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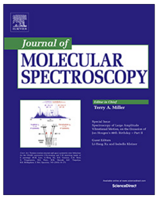

Spectroscopy of the low-frequency vibrational modes of CH_3^+ isotopologues

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ABSTRACT

The low-frequency stretching and bending vibrations of the isotopologues CH_2D^+, CD_2H^+ and CD_3^+ have been recorded at low temperature and low resolution. For this, a cryogenic 22-pole trapping machine coupled to an IR beamline of the FELIX free electron laser facility has been used. To record the overview spectra, the laser induced reactions $CD_mH_n^+ + H_2 \xrightarrow{h\nu} CD_{m-1}H_{n+1}^+ + HD$ have been applied for these species. As this scheme is not applicable to CH_3^+, the latter has been tagged with He and subsequently dissociated by the IR beam. For the resulting CH_3^+-He spectrum, broad features are observed below $1000\ cm^{-1}$ possibly related to vibrational motions involving the He atom. The extracted vibrational band positions for all species are compared to results from high-level quantum-chemical calculations.

1. Introduction

The spectroscopy of carbon containing cations was pioneered by Takeshi Oka and coworkers, who characterized many of these so-called carbocations [1–7] by their C-H stretching vibrations in the 3 μm spectral range. All these ions play important roles in hydrocarbon combustion chemistry as well as in astrochemistry. In the context of astrochemistry, CH_3^+ is a particularly important intermediate, as its non-reactivity with molecular hydrogen makes it amenable to deuteration by HD [8,9]. Its C-H stretching mode was discovered in the laboratory in 1985 [10], and later also those of its deuterated counterparts CH_2D^+ and CD_2H^+ were observed [11,12]. The deuterated versions have a permanent dipole moment and are therefore detectable by laboratory microwave and radioastronomical means. Additionally, they are thought to be responsible for the deuteration of other molecules observed in luke-warm ($T > 20$ K) interstellar environments [13,14]. Therefore there has been a long-standing search for the pure rotational lines of these two species. It was only in 2010 when Amano published the first rotational data, four high-frequency lines of CH_2D^+ [15] measured in a discharge cell. Recently, complete lists of rotational transitions of CH_2D^+ and CD_2H^+ up to 1.1 THz have been presented [16,17], measured by a novel IR-mm-wave double resonance method. Despite their low abundance in interstellar space, this renews the hope for a radioastronomical search of the CH_3^+ isotopic family.

Whereas the C-H stretches and the rotational spectra are thus well characterized, the lower frequency C-D stretches as well as the bending vibrations of the CH_3^+ isotopologues have not yet been investigated, most probably due to the lack of appropriate lower frequency IR sources. In particular, CD_3^+ has not at all been characterized by direct rovibrational spectroscopy. For this isotopologue, the only sources of vibrational information are high-level *ab initio* predictions as well as photoelectron spectra of the perdeuterated methyl radical [18].

In this paper, we investigate the experimentally missing vibrational modes of the CH_3^+ isotopologues. For taking low-frequency overview spectra of molecular ions and clusters, cryogenic radio-frequency ion traps have been used for a long time in combination with free electron lasers operating in the MIR range, in particular with FELIX (Free Electron Laser for Infrared eXperiments, [19]). In such experiments, the interrogation of the cold ions in their long wavelength fingerprint region by vibrational action spectroscopy yields compelling evidence of their structure and dynamics. Prominent examples include the investigation of the protonated water dimer [20], the overview spectrum of floppy protonated methane [21,22], as well as the determination of the cis-bending vibrational frequency of ground state $C_2H_2^+$ [23,24]. A particularly general action spectroscopic tool uses the formation of cation-helium complexes in the cryogenic ion trap, which has been pioneered by Asmis and coworkers [25] 15 years ago. For the CH_3^+ isotopologues,

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our interest has been triggered by the observation of a strong interaction of the ν_1 symmetric C-H stretch of CD_2H^+ [12,17] with a combination band consisting of lower frequency vibrations. This lead to the question about the nature and frequency positions of these fundamental modes, as well as their combination bands. In this work, the frequency positions of all these modes are extracted with the help of spectroscopic simulations and compared to values calculated *ab initio*.

2. Experimental methods

Central part of the current experiment is a cryogenic 22-pole ion trapping machine, called FELION, which has been used for high-resolution rotational spectroscopy of small cations in the Cologne laboratories [26,27]. It is nearly identical to the 22-pole machine documented in Ref. [28], and a detailed description of the combination of FELION with FELIX is in preparation. The CH_3^+ isotopologues were produced by ionization of pure methane gas (CH_4 5.5, Linde AG) or deuterated samples (CH_3D, CD_3H or CD_4, 98%, CIL Inc.) in an external storage ion source. In this source, electrons with small kinetic energy (<20 eV) are used to ionize and fragment the precursor gas. After mass selection in the first mass filter, an ensemble of several ten thousand ions were injected into the cold 22-pole ion trap [29] and stored there for a few seconds. During this trapping time, the ionic species were exposed to the tunable IR pulses of FELIX [19]. For the CH_3^+ tagging experiments, the trap was held at 4 K. A ∼ 100 ms He pulse at the beginning of the trapping cycle cooled the ions and led to the efficient formation of CH_3^+-He complexes by ternary collisions. For the CH_2D^+, CD_2H^+, and CD_3^+ experiments, on the other hand, hydrogen gas at low number density (on the order 10^{10} cm^{-3}) was admitted to the trap (kept at $T = 12$ K) so that the laser induced reaction method (LIR, see below) could be applied. After the storage period, the ion cloud was extracted from the trap, and the number of mass selected parent ions or reaction products were counted by an effective ion counter. Such storage cycles were repeated typically 2–3 times to improve the S/N ratio, after which the FELIX laser was moved to the next frequency.

The FELIX laser was operated at a repetition rate of 10 Hz. The pulses had an energy content varying from 10 to 30 mJ (at user station), depending on the wavelength region. The beam entered and exited the 22-pole trapping machine by a pair of KRS-5 windows, and after the exit window it was stopped by a power meter. The laser power was constantly monitored by this meter in order to normalize the obtained spectra to power. The bandwidth of FELIX is transform-limited with a typical resolution of 0.5% FWHM of the central frequency (e.g. $\Delta\nu = 5$ cm^{-1} at $\nu = 1000$ cm^{-1}). With this resolution, we are not able to resolve single rovibrational lines, but can only recover the envelopes of the *P*-, *Q*-, and *R*-branches of the vibrational modes. In our experiments, the trapping repetition time of a few seconds was synchronized to the frequency of the main electrical power supply. This way, synchronization with the 1 s cycle of the cold head was achieved (important for stable tagging with He at 4 K), as well as synchronization to the 10 Hz of the FELIX laser pulses.

For the IR spectroscopy of the deuterated isotopologues, the laser induced reaction method LIR [23,30,31] has been applied. For this, the rates of the endothermic reactions [8,9]

$$CD_mH_n^+ + H_2 \xrightarrow{h\nu} CD_{m-1}H_{n+1}^+ + HD \qquad (1)$$

have been enhanced by rovibrational excitation of the $CD_mH_n^+$ parent ions. These excitations are all above $E/hc = 1000$ cm^{-1} and thus exceed the reaction endothermicities, which are on the order of 300 cm^{-1} [32]. A spectrum can be recorded by counting the laser induced reaction products $CD_{m-1}H_{n+1}^+$ as a function of the FELIX excitation frequency. This scheme is well established and has been used for high-resolution rovibrational spectroscopy [17,33,34] and even for double resonance rotational spectroscopy [16,17] of these species. In this work, the spectral signal $s(f)$ is obtained by the normalization $s(f) = (c(f) - c_0)/P(f)$, with $c(f)$ being the laser induced reaction product counts, c_0 the background counts without laser, and $P(f)$ the frequency dependent IR power.

As the above LIR scheme (1) is not applicable to CH_3^+ (because there is no D atom which can be exchanged for an H atom), we used He-tagging in the cold ion trap, as shown in Fig. 1, with subsequent IR photodissociation (IRPD)

$$CH_3^+\text{-He} \xrightarrow{h\nu} CH_3^+ + \text{He}. \qquad (2)$$

The spectral signal for He-tagging has been obtained by counting the number $c(f)$ of CH_3^+-He ions and the normalization procedure $s(f) = (c_0 - c(f))/(c_0 \cdot P(f))$.

3. Quantum-chemical calculations

The measurements were complemented by molecular structural calculations of CH_3^+ which have been outlined previously [17]. Briefly, calculations were carried out using the CCSD(T) method [37] with the CFOUR suite of programs [38,39]. In the present investigation, Dunning's correlation consistent basis sets as large as aug-cc-pwCVQZ [40,41] were used when considering all electrons (ae) in the correlation treatment. Molecular structures were calculated using analytic gradient techniques [42]. Harmonic and anharmonic force fields of CH_3^+ isotopologues were calculated at the CCSD(T)/cc-pwCVQZ level of theory using analytic second-derivative techniques [43,44] followed by additional numerical differentiation to calculate the third and fourth derivatives needed for the anharmonic force fields [44,45]. Where possible, all vibrational wavenumbers compare very favorably with the ones given in Ref. [18]. Complementary force field calculations of CH_3^+ rare-gas clusters were performed in the frozen-core (fc) approximation at the fc-CCSD(T)/cc-pVTZ level. Theoretical ground state rotational constants were obtained from the calculated zero-point vibrational

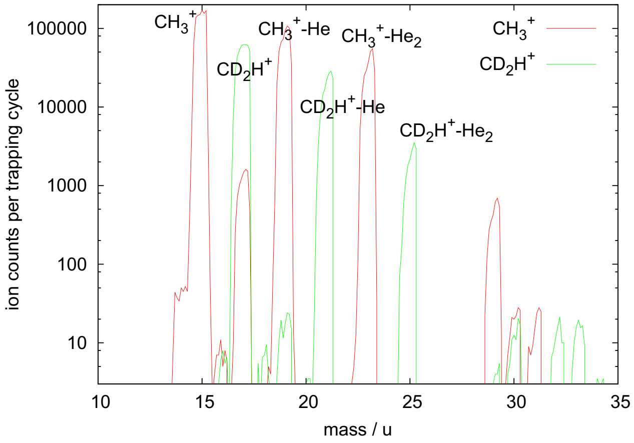

Fig. 1. Two mass spectra showing the ease of He tagging. CH_3^+ (red trace) or CD_2H^+ (green trace) ions have been injected into the 22-pole ion trap held at 4 K, and a short pulse of He atoms (100 ms) was applied at the beginning of the trapping sequence. The attachment of up to two He atoms by ternary collisions is very effective (dissociation energy $D_0 = 193$ cm^{-1} [35]), whereas there is no evidence for the attachment of a third one. This strongly supports the structure of p-orbital bound He atoms as brought forward by Dopfer and coworkers [36]. All other masses (e.g. 17 and 29 u for CH_3^+) are due to small H_2 and N_2 contaminations in the He pulse. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)