

Preliminary Note

Structure and stability of the gas phase complex of SO₂ with H₂O

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During recent years there has been evidence that the kinetics of certain reactions may be altered when the reactants are in the presence of another molecule to which one of them can become clustered. In particular, Hamilton and Naleway [1] suggested that reactions involving the free radical HO₂ may be influenced by the presence of H₂O or NH₃ that clusters with the HO₂. As part of the photochemical oxidation scheme proposed for the conversion of SO₂ to H₂SO₄ Davis [2] has proposed that HSO₃, formed on reaction of SO₂ with OH, becomes clustered with O₂ to form HSO₅. As part of the subsequent gas-to-particle conversion mechanism Calvert [3] and Holland and Castleman [4] suggested that the formation of H₂SO₄ aerosols from SO₃ commences [5] with the formation of the adduct SO₃·H₂O. The plausibility of this suggestion has been borne out by the calculations [4] of the structure and energy barrier to rearrangement of SO₃·H₂O to form H₂SO₄.

In order to account for their observations concerning the formation of aerosols via the photooxidation of SO₂, Friend *et al.* [6] postulated the role of clusters. Similar suggestions have been made independently by Friedlander and McMurray [7]. Very recently there has been considerable interest in the existence of adducts of SO₂ and H₂O in the atmosphere and a number of experiments are in progress concerned with this problem [8]. The purpose of this note is to report the results of complete neglect of differential overlap (CNDO/2) calculations of the structure of the SO₂·H₂O adduct.

To our knowledge these are the first molecular orbital calculations of the gas phase structure of the SO₂·H₂O adduct. The present calculations were carried out using a standard CNDO/2 program [9]; such calculations [10] have been successfully used by others for treating even-electron sys-

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tems of moderate size. This method was chosen as being relatively economical for the six atom-23 orbital system under consideration, particularly in view of the number of calculations necessary to optimize geometries and to investigate various configurations. It is well known that calculations made with this method tend to predict stabilities that are greater than those observed experimentally and also usually overestimate interatomic distances. Nevertheless, despite the relative simplicity of the calculational method, it often gives a good representation of relative stability and bond angles [11].

In our study, energy-minimized geometries were found for $\text{SO}_2 \cdot \text{H}_2\text{O}$, SO_2 and H_2O . Interatomic distances were obtained to 0.01 Å and bond angles were obtained to 0.5° (0.1° for H_2O). The geometry of minimum energy found for the $\text{SO}_2 \cdot \text{H}_2\text{O}$ adduct is shown in Fig. 1. The separate SO_2 and H_2O molecules were found respectively to have an O—S—O angle of 137° with S—O = 1.51 Å and an H—O—H angle of 104.1° with O—H = 1.03 Å. Energies corresponding to these geometries (in hartrees) are listed in Table 1.

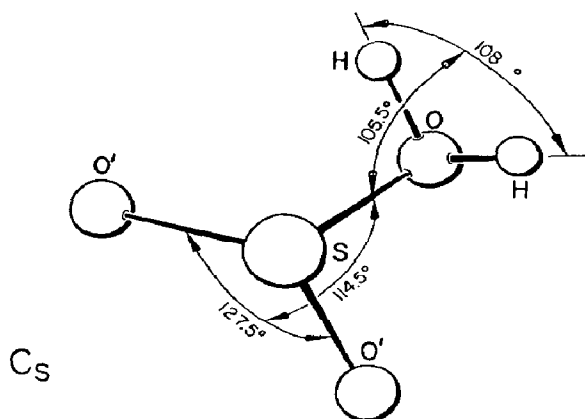


Fig. 1. CNDO/2 optimized geometry of the adduct of SO_2 and H_2O . The calculated interatomic distances are O—H = 1.04 Å, S—O = 1.75 Å and S—O¹ = 1.52 Å. The symmetry of the complex is C_s .

TABLE 1
Complete neglect of differential overlap
(CNDO/2) minimized energies

Molecule	Energy (hartrees)
$\text{SO}_2 \cdot \text{H}_2\text{O}$	-67.6430
SO_2	-47.6059
H_2O	-19.8912

In calculating the structure of the adduct, a number of different geometries of interaction between SO_2 and H_2O were found to give favorable bonding for the formation of a complex. Those in which the dipole moments of SO_2 and H_2O were aligned with respect to each other gave about 75% of the optimized bonding energy. Interestingly, those in which the dipole moments were oriented at right angles to each other gave a greater degree of interaction, about 85% of the optimized binding energy.

The geometry of the optimized $\text{SO}_2 \cdot \text{H}_2\text{O}$ adduct (Fig. 1) shows that the plane of the water molecule is tilted back from the S—O intermolecular axis, thus projecting a "lone electron pair" of H_2O at the sulfur of SO_2 . This result is very similar to that obtained for the $\text{SO}_3 \cdot \text{H}_2\text{O}$ adduct [4]. This configuration suggests that the adduct can be described as a Lewis acid-base pair, analogous to that of the $\text{SO}_2 \cdot \text{N}(\text{CH}_3)_3$ complex [12]. *Ab initio* calculations [13] on the $\text{SO}_2 \cdot \text{NH}_3$ and $\text{SO}_2 \cdot \text{N}(\text{CH}_3)_3$ complexes give geometries that are similar to that obtained for the $\text{SO}_2 \cdot \text{H}_2\text{O}$ adduct in the present work, namely a "lone electron pair" directed at the sulfur of SO_2 with the SO_2 bent back somewhat. The *ab initio* results give a bonding energy of $10.4 \text{ kcal mol}^{-1}$ [13] for the $\text{SO}_2 \cdot \text{NH}_3$ complex. Since NH_3 is a better Lewis base than H_2O is, the binding energy of an $\text{SO}_2 \cdot \text{H}_2\text{O}$ adduct should be less than 10 kcal mol^{-1} . Although there is no stable "sulfurous acid" structure for the $\text{SO}_2 \cdot \text{H}_2\text{O}$ adduct to which it can rearrange, a comparison with the results for the $\text{SO}_3 \cdot \text{H}_2\text{O}$ adduct is useful. The CNDO/2 results give a dipole moment of 6.94 D for the optimized $\text{SO}_2 \cdot \text{H}_2\text{O}$ adduct compared with 7.28 D and 0.62 D for the $\text{SO}_3 \cdot \text{H}_2\text{O}$ adduct and H_2SO_4 respectively. Since CNDO/2 calculations tend to overestimate bond lengths, these values are probably too high; for example, the calculated dipole moment of H_2O of 2.11 D compares with an experimental value [14] of 1.85 D. The CNDO/2 binding energy of $\text{SO}_2 \cdot \text{H}_2\text{O}$ is about 80% of that of the $\text{SO}_3 \cdot \text{H}_2\text{O}$ adduct [4].

In conclusion, CNDO/2 calculations suggest that an $\text{SO}_2 \cdot \text{H}_2\text{O}$ adduct should be stable in the gas phase although less strongly bound than other similar adducts. The optimized geometry of $\text{SO}_2 \cdot \text{H}_2\text{O}$ suggests that, similar to that of $\text{SO}_2 \cdot \text{NH}_3$, $\text{SO}_2 \cdot \text{N}(\text{CH}_3)_3$ and $\text{SO}_3 \cdot \text{H}_2\text{O}$, the adduct can be described as a Lewis acid-base pair. The results of the present study also suggest that an $\text{SO}_2 \cdot \text{H}_2\text{O}$ adduct would have a relatively large dipole moment.

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