Quenching of the C $^3\Pi_u$ State of N_2 (v = 0, 1) by Water Vapour ◇

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During the year 2004, the experimental setup for pulsed, low-energy electron beam excitation of gases [1] was used to perform various gas kinetic studies. Here we report on results concerning the quenching of emission from molecular nitrogen by water vapour. The experimental concept was first applied to measure the radiative lifetimes and collisional self-quenching rate constants of the molecular nitrogen state C $^3\Pi_u$ (vibrational levels 0 and 1). Since these data are already known, this application was a good test of the experimental technique. Then the technique was used to measure quenching rate constants of molecular nitrogen by water vapour [2], which had not yet been studied sufficiently.

The purity of nitrogen used in this study was 99.999%. Nitrogen pressure was monitored using a capacitive manometer (MKS Baratron 690A) temperature controlled to 45C. The manometer has an accuracy of 0.12% of the reading and an uncertainty of 0.02 hPa due to zero drift with temperature. To prepare nitrogen water-vapour mixtures, the evacuated gas cell was first filled with water vapour from a separate volume containing bi-distilled and degassed water and then nitrogen was added. Partial pressure of water vapour was monitored during the experiments using an impedance dewpoint hygrometer ("Easidew Transmitter" from Michell Instruments). The hygrometer showed a repeatability of water vapour pressure reading of about 10% and was calibrated using the capacitive manometer.

To determine the radiative lifetimes τ and the collisional quenching rate coefficients Q_{N2} for the two lowest vibrational levels of the molecular nitrogen state $C^3\Pi_u$, time spectra of two molecular bands were recorded at various pressures of nitrogen P_{N2} and the exponential decay rate R of the C state was derived from the intensity I of the C to B transition according to

$$I(t) = I_0 + M \cdot exp\{-R \cdot (t - t_0)\} \qquad (1)$$

where R is the total decay rate of the upper state, I_0 the background intensity and M the intensity at time t_0 (corrected for the background).

Since the total decay rate is a combination of radiative decay and collisional quenching:

$$R = 1/\tau + Q_{N2} \cdot P_{N2}, \qquad (2)$$

the radiative lifetime can be found from extrapolation of the decay rate to zero pressure and the quenching rate from the slope of the decay rate versus pressure. This procedure was applied for the N_2 band at 337 nm (v'=0 → v"=0 transition) and for the band at 316 nm (v'=1 → v"=0 transition). The pressure dependences of decay rates for the bands are shown in Fig.1.

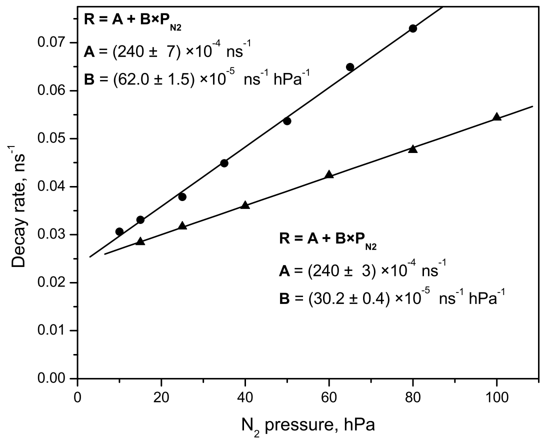

Fig. 1: Pressure dependences of the decay of the molecular nitrogen state C $^3\Pi_u$. Triangles: Emission from v'=0; dots: emission from v'=1.

Linear fits according to Eq.2 result in the following values for lifetimes τ and collisional quenching rate coefficients Q_{N2} for the N_2 C $^3\Pi_u$ state:

Vibrational level 0:
$\tau = 41.7 \pm 1.4$ ns,
$Q_{N2} = (3.0 \pm 0.4) \cdot 10^5 s^{-1}\mathrm{hPa}^{-1} \rightarrow$
$(1.2 \pm 0.1) \cdot 10^{-11}$ s^{-1}cm^3.
Vibrational level 1:
$\tau = 41.7 \pm 2.1$ ns,
$Q_{N2} = (6.2 \pm 0.2) \cdot 10^5 \mathrm{s}^{-1}\mathrm{hPa}^{-1} \rightarrow$
$(2.5 \pm 0.1) \cdot 10^{-11}$ s^{-1}cm^3.

Gas pressure was converted to gas density using a gas temperature of 293 K. The lifetimes and quenching rate coefficients obtained here are in very good agreement with data in the literature (see [3, 4] and references therein).

A technique similar to the one described above was applied to measure quenching rates of molecular nitrogen in the C $^3\Pi_u$ state by water vapour. For nitrogen water-vapour mixtures the decay rate R of the emission (see Eq. 2 for the pure nitrogen case) is proportional to the partial vapour pressure of water P_{H2O}:

$$R = 1/\tau + Q_{N2} \times P_{N2} + Q_{H2O} \times P_{H2O} \qquad (3)$$

Decay rates of light emission from vibrational levels 0 and 1 were recorded using gas mixtures at a fixed nitrogen pressure and different partial pressures of water vapour. Decay rates and results of a linear fit for vibrational level 0 (337 nm band) are shown in Fig. 2 as an example.

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The data result in the following quenching rate coefficients Q_{H2O}:

vibrational level 0:
$(17.5\pm1.8)\times10^6$ s^{-1}hPa^{-1} $\rightarrow$ $(7.1\pm0.7)\times10^{-10}$ s^{-1}cm^3
vibrational level 1:
$(16.5\pm1.7)\times10^6$ s^{-1}hPa^{-1} $\rightarrow$ $(6.7\pm0.7)\times10^{-10}$ s^{-1}cm^3.

The coefficients obtained in this work are about two times larger than data which can be found in the literature. There are two papers [3,5] where the quenching of nitrogen emission by water vapour has been studied. However, the values given in reference [5] have large uncertainties (up to 40%) and it is not described how the nitrogen water-vapour mixtures were prepared and how water vapour pressure was monitored.

In reference [3] the water vapour pressure was derived from the assumption that hydrogen and oxygen which were added as admixtures to nitrogen were completely converted to water vapour in the cell due to gas excitation. If this assumption was not valid, the actual water vapour pressure might have been lower than expected. In the present work [2], to avoid similar uncertainties with the actual content of the water in the gas phase, the partial pressure of water vapour was continuously monitored during the experiments.

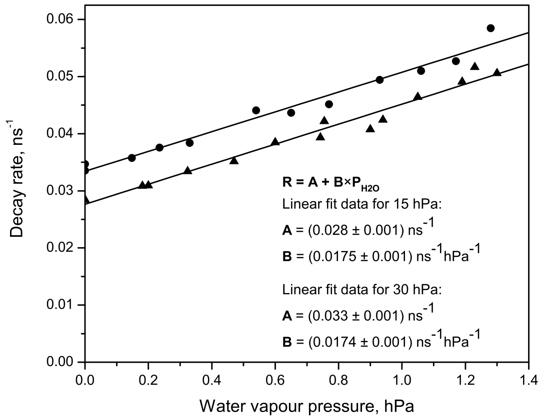

Fig. 2: Pressure dependence of the decay rate of the molecular nitrogen state C $^3\Pi_u$ (v'=0) in nitrogen water-vapour mixtures. Dots and triangles show the results for mixtures with 30hPa and 15hPa nitrogen pressure, respectively.

References

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