4158 *J. Phys. Chem. A* **2008,** *112,* 4158−4164

Coupled-Cluster Study of Isomers of H_2SO_2

Brian Napolion, Ming-Ju Huang, and John D. Watts*

Department of Chemistry, P.O. Box 17910, Jackson State University, Jackson, Mississippi 39217

Received: January 30, 2008

A theoretical study has been made on six isomers of H_2SO_2 using coupled-cluster singles and doubles with noniterative triple excitations (CCSD(T)). The isomers studied are sulfoxylic acid ($S(OH)_2$; C_2 and C_s conformers), sulfinic acid ($HS(=O)OH$; 2 C_1 conformers), dihydrogen sulfone (H_2SO_2; C_{2v}), sulfhydryl hydroperoxide (HSOOH; C_1), thiadioxirane (C_s), and dihydrogen persulfoxide (H_2SOO; C_s). Molecular geometries, harmonic vibrational frequencies, and infrared intensities of all species were obtained using the CCSD(T) method and the 6-311++G(2d,2p) basis set. All aforementioned species were found to be local minima, with the exception of thiadioxirane, which has one imaginary frequency. A prior possible infrared observation of sulfinic acid was reassessed on the basis of the present data. In agreement with previous MP2 results, the present CCSD(T) data provide support for at most 4 of the 8 observed frequencies. The CCSD(T) frequencies and intensities should be of assistance in future identification of H_2SO_2 isomers by vibrational spectroscopy. Relative energies were calculated using the CCSD(T) method and several larger basis sets. As found previously, the lowest energy species is C_2 $S(OH)_2$, followed by C_s $S(OH)_2$, $HS(=O)OH$, H_2SO_2, HSOOH, thiadioxirane, and H_2SOO. Expanding the basis set significantly reduces the relative energies of $HS(=O)OH$ and H_2SO_2. The CCSD(T) method was used with extended basis sets (up to aug-cc-pV(Q+d)Z) and basis set extrapolation in two reaction schemes to calculate the ΔH_f^o(25 °C) of C_2 $S(OH)_2$. The two reaction schemes gave −285.8 and −282.7 kJ mol^{-1}, which are quite close to a prior theoretical estimate (−290 kJ mol^{-1}).

Introduction

Species having the chemical formula H_2SO_2 are expected to be involved in the atmospheric and/or combustion chemistry of sulfur-containing compounds.[1−5] Examples include the reaction between H_2 and SO_2 and that between H_2S and O_2. Montoya et al.[6] have recently noted that although the reactions between H_2S and oxygen atoms and hydroxyl radicals have been quite well studied, comparatively little attention has been given to the kinetics and mechanism of the reaction between H_2S and O_2. Knowledge about species on the H_2SO_2 potential energy surface is important for the understanding of this and related reactions. Various H_2SO_2 isomers are also parents of several families of organosulfur compounds.

There are, of course, several possible structures that contain two hydrogen atoms, two oxygen atoms, and one sulfur atom. Hereafter, following the notation of several groups, we shall use [H_2, S, O_2] to denote general species of this composition. They include sulfoxylic acid, also called dihydroxysulfane ($S(OH)_2$), sulfinic acid ($HS(=O)OH$), sulfone or dihydrogen sulfone (H_2SO_2), sulfhydryl hydroperoxide (HSOOH), thiadioxirane (a three-membered SOO ring with H atoms bonded to S), and dihydrogen persulfoxide (H_2SOO). These species are shown in Figure 1. As might be expected from consideration of bond energies, theoretical calculations (discussed in more detail below) suggest that $S(OH)_2$ is the most stable species, followed by $HS(=O)OH$ and H_2SO_2, with the other isomers being somewhat higher in energy.

There have been very few experimental observations of [H_2, S, O_2] species. Fender at al.[7] attributed 8 infrared absorptions to sulfinic acid. These bands were observed after the photolysis of H_2S and SO_2 in an Ar matrix. On the basis of their calculated data, Steiger and Steudel[8] questioned whether all of the absorptions observed by Fender et al. should be assigned to sulfinic acid. About the same time, Laakso and Marshall[9] calculated frequencies that matched 3 of the observed frequencies reasonably, but there were large deviations from the other observed frequencies. Several years later, Otto and Steudel[10] repeated the concerns of Steiger and Steudel. Frank et al.[11] detected sulfoxylic acid by neutralization-reionization mass spectrometry (NRMS). Ionization of dimethyl sulfate ($O_2S(OCH_3)_2$) was followed by loss of 2 formaldehyde molecules, leading to the radical cation $S(OH)_2^+$, which then captured an electron by collisional neutralization with dimethyl disulfide

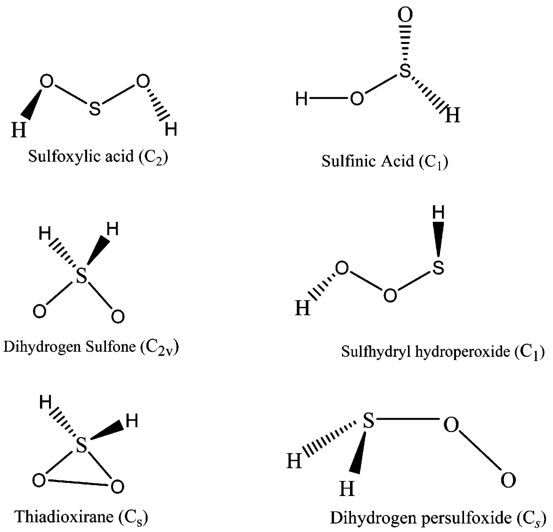

Figure 1. Isomers of the form [H_2,S,O_2].

10.1021/jp8009047 CCC: $40.75

$(CH_3S)_2$, yielding $S(OH)_2$. Otto and Steudel[10] referred to the work of Frank et al.[11] as the "only reliable experimental information on [H_2, S, O_2]". Wang and Zhang[12] cite an estimated standard enthalpy of formation of $S(OH)_2$ of -290 ± 17 kJ mol^{-1} that was derived by Benson[13] by his group additivity scheme.

Several prior theoretical studies have been made on various [H_2, S, O_2] isomers. Initial calculations were made by Plummer et al.[2] and Boyd et al.[14] using the STO-3G(*) basis set. Later Basch[15] performed some HF calculations with the 6-31G* basis set. The first calculations with a correlated method were those of Steiger and Steudel[8] and Laakso and Marshall.[9] The former authors performed calculations on C_2 and C_s conformers of $S(OH)_2$, sulfinic acid (one C_1 conformer), and dihydrogen sulfone (C_{2v}). Geometries and harmonic vibrational frequencies were obtained at the HF/6-31G(d) and MP2/6-31G(d) levels. MP4 single-point calculations were made at the MP2 geometries. It was found that C_2 $S(OH)_2$ was the most stable species, the C_s conformer being only 7−8 kJ mol^{-1} higher in energy. MP4 calculations indicated sulfinic acid and dihydrogen sulfone to be 57 and 129 kJ mol^{-1} higher in energy than C_2 $S(OH)_2$, respectively. As mentioned earlier, Steiger and Steudel[8] compared their MP2 frequencies of sulfinic acid to the observed values of Fender et al.,[7] but they found no conclusive match and questioned the assignment. Using MP2/3-21G(*) for geometry optimizations and MP4/6-31G* for single-point energies, Laakso and Marshall[9] studied C_2 $S(OH)_2$, two C_1 conformers of sulfinic acid, dihydrogen sulfone, sulfhydryl hydroperoxide, and the dihydrogen persulfoxide. They also compared their sulfinic acid frequencies with those reported by Fender et al., noting reasonable agreement with the 3 largest observed frequencies, but not for the other frequencies measured by Fender at al. The two conformers of sulfinic acid differ in energy by only 1 kJ mol^{-1}, and the lowest energy conformer is that studied by Steiger and Steudel.

Along with their experimental work, Frank et al.[11] performed calculations on C_2 and C_s $S(OH)_2$ and sulfinic acid, using MP2/6-31+G(d) for geometry optimizations and the G2(MP2) method for energies and enthalpies at the MP2/6-31+G(d) geometries. As well as these local minima of neutral [H_2, S, O_2], they studied transition states and various cationic species. Again, C_2 $S(OH)_2$ was found to be the most stable species, but the reported G2(MP2) enthalpy of sulfinic acid is only 20 kJ mol^{-1} higher, which is significantly smaller than the differences reported in earlier calculations. G2 and CBS calculations by Otto and Steudel[10] confirmed this smaller difference. Wang and Zhang[12] have used G3 methodology to estimate the heats of formation of both conformers of $S(OH)_2$. Using the B3LYP functional and G2, Montoya et al.[6] studied all of the structures in Figure 1, as well as several transition states.

In this paper we report a series of calculations on the species in Figure 1 using the highly correlated CCSD(T) method for geometry optimizations and vibrational frequency calculations. No prior calculations on [H_2, S, O_2] species have used a method of this quality for geometry optimizations and vibrational frequency calculations. Also, the G2 methodology depends on various additivity approximations and, and it is of interest to compare the G2 data on relative energies and heats of formation with calculations that do not depend on these approximations. The CCSD(T) frequencies can be used to make a reassessment of the results obtained by Fender et al. as well as make predictions for other species.

TABLE 1: CCSD(T)/6-311++G(2d,2p) Geometries and Energies of the C_2 and C_s Conformers of Sulfoxylic Acid ($S(OH)_2$)[a]

	C_2	C_s
r(S−O)	1.668	1.668
r(O−H)	0.962	0.962
θ(OSO)	102.8	103.2
θ(HSO)	106.9	107.4
τ(HOSO)	83.0	90.3
energy	−549.064972	−549.062817
ZPE	77.4	77.0

[a] Bond lengths are in Å; angles are in degrees. The electronic energies are given in atomic units, and the zero-point vibrational energies are given in kJ mol^{-1}.

Computational Methods

Calculations were performed with the ACES II,[16,17] Gaussian 98,[18] and PSI3[19] programs. The [H_2, S, O_2] species studied are as follows: C_2 and C_s conformers of $S(OH)_2$; two C_1 conformers of sulfinic acid; dihydrogen sulfone (C_{2v}); HSOOH (C_1); thiadioxirane (C_s); and H_2SOO (C_s). CCSD(T)[20] geometry optimizations were performed on the ground state of each isomer using the 6-311++G(2d,2p) basis set.[21−24] Harmonic vibrational frequencies and infrared intensities were calculated at this level for each stationary point located. Enthalpies were obtained using thermal corrections based on the standard rigid rotor/harmonic oscillator/ideal gas model. To provide improved relative energies and thermochemical data, single-point CCSD(T) energies were obtained with several other basis sets. These basis sets are as follows: (1) the improved correlation-consistent polarized valence double-, triple- and quadruple-ζ sets (cc-pV(D+d)Z, cc-pV(T+d)Z, and cc-pV(Q+d)Z)[25−27] (these include a larger and improved d set for sulfur,[27] which leads to improved energetics compared with the original cc-pVnZ set[28,29]); (2) the diffuse function-augmented cc-pV(T+d)Z and cc-pV(Q+d)Z basis sets (aug-cc-pV(T+d)Z and aug-cc-pV(Q+d)Z);[25−27,30] (3) the 6-311++G(3df,3pd) set;[21−24] (4) an atomic natural orbital set of triple-ζ valence plus polarization quality.[31,32] In all calculations, the core electrons were not correlated, and real spherical harmonic d, f, and g functions were used.

The CCSD(T) method[20] involves a coupled-cluster singles-and-doubles (CCSD)[33] calculation, followed by a noniterative estimate of the effect of connected triple excitations based on the CCSD amplitudes. The CCSD(T) method is complete through fourth order terms, and also includes fifth-order singles-triple terms. In the absence of large multireference effects, the CCSD(T) method, in combination with appropriate basis sets, is a highly reliable method for structures, energies and other molecular properties.[34−36] On the basis of the size of the CCSD amplitudes, the species studied in this work do not have significant multireference character, so the CCSD(T) method should be suitable for this study.

Results and Discussion

Sulfoxylic Acid ($S(OH)_2$). In agreement with prior work, conformers of C_2 and C_s symmetry were found and determined to be local minima. The planar C_{2v} species was determined not to be a local minimum, in contrast to what has been found for the cation. Table 1 shows the geometries and CCSD(T)/6-311++G(2d,2p) energies. The geometries of the species have been determined at the MP2 level in several prior studies. Steiger and Steudel[8] obtained MP2/6-31G* geometries. Laakso and Marshall[9] obtained MP2/3-21G(*) geometries. Frank et al.[11] reported MP2/6-31+G(d,p) geometries. Wang and Zhang[12] calculated MP2/cc-pVTZ geometries. Montoya et al.[6] also

TABLE 2: CCSD(T)/6-311++G(2d,2p) Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km mol^{-1}) of the C_2 and C_s Conformers of Sulfoxylic Acid

	C_2		C_s			
symmetry	ω	infrared intensity	symmetry	ω	infrared intensity	approximate description
A	333	0.9	A′	343	1.4	OSO bend
A	499	132.0	A″	446	54.6	Torsion
B	520	100.4	A′	542	112.2	Torsion
B	748	175.3	A″	749	184.3	SO stretch
A	759	58.3	A′	757	53.7	SO stretch
B	1220	47.6	A″	1205	59.7	HOS bend
A	1221	24.0	A′	1218	31.7	HOS bend
B	3810	121.3	A′	3818	87.3	OH stretch
A	3813	19.0	A″	3820	40.0	OH stretch

reported MP2/6-31G* geometries. They also obtained B3LYP/6-31G(d) and B3LYP/6-311++G(3df,2p) geometries, although these were not reported. Our CCSD(T)/6-311++G(2d,2p) geometries are in fact very close to the MP2/6-31G* geometries. This close correspondence is the result of two opposing effects: going from MP2 to CCSD(T) leads to an increase in bond lengths, and going from the 6-31G* to 6-311++G(2d,2p) basis sets decreases bond lengths. The primary difference between the CCSD(T)/6-311++G(2d,2p) and MP2/6-31G* geometries is in the O−H bond length, the CCSD(T) value being about 0.015 Å smaller than the MP2/6-31G*. In contrast, the S−O bond distances differ by only 0.002 Å. The angles differ by less than 1°. Regarding the MP2/6-31+G(d,p) geometries of Frank et al., the O−H distance is between our CCSD(T) value and the MP2/6-31G* value, and the S−O distance is about 0.002 Å longer than our CCSD(T) value. Presumably, the values Frank et al. report for the OSO angle (128.5° and 128.2° for the C_2 and C_s conformers, respectively) are typographical errors: quite possibly these values are the OSX angles, where, for the C_2 conformer, X is a point on the C_2 axis. The S−O bond distance reported by Wang and Zhang (1.651 Å) is 0.017 Å smaller than our value. They do not report a value for the O−H distance, and their torsional angle for the C_2 conformer (89.9°) is somewhat different from our value and other MP2 results.

HF, MP2, and B3LYP harmonic vibrational frequencies have been calculated in several prior studies. However, for the most part the frequencies have been used to calculate zero-point vibrational energies and thermal corrections but have not been analyzed further. An exception is the work of Steiger and Steudel,[8] who report HF/6-31G* and MP2/6-31G* frequencies and infrared intensities. We report (unscaled) CCSD(T)/6-311++G(2d,2p) results in Table 2. Overall there is broad agreement between our results and those of Steiger and Steudel. In particular, both sets of calculations indicate quite small splittings between the SO stretching modes, the OH stretching modes, and the HOS bending modes. The intensity patterns are quite similar in both sets of calculations, too. As expected from the Lewis structure, the SO stretching modes have frequencies in the range expected for single S−O bonds.

Sulfinic Acid (HS(=O)OH). Table 3 shows the CCSD(T)/6-311++G(2d,2p) structure of sulfinic acid. Also shown are the MP2/6-31G* data of Steiger and Steudel[8] and the MP2/3-21G(*) data of Laakso and Marshall.[9] The CCSD(T) bond lengths tend to be somewhat smaller than the MP2 values. In both sets of data, the formal S=O bond length is about 0.2 Å smaller than the S−O bond length. There is fairly close agreement between the angles.

CCSD(T)/6-311++G(2d,2p) vibrational frequencies and infrared intensities are shown in Table 4, along with the MP2 data from previous work. The two sets of frequencies have a similar general pattern. With one exception for each conformer, the CCSD(T) frequencies are all smaller than the MP2 values. For the O−H stretching mode, the CCSD(T) frequency is 98 cm^{-1} greater than the MP2 value, which is consistent with the smaller CCSD(T) value for the O−H bond length. The situation is not as clear for the modes that are nominally SO and SH stretching modes. The CCSD(T) frequencies for these modes are smaller than the MP2 values, yet the CCSD(T) SO and SH bond lengths are smaller (Table 3). In fact, it is an oversimplification to describe these modes as localized stretching modes, so the customary inverse relationship between bond length and frequency for a pure stretching mode is not observed. Regarding the infrared intensities, one sees not only some significant differences in the two sets of data but also some close similarities.

TABLE 3: CCSD(T)/6-311++G(2d,2p) and MP2/6-31G* Geometry and Energies of Sulfinic Acid[a]

	conformer 1		conformer 2	
	CCSD(T)	MP2/6-31G*	CCSD(T)	MP2/3-21G(*)
r(S−O$^{(1)}$)	1.685	1.690	1.666	1.668
r(S−O$^{(2)}$)	1.476	1.483	1.479	1.487
r(O$^{(1)}$-H$^{(1)}$)	0.963	0.978	0.966	1.000
r(S−H$^{(2)}$)	1.362	1.363	1.369	1.380
θ(OSO)	111.0	112.8	110.2	112.0
θ(H$^{(1)}$O$^{(1)}$S)	106.3	106.9	108.1	112.2
θ(H$^{(2)}$SO$^{(1)}$)	86.9	86.0	93.5	93.5
τ(H$^{(1)}$O$^{(1)}$SO$^{(2)}$)	88.8	84.4	45.1	44.4
τ(H$^{(2)}$SO$^{(1)}$O$^{(2)}$)	106.3	107.8	−106.8	−110.3
energy	−549.048337	−548.819404	−549.047925	−546.022954
ZPVE	72.4		71.5	

[a] Bond lengths are in Å, angles are in degrees, and energies are in atomic units. The electronic energies are given in atomic units, and the zero-point vibrational energies are given in kJ mol^{-1}. The MP2/6-31G* data are from ref 8. The MP2/3-21G(*) data are from ref 9. The labeling of atoms refers to the structural formula H$^{(2)}$S(=O$^{(2)}$)O$^{(1)}$H$^{(1)}$.

TABLE 4: CCSD(T)/6-311++G(2d,2p) and MP2 Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km mol^{-1}) of Sulfinic Acid

conformer 1				conformer 2				
CCSD(T)		MP2[a]		CCSD(T)		MP2[b]		approximate normal mode description[a]
ω	I	ω	I	ω	I	ω	I	
323	63.2	341	20	299	44.9	311		torsion
387	62.4	431	144	445	79.4	467		OSO bend
693	145.3	741	151	706	175.4	749		S−O stretch
988	27.5	1018	29	993	22.1	1003		HSO bend
1100	7.3	1153	15	1090	21.5	1151		HSO bend
1149	169.3	1241	135	1123	104.8	1185		S=O stretch
1264	52.8	1278	108	1213	66.3	1258		HOS bend
2404	71.7	2560	137	2335	114.7	2366		SH stretch
3820	88.8	3722	87	3781	67.1	3438		OH stretch

[a] Reference 8. [b] Reference 9.

Having obtained CCSD(T) frequencies for sulfinic acid for the first time, it is interesting to assess the observed frequencies of Fender et al.[7] that were thought to arise from sulfinic acid. As noted earlier, on the basis of their MP2 frequencies, Steiger and Steudel[8] questioned the assignments of some of the observed bands to sulfinic acid. Laakso and Marshall[9] also only found plausible agreement for 3 modes.

Fender et al. reported four frequencies below 500 cm^{-1}, namely 270, 340, 450, and 476 cm^{-1}. On the basis of the CCSD(T) harmonic frequencies of conformer 1, it appears that only the two lowest of these could reasonably be assigned to sulfinic acid. For conformer 2, only one CCSD(T) frequency seems to provide a plausible fit, i.e., 299 cm^{-1}. The CCSD(T) harmonic

TABLE 5: CCSD(T)/6-311++G(2d,2p) and MP2/6-31G* Geometries and Energies of Dihydrogen Sulfone[a]

	CCSD(T)	MP2/6-31G*
r(S−O)	1.445	1.458
r(S−H)	1.350	1.358
θ(OSO)	123.3	124.4
θ(HSH)	99.4	99.1
energy	−549.026261	−548.795048
ZPE	74.1	77.4

[a] Bond lengths are in Å; angles are in degrees. The electronic energies are given in atomic units, and the zero-point vibrational energies are given in kJ mol^{-1}. The MP2/6-31G* data are from ref 8.

TABLE 6: CCSD(T)/6-311++G(2d,2p) and MP2/6-31G* Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km mol^{-1}) of Dihydrogen Sulfone[a]

symmetry	CCSD(T) harmonic frequency	infrared intensity	MP2[b] harmonic frequency	infrared intensity	approximate description[b]
A_1	485	29.7	490	34	OSO bend
B_1	885	23.0	912	38	SH_2 rock
A_2	999	0	1019	0	HSH twist
A_1	1123	67.9	1171	62	SO sym str
B_2	1187	13.7	1273	8	SH_2 wag
A_1	1329	26.8	1366	60	SH_2 scis
B_2	1354	263.3	1445	303	SO antisym str
B_1	2490	58.1	2612	137	SH antisym str
A_1	2504	53.3	2635	121	SH sym str

[a] The MP2 data are from ref 8. [b] Reference 8.

TABLE 7: CCSD(T)/6-311++G(2d,2p) Geometries and Energies of Sulfhydryl Hydroperoxide, Thiadioxirane, and Dihydrogen Persulfoxide[a]

HSOOH (C_1)		thiadioxirane (C_s)		H_2SOO (C_s)	
r(O−O)	1.495	r(S−O)	1.713	r(O−O)	1.505
r(S−O)	1.675	r(S−H)	1.365	r(S−O)	1.571
r(O−H)	0.965	∠OSO	55.2	r(S−H)	1.358
r(S−H)	1.342	$\angle H_1SO_1$	89.8	∠SOO	101.3
∠SOO	110.0	$\angle H_2SO_2$	89.8	∠HSO	99.5
∠HOO	99.2	$\tau(H_1SO_1O_2)$	141.5	τ(HSOO)	±45.7
∠HSO	97.4	$\tau(H_2SO_2O_1)$	−141.5		
τ(D1)	102.8				
τ(D2)	82.2				
energy	−548.976177		−548.882866		−548.883448

[a] Distances are in Å, angles are in degrees, and energies are in atomic units.

TABLE 8: CCSD(T)/6-311++G(2d,2p) Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km mol^{-1}) of Sulfhydryl Hydroperoxide, Thiadioxirane, and Dihydrogen Persulfoxide

HSOOH			thiadioxirane			H_2SOO		
	ω	I		ω	I		ω	I
a	198	110.5	a″	394i	7.7	a″	310	7.0
a	350	23.9	a″	542	9.1	a′	335	43.8
a	397	0.8	a′	671	82.2	a′	698	8.1
a	676	8.8	a′	798	34.6	a′	765	8.7
a	726	23.1	a′	1020	5.3	a″	880	2.0
a	1008	8.4	a″	1075	5.0	a′	988	27.3
a	1340	41.9	a′	1429	25.2	a′	1263	8.9
a	2616	7.6	a″	2386	65.1	a″	2454	0.8
a	3785	42.6	a′	2413	75.1	a′	2493	46.1

frequency of 445 cm^{-1} is close to an observed *anharmonic* frequency, but it seems unwise to read much into this agreement. The next observed band is at 762 cm^{-1}. Whether this is from sulfinic acid is debatable: the CCSD(T) frequencies for mode 3 will probably increase with basis set expansion, but the corresponding fundamental frequency will be smaller, so one questions whether the fundamental frequency will be much above 700 cm^{-1}. The next two observed bands, at 1093 and 1209 cm^{-1}, are somewhat consistent with the CCSD(T) data. As for the band at 2591 cm^{-1}, it is hard to reconcile this with the CCSD(T) frequency to which it is closest. First, the closest CCSD(T) frequency is 2404 cm^{-1}, and the corresponding fundamental frequency will be lower. Of course, basis set expansion will probably raise it somewhat, but presumably not as much as 200 cm^{-1}. Second, the calculated infrared intensity is quite significant, yet the band at 2591 cm^{-1} is the weakest of the observed absorptions. In summary, it seems that only 4 bands observed by Fender et al.[7] can reasonably be attributed to sulfinic acid. At the same time, one must remember that the matrix effects and the effects of basis set expansion and anharmonicity have yet to be assessed.

Dihydrogen Sulfone. CCSD(T)/6-311++G(2d,2p) bond lengths and angles of dihydrogen sulfone are shown in Table 5 along with the MP2/6-31G* values from Steiger and Steudel.[8] MP2/6-31G* data have also been reported by Montoya et al.[6] The CCSD(T) bond lengths are about 0.01 smaller than the MP2 values. The angles are quite similar. One anticipates significant double-bond character for the SO bonds in dihydrogen sulfone. This is reflected by the bond lengths, which are quite close to that of the formal S═O bond in sulfinic acid.

Harmonic vibrational frequencies and infrared intensities are shown in Table 6. The CCSD(T) frequencies are somewhat smaller than the unscaled MP2 values, but greater than the scaled MP2 values. Both sets of calculations agree that the largest intensity is for the antisymmetric SO stretching mode. However, there are some significant differences, particularly for the two SH stretching modes. The CCSD(T) frequencies for the SH stretching modes are 90−100 cm^{-1} higher than for the corresponding mode in sulfinic acid. The CCSD(T) difference between the symmetric and antisymmetric SH stretching modes is 14 cm^{-1}, compared to the (unscaled) MP2 value of 23 cm^{-1}. The difference between the two SO stretching modes is much larger (231 cm^{-1} for CCSD(T) and 195 cm^{-1} for MP2).

Higher Energy Isomers: Sulfhydryl Hydroperoxide, Thiadioxirane, and Dihydrogen Persulfoxide. On the basis of prior calculations, these three isomers are at somewhat higher energies than those discussed above. Our CCSD(T)/6-311++G(2d,2p) results are shown in Tables 7 and 8. MP2/6-31G(d) geometries and vibrational frequencies have been reported by Montoya et al.,[6] who have also reported G2 energies. For the peroxide, the differences between our CCSD(T)/6-311++G(2d,2p) geometry and that of Montoya et al. are minor. For the lower frequency modes, the CCSD(T) frequencies tend to be similar or slightly below the scaled MP2 results, but for the 3 highest frequencies, the reverse is true. For thiadioxirane, there are again only minor differences between the MP2 and CCSD(T) geometries. The situation is different for the frequencies, however. According to the CCSD(T) calculations, the C_s structure has an imaginary A″ frequency of 394i cm^{-1}, implying a lower energy C_1 structure. In the C_s MP2/6-31G(d) structure reported by Montoya et al., all frequencies are real, although the smallest one is only 57 cm^{-1}. Interestingly, Shangguan and McAllister[37] report MP2 and QCISD calculations on a C_1 thiadioxirane, which is perhaps the structure that would arise if the C_s species were optimized without symmetry constraints. For the persulfoxide, the most significant difference in the MP2 and CCSD(T) geometries is the O−O bond distance, the CCSD(T) value being a little over 0.03 Å greater than the MP2 value. The overall patterns of vibrational frequencies are similar, although there are some differences in the details. The frequency of the CCSD(T) O−O stretching mode (698 cm^{-1}) is smaller than the scaled MP2 value (721 cm^{-1}).

TABLE 9: Comparison of CCSD(T) and QCISD(T) Relative Energies (6-311++G(3df,3pd) Basis Set) with the G2 Relative Energies and Enthalpies and CBS-Q Relative Enthalpies[a]

	QCISD(T)	CCSD(T)	G2[b]	G2[c]	CBS-Q[c]
$S(OH)_2$ (C_2)	0.0	0.0	0.0	0.0	0.0
S(OH)2 (C_s)	5.0	5.0	4.9	4.9	5.6
HS(=)OH	25.9	27.0	24.5	23.6	18.5
H_2SO_2	59.5	60.9	62.0	61.0	50.5
HSOOH	247.4	242.3	235.3		
thiadioxirane	467.3	468.9	455.6		
H_2SOO	475.9	477.8	461.5		

[a] The QCISD(T) and CCSD(T) calculations were performed at the CCSD(T)/6-311++G(2d,2p) geometries. The relative energies and enthalpies are in kJ mol^{-1}. [b] Reference 6. [c] Reference 10 (relative enthalpies).

TABLE 10: CCSD(T) Relative Energies of the Lowest Energy Conformers of Sulfoxylic Acid, Sulfinic Acid, and Dihydrogen Sulfone as a Function of Basis Set[a]

	$S(OH)_2$ (C_2)	HS(=)OH (C_1)	H_2SO_2 (C_{2v})
cc-pV(T+d)Z	0.0	32.0	62.3
cc-pV(Q+d)Z	0.0	25.3	52.3
extrapolation[b]	0.0	20.4	45.0
6-311++G(2d,2p)	0.0	43.7	101.6
6-311++G(3df,3pd)	0.0	27.0	60.9

[a] The calculations were performed at the CCSD(T)/6-311++G(2d,2p) geometries. The units are kJ mol^{-1}. [b] X^{-3} extrapolation of the cc-pV(T+d)Z and cc-pV(Q+d)Z results.

Relative Energies and Enthalpies of [H_2, S, O_2] Isomers. Since the 1992 studies of Steiger and Steudel[8] and Laakso and Marshall,[9] there has been a consensus on the stability order of the four lowest energy [H_2, S, O_2] isomers. Thus, the most stable species is the C_2 conformer of sulfoxylic acid, which is a few kJ mol^{-1} lower in energy than the C_s conformer. Next comes sulfinic acid, followed by dihydrogen sulfone. At the same time, there is not a consensus on the energies (or enthalpies) of sulfinic acid and dihydrogen sulfone relative to that of sulfoxylic acid. MP2 and MP4 calculations by Steiger and Steudel[8] place sulfinic acid about 56 kJ mol^{-1} above sulfoxylic acid, and they place dihydrogen sulfone 120 (MP2) or 129 (MP4) kJ mol^{-1} above sulfoxylic acid. Similar conclusions were reached by Laakso and Marshall.[9] In contrast, at least two sets of later calculations using the G2 methodology, indicated much smaller energy differences. First, Otto and Steudel[10] obtained G2 relative enthalpies of sulfinic acid and dihydrogen sulfone of 23.6 and 61.0 kJ mol^{-1}, respectively. These authors also reported CBS-Q relative enthalpies of 18.5 and 50.5 kJ mol^{-1}. Montoya et al.[6] report G2 relative energies of 24.5 and 62.0 kJ mol^{-1} for sulfinic acid and dihydrogen sulfone, respectively.

Otto and Steudel and Montoya et al. noticed the differences between their results and earlier MP2 and MP4 results, but they did not attempt to analyze the situation further. We have attempted to gain some further insight into the issue through several sets of calculations. First, we are able to use CCSD(T)/6-311++G(2d,2p) geometries: G2 calculations[38] are based on MP2/6-31G(d) geometries. Second, we have been able to perform CCSD(T) and QCISD(T) calculations using the 6-311++G(3df,3pd) basis set: the G2 method *estimates* QCISD(T)/6-311++G(3df,3pd) energies using additivity approximations. Third, we have tried to isolate the role of the effects of diffuse and multiple polarization functions on the relative energies. Fourth, we have performed a series of calculations using the cc-pV(T+d)Z, and cc-pV(Q+d)Z correlation-consistent basis sets.

The first results are shown in Table 9. This table includes the G2 relative energies from Montoya et al., the G2 and CBS-Q relative enthalpies from Otto and Steudel, and our CCSD(T) and QCISD(T) energies and relative energies. In general, there is a close correspondence between the G2 data and our QCISD(T) relative energies, thus indicating the reliability of the G2 additivity scheme in this case. There is only a minor difference between CCSD(T) and QCISD(T) results in this case, which reflects the fact that the cluster amplitudes are quite small and that methods such as CCSD(T) and QCISD(T) thus ought to be capable of giving a good account of electron correlation for the studied systems. The CBS-Q results are somewhat different from the G2 results, and it is not *a priori* clear which set are more accurate. The higher level correction employed in G2 has no effect on isomer energy differences, whereas the CBS-Q method uses a separate extrapolation for each system.

We have studied the basis set effects on the relative energies through a series of calculations with the cc-pV(T+d)Z, and cc-pV(Q+d)Z basis sets. The results are shown in Table 10. These show quite a significant basis set effect. This might be anticipated given the different environments of sulfur and the consequent need for multiple sets of polarization functions, as well as a good description of the valence space. One sees a significant decrease in the relative energies of sulfinic acid and dihydrogen sulfone on going from cc-pV(T+d)Z to cc-pV(Q+d)Z. The cc-pV(Q+d)Z relative energy is slightly above the G2 value for sulfinic acid (see Table 9), but it is somewhat below it for the sulfone (see Table 9). Extrapolation further lowers the relative energies so they are both below the G2 values. Compared with CBS-Q *relative enthalpies* (Table 9), our extrapolated result for sulfinic acid is slightly above the CBS-Q value, whereas our result for dihydrogen sulfone is below the CBS-Q value.

Thermochemistry. There have been a few prior attempts to calculate the heats of formation of one or more [H_2, S, O_2] isomers. Wang and Zhang[12] calculated ΔH_f^o in 2 ways using the G3B3 and G3//MP2 procedures. First, they calculated the enthalpy change for dissociation to atoms. Then they used experimental ΔH_f^o of atoms to obtain a ΔH_f^o for $S(OH)_2$. In this way they obtained values of −272.7 (G3B3) and −275.6 kJ mol^{-1} (G3//MP2), which are in line with Benson's estimate. However, Wang and Zhang were concerned about errors in the atomization procedure, so they also applied a procedure involving isodesmic reactions. This gave estimates in the range −290.3 to −290.8 kJ mol^{-1} (G3B3) and −285.9 to −293.0 kJ mol^{-1} (G3//MP2). Wang and Zhang's preferred value was −290 kJ mol^{-1}.

In this work we have obtained estimates of ΔH_f^o (298.15 K) for $S(OH)_2$ (C_2 conformer) from two reaction schemes using several basis sets:

SCHEME 1

The standard enthalpy change for the reaction

$$S(OH)_2\ (g) \rightarrow SO_2\ (g) + H_2\ (g)$$

was calculated. The ΔH_f^o was then calculated from

$$\Delta H_f^o = \Delta H_f^o(SO_2) + \Delta H_f^o(H_2) - \Delta H_{rxn}^o = -296.8\ \text{kJ mol}^{-1} - \Delta\ H_{rxn}^o$$

using the calculated ΔH_{rxn}^o and experimental data for SO_2 and H_2.

TABLE 11: CCSD(T) Results for ΔE and ΔH^o for the Reaction $S(OH)_2$ (g) → SO_2 (g) + H_2 (g) and ΔH_f^o of $S(OH)_2$ (g) (C_2 Conformer)[a]

basis set	ΔE	ΔH^o	ΔH_f^o
6-311++G(2d,2p)	34.1	7.4	−304.2
6-311++G(3df,3pd)	21.2	−5.5	−291.3
ANO-TZP	33.7	7.0	−303.8
cc-pV(D+d)Z	35.9	9.2	−306.0
cc-pV(T+d)Z	16.5	−10.2	−286.6
cc-pV(Q+d)Z	16.8	−9.9	−286.9
aug-cc-pV(D+d)Z	55.5	28.8	−325.6
aug-cc-pV(T+d)Z	23.0	−3.7	−293.1
aug-cc-pV(Q+d)Z	18.8	−7.9	−288.9
extrapolation[b]	17.0	−9.7	−287.1
extrapolation[c]	15.7	−11.0	−285.8

[a] ΔH^o and ΔH_f^o are for 25 °C. The units are kJ mol^{-1}. The thermal correction, i.e., the difference between ΔE and ΔH^o, is −26.7 kJ mol^{-1}, which was obtained at the CCSD(T)/6-311++G(2d,2p) level. [b] Extrapolation based on the cc-pV(T+d)Z and cc-pV(Q+d)Z data. [c] Extrapolation based on the aug-cc-pV(T+d)Z and aug-cc-pV(Q+d)Z data.

TABLE 12: CCSD(T) Results for ΔE and ΔH^o for the Reaction $S(OH)_2$ (g) → H_2S (g) + O_2 (g) and ΔH_f^o of $S(OH)_2$ (g) (C_2 Conformer)[a]

basis set	ΔE	ΔH^o	ΔH_f^o
6-311++G(2d,2p)	236.5	214.1	−234.3
6-311++G(3df,3pd)	261.9	239.5	−259.7
ANO-TZP	267.5	245.1	−265.3
cc-pV(D+d)Z	181.4	159.0	−179.2
cc-pV(T+d)Z	257.0	234.6	−254.8
cc-pV(Q+d)Z	273.4	251.0	−271.2
aug-cc-pV(D+d)Z	240.4	218.0	−238.2
aug-cc-pV(T+d)Z	270.2	247.8	−268.0
aug-cc-pV(Q+d)Z	278.7	256.3	−276.5
extrapolation[b]	285.4	263.0	−283.2
extrapolation[c]	284.9	262.5	−282.7

[a] ΔH^o and ΔH_f^o are for 25 °C. The units are kJ mol^{-1}. The thermal correction for the reaction, i.e., the difference between ΔE and ΔH^o, is −22.4 kJ mol^{-1}, was obtained at the CCSD(T)/6-311++G(2d,2p) level. [b] Extrapolation based on the cc-pV(T+d)Z and cc-pV(Q+d)Z data. [c] Extrapolation based on the aug-cc-pV(T+d)Z and aug-cc-pV(Q+d)Z data.

SCHEME 2

The standard enthalpy change for the reaction

$$S(OH)_2\ (g) \rightarrow H_2S\ (g) + O_2\ (g)$$

was calculated. The ΔH_f^o was then calculated from

$$\Delta H_f^o = \Delta H_f^o(H_2S) + \Delta H_f^o(O_2) - \Delta H_{rxn}^o = -20.15\ \mathrm{kJ\ mol^{-1}} - \Delta\, H_{rxn}^o$$

using the calculated ΔH_{rxn}^o and experimental data for H_2S and O_2.

For both reaction schemes the thermal corrections were based on the CCSD(T)/6-311++G(2d,2p) harmonic vibrational frequencies and geometries. CCSD(T) single-point calculations were performed at the CCSD(T)/6-311++G(2d,2p) geometries using the 6-311++G(3df,3pd), ANO-TZP, cc-pV(D+d)Z, cc-pV(T+d)Z, cc-pV(Q+d)Z, aug-cc-pV(D+d)Z, aug-cc-pV(T+d)Z, and aug-cc-pV(Q+d)Z basis sets. The results of calculations from Schemes 1 and 2 are shown in Tables 11 and 12. Before discussing these results, it is worth noting that ΔH_f^o (Scheme 1) − ΔH_f^o (Scheme 2) is equal to ΔH^o(Expt) − ΔH^o(Calc) for H_2S (g) + O_2 (g) → SO_2 (g) + H_2 (g). Our most complete results yield a difference of −3.1 kJ mol^{-1}, which is within "chemical accuracy". This indicates the suitability of our methodology for calculating the ΔH_f^o of $S(OH)_2$.

Tables 11 and 12 show 3 quantities. ΔE is the energy change of the reaction for stationary nuclei at 0 K. ΔH^o is the calculated standard enthalpy change of the reaction at 298.15 K, obtained from ΔE and the unscaled CCSD(T)/6-311++G(2d,2p) thermal correction (−26.7 and −22.4 kJ mol^{-1} for Schemes 1 and 2, respectively). ΔH_f^o is the calculated standard enthalpy of formation at 298.15 K, obtained as indicated above from ΔH^o and experimental data for SO_2, H_2, H_2S, and O_2. Looking first at Table 11, one can see that basis set extension usually lowers the ΔH^o, leading to less negative ΔH_f^o values. Evidently, a very large basis set is necessary to obtain well converged results. Going from 6-311++G(2d,2p) to 6-311++G(3df,3pd) increases the ΔH_f^o by 12.9 kJ mol^{-1}. The ANO-TZP results are very close to those from the 6-311++G(2d,2p) basis set. Looking at the results from the correlation-consistent basis sets, those from cc-pV(D+d)Z and aug-cc-pV(D+d)Z differ significantly from those with the larger basis sets. The difference between cc-pV(T+d)Z and cc-pV(Q+d)Z results, however, is very small (0.3 kJ mol^{-1}), whereas for the augmented sets the corresponding difference is more significant (4.2 kJ mol^{-1}) but not very large. The cc-pV(Q+d)Z and aug-cc-pV(Q+d)Z results are quite close to the extrapolated values, differing by 0.2 and 3 kJ mol^{-1}, respectively. The 6-311++G(3df,3pd) results are between the cc-pV(T+d)Z and aug-cc-pV(T+d)Z results, which is sensible given the composition of these basis sets. There is fairly close agreement between our most complete results and those of Wang and Zhang,[12] although our results favor the higher end of their suggested range (−285.9 to −293.0 kJ mol^{-1}). At the same time, it must be borne in mind that all calculated results are sensitive to the value of the thermal correction.

We now consider the results in Table 12. For complete theoretical methods, the ΔH_f^o values obtained from Schemes 1 and 2 would be identical. The ΔH_f^o values in Table 12 are somewhat higher (less negative) than those in Table 11. Also, the basis set effects in Table 12 are more pronounced. In particular, there are significant differences between the cc-pV(T+d)Z and cc-pV(Q+d)Z results (16.4 kJ mol^{-1}) and between the aug-cc-pV(T+d)Z and aug-cc-pV(Q+d)Z results (8.5 kJ mol^{-1}). Consequently, the difference between the extrapolated results and the cc-pV(Q+d)Z and aug-cc-pV(Q+d)Z results is larger than in Table 11. However, there is only a small difference (about 3 kJ mol^{-1}) between the extrapolated ΔH_f^o values in Tables 11 and 12. Given the larger basis set effects in Table 12, one might anticipate that the ΔH_f^o value in Table 11 is the more reliable. The present results and those of Wang and Zhang[12] therefore suggest that the ΔH_f^o of C_2 $S(OH)_2$ is probably between −285 and −290 kJ mol^{-1}, which is slightly above the mean of Benson's estimate,[13] but well within his range. It also appears that the decomposition of $S(OH)_2$ to SO_2 and H_2 is slightly exothermic, but entropy further favors the decomposition, of course. Decomposition to H_2S and O_2 is strongly endothermic.

Acknowledgment. This work was supported in part by the National Science Foundation (NSF300423-190200-21000 and HRD0318519). J.D.W. thanks the Army High Performance Computing Research Center for providing generous computing facilities. The content of this paper does not necessarily reflect the position or policy of the United States government, and no official endorsement should be inferred. Some of the calculations were run on a QuantumCube QS4-2800C computer from

Parallel Quantum Solutions, LLC. We thank Dr. Ajith Perera (University of Florida) for installing ACES II on the QuantumCube.

References and Notes

(1) Frenklach, M.; Lee, J. H.; White, J. N.; Gardiner, W. C. J. *Combust. Flame* **1981**, *41*, 1−16.

(2) Plummer, P. L. M.; Chen, T. S.; Law, K. Y. *Atmos. Environ.* **1984**, *18*, 2769−2774.

(3) Tyndall, G. S.; Ravishankara, A. R. *Int. J. Chem. Kinet.* **1991**, *23*, 483−527.

(4) *Kinetics and Mechanism of the Oxidation of Gaseous Sulfur Compounds*; Hynes, A. J., Wine, P. H., Eds.; Springer: New York, 2000.

(5) Schofield, K. *Combust. Flame* **2001**, *124*, 137−155.

(6) Montoya, A.; Sendt, K.; Haynes, B. S. *J. Phys. Chem. A* **2005**, *109*, 1057−1062.

(7) Fender, M. A.; Sayed, Y. M.; Prochaska, F. T. *J. Phys. Chem.* **1991**, *95*, 2811−2814.

(8) Steiger, T.; Steudel, R. *J. Mol. Struct. (THEOCHEM)* **1992**, *257*, 313−323.

(9) Laakso, D.; Marshall, P. *J. Phys. Chem.* **1992**, *96*, 2471−2474.

(10) Otto, A. H.; Steudel, R. *Eur. J. Inorg. Chem.* **2000**, 617−624.

(11) Frank, A. J.; Sadilek, M.; Feerrier, J. G.; Turecek, F. *J. Am Chem. Soc.* **1997**, *119*, 12343−12353.

(12) Wang, L.; Zhang, J. *J. Mol. Struct. (THEOCHEM)* **2002**, *581*, 129−138.

(13) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23−35.

(14) Boyd, R. J.; Gupta, A.; Langler, R. F.; Lownie, S. P.; Pincock, J. A. *Can. J. Chem.* **1980**, *58*, 331−338.

(15) Basch, H. In *The Chemistry of Sulfinic Acids, Esters, and their Derivatives*; Wiley: New York, 1990.

(16) ACES II, a program product of the Quantum Theory Project, University of Florida. Authors: Stanton, J. F.; Gauss, J.; Watts, J. D.; Nooijen, M.; Oliphant, N.; Perera, S. A.; Szalay, P. G.; Lauderdale, W. J.; Gwaltney, S. R.; beck, S.; Balková, A.; Bernholdt, D. E.; Baeck, K.-K.; Rozyczko, P.; Sekino, H.; Huber, C.; and Bartlett, R. J. Integral packages included are VMOL (J. Almlöf and P. R. Taylor); VPROPS (P. R. Taylor); ABACUS (Helgaker, T.; Aa Jensen, H. J.; Jørgensen, P.; Olsen, J.; and Taylor P. R.).

(17) Basis sets in ACES II were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory, which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06−76RLO 1830. Contact David Feller, Karen Schuchardt, or Don Jones for further information.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; et al. *Gaussian 98*, revision B.1; Gaussian, Inc.: Pittsburgh, PA.

(19) Crawford, T. D.; Sherill, C. D.; Valeev, E. F.; Fermann, J. T.; King, R. A.; Leininger, M. L.; Brown, S. T.; Janssen, C. L.; Seidl, E. T.; Kenny, J. P.; Allen, W. D. PSI 3.2, 2003.

(20) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479−483.

(21) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650−654.

(22) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639−5648.

(23) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294−301.

(24) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265−3269.

(25) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007−1023.

(26) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358−1371.

(27) Dunning,T. H., Jr.; Peterson, K. A.; Wilson, A. K. *J. Chem. Phys.* **2001**, *114*, 9244−9253.

(28) Wang, N. X.; Wilson, A. K. *J. Phys. Chem. A* **2003**, *107*, 6720−6724.

(29) Wilson, A. K.; Dunning, T. H., Jr. *J. Phys. Chem. A* **2004**, *108*, 3129−3133.

(30) Kendall, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796−6806.

(31) Widmark, P.-O.; Malmqvist, P.-A.; Roos, B. O. *Theor. Chim. Acta* **1990**, *77*, 291−306.

(32) Widmark, P.-O.; Persson, B. J.; Roos, B. O. *Theor. Chim. Acta* **1991**, *79*, 419−432.

(33) Purvis, G. D., III; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910−1918.

(34) Martin, J. M. L. *J. Chem. Phys.* **1994**, *100*, 8186−8193.

(35) Lee, T. J.; Scuseria, G. E. In *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*; Langhoff, S. R., Ed.; Kluwer Academic: Dordrecht, The Netherlands, 1994; p 47.

(36) Bartlett, R. J.; In *Modern Electronic Structure Theory, Part I*; Yarkony, D. R., Ed.; World Scientific: Singapore, 1995; pp 1047−1131.

(37) Shangguan, C.; McAllister, M. A. *J. Mol. Struct. (THEOCHEM)* **1998**, *422*, 123−132.

(38) Curtis, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293−1298.