

# A Density Functional Study of the Hyperfine Properties of Sulfur-Containing Radicals and Radical Ions<sup>†</sup>

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Martell, J. M., Eriksson, L. A. and Goddard, J. D., 1997. A Density Functional Study of the Hyperfine Properties of Sulfur-Containing Radicals and Radical Ions. – Acta Chem. Scand. 51: 229–232. © Acta Chemica Scandinavica 1997.

Geometries, electron affinities and isotropic hyperfine coupling constants are presented for a set of sulfur oxide radical anions,  $\text{SO}_x^-$  ( $x=2-4$ ), and the neutral SH and  $\text{HSO}_3$  radicals. The data reported are computed at the B3LYP and QCISD levels, using a large set of extended and/or decontracted basis sets. The geometries and electron affinities are in close agreement with previously calculated values. There is some variation in the hyperfine structures at various levels of theory. It is concluded that none of the approaches employed is sufficient to fully describe the distribution of unpaired spin for all systems investigated, and that further work is necessary before an approach is available that can accurately account for the reactivity and properties of these species. The computed sulfur and oxygen hyperfine coupling constants are at best within 25% of experimental data.

In a recent paper, McKee<sup>1</sup> presented a detailed theoretical study of the mono- and di-anions of several sulfur oxides, using both density functional theory (DFT) and correlated *ab initio* methods. In his work, he noted large discrepancies between the DFT/6-311+G(2d) calculated isotropic <sup>33</sup>S hyperfine coupling constants (HFCC) and previous experimental data, in some cases by as much as 130 G. After the original submission of this manuscript, we have learned that much of this discrepancy was due to the values being calculated in the unit MHz but reported as G by McKee. Still, McKee's corrected values<sup>2</sup> are in error by 30–60%. As the radical hyperfine properties reflect the distribution of unpaired spin in the molecule, disagreements of this order mean we cannot be certain that the theoretical approach can correctly describe chemical reactivity and other properties of the systems in question. In the present work we address the problem of calculated hyperfine properties of the sulfur oxide monoanions in more detail, using theoretical methods similar to those of McKee (B3LYP and QCISD), but exploring a large number of basis sets. We also include data for the neutral SH and  $\text{HSO}_3$  radicals.

## Results and discussion

*Optimized geometries and electron affinities.* The geometries and hyperfine properties of the radical anions of  $\text{SO}_x$

( $x=2-4$ ), have been investigated using the gradient-corrected B3LYP<sup>3,4</sup> density functional. The GAUSSIAN 94 program package<sup>5</sup> was used. Geometry optimizations were performed using the correlation-consistent polarized valence basis sets (CC-PVXZ, X=D,T) augmented with diffuse functions (denoted by the prefix 'aug-'), by Dunning.<sup>6</sup> In some cases, larger uncontracted bases were also employed. Resulting geometries are listed in Table 1. Compared with the previous data by McKee,<sup>1</sup> the use of the aug-CC-PVDZ basis set rather than 6-31+G(d) results in very minor changes in geometries. Overall we tend to get slightly longer S–O bonds, and slightly smaller O–S–O angles. The QCISD/aug-CC-PVDZ geometries obtained for the SH and  $\text{SO}_2^-$  radicals are also very similar to the corresponding B3LYP data.

We furthermore optimized the structures of the corresponding neutral sulfur oxides and of  $\text{HSO}_3$ , allowing for a comparison of the adiabatic electron affinities (EA), corrected for zero-point vibrational energies, at the different levels of theory. These are listed in Table 2, together with experimental data<sup>7,8</sup> and results reported by McKee.<sup>1</sup> Again, the present B3LYP/aug-CC-PVTZ//aug-CC-PVDZ results agree closely with the previously reported B3LYP/6-311+G(2d)//6-31+G(d) data, and seem to yield a more or less constant overestimation of the EA of 8–10 kcal mol<sup>-1</sup> compared with experiment. Using the G2 theoretical approach, EAs deviating by only 0.5 kcal mol<sup>-1</sup> were previously obtained.<sup>1</sup> The EAs of  $\text{SO}_4$  and  $\text{HSO}_3$  are 120.5 and

<sup>†</sup> Contribution at the 14th International Conference on Radical Ions, Uppsala, Sweden, July 1–5, 1996.

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Table 1. Optimized geometrical parameters. Bond lengths in ångströms, bond angles in degrees.

System	Sym.	Parameter	B3LYP/ aug-CC-PVDZ	B3LYP/ 6-31 + G(d) <sup>a</sup>	B3LYP/ u-aug-CC-PVDZ <sup>b</sup>	QCISD/ aug-CC-PVDZ
SH	$C_{\infty v}$	H-S	1.362			1.357
SO <sub>2</sub> <sup>-</sup>	$C_{2v}$	O-S	1.566	1.548	1.563	1.564
		O-S-O	113.9	115.1	114.4	113.4
SO <sub>3</sub> <sup>-</sup>	$C_{3v}$	O-S	1.535	1.516	1.531	
		O-S-O	113.6	113.7	113.7	
SO <sub>4</sub> <sup>-</sup>	$C_{2v}$	O-S	1.499	1.482		
		O-S'	1.568	1.546		
		O-S-O	114.3	114.2		
		O'-S-O'	93.4	94.5		
HSO <sub>3</sub>	$C_{3v}$	H-S	1.371			
		O-S	1.506			
		H-S-O	106.7			
		O-S-O	112.1			

<sup>a</sup> Ref. 1. <sup>b</sup> Fully decontracted.

Table 2. Adiabatic electron affinities (kcal mol<sup>-1</sup>), computed at the B3LYP level.

System	aug-CC-PVTZ <sup>a</sup>	6-311 + G(2d) <sup>b</sup>	Exptl.
SO <sub>2</sub>	35.4	34.1	25.5 <sup>c</sup>
SO <sub>3</sub>	58.2	57.7	50.7 <sup>d</sup>
SO <sub>4</sub>	120.5	121.9	
HSO <sub>3</sub>	102.8		

<sup>a</sup> This work. <sup>b</sup> Ref. 1. <sup>c</sup> Ref. 7. <sup>d</sup> Ref. 8.

102.8 kcal mol<sup>-1</sup>, respectively, at the present B3LYP/aug-CC-PVTZ level. Assuming we also have the same error of  $9 \pm 1$  kcal mol<sup>-1</sup> in EA for these species, we may predict more accurate estimates for these as  $111.5 \pm 1$  and  $94 \pm 1$  kcal mol<sup>-1</sup>. The former is in close agreement with QCISD(T)/6-31 + G(2df) data by McKee.<sup>1</sup>

*Isotropic hyperfine coupling constants.* Isotropic hyperfine coupling constants calculated at the present B3LYP/aug-CC-PVTZ level of theory are presented in Table 3, as

Table 3. Isotropic hyperfine coupling constants,  $A_{\text{iso}}$  (G), using the B3LYP method.

System	Atom	aug-CC-PVTZ <sup>a</sup>	6-311 + G(2d) <sup>b</sup>	Exptl.
SH	<sup>33</sup> S	13.0		
	<sup>1</sup> H	-13.5		-18.7 <sup>c</sup>
SO <sub>2</sub> <sup>-</sup>	<sup>33</sup> S	11.4	6.5	15 <sup>d</sup>
	<sup>17</sup> O	-4.2		-8.2 <sup>c</sup>
SO <sub>3</sub> <sup>-</sup>	<sup>33</sup> S	85.4	94.1	130 <sup>d</sup>
	<sup>17</sup> O	-6.5		
SO <sub>4</sub> <sup>-</sup>	<sup>33</sup> S	-6.0	-6.4	
	<sup>17</sup> O	0.5		
		-3.4		
HSO <sub>3</sub>	<sup>33</sup> S	-6.8		
	<sup>17</sup> O	0.0		
	<sup>1</sup> H	-3.7		

<sup>a</sup> This work. <sup>b</sup> Ref. 1. <sup>c</sup> Ref. 9. <sup>d</sup> Ref. 10.

well as data from experiment<sup>9,10</sup> and previous B3LYP/6-311 + G(2d) calculations.<sup>2</sup> Our results provide a significantly improved description of the hyperfine coupling for SO<sub>2</sub><sup>-</sup>, but give slightly worse agreement with experiment for SO<sub>3</sub><sup>-</sup>. In either case, the agreement is not close enough to be regarded as satisfactory. For the SH radical, we deviate by ca. 5 G for the proton at the B3LYP/aug-CC-PVTZ level, whereas performing full geometry optimization and HFCC calculation at the QCISD/aug-CC-PVDZ level (not shown) yields  $A_{\text{iso}}(^1\text{H}) = -21.1$  G (exp: -18.7 G) and  $A_{\text{iso}}(^{33}\text{S}) = 20.2$  G.

In a first attempt to improve upon the description of the DFT-computed sulfur HFCCs, a number of single-point calculations were performed on the SO<sub>2</sub><sup>-</sup> and SO<sub>3</sub><sup>-</sup> anions, using extended basis sets. For comparison, we also performed a set of calculations on SO<sub>2</sub><sup>-</sup> using the more accurate QCISD approach rather than B3LYP. These calculations are reported in Table 4. On comparison with the B3LYP/aug-CC-PVTZ data of Table 3, we note that a decontraction of the basis set (u-aug-CC-PVTZ of Table 4) leads only to minor changes. This is in contrast with previous work on, e.g., the OH radical.<sup>11</sup> The decontraction causes a slight lowering of the oxygen HFCCs in both systems (more negative values), and of the sulfur HFCC in the dioxide radical anion. In SO<sub>3</sub><sup>-</sup>, on the other hand, the sulfur HFCC increases by 3 G. The <sup>17</sup>O coupling in SO<sub>2</sub><sup>-</sup> thus comes in close agreement with experiment, whereas for the sulfur atoms it worsens in SO<sub>2</sub><sup>-</sup> and improves in SO<sub>3</sub><sup>-</sup>. Extending the basis to the aug-CC-PVQZ level, rather than decontracting the aug-CC-PVTZ basis, does not result in any marked improvement.

Changing the basis set to IGLO-III,<sup>12</sup> which can be described as a decontracted triple-zeta plus polarization basis, specially tailored for magnetic properties, the sulfur HFCCs improve somewhat whereas the oxygen couplings essentially remain unaltered, compared with the uncon-

Table 4. Isotropic hyperfine coupling constants,  $A_{\text{iso}}$  (G), using extended basis sets.<sup>a</sup>

System	Atom	B3LYP/u-aug-CC-PVTZ <sup>b</sup>	B3LYP/aug-CC-PVQZ	B3LYP/IGLO-III	B3LYP/TZVP	QCISD/TZVP	QCISD/TZVP
$\text{SO}_2^-$	<sup>33</sup> S	7.9	9.1	9.4	11.3	17.0	19.5
	<sup>17</sup> O	-7.3	-3.8	-7.7	-8.5	-11.1	-14.0
$\text{SO}_3^-$	<sup>33</sup> S	88.7		98.7	85.1		
	<sup>17</sup> O	-8.8		-8.4	-8.4		

<sup>a</sup> At B3LYP/aug-CC-PVDZ optimized geometries. <sup>b</sup> Fully decontracted aug-CC-PVTZ basis set.

tracted PVTZ results. The largest improvement is for the sulfur atom in  $\text{SO}_3^-$ , now being close to 100 G (exp: 130 G). If we instead employ the LSDA optimized TZVP basis set,<sup>13</sup> the HFCC of the oxygens improve slightly over the aug-CC-PVTZ data, whereas the sulfur atoms remain essentially unaltered (cf., Table 3). The overall agreement with experiment is fair, although not excellent, at both the B3LYP/IGLO-III and B3LYP/TZVP levels of theory.

For  $\text{SO}_2^-$ , the TZVP and IGLO-III basis sets were also tested together with the QCISD method. Compared with the corresponding B3LYP calculations, the absolute values of both the sulfur and the oxygen HFCCs increase considerably (by ca. 8 G for sulfur and by 4–6 G for oxygen). Thus, all HFCCs now become overestimated in magnitude. The results are highly similar to the data obtained at the QCISD/aug-CC-PVDZ//QCISD/aug-CC-PVDZ level (not listed), yielding 19.7 G for sulfur and -16.2 G for the oxygens.

In Table 5 we list the hyperfine parameters of  $\text{SO}_2^-$  and  $\text{SO}_3^-$ , obtained using either a decontracted basis set for the geometry optimizations, or larger still basis sets for the HFCC data. Using a fully uncontracted aug-CC-PVDZ basis set for the geometry optimizations followed by uncontracted aug-CC-PVTZ HFCC calculations results in very minor overall changes. Again, this is related to the close similarity in optimized structures, deviating only in the fourth or fifth significant figures from the contracted aug-CC-PVDZ data.

Recently, Gronert suggested that a double set of diffuse functions be used in combination with the G2 approach, in order to obtain improved results for anionic systems.<sup>14</sup> We hence added a second set of diffuse functions to the basis of McKee, using the recommended exponents of Gronert, and also extended the resulting basis set with an additional f-function [6-311'+G(2d) and

6-311'+G(2df)], respectively]. Both these basis sets render slightly improved data for the sulfur atom in  $\text{SO}_3^-$ , but worse results for  $\text{SO}_2^-$  compared with, e.g., the aug-CC-PVTZ results. The additional f-function has minor effects.

## Conclusions

We have performed detailed calculations of sulfur oxide monoanions, with the primary objective of finding a suitable approach for computing accurate isotropic hyperfine data. It is noted that, although generating highly similar geometries and electron affinities, the different basis sets employed within the B3LYP approximation show some variations in the sulfur HFCCs. Neither decontracting the basis sets, nor using basis sets previously shown to be highly accurate for HFCC calculations on systems containing other first- and second-row atoms (IGLO-III, TZVP) results in vast improvements over the data reported at the present B3LYP/aug-CC-PVTZ level. The best results obtained are reasonably close for  $\text{SO}_2^-$ , but the deviation for the sulfur atom in  $\text{SO}_3^-$  remains at ca. 30 G, or 24%. Using the more accurate QCISD approach instead appears to overestimate the spin density at the nuclei. It is noted that further work is necessary either by developing purposely tailored sulfur HFCC basis sets, or by improving the level of theory employed, to be able to accurately describe these systems.

*Acknowledgements.* We are grateful to the Natural Sciences and Engineering Research Council (NSERC) of Canada and the Swedish Natural Science Research Council (NFR) for financial support. We thank Fahmi Himo for technical assistance, and Professor McKee for supplying his corrected data prior to publication.

Table 5. Isotropic hyperfine coupling constants,  $A_{\text{iso}}$  (G), using extended basis sets and geometries.<sup>a</sup>

System	Atom	u-aug-CC-PVTZ <sup>b</sup>	6-311'+G(2d) <sup>c</sup>	6-311'+G(2df) <sup>c</sup>
$\text{SO}_2^-$	<sup>33</sup> S	7.2	5.8	
	<sup>17</sup> O	-7.9	-6.0	
$\text{SO}_3^-$	<sup>33</sup> S	88.0	93.7	91.3
	<sup>17</sup> O	-9.3	-9.4	-9.1

<sup>a</sup> All geometries obtained using the B3LYP functional. <sup>b</sup> Uncontracted aug-CC-PVTZ basis set at uncontracted aug-CC-PVDZ optimized geometry. <sup>c</sup> At 6-31'+G(d) optimized geometry; '+' indicates addition of second diffuse functions, using exponents recommended by Gronert.<sup>14</sup>

J. M. M. thanks members of the Quantum Chemistry Group, Department of Physics, S. U., for their hospitality during his stay there.

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Received July 1, 1996.