

METHYL TORSION EFFECTS IN THE ROTATIONAL PATTERNS OF THE HIGH RESOLUTION ROVIBRATIONAL SPECTRUM OF THE ACETYLENIC C-H STRETCH OF 1-BUTYNE

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

Determining the dynamical consequences of the internal rotation of symmetric rotors is an area of continued interest in the field of intramolecular vibrational energy redistribution (IVR). At high vibrational energies there can be extensive excitation of the rotor. Rotor excitation has been suggested to enhance the coupling between vibrational states leading to faster IVR. In the principal axis frame (as chosen for the PAM analysis of threefold rotors), excitation of the rotor generates strong angular momentum coupling between the degenerate rotor levels (E levels). The effect of rotor angular momentum on the high-resolution rovibrational spectrum of 1-butyne is studied through the correlation of the spectra for different asymmetric top rotational levels of the acetylenic bright state. Strong position correlation is observed for the E levels of the spectrum, but not the A levels, that is caused by interactions with highly torsionally excited states. This effect is proven through assignment of the A and E levels using rotational spectroscopy of single eigenstates. The analysis of the spectrum shows that highly torsionally excited states are involved in the IVR dynamics.