Heat of formation for C_{60} by means of the G4(MP2) thermochemical protocol through reactions in which C_{60} is broken down into corannulene and sumanene

Wenchao Wan and Amir Karton*

School of Chemistry and Biochemistry, The University of Western Australia, Perth, WA 6009, Australia

ABSTRACT

High-level heats of formation for C_{60} are obtained through the use of reactions in which C_{60} is broken down into its fundamental bowl-shaped aromatic fragments (corannulene and sumanene). The reaction enthalpies are obtained by means of the high-level G4(MP2) thermochemical protocol and reliable experimental (from the Active Thermochemical Tables, ATcT) or theoretical (from W1h theory) heats of formation are used for the molecules involved in these reactions. Our best theoretical estimate, $\Delta_f H^o_{298}[C_{60}(g)]$ = 2511.7 kJ mol^{-1}, suggests that the experimental value adopted by the NIST thermochemical database ($\Delta_f H^o_{298}[C_{60}(g)]$ = 2560 ± 100 kJ mol^{-1}) should be revised downwards.

Keywords: Buckminsterfullerene, C_{60}, corannulene, sumanene, CCSD(T), G4(MP2), W1 theory.

How to cite this paper:

W. Wan and A. Karton. *Chemical Physics Letters*, 643, 34–38 (2016).
http://dx.doi.org/10.1016/j.cplett.2015.11.009

1. Introduction

The fundamental importance of *Buckminsterfullerene*[1] as a molecular allotrope of carbon and as a key building block in nanotechnology and material science is clearly evident to any chemist.[2,3] However, its heat of formation has been a matter of controversy with reported experimental values extending over a wide energy range of 199 kJ mol^{-1}, from 2457 ± 16[4,5,6] to 2656 ± 25 kJ mol^{-1}.[7] In light of these very large differences, the NIST thermochemical database has adopted a value of $\Delta_f H^o_{298}[C_{60}(g)]$ = 2560 kJ mol^{-1} associated with an unusually high error bar of ± 100 kJ mol^{-1}. The first measurement of heat of formation for C_{60} was carried out by Beckhaus *et al.* in 1992,[8] who reported a standard heat of formation in the gas-phase ($\Delta_f H^o_{298}[C_{60}(g)]$) of 2464 ± 7 kJ mol^{-1}.[5,6] The same year, Steele *et al.*[7] revised this value substantially upwards to 2656 ± 25 kJ mol^{-1}.[9] The large discrepancy between these two experimental determinations has stimulated a series of subsequent macro- and micro-combustion calorimetric studies[4,6,10,11,12,13,14,15,16] (Table S1 of the Supplementary data summarizes the experimental $\Delta_f H^o_{298}[C_{60}(cr)]$ and $\Delta_f H^o_{298}[C_{60}(g)]$ values). The reasons for these large discrepancies include the difficulties associated with the production of samples of C_{60} of sufficiently high purity and the limited accuracy of calorimetric measurements on relatively small samples.[17,18] An additional contributor to the discrepancies between the $\Delta_f H^o_{298}[C_{60}(g)]$ values comes about because in some cases the enthalpies of sublimation (used for converting the crystalline heat of formation into the gaseous heat of formation) show a variation of as much as ~50 kJ mol^{-1} (Table S1, Supplementary data). However, even the reported solid-phase heats of formation span a wide energy range of 149 kJ mol^{-1}. In the light of this state of affairs, the NIST Webbook has adopted a standard heat of formation for C_{60} of 2560 ± 100 kJ mol^{-1}, which was obtained as the average of six $\Delta_f H^o_{298}[C_{60}(g)]$ values (Table S1, Supplementary data).[19] We note that the six $\Delta_f H^o_{298}[C_{60}(g)]$ values selected by NIST spread over the abovementioned energy range of 149 kJ mol^{-1}.

Two recent theoretical studies have obtained the heat of formation for C_{60} through the use of reactions in which C_{60} is broken down into prototypical hydrocarbons.[20,21] Reference 20 used reactions in which C_{60} is broken down into corannulene:

$$C_{60} + a\ \mathrm{Ar} \rightarrow b\ \text{corannulene} \qquad (\mathbf{1})$$

where Ar is benzene or naphthalene. These reactions were chosen because they conserve some of the unique chemical features present in C_{60} (such as curvature in the π system associated with pentagons

completely surrounded by hexagons). In order to obtain the heat of formation for C_{60} the reaction enthalpy was calculated at the DSD-PBEP86-D3/cc-pVQZ level of theory,[22] the heat of formation for corannulene was obtained from W1h theory,[23,24] and the heats of formation for Ar were taken from accurate experimental measurements. In this study the best theoretical heat of formation for C_{60} was reported to be $\Delta_f H°_{298}[C_{60}(g)] = 2522 \pm 14$ kJ mol^{-1}. Shortly thereafter, Dobek *et al*.[21] obtained the heat of formation for C_{60} from CBS-4M and APF-D calculations,[25,26] using a homologous sequence of isodesmic reactions in which C_{60} is broken down into CH_4, C_2H_4, C_2H_6, and C_6H_6. The chosen set of reactions allow for obtaining size-consistent empirical parameters determined from least-squares fitting to W1h enthalpies of formation1 for C_6H_6, $C_{10}H_8$, $C_{14}H_{10}$, and $C_{18}H_{12}$. Using this empirical approach Dobek *et al*.[21] arrived at $\Delta_f H°_{298}[C_{60}(g)] = 2531 \pm 15$ kJ mol^{-1}, in good agreement with the value reported in ref. 20.

The reactions used by Dobek *et al*.[21] for obtaining the heat of formation for C_{60} do not attempt to balance the strain energy on the two sides of the reaction, whereas reaction **1** attempts to do so using corannulene. It is important to note, however, that C_{60} is composed of two fundamental aromatic bowl-shaped fragments (i) a pentagon surrounded by five hexagons (corannulene) and (ii) a hexagon surrounded by three hexagons and three pentagons (sumanene). This is illustrated schematically in Figure 1.

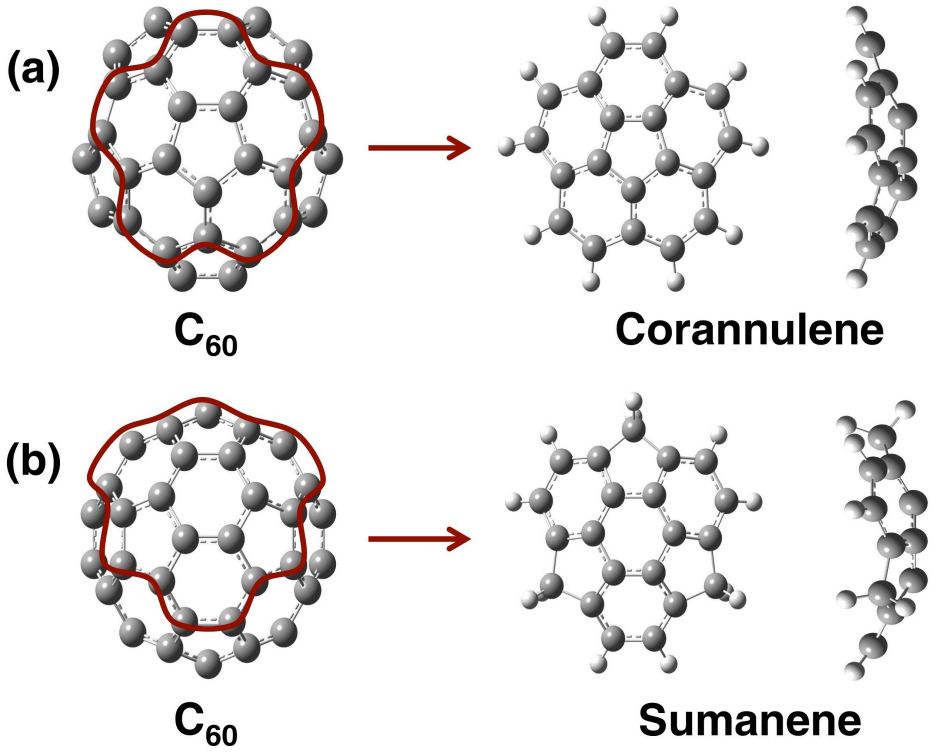

Figure 1. B3LYP/6-31G(2df,p) optimized structure of C_{60} and its two basic fragments (a) corannulene ($C_{20}H_{10}$) and (b) sumanene ($C_{21}H_{12}$).

In the present work, we obtain the heat of formation of C_{60} via reactions that conserve some of the unique chemical features present in C_{60} (such as strain energy resulting from curvature in the π system). There are two key differences between the approach taken here and in ref. 20. The first is that here C_{60} is broken down into both corannulene and sumanene, rather than just corannulene. Including sumanene in the thermochemical cycle used for obtaining the heat of formation of C_{60} is important, since corannulene accounts for only one type of strain energy involved in C_{60} (i.e., pentagons completely surrounded by hexagons), whilst sumanene accounts for the strain energy associated with hexagons surrounded by three hexagons and three pentagons (Figure 1). A number of studies have previously shown that it is important to conserve such features when calculating the heats of formation of fullerenes and PAHs.[27,28,29,30,31] The second difference is that the reaction energies are obtained at a much higher level of theory, namely, by means of the G4(MP2) protocol,[32] rather than by means of double-hybrid density functional theory (DHDFT). In this context, we note that the CCSD(T)/6-31G(d) calculation for C_{60} stretched our computational resources to the limit. This single-point energy

calculation ran for more than two weeks on eight Intel Xeon E5-4650L cores (at 3.1 GHz) with 512 GB of RAM.

2. Computational details

The geometries and harmonic vibrational frequencies of all structures have been obtained at the B3LYP/6-31G(2*df,p*) level of theory. Zero-point vibrational energies (ZPVEs) and enthalpic temperature corrections (H_{298}–H_0) have been obtained from such calculations, within the rigid-rotor harmonic oscillator (RRHO) approximation, and have been scaled using literature scaling factors.[33] All geometry optimizations and frequency calculations were performed using the Gaussian 09 program suite.[34]

The reaction enthalpies of reactions **2** and **3** (below) are obtained by means of the high-level, ab initio W1h thermochemical protocol[23,24] as described in detail in ref. 20 for corannulene. All the high-level ab initio calculations have been carried out with the Molpro 2012.1 program suite.[35,36] We use these W1h reaction enthalpies to obtain a reliable theoretical heat of formation for sumanene. W1h represents a layered extrapolation to the relativistic, all-electron CCSD(T) (coupled cluster with singles, doubles, and quasiperturbative triple excitations) basis-set-limit energy, and can achieve "sub-chemical accuracy". For example, the large set of 124 accurate atomization energies in the W4-11nonMR database, W1h attains a root-mean-squared deviation (RMSD) of 2.7 kJ mol^{-1}.[37,38] However, it should be pointed out that for reaction that conserve large molecular fragments on the two sides of the reaction (such as reactions **2** and **3**), W1h theory should yield even better performance due to a large degree of systematic error cancelation between reactants and products.[30,31,37,39,40,41,42]

The reaction enthalpies of the reactions involving C_{60} (reactions **4**–**9** below) have been obtained by means of the G4(MP2) thermochemical protocol.[32] The G4(MP2) protocol estimates the CCSD(T) energy in conjunction with a triple-ζ quality basis set and has been found to give chemical properties with "near-chemical accuracy". For example, for the set of 124 atomization energies in the W4-11nonMR database G4(MP2) attains an RMSD of 7.5 kJ mol^{-1}.[37] Whilst for the wide range of 454 experimental thermochemical properties considered in ref. 32 (such as enthalpies of formation, electron affinities, and ionization energies) G4(MP2) attains an RMSD of 6.2 kJ mol^{-1}. However, as pointed out above, for reaction that conserve large molecular fragments on both sides of the reaction, G4(MP2) theory should yield better performance due to a large degree of systematic error cancelation between reactants and products.[30,31,37,39,40,41,42] In this context, we note that reactions **4** and **6**–**9** conserve both

the numbers of each formal bond type and the numbers of carbon atoms in each hybridization state on the two sides of the reaction.

Since both W1h and G4(MP2) approximate the CCSD(T) energy, it is of interest to estimate whether post-CCSD(T) contributions are likely to be significant for the theoretical heats of formation obtained from reactions **2**–**9**. The percentage of the atomization energy accounted for by parenthetical connected triple excitations, %TAE[(T)], has been shown to be a reliable energy-based diagnostic indicating the importance of post-CCSD(T) contributions.[37,43,44] The %TAE[(T)] values for the species involved in reactions **2**–**9** (Table S2, Supplementary data) range between 0.7 (CH_4) and 3.0 (C_{60}). These values indicate that these systems are dominated by dynamical correlation effects and that post-CCSD(T) excitations are not expected to have a significant contributions to the reaction energies.

3. Results and discussion

3.1. W1h heat of formation for sumanene. We begin by calculating the heat of formation for sumanene by means of the W1h thermochemical protocol. We obtain an accurate theoretical heat of formation for sumanene via reactions that conserve the chemical environments of the reactants and products to various degrees. Specifically, the following reactions are considered:

$$\text{sumanene} + 3\ \text{methane} \rightarrow 4\ \text{benzene} \qquad (\mathbf{2})$$

$$\text{sumanene} + \tfrac{3}{5}\ \text{methane} \rightarrow \tfrac{6}{5}\ \text{triphenylene} \qquad (\mathbf{3})$$

Sumanene is essentially triphenylene in which the three outer phenyl rings are joined together with three CH_2 groups (Figure 1). Thus, apart from the strain energy involved in sumanene, reaction **3** conserves the chemical environments of the reactants and products to a large extent. The reaction enthalpies of reactions **2** and **3** are obtained from W1h theory, whilst accurate experimental heats of formation for methane and benzene are taken from the Active Thermochemical Tables (ATcT) network of Ruscic and coworkers (the ATcT values are summarized in Table 1).[45,46,47] An experimental heat of formation for triphenylene ($\Delta_f H°_{298}[C_{18}H_{12}(g)]$ = 270.1 ± 4.4 kJ mol^{-1}) is taken from Roux *et al.*[48] We note that this experimental value is in good agreement with the theoretical W1h value calculated in ref. 20. The component breakdown of the W1h reaction enthalpies and our resultant predicted heats of formation are gathered in Table 2. Both reactions **2** and **3** lead to similar heats of

formation for sumanene, namely $\Delta_f H°_{298}[C_{21}H_{12}(g)]$ = 535.3 ± 9 (reaction **2**) and 530.3 ± 8 (reaction **3**) kJ mol^{-1}. Using reaction **2** has the advantage that only highly accurate experimental values from ATcT are used, whereas reaction **3** has the advantage that larger molecular fragments are being conserved on the two sides of the reaction. Since we believe that our W1h reaction energy should be sufficiently converged for reaction **2**, we adopt the heat of formation obtained from this reaction since it involves only experimental data associated with well-defined error bars < 0.3 kJ mol^{-1}. We note that calculating the heat of formation of sumanene via an atomization reaction leads to a very similar value of $\Delta_f H°_{298}[C_{21}H_{12}(g)]$ = 536.7 kJ mol^{-1}.[49]

Table 1. Experimental ATcT heats of formation at 298 K ($\Delta_f H°_{298}$) for species involved in reactions **2**–**4** and **6**–**9** (kJ mol^{-1}).[45,46,47]

	$\Delta_f H°_{298}$
CH_4	–74.532 ± 0.057
C_2H_4	52.56 ± 0.15
C_2H_6	–83.79 ± 0.17
C_3H_8	–104.41 ± 0.29
C_6H_6	83.18 ± 0.26

Table 2. Component breakdown of the W1h reaction enthalpies and predicted theoretical enthalpies of formation for sumanene (kJ mol^{-1}).

Reaction	(2)	(3)
ΔHF[a]	–244.8	–153.3
ΔCCSD[b]	65.9	142.6
Δ(T)[c]	6.7	27.1
ΔCV[d]	–0.5	0.4
ΔRel[e]	–0.3	–0.6
ΔDBOC[f]	0.0	0.2
ΔZPVE[g]	5.6	18.7
Δ(H_{298}–H_0)[g]	0.9	–9.0
$\Delta_r H^\circ_{298}$[h]	–166.4	26.1
$\Delta_f H^\circ_{298}$[i,j]	535.3 ± 9	530.3 ± 8

[a]Extrapolated from the cc-pVQZ and cc-pV5Z basis sets. [b]Extrapolated from the cc-pVTZ and cc-pVQZ(no *f* on H) basis sets (see ref. 20 for further details). [c]Extrapolated from the cc-pVDZ and cc-pVTZ basis sets. [d]CCSD(T) core–valence correction obtained as: CCSD/cc-pwCVTZ + (T)/cc-pwCVTZ(no *f*) (see ref. 20 for further details). [e]CCSD(T)/cc-pVDZ-DK scalar relativistic correction. [f]HF/cc-pVTZ DBOC correction. [g]Scaled B3LYP/6-31G(2df,p) values. [h]Overall reaction enthalpy at 298 K. [i]Theoretical heats of formation at 298 K for sumanene obtained using the W1h reaction enthalpies and experimental heats of formation (see text). [j]The associated uncertainties are obtained using the reported experimental uncertainties and a conservative uncertainty of ± 7.7 kJ mol^{-1} for the W1h reaction enthalpies, taken from ref. 37.

3.2. Heat of Formation of C_{60}. Having obtained a reliable W1h heat of formation for sumanene paves the way for calculating the heat of formation for C_{60} via reactions in which C_{60} is broken down into sumanene and corannulene. In these thermochemical cycles we will use our best theoretical W1h heats of formation for corannulene ($\Delta_f H^\circ_{298}[C_{20}H_{10}(g)]$ = 485.2 ± 8, from ref. 20) and sumanene ($\Delta_f H^\circ_{298}[C_{21}H_{12}(g)]$ = 535.3 ± 9 kJ mol^{-1}). In these reactions we will only consider additional species for which accurate experimental heats of formation are available from the ATcT thermochemical network (Table 1). In all cases the reaction energies are calculated at the G4(MP2) level.

We begin by stressing that even though we are calculating the reaction energies at the G4(MP2) level, we still need to use reactions that conserve large molecular fragments on the two sides of the reaction. This is clearly demonstrated by considering the following isodesmic reaction, which was used in ref. 21:

$$C_{60} + 30\ C_2H_4 \rightarrow 20\ C_6H_6 \qquad \textbf{(4)}$$

Table 3 lists the G4(MP2) reaction enthalpy for reaction **4** as well as the resulting predicted heat of formation for C_{60} $\Delta_f H^o_{298}[C_{60}(g)]$ = 2420.7 kJ mol^{-1}. This heat of formation is lower than the experimental value adopted by NIST by nearly 140 kJ mol^{-1} and is also significantly lower than the theoretical values obtained via reactions that conserve larger molecular fragments on the two sides of the reaction (*vide infra*). The experimental uncertainties associated with C_2H_4 and C_6H_6 cannot account for more than about 10 kJ mol^{-1}. This leaves the G4(MP2) reaction enthalpy as the main source of error, and we conclude that the G4(MP2) level cannot accurately predict the enthalpy of this reaction. We note that using an atomization reaction calculated at the G4(MP2) level leads to an even lower heat of formation for C_{60}, namely, $\Delta_f H^o_{298}[C_{60}(g)]$ = 2402.5 kJ mol^{-1}.[49] In this context it should be pointed out that the quality of G4(MP2) heats of formation obtained from atomization reactions deteriorates with the size (and complexity) of the molecular system. For example, we obtain the following differences relative to our best W1h or ATcT heats of formation: 1.0 (CH_4), –1.8 (C_2H_4), 1.3 (C_2H_6), 1.4 (C_3H_8), –3.6 (C_6H_6), –31.5 ($C_{20}H_{10}$), and –30.0 ($C_{21}H_{12}$) kJ mol^{-1} (the differences are G4(MP2) – best expt./theor. value). These differences (in particular, the large underestimations obtained for $C_{20}H_{10}$ and $C_{21}H_{12}$) suggest that the G4(MP2) heat of formation for C_{60} obtained via an atomization reaction will be significantly underestimated.

Table 3. G4(MP2) reaction enthalpies for reactions **4–9** and predicted theoretical enthalpies of formation for C_{60} (kJ mol^{-1}).

Reaction	$\Delta_r H_{298}$[a]	$\Delta_f H^o_{298}[C_{60}(g)]$[b]
4	–2333.9	2420.7
5	–1619.7	2558.5
6	–475.9	2555.3
7	18.0	2511.7
8	61.9	2515.2
9	158.8	2515.0

[a]Reaction enthalpy calculated at the G4(MP2) level. [b]Theoretical heat of formation for C_{60} obtained from the G4(MP2) reaction enthalpies, theoretical W1h heats of formation for sumanene and corannulene, and experimental ATcT heats of formation for methane, ethene, ethane, propane and benzene (see Table 1 and text).

Let us now turn to reactions that conserve larger molecular fragments on the two sides of the reaction. We first consider a reaction that involves only sumanene and corannulene:

$$C_{60} + 20 \text{ sumanene} \rightarrow 24 \text{ corannulene} \qquad \textbf{(5)}$$

The predicted heat of formation for C_{60} from reaction **5** is 2558.5 kJ mol^{-1}. However, it is important to note that, due to the large stoichiometric coefficients of sumanene and corannulene (20 and 24, respectively), even a small error of ± 1 kJ mol^{-1} in the W1h heats of formation for these species could translate to an error of 44 kJ mol^{-1} in the predicted heat of formation for C_{60}. Given that our best W1h theoretical heats of formation for sumanene and corannulene are associated with uncertainties of 8–9 kJ mol^{-1}, it is desirable to use reactions with much smaller stoichiometric coefficients for these species. In addition, we note that reaction **5** does not conserve the numbers of each formal bond type, and the numbers of carbon atoms in each hybridization state on the two sides of the reaction. Two reactions in which these properties are conserved are:

$$C_{60} + 10\ C_6H_6 \rightarrow 6 \text{ corannulene} \qquad \textbf{(6)}$$

$$C_{60} + 10\ CH_4 \rightarrow \frac{10}{3} \text{ sumanene} \qquad \textbf{(7)}$$

Reaction **6** was used in ref. 20 for obtaining the heat of formation for C_{60}. Calculating the reaction energy with two DHDFT functionals in conjunction with the cc-pVQZ basis set (and using the ATcT heat of formation for benzene), ref. 20 obtained $\Delta_f H^o_{298}[C_{60}(g)]$ = 2535.2 (DSD-PBEP86-D3)[Error! Bookmark not defined.] and 2543.1 (B2GP-PLYP-D3)[50] kJ mol^{-1}. In the present work e obtain a higher value of $\Delta_f H^o_{298}[C_{60}(g)]$ = 2555.3 kJ mol^{-1} using the more accurate G4(MP2) reaction energy. In reaction **7** C_{60} is broken down into 3.3 sumanenes. Calculating the reaction energy at the G4(MP2) level (and using the ATcT heat of formation for methane) we obtain a significantly lower heat of formation for C_{60} of $\Delta_f H^o_{298}[C_{60}(g)]$ = 2511.7 kJ mol^{-1}. We note however, that since reaction **7** involves about three sumanenes, whereas reaction **6** involves six corannulenes, reaction **7** is less prone to the potential error resulting from the uncertainty in the

W1h heats of formation for corannulene and sumanene. Therefore, we deem the $\Delta_f H^o_{298}[C_{60}(g)]$ value obtained from reaction **7** more reliable.

What about reactions in which C_{60} is separated into both corannulene and sumanene? The following two reactions conserve the numbers of each formal bond type and the numbers of carbon atoms in each hybridization state on the two sides of the reaction:

$$C_{60} + 7.5\ C_2H_6 + 1.5\ \text{corannulene} \rightarrow 5\ \text{sumanene} \qquad (\mathbf{8})$$

$$C_{60} + 6\ C_3H_8 + 2.4\ \text{corannulene} \rightarrow 6\ \text{sumanene} \qquad (\mathbf{9})$$

These reactions result in essentially the same predicted heat of formation for C_{60}, namely, $\Delta_f H^o_{298}[C_{60}(g)]$ = 2515.2 (reaction **8**) and 2515.0 (reaction **9**) kJ mol^{-1}. These results are in close agreement with the $\Delta_f H^o_{298}[C_{60}(g)]$ value obtained via reaction **7**.

4. Conclusions

Corannulene (a pentagon surrounded by five hexagons) and sumanene (a hexagon surrounded by three pentagons and three hexagons) are the two basic building blocks of C_{60}. We obtain the heat of formation of C_{60} via ructions that involve corannulene and sumanene, and hence conserve the chemical environments of the reactants and products to large extents. We calculate the reaction energies by means of the high-level G4(MP2) thermochemical protocol, whilst the heats of formation for the reactants and products are calculated with the W1h thermochemical protocol (for corannulene and sumanene) or taken from the ATcT thermochemical network (for CH_4, C_2H_4, C_2H_6, C_3H_8, and C_6H_6). We show that there is a significant variation in the predicted heat of formation of C_{60} obtained via different reactions. In particular, reactions **5** and **6** result in $\Delta_f H^o_{298}[C_{60}(g)]$ = 2555.3–2558.5, whereas reactions **7–9** result in $\Delta_f H^o_{298}[C_{60}(g)]$ = 2511.7–2515.2 kJ mol^{-1}. Since the considered reactions conserve the chemical environments of the reactants and products to large extents we assume that our G4(MP2) reaction energies are sufficiently converged. Thus, the main source of error in the predicted heats of formation for C_{60} are the potential errors in the theoretical W1h heats of formation for corannulene and sumanene. We therefore adopt the $\Delta_f H^o_{298}[C_{60}(g)]$ value obtained from reaction **7** ($\Delta_f H^o_{298}[C_{60}(g)]$ = 2511.7 kJ mol^{-1}) as our best theoretical heat of formation for C_{60} since this reaction is the least prone for

this source of error. The revised $\Delta_f H^o_{298}[C_{60}(g)]$ value is lower by only 9.9 kJ mol^{-1} than the best theoretical estimate recommended in ref. 20, but should carry a smaller uncertainty since it is obtained at a considerably higher level of theory. Our best theoretical value is within the limits of the error bars of the experimental value adopted by the NIST thermochemical database (2560 ± 100 kJ mol^{-1}). However, it suggests that the NIST value should be revised downwards.

Supplementary data

Summary of reported experimental heats of formation for C_{60} (Table S1); Diagnostics indicating the importance of post-CCSD(T) correlation effects for the species involved in reactions **2**–**9** (Table S2); B3LYP/6-31G(2df,p) optimized geometries for all the species in reactions **2**–**9** (Table S3); and full references for ref 34 (Gaussian 09) and ref 35 (Molpro 2012.1) (Table S4).

Corresponding author

*E-Mail: amir.karton@chem.usyd.edu.au

Acknowledgments

We gratefully acknowledge the generous allocation of computing time from the National Computational Infrastructure (NCI) National Facility, and system administration support provided by the Faculty of Science at UWA to the Linux cluster of the Karton group. AK is the recipient of an Australian Research Council (ARC) Discovery Early Career Researcher Award (DECRA, project number: DE140100311).

References

(1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162.

(2) Hirsch, A.; Brettreich, M. *Fullerenes*; Wiley-VCH: New York, NY, 2005.

(3) Schwerdtfeger, P.; Wirz, L. N.; Avery, J. *WIREs Comput Mol Sci* **2015**, *5*, 96.

(4) Kiyobayashi, T.; Sakiyama, M. *Fullerene Sci. Technol.* **1993**, *1*, 269.

(5) The reported crystalline heat of formation was converted to a heat of formation in the gas phase using the enthalpy of sublimation from ref 6 ($\Delta H_s(C_{60}$, 298 K) = 183.7 ± 5.1 kJ mol^{-1}).

(6) Diky, V. V.; Kabo, G. J. *Russ. Chem. Rev.* **2000**, *69*, 95.

(7) Steele, W. V.; Chirico, R. D.; Smith, N. K.; Billups, W. E.; Elmore, P. R.; Wheeler, A. E. *J. Phys. Chem.* **1992**, *96*, 4731.

(8) Beckhaus, H. D.; Ruchardt, C.; Kao, M.; Diederich, F.; Foote, C. S. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 63.

(9) Note that using the enthalpy of sublimation from ref 6 ($\Delta H_s(C_{60}$, 298 K) = 183.7 ± 5.1 kJ mol^{-1}) to convert the reported crystalline heat of formation to a gas-phase heat of formation, we obtain $\Delta H_f(C_{60}, g)$ = 2606 ± 15 kJ mol^{-1}.

(10) Diogo, H. P.; Minas da Piedade, M. E. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 3541.

(11) Beckhaus, H. D.; Verevkin, S.; Ruchardt, C.; Diederich, F.; Thilgen, C.; ter Meer, H. U.; Mohn, H.; Muller, W. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 996.

(12) Kolesov, V. P.; Pimenova, S. M.; Pavlovich, V. K.; Tamm, N. B.; Kurskaya, A. A. *J. Chem. Thermodyn.* **1996**, *28*, 1121.

(13) Xu-wu, A.; Jun, H.; Zheng, B. *J. Chem. Thermodyn.* **1996**, *28*, 1115.

(14) Xu-wu, A.; Chen, B.; Jun, H. *Sci. Chin.* **1998**, *41*, 543.

(15) Rojas-Aguilar, A. *J. Chem. Thermodyn.* **2002**, *34*, 1729.

(16) Rojas-Aguilar, A.; Martinez-Herrera, M. *Thermochimica Acta* **2005**, *437*, 126.

(17) Diogo, H. P.; Minas da Piedade, M. E. Enthalpies of Formation of C_{60} and C_{70} in the Crystalline State: An Unfinished Tale?, In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*. Kadish, K. M. and Ruoff, R. S. Eds.; The Electrochemical Society: New Jersey, **1998**, v. 6, pp. 627.

(18) Biglova, Y. N.; Sigaeva, N. N.; Talipov, R. F.; Monakov, Y. B. Review of Fullerene Organic Chemistry. In Molecular And High Molecular Chemistry: Theory And Practice, Monakov, Y. B.; Zaikov, G. E. Eds. Nova Science Pub Inc, 2006, pp. 1.

(19) Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. Neutral Thermochemical Data. In *NIST Chemistry WebBook*, NIST Standard Reference Database Number 69, Eds. Linstrom, P. J. and Mallard, W. G. National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov, (retrieved October 12, 2015).

(20) Karton, A.; Chan, B.; Raghavachari, K.; Radom, L. *J. Phys. Chem. A* **2013**, *117*, 1834.

(21) Dobek, F. J.; Ranasinghe, D. S.; Throssell, K.; Petersson, G. A. *J. Phys. Chem. A* **2013**, *117*, 4726.

(22) Kozuch, S.; Martin, J. M. L. *Phys. Chem. Chem. Phys.* **2011**, *13*, 20104.

(23) Martin, J. M. L.; Oliveira, G. *J. Chem. Phys.* **1999**, *111*, 1843.

(24) Martin, J. M. L.; Parthiban, S.; W1 and W2 theory and their variants: thermochemistry in the kJ/mol accuracy range. Understanding Chemical Reactivity, Vol. 22: Quantum-Mechanical Prediction of Thermochemical Data, J. Cioslowski, ed. (Kluwer, Dordrecht, 2001), pp. 31.

(25) Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **2000**, *112*, 6532.

(26) Austin, A.; Petersson, G. A.; Frisch, M. J.; Dobek, F. J.; Scalmani, G.; Throssell, K. *J. Chem. Theory Comput.* **2012**, *8*, 4989.

(27) Sun, C. H.; Yao, D.; Lu, G. Q.; Cheng, H. M. *Chem. Phys. Lett.* **2007**, *434*, 160.

(28) Cioslowski, J.; Rao, N.; Moncrieff, D. *J. Am. Chem. Soc.* **2000**, *122*, 8265.

(29) Yu, J.; Sumathi, R.; Green, W. H. *J. Am. Chem. Soc.* **2004**, *126*, 12685.

(30) Ramabhadran, R. O.; Raghavachari, K. *J. Chem. Theory Comput.* **2011**, 7, 2094.

(31) Ramabhadran, R. O.; Raghavachari, K. *J. Phys. Chem. A* **2012**, 116, 7531.

(32) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K. *J. Chem. Phys.* **2007**, *127*, 124105.

(33) Merrick, J. P.; Moran, D.; Radom, L. *J. Phys. Chem. A* **2007**, *111*, 11683.

(34) Gaussian 09, Revision C.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; *et al.* Gaussian, Inc., Wallingford CT, 2009.

(35) Molpro 2012.1, Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Mitrushenkov, A.; Rauhut, G.; B. Adler, T.; *et al.* See: http:www.molpro.net.

(36) Werner, H.-J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M. *WIREs Comput. Mol. Sci.* **2012**, *2*, 242.

(37) Karton, A.; Daon, S.; Martin, J. M. L. *Chem. Phys. Lett.* **2011**, *510*, 165.

(38) Karton, A.; Martin, J. M. L. *J. Chem. Phys.* **2012**, *136*, 124114.

(39) Wheeler, S. E.; Houk, K. N.; Schleyer, P. v. R.; Allen, W. D. *J. Am. Chem. Soc.* **2009**, *131*, 2547.

(40) Wodrich, M. D.; Corminboeuf, C.; Wheeler, S. E. *J. Phys. Chem. A* **2012**, *116*, 3436.

(41) Wheeler, S.E. *WIREs Comput. Mol. Sci.* **2012**, *2*, 204.

(42) Karton, A.; Gruzman, D.; Martin, J. M. L. *J. Phys. Chem. A* **2009**, *113*, 8434.

(43) Karton, A.; Rabinovich, E.; Martin, J. M. L.; Ruscic, B. *J. Chem. Phys.* **2006**, *125*, 144108.

(44) Karton, A.; Martin, J. M. L. *J. Chem. Phys.* **2010**, *133*, 144102.

(45) Ruscic, B; Pinzon, R. E. Morton, M. L.; von Laszewski, G.; Bittner, S.; Nijsure, S. G.; Amin, K. A.; Minkoff, M.; Wagner, A. F. *J. Phys. Chem. A* **2004**, *108*, 9979.

(46) Ruscic, B.; Pinzon, R. E.; von Laszewski, G.; Kodeboyina, D.; Burcat, A.; Leahy, D.; Montoya, D.; Wagner, A. F. *J. Phys. Conf. Ser.* **2005**, *16*, 561.

(47) ATcT enthalpies of formation are taken from version 1.110 of the Thermochemical Network, see: http://atct.anl.gov/ (retrieved October 12, 2015).

(48) Roux, M. V.; Temprado, M.; Chickos, J. S.; Nagano, Y. *J. Phys. Chem. Ref. Data* **2008**, *37*, 1855.

(49) The atomization energy at 0 K was converted to a heat of formation at 298 K using ATcT atomic heats of formation at 0 K (H 216.034 ± 0.000 and C 711.38 ± 0.06 kJ mol^{-1}), and the CODATA enthalpy functions, $H_{298}-H_0$, for the elemental reference states (H_2(g) = 8.468 ± 0.001 and C(*cr*,graphite) = 1.050 ± 0.020 kJ mol^{-1}), while the molecular enthalpy function was obtained within the RRHO approximation from the B3LYP/6-31G(2df,p) calculated geometry and harmonic frequencies.

(50) Karton, A.; Tarnopolsky, A.; Lamère, J.-F.; Schatz, G. C.; Martin, J. M. L. *J. Phys. Chem. A* **2008**, *112*, 12868.