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Supplementary Information

Static and Dynamic Scavenging of Ammoniated Electrons by Nitromethane

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Diagram of the high-pressure optical cell

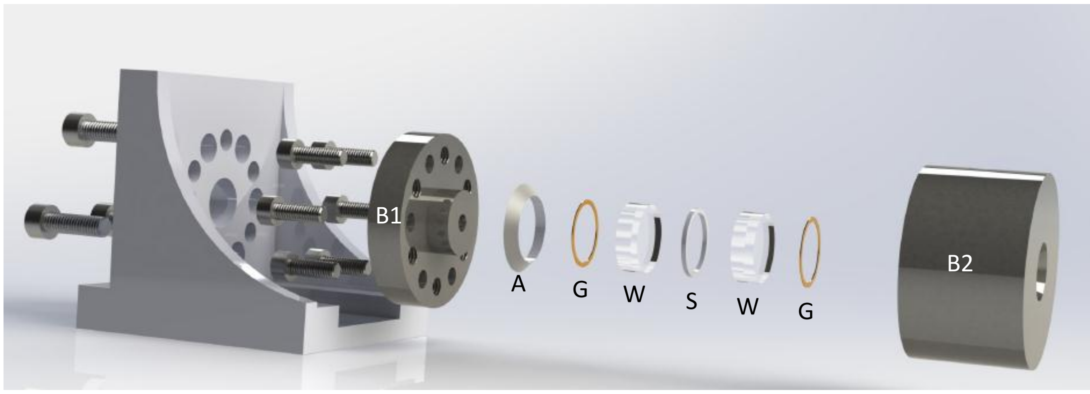

Figure S1. High-pressure optical cell: B1, cell cap; B2 cell body (magnetic stirrer housing graved inside, not shown); G, gold seals; W, sapphire windows; S, spacer (radial holes allow fluid access); A, centring piece.

Diagram of the fluid handling equipment

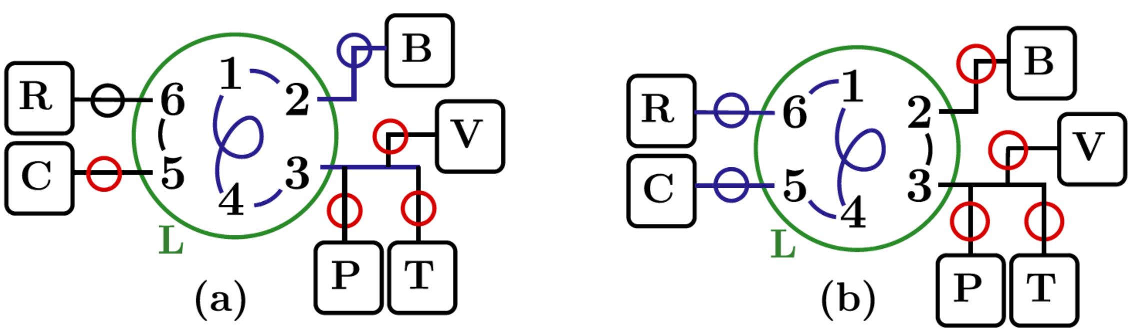

Figure S2. High-pressure ancillary fluid handling equipment: (a) load, (b) injection. L, six-port low-dead-volume valve with a 10 μL sampling loop; C, high-pressure optical cell; R, 3 cm^3 stainless steel auxiliary reservoir; B, stainless steel bottle with the nitromethane-ammonia mother solution; V, access port to the vacuum line; P, purge; T, access to high-pressure syringe pump filled with liquid ammonia and pressure transducer. Needle valves are represented by circles (in blue, open; in red, closed).

Electron distribution along the pathlength of the cell

The transient electron concentration decreases along the position x of the optical path following the intensity drop of the UV light. For a given delay τ, the transient electron concentration is: $c_{\mathrm{el}}(x,\tau) = c_{\mathrm{el}}(x=0,\tau)\, I(x)/I_0$, where $I(x) = I_0 \times 10^{-\epsilon_{\mathrm{CTTS}} c_{\mathrm{KI}} x}$, being ϵ_{CTTS} the molar extinction coefficient of the iodide's first CTTS band in liquid ammonia, and c_{KI} the KI concentration. We used for ϵ_{CTTS} the value 1.11x10^4 M^{-1}·cm^{-1}, which we determined carefully in a former stationary experiment.[1] Finally, the transient electron concentration profile can be related with the measured solution transient absorbance by the expression: $\Delta A(\tau) = \epsilon_{\mathrm{el}} \int c_{\mathrm{el}}(x,\tau)\mathrm{d}x,\ x: 0 \rightarrow b$, where ϵ_{el} represents the molar extinction of the solvated electron in liquid ammonia. We used for ϵ_{el} the value 4.5x10^4 M^{-1}·cm^{-1}, which was measured by Quinn and Lagowski[2] on ammoniated electrons produced by electrolitically-generated K-NH_3 solutions, at a wavelength of 1443 nm, and in presence of KI 0.1M.

In our experimental conditions, transient electron concentrations at the position of the front window were in the range of 2-5 mM, decreasing rapidly into the μM range when x is ~30 μm. The mean electron concentration, $\overline{c_{\mathrm{el}}}(\tau) = 1/b \int c_{\mathrm{el}}(x,\tau)\mathrm{d}x,\ x: 0 \rightarrow b$, can be related with the measured transient absorbance as: $\Delta A(\tau) = \overline{c_{\mathrm{el}}}(\tau)\epsilon_{\mathrm{el}} b$.

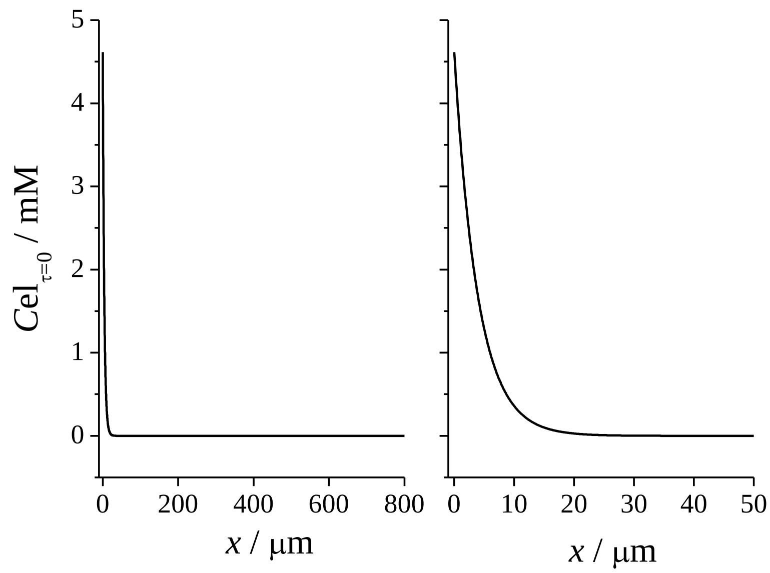

Figure S3. Concentration of electrons along the optical cell's pathlength, x.

References

1 R. Ferna, G. Sciaini, E. Marceca and R. Fernández-Prini, *Phys. Chem. Chem. Phys.*, 2006, **8**, 4839–4848.

2 R. K. Quinn and J. J. Lagowski, *J. Phys. Chem.*, 1969, **73**, 2326–2329.