Four hundred light-years from Earth in the constellation Ophiuchus—known as the snake bearer because it resembles a man grasping a serpent—floats an interstellar dust cloud. This relatively dense gathering of molecules and particles holds the makings of two future stars. Made mostly of hydrogen gas, the cloud also contains helium molecules and frozen dust grains of carbon and silicon sometimes coated with ice. The list of ingredients making up this star nursery is interesting, but perhaps pedestrian, to chemists on Earth. That is, until you get to the part of the list that mentions trihydrogen, or H$_3^+$. This unearthly molecule consists of three protons arranged in an equilateral triangle, sharing two electrons among them.

The cloud’s temperature hovers a few tens of degrees above absolute zero. In this environment, atoms and molecules occasionally collide and then bounce apart unchanged because they don’t have enough energy to react. The highly reactive H$_3^+$, however, is primed to donate a proton to anything it stumbles into. The little molecule enriches the chemistry of the cloud by launching chains of reactions that make larger and more diverse molecules involving mostly carbon, hydrogen, and oxygen. This extreme reactivity, a boon for interstellar chemistry, also means that in a dense molecular environment, such as that found on Earth, H$_3^+$’s existence is so short-lived, it’s rarely observed. As a result, it’s a relative unknown among chemists.

Astronomers, who are more familiar with the simple molecule, have exploited it as a temperature gauge and a cosmological clock, using it as a tool to understand conditions around planets in our solar system and beyond. “Every time we look at H$_3^+$, it helps us uncover some cool, crazy physics,” says James O’Donoghue, a planetary scientist at the Japan Aerospace Exploration Agency. Meanwhile, scientists here on Earth are using new technology to generate the triangular molecule and learn the atomic details of how it forms. H$_3^+$ is helping unravel the mysteries of planets, outer space, star formation, and fundamental chemical processes.

Discovery in Space
British physicist J. J. Thomson first discovered H$_3^+$ in 1911 in a plasma tube in his lab using an early form of mass spectrometry. By the 1960s, scientists speculated that H$_3^+$ might be found in space, but it was 1989 before researchers spotted its characteristic signal coming from Jupiter.

The discovery of H$_3^+$ in space hinged on a description of the molecule’s spectrum, parts of which had been defined in 1980 by the University of Chicago’s Takeshi Oka. The molecule emits infrared light at signature wavelengths that can penetrate the vast distances of space, arriving unimpeded at detectors here on Earth. Importantly, the ion unleashes its strongest emissions in a set of wavelengths rarely given off by other molecules, making it a relatively easy molecule to spot, even light-years away.

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Jupiter has spectacular auroras—colorful clouds of charged gas—but in the 1980s little was known of their chemistry, says Steve Miller, a planetary scientist at University College London. So Pierre Drossart of the Paris Observatory, Miller, and their colleagues focused an infrared telescope on the auroras hovering over Jupiter’s poles. With a sensitive new spectrometer hooked up to the telescope, they expected to see evidence of lots of hydrogen gas, H₂, the most abundant molecule on the gas giant. Indeed, they did. But the spectrometer also picked up another set of unexpected IR wavelengths; Miller and colleagues realized that their predicted IR spectrum of H₃⁺, which they had built from Oka’s work, was a perfect match for the mysterious light emissions coming from Jupiter. The unexpected first-time discovery of H₃⁺ in space inspired scientists to search for it elsewhere in the universe. In the past 30 years, researchers have found H₃⁺ nearly everywhere in outer space that they have looked. Its presence has given them a tool to directly observe processes in space that had previously been only theorized about.

“It’s not just that we can see H₃⁺ in the upper atmospheres of planets like Jupiter, Saturn, and Uranus, but we can derive properties such as the temperature and density of H₃⁺, which telegraphs the temperature and density of the molecule’s surroundings, O’Donoghue says.

Out in space, when sunlight strikes H₃⁺ or molecules bang into it, the ion absorbs energy and then releases light at particular IR wavelengths. The intensity of the energy emitted at each wavelength varies according to the molecule’s temperature, allowing H₃⁺ to act as a virtual thermometer of outer space.

Models can also predict the amount of light that a single molecule of H₃⁺ should emit at various temperatures. Because of this ability, measuring the light intensity that reaches their detectors enables researchers to derive the concentration of H₃⁺ above planets’ surfaces. Knowing this allows scientists to infer the density of other molecules, such as the water in Saturn’s upper atmosphere.

These kinds of measurements allowed O’Donoghue and colleagues this year to confirm a long-held hypothesis about the rings of Saturn. The rings are made of chunks and particles of ice, held in orbit by the balance between the planet’s gravity and the spinning rings’ centrifugal force. Scientists have long suspected that sometimes these particles rain down onto the planet. They proposed that ice particles might get charged by collisions with micrometeors rocketing across space or by ultraviolet light from the sun. These charged particles could then get captured by Saturn’s magnetic field and be drawn into the planet’s upper atmosphere, where they could sublimate into gaseous, neutrally charged water vapor, the scientists hypothesized. Neutral water reduces the density of electrons in the atmosphere, which in turn prolongs the life span of H₃⁺, so areas of the planet receiving such ring rain should have higher densities of H₃⁺.

Studies of H₃⁺ emissions from Saturn had observed high concentrations of the molecule encircling the planet right where water should be coming out of the rings and into the atmosphere. But a detailed analysis of temperature and density at different latitudes was missing, O’Donoghue says.

After carrying out such analyses, he and his team not only confirmed that H₃⁺ was present in patterns that backed up the ring rain theory but also calculated that the entire ring system will be gone in less than 300 million years, a blink of an eye in cosmological time, he says.

The H₃⁺ ion has also helped solve a mystery about Jupiter’s upper atmosphere. Jupiter is five times as far from the sun as Earth is, so its upper atmosphere should be extremely cold. And yet scientists have measured it to be about as warm as Earth’s upper atmosphere. Why?

Earlier modeling studies had suggested that sound waves emanating from the surface of Jupiter could be warming the upper atmosphere. Acoustic waves produced above thunderstorms are known to travel upward and heat Earth’s atmosphere. Jupiter’s famous Great Red Spot hosts the largest storm in our solar system, with winds gusting to over 600 km/h, so it would stand to reason that it might play a part in warming the planet’s atmosphere.

Using wavelengths emitted by H₃⁺, O’Donoghue and his team reported in 2016 that they had mapped the temperature of Jupiter’s upper atmosphere for the first time, finding that the maximum temperatures occurred right over the Great Red Spot. The team determined that the pattern of planetary temperatures was consistent with researchers’ hypothesis that sound waves from the Great Red Spot are heating the atmosphere. The sound waves...
travel upward, breaking at the outer layer of the atmosphere like waves on a beach, causing $\text{H}_3^+$ and other molecules there to vibrate and rotate more than normal. This increased kinetic energy means a heated atmosphere.

Such findings can help scientists understand more terrestrial matters, too. Building on these results has revealed that the low sound frequencies of ocean waves crashing into each other could be heating Earth’s upper atmosphere.

Beyond the Solar System

O’Donoghue is looking to find $\text{H}_3^+$ in the atmosphere of an exoplanet, a planet outside our solar system. Seeing the characteristic light emissions of $\text{H}_3^+$ around an exoplanet would indicate the presence of an ionosphere, a layer of charged particles in its upper atmosphere. By probing the ionosphere, scientists could learn about conditions on the planet, including whether it might harbor life.

In certain situations, a special form of $\text{H}_3^+$ can also act as a chemical clock, helping astronomers determine how long processes take far beyond our solar system. For instance, scientists have many questions about how long it takes to make a star, says Olli Sipilä, an astrochemist at the Max Planck Institute for Extraterrestrial Physics. Star formation occurs over tens of thousands of years, so conventional clocks can’t track them. But the relative concentrations of two types of hydrogen molecules—ortho- and para-$\text{H}_2$, each with a characteristic IR spectrum—change in a predictable way as a dust cloud ages, allowing scientists to derive the passage of time.

Sipilä and his colleagues had trained their sights on the cold, dense dust cloud in Ophiuchus, hoping to measure its age. The star-forming process underway there is analogous to the one that birthed our solar system, right? not our sun? so researchers are naturally keen to know how long it takes. Models have made predictions ranging from 100,000 years to more than 1 million years.

The scientists considered using the ortho and para forms of hydrogen to judge the age of the cloud. “But the problem is that this interstellar cloud is too cold to allow us to directly measure $\text{H}_3^+$ from IR emissions, Sipilä says. On the other hand, $\text{H}_3^+$ is easy to detect, but the problem is that “$\text{H}_3^+$ itself is not a good chemical clock,” Sipilä says. There is no straightforward connection to the ratios of ortho- and para-$\text{H}_3$ in $\text{H}_3^+$. Fortunately, in cold interstellar space, $\text{H}_3^+$ sometimes substitutes a deuterium ion—a proton and neutron—for a hydrogen ion, forming $\text{H}_2\text{D}^+$. The ortho and para forms of $\text{H}_2\text{D}^+$ emit light in different IR wavelengths. But until recently this ratio could not be used to determine the age of these distant clouds: while the light from ortho-$\text{H}_2\text{D}^+$ will reach a ground-based IR telescope, Earth’s atmosphere obstructs the IR wavelengths released from para-$\text{H}_2\text{D}^+$. Now, however, thanks to a new telescope onboard an airplane flying 14 km above Earth, unobscured by the atmosphere, the researchers measured the IR light emitted from para-$\text{H}_2\text{D}^+$ for the first time in 2014. Using these measurements, Sipilä and his team estimate the cloud core to be 1 million years old. The finding marks the first confirmed detection of para-$\text{H}_2\text{D}^+$ in space.

An Atomic View of $\text{H}_3^+$

The world of $\text{H}_3^+$ is not limited to the cold reaches of outer space. Under the right conditions, scientists can create the ion in earth-bound chemistry laboratories, says Marcos Dantus, a chemical physicist at Michigan State University. Dantus and his team specialize in using ultrafast lasers to make molecular movies, exciting atoms with strobe-like light pulses and watching how they change on a femtosecond scale. They thought they might learn more about the dynamics of $\text{H}_3^+$’s behavior by filming how it forms, timing how long it takes to break and form bonds, and determining where the atoms go. The 2017 project started from sheer curiosity, Dantus says.

Earlier studies observed that intense laser fields trained on small organic molecules such as methanol would cause $\text{H}_3^+$ to form, so Dantus and his team thought they could use this tactic to make $\text{H}_3^+$ for their molecular movies. Even so, the scientists predicted that making $\text{H}_3^+$ wouldn’t be easy. “Starting from methanol, the formation of $\text{H}_3^+$ requires us to doubly ionize the molecule; three chemical bonds need to break, and three new chemical bonds need to form,” he says. And all this needs to occur faster than the time it takes for atoms to fly away from each other and lose their chance to react.

To capture what really happens as $\text{H}_3^+$ forms, the scientists injected a thin beam of gaseous methanol into a vacuum. Then they zapped the methanol with an intense
laser beam to trigger the reaction. As they applied femtosecond laser pulses, which recur in less time than it takes a C−H bond to vibrate, time-of-flight mass spectrometry provided measurements of the energy state of the molecules. A computer simulation translated the data into a molecular movie of the reaction.

The researchers found that the reaction proceeds by forming a neutral H$_2$ molecule from two hydrogen atoms on methanol, which becomes doubly charged under the strong-field laser. But instead of flying away, the H$_2$ roams around—it liberates itself from the CHOH$^{2+}$ and then comes back to snatch a proton to form H$_3^+$. The entire reaction takes about 100 fs. “Our measurements are providing the first dynamic information at the molecular level for H$_3^+$ chemistry,” Dantus says. This is the first documented case of a so-called roaming H$_2$ reaction, which is significant because roaming mechanisms are a budding research area of chemistry, he says.

These methanol-based reactions are also relevant to astrochemistry, Dantus says. “Most of the galaxies have molecular clouds that contain methanol and small amounts of larger organic molecules. All those molecules are being bombarded by radiation and high-energy particles, both of which cause the formation of H$_3^+$,” he says. The reactions are likely similar to the ones he created in the laboratory. They also matter here on Earth in situations where high-energy beams are used: “Next time we have an X-ray, or when we have laser eye surgery we will know that H$_3^+$ is being formed,” even if it sticks around for only a short while, he says. What that means for situations like these, if anything, is yet unknown because the chemistry is just being discovered.

Meanwhile, H$_3^+$ continues to hurl its emitted wavelengths out into the universe for earth-bound scientists to detect. These scientists hope to probe more areas of the cosmos for the molecule’s reactive presence. H$_3^+$ was there at the beginning, University College London’s Miller says, and it will be there at the end.

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