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A theoretical study of the NCN ($^3\Sigma^-$) biradical thermochemical properties: Implications for combustion chemistry

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A B S T R A C T

Theoretical calculations are performed to obtain thermochemical properties ($\Delta_f H^{\circ}_{298K}$, S°_{298K}, $C_P = f(T)$) for the electronic ground state of the NCN ($^3\Sigma^-$) biradical. In order to validate our methodology, the thermochemical properties ($\Delta_f H^{\circ}_{298K}$, S°_{298K}, $C_P = f(T)$) are determined also for seventeen species involved in the prompt-NO mechanism. The standard enthalpies of formation at 298 K are estimated using atomization reaction based on the CBS-QB3, CBS-APNO, G3B3, G3, and G4 calculation levels. In the case of the NCN biradical, an isogyric set of four reactions is also used to assess its standard enthalpy of formation at 298 K. Standard molar entropies at 298 K and heat capacities at constant pressure are estimated at the B3LYP/cc-pVQZ level of theory. Based on our results, we recommend the use of our calculated thermochemical properties for the modeling of the prompt-NO mechanism: $\Delta_f H^{\circ}_{298K}$ (NCN) = (448.7 ± 3.4) kJ mol^{-1}, S°_{298K} = 225.8 J mol^{-1} K^{-1}, C_P (in J mol^{-1} K^{-1}) = 41.9, 45.8, 49.0, 51.6, 55.2, 57.3, 59.9, 60.9, 61.7, 62.0, 62.1 at 300, 400, 500, 600, 800, 1000, 1500, 2000, 3000, 4000, 5000 K, respectively.
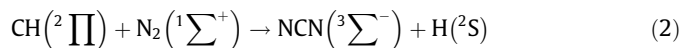
1. Introduction

Thermal NO$_x$ formation, which is highly temperature dependent, is recognized as the most relevant source when combusting natural gas [1]. Fuel NO$_x$ tends to dominate during the combustion of fuels, such as coal, which have significant nitrogen content, particularly when burned in combustors designed to minimize thermal NO$_x$. The contribution of prompt NO$_x$ is normally considered negligible.

The prompt-NO source is attributed to the reaction of atmospheric nitrogen, N$_2$, with radicals such as C, CH, and CH$_2$ fragments derived from fuel, where this cannot be explained by either the aforementioned thermal or fuel processes. Occurring in the earliest stage of combustion, it results in the formation of fixed species of nitrogen such as NH, HCN, and CN which can oxidize to NO. In fuels that contain nitrogen, the incidence of prompt NO$_x$ is especially minimal and it is generally only of interest for the most exacting emission targets.

There is a demand for further reducing NO$_x$ emissions from natural gas burners in heat and power production. It was well known that the prompt-NO formation was mainly initiated by the following reaction

$$CH\left(^2\textstyle\prod\right) + N_2\left(^1\textstyle\sum^+\right) \rightarrow HCN\left(^1\textstyle\sum^+\right) + N\left(^4S\right) \tag{1}$$
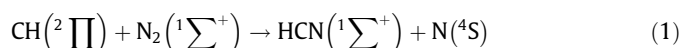
According to the known mechanism of Fenimore [2] even though this reaction was known to be spin-forbidden. Moskaleva and Lin [3,4] showed that the reaction between methylidyne radical (CH) and molecular nitrogen (N$_2$) yields NCN biradical and H atom according to the spin-allowed reaction pathway

$$CH\left(^2\textstyle\prod\right) + N_2\left(^1\textstyle\sum^+\right) \rightarrow NCN\left(^3\textstyle\sum^-\right) + H\left(^2S\right) \tag{2}$$

El Bakali et al. [5] introduced this key reaction in the GDF-kin®3.0_NCN mechanism. The rate constant has been therefore re-examined using both experimental measurements [6,7] and theoretical calculations [3,4,8,9]. NCN was moreover detected and quantified in a rich CH$_4$/O$_2$/N$_2$ flame [10] using the cavity ring down spectroscopy combined with laser induced fluorescence. Recently, experimental and modeling studies on the prompt-NO formation in low pressure premixed CH$_4$–O$_2$–N$_2$ and C$_2$H$_2$–O$_2$–N$_2$ flames were performed [7]. The examination of literature shows the thermochemistry of the NCN biradical suffers from lack of data. In particular, the values of its enthalpy of formation at 298 K are scattered. On one hand, Bise et al. [11,12] studied the photodissociation dynamics of the NCN biradical using beam photofragment spectroscopy leading to $\Delta_f H^{\circ}_{298K}$ = (465.1 ± 2.9) kJ mol^{-1}. On the other hand, Clifford et al. [13] estimated the enthalpy of formation

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to (451.9 ± 16.7) kJ mol^{-1} from electron affinity measurements. Other $\Delta_f H^{\circ}_{298K}$ have been also reported in the NIST-JANAF [14] and Burcat [15] databases. The corresponding values are (473 ± 21) and (465.89 ± 1.78) kJ mol^{-1}, respectively. For the enthalpy of formation of NCN biradical, the value of Clifford et al. [13] was adopted in the modeling of the prompt-NO mechanism subsequently by Benard et al. [16], El Bakali et al. [5], Xu and Lin [17,18], Zhu et al. [19], and Lamoureux et al. [7] while the value of Bise et al. [11,12] was chosen by other works [6,20–23].

The present work aims to contribute to a better understanding of the prompt-NO mechanism by reporting the thermochemical properties ($\Delta_f H^{\circ}_{298K}$, S°_{298K}, $C_P(T)$) for the NCN biradical in its electronic ground state ($^3\Sigma^-$). The determination of thermochemical data by means of quantum chemistry tools is a valuable solution to fill in the absence of experimental data. In this work, we extend the theoretical procedure used for the NCN biradical to seventeen other species involved in the prompt-NO mechanism. These computed thermochemical data could be therefore included in thermokinetic models.

This article is organized as follows: computational methods are reported in Section 2, while the results are presented and discussed in Section 3.

2. Computational methods

All calculations were performed using Gaussian03 [24] and Gaussian09 [25] suite of programs. The structural parameters were fully optimized at different levels of theory: (i) B3LYP/cc-pVQZ [26–31], (ii) CBS-QB3 [32,33], (iii) CBS-APNO [34], (iv) G3B3 [35], (v) G3 [36], and (vi) G4 [37]. Harmonic vibrational frequencies and zero-point vibrational energies were computed at the same levels. The absence of imaginary vibrational frequencies indicated that all optimized structures were minima. Vibrational frequencies have been scaled using appropriate scaling factors for the computation of the partition functions as a function of the temperature (0.969, 0.990, 0.9251, 0.960, 0.8929, and 0.9854 for B3LYP/cc-pVQZ [38], CBS-QB3 [32,33], CBS-APNO [34], G3B3 [35], G3 [36], and G4 [37], respectively). The CBS-QB3, CBS-APNO, G3B3, G3, and G4 are multilevel model chemistries that combine the results of several electronic structure calculations and empirical terms to predict molecular energies with high accuracy and relatively low computational costs.

2.1. Enthalpies of formation at 298 K ($\Delta_f H^{\circ}_{298K}$)

The $\Delta_f H^{\circ}_{298K}$ values of all studied species were determined using their atomization reaction at the CBS-QB3, CBS-APNO, G3B3, G3, and G4 levels of theory. The enthalpies of formation for the gaseous atoms (C, H, N, and O) were taken from the NIST-JANAF thermochemical database [14] whose values are in kJ mol^{-1}: 716.67, 217.999, 472.68, and 249.17, respectively.

For each i species, the values of $\Delta_f H^{\circ}_{298K}(i)$ calculated with each calculation method can be considered as the measurements of the same quantity, the true enthalpy of formation i. Hence, they are subjected to statistical analysis [39]. With a small number of measurements, the accurate determination of the confidence limits requires the use of Student's t distribution [39,40]. Therefore, the value of the uncertainty $u(\Delta_f H^{\circ}_{298K}(i))$ is calculated at a confidence level of 95% as the product of the t value by the sample standard deviation s of the $\Delta_f H^{\circ}$ values determined by the five different calculation methods, through:

$$u(\Delta_f H^{\circ}_{298K}(i)) = t \cdot s = t \sqrt{\frac{\sum_{j=1}^{5} (\overline{\Delta_f H^{\circ}_{298K}(i)} - \Delta_f H^{\circ}_{298K}(i,j))^2}{5-1}} \quad (I)$$

where t is the coefficient of Student's t distribution at a confidence level of 95% with four degrees of freedom (sample size minus 1) and $\overline{\Delta_f H^{\circ}_{298K}(i)}$ is the arithmetic average of the $\Delta_f H^{\circ}_{298K}(i)$ values across the four calculation methods and $\Delta_f H^{\circ}_{298K}(i,j)$ is the enthalpy of formation i calculated using the calculation method j. The t value is 2.776 at a confidence level of 95% with four degrees of freedom for a two-tailed t test [40].

For the NCN biradical, to improve upon the precision of the results obtained using the atomization reaction, an isogyric set of reactions has been used in this work:

$$NCN + CH \rightarrow CN + HCN \qquad (R1)$$
$$NCN + CO \rightarrow NCO + CN \qquad (R2)$$
$$NCN + CH_2 \rightarrow 2\,HCN \qquad (R3)$$
$$NCN + HCO \rightarrow NCO + HCN \qquad (R4)$$

The model chemistries CBS-QB3, CBS-APNO, G3B3, G3, and G4 provided independent determinations of the true $\Delta_r H^{\circ}_{298K}$ value for each reaction and hence the average of these gives an obvious (and statistically consistent) estimate of the true value that can be used in the subsequent calculations. The enthalpy of formation of the NCN target species was estimated based on our atomization values of the enthalpies of formation for CH, CN, HCN, CO, NCO, CH$_2$, and HCO. The final reported value $\Delta_f H^{\circ}_{298K,\text{final}}$ (NCN) is a weighted average across the values given by the four isogyric reactions and the five methods of calculation. The weights are the reciprocal square of the uncertainty in enthalpy of formation of the target species. $\Delta_f H^{\circ}_{298K,\text{final}}$ (NCN) values are calculated according to:

$$\Delta_f H^{\circ}_{298K,\text{final}}(NCN) = \frac{\sum_{i=1}^{4} \sum_{j=1}^{5} \frac{\Delta_f H^{\circ}_{298K}(NCN)_{i,j}}{u^2(NCN)_{i,j}}}{\sum_{i=1}^{4} \sum_{j=1}^{5} \frac{1}{u^2(NCN)_{i,j}}} \quad (II)$$

where $\Delta_f H^{\circ}_{298K}$ (NCN)$_{i,j}$ is the enthalpy of formation at 298 K of NCN target species calculated using the isogyric reaction i and the calculation method j and $u(NCN)_{i,j}$ is its uncertainty. This procedure discriminates against the isogyric reactions which involve less well known enthalpies of formation for reference species. As $u(NCN)_{i,j}$ is identical for each calculation method (see below), Eq. (II) can be rewritten as follows:

$$\Delta_f H^{\circ}_{298K,\text{final}}(NCN) = \frac{\sum_{i=1}^{4} \frac{1}{u^2(NCN)_{i,j}} \sum_{j=1}^{5} \Delta_f H^{\circ}_{298K}(NCN)_{i,j}}{5 \sum_{i=1}^{4} \frac{1}{u^2(NCN)_{i,j}}} \quad (III)$$

Let us consider a target species TS involved in the isogyric reaction i whose equation is:

$$TS + RS_{1,i} = RS_{2,i} + RS_{3,i}$$
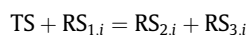
where $RS_{1,i}$, $RS_{2,i}$, and $RS_{3,i}$ are reference species whose the enthalpies of formation are known. Then, $\Delta_f H^{\circ}_{298K}$ (TS)$_{i,j}$ is calculated using an algebraic sum of enthalpies of formation of the reference species RS involved in the isodesmic reaction i and the enthalpy of reaction i at 298 K, $\Delta_r H^{\circ}_{298K,i}$, evaluated with the calculation method j as follows:

$$\Delta_f H^{\circ}_{298K}(TS)_{i,j} = -\Delta_r H^{\circ}_{298K,i} - \Delta_f H^{\circ}_{298K}(RS_1) + \Delta_f H^{\circ}_{298K}(RS_2) + \Delta_f H^{\circ}_{298K}(RS_3) \quad (IV)$$

As $\Delta_f H^{\circ}_{298K}$ of the reference species and $\Delta_r H^{\circ}_{298K,i}$ are independent measurements and have random uncertainties, the uncertainty in $\Delta_f H^{\circ}(TS)_{i,j}$ is the square root of the quadratic sum of their uncertainties [39] as shown by:

$$u(TS)_{i,j} = \sqrt{\sum_{k=1}^{3} u^2(RS_{k,i}) + u^2(\Delta_r H^{\circ}_{298K,i})} \quad (V)$$

where $u(RS_{k,i})$ is the uncertainty in $\Delta_f H^\circ_{298K}$ for the reference species $RS_{k,i}$ and $u(\Delta_r H^\circ_{298K,i})$ is the uncertainty in $\Delta_r H^\circ_{298K,i}$.

The values of $u(RS_{k,i})$ are taken from our calculations using the atomization reaction of the reference species. The values of $\Delta_r H^\circ_{298K,i}$ calculated with each calculation method can be considered as the measurements of the same quantity, the true enthalpy of reaction i. Therefore, the value of $u(\Delta_r H^\circ_{298K,i})$ is calculated at a confidence level of 95% as the product of the t value by the sample standard deviation s of the $\Delta_r H^\circ$ values determined by the five different calculation methods as described above.

2.2. Entropies (S°_{298K}) and heat capacities at constant pressure ($C_P(T)$, $300 \leqslant T/K \leqslant 5000$)

From the molecular properties obtained at the B3LYP/cc-pVQZ level of theory, the standard entropies (S°_{298K}) and heat capacities at constant pressure ($C_P(T)$, $300 \leqslant T/K \leqslant 5000$) were calculated using the rigid rotor harmonic oscillator approximation with the Thermo.pl program [41].

3. Results and discussion

3.1. Geometries and vibrational frequencies

For all species, Table 1 gathers the optimized geometry parameters calculated at the different levels of theory together with the available literature values. It can be noticed that the calculated geometric parameters do not vary a lot as a function of the level of theory and are in very good agreement with their literature counterparts. The global minimum for the C_2H ($^2\Sigma^+$) radical is found at the G3B3 and G4 levels of theory to be in a conformation in which the bond angle HCC is equal to about 162.8° while the other levels of theory predict a linear structure ($\theta(HCC) = 180°$). This problem can be attributed to the use of the 6-31G(d) and 6-31G(2df,p) basis sets as it was already reported [38]. The structure of the NCN biradical in its electronic ground state ($^3\Sigma^-$) is found to be linear at all levels of theory as reported in previous theoretical studies [13,42–46].

Scaled harmonic vibrational frequencies and their literature values are presented in Table 2. When comparing theoretical and

Table 1
Optimized geometry parameters[a] for the studied species at different levels of theory.

Species	Geometric parameters	B3LYP/cc-pVQZ	B3LYP/6-311G(d,p) [CBS-QB3]	HF/6-311G(d,p) [CBS-APNO]	B3LYP/6-31G(d) [G3B3]	HF/6-31G(d) [G3]	B3LYP/6-31G(2df,p) [G4]	Literature
H_2 ($^1\Sigma^+$)	r(HH)	0.742	0.744	0.735	0.743	0.730	0.743	0.741[b]
N_2 ($^1\Sigma^+$)	r(NN)	1.090	1.095	1.070	1.078	1.106	1.100	1.097[b]
CH ($^2\Pi$)	r(CH)	1.122	1.128	1.109	1.133	1.108	1.131	1.120[c]
CN ($^2\Sigma$)	r(CN)	1.161	1.166	1.154	1.174	1.162	1.170	1.172[c]
CO ($^1\Sigma$)	r(CO)	1.124	1.127	1.105	1.138	1.114	1.131	1.128[c]
NO ($^2\Pi$)	r(NO)	1.145	1.148	1.117	1.159	1.127	1.151	1.151[b]
CH_2 ($^3\Sigma^-$)	r(CH)	1.077	1.080	1.072	1.082	1.071	1.082	1.029[b]
	θ(HCH)	135.2	135.0	131.7	133.2	130.7	133.7	136.0[b]
C_2H ($^2\Sigma$)	r(CH)	1.063	1.064	1.057	1.070	1.058	1.065	1.061[b]
	r(CC)	1.198	1.202	1.209	1.226	1.215	1.212	1.207[b]
	θ(HCC)	180.0	180.0	180.0	162.8	180.0	168.4	180.0[b]
HCN ($^1\Sigma^+$)	r(CH)	1.066	1.066	1.069	1.071	1.069	1.067	1.066[b]
	r(CN)	1.145	1.149	1.159	1.157	1.176	1.152	1.153[b]
	θ(HCN)	180.0	180.0	180.0	180.0	180.0	180.0	180.0[e]
HCO ($^2A'$)	r(CH)	1.123	1.127	1.109	1.128	1.106	1.128	1.160[b]
	r(CO)	1.171	1.174	1.152	1.183	1.159	1.176	1.170[b]
	θ(HCO)	124.5	124.0	126.6	123.6	126.3	124.1	123.8[b]
CCO ($^3\Sigma^-$)	r(CC)	1.355	1.358	1.351	1.365	1.354	1.359	1.352[d]
	r(CO)	1.160	1.163	1.130	1.173	1.139	1.165	1.183[d]
	θ(CCO)	180.0	180.0	180.0	180.0	180.0	180.0	180.0[d]
NCO ($^2\Pi$)	r(CN)	1.221	1.222	1.207	1.230	1.213	1.226	1.230[b]
	r(CO)	1.174	1.177	1.150	1.187	1.160	1.179	1.180[b]
	θ(NCO)	180.0	180.0	180.0	180.0	180.0	180.0	180.0[b]
CNC ($^2\Pi$)	r(CN)	1.239	1.245	1.232	1.250	1.235	1.245	1.245[b]
	θ(CNC)	180.0	180.0	180.0	180.0	180.0	180.0	180.0[b]
CNN ($^3\Sigma^-$)	r(CN)	1.231	1.236	1.236	1.241	1.240	1.237	1.232[e]
	r(NN)	1.198	1.204	1.191	1.212	1.194	1.204	1.195[e]
	θ(CNN)	180.0	180.0	180.0	180.0	180.0	180.0	180.0[e]
NCN ($^3\Sigma^-$)	r(CN)	1.223	1.226	1.227	1.234	1.233	1.230	1.232[b]
	θ(NCN)	180.0	180.0	180.0	180.0	180.0	180.0	180.0[b]
NNO ($^1\Sigma^+$)	r(NN)	1.120	1.121	1.086	1.134	1.092	1.128	1.128[b]
	r(NO)	1.183	1.184	1.169	1.193	1.179	1.186	1.184[b]
	θ(ONN)	180.0	180.0	180.0	180.0	180.0	180.0	180.0[b]
NO_2 ($^2A_1$)	r(NO)	1.191	1.195	1.156	1.203	1.164	1.196	1.197[b]
	θ(ONO)	134.3	134.2	136.3	133.9	136.1	134.3	134.2[b]
HNCO ($^1A'$)	r(HN)	1.004	1.006	0.994	1.009	0.994	1.006	1.005[f]
	r(NC)	1.209	1.211	1.197	1.219	1.200	1.214	1.211[f]
	r(CO)	1.163	1.165	1.139	1.174	1.148	1.167	1.164[f]
	θ(HNC)	125.7	125.5	123.6	124.7	125.2	124.6	124.4[f]
	θ(NCO)	172.9	172.9	174.6	172.2	174.2	172.8	172.8[f]
	φ(HNCO)	180.0	180.0	180.0	180.0	180.0	180.0	180.0[f]

[a] Bond lengths r are in Angstroms, bond angles θ and dihedral angles φ are in degrees.
[b] The values in italics are taken from Ref. [14].
[c] The values in italics are taken from Ref. [85].
[d] The values in italics are taken from Ref. [86].
[e] The values in italics are taken from Ref. [81].
[f] The values in italics are taken from Ref. [87].

Table 2
Scaled vibrational frequencies (in cm^{-1}) for the studied species calculated at different levels of theory.

Species	B3LYP /cc-pVQZ	B3LYP/6-311G(d,p) [CBS-QB3]	HF/6-311G(d,p) [CBS-APNO]	B3LYP/6-31G(d) [G3B3]	HF/6-31G(d) [G3]	B3LYP/6-31G(2df,p) [G4]	Literature
H$_2$ ($^1\Sigma^+$)	4279	4377	4251	4275	4151	4401	4401[b]
N$_2$ ($^1\Sigma^+$)	2372	2423	2535	2359	2463	2395	2359[b]
CH ($^2\Pi$)	2738	2776	2802	2690	2732	2772	2861[a]
CN ($^2\Sigma$)	2087	2130	1848	2075	1769	2111	2069[b]
CO ($^1\Sigma^+$)	2145	2198	2258	2120	2178	2172	2170[b]
NO ($^2\Pi$)	1913	1969	2066	1911	1983	1956	1903[a]
CH$_2$ ($^3\Sigma^-$)	1019, 3028, 3259	1039, 3090, 3330	1111, 3021, 3216	1063, 3031, 3249	1106, 2969, 3148	1073, 3085, 3320	1056, 2954, 3123[a]
C$_2$H ($^2\Sigma$)	307, 307, 2028, 3341	300, 300, 2069, 3425	553, 553, 1719, 3308	359, 1568, 3304	496, 496, 1653, 3234	181, 181, 1823, 3431	375[c], 375 [c], 1841[d], 3299[e]
HCN ($^1\Sigma^+$)	739, 739, 2134, 3332	778, 778, 2178, 3327	824, 824, 2232, 3353	736, 736, 2125, 3342	794, 794, 2177, 3286	787, 787, 2166, 3439	713, 713, 2096, 3311[a]
HCO ($^2A'$)	1072, 1876, 2563	1099, 1922, 2596	1137, 1975, 2640	1085, 1870, 2556	1117, 1914, 2607	1100, 1919, 2602	1083, 1820, 2488[a]
CCO ($^3\Sigma^-$)	370, 370, 1070, 1969	368, 368, 1092, 2014	453, 453, 1078, 2059	327, 327, 1058, 1948	406, 406, 1045, 1983	389, 389, 1093, 2016	381, 381, 1074, 1978[a]
NCO ($^2\Pi$)	495, 576, 1257, 1924	500, 580, 1285, 1979	536, 614, 1301, 1837	462, 531, 1248, 1918	495, 563, 1256, 1749	518, 597, 1284, 1979	536, 536, 1275, 1922[a]
CNC ($^2\Pi$)	222, 392, 1263, 1473	230, 395, 1288, 1492	231, 403, 1161, 1268	230, 388, 1252, 1475	222, 390, 1146, 1232	224, 400, 1284, 1519	321, 321, 900, 1200[a]
CNN ($^3\Sigma^-$)	394, 394, 1244, 1467	395, 395, 1267, 1498	359, 359, 1088, 1646	376, 376, 1234, 1491	338, 338, 1060, 1617	398, 398, 1268, 1514	393, 393, 1241, 2847[a]
NCN ($^3\Sigma^-$)	434, 434, 1235, 1507	446, 446, 1260, 1549	370, 370, 1142, 1341	410, 410, 1228, 1516	336, 336, 1109, 1312	462, 462, 1257, 1581	423, 423, 1197, 1475[a]
NNO ($^1\Sigma^+$)	600, 600, 1289, 2272	602, 602, 1323, 2331	642, 642, 1291, 2421	580, 580, 1290, 2277	615, 615, 1244, 2351	615, 615, 1321, 2327	589, 589, 1276, 2223[a]
NO$_2$ ($^2A_1$)	745, 1350, 1642	758, 1385, 1699	787, 1492, 1736	719, 1347, 1651	743, 1440, 1680	745, 1379, 1698	750, 1318, 1618[b]
HNCO ($^1A'$)	558, 618, 773, 1296, 2259, 3564	563, 628, 775, 1326, 2332, 3652	544, 667, 802, 1344, 2293, 3599	540, 586, 769, 1285, 2262, 3530	527, 624, 763, 1303, 2217, 3499	569, 636, 799, 1321, 2323, 3637	577, 659, 777, 1327, 2274, 3531[a]

The literature values of the vibrational frequencies are in italics.
[a] These values are taken from Ref. [14].
[b] These values are taken from Ref. [49].
[c] These values are taken from Ref. [64].
[d] These values are taken from Ref [38].
[e] These values are taken from Ref. [47].

literature (experimental) data one should remember that the theoretical vibrational frequencies are obtained in the harmonic approximation while the experimental results are mostly anharmonic values. The calculated vibrational frequencies are however in reasonable agreement with their experimental counterparts. For the diatomic species, there are slight differences between calculated scaled harmonic vibrational frequencies and literature values with the exception of the CN ($^2\Sigma^+$) radical where the CBS-APNO and G3 methods underestimate the vibrational frequency by about 10 to 15%. For the ground states of C_2H ($^2\Sigma^+$), HCN ($^1\Sigma^+$), CCO ($^3\Sigma^-$), NCO ($^2\Pi$), CNC ($^2\Pi$), NCN ($^3\Sigma^-$), and NO_2 ($^2A_1$), the calculated lowest vibrational frequency exhibit largest differences (10–20%) by comparison to the literature values than the other vibrational frequencies.

For some species, there are large differences between our calculations and the literature values. A detailed discussion is given below.

C_2H ($^2\Sigma^+$): The vibrational frequencies for the ground state of C_2H are not well known due to a strong vibronic coupling. In particular, the C–H stretch mode has not yet been definitely assigned since its determination is complicated by the presence of the $X^2\Sigma^+$–$A^2\Pi$ system in the same region of the spectrum. Stephens et al. [47] proposed two possible values: 3547 and 3299 cm^{-1} while a value of 3612 cm^{-1} was previously derived from experiments [48–50]. We have calculated the vibrational frequencies at the theoretical equilibrium geometry of C_2H in the harmonic approximation. Our own calculations give 3341, 3425, 3308, 3234, 3431 cm^{-1} at the B3LYP/cc-pVQZ, CBS-QB3, CBS-APNO, G3, and G4 levels of theory, respectively, while most other theoretical determinations are closer to the upper value [51–63]. The CC stretching was reported to be in cm^{-1} 1848 [48–50], and 1841 [38]. Our calculations predict frequencies within about 15% of these two literature values. The lowest vibrational frequency can be attributed to a bending mode. Different experimental studies [64–67] report the value to be in the range of 371.6–389 cm^{-1}. Ab initio methods (CBS-APNO, and G3) overestimate the bending frequency while the DFT methods (B3LYP/cc-pVQZ, CBS-QB3, and G4 (B3LYP optimized geometry)) underestimate this frequency.

NCO ($^2\Pi$): The literature values are taken from the NIST-JANAF Thermochemical Tables [14] where the 1275 and 1922 cm^{-1} vibrational frequencies are from the matrix isolation data [68] whereas the doubly degenerate 536 cm^{-1} vibrational frequency is from Dixon [69,70]. Whatever the level of theory, the calculated vibrational frequencies do not reproduce the degeneracy of the lowest vibrational frequency. This is due to the Renner–Teller splitting of the

π vibrational modes. The doubly degenerate mode splits in two different modes (495 and 572 cm^{-1}) when taking into account the Renner–Teller effect [71]. Previous reported calculations on the NCO radical [72] and our theoretical results are in good agreement with the values given by Bolman and coworkers [71].

CNC ($^2\Pi$): Experimental observations about the fundamentals are scarce for CNC. Only bending fundamental of 321 cm^{-1} was reported for $\tilde{X}^2\Pi_g$ by Merer and Travis [73]. The CNC stretching vibrational frequency of 1453 cm^{-1} is available only for the $\tilde{X}$ state [74] and is not coherent with the reported values in the NIST-JANAF database [14] (900 and 1200 cm^{-1}) which were estimated by comparison with the $^1\Pi$ state of C_3(g) [75,76]. Vibrational frequencies (313, 313, 1264, 1284 cm^{-1}) for the $\tilde{X}^2\Pi_g$ ground state were determined using the CASSCF method [77]. The doubly degenerate mode splits in two different modes (223 and 382 cm^{-1}) when taking into account the Renner–Teller effect. Our computed values using the B3LYP/cc-pVQZ and the different composite methods are in good agreement with the literature values.

CNN ($^3\Sigma^-$): The highest band (2847 cm^{-1}) [78] is an extremely high frequency for a CN or NN stretch. The results of our calculations are not consistent with the observed spectra. It was already noticed in previous theoretical studies [43,44,77,79–81]. Fourier transform laser-induced fluorescence of CNN, $\tilde{A}^3\Pi \rightarrow \tilde{X}^3\sum^-$, in an argon matrix has been investigated by Wurfel and coworkers [82]. Eight new vibronic transitions have been found, indicating that the ground-state asymmetric stretch is 1419 cm^{-1}, about half the 2847 cm^{-1} value of earlier studies [78]. Our theoretical calculations are in good agreement with this value of 1419 cm^{-1}.

3.2. Enthalpies of formation

Table 3 gathers the literature values of the enthalpies of formation $\Delta_f H^\circ_{298K}$ for the i species which are taken from different databases (NIST-JANAF [14], Burcat [15], JPL-06 [83], and Sandia [84]). The enthalpies of formation at 298 K are calculated at different levels of theory through their atomization reactions. The corresponding values as well as their arithmetic averages ($\overline{\Delta_f H^\circ_{298K}(i)}$) and associated uncertainties at a confidence level of 95% ($u(\Delta_f H^\circ_{298K}(i))$) are given in Table 4.

The examination of the Table 3 shows that they are large differences between the literature values mainly between the NIST-JANAF and the other databases for eight species (C_2H, CCO, NCO, CNC, NCN, and HNCO). For example, the reported $\Delta_f H^\circ_{298K}$(NCO) values are 159.4, 128.040, 151, and 134.3 kJ mol^{-1} in the NIST-JA-

Table 3
Literature enthalpies of formation $\Delta_f H^\circ_{298K}$ for the studied species (kJ mol^{-1}).

Species	Literature			
	NIST-JANAF [14]	Burcat [15]	JPL-06 [83]	Sandia [84]
CH ($^2\Pi$)	594.128 ± 17.5	595.8 ± 0.6	597.4 ± 1.3	590.8 ± 4.3
CN ($^2\Sigma$)	435.1 ± 10	438.68 ± 2.0	440 ± 5	452.7 ± 15.3
CO ($^1\Sigma$)	−110.5 ± 0.2	−110.53 ± 0.17	−110.53 ± 0.17	−113.4 ± 4.8
NO ($^2\Pi$)	90.291 ± 0.17	91.3	91.29 ± 0.17	90.4 ± 4.3
CH_2 ($^3\Sigma^-$)	386.39 ± 4.2	391.2 ± 1.6	390.4 ± 0.8	388.3 ± 5.8
C_2H ($^2\Sigma$)	477 ± 29	568.522 ± 4	565.3 ± 2.9	576.1 ± 4.5
HCN ($^1\Sigma^+$)	135.1 ± 8.4	129.799 ± 0.38	132 ± 4	133.1 ± 4.2
HCO ($^2A'$)	43.5 ± 8.0	42.3 ± 0.3	44.15 ± 0.43	38.9 ± 6.9
CCO ($^3\Sigma^-$)	286.6 ± 63	385.68 ± 1.9	×	387.9 ± 8.5
NCO ($^2\Pi$)	159.4 ± 10.5	128.040 ± 4.2	151 ± 14	134.3 ± 19.1
CNC ($^2\Pi$)	556 ± 126	675.85 ± 5.89	×	×
CNN ($^3\Sigma^-$)	585 ± 126	591.87 ± 3.19	×	×
NCN ($^3\Sigma^-$)	473 ± 21	465.89 ± 1.78	×	×
NNO ($^1\Sigma^+$)	82.05 ± 0.4	81.6 ± 0.1	81.6 ± 0.5	77.8 ± 4.9
NO_2 ($^2A_1$)	33.10 ± 0.8	34.2 ± 0.5	34.19 ± 0.5	29.7 ± 17.4
HNCO ($^1A'$)	−101.7 ± 8	−118.6 ± 4.2	−104 ± 12	−119.7 ± 12.8

Table 4
Calculated enthalpies of formation $\Delta_f H^\circ_{298K}$ for the studied species using the atomization reaction (kJ mol^{-1}).

Species (i)	This work						
	CBS-QB3	CBS-APNO	G3B3	G3	G4	$\overline{\Delta f H^\circ_{298K}(i)}$	$u(\Delta_f H^\circ_{298K}(i))$
CH ($^2\Pi$)	596.3	596.8	590.3	590.7	591.8	593.2	8.7
CN ($^2\Sigma$)	446.1	445.0	439.3	446.8	442.7	444.0	8.5
CO ($^1\Sigma$)	−111.6	−109.8	−112.3	−110.8	−113.7	−111.6	4.1
NO ($^2\Pi$)	87.3	92.7	91.2	91.8	89.5	90.5	5.9
CH$_2$ ($^3\Sigma^-$)	396.3	392.5	386.5	386.8	390.0	390.4	11.4
C$_2$H ($^2\Sigma^+$)	573.1	575.3	563.2	570.8	564.9	573.1	9.9[a]
HCN ($^1\Sigma^+$)	132.8	134.0	128.4	131.4	128.5	131.0	7.0
HCO (^{2}A′)	41.3	40.8	40.3	41.5	39.7	40.7	2.0
CCO ($^3\Sigma^-$)	383.3	382.3	375.5	376.2	379.5	379.3	9.7
NCO ($^2\Pi$)	123.9	127.2	121.7	122.9	123.8	123.9	5.6
CNC ($^2\Pi$)	678.8	679.0	674.5	672.9	672.1	675.4	9.0
CNN ($^3\Sigma^-$)	577.1	579.2	575.9	579.8	575.1	577.4	5.7
NCN ($^3\Sigma^-$)	449.4	453.2	445.8	445.1	450.2	448.7	9.3
NNO ($^1\Sigma^+$)	77.3	80.6	81.0	89.9	80.1	81.8	13.2
NO$_2$ (^{2}A$_1$)	26.2	27.8	32.5	35.1	30.4	30.4	9.9
HNCO (^{1}A′)	−120.7	−119.5	−120.9	−119.5	−118.8	−119.9	2.4

[a] Mean and its uncertainty calculated without the G3B3 and G4 methods for which the structure is not linear. In this case, there are only two degrees of freedom corresponding to a t value of 4.304.

NAF [14], Burcat [15], JPL-06 [83], and Sandia [84] databases, respectively. These literature values should be therefore used with great caution. As it can be observed, the difference between our calculated $\overline{\Delta_f H^\circ_{298K}(i)}$ values and their literature counterparts is less than about 4 kJ mol^{-1} for eight species involved in the prompt-NO mechanism (CH, CO, NO, CH$_2$, HCN, HCO, NNO, and NO$_2$). In the case of the cyano radical (CN), our calculated enthalpy of formation at 298 K is in good agreement with the literature values especially if we take into account the associated uncertainties. For all species, our calculated $\overline{\Delta_f H^\circ_{298K}(i)}$ values are in very good agreement with

the ones given in the Burcat [15,84] database with the exception of CNN and NCN. It is worth noticing that CCO, CNC, CNN, and NCN are not in present in the JPL-06 [83] and Sandia [84] databases.

Table 5 reports the enthalpies of formation $\Delta_f H^\circ_{298K}$ (NCN) calculated at different levels of theory using a set of isogyric reactions which involve different species present in the prompt-NO mechanism (CH, CN, HCN, CO, NCO, CH$_2$, and HCO). The enthalpies of formation at 298 K for these species correspond to the values calculated in this work through atomization reactions. The use of the G3 method seems to slightly underestimate the $\Delta_f H^\circ_{298K}$ (NCN). The statistical treatment applied here to the four reactions and the five methods leads to a final value $\Delta_f H^\circ_{298K,final}$ (NCN) of (448.7 ± 3.4) kJ mol^{-1}. This value is in excellent agreement with the one obtained through atomization reaction which is (448.7 ± 9.3) kJ mol^{-1}. A smallest uncertainty is obtained when employing a set of isogyric reactions in the calculation of the enthalpy of formation at 298 K. Our recommended value of $\Delta_f H^\circ_{298K,final}$ (NCN) is also in excellent agreement with the one reported by Clifford et al. [13] (451.9 kJ mol^{-1}). This value is subsequently lower than the one given by Bise et al. [11,12] (465.1 kJ mol^{-1}).

Table 5
Calculated enthalpies of formation $\Delta_f H^\circ_{298K}$ for the NCN biradical (kJ mol^{-1}) using isogyric reactions.

Reactions	$\Delta_f H^\circ_{298K}$ (NCN)				
	CBS-QB3	CBS-APNO	G3B3	G3	G4
NCN + CH → CN + HCN	448.5	452.8	450.2	439.4	452.7
NCN + CO → NCO + CN	447.3	450.7	452.1	444.0	449.6
NCN + CH$_2$ → 2 HCN	451.7	449.3	447.2	440.7	454.9
NCN + HCO → NCO + HCN	448.1	447.1	450.3	446.4	451.8

Table 6
Absolute entropies S°_{298K} for the studied species.

Species	Literature				This work
	NIST-JANAF [14]	Burcat [15]	JPL-06 [83]	Sandia [84]	B3LYP/cc-pVQZ
CH ($^2\Pi$)	183.04 ± 0.04	183.037	183.04	177.0	182.9
CN ($^2\Sigma$)	202.64 ± 0.04	202.643	202.64	202.3	202.4
CO ($^1\Sigma$)	197.65 ± 0.04	197.657	197.660 ± 0.004	197.8	197.5
NO ($^2\Pi$)	210.758	210.748	210.76	204.8	210.6
CH$_2$ ($^3\Sigma^-$)	193.93 ± 0.5	194.418	194.90	201.2	195.2
C$_2$H ($^2\Sigma$)	207.744 ± 5.4	213.304	209.73	209.4	215.6
HCN ($^1\Sigma^+$)	201.828 ± 0.04	201.824	201.82	200.7	201.4
HCO (^{2}A′)	224.649 ± 0.04	224.28	224.34	223.7	224.3
CCO ($^3\Sigma^-$)	233.07	233.624	×	232.5	233.9
NCO ($^2\Pi$)	232.2 ± 0.8	232.229	232.38	226.5	232.2
CNC ($^2\Pi$)	230 ± 8	233.804	×	×	231.6
CNN ($^3\Sigma^-$)	231.716	232.398	×	×	231.9
NCN ($^3\Sigma^-$)	226.21 ± 0.42	225.814	×	×	225.8
NNO ($^1\Sigma^+$)	219.957	220.01	220.01	219.2	219.7
NO$_2$ (^{2}A$_1$)	240.034 ± 0.13	240.171	240.17	239.0	239.9
HNCO (^{1}A′)	238.228 ± 0.4	238.265	237.97 ± 0.8	238.7	238.7

Table 7
Heat capacities C_P as a function of the temperature (J mol^{-1} K^{-1}).

Species	Temperature (K)										
	300	400	500	600	800	1000	1500	2000	3000	4000	5000
CH ($^2\Pi$)	29.1	29.2	29.3	29.6	30.6	31.7	33.9	35.2	36.3	36.8	37.0
	29.2[a], 29.2[b]	29.2	29.4	29.8	31.0	32.6	36.5	39.3	41.4	41.9	42.4
CN ($^2\Sigma$)	29.1	29.4	29.8	30.5	32.0	33.2	35.1	36.0	36.8	37.0	37.2
	29.2[a], 29.2[b]	29.4	29.9	30.7	32.2	33.5	35.7	37.6	42.0	45.0	46.1
CO ($^1\Sigma$)	29.1	29.3	29.8	30.4	31.8	33.1	35.0	35.9	36.7	37.0	37.2
	29.1[a], 29.1[b]	29.3	29.8	30.4	31.9	33.2	35.2	36.3	37.2	37.7	38.1
NO ($^2\Pi$)	29.8	29.9	30.4	31.1	32.6	33.7	35.5	36.2	36.9	37.1	37.2
	29.8[a], 29.9[b]	29.9	30.5	31.2	32.8	34.0	35.8	36.6	37.5	37.9	38.2
CH$_2$ ($^3\Sigma^-$)	34.8	36.3	37.7	38.9	41.5	44.0	49.1	52.3	55.2	56.4	57.1
	34.6[a], 35.0[b]	36.1	37.7	39.2	42.4	45.6	51.3	54.3	57.2	58.4	59.0
C$_2$H ($^2\Sigma$)	43.1	44.4	45.6	46.7	49.1	51.3	55.5	57.9	60.1	61.1	61.5
	37.2[a], 42.0[b]	40.4	42.8	44.8	48.2	50.9	55.7	59.0	64.1	67.0	67.9
HCN ($^1\Sigma^+$)	35.5	38.9	41.4	43.5	47.0	49.9	54.8	57.5	59.9	60.9	61.4
	35.9[a], 35.9[b]	39.2	41.7	43.8	47.3	50.2	55.3	58.3	61.2	62.5	63.
HCO ($^2A'$)	34.7	36.5	38.6	40.8	44.7	47.8	52.4	54.6	56.5	57.2	57.6
	34.6[a], 34.7[b]	36.5	38.7	41.0	45.0	48.1	52.7	54.9	57.1	58.2	59.0
CCO ($^3\Sigma^-$)	43.3	46.6	49.2	51.3	54.5	56.6	59.4	60.6	61.5	61.9	62.1
	43.1[a], 43.1[b]	46.4	49.0	51.2	54.6	57.1	61.3	63.5	65.0	64.9	64.5
NCO ($^2\Pi$)	40.2	43.9	47.0	49.6	53.4	55.9	59.1	60.4	61.5	61.8	62.0
	40.1[a], 40.0[b]	43.9	47.0	49.5	53.4	55.9	59.0	60.4	61.5	61.9	62.4
CNC ($^2\Pi$)	44.0	47.1	49.9	52.2	55.6	57.6	60.0	61.0	61.7	62.0	62.1
	45.8[a], 45.0[b]	49.8	52.8	55.0	57.7	59.2	60.9	61.5	62.0	62.2	62.3
CNN ($^3\Sigma^-$)	42.7	46.3	49.4	51.9	55.4	57.5	60.0	61.0	61.7	62.0	62.1
	42.3[a], 42.7[b]	45.2	47.4	49.1	52.0	54.1	57.6	59.3	60.9	61.5	61.8
NCN ($^3\Sigma^-$)	41.9	45.8	49.0	51.6	55.2	57.3	59.9	60.9	61.7	62.0	62.1
	42.3[a], 41.9[b]	46.2	49.4	51.9	55.5	57.5	60.0	61.0	61.7	62.0	62.3
NNO ($^1\Sigma^+$)	38.5	42.5	45.6	48.2	52.0	54.7	58.3	59.9	61.2	61.7	61.9
	38.7[a], 38.6[b]	42.7	45.8	48.4	52.2	54.9	58.4	60.0	61.2	61.7	61.9
NO$_2$ ($^2A_1$)	37.1	40.3	43.4	46.0	49.8	52.3	55.3	56.5	57.4	57.8	57.9
	37.0[a], 37.2[b]	40.2	43.2	45.8	49.7	52.2	55.2	56.4	57.4	57.7	57.9
HNCO ($^1A'$)	45.8	51.3	55.5	58.8	63.9	67.7	73.8	77.1	80.2	81.4	82.0
	45.2[a], 45.1[b]	50.7	55.0	58.4	63.6	67.5	73.8	77.1	80.1	81.4	82.0

The literature values of the heat capacities are in italics.
[a] These values are taken from Ref. [14].
[b] These values are taken from Ref. [15].

3.3. Entropies and heat capacities at constant pressure

Calculated standard molar entropies S°_{298K} and heat capacities C_P as a function of temperature are given in the Tables 6 and 7, respectively. Available literature values are also listed for comparison purposes. There is an excellent agreement between our calculated S°_{298K} and the corresponding literature values for the eighteen studied species with the exception of the C$_2$H ($^2\Sigma^+$) radical. In this case, our B3LYP/cc-pVQZ calculated value of 215.6 J mol^{-1} K^{-1} is slightly different from the values reported in the NIST-JANAF [14] and JPL-06 [83] databases which were 207.744 and 209.73 J mol^{-1} K^{-1}, respectively while a good agreement between our value and the one taken from the Burcat [15] database (213.304 J mol^{-1} K^{-1}). Similar trend is observed in the case of the calculated S°_{298K} with the CBS-QB3 method (216.0 J mol^{-1} K^{-1}). When using the two other composite methods (CBS-APNO and G3), the values of the standard molar entropies at 298 K are 208.8 and 209.5 J mol^{-1} K^{-1}, respectively. This is in very good agreement with the reported values in the NIST-JANAF [14] and JPL-06 [83] databases. The calculated heat capacities at constant pressure are generally in excellent agreement over the studied temperature range with their literature counterparts. There are however slight differences of about 10–15% mainly at high temperatures for the following species: CH ($^2\Pi$) (2000–5000 K), CN ($^2\Sigma^+$) (3000–5000 K), CH$_2$ ($^3\Sigma^-$) (5000 K), C$_2$H ($^2\Sigma$) (300 and 4000–5000 K), HNCO ($^1A'$) (5000 K).

4. Conclusions

Theoretical calculations allowed to obtain thermochemical properties ($\Delta_f H^{\circ}_{298K}$, S°_{298K}, $C_P = f(T)$) for the electronic ground state of the NCN biradical. In order to validate our methodology, $\Delta_f H^{\circ}_{298K}$, S°_{298K}, $C_P = f(T)$ were determined also for seventeen species involved in the prompt-NO mechanism. The standard enthalpies of formation at 298 K were calculated using atomization reaction based on the CBS-QB3, CBS-APNO, G3B3, G3 and G4 calculation levels. In the case of the NCN biradical, an isogyric set of reactions was also used to assess its standard enthalpy of formation at 298 K. Standard molar entropies at 298 K and heat capacities at constant pressure were estimated at the B3LYP/cc-pVQZ level of theory. Based on our theoretical results, we recommend the use of our calculated thermochemical properties for the modeling of the prompt-NO mechanism: $\Delta_f H^{\circ}_{298K}$ (NCN) = (448.7 ± 3.4) kJ mol^{-1}, S°_{298K} = 225.8 J mol^{-1} K^{-1}, C_P (in J mol^{-1} K^{-1}) = 41.9, 45.8, 49.0, 51.6, 55.2, 57.3, 59.9, 60.9, 61.7, 62.0, 62.1 at 300, 400, 500, 600, 800, 1000, 1500, 2000, 3000, 4000, 5000 K, respectively.

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