Two-Photon Rotational Action Spectroscopy of Cold OH^- at 1 ppb Accuracy

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The fundamental rotational transition $J = 1 \leftarrow 0$ of the anion OH^- has been measured by cooling mass-selected OH^- ions to 10 K in a 22-pole ion trap and applying a novel rotational-rovibrational two-photon scheme. A transition frequency of $(1\,123\,101.0410 \pm 0.0014)$ MHz was obtained with so far unprecedented accuracy. The general application of the presented action-spectroscopy scheme to other anions and cations is discussed.

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In the field of molecular ion spectroscopy, trap setups offer the advantage of cooling and mass selecting the ion ensemble, leading to uncontaminated and assignable spectra. In addition, the stored ions can be exposed to the radiation field for rather long times, and, therefore, very high spectral resolution can be achieved in principle. The limited number of trapped ions, though, makes the application of some sort of action spectroscopy mandatory, with methods like predissociation spectroscopy [1,2], laser induced reactions (LIR) [3], infrared multiphoton dissociation (IRMPD) [4], or the messenger (tagging) technique [5,6] routinely being used for vibrational investigations. For rotational spectroscopy, however, the inherent low photon energy has limited the number of methods and examples so far [7,8]. The first demonstration of pure rotational spectroscopy in a cold ion trap was only feasible due to the large rotational spacing of the investigated ions H_2D^+ and D_2H^+, and also the low energy barrier which had to be surmounted in the LIR process [7]. Such a scheme cannot be transferred to other molecular ions in a direct manner. Recently, the ternary attachment of 4 K He to trapped cations has been used for a new action spectroscopic scheme called LIICG (laser induced inhibition of complex growth) [9] to record the electronic spectrum of cold N_2^+. We adapted this method for rovibrational spectroscopy of several molecular cations in a newly developed instrument [10]. Very recently we also demonstrated that He attachment depends on the rotational state of the cation, and thus changes in the rotational population also change the effective attachment rate. Recording the number of cation-He complexes as a function of the excitation wavelength turns out to be the first rotational spectroscopy method generally applicable to any trapped cation [11]. Such novel schemes for rotational spectroscopy are needed in radio astronomy and molecular physics for the identification and structural analysis of larger ionic species. In this Letter, we present an alternative scheme for direct rotational spectroscopy in ion traps, applicable to both cations and anions. It is a LIR IR-THz double resonance scheme, in which the wavelength of the IR photon is kept fixed on a rovibrational transition starting from a rotational level of the vibrational ground state, resulting in a detectable constant LIR signal. The THz photon then excites a rotational transition starting or ending on the same lower level (see inset of Fig. 3), thus decreasing or increasing the LIR signal, respectively. The rotational line is recorded by scanning the THz photon frequency. While a preliminary test of this two-photon scheme has been given earlier for the cation H_2D^+ [12] for which also the single photon rotational scheme works [7], we give here a full account on its first application to an anion, deprotonated water OH^-, for which, in contrast, the one photon THz excitation scheme does not work. This work is thus related to earlier ion trap investigations of the photodetachment of the electron from OH^- [13,14], and, in particular, on previous rovibrational [15] and rotational [16,17] work on this closed shell linear molecule. Because of cooling the ion trap to 10 K in the present work, the frequency of the fundamental rotational transition $J = 1 \leftarrow 0$ at 1.123 THz could be refined by more than 2 orders of magnitude to within 1 ppb accuracy. The corresponding improved transition frequencies and spectroscopic constants are given below.

The experiment has been performed in a 4 K 22-pole ion trapping machine. As the setup has been described in detail earlier [10,18], only the modifications relevant for this work are described here. Most importantly, the operation has been changed for the investigation of negative ions by using a multichannel plate (MCP) as ion detector, and by changing the voltages of all involved electrodes (further details of negative-ion operated 22-pole traps can be found in [13,14,19]). One of the advantages of the new ion trap setup [10] is an access flange in close proximity (140 mm) to the entrance of the 22-pole ion trap, facilitating easy adjustment of mm- and sub-mm-wave beams into the ion trap. This flange has been equipped with a 0.8 mm thick diamond window, through which the copropagating 2.85 μm IR radiation and the 276 μm THz radiation have been introduced. These two beams have been combined by an elliptical mirror containing a 1 mm diameter hole for the IR laser, as shown in Fig. 1. The IR radiation was provided

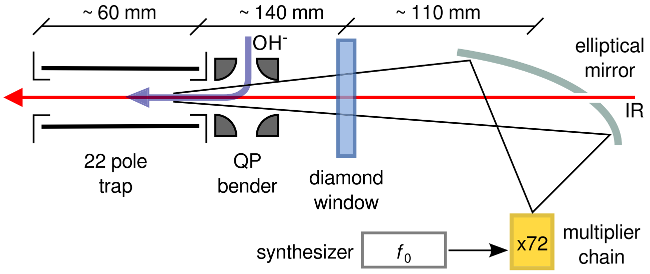

FIG. 1 (color online). Schematic drawing of the 22-pole trap setup with admitted IR and THz radiation. The IR radiation comes from the right side and passes through a 1 mm hole in the elliptical mirror ($f = 43.7$ mm), which also focuses the THz photons from the multiplier chain. Both wavelengths pass through a 0.8 mm thick diamond window before entering the trap. The shown electrostatic quadrupole (QP) bends the incoming, mass-selected OH^- bunch by 90° into the trap.

by a cw optical parametric oscillator [(OPO), Aculight Argos Model 2400], with power up to several hundred mW, and its frequency measured with a Bristol model 621 A wave meter, while the ~ 1 μW THz radiation was supplied by a multiplier chain (Virginia Diodes, Inc.) with a total multiplication factor of 72, driven by a E8257D Agilent synthesizer locked to a Rubidium atomic clock. The bandwidths of the radiation sources ($f_{\Delta,\mathrm{OPO}} < 1$ MHz, $f_{\Delta,\mathrm{THz}} \lesssim 1$ Hz) are negligible under the given experimental conditions. The OH^- anions were produced in an ion storage source by electron impact on a 2:1 mixture of N_2O and H_2 [20], and several thousands of them mass selected and trapped in the 22-pole ion trap. He attachment at 4 K turned out to be very ineffective as complexes between helium and the anionic partners are usually even weaker bound than their neutral analogues; for a review, see [21]. Therefore, the suppression of complex formation could not be employed. Instead, the endothermic anion-molecule reaction

$$OH^-(\nu, J) + H_2 \rightarrow [H_3O^-]^* \rightarrow H^- + H_2O \qquad (1)$$

was used for LIR, in which the rovibrational excitation of the OH^- ions can be probed by counting the reaction product H^-. Because of the usage of H_2 as a neutral reaction partner, the trap had to be heated to 10 K to avoid freezing.

Consequently, as a first step in the investigations, the rovibrational transitions of OH^- [15] have been revisited in a single photon LIR experiment using reaction (1). As OH^- has a large rotational spacing, the ion trap was heated slightly to a nominal temperature of 16 K, so that rotational levels up to $J = 3$ could be populated. Seven rovibrational lines that were recorded are listed in Table I. An example rovibrational LIR signal, where the reactant OH^- and product H^- ion counts are recorded as a function of the OPO frequency is shown for the $(v, J) = (1,1) \leftarrow (0,0)$ transition (at 3591.5 cm^{-1}) in Fig. 2. The detected lines have been fitted with a saturated Gaussian [for details, see Eq. (8) in [12]] to determine the frequency positions. Although the line center positions could, in principle, be determined with high precision (several 10^{-5} cm^{-1}), the wave meter used for frequency calibration has an accuracy of only 30 MHz, and thus our measurements improve the former investigations [15] by a factor of only 2.

TABLE I. Frequencies of the fundamental rotational and the seven lowest rovibrational transitions of OH^- measured in this work, compared to former measurements [15,17]. Because of the usage of a wave meter, our rovibrational data are accurate only within 0.001 cm^{-1}, while the fundamental rotational transition has been determined by seven separate measurements (as shown in Fig. 3) to its final precision of 1 ppb. Within the error limits, former and new data agree well.

$(\nu, J) \leftarrow (\nu, J)$	This work	Former work	Unit
$(0,1) \leftarrow (0,0)$	1 123 101.0410(14)	1 123 100.985(324)	MHz
$(1,1) \leftarrow (0,0)$	3591.5265 (10)	3591.5254 (20)	cm^{-1}
$(1,2) \leftarrow (0,1)$	3625.8566 (10)	3625.8537 (20)	cm^{-1}
$(1,3) \leftarrow (0,2)$	3658.5494 (10)	3658.5497 (20)	cm^{-1}
$(1,4) \leftarrow (0,3)$	3689.5617 (10)	3689.5591 (20)	cm^{-1}
$(1,0) \leftarrow (0,1)$	3518.1444 (10)	3518.1434 (20)	cm^{-1}
$(1,1) \leftarrow (0,2)$	3479.1860 (10)	3479.1834 (20)	cm^{-1}
$(1,2) \leftarrow (0,3)$	3438.7803 (10)	3438.7799 (20)	cm^{-1}

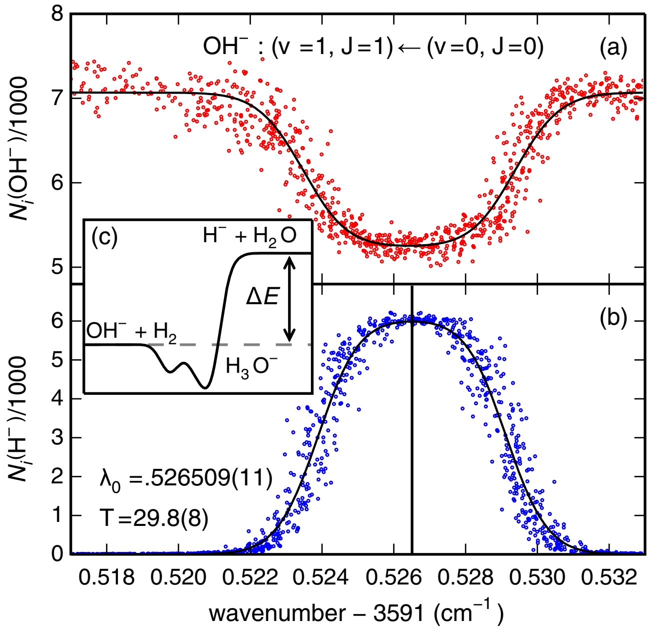

FIG. 2 (color online). Single photon LIR lines of the $(v, J) = (1,1) \leftarrow (0,0)$ rovibrational transition showing decrease (a) and increase (b) of reactant and product ion counts, respectively (the discrepancy between the ion count signal magnitudes is attributed to mass discrimination of the detection system). The 22-pole ion trap was kept at 16 K and the saturated Doppler fit yields a kinetic temperature of about 29 K. The inset (c) shows schematically the potential energy surface with the H_3O^- intermediate.

In principle, the full precision provided by the cold ion ensemble can be exploited by using a frequency comb system for absolute frequency calibration as demonstrated in previous experiments on rovibrational lines of the CH_5^+ molecule [22]. Note that the LIR signal of H^- is practically zero off resonance which shows that LIR is a background free spectroscopy method. It also shows that reaction (1) indeed needs to be activated. Time-dependent measurements of the LIR signal show that reaction (1) is very fast upon vibrational excitation and that the theoretically predicted endothermicity is surely overcome by the additional internal energy of 3591.5 cm^{-1} for the excitation into the (1,1) state as shown in Fig. 2. As shown in Table I, even excitation into (1,0) leads to a LIR signal. Therefore, our experiment safely sets an upper limit of 3556 cm^{-1}, the difference between (1,0) and (0,0), or $\Delta E < 0.44$ eV for its predicted endothermicity. This upper limit compares very well with literature values for ΔH in the range 0.365–0.462 eV [23–26]. A sketch of the previously calculated potential energy surface for H_3O^- [23,25], together with the barrier for the LIR process is shown as an inset in Fig. 2.

For the two-photon rotational spectroscopy of the fundamental $J = 1 \leftarrow 0\,(v = 0)$, the trap has been cooled to 10 K to maximize the population of the lowest $J = 0$ rotational state, with only moderate population ($< 10\%$) in the $J = 1$ state. For the second photon the rovibrational transitions $(v, J) = (1,1) \leftarrow (0,0)$ or $(1,2) \leftarrow (0,1)$ have been selected, starting at the lower and upper levels involved in the targeted fundamental rotational transition, respectively. The frequency of this rotational transition has been measured before by Matsushima *et al.* [17] in a discharge cell using a tunable far-infrared spectrometer. For the measurements in this work, the OPO has been kept at one of the rovibrational center frequencies (see Table I) by a feedback loop to generate a constant LIR signal [such as on top of the peak shown in Fig. 2(b)]. Scanning the synthesizer frequency (which is multiplied by a factor of 72) over the $J = 1 \leftarrow 0$ resonance, dips and peaks were superimposed onto the LIR signal background. To minimize background drifts, this scanning was done symmetrically up and down in frequency. As the peak generated with the $(1,2) \leftarrow (0,1)$ rovibrational transition showed a better signal-to-noise ratio, it was used for frequency determination by multiple measurements. The final result is given in Table I and an example measurement is depicted in Fig. 3 together with a Gaussian fit. The Doppler width of the shown signal reveals an OH^- kinetic ion temperature of 15 K. This effective cooling in combination with the atomic clock referenced synthesizer (the Rb clock is accurate within 10^{-11}), allows us to constrain the transition to within 1.4 kHz by seven separate measurements, and thus within 1 ppb. This is an improvement by more than 2 orders of magnitude compared to the former measurement [17]. The improved spectroscopic constants for the vibrational ground state are presented in Table II. As expected, only the rotational constant B_0 is substantially refined.

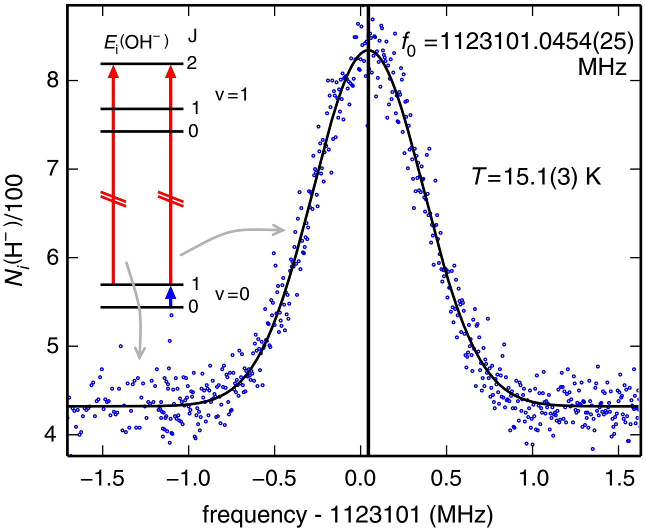

FIG. 3 (color online). Two photon LIR excitation, consisting of the rovibrational $(v, J) = (1,2) \leftarrow (0,1)$ and the rotational $(0,1) \leftarrow (0,0)$ transitions. With the trap at a nominal 10 K, the OH^- (0,1) level is moderately populated, leading to a stable background product count when only the rovibrational transition is kept on resonance (left side of inset). Scanning the rotational transition into resonance then pumps OH^- ions into the $J = 1$ rotational state, leading to additional product counts (right side of inset). This resonance is very narrow and indicates a kinetic ion temperature of about 15 K.

This work is the first demonstration of LIR for anions and, in particular, the first pure rotational spectroscopy of an anion in a cold ion trap. The presented two-photon method is quite general, it can be used for cations as well as for anions, provided there is a suitable reaction for which a sizable reaction product signal can be generated. The sensitivity of the method is inherently connected to the finite ensemble of ions prepared in the trap and therefore has tremendous advantages compared to other hole burning spectroscopy experiments. This new method of THz spectroscopy extends all rovibrational or rovibronic action spectroscopy methods of cold trapped ions into the rotational domain. The cryogenic cooling associated with action spectroscopy allows for a very high precision determination of the transition frequencies. Currently the precision of the experiment is limited by the thermal motion of the ions in

TABLE II. Improved molecular parameters for OH^- (in MHz) for the ground vibrational state only, obtained by feeding the program PGOPHER [27] with the values of the fundamental given in Table I and former rotational work [16,17]. The 1σ errors are given in brackets.

	This work	Matsushima *et al.* [17]
B_0	561 669.3002(58)	561 669.1865(944)
D_0	59.3981(30)	59.3928(55)
H_0	0.004 13(11)	0.004 09(9)

the trap. The actual width of the absorption signal is already below 1 MHz and can be lowered substantially in a lower temperature environment. For LIR this can be achieved, for instance, by a molecular beam of the condensable reaction partner traversing the 4 K cold ion trap. Thanks to the good overlap of the phase stable THz radiation with the ion cloud, the method is immune to transit time broadening effects. Therefore, frequencies of rotational transitions of molecular ions may be determined yet better by another 1 or 2 orders of magnitude and then serve for probing fundamental physics as it is approached for molecules like methanol [28].

Over the last eight years six anions have been detected in space based on their rotational spectrum [29]. With the mass selective, cold ion trap experiments, further rotational and rovibrational spectra of molecular anions will be measured. Deprotonated versions of abundant interstellar molecules are among the most promising candidates. Rotational spectra of these molecules will help to identify anions as well as cations in space as has been demonstrated for the l-C_3H^+ cation by our recent work [11]. This work will help to clarify the role of negative and positive ions on the chemistry of the interstellar medium.

The methods described in this work can be applied to other ions of fundamental interest, e.g., the intermediate H_3O^-. This ion has been used in photodetachment experiments [23] to probe the potential energy surface of the analogous neutral reaction $OH + H_2 \rightarrow H_2O + H$. Two isomers, $OH^- \cdot H_2$ and the lower-lying $H_2O \cdot H^-$, are predicted (see inset in Fig. 2). Both structures can be investigated using temperature dependent rovibrational action spectroscopy. For this lightly bound ion, predissociation into OH^- and H_2 seems feasible with a single photon $h\nu > 0.36$ eV. Moreover, applying the two-photon rotational scheme will yield rotational constants and the structure of this fundamental system, presenting a benchmark for future quantum calculations.

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