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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  $\sigma$   
 $A = \alpha \times l = \sigma \times [\text{NCN}] \times l$

#### 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  $|M_{K'K''}|$

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

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

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

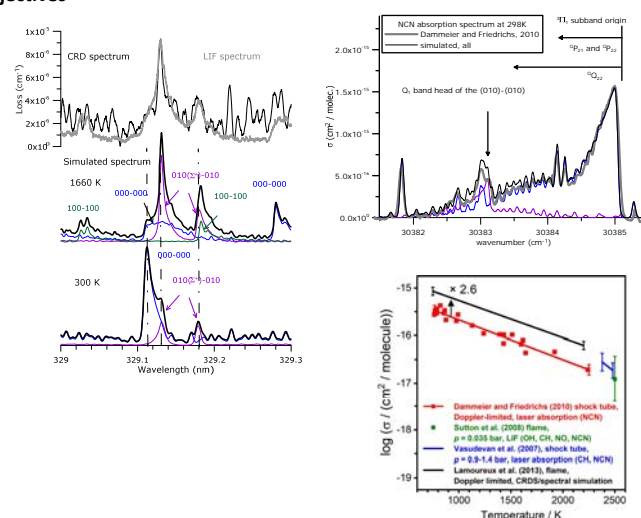
##### From experimental shock tube measurements (thermal decomposition of NCN<sub>3</sub> in Ar bath)

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

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

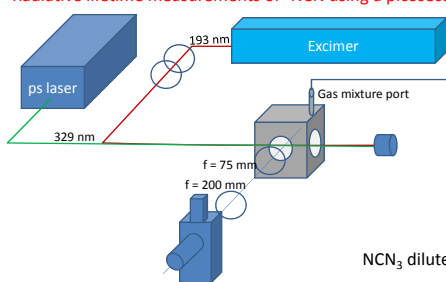
### Issues

- 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 <sup>3</sup>NCN using a picosecond laser



NCN<sub>3</sub> diluted in Ar was introduced into the reactor at 298 K and low pressures ( $p < 10$  mbar).

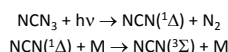
- Constant gas flow rate of NCN<sub>3</sub> (1 ppm diluted in Ar).
- Total pressure was increased by increasing the gas flow rate of Ar.
- Gas flow rate was adjusted at each pressure in order to have a complete renewal of the gas mixture every second.

### NCN<sub>3</sub> synthesis

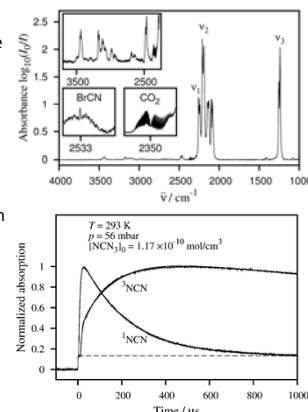
- Cyanogen azide (NCN<sub>3</sub>) served as NCN source
- NCN<sub>3</sub> (extremely explosive) synthesis from NaN<sub>3</sub> and BrCN
- Product characterisation by FTIR

### NCN<sub>3</sub> decomposition

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



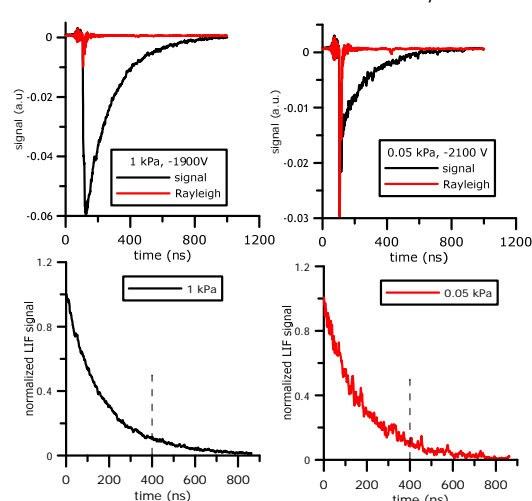
- [<sup>3</sup>NCN] = [<sup>1</sup>NCN]<sub>0</sub> was assumed after a delay time of 400 - 1000 μs. (Dammeier et al., Int. J. Chem. Kin. 45 (2013))



## Results

### <sup>3</sup>NCN fluorescence lifetime

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



### Summary

Methods	Smith et al. JCP (1989)	Present work
NCN( <sup>3</sup> Σ) source	Microwave discharge flow tube of CF <sub>4</sub> in N <sub>2</sub>	NCN <sub>3</sub> photolysis with a 193 nm wavelength radiation
Laser excitation at 329.13 nm	10 ns pulse length, 0.3 cm <sup>-1</sup> bandwidth	35 ps pulse length, 3.5 cm <sup>-1</sup> bandwidth
Bath gases	Xe, NO, NO <sub>2</sub> , CO, O <sub>2</sub> , N <sub>2</sub> O, Kr, SF <sub>6</sub> , 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 <sup>-18</sup> m <sup>3</sup> s <sup>-1</sup>	3.6 × 10 <sup>-19</sup> m <sup>3</sup> s <sup>-1</sup>

### Conclusion and Outlook

- <sup>3</sup>NCN 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 <sup>3</sup>NCN to <sup>1</sup>NCN that may have interfered with the lifetime measurements.
- NCN yield from the NCN<sub>3</sub> decomposition needs to be reassessed.
- Analysis of new shock tube measurements for NCN absorption cross section are in progress.

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