

A POSSIBLE TRANSITION STATE FOR THE $H_2 + D_2$ EXCHANGE REACTION

Lawrence L. LOHR Jr.

*Department of Chemistry, University of Michigan,
Ann Arbor, Michigan 48109, USA*

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A proposal for a possible transition state for the $H_2 + D_2$ exchange reaction follows from an analysis of the Jahn–Teller instability of tetrahedral H_4 . The suggested pathway involves pseudo-rotation in the e deformation space, with a compressed tetrahedral structure corresponding to the reaction saddle point.

1. Introduction

A considerable effort has been devoted to ab initio theoretical studies [1–16] * of the H_4 potential surface in order to locate a structure that might correspond to the transition state for the four-center exchange reaction $H_2 + D_2 \rightarrow 2HD$ and to characterize the long-range intermolecular interaction. To date a satisfactory structure for the transition state has not been located. Various shock-tube studies [17–19] of this reaction have been interpreted in terms of a bimolecular rate process having an activation energy of 39 to 42 kcal/mol. Recent atomic resonance absorption experiments [20] have been similarly interpreted, with a reported activation energy of 38 ± 5 kcal/mol. By contrast the ab initio barrier heights are typically 100 kcal/mol higher, with some representative values being 124 to 148 kcal/mol for a square planar structure [3–7,12] and 188 kcal/mol for a tetrahedral structure [7]. Of comparatively low energy but not suitable as the transition state is the collinear structure. As often pointed out, either the “correct” region of configuration space has not been explored in the ab initio studies, or the ex-

perimental activation energy does not correspond to a four-center bimolecular reaction pathway. It is the object of this letter to describe a bimolecular pathway that might be relevant either for this or for other four-center exchange reactions.

2. Proposition

The tetrahedral structure is highly unfavorable as a transition state not only because of its very high energy but also because it corresponds to three valleys meeting at a point, so that a lower energy pathway avoiding this structure is expected from the arguments [21] of Stanton and McIver. Their arguments apply even if the lowest energy spin singlet for the T_d structure were not orbitally degenerate. Pearson [22] has briefly discussed the possibility of exchange involving the perpendicular approach of two molecules to form a tetrahedral activated complex and has shown that such a process is forbidden by orbital symmetry. However, the full implications of the degeneracy of the 1E state appear not to have been considered.

Using an orbital description, the two components of the 1E term of the $a_1^2 t_1^2$ configuration may be written in Griffith's notation [23] as

$$|U\rangle = |^1E(^1A_1)\rangle \\ = 6^{-1/2} [(a_1 \bar{a}_1 \xi \bar{\xi}) + (a_1 \bar{a}_1 \eta \bar{\eta}) - 2(a_1 \bar{a}_1 \zeta \bar{\zeta})] \quad (1a)$$

* We note that the qualitative correlation diagram given in ref. [5] for the staggered approach of two H_2 molecules is in error for the region between the D_{4h} and T_d structures. The lowest singlet ($^1B_{1g}$) of the D_{4h} structure correlates with the lower Jahn–Teller branch of the lowest singlet (1E) of the T_d structure.

and

$$|V\rangle = |{}^1E({}^1B_1)\rangle = 2^{-1/2}[(a_1\bar{a}_1\eta\bar{\eta}) - (a_1\bar{a}_1\xi\bar{\xi})], \quad (1b)$$

where the symbols ξ , η , and ζ denote the t_2 orbital components transforming as x , y , and z , respectively, the bar superscripts denote "down" spin, the parentheses enclosing four spin-orbital symbols denote Slater determinants, and the 1E component labels 1A_1 and 1B_1 for U and V denote their irreducible representations in the D_{2d} subgroup. Instability of the T_d structure is confined in first order to the three-dimensional configuration space spanned by the symmetry coordinates Q_1 , Q_{2a} , and Q_{2b} , where Q_1 is the totally symmetric A_1 stretching mode, while Q_{2a} and Q_{2b} are the components of the E bending mode transforming as $3z^2 - r^2$ and $x^2 - y^2$, respectively. Assuming an orientation of the tetrahedron with atoms having spherical polar coordinates (r, θ, ϕ) , $(r, \theta, \phi + \pi)$, $(r, \pi - \theta, -\phi)$, and $(r, \pi - \theta, -(\phi + \pi))$, respectively, positive Q_{2a} is taken to mean an elongation along z (reduction in θ) while positive Q_{2b} is taken to mean a twist about z (reduction in ϕ). If the customary *plane* polar coordinates [24] are defined in Q_{2a} , Q_{2b} space by

$$\rho \equiv (Q_{2a}^2 + Q_{2b}^2)^{1/2}, \quad \alpha \equiv \tan^{-1}(Q_{2b}/Q_{2a}), \quad (2)$$

then the lower energy surface is associated with the electronic wavefunction

$$\Psi(\alpha) = \cos(\alpha/2)|U\rangle - \sin(\alpha/2)|V\rangle, \quad (3)$$

where the coefficients reflect the Jahn-Teller stabilization of the $|U\rangle$ component for an elongated tetrahedron ($\alpha = 0$) and the $|V\rangle$ component for a compressed tetrahedron ($\alpha = \pi$). The minimal symmetry in the three-space is D_2 , with D_{2d} symmetry occurring for arbitrary Q_1 and ρ for $\alpha = 0, 2\pi/3$, and $4\pi/3$, corresponding to tetrahedra elongated along the z , x , and y axes, respectively, and for $\alpha = \pi/3, \pi$, and $5\pi/3$, corresponding to tetrahedra compressed along the y , z , and x axes, respectively. Neglecting cubic and higher terms, the potential energy is independent of α at fixed r and ρ , giving rise the famous "Mexican hat" circular trough. The $|U\rangle$ component is further stabilized by a *second-order* Jahn-Teller mixing with the higher energy term transforming as 1A_1 in T_d and given by

$$|{}^1A_1\rangle = 3^{-1/2}[(a_1\bar{a}_1\xi\bar{\xi}) + (a_1\bar{a}_1\eta\bar{\eta}) + (a_1\bar{a}_1\zeta\bar{\zeta})], \quad (4)$$

so that a three-fold pseudo-rotational barrier is anticipated in ρ, α space.

Consider now the staggered approach of two I molecules having the same bond length so as to form an H_4 array of D_{2d} symmetry with respect to the z axis. This approach involves a *decrease* in both Q_1 and Q_{2a} , with $Q_{2b} = 0$. For some Q_{2a} the molecule is a Jahn-Teller minimum along the $\alpha = 0$ direction in space. A pseudo-rotation of $\alpha = \pm\pi/3$ produces y or x compressed structures corresponding to a potential energy maximum along α but to a local minimum with respect to ρ and Q_1 , while continuing the pseudo-rotation to $\alpha = \pm 2\pi/3$ produces x or y elongated structures equivalent to that initially formed along z , but with atoms now re-paired, so that increase of Q_1 and ρ leads to products (fig. 1). Thus it is suggested that a possible transition state is a *compressed* D_{2d} tetrahedral structure with a 1B_1 electronic state. The actual path of steepest ascent involves r and ρ changing simultaneously with α , except for $\alpha = \pm\pi/3$ and π , where the path is tangent to a circle of constant ρ .

Of paramount importance to the plausibility of the proposed reaction pathway is the continuity of the electronic wavefunction given by (3). While the individual t_2 orbitals transform as different irreducible representations (b_1, b_2 , and b_3) in D_2 symmetry, such that "orbital energy surfaces" are disjoint paraboloids intersecting but not interacting, the components of the 1E wavefunction *both* transform as 1A in D_2 symmetry, so that reactants and products are connected by a single poten-

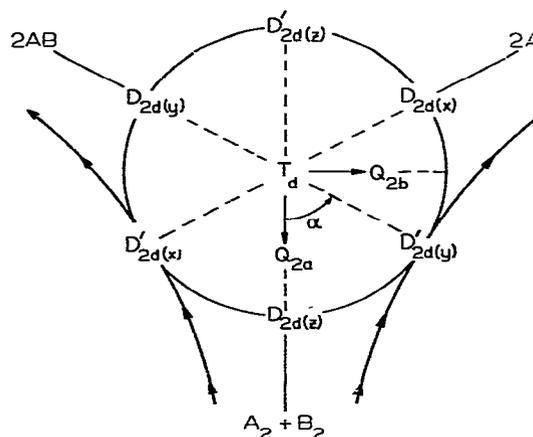


Fig. 1. Schematic projection of proposed exchange path in Q_{2a} , Q_{2b} (or ρ , α) space. The hexagonal array of lines emerging from the T_d origin denote loci of structures with D_{2d} symmetry, with primed symbols for compressed structure unprimed for elongated.

energy surface in Q_1, Q_{2a}, Q_{2b} space. In short, the exchange reaction is "allowed" in a term description, with only "essential" configuration interaction being considered. A recent quasiclassical dynamical trajectory study [25] employing a London-type potential energy surface indicated that the reactive collisions tend to be those for which each of the diatomics is roughly perpendicular to the line of motion and for which they are within 40° of being planar, so that a nearly planar arrangement, such as proposed compressed tetrahedral structure, seems plausible as the transition state provided that its energy is not too high.

3. Energy considerations

Since the ${}^1B_{1g}$ state of the D_{4h} structure has too high an energy to serve as the transition state, the proposed mechanism demands a significant second-order instability of this state with respect to the out-of-plane B_{1u} mode. This could arise from a combination of a decrease in the nuclear repulsion energy and second-order Jahn–Teller mixings with excited ${}^1A_{1u}$ states. While no ${}^1A_{1u}$ states arise from a basis consisting only of s AO's on each hydrogen, there is one arising from the singly-excited configuration $a_{1g}^2 e_u^1 e_g^1$, where the e_g MO is constructed from p AO's perpendicular to the molecular plane. Whether or not instability would be found from accurate ab initio calculations remains to be shown, although our single determinant \dagger calculations with either STO-3G or 4-31G s-type basis sets indicate *stability* for a D_{4h} structure with respect to the (cartesian) B_{1u} deformation. A major reason for this is that the displacement reduces the bonding of the a_{1g} MO. Thus it is possible that the flattened tetrahedron has an energy too high to serve as the transition state for the hydrogen exchange reaction, although it may be relevant in other cases where two-fold orbital degeneracy obtains for a tetrahedral structure.

\dagger The single-determinant corresponds to a superposition of the ${}^1B_{1g}$ and ${}^1A_{1g}$ states of the configuration $a_{1g}^2 e_u^2$.

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