may have been domesticated some hundreds, or even thousands, of kilometers away from the center of its founder-stock germ plasm. Thus, the location of founder germ plasm stocks without supplemental evidence cannot be used for confident reconstruction of the locale of final domestication.

Increasing archaeobotanical evidence indicates that the beginning of agriculture, as well as of crop domestication, was not necessarily a single event but a process of trial and error. For oats and rye, for example, the beginnings of cultivation and subsequent domestication are separated by millennia and great distances. For the Near East, current data suggest that at least three or four species can be considered as early pioneer crops, which predate the seven well-recognized species of founder crops. Because two of these pioneer species—barley and lentil—belong to the group of founder crops as well, our understanding of the domestication of these species must be revised. In the PPNA, Near Eastern human groups in two regions already possessed and applied agricultural knowledge: In the north, they planted lentil and perhaps rye; and in the south, they raised barley and probably oat, together with imported lentil. Although this early barley and lentil was eventually domesticated in the region, two of the crops raised or gathered there—rye and oats—were abandoned.

The transition to food production in eastern North America shows a notable similarity to the Near East. There, indigenous plants—chenopod (*Chenopodium berlandieri* subsp. *jonesianum*), marsh elder (*Iva annua* var. *macrocarpa*), squash (*Cucurbita pepo* subsp. *ovifera*), and sunflower (*Helianthus annuus* var. *macrocarpus*)—became domesticants under indigenous group management between 5000 and 4000 years before the present. In contrast, the cereal-like erect knotweed (*Polygonum erectum*), little barley (*Hordeum pusillum*), and maygrass (*Phalaris caroliniana*), though clearly of economic importance as cultivated crops by about 2500 to 2200 years before present, never became morphological domesticates. With the shift to maize-centered agriculture about 900 C.E. and the arrival of the common bean (*Phaseolus vulgaris*) several centuries later, local eastern crops became less important, and by 1800 C.E., only sunflower and squash were still being grown (*17*).

Thus, both in the Near East and early eastern North America, the first stage of agriculture was cultivating annual wild plants; the second stage was cultivating both wild types and domesticants; and the last stage was the cultivation of domesticants alone. Finally, the recent discovery of PPNA fig domestication (*18*) raises the question of whether, in worldwide locales of agriculture origin, fruit trees were domesticated contemporaneously with the annuals.


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10.1126/science.1127235

ASTRONOMY

# A Key Molecular Ion in the Universe and in the Laboratory

**T. R. Geballe and T. Oka**

The molecular ion $H_3^+$ is abundant in interstellar clouds and presents many interesting puzzles in the laboratory. A recent conference explored the current knowledge about this species and its implications for astrophysics.

The protonated hydrogen molecule, $H_3^+$ is the most abundant molecular ion in the universe and plays a pivotal role in interstellar chemistry. As the simplest of all polyatomic molecules, $H_3^+$ is fascinating to both physicists and chemists, but lately research in astronomy has been an important driver of both laboratory work and theory. Interstellar clouds are almost entirely molecular hydrogen, and anything that causes ionization of $H_2$ in them should lead to the production of $H_3^+$. On 16 to 18 January 2006, researchers from different fields in which $H_3^+$ plays a major role met in London, at the Royal Society and at University College London, to discuss this fundamental molecular ion from a variety of perspectives. A similar meeting on $H_3^+$ took place in 2000, but since then many exciting developments related to this ion and its deuterated species, both in the laboratory and in space, made a new discussion meeting a necessity.

$H_3^+$ was discovered in 1911 by J. J. Thomson (*1*). First observed as an "evanescent" trace product of a discharge in $H_2$, its abundance was soon found to exceed that of both $H^+$ and $H_2^+$ in most hydrogen plasmas, demonstrating both its ease of formation and stability. It was realized that $H_3^+$ was being formed by the efficient reaction, $H_2^+ + H_2 \rightarrow H_3^+ + H$ (*2*). $H_3^+$ is highly reactive, happily donating a proton to almost every atom and molecule it encounters. In astrophysical environments, the principal seed is cosmic rays, which, as they traverse interstellar clouds, leave trails of $H_2^+$ ions in their wakes, which are rapidly converted to $H_3^+$ by the aforementioned reaction. The importance of $H_3^+$ for interstellar chemistry was recognized in 1973 in two seminal papers (*3*, *4*), both of which demonstrated that $H_3^+$ is the base of a tree of ion-molecule reactions that produce many of the molecules found in space.

Although the presence of $H_3^+$ in dense clouds could be inferred, direct detection of $H_3^+$ proved to be elusive. The only method of observing the molecule in space is via the $\nu_2$ vibration-rotation band whose fundamental occurs near a wavelength of 4 μm. This spectrum was observed in the laboratory in 1980 (*5*). It took 16 additional years before $H_3^+$ was detected in interstellar space (*6*).

The 2000 Discussion Meeting took place less than 4 years after this detection, and roughly a decade after the ion had been found in the aurorae of Jupiter, Saturn, and Uranus (*7*–*9*). At that time it was already clear that there was a problem in understanding the interstellar data. Although the abundance of $H_3^+$ in dense clouds was roughly as expected, it was more than an order of magnitude higher than predicted in diffuse clouds where abundant electrons destroy $H_3^+$ (*10*). That difference has only become more striking in subse-

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quent years as unexpectedly large amounts of $H_3^+$ have been found in additional diffuse clouds (*11*). Now a combination of measurements in the laboratory and at the telescope have shown that the difference is likely a result of the cosmic-ray ionization rate being much larger in diffuse clouds than in dense clouds (*12*). Although the reason for this is not completely understood, it is well established observationally that, contrary to initial expectations, the abundance of $H_3^+$ relative to all forms of hydrogen is 10 times higher in diffuse clouds than in dense clouds, and the total amount of $H_3^+$ is much higher as well. $H_3^+$ has thus emerged as a unique and powerful astrophysical probe to study the diffuse interstellar medium.

An inspiring example of this is the recent discovery of a vast amount of high-temperature and low-density gas in the Central Molecular Zone of the Milky Way, a region of radius ~200 pc at the Galactic center (*13*). The physical state of the gas in that region, as clearly revealed by spectroscopy of three lines of $H_3^+$ and one line of carbon monoxide (see the figure), is unique in the Galaxy. The locations along the 8 kpc–long line of sight to the Galactic center where most of the narrow absorption components are formed were already well known from previous radio and infrared observations. However, because the two molecules probe different types of clouds (CO is much more abundant in dense clouds than in diffuse clouds, whereas the opposite is true for $H_3^+$), in combination they allow one to discriminate between cloud types. The new measurements strongly constrain the amount of dense molecular gas in the center. Together with other gaseous components in the nucleus observed at radio, infrared, and x-ray wavelengths, the $H_3^+$ measurements provide information vital for understanding the complex energetics of the Galactic center. $H_3^+$ has also been detected for the first time in an external galaxy (*14*), opening up a new and potentially fruitful area of study.

A remarkable manifestation of the fundamental role $H_3^+$ plays in interstellar chemistry has recently been revealed in the extremely high deuterium fractionation in the cold cores of dark clouds, where multiply deuterated molecules such as $D_2CO$, $ND_3$, and $CD_3OH$ have been discovered. In these clouds the usual destroyers of $H_3^+$ such as CO are frozen onto dust particles, and HD becomes the principal agent for removal of $H_3^+$, through the reaction $H_3^+ + HD \rightarrow H_2D^+ + H$. This reaction and similar ones producing more deuterated species proceed efficiently due to the low temperature. For some cases model calculations predict that, despite the extremely low abundance of deuterium, the abundance of $H_3^+$ isotopomers is in the order $H_3^+ < H_2D^+ < D_2H^+ << D_3^+$ (*15*). Recent detections of $H_2D^+$ and $D_2H^+$ support this prediction (*16*).

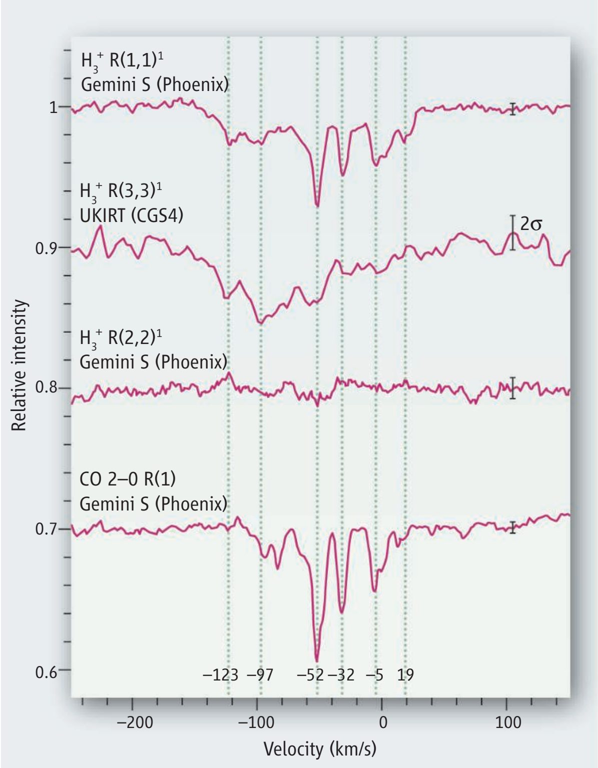
Studies of $H_3^+$ are yielding new and exciting results in planetary astronomy. Since its discovery in the jovian ionosphere in 1989, $H_3^+$ has been used to study plasmas in planetary ionospheres from ground-based observatories. Now it is becoming increasingly clear that $H_3^+$ also plays a major role in the dynamics of giant planets through both its efficient emission and ion-neutral coupling (*17*).

Although the new astronomical observations spearhead much of the progress in $H_3^+$ science, during the same period theoretical and laboratory progress in understanding $H_3^+$ has been no less exciting. Perhaps the most drastic change from the last meeting is the advent of the badly needed full-fledged theory of dissociative recombination. An extensive theoretical calculation that fully takes into account the multidimensionality of the process, including the Jahn-Teller effect (*18*), has given a value for the dissociative recombination rate that is more than two orders of magnitude higher than the one obtained in 2000 and is close to the experimental result. Measurements with rotationally cooled $H_3^+$ have also been performed (*11*). After decades of uncertainty, a reliable rate of dissociative recombination, which is of overwhelming importance for understanding the chemistry of the diffuse interstellar medium, appears to have been determined.

Interplay between theory and experiment has been the cornerstone of $H_3^+$ spectroscopy, and the past two decades have seen several theoretical groups competing to achieve a rigorous theory and the experimental groups vying to extend the observations to higher energy. Theoretical efforts have now reached the level where a first-principles calculation based only on natural constants gives spectroscopic accuracy of better than 1 $cm^{-1}$ for states up to 12,500 $cm^{-1}$ above ground (*19*). This may be likened to what the theory for $H_2$ had achieved in 1975. Theories of $H_3^+$ in the triplet state and asymptotic vibrational states near the dissociation limit have also been developed.

Meanwhile, laboratory spectroscopy of overtone and combination bands of $H_3^+$ has reached the visible region, probing high vibrational levels that exceed the barrier to linearity (the vigorously vibrating molecule is on average still an equilateral triangle, but instantaneously linear) (*20*). The higher the energy, the weaker the spectrum, but increases in sensitivity by many orders of magnitude afforded by various new techniques more than compensate. A new method of action spectroscopy, utilizing the ion-neutral reaction of $H_3^+$ with Ar, has been introduced. With the aforementioned discoveries of high deuterium fractionation in cold interstellar clouds, spectroscopy of deuterated species has been greatly developed (*21*). The new method of lowering the velocity of $H_3^+$ by sympathetic cooling with laser-cooled ultracold atomic ions (*22*) is noteworthy because it opens the path to ultrahigh-resolution spectroscopy of $H_3^+$ and its deuterated species.

Understanding the amazingly high interstellar deuterium fractionation has also required detailed information on the reaction rate of $H_3^+$ and HD and other similar reactions. In addition, the observation of high-temperature gas in the Galactic center




**Telltale molecules.** Spectra of three lines of $H_3^+$ at 3.5 to 3.7 μm and one line of CO at 2.34 μm toward the galactic center source GCS 3-2, observed at the Gemini South Telescope on Cerro Pachon, Chile, and the United Kingdom Infrared Telescope on Mauna Kea, Hawaii (*13*). The spectra are offset and are magnified by different factors. The sharp absorption components seen in the $H_3^+$ $R(1,1)^1$ and CO lines arise in dense clouds, mostly in spiral arms between the Sun and the center but some very close to the center. The broad absorption profile seen in the $H_3^+$ $R(3,3)^1$ line and overlying the sharp features in the $H_3^+$ $R(1,1)^1$ profile is thought to arise in gas within 200 pc of the nucleus. The presence of the $H_3^+$ $R(3,3)^1$ line demonstrates that the gas is warm and the absence of the $H_3^+$ $R(2,2)^1$ line shows that it is diffuse.



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requires detailed information on the state-specific collision rate and ortho-to-para conversions of $H_2$, $H_3^+$, and isotopomers. Such information is being provided by means of an ingenious temperature-variable cryogenic ion trap (*23*)

The Discussion Meeting contained many other exciting reports on $H_3^+$ and its deuterated species, as well as the related species, $H_3$, $H_3^-$, $H_3^{++}$, $H_5^+$, $H_3^+(H_2)_n$, etc. (*24*). With the 100th anniversary of the discovery of $H_3^+$ only 5 years away and research forging ahead on many fronts, it is likely that a centennial Discussion Meeting on this most interesting and important molecular ion and its relatives will be timely.


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10.1126/science.1126279

CLIMATE CHANGE

# Permafrost and the Global Carbon Budget

**Climate warming will thaw permafrost, releasing trapped carbon from this high-latitude reservoir and further exacerbating global warming.**

**Sergey A. Zimov, Edward A. G. Schuur, F. Stuart Chapin III**

The carbon content of Earth's atmosphere has increased from ~360 gigatons (Gt)—mainly as $CO_2$—during the last glacial maximum to ~560 Gt during preindustrial times and ~730 Gt today. These changes reflect redistributions among the main global carbon reservoirs. The largest such reservoir is the ocean (40,000 Gt, of which 2500 Gt is organic carbon), followed by soils (1500 Gt) and vegetation (650 Gt). There is also a large geological reservoir, from which ~6.5 Gt of carbon are released annually to the atmosphere by burning fossil fuels.

Permafrost (permanently frozen ground) is an additional large carbon reservoir that is rarely incorporated into analyses of changes in global carbon reservoirs. Here we illustrate the importance of permafrost carbon in the global carbon budget by describing the past and potential future dynamics of frozen loess (windblown dust, termed yedoma in Siberia) that was deposited during the glacial age, covering more than 1 million km$^2$ of the north plains of Siberia and Central Alaska to an average depth of ~25 m.

The frozen yedoma represents relict soils of the mammoth steppe-tundra ecosystem that occupied this territory during glacial times (*1*). As windblown or river-borne materials accumulated on the soil surface, the bottom of the previously thawed soil layer became incorporated into permafrost. These sediments contain little of the humus that characterizes modern ecosystems of the region, but they comprise large amounts of grass roots (see the figure) and animal bones, resulting in a carbon content that is much higher than is typical of most thawed mineral soils. Frozen yedoma deposits across Siberia and Alaska typically have average carbon contents from 2% to 5%—roughly 10 to 30 times the amount of carbon generally found in deep, nonpermafrost mineral soils.

Using an overall average carbon concentration for yedoma of ~2.6%, as well as the typical bulk density, average thickness, and ice-wedge content of the yedoma, we estimate the carbon reservoir in frozen yedoma to be ~500 Gt (*2*). Another ~400 Gt of carbon are contained in nonyedoma permafrost (excluding peatlands) (*3*), and 50 to 70 Gt reside in the peatbogs of western Siberia (*4*). These preliminary estimates indicate that permafrost is a large carbon reservoir, intermediate in size between those of vegetation and soils.

Our laboratory incubations and field experiments show that the organic matter in yedoma decomposes quickly when thawed, resulting in respiration rates of initially 10 to 40 g of carbon per m$^3$ per day, and then 0.5 to 5 g of carbon per m$^3$ per day over several years. These rates are similar to those of productive northern grassland soils. If these rates are sustained in the long term, as field observations suggest, then most carbon in recently thawed yedoma will be released within a century—a striking contrast to the preservation of carbon for tens of thousands of years when frozen in permafrost.

Some local thawing of yedoma occurs independently of climate change. When permafrost ice wedges thaw, the ground subsides (thermokarst), forming lakes. The abundant thermokarst lakes on yedoma territory migrate across the plains as thawing and subsidence occur along their margins. During the Holocene (the past 10,000 years), about half of the yedoma thawed beneath these migratory lakes and then refroze when the lakes had moved on.

The yedoma carbon beneath the thermokarst lakes is decomposed by microbes under anaerobic conditions, producing methane that is released to the atmosphere primarily by bubbling (*5*). Near eroding lake shores, methane bubbling is so high that channels through the lake ice remain open all winter. During a thaw/freeze cycle associated with lake migration, ~30% of yedoma carbon is decomposed by microbes and converted to methane. As a potent greenhouse gas, this methane contributes to climate warming.

In response to climate warming, permafrost sediments have already begun to thaw (*6*), with extreme projections that almost all yedoma will thaw by the end of the 21st century (*7*). What would happen to the carbon derived from permafrost if high-latitude warming continues?

The unique isotopic signature of permafrost carbon provides clues from past warming episodes, such as the transition from the last glacial maximum to the Holocene. The $^{13}C/^{12}C$ isotope ratio of the permafrost reservoir is similar to that of soil, vegetation, and

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