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Global nine-dimensional potential energy surface for the H₅ system.

I. *Ab initio* multiple reference single and double excitation configuration interaction computations

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The ground-state adiabatic potential energy surface was computed for 2836 conformations of H₅, using a multiple reference single and double excitation configuration interaction program and an extended basis set. The transition state obtained is that of a pentagon with *D*_{5h} symmetry. We find the energy barrier to lie at 81 kcal/mol within ± 1 kcal/mol if a multireference Davidson's correction is employed, while the *D*_e(H₂) at this level was 109 kcal/mol. The calculations presented here clearly show the energy of H₅ in *D*_{5h} symmetry to be 28 kcal/mol below the dissociation energy of H₂, and therefore a bimolecular mechanism, in the presence of hydrogen atoms, could indeed be considered for the exchange process: H₂+D₂+H→2HD+H. © 1999 American Institute of Physics. [S0021-9606(99)30716-9]

I. INTRODUCTION

The solution of a kinetic problem consists of four parts: calculation of an accurate *ab initio* potential energy surface (PES), fit of the *ab initio* data to a global (3*N*-6)-dimensional functional form—*N* being the number of atoms, quantum scattering calculations that provide a good description of the nuclear dynamics in chemical reactions, and a statistical analysis of the behavior of a macroscopic sample derived from the results of the previous step for comparison with experimental results.

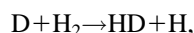
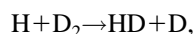
The application of the quantum theory to reactions in triatomic systems has made great progress starting from the H₃ system¹ and based on accurate three-dimensional (3D) PES fits.^{2,3} Recently, a remarkable interest in reactions involving four atoms has been addressed.⁴ A special kind of four-atom reaction, namely, the general exchange four-center (4C) reactions,



has been recently studied⁵ for the particular case of A₂+B₂→2AB, and collision induced dissociation (CID) A₂+B₂→A+B₂+A, being A≡H and B≡H, i.e., the H₄ system. These quantum scattering calculations are based on an accurate global six-dimensional (6D) PES fit for the H₄ system.⁵ In this study⁶ the authors conclude that the 4C reaction is a non-negligible process occurring in the high-energy H₂+H₂ collision dynamics, although the CID process is more important. Nevertheless, their results are based on 3D quantum scattering calculations that may change for full dimensional four-body dynamics.

The gas phase exchange reaction between hydrogen and deuterium has been studied in the past several decades in numerous experiments.⁷ This reaction has been the subject of great controversy on its mechanism.⁸ Large discrepancies exist between experimentally derived activation energies (about 40 kcal/mol⁷ or a lower bound of 70 kcal/mol⁹ on the

bimolecular energy barrier or 45 kcal/mol⁹ on the termolecular energy barrier) and very accurate theoretical calculations of barrier heights on the H₄ PES (about 110 kcal/mol^{10,11}). The role of low levels of impurities is a very important experimental problem. Burcat and Lifshitz¹² found that with impure HD the total order of the reaction 2HD→H₂+D₂ declined from 2 to approximately 3/2 and the measured activation energy rose by about 10 kcal. Experiments carried out with an ultraclean shock tube, under the conditions where no H atoms are present, found that no HD products of the reaction H₂+D₂→2HD are obtained.⁸ Lifshitz *et al.* consider that this reaction is strongly catalyzed by H atoms, that are present in the experiments formed from the absorbed pump oil impurities from the shock tube walls.⁸ They have proposed the following chain reaction mechanism for the homogeneous H atom catalysis:



involving five (H+D₂+H₂) atoms. They conclude that the formation of a 4C transition state is highly doubtful.⁸ A comparison between the ultraclean shock tube results⁸ and results obtained previously in conventional systems suggests that the high HD conversion observed in the past was caused by hydrogen atoms generated from impurities.⁸ Rabinowitz and Gardiner⁹ studied the isotope exchange reaction between hydrogen and deuterium in incident (and reflected) shock waves by vacuum ultraviolet absorption spectroscopy in order to get real time product formation rates far from the shock tube walls (to avoid the H-atom contamination due to impurities). They conclude⁹ that the isotope exchange reaction between H₂ and D₂, observed in single pulse and mass spectrometric studies, is confirmed to be attributable to atom chain reactions rather than molecular processes. They also gave⁹ lower bounds on the bimolecular and termolecular energy barriers of 70 and 45 kcal, respectively.

From a theoretical point of view the study of the chain reaction mechanism for the homogeneous H atom catalysis is possible using several accurate H_3 PESs (see Boothroyd *et al.*¹³ for a review on these PESs). However, the theoretical treatment of the proposed mechanisms, such as 4C or chain reaction, as well as other alternatives, such as a 4C mechanism in the presence of hydrogen atoms or the CID process in the presence of hydrogen atoms and many others, could be carried out if a global nine-dimensional (9D) PES for the H_5 system is available. Obviously, such a PES includes as particular cases the PES of smaller systems (H_4 , H_3 , and H_2). This last condition may be fulfilled by following the fitting procedure proposed by some of the authors for the H_4 system.⁵ Moreover, Wright¹⁴ in 1970, based on hexagonal H_6 calculations, suggested a molecular six-center exchange mechanism, the so-called termolecular reaction of $3H_2$. This mechanism has been proposed in two forms, either as a concerted trimolecular reaction^{14,15} or as a two-step bimolecular reaction.

The concerted trimolecular path has two drawbacks:¹⁴ very low reaction probability would be expected involving simultaneous trimolecular collisions, and it does not explain the observed effect of argon on the experimental reaction rate. However, the concerted trimolecular presents the advantage of a lower barrier to reaction.¹⁶

The two-step pathway proposed¹⁴ would be the formation of linear H_4 in a first step, which must then remain bound long enough to allow the approach of another H_2 (or D_2), followed by distortion to form the hexagonal H_6 , and decomposition of the hexagon to form $3H_2$ (or $H_2 + 2HD$). The first step of this two-step mechanism may be supported by recent molecular beam scattering experiments,¹⁷ that have shown that $H_2 \cdots H_2$ dimers have a substantially large survival probability, even at collision energies that correspond nearly to room temperature. This is a somewhat surprising result taking into account the very small binding energy of these dimers.

The complete study of the $3H_2$ exchange reaction, both for concerted trimolecular or two-step bimolecular mechanisms, requires the accurate *ab initio* calculation of the H_6 PES and the corresponding fit of the *ab initio* data to a global twelve-dimensional (12D) PES for the H_6 system, that requires also as particular cases the PES of smaller systems (H_5 , H_4 , H_3 , and H_2). This is a huge task that would be accessible in the future; our aim in the present paper is to deal with the accurate *ab initio* calculations of the H_5 PES, the first step of the kinetic problem. In Paper II of this series, we produce, based on the present calculations, the—to the best of our knowledge—first global fit to a 9D PES of a penta-atomic system up to date. This H_5 global 9D PES would be needed in the future to build a global 12D PES for the H_6 system.

We report here the results of an extensive *ab initio* study of a full-dimensional grid for the H_5 system (nine degrees of freedom). In our calculations we analyze several types of configurations, from those of greater symmetry to those with a total lack of symmetry.

II. COMPUTATIONAL METHODS AND PROCEDURES

Despite the fact that there are nine independent degrees of freedom allowed in the placement of nuclear centers for a five-atom system, symmetry constraints can reduce this number. The calculations include several structures of nuclear configurations with symmetry constraints. The most accessible geometries to study are those which maintain the highest symmetries having only one degree of freedom—pentagon, centered square, tetrahedron, and bitetrahedron. Nuclear configurations with two degrees of freedom are the square pyramid, centered rhombus, centered rectangle, bipyramid, distorted tetrahedron, and linear with inversion center. Geometries with three or more degrees of freedom are the rectangular pyramid, linear without inversion center, regular centered trapezium, as well as random points with a mirror plane (six degrees of freedom), and totally random geometries (nine degrees of freedom).

The choice of an appropriate basis set can be determinant to achieve a good precision in the calculations. The basis set should be as large and flexible as possible, in order to minimize the errors due to the basis set incompleteness. We have adopted the same basis set that has been used in previous studies of the H_3 PES by Liu and Siegbahn¹⁸ and by Boothroyd *et al.*,¹³ H_4^+ PES by Alvarez-Collado *et al.*,²³ and H_4 PES by Boothroyd *et al.*¹¹ This basis set consists of nine Gaussian *s*-type functions optimized to describe the hydrogen atom; the six innermost are contracted, given a total of four *s* functions by atom; three *p* functions optimized in complete configuration interaction (CI) calculations on the hydrogen molecule at its equilibrium distance; and two optimized *d* functions to give finally the (4*s*,3*p*,2*d*) basis set. The total size of this basis set is of 125 atomic orbitals.

The electronic energy for the lower three doublet spin state for H_5 has been calculated using the multiple reference single and double excitation configuration interaction (MRDCI) method of Buenker and co-workers.¹⁹ All the calculations were carried out by ignoring the symmetry of the possible nuclear configurations (C_1 group). We have calculated many of these points with higher symmetry operations by taking into account the symmetry group (or subgroup) to ensure that the ground state is obtained in each case.

All 125 molecular orbitals, obtained by a self-consistent field (SCF) procedure, are used in the CI step. The CI space of each irreducible representation was constructed using the reference configurations shown in Table I. In the calculations, a threshold of about 1–5 μ hartree was chosen, and the lowest three eigenvalues were calculated in all cases. With these choices, the number of total generated spin adapted functions (SAFT) ranges from 272 336 to 2 943 519, depending on the symmetry (see Table I), out of which between 5 656 and 23 344 were selected for the final CI calculation. Defining $C_R^2 = \sum_r C_r^2$ as the sum of the squares of the coefficients of all the reference configurations, our calculations of the H_5 PES have $0.93 \leq C_R^2 \leq 0.96$. To obtain these results in all the points it is necessary, in certain geometries, to use a higher number of reference configurations.

Extrapolation of the energy to zero threshold gives the MRDCI energy. Finally, we use the multireference analog²⁰

TABLE I. Distribution and properties of the calculated points.

Conformations	Group	Points	Number of RCs	Number of SAFTs
Tetrahedron	T_d	17	81	700 591
Pentagon	D_{5h}	17	73	918 086
Centered square	D_{4h}	17	60	1 059 480
Bitetrahedron	D_{3h}	17	69	765 775
Bipyramid	D_{3h}	142	69	483 715
Centered rhombus	D_{2h}	55	58	272 336
Centered rectangle	D_{2h}	57	79	347 594
Square pyramid	C_{4v}	52	60	474 776
Body triangular pyramid	$D_{3h}(C_1)$	36	83	2 943 519
Distorted tetrahedron	C_{2v}	35	76	2 867 313
Trapezium	C_{2v}	43	79	679 995
Rectangular pyramid	C_{2v}	51	56	474 776
Random (C_s)	C_s	663	188	1 012 308
Random (C_1)	C_1	1634	83	2 943 519
Total	C_1	2836	83	2 943 519

of the Davidson correction²¹ to obtain the full CI extrapolated energy that we use as final energy.

With the number of calculated points, i.e., 2836, that include all the possible degrees of freedom, we could achieve an analysis of a huge quantity of possibilities that can be present in the H_5 system. For a system with so many degrees of freedom, this analysis can be cumbersome in many cases, with excessively complex conclusions that darken the physical interpretation of the results. Therefore, in the following sections we will analyze those cases in which the conclusions appear clearly, and are not masked by the great number of degrees of freedom of the system.

A. Geometries with one degree of freedom

The spatial arrangement of the first symmetry structure is a centered tetrahedron (see the top panel in Fig. 1). We have selected the only degree of freedom as the distance between the central hydrogen and a vertex. In the bottom panel of Fig. 1 we plot the ground state energy versus the degree of freedom, which presents a minimum at $E = -2.5874$ hartree for $R = 2.3a_0$. For the sake of clarity, we plot in this, and in other figures, some interesting asymptotic limits of the H_5 system, i.e., 5H (corresponding to the five separated atoms or -2.5 hartree), $H+H_4$ (squared configuration local minimum), $2H+H_3$ (linear configuration transition state), $H+H_4$ (linear configuration saddle point), $3H+H_2$, H_2+H_3 (linear configuration transition state), and $H+2H_2$ (the reactants and products asymptote in the exchange reaction). We select as zero energy that corresponding to the reactants asymptote (-2.8489 hartree). In all the figures energies are given in kcal/mol with respect to the reactants asymptote (0 kcal/mol). Then, the minimum of the centered tetrahedron structure is 164 kcal/mol above the reactants. The number of calculated points with centered tetrahedron structure is 17, as is shown in Table I.

The configuration corresponding to five nuclei located in the vertices of a regular pentagon is given in Fig. 2. It is a conformation with one degree of freedom, which we have selected as the distance between two contiguous nuclei (R in Fig. 2). The curve of Fig. 2 plots the ground state energy

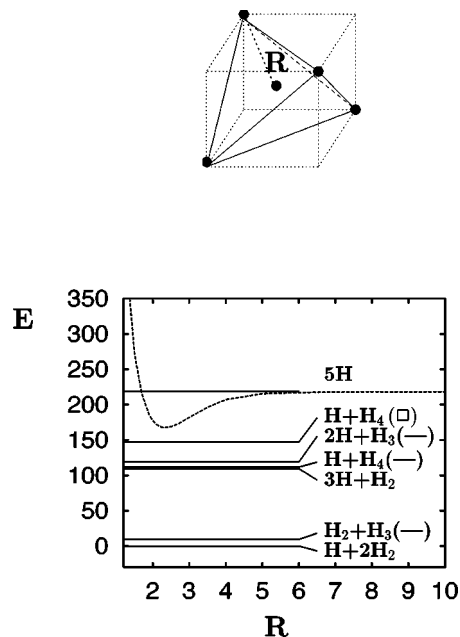


FIG. 1. Potential energy of tetrahedral H_5 as a function of the distance R (see the top). Several asymptotic energies have been indicated by horizontal lines, $H_3(-)$ means H_3 in its linear configuration transition state, $H_4(-)$ means H_4 in its linear configuration saddle point and $H_4(\square)$ means H_4 in its squared configuration local minimum. Energies are given in kcal/mol and distances in atomic units.

with respect to this degree of freedom. This conformation presents an energy minimum at $E = -2.7201$ hartree for $R = 2.1a_0$ (about 81 kcal/mol above the reactants). The calculation of this H_5 regular pentagonal structure was carried out by Varandas *et al.*²² at SCFMO (restricted Hartree-Fock) level, who found an optimum structure with the same length $R = 2.1a_0$, but with an energy of $E = -2.550$ hartree, prob-

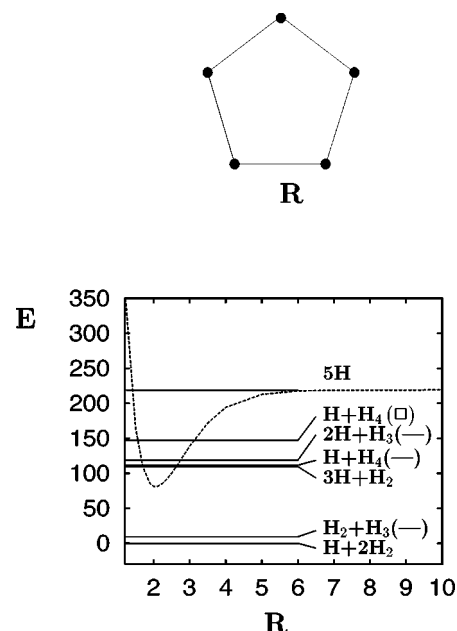


FIG. 2. Potential energy of pentagonal H_5 as a function of the distance R (see the top). Several asymptotic energies have been indicated by horizontal lines as in Fig. 1. Energies are given in kcal/mol and distances in atomic units.

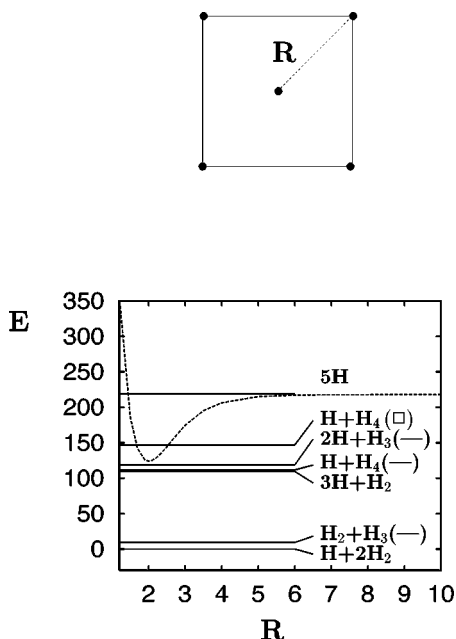


FIG. 3. Potential energy of centered square H_5 as a function of the distance R (see the top). Several asymptotic energies have been indicated by horizontal lines as in Fig. 1. Energies are given in kcal/mol and distances in atomic units.

ably due to the use of only one configuration in their calculations. This minimum is the lowest one of all the calculations presented in this paper, except for the asymptotic limits $2H_2+H$ and H_2+H_3 . The number of calculated points for this symmetry structure is 17, as is shown in Table I.

The nuclear configuration of the centered square symmetry structure is shown in Fig. 3, where there is a nucleus located in each vertex of the square and the remaining one is located in the symmetry center. The symmetry group of this nuclear configuration is D_{4h} . This is a conformation with one degree of freedom, which we have selected as the distance between the central nucleus and a vertex. As shown in Table I, the number of calculated points for this geometry is 17. In Fig. 3 we plot the ground state energy of this conformation with respect to this degree of freedom. The curve presents a minimum for $R=2.0a_0$ with $E=-2.6528$ hartree (about 123 kcal/mol above the reactants).

The spatial arrangement of the bitetrahedron symmetry structure is like two united tetrahedrons, as is shown in Fig. 4, with the five nuclei located in the vertices. This conformation has one degree of freedom, which we have selected as the distance between two contiguous nuclei. The curve of Fig. 4 plots the ground state energy with respect to this degree of freedom. It presents an energy minimum at $E=-2.5733$ hartree for $R=2.5a_0$ (about 173 kcal/mol above the reactants). The number of calculated points for this symmetry structure is 17, as shown in Table I.

B. Geometries with two degrees of freedom

The corresponding nuclear configuration for the bipyramidal arrangement is shown in Fig. 5, where we define the two independent coordinates. For these conformations we have calculated 142 points (see Table I). When the two indepen-

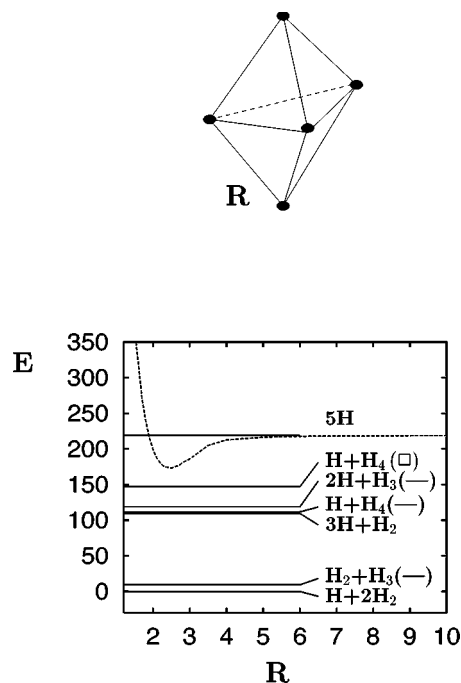


FIG. 4. Potential energy of bitetrahedral H_5 as a function of the distance R (see the top). Several asymptotic energies have been indicated by horizontal lines as in Fig. 1. Energies are given in kcal/mol and distances in atomic units.

dent coordinates coincide: $R_1=R_2$, we have the bitetrahedron symmetry structure (Fig. 4). In the bottom panel of Fig. 5 we plot the contour levels for this arrangement using cubic splines as for the remaining figures in this section. In this case the asymptotic limit for $R_1 \gg R_2$ corresponds to H_2+3H , and for $R_1 \ll R_2$ corresponds to $2H+H_3$, where the H_3 is an equilateral triangle arrangement.

The corresponding nuclear configuration to the centered rhombus symmetry structure is shown in Fig. 6. In the top

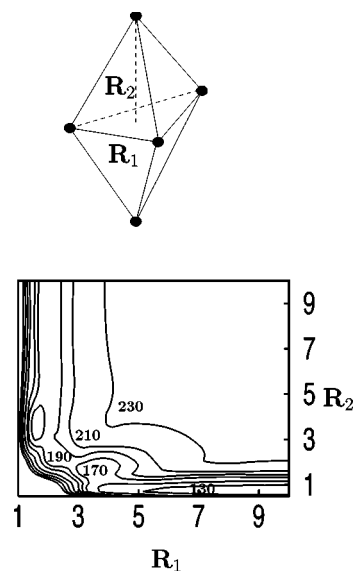


FIG. 5. Potential contours for bipyramidal H_5 as a function of the distances R_1 and R_2 (see the top). Contour labels are in kcal/mol with respect to the selected zero energy (reactants), all the distances are in atomic units.

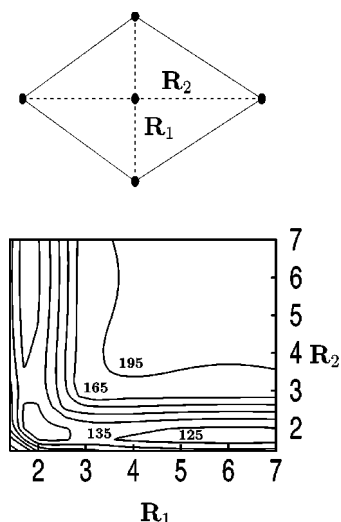


FIG. 6. Potential contours for centered rhombus H_5 as a function of the distances R_1 and R_2 (see the top). Contour labels are in kcal/mol with respect to the selected zero energy (reactants), all the distances are in atomic units.

panel of Fig. 6 the two degrees of freedom selected for this geometry are plotted. The number of calculated points for this geometry is 55 (see Table I). In the bottom panel of Fig. 6 we plot the two-dimensional contour levels for the ground state energy. The asymptotic limit when one of the two degrees of freedom is much greater than the other corresponds to $2H+H_3$, where the configuration of the H_3 consists of three hydrogen atoms placed in linear form with the equal internuclear distances. The configuration for $R_1=R_2$ corresponds to the centered square, which is slightly less stable than the configuration corresponding to the $2H+H_3$ asymptotic limit (see also Fig. 3).

In Fig. 7 we present the nuclear configuration for the centered rectangle symmetry structure. In Fig. 7 the two selected degrees of freedom have been plotted too. The number of calculated points for this geometry is 57 (see Table I). The bottom panel of Fig. 7 plots the contour levels of the H_5

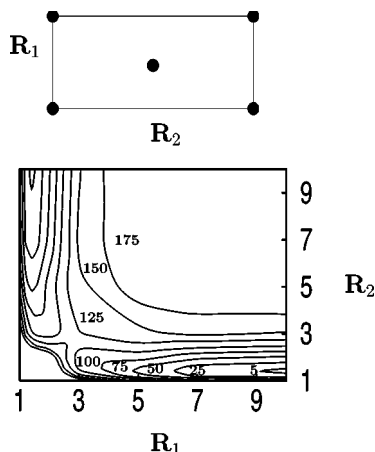


FIG. 7. Potential contours for centered rectangle H_5 as a function of the distances R_1 and R_2 (see the top). Contour labels are in kcal/mol with respect to the selected zero energy (reactants), all the distances are in atomic units.

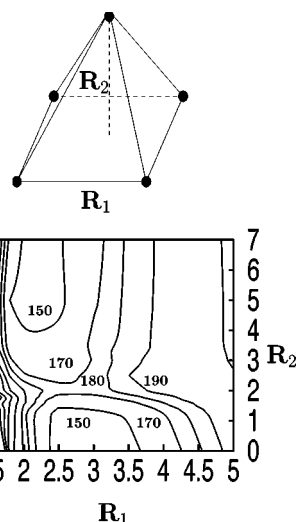


FIG. 8. Potential contours for squared pyramidal H_5 as a function of the distances R_1 and R_2 (see the top). Contour labels are in kcal/mol with respect to the selected zero energy (reactants), all the distances are in atomic units.

potential for the ground state energy. The asymptotic limit when one of the two degrees of freedom is much greater than the other one corresponds to $H+2H_2$. As in the centered rhombus, the configuration for $R_1=R_2$ corresponds to the centered square, this is a saddle point that connects the $H+2H_2$ corresponding channels. This saddle point is more stable than that corresponding to the rectangular arrangements of the H_4 system,⁵ as shown in Fig. 3.

The distances between the atoms of the squared pyramid located at the pyramid base are different from the distances corresponding to vertex atom—base atoms (see Fig. 8). Therefore, it is a conformation with two degrees of freedom. One of them (R_1) has been selected as the distance between two contiguous base atoms. The other one (R_2) have been taken as the shortest distance between the pyramid vertex atom and the pyramid base. The number of calculated points for this geometry is 52 (see Table I). The bottom panel of Fig. 8 plots two-dimensional contour levels for the ground state energy. The limit for $R_2 \gg R_1$ corresponds to $H+H_4$, where the configuration of the H_4 consists of four hydrogens in the vertices of a square. The asymptotic limit for $R_1 \gg R_2$ corresponds to $5H$. As it is shown in Fig. 8, at short distances a minimum appears corresponding to the centered square configuration (with $R_1=2.83a_0$, $R_2=0.0a_0$, and with an energy of $E=-2.6528$ hartree). This energy is lower than that corresponding to the asymptotic limit $H+H_4$, i.e., the insertion of a hydrogen atom makes the H_5 system more stable than the squared H_4 . In the path from one limit to the other one there is a saddle point, as can be observed in Fig. 8, at $R_1=2.54a_0$, $R_2=2.02a_0$, and with an energy of $E=-2.5706$ hartree.

The corresponding nuclear configuration to the distorted tetrahedron symmetry structure is considered in Fig. 9, where $R_{C.M.}$ (the distance between the lines defining R_1 and R_2 , see Fig. 9) is fixed at $3a_0$. Therefore, a particular case of the trapezoid (4D) is considered, but with only two degrees of freedom. The number of calculated points for this

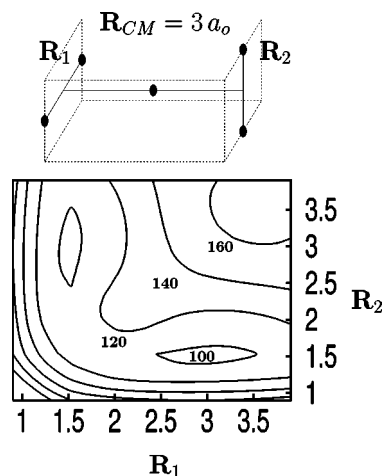


FIG. 9. Potential contours for distorted tetrahedral H_5 as a function of the distances R_1 and R_2 (see the top). Contour labels are in kcal/mol with respect to the selected zero energy (reactants), all the distances are in atomic units.

geometry is 25 for $R_{CM} = 3a_0$ and 10 for $R_{CM} = 4a_0$. In the bottom panel of Fig. 9 we plot the contour levels for the ground state energy with respect to the distances between two hydrogen molecules (R_1 and R_2). The asymptotic limit when one of the two degrees of freedom is much greater than the other corresponds to $2H + H_3$. The nuclei of H_3 in this asymptotic limit form an isosceles triangle. When the two distances are $R_1 = R_2 = 1.69a_0$ there is a saddle point with an energy of $E = -2.6740$ hartree (about 110 kcal/mol above the reactants).

C. Geometries with more than two degrees of freedom

Some of the conformations with symmetry structures such as body triangular pyramid, trapezium, rectangular pyramid, and random geometries with or without a symmetry plane (C_s or C_1), have more than two degrees of freedom. In these cases, except for random geometries, we have also generated small n -dimensional grids (being n the number of degrees of freedom) around the corresponding equilibrium geometries. Two or three points by degree of freedom were selected to form the grids giving a total of 2^n to 3^n calculated points. Moreover, in those regions with a greater energy change we computed additional points (see Table I for the number of calculated points at each symmetry structure).

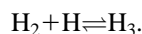
For those conformations corresponding to symmetry structures with only one symmetry plane (C_s) or without symmetry elements except for identity operation (C_1), the degrees of freedom is so high that we generated random geometries for the calculations. Due to the high number of degrees of freedom the number of calculated points must be much higher than those obtained for conformations with less than three degrees of freedom (see Table I).

III. DISCUSSION

A very important difference between the calculations carried out here on the H_5 system and those corresponding to the H_4 system^{10,11} is that in H_5 system we have covered

geometries through which there exists a reaction path for exchange requiring less than the dissociation energy of one H_2 molecule (about 109 kcal/mol) assuming that one hydrogen atom is present together with the two H_2 reactant molecules as has been stated experimentally.^{8,9} The transition state corresponding to this path is a pentagonal H_5 . Taking into account the results of the present study, a possible mechanism for the $H_2 + D_2$ exchange reaction in the presence of hydrogen atoms may be proposed as a two-step bimolecular pathway in a form similar to that of the proposed mechanisms¹⁴ of the so-called termolecular reaction of $2H_2 + D_2$, with hexagonal H_6 ^{15,16} as the transition state.

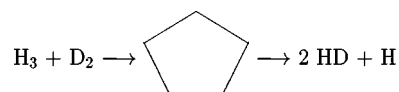
We propose a mechanism involving two steps. The first step would be the formation of H_3 :



The discovery of emission spectra of metastable Rydberg states of D_3 and H_3 by Herzberg *et al.*²⁴ would support this step. Although the H_3 molecule does not exist in its ground state the H_3^+ molecular ion is a stable species with a well-known structure.²⁵ H_3^+ can combine with electrons to form short-lived excited states of H_3 .

Furthermore, recent molecular beam scattering experiments have shown that $(H_2)_2$ dimers have a substantially large survival probability even at collision energies that correspond nearly to room temperature.¹⁷ This result is somewhat surprising because the binding energy of $(H_2)_2$ van der Waals dimer is very small. Collisions of weakly bound quantum clusters with atoms and molecules were studied by time-dependent calculations²⁶ and substantial survival probabilities of the clusters were found, even for collision energies which exceed the cluster binding energy by orders of magnitude. This situation may be very similar for $H_2 \cdots H$ with a very small binding energy of about $75 \pm 3 \mu E_h$.²⁷ Moreover, the argon diluent did play a significant role in shock tube experiments,⁷ that was first interpreted as the participation of the argon in vibrationally exciting the exchange partners⁷ and second, interpreted as to its hydrocarbon impurities and its function in stripping off the absorbed pump oil impurities from the shock tube walls with subsequent production of hydrogen atoms.⁸ In the proposed first-step pathway we expect that argon would play an important role both for recombination of hydrogen atoms to form H_2 and for direct association or enhancing the H atoms production.

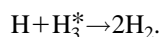
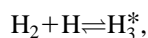
The second step is the rate-determining process due to the first step is considered to be in rapid equilibrium and energetically favored. The H_3 formed in the first step must remain bound long enough to allow the approach of D_2 molecule, followed by distortion to form the pentagon as transition state:



Here, the transition state energy is about 81 kcal/mol above the reactants ($H + 2H_2$), this barrier is already above that for the termolecular reaction $3H_2 \rightarrow (H_6) \rightarrow 3H_2$, with a hexagonal transition state that lies at 66.5 kcal/mol above the reactants ($3H_2$).¹⁶ However, the low probability of simultaneous trimolecular collisions¹⁴ may compensate for this en-

ergy difference making more feasible the mechanism proposed here. Moreover, Dixon *et al.*¹⁵ estimate that, for shock tube studies, the termolecular exchange is several orders of magnitude too slow, which may be compensated for by the very high activation energy of the bimolecular reaction $2\text{H}_2 \rightarrow (\text{H}_4) \rightarrow 2\text{H}_2$, that is about 110 kcal/mol,^{10,11} but this value is 29 kcal/mol higher than that of the present results. Furthermore, the two-step bimolecular reaction $3\text{H}_2 \rightarrow (\text{H}_4) + \text{H}_2 \rightarrow (\text{H}_6) \rightarrow 3\text{H}_2$, proposed by Wright¹⁴ may be the most feasible taking into account both factors, collision probability and transition state energy.

Several processes are omitted from the present discussion, namely the possibility of direct association from the continuum as well as contributions to the recombination of hydrogen atoms to form H_2 in the presence of H_2 :²⁸ $\text{H} + \text{H} + \text{H}_2 \rightarrow 2\text{H}_2$ and other processes involving quasibound states, e.g., the chaperon mechanism



Estimates from Roberts *et al.* indicate that direct association from the nonresonant continuum relative to the association from the quasibound states will become more important as the temperature increases.²⁹ On the other hand, in these processes tunneling plays an important role because of the presence of hydrogen atoms. In addition, the formation and decay of the quasibound states can undergo large amounts of tunneling.

Unfortunately, a complete quantum dynamical study of the mechanisms mentioned above requires global full-dimensional potential energy surfaces for both H_5 and H_6 systems. In Paper II of this series we deal with the global 9D potential energy surface of the H_5 system. In the future we are planning a complete study of the global 12D potential energy surface of the H_6 system.

IV. CONCLUSIONS

The calculations presented here for the H_5 system cover all the possible degrees of freedom of the system (9D) with a total of 2836 calculated points of similar accuracy than those obtained previously for the H_4 system.^{10,11} The present calculations can be used for fitting a global 9D PES for the H_5 system valid for molecular dynamics studies. The next paper of this series is devoted to obtaining a fit of the data presented here by using a generalization of the corresponding procedure for tri- and tetra-atomic systems including the functional form previously proposed by some of the authors.⁵

Finally, a new reaction mechanism for exchange $\text{H}_2 + \text{D}_2$ in presence of hydrogen atoms is proposed based on the existence, in the present calculations, of a reaction path for

exchange requiring less than the dissociation energy of an H_2 molecule.

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