Theoretical Evidence for Rotational Energy Cluster Formation in the Vibrational Ground State of SO_3

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In previous work [1] we have computed energy levels and transition intensities for SO_3 adequate for simulating a room-temperature spectrum. This involved the calculation of ro-vibrational energy levels and associated eigenfunctions, for rotational states up to and including J = 85, using the TROVE program [2]. The theoretical microwave spectrum composed from pure-rotational transitions exhibits some interesting features indicating the presence of localized stable rotation axes at high J. In this work we aim to investigate the rotational dynamics of SO_3 using our theoretical approach. Following a previous, analogous study of PH_3 [3], we compute the rotational energy levels in the vibrational ground state of SO_3 up to a high value of rotational quantum number J (> 200). At such high values of J we observe a clustering of rotational energy levels with a six-fold pattern similar to that observed for PH_3. To our knowledge this is the first time such effects have been observed for a trigonal D_{3h} planar molecule.
We also present some details of our efforts to extend upon our initial room-temperature line-list, including a spectroscopic refinement of our previous *ab initio* potential energy surface and some computational difficulties we have observed in attempting to prepare for a hot line-list calculation.

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