K-SCRAMBLING IN A NEAR-SYMMETRIC-TOP MOLECULE CONTAINING AN EXCITED NON-COAXIAL INTERNAL ROTOR

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Classical trajectories on rotational energy surfaces and coherent-state quantum projections have been used to study an asymmetric-top molecule containing a freely rotating internal symmetric top whose symmetry axis is not coincident with a principal axis of the molecule. Stationary points on the rotational energy surface, which strongly influence the trajectories, increase in number from two to four to six as J/n increases from zero to infinity (where J is the total and n is the free-internal-rotor angular momentum). For some J/n values trajectories can arise which sample a large fraction of K values (where K is the z-axis projection of J), corresponding in quantum wavefunctions to extensive K-mixing in the symmetric-top basis set $|J, K\rangle$. When such mixing cannot be made small for any choice of z axis we call it K-scrambling. For typical values of the torsion-rotation coupling parameter ρ, rotational eigenfunctions for given J and torsional state turn out to be quite different from eigenfunctions for the same J in some other torsional state. Nonzero rotational overlap integrals are then distributed among many rotational functions for each (n, n') pair, which may in turn contribute to internal rotation enhancement of intramolecular vibrational energy redistribution. We have also examined near-free-rotor levels of our test molecule acetaldehyde, which arise for excitation of ten or more quanta of methyl group torsion, and find that barrier effects do not change the qualitative picture obtained from the free-rotor treatment.