USING ROTATIONAL SPECTROSCOPY TO EXPLORE INTRAMOLECULAR DYNAMICS

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Pure rotational spectroscopy is a powerful tool in the study of the structure of molecules in the gas phase. At the simplest level, structure determination is made through the connection between the rotational transition frequencies and the moments-of-inertia of the static structure. (Although, in practice, unambiguous structure determination in large molecules often requires secondary information such as dipole moment components in the principal axis system and the analysis of nuclear quadrupole hyperfine structure.) The direct connection between transition frequencies and molecular structure make rotational spectroscopy ideally suited to quantitative measurements of isomerization kinetics of highly excited molecules. Vibrationally excited molecules can display new behavior associated with the flow of vibrational energy, or intramolecular vibrational energy redistribution (IVR), and isomerization. In these energy regions the molecular structure is no longer static and the description of molecular rotational spectroscopy must be extended to include the effects of the time-dependent nuclear motion associated with the intramolecular dynamics. Many of the new features of "dynamic rotational spectroscopy", like motional narrowing and coalescence of the rotational spectrum, have analogs in NMR spectroscopy. Other features, such as gyroscopic effects in molecules where a symmetric internal rotor can be energized by IVR, are unique to rotational spectroscopy. The basic principles of this new application of rotational spectroscopy will be presented using recent measurements from our laboratory. These experiments demonstrate the ability to determine isomerization rates on the picosecond time scale using rotational spectroscopy. There are significant experimental challenges to acquire rotational spectra in energy regions where intramolecular dynamics occur. New developments in spectrometers for rotational spectroscopy that were motivated by the requirements of dynamic rotational spectroscopy, such as the introduction of a true broadband Fourier transform microwave spectrometer capable of acquiring the rotational spectrum in the 7.5 – 18.5 GHz range in a single data acquisition event, will also be described.