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Spur Decay Kinetics of the Solvated Electron in Heavy Water Radiolysis[†]

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Spur decay kinetics of the hydrated electron following picosecond pulse radiolysis of heavy water have been measured using a time-correlated absorption spectroscopy (TCAS) technique. The TCAS data collected for the first 40 ns of the decay was matched up with single-shot transient digitizer data out to microsecond time scales. The decay shape in heavy water looks exactly like the decay in light water except in the first 10 ns. The "time zero" solvated electron yield in heavy water radiolysis must be approximately 7% larger than in light water, to match the best available scavenger product measurements. We propose an explanation in terms of the larger distances traveled by electrons in heavy water prior to localization. The implication is that presolvated H_2O^+ "holes" are very efficient scavengers for the presolvated conduction band electrons.

Introduction

The interaction of ionizing radiation with pure water has great importance in many areas of biology, medicine, nuclear energy, and other technologies where radiation is used or radiation effects must be dealt with and understood.[1,2] Much of the basic mechanistic information was already collected by the 1970s, particularly using the convenient technique of electron pulse radiolysis.[3−10] Briefly, high energy electrons (beta radiation) or gamma photons leave a sparse track of ionization events in the liquid. The secondary electrons produced have sufficient energy to cause secondary ionization and excitation close to the primary event, resulting in "clusters" of ionization and excitation called "spurs". The electrons eventually become solvated $(e^-)_{aq}$, while the H_2O^+ "holes" disproportionate into $(H_3O^+$, OH) pairs. Following these initial events in the first picosecond, the reactive fragment species diffusively recombine over a time scale of several hundred nanoseconds. The entire process can now be efficiently modeled using Monte Carlo and other stochastic methods,[11−15] but despite its importance and long history, several qualitative and quantitative aspects of the water radiolysis problem remain unresolved.

A new time-correlated absorption spectroscopy (TCAS) technique[16] was recently applied in our laboratory to reinvestigate spur recombination kinetics in picosecond pulse radiolysis of water.[5−10] Our new method was devised in order to extend the time-range and improve the S/N ratio of earlier stroboscopic measurements,[5,6] and overcome the universal problem of nonlinear secondary response of fast detectors in nanosecond or faster transient absorption experiments. The 10-ns full scale of the TCAS method was combined with reliable transient digitizer data taken out to a microsecond, to carefully characterize the shape of the hydrated electron decay over many orders of magnitude in time. Given the shape of the electron decay in pure water, it was possible to predict scavenger yields as a function of scavenger concentration, and extrapolate to a "time-zero" solvated electron yield of $G°|_{t=0} = 4.0$ electrons per 100 eV of absorbed radiation. This represents a surprisingly large 20% reduction over some earlier estimates.[17]

The same method has now been applied to determine the radiolysis yield of solvated electrons in heavy water. The spur decay is slower, and the initial yield is larger in heavy water. We argue that both effects result from the greater distance of secondary electron travel in heavy water.

Experimental Section

The technique of time-correlated transient absorption used in these experiments was explained in some detail in our previous publication,[16] and only minor changes will be described here. Briefly, the beam from a mode-locked Ti:sapphire laser crosses a 1 cm flow cell at right angles in front of a 20 MeV electron linac beam (60 Hz, 30ps pulses), and is then detected by a Hamamatsu S5972 silicon photodiode. The basic idea is to measure absorption of the one laser pulse that is nearly coincident with the 30 ps electron pulse, and to simultaneously measure the time delay between the electron and laser pulses with a time-to-amplitude converter. A histogram of absorption vs time events can then be constructed.

In our previous experiments, the time full scale was approximately 11 ns, the spacing of pulses in the mode-locked pulse train. Roughly 440 channels were used to obtain 25 ps/channel time resolution. The rise time of the absorption was limited by trigger jitter to approximately 100 ps. In the present experiments, we have extended the time full scale to 44 ns, and used 880 channels. This is accomplished merely by counting down the laser "clock", so that the electronics are only aware of every fourth laser pulse. The rise time was observed to be one or two channels, as might be expected from the noncollinear arrangement of laser and radiolysis pulse. The longer time scale makes it possible to very rigorously match decay profiles from the TCAS experiment with data obtained from single shot experiments using a transient digitizer and continuous light source.

A problem noted in our previous experiments was the apparent buildup of peroxide product in "dead" flow regions of the absorption cell, which could slightly distort the kinetics. In the present experiment we have added 10^{-3} M methanol and 10^{-5} M sodium hydroxide to scavenge hydroxyl radicals and

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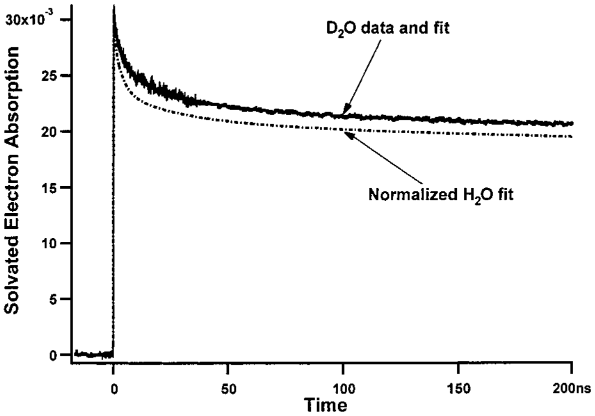

Figure 1. Spur decay of solvated electron in heavy water following 30 ps radiolysis pulses. The first 40 ns of the decay is from time-correlated absorption. The remainder (out to a microsecond, not shown) is recorded with a transient digitizer and photodiode. Superimposed is a fit to the corresponding decay in light water,[16] normalized to the same absorption at $t = 0$.

control the pH of the recirculated heavy water sample. The half-life for electron absorption was well in excess of a microsecond in all cases. The effect of this small scavenger concentration should be negligible in the first 40 ns of solvated electron kinetics, based on the known reaction rate constants.[4] The TCAS decay does match up well with the single-shot kinetics measured in pure degassed heavy water.

Results and Discussion

Result of the present set of experiments on heavy water is shown in Figure 1. Most of the 200 ns full scale represents data collected at 750 nm with a biased FND100 photodiode and 250 MHz analogue bandwidth transient digitizer system (samples every 200 ps, data not shown taken out to a microsecond). The first 40 ns of the photodiode transient was replaced by the TCAS data, after scaling it to match the absorption in the 10−40 ns range. (Photodiode data at earlier times is distorted by rise time and secondary response problems.[16]) Also shown in Figure 1 is the function fitted to the light water data of ref 16. It has been scaled to match the heavy water data at $t = 0$. The initial decay is faster in light water, as reported previously by Chernovitz and Jonah.[18,19] Except in the first five to 10 ns, however, the two decays are indistinguishable.

The fitting procedure followed here is identical to that followed in ref 16. We assume that the long-time limiting decay is due to reaction of hydrated electron with impurities or by second-order recombination. The overall decay is cast in the form

$$G(t) = G°(t)\exp(-k_s[S]t) \tag{1}$$

where $G°(t)$ is the intrinsic decay of electron due to spur recombination processes, and $k_s[S]$ is a scavenging (or impurity) rate. In the spirit of an "isolated spur" model where the reactive radicals can escape to infinity, we represent $G°(t)$ as a sum of exponentials plus a constant. A good (not unique) representation of the heavy water data is given by

$$G°(t)/G_{\text{inf}} = 1 + 0.080\exp(-t/192\text{ ns}) + 0.089\exp(-t/45.7\text{ ns}) + 0.165\exp(-t/11.6\text{ ns}) + 0.185\exp(-t/1.85\text{ ns}) \tag{2}$$

Excellent separation of the spur decay from the "impurity" kinetics is obtained, as the limiting lifetime in Figure 1 is 10 μs, while the longest component of spur decay has 192 ns time constant. By inspection of eq 2, the fitted value of $G°$ ($t = 0$) is 1.519 times the escape yield G_{inf}. Although we have not carried out any sensitivity analysis of the data, we believe this ratio should be correct to within about 3%.

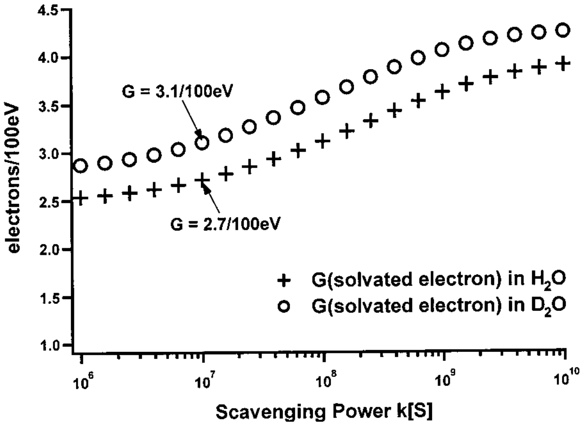

Figure 2. Predicted product yields vs the scavenging power for solvated electrons, based on the time-dependent survival probabilities measured in this work (D_2O) and ref 16 (H_2O). The curves were normalized to product yields obtained with $k_s[S]$ equal to 1 × 10^7, as indicated.

We have carried out no dosimetry in the present study, and report only the shape of the hydrated electron decay as a function of time. However, we can readily predict a yield of scavenged product by integration of eqs 1 and 2 over time, if we know the product $k_s[S]$ of scavenger concentration and reaction rate constant (the "scavenging power"). In our previous study the value of G_{inf} was selected to match the best scavenged product data for light water, which is 2.7 product molecules per 100 eV of energy deposited in solution, when the scavenging power is $1 \times 10^7\ s^{-1}$.[16] Fewer measurements of this quantity are available in heavy water. Elliot and co-workers[20] measure 3.0−3.2 electrons/100 eV. Buxton and co-workers obtain 3.1 electrons /100 eV.[21] Fielden and Hart[22] measured 3.0 for this quantity, also at a scavenging power of $10^7\ s^{-1}$. Taking 3.1 ± 0.1 as a best experimental value, we can predict these scavenger yields if we take $G_{\text{inf}} = 2.82$ in eq 2.

Figure 2 compares the predicted yields for scavenged products in light and heavy water as a function of the scavenging power. Even with the smaller recombination fraction in D_2O (cf. Figure 1), we cannot explain the difference in scavenged yields unless there is a larger initial yield of electrons in heavy water. The extrapolation of eq 2 to $t = 0$ gives a yield $G°|_{t=0} = 4.3$ in heavy water in comparison with the corresponding result $G°|_{t=0} = 4.0$ in light water.[16] If we normalize the decay curves at time zero as in Figure 1, the scavenged yields in H_2O and D_2O should differ by only about 4%, rather than the 13% difference between 2.7 and 3.1. This appears to be outside of the combined range of uncertainty in the data sets.

Discovery of this isotope effect in the prompt radiolysis yield of hydrated electrons is a new result. Chernovitz and Jonah[18,19] measured a slower decay of electrons in heavy water, but never compared the amplitudes on an absolute scale. Nevertheless, the arguments used in their paper can also be used to explain the present result. It is well established that secondary electrons produced in radiolysis quickly lose kinetic energy by inelastic scattering into electronic modes of the solvent.[1−3,11−15] (This gives rise to the radiolysis "spur" in which several electronic excitations occur close together.) Once the electron energy degrades below the electronic band-gap the most efficient energy loss process is scattering into the stretching vibrations. Given that these vibrations are $\sqrt{2}$ lower in frequency in heavy water, one can expect on average that 40% more inelastic scattering events will need to occur in D_2O than H_2O, to reach sufficiently low energy for electron trapping. This implies that the electrons will cover 40% greater distance in heavy water. Assuming that the elastic scattering cross-section is large for these low-energy electrons, we might expect a "random walk" and a near-Gaussian distribution of distances between the trapped electrons and their geminate partners. The standard deviation of the final distance distribution should scale as the square root of the random walk distance. Thus we are led to predict on the order of 20% larger standard deviation of distances in heavy water relative to light water.

A straightforward spur modeling calculation performed by Chernovitz and Jonah[18] demonstrates that this argument qualitatively explains the slower recombination kinetics and larger escape fraction of electrons in heavy water. We suggest that the same argument applies to the "initial yield" of electrons, if it is recognized that some electrons recombine prior to trapping, or at very short times when they are trapped near to their geminate partners.[14] Once again assuming the three-dimensional random walk model, for a standard deviation of distances 20% larger, the probability amplitude for an electron to localize near the origin must be smaller by a factor of $(1.2)^{-3} = 0.58$ (i.e., it is necessary to conserve total probability.) It follows that 42% less "prompt" recombination with H_2O^+ or (H_3O^+,OH) pairs might occur in heavy water.[23] Assuming that the total direct ionization yields are the same in H_2O and D_2O,[24] then the difference $4.3 - 4.0 = 0.3$ in the "time zero" solvated electron yields should be a measure of the difference in "prompt" recombination in the two liquids. Application of our simple geometrical argument implies that we have a prompt "recombination yield" $G_{\mathrm{rec}} = 0.3/0.42 = 0.7$ in light water but only 0.4 in heavy water. In this case the yield of "pre-solvated" electrons must be at least $G_{\mathrm{ps}} = 4.7$.

It has long been known that the yield of "presolvated" electrons must be larger than the final yield of solvated electrons observed on picosecond time scales. Some scavengers will efficiently trap electrons prior to their solvation,[7,8] and the yield of product from such scavengers is demonstrably larger than the prompt yield of solvated electrons. Wolff et al.[10] suggested the presolvated electron yield is $G_{\mathrm{ps}} = 4.8$ and the solvated electron yield is $G°|_{t=30\mathrm{ps}} = 4.0$ in light water, based on measurements with Cd^{2+} and cystamine scavenging. Jonah et al.[6] noted that this experiment failed to account for spur recombination of Cd^+ radical, and therefore scaled up the presolvated electron yield estimate to $G_{\mathrm{ps}} = 5.4$. The recent work of Pastina and LaVerne[26] using both cadmium and selenate scavengers appears to be consistent with a pre-solvated electron yield on the order of $G_{\mathrm{ps}} = 6.0$.

The fate of these "missing" electrons remains an interesting question. Recent femtosecond laser work suggests that "pre-solvated electrons", as defined by the total radiolysis yield from concentrated presolvated electron scavengers such as selenate, include pre-solvated conduction band electrons, localized partially solvated electrons, and even water excited states.[27,28] The yield G_{ps} on the order of 6.0 should represent both the direct ionization of water to produce energetic conduction band electrons and the electronic excitation to produce water "localized excitons". Laser photoionization experiments have shown the latter are produced for excitation energies below about 9.5 eV, and the former are exclusively generated at energies slightly higher.[25,29,30] The number of water excitons produced is expected to be substantially smaller than the total number of electrons in the conduction band.[11,12] The localized excitons produced by laser photolysis do decay (via electron transfer to preexisting traps[25]) to give solvated electrons, but the quantum yield is substantially less than unity, and the isotope effect is found to give fewer solvated electrons in D_2O than in H_2O.[25] Clearly, the localized excitons cannot explain the isotope effect found in the present study.

Another possible isotope effect that should be considered involves dissociative capture of pre-solvated electrons by water. This low cross-section process, leading to a hydride ion and OH radical, has been demonstrated to occur in amorphous ice.[31] It may be responsible for a part of the H_2 yield in water radiolysis, as the H^- ion reacts with water to give H_2 and OH^-.[13,32] However, it was also shown that the efficiency of the process in both light and heavy water must be very similar.[31] To account for the difference in yields of solvated electrons in light and heavy water, the isotope effect in this minor process would need to be very large indeed, so dissociative electron capture can be safely discounted in the present discussion.

If we discount both water exciton decay and dissociative electron capture as the source of our isotope effect, short-time recombination seems to be the only remaining mechanism. However, the size of the effect is surprisingly large. Based on our simple geometrical argument, the probability for recombination in light water would be at least 0.7/4.7, or 15%. This is a very large fraction, given the large electron distributions estimated in recent models of spur chemistry to account for the observed decay rate and yields.[12] Given a probability for electron localization $P(r) = \sqrt{(2/\pi)}*\sigma^{-3}*r^2*\exp(-r^2/2\sigma^2)$ about the center of a typical "spur", only 3% of the total probability is contained in the volume with $r < \sigma/2$. This corresponds to a sphere of 20−25 Å radius for estimated spur distributions with sigma of 40−50 Å.[12] Even allowing for significant error in our estimation of the "prompt" isotope effect (e.g., if there is really only 10% recombination rather than 15%), the demonstration of an isotope effect favoring electron solvation in D_2O implies that the recombination is a very efficient process, with large cross-section or scavenging radius.

It is interesting to note that no additional recombination has been observed in the recent suppressed geminate recombination laser experiments of Barbara and co-workers.[27,28] These experiments involve exciting to the conduction band those solvated electrons which are relatively close to their (fully solvated) geminate partners; the electrons move (>30 Å) away from their geminate H_3O^+ and OH radical partners, and the recombination is effectively turned off. If either H_3O^+ or OH radical were an efficient reaction partner for conduction band electrons, one might expect 5−15% sudden additional recombination. This result suggests that the presolvated H_2O^+ holes are exclusively responsible for the prompt recombination in radiolysis.

More quantitative support for our explanation can be found in the detailed Monte Carlo random flight simulations of Goulet et al.[14] Using an electron-energy-dependent (e^-, H_2O^+) recombination cross-section taken from gas-phase data, and differential electron scattering cross-sections measured for amorphous ice, they calculated an average 5% recombination probability for conduction band electrons. (The initial electron energies of less than 7.2 eV were taken from a realistic distribution based on the water energy-loss spectrum.) They noted that the electrons "which recombine tend to be the ones which, in the absence of cation, would be thermalized relatively close to their starting position." Increasing the recombination cross-section by a factor of 10 over the gas-phase value lead to 14% recombination. Such a large cross-section is consistent with the isotope effect found in this study.

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(23) Note that this argument will change quantitatively, but not qualitatively, if the range parameter (sigma) scales directly by the $\sqrt{2}$ factor, or some factor between 1.4 and 1.2.

(24) The molar densities of H_2O and D_2O are very similar, and the vibrational zero-point energy imposes only a 0.16 eV shift in the electronic spectrum.[25] Thus, it is difficult to imagine a significant difference in the integrated heavy water ionization probability, and any difference ought to favor more ionization in light water where the threshold is lower.

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