



# Threshold photoelectron spectroscopy and dissociative photoionization of NCN and NCN<sub>3</sub>: The NCN enthalpy of formation

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## ARTICLE INFO

Dataset link: <https://pepisco.psi.ch>

### Keywords:

NCN radical  
Enthalpy of formation  
Thermochemistry  
Prompt-NO modeling  
Threshold photoionization

## ABSTRACT

The NCN radical is a key intermediate in prompt-NO formation. For flame simulations that involve detailed NCN radical chemistry such as the prompt-NO switch reaction  $\text{NCN} + \text{H}$ , it is vital to have both accurate kinetic and thermodynamic data on NCN available. This study employed synchrotron-based imaging photoelectron photoion coincidence (iPEPICO) spectroscopy on NCN<sub>3</sub> and NCN to determine a consistent and accurate enthalpy of formation for NCN. The obtained value of  $\Delta_f H_{0\text{K}}^\circ(\text{NCN}) = 450.5 \pm 3.5 \text{ kJ/mol}$  ( $\Delta_f H_{298\text{K}}^\circ(\text{NCN}) = 451.0 \pm 3.5 \text{ kJ/mol}$ ) provides experimental evidence for the recently recommended, similarly low theoretical values. The determination is based on thermodynamic cycles with input from the first reported threshold photoelectron spectrum (TPES) of the NCN radical, indicating an adiabatic ionization energy of  $\text{IE}_{\text{NCN}} = 12.608 \pm 0.027 \text{ eV}$ , complemented by the appearance energy of  $\text{NCN}^+$  from dissociative ionization of NCN<sub>3</sub>,  $\text{AE}_{\text{NCN}^+} = 12.060 \pm 0.015 \text{ eV}$ . We also report the adiabatic ionization energy of NCN<sub>3</sub>,  $\text{IE}_{\text{NCN}_3} = 10.995 \pm 0.010 \text{ eV}$  along with Franck–Condon spectral modeling.

**Novelty and significance statement:** The enthalpy of formation of the biradical NCN has been a subject of debate until recently. Over the years, theoretical calculations, kinetic models and experiments have yielded very different values, ranging from 445 - 473 kJ/mol. However, most recent high-level theoretical calculations seem to converge to a consensus value of about 451 kJ/mol, but an independent experimental verification of this value is still lacking to clarify the discrepancy between two previously reported spectroscopic measurements of 452 kJ/mol and 466 kJ/mol. We took advantage of the synchrotron-based imaging photoelectron photoion coincidence spectroscopy setup at the Swiss Light Source to record the first threshold photoelectron spectrum of NCN, where NCN radicals were generated by a flash pyrolysis of NCN<sub>3</sub>. By combining the derived adiabatic ionization energy with the appearance energy of  $\text{NCN}^+$  from the dissociative photoionization of NCN<sub>3</sub>, we were able to verify the lower enthalpy of formation value.

## 1. Introduction

The cyanonitrene diradical <sup>3</sup>NCN in its triplet electronic ground state, hereafter referred to as NCN, is a key intermediate for prompt-NO formation under fuel rich combustion conditions [1–5]. NCN is a direct reaction product of the reaction  $\text{CH} + \text{N}_2$  (1) [6–8] and subsequent bimolecular reactions of NCN are involved in oxidative pathways that result in the production of NO at high temperatures [4,5]. In modeling the formation of prompt-NO, the rate constant and the branching ratio for the two primary reaction channels of the  $\text{NCN} + \text{H}$  (2) reaction, known as the *prompt-NO* switch, proved to be essential:  $\text{NCN} + \text{H} \rightarrow \text{CH} + \text{N}_2$  (2a) and  $\text{NCN} + \text{H} \rightarrow \text{HCN} + \text{N}$  (2b). Whereas reaction

channel (2b) feeds into the traditional Fenimore pathway for NO formation through the formation of HCN [9], reaction channel (2a) simply represents the reverse of the NCN formation reaction (1).

Although the exact switch-temperature between channel (2a), dominating at overall low temperature, and channel (2b), gaining importance at high temperature, is still subject to a debate [10,11], in the context of this paper it is more important to note that the consistent description of NCN formation and consumption via the equilibrium reaction  $\text{CH} + \text{N}_2 \rightleftharpoons \text{NCN} + \text{H}$  critically depends on the assumed enthalpy of formation of the NCN radical. The important role of NCN thermochemistry in prompt-NO formation has been pointed out earlier by Harding et al. [12] and Goos et al. [13], and has recently been

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<https://doi.org/10.1016/j.proci.2026.106251>

Received 13 March 2026; Accepted 7 June 2026

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discussed and reviewed by Klippenstein et al. [4] and Lamoureux et al. [5]. Interestingly, even though the NCN radical appears to be a straightforward triatomic molecule, its precise enthalpy of formation was subject of considerable uncertainty for a long time. An early experimental value of  $\Delta_f H_{0\text{ K}}^\circ(\text{NCN}) = 451.4 \pm 16.7$  kJ/mol had been reported with fairly high uncertainty limits by Clifford et al. [14]. It was based on electron affinity measurements of  $\text{NCN}^-$ . Later, by using photofragment translational spectroscopy following NCN photodissociation, a seemingly more precise (but now considered significantly too high) value of  $466.5 \pm 2.9$  kJ/mol has been derived by Bise et al. [15]. First single-determinant quantum-chemical calculations yielded significantly lower values of  $448.7 \pm 3.4$  kJ/mol [16], higher-level multireference calculations resulted in  $457.8 \pm 2.0$  kJ/mol [12,13]. The latter values turned out to be inconsistent with a low pressure flame modeling study [17–19], where an enthalpy value of 444 kJ/mol was required to reproduce measured species profiles, including that of NCN. Also the kinetic analysis of the thermochemistry of the  $\text{CH} + \text{N}_2 \rightleftharpoons \text{NCN} + \text{H}$  equilibrium as performed by Faßheber et al. [20] favored an enthalpy of formation of 450 kJ/mol. Their analysis was based on direct measurements of NCN concentration–time profiles in shock tube experiments targeting the rate of the reaction  $\text{NCN} + \text{H}$ .

In the meantime, thanks to state-of-the art thermochemical quantum chemical calculations using high-level compound methods (ANL0, ANL1, HEAT456-QPH), the issue seems to be largely resolved [4,21]. In particular, it turned out that the sensitivity of the calculated wavenumber for the asymmetric stretching vibration of NCN to spin restriction at the Hartree–Fock and/or the CCSD(T) level of theory caused errors in the quantum-chemically predicted vibrational zero-point energy and the derived enthalpy of formation of up to 12 kJ/mol [4]. The latest recommended enthalpies of formation from different sources now agree within  $< 1$  kJ/mol, with values of  $\Delta_f H_{0\text{ K}}^\circ(\text{NCN}) = 451.4 \pm 0.4$  kJ/mol recommended in the most recent update of the Active Thermochemical Tables (ATcT) [22] and  $451.0 \pm 1.0$  kJ/mol in the NCN review by Lamoureux et al. [5]. However, the authors clearly emphasize that this value has yet to be experimentally confirmed because even a few kJ/mol level of uncertainty cause large effects in  $\text{NO}_x$  modeling. For example, Faßheber et al. [20] demonstrated that changing the enthalpy value strongly influenced their analysis of the  $\text{NCN} + \text{H}$  rate constant measurements, leading to prompt-NO switch branching fractions between 52% and 20% when the enthalpy was varied from  $\Delta_f H_{298\text{ K}}^\circ(\text{NCN}) = 445.7$  kJ/mol to 457.8 kJ/mol at a representative flame temperature of  $T = 1300$  K. This, in turn, directly affects the NO mole fractions predicted in flames. In their modeling work, Goos et al. [13] showed that the same enthalpy change reduced the calculated peak NCN mole fraction by a factor of 1.7, accompanied by a reduction in NO formation by a factor of 1.6 for a fuel-rich low-pressure  $\text{CH}_4/\text{O}_2/\text{N}_2$  flame. The aim of this work was to provide an accurate experimental value for the NCN enthalpy of formation by using imaging photoelectron photoion coincidence (iPEPICO) spectroscopy. Synchrotron-based iPEPICO has proven successful to provide gas-phase enthalpies of formation with 1–2 kJ/mol accuracy based on the determination of highly accurate ionization (IE) and appearance energies (AE) in combination with thermochemical cycles [23–27]. Next to ionization energies of NCN and its precursor  $\text{NCN}_3$ , we also measured the appearance energy for dissociative photoionization of  $\text{NCN}_3$  forming  $\text{NCN}^+ + \text{N}_2$ . From these data, a consistent value for the NCN enthalpy of formation can be derived using two thermodynamic cycles, employing either the literature values for the enthalpy of formation of  $\text{NCN}_3$  or the  $\text{NCN}^+$  ion.

## 2. Experimental section

iPEPICO experiments were carried out at the VUV beamline of the Swiss Light Source, providing monochromatic VUV radiation. The photon energy resolution was determined by scanning the argon Rydberg series in both first and second order of the 150 lines/mm grating,

yielding a photon energy resolution of 5 meV. The kinetic energy resolution of the photoelectrons was limited to a maximum of 10 meV, resulting in an overall error propagation of approximately 11 meV (1 kJ/mol) for the instrument. No correction has been applied to the finally determined IE and AE values for potential Stark shifts, as we have recently found that the observed peak maxima are only affected by a few meV [28]. Further details of the experimental setup and application examples are described elsewhere [28–31].

Dissociative photoionization or thermal decomposition of cyanogen azide ( $\text{NCN}_3$ ) served as  $\text{NCN}^+$  and NCN source, respectively. Due to the tendency of the highly toxic  $\text{NCN}_3$  to violently explode, it cannot be stored and needs to be synthesized in the gas phase directly before the experiments. The synthesis has been accomplished according to Dammeier et al. [32,33] using solid sodium azide ( $\text{NaN}_3$ ) and gaseous cyanogen bromide as precursors. The gaseous product, containing mostly  $\text{NCN}_3$ , residual  $\text{BrCN}$ , and the side product  $\text{N}_2$ , was passed into a glass flask and was diluted to 0.1 – 1% with Ar/He. In the dissociative photoionization experiments,  $\text{NCN}^+$  was generated by single photon ionization according to  $\text{NCN}_3 + h\nu \rightarrow {}^3\text{NCN}^+ + \text{N}_2 + \text{e}^-$  by directly expanding the  $\text{NCN}_3/\text{Ar}$  mixture through a 6 mm outer diameter Teflon tube into the ionization zone of the iPEPICO endstation (effusion setup). Alternatively, a Chen-type flash-pyrolysis setup [34] has been used (pyrolysis setup). It consisted of a 100  $\mu\text{m}$  pinhole, connected to a resistively heated SiC microreactor with inner diameter of 1.0 mm and a heated length of about 10 mm. The thermal decomposition of  $\text{NCN}_3$  yields NCN radicals according to  $\text{NCN}_3 + \text{M} \rightarrow {}^1\text{NCN} + \text{N}_2 + \text{M} \rightarrow {}^3\text{NCN} + \text{N}_2 + \text{M}$  [33,35]. After passing the reactor, the reactive mixture expanded into the source chamber ( $10^{-4}$  mbar) and the effusive gas beam was further skimmed before entering the ionization chamber ( $10^{-6}$  mbar).

Photoelectrons were velocity map imaged and served as start signal for the photoion time-of-flight analysis. Threshold electrons were focused onto the center of the imaging detector. Subtraction of kinetic energy electrons detected in a small ring region around this center spot yielded the photoionization mass-selected threshold photoelectron spectrum (ms-TPES) [36]. At higher photon energies, the parent molecule undergoes dissociative photoionization. While the TPE signal of the parent ion decreases, the one of the fragment ion increases. Above the dissociation limit (appearance energy, AE) only the TPE signal of the fragment ion remains. To analyze the dissociative photoionization in detail and to extract precise AE values, the fractional abundance of the parent and fragment ions is plotted against the photon energy in a so-called breakdown diagram. Details of the analysis of breakdown diagrams including the treatment of internal energies in the neutral and the fragments are outlined in Sztáray et al. [26]. Briefly, in threshold ionization, the internal energy distribution of the neutral is transferred to the ions' manifold, resulting in a well-defined parent ion energy distribution. This rovibrational energy distribution leads to a red-shift of the onset of fragmentation and thus to a broadening of the breakdown diagram, but does not shift the underlying 0 K appearance energy. In our experiment, fragmentation is prompt on the time scale of the experiment, as indicated by the absence of a kinetic shift (i.e. symmetric fragment ion peak). Thus all ions with internal energy above the dissociation threshold will dissociate and only the thermal energy distribution of the neutral has to be considered when fitting the breakdown diagram.

Gaussian 09/16 has been utilized, applying the B3LYP functional and the 6-311++G(d,p) basis set, to calculate the equilibrium geometry and force constant matrices [37]. Composite method calculations (CBS-APNO, G4, W1BD) were used to further refine thermochemical data. For the analysis of the ms-TPE spectra, Franck–Condon factors were calculated with the program ezSpectrum [38] utilizing MP2/6-31G(d) geometries and force constant matrices. The obtained stick spectra were convoluted by a 30–50 meV Gaussian function to enable comparison with the experiment.

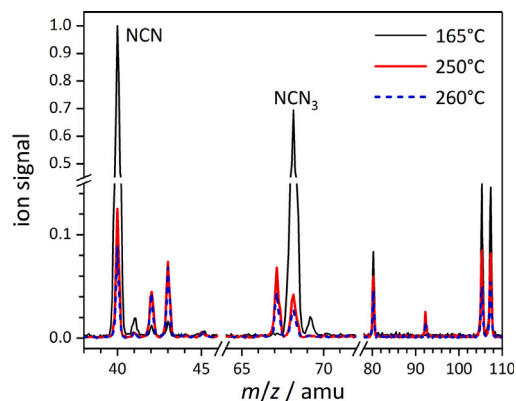


Fig. 1. Time-of-flight mass spectra following  $\text{NCN}_3$  pyrolysis at different temperatures and a photon energy of 12.7 eV.

### 3. Results and discussion

#### 3.1. Mass spectra

Fig. 1 shows time-of-flight (TOF) mass spectra recorded at a photon energy of 12.7 eV at three different pyrolysis temperatures of 165°C (black curve), 250°C (red curve) and 260°C (blue dashed curve). The mass signals of the parent ion  $\text{NCN}_3^+$ , with a mass-to-charge ratio  $m/z$  68, and the  $\text{NCN}_3$  fragment or parent  $\text{NCN}^+$  from  $\text{NCN}$  formed in the pyrolysis,  $m/z$  40, are clearly visible in all three spectra. The relative intensities of the isotopic peaks at  $m/z$  41 and  $m/z$  69 are fully consistent with the expected relative isotopic abundances of the sum of the  $^{13}\text{C}$  and  $^{15}\text{N}$  substituted species (1.81% for  $\text{NCN}$  and 2.54% for  $\text{NCN}_3$ ). With increasing temperature, the  $m/z$  68 peak diminishes but does not disappear completely. Also the  $m/z$  40 signal decreases, but the  $m/z$  40/68 ratio increases from 1.4 (165°C) to 3.0 (250°C) and 3.2 (260°C). Whereas at 165°C the  $\text{NCN}^+$  signal only originates from the dissociative photoionization of thermally stable  $\text{NCN}_3$ , we attribute the relative increase of the  $\text{NCN}^+$  signal to the direct ionization of  $\text{NCN}$  formed from the thermal decomposition of  $\text{NCN}_3$ . However, several other mass peaks were present in the TOF spectra as well, where the signals at  $m/z$  80, 105, and 107 decreased and the signals at  $m/z$  42, 43, 67, and 92 increase or newly appeared at the higher pyrolysis temperatures. Tentatively, these signals originate from pyrolysis products and fragments of  $\text{NCN}_3$  polymer species or minor contaminations (e.g., the acetyl ion at  $m/z$  43 as a fragment of acetone). Interfering polymerization during storage and handling of  $\text{NCN}_3$  has already been mentioned by Faßheber et al. [39] (as inferred from Fourier transform infrared spectra, gas chromatography, and mass spectrometric measurements) and is also evident from our signals at higher  $m/z$ . For example, the  $m/z$  92 peak could be due to  $\text{C}_3\text{N}_4^+$ ,  $m/z$  80 to  $\text{C}_2\text{N}_4^+$ , and  $m/z$  42 to  $\text{N}_3^+$ . Finally, the double peak at  $m/z$  105 and 107 originates from residual  $\text{BrCN}$  (ionization energy 11.84 eV [40]) from  $\text{NCN}_3$  synthesis. Even though this overlapping ion signals from impurities are likely to complicate the analysis of simple photoionization curves, ms-TPE spectra and breakdown curves obtained from iPEPICO should still enable the determination of accurate ionization and appearance energies.

#### 3.2. ms-TPE spectrum and breakdown diagram of $\text{NCN}_3$

**TPE spectrum:** Fig. 2 shows the ms-TPE spectrum of  $\text{NCN}_3$  obtained from the effusive measurements utilizing an  $\text{NCN}_3/\text{Ar}$  gas mixture together with the corresponding Franck-Condon simulation. The onset of the TPE signal is seen around 10.9 eV with a first intense peak maximum at a photon energy of  $10.995 \pm 0.010$  eV ( $1060.9 \pm 1.0$  kJ/mol). This peak is assigned to the adiabatic ionization energy (IE) of  $\text{NCN}_3$ , which is in excellent agreement with composite method calculations

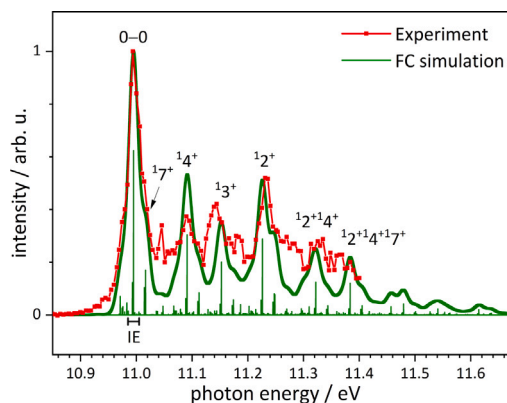


Fig. 2. ms-TPE spectrum of  $\text{NCN}_3$  (red) and the corresponding Franck-Condon simulation (green, stick spectrum and convoluted band shape). Vibrational transitions are labeled in the Mulliken notation, where the modes are sorted by symmetry in descending order. Adiabatic ionization energy  $\text{IE} = 10.995 \pm 0.010$  eV.

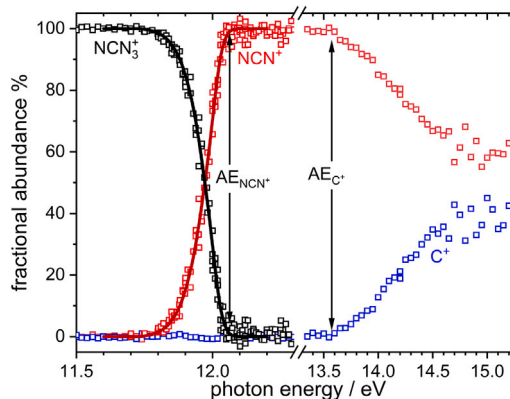


Fig. 3. Threshold photoionization breakdown diagram for dissociative  $\text{NCN}_3$  photoionization.  $\text{AE}_{\text{NCN}^+} = 12.060$  eV,  $\text{AE}_{\text{C}^+} = 13.57$  eV.

at 10.98 eV (CBS-APNO), 11.02 (G4) and 11.03 (W1BD). First photoelectron spectra of  $\text{NCN}_3$  were recorded by Bak et al. [41] and Frost et al. [42]. Our IE value is in quantitative agreement with their reported  $\text{NCN}_3$  ionization energies of 10.96 eV and 11.00 eV. To confirm the IE assignment, we carried out Franck-Condon simulations at MP2/6-31G(d) level of theory at 300 K. The vibrational progression and the relative intensities match very well with the experiment, showing that the spectrum can be clearly attributed to  $\text{NCN}_3$  photoionization.

The highest occupied molecular orbital (HOMO) of  $\text{NCN}_3$  (N1-C-N2-N3-N4) exhibits  $\pi$  character with a node at the carbon atom and at the nitrogen atom N3. Consequently, the N1-C and the N2-N3 bond length increases, while the C-N2 bond decreases upon ionization. In addition, both the N1-C-N2 and N2-N3-N4 angles decrease by  $3^\circ$ . This change in geometry is mirrored by four totally symmetric modes in the FC simulation. We obtained calculated values of  $1863\text{ cm}^{-1}$  (N-C-N stretch,  $\nu_2$ ),  $1271\text{ cm}^{-1}$  (C-N & N-N antisymmetric stretch,  $\nu_3$ )  $774\text{ cm}^{-1}$  (C-N and N-N symmetric stretch,  $\nu_4$ ) and  $174\text{ cm}^{-1}$  (N-C-N & N-N-N bending,  $\nu_7$ ), respectively. These are in very good agreement with the experimental values of  $1940\text{ cm}^{-1}$  ( $\nu_2$ ),  $1160\text{ cm}^{-1}$  ( $\nu_3$ ) and  $720\text{ cm}^{-1}$  ( $\nu_4$ ), derived from the peaks at 11.236 eV, 11.139 eV, and 11.084 eV in the ms-TPE spectrum, with an estimated uncertainty in the peak positions relative to the 0-0 transition of  $\pm 15$  meV ( $\pm 120\text{ cm}^{-1}$ ). Above 11.3 eV,  $\nu_2\nu_4$  and  $\nu_2\nu_4\nu_7$  combination bands are responsible for the two less well resolved intensity features.

**Breakdown diagram:** In the mass spectra, at photon energies below 11.75 eV, only the parent peak of  $\text{NCN}_3^+$  at  $m/z$  68 was observed. By

further increasing the photon energy, fragment peaks at  $m/z$  40 ( $\text{NCN}^+$ ) and  $m/z$  12 ( $\text{C}^+$ ) became visible. To determine the appearance energy of  $\text{NCN}^+$ , a breakdown diagram has been plotted, as shown in Fig. 3. Between 11.7 and 12.2 eV, dissociative photoionization of  $\text{NCN}_3^+$  (black symbols) takes place, where the decrease of the fractional abundance of the  $\text{NCN}_3^+$  signal is accompanied by a corresponding  $\text{NCN}^+$  increase. A fit of the breakdown curves assuming a room temperature Boltzmann distribution (red and black curves) yields an appearance energy for  $\text{NCN}^+$  of  $\text{AE}_{\text{NCN}^+} = 12.060 \pm 0.015$  eV ( $1163.6 \pm 1.4$  kJ/mol). In good agreement with the experiment, our composite method calculations find values of 12.06 eV (G4), 12.14 eV (W1BD) and 12.10 eV (CBS-APNO), respectively. Due to the absence of a reverse barrier along the  $\text{NCN}-\text{N}_2$  coordinate, the bond energy in the cation can be determined by subtracting the adiabatic IE of  $\text{NCN}_3$  from the appearance energy AE of the  $\text{NCN}^+$  fragment, resulting in 1.065 eV (102.8 kJ/mol). Note that the vanished parent ion reflects the 0 K appearance energy, i.e., the threshold for fragmentation of a rovibrationally cold molecule. Moreover, since fragment ions only carry internal energy after crossing the 0 K dissociation threshold, this does not influence the determination of the enthalpy of formation of  $\text{NCN}$ .

In principle, reaction channels with higher barriers can be tracked by increasing the photon energy even more. Indeed, at energies  $> 13.5$  eV, the fractional abundance of the  $\text{NCN}^+$  ion starts to decrease for the sake of an increase of the  $m/z$  12 signal, indicating  $\text{C}^+$  formation. In contrast to the simple bond fission process yielding  $\text{NCN}^+$  and  $\text{N}_2$ , the formation of the  $\text{C}^+$  fragment involves energy partitioning between the  $\text{NCN}$  and  $\text{N}_2$  fragments and a more complicated elimination step, presumably with reaction barrier over a cyclic transition state [15]. The appearance energy for  $\text{C}^+$ ,  $\text{AE}_{\text{C}^+} = 13.57$  eV ( $\leq 1309$  kJ/mol), is taken from the onset of the second breakdown signal, corresponding to the upper limit of the reaction energy for  $\text{C}^+$  fragment formation. Note that the fragments  $\text{N}_3^+$  and  $\text{CN}^+$  were not detected, as they would only be expected to appear at photon energies above 15 eV, which lies beyond the photon energy range used in the present study.

### 3.3. ms-TPE spectrum of NCN

Flash pyrolysis of  $\text{NCN}_3$  at  $T = 255^\circ\text{C}$  led to almost complete thermal decomposition of  $\text{NCN}_3$ , so that the  $m/z$  40 signal can be attributed primarily to  $\text{NCN}^+$  generated by direct photoionization of  $\text{NCN}$  radicals, rather than to a fragment ion of  $\text{NCN}_3$  (see Section 3.1). Fig. 4a illustrates three experimental ms-TPE spectra of the free  $\text{NCN}$  radical, depicted in varying shades of red, each recorded using a different photon-energy step size. To the best of our knowledge, these are the first reported TPE spectra for  $\text{NCN}$ . Overall, the spectra exhibit rather low signal-to-noise ratio, but a broad peak centering around 12.6 eV can be clearly identified in all spectra. This peak disappears for a scan with the pyrolysis temperature set to only  $165^\circ\text{C}$  (blue square symbols in Fig. 4a), as expected for a temperature with negligible thermal  $\text{NCN}$  formation. Additionally, Fig. 4a shows an  $\text{NCN}$  TPES recorded from effusive  $\text{NCN}_3$  at room temperature (dark gray squares), scaled to match the signal intensity of the pyrolysis experiments to compensate for the higher count rate. This spectrum likewise exhibits a flat baseline, with no sign of peak structure. Unlike conventional photoelectron spectroscopy, the iPEPICO method efficiently suppresses possible contributions from other mass channels. Although polymerization products at  $m/z$  80 and 92 were observed in the mass spectrum (Fig. 1) and their fragmentation could, in principle, yield  $m/z$  40 fragments, any impact on the high-temperature ms-TPE signal of  $\text{NCN}$  can be regarded as negligible, since the intensity of the  $165^\circ\text{C}$  ms-TPES in Fig. 4a is essentially zero.

We also attempted to collect data for the dissociative photoionization channel yielding  $\text{C}^+ + \text{N}_2$ . At higher photon energies, a very weak  $m/z$  12 signal was indeed detected. However, the very weak signals for both  $\text{NCN}^+$  and  $\text{C}^+$  prevented a more accurate breakdown-diagram analysis. We note, though, that the onset of  $\text{C}^+$  formation at around

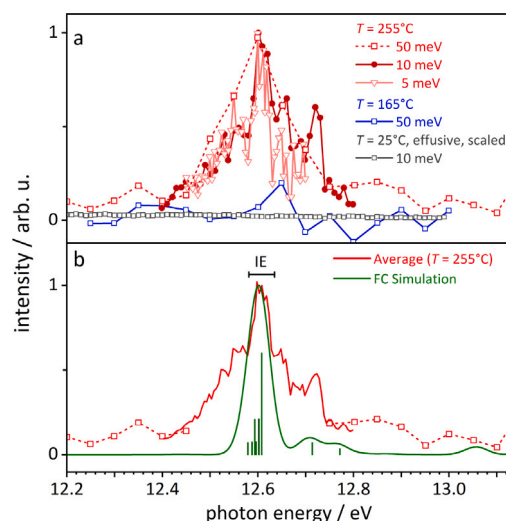


**Fig. 4.** ms-TPE spectrum of the free  $\text{NCN}$  radical. (a) Three scans with variable step size (red symbols and curves) in comparison with a residual TPE signal for an experiment with a pyrolysis temperature too low for thermal decomposition of  $\text{NCN}_3$  (blue symbols and curve) and the corresponding room temperature signal using the  $\text{NCN}_3$  effusion setup (black symbols). (b) Average TPE spectrum for the overlap region of the three scans (red), in comparison with the Franck–Condon simulation (green, stick spectrum and convoluted band shape). Adiabatic ionization energy  $\text{IE} = 12.608 \pm 0.027$  eV.

14 eV lies clearly above the 13.57 eV appearance energy of  $\text{C}^+$  from  $\text{NCN}_3$  dissociative photoionization, providing further evidence that the  $m/z$  40 signal is not due to  $\text{NCN}_3$  fragment ions. Finally, in the scan with 10 meV step size (red circles in Fig. 4a), an additional weak and narrow peak seems to develop at 12.72 eV. However, because an unusual peak was also detected in the total photoelectron curve at precisely the same photon energy, this could be an experimental artifact, possibly caused by an instability in the pyrolysis temperature or in the  $\text{NCN}_3$  gas supply.

Fig. 4b displays the averaged ms-TPE spectrum (red) in comparison with a Franck–Condon simulation (green) with the temperature set to 600 K. Within the harmonic approximation, essentially only one intense spectral feature is predicted, hence in qualitative agreement with the experiment. Taking the FC envelope into account, the maximum of the TPE spectrum can be pinned down to 12.602 eV, whereby the adiabatic ionization energy (corresponding to the most intense transition in the stick spectrum) is expected to be slightly blue-shifted, since several red-shifted hot bands significantly contribute to the predicted TPE spectral shape. As the best fit, we determine a 6 meV shifted value of  $\text{IE}_{\text{NCN}} = 12.608 \pm 0.027$  eV ( $1216.5 \pm 2.6$  kJ/mol). This value compares well with an early theoretical estimate of Armstrong et al. [43]. Based on quantum-chemical calculations on G2 level of theory, they have reported an adiabatic ionization energy of 12.52 eV (1208 kJ/mol) for  $\text{NCN}$  and  $\text{NCN}^+$  in their linear  $^3\Sigma_g^-$  and  $^2\Pi_g$  electronic ground states, respectively. Our CBS-APNO, G4 and W1BD calculations differ only slightly and result in 12.63 eV, 12.59 eV and 12.67 eV, respectively.

Note that the overall very broad band is not fully reproduced by the FC simulation. This is most probably caused by subtle effects of the pyrolytic formation of  $\text{NCN}$  [34], including signal contributions from thermally highly excited  $^3\text{NCN}$  biradicals or residual interfering signal contributions from dissociative photoionization of  $\text{NCN}_3$ . Another possible contribution to the broad band may be related to a Renner–Teller effect. According to the literature, the  $^2\Pi_g$  electronic state of the  $\text{NCN}$  cation feels a Renner–Teller coupling, which breaks the degeneracy of the bending mode, effectively reducing the symmetry from  $D_{\infty h}$  to  $C_{2v}$  [43,44]. Thus, we refrain from a detailed vibrational assignment of the predicted band structure from our FC simulation. A Renner–Teller splitting is expected to broaden the observed TPE band and also slightly

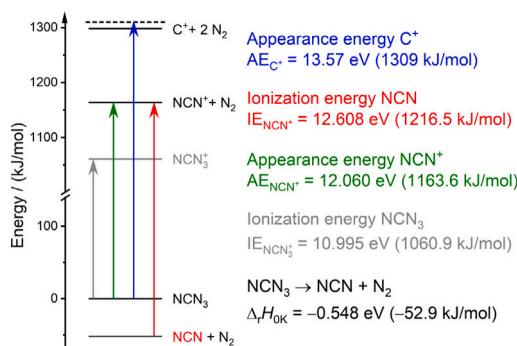


**Fig. 5.** Energy diagram summarizing the determined ionization and appearance energies.

**Table 1**

Thermodynamic cycles.

|                                                                                                                               |            |
|-------------------------------------------------------------------------------------------------------------------------------|------------|
| $\text{NCN}_3 \rightarrow \text{NCN}^+ + \text{N}_2 - \text{AE}_{\text{NCN}^+}$                                               | I          |
| $\text{NCN} \rightarrow \text{NCN}^+ - \text{IE}_{\text{NCN}}$                                                                | II         |
| $\text{NCN}_3 \rightarrow \text{C}^+ + 2 \text{N}_2 - \text{AE}_{\text{C}^+}$                                                 | III        |
| $\text{NCN}_3 \rightarrow \text{NCN} + \text{N}_2 - \text{AE}_{\text{NCN}^+} + \text{IE}_{\text{NCN}}$                        | IV = I–II  |
| $\text{NCN} \rightarrow \text{C}^+ + \text{N}_2 - \text{AE}_{\text{C}^+} + \text{AE}_{\text{NCN}^+} - \text{IE}_{\text{NCN}}$ | V = III–IV |

shifts the adiabatic ionization energy of the vibrational ground state corresponding to the lower Renner-Teller component. According to Armstrong et al. [43], the bending vibration of the split components are 378 and 235  $\text{cm}^{-1}$ , hence only a small shift of the zero-point vibrational energy of about 35  $\text{cm}^{-1}$  (0.42 kJ/mol, 0.0043 eV) is expected. For a quantitative treatment of the Renner-Teller coupling and its effect on the TPE spectrum, a full quantum chemical treatment of the rovibronic problem such as the one presented by Coudert et al. [44] for the photoelectron spectra of CNC, CCN, and HCCN, is needed. Although such a detailed analysis of the system is outside the scope of this experimental study, it is worth mentioning that our observed  $-6$  meV shift of the peak maximum (relative to the adiabatic ionization energy) is comparable to the  $-12$  to  $21$  meV peaks shifts calculated by Coudert et al. To account for the extra uncertainties that may arise from all the mentioned effects, we have assigned a relatively large uncertainty of 27 meV (2.6 kJ/mol) to the adiabatic ionization energy (as indicated by the error bar in Fig. 4b). It corresponds to the peak half width (FWHM) of the Franck-Condon envelope.

### 3.4. NCN formation enthalpy

We use the combined results from the  $\text{NCN}_3$  and NCN photoionization measurements to determine the NCN enthalpy of formation based on thermodynamic cycles outlined in Table 1. The energy diagram in Fig. 5 summarizes the results of the iPEPICO measurements. A first estimate of the NCN enthalpy of formation can directly be obtained from reaction (II) using  $\text{IE}_{\text{NCN}}$  and a literature value of  $\Delta_f H_{0\text{K}}^\circ(\text{NCN}^+) = 1672.4 \pm 2.6$  kJ/mol, the latter adopted from the most recent ATcT update [22]. Taking possible error compensation into account by standard Gaussian error propagation,  $\Delta_f H_{0\text{K}}^\circ(\text{NCN}) = 455.9 \pm 2.8$  kJ/mol is obtained. However, it is possible that an estimate based on  $\text{NCN}^+$  has a certain bias, as the ATcT data for  $\text{NCN}^+$  are closely linked to the data for NCN itself. Therefore, we prefer reaction (IV) that cancels out the contribution of  $\text{NCN}^+$  and instead relies on  $\text{IE}_{\text{NCN}}$ ,  $\text{AE}_{\text{NCN}^+}$  and the independent knowledge of the enthalpy of formation of  $\text{NCN}_3$ , yielding  $\Delta_f H_{0\text{K}}^\circ(\text{NCN}) = -52.9 \text{ kJ/mol} + \Delta_f H_{0\text{K}}^\circ(\text{NCN}_3)$ .

Based on CCSD(T)-F12a/aug-cc-pVTZ ab-initio calculations with a higher-order correction for connected quadruple excitations obtained as CCSDT(Q) - CCSD(T) in a smaller basis, Pfeifle et al. [45] reported a value of  $\Delta_f H_{0\text{K}}^\circ(\text{NCN}_3) = 504.6$  kJ/mol. Literature benchmarks for such post-CCSD(T) composite approaches suggest an uncertainty of

roughly 2–4 kJ/mol for well-behaved single-reference systems [46,47], but can degrade for multireference cases. Therefore, Pfeifle et al. further reduced this uncertainty through an isodesmic reaction scheme,  $\text{HN}_3 + \text{HCN} \rightarrow \text{NCN}_3 + \text{H}_2$ , leading us to estimate the accuracy to approximately 2 kJ/mol due to enhanced error cancellation. Another accurate value,  $501 \pm 4$  kJ/mol, has been determined by Dorofeeva et al. [48] using a G4 approach with 16 isodesmic reactions and 5 reference azides, with  $\text{HN}_3$  chosen as a key reference compound. Here, the stated uncertainty range includes all determined values for the 16 isodesmic reactions. Adopting the weighted average of the two high-level theoretical estimates as a consensus value,  $\Delta_f H_{0\text{K}}^\circ(\text{NCN}_3) = 503.4 \pm 1.8$  kJ/mol, the enthalpy of formation becomes  $\Delta_f H_{0\text{K}}^\circ(\text{NCN}) = 450.5 \pm 3.5$  kJ/mol. Here, the error estimate is based on standard error Gaussian propagation of the uncertainties 1.8 kJ/mol, 1.4 kJ/mol (15 meV), and 2.6 kJ/mol (27 meV) for  $\Delta_f H_{0\text{K}}^\circ(\text{NCN}_3)$ ,  $\text{IE}_{\text{NCN}}$ , and  $\text{AE}_{\text{NCN}^+}$ , respectively. Finally, with an enthalpy difference of  $\Delta(298 \text{ K} - 0 \text{ K}) = 0.47$  kJ/mol [5] this corresponds to a room temperature value of  $\Delta_f H_{298 \text{ K}}^\circ(\text{NCN}) = 451.0 \pm 3.5$  kJ/mol.

Ideally, we would have liked to calculate the NCN enthalpy by reaction (V) in Table 1 as it can be referenced to the very accurately known enthalpy of formation of the  $\text{C}^+$  ion ( $1797.837 \pm 0.0039$  kJ/mol [22]). However, as the dissociative photoionization reaction III takes place over an exit barrier and therefore  $\text{AE}_{\text{C}^+}$  from the  $\text{NCN}_3$  breakdown diagram serves as an upper limit for its reaction energy, we can only specify a lower limiting value of  $\Delta_f H_{0\text{K}}^\circ(\text{NCN}) > 435.9$  kJ/mol from these data.

Our new experimental value  $\Delta_f H_{0\text{K}}^\circ(\text{NCN}) = 450.5 \pm 3.5$  kJ/mol serves as an independent experimental verification of previously reported spectroscopic measurements of  $451.4 \pm 16.7$  kJ/mol by Clifford et al. [14] and  $466.0 \pm 2.9$  kJ/mol by Bise et al. [15]. Clifford et al. [14] used negative ion photoelectron spectroscopy to measure the electron affinities of the NCN and the cyanoamino radical ( $\text{HNCN}$ ), where  $\text{NCN}^-$  and  $\text{HNCN}^-$  has been generated by  $\text{O}^-$  and  $\text{OH}^-$  reactions with cyanamide ( $\text{NH}_2\text{CN}$ ). The kinetic energy of the photodetached electrons were analyzed with an instrumental resolution of 6–10 meV, yielding the electron affinities of  $\text{EA}_{\text{HNCN}} = 2.622 \pm 0.005$  eV and  $\text{EA}_{\text{NCN}} = 2.484 \pm 0.006$  eV, the latter in excellent agreement with the results of a similar work of Taylor et al. [49] reporting  $\text{EA}_{\text{NCN}} = 2.481 \pm 0.008$  eV. Clifford et al. deduced the enthalpy of formation of NCN from two thermochemical cycles, the first including the gas phase acidity of  $\text{NH}_2\text{CN}$  [50], the second the gas phase acidity of  $\text{HNCN}$ . As the latter was not experimentally available, it was calculated with complete basis set (CBS) ab initio electronic structure calculations, which were checked to reliably reproduce the experimental gas phase acidity of  $\text{NH}_2\text{CN}$  beforehand. Together with the well-known ionization energy of the H atom and the enthalpy of formation of  $\text{NH}_2\text{CN}$  [51], the NH bond dissociation energy of  $\text{NH}_2\text{CN}$  and with it the enthalpy of formation of  $\text{HNCN}$  was calculated first. This value has then been adopted in the second thermodynamic cycle to finally deduce the enthalpy of formation of NCN. Although this method is expected to yield a robust absolute value, error propagation limited the determination of the NCN enthalpy of formation to an uncertainty of  $\pm 16.7$  kJ/mol. However, using the currently accepted value of the enthalpy of formation of  $\text{NCN}^-$  from the ATcT database [22],  $\Delta_f H_{0\text{K}}^\circ(\text{NCN}^-) = 211.91 \pm 0.60$  kJ/mol, together with the EA value from Clifford et al. results in  $\Delta_f H_{298 \text{ K}}^\circ(\text{NCN}) = 452.1 \pm 1.0$  kJ/mol. Even though this value and its very small uncertainty are somewhat biased — since the ATcT values rely by 50% on the electron affinities reported by Clifford et al. and Taylor et al. themselves — this exercise clearly demonstrates not only that Clifford's value quantitatively matches our measurement, but also that the currently adopted values for the NCN system are thermodynamically consistent.

Finally, Bise et al. [15] determined the NCN enthalpy of formation based on fast beam photofragment translational spectroscopy (PTS). Following a pulsed electric discharge of  $\text{H}_2\text{NCN}$ , NCN radicals were

generated by mass-selective photodetachment of  $\text{NCN}^-$  ions. In a second step, the relative kinetic energy distribution of the fragments formed from photodissociation by a second laser were imaged on a time-and-position sensitive microchannel plate detector. For the photodissociation channel  $\text{NCN} \rightarrow \text{N}_2 + \text{C}$ , the enthalpy of formation of ground state NCN can be deduced from the measured maximum relative kinetic energy  $E_T^{\text{max}}$  of the fragments by the energy balance equation  $h\nu + E_{\text{int}}(\text{NCN}) = D_0(\text{NCN}) + E_T^{\text{max}}$ . Here,  $E_{\text{int}}(\text{NCN})$  is a small rotational energy contribution of the parent radical ( $\approx 33 \text{ cm}^{-1}$ ) and  $D_0 = \Delta_f H_{0\text{K}}^\circ(\text{C}) - \Delta_f H_{0\text{K}}^\circ(\text{NCN})$  is the enthalpy of reaction at  $T = 0 \text{ K}$ . Clear onsets of the translation energy distributions have been observed in Ref. [15], hence the determination of an accurate  $\Delta_f H^\circ(\text{NCN})$  from  $E_T^{\text{max}}$  and the well-known enthalpy of formation of the C atom was straightforward. Therefore, the remaining discrepancy of the reported enthalpy of about 16 kJ/mol is surprising. In principle, due to the underlying dissociation dynamics and in particular for dissociation channels with exit barrier, the experimentally derived  $E_{\text{max}}$  may underestimate the thermochemical limit [52]. However, as a higher  $E_{\text{max}}$  value would result in an even higher  $\Delta_f H^\circ(\text{NCN})$  and as the reported PTS data are of high quality, the reason for the deviation must remain unclear at this point.

#### 4. Conclusion

iPEPICO spectroscopy has been successfully applied to measure the first threshold photoelectron spectrum of the triplet ground state NCN radical. Taking advantage of (i) the directly measured adiabatic ionization energy of NCN and (ii) the  $\text{NCN}^+$  appearance energy from dissociative photoionization of  $\text{NCN}_3$ , we were able to constrain the enthalpy of formation of the NCN radical to  $\Delta_f H_{0\text{K}}^\circ(\text{NCN}) = 450.5 \pm 3.5 \text{ kJ/mol}$ . This result is significantly lower than previous estimates, but in excellent agreement with the most recent quantum-chemical predictions (450.3 kJ/mol [4], 451.7 kJ/mol [21]), recommended values (451 kJ/mol [5], 451.4 kJ/mol [22]), and also the early experimental value of  $451.4 \pm 16.7 \text{ kJ/mol}$  reported by Clifford et al. [14]. In this sense, we hope that our experimental data help to conclude the longstanding debate about the enthalpy of formation of NCN and further improve the thermodynamic consistency of detailed NCN flame chemistry models.

#### CRediT authorship contribution statement

**Nancy Faßheber:** Writing – original draft, Visualization, Investigation, Formal analysis. **Patrick Hemberger:** Writing – review & editing, Validation, Software, Methodology, Investigation. **Elke Goos:** Writing – review & editing, Project administration, Investigation, Funding acquisition, Conceptualization. **Gernot Friedrichs:** Writing – review & editing, Investigation, Funding acquisition, Formal analysis, Conceptualization.

#### Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work the authors have used ChatGPT/TextGPT (OpenAI) and DeepL for minor grammatical and spelling corrections. After using this tools, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Acknowledgments

This work has been conducted at the VUV beamline of the Swiss Light Source (Paul Scherrer Institute, PSI) under Proposal No. 20131144. We acknowledge the German Science Foundation (DFG 134123282, 546036961), the German Aerospace Center, and the Christian-Albrechts University Kiel for ongoing financial support.

#### Data availability

The ms-TPE spectra of NCN and  $\text{NCN}_3$  are available in the Photoelectron PhotoIon Spectral Compendium (<https://pepisco.psi.ch>) [28].

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