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MEASUREMENT OF X-RAY PULSES USING HYDRATED ELECTRONS

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TO: All holders of UCRL-51206 "Measurement of X-Ray Pulses
Using Hydrated Electrons"
FROM: Technical Information Department, L-9

ERRATA

Please note the following corrections to your copy of UCRL-51206:

Page 15

Figure 9(d) is upside down.

Page 16

The first sentence of the Acknowledgments should read:

I would like to express my appreciation to H. Koehler whose memorandum initiated this work, and to L. J. Ferderber for his helpful discussions.

Page 25

The sixth name down should read H. Koehler.

Technical Information Department

MEASUREMENT OF X-RAY PULSES USING HYDRATED ELECTRONS

Abstract

This article presents an engineering discussion of the role of the hydrated electron in a transient dosimetry system. The pertinent rate equations for this system

are presented and practical assumptions are made concerning a simple theoretical solution for the system. This solution is compared with empirical results.

Introduction

One of the most meaningful contributions to the radiation chemistry of aqueous systems has been the discovery of the hydrated electron. Its theoretical prediction by Platzman and its experimental verification by Boag and Hart have profoundly modified the concepts of primary actions in the radiolysis of water and other solvents with similar molecular structures.¹ In addition to advancing the understanding of polar solvents, the dis-

covery of hydrated electrons has also benefited photochemistry and related sciences. In radiation dosimetry, the optical absorption property attributed to the hydrated electron can be used to measure transient radiation pulses.²⁻⁴

The existence of this transient absorption band coupled with the development of high power light sources, such as dye lasers, have made a fast response pulse dosimetry system feasible.

Theory

When water is irradiated, a complex reaction sequence leading to the production of thermalized electrons (e^-) is initiated. If the thermalized electron is trapped in a potential well formed by a polarized water molecule, it is termed a hydrated or solvated electron (e^-_{aq}).⁵⁻⁸ In 1966, E. J. Hart published an article that demonstrated the linear dependence

between radiation dose and hydrated electron yield.⁹ In 1968, N. Klein et al., experimentally determined the solvated electron yield to be on the order of $2.76 \pm 0.17 \mu\text{moles-liter}^{-1}\text{-kilorad}^{-1}$. Klein suggested that this number was constant over a dose range from 0 to 10,000 rads.¹⁰ Thus, assuming the yield to be independent of dose rate

$$\left(\frac{d[e_{aq}^-]}{dt}\right)_p = k \frac{dR}{dt} \quad (1)$$

Here $(d[e_{aq}^-]/dt)_p$ is the number of moles-liter⁻¹-sec⁻¹ of hydrated electrons produced by ionizing radiation that has a dose rate of dR/dt rads/sec. As previously stated, k was experimentally determined to be about 2.76×10^{-9} moles/liter-rads-sec.

Equation (1) compares the rate of change of the hydrated electron concentration to the radiation dose rate in an irradiated aqueous solution. To predict the solvated electron concentration at any time (t), it is necessary to know the e_{aq}^- mean lifetime. Experimental investigation has shown that the mean lifetime is a strong function of water purity.^{11,12}

Using the strong optical absorption band attributed to the hydrated electron, E. J. Hart et al., were able to demonstrate that in highly purified H₂O samples, the mean lifetime approached the 100 μ sec region.¹³

The reason for the long lifetime was attributed to the relatively low concentra-

tion of species with which the hydrated electron could react and disappear. A few of the more significant reactions that account for the disappearance of solvated electrons are given in Table 1 along with their associated rate constants.^{3,12} The equation that relates the rate of annihilation of the e_{aq}^- radical to the concentration of those species (A_n) listed in the table is

$$\left(\frac{d[e_{aq}^-]}{dt}\right)_a = \sum_{n=1}^7 k_n [e_{aq}^-] A_n \quad (2)$$

Combining Eqs. (1) and (2) gives a first order rate equation for the $[e_{aq}^-]$ in an irradiated aqueous solution, i.e.,

$$\frac{d[e_{aq}^-]}{dt} = \left(\frac{d[e_{aq}^-]}{dt}\right)_p + \left(\frac{d[e_{aq}^-]}{dt}\right)_a$$

or,

$$\frac{d[e_{aq}^-]}{dt} = k \frac{dR}{dt} - k_1 [H_2O] [e_{aq}^-]$$

Table 1. Reactions that cause the disappearance of hydrated electrons.

Reaction No. (n)	Species A_n	Reaction	Rate constant (k_n) moles ⁻¹ -sec ⁻¹
1	H ₂ O	$e_{aq}^- + H_2O \rightarrow H + OH^-$	16
2	H ⁺	$e_{aq}^- + H^+ \rightarrow H$	$2.36 \pm 0.24 \times 10^{10}$
3	H	$e_{aq}^- + H \rightarrow H_2 + OH^-$	$\sim 2.5 \times 10^{10}$
4	H ₂ O ₂	$e_{aq}^- + H_2O_2 \rightarrow OH + OH^-$	$1.23 \pm 0.14 \times 10^{10}$
5	OH	$e_{aq}^- + OH \rightarrow OH^-$	3.0×10^{10}
6	O ₂	$e_{aq}^- + O_2 \rightarrow O_2^-$	$1.88 \pm 0.2 \times 10^{10}$
7	e_{aq}^-	$e_{aq}^- + e_{aq}^- \rightarrow H_2 + 2OH^-$	4.5×10^{10}

$$\begin{aligned}
 & -k_2[H^+][e_{aq}^-] - k_3[H][e_{aq}^-] \\
 & -k_4[H_2O_2][e_{aq}^-] - k_5[OH][e_{aq}^-] \\
 & -k_6[O_2][e_{aq}^-] - k_7[e_{aq}^-]^2. \quad (3)
 \end{aligned}$$

The remaining rate equations are

$$\frac{d[H_2O]}{dt} = -k_1[H_2O][e_{aq}^-]. \quad (4)$$

$$\frac{d[H^+]}{dt} = -k_2[H^+][e_{aq}^-] + k_{2,0} \frac{dR}{dt}. \quad (5)$$

$$\begin{aligned}
 \frac{d[H]}{dt} = & -k_3[H][e_{aq}^-] + k_1[H_2O][e_{aq}^-] \\
 & + k_2[H^+][e_{aq}^-] + k_{3,0} \frac{dR}{dt}. \quad (6)
 \end{aligned}$$

$$\frac{d[H_2O_2]}{dt} = -k_4[H_2O_2][e_{aq}^-] + k_{4,0} \frac{dR}{dt}. \quad (7)$$

$$\begin{aligned}
 \frac{d[OH]}{dt} = & -k_5[OH][e_{aq}^-] + k_4[H_2O_2] \\
 & + k_{5,0} \frac{dR}{dt}. \quad (8)
 \end{aligned}$$

Here $k_{n,0}$ is the yield for the species A_n listed in Table 1.

The previous set of rate-equations, although not complete, is too complex for simple analysis. However, if a few assumptions are made, analysis becomes possible. The first assumption is that the molar concentration of H, H_2O_2 , and OH is smaller than the concentration of H^+ . Such a condition is readily achieved in an acidic solution containing a 10^{-2} (or larger) molar concentration of H^+ .³ Thus, those terms involving H, H_2O_2 , and OH can be neglected.

Likewise, the term involving O_2 can be dropped if the molar concentration of dissolved O_2 is kept at least one or two orders of magnitude below the H^+ concentration. This is achieved if the sample is deaerated and kept in an oxygen free atmosphere. Nothing can be done physically about the term originating from reaction 1. However, a simple evaluation of the coefficients in Eq. (3) reveals that its effect is negligible for H^+ molar concentration of 10^{-5} or larger

$$k_1[H_2O] = 16[55] = 880$$

$$k_2[H^+] = 2.3 \times 10^{10}[10^{-5}] = 2.3 \times 10^5.$$

The effect of reaction 7 on Eq. (3) can only be neglected if the dose rate is limited to a value where the maximum expected e_{aq}^- concentration is kept below 10^{-5} moles/liter. This requires that the radiation dose be kept below 10^4 rads.

If all the above conditions are met, then the pertinent rate equations are

$$\frac{d[e_{aq}^-]}{dt} = k \frac{dR}{dt} - k_2[H^+][e_{aq}^-], \quad (9)$$

and

$$\frac{d[H^+]}{dt} = -k_2[H^+][e_{aq}^-] + k_{2,0} \frac{dR}{dt}. \quad (10)$$

In the absence of any radiation,

$$\frac{d[e_{aq}^-]}{dt} = -k_2[H^+][e_{aq}^-] = \frac{d[H^+]}{dt}.$$

In other words, the rate of change of $[e_{aq}^-]$ is equal to the rate of change in $[H^+]$. This fact is also obvious from reaction 2 in Table 1. The foregoing conclusion

suggests that for radiation doses less than 10^4 rads, a change in the H^+ concentration of no more than 1 part in 10^3 is expected. Therefore, the value of $[H^+]$ can be assumed constant. Thus, Eq. (10) can be neglected. This only leaves Eq. (9) to predict the temporal dependence of the e_{aq}^- concentration in pulse irradiated samples where the total dose is kept below 10^4 rads.

An analytical solution to Eq. (9) is readily achieved using Laplace transforms. Taking Laplace transforms of each term in Eq. (9) gives

$$s \mathcal{L}\{[e_{aq}^-](t)\} - [e_{aq}^-](0) = k \mathcal{L}\left\{\frac{dR(t)}{dt}\right\} - k_2[H^+]\mathcal{L}\{[e_{aq}^-](t)\}.$$

Solving for $\mathcal{L}\{[e_{aq}^-](t)\}$ gives

$$\mathcal{L}\{[e_{aq}^-](t)\} = \frac{k \mathcal{L}\left\{\frac{dR(t)}{dt}\right\} + [e_{aq}^-](0)}{s + k_2[H^+]}$$

Since $[e_{aq}^-](0) = 0$,

$$\mathcal{L}\{[e_{aq}^-](t)\} = \frac{k \mathcal{L}\left\{\frac{dR(t)}{dt}\right\}}{s + k_2[H^+]}$$

Using the convolution theorem for Laplace transforms gives the solution for $[e_{aq}^-]$,

$$[e_{aq}^-](t) = \int_0^t k e^{-k_2[H^+](t-\tau)} \frac{dR(\tau)}{dt} d\tau$$

or

$$[e_{aq}^-](t) = k e^{-k_2[H^+]t}$$

$$\times \left[\int_0^t e^{-k_2[H^+]\tau} \frac{dR(\tau)}{dt} d\tau \right]. \quad (11)$$

Using Eq. (11) and knowing $[H^+]$, k , and k_2 we can predict $[e_{aq}^-](t)$ in samples irradiated by dose rates given by $dR(t)/dt$.

Figure 1 shows the predicted e_{aq}^- concentration in several irradiated samples with different H^+ concentrations. The irradiation pulse in each case is similar to that expected from a 705 Febetron.^{*} Note how well the shape of the electron concentration follows the shape of the radiation pulse. This fidelity becomes more obvious as the H^+ concentration is increased. Note also how the maximum e_{aq}^- concentration decreases as the hydrogen ion concentration is increased. Figure 2 shows similar results using a shorter radiation pulse (3 nsec FWHM). Note how the H^+ concentration must be increased in order to achieve a fidelity comparable to that shown in Fig. 1.

As mentioned before, there is a strong absorption band associated with the solvated electron. In an irradiated sample where the hydrated electron concentration is space homogeneous, the optical transmission at wavelength λ (T_λ) is given by⁴

$$T_\lambda = e^{-\epsilon_\lambda [e_{aq}^-] L}. \quad (12)$$

Here ϵ_λ is the molar absorptivity at the wavelength of interest (Fig. 2) and L is the sample thickness.

*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Atomic Energy Commission to the exclusion of others that may be suitable.

(a) Febetron pulse, 20 nsec FWHM.

(b) H^+ concentration, 0.001 moles/liter.

(c) H^+ concentration, 0.002 moles/liter.

(d) H^+ concentration, 0.008 moles/liter.

(e) H^+ concentration, 0.03 moles/liter.

(f) H^+ concentration, 0.16 moles/liter.

Fig. 1. Theoretical predicted concentration of hydrated electrons for various irradiated weakly acidic solutions. Radiation source was a 20 nsec FWHM Febetron pulse. Hydrogen ion concentration was varied as specified.

(a) Irradiation pulse, 3 nsec FWHM.

(b) H^+ concentration, 0.008 moles/liter.

(c) H^+ concentration, 0.02 moles/liter.

(d) H^+ concentration, 0.08 moles/liter.

(e) H^+ concentration, 0.2 moles/liter.

(f) H^+ concentration, 0.8 moles/liter.

Fig. 2. Theoretical predicted hydrated electron concentration for various irradiated acidic solutions of H_2SO_4 . A 3-nsec FWHM radiation pulse was used as a basis for prediction. H^+ concentration was varied as specified.

Solving Eq. (12) for $[e_{aq}^-]$ gives

$$[e_{aq}^-](t) = \frac{\ln T_{\lambda}(t)}{\epsilon_{\lambda} L}. \quad (13)$$

Thus, combining Eqs. (13) and (9),

$$\frac{dR(t)}{dt} = \left(\frac{d \ln[T_{\lambda}(t)]}{dt} + k_2[H^+] \ln[T_{\lambda}(t)] \right) \frac{1}{k \epsilon_{\lambda} L}. \quad (14)$$

Therefore, by knowing the geometry of the system we can calculate the radiation incident on the aqueous cell.

Theoretical Limitations

In this section we briefly evaluate optical transmission magnitude and dosimetry system limitations. With Eq. (12) and Fig. 3, we can generate plots of sample transmissions (at various wavelengths) vs aqueous electron concentrations. Figure 4 represents a family of curves plotted for several different laser wavelengths. The curves relate optical transmission in a 0.5-cm cell to hydrated electron concentration. They suggest that a greater change in sample transmission

Fig. 3. Extinction coefficient vs wavelength for hydrated electrons.

Fig. 4. Optical transmission vs solvated electron concentration for various laser wavelengths.

can be achieved at the ruby laser wavelength because that wavelength falls nearly at the peak of the hydrated electron absorption spectrum. Therefore, dosimetry systems requiring a large dynamic range (10^3 or more) would find ruby lasers attractive because the systems can have optical transmissions down to one-tenth of one percent and still not require unreasonable hydrated electron concentrations.

(a) Results using Eq. (9) with a maximum dose rate of 1.55×10^{14} rads/sec. Ratio of $k_7[e_{aq}^-]_{\max}/k_2[H^+]$ is 3.22×10^{-3} .

(b) Result using Eq. (9) with a maximum dose rate of 1.55×10^{16} rads/sec. Ratio of $k_7[e_{aq}^-]_{\max}/k_2[H^+]$ is 2.64×10^{-1} .

(c) Results using Eq. (9) with a maximum dose rate of 1.55×10^{18} rads/sec. Ratio of $k_7[e_{aq}^-]_{\max}/k_2[H^+]$ is 5.41.

(d) Results using Eq. (15) with a maximum dose rate of 1.55×10^{14} rads/sec. Ratio $k_7[e_{aq}^-]_{\max}/k_2[H^+]$ is 3.22×10^{-3} .

(e) Results using Eq. (15) with a maximum dose rate of 1.55×10^{16} rads/sec. Ratio $k_7[e_{aq}^-]_{\max}/k_2[H^+]$ is 2.64×10^{-1} .

(f) Results using Eq. (15) with a maximum dose rate of 1.55×10^{18} rads/sec. Ratio $k_7[e_{aq}^-]_{\max}/k_2[H^+]$ is 5.41.

Fig. 5. Deviation in (e_{aq}^-) caused by including reaction 7 in the system differential equation. A pH of 2.0 was assumed for all calculations. Radiation sources were similar to those of Fig. 2a, with the exception of dose rate which was varied as specified.

To achieve transmissions approaching one percent or less, a system requires a hydrated electron concentration of 9×10^{-4} moles/liter for 6943 Å light. At this higher concentration Eq. (9) may no longer represent a valid relationship between dose rate and hydrated electron concentration. The discrepancy is a result of reaction 7 shown in Table 1. At e_{aq}^- concentrations where $k_2[H^+]$ is of the same order as $k_7[e_{aq}^-]$, reaction 7 should be considered when relating dose rate and aqueous electron concentration. If reaction 7 is considered, the system equation becomes

$$\frac{d[e_{aq}^-]}{dt} = k \frac{dR(t)}{dt} - k_2[H^+][e_{aq}^-] - k_7[e_{aq}^-]^2. \quad (15)$$

Consideration of reaction 7 gives a first order nonlinear differential equation. The relationship between $[e_{aq}^-]$ and $dR(t)/dt$ can be best evaluated using a computer. Appendix B is a copy of the computer code that evaluates $[e_{aq}^-](t)$ using Eqs. (9) and (15) and a given function for $dR(t)/dt$. Figure 5 shows the results of including reaction 7 in the system differential equation. Note that as $k_2[H^+]$ and $k_7[e_{aq}^-]_{max}$ become comparable in magnitude, there is a noticeable difference in the two calculated values of e_{aq}^- concentrations.

This deviation is caused by reaction 7 which, in effect, causes the mean lifetime of the hydrated electrons in solution to be time dependent. Actually, an accurate description of the behavior of acidic H_2O in a radiation environment where the aqueous electron concentration approaches 10^{-3} moles/liter would require consideration of all seven reactions in Table 1. Equation (9) will only give an approximate solution to the temporal dependence of the solvated electron concentration if the initial H^+ concentration is kept well above the maximum expected e_{aq}^- concentration. For a system where the hydrated electron concentration is expected to reach 10^{-3} moles/liter, the H^+ concentration should be kept above 1×10^{-2} moles/liter. With this concentration, reactions 3 and 7 should have limited second order effect. To obtain an e_{aq}^- concentration of 10^{-3} moles/liter in a 10^{-2} molar H^+ solution, a dose rate of approximately 1.75×10^{14} rads/sec is required. In other words a pulse width of 5 nsec would require one million rads—a considerable amount of ionizing radiation. At this level of radiation, most optical glasses exhibit irreversible optical damage unless chemically stabilized.¹⁴ This optical damage represents another factor that must be considered in fabricating optical dosimetry systems to measure high flux levels.

Experimental Arrangement

Measuring optical transmission of aqueous samples irradiated with short radiation pulses requires a fast response optical system. Figures 6a and 6b show

two systems that measure the optical transmission of samples irradiated with bremsstrahlung from a 705 Febetron. In system 6a (which is similar in concept to

Fig. 6. (a) Experimental arrangement used to measure transmission of irradiated samples at 5400 Å.
 (b) Experimental arrangement used to measure transmission of irradiated samples at 4600 Å.

that used by Hunt and Thomas in 1967),¹⁵ the light source was a Xenon flash lamp excited with a 12 kV capacitor bank. The light emitted by the flash lamp was focused on the sample with a parabolic reflector and a large condensing lens system. A 100 Å FWHM, 5400 Å color filter was placed in front of the sample to achieve quasi-monochromatic light. At first, there was concern over the effect of the radiation pulse on the color filter. However, investigation showed that there was no significant effect at 5400 Å. The light that passed through the sample was collected with another large lens and focused onto the photocathode of an FW114A after passing through another 5400 Å color filter. The output of the photodiode was displayed on a 519 oscilloscope. As shown in Fig. 6a, this system did not contain a separate scope and photodiode to monitor the light incident on the test sample. Instead, a reference light sweep was taken before irradiation. This scope trace was then normalized to the same amplitude as the trace showing the induced absorption and used as an approximation of the incident light. Investigation into the repeatability of this method showed that little experimental error was introduced.

The system shown in Fig. 6b has several advantages over the 6a system. The 6b system replaces the flash lamp with a dye laser. Thus, a color filter is no longer necessary in the high radiation environment. Also, enough well-collimated monochromatic light is obtained to measure optical transmission in a specific region of the sample cell. This fact allows simpler and more accurate reduction of data. Because of the nonrepeatability of the dye

laser output, it was necessary to install a scope and photodiode system that would measure light incident on the test cell. In addition, care was taken to cross-time all three scopes.

The sensitivity of the detection system is dependent on the maximum linear voltage obtainable from the light detection system. For the systems shown in Fig. 6 FW114 photodiodes were used. These detectors and the light sources previously described generated a maximum linear voltage of about 60 V at each detector. To reliably obtain a display of the light transmitted through the test cell, the scope base line was offset an amount equivalent to -40 V and the scope sensitivity was adjusted to 18.4 V/cm. By applying the derivative of Eq. (12) to the above parameters and to the trace width (0.01 cm) of the scope, we can estimate a minimum detectable transmission change

$$dT_{\lambda} = \left(\epsilon_{\lambda} L e^{-\epsilon_{\lambda} [e_{aq}^{-}] L} \right) d[e_{aq}^{-}]$$

or

$$\Delta[e_{aq}^{-}] = \frac{\Delta T_{\lambda}}{\epsilon_{\lambda} L} e^{+\epsilon_{\lambda} [e_{aq}^{-}] L}.$$

Since

$$\begin{aligned} \Delta T &= (0.01 \text{ cm})(18.4 \text{ V/cm})/60 \text{ V} \\ &\approx 3.06 \times 10^{-3}, \end{aligned}$$

$$L = 2 \text{ cm},$$

and

$$\epsilon_{\lambda} = 8.4 \times 10^3 \frac{1}{\text{cm} \frac{\text{moles}}{\text{liter}}} \text{ (Fig. 3);}$$

the minimum detectable change in

$[e_{aq}^-]$ is 1.825×10^{-7} moles/liter. For a system where the e_{aq}^- concentration is on the order of 10^{-5} moles/liter the system's relative error ought to be about 0.5%. To get an accurate picture of the change in optical transmission, the photodiode should have a fall time that is on the order of 1 nsec or better. We confirmed this fall time with a Q-switched, cavity-dumped, frequency-doubled Nd^{+3} laser. The output pulse of this laser was about 3 nsec FWHM with a fall time of about 1 nsec.

A calibrated lithium drifted detector measured the radiation transmitted through the sample cell. The rise time of this detector is reported to be 2 to 3 nsec.¹⁶ By using data obtained with this detector, and by knowing radiation parameters for the 705 Febetron, we estimated dose rate in the cell sample (Appendix A). The relative accuracy of the radiation is limited by the trace width of the scope monitor. For a trace width of 0.01 cm and a 1-cm deflection the relative uncertainty should not be more than 1%.

Results

Three different weakly acidic H_2SO_4 solutions were irradiated with bremsstrahlung from a 705 Febetron. The particular acidic concentrations investigated with the flash lamp system were 0.001, 0.002, and 0.004M. Because of system sensitivity, samples with concentrations above 0.004M were not investigated.

Figures 7, 8, and 9 show the typical results obtained with the three irradiated samples. To predict the average dose rate the radiation detector was calibrated with TLD's and an adjustment was made for sample transmission losses. (Appendix A). Figures 7a, 8a, and 9a are the scope traces that were used to predict the average dose rate in each of the three sample cells. Figures 7b, 8b, and 9b are curves that represent the mean dose rate in each cell sample. Using Figs. 7b, 8b, and 9b and Eq. (9), we calculated a theoretical prediction of the mean or average hydrated electron concentration. The results of these predictions are shown in Figs. 7c, 8c, and 9c.

Figures 7d, 8d, and 9d show the photocurrent in the diode that monitored sample cell transmission. Using these figures and Eq. 13, we calculated the mean hydrated electron concentration. The results of that calculation are shown in Figs. 7e, 8e, and 9e.

A comparison of Figs. 7c, 8c and 9c with Figs. 7e, 8e, and 9e reveals that in all cases the maximum predicted hydrated electron concentration was lower than the maximum empirical value. This fact could be readily explained as an underestimate of the mean dose rate in the irradiated sample cell. If an underestimate of the dose rate were made, then the ratio between peak empirical and peak theoretical $[e_{aq}^-]$ should be a constant. The empirical to theoretical ratios for 0.001, 0.002, and 0.004M solutions are 4.56, 4.86, and 5.09 respectively. The average deviation from a mean value of 4.82 is about 4.3%. This deviation is a little higher than one would expect given the relative experimental errors quoted

(a) Scope trace used to estimate dose rate in 0.001M H_2SO_4 sample. A 20 nsec/cm sweep with 90 V/cm vertical sensitivity.

(d) Scope trace used to measure optical transmission changes in irradiated sample. A 20 nsec/cm sweep and 18.4 V/cm vertical sensitivity with 40 V offset.

(b) Estimated average dose rate vs time for irradiated H_2SO_4 sample.

(c) Theoretical average concentration of hydrated electrons vs time in irradiated sample.

(e) Estimated hydrated electron concentration in 0.001M H_2SO_4 sample.

Fig. 7. Experimental results and theoretical prediction of hydrated electron concentration in irradiated 0.001M H_2SO_4 .

(a) Scope trace used to estimate dose rate in 0.002M H_2SO_4 sample. A 20 nsec/cm sweep with 90 V/cm vertical sensitivity.

(d) Scope trace used to measure optical transmission change in irradiated H_2SO_4 sample. A 20 nsec/cm sweep and 18.4 V/cm vertical sensitivity with 40 V offset.

(b) Estimated average dose rate vs time for irradiated H_2SO_4 sample.

(c) Theoretical average concentration of hydrated electrons vs time in irradiated sample.

(e) Estimated hydrated electron concentration in 0.002M H_2SO_4 sample.

Fig. 8. Experimental results and theoretical prediction of hydrated electron concentration in irradiated 0.002M H_2SO_4 .

(a) Scope trace used to estimate dose rate in 0.004M H_2SO_4 sample. A 20 nsec/cm sweep with 90 V/cm vertical sensitivity.

(d) Scope trace used to measure optical transmission change in irradiated H_2SO_4 sample. A 20 nsec/cm sweep and 18.4 V/cm vertical sensitivity with 40 V offset.

(b) Estimated average dose rate vs time for irradiated H_2SO_4 sample.

(c) Theoretical average concentration of hydrated electrons vs time in irradiated sample.

(e) Estimated hydrated electron concentration in 0.004M H_2SO_4 sample.

Fig. 9. Experimental results and theoretical prediction of hydrated electron concentration in irradiated 0.004M H_2SO_4 .

previously. However, it is certainly within acceptable limits considering the accuracy ($\pm 5\%$) with which the data were reduced.

A comparison of the shape of the theoretical and empirical data indicates an empirical mean lifetime for the solvated electron that is almost a factor of two greater than the theoretically predicted value. This fact is readily seen by comparing Figs. 1a with 7e; 7c with 8c; and 8c with 9e. The measurement of a longer lifetime for the solvated electron indicates that there were less H^+ ions present in solution than we assumed in the theoretical calculations. An investigation

into the disassociation of H_2SO_4 in water showed that H^+ concentrations used in the theoretical calculations were somewhat overestimated (complete dissociation was assumed). However, measurements of pH's in samples similar to those used in this experiment indicate the overestimate should not have exceeded 30%. A change in the H^+ concentration of 30% could not account for the discrepancy measured here. This suggests that the samples were either contaminated or a deviation from theory has resulted. However, before any concrete statement can be made the experiment should be repeated and sample purity scrutinized.

Conclusions

The system shown in Fig. 6a has demonstrated its limited usefulness in monitoring the concentration of hydrated electrons in pulse irradiated aqueous solutions. Problems associated with the system can be greatly reduced by using the dye laser system shown in Fig. 6b. The ability to probe the irradiated sample with a well collimated light beam should increase the accuracy of dose rate

prediction. In addition, the higher intensity of monochromatic light suggests a potential for increasing the system sensitivity. An increase in system sensitivity should allow investigations of samples with shorter hydrated electron mean life times. This increased potential should be very useful in calibrating samples for use in pulse radiation detector systems.

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Appendix A

Estimation of Dose Rate in Irradiated Sample Cells

To estimate the mean dose or dose rate in the test cell, the radiation monitor system must be calibrated. Several TLD's were used to accomplish this task. We calibrated the system by first positioning the radiation detector a fixed distance from the Febetron output faceplate (about 2 m). The TLD's were then placed adjacent to the radiation detector. After flashing the x-ray machine, we digitized and integrated the Febetron scope trace recorded on the 519. The integrated value, in volt-seconds, was then divided by the roentgens measured by the TLD's. This division yielded the sensitivity of the detector system in volt-seconds/roentgen. This process was repeated several times to achieve a good mean value for system sensitivity. Since we knew that relative dose rate in air was a function of distance from the Febetron target (Fig. A-1), and we already knew system sensitivity, we

Fig. A-1. Relative dose rate, in air, vs axial distance from Febetron target.

Fig. A-2. Y-axis scale factor required to make Febetron scope trace reflect the dose rate in the irradiated sample at any distance from target.

could scale the y-axis of the scope trace to show the dose rate at any distance from the Febetron faceplate. Using the curve shown in Fig. A-1 and compensating for x-ray transmission losses in the irradiated sample, we can generate a plot that shows the y-axis scale factor. This factor scales the Febetron scope trace to reflect the dose rate in the irradiated sample at any distance from the Febetron faceplate. Obviously, the curve shown in Fig. 8 does not reflect the correct scale factor if the Febetron 519 is to represent the dose rate for all cell incremental

volumes that are a specified distance from the target. The curve shown in Fig. A-2 only represents the approximate scale factor associated with incremental volumes along the radiation symmetry axis. Because of the complex system geometry, a true estimate of the dose rate associated with every incremental volume would require evaluation by computer code. A code specifically designed for this purpose

is in the process of development but it is not available at this time. Therefore, the mean dose rate for the entire sample will be assumed equal to the average dose rate associated with incremental cells along the axis symmetry. It is evident that this dose rate will be higher than the actual dose rate. The degree to which the theoretical and experimental are compared must be made with this fact in mind.

Appendix B

Computer Program

```

PROGRAM H20SOL (SPECT, TAPE2=SPECT, MATL, TAPE5=MATL, HGRA
FX, TAPE3=HGR
13FK, TGRAF, TAPE14=TGRAF, ASCII, TAPE100=ASCII, TAPE59)
CALL CHANGE(7H+H20SOL)
CALL DEVICE(6HCREATE, 6HHGRAFX, 120000, 1R)
CALL ASSIGN(3, 6HHGRAFX)
CALL DEVICE(6HCREATE, 5HTGRAF, 10000)
DIMENSION XCRT(10), YCRT(10), IC(15), DEIN(1000), T(1000),
EIN(1000),
ITR(1000), X(1000), Y(1000), BLT(1000), BL(1000), TEL(1000),
TRA(1000),
REINT(1000), TF(1000), RF(1000), RFI(1000), DEINI(1000), EPK
3(20),
3TEPK3(20), EPK2(20), TEPK2(20)
CALL CLOCK (PART, PARM)
CODE=10HH20SOL
OPER=10HG-V-COUTTS
WRITE(59,900)OPER, CODE, PART, PARM
900 FORMAT(4(2X, A10))
I=0
901 CONTINUE
I=I+1
WRITE( 3,900)OPER, CODE, PART, PARM
IF(1-50)901,902,900
902 CONTINUE
CALL DD80ID (19HBOX N04 COUTTS WAT ,1)
CALL KEEP80(1)
C READING IN PULSE SHAPE
SPEC=3HFEB
CALL ASSIGN(2, SPEC)
I=0
TENS=1.0E+07
TENS=1.0E+06
TENS=1.0E+04
131 I=I+1
READ(2,13)L, T(1), DEIN(1)
13 FORMAT(1E10, 3, 2X, E10, 3)
DEIN(1)=DEIN(1)+TENS
T(1)=1.0E-09+T(1)
T(I)=.15+T(I)
IF(L)132,132,133
132 CONTINUE
WRITE(3,15)T(1), DEIN(1)
15 FORMAT(2X, E10, 3, 2X, E10, 3)
GO TO 131
133 CONTINUE
IPS=I-1
CALL LPRAM (IC)
XCRT(1)=10H
XCRT(8)=10H
XCRT(3)=10H
XCRT(4)=10H*TIME - SEC
XCRT(5)=10H
XCRT(6)=10H
XCRT(7)=10H
YCRT(1)=10H
YCRT(2)=10H
YCRT(3)=10H*INPUT - RA
YCRT(4)=10H*DS/SEC
YCRT(5)=10H
YCRT(6)=10H
YCRT(7)=10H
CALL PIX (T, DEIN, IPS, IC, XCRT, YCRT)
IC(14)=72

```

```

REWIND 8
CALL DEVICE (SMCLOSE, SPEC)
SPEC=4HEQPR
CALL ASSIGN (2, SPEC)
32 CONTINUE
READ(2,1) DT1, CK1, CON, TMAX
1 FORMAT(4(2X, E10.3))
XCRT(18)=CON
IF(DT1) 30, 30, 31
31 CONTINUE
CK2=CON*2.38E+10
WRITE(3,10) CON
10 FORMAT(// ,17HH+ CONCENTRATION , E10.3,12H MOLES/LI
TER )
TMAX=T(IPS)
DT1=TMAX/990.
CK3=.4.5E+10
TH=.2.0
EXCO=8.3E+03
EAG=0.0
TMAXR=TMAX/100.
TI=0.0
TIN=0.0
I=0
EING=0.0
TING=0.0
DTING=DT1/5
5 TI=TI+DT1
I=I+1
TR(I)=TI
CALL TERP(T, DEIN, IPS, TI, EA, 0)
X(I)=EA
DEAG=((CK1*EA)-(CK2*EAG)-(CK3*EAG*EA))*DT1
EAG=EAG+DEAG
EIN(I)=EAG
AL=-EXCO*TH*EIN(I)
TRA(I)=EXP(AL)
20 CONTINUE
TING=TING+DTING
CALL TERP(T, DEIN, IPS, TING, EAING, 0)
SUMI=EXP(CK2*TING)
SUMI=SUMI*EAING*DTING
EING=EING+SUMI
IF(TING-TI) 20, 21, 21
21 CONTINUE
EAGT=EXP(-CK2*TI)
EINT(I)=EAGT*CK1*EING
IF(TI-TMAX) 5, 6, 6
6 CONTINUE
YCRT(1)=.0H AVERAGE
YCRT(2)=10HHYDRATED E
YCRT(3)=10HLECTRON CO
YCRT(4)=10HNCENTRATIO
YCRT(5)=10HN - MOLES/
YCRT(6)=10HLITER
YCRT(7)=10H
CALL PIX (TR, EINT, I, IC, XCRT, YCRT)
CALL PIX (TR, EIN, I, IC, XCRT, YCRT)
YCRT(1)=10H
YCRT(2)=10H
YCRT(3)=10HTRANSMISSI
YCRT(4)=10HON THROUGH
YCRT(5)=10H 2CM SAMPL

```



```

YCRT(6)=10HE
YCRT(7)=10H
CALL PIX(TR,TRA,I,IC,XCRT,YCRT)
GO TO 3E
30 CONTINUE
IC(14)=0
YCRT(1)=10H
YCRT(2)=10H
YCRT(3)=10HINPUT - RA
YCRT(4)=10HDS/SEC
YCRT(5)=10H
YCRT(6)=10H
YCRT(7)=10H
CALL PIX (TR,X,I,IC,XCRT,YCRT)
CALL FRAME (I)
51 CONTINUE
CALL PLOTE
CALL EXIT
END
SUBROUTINE TERP (X,Y,N,XA,YA,IT)
DIMENSION X(N),Y(N)
REVISED 9 OCT 67
IL = 0
DO 5 I=0,N
  IF(XA-X(I)) 7,6,5
6 CONTINUE
YA = 0.0
GO TO 50
7 YA = Y(I)
GO TO 50
7.1 I = 1
  IF(IT-1) 10,14,10
10 XV = XA
  XVA = X(I-1)
  XVB = X(I)
12 IF(IT-2) 19,16,14
14 XV = LOGF(XA)
  XVA = LOGF(X(I-1))
  XVB = LOGF(X(I))
15 IF(IT-2) 16,16,19
16 IF(Y(I-1)) 60,60,17
17 IF(Y(I)) 60,60,18
60 YA = 0
GO TO 50
18 YVA = LOGF(Y(I-1))
  YVB = LOGF(Y(I))
  IL = 1
GO TO 20
19 YVA = Y(I-1)
  YVB = Y(I)
DO INTERPOLATION
20 YA = YVA + (YVB-YVA) * (XV-XVA) / (XVB - XVA)
  IF(IL) 50,50,22
22 YA = EXPF(YA)
50 RETURN
END
SUBROUTINE PIX (X,Y,N,IC,XCRT,YCRT)
DIMENSION X(N),Y(N),IC(20),XCRT(20),YCRT(20)
IF(IC(13)-1) 4,1,2
1 CALL FRAME (1)
2 IYL = 1
GO TO 3E

```

```

C      1 FRAMING
      4 IF(1C(1)) 5,5,20
      5 CALL FRAME(1)
C      2 LIMITS OF GRAPH
      IF(1C(3)) 6,6,67
      67 CONTINUE
      CALL LOGMM(4,N,XMIN,XMAX,X,1)
      CALL LOGMM(4,N,YMIN,YMAX,Y,1)
      GO TO 3
      6 CALL CARTMM(N,XMIN,XMAX,X,1)
      CALL CARTMM(N,YMIN,YMAX,Y,1)
      3 IF(1C(2)-1) 9,7,8
      7 XMIN = XCRT(16)
      XMAX = XCRT(17)
      GO TO 9
      8 YMIN = YCRT(16)
      YMAX = YCRT(17)
      IF(1C(2)-2) 9,9,7
C      3 TYPE OF PLOT
      9 IF(1C(1)) 10,10,20
      10 IF(1C(3)-1) 12,13,11
      11 IF(1C(3)-3) 14,15,15
      12 CALL MAPG(XMIN,XMAX,YMIN,YMAX,.12,.9999,.12,.8888)
      GO TO 20
      13 CALL MAPGLL(XMIN,XMAX,YMIN,YMAX,.12,.9999,.12,.8888)
      GO TO 20
      14 CALL MAPGSL(XMIN,XMAX,YMIN,YMAX,.12,.9999,.12,.8888)
      GO TO 20
      15 CALL MAPGLS(XMIN,XMAX,YMIN,YMAX,.12,.9999,.12,.8888)
C      4 TYPE OF POINT
      20 IF(1C(4)) 22,22,21
      21 IF(1C(4)-4) 24,28,28
      22 DO 23 I=2,N
      CALL LINE(X(I-1),Y(I-1),X(I),Y(I),0,0)
      23 CONTINUE
      GO TO 35
      24 CALL SETPCH(0,0,0,0,1)
      IF(1C(4)-2) 25,26,27
      25 CALL POINTC(1H*,X,Y,N,1,1)
      GO TO 35
      26 CALL POINTC(1H0,X,Y,N,1,1)
      GO TO 35
      27 CALL POINTC(1H*,X,Y,N,1,1)
      GO TO 35
      28 CALL SETCRT(X,Y,0,0)
      CALL TRACEF(X,Y,N,-2,1,1)
C      LABELS
      35 IYL = 0
      IF(1C(1)) 38,38,100
C      X-AXIS LABEL
      38 XLX = 1C(7)
      XLY = 1C(8)
      CALL SETCH(XLX,XLY,1,0,1C(5),0,0)
      ICK = 1C(6)
      WRITE(100,200)XCRT(1),XCRT(2),XCRT(3),XCRT(4),XCRT(5),
XCRT(6),XCRT
      1(7)
      200 FORMAT(7A10)
      CALL SETCHW0
      IF(IYL) 40,40,100
C      Y-AXIS LABEL
      40 YLX = 1C(11)
      YLY = 1C(12)

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```

      CALL SETCH (YLY,YLY,1,0,IC(9),1,0)
      ICY = IC(10)
      WRITE(100,200)YCRT(1),YCRT(2),YCRT(3),YCRT(4),YCRT(5),
YCRT(6),YCRT
      1(7)
      CALL SETCHWO
C      X-AXIS INSERT
      IF(IC(14)) 45,60,45
45      XLI =XABSF(IC(14))
      XCY=0.0
      CALL SETCH (XLI,XCY,1,0,IC(5),0,1)
      IF(IC(14)) 46,60,45
46      IV = YCRT(18)
      WRITE(100,47)IV
47      FORMAT(15)
      CALL SETCHWO
      GO TO 60
48      WRITE(100,49)YCRT(18)
49      FORMAT(E10.3)
      CALL SETCHWO
C      Y-AXIS INSERT
60      IF(IC(15)) 61,100,61
61      YLI =XABSF(IC(15))
      CALL SETCH (YLY,YLI,1,0,IC(9),1,1)
      IF(IC(15)) 64,100,66
64      IV = YCRT(18)
      WRITE(100,47)IV
      CALL SETCHWO
      GO TO 100
66      WRITE(100,49)YCRT(18)
      CALL SETCHWO
100      CONTINUE
      RETURN
      END
      SUBROUTINE LPRAM (IC)
      DIMENSION IC(20)
      IC(1)=0
      IC(2)=0
      IC(3)=0
      IC(4)=4
      IC(5)=1
      IC(6)=7
      IC(7)=9
      IC(8)=1
      IC(9)=1
      IC(10)=7
      IC(11)=1
      IC(12)=9
      IC(13)=0
      IC(14)=0
      IC(15)=0
      RETURN
      END

```

NOTICE

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