Supporting Information

Photochemistry of Rose Bengal in Water and Acetonitrile: A Comprehensive Kinetic Analysis

Lucie Ludvíková, Pavel Friš, Dominik Heger, Peter Šebej, Jakob Wirz, Petr Klán**

RECETOX, Faculty of Science, Masaryk University, Kamenice 5, 625 00 Brno, Czech Republic

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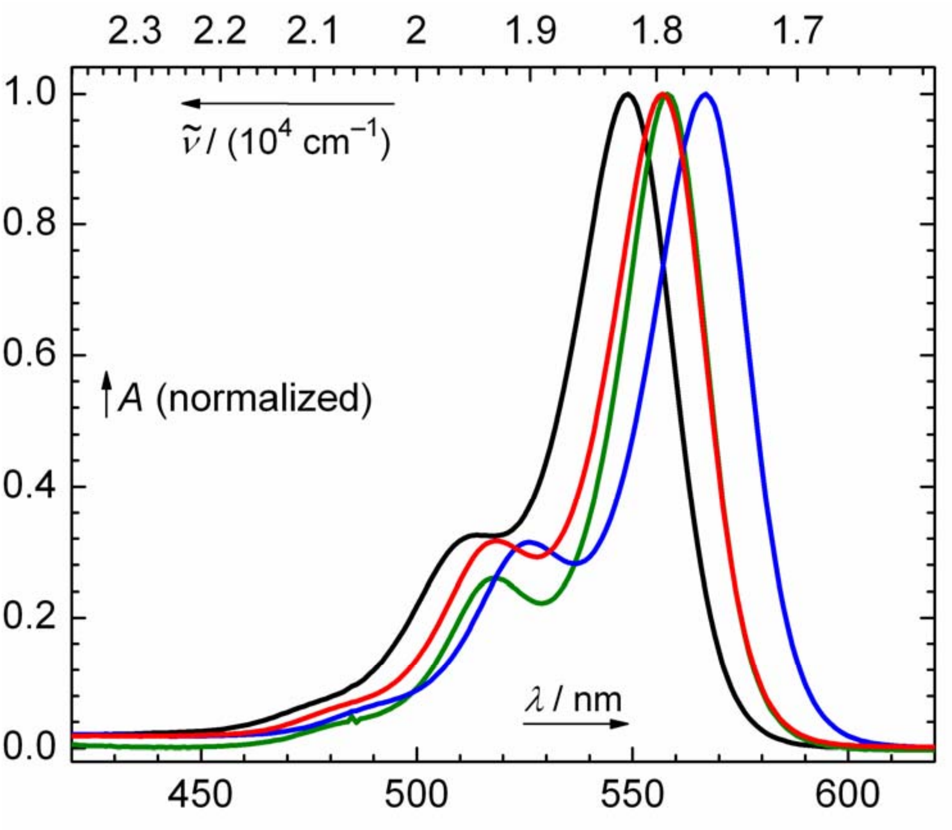
Steady-State Spectra of RB^{2-}. The singlet-state energies were obtained from the 0−0 transition estimated from an intersection point of the normalized absorption and fluorescence spectra. The triplet-state energies were estimated from the phosphorescence spectra (the 0−0 transition was placed at the wavelength at which the emission intensity at a short-wavelength tail of the band was 10% of the maximum).

a)



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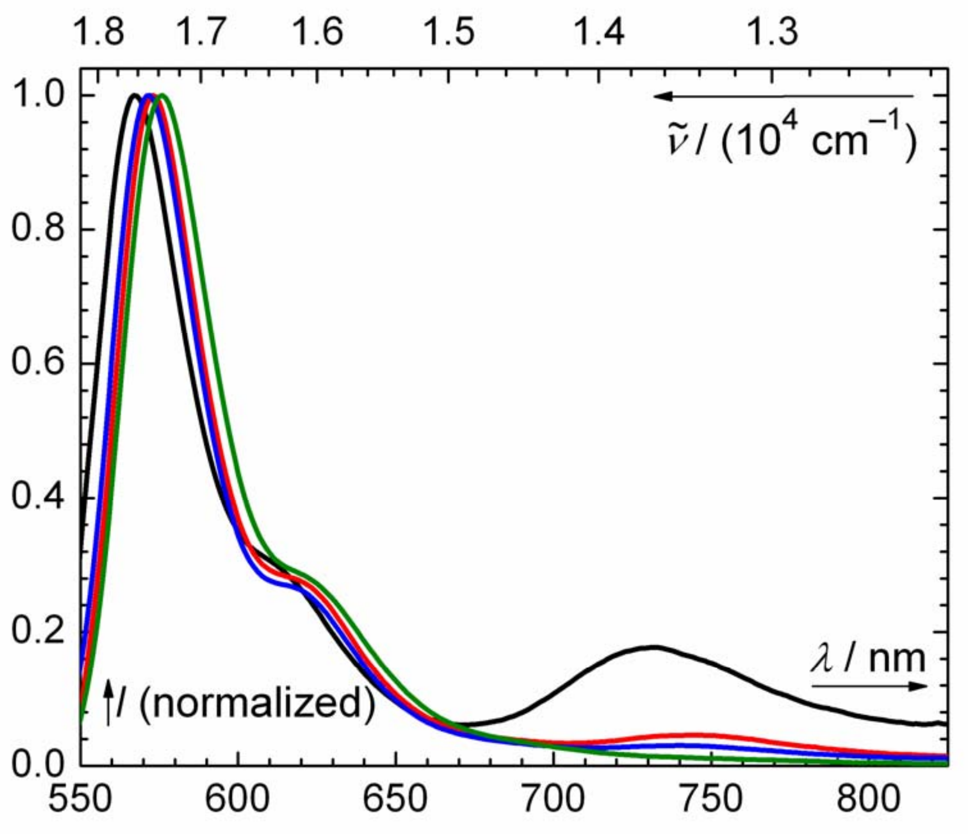


Figure S1. Normalized (a) absorption and (b) luminescence spectra of RB^{2-} in water (black line), methanol (red line), propan-2-ol (blue line) and acetonitrile (green line) degassed solutions at (25 ± 1) °C. The sample concentrations were adjusted to keep the absorbance below 0.1 at λ_{exc} = 530 nm.

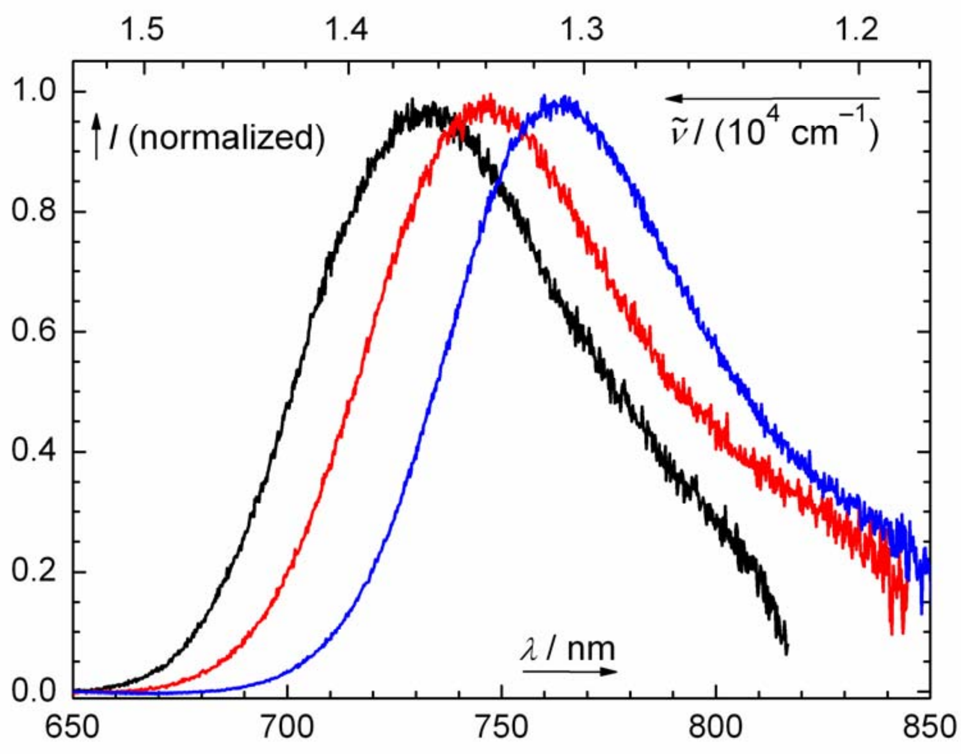


Figure S2. Normalized phosphorescence spectra of RB^{2-} in water (black line), methanol (red line), and propan-2-ol (blue line) degassed solutions at (25 ± 1) °C; the sample concentrations were adjusted to keep the absorbance below 0.1 at $\lambda_{exc} = 530$ nm. The phosphorescence spectra were measured with a microsecond flash xenon lamp with the delay time of 100 μs after the flash.

Transient Absorption Spectra of RB Species. Difference absorption spectra of degassed RB^{2-} aqueous solutions at a particular time were obtained for various RB concentrations (Figure S3). The ground-state bleach signal in its full range for a low concentrated RB sample ($c = 2.5 \times 10^{-6}$ mol dm^{-3}) is shown in the spectrum recorded 50 ns after the flash (Figure S3, red line). However, the ground state bleach signal is cut for a higher concentrated sample ($c = 1.5 \times 10^{-5}$ mol dm^{-3}, Figure S3, black line) due to a limited dynamic range of our ICCD chip. On the other hand, the ground state signal is almost fully recovered at 400 μs after the flash as shown in the same figure ($c = 1.5 \times 10^{-5}$ mol dm^{-3}; Figure S3, blue line). The remaining bands below 500 nm correspond to the redox forms of RB^{2-} (see the main text).

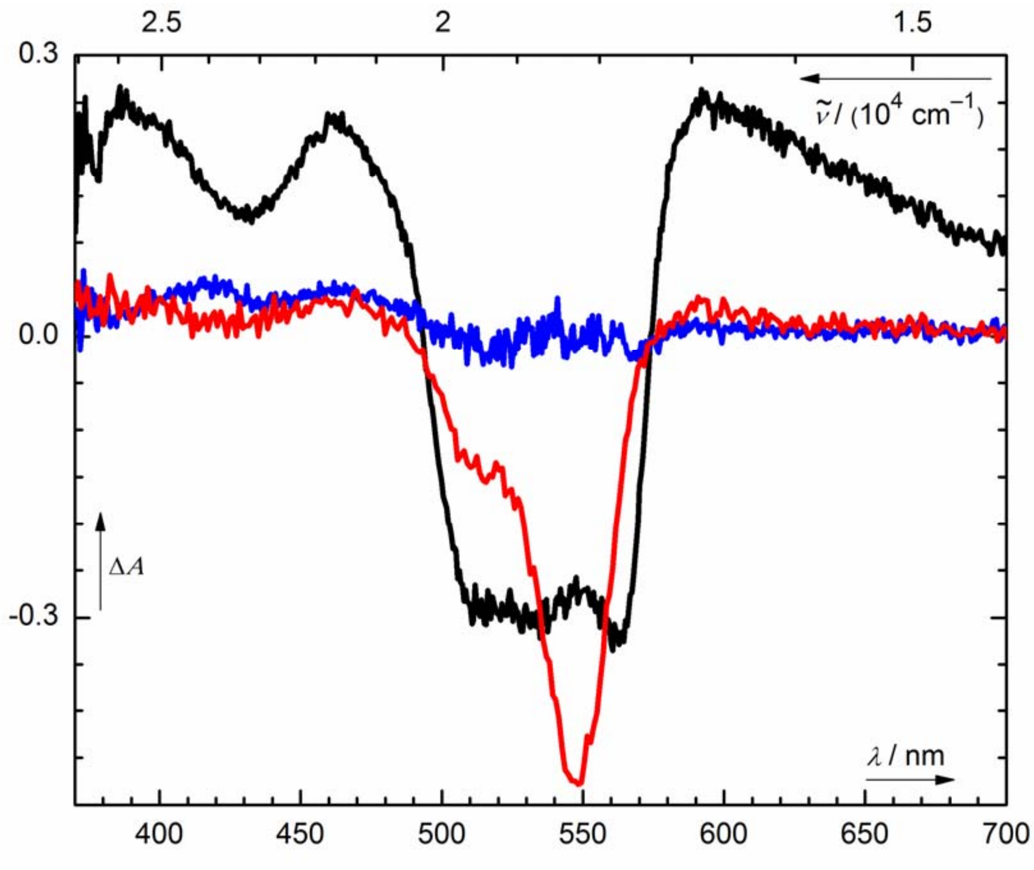


Figure S3. Difference absorption spectra of degassed RB^{2-} solutions in water recorded 50 ns (black line, $c = 1.5 \times 10^{-5}$ mol dm^{-3}), 400 µs (blue line, $c = 1.5 \times 10^{-5}$ mol dm^{-3}) and 50 ns (red line, $c = 2.5 \times 10^{-6}$ mol dm^{-3}) after the 532 nm flash (E = 240 mJ) with a 5 ns integration window.

The transient absorption spectra of RB redox forms (Figure S4) were measured by reductive and oxidative quenching of $^3RB^{2-}*$ with tris(2-hydroxyethyl)amine ($c = 25 \times 10^{-3}$ mol dm^{-3}, red line) as an electron donor or 4-nitroimidazole ($c = 5 \times 10^{-3}$ mol dm^{-3}, black line) as an electron acceptor, as also reported in the literature.[1,2] The absorption spectra of RB redox forms are similar to those measured by pulse radiolysis[3] and also comparable to the measured transient absorption spectra of a RB^{2-} degassed solution recorded 400 µs after laser flash (Figure S4, blue line).

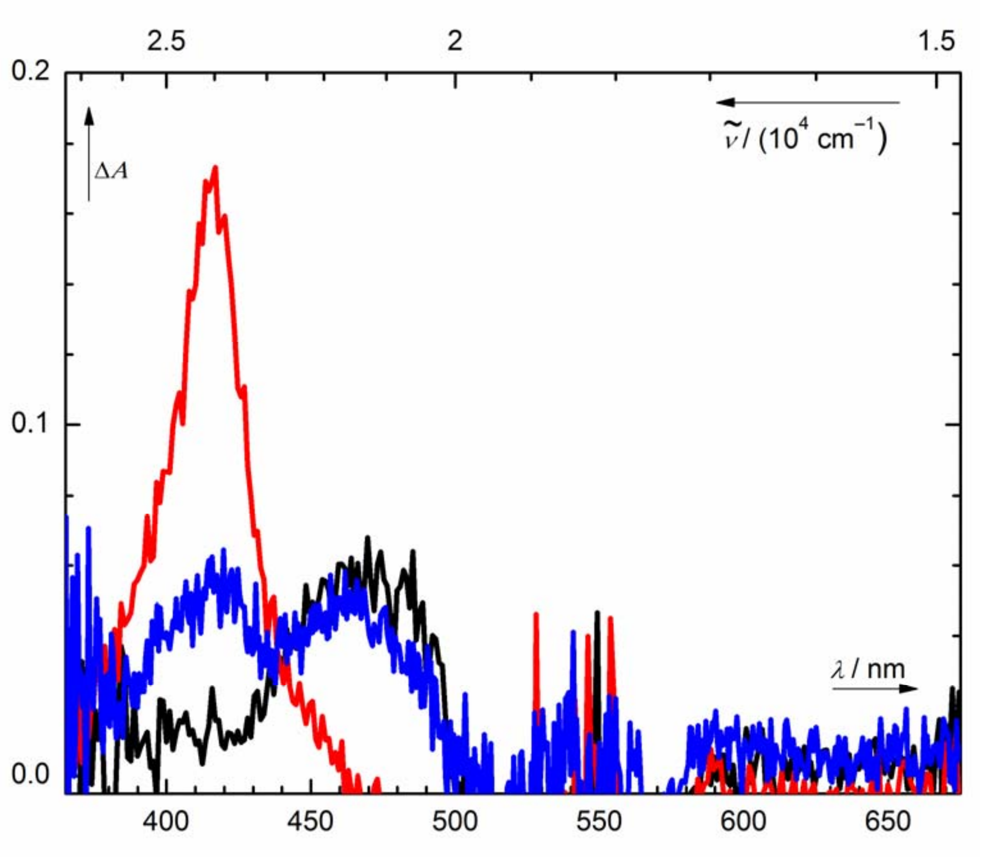


Figure S4. Difference absorption spectra of reduced (red line) and oxidized (black line) RB forms in water ($c = 1.5 \times 10^{-5}$ mol dm^{-3}) in the presence of tris(2-hydroxyethyl)amine ($c = 25 \times 10^{-3}$ mol dm^{-3}) or 4-nitroimidazole ($c = 5 \times 10^{-3}$ mol dm^{-3}) recorded 5 μs after the 532 nm flash (E = 240 mJ), and the difference absorption spectra of a degassed RB^{2-} solution in water ($c = 1.5 \times 10^{-5}$ mol dm^{-3}) recorded 400 μs after a 532 nm flash (E = 240 mJ) with a 5 ns integration window (blue line).

The triplet-triplet absorption spectrum of a degassed RB^{2-} aqueous solution ($c = 1.5 \times 10^{-5}$ mol dm^{-3}) was measured in the near infrared region at 10 ns after the 532 nm laser pulse (Figure S5). We should note that the sensitivity of our ICCD sharply decays at this region. The kinetic traces observed at 830 and 900 nm were similar in the shape to that observed at 620 nm (Figure S6).

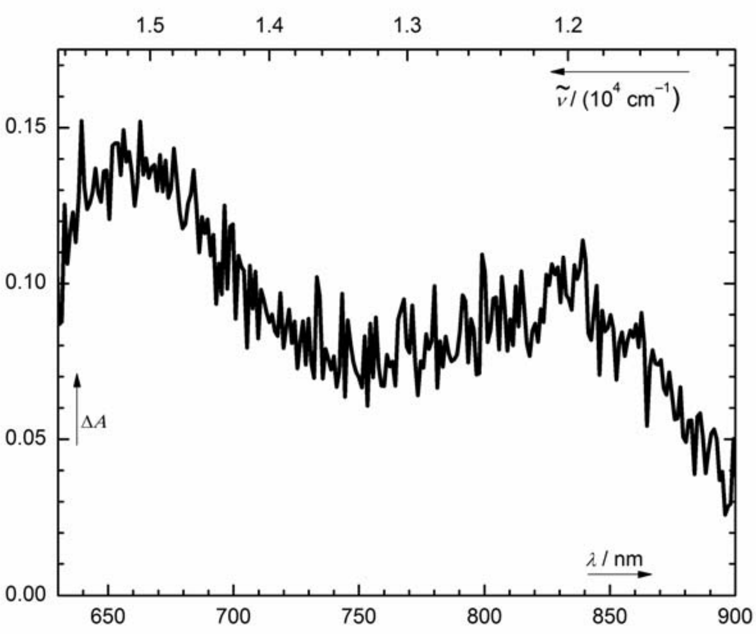


Figure S5. Triplet-triplet absorption spectrum of $^3RB^{2-}*$ in an aqueous solution ($c = 1.5 \times 10^{-5}$ mol dm^{-3}) in near infrared region recorded 10 ns after the 532 nm flash (E = 240 mJ) with a 5 ns integration window.

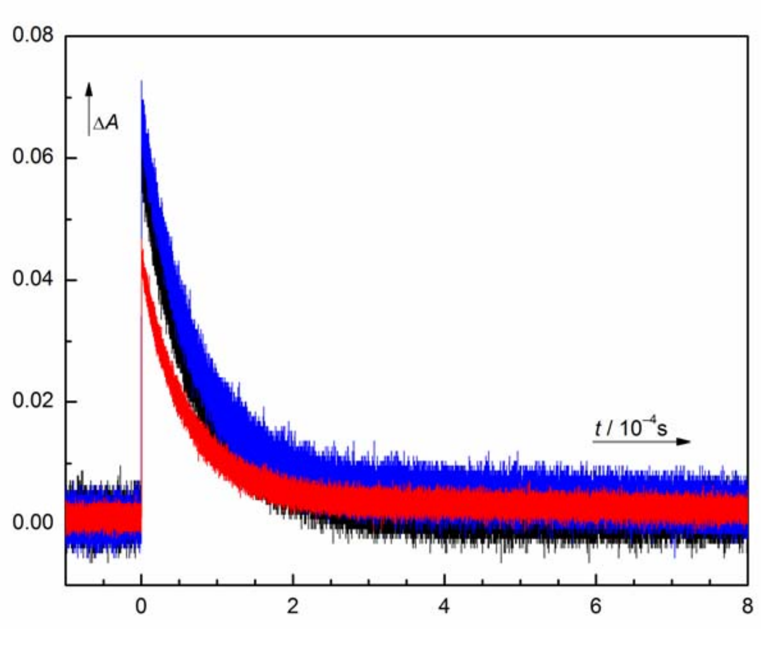


Figure S6. Kinetic traces recorded upon excitation (λ_{exc} = 532 nm) of RB in aqueous solutions (c = 15 μmol dm^{-3}, $E_{\text{laser pulse}}$ = 240 mJ) at λ_{obs} = 620 (black line), 830 (red line), and 900 nm (blue line).

Efficiency of the RB Triplet-State Formation. In the calculation of the molar absorption coefficients of $^{3}RB^{2-}$, we assumed that essentially all RB^{2-} molecules form $^{3}RB^{2-}$ at low concentrations of RB^{2-} and a high energy of the laser pulse (see the main text). For simplification, we considered only the energy levels and processes depicted in Figure S7 (k is a reciprocal value of the singlet state lifetime because the quantum yield of ISC is close to unity in aqueous media.[4,5]). We neglected higher vibrational levels of $^{1}RB^{2-*}$ due to the fast relaxation to the zero vibrational level of $^{1}RB^{2-*}$ (in the order of ps),[6] and we also neglected the decay from $^{1}RB^{2-*}$ to RB^{2-} because of the low effectivity of this process (under 2%).[4] In our work, RB^{2-} is excited to higher vibrational levels of the S_1 state because the laser energy is higher (532 nm = 225 kJ mol^{-1}) than that of the lowest vibrational level of this state (213 kJ mol^{-1}, Table 1). In case that these energies were matched, a very efficient $^{1}RB^{2-*} \rightarrow RB^{2-}$ transition would occur to the detriment of the isc due to stimulated emission.

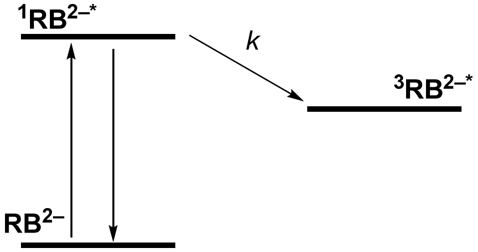


Figure S7. Energy levels of RB considered in equations S1-S5

Thus, our laser delivers a pulse of 210 mJ energy within 700 ps at 532 nm (see the Experimental part). The concentration of photons in a 4 mL cuvette was $c = 3.325 \times 10^{-7}$ mol dm^{-3} per 1 ps. Considering the initial absorbance, A, of 0.11 at 532 nm, the time for reaching population saturation is under 100 ps when 50% of molecules of RB are in the ground state and 50% in the excited state ($^{1}RB^{2-*}$). Therefore, we consider the concentration of RB^{2-} and $^{1}RB^{2-*}$ to be equal during the full duration of the laser pulse (Equation S1). We constructed the equations describing depletion of RB^{2-} and decay of $^{1}RB^{2-*}$ (Equation S2), as well as mass conservation (Equation S3) and the initial boundary conditions of saturation in the beginning of the laser pulse (Equation S4). The 0 index denotes the initial time, whereas t stands for the time of reaction progress. Thus, $[RB^{2-}]_{0w}$ is the initial weighed concentration of the ground state of RB (c = 2.5 μmol dm^{-3}), $[RB^{2-}]_t$ is the concentration of the RB ground state at t, $[^{1}RB^{2-*}]_0$ is the initial concentration of the singlet excited state of RB, $[^{1}RB^{2-*}]_t$ is the concentration of the singlet excited state of RB at t, $[^{3}RB^{2-*}]_t$ is the concentration of the triplet excited state of RB at t.

$$\left[\mathrm{RB}^{2-}\right]_t = \left[{}^{1}\mathrm{RB}^{2-*}\right]_t \qquad \text{(Eq. S1)}$$

$$\left[{}^{1}\mathrm{RB}^{2-*}\right]_t = [\mathrm{RB}^{2-}]_t = \left[{}^{1}\mathrm{RB}^{2-*}\right]_0 \cdot e^{-kt/2} \qquad \text{(Eq. S2)}$$

$$\left[\mathrm{RB}^{2-}\right]_t + \left[{}^{1}\mathrm{RB}^{2-*}\right]_t + \left[{}^{3}\mathrm{RB}^{2-*}\right]_t = \left[\mathrm{RB}^{2-}\right]_{0\mathrm{w}} \qquad \text{(Eq. S3)}$$

$$\left[{}^{1}\mathrm{RB}^{2-*}\right]_0 = \frac{\left[\mathrm{RB}^{2-}\right]_{0\mathrm{w}}}{2} \quad \text{(Eq. S4)}$$

A solution of these equations for the triplet excited state is given in Equation S5. This approach has already been applied to determine the triplet molar absorption coefficient at a single wavelength.[4,7,8]

$$\left[{}^{3}\mathrm{RB}^{2-*}\right]_t = \left[\mathrm{RB}^{2-}\right]_{0\mathrm{w}} \cdot \left(1 - e^{-kt/2}\right) \quad \text{(Eq. S5)}$$

Within these approximations, the population of the triplet state is found to be 95.75% and 97.49% in the sample in 600 and 700 ps, respectively. These values suggest that all excited molecules should be efficiently converted to the triplet state in 5 ns after the flash, which corresponds to the time of our measurement.

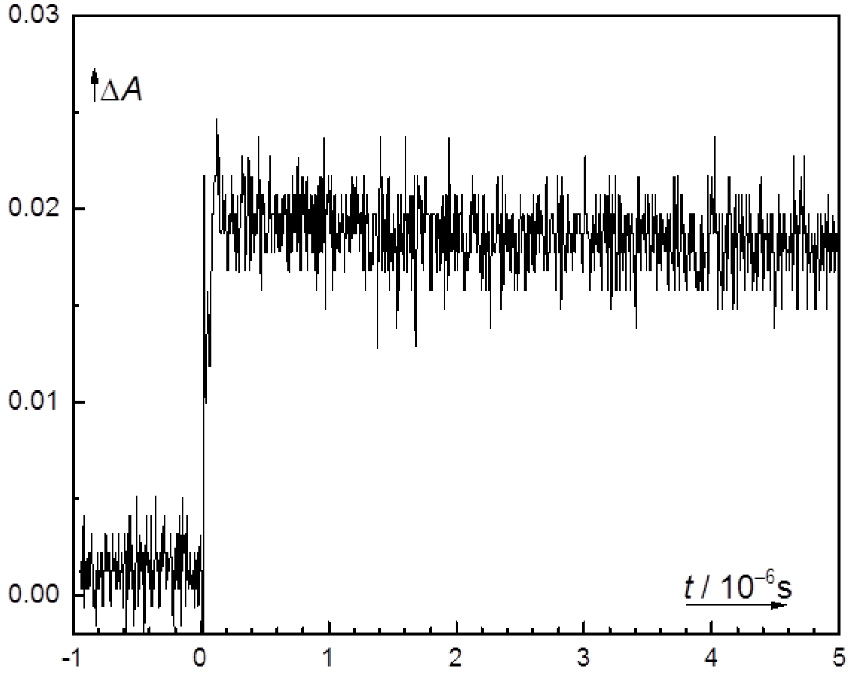
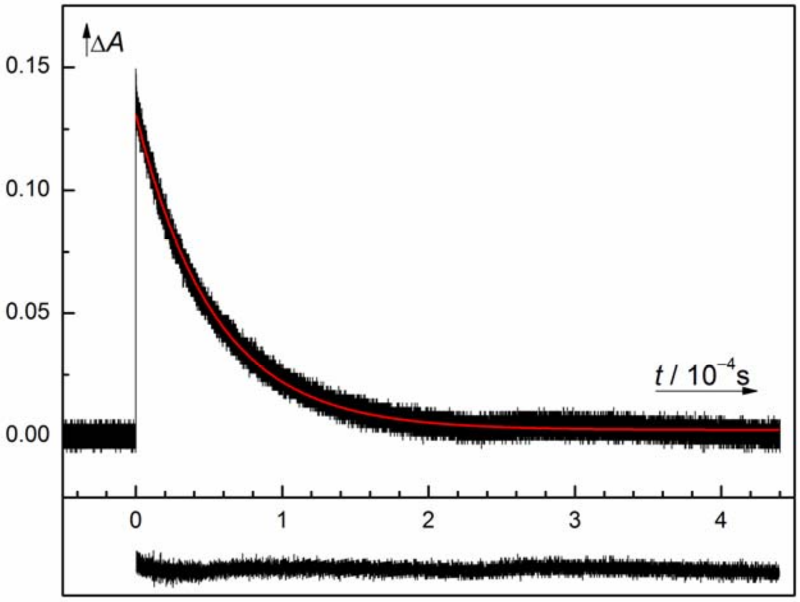


Figure S8. A differential absorbance kinetic trace of ${}^{3}\mathrm{RB}^{2-}$ at 620 nm (at 532 nm; E = 210 mJ) in a degassed aqueous solution (c = 2.5 µmol dm^{-3}).

Transient Kinetics. The laser energy values provided in this work are the energies of a 1 cm circular laser beam. The laser beam was expanded to a 4 cm cuvette by a cylindrical quartz lens, so that the final energy density targeting the sample is approximately one quarter of the original energy value.

a)



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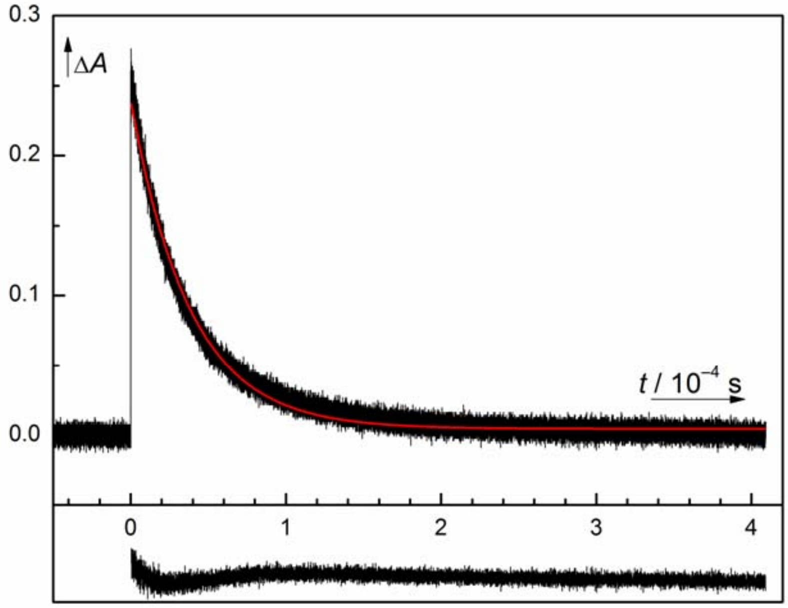

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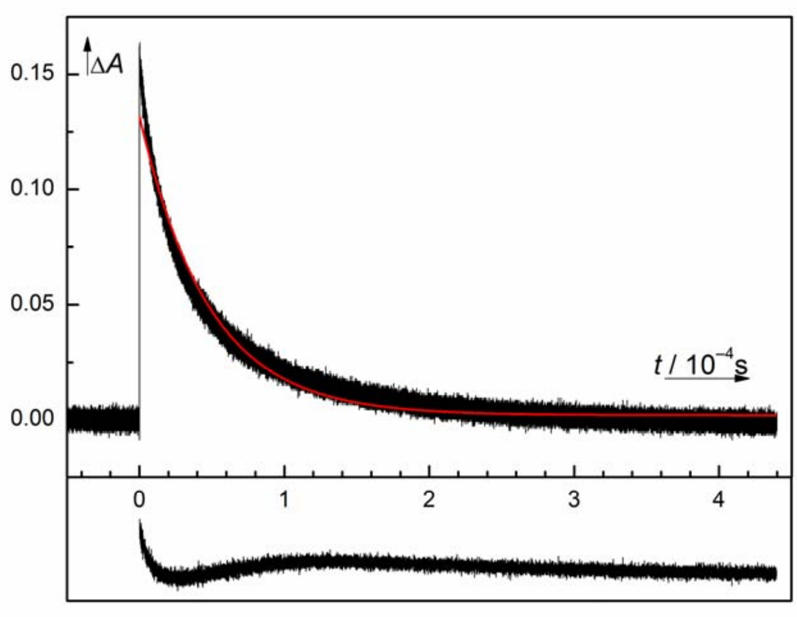

Figure S9. Kinetic traces recorded upon RB excitation: (a) c = 15 µmol dm^{-3}, $E_{\text{laser pulse}}$ = 20 mJ; an aqueous solution; (b) c = 48 µmol dm^{-3}, $E_{\text{laser pulse}}$ = 50 mJ, an aqueous solution; (c) c = 167 µmol dm^{-3}, $E_{\text{laser pulse}}$ = 34 mJ, acetonitrile solution, measured at λ = 620 nm and fitted by the first-order rate constant. The brief inspection of the residuals in individual plots (below abscissa) reveals that the fit is indeed unsatisfactory.

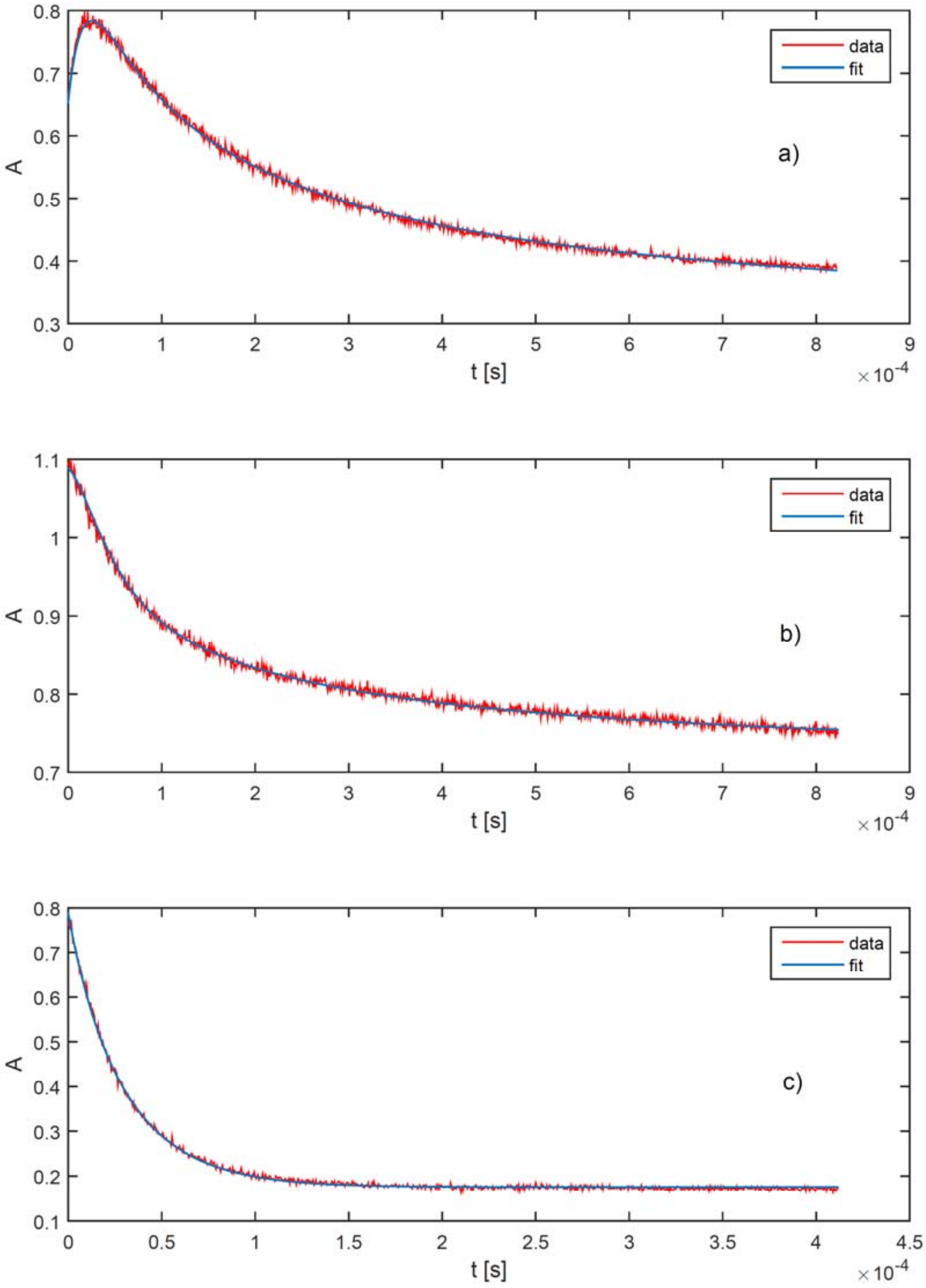

Figure S10. Kinetic traces recorded upon RB excitation: c = 48 μmol dm^{-3}, $E_{\text{laser pulse}}$ = 240 mJ; aqueous solution; measured at (a) λ = 420 nm, (b) λ = 470 nm, and (c) λ = 620 nm, and fitted all together using a global kinetic model.

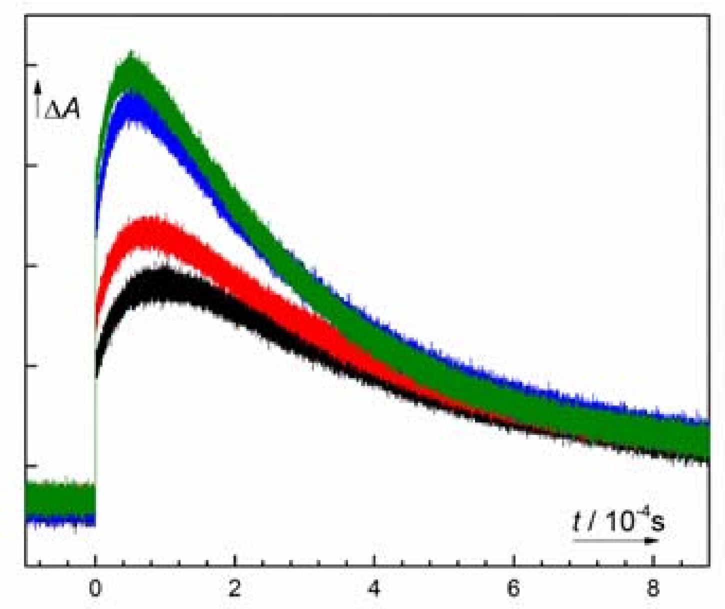

Figure S11. Kinetic traces recorded upon RB excitation in acetonitrile solutions (λ_{exc} = 532 nm, λ_{obs} = 440 nm, c = 35 µmol dm^{-3}): $E_{\text{laser pulse}}$ = 25 (black line), 50 (red line), 120 (blue line) and 180 mJ (green line).

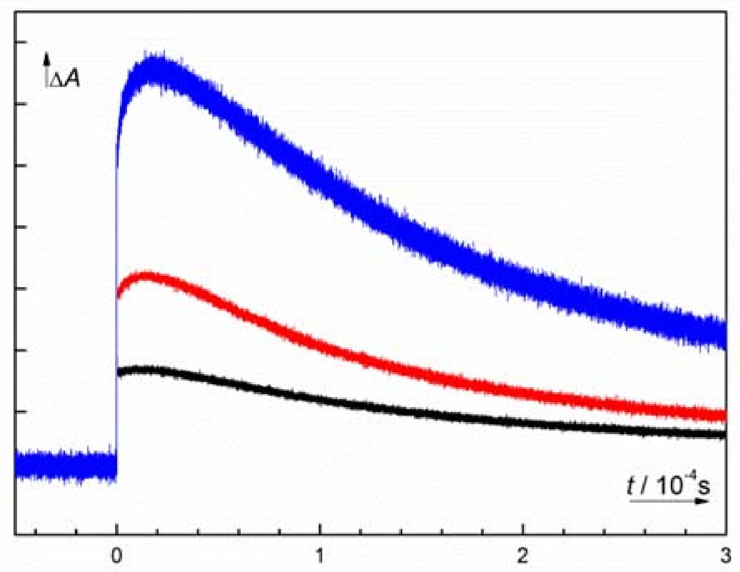

Figure S12. Kinetic traces recorded upon RB excitation in aqueous solutions (λ_{exc} = 532 nm, λ_{obs} = 420 nm, $E_{\text{laser pulse}}$ = 240 mJ): c = 15 (black line), 35 (red line) and 60 µmol dm^{-3} (blue line).

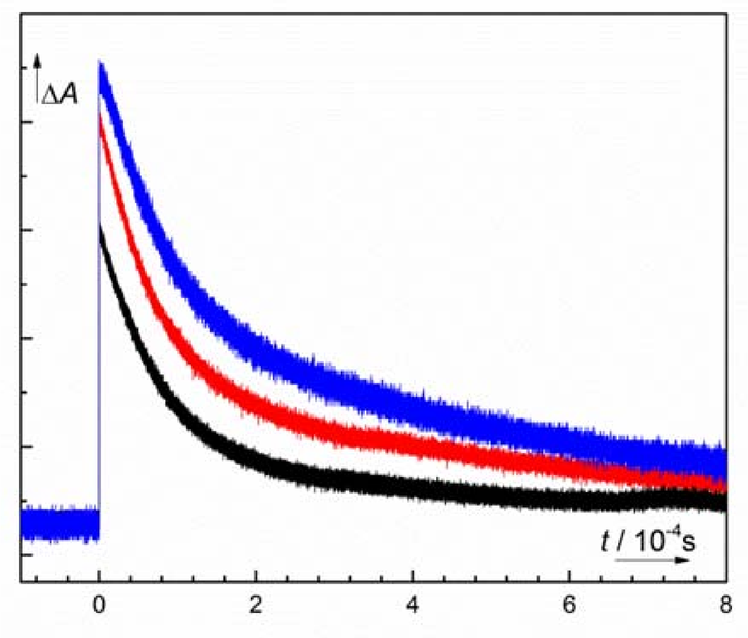

Figure S13. Kinetic traces recorded upon RB excitation in aqueous solutions (λ_{exc} = 532 nm, λ_{obs} = 470 nm, $E_{\text{laser pulse}}$ = 240 mJ): *c* = 15 (black line), 35 (red line) and 48 µmol dm^{-3} (blue line).

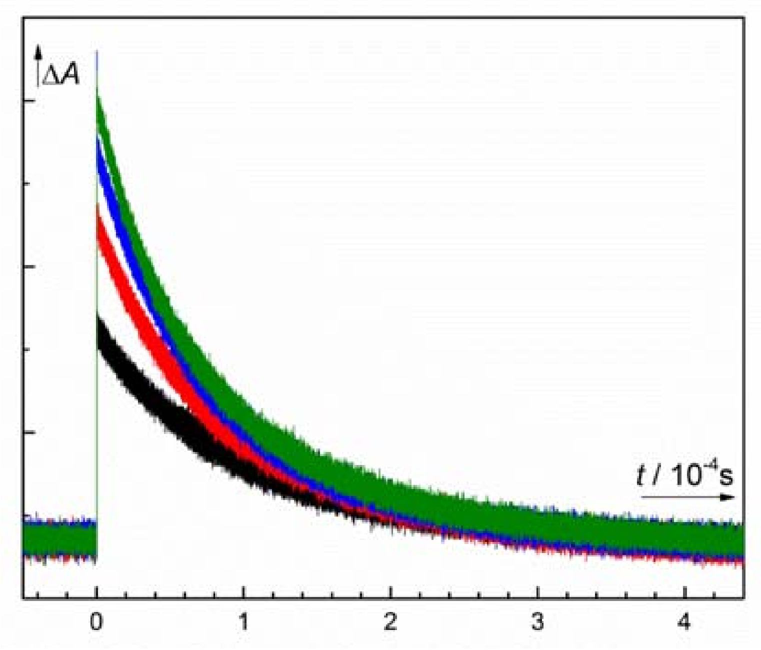

Figure S14. Kinetic traces recorded upon RB excitation (λ_{exc} = 532 nm, λ_{obs} = 620 nm) of RB in acetonitrile solutions (*c* = 35 µmol dm^{-3}, $E_{\text{laser pulse}}$ = 25 (black line), 50 (red line), 120 (blue line) and 240 mJ (green line).

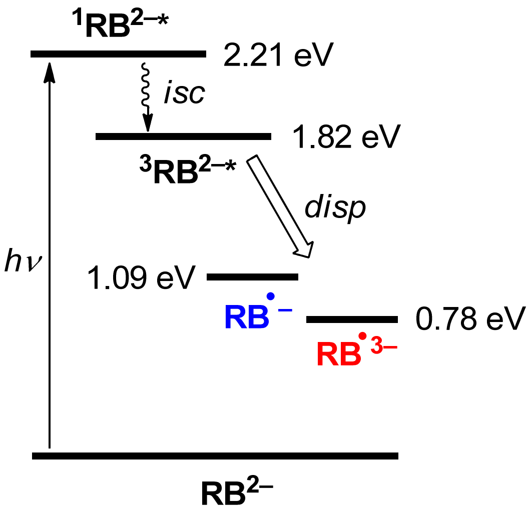

Figure S15. A diagram showing all RB forms and their relative energies (disp = disproportionation).

References

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