

Astrochemistry Examples in the Classroom

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For over 20 years I have taught undergraduate courses in general and physical chemistry as well as in astronomy and astrobiology. During that time I also have maintained an active research collaboration with scientists at NASA's Goddard Space Flight Center and have been a member of both the American Chemical Society and American Astronomical Society. These activities have placed me on the chemistry–astronomy interface and have given me insight and experience into how astronomical topics can be used in chemistry courses.

In this article I will describe some of my own experiences with astrochemical examples in the classroom and offer suggestions for chemistry instructors. These suggestions are suitable for the first or second year in U.S. college chemistry curricula, although some of them might fit into high-school classes. A future article will cover applications and examples for more-advanced chemistry students. The suggestions made here are largely taken from my own research, and all have been student-tested in chemistry classrooms.

Some Background

Most of my students have studied chemistry in high school, but lack all but the most elementary knowledge of either astronomy or geology. These same students are largely from urban environments, and I suspect that that is true for most students in the United States. Early in a general chemistry course I find it useful to say that while the Earth's air and water are vital to our existence, the Earth's total reservoir of water accounts for a trivial amount of our planet's mass, and the height of our atmosphere, compared to the Earth's radius, is akin to the skin on an onion. At this point I add that chemists and chemistry are concerned with all of nature and not just what we experience on the Earth's surface. I also find it helpful to review some basic astronomical facts such as the following:

- The Sun is a star.
- All individual stars that can be seen with the unaided eye are part of a grand collection of stars called the Milky Way galaxy.
- The Milky Way is one galaxy among billions.
- The Milky Way's shape is roughly that of a music or data CD with a diameter of about 10^{18} km.
- To reach the Earth, a ray of light travels about 8 minutes if it comes from the Sun, 4 years if coming from the next closest star, 50,000 years if coming from the center of the Milky Way, and about 2.9 million years if coming from the next nearest sizable galaxy.
- For the overwhelming majority of its existence, over 98% of a star's mass is due to hydrogen and helium.

All of this places the Earth in a context within the Milky Way, but what of our astronomical neighbors therein? The Milky Way is home to about two hundred billion stars and

Table 1. Typical Characteristics of Cool Interstellar Nebulae

Type of Nebula	Mass/ kg	Diameter/ km	Number Density/ cm^{-3}	Temp/ K	Pressure/ atm
Diffuse	10^{32}	1×10^{14}	50	80	5×10^{-19}
Dense or Molecular	10^{34}	2×10^{14}	5000	10	7×10^{-18}

their attendant planets, including those in our solar system. The largest entity in the Milky Way, by volume, is the interstellar medium (ISM), the space between the stars. Far from being empty, the ISM accounts for about 10% of the galaxy's visible mass, mostly in the form of interstellar H atoms at a density of ~ 1 H per cm^3 (1, 2).

The ISM also contains a vast number of clouds, called nebulae (singular is nebula). The physical and chemical conditions within these clouds vary greatly, but their composition is largely hydrogen and helium gas ($\sim 98\%$) and dust grains on the order of $0.1 \mu\text{m}$ in size. Although interstellar dust is known to have an amorphous silicate component, grain chemistry and physics remain active areas of research (3, 4). Characteristics of two types of interstellar nebulae of interest to astrochemists (5) are given in Table 1. Note that entries in the last column follow from the ideal gas law.

Visual aids are useful in presenting this background material to chemistry students, not to mention helpful in removing the misconceptions that chemistry's domain is only the microscopic and solely the terrestrial. A photograph of the Andromeda Galaxy, which is thought to be similar to our own Milky Way, is shown in Figure 1. The Andromeda Galaxy contains several hundred billion stars, is about 2.9 million light years (2.7×10^{19} km) away, and has a diameter of



Figure 1. The unaided eye can see the Andromeda Galaxy on a clear, dark night but cannot resolve its component stars. This galaxy is external to our own, as all other galaxies are, and has a diameter of about 170,000 light years (1.6×10^{18} km). (Courtesy of Robert Gendler; <http://www.robgendlerastropics.com>, accessed June 2006).

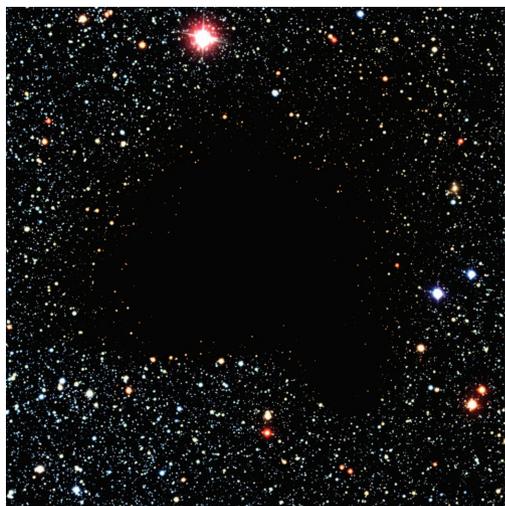


Figure 2. B68, a dark absorption nebula within our own galaxy, is about half a light year (5×10^{12} km) across. (Courtesy of the European Southern Observatory; <http://www.eso.org>, accessed Jun 2006).

about 170,000 light years (1.6×10^{18} km). It is external to the Milky Way galaxy.

A much smaller and closer object, a dark nebula known as B68 (Figure 2) is “only” about 500 light years (5×10^{15} km) away and half a light year (5×10^{12} km) across. This interstellar object is within the Milky Way. B68 looks dark because it contains cold (~ 10 K) dust grains and gas, which block starlight behind the cloud from reaching us. Because the dust grains are cold, gas-phase atoms and molecules in the cloud can stick to them. Over time the grains acquire an icy coating of material that undergoes chemical reactions from, for example, exposure to cosmic radiation. If the reactions are energetic enough, the product molecules can be ejected back into the gas phase. Grain–grain collisions, sputtering, photoejection, and shock waves from exploding stars (supernovae) are other ways proposed to move material from icy grain mantles to the surrounding gas phase (see, for example Bringa and Johnson (6) and references therein).

The remainder of this article focuses on chemistry classroom examples, mainly taken from studies of the ISM. Since the matter forming stars, and ultimately planets, comes from the ISM, its chemistry can tell us much about the early Earth and its environment. Remnants of the formation of our own solar system, and ancient ISM chemistry, are still with us in the form of cometary and meteoritic material.

What Is a Natural Product?

The term “natural product” is often used by chemists to identify an organic compound produced on the Earth with minimal assistance from *homo sapiens*. Nature, however, goes beyond 25°C and 1 bar in her choice of environments. It is important that chemistry students recognize this and be made aware that unconventional environments with extremes of temperature, radiation, pressure, salinity, and acidity, among other factors, are all the subject of research by scientists. Further, students should realize that the chemical concepts they

study, even in elementary courses, apply to a wide variety of environmental conditions.

This brings us back to the title of this section. To astrochemists, natural products can form under conditions that are quite exotic by terrestrial standards. Nebulae scattered among the Milky Way galaxy can be found with densities of only 1000 atoms and molecules per cubic centimeter and temperatures on the order of 10 K. Chemical reactions under these conditions have to be powered by nonthermal energy sources, such as cosmic rays (mostly high-energy protons) and UV light from stars. The products of such reactions include familiar molecules as well as species that are difficult or impossible to make in terrestrial laboratories, but they are all natural products to the astrochemist.

Interstellar Molecules

The development of astrochemistry largely parallels the development of spectroscopy, and for good reason. Most astronomical objects are so distant that only remote sensing is feasible. Among the spectroscopic pioneers were Robert Bunsen (1811–1899) and Gustav Kirchhoff (1824–1887), who are well known to most chemists, and William and Marie Huggins, of the late 19th century. They, their contemporaries, and their successors demonstrated the utility of spectroscopy for probing the chemistry and physics of extraterrestrial objects (7).

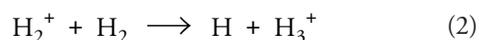
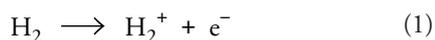
The first century of astronomical spectroscopy was restricted to observations with visible light, but other spectral regions became increasingly accessible and important in the 20th century. Observations have now been made with both Earth-based and orbiting spectrometers and with light ranging from X-rays to radio wavelengths.

The molecules so far detected in interstellar space (8) are summarized in Table 2. Students seeing this list for the first time are often surprised that supposedly empty space contains such an extensive and varied set of compounds. Within this list are both organics and inorganics, ranging from diatomics to long-chain unsaturated polyynes. When teaching introductory chemistry courses I have often found that Table 2 can be used to raise students’ interest in such tasks as nomenclature, assigning oxidation numbers, molecular structure, Lewis dot formulas, and chemical bonding. For example, adding “These molecules have been discovered in interstellar space” to a worksheet on Lewis structures can help motivate students while demonstrating the wide (literally!) applicability of chemical concepts. Many examples of isomers are found in Table 2, such as $(\text{CH}_3)_2\text{O}/\text{CH}_3\text{CH}_2\text{OH}$, HCN/HNC , and $\text{HCO}^+/\text{HOC}^+$. The ability of one element to substitute for another, within the same family on the periodic table, can be illustrated with $\text{H}_2\text{O}/\text{H}_2\text{S}$, CH_4/SiH_4 , HNCO/HNCS , and $\text{H}_2\text{CO}/\text{H}_2\text{CS}$. Pairs such as $\text{CH}_3\text{CN}/\text{NH}_2\text{CN}$, $\text{H}_2\text{C}=\text{CH}_2/\text{H}_2\text{C}=\text{NH}$, and $\text{CH}_3\text{OH}/\text{CH}_3\text{NH}_2$ can help demonstrate the concept of isoelectronicity. Table 2 also suggests some future interstellar molecular discoveries. Since SO_2 is known, it is safe to assume that interstellar O_3 might eventually be found, oxygen having a much greater cosmic abundance than sulfur. Also, the existence of CH_3CN and CH_3NC , and HCN and HNC , suggests that other nitrile–isonitrile pairs await detection.

Extraterrestrial Acid–Base Chemistry

Discussions of acid–base chemistry in most introductory chemistry texts focus on aqueous solutions, but most of the known universe does not permit the existence of liquid water. Nevertheless, acid–base concepts are still applicable in extraterrestrial environments and cover molecules few students would consider either acidic or alkaline.

The most abundant interstellar molecule is H_2 , as one might expect from the high cosmic abundance of hydrogen. Cosmic radiation ionizes H_2 in a dense nebula at a rate of about 10^{-17} molecule $^{-1}$ s $^{-1}$, to give H_2^+ . From there a proton-transfer reaction produces H_3^+ , the entire sequence being as follows:

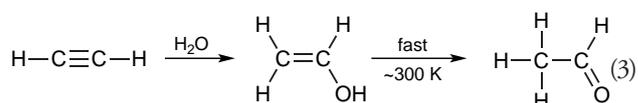


Pathways similar to the above are thought responsible for the formation of a variety of interstellar acid–base pairs. The known interstellar conjugate acids and bases as of July 2006 (Table 3) were all detected spectroscopically. With the exception of H_3O^+ , most of the conjugate acids in the table probably are new to chemistry students. In using this table in my own lectures, I have found that even students who know the definition of a conjugate acid or conjugate base

are surprised that N_2 or CO can serve as proton acceptors. As for what's not in Table 3, although radio astronomers have identified NH_3 , the corresponding conjugate acid, NH_4^+ , has not been found. This is likely due to the ammonium ion's lack of pure rotational transitions. The data in Tables 2 and 3 suggest that other conjugate acid–base couples may await discovery. Aside from NH_4^+ , one expects hardy anions such as CN^- , CH_3COO^- , and OH^- to exist under the right conditions. An assignment of $HCOO^-$ has been suggested for two solid-phase infrared features in the spectra of several protostellar sources (9).

Erlenmeyer's Rule and Keto–Enol Tautomerism

Many of the molecules in Table 2 carry a story that can be used to both capture student attention and illustrate a concept. Vinyl alcohol is one such molecule. As long ago as 1881, Emil Erlenmeyer (1825–1909) found that direct hydration of alkynes gave an aldehyde, as opposed to the enol tautomer one might predict (10). This preference for the keto product is still sometimes referred to as Erlenmeyer's Rule. To take a specific example, the expected path for addition of H_2O to acetylene is



Organic chemistry texts often display such a reaction sequence, with comments about the instability of the expected enol compared to the observed aldehyde. The instability of vinyl alcohol, $CH_2CH(OH)$, relative to acetaldehyde, $CH_3C(O)H$, is such that the alcohol's preparation usually requires decomposition of a larger molecule (11–13) or synthesis from ethylene and a source of atomic oxygen, followed by trapping (14). Gas-phase IR (13) and microwave spectra (15) have been obtained for vinyl alcohol, while more complex variants, with somewhat greater stability, have been studied with NMR and other methods (16).

Experiments in 1998 suggested that the Erlenmeyer's rule prediction of acetaldehyde from the addition of H_2O to acetylene might be circumvented if the reaction took place at a low temperature, such as in interstellar space (17). Subsequently, radio astronomers announced that vinyl alcohol had been detected in a region of space near the center of our galaxy (18). Additional experiments soon showed that vinyl al-

Table 2. Interstellar Molecules by Number of Atoms

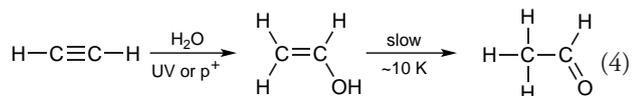
No of Atoms	Molecules
2	H_2 , CO, CSi, CP, CS, NO, NS, SO, HCl, NaCl, KCl, AlCl, AlF, PN, SiN, SiO, SiS, NH, OH, C_2 , CN, HF, FeO, LiH, CH, CH^+ , CO^+ , SO^+ , SH, N_2 , O_2
3	H_2O , H_2S , HCN, HNC, CO_2 , SO_2 , MgCN, MgNC, NaCN, N_2O , NH_2 , OCS, CH_2 , HCO, C_3 , C_2H , C_2O , C_2S , AlNC, HNO, SiCN, N_2H^+ , SiNC, c-SiC $_2$, HCO^+ , HOC^+ , HCS $^+$, H_3^+ , OCN $^-$
4	NH_3 , H_2CO , H_2CS , C_2H_2 , HNCO, HNCS, H_3O^+ , SiC $_3$, C_3S , H_2CN , c-C $_3H$, l-C $_3H$, HCCN, CH_3C_2CN , C_3O , HCNH $^+$, HOCO $^+$
5	CH_4 , SiH $_4$, CH_2NH , NH_2CN , CH_2CO , HCOOH, HCCCN, HCCNC, c-C $_3H_2$, l-C $_3H_2$, CH_2CN , H_2COH^+ , C_4Si , C_5 , HNC CC , C_4H
6	CH_3OH , CH_3SH , C_2H_4 , H(CC) $_2H$, CH_3CN , CH_3NC , HC(O)NH $_2$, HCCC(O)H, HC_3NH^+ , HC_4N , C_5N , C_5H , H_2CCCC , c-C $_2H_2C(O)$, H_2CCNH
7	HC(O)CH $_3$, c-C $_2H_4O$, $CH_2CH(OH)$, CH_3CCH , CH_3NH_2 , $CH_2CH(CN)$, H(CC) $_2CN$, C_6H
8	CH_3COOH , HC(O)OCH $_3$, HOCH $_2C(O)H$, CH_3CCCN , H_2C_6 , H(CC) $_3H$, $C_2H_3C(O)H$, C_7H , $H_2CCCH(CN)$
9	(CH_3) $_2O$, CH_3CH_2OH , CH_3CH_2CN , CH_3C_4H , HC_7N , C_8H , $CH_3C(O)NH_2$
10	(CH_3) $_2CO$, HOCH $_2CH_2OH$, $C_2H_5C(O)H$, $CH_3(CC)_2CN$
11	HC $_9N$, CH_3C_6H
12	C_6H_6
13	HC $_{11}N$

NOTE: The list is accurate as of July 1, 2006. See ref 8 for methods of detection. Some molecules detected in circumstellar regions. c = cyclic and l = linear.

Table 3. Gas-Phase Interstellar Acid–Base Pairs

Conjugate Base	Conjugate Acid
H_2	H_3^+
N_2	HN_2^+
CO	HCO^+/HOC^+
CS	HCS $^+$
CO_2	HOCO $^+$
H_2O	H_3O^+
HCN	HCNH $^+$
H_2CO	H_2COH^+
HC $_3N$	HC $_3NH^+$

cohol can indeed form in interstellar space by the addition of H₂O across the C≡C bond of acetylene and that the necessary energy can come from either UV photons or cosmic rays (19):



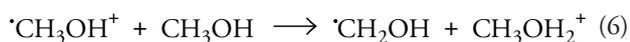
Given the great difference in temperatures between cold, dark nebulae (~10 K) and typical lab-bench conditions, it is not surprising that the tendency of vinyl alcohol to tautomerize is altered in interstellar regions.

Interstellar Antifreeze

Methyl alcohol was first identified as a gas-phase interstellar molecule in 1970 (20), and more recent observations indicate that it also exists frozen on the surfaces of cold interstellar grains (21). The low temperatures of such grains prohibit thermally-initiated chemical reactions, and the opacity of the surrounding clouds hinders photo-initiated processes. However, as noted earlier, ionizing radiation, such as cosmic rays, can penetrate such environments and initiate chemistry on any icy material coating an interstellar grain.

Chemists have long known (22) that room-temperature radiolysis of liquid CH₃OH yields ethylene glycol, HOCH₂CH₂OH, through formation and coupling of •CH₂OH radicals, but only recently have irradiations of solid-phase methanol been done. Experiments in 2000 showed that cosmic-ray bombardment of frozen methanol will yield the glycol, suggesting that this molecule was a good candidate for astronomical searches (9). Radio astronomers subsequently found ethylene glycol in interstellar space (23), as did astronomers observing the gaseous products emanating from Comet Hale-Bopp (24).

While the existence of extraterrestrial ethylene glycol is of inherent interest, its presumed synthetic path offers examples of ionization, proton transfer, and radical-radical reactions for students. The sequence is given in eqs 5–7:

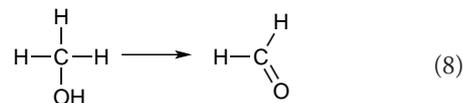


Other routes to •CH₂OH are possible, such as the initial formation of CH₃O• followed by isomerization.

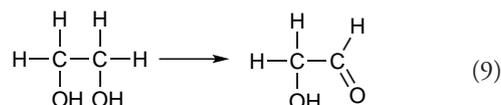
Carbohydrate Astrochemistry

An important lesson from these examples is that differences in terrestrial and extraterrestrial conditions can change what one regards as a stable molecule. Glycolaldehyde provides yet another illustration. As purchased from commercial suppliers, crystalline glycolaldehyde is actually a cyclic dimer, which can be heated to about 80 °C under vacuum to produce the monomer, HC(O)CH₂OH. Given the monomer's empirical formula of C₂(H₂O)₂, and its structure, glycolaldehyde is sometimes considered an elementary sugar.

In 1999 the discovery of interstellar monomeric glycolaldehyde was reported (25). As of this writing, unambiguous laboratory evidence for a feasible synthesis of this molecule, under interstellar conditions, has not been published, but at least two possibilities suggest themselves. Since the photochemical decomposition of methanol yields form-aldehyde as



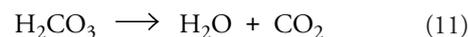
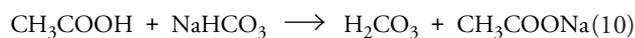
then the decomposition of ethylene glycol, a known extraterrestrial molecule, should make glycolaldehyde as shown below.



Alternatively, radiation- or photoinduced solid-phase dimerization of H₂CO at interstellar temperatures could be a source of glycolaldehyde (26), perhaps roughly analogous to the formose reaction for making sugars (27).

Carbonic Acid

As a last astrochemical example, consider a molecule that is *not* among the interstellar species of Table 2, namely carbonic acid, H₂CO₃. Perhaps like some other readers of this *Journal*, I was first introduced to chemistry with a reaction involving H₂CO₃, the combination of vinegar and baking soda to make carbon dioxide. Only later did I learn that the CO₂ evolution could be explained by a double-replacement reaction followed by the decomposition of the unstable H₂CO₃, as summarized in eqs 10 and 11:



Many introductory chemistry texts include carbonic acid in discussions of buffers and acid–base reactions in the bloodstream and in all cases mention the instability of H₂CO₃ relative to H₂O and CO₂. Although H₂CO₃ does exist in aqueous solution, with well-known *K_a* values, its low concentration (< 10⁻⁸ M at 25 °C and 1 bar) makes its direct study difficult.

In contrast to its behavior under typical laboratory conditions, if H₂CO₃ is formed at the temperature of many extraterrestrial environments, its dissociation might be hindered. This was the reasoning behind the first isolation and IR spectra reported for carbonic acid (28). A 1:1 H₂O:CO₂ mixture was frozen at 20 K in a vacuum chamber and then bombarded with 700 keV protons, from a Van de Graaff accelerator, to simulate exposure to cosmic rays. Infrared (IR) spectroscopy was used to examine both the initial reaction mixture and the final products. After proton irradiation, the sample had an IR spectrum showing unreacted starting material, some expected products (CO, O₃, and CO₃) and IR absorbances from an unknown carrier. Subsequent warming from 20 K to 250 K removed the starting materials, CO, O₃, and CO₃,

and left only a distinct set of IR features that soon were assigned to H_2CO_3 . Warming H_2CO_3 above 250 K in the vacuum chamber resulted in the molecule's rapid sublimation.

To confirm the synthesis of H_2CO_3 , isotopic substitution (28, 29) and independent syntheses (30, 31) were used. Later work included ab initio calculations of the IR spectrum and potential energy surface of H_2CO_3 (32) and searches for H_2CO_3 in Martian spectra (33). Gerakines et al. (34) showed that H_2CO_3 could be destroyed photolytically and used this observation to measure the molecule's intrinsic IR band strengths. More recently, both experimental (35) and theoretical (36) work have demonstrated that the presence of H_2O molecules is a critical factor in carbonic acid's decomposition into H_2O and CO_2 .

One of the first IR spectra of pure H_2CO_3 (28), along with the molecule's lowest-energy conformation (32), is shown in Figure 3. With the molecule drawn this way, students can see that it is merely a special type of carboxylic acid. Undergraduates who have been introduced to IR spectroscopy may recognize a few features in Figure 3, such as the C=O stretch near 1700 cm^{-1} and the network of OH stretches in the 3000 cm^{-1} region, probably broadened by hydrogen bonding. It is worth telling students that if one melted the solid sample from which this IR spectrum was taken, the resulting pure liquid H_2CO_3 would have a concentration near 13 M, nine orders of magnitude above that of H_2CO_3 in natural rainwater, $\sim 10^{-8}\text{ M}$.

The H_2CO_3 story is valuable in itself since students find it interesting that a three-element, six-atom molecule commonly found in soft drinks has so far eluded most attempts at isolation and direct detection. Significantly, it has been shown that H_2CO_3 can be sublimed under vacuum and then recondensed without dissociation (37). This gives cause to hope that gas-phase interstellar H_2CO_3 may one day be detected, adding this elusive species to the other interstellar molecules of Table 2. Along these lines, it is useful to remind students that there are many exciting problems, such as the astronomical detection of H_2CO_3 , awaiting the next generation of scientists.

Other Examples and Material

For additional background material, the review in this *Journal* by Carbó and Ginebreda (38) is still useful as an introduction, although it lacks coverage of laboratory-related work, newer molecular detections, and developments in theoretical models. Other earlier articles in this *Journal* have treated somewhat more-specialized astronomy-related topics such as nuclear chemistry and subatomic particles (39), ab initio calculations (40), and a lab assignment for "advanced physical chemistry" students (41). The present article has emphasized astrochemical examples of *molecular* properties such as structure and reactivity, two concerns of essentially all who teach and study beginning chemistry.

Many of the citations in this article are to papers and books that are easily located, but some of the periodicals may be unfamiliar and unavailable to chemistry instructors. Fortunately, many of the best astronomical journals allow free online access to back issues older than about five years. Searches covering almost all of the astrochemical literature

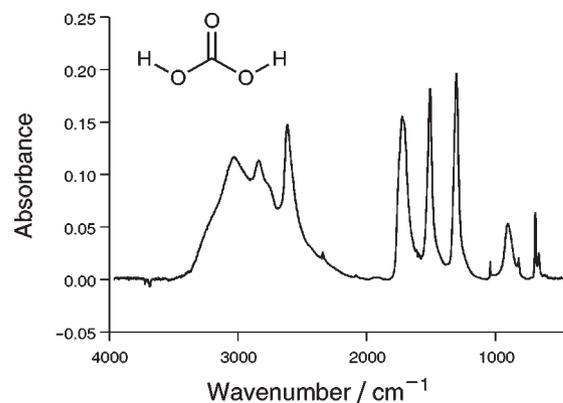


Figure 3. An early infrared spectrum of solid H_2CO_3 at 250 K. The lowest-energy structure is shown.

are free and online at the Harvard ADS abstract service (42). Also, the NASA Cosmic Ice Laboratory Web site (43) has links to some active astrochemistry research groups and to original articles.

Finally, while the suggestions described here have mostly been drawn from recent work on interstellar chemistry, the astrochemistry of the solar system also provides many interesting case-histories for classroom use. For example, organic molecules, including amino acids, have been found in meteorites (44), H_2SO_4 clouds exist on Venus (45), H_2O acts like dry ice on Mars (46), and the $\cdot\text{CH}_3$ radical has been discovered in the atmospheres of the planets Saturn (47) and Neptune (48). To borrow from Descartes, these case-histories have been "intentionally omitted so as to leave to others the pleasure of discovery" (49).

Acknowledgments

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