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COMPUTATIONAL SOLUTION OF CHEMISTRY PROBLEMS

By

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THE HYDRATION OF SO₂: AN AB INITIO INVESTIGATION

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AB initio quantum chemical techniques have been used to investigate weakly bound complexes of $\overline{\text{H}_2\text{O}}$ and SO_2 . An energy gradient program was used to locate stable structures for the $\text{H}_2\text{O} \cdots \text{SO}_2$ complexes and SCF calculations were carried out to determine the binding energies of complexes with multiple water molecules. A 4-31G basis set was used for most potential energy searches. More accurate basis sets including a generally contracted basis set with d orbitals on the sulfur were used for geometry and binding energy verification. For single water complexes, five different stable geometries were located with binding energies between 4 and 11 Kcal mol⁻¹ suggesting a binding shell for $\overline{\text{H}_2\text{O}}$ around SO_2 and a mechanism for the formation of an $\overline{\text{SO}_2}$ -containing water droplet. Calculations on one of the complexes utilizing a larger double zeta basis and d functions on the sulfur atom lead to adjusted binding energies in the range 3 to 8 Kcal mol⁻¹. Very little charge transfer between $\overline{\text{SO}_2}$ and $\overline{\text{H}_2\text{O}}$ was present. Addition of more than one H_2O was found to be energetically

favorable although the addition of the fourth water in certain geometries did not increase the stability of the complex. An alternative mechanism for the tropospheric, gas phase production of acid rain is suggested.

Introduction

The oxidation of SO_2 is an important chemical process. The phenomenon of "acid rain" involves the oxidation of sulfur containing species including SO_2 to form SO_3 . Hydration is involved to give H_2SO_4 which in turn is ultimately precipitated as sulfates.¹ The influence which water plays on the kinetics of oxidation is less clear. However, Reiss noted a 4.7×10^3 fold increase in the rate of photo oxidation of SO_2 in the 283% relative humidity of a Wilson cloud chamber over that in the absence of water² and Ravishankara noted that the formation of aerosol upon the irradiation of gaseous mixtures containing H_2O and SO_2 and the formation of aerosol in $\text{H}_2\text{O} \cdot \text{SO}_2 \cdot \text{O}_2$ mixtures. Ravishankara further noted that aerosol formation occurred only for sufficiently high water vapor concentrations.³

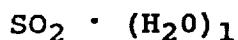
The stability of a complex of SO_2 and H_2O was first suggested by Phillips on the basis of results of semiempirical calculations.⁴ Holland and Castleman using CNDO/2 calculations suggested that an $\text{SO}_2 \cdot \text{H}_2\text{O}$ adduct should be stable in the gas phase and reported a binding energy of 145 mH and a large dipole moment.⁵

Evidence for the existence of $\text{H}_2\text{O} \cdot \text{SO}_2$ produced from the photolysis of H_2S in solid O_2 at 15K by ultraviolet light is presented by Tso and Lee who conducted an FTIR study of the photolysis mixture.⁶ Identification was based on shifted vibrational bands of SO_2 and H_2O .

The stability of SO_2 -water complexes has also been suggested from molecular beam measurements, and electric deflection experiments indicate a large dipole moment for the complex.⁷

Ab initio calculation on $\text{SO}_2 \cdot \text{NH}_3$ ⁸ and $\text{SO}_2 \cdot \text{HF}$ ⁹ show stable complexes for a variety of geometries. An important pair of calculations was done on the closely related complex $\text{H}_2\text{O} \cdot \text{SO}_3$ and its rearrangement to H_2SO_4 . A semiempirical CNDO/2 calculation by Holland and Castleman⁻¹⁰ has been followed by a recent ab initio calculation by Chen and Plummer.¹¹ After the completion of the calculations reported here, the authors became aware of a articles by Plummer¹² and by Plummer, Chen, and Law¹³ which reported ab initio results on two structures of the monohydrate of SO_2 obtained using an STO-3G basis set augmented by a set of d functions on the sulfur atom. Plummer reported binding energies of 10 and 2.3 Kcal/mol respectively for the two monohydrate structures studied. The structures reported by Plummer are similar to two of the monohydrates investigated in the present study, but the results differ significantly in detail from those reported here (vide infra).

In an effort to shed some light on a possible role of H₂O in the oxidation of SO₂ and elucidate the structure and energetics of formation of water complexes of SO₂, we have undertaken an ab initio study.



To explore the possibility of bound conformations of H₂O · SO₂ an SCF energy gradient program¹⁴ was used to locate stable structures for the complex. The 4-31G basis set was used for the initial potential energy searches. The minimum energy geometry was established when the largest component of the energy gradient was reduced to the order of 1 milliHartree per Bohr.

Five distinct conformations of the single water complex were found to be bound. These are shown in Figure 1. The total energies for the complexes and the molecular fragments as well as the binding energies are given in Table 1. The minimum energy geometry information is given in Table 2.

Conformations III and IV bear the closest relationship to classical hydrogen bonded structures, having respectively, one and two such bonds, and no significant binding interaction between the water oxygen and the sulfur atom. Conformation I, the most weakly bound, is at the opposite end of the scale with no hydrogen bonding, but has a favorable dipole interaction and a loose coordination between the water oxygen and the sulfur atom. Conformations II and V exhibit intermediate characteristics with both hydrogen bonding and O-S coordination. Except for the

interplanar angle between the two moieties, conformation V, the most strongly bound, exhibits the most favorable alignment of the fragment dipoles.

Hydrogen transfer with subsequent charge and structural relaxation from either conformation II or V would lead to the presumed structure of sulfurous acid. The coordination of the water oxygen and sulfur atom in conformations I, II, and V could also facilitate other reactions leading to oxidation of SO_2 .

In conformation III the out-of-plane angle of rotation of the nonhydrogen-bonded OH is very soft energetically and no angle is favored by more than a few tenths of a milliHartree. Conformation III is similar to the more weakly bound structure reported by Plummer except that the present conformation is for a cis arrangement of the two fragments while Plummer's structure is trans. The interfragment separations resulting from the two investigations were almost the same but Plummer found a binding energy (2.3 Kcal/mole) which is significantly smaller than that given in Table I for conformation III. The present structure provides a favorable electrostatic interaction between H2 and O1 of conformation III (Fig 1) and would be expected to yield a lower energy. Although the potential energy was found to be weakly dependent on the rotation angle of the nonhydrogen-bonded OH near the cis minimum, the calculations along this coordinate were not carried out at sufficiently large angles to determine if there is a significant potential energy barrier between the cis and trans structures.

Conformation V was suggested by the results of a semiempirical calculation⁵ but the minimum energy geometry result here indicates a preference for a cis arrangement rather than the trans arrangement of the semiempirical calculation. The potential energy surface search which led to conformation V was started near the geometry found by Castleman and migrated toward the cis conformation as the iterations continued. However, the calculations were converging quite slowly and were terminated with a structure similar to the more stable of the structures reported by Plummer. The calculations were restarted in a cis configuration and subsequent iterations produced a fairly rapid decrease in the interfragment bond length and a significant increase in the binding energy. In light of Plummer's results it appears that a trans structure was probably skipped over in carrying out the search. Although the literature contains a significant amount of information on the performance of various basis sets on covalently bonded molecules, the information available for evaluating the results obtained on weakly bound complexes using different basis sets is much more limited and somewhat contradictory. For example, while Raffenetti and Phillips¹⁵ found that SCF calculations utilizing an unpolarized ST0-3G basis set overestimated the binding energy of $\text{H}_3\text{N}-\text{HCl}$ by almost a factor of two, Lucchese, Haber, and Schaefer⁸ found that this basis set underestimated the binding energy of $\text{H}_3\text{N}-\text{SO}_2$ by a similar factor. The results obtained by the latter authors and the results of the present investigation are in agreement with respect to the relative importance of the completeness of the s and p

basis and the inclusion of d functions on the sulfur atom for the determination of binding energies. The fact that Plummer, Chen, and Law¹³ found that the binding energy of the structure reported by Plummer¹² decreased by 0.8 Kcal/mole when the flexibility of the STO-3G* basis was increased somewhat by splitting it to 3-21G* suggests that the minimum basis set results in an overestimation of the binding energy in this case. Qualitatively, the increased interaction energy resulting from the favorable arrangement of the fragment dipole moments in the cis structure also suggests that this structure should be more stable than the trans structure. The shorter interfragment bond length found for the cis conformation would be expected for a more tightly bound structure.

Figures 2 in the articles by Plummer and Plummer, Chen, and Law give a value of 2.7 Debye for the dipole moment of their more stable monohydrate structure^{12,13}. The value obtained for the cis structure in the present treatment with the DZP basis set is slightly smaller than these values, but the trans structure would be expected to have a larger dipole moment than the cis conformation.

To examine the effect of basis set size on the binding energy and geometry two additional SCF energy gradient calculations were performed on conformation V. In the first calculation a double zeta basis set was employed. The primitive basis set, a Huzinaga sulfur (12s/8p), oxygen (9s/5p), hydrogen (4s) set, was segmentally contracted.^{16,17} A Dunning contraction of the hydrogen and oxygen orbitals, O(9s/5p)/<6111/41>, H(4s)/<31>, and a McLean contraction of the sulfur orbitals, S(12s/8p)/<62211/621>, were

chosen.^{18,19} The binding energy decreased by 3.0 mH, a rough measure of the superposition error in the poorer basis set. In the second calculation a set of sulfur 3d orbitals ($\zeta_{3d} = 0.6$) was added to this basis set. The polarization functions reduced the SO₂ bond lengths and bond angle, decreased the SO₂ dipole moment, and lowered the binding energy of the complex by an additional 2.4 mH. The results of these two calculations are given in Tables 1 and 2.

Although the changes in the SO₂ structure and the complex binding energy were significant, the changes in the interfragment structural parameters were small. The decrease in the binding energy in the going from the 4-31G basis set to the more complete basis is very close to the percentage reduction which has been observed in previous treatments of similar complexes.¹⁵ The present results indicate that more than half of the discrepancy in the binding energy is due to the incompleteness of the s and p functions in the poorer basis with the balance being due to the absence of polarization functions. Further augmentation of the basis set with polarization functions would be expected to lead to monomer structures and dipole moments in better agreement with experiment and a slight further decrease in the predicted binding energies. The inclusion of electron correlation corrects for the tendency of the SCF model to predict too much charge separation and produces more accurate dipole moments for monomers. The net effect of including correlation for complexes such as those investigated here is to increase the binding energy of the complex

by an increment on the order of 1 Kcal/mol.^{15,20,21}



Selected two-water complexes were studied using the energy gradient program with the 4-31G basis set. The conformations are shown in Figure 2. Conformations VI and VII are mirror image doublings of conformations I and V, respectively.

The interatomic distances did not change significantly in going to the two-water complexes. The energies are given in Table 1. In both cases the binding energy of the two-water complexes are a little less than twice the binding energies of the one-water complexes indicating relatively little interaction between the water molecules and almost independent addition of the second water molecule.

In order to examine the energetics of adding multiple waters to SO_2 with the double zeta plus sulfur d orbital basis set, SCF calculations were run using a generally contracted basis set at fixed geometries predicted by the earlier gradient results. The primitive basis set was again the Huzinaga sulfur (12s/8p), oxygen (9s/5p), hydrogen (4s) set generally contracted to <4s/3p>, <3s/2p>, and <2s>, respectively.^{16,17,22} This set was augmented by a single set of 3d functions ($\alpha_{3d} = 0.6$) on the sulfur atom. This basis set was similar to the previous double zeta plus d set and the binding energy of conformation V obtained with this new basis set differed by only 0.2 mH from the previous result. Based on the results of optimizing the structure of complex V, the major effects of relaxing the geometry rather than using the

fixed geometries would be expected to be changes in the SO₂ structure with some attendant lowering of the energy of the complex. Thus the binding energies obtained using fixed geometries are lower limit SCF binding energies for the complexes.

The multiple-water complexes studied are shown in Figure 2. The total energies and binding energies are given in Table 1. Conformation I with this basis set produces a binding energy which is 72% of the binding energy derived from the earlier 4-31G calculation. This reduction in binding energy is virtually identical to that obtained for conformation V. The multiple-water complexes SO₂ (H₂O)_n with n = 3 and 4 differ by only a few mH from the sum of the binding energies of the separate bound pairs. This assumes that the energies of the conformations II and IV (which were not calculated with the larger basis) can be approximated by taking 70% of the binding energy obtained with the 4-31G basis set. The binding energy of the five-water complex is, however, significantly less than the sum of the binding energies of the separate bound-pairs.

The implications of the additivity of the binding energies supports the notion that the bonding interaction is nearly purely electrostatic. Only when the waters were close enough to interact with each other, as in the five-water complex, did the binding energy fall significantly below the sum of the binding energies of the separate bound pairs. An interesting corollary to the approximate additivity of the binding energies occurred in the three water complex, conformation VIII, which was slightly

more stable than predicted from the binding energy additivities perhaps due to a favorable alignment of the water dipoles. These results suggest that the binding energy of some multiple water complexes which could be modeled by superposition of smaller complexes, but which have not been investigated here, would deviate significantly from additivity due to water-water interactions.

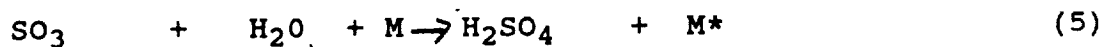
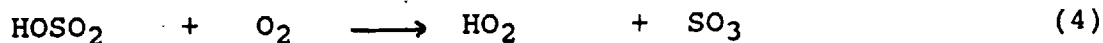
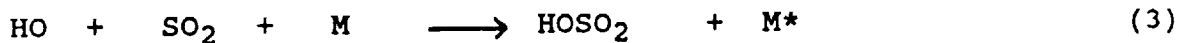
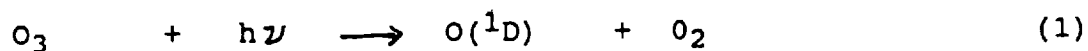
Although a Morakuma component analysis²³ of the energy components of the $\text{H}_2\text{O} - \text{SO}_2$ interaction was not made, the results obtained here suggest that the analysis would follow that for the $\text{NH}_3 \cdot \text{SO}_2$ complex⁷ as discussed by Kollman.²⁴ Mulliken population analyses²⁵ of the results of SCF calculations on the $\text{H}_2\text{O}-\text{SO}_2$ complex using the best basis set show a small charge transfer resulting in a small negative charge on the SO_2 . See Table 1. With the 4-31G basis set the charge transfer was about fifty percent larger, a consequence of basis set superposition error. The 4-31G basis set calculation for conformation IV produced the unique result of a charge transfer in the opposite direction from all the other results. Since the charge transfer and polarization effects are small, the minimum energy geometry is determined by a balance of the electrostatic energy and the exchange repulsion energy. However, unlike the $\text{NH}_3 \cdot \text{SO}_2$ complex, the minimum energy orientation for the H_2O and SO_2 fragments in conformation V is closer to that predicted solely from consideration of the dipole-dipole interaction.

The H-bonded complex, conformation III, has a binding energy (4.7 Kcal) which is virtually the same as that obtained for the HF · SO₂ complex (5Kcal).⁹ The minimum energy complex, conformation V, has a binding energy (10.9 Kcal) very close to that obtained for the NH₃ · SO₂ complex (9.3 Kcal).⁸ It should be noted that inclusion of d orbitals in the sulfur basis set reduced the binding energy of NH₃ · SO₂ from 10.4 Kcal to 9.3 Kcal, an effect that was also observed in the H₂O · SO₂ calculations. The CNDO/2 results of Castleman gave a much larger binding energy (98.3 Kcal) and a different minimum energy geometry.⁵

In the analysis of his molecular beam electric deflection results Castleman, remarks on the existence of species with large dipole moments that he attributes to H₂O · SO₂ complexes.⁷ The dipole moments for some of the complexes were calculated in this study and are reported in Table 2. These values are all overestimated, particularly those from calculations which did not include sulfur d orbitals in the basis set.

The gradient SCF program can also be used to produce force constants and fundamental frequencies for vibrational modes. However, the equilibrium geometries were not converged to sufficient accuracy to enable predicting the sizes and signs of the frequency shifts of SO₂ and H₂O vibrations upon complexation. Better convergence would allow comparison with the experimental IR spectroscopic results of Tso and Lee who claim to have evidence for the existence of the H₂O · SO₂ complex.⁶

The gas phase reactions of SO₂ with a number of oxidants are exothermic, but the measured bimolecular rates for most such reactions are quite small.²⁶ In some cases, such as the reaction between SO₂ and CH₃O₂, complexes which subsequently decompose to the reactants are believed to be formed in preference to the bimolecular reaction.²⁶ Thus oxidants like O₃, NO₂, H₂O₂, HO₂, and CH₃O₂ which have the highest concentrations in the troposphere aren't considered important in the homogeneous oxidation of SO₂, except in moderately to highly polluted air. Instead, most of the gas phase oxidation of SO₂ to H₂SO₄ is believed to proceed by the following mechanism:



At 300K, this mechanism requires a steady state OH concentration of about 10⁷ cm⁻³ in order to yield an SO₂ lifetime on the order of hours. Unfortunately, the distribution of OH in the troposphere is not known accurately. Since the above mechanism is driven by photochemistry and the lifetime of the OH radical is very short,

it is operative only in daylight hours.

Heterogeneous removal of SO_2 by H_2O_2 , NO_2 , and other species has been observed in aqueous solutions, however^{1,27}. Heterogeneous oxidation of SO_2 in cloud droplets is now considered to be significant but remains to be accurately quantified. Estimates of SO_2 removal rates due to heterogeneous oxidation by H_2O_2 dissolved in cloud droplets range up to several hundred per cent per hour.¹

Penzhorn and Canosa²⁸ have reported water vapor catalysis of the reaction with NO_2 . The results of the present investigation raise the possibility that complexes of SO_2 and H_2O may provide a homogeneous mechanism for catalyzing the oxidation of the former by oxidants which are present in the atmosphere at concentrations significantly greater than those of OH. This mechanism would not be subject to the pH quenching observed for many of the heterogeneous reactions. Such a mechanism could be important if the product of the equilibrium constant for the complex, the concentration of water vapor, the reaction rate, and the concentration of the oxidant were on the order of 10^{-5} . This is equivalent to the oxidation rate due to 10^6 OH molecules cm^{-3} at 300K. A somewhat smaller product would be significant for oxidants which do not drop to zero concentration in the absence of sunlight.

Determining an accurate first principals estimate of the temperature dependent equilibrium constant would require knowledge of the barriers separating the various structures identified for the single water complex, barriers to free internal rotation,

vibrational frequencies, and the vibrational anharmonicities. A rough estimate of the range into which the equilibrium constant might be expected to fall can be obtained by comparison with the information available on other weakly bound complexes. Curtiss, Frurip, and Blander have determined K for both H_2O and D_2O dimers between 358K and 387K.²⁹ At 358K their results for D_2O give K as $7 \times 10^{-19} \text{ cm}^3 \text{ molec}^{-1}$. Extrapolating their results to 300K yields an association constant of about $1.4 \times 10^{-18} \text{ cm}^3 \text{ molec}^{-1}$. The calculated electronic binding energy for H_2O-SO_2 is higher than that of the D_2O dimer which would lead to a somewhat higher enthalpy of formation. Curtiss et. al obtained a standard entropy change of association of $-18.67 \text{ cal/deg-mol}$ for the D_2O dimer. The possibility that the multiple binding sites for H_2O in the H_2O-SO_2 complex may contribute to the entropy change makes estimates of the latter subject to considerable uncertainty, but for the present purposes we may assume that it is approximately equal to that of the D_2O dimer. This would lead to a lower limit of about $10^{-18} \text{ cm}^3 \text{ molec}^{-1}$ for the association constant with an upper limit as much as a factor of 100 larger.

For the smaller of these two limits and water vapor concentrations appropriate for humid summer conditions, the reaction rate required to meet the above criteria would be on the order of $10^{-17} \text{ cm}^3 \text{ molec}^{-1}\text{s}^{-1}$ for ozone and $10^{-13} \text{ cm}^3 \text{ molec}^{-1}\text{s}^{-1}$ for oxidants present at relative concentrations of a few parts per trillion.

For a number of oxidants, such as H_2O_2 , which are present in moderately polluted air at relative concentrations on the order of 1 ppb, an intermediate rate of about $10^{-16} \text{ cm}^3 \text{ molec}^{-1}\text{s}^{-1}$ would be required. With an equilibrium constant near the upper limit, the rates required for oxidants to be effective according to the criteria above would be proportionately lower. Currently recommended upper limits for the uncatalyzed reactions of trace oxidants other than OH with SO_2 range from $5 \times 10^{-17} \text{ cm}^3 \text{ molec}^{-1}\text{s}^{-1}$ for CH_3O_2 to $2 \times 10^{-26} \text{ cm}^3 \text{ molec}^{-1}\text{s}^{-1}$ for NO_2 . The formation of $\text{H}_2\text{O}-\text{SO}_2$ complexes is undoubtedly the basis for the mechanism by which H_2O enhances the rate of the NO_2 reaction by many orders of magnitude. It appears likely that such complexes may react with other oxidants at rates much higher than those with SO_2 and that one or more such reactions may make a significant contribution to the observed rate of SO_2 oxidation in the atmosphere.

The dependence of this H_2O catalyzed mechanism on oxidant concentrations would lead to the observed seasonal dependence of SO_2 oxidation rates. (1)

In summary, an energy gradient program was used to locate stable structures for $\text{H}_2\text{O} \cdot \text{SO}_2$ complexes and SCF calculations were carried out to determine the binding energies of complexes with multiple water molecules. A 4-31G basis set was used for most potential energy searches. More accurate basis sets including a generally contracted basis set with d orbitals on the sulfur atom were used for geometry and binding energy verification. For one water complexes five different stable geometries were located

with adjusted binding energies between 3 and 8 Kcal mol⁻¹ suggesting a binding shell for H₂O around SO₂. Very little charge transfer between SO₂ and H₂O was present. Addition of more than one H₂O was found to be energetically favorable and approximately additive up to four added waters. An alternative mechanism for the tropospheric, gas phase production of acid rain is suggested. A process for the formation of an SO₂ containing water droplet is advanced.

Acknowledgement. This work was supported by NASA Grant NAG-1-596.

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Table 1. SCF total energies (Hartrees), binding energies (Kcal mol⁻¹), in parentheses, and total charge on SO₂ of SO₂ (H₂O)_n complexes.

	Geometry Optimized			Geometry Fixed	
H ₂ O	-75.9086	-76.0110	-76.0110	-76.012 ¹	-
SO ₂	-546.3733	-546.9719	-547.1540	-547.1755	-
I	-622.2894(4.7)	-	-	-623.1930(3.4)	-0.003
II	-622.2943(7.8)	-	-	-	-
III	-622.2894(4.7)	-	-	-	-
IV	-622.2902(5.8)	-	-	-	-
V	-622.2993(10.9)	-622.9974(9.1)	-623.1770(7.5)	-623.1998(7.6)	-0.035
VI	-698.2120(13.5)	-	-	-	-
VII	-698.2236(20.8)	-	-	-699.2212(13.5)	-0.067
VIII	-	-	-	-775.2437(20.0)	-0.061
IX	-	-	-	-851.2560(20.1)	-0.056
X	-	-	-	-927.2703(21.5)	-

Basic Set A B C D D

A: 4-31G
 B: Double Zeta S(12s/8p)/<62211/621>, O(9s/5p)/<6111/41>, H(4s)/<31>
 C: Double Zeta + Sulfur d
 D: S(12s/8p/1d)/<4s/3p/1d>, O(9s/5p)/<3s/2p>, H(4s)/<2s>

Table 2. Bond distances, bond angles, and dipole moments for fragments and complexes from SCF geometry optimizations

	Basis set	R(SO)	L(OSO)	R(OH)	L(HOH)	LA LB	RA	Dipole moment
H ₂ O	A	--	----	0.951	111.2	--	--	2.49
	B	--	----	0.952	112.5	--	--	2.53
SO ₂	A	1.530	114.2	---	---	--	--	3.30
	B	1.535	113.0	---	---	--	--	3.44
	C	1.428	118.1	---	---	--	--	2.67
I	A	1.531	113.1	0.951	111.0	--	3.27	--
							2.86	
II	A	1.528 / 1.534	112.9	0.953 / 0.949	112.1	--	2.54	--
III	A	1.525 / 1.531	114.3	0.953 / 0.950	110.6	--	2.02	6.10
IV	A	1.531	112.8	0.951	110.3	--	2.37	6.35
						90.4		
V	A	1.533	113.6	0.953	112.5	124.4	2.48	2.95
						89.4		
	B	1.541	112.6	0.953	113.2	125.9	2.49	2.92
						87.6		
	C	1.427	115.7	0.953	113.8	129.0	2.52	2.51
							2.85	
VI	A	1.534	112.5	0.951 / 0.949	112.3	--	2.54	--
						90.3		
VII	A	1.541	113.0	0.953	112.5	124.7	2.48	0.07

All distances are in Angstroms. Dipole moments are in Debyes. A second set of bond lengths is given for asymmetric complexes.

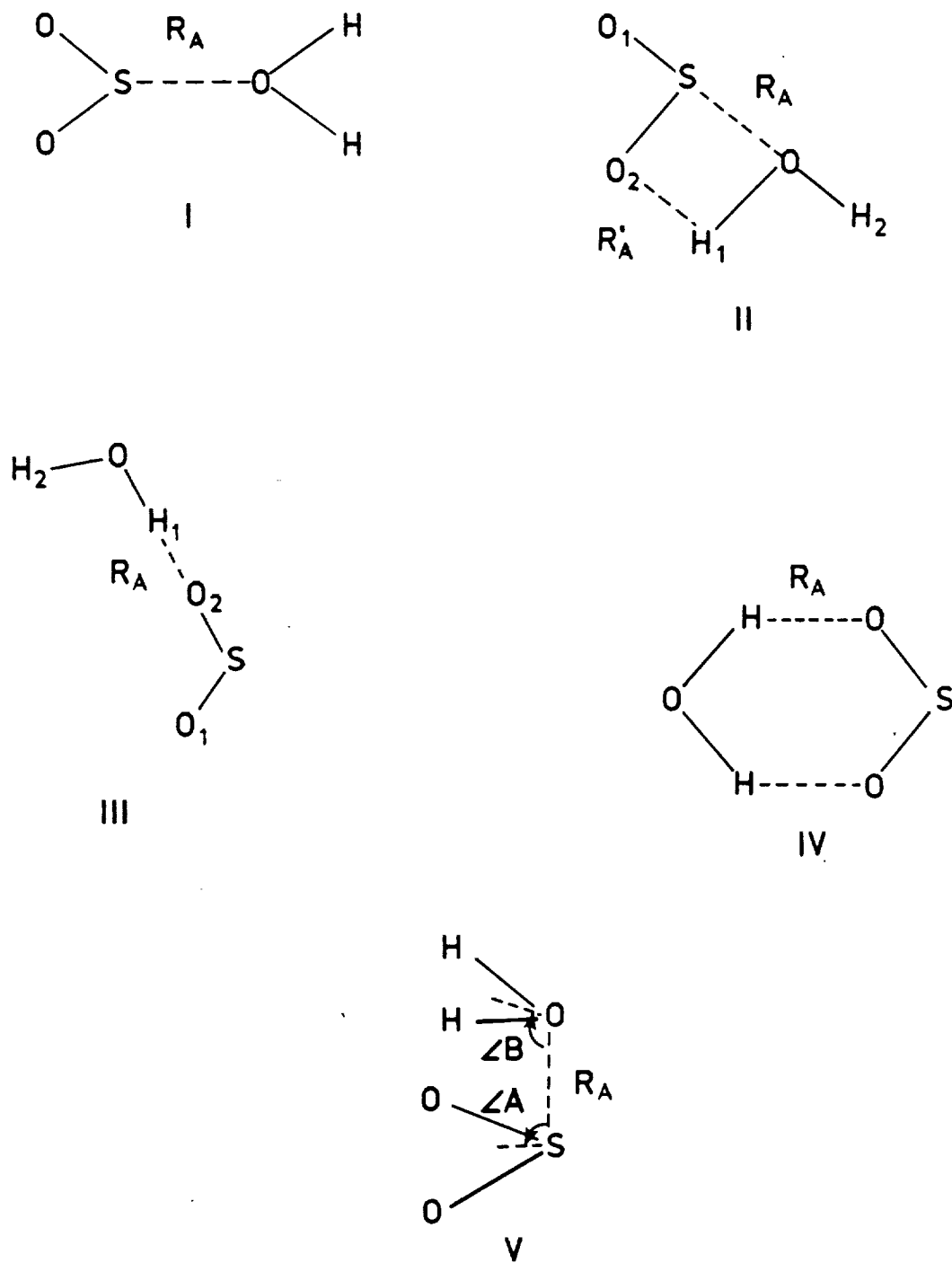
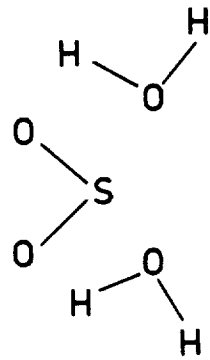
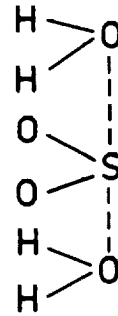


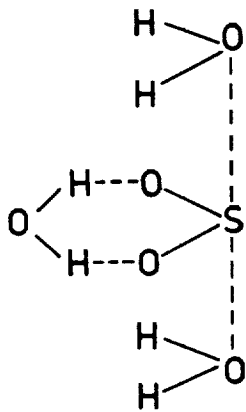
FIGURE 1. CONFORMATIONS OF $\text{SO}_2 \cdot \text{H}_2\text{O}$ COMPLEXES



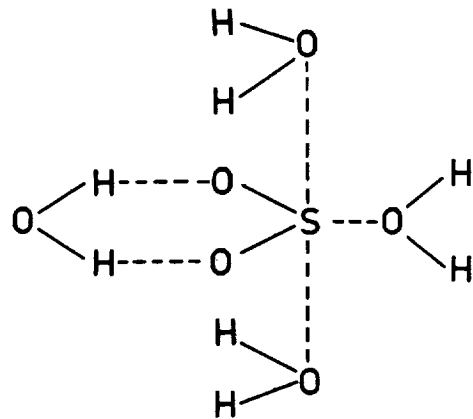
VI



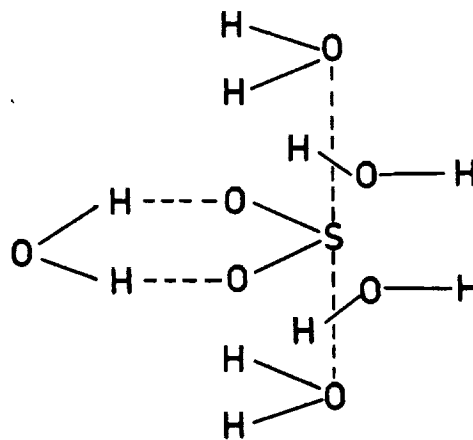
VII



VIII



IX



X

FIGURE 2. CONFORMATIONS OF MULTIPLE WATER COMPLEXES OF SO_2 .