VIBRATIONAL ANHARMONIC CALCULATIONS IN ELECTRONIC STRUCTURE PACKAGES FOR APPLICATIONS IN INTRAMOLECULAR DYNAMICS

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The addition of anharmonic calculation capabilities to the Gaussian 03 computational chemistry package has made it possible to determine a number of quantities useful in the realm of intramolecular vibrational dynamics. We will be testing the utility of these calculations in three areas. First, for buytne and cyclopropylacetylene, we have tested (versus high-resolution IR spectra with full eigenstate resolution) whether or not the inclusion of anharmonicities can a) provide us with accurate vibrational frequencies without the need for scaling factors and b) provide improved accuracy for vibrational state density calculations. In particular, accurate vibrational state densities are crucial for the calculation of rate constants via RRKM. Second, for cyclopropylacetylene and phenylacetylene, we have used the calculated cubic and quartic anharmonic matrix elements to model intramolecular vibrational relaxation (IVR). The initial steps of IVR are governed by low-order couplings, but the interesting question is whether or not the calculated matrix elements can account for the presence of multiple time scales in the relaxation (*i.e.*, through chains of low-order couplings). Finally, we have tested the predicted vibration-rotation interaction constants (α_ν) against measured constants in small molecules as well as against measured rotational frequencies in the dynamic rotational spectra of highly excited propyne, trifluoropropyne, and phenylacetylene.