Rotational Raman Spectroscopy with 5 THz Bandwidth, 3 MHz resolution, and sub-kHz accuracy.

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Scientific progress is always based on the observation of the natural world. In the field of spectroscopy, we construct ever more powerful spectroscopic tools to increase the fidelity and accuracy of our observations. Modern spectroscopy often operates at the physical limits of observation, e.g., the quantum limit of observing single particles or the precision limit of the Heisenberg uncertainty principle. Further progress requires ingenious measurement concepts, such as the correlation of observables in multidimensional NMR,[1] or the direct coupling of optical frequencies to high-precision clocks in extreme-resolution frequency-comb atomic spectroscopy.[2]

We correlated high-resolution rotational spectra with observables from ultra-fast laser spectroscopy in the technique of correlated rotational alignment spectroscopy (CRASY).[3] As in multidimensional NMR, we coherently excite and probe angular momentum wave packets in the time domain. Instead of nuclear spins, our experiment excites and probes molecular rotations using short optical laser pulses. As in frequency-comb measurements, we couple our experiment to a high-precision clock to obtain absolute frequency results without systematic errors.

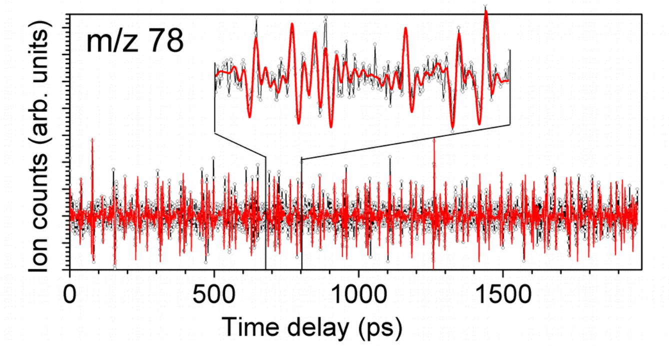

Figure 1: Rotational coherence trace for the $^{32}S^{12}C^{34}S$ isotope (m/z 78). Signal modulations are due to a rotationally coherent wave-packet excited at time delay 0. Extending range of observed time delays increases the spectroscopic resolution of the Fourier-domain spectrum (cf. Figure 2).

Figure 1 shows the measured rotational coherence signal for a mass-selected isotope of carbon disulfide. An 800 nm picosecond laser pulse excited a rotationally coherent wave packet in a beam of neutral, cold molecules. The temporal evolution of the wave packet was probed by 200 nm photoexcitation and photoionization. The formed ions were detected in a mass spectrometer.

The spectroscopic resolution of rotational spectra measured by CRASY, or by the related methods of rotational coherence spectroscopy (RCS),[3] is fundamentally limited by Heisenberg's uncertainty principle $\Delta E \cdot \Delta t \geq \hbar/2$. The observation time Δt corresponds to the length of the delay range over which we observe the rotational coherence modulations. Our experiment operates at the Heisenberg limit and any increase in observation range directly results in a proportionally higher resolution. To reduce the energy uncertainty, our new spectroscopic set-up at UNIST employs electronic pulse-picking of femtosecond oscillator pulses. This extends the delay range Δt into the sub-microsecond regime, a factor 50 beyond the best published RCS data.

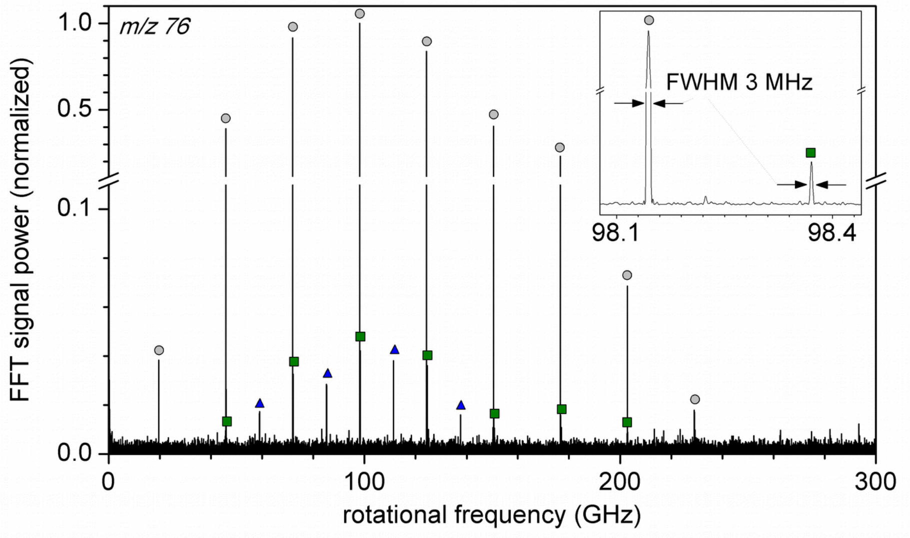

Figure 2: Fourier-transform rotational Raman spectrum for the main isotope of carbon disulfide (mass m/z 76). The vibrational ground state shows a regular progression with frequencies $\omega_J = B\cdot(4J + 6)$ for even J and $\Delta J = 2$ (circles). The lowest vibrational bending mode with angular momentum $l = \pm 1$ gives progressions for even/odd J quantum numbers (marked with squares and triangles, respectively).

Figure 2 shows a mass-CRASY spectrum for the main isotope of carbon disulfide, obtained by the Fourier transformation of a signal trace as shown in Fig. 1. In this mass channel, we resolved progressions for the vibrational ground state of carbon disulfide and the lowest vibrational bending state. A fit of the line positions gave a rotational constant of B = 3271517.2 ± 0.6 kHz and a centrifugal distortion of D = 356 ± 3 Hz for the ground state, and B = 3277905 ± 12 kHz, D = 406 ± 81 Hz for the first bending mode with an l-type splitting of q = 1160 ± 12 kHz.

Our electronic pulse-picking method directly relates the measured rotational frequencies to the laser repetition rate. We monitored the laser repetition rate against a GPS stabilized clock with absolute errors of $\Delta t/t <= 10^{-10}$. Accounting for possible short-term drifts of clock or laser, we can determine absolute frequency values with relative errors $<<10^{-8}$, well below our current measurement accuracy of $2\cdot10^{-7}$.