THE EFFECTS OF INTERNAL ANGULAR MOMENTUM ON DYNAMIC ROTATIONAL SPECTRA

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When molecules are excited to regions of high state density (greater than 10 states/ cm^{-1}), intramolecular vibrational redistribution (IVR) can occur. When a molecule contains a source of internal angular momentum, such as a methyl rotor, activation of the rotor via IVR flow can have profound effects on the rotational spectrum of the molecule. Because the total angular momentum of the molecule is a conserved quantity, internal angular momentum generated by activation of the internal rotor must be compensated for by counter-rotation of the frame. This counter-rotation of the frame produces a "gyroscope effect" within the molecule. In the presence of IVR, the inertial axes become time-dependent quantities where the rotation of the molecule is described somewhere between the asymmetric top and gyroscope limits. 3-butyn-2-one and 3-methyl but-1-yne are isoelectronic molecules with barrier heights to internal rotation that differ by almost an order of magnitude. Infrared excitation of the acetylenic CH stretches prepares the molecules with approximately 3330 cm^{-1} of internal energy which can be transferred to torsional motion via IVR. The resulting spectra were probed through a combination of infrared-microwave-Fourier transform microwave triple resonance techniques. The effects of internal angular momentum on the dynamic rotational spectra in the low barrier (3-butyn-2-one, gyroscope rotor) and high barrier (3-methyl but-1-yne, asymmetric top rotor) limits will be compared.