Ab Initio Study of $SO_2 + H_2O$

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We present quantum chemical calculations of several stationary points in the $SO_2 + H_2O$ system. Final calculations at the QCISD(T)/ 6-311++G(d,p)//MP2/6-31G(d) level predict the following gas-phase thermochemistry at 270 K. (1) $SO_2 + H_2O \rightarrow H_2SO_3$($\Delta H° = +44.9$ kJ mol^{-1}; $\Delta G° = +92.7$ kJ mol^{-1}; $E_a \geq 130$ kJ mol^{-1}). (2) $SO_2 + H_2O \rightarrow (SO_2{-}H_2O)$ ($\Delta H° = -7.6$ kJ mol^{-1}; $\Delta G° = +20.1$ kJ mol^{-1}; $K_p = 1.29 \times 10^{-4}$). The high activation barrier for H_2SO_3 formation and its large positive $\Delta G°$ are consistent with this species having never been detected. Lower level calculations on reaction 1 in the aqueous phase indicate a positive $\Delta G°$ and high activation barrier in solution as well. The calculated 1:1 SO_2−water complex geometry, vibrational frequencies, and rotational constants are in good agreement with experimental results. Its low binding energy suggests that it is unimportant in the atmosphere.

Introduction

The atmospheric oxidation of SO_2 to sulfuric acid[1,2] is thought to occur predominantly within cloud droplets, except in conditions of very low relative humidity. The first step in this process is the entry of SO_2 into the drop and its solvation and hydrolysis. These steps are generally written as

$$SO_2\,(g) \rightarrow SO_2\,(aq)$$

$$SO_2\,(aq) + H_2O \rightarrow HSO_3^- + H^+$$

The second step formally involves H_2SO_3, sulfurous acid, though this species has never been isolated. The infrared[3] and Raman[4] spectra of aqueous solutions of SO_2 are essentially identical with those of gas-phase SO_2, suggesting that "H_2SO_3" is in fact a loosely aquated SO_2 molecule. The near-UV spectrum of "sulfurous acid" solutions consists of a broad, featureless band centered about 278 nm,[5] about a 10 nm blue shift from the maximum of the gas-phase SO_2 ($^1A_2;^1B_1 \leftarrow X^1A_1$) transition. No explanation of why H_2SO_3 does not exist in molecular form (whereas sulfuric acid, H_2SO_4, is very stable) appears in any of the standard texts.[6−9]

Recently, a further step in the air−aqueous transport of SO_2 has been identified. On the basis of kinetic measurements of SO_2 uptake in aqueous droplets, Jayne et al.[10] proposed that a surface complex could be formed between SO_2 and H_2O at the air−water interface. Their model was of a contact ion pair of H^+ and HSO_3^- bound at the interface by $\Delta G^0_{ads} = -29$ kJ mol^{-1}. Following that suggestion, we presented further evidence that such a complex might exist.[11] A combination of surface second harmonic generation (SHG) and surface tension measurements showed that a S(IV) species does adsorb at the air−water interface. These measurements provided an upper limit to the room temperature ΔG^0_{ads} (from the gas phase) of -23 kJ mol^{-1}. The nature of this adsorbed species could not be ascertained from the surface SHG measurements.

A complex of SO_2 with water has been reported in the gas phase by microwave spectroscopy[12] and in a frozen matrix by infrared spectroscopy.[13] The analogous $SO_3{-}H_2O$ complex is also known both from experimental results[14] and ab initio[15−17] calculations; that complex is thought to be critical in the gas-phase transformation of SO_3 to H_2SO_4.[18,19] However, unlike SO_3, SO_2 does not react with water in the gas phase. Again, no explanation for this observation has been proposed.

In the following we present ab initio calculations of several stationary points in the SO_2−water system. The issues we wish to address are the following. What are the thermodynamics and kinetics of H_2SO_3 formation, and why has it not been isolated? What is the binding energy of the $SO_2{-}H_2O$ complex? Is this an important atmospheric species? Does such a complex play a role in the adsorption of SO_2 at the water surface? Is it important for the understanding of "sulfurous acid"?

Details of Calculation

All calculations were performed using GAUSSIAN suites of programs.[20,21] The smaller calculations used GAUSSIAN 94W [20] on a Windows-based computer; the rest used GAUSSIAN 92 [21] running on a Unix-based system. The basis sets used were the standard split-valence sets available in the program suites. A 6-31G(d) basis set was used to perform a survey of all aspects of the chemistry; subsequently, various points of interest were calculated using a 6-311++G(d,p) basis set as well. Electron corelation effects were included by use of Moller−Plesset perturbation theory[22] to second (MP2) and fourth (MP4) order and by the quadratic configuration interaction method,[23] including single, double and triple excitations (QCISD(T)).

Geometry optimizations of all species were carried out at the MP2 level using the 6-31G(d) basis set. Further geometry optimizations of the 1:1 complex were carried out at the MP2 level using a basis set augmented by diffuse functions and p-functions on the hydrogens (MP2/6-31+G(d,p)). Final MP4SDQ and QCISD(T) energies using a 6-311++G(d,p) basis set were calculated at the optimized geometries of all the species except the transition state. To test the effect of including

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TABLE 1: Ab Initio Energies of Species Involved in Reaction 1[a]

	6-31G(d)		6-311++G(d,p)	
	MP4SDQ	QCISD(T)	MP4SDQ	QCISD(T)
SO_2	−547.681 06	−547.699 25	−547.782 98	−547.806 14
H_2O	−76.204 94	−76.207 46	−76.281 21	−76.286 69
$SO_2 + H_2O$	−623.886 00 (0.0)	−623.906 71 (0.0)	−624.064 19 (0.0)	−624.092 83 (0.0)
TS	−623.834 77 (+134.5)	−623.857 70 (+128.7)		
H_2SO_3	−623.882 70 (+8.7)	−623.901 58 (+13.5)	−624.050 23 (+36.7)	−624.077 82 (+39.4)

[a] Energies in hartrees (relative energies in parentheses in kJ mol^{-1}) calculated at the MP2/6-31G(d) optimized geometries.

additional high angular momentum functions in the basis set, a series of MP2/6-311+G(2df,2p) calculations were performed at the optimized geometries as well.

Transition-state calculations used the synchronous transit-guided quasi-Newton method[24] at the MP2/6-31G(d) level. In this approach, the program generates an initial guess for the transition-state structure, given optimized reagent and product geometries. It then performs a full geometry optimization on this guess, resulting in an optimized transition state. At all the calculated stationary points, vibrational frequency calculations were performed to ensure that these were true minima (or a true saddle point, in the case of the transition state.) These determinations were done at the MP2/6-31G(d) level by analytical calculation of the harmonic force constants at the stationary point. Since calculations of this type typically overestimate the harmonic force constants, the calculated harmonic frequencies were corrected by the factor 0.9427.[25] An intrinsic reaction coordinate (IRC) calculation was performed, starting at the optimized geometry, to confirm that the transition state does, indeed, connect the $SO_2{-}H_2O$ complex and H_2SO_3.

The basis set superposition error (BSSE)[26] in the calculations involving the complex was estimated using the full counterpoise correction.[27] Although there has been some discussion over the merits of using the full correction, especially at the CI level, debate seems to be settled in favor of the full correction.[28] At the geometry of the complex, the total energy was calculated using "ghost" orbitals on H_2O (i.e., with the water nuclear charges set to zero); the difference between this energy, designated $E(SO_2(H_2O)^{gh})$, and the energy of isolated SO_2 gives the artificial lowering of the SO_2 energy by the presence of the basis functions on water. This energy and the corresponding energy of water in the presence of "ghost" SO_2 orbitals are subtracted from the energy of the complex to give the binding energy corrected for BSSE: $\Delta E = E(SO_2{-}H_2O) - E(SO_2(H_2O)^{gh}) - E(H_2O(SO_2)^{gh})$. This calculation was performed only at the optimized geometry of the complex.

The effect of solvation in water for SO_2, H_2O, $SO_2{-}H_2O$, the transition state, and H_2SO_3 was calculated at the MP2/6-31G(d) level using a variant of the polarizable continuum model (PCM) of Tamasi and co-workers.[29] In that model the solute molecule is embedded in a polarizable continuum dielectric medium; the cavity it forms is modeled by a series of overlapping spheres, centered on the constituent atoms of the solute molecule. The coupling of the solute charge distributrion to the solvent electric field is evaluated from the charges induced on the surface of the solute cavity. In the variant used here, the isodensity polarized continuum model (IPCM),[30] this surface is defined by a surface of constant electron density, calculated in an iterative manner. We simulate aqueous solution in this approach as a continuum dielectric with $\epsilon = 78.85$.

Results and Discussion

(a) Overall Aspects of the Chemistry. A survey set of calculations were done using the 6-31G(d) basis set to examine the general features of the chemistry—sulfurous acid formation and complex formation. Higher level calculations were used to determine more accurately the energetics of these processes. At all levels of calculation a bound complex is formed between SO_2 and H_2O and the formation of H_2SO_3 is endothermic with a significant positive ΔG^0. By use of the 6-31G(d) basis set, a high barrier to the formation of H_2SO_3 is predicted. At the MP2/6-31G(d) level the results carry over into the solution phase as well, consistent with no experimental observations of molecular H_2SO_3 in either gas or solution phase.

(b) Reaction 1: $SO_2 + H_2O \rightarrow H_2SO_3$. There have been a small number of previous calculations that deal with this reaction. Baird and Taylor[31] calculated SCF reaction energies using STO-3G* and 4-31G* basis sets and reported $\Delta E_{el} = E(H_2SO_3) - E(SO_2) - E(H_2O)$ for reaction 1 of −117 and −30 kJ mol^{-1}, respectively. Recently, Brown and Barber[32a] and also Li and McKee[32b] gave results using accurate G2 level energies;[33] the calculated ΔE_{el} is +24.0 kJ mol^{-1}. With a zero-point correction of 11.7 kJ mol^{-1}, the ΔE_0 derived from these authors' results becomes +35.8 kJ mol^{-1}. The ΔH^0_{298} is given as +18.4 kJ mol^{-1} at the G2 level,[32] compared with the experimental estimate[34] of +7.1 kJ mol^{-1}.

Our results are presented in Tables 1 and 2, and the optimized geometries of H_2SO_3 and the transition state are shown in Figure 1. The SO_2 and H_2O geometries, frequencies and rotational constants are in reasonable accord with experimental results.[35] The calculated structure of H_2SO_3 is in excellent agreement with that given by Baird and Taylor.[31] The calculated transition-state geometry is qualitatively quite similar to that calculated for the $SO_3 + H_2O$ reaction,[16,17] with the concerted creation of an S−O bond out of the SO_2 plane and the transfer of a hydrogen from the oxygen atom of water to one of those in SO_2.

We obtain a ΔE_{el} for reaction 1 of +8.8 kJ mol^{-1} at the MP4SDQ/6-31G(d) level and of +13.6 kJ mol^{-1} using a QCISD(T)/6-31G(d) calculation. The zero-point correction is +13.6 kJ mol^{-1}, yielding ΔE_0's of 22.2 and 27.2 kJ mol^{-1}, respectively. By use of the larger 6-311++G(d,p) basis set, the values of ΔE_0 are +50.2 and +53.1 kJ mol^{-1} at the MP4SDQ and QCISD(T) levels, respectively. These values are somewhat higher than the endoergicities calculated at the G2 level.[32] However, it is clear that the calculations that use larger basis sets all show a significant positive value of ΔE_0 for the reaction.

Since the energies quoted here are calculated as $E(H_2SO_3) - E(SO_2) - E(H_2O)$, there is a potential error due to the lack of size consistency[24,36] in the CI calculation. This arises because the size of the orbital space in the H_2SO_3 calculation is larger than those in the SO_2 and H_2O calculations, allowing a wider selection of electron excitations to take place at the CI step. The quadratic configuration interaction approach used here is designed to be size-consistent.[23] As well, perturbation methods, such as Moller−Plesset perturbation theory, are rigorously free of this effect.[36]

TABLE 2: Rotational and Vibrational Constants in $SO_2 + H_2O$[a]

	SO_2	expt[b]	H_2O	expt[b]	TS	H_2SO_3	SO_2-H_2O	expt[c,d]
Rotational Constants (cm^{-1})								
A	1.880	2.027	27.26	27.88		0.275	0.270	0.293
B	0.322	0.344	14.00	14.51		0.250	0.130	0.127
C	0.275	0.293	9.25	9.28		0.157	0.0970	0.0967
Uncorrected Harmonic Frequency (cm^{-1})								
	486.4	517.7	1765.2	1594.8	1650.5 i	159.9	40.5	
	1077.5	1151.4	3537.4	3657.0	225.7	312.1	95.5	80.1
	1305.5	1361.8	3678.6	3755.8	453.9	442.0	124.4	
					501.0	452.6	145.2	
					523.8	482.1	219.3	
					707.5	776.9	270.3	
					882.0	783.9	487.0	522
					1034.4	1130.6	1077.4	1150
					1280.4	1157.5	1280.8	1343
					1305.2	1293.5	1637.2	1591
					1937.1	3635.7	3850.9	3630
					3667.6	3637.9	3992.9	3722

[a] MP2/6-31G(d) optimized geometries and frequencies except for the complex, calculated at MP2/6-31+G(d,p). [b] From ref 35. [c] Rotational constants from ref 12. [d] Vibrational constants from ref 13.

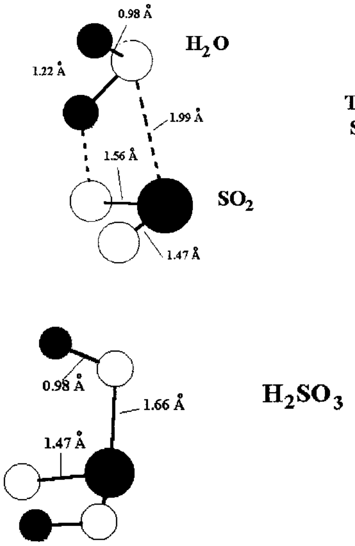

Figure 1. Geometries of H_2SO_3 and the transition state for reaction 1 optimized at the MP2/6-31G(d) level.

TABLE 3: IPCM Gas−Aqueous Solution Energies[a]

	isolated molecule (hartree)	aqueous solution (hartree)	$E_{soln} - E_{isolated}$ (kJ mol^{-1})
SO_2	−547.682 48	−547.687 31	−12.7
H_2O	−76.196 85	−76.210 08	−34.7
TS	−623.828 90	−623.840 48	−30.4
H_2SO_3	−623.867 78	−623.885 46	−46.4
SO_2-H_2O	−623.889 23	−623.899 59	−27.2

[a] MP2/6-31G(d), calculated at the optimized geometry of the isolated molecule.

The calculated rotational and vibrational constants are given in Table 2. Using these, we can determine the partition functions for reagents and products and hence the reaction free energy change. With our largest basis set, we calculate $\Delta G^0 = +91.7$ kJ mol^{-1} at 270 K for reaction 1, corresponding to an equilibrium constant of 1.82×10^{-18} (bar^{-1}) for formation of H_2SO_3. The standard enthalpy and entropy changes are calculated to be $\Delta H° = +44.9$ kJ mol^{-1} and $\Delta S° = -175$ J K^{-1} mol^{-1}. These unfavorable thermodynamics could well explain the lack of observation of free H_2SO_3 molecules.

The present study is the second report of the barrier to reaction 1. We calculate ΔE_{el} for formation of the transition state to be +128.5 kJ mol^{-1} at the QCISD/6-31G(d) level. Inclusion of the zero-point energy correction gives a ΔE_0 of 132 kJ mol^{-1}, in excellent agreement with the value of +134.3 kJ mol^{-1} given by Li and McKee[32b] and very much higher than the corresponding barrier for the $SO_3 + H_2O$ reaction. Hofmann and Schleyer[16] report a barrier of +62.3 kJ mol^{-1} for SO_3 hydrolysis, using the 6-31G(d) basis set at the MP2 level. At the MP2/6-31G(d) level, we calculate a barrier for reaction 1 of +136 kJ mol^{-1}. In the calculations of Hofmann and Schleyer,[16] higher level calculations (MP4SDQ/6-311+G(2df,p)) gave rise to a slight increase in the predicted barrier height for SO_3 hydrolysis, to approximately 87.9 kJ mol^{-1}. This is in reasonable agreement with the 99.6 kJ mol^{-1} given by Morokuma and Muguruma at the MP4SDQ/6-311+G(d,p) level.[17] We can anticipate that the barrier to reaction 1 is probably not much lower than the +132 kJ mol^{-1} calculated here.

The gas−aqueous solution energies were calculated at the MP2/6-31G(d) level, using the gas-phase geometries. They are given in Table 3. There is very little change in the reaction energy in going to solution. At this level of theory, the gas-phase reaction has ΔE_{el} of +30.3 kJ mol^{-1}; in aqueous solution $\Delta E_{el} = 31.3$ kJ mol^{-1}. Although the ΔE_{el} is only one factor in the reaction thermodynamics, it is a major contributer to the final $\Delta G°$. At the same time, the predicted activation barrier is higher by about 15 kJ mol^{-1} in solution than in the gas -phase. Thus, it is reasonable to conclude that the $SO_2 + H_2O \rightarrow H_2SO_3$ reaction is both thermodynamically and kinetically unfavored in the solution phase as well as in the gas phase.

(c) Reaction 2: $SO_2 + H_2O \rightarrow (SO_2\text{-}H_2O)$. The SO_2-H_2O 1:1 complex has been the subject of two experimental reports. In 1988 Schriver et al.[13] reported infrared spectra of matrix-isolated 1:1, 1:2, and 2:1 complexes of water and sulfur dioxide. In the 1:1 complex, the vibrational frequencies of each partner in the complex are close to the values of the isolated molecules. The results were modeled well by assuming two equivalent OH oscillators on the water moiety. These data suggest that each partner in the complex exists in a local C_{2v} environment. The ν_3/ν_1 intensity changes in the water moiety upon complexation were taken as evidence of a charge-transfer interaction, with the water's oxygen as the electron donor.

A microwave spectrum and the resulting structure derived for the gas-phase complex were given by Matsumura et al. in 1989.[14] Consistent with the IR results, the complex was reported to consist of essentially unperturbed SO_2 and H_2O moieties,

TABLE 4: Ab Initio Energies of Species in Reaction 2

	6-31G(d)[a]		6-311++G(d,p)[b]	
	MP4SDQ	QCISD(T)	MP4SDQ	QCISD(T)
SO_2[c]	−547.681 06	−547.699 25	−547.782 98	−547.806 14
$SO_2(H_2O)^{gh}$ [c]	−547.682 51	−547.700 70	−547.784 18	−547.807 58
H_2O[c]	−76.204 94	−76.207 46	−76.281 21	−76.286 69
$H_2O(SO_2)^{gh}$ [c]	−76.209 03	−76.211 59	−76.282 54	−76.288 11
SO_2-H_2O[c]	−623.896 91	−623.917 36	−624.072 45	−624.101 40
ΔE_{el}[d]	−14.1	−13.3	−15.0	−15.0
zero-point correction[d]	+8.4	+8.4	+7.8	+7.8
ΔE^0 [d]	−5.7	−4.9	−7.2	−7.2

[a] Calculated using the MP2/6-31G(d) optimized geometries and frequencies. [b] Calculated using the MP2/6-31+G(d,p) optimized geometries and frequencies. [c] Energies in hartrees. [d] Energies in kJ mol^{-1} .

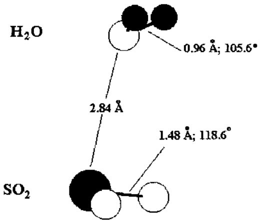

Figure 2. Geometry of the SO_2-H_2O complex, calculated at the MP2/6-31+G(d,p) level.

forming a “sandwich” type structure with the O atom of the H_2O lying roughly above the S atom in SO_2, the water H atoms and sulfur dioxide O atoms pointing in the same direction and the planes containing the two molecules forming an included angle of 44°.

Table 2 lists the results obtained here for the vibrational frequencies and rotational constants of the free molecules and complex, and the experimental values for comparison. The calculated geometry of the complex is illustrated in Figure 2. Although the vibrational frequencies are not quantitatively reproduced at this level of theory, the small shifts in going from free molecule to complex are all consistent with experimental results. The rotational constants are reproduced to better than 10% for the free molecules and for the complex, giving some confidence in the complex’s calculated geometry.

After correction for BSSE and zero-point differences, the SO_2-H_2O complex is predicted to be bound by 4−10 kJ mol^{-1}, depending on the level of calculation. Table 4 lists the ab initio energies as well as the binding energy of the complex for each of the basis sets and levels of calculation used here. As expected, the counterpoise correction, obtained by taking the difference between the energy of the free molecule (e.g., SO_2) and the molecule in the presence of “ghost” orbitals (e.g., $SO_2(H_2O)^{gh}$), decreases with increasing basis set size and increases with increasing inclusion of correlation effects. The final results at the MP4 and the QCISD(T) levels are essentially identical. Calculations at the MP2/6-311+G(2df,2p) level and the MP2/6-31G(d) level yield binding energies (corrected for BSSE and zero-point energies) of 5.9 and 4.7 kJ mol^{-1}, respectively, indicating that exclusion of high angular momentum basis functions does not significantly alter the calculated thermochemistry.

Using the results in Tables 2 and 4 allows calculation of the relevent partition functions and hence the thermodynamics of complex formation. (Li and McKee[32b] report a binding energy of 14.6 kJ mol^{-1} at the G2 level, but this value is uncorrected for BSSE.) At 270 K the QCISD(T)/6-311++G(d,p)//MP2/6-31+G(d,p) calculation yields $\Delta H^\circ = -7.60$ kJ mol^{-1}, $\Delta G^0 = +20.1$ kJ mol^{-1} and $\Delta S^\circ = -102$ J K^{-1} mol^{-1} for reaction 2. The equilibrium constant for complex formation at this temperature is 1.29×10^{-4} bar^{-1}. The small binding energy and rather unfavorable equilibrium constant argue against the complex being atmospherically important. At 270 K and a water mixing ratio of 10^{-3}, the fraction of SO_2 bound in a complex with water is only 5×10^{-8}. By contrast, the SO_3-H_2O complex has a calculated binding energy $\Delta E^\circ = -(30-35)$ kJ mol^{-1} [16,17] and plays an important role in the atmospheric reaction of SO_3 with H_2O.

TABLE 5: Mulliken Electron Populations in the SO_2-H_2O Complex

	O−S−O			H−O−H		
	O	S	O	H	O	H
isolated molecules:	−0.40	+0.80	−0.40	+0.25	−0.51	+0.25
in complex:	−0.42	+0.84	−0.42	+0.29	−0.57	+0.29

Examination of the Mulliken electron populations suggests that dipole−dipole and dipole-induced dipole interactions are important in the complex binding. There is a mutual polarization effect such that both the SO_2 and the H_2O dipole moments are increased in the complex. Table 5 displays the calculated electron population of each atom in the complex and in the isolated molecules. Although there is clearly a shift of electron density, from sulfur to oxygen in SO_2 and from hydrogen to oxygen in water, there is no overall electron transfer from water to sulfur dioxide predicted.

At the MP2/6-31G(d) level, the binding energy of the complex (not corrected for zero-point energies or BSSE) is predicted to decrease in aqueous solution, from $\Delta E_{el} = -26.0$ kJ mol^{-1} in the gas phase to -5.8 kJ mol^{-1} in solution. Inclusion of zero-point and BSSE corrections will reduce this further, suggesting that the 1:1 complex may be unstable in solution with respect to the solvated SO_2 and H_2O species. This may be an artifact of the way in which the solvation energy is calculated in the ICPM model, since the dipole moment of the complex as a whole is significantly smaller than the dipole moments of the free molecules in the gas phase. There is a suggestion, though, that the 1:1 complex may not be an important species in aqueous solution.

Conclusions

We have demonstrated that the formation of H_2SO_3 from reaction 1 is significantly endoergic, with a high positive ΔG° and a large activation barrier. ICPM calculations indicate that this large endoergicity carries over into aqueous solution as well. The equilibrium constant we calculate for sulfurous acid formation from water and sulfur dioxide is 1.8×10^{-18}, a value consistent with the fact that H_2SO_3 has not been observed experimentally. We conclude that H_2SO_3 is too thermodynamically unstable to be observed.

A 1:1 complex is calculated to be formed between H_2O and SO_2; it has a binding enthalpy of 7.2 kJ mol^{-1} and a geometry in excellent agreement with that determined experimentally. The low binding energy suggests that this complex is not likely to play an important role in atmospheric SO_2 oxidation chemistry. The complex is predicted to become less strongly bound in aqueous solution, so it is probably not important in describing aquated SO_2. The positive $\Delta G°$ and the modest dipole−dipole interaction indicate that the 1:1 complex is probably not the "surface-bound" SO_2 species reported experimentally.[10,11]

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