SCIENCE'S COMPASS

PERSPECTIVES: MOLECULAR SPECTROSCOPY

H₃⁺—an Ion with Many Talents

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The H₃⁺ ion plays an important role in diverse fields from chemistry to astrophysics (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 H₃⁺ and take a glimpse into its future.

The H₃⁺ molecular ion consists of three protons bound by two electrons and can be thought of as a hydrogen molecule (H₂) with an extra proton attached (H⁺). 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 H₃⁺ 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 H₃⁺ 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 H₃⁺ is the simplest polyatomic molecule, these calculations for H₃⁺ 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 H₃⁺ 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 H₃⁺ 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
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. 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\(_n\)H\(_{2n+2}\)) may be transformed into olefins (C\(_n\)H\(_{2n}\)) by 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 π electron systems, undergo a variety of reactions with Lewis or Brønsted 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 heterogeneous 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 contain 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 tungsten borane complex (L\(_2\)W–BR\(_3\)) in a photocatalytic reaction to give a boron functionalized alkane (R’–BR\(_3\)) (6). The alkylboron products can be converted into a wide variety of derivatives with well-established properties. With a related rhenum complex,