SPECTROSCOPIC CHARACTERIZATION OF ISOMERIZATION TRANSITION STATES

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Transition state theory is central to our understanding of chemical reaction dynamics. We demonstrate here a method for extracting transition state energies and properties from a characteristic pattern found in frequency domain spectra of isomerizing systems. This pattern, a dip in the spacings of certain barrier-proximal vibrational levels, can be understood using the concept of effective frequency, ω^{eff}. The method is applied to the *cis-trans* conformational change in the S_1 state of C_2H_2 and the bond-breaking HCN-HNC isomerization. In both cases, the barrier heights derived from spectroscopic data agree extremely well with previous *ab initio* calculations. We also show that it is possible to distinguish between vibrational modes that are actively involved in the isomerization process and those that are passive bystanders. (This work has been published in J. H. Baraban, P. B. Changala, G. Ch. Mellau, J. F. Stanton, A. J. Merer, and R. W. Field. Spectroscopic characterization of isomerization transition states. *Science*, 350(6266):1338–1342, 2015.)