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Coupled-cluster vibrational frequencies for open, ring and superoxide sulfur dioxide

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Abstract. The harmonic vibrational frequencies of the open, ring and superoxide isomers of sulfur dioxide are predicted with the coupled-cluster including all single and double excitations (CCSD) and coupled cluster singles and doubles with perturbative connected triples [CCSD(T)] methods. The reliability of the results is discussed and comparisons are made to the recent observations of the matrix-isolated SOO molecule reported by Chen, Lee and Lee.

Key words: Equilibrium geometrics – Infrared intensities – Isotope effects

The existence of the ring and superoxide isomers of $^1A_1$ sulfur dioxide has been strongly suggested by theoretical investigations [1,2]. However, no conclusive experimental observation of either isomer was reported until the recent investigations of Chen et al. [3]. Chen and coworkers report that they have observed the superoxide isomer, SOO, in an argon matrix via infrared spectroscopy. The presence of an absorption continuum in the flash photolysis spectra of S containing species in 1957 prompted Meyerson et al. [4] to propose the existence of a high-temperature isomer of SO_2, and suggested that this isomer might be the superoxide, SOO. Although early Hartree-Fock studies of O_3 [5] supported the existence of a relatively low-lying cyclic isomer of the valence-isoelectronic SO_2, subsequent studies of O_3 revealed that the HF model was especially poor for ozone [6, 7] and that multi-reference treatment was necessary for accurate predictions of the energetic separations of its various isomers [8]. Ab initio studies of SO_2 have found that, while it possesses significantly less multi-reference character than ozone [9], the excitation energies for the lowest closed-shell isomers are still too large [1, 2] for them to be responsible for the curious absorption observed by Meyerson et al. and others [10–12].

The theoretical characterization of such properties as equilibrium geometries and harmonic vibrational frequencies can often help to guide or confirm spectroscopic investigations. In our previous work on the open, ring and superoxide isomers, the main aim was to provide an accurate estimate of the relative energetics of the three species [1]. The SCF and CISD harmonic frequencies which were predicted were presented mainly to provide an estimate of the ZPVE for each of the three species, and thereby refine our predictions of their energetic separation. The poor agreement between the highest level predictions for the harmonic vibrational frequencies of the open isomer, obtained at the TZ2P(*f*) CISD level of theory, and the experimental values of the fundamental frequencies indicates that the TZ2P(*f*) CISD predictions for the other two isomers may also be unreliable.

The new experimental investigations of Chen et al. point out a clear need for reliable predictions of the harmonic vibrational frequencies and infrared intensities for the open, ring and superoxide isomers of SO_2. This work attempts to provide a more definitive characterization of the harmonic vibrational frequencies for the three isomers (Fig. 1) by employing the TZ2P(*f*) CCSD and TZ2P(*f*) CCSD(T) methods. The investigations of Thomas et al. [13] indicate that TZ2P(*f*) CCSD and TZ2P(*f*) CCSD(T) provide predicted harmonic frequencies which reproduce experimentally deduced harmonic frequencies with an average error of 1.5% and 0.6%, respectively, for a group of relatively well behaved systems. Although such accuracy is not likely for SO_2, which exhibits more multi-reference character than those systems studied by Thomas et al. TZ2P(*f*) CCSD and CCSD(T) should still provide predictions which are superior to TZ2P(*f*) CISD predictions, since coupled-cluster methods are generally less sensitive to the quality of the reference function than are CI techniques.

The basis set used in this investigation consisted of the Huzinaga-Dunning-McLean-Chandler triple-ζ set of contracted gaussian functions with two sets of d-type polarization functions and one set of higher angular

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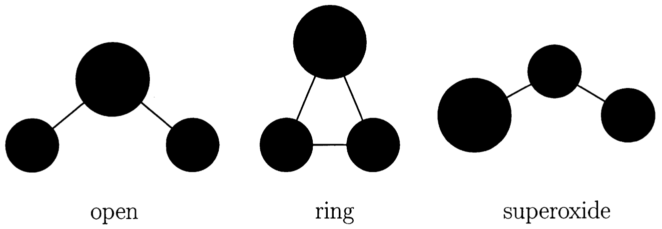

Fig. 1. Pictoral representations of the open, ring and superoxide isomers of sulfur dioxide

momentum f-type functions appended to each atom, designated TZ2P(f) [14, 15]. The basis may be expressed as O($10s\ 6p\ 2d\ 1f/\ 5s\ 3p\ 2d\ 1f$) for oxygen and S($12s\ 9p\ 2d\ 1f/\ 6s\ 5p\ 2d\ 1f$) for sulfur. The orbital exponents for the polarization functions of the TZ2P(f) basis are $\alpha_d(\mathrm{O}) = 1.70, 0.425$, $\alpha_d(\mathrm{S}) = 1.4, 0.35$. Exponents for the f functions on oxygen and sulfur were $\alpha_f(\mathrm{O}) = 1.40$; and $\alpha_f(\mathrm{S}) = 0.55$, respectively.

Selected orbitals were not allowed to participate in the correlated studies. For the C_{2v} symmetry ring and open isomers, four core-like orbitals of a_1 symmetry, one orbital of b_1 symmetry and two orbitals of b_2 symmetry were excluded from the active space, as were three a_1 virtual orbitals, one b_1 virtual orbital, and two b_2 virtual orbitals. For the superoxide isomer, six core orbitals of a' symmetry and one core orbital of a'' symmetry, as well as five virtual orbitals of a' symmetry and one virtual orbital of a'' symmetry were excluded from the orbital active space. The justification for this choice (seven frozen core, six deleted virtual orbitals) of active space may be found in Ref. [1].

Geometry optimizations at the CCSD [16] and CCSD(T) [17] levels of theory proceeded by means of analytic first derivative methods [18, 19]. Force constants for the optimizations at all levels of theory were taken from SCF second derivative values at the SCF optimized geometries [20]. Harmonic vibrational frequencies were determined by means of numerical differentiation of analytic gradients taken at finitely displaced geometries. Vibrational intensities were computed by means of numerical differentiation of dipole moments determined at finitely displaced geometries. All research was performed on IBM RS6000 workstations using the PSI 2.0.8 program package [21].

The optimized CCSD and CCSD(T) geometries of the open, ring and superoxide isomers may be found in Table 1. These geometries were obtained in the previous study of the energy separation of the three isomers. The predicted harmonic vibrational frequencies at the TZ2P(f) CCSD and CCSD(T) levels of theory are presented in Tables 2–4. In Table 5 the ratios of the predicted harmonic vibrational frequencies of the isotopically substituted species to the predicted harmonic frequencies of the unsubstituted $^{32}S\ ^{16}O_2$ species for each isomer are reported. The observed isotopic ratios for the open isomer and the recent observations of the superoxide isomer reported by Chen et al. are also presented.

Comparison of the TZ2P(f) CCSD(T) predicted harmonic frequencies for the unsubstituted open isomer with the experimentally observed vibrational fundamentals, $\nu_1 = 1151$, $\nu_2 = 517$ and $\nu_3 = 1361$, reveals an exceptionally close correspondence, and a far better agreement than was obtained at either the TZ2P(f) CISD or CCSD levels of theory. The proximity of the predicted harmonic frequencies to the observed fundamentals may be somewhat fortuitous, since anharmonic contributions, which could be in the order of $\sim 25\ \mathrm{cm}^{-1}$, must be taken into account for a rigorous comparison. The predicted CCSD and CCSD(T) harmonic frequencies for the open isomer agree to within at least $60\ \mathrm{cm}^{-1}$ for all three modes, indicating that the frequencies are relatively well converged with respect to the level of electron correlation. If we assume that the anharmonic contributions are relatively small for the open isomer, then the remaining discrepancy between the predicted harmonic frequencies and the observed fundamentals may be attributed to basis set inadequacy. Given the close agreement of the predicted and observed frequencies and isotopic ratios, it would appear that basis set inadequacy is not a significant concern.

Table 1. Predicted equilibrium geometries of the open, ring and superoxide isomers of SO_2 at the TZ2P(f) CCSD and CCSD(T) levels of theory

Open isomer	r_{so}	θ_{oso}	
CCSD	1.4345	118.71°	
CCSD(T)	1.4476	118.70°	
Ring isomer	r_{so}	r_{oo}	θ_{oso}
CCSD	1.6740	1.4782	52.40°
CCSD(T)	1.6900	1.5001	52.69°
Superoxide isomer	r_{so}	r_{oo}	θ_{soo}
CCSD	1.6088	1.2804	121.00°
CCSD(T)	1.6294	1.3139	119.80°

Table 2. Harmonic vibrational frequencies (cm^{-1}) and infrared intensities ($\mathrm{km\ mol}^{-1}$) for various isotopomers of the open isomers of SO_2 as predicted by the TZ2P(f) CCSD and CCSD(T) methods

Isotopomer	Method	$\omega_1(A_1)$	$\omega_2(A_1)$	$\omega_3(B_2)$
$^{32}S\ ^{16}O_2$	CCSD	1206.8 (32)	538.7 (33)	1407.9 (217)
	CCSD(T)	1139.0 (24)	516.6 (29)	1344.0 (180)
	Experiment[a]	1151.3	517.6	1361.7
$^{32}S\ ^{18}O\ ^{16}O$	CCSD	1177.2 (33)	527.6 (32)	1387.9 (209)
	CCSD(T)	1111.3 (25)	506.0 (27)	1324.8 (174)
	Experiment[a]	1123.7	506.7	1342.6
$^{32}S\ ^{18}O_2$	CCSD	1153.3 (32)	516.3 (30)	1362.1 (204)
	CCSD(T)	1088.7 (23)	495.1 (26)	1300.3 (170)
	Experiment[a]	1100.6	495.9	1318.1
$^{33}S\ ^{16}O_2$	CCSD	1202.7 (31)	536.3 (33)	1398.8 (214)
	CCSD (T)	1135.2 (23)	514.4 (29)	1335.3 (178)
$^{33}S\ ^{18}O\ ^{16}O$	CCSD	1172.9 (33)	525.3 (32)	1378.8 (206)
	CCSD(T)	1107.2 (24)	503.8 (27)	1316.0 (171)
$^{33}S\ ^{18}O_2$	CCSD	1149.1 (31)	514.0 (30)	1352.7 (201)
	CCSD(T)	1084.6 (23)	492.9 (26)	1291.3 (167)
$^{34}S\ ^{16}O_2$	CCSD	1199.0 (30)	534.1 (33)	1390.2 (211)
	CCSD(T)	1131.6 (22)	512.2 (29)	1327.1 (175)
$^{34}S\ ^{18}O\ ^{16}O$	CCSD	1168.9 (32)	523.2 (32)	1370.1 (203)
	CCSD(T)	1103.4 (24)	501.7 (27)	1307.7 (169)
$^{34}S\ ^{18}O_2$	CCSD	1145.0 (30)	511.9 (30)	1343.8 (198)
	CCSD(T)	1080.9 (22)	490.9 (26)	1282.8 (165)

[a] Fundamental frequencies [3, 22]

Table 3. Harmonic vibrational frequencies (cm^{-1}) and infrared intensities (km mol^{-1}) for various isotopomers of the ring isomer of SO$_2$ as predicted by the TZ2P(f) CCSD and CCSD(T) methods

Isotopomer	Method	$\omega_1(\mathrm{A}_1)$	$\omega_2(\mathrm{A}_1)$	$\omega_3(\mathrm{B}_2)$
$^{32}\mathrm{S}\ ^{16}\mathrm{O}_2$	CCSD	1002.9 (13)	677.9 (3)	755.1 (12)
	CCSD(T)	939.2 (10)	633.8 (2)	718.5 (8)
$^{32}\mathrm{S}\ ^{18}\mathrm{O}\ ^{16}\mathrm{O}$	CCSD	980.3 (13)	664.9 (3)	736.3 (11)
	CCSD(T)	918.5 (10)	621.5 (2)	700.5 (8)
$^{32}\mathrm{S}\ ^{18}\mathrm{O}_2$	CCSD	955.4 (13)	651.9 (2)	719.0 (11)
	CCSD(T)	895.4 (10)	609.0 (2)	684.3 (7)
$^{33}\mathrm{S}\ ^{16}\mathrm{O}_2$	CCSD	1000.5 (13)	674.4 (3)	753.2 (12)
	CCSD(T)	936.7 (10)	630.7 (2)	716.7 (8)
$^{33}\mathrm{S}\ ^{18}\mathrm{O}\ ^{16}\mathrm{O}$	CCSD	977.7 (13)	661.4 (3)	734.4 (11)
	CCSD(T)	915.8 (10)	618.4 (2)	698.7 (7)
$^{33}\mathrm{S}\ ^{18}\mathrm{O}_2$	CCSD	952.6 (12)	648.6 (3)	717.1 (11)
	CCSD(T)	892.6 (10)	606.0 (2)	682.4 (7)
$^{34}\mathrm{S}\ ^{16}\mathrm{O}_2$	CCSD	998.2 (13)	671.1 (3)	751.4 (12)
	CCSD(T)	934.4 (10)	627.7 (2)	715.0 (8)
$^{34}\mathrm{S}\ ^{18}\mathrm{O}^{16}\mathrm{O}$	CCSD	975.3 (13)	658.1 (3)	732.6 (11)
	CCSD(T)	913.4 (10)	615.4 (2)	697.0 (7)
$^{34}\mathrm{S}\ ^{18}\mathrm{O}_2$	CCSD	950.1 (12)	645.3 (3)	715.2 (11)
	CCSD(T)	890.1 (10)	603.1 (2)	680.6 (7)

Table 4. Harmonic vibrational frequencies (cm^{-1}) and infrared intensities, in (km mol^{-1}) for various isotopomers of the superoxide isomer of SO$_2$ as predicted by the TZ2P + (f) CCSD and CCSD(T) methods

Isotopomer	Method	$\omega_1(\mathrm{A}')$	$\omega_2(\mathrm{A}')$	$\omega_3(\mathrm{A}')$
$^{32}\mathrm{S}\ ^{16}\mathrm{O}\ ^{16}\mathrm{O}$	CCSD	1185.0 (148)	837.6 (21)	497.5 (0.3)
	CCSD(T)	929.8 (91)	758.0 (29)	467.8 (0)
	Experiment[a]	1006.1 1004.7	739.9	–
$^{32}\mathrm{S}\ ^{18}\mathrm{O}\ ^{16}\mathrm{O}$	CCSD	1152.2 (138)	805.3 (20)	490.7 (0.3)
	CCSD(T)	907.0 (86)	726.4 (28)	461.4 (0)
	Experiment[a]	978.0 976.6	738.9	–
$^{32}\mathrm{S}\ ^{16}\mathrm{O}\ ^{18}\mathrm{O}$	CCSD	1151.3 (142)	836.0 (19)	483.9 (0.4)
	CCSD(T)	901.8 (84)	756.8 (31)	455.5 (0)
	Experiment[a]	980.2 978.8	710.9	–
$^{32}\mathrm{S}\,^{18}\mathrm{O}\ ^{18}\mathrm{O}$	CCSD	1117.1 (132)	803.9 (19)	477.4 (0.3)
	CCSD(T)	878.0 (79)	725.3 (29)	449.5 (0)
	Experiment[a]	950.8 949.4	709.9	–
$^{33}\mathrm{S}\ ^{16}\mathrm{O}\ ^{16}\mathrm{O}$	CCSD	1185.0 (148)	834.0 (21)	495.3 (0.3)
	CCSD(T)	929.4 (92)	755.2 (29)	465.5 (0)
$^{33}\mathrm{S}\ ^{18}\mathrm{O}\ ^{16}\mathrm{O}$	CCSD	1152.2 (138)	801.4 (20)	488.6 (0.3)
	CCSD(T)	906.6 (87)	723.5 (27)	459.2 (0)
$^{33}\mathrm{S}\ ^{16}\mathrm{O}\ ^{18}\mathrm{O}$	CCSD	1151.3 (142)	832.3 (19)	481.6 (0.4)
	CCSD(T)	901.5 (85)	754.1 (30)	453.2 (0)
$^{33}\mathrm{S}\ ^{18}\mathrm{O}\ ^{18}\mathrm{O}$	CCSD	1117.1 (132)	800.0 (19)	475.2 (0.3)
	CCSD(T)	877.6 (80)	722.3 (28)	447.2 (0)
$^{34}\mathrm{S}\ ^{16}\mathrm{O}\ ^{16}\mathrm{O}$	CCSD	1185.0 (148)	830.6 (20)	493.1 (0.3)
	CCSD(T)	929.1 (93)	752.5 (28)	463.4 (0)
$^{34}\mathrm{S}\ ^{18}\mathrm{O}\ ^{16}\mathrm{O}$	CCSD	1152.2 (138)	797.8 (20)	486.5 (0.3)
	CCSD(T)	906.2 (87)	720.8 (26)	457.1 (0)
$^{34}\mathrm{S}\ ^{16}\mathrm{O}\ ^{18}\mathrm{O}$	CCSD	1151.3 (142)	828.9 (19)	479.4 (0.4)
	CCSD(T)	901.1 (86)	751.4 (29)	451.0 (0)
$^{34}\mathrm{S}\ ^{18}\mathrm{O}\ ^{18}\mathrm{O}$	CCSD	1117.1 (132)	796.3 (19)	473.1 (0.3)
	CCSD(T)	877.2 (80)	719.6 (27)	445.1 (0)

[a] Fundamental frequencies [3]

Table 5. Ratios of the harmonic vibrational frequencies of the isotopically substituted species to the harmonic frequencies of the unsubstituted $^{32}\mathrm{S}\ ^{16}\mathrm{O}_2$ species for the open, ring and superoxide isomers of SO$_2$, as predicted by the TZ2P + (f) CCSD and CCSD(T) methods

Isotopomer	Method	$\omega_1(\mathrm{A}')$	$\omega_2(\mathrm{A}')$	$\omega_3(\mathrm{A}')$
Open				
$^{32}\mathrm{S}\ ^{18}\mathrm{O}\ ^{16}\mathrm{O}$	CCSD	0.9755	0.9794	0.9858
	CCSD(T)	0.9757	0.9795	0.9857
	Experimental[a]	0.9760	0.9790	0.9860
$^{32}\mathrm{S}\ ^{18}\mathrm{O}_2$	CCSD	0.9557	0.9584	0.9675
	CCSD(T)	0.9558	0.9584	0.9675
	Experimental[a]	0.9560	0.9580	0.9680
Ring				
$^{32}\mathrm{S}\ ^{18}\mathrm{O}\ ^{16}\mathrm{O}$	CCSD	0.9975	0.9808	0.9751
	CCSD(T)	0.9780	0.9806	0.9749
$^{32}\mathrm{S}\ ^{18}\mathrm{O}_2$	CCSD	0.9526	0.9616	0.9522
	CCSD(T)	0.9534	0.9609	0.9524
Superoxide				
$^{32}\mathrm{S}\ ^{18}\mathrm{O}\ ^{16}\mathrm{O}$	CCSD	0.9723	0.9614	0.9863
	CCSD(T)	0.9755	0.9583	0.9863
	Experimental[a]	0.9742	0.9605	–
$^{32}\mathrm{S}\ ^{16}\mathrm{O}\ ^{18}\mathrm{O}$	CCSD	0.9716	0.9981	0.9727
	CCSD(T)	0.9699	0.9984	0.9737
	Experimental[a]	0.9720	0.9986	–
$^{32}\mathrm{S}\ ^{18}\mathrm{O}\ ^{18}\mathrm{O}$	CCSD	0.9427	0.9598	0.9596
	CCSD(T)	0.9443	0.9569	0.9609
	Experimental[a]	0.9450	0.9592	–

[a] Ratios of the observed fundamentals [3, 22]

The geometries, harmonic frequencies and isotopic ratios of the ring isomer exhibit a convergence with respect to level of electron correlation which is similar to that of the open isomer. Therefore, it is reasonable to conclude that the CCSD(T) predictions are reliable and should provide a reasonable guide for future experimental observations. The superoxide isomer, on the other hand, does not appear to be as well converged by TZ2P(f) CCSD(T). The differences between the predicted CCSD and CCSD(T) equilibrium geometries are somewhat larger than the analogous differences between the predicted geometries for the open and ring isomers. The corresponding predicted harmonic frequencies and isotopic ratios also exhibit significant differences, indicating that perhaps the CCSD(T) predicted properties are not as well converged with respect to the treatment of electron correlation as are the properties of the ring and open isomers. The poor agreement between the predicted harmonic frequencies and the observed fundamentals makes it difficult to place confidence in either the CCSD or CCSD(T) predictions. It is important, however, to consider that such factors as vibrational anharmonicity and matrix isolation effects could give rise to significant differences between the exact gas phase harmonic frequencies and the observed fundamentals. The predicted isotopic ratios of the harmonic frequencies for the superoxide isomer appear to be relatively good, but neither the CCSD nor CCSD(T) predictions match the observations as well as the predicted isotopic ratios for the open isomer, and it is difficult to discriminate between the methods based on their ability to reproduce the observed ratios. Chen et al. report that the ν_1 emission is approximately ten times more intense than that for ν_2. The CCSD prediction of the ratio of the intensities, ~7, is more consistent with this observation than the CCSD(T) prediction of ~3. However, given the ambiguity of the comparisons of the predicted results of the two methods with the other observed properties, this does not represent very strong evidence for the relative accuracy of CCSD over CCSD(T).

In conclusion, the TZ2P(*f*) CCSD(T) method has been shown to provide high-quality predictions of the harmonic vibrational frequencies and isotopic ratios of the open isomer of SO_2, in contrast to previous predictions made by TZ2P(*f*) CISD. The ring isomer of SO_2 also appears to be well described by TZ2P(*f*) CCSD(T), and the predicted harmonic vibrational frequencies $\omega_1 = 939.2\ \mathrm{cm}^{-1}$, $\omega_2 = 633.8\ \mathrm{cm}^{-1}$ and $\omega_3 = 718.5\ \mathrm{cm}^{-1}$ represent a relatively accurate estimate of the fundamental vibrational frequencies. Comparison of the TZ2P(*f*) CCSD and TZ2P(*f*) CCSD(T) predictions for the superoxide isomer are complicated by potential matrix isolation effects and the lack of information about the vibrational anharmonicity of the superoxide isomer, either experimental or theoretical. Future ab initio investigations of this species should involve characterization of the anharmonic contributions to the vibrational fundamentals, as well as higher-level correlated studies, such as CCSDT, with at least a TZ2P(*f*) basis.

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