Gyroscopic destabilisation of molecular rotation and quantum bifurcation observed in the structure of the ν_{23} fundamental of dimethylsulfoxyde (DMSO)

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Following the first successful high-resolution study of the "perpendicular" band of dimethylsulfoxyde (DMSO) at 324 cm^{-1}, associated with the ν_{23} bending vibration, we discovered a sequence of four-fold degenerate clusters of rotational levels at high angular momenta $J > 40$. This unusual system of localized states corresponds to classical rotations about a pair of "tilted" axes, which become stationary at high J, after the principal axis of inertia A loses stability and bifurcates for $J \approx 27$.

FIG. 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. Photograph by Erik Gustafson, courtesy AIP Emilio Segrè Visual Archives, Margrethe Bohr Collection (http://photos.aip.org)
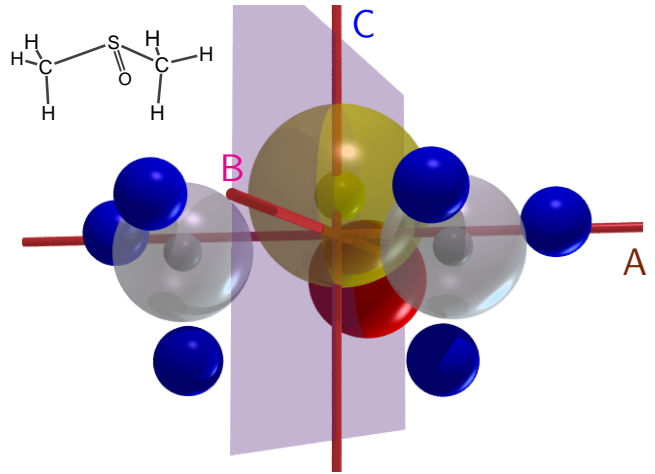

FIG. 2. Equilibrium configuration of $(CH_3)_2SO$ (DMSO) [1]; the three principal axes of inertia cross at the center of mass, axes B and C (vertical) lie in the the symmetry plane.

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. A standard Lagrange top with friction simply falls down, a *tippe top*, like the one played with by Bohr and Pauli in Fig. 1, turns upside down and continues to rotate.

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 our system, a freely rotating DMSO molecule (fig. 2). In its ground vibrational state $|0\rangle$, the ν_{11} fundamental excited state [1], and, generally, for low j, this molecule is qualitatively similar to a rigid oblate asymmetric Euler top. Specifically, its set of stationary rotation axes consists of three principal axes of inertia [2], stable axes A and C, and unstable B, with inertia moments $I_A < I_B \ll I_C$. We have found that the situation changes in the excited vibrational fundamental state ν_{23} at large j, when axis A *loses stability* and two *new stable stationary rotation axes*, which we call X, emerge in the plane AB at a certain tilt angle to A.

Phenomena of this kind occur due to the *nonrigidity* of molecular tops; their quantum manifestations, and the underlying classical dynamics were well understood by the mid-80's [3, 4] within the general concept of molecular quantum bifurcations [5–7], and were studied recently in relation to BEC [6] and quantum entanglement [8]. In our particular case, the asymmetric ν_{23} bending vibration "softens" the C_2SO frame, induces specific deformations of its averaged geometry, and amplifies specific dynamical responses to the centrifugal forces. These forces cause the bifurcation at reasonable j if the rotational constants [2] of the molecule are "accidentally" close to an exceptional, more symmetric configuration. This is why only a small

number of "molecular tippe tops" have been discovered, notably the somewhat exotic H_2Se and H_2Te molecules [9–11]. Their almost 90° bond angle makes them nearly symmetric tops, and in their ground vibrational state, they exhibit a bifurcation, which is very similar to the one we report here for the ν_{23} state of DMSO.

The Hamiltonian $\hat{H}_{\rm rot}(\mathbf{J})$ describing the rotational level structure of an isolated vibrational state is typically Taylor expanded in even powers of the body-fixed [2] components of the angular momentum vector operator $\mathbf{J} = (J_a, J_b, J_c)$ [12]. The series begins with the rigid rotor term

$$\hat{H}^0_{\rm rot}(\mathbf{J}) = AJ_a^2 + BJ_b^2 + CJ_c^2,$$

is symmetric under the momentum reversal $\mathbf{J} \to -\mathbf{J}$, and is invariant under the rotations by π about any of the axes (J_a, J_b, J_c) [13]. The classical equivalent of $\hat{H}_{\rm rot}$ is a similar series $\mathcal{H}_{\rm rot}(\mathbf{j})$ with $\mathbf{j} = (j_a, j_b, j_c)$, whose $\mathcal{H}^0_{\rm rot}(\mathbf{j})$ term describes the reduced motion of an Euler top. Scaling quantum angular momenta by $\hbar$, we have $\|\mathbf{J}\| = \sqrt{J(J+1)}$ with quantum number $J = 0, 1, 2, \ldots$. Then the length j of $\mathbf{j}$ equals $\hbar\|\mathbf{J}\|$, and consequently, the classical limit of $\hbar \to 0$ corresponds to $J \to \infty$.

Contrary to the tippe top toy and other such dissipative systems—the amplitude j (and the laboratory frame orientation) of the angular momentum $\mathbf{j}$ are conserved. The set of points representing all instantaneous body-fixed orientations of the classical rotation axis and two possible directions of rotation for a given j is an $\mathbb{S}^2_j$ which embeds in $\mathbb{R}^3_{(j_a, j_b, j_c)}$ as a 2-sphere of radius j. This space is a phase space of the classical one-degree-of-freedom dynamical system that has Hamiltonian $\mathcal{H}_{\rm rot}$ and can be qualified as a nonrigid reduced Euler top system, whose equilibria correspond to the stationary rotation axes.

Fixing angular momentum, we can visualize the function $\mathcal{H}_{\rm rot} : \mathbb{S}^2_j \to \mathbb{R}$ as a *closed surface in* $\mathbb{R}^3$ [3, 6, 14] using spherical angles (θ, φ) to define the axis and the direction of rotation, and using the distance from the origin to give the value of $\mathcal{H}_{\rm rot}$. The surface inherits the symmetries of $\mathcal{H}_{\rm rot}$ [13], and in particular, it is $\mathbf{j}$-inversion invariant, so that any axis is represented by two equivalent opposite points corresponding to two rotation directions about this axis. For DMSO, as illustrated in Fig. 3, such surface has a deep minimum on axis C (north and south poles) and small height variations in the equatorial region, i.e., for C-projections $|j_c| \ll j$. In the ground vibrational state $|0\rangle$, we see two A maxima and two B saddles. This means that, as for a rigid oblate asymmetric Euler top (a "pumpkin"), rotations about A and C are stable and have, respectively, maximal and minimal energies for a given J, while rotation about B is unstable.

In the fundamental excited vibrational state ν_{23} (see Fig. 3, top), the equatorial region is *qualitatively different* for $J = 50$. Here *both* principal axes A and B are unstable, while near A we see a pair of new equivalent maxima
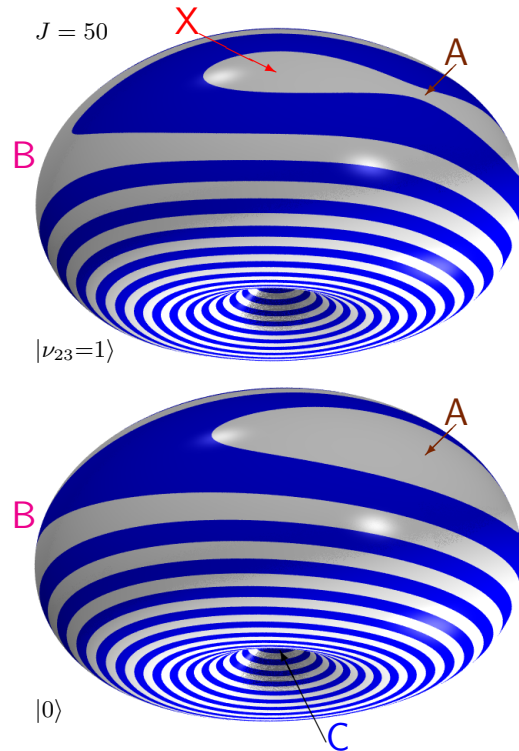

FIG. 3. Classical rotational energy of DMSO in the ν_{23} vibrational excited state (top) and the ground state (bottom) with angular momentum $J = 50$ shown in slightly rotated coordinates (J_a, J_b, J_c) of Fig. 2. To the same fixed additive constant and scale in both plots, the energy is given by the radial distance from the origin as function of the position of the instantaneous axis of rotation. Equidistant constant energy sets are stripe painted to emphasize the shape of the surfaces.

X. These maxima emerged from A at some $J_{\rm crit} < 50$ after a pitchfork bifurcation. They correspond to a pair of new stationary rotation axes that lie in the plane AB at some angle to axis A. So in order to parallel the amusement of the two men in Fig. 1, imagine the following. Suppose that for a sufficiently small J, when A is still stable, the molecule is found spinning about A with small precession. Then—if we had the liberty to increase J smoothly up to 50, we would have seen, after some critical $1 \ll J_{\rm crit} < 50$, the axis of this nearly stationary rotation tilting away from A in the plane AB.

In reality, we uncover axes X due to their specific "signature" in the rotational energy level structure [3]: while stable principal axes A and C correspond to sequences of nearly degenerate A and C-type level doublets, a common feature of any asymmetric top J-multiplet [15], the pair of X axes manifests itself in the formation of *quadruples*, or *4-clusters*. It follows that one should either observe such quadruples directly in the spectroscopic experiment, or at least accumulate sufficient data to make sure that the Hamiltonian $H_{\rm rot}$ predicting their existence is sufficiently stable, and the prediction is not an artifact
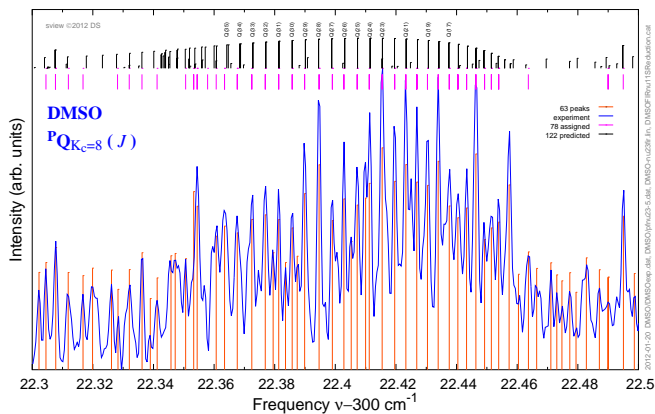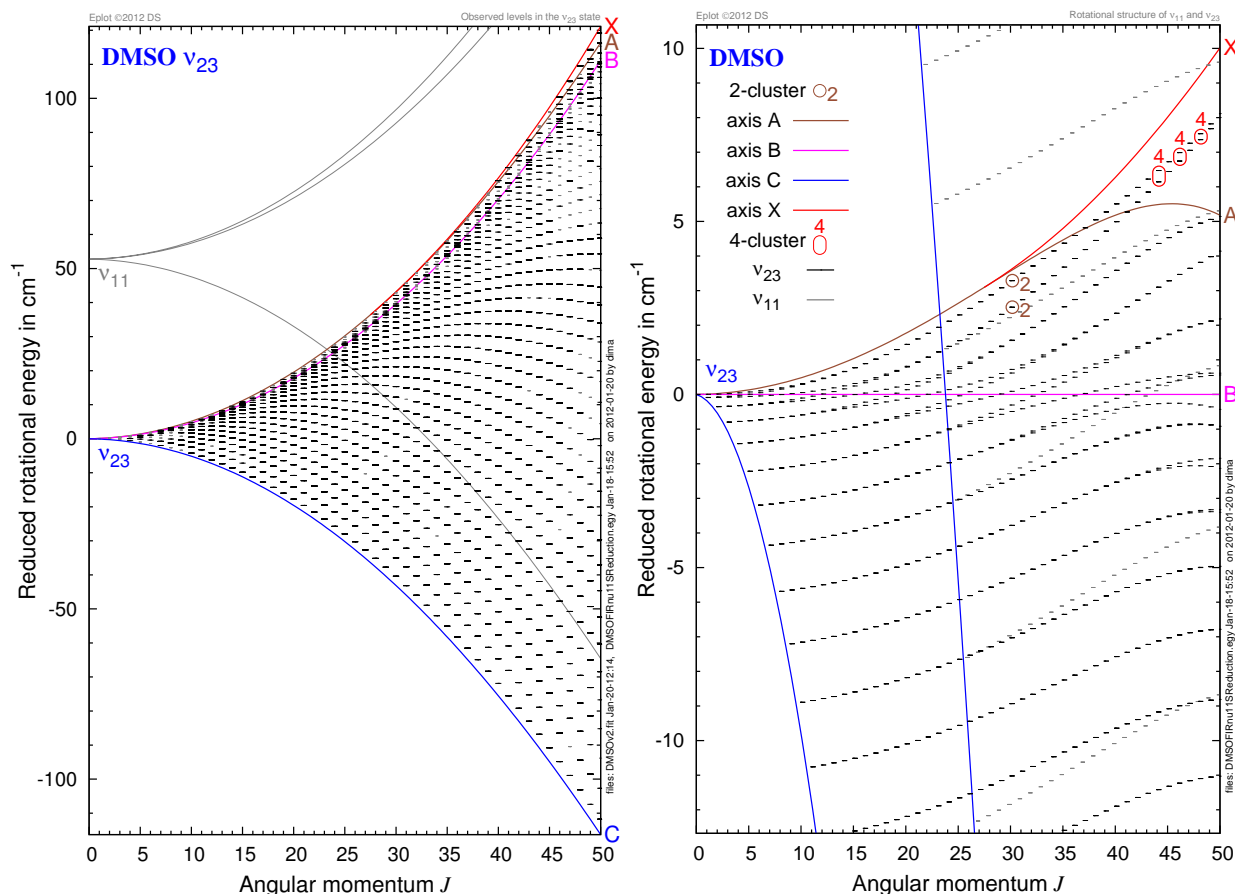
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FIG. 5. Rotational structure of the fundamental excited state ν_{23} of DMSO (left): observed and predicted levels are indicated by short and long dashes, respectively. Solid lines (gray for the ν_{11} multiplet) give energies of classical stationary rotations. The zoomed part (right) shows ν_{23} levels of type A, X (see encircled 2 and 4-clusters), and C and ν_{11} levels of type C. Average ν_{23} multiplet energy is subtracted in the left plot, and the energy of rotation about axis B is subtracted in the right plot.

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[11] Bifurcations in systems with excited resonant vibrations, notably H_2S and again H_2Se, or spherical tops, should be treated within a broader framework of *rovibrational relative equilibria*, i.e., vibrational nonlinear normal modes associated with particular axes of stationary rotation. Such approach covers the whole range of critical phenomena from axis reorientation in an isolated nondegenerate vibrational state [3] to the formation of *local modes* [6].

[12] By convention for oblate tops [21], standard commutation relations correspond to indices $(b, a, c) = (x, y, z)$.

[13] The momentum (or time) reversal invariance of $H_{\rm rot}$ reflects the independence of the classical free rotation energy on the direction of rotation. Rotations by π about the principal axes of inertia form a dihedral group D_2; reduction of $H_{\rm rot}$ to a D_2 symmetric form was given by Watson [18].

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[15] Near any sufficiently stable axis ξ, rotational states localize similarly to the symmetric top eigenstates $|J, J_\xi\rangle$ with projection $J_\xi = \pm J$ (for the most localized states), $\pm(J-1)$, etc. Spectroscopists call $K_\xi = |J_\xi|$ and ξ *good quantum number* and *quantization axis*. Due to the reversal symmetry [13], localized states form nearly degenerate *doublets* with dominant contribution from $|J, \pm J_\xi\rangle$.

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