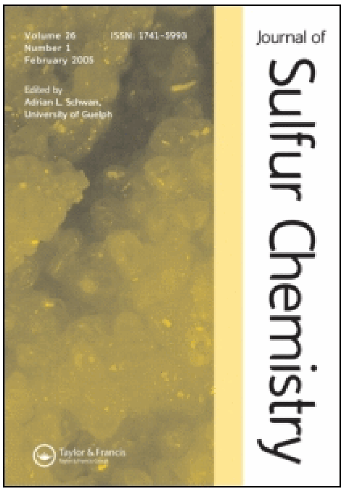

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Thermochemistry of 35 selected sulfur compounds, a comparison between experiment and theory

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Thermochemistry of 35 selected sulfur compounds, a comparison between experiment and theory

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The thermochemistry of 35 diatomic, triatomic and tetratomic, sulphur-containing molecules was investigated. For each molecule, we have estimated its enthalpy of formation at the CCSD(T)/CBS level, including corrections for, scalar relativistic, core-valence and spin-orbit effects. When experimental data was available we also included a correction for anharmonicities in Zero point energies. The molecules investigated are involved in several areas, atmospherical chemistry, astrochemsitry, nanotechnology, and biology. The present results demonstrate that from the previous landmark review of Benson, published in 1978, we had advanced only a little and much work must be done to have sulfur thermochemistry well established. It was very difficult to obtain a meaningful mean absolute deviation (MAD) because of the reduced number of accurate enthalpies of formation available. For a selected set of eight molecules the MAD = 0.4 kcal/mol. For the 27 remaining molecules we discussed the available experimental and theoretical data and suggested new values. The consistency of our propositions has been double checked employing homodesmic and isodesmic reactions. In all cases, except one that involved S_2, the results were perfectly consistent. We expect that the present work motivates new theoretical and experimental investigations of these fascinating species that contain sulfur.

Keywords: sulfur thermochemsitry; atmospherical chemistry; benchmark calculations; combustion chemistry; theoretical chemistry

1. Introduction

Sulfur has been known by the humanity since ancient times. The Egyptians used it to purify temples and it is mentioned several times in the Bible (brimstone and fire). However, it was not until the eighteenth century Lavoisier demonstrated that sulfur was an element and not a compound. Sulfur is among the most abundant elements in earth's crust, it is placed 16th, with abundance between 0.052% and 1% (*1*). It can be found near volcanoes and hot springs. The most common minerals which forms are: cinnabar, galena, iron pyrites, gypsum, barite and celestite. It also occurs in high percentage in natural gas, petroleum, and coals. It must be removed from these sources of energies because sulfur is one of the most important contaminants of the earth's atmosphere. It causes acid rain and it forms polar stratospheric clouds, which are one of the causes of the stratospheric ozone depletion (*2*).

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In the industry it has several applications, it is the component of the most important manufactured chemical in the world, sulfuric acid, and it also is needed to fabricate black gun powder, semiconductors, perform the vulcanization process of black rubber and to make fertilizers, insecticides, and fungicides (*1, 3*).

The importance of sulfur is not limited to the facts mentioned above. Sulfur is playing an important role is nanotechnology. MoS_2 was the first inorganic nanotube synthesized (*4*) in the 1990s and that opened several new avenues of research that are still investigated nowadays. The second area that we can highlight is nanotechnology in which sulfur is important, is the sulfur–gold interaction (*5, 6*); it is widely used today to create self-assembled monolayers (*5*) or to synthesize free standing nanotubes over gold substrates (*6*). To build these nanostructures single wall carbon nanotubes are functionalized with sulfur-containing molecules. Then, the strong affinity between sulfur and gold is used to attach the tube to the gold substrate. Finally, two important properties of solid-state materials have recently been demonstrated: the superconductivity of the sulfur–graphite composites (*7*) and the metallic properties of polymeric sulfur nitrides (*8*).

We can continue for several pages describing the properties, applications, and the importance of sulfur in earth and space; over 10 sulfur-containing molecules have been detected in space (*9, 10*). However, we feel that they are going to be highlighted by the several articles that are published in this special issue of the *Journal of Sulfur Chemistry*, ‘Sulfur in extreme environments’ edited by Prof. Dr. Greer and Prof. Dr. Aebisher.

To understand all the processes in which sulfur participates there is one property that is crucial, the bond energies (*11*). They determinate which compounds are formed and which not, driving all the chemical reactions together with kinetics. In the present work, we have selected 35 diatomic, triatomic and tetratomic, sulfur-containing molecules of paramount importance in atmospherical chemistry (*2*), flame chemistry (*12, 13*), industrial processes, nanotechnology (*5–8*), and biology (*14*) and estimated its enthalpy of formation employing first principles calculations. We have compared our results with the experimental data available and also with the theoretical values derived by other investigators. The present results indicate that only a few molecules have thermochemical properties well established. We expect that the present work will motivate new theoretical and experimental investigations of the thermodynamic properties of sulfur compounds, and help to perform good parameterizations of force fields, semiempirical and density functional methodologies, which are very important to investigate large systems. One important missing issue in the present article, is the thermochemistry of large organic sulfur-containing molecules such us dimethysulfide, sulfoxide, sulfine, and many others. For these species we refer the readers to the excellent reviews available (*15–18*). In future works we are planning to investigate the thermochemistry of these species employing high level ab initio methodologies. The present article is organized as follows: in Section 2 we describe the theoretical methods employed; we have performed a brief discussion about them. In the third section we show our results for, diatomic, triatomic, and tetratomic molecules and compare them with the data available in the literature. It is important to note that we have divided the 35 in the diatomic, triatomic, and tetratomic subgroups and not by the environments in which they are present because, almost all molecules are important in more than one environment. Finally, we included a conclusion section and recommended values for the molecules investigated.

2. Theoretical methods

In theoretical chemistry there are two main approaches to estimate enthalpies of formation. The first one only involves the use of pure ab initio methodologies and does not rely on empirical parameters (*19, 20*). All the information used is obtained only by theoretical calculations.

The later procedure is tremendously expensive from a computational stand point. However, it has the advantage of being 100% independent. It is not affected by external errors. By external errors we mean, the uncertainties inherent to any determination, which can be quite large. The core of the procedure is the combination of basis sets and theoretical formulations. The basis sets selected are those developed by Dunning (*21*) and coworkers in the 1990s, and the theoretical methodology is coupled cluster theory in all its flavors (*22, 23*). The second approach employs reference data obtained by other theoretical or experimental procedures to yield accurate results. The most common examples are the use of isodesmic or homodesmic reactions in conjunction with an *ab initio* (*24, 25*) or density functional method (*26–31*). Others procedures that can be included here are the model chemistries, G1, G2, G3, (*32*) CBS_APNO (*33*) methodologies of Peterson and coworkers that use well-established enthalpies of formation to adjust some parameters and yield tremendously, inexpensive and accurate results.

2.1. *Extremely accurate determinations employing the atomization reaction*

There are six factors that need to be considered when we estimate the enthalpies of formation using the atomization reaction:

1. CCSD(T)/basis bond energies.
2. Core-valence correlation effects.
3. Scalar relativistic and spin-orbit splitting.
4. Anharmonic corrections to zero point energies.
5. High-order correlation effects (quadruple, quintuple excitations, etc.).
6. Born-Oppenheimer diagonal corrections.

These contributions have already been discussed in the literature (*19, 34–36*). However, in the present work we are going to provide a brief discussion about their importance in sulfur-containing molecules.

2.1.1. *CCSD(T)/basis: (a) Method*

The theoretical chemistries have been looking for several decades at a theoretical methodology that can yield ‘chemical accuracy’, an error of 1 kcal/mol for bond energies. Unfortunately, experience has demonstrated that while it is possible to obtain an average error of 1 kcal/mol, it is not possible to obtain an error below 1 kcal/mol in all cases. It is important to note, that in some cases an even smaller average error is claimed, about 1kJ/mol (0.239 kcal/mol) (*35, 37*). The problem behind those cases in which it is not possible to obtain chemical accuracy, is almost always the same; the wave function is not dominated by a single reference and a strong multiconfigurational character is observed. In principle, the solution would be to use a multiconfigurational configuration interaction approach. However, the analysis of the results published by Dunning and coworkers (*21, 38, 39*) for coupled cluster and mutirreference configuration interaction (MRCI) methodologies, clearly demonstrates that the convergence of the binding energy in the CI expansion is too slow and it is next to impossible to obtain the same accuracy as the CCSD(T) methodology. Thus, for those cases in which the strong muticonfigurational approach is evident we need to go beyond the CCSD(T) methodology. The multirreference coupled cluster (MRCC) methodologies had advanced tremendously in the recent years. However, the evidence obtained by us suggests that it may be possible to avoid the use of MRCC methodologies if we use quadruple excitations or higher. In the case of BN, a molecule with a very strong muticonfigurational character, it has been demonstrated that the CCSDTQ methodology yields results that are very similar to those obtained by very large MRCI calculations (*40, 41*). In addition to this, our results for FOO have demonstrated (*40, 42*) that even a modest CCSDT calculation can yield results that are as good as the determined at the MRCI level (*43*). Therefore, the lowest level of theory acceptable to investigate the thermochemistry of sulfur compounds is CCSD(T) and at least the CCSDTQ methodology is necessary for molecules with strong multiconfigurational character. Another factor that may be needed to be taken into account is the CCSD(T) formulation employed. In some cases there are differences between the UHF/UCCSD(T) (*22, 23*) results and those obtained at the ROFH/UCCSD(T) level (*35, 44*). In general the differences are small, around 0.1 kcal/mol. However in kJ/mol this is 0.418 kJ/mol, thus if the desired accuracy is 1 kJ/mol, this problem must be considered. In some extreme cases, like the FOO radical, we have showed that the completely unrestricted formulation gives a total atomization energies that are 0.5 kcal/mol (2 kJ/mol) larger than those determined at the restricted-unrestricted level (*40, 42*).

2.1.2. *(b) Basis set*

This is likely to be the most problematic issue when we estimate the enthalpies of formation. The CCSD(T) contribution to the bond energies can be divided in three quantities: i) Hartee-Fock, ii) singles and doubles contributions, (SD) determined as the difference between the HF and CCSD bond energies, and iii) the perturbative triples contribution (T) determined as the CCSD-CCSD(T) difference. In general, the HF contributions can be considered to be converged if we employ the aug-cc-pV(6 + d)Z or in most cases the aug-cc-pV(5 + d)Z basis set. The (T) contribution also present a fast convergence against the size of the basis set, but to reach the complete basis set limit (CBS), extrapolation is mandatory. The difference between the (T) contribution estimated employing the cc-pV(Q + d)Z basis set and the extrapolated result is very small, as we can appreciate in Table 1. Thus, the error introduced by the extrapolation procedure is almost unimportant. However, the SD contribution presents major problems. Its convergence against basis set size is very slow and the extrapolation employing the two parameter equation, suggested by Halkier *et al.* (*45*) increases the binding energies in several kcal/mol. Thus, a large error is expected. In Table 1, we show the different SD contributions obtained for several sulfur-containing molecules with basis sets up to quintuple zeta. In addition to this, we need to consider that several extrapolation schemes have been suggested. Some of them have a strong theoretical basis, for example the two parameter equation is based on the work of Schwartz (*46*) about the

Table 1. Singles and doubles (SD) and perturbative (T) contributions determined for several sulphur-containing molecules.

		SO	SO_2	SH	SH_2	SSH_2	FSSF	SSF_2
SD	cc-pv(T + d)Z		120.98	22.8	46.80	72.13	106.98	110.72
	cc-pV(Q + d)Z		127.89	24.36	49.85	78.44	115.90	119.75
	∞(T,Q)		132.93	25.50	52.07	83.05	121.62	126.34
	aug-cc-pV(T + d)Z	57.87		23.43	48.25			
	aug-cc-pV(Q + d)Z	59.96		24.58	50.24			
	aug-cc-pV(5 + d)Z	60.96		24.91				
	∞(Q,5)	62.01		25.26				
	∞(T,Q)	61.48		25.42	51.69			
(T)	cc-pv(T + d)Z		14.66	0.93	2.03	6.10	12.74	14.04
	cc-pV(Q + d)Z		15.57	1.03	2.24	6.55	13.98	15.60
	∞(T,Q)		16.23	1.10	2.42	6.87	14.89	16.74
	aug-cc-pV(T + d)Z	7.11		1.03	2.23			
	aug-cc-pV(Q + d)Z	7.40		1.07	2.32			
	aug-cc-pV(5 + d)Z	7.55		1.09				
	∞(Q,5)	7.71		1.11	2.39			
	∞(T,Q)	7.61		1.10				

correlation energy. However, others like the exponential schemes suggested by Feller *et al.* (*47*) are based in the empirical observations of the convergence of the correlation energy against basis set size. It is important to note that in the later procedure, total energies are extrapolated, without performing a separation of the different contributions like that discussed above.

Let's consider SO, in Table 2 we included the total atomization energies obtained with different basis sets and different extrapolation schemes. On the one hand, first we separate HF and correlation contributions. The former was considered to be converged. Then, we employ the two parameter equation and the aug-cc-pV(X + d)Z X=Q,5 results, to extrapolate the correlation contribution to the CBS limit. Therefore, we obtain a total atomization energy of 125.59 kcal/mol. On the other hand, if we use the three parameter equation suggested by Peterson (*47*), and the energies obtained with the aug-cc-pV(X + d)Z X=,T,Q,5 basis sets to perform an extrapolation of total energies, *i.e.* we did not separate HF and correlation contributions. Thus, employing Peterson's procedure we obtain that TAE = 125.06 kcal/mol. We have obtained two values for TAE(SO); which value is the correct one? Unfortunately to answer the later questions we need to perform CCSD(T) calculations with sextuple basis sets and higher which are not affordable to us at present time. Thus, the selection of the extrapolation scheme is based on the experience of the investigator and to some extent in the results obtained for first row compounds for a limited set of molecules. Other authors prefer to use the average of the values estimated with the procedures above mentioned (*48*). To our knowledge, no detailed investigation has been performed for sulfur compounds. In the present work, we have decided to use the extrapolation scheme that gives the most reliable results. Test calculations were performed for all the molecules investigated to find a scheme that is accurate and cheap from a computational stand point. The best agreement with experiment is not obtained with the separated two parameter procedure of Halkier *et al.* (*45*) or the joint three parameter exponential scheme suggested by Peterson (*47, 48*), but with one that combines both. We have selected to study most of these compounds a two parameter extrapolation of the CCSD(T) bond energies employing the results obtained with the cc-pV(T + d)Z and cc-pV(Q + d)Z basis sets. The difference between a joint and a separated extrapolation – employing the two parameter equation of Halkier *et al.*– and the triple and quadruple zeta basis set is that, if we perform a separated extrapolation, the TAE are systematically too low. However, the joint extrapolation gives improved results that are closer to the experimental values. The later effect is probably because an error cancellation. The inclusion of the HF contribution in the two

Table 2. Enthalpies of formation obtained for SC, SO employing different extrapolation schemes.

Basis	SC	SO
aug-cc-pV(D + d)Z	156.74	108.65
aug-cc-pV(T + d)Z	164.75	119.53
aug-cc-pV(Q + d)Z	168.36	123.03
aug-cc-pV(5 + d)Z	169.72	124.31
∞(T,Q,5)	170.52	125.06
∞(D,T,Q)	170.56	125.04
∞(Q,5)-joint[b]	171.15	125.65
∞(T,Q)-joint[b]	170.99	125.58
∞(Q,5)-separated[a]	170.86	125.59
∞(T,Q)-separated[a]	168.36	124.76
cc-pV(T + d)Z	163.49	116.98
cc-pV(Q + d)Z	167.69	121.77
∞(T,Q)-joint[b]	170.75	125.27

[a] The HF contribution was removed after extrapolation.

[b] The HF contribution was included to perform the extrapolation to allow error cancellation.

Table 3. Estimated enthalpies of formation employing the cc-pV(X + d) X = T,Q basis sets and joint and separated extrapolations.

	∞(T,Q)-separated[a]	∞(T,Q)-joint[b]	Exp
SO_2	−68.5	−70.2	−70.94
CSO	−33.1	−33.7	−33.9
SSO	−11.6	−12.4	−13.2
SF_2	−69.69	−71.0	−70.9

[a] The HF contribution was removed after extrapolation.
[b] The HF contribution was included to perform the extrapolation to allow error cancellation.

parameter extrapolation scheme is the key step to avoid the observed underestimation of the TAE employing the separated two parameter extrapolation with the cc-pV(X + d)Z X = T, Q basis sets. In Table 3, we show the enthalpies of formation estimated for several molecules employing the joint and separated extrapolations to illustrate this situation. We have performed this test for all the molecules investigated and in almost all cases the joint extrapolation gives a better agreement, and in two both give the same value. Thus, the later results confirm our procedure.

We were able to perform one more test for the tetraatomic molecules FSSF and SSF_2. For the later molecules, very accurate enthalpies of formation were suggested by Ornellas (*50*). He used basis sets up to aug-cc-pV(5 + d)Z. For these two molecules our results are within 1 kcal/mol with those recommended by Ornellas (*50*). It is important to note that Ornellas employed the joint three parameter exponential scheme of Peterson (*47, 48*). If we use the data obtained by Ornellas and the two parameter extrapolation scheme, the agreement is better, close to 0.5 kcal/mol. Thus, this is another confirmation that the results obtained with quintuple zeta basis sets can be reproduced employing our scheme. Finally, we want to stress that the extrapolation recommended above is useful when it is not possible to perform calculations with larger basis sets like the quintuple or sextuple zeta. Indeed, all the diatomic molecules, except SBr, were investigated employing the aug-cc-pV(X + d)Z X=Q,5. basis sets. However, our results suggest that it is possible to obtain an average error below 1 kcal/mol with the extrapolation recommended.

2.1.3. *Core correlation*

Evaluated as the difference between the full and frozen core CCSD(T) calculations. It is important to note that to evaluate this effect only the next lower shell must be correlated for sulfur. The 1s electron are not correlated in the full calculations (employing the rw option in Gaussian or DROPMO in aces2). For this correction is not important to perform geometry optimizations. It can be evaluated performing single point calculations. However, if one desires to estimate very accurate geometries the contribution must be included because it contracts the bond distances as we have showed in previous works about sulfur compounds (*51, 52*). The results presented in Table 4 indicate that the cc-pwCVTZ basis set (*53*) is enough to estimate this contribution. In general, the use of the quadruple zeta basis set is only necessary when the desired accuracy is around 1 kJ/mol.

2.1.4. *Scalar relativistic and spin-orbit effects*

To evaluate this contribution we need to perform DK_CCSD(T) (*54, 55*) calculations employing the cc-pVX_DK basis sets, where the cc-pVXZ_DK basis sets (*56*) are a recontraction of the cc-pVXZ basis set for relativistic calculations. The results indicate that the cc-pVTZ_DK basis set is enough to estimate this contribution. In principle, one is tented to think that relativistic contributions are not important to estimate enthalpies of formation. However, evidence showed

Table 4. Core-valence correction for a selected set of molecules.

	cc-pwCVTZ	cc-pwCVQZ
SC	0.95	1.02
SO	0.59	0.61
SF	0.33	0.28
SAl	0.08	0.13
SSi	0.73	0.76
SP	0.75	0.82
S_2	0.71	0.75
SCl	0.46	0.41

that scalar relativistic contributions can be very important, affecting the estimated enthalpy of formation several kJ/mol. As expected, the effect is more serious if the size of the molecule is larger.

Spin-orbit splitting is the other relativistic contribution that one must consider when we work in sulfur thermochemistry. The splitting can be estimated employing several approaches, or one can use experimental information. For atoms, the splitting is necessary to estimate the enthalpies of formation, since we are using the atomization reaction. For example, in the case of atomic Bromine, the spin-orbit splitting correction is 3.51 kcal/mol per Br atom and the spin-orbit correction for atomic sulfur is 0.56 kcal/mol. The tables published by Moore (*57*) have tremendously accurate data. However, for molecules the data are scarce. The spin-orbit contribution affects the estimated enthalpies of formation tremendously.

2.1.5. *Evaluation of anharmonic corrections to zero point energies*

In general, when we estimate the IR vibrations theoretically, we obtain harmonic frequencies. In most experiments the fundamental frequencies are obtained. Thus, to compare the right quantities we must compare fundamentals with fundamentals and harmonics with harmonics. Theoretically it is possible to determine fundamentals and the use these information determine accurate ZPEs. The procedure is very time consuming because several points needs to be evaluated on the potential energy surface. Fortunately, Grev *et al.* (*58*) developed a procedure that simplifies the problem. They used harmonic and fundamentals to determined zero point energy corrections. As they have demonstrated the results are accurate enough to be used in thermochemistry now the procedure is widely used.

2.1.6. *Born-Openheimer diagonal corrections*

This contribution is expected to be very small, but they must be included to obtain and error below 1 kJ/mol. In general we can avoid these corrections (*35*).

2.1.7. *Evaluation of high-order correlation effects*

High-order excitations are very difficult to estimate because of the computational cost involved. Fortunately, it has been demonstrated that because an error cancellation between the missing triple excitations in the CCSD(T) approach and the quadruples ones, the CCSD(T) results are of nearly CCSDTQ quality (*59, 60*). A consequence of the later effect is that the enthalpies of formation estimated at the CCSDT level are worse than those determined at the CCSD(T) level (*61*). In Table 5, we include some results obtained by us at the CCSDT and CCSD(T) levels to

Table 5. Enthalpies of formation estimated at the CCSD(T) and CCSDT levels.

Molecule	Basis set	$\Delta H^{\circ}_{f,298}$ CCSD(T)	$\Delta H^{\circ}_{f,298}$ CCSDT
SH	cc-pVQZ	35.17	35.17
SB	aug-cc-pV(T + d)Z	69.44	69.45
SC	aug-cc-pV(T + d)Z	70.26	70.83
SN	aug-cc-pV(T + d)Z	69.91	70.55
SF	aug-cc-pV(T + d)Z	2.46	2.61
Sal	aug-cc-pV(T + d)Z	49.64	49.84
SSi	aug-cc-pV(T + d)Z	30.38	30.93
SS	aug-cc-pV(T + d)Z	32.24	32.67
SCl	aug-cc-pV(T + d)Z	29.43	29.61
SO_2	aug-cc-pV(T + d)Z	−57.91	−56.73
SF_2	aug-cc-pV(T + d)Z	−63.32	−62.87
SCS	aug-cc-pV(T + d)Z	38.47	39.62
SCO	aug-cc-pV(T + d)Z	−22.95	−21.92
SO_3	aug-cc-pVDZ	−12.77	−11.80
HSO	cc-pVTZ	9.10	9.37
HSS	aug-cc-pV(T + d)Z	31.83	32.02

illustrate the situation. Therefore, unless the molecule has an extremely strong multiconfigurational character the CCSD(T) methodology is preferred over the CCSDT as we have showed for sulfur compounds. The limited results available for sulfur compounds confirm that quadruple excitations are important. In the case of SO, SC, SCO, SO_2, they increase the binding energies in about 0.5 kcal/mol (*35*). However, for SH_2 the increment is more modest, around 0.1 kcal/mol (*35*).

2.2. *Determinations employing isodesmic, isogyric or homodesmic reactions*

The idea behind this procedure is to construct reactions where the bonds that are formed are similar to those broken. For example, the following reaction can be considered isodesmic:

$$\mathrm{SSO} + \mathrm{SO} \longrightarrow \mathrm{OSO} + \mathrm{SS}. \qquad (1)$$

We have one SS bond and two SO bonds on the left side and the same number and kind on the right side. The use of isodesmic reactions has two strong advantages. First, the enthalpy change can be accurately estimated with small basis sets, namely double and triple zeta, because the basis set dependence is not strong. The second important fact is that because of the similarity of the formed and broken bonds the correlation effects tend to cancel making high-order contributions almost unimportant (*62*). However, there is a big problem that prevents us from using isodesmic reactions extensively. It is not possible to always construct an isodesmic or homodesmic reaction and even if it possible, the enthalpies of formation of the participating molecules could not be known with enough accuracy to make predictions. For example, in reaction 1 the enthalpy of formation of Sulfur dioxide is the only one that is known with low-error bars, –70.939 ± 0.048 kcal/mol and that of SO is 1.2 kcal/mol, but the error bars are ±0.3 kcal/mol. Thus the enthalpy of formation of SO is between 0.9 and 1.5 kcal/mol. In the case of SS our results suggest that the experimental result may be too large by at least 0.5 kcal/mol and for SSO the suggested value is –13.22 ± 0.26 kcal/mol. Considering all these uncertainties, it is very difficult to make accurate predictions employing the isodesmic reactions because the total error can be too large. However, they are valuable tool to check the consistency of the results obtained employing the atomization reaction, as we have showed recently for HOCl, HOBr (*63*) and HSO (*26, 51*), HSO_2 (*23*). It is important to remark the importance of checking the consistency of the proposed values. Indeed, Ruscic *et al.* (*64*) have used this concept in a more advanced procedure to design a self consistent thermochemical network approach.

In an isodesmic reaction the scalar relativistic, core valence, anharmonic corrections tend to cancel, however spin-orbit effects can be important. For example, in the following homodesmic reaction the spin-orbit splitting of SBr (*65*) and SCl (*52, 66*) are different and must be considered:

$$\mathrm{SCl} + \frac{1}{2}\mathrm{BrBr} \longrightarrow \mathrm{SBr} + \frac{1}{2}\mathrm{ClCl}. \tag{2}$$

In the present work, we did not use DFT methods to estimate enthalpies of formation. However, it is important to remark that another problem that may be faced, in cases where Density Functional Theory (DFT) methods are employed. When we have molecules with different multiplicities, large error are introduced as we have showed for sulfine (*27, 28, 30*) and the following reactions:

$$\mathrm{CH_2S} + \mathrm{SO_2} \longrightarrow \mathrm{CH_2SO} + \mathrm{SO} \tag{3}$$

$$\mathrm{CH_2S} + \mathrm{SO_3} \longrightarrow \mathrm{CH_2SO} + \mathrm{SO_2}. \tag{4}$$

At the B3LYP/6-311++G(3df,2p) level, the use of reaction 3 to estimate the enthalpy of formation of sulfine gives a larger error ($\Delta H^{\circ}_{f,298}(CH_2SO) = -14.6$ kcal/mol) because on the right side we have SO, which has a triplet ground state. However, this problem can be avoided employing reaction 4 that includes sulfur trioxide. Indeed, the $\Delta H^{o}_{f,298}(CH_2SO)$ estimated employing reaction is -9.1 kcal/mol much more closer to the CCSD(T) results (*27, 28, 30*).

2.3. *Methodology employed*

The UCCSD(T) methodology as implemented in Gaussian 2003 (*67*) or ACESII (*68*) was employed, in conjunction with the cc-pV(X + d)Z and aug-cc-pV(X + d)Z X=D,T,Q,5 (*21, 38, 39*) basis sets. Basis sets were obtained from the database of PNNL (*69*). The frozen core approximation was used for the UCCSD(T) calculations. Core-valence correlation effects were estimated as the difference between the full and frozen core CCSD(T) calculations employing the cc-pwCVTZ basis sets (*53*), although in some cases calculations were performed using the cc-pwCVQZ basis set to investigate the convergence of this contribution. It is important to note that the 1s electrons of sulfur were not correlated because the cc-pwCVXZ basis sets (*53*) were not designed to include those electrons, since they are expected to lie too low in energy to make a significant contribution. As expressed above, the extrapolation selected was that with two parameters, the $E = B + C/L^3$ (*45*), modified to include HF contributions when cc-pv(X + d)Z X=T,Q basis sets were used. When the aug-cc-pV(X + d)Z X=Q,5 were used the separated extrapolation was employed. For comparative purposes, in some cases we carried out a separated extrapolation of the correlation energies from the HF energies. The later were determined with the cc-pV(5 + d)Z or aug-cc-pV(Q + d)Z basis sets. Scalar relativistic effects were estimated at the DKCCSD(T)/cc-pVQZ_DK level of theory (*54, 55*), where the cc-pVQZ_DK basis set is a recontraction of the cc-pVQZ for relativistic calculations (*56*).

The spin-orbit splitting for atoms were taken from Moore (*57*). In the case of diatomic molecules – except SBr – the HSO and SOH radicals we optimized geometries for all the basis set employed, *i.e.* aug-cc-pV(5 + d)Z. However, for the remaining molecules the energies were estimated employing the cc-pV(T + d)Z geometry. Zero point energies were estimated as one half of the sum of the theoretical harmonics and experimental fundamentals, following the recommendation of Grev *et al.* (*58*). The theoretical harmonic vibrational frequencies were determined at the CCSD(T)/cc-pV(T + d)Z level of theory and experimental fundamentals were taken from different sources to estimate anharmonic corrections to zero point energies.

3. Results and discussion

3.1. *Diatomic sulfur-containing molecules*

3.1.1. *SH*

According to Thaddeus, the mercapto radical is one of the molecules that has been detected in space (*9, 10*), its abundance has been considered in several models. As explained by Kilsh *et al.* (*9, 10*) the relatively low abundance of SH occurs because the natural ion molecule reactions leading to the precursor ions SH^+ and SH_2^+ are endothermic. To model the reactions in the interstellar medium it is essential to have thermochemical properties well established. SH is an important intermediate in the atmospheric oxidation of one of the most important sulfur emissions to the atmosphere, hydrogen disulfide, SH_2. It is believed that the oxidation of SH_2 by OH leads to the production of water and the SH radical. However, in spite of the importance of the SH radical, its enthalpy of formation has originated some debate that seems to be approaching to an end. Indeed, the theoretical and experimental estimations present small disagreements. In the case of SH we were able to perform the extrapolation using large basis sets, aug-cc-pV(X + d)Z, X = 5, Q. The estimated enthalpy of formation is 33.7 kcal/mol. The later result is only 0.1 kcal/mol larger than the obtained employing the standard procedure described in the methods section, that which involves the use of smaller basis sets, cc-pV(T + d)Z and cc-pV(Q + d)Z. There are several theoretical and experimental estimations about the enthalpy of formation of the SH radical. These have been reviewed in a recent article by Csaszar *et al.* (*70*). Among the theoretical values we can highlight three, by Csaszar *et al.* (*70*), Parthiban *et al.* (*34*), and Peebles *et al.* (*71*). All of them have employed coupled cluster theory and correlation consistent basis sets. The recommended enthalpies of formation are: 33.9, 33.6, and 34.2 kcal/mol by Csaszar *et al.* (*70*), Parthiban and Martin (*34*), and Peebles *et al.* (*71*), respectively. The agreement between the theoretical estimations is extremely satisfactory if we neglect Peebels *et al.* (*71*) value. Our estimation, that of Csaszar *et al.* (*70*), Parthiban and Martin (*34*) lie within 0.3 kcal/mol. The later results can be compared with the experimental data available. The most recent experimental investigation is that of Nicovich *et al.* (*72*) whom determined $\Delta H^\circ_{f,298}(SH) = 34.15 \pm 0.67$ kcal/mol. However, one year before, Nourbakhsh (*73*) *et al.* determined $\Delta H^\circ_{f,298}(SH) = 34.01 \pm 1.51$ kcal/mol. There are other older experimental values, for example, Traeger (*74*) and Benson (*75*), whom recommended, $\Delta H^\circ_{f,298}(SH) = 33.1 \pm 0.1$ and 33.6 ± 1 kcal/mol, respectively. Comparing the most recent experimental measurements and the best theoretical estimation (Csaszar *et al.*) value, we can appreciate that the difference is 0.27 kcal/mol if we consider Nicovich *et al.* (*72*) value and 0.1 kcal/mol if we consider Nourbakhsh *et al.* (*73*) determination. Since the correlation effects at the CCSD(T) level seems to be well converged with the sextuple zeta basis sets, and that it has been demonstrated that quadruple excitations increase binding energies, we suggest $\Delta H^\circ_{f,298}(SH) = 34.0 \pm 0.3$ kcal/mol.

3.1.2. *SC*

Carbon monosulfide is an important intermediate in the oxidation of CS_2 in the atmosphere by the O atom and it is produced in several combustion processes. The importance of SC is not limited to earth, since it has been identified in the space (*9*). Its thermochemsitry seems to be well established as it is included in the G2 set (*32*). At least three experimental values for its enthalpy of formation can be found in the literature, 66.86 ± 0.23 kcal/mol by Huber and Herzberg (*76*), 67.07 ± 0.9 kcal/mol by the JANAF tables (*77*), and 66.5 kcal/mol by Gurvich *et al.* (*78*). In a previous work (*52*), employing basis sets up to aug-cc-pV(5 + d)Z, we have determined $\Delta H^\circ_{f,298}$ (SC) $= 67.4 \pm 0.5$ kcal/mol. As we have expressed above, the standard procedure suggested, that which employs the cc-pV(X + d)Z X=T,Q basis sets yields a result that is only 0.13 kcal/mol lower.

There are other theoretical estimations of the enthalpy of formation of SC. Three of them were performed by Martin at the W1, W2 (*34*), and W4 levels (*35*), the results obtained were 67.76, 67.36, and 67.0 kcal/mol, respectively. The most important difference between the W4 and W2 determinations is the inclusion of quadruple excitations. Considering Martin's results (*35*) we have calculated the CCSD(T)-CCSDTQ difference is going to increase the SC binding energy in 0.6 kcal/mol. Thus, our CCSD(T) estimation becomes, 66.8 ± 0.5 kcal/mol, in excellent agreement with the experimental values obtained by Huber and Herzberg (*76*) and the value proposed in the JANAF tables (*77*). Taking into account the experimental and theoretical results we recommend a $\Delta H^\circ_{f,298}(SC) = 66.9 \pm 0.5$ kcal/mol, which is essentially the same as recommended by Huber and Herzberg (*76*).

3.1.3. *SN*

This radical is known to be important in combustion chemistry, atmospherical chemistry, and space chemistry (*9*). It has been detected in interstellar gas and circumstellar shells (*9*). The enthalpy of formation of the SN radical has been estimated by us (*52*) and by Peebles and Marshal (*79*) employing CCSD(T) methodologies and basis sets up to aug-cc-pV(5 + d)Z as 66.7 and 66.4 kcal/mol, respectively. The later result is in good agreement with the recent result value by Lodders (*80*), $\Delta H^\circ_{f,298}(SN) = 67.7 \pm 5.7$ kcal/mol, who performed a reanalysis of the values listed in the JANAF tables and obtained by Gurvich *et al.* (*78*). In the later work, Lodders (*80*) described several mistakes that were present in the JANAF (*77*) tables and reanalyzed the recommendations of Gurvich *et al.* (*78*). Considering the large uncertainties in the experimental determinations, we propose that $\Delta H^\circ_{f,298}(SN) = 66.7 \pm 0.5$ kcal/mol.

3.1.4. *SO*

As most of the diatomic analyzed previously sulfur monoxide participates in several combustion and atmospheric process. The enthalpy of formation of SO seems to be well established, although it has a rather large uncertainty. The value recommended by most thermochemical tables is $\Delta H^\circ_{f,298}(SO) = 1.2 \pm 0.3$ kcal/mol. In our previous work (*52*) about first and second row SX, we obtained $\Delta H^\circ_{f,298}(SO) = 1.6 \pm 0.5$ kcal/mol, nearly the same as obtained in the present work with a different extrapolation scheme, $\Delta H^\circ_{f,298}(SO) = 1.4 \pm 0.5$ kcal/mol. The results can be improved if we include quadruple excitations. Indeed, employing the CCSDTQ results of Martin (*35*) we obtain that the CCSD(T)-CCSDTQ correction increases the binding energy in 0.4 kcal/mol. The later correction improves the agreement with experiment for the estimation made by us. Thus the recommended value is the same as suggested by the JANAF tables, 1.2 ± 0.3 kcal/mol (*77*).

3.1.5. *SF*

It is the simplest sulfur fluoride, thus is it extremely important to determine its bond energy accurately to perform parameterizations that allow a proper treatment of the SF bond. Sulfur fluorides are very important molecules in industry, combustion chemistry, and atmospherical chemistry. For example, SF_6 is used as the source of F atoms in lasers and semiconductor industry, since SF_6 presents excellent insulating properties (*3*). The thermochemsitry of sulfur fluoride has presented some problems. The value recommended by the JANAF tables is 3.1 ± 1.5 kcal/mol (*77*). However, the theoretical estimations available suggest that the SF radical is more stable.

Bauschlicher and Ricca (*81*) determined $\Delta H^\circ_{f,298}(SF) = 0.71$ kcal/mol, whereas Irikura, obtained a slightly larger value 1.7 kcal/mol (*82*). Our estimation, employing basis sets up to aug-cc-pV(5 + d)Z is $\Delta H^\circ_{f,298}(SF) = 0.83 \pm 0.5$ kcal/mol (*52*), in good agreement with the results suggested by Bauschlicher and Ricca (*81*). It is important to note that our estimation and that of the later authors are not dependent on other values thus they are expected to be more accurate.

3.1.6. *SB*

This is the last first row SX investigated, our proposed enthalpy of formation is the same as our previous work (*52*) 67.6 ± 0.5 kcal/mol. About 10 kcal/mol larger than the JANAF (*77*) value 58 kcal/mol. Our recommendation are supported by the result obtained by Chin *et al.* (*83*) 67.6 kcal/mol and by the recent MRCI calculations of Yang and Boggs (*84*), whom obtained $D_e = 5.82$ eV at the ic-MRCISD+Q level.

3.1.7. *SAl*

For aluminum sulfide we propose $\Delta H^\circ_{f,298}(SAl) = 47.4 \pm 0.5$ kcal/mol, obtained employing basis sets up to aug-cc-pV(5 + d)Z (*52*). It is important to note that performing the extrapolation with the cc-pV(X + d)Z basis sets, the estimated enthalpy of formation changes in only 0.2 kcal/mol, showing one more time the robustness of this procedure. As observed for SB, the experimental result is in marked disagreement The JANAF (*77*) value is 57.0, almost 10 kcal/mol larger. Thus at present time, to our knowledge the most accurate estimation is $\Delta H^\circ_{f,298}(SAl) = 47.4 \pm 0.5$ kcal/mol.

3.1.8. *SS*

Disulfur is another important molecule in atmospherical chemistry and combustion processes. Its enthalpy of formation is very important because it is strongly related to that of sulfur. The recommended experimental value is $\Delta H^\circ_{f,298}(SS) = 30.7 \pm 0.1$ kcal/mol (*13*). However, our estimation suggests that it must be slightly lower. Our result is $\Delta H^\circ_{f,298}(SS) = 29.4 \pm 0.5$ kcal/mol. In a recent work, Grant *et al.* (*48*) performed the same investigation as our previous work for SS (*52*) and obtained a value that is essentially the same, $\Delta H^\circ_{f,298}(SS) = 29.5$ kcal/mol. However, the later authors did not suggest that there could be an error in the experimental determination, because they compared their value at 0 K 29.8 kcal/mol with the experimental enthalpy of formation at 0 K 30.66 ± 0.07 kcal/mol. No comparison was made at 298 K. In another work, Peterson *et al.* (*85*) determined $\Delta H^\circ_{f,0}(SS) = 29.9$ kcal/mol employing CCSD(T) methodologies and basis sets up to aug-cc-pV(6 + d)Z, in agreement with Grant *et al.* (*48*) and Denis (*52*).

Since the expected sources of error in the theoretical calculations indicated that the correct value might be lower than our proposed values we are convinced that the experimental value must be revised. For example, the inclusion of high-order excitations increases binding energies augmenting the differences between experiment and theory; and an error of 1.3 kcal/mol in the binding energy due to basis set incompleteness seems to be unlikely, since our results was obtained employing a very large basis set, the aug-cc-pV(5 + d)Z. Indeed, the singles and doubles contribution, which is the most problematic as we have explained previously, is increased 1.26 kcal/mol when it is estimated employing the aug-cc-pV(5 + d)Z basis set instead of the aug-cc-pV(Q + d)Z basis set. Finally, we want to note that the SD contribution at the CBS limit is 44.35 kcal/mol, 1.32 kcal/mol larger than the obtained with the quintuple zeta basis set. Thus, we must admit that some error to the extrapolation scheme selection, but it is next to impossible that this error can solve the discrepancy between experiment and theory, because to have an agreement the SD contribution must have converged with the aug-cc-pV(5 + d)Z basis set, and that is not true. As we will show below the problem in the enthalpy of formation of SS becomes evident when we estimate the enthalpy of formation of SSO employing isodesmic reactions.

Finally, we decided to perform a final test employing the homodesmic reaction:

$$2\mathrm{SO} \longrightarrow \mathrm{SS} + \mathrm{OO}. \tag{5}$$

The enthalpy change at the CCSD(T)/cc-pV(T + d)Z and CCSD(T)/cc-pV(Q + d)Z levels are 25.22 and 26.69 kcal/mol respectively, which yields an enthalpy change at the CCSD(T)/CBS limit of 27.76 kcal/mol. Employing the experimental enthalpy of formation of SO, 1.2 ± 0.3 kcal/mol (*77*) and including scalar relativistic, and core-valence effects we can infer that the enthalpy of formation of SS is equal to 30.10 ± 0.6 kcal/mol, almost in the middle of our estimation and the experimental result, more precisely, 0.61 kcal/mol lower than the experimental result and 0.70 kcal/mol larger than our estimation. We expect that the enthalpy change calculated at the CCSD(T) level to be very accurate for three reasons: (1) due to the homodesmic character of Equation 5, high-order correlation effects are expected to be cancelled, (2) the basis set dependence in indeed small, and (3) all the effects that needs to be included when we estimate the enthalpies of formation employing the atomization reaction tend to cancel. Indeed, if we consider the scalar relativistic and core-valence effects of S_2 and SO listed in Table 6 and those calculate for O_2, 0.34 core-valence and 0.15 kcal/mol for the scalar relativistic effects we get that the net correction is extremely small -0.06 kcal/mol. Thus, our results seem to indicate that at least, the correct value for SS should be about 0.6 kcal/mol lower.

3.1.9. *SSi*

The interest in SSi is two-fold. First, SSi is one of the prebiotic molecules that has been detected in space (*9*). Second, because of the importance of silicon in semiconductor industry, the properties of its compounds with other elements of the p block have been studied extensively. In particular, we can mention the spectroscopic investigation of SSi made by Chattopadhyaya *et al.* (*86*). However, the thermodynamic properties of SSi are not well established. In our previous work (*52*), we have obtained $\Delta H^{\circ}_{f,298}(\mathrm{SSi}) = 27.9 \pm 0.5$ kcal/mol, within the error bars of the values recommended in the JANAF tables, 25.3 ± 3 kcal/mol. Since an error of 2.6 kcal/mol seems to be unlikely at the CCSD(T) level of theory, and because of its strong monofigurational character, we recommend that the experimental measurement should be performed again.

3.1.10. *SP*

The enthalpy of formation of SP has been reanalyzed quite recently by Lodders (*80*). In the later work she proposed $\Delta H^{\circ}_{f,298}(\mathrm{SP}) = 36.41 \pm 2.39$ kcal/mol. This value is 1.73 kcal/mol lower than our estimation $\Delta H^{\circ}_{f,298}(\mathrm{SP}) = 38.14 \pm 0.5$ kcal/mol (*52*). We expect that part of the differences between experiment and theory can be solved if CCSDTQ calculations are performed. It is important to note that in the case of SC and SO their contribution was very important, 0.4 and 0.6 kcal/mol, respectively. In the case of SP, as well as SN we expect the later contribution to be important because the wavefuntions present some instabilities that have been discussed in our previous work (*52*). For example, in the case of SP the inclusion of complete triple excitations decreased the SP bond distance in 0.0037 Å.

3.1.11. *SCl*

This is the last second row diatomic investigated. The value proposed by us (*58*) was obtained employing the aug-cc-pV(X + d)Z X = Q,5 basis sets, and it is $\Delta H^\circ_{f,298}(SCl) = 27.13 \pm 0.5$ kcal/mol, about 10 kcal/mol lower than the value recommended by the JANAF (*77*) tables, 37.37 ± 4 kcal/mol. As expressed above, such difference between the CCSD(T) results and the experimental value is unacceptable. Thus, we recommend that the experimental measurement should be carried out again.

3.1.12. *SBr*

This is the last sulfur diatomic investigated in the present work. Accurate values are available. On one hand Ornellas (*65*) have estimated its enthalpy of formation as 36.07 kcal/mol at the CCSD(T)/CBS limit employing very large basis sets. The later value is in good agreement with the inferred experimental value, 36.15 kcal/mol, which was obtained by Ornellas (*65*), employing the experimental enthalpies of formation of: BrO, Br, and oxygen. On the other hand, our estimation is 35.1 kcal/mol in good agreement with the value obtained by Ornellas (*65*).

To check whether or not the suggested enthalpies of formation of SCl and SBr are consistent with each other we have built the following homodesmic reaction:

$$\frac{1}{2}\mathrm{BrBr} + \mathrm{SCl} \longrightarrow \mathrm{SBr} + \frac{1}{2}\mathrm{ClCl}. \tag{6}$$

The homodesmic character of the reaction is reflected by the small basis set dependence that is observed. Indeed, the enthalpy change at the CCSD(T)/cc-pV(T + d)Z and cc-pV(Q + d)Z levels are 3.74 and 3.85 kcal/mol, respectively, which yield an enthalpy change at the CCSD(T)/CBS limit of 3.94 kcal/mol. The scalar relativistic and core-valence effects increase the endothermicity of the later reaction in only 0.1, as expected because of the homodesmic character of the reaction. However, there is one effect that must be addressed before proceeding to check the values for SBr and SCl. The later radicals present spin-orbit splitting (*52, 65, 66*), and that of bromine sulfide is much larger than for the chlorine sulfide. Considering the scalar relativistic, spin-orbit, and core-valence correction the enthalpy change becomes, 3.68 kcal/mol. Employing the enthalpy of formation of Br_2, 7.388 kcal/mol we obtain that, $\Delta H^\circ_{f,298}(SBr) = 7.64 + \Delta H^\circ_{f,298}(SCl)$. For SCl we have explained above that the experimental enthalpy of formation presents a large error, thus we employed our determination 27.13 kcal/mol to get $\Delta H^\circ_{f,298}(SBr) = 34.77$ kcal/mol, in good agreement with our estimation and slightly lower than the value recommended by Ornellas (*65*). With the evidence given above we propose a value that is the average of our estimation and that of Ornellas, $\Delta H^\circ_{f,298}(SBr) = 35.59 \pm 1$ kcal/mol.

3.2. ***Triatomic sulfur-containing molecules***

3.2.1. *SH_2*

Dihydrogen sulfide is one of the most important natural and anthropogenic emissions of sulfur to the atmosphere and it is probably the precursor of SH in the space (*9*). Volcanoes contribute in a large amount to the natural emissions. SH_2 is oxidized in the atmosphere to sulfuric acid which leads to the formation of polar stratospheric clouds, which are believed to be one of the reservoirs of bromine-containing molecules. SH_2 is a close shell molecule and its wave function is dominated by a single reference. However, the determination of its enthalpy of formation is somewhat problematic, much more than what would be expected. Our best estimation, employing basis sets up to cc-pV(Q + d)Z is $\Delta H^\circ_{f,298}(SH_2) = -5.8$ kcal/mol and if we use basis sets up to aug-cc-pV(Q + d)Z the result becomes –6.0 kcal/mol. The later values are about, 1 kcal/mol lower than the experimental recommended values −4.9 kcal/mol. At first sight one can be tempted to think that the problem behind this overestimation of the binding energy is that we did not use quintuple zeta or sextuple zeta basis sets. For that reason we searched the literature for other estimations. Parthiban and Martin (*34*) determined $\Delta H^\circ_{f,298}(SH_2) = -5.3$ kcal/mol at the W2 level. Some years later, Martin (*35*) revisited his estimation employing a more advanced methodology, the W4 theory which includes up to quadruple excitations in the coupled cluster treatment and obtained $\Delta H^\circ_{f,298}(SH_2) = -5.35$ kcal/mol. Another investigation about the total atomization energy of SH_2 was performed by Peebles and Marshall (*71*). They obtained that a TAE that was 1 kJ/mol (0.24 kcal/mol) larger than the values recommended by Gurvich (*78*) and the JANAF tables (*77*). The determinations of Peebles and Marshall (*71*) employed basis sets up to aug-cc-pV6Z, which are much extended. However, caution must be taken because it has been demonstrated that tight d functions are extremely important to investigate sulfur compounds. Thus, in our opinion, the most confident determination is that of Martin at the W4 level (*35*). The question that arises is why for a simple molecule like SH_2 we cannot obtain a better accuracy than 0.45 kcal/mol (1.88 kJ/mol) even at the CCSDTQ level. Maybe to answer that question we need to use basis sets up to aug-cc-pV(7 + d)Z, without, the later results, or at least the obtained at the CCSD(T)/aug-cc-pV(6 + d) level it is not possible to challenge the very accurate experimental value, which has an uncertainty of ±0.12 kcal/mol.

3.2.2. *SO_2*

Sulfur dioxide is another step in the oxidation of dihydrogen sulfide in the atmosphere and as well as SH_2 it is one of the prebiotic molecules observed in the space. Its enthalpy of formation was determined very early and it has a small uncertainty. The estimation of $\Delta H^\circ_{f,298}(SO_2)$ was extremely important to understand the problematic basis set dependence of sulfur-containing molecules. Early works by Bauschlicher (*87*) and Martin (*88*) showed the importance of including tight d functions. Martin (*87*) recommended the inclusion of 2d and 1f function to the standard correlation consistent basis sets. However, in a recent article, Dunning and coworkers (*38*) revisited the correlation consistent basis sets and introduced the cc-pV(X + d)Z basis sets. This problem is not only limited to *ab initio* methodologies. We have showed (*89*) that even the density functional methods require more than sextuple zeta basis sets to obtain a converged TAE for SO_2. Employing the procedure describe above joint-∞(T,Q) we have determined $\Delta H^\circ_{f,298}(SO_2) = -70.2$ kcal/mol in reasonable agreement with the experimental value, –70.95 kcal/mol. The error in our estimation can be considered small if we take into account two factors: (1) we used only basis sets up to cc-pV(Q + d)Z and (2) we did not include quadruple and quintuple excitations in the coupled treatment, which are expected to increase the binding energy in 0.42 kcal/mol (*35*).

3.2.3. *SSO*

Disulfur monoxide is included in the set of molecules which are important in atmospherical chemistry and air pollution (*13*). In 1988, Lias *et al.* suggested that $\Delta H^\circ_{f,298}(SSO) = -12.0 \pm 0.2$ kcal/mol (*90*). However, in a recent article on the same journal Lodders (*80*) reanalyzed two values, the proposed in the JANAF tables (*71*), $\Delta H^\circ_{f,298}(SSO) = -13.5 \pm 8$ kcal/mol and that by Gurvich *et al.* (*78*) $\Delta H^\circ_{f,298}(SSO) = -13.38 \pm 0.33$ kcal/mol. Lodders (*80*) suggested that $\Delta H^\circ_{f,298}(SSO) = -13.22 \pm 0.26$ kcal/mol. Our best estimation is $\Delta H^\circ_{f,298}(SSO) = -12.4$ kcal/mol, employing the same basis sets as for SO_2. In this case we are underestimating the $\Delta H^\circ_{f,298}(SSO)$ by 0.8–1 kcal/mol. To shed light into this discrepancy we have built the following isodesmic reaction:

$$\mathrm{SSO} + \mathrm{SO} \longrightarrow \mathrm{OSO} + \mathrm{SS}. \tag{7}$$

The enthalpy change at the CCSD(T)/cc-pV(T + d)Z and CCSD(T)/cc-pV(Q + d)Z levels of theory are –29.69 and –29.5 kcal/mol, respectively, which give an enthalpy change at the CBS limit of –29.36 kcal/mol. It is very nice to appreciate the small basis set dependence of the later reaction, confirming its isodesmic character. The next step is to check importance of core-valence and correlation effects on the enthalpy change. As expected, because of the isodesmic character of the reaction, the later effects increase the exothermicity to –29.54 kcal/mol, only 0.18 kcal/mol of difference. The main problem to use the isodesmic reaction is that in the previous sections we have concluded that the enthalpy of formation of S_2 is somewhat problematic. Thus, employing the enthalpies of formation of SO_2 and SO we obtain that:

$$\Delta H^{\circ}_{f,298}(\mathrm{SSO}) = -41.41 + \Delta H^{\circ}_{f,298}(\mathrm{S_2}).$$

On the one hand, if we employ the enthalpy of formation suggested in the JANAF tables (*77*), 30.71 kcal/mol we get that $\Delta H^{\circ}_{f,298}(\mathrm{SSO}) = -10.7$ kcal/mol, almost 3 kcal/mol lower than the experimental value suggested in the JANAF tables (*77*). On the other hand, if we use our value, $\Delta H^{\circ}_{f,298}(\mathrm{S_2}) = 29.4$ kcal/mol, we obtain $\Delta H^{\circ}_{f,298}(\mathrm{SSO}) = -12.0$ kcal/mol, in better agreement with all the experimental values and with our parameter-free estimation employing the isodesmic reaction. Since it seems to be very unlikely an error of 2–3 kcal/mol in the enthalpy change of reaction 1 at the CCSD(T) level, the later results led us to confirm our initial idea of a problem in the enthalpy of formation of S_2 and also in that of SSO.

3.2.4. *SCS*

Carbon disulfide is an important molecule in atmospherical and combustion chemistry. It is oxidized by atomic oxygen to produce SC and SO, or SCO and S or CO, and S_2. Employing basis sets up to cc-pV(Q+d)Z we have determined $\Delta H^{\circ}_{f,298}(\mathrm{SCS}) = 27.7$ kcal/mol, in good agreement with the values recommended in the JANAF tables 27.949 kcal/mol (*77*) and by Gurvich, 27.9 ± 0.24 kcal/mol (*78*). The enthalpy of formation of SCS has also been determined by Parthiban and Martin at the W2 level as 27.2 kcal/mol (*34*) in reasonable agreement with the experimental determination. The small difference between our estimation and that of Martin probably relies on the different basis set employed. Further theoretical work would be desirable to solve the discrepancy between the results of Martin (*34*) and experiment. The inclusion of quadruple excitations is going to lower the $\Delta H^{\circ}_{f,298}(\mathrm{SCS})$, thus the problem may be related with basis set size. It is important to note that for a similar molecule, SCO, the quadruple and quintuple excitations increased the binding energy in 0.29 kcal/mol (*29*). Thus, a similar contribution may be expected for SCS, augmenting the difference with the JANAF value (*71*).

3.2.5. *SCO*

SCO has been detected in the interstellar medium and it can be produced by the oxidation of SCS by atomic O (*91*). We have determined $\Delta H^{\circ}_{f,298}(\mathrm{SCO}) = -33.7$ kcal/mol in good agreement with the value suggested in the JANAF (*77*) tables –34.0, although it is closer to the value compiled by Gurvich –33.9 ± 0.5 kcal/mol (*78*). Parthiban and Martin (*34*) determined $\Delta H^{\circ}_{f,298}(\mathrm{SCO})$ at the W1 and W2 levels as –34.0 and –34.1 kcal/mol, in excellent agreement with our estimation. Some years later Martin reinvestigated the $\Delta H^{\circ}_{f,298}(\mathrm{SCO})$ at the W4 level (*35*) and obtained a total atomization energy that is only 0.12 kcal/mol larger than the value compiled in the Active Thermochemical Tables Benchmark (*13*), which is Gurvich's value (*78*). Considering our estimation and that of Martin (*29*) we recommend a value that is closer to Gurvich's (*78*) determination and not that of the JANAF tables (*77*), $\Delta H^{\circ}_{f,298}(SCO) - 33.9 \pm 0.5$ kcal/mol.

To check the consistency of values proposed we have built the following homodesmic reaction:

$$SCS + SO \longrightarrow SCO + SS. \tag{8}$$

The enthalpy change at the CCSD(T)/cc-pV(T + d)Z and CCSD(T)/cc-pV(Q + d)Z levels of theory are –33.60 and –33.65 kcal/mol, respectively, which gives an enthalpy change at the CBS limit of –33.69 kcal/mol. As expected for a homodesmic reaction, the core-valence and scalar relativistic effects change the enthalpy change in only 0.08 kcal/mol, thus the enthalpy of reaction at 298 K is –33.77 kcal/mol. The problem with the later reaction is that many values present discrepancies. The enthalpy of formation of SO is 1.2 ± 0.3 kcal/mol, for SCO we adopt the value suggested by Gurvich (*77*), which has been confirmed by us above, $\Delta H^{\circ}_{f,298}(SCO) - 33.9 \pm 0.5$ kcal/mol. Employing our value for SS, $\Delta H^{\circ}_{f,298}(S_2) = 29.4$ kcal/mol we obtain $\Delta H^{\circ}_{f,298}(SCS) = 28.07$ kcal/mol in excellent agreement with the experimental value 27.9 kcal/mol. However, if we use the JANAF value, we get $\Delta H^{\circ}_{f,298}(SCS) = 29.37$ kcal/mol, in worse agreement with the value suggested by Gurvich (*77*). Therefore, this is the second homodesmic reaction that suggests a lower enthalpy of formation to achieve consistency.

3.2.6. *HSO*

This radical is one of the most controversial species that are included in the present work. HSO is an important intermediate in the oxidation of SH_2 in the atmosphere. Its enthalpy of formation is crucial to determine whether or not HSO and SH can be involved in a catalytic cycle that destroys ozone (check refs. *26*, *51*). For a detailed review of previous determinations we refer the readers to references (*26*) and (*51*). The most recent experimental determinations of its $\Delta H^{\circ}_{f,298}$ are based on the investigations of the reaction between SH_2 and atomic O. In 1985 and 1993, Davidson *et al.* (*92*), and Balucani *et al.* (*93*) determined that $\Delta H^{\circ}_{f,298}(HSO) = -1.4 \pm 2$ and -1.6 ± 0.7 kcal/mol, respectively. However, in 2004 Balucani *et al.* (*94*) revisited the experiment and obtained a lower limit for the $\Delta H^{\circ}_{f,298}$(HSO) of –3.7 kcal/mol. The later results are larger than our recent CCSD(T) estimation that employed basis sets up to aug-cc-pV(5 + d)Z, $\Delta H^{\circ}_{f,298}(HSO) = -5.2 \pm 0.5$ kcal/mol. The later theoretical estimation is supported by several theoretical investigators. Among them, we can highlight that of Xantheas and Dunning (*95*) that employed icMRCI+Q/CBS calculations to get $\Delta H^{\circ}_{f,298}(HSO) = -6.1 \pm 1.3$ kcal/mol, or that by Wilson and Hirst (*96*) at the G2 level in conjunction with isodesmic reactions $\Delta H^{\circ}_{f,298}(HSO) = -4.9 \pm 1.3$ kcal/mol. The nice agreement between the MRCI, CCSD(T),G2-isodesmic and DFT-isodesmic determination strongly suggests that the enthalpy of formation of HSO is close to our determination, $\Delta H^{\circ}_{f,298}(HSO) = -5.2 \pm 0.5$ kcal/mol.

3.2.7. *SOH*

This isomer of HSO is another key intermediate in atmospherical and combustion chemistry, its enthalpy of formation has presented fewer problems. Bierbaum (*97*) determined its enthalpy of formation in a combined experimental-theoretical work as $\Delta H^{\circ}_{f,298}(SOH) = -0.5 \pm 2.0$ kcal/mol, in excellent agreement with our theoretical estimation $\Delta H^{\circ}_{f,298}(SOH) = -1.6 \pm 0.5$ kcal/mol (*51*). The similarity between the $\Delta H^{\circ}_{f,298}$(SOH) and the results derived for $\Delta H^{\circ}_{f,298}$(HSO) in the experimental investigations of the reaction between SH_2 and O have tempted us to suggest that maybe SOH is formed in these experiments and not HSO. At present time we are studying the experimental procedure to give a theoretical basis to our proposition.

3.2.8. *HSS*

This radical presents an electronic structure similar to HSO because of the similarities between oxygen and sulfur. Several properties have been determined for its ground and excited states in experimental and theoretical investigations. Fortunately, there is a good agreement among them. In a previous work (*98*), employing basis sets up to cc-pV(Q + d)Z we have determined $\Delta H^\circ_{f,298}(HSS) = 25.02 \pm 1$ kcal/mol, in superb agreement with the experimental determination of Decker *et al.* 25 ± 2.5 kcal/mol (*99*). However, the later values are larger than the suggested by Benson 22.1 ± 1 kcal/mol (*11*). The excellent agreement between our estimations and that of Decker *et al.* (*99*) suggest that $\Delta H^\circ_{f,298}(HSS) = 25.02 \pm 1$ kcal/mol.

Considering the nice agreement obtained for HSS we can use it to construct a homodesmic reaction that includes HSO and checks the consistency of our values.

$$SS + HSO \longrightarrow HSS + SO. \tag{9}$$

The enthalpy change at the CCSD(T)/cc-pwCVTZ and CCSD(T)/cc-pwCVQZ levels of theory are 0.31 and 1.18 kcal/mol, respectively, which gives an enthalpy change at the CBS limit of 1.81 kcal/mol. As expected for a homodesmic reaction, the core-valence and scalar relativistic effects change the enthalpy change in only 0.06 kcal/mol, thus the enthalpy of reaction at 298 K is 1.87 kcal/mol. With the aid of the enthalpies of formation of SO and HSS, 1.2 and 25.0 kcal/mol, respectively we obtain that $\Delta H^\circ_{f,298}(HSO) = 24.33 - \Delta H^\circ_{f,298}(S_2)$. As observed for the other homodesmic reactions discussed above, the $\Delta H^\circ_{f,298}(S_2)$ is somewhat problematic. On the one hand, if we use our estimation, 29.4 kcal/mol we obtain $\Delta H^\circ_{f,298}(HSO) = -5.07$ kcal/mol, in excellent agreement with our estimation for HSO employing the atomization reaction, −5.2 kcal/mol. On the other hand, the JANAF (*71*) value of $\Delta H^\circ_{f,298}(S_2)$ gives $\Delta H^\circ_{f,298}(HSO) = -6.38$ kcal/mol, although the later result is more than 1 kcal/mol far from the $\Delta H^\circ_{f,298}(HSO)$ estimated with the atomization reaction, it is much more negative than the results obtained in the experimental investigations of the reaction between SH_2 and O. Therefore, this new evidence confirms our initial idea of a more negative enthalpy of formation for the HSO radical.

3.2.9. *HSN*

Several properties of HSN and substituted derivatives were investigated by us in a recent article (*100*). No experimental determination is available for its enthalpy of formation. In the present work we have revisited the proposed enthalpy of formation because in the previous work we did not include scalar relativistic effect. Employing the results up to the aug-cc-pV(Q + d)Z level we obtained $\Delta H^\circ_{f,298}(HSN) = 75.0 \pm 0.5$ kcal/mol, only 0.4 kcal/mol lower than our previous determination.

3.2.10. *HNS*

The thionitroso isomer (HNS) of the thiazyl derivative (HSN) was also investigated our previous work (*100*). We have found that the former is more stable. As we did for HSN, if we include scalar relativistic effects and use the results obtained with basis sets up to aug-cc-pV(Q + d)Z, we obtain $\Delta H^\circ_{f,298}(HNS) = 55.0 \pm 0.5$ kcal/mol, only 0.3 kcal/mol lower than the previous estimation.

3.2.11. *ClNS*

The chlorine analog of HNS is expected to be less stable than the thiazyl isomer NSCl. Employing basis sets up to cc-pV(Q + d)Z, we have determined that $\Delta H^\circ_{f,298}(ClNS) = 64.9 \pm 1$ kcal/mol. The later result is more accurate and in reasonable agreement with our previous G3 estimation, 63.2 kcal/mol (*100*). However, it is larger than the CBS-QB3 result, 61.7 kcal/mol.

3.2.12. *NSCl*

The thiazyl chloride has been recently investigated by IR spectroscopy by Robertson *et al.* (*101*). Our previous G3 estimation (*100*) suggested, $\Delta H^\circ_{f,298}(HNS) = 42.3$ kcal/mol. In the present work, we have improved the result employing CCSD(T) methodologies and basis sets up to cc-pV(Q + d)Z. The improved estimation is $\Delta H^\circ_{f,298}(NSCl) = 41.1 \pm 1$ kcal/mol.

3.2.13. *NSO*

This is another molecule that participates in several atmospherical and combustion processes. In this case, we have employed basis sets up to aug-cc-pV(Q + d)Z and the corrections listed in Table 6. The proposed value is $\Delta H^\circ_{f,298}(NSO) = 41.9 \pm 1$ kcal/mol.

3.2.14. *SF₂*

Sulfur difluoride is an important molecule in semiconductor industry. It is produced in the DC plasma etching of silicon by sulfur hexafluoride. The JANAF tables recommend $\Delta H^\circ_{f,298}(SF_2) = -70.9$ kcal/mol (*77*). According to the active thermochemical tables, the uncertainty is ±4 kcal/mol (*13*). Our best estimation is $\Delta H^\circ_{f,298}(SF_2) = -71.1 \pm 1$ kcal/mol, in excellent agreement with the experimental value. It is important to note that it was obtained employing basis sets up to cc-pV(Q + d)Z.

3.2.15. *SCl₂*

Sulfur chloride is an important molecule in industry, it is a powerful chlorinating agent and is used in the cold vulcanization of rubber. It is very corrosive and dangerous to the environment (*1*). It has also been detected in the photolysis of ClSSCl (*102*). We have estimated $\Delta H^\circ_{f,298}(SCl_2) = -5.4$ kcal/mol, 1.2 kcal/mol more negative than the value included in the JANAF tables (*77*), −4.199 kcal/mol, the uncertainty quoted in the active thermochemical tables is ±0.79 (*13*). Thus our estimation is outside the error bars. However, it is closer to the value recommended by Benson −4.7 kcal/mol.

3.2.16. *SBr₂*

The last triatomic investigated in this work is sulfur dibromide. Benson (*11*) suggests $\Delta H^\circ_{f,298}(SBr_2) = 5 \pm 4$ kcal/mol. The later value was estimated using group additivity methods. Employing basis sets up to cc-pV(Q + d)Z we have determined $\Delta H^\circ_{f,298}(SBr_2) = 12.6$ kcal/mol, much larger than Benson's recommendation (*11*). As we have made above for SCl and SBr, we can check the consistency of our results employing the following homodesmic reaction:

$$Br_2 + SCl_2 \longrightarrow Cl_2 + SBr_2. \tag{10}$$

Table 6. Estimated enthalpies of formation and the corrections employed, Core-valence, Scalar relativistic, Spin-orbit and ZPE anharmonicities.

	$\Delta H^{\circ}_{f,298}$ CCSD(T)/CBS	Core correction	Scalar relativistic	Anharmoic Spin-orbit	Zpe	High order	Best
SH^a	33.79	−0.23	0.18	0.01	−0.01		33.7
SB^a	68.03	−1.27	0.26	0.59	−0.01		67.6
SC^a	67.67	−1.11	0.15	0.64	−0.01		67.4
SN^a	67.0	−0.87	0.25	0.32	0.00		66.7
SO^a	1.16	−0.63	0.33	0.78	0.00		1.6
SF^a	0.48	−0.45	0.23	0.57	0.00		0.8
SAl^a	46.38	−0.20	0.41	0.77	0.00		47.4
SSi^a	27.40	−0.78	0.29	0.99	−0.01		27.9
SP^a	38.30	−0.82	0.30	0.46	NA		38.2
SS^a	28.68	−0.75	0.30	1.12	0.00		29.4
SCl^a	26.81	−0.41	0.22	0.57	NA		27.2
SBr^b	32.34	−0.60	0.51	2.87	NA		35.1
SH_2^b	−6.10	−0.45	0.38	0.56	−0.15		−5.8
SF_2^b	−72.33	−0.52	0.48	1.33	0.00		−71.0
SCl_2^b	−6.18	−0.76	0.33	1.39	−0.13		−5.4
SBr_2^b	5.4	−0.90	0.53	7.58			12.6
HSO^a	−5.76	−0.64	0.53	0.76	−0.12		−5.2
SOH^a	−1.91	−0.67	0.37	0.76	−0.12		−1.6
SSO^b	−13.51	−0.82	0.59	1.34	0.02		−12.4
SO_2^b	−70.98	−0.99	0.73	1.01			−70.2
SCO^b	−33.90	−1.50	0.52	0.86			−34.0
SCS^b	27.60	−1.69	0.59	1.20			27.7
HSS^b	24.22	−0.66	0.46	1.12	−0.12		25.0
HSN^c	74.91	−0.80	0.45	0.56	−0.12		75.0
HNS^c	55.92	−0.80	0.43	0.56	−0.12		56.0
$ClNS^b$	64.05	−0.75	0.27	1.37			64.9
$NSCl^b$	40.23	−0.75	0.27	1.37			41.1
NSO^c	41.58	−1.07	0.63	0.78			41.9
H_2SO^b	−13.08	−0.72	0.75	0.78	−0.19		−12.5
H_2SS^b	28.53	−0.65	0.65	1.12	−0.19		29.5
$HSSH^b$	2.89	−0.83	0.64	1.12	−0.19		3.6
$FSSF^b$	−78.77	−1.07	0.73	1.9	−0.07		−77.3
CH_2S^b	28.25	−1.45	0.42	0.64	−0.24		27.6
$HSOH^b$	−28.73	−0.72	0.58	0.78	−0.28		−28.4
SSF_2^b	−81.61	−0.67	0.74	1.9	−0.1		−79.7

[a] aug-cc-pV(X + d)Z X = Q, 5 were employed; [b] cc-pV(X + d)Z X = T, Q were employed; [c] aug-cc-pV(X + d)Z X = T, Q were employed.

The enthalpy change at the CCSD(T)/cc-pV(T + d)Z and cc-pV(Q + d)Z levels are 8.78 and 9.12 kcal/mol, respectively, which yield an enthalpy change at the CCSD(T)/CBS limit of 9.37 kcal/mol. The scalar relativistic and core-valence effects increase the endothermicity of the later reaction by only 0.06 kcal/mol, as expected because of the homodesmic character of the reaction. Employing $\Delta H^{\circ}_{f,298}(Br_2) = 7.388$ kcal/mol (*13*) we obtain:

$$\Delta H^{\circ}_{f,298}(SBr_2) = 16.79 + \Delta H^{\circ}_{f,298}(SCl_2).$$

If we use the JANAF (*77*) value for $\Delta H^{\circ}_{f,298}(SCl_2)$ we obtain $\Delta H^{\circ}_{f,298}(SBr_2) = 12.59$ kcal/mol. However, if we select our estimation for sulfur dichloride we get $\Delta H^{\circ}_{f,298}(SBr_2) = 11.6$ kcal/mol. Therefore, the present result indicates that we are overestimating the stability of SCl_2 and the correct value is closer to the suggested in the JANAF tables (*77*). For sulfur bromide we propose $\Delta H^{\circ}_{f,298}(SBr_2) = 13.3 \pm 1$ kcal/mol.

3.3. *Tetraatomic sulfur-containing molecules:*

3.3.1. *CH_2S*

Despite its importance in several processes and that it is one of the few tetratomic molecules detected in the space (*9*), the enthalpy of formation of thioformaldehyde is not well established. The JANAF tables (*77*), based on the experimental determinations of the ionization potential of CH_2S (*103, 104*), recommend $\Delta H^\circ_{f,298}(CH_2S) = 28.3 \pm 2$ kcal/mol, whereas Benson (*11*) recommends a much lower value, 24.3 kcal/mol. Our best estimation was made employing basis sets up to cc-pV(Q + d)Z. We propose $\Delta H^\circ_{f,298}(CH_2S) = 27.6 \pm 1$ kcal/mol, in fair agreement with the value proposed in the JANAF tables (*77*).

3.3.2. *H_2SO*

This molecule may be produced in the oxidation of reduced sulfur molecules in the atmosphere or in several combustion processes. We have estimated its enthalpy of formation employing the same basis sets as for thioformaldehide as -12.5 ± 1 kcal/mol.

3.3.3. *HSOH*

A structural isomer of H_2SO which also participates in several atmospheric reactions. It is more stable than H_2SO, according to our calculations by 15.9 kcal/mol. Employing the same methodology as for H_2SO, we propose $\Delta H^\circ_{f,298}(HSOH) = -28.4 \pm 1$ kcal/mol.

3.3.4. *HSSH*

we have estimated the enthalpy of formation of HSSH in a recent article (*98*). The value obtained was 3.6 ± 1 kcal/mol in excellent agreement with the value quoted by Lias 4.0 kcal/mol (*85*) and also with the value recommended by Benson, 3.8 kcal/mol (*11*). The active thermochemical tables list a value by Kerr (*13*) that is 3.7 kcal/mol in excellent agreement with our determination and that of Benson (*11*). Thus, for HSSH we propose $\Delta H^\circ_{f,298}(HSSH) = -3.6 \pm 0.5$. We can use HSSH to construct another homodesmic reaction to investigate the consistency with the value proposed for HSOH:

$$SO + HSSH \longrightarrow SS + HSOH. \tag{11}$$

The enthalpy change at the CCSD(T)/cc-pv(T + d)Z and CCSD(T)/cc-pV(Q + d)Z levels of theory are -1.94 and -2.25 kcal/mol, respectively. The enthalpy change at the CBS limit is -2.44 kcal/mol. As expected for a homodesmic reaction, the core-valence, and scalar relativistic effects are not important. For this reaction, they do not affect the enthalpy change. With the aid of the enthalpies of formation of SO and HSSH, 1.2 and 3.6 kcal/mol, respectively we obtain that $\Delta H^\circ_{f,298}(HSOH) = 2.36 - \Delta H^\circ_{f,298}(S_2)$. As observed for the other homodesmic reactions discussed above, the $-\Delta H^\circ_{f,298}(S_2)$ is somewhat problematic. On the one hand, if we use our estimation, 29.4 kcal/mol we obtain $\Delta H^\circ_{f,298}(HSOH) = -27.0$ kcal/mol, in reasonable agreement with our estimation for HSOH employing the atomization reaction, -28.4 kcal/mol. On the other hand, the JANAF (*77*) value of S_2 gives $\Delta H^\circ_{f,298}(HSOH) = -28.34$ kcal/mol in excellent agreement with our estimation employing the atomization reaction. This is the first case in which the use of the JANAF (*77*) value for S_2 gives better consistency. However, due to the size of

HSOH, a tetratomic molecule, it is possible that the atomization reaction is giving an error of 1 kcal/mol.

3.3.5. *H_2SS*

This is the tetravalent isomer of HSSH. Employing the same methodology as for HSSH we have estimated its enthalpy of formation as 29.5 kcal/mol. The later value indicates that the HSSH isomer is more stable than the H_2SS by 25.9 kcal/mol.

3.3.6. *FSSF*

Difluorosulfane has been recently investigated by Ornellas (*50*) at the CCSD(T) level and by Wilson at the CCSD(T) and DFT levels (*105*). The isoelectronic molecule, FOOF is one of the most difficult systems to describe (*106, 107*) because of the short OO bond distance. The OO distance in FOOF is 1.217 Å only slightly larger than the observed in the ground state of O_2 (1.204 Å). The most accurate estimation of $\Delta H^\circ_{f,298}$(FOOF) is that of Feller and Dixon that employed CCSD(T) methodologies and large basis sets. The predicted enthalpy of formation at 298 K was, 9.6 ± 0.9 kcal/mol, 4–5 kcal/mol larger than the experimental values. The experimtal determinations of $\Delta H^\circ_{f,298}$(FOOF) lie within 1.3 kcal/mol. Thus, considering the evidence presented for FOOF we can expect some problems in the determination of $\Delta H^\circ_{f,298}$(FSSF). Indeed, the bond distances indicate that the situation is similar to that observed for FOOF. The SS distance in FSSF is nearly identical to the observed in S_2, 1.8889 and 1.8892 Å, respectively.

The most accurate value is that of Ornellas (*50*) that employed basis sets up to aug-cc-pV(5 + d)Z. The value obtained by Ornellas (*50*) was −76.77 kcal/mol. It is 3.6 kcal/mol larger than the recommended in the JANAF (*77*) tables, −80.41 ± 10 kcal/mol. We have estimated $\Delta H^\circ_{f,298}(\mathrm{FSSF}) = -77.3$ kcal/mol, in excellent agreement with the value obtained by Ornellas (*43*). It is important to note that in the case of FSSF the theoretical value is 3 kcal/mol less negative than the JANAF value. Thus, the error is in the same direction as FOOF, although in our case it is much more difficult to make a comparison with experiment because the uncertainty in the experimental value is too large, 10 kcal/mol.

Considering the later fact, we propose a value which is the average of Ornellas (*50*) and our value, −77.0 ± 1 kcal/mol. It is important to note that the discrepancy between the estimation of Ornellas (*50*) and our estimation is due to the use of a different extrapolation scheme. That employed by Ornellas (*50*), the three parameter exponential almost always gives binding energies that are lower than the determined performing the extrapolation with the two parameter equation, as we can appreciate in Table 2. We expect that future CCSDTQ calculations and new experimental determinations of $\Delta H^\circ_{f,298}$(FOOF) can decide whether or not we are underestimating the stability of FOOF:

3.3.7. *SSF_2*

Thiothionyl fluoride is the structural isomer of FSSF, it is slightly more stable. We have determined $\Delta H^\circ_{f,298}(\mathrm{SSF_2}) = -79.7$ kcal/mol in good agreement with the value calculated by Ornellas (*50*), −78.87 kcal/mol. Again the main difference is due to the different extrapolation scheme. Both theoretical values are around 16 kcal/mol far from the value recommended in the JANAF tables −95.939 ± 10 kcal/mol (*77*). Since an error of 16 kcal/mol is not possible at the CCSD(T) level for a molecule that is dominated by a single reference, we propose a value that is the average of the results obtained by Ornellas (*50*) and by us, $\Delta H^\circ_{f,298}(\mathrm{SSF_2}) = -79.3$ kcal/mol.

Table 7. Enthalpies of formation available for the set of molecules investigated and proposed values.

	This work	Theory 1	Theory 2	Theory 3	Exp	Exp	Exp	Recommended value
SH	33.7	33.6(34)	33.9(70)	34.2[71]	33.6 ± 1.1(75)	34.2 ± 0.67(72)	34.0 ± 1.5(73)	34.0 ± 0.3
SB	67.6				58.0(77)			67.6 ± 0.5
SC	67.4	67.36(34)	67.0(35)		67.1 ± 0.9(77)	66.5(78)	66.9 ± 0.2(76)	66.9 ± 0.2
SN	66.7	66.4(79)			63.0(77)	67.7 ± 5.7(80)		66.7 ± 0.5
SO	1.6				1.2 ± 0.3(77)			1.2 ± 0.3
SF	0.8	0.71(81)	1.7(82)		3.1 ± 0.5(77)			0.8 ± 0.5
Sal	47.4				57.0(77)			47.4 ± 0.5
SSi	27.9				25.3 ± 3(77)			27.9 ± 0.5
SP	38.2				33.1(77)	36.4 ± 2.39(80)		38.2 ± 0.5
SS	29.4	29.5(48)			30.7 ± 0.1(77)			30.1
SCl	27.2				37.4 ± 0.4(77)			27.2 ± 0.5
SBr	35.6	36.1(57)						35.5 ± 0.5
SH_2	−5.8	−5.3(34)	−5.35(35)		−4.9(77)			−4.9 ± 0.5
SF_2	−71.0				−70.9 ± 0.04(77)			−71 ± 1
SCl_2	−5.4				−4.2 ± 0.7(77)	−4.9(9)		−4.9 ± 1
SBr_2	13.3				5 ± 4(11)			13.3 ± 1
HSO	−5.2	−6.1 ± 1.3(95)	−4.9 ± 1.3(110)	−4.9 ± 1.3(96)	−3.0(109)	−1.4 ± 2(92)	−1.6 ± 0.7(93)	−5.2 ± 0.5
SOH	−1.6				−0.5 ± 1.1(97)			−1.6 ± 0.5
SSO	−12.4				−13.5 ± 8(77)	−13.4 ± 0.3(78)	−13.2 ± 0.3(80)	−12.4 ± 1
SO_2	−70.2				−70.94 ± 0.05(77)			−70.94 ± 0.05
SCO	−33.7	34.1(34)	34.0(35)		−33.0(77)	−33.9 ± 0.6(78)		−33.9 ± 0.6
SCS	27.7	27.2(34)			27.95(77)	27.9 ± 0.24(78)		27.9 ± 0.3
HSS	25.0	24.9(108)			23.60(77)	25.0 ± 2.5(99)	22.1 ± 1(11)	25.0 ± 0.5
HSN	75.0							75.0 ± 0.5
HNS	56.0							55.0 ± 0.5
ClNS	64.9							64.9 ± 0.5
NSCl	41.1							41.1 ± 0.5
NSO	41.9							41.9 ± 0.5
H_2SO	−12.5							−12.5 ± 1
H_2SS	29.5							29.5 ± 1
HSSH	3.6				4.0(90)	3.7(13)	3.7(11)	3.7 ± 0.5
FSSF	−77.3	−76.8(50)			−80.41 ± 10(77)			−77.0 ± 0.5
CH_2S	27.6				28.3 ± 2(77)	24.3(9)		27.6 ± 1
HSOH	−28.4							−28.4 ± 1
SSF_2	−79.7	−78.9(50)			−95.4 ± 10(77)			−79.3 ± 0.5

4. Conclusions

In Table 7, we have compared the theoretical values determined by us, and other investigators, as well as the most important experimental enthalpies of formation. Finally, in the last column we recommend values for all the species investigated. The set of 35 molecules can be divided in to five categories:

(1) Molecules for which there is an excellent agreement between experiment and theory, their $\Delta H^\circ_{f,298}$ can be considered established. They are: SC, SH, SO, SF_2, SO_2, SCS SCO, SH_2, and HSSH. We expect that future theoretical and experimental works only reduce the uncertainty.

(2) Then we have a set of seven molecules for which there is a good agreement between experiment and theory, but the uncertainty in the experimental determination is large. These are: SN, SOH, HSS SCO, SCl_2, and CH_2S, SP. Experimental determinations must be performed with more accurate techniques.

(3) Molecules that do not present problems at the theoretical level but need an experimental verification. This subset if composed by: SSi, SBr, SBr_2, HSN, HNS, SNCl, NSCl, NSO, HSOH, H_2SO, H_2SS.

(4) Controversial molecules: For these, the difference between experiment and theory is large, and no agreement has been reached up to now. They are: SB, SF, SAl, SCl, HSO, SSO, SSF_2, and FSSF.

(5) The last group is composed by only one molecule, S_2. For the later molecule our estimated $\Delta H^\circ_{f,298}(S_2)$ is 1.3 kcal/mol lower than the experimental value suggested in the JANAF tables (*77*), 30.71 kcal/mol. During the first step of the investigation we thought that the problem was that we did not use more extended basis sets, like the aug-cc-pV(6 + d)Z. However, posterior investigations that used sextuple zeta basis sets determined values that were in excellent agreement with us (*48, 85*). Indeed, Grant *et al.* determined $\Delta H^\circ_{f,298}(S_2) = 29.8$ kcal/mol. It is important to note that the agreement obtained by Grant *et al.* (*48*) at 0 K is much better than at 298 K. At 0 K the theoretical estimation is 0.86 kcal/mol lower than the experimental. To check the consistency of our values and to minimize the effect of higher excitation we used six homodesmic or isodesmic reactions. However, in five cases the results suggested a value that was closer to our estimation and not to the JANAF value (*77*). Therefore, considering the evidence given above and that a CCSDTQ treatment is going to increase the differences between experiment and theory, we believe that the $\Delta H^\circ_{f,298}(S_2)$ needs to be reinvestigated by new experimental and theoretical procedures. Experimentally, to confirm or not the value and theoretically, to investigate if it is possible an overestimation of the binding energies at the CCSD(T) and CCSDTQ levels, like we have observed for SH_2.

We expect that future experimental and theoretical works can help us to expand the set number 1 and reduce the others. At present time we are working to establish the thermochemical properties of many other sulfur-containing molecules.

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