

Scientific paper

H-Bonded $\text{CH}_3\text{SO}/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ 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 $12.2 \text{ kcal mol}^{-1}$ for the most stable $\text{CH}_3\text{SO}-\text{H}_2\text{SO}_4$ complex, $19.1 \text{ kcal mol}^{-1}$ for $\text{CH}_3\text{SO}-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ complex and $28.8 \text{ kcal mol}^{-1}$ for $\text{CH}_3\text{SO}-\text{H}_2\text{SO}_4-2\text{H}_2\text{O}$ 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 $\text{CH}_3\text{SO}-\text{H}_2\text{SO}_4$ 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 anthropoge-

nic 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 $\text{CH}_3\text{SO}-\text{H}_2\text{SO}_4$ 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 functional⁸ 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 $\langle S^2 \rangle$ 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.

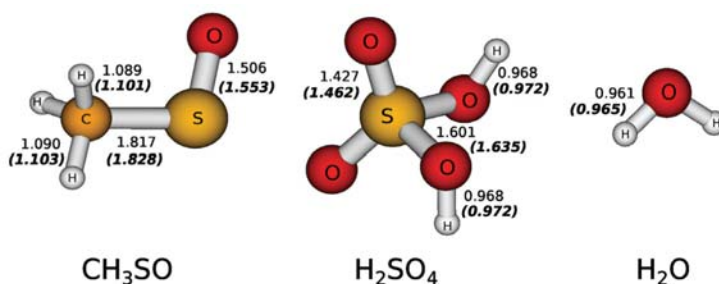


Figure 1. B3LYP/6-311++G(2df,2pd) optimised structures of the CH_3SO radical, H_2SO_4 and H_2O molecules. In parentheses are the CCSD/aug-cc-pVDZ parameters. Bond lengths are in Å.

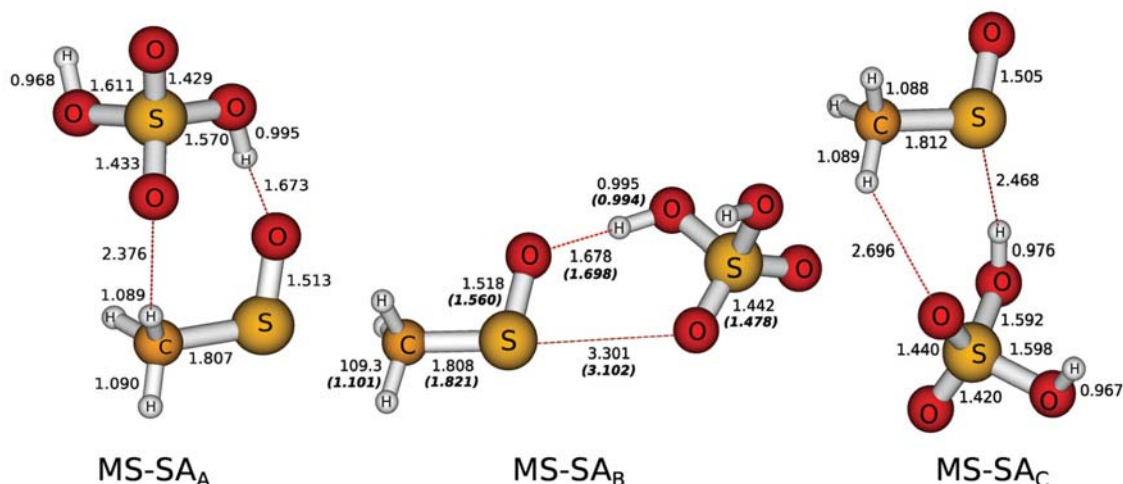


Figure 2. B3LYP/6-311++G(2df,2pd) optimised structures of the $\text{CH}_3\text{SO}-\text{H}_2\text{SO}_4$ complexes. In parentheses are the CCSD/aug-cc-pVDZ parameters. Bond lengths are in Å.

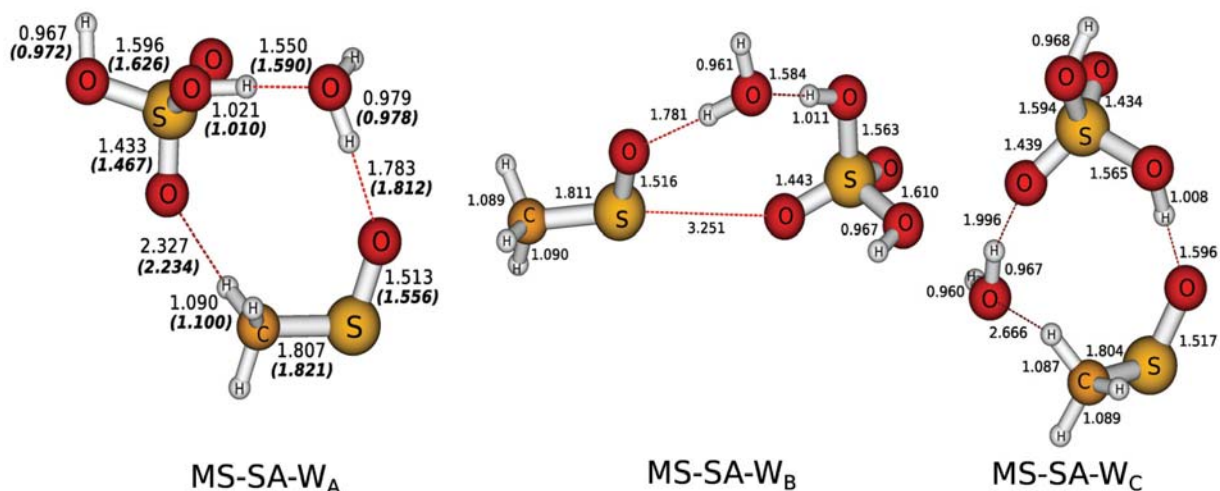


Figure 3. B3LYP/6-311++G(2df,2pd) optimised structures of the $\text{CH}_3\text{SO}-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ complexes. In parentheses are the CCSD/aug-cc-pVDZ parameters. Bond lengths are in Å.

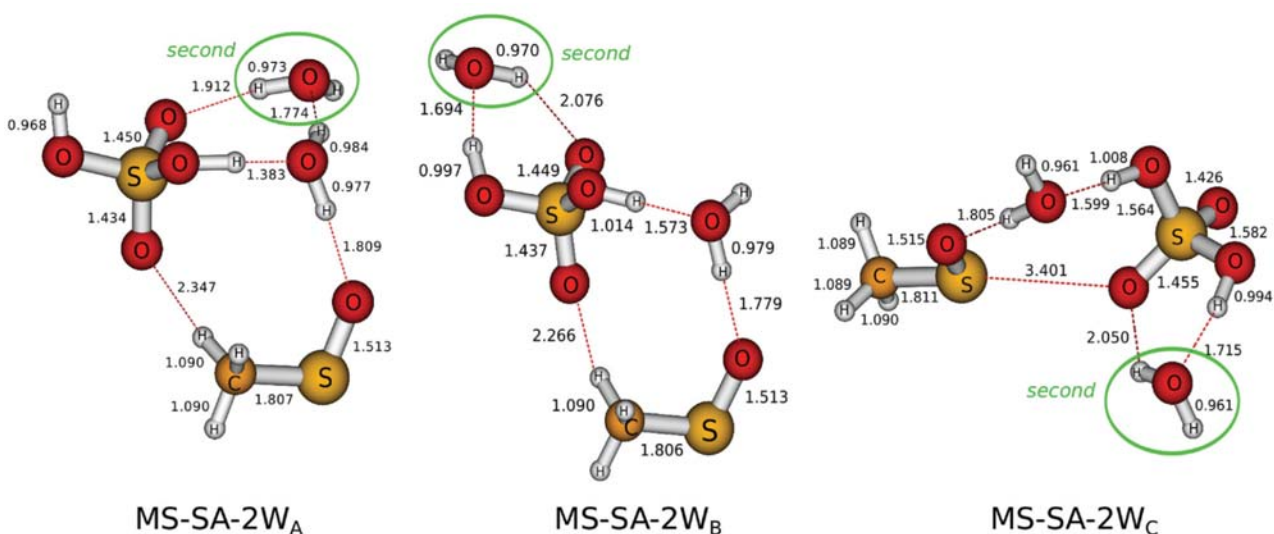


Figure 4. B3LYP/6-311++G(2df,2pd) optimised structures of the $\text{CH}_3\text{SO}-\text{H}_2\text{SO}_4-2\text{H}_2\text{O}$ complexes. Bond lengths are in Å.

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 0.87¹⁶ 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

CH₃SO–H₂SO₄ Complexes. A large set of initial guess configurations for the CH₃SO–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 H₂SO₄ forms a strong H-bond through the inte-

reaction of its H atom with the lone oxygen electron pair of CH₃SO. 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 CH₃SO 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.

CH₃SO–H₂SO₄–H₂O Complexes. The optimisation of the extensive set of initial geometrical structures for the CH₃SO–H₂SO₄–H₂O 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. H₂O molecules in this complex act as an H acceptor from the H₂SO₄ 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 CH₃SO 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 CH₃SO 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 CH₃SO–H₂SO₄, CH₃SO–H₂SO₄–H₂O and CH₃SO–H₂SO₄–2H₂O 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.

CH₃SO–H₂SO₄–2H₂O Complexes. We have studied the addition of a second water molecule to the CH₃SO–H₂SO₄–H₂O 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 CH₃SO-sulphuric acid complex with a binding energy of 12.2 kcal mol⁻¹ is relatively stable. The subsequent hydration of the CH₃SO-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 CH₃SO radical, and for the CH₃SO–H₂SO₄, CH₃SO–H₂SO₄–H₂O and CH₃SO–H₂SO₄–2H₂O complexes at the B3LYP/6-311++G(2df,2pd) level of theory.

	A	B	C
CH ₃ SO	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-2W _A	1.816	0.497	0.436
MS-SA-2W _B	1.967	0.454	0.402
MS-SA-2W _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 CH₃SO radical, sulphuric acid and water molecule are presented in Table SI-2 of the Supplementary data, where the available experimental values for the CH₃SO radical,³ sulphuric acid¹⁹ and water molecule^{20,21} are also quoted. The data for the CH₃SO–H₂SO₄, CH₃SO–H₂SO₄–H₂O and CH₃SO–H₂SO₄–2H₂O complexes are given in Tables SI-3, SI-4 and SI-5, respectively. The calculated anharmonic frequencies of the CH₃SO 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 H₂SO₄, 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*₀, in kcal mol⁻¹) and Gibbs free energies (*G*₀, in kcal mol⁻¹) for the CH₃SO–H₂SO₄, CH₃SO–H₂SO₄–H₂O and CH₃SO–H₂SO₄–2H₂O complexes.

	<i>D</i> ₀ (kcal mol ⁻¹)			<i>G</i> 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.

CH₃SO–H₂SO₄ 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 sul-

phuric 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 CH₃SO–H₂SO₄, CH₃SO–H₂SO₄–H₂O and CH₃SO–H₂SO₄–2H₂O complexes at the B3LYP/6-311++G(2df,2pd) level of theory.

		Moiety in complex					
		H ₂ SO ₄		H ₂ O		H ₂ O _{second}	
		OH-free	OH-bonded	OH-free	OH-bonded	OH-free	OH-bonded
H ₂ SO ₄	H	3774	3770				
	A	3578	3574				
	I	50	210				
H ₂ O	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.

CH₃SO–H₂SO₄–H₂O 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.

CH₃SO–H₂SO₄–2H₂O 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 CH₃SO 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) geome-

tries for the CH₃SO radical and for its complexes with sulphuric acid and water are summarised in Table 5. The UV/Vis absorption spectrum of CH₃SO 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 CH₃SO–H₂SO₄ 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 CH₃SO–H₂SO₄–H₂O 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 CH₃SO–H₂SO₄–2H₂O 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 excited states of the CH₃SO-complexes and CH₃SO 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. TDDFT 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 CH₃SO radical (experimental values from ref. 3.) and for the CH₃SO–H₂SO₄, CH₃SO–H₂SO₄–H₂O and CH₃SO–H₂SO₄–2H₂O complexes at the B3LYP/aug-cc-pVTZ level of theory.

	Transition	ΔE [eV]	λ _{max} [nm]	f	Exp.
CH ₃ SO	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 CH₃SO 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 CH₃SO–H₂SO₄ (MS-SA_A), H₃SO–H₂SO₄–H₂O (MS-SA-W_A) and CH₃SO–H₂SO₄–2H₂O (MS-SA-2W_A) complexes, respectively.

From the calculated vibrational frequencies and the IR intensities, it follows 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 CH₃SO-sulphuric acid and CH₃SO-sulphuric acid-water complexes indicate significant spectral shifts in comparison to the free CH₃SO 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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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 $12,2 \text{ kcal mol}^{-1}$ za najstabilnejši $\text{CH}_3\text{SO}-\text{H}_2\text{SO}_4$ skupek, $19,1 \text{ kcal mol}^{-1}$ za $\text{CH}_3\text{SO}-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ in $28,8 \text{ kcal mol}^{-1}$ za $\text{CH}_3\text{SO}-\text{H}_2\text{SO}_4-2\text{H}_2\text{O}$ 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 $\text{CH}_3\text{SO}-\text{H}_2\text{SO}_4$ kompleks verjetno razpade s fotolizo na sončni svetlobi.

H-Bonded CH₃SO/H₂SO₄/H₂O Complexes: Quantum Chemical Study

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Dedicated to Prof. Dr. Joe Koller on the occasion of his 70th birthday

Supplementary Data

Table SI-1: Cartesian coordinate in Å for all structures studied in this work.

Table SI-2: B3LYP/6-311++G(2df,2pd) harmonic and anharmonic (cm⁻¹) frequencies together with IR intensities (I, in km mol⁻¹) of CH₃SO radical, H₂SO₄ and H₂O molecule.

Table SI-3: B3LYP/6-311++G(2df,2pd) harmonic and anharmonic (cm⁻¹) frequencies together with IR intensities (I, in km mol⁻¹) for CH₃SO-H₂SO₄ complexes.

Table SI-4: B3LYP/6-311++G(2df,2pd) harmonic and anharmonic (cm⁻¹) frequencies together with IR intensities (I, in km mol⁻¹) for CH₃SO-H₂SO₄-H₂O complexes.

Table SI-5: B3LYP/6-311++G(2df,2pd) harmonic and anharmonic (cm⁻¹) frequencies together with IR intensities (I, in km mol⁻¹) for CH₃SO-H₂SO₄-2H₂O complexes.

Table SI-1. Cartesian coordinate in Å for all structures studied in this work.

CH₃SO						
	B3LYP/6-311++G(2df,2pd)			CCSD/aug-cc-pVDZ		
O	1.245682	0.607973	0.000015	1.259622	0.628078	-0.000006
S	0.226446	-0.501169	0.000008	0.218014	-0.523920	-0.000010
C	-1.404128	0.300882	-0.000030	-1.402817	0.320911	-0.000002
H	-2.160317	-0.483992	-0.001712	-2.186249	-0.455515	0.000091
H	-1.500815	0.918097	-0.891509	-1.481282	0.944148	-0.904076
H	-1.502681	0.915529	0.893153	-1.480759	0.943995	0.904210
H₂SO₄						
	B3LYP/6-311++G(2df,2pd)			CCSD/aug-cc-pVDZ		
O	-0.515762	0.496061	0.657449	-0.002745	0.003610	-0.039658
S	0.194842	-0.332201	1.576467	0.008355	0.000037	1.422287
O	1.600978	-0.567132	1.520097	1.212291	-0.003655	2.251710
O	-0.096703	0.184158	3.063908	-0.880159	1.265122	1.953102
H	-0.960199	0.621629	3.081825	-1.535727	1.463274	1.263661
S	-0.562314	-1.742955	1.559748	-0.929696	-1.264900	1.860041
H	0.021913	-2.418467	1.933516	-0.726983	-1.462902	2.789592
H₂O						
	B3LYP/6-311++G(2df,2pd)			CCSD/aug-cc-pVDZ		
O	0.000000	0.000000	0.116800	0.000000	0.000000	0.118740
H	0.000000	0.763077	-0.467198	0.000000	0.760299	-0.474961
H	0.000000	-0.763077	-0.467198	0.000000	-0.760299	-0.474961

Table SI-1. Continued.

MS-SA_A

	B3LYP/6-311++G(2df,2pd)		
O	0.332699	0.804917	-0.125607
S	0.029616	0.757528	1.356394
C	1.459144	0.008029	2.167803
H	1.209643	-0.083978	3.224687
H	2.325662	0.656003	2.041851
H	1.653942	-0.967579	1.725753
H	1.196162	-0.058090	-1.268840
O	1.644165	-0.534379	-2.019223
S	2.660546	-1.609410	-1.494595
O	2.197937	-2.160583	-0.255399
O	3.017024	-2.422941	-2.613467
O	3.938397	-0.717330	-1.086710
H	4.443219	-0.515773	-1.887212

MS-SA_B

	B3LYP/6-311++G(2df,2pd)			CCSD/aug-cc-pVDZ		
O	0.060500	-0.218138	0.858442	-0.077942	-0.147128	0.038226
S	0.994610	0.689066	1.637853	0.009682	0.339633	1.518190
C	2.445695	-0.337641	1.967804	1.741673	-0.016586	1.954052
H	3.153597	0.268155	2.532568	1.891748	0.294286	3.001146
H	2.885647	-0.650355	1.022369	2.401869	0.555450	1.284175
H	2.145576	-1.208349	2.548298	1.922574	-1.096795	1.843231
H	-1.336863	0.358737	0.130478	-1.453108	0.294367	-0.855073
O	-2.143641	0.683760	-0.352847	-2.244873	0.581695	-1.382314
S	-2.749385	1.944700	0.366691	-3.515369	0.580224	-0.397403
O	-1.797077	2.424353	1.337118	-3.031041	0.664083	0.996700
O	-3.994503	1.324733	1.170627	-4.120360	-0.930388	-0.602612
H	-3.689522	1.026664	2.038094	-3.723255	-1.484818	0.087744
O	-3.322807	2.785732	-0.627063	-4.507043	1.486569	-0.960210

MS-SA_C

	B3LYP/6-311++G(2df,2pd)		
O	1.078258	2.019338	0.735267
S	0.587920	0.928130	1.648910
C	1.833292	-0.387384	1.640158
H	1.490050	-1.159140	2.326950
H	2.785322	0.022533	1.972639
H	1.925216	-0.780177	0.629314
O	-0.212680	-0.847080	4.394369
S	-0.506117	0.085014	5.452599
O	-0.123019	1.543755	4.943306
H	0.035761	1.520920	3.980504
O	0.003832	-0.047048	6.770887
O	-2.094355	0.182343	5.602769
H	-2.513425	-0.080402	4.771370

Table SI-1. Continued.

MS-SA-W_A						
	B3LYP/6-311++G(2df,2pd)			CCSD/aug-cc-pVDZ		
O	1.555753	-1.344575	0.394866	-0.178659	-0.032691	0.007460
S	1.614859	-0.815221	1.810859	-0.042652	0.050075	1.555042
C	0.694456	0.739386	1.833657	1.748858	0.034504	1.881440
H	0.766708	1.133205	2.847503	1.877289	0.059593	2.976182
H	-0.347751	0.555902	1.573705	2.215085	0.918947	1.422955
H	1.148552	1.434945	1.129122	2.172146	-0.894918	1.468693
H	-1.103516	-0.147747	-1.698770	3.029102	1.121014	-1.510682
O	-1.858475	0.515273	-1.517526	3.922584	1.452200	-1.174488
S	-2.897915	-0.112963	-0.528105	3.661362	2.910761	-0.553407
O	-3.233735	-1.442860	-0.961941	2.862184	3.703144	-1.504675
O	-4.133990	0.861801	-0.790436	5.190876	3.460546	-0.524521
H	-4.561755	0.615462	-1.622533	5.421282	3.720672	-1.431746
O	-2.510884	0.125734	0.831158	3.259828	2.809987	0.854458
H	0.626524	-1.216734	-1.121415	0.974268	0.337260	-1.340200
O	0.060868	-1.147403	-1.917239	1.617754	0.601847	-2.027205
H	-0.268617	-2.034697	-2.091341	1.174891	1.296146	-2.531437

MS-SA-W_B			
	B3LYP/6-311++G(2df,2pd)		
O	0.193683	-0.305100	-0.131485
S	-0.308718	0.007102	1.263951
C	1.193514	0.210378	2.253955
H	0.885454	0.433584	3.275049
H	1.782051	1.032525	1.850088
H	1.770604	-0.712470	2.227127
H	-2.728931	0.056651	-2.316272
O	-3.616016	0.539529	-2.266886
S	-4.326991	0.278464	-0.899159
O	-3.338425	-0.083129	0.088043
O	-5.207730	-1.036774	-1.191593
H	-4.672567	-1.816678	-0.992191
O	-5.265494	1.327302	-0.684583
H	-0.812934	-0.561681	-1.578763
O	-1.339532	-0.699856	-2.393762
H	-0.761614	-0.495936	-3.133740

MS-SA-W_C			
	B3LYP/6-311++G(2df,2pd)		
O	0.434094	-0.071181	0.044610
S	0.109631	-0.689251	1.391578
O	1.662267	-0.805452	2.303244
H	1.415653	-1.177083	3.296931
H	2.109604	0.182554	2.377883
H	2.328942	-1.498723	1.792031
H	1.647926	0.820135	-0.483299
O	2.409579	1.368340	-0.851270
S	2.520111	2.759087	-0.142660
O	1.628997	3.713204	-0.735317
O	4.014041	3.128791	-0.556216
H	3.991441	3.631851	-1.382340
O	2.535996	2.576862	1.285134
H	1.078342	2.478267	2.644517
O	0.436223	2.070015	3.241874
H	-0.224795	2.745896	3.410334

Table SI-1. Continued.

MS-SA-2W_A

B3LYP/6-311++G(2df,2pd)

O	0.000000	0.000000	0.000000
S	0.000000	0.000000	1.512599
C	1.727805	0.000000	2.042981
H	1.722605	-0.042617	3.132266
H	2.219258	0.911227	1.703035
H	2.227882	-0.878301	1.637022
H	2.960402	0.934273	-1.548180
O	3.899895	1.265529	-1.126314
S	3.845341	2.710122	-0.590571
O	3.379670	3.612599	-1.625915
O	5.396519	2.995509	-0.347697
H	5.832504	3.137963	-1.199589
O	3.236160	2.776112	0.705809
H	1.117837	0.294114	-1.391764
O	1.762140	0.509897	-2.093735
H	1.397434	1.262137	-2.611901
H	1.927359	3.338375	-2.838720
O	1.248385	2.867407	-3.351660
H	0.453494	3.405167	-3.311901

MS-SA-2W_B

B3LYP/6-311++G(2df,2pd)

O	0.258473	-0.909281	0.022669
S	0.347507	-1.054643	1.526146
C	2.020196	-0.567594	2.003404
H	2.087729	-0.685666	3.084909
H	2.187438	0.471959	1.722781
H	2.738365	-1.221298	1.510071
H	2.569010	1.533828	-1.549507
O	3.278554	2.199821	-1.262837
S	2.696004	3.249516	-0.258426
O	1.853168	4.191563	-0.966833
O	4.021164	3.972504	0.169360
H	4.133597	4.802682	-0.371482
O	2.156506	2.580126	0.892528
H	1.093741	-0.041262	-1.287030
O	1.519190	0.457744	-2.013899
H	0.806506	0.794253	-2.564377
H	2.952918	5.849934	-1.558907
O	3.869938	6.124035	-1.398909
H	3.830293	7.010426	-1.028811

Table SI-1. Continued.

MS-SA-2W_C			
B3LYP/6-311++G(2df,2pd)			
O	0.228145	0.026523	-0.030226
S	0.228233	0.209150	1.473832
C	1.965731	0.478786	1.906043
H	2.017218	0.616212	2.985745
H	2.328364	1.369306	1.395424
H	2.550574	-0.389586	1.607424
H	-3.162762	0.844126	-0.810372
O	-3.803052	1.418233	-0.284354
S	-4.227418	0.737666	1.058387
O	-3.154930	-0.141502	1.499153
O	-5.451775	-0.172001	0.640074
H	-5.174034	-1.126115	0.631380
O	-4.714984	1.765130	1.917995
H	-1.249013	-0.053393	-1.064443
O	-2.070242	-0.020827	-1.594535
H	-1.819155	0.260625	-2.478180
H	-3.597365	-2.124092	1.225552
O	-4.345712	-2.611839	0.846391
H	-4.667280	-3.196686	1.538433

Table SI-2. Harmonic and anharmonic frequencies (cm^{-1}) with IR int. (km mol^{-1}) for CH_3SO , H_2SO_4 and H_2O molecules.

CH_3SO				H_2SO_4				H_2O			
H	A	IR int.	Exp ^a	H	A	IR int.	Exp ^b	H	A	IR int.	Exp ^{c,d}
3131	2981	2	2995 vw	3774	3578	50	3609	3818	3647	8	3661
3130	2979	4		3770	3574	210		1630	1575	72	1596
3037	2917	3	2919 vw	1449	1418	304	1465	3921	3736	64	3751
1460	1419	8	1417 w	1201	1180	165	1220				
1446	1404	10	1405 w	1166	1124	84	1157				
1323	1299	1	1289 w	1152	1116	79	1138				
1061	1408	47	1068 vs	851	831	342	891				
947	921	11	927 m	799	781	113	834				
887	869	1	868 vw	540	532	24	568				
662	646	14	670 w	531	525	39	550				
332	333	7	341 w	485	476	42					
137	93	0	n.o.	429	397	17					
				365	346	2	281				
				327	265	59					
				251	219	98	216				

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Table SI-3. Harmonic and anharmonic frequencies (cm^{-1}) with IR int. (km mol^{-1}) for MS-SA complexes.

MS-SA _A			MS-SA _B			MS-SA _C		
H	A	IR int.	H	A	IR int.	H	A	IR int.
3778	3583	119	3791	3593	100	3781	3613	115
3230	2929	1733	3226	2941	2028	3588	3366	719
3139	2990	2	3136	2983	2	3147	2999	0
3128	2983	3	3134	2983	0	3136	2988	1
3036	2920	4	3040	2918	1	3043	2926	2
1462	1423	2	1457	1413	6	1457	1417	17
1443	1408	51	1445	1405	13	1451	1409	4
1428	1398	286	1437	1404	304	1439	1408	338
1336	1289	4	1331	1284	1	1326	1295	2
1288	1249	62	1301	1263	97	1205	1170	160
1194	1172	185	1183	1162	196	1173	1152	60
1157	1122	96	1150	1105	57	1146	1115	66
1066	1049	106	1046	1033	95	1058	1045	41
961	938	18	959	933	12	958	937	11
897	878	161	892	873	193	897	887	2
893	877	81	891	873	140	864	843	370
802	783	191	807	785	182	806	788	94
764	705	23	771	701	23	667	673	8
673	659	9	676	653	16	544	535	27
544	538	33	546	537	38	532	525	26
538	530	40	535	528	31	503	503	7
510	503	10	509	501	23	450	443	66
421	381	31	419	394	14	403	399	39
379	358	2	376	363	39	356	308	4
346	351	8	362	344	2	333	335	5
270	170	61	219	130	78	192	129	63
180	175	40	156	136	12	141	117	0
157	204	3	141	78	1	93	93	2
107	108	0	120	106	5	69	95	9
93	94	5	52	24	3	62	51	2
59	75	1	45	29	3	47	51	9
36	48	2	35	-10	1	29	66	3
20	106	3	24	-31	2	19	-7	3

Table SI-4. Harmonic and anharmonic frequencies (cm^{-1}) with IR int. (km mol^{-1}) for MS-SA-W complexes.

MS-SA-W _A			MS-SA-W _B			MS-SA-W _C		
H	A	IR int.	H	A	IR int.	H	A	IR int.
3857	3683	118	3877	3682	116	3892	3683	116
3780	3591	120	3790	3603	99	3782	3573	132
3527	3274	839	3500	3324	1048	3737	3549	254
3129	2978	29	3133	2985	2	3152	3000	5
3128	2982	2	3132	2987	1	3133	2988	1
3031	2931	22	3038	2923	2	3043	2920	8
2775	2342	1981	2936	2489	1903	2990	2624	2253
1663	1618	38	1661	1633	43	1645	1582	58
1467	1427	7	1467	1418	189	1452	1387	7
1446	1400	10	1457	1413	9	1442	1385	10
1406	1149	180	1446	1405	11	1383	1372	301
1371	1371	241	1369	1354	236	1334	1285	15
1339	1297	2	1328	1282	0	1322	1254	91
1186	1163	147	1183	1162	249	1186	1171	169
1158	1126	123	1150	1107	55	1159	1132	105
1074	1004	22	1050	1039	92	1062	1044	91
1062	1032	138	955	932	13	960	940	19
960	938	11	938	862	203	907	887	322
910	892	283	910	888	188	896	876	1
897	879	3	888	873	1	832	782	123
822	803	143	801	783	148	811	707	101
704	694	129	711	673	52	677	653	8
673	661	8	672	650	17	547	535	19
549	539	38	554	543	23	543	540	58
543	534	22	540	526	27	518	514	8
517	513	32	536	527	34	477	470	102
463	485	34	476	468	51	407	396	30
413	363	30	419	391	4	391	365	40
405	403	17	367	348	1	351	357	15
343	345	15	363	359	29	321	369	92
330	241	102	297	202	134	225	226	62
279	244	22	270	244	35	202	200	58
248	114	74	209	139	48	151	37	18
183	104	3	162	148	15	140	68	23
175	165	35	142	124	0	118	55	12
99	93	14	101	85	6	113	-183	62
77	101	8	65	42	2	89	142	5
67	74	14	52	24	6	60	79	2
47	78	3	43	20	2	46	65	3
30	42	3	34	-14	1	31	98	4
26	31	1	29	26	2	26	99	2
23	22	3	21	-45	4	20	51	3

Table SI-5. Harmonic and anharmonic frequencies (cm^{-1}) with IR int. (km mol^{-1}) for MS-SA-2W complexes.

MS-SA-2W _A			MS-SA-2W _B			MS-SA-2W _C		
H	A	IR int.	H	A	IR int.	H	A	IR int.
3885	n/a	112	3879	3685	120	3878	3618	101
3780		120	3870	3694	116	3877	3683	139
3651		474	3702	3507	176	3700	3505	201
3563		913	3520	3311	867	3538	3326	923
3436		607	3194	2964	1121	3250	3051	1087
3129		19	3130	2987	56	3134	2982	2
3128		5	3128	2974	4	3133	2977	1
3031		17	3030	2914	41	3039	2913	1
1871		2666	2882	2697	2158	2988	2579	1634
1676		79	1665	1615	38	1657	1601	40
1643		56	1633	1578	62	1633	1580	53
1468		52	1469	1410	6	1457	1411	11
1464		69	1445	1387	16	1452	1393	224
1446		22	1428	1381	202	1446	1398	9
1355		377	1361	1296	122	1375	1314	79
1339		8	1337	1292	1	1329	1280	2
1300		68	1305	1265	256	1321	1277	212
1158		206	1166	1147	178	1149	1133	212
1156		112	1063	1047	78	1051	1037	76
1063		73	1033	901	80	957	903	49
962		204	961	936	12	953	898	165
960		77	931	905	355	924	896	278
897		3	901	882	2	889	857	1
874		114	859	841	76	843	825	86
829		195	804	748	86	778	626	69
730		45	697	623	102	675	628	68
673		9	674	661	9	670	630	39
626		176	584	513	183	587	516	135
590		16	554	540	18	558	540	41
554		25	551	545	40	548	507	68
535		87	526	502	43	542	533	33
522		34	454	509	24	467	384	14
420		60	414	409	11	411	376	28
413		109	387	371	46	367	357	11
388		29	352	258	109	361	340	27
344		2	344	338	13	328	192	93
321		97	285	367	97	285	20	141
244		160	270	260	11	261	231	57
238		43	256	135	113	247	209	28
227		26	217	194	17	208	183	22
180		1	182	87	0	161	126	18
161		31	172	153	35	153	85	17
148		3	152	117	46	139	137	0
115		18	113	85	8	102	14	1
91		2	90	94	2	65	-23	2
76		4	72	27	1	49	-45	7
54		2	48	55	8	36	-21	2
47		1	42	39	2	32	-101	3
38		6	28	-7	3	27	-180	1
29		3	15	5	2	20	-131	2
26		1	14	-52	1	8	-340	1