HOW SPHERICAL COULD A NONRIGID SPHERICAL TOP MOLECULE BE?

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The classical rotational energy surface for any rigid spherical top molecule is an ideal spherical surface: the energy of rotation is independent on the orientation of the angular momentum in the body-fixed frame. For a nonrigid molecule even a small rotational excitation leads to deformation of the rotational energy surface. This surface takes generically the form of (one of) the simplest Morse type function(s) on the sphere. The number of minima and maxima of this function minimize the Morse inequalities which take into account the topology of the sphere and the symmetry. Additional accidental relations between harmonic frequencies can result (in the limit of small deformation) in the rotational energy surface with higher number of stationary points (non-simplest Morse type functions).

Classical analysis of the centrifugal distortion effects is used to relate the form of the rotational energy surface with the vibrational frequencies in the harmonic approximation. Spherical tops with the T_d point symmetry group are studied in detail. There are two simplest Morse type functions in this case: one has maxima at C_{3v} symmetric positions and the other has minima at these positions. Special relation between harmonic force constants which splits molecules into two classes with "normal" and "inverted" rotational energy surface gives at the same time the condition for the molecule to be exceptionally spherical. The "unusual" rotational energy pattern for such exceptionally spherical molecule is discussed.