Experimental study of a sequence of quantum bifurcations leading to the crossover of a rotational multiplet

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The "crossover" of the energy spectrum of a molecule during rotational excitation corresponds to a series of bifurcations in the classical limiting problem. The sequence and type of these bifurcations are determined by the symmetry conditions. This effect is studied in the high-resolution spectrum of R_3^- band of the ν_3 state of the CF_4 molecule.

The simplest qualitative changes occurring in the energy spectrum of a quantum system as its motion integrals change are the subject of extensive studies in nuclear and molecular physics, using various model Hamiltonians.[1–5] Elementary qualitative (critical) phenomena correspond to elementary bifurcations in the classical problem,

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which is obtained from the initial quantum problem on passing to the classical limit on the basis of generalized coherent states. A special role in the study of quantum bifurcations is played by the stratification of the phase space of the classical problem under action of symmetry group G. The local symmetry of stationary points $g \subset G$ makes it possible to give a general classification of bifurcations.[1]

If in the phase space acted on by group G, in addition to the 0-D striations whose points are included in the minimum set of stationary points of the problem, striations of a large number of dimensions are formed, qualitative changes of a more complex nature become possible. Of particular interest for the one-parameter problem is a system of 0-D striations which we connected by 1-D striations. In this case, as the parameter changes, stationary currents move along a 1-D striation, causing a sequence of elementary bifurcations in stationary currents which are located on zero-dimensional striations. The sequence is determined by the relative positions of the striations, i.e., by the action of G. Such a sequence is represented as one complex qualitative change which, in contrast to the bifurcations contained in it, has a global nature.

In the area of molecular problems, one of the most convenient subjects for an experimental study of the effects discussed was found to be the rotational multiplets of spherical-top molecules.[6] In this case, in phase space S^2, the action of the group $G = O_h$ generates a system of 0-D striations which are characterized by a local symmetry $g = C_2$, C_3, C_4, and which are connected by 1-D striations C_S, and a 2-D striation of common position (Fig. 1). The sequence of bifurcations for a given stratification is caused by the motion of the stationary point C_S during a change in the parameter of the problem—the total angular momentum **J**, i.e., during rotational excitation.[7] In the quantum problem, this sequence of classical bifurcations is associated with crossover

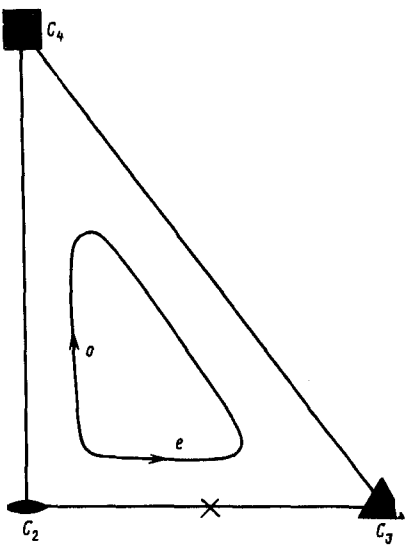

FIG. 1. Unit cell of the O_h group and location of stationary points. Motion of point C_S in the plane of symmetry σ at different stages of crossover.

of a rotational multiplet. This effect was noted earlier in Ref. 8 in a study of the ν_3 band of the CH_4 molecule, but the nature of the change in the energy spectrum near the crossover point had not been analyzed before, either theoretically or experimentally. At the same time, a general theoretical analysis leads to the following conclusions: (a) for spherical-top molecules, the crossover consists in a sequence of elementary bifurcations of the type $e = C_2 \to C_3 \to C_4 \to C_2$ or $o = C_2 \to C_4 \to C_3 \to C_2$ (Fig. 1) and is associated with the formation of 12-tuple clusters of energy levels at values of **J** corresponding to the crossover stage; (b) a detailed experimental study of the sequence of bifurcations in the spectrum of a quantum system, in particular, the formation of 12-tuple clusters, is possible at sufficiently high values of **J**; (c) a phenomenological description of the rotational spectrum by means of a parametric effective Hamiltonian is highly sensitive to information on rotational transitions in the crossover region; (d) as a result of a marked narrowing of the rotational multiplet near the crossover, its

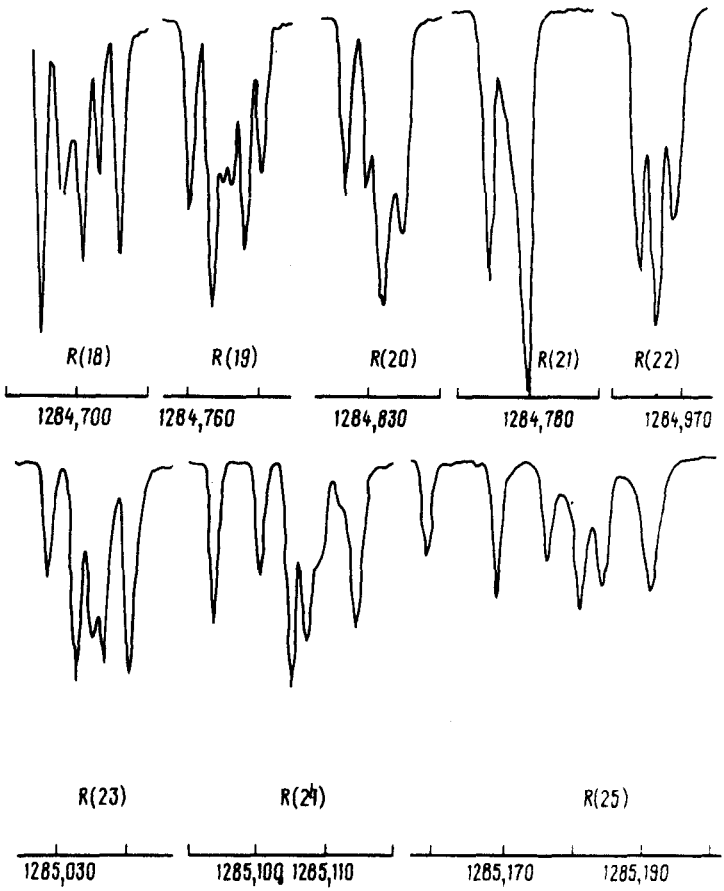

FIG. 2. High-resolution IR spectrum of the R_3^- band of the ν_3 vibrational state of the CF_4 molecule, corresponding to the crossover region of the F^- multiplet.

experimental study requires a higher spectral resolution than in the neighboring regions of the spectrum.

Of particular interest in this connection was the rotational structure $F^-(R=J-1)$ of the branch of the $\nu_3(F_2)$ state of the CF_4 molecule, where the available experimental information[9] did not cover the crossover region for $J\approx 22$. We recorded the experimental spectrum of the R_3^- band of the CF_4 molecule (Fig. 2) on a diode laser spectrometer. The instrumental resolution of the apparatus amounts to $\approx 10^{-4}\text{cm}^{-1}$ for a Doppler linewidth $\approx 1.7\times 10^{-3}\text{cm}^{-1}$ ($T=77$ K). The pressure of CF_4 gas was 0.05 Torr. The precision of calibration of the absolute scale of wave numbers against the reference spectra of N_2O, H_2O, HDO, and D_2O was $\approx 5\times 10^{-4}\text{cm}^{-1}$. The crossover effect causes an anomalous narrowing of the $R(21)$ and $R(22)$ lines corresponding to transitions to levels in the region of maximum compression of the F^- multiplet (Fig. 2). According to a preliminary analysis, a crossover of type $-e$ is observed in CF_4. A separate article will discuss in more detail the results of an analysis of the spectrum and cluster structure of the F^- multiplet. The authors are grateful to G. Pierre for conducting collaborative studies which considerably stimulated this work.

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