Gyroscopic destabilization in a polyatomic molecule revealed by gas phase high-resolution THz spectroscopy

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Many of us have enjoyed the spectacle of a spinning top influenced by friction: rotating rapidly about a stable stationary axis, the top loses slowly its angular momentum j (and energy), slows down gradually, and then, suddenly, its axis becomes unstable, the top wobbles, and an abrupt change of the top's position follows. In other words, the system undergoes a bifurcation. In the case of the tippe-top, rotation about its lower point is stable at low values of angular momentum J and becomes unstable at large J. Something quite similar occurs in a freely rotating dimethylsulfoxyde (DMSO, $(CH_3)_2SO$) molecule. For the first time in such large polyatomic molecule, a quantum bifurcation induced by a gyroscopic destabilization was observed. [1,2] This unusual phenomenon in rotational dynamics was discovered in the rovibrational states of the asymmetric bending fundamental v_{23} band of DMSO whose high-resolution gas phase absorption spectrum was observed along with that of the symmetric bending v_{11} by Cuisset et al. [2,3] using the exceptional properties of AILES in the Far-Infrared domain (300 - 400 cm^{-1} spectral region). [4]

In order to explain this phenomenon, we looked for the system bifurcation in the pure rotational transitions in the lowest vibrationnally excited states of DMSO. Therefore the high-resolution ground state THz spectrum of DMSO has been recorded with a sub-THz spectrometer based on a frequency multiplication chain. [5] We obtained rotational constants and centrifugal corrections to order J^8 of all low frequency fundamental vibrational states of DMSO, specifically those corresponding to the two methyl rocking modes v_{13} and v_{24}, the absorption inactive symmetric methyl bending mode v_{12} of the OSC_2 frame, as well as the other symmetric and the only asymmetric bending modes v_{11} and v_{23} of OSC_2. Neglecting splittings due to the internal rotation of methyl groups, the spectrum was reproduced to the subMHz experimental accuracy. [6] We have found that the state v_{23} is the only low frequency vibrational state with the "anomalous" rotational structure uncovered in [1].

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