CH_5^+

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Abstract

The infrared spectrum of CH_5^+ is known to be very irregular and congested. Using laser induced action spectroscopy we have measured it with high resolution and high precision in the CH-stretching region, from 2900 to 3100 cm^{-1}. The ion trap constructed and operated at the University of Cologne was employed as a reaction vessel at cryogenic temperatures. We were able to greatly reduce the number of lines in the observed spectra. This gives hope that we can tame this "enfant terrible."

Introduction

Since Oka and coworkers first reported the infrared spectrum of the CH_5^+ ion [1], this ion has attracted the interest of many scientists. The spectra they reported cover the CH-stretching region (917 lines in the range from 2782 to 3133 cm^{-1}), and are so congested and irregular that attempts to assign the lines have so far failed. To try to break this deadlock we have measured the infrared spectra of CH_5^+ in the Cologne ion trap, employing two kinds of action spectroscopy (LIR and LIICG) with high resolution and high precision. By cooling the ion trap to cryogenic temperatures the observed spectra are much less congested than those reported in Ref. [1] which were measured in a liquid nitrogen cooled discharge cell.

Experimental procedure

The ion trap spectrometer used in the present study is described in detail in Ref. [2]. The CH_5^+ ion was produced in a Gerlich-type storage ion-source [3] and mass-selectively guided to a 22 pole ion trap [4,5] by a quadrupole mass-filter. The ion trap is mounted on the cold head of a He-refrigerator. The trap compartment can be evacuated to 10^{-7} Pa without cooling. By introducing He gas into the trap the ion can be collisionally cooled to cryogenic temperatures. 3 μm wavelength infrared laser radiation produced as the idler of a cw optical parametric oscillator (OPO) was employed to obtain the action spectra of the ion in the following two ways:

In **LIR** (Laser Induced Reaction) experiments we introduced CO_2 into the trap and observed the endothermic proton transfer reaction,

$$CH_5^+ + CO_2 \rightarrow CH_4 + HOCO^+. \quad (1)$$

The product ion, $HOCO^+$, was guided mass-selectively to a Daly-type ion-detector using a second quadrupole mass-filter. Introducing infrared laser radiation into the trap can modify the reaction rate since the production rate of the $HOCO^+$ ion *increases* when the laser frequency is on resonance with a transition of CH_5^+. The spectrum is obtained by monitoring the production of $HOCO^+$ as a function of the frequency of the infrared light. This scheme can be applied in the temperature range 10 K < T_{trap} (temperature of the trap) < 100 K.

In **LIICG** (Laser Induced Inhibition of Cluster Growth) experiments, a technique first introduced by Maier and coworkers [6], we observed the formation rate of He-clusters,

$$CH_5^+ + 2He \rightarrow HeCH_5^+ + He. \quad (2)$$

In this scheme, we observed the rate of formation of cluster ions, $HeCH_5^+$, as a function of the introduced laser light. In this case the reaction rate *decreases* when the laser frequency is on resonance with a transition of CH_5^+. This method can be applied in the temperature range 4 K < T_{trap} < 10 K.

The idler frequency in the MIR (Mid Infrared) range of the OPO was monitored by a wavemeter with an uncertainty of less than 20 MHz. The pump and signal frequency of the OPO, both in the NIR (Near Infrared), were measured by monitoring the beat frequency with NIR frequency combs. The MIR idler frequency can be determined with an uncertainty of about 100 kHz [7].

Observed spectra

The action spectra of CH_5^+ were recorded in the spectral range 2900 to 3100 cm^{-1}. This is the highest wavenumber region of the very broad CH stretching bands. In this range we observed about 2900 lines with T_{trap}≃10 K and 180 lines with T_{trap}≃4 K, with Doppler-limited resolution in both cases. Although the idler frequency can be measured with very small uncertainty the uncertainty of the transition frequency is much larger. Even for T_{trap}≃10 K the spectra are so dense that we cannot exclude the possibility of overlapping lines within the line width. In such cases the observed line center may deviate from the transition frequency by about 30 MHz.

Group theoretical considerations

At a very early stage in research on CH_5^+, Bunker published a stimulating paper on this ion [8]. There he introduced the group G_{240} as the appropriate symmetry group. He extended this investigation further with coworkers, examining the ro-contortion energy levels of the ion by employing the potential energy surface predicted by *ab-intio* calculations, e.g. Ref. [9].

The 32 nuclear spin functions for the five protons can be classified in G_{240} as $6A_1^+ + 4G_1^+ + 2H_1^+$, corresponding to the spin modification I=5/2, 3/2, and 1/2, respectively. Following the Pauli principle the ro-contortion energy levels of $A_2^\pm$, $G_2^\pm$, and $H_2^\pm$ have non-zero spin statistical weights. All others have zero weight. Consequently, although the energy splitting due to the tunneling motion is expected to be very complicated, the molecular symmetry of G_{240} dramatically reduces the number of actual energy levels. The electric dipole selection rules are also simple: transitions are allowed only between ro-contortion energy levels of Γ^+ and Γ^-, where $\Gamma = A_2, G_2,$ and H_2.

Temporary conclusion

Because the spin modifications should be conserved in the cooling process in the trap (collision with He) only the lowest ro-contortion energy levels for each nuclear spin modification will be populated at T_{trap}≃4 K. The number of transitions that were expected to be observed was therefore quite small. However, the actual number of lines observed is much larger than expected. So far we have not reached any definitive assignments. We may therefore have to consider additional possible isomers, low frequency vibrations, combination bands, and so on. We are continuing to search for crucial evidence in the observed spectra to help in the disentanglement of this still very complex spectrum. Further refinement of the experiment may also help in this regard.

References

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