Direct EPR detection of atomic nitrogen in a nitrogen plasma jet

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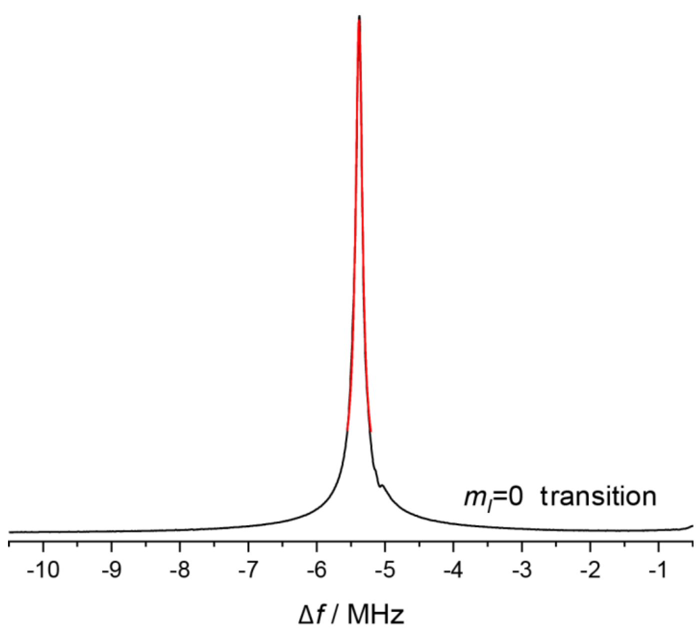
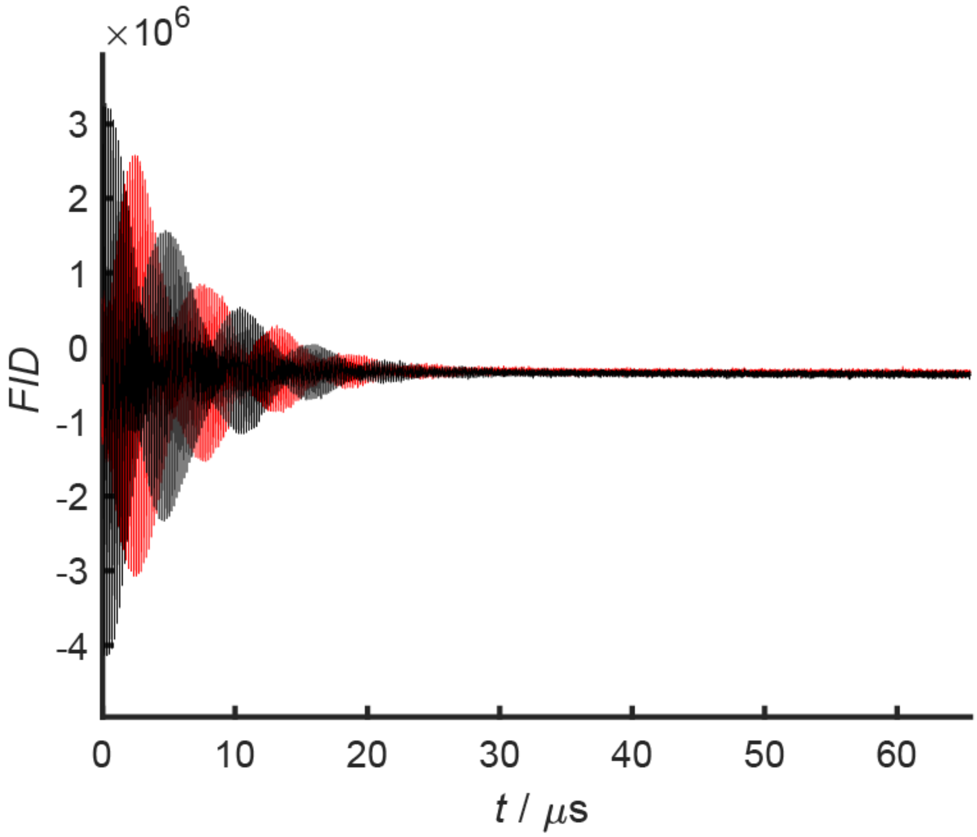
Supporting Information

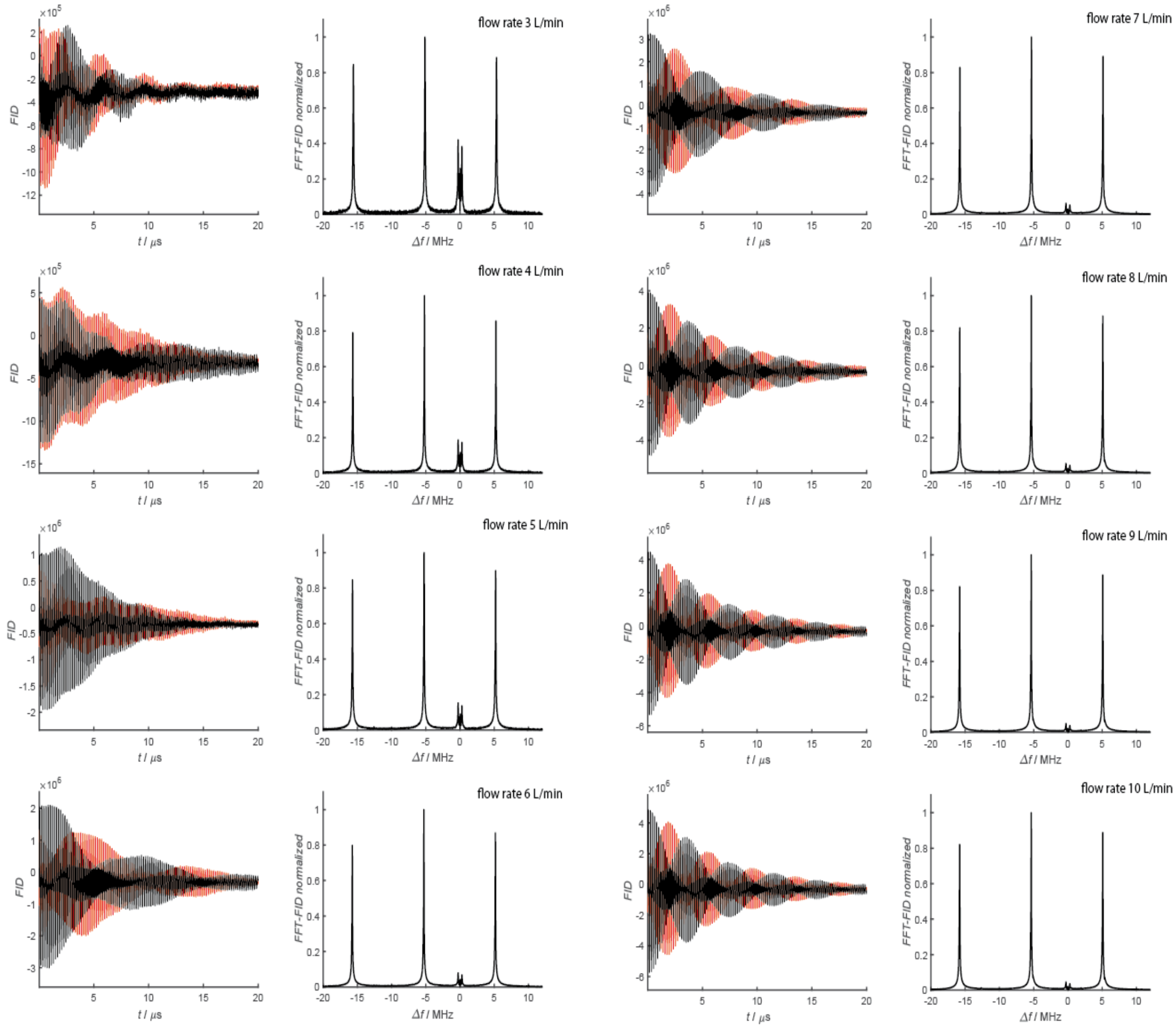
A. Additional EPR spectra



Supporting Figure 1: Exemplary standard Voigt function fit (red) of the FID-detected EPR spectrum (m_I = 0 transition, black) using the following parameters: y_0 (offset = $7.40 \cdot 10^9 \pm 9.35 \cdot 10^8$), X_c (center = $-5.38 \pm 4.17 \cdot 10^{-4}$) MHz, A (area = $1.10 \cdot 10^{10} \pm 5.97 \cdot 10^8$) MHz, w_G (Gaussian width = $4.38 \cdot 10^{-9} \pm 96.6$) MHz, w_L (Lorentzian width = 0.12 ± 0.01) MHz. The FWHM (0.12 ± 0.003) MHz was calculated as follows: $0.5346 * w_L + \mathrm{sqrt}(0.2166 * w_L^2 + w_G^2)$.



Supporting Figure 2: Exemplary full FID (black: real part; red: imaginary part) recorded at a flow rate of 7 l/min.



Supporting Figure 3: FIDs (black: real part; red: imaginary part) and corresponding FID-detected EPR spectra recorded at indicated flow rates. Please note that the signal-to-noise ratio increases significantly with the flow rate.

B. Calculation of the Reynolds numbers and the collision rates.

The following values were used (exemplary done for 3 $\frac{\mathrm{l}}{\mathrm{min}}$):

- Temperature: $T = 293\ \mathrm{K}$
- Pressure: $p = 1atm = 1.01325 \cdot 10^5\ \mathrm{Pa}$
- Density of the nitrogen gas: $\rho = 1.25\,\frac{\mathrm{kg}}{\mathrm{m}^3}$
- The quartz tube has a radius of $r = 1.5\ \mathrm{mm}$ und an effective length of the EPR resonator of $l = 3\ \mathrm{cm}$
- The cross sectional surface is $A = \pi \cdot r^2 \approx 7.0686 \cdot 10^{-6}\ \mathrm{m}^2$
- The perimeter is $U = 2\pi r \approx 0.09425\ \mathrm{m}$
- The effective volume is $V = A \cdot l \approx 2.1206 \cdot 10^{-7}\ \mathrm{m}^3$
- The gas flow volume is $\dot{V} = 3\ \frac{\mathrm{l}}{\mathrm{min}} = 5 \cdot 10^{-5}\,\frac{\mathrm{m}^3}{\mathrm{s}}$
- The viscosity of nitrogen gas at $T = 293\ \mathrm{K}$ and $p = 1\ \mathrm{atm}$ is $\eta = 17.58\ \mu\mathrm{Pa} \cdot \mathrm{s}$
- The molecular mass of nitrogen is $M = 28\ \frac{\mathrm{g}}{\mathrm{mol}} = 0.028\ \frac{\mathrm{kg}}{\mathrm{mol}}$

Calculation of the Reynolds number R_e:

The Reynolds number is calculated by using: $R_e = \frac{\rho v_g d_h}{\eta}$

with:

- v_g is the velocity of the gas: $v_g = \frac{\dot{V}}{A} \approx 7.1\ \frac{\mathrm{m}}{\mathrm{s}}$
- The hydraulic diameter $d_h = 4\frac{A}{P}$, can be calculated, if the wetted perimeter (P) is assumed to be identical to the inner perimeter of the quartz tube (U): $d_h = 4\frac{A}{U} = 2r = 0.003\ \mathrm{m}$

This results in a Reynolds number of $R_e = 1509$ for a flow rate of 3 $\frac{\mathrm{l}}{\mathrm{min}}$.

The following Table shows the flow rates, the gas velocity v_g and the Reynolds numbers R_e:

Flow rate / $\frac{\mathrm{l}}{\mathrm{min}}$	v_g / $\frac{\mathrm{m}}{\mathrm{s}}$	**Reynolds number R_e**
3	7	1509
4	9	2011
5	12	2515
6	14	3017
7	17	3520
8	19	4023
9	21	4527
10	24	5030

These numbers result in Reynolds numbers of $R_e \approx 1509$ (3 l/min) to $R_e \approx 5030$ (10 l/min). The calculated Reynolds number in case of a flow rate of 3 l/min is lower than the critical Reynolds number of about 2300, but is higher in case of flow rates between 4 and 10 l/min. Therefore, the plasma flow is turbulent in most cases.

Calculation of the influence of the wall

To estimate the influence of the quartz tube wall on the nitrogen gas, the inter-molecular collision rate of the nitrogen is compared to the collision rate of the nitrogen molecules with the tube wall.

Inter-molecular collision rate:

The total inter-molecular collision rate Z_{gas} can be calculated by $\boldsymbol{Z_{gas} = N_t \cdot \nu_c}$, with N_t being the effective number of molecules in the quartz tube and ν_c the collision frequency of one molecule with another molecule. The effective number of nitrogen molecules inside the tube can be calculated by assuming the ideal gas law:

$$N_t = \frac{pV}{k_B T} = \frac{1.01325 \cdot 10^5 \mathrm{Pa} \cdot 2.1206 \cdot 10^{-7} \mathrm{m}^3}{1.3806 \cdot 10^{-23} \mathrm{JK}^{-1} \cdot 293\mathrm{K}} = 5.31 \cdot 10^{18}$$

The collision rate ν_c can be calculated from the mean free path, λ, and the mean velocity of gas molecules, v.

$$\nu_c = \frac{v}{\lambda}$$

The mean free path way λ can be calculated by the classical gas theory and assuming hard spheres:

$$\lambda = \frac{k_B T}{\sqrt{2}\pi d^2 p}$$

with d being the kinetic diameter of the molecule (which takes scattering events into account and therefore differs from the van-der-Waals diameter). For nitrogen gas: $d = 3.7 \cdot 10^{-10}$ m. This results in: $\lambda = 6.56 \cdot 10^{-8}$ m.

The mean velocity can be calculated by using the Maxwell Boltzmann distribution

$$v = \sqrt{\frac{8RT}{\pi M}}$$

using the ideal gas constant $R = 8.314 \ \mathrm{Jmol^{-1}K^{-1}}$ and $M = 28 \ \mathrm{kg \cdot mol^{-1}}$. This leads to $= 4.71 \cdot 10^2 \ \frac{\mathrm{m}}{\mathrm{s}}$, which results in an inter-molecular collision rate of: $\nu_c = 7.17 \cdot 10^9 \ \mathrm{s}^{-1}$. Finally, the number of inter-molecular gas collisions can be calculated as:

$$Z_{gas} = N_t \cdot \nu_c = 3.81 \cdot 10^{28} \ \mathrm{s}^{-1}$$

The gas flow does not influence this value because for each gas molecule leaving the gas tube, a new one comes in. Moreover, we note that a molecule moves on average at about 60–20 times the speed of the overall gas flow.

Collision rate with the wall:

Now, we calculate the total collision rate of the nitrogen molecules with the wall (Z_{wall}). To do so, we calculate the number of gas molecules that can hit the wall within a mean inter-molecular collision time, $t_c = {}^{1}/_{\nu_c}$. Those molecules are therefore within a distance of the mean free path λ to the wall. Molecules outside this layer will not be able to hit the wall within the considered time. Within this layer, one half of the molecules are moving to the wall and the other half to the inside of the quartz tube. Thus, the number of collisions to the wall within the mean collision time is

$$N_{coll} = \frac{1}{2}\frac{N}{V}S\lambda$$

with $\frac{N}{V}$ being the particle density inside the tube. For an ideal gas this can be calculated by:

$$\frac{N}{V} = \frac{p}{k_B T}$$

S is the surface of the quartz tube given by $S = 2\pi r l$ and $S\lambda$ is the volume the layer.
This leads to:

$$N_{coll} = \frac{1}{2}\frac{p}{k_B T}2\pi r\ l\ \frac{k_B T}{\sqrt{2}\pi d^2 p} = \frac{r\ l}{\sqrt{2}d^2} = 2.32 \cdot 10^{14}$$

The total collision rate with the wall can be calculated by:

$$Z_{wall} = \frac{N_{coll}}{t_c} = N_{coll} \cdot \nu_c = 1.67 \cdot 10^{24}\mathrm{s}^{-1}$$

Finally, the ratio of the two collision rates can be estimated:

$$\frac{\boldsymbol{Z_{wall}}}{\boldsymbol{Z_{gas}}} = \frac{1.67 \cdot 10^{24}\mathrm{s}^{-1}}{3.81 \cdot 10^{28} s^{-1}} \approx \mathbf{4{,}383 \cdot 10^{-5}}$$

Summary: The collision frequency of gas molecules to the wall is much lower than the gas-gas collision frequency ($Z_{wall} = 1.67 \cdot 10^{24}$ s^{-1} versus $Z_{gas} = 3.81 \cdot 10^{28}$ s^{-1}). From these results it can be concluded that the lifetime of the plasma state is much longer than the collision rate, if it is assumed that collisions with the wall are a primary source of energy dissipation.