Methanol Radiolysis of Astrochemical Interest

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Abstract

Using infrared reflection absorption spectroscopy (IRAS), we have investigated low-energy (5-20 eV) electron-induced reactions in condensed methanol (CH$_3$OH) under ultrahigh vacuum conditions ($\sim 4 \times 10^{-10}$ torr). In contrast to temperature programmed desorption (TPD), a post-irradiation technique we have used previously to study methanol radiolysis, IRAS does not require thermal processing prior to product detection. Our goal is to simulate processes which occur when high-energy cosmic rays interact with interstellar and cometary ices, where methanol, a precursor of several prebiotic species, is relatively abundant. The interactions of high-energy radiation, such as cosmic rays ($E_{\text{max}} \sim 10^{20}$ eV), with matter produces large numbers of low-energy (< 15 eV) secondary electrons, which are thought to initiate radiolysis reactions in the condensed phase. Using IRAS we have found compelling evidence for the formation of ethylene glycol (HOCH$_2$CH$_2$OH), formaldehyde (CH$_2$O), dimethyl ether (CH$_3$OCH$_3$), methane (CH$_4$), carbon dioxide (CO$_2$), carbon monoxide (CO), and the hydroxyl methyl radical (•CH$_2$OH) upon low-energy electron irradiation of condensed methanol at $\sim 85$ K. We have also identified the same nascent radiolysis products following high-energy ($\sim 900$ eV) electron irradiation of condensed methanol, a finding which is consistent with the hypothesis that high-energy condensed phase radiolysis is mediated by low-energy electron-induced reactions. The observed formation of radiolysis products at electron energies below 10 eV demonstrates that electron impact ionization cannot be the sole reaction mechanism. The results of experiments such as ours may provide a fundamental understanding of how complex molecules are synthesized in the interstellar medium and comets.
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1.0 Introduction

Dense interstellar clouds of molecules and dust become the building blocks of protostellar disks, from which stars, planets, asteroids, comets, and other macroscopic objects form.\textsuperscript{1,2} Observations at infrared, submillimeter, millimeter, and radio frequencies show that a large variety of organic molecules (over 140 species) are present in these interstellar clouds.\textsuperscript{2,3} In fact, these regions of star formation, called protostars, are defined by a relative abundance of organic molecules such as methanol (CH\textsubscript{3}OH).\textsuperscript{3} Organic molecular classes identified within these regions include nitriles, aldehydes, alcohols, acids, ethers, ketones, amines, and amides.\textsuperscript{4,5,6} Although the majority of identified species consist of only a few atoms, larger molecules such as quinones, fullerenes, and polycyclic aromatic hydrocarbons (PAHs) have also been observed.\textsuperscript{2,7} The growth of molecular complexity in the interstellar medium is an active area of current research.\textsuperscript{8}

Methanol (CH\textsubscript{3}OH) is of astrochemical interest because of its relatively high abundance in protostar environments. Relative to that of water, observed methanol abundance values range from 7\% to as high 30\%.\textsuperscript{9,10} Moreover, methanol is thought to be an important precursor not only to simple species such as methyl formate (HCOOCH\textsubscript{3}) and dimethyl ether (CH\textsubscript{3}OCH\textsubscript{3}), but also to many prebiotic species such as simple sugars and amino acids.\textsuperscript{7,11,12} It has been proposed that CH\textsubscript{3}OH evolves through the successive hydrogenation of CO molecules on interstellar silicate dust grains.\textsuperscript{13} Laboratory experiments simulating these processes have demonstrated the formation of formaldehyde (CH\textsubscript{2}O) and methanol in amounts consistent with observed abundances in the interstellar medium (ISM).\textsuperscript{13}
Physical conditions of dense molecular clouds vary greatly across the ISM, with molecular densities ranging from $10^4$ to $10^8$ hydrogen atoms cm$^{-3}$ and temperatures ranging from 10 to 300 K.$^{1,14}$ The abundance of relatively complex organic and prebiotic molecules in the ISM environment has led to debate concerning the reaction mechanisms involved in interstellar molecular synthesis. Gas-phase reactions, surface reactions on dust grains, and UV- and cosmic ray-induced chemistry in ice mantles have all been suggested as possible paths for chemical synthesis, as described in detail below.$^{15}$

Gas phase chemistry in the ISM is sufficiently efficient to account for the formation of simple species such as CO, N$_2$, O$_2$, C$_2$H$_4$, HCN, and simple carbon chains.$^{16}$ However, recent studies have shown that gas-phase processes are much too inefficient to account for the observed abundance of species such as methyl formate (HCOOCH$_3$) in star-forming regions, suggesting that gas phase processes play only a minor role in the formation of more complex species.$^{17}$ Although surface reactions on dust grains have yet to be studied quantitatively, experiments of surface hydrogenation reactions have shown the favored mechanism to be the dissociation, rather than the synthesis, of complex molecules. Thus, surface reactions may serve to slow the buildup of complex molecules.$^{18}$

UV- and cosmic ray-induced chemistry in interstellar ices is thought to be the most probable route in the synthesis of organic species. In this model, CH$_3$OH and other simple species in ice mantles, such as CO and H$_2$O, are dissociated into radical species by UV photolysis or cosmic ray radiolysis. Then during a crucial warm-up period that promotes diffusion, radicals recombine to form more complex species.$^{3}$ The absence of any energy barrier for radical-radical encounters allows these reactions to proceed rapidly, even at low temperatures. The possible
combinations of radicals thought to form during irradiation of \( \text{CH}_3\text{OH} \) can lead to a rich and varied chemistry, as shown in Table 1. It has been claimed that radiation-induced ice chemistry can explain the observed abundances of complex organic molecules within protostars, and can furthermore predict the abundances of complex species that have yet to be detected.\(^3\) For example, the formation of the amino acid glycine has been successfully demonstrated in laboratory experiments simulating cosmic ray irradiation of ISM ice film analogs.\(^{19}\) This laboratory result has led astronomers to develop new strategies to identify glycine within the ISM.\(^{20}\)

Radiation-induced chemistry in extraterrestrial ices is also thought to play a significant role in the synthesis of organic species detected in comets.\(^{21}\) Tellingly, recent UV photolysis experiments with pure \( \text{CH}_3\text{OH} \) ices have shown that this mechanism can account for the composition of complex ices in the comet Hale-Bopp.\(^{12}\)

<table>
<thead>
<tr>
<th>Radical 1</th>
<th>( \bullet\text{CH}_2\text{OH} )</th>
<th>( \bullet\text{HCO} )</th>
<th>( \bullet\text{CH}_3\text{O}^\bullet )</th>
<th>( \bullet\text{CH}_3 )</th>
<th>( \bullet\text{OH} )</th>
<th>( \bullet\text{H} )</th>
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<td>( \bullet\text{CH}_2\text{OH} )</td>
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<td>Glycolaldehyde</td>
<td>CHOCHO</td>
<td>Methyl Formate</td>
<td>( \text{CH}_3\text{OCH}_3 )</td>
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<td></td>
</tr>
<tr>
<td>( \bullet\text{CH}_3\text{O}^\bullet )</td>
<td>Methoxymethanol</td>
<td>CH(_2)OCH(_3)</td>
<td>Dimethyl Peroxide</td>
<td>( \text{CH}_3\text{OCH}_3 )</td>
<td>Dimethyl Ether</td>
<td></td>
</tr>
<tr>
<td>( \bullet\text{CH}_3 )</td>
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<td>CH(_3)CHO</td>
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<td>Methyl Hydroperoxide</td>
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<tr>
<td>( \bullet\text{H} )</td>
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<td>( \text{H}_2\text{CO} )</td>
<td>Methanol</td>
<td>( \text{CH}_4 )</td>
<td>Methane</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Possible radical-radical combinations for irradiated \( \text{CH}_3\text{OH} \).
Several studies have investigated the effects of radiation on CH$_3$OH ices using infrared reflection absorption spectroscopy (IRAS) to identify photolysis/radiolysis products. In order to stimulate dissociation of condensed CH$_3$OH, UV Ly$\alpha$ photons (energy $\sim$10 eV) have been used to simulate UV rays in the ISM; 1 MeV protons, 3 KeV He$^+$ ions, and high-energy electrons have been used to simulate high-energy cosmic rays. Identified methanol photolysis and high-energy radiolysis products include formaldehyde (H$_2$CO), carbon monoxide (CO), carbon dioxide (CO$_2$), methane (CH$_4$), methyl formate (CH$_3$OCHO), dimethyl ether (CH$_3$OCH$_3$), ethylene glycol (HOCH$_2$CH$_2$OH), glycolaldehyde (HCOCH$_2$OH), ethanol (CH$_3$CH$_2$OH), ethane (CH$_3$CH$_3$), acetaldehyde (CH$_3$CHO), acetone (CH$_3$COCH$_3$), water, and the hydroxyl methyl (•CH$_2$OH) and formyl (•HCO) radicals. Although the results and conclusions of these studies are similar, disagreements among the findings merit closer examination. Moreover, prior to the work described herein, low-energy electron interaction with CH$_3$OH ices had yet to be examined using IRAS. Our motivation for this study is the hypothesis that low-energy electron interactions with condensed matter play a critical role in astrochemistry, as described in detail below.

Organic synthesis in protostar environments is dependent upon energetic processing involving UV photons and high-energy cosmic rays.$^1$ However, the interstellar UV radiation field is not able to penetrate into the interior of dense clouds.$^{29}$ H$_2$ molecules excited by cosmic rays decay by emitting UV photons, leading to a cosmic ray-induced UV radiation field within the ISM.$^{29}$ Essentially, high-energy cosmic rays are thought to be the sole drivers of energetic processes within the protostar environment.$^{29}$ In addition to UV photons, the interaction of high-energy radiation with matter results in the formation of copious amounts of low-energy
secondary electrons, which form distinct energetic species that are thought to promote a variety of radiation-induced chemical reactions.\textsuperscript{30} The majority of the resulting secondary electrons have energies below 15 eV and react with matter via one of three mechanisms: (1) dissociative electron attachment (DEA), (2) electron impact excitation, or (3) electron impact ionization.\textsuperscript{31} The three mechanisms are illustrated below for a generic molecule AB.

1. \( e^- + AB \rightarrow [AB]^ - \rightarrow A^* + B^- \)

2. \( e^- + AB \rightarrow [AB]^* + e^- \rightarrow A^* + B + e^- \)

3. \( e^- + AB \rightarrow [AB]^{1*} + e^- \rightarrow A + B^{**} \)

Dissociative electron attachment, a resonant process occurring at low electron energies (< 15 eV), is characterized by the initial capture of an electron by a molecule to form a transient negative ion, which subsequently dissociates into a radical and an anion.\textsuperscript{31, 32} Electron impact excitation and ionization occur at electron energies typically above 6 eV and 10 eV, respectively.\textsuperscript{31}

The energy distribution of secondary electrons resulting from the interaction of high-energy radiation with matter has a quasi-bell-shaped curve, with the majority of electrons having energies below \( \sim 15 \text{ eV} \). The dissociation cross-section as a function of electron energy shows DEA resonances at low energies, followed by an increase at higher electron energies due to electron impact excitation and ionization. Multiplying the energy distribution by the dissociation cross-section gives the dissociation yield as a function of electron energy. Even though the dissociation probability increases above a threshold of \( \sim 10 \text{ eV} \), the yield function indicates that dissociation due to secondary electrons is far more likely at energies below \( \sim 15 \)
Few experimental studies, however, have examined the relationship between the effects of high-energy irradiation and low-energy electron irradiation of condensed matter.\textsuperscript{31, 33}

Results of previous temperature programmed desorption (TPD) studies of CH\textsubscript{3}OH thin films irradiated with low-energy (≤ 50 eV) electrons demonstrated the formation of ethylene glycol (HOCH\textsubscript{2}CH\textsubscript{2}OH), ethanol (CH\textsubscript{3}CH\textsubscript{2}OH), dimethyl ether (CH\textsubscript{3}OCH\textsubscript{3}), formaldehyde (H\textsubscript{2}CO), methoxymethanol (CH\textsubscript{3}OCH\textsubscript{2}OH), methane (CH\textsubscript{4}), methyl formate (CH\textsubscript{3}OCHO), glycolaldehyde (HCOCH\textsubscript{2}OH), and water.\textsuperscript{34, 35} Because the TPD technique requires a thermal processing step after electron irradiation, products identified by this technique may not be nascent radiolysis products formed at liquid nitrogen temperatures. Because of this limitation of TPD, we have investigated low-energy electron interactions with CH\textsubscript{3}OH thin films using infrared reflection absorption spectroscopy.

Results of our IRAS experiments show that low-energy (14 eV) electron irradiation of condensed CH\textsubscript{3}OH at ~85 K results in the formation of ethylene glycol (HOCH\textsubscript{2}CH\textsubscript{2}OH), formaldehyde (CH\textsubscript{2}O), dimethyl ether (CH\textsubscript{3}OCH\textsubscript{3}), methane (CH\textsubscript{4}), carbon dioxide (CO\textsubscript{2}), carbon monoxide (CO), and the hydroxyl methyl radical (•CH\textsubscript{2}OH) without thermal processing above liquid nitrogen temperatures. Interestingly, the same radiolysis products are produced following irradiation with high-energy (900 eV) electrons. These qualitative findings suggest that high-energy radiation-induced changes may be attributable to low-energy secondary electron interactions with condensed matter.

2.0 Experimental Section
Experiments were performed in a custom-designed stainless steel UHV chamber with a base pressure of $4 \times 10^{-10}$ torr. A Mo(110) single crystal substrate was mounted on a precision sample manipulator capable of x, y, and z translations at the chamber center. Polar rotation of the crystal mount was provided for via a differentially pumped rotary feedthrough. The crystal substrate could be cooled to $\sim 85$ K with liquid nitrogen and heated to 800 K radiatively or to 2200 K by electron bombardment. Temperature measurements were made using a tungsten-rhenium, W-5% Re vs. W-26% Re thermocouple spot welded to the edge of the crystal. The crystal was routinely cleaned by heating to 2200 K, exceeding the desorption temperature of oxygen.

IRAS measurements were performed using a TENSOR$^\text{TM}$ 27 FTIR spectrometer (Bruker Optics) equipped with a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector (see Appendix 1). A background spectrum (1000 scans at 8 cm$^{-1}$ resolution) of the clean crystal was subtracted from all sample IRAS spectra. Unless otherwise noted, all sample spectra were collected at 8 cm$^{-1}$ resolution with 250 scans for each spectrum.

An EGPS-1106A electron gun (Kimball Physics Inc.) was used to irradiate condensed methanol samples on the crystal substrate. The incident current was set at 2 microamps on the clean crystal for all experiments. Incident electron energy was varied between 5 and 900 eV.

All samples [CH$_3$OH (Aldrich, 99.9+ %), $^{13}$CH$_3$OH (Aldrich, 99%), CH$_3$CH$_2$OH (Pharmco, anhydrous absolute), HCOOCH$_3$ (Aldrich, anhydrous 99%), CH$_3$OCH$_3$ (Aldrich, 99%), HOC$\text{H}_2$CH$_2$OH, (Aldrich, anhydrous 99.8%) HCOCH$_2$OH (Aldrich, crystalline dimer), CH$_3$COOH (EMD, glacial)] were stored in cleaned (baked) Schlenk tubes and degassed by three freeze–pump–thaw cycles before use. The two exceptions were HCOCH$_2$OH, a solid dimer sample
which was gently heated to produce monomer fragments before introduction to the chamber, and CH$_3$OCH$_3$, which was packaged in a pressurized canister and introduced directly into the UHV chamber.

Dosers with precision leak valves allowed for highly-controlled deposition of methanol onto the Mo(110) crystal surface. Temperature-programmed desorption experiments in the absence of electron irradiation were used to determine the coverage of CH$_3$OH. One monolayer (1 ML) is defined as the coverage achieved by the maximum exposure of the adsorbate that does not yield a multilayer peak. Film thickness (usually 100 ML) was sufficient to rule out any contribution from Mo surface interactions. Multilayers of methanol at 85 K form an amorphous solid (glass), because crystallization of methanol occurs only above 128 K.$^{36}$

### 3.0 Results and Discussion

#### 3.1 Radiolysis Products Identification

Multiple methods based on IR spectroscopy were utilized to identify low-energy electron-induced radiolysis products formed within methanol thin films at 85 K. First, IR peak positions were compared to literature values (Table 2). Second, these peak assignments were further verified by annealing experiments during which the irradiated CH$_3$OH thin film was heated to various temperatures before IR analysis at 85 K. The temperatures corresponding to the loss of IR peaks were compared with previously recorded radiolysis product desorption temperatures (Table 3).$^{34}$ Third, mixtures of CH$_3$OH with approximately 10-30% of potential radiolysis product were dosed onto the crystal at 85 K. IR spectra of these unirradiated mixed thin films were used as additional evidence for peak assignments in electron-irradiated condensed methanol.
| ν   | CH₃OH | H₂CO | H₂CO | H₂CO | HCO | CO | CO₂ | CO₂ | CH₄ | CH₄ | CH₃OCHO | CH₃OCHO | CH₃OCHO | HOC₆H₂OH | HOC₆H₂OH | HOC₆H₂OH | HOC₆H₂OH | HOC₆H₂OH | CH₃H₂O | CH₃CH₂OH | CH₃CH₂OH | CH₃COCH₃ | CH₃COCH₃ | CH₃COCH₃ | CH₃COCH₃ | H₂? | HCOO⁻ | HCOO⁻ | H₂O |
|-----|-------|------|------|------|-----|----|-----|-----|-----|-----|---------|---------|---------|----------|----------|----------|----------|----------|--------|---------|---------|------|
| ν₁  | 1195  | 1195 | 1192 | 1195 | 1197|     |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₂  | 1724  | 1720 | 1726 | 1720 | 1727| 1719| 1712| 1720| 1720|     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₃  | 1496  | 1500 | 1498 | 1497 | 1499|     |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₄  | 1249  | 1249 | 1245 | 1245 | 1244| 1248|     |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₅  | 2133  | 2134 | 2137 | 2135 | 2138| 2135| 2136| 2136|     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₆  | 2087  | 2087 |     |      | 2092|     |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₇  | 2341  | 2341 | 2345 | 2343 | 2340| 2342| 2344| 2344|     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₈  | 2276  | 2276 |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₉  | 1303  | 1303 | 1303 | 1304 | 1301| 1304| 1303| 1305| 1308|     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₁₀ | 1161  | 1161 |     |      | 1160|     |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₁₁ | 1160  | 1160 |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₁₂ |      |      |      |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₁₃ | 1610  | 1610 |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₁₄ |      |      |      |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₁₅ | 525   | 524  |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₁₆ | 1747  |      |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₁₇ | 1382  |      |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₁₈ | 885   |      |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₁₉ | 1372  |      |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₂₀ | 822   |      |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₂₁ | 1350  |      |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₂₂ | 1720  |      |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₂₃ | 1444  |      |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₂₄ | 1232  |      |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₂₅ | 1090  |      |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₂₆ | 4140  |      |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₂₇ | 1382  |      |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₂₈ | 1384  |      |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₂₉ | 1589  |      |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |
| ν₃₀ |       |      |     |      |     |      |      |      |     |     |         |         |         |           |           |           |           |           |        |          |          |     |

Table 2. Comparison of several studies which investigated the effects of various radiations on CH₃OH thin films using IRAS. Highlighted in yellow are peak values and identifications that agree with the results from this work. Expansion of table in Kaiser 2007.²⁸
3.1.1 Evidence for Ethylene Glycol (HOCH$_2$CH$_2$OH) Formation

Post-irradiation IR spectra (Figure 1) demonstrate the formation of ethylene glycol (HOCH$_2$CH$_2$OH) at 85 K upon low-energy electron irradiation of condensed methanol. High-energy methanol radiolysis leading to ethylene glycol formation has been previously attributed to the dimerization of two hydroxyl methyl (•CH$_2$OH) radicals. Ethylene glycol formation at 85 K was verified by the presence of a prominent IR peak at 1090 cm$^{-1}$, as well as weaker peaks at 890 and 865 cm$^{-1}$, observed following electron irradiation of methanol thin films. Ethylene glycol production was observed when methanol films were irradiated with electrons with energies as low as 7 eV (electron dose of 2.4 × 10$^3$ µC). During annealing experiments, IR peaks associated with ethylene glycol disappeared between 200 and 250 K, consistent with the ~210 K ethylene glycol desorption temperature found during temperature programmed desorption following low-energy electron irradiation of condensed methanol (Table 3). Furthermore, IR spectra of thin films formed from a mixture of ~10% ethylene glycol (v/v) in CH$_3$OH dosed onto the cooled crystal evinced prominent peaks that were in good agreement with features identified in the irradiated CH$_3$OH thin film.
Figure 1. IRAS spectrum of 100 ML of unirradiated CH$_3$OH (black curve). Same CH$_3$OH sample after irradiation with 14 eV electrons (electron dose of 2.4 × 10$^3$ µC)(red curve).
<table>
<thead>
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Table 3. 100 ML CH\textsubscript{3}OH after electron dose of 2.4 × 10\textsuperscript{3} µC with 14 eV electrons annealed to various temperatures. Peaks identified as evidence for specific species are listed at the temperatures they were present. Desorption of the various species at differing temperatures can be seen.

3.1.2 Evidence for Formaldehyde (H\textsubscript{2}CO) Formation

Formaldehyde (H\textsubscript{2}CO) formation at 85 K following electron irradiation of condensed methanol was confirmed by IR peaks at 1724 and 1242 cm\textsuperscript{-1}. Formaldehyde is thought to be produced through the combination of •H and •HCO radicals and/or disproportionation of the hydroxymethyl radicals within the irradiated CH\textsubscript{3}OH thin film.\textsuperscript{23,34} Formation of formaldehyde was seen after irradiation with electrons with energies as low as 9 eV (electron dose of 2.4 ×10\textsuperscript{3} µC). Results of annealing experiments showed the disappearance of formaldehyde IR peaks between 120 and 135 K, above the desorption temperature of ~90 K reported in a previous post-irradiation TPD study of condensed methanol.\textsuperscript{34}
3.1.3 Evidence for Dimethyl Ether (CH$_3$OCH$_3$) Formation

The low-energy electron-induced production of dimethyl ether (CH$_3$OCH$_3$) at 85 K from condensed methanol was confirmed by the prominent IR peak at 1090 cm$^{-1}$ as well as weaker peaks at 1161 and 922 cm$^{-1}$. Previous studies have demonstrated that dimethyl ether (CH$_3$OCH$_3$) is a methanol ice radiolysis/photolysis product,$^{34}$ which is thought to form from the combination of CH$_3$O• and •CH$_3$ radicals.$^{23}$ Formation of this product was seen after irradiation with electrons with energies as low as 7 eV (electron dose of $2.4 \times 10^3$ µC). During annealing experiments, CH$_3$OCH$_3$ was seen to desorb between 100 and 120 K, consistent with the desorption temperature of ~100 K observed for dimethyl ether in a previous post-irradiation TPD study of condensed methanol.$^{34}$

In previous IRAS studies of irradiated CH$_3$OH, the peaks at 1161 and 922 cm$^{-1}$ were attributed to either dimethyl ether$^{23}$ or another methanol radiolysis product, methyl formate (HCOOCH$_3$).$^{28,26,38}$ In order to resolve this discrepancy, IR spectra of condensed films of a mixture of ~20% dimethyl ether in CH$_3$OH were compared to those of a mixture of ~30% methyl formate in CH$_3$OH. IR peaks of the dimethyl ether/CH$_3$OH thin film better matched those of the electron irradiated CH$_3$OH ice (Figure 2). Although IR features of the methyl formate also align well with features in the irradiated CH$_3$OH sample, particularly the band at 1161 cm$^{-1}$, the absence of the even more prominent methyl formate peak at 1207 cm$^{-1}$ in the irradiated CH$_3$OH sample supports our IR peak assignments.
3.1.4 Evidence for Hydroxy Methyl radical (\(\cdot\)CH\(_2\)OH) Formation

Consistent with the results of multiple previous IRAS studies of irradiated methanol ices, the hydroxy methyl radical (\(\cdot\)CH\(_2\)OH) was identified by a single peak at 1195 cm\(^{-1}\) at 85 K following low-energy electron irradiation of condensed methanol.\(^{23,24,28}\) Although formation of HOCH\(_2\)CH\(_2\)OH was detected at energies as low as 7 eV, evidence for the production of hydroxy methyl radical was only seen after irradiation with 14 eV electrons (electron dose of 2.4 \(\times\) 10\(^3\) \(\mu\)C). This discrepancy is attributed to rapid radical diffusion, even at 85 K, leading to facile ethylene glycol formation from the dimerization of hydroxymethyl radicals.
3.1.5 Evidence for CO$_2$ Formation

IR evidence for CO$_2$ production when condensed methanol was irradiated with low-energy (14 eV) electrons was detected only following a high total electron dose of $1.4 \times 10^4$ µC. Background signals for CO$_2$ present in our experimental setup necessitated the use of $^{13}$CH$_3$OH in order to clearly detect IR peaks attributable to carbon dioxide. A prominent IR peak at 2276 cm$^{-1}$ was assigned to $^{13}$CO$_2$ (Figure 3), in good agreement with literature values (Table 2).$^{24}$ CO$_2$ is thought to be produced by the reaction of CO and the hydroxyl radical (•OH) formed during the radiolysis of methanol.$^{39}$

3.1.6 Evidence for CO Formation

Similar to CO$_2$, an IR peak attributable to carbon monoxide (CO) was detected at 85 K only after irradiation of condensed methanol with a high total electron dose ($1.4 \times 10^4$ µC) of low-energy (14 eV) electrons. A single peak in both irradiated CH$_3$OH (at 2134 cm$^{-1}$) and $^{13}$CH$_3$OH (at 2087 cm$^{-1}$) thin films was attributed to carbon monoxide (Figure 3) in good agreement with literature values (Table 2).$^{22,23,24,25,26,27,28}$ Dissociation of the formyl radical (•HCO) is thought to yield CO.$^{23}$

3.1.7 Evidence for CH$_4$ Formation

A high total electron dose ($1.4 \times 10^4$ µC) was also necessary to detect formation of methane (CH$_4$) in CH$_3$OH thin films irradiated with low energy (14 eV) electrons at 85 K. A single IR peak at 1303 cm$^{-1}$ was attributed to CH$_4$ (Figure 3), in good agreement with literature values (Table 2).$^{22,23,24,25,26,27,28}$ CH$_4$ formation is thought to occur via the combination of •CH$_3$ and •H radicals.$^{23}$
3.2 IRAS of High-Energy Electron Irradiated Condensed Methanol

IR spectra were acquired of thin films (100 ML) of CH$_3$OH irradiated with 900 eV electrons in order to examine possible differences in chemical synthesis during high- vs. low-energy electron irradiation. Total electron dose was kept small (60 µC) relative to low-energy electron experiments because of the large quantities of low-energy secondary electrons thought to be produced from high-energy electron interactions. Interestingly, all previously identified low-energy electron-induced radiolysis products were also identified following high-energy electron irradiation (Table 2). A comparison of the CO$_2$, CO, and CH$_4$ IR peaks in low- and high-energy electron irradiated methanol is shown in Figure 3. Several small new IR peaks were also observed but have yet to be identified. These new peaks do not correspond with literature values or IR peaks in spectra of thin films of CH$_3$OH / suspected radiolysis product (ethylene glycol, methyl formate, glycolaldehyde (both monomer and dimer), acetic acid, dimethyl ether, or ethanol) mixtures.
Figure 3. IRAS scan of 100 ML of CH$_3$OH irradiated (electron dose $1.4 \times 10^4$ µC) with 14 eV electrons (black curve), and 100 ML of CH$_3$OH irradiated (electron dose 60 µC) with 900 eV electrons (red curve). $^{13}$CH$_3$OH was used to detect $^{13}$CO$_2$ formation without interference from background $^{12}$CO$_2$.

3.3 Annealing Experiments Reveal New IR Peaks

IR spectra collected at 85 K following post-irradiation annealing of the CH$_3$OH thin films demonstrated the desorption of radiolysis products at characteristic temperatures (Table 3). Upon annealing to 120 K, new IR peaks, some quite prominent, were also observed (Figure 4) and were later seen to disappear between 135 and 150 K along with those of CH$_3$OH. These IR peaks were not seen when nonirradiated CH$_3$OH was annealed. Because these new peaks do not correspond with known/suspected methanol radiolysis products, we attribute these IR features to surface reaction products or phase changes of methanol radiolysis products. An IR band at 991 cm$^{-1}$, detected upon annealing irradiated methanol to 550 K, was attributed to Mo
/ O double bond stretching on the oxidized Mo surface.\textsuperscript{40, 41} This species was observed to desorb upon annealing to 870 K. A similar IR peak was also detected when unirradiated methanol thin films were annealed.

![Figure 4](image)

**Figure 4.** IRAS scan of 100 ML of unirradiated CH3OH (green curve). Same sample irradiated with 14 eV electrons, total electron dose of $2.4 \times 10^3 \, \mu\text{C}$ (red curve). Same CH$_3$OH sample now annealed to $\sim 120$ K, cooled, and rescanned (blue curve). New unidentified peaks formed upon annealing.

### 3.4 Potential Radiolysis Products Not Observed

Several potential radiolysis products of methanol, including methyl formate, glycolaldehyde, acetic acid, and ethanol, have been detected in the ISM,\textsuperscript{42, 43} as well as in previous photolysis/radiolysis laboratory experiments.\textsuperscript{23, 24, 28, 34} However, these products were not detected in our IRAS data collected at 85 K following either low-energy or high-energy electron irradiation. IR spectra acquired at 85 K after annealing the irradiated methanol films to higher
temperatures also failed to evince peaks characteristic of these reaction products. These results were verified by acquiring IR spectra of thin films made from mixtures of CH$_3$OH / ~10%-30% potential product. Results of temperature programmed desorption experiments, however, demonstrate the formation of methyl formate, glycolaldehyde, acetic acid, and ethanol following low-energy electron irradiation of condensed methanol.  

3.5 Unidentified Peaks in Irradiated CH$_3$OH

Several IR peaks of irradiated CH$_3$OH at 85 K remain unidentified (Figure 1). These peaks, located at 1408, 1269, and 985 cm$^{-1}$, do not correspond to literature values or to peaks seen in IR spectra of thin films of mixtures of potential product in CH$_3$OH. These unidentified peaks are reproducible and provide an interesting area for future research.

Interestingly, for a total electron dose of $2.4 \times 10^3 \mu$C, the IR peak at 985 cm$^{-1}$ is observed only when the methanol thin film is irradiated with electrons with energies between 5 and 17 eV, with maximum formation at 14 eV. This finding is suggestive of dissociative electron attachment. This IR peak is not detected upon irradiation with 14 eV electrons at a total electron dose is $3.6 \times 10^3 \mu$C, suggesting that the species responsible for this IR peak is decomposed at high electron fluence. This IR peak was seen to disappear between 100 and 120 K during post-irradiation annealing experiments. IR features seen in thin films of mixtures of CH$_3$OH / potential radiolysis products did not align with this peak. Further experiments concerning the formation of this unknown species provide an intriguing direction for future research.

3.6 Implications for Interstellar Chemistry?
The excellent correlation between results of low- and high-energy electron interactions suggests that low-energy secondary electrons may be responsible for initiating chemical processes within interstellar ice films. Within protostellar environments, low-energy secondary electrons from interstellar cosmic rays may interact with ice films rich in CH$_3$OH to form radical species whose subsequent reactions may lead to the production of some of the diverse observed interstellar molecules, including prebiotic species. These prebiotic molecules may then be delivered to planets by comets, providing essential ingredients for the origins of life.¹

4.0 Conclusion

We have investigated the effects of low-energy electron irradiation of nanoscale thin films of CH$_3$OH at 85 K under ultrahigh vacuum conditions. Results collected using IRAS indicate that ethylene glycol, formaldehyde, dimethyl ether, carbon dioxide, carbon monoxide, methane, and the hydroxyl methyl radicals are nascent low-energy electron-induced radiolysis products of condensed methanol. Analysis of methanol thin films irradiated with high-energy electrons demonstrated the formation of the same radiolysis products, suggesting that high-energy radiation-induced changes may be attributable to low-energy secondary electron interactions with condensed matter. The observed formation of radiolysis products at electron energies below 10 eV demonstrates that electron impact excitation and/or dissociative electron attachment must contribute to methanol radiolysis relevant to astrochemistry.
Appendix 1: IRAS Setup in Detail

A TENSOR™ 27 FTIR spectrometer from Bruker Optics was coupled to our ultrahigh vacuum (UHV) system and made operational for IRAS experiments. Because the amount of radiolysis products formed in nanoscale films was expected to be approximately ten orders of magnitude smaller than the amount of sample material used in typical IR experiments, several modifications, discussed in detail below, were made to optimize IRAS experiments.

A liquid nitrogen-cooled mercury cadmium telluride (MTC) detector was selected for our system due to its ability to produce a spectrum with a noise level 10 to 100 times lower than that from a standard Deuterated Tri-Glycine Sulfate (DTGS) detector working at room temperature. This reduction in noise level provides two improvements: first, the minimum detection limit is significantly lowered, and second, the concentration range over which measurements can be made is widened.

The absorption of IR light incident on a metal crystal surface is dependent on the angle of incidence. Maximum absorbance occurs when the beam is near grazing incidence, ~80° to the surface normal. IR light was reflected onto the substrate using external gold-coated plane and parabolic mirrors. The size of the beam spot at the crystal was calculated to be 20 x 115 mm for an 80° angle of incidence. Therefore the crystal, being about one centimeter in diameter, is exposed to less than 5% of the incident IR light. A significant increase in the IR light incident on the crystal can only be achieved by shortening the beam path, an impossible task given our current UHV system.
Figure 5. Spectral intensity as a function of incidence angle of the IR beam. Two curves show p-polarized (Ap) and s-polarized (As) light. Absorption of s-polarized light remains at zero due to image dipole effect. Figure obtained from J. Ferraro and L. Basile, 1985.

Figure 6. Schematic of IR beam path into and out of UHV chamber. Parabolic mirrors focus beam onto crystal surface within chamber. F is the focal length in mm. Figure obtained from Bruker Optics.

Due to the delicate alignment of the beam path, small vibrations of the system could be a significant source of noise. In order to minimize the effects of vibrations, tables built to support the spectrometer and detector were coupled to the frame supporting the UHV chamber, thus ensuring that the IR source, sample, and detector experience the same vibrations. Furthermore, Sorbothane, a viscoelastic material designed to absorb shocks and
vibrations, was placed beneath the IR spectrometer and detector. The rotary vane pump was also repositioned to minimize vibrations.

Custom-designed angled ports were fabricated to allow for normal incidence of the IR beam on the port windows (Figure 7) made of KBr, a material transparent to IR light. Compared to other materials transparent to IR light, KBr has many advantages, such as transmittance of a wide spectral range and low cost. However, KBr is susceptible to cleavage when stressed and hence could not be mated to the stainless steel ports with metal gaskets. In order to resolve this problem, as well as maintain good vacuum, a KBr window was placed in each port with Viton O rings on either side. A differential pumping system was installed to minimize leaks across the Viton seals. Atmospheric water-induced degradation of the KBr windows in our system is not a major concern, because the KBr windows are only exposed to vacuum conditions or nitrogen purge conditions.
Figure 7. Diagram of UHV chamber highlighting beam path. Angled ports on either side can be seen. SolidWorks figure prepared by Christopher Fitzhugh (Olin College undergraduate).

During each IRAS measurement, optical alignment was optimized by adjusting the x and y positions of the crystal stage using precision micrometers. The crystal’s θ coordinate was optimized by observing the amplitude of IR signal at the detector.

Image dipole effects caused by the metal surface mirroring dipoles in the adsorbed species cancels the ability of the s-polarized component of light to excite a dipole along the metal surface (Figure 5). The addition of a polarizer to allow only p-polarized incident light for data collection has been suggested, and could possibly contribute to future system improvements.
Figure 8. Top view of UHV chamber with IRAS setup implemented. IR beam path is highlighted in red. SolidWorks figure prepared by Christopher Fitzhugh (Olin College undergraduate).
Appendix 2: Merits of Continuous Purge

Because the IR beam is routed externally, reducing background signals from atmospheric gases such as water and carbon dioxide is imperative for high-quality data collection. Plexiglas purge boxes were custom-designed and built along the external beam path. \( \text{N}_2 \) gas flowing at a rate of 6 liters/minute was used to purge these boxes (Figure 9).

Figure 9. Custom-built Plexiglas box allows \( \text{N}_2 \) purging for external beam path.

1. **Background Scan Analysis**

   Background IR spectra were collected to ascertain the amount of time needed for sufficient \( \text{N}_2 \) purging (Figure 10). Results led to the conclusion that continuous purge produced the highest quality data.
2. Resolution

Although N₂ purging leads to a significantly reduced background signal, background interference remains an obstacle for high-quality data collection. In order to visualize IR peaks in spectral regions of H₂O and CO₂ background signals, resolution was lowered to 8 cm⁻¹. As shown in the equation below, the signal to noise ratio can be improved by lowering the resolution value.

\[
\text{Signal to Noise Ratio} \propto \sqrt{\text{number of scans} \times \text{resolution} \ (cm^{-1})}
\]

Despite this seemingly low resolution, our IRAS data was reproducible and generally consistent with previous studies involving other radiation sources.
3. Design for One-way Purge Box Valve (Not Yet Installed)

To decrease atmospheric contributions along the external beam path, edges and any openings of the Plexiglas purge boxes were sealed with weld-on acrylic cement. However, it was hypothesized that sealing the boxes resulted in a decreased ability to remove atmospheric contaminants. In order to improve the purging capability of our system, it has been suggested that one-way valves be installed on top of each purge box.

The design of these simple one-way valves is as follows. A small cup with a short tube attached to the bottom would be inserted into a small hole drilled into each of the two Plexiglas purge box lids. A rubber ball would be placed into each cup to close off the opening. However, once pressure in the purge box is increased, the ball would be lifted up to allow outward airflow. Once this valve is installed, all other openings of the purge boxes will be sealed completely. The usefulness of such a design is currently being discussed, and the final design and installation of these valves have yet to be completed.
References


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