Gyroscopic Destabilization of Molecular Rotation and Quantum Bifurcation Observed in the Structure of the ν_{23} Fundamental of Dimethylsulfoxyde

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Following the first successful high-resolution study of the "perpendicular" band of dimethylsulfoxyde at 324 cm^{-1}, associated with the ν_{23} bending vibration, we discovered a sequence of fourfold 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 $J \approx 27$.

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 dimethylsulfoxyde (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-1980s [3,4] within the general concept of molecular quantum bifurcations [5–7], and were studied recently in relation to Bose-Einstein condensation [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 $\hat{H}_{rot}(\mathbf{J})$ 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

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

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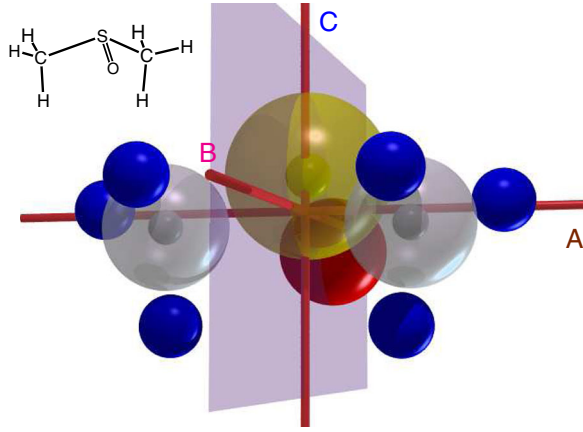
FIG. 2 (color online). Equilibrium configuration of $(CH_3)_2SO$ (DMSO) [1]; the three principal axes of inertia cross at the center of mass, axes B and C (vertical) lie in the symmetry plane.

is symmetric under the momentum reversal $\mathbf{J} \rightarrow -\mathbf{J}$, and is invariant under the rotations by π about any of the axes (J_a, J_b, J_c) [14]. The classical equivalent of $\hat{H}_{\text{rot}}$ is a similar series $\mathcal{H}_{\text{rot}}(\mathbf{j})$ with $\mathbf{j} = (j_a, j_b, j_c)$, whose $\mathcal{H}_{\text{rot}}^0(\mathbf{j})$ 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 $\hbar \rightarrow 0$ corresponds to $J \rightarrow \infty$.

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 $\mathbb{S}_j^2$ which embeds in $\mathbb{R}_{(j_a, j_b, j_c)}^3$ 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 $\mathcal{H}_{\text{rot}}$ 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 $\mathcal{H}_{\text{rot}}: \mathbb{S}_j^2 \rightarrow \mathbb{R}$ as a *closed surface in* $\mathbb{R}^3$ [6,16] 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 $\mathcal{H}_{\text{rot}}$. The surface inherits the symmetries of $\mathcal{H}_{\text{rot}}$ [14], 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.
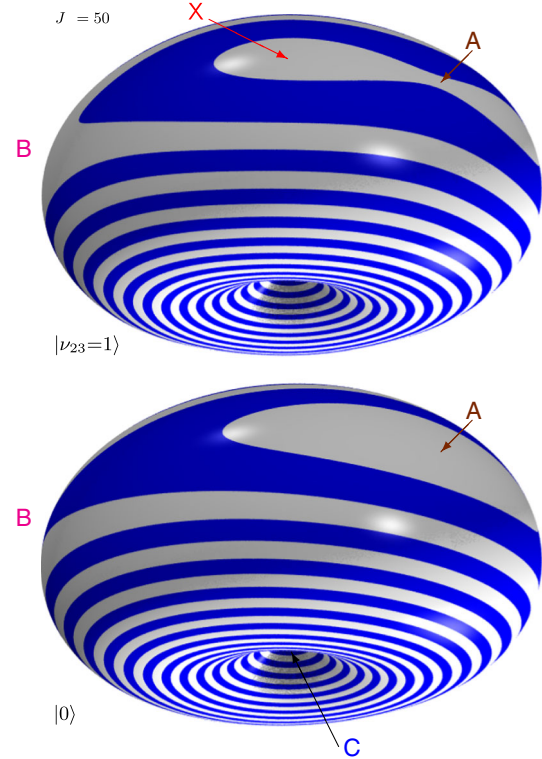

FIG. 3 (color online). Classical rotational energy of DMSO in the ν_{23} vibrational excited state (top) and the ground state (bottom) with angular momentum $J = 50$ shown in slightly rotated coordinates (J_a, J_b, J_c) of Fig. 2. To the same fixed additive constant and scale in both plots, the energy 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 painted with stripes to emphasize the shape of the surfaces.

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 X. These maxima emerged from A at some $J_{\text{crit}} < 50$ 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 $1 \ll J_{\text{crit}} < 50$, 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 [17], the pair of X axes manifests itself in the formation of
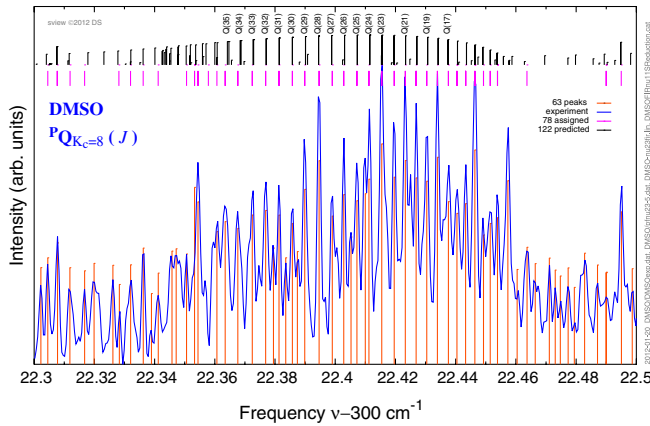
FIG. 4 (color online). A characteristic $^P Q$ sub-branch of transitions to C-type levels with $K_c^l = 8$ of the $\nu_{23} \leftarrow 0$ band of DMSO; all assignments are confirmed by combination differences.

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_{rot} predicting their existence is

sufficiently stable, and the prediction is not an artifact of extrapolating a power series too far. In the present study, we achieved both objectives.

DMSO, a relatively common organosulphur compound, has long been known for being a near symmetric top [18,19] and was used to discuss K-doubling and Watson's S-reduction [18]. Its low vapor pressure made conventional far infrared sources ineffective for high-resolution spectroscopic studies, and the information on the rotational structure of the bending vibrational states of DMSO remained inaccessible up until most recently [1]. The exceptional properties of the far infrared synchrotron radiation sources [20], specifically those of the AILES beam line of the SOLEIL synchrotron that became operational at the end of 2008, made this study possible.

The ν_{23} and ν_{11} spectral absorption bands of the gas phase DMSO were recorded at room temperature and 0.0015 cm^{-1} resolution using the IFS 125 Fourier-transform infrared spectrometer connected to a multipass cell with a 150 m optical path. The simpler ν_{11} band was analyzed successfully in Ref. [1]. The key to the ν_{23} band was in the series of fairly regular $^{P,R}Q$ sub-branches with
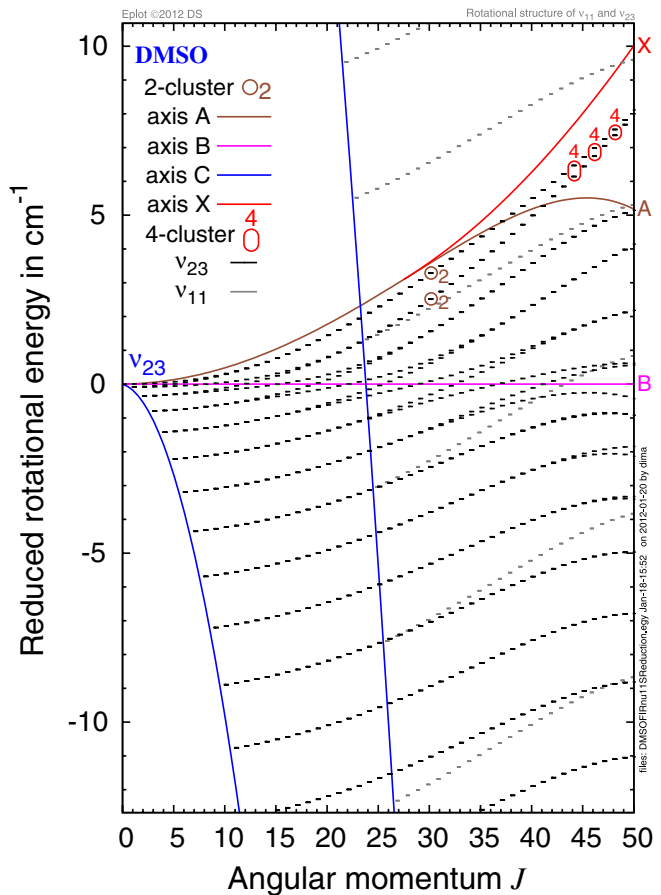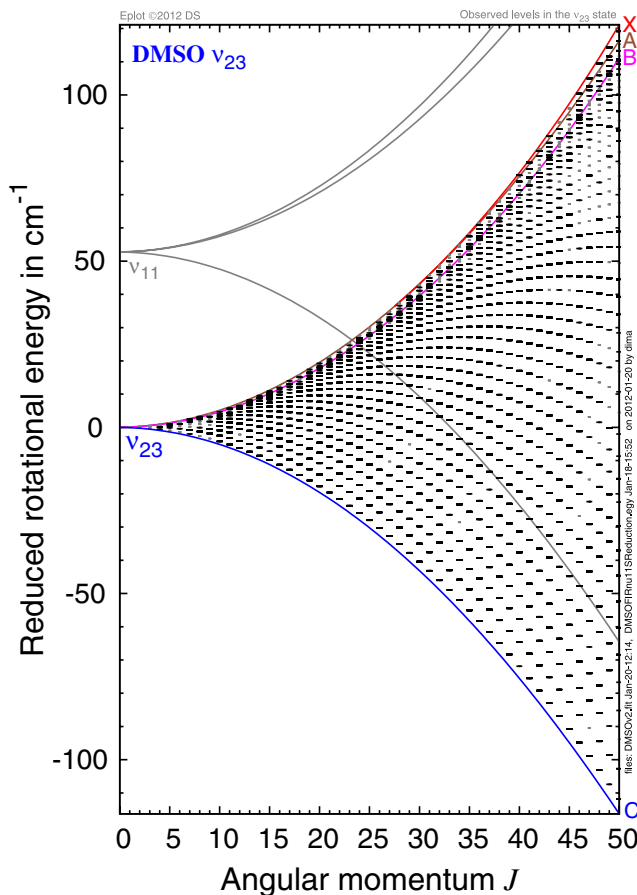

FIG. 5 (color online). Rotational structure of the fundamental excited state ν_{23} of DMSO (left): observed and predicted levels are indicated by short and long dashes, respectively. Solid lines (gray for the ν_{11} multiplet) give energies of classical stationary rotations. The zoomed part (right) shows ν_{23} levels of type A, X (see encircled 2- and 4-clusters), and C and ν_{11} levels of type C. The 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.

$\Delta K_c = \pm 1$ situated off the unresolved main Q branch (see Fig. 4). After finding and combining the reciprocal $^PQ_{K_c}(J)$ and $^RQ_{K_c-2}(J)$ lines so that their frequency differences of order 4–6 cm^{-1} reproduce to at least 10^{-3} cm^{-1} the lower state splittings known very accurately from Ref. [21], a computer aided assignment procedure based on a systematic search of all combination frequencies became possible. The Hamiltonian $H_{\rm rot}(\mathbf{J})$ in Watson's S form, which is most adequate for a nearly symmetric top, was developed to terms of combined degree 8 in the components of $\mathbf{J}$. As the assignment progressed, its parameters were adjusted using the programs by Pickett [13]. About 7500 transitions $\nu_{23} \leftarrow 0$ with angular momenta between 4 and 60, including more than 400 transitions to levels of type A and X, were assigned in the 300–350 cm^{-1} spectral range and reproduced to 5×10^{-4} cm^{-1} (15 MHz), which is, essentially, the experimental accuracy.

Figure 5 presents the rotational energy-momentum spectrum of ν_{23} given by $\hat{H}_{\rm rot}$ and the classical interpretation of this spectrum, notably the energies of classical rotation about axes A, B, C, and X, obtained from $\mathcal{H}_{\rm rot}$ (cf. the surface in Fig. 3, top). Because rotational constants A and B are very close, most of the states (up to 85%) are of type C. They are described primarily by the diagonal part of $\hat{H}_{\rm rot}$, a series in J and $K := J_c$. In order to determine unambiguously the parameters of the S-form tensorial terms $J_+^{2n} + J_-^{2n}$, we made a special effort to observe practically *all* A states. So no part of the energy-momentum spectrum in Fig. 5 is a result of a mere extrapolation unsupported by direct observations.

The low-J structure of ν_{23} resembles that of a rigid oblate asymmetric top: sequences of C and A-type doublets of rotational levels ascend and descend from the respective minimum and maximum energies of J multiplets towards the transition region B. When J reaches ≈ 30, the $J_\pm^4$ term becomes dominant at low K_c, and a classical pitchfork bifurcation takes place at A (see the branch point of the A and X lines in Fig. 5) creating a pair of new stationary rotation axes X. For larger J, rotation about X requires the maximal energy. Quantum states of type X, i.e., states with a new unusual localization pattern, lie in the energy-momentum domain between the energies of X and A. We see them being formed out of two neighboring sequences of A-type doublets crossing into the X domain and merging into quadruples. Even though these quadruple states do not give rise to any prominent spectroscopic transitions, we actually observed most of them in about 20 out of the 7500 assigned transitions.

It is always a matter of considerable satisfaction to participate in a fresh important development in a field where such advancement seemed unlikely just a few years ago. The far infrared synchrotron radiation made a great number of complex molecular systems accessible. The interesting dynamics that we have uncovered in one of these systems, and the way this dynamics was observed have many analogs in different areas of modern nonlinear physics.

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[11] Bifurcations in systems with excited resonant vibrations, notably H$_2$S and again H$_2$Se, 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 an 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 [13], standard commutation relations correspond to indices $(b, a, c) = (x, y, z)$.

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[14] 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 [15].

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[17] 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 a good quantum number and quantization axis. Due to the reversal symmetry [14], localized states form nearly degenerate doublets with dominant contribution from $|J, \pm J_\xi\rangle$.

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