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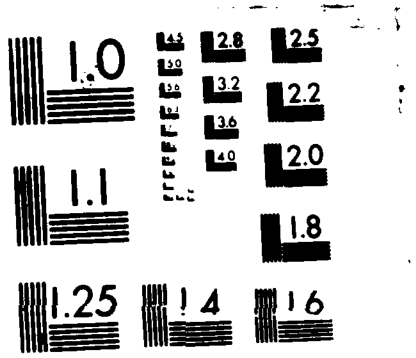

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Final Report
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30 Sept 1985 to
29 Sept 1986

Potential Energy Surface Stability and Decay Mechanisms of Excited Tetrahydrogen H_4

March 1987

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prepared for the: **Air Force Rocket Propulsion Laboratory**

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NOTICE

FOREWORD

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This technical report has been reviewed and is approved for distribution in accordance with the the distribution statement on the cover and on the DD Form 1473.

Walter J Lauderdale

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Project Manager

FOR THE COMMANDER

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TRIGONAL PYRAMIDAL HYDROGEN

As a first attempt to study the stability of the ~~H_4~~ (C_{3v}) cluster we have used the MRD-CI method and a medium size basis set to calculate various sections of the potential energy surfaces of its ground and first excited states. We show that these correlate to the ~~$(X^1\Sigma_g^+ X^1\Sigma_g^+)$ and $(X^1\Sigma_g^+ B^1\Sigma_u^+)$~~ states of the two HYDROGEN ~~H_2~~ constituents. ~~respectively~~. Finally, we report on the calculation of the diabatic matrix elements of the vibronic interaction in the region of avoided crossing which is crucial to the stability of ~~H_4~~ TETRAGONAL HYDROGEN

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INTRODUCTION

In a series of papers from this institute, an excited state in a trigonal pyramidal geometry of H_4^* (C_{3v}) has been predicted theoretically and shown computationally to be bound, employing a relatively small basis set (Ref. 1). The prediction is based on the Maximum Ionicity of the Excited State (MIES) model, which relates the chemical binding and the geometry of the bound species to the strong charge transfer in the H_2^* $B^1\Sigma_u^+$ excited state. The calculations, done at C_s symmetry, show that the first excited A $^1A'$ state of H_4^* has a relatively deep minimum near an avoided crossing with the ground X $^1A'$ state. At this minimum, the geometrical arrangement of four H atoms is shown in Fig. 1 with R = 3.8 bohr and r = 1.7 bohr.

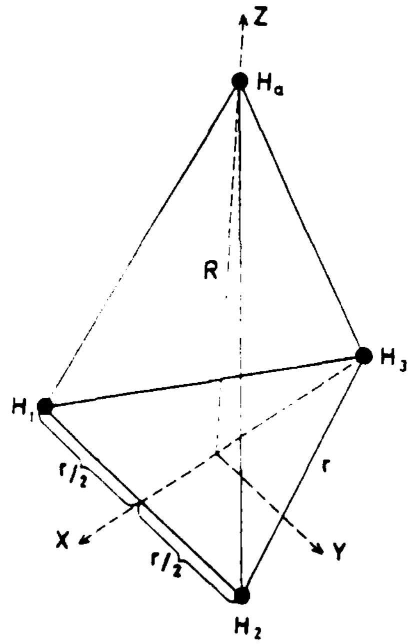

Figure 1. Geometry of the H_4 Molecule. The basis for the pyramid is an equilateral triangle of side r while R is the distance of the H_4 atom at the apex of the pyramid from the center of the triangle. An auxiliary angle θ (not shown) may be defined on the XZ plane between the vector R and the Z axis so that it is positive if Ha is in the first quadrant, negative if it is in the fourth quadrant, and zero if it is on the Z axis ($-90^\circ \leq \theta \leq +90^\circ$).

We have verified the above results via calculations of higher accuracy which employed a larger basis set. We also performed optimized calculations to show that, as long as the C_{3v} symmetry is maintained, there can be no dissociation except via a diabatic crossing to the ground X $^1A'$ state or via a high vibrational excitation of A' (A_1) symmetry. In addition, we computed the diabatic matrix elements of the vibronic interaction in the region of the avoided crossing, which is related to the probability of a diabatic crossing.

There has been some speculation as to whether the X $^1A'$ state represents the true ground state (relative to two hydrogen molecules). In this report we show that this state belongs to the ground state hypersurface since it correlates to $H_2(X^1\Sigma_g^+)$ + $H_2(X^1\Sigma_g^+)$, while the first excited A $^1A'$ state is shown to correlate to $H_2(X^1\Sigma_g^+)$ + $H_2(B^1\Sigma_u^+)$ (an excimer state).

TECHNICAL DETAILS

We have used the MRD-CI programs of Buenker and Peyerimhoff (Ref. 2) with the basis set taken from a paper by Romelt et al. (Ref. 3). However, using their full set (7s/3p) resulted in an unmanagably high CPU time per point and it became evident that a few functions had to be removed. By running a few tests we concluded that the best choice was to remove from each H center the set of p functions with the exponent 0.035. With this somewhat smaller basis set, the CPU time per point became considerably better. Calculations for both the C_{3v} and the C_s symmetries have been carried out at C_s symmetry due to limitations of the MRD-CI programs, which can handle Abelian groups only. Additional calculations for the planar T geometry (see discussion) have been carried out at C_{2v} symmetry. In all cases a selection threshold of 10 μH has been maintained and enough reference configurations have been used to ensure a $\sum_n c_n^2 > 0.95$, where c_n is the coefficient of the n^{th} reference CI vector. For the diabatic matrix elements of the vibronic interaction we have used the finite differences method of Lorquet (Ref. 4) as it has been adapted to the MRD-CI programs by Hirsch et al. (Ref. 5). The method requires two separate energy calculations at two intermolecular separations differing by a small increment, which here is taken to be 0.0001 bohr. The accuracy of the method is estimated to be to two significant figures.

DETAILS OF THE CALCULATION

This calculation may be divided into four parts:

1) Finding the new minimum of the A $^1A'$ state in the new basis set.
2) Generating the potential energy curves of X $^1A'$ and A $^1A'$ as the R coordinate changes, everything else being kept constant.
3) Computing the non-adiabatic matrix elements at and around the avoided crossing.
4) Additional calculations to determine whether the potential minimum of the A $^1A'$ state in the R dimension is a real minimum or a saddle point.
5) Calculations to establish that the X $^1A'$ and A $^1A'$ states of $H_4(C_{3v})$ correlate to $H_2(X^1\Sigma_g^+)$ + $H_2(X^1\Sigma_g^+)$ and to $H_2(X^1\Sigma_g^+)$ + $H_2(B^1\Sigma_u^+)$ states of two H_2 molecules respectively.

Finding the new minimum

Figure 1 describes the relevant parameters of the H_4 trigonal pyramidal geometry: r is the length of the side of the equilateral triangular base and R is the distance between the hydrogen atom at the apex of the pyramid (H_a) and the center of the triangle. By varying both r and R we have found that the minimum of the first excited $^1A'$ state is now at r = 1.8 and R = 4.2 bohr and the depth of its well is 2.476 eV.

Generating the potential energy curves

Figure 2 shows the variation of the potential for ground and the first excited $^1A'$ states of H_4 as R varies while r is kept fixed at 1.8 bohr. Similar potential curves obtained previously with the smaller basis set (Ref. 1) are also shown in Fig. 2 for comparison. The potential was calculated at intervals appropriate to the steepness of the curve, and to the detail required. This was typically between 0.1 and 1.0 bohr.

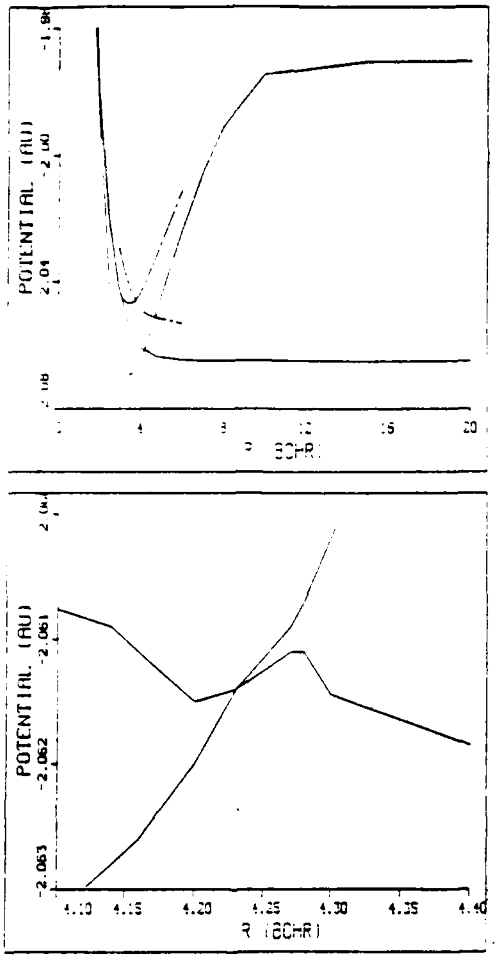

Figure 2. Potential Energy Surface of the X $^1A'$ and A $^1A'$ States of the trigonal pyramidal H_4 corresponding to r = 1.8 bohr (solid line). For comparison, the upper plot displays the same section from the results of Ref. 6 (chained dashed line). The lower plot is a blow up of the region of pseudocrossing. The dissociation limit for the ground state is $H_3(^2E') + H(^2S)$, while for the excited state it is $H_3(^2A_1) + H(^2S)$.

Computation of the non-adiabatic matrix elements

To compute the lifetime of the bound excited state, its transition probability (both radiative and nonradiative) to the lower X $^1A'$ state must be calculated. As a first step toward this goal we have computed the diabatic matrix elements of the vibronic interaction d/dR in the area of the avoided crossing. These matrix elements are shown in Table 1 from which one notes the sharpness of this interaction. The dominant configurations interchange completely somewhere between R = 4.23 and R = 4.24 bohr, while the area where the matrix elements are significant extends from 4.20 to 4.25 bohr. Because the interaction region is so narrow, one may assume that the probability of diabatic crossing could be relatively low.

Table 1. Diabatic matrix elements of d/dR
in the area of avoided crossing (in a.u.) for r = 1.8 bohr.

R	$X\ {}^1A'\,\lvert d/dR\rvert\,A\ {}^1A'$
4.10	0.07
4.20	1.1
4.21	1.0
4.22	2.6
4.23	24.
4.24	10.
4.25	1.5
4.26	0.57
4.27	0.12
4.28	0.09

Calculations to discriminate between true minimum and saddle point

To achieve such a discrimination one has to distort the C_{3v} symmetry in various ways and see whether the energy at the minimum goes always up. As a first step, we have moved the H at the apex of the H_4 pyramid (H_a) around the XZ plane thus obtaining a section of the H_4 surface. This section is shown in Fig. 3. It represents the variation of the potential of the ground and the first excited ${}^1A'$ state as the H_a atom moves curvelinearly on the XZ plane. The variable is the angle θ between the R vector and the Z axis. $\theta = 0^o$ is the original vertical position of H_a; for $\theta = 90^o$ H_a is positioned on the + X axis (kite geometry) while for $= -90^o$ it is positioned on the - X axis towards the H atom (T geometry). For $0^o<\theta<90^o$ C_s is the true symmetry while for $\theta = 90^o$ the symmetry is C_{2v}. For each θ the first excited ${}^1A'({}^1A)$ state is minimized with respect to R. For two angles $\theta = -45^o$ and $\theta = -90^o$ the energy is also minimized with respect to r. The solid circles in Fig. 3 show these points, while the dashed line connects them with the known $\theta = 0^o$ points. The dashed lines show roughly the expected change due to r optimization at various

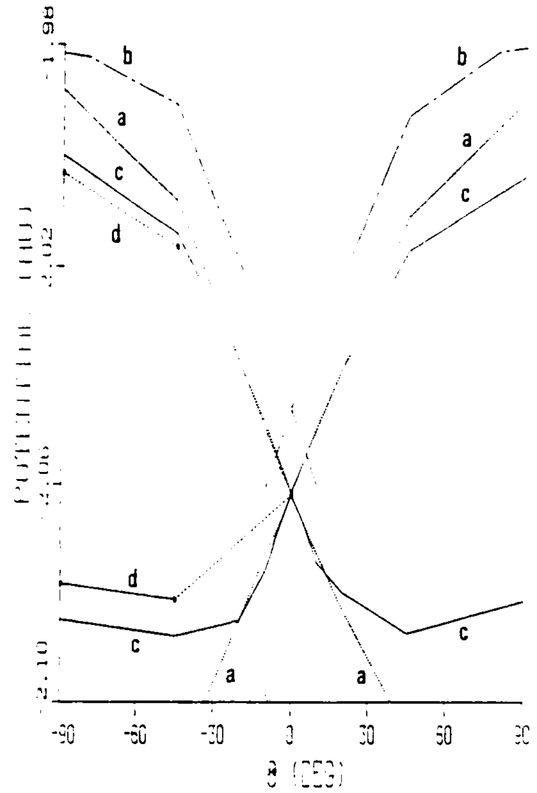

Figure 3. Potential Energy Surfaces for H_a rotation. A section of the X $^1A'$ and A $^1A'$ potential energy surfaces of H_4 corresponding to a motion of H_a on the XZ plane from θ = -90 to θ = +90. a) Dotted line: A circular motion with r = 1.8 and R = 4.2 bohr. b) Chained dashed line: A circular motion with r = 1.7 and R = 3.8 bohr from the results of Ref. 1. c) Solid line: A curvilinear motion so that the energy of the A $^1A'$ state is minimized with respect to R. d) Solid circles and connecting dashed line: A curvilinear motion so that A $^1A'$ is minimized with respect to both r and R.

θ. Two more curves are shown in Fig. 3. One of them (dotted line) corresponds to a circular sweep of H_a in the same plane as above with r = 1.8 and R = 4.2 bohr. The other one (chained dashed line) corresponds to the same circular sweep of H_a but with r = 1.7, R = 3.8 bohr and using the small basis set employed in Ref. 1. The chained dashed line has been added for comparison.

By looking at Fig. 3 it is obvious that the effect of optimization becomes more and more pronounced as θ increases and it is maximum at θ = 90°.

It is also very interesting to see how rapidly the ground state varies as a function of R (and r) since it is extremely affected by the optimization with respect to the first excited state. The effect of (r,R) optimization is smaller than that of R optimization and it again increases as θ increases. Note that if the optimum values of R (and r for the r optimized points) vary from the values shown in Fig. 3, the potential energy increases. Thus, one concludes that the r = 1.8, R = 4.2, $\theta = 0^{\circ}$ position of H_a is a true equilibrium position (momentarily disregarding a possible diabatic crossing to X $^1A'$) since the potential energy goes up for any movement of H_a away from it. Thus, only a high vibrational excitation to the dissociation limit or a diabatic crossing to the ground state may result in dissociation of H_4 (C_{3v}) to H_3 (D_{3h}) + H.

Correlations to $H_2 + H_2$

Here, we set out to show that if one starts with two H_2 molecules at infinite separation and brings them together in the trigonal pyramidal geometry which we have already discussed, the pairs $(X^1\Sigma_g^+ X^1\Sigma_g^+)$ and $(X^1\Sigma_g^+ B^1\Sigma_u^+)$ correlate to the first two $^1A'$ states of $H_4(C_{3v})$. We begin with two H_2 molecules at a large separation (20-30 bohr) approaching each other in a T geometrical arrangement (C_{2v} symmetry). Their large separation allows us to assume that initially the H_2 corresponding to the "horizontal" bar of T is in the $X^1\Sigma_g^+$ state while the "vertical" H_2 may be either in the $X^1\Sigma_g^+$ state or in the $B^1\Sigma_u^+$ state.

When they have approached closely enough, the two H_2 molecules are stretched so that three H atoms form an equilateral triangle with r = 1.8 bohr while the fourth H atom (H_a) has a distance R = 4.2 bohr from the center of the triangle. Now, H_a is moved upward circularly until it positions itself vertically above the center of the triangle. During the circular motion of H_a, a C_s symmetry is maintained ($\sigma = \sigma_v$) until a trigonal pyramidal geometry with C_{3v} symmetry is reached. This is exactly the opposite motion of H_a from that followed in the first set of calculations and it corresponds to a change of θ from -90° to 0°.

The purpose of the above calculations is to check the energetics of the following correlations which arise under the conditions previously mentioned:

$$(X\ ^1\Sigma_g^+)(X\ ^1\Sigma_g^+) \dashrightarrow X\ ^1A_1\ (C_{2v}) \dashrightarrow X\ ^1A'\ (C_s)$$
$$(X\ ^1\Sigma_g^+)(B\ ^1\Sigma_g^+) \dashrightarrow A\ ^1A_1\ (C_{2v}) \dashrightarrow A\ ^1A'\ (C_s).$$

One starts with reference vectors corresponding to the ground and first excited $^1A_1$ states of the C_{2v} structure at large separations. The interatomic distances of the H_2 molecules are selected to be the equilibrium distances of the $X\ ^1\Sigma_g^+$ and $B\ ^1\Sigma_u^+$ states and a third distance between them (they could be at any other reasonable distance). To ensure similar conditions, the $X\ ^1\Sigma_g^+$ and $B\ ^1\Sigma_u^+$ energies of H_2 at the selected interatomic distances were recalculated with the MRD-CI method, using the larger basis set employed for H_4. The results of both calculations are shown in Table 2. By comparing the first two $^1A_1$ energies with the computed energies of $X\ ^1\Sigma_g^+ + X\ ^1\Sigma_g^+$ and $X\ ^1\Sigma_g^+ + B\ ^1\Sigma_u^+$ of the two H_2 constituents it is found that they are identical within the accuracy of the method. Thus, one is now assured of the first part of the above correlations. Now, as the $\theta = -90^o$, $r = 1.8$ and $R = 4.2$ geometry is approached and then continues into the C_s and C_{3v} geometries, more and more reference vectors are added while others are no longer important and may be removed. The important thing is that at $\theta = -90^o$, $\theta = -45^o$, and $\theta = 0^o$ the important reference configurations and, of course, the calculated energies are the same as those found starting directly with reference vectors corresponding to the $\theta = 0^o$ equilibrium C_{3v} geometry and moving downwards to the $\theta = -90^o$, $r = 1.8$, $R = 4.2$ geometry. Thus, the second part of the above correlations is also established.

CONCLUSION

By using a larger basis set than previous calculations (Ref. 1) and by optimizing some variables (r and/or R) to minimize the energy of the first excited $^1A'$ state of $H_4(C_{3v})$, we have improved the previous results and have estimated the effect of optimization. We have also computed the diabatic matrix elements of the vibronic interaction near the avoided crossing and have found that they are significant only within a narrow region. Moreover, by starting with two H_2 molecules at a large distance and proceeding to the C_{3v}

Table 2. Comparison of Potential Energies of 2 H_2 molecules and the H_4 molecule.

	1 ρ(a.u.)			2 H_4 (r = 1.8, R = 4.2 a.u.)		
Geometry	1.4	1.5	2.43	C_{2v}	Cs*	Cs+
$X^1\Sigma_g^+ + X^1\Sigma_g^+$	-2.3400	-2.3375	-2.1942	-2.1418	-2.1139	-2.0619
$X\ ^1A_1$	-2.3393	-2.3369	-2.1947	-2.1421	-2.1137	-2.0620
$X^1\Sigma_g^+ + B^1\Sigma_u^+$	-1.8735	-1.8867	-1.8513	-1.9875	-2.0084	-2.0612
$A\ ^1A_1$	-1.8730	-1.8863	-1.8506	-1.9882	-2.0080	-2.0615
$H_2\ (X^1\Sigma_g^+)$	-1.1699	-1.16874	-1.09711			
$H_2\ (B^1\Sigma_u^+)$	-0.70350	-0.71799	-0.75424			

*θ= 45 deg (Cs) + θ = 0 deg (c_{3v})

Comparison between 1) the sums of the potential energies of two hydrogen molecules at infinite separation and a T shaped C_{2v} H_2-H_2 complex at large intermolecular separations (1st three columns) and 2) the potential energies of H_4^* computed with reference configurations initially corresponding to H_2-H_2 (C_{2v}) and H_4^* (C_{3v}/Cs) (last three columns). The MRDIC potential energies of the H_2 molecules are also given. For the Cs symmetries, $^1A_1$ should be replaced with $^1A'$; r,R and θ have the meaning given in the text; ρ is the bond length of an H_2 diatom.

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geometry of H_4 we have shown that the first $^1A'$ state of H_4 correlates to the $X\ ^1\ _g^+$ ground state of the two separated H_2 molecules. The first excited $^1A'$ state is found to correlate to the ($X\ ^1\Sigma g$, $B\ ^1\Sigma u$) state of two H_2 molecules.

RECENT DEVELOPMENTS

During the summer of 1986, one of the authors traveled to the Ballistic Research Laboratory (BRL) at Aberdeen Proving Ground, MD to become familiar with the geometry optimization and vibronic coupling programs of Dr Byron H. Lengsfield III. This trip was sponsored by the U. S. Air Force, but was only partially successful due to the limited time spent at BRL and due to hardware difficulties existing there at the time.

While discussing the H_4 project with Dr Lengsfield, it became evident that the $^1A'$ state in the C_{3v} geometry is really a component of an ^1E state and that as a consequence, we are faced with a pseudo Jahn-Teller distortion. This means that the avoided crossing would occur not at a C_{3v} symmetry but probably at a C_s symmetry. Preliminary calculations to investigate this possibility were performed on the return of Dr Metropoulos from BRL and covered a period from early September to late October 1986.

These calculations were performed at C_1 symmetry and at a threshold of 2 μH. It was found that there is indeed a ^1E state crossing the X $^1A_1$ state at R = 4.22 bohr and at an energy of approximately -2.06173 a.u. It was also found that upon distortion of the triangular base to a C_{2v} geometry, a true avoided crossing exists between the $^1A'$ component of the old ^1E state and the X $^1A'$ state at an energy lower by about 72 meV relative to the C_{3v} crossing point. This new minimum occurs at R = 4.22 bohr and for an isosceles triangular base which has one side equal to 1.65 bohr and the other two sides equal to 1.80 bohr. Further calculations to optimize this structure are underway.

The most recent results (January 1987) show that the optimum geometry occurs at R = 3.90 bohr and for an isosceles triangular base which has one side equal to 1.62 bohr and the other two sides equal to 1.78 bohr; the energy at the minimum is -2.06739 a.u., which is about 154 meV lower than the C_{3v} crossing point.

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