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 ∼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-

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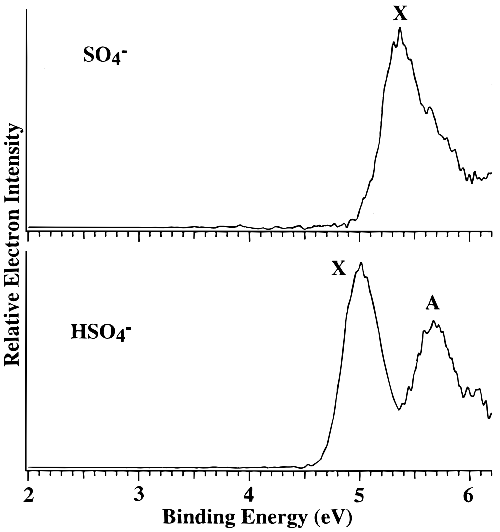


Figure 1. Photoelectron spectra of SO_4^- and HSO_4^- at 193 nm (6.424 eV).

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.

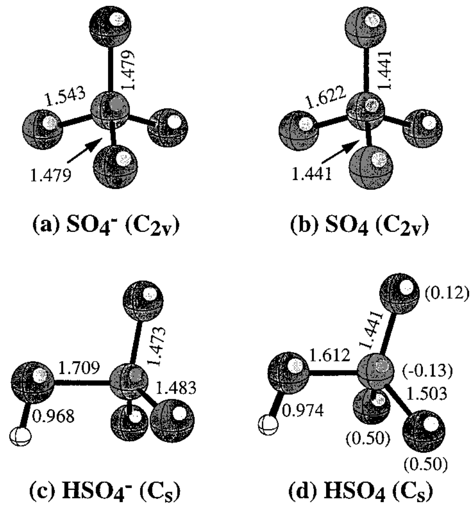
IV. Experimental Results

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 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.

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.



(a) SO_4^- (C_{2v}) (b) SO_4 (C_{2v})

(c) HSO_4^- (C_s) (d) HSO_4 (C_s)

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.

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

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

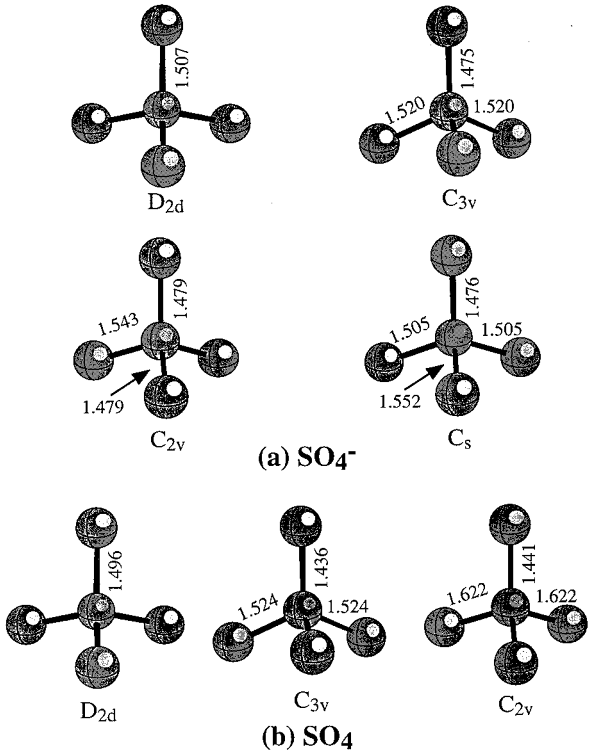
	ADE (eV)	VDE (eV)
B3LYP/tzvp+	5.25	6.67
MP2/6-311+G*[a]	4.71	6.11
MP4(sdq)/6-311+G*[a]	4.82	6.27
CCSD/6-311+G*[a]	4.95	6.40
CCSD(T)/6-311+G*[a]	4.79	5.64
exp	5.10(0.10)	5.40(0.10)

[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.



(a) SO_4^-

(b) SO_4

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.

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 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.

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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 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.

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

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/

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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