Closing in on the elusive rotational-vibrational CH5+ spectra

May 24 2016

Protonated methane, a.k.a. CH5+, is a highly unusual molecule that scientists and astronomers suspect may be found within the interstellar medium where stars and planets are formed.

To identify molecules on Earth or in outer space, scientists typically record the spectrum of light absorbed—each molecule has its own unique spectrum. CH5+, consists of a central carbon atom with five hydrogen atoms constantly moving around it, which makes it difficult to interpret its spectrum.

In *The Journal of Chemical Physics*, Queen's University researchers in Canada report comparing, for the first time at a detailed level, experimental v. theory for CH5+.

The group's work was inspired by the complexity of CH5+. "No one has been able to understand its spectrum," said Tucker Carrington Jr., a professor of theoretical chemistry. "Spectroscopists usually attempt to sort rotational-vibrational levels into groups, each of which is associated with a vibrational state, but it completely fails for CH5+."

By focusing on quirks of molecules that don't fit neatly into paradigms, new ideas tend to emerge. "Using experimental methods in 2015, Asvany, Yamada, Schlemmer, and colleagues at the University of Cologne, for the first time, observed and assigned differences of CH5+ energy levels, which opened the door to a detailed comparison between theory and experiment," Carrington said.

To gain a better understanding of the motion of nuclei, "it's common to first approximately separate vibration and rotation, and then to assume that small amplitude vibration occurs within the vicinity of the equilibrium geometry of the molecule," he explained.

Vibration and rotation are inseparable in CH5+ because there are 120 low-lying equivalent equilibrium structures, and the amplitude of vibration is quite large.

Computing and analyzing the spectrum of CH5+, as you might expect, involves complex mathematics. "It's necessary to numerically solve the Schrodinger equation by calculating eigenvalues of a large Hamiltonian matrix," Carrington pointed out. "This is extremely difficult because the size of the matrix is larger than 10^9, so we use the Lanczos algorithm."

The significance of this work, done together by Xiao-Gang Wang, research associate, and Carrington, is that by comparing experiment and theory for CH5+ they were able to develop the first possible new assignment of the experimental results—something no one expected so soon.

"Our theoretical understanding is far from complete, but it's a good start," Carrington noted. "A year ago, most researchers within this field wouldn't have expected that theory would be good enough to suggest a possible experimental misassignment. Our new assignment reduces errors from about 30 cm-1 to 2 cm-1."

The success of the group's calculations implies that it may now be possible to begin interpreting and understanding the detailed rotational-vibrational CH5+ spectra previously recorded by several other groups. For example, CH5+ plays a key role in George A. Olah's "superacid chemistry," which earned him the 1994 Nobel Prize in chemistry.

Next, Carrington and colleagues will "compute the intensities of transitions, which will enable a more complete comparison with experimental spectra," he added.

More information: "Calculated Rotation-Bending Energy Levels of CH+5 and a Comparison with Experiment," by Xiao-Gang Wang and Tucker Carrington Jr. The *Journal of Chemical Physics* on May 24, 2016. DOI: 10.1063/1.4948549