

Broadband Molecular Rotational Spectroscopy

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Advances in high-speed digital electronics have ushered in the era of broadband molecular rotational spectroscopy where spectral bandwidths as large as 30 GHz can be detected in a single time-domain experiment with duration on the order of a few microseconds. Advances in both arbitrary waveform generators (AWGs) and high-speed digitizers are critical to these designs. High-speed AWGs make it possible to create tailored broadband excitation pulses for molecular rotational spectroscopy. Following broadband excitation, the coherent molecular emission is captured using a high-speed digitizer and the frequency spectrum is obtained by fast Fourier transform. The two most common gas samples in molecular spectroscopy are molecular beams, with rotational temperatures $\sim 10\text{K}$, and room-temperature samples. The rotational cooling achieved in pulsed molecular beams leads to a peak in the spectral intensity of the rotational spectrum in the microwave region for molecules with three or more heavy atoms. Chirped-pulse Fourier transform microwave (CP-FTMW) spectrometers at frequencies from 2-40 GHz have been developed using high-power traveling wave tube amplifiers. Perhaps the most significant performance gains for CP-FTMW spectroscopy over Balle-Flygare FTMW spectroscopy are achieved at low-frequency (2-8 GHz) where the design of a microwave cavity becomes difficult. Results from a recently redesigned 2-8 GHz CP-FTMW spectrometer will be presented including the structural characterization of water clusters up to $(\text{H}_2\text{O})_{15}$. For room-temperature samples, the peak spectral intensity for molecules with about three heavy atoms occurs in the mm-wave region of the spectrum. Recent advances in high-power solid state active multiplier chain mm-wave sources, which can produce $\sim 30\text{ mW}$ at 300 GHz, give the extension of chirped-pulse FT techniques to mm-wave spectroscopy significant measurement benefits. In addition to reducing measurement times by a factor of 1000 over previous high-speed mm-wave absorption spectroscopy methods, the move to an arbitrary waveform based mm-wave excitation source makes it possible to implement pulse sequence measurements that can speed spectroscopic analysis. The implementation of CP-FT mm-wave double-resonance spectroscopy, pulse echoes, and saturation recovery experiments will be described. These capabilities increase the power of mm-wave rotational spectroscopy as a trace gas analysis technique and the initial design of a compact mm-wave spectrometer based on coherent spectroscopy will be presented. Finally, the coupling of these rotational spectroscopy measurement techniques with tunable, pulsed lasers for chemical kinetics experiments will be described. This discussion will include a brief introduction to dynamic effects in the rotational spectroscopy of highly excited molecules.