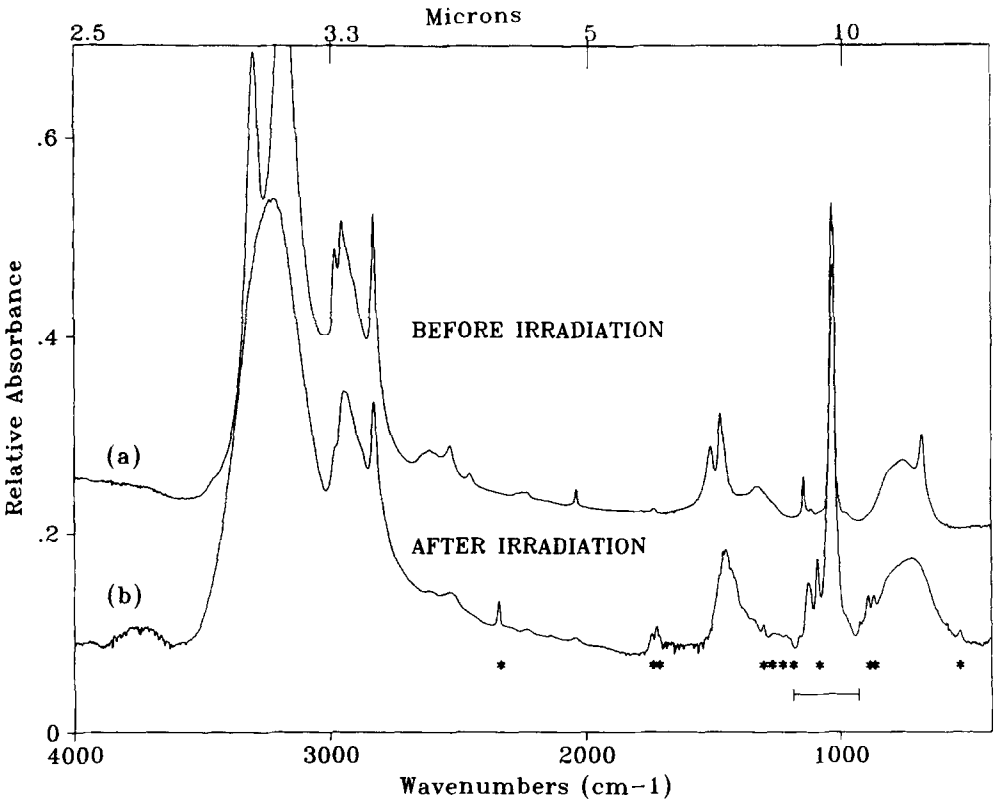

Fig. 6. (a) Infrared spectrum of CH_3OH ice formed on a silicate smoke layer at $T < 20$ K. (b) The same ice after proton irradiation. Before irradiation the ice is mostly crystalline in phase. Irradiation amorphization occurs during bombardment. Most synthesized species marked with an asterisk are identified in Table 1. The 10 μm silicate feature has been removed by ratioing each trace with the spectrum of the silicate smoke before any ice condensed. Ratioing may cause some irregularity in the baseline in the wavelength region marked with a line

comets. A comet originally containing a similar H_2O and CH_3OH ice component would have a decreasing concentration of CH_3OH toward its outer layers due to cosmic ray processing during storage in the Oort cloud (if independent of all other sources and sinks). When dynamically new, the release of volatiles from the most heavily irradiated outer layers of ices could give CH_3OH/H_2O ratios a factor of at least 4 lower than the deep ices which are most pristine and minimally processed. Dynamically new comets would have $CO > CO_2$ by a factor of ~ 1.5. As these comets age, in the absence of additional processing, you would expect to see a continuous increase in the CH_3OH abundance and a decrease in H_2CO, CH_4, CO, and CO_2 as less irradiated ices are exposed.

The CH_3OH abundance has been tabulated for several recent comets (Eberhardt *et al.*, 1994). There exists clear variations between comets; abundances from values near a few tenths of a percent to 7% (relative to H_2O) have been reported. In general these values are compatible with the range of values observed in interstellar environments. Mumma *et al.* (1993b) have argued that, based on the CH_3OH abundance, comets tend to fall into two groups. Those comets with higher CH_3OH abundances tend to be dynamically new, and those with lower abundances tend to be short-period. Mumma *et al.* (1993b) suggest that a cosmogenic connection could account for the compositional dichotomy. These CH_3OH abundances are opposite to what we would expect based on our laboratory experiments *if* short-period comets are assumed to be evolved older comets, but this assumption is a simplification of a complex problem. Comets might form in different regions with different CH_3OH enrichments, or comets might form in the same region but at different times when the precomet material contains different CH_3OH enrichments. For example, late forming comets could contain less CH_2OH if the precomet material has undergone increased irradiation due to a decrease in the opacity of the nebula. Additional comet observations are necessary to improve the statistics of the CH_3OH abundance–dynamic age correlation as pointed out by Eberhardt *et al.* (1994).

Infrared spectra of CH_3OH at $T < 20$ K on silicate smokes reveal that predominantly crystalline phase ice forms directly on deposit. A mechanism to explain this is currently under investigation. In a separate experiment with silicate smokes, we have found that condensed H_2CO in a mixture with H_2O is not retained during warming to as high a temperature as similar deposits (which form as amorphous phase deposits) on aluminum substrates (Ferrante *et al.*, 1994). We have not completed the study of the residues formed from these irradiated ice/silicate composites. More realistic cometary type mixtures may be quite complex. For example, from past experiments we know that noble gases are more effectively trapped in irradiated silicates than in unirradiated silicates (Nichols

et al., 1992). The idea that irradiation produces active sites in silicates which are in intimate association with icy mixtures suggests that in these more complex mixtures, volatile material may compete for trapping sites after irradiation. The idea that amorphous ices retain volatile species is central to many cometary theories. Since the laboratory produced silicates have such a dramatic effect on the phase of the ice, and radiation may change trapping sites within the silicate, we are studying ices/silicate composites and their radiation products in an effort to understand the ice/surface interactions which affect the retention of volatiles.

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