Pseudo-Jahn-Teller Effect in Transition States of Chemical Reactions

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The basic idea of the Jahn-Teller effect as the source of any symmetry breaking in polyatomic systems [1-4] is presented for three fundamental cases of nuclear instability of high-symmetry configurations: formation of the hydrogen bond, planar-to-pyramidal instability in trigonal pyramidal molecules, and the transition state of several chemical reactions.

1. Often termed the hydrogen bond [5,6], the proton transfer between two molecular systems is shown to be the case of the pseudo-Jahn-Teller effect (PJTE). Illustrative examples include the proton transfer in deprotonated $H_3O_2^-$ and protonated $H_5O_2^+(H_2O)_4$ water clusters, several proton-bound dimers $MH^+ + M \leftrightarrow M + HM^+$, and other similar systems.
2. An essential case of nuclear instability is the transition state in chemical reactions as the saddle point on the adiabatic potential energy surface. The two linear collision reactions, $H+H_2 \rightarrow H_2+H$ and $F+H_2 \rightarrow FH+H$, show the PJTE nature of the negative curvature at the transition state of the adiabatic potential curve along the reaction path. In addition, as a natural implication of the PJTE, we show the existence of the stable excited states, in which vibronic coupling to the ground state causes the instability of the activated complex of the reaction [7].
3. For several trigonal pyramidal molecules AB_3 and a series of planar X_2CE compounds (X = H, F; E = O, S), with a pyramidal structure in their anionic and the first excited states, we reveal the PJTE as the origin of the instability of their planar nuclear configuration to inversion of the pyramidal structure.

In all the cases considered, the theory of the PJTE provides a feasible model of the potential energy along the instability coordinate. Moreover, the corresponding parameters evaluated from quantum chemical calculations help simulate the nuclear dynamics of the respective phenomena.

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