

# Gas phase Far-Infrared high-resolution spectroscopy of DMSO: an unusual rotational behaviour revealed by the AILES beamline.

Following the first successful high-resolution of the far-infrared spectrum of DMSO recorded with the AILES beamline, Arnaud Cuisset and Dmitrii Sadovskii, from the Laboratory of Physical Chemistry of the Atmosphere in Dunkerque, discovered a sequence of fourfold clusters of rotational levels. This unusual system of localized states corresponds to classical rotations about a pair of tilted axes, which become stationary at high angular momenta. These results were recently published in Physical Review Letters (A. Cuisset et al. Phys. Rev. Lett. Vol. 109, 094101, (2012)).



Figure 1 : Wolfgang Pauli and Niels Bohr watching a tippe top at the opening of the Institute of Physics, University of Lund, Sweden on May 31 1951.

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 dimethylsulfoxide (DMSO,  $(\text{CH}_3)_2\text{SO}$ ) molecule. For the first time in such large polyatomic molecule a quantum bifurcation induced by a gyroscopic destabilization was observed. This unusual phenomenon in rotational dynamics was discovered in the rovibrational states of the bending fundamental  $\nu_{23}$  band of DMSO whose high-resolution gas phase absorption spectrum was observed along with that of  $\nu_{11}$  by Cuisset *et al.* (Chem. Phys. Lett. 492, 30, (2010)) using the exceptional properties of AILES in the Far-Infrared domain.

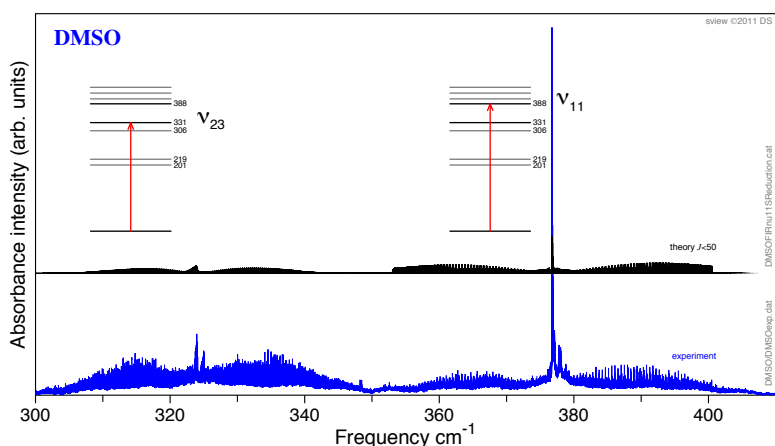


Figure 2 : Experimental (blue) and theoretical (black) spectra of DMSO.  $\nu_{23}$  and  $\nu_{11}$  bands are associated respectively to the symmetric and asymmetric bending vibrations.

In order to observe this phenomenon, it was necessary to assign a large number of spectral lines. The analysis was complicated by a large number and high density of spectral lines and had to account for the specific spectral structures reflecting the accidental closeness of DMSO to the symmetric top. 4500 rovibrational transitions of the  $\nu_{11}$  band were firstly assigned using a common procedure in rovibrational spectroscopy to adjust the molecular parameters. For the  $\nu_{23}$  band, a computer aided assignment procedure based on a systematic search of all combination frequencies was necessary to assign more than 7500 transitions and to reproduce the spectrum at the experimental accuracy. By analyzing the obtained spectroscopic constants, the interesting classical rotational dynamics with additional stationary axes of rotation was uncovered for  $\nu_{23}$ .

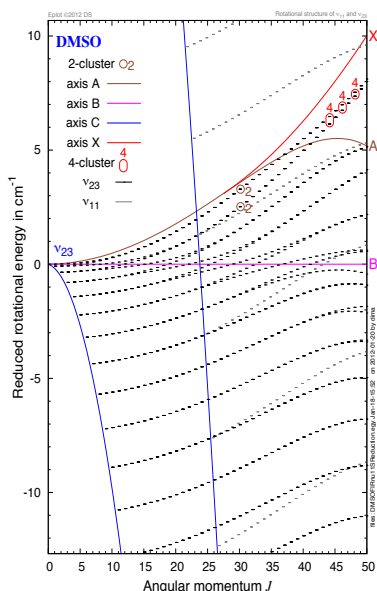


Figure 3 : Fourfold clusters observed for  $J > 40$  in the rotational energy-momentum spectrum of DMSO.  $\nu_{23}$

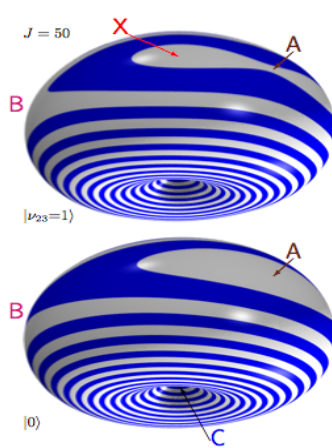


Figure 4 : Classical rotational energy of DMSO in the  $\nu_{23}$  state (top) and in the ground state (bottom)

Figure 3 presents the observed and predicted doublet energy levels of  $\nu_{23}$  (respectively short and long dashed) and the energies of classical rotations (solid lines) around the stationary axes. The low- $J$  structure of  $\nu_{23}$  resembles that of a rigid oblate asymmetric top: sequences of C and A-type rotational levels ascend and descend from the respective minimum and maximum energies towards the transition region B. For  $J > 27$ , a classical pitchfork bifurcation takes place at A creating a pair of new stationary rotation axes X. A-type doublets crossing into the X domain and merging into quadruplets. These 4-fold clusters were actually observed in about 20 out of the 7500 transitions! The far infrared synchrotron radiation made a great number of complex molecular systems such as DMSO accessible. The interesting rotational dynamics uncovered in DMSO, and the way this dynamics was observed has many analogs in different areas of modern nonlinear physics.