

## A BEHIND THE SCENES LOOK AT INTRAMOLECULAR VIBRATIONAL ENERGY REDISTRIBUTION

B. H. PATE, *Department of Chemistry, University of Virginia, McCormick Rd., Charlottesville, VA 22901.*

The flow of vibrational energy in polyatomic molecules is the fundamental physical process of chemical kinetics. Statistical theories of reaction rates, such as Rice-Ramsperger-Kassel-Marcus (RRKM) theory, assume that the redistribution of vibrational energy is rapid compared to reaction times. Over the past decade high-resolution infrared spectroscopy techniques in molecular beams have been used to quantitatively determine the time scale for energy redistribution in isolated molecules. We have developed high-sensitivity infrared-microwave double-resonance techniques that permit rapid and accurate assignment of these complex spectra. However, single photon infrared spectroscopy still provides limited information on the intramolecular dynamics because the dynamical information is filtered through a single vibrational state. One important problem in intramolecular dynamics that is difficult to study through infrared spectroscopy is conformational isomerization. To study this fundamental chemical process we have developed the theory for the rotational spectrum of a single molecular quantum state in an energy region where vibrational energy flow and isomerization occur. The theory is an extension of the exchange (or motional) narrowing theories first formulated for NMR spectroscopy. To make the measurements of the rotational spectrum of a highly excited quantum state we employ infrared-microwave double-resonance and infrared-microwave-triple resonance techniques that exploit the Autler-Townes splitting of states (or AC Stark effect). The theory of this type of spectroscopy and useful features of our spectroscopy techniques will be illustrated through the spectra we have measured for propargyl alcohol, allyl fluoride, 2-fluoroethanol, and 4-chlorobut-1-yne.