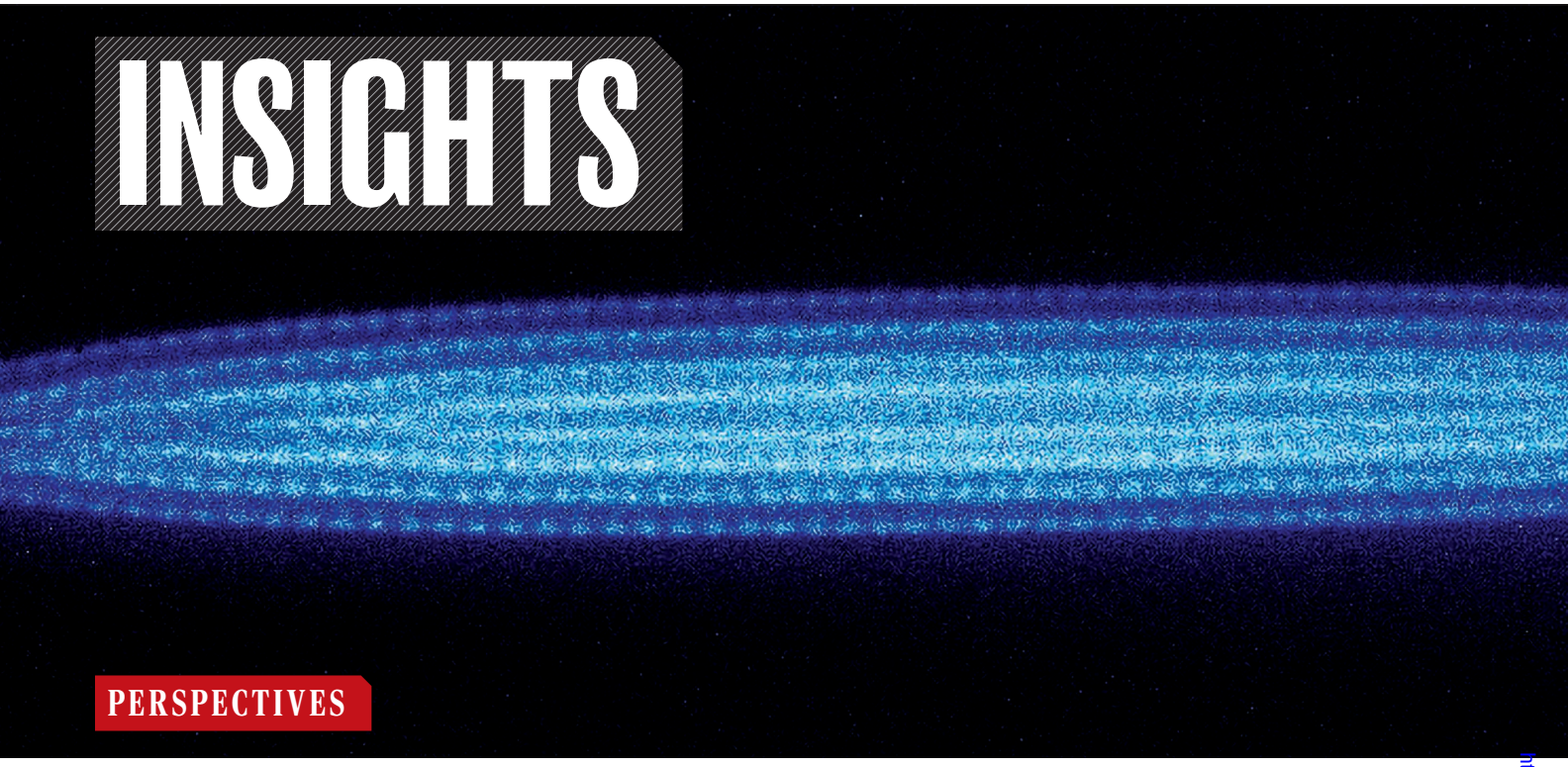

METROLOGY

High-precision molecular measurement

Spectroscopy of hydrogen deuteride ions provides the proton-to-electron mass ratio

By **Masaki Hori**

The hydrogen molecular ion ($H_2^+ \equiv p^+ + p^+ + e^-$) is the simplest molecule with two protons bound by an electron. Historically, it was the first molecule to be studied by using quantum mechanics, and it remains on the short list of experimentally accessible molecules for which a truly precise theoretical understanding is possible. However, several characteristics make precision optical spectroscopy of H_2^+ a formidable challenge in laboratory experiments. Hydrogen deuteride molecular ion ($HD^+ \equiv p^+ + d^+ + e^-$), in which one of the protons of H_2^+ is replaced by a deuteron (*1*–*3*), has an asymmetric dipolar structure that allows numerous vibrational-rotational transitions. These "rovibrational" transitions (ν_{rv}) have exceptionally narrow relative widths of less than 10^{-13} and occur at much higher rates when compared to the even narrower H_2^+ transitions. On page 1238 of this issue, Patra *et al.* report two frequencies with a precision of 2.9 parts per trillion and determine the mass ratio between the proton and electron (*2*).

Quantum electrodynamics (QED) is the relativistic quantum field theory that describes the electromagnetic interaction, which is among the four known fundamental interactions of nature. QED reveals the forces that act between the bound electron, proton, and deuteron in HD^+ that arise from an infinite series of elementary processes of progressively higher complexity. These involve the exchange of virtual photons that exist as transient quantum fluctuations of the underlying electromagnetic field. The fluctuations can temporarily transform into pairs of virtual electrons and positrons that immediately annihilate back into photons. This gives rise to minute but measurable changes in the structure of HD^+. Some processes involving multiple virtual particles that cause sub–parts-per-billion scale shifts in the HD^+ energies have taken a decade to calculate (*2*–*5*). Despite these difficulties, QED remains the most stringently tested part of the standard model.

"So high a consistency between multiple experiments at the forefront of precision measurements is unusual."

The authors compared their measured HD^+ frequencies with the results of QED calculations. Under the assumption that there are no deviations from QED predictions, the authors determined the proton-to-electron mass ratio M_p/m_e with a precision of 21 parts per trillion. This value lies within 30 and 350 parts per trillion of other experiments that instead measured the characteristic motions of a proton (*6*) or a H_2^+ ion (*7*) confined within the magnetic fields of ion traps. The result is also in excellent agreement with the ratio determined to a similar precision by a recent measurement carried out in Düsseldorf (*3*) of several hyperfine components of a HD^+ rotational transition. So high a consistency between multiple experiments at the forefront of precision measurements is unusual.

The experiment required samples of the reactive HD^+ ions to be isolated in an ultrahigh-vacuum environment and cooled

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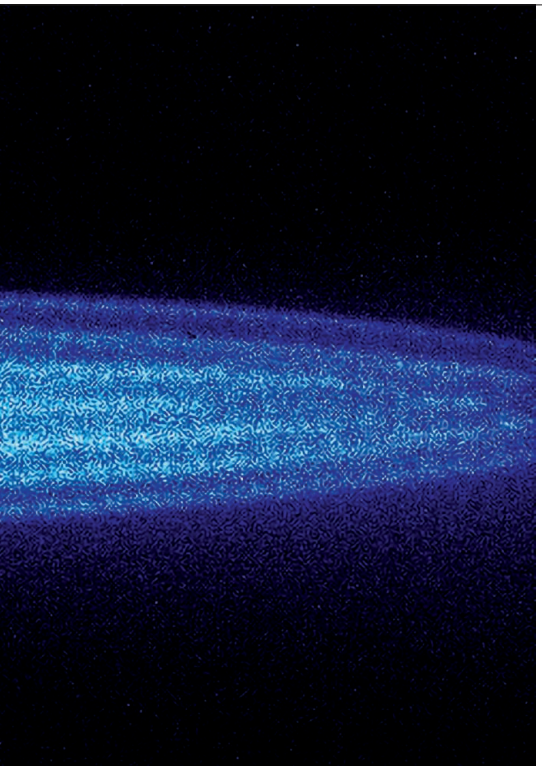
IMAGE: SAYAN PATRA/VU AMSTERDAM



False-color image of a Coulomb crystal containing some 1000 Be^+ ions cooled to a temperature of less than 10 mK. The long dimension of the ellipsoidal crystal is ~1 mm. A small number of HD^+ molecular ions (not visible) are suspended in the darker horizontal band at the center of the crystal.

to temperature $T \approx 10$ mK to minimize the Doppler broadenings of the spectral resonances due to the thermal motions. The authors achieved this by first confining a cloud of beryllium ions (Be^+) in the oscillating electric field of a radiofrequency ion trap. The Be^+ ions were irradiated with an ultraviolet laser beam, so that higher-velocity ions would scatter more laser photons. This velocity-selective scattering eventually cooled an ensemble of ≈1000 Be^+ ions into the ordered structure of a so-called "Coulomb crystal" (*8*). The HD^+ ions were suspended in the center of the crystal and allowed to thermalize (see the figure). The ions were then irradiated with two counterpropagating laser beams with infrared frequencies ν_1 and ν_2 that excited the HD^+ transition when the sum $\nu_1 + \nu_2$ was tuned to ν_{rv}. The motion of each HD^+ ion in the trap was strongly confined within its own micrometer-sized volume, which allowed the observation of particularly narrow spectral lines.

Although the early pioneers (*1*) realized the potential of HD^+ experiments to eventually determine the physical constants, the numerous degrees of freedom in a three-body molecule made the theoretical evaluation vastly complicated. At the time, the HD^+ molecular frequencies were typically calculated with parts-per-million scale precision. This appeared to limit any determination of the proton-to-electron mass ratio to a similar precision. Development of computational techniques based on variational trial functions that included the molecular degrees of freedom occurred in the 1980s. These techniques were used to study muonic molecular heavy hydrogen ions [$(dd\mu)^+ \equiv d^+ + d^+ + \mu^-$ and $(dt\mu)^+ \equiv d^+ + t^+ + \mu^-$] to estimate some of the reaction rates relevant for the possibility of energy production by muon-catalyzed fusion. The methods were used to calculate the transition frequencies of neutral antiprotonic helium atoms ($\bar{p}He^+ \equiv \bar{p} + He^{2+} + e^-$) (*4, 5*), which eventually allowed the determination of the antiproton-to-electron mass ratio to a precision of 8 parts in 10^{10} (*9*). Advances in the calculations and measurements of the HD^+ frequencies (*2*–*4*) cumulated in the 2 parts per 10^{11} determination of the M_p/m_e ratio.

Several advances in fundamental physics could result from these observations. Other physical constants such as the Rydberg constant, the charge radii of protons and deuterons (*10*–*13*), and the deuteron-to-electron mass ratio (*14*) may eventually be determined. The charge radii are especially interesting, as deviations of up to 4% have been reported among the results of a few experiments (*10*–*13*). Some of these physical constants until recently could only be precisely determined on the basis of either the elegant simplicity of a single proton confined in an ion trap (*6*) or two-body systems, such as atomic hydrogen ($H \equiv p^+ + e^-$) (*10*–*12*), muonic hydrogen and deuterium atoms ($\mu H \equiv p^+ + \mu^-$ and $\mu D \equiv d^+ + \mu^-$) (*13*), or hydrogenic carbon ions ($^{12}C^{5+} \equiv {}^{12}C^{6+} + e^-$) (*15*). Upper limits have also been set on phenomena that may cause deviations from the predictions of QED like the possible existence of a fifth fundamental force that may act between the constituent particles of HD^+ ions (*3*). ■

REFERENCES AND NOTES

1. W. H. Wing, G. A. Ruff, W. E. Lamb, J. J. Spezeski, *Phys. Rev. Lett.* **36**, 1488 (1976).
2. S. Patra *et al.*, *Science* **369**, 1238 (2020).
3. S. Alighanbari, G. S. Giri, F. L. Constantin, V. I. Korobov, S. Schiller, *Nature* **581**, 152 (2020).
4. V. I. Korobov, L. Hilico, J.-P. Karr, *Phys. Rev. Lett.* **112**, 103003 (2014).
5. Z.-X. Zhong *et al.*, *Chin. Phys. B* **24**, 053102 (2015).
6. F. Heiße *et al.*, *Phys. Rev. Lett.* **119**, 033001 (2017).
7. A. Solders, I. Bergström, S. Nagy, M. Suhonen, R. Schuch, *Phys. Rev. A* **78**, 012514 (2008).
8. M. Drewsen, C. Brodersen, L. Hornekær, J. S. Hangst, J. P. Schifffer, *Phys. Rev. Lett.* **81**, 2878 (1998).
9. M. Hori *et al.*, *Science* **354**, 610 (2016).
10. A. Beyer *et al.*, *Science* **358**, 79 (2017).
11. H. Fleurbaey *et al.*, *Phys. Rev. Lett.* **120**, 183001 (2018).
12. N. Bezginov *et al.*, *Science* **365**, 1007 (2019).
13. R. Pohl *et al.*, *Science* **353**, 669 (2016).
14. D. J. Fink, E. G. Myers, *Phys. Rev. Lett.* **124**, 013001 (2020).
15. S. Sturm *et al.*, *Nature* **506**, 467 (2014).

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BIOGEOCHEMISTRY

Soil age alters the global silicon cycle

As rocks undergo prolonged chemical weathering, plants become more important for supplying bioavailable silicon

By **Joanna Carey**

Silicon (Si)—the second most abundant element in Earth's crust—relies largely on geological factors to control its mobilization. Thus, Si cycling through Earth's systems was often believed to be buffered from human disturbance (*1*). However, research over the past several decades has awakened scientists to the central role of vegetation in regulating Si availability in the biosphere (*2*, *3*). It is now beyond doubt that human disturbance affects Si biogeochemistry and its associated impact on carbon (C) sequestration rates. Attempts to decipher how human activities (namely deforestation and agricultural expansion) influence Si cycling have left scientists to reconcile conflicting data on the importance of geochemical versus biological controls on Si biogeochemistry (*4*, *5*). On page 1245 of this issue, de Tombeur *et al.* provide new insights into this debate by demonstrating the importance of soil age in regulating Si cycling (*6*).

The Si and C cycles are intricately linked at the global level. On geological time scales, the chemical weathering of mineral silicates consumes atmospheric carbon dioxide (CO_2), thus regulating Earth's climate (*1*). On biological time scales, the uptake of CO_2 by Si-requiring microscopic phytoplankton known as diatoms accounts for roughly half of the photosynthesis that occurs in global oceans (*7*). As such, the amount of Si exported from terrestrial uplands to marine waters can directly control the rate of photosynthetically driven CO_2 uptake (*8*).

However, Earth's biological Si cycle is not relegated only to aquatic systems. Terrestrial vegetation performs an integral function in Si biogeochemistry and provides

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