

NOTE

IR Spectra of Irradiated Cometary Ice Analogues Containing Methanol: A New Assignment, a Reassignment, and a Nonassignment

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The IR spectra and radiation chemistry of water-methanol ices near 16 K have been reinvestigated. In contrast to earlier work, no evidence is found for the formation of acetone, and a band previously attributed to ethanol is reassigned to ethylene glycol. Three new features are reported, assigned to the formate ion, and compared to the ISO spectrum of a protostellar source. © 2000 Academic Press

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The possibility that comets may have delivered organic molecules to the early Earth has generated considerable interest both in professional (Thomas *et al.* 1997) and “popular” publications (Bernstein *et al.* 1999). The original source of these organics is unknown, but it is likely that some were formed by cosmic-ray and/or UV processing of cometary ices before, during, and after accretion. For many years laboratory experiments have probed the chemical reactions which accompany ion irradiation and UV photolysis of cometary ice analogues. These experiments have demonstrated that small molecules, such as CO, can be converted into larger ones, such as H₂CO and CH₃OH (Hudson and Moore 1999, Schutte *et al.* 1996a, Allamandola *et al.* 1988). In many ice analogues, a small percent of the starting material is converted into a residual mixture of organics (Moore *et al.* 1983, Bernstein *et al.* 1995).

Methanol, CH₃OH, is a molecule of high interest in ice analogue experiments. It is among the most abundant molecules found in cometary comae, and it is the most abundant organic seen in interstellar ices (Bockelée-Morvan 1997, Crovisier 1998, Schutte 1999). Recent experiments on the ion irradiation of H₂O + CO mixtures at ~16 K have shown that CH₃OH readily forms at levels comparable to those seen in cometary comae and interstellar ices (Hudson and Moore 1999). Experiments have also demonstrated that UV photolysis with H₂-discharge lamps produces CH₃OH from H₂O + CO mixtures, although not to the degree seen from proton bombardment (Schutte *et al.* 1996a). Once formed in ices, CH₃OH can undergo other reactions, perhaps to make even more complex molecules. Here, however, the results from radiation and photolysis experiments disagree. UV photolysis of H₂O + CH₃OH has long been known to make primarily CO, CO₂, and H₂CO (Allamandola *et al.* 1988). These same products have been reported in ion-irradiated H₂O + CH₃OH ices but with the additional suggestion of acetone, (CH₃)₂CO, formation.

To the best of our knowledge, the possibility that acetone might be synthesized in CH₃OH-containing ices originated with a tentative IR identification by Baratta *et al.* (1994) which was repeated in subsequent papers (e.g., Strazzulla *et al.* 1995, Palumbo *et al.* 1999), and later considered by Moore *et al.* (1996). This synthesis, if confirmed, would have possible applications to both interstellar and Solar System chemistry. Herbst *et al.* (1990) suggested that acetone formation on grains in the interstellar medium might reconcile the discrepancy between observed acetone abundances and predictions of gas-phase models. Delitsky and Lane (1998) included acetone as a possible radiation product on jovian satellites, the reaction sequence being CO₂ → CO → CH₃OH → (CH₃)₂CO. Even more recently, Cruikshank *et al.* (1998) considered (CH₃)₂CO production from CH₃OH in their study of the composition of Centaur 5145 Pholus.

Given this interest in acetone formation we present a reexamination of ion-irradiated H₂O + CH₃OH ice using IR spectroscopy. Our conclusion is that there is *no IR evidence* for acetone synthesis. However, there is evidence for ethylene glycol and the formate anion, two species not yet reported in CH₃OH and H₂O + CH₃OH ices.

Our experimental techniques have been described in previous papers. An ice mixture is formed on a cold (~16 K) aluminum substrate in a vacuum chamber. The mid-IR spectrum of the ice can be recorded with an attached FTIR spectrometer before and after radiation doses from an interfaced Van de Graaff accelerator. For details see Moore and Hudson (1998) and references therein.

The upper two traces of Fig. 1 are mid-IR spectra of H₂O + CH₃OH ice (3:1) before and after 0.8 MeV proton irradiation at ~16 K. These spectra have been enlarged to display absorptions not easily seen in earlier papers. The bottom spectrum in Fig. 1 is from an unirradiated reference mixture of H₂O + CH₃OH + acetone (10:10:1) at ~16 K. Acetone features at 1701, 1422, 1368, 1238, and 1097 cm⁻¹ are marked by vertical dashed lines. Although these five acetone bands are close to absorptions in irradiated H₂O + CH₃OH, *a careful comparison reveals that there is not even a single unambiguous match.* An absorbance at 1427 cm⁻¹ in irradiated H₂O + CH₃OH is the closest match for acetone, but CH₃OH has a band there. The other four bands listed above for acetone simply do not appear in irradiated H₂O + CH₃OH.

Assignments for most peaks in the spectrum of irradiated H₂O + CH₃OH are straightforward, as can be seen working from left to right in the middle spectrum of Fig. 1. A weak HCO absorption is present at 1848 cm⁻¹. A broad feature from about 1750 to 1525 cm⁻¹ is due to both water and an organic molecule having a carbonyl (C=O) group, the organic contribution peaking at 1712 cm⁻¹. The broad band starting near 1520 cm⁻¹ and peaking near 1450 cm⁻¹, topped by several weak bumps, is from residual CH₃OH. A peak at 1499 cm⁻¹ can be

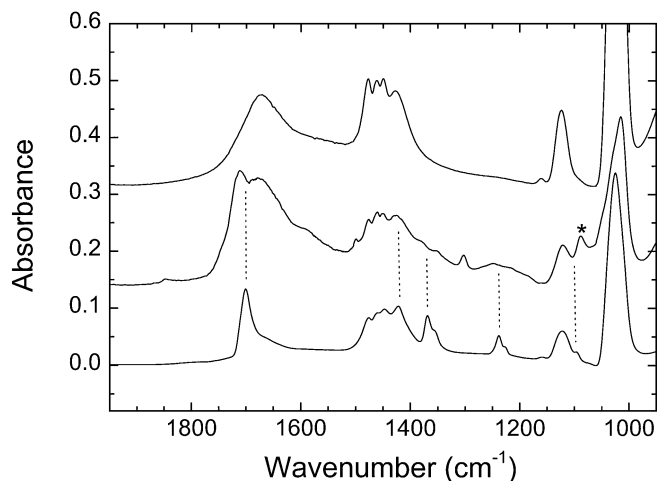


FIG. 1. Mid-IR spectra of an $\text{H}_2\text{O} + \text{CH}_3\text{OH}$ (3:1) ice before (upper) and after (middle) an irradiation to $\sim 18 \text{ eV molecule}^{-1}$ with 0.8 MeV protons. At the bottom is a reference spectrum of unirradiated $\text{H}_2\text{O} + \text{CH}_3\text{OH} + \text{acetone}$ (10:10:1). Dotted lines indicate acetone features in the bottom spectrum. All spectra, and the irradiation itself, were at $\sim 16 \text{ K}$.

assigned to H_2CO which then explains the carbonyl absorption at 1712 cm^{-1} ; a band at 1248 cm^{-1} is also assigned to H_2CO . Features at 1384 and 1353 cm^{-1} , as well as a shoulder near 1589 cm^{-1} , are assigned to formate ion, HCOO^- , as described below. The sharp line at 1303 cm^{-1} is from CH_4 , and features from residual CH_3OH are again encountered at 1121 and 1015 cm^{-1} . Not shown in Fig. 1 are weak bands at 885 , 861 , and 524 cm^{-1} . These three features were strongest when “neat” CH_3OH was irradiated (no H_2O initially present), and can be seen in Fig. 1b of Moore *et al.* (1996). In fact, all the bands just described were somewhat stronger when the initial sample was neat CH_3OH .

Our identification of features near 1589 , 1384 , and 1353 cm^{-1} with HCOO^- , formate ion, is based on separate experiments (Hudson and Moore, in preparation). Knowing that irradiation of $\text{H}_2\text{O} + \text{CO}$ (Hudson and Moore 1999) gives HCOOH , formic acid, we irradiated $\text{H}_2\text{O} + \text{CO} + \text{NH}_3$, with the base NH_3 being added to convert the HCOOH into HCOO^- . The resulting IR spectra showed strong features near 1589 , 1384 , and 1353 cm^{-1} . To confirm that these three were indeed due to HCOO^- , separate $\text{H}_2\text{O} + {}^{13}\text{CO}$ and $\text{H}_2\text{O} + \text{C}^{18}\text{O}$ ices were prepared and irradiated. These same three IR features showed ${}^{13}\text{C}$ shifts of 38, 3, and 20 cm^{-1} (expected for HCOO^- were 39, 0, and 23 cm^{-1} , Spinner and Rowe 1979) and ${}^{18}\text{O}$ shifts of 9, 0, and 19 cm^{-1} (expected for HCOO^- were 10, 2, and 20 cm^{-1} , Spinner and Rowe 1979). The relative intensities of these three bands were scarcely changed on isotopic substitution. Returning now to the central spectrum of Fig. 1, the shoulder near 1589 cm^{-1} and the bands at 1384 and 1353 cm^{-1} match the HCOO^- features in the experiments just described, both in positions and relative intensities. Thus the assignment of these three features to HCOO^- , in both irradiated CH_3OH and irradiated $\text{H}_2\text{O} + \text{CH}_3\text{OH}$, can be made with confidence.

The only distinct unassigned band remaining in the central spectrum of Fig. 1 is at 1088 cm^{-1} , marked with an asterisk. Although this band has been attributed to $\text{C}_2\text{H}_5\text{OH}$ (Moore *et al.* 1996), we favor a reassignment to $\text{C}_2\text{H}_4(\text{OH})_2$, ethylene glycol, for three reasons. First, irradiated CH_3OH has been studied for at least 40 years, using analytical techniques far more sensitive than IR spectroscopy (e.g., Meshitsuka and Burton 1958). To our knowledge, all papers agree that ethylene glycol is a major organic product and that little, if any, $\text{C}_2\text{H}_5\text{OH}$ is made. A second argument for ethylene glycol is that weak features at 885 , 861 , and 524 cm^{-1} in irradiated $\text{H}_2\text{O} + \text{CH}_3\text{OH}$ and irradiated CH_3OH (Moore *et al.* 1996) have the same positions and relative intensities as $\text{H}_2\text{O} + \text{C}_2\text{H}_4(\text{OH})_2$ does in those regions. Finally, the formation of $\text{C}_2\text{H}_4(\text{OH})_2$ can be explained by straightforward reaction chemistry. Hydroxymethyl radicals, CH_2OH , are produced by proton irradiation of CH_3OH and combine to make the glycol: $2\text{CH}_2\text{OH} \rightarrow \text{C}_2\text{H}_4(\text{OH})_2$. Although some $\text{C}_2\text{H}_5\text{OH}$ formation may occur in irradiated $\text{H}_2\text{O} + \text{CH}_3\text{OH}$, we

TABLE I
IR Positions of Products in Irradiated CH_3OH -Containing Ices (Positions in cm^{-1})

HCOO^- : 1589 (shoulder), 1384, 1353
$\text{C}_2\text{H}_4(\text{OH})_2$: 1088, 1046 (shoulder), 885, 861, 524
H_2CO : 1712, 1499, 1248
CH_4 : 1303
CO : 2135
CO_2 : 2341, 654 (broad)
HCO : 1848

Note. Reference positions: $\text{H}_2\text{O} + \text{HCOO}^-$ mixture, 1587, 1382, and 1354 cm^{-1} (irradiated $\text{H}_2\text{O} : \text{CO} = 5 : 1$, this work); $\text{H}_2\text{O} + \text{ethylene glycol}$ (5:1 mixture), 1086, 1047, 884, 865, and 523 cm^{-1} (this work). Literature references for H_2CO , CH_4 , CO , CO_2 , and HCO are widely available (e.g., Hudson and Moore 1999, and references therein). All measurements were made at $\sim 16 \text{ K}$. For ethylene glycol, a reference spectrum is also available from the authors at http://www.eckerd.edu/academics/nas/chn/cosmic_ices/ and at http://www-691.gsfc.nasa.gov/cosmic_ices/ in several formats.

have no IR-spectral evidence for it. Bernstein *et al.* (1995) have found trace amounts of $\text{C}_2\text{H}_5\text{OH}$ in room temperature residues from more complex UV-photolyzed ices containing CH_3OH , but using more sensitive analytical techniques than IR absorption.

To summarize, we find no IR evidence for acetone formation in ion-irradiated $\text{H}_2\text{O} + \text{CH}_3\text{OH}$; any acetone contribution is so small as to be negligible. Ethylene glycol has been identified for the first time in this ice mixture, indicating its radiation synthesis at $\sim 16 \text{ K}$, and explaining unidentified bands reported earlier. Three features from HCOO^- have permitted its identification in irradiated $\text{H}_2\text{O} + \text{CH}_3\text{OH}$. Table I summarizes the spectral assignments of carbon-containing products.

Since CH_3OH exists in comets and interstellar ices, our work suggests HCOO^- and $\text{C}_2\text{H}_4(\text{OH})_2$ as candidates for searches by observers. In the case of $\text{C}_2\text{H}_4(\text{OH})_2$, the largest band we detected (1088 cm^{-1}) is in a region typically obscured by silicates. However, the two HCOO^- lines form a distinctive pair near 1384 and 1353 cm^{-1} . Figure 2 compares our spectrum of irradiated

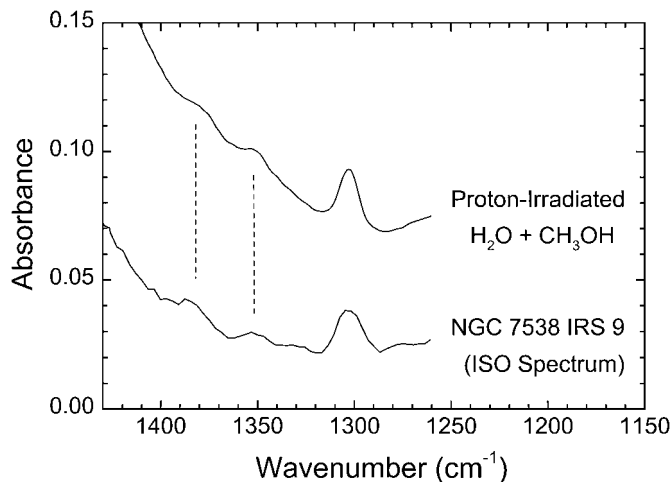


FIG. 2. Mid-IR spectrum from Fig. 1 of an irradiated $\text{H}_2\text{O} + \text{CH}_3\text{OH}$ (3:1) ice (upper) compared to an ISO spectrum of NGC 7538 IRS 9. Two vertical dashed lines are drawn from the formate ion features in the upper spectrum to the lower, ISO spectrum.

$\text{H}_2\text{O} + \text{CH}_3\text{OH}$ from Fig. 1 with a spectrum taken by the Infrared Space Observatory of the protostellar object NGC 7538 IRS 9 (Schutte *et al.* 1996b, Fig. 3). In both traces of our Fig. 2, a pair of absorbances near 1384 and 1353 cm^{-1} is present. These same features can be seen in the published spectra of RAFGL 7009S (Demyk *et al.* 1998, Fig. 8) and W33A (Schutte *et al.* 1998, Fig. 1). Although other interpretations for these IR bands are possible, the close matches in position, width, and relative intensity with our laboratory spectrum lend support to the HCOO^- assignment. If these features in NGC 7538 IRS 9, RAFGL 7009S, and W33A are indeed due to HCOO^- , they may indicate a history of radiation exposure for interstellar and hence cometary ices. Alternatively, some type of acid–base reaction may produce HCOO^- from HCOOH , although it is difficult to see how such a reaction could be initiated at ~ 16 K without either ion irradiation or UV photolysis. Even here, new experiments may be needed, as we are unaware of published work showing HCOO^- synthesis in the UV photolysis of $\text{H}_2\text{O} + \text{CH}_3\text{OH}$ or other ices.

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