CH_5^+: the ground-state combination differences

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Infrared (IR) spectra of CH_5^+ in the CH-stretching region were measured employing two types of action spectroscopy. Ions were stored in a 22-pole ion-trap. The IR absorption signal was detected by Laser Induced Reaction (LIR) with CO_2 at the trap temperature of 10 K, and by Laser Induced Inhibition of Cluster Growth (LIICG) with He at 4 K. Careful inspection allows the identification of several ground-state combination differences in the observed spectra.

Introduction

The infrared spectra of CH_5^+ were first detected by Oka's group. The spectra they recorded were so chaotic that not a single line out of the many hundreds was understood or assigned [1]. This has been considered one of the last mysteries of molecular physics. We recently succeeded in taming this enfant terrible of molecular physics as published in *Science* magazine [2]. Oka wrote an excellent perspective concerning our study in the same issue [3], which may be the best introduction for the present work.

Experimental procedure

As reported in SMS14 (Tokyo, 2014) we used an ion trap to store several thousand CH_5^+ ions and cooled them down to cryogenic temperatures. Then, IR laser light produced by a Comb-assisted OPO was introduced into the trap. Two different action spectroscopic methods have been applied on a few thousand mass-selectively trapped CH_5^+ ions: laser induced reaction (LIR) with CO_2 at a trap temperature of 10 K, and laser-induced inhibition of complex growth (LIICG) with He at a trap temperature of 4 K. In LIICG, the attachment of helium is hindered by resonant excitation of CH_5^+ ions.

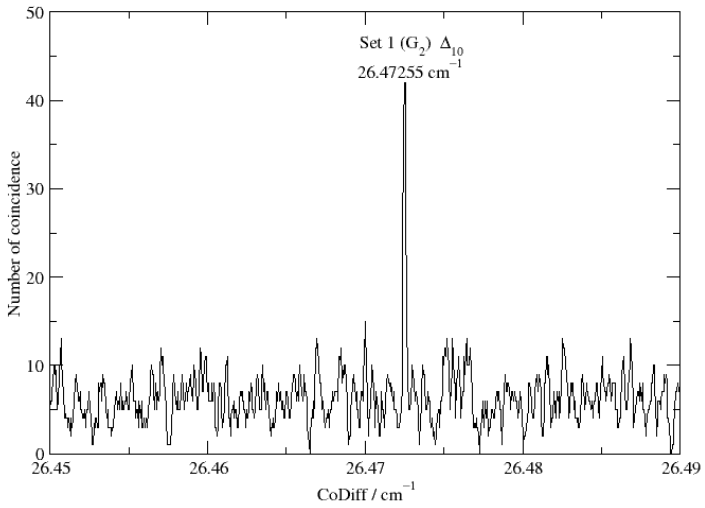
Thanks to the frequency comb, line centers of the observed transitions were determined with high accuracy and precision, often below 1 MHz. The obtained LIR-spectra contain 2897 lines in the range 2886 through 3116 cm^{-1}, and the LIICG spectra only 185 lines. The observed temperature dependence supplies us with information valuable for assigning the lines.

Combination differences

So far no good effective Hamiltonian is known for CH_5^+. Thus, the only criteria for assigning lines is the Rydberg-Ritz combination principle. The frequency differences for all pairs of transitions (combination differences, CoDiff) were inspected. We counted the number of coincidences within a certain tolerance limit for a given CoDiff. If the coincidence number is two, the two pairs of transitions (four lines) form a set of so called 4LCD. In the

spectra of CH_5^+, however, we should find mLCD with m>>4, because the number of levels in the excited states, to which transitions are allowed from a single level in the ground state, is expected to be very large. The figure below shows a small portion of the obtained"CoDiff spectrum"; the number of coincidences (tolerance limit of 0.001 cm^{-1}) is plotted versus CoDiff, with a step of 0.00005 cm-1. The number of coincidences for the CoDiff=26.47255 cm-1 is very large, 42 (including undesired false or accidental pairs), as shown there. Taking the temperature effect into consideration, we assigned this CoDiff to one of the ground-state combination differences.

In this symposium we present all ground-state CoDiffs so far found using a more sophisticated CoDiff spectrum technique, and some "speculative" assignments for them.



References

[1] E. T. White, J. Tang, T. Oka, *Science* **284**, 135(1999).

[2] O. Asvany *et al*., *Science* **347**, 1346 (2015).

[3] T. Oka, *Science* **347**, 1313 (2015).