ASTROCHEMISTRY

Water on the Sun: Molecules Everywhere

Takeshi Oka

Ordinary polyatomic molecules like H_2O are not supposed to exist on the surface of the sun; at the high temperature of ~5800 K, a water molecule should dissociate into a free-radical OH and an H atom or further into an O atom and two H atoms. I therefore found the title of the 1995 report by Wallace *et al.* (*1*) "Water on the Sun" quite incredible, although completely believable after seeing the data. This reaction was in contrast to the possible discovery of water on the moon, which was sensationally reported in newspapers by way of a press release from the Pentagon. In this case, the scientists themselves were cautious (*2*), even though from a chemical point of view the presence of water on the moon is less surprising than that on the sun. The decisive difference between the two detective stories is the presence of an unmistakable fingerprint for the case of the sun: the laboratory infrared spectrum of hot water taken by Bernath and his co-workers matched exactly with the observed solar spectrum (*1*). On page 346 of this issue, Polyansky *et al.* (*3*) answer some of the theoretical questions about the spectra. Their results not only confirm the already solid evidence for H_2O on the sun but also demonstrate the power of a recent method of spectral analysis based on variational treatment of nuclear motions in a molecule.

Part of the solution to the puzzle is that H_2O is not found all over the surface of the sun but only in sunspot umbrae (central dark spots), where the temperature is lower, around 3200 K. The existence of molecules on "cool" stars—such as highly luminous red giants or obscure dwarfs, whose temperature in the photosphere is below 4000 K—has been well established observationally. Over the years, Tsuji has been studying chemical models to explain molecular abundance and opacity in such stars (*4*). His model predicts that water, methane, and ammonia are the most abundant species after hydrogen molecules in objects with temperature $T < 1000$ K, such as brown dwarfs. Nevertheless, the identification of H_2O in sunspots with the substantial column density of 2×10^{19} cm^{-2} is still very exciting.

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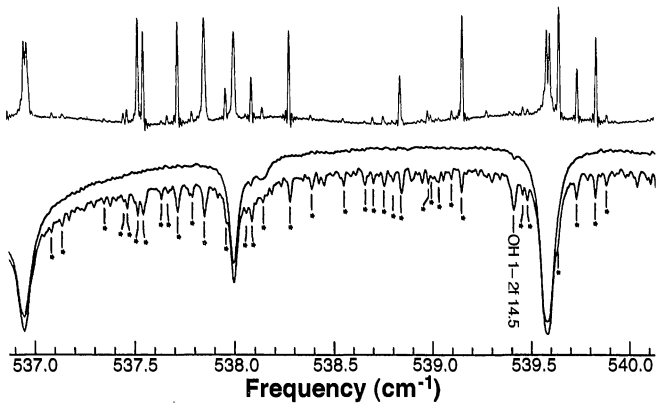
Wallace *et al.* (*1*) gave a comparison (see figure) of the observed infrared absorption spectra of a sunspot umbra and a penumbra (half dark spot), along with a laboratory emission spectrum. The three strong, broad features in the two lower curves are due to terrestrial water absorption and are incidental. The key feature is the extremely rich spectral structure in the umbra and laboratory spectra. Such intricate structure in the near-infrared region of 2.5 to 1.1 μm has been known for many years and was compiled in 1970 (*5*). Specialists of the water spectrum such as Benedict [cited in (*5*)], Flaud, and Camy-Peyret (*6*) proposed H_2O as the source of the spectrum and took laboratory flame spectra (at 2900 K), but somehow the identification of the spectrum had not been clearly claimed. The sunspot spectrum in the figure is not new either; it is a small portion of the spectrum recorded from 470 to 1233 cm^{-1} by Noyes *et al.* in 1982 (*7*). It is really the new laboratory spectrum of hot H_2O that has led to the identification.



Hot and hotter. The laboratory emission spectrum (**top trace**) of hot water at 1820 K and the observed spectra of a sunspot penumbra (**middle trace**) and a sunspot umbra at 3200 K (**lower trace**) (water peaks are indicated by the asterisks). The broad water features at 537, 538, and 539.6 cm^{-1} are due to terrestrial water in the lower two traces. [Adapted from Wallace *et al.* (*1*)]

The two spectra may look different at a glance, but closer examination shows exact coincidence in the frequencies of the spectral lines. Matching frequencies between astronomical and laboratory spectra has been the cornerstone in discoveries of molecules in space. The discriminative power of high-resolution spectroscopy is so high that many important radioastronomical discoveries have been claimed after the observation of one line (with few mistakes). The discovery of interstellar water by Townes and his colleagues was based on the only line of H_2O that appears in the centimeter-wavelength region (*8*). The matching of the frequencies of tens of spectral lines, as in the figure, is foolproof evidence of the H_2O detection. The two spectra look different because relative intensities of the lines are different and many spectral lines in the umbra spectrum are missing in the laboratory spectrum. This difference is because the temperature of Bernath's sample cell, 1820 K, was much lower than the umbra temperature of 3200 K, an example of the limit laboratory astrophysicists always experience in trying to mimic nature. This restriction sets a limit on empirical fingerprint matching by experiment; beyond this, we have to rely on theory.

The equilibrium structure of H_2O is an isosceles triangle with the apex angle of 104°, but in a real molecule, the nuclei do not stay still, deviating from this structure at any moment. The molecule vibrates and rotates, forming tens of thousands of quantized vibration-rotation levels. The spectrum (figure) is the result of transitions of H_2O between rotational levels and are more than 10 times stronger than the near-infrared transitions between vibrational states. As the temperature increases, higher quantum levels get populated and more spectral lines are observed. At room temperature (~300 K), the spectrum in the figure would be composed of the three strong atmospheric lines, whereas for the temperatures of 1820 and 3200 K, the number of lines increases by a factor of ~10 and ~30, respectively. Thus, in order to analyze a spectrum at high temperature, one needs to analyze higher energy quantum states. The traditional approach, in which vibrational and rotational motions are separated and interactions between them are treated by the perturbation method, does not work well.

Polyansky *et al.* (*3*) use a high-quality ab initio Born-Oppenheimer potential-energy surface given by Partridge and Schwenke (*9*) and solve the Schrödinger equation for the nuclear motion directly using a variational method. This type of brute force calculation made possible by the advent of modern computers is becoming the norm in high-resolution theoretical spectroscopy for simple and light polyatomic molecules. Such calculations by

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Miller, Tennyson, and Sutcliffe and many others has played a great role in understanding the H_3^+ spectrum in the laboratory and in space (*10*). Polyansky *et al.* (*3*) have demonstrated the power of this new method in approximately doubling the energy range for which assignments of the quantum states of H_2O have been made. This has led to an understanding of the spectral lines in the figure and a great many more in other frequency regions. It also revealed new spectroscopic features of hot water, such as strong rotational difference transitions induced by Fermi resonance and large splittings of normally nearly degenerate levels.

Over a longer term, the following two points come to mind. (i) The discovery of water on the sun, together with the recent observation of H_2O on many objects based on data from the Infrared Space Observatory satellite (*11*), is a part of the ongoing development of molecular astrophysics. Molecules are found everywhere, and it is now accepted that half of visible interstellar matter in this galaxy is in the form of molecules (*12*). This interplay of astronomy and chemistry will no doubt increase. (ii) The major remaining approximation in calculations of the sort that Polyansky *et al.* have done is the Born-Oppenheimer separation of electronic and nuclear motion. We can hope that full quantum mechanical treatment of the whole system without this approximation may now be possible, at least for simple molecules like H_3^+, with development of even more powerful computers.

References and Notes

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PROTEIN STRUCTURE

GAP into the Breach

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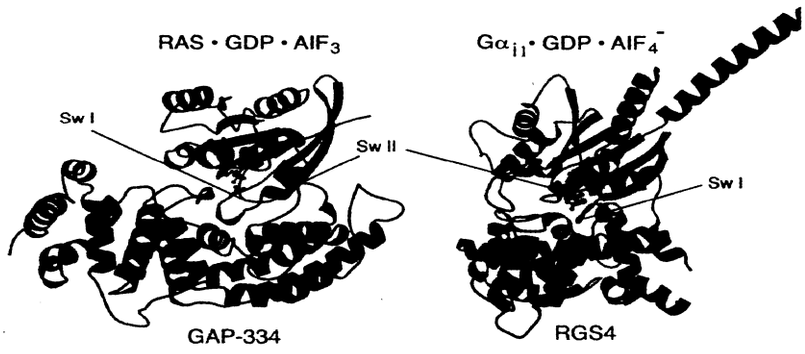
Regulatory pathways inside cells often make use of guanosine triphosphatases (GTPases) to turn cellular functions on and off. The signals transduced by GTPases such as Ras and heterotrimeric GTP-binding protein α subunits (Gα) (*1*) are transient. In the guanosine triphosphate (GTP)–bound state, these enzymes interact with downstream effectors but dissociate upon GTP hydrolysis. If Ras and Gα were efficient enzymes, the signals would be too short-lived to be effective; consequently they have evolved low catalytic rates. Ras, for example, hydrolyzes GTP with a rate constant of only 0.02 min^{-1}. These signals are switched off by GTPase-activating proteins (GAPs), which accelerate the rate of Ras-catalyzed GTP hydrolysis by a factor of 10^5 (*2*, *3*). Efforts to understand how GAPs function have now culminated in the crystal structure of the complex between Ras and the active, 334-residue fragment of $p120^{GAP}$, reported on page 333 of this issue by Scheffzek, Wittinghofer, and their colleagues (*4*). In this complex, guanosine diphosphate (GDP), aluminum trifluoride, and Mg^{2+} are bound to Ras and mimic the transition state for GTP hydrolysis.



The structures of Ras-GAP and $G\alpha_{i1}$-RGS. (**Left**) The complex between GAP-334 (red and green) bound to Ras•GDP•Mg^{2+}•AlF_3 (mustard yellow), with switch I and II segments in cyan. (**Right**) Shown in a similar orientation is the complex between RGS4 (red) and $G\alpha_{i1}$•GDP•Mg^{2+}•AlF_4^- (*15*) (yellow, helical domain in charcoal), with switch I and II in cyan.

GAPs are not unique to the Ras family. In light of recent biochemical data, genetic studies of yeast mating pheromone regulation can be seen to have long pointed to the existence of GAPs for heterotrimeric G proteins (*5*). These regulators of G protein signaling, or RGS, accelerate Gα–catalyzed GTP hydrolysis nearly 100-fold (*6*). RGS proteins and Ras-GAPs are completely unrelated (though both are α-helical proteins) and do not act on each other's substrates. The degree of stimulation afforded by RGS4 is at least three orders of magnitude less than that effected by GAP. On the other hand, the intrinsic rate of GTP hydrolysis catalyzed by Gα subunits (about 3 min^{-1}) is correspondingly higher than that of Ras. When stimulated by GAP and RGS4, respectively, the catalytic rates of Ras and $G\alpha_{i1}$ are within an order of magnitude of each other. As had been suspected (*7*, *8*), and the structures now demonstrate, GAP provides a catalytic residue, Arg^{789}, that is lacking in Ras but is intrinsic to Gα. This could account for at least two orders of magnitude of the total rate acceleration. However, the source of the remaining stimulatory power of GAP, and all of the acceleration provided by RGS proteins, is less easily understood.

To understand how GAP (or RGS4) causes rate acceleration, consider the conserved features in the active sites of Ras and Gα (*9*). In Ras, GTP is held between two flexible segments of chain, known as switch I and switch II. There are also inflexible elements that recognize the purine ring and the α and β phosphate groups, so there is no danger of nucleotide escaping from the active site. However, it is the switch regions that provide the essential catalytic residues. In Gα subunits, switch I is preceded by an α-helical

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