

IS THE COUPLING OF C_{3V} INTERNAL ROTATION AND NORMAL VIBRATIONS A TRACTABLE PROBLEM?

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The solution of a C_{3V} internal rotation problem for the torsional manifold of an isolated vibrational state such as the ground state is well established. However, once an interacting small amplitude vibrational state is involved the path to a solution becomes far less clear and there is little guidance in the literature on how to proceed. The fundamental challenge is that the torsional problem and the internal axis system are unique to each torsional manifold of a specific vibrational state. In an asymmetric top molecule vibrational angular momentum can be rotated away, but this sort of rotation changes the angle between the internal rotation axis and the principle axis when there is an internal rotor. This means that there is an angle between the internal axis systems of each torsional manifold of a vibrational state. The net result is that the coupling between the two states must account for the difference in internal axis angle and will have some significant consequences to the selection rules and interactions. Two cases will be discussed, methanol and ethyl cyanide.