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H-Bonded $CH_3SO/H_2SO_4/H_2O$ Complexes: A Quantum Chemical Study

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Dedicated to prof. Jože Koller on the occasion of his 70th birthday.

Abstract

The structural, electronic, and spectroscopic properties of complexes of the methyl sulfinyl radical, sulphuric acid and water molecules have been studied by density functional theory and ab initio methods. The hydrogen bond interactions between the CH_3SO radical, H_2SO_4 and H_2O molecules have been characterised. The calculations predict relatively large binding energies for the complexes of 12.2 kcal mol^{-1} for the most stable $CH_3SO–H_2SO_4$ complex, 19.1 kcal mol^{-1} for $CH_3SO–H_2SO_4–H_2O$ complex and 28.8 kcal mol^{-1} for $CH_3SO–H_2SO_4–2H_2O$ complex at the CBS–QB3 level of theory. The relatively high stabilisation of the complexes is likely to have significant effects on the overall processes that lead to the formation of new-particles in the atmosphere. Infrared spectroscopy is suggested to be a potentially useful tool for the detection of these complexes either in laboratory experiments or in atmospheric observations. The electronic spectra of the complexes have been examined, and their photochemical spectral features are discussed. The hydrated $CH_3SO–H_2SO_4$ complexes can be expected to undergo photolysis in sunlight.

Keywords: hydrogen-bond complexes, methyl sulfinyl radical, sulphuric acid, water, nucleation precursors, quantum-chemical methods

1. Introduction

Sulphur-containing species are of significant interest in the atmospheric chemistry of the marine boundary layer. The methyl sulfinyl radical CH_3SO is a key intermediate in the atmospheric oxidation of dimethyl sulphide CH_3SCH_3, which is the largest natural source of reactive sulphur emitted into the troposphere.[1] The radical is relatively stable,[2] but the concentration in the atmosphere is small, making its direct observation difficult. The recent work of Reisenauer et al.[3] is dedicated to the matrix-isolation technique, investigating the spectroscopic properties of the CH_3SO radical by UV/Vis spectroscopy. As the most abundant greenhouse gas, water can form complexes with this radical, affecting its stability and changing its photochemical features, which has been studied in detail.[4]

Sulphuric acid is one of the most important vapours leading to the formation of secondary aerosols.[5] Sulphate aerosols have a large cooling effect on the global climate. In contrast to primary aerosols, which are released directly into the atmosphere from geogenic and anthropogenic sources, secondary aerosols are produced in the atmosphere by nucleation from gas-phase species.[6] The new-particle formation is initiated by the interaction between various atmospheric constituents or/and contaminants. The atmospheric nucleation processes are not yet well understood and are difficult to probe by experimental means. A physical understanding of the nucleation process would enable researchers to predict the nucleation rate, an essential variable in improved atmospheric models. High-level density functional and ab initio calculations represent a powerful tool for gaining insight into the nucleation mechanism at the molecular level: for instance, they are able to describe the very first step of particle formation in the atmosphere.

This work presents a comprehensive series of electronic structure calculations on H-bonded complexes of the CH_3SO radical with one molecule of H_2SO_4 and their subsequent hydration with one or two molecules of water. The primary focus of the study is to characterise the structure, calculate the binding energy and predict the influence of H-bonding on the infrared spectra of the H-bonded

OH stretching modes in these complexes. Finally, the vertical excited state energies of the complexes will be calculated to determine to what extent the complexation might influence the electronic spectra of radicals within the acid and water complexes.

The CH_3SO–H_2SO_4 complexes and their hydration have not, to the best of our knowledge, been reported before, either experimentally or theoretically. Due to their role in new-particle formation in the troposphere, proposed studies are highly desirable.

2. Computational Methods

Electronic structure calculations for systems containing the methyl sulfinyl radical, sulphuric acid and water were performed with the GAUSSIAN 09 program.[7] All complex geometries were optimised using the Becke three-parameter non-local exchange functional[8] with the non-local correlation of Lee, Yang and Parr (B3LYP)[9,10] and the People-type 6-311++G(2df,2pd)[11] basis set. The proposed level of calculations has been proven to be an economical and accurate computational model for obtaining reliable results and has been employed widely.[4] The spin contamination was monitored for all species, and the $<S^2>$ value showed insignificant deviation from the expectation value of 0.75 for open shell species. The harmonic and anharmonic frequencies of all species were computed at the same level of theory to confirm the nature of the stationary points and to determine the zero-point energies. The geometries of the certain complexes have been reoptimised by the coupled cluster with single and double excitation method (CCSD)[12,13] in conjunction with the Dunning aug-cc-pVDZ basis set[14,15] to further verify the reliability of the density functional method for the prediction ground-state geometrical parameters of hydrogen-bonded complexes. It is known that coupled cluster methods are well suited for determining hydrogen bonding interactions. The rotational constants were evaluated for the B3LYP/6-311++G(2df,2pd) geometrical parameters. The final energies of the complexes were improved using the CBS-QB3 level of theory.[16] Additionally, for the purpose of comparison, the energies were also evaluated by the G4 method.[17] Vertical excitation energies were calculated with time-dependent DFT (TDDFT).[18] TDDFT calculations were performed with the B3LYP functional and the aug-cc-pVTZ basis set on the B3LYP/6-311++G(2df,2pd) geometry.

3. Results and Discussion

The optimised geometry for the structures of the CH_3SO radical, H_2SO_4 and H_2O molecules at the B3LYP/6-311++G(2df,2pd) level of theory are shown in Figure 1.

The structures of 1:1 CH_3SO-sulphuric acid complexes are illustrated in Figure 2, and 1:1:1 and 1:1:2 CH_3SO-sulphuric acid-water complexes are given in Figure 3 and Figure 4, respectively. The particular type of complexes are labelled as MS-SA, MS-SA-W and MS-SA-2W, respectively, where MS denotes methyl sulfinyl radical, SA denotes sulphuric acid and W denotes a water molecule.

The descriptive bond lengths of the structures are displayed in the figures, and the CCSD/aug-cc-pVDZ parameters for a few complexes are also provided. The Cartesian coordinates for all of the studied structures (Table SI-1) are available in the Supplementary data. The harmonic and anharmonic vibrational frequencies, along with the IR intensities for the water, sulphuric acid and CH_3SO radical (Table SI-2), and sulphuric acid-complexes, sulphuric acid-water complexes and sulphuric acid-2water complexes (Table SI-3, Table SI-4, Table SI-5, respectively), are also available in the Supplementary data. The reasonable agreement between the B3LYP and CCSD geometrical parameters indicate that more the economical B3LYP method would be relevant for the geometry prediction of these species.

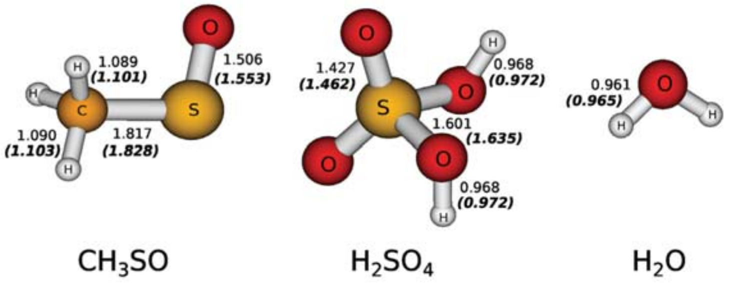

Figure 1. B3LYP/6-311++G(2df,2pd) optimised structures of the CH_3SO radical, H_2SO_4 and H_2O molecules. In parentheses are the CCSD/aug-cc-pVDZ parameters. Bond lengths are in Å.

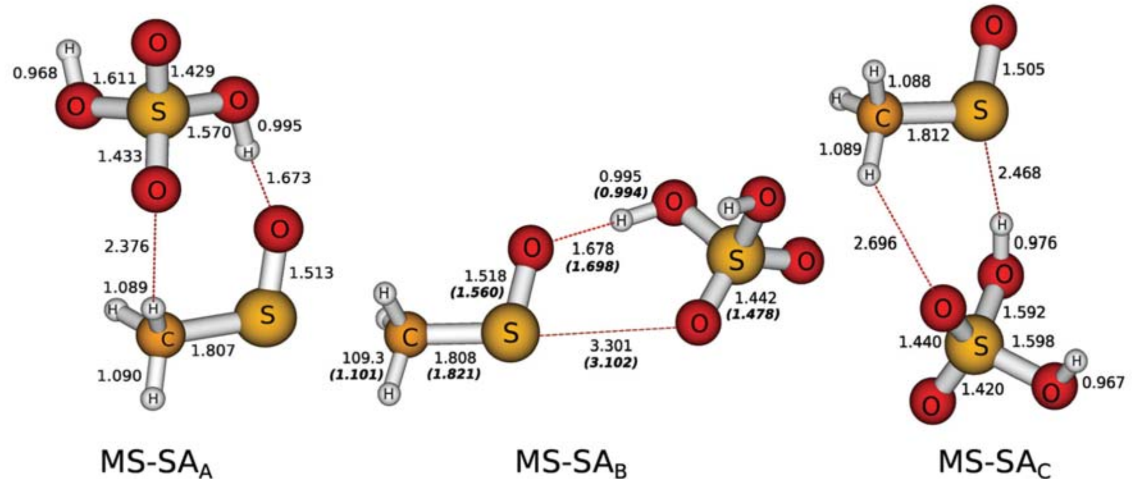

Figure 2. B3LYP/6-311++G(2df,2pd) optimised structures of the $CH_3SO–H_2SO_4$ complexes. In parentheses are the CCSD/aug-cc-pVDZ parameters. Bond lengths are in Å.

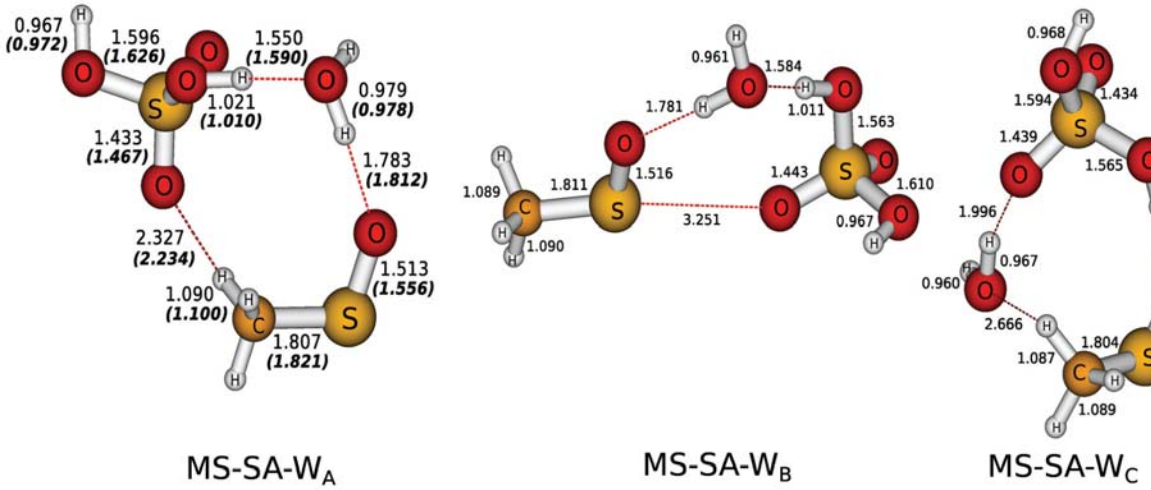

Figure 3. B3LYP/6-311++G(2df,2pd) optimised structures of the $CH_3SO–H_2SO_4–H_2O$ complexes. In parentheses are the CCSD/aug-cc-pVDZ parameters. Bond lengths are in Å.

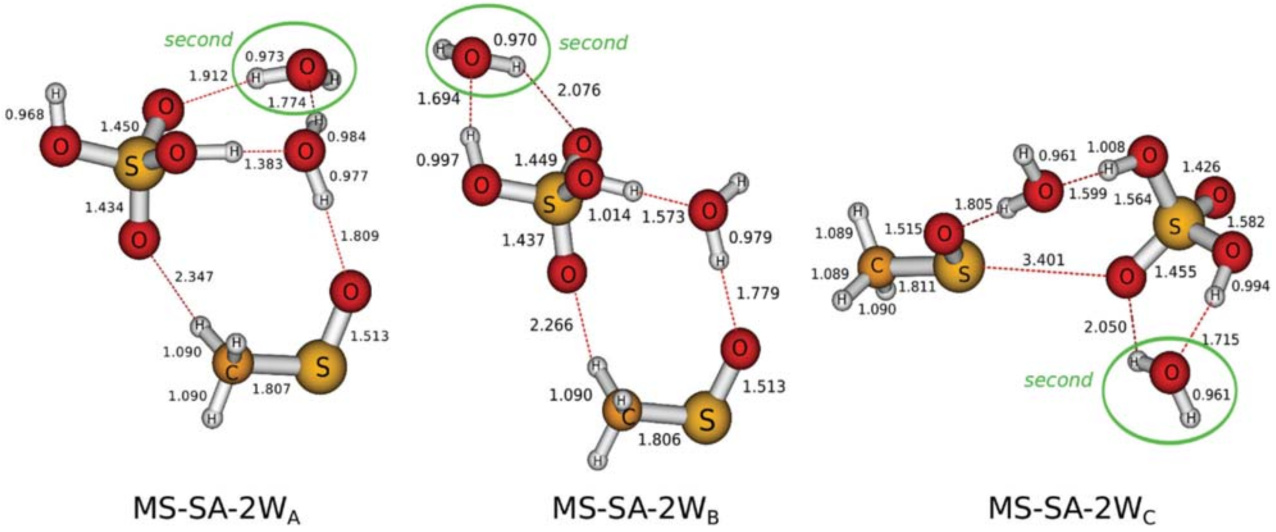

Figure 4. B3LYP/6-311++G(2df,2pd) optimised structures of the $CH_3SO–H_2SO_4–2H_2O$ complexes. Bond lengths are in Å.

The hydrogen bond distances for the complexes are summarised in Table 1. Table 2 presents the binding energies for the CBS-QB3 and G4 composite methods, along with the B3LYP/6-311++G(2df,2pd) binding energies. The CBS-QB3 and G4 Gibbs free energies are also involved in Table 2. The comparison of the binding energies obtained with both compound methods shows good agreement between the two values, and the G4 values are on average 1.4 kcal mol^{-1} higher. The CBS-QB3 and G4 methods are estimated to be accurate to 0.87[16] and 0.83 kcal mol^{-1},[17] respectively. In the following discussion, the B3LYP/6-311++G(2df,2pd) geometrical parameters and the CBS-QB3 binding energies will be used unless stated otherwise. The equilibrium rotational constants calculated at the B3LYP/6-311++G(2df,2pd) level of theory are presented in Table 3 and would be valuable for eventual identification by microwave spectroscopy. Selected IR spectroscopic findings are collected in Table 4, and Table 5 presents the vertical excitation energies.

3. 1. Geometrical Parameters and Binding Energies

CH_3SO–H_2SO_4 Complexes. A large set of initial guess configurations for the CH_3SO-sulphuric acid complexes have converged after full geometry optimisation to the three stable hydrogen-bonded structures, designated as MS-SA$_A$, MS-SA$_B$ and MS-SA$_C$, shown in Figure 2. In the MS-SA$_A$ cyclic complex, the shorter H-bond is 1.673 Å long, resulting from the interaction between the lone pair on the oxygen atom of the MS and H atom of SA, thus with SA as hydrogen donor. The second H-bond is longer at 2.376 Å with MS as the hydrogen donor. The complex is quite stable, and the binding energy of the complex is 12.2 kcal mol^{-1}. The next structure, the MS-SA$_B$ complex, has slightly lower binding energy, 10.0 kcal mol^{-1}, compared to the MS-SA$_A$ complex and possesses only a single H-bond with the SA molecule acting as a hydrogen donor. However, the MS-SA$_B$ complex is relatively stable, suggesting that H_2SO_4 forms a strong H-bond through the interaction of its H atom with the lone oxygen electron pair of CH_3SO. In addition, the MS-SA$_B$ complex is stabilised by the van der Waals interaction between the oxygen atom of sulphuric acid and the sulphur atom of the CH_3SO radical. The last stable structure found, a cyclic MS-SA$_C$ complex, is formed by intermolecular C–S···H–O and C–H···O–S bonds with bond lengths of 2.468 Å and 2.696 Å, respectively. Due to the two weak bonds in the complex the binding energy is small, 4.2 kcal mol^{-1}.

CH_3SO–H_2SO_4–H_2O Complexes. The optimisation of the extensive set of initial geometrical structures for the CH_3SO–H_2SO_4–H_2O complex again yields three different structures, MS-SA-W$_A$, MS-SA-W$_B$ and MS-SA-W$_C$, which are presented in Figure 3. The MS-SA-W$_A$ complex is a cyclic structure with triple H-bonds. H_2O molecules in this complex act as an H acceptor from the H_2SO_4 molecule with a strong O–H···H bond with a length of 1.550 Å and as an H donor to the oxygen atom of the CH_3SO radical, also with a relatively strong O···H–O bond that is 1.783 Å long. The third intermolecular H–bond is longer at 2.327 Å and results from interaction of the methyl hydrogen atom and the sulphuric acid oxygen atom. The complex is fairly stable, with a binding energy of 19.1 kcal mol^{-1}. Further, the MS-SA-W$_B$ complex, with a computed binding energy of 17.4 kcal mol^{-1}, is held together by two hydrogen bonds and one van der Waals interaction. The nature of the two hydrogen bonds are similar to those in the MS-SA-W$_A$ complex: thus, their bond lengths of 1.584 and 1.781 Å are also comparable to those in the MS-SA-W$_A$ complex. The van der Waals interaction occurs between the oxygen atom of sulphuric acid and the sulphur atom of the CH_3SO radical. The last three-body complex, MS-SA-W$_C$, is again stabilised by three hydrogen bonds. The stronger bond with sulphuric acid as proton donor is 1.596 Å long, whereas the H-bond with sulphuric acid as proton acceptor is 1.996 Å long. The third H-bond is significantly longer, 2.666 Å, for which water acts as the proton acceptor. The binding energy of the MS-SA-W$_C$ complex is predicted to be 16.2 kcal mol^{-1}, which is 2.9 kcal mol^{-1} and only

Table 1. Hydrogen bond distances (Å) for the CH_3SO–H_2SO_4, CH_3SO–H_2SO_4–H_2O and CH_3SO–H_2SO_4–$2H_2O$ complexes.

	B3LYP / 6-311++G(2df,2pd)					
	CSO···H	**SCH···O**	**CS···H**	**SOH···O**	**SO···HO**	**O···HO**
MS-SA$_A$	1.673	2.376				
MS-SA$_B$	1.678					
MS-SA$_C$		2.696	2.468			
MS-SA-W$_A$	1.783	2.327		1.550		
MS-SA-W$_B$	1.781			1.584		
MS-SA-W$_C$	1.596	2.666			1.996	
MS-SA-2W$_A$	1.809	2.347		1.38	1.912	1.774
MS-SA-2W$_B$	1.779	2.266		1.573 1.694	2.076	
MS-SA-2W$_C$	1.805			1.599 1.715	2.050	

1.2 kcal mol^{-1} lower than the binding energies of the MS-SA-W$_A$ and MS-SA-W$_B$ complexes, respectively.

$CH_3SO–H_2SO_4–2H_2O$ Complexes. We have studied the addition of a second water molecule to the $CH_3SO–H_2SO_4–H_2O$ complexes, and all of our attempts with various initial guess configurations resulted in the three stable structures that are illustrated in Figure 4. In the MS-SA-2W$_A$ complex, the second water molecule acts as an H acceptor with a stronger H-bond (1.774 Å) to the first water molecule and as an H-donor, forming a weak H bond (1.912 Å) with the free electron pair of sulphuric acid double-bonded oxygen. The MS-SA-2W$_B$ complex also involves a weak H-bond (2.076 Å) between the water hydrogen atom and the free electron pair of sulphuric acid double-bonded oxygen, whereas the main H-bonding is generated by the acidic H atom of sulphuric acid and the oxygen atom of the second water molecule. The binding energy of both configurations is equal at 28.8 kcal mol^{-1}. Similarly, the second water molecule in the third complex labelled as MS-SA-2W$_C$ interacts with the free electron pair of sulphuric acid double-bonded oxygen and the acidic H atom of sulphuric acid, with bonds that are 2.050 and 1.715 Å long, respectively. Its binding energy is only 1.8 kcal mol^{-1} lower than in the previous two structures.

An inspection of the relative Gibbs free energies from Table 1 shows that the formation of the complexes, in particular those with the higher binding energies, are spontaneous processes.

When we analyse the binding energies of the complexes studied, we can conclude that the lowest energy structure of CH_3SO-sulphuric acid complex with a binding energy of 12.2 kcal mol^{-1} is relatively stable. The subsequent hydration of the CH_3SO-sulphuric acid complex significantly increases the binding energy, to 19.1 kcal mol^{-1} and to 28.8 kcal mol^{-1}, when one and two additional water molecules, respectively, participate in the hydration process.

Table 3. Rotational constants (GHz) for the CH_3SO radical, and for the $CH_3SO–H_2SO_4$, $CH_3SO–H_2SO_4–H_2O$ and $CH_3SO–H_2SO_4–2H_2O$ complexes at the B3LYP/6-311++G(2df,2pd) level of theory.

	A	B	C
CH_3SO	27.367	8.336	6.660
MS-SA$_A$	3.086	0.674	0.626
MS-SA$_B$	4.108	0.564	0.554
MS-SA$_C$	3.140	0.588	0.558
MS-SA-W$_A$	1.816	0.497	0.436
MS-SA-W$_B$	1.967	0.454	0.402
MS-SA-W$_C$	1.664	0.596	0.528
MS-SA-2W$_A$	1.056	0.475	0.371
MS-SA-2W$_B$	1.807	0.337	0.309
MS-SA-2W$_C$	1.181	0.394	0.382

3. 2. Infrared Spectra

For the sake of completeness the harmonic and anharmonic frequencies, along with the IR intensities calculated at the B3LYP/6-311++G(2df,2pd) level of theory for the CH_3SO radical, sulphuric acid and water molecule are presented in Table SI-2 of the Supplementary data, where the available experimental values for the CH_3SO radical,[3] sulphuric acid[19] and water molecule[20,21] are also quoted. The data for the $CH_3SO–H_2SO_4$, $CH_3SO–H_2SO_4–H_2O$ and $CH_3SO–H_2SO_4–2H_2O$ complexes are given in Tables SI-3, SI-4 and SI-5, respectively. The calculated anharmonic frequencies of the CH_3SO radical, sulphuric acid and water molecule are in very good agreement with the observed gas-phase fundamental frequencies, which has been extensively discussed in our previous work.[4]

The harmonic and anharmonic OH stretching vibrations and IR intensities of H_2SO_4, water and the complexes studied are summarised in Table 4. An examination of the calculated frequencies and intensities shows that the frequencies and intensities of the hydrogen-bonded OH stretching regions are most affected by complex forma-

Table 2. Binding energies (D$_o$, in kcal mol^{-1}) and Gibbs free energies (G$_o$, in kcal mol^{-1}) for the $CH_3SO–H_2SO_4$, $CH_3SO–H_2SO_4–H_2O$ and $CH_3SO–H_2SO_4–2H_2O$ complexes.

	D$_0$ (kcal mol^{-1})			G$_0$ (kcal mol^{-1})	
	B3LYP 6-311++G(2df,2pd)	**CBS-QB3**	**G4**	**CBS-QB3**	**G4**
MS-SA $_A$	9.7	12.2	13.6	–2.4	–4.5
MS-SA $_B$	7.7	10.0	11.2	–0.9	–2.0
MS-SA $_C$	1.4	4.2	5.4	5.9	3.1
MS-SA-W $_A$	16.3	19.1	20.7	–1.5	–3.7
MS-SA-W $_B$	15.0	17.4	19.4	1.1	–1.8
MS-SA-W $_C$	12.8	16.2	17.4	2.1	1.2
MS-SA-2W $_A$	25.3	28.8	30.4	–0.4	–3.2
MS-SA-2W $_B$	24.8	28.8	29.7	–2.6	–2.8
MS-SA-2W $_C$	22.4	27.0	28.1	–1.6	–2.0

tion: thus, the large frequency shift is mainly related to the OH bonds involved in the hydrogen-bonding interaction.

CH_3SO–H_2SO_4 Complexes. This particular complex has six modes that correspond to the unique intermolecular modes. A comparison of the OH stretching modes in the MS-SA$_A$, MS-SA$_B$ and S-SA$_C$ complexes with the sulphuric acid monomer shows that the OH stretching frequencies for the 'free' OH bonds in the complexes are only slightly blue-shifted. By contrast, for the MS-SA$_A$ and MS-SA$_B$ complexes, the H-bonded OH-stretching frequencies are red-shifted by approximately 650 cm^{-1}, and for MS-SA$_C$ complex, the shift is lower at 208 cm^{-1}. At the

Table 4. Harmonic (H) and nharmonic (A) OH-stretching vibrations (cm^{-1}) with IR intensities (I, km mol^{-1}) for the CH_3SO–H_2SO_4, CH_3SO–H_2SO_4–H_2O and CH_3SO–H_2SO_4–$2H_2O$ complexes at the B3LYP/6-311++G(2df,2pd) level of theory.

		Moiety in complex					
		H_2SO_4		**H_2O**		**H_2O_{second}**	
		OH-free	**OH-bonded**	**OH-free**	**OH-bonded**	**OH-free**	**OH-bonded**
H_2SO_4	H	3774	3770				
	A	3578	3574				
	I	50	210				
H_2O	H		3921	3818			
	A		3736	3647			
	I		64	8			
MS-SA$_A$	H	3778	3230				
	A	3583	2929				
	I	119	1733				
	shift	5	–645				
MS-SA$_B$	H	3791	3226				
	A	3593	2941				
	I	100	2027				
	shift	15	–633				
MS-SA$_C$	H	3781	3588				
	A	3613	3366				
	I	115	719				
	shift	35	–208				
MS-SA-W$_A$	H	3780	2775	3857	3527		
	A	3591	2342	3683	3274		
	I	120	1981	118	839		
	shift	13	–1232	–53	–373		
MS-SA-W$_B$	H	2790	2936	3877	3500		
	A	3603	2489	3682	3324		
	I	99	1903	116	1048		
	shift	25	–1085	–54	–323		
MS-SA-W$_C$	H	3782	2990	3892	3737		
	A	3573	2624	3683	3549		
	I	132	2253	116	254		
	shift	–5	–950	–53	–98		
MS-SA-2W$_A$	H	1871	3780[a]	3563[b]	3436	3885	3651
	A	n/a	n/a	n/a	n/a	n/a	n/a
	I	2666	120	913	607	112	474
MS-SA-2W$_B$	H	2882	3194	3870	3520	3879	3702
	A	2697	2964	3694	3311	3685	3507
	I	2158	1121	116	867	120	176
	shift	–877	–614	–42	–336	–51	–140
MS-SA-2W$_C$	H	2988	3250	3878	3538	3877	3700
	A	2579	3051	3618	3326	3683	3505
	I	1634	1087	101	923	139	201
	shift	–995	–527	–118	–321	–53	–142

[a] OH-free, [b] OH-bonded

same time, the intensities are significantly larger, implying the strong participation of the sulphuric acid OH in the H-bonding.

$CH_3SO–H_2SO_4–H_2O$ Complexes. An examination of the anharmonic frequencies of the H-bonded OH-stretching modes in the MS-SA-W_A, MS-SA-W_B and MS-SA-W_C complexes also reveals strong participation of the sulphuric acid OH in the H-bonding: the red shifts are 1232, 1085 and 950 cm^{-1}, respectively. For the water subunit in the complexes, the OH stretching frequencies in the H-bonding are changed by 373, 323 and 98 cm^{-1}, respectively, which is in line with the weaker H-bonds.

$CH_3SO–H_2SO_4–2H_2O$ Complexes. When the anharmonic frequencies of the OH-stretching modes in the MS-SA-2W_A, MS-SA-2W_B, MS-SA-2W_C complexes are considered, the red shift on average of 940 cm^{-1} for the OH modes of the sulphuric acid moiety involved in H-bonding is observed. The OH-stretching modes of both water subunits in the complex are also affected by complexation. The OH modes participating in H-bonding are shifted by approximately 140 cm^{-1} to the red region of the spectrum compared to the symmetric stretching frequencies of the free water molecule.

The present data provide strong evidence that the complexation of the methyl sulphinyl radical with sulphuric acid, as well as the subsequent hydration of these complexes with one or two water molecules, induces large frequency shifts and an intensity enhancement of the H-bonded OH-stretching vibrations in relation to that of the corresponding parent monomers. The modes that are similar to the isolated monomers are changed with respect to the monomers, mainly due to the geometry modification induced by the new interaction with the other atoms in the complexes.

3. 3. Vertical Excitation Energies

It is also important to consider the photochemistry of the system in the atmosphere: thus, an investigation of the excited states of the complexes can provide other spectroscopic features that should aid in an experimental characterisation. In this study, we will especially concentrate on determining to what extent the complexation might affect the electronic spectra of the CH_3SO radical within the sulphuric acid and water complexes. Electronic excitations in water and sulphuric acid require very high energy, and the transitions occur in the VUV region, well above those available from the sun in the troposphere. Water has its first electronic transition at approximately 180 nm,[22] whereas for sulphuric acid, the electronic excitations are below 150 nm.[23,24]

The vertical excitation energies for three low-lying singlet electronically excited states and the oscillator strengths calculated from the TDDFT B3LYP/aug-cc-pVTZ calculations on the B3LYP/6-311++G(2df,2pd) geometries for the CH_3SO radical and for its complexes with sulphuric acid and water are summarised in Table 5. The UV/Vis absorption spectrum of CH_3SO shows two absorption bands.[3] One is a very weak, broad band starting at 635 nm and terminating at approximately 450 nm, with maximum at approximately 530 nm. The second is much more intense, starting near 320 nm with a maximum at approximately 260 nm. Both bands are in reasonable agreement with our computed electronic transitions, found at 556 nm and 234 nm, respectively. From comparison of the experimental and calculated absorption bands, we have estimated that the excitation energies would be provided to within 0.3 eV or 25 nm. Thus, we can expect that the excitation energies for the complexes predicted by our calculations would be sufficiently reliable for qualitative prediction of the general trends or shift of the absorption energies.

Among the $CH_3SO–H_2SO_4$ complexes, the most intense band is calculated at 258 nm for the relatively least stable structure, the MS-SA_C complex. Although the photolysis in the sunlight occurs at the threshold of approximately 300 nm, this complex is expected not to photolyse under sunlight. Eventually, the MS-SA_B complex with the third singlet electronic transition calculated at 301 nm can undergo photolysis. For the $CH_3SO–H_2SO_4–H_2O$ complexes, the highly intense absorption band appears at 321 nm for MS-SA-W_C structure. Further, the MS-SA-2W_A and MS-SA-2W_B structures for the $CH_3SO–H_2SO_4–2H_2O$ complexes have electronic transitions slightly above 300 nm, at 302 and 312 nm, respectively, with moderate intensities.

When the calculated electronic transitions related to the first singlet exited states of the CH_3SO-complexes and CH_3SO radical are compared, it is found that the transitions in the complexes are approximately 35 nm blue-shifted relative to those for the free radical, except in the case of the MS-SA_C complex, for which the transition is red-shifted by 32 nm. TTDFT calculations demonstrate that the character of the first electronic transitions is the same in the radical and in all complexes and that they correspond to the HOMO-1 → LUMO excitations or an n(O),σ(S-O) → π*(S-O) type transitions. The vertical transition energies for the most intense peaks in the radical at 234 nm and in the MS-SA_C complex at 258 nm are considered to be π(S-O) → π*(S-O) type transitions. The second electronic transition for the MS-SA-W complexes and also for the MS-SA-2W complexes are associated with the n(O) → π*(S-O) type transitions with the difference that, for the former complexes, the n(O) type lone-pair orbitals are at water oxygen centres, whereas in the latter, the complexes the n(O) lone-pair orbitals are at sulphuric acid oxygen centres. For example, this type of transition is computed to be located at 321 and 312 nm for the MS-SA-W_C and MS-SA-2W_B complexes, respectively.

Table 5. TDDFT vertical excitation energies (in eV and in nm) and oscillator strengths f for the CH_3SO radical (experimental values from ref. 3.) and for the $CH_3SO–H_2SO_4$, $CH_3SO–H_2SO_4–H_2O$ and $CH_3SO–H_2SO_4–2H_2O$ complexes at the B3LYP/aug-cc-pVTZ level of theory.

	Transition	ΔE [eV]	λ_{max} [nm]	f	Exp.
CH_3SO	16β → 17β	2.23	556	0.0005	530 nm
	17α → 19α	4.92	252	0.0001	
	15β→ 17β	5.29	234	0.0019	260 nm
MS-SA$_A$	41β →42β	2.38	521	0.0006	
	40β →42β	4.16	298	0.0005	
	38β →42β	4.53	274	0.0006	
MS-SA$_B$	41β →42β	2.39	519	0.0004	
	40β →42β	3.88	319	0.0000	
	39β →42β	4.12	301	0.0015	
MS-SA$_C$	41β →42β	2.11	588	0.0008	
	37β →42β	4.81	258	0.0432	
	40β →42β	4.93	251	0.0015	
MS-SA-W$_A$	46β→47β	2.36	525	0.0005	
	45β→47β	4.05	306	0.0009	
	44β→47β	4.66	266	0.0003	
MS-SA-W$_B$	46β→47β	2.36	525	0.0003	
	45β→47β	4.04	307	0.0003	
	44β→47β	4.28	290	0.0005	
MS-SA-W$_C$	46β→47β	2.53	490	0.0007	
	45β→47β	3.86	321	0.0094	
	44β→47β	4.19	296	0.0004	
MS-SA-2W$_A$	51β→52β	2.36	526	0.0005	
	50β→52β	4.11	302	0.0012	
	49β→52β	4.64	267	0.0025	
MS-SA-2W$_B$	51β→52β	2.37	523	0.0005	
	50β→52β	3.97	312	0.0016	
	49β→52β	4.55	273	0.0002	
MS-SA-2W$_C$	51β→52β	2.35	527	0.0003	
	50β→52β	3.84	323	0.0001	
	49β→52β	4.12	301	0.0001	

4. Conclusions

The primary aim of this study was to characterise structural and spectroscopic properties of complexes involving the CH_3SO radical, sulphuric acid and water molecules. Quantum chemical calculations at the density functional theory (B3LYP) level in conjunction with the 6-311++G(2df,2pd) basis set determined multiple H-bonded cyclic complexes for all studied stoichiometries, with H-bond lengths in the range of 1.38 to 2.70 Å. The CBS-QB3 level of theory predicts that the complexes are bonded strongly, with binding energies of 12.2, 19.1 and 28.8 kcal mol^{-1} for the minimum-energy structure $CH_3SO–H_2SO_4$ (MS–SA$_A$), $H_3SO–H_2SO_4–H_2O$ (MS-SA-W$_A$) and $CH_3SO–H_2SO_4–2H_2O$ (MS-SA-2W$_A$) complexes, respectively.

From the calculated vibrational frequencies and the IR intensities, it follow that complex formation through H-bonding induces a large spectral red-shift and enhancement of the IR intensities for the H-bonded OH stretching vibrational mode, relative to the modes in the monomers forming the complex. TDDFT calculations of the vertical excitation energies for the CH_3SO-sulphuric acid and CH_3SO-sulphuric acid-water complexes indicate significant spectral shifts in comparison to the free CH_3SO radical, which suggests that the radical and complexes are experimentally distinguishable using standard UV/Vis absorption spectroscopy. In the troposphere, complexes of the MS-SA-W and MS-SA-2W types can be expected to undergo photolysis in the sunlight.

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6. References

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Povzetek

V tem delu smo preučevali strukturne, elektronske in spektroskopske lastnosti kompleksov metil-sulfilnega radikala, žveplove kisline in vodne molekule s pomočjo teorije gostotnega funkcionala in ab initio metod. Določili smo vodikovo med vez med CH_3SO radikalom, H_2SO_4 in H_2O. Dobili smo relativno velike vezne energije kompleksov in sicer 12,2 kcal mol^{-1} za najstabilnejši $CH_3SO–H_2SO_4$ skupek, 19,1 kcal mol^{-1} za $CH_3SO–H_2SO_4–H_2O$ in 28,8 kcal mol^{-1} za $CH_3SO–H_2SO_4–2H_2O$ pri CBS-QB3 približku. Relativno visoka stabilizacija skupkov je verjetno razlog za tvorjenje novih struktur v atmosferi. S pomočjo infrardeče spektroskopije lahko opazimo te komplekse v laboratoriju kot tudi v atmosferi. Določili in razložili smo tudi elektronski spekter preučevanih skupkov ter fotokemični spekter. Hidratiran $CH_3SO–H_2SO_4$ kompleks verjetno razpade s fotolizo na sončni svetlobi.