STATISTICAL ASPECTS OF THE CONFORMATIONAL ISOMERIZATION RATE OF 4-FLUOROBUT-1-YNE MEASURED BY DYNAMICAL ROTATIONAL SPECTROSCOPY

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The vibrational dynamics of large polyatomic molecules cannot be discussed in terms of the exact molecular Hamiltonian. Intramolecular vibrational energy redistribution (IVR) and isomerization occurs in regions where the rovibrational state density exceeds 100 states/cm^{-1}. Current theoretical methods are far from being able to determine the parameters in the Hamiltonian (interaction constants, anharmonicities, and rotational constants) to sufficient accuracy to perform traditional spectroscopic assignment of the spectrum. In these cases, the statistical properties of the spectrum and kinetics are often modeled using methods from random matrix theory. However, there have been few cases where sufficient data exists to quantitatively test the model predictions. We present a simple random matrix model to describe conformational isomerization reactions. The predictions of this model are compared to high-resolution infrared spectroscopy and dynamical rotational spectroscopy measurements of 4-fluorobut-1-yne. We show that this model provides a good description of the eigenstate-level fluctuations of the isomerization rate, the intensity correlations between separate single-eigenstate rotational spectra, and the nearest-neighbor level spacing statistics. The fact that the random matrix model predictions are in good agreement with the experiment indicates that a master equation description for isomerization reactions of isolated molecules is valid and that a simple Bloch-vector approach to describing the rotational spectrum of an isomerizing molecule is justified.