UNUSUAL INTERNAL ROTATION COUPLING IN THE MICROWAVE SPECTRUM OF PINACOLONE

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The molecular-beam Fourier-transform microwave spectrum of pinacolone (methyl tert-butyl ketone) has been measured in several regions between 2 and 40 GHz. Assignments of a large number of A and E transitions were confirmed by combination differences, but fits of the assigned spectrum using several torsion-rotation computer programs based on different models led to the unexpected conclusion that no existing program correctly captures the internal dynamics of this molecule. A second puzzle arose when it became clear that roughly half of the spectrum remained unassigned even after all predicted transitions were added to the assignment list. Quantum chemical calculations carried out at the MP2/6-311++G(d,p) level indicate that this molecule does not have a plane of symmetry at equilibrium, and that internal rotation of the light methyl group induces a large oscillatory motion of the heavy tert-butyl group from one side of the C₆ saddle point to the other. The effect of this non-C₆ equilibrium structure was modeled for \( J = 0 \) levels by a simple two-top torsional Hamiltonian, where magnitudes of the strong top-top coupling terms were determined directly from the \textit{ab initio} two-dimensional potential surface. A plot of the resultant torsional levels on the same scale as a one-dimensional potential curve along the zig-zag path connecting the six (unequally spaced) minima bears a striking resemblance to the 1:2:1 splitting pattern of levels in an internal rotation problem with a six-fold barrier. A plot of the six minima closely resembles the potential surface for methylamine. This talk will focus on implications of these resemblances for future work.