Multiple Detection Schemes for Investigating High-Temperature Radical Cross Reactions of NCN behind Shock Waves

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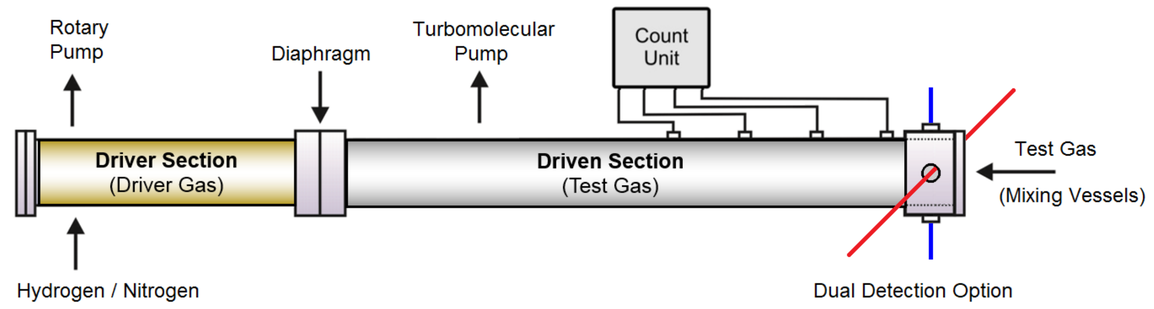
Introduction and Motivation

The kinetic study of elementary reactions demands for fast and sensitive detection techniques for radicals that can be tailored to the specific case of application. Another challenge is the availability of suitable and stable precursors. Here, we present three variations of laser absorption based setups for NCN, OH, CN, and HCN (!) detection for shock tube studies of four different reactions of the highly reactive diradical cyanonitrene, NCN. The NCN radical is a key species for prompt-NO formation – one of the main pollutant processes in fuel-rich hydrocarbon combustion.[1]

Many reactions of NCN have been studied both experimentally and theoretically, but some crucial issues still remain unsolved: **1.** Accurate rate constant for the self-reaction NCN + NCN needs to be known for the study of other NCN reactions, in particular if pseudo-first order conditions can not be achieved. **2.** The methyl and hydroxyl radical, CH_3 and OH, appear in comparably high levels in the reaction zone of rich methane flames. As yet, their reactions with NCN have only been addressed theoretically. **3.** The channel branching of the utmost important reaction NCN + H determines the chemical propagation in the prompt-NO pathway. So far, the transition temperature of the two main channels, the so-called prompt-NO switch temperature, remained an open, pivotal question.

The Kiel Shock Tube

The Kiel Shock Tube enables the investigation of fast gas phase reactions, such as radical cross reactions at high temperatures (700 – 3500 K). Shock wave conditions (T, p) are stable for several hundreds micro- (incident shock wave) up to two milliseconds (reflected shock wave). The electropolished 8.35 m stainless steel tube has an inner diameter of 81 mm, large enough to neglect possible wall effects. Two independent detection systems can be used for simultaneous radical detection through 4 windows in the shock tube head.



NCN radical source and spectroscopy

Cyanogen azide (NCN_3) as a quantitative source for NCN.
Thermal decomposition proceeds as follows: [2]

$NCN_3 + M \rightarrow NCN(^1\Delta) + N_2(^1\Sigma) + M$
$NCN(^1\Delta) + M \rightarrow NCN(^3\Sigma) + M$ (CIISC)

NCN_3 Synthesis

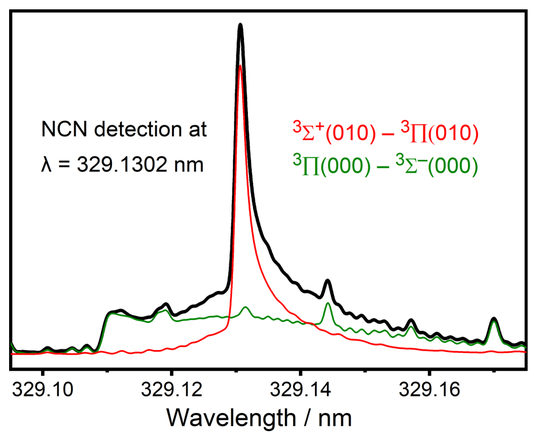
Modified version of the method of Milligan et al.: [3]

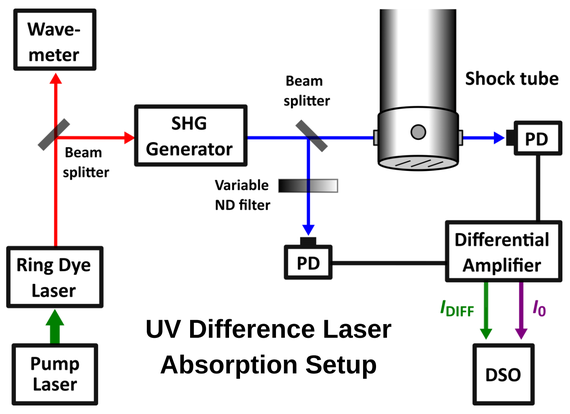
$NaN_3(s) + BrCN(g) \rightarrow NCN_3(g) + NaBr(s)$

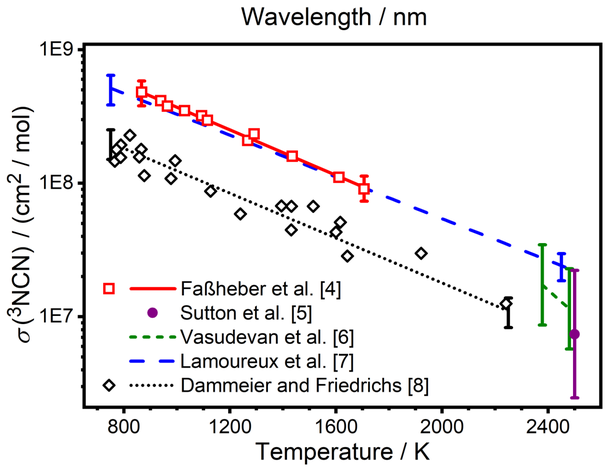
Mixture Composition

FTIR, GC and MS (ToF) analysis reveals side reaction:

$NCN_3 + NCN_3 \rightarrow$ Polymer + 2 N_2 → approx. 25 % N_2







1. The Reaction NCN + NCN → 2 CN + N_2

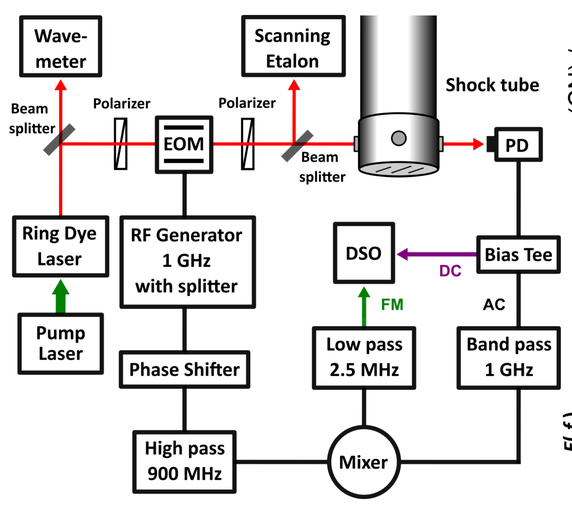
Time-resolved NCN detection by UV difference laser absorption spectroscopy yields the rate constant
k / cm^3 mol^{-1} s^{-1} = 1.10×10^{13} exp(−11.7 kJ mol^{-1} / RT)

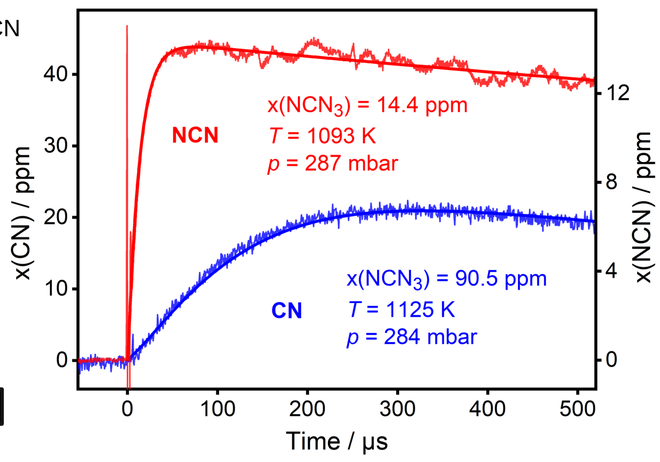
Validation of the assumed CN formation by detection of the CN radical using an **analog frequency modulation setup** at 622.2733 nm, $^2\Pi - {}^2\Sigma^+$, (5 – 1), $Q_1(10)$.

Thermal decomposition of BrCN for calibration of CN

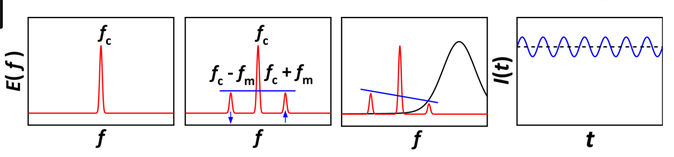
BrCN + M → Br + CN + M

Analog Frequency Modulation Setup





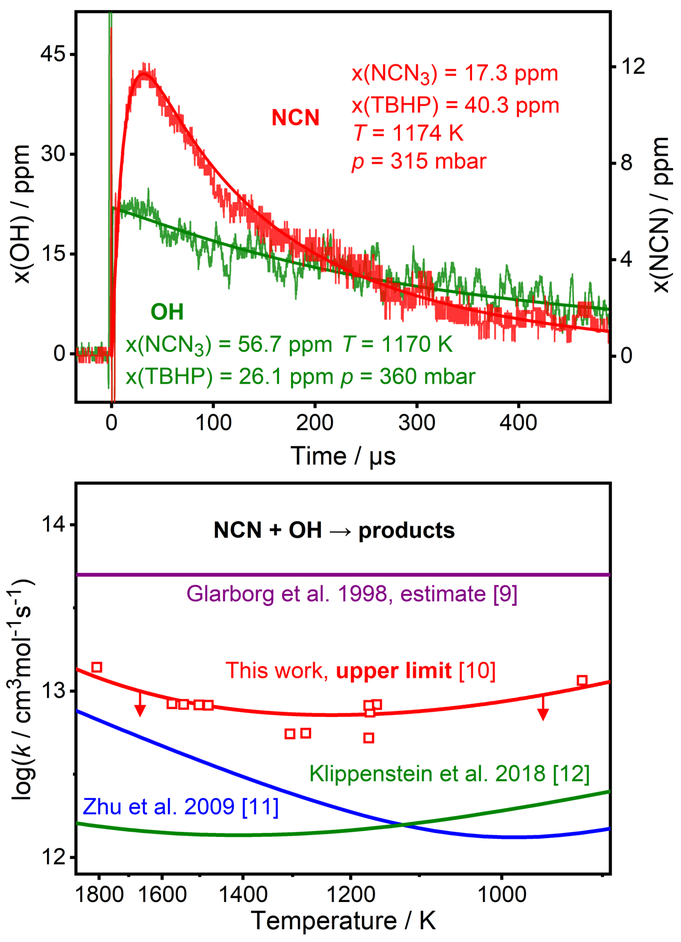
Principle of Frequency Modulation Spectroscopy

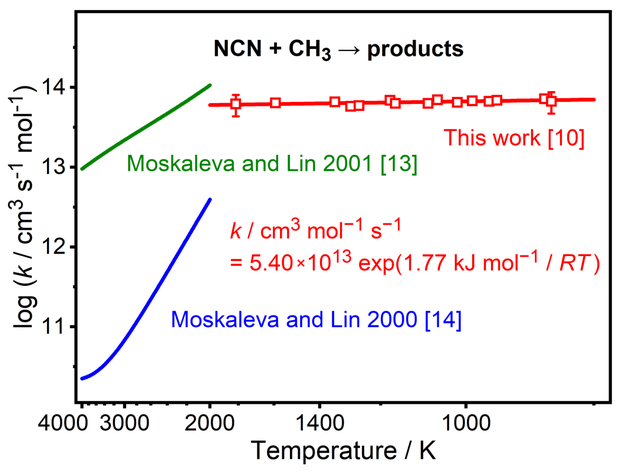


2. The Reactions NCN + OH and NCN + CH_3

tert-Butyl hydroperoxide (TBHP) as precursor for OH and CH_3 radicals:

NCN and OH profiles were recorded by using the **UV difference absorption setup**. OH detection at 310.2131 nm, $^2\Sigma^+ - {}^2\Pi$, (0 – 0), $P_1(5)$



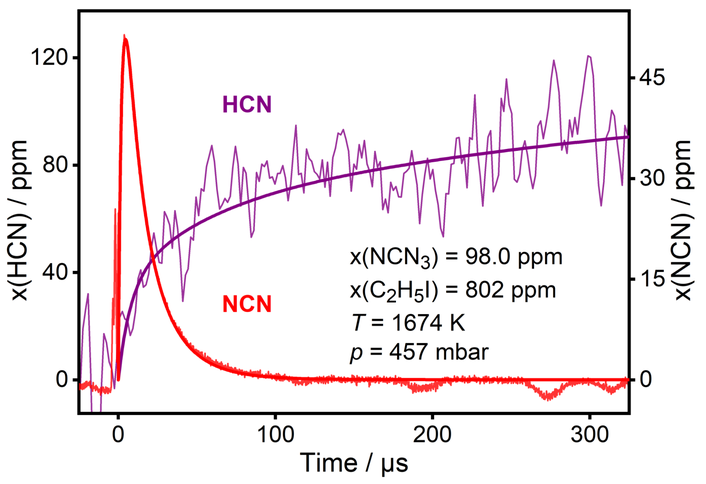


3. Channel Branching of the Reaction CH + N_2 $\overset{k_a}{\leftarrow}$ NCN + H $\overset{k_b}{\rightarrow}$ HCN + N

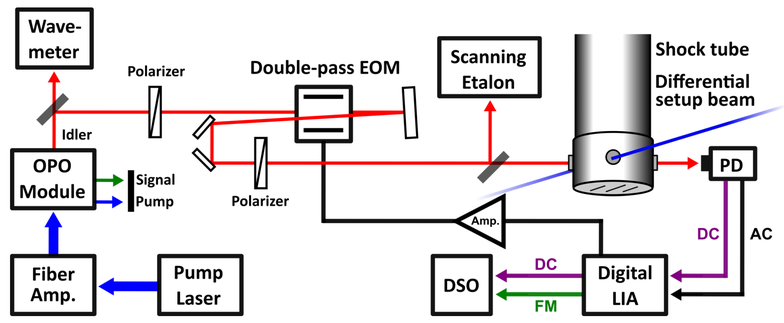
Thermal decomposition of ethyl iodide (C_2H_5I) as a source for H radicals:

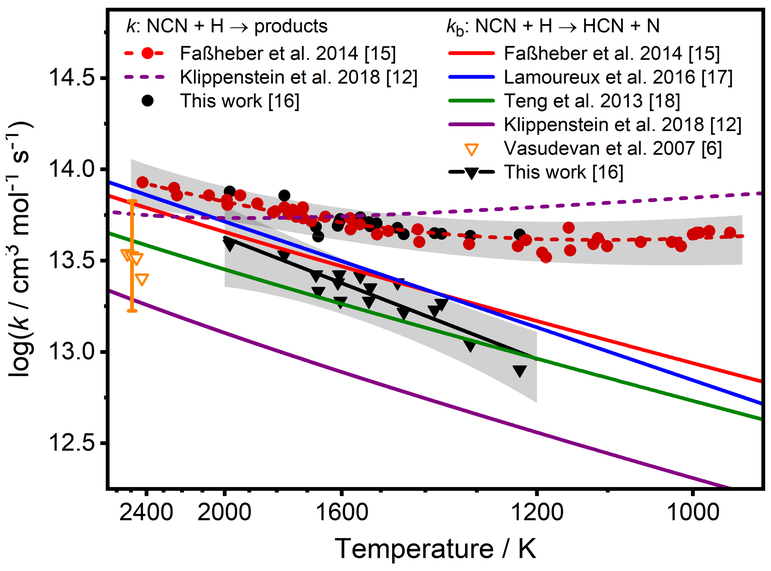
$C_2H_5I + M \rightarrow C_2H_5 + I + M$
$C_2H_5 + M \rightarrow C_2H_4 + H + M$

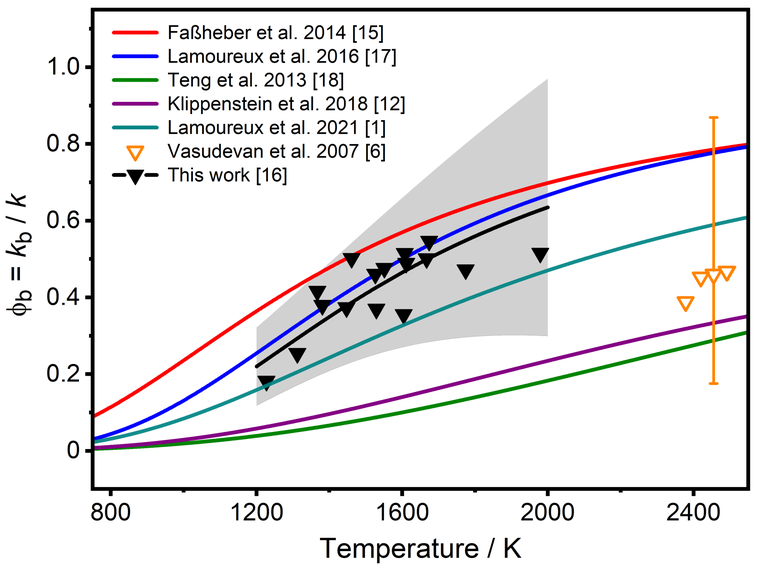
NCN and HCN profiles were recorded simultaneously by combining the UV difference absorption setup for NCN with an all-digital MIR frequency modulation scheme detecting HCN at 3097.846 nm, $^1\Sigma^+$ (1 – 0), P(26).



Dual NCN / HCN Detection Scheme: All-digital MIR Frequency Modulation Setup







References

[1] N. Lamoureux, P. Desgroux, M. Olzmann, G. Friedrichs, *PECS 87* **2021**.
[2] J. Dammeier, B. Oden, G. Friedrichs, *IJCK 45* **2013**.
[3] D. E. Milligan, M. E. Jacox, A. M. Bass, *JCP 43* **1965**.
[4] N. Faßheber, L. Bornhorst, S. Hesse, Y. Sakai, G. Friedrichs, *JPC A 124* **2020**.
[5] J. A. Sutton, B. A. Williams, J. W. Fleming, *CF 153* **2008**.
[6] V. Vasudevan, R. K. Hanson, C. T. Bowman, D. M. Golden, D. F. Davidson, *JPCA 111* **2007**.
[7] N. Lamoureux, C. M. Western, X. Mercier, P. Desgroux, *CF 160* **2013**.
[8] J. Dammeier, G. Friedrichs, *JPC A 114* **2010**.
[9] P. Glarborg, M. U. Alzueta, K. Dam-Johansen, J. A. Miller, *CF 115* **1998**.
[10] S. Hesse, L. Nazari, G. Friedrichs, will be published soon.
[11] R. S. Zhu, H. M. T. Nguyen, M. C. Lin, *JPC A 113* **2009**.
[12] S. J. Klippenstein, M. Pfeifle, A. W. Jasper, P. Glarborg, *CF 195* **2018**.
[13] L. V. Moskaleva, M. C. Lin, *CPPC* **2001**.
[14] L. V. Moskaleva, M. C. Lin, *PROCI 28* **2000**.
[15] N. Faßheber, J. Dammeier, G. Friedrichs, *PCCP 16* **2014**.
[16] M. Stuhr, S. Hesse, G. Friedrichs, *PROCI 39* **2022**. Under revision.
[17] N. Lamoureux, H. E. Merhubi, L. Pillier, S. de Persis, P. Desgroux, *CF 163* **2016**.
[18] W.-S. Teng, L. V. Moskaleva, H.-L. Chen, M. C. Lin, *JPCA 117* **2013**.

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