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Theoretical values of the enthalpies of formation of the NH_x ($x = 1, 2, 3$) compounds. Importance of the core-correlation effects

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Abstract

The enthalpies of formation of the NH_x ($x = 1, 2, 3$) compounds were theoretically estimated using the isogyric and hydrogenation reactions as working chemical reactions. Energy differences were computed at seven levels of calculation, using MP4 (with spin projection and post-PMP4 corrections), QCI, CC, and multireferential methods with two extended basis sets. Using NH_3 as the test molecule, we found that accurate results can be obtained with theoretical methods using large basis sets, elaborate correlated wavefunctions, and, above all, with the core-correlation effects explicitly considered. The value obtained for the NH_2 radical is $\Delta H_{f,298\text{ K}} = 43.8 \pm 0.6 \text{ kcal mol}^{-1}$, which is smaller than the recommended JANAF value and the latest experimental values. For the NH species, the value obtained is $\Delta H_{f,298\text{ K}} = 86.3 \pm 0.8 \text{ kcal mol}^{-1}$, in excellent agreement with other high-quality results. This last value confirms indirectly the accuracy of our proposed value for the NH_2 radical.

1. Introduction

Interest in the thermochemistry of the NH_x ($x = 1, 2, 3$) compounds is due to the important role that they play in nitrogen combustion chemistry, and to the N–H bond being among the most frequently encountered in chemistry and biochemistry.

While the enthalpy of formation of NH_3 is well determined ($\Delta H_{f,298\text{ K}} = -10.97 \pm 0.1 \text{ kcal mol}^{-1}$ [1], $\Delta H_{f,0\text{ K}} = -9.30 \pm 0.1 \text{ kcal mol}^{-1}$ [1], $\Delta H = -9.31 \pm 0.08 \text{ kcal mol}^{-1}$ [2]), the NH_2 and the NH

species present a lack of coincidence among proposed experimental values. Thus, for the enthalpy of formation of the NH_2 radical, the proposed experimental values vary between $\Delta H_{f,0\text{ K}} = 44.7 \pm 2.4 \text{ kcal mol}^{-1}$ ($\Delta H_{f,298\text{ K}} = 44.0 \pm 2.3$) based on a bracketing of the proton affinity of NH_2 [3] and $\Delta H_{f,0\text{ K}} = 48.8 \pm 3.5 \text{ kcal mol}^{-1}$ ($\Delta H_{f,298\text{ K}} = 48.1 \pm 3.5$) based on the enthalpy of formation of benzylamine [4]. However, the latest compilations diminish this range. The Russian compilation [2] proposed a value of $\Delta H_{f,0\text{ K}} = 46.1 \pm 2.4 \text{ kcal mol}^{-1}$, the most recent JANAF tables [1] recommend $\Delta H_{f,0\text{ K}} = 46.2 \pm 1.5 \text{ kcal mol}^{-1}$ ($\Delta H_{f,298\text{ K}} = 45.5 \pm 1.5$), and Anderson [5] after critical examination of all pertinent

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papers in the literature recommended $\Delta H_{f,0K} = 45.9 \pm 0.2$ kcal mol⁻¹. More recent experimental values also point in this direction: for example, $\Delta H_{f,0K} = 45.8 \pm 0.3$ [6] and $\Delta H_{f,298K} = 45.3$ kcal mol⁻¹ [7]. With respect to the enthalpy of formation of the NH species, there has unfortunately been less coincidence. Thus, the proposed experimental values vary between $\Delta H_{f,0K} \leq 94.6 \pm 1.9$ kcal mol⁻¹ [8] and $\Delta H_{f,0K} \leq 77.2 \pm 1.7$ kcal mol⁻¹ [9]. The latest compilations do not clarify this situation. The JANAF tables [1] and the Russian compilation [2] recommended $\Delta H_{f,0K} = 90 \pm 4$ and 81.0 ± 2.4 kcal mol⁻¹, respectively, and Anderson [5] proposed 85.4 ± 0.3 kcal mol⁻¹.

From a theoretical viewpoint, the controversies persist for both species. Thus, for the NH₂ radical, the values vary between $\Delta H_{f,0K} = 47.1$ [10] and 46.6 kcal mol⁻¹ [11,12], although the range is greater if we consider the theoretical values obtained by Sana and Leroy [13] at the MP4 level, which range between $\Delta H_{f,298K} = 43.98$ and 45.93 kcal mol⁻¹, depending on the reaction used in the evaluation. For the NH species, the latest values present a narrow range $86.5 \leq \Delta H_{f,0K} < 87.0$ kcal mol⁻¹ [10–12,14]. Refs. [11,12] calculate the energies at the MP4 level with frozen core approximation. Although this approximation normally seems to work well, we later see that for these compounds the core-correlation effects are important.

In the present work, we estimate theoretically the enthalpy of formation of the NH and NH₂ species, considering explicitly the core-correlation effects.

2. Methods

Molecular calculations were carried out using the GAUSSIAN 92 [15], HONDO 8.4 [16], and CIPSI [17] systems of programs. The geometrical parameters were fully optimized at the second order of Møller–Plesset perturbation theory with full electron correlation (MP2=FULL level), using the 6-31G(d, p) basis set. Then we used seven levels of calculation.

Level I. We made a single-point calculation at fourth-order Møller–Plesset perturbation theory, with full electron correlation and single, double, triple and quadruple replacements (MP4sdtq=FULL) with a

larger basis: namely, 6-311 + G(d, p). We denote this energy as

$$(R-U)MP4sdtq=FULL/6-311 + G(d, p) //$$

$$(R-U)MP2=FULL/6-31G(d, p) .$$

Level II. Continuing with the perturbational methods, we made a single-point calculation at MP4sdtq=FULL, but augmented the basis set, i.e. we used the (augmented) correlation-consistent polarized valence triple-zeta sets developed by Dunning et al. [18] (AUG-CC-PVTZ). We denote this energy as

$$(R-U)MP4sdtq=FULL/AUG-CC-PVTZ //$$

$$(R-U)MP2=FULL/6-31G(d, p) .$$

As the UHF wavefunction is not necessarily an eigenfunction of the S^2 operator, we find spin contamination. The small spin contamination has been corrected by use of a projection operator implemented in GAUSSIAN 92 (PMP4 level: projected MP4). However, it is well known that the unrestricted Møller–Plesset perturbation theory converges slowly, especially in the case of free radicals [19]. In this work, we use the fourth-order invariant quantity of Feenberg [20] with the aim of taking the post-PMP4 energy into account.

Level III. We made a single-point calculation at the quadratic configuration interaction level [21], with full electron correlation, QCISd(t)=FULL, and the same basis set as in level II. This method consists of an iterative treatment of single and double substitutions (QCISd approach) followed by a non iterative perturbative treatment of triple substitutions. We denote this energy as

$$QCISd(t)=FULL/AUG-CC-PVTZ //$$

$$(R-U)MP2=FULL/6-31G(d, p) .$$

Level IV. We made a single-point calculation with the singles and doubles coupled-cluster approach including a perturbative estimate of connected triple excitations with full electron correlation [22], CCsd(t)=FULL, and the same basis set as in level II. Scuseria and Lee [23] have shown that the average difference between CCsdt (where now the triple excitations are also included in an iterative manner),

and CCsd(t) in their fourteen test cases is 0.42 kcal mol⁻¹, and if we exclude the maximum error of 1.89 kcal mol⁻¹ for the difficult system CN⁺, the average difference is smaller still. We denote this energy as

$$\text{CCsd(t)} = \text{FULL/AUG-CC-PVTZ} //$$

$$(\text{R-U})\text{MP2} = \text{FULL}/6\text{-}31\text{G(d,p)}.$$

Levels V–VII. Single point calculations using the complete active self-consistent-field (CASSCF) approach were performed including all valence electrons in the active space and the same basis set as in level II. Taking these CASSCF wavefunctions as reference, all determinants arising from single and double excitations from this multireference wavefunction were generated and their contributions to the correlation energy computed through Møller–Plesset perturbation theory (level V, CASPT2). The most important of those determinants (up to 70000) were then diagonalized and the convergence limit of the series was estimated by extrapolation (level VI, multireference configuration–interaction approach, MR-sdCI). The full-CI correction (level VII, MR-sd{Q}CI) was obtained as proposed by Langhoff and Davidson, denoted {Q} [24].

Theoretically, the accuracy of the enthalpies of formation is conditioned mainly by just a few factors: the reliability of the enthalpies of formation of reference compounds, the uncertainty in the thermal corrections, the level and accuracy of the electronic energy, the spin contamination (if radicals are involved), and, most importantly, the choice of the working chemical reaction used in the evaluation. Sana et al. [13,25], for XH_n compounds, carried out an exhaustive study with extended basis sets of two types of reaction: isogyric and abstraction on H₂ (for radicals). They conclude that, on average, these two reactions give close results, with errors of ±1 kcal mol⁻¹.

3. Results and discussion

The zero-point energies (ZPE) and thermodynamic corrections (TC), and the enthalpies of formation of reference compounds are listed in Table 1. To avoid errors from the local potential shape we use experimental thermal corrections when available,

even if it was known that the uncertainty in the theoretical thermal corrections was not larger than a few tenths of a kcal mol⁻¹.

3.1. NH₃ molecule

The purpose of introducing the study of the NH₃ molecule into the present work is because it can be used as a test of several variables in the subsequent study of the NH₂ and NH species: namely, the basis set, the method for introducing correlation energy, and the working chemical reaction used in the evaluation of the enthalpy of formation.

As the working chemical reaction, we used the isogyric reaction



The enthalpies of formation of NH₃, $\Delta H_{f,298\text{K}}$, are listed in Table 2, with and without core-correlation effects. First, we must point out that the level I result shows that the 6-311 + G(d, p) basis set is poorly suited to describing this system. Similarly, the CASPT2 result (level V) shows this method to be inadequate for the description of the correlation effects in this system. The core-correlation contribution to the enthalpy of formation is quite constant, 3–4 kcal mol⁻¹ at levels II–VI. Levels II and VI slightly overestimate the experimental value. The agreement at the all electrons correlation level between the predictions based on the QCI, CC, and MR-sd{Q}CI methods lends confidence to the value that we have obtained as the average of levels III, IV, and VII: $\Delta H_{f,298\text{K}} = -11.3$ kcal mol⁻¹ ($\Delta H_{f,0\text{K}} = -9.8$ kcal mol⁻¹), which is only ≈0.4 kcal mol⁻¹ more than the experimental value ($\Delta H_{f,298\text{K}} = -10.97 \pm 0.1$, $\Delta H_{f,0\text{K}} = -9.30 \pm 0.1$ kcal mol⁻¹ [1]).

Table 1
Thermal corrections^a, and enthalpies of formation^a (kcal mol⁻¹)

Compound	ZPE	TC _{298K}	$\Delta H_{f,0\text{K}}$
H	0.0	1.48	51.68
H ₂	6.30	2.02	0.0
N	0.0	1.48	112.53
NH	4.69	2.06	90
NH ₂	11.28	2.37	46.2
NH ₃	21.53	2.41	-9.30

^a Ref. [1].

Table 2

Core-correlation effects on the enthalpy of formation (298 K) of the NH_x species (kcal mol^{-1}) using several levels of calculation

Level	Valence electrons correlated	All electrons correlated	Core-correlation contribution to $\Delta H_{f,289\text{K}}$ ^a
NH_3 ^b (exp. -10.97 ± 0.1 ^c)			
I	-1.62	-2.04	0.42
II	-7.85	-12.10	4.25
III	-7.15	-11.38	4.23
IV	-7.08	-11.30	4.22
V	1.2	-2.72	3.94
VI	-9.52	-12.48	2.96
VII	-11.12	-11.32	0.20
others	$-10.8^d, -10.3^e$ -9.2^e	-11.21^f	
NH_2 ^g			
I	51.14	50.75	0.61
	41.80	41.93	0.13
II	45.78	42.69	3.09
	42.66	43.82	1.16
III	46.49	43.41	3.08
	42.68	43.82	1.14
IV	46.55	43.46	3.09
	42.66	43.80	1.14
V	39.82	35.80	4.07
	52.04	49.18	2.86
VI	44.04	36.21	7.83
	45.49	42.85	2.64
VII	45.95	38.37	7.58
	45.79	43.18	2.61
others		43.83^f 44.08^f	
NH ^{g,h}			
I	89.55	89.41	0.14
	83.90	84.14	0.24
II	86.80	84.98	1.82
	86.52	87.80	1.28
III	87.24	85.46	1.78
	86.24	87.54	1.30
IV	87.27	85.50	1.77
	86.21	87.54	1.33
V	90.65	89.06	1.59
	84.11	85.38	1.27
VI	89.54	87.58	1.96
	89.56	90.22	0.66
VII	88.65	86.52	2.13
	88.40	88.83	0.43
others		86.3^i	

^a Mean absolute deviate. ^b Using isogyric reaction (Eq. (1)).^c Ref. [1]. ^d Ref. [11]. ^e Ref. [13]. ^f Ref. [26].^g At each level, the first entry corresponds to the isogyric reaction and the last entry to the hydrogenation reaction.^h Here, we use the JANAF value for the enthalpy of formation of the NH radical (45.5 ± 1.5 kcal mol).ⁱ Ref. [14], from the bond dissociation energy.

To test the quality of the basis set used, let us compare our result at level IV (CCsd(t)=FULL/AUG-CC-PVTZ) with the results obtained using the energies of Kraka et al. [26]¹ with a larger basis (CCsd(t)=FULL/AUG-CC-PVQZ). With these energies and full correlation correction, we obtain $\Delta H_{f,298\text{K}} = -11.21$ kcal mol⁻¹, in excellent agreement with our value of -11.3 kcal mol⁻¹. Therefore, we can consider the AUG-CC-PVTZ basis used in this work to be sufficient for a correct description of the system.

The agreement with experiment found by other authors [11,13] could be fortuitous or due to error cancellation. If one analyzes carefully the results of Ref. [13] (see also Ref. [25]) one finds two effects.

(i) Basis set effect. In the frozen core approach, when the basis set is larger, the enthalpy of formation is worse,

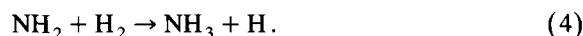
$$D(6-311 + + G(3df, 2p) - 6-31 + G(2df, p)) \\ = +1.31 \text{ kcal mol}^{-1}.$$

(ii) Post-MP4 effect. In the frozen core approach, when the post-MP4 corrections are included via $\Delta E(\text{QCI})$, as defined by Pople et al. [27] ($\Delta E(\text{QCI}) = E(\text{QCISd}/6-311\text{G}(\text{d}, \text{p}) - E(\text{MP4}/6-311\text{G}(\text{d}, \text{p}))$), the enthalpy of formation is also worse: $\Delta E(\text{QCI}) = +1.2$ kcal mol⁻¹.

Therefore, considering these two effects, $\Delta H_{f,298\text{K}}$ goes from -10.33 to -7.82 kcal mol⁻¹. To obtain agreement with experiment again, it is necessary to introduce the full core correlation, as has just been seen.

3.2. NH_2 radical

As the working chemical reactions we use the isogyric (3) and the hydrogenation (4) reactions,



To reject the geometrical optimization effect, we optimized the NH_2 radical at UMP2=FULL/6-31G(d, p) and QCISd(t)=FULL/6-31G(d, p) levels.

¹ We thank Prof. Kraka for the unpublished energy of N.

At the MP2 (and QCI) levels, we obtain N–H: 1.023 Å (1.029 Å) and HNH: 102.7° (102.3°). Comparison with the experimental geometry [1], 1.024 Å and 103°, shows that the MP2 level adequately describes the geometrical parameters of this system.

The enthalpies of formation of the NH_2 radical, $\Delta H_{f,298\text{K}}$, with and without core-correlation effects, are also listed in Table 2. Firstly, if we use the isogyric reaction (3) the core-correlation contribution to the enthalpy of formation is $\approx 3 \text{ kcal mol}^{-1}$ at levels II–IV and larger ($7\text{--}8 \text{ kcal mol}^{-1}$) at levels VI and VII. This behaviour is like the NH molecule. However, if we use the hydrogenation reaction (4) the core-correlation effect is considerably smaller ($\approx 1.5 \text{ kcal mol}^{-1}$ at levels II–IV and $\approx 2.6 \text{ kcal mol}^{-1}$ at levels VI–VII). Therefore, as can be seen, the hydrogenation reaction is less sensitive to the core-correlation effects.

As with the conclusions obtained for the NH_3 molecule, we use the values obtained at levels III, IV and VII, because the results of levels II and VI seem to be overestimated. Using the isogyric reaction with the frozen-core approach we obtain an average value of $\Delta H_{f,298\text{K}} = 46.3 \text{ kcal mol}^{-1}$ at less than 1 kcal mol^{-1} from the recommended value, 45.5 ± 1.5 [1], while if we use the hydrogenation reaction (4) with the frozen core approach we obtain a smaller value, $43.7 \text{ kcal mol}^{-1}$. However, as we have just demonstrated for the NH_3 molecule, the core-correlation contribution to the enthalpy of formation is important, which leads us to think that the agreement of the isogyric reaction (frozen core approach) with experiment is fortuitous. Using the full correlation, we obtain an average value of $\Delta H_{f,298\text{K}} = 41.7$ and $43.6 \text{ kcal mol}^{-1}$ using the isogyric and the hydrogenation reactions, respectively. With the energies of Kraka et al. [26] we obtain 43.8 and 44.1 kcal mol^{-1} , respectively. Due to the hydrogenation reaction being less sensitive to the core-correlation effects, we will only use these values. The agreement between the predictions based on the various methods (hydrogenation reaction with full correlation) and basis sets lends confidence to the value that we recommend: $\Delta H_{f,298\text{K}} = 43.8 \pm 0.6 \text{ kcal mol}^{-1}$ ($\Delta H_{f,0\text{K}} = 44.4 \pm 0.6 \text{ kcal mol}^{-1}$). This value is smaller than the recommended values [1,2,5] and the latest experimental results [6,7], although it is in agreement with the value of DeFrees et al. [3]. We

will return to this result when we analyze the enthalpy of formation of the NH species.

In the light of these results and bearing in mind the quality of the energies of this work, we think that a revision of the experimental results of the NH_2 enthalpy of formation is advisable.

3.3. NH species

As for the NH_2 radical, we use the isogyric (5) and the hydrogenation (6) reactions as working chemical reactions,



The enthalpies of formation, $\Delta H_{f,298\text{K}}$, with and without core-correlation effects, are also listed in Table 2. The core-correlation contribution to the enthalpy of formation of the NH species is 1.9 and $1.0 \text{ kcal mol}^{-1}$ using the isogyric and the hydrogenation reaction, respectively. Again, the hydrogenation reaction is less sensitive to the core-correlation effects, although now the difference is smaller.

Again, we will only use the values obtained at levels III, IV and VII. Using the isogyric reaction with full correlation, we obtain an average value of $\Delta H_{f,298\text{K}} = 85.8 \text{ kcal mol}^{-1}$. Note that in this reaction (Eq. (5)), the enthalpies of formation of the reference compounds, N, H and H_2 , are well determined. However, in the hydrogenation reaction (6) we use the NH_2 radical for which we have just proposed a new value of $\Delta H_{f,298\text{K}} = 43.8 \pm 0.6 \text{ kcal mol}^{-1}$ ($\Delta H_{f,0\text{K}} = 44.4 \pm 0.6$) versus the recommended value of 45.5 ± 1.5 ($\Delta H_{f,0\text{K}} = 46.2 \pm 1.5$) [1]. In this reaction, if we use the latter value of $45.5 \pm 1.5 \text{ kcal mol}^{-1}$ for the reference compound NH_2 , we obtain an average value of $\Delta H_{f,298\text{K}} = 88.0 \text{ kcal mol}^{-1}$ for the NH species, while if we use our new proposed value ($43.8 \pm 0.6 \text{ kcal mol}^{-1}$) we obtain $\Delta H_{f,298\text{K}} = 86.3 \text{ kcal mol}^{-1}$. This last result is in excellent agreement with the value obtained with the isogyric reaction. Therefore, we propose a value of $\Delta H_{f,298\text{K}} = 86.3 \pm 0.8 \text{ kcal mol}^{-1}$ ($\Delta H_{f,0\text{K}} = 86.5 \pm 0.8$) for the NH species.

Indirectly, the agreement between these two reactions lends confidence to our new proposed value for the enthalpy of formation of the NH_2 radical.

Table 3

	$\text{NH}_2 + \text{H}_2 \rightarrow \text{NH}_3 + \text{H}$		Ratio
FC approach	$(7 \times 6/2)1$	$(8 \times 7/2)$	$28/22 = 1.27$
FULL approach	$(9 \times 8/2)1$	$(10 \times 9/2)$	$45/37 = 1.22$

To examine the accuracy of our result for the NH species (and indirectly for the NH_2 radical), we calculated the bond dissociation energy for the NH species. With our enthalpy of formation of NH, we obtain $D_0 = 77.7 \pm 0.8 \text{ kcal mol}^{-1}$, within the range of experimental values $80.02 < D_0 < 75.87$ [28–30], and in excellent agreement with the high-quality result of Bauschlicher and Langhoff [14]: $77.71 \pm 0.69 \text{ kcal mol}^{-1}$. These results also seem to confirm the new enthalpy of formation found for the NH_2 radical.

Finally, one explanation as to why the hydrogenation reactions are less sensitive to the core-correlation effects than the isogyric reactions can be seen by considering the difference between the number of interacting electron pairs for products and reactants. Following the reasoning of Harding [31], there will always be some residual correlation error for each interacting pair of electrons in any basis set expansion of finite size. For the hydrogenation reactions (Eqs. (4) and (6)), the ratio of the number of interacting pairs of electrons between products and reactants is ≈ 1.3 , in the frozen-core and in the full approach, (see Appendix A for more detail). However, for the isogyric reactions (Eqs. (5), (3) and (1)) this ratio is larger: 1.3 (1.4), 1.6 (1.8) and 2.0 (2.5) for the NH, NH_2 and NH_3 full approach (frozen-core), respectively. We can see that in the frozen-core approach the difference is greater.

This reasoning leads us to the interesting conclusion that the difference of the number of interacting pairs of electrons between products and reactants is the key to the choice of the working chemical reaction if we use correlated wavefunctions. Thus, while the isogyric reactions present a large difference, the hydrogenation reactions present a small difference, i.e. the latter presents a better conservation of the nature of the pairs between reactants and products, and the inter-pair correlation error (core-valence) will thus be of the same magnitude between reactants and products. This will certainly not be the case in isogyric reactions. On the other hand, when larger

molecules are involved, the more economical isodesmic approach must be used. By definition, in this type of process, all the bonds are conserved (in number and nature) and this leads to approximate cancellations not only of correlation errors but also of ZPE and thermal corrections. Thus, the energy change is obtained theoretically at the SCF level. This error correlation cancellation can also be explained because the number of interacting pairs of electrons between products and reactants is similar or even, at times, equal for this type of reaction.

4. Appendix A

Following the suggestions of the referee, in this Appendix we give an explicit example. For reaction (4), the ratio of the number of interacting pairs of electrons between reactants and products is given in Table 3.

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