

saically among and even within living snake species. External hindlimbs may be present as clawlike vestiges in both sexes or in males only, or may be absent; pelvic elements vary from none to three among basal snake taxa (11, 16).

Conversely, well-developed hindlimbs in *Haasiophis* and *Pachyrhachis* might reflect a second evolutionary origin of the tetrapod hindlimb (see the figure, bottom of previous page). Thus, although the Tchernov fossil seems to have bones that closely resemble the femur, tibia and fibula, tarsals, and tiny toes of other tetrapods, they may not be strictly homologous. This surprising conclusion is bolstered by recent evidence for the regulation of vestigial leg morphogenesis in living pythons by the hox family of genes (10). In terms of evolutionary biology, those fossil hindlimbs are neomorphs (nonhomologs) because tetrapod hindlimbs are not found in the common ancestor of *Haasiophis*,

*Pachyrhachis* and other snakes. However, they could be "latent homologs" (17) if genes that regulate hindlimb development (such as hox genes) persisted in those legless ancestors.

However much controversy the beautifully preserved skulls and bones described by Lee *et al.* (4–7) and Tchernov *et al.* (3) continue to generate, they are sure to figure prominently in our growing understanding of snake evolution. These Cretaceous Middle Eastern fossils also significantly broaden our understanding of the spectrum of possible relationships between body elongation and limb reduction in snakes (1, 10, 11). An unusual combination of hindlimb and skull features in these extinct forms, together with the considerable morphological variation among living taxa, and the proven applicability of molecular genetics, confirm that snakes will prove particularly valuable for integrative studies of development and evolution.

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## PERSPECTIVES: MOLECULAR SPECTROSCOPY

H<sub>3</sub><sup>+</sup>—an Ion with Many Talents

Benjamin J. McCall and Takeshi Oka

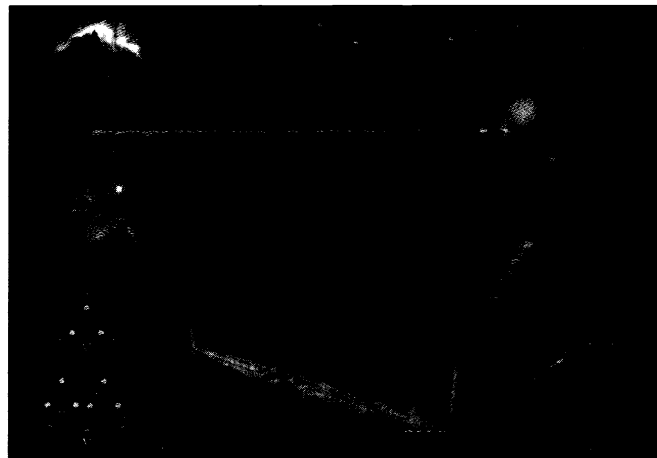
The H<sub>3</sub><sup>+</sup> ion plays an important role in diverse fields from chemistry to astronomy (see the figure). Not only does this most fundamental of molecular ions serve as a benchmark for quantum chemists, it was recently discovered both in molecular clouds (1) and in the diffuse interstellar medium (2), and it provides a tool for characterizing Jupiter's atmosphere from afar. At a recent discussion meeting in London (3), chemists, physicists, and astronomers came together to take stock of what is known about H<sub>3</sub><sup>+</sup> and take a glimpse into its future.

The H<sub>3</sub><sup>+</sup> molecular ion consists of three protons bound by two electrons and can be thought of as a hydrogen molecule (H<sub>2</sub>) with an extra proton attached (H<sup>+</sup>). This ion is the dominant positively charged ion in molecular hydrogen plasmas and was first identified in 1911 by J. J. Thomson, using an early form of mass spectrometry (4). Because H<sub>3</sub><sup>+</sup> lacks a stable electronic excited state (necessary for electronic spectroscopy) and a permanent dipole moment (necessary for rotational spectroscopy), the only spectroscopic probe of this ion is its infrared rotation-vibration spectrum, which was first observed in the laboratory in 1980 (5).

In the two decades since this initial spectroscopic observation, over 600 spectral lines of H<sub>3</sub><sup>+</sup> in low-energy ro-vibrational states have been detected. Using state-of-the-art computers, theoretical spectroscopists are now able to reproduce this laboratory spectrum with high accuracy from first principles and provide predictions of

new lines to help guide laboratory work. Because H<sub>3</sub><sup>+</sup> is the simplest polyatomic molecule, these calculations for H<sub>3</sub><sup>+</sup> serve as a benchmark for calculations on other polyatomic molecules, such as water. In contrast to the low-energy spectrum, theorists have not yet been able to assign any of the over 27,000 spectral lines in the H<sub>3</sub><sup>+</sup> near-dissociation spectrum (6). If the sensitivity of the low-energy experiments can be substantially increased so that higher energy bands can be studied, and if the near-dissociation experiments can reach lower energies using visible lasers, the two techniques may eventually converge, leading to a complete theoretical understanding of this ion.

A controversy surrounds the recombination of H<sub>3</sub><sup>+</sup> with electrons (7), the dominant destruction mechanism in some plasmas. In the past three decades, laboratory measurements of this recombination rate have differed by four orders of magnitude. The situation has improved, but discrepancies between different experiments remain, and the rate is still uncertain to within a factor of 10. To make matters worse, the best theoretical estimates of the recombination rate are



**A collage of images related to H<sub>3</sub><sup>+</sup>.** In the laboratory, H<sub>3</sub><sup>+</sup> is produced in plasma tubes. The laboratory spectrum of the v<sub>2</sub> vibrational mode (from A. R. W. McKellar) can be understood in terms of the H<sub>3</sub><sup>+</sup> potential energy surface. The emission of H<sub>3</sub><sup>+</sup> from Jupiter (from J. E. P. Connerney, shown here overlaid on a visible image) allows remote probing of the jovian aurora. H<sub>3</sub><sup>+</sup> also plays a key role in the chemistry of molecular clouds, such as the one in the upper left (imaged by the Hubble Space Telescope), and has been spectroscopically detected in absorption from sources such as NGC 2024 IRS 2 near the Horsehead nebula.

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100 times lower than the experimental data. This enigma extends from the laboratory to interstellar space: Because the recombination process is the dominant destruction mechanism for  $H_3^+$  in diffuse clouds, the uncertainty in the electron recombination rate translates to a large uncertainty in the size of the diffuse clouds where  $H_3^+$  has been measured with the use of its infrared spectrum (2). The importance of reconciling theory and experiment and of reducing the present uncertainty in the value of the  $H_3^+$  electron recombination rate cannot be overemphasized.

$H_3^+$  also plays an important role in planetary science. Ever since it was first spectroscopically detected in emission from Jupiter's aurora (8), the ion has served as a useful remote probe of Jupiter's upper atmosphere (9). Because the strongest spectral lines of  $H_3^+$  are in a spectral region where few other molecules have lines,  $H_3^+$  can be observed on Jupiter with only an infrared camera with a narrow filter. With this technique, Jupiter's aurora can be imaged with ground-based telescopes, and the images can be used to create and evaluate detailed models of the jovian magnetosphere and the interaction between Jupiter and its moon Io. As the only hydrogenic species in this environment with efficient spontaneous emission,  $H_3^+$  is the dominant coolant of the jovian ionosphere. During the meeting, it was proposed that  $H_3^+$  may also play a major

role in the energy budget and the overall dynamics of the jovian magnetosphere. It was even suggested that  $H_3^+$  emission might be detectable from Jupiter-like planets orbiting other stars such as  $\tau$  Boötis.

In interstellar space,  $H_3^+$  forms the basis for an extensive network of ion-molecule reactions that are responsible for the creation of most of the molecules observed in interstellar space (10). This scheme of interstellar chemistry was directly confirmed when the infrared spectrum of  $H_3^+$  was observed in molecular clouds (1). Thanks to improvements in astronomical spectrometers, the detection of interstellar  $H_3^+$  is now almost routine, and observations of  $H_3^+$  can now be combined with those of other important molecules such as  $H_2$  and CO to characterize the physical and chemical conditions in interstellar clouds. The observations of dense molecular clouds are generally in accord with theoretical models of interstellar chemistry.

The present understanding of the chemistry of diffuse clouds is, in contrast, quite primitive. In addition to the long-standing enigmas of the high abundance of  $CH^+$  and the ubiquitous but unexplained diffuse interstellar bands, the  $H_3^+$  ion presents a new mystery. Given the current experimental values of the  $H_3^+$  electron recombination rate, the observations (2) suggest that  $H_3^+$  in diffuse clouds extends for unreasonably long distances (over a thousand light years).

The physics and chemistry of  $H_3^+$ , combined with the low density and temperature of interstellar space, lead to interesting phenomena such as extraordinary deuterium fractionation, bistability of chemical models, and radiative thermalization through forbidden rotational transitions. The discussions between astronomers, physicists, and chemists about the various processes in which  $H_3^+$  plays the pivotal role were inspiring, but, as expected, there are still more questions than answers. Hopefully, more astronomical observations and laboratory and theoretical studies will provide solutions to these problems in the coming years.

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#### PERSPECTIVES: HYDROCARBON CHEMISTRY

## Conquering the Carbon-Hydrogen Bond

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Considering the vast quantities of liquid and gaseous hydrocarbons brought annually from beneath Earth's surface, it is a pity that the vast majority of these precious raw materials

are burned as simple fuels for heating and transportation.

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Only a modest portion of these hydrocarbons—alkanes and aromatics—are converted into large-scale chemical intermediates for use in the chemical industry. But the controlled conversion of these hydrocarbons into the desired products remains a challenge. In this issue, Jia *et al.* on page 1992 (1) and Chen *et al.* on page

1995 (2) report important advances in the catalytic conversion of aromatic (1) and aliphatic (2) hydrocarbons into useful, reactive products.

The reactions of saturated alkanes themselves are limited to partial oxidations, such as the conversion of butane and oxygen into acetic acid. Saturated alkanes ( $C_nH_{2n+2}$ ) may be transformed into olefins ( $C_nH_{2n}$ ) by way of a high-temperature process called cracking. The unsaturated olefins easily react with both electron-deficient reagents (electrophiles) and electron-rich reagents (nucleophiles). Similarly, aromatics, with their  $\pi$  electron systems, undergo a variety of reactions with Lewis or Bronsted acids to give substituted derivatives. The resulting derivatized hydrocarbons can be used to produce more desirable, value-added materials.

Many of the industrial processes used to derivatize hydrocarbons are based on hetero-

geneous catalysts. Homogeneous transition metal complexes have long been believed to also be capable of catalyzing these processes. Already in 1970, the strong C-H bonds of aromatics were found to undergo addition to metal complexes, followed by conversion to a product with a more reactive functional group (3). Similar addition reactions of alkanes to transition metal complexes (4, 5) offered the hope of facile, selective conversion of the abundant alkanes into higher value products. These complexes typically contained electron-donating ligands and metals in low formal oxidation states. The hydrocarbon is effectively "reduced" upon cleavage of the C-H bond, whereas the metal is "oxidized," a process commonly referred to as "oxidative addition."

Despite this early progress in C-H activation, little progress toward catalytic hydrocarbon functionalization was not made until Waltz and Hartwig showed that linear alkanes could be reacted with a tungstenborane complex ( $L_nW-BR_2$ ) in a photochemical reaction to give a boron functionalized alkane ( $R'-BR_2$ ) (6). The alkylboron products can be converted into a wide variety of derivatives with well-established properties. With a related rhenium complex,

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