Observation of dissociative quasi-free electron attachment to nucleoside via excited anion radical in solution

Jun Ma, Anil Kumar, Yusa Muroya, Shinichi Yamashita, Tsuneaki Sakurai, Sergey A. Denisov, Michael D. Sevilla, Amitava Adhikary, Shu Seki & Mehran Mostafavi

Damage to DNA via dissociative electron attachment has been well-studied in both the gas and condensed phases; however, understanding this process in bulk solution at a fundamental level is still a challenge. Here, we use a picosecond pulse of a high energy electron beam to generate electrons in liquid diethylene glycol and observe the electron attachment dynamics to ribothymidine at different stages of electron relaxation. Our transient spectroscopic results reveal that the quasi-free electron with energy near the conduction band effectively attaches to ribothymidine leading to a new absorbing species that is characterized in the UV-visible region. This species exhibits a nearly concentration-independent decay with a time constant of ~350 ps. From time-resolved studies under different conditions, combined with data analysis and theoretical calculations, we assign this intermediate to an excited anion radical that undergoes N1-C1′ glycosidic bond dissociation rather than relaxation to its ground state.
Radiation-induced cellular DNA damage stems not only from the impact (i.e. direct effect) of primary high-energy photons and charged particles, but also from secondary species (excited molecules, free radicals, and free electrons) that are produced via radiolysis of cell components along the radiation tracks. Secondary electrons are ubiquitous in an irradiated medium with an estimated quantity of ~4 × 10^6 electrons per 1 MeV energy deposited. They cause cascades of additional ionizations and excitations through inelastic scattering with molecules. As a result, low-energy electrons (LEEs) are generated with an excess kinetic energy of 0–20 eV.

DNA strand breaks, especially double strand breaks (DSBs), are the most important DNA damage that has been shown to lead to cell death and neoplastic transformation. It is known that fully solvated electrons (esol-) are ineffective at triggering DNA bond cleavage because they generally reside on biomolecules as stable anions. For this reason, the conventional notion of electron-induced damage to the genome is mainly due to those electrons with sufficient energy to ionize or excite DNA, thereby leading to the formation of electron-loss radicals (holes) and excited states that cause subsequent molecular fragmentation. In 2000 and onwards, the experimental observations from Sanche and coworkers showed that LEEs were able to cause single strand breaks (SSBs), as well as DSBs via dissociative electron attachment (DEA). This observation motivated a great number of mechanistic studies on the interaction of LEEs with DNA and its components in both the gas and condensed phases. The low-energy resonance features in the yield of DSBs, SSBs, and anions produced by the impact of LEEs on model pyrimidine bases suggested that the initial step involves electron capture into the unoccupied molecular orbitals that are above the lowest unoccupied molecular orbitals (LUMOs) of the parent nucleobase, creating excited transient negative ions (TNI*s*). Once the TNIs* are formed, they are shown to decay very rapidly leading either to a SSB via phosphate-sugar C bond cleavage or to a DSB via bond breaking. The rightmost transient species (epre-, e sol- and TNI*) of the LEE interaction with DNA and its model components can be studied using transient absorption spectrometry (Supplementary Figure 1).

Results

Electron solvation in liquid DEG. The transient absorption spectra of neat DEG is shown in Fig. 2a. A significant fraction of electrons formed in DEG immediately after the electron pulse have undergone relaxation. A transient feature absorbing above 900 nm rapidly diminishes, and a broad intense signal with a maximum at around 750 nm undergoes a continuous blue shift of
ca. 120 nm, accompanied with a growing amplitude of about hundreds of picoseconds (e.g. 250 ps, Fig. 2a). At the end of the spectral evolution (Fig. 2a), a broad and featureless absorption band builds up with a peak at 630 nm. Based on previous studies in various alcohols\textsuperscript{24}, this band is assigned to the spectrum of \( \text{e}_{\text{sol}}^- \). Quenching of the signals by adding acetone (an electron scavenger) confirms this assignment and nanosecond pulse radiolysis measurements indicated that the lifetime of \( \text{e}_{\text{sol}}^- \) in neat DEG is around 5 μs. Alcohol radicals are formed by ionization, but they absorb only in the UV region below 300 nm. As a result, the time-dependent spectral changes in Fig. 2a clearly show that the electron solvation essentially consists of at least two distinct states, one absorbing in the near-infrared, and one in the visible range.

Figure 2b presents kinetic traces of the transient electrons in DEG at various wavelengths (390–1000 nm) with a non-monotonic kinetics and with no isosbestic point. Figure 2b clearly shows that the signals at 390 and 600 nm rise fast, then remain almost constant for the next hundreds of ps, and the one at 900–1000 nm follows a continuous decrease. The overall kinetics are shown in Fig. 3. Rapid electron capture by rT generates a new transient signal that is immediately and clearly visualized in the UV–visible regions shown in Fig. 2c. In contrast to the slight increase in neat DEG, the transient kinetics in the UV–visible region (370–600 nm) shown in Fig. 2d and Fig. 3a, b of rT solutions display an obvious decay. From Fig. 3c, d, we observe a substantial decrease of the initial near-infrared absorbance that correlates exponentially with increasing rT.

**Electron attachment to rT leading to TNI\(^+\) formation.** To investigate the electron attachment to rT and the consequent formation of rT\(^+\), picosecond pulse radiolysis studies were performed in rT solutions (50–500 mM) in DEG. In these solutions, direct ionization or excitation of solute itself is not significant. As an example, the transient spectra and the kinetics at 300 mM in Fig. 2c, d, and the effect of the rT concentration on the kinetics are shown in Fig. 3. Rapid electron capture by rT generates a new transient signal that is immediately and clearly visualized in the UV–visible regions shown in Fig. 2c. In contrast to the slight increase in neat DEG, the transient kinetics in the UV–visible region (370–600 nm) shown in Fig. 2d and Fig. 3a, b of rT solutions display an obvious decay. From Fig. 3c, d, we observe a substantial decrease of the initial near-infrared absorbance that correlates exponentially with increasing rT.

**Fig. 2** Transient absorption profiles of pure diethylene glycol and ribothymidine solutions under ambient conditions. Spectra (a, c) and kinetics (b, d) for neat DEG and 0.3 M ribothymidine (rT) solutions, respectively. The region at 780 nm is filtered out. The duration of the electron pulse is ~7 ps. The dose per electron pulse is 25.3 Gy.
concentrations. These results clearly show that rT has scavenged a significant fraction of the electrons prior to their being trapped in DEG. For instance, about 12% and as high as 75% of electrons are captured by rT molecules at the concentration of 0.05 and 0.5 M, respectively. Analyses of normalized kinetics at the infrared region from 720 to 1000 nm, at which the absorptions are only associated with e_{pre}^−, are found to be nearly identical (Fig. 3d, inset) with those observed in neat DEG (Fig. 2b). Also, the global fitting for the transient in each rT solution at the higher wavelength (>720 nm) shows that the characteristic times of two components (τ1 and τ2) remain almost unchanged. Therefore, these results establish that even such a significant extent of electron scavenging takes place before electron localization in pre-existing traps, the presence of rT does not affect significantly the subsequent electron solvation process in DEG (Fig. 3); also, rT does not react with e_{pre}^− on the time scale of hundreds of ps. Based upon our assignments of the states of e_{pre}^− and e_{sol}^−, we conclude that the electrons captured by rT within the pulse duration (≤7 ps) are most likely attributed to e_{qf}^− at or above the conduction band. Because energy levels of trapped electrons in a solvent strongly correlate with time of electron solvation, the lifetime of this species is estimated to be ~350 ps based on the lineally fitting of the kinetic in logarithm, as well as the half-life of TNI• shown in Fig. 4b, which agrees with previously measured rates of charge-induced dissociation.

In the liquid phase, electron attachment to rT results in the formation of excited rT•• (i.e., TNI•) or ground state, rT••, i.e., TNI. rT•• will subsequently, either dissociate to a neutral radical (R*) and an anion when the energy is accessible or relax to a stable anion radical by liberating energy to the solvent. This latter species, rT••, is essentially, identical in nature with that from the reaction of the fully e_{sol}^− (see Fig. 1). It is less likely that the transient kinetics correspond to the decay of fragment radicals R*. This is because in DEG (viscosity = 35.7 cP; 25 °C), R* should react with other radicals through nearly diffusion-limited reactions on timescale of tens of nanoseconds. In addition, the decay rate should be affected by the concentration of R*. More importantly, the initial absorbance of the new species at various concentrations is linearly correlated with the number of electrons captured (Supplementary Figure 4). After ruling out this possibility, the key question now is whether it corresponds to the excited anion radicals or fully solvated anion radicals or both.

To answer this question, the MCR-ALS analysis of a data matrix (Supplementary Figure 2) previously described and via simply subtracting the initial absorbance of e_{pre}^− and the observed IR spectra of e_{pre}^− are identical with that in DEG. Consequently, the transient profiles of rT intermediates were obtained as shown in Fig. 4, via a combination of a multivariate curve resolution alternating least squares (MCR-ALS) analysis of a data matrix (Supplementary Figure 2) previously described and via simply subtracting the e_{pre}^− absorption in neat DEG (Supplementary Figure 3). In studied wavelength range, the spectra of this species are characterized as a mono-peak absorption band extending to the UV (Fig. 4a) and it does not evolve with the delay time (Supplementary Figure 3). Figure 4a inset also showed that this species undergoes a decay that is nearly independent of the concentration. The lifetime of this species is estimated to be ~350 ps based on the lineally fitting of the kinetic in logarithm, as well as the half-life of TNI• shown in Fig. 4b, which agrees with previously measured rates of charge-induced dissociation.

As described above, the presence of rT has only changed the initial absorbance of e_{pre}^− and the observed IR spectra of e_{pre}^− are identical with that in DEG. Consequently, the transient profiles of rT intermediates were obtained as shown in Fig. 4, via a combination of a multivariate curve resolution alternating least squares (MCR-ALS) analysis of a data matrix (Supplementary Figure 2) previously described and via simply subtracting the e_{pre}^− absorption in neat DEG (Supplementary Figure 3). In studied wavelength range, the spectra of this species are characterized as a mono-peak absorption band extending to the UV (Fig. 4a) and it does not evolve with the delay time (Supplementary Figure 3). Figure 4a inset also showed that this species undergoes a decay that is nearly independent of the concentration. The lifetime of this species is estimated to be ~350 ps based on the lineally fitting of the kinetic in logarithm, as well as the half-life of TNI• shown in Fig. 4b, which agrees with previously measured rates of charge-induced dissociation.

In the liquid phase, electron attachment to rT results in the formation of excited rT•• (i.e., TNI•) or ground state, rT••, i.e., TNI. rT•• will subsequently, either dissociate to a neutral radical (R*) and an anion when the energy is accessible or relax to a stable anion radical by liberating energy to the solvent. This latter species, rT••, is essentially, identical in nature with that from the reaction of the fully e_{sol}^− (see Fig. 1). It is less likely that the transient kinetics correspond to the decay of fragment radicals R*. This is because in DEG (viscosity = 35.7 cP; 25 °C), R* should react with other radicals through nearly diffusion-limited reactions on timescale of tens of nanoseconds. In addition, the decay rate should be affected by the concentration of R*. More importantly, the initial absorbance of the new species at various concentrations is linearly correlated with the number of electrons captured (Supplementary Figure 4). After ruling out this possibility, the key question now is whether it corresponds to the excited anion radicals or fully solvated anion radicals or both. To answer this question, the MCR-ALS analysis of a data matrix showed several important features of species involved as displayed in Fig. 4: (i) only two absorbing species (e•− and rT••) exist at the early time. rT•• is formed within the pulse and not
after the electron pulse (ii). rT** decays in a few 100 ps and the decay of the electron during this time is almost negligible (Fig. 4b). (iii) The decay of the rT** does not form the rT* because the formation of the latter only correlates with the decay of e_{sol} at longer time (Fig. 4b). Besides, to compare the spectral difference (the band shape, lifetime, and extinction coefficient) between rT** and rT*, we performed additional measurements of DEG solution at low concentrations (1–10 mM), in which e_{eq} and e_{pre} are not scavenged by rT* at long range and all of them are converted into rT* (Fig. 1). The resulting anion radicals rT* at microsecond timescale show a distinct transient spectrum (blue curve in Fig. 4a) and remain stable over a long period of time (lifetime >10 μs, see Supplementary Figure 5). These results conclude that the transient signals are attributed to the excited anion radical rT** formed from e_{eq} attachment to rT in liquid DEG.

In contrast to the results obtained in DEG solutions, studies using aqueous rT did not provide any evidence of the bond breaking. All TNIs* relaxed to rT* (Fig. 1), which is in the agreement with our previous work. For a given rT concentration, e.g., 0.5 M, the scavenging time of e_{pre} is about 400 fs both in water and in DEG as the rate constant of e_{pre} scavenging by rT is found to be similar, ~5 × 10^{12} M^{-1} s^{-1}. However, as the solvation dynamics in water is much faster, the time for excess electrons reaching into the pre-existing traps of liquid water is on the order of tens of fs and the lifetime of p-like states of electron was around 300 fs. Thus, rT in liquid water cannot react with the higher electronic states of electrons, such as p-like states or conduction states, which, in turn, do not offer enough energy for the bond rupture of TNIs*. Thus, our results clearly point out the energy states of a single electron and pre-existing traps in the solvent medium are the decisive factor for the occurrence of TNIs* fragmentation.

**Modeling of excited TNI surfaces leading to N1–C1' bond breakage.** It is well-known that LEEs on interacting with a molecule create TNI resonances which are equivalent to vertical excited states of the electron adduct of the parent molecule. Based on this understanding, calculations of the transition energies to vertical excited states of a TNI can predict the specific resonance energies available for direct capture of LEEs. In this work, the transition energies of TNI of rT in DEG (ε_{c} = 31.69) are calculated using the time-dependent DFT (TD-DFT) implemented in Gaussian 16. The complete methodology is abbreviated as TD-ωB97XD-PCM/6-31G**. Use of a compact basis set (6–31G**) in these calculations avoids mixing of resonances with the continuum. From the nature of the TNI potential energy surface (PES) (Fig. 5), we see that as the N1–C1' bond elongates the energy of ground state of the TNI (\(\tilde{\pi}_{\text{TNI}}\)) surface increases until it crosses the dissociative \(\tilde{\pi}\) surface with a barrier of 1.6 eV. The energy of the first excited state \(\tilde{\pi} \rightarrow \tilde{2\pi}^{*}\) (\(\tilde{\pi}^{*}\) surface) also increases as N1–C1’ bond elongates and at 1.8 Å it crosses the dissociative \(\tilde{\pi}\) surface having a barrier of ca. 1 eV. We also optimized the \(\tilde{2\pi}^{*}\) excited state (The \(\tilde{2\pi}^{*}\)) was not fully optimized because during optimization this excited state switches to another excited state after few cycles of the optimization steps. Thus, we use the energy of \(\tilde{2\pi}^{*}\) just before the switch.

**Fig. 5** Potential energy surface profiles for N1–C1’ bond cleavage. Shown for the ground and vertical excited states of rT anions (TNI*). The energies were scaled by adding −1.6 eV to the actual calculated values (Supplementary Figure 8) to match with the theoretical adiabatic electron affinity (2.1 eV) of rT. The light blue solid line is the proposed path leading to barrierless fast N1–C1’ bond dissociation.
to the other excited state.) designated as $2\pi^*_{\text{OPT}}$ in Fig. 5. As expected, the adiabatic state, $2\pi_{\text{OPT}}$, lies lower than the vertical $2\pi$ surface and after surpassing a small barrier of ca. 0.6 eV, the N1–C1’ bond dissociates. The light blue solid line in Fig. 5, denotes a proposed barrier-free dissociation path which occurs on capture of a quasi-free electron into the vertical $\pi$-MO of rT ($2\pi^*$) which upon extension of the N1–C1’ bond, relaxes from the vertical to the adiabatic surface.

The ground state adiabatic PES of rT anion radical ($2\pi_{\text{OPT}}$, Fig. 5) shows that the N1–C1’ bond dissociation involves a substantial barrier ca. 1 eV as reported earlier. From the overall nature of the PESs, we inferred that the energy of the lowest excited state of the TNI is located at $-0.3$ eV ($2\pi^*$) and provides the most likely path for immediate dissociation of rT via electron attachment. To mimic the experiment, we scaled the energy in Fig. 5 by adding $-1.6$ eV to the calculated values for matching the adiabatic electron affinity (AEA) (2.1 eV) of rT that were calculated using theωB97XD-PCM/6-31+G** method with actual energy values presented in the supporting information (Supplementary Figures 6–9). From Fig. 5, it is evident that the vertical $\pi^*$ excited state of TNI has energy of $-0.3$ eV which lies within the conduction band energy range. An overview of the energies of the electron and TNI of rT in DEG is shown in Fig. 1 and Supplementary Figure 9. Thus, electrons generated in the conduction band should be efficiently captured into the excited state $\pi^*$-MO of the rT TNI and proceed via gradual relaxation of the structure on bond elongation to a barrier-free N1–C1’ glycosidic bond cleavage leading to thymine release.

Discussion
Our spectroscopic observations in DEG establish that the quasi-free electrons form two localized electron-solvent configuration states (in the infrared region and in the visible region) within the timescale of the electron pulse (<7 ps); the former is characterized as a p-like state and the latter is assigned to a vibrationally hot ground state which gradually relaxes to form a solvated electron $e_{\text{solv}}^-$. In the presence of rT, our results show that dissociative electron transfer occurs only by the quasi-free electrons at or above the conduction band rather than via $e_{\text{WA}}^-$ and $e_{\text{solv}}^-$. The resulting excited rT anion radical rT** observed on a picosecond timescale has been fully characterized, and it exhibits a spectrum that is different from the spectrum of the stable anion radical rT* which is observed on the microsecond timescale in dilute DEG solutions at room temperature. The combination of time-resolved results and DFT calculations establishes that the observed transients rT** can be attributed to the excited state $\pi^*$-MO of the TNI of rT, and its dissociation proceeds via gradual relaxation of the structure on bond elongation through a barrier-free N1–C1’ glycosidic bond cleavage. Our results further imply the generation of biomolecular damage does not necessarily require electrons carrying kinetic energy. In cellular systems the water molecules have inherently long relaxation times. Conduction band electrons ($e_{\text{CB}}$) formed in cells should have longer lifetimes than those found in water or in DEG; as a result, these longer-lived $e_{\text{CB}}$ would contribute to biomolecular damage. Thus, the insights gained in our present study could pave the way to directly investigate the long-standing mystery of electron-driven reactions in radiation chemistry and biology.

Methods
Pulse radiolysis experiment. The chemical compounds (rT and DEG; purity, >99%) were purchased from Sigma-Aldrich and used without further purification. The 7 ps pulse radiolysis coupled with transient absorption measurements were performed at the electron facility LINAC (Tokyo University) coupled to a transient absorption broadband probe spectroscopy (380–1050 nm) instrument. Additional time-resolved radiolysis results were also carried out at ELYSE facility (Paris-Saclay University) for comparison. The experimental data matrices were analyzed by a MCR-ALS approach as previously described. Details about experimental apparatus, methodologies, and data analysis are provided in Supplementary Notes 1 and 2.

TD-DFT calculations. In this study, the ωB97XD density functional and 6–31G** basis set were used and the effect of bulk solvent with dielectric constant of DEG ($\varepsilon = 31.69$) was incorporated via the use of the integral equation formalism polarized continuum model (IEF-PCM). Details about the TD-DFT calculations are provided in Supplementary Note 3.

Data availability
The data that support the findings of this study are available from the corresponding authors upon request.

Received: 26 August 2018 Accepted: 11 December 2018
Published online: 09 January 2019

References
1. von Sonntag, C. Free Radical-Induced DNA Damage and Its Repair: A Chemical Perspective (Springer, Berlin, Heidelberg, 2006).
2. Alizadeh, E. & Sanchez, L. Precursors of solvated electrons in radiobiological physics and chemistry. Rev. Chem. Rev. 112, 5578–5602 (2012).
3. Cobut, V. et al. Monte Carlo simulation of fast electron and proton tracks in liquid water. I. Physical and physicochemical aspects. Radiat. Phys. Chem. 51, 229–243 (1998).
4. Pimblott, S. M. & LaVerne, J. A. Production of low-energy electrons by ionizing radiation. Radiat. Phys. Chem. 76, 1244–1247 (2007).
5. Khanna, K. K. & Jackson, S. P. DNA double-strand breaks: signaling, repair and the cancer connection. Nat. Genet. 27, 247–254 (2001).
6. Nabben, F. J., Karman, J. P. & Loman, H. Inactivation of biologically active DNA by hydrated electrons. Int. J. Radiat. Biol. 42, 23–30 (1982).
7. Becker, D., Adhikary, A. & Sevilla, M. D. in Mechanisms of Radiation-induced DNA Damage: Direct Effects. Recent Trends in Radiation Chemistry (eds. Wishart, J. F. & Rao, B. S. M.) 21–58 (World Scientific Publishing Company, 2010).
8. Boudaïf, B., Cloutier, P., Hunting, D., Huels, M. A. & Sanche, L. Resonant formation of DNA strand breaks by low-energy (3 to 20 eV) electrons. Science 287, 1658–1660 (2000).
9. Martin, F. et al. DNA strand breaks induced by 0–4 eV electrons: the role of shape resonances. Phys. Rev. Lett. 93, 068101 (2004).
10. Ptasińska, S., Denilf, S., Scheier, P., Illenberger, E. & Märk, T. D. Bond- and site-selective loss of H atoms from nucleobases by very-low-energy electrons (<3 eV). Angew. Chem. Int. Ed. Engl. 44, 6941–6943 (2005).
11. Yandell, M. A., King, S. B. & Neumark, D. M. Time-resolved radiation chemistry: photoelectron imaging of transient negative ions of nucleobases. J. Am. Chem. Soc. 135, 2128–2131 (2013).
12. Gu, J., Leszczynski, J. & Schafer, H. F. III. Interactions of electrons with bare DNA by hydrated electrons. Int. J. Radiat. Biol. 42, 23–30 (1982).
13. Cooper, D., Adhikary, A. & Sevilla, M. D. in Mechanisms of Radiation-induced DNA Damage: Direct Effects. Recent Trends in Radiation Chemistry (eds. Wishart, J. F. & Rao, B. S. M.) 21–58 (World Scientific Publishing Company, 2010).
14. Chase, W. J. & Hunt, J. W. Solvation time of the electron in polar liquids. J. Phys. Chem. 86, 2572–2579 (1982).
15. Migus, A., Leszczynski, J. & Schaefer, H. F. III. Electron reactions in radiation chemistry: photoelectron imaging of transient negative ions of nucleobases. J. Am. Chem. Soc. 135, 2128–2131 (2013).
16. Migus, A., Gauduel, Y., Martin, J. L. & Antonetti, A. Excess electrons in liquid water: first evidence of a prehydrated state with femtosecond lifetime. Phys. Rev. Lett. 58, 1539–1542 (1987).
17. Shkrob, I. A. in The Structure and Dynamics of Solvated Electrons.Recent Trends in Radiation Chemistry (eds. Wishart, J. F. & Rao, B. S. M.) 21–58 (World Scientific Publishing Company, 2010).
18. Chase, W. J. & Hunt, J. W. Solvation time of the electron in polar liquids. Water Alcohols J. Phys. Chem. 79, 2835–2845 (1975).
19. Tani, I. et al. Reactivity of prehydrated electrons toward nucleobases and nucleotides in aqueous solution. Sci. Adv. 1, 1–7 (2017).
20. Kenney - Wallace, G. A. & Jonah, C. D. Picosecond spectroscopy and solvation clusters. The dynamics of localizing electrons in polar fluids. J. Phys. Chem. 86, 2572–2586 (1982).
21. Goncharenko, A. V. & Chang, Y. C. Effective dielectric properties of biological cells: generalization of the spectral density function approach. J. Phys. Chem. B 111, 9924–9931 (2009).
22. Eliasson, R., Hammarsten, E., Lindahl, T., Björk, I. & Laurenti, T. C. The stability of deoxyribonucleic acid in glycol solution. *Biochim. Biophys. Acta* **68**, 234–239 (1963).

23. Muruya, Y., Lin, M. Z., Iijima, H., Ueda, T. & Katsumura, Y. Current status of the ultra-fast pulse radiolysis system at NERL, the University of Tokyo. *Res. Chem. Intermed.* **31**, 261–272 (2005).

24. Jou, F. J. & Freeman, G. R. Band resolution of optical spectra of solvated electrons in water, alcohols, and tetrahydrofuran. *Can. J. Chem.* **57**, 591–597 (1979).

25. Pépin, C., Goulet, T., Houde, D. & Jay-Gerin, J.-P. Observation of a continuous spectral shift in the solvation kinetics of electrons in neat liquid deuterated water. *J. Phys. Chem. A* **101**, 4351–4360 (1997).

26. Yokoyama, K., Silva, C., Son, D. H., Walhout, P. K. & Barbara, P. F. Detailed Investigation of the femtosecond pump-probe spectroscopy of the hydrated J. Phys. Chem. A **102**, 6957–6966 (1998).

27. Pépin, C., Goulet, T., Houde, D. & Jay-Gerin, J.-P. Femtosecond kinetic measurements of excess electrons in methanol: substantiation for a hybrid solvation mechanism. *J. Phys. Chem.* **98**, 7009–7013 (1994).

28. Silva, C., Walhout, P. K., Reid, P. J. & Barbara, P. F. Detailed investigations of the pump-probe spectroscopy of the equilibrated solvated electron in alcohols. *J. Phys. Chem. A* **110**, 5071–5076 (1998).

29. Soroushian, B. et al. Solvation dynamics of the electron produced by two-photon ionization of liquid polyols. I. Ethyl glycol *J. Phys. Chem. A* **110**, 1705–1717 (2006).

30. Bonin, J., Lapre, J., Pernot, P. & Mostafavi, M. Solvation dynamics of electron produced by two-photon ionization of liquid polyols. II. Propanediols. *J. Phys. Chem. A* **111**, 4902–4913 (2007).

31. Turi, L. & Rossky, P. J. Theoretical studies of spectroscopy and dynamics of hydrated electrons. *Chem. Rev.* **112**, 5641–5674 (2012).

32. Schwartz, B. J. & Rossky, P. J. Aqueous solvation dynamics with a quantum mechanical solute: computer simulation studies of the photoexcited hydrated electron. *J. Chem. Phys.* **101**, 6902 (1994).

33. Zharkin, A. A. & Fischer, S. F. Theory of electron solvation in polar liquids: a continuum model. *J. Chem. Phys.* **124**, 054506 (2006).

34. Elkins, M. H., Williams, H. L., Shreve, A. T. & Neumark, D. M. Relaxation mechanism of the hydrated electron. *Science* **342**, 1496–1499 (2013).

35. Karasahina, S., Yamamoto, Y. & Suzuki, T. Resolving non-adiabatic dynamics of hydrated electrons using ultrafast photoemission anisotropy. *Phys. Rev. Lett.* **116**, 137601 (2016).

36. Nordlund, D. et al. Probing the electron delocalization in liquid water and ice at attosecond time scales. *Phys. Rev. Lett.* **99**, 217406 (2007).

37. Stahler, J., Deinert, J. C., Wegkamp, D., Hagen, S. & Wolf, M. Real-time measurement of the vertical binding energy during the birth of a solvated electron. *J. Am. Chem. Soc.* **137**, 3520–3524 (2015).

38. Savolainen, J., Uhlig, F., Ahmed, S., Hamm, P. & Jungwirth, P. Direct observation of the collapse of the delocalized excess electron in water. *Nat. Chem.* **6**, 697–701 (2014).

39. Tang, Y. et al. Direct measurement of vertical binding energy of a hydrated electron. *Phys. Chem. Chem. Phys.* **12**, 3653–3655 (2010).

40. Kumar, A., Adhikary, A., Shamoun, L. & Sevilla, M. D. Do solvated electrons in water, alcohols, and tetrahydrofuran: a theoretical rationale. *J. Phys. Chem. Lett.* **7**, 3401–3405 (2016).

41. Gu, J., Xie, Y. & Schaefer, H. F. Glycosidic bond cleavage of pyrimidine nucleosides by low-energy electrons: a theoretical rationale. *J. Am. Chem. Soc.* **127**, 1053–1057 (1965).

42. Kumar, A. & Sevilla, M. D. The role of n* excited states in electron-Induced DNA strand break formation: a time-dependent density functional theory study. *J. Am. Chem. Soc.* **130**, 2130–2131 (2008).

43. Kumar, A. & Sevilla, M. D. Role of excited states in low-energy electron (LEE) induced strand breaks in DNA model systems: influence of aqueous environment. *Chem. Phys. Chem.* **10**, 1426–1430 (2009).

44. Kumar, A. & Sevilla, M. D. In *Handbook of Computational Chemistry* (eds. Leszczynski, J. et al.) 1–63 (Springer Science+Business Media, Dordrecht, 2015).

45. Schulz, G. J. Resonances in electron impact on diatomic molecules. *Rev. Mod. Phys.* **45**, 423–486 (1973).

46. Frisch, M. J. et al. Gaussian v16 (Gaussian Inc., Wallingford, CT, 2009).

47. Li, X., Cai, Z. & Sevilla, M. D. DFT calculations of the electron affinities of nucleic acid bases: dealing with negative electron affinities. *J. Phys. Chem. A* **106**, 1596–1603 (2002).

48. Ruckebusch, C., Sliwa, M., Pernot, P., Juan, A. De & Tauler, R. Comprehensive data analysis of femtosecond transient absorption spectra: A review. *J. Photochem. Photobiol. C* **13**, 1–27 (2012).