Supplementary Materials: Isotope Labelling for Reaction Mechanism Analysis in DBD Plasma Processes

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2. Results and Discussion

2.1. Analysis of Plasmas Induced Isotope Exchange Reactions

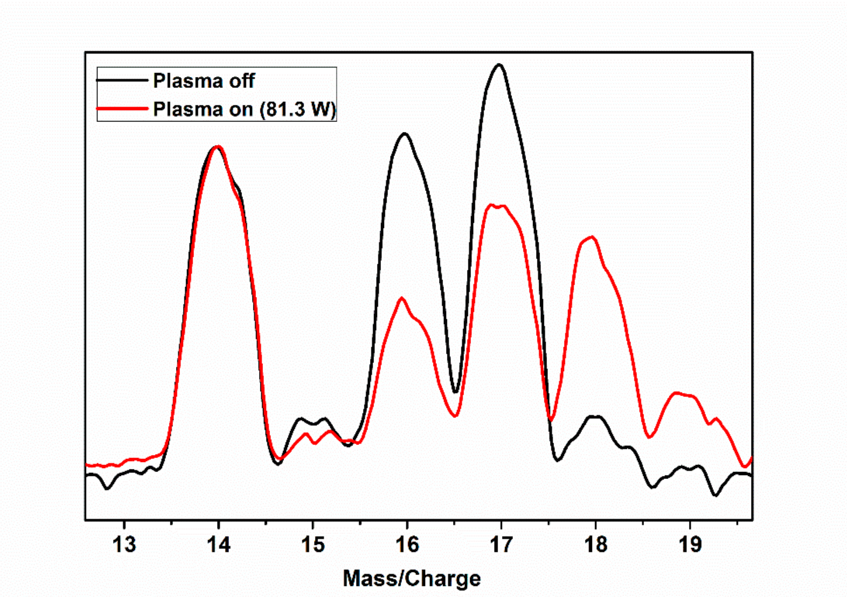

Figure S1. MS spectra (zone *m/z* from 13 to 20) taken for the ternary mixture N_2+D_2+NH_3 before (black line) and after (red line) switching on the plasma. The residual intensity at *m/z*=18 is due to the residual water always present in the MS chambers. After application of plasma there is a change in the relative intensities of *m/z* peaks at 16, 17, 18 and 19, while the m/z peak at 14 remains constant. These changes are attributed to isotope exchange processes affecting to some of the initially detected NH_3 molecules that become transformed into NH_2D, NHD_2 and ND_3 (see the text).

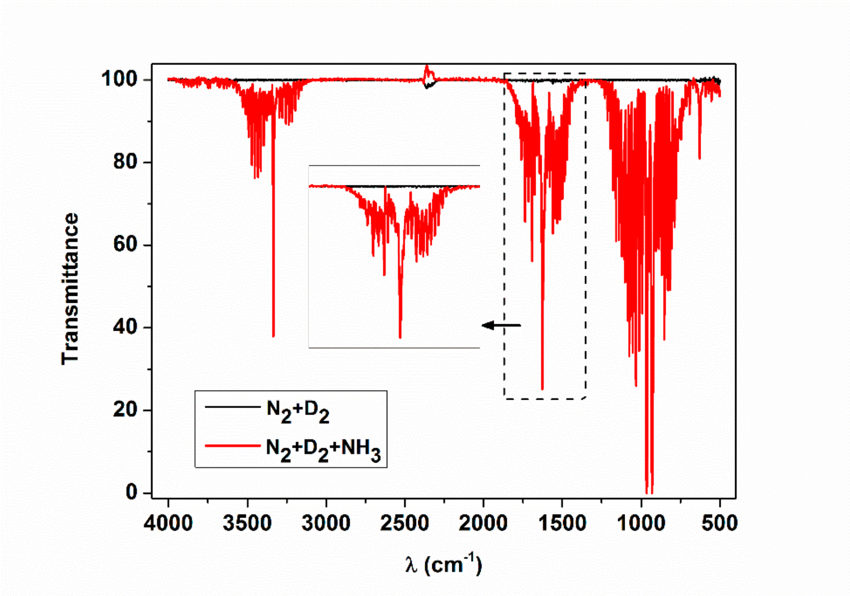

Figure S2. FTIR spectra recorded for binary N_2+D_2 (black line) and ternary $N_2+D_2+NH_3$ (red line) mixtures before plasma ignition. This analysis disregards the presence of water in the reactor chamber, since the zone 1300-2000 cm^{-1} only presents bands for the ternary mixture, which correspond to NH_3.

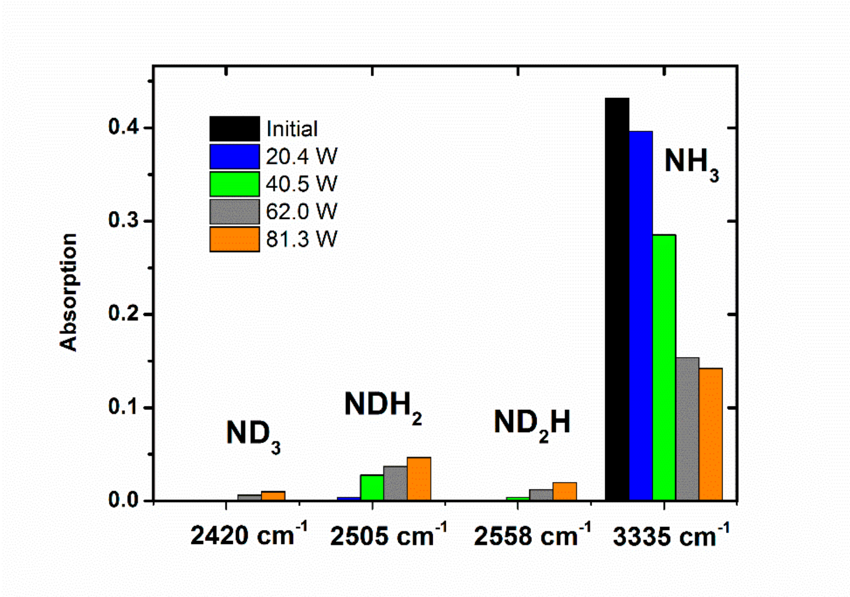

Figure S3. Evolution of the intensity of the IR absorption bands attributed to different ammonia species during isotope labelling processes induced by DBD plasma.

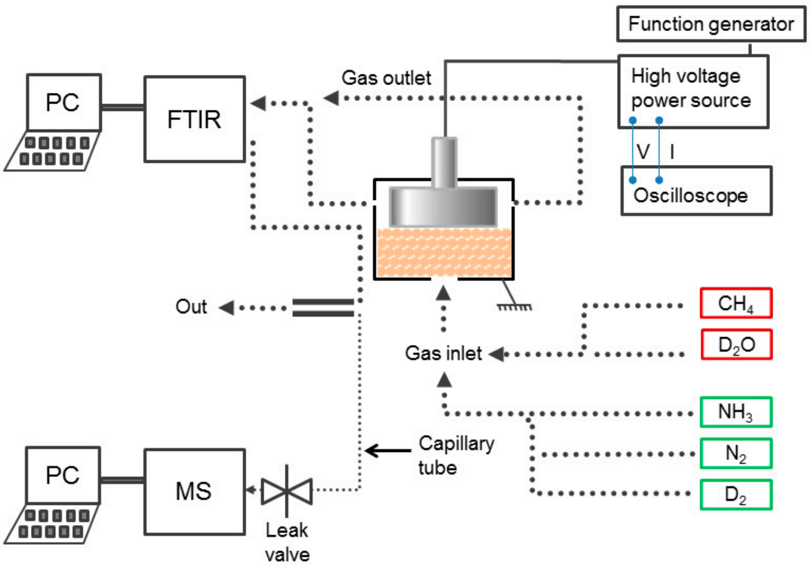

Figure S4. Scheme of the experimental set-up. A more detailed description of the reactor and the electrical supply can be found in our previous works [1–3]. Outlet gas flow is represented with the point line.

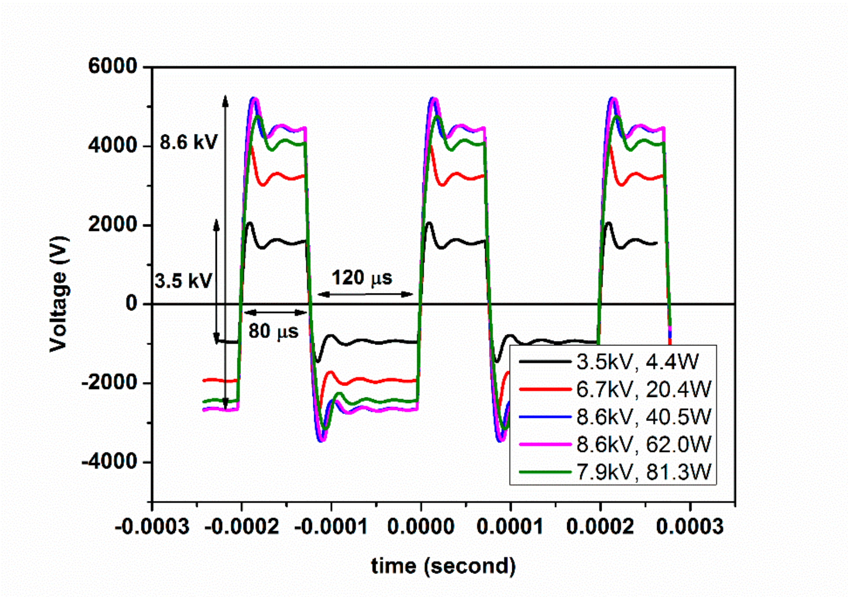

Figure S5. Squared AC curves for the different maximum to minimum voltage difference (3.5, 6.7, 8.7, 8.7 and 7.9 kV) and power (4.4, 20.4, 40.5, 62.0 and 81.3 W) in the case of the $NH_3/D_2/N_2$ mixture. Squared signals are expected to provide a higher efficiency that sinusoidal ones due to their higher V_{rms} value.

References

1. Montoro-Damas, A.M.; Gómez-Ramírez, A.; Gonzalez-Elipe, A.R.; Cotrino, J. Isotope labelling to study molecular fragmentation during the dielectric barrier discharge wet reforming of methane. *J. Power Sources* **2016**, *325*, 501–505.
2. Gómez-Ramírez, A.; Montoro-Damas, A.M.; Cotrino, J.; Lambert, R.M.; González-Elipe, A.R. About the enhancement of chemical yield during the atmospheric plasma synthesis of ammonia in a ferroelectric packed bed reactor. *Plasma Process. Polym.* **2017**, *14*, 1600081.
3. Gómez-Ramírez, A.; Cotrino, J.; Lambert, R.M.; González-Elipe, A.R. Efficient synthesis of ammonia from N_2 and H_2 alone in a ferroelectric packed-bed DBD reactor. *Plasma Sources Sci. Technol.* **2015**, *24*, 065011.