# Photoelectron Spectroscopy and Theoretical Calculations of $SO_4^-$ and $HSO_4^-$: Confirmation of High Electron Affinities of $SO_4$ and $HSO_4$

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We present a combined photoelectron spectroscopic and theoretical study of $SO_4^-$ and $HSO_4^-$ and their corresponding neutral species in the gas phase. We measured very high electron affinities for $SO_4$ and $HSO_4$, which are 5.10(0.10) and 4.75(0.10) eV, respectively. Theoretical calculations of the neutral and anionic species using both density functional and ab initio molecular orbital theory confirm the high electron affinities of the two species. The theoretically predicted vertical and adiabatic detachment energies are in good agreement with the experimental measurements. We find that both $SO_4^-$ and $SO_4$ have $C_{2v}$ symmetry, whereas both $HSO_4^-$ and $HSO_4$ have $C_s$ symmetry. We predict significant geometry changes between the equilibrium geometries of the anion species and the neutral species for both systems that are consistent with the broad nature of the measured photoelectron spectra.

## I. Introduction

$SO_4^-$ and $HSO_4^-$ are important anions in both the condensed phase and the gas phase. It is believed that $SO_4^-$ plays a large role in the chemistry of the ionosphere.[1] The $SO_4$ molecule is also known to be an intermediate in the reaction of sulfur trioxide with atomic oxygen and is an important atmospheric intermediate.[2] The vibrational frequencies of $SO_4$ were measured using IR spectroscopy in a low-temperature matrix.[3] Recently, McKee predicted $SO_4$ to be a $C_{2v}$ molecule with a very high electron affinity (EA) of 5.28 eV.[4] While many experimental studies have dealt with the oxidative ability of $SO_4$ in solution,[5,6] its gas-phase properties remain almost completely unknown. The $HSO_4^-$ anion is known to be thermodynamically stable in high-temperature acidic solutions.[7,8] Vibrational spectral studies of $HSO_4^-$ have been carried out, and its ionic dissociation constant is well-known.[9−11] $HSO_4^-$ has also been theoretically investigated and found to have $C_s$ symmetry with the $OSO_3$ unit having a local $C_{3v}$ symmetry.[12] Viggiano et al. have investigated the protonation reactions of $HSO_4^-$ in the gas phase and obtained a very high electron affinity of 4.7(0.2) eV for $HSO_4$.[13] Recently, we have studied the ion pairs $NaSO_4^-$ and $KSO_4^-$, and their dimers, in the gas phase.[14] However, there have been no direct measurements of the EAs of $SO_4$ and $HSO_4$, and the EA of $SO_4$ is still unknown. The scarcity of experimental and theoretical studies of gaseous $SO_4$ and $HSO_4$ and their anions is surprising.

In this paper, we report a photoelectron spectroscopy (PES) study of $SO_4^-$ and $HSO_4^-$, which were produced using an electrospray ionization (ESI) source.[15] We directly measured the EA's and electronic structures of the corresponding neutral species. We obtained for the first time the EA of $SO_4$, which we found to be 5.10(0.10) eV. We measured the EA of $HSO_4$ to be 4.75(0.10) eV. We also carried out theoretical calculations on both anions, and their corresponding neutrals, and compared

the calculated energetic information with the experimental data. Our theoretical calculations predicted that the lowest energy conformations of both $SO_4^-$ and $SO_4$ have $C_{2v}$ symmetry. We found considerable changes in geometry between the anion and neutral structures that were consistent with the broad PES features observed. We predicted that both $HSO_4^-$ and $HSO_4$ have $C_s$ symmetry.

The paper is organized in the following manner: In the next section, the experimental aspects will be briefly described. In section III, the theoretical methods are presented. We report the experimental results in section IV, followed by the presentation of the theoretical results and discussion in section V. A brief conclusion is given in section VI. Finally, detailed calculations for the various isomers of $SO_4^-$ and $SO_4$ at different levels of theory are presented in the Appendix.

## II. Experiment

The experiments were carried out with an apparatus that involves a magnetic-bottle TOF photoelectron analyzer and an ESI source. Details of the experimental setup have been published elsewhere.[15] To produce the desired anions, we used a $10^{-4}$ M solution of the corresponding salts ($NaHSO_4$) at pH $\sim$7 in a water/methanol mixed solvent (2/98 ratio), spraying it through a 0.01 mm diameter syringe needle at ambient atmosphere and −2.2 kV high voltage. To generate $SO_4^-$, a $Na_2S_2O_8$ solution was used, in which the $S_2O_8^{2-}$ dianions dissociated to give $SO_4^-$. Negatively charged molecular ions emerging from a desolvation capillary were guided by an rf-only quadrupole ion guide into an ion trap, in which the ions were accumulated for 0.1 s before being pushed into the extraction zone of a TOF mass spectrometer.

In each PES experiment, the anions of interest were mass-selected and decelerated before being intercepted by a laser beam in the detachment zone of the magnetic-bottle photoelectron analyzer. For the current study, the 193 nm (6.424 eV) light from an ArF excimer laser was primarily used. The photoelec-
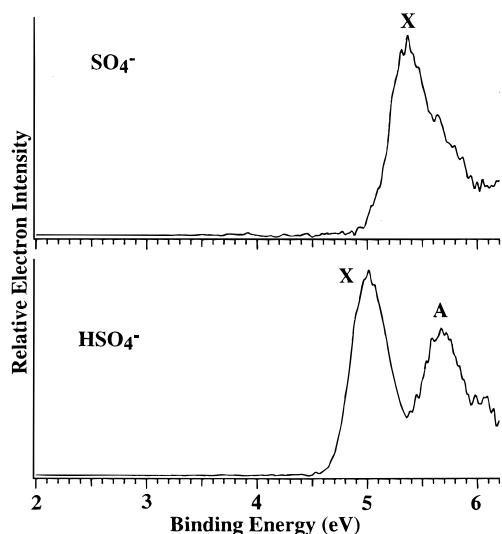
**Figure 1.** Photoelectron spectra of $SO_4^-$ and $HSO_4^-$ at 193 nm (6.424 eV).

trons were collected at nearly 100% efficiency by the magnetic-bottle and analyzed in a 4 m TOF tube. Photoelectron TOF spectra were measured and then converted to kinetic energy spectra that were calibrated by the known spectra of $I^-$ and $O^-$. The binding energy spectra were obtained by subtracting the kinetic energy spectra from the photon energy. The energy resolution was ~11 meV fwhm at 0.4 eV kinetic energy, as measured from the spectrum of $I^-$ at 355 nm, and deteriorated at 193 nm and higher kinetic energies.

## III. Theoretical Details

We used theoretical chemistry to determine the geometry and electronic structure of $SO_4^-$, $HSO_4^-$, and the corresponding neutrals, and as verification of our interpretation of the PES spectra. All of the species were optimized with density functional theory (DFT).[16,17] The optimizations used the hybrid B3LYP exchange-correlation functional.[18,19] We used the tzvp+ basis set, which is derived from the DFT-optimized tzvp basis set of Godbout and co-workers,[20] with the addition of a diffuse s (H, O, and S) and p (O and S only) function. The exponents of the diffuse functions were derived from an even-tempered expansion of the outermost functions in the original basis set. Frequencies were calculated for all species to verify that the geometries were minima on the potential energy surface.

Following the DFT optimizations, single-point energies were obtained using coupled-cluster theory with perturbative triples (CCSD(T)) and the 6-311+G* basis set. The vertical detachment energy was taken as the difference in total energy between the anion and the corresponding neutral molecule at the anion geometry. The reported adiabatic detachment energy is the difference in total energy between the optimized geometries of the anion and neutral. All the theoretical calculations were performed using Gaussian94.[21]

During the course of our work, we found that $SO_4$ required more extensive theoretical treatment. The details of this aspect of the theoretical study are included in the Appendix.

## IV. Experimental Results

Figure 1 shows the 193 nm spectra of $SO_4^-$ and $HSO_4^-$. We observed one broad feature for $SO_4^-$ (X) and two broad features (X and A) for $HSO_4^-$. The feature of $SO_4^-$ yields an adiabatic (ADE) and vertical (VDE) detachment energy of 5.10(0.10) and 5.40(0.10) eV, respectively. The first feature (X) of $HSO_4^-$ is

**TABLE 1: The Measured Adiabatic (ADE) and Vertical Detachment (VDE) Energies for $SO_4^-$ and $HSO_4^-$**

| | | ADE (eV) | VDE (eV)[c] |
|---|---|---|---|
| $SO_4^-$ | X | 5.10 (0.10)[a] | 5.40 (0.10) |
| $HSO_4^-$ | X | 4.75 (0.10)[a] | 5.00 (0.10) |
| | A | 5.4 (0.1) | 5.65 (0.10) |

[a] Also represents the adiabatic electron affinity of the neutral.
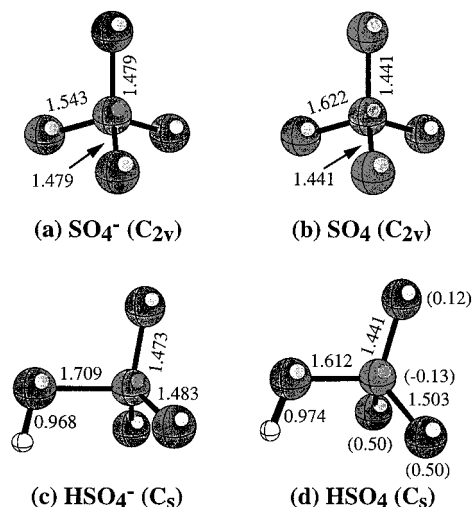


**Figure 2.** Ground-state geometries of (a) $SO_4^-$, (b) $SO_4$, (c) $HSO_4^-$, and (d) $HSO_4$, optimized at B3LYP/tzvp+. All bond lengths in Å are indicated. The numbers in the parentheses in (d) indicate the distribution of the unpaired spin.

slightly narrower than that of $SO_4^-$, yielding an ADE and VDE of 4.75(0.10) and 5.00(0.10) eV, respectively. The second feature (A) of $HSO_4^-$ overlaps feature X slightly. We estimate an ADE of 5.4(0.1) eV and a VDE of 5.65(0.10). The energetic data for $SO_4$ and $HSO_4$ are summarized in Table 1.

The ADE of the X feature in each spectrum should correspond to the adiabatic EA of the neutral species. However, for cases in which there are large structural changes between the anion and neutral ground states, the ADE can only be viewed as an upper limit of the EA, because the Franck–Condon factors for the 0–0 transition may be negligible. The broad nature of the PES spectra of $SO_4^-$ and $HSO_4^-$ suggests that there should be significant geometry changes between the anion and neutral ground states for the two molecules. As will be shown below, this is indeed born out from the theoretical calculations.

## V. Theoretical Results and Discussion

**A. $SO_4$ and $SO_4^-$.** The lowest energy geometries of both $SO_4^-$ and $SO_4$ have $C_{2v}$ symmetry. The B3LYP/tzvp+ optimized geometries of $SO_4^-$ and $SO_4$ are presented in Figure 2, parts a and b, respectively. Although both the anion and neutral have the same symmetry, there are considerable structural changes. In the anion, the two types of S–O bonds are different by only 0.064 Å, whereas they are different by almost 0.2 Å in the neutral. This large geometry change between the anion and neutral ground states is consistent with the broad PES spectrum observed for $SO_4^-$. At the B3LYP/tzvp+ level, we obtain a VDE of 6.67 eV and an ADE of 5.25 eV (Table 2). The large difference between the predicted VDE and ADE is consistent with the large equilibrium geometry changes between the anion and the neutral. The predicted values reasonably compare to the experimental ADE value of 5.10 eV and VDE value of 5.40 eV. While the predicted ADE is in good agreement with the experiment, the VDE is much too high. This large disagreement

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**TABLE 2: Calculated Adiabatic and Vertical Detachment Energies for $SO_4^-$**

| | ADE (eV) | VDE (eV) |
|---|---|---|
| B3LYP/tzvp+ | 5.25 | 6.67 |
| MP2/6-311+G*[a] | 4.71 | 6.11 |
| MP4(sdq)/6-311+G*[a] | 4.82 | 6.27 |
| CCSD/6-311+G*[a] | 4.95 | 6.40 |
| CCSD(T)/6-311+G*[a] | 4.79 | 5.64 |
| exp | 5.10(0.10) | 5.40(0.10) |

[a] Calculated at the B3LYP/tzvp+ optimized geometry.

is corrected at the CCSD(T)/6-311+G*//B3LYP/tzvp+ level, which predicts a VDE of 5.64 eV, much closer to the experimental value. However, the CCSD(T) ADE of 4.79 eV is in somewhat poorer agreement with the experimental value than the B3LYP/tzvp+ value. Therefore, the theoretical calculations consistently predict a larger difference between the VDE and ADE than the experimental measurements indicate. This suggests that the experimentally measured ADE may not be the true ADE because of the negligible Franck−Condon factor for the 0−0 transition. Rather, the measured ADE should only be viewed as an upper bound.

The ground state of $SO_4^-$ is open shell with an unpaired electron. The neutral $SO_4$ is closed shell with a singlet ground state. The considerable lengthening of two of the S−O bonds upon electron detachment in the neutral $SO_4$ suggests that the unpaired electron in $SO_4^-$ occupies a bonding molecular orbital primarily consisting of bonding interactions in these two S−O bonds. The large geometry changes between the $C_{2v}$ anion and $C_{2v}$ neutral are consistent with our experimental observation of a broad band. As will be shown in the Appendix, three other isomers of the $SO_4^-$ anions with higher energies are also found in our theoretical studies. We can rule out the $D_{2d}$ and $C_{3v}$ isomers, because there is little geometry change between their anions and neutrals (Figure 3), which would yield sharp photodetachment features, inconsistent with our experimental observation.

**B. $HSO_4$ and $HSO_4^-$.** Both $HSO_4^-$ and $HSO_4$ are found to have $C_s$ symmetry. The B3LYP/tzvp+ optimized geometries of the two species are shown in Figure 2 parts c and d, respectively. Contrary to the result obtained for $SO_4^-$, the VDE obtained at the B3LYP/tzvp+ level was very close to that predicted by CCSD and CCSD(T) single point calculations (Table 3). Both B3LYP and CCSD(T) VDEs are within the experimental error. MP2 and MP4 VDEs are ∼0.5 eV higher than those of B3LYP and CCSD(T) and are, consequently, in poorer agreement with experiment. The predicted values of the ADE vary less between the different levels of theory, although the MP2 value again appears too large. The best agreement with the experimental value was obtained from the B3LYP/tzvp+ calculations.

There are also substantial geometric changes between the ground states of $HSO_4^-$ and $HSO_4$, which is consistent with the broad ground-state PES feature (X) of $HSO_4^-$ (Figure 1). The structure of $HSO_4^-$ is similar to that obtained from a previous theoretical calculation.[12] $HSO_4^-$ has three nearly equal S−O bonds and a much longer S−O bond between S and the O bonded to the H. In the $HSO_4$ neutral, the biggest change occurs at the S−O bond in which the O is bonded to H; it is shortened by nearly 0.1 Å, relative to the anion. The changes in the S−O bonds of the $SO_3$ moiety are similar to the $SO_4$ case. The short S−O bond (1.441 Å) is identical to that in $SO_4$, but the two longer S−O bonds in $HSO_4$ did not change very much, relative to the anion. Because $HSO_4^-$ is closed shell, the $HSO_4$ neutral must be a doublet with an unpaired electron. As
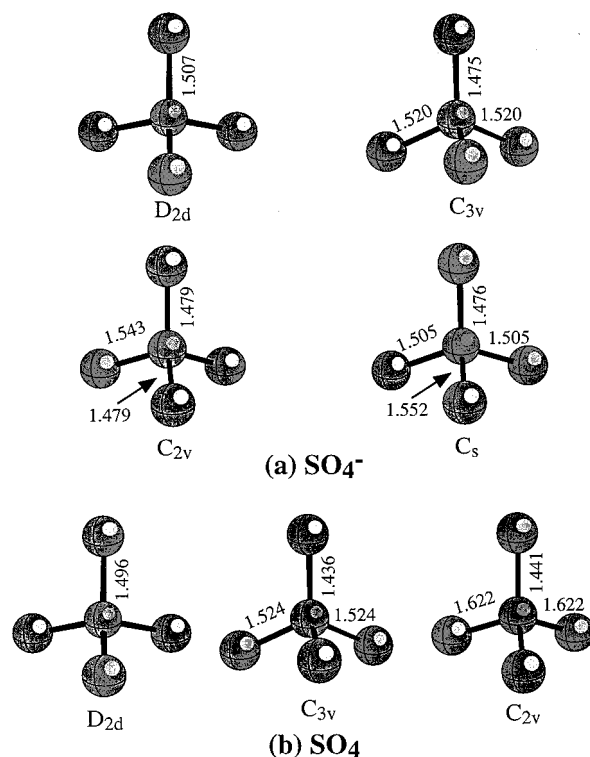


**Figure 3.** Geometries of various isomers of (a) $SO_4^-$ and (b) $SO_4$, optimized at B3LYP.tzvp+. All bond lengths in Å are indicated.

**TABLE 3. Calculated Adiabatic and Vertical Detachment Energies for $HSO_4^-$**

| | ADE (eV) | VDE (eV) |
|---|---|---|
| B3LYP/tzvp+ | 4.76 | 4.99 |
| MP2/6-311+G*[a] | 5.01 | 5.68 |
| MP4(sdq)/6-311+G*[a] | 4.74 | 5.42 |
| CCSD/6-311+G*[a] | 4.65 | 5.09 |
| CCSD(T)/6-311+G*[a] | 4.59 | 4.93 |
| exp | 4.75(0.10) | 5.00(0.10) |

[a] Calculated at the B3LYP/tzvp+ optimized geometry.

shown in Figure 2d, the electron spins are mainly localized on the two O atoms with the longer S−O bonds. Compared to the geometry changes between $SO_4^-$ and $SO_4$, the geometry changes between $HSO_4^-$ and $HSO_4$ are smaller. The smaller geometry changes are also consistent with the relatively narrower ground-state PES feature of $HSO_4^-$. The difference between the predicted ADE and VDE of $HSO_4^-$ is also smaller. The good agreement between the predicted and experimental ADE and VDE indicates that the experimentally measured ADE is the true value for $HSO_4^-$. Our measured EA for $HSO_4$ is in excellent agreement with the value obtained previously by Viggiano et al., and it is slightly more accurate.

## V. Conclusion

In conclusion, we present the first photoelectron spectra of $SO_4^-$ and $HSO_4^-$ and a theoretical investigation of both the anion and neutral species. We observe one broad feature in the PES spectrum of $SO_4^-$. Two broad features, separated by ∼0.65 eV, were observed in the PES spectrum of $HSO_4^-$. We measured the electron affinity of $SO_4$ for the first time in the gas phase and found it to be very high (∼5.10 eV). We also measured a more accurate electron affinity (4.75 ± 0.10 eV) for $HSO_4$ that compares well with a previous estimate using a thermodynamical cycle. Theoretical calculations, which predicted $C_{2v}$ symmetry for both $SO_4^-$ and $SO_4$, were performed. The predicted

**TABLE 4: Relative Energies (kcal/mol) and Number of Imaginary Frequencies of the Various Symmetries of $SO_4^-$ at B3LYP/TZVP+, B3LYP/6-31+G*, and MP2/6-31+G***

| | B3LYP/tzvp+ | | B3LYP/6-31+G* | | MP2/6-31+G* | |
|---|---|---|---|---|---|---|
| symmetry | energy | imaginary | energy | imaginary | energy | imaginary |
| $D_{2d}$ $^2A_2$ | 1.98 | 2 | 3.63 | 2 | 0.0 | 0 |
| $C_{3v}$ $^2B_1$ | 1.90 | 2 | 1.90 | 2 | 0.54 | 0 |
| $C_{2v}$ $^2A_2$ | 0.0 | 0 | 0.0 | 0 | 3.08 | 0 |
| $C_s$ $^2A"$ | 1.65 | 1 | 1.64 | 1 | 12.67 | 1 |

ADE and VDE values of $SO_4^-$ were in good agreement with the experimental values. However, the difference between the calculated ADE and VDE was much larger than that which was experimentally determined, at the highest level of theory carried out, suggesting that the measured ADE may only represent an upper limit of the real adiabatic electron affinity. Theory predicts that both $HSO_4^-$ and $HSO_4$ have $C_s$ symmetry. The calculated VDE and ADE for $HSO_4^-$ are in excellent agreement with the experimental values.

## Appendix

In a recent paper,[4] McKee presented a theoretical study of a variety of sulfur-containing complexes, including $SO_4$ and $SO_4^-$. B3LYP/6-31+G* and MP2/6-31+G* optimizations were reported for $SO_4$ and $SO_4^-$, with single-point energies calculated at higher levels of theory. Frequencies were also obtained at the B3LYP/6-31+G* level. The zero-point energies from these frequency calculations were given, but no other details were presented. McKee reported one geometry for $SO_4$ ($C_{2v}$) and three for $SO_4^-$ ($D_{2d}$, $C_{3v}$, and $C_{2v}$). We found that the relative energies of the three isomers of $SO_4^-$ were different at the B3LYP/6-31+G* level from those found at the MP2/6-31+G* level. To obtain the ADE and VDE for $SO_4^-$, for comparison to the experiment, we had to determine which of these three states to choose as the anion ground state. Our optimizations and frequency calculations at the B3LYP/tzvp+ level indicated that the $D_{2d}$ and $C_{3v}$ geometries were not stable points. We thus decided to duplicate the B3LYP/6-31+G* and MP2/6-31+G* optimizations and frequency calculations to clarify the situation. The relative energies and number of imaginary frequencies for the various states are presented in Table 4. We were also able to optimize a geometry of $C_s$ symmetry. At the B3LYP/tzvp+ and B3LYP/6-31+G* levels; only the $C_{2v}$ geometry is a minimum. The $C_{2v}$ molecule is also the lowest in energy. The other isomers have one or two large imaginary frequencies. However, at the MP2/6-31+G* level, only the $C_s$ isomer has a negative frequency. In this case, the $D_{2d}$ geometry is the lowest in energy. The B3LYP/tzvp+ structures of the four symmetries of $SO_4^-$ are shown in Figure 3a.

The only isomer that is a minimum at both levels of theory is that of $C_{2v}$ symmetry. To verify which symmetry was the lowest energy state, we obtained CCSD(T)/6-311+G* single-point energies for each species. Although the geometries at all

**TABLE 5: Energies (kcal/mol) of Various Symmetries of $SO_4^-$ Relative to $C_{2v}$ from CCSD(T)/6-311+G*//B3LYP/ tzvp+ Calculations**

| symmetry | MP2 | MP4(sdq) | CCSD | CCSD(T) |
|---|---|---|---|---|
| $D_{2d}$ $^2A_2$ | −3.94 | 8.39 | 9.68 | 5.88 |
| $C_{3v}$ $^2B_1$ | −3.52 | 3.75 | 4.56 | 2.85 |
| $C_{2v}$ $^2A_2$ | 0.0 | 0.0 | 0.0 | 0.0 |
| $C_s$ $^2A"$ | 12.59 | 6.20 | 2.80 | 2.59 |

**TABLE 6: Relative Energies (kcal/mol) of the Various Symmetries of $SO_4$ at B3LYP/6-31+G* and MP2/6-31+G***

| symmetry | B3LYP/tzvp+ | B3LYP/6-31+G* | MP2/6-31+G* |
|---|---|---|---|
| $D_{2d}$ $^1A_1$ | 28.20 | 27.11 | 0.0 |
| $C_{3v}$ $^1A_1$ | 33.78 | 32.71 | 12.47 |
| $C_{2v}$ $^1A_2$ | 0.0 | 0.0 | 17.53 |

**TABLE 7: Relative Energies (kcal/mol) of the Various Symmetries of $SO_4$ from CCSD(T)/6-311+G*//B3LYP/tzvp+ Calculations**

| symmetry | MP2 | MP4(sdq) | CCSD | CCSD(T) |
|---|---|---|---|---|
| $D_{2d}$ $^1A_1$ | −10.12 | 43.92 | 36.87 | 15.68 |
| $C_{3v}$ $^1A_1$ | 5.18 | 35.19 | 34.07 | 17.89 |
| $C_{2v}$ $^1A_1$ | 0.0 | 0.0 | 0.0 | 0.0 |

three levels of theory were in close agreement with each other, despite the differing numbers of negative frequencies, we used only our B3LYP/tzvp+ geometries. The relative CCSD(T)/6-311+G* energies, including the MP2, MP4(sdq), and CCSD predictions, also obtained from these single-point calculations, are shown in Table 5.

Only the MP2/6-311+G* calculation predicts that the $D_{2d}$ symmetry is lowest in energy. All of the more extensive treatments of electron correlation predict the lowest energy for the $C_{2v}$ geometry, which is consistent with the DFT results. The difference in energy between the various states becomes less when the triple excitations are included, but CCSD(T) still gives larger relative energy differences than those given by B3LYP. From these results, we tentatively concluded that the lowest-energy geometry of $SO_4^-$ has $C_{2v}$ symmetry. We still cannot reach a firm conclusion, because the energy differences among the various isomers of $SO_4^-$ are not great enough (Table 5). In principle, they might even be accessible at our experimental conditions (room temperature). Frequency calculations at a higher-order level of correlation (i.e., MP4) would be needed to verify whether the $D_{2d}$ and $C_{3v}$ geometries are stable points. Such studies are beyond the scope of the current investigation.

Extending this approach to $SO_4$, we find that B3LYP again predicts that the lowest energy isomer is that of $C_{2v}$ symmetry, whereas MP2 predicts that the $D_{2d}$ isomer is the lowest in energy. However, contrary to the results for $SO_4^-$, both DFT and MP2 predict that all the symmetries are stable points. In addition, during attempts to optimize a $C_s$ geometry, the molecule reverted to $C_{2v}$ symmetry at both levels of theory. The relative energies of the various isomers are given in Table 6, and the B3LYP/tzvp+ structures are shown in Figure 3b.

To again clarify the correct symmetry, we obtained CCSD-(T)/6-311+G* single-point energies for each species. As before, we used the B3LYP/tzvp+ geometries for the single point calculations. The calculated energies, relative to those of the $C_{2v}$ isomer, are shown in Table 7.

Once again, the MP2/6-311+G* single-point energy is the lowest for the $D_{2d}$ geometry, whereas all the other results indicate that the $C_{2v}$ geometry is the energy minimum. The relative energies from the more extensive treatment of electron correlation are not close to those obtained with DFT; CCSD-(T) gives predictions of the relative energies that are ~10 kcal/

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mol lower than those given by B3LYP. However, we can still conclude that the lowest energy isomer of $SO_4$ has $C_{2v}$ symmetry.

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