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Study of the Hydrogen Bond and of the Proton Transfer between Two H_2S Molecules*

Krzysztof Pecul

Quantum Chemistry Group, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland

The potential energy surface for the H_2S dimer is calculated as the sum of the SCF-MO-LCGO energy with a new, modified, basis set and the estimated dispersion energy. Proton affinities for SH^- and H_2S, and, as their difference, the energy of the proton transfer between two H_2S molecules, are also calculated. Despite the limited basis set used, the results are consistent with experimental data.

Key words: Weak hydrogen bonds - H_2S dimer - Proton transfer - Proton affinities

1. Introduction

The hydrogen bond between two H_2O molecules has been investigated by many quantum chemists and numerous studies on this problem have been published (see e.g. [1–4] and references therein). However, for the H-bond between two H_2S molecules, despite their similarity to those in H_2O, only one *ab initio* study (Sabin [5]) had been available for a lengthy period. Veillard's basis set [6], which has been used, after strong contraction, by Sabin, is too large to be used for larger systems with SH . . . S bonds and/or in research centres which have no access to large computers. The well-known STO-3G and STO-4G basis sets [7] (the latter being almost as large as Veillard's) give too great H-bond energy for the second-row hydrides, due to overestimating the dipole moments and to the basis set defect spurious stabilization energy [8, 9]. On the other hand, it is possible to reproduce qualitatively some experimental facts for the CH_3SH dimer (Ref. [10], hereafter referred to as Paper I), using a very limited basis set (called hereafter Basis I). Basis I exhibited similar defects as the STO-3G and STO-4G basis sets, but was much less time consuming and the results were to some extent encouraging. Therefore, the author made an attempt to choose a basis set which is small but useful for the study of the SH...S bond and better than Basis I. Moreover, it was interesting to estimate the relative contribution of the Hartree-Fock and dispersion parts of the interaction energy in the H_2S dimer.

Whilst the present investigation was in progress, the papers by Yamabe *et al.* [11] and by Kollman *et al.* [12] appeared, where the proton affinity of H_2S with STO-3G and the potential energy curve for two rigid H_2S monomers with STO-4-3/1G (denoted

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in [12] by 431G) basis set, respectively, were calculated. Their results present interesting material for comparison with ours. However, we have calculated the potential energy curves along with proton affinities using our new basis set (called hereafter Basis II) for both and it seems that our results are more consistent with experiment. The last point will be discussed later.

2. Method

Our Basis II is given in Table 1. It differs from Basis I (given and described in Paper I) in the following points.

1) Instead of the two greatest *s* exponents for the S atom, three exponents are introduced and energy optimized for the experimental geometry in the uncontracted basis set.
2) When point 1) is completed, the greatest *p* exponent is optimized, also in the uncontracted basis set. After this optimization, the two greatest *s* exponents are contracted.
3) New lobes, one on each S-H bond, are added. The centre and the exponent of such a lobe is optimized. After this optimization, the two greatest *p* exponents are contracted in the same way, as in Basis I.

Using Basis II, with the parameters optimized for the experimental geometry of H_2S [13] in the manner described above, the geometries of H_2S, SH^- and H_3S^+ were energy optimized. With the optimum geometry of H_2S, the potential energy curve for the system of the two rigid H_2S monomers was calculated, assuming that the dimer contains a linear SH ... S hydrogen bond and that the pi-type orbitals of the monomers are perpendicular. This assumption is consistent with the results of the analysis of infrared and Raman spectra of the matrix-isolated hydrogen sulphide [14, 15]. Sabin [5] found the lowest energy for such a dimer geometry, which was also assumed for the CH_3SH dimer in Paper I.

At the first stage of the dimer study, only the distance between the S nuclei, R_{SS}, was energy optimized. In order to compare Basis II with Basis I, the same optimization for the H_2S monomer and dimer was also performed with Basis I. The potential energy curve for the hydrogen-bonding proton motion along the S ... S axis was calculated for Basis II only, assuming the optimum value of R_{SS}.

In order to estimate the influence of the intermolecular correlation on the H bond, the H_2S-H_2S dispersion energy was calculated by the London formula [16, 17] and added to the SCF interaction energy. The proton affinities of SH^- and H_2S were calculated as the difference between the respective SCF energies, found for Basis II with the energy minimum geometries and exponents optimized for H_2S.

All SCF calculations were performed on the CDC CYBER 72 computer of the Institute of Nuclear Research, using the MOLPRO program, which had been used in calculations published in Paper I.

3. Results and Discussions

Numerical results are presented in Tables 1-4. Table 1 contains the exponents and contraction coefficients of Basis II. The symbol "S + 0.35(SH)" denotes the centre of the lobe placed on the SH bond and shifted from the S nucleus by 0.35 of the SH bond length.

The best SCF results for H_2S [18], known so far, and some results with basis sets used for the study of intermolecular interactions and proton affinities, are given in Table 2. The content of Table 2 is as follows: name of the monomer and reference to the basis set, i.e. our type of basis set or reference number, the energy optimized, SH bond length, R, the optimized HSH angle, A, the energy of the system, E, the dipole moment, d.m.

Table 1. Gaussian basis set used

Centre	Type	Nr.	Exponent	Coefficient
S	*s*	1	1039.3	1.0
			189.3	4.73
		2	44.7	1.0
		3	6.061	1.0
		4	2.448	1.0
		5	0.604	1.0
		6	0.230	1.0
	p	1	18.30	1.0
			3.68	1.854
		2	0.737	1.0
		3	0.202	1.0
H	*s*	1	1.127	1.0
		2	0.201	1.0
S + 0.35(SH)	*s*	1	0.60	1.0

Table 2. Results for monomers

Ref.	R	A	E	d.m.
H_2S, expt.	2.51	92.2	−400.81	0.401
H_2S, Ref. [18]	expt.	expt.	−398.68	0.502
H_2S, Ref. [12]	2.55	97	−398.20	0.696
H_2S, Ref. [5]	2.79	94	−398.08	0.599
H_2S, Basis II	2.595	92.8	−394.67	0.454
H_2S, Basis II	2.595	92.2	−394.67	0.452
H_2S, Basis II	expt.	expt.	−394.67	0.472
H_2S, Ref. [11]	expt.	93.5	−394.06	–
H_2S, Basis I	2.65	94	−387.96	0.665
H_2S, Basis I	2.657	expt.	−387.96	0.660
H_2S, Ref. [19]	expt.	expt.	−381.04	0.688
SH^-, Basis II	2.64	–	−394.05	−0.053
H_3S^+, Basis II	2.61	95.4	−394.95	0.938

The angle A is given in degrees, other quantities in atomic units. The latter are used in the present paper unless otherwise stated. The d.m. for SH^- and H_3S^+ is calculated with respect to the S nucleus. If, instead of an R or A value, the symbol "expt." is written, it means that the experimental value is assumed. There are small differences (the relative differences are smaller than 2%) between the experimental values of R or A, assumed by different authors, but it has practically no influence on the E or d.m. values.

It can be seen from Table 2 that Basis II is superior to Basis I. This is the reason why interaction calculations were preformed with Basis II. However, the potential energy curve for two rigid H_2S monomers was also calculated with Basis I, for the sake of comparison. In the calculations on the dimer, the value of $A = 92.2°$ was assumed, which was the result of a preliminary minimization. The difference between this and the energy minimum A value is only $-0.6°$ and has no influence on the interaction energy.

The total energy, E, calculated with Basis II, lies above those of Refs. [18], [12] and [5], but below those of Refs. [11] and [19]. However, the total computation time for the dimer is much smaller with Basis II than with the basis sets used in Refs. [18], [12] and [5] (the computation time is estimated to be smaller by an order of magnitude) and is probably not greater than those of Refs. [11] and [19]. Basis II gives comparable accuracy in the geometry of H_2S and a considerably better value of the dipole moment (the experimental value of d.m. was assumed to be the one given in Ref. [20]). The relation of our d.m. to the experimental value is fairly close to that calculated for H_2O with the basis sets used in the most accurate calculations for the water dimer ([1], [3], [4]). This agreement enables us to use Basis II to study the H_2S dimer.

Table 3 gives the most important results for the dimer. The binding energies, the first one denoted by *B.E.*(SCF) being the difference between the sum of two SCF monomer energies and the SCF dimer energy, and the second one denoted by *B.E.*(Sum) being the sum of *B.E.*(SCF) and of the absolute value of the dispersion energy defined above, are given in kcal/mole. The experimental value of the binding energy ([21], quoted after [12]) is given in the first row. The results of the minimization of the total interaction energy (negative value of *B.E.*(Sum)) are given in the rows denoted by Basis IId and Basis Id, those for *B.E.*(SCF) in other rows.

The results given in Table 3 need some comment. We use the London formula to estimate the H_2S dispersion energy. In this case it is justified because for H_2S the electron density

Table 3. Results for H_2S dimer

Ref.	R_{SS}	*B.E.*(SCF)	*B.E.*(Sum)
expt.	–	–	1.7
Ref. [12]	8.3	1.8	2.2
Ref. [5]	8.5	0.7	1.0
Basis II	8.2	1.0	1.4
Basis IId	8.0	0.9	1.4
Basis I	8.1	1.5	1.9
Basis Id	7.9	1.4	1.9

distribution is very close to the spherical one. In particular, the anisotropy of the polarizability tensor (Ref. [22], quoted after [23]) is small. A similar method of estimation of the dispersion energy was used for H_2O by Kistenmacher *et al.* [24]. The ionization potential of H_2S, *I.P.*(H_2S), was taken from Ref. [25]; the value of Ref. [26] is almost the same.

Zeiss and Meath [17] found that the value of the dispersion energy, calculated for H_2O by the London formula, is only about 70% of their "experimental" dipole-dipole dispersion energy. Moreover, the London dispersion energy in the H_2O dimer at the equilibrium R_{OO} distance represents less than 40% of the *ab initio* dispersion energy calculated by Jeziorski and van Hemert [4]. This suggests that the dispersion energy for H_2S is probably also much greater than our estimate and the dispersion effects are important in the hydrogen bond (also in the H-bonding proton motion) for the H_2S dimer and probably also in some other H bonds involving second-row atoms, in disagreement with the suggestion of Kollman *et al.* [12]. Their opinion has been supported by the agreement of their *B.E.*(SCF) for H_2S with the experimental results [21]. As can be seen in Table 3, this agreement is not so good if the dispersion energy is taken into account. Moreover, the *B.E.*(SCF) found by them is, in the case of the H_2O dimer, about twice as great as the best SCF results [1, 3, 4] and the ratio of their d.m. to the experimental value is greater for H_2S than for H_2O. The reasons presented above suggest that the agreement of their *B.E.*(SCF) with experiment is fortuitous.

Our London dispersion energy is greater than the value of $2m_1 \cdot m_2$, i.e. the electrostatic energy of two dipoles situated at the S nuclei and equal to the total dipole moments of the H_2S monomers. This suggests that the H_2S dimer can be stable at any orientation of the monomers.

The difference between the energy of the monomer in the monomer and in the dimer basis set, being the best known estimate of the basis set superposition error [3, 4, 8, 9, 12], is for Basis II at $R = 8.2$ equal to 0.8 kcal/mole. The same value was found by Kollman *et al.* for their basis set [12]. For the STO-3G basis set, which seems to be more time-consuming than Basis II, this difference is probably greater [12, 9]. For Basis I it is equal to 1.0 kcal/mole.

Table 2 shows that the optimum R_{SS} is relatively independent of the basis set. The R and *B.E.*(SCF) for Basis I are almost equal to the respective quantities for the CH_3SH dimer reported in Paper I.

The potential energy curve for the proton motion along the S-S axis in the H_2S dimer exhibits practically no difference with respect to that in the H_2S monomer. In particular, no proton shift from "proton donor" to "proton acceptor" is observed. The same effect has been found for the CH_3SH dimer (Paper I) and for many other H bonds [12]. Unfortunately, no estimate of the influence of the dispersion energy on the proton motion in the SH... S bond has been given until now. This influence probably causes the proton shift and the lowering of the fundamental stretching vibration frequency.

Table 4 gives proton affinities in kcal/mole for SH^- and H_2S along with their difference, denoted by *PA*(SH^-), *PA*(H_2S) and *Diff.*, respectively. Up to now, quantum mechanical calculated proton affinities for these systems have been found in the literature only in

Table 4. Proton affinities in kcal/mole

Ref.	$PA(SH^-)$	$PA(H_2S)$	Diff.
expt.	350–368	169–199	151–199
Basis II	388	181	207
Ref. [11]	–	225	–
Ref. [25]	262	–	–
Ref. [19]	711	324	387

Refs. [11, 17, 27]. In the last work, the calculations were made for the minimal one-centre Slater basis set. It is known that the area of application of such a basis set is rather small. The basis set STO-3G from [11] resulted in higher energy than Basis II and the basis set from [19] in much worse agreement with good SCF results both for energy and for dipole moment. As one may expect, the agreement of the proton affinities with experiment is better for Basis II than for the basis sets mentioned above.

Experimental data for $PA(H_2S)$ are taken from works quoted in Ref. [11]. "Experimental" $PA(SH^-)$ is calculated from the formula

$$PA(SH^-) = (E(SH^-) - E(SH)) + (E(SH) - E(H_2S)) \tag{1}$$

The first term in (1), i.e. the electron affinity of the SH radical, is taken from Refs. [28–30], the second term from [31]. All these values are given in Refs. [32, 33].

It should be taken into account, when comparing *PA*'s calculated for Basis II with the experimental values, that the exponents of Basis II were optimized for H_2S only. Such an optimization was not performed for SH^- and H_3S^+, because it would be time-consuming and calculation of *PA*'s is not the main purpose of our contribution. As a result, $PA(SH^-)$ is greater, $PA(H_2S)$ less than (the latter effect is probably not as great as the former) and *Diff.* greater than if the exponents were optimized for SH^-, H_2S and H_3S^+ with the same degree of accuracy. A relatively good agreement, with experiment, of *PA*'s and *Diff.*, the latter being the energy of the proton transfer between two H_2S molecules, can be considered as an additional argument showing that even a relatively small basis set can be useful for the investigation of the hydrogen bond and of the proton transfer.

Results of the present contribution seem to suggest that it is possible to investigate *ab initio* the hydrogen bond with an accuracy comparable to that of elaborate SCF calculations, but with a much lower computational effort. Further investigations in this field have commenced in our laboratory.

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