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Original Investigations

Theoretical study of three-body nonadditive interactions for the H_2S–$(H_2O)_2$ system

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An *ab initio* SCF MO study of the hydrogen-bonded system formed by an H_2S molecule interacting with two water molecules is presented. The nonadditive contributions to the interaction energies are obtained using the 4-31G basis sets which tend to overestimate the dipole moments of the H_2S and H_2O molecules. Thus possibly too large interactions, including upper-limit values for the nonadditive three-body contributions, were obtained. The nonadditive corrections were found to be comparable in magnitude to the cases of other first-row hydride trimers. On this basis one can infer that they probably do not affect the proton and deuterium exchange in hydrated H_2S (as occurs in the G–S heavy water enrichment process) and that they do not play an important role in the formation of clathrates involving hydrogen sulphide.

Key words: H_2S hydration—Three-body nonadditive effects—Hydrogen bonding—Proton and deuterium transfer.

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1. Introduction

The problem to be studied here concerns the hydrogen bonded system H_2S–$(H_2O)_2$ and the importance of its nonadditive energy terms. The need for an understanding of the hydrogen bond, with its many implications for biological, physical and chemical phenomena hardly needs to be emphasized. As concerns quantum mechanical calculations the most studied hydrogen-bonded system is perhaps the one consisting of interacting water molecules. A few among many such studies [1–4] have analysed the water trimers separating explicitly the pairwise additive interactions from the essentially nonadditive three-body effects. In Ref. [1] it is shown that three-molecule nonadditivities are not small in magnitude and vary in sign according to the system's geometry, leading to changes in the binding energies and bond distances for aqueous liquids and solids. Clementi [4] however, has claimed that for the bulk properties of water the nonadditive contributions actually average out and that if simple pairwise additive potentials are used in Monte Carlo calculations, one reproduces experimental data quite adequately.

Furthermore, there have appeared a couple of papers involving hydrogen bonds for hydrogen sulfide molecules. One is the work by Pecul on the H_2S dimer [5] and another a paper by our group [6] on the hydrogen-bonded mixed dimer H_2S–H_2O. For other first-row hydrides such as methane and ammonia the nonadditive effects on the respective trimers have also been studied [7, 8]. However, no estimation of three-body effects for hydrogen-bonded hydrogen sulfide exist to date, as far as we know.

In trying to establish whether three-body effects are significant one must first clarify what level of precision is involved in a particular physical situation. Small energy contributions, quite negligible as concerns a liquid say at room temperatures may become crucial to understand low temperature phenomena. Such is the case of the study of the nonadditive terms in the (NH_3) trimer which amount to only two or three kilocalories [8] but which are essential to understand the experimental data of collision processes of ammonia molecules by Odutola et al. [9]. These authors in fact find that the most stable ammonia trimers have shorter internuclear separations and strained hydrogen-bond angles than one would predict using purely pairwise additive potentials. Their results on the other hand are very well accounted for if a theory with three-body corrections is used [8]. Even weakly interacting He_2 dimers are affected by nonadditive (solvent) effects at the low temperatures of liquid helium [10, 11].

On the other hand, a different order of magnitude is necessary so that nonadditive effects become significant at the relatively high temperatures at which most of the phenomena in biological or industrial processes occur. To be important in such cases three-body nonadditive terms should at least be, when averaged over the different mutual orientations of the interacting molecules, as large as the thermal motions within the liquid and comparable in magnitude to the purely pairwise additive energies. One recent case in point is the study of nonadditive effects for hydrated ions like Li^+ [12], Mg^{2+} and Ca^{2+} [13]. Here the three-body terms were found to be quite large (especially for Mg^{2+} where it reaches up to 60 kcal/mol when water molecules from the first and second hydration shells interact with it). Thus these effects are certainly structure determining for the hydration shell. So this way is a confirmation of "through-water" type binding for hydrated ions in biology first proposed by Pullmans' [14].

Going back to the problem of hydrogen-bonded interactions between H_2S and H_2O studied in Ref. [6] the study of the nonadditive three-body corrections obtained introducing another H_2O molecule seems very interesting in order to attempt to answer some physical questions at the two levels mentioned before. At the level of the sensitive phenomena that occur at lower temperatures and pressures one could ask whether the hydrated H_2S that leads to clathrate formation [15] induces structure formation of the hydration shells as the metallic ions discussed above do. This could conceivably have relevance to understand–at a molecular level–the way that H_2S gas hydrates freeze at higher temperatures than pure water itself and the interesting structural nature of the combined gas-water solids known as clathrates. For the case of phenomena that would require large nonadditive effects such as is the case of relatively high temperatures and pressures we could mention the dissolution in water of gaseous H_2S (and its isotopes HDS and D_2S) at high pressures and at two temperatures, during the heavy water enrichment process industrially known [16] as Girdler–Sulphide or GS process. In Ref. [6] the proton donor nature of the H_2S towards the water molecule was established. One can also estimate the proton (and what is even more relevant the deuteron) transfer for the two hydrogen bonded structures of the pair H_2O–H_2S in the lines of Pecul's work on proton transfer for the H_2S–H_2S dimer [5]. Before doing this we would like to know whether the presence of the other water molecules does not effect the hydrogen bond of the original pair through nonadditive corrections.

For all the above reasons it seems interesting to study the interaction energy and its purely nonadditive contributions of the H_2S-$(H_2O)_2$ system. We shall do this using the method described in the following section.

2. Method

The present study is based on LCAO-MO-SCF calculations using a modified Gauss 70 program [17]. The $H_2S(H_2O)_2$ system was analyzed in various different hydrogen-bonded structures to be described in the following section. The calculations were mainly obtained using the internal 4-31G set of the program [17], although several tests using minimal sets or 4-31G plus polarization functions on O, S and H were performed as shall be described below. Also some attempts to obtain a measure of the dispersion contributions to the intermolecular interactions were made.

Before we report these tests, however, it is worthwhile to remember the meaning of nonadditive and additive contributions to intermolecular potentials (and it is also worth mentioning that no discussion is given here about three-body *intra*molecular effects within H_2S or H_2O as is discussed for example by Murrell [18]). In a system of n-interacting molecules the total interaction energy can be written as

$$E(n) = \sum_{k=2}^{n} E(k, n) \tag{1}$$

where $E(k, n)$ represents the sum of all k-body contributions to $E(n)$:

$$E(k, n) = \sum_{\alpha_1<\alpha_2<\cdots<\alpha_k}^{n} V(\alpha_1, \alpha_2, \ldots, \alpha_k) \tag{2}$$

where $V(\alpha_1, \ldots, \alpha_k)$ is the k-body contribution to the interaction energy of the system of k molecules denoted as $\alpha_1, \ldots, \alpha_k$.

For our three molecule system $n = 3$ and obviously we have a two-term expansion (up to three-body terms):

$$E(n) = E(2, n) + E(3, n) \tag{3}$$

but precisely this expression is generally used as the approximation to Eq. (1) that can give relatively good results for extended systems with $n > 3$ (for example in the cases of atomic clusters [19, 20]. This at least is far superior to the even more common approximation that expresses the interaction energy of a many-component system as simple sum of pair interactions, i.e. identifying $E(n)$ with $E(2, n)$.

The choice of the 4-31 G basis set was based in the reasonable representation of the molecular orbital levels of the H_2O and H_2S molecules as can be seen in Tables 1 and 2 where results using this set *versus* minimal sets and a modified 4-31 G set including polarization functions, are reported. It is obvious that STO-3G set is frankly incapable of giving the orbital energies anywhere near the Hartree–Fock limit values for either molecule. Also one can see that the results of the 4-31 G sets augmented by d-polarization functions generally tend to worsen this agreement which is quite reasonable for the original 4-31 G set. In the next section it will also be shown that the description of the H_2S–H_2O dimers with this set is also relatively similar to previous results reported in [6] using an extended set without polarization functions. On the other hand it is evident that the dipole moments predicted by the 4-31 G set are too large and in fact it is also known that at the Hartree–Fock limit the dipole moment is not given correctly for H_2O or H_2S. The minimal set STO-3G gives a better value for this property, albeit *via* a compensation of errors. Considering that our 4-31 G set exaggerates the polarity of molecular electron density as indicated by too large dipole moments we may expect an overestimation of the two- and three-body interaction energies. An interesting example of this situation is the case of H_2O–H_2O interactions for which one of the best calculations is that of Jeziorski et al. [21]. Near the minimum of the potential well (at 5.67 a.u.) they estimate the attraction as −3.87 kcal/mole while our calculations with STO-3G, 4-31G and 4-31G plus set of polarization functions give respectively: −4.54 kcal/mole,

Table 1. Cumulative results on H_2O

	a	b	c	c'	c''	c'''	d
GTO	(6, 3/3)	(8, 4/4)	(8, 4/4)	(8, 4, 1/4)	(8, 4, 1/4, 1)	(8, 4, 1/4, 1)	(11, 7.2/5.1)
CGTO	[2, 1/1]	[2, 1/1]	[3, 2/2]	[3, 2, 1/2]	[3, 2, 1/2, 1]	[3, 2, 1/2, 1]	[6, 5, 2/3, 1]
−E	74.963	75.497	75.907	75.938	75.953	75.953	76.062 (76.066)*
$-\varepsilon(1a_1)$	20.242	20.429	20.519	20.529	20.528	20.529	20.563
$-\varepsilon(2a_1)$	1.268	1.276	1.352	1.338	1.336	1.336	1.351
$-\varepsilon(3a_1)$	0.453	0.458	0.558	0.568	0.566	0.566	0.584
$-\varepsilon(1b_1)$	0.391	0.396	0.500	0.496	0.495	0.495	0.508
$-\varepsilon(1b_2)$	0.618	0.620	0.708	0.705	0.701	0.702	0.717
Net charge on oxygen $(-q)$	0.367	0.385	0.785	0.832	0.528	0.522	—
Dipole Moment (Debyes)	1.73	1.76	2.61	2.28	2.13	2.17	2.08 (2.21)**

a: Standard STO-3G basis set [17].
b: Standard STO-4G basis set [17].
c: Standard 4-31 G basis set [17].
c': Basis c) plus polarization on oxygen d(1.0).
c'': Basis c) plus polarization on oxygen d(1.0) and polarization on hydrogen p(0.75). Exponents of polarization functions taken from Ref. [T1].
c''': Basis c) plus polarization on oxygen d(1.3) and polarization on hydrogen p(0.80). Exponents of polarization functions are close to the best estimates of Roos and Siegbahn, Ref. [T2].
d: Near the limit of Hartree-Fock calculations, Ref. [T3].
* Basis (13, 8, 3, 1/6, 2, 1) contracted to [8, 5, 3, 1/4, 2, 1], Ref. [T1].
** Basis (12, 7, 1/7, 1) uncontracted, $E = -76.060$ a.u., Ref. [T1].

T1. Clementi, E., Popkie, H., J. Chem. Phys. **57**, 1077 (1972).
T2. Roos, B., Siegbahn, P., Theor. Chim. Acta (Berl.) **17**, 199 (1970).
T3. Dunning, T. H., Jr., Pitzer, R. M., Aung, S., J. Chem. Phys. **57**, 5044 (1972).

Table 2. Cumulation results on H_2S

	a	b	c′	c″	c‴	d
GTO	(9, 6/3)	(12, 8/4)	(12, 8/4)	(12, 8, 1/4)	(12, 8, 1/4, 1)	(12, 9, 2/4, 1)
CGTO	[3, 2/1]	[3, 2/1]	[4, 3/2]	[4, 3, 1/2]	[4, 3, 1/2, 1]	[6, 4, 2/2, 1]
$-E$	394.312	396.571	398.203	398.257	398.265	398.682
$-\varepsilon(1a_1)$	90.746	91.521	91.795	91.817	91.821	91.976
$-\varepsilon(2a_1)$	8.648	8.645	8.946	8.940	8.941	8.958
$-\varepsilon(3a_1)$	6.278	6.310	6.631	6.630	6.631	6.646
$-\varepsilon(4a_1)$	0.898	0.895	0.997	0.975	0.974	0.982
$-\varepsilon(5a_1)$	0.395	0.395	0.484	0.491	0.489	0.500
$-\varepsilon(1b_1)$	6.275	6.312	6.628	6.627	6.628	6.644
$-\varepsilon(2b_1)$	0.278	0.279	0.383	0.373	0.373	0.382
$-\varepsilon(1b_2)$	6.281	6.306	6.633	6.632	6.632	6.647
$-\varepsilon(2b_2)$	0.507	0.508	0.586	0.584	0.581	0.592
Net charge on sulphur ($-q$)	−0.072	−0.081	0.183	0.332	0.157	0.164
Dipole Moment (Debyes)	1.02	1.00	1.78	1.26	1.20	1.28

a: Standard STO-3G basis set [17].
b: Standard STO-4G basis set [17].
c: Standard 4-31 G basis set [17].
c′: Basis c) plus polarization on sulphur d(0.5).
c″: Basis c) plus polarization on sulphur d(0.5) and on hydrogen p(0.75).
d: Extended basis set, see Ref. [T2] of Table 1.

−7.37 kcal/mole and −5.65 kcal/mole. Therefore our 4-31 G results overestimate the SCF binding energy almost by a factor of two. One of us (AL) performed the pseudopotential calculations on H_2O–H_2S dimer using the molecularly optimized basis sets augmented by polarization functions. Near minimum the interaction energy in geometries *B* and *A* were found to be weaker by 40% and 60%, respectively, of the values calculated in the 4-31 G basis set, in full rapport with the estimations we made for water dimer. Work on this subject is in progress and results will be published elsewhere. Hence we may also expect an overestimation of H_2S–H_2O interactions and of the three-body energy values, which will then be considered an upper-limit to the actual non-additive effects. This, on the other hand, will be quite convenient as concerns the possibility of drawing definite conclusions to actual physical and chemical effects, as shall be discussed in the following sections. Also we must note that all our calculations of the interaction energies, including those of H_2O–H_2S dimer, have been obtained in a standard way, i.e. being not corrected by the counterpoise method, see for example [22]. Nevertheless, for the 4-31 G basis set this correction was found to be considerably small [7, 8] and consequently it should not affect any of our conclusions.

The main error present in the Hartree–Fock calculations of intermolecular interactions is the lack of dispersion energies therein. A rough estimation of dispersion terms can be achieved using the method outlined by Kołos [22]. For the two-body dispersion energy we use the following formula:

$$E_{\mathrm{disp}}(2,2) = -\mathrm{C}_6\mathrm{R}^{-6}. \tag{4}$$

The relevant values of the C_6 coefficient were taken from the literature (see Table 3). For the estimation of $E_{\mathrm{disp}}(3,3)$ for the H_2O–H_2O–H_2S trimer we shall use the Axilrod–Teller nonadditive dispersion energy formula:

$$E_{\mathrm{disp}}(3,3) = C_9(3\cos\gamma_1\cos\gamma_2\cos\gamma_3+1)R_{12}^{-3}R_{13}^{-3}R_{23}^{-3} \tag{5}$$

where γ_i and R_{ij} denote the angles and sides of triangle formed by oxygen and sulphur atoms. The value of $C_9 = 699$ a.u. was estimated from the combination rule (see Table 3.).

It should be noted that in formulas (4–5) no information concerning the internal structure of H_2S and H_2O is given. As in the case of ammonia trimers [8] we shall find that the actual values of the dispersion non-additivity is but a fraction of the SCF values for the non-additivity and therefore the crudeness of the method used for obtaining the former cannot introduce any notable effects in our conclusions.

3. Results

In a previous study of the H_2S–H_2O dimer [6] the two possible hydrogen-bonded situations were analysed with each molecule acting alternatively as a proton donor to the other. The dimer was constructed, in both cases, assuming fixed (experimental [23]) geometries for the internal structures of the individual H_2O and H_2S molecules. Furthermore the hydrogen bonds S–H···O and O–H···S

Table 3. Dispersion energies obtained from London-formula as a function of the internuclear separation between the heavy atoms (kcal/mole)

R(a.u.)	H_2O–H_2O[a]	H_2O–H_2S[b]	H_2S–H_2S[c]
5.5	−1.03	−2.02	−4.24
6.0	−0.61	−1.20	−2.52
6.5	−0.38	−0.74	−1.56
7.0	−0.24	−0.47	−1.00
7.5	−0.16	−0.31	−0.66
8.0	−0.11	−0.21	−0.45

[a] $C_6 = 45.37$ a.u., [T1].

[b] $C_6 = 89.0$ a.u. calculated from the combination rule [T2].
$C_6^{AB} = 2\alpha_A \alpha_B C_6^A C_6^B / (\alpha_B^2 C_6^A + \alpha_B^2 C_6^A)$.

[c] $C_6 = 187$ a.u. calculated from the London formula:
$C_6 = -(3/4) U \alpha^2$, with $U = 0.3837$ a.u. [T3] and
$\alpha = 25.5$ a.u. [T4].

T1. Zeiss, G. D., Meath, W. J., Donald, J. C. F., Dawson, D. J. Mol. Phys. **39** (1980) 1055.

T2. Margoliash, D. J., Proctor, T. R., Zeiss, G. D., Meath, W. J.: Mol. Phys. **35** (1978) 747.

T3. Watanabe, K. J. Chem. Phys. **26** (1957) 542.

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were first assumed linear. The calculations used an extended gaussian set containing $10s6p$ for sulphur and $6s3p$ for oxygen, then contracting to (5, 1, 1, 1, 1, 1; 3, 1, 1, 1) and (5, 1, 1, 1; 1, 1), respectively. This, including the $4s$ functions on the hydrogens, contracted (3, 1) implied double-zeta quality calculations. Such a set is rather time consuming for the H_2S–$(H_2O)_2$ trimers that interest us here, so the choice of the 4-31 G set [17] which also has double-zeta quality for the *valence* electrons seems natural. Also the size $12s8p$ for S and $8s4p$ for O and $4s$ for H gives *total* energies slightly lower than the set of Ref. [6] for H_2S and H_2O. But most importantly, the main qualitative features of the H_2S–H_2O system using the 4-31 G set are similar to those of Ref. [6]. Let us remember the main conclusions therein.

Firstly the two alternatives for the hydrogen-bonded pair H_2S–H_2O are *not* equivalent. The one where the H_2S acts as proton donor has a substantially deeper well and a shorter equilibrium distance than the other one. Furthermore this most stable structure presents a large charge transfer (from the water to the hydrogen sulfide) and a relatively large bond order between the sulphur hydrogen and the oxygen, results that are *not* present in the other structure.

The first question is whether our 4-31 G set gives a similar representation of the H_2S–H_2O pairs. This is answered in Figs. 1 and 2 where the same situation above is clearly represented. Thus the 4-31 G set results are capable (contrary to what could be inferred from the work of Kollman [24]) of predicting the proton donor and electron acceptor role of H_2S in hydrogen bonded situations, quite in rapport with other theoretical studies [6, 25].

To further compare the predictions of different sets for the H_2S–H_2O dimer, we present Figs. 3 and 4 including the minimal sets STO-4 G and the 4-31 G and extended sets. Naturally the minimal set gives a less profound well for both structures due to their inherent limitations but also (see discussion in preceeding section) influenced by the excessively large dipole moment that Hartree–Fock calculations introduce for H_2S and H_2O. This means that while we can accept that 4-31 G has double-zeta quality concerning these hydrogen bonded structures, still all interaction energies, including our desired three-body effects, are probably

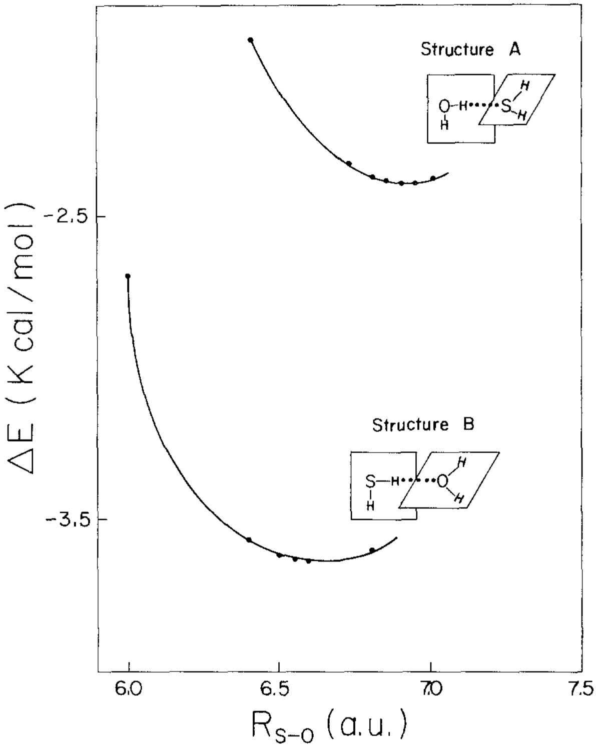

Fig. 1. Interaction energies for both dimers (structures A and B in the terminology of [6]) using the 4-31 G basis set

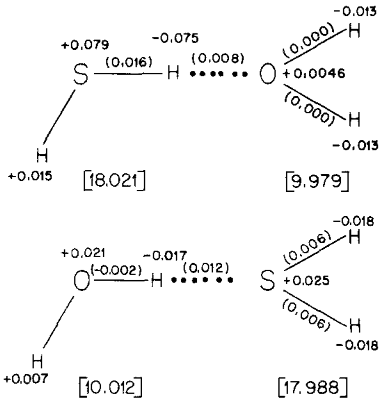

Fig. 2. Changes in the atomic charges and bond orders of the isolated H_2S and H_2O molecules when forming structure B and A at their respective equilibrium distances (6.6 and 6.95 a.u.) as given by the Mulliken population analysis of the 4-31 G basis set calculations. Also the total populations of each molecule (in square brackets) are reported

exaggerated and the latter should be considered as upper limit values as concerns their use in interpreting physical situations.

The structures chosen for the H_2S–$(H_2O)_2$ trimers are depicted in Fig. 5 and consist of configurations quite similar to those proposed first by Hankins, Moskowitz and Stillinger [1] for $(H_2O)_3$ and then used by our group for the ammonia trimer [7]. The geometries of the water trimer were of double donor, double acceptor and sequential (called chain structure in [7]), with the latter being by far the most stable [1]. For $(NH_3)_3$ these same three geometries plus a cyclic structure (which would be of little interest in a mixed system as $H_2S(H_2O)_2$) were studied reaching the conclusion that all were relatively stable except for the double acceptor. Here we concentrate in chain and double donor structures which due to the presence of two different molecules in the trimer give the five geometries of Fig. 5.

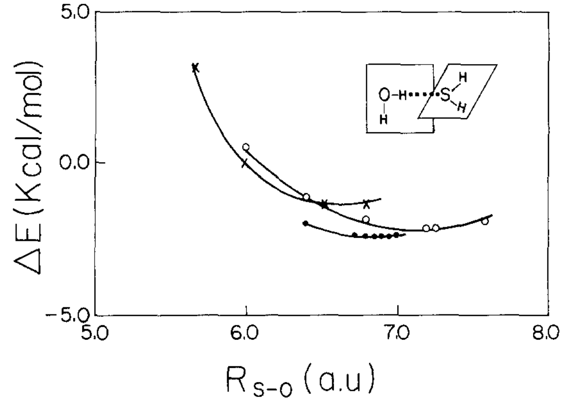

Fig. 3. Interaction energy curves obtained with several basis sets (××× = STO-4, ··· = 4-31 G, OOO = extended basis set from [6]) for Structure A

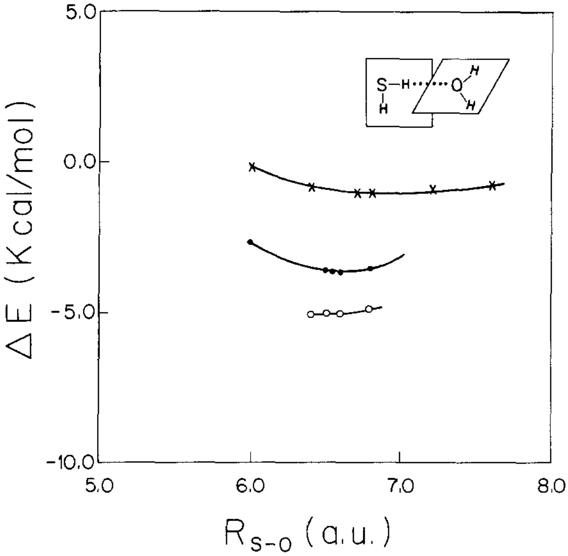

Fig. 4. Interaction energy curves obtained with several basis sets (××× = STO-4 G, ··· = 4-31 G, OOO = extended basis set from [6]) for Structure B

In Table 4 we report the total interaction energy, pair-wise-additive and non-additive three-body contributions (see Sect. 1) for each structure. As in the case of $(H_2O)_3$ and $(NH_3)_3$ we see that the chain- or sequential-structure III is the most stable (the cyclic structure of Ref. [7] can be considered a closed chain, of course). This and the other chain structures (II and III) have an attractive three-body energy. Both double donor structures (I and V) on the other hand have repulsive non-additivity, also in full rapport with the cases of $(H_2O)_3$ and $(NH_3)_3$. Such a repulsion is particularly large when H_2S is the double donor. Structure I in fact is the least stable of all trimers studied and in spite of the fact that H_2S is an efficient single-proton donor to H_2O, with a large pair interaction to which it can establish another S–H···O bond (see Fig. 5) is actually destabilizing

Table 4. Total interaction energies and its additive and non-additive components (in kcal/mole) for the geometries of Fig. 5

Geometry	Total interaction energy E(3)	Pairwise additive energy E(2, 3)	Non-additive energy E(3, 3)
I	−5.33	−6.09	+0.76
II	−7.07	−6.48	−0.59
III	−12.40	−11.55	−0.85
IV	−10.50	−10.11	−0.39
V	−8.60	−9.06	+0.46

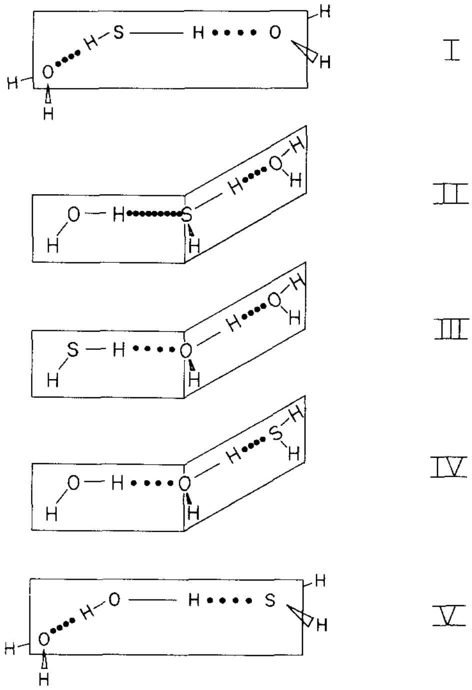

Fig. 5. Geometries of the five trimers studied

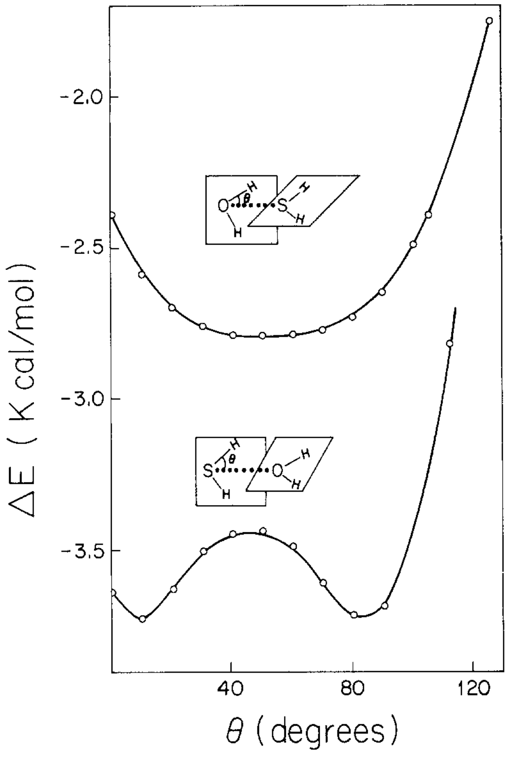

Fig. 6. Interaction energy curves obtained when the -OH or -SH bonds deviate from the S–O line

it. The other double-donor structure V (with a water in the central position) is reasonably stable in spite of its three-body repulsion. Of the three chains structure II in Fig. 5, which has H_2S intermediate between two water molecules also has a relatively smallish total interaction energy but has a three-body attraction comparable to the other two in which H_2S occupies a terminal position. All in all we see that the most stable structures are naturally III, IV and V because they maintain a hydrogen bonded water dimer. Out of these structures III, (i.e., the one maintaining the H_2S on a proton donating position) is particularly stable, which again is quite normal. But this is a relatively smallish contribution of H_2S to water-water interactions in say, a solvent-solvate situation, specially contrasting with the very important changes observed for other hydrated species, like double cations (see Ref. [13]).

Now we want to analyse the changes in the charge distribution when three-body effects are present. In Fig. 2 we already presented the situation for the dimers *A* and *B* essentially showing all the same features already reported in Ref. [6] where an extended set was used. Our 4-31 G results coincide almost perfectly with them *except* that the bond order of structure *B* is not as large as the extended set value, perhaps due to the substantially more profound energy well given by the latter set as can be seen in Fig. 4.

The charge distribution does not change so much in the trimers of Fig. 5 when compared with the dimers to justify including another figure. Let us rather try to state in a few short sentences the main changes, emphasizing these affecting the H_2S molecule and its bonds.

We shall start with structures I and II, where H_2S occupies the central position in the trimer and structure III where it is at the initial position of the hydrogen bonded chain (see Fig. 5). In all three of these structures one must compare with the dimer structure *B* in Fig. 2. They all have some common aspects, showing an increased polarity (specially in I and II perhaps in an attempt to compensate for their very small binding energy, see Table 4). Also in all of them the charge transfer towards H_2S is increased over the already notable value of dimer *B*. This confirms the proposition of Ref. [6] that H_2S acts both as a proton donor and electron acceptor in hydrogen bonded situations. It is notable that such similarities exist in spite of the fact that structure I presents repulsive three-body energy while II and III have attractive $E(3,3)$. This last fact however does introduce a difference concerning the bond orders. For the internal bonds in H_2S and of its H-bonds towards water of structures II and III bond orders are reinforced while for I, they are weakened, the same trend as for the non-additive energies in each case. Also noteworthy is the large H-bond population for III which precisely has the highest total and non-additive interaction energies of all trimers (see Table 4).

As concerns trimer structures IV and V which are related to dimer structure *A* we find that the former, which is stabilized by three-body attractions presents reinforcement of the effects present in dimer *A* including more charge transfer and increased H-bond order. The double-donor structure V on the contrary has a repulsive non-additivity and all the characteristics of dimer *A* in H_2S go down by 50%. These results show that when H_2S interacts with two layers of water as in structures III and IV (see Fig. 5) the sequential or chain structures are greatly stabilized. This may be compared with the similar situation of hydrated ions [13]. When H_2S is inserted within the water structure as in double donor structure V three-body effects destabilize the trimer both energetically and as concerns the charge distribution.

Up to now we have kept the proton of the H-bond strictly in the line of the heavy nuclei. To further relax the hydrogen bonded structures, we now relieve on the constrictions on the H_2S–H_2O structure by allowing the H-bond proton to rotate freely away from the S–O direction. The results given in Fig. 6 show relatively small energy changes. For the configuration *A* where H_2O acts as the proton donor the most stable situation is not with one O–H bond lying on the O–S line but rather when both O–H bonds can interact symmetrically with *S*. In any case the energy curve shows a rather flat and shallow minimum and energy changes of less than one half of a kcal/mole occur over a range of over 100° away from the O–S line. The other structure undergoes even smaller energy changes (of the order of only one fourth of a kcal/mole) over a similar range although now the preferential position of the SH_2 is with either of the S–H bonds

Table 5. Dispersion non-additive corrections calculated by the Axilrod–Teller formula, for the geometries of Fig. 5

Geometry	Non-additive Corrections (kcal/mole)
I	+0.0067
II	−0.0016
III	−0.0032
IV	−0.0032
V	+0.0052

very near to the S···O line (see Fig. 6). The possible consequences of this lack of directionality will be discussed in the following section.

Now we want to report the estimations of the dispersion contributions to the interaction energies obtained from the formulas of Eqs. (4–7). The two-body dispersion energies obtained from the London formula of Eq. (4) are reported in Table 3, as a function of the internuclear separation between the heavy atoms S and O. Not only the pairs contained in our trimers, e.g. water-water and H_2S-water, but also the H_2S–H_2S values are reported because in Ref. [5] it was implied that dispersion terms were dominant over the SCF pair energies for this last dimer. First of all we see that the dispersion pair energies are substantially smaller for the other two dimers which are the ones that interest us here. Even if we have an overestimation of the SCF energies and perhaps an underestimation of the dispersion correction by the London formula, we still can expect, specially at the distances pertinent to the minima, that the SCF will be dominant.

Now we pass to the three-body corrections given by the Axilrod–Teller formula of Eq. (5), which are reported in Table 5. From them we see that the non-additive corrections are very small, two orders of magnitude smaller, in fact, than the values reported in Table 3 for the SCF non-additive values. However, we also notice that the general trends in both these tables are quite similar, the double donor geometries showing a repulsive three-body effect, the chain structure an attraction, etc. This is remarkable considering that no structural information about the monomers is included in Eqs. (4–5). From the freely rotating picture derived above for the H_2S–H_2O pairs such an information should not, however, alter the main features of Tables 4 and 5.

4. Discussion

Now we shall try to discuss and correlate the results on the three-body non-additive effects of the H_2S–$(H_2O)_2$ trimer to well-known experimental situations. Specifically we want to consider the proton and deuterium transfer process between H_2S (and its isotopes) and water in the so-called G–S two-temperature process [16], as well as the role of H_2S clathrate formation [15]. These two aspects are not totally unrelated, due to the undesired possibility of clathrate formation which imposes a lower limit to the low-temperature that can be used in the G–S plants [26]. As concerns clathrate formation we thought that the fact that the H_2S gas hydrate freezes more readily than pure water, could conceivably be related to structure formation induced in the solvent layers by the H_2S solute molecules, in analogy to the situation found for hydrated divalent cations. For example three-body effects for solvated Ca^{++} and Mg^{++} are particularly large when they interact with two waters coming from two different solvation shells [13]. For the latter ion the non-additive contribution outweighs the water-water two-body attractions being of the order of 60 kcal/mole. This indeed indicates that a propagating effect from the metal on the 1st and 2nd hydration shell is present and indeed even the internuclear distances and angles of the hydrogen bonded water pairs is modified by its presence.

As concerns the H_2S solvate we find that a similar structure, where this said solvate also is interacting with two hydration shells (i.e. with two waters in the chain structure III of Fig. 7) is the one that introduces the largest three-body non-additive effect. This could also be considered a propagating effect over two solvent layers *but* the order of magnitude is so small (less than 1 kcal/mole) that this has but nominal consequences. This and the fact that the H_2S is relatively free to rotate, even when it is hydrogen bonded to a water molecule, lead us to think that there are no real structural effects on the clathrate formation by the H_2S. Even if this is a negative conclusion it deserves to be discussed in relation to the experimental knowledge.

First, it is known that clathrates contain almost spherical holes in an icelike lattice where each water molecule is hydrogen bonded to four nearest neighbor waters in geometries not too different from tetrahedral ice [15]. Furthermore the "guest molecules" have a remarkable degree of rotational mobility which makes clathrates quite different from other solids [15]. This is quite natural viewed from the point of view of our results, non-additivity is not large enough to change the H_2O–H_2O structures significantly. Also as we have seen from Fig. 7, H_2S can rotate so freely and it can interact with one H_2O with both protons simultaneously, etc. that one must conclude that if it is surrounded by six individual molecules in a clathrate cavity, then for all practical purposes it can take any imaginable position within it and also be absolutely free to rotate.

If three-body effects are not important as concerns H_2S clathrates, it is even less likely that they will be relevant to the H_2S–H_2O interactions when H_2S is bubbled in water during the two temperature G–S process. It seems natural to assume that the proton- and deuterium-transfer rate constants obtained recently [27] from the reaction between two molecules:

$$H_2O + HDS \rightleftarrows H_2S + HDO \tag{6}$$

using quantum mechanical partition functions will not be affected by the consideration of another H_2O molecule. The only way that three-body effects could change the results of Dave et al. [27] would be that the vibrational frequencies for the different species in Eq. (8) would be affected by the presence of another water molecule. We, however, have seen that no really significant modifications of the pair potentials are introduced by a third partner so we can see that the conclusions of Ref. [27] are valid and no correction due to non-additivity can change the equilibrium constant. This is not surprising considering that Dave et al. [27] have in fact shown that the gas-gas value of the equilibrium constant (relevant to the reaction of the two isolated molecules of Eq. (8) interacting in vacuum) does not change significantly when going to the gas-liquid reaction (which is the one relevant to the industrial G–S process). Remembering that the introduction of three-body effects can be considered as first step into solvent effects [4, 10–11] then it seems obvious that if the latter do not change the conclusions of the purely pairwise additive equilibrium constant, then neither can the former effects.

Obituary note

Three of us (O.N., M.G. and A.L.) have the sad duty to inform the scientific community of the premature and unexpected death of our dear friend and co-author Guillermo del Conde who was participating in the planning and development of this work. We know that anyone who ever met him will share our great sense of loss of the very dear friend and promising young scientist.

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