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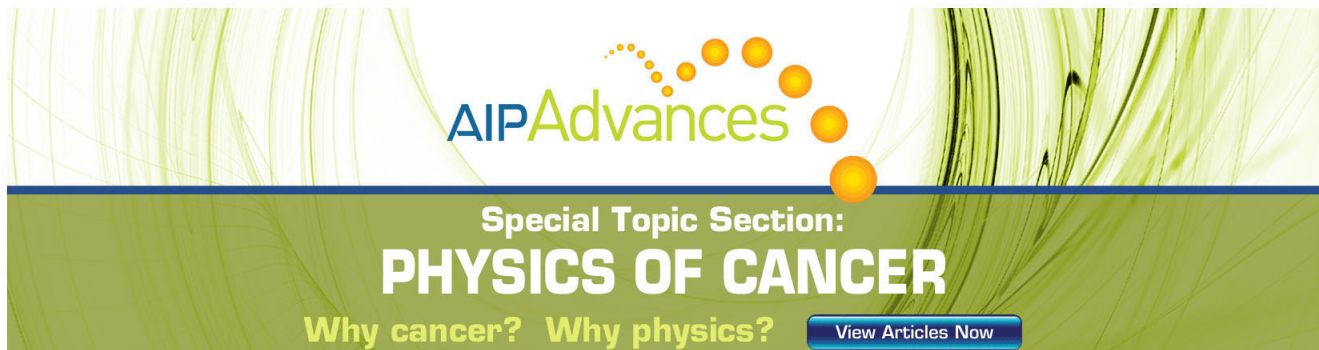
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# Frequency comb assisted mid-infrared spectroscopy of cold molecular ions

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A mid-infrared spectrometer consisting of a high power optical parametric oscillator, a frequency comb, and a cold ion trap is described and characterized. The idler frequency at 3  $\mu\text{m}$  is measured accurately by analyzing the pump and signal beat frequencies with the comb. This is done via two spectrum analyzers, allowing for a wide and continuous scanning ideal for spectroscopy of cold molecules with unknown spectra. The potential of this approach is demonstrated by measuring a ro-vibrational line of  $\text{CH}_5^+$  in a 22-pole ion trap via action spectroscopy of only several thousand cold ions. The current setup limits the precision of the line center frequency determination to some 100 kHz with ample room for future improvements. Following this approach, ground state combination differences of molecular ions can be predicted in order to identify them in astronomical objects. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4753930>]

## INTRODUCTION

The development of the frequency comb<sup>1,2</sup> has its roots in high precision spectroscopy of the benchmark hydrogen and other atomic systems, where a laser is locked to or scanned over a single Doppler-free transition and its frequency measured in small bandwidth. It made it recently possible to measure the 1S-2S transitions of the hydrogen atom with a fractional uncertainty of  $4.2 \times 10^{-15}$ ,<sup>3</sup> and is the clockwork mechanism of optical clocks.<sup>4</sup>

Due to their commercial availability frequency combs are increasingly applied for the spectroscopy of molecules, usually in the visible or near-infrared (NIR) spectral range. Selected examples from the rapidly growing literature are cavity ring-down spectroscopy of oxygen,<sup>5</sup> highly sensitive spectroscopy of  $\text{N}_2^+$  in a discharge or an ion beam,<sup>6,7</sup> and high-precision spectroscopy of  $\text{HD}^+$  for fundamental science.<sup>8</sup>

One of the most important regions for vibrational molecular spectroscopy is the 3  $\mu\text{m}$  mid-infrared (MIR) region where many carbon containing molecules have their fundamental CH stretches. Up to date, femtosecond sources only scarcely operate in this region, so some kind of conversion is usually applied (for a recent comprehensive review, please confer Ref. 9). This can be achieved, for example, by down-converting a comb to the MIR region by difference frequency generation (DFG) with a phase locked laser in a nonlinear crystal,<sup>10</sup> or even by pumping an optical parametric oscillator (OPO) with an amplified NIR comb, obtaining idler comb radiation which is so powerful that the comb modes themselves can be used for spectroscopy.<sup>11</sup> A further feasible approach is to keep the comb in the NIR range, and to determine the absolute frequency of a DFG-source by measuring the frequencies of the two contributing beams.<sup>12-14</sup>

Optical parametric oscillators are favorite tools for spectroscopy in the MIR range due to their wide tunability, narrow line-width, stability, and output power much higher than DFG-sources. Phase locking a MIR-OPO to a Ti:Sa frequency comb (operating at 0.5–1.1  $\mu\text{m}$ ) requires the use of intermedi-

ate (for example, doubled) frequencies.<sup>15,16</sup> The availability of erbium doped fiber frequency combs (operating at 1–2.1  $\mu\text{m}$ ) made it recently possible to directly link a MIR-OPO to a comb<sup>17</sup> by phase locking both signal and pump beams. Scanning of the idler over 70 MHz has been achieved by shifting the pump frequency with help of an electro-optic modulator.<sup>17</sup>

In this work, we describe a free-running OPO whose idler frequency (in the MIR) is determined by measuring its pump and signal frequencies by a NIR-comb. In this sense, our approach is somewhat similar to that of Ricciardi *et al.*,<sup>17</sup> though our system has been tailored to the specific needs of action spectroscopy of  $\text{CH}_5^+$ : Due to its floppiness,<sup>18</sup> many thousand CH-stretching lines are expected in a very wide frequency range (2300–3200  $\text{cm}^{-1}$ , see Fig. 2 of Ref. 19) even at very low temperatures. Sacrificing locking of the OPO to the comb, our system has been optimized to feature automatic and easy handling, and permits wide scans of 3  $\text{cm}^{-1}$  (90 GHz, limited by OPO pump) in a single piece. The latter has been achieved by a software which detects changes in the sign of the pump beat note. With this system we demonstrate that individual ro-vibrational lines of only a few thousand cold  $\text{CH}_5^+$  parent ions can be determined to a precision of some 100 kHz. With such a precision ground-state combination differences and thus pure rotational transitions can be determined well below 1 MHz allowing identifications of molecular ions in radio-astronomical observations based on high-resolution ro-vibrational spectroscopy.<sup>20</sup>

## OPTICAL SETUP

The optical setup of the spectrometer consisting of OPO and the frequency comb is illustrated in Fig. 1. The cw OPO is a Aculight Argos Model 2400 operating in the range 2560–3130  $\text{cm}^{-1}$ . It is pumped by 1064 nm radiation with power up to 15 W and emits idler and signal beams with their frequencies obeying energy conservation  $hf_p = hf_s + hf_i$ . The signal and pump beams are dumped into beam traps, while small fractions of them (2–5 mW) are sent via beam couplers

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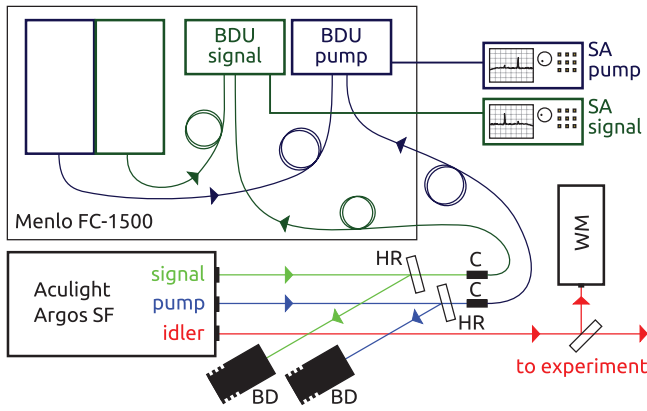


FIG. 1. Optical setup consisting of OPO and frequency comb (HR: high reflectivity mirror, C: fiber coupler, BD: beam dump, BDU: beat detection unit, SA: spectrum analyzer, WM: wavemeter). As the signal beat is fixed during a scan, a counter can be used instead of a spectrum analyzer. See text for more details.

and fibers to the frequency comb (Menlo System FC1500) which is referenced to a rubidium clock (Rohde&Schwarz XSRM, not shown in Fig. 1) with a stability of about  $10^{-11}$ . The frequency of the idler radiation is measured by a wavemeter (Bristol Instruments Model 621A-IR) and the main beam sent to the experiment. The absolute accuracy of the wavemeter is  $\pm 0.2$  ppm, corresponding to  $\pm 20$  MHz in the  $3\mu$  region. The signal and pump beams generate two beat notes  $f_{b,p}$  and  $f_{b,s}$  in two beat detection units of the frequency comb, whose frequencies are read out by two spectrum analyzers (HAMEG HMS 1000E, referenced to the rubidium clock). Alternatively, for the signal beat, the counter delivered with the comb can be used for the readout. As the frequency of interest is the difference between pump and signal, a measurement of the comb offset frequency  $f_{\text{off}}$  is not necessary. In fact, our frequency comb currently does not have any interferometer to measure and lock the offset  $f_{\text{off}}$ . The measurement of the idler frequency  $f_i$  is done in following way. The frequencies of pump and signal are given by the usual formula for frequency combs (see, e.g., Refs. 1 and 21)

$$f_p = f_{\text{off}} + n_p \cdot f_{\text{rep}} + f_{b,p}, \quad (1)$$

$$f_s = f_{\text{off}} + n_s \cdot f_{\text{rep}} + f_{b,s}, \quad (2)$$

with  $f_{\text{rep}} = 250$  MHz being the repetition rate of the comb. The idler is the difference of these frequencies

$$f_i = f_p - f_s = (n_p - n_s) \cdot f_{\text{rep}} + f_{b,p} - f_{b,s} \quad (3)$$

$$= n_i \cdot f_{\text{rep}} + f_{b,p} - f_{b,s}. \quad (4)$$

As the idler frequency is approximately measured by the wavemeter  $f_i \approx f_w$ , the comb number  $n_i$  can be determined by rounding

$$n_i = \frac{f_w - f_{b,p} + f_{b,s}}{f_{\text{rep}}} \quad (5)$$

to the nearest integer. For this, the accuracy of the wavemeter must be better than  $f_{\text{rep}}/2 = 125$  MHz which is fulfilled. The idler frequency  $f_i$  as measured by the frequency comb is finally determined by using Eq. (4). Please observe that the two

beat frequencies  $f_{b,p}$  and  $f_{b,s}$  have a sign which is taken care of by the following procedure: Before starting the OPO-scan, when the pump and signal frequencies have settled and show negligible drifts (typical drifts are shown in Fig. 3), the beat signs are automatically determined by slightly changing the repetition rate  $f_{\text{rep}}$  and observation of the change in beat note. Tuning of the OPO (tuning  $3 \text{ cm}^{-1}$  without readjustment is possible) is done by tuning the pump frequency while keeping the signal resonant in the OPO cavity. Thus, the change of beat note sign of the pump has to be detected by the measurement program (implemented in LabVIEW running on the comb computer). These sign changes happen at the beat frequencies  $0 \text{ Hz}$  and  $f_{\text{rep}}/2 = 125 \text{ MHz}$ , and the span of the pump spectrum analyzer is adjusted to this range. For the software detection to work properly, the scan direction (up/down) and the pump scan steps, usually  $\Delta f_p = 6 \text{ MHz}$ , are given as parameters to the program. When the pump beat approaches the borders of the analyzer span, where a beat sign change is to be expected (for instance, in the upward scanning direction these are the frequency ranges  $[0, \Delta f_p]$  for negative beat sign and  $[125 - \Delta f_p, 125]$  for positive beat sign), a subsequent move of the pump beat will lead to a change in sign. This turned out to work extremely well, though some glitches can occur when scanning fast. These glitches are mostly due to the hysteresis of the piezo-actuator responsible for the pump tuning. Due to the high accuracy of the wavemeter, these glitches can be immediately detected when  $n_i$  as determined by Eq. (5) deviates from an integer more than  $\sim \pm 0.15$  (corresponding to a frequency deviation of  $\pm 38 \text{ MHz}$ ). The measurement is then paused by the software, and the user can then change the pump beat sign by pressing a button.

## TEST MEASUREMENTS

### Beat note measurement by spectrum analyzers

As mentioned above, the beat frequencies of pump and signal beams are measured by the peakfinder utility of the spectrum analyzers, allowing for an update rate of the idler frequency of about  $6 \text{ s}^{-1}$ . As the signal beat is not changing in a scan (apart from a slow drift, see Fig. 3), the spectrum analyzer for the signal can be zoomed into the given region, or even a counter with small bandwidth can be used. On the other hand, the pump beat is scanning over the entire range between  $0$  and  $125 \text{ MHz}$ . To estimate the frequency error induced by such an operation mode, the  $-35 \text{ dBm}$  output of a Hewlett Packard 8648B signal generator has been fed into one spectrum analyzer. In Fig. 2, the deviation between input frequency (signal generator) and measured frequency (analyzer) is shown for three different spans of the spectrum analyzer. Very systematic patterns are obtained. They originate from sorting the measured frequencies into a fixed number of 500 bins. For example, with a frequency span of about  $125 \text{ MHz}$  the bin width is  $125/500 = 0.25 \text{ MHz}$ . About half of this value, i.e.,  $0.125 \text{ MHz}$ , is the amplitude of the binning error seen for the red points in Fig. 2. Apart from this readout error, there is also a systematic shift of the spectrum analyzer to higher frequencies, indicated by the fitted red line



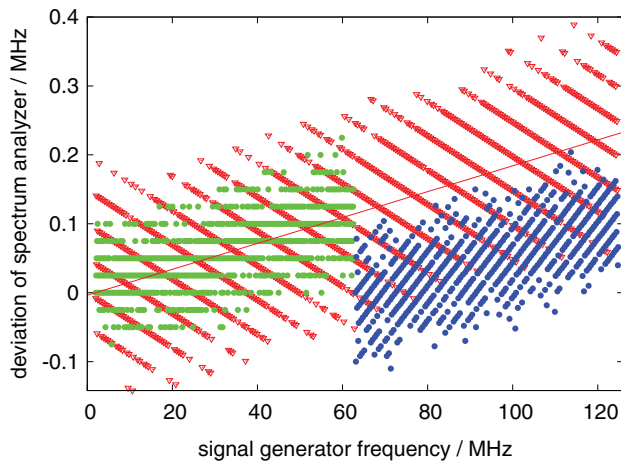


FIG. 2. Systematic deviation and binning error obtained by measuring the pump beat frequency  $f_{b,p}$  with a spectrum analyzer. The span of the analyzer has been set to 0.5–125 MHz (red points) and the signal generator stepped in 100 kHz steps. The binning error can be reduced by dividing this span into two parts (green points: 0.5–63 MHz, blue points: 62–125 MHz). The resolution bandwidth has been set to 300 kHz.

in Fig. 2.<sup>22</sup> As the shown patterns and the systematic shifts are very reproducible, the shift can be corrected for in the measurement program, leaving the pump beat measurement only with a binning error of about 0.125 MHz. For the current Doppler-limited measurements (see Fig. 4), these deviations are not of concern yet. If a lower binning error is required in the future, this can be achieved by switching to smaller spans as shown by the green and blue points in Fig. 2.

### Drift and jitter of OPO

Figure 3 shows a measurement where the beat notes of signal  $f_{b,s}$  and pump  $f_{b,p}$  (which is not scanned here) have been recorded and the idler frequency  $f_i$  determined

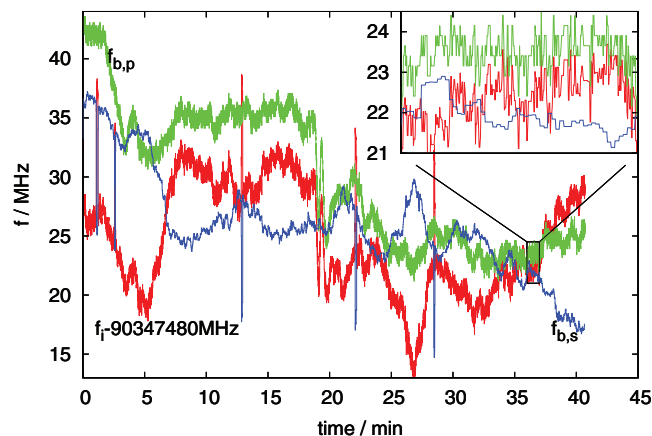


FIG. 3. Idler frequency  $f_i$  (red trace) determined from the shown positive beats (blue: signal, green: pump). The repetition rate has been kept at  $f_{\text{rep}} = 250.00000225$  MHz and the idler comb number measured to be  $n_i = 361\,390$ . The reproducible jumps of about  $10.4 \pm 0.8$  MHz in signal and idler instantaneously happened when opening the laboratory door, thereby changing the laboratory pressure. The inset zooms into a 1 min period, in which the 0.25 MHz binning and the update rate  $6 \text{ s}^{-1}$  of the pump beat is visible. In this measurement, the signal beat has been measured with the counter of the frequency comb and is updated only at a rate of  $1 \text{ s}^{-1}$ .

via formulae (4) and (5). The sign of both beats has been adjusted to be positive. As neither the pump nor the signal frequencies are locked in the current setup, all frequencies in Fig. 3 show slight drifts and jitter. In some measurements, a small common drift of pump and signal is observed and attributed to the slow drift of the offset frequency  $f_{\text{off}}$ , which is not measured nor locked. The shown slow drifts do not present a drawback in the ion spectroscopy measurements (see Spectroscopy of cold ions section), as long as the idler frequency is correctly measured on the timescale of an ion trapping cycle (about 600 ms). Notable are the sudden jumps of about  $\Delta f_s = 10.4$  MHz in the signal (and consequently also in the idler) which occurred when someone opened the laboratory door. These are caused by an increase in pressure in the laboratory which is maintained under slight underpressure by a ventilation system. By increasing the pressure (opening the door), the refractive index  $n(p)$  of air is increased and thus with  $c = c_0/n(p) = \lambda \cdot f_s$  the signal frequency (with  $\lambda$  held constant in cavity) is decreased as observed for the blue trace in Fig. 3. Using the relation  $(n(p) - 1) \sim p$  with proportionality factor  $(n_0 - 1)/p_0$ , one arrives finally to a relation to calculate the air pressure change

$$\Delta p = p_0 \frac{n_0}{1 - n_0} \frac{\Delta f_s}{f_s}. \quad (6)$$

The laboratory pressure at the day of measurement was about  $p_0 = 1006$  mbar, measured with a simple USB barometric data logger (Gulf Coast Data Concepts, LLC) and also obtained online from a local meteorological station. For this pressure and the signal frequency of about  $f_s = 191.3$  THz (1567.1 nm), a refractive index of about  $n_0 = 1.000261$  can be looked up.<sup>23</sup> Using Eq. (6), a pressure change of  $\Delta p = 0.21$  mbar is obtained when opening the door. Pressure changes in this range have also been observed by the datalogger, but of course the reproducibility and the sensitivity of the signal cavity is much better. With this sensitivity, one could even detect pressure changes smaller than  $20 \mu\text{bar} = 2 \text{ Pa}$ . Also, as the atmospheric pressure can vary more than 5 mbar during a day, frequency shifts of the signal frequency exceeding 260 MHz can be expected just due to this effect. This can simply be counteracted by manually adjusting the voltage applied to the signal cavity piezo.

The inset in Fig. 3 shows the jitter of the pump and signal and the resulting idler radiation during a 1 min period. The pump beat is updated at about 6 Hz (measured by the spectrum analyzer) while the signal beat is updated at 1 Hz (the counter value is obtained from the server of the frequency comb software). As can be seen, the jitter of the OPO idler is dominated by the jitter of the pump radiation. The jitter of the pump in turn is somewhat larger than the frequency binning of 0.25 MHz of the spectrum analyzer. Thus, for future work the jitter has to be counteracted by some locking scheme (see Summary and outlook section).

### Spectroscopy of cold ions

The suitability of the system for the search of unknown molecular lines over a wide range of IR frequencies has been tested on the fluxional molecule  $\text{CH}_5^+$ , the “enfant terrible” of

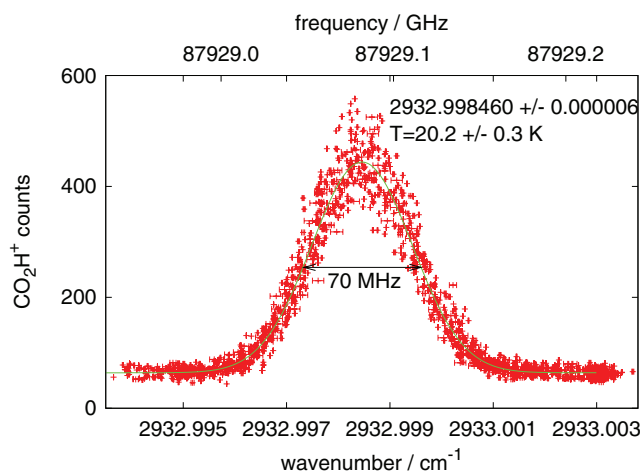


FIG. 4. Single rovibrational transition of  $\text{CH}_5^+$  detected by inducing the reaction  $\text{CH}_5^+ + \text{CO}_2 \rightarrow \text{CH}_4 + \text{CO}_2\text{H}^+$  with the OPO and counting the reaction product  $\text{CO}_2\text{H}^+$ . A fit with a Doppler profile yields a frequency position of  $(2932.998460 \pm 0.000006) \text{ cm}^{-1}$  and a temperature  $(20.2 \pm 0.3) \text{ K}$ .

molecular spectroscopy.<sup>18</sup> The test has been performed with a special kind of action spectroscopy called laser induced reaction (LIR). The LIR spectroscopy is capable of detecting ro-vibrational or even pure rotational transitions of molecular ions trapped in a cryogenic ion trap,<sup>24</sup> for details please see Refs. 25–27. In the current measurements, about 10 000  $\text{CH}_5^+$  ions were trapped, cooled to the trap temperature by a short He pulse, and during the subsequent irradiation with the  $\sim 800 \text{ mW}$  idler beam subjected to  $\text{CO}_2$  gas. The  $\text{CO}_2$  gas was diluted in He in a ratio of about 1:5 and supplied from a pulsed valve in three short pulses in order to circumvent problems with freeze out which hindered cooling to the lowest possible trap temperature up to date.<sup>19</sup> The reaction with  $\text{CO}_2$  serves to detect the excitation of the  $\text{CH}_5^+$  by counting the reaction products of the endothermic reaction  $\text{CH}_5^+ + \text{CO}_2 \rightarrow \text{CO}_2\text{H}^+ + \text{CH}_4$ .<sup>19,28</sup> The described cycle takes about 600 ms. After every 4th cycle, the idler was tuned by about 6 MHz.

An example measurement of a single ro-vibrational line is shown in Fig. 4, with the line position and Doppler temperature fitted to  $(2932.998460 \pm 0.000006) \text{ cm}^{-1}$  and  $(20.2 \pm 0.3) \text{ K}$ , respectively. The discrepancy between the nominal trap temperature ( $\sim 10 \text{ K}$ ) and the Doppler temperature is caused by radio frequency heating effects<sup>29</sup> and the room temperature  $\text{CO}_2/\text{He}$  gas pulses entering the trap. The shown measurement yields the first new published line position for this enigmatic molecule since the tedious work of Oka and co-workers more than 10 years ago. Please note that assignment of the  $\text{CH}_5^+$  lines is not possible to date.<sup>18</sup> The center of the Doppler profile can be fitted within 200 kHz, giving a relative precision of this single measurements of  $2 \times 10^{-9}$ . When carefully measured with a good signal-to-noise ratio and stable background, tests on several lines have shown that the scatter of the single measurements is in the same range, so that a final combined standard deviation of their frequency positions below 200 kHz can be obtained by a couple of measurements. At this level, we do not expect any systematic errors of the frequency determination of the

peak positions, as the binning error discussed earlier only introduces some “frequency noise” and will thus cancel out in a single line measurement. Furthermore, the  $\text{CO}_2/\text{He}$  pressures applied in the current LIR scheme are too low (max.  $10^{-8} \text{ mbar}$ ) to induce any systematic pressure shifts.

## SUMMARY AND OUTLOOK

The presented combination of a free-running OPO, a NIR-frequency comb and a cold 22-pole ion trap allows to perform wide scans of  $3 \text{ cm}^{-1}$  in one piece in the MIR range at high resolution. Our relative line position precision of about  $10^{-9}$  is currently limited by the Doppler width of the cooled ions, and to a lesser extent by the signal-to-noise ratio of the ion counts, the OPO jitter and the limitations imposed by the usage of the spectrum analyzers.

First ro-vibrationally resolved LIR-spectra of trapped molecular ions have been obtained for  $\text{C}_2\text{H}_2^+$  some ten years ago using a DFG scheme with pulsed lasers, showing that action spectroscopy of only a few thousand ions is possible.<sup>26,30</sup> However, even at the low temperatures of our trap experiments many more rotational levels are populated for an asymmetric rotor like  $\text{CH}_5^+$  leaving much fewer ions in the pumped rotational state. In addition, population of internal rotor states of this exceptionally floppy molecule increases the partition function substantially. The ultimate sensitivity of the LIR technique allows to overcome these limitations. As can be seen from Fig. 4, the spectrum is almost background free since the proton transfer from  $\text{CH}_5^+$  to  $\text{CO}_2$  does not occur without laser excitation. The high spectral intensity of the MIR OPO system and the many collisions of the parent ions with the He buffer gas repopulating the rotational state of interest lead to rather high signal-to-noise ratios of product ion counts enabling high-resolution ro-vibrational spectra of a finite number of parent ions. It is gratifying to see that high-resolution LIR spectroscopy can be extended to such difficult cases.

As pointed out by several authors,<sup>14,20</sup> high resolution vibrational spectroscopy can yield accurate rotational data not only on the ground but also for the vibrational excited state. A prominent example for such an approach is the interstellar important  $\text{CH}_2\text{D}^+$ ,<sup>31</sup> whose rotational lines became available only recently from microwave spectroscopy.<sup>32</sup> It has been shown with our home-built OPO system that ground state combination differences of ro-vibrational lines can be determined to an accuracy sufficient to meet the precision of radio astronomical observations which usually aim for 1 MHz<sup>20</sup> in the determination of line center frequencies. Comparison of ro-vibrational with microwave data are possible for cases like  $\text{CH}_2\text{D}^+$ .

However, for  $\text{CH}_5^+$  no high-quality structural information is available to date. No assignment of the many ro-vibrational lines of warm  $\text{CH}_5^+$  could be made.<sup>18</sup> The rotational spectrum of  $\text{CH}_5^+$  is missing and only theoretical predictions of its layout are available.<sup>33</sup> Therefore, the search of ground state combination differences of ro-vibrational lines of  $\text{CH}_5^+$  is currently the most promising way to unravel the structure of this non-classical molecule. The current work is the first and necessary step to demonstrate that high-resolution LIR

action spectroscopy can solve this problem since the accuracy and precision of combination differences will be sufficient to separate term differences of the ground state and the vibrational excited state of  $\text{CH}_5^+$ .

In the future, much higher precision spectroscopy is envisaged based on the instrument described here. Short term simple improvements in this direction are colder ions, for which a 4 K-instrument is close to completion in our laboratory, but a further narrowing of the transition line, for example, by ion trap Lamb dip spectroscopy, seems mandatory. The high idler power of the OPO (at least 1 W over the entire tuning range) is a perfect basis for this challenge. Additionally, it will be necessary to stabilize the used idler radiation. As the slow repetition rate of the action spectroscopy measurement cycle (several 100 ms) does not permit a locking of the laser to the transition, it will be necessary to lock the OPO to the comb. Since our frequency comb lacks the stabilization of the carrier envelope offset, neither locking schemes of only pump or only signal to the comb would yield a stable idler frequency. However, this can be reached by locking both frequencies at once to the comb, and scanning the idler frequency by shifting the pump frequency in a small range with help of an electro-optic modulator.<sup>17</sup> Alternatively, both beat frequencies can be mixed and the difference frequency of those can be phase-locked to a DDS (direct digital synthesis) using only one single feedback loop controlling the frequency of either pump or signal, similar to the system described in Ref. 13. With this approach, the idler frequency could be set and stabilized to a given value instead of just being measured accurately. Especially for transitions with a smaller line width such as the mentioned Lamb dip, this locking is crucial to retrieve the proper line shape.

## ACKNOWLEDGMENTS

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