

## SPECTROSCOPY

# Frequency-comb spectroscopy on pure quantum states of a single molecular ion

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Spectroscopy is a powerful tool for studying molecules and is commonly performed on large thermal molecular ensembles that are perturbed by motional shifts and interactions with the environment and one another, resulting in convoluted spectra and limited resolution. Here, we use quantum-logic techniques to prepare a trapped molecular ion in a single quantum state, drive terahertz rotational transitions with an optical frequency comb, and read out the final state nondestructively, leaving the molecule ready for further manipulation. We can resolve rotational transitions to 11 significant digits and derive the rotational constant of  $^{40}\text{CaH}^+$  to be  $B_R = 142\,501\,777.9(1.7)$  kilohertz. Our approach is suited for a wide range of molecular ions, including polyatomics and species relevant for tests of fundamental physics, chemistry, and astrophysics.

**M**olecular spectroscopy is essential to understand molecular properties, which underpin chemistry and biology. Improved spectroscopic precision and state control can uncover obfuscated molecular properties and enable direct manipulation of molecular quantum states. However, because numerous effects crowd and blur molecular spectra, spectroscopic experiments often fail to resolve the natural linewidth of the transitions. Some of these effects can be ameliorated by using cold trapped molecules. Laser cooling and trapping (1) have enabled molecule formation from cold atoms (2) and precision molecular spectroscopy (3). Direct laser cooling shows promise for molecular species with advantageous level structures (4, 5). Long interrogation times and low translational temperature yield high resolution (6), which has enabled, for example, the most stringent test of fundamental theory carried out by molecular ions (7). Yet, even with trapped and cooled molecules (8), commonly used detection methods, such as state-dependent photodissociation or ionization, are destructive, preventing further manipulation. For larger molecules with more hyperfine and spin-rotation couplings, spectra typically become more complex and assignment of features more difficult.

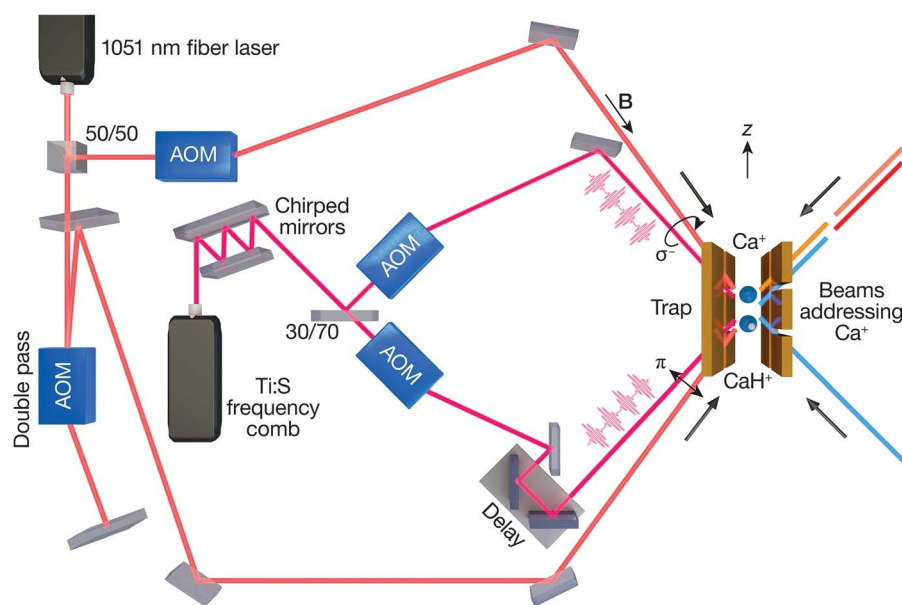
We perform high-resolution rotational spectroscopy of a single  $^{40}\text{CaH}^+$  molecular ion

using methods applicable to a broad range of molecular ion species. We coherently drive stimulated terahertz Raman rotational transitions using an optical frequency comb (OFC) (9–12) with a spectrum far off-resonant from most vibrational and all electronic transitions (10). We demonstrate <1-kHz spectral linewidth and determine the transition centroid frequencies with  $\sim 1$  part per billion (ppb) accuracy. Using OFCs with broader spectra, we could interrogate molecular transitions up to optical frequencies in a similar way (13) for applications such as testing fundamental physics,

benchmarking molecular theories, and assigning spectral lines observed in the interstellar medium (14). In this direction, we determine the frequency differences between rotational centroids from measured transition frequencies (13) to derive precise  $^{40}\text{CaH}^+$  rotational constants up to fourth order. We detect both the initial and final states of the attempted rotational transition, demonstrating a capability that simplifies the spectra and facilitates line assignment. We independently confirm our assignments by comparison with quantum-chemical calculations (15).

In our experiments (Fig. 1), a  $^{40}\text{Ca}^+ - ^{40}\text{CaH}^+$  ion pair, trapped in a linear Paul trap in ultrahigh vacuum, is studied with quantum-logic spectroscopy (16–19). At room temperature, the  $^{40}\text{CaH}^+$  is in its  $^1\Sigma$  vibronic ground state, but its rotation is thermalized with the environment. Blackbody radiation continuously perturbs the molecule, causing rotational state jumps on a time scale of tens of milliseconds to seconds for the states that we study.

We label the molecular eigenstates in a static external magnetic field  $\mathbf{B}$  as  $|J\rangle = |J, m, \xi\rangle$ , where  $J$  is the rotational quantum number,  $m$  is the projection quantum number of the total (rotational and proton nuclear spin) angular momentum on the  $\mathbf{B}$  direction, and  $\xi \in \{+, -\}$  labels the two eigenstates that share the same  $J$  and  $m$ , or is the sign of  $m$  for the case  $m = -J - 1/2$  or  $J + 1/2$  (17). For  $1 \leq J \leq 6$



**Fig. 1. Experimental setup.** A  $^{40}\text{CaH}^+ - ^{40}\text{Ca}^+$  ion pair is held in a linear Paul trap. The  $^{40}\text{CaH}^+$  is projectively prepared using Raman beams from a 1051-nm fiber laser (red) (17). A Ti:S OFC is divided into two Raman beams (pink). The frequencies and powers of the beams are controlled by AOMs. The normal mode of motion used for quantum-logic operations is along the  $z$  axis. The two pairs of Raman beams have  $\pi$  and  $\sigma^-$  polarizations relative to the quantization axis defined by the static magnetic field  $\mathbf{B}$ . They drive two-photon SRTs in the molecule, for which selection rules  $\Delta J = 0, \pm 2$  and  $\Delta m = \pm 1$  apply. Group delay dispersion introduced by optical elements is precompensated with chirped mirrors, and a tunable delay stage ensures that the pulses from both arms temporally overlap on the molecular ion.

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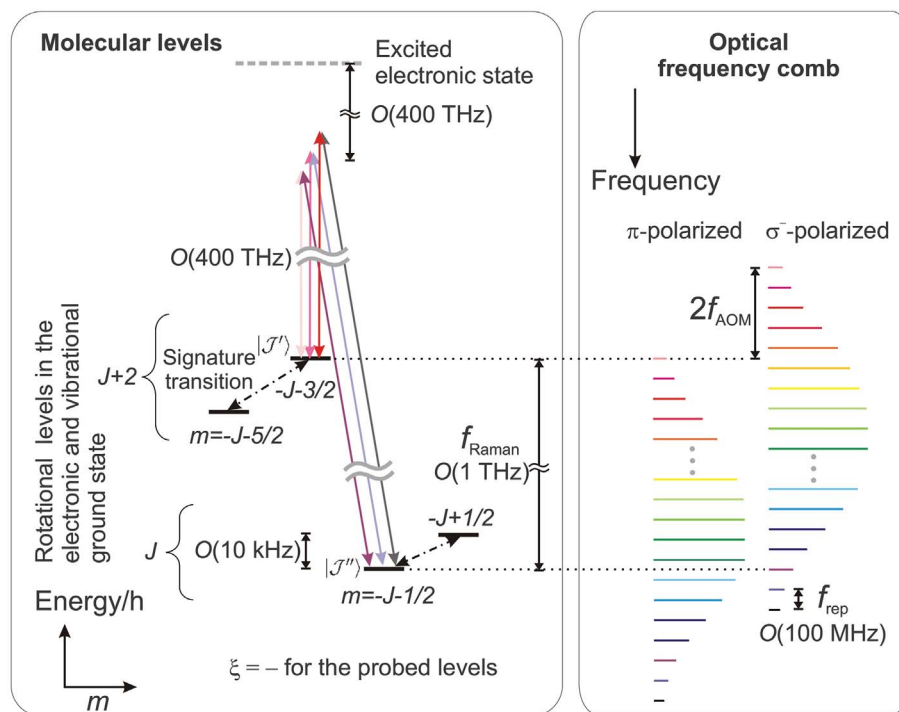
and our  $\sim 0.357$ -mT quantization field, each rotational manifold contains a signature transition (Fig. 2) with a unique frequency (13). Two states connected by such a signature transition can be used for high-fidelity state preparation and detection for the corresponding manifold (13, 17).

Our spectroscopy starts with heralded projective molecular state preparation (17). First, the molecular population is pumped toward a state connected by a signature transition. Then, one normal mode of the coupled harmonic motion of the atomic and molecular ions in the external potential of the trap is initialized in the ground  $|n=0\rangle$  or first excited  $|n=1\rangle$  state by manipulation of the atom (20, 21). We subsequently attempt to drive the signature transition with a  $\pi$  pulse on a sideband of the shared motion  $|J, m = -J+1/2, -\rangle|n=0\rangle \leftrightarrow |J, -J-1/2, -\rangle|n=1\rangle$  using a pair of Raman beams derived from a 1051-nm continuous-wave (CW) fiber laser (17). With finite probability, successful state preparation is heralded by a motional state change, detected with operations on the atom (13, 17). The sequence is repeated to suppress molecular preparation errors. The CW Raman beams can prepare and read out the  $|\mathcal{J}'' = \{J, -J-1/2, -\}\rangle$  and  $|\mathcal{J}' = \{J+2, -J-3/2, -\}\rangle$  states [ $J \in \{1, 2, 3, 4\}$  in this work], each connected by the signature transition in the respective manifold.

We then probe a rotational transition and detect the molecular state. We coherently excite the rotational transitions  $|\mathcal{J}''\rangle \leftrightarrow |\mathcal{J}'\rangle$  with Raman beams derived from a titanium:sapphire (Ti:S) femtosecond laser OFC with a repetition rate  $f_{\text{rep}} \sim 80$  MHz and 800- to 850-nm center wavelength (Fig. 2). The frequencies of the Raman beams are shifted oppositely by  $f_{\text{AOM}}$  with acousto-optic modulators (AOMs) (Figs. 1 and 2). The comb teeth in one beam together with the corresponding ones in the other beam collectively drive a stimulated Raman transition (SRT) of frequency  $f_{\text{Raman}} = |Nf_{\text{rep}} - 2f_{\text{AOM}}|$  ( $N$  is an integer) (9–13) (Fig. 2). By sequentially detecting the  $|\mathcal{J}''\rangle$  and  $|\mathcal{J}'\rangle$  states, we confirm excitation of the attempted transition. With the molecule prepared in a known state, the  $\sim 10$ -THz bandwidth OFC can probe all allowed transitions up to several terahertz by scanning  $f_{\text{AOM}}$  over  $f_{\text{rep}}/2$ . This facilitates the search for transitions when knowledge of the molecular constants is limited.

Figure 3A shows the spectra of a transition between the  $J=2$  and  $J=4$  rotational manifolds. When  $f_{\text{Raman}}$  of the comb Raman pulse train (CRPT) is tuned near the  $\sim 2$ -THz resonance frequency, the molecular population is transferred from the prepared state  $|\mathcal{J}'' = \{2, -5/2, -\}\rangle$  to the final state  $|\mathcal{J}' = \{4, -7/2, -\}\rangle$ .

Rabi flopping between  $|\mathcal{J}''\rangle$  and  $|\mathcal{J}'\rangle$  is driven by setting  $f_{\text{Raman}}$  on resonance with



**Fig. 2. Molecular levels probed with comb Raman beams.** Within the  $J$ th manifold, either of the  $|J, -J-1/2, -\rangle$  and  $|J, -J+1/2, -\rangle$  states connected by the signature transition (dot-dash arrow) can be nondestructively detected and prepared with the CW Raman beams. The comb teeth in each comb Raman beam are spaced in frequency by  $f_{\text{rep}}$ . Within the limit of the comb spectrum, any comb tooth from one beam (e.g., the tooth in red from the  $\pi$ -polarized beam) can have a target difference frequency  $f_{\text{Raman}}$  with a corresponding comb tooth from the other beam (the tooth in dark gray from the  $\sigma$ -polarized beam). The  $\Delta J = \pm 2$  transition  $|\mathcal{J}' = \{J+2, -J-3/2, -\}\rangle \leftrightarrow |\mathcal{J}'' = \{J, -J-1/2, -\}\rangle$ ,  $J \in \{1, 2, 3, 4\}$  is interrogated by a CRPT. The gray dashed line indicates off-resonant excited electronic states of the molecule.  $O(\dots)$  indicates “on the order of.”

**Table 1. Measured and inferred rotational transition frequencies.** The transition frequencies  $f_{\mathcal{J}'', \mathcal{J}'}$  were determined at a magnetic field of 0.357(1) mT with statistical uncertainties  $\delta f_{\mathcal{J}'', \mathcal{J}'}$  representing 95% confidence intervals of the line centers. The centroid frequencies  $cf_{\mathcal{J}'', \mathcal{J}'}$  are calculated from measured frequencies by subtracting shifts due to finite magnetic field and spin-rotation coupling. The uncertainties in these corrections and the systematic uncertainty due to the trap radio-frequency electric field at the molecule are included in the 95%-confidence systematic uncertainties  $\delta cf_{\mathcal{J}'', \mathcal{J}'}$  of the centroid that are substantially larger than the statistical uncertainties of the measured resonances.

$J''$	$J'$	$f_{\mathcal{J}'', \mathcal{J}'}$ (THz)	Statistical uncertainty $\delta f_{\mathcal{J}'', \mathcal{J}'}$ (Hz)	$cf_{\mathcal{J}'', \mathcal{J}'}$ (THz)	$\delta cf_{\mathcal{J}'', \mathcal{J}'}$ (kHz)
1	3	1.424 204 460 565	14	1.424 204 457 7	2.4
2	4	1.992 911 000 121	16	1.992 910 990 8	3.3
3	5	2.560 643 630 446	20	2.560 643 614 2	3.7
4	6	3.127 125 998 610	63	3.127 125 974 8	4.5

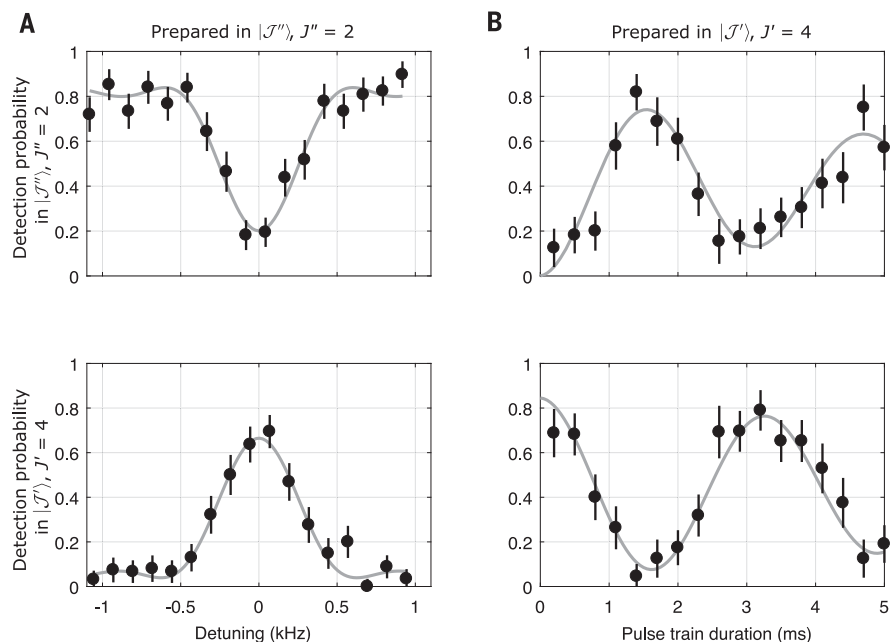
a transition and varying the duration of the CRPT. This puts the molecular ion into superpositions of the form  $\alpha|\mathcal{J}''\rangle + \beta|\mathcal{J}'\rangle$ ,  $|\alpha|^2 + |\beta|^2 = 1$ , as shown for  $J''=2$  to  $J'=4$  in Fig. 3B. Any set of two states can implement a qubit that can, in principle, be coherently rotated or entangled with atomic ions or other molecular ions using standard quantum information-processing techniques (22), poten-

tially enabling precision measurements with quantum advantages on molecular ions.

The measured frequencies of transitions with  $J$  between 1 and 6 are presented in Table 1. With  $<1$  kHz full width at half-maximum (FWHM) Fourier-limited spectroscopic line shapes, we reach statistical uncertainties in the line centers below 100 Hz, but uncertainty in the trap radio-frequency electric field in

**Fig. 3. Spectra and Rabi flopping for a frequency-comb driven  $\Delta J = 2$  transition.** (A) Spectra.

$^{40}\text{CaH}^+$  is prepared in  $|\mathcal{J}'' = \{2, -5/2, -\}\rangle$ , followed by a CRPT probing the  $|\mathcal{J}' = \{4, -7/2, -\}\rangle \leftarrow |\mathcal{J}''\rangle$  transition. After excitation, we determine the probabilities of the molecule being in either state. The horizontal axis shows the offset of the Raman difference frequency from the resonant value. The solid lines are fits to line shapes corresponding to a  $\sim 1.6$ -ms square pulse excitation. (B) Rabi flopping. Starting in  $|\mathcal{J}'\rangle$ , the state of the  $^{40}\text{CaH}^+$  ion is driven on resonance coherently to and from  $|\mathcal{J}''\rangle$  by a CRPT of variable duration. The solid curves are fits to decaying sinusoidal functions. The error bars indicate  $\pm 1$  SD derived from Bayesian inference.



**Table 2. Experimental values of the molecular constants in Eq. 1 inferred from measured rotational transition frequencies and ab initio values.**

$k$	Experimental $C_k$ (Hz)	Ab initio $C_k$ (Hz)	Comments
1	$1.42\ 501\ 777\ 9\ (17) \times 10^{11}$	$1.427\ (11) \times 10^{11}$	$B_R$ (rotational constant)
2	$-5.81217\ (19) \times 10^6$	$-5.831\ (19) \times 10^6$	$-D_R$ (centrifugal correction)
3	222.9 (7.2)	222.6 (0.6)	$H_R$ (second centrifugal correction)
4	-0.021 (88)	-0.0158 (4)	Third centrifugal correction

our current setup limits uncertainties in extrapolation ( $I\mathcal{B}$ ) of line centers to zero electric field to hundreds of hertz. A more detailed study of these effects is ongoing, and we expect that they can be better controlled in future experiments.

We derive precise values for the rotational constants from the unperturbed rotational transition frequencies. The centroid energy  $E_J$  of the  $J$ th manifold can be parametrized:

$$E_J = \hbar \sum_{k=1,2,3,\dots} C_k J^k (J+1)^k \quad (1)$$

where  $\hbar$  is the Planck constant and the coefficients  $C_k$  are the rotational constants. The inferred frequencies corresponding to the energy differences between the centroids of the rotational manifolds, obtained by subtracting the energy arising from the interactions of the proton and the rotational magnetic moment with the external magnetic field and among themselves ( $I\mathcal{B}$ ), are also listed in Table 1 ( $I\mathcal{B}$ ). The rotational constants derived from our measured transition frequencies are shown in Table 2.

We compare the experimentally determined rotational constants to ones obtained from ab initio calculations. To compute the rotational constants of  $^{40}\text{CaH}^+$ , complete basis set extrapolated coupled-cluster calculations at the CCSD(T) level ( $2\mathcal{B}$ ) were used in conjunction with incremental corrections for electron correlation up to the CCSDTQ level ( $24, 25$ ), with relativistic and diagonal Born-Oppenheimer corrections. The computed rotational constants (Table 2) are in good agreement with experiment. The  $1.2 \times 10^{-8}$  relative precision of our  $^{40}\text{CaH}^+$  rotational constant  $B_R$  determination is orders of magnitude higher than achievable from ab initio molecular structure calculations. For  $^{40}\text{CaH}^+$ , the accuracy of the computed constants is mainly limited by the one-electron basis sets. The comparison between calculated and experimental results clearly shows that the relative accuracy of computational methods sensitively depends on the computed property.

Our resolution is currently limited by the coherence of the microwave-referenced OFC and can be further improved to the sub-hertz level ( $26$ ). The measurement accuracy could

be improved to the sub-hertz ( $<1$  part per trillion) level with improvements of the apparatus or for molecules that are less sensitive to the trap field. This may enable tests of fundamental physics on a much larger variety of molecular species than currently considered. They may include searches for electron-to-proton mass ratio variations ( $27, 28$ ) and measurements of isomer transition frequency differences, including those for chiral molecules ( $29, 30$ ). When extended to excited vibrational levels, the full ro-vibrational energy-level structure of molecules can be probed for information that can benchmark accurate theoretical models of the potential energy surfaces of molecular ground states. Combined with frequency-comb-enabled coherent manipulation, the current protocol could elucidate molecular dynamics and complement studies based on ultrafast laser techniques. Moreover, coherent manipulation of molecular states may enable precise alignment and orientation of molecules, preparation of squeezed or Schrödinger cat-type states of rotation, and precisely state-controlled dissociation.

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bw17D01). **Author contributions:** C.W.C., A.L.C., C.K., T.F., S.D., D.L., and D.R.L. developed components of the experimental apparatus. C.W.C., A.L.C., and C.K. collected and analyzed data. C.W.C., Y.L., D.L., and D.R.L. designed the experimental methods and pulse sequences. M.E.H. and P.N.P. computed rotational transition frequencies and constants. All authors provided experimental suggestions, discussed the results, and contributed to writing the manuscript. **Competing interests:** The authors declare no competing interests. **Data and materials availability:** The data from the main text and supplementary materials are available from the NIST Public Data Repository (31). This is a contribution of the National Institute of Standards and Technology, not subject to U.S. copyright.

#### SUPPLEMENTARY MATERIALS

science.sciencemag.org/content/367/6485/1458/suppl/DC1  
Supplementary Text  
Fig. S1  
Tables S1 to S5  
References (32–45)

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## Frequency-comb spectroscopy on pure quantum states of a single molecular ion

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### Precision spectroscopy with single ions

Spectroscopy is a powerful tool that can identify chemical species used in a wide range of settings. Usually, the samples are formed of ensembles, and this can limit the resolution with which the different species can be detected or identified. Chou *et al.* demonstrate an optical frequency comb technique with a single pair of trapped ions,  $\text{Ca}^+$  and  $\text{CaH}^+$ , to obtain the rotational spectrum of a single trapped ion,  $\text{CaH}^+$ . With the ions isolated and the ensemble interactions removed, the rotational structure of the trapped molecular ion can then be obtained with high precision. As the trapping and manipulation process is general, this technique could be applied to a number of chemical species for specific purposes.

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