Theoret. Chim. Acta (Berl.) 51, 79–83 (1979)

THEORETICA CHIMICA ACTA

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Short Communication

Ab initio SCF MO Study of Hydrogen Bonds between H_2S and H_2O Molecules

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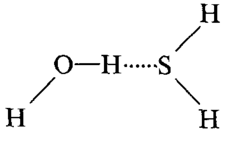
The hydrogen bonds between H_2S and H_2O molecules are calculated through an *ab initio*, LCAO MO SCF method using a Gaussian type orbital double-zeta basis set. The capacity of the H_2S molecule to act as an electron acceptor is confirmed.

Key words: H_2S–H_2O hydrogen bonds

Hydrogen bonds involving sulphydryl groups SH are important in several biochemical problems, such as their interactions with proteins [1, 2]. This has motivated some recent theoretical studies to establish whether H_2S is an electron donor or acceptor towards formamide [3] and the nature of the sulphydryl hydrogen bonding to the protein [4]. In nuclear chemistry the H_2S–H_2O system is of great importance, since the most developed industrial process for the production of heavy water (the so-called G-S process) involves the exchange reaction between H_2O and HDS [5]. Our main concern here is the study of the H_2O–H_2S supersystem in relation to the deuteration of heavy water. The complete potential energy surface of this supersystem is being obtained [6] following the work of Clementi and coworkers [7] on the water dimer and using different methods. We here present some preliminary results on the interaction energies of the two hydrogen bonded systems:



(A)

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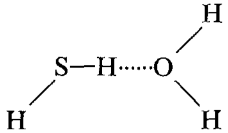

(B)

The method employed here is an *ab initio* molecular orbital calculation using the combined MOLECULE [8] and Hehenberger's [9] SCF program on a Burroughs 6700 computer. The basis set was selected to obtain essentially double zeta quality, as follows: for sulphur the one optimized by Roos and Siegbahn [10], for oxygen the Van Duijneveldt $8s3p$ set [11] and for hydrogen the Huzinaga $4s$ set [12]. We contracted the basis set according to a suggestion by Clementi [13]: S(5, 1, 1, 1, 1, 1; 3, 1, 1, 1); O(5, 1, 1, 1; 1, 1, 1) and H(3,1). Our computed total energies for H_2S and H_2O at their experimental equilibrium conformation [14] are -398.159490 and -75.897693 hartrees respectively. It should be pointed out that this energy for H_2S is obtained using the exponents as they appear in Ref. [10], namely the fifth exponent was 97.0448. However a referee, to whom we are grateful, pointed out a misprint in Ref. [10] where the exponent should read 79.0048. When this exponent is used the energy of H_2S is -398.496363. All the calculations that we report in this note were carried out with the published fifth exponent, however as it will be discussed later this does not affect our results for the interaction energies between H_2S and H_2O molecules. These values are in reasonable agreement with other calculations found in the literature (good compendia are given by Richards *et al.* [15]).

For the H_2S–H_2O supersystem we have kept the relative orientations fixed corresponding to the most stable configuration found by Clementi and coworkers [7] for the H_2O–H_2O system (in their notation the $\alpha=0$, $\beta=0$ configuration). Thus the only intermolecular parameter we allowed to vary was the oxygen sulphur separation distance R for each of the structures A and B.

In Table 1 the intermolecular interaction energies for structures A and B as a function of R are given, for the region near their respective minima. There are several interesting points to be noted. Structure A is stabilized when R is about 7.25 bohrs, with an energy of 2.08 kcal/mole while structure B is stable (with $\Delta E = 5.1$ kcal/mole) at about $R=6.5$ bohrs.

A calculation performed on the structure B at $R=6.6$ bohrs with the corrected exponent on the sulphur atom yields a relative energy of -0.008102 which is very close (0.000012 a.u.) to that obtained with the published fifth sulphur exponent. This gives us confidence in the quality of the double zeta basis we employed, further the population analysis shows changes of the order of 0.001 electron which do not affect the present discussion.

Kollman *et al.* [16], in their work on hydrogen bonded dimers include the S–H···O and O–H···S structures for the H_2S–H_2O supersystem. These authors report an energy of about 3.8 and 3.9 kcal/mole and an equilibrium distance of roughly 3.6 Å for both structures. This is a rather surprising result and an exception among the total of 144 hydrogen complexes reported in Ref. [16]. For all other hydrogen bonded molecular dimers they obtain a frankly asymmetric behaviour when the proton donor of the pair is changed to proton acceptor and vice versa. Energies change by a factor of two or three, the equilibrium distances by as much as one bohr when the hydrogen bond X–H···Y changes to Y–H···X for all the hydrides, except for the H_2S–H_2O supersystem. Thus we feel that the present results showing an asymmetry between our structures A and B are more in line with the general conclusions of Ref. [16].

Table 1. Intermolecular energies (hartrees) as a function of $R_{S\text{-}O}$ (bohrs) for S–H···O and as a function of $R_{O\text{-}S}$ for O–H···S

Structure B	
$R_{S\text{-}O}$	ΔE^a
6.0	0.022684
6.4	−0.008125
6.5	−0.008129[b]
6.6	−0.008114
6.8	−0.007943
Structure A	
$R_{S\text{-}O}$	ΔE^a
6.0	0.000871
6.4	−0.001893
6.8	−0.002885
7.2	−0.003317
7.25[b]	−0.00332[b]
7.6	−0.003057

[a] Defined as E_{syst}–($EH_2O + EH_2S$).
[b] Interpolated values.

Figure 1 shows the gross and overlap populations of the structures A and B referred to the infinitely separated molecule values. For structure A we find a very small charge transfer and weak polarization effect. The bond orders of the H_2S group are strengthened while those of H_2O are weakened. The situation for structure B is quite different, we notice that here the water molecule exerts a certain polarizing effect on the H_2S molecule. The charge transfer from H_2O to H_2S is not negligible amounting to 0.042 electrons and H_2S is consequently an electron acceptor. The bond order between the sulphur hydrogen and the oxygen is over five times larger for structure B that for structure A.

The results for structure B give us some grounds for comparison with the results of Otto *et al.* [3] in their analysis of the H_2S–formamide system as a model of sulphur hydrogen bonds with proteins. These authors conclude that H_2S acts as an electron acceptor with respect to the S–H···O hydrogen bond with formamide and consider this an unexpected result. But as seen above this is in full agreement for the same hydrogen bonded situation for the H_2S–H_2O supersystem. Furthemore they propose the S–O distance to be $R = 2.0$ Å which matches very reasonably with our

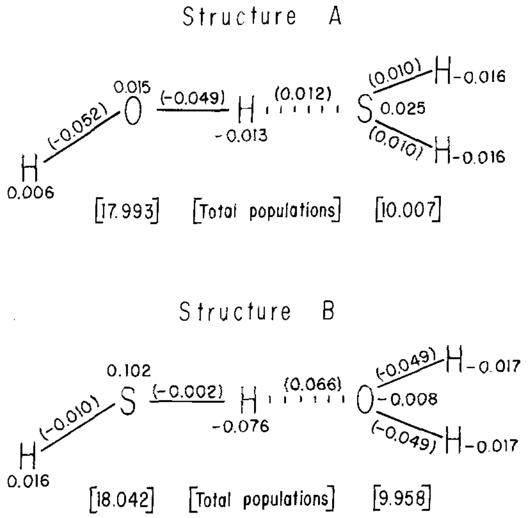

Fig. 1. Mulliken populations for internuclear distances of 7.2 a_0 (structure A) and 6.4 a_0 (structure B). Changes in the net atomic charges and overlap populations (in round brackets) as compared to the infinitely separated molecules are reported. Also the total populations of the molecules (in square brackets quoted in electrons) are given

value of $R = 2.3$ Å. The relevance of the present results in relation to the H_2O–HDS selective exchange will be discussed elsewhere [6].

Acknowledgements. We would like to express our gratitude to Paul S. Bagus for his interest and encouragement as well as to E. Clementi for discussions concerning the basis sets and contraction schemes used here and to M. Hehenberger for the use of his SCF programme. We also acknowledge interesting discussions with J. Pineda, J. L. Mateos and V. Coronado as well as the effective help of the computing center of UNAM.

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Received June 14, 1978/September 23, 1978