Title of Paper: Radiation Chemical Effects of X-rays on Liquids

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INTRODUCTION

This chapter describes some of the chemical changes induced by photoelectrons which are released in liquids when X-rays are absorbed. Both experimental studies and theory are discussed. In part I, the basic processes occurring upon absorption of X-rays are described. Parts II and III deal with hydrocarbon liquids; in part II the ion yields, including effects at *K*-edges, and in part III, the yields of excited states. Part IV discusses chemical effects of X-rays in aqueous solutions. We end with a summary of future needs and directions.

I. BASIC PROCESSES

Photons interact with matter in several different ways, but for X-rays, the two main processes that occur are ejection of photoelectrons and incoherent (Compton) scattering.¹ Both processes release electrons. In the photoelectric effect the X-ray is completely absorbed and a photoelectron is ejected with kinetic energy, (E_e), equal to the X-ray photon energy less the binding energy, E_b :

$$E_e = E_x - E_b \quad (1)$$

Water and hydrocarbon liquids are usually considered, so that the photoelectrons originate from oxygen or carbon. For the X-ray energies considered here, generally well above 1 keV, photoelectrons are knocked out of the *K*-shell, for which E_b is 543 eV for oxygen and 284 eV for carbon.²

The ion left by the loss of an electron is in an excited state and relaxes either by emission of Auger electrons or by emission of fluorescence photons. In the case of carbon, the Auger process dominates, and an Auger electron is released. For molecules, Auger spectra are generally broad; that is, the electrons have a range of energies. For alkanes the spectra are peaked at 249 eV.³

Fluorescence is a minor channel for carbon and oxygen (less than 1%)⁴, but in liquids, the fluorescent photons are often reabsorbed, producing more electrons. Overall, the net result of the photoelectric effect in a liquid hydrocarbon or water will be the release of electrons, the total energy of which equals that of the photon energy. The situation is quite different if the sample contains a higher-Z element with an accessible *K*- or *L*-edge. In that case, the photoelectron has near-zero energy just above the edge, and all of the energy goes into the electrons in the Auger cascade or into fluorescence X-rays.

The photoelectric effect dominates up to 30 keV of absorbed energy. At that energy, for carbon, the cross section for incoherent scattering becomes comparable to that for photoelectric absorption. However, for incoherent scattering only a fraction of the photon's energy is given up to the recoil electron: at 30 keV the fraction is 5%. Although incoherent scattering dominates at higher energies, for the studies described here that utilize X-rays with energies between 1 and 30 keV, the photoelectric process is the most important. The absorption cross sections decrease with increasing energy and the penetration depth increases dramatically as is shown in Table 1.

In liquids, chemical changes come about as a result of the ionizations and excitations formed along the path (*track*) of the photoelectrons as they slow down in the liquid. The ranges of these electrons in liquids are short (see Table 2), on the order of micrometers. The ranges, *R*, in water can be calculated from an empirical relationship given by Paretzke:⁵

$$R = 40E(1 + E_e/2) \quad (R \text{ in nm}) \quad (2)$$

where E_e is in keV. As the electron energy decreases, the range decreases much faster than the energy, and the rate of energy loss (dE/dx) increases. As a consequence, the ionizations and excitations become closer together along the track as the energy of the electrons decreases. The

effect is similar in water where the rate of energy loss may be estimated from Eq. 3 as given by Allen,⁷

$$\frac{dE}{dx} = (10190/E_e) \log_{10}(E/56.6) \quad (3)$$

where E_e is in eV and dE/dx in eV/nm. Recent calculations by Paretzke *et al.*⁸, utilizing cross-section data, lead to energy loss values comparable to those given by Eq. 3 in the higher energy range, but slightly lower values for lower energies. The total number of initial ionizations per 100 eV absorbed energy (the G -value) is not known precisely for liquids. Calculations indicate $G = 3.9$ for water⁸ for energies above 1 keV. A similar value is assumed for hydrocarbons.⁹

The track of ionizations and excitations left by the photoelectrons depends on their energy. From the above data it can be estimated that for a 30-keV electron, ionizations will occur (on average), 24 nm apart. For a 2-keV electron, ionizations will occur 2.9 nm apart. Electrons frequently change directions as they lose energy, so that the actual track is far from a straight line. Of interest here also are the fates of Auger electrons. The rate of energy loss for a 245-eV carbon Auger electron is near the maximum for electrons, approximately 20 eV/nm. Thus, ionizations will occur about 1 to 2 nm apart for such electrons, or the track will be very dense.

The final aspect of the physical process of X-ray absorption in a liquid is charge separation. The secondary electrons released travel considerable distances from their ion partners. Their thermalization range depends on the liquid. In most of the thermalization range, the secondary electrons have subexcitation energies. The ranges can be inferred from free-ion yields, for example. As will be shown in the next section, the probability of escape of an electron from an ion in a hydrocarbon is distance dependent. For *n*-hexane the mean thermalization range is 6.7 nm, for 2,2,4,4-tetramethylpentane it is 17 nm,⁹ whereas, for water the electron range is taken as 2.46

nm.¹⁰ These ranges are comparable to the average separation between ionizations. The phenomena discussed below are a consequence of this overlap of ionizations along the track of the photoelectron.

The absorption processes described above occur very fast, on the order of femtoseconds. In the next stage, the ions and electrons diffuse subject to the Coulombic forces of the other particles and any external applied field. In polar liquids like water, the Coulombic forces can be ignored. Recombination of electrons with ions will produce more excited states in the case of liquid hydrocarbons. This nonhomogeneous recombination in the track lasts up to a few hundred picoseconds. Some fraction of the ions will escape the track; these are termed *free ions*. Section II considers how the yield of free ions varies with photon energy. Section III considers yields of excited states.

II. FREE ION YIELDS IN HYDROCARBONS VS. X-RAY ENERGY

Theoretical yields. The yield of ions escaping the track relative to recombination has been modeled for electrons with energies from 40 eV to 1 MeV. In these computer studies, the initial positions of the positive ions along the track are first defined, then some distribution of electrons around the positive ions is assumed. Next, the charges are allowed to diffuse randomly subject to drift of the charges in the net electric field due to other ions and any external applied field. In one study, the authors¹¹ assumed the track to be straight so that cylindrical geometry could be used; the separation between charges was that derived from range data; it was also assumed that four ion-pairs were formed for every 100 eV of energy ($G = 4/100$ eV). In another study,¹² the positions of the positive ions were simulated by a Monte Carlo procedure, utilizing energy dependent mean free paths obtained from theory. From optical oscillator strengths a

universal expression (Eq. 4) for the mean free path Λ , (in Ångstroms) in an organic material for an electron of energy E_e (in eV) has been derived,¹³

$$\Lambda \rho_e = E_e / (14.1 \ln E_e - 25.5 - 1500 / E_e) \quad (4)$$

where ρ_e is the valence electron density (mol/cm³) of the material. This equation indicates that the mean free path is energy dependent and that the ions in a track are not uniformly spaced, but are produced closer together near the end of the track. For example, for a 2 keV electron in hexane the ions are ≈ 8.5 nm apart at the beginning of the track and ≈ 2 nm apart at the end.

The secondary electrons thermalize at some distance from the positive ion. A distribution of distances is assumed. Typically, Gaussian and exponential distributions are used. Calculations are generally performed for various mean thermalization distances to find the best match to experiment. The simulation begins by calculating the displacement of a particle, dr , during a time interval, dt . The displacement in the electric field, E due to all the other particles and the external field is given by $\mu E dt$, where μ is the mobility of the particle. The displacement due to random diffusion is given by $(6Ddt)^{1/2}$, where D is the diffusion coefficient of the particle. After each step, recombination of opposite charges is assumed to occur if the distance between them is less than some predetermined reaction radius, typically 1.5 nm. The calculation is continued until only one pair of ions per track remain. The escape probability of this pair is calculated from the Onsager formula given by:¹⁴

$$P_{\text{esc}} = \exp(-e^2 / r \epsilon k_B T) \quad (5)$$

In this way the escape probability, or equivalently the free ion yield, G_{fi}^0 , is calculated as a function of electron energy up to 30 keV. Some examples are shown by the lines in Fig. 1. For

the two lower lines, a Gaussian distribution of ion-electron separation distances was assumed.¹¹ Examples for a mean thermalization range, b , equal to 6.8 and 10.6 nm are shown. The upper line was calculated assuming an exponential distribution with the average thermalization range, $r_{av} = 26.5$ nm.¹²

The calculations have been extended to higher energies where the ion yield increases because of the increasing importance of isolated groups (spurs) of ionization along the path of the electron. The probability of escape from these spurs is higher than for dense tracks. The predicted ion yields for high energy (MeV) electrons are significantly higher than for electrons of 2 to 4 keV, which is near the minimum shown in Fig. 1. For a thermalization range of 6.8 nm (lower curve) the difference is a factor of two; however, for a range of 26.5 nm the difference in yield is a factor of six.

At energies below 2 keV the curves all rise again, and at 100 eV the ion yields are predicted to be very comparable to those observed at very high energy. This is not coincidental but due to the fact that 100 eV is near the average energy deposited in a single spur for a high energy electron and the escape yields are thus expected to be similar. The decrease in yield as the energy increases above 100 eV is very rapid. This follows from the high rate of energy loss from electrons of this energy (≈ 20 eV/nm).⁸ The tracks are thus short but very dense favoring recombination. The escape probability in this energy range is thus largely that for the last pair remaining as given by the Onsager probability.

Experimental Yields. Free ion yields have been measured for several hydrocarbons as a function of X-ray energy using synchrotron radiation. The yields were derived from measurements of the steady state current from a liquid-filled ionization cell during exposure to an X-ray beam. The first study⁹ of this type was done at CHESS for X-ray energies from 6 to 29

keV. The cell used was long since the X-rays are more penetrating (see Table 1), with electrodes parallel to the beam. Studies at X-ray energies from 1.6 to 4 keV,^{15,16} were done at ALADDIN. X-rays of this energy are absorbed in a thin layer near the window; thus, a short cell with electrodes perpendicular to the beam was used. The current from the cell, divided by the electronic charge, gives the number of ion pairs formed per second.

The X-ray flux is obtained simultaneously from an ionization chamber, filled with Ar or N₂ gas, placed ahead of the liquid-filled cell. The ion chamber measures a current which is proportional to the flux in photons/sec absorbed by the ion chamber. The flux of photons transmitted by the chamber is calculated from the absorbed flux knowing the cross sections and density for the gas used. The transmitted X-ray beam goes through various windows before reaching the liquid. The resulting losses in flux are calculated from the thickness of the windows and the cross sections and densities of the constituents in the windows. The fraction of the beam actually absorbed in the liquid is then calculated from the absorption cross sections for carbon and hydrogen and the density of the hydrocarbon. This fraction is close to 1 for energies near 2 keV, but for energies near 30 keV most of the beam passes through the cell (path length 3 cm). This procedure gives the absorbed dose rate in photons/sec. Multiplying by the photon energy yields the absorbed dose rate in eV/sec. The free ion yield is then given by:

$$G_{fi} = \frac{\text{ion pairs/sec}}{\text{eV/sec}} \times 100 \quad (6)$$

The ion yields were measured with an electric field applied. Typically, several different voltages were used. A linear dependence of yield on field was observed experimentally^{9,16} and is predicted by computer models.¹² The extrapolated yield at zero field, G_{fi}^0 , can be compared to theory, which is usually done with no external field applied. This method gives satisfactory results

providing a sufficiently low dose rate and a sufficiently high electric field are used in order to avoid losses due to volume recombination of ions.

The measured yields of free ions, G_{fi} , from hydrocarbon liquids decrease with decreasing X-ray energy from 30 keV down to about 2 keV. The results for three liquids are shown in Fig. 1. This energy effect was correlated, in an early study,⁹ with the rate of energy loss of the photoelectrons or the density of ionization along the track of the electron. The results shown are in good agreement with the computer simulations discussed above, indicating that thermalization ranges are 6.8 nm for hexane, 10.6 nm for 2,2,4-trimethylpentane, and 26.5 nm for 2,2,4,4-tetramethylpentane. Also shown on the figure are the results obtained for high energy photons (≈ 1 MeV); there are large changes in yield between 1 MeV and 2 keV. The change is largest for the highly branched hydrocarbon, 2,2,4,4-tetramethylpentane. For this liquid the probability of escape is close to 20% at 1 MeV and decreases to 2% near 2 keV. The latter yield corresponds to a quantum yield of only two ion-pairs escaping per photon absorbed.

Recently, the ion yield measurements were extended down to 1.6 keV¹⁶ in order to search for the minimum in yield predicted by the computer simulations. Minima were observed, as predicted, between 2 and 2.5 keV for the liquids mentioned above and also for *n*-pentane and cyclohexane. Since X-rays of higher as well as lower energies are available at synchrotron sources, extension of these measurements over a wider range are possible and would be of interest.

Ion Yields at K-edges. Early conductivity studies showed that sharp minima are observed at the *K*-edge of a constituent atom of the liquid and that the apparent ionization yield is lower above the edge than below. In a study at the Fe *K*-edge of ferrocene dissolved in 2,2,4-trimethylpentane, a drop in the conductivity was observed at the *K*-edge for optically thick

samples.¹⁷ The structure in the conductivity spectra, although attributed to inefficiency of charge collection, was shown to provide a useful EXAFS spectrum, from which valid structural information could be obtained.

Similar studies done for tetramethyltin solutions at the Sn *K*-edge showed that the conductivity spectra were concentration dependent.¹⁸ At low concentrations the conductivity spectra resemble the absorption spectrum, while at higher concentrations the conductivity spectra are inverted; that is, the current decreases at the Sn *K*-edge as was found for Fe. Two factors contributing to the lower yield above the edge were recognized. Above the edge, X-ray fluorescence is highly probable (86%) in the case of tin.¹⁹ It was also suggested that the electrons from the Auger cascade may be less effective than the photoelectron that is emitted below the edge, in producing free ions.²⁰ The phenomenon of lower yields above edges is not limited to *K*-edges. A similar drop in conductivity has been observed at the Sn *L*_{III}-edge for a solution of tetramethyltin in 2,2,4,4-tetramethylpentane.²¹

Absolute yields of free ions have been measured across the chlorine *K*-edge in CCl₄¹⁵ and across the Si *K*-edge in tetramethylsilane.¹⁶ The yield above the edge is 10% less than below the edge in CCl₄, and 21% less in Si(CH₃)₄ (see Fig. 2). The drop in the case of CCl₄ can be attributed to X-ray fluorescence, which is 9.7% for chlorine.¹⁹ The drop in the case of Si(CH₃)₄ is only partially accounted for by X-ray fluorescence (5% for Si).¹⁹

Another characteristic feature of these *K*-edge spectra is the appearance of a sharp minimum in ion yield at or just below the edge. This is shown for Si(CH₃)₄ in Fig. 2 and has also been seen in CCl₄.¹⁵ The minimum in the ion yield curve (Fig. 2 - lower) occurs at the position of

the $1s \rightarrow \sigma^*$ transition at which there is a peak in the photoionization curve (Fig. 2 - upper)²². The liquid ion-yield curve further mirrors the gas phase ionization curve in showing a dip at the position of the shape resonance (labeled 3 in Fig. 2). The nature of the transition occurring at an edge is described as non-radiative resonance Raman scattering, whereby X-ray absorption results in the emission of two electrons, leaving a doubly charged ion: $A + h\nu \rightarrow A^{++} + e + e_A$ (see Chapter by W. Drube). Above the edge, the Auger cascade occurs as a result of a core hole and excess energy is carried away by the photoelectron. The fact that the energies of Auger electrons are expected to be similar at, as well as above the resonance should result in yields of free ions at the resonance similar to the yields found above the edge. Thus, it is difficult to explain these minima. Several reasons have been suggested; one is a difference in fluorescence yield at and above the edge, but there is no confirming evidence that this is the case. Another reason may be the simultaneous emission of several electrons in the Auger cascade and the role of multiple charges on the Si ion. The multiply-charged ion, combined with the fact that the Auger electrons from Si are of low energy and therefore short range, may make escape much less efficient.

Another possibility are changes in the initial yield of ionization formed in the tracks by the photoelectron. As noted in section I above, values of the initial yields must be assumed for liquids. They can be measured directly in the gas phase and have been measured across the carbon *K*-edge for methane²³ and propane.²⁴ For both gases, structure in the ion yield spectra is observed: a minimum in the ion yield at 291 eV and a yield that is lower just above the edge than below. These "structures" are attributed to changes in the energy distribution of the ejected electrons. How yields change across the edges for other elements is not known. The correct explanation for these minima and the structure in the conductivity spectra is not yet clear.

III. EXCITED STATE YIELDS IN HYDROCARBONS VS. X-RAY ENERGY

Theoretical Predictions. Excited states are formed in hydrocarbons as a result of neutralization of cations by electrons (or anions) in the tracks of the photoelectrons. Neutralization of charged species is the complement of escape, which leads to free ions as discussed in section II. Because the Coulomb interaction is long range, the majority of charged species neutralize in nonpolar liquids to form excited states, which can be either singlet or triplet. Where ionizations are widely separated, the electrons will return mainly to their parent cations. Only singlet excited states will be formed by this geminate recombination, providing spin relaxation during charge separation is unimportant. This is likely to be the case since neutralization in hydrocarbons occurs rapidly. In *trans*-decalin, for example, most of the neutralization occurs between 4 and 100 ps.²⁵

In tracks of photoelectrons or in clusters of ionizations (called *spurs*), the probability of cross-neutralization increases, leading to the formation of triplet as well as singlet states. Bartczak, *et al.*²⁶ have shown explicitly that such cross neutralization leads to triplet states 75% of the time. Thus the probability for singlet formation becomes:

$$P_{\text{singlet}} = P_{\text{geminate}} + \frac{1}{4}(1 - P_{\text{geminate}}) \quad (7)$$

If the neutralization is truly random in a spur, P_{geminate} is $1/N$, where N is the number of ion-pairs present. Thus, from Eq. 7, for 2 ion-pairs, $P_{\text{singlet}} = 0.625$; for 3 ion-pairs, $P_{\text{singlet}} = 0.5$; and for N large, P_{singlet} is nearly 0.25.

The probability of singlet formation has been calculated for electrons of initial energy from 25 eV to 1 MeV.²⁵ The computation was similar to that employed in simulating the free ion yield

(see section II). The initial positions of the positive ions were taken to be on a straight line with the average separation given by range data. For example, for 50 ion-pairs, produced by a 1250 eV electron, a separation of 1 nm was used, corresponding to a range of 50 nm. It was assumed that the average energy required to form an ion pair is 25 eV. Again, the negative charges were assumed to be spherically distributed around each positive charge. The charges were then allowed to diffuse and drift; opposite charges neutralized one another if they came within a reaction radius (1.5 nm). For this calculation it is noted whether the electron returns to its parent cation (geminate) or otherwise (cross). When only one pair remains the probability of combination is given by $1 - P_{\text{esc}}$ (see Eq. 5).

The results of this simulation are shown by the curves in Fig. 3 for Gaussian distributions of cation-electron distances, with mean thermalization ranges (b) of 4.4 and 10.6 nm. At 25 eV (one ion-pair) the singlet probability is one, and at high energy the probability is near 0.6, which is close to that expected for a two-ion-pair spur. Near 1 keV both curves go through a minimum, where the singlet probability is close to the value of $\frac{1}{4}$ expected for random combination. The singlet probability is less for b equal to 10.6 nm than for 4.4 nm, especially in the 10-100 keV region, reflecting the increased cross neutralization occurring for the larger b -value.

Experimental Results. Synchrotron radiation has been used to measure yields of excited states in a few hydrocarbon liquids. One type of measurement utilizes the effect of a magnetic field on the UV fluorescence of a scintillator, *p*-terphenyl, added to the solvent. The magnetic field effect is based on the premise that the spins of ions relax over time in the absence of a field and a random mixture of 25% singlet and 75% triplet ion-pairs is reached within 100 ns.²⁷ In the presence of a magnetic field, the spins remain aligned so that the ratio of the fluorescence intensity

at 100 ns with a field on ($F_{B,t}$) to that in the absence of a field ($F_{0,t}$) provides a measure of the initial singlet fraction, x_0 , according to the relationship:²⁸

$$x_0 = 1.25[F_{B,t} / F_{0,t}] - 1 \quad (8)$$

The fluorescence ratio was found to decrease as the photon energy increased from 15 to 150 eV.²⁹ Eq. 8 was used²⁸ to obtain the initial singlet fractions which are shown in Fig. 3 for the VUV (15-150) eV and X-ray (4-15 keV) regions. For single ion pairs the fluorescence ratio was found to be 1.6,³⁰ corresponding to $x_0 = 1$ and for an initial random mixture there is no effect of the field or the fluorescence ratio is 1 and $x_0 = 0.25$. The actual results, which lie between these two extremes, are in quite good agreement with theory.

For the magnetic measurements the liquid hydrocarbon used was squalane (2,6,10,15,19,23-hexamethyltetracosane), which has a sufficiently low vapor pressure to be placed in the vacuum chamber. The VUV light was reflected down onto the sample, where it was absorbed in a surface layer ≈ 30 nm thick.²⁷ Oxygen quenches excited states, but oxygen is effectively removed from this surface layer by the vacuum. Magnetic fields of 0.11 T were used. For the magnetic measurements using 4 to 15 keV X-rays, the beam was extracted through a Be window and the squalane samples were degassed prior to use by bubbling with N_2 .

Another type of measurement³¹ uses the UV fluorescence from the excited state of the hydrocarbon directly, without addition of a scintillator. The yield of excited singlets is then deduced from the fluorescence yield. This method requires absolute measurements of the absorbed dose rate and the fluorescence yield, $G(\text{photons})$. The former is derived from the

current recorded in an ionization chamber ahead of the sample cell. The yield of singlet states, $G(^1S^*)$, is then calculated from:

$$G(^1S^*) = G(\text{photons}) \times (\tau_{\text{UV}} / \tau_{\text{x-ray}}) (\Phi_F \times F_{\text{eff}}) \quad (9)$$

where Φ_F is the quantum yield of fluorescence and F_{eff} is a correction factor for filter losses and collection efficiency. A correction is made for fluorescence lifetime (τ) which depends on X-ray energy and is less than is observed for UV excitation.^{31,32} The yields are relative to the yields of singlets for liquid benzene exposed to X-rays. Singlet yields obtained this way for *cis*- and *trans*-decalin are shown in Fig. 3; measured G -values have been divided by four, the assumed total yield of excited states, to give the singlet fraction. The yields observed near 5 keV are close to the predicted curve for $b = 4.4$ nm and the yields increase with increasing energy. The increase is somewhat more than predicted by theory for this energy range.

Edge Effects. The changes in the yields of excited states across an L - or K -edge is an interesting subject for which only qualitative information is available at present. Although the total energy carried away by the electrons is expected to be comparable just below and above an edge, differences in yield of excited states may occur either because of changes in the spectrum of electron energies or because of changes in the density of ionization. Below a K -edge, for example, absorption of an X-ray releases an energetic photoelectron from the L -shell, whereas just above the edge the photoelectron energy will be small and the energy will go into the electrons released in the Auger cascade. Some of these electrons may be of quite low energy and their tracks may overlap. Consequently these electrons, which are released simultaneously, produce dense regions of excitation near the ion of origin.

In one experimental study, excited singlet states were detected at the Sn *K*-edge in a solution of tetramethyltin in toluene, to which a scintillator was added.²⁰ The UV fluorescence dropped 10% at the *K*-edge, matching the drop in conductivity. The drop in conductivity indicated a lower free ion yield above the edge (see section II). The similarity of the fluorescence and conductivity XANES spectra across the edge supported the mechanism suggested: that excited states arise by in-track combination of ions (reactions 10-11) and that only a small but constant fraction of the ions

escape the track to contribute to the conductivity.

A similar effect was reported to occur at the Sn *L*₃-edge at 3.93 keV, where the UV fluorescence yield drops 7% at the edge.²⁰ The fluorescence and conductivity XANES spectra are again quite similar, supporting the mechanism of excited state formation shown above.

Although the fluorescence and ion yield spectra are similar, the reason for the decreases in yield at edges remains unexplained. We can speculate that excited states may be quenched, by free radicals perhaps, in the denser regions of excitation, which reduces the fluorescence. Further study of these effects is in order.

While this chapter is mainly about effects in liquids, there are some related measurements of singlet yields in solids across *K*-edges. Quantum yields of singlet exciton formation in crystalline anthracene were measured versus the X-ray energy from 100 to 600 eV.³³ The yields increased monotonically with energy; there was no significant decrease at the carbon edge. In contrast, the UV fluorescence from sodium salicylate was measured over a similar energy range.

The fluorescence efficiency generally increased with photon energy, but decreased 70% at the carbon *K*-edge and 15% at the oxygen *K*-edge.³⁴ The fluorescence efficiency, in this case defined as the ratio of the number of UV photons emitted per second to the number of incident X-ray photons per second, is a measure of the yield of excited singlet states. The explanation for the conflicting picture of excited state yields presented by these two studies is unclear at present.

IV. DECOMPOSITION OF WATER AND AQUEOUS SOLUTIONS

The theoretical understanding of the effects of X-rays on the decomposition of water is well advanced but there are few experimental measurements for comparison. As indicated in the Introduction, for water, X-rays are primarily absorbed in the *K*-shell of oxygen for energies above 532 eV. The photoelectrons produced have energies given by $E_x - 532$ eV, and Auger electrons are emitted with an average energy of 518 eV. Absorption of X-rays with energy below 532 eV produce photoelectrons with energies $E_x - 24$ eV.

The energetic photoelectrons ionize other water molecules along their tracks. In a very short time the secondary electrons become solvated, e_{aq}^- , and the ions form OH radicals and H_3O^+ . These species along with some H-atoms are formed initially; that is, within a few picoseconds. We should note that charge recombination, so important at short times in hydrocarbons, can be ignored due to shielding of the Coulombic force by the high dielectric constant of water. Nonetheless, there are track effects in water between the initial radical species, which are formed nonhomogeneously in spurs and along the tracks. In these regions, where the local concentrations of these species is high, radical-radical reactions like:

will be favored. At the same time, the radicals diffuse outward from the center of the track or spur due to the concentration gradient and in a matter of a few nanoseconds radical concentrations become homogeneous. The yields of e_{aq}^- , OH, H, H_2 and H_2O_2 present at this time are the yields of interest to the experimentalist, since they are the species that remain at this time that can react with solutes, and it is the yields of these species that are calculated by theory.

Radical and Molecular Yields - Theory. Various models have been developed to calculate the yields of radicals (e_{aq}^- , H, and OH) and molecular products (H_2 and H_2O_2) that survive the spur or track recombination process as a function of electron or photon energies. As an overall measure of the yield of water decomposition, the yield of the Fricke dosimeter is calculated because this is measurable experimentally. The Fricke dosimeter contains 1 mM Fe^{+2} ion in aerated, acid solution. Radiation of this solution causes oxidation of the ferrous to ferric ion, the yield of which is:

$$G(Fe^{+3}) = 3G(H) + 3G(e_{aq}^-) + 2G(H_2O_2) + G(OH)$$

This comes about because each H-atom and each electron react with O_2 to form HO_2 , and each HO_2 oxidizes a Fe^{+2} ion but, in addition, forms another hydrogen peroxide:

Each H_2O_2 oxidizes two ferrous ions:

and each OH oxidizes one ferrous ion:

In an early paper³⁵ the decomposition of water was modeled by considering that at low energies (from 0.1 to 20 keV) tracks are formed and at higher energies (above 20 keV) mainly

spurs. The number of radicals which avoid track recombination of radicals was calculated by a prescribed diffusion model, which requires knowing the diffusion constants, D , of the H and OH radicals. The predicted dependence of the Fe^{+3} yield on electron energy is shown in Fig. 4. There is a minimum in the yield around 1 keV, where the radical concentrations are the highest along the track. At lower, as well as higher energies, the radical concentrations in the track are less and the Fe^{+3} yield is higher.

In a later calculation, Yamaguchi³⁶ used a modified prescribed diffusion model. Whereas the earlier model had assumed constant interspur distances for a given electron energy, this model took into account the fact that ionizations generally get closer together as the electron loses energy. Values for the rate constants of reactions like (11) and (12) were used, as well as diffusion constants, initial radii, and yields for the species present (see Table 3). Yields for species remaining after a time of 0.3 μs were calculated. Although not shown in Fig. 4, this calculation predicts a minimum in the Fe^{+3} yield of 9.4 per 100 eV around 400 eV.

A more recent paper by Yamaguchi³⁷ not only takes the track structure into account, but calculates specifically for irradiation of water by monoenergetic photons. Thus the effects of photoelectrons, whose energies are given by Eq. 1, and Compton recoil electrons, more important at high energies, are considered. The calculated yield of ferrous oxidation shows a double minimum around 500 eV, as shown by the dotted line in Fig. 4. This structure may be related to the K -edge of oxygen which occurs at 532 eV. Also shown on the figure is the calculated curve for the yield of e_{aq}^- ; the curve for OH is similar. Both show the double minimum. The yields of H_2O_2 and H_2 are a maximum in this region near 500 eV.

Recently Pimblott and LaVerne³⁸ used a Monte Carlo method, employing known photon cross sections to model the X-ray tracks. The subsequent reactions of radical species in the tracks are followed by an independent reaction times model. The results of this model, shown by the solid line in Fig. 4, predict a minimum in yield near 1 keV.

Radical and Molecular Yields - Experimental. The individual yields of radicals and molecular species are available for high energy (MeV) photons but have not been measured with synchrotron radiation. There have, however, been measurements of ferrous oxidation for X-ray energies down to 1.5 keV.

The results of two studies done at the 2.5 GeV synchrotron of the Photon Factory are shown in Fig. 4. The first study was done at X-ray energies near 10 keV.³⁹ A Lucite cell was used and the sample irradiated through a wall of the cell. The dose rate was approximately 14 kR min⁻¹. The second study covered the energy range from 1.8 to 10 keV.⁴⁰ A cell with a Mylar window was used and the sample was stirred during irradiation. An InSb double monochromator provided energies below 5 keV; higher orders were negligible. Dose rates were approximately 105 R min⁻¹. The energy dependence of the Ferric yield shown by the second study is similar to that predicted by Yamaguchi. However, the actual yields are lower and in better agreement with the calculations of Magee and Chatterjee. The point at 1.5 keV, was measured using Al K X-rays, and the yield is 57% of its high-energy value.⁴¹

Effects at K-edges. To the extent that electrons in the Auger cascade have the same effect as photoelectrons, there may be no change in yields at edges. However, some unexplained changes in yields at K-edges have been seen in hydrocarbons and solids, and there are similar effects in aqueous solutions. Bond scission in molecules which are specifically associated with the atom where the hole is created can be important

In the cited study by Watanabi, *et al.* of ferrous oxidation,⁴⁰ measurements were made across the *K*-shell absorption edges of iron and sulfur. The ferric yield remained constant below, at, and above each edge. However, the X-rays are absorbed primarily by water; the concentration of iron (1 mM) in the Fricke dosimeter is too small to have a significant effect. Absorption by sulfur in the solution is also small below its *K*-edge, at 2.47 keV, and only 8% above the *K*-edge.

In contrast to the above, studies of more concentrated solutions have shown remarkable effects occurring at *K*-edges. A solution of 5-bromo-2'-deoxyuridine-5'-monophosphate (Br-dUMP) (0.52 M) was irradiated at four X-ray energies, two below and two above the bromine *K*-edge.⁴² The yields of bromine release, as measured by the formation of 2'-deoxyuridine-5'-monophosphate (dUMP), are shown in Table 4. The bromine edge is at 13.47 keV and the measurements at 13.43 and 13.49 keV show a 120% enhancement of the *G*-value at the edge. This was attributed by the authors to the selective absorption of photons by bromine creating a hole in the *K*-shell. The absorption of X-rays by bromine in the sample increases from 26% below the edge to 70% above. Bromine release is known to be initiated by electrons giving a radical on the uracil moiety and Br⁻.⁴³ This radical is quite reactive and will abstract an H-atom, most likely from the sugar moiety, forming dUMP. The yield of electrons is predicted to be 2.4 (per 100 eV) for 13.5 keV photons (see Fig. 4) and the yields of dUMP are larger. If the sugar radical can attack another Br-dUMP a short chain could be created, explaining the yields. However, the mechanism of enhancement at the edge is unclear. Further, it is difficult to explain why the yield at 14.12 keV is lower than at the edge, since a hole in the *K*-shell is created at both energies. These results suggest that some unique processes occur at energies near the *K*-edge.

A similar result was found for irradiation of a solution of adenosine 5'-triphosphate (0.28 M) near the phosphorous *K*-edge at 2.153 keV.^{44,45} The *G*-value of adenine was 30% higher

above the edge than below it. However, the yields of adenosine 5'-monophosphate increased from 0.14 (per 100 eV) just below the edge to 0.48 (per 100 eV) at the edge. A similar increase was found for adenosine-5'-diphosphate, showing unique bond rupture processes are induced by absorption of photons that ionize phosphorus at the *K*-shell.

The above examples illustrate effects that have been observed at *K*-edges for nucleotides. Enhanced yields of double and single strand breaks have also been reported for solutions of DNA at the phosphorous edge.⁴⁵ In contrast, no enhancement is observed in solid biological samples. A review of all the literature in this area is beyond the scope of this chapter but the reader is referred to recent reviews.⁴⁵⁻⁴⁷ For specific effects occurring at *K*-shells, the reader is also referred to the chapter in this book on *Photofragmentation of Molecules* by D. Hanson.

CONCLUDING REMARKS

As this review shows, chemical effects result from ionizations and excitations produced by photoelectrons and Compton scattering. The changes in yields of ions, excited states, and radicals is shown by theory and experiment to be a result of differences in density of ionizations along the tracks of the photoelectrons. The experimental measurements cover only a limited energy range; there are gaps at low and high X-ray energy where experimental data are needed.

A satisfying explanation of results near *K*-edges is yet to be found. Perhaps there are changes in the initial yields of ions across *K*-edges. Gas-phase measurements for atoms other than carbon, where structure in the *W*-value has been observed, are not yet available. Modeling of the high density of ionizations expected as a result of multiple electron emission in Auger decay may provide some insight. A decrease in the initial yield of Auger electrons occurring at the *K*-edge resonance energy would explain the "mirror-like" similarity of ion yield and absorption spectra at

the *K*-edge of Si and other elements. Whether the non-radiative resonant Raman effect, occurring at absorption edges, affects the subsequent chemical events needs to be determined.

Synchrotron radiation, providing monochromatic X-rays over a wide energy range, has to date been underutilized by chemists. In the future more chemical studies are anticipated. The brighter sources of the newer machines will facilitate these studies.

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References

1. E. Storm and H.I. Israel, *Nuclear Data Tables A7*, 565 (1970).
2. G.P. Williams, *Electron Binding Energy of the Elements*, 1992.
3. R.R. Rye, D.R. Jennison, J.E. Houston, *J. Chem. Phys.* **73**, 4867 (1980).
4. M.O. Krauss, *J. Phys. Chem. Ref. Data* **8**, 307(1979).
5. H.G. Paretzke, in *Kinetics of Nonhomogeneous Processes*, ed. G.R. Freeman (Wiley & Sons, New York, 1987) p. 123.
6. A. Hummel, A.O. Allen, F.H. Watson, Jr., *J. Chem. Phys.* **44**, 3431 (1966).
7. A.O. Allen, *Radiation Chemistry of Water and Aqueous Solutions* (D. Van Nostrand Co., Princeton, 1961).
8. H.G. Paretzke, J.E. Turner, R.N. Hamm, H.A. Wright, R.H. Ritchie, *J. Chem. Phys.* **84**, 3182 (1986).
9. R.A. Holroyd, T.K. Sham, *J. Phys. Chem.* **88**, 2909 (1985).
10. H. Yamaguchi, *Radiat. Phys. Chem.* **30**, 279 (1987).
11. W.M. Bartczak, A. Hummel, *J. Phys. Chem.* **97**, 1253 (1993); *Radiat. Phys. Chem.* **49**, 675 (1997).
12. L.D.A. Siebbeles, W.M. Bartczak, M. Terrissol, A. Hummel, *J. Phys. Chem.* **101**, 1619 (1997).
13. J.C. Ashley, *J. Electron Spectroscopy and Related Phenomena* **28**, 177 (1982).
14. L. Onsager, *Phys. Rev.* **54**, 554 (1938).
15. R.A. Holroyd, T.K. Sham, B.-X. Yang, X.-H. Feng, *J. Phys. Chem.*, **96**, 7438 (1992).
16. R.A. Holroyd, T.K. Sham, *Radiat. Phys. Chem.* **51**, 37 (1998).
17. T. K. Sham, R. A Holroyd, *J. Chem. Phys.* **80**, 1026 (1984).
18. T.K. Sham, R. A. Holroyd, *Phys. Rev.* **B39**, 8257 (1989).

19. M.O. Krause, *J. Phys. Chem. Ref. Data*, **8**, 307 (1979).
20. T.K. Sham, R.A. Holroyd, R.C. Muñoz, *Nucl. Inst. Methods* **A249**, 530 (1986).
21. T.K. Sham, P. Kristof, R.A. Holroyd, *Rev. Sci. Instrum.* **63**, 1198 (1992).
22. S. Bodeur, P. Millié, I. Nenner, *Phys. Rev.* **A41**, 252 (1990).
23. N. Saito, I.H. Suzuki, *Chem. Phys.* **108**, 322 (1986).
24. I.H. Suzuki, N. Saito, *Bull. Chem. Soc. Jpn.* **58**, 3210 (1985).
25. W. M. Bartczak, A. Hummel, *Chem. Phys. Lett.*, **208**, 232 (1993).
26. W. M. Bartczak, M. Tachiya, A. Hummel, *Radiat. Phys. Chem.* **36**, 195 (1990).
27. B. Brocklehurst, A. Hopkirk, I.H. Munro, *Radiat. Phys. Chem.* **37**, 487 (1991).
28. B. Brocklehurst, *Chem. Phys. Lett.*, **211**, 31 (1993).
29. G. J. Baker, B. Brocklehurst, I. R. Holton, *Chem. Phys. Lett.*, **134**, 83 (1987).
30. G. J. Baker, B. Brocklehurst, M. Hayes, A. Hopkirk, D.M.P. Holland, I.H. Munro, D.A. Shaw, *Chem. Phys. Lett.*, **161**, 327 (1989).
31. R. A. Holroyd, J.M. Preses, J.C. Hanson, *J. Phys. Chem.*, **101**, 6931 (1997).
32. R. A. Holroyd, J. M. Preses, J. C. Hanson, *Radiat. Res.* **135**, 312 (1993).
33. A. Kimura, K. Nakagawa, K. Tanaka, M. Kotani, R. Katoh, *Nucl. Inst. and Methods in Phys. Res.* **B91**, 67 (1994).
34. G.C. Angel, J.A.R. Samson, G. Williams, *Applied Optics*, **25**, 3312 (1986).
35. J.L. Magee, A. Chatterjee, *J. Phys. Chem.*, **82**, 2219 (1978).
36. H. Yamaguchi, *Radiat. Phys. Chem.*, **30**, 279 (1987).
37. H. Yamaguchi, *Radiat. Phys. Chem.*, **34**, 801 (1989).
38. S.M. Pimblott, J. LaVerne, *J. Phys. Chem.*, **101**, 5828 (1997).

Y. Yamamoto, S. Sawada, T. Asai
Sawada, *Int. J. Radiat. Biol.*, **61**, 21

67m pr

. Y.

40. W. Watanabe, N. Usami, K. Kobayashi, *Int. J. Radiat. Biol.*, **68**, 113 (1995).
41. J. P. Freyer, M. E. Schillaci, M.R. Raju, *Int. J. Radiat. Biol.*, **56**, 885 (1989).
42. K. Takakura, *Radiat. Environ. Biophysics*, **28**, 177 (1989).
43. J.D. Zimbrick, J.F. Ward, L.S. Myers, Jr., *Int. J. Radiat. Biol.*, **16**, 505 (1969).
44. R. Watanabe, M. Ishikawa, K. Kobayashi, K. Takakura, *Biophysical aspects of Auger Processes, AAPM Symposium Series No. 8*, **24** (1992), R.W. Howell, V.R. Narra, K.S.R. Sastry, D.V. Rao, eds.
45. K. Takakura, K. Kobayashi, in *Polymeric Materials Encyclopedia* J.C. Salamone, ed. CRC Press Boca Raton **3**, 1926 (1996).
46. K. Kobayashi, in *Proceedings of the International School of Physics CXXVIII*, E. Burattini and A. Balerna eds. IOS Press, Amsterdam (1996).
47. K. Takakura, H. Maezawa, K. Kobayashi, K. Hieda, in *Synchrotron Radiation in the Biosciences*, B. Chance, *et al.* eds. Oxford Univ. Press 756 (1994).

Table 1 - Absorption data of X-rays			
E _x (keV)	1/e depth ^a (cm)		
	2	10	30
water	0.003	0.21	6.6
hexane	0.006	0.92	27

a) cross section data from Ref. 1

Table 2 - Electron Range Data			
$E_x(\text{keV})$	2	10	30
Range - in water ^a	0.16	2.4	19.2
(μm)			
- in hexane ^b	0.23	4.0	29
$\frac{dE}{dx}$ - in water ^c	7.9	2.3	0.92
- in hexane ^d	8.7	2.5	1.0

a)Ref. 5; b) Ref. 6; c) Eq. 2; d) Average rates of energy loss based on ranges

Table 3			
Diffusion Constants, Initial Radii, and Initial Yields ^a			
Species	$D (\times 10^5 \text{ cm}^2 \text{ s}^{-1})$	$R^0 (\text{nm})$	$G^0 (100 \text{ eV}^{-1})$
e_{aq}^-	4.5	2.46	5.03
H	7	1.14	0.65
OH	2.8	1.14	6.0
H ₂ O ₂	2.2	1.14	0
H ₂	8	1.14	0.16

a) ref. 35

Table 4
G-Values for Products from Exposure of Bromo-deoxyuridine-monophosphate to X-rays^a

X-ray Energy (keV)	<i>G</i> (dUMP) (per 100 eV)
12.89	3.8
13.43	4.7
13.49	10.5
14.12	3.2

a) See Fig. 4 of Ref. 44.

Figure Captions

Figure 1. Yield of free ions vs. energy. Points are G_{fi} for X-rays. ■: 2,2,4,4-tetramethylpentane; O: 2,2,4-trimethylpentane; ●: n-hexane;^{9,15,16} Lines are calculated escape probabilities for electrons. Dotted line: for exponential distribution of thermalization distances, $r = 26.5$ nm; dashed line: for Gaussian distribution of distances $b = 10.6$ nm and 6.8 nm.^{11,12}

Figure 2. XANES Spectra at the Si K-edge. Upper is absorption spectrum of $\text{Si}(\text{CH}_3)_4$ vapor.²² Lower is free ion yield spectrum of liquid $\text{Si}(\text{CH}_3)_4$.¹⁶

Figure 3. Fraction of excited states that are singlet vs. energy. Points are for synchrotron X-rays. O; from magnetic field effects²⁸; ■; from fluorescence,³¹. Lines are calculated for electrons with a Gaussian distribution of cation-electron distances; dashed line: $b = 4.4$ nm; solid line: $b = 10$ nm.²⁵

Figure 4. Yields for decomposition of water. Upper three lines are calculated yield of Fe^{+3} :; from Ref. 37. — — — — —; from Ref. 35. —————; from Ref. 38. ●; synchrotron measurements from Refs. 39 and 40. O; from Freyer.⁴¹. — — — — —; calculated yield of e_{aq}^- from Ref. 37. — — — — —; H_2O_2 from Ref. 37.

FIGURE 1

FIGURE 2

G-values for Water vs. X-Ray Energy