Radiation chemical alterations in solar system ices: An overview

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Abstract. Many solar system objects, such as planets, satellites, rings, and comets, are known to either be made of ices or to have icy surfaces. Because these ices are subjected to radiation processing by keV–MeV ions and UV photons, their chemical and physical properties evolve over time. We have employed a laboratory approach to investigate these radiolytic and photolytic changes. Ices, either pure or mixtures, are subjected to ionizing radiation and UV photons and then probed by IR spectroscopy. It has been found that radiolysis and photolysis destroy reactant molecules, synthesize new molecules, cause changes of phase in pure materials, and eject molecules from ices. Although our laboratory approach initially focused on product identification, it has become increasingly necessary to work toward a comprehensive understanding of ice chemistry. To this end, we describe recent radiation experiments on some of the most important solar system and interstellar ice molecules, such as H_2O, CO, CO_2, and hydrocarbons. Chemical reactions are given to account for our observations, and these reactions include such general types as acid-base, electron-transfer, radical-radical combination, and H-atom addition. Comparisons of ion and UV processing are described for pure H_2O and for two binary mixtures, $H_2O + CO_2$ and $NH_3 + CO$. Predictions of molecular evolution in complex ices, both H_2O- and N_2-dominated, are made. Applications are described for cometary organic chemistry, ion processing in interstellar ices, and the recent discovery of H_2O_2 on the surface of Europa.

1. Introduction

It has been known since the earliest days of radiation research that high-energy particles and photons cause irreversible chemical and physical changes in a variety of materials [*Spinks and Woods*, 1990]. Therefore, because solar system ices have been exposed to ionizing radiation at several stages of their evolution, they have been altered over time. Direct investigation of these changes by sampling is not yet possible, so that a combination of astronomical and laboratory spectroscopy is employed, and for many years we have been involved in this effort. In this paper we review some of our most recent work on irradiated solar system ice analogues. Although some results from other laboratories are presented, we will restrict most of our comments to work with which we have been directly involved.

Before beginning, it is appropriate to explain the expression "ice," to ask what molecules make up solar system ices, and to describe how ionizing radiation can alter ices. As used by astrochemists and astronomers, the term "ice" typically refers to a solid composed of molecules which, at 25°C and 1 bar, form a gas or a liquid. There are exceptions to this usage but they are few. When a distinction between a one-component and a multicomponent solid is needed, expressions such as "pure ice" and "mixed-molecular ice," respectively, can be employed. Table 1 lists the ice molecules identified on planets and satellites as of January 2001. Other molecules have been

reported but await independent confirmation. Cometary ice is thought to be the most primitive in the solar system, being closest to interstellar ice. To illustrate the similarities of these ices, Table 2 compares molecules detected in the coma of Comet Hale-Bopp [*Campins*, 1998] with molecules detected in interstellar ice mantles of NGC 7538 IRS 9 [*Gibb et al.*, 2000]. Table 1 shows that H_2O is by far the most commonly reported ice molecule for planets and satellites, and Table 2 shows that it is the most abundant ice in comets and the interstellar medium as well. Note that our Table 2 is not an exhaustive list of cometary and solid-phase interstellar molecules. For example, solid carbonyl sulfide (OCS) has been reported in interstellar sources [*Palumbo et al.*, 1997]. See also *Ehrenfreund and Charnley* [2000, Table 2].

Among the ionizing radiations acting on solar system ices are cosmic rays (mostly H^+ and He^+), solar wind particles, and, around selected planets, magnetospheric particles [*Johnson*, 1990]. The influence of these radiations on molecules is known in general terms, but quantitative predictions for particular cases are challenging. As a specific example of radiation chemical effects, consider the case of a ~1 MeV proton (H^+) passing through H_2O ice. A trail of thousands of ionizations and excitations will be left along the path of the H^+ as its energy is slowly degraded. Some of the ionizations will produce secondary electrons which, in turn, travel through the ice, creating separate tracks of yet more ionizations and excitations which lead to chemical changes. In this way, the direct chemical action of the incident radiation is completely overshadowed by the chemistry produced by the secondary electrons. This implies that to a first approximation, the chemical reactants produced by various ionizing radiations (X-rays, γ-rays,

Table 1. Molecules Detected as Ices on Outer Solar System Planets and Satellites[a]

Planet	Satellite	Ices (Molecules) Detected
Jupiter	Io	SO_2, SO_3, H_2S (?), H_2O (?)
	Europa	H_2O, SO_2, H_2O_2, CO_2
	Ganymede	H_2O, O_2, O_3, CO_2, SO_2
	Callisto	H_2O, CO_2, SO_2
Saturn	Mimas	H_2O (?)
	Enceladus	H_2O
	Tethys	H_2O
	Dione	H_2O, O_3
	Rhea	H_2O, O_3
	Hyperion	H_2O
	Iapetus	H_2O, H_2S(?)
	Phoebe	H_2O
	[Rings]	H_2O
Uranus	Miranda	H_2O
	Ariel	H_2O
	Umbriel	H_2O
	Titania	H_2O
	Oberon	H_2O
Neptune	Triton	N_2, CH_4, CO, CO_2, H_2O
Pluto	(itself)	N_2, CH_4, CO, H_2O, C_2H_6[b]
	Charon	H_2O, NH_3

[a]After *Cruikshank et al.* [1998], *Roush* [2001], *Moore and Hudson* [2000], and references therein.
[b]See *Nakamura et al.* [2000].

e^-, H^+, and He^+) are the same. Differences in yields are expected depending on the rate of energy deposition (stopping power) of the radiation and its effect on the chemical reaction rates, and these are observed in a variety of experiments.

A few other points about the above illustration deserve emphasis. First the incident 1 MeV proton will have a range near 20 μm, several orders of magnitude greater than that of solar UV-visible photons. This means that after accretion, solar system bodies are altered at a greater depth by radiation chemistry than by photochemistry. Second, while UV-visible photons interact with ice molecules and transfer their energy in a single encounter, 1 MeV protons will pass through an ice losing energy in multiple events. Finally, in our study of the radiation chemistry of covalently bonded molecules, it is safe to ignore displacement effects through elastic collisions, which often dominate radiation damage to metal targets. However, such

Table 2. Selected Molecular Abundances in Comet Hale-Bopp and Interstellar Ices of NGC 7538 IRS9

Molecule	Comet Hale-Bopp[a]	NGC 7538 IRS 9[b]
H_2O	=100	=100
CO	20	16
CO_2	6	22
CH_3OH	2	5
H_2CO	1	4 (tentative)
HCOOH	0.05	3 (tentative)
CH_4	~1	2
C_2H_2	~0.5[c]	...
C_2H_6	~0.5[c]	...
NH_3	0.6	13
OCN^-	0.37	1
OCS, XCS	0.7	see note[d]
SO_2	0.15	...

[a]*Crovisier* [1998].
[b]*Gibb et al.* [2000].
[c]*Campins* [1998].
[d]See also *Palumbo et al.* [1997] and *Ehrenfreund and Charnley* [2000].

collisions are important in ejecting molecules from ices during radiolysis, particularly with particle radiations of lower energy than our ~1 MeV protons. Additional information can be found in standard texts on radiation chemistry [e.g., *Swallow*, 1973; *Spinks and Woods*, 1990] and charged-particle interactions [*Johnson*, 1990].

Although the molecules in Tables 1 and 2 are relatively simple, predicting their responses to radiation in space remains difficult. First of all, there are uncertainties regarding the radiation environments. What, for example, are the doses experienced by the icy Jovian satellites, cometary ices stored in the Oort Cloud, or the ice on the rings of Saturn? What are the temperatures of such environments, and what types of radiation are most abundant? Such questions presently are answered by theoretical models, by terrestrial observations, and, in favorable cases, by spacecraft. Most workers in the field probably believe that the answers are good to "first order," while recognizing that details remain to be discovered.

Another difficulty in predicting solid-phase radiation effects concerns the dearth of fundamental data. Unlike the situation with gas-phase astrochemistry, no database of rate constants or thermodynamic data exists for solid-phase reactions. In many cases, it is not even known how such data might be measured, much less calculated from first principles. This means that research into all astronomical ices relies heavily on laboratory work to identify radiation products, measure yields, determine reaction pathways, elucidate mechanisms, evaluate identifications, and suggest new molecules for observations. Without laboratory measurements, few qualitative, and essentially no quantitative, interpretations of astronomical ice data would be possible.

2. Three Examples of Radiation Effects in Ices

Before turning to our own radiation experiments on astronomical ice analogues, we briefly describe results from several other laboratories. These examples illustrate three general effects observed in ice radiation chemistry: amorphization, the formation of room-temperature residues, and sputtering. For the first of these, it is thought that H_2O-ice exists in both crystalline and amorphous forms in the solar system, the former applying to some planetary satellites and the latter to comets. Knowledge of an ice's phase potentially can provide important information about the local astronomical environment. It is known from laboratory work that radiation can promote phase changes in solid H_2O, the change most often studied being of crystalline H_2O to amorphous H_2O. This amorphization has been reported after exposure of crystalline H_2O-ice at 10–77 K to energetic e^-, vacuum UV photons, and He^+, and has been followed both by electron diffraction and IR spectroscopy [*Heide*, 1984; *Kouchi and Kuroda*, 1990; *Baratta et al.*, 1991].

In addition to promoting phase changes in ice, ionizing radiation will, of course, make new molecular products. A small fraction of these are ejected from the ice, even at low temperatures (vide infra), but the great majority stay trapped within the bulk of the solid. In some cases, products are stable enough to remain behind as a residue at room temperature, even after most of the ice has sublimed and the volatiles have left under vacuum. Because the spectral properties of the residual material may differ from those of the original ice, it has been suggested that colors of some solar system objects are due to their radiation exposure. (For a summary see *Strazzulla*

[1998].) It has also been suggested that radiation and photochemically produced residues may have been a source of organics for the early Earth. (For a summary see *Bernstein et al.* [1999].) Thus the residual materials in laboratory radiation experiments are of high interest. Although more work is needed, for H_2O-dominated ices conversions on the order of a few percent of original material into residue appear typical [*Moore et al.*, 1983], but as concerns these residues' composition, it is only in recent years that they have faced the full range of modern analytical chemical methods. What is possible at the "state of the art" is exemplified by *Bernstein et al.* [1999] who used powerful laser-desorption techniques to analyze photochemically produced residues. They found a diverse set of residual products, including such important organics as alcohols, ethers, and quinones. Similar analytical techniques could be applied to residues generated by ionizing radiation.

A very different radiation effect is the sputtering of material from an ice during radiolysis. In the case of water at ~10 K, ejection of H_2O molecules, as well as the radiation products H_2 and O_2, takes place on bombardment with MeV ions, and has been followed with mass spectrometry [*Brown et al.*, 1978; *Reimann et al.*, 1984]. The astronomical relevance of this effect is that sputtering from ices by cosmic rays, solar wind particles, and magnetospheric radiation can both create and eject surface materials from a planetary satellite, such as the Galilean moons Europa and Ganymede, resulting in the formation of an atmosphere about the satellite, resurfacing, and the transport of material from one location to another. A more complete discussion of the sputtering process, its astrophysical relevance, and some results for H_2O-ice is given by *Johnson* [1990].

Although we have contributed to each of the above three areas, our most recent work has focused on investigations of ice radiation chemistry with mid-IR spectroscopy. The molecules selected for study have been taken largely from Tables 1 and 2, and a long-term goal is to study the radiation chemistry of all known cometary and interstellar molecules. When these types of experiments commenced some 20 years ago, it was important to show that radiation and photochemistry could produce molecules in "cosmic-ice" analogues at the appropriate solar system temperatures.

Multicomponent mixtures, assumed relevant for astronomical problems, were investigated, and new spectral bands were reported after irradiation. As the field has matured, it has become increasingly important to identify radiation products unambiguously, to determine reaction pathways, and, when possible, to unravel the underlying reaction mechanisms. It is only by knowing the conditions and pathways for specific chemical reactions that predictions can be made for individual astronomical environments. This has necessitated using a systematic laboratory approach as will be described below.

3. Experimental Methods

In a typical "cosmic-ice" radiation experiment, a sample consisting of the molecule(s) of interest is prepared by slow condensation of a room-temperature vapor onto a precooled substrate in a vacuum chamber. The substrate temperature is usually selected with the temperature of a specific astronomical environment in mind. Either during or after the ice's growth, the sample is exposed to ionizing radiation, and some property is measured.

Figure 1 shows our own experimental arrangement, details of which have been described in many earlier papers [*Hudson*
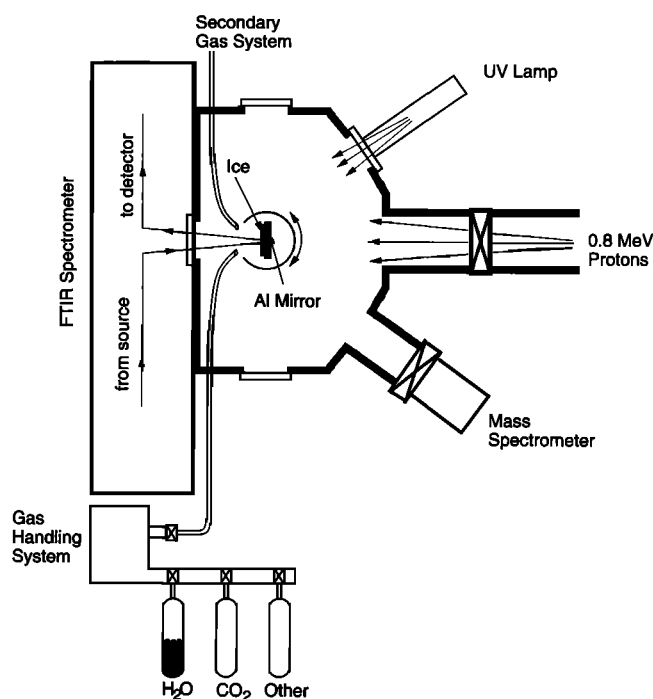

Figure 1. Schematic of experimental set-up showing FTIR spectrometer, gas handling system, protons from Van de Graaff accelerator, and ice sample. Note that the ice and substrate can be oriented to face either the spectrometer or the proton beam.

and Moore, 1995, 1999, and references therein]. The temperature of the aluminum substrate, on which ices are grown, can be varied in the 15–300 K range, all while under vacuum (10^{-8} torr or better). The ice's mid-IR spectrum (400–4000 cm^{-1}) is recorded before and after exposure to a 0.8 MeV proton beam from a Van de Graaff accelerator. IR spectra usually are recorded as 60-scan accumulations at a resolution of 4 cm^{-1}, although longer accumulations and higher resolutions are sometimes employed. Earlier papers discuss chemical reagents, ice thicknesses, sample deposition rates, and radiation dose rates. We note here that since sample thicknesses are of the order of a few micrometers, the incident protons, having a range of 16 μm [*Northcliffe and Shilling*, 1970], penetrate the ices and come to rest in the underlying metal substrate, not in the ice itself. Although the bulk of our work in recent years has involved proton irradiations, we have recently added a microwave-discharge hydrogen-flow lamp to our system. This lamp produces primarily Lyman-α photons (10.2 eV, 121.6 nm), and details are given by *Gerakines et al.* [2000] and references therein.

As the purpose of this article is to describe radiation chemical pathways, we say very little here about radiation chemical yields. These are of interest and importance and can be quantified in our experiments [*Moore and Hudson*, 2000; *Hudson and Moore*, 1999; *Moore and Hudson*, 1998]. Measuring a radiation yield requires that the strength of an IR band for a molecule be compared to the intrinsic (absolute) strength of that same IR feature, and this implies that the detection limit varies from molecule-to-molecule. As a "rule of thumb," we estimate that we can detect products present near 0.1% of the total sample. (See *Hudgins et al.* [1993] for details on measuring absolute band strengths.)
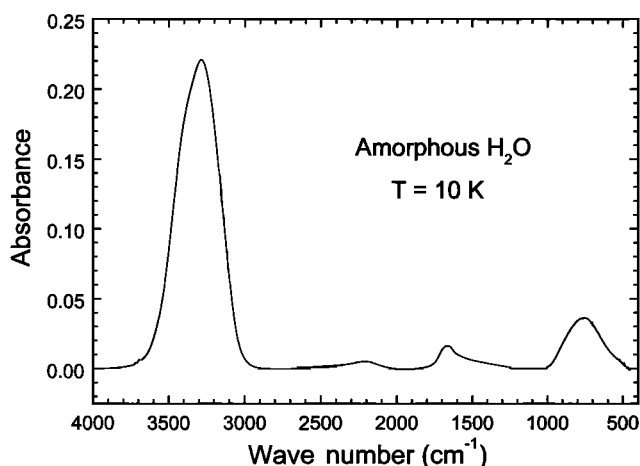
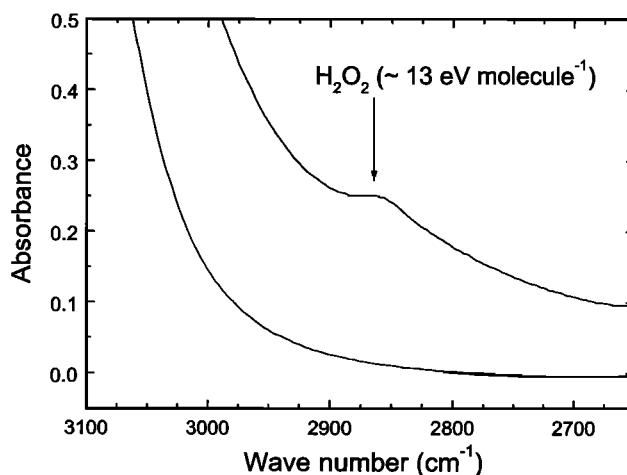**Figure 2.** Mid-IR spectrum of amorphous H_2O-ice at 10 K. See text for reference.

Figure 3. Mid-IR spectra of amorphous H_2O-ice at 16 K before (bottom line) and after (top line) irradiation to a dose of ~ 13 eV molecule^{-1}. Spectra have been offset for clarity.

4. Selected Results

Although we have investigated radiation effects in many molecules, we will discuss only a few here. We first consider frozen H_2O, then hydrocarbons, and then carbon oxides, all important solar system and interstellar ices. In each case we describe typical radiation chemical alterations, writing reactions where possible. We then comment on irradiated apolar ices and the so-called "XCN" IR feature and conclude with brief comparisons of radiation and photochemistry in three systems.

4.1. H_2O and Hydrocarbon Experiments

Water is the dominant ice molecule in many of our experiments, and in many astronomical settings, and so we start with its radiation chemistry. On encountering either a high-energy proton or an energetic secondary electron, a water molecule will be either ionized or electronically excited. These events give rise to a set of primary products that include charged species, radicals, and closed-shell molecules, summarized as follows:

$$H_2O \rightarrow H_3O^+ + e^- + H + OH + H_2 + H_2O_2.$$

In addition, secondary reactions form HO_2 and O_2 and electron attachment to OH (hydroxyl) produces OH^- (hydroxide). (See Buxton [1987] and Spinks and Woods [1990] for more detailed reviews of H_2O radiolysis.) Given these radiation products from H_2O, subsequent possible reactions with other molecules in the original ice may include H^+ transfer (acid-base reaction), e^- transfer (oxidation-reduction), and free-radical reactions, such as radical combinations, H and OH addition, disproportionation, and atom abstraction by H and OH.

Figure 2 is a spectrum of unirradiated amorphous H_2O near 10 K, taken from the Leiden database (http://www.strw.leidenuniv.nl/~schutte/database.html). The four broadbands seen will also be present in some of the other spectra we show. On proton irradiation of amorphous ice, the spectrum scarcely changes, except for a band that appears near 2860 cm^{-1}. Figure 3 shows an enlargement of the relevant region, before and after irradiation. The band near 2860 cm^{-1} is due to H_2O_2 [Lannon et al., 1971], which we have verified by comparison with frozen H_2O_2 solutions. Although H_2O_2 has been a known

radiolysis product of liquid H_2O for almost a century [Kernbaum, 1910], the spectra in Figure 3 constitute its first in situ observation in irradiated H_2O-ice [Moore and Hudson, 2000]. The accepted mode of H_2O_2 formation is combination of OH radicals:

$$OH + OH \rightarrow H_2O_2.$$

Our work on H_2O was motivated by the recent detection of a 2860 cm^{-1} feature on Europa's icy surface by Carlson et al. [1999], which they assigned to H_2O_2. Jovian magnetospheric radiation striking Europa will dissociate H_2O-ice into H and OH and the above OH-OH reaction will follow. We will return to the Europa H_2O_2 detection later in this paper.

Another example of the formation of a radical, and its subsequent reaction, is provided by CH_4, methane. Irradiated CH_4-ice has been studied by several groups [e.g., Kaiser and Roessler, 1997; Foti et al., 1984] and is of interest because it is both a solar system and an interstellar ice component. Figure 4 shows IR spectra of CH_4-ice before (bottom line) and after

Figure 4. Mid-IR spectra of amorphous CH_4-ice at 16 K before (bottom line) and after (top line) irradiation to a dose of ~ 12 eV molecule^{-1}. Spectra have been offset for clarity. Asterisks indicate five features of C_2H_6.
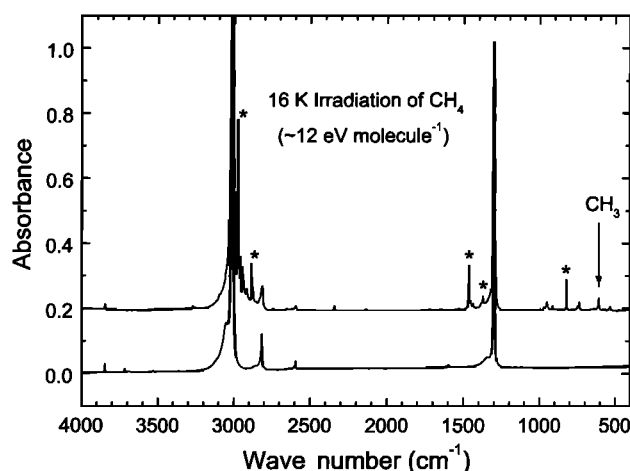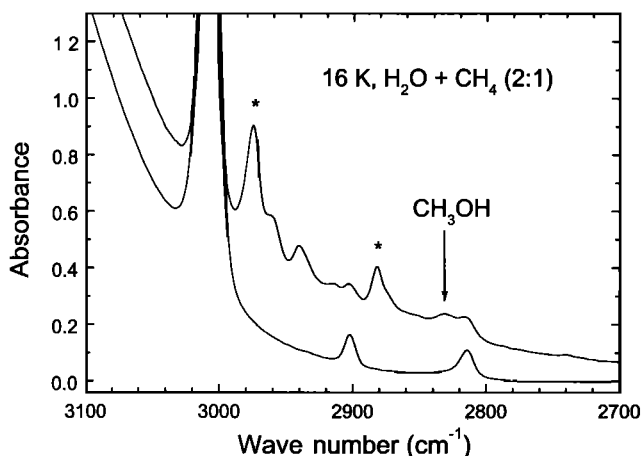
Figure 5. Mid-IR spectra of an amorphous H_2O + CH_4 (2:1) mixture at 16 K before (bottom line) and after (top line) irradiation to a dose of ~24 eV molecule^{-1}. Spectra have been offset for clarity. Asterisks indicate two features of C_2H_6.

Figure 6. Mid-IR spectrum of an H_2O + CO (5:1) ice at 16 K before and after proton irradiation to two different doses. Spectra have been offset for clarity.

(top line) irradiation at 16 K. Radiolysis forms the methyl radical, CH_3, which is indicated in Figure 4 with an arrow. Combination of methyl radicals by

$$CH_3 + CH_3 \rightarrow C_2H_6$$

gives C_2H_6, ethane, which is also marked in the Figure 4. The remaining features are due to other hydrocarbon products and can be identified by reference spectra of various alkanes, alkenes, and alkynes.

Knowing that radical combination reactions occur in both irradiated H_2O and irradiated CH_4 makes it possible to predict a new product in irradiated H_2O + CH_4 mixtures. Methyl radicals from CH_4 and OH radicals from H_2O should combine to give CH_3OH, methanol, by

$$CH_3 + OH \rightarrow CH_3OH,$$
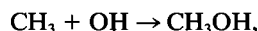
and indeed CH_3OH is observed as Figure 5 shows. Confirmatory bands for CH_3OH are present near 1124 and 1018 cm^{-1} (not shown) and were documented by us earlier [*Moore and Hudson*, 1998].

These examples involving H_2O and CH_4 were part of our efforts to understand the radiation chemistry of saturated and unsaturated hydrocarbons in H_2O-ice. An important aspect of this work was the investigation of H-atom and OH-radical addition reactions to carbon-carbon double and triple bonds. Specifically, the discovery of abundant C_2H_6 in comet C/1996 B2 Hyakutake by *Mumma et al.* [1996] led them to propose H-atom addition to C_2H_2, acetylene, as a source of C_2H_6. We have confirmed that the sequence

$$C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_6$$

does occur in frozen H_2O + C_2H_2 at the temperatures thought to characterize comets stored in the Oort Cloud [*Hudson and Moore*, 1997; *Moore and Hudson*, 1998]. Moreover, our work demonstrated that C_2H_5OH, ethanol, forms in irradiated H_2O + C_2H_2 mixtures. This conversion of C=C and C≡C bonds to C–C bonds of alkanes and alcohols also occurs in irradiated three-carbon molecules (R. L. Hudson and M. H. Moore, unpublished work, 2000). The reverse process, formation of
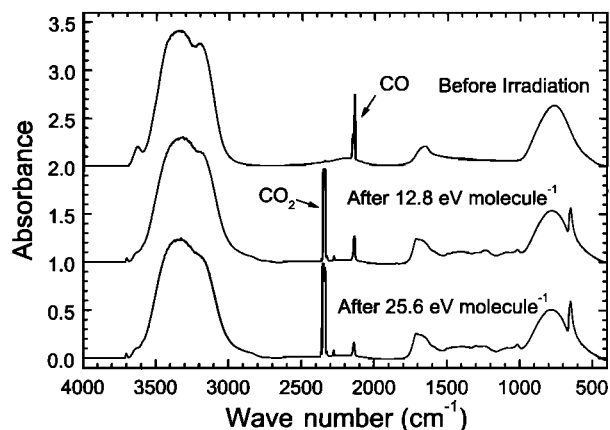
C=C and C≡C bonds from C–C bonds, occurs less readily in irradiated H_2O-rich ices.

4.2. H_2O + CO Experiments

The extremes of chemical oxidation for carbon are represented by hydrocarbons (reduced carbon) and carbon oxides. Having commented on hydrocarbon radiation chemistry we now turn to CO and CO_2, two important molecules found in the solar system and the interstellar medium. Figure 6 shows IR spectra of an H_2O + CO mixture near 16 K before and after proton irradiation [*Hudson and Moore*, 1999]. The formation of CO_2 is obvious and is indicated. The relevant reaction is thought to be

$$OH + CO \rightarrow H + CO_2.$$
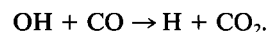
An enlargement of the 1500–1000 cm^{-1} region is displayed in Figure 7a and shows many product features. Four of these are identified in Figures 7b–7e.

The bands in Figure 7a, and elsewhere in this paper, are broad and overlap one another, and so it is necessary to use
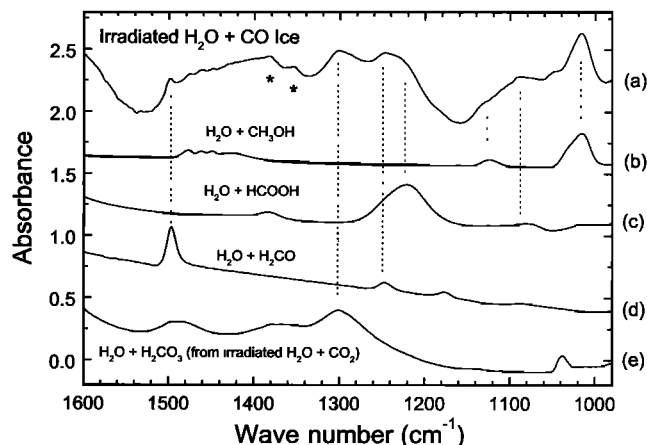

Figure 7. New species formed in an H_2O + CO (5:1) ice irradiated to 26 eV molecule^{-1} at 16 K are identified by comparison with reference spectra of other molecules in H_2O at ~16 K. Spectra have been offset for clarity. The two features marked by asterisks in the upper spectrum are due to HCOO$^-$, formate ion.

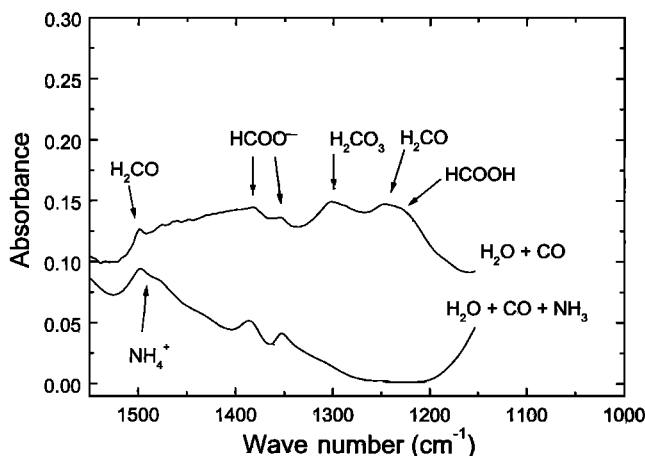**Figure 8.** Mid-IR spectra at 16 K of an irradiated H_2O + CO (5:1) ice compared to an irradiated H_2O + CO + NH_3 (5:1:1) ice. Both mixtures were irradiated to a dose of about 26 eV molecule^{-1}. Note the absence of the two acids, HCOOH and H_2CO_3, in the lower spectrum.

multiple techniques to confirm assignments. In general these techniques include (1) comparisons with reference spectra, (2) "blank" experiments involving the irradiation of a single component, (3) isotopic substitution, and (4) selective removal or enhancement of bands by adding scavengers for e$^-$, H$^+$, and radicals. A fifth method of assigning IR features is to consider what radiation products are expected based on related systems. In the case of CO one has a triply bonded molecule which is isoelectronic to C_2H_2, which possesses a carbon-carbon triple bond. Since radiation reactions and products of H_2O + C_2H_2 were already known [*Hudson and Moore*, 1997; *Moore and Hudson*, 1998], some reactions and products of H_2O + CO could be predicted. Specifically, because the radiation products of H_2O + C_2H_2 can be summarized as

$$H_2O + C_2H_2 \rightarrow C_2H_4, C_2H_6, C_2H_5OH$$
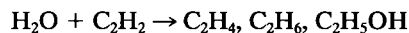
then chemical expectations lead to the predicted radiolysis products of H_2O + CO as

$$H_2O + CO \rightarrow H_2CO, CH_3OH, HCOOH.$$
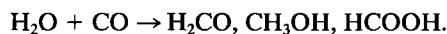
The latter three products were indeed found, along with a band near 1853 cm^{-1} (not shown) for the formyl radical, HCO. Two additional contributors in Figure 7a, without counterparts in the C_2H_2 experiments, were HCOO$^-$, formate ion, and H_2CO_3, carbonic acid. These are indicated in Figure 7 and were confirmed with the techniques already described. Radiation chemical yields ($G \equiv$ molecules formed/100 eV absorbed) were of the order of 0.1 for H_2CO, CH_3OH, and HCOOH in H_2O + CO (5:1) mixtures, and the conversion of CO to CH_3OH was ~12%. Tables of yields are given by *Hudson and Moore* [1999].

As a second illustration of how broad, overlapping IR bands are assigned, consider Figure 8. The sample giving the upper spectrum was originally composed of H_2O + CO (5:1), while the sample giving the lower spectrum was originally composed of three components, H_2O + CO + NH_3 (5:1:1). NH_3 is a weak base, an H$^+$ scavenger, and acts to alter the abundances of acid products. Comparison of the upper and lower spectra shows that the features in the 1300–1200 cm^{-1} region assigned to HCOOH and H_2CO_3 are almost completely absent when

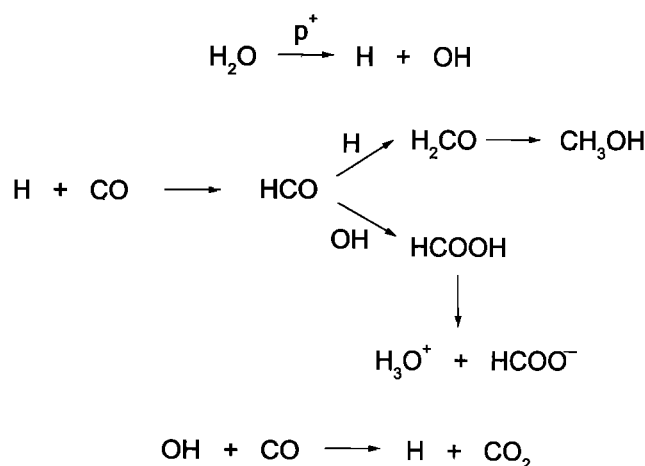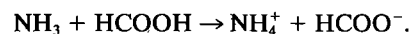**Figure 9.** Radiation-induced reactions in H_2O + CO ices.

NH_3 is present. Enhancement of a pair of features at 1386 and 1353 cm^{-1}, owing to HCOO$^-$ [*Hudson and Moore*, 2000a], confirms that NH_3 shifts the balance between HCOOH and HCOO$^-$ toward the ion by forming NH_4^+. A possible reaction is as follows

$$NH_3 + HCOOH \rightarrow NH_4^+ + HCOO^-.$$

As an alternative, HCOO$^-$ may be produced first, with NH_3 blocking HCOOH formation. Absorptions due to CO_3^{2-} (carbonate) and HCO_3^- (bicarbonate) also may be present in Figure 8, between 1600 and 1400 cm^{-1}, but they are insufficiently distinct in shape or intensity to allow identification. This contrast between H_2O + CO and H_2O + CO + NH_3 shows that one- and two-component ices are useful in making spectral assignments, but more complex ice mixtures sometimes give rise to reactions not seen in the simpler cases.

Figure 9 summarizes the radiation chemistry we observed for CO in H_2O-ice. At present, radiation processing represents the only known way to reach the CH_3OH abundances reported for many protostars [*Hudson and Moore*, 1999]. The HCOOH abundance we find in H_2O + CO ice can be much larger than that suggested for interstellar ice but, as shown in Figure 8, the HCOOH abundance can be radically altered by the presence of NH_3, producing HCOO$^-$ at the expense of HCOOH. The features we observed at 1386 and 1353 cm^{-1} for HCOO$^-$ match the relative intensities, positions, and widths of two bands detected in interstellar ices [*Schutte et al.*, 1999], and at present, the only known way to produce these bands under astrophysically relevant conditions is by ion irradiation. For a comparison of HCOO$^-$ to features in interstellar ices, see *Hudson and Moore* [2000b].

4.3. H_2O + CO_2 Experiments

The broad feature at 1300 cm^{-1} in Figure 7a was assigned to H_2CO_3, carbonic acid, whose IR spectrum was first reported and analyzed by *Moore and Khanna* [1991]. Figure 10 shows spectra of an H_2O + CO_2 ice before (top line) and after (middle line) ion irradiation. New features in the 1700–1300 cm^{-1} region correspond to H_2CO_3, with a contribution from CO near 2140 cm^{-1} and, perhaps, some contributions from CO_3^{2-} and HCO_3^- between 1600 and 1400 cm^{-1}. The bottom spectrum was obtained after irradiated H_2O + CO_2 was warmed to ~250 K, to drive off H_2O, CO_2, and CO, and then
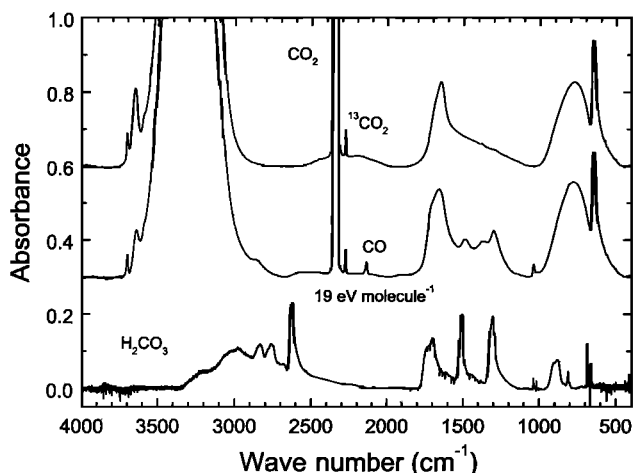
Figure 10. Mid-IR spectrum of an H_2O + CO_2 (10:1) ice 17 K before (top line) and after (middle line) irradiation. The bottom spectrum was recorded at 17 K after an annealing of the sample to about 250 K. Spectra have been offset for clarity.

Figure 11. Radiation-induced reactions in H_2O + CO_2 ices.

recooled. The resulting spectrum is interpreted as essentially pure crystalline H_2CO_3 [*Moore and Khanna*, 1991; *Gerakines et al.*, 2000]. Minor products in these experiments included HCO (1853 cm^{-1}), O_3 (1038 cm^{-1}), and CO_3 (2044 cm^{-1}).

As H_2O and CO_2 have been reported on several astronomical objects (Tables 1 and 2), the possible formation of H_2CO_3 is of interest. We have found that H_2CO_3 is made on irradiation of H_2O + CO_2 ices from 16 to 100 K, approximately the range of temperatures in the outer solar system. However, we also have found that formation of H_2CO_3 is almost totally blocked in certain cases. The three cases examined to date are H_2O + CO_2 + X ices where X is a radical scavenger (e.g., CO or C_2H_4), an electron scavenger (e.g., N_2O or SF_6), or an H^+ scavenger (e.g., NH_3). This puts important chemical constraints on H_2CO_3 formation. Conversely, the detection of H_2CO_3 on an astronomical object can be used to draw conclusions about the chemical composition of the object's surface. In Figure 11 we give reactions for H_2CO_3 formation in irradiated H_2O + CO_2 ices consistent with our experiments. Two pathways to H_2CO_3 are possible, both going through the bicarbonate ion, HCO_3^-.

Table 3 summarizes the products observed by IR spectroscopy for irradiated H_2O + CO and H_2O + CO_2 mixtures. Yields for most of these products have been reported [*Gerakines et al.*, 2000; *Hudson and Moore*, 1999].

4.4. H_2O_2 on Europa: Part II

Earlier in this paper we described how H_2O_2 was detected in irradiated H_2O-ice, shown in Figure 3, and we noted that an H_2O_2 detection has been reported for Europa [*Carlson et al.*, 1999]. However, our laboratory detection was at 16 K, whereas Europan ice is closer to 80 K. Therefore we repeated our experiment at the higher temperature but, somewhat surprisingly, detected no H_2O_2. In later experiments [*Moore and Hudson*, 2000] we found that at 80 K we could detect H_2O_2 only when a known electron scavenger (e.g., CO_2, N_2O, O_2, or SF_6) was initially added to the H_2O-ice. This suggests that at 80 K the H_2O_2 level is kept low by a reaction such as

$$H_2O_2 + e^- \rightarrow OH + OH^-$$
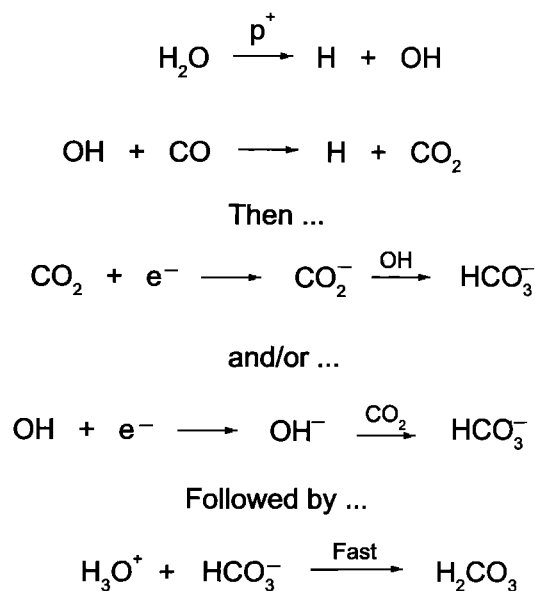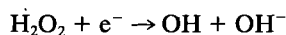
but that electron scavengers "protect" the H_2O_2 from this destruction. We also note that neither inert molecules (e.g., N_2 or Kr) nor radical scavengers (e.g., CO or C_2H_4) were able to raise the H_2O_2 level at 80 K to a detectable value in our experiments. The radical scavengers even prevented H_2O_2 detection at 16 K, presumably by reacting with OH radicals. Thus an implication for H_2O_2 on Europa is that relatively few unsaturated hydrocarbons are present near the surface compared to molecules such as CO_2. In a separate paper [*Moore and Hudson*, 2000] we have shown quantitatively that radiolysis of H_2O + O_2 ice under Europan conditions can account for the observed H_2O_2. Table 4 gives a qualitative summary of our results on H_2O_2 detection.

4.5. Other Molecules

One of our long-term goals is to study the radiation chemistry of all known solar system and interstellar molecules and representatives of the main classes of organics. Table 5 lists the molecules studied to date. In each case the molecule was irradiated in H_2O-ice, usually at a concentration of 20% or less, IR spectra were taken, and product identifications were made. This work will eventually be published, and interested readers are invited to contact the authors. The results of these experiments will reveal the main products of radiation processing in each case and allow us to determine radiation lifetimes for various molecules.

Table 3. Products Observed After Irradiation of Two H_2O-Containing Ices[a]

H_2O + CO (5:1)[b]	H_2O + CO_2 (10:1)[c]
HCO, H_2CO, CH_3OH HCOOH, HCOO$^-$ CO_2, H_2CO_3	CO, H_2CO_3 (Minor: HCO, O_3, CO_3)

[a]Irradiations at ~16 K with 0.8 MeV protons.
[b]Hudson and Moore [1999].
[c]See *Gerakines et al.* [2000] and *Moore and Khanna* [1991].

Table 4. When is H_2O_2 Observed After Irradiation of H_2O-Containing Ices

Ice Mixture	16 K	80 K
H_2O (neat)[a]	yes	no
H_2O + Kr	yes	no
H_2O + N_2	yes	no
H_2O + CO	no	no
H_2O + C_2H_4	no	no
H_2O + O_2[a]	yes	yes
H_2O + CO_2[a]	yes	yes
H_2O + N_2O	yes	yes
H_2O + SF_6	yes	yes

[a]See *Moore and Hudson* [2000] for quantitative details.

4.6. Apolar Ices and the "XCN" Spectral Feature

In contrast to our extensive work on the radiation chemistry of H_2O-dominated ice mixtures, much less has been done with apolar ices, such as the nitrogen-rich ice of Pluto. Nevertheless, statements can be made about radiation products in apolar ices using the experiments already described here, experiments in the literature, a matrix's solvating ability, and the stability of potential radiation products. Specifically, we expect much better stabilization of ions in a polar matrix, such as H_2O-ice, than in nonpolar matrix, such as N_2. Trapping of free radicals will be more efficient in solid N_2 than in the more reactive H_2O-ice. Another observation is that CO_2 is all but ubiquitous in our irradiated ices, reflecting its high thermodynamic stability. Consequently, we expect other 16-valence electron, linear triatomic species, such as N_2O and OCN^-, to form in high yield under the appropriate conditions.

These considerations lead to specific expectations for both laboratory and astronomical ices. Irradiation of a N_2-rich ice containing CO will produce CO_2, and irradiation of a N_2-rich ice containing CO_2 will produce CO. In both cases we expect an IR spectrum showing N_2O, little or no OCN^-, and IR features of neutral free radicals, such as CO_3, OCN, and NO. Conversely, irradiations of more polar ices, such as H_2O + CO + N_2 and H_2O + CO + NH_3 ices, are expected to yield both N_2O and OCN^-, but few bands are expected from reactive radicals. The balance between OCN^- and HNCO, its conjugate acid, will be influenced by the matrix, just as in the case we showed for HCOOH and $HCOO^-$ (Figure 8). Experiments support these conclusions [*Hudson et al.*, 2001].

Table 5. Molecules Irradiated in H_2O (~16 K, ~1 MeV p^+)

Class of Molecule	Molecules Studied
Carbon Oxides	CO, CO_2
Alkanes	CH_4, C_2H_6
Alkenes	C_2H_4, C_3H_6
Alkynes	C_2H_2, C_3H_4
Dienes	C_3H_4
Alcohols	CH_3OH, C_2H_5OH
Aldehydes	H_2CO, CH_3COH
Ketones	$(CH_3)_2CO$
Acids	HCOOH, CH_3COOH
Ethers	$(CH_3)_2O$, c-C_2H_4O
Esters	$HCOOCH_3$
Amines	NH_3
Assorted	O_2, N_2, N_2O
	HCN, H_2O_2, OCS
	SF_6, SiH_4, Kr

Going further, these predictions are directly related to the oft-debated "XCN" feature near 2165 cm^{-1} (4.62 μm) in interstellar ices. Refractory residues have been suggested as a contributor to the "XCN" feature by *Palumbo et al.* [2000]. *Pendleton et al.* [1999] considered various nitriles and observed that "a true identification of the carrier of the 4.62 μm band still cannot be made on spectroscopic arguments alone," a statement with which we agree. We find [*Hudson and Moore*, 2000b] that a consideration of radiation effects and reaction chemistry leave no doubt that OCN^- will form in irradiated polar ices in the laboratory, in the solar system, and in the interstellar medium. We know of no published evidence that any other species contributes to the so-called "XCN" band at 2165 cm^{-1}. See also the recent work of *Demyk et al.* [1998]. *Hudson et al.* [2001] present an extensive analysis of OCN^- formation based on laboratory experiments.

4.7. Comparison of Photochemical and Radiation Chemical Effects

Astronomical ices are subject to both UV photolysis and ion irradiation, but it is very difficult to find experiments comparing the chemical effects of these two processes. Our Table 4 gives conditions under which H_2O_2 has been observed at 16 and 80 K in radiation experiments. We have extended this work by UV photolyzing the mixtures of Table 4 (Hudson et al., unpublished work, 2000). We find that those ices which show H_2O_2 in radiation experiments also show H_2O_2 in photolysis experiments and that those which do not show H_2O_2 in radiation experiments do not show H_2O_2 in photolysis experiments. A quantitative comparison of yields remains to be done.

We also have compared UV and ion processing of CO + NH_3 and H_2O + CO_2 mixtures. UV-photolyzed and ion-irradiated CO + NH_3 ices yield many products, so only a qualitative comparison was attempted. We determined that the same chemical species were formed with about the same relative abundances in the radiation and photochemical experiments, suggesting a common underlying chemistry [*Hudson and Moore*, 2000b]. In the case of H_2O + CO_2 mixtures, only CO and H_2CO_3 were observed as major products, so a quantitative comparison was undertaken. We found that both of these products were formed in UV-photolyzed and ion-irradiated ices at essentially the same rate for the two types of energetic processing [*Gerakines et al.*, 2000].

Finally, we note that it is sometimes assumed that UV and ion experiments on triply bonded molecules, such as N_2, will give different results, although few direct comparisons are available. While a mere quantitative difference in products would not be particularly interesting, a qualitative difference would be very useful. Were the radiation chemical and photochemical products found to differ, then either set of products might be used by observers as indicators of that particular type of energetic processing in astronomical ices. We are presently comparing UV and ion processing for many ices, including N_2 and CO mixtures.

5. Discussion and Conclusions

Our experiments on radiation chemical effects have led to some general observations. One is that radiation processing is very efficient in producing certain "small" molecular species in ices. These species include CO, CO_2, OCN^-, CH_3OH, and HCOOH. Each of these can be produced in sufficient yield

from suitable laboratory precursors to account for observed abundances in many astronomical ices. A challenge for experimentalists is to determine the conditions under which the formation of such molecules might either be enhanced or hindered.

In contrast to these "favored" molecules, we have found it difficult to detect certain other types. Large molecules, such as polycyclic aromatic hydrocarbons (PAHs), polymers, and biomolecules were not seen in any of our IR spectra. These molecules may form part of the residual material already described, but such material is not easily analyzed by conventional IR spectroscopy. On the other end of the dimensional scale, certain classes of small molecules have also proven difficult to detect. These include ethers and organic acids beyond HCOOH. Unfortunately, ethylene oxide [*Nummelin et al.*, 1998] and acetic acid [*Mehringer et al.*, 1997] are two molecules which have been detected in the interstellar medium but whose formation is thought to proceed through solid-phase reactions. The likelihood of observing either in the solid state by remote sensing appears slim.

A useful concept in our ice work is that of thermodynamic stability. Ionizing radiation drives an ice toward a more stable composition, reactants to products. However, if the experiment is repeated starting with the products, the original reactants are recovered as the ice approaches an equilibrium composition. Many examples can be given. Irradiation of CO in amorphous H_2O-ice generates CO_2, CH_3OH, and the other products already described. However, irradiation of either H_2O + CO_2 or H_2O + CH_3OH ices generates CO. Some other pairs of reactants and products showing this behavior, all in H_2O-dominated ices, are {CO_2, H_2CO_3}, {CH_4, C_2H_6}, {CH_4, CH_3OH}, {H_2CO, CH_3OH}, {CH_3COH, C_2H_5OH}, and {CO, H_2CO}. This implies that in multicomponent ices, such as H_2O + CO + NH_3, that complex organics are formed by radiolysis, albeit in low yields. Conversely, it also implies that organic molecules, such as amino acids or organic polymers, will be destroyed in H_2O-ice by radiation, forming CO_2, NH_3, and other simple products. Similar conclusions will apply to inorganics, such as C_3O_2 and, perhaps, simple salts.

Turning from radiation products to radiation processes, we have observed that certain chemical reactions occur in a variety of molecules in H_2O-dominated ices. Double and triple bonds of types C=C, C≡C, C=O, and C≡O are converted to single bonds by irradiation in H_2O-ice. Radical-radical reactions to make molecules like H_2O_2, C_2H_6, CH_3OH, and ethylene glycol [*Hudson and Moore*, 2000a] readily occur and are so common that they can be relied on in ices not yet studied. Electron-transfer reactions are important in some systems, notably H_2O_2 and CO_2. Acid-base reactions (H^+ transfer) are at the heart of the radiolysis of H_2O-ice and certainly take place in H_2O-dominated mixtures, as evidenced by our work on H_2O + CO + NH_3 ices.

Elsewhere we have argued that reactions occurring in one-component ices may have little relevance to ice mixtures [*Hudson and Moore*, 1999]. Nevertheless, our work has shown that one key to unraveling complex ice chemistry is to look at simple systems. Multicomponent ices display such a rich chemistry that it is almost impossible to understand them without considerations such as chemical theory, isotopic substitution, and a consistent set of experiments on model systems. Certainly there is a need to investigate and understand simple laboratory ices for comparisons to solar system and interstellar ices.

As concerns the question of UV versus ion processing, we have found that the major products of radiation and far-UV processing are very similar for the ices studied so far. However, very few ices have been subjected to quantitative examination by both techniques, and so additional experiments are certainly needed.

Finally, and perhaps most exciting, the data are almost in hand for predictions of radiation products in specific astronomical environments. Enough is known about the behavior of individual molecules in the pure state, in H_2O, and, in some cases, in N_2 that, given a specific set of temperature, radiation, and compositional constraints, one can turn to a radiation astrochemist for a reasonable set of chemical reactions and products. The situation that has existed up until now, in which each astronomical ice analogue studied represented a unique chemical problem, is changing as a comprehensive picture of energetic processing emerges.

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