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NCN absorption cross section determination; Re-assessment of the zero-pressure radiative lifetime measurements

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Motivations and Objectives

Aim

Measurement of absolute NCN concentrations in flames by CRDS.

- Species concentration of NCN can be determined from the absorbance A and the absorption cross section σ
 $A = \alpha \times l = \sigma \times [\text{NCN}] \times l$

Determination of the absorption cross-section

From spectral simulations and the experimental radiative lifetime

- Temperature dependent simulation of the absorption spectrum using PGOPHER (Western, JQSRT 186 (2017))
- Excitation LIF spectra recorded at room temperature (Smith et al., J. Chem. Phys. 91 (1989)) and 1660 K (Lamoureux et al., Combust. Flame 160 (2013))
- Absorption spectrum recorded at room temperature (Dammeier and Friedrichs, J. Phys. Chem. A 114 (2010))
- Excellent ability of the simulated spectrum to fit the experimental ones over a wide temperature range
- The hot band (010) - (010) peaks in the vicinity of the cold band (000) - (000) (separation by only 0.03 nm)
- Quantification requires the calculation of the electronic transition dipole moment $|M_{K'K''}|$

$$\frac{1}{\tau_{K'}} = \frac{16\pi^3}{3\epsilon_0\hbar} \nu_{K'K''}^3 |M_{K'K''}|^2 (1 + \delta_{K'0}\delta_{K''1}) \quad (\text{Hansson and Watson, J. Mol. Spectrosc. 233 (2005)})$$

- Using the radiative lifetime, which was reported **only once** for NCN (Smith et al., 1989), one obtains:

$$\sigma (\text{cm}^2 \text{ molecule}^{-1}) = 3.3 \times 10^{-15} \exp(-1.80 \times 10^{-3} \times T(\text{K})) (\pm 22\%)$$

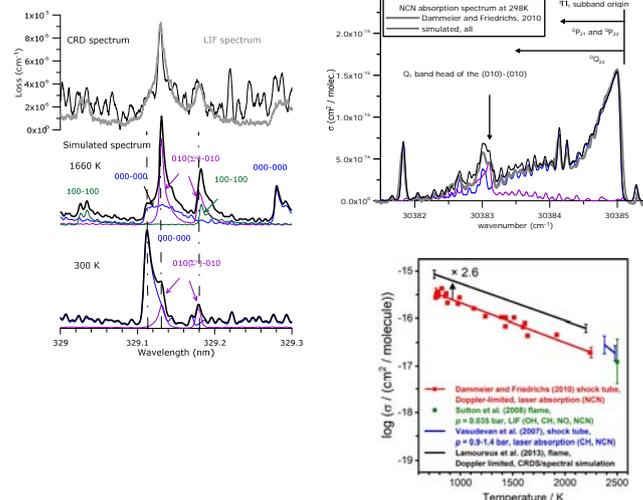
From experimental shock tube measurements (thermal decomposition of NCN₃ in Ar bath)

- Has been measured directly **only once** (Dammeier and Friedrichs, 2010), yielding

$$\sigma (\text{cm}^2 \text{ molecule}^{-1}) = 1.43 \times 10^{-15} \exp(-1.91 \times 10^{-3} \times T(\text{K})) (\pm 25\%)$$

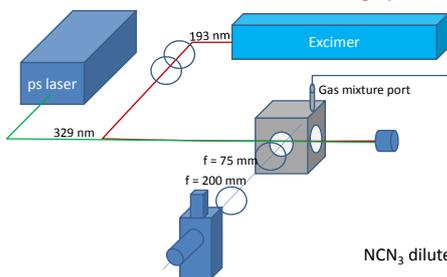
Issues

- Disagreement between the experimental and the calculated NCN absorption cross-section by a factor of 2.6.
- What are the reasons? 1.) Radiative lifetime or 2.) Expected NCN concentrations in shock tube experiments.



Experimental Approach

Radiative lifetime measurements of ³NCN using a picosecond laser



NCN₃ diluted in Ar was introduced into the reactor at 298 K and low pressures ($p < 10$ mbar).

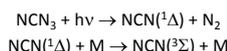
- Constant gas flow rate of NCN₃ (1 ppm diluted in Ar).
- Total pressure was increased by increasing the gas flow rate of Ar.
- Gas flow rate was adjusted at each pressure in order to have a complete renewal of the gas mixture every second.

NCN₃ synthesis

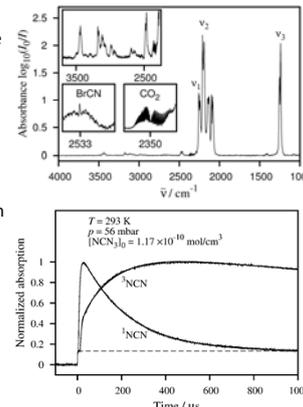
- Cyanogen azide (NCN₃) served as NCN source
- NCN₃ (extremely explosive) synthesis from NaN₃ and BrCN
- Product characterisation by FTIR

NCN₃ decomposition

- ¹NCN is generated from the 193 nm excimer laser photolysis of NCN₃, followed by collision induced intersystem crossing (CIISC) forming ³NCN



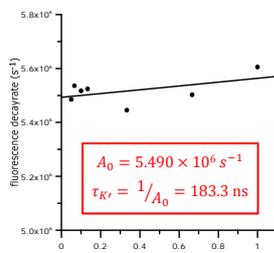
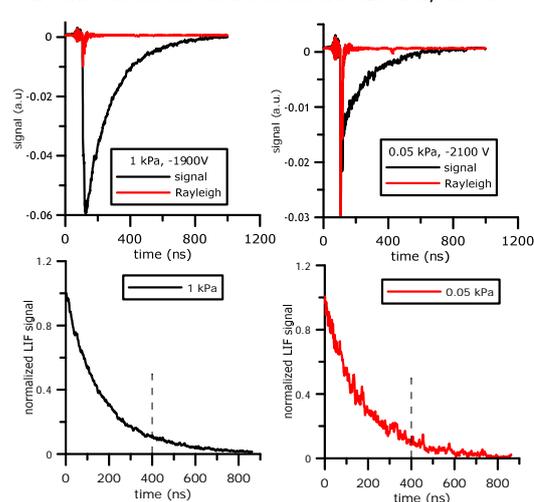
- [³NCN] = [¹NCN]₀ was assumed after a delay time of 400 - 1000 μs. (Dammeier et al., Int. J. Chem. Kin. 45 (2013))



Results

³NCN fluorescence lifetime

- Excitation of ³NCN by using the ps-laser at $\lambda = 329.1$ nm.
- ³NCN fluorescence lifetime collected at 329 nm by fast PMT.



Summary

Methods	Smith et al. JCP (1989)	Present work
NCN(³ Σ) source	Microwave discharge flow tube of CF ₄ in N ₂	NCN ₃ photolysis with a 193 nm wavelength radiation
Laser excitation at 329.13 nm	10 ns pulse length, 0.3 cm ⁻¹ bandwidth	35 ps pulse length, 3.5 cm ⁻¹ bandwidth
Bath gases	Xe, NO, NO ₂ , CO, O ₂ , N ₂ O, Kr, SF ₆ , Ar	Ar
Collection at 329 nm	Boxcar	Fast PMT (rise time 1.5 ns), oscilloscope 12 bit vertical resolution, 1 GHz
Radiative lifetime	183 ± 6 ns	183.3 ± 3.5 ns
Quenching rate in Ar	1.2 × 10 ⁻¹⁸ m ³ s ⁻¹	3.6 × 10 ⁻¹⁹ m ³ s ⁻¹

Conclusion and Outlook

- ³NCN fluorescence lifetimes could be measured down to pressures of $p = 1$ kPa.
- Measurements confirmed the value of $\tau = 183$ ns measured by Smith et al., hence the previously used lifetime is not the reason for the disagreement in the NCN absorption cross section.
- We also could not identify potential collisionless intersystem crossing processes from ³NCN to ¹NCN that may have interfered with the lifetime measurements.
- NCN yield from the NCN₃ decomposition needs to be reassessed.
- Analysis of new shock tube measurements for NCN absorption cross section are in progress.

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