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REGULAR ARTICLE

On the enthalpy of formation of thiophene

Pablo A. Denis

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Abstract Thiophene is an important contaminant of petroleum-derived fuels, and it also plays an important role in molecular electronics. We have calculated the enthalpy of formation of thiophene employing the CCSD(T) methodology and the cc-pV($X + d$)Z $X =$ T,Q,5 basis sets. At the CCSD(T)/CBS limit and including corrections for scalar relativistic effects, anharmonic effects, spin–orbit and core-valence correlation effects, the estimated enthalpy of formation is $25.15^{+0.5}_{-1}$ kcal/mol. Our estimation is 2.3 kcal/mol lower than the experimental value. The discrepancies between experiment and theory are expected to be increased if higher-order correlation effects are taken into account. Thus, a new determination of the experimental value is highly recommended. Finally, we discuss the problems faced to make this estimation, in particular the determination of accurate Zero-point energy corrections and the evaluation of core-valence correlation effects.

Keywords Correlation consistent basis sets · Sulfur compounds · Thiophene

1 Introduction

The oxidation of sulfur compounds in the atmosphere produces sulfuric acid which is one of the constituents of the polar stratospheric clouds [1]. The latter are very harmful for the stratospheric ozone because they are one of the winter reservoirs of bromine and chlorine compounds [2, 3]. For this reason, there have been sustained efforts to reduce the anthropogenic emission of sulfur compounds. In this regard, the extraction of sulfur compounds from oil-derived fuels is one of the keys [4]. In effect, most of the sulfur produced worldwide is extracted from petroleum [5] derived fuels and natural gas by procedure called hydrodesulfurization [6]. The interest elicited by thiophene is not limited only to the contamination of the atmosphere. Indeed, thiophene and its polymerized derivatives are widely used in organic electronic devices and molecular electronics because the presence of a sulfur atom in an aromatic molecule gives a particular stabilization and excellent transport properties to its oligomers [7] and nanocomposites [8]. Due to the importance of thiophene and its derivatives [9–18] several efforts have been performed to determine the spectroscopic and structural parameters of thiophene [19–25]. However, the currently accepted enthalpy of formation dates from 1955 [26] 27.47 ± 0.24 kcal/mol. In 1994, Dorofeeva and Gurvich [27] studied the experimental data available and confirmed the latter value. This estimation was included in the reference compounds of G3 theory [28], and the deviation between experiment and theory was 0.2 kcal/mol.

Over the last years several experimental and theoretical studies were performed to characterize small sulfur containing molecules [29–70, 9–18]. While it is true that we had advanced in the spectroscopic characterization, much more work is needed to determine the enthalpies of formation of these molecules. In a recent work we discussed the thermochemistry of 35 small sulfur-containing molecules. We concluded that, only for nine molecules the enthalpies of formation determined experimentally are in good agreement with those predicted by theory [36]. The problem of establishing the thermochemical properties is

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P. A. Denis (✉)
Computational Nanotechnology,
DETEMA Facultad de Química, Gral, UDELAR,
Flores 2124, CC 1157, 11800, Montevideo, Uruguay
e-mail: pablod@fq.edu.uy

so difficult that even for diatomic S_2, the theoretical results obtained by us [31, 36] and Feller et al. [71] recommend revision of the experimental value by more than 1 kcal/mol. In a recent experimental investigation [72], the theoretical values [31, 36, 72] were confirmed and the enthalpy of formation of S_2 was revised because in the original work there was a problem with the transitions (for details see ref. [72]). The accurate estimation of enthalpies of formation employing coupled cluster theory and extrapolation schemes is usually limited to small highly symmetric molecules because of its high computational cost, although there are examples of large molecules like the estimation of the enthalpy of formation of benzene [73, 74] and that of octane [75]. Herein, we have applied the state of the art methodologies to thiophene and performed a highly accurate calculation of its enthalpy of formation. The result was compared with the experimental data available and a revision of the experimental $\Delta H^{\mathrm{o}}_{\mathrm{f},298}(C_4H_4S)$ by more than 2 kcal/mol is recommended. The present results affect several works that employed the experimental $\Delta H^{\mathrm{o}}_{\mathrm{f},298}(C_4H_4S)$ [10] and may serve to construct a reliable database of thermochemical properties, in particular those of large sulfur containing heterocycles which can be used to understand combustion processes [39] and to benchmark new density functionals.

2 Theoretical methods

Coupled cluster theory with single-, double-, and perturbative treatment of triple excitations, namely CCSD(*T*), was employed [76–79], along with the cc-pV($X + d$)Z $X = D, T, Q, 5$ [80] basis sets. The HF energy was estimated employing the cc-pV($6 + d$)Z basis set. 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 UCCSD(*T*) calculations employing the cc-pwCVXZ basis sets $X = T, Q$ [81]. It is important to note that the 1 s electrons of sulfur were not correlated because the cc-pwCVXZ basis sets were not designed to include those electrons, since they are expected to lie too low in energy to make a significant contribution. The extrapolation of correlation energies to the complete basis set limit was performed employing the two parameter expression $E = B + C/l^3$ [82, 83]. Scalar relativistic effects were estimated using perturbative techniques at the MVD2 level as implemented in CFOUR [84] and using the cc-pwCVTZ basis set. The spin–orbit splitting for atoms were taken from Moore [85]. We performed geometry optimizations for basis sets up to cc-pV($Q + d$)Z, except for the cc-pV($X + d$)Z $X = 5,6$ ones, for which the cc-pV($Q + d$)Z geometry was employed. In the case of the CCSD(*T*)/cc-pwCVQZ calculations the CCSD(*T*)/cc-pwCVTZ geometry was used. The harmonic vibrational frequencies were determined analytically at the CCSD(*T*)/cc-pV($T + d$)Z, respectively. To evaluate anharmonic contributions to Zero-point energy corrections we employed two procedures. In one of them we evaluated fundamentals at the B3LYP/6-311 + (3*df*,2p) level [86–88]. The second procedure used is the one recommended by Grev et al. [89] which calculates ZPE employing theoretical harmonic frequencies and experimentally measured fundamentals. All the CCSD(*T*) calculations were performed with CFOUR [84] and whereas the DFT calculations were computed with Gaussian [90].

3 Results

Although it is not the purpose of the present work to discuss in detail the structure of thiophene, we present the key structural parameters in Fig. 1. Overall, there is good agreement between experiment and theory. However, it is quite surprising that at the CCSD(*T*)/cc-pV($Q + d$)Z level two distances are shorter than the experimental values, namely one of the CC distances and one of the CH bonds. It would be interesting to perform more detailed calculations to explain such differences because our previous results for sulfur-containing molecules [30–38] suggest that bond distances calculated at this level should be larger than the experimental values. To make an accurate estimation of the enthalpy of formation of thiophene employing the atomization reaction, these factors must be taken into account: (a) extrapolation to the complete basis set limit (b) Core-valence correlation effects (c) Spin–orbit and scalar relativistic effects (d) anharmonic corrections to ZPE (e) higher-order correlation effects. We discuss them in detail.

a) The extrapolation to the complete basis set limit is one of the most important sources of error because the singles and doubles contribution makes the most significant contribution. However, the perturbative triples one rapidly converges with basis set. In the case of thiophene, the results reported in Table 1 show that there is a good agreement between the total atomization energies calculated employing the $\infty(5, Q)$ and $\infty(Q, T)$ extrapolations, being the difference 0.49 kcal/mol. This agreement is quite unusual because in our previous works [30–38] we have observed that the $\infty(Q, T)$ extrapolation deviates more from the $\infty(5, Q)$ and $\infty(6,5)$ ones. However, the latter two do not deviate by more than 0.5 kcal/mol, so it is possible to avoid the calculation with the sextuple zeta basis set. For the purposes of the present work, the

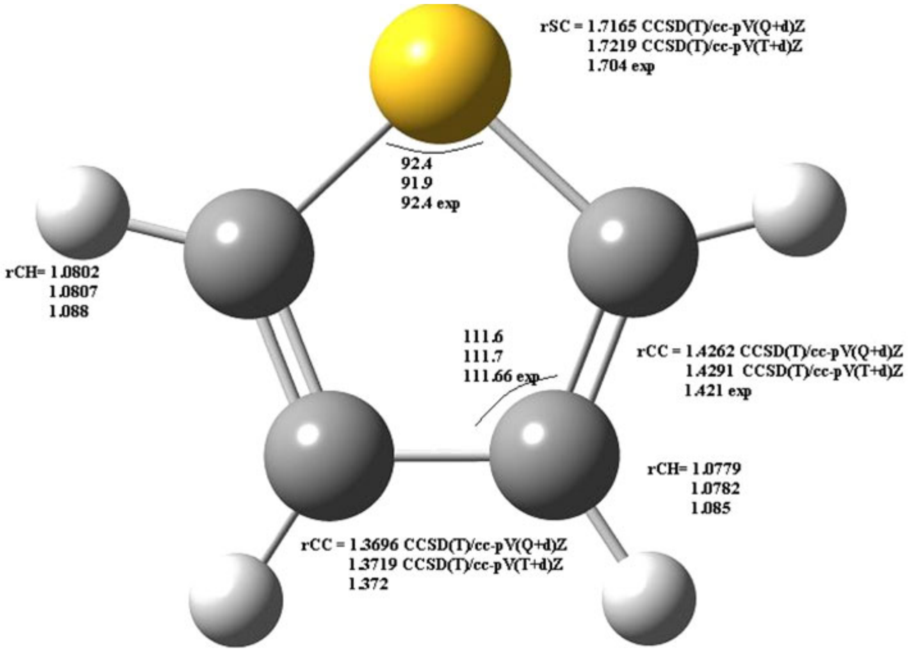

Fig. 1 Structural parameters determined for thiophene (Å,°). First value is CCSD(*T*)/cc-pV(*Q* + *d*)*Z*, the second corresponds to CCSD(*T*)/cc-pV(*T* + *d*)*Z*, whereas the last one is from the experimental work [20]

Table 1 Total atomization energy and enthalpy of formation of thiophene (kcal/mol), estimated at the CCSD(T) level

	TAE
CCSD(*T*)/cc-pV(*T* + *d*)*Z*	934.51
CCSD(*T*)/cc-pV(*Q* + *d*)*Z*	950.58
CCSD(*T*)/cc-pV(5 + *d*)*Z*	955.90
CCSD(*T*)/cc-pV(6 + *d*)*Z*	
CCSD(*T*)/∞(5, *Q*)	961.24
CCSD(*T*)/∞(*Q*, *T*)	961.73
$\mathrm{TAE_e}$	961.24
Core-valence (cc-pwCQZ)	5.51
Scalar relativistic (cc-pwCVTZ)	1.09
Spin–orbit	0.88
$\mathrm{TAE_{0K}}$	923.42
$\Delta H^{\mathrm{o}}_{\mathrm{f},0}$	28.12
$\Delta H^{\mathrm{o}}_{\mathrm{f},298}$	25.15

convergence of the correlation energy with respect to basis set size does not show an unusual behavior and a large error seems to be unlikely.

b) In our previous works [30–38] we calculated the core-valence correlation effects employing a cc-pwCVTZ basis set. However, because thiophene is a larger molecule than the ones previously studied by us, we increased the basis set to the cc-pwCVQZ. The effect is noticeable since the correction was augmented by a 10%. The values are reported in Table 1, and the correction to the total atomization energy (TAE) determined was 5.51 kcal/mol.

c) Since thiophene is a closed shell molecule composed by first and second row atoms, we consider only the spin–orbit effects for atoms from the work of Moore [85]. The spin orbit correction is 0.88 kcal/mol. The scalar relativistic effect did not show an appreciable variation with respect to basis set size. The correction obtained was 1.09 kcal/mol.

d) The calculation of accurate ZPE for large molecules becomes increasingly difficult, with the number of atoms. In the case of thiophene, at the CCSD(*T*)/cc-pV(*T* + *d*)*Z* level the harmonic ZPE is 41.71 kcal/mol. The value calculated at the B3LYP/6-311 + (3*df*,2p) level is essentially the same, 41.73 kcal/mol. To correct for anharmonic effects, we have calculated the anharmonic force field at the DFT level. After correcting for anharmonic effects, the ZPE = 41.36 kcal/mol. The latter value is 0.37 kcal/mol lower than the harmonic one. To confirm the accuracy of the latter procedure we have employed the scheme described by Grev et al. [89] to compute the anharmonic ZPE. The theoretical harmonics and experimental fundamentals employed are reported in Table 2. The ZPE predicted by this procedure is 41.16 kcal/mol, 0.20 kcal/mol lower than the value obtained by fitting the anharmonic force field. It is important to note that the result is the same if we use the B3LYP or the CCSD(*T*) harmonic frequencies because they are very similar, as reflected by the harmonic ZPE calculated with both methodologies.

4 Discussion

The total atomization energy calculated at the CCSD(*T*)/∞(5, *Q*) level and the corrections can be used to estimate

Table 2 Harmonic and fundamental vibrational frequencies of thiophene at different levels

	B3LYP 6-311 + *G*(3*df*,2p) Harmonics	CCSD(T) cc-pV(*T* + *d*)*Z* Harmonics	B3LYP 6-311 + *G*(3*df*,2p) Fundamentals	Exp. (cm^{-1}) Refs. [19, 20]
A_1(cm^{-1})				
	3,244	3,259	3,127	3,126
	3,207	3,228	3,092	3,098
	1,438	1,443	1,406	1,409
	1,394	1,396	1,365	1,360
	1,105	1,098	1,094	1,083
	1,056	1,052	1,039	1,036
	843	846	831	839
	617	610	610	608
A_2(cm^{-1})				
	932	903	920	898
	696	688	693	683
	579	566	573	565
B_1(cm^{-1})				
	893	876	879	867
	728	726	725	712
	463	453	458	452
B_2(cm^{-1})				
	3,241	3,256	3,125	3,125
	3,194	3,213	3,079	3,086
	1,546	1,545	1,513	1,504
	1,282	1,279	1,260	1,256
	1,106	1,101	1,095	1,085
	877	878	869	872
	756	759	746	751
ZPE (kcal/mol)	41.73	41.71	41.36	41.16[a]

[a] Estimated employing the procedure described in Ref. [89]

the $\Delta H^{o}_{f,298}(C_4H_4S)$ as 25.15 kcal/mol. The latter value can be compared with the one measured by Hubbard et al. [26], which is the recommended by Dorofeeva and Gurvich [27], namely 27.44 ± 0.25 kcal/mol. The difference between our estimation and the experimental value is 2.3 kcal/mol, quite large at this level of theory, even for a large molecule like thiophene. The largest sources of error in our procedure are expected to be three: the extrapolation of the correlation contribution, higher-order correlation effects, and the calculation of the $\mathrm{ZPE}_{\mathrm{anharmonic}}$. We analyze the effect of each one:

i. Correcting the ZPE for anharmonic effects increases the total atomization energy making more significant the difference between experiment and theory. It is important to note that we have used the ZPE obtained at the DFT level which is 0.20 kcal/mol larger than the one obtained employing the procedure described in Ref. [89]. Thus, if the latter ZPE is to be used, the discrepancy with respect to experiment would be 2.5 kcal/mol kcal/mol instead of 2.3 kcal/mol. In short, this error, if corrected, is likely to increase the discrepancy.
ii. The extrapolation to the complete basis set limit can introduce an important error, because reaching the CBS limit increases the TAE by 5.34 kcal/mol. However, we can expect a small error because the values obtained using the $\infty(5, Q)$ and $\infty(Q, T)$ extrapolations did not differ by more than 0.5 kcal/mol. The calculation employing the sextuple zeta basis set will not solve the problem because it gives values that are similar to those obtained with the $\infty(5, Q)$ extrapolation [30–38]. This error may augment or decrease the discrepancy.
iii. A CCSDTQ with a meaningful basis set, like a triple zeta one is out of our computation resources. However, it is possible to predict the effect of this correction. Previous works showed that higher-order correlations effects increase binding energies in almost all cases investigated (decrease enthalpies of formation) [71, 91–95]. Thus, they are going to make

discrepancy between experiment and theory more severe.

Considering the effects of the three aforementioned sources of error, two of them are likely to increase the discrepancy. For the extrapolation we cannot predict the sign of this correction but given the observed convergence with the basis set employed it is unlikely that it will resolve the discrepancy of 2.3–2.5 kcal/mol between experiment and theory. Thus, it will be desirable to perform a new experimental determination of the enthalpy of formation of thiophene to check whether revision is required for the accepted enthalpy of formation of thiophene. We suggest that the enthalpy of formation of thiophene should be $25.15^{+0.5}_{-1}$ kcal/mol. Finally, we would like to note that one of the anonymous reviewers suggested that a possible explanation for the discrepancy may be the contamination of thiophene by benzene in experimental investigations.

5 Conclusions

We have calculated the enthalpy of formation of thiophene employing the CCSD(T) methodology and the cc-pV($X + d$)Z $X =$ T,Q,5 basis sets. At the CCSD(T)/CBS limit and including corrections for scalar relativistic effects, anharmonic effects, spin–orbit and core-valence correlation effects, the estimated enthalpy of formation is $25.15^{+0.5}_{-1}$ kcal/mol. The latter value is 2.3 kcal/mol lower than the experimental value. The discrepancies between experiment and theory are expected to be increased if more refined calculations are performed. Thus, revision of the experimental value is recommended. The present results affect several works that employed the experimental $\Delta H^{o}_{f,298}(C_4H_4S)$ like reference [10]. Finally, we found a good agreement between experiment and theory for the structural parameters of thiophene, although for two distances we observed unexpected differences. Further calculations at a higher level of theory would be desirable to understand this deviation. We expect that this work can stimulate new experimental investigations of the structure and enthalpy of formation of thiophene.

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