The Jahn–Teller Theorem applies to Transition States

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Summary It is shown that the Jahn–Teller theorem applies to transition states and the implications of this to the geometry of the transition states of the $H + H_2$ and $H_2 + H_2$ reactions are noted.

THE Jahn–Teller theorem may be stated as:[1] the equilibrium nuclear configuration of any molecular electronic state cannot have spatial degeneracy except when the configuration is linear. In other words, if for a particular configuration the electronic wave function is found to be degenerate, then it is always possible to find some nuclear displacement vector along which the potential energy decreases. I have not seen the statement that this theorem may be applied to transition states (activated complexes), and the extension to these is not completely trivial because a transition state is unstable to distortions in one direction. At first sight it appears that the Jahn–Teller distortion could be along the reaction co-ordinate.

A transition state is defined as a saddle on a potential energy surface, and for this the gradient of the surface in any direction is zero. To prove the Jahn–Teller theorem one establishes that when starting with a configuration that has a degenerate state there is always some co-ordinate vector for which the change in energy is *first-order* in the displacement. In fact, there are at least two such directions. A doubly degenerate state is stabilized by displacement along two directions of a doubly degenerate normal mode. A triply degenerate state may be stabilized by a triply or doubly degenerate mode. The important point is that a first-order energy change implies a gradient of the potential energy in these directions and this is incompatible with the definition of a transition state.

The following are simple examples of the principle we have established. 1. The transition state in the $H + H_2 \rightarrow H_2 + H$ reaction cannot be an equilateral triangle H_3 because from simple molecular orbital arguments this has a ground state of E' symmetry. 2. The transition state for the $H_2 + H_2$ atom exchange reaction cannot be a tetrahedral H_4. The lowest energy molecular orbital configuration is $a_1^2t_2^2$ and the singlet spin ground state from this would be T_2. However, the transition state could be square planar because the lowest energy configuration $a^2_{1g}e_g{}^2$ gives only the non-degenerate singlet states, A_{1g}, B_{1g}, and B_{2g}. On the other hand a square planar configuration H_4^+ could not be a transition state for a reaction between H_2 and H_2^+, as this configuration would have a degenerate ground state. These conclusions are in agreement with the results of accurate potential energy surfaces by Conroy and his co-workers.[2,3]

The above conclusions about the allowed symmetry for transition states is additional to the arguments presented by Murrell and Laidler[4] which were based on the symmetry of normal modes. They pointed out that at the transition state there could not be two orthogonal directions for which the surface had negative curvative, because if this is the case there must be a lower energy path for the reaction than the one passing through the transition state. A reaction co-ordinate at the transition state cannot have the symmetry of a degenerate mode. Because the reaction co-ordinate for triangular H_3 to give $H_2 + H$ has E' symmetry, this is a separate argument against this configuration being the transition state for the $H + H_2$ exchange reaction.

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