POTENTIAL FUNCTIONS FOR TWO-ROTOR MOLECULES FROM AB INITIO CALCULATIONS AND EXPERIMENT: WHAT TO COMPARE?

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The potential function for molecules with two threefold internal rotors restricted to the lowest terms may defined as
$V(\tau_1, \tau_2)$ = (1/2) [V_{30}(1 - cos3τ_1) + V_{03}(1 - cos3τ_2) + V'_{30} sin3τ_1 + V'_{03} sin3τ_2 + V_{60}(1 - cos6τ_1) + V_{06}(1 - cos6τ_2) + V'_{60} sin6τ_1 + V'_{06} sin6τ_2 + V_{33}(1 - cos3τ_1)(1 - cos3τ_2) + V'_{33} sin3τ_1 sin3τ_2 + V''_{33} sin3τ_1 (1 - cos3τ_2) + V'''_{33} (1 - cos3τ_1) sin3τ_2].
The determination of the coefficients of this function from ab initio or experimental data is fairly straightforward if the internal rotor axes are in a plane of symmetry such as in CH_3OCH_3 or CH_3OSiH_3. In cases with lower symmetry, this is no longer the case. In one example, the standard deviation of a fit of energies obtained from ab initio calculations was quite satisfactory but the coordinates for the minimum of the potential function were about 8 degrees off and the energy was about 140 cm^{-1} lower than the fitted optimized energy. A more satisfactory set of potential coefficients was obtained from the same data after the equations for zero derivatives for minima, maxima and saddle points of the potential energy were introduced. The choice of relative weights for the energies and the derivatives is critical. In order to compare potential coefficients between theory and experiment, the potential function must be transformed into standard form where the coefficients V'_{30} and V'_{03} vanish.