Mid- and far-infrared spectroscopic studies of the influence of temperature, ultraviolet photolysis and ion irradiation on cosmic-type ices

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Abstract

Infrared (IR) studies of laboratory ices can provide information on the evolution of cosmic-type ices as a function of different simulated space environments involving thermal, ultraviolet (UV), or ion processing. Laboratory radiation experiments can lead to the formation of complex organic molecules. However, because of our lack of knowledge about UV photon and ion fluxes, and exposure lifetimes, it is not certain how well our simulations represent space conditions. Appropriate laboratory experiments are also limited by the absence of knowledge about the composition, density, and temperature of ices in different regions of space. Our current understanding of expected doses due to UV photons and cosmic rays is summarized here, along with an inventory of condensed-phase molecules identified on outer solar system surfaces, comets and interstellar grains. Far-IR spectra of thermally cycled H2O are discussed since these results reflect the dramatic difference between the amorphous and crystalline phases of H2O ice, the most dominant condensed-phase molecule in cosmic ices. A comparison of mid-IR spectra of products in proton-irradiated and UV-photolyzed ices shows that few differences are observed for these two forms of processing for the simple binary mixtures studied to date. IR identification of radiation products and experiments to determine production rates of new molecules in ices during processing are discussed. A new technique for measuring intrinsic IR band strengths of several unstable molecules is presented. An example of our laboratory results applied to Europa observations is included. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: IR spectroscopy; Condensed-phase; Ices; Energetic processing; Radiation chemistry; UV photolysis

1. Introduction

One of the major questions in the formation and evolution of condensed-phase molecules in interstellar environments is their production, which may proceed either via grain-surface chem-
istry or by accretion of simple molecules with subsequent processing by cosmic rays, UV photons, or a combination of both. Although research on grain-surface reactions represents the future direction of several laboratories, our experiments have focused on the processing of ices by protons and UV photons. The goal is to study the infrared spectra of key molecules and mixtures of molecules, and from those experiments identify new species formed during processing, and to measure the yield of major products. Many experiments also apply to ices in solar system environments when the ice composition, temperature, or bombarding flux is varied to simulate what is known about each icy-satellite, planetary, or cometary environment.

Laboratory experiments on UV-photolyzed and ion irradiated ices lead to the formation of many complex organic molecules, and seem to be representative of processes occurring in space. However, the exact nature of complex space environments is a major question connected to the correct dose of energetic processing in different regions. The flux of cosmic-ray ions onto the surface of a cometary nucleus stored for $10^9$ years in the Oort cloud (or Kuiper belt) or the flux of ions onto the surface of the Galilean satellites is more accurately modeled than the cosmic-ray flux encountered in various molecular clouds. Possible evidence for processing in interstellar ices includes the so-called ‘XCN’ feature at 4.62 μm [1–3], the 6.8 μm band [4,5], and the triple peak structure of the bending mode of CO$_2$ at 15.2 μm indicative of thermally-processed H$_2$O–CO$_2$–CH$_3$OH = 1:1:1 ice seen towards a number of massive protostellar sources [6,7]. Analysis of band shapes of CO$_2$ in many sources observed by the Infrared Space Observatory (ISO) reveals that CO$_2$ exists in both polar (H$_2$O and CH$_3$OH) ice matrices and in non-polar ices such as N$_2$, CO, or O$_2$ [6,8]. Another observational clue supporting thermal processing is the interstellar (IS) signature of the apolar CO$_2$ ice component which resembles that of annealed CO$_2$, rather than CO$_2$ condensed at 10 K. Evidence for energetic processing of cometary ices prior to accretion comes from the detection of abundant C$_2$H$_6$ in comet Hyakutake [9]. An abundance of C$_2$H$_6$ comparable with that of CH$_4$ implies that the ices did not originate in a thermochemically-equilibrated region of the solar nebula, but were produced by UV or radiation processing of interstellar icy grain mantles (see [10,11] for discussions of relevant experiments). Evidence for processing on the Jovian satellite, Europa, comes from the detection of H$_2$O$_2$ formed by ion bombardment of its H$_2$O-dominated surface ice [12] (for discussions of relevant experiments see [13]).

The bulk of solar system spectroscopic observations are obtained at visible and near-IR wavelengths (0.4–5 μm) since icy surfaces are observed in reflection or emission. However, laboratory experiments that focus on the identification of molecules, use the mid-IR (2–20 μm) spectral region. The fundamental vibration bands found in the mid-IR are much stronger than their overtones found in the near-IR, and are, therefore, more accurate indicators of molecular abundances in laboratory experiments. The far-infrared region (20–100 μm) contains absorptions due to intermolecular vibrations (lattice vibrations) and is often used for structural information. In the laboratory, good quality transmission spectra of thin ice films are used to identify molecular positions, and to calculate intrinsic band strengths of molecules. The detailed comparison of these spectra to observations requires modeling to account for effects such as grain size and shape distribution (see discussions in [14]).

1.1. Nature of radiation environments

In IS space, the galactic cosmic-ray environment is thought to have an isotropic flux which, on average, has been the same throughout the age of the solar system, $4.6 \times 10^9$ years. It is estimated that cosmic rays are 87% protons, 12% helium nuclei, and 1% heavier nuclei. The IS electron cosmic-ray flux is a factor of 10 to 100 times smaller than the proton flux for energies below 100 MeV. Radiation processing of ices by cosmic rays is dominated by protons, whose intensity is largest in the low MeV range and whose energy spectrum decreases with a power law index of 2.5 at higher energies.
The energy deposited per cm as a proton moves through a solid (the stopping power) has a maximum value for proton energies near 0.1 MeV. A typical 1 MeV proton has a stopping power of \( \sim 300 \text{ MeV cm}^{-2} \text{ g}^{-1} \) and a range near 23 \( \mu \text{m} \) in \( \text{H}_2\text{O} \) ice. In an ice, MeV protons cause numerous excitations and ionizations and produce many secondary electrons, which cause additional nearby ionizations. See Moore [15] and references therein for a more detailed discussion of cosmic-ray interactions with solids. Although the flux of low energy (\( \sim \text{MeV} \)) galactic cosmic-ray protons cannot be directly measured, it is estimated from observations of \( \text{H}_3^+ \) absorption and \( \text{H}^{13}\text{CO}^+ \) emission lines, combined with models of the temperature and density structure of the sources. The average cosmic-ray ionization rate is \( 2.6 \pm 1.8 \times 10^{-17} \text{ s}^{-1} \) with variations of order 50% on a scale of \( \approx 10,000 \) light years [16]. The inferred flux of low energy MeV protons is calculated from the ionization rate using an appropriate ionization cross-section. In the diffuse IS medium, the estimated flux range is from about 1 to 10 \( \text{cm}^{-2} \text{ s}^{-1} \). A flux of 1 MeV protons of 10 \( \text{cm}^{-2} \text{ s}^{-1} \) (1 \( \times 10^7 \) eV cm\(^{-2}\) s\(^{-1}\)) is used by Strazzulla and Johnson [17] for calculations of energy deposited in materials exposed to galactic cosmic-ray environments.

UV photons are also present in space environments, and those with wavelengths below \( \sim 200 \) nm cause ice photochemistry. Interstellar UV photons (mostly Lyman-\( \alpha \)) are produced primarily by hot O and B stars, and the estimated number density of these sources results in a calculated intensity of \( 9.6 \times 10^8 \text{ eV cm}^{-2} \text{ s}^{-1} \) between 91 and 180 nm. UV photons are absorbed in a single excitation or ionization event. In \( \text{H}_2\text{O} \) ice, with \( \rho = 1 \text{ g cm}^{-3} \), the UV transmission drops to 37% in 0.15 \( \mu \text{m} \) assuming a UV cross-section of \( 2 \times 10^{-18} \text{ cm}^2 \) from Okabe [18].

1.2. Effects of radiation environments

1.2.1. Interstellar ices

IS icy grain mantles (\( \sim 0.02 \mu \text{m} \) thick) are subjected to both Lyman-\( \alpha \) UV photons and cosmic rays, but since icy grains can exist within molecular clouds of varying gas and dust densities, the UV contribution varies. Models predict that in cold dark clouds (10–20 K) dust shields the interior ices from IS UV photons. However, cosmic ray induced fluorescence of molecular hydrogen produces UV inside the cloud. The energy dose from this internal UV source is thought to be similar in value to the energy contribution from the incoming cosmic rays. In cold diffuse clouds (\( \sim 100 \) K), there is less UV attenuation and the dose due to the IS radiation field is orders of magnitudes greater than the dose from cosmic rays. Total doses for ices in these different regions for different time scales are summarized in Table 1.

1.2.2. Comets

Radiation modification of ices in comets can occur while they are stored in the Kuiper Belt or the Oort Cloud, where the radiation environment is dominated by cosmic-ray protons. It is estimated that the total dose accumulated in the upper 10 cm of cometary ice is larger than 150 eV mol\(^{-1}\) when the veneer of heavily UV-processed ice is included. However, deeper layers accumulate smaller ion doses and no UV processing, so the greatest modification takes place in the surface material of comets. Table 1 also summarizes current ideas of cosmic-ray doses in comets.

1.2.3. Satellites

Radiation modification of ices on outer solar system objects in some cases is dominated by the local magnetospheric radiation environment instead of galactic cosmic rays. For example, the icy Galilean satellites experience an average magnetospheric Jovian energy flux of \( 4 \times 10^{13} \text{ eV cm}^{-2} \text{ s}^{-1} \) from \( \text{e}^- , \text{p}^+ , \text{O}^n^+ , \text{and S}^n^+ , \) which is greater than the energy flux from galactic cosmic rays [22]. UV photochemistry plays a diminished role in these ices, since the flux from solar photons with energies greater than 6 eV is only 1% of the magnetospheric flux. Moreover, the contribution of UV products to the total abundance of observed molecules on these icy surfaces is likely to be insignificant because IR observations sample the top \( \sim 50 \mu \text{m} \) of the surface, whereas, UV photons only process the top 0.2 \( \mu \text{m} \). Any chemical model of the abundance of radiation products on a dynamic icy surface needs to include the
Table 1
Predicted UV photon (E $\approx$ 10 eV) and 1 MeV proton fluxes in diffuse and dense IS cloud regions are used to calculate absorbed energy in 0.02 $\mu$m ice coated-grains and in the icy layers of a comet nucleus$^a$

<table>
<thead>
<tr>
<th>Resident time of ices in region (years)</th>
<th>UV</th>
<th>Protons</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flux 10 eV photon (eV cm$^{-2}$s$^{-1}$)</td>
<td>Energy absorbed (eV cm$^{-2}$s$^{-1}$)</td>
</tr>
<tr>
<td>IS ices in cold diffuse clouds</td>
<td>$9.6 \times 10^8$</td>
<td>$5 \times 10^8$ (0.02 $\mu$m mantle)</td>
</tr>
<tr>
<td>10$^5$</td>
<td>$10^7$</td>
<td>$1 \times 10^6$</td>
</tr>
<tr>
<td>10$^7$</td>
<td>$1.4 \times 10^7$</td>
<td>$1.7 \times 10^7$ (0.02 $\mu$m mantle)</td>
</tr>
<tr>
<td>10$^9$</td>
<td>$10^9$</td>
<td>$&lt; 1$</td>
</tr>
<tr>
<td>IS ices in cold dense clouds</td>
<td>$1.4 \times 10^4$</td>
<td>$1.7 \times 10^4$ (0.02 $\mu$m mantle)</td>
</tr>
<tr>
<td>10$^5$</td>
<td>$1.7 \times 10^3$</td>
<td>$&lt; 1$</td>
</tr>
<tr>
<td>10$^7$</td>
<td>$10^3$</td>
<td>$10^3$</td>
</tr>
<tr>
<td>10$^9$</td>
<td>$10^9$</td>
<td>$&lt; 1$</td>
</tr>
<tr>
<td>Cometary ices in Oort cloud</td>
<td>$9.6 \times 10^8$</td>
<td>$9.6 \times 10^8$</td>
</tr>
<tr>
<td>4.6 $\times 10^7$</td>
<td>$10^9$</td>
<td>$10^9$</td>
</tr>
<tr>
<td>Typical laboratory experiment</td>
<td>$8.6 \times 10^{14}$</td>
<td>$8.6 \times 10^{14}$ (0.26 $\mu$m)</td>
</tr>
<tr>
<td>4.6 $\times 10^{-4}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The absorbed energy dose from 1 MeV cosmic-ray protons is calculated assuming a 300 MeV cm$^2$ g$^{-1}$ stopping power and assuming that protons deposit energy in both the entrance and exit ice layer of an ice coated grain. The ice density is assumed to be 1 g cm$^{-3}$. Calculations for the IS environments are based on Jenniskens et al [19], Strazzulla and Johnson [17], Wdowiak [20] and Duley and Williams [21]. An energy dependent flux, $\phi(E)$, is used to calculate the resulting energy dose at different depths in a comet nucleus (for details see Strazzulla and Johnson [17] and references therein). Typical UV and proton fluxes and doses measured in our laboratory are shown in the last line for comparison.
effects of removal processes (e.g. sputtering and thermal sublimation) and burial mechanisms (e.g. impact gardening). Impact gardening on solid solar system surfaces can mix surface material on a short time scale to depths greater than the penetration depth of bombarding ions.

1.3. Inventory of condensed-phase molecules

A typical inventory of molecules in IS ice mantles is represented by the spectrum recorded by ISO of a source called NGC 7538 IRS9 [23]. One surprising observation about this spectrum is that unprocessed laboratory ice mixtures can explain most of the features. The only exceptions are the so-called ‘XCN’ feature at 4.62 μm and the unidentified 6.8 μm band, which may be indicators of energetic processing [1–5].

H$_2$O is the dominant condensed-phase molecule in the NGC 7538 IRS9 spectrum and in other cosmic ices. A clue to the ice temperature comes from the spectral identification of the ice phase. Evidence for both amorphous and crystalline phase H$_2$O in different IS sources is discussed in Section 3. Observations of most icy solar system surfaces, including the rings of Saturn, reveal that H$_2$O is crystalline [24]. In comet Hale–Bopp, evidence for amorphous phase icy grains of H$_2$O was detected in near-IR spectra based on the absence of the 1.65 μm absorption feature [25].

Table 2 lists the molecules observed in IS ices, cometary ices, and ices on satellites and Pluto. Mid-IR laboratory spectra of the majority of the molecules in Table 2 are known in the condensed-phase, as are the spectra of each mixed with solid H$_2$O. In general, less information is available for ices containing sulfur, for molecules such as HCN and for N$_2$.

2. Experimental

Details concerning our laboratory setup and techniques are already in print [29,30,32]. IR spectra of thin ice films are measured before and after ion bombardment or UV photolysis to identify radiation products and to determine changes in spectral band strength with dose or with thermal processing. Fig. 1 is a schematic of our experimental arrangement. Ices were formed by slow condensation from appropriate vapor-phase mixtures at room temperature onto a cold (16 K) polished aluminum mirror (area 5 cm$^2$) mounted on the tail of a cryostat. A vacuum of about 10$^{-8}$ torr was maintained within the cryostat. A heater provided the capability of maintaining samples at temperatures between 16 and 300 K. Ice thicknesses were on the order of a few micrometers for ion irradiation experiments, and were measured using a laser interference system assuming an index of refraction of 1.3 for H$_2$O-dominated ices [32]. Deposition rates were roughly 1–5 μm h$^{-1}$.

Ice thicknesses for UV-photolysis experiments were as small as 0.1 μm. An FTIR spectrometer was used to record mid-IR (4000–400 cm$^{-1}$) spectra with a resolution of 4 or 1 cm$^{-1}$, depending on the nature of the experiment. Since the IR beam passed through the ice before and after reflection at the ice-mirror interface, this IR measurement is called transmission-reflection-transmission (TRT).

Table 2

<table>
<thead>
<tr>
<th>Sources</th>
<th>Detected condensed-phase molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>IS molecular cloud, NGC 7538 IRS9</td>
<td>H$_2$O, CO$_2$, CO, NH$_3$, CH$_3$OH, CH$_4$, OCN$^-$, HCOO$^-$</td>
</tr>
<tr>
<td>Comet Hale–Bopp</td>
<td>H$_2$O, CO, CO$_2$, CH$_3$OH, H$_2$S, H$_2$CO, CH$_3$$_2$, NH$_3$, C$_2$H$_5$</td>
</tr>
<tr>
<td></td>
<td>OCS, CS$_2$, SO$_2$, SO, HNCO, HCOOH, HCOOCH$_3$, HCN, CH$_3$CN, H$_2$CS, H$_2$CN, NH$_2$CHO, S$_2$, HNC</td>
</tr>
<tr>
<td>Ices on satellites and Pluto</td>
<td>H$_2$O, H$_2$O$_2$, CO$_2$, CO, CH$_4$, O$_2$, O$_3$, N$_2$, NH$_3$, SO$_2$, SO$_3$, H$_2$S, NH$_3$</td>
</tr>
</tbody>
</table>

$^a$ Ices on comets are inferred from the identification of parent molecules in emission spectra of the coma (with the exception of H$_2$O ice detected in comet Hale–Bopp [24]).

$^b$ See reviews; Tielens and Whittet [23] and Gibb et al [26].

$^c$ Icy material from the comet nucleus sublimes releasing these gas-phase molecules into the coma. For abundances see review by Crovisier [27].

$^d$ See reviews by Cruikshank et al [28] and Schmitt et al [14].
Far-IR measurements (500–1000 cm⁻¹) reported in this paper were recorded in conventional transmission by repositioning the spectrometer so that the IR beam passed through polypropylene windows, located at W1 and W2, and through the ice formed on a silicon substrate. Temperature-sensitive bands in the p-type silicon were removed from each spectrum by ratioing with a background spectrum at the same temperature. The silicon substrate provided a better thermal connection to the cryostat than a polyethylene substrate used in measurements by Smith et al. [33], Hudgins et al. [32], or Schmitt et al. [14]. Transmission measurements avoided possible errors from added signals due to front surface reflections and internal reflections that appear in the TRT technique.

To process a sample by ion bombardment, the ice was rotated to face a beam of 0.8 MeV protons generated by a Van de Graaff accelerator. Typically, a beam current of 0.1 μA and incident fluences of 10¹³–10¹⁵ protons cm⁻² was used. Incident fluences were converted into eV mol⁻¹ by way of the stopping power of the energetic proton, which in turn required knowing the ice density. However, since the density was largely unknown, we assumed a value of 1 g cm⁻³ for H₂O-dominated ices. For pure water, a fluence of 1 × 10¹⁵ protons cm⁻² corresponded to 11.4 eV mol⁻¹. For mixed ices, weighted averages of the stopping powers for each initial component were used. Details about these techniques and calculations are given in Hudson and Moore [30] and Moore and Hudson [10]. Since the incident 0.8 MeV protons had a range of 16 μm [34], they penetrated each ice sample and came to rest in the aluminum mirror. The bombarding proton was not implanted into the ice. Ionizations and excitations caused by the incident radiation initiated the radiation chemistry pathways.

A microwave-discharge hydrogen flow lamp that produced primarily Lyman-α photons (λ = 121.6 nm, E = 10.2 eV; see e.g. Warneck [35]) was interfaced with the vacuum chamber as shown in Fig. 1. The lamp discharge was separated from the vacuum system by a UV-transmitting lithium fluoride window. The lamp’s flux at the ice was calculated to be 8.6 × 10¹³ photons cm⁻² s⁻¹ (for λ < 185 nm) by measuring the O₂ → O₃ conversion rate during the photolysis of pure O₂ ice at 18 K. Details of these calculations are given by Gerakines et al. [31]. To ensure UV processing throughout the bulk of the ice, samples were less than 0.5 μm thick. Thicker processed samples could be formed by simultaneously depositing and photolyzing.

3. Results and discussion

3.1. Far-IR spectra of water ice

H₂O ice and H₂O-dominated icy mixtures are important constituents of IS grain mantles, of comets, and many of the outer planetary satellites. The far-IR spectrum of H₂O is of interest to astronomers since distinct lattice vibrations in this region reveal the ice phase. For the first time, a continuous view of IR sources from 2.5 to near 200 μm was possible with the wide spectral coverage provided by ISO. Although the spectra of cold molecular clouds show many far-IR signatures, they often have blended features of various
silicate grain mineralogies with (in some cases) water ice. Dartois et al. [36] reported evidence for the 44-μm band of crystalline phase H₂O ice in absorption toward IRAS 19110+1045 and in another source, IRAS 18316-0602, identified amorphous phase H₂O. Waters [37] detected both the 44 μm and 62 μm bands of ~65 K crystalline ice toward the source HD 161796.

Identifying water-ice’s phase in a particular line of sight may help determine its temperature history in an IS environment. H₂O is amorphous, if condensed at temperatures below ~100 K, crystalline H₂O forms at higher temperatures. Amorphous H₂O irreversibly crystallizes when warmed. There is a dramatic difference between the far-IR spectrum of amorphous H₂O, with a featureless broad absorption peak near 45 μm, and crystalline H₂O with two peaks (the so-called 44 and 62 μm bands). Although a good observational clue, the ice phase may not be sufficient to determine the temperature or thermal history of the ice since crystalline ice can be amorphized with sufficient energetic processing (ions and UV photons) at temperatures below ~50 K. This effect cannot be excluded until the dose of energetic processing is better known in IS regions.

The far-IR spectrum of H₂O ice also shows changes in peak position and intensity with temperature. The peak position of amorphous H₂O shifts to smaller wavenumbers as the temperature increases. After the irreversible crystallization of H₂O at 160 K, the peak near 222 cm⁻¹ (45 μm) shifts to larger wavenumbers (reversibly) with cooling. Fitting an IS H₂O ice band ultimately depends on appropriate laboratory spectra and optical constants. Far-IR band positions and band profiles for H₂O between ~14–160 K have been examined by Moore and Hudson [38], Smith et al. [33], and Schmitt et al. [28]; absorbance values were published by Schmitt et al. [14], and Coustenis et al. [39], and optical constants by Hudgins et al. [32].

Here we report our best illustration of the combined effects of temperature and thermal history on the bands of water ice. Fig. 2a shows the spectrum of water deposited at 14 K and warmed to 30, 80, 100, 120, 140 and 160 K. The spectrum at 14 K had a maximum absorbance of 0.37 at 218 cm⁻¹. Using the optical constants of Hudgins et al. [32] and our known deposition time, this corresponds to a thickness of 7.2 μm and a deposition rate of 11 μm h⁻¹. Fig. 2b shows the spectrum of water deposited at 160 K and cooled to 140, 120, 100, 80, 30 and 14 K. The spectrum at 160 K had a maximum absorbance of 0.75 at 225 cm⁻¹. Using our known deposition time and the optical constants of Bertie et al. [40], or comparing with the measurements of Smith et al. [33], a thickness of ~5 μm was estimated for the ice, corresponding to a deposition rate of ~5 μm h⁻¹. A third set of data, shown in Fig. 2c, was obtained when water was deposited at 140, 120, 100, 80 and 30 K. The complete set of data in Fig. 2 is available at: www-691.gsfc.nasa.gov/cosmic_ices. Fig. 3a plots the reversible changes we measured in the 44 and 62 μm peak positions of crystalline water (deposited at 160 K) with temperature. Also shown is the data of Smith et al. [33] and Schmitt et al. [14]. This plot compares three very similar data sets recorded in three different laboratories. Overall, the plot shows comparable results were obtained and differences are within the spectral resolution (4 cm⁻¹ for Smith et al. [33] and 2 cm⁻¹ for Schmitt et al. [14]). In Fig. 3b we have included the 44/62-μm peak height ratio of crystalline water at different temperatures. These laboratory results can be fitted to observations in order to determine ice temperature (in the absence of any processing effects) and to search for minor species whose spectral signatures may be present in the sub-structure of the 44 or 62 μm H₂O bands.

3.2. First laboratory comparison of ion irradiation with UV photolysis-carbonic acid

When considering ices in different space environments and the variety of molecules present, it is obvious that a complex array of radiation- and photo-chemistries may occur. An unsolved problem in laboratory astrophysics is the quantitative comparison between ion bombardment and UV photolysis of cosmic-type ices. In the absence of relevant experiments, it is usually assumed that UV photolysis and ion irradiation produce identical results. Therefore, studies to determine whether the action of photons and energetic particles form the same major products, with the same efficiency, are warranted.
We have completed the first set of experiments to compare the effects of proton irradiation and UV photolysis on ices [31]. The formation of H$_2$CO$_3$ by proton bombardment of H$_2$O + CO$_2$ ice mixtures has been shown in previous experiments [41]. Now, H$_2$CO$_3$ has also been identified in photolyzed H$_2$O + CO$_2$ ices [31]. Crystalline-phase H$_2$CO$_3$ is less volatile than H$_2$O, and its IR signature is measured after slow warming of the ice to near 200 K. Fig. 4 shows the spectrum of H$_2$O + CO$_2$ and the carbonic acid formed after proton bombardment and after photolysis. Since the formation of H$_2$CO$_3$ by UV photolysis is limited to the penetration depth of the photons, its IR identification was not secured until a careful set of experiments were completed in which ice samples were created by simultaneous condensation and UV photolysis of the H$_2$O + CO$_2$ gas$^2$.

$^2$Simultaneous condensation and UV photolysis is a technique used to increase the amount of UV exposure in the bulk of the ice. While gas-phase reactions during condensation could occur, observed photolysis products in the ‘condense and then photolyze’ case are identical to those in the ‘simultaneous condensation and photolysis’ case.
Determination of the intrinsic band strength of H$_2$CO$_3$ ($A$(H$_2$CO$_3$)) is discussed in Section 3.3. Using $A$(H$_2$CO$_3$), the formation rates of H$_2$CO$_3$ as a function of dose, shown in Fig. 5, seem to be independent of the type of energetic processing. CO, the other major product, is also formed at a rate independent of the processing type. $A$(H$_2$CO$_3$) and the change in the H$_2$CO$_3$ band area as a function of time due to sublimation lead to a vapor pressure at 250 K of $1.5 \times 10^{-7}$ torr for crystalline H$_2$CO$_3$. The corresponding vapor pressure for crystalline H$_2$O at 250 K is 1 torr.

Recent experiments with H$_2$O + CH$_3$OH, H$_2$O + CH$_3$OH + CO$_2$, and H$_2$O + CH$_4$ ices also show the same rate of formation of major products independent of the two types of processing (spectra not shown). There is one difference in that the formate ion, HCOO$^-$, seen in ion bombarded H$_2$O + CH$_3$OH and H$_2$O + CH$_3$OH + CO$_2$, is not detected when the mixture is photolyzed. This is discussed further in the next section. It is possible that other differences will be seen e.g. for molecules with high dissociation energies such as CO (11.1 eV) and N$_2$ (9.8 eV), since MeV protons may have a much larger impact on these molecules than 10.2 eV photons and allow them to more effectively take part in the chemical reactions. Relevant experiments are currently in progress.

### 3.3. Band strengths of unstable molecules and radicals

The intrinsic band strength of a condensed phase molecule can be used to determine its concentration, or rate of formation in irradiated ices and to assess its role in a reaction pathway. There are a few reliable measurements of absolute band strengths ($A$ cm mol$^{-1}$, intrinsic absorbances) of condensed-phase molecules, but too often the information is limited by temperature, wavelength, or matrix. Standard measurement methods involve condensing an ice of measured thickness whose composition and density are (poorly) known. These parameters can be used to determine the column density ($N$) of an individual molecular component in an ice. Values of the band area and $N$, lead to an $A$-value:

$$A(v_1,v_2) = \frac{1}{N} \int_{v_1}^{v_2} \ln(I_0/I)dv$$

An alternate procedure, applied when the intrinsic band strength is unknown, has been to use the gas-phase value, but this can lead to errors because band strengths can depend on the molecular environment. For example, the 1300 cm$^{-1}$ band of CH$_4$ has $A_{\text{gas}} = 5.23 \times 10^{-18}$ cm mol$^{-1}$ [42], $A_{\text{solid}} = 3.8 \times 10^{-18}$ cm mol$^{-1}$ for pure CH$_4$. 

![Fig. 3](image-url)
ice and $A_{\text{solid}} = 4.7 \times 10^{-18}$ cm mol$^{-1}$ for CH$_4$ in an H$_2$O matrix [32]. The affect of the environment is often band dependent as well (e.g. stretch, bend, or liberation), e.g. $A_{\text{solid}}/A_{\text{gas}} = 0.62$ for the $v_3$ band of C$_2$H$_2$, but this ratio is 5.5 for the $v_3$ band [43].

Properly determined laboratory values of $A$ for condensed-phase molecules in matrices dominated by H$_2$O are relevant for many IS and planetary ice observations. Standard methods, however, cannot be used to measure the $A$-values of unstable species formed in some irradiation experiments. Instead the $A$-value of some unstable species can be determined, if they photodissociate into a product, P, whose intrinsic band strength is known. The $A$-value of the unstable species is determined by observing the balance between its disappearance and the formation of P. Two examples are discussed — H$_2$CO$_3$, which is unstable at STP, and the radical HCO, which is stable in H$_2$O matrices to $\sim 100$ K on laboratory time scales.

![Fig. 4. Mid-IR spectra of H$_2$O + CO$_2$ before processing (a) is compared with (b) H$_2$CO$_3$ at 250 K formed after warming proton irradiated H$_2$O + CO$_2$ at 20 K and (c) H$_2$CO$_3$ at 250 K formed after warming UV processed H$_2$O + CO$_2$ at 20 K.](image)

Since both H$_2$O and CO$_2$ have been detected in different astrophysical environments (IS, comets, icy Galilean satellites, Triton and Mars), it is possible that H$_2$CO$_3$ may form as a radiation product. Predicting the abundance of H$_2$CO$_3$ in a cosmic ice is based on its calculated formation rate in laboratory ices, a rate that requires knowing the intrinsic band strength. We determined $A$(H$_2$CO$_3$) by measuring its IR spectrum during photodissociation into CO$_2$, a product with a known band strength. When pure H$_2$CO$_3$ is photolyzed, H$_2$CO$_3$ + hv $\rightarrow$ H$_2$O + CO$_2$, and since the intrinsic IR band strength of CO$_2$ has already been determined (pure CO [44]; pure CO$_2$ [45]; H$_2$O-dominated mixtures with CO and CO$_2$ [46]), the column density of CO$_2$ can be calculated. The number of CO$_2$ molecules produced equals the number of H$_2$CO$_3$ molecules destroyed. CO is also taken into account once a significant amount is created from the CO$_2$. Fig. 6b shows three bands of H$_2$CO$_3$ at 20 K before and after photolysis. From the decrease in the H$_2$CO$_3$ bands, and the increase in the CO$_2$ band area shown in Fig. 6a, $A$(1485 cm$^{-1}$, H$_2$CO$_3$) $\sim 6 \times 10^{-17}$ cm mol$^{-1}$ is calculated [31].

The second example, is the 1853 cm$^{-1}$ band of the formyl free radical (HCO) identified in photolyzed H$_2$O + CO and H$_2$O + H$_2$CO ices [47]. We
Fig. 6. During UV photolysis of pure H2CO3 at 20 K, H2CO3 → H2O + CO2. Decreases in the band areas of H2CO3 occur as CO2 is formed.

observe a similar feature in proton-bombarded ices. HCO formation is the first step in the production of H2CO, CH3OH and other organic molecules in photolyzed or ion-bombarded ices containing H2O, and in grain-surface reactions, by the addition of hydrogen atoms. Predicting the abundance of HCO in cosmic ices is based on its formation rate in our laboratory ices, a value requiring $A$(H2CO3). To determine $A$(HCO), we exposed an irradiated H2O + H2CO ice, showing the HCO band, to unfiltered visible light from a 60 W tungsten lamp. Fig. 7b shows the decrease in absorbance of the HCO band over a few hours along with an increase in CO, Fig. 7a. These observations show that photobleaching causes HCO → H + CO; the number of CO formed equals the number of HCO destroyed. From the decrease in HCO, the corresponding increase in the CO band, at 2137 cm$^{-1}$, and CO’s known band strength (1.7 × 10$^{-17}$ cm mol$^{-1}$ [48]), we have calculated a value of $A$(HCO) ≈ 2.1 × 10$^{-17}$ cm mol$^{-1}$. This value can be used to determine an upper limit for the abundance of the HCO radical, which has not been detected in ISO observations.

3.4. Identification of new species after energetic processing

IR spectroscopy is the key to identifying new species formed after energetic processing of ices. Spectroscopy is also used to track the products retained in the ice during warming and to monitor the formation of new bands due to any reactions (e.g. radical, acid-base) that occur. Some new species are more volatile than the original parent molecule (e.g. CO synthesis from CO2) and some are less volatile (e.g. ethylene glycol, C2H4(OH)2, from CH3OH). The motivation for our choice of experiments comes from astrophysical problems.

We have examined many icy mixtures using different concentrations of hydrocarbons to determine if yields of C2H6 from CH4 due to dimerization were similar to yields of C2H6 from C2H2 due to H-addition reactions [11,10]. These experiments were motivated by the detection of C2H6, CH4 [9], and C2H2 [49] in Comets Hyakutake and Hale–Bopp [50]; the surprisingly high abundance of C2H6 relative to CH4 suggested solid-phase UV or radiation processing of cometary ices prior to accretion [9].

In a different set of experiments, we showed that IR spectroscopy of radiation-processed icy mixtures of H2O and CO formed HCO, H2CO,
HCOOH, and CH3OH [51]. We used isotopic labeling to study an H-atom addition mechanism for the low-temperature solid-phase reaction sequence from CO to CH3OH. In the next phase of experiments, we measured the formation rate of CH3OH, which is relevant to IS ices since an efficient pathway for its formation has not been demonstrated. Our experiments were the first to quantify a relatively high conversion rate of CO→CH3OH in ion bombarded H2O+CO. The identification of products in irradiated CH3OH and H2O+CH3OH ices, relevant to both IS and cometary ices, was discussed by Hudson and Moore [52]. Table 3 lists products we have identified in several simple ice mixtures after irradiation and photolysis.

Many of the mid-IR identifications discussed in this paper required appropriate reference spectra. Since no published library of spectra of relevant molecules in polar and/or non-polar ice matrices is available, we have created a spectral reference set of molecules in H2O-dominated ices at 15–20 K measured from 4000 cm⁻¹ (2.5 μm) to 400 cm⁻¹ (25 μm) at 4 cm⁻¹ resolution. It includes the following: carbon oxides CO, CO2; alkanes CH4, C2H6, C3H8, C4H10; alkenes C2H4, C3H6; alkynes C2H2, C3H4, C4H6; dienes C2H4, C3H6; ethers CH3OH, CH2=CH2; aldehydes CH3CHO, CH3COH; ketones (CH3)2CO, (CH3)2CH; acids HCOOH, CH3COOH; ethers (CH3)2O, C6H5O; esters HCOOCH3; amines NH3, CH3NH2; assorted N2O, HCN, H2O2, OCS. Spectral files are available at: www-691.gsfc.nasa.gov/cosmic_ices.

Confirming the identity of radiation products can be done in separate experiments using isotopically-labeled molecular components. A good example of this is our recent identification of the formate ion, HCOO⁻, in irradiated H2O+CH3OH ices. This identification was made by matching both the position and relative intensity of a feature near 1589 cm⁻¹ and bands at 1384 and 1353 cm⁻¹ with similar features in irradiated

Table 3
A comparison of products identified after proton irradiation or UV photolysis for several binary icy mixtures relevant to IS molecular clouds

<table>
<thead>
<tr>
<th>Initial mixture</th>
<th>Products identified after proton irradiation or UV photolysis a</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2O+CO</td>
<td>CO2, HCO, H2CO, CH4(?) CH3OH, HCOOH, H2CO3, HCOO⁻</td>
</tr>
<tr>
<td>H2O+CO2</td>
<td>H2CO3, CO2, CO3, O3, H2O2</td>
</tr>
<tr>
<td>H2O+CH3OH</td>
<td>CO3, CO, HCO, H2CO, CH4, HCOO⁻, C2H5OH(OH)</td>
</tr>
<tr>
<td>H2O+CH4</td>
<td>CO2, CO, C2H4, C2H6, CH3OH, C3H5OH, H2CO, CH3CHO, C2H4</td>
</tr>
</tbody>
</table>

a Products in bold-face are detected only in ion-irradiated ices.
H$_2$O + CO. The H$_2$O + CO features were identified as HCOO$^-$ through separate radiation experiments with H$_2$O + $^{13}$CO and H$_2$O + C$^{18}$O to form H$^{13}$COO$^-$ and HC$^{18}$OO$^-$, respectively. Fig. 8 compares the CH in-plane bending mode and CO stretching mode of the formate ion in the 1425 to 1300 cm$^{-1}$ region. Spectra (b) and (c) show the similarity between the features in irradiated H$_2$O + CH$_3$OH and H$_2$O + CO at $\sim$ 20 K. Features for H$_2$O + CO are at 1381 and 1354 cm$^{-1}$. Spectrum (d) shows that the features in irradiated H$_2$O + $^{13}$CO at 1381 and 1331 cm$^{-1}$ are shifted 0 and 23 cm$^{-1}$, respectively, from the $^{12}$CO position (expected shifts are 0 and 23 cm$^{-1}$ [53]). Spectrum (e) shows that the features in irradiated H$_2$O + C$^{18}$O at 1381 and 1334 cm$^{-1}$ are shifted 0 and 20 cm$^{-1}$, respectively, from C$^{18}$O (expected shifts are 2 and 20 cm$^{-1}$ [53]).

Fig. 8(a) shows the ISO spectrum of NGC 7538 IRS 9 in the 7.5 $\mu$m region. A pair of features near 1384 and 1353 cm$^{-1}$ appear similar to those in our irradiated H$_2$O + CH$_3$OH and H$_2$O + CO ices. We suggest [52] that HCOO$^-$ may be present in this and other IS ices, and may be a marker of CO or CH$_3$OH radiation processing in similar protostellar regions. Another identification of HCOO$^-$ in ices has involved acid-base reactions during warming H$_2$O + HCOOH + NH$_3$ [54] and H$_2$O + HCOOH + N$_2$H$_4$ [55].

3.5. Laboratory studies of H$_2$O$_2$ formation on Europa

Our study of H$_2$O$_2$ formation in irradiated 80 K ice was motivated by observations of this molecule on Europa [12]. An outline of our experiments is presented here as an example of how a combination of IR measurements, encompassing many of the techniques we have discussed, can be used to investigate such a problem. Hydrogen peroxide was identified on Europa, one of Jupiter’s icy satellites, based on a 3.5 $\mu$m absorption feature in spectra obtained by the Galileo’s near infrared mapping spectrometer[12]. Carlson et al. [12] matched the position and width of the observed IR feature with a laboratory reflectance spectrum of H$_2$O + H$_2$O$_2$ ice, where the H$_2$O$_2$ concentration was 0.13% by number relative to H$_2$O. The dominant ice on Europa H$_2$O is at a temperature near 100 K, and receives a constant flux of energetic ions from the Jovian magnetosphere. H$_2$O$_2$ was suggested by Carlson et al. [12]
since it is a radiation product consistent with early X- and γ-ray experiments on H₂O. We examined the conditions of H₂O₂ formation and detection at 3.5 μm in irradiated H₂O maintained at 80 K.

Simulation of Europa’s icy surface and radiation environment in the laboratory involved H₂O ice films at 80–100 K, irradiated with MeV protons simulating different exposure times. We measured the IR reference spectrum of H₂O + H₂O₂ (100:1.4) at 16 K and determined A(H₂O₂) = 2.7 × 10⁻¹⁷ cm mol⁻¹ for the 3.5 μm band [13]. Fig. 9a shows the spectrum of H₂O in the 3.5 μm region before and after irradiation at 16 K. H₂O₂ was detected on the wing of the H₂O band at 3.49 μm. The experiment was repeated at 80 K, but no H₂O₂ was detected after irradiation (Fig. 9b).

Radiolysis of mixtures of H₂O with O₂ and with CO₂ did produce H₂O₂ at 80 K (Fig. 9c). CO₂ and O₂ are relevant to Europa since CO₂ has been detected on the surface of Europa and O₂ is found in its tenuous atmosphere. Formation mechanisms were suggested for H₂O₂ and these were supported by a variety of isotope studies (Moore and Hudson [13]). It is possible that destruction mechanisms for H₂O₂ in pure H₂O are more efficient at 80 K. The addition of O₂ to the ice increases the amount of H₂O₂ detected since H atom addition to O₂ can form H₂O₂ with little difficulty. The addition of CO₂ to the ice raises the abundance of H₂O₂, since CO₂ is an effective electron scavenger. Spectra of the H₂O₂ band formed in 80 K irradiated H₂O containing O₂ and CO₂ are shown in Fig. 9c and are compared with the observed Europan spectrum [12].

4. Summary

IR spectroscopy plays a major role in identifying new products in astrophysically relevant icy mixtures after UV photolysis and/or ion irradiation. In addition, spectroscopy may be used to monitor the stability of products at different temperatures. Identification is often based on a combination of techniques; matching an unknown spectral feature with appropriate reference spectra and performing relevant isotope experiments. We have placed TRT reference spectra of a variety of molecules in H₂O-dominated ice mixtures at 20 K at: http://www-691.gsfc.nasa.gov/cosmic_ices.

An important feature of recorded spectra is that the integrated absorbance value for IR bands of condensed-phase molecules, along with information about thickness, composition and ice density, can be used to calculate an intrinsic band strength, A. A-values are required to calculate the rate of formation and destruction of molecules during processing. Formation rates in UV-photolized and ion-processed ices can be compared to determine if one form of processing is more
effective than the other. Formation and destruction rates are also used to predict abundances in similarly processed cosmic ices.

Many IR studies have focused on H2O, the dominant molecule in most cosmic environments. Far-IR spectroscopy can be used to identify the phase of H2O ice. Since the 44 and 62 \( \mu \)m bands of crystalline H2O shift position with temperature, the observation of their band location (or the ratio of their peak intensities) can be used as a thermometer for astronomical ices. Our laboratory far-IR H2O spectra (available at: http://www-691.gsfc.nasa.gov/cosmic_ices) can be fitted to far-IR observations; matched band shapes can determine the H2O ice phase and band positions can be a clue to the cosmic ice temperature.

Processing in laboratory experiments is thought to be representative of processes in space in spite of limited information about appropriate UV and ion radiation doses. Although the majority of absorption features detected in IS ices can be fitted with the spectrum of unprocessed ices, features at 4.6 and 6.8 \( \mu \)m in several IS sources may be markers of UV and/or ion (cosmic ray) processing. Evidence also exists for cosmic ray and/or UV processing in comet Hyakutake and ion (magnetospheric ions) processing on Europa’s icy surface.

A quantitative comparison between ion bombardment and UV photolysis experiments for several H2O-dominated mixtures containing CO2, CH3OH, or CH4 shows that the formation rate of most major products is the same, independent of the energy source; e.g. the yield of H2CO3 and CO in UV-photolyzed and ion-bombarded H2O + CO2 is the same. However, one difference was found — the HCOO\(^-\) radical is identified in proton-irradiated ices and not in those processed by UV-photolysis. Future experiments will compare the formation rate of products in ices containing N2 and CO.

A recent example of the application of laboratory studies to astronomical observations is our work on H2O2 formation in 80 K water ices relevant to Europa. It is expected that future observations by space-based telescopes, such as SIRTF, NGST, or the IR spectrometer onboard the Saturn-bound Cassini spacecraft, may provide spectra of icy objects of higher quality than currently available. It is possible that spectroscopic evidence for the presence of complex organics may be found. A challenge will be simulating new icy environments in laboratory experiments, understanding any new identifications and possibly identifying less abundant species in both laboratory and astronomical spectra.

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