Standard Gibbs energies of formation and equilibrium constants from ab-initio calculations: Covalent dimerization of NO₂ and synthesis of NH₃

Neha Awasthi a,*, Thomas Ritschel b, Reinhard Lipowsky a, Volker Knecht a

a Department of Theory & Biosystems, Max Planck Institute of Colloids and Interfaces, Am Mühlenberg 1, D-14476 Potsdam, Germany
b Institut für Chemie, Universität Potsdam, Karl-Liebknecht-Str. 24–25, D-14476 Potsdam, Germany

ARTICLE INFO

Article history:
Received 4 January 2013
Received in revised form 11 March 2013
Accepted 13 March 2013
Available online 30 March 2013

Keywords:
Equilibrium constants
Thermochemical properties
Ab-initio calculations

ABSTRACT

Standard quantum chemical methods are used for accurate calculation of thermochemical properties such as enthalpies of formation, entropies and Gibbs energies of formation. Equilibrium reactions are widely investigated and experimental measurements often lead to a range of reaction Gibbs energies and equilibrium constants. It is useful to calculate these equilibrium properties from quantum chemical methods in order to address the experimental differences. Furthermore, most standard calculation methods differ in accuracy and feasibility of the system size. Hence, a systematic comparison of equilibrium properties calculated with different numerical algorithms would provide a useful reference. We select two well-known gas phase equilibrium reactions with small molecules: covalent dimer formation of NO₂ (2NO₂ → N₂O₄) and the synthesis of NH₃ (N₂ + 3H₂ → 2NH₃). We test four quantum chemical methods denoted by G3B3, CBS-APNO, W1 and CCSD(T) with aug-cc-pVXZ basis sets (X = 2, 3, and 4), to obtain thermochemical data for NO₂, N₂O₄ and NH₃. The calculated standard formation Gibbs energies ∆G°f are used to calculate standard reaction Gibbs energies ∆G° and standard equilibrium constants K°eq for the two reactions. Standard formation enthalpies ∆H°f are calculated in a more reliable way using high-level methods such as W1 and CCSD(T). Standard entropies S° for the molecules are calculated well within the range of experiments for all methods, however, the values of standard formation Gibbs energies ∆G° show some dependence on the choice of the method. High-level methods perform better for the calculation of molecular energies, however, simpler methods such as G3B3 and CBS-APNO perform quite well in the calculation of total reaction energies and equilibrium constants, provided that the chemical species involved do not exhibit molecular geometries that are difficult to handle by the applied method. The temperature dependence of standard reaction Gibbs energy ∆G° for the NH₃ reaction is discussed by using the calculated standard formation Gibbs energies ∆G°f of the reaction species at 298.15 K. The corresponding equilibrium constant K°eq as a function of temperature is found to be close to experimental values.

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1. Introduction

Thermodynamics of equilibrium reactions provides valuable information about the underlying reaction mechanism. Accurate experimental measurements to determine equilibrium properties such as enthalpy, Gibbs energy of reaction and equilibrium constant, K°eq, are often challenging. Computational methods provide a useful tool to corroborate these experimental measurements. Molecular dynamics (MD) simulations have been used to predict K°eq for weak complexes with non-covalent interactions and the lifetime of non-covalently formed dimers [1]. Although MD simulations are useful for large systems and can include solvent interactions, the prediction of K°eq is limited in accuracy because of the classical treatment of formation and dissociation of reaction species. Quantum chemical calculations are useful to get accurate thermodynamic data [2] as well as information about dynamical properties such as reaction intermediates, activation energies, and rate constants [3].

Experimentally, the equilibrium constant K°eq can be determined by measurements of infrared (IR) or ultra-violet(UV)-visible spectra [4,5], or by measurements of the sound velocity in the equilibrium mixture [4]. For gas phase reactions, K°eq is also calculated from pressure measurements [4]. Equilibrium reactions are strongly temperature dependent [5] and direct experimental measurements can be conducted for a range of temperatures using methods such as flash photolysis-shock tube techniques [6]. The temperature dependence of K°eq is often used to calculate enthalpies and Gibbs energies of reactions [7,8]. Standard formation enthalpies, ∆H°f, for molecules are determined from calorimetric experiments [9,10] or vapor pressure measurements [10]. K°eq for
a reaction can also be calculated by constructing a reaction scheme [5], with Gibbs energies, \( \Delta G \), and \( K^{eq} \) of intermediate reactions involved as input. Input values may be from sources that differ in accuracy (literature or additional experiments), which can give rise to possible discrepancies. \( K^{eq} \) values are extrapolated using thermodynamic data, which also contributes to the uncertainty. Many recent experimental calorimetry studies also include quantum chemical calculations to support experimental measurements [10–12]. Furthermore, unconventional reaction conditions (temperature, pressure, absence of catalysts, solvents) which are not easily accessible in a laboratory can be probed using simulations. In fact, density functional and other model chemistry simulation methods have been used to check experimental data, such as \( \Delta H_f \), and to resolve discrepancies between reported values [13,14,11,15]. Ruscic et al. [16] presents a critical evaluation of thermochromy data from various experimental sources (kinetic, spectroscopic, and ion cycle studies) for some organic radicals, and includes high-level theoretical calculations to settle discrepancies. Quantum chemical calculations have also been used to provide accurate structural parameters, such as the equilibrium N–H bond length in molecules including NH3, using three different methods [17]. Demaison et al. [17] also provides the evolution of the estimates of the structure of NH3 with time. Apart from stable molecules, thermochromical calculations are quite useful in the characterization of structural and thermochemical properties of radicals and ions, such as NH4+ [17] and NO3− [18].

For simple chemical reactions involving small molecules, quantum mechanical methods are efficient for calculating \( \Delta H, \Delta G \), and \( \Delta G^{eq} \), and hence, predicting \( K^{eq} \). Benchmark thermochromical calculations have been reported in the literature for several molecular species and the NIST thermochromy database is a collection of such data [19]. We emphasize that our investigation with the choice of reaction species using four different compound thermochromy methods does not correspond to an existing entry in the database. In fact, our work reporting structural, vibrational and thermochromical data makes a useful addition to the NIST repository [19].

We consider two well investigated gas phase reactions involving small molecules consisting of less than 10 atoms: Covalent dimer formation of NO2 and uncatalyzed synthesis of NH3. Experimental values for \( K^{eq} \) are available for both of these reactions [4,20,21]. For the NO2 reaction, a critical review of the measurements of \( K^{eq} \) as a function of temperature using several experimental techniques is provided in Ref. [4]. We note that the equilibrium constants for both these reactions have not been discussed from a computational perspective with comparison between several methods. We present a systematic study comparing four \textit{ab initio} methods such as G3B3, CBS-APNO, W1 and CCSD(T), of different accuracy and computational intensity, to calculate the Gibbs energies \( \Delta G^{eq} \), and \( \Delta G \), as well as the equilibrium constants \( K^{eq} \). To our knowledge, our study is the first comparing equilibrium constants obtained from different methods, and discussing the temperature dependence of calculated versus experimental equilibrium constants.

The four methods that we consider have been developed starting from different theoretical frameworks. Hence, there is a significant difference in their performance, with respect to accuracy and computational expense. However, the choice of a given method cannot be naively made on the basis of performance alone. The application of a particular method for a given molecule may lead to unexpected results, as we see later in our work. Therefore, it is useful to have studies that offer a comparative perspective and report interesting outliers/limitations for a method. Our work also contributes towards this goal. We use Ref. [22] as a source for experimental data, and we have checked that there are no computational results reported for the combination of reactions and methods that we study here.

The higher level methods, such as W1 and CCSD(T), though accurate, are not feasible for molecules that contain more than 10 atoms. Our study provides a comparison between different methods which can be used for a range of molecular sizes. We note that our aim is not to repeat the earlier works, which computed geometries and energies up to very high levels of accuracies (see Ref. [23]), but to show that one can study formation and equilibrium processes at an intermediate level of accuracy, with some extrapolation of the incompleteness of the basis set. Such computationally inexpensive methods are useful if one can expect to find reasonable agreement between calculated and experimental thermochromy data. We compare our results, such as structural parameters, vibrational frequencies, and energies, with those of previous studies. There has been a previous quantum chemical calculation for the formation of oxides of nitrogen (NO2 and N2O4, among others) [24] using the CCSD(T) method which reports structural parameters, enthalpies, entropy [24]. We show that our CCSD(T) data are consistent with the results in Ref. [24]. Our paper is organized as follows: Section 2 describes the details of the methods used. The results and the discussion are presented in Section 3, followed by conclusions in Section 4.

2. Method

We study two gas phase equilibrium reactions, covalent dimer formation of NO2 and synthesis of NH3, for which the experimental equilibrium data are given in table 1. The Gibbs energy \( \Delta G \) for these equilibrium reactions can be expressed as

\[
\Delta G = \Delta G^{eq} + RT \ln Q,
\]

where \( R \) is the gas constant and \( T \) the absolute temperature. \( Q \) is the reaction quotient, which is given by

\[
Q = \left( \frac{P_{NO2}/P_r}{P_{N2O4}/P_r} \right)^{1/2},
\]

for the NO2 dimerization reaction, where \( P \) is the standard pressure and \( P_{NO2} \) or \( P_{N2O4} \) denote the partial pressures for the product or reactant, respectively. At chemical equilibrium, \( \Delta G = 0 \) and \( Q \) becomes equal to the equilibrium constant \( K^{eq} \), such that

\[
\Delta G^{eq} = -RT \ln K^{eq}.
\]

The standard reaction Gibbs energy, \( \Delta G^{eq} \), is equal to the difference in the standard Gibbs energies of formation, \( \Delta G_f \) [25], of the products and reactants. Hence, the equilibrium constant \( K^{eq} \) for the NO2 reaction is given as

\[
K^{eq} = e^{\Delta G_f(N_{O2}) - \Delta G_f(2N_{O4})},
\]

For the NH3 reaction, as given in table 1, one has

\[
K^{eq} = e^{\Delta G_f(NH_3) - \Delta G_f(2NH_2)}.
\]

The Gibbs energy of formation, \( \Delta G_f \), is defined as the standard reaction Gibbs energy for the formation of the compound from its

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( K^{eq} )</th>
<th>( \Delta G/kJ \cdot mol^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 2NO_2 \rightleftharpoons N_2O_4 )</td>
<td>6.54–10.64</td>
<td>(-4.73 \text{ to } -5.86)</td>
</tr>
<tr>
<td>( N_2 + 3H_2 \rightleftharpoons 2NH_3 )</td>
<td>5.94 \times 10^5</td>
<td>(-32.90)</td>
</tr>
</tbody>
</table>
elements in their reference states, where reference state is the most stable state of the element at the specified temperature (298.15 K for our calculations) and pressure of 1 bar [25].

The equilibrium constant calculated via ΔG° using statistical thermodynamic calculations is dimensionless. According to the IUPAC recommendation [26], the dimensionless equilibrium constant defined at standard conditions is also called the thermodynamic equilibrium constant. However, experimental studies often report equilibrium constants in units of pressure for gas phase reactions, which will be denoted as Kp. For the reactions shown in Table 1, the equilibrium constants Kp are defined in terms of the partial pressures at equilibrium and given by

\[ K_p = \frac{P_{(NO)}}{P_{(NO_2)}} \]  

(6)

and

\[ K_p = \frac{(P_{(NH_3)})^2}{(P_{(N_2)})(P_{(H_2)})^2} \]  

(7)

Using the ideal gas law for a reaction in the gas phase at constant temperature (standard temperature 298.15 K in our case), we obtain the relation

\[ K_p = K_{eq} (P^\Lambda n) \]  

(8)

where P is the standard pressure, 10^5 Pa or 1 bar and \( \Lambda n \) denotes the difference between the sum of the stoichiometries of the products and the reactants. For the NO2 dimerization reaction, \( \Lambda n = -1 \) while for the synthesis of NH3, \( \Lambda n = -2 \) (see Table 1). We use the dimensionless equilibrium constant, denoted by \( K_{eq} \) in our work, and all experimental values of \( K_p \) are duly converted for consistent comparison.

The standard formation Gibbs energy, \( \Delta f G_m \), was determined via ab-initio calculations using the Gaussian 03 [27] and MOLPRO [28] packages. Geometry optimizations and thermochemistry calculations were performed using the G3B3 [29], CBS-APNO [30], W1 [31], and CCSD(T) [32] methods for the NO2, N2O4 and NH3 molecules in the gas phase. In order to calculate formation energies, we also performed the same set of calculations for the N2, O2, and H2 molecules.

These standard methods differ in the underlying theoretical procedure as well as the accuracy. G3B3, CBS-APNO, and W1 are compound thermochemistry methods, which employ several steps of calculations using various basis sets and correction factors (except W1). Hence, there is a dependence of calculated Gibbs energies and equilibrium constants on the basis sets and the level of theory. G3B3, one of the Gaussian model chemistry (GX) methods [33], uses the B3LYP functional for structure and frequency (at the B3LYP/6-31G(d,p) level) calculations. Calculations do not require excessive time or computing resources, and thermochemistry data are obtained within the accuracy of \( \pm 4.13 \) kJ·mol\(^{-1}\) [29]. The CBS-APNO method utilizes the asymptotic convergence of pair natural orbitals to overcome the error introduced due to the single-electron basis set truncation [30]. This method includes higher order correlations, as compared to GX methods, with a relatively smaller basis set. The calculated energy is extrapolated to the complete basis limit, which improved the accuracy to \( \pm 2.09 \) kJ·mol\(^{-1}\) [30] at a relatively low computational expense. Frequencies are calculated at the HF/6-311G(d,p) level [30]. Both GX and CBS methods have issues with spin-contamination in open-shell molecules, low-lying virtual orbitals and molecules having multiple lone pairs on the same atom.

The W1 level of theory [31] performs a CCSD calculation [32] using Dunning's augmented polarized correlation-consistent polarized valence basis sets (aug-cc-pVXZ avdz) [34,35], and does not use empirical corrections like the GX and CBS methods. It is one of the most intensive methods with an accuracy on the order of \( \pm 1.25 \) kJ·mol\(^{-1}\) [31]. The computational cost makes it feasible for small molecules only. For the open-shell systems N2O and O2, the spin-unrestricted W1U method is used. Frequency calculation is done at the B3LYP/aug-cc-pVTZ level. We also performed coupled cluster calculations with single and double excitation and non-iterative triples [32] CCSD(T) [closed shell systems] and UCCSD(T) using aug-cc-pVXZ (a = 2, 3, 4, =D, T, Q for double-\( \zeta \), triple-\( \zeta \), and quadruple-\( \zeta \), respectively) levels, closely following the procedure described in [24]. This approach starts with geometry optimization and computation of vibrational frequencies using the aug-cc-pVQZ basis set. For open shell molecules, like NO2 and O2, spin-unrestricted UCCSD(T) calculations (based on ROHF orbitals) are conducted. In order to estimate the electronic energies in the complete basis set (CBS) limit, single point calculations are performed for the triple-\( \zeta \) and quadruple-\( \zeta \) basis sets (aug-cc-pVTZ and aug-cc-pVQZ, respectively), using the geometries obtained at the double-\( \zeta \) level. Following the work of Peterson et al. [36], the CBS-extrapolated energies \( E_{CBS} \) are obtained by representing the calculated energies as the following mixed exponential plus Gaussian function:

\[ E[X] = E_{CBS} + a e^{-(X-1)^2} + b e^{-(X-1)^2/2}. \]  

(9)

Here, X denotes the ordinal number for the basis set as explained above, \( E_{CBS} \) is the extrapolated energy in the complete basis set limit, whereas a and b are fitting parameters. The expected accuracy of this method is \( \pm 2.0 \) kJ·mol\(^{-1}\) [37].

In order to determine \( \Delta f G_m \) for a compound X of composition \( \text{A}_n \text{B}_m \), thermochemistry calculations using a particular method are performed for \( \text{A}_n \text{B}_m \), and the stable form of constituent elements A and B. Effectively, one considers the formation of the molecule from its constituent elements, being diatomic gases H2, N2, and O2 in our case.

We directly compute of the enthalpies and Gibbs energies by taking the appropriate differences in energies according to the formation reactions. This can be done since all the reference elemental standard states are diatomic gases (H2, N2, and O2). Furthermore, this procedure does not require the actual computation of atomization energies which might be problematic for O and N, e.g., due to spin contributions. It should be noted that this is in contrast to the procedure based on atomization energies which is typically used for molecules containing carbon or other elements, for which the computation of the elemental standard states is not feasible. This latter procedure does not correspond to a full ab-initio calculation since it also makes use of experimental data. In contrast, we use an unbiased ab-initio approach. We note that formation energies can also be calculated accurately using isodesmic reactions. However, in our case of simple gas phase reaction with few species, the calculation of formation energies using formation reactions is quite accurate and reasonable.

It is required that the enthalpies and Gibbs energies are calculated for optimized structures corresponding to a local minima. To validate this, vibrational frequencies were calculated for each species, and compared with available experimental data [20]. Unless stated otherwise, all calculations were performed at

1 Error is the average absolute deviation from experiment in energies calculated for a test set with 299 molecules.
2 Error is the mean absolute deviation of a model from experiment, for the 125 energies of the G2 test set. The maximum deviation from experiment observed within the test set is 6.27 kJ·mol\(^{-1}\).
3 Error is the mean absolute error and the method includes only a single, molecule-independent empirical parameter.
298.15 K and 1 atm pressure. The frozen core approximation was used for all calculations. We note that standard pressure is 1 bar for the definition of $\Delta C_p$, however, in both MOLPRO and Gaussian, thermochemical calculations assume a pressure of 1 atm ($=1.01325$ bar). Hence, one expects a deviation of $\pm 1\%$ between calculated and experimental data.

3. Results

The results in this section are organized as follows. We first summarize the structural parameters such as bond lengths, bond angles and vibrational frequencies. Thermochemistry data such as $\Delta H$, $S$, and $\Delta C_p$ are given in Section 3.2, followed by equilibrium constants. Finally, in Section 3.4, the temperature dependence of $\Delta C_p$ is discussed.

3.1. Structural parameters and vibrational frequencies

Structural data for the reaction species involved in the two equilibrium reactions described in Section 2 are shown in Table 2. Experimental data are taken from [40] for N2O4, and from [41] for NO2 and NH3. The structural data we report for the three molecules are a set for comparison between the four methods (see Section 2 for details) tested in this work. Some of the methods we have tested have been reported for one of the species earlier [24,23,42]. We present all our results for the sake of completeness.

Table 2 shows the comparison of bond lengths and bond angles for the equilibrated structures of N2, H2, O2, NH3, NO2 and N2O4 calculated for all the four methods considered. In fact, we observe that structural parameters for small molecules can be reproduced with little computational cost and time, using methods such as G3B3. We see a consistent agreement between calculated and experimental parameters for all the three molecules, for the four methods we have tested. The bond lengths for N2, H2 and O2 calculated in our study are in good agreement with those predicted from experiments [22]. The bond lengths obtained at the CCSD(T)/aug-cc-pVDZ level are typically a bit too large, especially for the diatomics, which is due to the relatively small basis set.

For NH3, a dummy atom denoted as X was placed on the C3 axis above the N atom in NH3 in order to obtain the optimized structure with the correct C3v symmetry. The improper dihedral angle of 120 degrees was kept constant during geometry optimization. Bond lengths and angles calculated using the W1 method are in best agreement with the experimental data, while the CBS-APNO parameters show the largest deviation from the experimental values. The structure of N2O4 is planar (D$_{2h}$ symmetry) and the dihedrals angles (O–N–N–O) are 0 and 180 degrees. The parameters for NO2 and N2O4 calculated in this work using the CCSD(T) method agree well with those reported in an earlier study [24]. For CBS-APNO, we note a rather short N–N bond (0.1688 nm) in the N2O4 molecule. This indicates that the underlying RHF level of theory used in CBS-APNO for obtaining the geometry partly fails here. Our CBS-APNO N–O and N–N bond lengths for N2O4 are identical to those reported in [42].

Table 2 shows unscaled vibrational frequencies for NH3, NO2 and N2O4. We compare the data obtained from the four different methods and also with experiments. Experimental frequencies for N2O4 are taken from [43], for NO2 from [44,45] and for NH3 from [44]. All frequencies, for the three reaction species, calculated using W1 and CCSD are in better agreement with experiments as compared to those calculated using G3B3 and CBS methods.

For NH3, the maximum deviation from the experimental measurement is observed for the $a_1$ mode of 950 cm$^{-1}$, for all the four methods. This mode corresponds to the umbrella mode with symmetric deformation motion. The other modes agree with the experimental data, with W1 and CCSD(T) performing better, as expected. We see a maximum deviation for the CBS-APNO frequencies, and this can be attributed to the rather strained optimized structure of NH3 modeled by this method.

For NO2 and N2O4, the vibrational frequencies calculated using CCSD(T) are consistent with those reported in [24] and in best agreement with experiments. Those calculated using W1 are also in good agreement with experiments. Among the four methods, the CBS-APNO frequencies show the largest deviation for both NO2 and N2O4 for all the modes. In case of N2O4 the largest deviations are apparent for the symmetric stretch mode $a_2$ which is directly affected by the short N–N distance. For the other modes, the effect is less pronounced.

Vibrational frequencies are obtained in the harmonic approximation. Scaling factors, between 0.8–1.0, are defined by the average ratio of experimental to calculated frequencies. These factors compensate for the approximation used in the calculations and the inaccuracies of a given level of theory. Table 3 shows the scaling factors calculated from our data, averaged over all modes for each molecule, for a given method. Values in parentheses are scaling factors recommended for a particular method from other studies [29–31]. We observe that the scaling factor for G3B3 is

<table>
<thead>
<tr>
<th>Molecule (symmetry)</th>
<th>Parameter</th>
<th>G3B3</th>
<th>CBS-APNO</th>
<th>W1</th>
<th>CCSD(T)</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2 (D$_{2h}$)</td>
<td>$r_{\text{a,b}}$</td>
<td>0.1055</td>
<td>0.11041</td>
<td>0.10915</td>
<td>0.1121</td>
<td>0.1098</td>
</tr>
<tr>
<td>H2 (D$_{2h}$)</td>
<td>$r_{\text{a,b}}$</td>
<td>0.07428</td>
<td>0.07355</td>
<td>0.07409</td>
<td>0.0762</td>
<td>0.0741</td>
</tr>
<tr>
<td>O2 (D$_{2h}$)</td>
<td>$r_{\text{a,b}}$</td>
<td>0.12146</td>
<td>0.11569</td>
<td>0.12059</td>
<td>0.1220</td>
<td>0.1208</td>
</tr>
<tr>
<td>NH3 (C3v)</td>
<td>$r_{\text{a,b}}$</td>
<td>0.1019</td>
<td>0.1000</td>
<td>0.1014</td>
<td>0.1024</td>
<td>0.1012</td>
</tr>
<tr>
<td>$\alpha_{\text{a,b}}$</td>
<td>105.785</td>
<td>107.46</td>
<td>106.50</td>
<td>105.9</td>
<td>106.67</td>
<td></td>
</tr>
<tr>
<td>NO2 (C2v)</td>
<td>$r_{\text{a,b}}$</td>
<td>1.203</td>
<td>0.1194</td>
<td>0.1192</td>
<td>0.1211</td>
<td>0.1193</td>
</tr>
<tr>
<td>N2O4 (D$_{3h}$)</td>
<td>$r_{\text{a,b}}$</td>
<td>0.1782</td>
<td>0.1688</td>
<td>0.1751</td>
<td>0.1780</td>
<td>0.1782</td>
</tr>
<tr>
<td>$\alpha_{\text{a,b}}$</td>
<td>112.65</td>
<td>112.85</td>
<td>112.58</td>
<td>112.6</td>
<td>112.3</td>
<td></td>
</tr>
<tr>
<td>$\alpha_{\text{a,b}}$</td>
<td>134.69</td>
<td>134.29</td>
<td>134.83</td>
<td>134.80</td>
<td>135.4</td>
<td></td>
</tr>
</tbody>
</table>
within the range recommended for NO2 and N2O4 and a slightly lower value for NH3. For CBS-APNO, the scaling factor we obtain is quite low as compared to the expected value of 0.9251. The CBS-APNO method is known to have issues with the geometries of nitrogen oxide species [42]. This drawback is highlighted further in the thermochemistry data and is discussed in detail in the following subsection. For W1, the scaling factor is recommended to be 0.985 for the fundamental modes and our data are close, though somewhat below this value. CCSD(T) frequencies are typically reported unscaled and no scaling factors are applied. It is important to note that we report unscaled frequencies for all the molecules from the four methods. These scaling factors are a measure for the agreement between experimental and computed frequencies, and therefore also an indirect measure for anharmonicity effects in such calculations.

The optimized structures for all the species reproduced the correct symmetry group for all the four methods, and no degree of freedom was missing in the vibrational analysis. In particular, the deviations between calculated and experimental frequencies of N2O4 cannot be attributed to lack of proper symmetry. For N2O4, we observe that there are five low lying modes (table 4) which need careful examination with respect to the harmonic oscillator approximation used for vibrational calculations. Our calculations, for all the four methods, detect the a1 mode (82 cm−1, see table 4) as a hindered internal rotor, which corresponds to the rotation of the two NO2 groups against each other. Hence, the electronic energy and entropy calculated using the harmonic oscillator approximation for N2O4 should be corrected by the contribution from this internal rotation mode.

Table 5 shows the energetic and entropic contributions of the a1 mode calculated with the harmonic oscillator and the hindered rotor analysis at 298 K for all four methods. The difference between the two contributions is calculated using the Pitzer–Gwinn scheme [46,47]. Corrections were calculated using the respective a1 vibrational frequencies corresponding to each method. Corrections in electronic energy, Ec for CBS-APNO are small (0.06–0.08 kJ·mol−1) for G3B3, W1 and CCSD(T), while the largest Ec ≈ 0.19 kJ·mol−1 for CBS-APNO. The corrections for W1 and CCSD(T) values are almost equal. This is expected since the frequencies are similar and the scaling factor for W1 is close to unity. There is no significant difference between the energy corrections for scaled and unscaled analysis, except for CBS-APNO. We recall that the deviation from experimental value for the CBS-APNO a1 mode is the largest amongst the four methods. Adding the hindered rotor correction does not improve the energies significantly, although the correction is relatively larger for the CBS-APNO value as compared to other methods. A similar trend is observed for the entropic correction Scor for the four methods. However, the inclusion of the scaling factors has some impact on the entropy corrections, which are significantly larger than the unscaled ones. Scor for CBS-APNO is more than twice as large as the other ones. This difference reflects the lower predicted frequency (71 vs. 86/88/95), lower scaling factor (0.9251 vs. 0.96/0.985) and the smaller reduced moment (primarily attributed to the shorter N–N distance).

Since compound methods use a scaling factor (e.g., 0.985 for W1) for the harmonic frequencies, the same factor should also be used for the hindered rotor correction. However, we found that Gaussian by default uses unscaled frequencies for the hindered rotor analysis performed for the compound methods. Therefore, the values given in table 5 are recomputed manually using the proper scaling factors following the Pitzer–Gwinn scheme [47] as used in Gaussian. In particular, this means that the procedure as done by Gaussian (using the unscaled frequencies) slightly overcompensates the errors caused by the improper vibration. For the CCSD(T) results, the same Pitzer–Gwinn scheme was used, since MOLPRO does not provide a hindered rotor detection and correction at all. For the MOLPRO computation a reduced moment of 17.64 amu ×
bohr$^2$ was used. Thermochemical quantities reported in the following subsection include the hindered rotor correction for N$_2$O$_4$ at 298 K.

It is important to note that energies are obtained at the final step of the compound thermochemistry methods, however frequencies are calculated at intermediate levels. The CBS-APNO method uses a larger basis set at the HF level, as compared to G3B3 for calculation of frequencies, however, G3B3 performs better due to inclusion of correlation with the 3LYP functional. With the W1 method, using a correlation consistent basis set [34,35] along with the B3LYP functional, improves the results further, as seen in table 4.

Thermochemical data are obtained by combining the vibrational data with the electronic energies calculated with a given method. Table 6 shows the zero point energy correction, ZPE, and the electronic reference energy at 0 K, $E_0$, for all the reaction species. The ZPE are scaled by the respective scaling factor for a given method. $E_0$ is the reference energy to which the ZPE and the thermal corrections are added to obtain the thermochemical quantities for a given temperature. For standard methods (such as RHF and B3LYP) $E_0$ is the electronic energy. However, for the compound methods, the reference energy itself is the sum of the electronic energy plus some corrections. Hence, we denote $E_0$ as the electronic reference energy.

For CCSD(T) data, calculated electronic energies are extrapolated to the complete basis set limit ($E_{CBS}$). This extrapolation of CCSD(T) energies is described in Section 2. Fig. 1 shows the CBS-extrapolated energies obtained using the mixed exponential plus Gaussian function (equation (9)) for the CCSD(T) calculations performed for H$_2$, N$_2$, O$_2$, N$_2$H, and N$_2$O$_4$. As expected, increasing the cardinal number of the basis set, we observe the electronic energy tending towards the (extrapolated) basis set limit. The CCSD(T) $E_0$ values listed in table 6 are $E_{CBS}$ values.

Furthermore, the absolute enthalpy at 0 K, $H_0$, absolute enthalpy at 298 K, $H_{298}$, and absolute Gibbs energy at 298 K, $G_{298}$ for all the species are presented in table 6. These are the quantities used for the calculation of the formation enthalpies and Gibbs energies in the following subsection.

### 3.2. Thermoch emistry: enthalpy of formation, Gibbs energy of formation and absolute entropy

In this section the results for $\Delta H_f^0$, $H_f^0$, and $\Delta G_f^0$ for NH$_3$, NO$_2$, and N$_2$O$_4$ in the gas phase at standard conditions (298.15 K and 1 atm) are presented. The respective formations of NH$_3$, NO$_2$, and N$_2$O$_4$ are considered from N$_2$, H$_2$, and O$_2$ in appropriate stoichiometric ratio. $\Delta H_f^0$ and $\Delta G_f^0$ for H$_2$, N$_2$, O$_2$ corresponding to the stable forms of the respective elements are set to zero. Absolute entropies $S_f$ for all species are reported from the respective calculations of NH$_3$, NO$_2$, and N$_2$O$_4$ without any reference value. For N$_2$H, H$_2$, and O$_2$ calculated $S_f$ are in good agreement with the experimental values, for all the methods we have tested. For N$_2$O$_4$ the energies are corrected for the internal rotation contribution as discussed in the previous subsection (see table 5).

We calculated $\Delta H_f^0$ at 0 K and at 298 K, $S_f$ at 298 K, and $\Delta G_f^0$ at 298 K for NH$_3$, NO$_2$, and N$_2$O$_4$. This data are presented in tables 7–9, along with experimental values available from thermochemical tables [20]. Relative deviations from the experimental values are given in parentheses. This relative deviation is calculated as $|X_{calc} - X_{exp}| / X_{exp}$, where $X$ is the thermodynamic quantity such as $\Delta H_f^0$ or $\Delta G_f^0$. The accuracy of computed $\Delta G^0$ depends on the accuracy of the computed $\Delta H^0$ and $S$. Using a high-level method, such as W1 and CCSD(T), significantly improves the contribution of $\Delta H^0$. We observe this consistently in our data, shown in tables 7–9.

$\Delta H_f^0$ at 298 K from W1 and CCSD(T) methods are always in better agreement with the experimental values, for all the methods we have tested. For N$_2$O$_4$ the energies are corrected for the internal rotation contribution as discussed in the previous subsection (see table 5).

### Table 6

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Parameter (hartree)</th>
<th>G3B3</th>
<th>CBS-APNO</th>
<th>W1</th>
<th>CCSD(T)</th>
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<tr>
<td>N$_2$</td>
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4 Standard enthalpies of formation in all references are zero at all temperatures because they are the enthalpies of such null reactions as N$_2$(g) $\rightarrow$ N$_2$(g).
the choice of method because the respective standard scaling factors are applied to the calculated vibrational frequencies. For NH$_3$, the results from CCSD(T) and W1 are in good agreement with experimental values, as shown in Table 7. $\Delta H_{298}$ and $\Delta G_{298}$ calculated using the W1 and CCSD(T) methods are within ±2 kJ·mol$^{-1}$ of the experimental value. $S_{298}$ predicted by CCSD(T) and W1 are quite

FIGURE 1. CBS-extrapolation of electronic energies using the mixed exponential plus Gaussian function (equation (9)) for H$_2$, N$_2$, O$_2$, NO$_2$, NH$_3$, and N$_2$O$_4$ calculated using the CCSD(T) method. The curves are fits of equation (9) to the data and the horizontal lines are the thus extrapolated asymptotic values.

TABLE 7
Enthalpy, $\Delta H_f$, absolute entropy, $S$, and Gibbs energy, $\Delta G_f$ of formation for NH$_3$ calculated using the G3B3, CBS-APNO, W1, and CCSD(T) methods. Exp refers to experimental values [22,20]. The relative deviations from experimental values are given in parentheses. Energies are in kJ·mol$^{-1}$ and entropies in J·K$^{-1}$·mol$^{-1}$.

<table>
<thead>
<tr>
<th>Method</th>
<th>G3B3</th>
<th>CBS-APNO</th>
<th>W1</th>
<th>CCSD(T)</th>
<th>Exp</th>
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</thead>
<tbody>
<tr>
<td>$\Delta H_{298}/$kJ·mol$^{-1}$</td>
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<td>$\Delta H_{298}/$kJ·mol$^{-1}$</td>
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<tr>
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<tr>
<td>$\Delta G_{298}/$kJ·mol$^{-1}$</td>
<td>-12.21 (0.25)</td>
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TABLE 8
Enthalpy, $\Delta H_f$, absolute entropy, $S$, and Gibbs energy, $\Delta G_f$ of formation for NO$_2$ calculated using the G3B3, CBS-APNO, W1, and CCSD(T) methods. Exp refers to experimental values [22,20]. The relative deviations from experimental values are given in parentheses. Energies are in kJ·mol$^{-1}$ and entropies in J·K$^{-1}$·mol$^{-1}$.

<table>
<thead>
<tr>
<th>Method</th>
<th>G3B3</th>
<th>CBS-APNO</th>
<th>W1</th>
<th>CCSD(T)</th>
<th>Exp</th>
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<td>$S_{298}/$J·K$^{-1}$·mol$^{-1}$</td>
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<td>$\Delta G_{298}/$kJ·mol$^{-1}$</td>
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<td>53.41 (0.04)</td>
<td>52.01 (0.01)</td>
<td>51.31</td>
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</table>

TABLE 9
Enthalpy, $\Delta H_f$, absolute entropy, $S$, and Gibbs energy of formation, $\Delta G_f$ for N$_2$O$_4$ calculated using the G3B3, CBS-APNO, W1, and CCSD(T) methods. Exp refers to experimental values [22,20]. The relative deviation from experimental values are given in parentheses. Data corrected for the hindered rotor motion are indicated as corr. Energies are in kJ·mol$^{-1}$ and entropies in J·K$^{-1}$·mol$^{-1}$.

<table>
<thead>
<tr>
<th>Method</th>
<th>G3B3</th>
<th>CBS-APNO</th>
<th>W1</th>
<th>CCSD(T)</th>
<th>Exp</th>
</tr>
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<td>$\Delta H_{298}/$kJ·mol$^{-1}$</td>
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<td>$\Delta H_{298}/$kJ·mol$^{-1}$</td>
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<tr>
<td>$S_{298}/$J·K$^{-1}$·mol$^{-1}$</td>
<td>301.34 (0.01)</td>
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<td>304.29</td>
</tr>
<tr>
<td>$\Delta G_{298}/$kJ·mol$^{-1}$</td>
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<td>93.89 (0.04)</td>
<td>100.69 (0.02)</td>
<td>97.32 (0.00)</td>
<td>97.89</td>
</tr>
<tr>
<td>$\Delta G_{298}/$kJ·mol$^{-1}$</td>
<td>91.33 (0.07)</td>
<td>93.74 (0.04)</td>
<td>100.62 (0.02)</td>
<td>97.25 (0.00)</td>
<td>97.89</td>
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</tbody>
</table>
accurate. $S_{298}$ calculated by G3B3 is closer to the experimental value as compared CBS-APNO, however, $\Delta H_{298}$ estimate from CBS-APNO are better due to a more accurate calculation of $\Delta H_{298}$.

For NO$_2$, the data from CCSD(T) show best agreement with experiments followed by W1. $S_{298}$ for all four methods are consistently close with experiments. The differences in the respective $\Delta H_{298}$ and $\Delta G_{298}$ values for G3B3, CBS-APNO and W1 are significant. This is due to the better computation of electronic energy in the W1 scheme as compared to G3B3 and CBS-APNO. Apart from the diatomic O$_2$, NO$_2$ is the only molecule in our study where spin effects play a role, and the two latter methods are known to have issues with spin contamination [48,30]. In fact, G3B3 based on the density-functional approach using B3LYP correlation functional is known to have fewer spin-contamination issues for open-shell systems such as NO$_2$, as compared to CBS-APNO. Hence, the former is known to have fewer spin-contamination issues for open-shell species (both N–O and N–N bonds) due to the inadequacy of the QCISD geometry [30]. In fact, for the case of ONOO$^-$ ion, a difference of 71 kJ · mol$^{-1}$ between the predicted heats of formation from G3 and CBS-APNO methods is reported [42]. We observe the maximum relative deviation from experiments for $\Delta H_{298}$ and $\Delta G_{298}$ for the CBS-APNO results. Our attempt to improve the QCISD/6-31 G step (of the CBS-APNO calculation) by geometry optimization at this level, as suggested in [42], followed by an appropriate calculation of the compound energies did not improve the description (geometry and energies) significantly.

For NO$_2$, $\Delta H_{298}$ is largely underestimated by the G3B3 and CBS-APNO methods. W1 and CCSD(T) methods are far better and the calculated values are well within the range of expected errors. Our $\Delta H_{298}$ is closer to the experimental value than the ones reported in reference [42]. In fact, G3B3 and CBS-APNO both predict similar numbers for $\Delta H_{298}$ and $\Delta G_{298}$. Again, the errors are not that significant for $S_{298}$ as compared to those for $\Delta G_{298}$. The better performance of W1 and CCSD(T) is again a result of a better description of the underlying geometry of the NO$_2$ molecule. As already stated in Section 2, the geometry optimization is done for both methods at the more sophisticated CCSD(T) level, while the other two methods rely on either B3LYP (G3B3) or RHF (CBS-APNO) geometries.

We also report the same quantities corrected for the hindered rotor motion. For $\Delta H$, the corrected values are close to the uncorrected ones for all methods. Relative errors for corrected data are similar to the uncorrected ones. The largest correction is $\pm 0.19$ kJ · mol$^{-1}$ observed for the CBS-APNO data. Corrected $S_{298}$ are closer to the experimental value, however, this improvement is not significantly reflected in the relative errors. The CCSD(T) result is almost identical to the experimental value. The correction for CBS-APNO is the largest $\sim 1.13$ J · K$^{-1}$ · mol$^{-1}$. Finally, the corrections are applied to $\Delta G$. Although the corrections for CBS-APNO were the largest amongst the four methods, the overall prediction of $\Delta G$ is not the worst. In fact, it is better than G3B3, due to the marginally better prediction of $\Delta H$. For the calculation of $\Delta G$ for the NO$_2$ dimerization reaction, corrected energies for NO$_2$ have been used. In fact, a particular choice of method (level of theory and basis sets) can give excellent results for some species, while not giving the best expected results for another species. This is attributed to the molecular symmetry of the species and the error compensation when its chemical structure is modeled using a specific compound thermochrometry method.

3.3. Equilibrium constants

For the NO$_2$ reaction, the experimental data for $\Delta G$ and $K_{eq}$ show a spread, as seen in table 10. For 298.15 K, the measured value of $K_{eq}$ varies between 0.136 and 0.147 [4] for the dissociation of NO$_2$. Reference [21] presents an IR spectroscopic study of the NO$_2$ dissociation reaction where $K_{eq}$ at room temperature is measured within the same range as Ref. [4]. For the dimerization reaction we consider in our study, the corresponding $K_{eq}$ is in the range between 6.54–7.36. From [24] and the corresponding $\Delta G$, $K_{eq}$ is estimated to be in the range between 6.74–10.64. For the NH$_3$ reaction, a $K_{eq}$ value of 5.4 × 10$^5$ is obtained from the $\Delta G$ value given in [20].

Table 10 shows $\Delta G$ and $K_{eq}$ for the two chemical equilibrium reactions discussed in Section 2. As shown in equation (3), $K_{eq}$ is exponentially related to $\Delta G$. A small error in the computation of $\Delta G$ for reaction species, and hence $\Delta G$, leads to a significant error in the calculation of $K_{eq}$. It is possible that $\Delta G$ is closer to the experimental value than $\Delta G$, due to cancellation of systematic errors in the calculation of individual $\Delta G$ or vice versa. We observe this in the case of the NO$_2$ reaction.

For the NO$_2$ reaction, the experimental data for $\Delta G$ and $K_{eq}$ show a spread, as seen in table 10. Using the G3B3 method, we obtain $\Delta G = -6.03$ kJ · mol$^{-1}$, close to the experimental value from reference [24], and the $K_{eq} \approx 11.39$ is also in good agreement with the range of experimental measurements. The CBS-APNO calculations yield $\Delta G = 4.70$ kJ · mol$^{-1}$ and $K_{eq} = 0.15$ which are in poor agreement with the experiments. The CBS-APNO $\Delta G$ for NO$_2$ shows a large deviation from the experimental value, as shown in table 8, and this leads to the large deviation in the estimate for $\Delta G$. We also tested the CBS-QB3 method [49] and found similar results for $\Delta G$ and $K_{eq}$. $\Delta G$ from the W1 and CCSD(T) methods are $-6.20$ kJ · mol$^{-1}$ and $-6.77$ kJ · mol$^{-1}$ respectively, with relative deviations of $\sim 6\%$ and $\sim 15\%$ from the largest experimental value of $\Delta G$. The $K_{eq}$ from W1 and CCSD(T), being 12.19 and 15.35 respectively, are higher than the experimental values but within the same order of magnitude. Our CCSD(T) $\Delta G$ value differs from [24] due to a difference in the fitting procedure used for getting the extrapolated complete basis set energies (see Section 2).

For the NH$_3$ reaction, we obtain $\Delta G = -24.42$ kJ · mol$^{-1}$ and $K_{eq} \approx 1.90 \times 10^6$ from the G3B3 method. This is about 30 times lower than the experimental value. Out of the other three methods, CBS-APNO performs best, underestimating the experimental $\Delta G$ by just 2 kJ · mol$^{-1}$, while both W1 and CCSD(T) overestimate $\Delta G$ by $\sim 4$ kJ · mol$^{-1}$. $\Delta G$ from W1 shows the largest relative deviation of $\sim 13\%$ from the experimental value. The $K_{eq}$ for W1 is $\sim 3.47 \times 10^6$, which is six times higher than the experimental value of $5.43 \times 10^5$ [20]. The CCSD(T) prediction of $K_{eq}$,
2.81 \times 10^6 \text{ is also five times higher. The CBS-APNO result of } \approx 2.36 \times 10^5 \text{ is closest to the experimental value.}

3.4. Temperature dependence of $\Delta G$ and $K_{eq}$

In order to discuss the temperature dependence of $\Delta G$, we first discuss the temperature dependence of the enthalpy, $H$, given by Kirchoff's equation [50],

$$H_f = H_{298} + \int_{298}^{T} C_p(T) \, dT,$$

(10)

where $C_p$ is the specific heat capacity, typically expanded in a polynomial series [51].

$$C_p(t) = a + bt + ct^2 + dt^3 + e/t^2,$$

(11)

where $t = T/(1000K)$, and the constants $a, b, c, d$, and $e$ are listed in thermochemical tables [22]. Equations (10) and (11) motivate the relation

$$H_f = H_{298} + at + bt^2/2 + ct^3/3 + dt^4/4 - e/t + f - h,$$

(12)

where $f$ and $h$ are additional constants also available from [22]. The temperature dependence of $S$ is given as,

$$\Delta S = \int_{298}^{T} \frac{C_p(T)}{T} \, dT.$$  

(13)

Equations (11) and (13) yield

$$S_f = a \ln t + bt^2/2 + dt^3/3 - e/(2t^3) + g.$$

(14)

In the following, the temperature dependence of reaction thermodynamics is studied using the NH$_3$ synthesis reaction as an example. Using experimental $H_{298}$ and appropriate constants $(a, b, c, d, e, g)$ from [22] in equations (12) and (14), we calculate $H_f$, $S_f$, and $G_f$ for NH$_3$, H$_2$, and N$_2$ at each $T$. Subsequently, we calculate $\Delta H$, $-T\Delta S$, and $\Delta G$ for the NH$_3$ formation reaction and denote them with the subscript exp.

Quantum chemical thermochemistry calculations use a simplified scheme (harmonic oscillator, ideal gas approximation, neglecting first and higher excited states) for including temperature dependent contributions. The electronic ground state energy is taken as the reference and contributions from the rotational, translational and vibrational degrees of freedom are added, including temperature dependence where applicable [38]. We use the W1 data from our calculation at 298.15 K to obtain $\Delta G^\text{eq}$ at higher $T$ by following the procedure prescribed in [38]. This fully ab-initio procedure that does not involve any experimental data requires the calculation of electronic energies, vibrational modes, moments of inertia, molecular mass, spin multiplicity, symmetry number and frequency scaling factor (if applicable, as for W1 data) as input from the thermochemistry calculation at 298 K for N$_2$, H$_2$ and NH$_3$. The $T$-dependent enthalpy (or entropy) is decomposed in two contributions: the $T$-independent electronic energy (at 0 K) and the $T$-dependent correction term. The calculated electronic reference energy at 0 K is the fundamental value, to which the respective thermal contributions are added to yield the $T$-dependent enthalpy and entropy. For a given $T$, the thermal contributions to internal energy, enthalpy and entropy are calculated using standard statistical mechanical formulae [38]. All the input parameters used in these formulae are obtained from the W1 calculation at 298 K, and no experimental data are used. This is repeated for the appropriate range of $T$, for each of the three species, N$_2$, H$_2$ and NH$_3$. Reaction energies are subsequently calculated at each $T$.

The enthalpic and entropic contributions are denoted as $\Delta H_{W1}$ and $-T\Delta S_{W1}$ respectively. $\Delta G$ calculated using the W1 theory at different temperatures are denoted as $\Delta G_{W1}$.

Fig. 2 shows a comparison between experimental and W1 calculated $\Delta H$, $-T\Delta S$ and $\Delta G$ for NH$_3$ as a function of temperature for $T \geq 298$ K. For all temperatures, the experimental and W1 data agree well. We observe that $-T\Delta S$ and $\Delta G$ have a strong $T$ dependence. $\Delta H$ contains the temperature independent ground state electronic energy, and temperature dependent contributions from rotational, translational and vibrational degrees of freedom. Hence, $\Delta H$ is expected to show a weaker $T$ dependence. At 298.15 K, the difference between the W1 and the experimental value for $\Delta G$ is $\approx 2.3 \text{ kJ} \cdot \text{mol}^{-1}$, which is attributed to the $\Delta H$ contribution, and this difference remains approximately constant for higher $T$.

The $-T\Delta S$ values are almost identical for both data sets (with differences $\leq 1 \text{ kJ} \cdot \text{mol}^{-1}$). This can be explained as follows. For N$_2$, H$_2$ and NH$_3$, the W1 calculations for $S_{298 \text{ K}}$ are in excellent agreement to experimental values (see Section 3.2) due to the application of the appropriate scaling factor that compensates for
the method-dependent inaccuracies (Section 3.1 and table 3). Initial
data have been used to obtain the T-dependence of S without any further loss of accuracy. Hence – $T \Delta S_K$ values for the reaction do not differ significantly from the experimental values. When $\Delta G \geq 0$, the formation reaction of $NH_3$ will be endothermic, and this corresponds to $T \gtrsim 470$ K for the W1 calculation and $T \gtrsim 450$ K from the experimental data. For $T \gtrsim 298$–470 K where $\Delta G \leq 0$, $NH_3$ will be thermodynamically stable.

We use experimental and W1 calculated values of $\Delta G$ to compute $K^{eq}$ from equation (3) and its natural logarithm is denoted as $ln K^{eq}$. A widely used relation for the temperature dependence of $K^{eq}$ is given by the Van't Hoff equation [50] which approximates the enthalpies to be temperature independent, leading to

$$\left(\frac{\partial \ln K^{eq}}{\partial T}\right)_P = \frac{\Delta H^r}{RT^2}.$$  (15)

$ln K^{eq}$ is calculated using the definite integral form of equation (15) and experimental $\Delta H^r = -45.90 \text{ kJ} \cdot \text{mol}^{-1}$ at $T_0 = 298.15$ K. Fig. 3 shows W1 calculated $ln K^{eq}_W$ and $ln K^{eq}_W$ versus $ln K^{eq}$ for 298 K $\leq T \leq 1000$ K. As expected, at 298.15 K, only $ln K^{eq}_W$ shows a deviation from $ln K^{eq}_W$ is exact. We observe that the deviation of $ln K^{eq}$ with respect to $ln K^{eq}_W$ increases for higher $T$ as the approximation of a temperature-independent enthalpy is good for a limited range of temperature around 298.15 K only. On the other hand, the relative deviation of $ln K^{eq}_W$ from $ln K^{eq}$ remains almost constant up to $\sim 600$ K, and decreases at $T \gtrsim 600$ K. In order to compare the two schemes, one can plot $ln K^{eq}$ versus $1/T$ and extract $\Delta H^r$ from the linear fit of the curve. For the Van't-Hoff data, this analysis yields experimental $\Delta H^r = -45.86 \text{ kJ} \cdot \text{mol}^{-1}$ used as input. For $ln K^{eq}_W$, we obtain $\Delta H^r = -52.14 \text{ kJ} \cdot \text{mol}^{-1}$ with a standard error of 0.6. Hence, by using the W1 data for $\Delta G^r$ at 298.15 K for each species, combined with appropriate temperature dependent contributions, we obtain $\Delta G$ in good agreement with experimental data over a range of $T$. Calculation of $K^{eq}$ from the $T$ dependent $\Delta G$ gives consistent results. The accuracy of the initial $\Delta G^r$ calculation at 298.15 K influences the accuracy of predicted $K^{eq}$ as a function of $T$.

4. Conclusions

Using ab-initio calculations, we show that reliable values of $\Delta G_X$, $\Delta G^r$ and $K^{eq}$ can be obtained for equilibrium reactions of $NO_2$ dimer formation and $NH_3$ synthesis. All methods we tested produce reliable structural parameters for all the reaction species involved. For $\Delta H^r$ and $\Delta G^r$, the quantum-chemical method CBS-APNO performs best for $NH_3$, while CCSD(T) data are closest to experiments for $NO_2$ and $N_2O_4$. For all molecules, $S_{298} K$ calculated using all the four methods are quite close to experimental values. Both G3B3 and CBS-APNO $\Delta H^r$ data show significant deviations from experiment for $N_2O_4$, a species for which better basis sets and the calculation of electronic energies incorporating higher level of correlation are important factors.

There is a difference in the performance of these methods when comparing standard reaction Gibbs energies, $\Delta G^r$, and equilibrium constants, $K^{eq}$. For the $NO_2$ dimerization reaction, our best result is obtained from the G3B3 calculation, with $\Delta G^r = -6.03 \text{ kJ} \cdot \text{mol}^{-1}$ and $K^{eq} \approx 11$. The values for $\Delta G^r$ from W1 and CCSD(T) are $-6.20 \text{ kJ} \cdot \text{mol}^{-1}$ and $-6.77 \text{ kJ} \cdot \text{mol}^{-1}$ respectively and the corresponding $K^{eq}$ are $\approx 12$ and 15. Our calculations support higher values of $\Delta G^r$ within the range of experimental data from different sources. All four calculated values for $K^{eq}$ are of the same order of magnitude as the experimental data. The CBS-APNO calculations yield poor results, and are not well-suited for this reaction, due to issues with the molecular geometry (N–O and N–N bonds) of nitrogen oxides. For the $NH_3$ synthesis, we obtain $\Delta G = -30.66 \text{ kJ} \cdot \text{mol}^{-1}$ and $K^{eq} \approx 2.36 \times 10^5$ from the CBS-APNO calculation. $\Delta G^r$ calculated from G3B3, W1, and CCSD(T) are $-24.42$, $-37.32$, and $-36.80 \text{ kJ} \cdot \text{mol}^{-1}$ respectively. The corresponding $K^{eq}$ are about $1.9 \times 10^5$, $3.47 \times 10^6$, and $2.81 \times 10^6$. For this reaction, both W1 and CCSD(T) overestimate the energies and $K^{eq}$. G3B3 performs reasonably well in the calculation of $\Delta G^r$ for the $NH_3$ synthesis reaction, and predicts $K^{eq}$ close to the experimental data. Interestingly, we see that CBS-APNO predicts the best result for this reaction.

We conclude that quantum-chemical methods such as G3B3 and CBS-APNO are quite robust in the calculation of equilibrium properties such as $\Delta G^r$ and $K^{eq}$, provided that the species of interest do not have known difficulties in modeling using a particular method. W1 and CCSD(T), which are relatively expensive calculations, are preferred for larger molecules where correlation, relativistic, and spin effects may be crucial for accuracy. Depending on the molecules involved, a reasonable choice can be made by referring to thermochemistry data for different methods. Systematic cancellation of errors and issues such as spin contamination, low lying virtual orbitals, and modeling of open-shell systems must be examined while selecting a compound thermochemistry method for the calculation of reaction energies.

We discuss the temperature dependence of $\Delta G^r$ and $K^{eq}$ for the formation reaction of $NH_3$. Standard formation Gibbs energies, $\Delta G^r$, for higher temperatures are obtained by using W1 calculations of $\Delta G^{298 K}$. We compare the experimental value of $\Delta G^r$ with explicit W1 calculated $\Delta G^r$ and find good agreement between the two. We show that the calculations of $\Delta G^{298 K}$ and hence $\Delta G$ within reasonable accuracy, predict $K^{eq}$ consistent with the experimental data over a range of temperatures. This is useful since calorimetric experimental data are usually available for limited temperature conditions only.

Equilibrium constants $K^{eq}$ are measured at the restricted set of accessible laboratory conditions (temperature and solvents) and simulation data such as those presented here can provide access to a wider range of temperatures. For reactions where experimental measurements of equilibrium are carried out in the presence of solvents [52], formation Gibbs energy and equilibrium constant calculations are sensitive to the choice of the solvation model implemented in quantum chemical calculations [38].

References
