

Computational Study of the Mono- and Dianions of SO₂, SO₃, SO₄, S₂O₃, S₂O₄, S₂O₆, and S₂O₈

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DFT theory (B3LYP/6-311+G(2d)//B3LYP/6-31+G(d)) has been used to characterize sulfoxy anions and dianions as large as S₂O₈²⁻, while post-HF theory ([QCISD(T)/6-31+G(2df)]/MP2/6-31+G(d)) has been used for systems as large as S₂O₃²⁻. Adiabatic and vertical ionization potentials have been computed to assess the gas-phase stability of the dianions. Three dianions (S₂O₆²⁻, S₂O₈²⁻, and SO₄²⁻·4H₂O) are predicted to have positive vertical ionization energies. S₂O₆²⁻ is predicted to have a negative (exothermic) adiabatic ionization potential; however, a large predicted geometry change between the dianion and monoanion rationalizes the measurable experimental lifetime of the dianion in the gas phase. Isotropic hyperfine coupling constants for ³³S have been calculated for the sulfoxy monoanions and compared with experiment.

Introduction

There has been considerable recent interest in gas-phase molecular anions and dianions.^{1–8} In polar solvents, polyanions such as SO₄²⁻ and PO₄³⁻ are quite stable due to the interaction of the negative charge with the solvent. In the gas phase, such stabilization is not possible and common anions such as SO₄²⁻ and PO₄³⁻ are unstable with respect to electron autodetachment.^{9,10} However, larger molecular systems have been designed which are stable in the gas phase with two or more extra electrons. For example C_n²⁻ with $n \geq 7$ are predicted to be stable in the gas phase.³ In addition, C₆₀ⁿ⁻ with $n \leq 3$ have been prepared experimentally.² The key to success is to have the charge separated, either radially as in MY₃²⁻ where M is positively charged and Y negatively charged, or to allow charge to localize at opposite ends of a linear molecule (C_n²⁻).

The recent development of electrospray mass spectrometry¹¹ has enabled solution-phase ions to be transferred into the gas phase. Using this technique, Blades and Kebarle¹² have produced gas phase ions of S₂O₆²⁻, S₂O₈²⁻, and SO₄²⁻·4H₂O. Clusters smaller than SO₄²⁻·3H₂O could not be prepared due to intramolecular proton transfer which forms HSO₄⁻ and OH⁻.¹²

Method

Calculations have used the GAUSSIAN 92 and 94 systems.¹³ Geometries were fully optimized within the appropriate point group and frequencies calculated at the B3LYP/6-31+G(d) level, while single-point calculations were carried out at the B3LYP/6-311+G(2d) level.¹⁴ For smaller systems, geometries have also been optimized at the MP2/6-31+G(d) level. Additional single-point calculations on MP2/6-31+G(d) geometries were made at the MP2/6-31+G(2df) and QCISD(T)/6-31+G(d) levels in order to estimate relative energies at the [QCISD(T)/6-31+G(2df)] level. Zero-point corrections are included without any weighting factor at the B3LYP/6-31+G(d) level. The standard DFT level is B3LYP/6-311+G(2d)//B3LYP/6-31+G(d)+ZPC and the standard QCI level is [QCISD(T)/6-31+G(2df)]/MP2/6-31+G(d)+ZPC/DFT. All post-HF calculations employed the frozen-core approximation. A table of total energies (hartrees) and zero-point energies (kcal/mol) is provided as supporting information.

For the anions S₂O₄⁻, S₂O₆⁻, and S₂O₈⁻, a small imaginary frequency remained in the lowest-energy structure, indicating

that the global minimum was not found. In each case, an inspection of the transition vector revealed that a distortion to C₁ symmetry was favorable. Previous experience has shown that these distortions result in a stabilization of less than 1 kcal/mol and are often reversed when the effects of zero-point corrections are added.

Adiabatic electron affinities of the monoanions were calculated at DFT and QCI levels for smaller systems and at the DFT level for larger systems. Calculated electron affinities were available^{15,16} for O, S, O₂, and SO₂ at G2¹⁵ which is effectively at the [QCISD(T)/6-311+G(3df,2p)]/MP2/6-31G(d) level with zero-point and higher level corrections. G2 calculations made in this work extend the list of electron affinities for sulfoxy compounds to include SO and SO₃.

Vertical ionization energies of the dianions were calculated in two ways. The first was the Δ method at the B3LYP/6-311+G(2d) level and the second was outer valence Green's function (OVGF) method¹⁷ using the 6-31+G(d) basis set. Discussion of electron affinities and ionization energies will be in units of kcal/mol rather than the more common units of eV in order to maintain uniformity.

Calculations on small dianions present special difficulties for ab initio calculations.³ If the dianion is unstable to electron autodetachment, then a sufficiently flexible method should give the monoanion and a free electron as the lowest energy solution. Some closed-shell dianions, such as SO₄²⁻, are unstable to electron autodetachment but have all negative eigenvalues of the HF wave function, signifying that all pairs of electrons are bound. Such systems can probably be treated reliably with conventional computational methods. However, closed-shell dianions with at least one positive eigenvalue of the HF wave function, such as SO₂²⁻ or S₂O₄²⁻ require, special care.¹⁸ All calculations were checked to ensure that diffuse functions were not significantly occupied.

Results and Discussion

Smaller Systems (O, S, O₂, SO, SO₂, SO₃, SO₄, S₂O₃). The computed and experimental^{19,20} geometries of SO (triplet), SO₂, SO₂⁻, and SO₃ are compared in Table 1. The B3LYP/6-31+G(d) values are closer to experiment than MP2/6-31+G(d) but still too long by about 0.03 Å. As the SO_x species becomes negatively charged, the S–O bond length increases and the O–S–O bond angle decreases (Table 2) due to the increase of

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TABLE 1: Comparison of Calculated and Experimental Geometries for SO, SO₂, SO₂⁻, and SO₃

	MP2/6-31+G(d)	B3LYP/6-31+G(d)	exptl ^a
SO(triplet)	1.524	1.516	1.481
SO ₂	1.482	1.466	1.432
SO ₂ ⁻	1.550	1.548	1.523 ^b
SO ₃	1.463	1.454	1.43

^a Reference 19. ^b Reference 20.**TABLE 2: Increase of SO Bond Distance (Å) or Decrease of OSO Bond Angle (deg) with Increase of Negative Charge**

charge	MP2/6-31+G(d)				B3LYP/6-31+G(d)			
	SO ₂	SO ₃	SO ₄ ^a	S ₂ O ₃ ^a	SO ₂	SO ₃	SO ₄ ^a	S ₂ O ₃ ^a
Bond Distance Change								
0 → -1	0.068	0.049			0.082	0.062		
-1 → -2	0.078	0.057	0.017	0.029	0.075	0.056	0.018	0.028
Bond Angle Change								
0 → -1	-4.1	-5.8			-3.6	-6.3		
-1 → -2	-4.4	-6.5			-4.2	-5.9		

^a From C_{3v} symmetry structure for monoanion.

antibonding character of the S—O bond. The electron affinities for S/O compounds are compared in Table 3. In almost every case, the DFT and QCI values bracket the experimental value. For O, S, SO, and SO₂, the DFT value is an average of 4.2 kcal/mol too high, while the QCI value is an average of 4.1 kcal/mol too low. Electron affinities at G2 theory (available for O, S, O₂, SO, and SO₂) have an average deviation of 1.6 kcal/mol.

The standard experimental EA of SO₃ (39.2 kcal/mol) is a lower bound determined by collisional ionization.²¹ Both calculated values are higher (57.7 kcal/mol, DFT; 49.8 kcal/mol, QCI) and suggest that the experimental value from Lias²¹ is too low. Two alternative values are available from the literature. One is from electron-transfer experiments²² (43.8 kcal/mol) and the other is from ion/molecular equilibrium techniques²³ (50.7 kcal/mol). Present calculations at the G2 level give an electron affinity of 49.5 kcal/mol, in closest agreement with the ion/molecular equilibrium measurement.²³

Neutral SO₄ and S₂O₃ have been previously studied at the MP2/6-31+G(d) level.²⁴ The most stable structure for both species is a three-membered ring (SOO for SO₄ and SSO for S₂O₃) with two terminal oxygens attached to a ring sulfur. In SO₄, the ring O—O distance is sensitive to computational method. At the DFT level, the O—O distance (1.586 Å) is significantly shorter than that computed at the MP2 level (1.632 Å). An optimization at the QCISD/6-31+G(d) level produced an intermediate O—O distance of 1.614 Å. In an earlier study of SO₄, MP2/6-31+G(d) frequencies of the three-membered ring were compared with the measured frequencies of a matrix-isolated species²⁵ in an attempt to determine its structure. Table 4 extends the comparison to DFT and QCISD/6-31+G(d) frequencies. The agreement between both methods and experiment remains acceptable, and further supports the identification of the C_{2v} structure.²⁴

While many experimental papers have dealt with the oxidative ability of SO₄⁻ in solution phase,²⁶ its gas-phase properties remain almost completely unknown. In earlier work on single crystals at 300 K, Morton et al.²⁷ tried to determine the ESR parameters of SO₄⁻ and S₂O₃⁻. The hyperfine structure of ³³S in SO₄⁻ could not be detected, however; it was determined that the symmetry of SO₄⁻ could not be higher than C_{2v}.

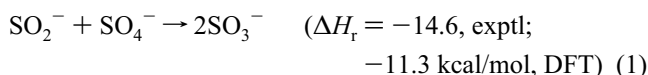
Three different structures of C_{2v}, C_{3v}, and D_{2d} symmetries were considered for SO₄⁻. Spin contamination was serious for the HF/MP2 calculations and probably accounted for the 8 kcal/mol change (Table 5) in relative energies between MP2/6-

31+G(d) and MP2/6-31+G(2df). The spin-squared values for the three structures were 0.80, 0.85, and 0.83 for the C_{2v}, C_{3v}, and D_{2d} symmetry structures, respectively.

In contrast, spin contamination was not as serious at the DFT level as found at the HF level, which is recognized as one of the advantages of the DFT method.²⁸ At the DFT level, the C_{2v} symmetry structure was 0.5 kcal/mol more stable than the C_{3v} structure and 1.6 kcal/mol more stable than the D_{2d} structure (Table 5). The SO₄⁻ C_{2v} structure can best be viewed as derived from neutral SO₄ with the extra electron added to the σ*_{OO} LUMO. The resulting O—O interaction is an example of an internal two-center three-electron bond (σ²σ*¹) which has increased in length from 1.586 Å in SO₄ to 2.271 Å in SO₄⁻ (nonbonded O—O distances in D_{2d} SO₄⁻ are 2.445 and 2.506 Å). An analysis of the unpaired spin density reveals that all of the unpaired spin is equally distributed between the two oxygen centers of the 2c—3e bond.

The lowest-energy C_{3v} state of S₂O₃⁻ is formed by removing one electron from the HOMO of S₂O₃²⁻ which is of e symmetry. The resulting ²E state is Jahn—Teller unstable and can distort to C_s symmetry and form a lower-symmetry ²A' or ²A'' state. The ²A' state is predicted to be more stable than the ²A'' by 0.2 and 0.6 kcal/mol more stable than the ²E state at the DFT level *without zero-point correction*. Inclusion of zero-point correction leads to the paradoxical result that the ²E state is slightly more stable than the ²A' or ²A'' state. A rigorous study of the S₂O₃⁻ surface would require solving the electronic and nuclear (vibrational) wave functions simultaneously. Since the J—T distortion from C_{3v} is likely to be very small, the ²E state of S₂O₃⁻ will be taken as the ground state.

The first electron affinity of SO₄ is larger than S₂O₃ indicating that the first added electron is more tightly bound in SO₄⁻. The EA of SO₄ is 121.9 kcal/mol by DFT and 111.5 by QCI, while for S₂O₃ the EA values are 94.8 and 86.5 kcal/mol by DFT and QCI, respectively. The second EA (SO₄⁻ → SO₄²⁻) is negative (i.e., unbound) for both SO₄⁻ (-39.0, DFT; -36.1 kcal/mol, QCI) and S₂O₃⁻ (-37.0, DFT; -38.1 kcal/mol, QCI). Previous calculations^{9,10} have been reported for the vertical IP of SO₄²⁻ in which the SO₄⁻ energy is evaluated at the SO₄²⁻ optimized geometry. These calculations show that gaseous SO₄²⁻ should spontaneously emit an electron. Using experimental heats of formation of gaseous SO₄⁻ and SO₄²⁻,^{29,30} the EA of SO₄⁻(g) is 3 kcal/mol. It is likely that the experimental estimate of ΔH_f(SO₄²⁻(g)) is too low, since the predicted exothermicity of eq 1 is in good agreement with experiment.



Oxygen atom and oxygen anion (O⁻) affinities are tabulated in Tables 6 and 7, respectively, at the DFT level. The addition of O and O⁻ is predicted to be exothermic in all cases except for addition of O⁻ to SO⁻ and SO₂⁻. The most exothermic process is the addition of O to SO₂²⁻ and SO₃²⁻, where the stabilization is due to the additional center for charge delocalization. The exothermic process O⁻ + SO₃⁻ → SO₄²⁻ (6.3 kcal/mol) indicates that the gas-phase sulfate ion (if it existed) would be stable to fragmentation.

Larger Systems (SO₅, S₂O₄, S₂O₆, S₂O₈, SO₄·4H₂O). The previous discussion indicates that geometries by DFT closely parallel geometries by MP2 and the DFT energetics are similar in quality to QCI. Therefore, the larger systems were only studied with DFT.

SO₅²⁻ and SO₅⁻. The most stable forms of SO₅²⁻ and SO₅⁻ have a tetracoordinate sulfur and a peroxide linkage. A X-ray

TABLE 3: Adiabatic Electron Affinities (kcal/mol) of Various Sulfoxy Compounds

	1st electron affinity ^a				2nd electron affinity ^a	
	DFT ^b	QCIC ^c	G2 ^d	exptl ^e	DFT ^b	QCIC ^c
O	37.1 (1.61)	27.3 (1.18)	32.3 (1.40)	33.7 (1.46)		
S	50.6 (2.19)	41.0 (1.78)	46.1 (2.00)	47.9 (2.08)		
O ₂	13.6 (0.59)	7.1 (0.31)	10.9 (0.47)	10.1 (0.44)		
SO	27.8 (1.20)	22.0 (0.95)	27.7 (1.20) ^f	25.1 (1.09)		
SO ₂	34.1 (1.48)	24.3 (1.05)	26.7 (1.16) ^g	25.5 (1.10)	-125.9 (-5.46)	-129.7 (-5.62)
SO ₃	57.7 (2.50)	49.8 (2.16)	49.5 (2.15) ^f	39.2 (1.70)	-78.2 (-3.39)	-80.3 (-3.48)
				43.8 (1.90) ^h		
				50.7 (2.20) ⁱ		
SO ₄	121.9 (5.28)	111.5 (4.84)			-39.0 (-1.69)	-36.1 (-1.56)
S ₂ O ₃	94.8 (4.11)	86.5 (3.75)			-37.0 (-1.60)	-38.1 (-1.65)
SO ₅	78.1 (3.39) ^j			<76.2 (3.30) ^k	-62.7 (-2.72)	
S ₂ O ₄					-61.3 (-2.66)	
S ₂ O ₆					-9.1 (-0.39)	
S ₂ O ₈					8.1 (0.35)	

^a The ionization potential in eV is given in parentheses. ^b At the B3LYP/6-311+G(2d)+ZPC level. ^c At the [QCISD(T)/6-31+G(2df)]+ZPC level. ^d Reference 15. ^e Reference 19. ^f This work. ^g Reference 16. ^h Reference 22. ⁱ Reference 23. ^j Neutral SO₅ assumed to be SO₃ + O₂. ^k Heat of formation of SO₅⁻(g) taken from ref 33.

TABLE 4: Calculated Vibrational Frequencies (cm⁻¹) for SO₄ and SO₄⁻

mode	SO ₄ neutral				SO ₄ ⁻
	MP2/ 6-31+G(d) ^a	B3LYP/ 6-31+G(d)	QCISD/ 6-31+G(d)	exptl ^b	B3LYP/ 6-31+G(d)
b ₁	1436	1378	1401	1437	1174
a ₁	1245	1214	1237	1267	1095
a ₁	876	932	921	927	889
b ₂	795	683	730	777	709
a ₁	643	662	637	611	517
b ₂	455	456	475		427
a ₁	460	454	469	498	341
b ₁	450	447	463	490	501
b ₂	283	287	298		337

^a Reference 24. ^b Reference 25.

structure of the HSO₅⁻ anion (related to SO₅²⁻) reveals three S—O distances of 1.44 Å and one of 1.63 Å.³¹ The calculated gas-phase O₃SOO²⁻ structure has three S—O distances of 1.509 Å and one of 1.657 Å (Figure 1). Two SO₅²⁻ structures with a pentacoordinate sulfur were calculated and found to be much higher in energy. A C_{4v} symmetry structure was 64.2 kcal/mol higher than the trans C_s structure and a D_{3h} symmetry structure was 80.5 kcal/mol higher in energy (Table 8). Rotation about the O—O bond in SO₅²⁻ is quite facile as shown by a calculated 3.4 kcal/mol barrier.

In the absence of a stabilizing medium (solid-state ionic lattice or polar solvent) SO₅²⁻ is unstable to decomposition to SO₄⁻ + O⁻ (42.1 kcal/mol exothermic, Table 9) or to SO₃⁻ + O₂⁻ (-55.9 kcal/mol exothermic, Table 9). The best way to view the bonding in SO₅²⁻ is the coupling of the unpaired electrons in SO₃⁻ and O₂⁻ to form a long (and weak) σ bond similar to the formation of O₂NNO₂ from two NO₂ radicals.³²

Removing an electron from SO₅²⁻ to form SO₅⁻ does not change the preferred structure. In the radical anion, three S—O bonds have shortened to 1.475 Å and one S—O bond has lengthened to 1.885 Å. Despite the longer S—O bond, SO₅⁻ is stable with respect to dissociation into SO₃⁻ and O₂ (20.4 kcal/mol endothermic). The only pentacoordinate SO₅⁻ species considered was a π-complex between SO₃ and O₂⁻ which was 67.1 kcal/mol higher in energy than the global minimum (Table 8). Both the cis and trans orientations of the OOS bond in SO₅⁻ are predicted to be minima which indicates that the rotational transition state must have C₁ symmetry.

Using the flowing afterglow technique, Möhler et al.³³ showed that SO₅⁻ forms in the gas phase by association of O₂ and SO₃⁻. From the estimated upper limit of ΔH_f(SO₅⁻(g)) (-170.9 kcal/

mol), the exothermicity of the process SO₃ + O₂ + e⁻ → SO₅⁻ can be placed at less than 76.2 kcal/mol. The corresponding DFT value (78.1 kcal/mol) is consistent with this estimate since electron affinities are overestimated by an average of 4 kcal/mol (Table 3).

The bonding in SO₅⁻ can be viewed as the interaction of SO₃⁻ with O₂ or of SO₃ with O₂⁻. Since the EA of SO₃ is 44.0 kcal/mol greater than O₂, the SO₃ moiety is more likely to have the negative charge. However, SO₃ is "an extremely strong Lewis acid",³⁴ and the donor/acceptor interaction could provide a strong thermodynamic driving force.

The SO₃⁻/O₂ interaction can be placed in context of a recent discussion of other radicals interacting with O₂.³² Depending on the strength of the 2c—2e O₂⁻ radical bond compared to promotion energy, O₂ can rehybridize to form a strong 2c—2e bond or avoid rehybridization and form a weak 2c—3e interaction with the π-bond. The fact that the O—O bond increases from 1.215 Å (O₂) to 1.308 Å (SO₅⁻) indicates that rehybridization takes place.

S₂O₄²⁻ and S₂O₄⁻. The X-ray structure of Na₂S₂O₄ reveals a dianion with eclipsed SO₂ units (C_{2v} symmetry) and a S—S distance of 2.39 Å.³⁵ In solution, spectroscopic evidence has been present for a centrosymmetric (C_{2h}, staggered) orientation.³⁶ Computationally, Leszczynski and Zerner³⁷ found the S₂O₄²⁻ staggered structure (C_{2h}) to be lower than the eclipsed structure (C_{2v}) by 9.2 kcal/mol at the MP2/6-31G*/3-21G level. Carter et al.³⁸ used a charge-stabilized LCAO-Xα method to calculate the relative energies of the staggered, gauche, and eclipsed conformers as 0.0, 0.6, and 6.0 kcal/mol, respectively. In the present work, the staggered (C_{2h}), gauche (C₂), and eclipsed (C_{2v}) conformers are ordered 0.0, 0.1, and 4.4 kcal/mol, respectively. It should be pointed out that at the B3LYP/6-31+G(d) level, the C_{2h} structure is a transition state and the C₂ structure a minimum but that the order reverses at the B3LYP/6-311+G(2d) level.

The dithionite anion is predicted to be unstable to autodecomposition by 61.3 kcal/mol (S₂O₄²⁻ → S₂O₄⁻ + e⁻) and to fragmentation (S₂O₄²⁻ → 2SO₂⁻) by 68.0 kcal/mol.

The monoanion S₂O₄⁻ has been studied by both experimental^{39,40} and theoretical⁴¹ techniques. Keesee et al.³⁹ have determined the binding energy of (SO₂)₂⁻ to be 24.0 kcal/mol. Bowers and co-workers⁴⁰ have studied the photodissociation dynamics of (SO₂)₂⁻ using a high pressure mass spectrometer. Applying an impulse model⁴² to their data, they concluded that the two SO₂ moieties were bound through two oxygen atoms rather than through the sulfurs. At the PMP4/6-31+G*/MP2/

TABLE 5: Comparison of Relative Energies (kcal/mol) at the DFT and QCI Levels for Several Sulfoxy Anions^a

	DFT level			QCI Level				
	B3LYP/a	B3LYP/b	+ZPC	MP2/a	MP2/c	QCISD(T)/a	[QCI/c] ^b	+ZPC
SO ₄ ²⁻ C _{2v} (² B ₁)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SO ₄ ²⁻ C _{3v} (² E)	1.8	1.7	0.5	-0.2	3.1	0.6	4.0	2.8
SO ₄ ²⁻ D _{2d} (² A ₂)	3.7	3.5	1.6	-1.9	6.2	-0.9	7.2	5.2
S ₂ O ₃ ²⁻ C _{3v} (² E)	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
S ₂ O ₃ ²⁻ C _s (² A')	-0.7	-0.6	0.1	-0.4	-0.6	-0.5	-0.6	0.1
S ₂ O ₃ ²⁻ C _s (² A'')	-0.4	-0.4	0.1	-0.2	-0.4	-0.3	-0.3	0.1

^a Basis set "a" is 6-31+G(d); basis set "b" is 6-311+G(2d); basis set "c" is 6-31+G(2df). "+ZPC" indicates inclusion of zero-point energies.

^b Additivity approximation. $\Delta E[\text{QCI}/c] = \Delta E(\text{MP2}/c) + \Delta E(\text{QCI}/a) - \Delta E(\text{MP2}/a)$.

TABLE 6: O Atom Affinities (kcal/mol) Calculated at the DFT Level

	binding		binding		binding	
SO	113.9		SO ⁻	120.1		
SO ₂	70.0		SO ₂ ⁻	93.7	SO ₂ ²⁻	141.3
SO ₃	17.4		SO ₃ ⁻	82.4	SO ₃ ²⁻	121.6

TABLE 7: O⁻ Atom Affinities (kcal/mol) Calculated at the DFT Level

	binding		binding	
SO	110.8		SO ⁻	-42.9
SO ₂	90.6		SO ₂ ⁻	-21.7
SO ₃	102.9		SO ₃ ⁻	6.3

6-31+G* level, Berthe-Gaujac et al.⁴¹ calculated the S-S one-electron-bonded structure and found the staggered conformer (2.1 kcal/mol lower in energy than the eclipsed conformer) to be bound by 20.1 kcal/mol.

In this study, three conformers of the 2c-1e bonded complex (staggered, gauche, and eclipsed) were considered, with relative energies of 0.0, 0.1, and 1.8 kcal/mol, respectively. At the B3LYP/6-31+G(d) level, the C₂ structure is lower in energy than the C_{2h} or C_{2v} structures but still characterized by an imaginary frequency. Further optimization was not undertaken since the B3LYP/6-311+G(2d) level reversed the energy order of the C₂ and C_{2h} structures. At the DFT level, (SO₂)₂⁻ is bound by 27.5 kcal/mol. The next higher product channel is SO₃⁻ + SO with an endothermicity of 47.8 kcal/mol.

A number of alternative geometries were considered for the cluster with a O-O or S-O intermolecular interaction. However, no reasonable candidate structures could be found and we are unable to support the interpretation of Bowers and co-workers⁴⁰ for the structure of the (SO₂)₂⁻ cluster.

S₂O₆²⁻ and S₂O₆⁻. The S₂O₆²⁻ anion has very recently been observed in the gas phase using electrospray mass spectrometry.¹² Since the SO₄²⁻ anion could not be observed in the gas phase, it is likely the larger size of the anion, which allows the negative charge to be distributed over more atoms,^{43,44} is the reason for its increased stability.

Several X-ray structures have been determined for S₂O₆²⁻ with various counterions.⁴⁵ Most recently, Kirfel and Will^{45a,b} solved the structure of Na₂S₂O₆·2H₂O in which the anion was staggered with a S-S bond length of 2.14 Å. The S-S bond in the anion was calculated longer than the X-ray distance (2.20 Å) by the LCAO-Xα method,³⁸ but the agreement was improved considerably (2.16 Å) when the charge-stabilized LCAO-Xα method was used.³⁸

Two different structures of the S₂O₆²⁻ anion were considered, D_{3d} with staggered SO₃ groups and a O₂SO-OSO₂²⁻ structure of C_{2h} symmetry (Figure 1) with a peroxy linkage. While the latter structure is the known structure for S₂O₈²⁻, it is predicted to be 58.9 kcal/mol higher than the D_{3d} structure for S₂O₆²⁻ (Table 8).

The adiabatic ionization potential of S₂O₆²⁻ is predicted to be positive (bound) by 9.1 kcal/mol. This result does not con-

tradict the fact that S₂O₆²⁻ can be observed in the electrospray experiments¹² since, as will be discussed below, the *vertical* ionization potential is negative (unbound). Decomposition into monocharged anions is predicted to be exothermic; 39.7 kcal/mol to two SO₃⁻ and 28.4 kcal/mol into SO₄⁻ plus SO₂⁻.

The S₂O₆⁻ ion is perhaps the most interesting of the sulfoxy anions in that the global minimum has a SOS linkage (O₂SOSO₃⁻) while the dianion has a SS linkage (O₃SSO₃²⁻). Four O₂SOSO₃⁻ structures (Figure 1) were calculated within 1.6 kcal/mol of each other. The precise nature of the conformer surface is ambiguous since three of the four structures (including the lowest-energy one) had at least one (albeit small) imaginary frequency. However, it can be concluded that rotation about the SO bond on either side of the SOS linkage is nearly unhindered.

The lowest energy pathway for S₂O₆⁻ decomposition is to SO₄⁻ plus SO₂ which is 16.3 kcal/mol endothermic, followed by SO₃⁻ plus SO₃, which is 27.1 kcal/mol endothermic. Since the SO₄⁻/SO₂ channel is more exothermic, it might be expected that the oxygen in the SOS linkage would be shorter on the SO₃ side rather than the SO₂ side. However, exactly the opposite is observed (Figure 1).

The dominant interaction between SO₃ and SO₃⁻ is an acceptor-donor interaction, O₃S ← OSO₂⁻, while between SO₄⁻ and SO₂ it is a 2c-3e interaction to form O₃SO:SO₂⁻. If SO₄⁻ and SO₂ are brought together, the 2c-3e interaction between SO₄⁻ and SO₂ is converted into a donor-acceptor interaction between SO₃⁻ and SO₃ by the transfer of an oxygen atom (Figure 2). Thus, the donor-acceptor interaction controls the geometry of the cluster. As the S-S distance is increased, the oxygen atom should transfer back toward the SO₃ so that the products begin to resemble SO₄⁻/SO₂.

The 2c-1e S·S bonded complex is 4.9 kcal/mol higher in energy than the global minimum with a S-S distance of 2.683 Å (Figure 1). With respect to SO₃⁻ and SO₃, the 2c-1e complex is bound by 32.0 kcal/mol, a relative strong S-S interaction.⁴⁶ The highest energy form of S₂O₆⁻ considered was the peroxy structure (Figure 1) which was calculated to be 33.8 kcal/mol above the global minimum on the S₂O₆⁻ potential energy surface (Table 8).

S₂O₈²⁻ and S₂O₈⁻. Peroxodisulfate ion, S₂O₈²⁻, has been described as "one of the most powerful and useful of oxidizing agents".⁴⁷ While the properties of S₂O₈²⁻ in the aqueous phase have been well studied,^{47b} its gas-phase properties have received only recent attention. In their study using electrospray mass spectrometry, Blades and Kebarle¹² noted that S₂O₈²⁻ was not prone to thermal detachment. Our adiabatic ionization potential is in agreement with this observation since it is the first sulfoxy dianion with an endothermic IP (8.1 kcal/mol). It was determined from the CID of S₂O₈²⁻, that the major daughter ions are SO₃⁻ and SO₅⁻. From a careful analysis of intensity patterns (due to natural isotopic abundances),¹² it was also concluded that S₂O₈²⁻ also decomposed into two SO₄⁻ ions. The DFT results predict three exit channels for S₂O₈²⁻ to be exothermic:

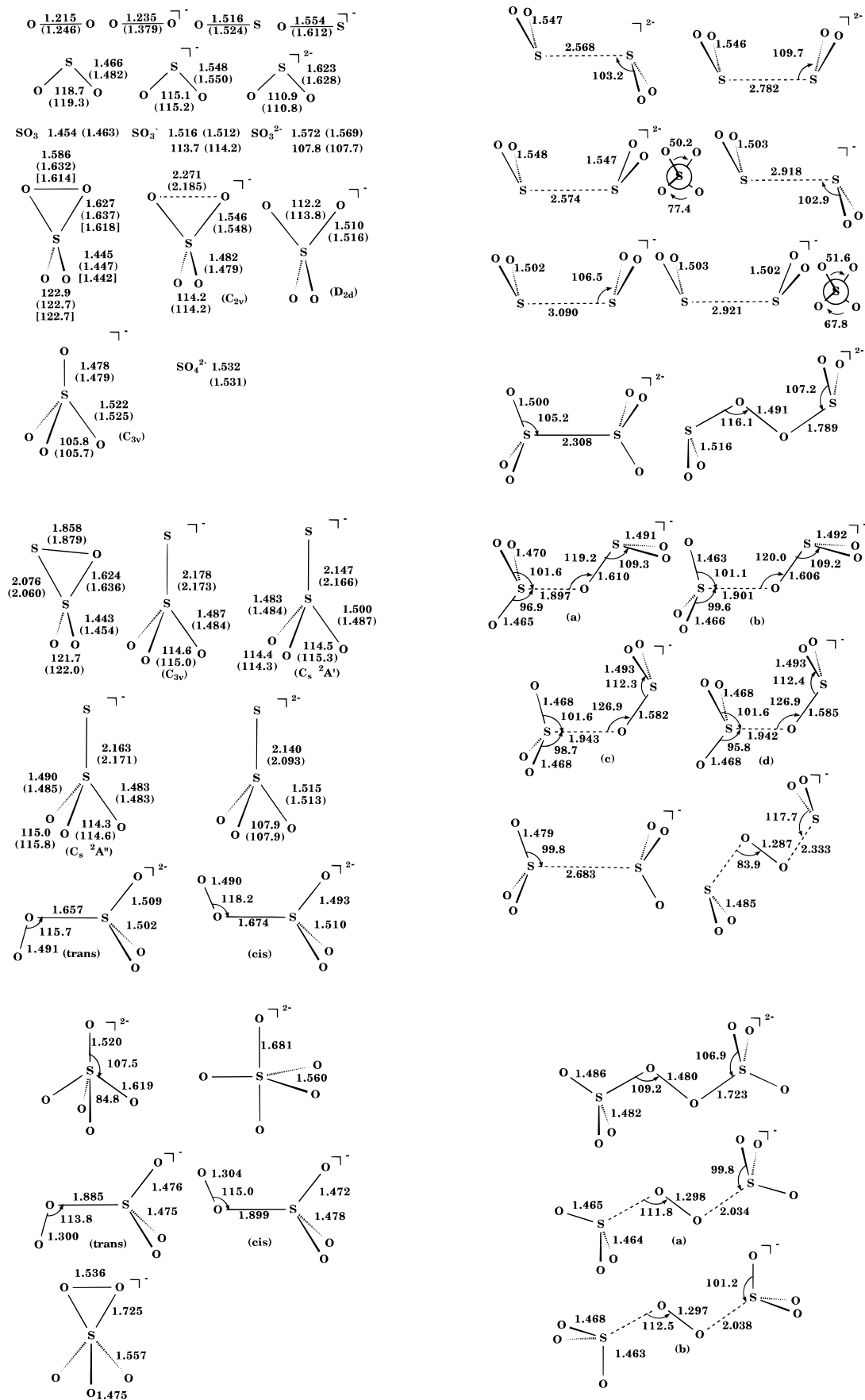


Figure 1. Selected geometric parameters (in angstroms and degrees) are given at the B3LYP/6-31+G(d) level for various species. Values in parentheses are at the MP2/6-31+G(d) level and values in brackets (for SO_4) are at the QCISD/6-31+G(d) level.

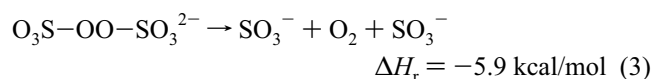
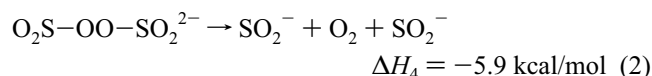
−50.9 kcal/mol to two SO_4^- , −26.2 kcal/mol to SO_5^- plus SO_3^- , and −5.9 kcal/mol to two SO_3^- plus O_2 .

Removing one electron from $\text{S}_2\text{O}_8^{2-}$ produces an anion with a short O—O bond (1.298 Å) and two long SO bonds (2.034

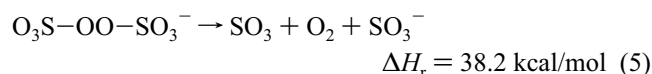
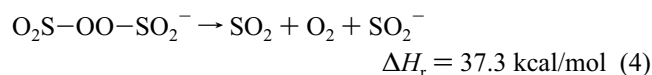
Å). Thus, the cluster resembles three interacting species, SO_3^- , SO_3 , and O_2 . However, noting that the S–O distance is very long in SO_5^- (1.885 Å), the molecule may also be thought of as SO_5^- interacting with SO_3 . The first available fragmentation pathway for $\text{S}_2\text{O}_8^{2-}$ is to SO_5^- plus SO_3 which is endothermic by 24.0 kcal/mol. Once SO_5^- is formed, elimination of O_2 to form a second SO_3^- is predicted to be endothermic by 20.4 kcal/mol. Forming SO_4^- and SO_4 from $\text{S}_2\text{O}_8^{2-}$ is much more endothermic (64.3 kcal/mol, Table 9).

Two structures were considered for $\text{S}_2\text{O}_8^{2-}$, differing only in the orientation of the SO_3 group. A staggered arrangement of the O_2 group with SO_3 is preferred for the anion but only by 0.6 kcal/mol (Table 8).

It is interesting to compare the decomposition of the peroxy structure of $\text{S}_2\text{O}_8^{2-}$, which is the known dianion structure, and the peroxy structure of $\text{S}_2\text{O}_6^{2-}$, which is not the known structure (eq 2 and 3). For both species, the structural parameters are



very similar (Figure 1) as well as the decomposition energetics. Therefore, the difference in observed structure is not due to a difference in the nature of the peroxy bonding. Rather, it is due to the fact that in $\text{S}_2\text{O}_6^{2-}$, SO_3 , a strong Lewis acid, can interact with sulfur in the Lewis base, SO_3^{2-} , to form the dative-covalent S–S bond. In $\text{S}_2\text{O}_8^{2-}$, such a S–S dative-covalent bond is not possible, which leaves the Lewis acid, SO_3 , interacting with the Lewis base, $\text{O}_3\text{SOO}^{2-}$, as the next best alternative. The similarity of the peroxy structure is retained, even after one electron is removed as shown in Figure 1 and eqs 4 and 5. The peroxy structure is the global minimum on



the $\text{S}_2\text{O}_8^{2-}$ potential energy surface but not on the $\text{S}_2\text{O}_6^{2-}$ surface.

$\text{SO}_4^{2-} \cdot 4\text{H}_2\text{O}$. While the SO_4^{2-} dianion could not be observed in the gas phase by electrospray methods, the tetraaqua species $\text{SO}_4^{2-} \cdot 4\text{H}_2\text{O}$ could be.¹² The four coordinated waters allow the negative charge to be delocalized sufficiently for autodetachment not to be spontaneous.

In a recent condensed-phase simulation of SO_4^{2-} ,⁴⁸ it was determined that the first solvation shell contained approximately 13 waters arranged such that one hydrogen pointed toward a sulfate oxygen and the other toward a water oxygen. For the discrete $\text{SO}_4^{2-} \cdot 4\text{H}_2\text{O}$ cluster, a structure of C_2 symmetry was considered with the aforementioned orientation of water around sulfate (Figure 3). While a thorough search of conformational minima was not attempted, it was confirmed that the C_2 structure is a minimum at the DFT level. At our standard level, the waters are bound by an average of 21.9 kcal/mol (24.5 kcal/mol without zero-point correction). The interaction energy of one water with sulfate is not known. However, a theoretical value of –26.4 kcal/mol has been calculated⁴⁸ at the [MP4/6-311+G(d)] level (with additivity approximation and without zero-point correction). As more waters are added, it is expected that the binding energy will decrease. It is interesting that the average water binding energy in $\text{SO}_4^{2-} \cdot 4\text{H}_2\text{O}$ (21.9 kcal/mol) is not much less

TABLE 8: Relative Energies (kcal/mol) of Various Sulfoxy Mono- and Dianions at the DFT Level^a

	B3LYP/a	B3LYP/b	+ZPC
SO_5^{2-} trans C_s ($^1A'$)	0.0	0.0	0.0
SO_5^{2-} cis C_s ($^1A'$)	3.5	3.8	3.4
SO_5^{2-} C_{4v} (1A_1)	65.4	66.3	64.2
SO_5^{2-} D_{3h} ($^1A_1'$)	82.3	82.9	80.5
SO_5^- trans C_s ($^2A''$)	0.0	0.0	0.0
SO_5^- cis C_s ($^2A''$)	0.7	0.8	0.7
SO_5^- C_s ($^2A'$)	66.3	68.3	67.1
$\text{S}_2\text{O}_4^{2-}$ C_{2h} (1A_g)	0.0	0.0	0.0
$\text{S}_2\text{O}_4^{2-}$ C_2 (1A)	0.0	0.1	0.1
$\text{S}_2\text{O}_4^{2-}$ C_{2v} (1A_1)	4.7	4.7	4.4
$\text{S}_2\text{O}_4^{2-}$ C_{2h} (2A_g)	0.0	0.0	0.0
$\text{S}_2\text{O}_4^{2-}$ C_2 (2A)	–0.1	0.5	0.6
$\text{S}_2\text{O}_4^{2-}$ C_{2v} (2A_1)	2.1	1.9	1.8
$\text{S}_2\text{O}_6^{2-}$ D_{3d} ($^1A_{1g}$)	0.0	0.0	0.0
$\text{S}_2\text{O}_6^{2-}$ C_{2h} (1A_g)	50.1	61.5	58.9
$\text{S}_2\text{O}_6^{2-}$ a C_s ($^2A'$)	0.0	0.0	0.0
$\text{S}_2\text{O}_6^{2-}$ b C_s ($^2A'$)	0.3	0.4	0.3
$\text{S}_2\text{O}_6^{2-}$ c C_s ($^2A'$)	2.0	1.2	1.1
$\text{S}_2\text{O}_6^{2-}$ d C_s ($^2A'$)	2.4	1.6	1.6
$\text{S}_2\text{O}_6^{2-}$ D_{3d} ($^2A_{1g}$)	10.3	5.1	4.9
$\text{S}_2\text{O}_6^{2-}$ C_{2h} (2B_g)	30.3	36.4	33.8
$\text{S}_2\text{O}_8^{2-}$ a C_{2h} (2B_g)	0.0	0.0	0.0
$\text{S}_2\text{O}_8^{2-}$ b C_{2h} (2B_g)	0.5	0.6	0.6

^a Basis set “a” is 6-31+G(d); basis set “b” is 6-311+G(2d). “+ZPC” indicates inclusion of zero-point energies.

than the water binding energy in $\text{OH}^- \cdot \text{H}_2\text{O}$ (26.7 kcal/mol).⁴⁹ The extent of charge transfer from SO_4^{2-} to the four water is 0.13 e^- as determined by a Mulliken analysis at the DFT level.

The water-sulfate cluster with only four waters is already beginning to resemble the structure found from simulations of the bulk solution.⁴⁸ For example, the S–O_w distances of 3.40 and 3.90 Å in $\text{SO}_4^{2-} \cdot 4\text{H}_2\text{O}$ (Figure 3) can be compared to a peak in the pair correlation function at 3.8 Å and the O_s–O_w distances of 2.77 and 2.81 Å can be compared to an O_s–O_w peak at 2.7 Å.

Vertical Ionization Energies of Dianions. Dianions may be observed in the gas phase if (1) their vertical ionization energy is positive (endothermic) and (2) all fragmentation pathways are either endothermic or have kinetic barriers. For all dianions considered in this study, except $\text{SO}_4^{2-} \cdot 4\text{H}_2\text{O}$, exothermic fragmentation pathways exist where both fragments carry a negative charge, which means that for these dianions to be observable, kinetic barriers to fragmentation must exist. For all dianions, the thermodynamically unstable bond is a 2c–2e bond which means that considerable electronic reorganization must take place prior to bond breaking. Using $\text{S}_2\text{O}_6^{2-}$ as an example with a thermodynamically unstable S–S bond (BDE = –39.7 kcal/mol), the short S–S 2c–2e bond (2.308 Å) and positive stretching frequency (198 cm^{-1}) both indicate a significant barrier to cleavage. Very similar arguments were used³ to suggest that a significant kinetic barrier exists for cleavage of the thermodynamically unstable Si–Si bond in $\text{Si}_2\text{O}_4^{2-}$.

Vertical ionization energies have been calculated directly by use of the outer-valence Green's function (OVGF) approach^{8,17} and by computing the difference in energy (at the DFT level) between the dianion and the monoanion fixed in the optimized geometry of the dianion (ΔDFT method, Table 10). The OVGF approach and other propagator-based approaches have enjoyed great success in predicting a number of properties including ionization energies and electron affinities.¹⁷ In particular, several research groups have used OVGF to predict the ionization energies of dianions such as C_n^{2-} , $\text{C}_2\text{O}_n^{2-}$, and $\text{Si}_2\text{O}_4^{2-}$.^{3–5,8}

Ionization energies in kcal/mol are given in Table 10 by Koopmans' theorem, OVGF, and ΔDFT . Several features are

TABLE 9: Calculated Fragmentation Energies for Various Sulfoxy Monoanions and Dianions at the DFT Level

reactant	product	anion reaction energies			reactant	product	dianion reaction energies		
		B3LYP/a	B3LYP/b	+ZPC			B3LYP/a	B3LYP/b	+ZPC
SO ₅ [−]	SO ₄ [−] + O	60.8	60.1	57.7	SO ₅ ^{2−}	SO ₄ [−] + O [−]	−37.0	−40.1	−42.1
	SO ₄ + O [−]	145.0	144.9	143.3		SO ₃ [−] + O ₂ [−]	−53.9	−52.9	−55.9
	SO ₃ [−] + O ₂	20.2	22.6	20.4	S ₂ O ₄ [−]	2SO ₂ [−]	−67.6	−66.4	−68.0
	SO ₃ + O ₂ [−]	68.5	66.9	64.4		SO ₃ [−] + SO [−]	−42.4	−40.8	−41.5
S ₂ O ₄ [−]	SO ₂ [−] + SO ₂	27.1	28.4	27.5		2SO [−] + O ₂	43.2	56.0	52.6
	SO ₃ + SO [−]	76.7	77.5	77.6		SO + SO [−] + O ₂ [−]	58.7	71.1	66.8
	2SO + O ₂ [−]	145.0	160.2	156.1	S ₂ O ₆ ^{2−}	2SO ₃ [−]	−40.7	−37.1	−39.7
	SO + SO [−] + O ₂	129.5	145.1	141.8		SO ₄ [−] + SO ₂ [−]	−30.2	−25.1	−28.4
S ₂ O ₆ [−]	SO ₃ [−] + SO ₃	31.2	28.3	27.1		SO ₅ [−] + SO [−]	24.8	37.0	34.0
	SO ₄ [−] + SO ₂	21.0	20.4	16.3		SO ₅ ^{2−} + SO	114.3	127.7	124.5
	SO ₄ + SO ₂ [−]	101.4	105.5	103.4		2SO ₂ [−] + O ₂	19.8	34.0	27.9
	SO ₅ [−] + SO	63.9	73.3	70.9		SO ₂ + SO ₂ [−] + O ₂ [−]	43.6	54.9	48.4
	2SO ₂ + O ₂ [−]	91.1	96.8	91.5	S ₂ O ₈ ^{2−}	2SO ₄ [−]	−44.4	−47.9	−50.9
S ₂ O ₈ [−]	SO ₂ + SO ₂ [−] + O ₂	67.3	76.0	71.1		SO ₅ [−] + SO ₃ [−]	−25.1	−23.4	−26.2
	SO ₄ [−] + SO ₄	64.8	65.9	64.3		SO ₅ ^{2−} + SO ₃	97.3	96.4	94.1
	SO ₅ [−] + SO ₃	24.5	25.1	24.0		2SO ₃ [−] + O ₂	−4.9	−0.8	−5.9
	2SO ₃ + O ₂ [−]	92.9	92.0	88.4		SO ₃ + SO ₃ [−] + O ₂ [−]	43.4	43.5	38.2
	SO ₃ + SO ₃ [−] + O ₂	44.6	47.8	44.3					

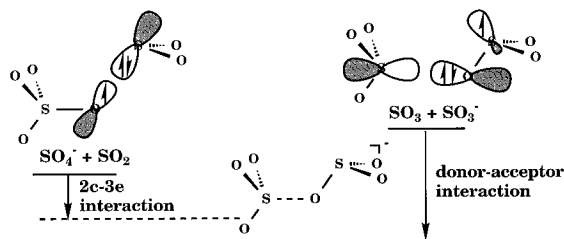


Figure 2. Depiction of the S₂O₆^{2−} global minimum with respect to the fragments SO₄[−]/SO₂ or SO₃/SO₃[−]. From the lower-energy SO₄[−]/SO₂ fragments, only a weak 2c–3e interaction between O and S is possible. From the higher energy SO₃/SO₃[−] fragments, a donor–acceptor interaction between SO₃[−] and the strong Lewis acid, SO₃, is possible. The donor–acceptor interaction determines the geometry of the complex.

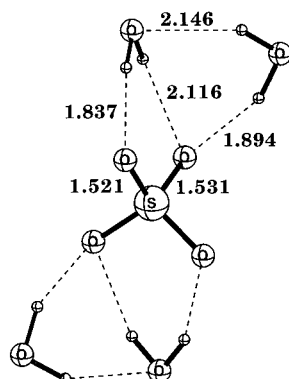


Figure 3. Plot of the SO₄^{2−}·4H₂O cluster optimized at the B3LYP/6-31+G(d) level in C₂ symmetry. Hydrogen bonding interactions are shown as dotted lines.

revealed: first, the IEs become more positive (more bound) by all three methods as the number of sulfur and oxygen atoms increase; second, the OVGF method gives IEs more negative (less bound) than Koopmans' theorem; and third, ΔDFT gives IEs slightly more negative (less bound) than OVGF. At the OVGF and ΔDFT levels, only S₂O₆^{2−}, SO₄^{2−}·4H₂O, and S₂O₈^{2−} have positive IEs.

The lifetime of the S₂O₆^{2−} is expected to be relatively short because, while the vertical IE is positive (14.4 kcal/mol, Table 10), the adiabatic IE is negative (−9.1 kcal/mol, Table 3). Following Cederbaum,³ the dianion lacks adiabatic stability because the monoanion potential energy surface crosses below

TABLE 10: Calculated Vertical Ionization Energies (kcal/mol)^a

	Koopmans' Theorem	OVGF ^b	ΔDFT ^c
SO ₂ ^{2−}	−103.0(−4.47)	−115.3(−5.00)	−119.7(−5.19)
SO ₃ ^{2−}	−44.1(−1.91)	−61.1(−2.65)	−65.7(−2.85)
SO ₄ ^{2−}	18.1(0.78)	−15.2(−0.66)	−30.8(−1.34)
S ₂ O ₃ ^{2−}	−6.1(−0.26)	−32.5(−1.41)	−30.6(−1.33)
SO ₅ ^{2−}	15.0(0.65)	−31.4(−1.36)	−37.8(−1.64)
S ₂ O ₄ ^{2−}	−38.0(−1.65)	−55.2(−2.39)	−51.5(−2.23)
S ₂ O ₆ ^{2−}	46.7(2.02)	14.1(0.61)	14.4(0.62)
S ₂ O ₈ ^{2−}	102.5(4.44)	63.2(2.74)	36.1(1.56)
SO ₄ ^{2−} ·4H ₂ O	80.8(3.50)	43.5(1.89)	29.1(1.26)

^a The ionization potential in eV is given in parentheses. ^b Outer valence Green's function approach. References 8 and 17. ^c At the B3LYP/6-311+G(2d) level.

the dianion surface. If the crossing occurs for a geometry very different from the dianion geometry, Franck–Condon factors will be small which will increase the lifetime of the anion. For S₂O₆^{2−}, the dianion geometry (*D*_{3d} symmetry with a S–S bond) is very different from the global minimum of the monoanion (*C*_s symmetry with a S–O–S linkage).

For S₂O₈^{2−}, the IE is positive by both OVGF and ΔDFT, although the difference between the two methods is rather large (27.1 kcal/mol). It is possible that the OVGF method is not converged with respect to the size of the basis set (6-31+G(d)). For SO₄^{2−}, where the OVGF and ΔDFT methods differ by 15.6 kcal/mol, higher level calculations at the ΔQCISD(T) level¹⁰ agree much better with the ΔDFT value (−30.9 and −30.8 kcal/mol, respectively). In the case of S₂O₈^{2−}, both the vertical IE (36.1 kcal/mol) and the adiabatic IE (8.1 kcal/mol) are positive, suggesting that the S₂O₈^{2−} lifetime will be much longer than S₂O₆^{2−}.

The calculated vertical IE for SO₄^{2−}·4H₂O is positive for OVGF and ΔDFT methods (43.5 and 36.1 kcal/mol, respectively). Since fragmentation pathways will be endothermic (waters are more electrostatically bound to the dianion than the monoanion), a positive IE indicates that the sulfate–water cluster should be observable in the gas phase which is in agreement with the electrospray results of Blades and Kebarle.¹² Upon associating with four water molecules, the IE is predicted to increase 58.7 kcal/mol by OVGF and 59.9 kcal/mol by ΔDFT. While the adiabatic IE was not calculated for the sulfate–water cluster, the size of the vertical IE would suggest that the dianion should have adiabatic stability as well. If the increase in vertical

TABLE 11: Comparison of DFT ^{33}S a_{hfcc} (G) with Experiment for Sulfoxy Anions

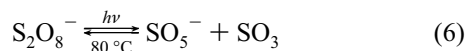
	DFT/b ^a	exptl
$\text{SO}^- \text{C}_{\infty\nu}$	0.0	
$\text{SO}_2^- \text{C}_{2\nu}$	18.2	$\pm 15^b$
$\text{SO}_3^- \text{C}_{3\nu}$	263.8	$\pm 130^b$
$\text{SO}_3^- \text{D}_{3h}^c$	587.0	
$\text{SO}_4^- \text{C}_{2\nu}$	-17.9	
$\text{S}_2\text{O}_3^- \text{C}_{3\nu}^d$	-7.9/4.4(exo)/-1.8(ave)	$\pm 131^e$
$\text{SO}_5^- \text{C}_s$	-8.2	$< \pm 3^f$
$\text{S}_2\text{O}_4^- \text{C}_{2h}$	-2.7	
$\text{S}_2\text{O}_6^- \text{C}_s$	279.9(SO_3)/-1.2(SO_4)/139(ave)	$\pm 142^b$
$\text{S}_2\text{O}_6^- \text{D}_{3d}$	45.2	$\pm 142^b$
$\text{S}_2\text{O}_8^- \text{C}_{2h}$	-1.8	$\pm 3.5^f$
$\text{SO}_4^- \text{C}_{2\nu}^g$	-19.6	
$\text{SO}_4^- \cdot 4\text{H}_2\text{O} \text{C}_{2\nu}^g$	-18.8	

^a B3LYP/6-311+G(2d) method. ^b Reference 55. ^c Inversion barrier is 32.3 kcal/mol at standard DFT level. ^d The value of ^{33}S a_{hfcc} for the $^2\text{A}'$ state are -8.4/6.0(exo) and for the $^2\text{A}''$ state -8.3/4.8(exo). ^e Reference 27. ^f Reference 56. ^g Geometry fixed to the dianion.

IE is linear with number of water molecules (15 kcal/mol per H_2O), the present ΔDFT results would predict that the IE would remain positive for three water molecules but not two.

Spin Densities and Predicted ESR Parameters. There is ample evidence that DFT can provide reliable spin densities for radical systems.^{50–54} Since experimental ESR data is available for several sulfoxy radical anions, comparison with theoretical values may aid interpretation.

In a methanol glass at 77 K, Mishra and Symons⁵⁵ recently measured the ESR spectra (and the ^{33}S isotropic hyperfine coupling constant) for SO_2^- , SO_3^- , and S_2O_6^- . For S_2O_3^- , Morton et al.²⁷ measured an isotropic hyperfine coupling constant of 131 G for ^{33}S . While the authors²⁷ noted that the ^{33}S isotropic a_{hfcc} in S_2O_3^- was almost identical to that in SO_3^- , they discard the possibility that S_2O_3^- had undergone S–S bond cleavage to form SO_3^- .⁵⁶ By irradiating a crystal or powder of $\text{K}_2\text{S}_2\text{O}_8$, Symons and Barnes⁵⁷ detected ESR signals which they attributed to the radicals, SO_5^- and S_2O_8^- . Over many heat–light cycles, they were able to interconvert the two radical through eq 1. The present calculation predict eq 6 to be the most favorable fragmentation pathway with an endothermicity of 24.0 kcal/mol.



While a glass or single crystal may represent conditions very different from the gas phase, comparisons are warranted if used with caution (Table 11). For example, calculations show that the ESR parameters of $\text{H}_2\text{S} \cdot \text{SH}_2^+$ are not sensitive to the present of explicitly coordinated waters.⁴⁶ Similarly, if one compares the ^{33}S isotropic a_{hfcc} for SO_4^- (-19.6 G) and $\text{SO}_4^- \cdot 4\text{H}_2\text{O}$ (-18.8 G) evaluated using the dianion optimized geometry, the shift is less than 1 G (Table 11).

There is reasonable agreement between theory and experiment for SO_2^- , SO_5^- , and S_2O_8^- . However, for several radicals there are serious disagreements between DFT and experiment. Perhaps most baffling is for SO_3^- , a radical of $\text{C}_{3\nu}$ symmetry, where the disagreement is over 130 G (Table 11). Geometric averaging over the umbrella mode of SO_3^- will not improve agreement because the inversion barrier is too high to be accessible (32.3 kcal/mol at DFT level) and the predicted isotropic a_{hfcc} constant of the D_{3h} structure is even further from the experimental value (587.0 G, DFT; ± 130 G, exptl⁵⁵). It is possible that the measured values in the glass correspond to a different species such as $\text{O}_3\text{S} \cdot \text{SO}_3^-$ or $\text{O}_3\text{S} \cdot \text{SO}_3^{3-}$. The predicted a_{hfcc} for D_{3d} $\text{O}_3\text{S} \cdot \text{SO}_3^-$ is 45.2 G, a significant change

from the free SO_3^- values, which is due to the fact that the spin density is symmetric distributed between the two sulfur centers.

For S_2O_3^- , the calculated ^{33}S a_{hfcc} values are so different from experiment (-7.9 and 4.4 G, DFT; ± 131 G, exptl²⁷), that the experiment spectrum is likely due to a different species. Mishra and Symons⁵⁵ report an a_{hfcc} value of ± 142 G for S_2O_6^- in a D_{3d} orientation. However, the predicted a_{hfcc} for the D_{3d} structure is nearly 100 G different from the observed value. As mention in the section above, the D_{3d} structure is 4.9 kcal/mol above the gas-phase global minimum. The a_{hfcc} of the two different sulfurs in the global minimum are 270.9 G (tricoordinate sulfur) and -1.2 G (tetracoordinate sulfur). If the tricoordinate and tetracoordinate sulfurs were to rapidly exchange through the symmetrical D_{3d} structure, the average a_{hfcc} of 139 G is very close to the experimental value of ± 142 G. If the D_{3d} structure were the transition state, the process would have an activation barrier of 4.9 kcal/mol.

Conclusion

There is fair agreement between DFT and QCI for the electron affinities of SO_2 , SO_3 , SO_4 , and S_2O_3 ; the DFT values are too large and the QCI values too small. The G2 EA of SO_3 (49.5 kcal/mol) is 10.3 kcal/mol larger than the standard experimental value but close to a more recent value. For SO_5^{2-} , $\text{S}_2\text{O}_4^{2-}$, and $\text{S}_2\text{O}_8^{2-}$, the preferred structure does not change when an electron is removed. However, for $\text{S}_2\text{O}_6^{2-}$, the lowest energy structure is characterized by a S–S bond, while for S_2O_6^- it is a structure with an SOS linkage. The $\text{S}_2\text{O}_6^{2-}$ dianion has a positive (endothermic) vertical ionization energy (14.4 kcal/mol) but a negative adiabatic ionization energy (-9.1 kcal/mol). $\text{S}_2\text{O}_6^{2-}$ can be observed in the gas phase because there is a significant change in geometry between the dianion and monoanion. The dianions, $\text{S}_2\text{O}_8^{2-}$ and $\text{SO}_4^{2-} \cdot 4\text{H}_2\text{O}$, which have both been observed in the gas phase, also have positive ionization energies. The calculated ^{33}S hyperfine coupling constants (a_{hfcc}) for SO_3^- and S_2O_3^- are in very poor agreement with experimental assignments.

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Supporting Information Available: Table of total energies (hartrees) and zero-point energies (kcal/mol) (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering instructions and Internet access instructions.

Note Added in Proof. Experimental free energies of hydration in the gas phase have recently been reported for the dianions SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, $\text{S}_2\text{O}_6^{2-}$, and $\text{S}_2\text{O}_8^{2-}$ (Blades, A. T.; Klassen, J. S.; Kellarle, P. *J. Am. Chem. Soc.* **1995**, *117*, 10563).

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