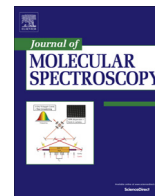




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High-resolution vibrational and rotational spectroscopy of CD_2H^+ in a cryogenic ion trap

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ABSTRACT

The low-lying rotational states ($J = 0, \dots, 5$) of CD_2H^+ have been probed by high-resolution ro-vibrational and pure rotational spectroscopy, applying several action spectroscopic methods in a cryogenic 22-pole ion trap. For this, the ν_1 ro-vibrational band has been revisited, detecting 108 transitions, among which 36 are new. The use of a frequency comb system allowed us to measure the ro-vibrational transitions with high precision and accuracy, typically better than 1 MHz. The high precision has been confirmed by comparing equal combination differences in the ground and excited state. Moreover, precise predictions of pure rotational transitions were possible for the ground state. Twenty-five rotational transitions have been detected directly by a novel IR-mm-wave double resonance method, giving rise to highly accurate ground state spectroscopic parameters.

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1. Introduction

The vivid interplay between rotational spectroscopy in the laboratory and astronomical observations enabled the detection and identification of many key cationic species in the last decades, recent examples (with our involvement) being $p\text{-H}_2\text{D}^+$ [1,2], $l\text{-C}_3\text{H}^+$ [3,4], or the quest for detecting CH_2D^+ in space [5–11]. For the last two cases it actually were the astronomical activities that boosted a search for those species in the laboratory. In the case of CH_2D^+ , for instance, high-resolution rovibrational data from the Oka laboratory enabled to bracket the rotational transitions to within some 10 MHz [5,6] already 25 years ago. Some tentative observations based on those predictions in 2008 [10] and 2009 [11] then triggered a reinforced laboratory search for any pure rotational line of that ion. Finally, Amano [7] measured four high-frequency rotational lines in a discharge cell, while our group concentrated on revisiting the ν_1 and ν_4 IR bands of CH_2D^+ at higher resolution using a cold ion trap experiment combined with narrow-band IR radiation [8,9]. Only very recently a full set of 21 low-lying rotational transitions up to 1.1 THz has been measured in the Cologne laboratories by a novel double resonance method [12]. This leaves a situation in which the transition

frequencies are very well defined, while the astronomical detection of this key ionic molecule is hampered, apparently because of low column densities.

The above example shows that there is a need for advanced laboratory techniques, in particular for rotational spectroscopy. In our group, we exploit the advantages of ion trapping (foremost cryogenic operation and mass selectivity) to do spectroscopy in the rotational domain. One of the emerging methods is Laser Induced Inhibition of Complex Growth (LIICG) [4,13–17], a novel action spectroscopy method in which attachment of He atoms to cold cations is hindered by resonant excitation. Its unique advantage is the apparent applicability to any cation, without the need of specific reaction schemes. This was nicely demonstrated by measuring four pure rotational transitions of $l\text{-C}_3\text{H}^+$ [4], ending the discussion about the charge state of the observed carrier in space [3]. Another powerful method for rotational action spectroscopy is IR - (sub)mm-wave double resonance, in which the cold ions are excited in two steps, first by a rotational photon into a higher rotational level, and then into a vibrationally excited state by a resonant IR photon. Keeping the IR excitation fixed on resonance, the frequency of the (sub)mm-wave photon can be scanned to obtain a rotational spectrum. This method has been tested and applied on single rotational transitions first for $p\text{-H}_2\text{D}^+$ [9] and later for OH^- [18], and very recently for a complete set of low-lying transitions of CH_2D^+ [12]. Also quite recently, the rotational double

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resonance technique has been extended by using photodetachment with a visible photon as the detection method. By enhancing the photodetachment rate of OD^- anions by rotational excitation, the two lowest rotational transitions of this anion could be recorded [19].

In this work, we turn our attention from CH_2D^+ to its next deuterated sibling, CD_2H^+ , for which no rotational data have been published before, and demonstrate in particular the capabilities of the mentioned rotational action spectroscopic methods. This paper is organized as follows: The experiment and the different action spectroscopic techniques are briefly described in Section 2. As a preparation for the rotational measurements the ν_1 IR band has been revisited using a frequency comb, with 108 accurate rovibrational lines summarized in Section 3. The resulting combination differences allow to scrutinize the accuracy, and lead to sub-MHz predictions of the rotational lines. The rotational action spectroscopic methods are then used to detect the rotational transitions directly. For CD_2H^+ , the IR-(sub)mm-wave double resonance method turned out to be extremely effective, with a total of 25 low-lying rotational transitions measured in a range up to 1.1 THz. These transitions are collected in Table 3 in Section 4. The relative uncertainties of these rotational frequencies approach values of 1 ppb, giving rise to highly accurate spectroscopic parameters for the ground state given in Section 5.

2. Experimental

2.1. Ion trap machine

The spectroscopy of CD_2H^+ has been conducted in a 4 K 22-pole trapping apparatus described in detail in Ref. [14]. The experiments of this work are very similar to those done for CH_2D^+ [8,9,12]. The CD_2H^+ ions are generated by electron impact (electron energy about 20 eV) in a storage ion source, using CD_3H gas (Cambridge Isotope Laboratories, Inc.: Methane (D3, 98%)) as precursor. At the beginning of each experimental cycle (usually 1 s cycle synchronized to cold head), a short pulse of ions is extracted from the storage ion source, mass filtered for CD_2H^+ in a quadrupole mass spectrometer, and injected into the 22-pole ion trap [20]. This trap is mounted on a 4 K cold head, with an attached heater allowing to adjust the temperature in the range 4–40 K. On entrance, several thousand CD_2H^+ ions are trapped and cooled down to the ambient cryogenic wall temperature by a short helium gas pulse. During the storage time of typically 700 ms the ensemble of trapped CD_2H^+ ions is irradiated by IR and/or mm-wave radiation (delivered by an OPO and multiplier chain, see below). The resonant absorption of a photon is detected by different action spectroscopic methods which are described in detail in the subsequent section. On resonant absorption, these methods induce a change of the ionic composition of the trapped ensemble, which is measured by extracting the ions through a second quadrupole mass spectrometer and counting the mass-filtered ions in an ion counter. By counting these mass-filtered ions as a function of the irradiation frequency, rovibrational or rotational spectra can be produced.

2.2. Action spectroscopy methods: LIR, LIICG and IR-mm-wave double resonance

In this work, we used three different action spectroscopic methods for rovibrational and rotational spectroscopy. We started our experiments by using a relatively new method called Laser Induced Inhibition of Complex Growth (LIICG), in which attachment of He atoms to ionic species is hindered by resonant excitation. This excitation can be of any kind. It has been demonstrated first for electronic spectroscopy [13], and adapted in our group to

rovibrational [14,15] as well as pure rotational spectroscopy [4,16]. Important features of LIICG are operation close to 4 K and its apparent applicability to any cation. In this work, we applied both rovibrational and rotational LIICG spectroscopy. For this, an ensemble of CD_2H^+ ions has been injected into the 4 K ion trap filled with He at a constant number density of approximately 10^{14} cm^{-3} . Three-body collisions then lead to an efficient formation of $\text{He}\cdot\text{CD}_2\text{H}^+$ complexes. The resonant excitation of the bare ions before complexation counteracts this formation, so that the LIICG signal is observed as a dip in the number of complexes. Examples of rovibrational LIICG signals are shown in the upper panel of Fig. 1. Due to the low temperature operation of LIICG, only seven rovibrational transitions from the lowest $J = 0$ and $J = 1$ states have been detected in this work.

Laser induced reactions (LIR), on the other hand, is a more established method and has been extensively used for the spectroscopy of deuterated species [1,8,9,15,21] in the Cologne laboratories. Energetic reasons make it typically suitable for rovibrational or electronic investigations, and only in one exceptional case it has been used for rotational spectroscopy [1]. For its operation, a suitable endothermic ion-molecule reaction is required, preferably with a reaction partner not condensing at low temperatures. In the current case, the endothermic reaction [9,22]



has been used. On excitation of the CD_2H^+ ions, the LIR signal is thus observed as an increase of the CH_2D^+ ion count. LIR features low background counts and excellent signal-to-noise ratio, as well as operation in a wider temperature range. For these advantageous reasons, the rovibrational data given in this work is based on LIR only. Adjusting the nominal trap temperature between 4 and about 24 K, the lowest rotational levels $J = 0, \dots, 5$ could be addressed by rovibrational LIR. Example transitions are shown in the lower panel of Fig. 1. For the depicted transitions, the IR power has been limited to below 1 mW in order to obtain sufficient signal without running into saturation.

For rotational spectroscopy of CD_2H^+ we primarily applied a recently developed IR-(sub)mm-wave double resonance method [9,12,18]. A recent application of this method to six submm-wave rotational transitions of H_2D^+ and D_2H^+ [23] can be found in this special issue “Spectroscopy in Traps”. The double resonance method is based on rovibrational action spectroscopy, in which the

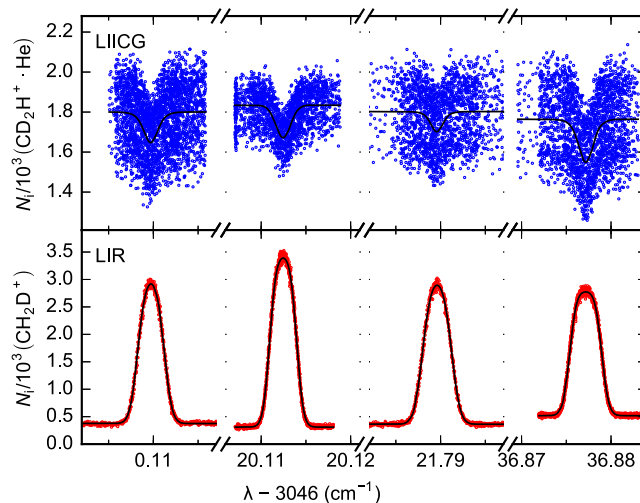


Fig. 1. Rovibrational LIICG (upper panel) and LIR (lower panel) lines recorded at a nominal temperature of 4 K and 10 K, respectively. Shown are the transitions $0_{00} \leftarrow 1_{11}$, $1_{11} \leftarrow 0_{00}$, $2_{02} \leftarrow 1_{11}$, and $2_{20} \leftarrow 1_{11}$ of the ν_1 band. For the LIR lines, less than 1 mW is sufficient to excite the shown strong transitions, while LIICG is operated typically with higher excitation power (up to 1 W).

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