MEASURING ISOMERIZATION RATES OF ISOLATED MOLECULES FROM THE ROTATIONAL SPECTRUM OF SINGLE, HIGHLY VIBRATIONALLY MIXED QUANTUM STATES

BROOKS H. PATE and DAVID A. McWHORTER, *Department of Chemistry, University of Virginia, Charlottesville, VA 22903*.

The rotational spectrum of a single quantum state in an energy region where extensive intramolecular vibrational energy redistribution (IVR) and isomerization occurs contains quantitative information about the isomerization rate. In this way, the rotational spectrum of a single quantum state of an isolated molecule provides a direct measure of the unimolecular isomerization reaction rate. This form of spectroscopy is similar to dynamic nuclear magnetic resonance spectroscopy. For example, under certain conditions the rotational spectrum displays coalescence behavior. It is shown that the spectrum of single eigenstates is well described by the Bloch formalism in the case of chemical exchange. In this way, empirical kinetics parameters can be obtained from the lineshape of the single eigenstate spectrum. These empirical kinetics rates are equal to the Fermi Golden Rule intramolecular dynamics rates. Application of the theory to the rotational spectrum of single eigenstates of 2-fluoroethanol will be presented.