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Original Investigations

Clusters of Hydrogen Molecules: *Ab initio* SCF Calculations Corrected Semiempirically for Correlation Energies

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Stabilization energy of the $(H_2)_n$ clusters ($n = 2$–8) was calculated as a sum of the SCF interaction energy and the semiempirical interaction correlation energy estimated according to Sinanoğlu and Pamuk. Optimum successive attachment of hydrogen molecules leads to the formation of a gas-phase "solvation" shell consisting of seven hydrogen molecules. Basis set effect has been found to be important with all clusters under study. The non-additivity effect was investigated with the $(H_2)_4$ cluster. Vertical ionization potentials of the clusters considered are predicted to be 0.4–0.6 eV lower than the ionization potential of the parent H_2 molecule.

Key words: Hydrogen molecule clusters, correlation energy of ~

1. Introduction

Molecular and ionic-molecular clusters play a role in modelling liquid and solid phases and processes which take place in sources of mass spectrometers. Calculation of the stability of clusters is not an easy task. Ordinarily, the size of system prevents a direct use of the supermolecule approach. On the other hand, use of pair potentials is limited because of the many-body effect.

So far only clusters of polar molecules were investigated nonempirically [1–4]. This is due to the fact that the calculation of interaction energy with nonpolar systems is much more involved. With polar molecules the SCF interaction energy (ΔE^{SCF}) matches satisfactorily the total interaction energy (ΔE). With nonpolar molecules ΔE^{SCF} forms only a part of ΔE, which means that the interaction correlation energy (ΔE^{corr}) cannot be disregarded. However, the calculations by existing methods that recognize electron correlation are impractical, unless very small systems are treated. For the sake of feasibility we selected a semiempirical approach

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to ΔE^{corr}, viz. the method of Sinanoğlu and Pamuk [5, 6] and applied it to clusters containing 2–8 hydrogen molecules. The goal of our study was to predict the structure and the stability of these clusters.

2. Calculations

SCF calculations were performed with the Gaussian double-zeta (DZ) basis set (referred to as III in Ref. [7]). ΔE^{SCF} of the cluster composed of n hydrogen molecules were determined by means of the following equation:

$$\Delta E^{\mathrm{SCF}} = E^{\mathrm{SCF}} - nE^{\mathrm{SCF}}(\mathrm{H}_2), \tag{1}$$

where E^{SCF} is the total SCF energy of the cluster and $E^{\mathrm{SCF}}(\mathrm{H}_2)$ is the SCF energy of the H_2 molecule. The importance of the basis set effect was pointed out with the $(H_2)_2$ dimer [8]. To eliminate this effect at least in part, we calculated also the "corrected" SCF interaction energies by means of the expression

$$\Delta E_{\mathrm{c}}^{\mathrm{SCF}} = E^{\mathrm{SCF}} - nE_{\mathrm{ghost}}^{\mathrm{SCF}}(\mathrm{H}_2) \tag{2}$$

in which the SCF energy of H_2 was given by the basis set containing so-called ghost orbitals, i.e., by the set containing basis functions of the whole cluster. The $\Delta E_{\mathrm{c}}^{\mathrm{SCF}}$ values were calculated only for geometries that were found optimum for the respective clusters.

The ΔE^{corr} were determined by the semiempirical EPCE-F2σ method according to Sinanoğlu and Pamuk [5, 6]. The calculation of effective pair correlation energies (EPCE) was based on CNDO/2 wave functions. The utility of the EPCE method in the field of weak interactions was shown recently with the $(H_2)_2$ dimer [9], with some hydrogen clusters [9], and some other van der Waals systems [10]. It should be noted that the EPCE-F2σ approach is size-consistent in our case. Previously we have shown [10] that with complexes at the dissociation limit EPCE-F2σ behaves incorrectly if the SCF wave function itself behaves incorrectly or if the highest molecular orbital (delocalized) of the cluster is formed by a single atomic orbital of one constituent and if it is housed by one electron (e.g. the $H_3 \rightarrow H_2 + H$ dissociation).

Total interaction energies, ΔE and ΔE_{c}, were obtained as a sum of the SCF interaction energy (either ΔE^{SCF} or $\Delta E_{\mathrm{c}}^{\mathrm{SCF}}$) and the interaction correlation energy. The SCF energies were calculated with a DZ basis set which was so selected that it mimics the potential energy curves for H_2–H_2 interactions given by large basis sets [7]. EPCE-F2σ is based on a minimum basis set but the empirical parameters involved are adjusted so that the whole correlation energy would be accounted for. So in spite of the fact that the SCF and post-SCF energies are treated on different levels, the model should be intrinsically consistent.

3. Results and Discussion

Total interaction energies calculated for the $(H_2)_n$ clusters ($n = 2$–8) are summarized in Table 1. Let us comment briefly on the data. Geometry of the individual

Table 1. Total interaction energy (ΔE), total corrected interaction energy (ΔE_c) and optimum geometries for the $(H_2)_n$ clusters given by the DZ basis set (all entries in a.u.)

n	Structure[a]	r[a,b]	$-\Delta E$	$-\Delta E_c$
2	C_{2v}	5.6	0.0001442	0.0000907
3	D_{2h}	5.6	0.0002877	0.0001710
4	D_{3h}	5.6	0.0004224	0.0002305
4	$D_{2h} + 1$	5.6, 5.6	0.0003790	—
5	D_{4h}	5.6	0.0005537	0.0002963
5	$D_{3h} + 1$	5.6, 5.6	0.0004953	—
6	D_{5h}	5.5	0.0007709	0.0004377
6	$D_{4h} + 1$	5.6, 5.6	0.0006144	
7	D_{6h}	5.8	0.0004995	0.0001563
8	$D_{5h} + 2$	5.5, 5.6	0.001218	—

[a] Cf. Fig. 1.

[b] In complexes possessing one H_2 molecule in the second shell the numbers refer to distances between the central molecule and first-shell molecules and first- and second-shell molecules, respectively.

H_2 molecules was kept constant (1.4 a.u.) during the geometry optimization of the clusters. The T-shaped cluster (C_{2v}) represents the most stable form for the $(H_2)_2$ dimer. This structure is favoured over the linear, tetrahedral and oblong structures due to the quadrupole–quadrupole Coulombic interaction and partially also to dispersion interaction [9]. The significant energy difference between the T-shaped structure and the other structures of the $(H_2)_2$ complex leads us to the assumption about preference of the T-form also in larger clusters. With the $(H_2)_3$ complex we have two possibilities to construct the respective structures – either a "double T"-form (–|–), or the H-form (|–|). The energy optimization with the $(H_2)_3$ complex favours the first structure. The fourth H_2 molecule can be located either into the first shell (D_{3h} cluster, Fig. 1) or into the second shell. Evidently (Table 1), the D_{3h} cluster is favoured. The further molecules can be added analogously. It is seen from Table 1 that the D_{4h} and D_{5h} structures are lower in energy than the structures possessing one H_2 molecule in the second shell.

The addition of the seventh molecule ($(H_2)_7$ cluster) requires special attention. The addition of this molecule into the first shell is connected with a significant change in both the equilibrium distance between the central and surrounding H_2 molecules and the stabilization energy of the cluster. The introduction of the seventh molecule makes the first shell overcrowded; from the energetical point of view the location of this molecule into the second shell is more favourable. This is obvious because $-\Delta E$ of the D_{5h} complex is considerably higher than that of the D_{6h} complex (Table 1). Clearly, the energy difference between the $D_{5h} + 1$ and D_{6h} complexes must be even greater. The most stable cluster containing eight molecules ($(H_2)_8$) consists of the D_{5h} unit, and the remaining two H_2 molecules are located on the C_5 symmetry axis above and below the plane containing five H_2 molecules, in the T-shaped orientation with respect to the central molecule (Fig. 1).

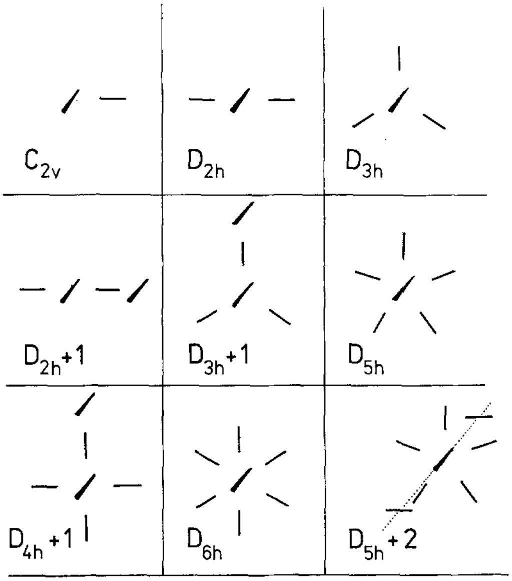

Fig. 1. Assumed $(H_2)_n$ structures

As noted above, we only assumed structures with the T-type bonding since these appear to be favoured on energy grounds. Finding the lowest energy does not assure, however, that the particular structure corresponds to a real minimum on the energy hypersurface $(H_2)_n$. To support our assumption about the preferential T-type bonding in larger clusters, we performed the vibrational FG analysis for the trimer $(H_2)_3$. We used a set of symmetry coordinates suggested by Vizi and Cyvin [11] for molecules $X_2Y_2Z_2$ of the D_{2h} symmetry but we dropped symmetry coordinates corresponding to intramolecular stretching modes. All eigenvalues obtained were positive and the respective vibrational wavenumbers fell into the range 130–250 cm^{-1}, though for the B_{2u} rock and B_{3u} torsion we obtained a very low value of 6 cm^{-1} and 7 cm^{-1}, respectively. The predicted wavenumbers are, of course, only qualitative because of the harmonic approximation used and because of low precision in some cases. Nevertheless, the result also suggests that the structures assumed for larger $(H_2)_n$ clusters correspond to real minima on the energy hypersurfaces.

3.1. Basis Set Effect

Although the DZ basis set used is associated with a rather small additional stabilization owing the ghost orbitals [8], we calculated the corrected SCF interaction energy with each cluster. ΔE_c^{SCF} (Eq. (2)) prefers, similarly as ΔE^{SCF}, the D_{5h} structures. The absolute value of ΔE_c^{SCF} is, as expected, smaller than ΔE^{SCF}, the factor ranging from 0.63 to 0.54.

Let us comment briefly on the calculation of ΔE_c^{SCF}. In the first step the standard SCF calculation is performed for the supermolecule. In the second step the energy of the hydrogen molecule is calculated in the basis set of the whole cluster. Of course, an individual calculation has to be performed for each nonequivalent hydrogen molecule; e.g. in the case with the most stable D_{5h} cluster we calculated the energy of the central H_2 molecule and of one of five equivalent H_2 molecules forming the shell. The ΔE_c^{SCF} is given, in this particular case, by the following equation:

$$\Delta E_c^{SCF} = \Delta E^{SCF} - [E_{ghost}^{SCF}(H_2, \text{central}) + 5 \times E_{ghost}^{SCF}(H_2, \text{shell})] \tag{3}$$

Let us present here, for the sake of illustration, energies of an isolated H_2 molecule, for the central and to the shell belonging H_2 molecules in the D_{5h} cluster: −1.1247602; −1.1250016; and −1.1247642 a.u. Obviously, the basis set effect influences significantly the energy of the central molecule. This can be explained as follows: all the additional functions of the shell-molecules are located in the vicinity of the central molecule meanwhile, with the shell-molecule, only functions of three H_2 molecules (two in the shell and one central) are located in the nearest vicinity.

3.2. Ionization Potentials

Recent development in photoelectron spectroscopy makes it possible now to determine ionization potentials of van der Waals molecules [12, 13]. We considered it useful, therefore, to calculate also the ionization potentials for the H_2 clusters. Our theoretical approach to vertical ionization potentials is based on orbital energies given by our *ab initio* SCF calculations (Koopmans' theorem). The change in correlation energy upon ionization is recognized by the difference in EPCE-F2σ correlation energies for the parent closed-shell cluster and its cation, assuming for both the same geometry (given in Table 1). The reorganization energy was assumed to be small and its effect on the ionization potentials was disregarded. From Table 2 it is seen that the effect of structure on the vertical ionization potential is small and that for all clusters considered we may expect a lowering of about 0.4–0.6 eV with respect to the parent H_2 molecule.

Table 2. Estimated vertical ionization potentials (VIP) for the $(H_2)_n$ clusters[a]

n	Structure[b]	Koopmans theorem	$-\Delta E_{corr}$	Estimated VIP
1	—	16.14	1.02	17.16
2	C_{2v}	15.86	0.91	16.77
3	D_{2h}	15.75	0.96	16.71
4	D_{3h}	15.67	0.99	16.66
5	D_{4h}	15.65	1.01	16.66
6	D_{5h}	15.67	1.04	16.71
7	D_{6h}	15.67	0.98	16.65
8	D_{5h} + 2	15.54	0.99	16.53

[a] All entries in eV.
[b] See footnotes in Table 1.

Table 3. Additivity of individual many-body terms (in a.u.) in expansion of ΔE^{SCF} and $\Delta E_c^{\mathrm{SCF}}$ for the D_{3h} cluster ($n = 4$, see Fig. 1)

	ΔE^{SCF}	$\Delta E_c^{\mathrm{SCF}}$
Total	0.0016738	0.0018657
Sum of two-body terms	0.0016758	0.0018405
Sum of three-body terms	−0.0000013	−0.0000238
Four-body term	−0.0000007	0.0000490

3.3. *Additivity of Many-Body Terms in* ΔE^{SCF}

ΔE^{SCF} of a cluster containing n molecules can be formally expressed as

$$\Delta E^{\mathrm{SCF}} = \Delta E^{\mathrm{SCF}}(ij) + \Delta E^{\mathrm{SCF}}(ijk) + \Delta E^{\mathrm{SCF}}(ijkl) + \cdots \tag{4}$$

The individual terms on the right-hand side represent two-, three- and four-body interaction terms. A question can be asked concerning the importance of three- and other many-body terms. This problem is of special importance with Monte Carlo calculations for the liquid state in which a large number of molecules has to be taken into consideration.

Numerical values of the individual terms of Eq. (3) were obtained for the D_{3h} cluster ($n = 4$) (Table 3). From this table it is evident that the members of the expansion (4) are different for ΔE^{SCF} and $\Delta E_c^{\mathrm{SCF}}$. The four-body term is smaller than the sum of the three-body terms with ΔE^{SCF} and both terms are attractive. The four-body term, with $\Delta E_c^{\mathrm{SCF}}$ is considerably larger than the sum of the three-body terms and, moreover, it is repulsive. If we determine the total potential as a sum of the two-body terms, the percentual value of the non-additivity contribution is rather small (1.4%). Remarkably enough, the inclusion of three-body terms does not manifest itself by expected decrease, but by an increase of the non-additivity contribution (2.6%).

The non-additivity contributions given in Table 3 suggest that, with van der Waals interactions, they are not so important as with hydrogen bond [2] interaction or even with chemical interactions [14] acting in clusters of some atoms.

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