Advances in high-speed digital electronics have enabled a new generation of molecular rotational spectroscopy techniques that provide instantaneous broadband spectral coverage. These techniques use a chirped excitation pulse to coherently excite the molecular sample over a spectral bandwidth of 10 GHz or larger through rapid passage. The subsequent time-domain emission is recorded using high-speed digitizers (up to 100 Gigasample/s) and the frequency domain spectrum is produced by fast Fourier transformation. The chirped-pulse Fourier transform (CP-FT) method has been implemented in the microwave frequency range (2-40 GHz) for studies of cold samples in pulsed jet sources and in the mm-wave/terahertz (THz) frequency range for studies of samples at room-temperature. The method has opened new applications for molecular rotational spectroscopy in the area of chemical kinetics where dynamic rotational spectroscopy is used to measure the rates of unimolecular isomerization reactions in highly excited molecules prepared by pulsed infrared laser excitation. In these applications, the isomerization rate is obtained from an analysis of the overall line shapes which are modified by chemical exchange leading to coalescence behavior similar to the effect in NMR spectroscopy. The sensitivity of the method and the ability to extend it to low frequency (2-8 GHz) have significantly increased the size range of molecules and molecular clusters for structure determination using isotopic substitution to build up the 3D molecular structures atom-by-atom. Application to the structure of water clusters with up to 15 water molecules will be presented. When coupled with advances in solid-state mm-wave/THz devices, this method provides a direct digital technique for analytical chemistry of room-temperature gases based on molecular rotational spectroscopy. These high-throughput methods can analyze complex sample mixtures with unmatched chemical selectivity and short analysis times.

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