

## Science & Technology

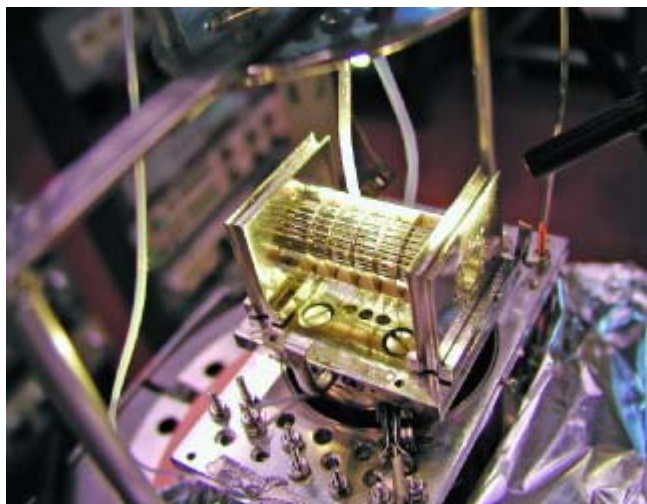
July 25, 2005

Volume 83, Number 30

pp. 45-48

# PROTONATED METHANE PROBED

Researchers obtain the first broad-frequency infrared spectrum of the  $\text{CH}_5^+$  carbocation



**GOTCHA** This ion trap, developed by Gerlich and coworkers, was the heart of the new experiments on  $\text{CH}_5^+$ . The trap is composed of 22 small rods, which are visible in the photo. A radiofrequency voltage applied to the rods causes cooled  $\text{CH}_5^+$  ions to be confined in the trap during the experiments.

COURTESY OF STEPHAN SCHLEMMER

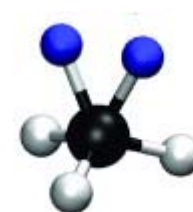
[STU BORMAN, C&EN WASHINGTON](#)

A new spectroscopic study of protonated methane,  $\text{CH}_5^+$ , is allowing long-standing questions about the mysterious ion's structure and dynamics to be answered with greater clarity than ever before.

$\text{CH}_5^+$ , also called methonium ion, is a carbocation formed in the gas phase by a chemical reaction that adds a proton to methane, and it has also been reported to be present in very acidic solution. It has resisted complete spectroscopic characterization since it was discovered in the early 1950s, but researchers have now obtained the first broad-frequency infrared (IR) spectrum of the ion.

The spectrum reveals new details about the structure and dynamics of  $\text{CH}_5^+$ . More work still needs to be done for the ion's structure and dynamics to be fully characterized, but the new study represents a key step toward that goal.

The work was carried out by a collaborative team including Britta Redlich, manager of the [Free Electron Laser for Infrared Experiments \(FELIX\) Facility](#) at the



**ELUSIVE**  $\text{CH}_5^+$  model, showing  $\text{CH}_3$  tripod structure (black and gray) and  $\text{H}_2$  moiety (blue).

REPRINTED FROM *SCIENCE*,  
© 2005 AAAS

Foundation for Fundamental Research on Matter (FOM) Institute for Plasma Physics, Nieuwegein, the Netherlands; physics professor [Stephan Schlemmer](#) of the University of Cologne, Germany; and professor of theoretical chemistry [Dominik Marx](#) of Ruhr University, Bochum, Germany (*Science*, published online June 30, [dx.doi.org/10.1126/science.1113729](https://doi.org/10.1126/science.1113729)).

Elucidating the fundamental nature of  $\text{CH}_5^+$  and similar carbocations is considered important because the ions serve as highly reactive intermediates in hydrocarbon reactions catalyzed by very strong "magic acids" and also play a key role in electrophilic substitution reactions of aliphatic hydrocarbons. The field of carbocation chemistry was developed by organic chemistry professor [George A. Olah](#) of the University of Southern California, Los Angeles, who received the 1994 Nobel Prize in Chemistry for his pioneering work in the area, including studies of  $\text{CH}_5^+$ .

Asked to comment on the new study, Olah says: "Professor Marx and his coworkers have made a significant new contribution to the study of protonated methane.  $\text{CH}_5^+$  has long continued to elude definitive experimental structural assignment [and has] challenged both theory and experiment." The study "gives a solid experimental and theoretical foundation to the structural question of  $\text{CH}_5^+$ ."

**ANOTHER REASON** for studying  $\text{CH}_5^+$  is the substantial astrochemical interest in the ion. It is "implicated in reactions that form part of the intricate synthesis of polyatomic species in cold interstellar clouds," Marx writes in a review.

"Experimental and theoretical colleagues have hunted for about 50 years for the spectrum of  $\text{CH}_5^+$  and about 30 years for an understanding of its structural dynamics," Marx tells C&EN. But success has been limited, primarily because the ion is unconventional. The component atoms of most ions and molecules occupy equilibrium positions.  $\text{CH}_5^+$  instead seems to have a constantly fluctuating "fluxional" or "floppy" structure that belies easy characterization.

"Lots of people worldwide are attacking this species," says chemistry professor [Mark A. Johnson](#) of Yale University. "It represents one of the most important unsolved spectroscopy problems involving small molecules." Johnson and a collaborative team recently helped solve a similar problem by obtaining the previously inaccessible low-energy part of the IR spectrum of the hydrated proton,  $\text{H}_3\text{O}^+$  ([C&EN, July 4, page 26](#)).



**RAD SOURCE** This free-electron laser at the FELIX Facility ([www.rijnh.nl/felix](http://www.rijnh.nl/felix)) was used to generate IR radiation for experiments on  $\text{CH}_5^+$ .

FOM INSTITUTE FOR PLASMA PHYSICS

Redlich, Schlemmer, Marx, and coworkers have now obtained the IR spectrum of  $\text{CH}_5^+$  over a much wider frequency range than has been accessible previously. And they used theoretical means to assign the ion's IR absorptions to specific motions in the ion.

The new  $\text{CH}_5^+$  spectrum ranges from about 600 to 3,200  $\text{cm}^{-1}$ . This covers not only  $\text{CH}_5^+$ 's full CH stretching band but also its complete CH bending band. The spectrum does not have sufficiently fine detail to resolve  $\text{CH}_5^+$ 's rotational structure, however.

A major conclusion of the study is that  $\text{CH}_5^+$  can be usefully considered to be a  $\text{CH}_3^+$  tripod structure with an added  $\text{H}_2$  group linked to the carbon by a three-centered (C-H-H), two-

electron bond, notes chemistry professor [Peter R. Schreiner](#) of Justus Liebig University, Giessen, Germany. "But this does not imply that its overall, time-averaged structure can be statically depicted" that way, he says.

Chemistry professor [Kenneth D. Jordan](#) of the University of Pittsburgh, a collaborator of Johnson's on the recent hydrated proton study, agrees that the new study indicates that "the  $\text{CH}_5^+$  ion, at least when sufficiently cold, can be viewed as having three-center, two-electron bonding." Given the low energetic barriers for structural interconversion of the ion, it has not been clear up to now "whether this bonding motif is the dominant one in the cluster," he notes.

"The three-center, two-electron bond coordinates the five protons, which, roughly speaking, move on a sphere about the carbon nucleus," Marx explains.

A separate  $\text{H}_2$  group can indeed be identified in the  $\text{CH}_5^+$  spectrum, but its hydrogens continually exchange with the ion's three other hydrogens, a process called scrambling. Hence, the  $\text{H}_2$  group constantly rotates about the carbon center as its hydrogens change, as shown in an animation at [www.theochem.rub.de/go/ch5p.html](http://www.theochem.rub.de/go/ch5p.html). The ion's three-center, two-electron bonding pattern and the rotating motions of its five protons are the keys to understanding its IR spectrum.

This new study and an earlier one by another group, "are likely to be taken as models for thoroughly understanding the IR spectra of highly fluxional molecules by elaborate molecular dynamics techniques," Schreiner says. The earlier study, reported in 2003, was one in which chemistry professor [Joel M. Bowman](#) of Emory University and coworkers first calculated the vibrational spectrum of  $\text{CH}_5^+$  by ab initio techniques.

Other notable earlier studies on  $\text{CH}_5^+$  included late-1960s work by several groups, including Olah's, that proposed the possibility of viewing  $\text{CH}_5^+$  as a  $\text{CH}_3^+$  tripod with a three-center, two-electron-bonded  $\text{H}_2$  moiety. In the early 1970s, [Werner Kutzelnigg](#) of Ruhr University, Bochum, and coworkers conducted theoretical studies on  $\text{CH}_5^+$ , one of which was the first "where the claim or conjecture concerning the ion's fluxional nature was spelled out, based on ab initio theory," Marx says.

Accurate ab initio calculations of the ion's potential surface and an explicit expression of its highly fluxional nature were obtained in 1993 by chemistry professors [Henry F. Schaefer III](#) at the University of Georgia, Athens; [Paul von Ragué Schleyer](#) at the University of Erlangen-Nuremberg, Germany; and coworkers, including Schreiner. The paper caused quite a stir, Schreiner says, by showing that  $\text{CH}_5^+$  is an unusual ion because a single equilibrium structure seemingly could not be assigned to it.

Further progress was made in a 1997 theoretical study led by Kutzelnigg; [Jozef Noga](#) of the Slovak Academy of Sciences, Bratislava, Slovakia; and chemistry professor [Willem M. Klopper](#) of the University of Karlsruhe, Germany. "They used a novel electron correlation approach to determine the energetics underlying the hydrogen motions around  $\text{CH}_5^+$ 's central carbon with ultimate precision," Marx says.

In 1999, the first IR spectrum of  $\text{CH}_5^+$  was obtained after a 16-year effort by now-emeritus professor of chemistry and of astronomy and astrophysics Takeshi Oka of the University of Chicago and coworkers. Their spectrum achieved rotational resolution, but the vibrational part of the spectrum was incomplete. It covered only part of  $\text{CH}_5^+$ 's CH stretching band, from about 2,800 to 3,100  $\text{cm}^{-1}$ . The spectral bands were so complex that "I did not even know where to begin" to assign them, Oka says.

The Oka group's study thus did not reveal much about  $\text{CH}_5^+$ 's structure, but it did help confirm the 1993 Schaefer-Schleyer study's claims about the ion's floppy character. In addition, recent theoretical studies of  $\text{CH}_5^+$ --by chemistry professor [Anne B. McCoy](#) of Ohio State University, Bowman, and coworkers, and independently by senior lecturer in chemistry [Meredith J. T. Jordan](#) of the University of Sydney, Australia, and coworkers--helped confirm the same claims computationally.

This year, professor of chemistry and biochemistry [David J. Nesbitt](#) of the University of Colorado, Boulder, and coworkers obtained a high-resolution IR spectrum of jet-cooled  $\text{CH}_5^+$  that, like the Oka group's study, achieved rotational resolution, but it was less congested and easier to understand. Oka calls this low-temperature spectrum "a great breakthrough," in part because it is simpler to analyze.

The Redlich-Schlemmer-Marx study now makes further inroads on  $\text{CH}_5^+$  by greatly extending the range of its IR spectrum. The researchers irradiated  $\text{CH}_5^+$  with IR light from a free-electron laser at the FELIX Facility while the ion was isolated in a low-temperature ion trap, a device developed by physics professor [Dieter Gerlich](#) and coworkers at the University of Technology, Chemnitz, Germany. They used laser-induced reaction (LIR), a technique developed by Gerlich, Schlemmer, and coworkers, to generate the ion's IR spectrum. In all previous IR studies of  $\text{CH}_5^+$ , Schlemmer says, spectra were recorded using a different technique called vibrational predissociation, which can cause artifacts in the data, whereas LIR does not.

With LIR, the experimentalists "monitored the product of an endothermic reaction with  $\text{CO}_2$  that selectively occurs with excited  $\text{CH}_5^+$  ions," Johnson says. Using that to get the  $\text{CH}_5^+$  spectrum was "a real tour de force."

**THE RESEARCHERS** then assigned the spectrum. They also computed the ion's IR spectrum using ab initio molecular dynamics and found that the theoretical and measured spectra agreed closely.

They plausibly assigned  $\text{CH}_5^+$ 's vibrational features, despite the ion's fluxional nature, by using computational tricks to artificially freeze the ion's rotational and structural properties. "The computations significantly helped in analyzing the IR spectrum," Schreiner says.

"The paper is very nice in that they have given for the first time the overall spectrum of this important species, albeit in low resolution," Oka says. "This is clearly a step forward."

The study provides "a survey spectrum that exquisitely shows the overall pattern of vibrational transitions, and that is a great achievement," Johnson says. "Now we need to look at these bands at much higher resolution to decode the energy-level pattern and reveal the intrinsic physics at play in this prototype molecule."

Oka agrees, noting that despite the study's success, "I do not think the problem of  $\text{CH}_5^+$  is close to a solution. It is clear to me that observation of the ion's rotational spectrum will be the key to understanding this beast." Professor of astrophysics and planetary sciences



**TOUR DE FORCE** The LIR setup used to obtain  $\text{CH}_5^+$ 's IR spectrum is a bench including an ultra-high-vacuum chamber and ion source (left), a 22-pole ion trap mounted on a helium refrigerator (center), and an ion-counting detector (right). The setup is axially transparent, so laser light from the FELIX free-electron laser can reach the trap after being introduced on the right side.

COURTESY OF STEPHAN SCHLEMMER

[Takayoshi Amano](#) of Ibaraki University, Japan, now moving to the University of Waterloo, Canada, is attempting to observe such a spectrum.

"In 1999 when I published our paper, I believed it would take at least 20 years to completely understand the spectrum of  $\text{CH}_5^+$ ," Oka says. "Several people challenged me and said that such an understanding would be obtained in a few years. It is already six years since then, and there is still no solution in sight. I personally think that 20 years is a gross underestimate."

"I agree that a full analysis will take some time," Nesbitt says. " $\text{CH}_5^+$  still has a few tricks up its sleeve."

**Chemical & Engineering News**  
**ISSN 0009-2347**  
**Copyright © 2005**