# Laboratory Studies of Astronomical Ices - Reaction Chemistry and Spectroscopy

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CONSPECTUS: Scientists have had evidence for molecules in both comets and interstellar space since the 19th and early 20th centuries. Since then, extraterrestrial molecules ranging from simple diatomics to $C_{70}$ to amino acids have been detected and identified through remote spectroscopy, spacecraft, and sample return missions. These achievements have been made through the efforts of astronomers and laboratory chemists collaborating to identify molecules in a myriad of exotic environments. It is now understood that even in the coldest depths of dense molecular clouds, there is a wealth of chemistry to explore, much of it driven by exposure to radiation. As molecular clouds condense to protostellar disks and eventually form new planetary systems, chemical processes continue and evolve. An understanding of these processes is paramount for explaining the compositions of different bodies in the Solar System and may provide insight into the origins of life.

In this article, we will describe the work of the Cosmic Ice Laboratory at NASA's Goddard Space Flight Center to characterize the composition of and to understand the chemistry occurring in icy bodies in the Solar System and beyond. Our work has touched on a wide range of extraterrestrial environments including icy interstellar grains, small bodies such as comets and asteroids, and planets and moons. We are especially interested in the chemical and physical changes that occur in ices as a result of thermal changes or exposure to radiation. To this end, we conduct experiments designed to simulate cold extraterrestrial environments and measure physical properties of single- and multi-component ices. We expose ices to radiation (e.g., MeV protons or keV-MeV electrons) or high-energy photons (e.g., UV) to initiate physical and chemical changes. We conduct experiments using cryo-vacuum chambers equipped with analytical tools and radiation sources to make most of our measurements, including the collection of all spectroscopic data, *in situ*. When possible and appropriate, we also collect reaction products for further *ex situ* analysis. The work of the Cosmic Ice Lab provides critical data to astrochemists and others seeking to understand observations, make predictions, and plan future space missions.

Key References:

- Hudson, R. L.; Moore, M. H. Laboratory Studies of the Formation of Methanol and Other Organic Molecules by Water + Carbon Monoxide Radiolysis: Relevance to Comets, Icy Satellites, and Interstellar Ices. *Icarus* **1999**, 140, 451-461.[1] *We showed that chemistry induced by the radiolysis of ices could fill the gap between the observed abundances of interstellar $CH_3OH$ and the available gas-phase synthetic pathways*.

- Hudson, R. L., Moore, M. H.; Gerakines, P. A. The Formation of Cyanate Ion ($OCN^-$) in Interstellar Ice Analogues. *ApJ* **2001**, 550, 1140-1150.[2] *We used reaction chemistry to identify $OCN^-$ as the source of the 'XCN' band observed in astronomical data and in the laboratory.*

- Gerakines, P. A.; Hudson, R. L. First Infrared Band Strengths for Amorphous $CO_2$, an Overlooked Component of Interstellar Ices. *ApJL* **2015**, 808, L40-L46.[3] *We measured the* *first band strengths for truly amorphous $CO_2$ and resolved problems and inconsistencies in the literature.*

- Gerakines, P. A.; Hudson, R. L.; Moore, M. H.; Bell, J-L. In-situ Measurements of the Radiation Stability of Amino Acids at 15 - 140 K. *Icarus* **2012**, 220, 647-659.[4] *We measured the radiolytic destruction of amino acids under conditions relevant to numerous extraterrestrial environments.*

## 1. INTRODUCTION

Chemistry might not be one's first thought upon contemplation of outer space, but chemists have long been interested in the extraterrestrial realm. Chemist William Miller (1817-1870) was a close collaborator of stellar spectroscopist William Huggins (1824-1910), and chemist Robert Bunsen (1811-1899) and physicist Gustav Kirchhoff (1824-1887) collaborated to identify elements in the Sun's photosphere. John Draper (1811-1882), an early lunar photographer, was the American Chemical Society's first president. Closer to the present, chemist Harold Urey (1893-1981) and astronomer Bertram Donn (1919-2012) proposed a free-radical mechanism in ices and on dust grains to explain cometary outbursts [5], and later Donn established our NASA group, the Cosmic Ice Laboratory, to investigate solid-phase chemistry at low temperatures, typically 10 to 100 K.

Our group's work began with studies of the effects of high-energy radiation on water-rich ices near 10 K, motivated by cosmic radiation acting on the surfaces of comets. An important goal was to determine if compositional changes could be detected in laboratory analog ices without warming to higher temperatures. Infrared (IR) spectroscopy was chosen as the analytical technique partly because of its amenability to *in situ* analysis without altering the sample. Pimentel and others had demonstrated the value of IR spectra for following photon-induced changes in rare-gases matrices [6], but astronomical constraints required the use of ices dominated by such molecules as $H_2O$, $CO_2$, and $CH_4$ to understand cometary and interstellar chemistry. Early experiments were promising, clearly showing IR spectral changes upon the irradiation of ices near 10 K, and that such changes could be assigned to the formation of molecules already identified in extraterrestrial environments, both within the Solar System and in cold interstellar regions.

These first experiments soon led to a larger research program to document photo- and radiation-chemical changes in single- and multi-component molecular ices. The types of reactions that could occur were of particular interest as they could help understand the formation of known extraterrestrial molecules and lead to predictions of unidentified ones. Further, the IR spectra themselves could aid in investigations of extraterrestrial environments, such as icy worlds within the Solar System, by both laboratory chemists and astronomical observers. Finally, the composition and fate of irradiated icy solids on warming was and remains of much interest because of questions about the molecules the Earth inherited or gave rise to before life emerged.

Here we present some of our work on these topics. We first review experiments describing specific chemical changes studied in our labs and that occur in extraterrestrial environments. We then turn to questions concerning IR spectra and how they can aid in quantitative studies. Lastly, we examine some results in light of astrobiology, broadly defined. For representative, albeit narrow examples of each of the topics mentioned here, please see the articles highlighted in the key references [1, 2, 3, 4]

## 2. ASTRONOMICAL BACKGROUND AND LABORATORY METHODS

Large clouds of gas and dust exist in the interstellar medium (ISM), the regions between stars. Astronomical theory says that when such clouds are sufficiently massive, they collapse to form one or more stars with any remaining material left to produce planets and smaller bodies. The most distant of the small bodies are very cold with temperatures of only 10 - 20 K. Thus, interstellar matter is the ancestral material from which the Earth and other planets form, with comets being the remnants of the ISM that produced them.

Of special interest are interstellar molecular clouds near 10 K and with densities of $10^3$ - $10^4$ atoms $cm^{-3}$. Molecular clouds typically last around $10^7$ years [7]. Within these clouds, or nebulae, are cold dust grains, largely amorphous silicates about 0.1 µm in size, and so cold that atoms condense and stick onto them, forming an icy mantle. Such grain mantles concentrate molecules and promote reactions that otherwise could not occur in the gas-phase ISM because of low molecular densities. In addition, chemical reactions occur in ices exposed to ionizing radiation, either cosmic rays or vacuum-UV photons, with the resulting chemical evolution subject to both thermodynamic and kinetic control. Similar chemical changes can occur on the icy surfaces of comets and other cold Solar System bodies, albeit with differences in the importance of various radiation sources, such as magnetospheric radiation from a nearby planet sometimes being more influential than cosmic rays.

We study the chemistry of cold icy environments using cryo-vacuum chambers ($10^{-10}$-$10^{-7}$ torr) interfaced to radiation sources (e.g., 1-MeV $H^+$ accelerator, keV $e^-$ gun, vacuum-UV lamp) (**Figure 1**). Infrared spectroscopy is our analytical method of choice for *in situ* measurements of ices, with techniques such as chromatography and mass spectrometry used for room-temperature *ex situ* studies of stable reaction products. In general, the equipment we use to study ices resembles that of matrix-isolation experiments, with ices being made by deposition onto a pre-cooled substrate (IR-transparent material or metal mirror), with ice thickness monitored by interference fringes. See our recent papers for details [8; 9].

As already stated, radiation drives chemistry on or near surfaces of Solar System bodies and in icy mantles of interstellar grains. Doses can be on the order of several eV $molecule^{-1}$ (a few $10^2$ kJ $mol^{-1}$) over the lifetime of a molecular cloud, with larger doses for Solar System objects. Although $10^{14}$-MeV cosmic rays have been detected, the great majority of such rays, which are primarily $H^+$ and $He^{2+}$, have energies below $10^2$ MeV. To the non-specialist this might seem like an enormous energy input, but it has been known for at least a century that the incident radiation's energy is degraded in a series of ionizations and excitations, with the final chemical products resulting from so-called secondary electrons with energies of 20 eV or less [10]. Notably, energetic particles and their secondary electrons can simultaneously excite or dissociate multiple molecules, while a single UV-photon cannot. As a result, the chemical products of various ionizing radiation sources are very similar and often resemble the products of lower energy UV-photochemistry, but subtle differences may remain [11]. In our lab, we use a 1-MeV $H^+$ beam as the energy source for most of our radiation experiments.

## 3. ICE RADIOLYSIS

Early work in our field involved ices that were representative, or thought to be, of interstellar and cometary material, such experiments clearly showing the radiolytic and photolytic formation of reaction products. The disadvantage of this approach was that it revealed little about the products made from specific reactants, much less mechanistic details. Subsequent work by our group and others has addressed this concern by focusing on specific compounds and classes of compounds.

### *Europa and $H_2O$-Ice*

We begin with frozen $H_2O$, the most-abundant astronomical ice. It has long been known that the irradiation of $H_2O$ ice would yield $H_2O_2$ at temperatures near 0°C, however the cold ISM and icy satellites (moons) required *in situ* experiments at much lower temperatures. We ion-irradiated $H_2O$-ice near 20 K, producing an IR feature that we assigned to $H_2O_2$ on the basis of isotopic substitution and reference spectra [12]. Surprisingly, this $H_2O_2$ band was not seen when the ice was irradiated near 80 K, a temperature more relevant to the outer Solar System's moons. Just prior to our work, $H_2O_2$ was identified on the surface of Europa, an ice-covered moon of Jupiter, setting up a disagreement between the lab and spacecraft results [13]. Resolution was achieved in several ways, such as when $H_2O + CO_2$ ices were irradiated, $CO_2$ being a Europa-ice component, such experiments clearly showing $H_2O_2$ formation at 80 K and higher. This unexpected temperature-dependent $H_2O_2$ yield was confirmed by others [14] and its underlying reason, addressed in our original paper, has received theoretical support [15].

### *Comets and Hydrocarbons*

Variations of ice composition have revealed reaction paths and products, as seen in our work on cometary chemistry. Comet C/1996 B2 Hyakutake was the first comet in which gas-phase $C_2H_6$ was identified, the observation being made by IR spectroscopy [16]. The discovery paper suggested that H-atom addition to $C_2H_2$ was the ethane's source. Subsequently, we ion-irradiated $H_2O + C_2H_2$ ices, finding that both $C_2H_4$ and $C_2H_6$ were produced [17]. **Figure 2** shows a typical result, with Scheme 1 summarizing pathways.

$$C_2H_2 \rightarrow C_2H_4 \rightarrow C_2H_6 \qquad (1)$$

In agreement with sequence (1), as the $C_2H_2$ abundance decreased, $C_2H_4$'s abundance first rose and then fell, and the $C_2H_6$ abundance simply rose with increasing radiation dose [17]. As an aside, these experiments also showed formation of vinyl alcohol, $C_2H_3(OH)$, by hydration of acetylene, the first clear demonstration of this process in an ice.

### *Alcohols and Interstellar Ices*

Our $H_2O$ + $C_2H_2$ work leads to an example of how we vary reactants and build on earlier results. Knowing that acetylene and CO are isoelectronic ($HC{\equiv}CH$ vs. $:C{\equiv}O:$), and that irradiation in a $H_2O$-rich ice reduced $C_2H_2$, we next addressed the radiolytic reduction of CO to give $CH_3OH$. Interstellar methanol's formation is a problem of long-standing interest as no gas-phase synthesis appears capable of making enough $CH_3OH$ to match astronomical observations [1]. With our $C_2H_2$ experiments as a guide, we used IR spectroscopy to examine $H_2O$ + CO ices near 10 K before and after irradiation with 1-MeV protons. As expected, reduction sequence (2) was observed.

$$CO \rightarrow H_2CO \rightarrow CH_3OH \tag{2}$$

The formyl radical, HCO, was identified, an intermediate in the first step of (2), but only weak evidence was obtained for a second radical intermediate ($CH_2OH$ or $CH_3O$). Scheme 2 summarizes the main reaction pathways. The formic acid (HCOOH) detection was confirmed with reference spectra and acid-base chemistry (see **Figure 3**). On including $NH_3$ in the initial ice to give $H_2O$ + CO + $NH_3$, in the subsequent irradiation HCOOH was replaced by formate ($HCOO^-$). Two formate IR peaks match two weak features seen in interstellar ices, as recorded by the Infrared Space Observatory [18]. We also note the ease with which irradiated $H_2O$ + CO ices made $CO_2$ in these experiments, presumably by $OH + CO \rightarrow H + CO_2$. Another significant observation in Scheme 2 is the path from $CH_3OH$ to $(CH_2OH)_2$, ethylene glycol, a prediction from our ice experiments that later was confirmed by detection of the glycol in the ISM [19]. Finally, there is the formation of elusive carbonic acid, $H_2CO_3$, which was first prepared, identified, and characterized in our labs [20].

### *The Cyanate Wars*

Having changed our $H_2O$ + $C_2H_2$ ice to $H_2O$ + CO, we next altered the other reactant, changing $H_2O$ to the isoelectronic $NH_3$ to give $NH_3$ + CO, but before presenting the result we first describe the astronomical motivation. For over two decades, the astronomical community was vexed by the assignment of a broad featureless IR absorption at 2165 $cm^{-1}$ (4.62 $\mu$m) in interstellar ices. This band initially was thought to be from solid CO, based on low-resolution spectra, but Moore et al. [21] showed that irradiation of an $H_2O$ + $NH_3$ + CO ice mixture gave the same IR feature separate from CO's peak near 2140 $cm^{-1}$ (see **Figure 4**). The 2165 $cm^{-1}$ feature eventually was dubbed the XCN band with numerous suggestions being made for its assignment, such as cyanides ($CN^-$), cyanates (ROCN), and others [22; 23]. From photolysis of $NH_3$ + CO ices, Grim and Greenberg [24] concluded that XCN was likely $OCN^-$, their evidence being spectroscopic matches of the two bands' profiles and positions.

Instead of relying only on spectroscopy, as previously done, we approached XCN from the perspective of reaction chemistry [2]. Knowing the results of the isoelectronic systems already studied, such as irradiated $H_2O$ + CO, it was relatively easy to predict the products for irradiated $NH_3$ + CO ices. For example, since $H_2O$ + CO gave $CO_2$, we could expect HNCO and $OCN^-$ from $NH_3$ + CO. See the reactions below for the similarity of the two systems. Reactions also can be written in terms of O atoms from $H_2O$ and the NH radical from $NH_3$. Approached this way, it would have been remarkable had $OCN^-$ *not* been observed.

$$H_2O \rightarrow H + OH \tag{3}$$
$$OH + CO \rightarrow H + CO_2 \tag{4}$$

$$NH_3 \rightarrow H + NH_2 \tag{5}$$
$$NH_2 + CO \rightarrow H + HNCO \tag{6}$$
$$NH_3 + HNCO \rightarrow NH_4^+ + OCN^- \tag{7}$$

Our initial experiments were accompanied by checks with isotopically labeled reagents, warming experiments to drive off volatile components, independent syntheses involving many radiolytic, photolytic, and thermal pathways, and blanks and tests that constrained $OCN^-$ formation. This work allowed the XCN band in our irradiated interstellar ice analogs to be firmly assigned to $OCN^-$. Extrapolation of our laboratory results suggested that $OCN^-$ should readily form in the icy mantles of dust grains in quantities sufficient to explain the interstellar XCN feature. Subsequent work identified $OCN^-$ in the line of sight toward the center of our galaxy [25].

These examples have emphasized reductions, but the radiolytic degradation of many icy compounds often results in oxidations, such as the reverse of sequences (1) and (2). Irradiated alcohol-ices make the corresponding aldehydes and ketones [9]. Low-temperature oxidations by O-atom addition give ketene from $C_2H_2$ and propylene oxide from propylene, among other examples [8; 26]. From the inorganic realm, irradiated $H_2O$ + $H_2S$ ices produces $SO_2$ and subsequently $SO_4^{2-}$, chemistry important for Europa [27].

## 4. INFRARED SPECTROSCOPY

### *Infrared Intensities*

The work just described required a knowledge of the IR spectra of compounds known or suspected to exist in extraterrestrial ices and their laboratory analogs. An extensive literature exists on the spectra of many common classes of organics and inorganics, but not always for measurements under the desired conditions. Moreover, such work usually lacks quantitative measures of IR intensities, either band strengths or absorption coefficients, but intensities are needed to convert spectra into molecular abundances, both in the laboratory and with spacecraft and telescopic data.

In principle, IR intensity measurements are straightforward. An ice of known thickness and density is prepared, its spectrum recorded, and the process is then repeated for other thicknesses. Similar to a Beer's Law calibration, either peak heights or band areas are measured as a function of ice thickness. In practice, however, determinations of ice thickness and density are non-trivial. Our preference is to use data from a quartz-crystal microbalance to derive ice densities ($\rho$) and interference fringes from an ice to determine thickness, which require a separate measurement of a reference visible-region refractive index ($n_{\text{vis}}$). We recently have summarized these methods and presented $n_{\text{vis}}$ and $\rho$ results for about thirty compounds covering a variety of types [28].

A more elegant, but computationally demanding, approach to quantifying IR intensities involves optical constants $n(\tilde{\nu})$ and $k(\tilde{\nu})$, the real and imaginary parts, respectively, of a sample's complex refractive index, $n(\tilde{\nu}) - ik(\tilde{\nu})$. With $n(\tilde{\nu})$ and $k(\tilde{\nu})$, a spectrum with correct intensities can be calculated, a practice used by planetary scientists to study atmospheres and surfaces of icy worlds. The underlying theory goes back to Kramers and Krönig, but the method used in practice is largely from Rice's group [29]. Despite the demand for IR optical constants by astrochemists, only recently has an open-source computational package become available [30].

**Table** 1 summarizes our recent optical-constants work and band-strength measurements. See the referenced papers for details such as temperatures and wavenumber range.

### *Ice Spectra and Ice Structure*

Before beginning laboratory work on ices, a sample is needed. Our ices usually are made by vapor-phase deposition onto a pre-cooled substrate inside a vacuum chamber. The ice's form is described as crystalline or amorphous, with the term "phase" loosely used for each. Substrate temperature strongly influences crystallinity, but deposition rate also is important. Significant differences were found in IR spectra collected near 10 K from four different laboratories of the $\nu_3$ and $\nu_2$ features of solid $CO_2$ (**Figure 5)**. A judicious choice of deposition rates allowed us to prepare the amorphous and crystalline forms of solid $CO_2$, with the spectra of **Figure 6**, and to assign the spectra of **Figure 5** to mixtures of the two phases [3]. This influence of deposition rate on crystallinity comes from the energy that must be dissipated to form a solid near 10 K from a room-temperature vapor, an energy release that can be sufficient to crystallize an ice if not removed by a cooling system.

An interesting extension of this $CO_2$ work is our study of the isoelectronic molecule $N_2O$. **Figure 7** shows $N_2O$ spectra with the upper and lower traces being for crystalline and amorphous forms of the compound, respectively. The middle trace is for an $N_2O$ ice made at about twice the rate as the amorphous ice of the bottom spectrum. The sharp and broad shapes in the middle spectrum show that the ice had both amorphous and crystalline components. It also is interesting that selected IR bands of amorphous $N_2O$ and $CO_2$ show an asymmetric shape indicating inhomogeneous broadening [3].

Identifying an ice's phase might seem trivial, but well-characterized reference spectra are needed to identify molecules in cold environments. The spectrum of an ice made under conditions that are not astronomically relevant can result in missed or incorrect identifications. See, for example, our paper on the IR spectrum of the stable low-temperature crystalline phase of propionitrile, $C_2H_5CN$ [52]. The lack of attention to thermodynamic and crystallographic work led to attempts, spanning several decades, to interpret spacecraft IR spectra using the high-temperature $C_2H_5CN$ phase. For other examples of multiple crystalline phases in simple compounds, see our work on $CH_3SH$ (which corrected a 40-year-old error) and $C_3H_8$ [46; 33].

Finally, we note the value of nominally forbidden IR transitions for distinguishing amorphous and crystalline solids. An elegant example is the IR spectrum of crystalline $NH_4SH$ in which the symmetric stretching vibration of $NH_4^+$ is not seen, but appears after the ice is amorphized by irradiation, only to again vanish as the ice is warmed to recrystallize it [53]. These experiments were conducted to test irradiated $NH_4SH$ as a candidate for the colors of Jupiter's Great Red Spot [54].

## 5. ASTROBIOLOGY AND ICES

Astrobiology seeks to understand the origins and distribution of life in the universe, and the Cosmic Ice Lab contributes to this effort. We study the role of ice radiolysis in the formation and destruction of biomolecules including amino acids and nucleobases. Radiolytic processes that lead to the abiotic formation of these compounds may be important for understanding the origin of life. Moreover, since amino acids and nucleobases are possible biomarkers, understanding their formation and destruction is key for understanding their detection in materials exogenous to the Earth.

### *Isovaline*

Our earliest foray into astrobiology sought to understand differences in the distributions of valine and the non-biological amino acid isovaline, and their respective enantiomers in meteorites [55]. Our experiments tested the impact of solid-phase radiation chemistry on the formation or modification of these compounds. Samples were analyzed *in situ* by IR spectroscopy and later *ex situ* by ultrahigh-performance liquid chromatography with UV fluorescence and time of flight mass spectrometry (LC-FD/ToF-MS). We found that isovaline and valine had similar radiation stabilities, demonstrating that differences in their distribution could not have resulted from the preferential destruction of one or the other isomer. There was no evidence of radiation-induced interconversion between isovaline and valine. For both compounds, there was evidence of racemization in samples that originally contained only one enantiomer, but the effect was modest at the radiation doses expected for meteoritic materials. Finally, we demonstrated that valine and isovaline could form by radiolysis of $CO_2$ and either isobutylamine or *sec*-butylamine ice mixtures.

### *Amino acid synthesis*

The formation of amino acid precursors was examined using acetonitrile-containing ices [56]. Acetonitrile has been detected in comets (e.g., [57]) and contains three of the major bioorganic elements (carbon, nitrogen, hydrogen). In our experiments, we irradiated $H_2O$ + acetonitrile mixtures at 10-25 K and monitored them by IR spectroscopy.

IR spectra of the irradiated ices allowed us to identify radiolysis products including $OCN^-$, $CH_3NC$, HCN, $H_2CCNH$, and $CH_4$. No other products were identified from IR spectra alone, but more were found with sensitive *ex situ* techniques including gas chromatography coupled with mass spectrometry and LC-FD/ToF-MS. Although no free amino acids were detected in the room-temperature residues, their acid hydrolysis yielded several (**Table 2**). The total yields of all amino acids identified relative to the initial acetonitrile abundances was ~0.1%. Importantly, the amino acids produced were highly similar (see **Table 2**) to those formed by the radiolysis or photolysis of different and often more complicated multi-component ices [58-61]. This suggests that irradiation of almost any ice containing C, H, N, and O will likely result in the production of amino acids or their precursors.

We note that some molecules detected in room-temperature *ex situ* analyses could have formed during warming and sublimation of the sample, and may not have been present after the ice's low-temperature irradiation. However, this does not diminish such molecules' astrobiological relevance because ice-covered dust grains in planetary nebulae are believed to undergo warming and cooling cycles as they migrate through their parent disk [62]. Additionally, amino acids generated by acid hydrolysis could form in the ocean of a telluric planet.

### *Destruction of amino acids and nucleobases*

Since these compounds are found in all known forms of life, amino acids and nucleobases and their distributions in extraterrestrial environments are important. Like amino acids, nucleobases have been produced abiotically in ice photolysis experiments (e.g., [63; 64]) and have been identified and quantified in carbonaceous chondrites [65]. Amino acids and nucleobases may be present in a range of Solar System ices including near the surfaces of icy worlds, arising from both endogenous and exogenous sources. Ionizing radiation will modify these biomolecules, and so we investigated the destruction kinetics and radiation stabilities of both classes of compounds for a range of ice compositions and temperatures, and applied the results to interstellar and planetary conditions. Ultimately, the stability and distribution of compounds from each class might be predicted.

Glycine, alanine, and phenylalanine were studied at 10 to 150 K and at several concentrations in $H_2O$-ice [4] with follow-up work on the destruction of glycine diluted either in $H_2O$- or $CO_2$-ice

[66; 67]. Our work was the first to quantify radiolytic amino acid-destruction *in situ* at cryogenic temperatures. Amino acids and mixtures were irradiated with 1-MeV protons and amino-acid destruction monitored by IR spectroscopy. We found that rates of radiolytic destruction depend on temperature, with a trend of higher destruction rate constants (*k*) at lower temperatures for all three compounds in an $H_2O$-ice, whereas the opposite trend with temperature was seen in $CO_2$ mixtures (see **Figure 8**). Furthermore, this work demonstrated that glycine is significantly more stable in an $H_2O$-ice than in solid $CO_2$, a result with important implications for the search for amino acids on Mars.

We performed similar experiments that tracked thymine destruction [69]. Our results demonstrated that the composition of the ices and the temperatures at which they were formed and irradiated play significant roles in thymine's stability. Specifically, we found that the destruction rate constant *k* of thymine increases as thymine becomes increasingly diluted in water (**Figure 9**). It can be inferred that the effect of dilution on *k* would asymptotically reach a maximum when the thymine molecules are sufficiently separated to the point of effective non-interaction. It was also observed that *k* generally decreased with increasing temperature (**Figure 9**). Importantly, the deposition temperature of the ice appeared to have a large effect on *k* between 13 and 100 K, as ices deposited at 100 K, cooled to 20 K, and then irradiated yielded *k* values similar to those of ices that were both deposited and irradiated at 100 K. We hypothesized that this effect might be related to the structure of the ice and that a more-ordered solid produced at higher temperature might increase thymine's radiolytic stability.

The results of this work suggest that thymine is best preserved under conditions where it is most highly concentrated and where any surrounding water-ice is more ordered. Interestingly, it was determined that the half-life of thymine in a dense cloud would likely be significantly shorter than the typical lifetime of the cloud itself. This short lifetime may play a role in the lack of detection of thymine in meteoritic samples to date.

## 6. CONCLUSION

In this account we have highlighted some ways that we have used laboratory ice experiments to address critical topics in astrochemistry, observational astronomy, and astrobiology. Our work clearly demonstrates the important role of solid-state radiolysis in the creation and alteration of complex molecules throughout the Solar System and beyond. Importantly, beyond serving as curious case studies of chemistry in exotic environments, ice radiolysis experiments may allow us to better understand the origins of the building blocks of life. Furthermore, such experiments allow us to predict where it is plausible for future spacecraft missions to detect biomarkers. Our work has also resulted in the production of reference spectra, often including optical constants, for molecules of importance to astrochemistry. We have shown that it is essential to collect these data under conditions relevant to target extraterrestrial environments to enable proper identification and quantification of the carriers of spectral features found in observational data. We have demonstrated laboratory astrochemistry, and ice experiments in particular, have predictive power, especially when combined with chemical theory.

Importantly, application of chemical theory to these experiments often enabled us to generalize our findings, meaning that individual ices need not be treated as islands of research.

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### Notes

The authors declare no competing financial interest.

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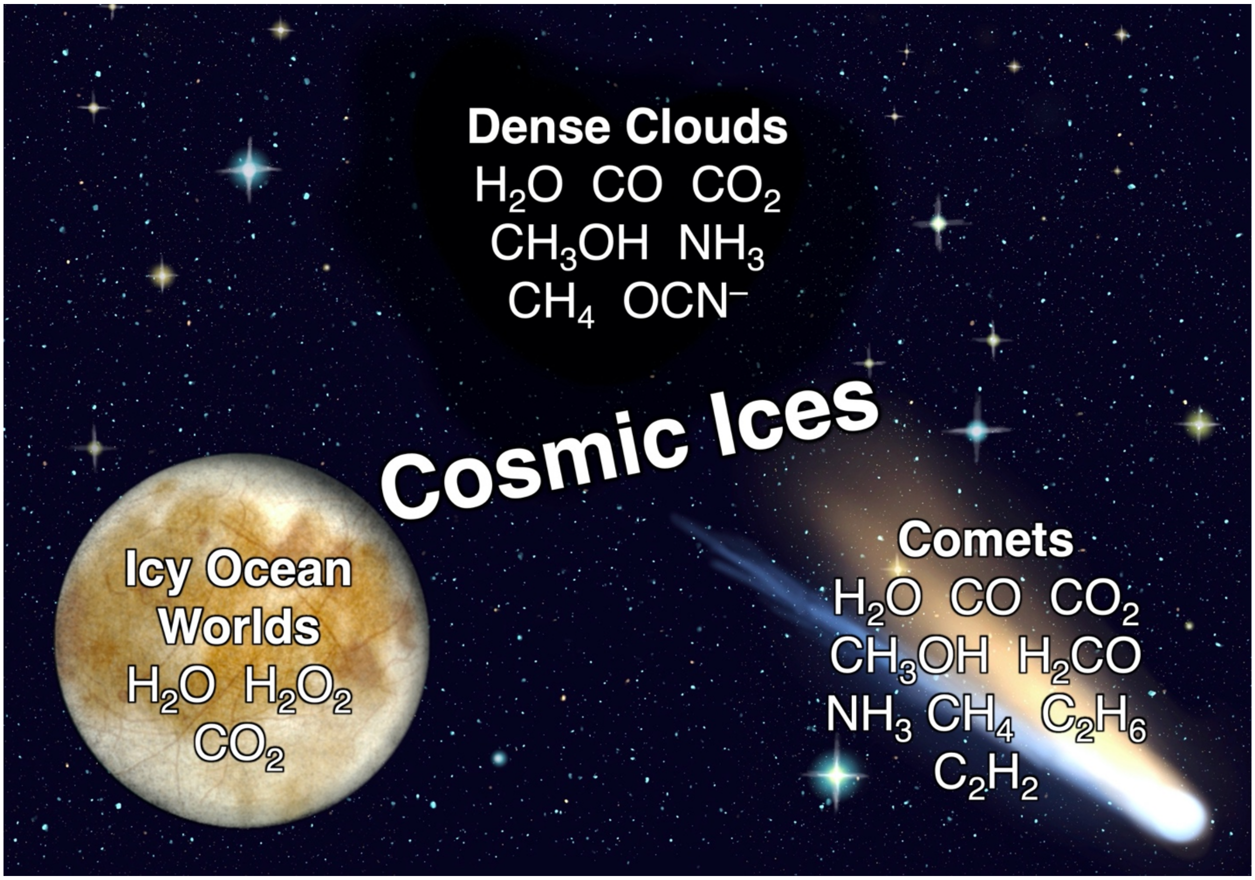

Dense Clouds
$H_2O$ $CO$ $CO_2$
$CH_3OH$ $NH_3$
$CH_4$ $OCN^-$
Cosmic Ices
Icy Ocean Worlds
$H_2O$ $H_2O_2$
$CO_2$
Comets
$H_2O$ $CO$ $CO_2$
$CH_3OH$ $H_2CO$
$NH_3$ $CH_4$ $C_2H_6$
$C_2H_2$

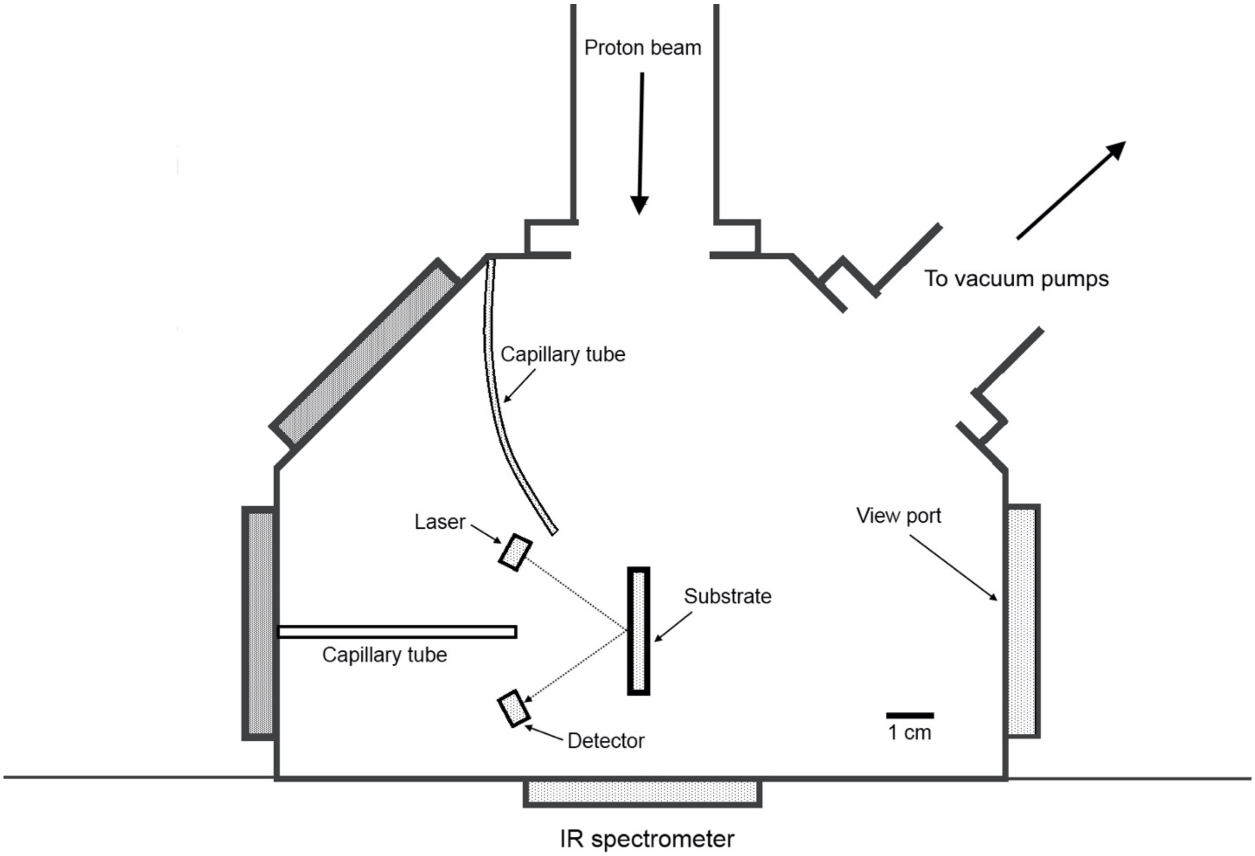


Figure 1. A schematic of one of our vacuum chambers interfaced to a Van de Graaff proton accelerator. Gases are introduced through the capillary tubes and the substrate can be rotated to face the proton beam or the IR spectrometer.

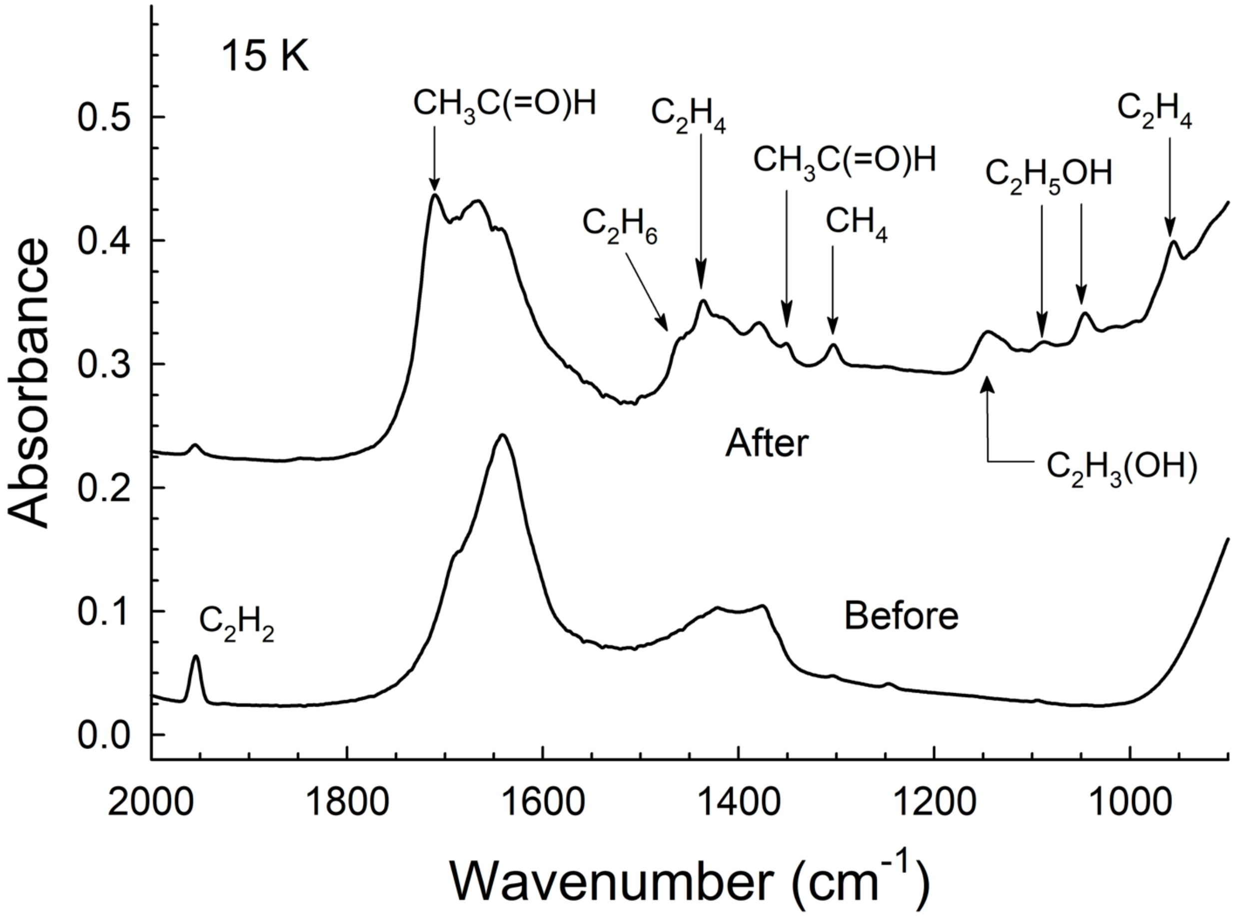


Figure 2. Infrared spectra of an $H_2O$ + $C_2H_2$ (4:1) ice before and after irradiation (dose = 17 eV molecule$^{-1}$) demonstrating the formation of products.

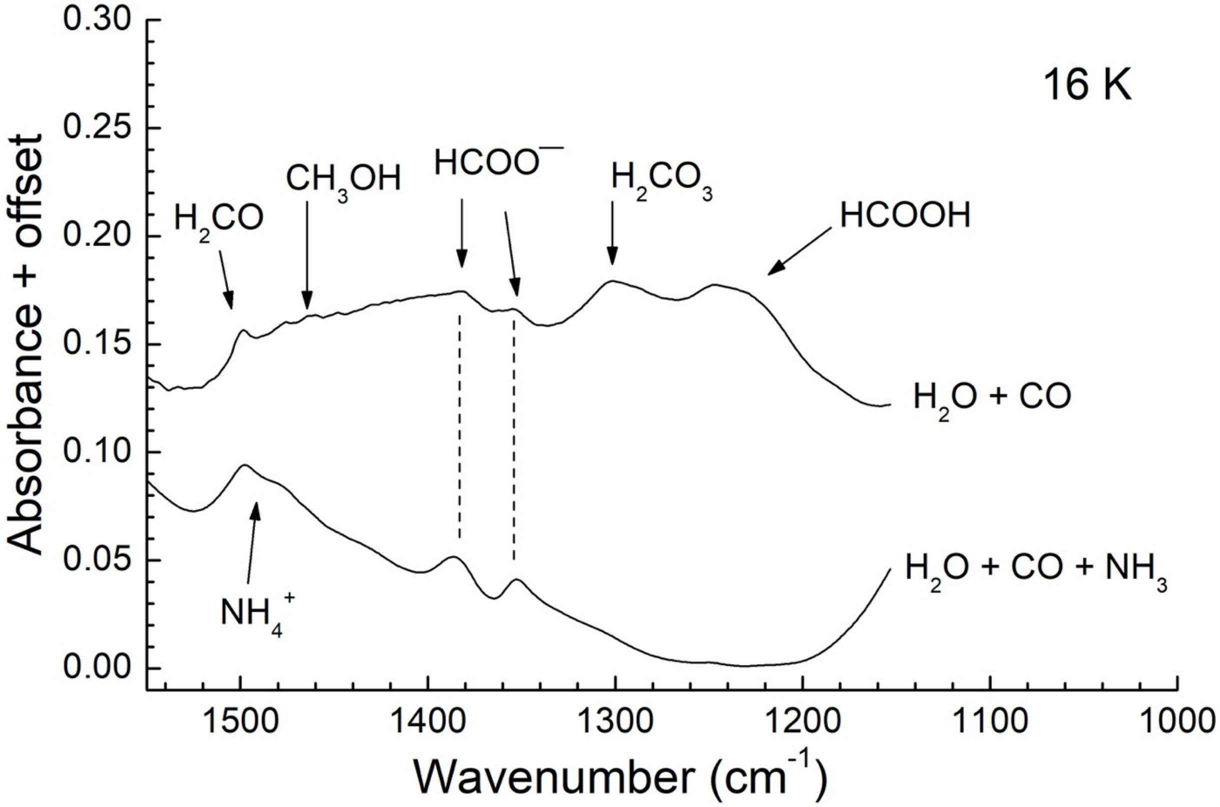


Figure 3. Infrared spectra of irradiated $H_2O$ + CO (5:1) and $H_2O$ + CO + $NH_3$ (5:1:1) ices demonstrating acid-base chemistry. Spectra recorded at 16 K after a radiation dose of 25 eV molecule$^{-1}$.

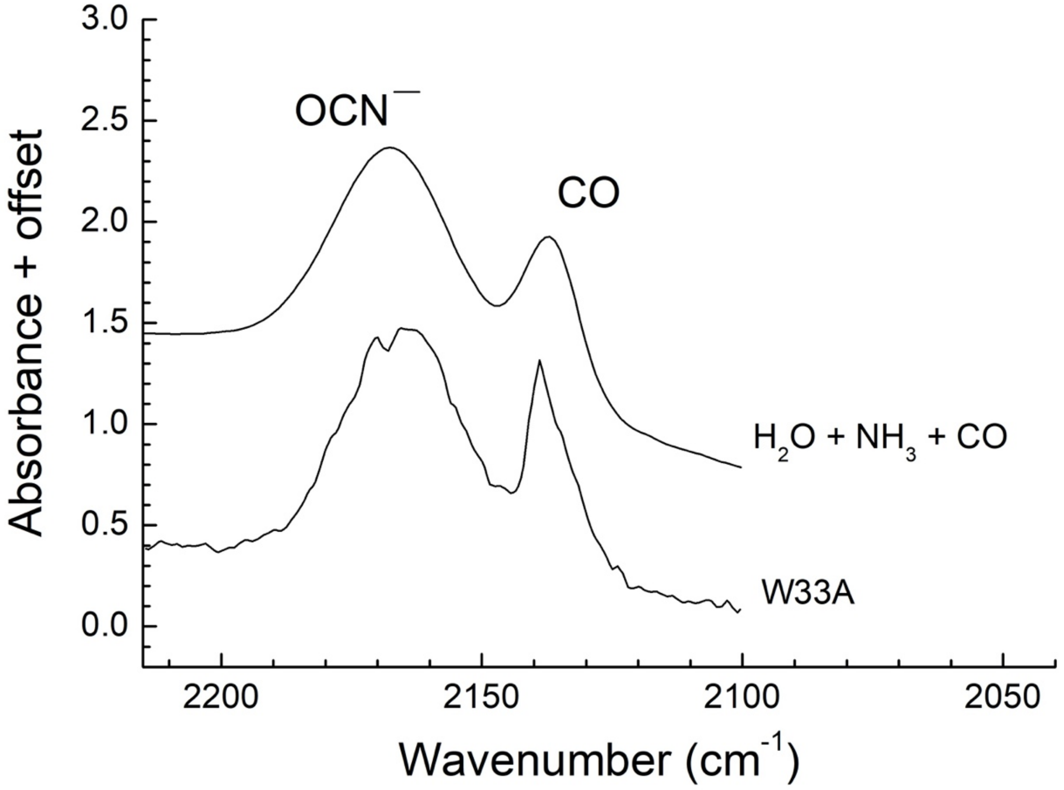


Figure 4. Comparison of the OCN⁻ feature in irradiated (19 eV molecule$^{-1}$) $H_2O + NH_3 + CO$ ice at 17 K (*top*) with the spectrum of W33A from the *Infrared Space Observatory* (*bottom*).

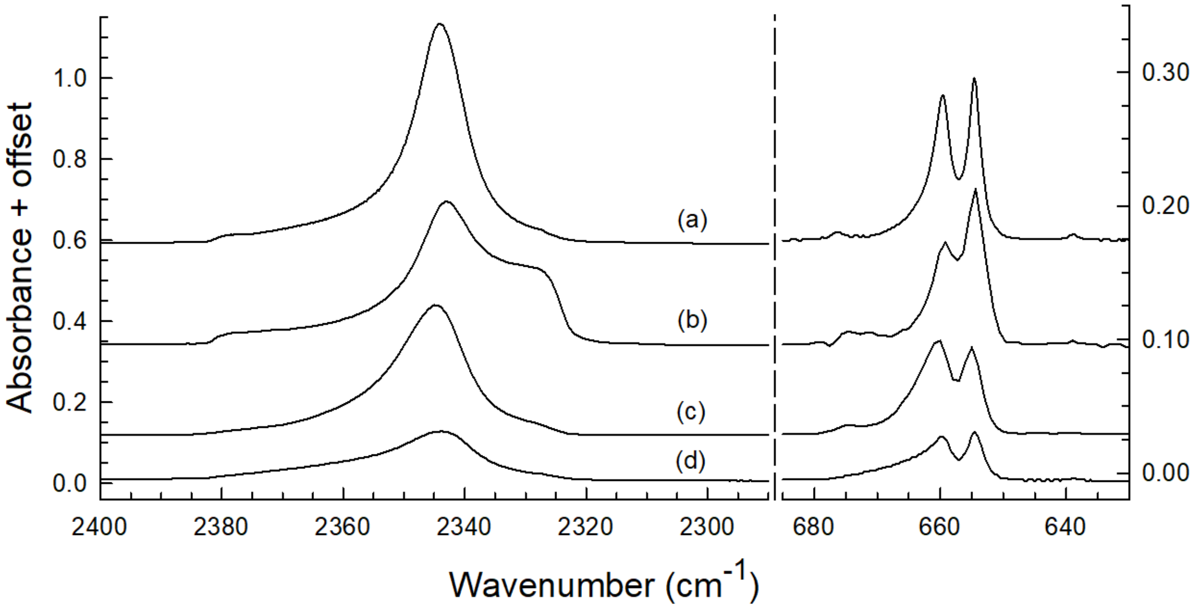


Figure 5. Infrared spectra of the $\nu_3$ (*left*) and $\nu_2$ (*right*) bands of $CO_2$ ices made near 10 K. Method and data from refs [47-51]

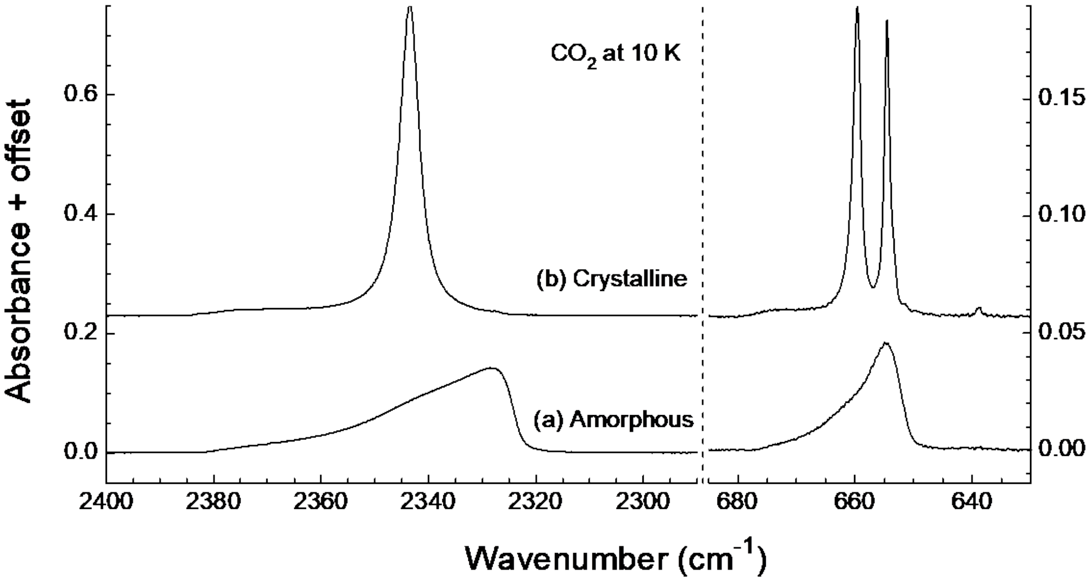


Figure 6. Infrared spectra of amorphous and crystalline $CO_2$ collected at 10 K.

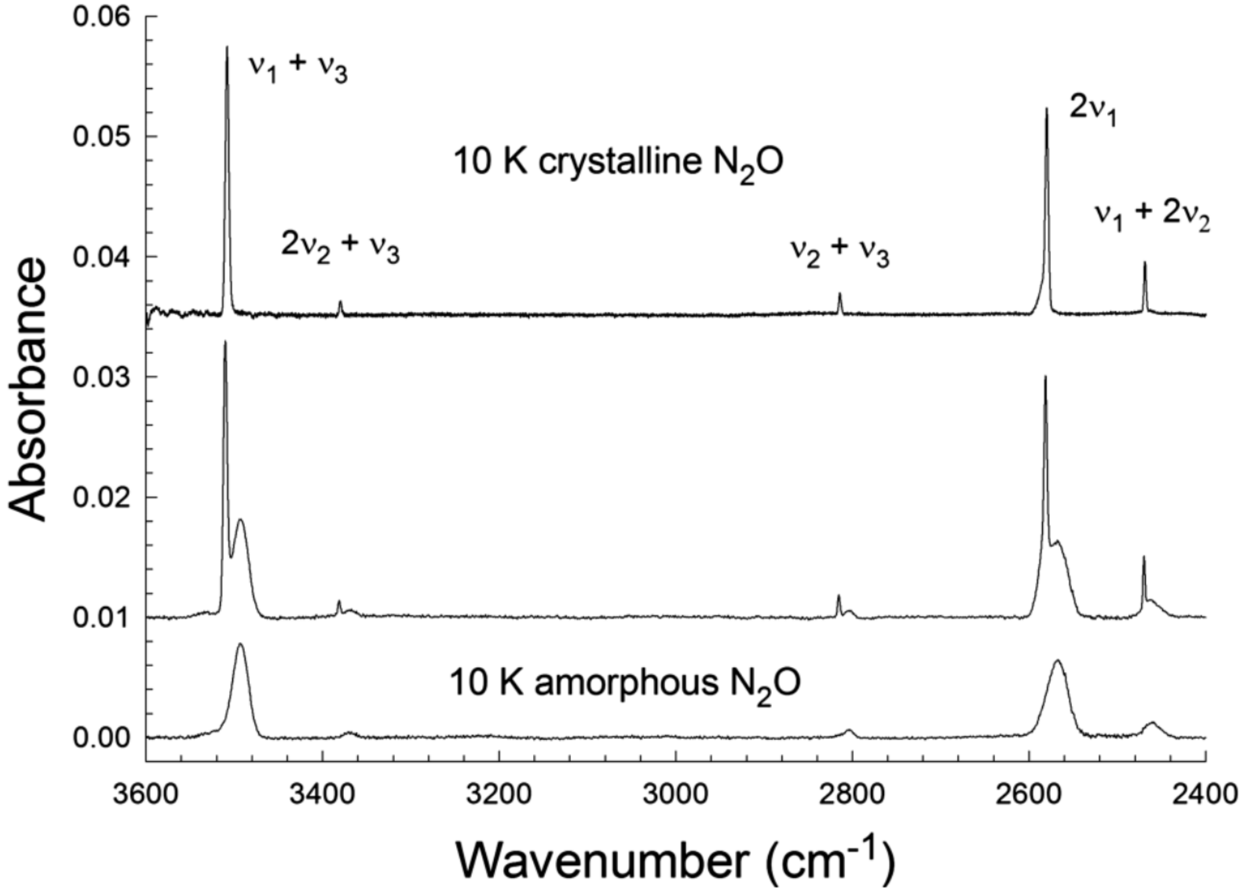


Figure 7. Spectra of $N_2O$ ices at 10 K: Crystalline $N_2O$ made at 70 K and cooled to 10 K (*top*), two-phase $N_2O$ ice (*middle*), and amorphous $N_2O$ (*bottom*).

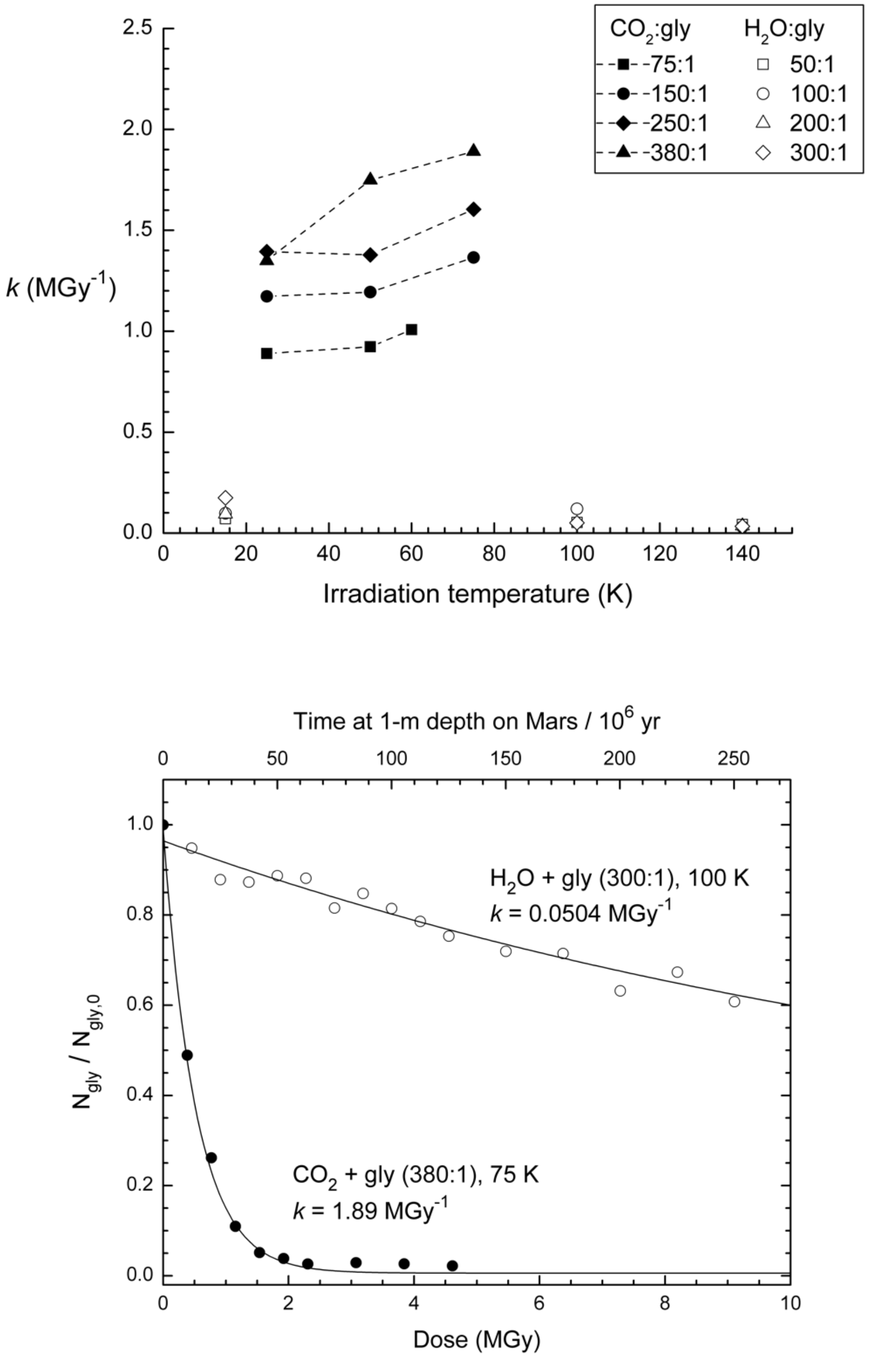


Figure 8. Destruction of glycine in $H_2O$ ice compared to that in $CO_2$. (top) Glycine destruction rate constants (in $MGy^{-1}$) versus temperature. (bottom) The surviving fraction of glycine molecules versus dose (in MGy) in dilute mixtures. The top axis gives corresponding times at a depth of 1 m on Mars based on the dose rate of 36.4 mGy $yr^{-1}$. Dose rate data from ref [68].

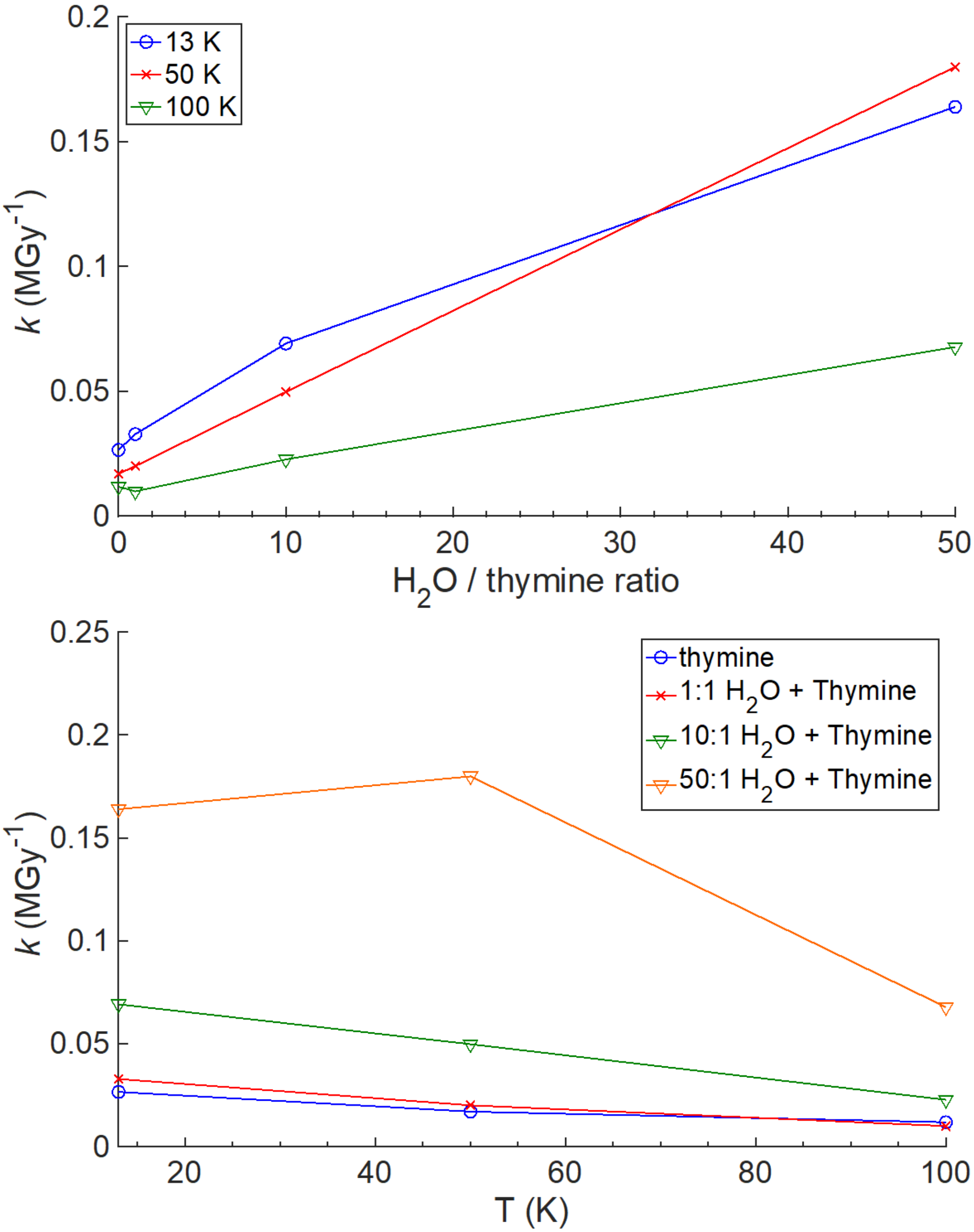
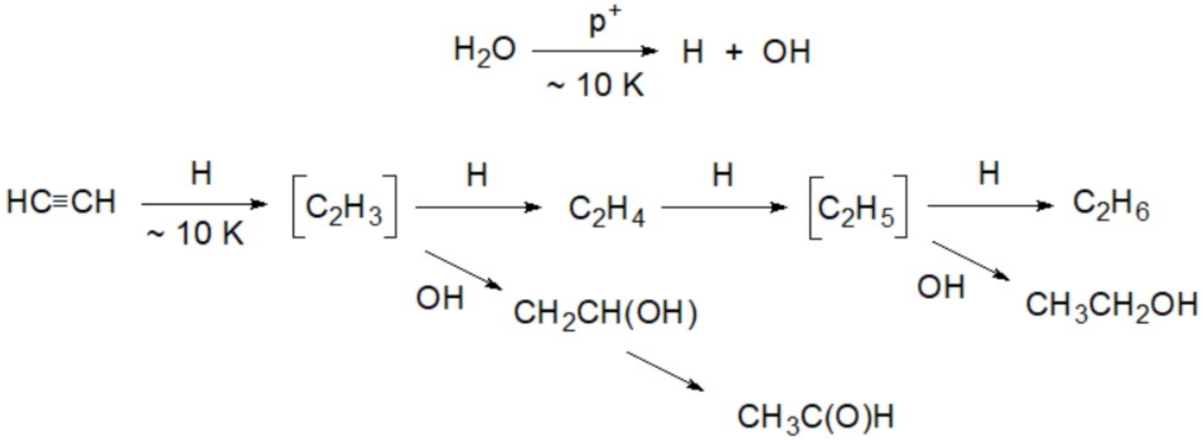


Figure 9. The radiolytic destruction rate constant *k* of thymine as a function of: (top) the ratio of water to thymine and (bottom) the temperature.

Scheme 1. Radiolysis of solid $C_2H_2$ in $H_2O$ ice.



Scheme 2. Radiolysis of CO in $H_2O$ ice.

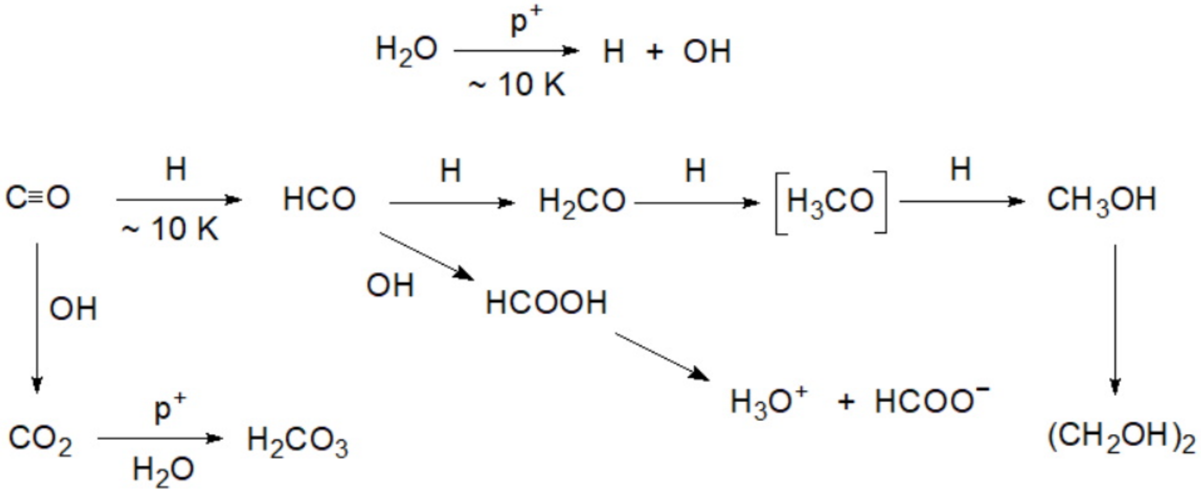


**Table 1. Measurements of Infrared Band Strengths and Optical Constants of Ices**

| Ice Studied | Reference(s) |
|---|---|
| $CH_4$ | 30 |
| $C_2H_6$ | 31 |
| $C_2H_4$ | 31 |
| $C_2H_2$ | 32 |
| $C_3H_8$ | 33 |
| $C_3H_6$ | 33 |
| $C_3H_4$ | 33 |
| $CH_3OH$ | 30 |
| $C_2H_5OH$ | 34[a] |
| $CO_2$ | 30, 3 |
| $N_2O$ | 30, 35 |
| $HC(O)CH_3$ | 36[a] |
| $HC(O)CH_2CH_3$ | 37 |
| $HCC\text{-}C(O)H$ | 38 |
| $(CH_3)_2CO$ | 39 |
| $(CH_3)_2O$ | 40 |
| $c\text{-}C_3H_6O$ | 26[a] |
| $C_2H_5COOCH_3$ | 41[a] |
| $(OCH_3)_2CO$ | 42[a] |
| $c\text{-}C_3H_5\text{-}C(O)H$ | 43[a] |
| $HCN$ | 44 |
| $C_2N_2$ | 44 |
| $CH_3CN$ | 44 |
| $C_2H_5CN$ | 44 |
| $HC_3N$ | 44 |
| $H_2S$ | 45 |
| $CH_3SH$ | 45, 46[a] |
| $C_2H_5SH$ | 45[a] |
| $C_3H_7SH$ | 45[a] |
| $CH_3CH(SH)CH_3$ | 45[a] |

[a] Band strengths published, but not optical constants.

**Table 2. Amino acids identified in hydrolyzed refractory residues from irradiated ices**

| Amino Acid | $H_2O$ $CH_3OH$ $NH_3$ HCN Far-UV photolysis [58] | $H_2O$ $CH_3OH$ $NH_3$ CO $CO_2$ Far-UV photolysis [59] | $H_2O$ $CH_3OH$ $NH_3$ Far-UV photolysis [60] | $H_2O$ $CH_4$ $NH_3$ 3-MeV p+ radiolysis [61] | $CH_3CN$ and $H_2O$ $CH_3CN$ 1-MeV p+ radiolysis [56] |
|---|---|---|---|---|---|
| glycine | ✓ | ✓ | ✓ | ✓ | ✓ |
| α-alanine | ✓ | ✓ | ✓ | ✓ | ✓ |
| β-alanine | ✓ | ✓ | ✓ | ✓ | ✓ |
| serine | ✓ | ✓ |  |  |  |
| aspartic acid |  | ✓ | ✓ |  | ✓ |
| α-aminobutyric acid |  | ✓ | ✓ | ✓ | ✓ |
| β-aminobutyric acid |  |  |  | ✓ | ✓ |
| γ-aminobutyric acid |  |  |  | ✓ | ✓ |
| glutamic acid |  |  |  |  | ✓ |
| valine |  | ✓ |  |  |  |
| di- and secondary amino acids |  | ✓ | ✓ |  |  |