Correlated Rotational Alignment Spectroscopy: High-Resolution, Absolute Frequency Spectroscopy in the Time Domain

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We describe the measurement of absolute frequency, high-resolution, broad-bandwidth rotational Raman spectra that are correlated with molecular mass. The Raman spectra have order-of-magnitude higher resolution as compared to preceding literature data. Rotational constants were determined with single-kHz accuracy, competitive with uncorrelated high-resolution Fourier-transform microwave experiments.

The experiment is based on correlated rotational alignment spectroscopy (CRASY, [1]): A femtosecond 'alignment' laser pulse excites a coherent rotational wave packet in a cold molecular beam. The wave packet evolution is probed by resonant multi-photon ionization with a second laser pulse, followed by ion detection in a mass spectrometer. Figure 1 shows resulting data: A mass spectrum of a carbon disulfide sample shows multiple isotopes (76 u to 82 u) and fragments (12 u to 66 u). Scanning of the alignment-ionization delay reveals signal modulations in each mass channel, as plotted for mass 76 u in the alignment trace. Fourier transformation of the alignment trace gives a rotational Raman spectrum for the selected mass. Insets show signals with 50-fold enlarged abscissa.

The spectroscopic resolution and bandwidth is determined by the range and step size of probed time-delays. A 1 picosecond step-size (0.5 THz spectroscopic bandwidth) was sufficient to resolve the complete rotational spectrum of carbon disulfide in a cold molecular beam. A delay range up to few nanoseconds can be scanned by opto-mechanical delays (moving mirrors on a motorized stage), leading to resolutions in the 100 MHz range (cf. Fig. 1).

We exploited the discrete time-domain property of the 80 MHz Ti:Sa laser oscillator pulse train to increase the spectroscopic resolution and accuracy. Pulse-selection for alignment and ionization pulses added discrete (80 MHz)$^{-1}$ = 12.5 ns delays and extended the delay range to the sub-microsecond regime (few-MHz resolution). A simple measurement of the oscillator repetition rate tied measured spectroscopic frequencies to a reference clock, creating a time-domain equivalent to frequency comb spectroscopy. Spectroscopic data for carbon disulfide allowed to determine rotational constants with kHz accuracy for multiple isotopologues [2].

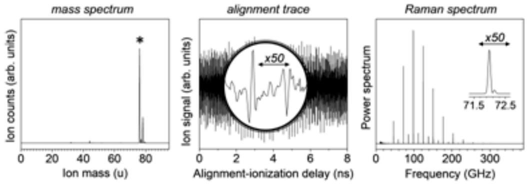
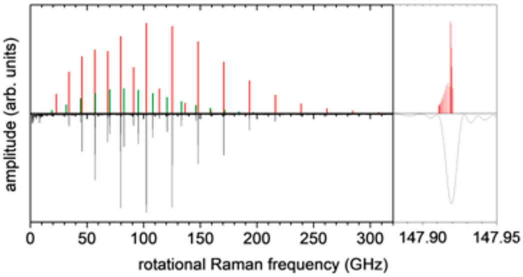


Figure 2 shows unpublished data for a mixture of carbon disulfide and benzene. The spectrum (bottom) at mass 78 u is compared to the best PGOPHER fit (top) for the main benzene isotopologue (red) and the rare ^{32}S^{12}C^{34}S isotopologue (green). The right hand side shows a small section of a non-apodized higher-resolution (11 MHz) measurement.



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[1] Schröter C., Kosma K., Schultz T., Crasy: Mass- or electron-correlated rotational alignment spectroscopy. *Science* **333**, 1011–1015 (2011).

[2] Schroter, C., Lee, J. C., Schultz, T., Mass-Correlated Rotational Raman Spectra with High Resolution, Broad Bandwidth, and Absolute Frequency Accuracy. *PNAS* **115**, 5072 (2018).

Space exploration of Venus, Mars and beyond using (relatively) high resolution spectroscopy

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Mars has been monitored for decades now, either from Earth using large telescopes and sensitive spectrometers, from the Hubble Space Telescope, from rovers or platforms on the surface of Mars and of course from instruments in orbit around the planet. The last atmospheric mission to Mars, the ESA/ROSCOSMOS ExoMars Trace Gas Orbiter, launched in 2016, just started its Science phase in April 2018. On board, two spectrometers' suites will probe the atmosphere covering the UV to IR range. The Venus Express mission observed the atmosphere of Venus down to its surface with a wide range of spectrometers. Cassini-Huygens probed the Saturnine system with UV and IR instruments, while Juno is observing Jupiter. New missions are being prepared to go back to Venus or to the moons of Jupiter. Ground-based and space telescopes in Earth orbit are also being improved or built, providing us with spectra of a wide variety of objects. The James Webb Space Telescope will (soon) replace the Hubble Space Telescope, although its launch has again been postponed. Missions to observe exoplanets are being prepared, with CHEOPS to be launched in 2018, followed by PLATO and ARIEL. I will review the capabilities in terms of spectral coverage and resolution of these space missions and instruments on board, showing that although their resolutions might not be as high as spectroscopists might wish, they allow for very interesting science.