Theor Chim Acta (1988) 73: 201–206

Theoretica
Chimica Acta

Potential energy surface of the $(H_2)_2$ dimer: an MP2 study*

Bohdan Schneider[1], **Pavel Hobza**[2,]**, **and Rudolf Zahradník**[3]

[1] Research Institute for Pharmacy and Biochemistry, Kouřimská 17, CS-130 60 Prague 3, Czechoslovakia
[2] Institute of Hygiene and Epidemiology, Šrobárova 48, CS-100 42 Prague 10, Czechoslovakia
[3] J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, Máchova 7, CS-121 38 Prague 2, Czechoslovakia

(Received October 1/Accepted October 7, 1987)

Fifteen structures of the $(H_2)_2$ dimer have been investigated at the MP2/[4s3p] level. The SCF and MP2 (2nd order Møller-Plesser treatment) interaction energies have been corrected for the basis set superposition error. Only the T-shaped structure has been established as a minimum on the potential energy surface. Two equivalent T-shaped structures are connected by a saddle point with a rhomboid structure.

Key words: Hydrogen molecule dimer — MP2 stationary points — Potential energy surface

1. Introduction

The $(H_2)_2$ dimer is among the van der Waals (vdW) molecules that have been studied frequently both experimentally and theoretically. Rather numerous experimental data are available for $(H_2)_2$; however, the agreement of the experimental values originating from various laboratories is not always good. The most reliable data obtained so far suggest that the r_0 value (the distance at which the isotropic potential attains zero value) is about 298 ± 30 pm [1] and the ε_0 value

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

** *Present address*: Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Flemingovo n. 2, CS-16610 Prague 2, Czechoslovakia

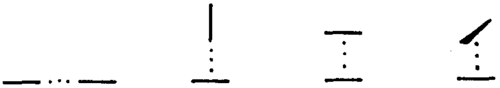

Fig. 1. Structures of the $(H_2)_2$ dimer

(the depth of the isotropic potential) amounts to 104.0 μH [2] or 110.1 μH [3]. Although the anisotropy of the intermolecular potential is not large, it needs to be known for correct interpretation of experimental data. The anisotropy cannot be obtained from experiments, and only a good-quality quantum-chemical calculation can provide this information. The $(H_2)_2$ vdW molecule has been the subject of theoretical studies for a number of years and the first non-empirical calculations were carried out in the early 1970s [4, 5]. The *T*-type structure occupies a special position among the four configurations most frequently studied (see Fig. 1): this structure is stabilized by the interaction of two quadrupoles associated with the hydrogen molecules, i.e. a stabilization should be found at the Hartree-Fock (HF) level. The stabilization of other structures comes exclusively from the electron correlation effects; hence, calculations beyond HF must be performed. Several papers have been devoted to the theoretical study of the dimer [6–13]; in nearly all these papers only the four structures proposed originally by Tapia and Bessis [4] were taken into consideration. Only in papers [12, 13] were more structures taken into account. To our knowledge, no attempt has been made to prove whether the structures suggested represent stationary points of the potential energy surface; if not, there would be no reason to prefer these structures over others, e.g. non-symmetrical structures. Furthermore, the nature of the stationary points (in the sense of minima or saddle points) has not yet been determined.

It is the aim of the present paper to investigate parts of the $(H_2)_2$ potential energy surface in detail, giving special attention to the determination of the nature of selected stationary points.

2. Calculations

The interaction energy (ΔE) of the dimer was evaluated as follows:

$$\Delta E = \Delta \mathrm{E}^{\mathrm{HF}} + \mathrm{BSSE}\,(\mathrm{HF}) + \Delta \mathrm{E}^{\mathrm{MP2}} + \mathrm{BSSE}\,(\mathrm{MP2}), \tag{1}$$

where $\Delta \mathrm{E}^{\mathrm{HF}}$ and $\Delta \mathrm{E}^{\mathrm{MP2}}$ are the HF interaction energy and correlation interaction energy determined at the MP2 level; BSSE (HF) and BSSE (MP2) are the basis set superposition errors at these two levels. It was shown previously [14] that the BSSE reaches significant values at both levels even when working with extended basis sets; it is therefore necessary to take the BSSE into account. Evidence of the necessity to take the full BSSE into account can be found in our recent paper [15]. For the $(H_2)_2$ dimer, the MP2 level covers a rather large portion of the correlation energy; for the *T*-shaped structure it is more than 80% [14]. One of the reasons for this relative success is the compensation at the MP4 level of contributions from triples on the one hand and singles, doubles and quadruples on the other [14]. For computational economy, we selected the [4*s*3*p*] basis set [14]; the exponents of the polarization functions amount to 1.0, 0.15 and 0.08.

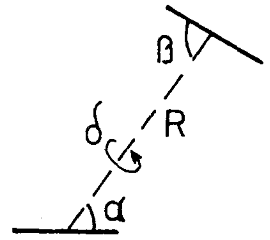

Fig. 2. Intersystem coordinates of the $(H_2)_2$ dimer

This basis set yields values of the interaction energy that are comparable with those obtained with extended basis sets containing d-functions (for details, see [14]).

The geometry of the complexes was optimized by the point-by-point method, first because of the necessity to optimize the corrected ΔE values (i.e. the values including BSSE at each point), and secondly because of the flatness of the potential energy surface. For the sake of comparison, the MP2 gradient optimization, implemented in the GAUSSIAN 82 program [16], was applied to selected stationary points.

3. Structure of the $(H_2)_2$ dimer

The intrasystem bond lengths were fixed at their experimental values (0.076678 nm [9]). In order to keep the number of structures at a reasonable level, we considered 45° steps for the angular coordinates, α, β and δ (see Fig. 2); the resulting 15 geometrically non-degenerate structures are depicted in Fig. 3. The intersystem distance was optimized for these structures.

4. Results and discussion

Stabilization energy

Table 1 collects the optimized intersystem distances and stabilization energies for all the 15 structures. The structures can be divided into three groups on the basis of the values of the interaction energy. The first group, with the stabilization energy between 15 μH and 35 μH, consists of structures 1, 10–14. The second group, including structures 2, 6–9 and 15 is characterized by stabilization energies in the range from 55 μH to 70 μH. Finally, the last group consists of the most stable structures, with stabilization energy ranging from 89 μH to 110 μH. Of the four originally proposed structures for the dimer (see Fig. 1), three belong to the energetically least favourable group.

The MP2 gradient optimization was applied to the energetically most favourable structures, 3 and 4; an intersystem distance of 6.59 and 6.61 a.u. respectively was obtained. These should be compared with 6.73 and 6.78 a.u. found for those structures by the point-by-point method (see Table 1). The optimization of the corrected MP2 interaction energy (BSSE included) results, as expected, in larger

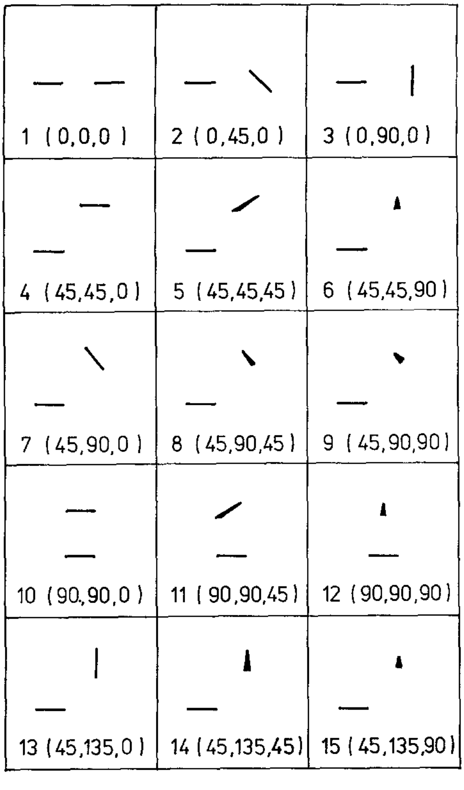

Fig. 3. Structures of the $(H_2)_2$ dimer under study. (The α, β and δ angles are specified in parentheses)

intersystem distances. For the linear structure 1, the MP2 gradient optimization repeatedly failed because of the flatness of the potential energy curve.

Nature of the stationary points

Determination of the nature of stationary points requires evaluation of the second derivatives of the potential energy with respect to all the internal coordinates;

Table 1. Optimized intersystem distances (R) and interaction energies (ΔE) for all the 15 structures of the $(H_2)_2$ dimer

Structure[a]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
R(a.u.)	7.69	7.09	6.73	6.78	6.83	7.02	7.02	6.83	6.93	7.58	7.33	7.22	7.62	7.32	7.05
$-\Delta E(\mu H)$	15.1	57.2	109.1	100.1	89.3	62.4	56.9	65.8	66.3	18.7	25.8	32.1	22.3	32.6	62.1

[a] See Fig. 3

the second derivatives represent the respective force constants. The Wilson FG (F and G stand for potential and kinetic energy matrices) analysis [17] leads to the eigenvalues and eigenvectors of the vibrational problem; the nature of the stationary point is deduced from the number of negative eigenvalues. Such a calculation for the system under study is tedious and time-consuming. We have tried, therefore, to develop a simpler procedure, which may rationalize the selection of stationary points.

Each stationary point for the dimer is characterized by three angular coordinates and the distance coordinate, which was optimized. If the change of any of the angular coordinates leads to an increase in the stabilization energy, the structure in question does not correspond to a minimum. Of all the structures studied, only two do not exhibit such an increase: the T-shaped structure, 3, and rhomboid structure, 4. Structures 5 and 9 possess just one stabilization energy increase; a change in the other coordinates leads to a decrease in the stabilization energy. These structures may, therefore, correspond to the saddle points. Finally, structures 1, 10 and 13 exhibit a stabilization energy increase upon changes of any angular internal coordinate. Clearly, these structures may correspond to the local maxima or saddle points of higher order on the $(H_2)_2$ energy hypersurface. This very simple analysis can be employed to reduce the number of candidates for the tedious FG analysis, but it is by no means a tool for a definite answer about the nature of stationary points.

For the two most attractive systems, 3 and 4, the force constant matrices were constructed and the FG problem solved. All eigenvalues belonging to structure 3 were positive, while structure 4 had one negative eigenvalue. This result permits us to visualize the transition of the saddle point, 4, into two equivalent minima, 3 (see Fig. 4); it would be possible to distinguish between the minima if HD molecules were used instead of H_2. In Fig. 4, relative energy values are plotted against relative changes in the α and β angles. Let us conclude by saying that

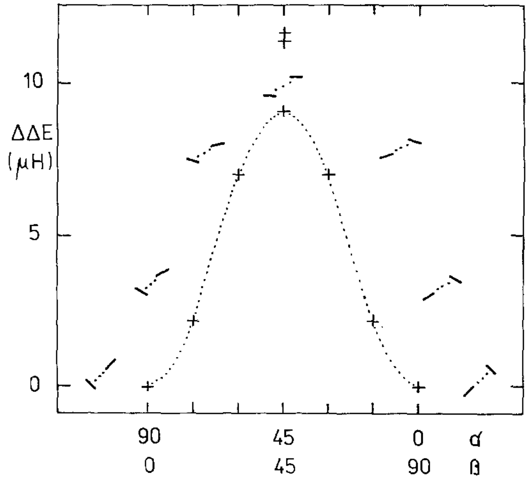

Fig. 4. The potential energy curve connecting the minima (the T-shaped structures) through the saddle point (≠) (rhomboid structure). Relative energy changes, $\Delta\Delta E$, plotted against the angular coordinates α, β (see Fig. 2).

the calculated stabilization energy for the T-structure of the dimer (109 μH) lies in the middle of the above-mentioned experimental values (104 μH and 110 μH). A deeper analysis concerning this comparison will be performed in a subsequent paper.

References

1. Buck U, Huisken F, Schleusener J, Schaefer J (1981) J Chem Phys 74:535
2. Schaefer J, Meyer W (1979) J Chem Phys 70:344
3. Buck U, Huisken F, Maneke G, Schaefer J (1983) J Chem Phys 78:4430
4. Tapia O, Bessis G (1972) Theor Chim Acta 25:130
5. Bender CF, Schaefer III HF (1972) J Chem Phys 57:217
6. Kochanski E (1973) J Chem Phys 58:5823
7. Kochanski E, Roos B, Siegbahn P, Wood MH (1973) Theor Chim Acta 32:151
8. Jaszuński M, Kochanski E, Siegbahn P (1977) Mol Phys 33:139
9. Burton PG, Senff UE (1982) J Chem Phys 76:6073
10. Burton PG (1983) Chem Phys Lett 100:51
11. Chałasiński G (1986) Mol Phys 57:427
12. Ree FH, Bender CF (1979) J Chem Phys 71:5362
13. Burton PG, Senff UE (1983) J Chem Phys 79:526
14. Hobza P, Schneider B, Sauer J, Čársky P, Zahradník R (1987) Chem Phys Lett 134:418
15. Hobza P, Sandorfy C (1987) J A Chem Soc 109:1302
16. Binkley JS, Frisch MJ, De Frees DJ, Raghavachari K, Whiteside RA, Schlegel HB, Fluder EM, Pople JA (1982) Program Gaussian 82 (release H version), Carnegie-Mellon-University, Pittsburgh, PA
17. Wilson EB, Decius JC, Cross PC (1955) Molecular vibrations. McGraw-Hill, New York