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STUDY OF MECHANISMS CONTROLLING THE ULTRAVIOLET PHOTOCHEMISTRY OF ASSOCIATED AND POLYMERIC SYSTEMS

by Michael Anbar and G. A. St. John

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16. Abstract

Liquid water and alcohols have been shown to undergo photoionization when subjected to vacuum ultraviolet in the range 210-180 nm. Hydrated electrons have been identified as the products of photolysis in liquid water by a number of characteristic reactions using competition kinetics as a quantitative criterion. The reactions $e^-aq + SF_6$, $e^-aq + H_3O^+$ and $e^-aq + Cd$ have been used as the principal analytical tools of investigation. The photoproduction of electrons was shown to be the result of a single photon process. A parallel investigation of the photodissociation of water to H + OH suggests that photoionization and photodissociation of liquid water involve the same excited state; the cross section for photodissociation is about ten times larger than for photoionization.

Photoionization of liquid water occurs at energies significantly (>6.5 eV) below the ionization potential mainly by solvation of the positive ion, H_2O^+ though the formation of excimers should also be considered.

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ABSTRACT

Liquid water and alcohols have been shown to undergo photoionization when subjected to vacuum ultraviolet in the range of 180 to 260 nm. Hydrated electrons have been identified as products of photolysis in liquid water by a number of characteristic reactions using competition kinetics as a quantitative criterion. The reactions

$$e^-_{aq} + SF_6 \rightarrow 6F^- + \tfrac{1}{2}SO_3^{2-} + \tfrac{1}{2}SO_4^{2-}$$

were used as the principal analytical tool, and the reactions

$$e^-_{aq} + H_3O^+,\ e^-_{aq} + Cd^{2+},\ \text{and}\ e^-_{aq} + Yb^{3+}$$

were used as diagnostic competing reactions. The photoproduction of electrons was shown to be the result of a single photon process with a cutoff wavelength of 205 nm. Photoionization of liquid water thus occurs at energies significantly (> 6.5 eV) below the ionization potential in the gas phase. A parallel investigation of the photodissociation of water to H + OH suggests that photoionization and photodissociation of liquid water involve the same excited state; the cross section for photodissociation of water is about seven times larger than that for photoionization. The quantum yield of e^-_{aq} in water is 0.077.

The photolysis of D_2O and of methanol show analogous behavior. The photoionization like the photodissociation of D_2O was found shifted to shorter wavelengths in accord with the absorption spectrum of D_2O. The photoionization of methanol was shown to involve the same excited state, leading to the cleavage of the C-O bond and resulting in the formation of methane. The quantum yield of photoionization of methanol in the range 240 to 260 nm may be as high as 0.5. n-Butanol was also found to undergo photoionization, though apparently with a lower quantum yield.

The possible mechanisms of photoionization of protonic associated liquids are discussed. The photoionization of liquid water at relatively long wavelengths has geochemical and cosmochemical implications, as well as important inputs to photochemistry and radiation chemistry. These topics are presented in the last part of this report.

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I INTRODUCTION

This is a final report of Project NAS-2-5937, started on April 20, 1970, and completed on April 9, 1971. It was a continuation of Project NAS-2-5119, started on October 1, 1968, and continued until September 30, 1969. The prime objectives of this project were to establish the occurrence of photoionization of liquid water at the threshold of the vacuum uv ($\lambda > 180$ nm) and to elucidate its mechanism. These objectives have been accomplished in full. During Project NAS-2-5119, preliminary results were obtained that have been substantiated and extended during the 1970-1971 project. The total level of effort of both projects has been only 13 man-months, and the extensive amount of work accomplished is due in part to the assistance of the technical staff of the Materials Research Branch, NASA-Ames Research Center, who provided the facilities used in this project.

Part of the results of this project were presented at the 16th National Meeting of the American Chemical Society on March 28, 1971, within the framework of a symposium on water structure at the water-polymer interface, and will be published in the proceedings.

II LITERATURE REVIEW

A. The Absorption Spectrum of Water Vapor

The 1953 experiments of Watanabe, Inn, and Zelikoff[1] are the most complete study to date. The data extend from 106 nm (the limit imposed by the LiF cutoff) to 186 nm (imposed by an apparatus limitation to absorption coefficients > 1 cm^{-1}). The earlier data of Wilkinson and Johnston[2] in the range 145 to 185 nm are in general agreement with the data of Watanabe *et al*. The more recent measurements of Thompson, Harteck, and Reeves[3] extended Watanabe's data from 186 to 198 nm (to absorption coefficients of 0.001 cm^{-1}). The extinction coefficients reported recently by Stevenson[4] for the range 170 to 191 nm are almost a factor of two lower than the data of Watanabe *et al*. in the same wavelength region. This discrepancy has not been explained.

Stevenson[5] has also measured the absorption spectrum of heavy water vapor in the range 170 to 185 nm. In the region of overlap, his results are lower by a factor of two than the measurements of Laufer and McNesby,[6] whose measurements cover the range 125 to 180 nm. A systematic error in Stevenson's measurements may be suspected. The absorption spectrum of D_2O parallels that of H_2O with a shift of $\sim$ 5 nm to shorter wavelengths.

B. The Absorption Spectrum of Liquid Water

The most extensive recent study in the region < 200 nm was done by Painter, Birkhoff, and Arakawa.[7] Earlier data by Weeks, Meaburn, and Gordon[8] are in the range of 170 to 190 nm with a tentative extrapolation to 160 nm and show a steadily increasing absorption coefficient with no fine structure. Other measurements substantially in agreement with the above are those of Barrett and Mansell[9] in the range 185 to 190 nm, Price *et al*.[10] in the range 180 to 192 nm, Barrett and Baxendale[11] at 185 nm, Kaye and Poulson[12] at 175 nm, Stevenson[4] in the range 175 to 195 nm, Halmann and Platzner[13] at 185 nm, and Onaka and Takahashi[14] in the range down to 147 nm.

Heavy water has been studied both by Stevenson[5] in the range 172.5 to 182.5 nm and by Barrett and Mansell[9] in the range 185 to 190 nm. Again no fine structure was observed, and the absorption curve parallels that of $H_2O_{(\ell)}$ with a shift of approximately 5 nm to shorter wavelengths.

C. The Absorption Spectrum of Ice

The recent measurements of Stevenson[5] in the range 175 to 180 nm give an upper limit for the absorption coefficient at 175 nm, which is almost two orders of magnitude lower than the earlier measurements of Dressler and Schnepp.[15] These latter workers found that the absorption coefficient rose steadily by almost four orders of magnitude from 175 to 150 nm and then remained constant down to 140 nm. It appears that a large part of the attenuation found in the earlier work could result from light scattering and was not due to absorption. The absorption spectrum of D_2O ice has not been measured to date to the best of our knowledge.

D. The Photochemistry of Water Vapor

For water and photons up to 10 eV, the following primary processes are possible:[16]

$$H_2O \xrightarrow{\lambda \leq 246.8\ \text{nm}} H_2 + O(^3P) \qquad (1)$$

$$\xrightarrow{\lambda \leq 242.0\ \text{nm}} H(^2S) + OH(X^2\Pi) \qquad (2)$$

$$\xrightarrow{\lambda \leq 176.3\ \text{nm}} H_2 + O(^1D) \qquad (3)$$

$$\xrightarrow{\lambda \leq 135.6\ \text{nm}} H(^2S) + OH(A^2\Sigma^+) \qquad (4)$$

$$\xrightarrow{\lambda \leq 135.0\ \text{nm}} H_2 + O(^1S) \qquad (5)$$

$$\xrightarrow{\lambda \leq 122.9\ \text{nm}} 2H(^2S) + O(^3P) \qquad (6)$$

Most of the experimental studies have been made in the first continuum extending from 145 to 190 nm. Some studies, however, have been made in the second continuum extending from 125 to 143 nm and in the banded region below 125 nm (extending to at least 105 nm). The primary processes that have been found and their importance are summarized in Table I.

Table I

PHOTOLYSIS OF WATER VAPOR[a]

105 - 125 nm (Banded Region)	125 - 143 nm (2nd Continuum)	145 - 190 nm (1st Continuum)
123.8 nm $H_2O \rightarrow H+OH$ or $OH(A^2\Sigma^+)$ } 75% (22) $2H+O$ $\rightarrow H_2+O$ or $O(^1D)$ } 25% (22) or $O(^1S)$ } >50% (23)	$\lambda < 135$ nm H_2O $H+OH(A^2\Sigma^+)$ ($\varphi \sim 0.05$ at 121.6 nm) (24,25)	$H_2O \rightarrow H+OH$ $\varphi \sim 1$ (17,18,19)[b] 184.9 nm $H_2O \rightarrow H_2+O$ $\varphi < 0.05$ (19,20)
		147 nm $D_2O \rightarrow D+OD$ 94% (21) D_2+O or $O(^1D)$ } 6%

[a]Unless otherwise shown, products are in their ground electronic state.

[b]Numbers in parentheses are reference numbers.

E. The Photochemistry of Liquid Water

The photolysis of liquid water has been investigated over a wide range in the vacuum uv as summarized in Table II. In this project we limited our investigation to the region $\lambda > 175$ nm.

The first absorption continuum of liquid water in the far ultraviolet peaks at about 155 nm and tapers off down to about 200 nm.[4,7,8] The absorption of photons in this range results in a substantial photodissociation of liquid water to H + OH ($\varphi \sim 0.5$).[11,26] Using flash photolysis, Boyle et al. have shown that photoionization also takes place in the same spectral range.[27] In their experiments, they were able to demonstrate the transient absorption spectrum of hydrated electrons, e^-_{aq}, formed as a direct result of photoabsorption.

In fact, Boyle et al. were not the first to observe the photoionization of liquid water. Hydrated electrons were observed by Matheson et al.[28] in the flash photolysis of methanol-containing solutions (0.2 M). The very small yields obtained and the presence of methanol prevented at the time a positive identification of water as the source of e^-_{aq}. In view of our results described in this report, it is very likely that the e^-_{aq} observed did originate from the photolysis of water.

In two steady-state studies on the photolysis of water there was an indication for the formation of e^-_{aq}.[26,29] Sokolov and Stein[26] set an upper limit of $\varphi(e^-_{aq}) < 0.05$, but they were limited by the absorption of N_2O--their e^-_{aq} scavenger--which produces N_2 on photolysis, and by the relatively inadequate analytical procedures of determining small amounts of N_2 in the presence of much larger quantities of hydrogen. Getoff and Schenk estimated $0.02 < \varphi(e^-_{aq}) < 0.04$ at 184.5 nm from a complex system of scavengers including CO_2 as e^-_{aq} scavenger.[29] Because of a gross error in assessment of the relative absorption coefficients of H_2O and CO_2 (in their assessment they used ϵH_2O for water vapor, which is about 3 orders of magnitude higher than that of liquid water), their measured quantum yields are expected to be low.

Table II

PHOTOLYSIS OF LIQUID WATER

123.6 nm	147.0 nm	184.9 nm
$\Phi(H,OH) = 1.03 \pm 0.02$ (29)[a]	$\Phi(H,OH) = 0.7 \pm 0.1$ (33) $= 0.72 \pm 0.02$ (29)	$\Phi(H,OH) = 0.6$ (30) 0.3 (31) 0.45 (26) 0.33 (32)
$0.06 < \Phi(e^-_{aq}, H_2O^*) < 0.12$ (29)	$0.037 < \Phi(e^-_{aq}, H_2O^*) < 0.075$ (29)	$\Phi(e^-_{aq}) \leq 0.045$ (26) $0.02 < \Phi(e^-_{aq}, H_2O^*) < 0.04$ (32)

[a]Numbers in parentheses are reference numbers.

III RATIONALE OF THE PROJECT

Although the quantum yield of e^-_{aq} in the photolysis of water above 180 nm remained an open question, ranging from 0.004[27] to 0.045,[26] there were strong indications that water undergoes photoionization, although with a very small yield, some 6 eV below its ionization potential in the gas phase. Such a rather unexpected result required independent verification that the electrons observed are not due to the photoionization of a trace impurity. Even if found true, this observation poses a number of interesting questions as to the mechanism of the photoionization of water. Is this a single photon process, or is it caused by photoionization of an electronically excited species? Does this photoionization result from the same excited state that leads to photodissociation? Is the observed photoionization a manifestation of a far more extensive photoionization that results in H atom formation by a fast vicinal recombination of $H_2O^+ + e^-_{aq}$? Is this photoionization at such a low energy a unique phenomenon of water, or is it the property of other associated liquids as well?

Using a more sensitive as well as more specific analytical technique than previously employed, we were able to establish the photoionization of water above 180 nm beyond any reasonable doubt, to determine its quantum yield, and to get far better insight into the mechanism of photoionization of water. This process seems to be the manifestation of a more general phenomenon shared by other associated liquids.

IV FACILITIES, MATERIALS, AND EXPERIMENTAL PROCEDURES

Light Source. The light source used was a 10-kW, vortex stabilized, high-pressure, argon plasma arc, "Plasmatron," with magnesium fluoride window (Gianini Scientific Corp., Santa Ana, Calif.)

Monochromators. For F^- production, we used a McPherson vacuum monochromator of the 1/2-m Seya-Namiyoka configuration with the grating blazed at 150 nm, using 2-mm slits.

H_2 production was carried out with a Diffraction Products, Inc., monochromator, 1/2-m, with 6.6-nm bandpass and grating blazed for 300 nm, flushed with flowing N_2.

Cutoff Filters. Cutoff filters consisted of solutions of NaCl, KBr, and KI. Analytical grade reagents were dissolved in triply distilled conductivity water and interposed between lamp and sample in a 1-cm Beckman quartz sample cell.

Neutral Intensity Filters. Perforated black anodized aluminum screens supplied with the Cary Spectrophotometer were used to decrease light intensity by known amounts (50, 30, and 8%).

Irradiation Cell. The photolysis was carried out in a 10-cm path-length quartz cell with sapphire windows (manufactured by Unified Science, Pasadena, Calif.) attached to a pyrex sample vessel for degassing by 3 freeze-thaw cycles and saturation with SF_6.

Reagents.

1. Water - Conductivity water, Chematics Research, Reseda, Calif.
2. D_2O - Biorad Labs., Richmond, Calif. Double redistilled in all-glass apparatus under N_2.
3. Methanol - J. T. Baker Spectrophotometric Grade.
4. SF_6 - Matheson.
5. $HClO_4$, NaOH, reagent grade - Mallinckrodt; $CdClO_4$ $YbClO_4$ - Electronic Space Products, Inc., Los Angeles, Calif.

The radiolysis experiments were carried out with a Co^{60} gamma source with a dose rate of 0.8 krad/min determined by the Fricke dosimeter.

A. Rationale of Analytical Procedure

As a specific e^-_{aq} scavenger, we chose SF_6. Because of its high electron affinity,[34] this compound has been used as an electron scavenger in gas phase studies[35] as well as in organic systems.[36] In aqueous solutions, SF_6 reacts with e^-_{aq} at a diffusion controlled rate ($k = 1.65 \times 10^{10}$ $\underline{M}^{-1}$ sec^{-1})[37] to give six equivalents of fluoride ions for every e^-_{aq} scavenged.[37] The following sequence of reactions was suggested to explain the formation of the six fluoride ions.[37]

$$SF_6 + e^-_{aq} \rightarrow SF_6^- \rightarrow SF_5\cdot + F^-$$
$$SF_5\cdot + 2H_2O \rightarrow SF_4 + F^- + OH + H_3O^+$$
$$SF_4 + 9H_2O \rightarrow SO_3^{2-} + 6H_3O^+ + 4F^-$$
$$SO_3^{2-} + 2OH \text{ (or } H_2O_2) \rightarrow SO_4^{2-} + H_2O$$

or

$$SO_3^{2-} + 2SF_5\cdot + 2H_2O \rightarrow SO_4^{2-} + 2SF_4 + 2F^- + H_3O^+$$

Hence each e^-_{aq} gives $6F^-$ and, by monitoring F^-, advantage can be taken of this chemical amplification.

The rate of reaction of SF_6 with H atoms is relatively slow. Assuming that no H atom scavenger was present in the system,[37] SF_6 + H did not compete at all with the H + H and H + OH reactions. Thus SF_6 + H must proceed at a rate slower than 10^2 $\underline{M}^{-1}$ sec^{-1}, if it proceeds at all. SF_6 is transparent to light down to $\lambda > 142$ nm.[38,39] In spite of its low solubility in water, it seems to be ideally suited for competition kinetics of photolytic electrons in aqueous solutions.

B. Measurement of the Photolytic Yield of F^- in SF_6 Saturated Aqueous Solutions

A 25-ml sample of triply distilled water was degassed in the Pyrex bulb by repeated freeze-pumping to $\sim 10^{-5}$ torr. SF_6 was then introduced into the cell at atmospheric pressure and the water saturated by vigorous shaking. Under these conditions the concentration of SF_6 in the water reached 2.2×10^{-4} $\underline{M}$.[40] The water was then tilted into the sapphire cell and irradiated with the light from the Plasmatron arc lamp with a MgF_2 window at a distance of 15 cm (arc to sapphire window). The space

between the lamp and cell was continuously swept with N_2 as a coolant and to maintain transparency in the vacuum ultraviolet.

Fluoride ion concentrations in the photolyzed solutions of SF_6 were determined by an Orion fluoride specific ion electrode (94-09) in conjunction with an Orion single-junction silver-silver chloride reference electrode (90-01); the electrode potentials were measured by a Beckman Model GS pH-meter. The electrodes were calibrated with standard sodium fluoride solutions. These calibrations gave excellent straight lines in the range 10^{-7} to 10^{-3} M F^-, exhibiting a 59-mV change in potential for each tenfold change in fluoride ion activity (Fig. 1). Values from 10^{-6} to 10^{-7} can be reliably measured if the electrode is preconditioned by soaking and standardizing in fresh solution and not exposed to F^- concentrations above 10^{-6} after conditioning.

The yield of H_2 produced in methanol-containing solutions was determined by gas chromatography using a 10-ft × 1/4-in Poropak Q column at 50°C, 15 ml/min nitrogen flow, with a thermoconductivity detector at 160 mA current on an F&M Model 720 gas chromatograph. Calibration of the system was carried out as follows:

To test recovery of H_2 from solution, a series of seven 50-μl samples were radiolytically produced in a H_2O-KBr solution, assuming $G_{H_2} = 0.45$. The H_2 was freeze-thaw released from solution into a closed, evacuated system with a liquid-nitrogen cooled trap. The H_2 was collected by a Toepler pump and transferred by syringe to the gas chromatographic inlet. The photolytically produced samples were handled in the same manner. The detector was calibrated before or after each sample by the direct injection of H_2 into the chromatograph.

The yield of methane produced in the photolysis of methanol was measured in the same way as the hydrogen produced. The methanol was prepared by repeated freeze-thaw cycles in the sample irradiation cell, followed by the addition of 1 atm SF_6. The solution was shaken to attain saturation of the gas in the liquid (0.02 M). Irradiation with polychromatic light was typically 10 min. The gas fraction, predominantly SF_6 but containing methanol, hydrogen, and methane, was passed through

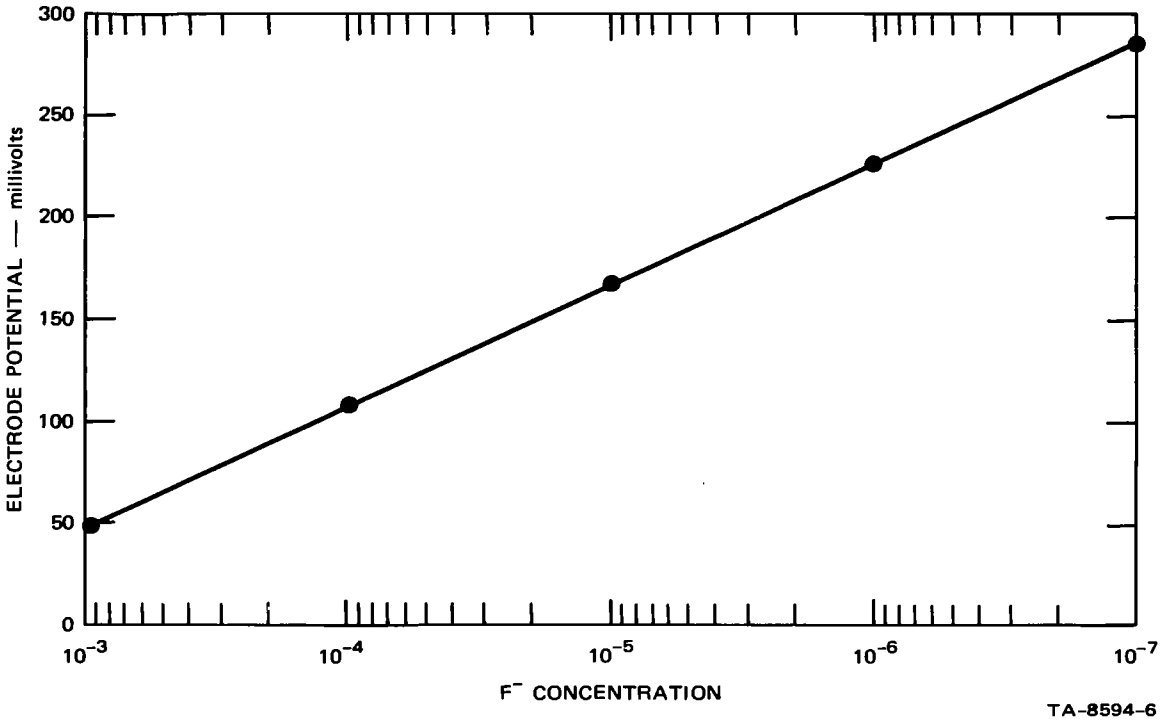

FIGURE 1 POTENTIAL OF SPECIFIC ION ELECTRODE AS A FUNCTION OF FLUORIDE ION CONCENTRATION

a liquid nitrogen cold trap to remove the SF_6 and the methanol and compressed by a Toepler pump into a capillary volume with a rubber septum for extraction of the gas. The total gas fraction was transferred by hyperdermic syringe to the gas chromatograph where the hydrogen and methane were quantitatively assayed.

The F^- concentrations in pure methanol were measured by diluting a milliliter aliquot to 10 ml with 15% sodium acetate buffer solution. The resulting F^- measurement with the specific ion electrode was consistent with a standard F^- in 10% alcohol, 90% buffer. The same method was used for measuring F^- production in n-butanol.

C. Measurement of the Isotopic Composition of the Photolytic Hydrogen

This measurement was carried out following the procedure of Farkas and Farkas.[41] A thermoconductivity cell was constructed in which we could accurately measure the resistance of a fine platinum wire. The sensing wire was 7.5-cm long and 10-μm in diameter. The exterior of the cell surrounding the wire was maintained at liquid nitrogen temperature. Calibration of the thermoconductivity isotope ratio cell was carried out with H_2 produced by photolysis of conductivity water containing 0.1 M methanol (spectroscopic grade). An irradiation period of 20 minutes with polychromatic light yielded enough H_2 to supply the cell and reserve volume with adequate pressure (0.1-0.2 torr). The produced H_2 was released from the reaction cell by shaking and transferred to the evacuated collection volume containing a liquid nitrogen cold trap. A Toepler pump transferred and compressed the hydrogen into the 200-cc test cell and reserve 100-cc volume. Hydrogen was admitted into the test cell (at liquid nitrogen temperature) until the conductivity wire reached a resistance of 50.0 Ω at 10.0 mA. This corresponds to a wire temperature of 160°K. At 77°K the wire had a resistance of 19 Ω. After careful adjustment at thermal equilibrium by liquid nitrogen level control of pressure to 50.0 Ω at 10.00 mA, the current in the wire was increased to 10.40 mA, raising the wire resistance to 59.8 Ω (185°K). A repeat of the process to photolyze D_2O (99.8%) containing 0.1 M methanol yielded pure HD gas. This gas in the test cell came to isotopic equilibrium ($2HD \rightleftarrows H_2 + D_2$) when the

platinum wire was held at 150 Ω (~ 400°K) until no further changes in conductivity of the gas occurred. Pressure was then adjusted to the 50.0 Ω, 10.00 mA point. This gas, because of its poorer thermal conductivity and its almost constant heat capacity with temperature change, reached a higher resistance (65.6 Ω) at 10.40 mA. The values 59.8 and 65.6 Ω represent the extreme values of gas composition resulting from photolysis of pure H_2O and pure D_2O in the presence of methanol. The work of Farkas,[41] which describes the technique and apparatus used in determining isotope ratios, shows a straight line relationship for mole fraction versus resistance obtained at the second current setting.

V RESULTS AND DISCUSSION

A. The Production of Fluoride Ions from SF_6 in Photolyzed Water as a Function of Time

The production of fluoride ions from SF_6 in photolyzed water was studied as a function of time at neutral pH using polychromatic light. Owing to the absorption coefficient of liquid water, the practical cutoff wavelength was as high as 175 nm under the experimental conditions. Light of shorter wavelength is absorbed in the first few microns (at 180 nm, 1 mm of water has an optical density of 2, and at 175 nm, 90% of the light is absorbed in 50 microns of water).[4] The e^-_{aq} scavenger is thus depleted to zero within a few seconds in the layer adjacent to the sapphire window producing at the same time a thin layer of $SO_4^=$ ions, which act as a cutoff filter. It has been found that the rate of F^- production was cut by 70% when a filter of 1-cm water was interposed between the light source and the photolysis cell. Using the absorption curve of water,[4] this means an "effective" wavelength of 187 nm. In other words, the photolyzed system behaved as if all the light was of 187 nm. Because some of the absorption took place at considerably longer wavelengths, a significant part of the photolysis took place at shorter wavelengths, but probably not much shorter than, say, 182 nm. It may be inferred that the contribution of the strongly absorbing boundary layers was limited and that all the active photons were absorbed in the 10-cm cell.

The F^- production was found linear with time from 5 to 60 minutes (Fig. 2). At the given geometry and light intensity, 0.12 μmoles F^- (0.02 μmoles e^-_{aq}) were produced per minute. This linear production of F^- indicates no exhaustion of reagent and no buildup of interfering substances in one hour. At longer irradiation times the rate of e^-_{aq} production decreased owing to the buildup of H_3O^+. On the other hand, the formation of SO_4^{2-} added a solute that generated e^-_{aq} on photolysis, thus increasing the overall e^-_{aq} yield. By measuring the absorption spectrum of SO_4^{2-} in the given spectral region, we concluded that its contribution

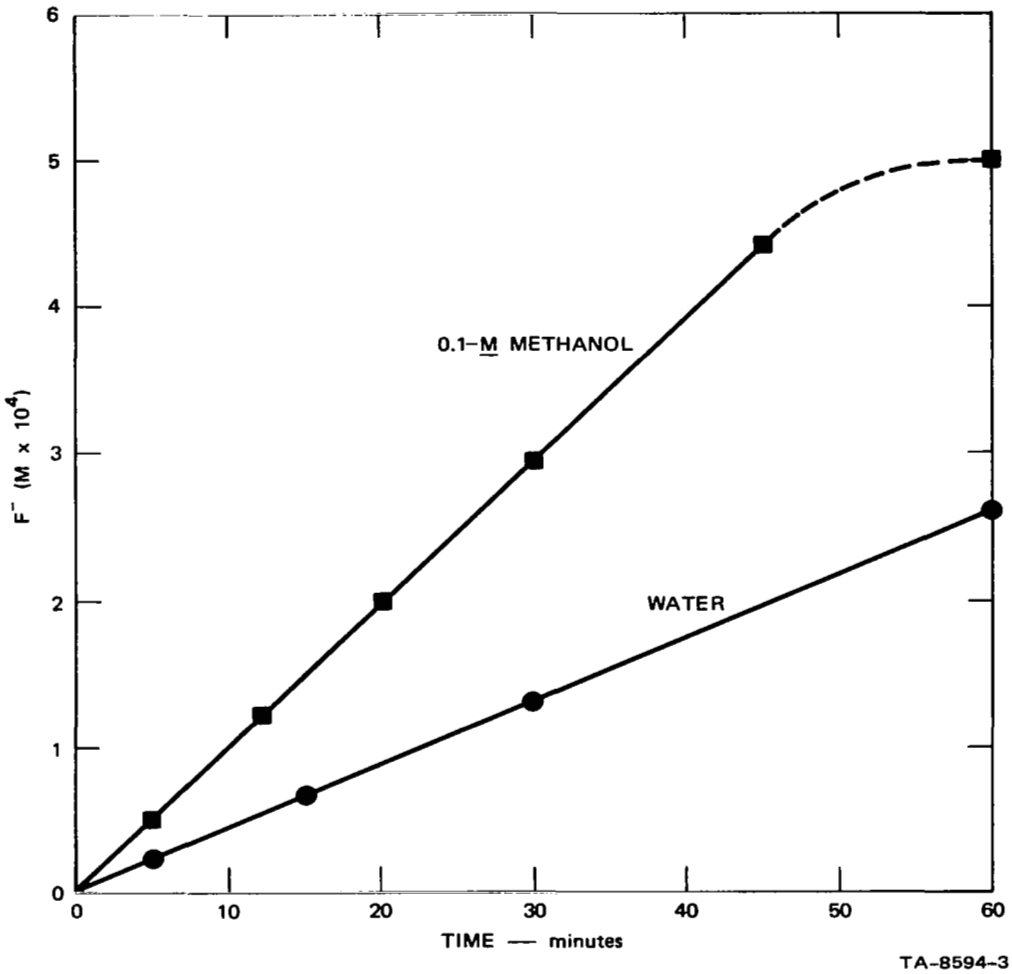

FIGURE 2 THE RATE OF PHOTOLYTIC FLUORIDE ION PRODUCTION FROM SF_6 AS A FUNCTION OF TIME IN THE ABSENCE AND PRESENCE OF 0.1-M METHANOL

would be minimal unless it reaches the 10^{-4} M level. As most of our work with "polychromatic light" was carried out with irradiation times of ten minutes, the final SO_4^{2-} concentration was lower than 10^{-5} M.

The same yield of fluoride ions, within 5%, was obtained for SF_6-saturated distilled water from three different sources: commercial water, triple distilled; SRI Physical Sciences, triple distilled water; and Ames, double distilled water. These results indicate that the hydrated electrons formed originate by photoionization of the water and not as a result of the photoionization of an adventitious impurity.

B. The Effect of Added Methanol or Ethanol on the Rate of F^- Production

The yield of F^- was found to increase when methanol was added to the water, and the F^- yield leveled off at [MeOH] = 0.03 M, staying constant up to 10^{-1} M MeOH (Fig. 3); the same yield of F^- was observed in 0.5 M MeOH. A similar increase was observed on addition of ethanol, reaching the same limiting value of 0.25 μmole F^- (= 0.042 μmole e^-_{aq}) produced per minute. The effect of ethanol was, however, more pronounced than that of methanol; ethanol had an effect equivalent to methanol at about half the concentration. The most plausible explanation for the effect of these alcohols is that they scavenge OH radicals vicinal to the e^-_{aq}, thus inhibiting geminate recombination.

$$H_2O \xrightarrow{h\nu} H_2O^+ + e^- \rightarrow H_3O^+ + OH + e^-_{aq}$$
$$e^-_{aq} + OH \rightarrow OH^-$$
$$CH_3OH + OH \rightarrow H_2O + CH_2OH$$

This suggestion finds its support in the nonlinear dependence of F^- production rate on alcohol concentration, which is typical for nonhomogeneous competition kinetics,[42] and by the twofold higher efficiency of EtOH, which is in line with the corresponding rates of reaction of OH radicals with MeOH and EtOH ($k = 6.1$ and 11.0×10^8 M^{-1} sec^{-1}, respectively[43]).

The possibility that the increase in F^- production in the presence of alcohols is due to the reaction of SF_6 with CH_2OH radicals, produced by hydrogen abstraction from methanol, has been ruled out by a series of

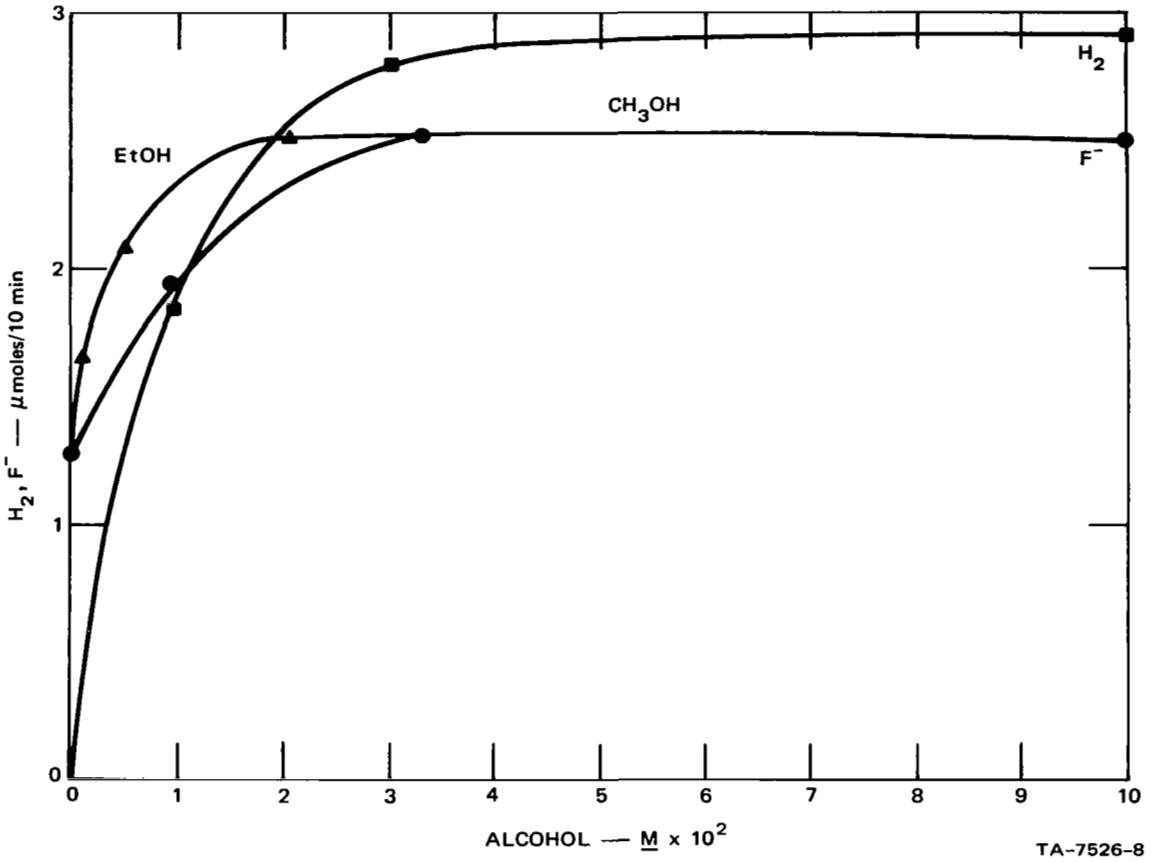

FIGURE 3 THE RATES OF PHOTOLYTIC FLUORIDE ION AND MOLECULAR HYDROGEN PRODUCTION AS A FUNCTION OF ADDED METHANOL AND ETHANOL

radiolytic experiments. SF_6-saturated solutions containing 0.1 M MeOH were irradiated by gamma rays at neutral pH in the presence and absence of N_2O (1×10^{-2} M) and in acid solution (10^{-2} M $HClO_4$). In the presence of N_2O and in acid solution the yield of F^- dropped by a factor of over 100 to the limit of detection. Under the latter conditions, the CH_2OH radicals are being produced with a G value of about 6, but all the e^-_{aq} are converted into OH radicals or H atoms.

C. The Effect of pH on the Rate of Production of F^-

The rate of F^- production was measured in the pH range 2.7 to 10.6 in absence and presence of 0.1 M MeOH. The results are presented in Fig. 4. It is evident that the rate of production of F^- is pH independent between pH 4.5 and 9. Below pH 4.5 there is a fast decline in the rate of F^- production, which may be easily explained by the competition of H_3O^+ for e^-_{aq}.

$$e^-_{aq} + H_3O^+ \rightarrow H + H_2O.$$

If we take pH = 4 as the point at which the rate of F^- production falls to half its original value, it appears that H_3O^+ is 2.2 times more efficient as e^-_{aq} scavenger than SF_6, which is higher than the value of 1.6 found by Asmus and Fendler[37] under radiolytic conditions. Now we have to remember that SF_6 at 2.2×10^{-4} M concentration picks up part of the e^-_{aq} from vicinal pairs with OH. Under these conditions, the relative rates of diffusion of H_3O^+ and SF_6 become critical, and H_3O^+ becomes more competitive as its rate of diffusion is higher by an order of magnitude. When methanol is added, the vicinal OH radicals are scavenged and the relative effectiveness of H_3O^+ falls from 2.2 to 1.2, which is even lower than 1.4--the ratio between the best known specific rate constants of e^-_{aq} with H_3O^+ and SF_6.[44] This apparent higher scavenger efficiency of SF_6 (by about 15%) may be partly or perhaps wholly due to a correspondingly slightly higher solubility of SF_6 in 0.1 M MeOH; we have found that the solubility of SF_6 in pure methanol is about a hundred times higher than in water.

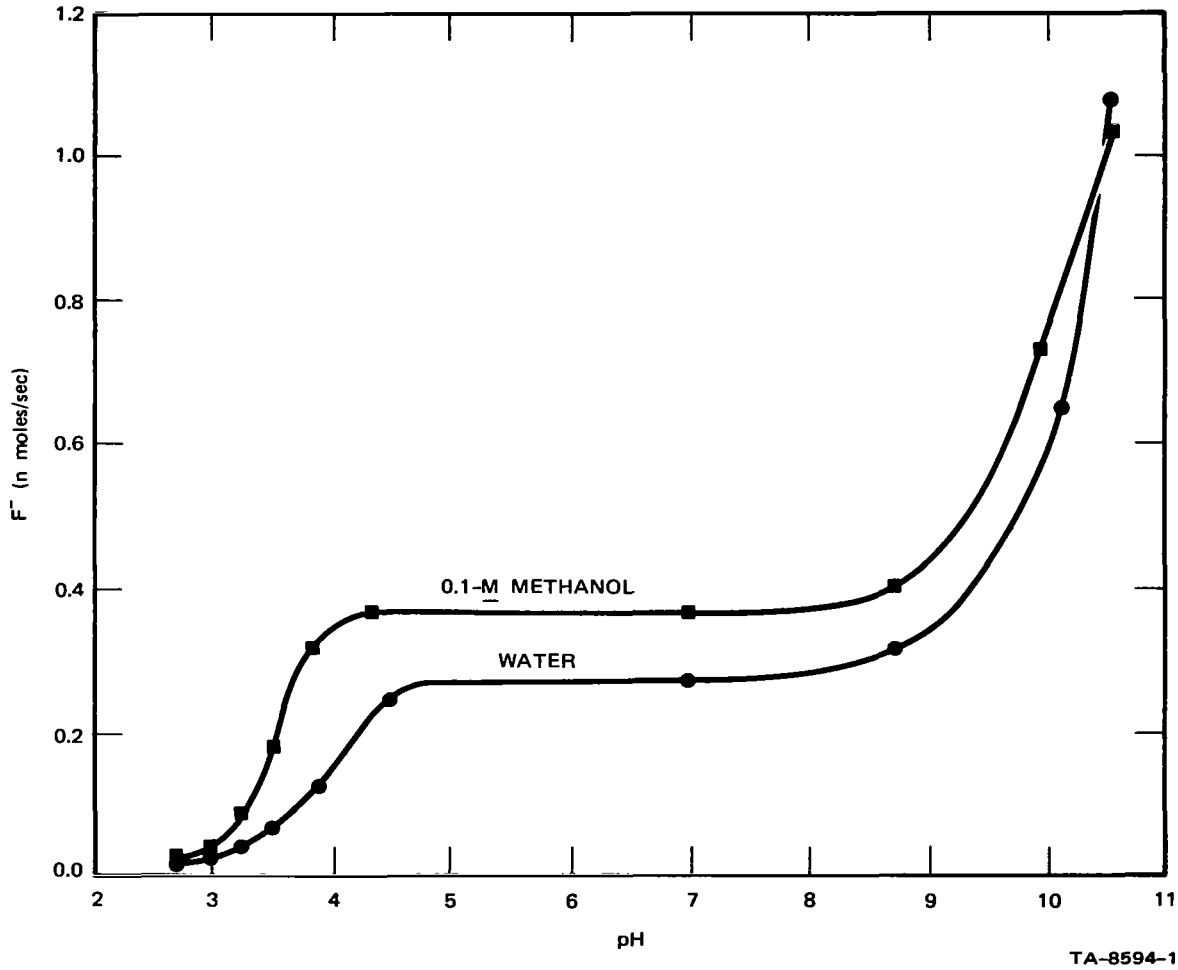

FIGURE 4 THE RATE OF PHOTOLYTIC FLUORIDE ION PRODUCTION AS A FUNCTION OF pH

At the other end of the pH range, the increase in F^- production (Fig. 4) is due to the photoionization of OH^- [33] as well as to the conversion of H to e^-_{aq} by the reaction[45]

$$OH^- + H \rightarrow e^-_{aq}.$$

This pathway for e^-_{aq} production is suppressed in the presence of methanol because 0.1 M MeOH effectively competes for H atoms in the pH range 9 to 11. The lower yields of F^- at high pH in the presence of MeOH are therefore expected.

The pH profile of the rate of F^- production in the absence and in the presence of methanol is thus completely consistent with the assignment of e^-_{aq} as the sole precursor of F^- and with the assumption that e^-_{aq} is produced by photoionization of H_2O in the pH range < 8.

The identification of e^-_{aq} as the precursor of F^- in our system has been corroborated by another series of competition kinetics experiments where e^-_{aq} scavengers other than H_3O^+ were used. Cd^{2+} and Yb^{3+}, which react rapidly with e^-_{aq}, have little uv absorption in the range 180 to 200 nm. Thus they could be added at 10^{-4} concentrations to the SF_6 photolyzed solutions. They were found to diminish the rate of F^- production, and their scavenging efficiency was compared with that of SF_6. The results are summarized in Table III.

Table III

REACTION RATES OF e^-_{aq} AS CALCULATED FOR COMPETITION KINETICS[a]

	Pure Water	0.1 M MeOH	Literature Value[44]
SF_6	1.1 ± 0.1^b	1.9 ± 0.2^b	1.65
Cd^{++}	6.8 ± 2.2^c	6.6 ± 2.0^c	4.8-5.2
Yb^{3+}	-	3.9 ± 1.0^c	3.7-4.3

[a] In units of 10^{10} M^{-1} sec^{-1}.

[b] Assuming $e^-_{aq} + H_3O^+ = 2.3 \times 10^{10}$ M^{-1} sec^{-1}.

[c] Assuming $e^-_{aq} + SF_6 = 1.65 \times 10^{10}$ M^{-1} sec^{-1}.

It is evident that, unlike the competition of H_3O^+, Cd^{++} ions do not show a significant change in apparent reactivity in the presence of 0.1 M MeOH. This corroborates our suggestion on the unique mode of action of H_3O^+ in scavenging e^-_{aq} from the vicinity of OH radicals. The slightly higher values of Cd^{++} compared with the pulse radiolysis data are in accord with other competition reactions of SF_6, where even the reactivity of H_3O^+ is found higher by over 10% from the pulse radiolysis value.[37] It is thus possible that the measured value of 1.65×10^{10} M^{-1} sec^{-1} for the $e^-_{aq} + SF_6$ reaction is slightly too high or that the solubility of SF_6 in water is somewhat lower than assumed.[40] In any case the agreement between the competition kinetics data and the absolute pulse radiolysis rate constants for H_3O^+, SF_6, Cd^{++}, and Yb^{3+} is sufficient to corroborate our conclusion that e^-_{aq} is the sole precursor of F^- in our photolyzed system.

D. The Formation of H_2 and the Quantum Yield of the Photoionization of Water

The rate of photodissociation of water was monitored by measuring the rate of H_2 evolution from photolyzed methanol-containing solutions. Under these conditions the following reactions take place:

$$H_2O \xrightarrow{h\nu} H + OH$$
$$CH_3OH + H \rightarrow CH_2OH + H_2$$
$$CH_3OH + OH \rightarrow CH_2OH + H_2O$$
$$2CH_2OH \rightarrow CH_3OH + HCOH \text{ or } (CH_2OH)_2.$$

The effect of methanol concentration on the H_2 yield is presented in Fig. 3. It can be seen that the H_2 yield levels off at $[MeOH] > 3 \times 10^{-2}$ M, just where the increase in F^- yield levels off. The production rate of H_2 is 1.16 times higher than that of F^- and therefore sevenfold higher than that of e^-_{aq}. Taking the quantum yield of H_2 in our spectral range in the presence of 0.1 M MeOH, $\varphi = 0.54$,[26] the quantum yield of e^-_{aq} is: $\varphi(e^-_{aq}) = 0.077$.

This quantum yield is substantially higher than that observed by Boyle *et al.*[27] using flash photolysis. A possible explanation is that, in that investigation, only the electrons that escaped from the "cages"

were observed, whereas, in our system, even in the absence of MeOH, SF_6 must have scavenged some electrons that would otherwise have recombined with their vicinal OH radicals or H_3O^+ ions. Interestingly enough, the relative yield of "free" $H/e^-_{aq} = 20$ obtained in flash photolysis is significantly higher than the ratio $H/e^-_{aq} = 7$ obtained by us in the presence of 0.1 M MeOH. The reason for the difference is most probably the greater chance for geminate recombination of e^-_{aq} with both H_3O^+ ($k = 2.3 \times 10^{10}$ M^{-1} sec^{-1})[44] and OH ($k = 3 \times 10^{10}$ M^{-1} sec^{-1})[44] compared with the single process H + OH ($k = 2 \times 10^{10}$ M^{-1} sec^{-1}).[46,47] In other words, e^-_{aq} "sees" in its cage two scavengers, whereas the H atom encounters only one.

The quantum yield found by us in the presence of MeOH is higher than that estimated by Sokolov and Stein,[26] namely, $\varphi(e^-_{aq}) \leq 0.05$. Their value was, however, obtained in a 1.3×10^{-3} M isopropanol solution where $\varphi(H_2)$ was just 0.33. Extrapolation of Sokolov and Stein's data for $\varphi(H_2) = 0.54$ would give $\varphi(e^-) \leq 0.08$. On the other hand, our quantum yield in the presence of 2.2×10^{-4} M SF_6 and in the absence of MeOH, $\varphi(e^-_{aq}) = 0.037$, is well below the upper limit of Sokolov and Stein. We must also remember that their determination of $\varphi(e^-_{aq})$ was carried out with a light source that emitted about 2×10^{-11} einstein sec^{-1} of the 184.9 nm photons into their photolyzing cell. Our light intensity was about 1.5×10^{-6} einstein sec^{-1} in the same spectral range. This dramatic difference in light intensity allowed us to obtain substantial yields of e^-_{aq}, whereas the previous study had to rely on marginal differences in the measured N_2 pressure. Sokolov and Stein should be complimented therefore for having obtained a result so close to ours with such inferior instrumentation and analytical technique. The other study[29] that has estimated $\varphi(e^-_{aq})$ is much less reliable, as was pointed out in the Introduction. The internal filtering effect of the scavenger, CO_2, might have resulted in low apparent quantum yield. Surprisingly, however, Getoff and Schenck's $\varphi(e^-_{aq})$ estimate for 0.01 M formate + 0.02 M CO_2, $0.02 < \varphi(e^-_{aq}) < 0.04$, is still in fair agreement with our $\varphi(e^-_{aq})$ measured in the absence of methanol.

E. The Energy Threshold of Photoionization of Water

The yield of photolytic hydrogen and F^- in 0.1 M MeOH was measured as a function of wavelength.

The wavelength cutoff for the production of hydrogen was obtained with relatively little difficulty, although the production was on the order of 0.1 μl H_2 in an hour compared with the polychromatic production rate of 50 μl in 10 minutes. Using 5-nm increments of wavelength advance, the production shows a peak at 190 nm. It then drops with wavelength to a cutoff at 203 nm (Fig. 5). Production of hydrogen also falls, as expected, below 190 nm because the high absorption of the water results in a pronounced self-filtering effect by thin layers, which may become depleted in SF_6 and methanol.

Because of the detection limit of F^- ($\sim 10^{-7}$ M), the measurement of the wavelength cutoff of fluoride was carried out by the attachment of a McPherson Vacuum Spectrometer to the lamp to minimize the internally scattered light during the long exposures. By extrapolation we obtained a cutoff of F^- production at 206 nm (Fig. 5).

Owing to the large experimental errors occurring in the determination of H_2 and F^- close to the cutoff wavelength, the value of the latter is estimated at 205 ± 2 nm. In any case, it can be seen from Fig. 5 that the photolytic yields of H_2 and F^- follow the same wavelength dependence. It may be thus concluded that both photodissociation and photoionization of water originate from the same excited state.

$$H_2O \xrightarrow{h\nu} H_2O^* \begin{cases} \nearrow H + OH \\ \searrow H_2O^+ + e^- \end{cases}$$

F. The Dependence of Photoionization of Water on Light Intensity

The cutoff wavelength for photoionization of water, 205 nm, corresponds to a quantum energy of 6.05 eV. This energy is in excess of the energy required to break the H-OH bond, 5.16 eV,[48] but is over 6.5 eV lower than the ionization potential of water in the gas phase (12.6 eV).[49] One simple explanation of this difference would be that photoionization

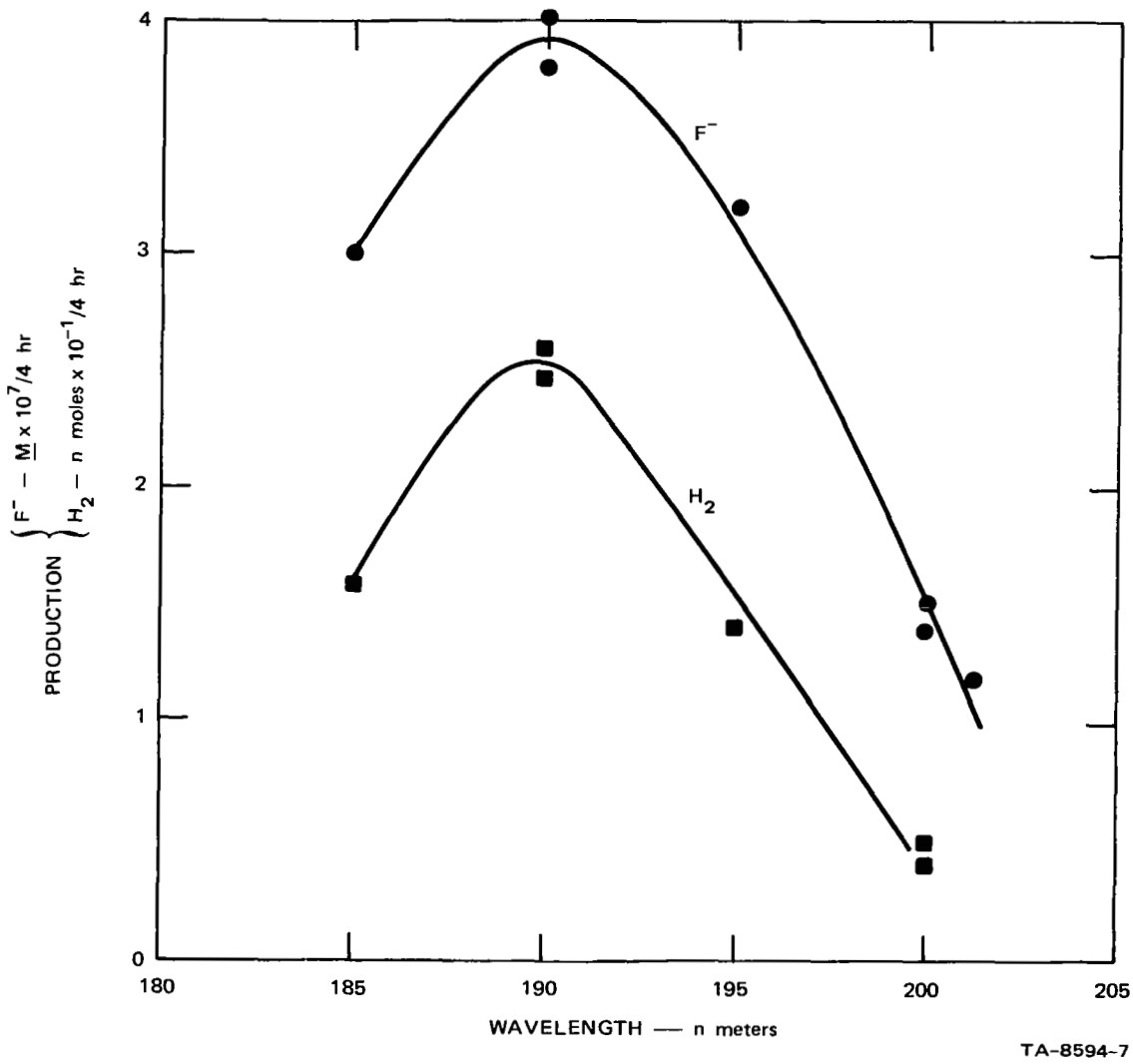

FIGURE 5 THE RATES OF PHOTOLYTIC FLUORIDE ION AND MOLECULAR HYDROGEN PRODUCTION IN WATER AS A FUNCTION OF WAVELENGTH

of water is the result of a double photon process--the photoionization of a relatively longlived, electronically excited H_2O^* molecule.

$$H_2O \xrightarrow{h\nu} H_2O^* \xrightarrow{h\nu} H_2O^+ + e^-$$

We have studied therefore the yield of photoproduced F^- as a function of light intensity by inserting neutral density filters in the light path. The results presented in Fig. 6 show a linear dependence of the F^- yield obtained in a given time on the light intensity. In other words, the quantum yield of e^-_{aq} is independent of light intensity. This conclusion is further corroborated by the comparable quantum yields obtained by Sokolov and Stein,[26] who photolyzed their solutions with light intensities lower by a factor of 10^5. We must conclude therefore that the photoionization of water is a single photon process.

G. The Photolysis of D_2O

A series of experiments was carried out in D_2O saturated with SF_6, both in the presence and in the absence of CD_3OD. The D_2O absorption band is shifted by about 5 nm to the shorter wavelength region.[5,11]

The experiments with heavy water confirm the results with light water. Production of F^- in heavy water irradiated with polychromatic light is about 90% of that with light water. This 90% is the result of the lower light output of the lamp at the shorter wavelengths necessary to photoionize D_2O as well as the decreased transmission of the windows at these wavelengths. The deuterium, D_2, production closely follows the e^-_{aq} production in heavy water as in light water. The ratio of e^-_{aq} to $H_2(D_2)$ is 16 ± 4% in D_2O compared with 14 ± 2% in H_2O; the difference being insignificant.

Inserting a Beckman 1-cm quartz cell between the lamp and the sample cell decreases the rate of F^- production in D_2O by 40%, while reducing F^- yield in light water by 13%. The 1-cm cell filled with H_2O cuts the F^- in D_2O production to 12%, and 1 cm 10^{-3} M NaCl reduces it to 8%. The results are summarized and compared with the corresponding H_2O data in Table IV.

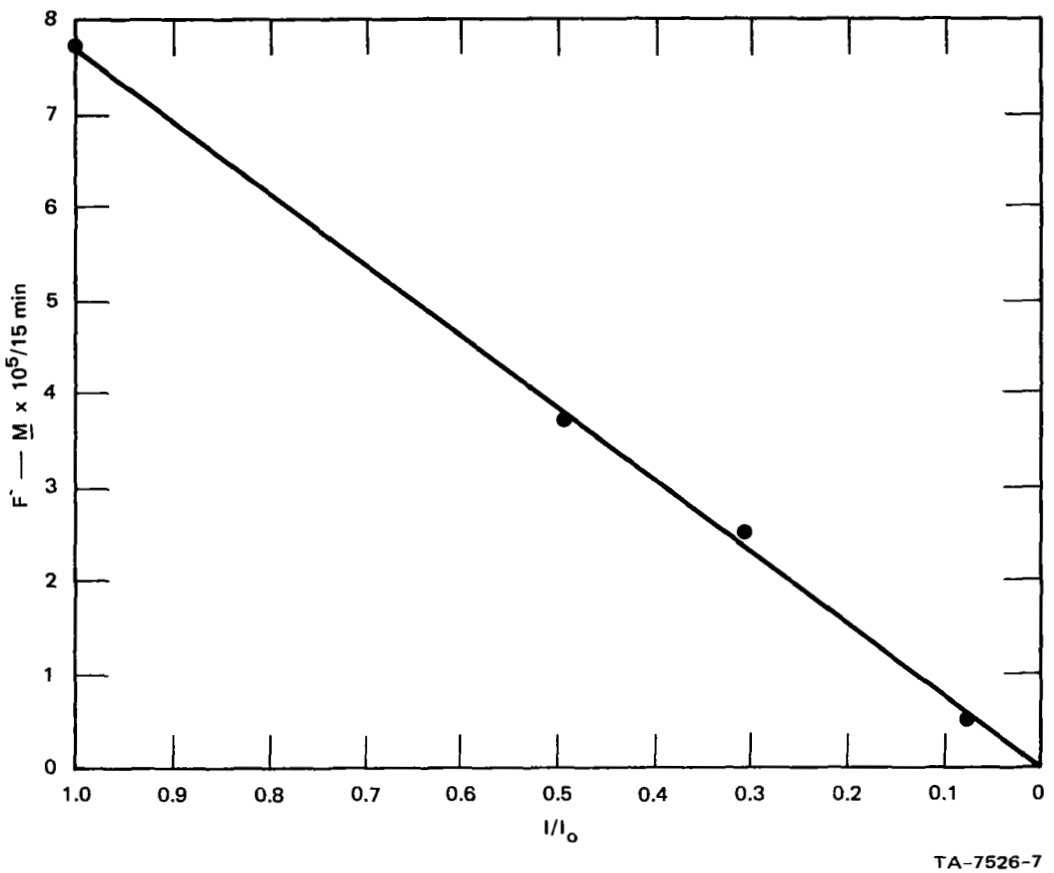

FIGURE 6 THE EFFECT OF LIGHT INTENSITY ON THE RATE OF FLUORIDE ION PRODUCTION

Table IV

EFFECT OF CUTOFF WAVELENGTH
ON THE PHOTOLYTIC YIELDS IN H_2O AND D_2O

Filter	D_2O-CD_3OD				H_2O-CH_3OH			
	F^-		D_2		F^-		H_2	
Polychromatic, no filter	.58[a]	100%	.56[a]	100%	.66[a]	100%	.75[a]	100%
Quartz cell, empty	.35	60	.30	54	.57	87	.64	85
1 cm H_2O	.07	12				34		29
1 cm 10^{-3} M NaCl	.045	8				15		12

[a]Data in μmoles in 10 min radiation.

A Cary scan of the 1-cm quartz cell showed an absorption density of .13 at 185 nm, so the marked effect of this cell in diminishing the rate of production of e_d^- and D_2 in heavy water is caused by wavelengths below this level. Water (H_2O) in 1-cm pathlength showed a density of 0.7 at 188 nm, and 1-cm 10^{-3} M NaCl gave a density of 0.7 at 192 nm.

The spectral shift of the F^- production in D_2O, which follows the shift in the first continuum absorption band of heavy water, provides an independent proof that the photolytic hydrated electrons are produced from the water and not from any trace impurity therein. The absence of any significant isotope effect on the branching of H_2O^* to ionization or dissociation is expected because the excitation energies of H_2O^* and D_2O^* are so far from the zero-point-energy level. This is in accord with the extremely small difference between the ionization potentials of H_2O and D_2O in the gas phase (12.614 ± 0.005 and 12.637 ± 0.005 eV, respectively).[5c]

H. The Photolysis of Methanol

Methanol saturated with SF_6 was photolyzed under conditions similar to those of the water photolysis. When photolyzed with polychromatic light, the F^- yield was 85% of that obtained in H_2O. The addition of 0.2, 1, and 10% H_2O to MeOH did not significantly change the rate of F^- production. The yield of H_2 from photolyzed methanol amounted to 5 times the fluoride production (or 30 times the e^-_{MeOH} yield).

In an independent series of radiolytic experiments, solutions of SF_6 in MeOH were irradiated in the presence and absence of N_2O and $HClO_4$. The fluoride yield was cut to less than 10% in the presence of these electron scavengers, indicating that, as in the water system, solvated electrons are the sole precursors of fluoride ions produced from SF_6.

The wavelength dependence of the photolytic F^- yield in methanol was determined, and the results are presented in Fig. 7. The F^- formation seems to follow the first absorption continuum in methanol.[51,52]

In short, methanol seems to behave similarly to water and undergoes photoionization with a cutoff wavelength of approximately 265 nm (4.7 eV); this is again 6.1 eV lower than the ionization potential of methanol in the gas phase (10.83 eV).[49]

The production of hydrogen in the photolysis of methanol was found to involve a different excited state from the production of the electron-ion pair. A Vycor glass window with sharp cutoff of uv transmission below 230 nm lowered the F^- production to 27%, while lowering that of hydrogen to $\sim$ 1% of the values produced by polychromatic light.

In the wavelength dependence experiments with pure methanol, it was found that methane was produced as a product in addition to hydrogen and solvated electrons. In three experiments using (1) no wavelength limiting window, (2) a quartz window, and (3) a Vycor window, we found the methane to be in molar ratio of 1.1:1 with e^-_{sol} under all three conditions, whereas the hydrogen to e^-_{aq} ratio ranged from 30:1 in (1) to 26:1 in (2) and to 0.3:1 in (3). This strongly suggests that photoionization and methane formation involve the same excited state of methanol, a state lower than the one leading to the hydrogen atom formation.

I. Photoionization of n-Butanol

Spectro grade n-butanol was photolyzed in the sample cell in the presence of 1 atm SF_6. Fluoride ion production (e^-_{sol}) was identical to that of methanol, and hydrogen production was slightly lower (25:1 relative to e^-_{sol} versus 30:1 in methanol). A chromatographic peak in the region of C_4 or C_5 hydrocarbon elution was detected but not identified

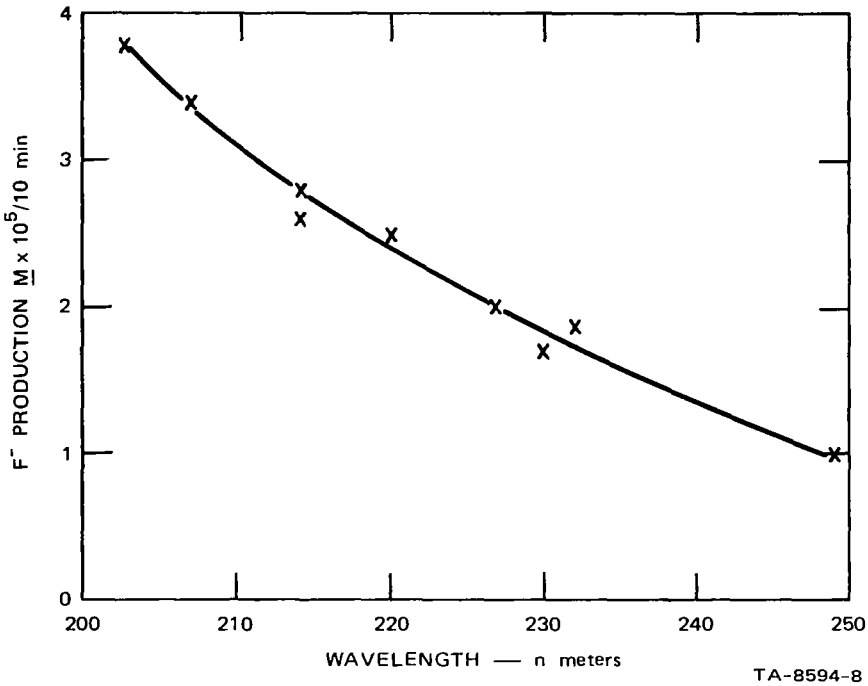

FIGURE 7 THE RATE OF PHOTOLYTIC FLUORIDE ION PRODUCTION IN PURE METHANOL AS A FUNCTION OF WAVELENGTH

in the gas evolved from the alcohol. The ionization process thus seems to be common to normal alcohols; confirmation experiments with radiolysis and competition kinetics were not conducted.

J. Photolysis of Methanol-Water Mixtures

Following our experiments in pure water, pure methanol, and dilute methanol solutions, it was of interest to investigate the yield of solvated electrons in a mixed solvent. This series of measurements of F^- yield in solutions containing from 5 to 95 mol % of H_2O in MeOH was intended to answer a number of questions:

(1) Are all the oxidizing species of the geminate ion pairs $H_2O^+ - e^-_{aq}$ scavenged in the presence of 0.1 M MeOH (Section B) to leave e^-_{aq} for reaction with SF_6, or are there additional ion pairs that undergo recombination to give H_2O^{**}, which may then dissociate to H + OH? The latter possibility would mean that photoionization is the predominant route of decomposition of the primary H_2O^*, excited by the incident photon.

(2) What is the lifetime of the primary H_2O^*? Can it be scavenged by a solute, say MeOH, and react with it? The possible reactions in this case could be:

$$H_2O^* + MeOH \rightarrow H_2O + MeOH^* \qquad (1)$$

Reaction 1 is an energy transfer reaction to be followed by $MeOH^* \rightarrow e^- + MeOH^+$, as well as by $MeOH^* \rightarrow MeO + H$ and $CH_3OH^* \rightarrow CH_3 + OH$. Reaction 1 is feasible because the energy levels of H_2O^* are higher than those of $MeOH^*$.

$$H_2O^* + MeOH \rightarrow \begin{cases} OH + H_2 + CH_2OH \\ H + H_2O + CH_2OH \\ H_2 + H_2O + HCOH \end{cases} \qquad (2)$$

In Reaction 2, MeOH acts as a hydrogen atom donor to H_2O^*, which may react either as an H atom or as an OH radical carrier. In any case each of the routes described under Reaction 2 is strongly thermodynamically favored and could proceed at a very high rate.

$$H_2O^* + MeOH \rightarrow e^- + OH + MeOH_2^+ \quad (3)$$

In Reaction 3, which will be discussed in greater detail in the section on the mechanism of photoionization (Part VI), MeOH acts as a proton acceptor that facilitates the ionization of H_2O^* to a greater extent than a neighboring H_2O molecule because of the high proton affinity of MeOH.

To minimize the formation of primary $MeOH^*$ by direct photon absorption by MeOH, we filtered out a major fraction of the light in the region 200 to 260 nm by placing a 1-cm quartz cell containing 10^{-3} M KBr in aqueous solution. The photolytic yield of F^- as function of H_2O mole-fraction is presented in Fig. 8.

In solutions containing a small mole-fraction of H_2O ($\leq$ 10%), water seems to diminish the yield of e_s^- from MeOH, which must be the main absorbing species at these concentrations. This result could be explained if we assume that the e_s^- from pure MeOH under the experimental conditions originates from a state < 200 nm, which has high probability for ionization and which is scavenged by H_2O to give H_2O^* with a lower probability for ionization.

Methanol has a strong absorption in the range 180 to 200 nm[52,53] leading to its photolysis.[54,55] Since the latter process in the gas phase has been shown to involve a fairly long-lived predissociative excited state,[56,57] the energy transfer mechanism seems plausible.

Another explanation could be based on the assumption that the photoionization of methanol, like that of water, requires the concerted effect of a large number of MeOH molecules (see Part VI). The presence of one H_2O molecule in 10 or even in 20 MeOH impairs the chances for such a process.

In another series of experiments using "polychromatic" light, which contains relatively more intensity in the range > 200 nm, it was found that concentrations of 0.4, 1.8, and 15 mol % of H_2O in MeOH did not affect the F^- yield. Thus the energy transfer mechanism seems more plausible. This hypothesis could be corroborated by measuring the CH_4 yield for alcoholic solutions irradiated by photons < 200 nm. If $MeOH^*$

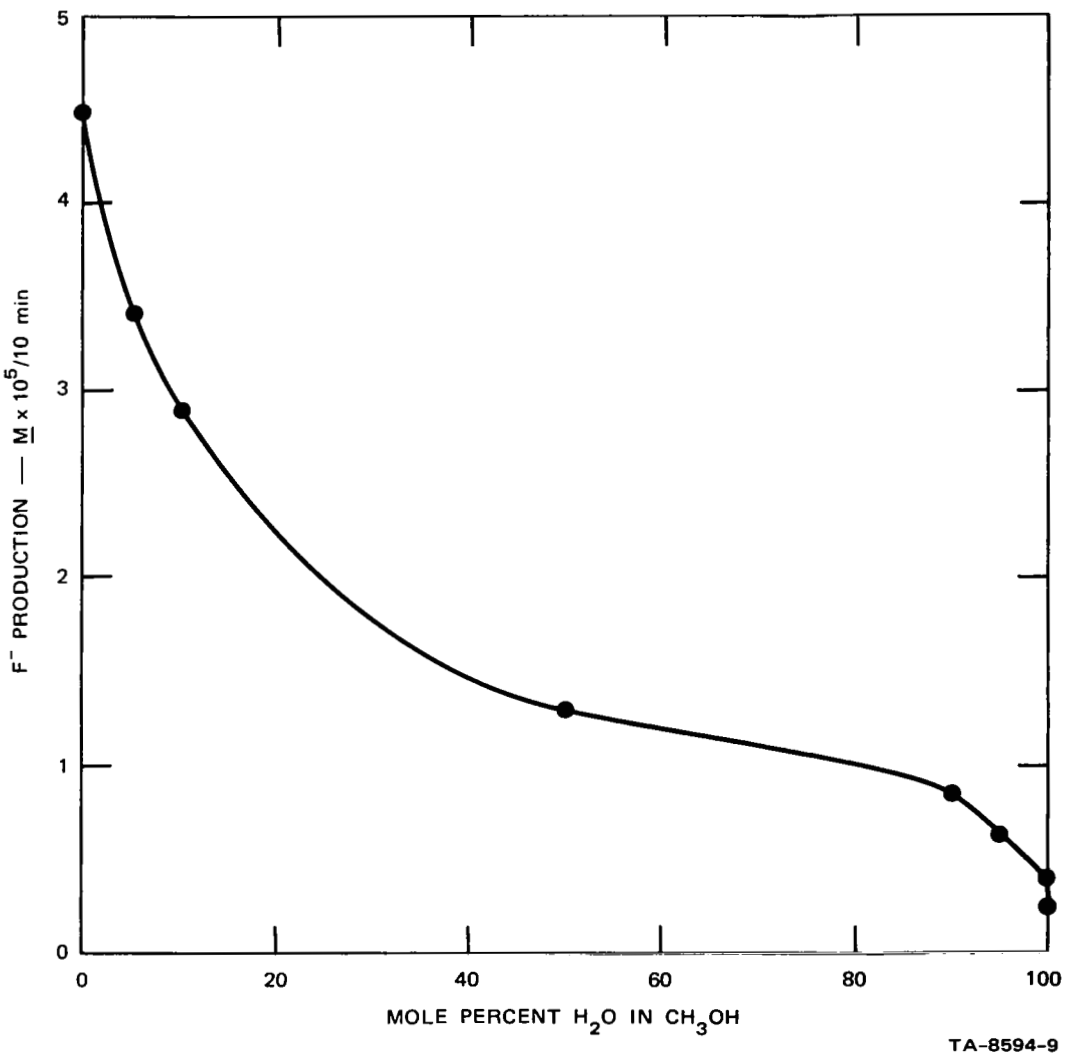

FIGURE 8 THE RATE OF FLUORIDE ION PRODUCTION AS A FUNCTION OF MOLE-FRACTION OF WATER IN METHANOL. Photolytic light has been filtered by 1-cm 10^{-3} M KBr solution.

transfers energy to H_2O, CH_4 yield should decrease with H_2O concentration faster than the F^- yield. If the presence of H_2O diminishes the probability of $MeOH^*$ to undergo ionization, the yield of CH_4 should not be affected by the presence of small amounts of H_2O and it might even increase under these conditions.

The effect of MeOH on the F^- in the concentration range 0 to 50 mol % may be subdivided into two regions: 0 to 1 mol %, which has its plateau, $\varphi = 0.077$ (see Section B), and 1 to 50 mol %, which again shows a plateau effect ($\varphi \simeq 0.18 \pm 0.01$); the slight increase in F^- yield observed between 10 and 50 mol % of MeOH may be easily attributed to the direct photolysis of MeOH. The lack of dependence of the F^- yield on MeOH over a wide range of concentrations indicates a mechanism of "indirect action." In other words, it is suggested that MeOH enhances the formation of e^-_{aq} from excited water molecules. This assumption could be corroborated by measuring the H_2 yield under the same conditions and finding a decrease in $\varphi(H_2)$ corresponding to the increase in $\varphi(e^-_{aq})$.

As in the case above, there are two alternative explanations for this effect. First, it is possible that there exist a substantial number of geminate $H_2O^+ + e^-$ pairs ($\varphi = 0.1 \pm 0.02$) that end up as H + OH and that are attacked by MeOH to give $H_2O + CH_2OH + H_3O^+ + e^-_{aq}$. Alternatively, MeOH may interact with H_2O^*, which should then have a lifetime of $\geq 10^{-12}$ sec, to give an e^-_{aq} by either reactions (1) or (3). Reaction (1), which could lead to the formation of e^-_{aq} by way of $MeOH^*$ as intermediate, would result in the simultaneous formation of methane; this could be experimentally checked out. The distinction between the scavenging of geminate H_2O^+ or OH and the involvement of MeOH as proton acceptor is not easy, because the <u>final</u> products will be identical and so will be the kinetic dependence on [MeOH], provided the half-life of H_2O^* does not exceed 10^{-12} sec.

One way to decide between these alternative mechanisms is to add to the water increasing amounts of a mixture dioxane-MeOH 1:10. As the ratio in reactivity of these two reagents is 2:1,[44] dioxane should scavenge 20% of all homogeneously distributed OH radicals. Now, if reaction (3) is involved, methanol will not alter the distribution of OH

radicals throughout the medium, and the yield of CH_2OH and therefore of HCOH will be independent of the concentration of MeOH--as long as the MeOH to dioxane ratio is kept constant. If, on the other hand, MeOH scavenges OH radicals from geminate pairs, where the reactivity difference between MeOH and dioxane has less effect than their relative concentrations,[42] then the yield of HCOH should increase with MeOH concentration, in spite of a simultaneous proportional increase in dioxane concentration.

It is evident that the mixed solvent experiments are an excellent tool for the investigation of the mechanism of photoionization, and they should be one of the first tasks in any extension of this project.

K. H/D Isotope Effects in the Photolytic Dissociation of Water

The H/D isotope effect in the photolysis of water has been measured by Sokolov and Stein,[26] who have measured the HD/H_2 ratio in hydrogen evolved from 10^{-3} M ethanol aqueous solutions containing 2 or 8% H and photolyzed at 184.9 nm. The hydrogen evolved from these solutions had a ratio of H_2/HD of 0.28 and 0.72, respectively. As H/D in the water was 0.02 and 0.087, respectively, isotopic fractional factors, S', of 14 and 8.3 can be calculated for the given conditions. This overall isotope effect does not represent the ratio between the rates of decomposition of HDO, the only H-containing species in the system,[58] to give H or D--because the effect has to be corrected for the absorption of photons by D_2O versus HDO.[26] An attempt was made to correct for the differential absorption of HDO and D_2O at 184.9 nm.[26] Using the absorption coefficient values of Barrett and Mansell,[9] namely 0.554 and 0.12 cm^{-1}, respectively, and applying the correct formula

$$S'' = [S'(HD/H_2)_g]/[(\alpha_{D_2O} + \tfrac{1}{2}\alpha_{HDO})/\tfrac{1}{2}\alpha_{HDO}]$$

(where α is the fraction of photons absorbed by the respective species), we can calculate the isotope effect for the differential dissociation of HOD, giving values of 4.5 and 3.3 for 98 and 92% D_2O, respectively.

It should be pointed out, however, that Barrett and Mansell have used Urey's thermodynamic data[58] for water in the gas phase to calculate their HDO concentration.[9] Now, if the absorption of photons in liquid

water is due to nonassociated water molecules,[59] the relative concentration of nonassociated HDO molecules compared with that of H_2O and D_2O may differ significantly from the thermodynamic equilibrium value between water molecules in the gas phase. In fact it is expected that in a one-to-one H_2O, D_2O solution most of the absorption will be still due to nonassociated H_2O molecules. Thus, the absorption coefficient of HDO at 184.9 nm is likely to be lower than 0.55 cm^{-1}. A lower value for α_{HDO} would result in a higher calculated isotope effect S". Furthermore, in 92 or 98% D_2O the ratio of nonassociated HDO/D_2O is not necessarily equal to the thermodynamic HDO/D_2O ratio. In fact the former ratio is expected to be significantly higher because of the weaker H····O compared with D····O hydrogen bonds.[59] This effect is expected to result again in a larger value for the calculated isotopic fractionation of HDO. It may be concluded therefore that the value (4 ± 0) calculated for the isotopic fractionation of HDO[26] is too low.

We have measured the isotopic fractionation of photolyzed water containing 0.1 M MeOH. Water containing 90% D photolyzed with polychromatic light gave hydrogen that contained 9% HD. An overall isotope effect of (91/9)/(10/90) = 91 was therefore observed. The experiment was repeated interposing a 1-cm filter of pure liquid D_2O. The hydrogen production was now diminished to 25% of its original value; however, the isotopic composition of the evolved hydrogen remained unchanged. In the second experiment we cut off the shorter wavelength portion of the spectrum, thus affecting primarily the photon absorption by D_2O. The lack of an effect on the isotopic composition of the evolved hydrogen indicates that the D atoms produced originate solely from the decomposition of HDO. Furthermore, the results suggest an effective energy transfer mechanism from D_2O^* to HDO. We conclude therefore that the rates of the two processes (1) HDO → H + DO and (2) HDO → D + HO differ in rates of a factor of (91/9)/(1/1) = 10. This is a rather high value considering that ΔH of reactions (1) and (2) are comparable, 118.27 and 119.70 kcal/mole, respectively;[60] proton tunneling may thus be involved in the dissociation process. The overall isotope effect would obviously be dependent on the H content of the heavy water, but the isotopic composition of the evolved

hydrogen is expected to remain constant, namely close to 10. When the concentration of H in D_2O increases to the point where H_2O molecules reach a significant concentration, the overall isotope effect is expected to increase considerably, because part of the photons would then be absorbed by the H_2O, producing H atoms exclusively. Further, energy transfer between HDO^* and H_2O, which is expected in analogy to the D_2O^* to HDO transfer, will amplify the effect of H_2O.

Our experimental results differ significantly from the two values measured by Sokolov and Stein.[26] Our value for the differential dissociation of HDO to H or D is higher by about a factor of two than the value calculated by them. We have no explanation for the discrepancy, and only further experiments would allow us to settle this point.

VI THE MECHANISM OF PHOTOIONIZATION OF ASSOCIATED LIQUIDS

It has been pointed out[27] that the combined energies of hydration of H_3O^+ and e^-_{aq} are sufficient to allow the photoionization of water with 6.5 eV photons, i.e., 6.0 eV below the ionization potential in gas phase.[27]

$$2H_2O \xrightarrow{h\nu} e^-_{aq} + H_3O^+_{aq} + OH_{aq} - 5.8 \text{ eV}$$

Following the same arguments, even photons with energies $\geq$ 6.05 eV are sufficient according to our experimental results to induce ionization. Obviously, this overall process is far too complicated to take place in a fast single step, and it is certainly in violation of the Franck-Condon principle. This mechanism involves a proton transfer reaction in addition to a series of rearrangements of water molecules around the newly formed H_3O^+ and e^-_{aq}. It requires, therefore, the formation of a long-lived, electronically excited H_2O^*, which managed somehow to orient its neighboring molecules to accept and solvate simultaneously a H^+ ion and an electron with just 0.25 eV excess energy. It is evident that this mechanism as it stands is highly improbable.

It should be emphasized that only partial solvation energy becomes available in the photoionization process, because complete solvation would require the rearrangement of water molecules around H_2O^*; this could hardly take place within 10^{-13} sec, the estimated lifetime of H_2O^*. Our conclusion that H_2O^*, produced as intermediate, dissociates or ionizes within 10^{-13} sec without any substantial atomic rearrangement of the solvent matrix could be supported by the fact that the ratio ionization/dissociation does not change with temperature.[27] If rearrangement of water molecules around the nascent H_2O^+ is a prerequisite for its formation, a significant temperature effect would be expected between 30 and 73°C.

It is evident that the photoionization of liquid water differs in nature from that in the gas phase. It requires 12.6 volts to produce an electron plus a H_2O^+ ion in the gas phase. On the other hand, it should

be noted that the absorption band leading to photoionization of liquid water peaks at 147 nm (8.4 eV)[61] or perhaps at 8.0 eV,[7,62] and that leading to the photoionization of methanol peaks about 7.3 eV.[8,12] Thus the difference between ionization potentials in the gas and liquid state, ΔI, is 4.6 eV for water and 3.5 eV for methanol. There is no reason to use the cutoff energies or any arbitrary energy in calculating ΔI.

In the liquid phase we gain the medium effect. From a purely electrostatic viewpoint, less energy will be needed to extract an electron from a molecule and detach it from the Coulombian Field of the parent ion. If this molecule is placed in a medium with a dielectric constant ϵ, the decrease in ionization energy will be equal to the solvation energy of the positive ion formed. This energy difference can be calculated by the continuous-medium Born formula[63]

$$\Delta I = \frac{e^2}{2r}\left(1 - \frac{1}{\epsilon_\infty}\right)$$

Taking $r = 0.147$ nm (the radius of H_2O as determined from the van der Waals equation in the gas phase,[64] which is very close to $r = 0.144$ nm obtained from x-ray diffraction of liquid water[65]) and the high frequency dielectric constant of water, $\epsilon_\infty = 6.0$,[66] we obtain $\Delta I = 4.05$ eV.

It has been pointed out[67] that this mode of calculation of ΔI in liquids suffers from a number of oversimplifications and can be applied as a first-order approximation at best. The main source of error is the necessity of reorienting molecules around the newly formed ion in order to accomplish solvation. In fact, the calculated value of ΔI, which should be equal to $\Delta H_h(H_2O^+)$, the enthalpy of hydration of H_2O^+,[68] is just a little smaller than ΔH_h of H_3O^+ calculated from

$$\Delta H_f(H_3O^+_{aq}) - \Delta H_f(H_3O^+) = 11.3\ ^{69} - 7.15\ ^{70} = 4.15 \text{ eV}$$

The value for ΔH_h of H_3O^+ includes, however, all the gain in energy following a <u>complete</u> orientation of water molecules around H_3O^+. Considering that $r(H_3O^+)$ and $r(Li^+)$ in solution are comparable[71] and taking the effective radius of Li^+ as 0.148 nm,[72] we may calculate ΔH_h of the photolytically formed H_2O^+ to be equal to $\Delta H_h(H_3O^+)$ within the uncertainties of the theory. It seems, therefore, that the Born treatment gives a too

high value for ΔI because it is unlikely that ΔI, which should not include any reorientation of the neighboring molecules, should be equal within the uncertainties of calculation to the total hydration energy of the given ion. (It is likely that the diameter of H_2O^+ at its ground state is smaller than that of water by some 10%, and thus its real ΔH_h will then be approximately 4.6 eV.) A more realistic calculation taking into consideration only the polarization of the adjacent molecules without any reorientation[65] would lead to ΔI of approx 3.5 eV.

It should be noted that even the overestimated ΔI of 4.05 eV is still over 0.5 eV short of the observed ΔI. If we add, however, to the ΔI due to solvation of H_2O^+ the gain in energy owing to the solvation of the electron (ΔH_h = 1.65 eV)[73] and assume that the latter solvation is predominantly due to polarization of the water molecules without reorientation,[46] we have gained more than 4.05 + 1.65 = 5.7 eV. This value may be overestimated by about 1 eV, because of the hydration by oriented water molecules. Even so, we have available some 4.7 eV, which is equal to or larger than the observed ΔI.

If we now look at photoionization in methanol, using the same arguments but taking $r(MeOH^+)$ = 0.304 nm,[64] and ε_∞ = 12.8,[74] we obtain ΔI = 2.17 eV. Here the reorientation of the solvent molecules has less effect than it does in water, and the true ΔI is estimated at 1.90 eV. If we add to this value the estimated ΔH_h of e^-_{MeOH} = 2.0 eV (estimated from its absorption spectrum),[75] we obtain ΔI = 3.90, which again is higher than the observed ΔI. The findings in the case of methanol confirm our conclusion[46] that most of ΔH_h of e^-_{solv} is due to solvent polarization and does not involve reorientation of solvent molecules. We have to conclude that the photionization of water and methanol follows the same pattern of behavior of nonassociated liquids.[67,76]

An alternative interpretation of the photoionization of water and methanol is to assume that H_2O^* undergoes ionization to give an excited $(OH^-)^*$ ion.

$$H_2O \xrightarrow{h\nu} H_2O^*$$
$$H_2O^* + H_2O \rightarrow H_3O^+ + (OH^-)^*$$
$$(OH^-)^* \rightarrow H + e^-$$

The released electron will undergo hydration to form e^-_{aq} only at a later stage. The transfer of the hydrogen-bond bridging proton is a very fast process, $t_{\frac{1}{2}} \sim 10^{-13}$, comparable in rate to the dissociation step

$$H_2O^* \rightarrow H + OH$$

This proton transfer may thus be significantly faster than the diffusion-controlled $H_3O^+ + OH^-$ reaction.[77]

We know very well that excited protonic acids have much higher dissociation constants than protonic acids at their ground states.[78,79] The ΔH of the reaction

$$H_2O + nH_2O \rightarrow H_3O^+_{aq} + OH^-_{aq}$$

is only 0.585 eV.[80] Thus, if the same reaction took place with H_2O^* excited to 8 eV, it could leave an OH^- ion with over 7 eV of excitation energy. This is considerably higher than the electron affinity of OH^-_{aq}, which is 6.35 eV (being about halfway between those of Cl^- and Br^-).

In this treatment we have assumed complete rearrangement of solvent molecules around H_3O^+ and OH^-. Let us assume now that we act without solvent rearrangement; thus the gain of energy in the proton attachment is just 7.15 eV, the proton affinity of H_2O,[69] and not $\Delta H_h(H_3O^+_{aq})$, which is 11.3 eV. In this case ΔH of the reaction

$$H_2O^*_{aq} + H_2O \rightarrow (OH^-)^* + H_3O^+$$

will be 8.0 - 11.3 + 7.15 - 0.59 = 3.26 eV. The latter value is considerably higher than the electron affinity of the nonhydrated OH, namely 1.89 eV.[81] In this treatment we did not take into account the stabilization of the OH^- by the polarization of the neighboring molecules, which may amount to about one eV out of the total $\Delta H_h(OH^-) = 4.85$.[73] This correction would have lowered ΔH to 1.4 eV and increased the electron affinity of the semisolvated OH^- to 2.9 eV. When we make use of the hydration energy of the electron, the ionization potential of the nonhydrated OH^- would decrease to < 1.3 eV. In spite of the uncertainties in the calculations, it seems that the proton transfer mechanism could account for the photoionization of water, whether it involves solvent molecule reorientation or not.

Repeating the same treatment for methanol, we know that its proton affinity is 7.8 eV,[82] whereas the ΔH_{solv} of H^+ in methanol is 10.0 eV and that of MeO^- is only about 1.7 eV. On the other hand, ΔH of the dissociation of methanol is not much higher than that of water as its pK is only about 2 units higher than pK_w.[83] We estimate ΔH of the autodissociation of methanol at < 0.75 eV. Thus

$$(MeOH^*)_{solv} + nMeOH \rightarrow (MeOH_2^+)_{solv} + (MeO^-)^*_{solv}$$

may result in MeO^- excited to 7.3 - 0.75 = 6.55 eV, which is by far higher than the electron affinity of MeO^-. Under nonsolvated conditions

$$(MeOH^*)_{solv} + MeOH \rightarrow MeOH_2^+ + MeO^-$$

Assuming a polarization solvation energy of 1.2 eV for MeO^-

$$\Delta H = 7.3 + 7.8 - 10.0 - 0.75 - 0.5 = 3.95 \text{ eV}$$

This is by far higher than electron affinity of the nonsolvated MeO^-, namely 0.39 eV,[84] and that of MeO^- solvated by polarization, only EA = 1.6 eV. Adding $\Delta H_h(e^-_{solv})$ to the process would make the ionization of the nonsolvated MeO^- an exothermal process. Even if solvation stabilizes MeO^- to an extent of 1.7 eV, its ionization would still be energetically favored.

In spite of the favorable energetics, methanol undergoes less extensive photoionization than water. The ratio e^-/H in MeOH is 1/30 compared with 1/7 in water. This difference may be explained by the less favorable orientation in the liquid phase, which does not allow every hydroxylic H to be in the optimal distance from an adjacent oxygen. Furthermore, the weaker C-H and O-H bond strengths in methanol (4.05 and 4.45 eV, respectively)[85] facilitate dissociation rather than ionization. The same trend is also observed in the radiolysis of methanol where the e^-/H is 1:2.2,[86] compared with 5.4:1 in water.[46]

The proton transfer mechanism without reorientation of solvent molecules may explain the increase of $\varphi(e^-_{aq})$ in the presence of molar concentration of methanol. In this case the reaction

$$H_2O^* + MeOH \rightarrow OH^- + MeOH_2^+$$

would be more exothermal by 7.8 - 7.15 = 0.65 eV than the analogous

$$H_2O^* + H_2O \rightarrow OH^- + H_3O^+.$$

The proposed mechanism differs from that of Boyle *et al.*[27] by not requiring any solvent molecule rearrangement that would take $> 10^{-11}$ sec; thus solvated H_3O^+ or e^- are not produced as primary products in our mechanism.

We have at present no evidence to help us to choose between the solvent effect mechanism, which is based on a rather approximate and simpleminded theory,[67] and the proton transfer mechanism, which is unique for protonic associated liquids but which is rather semiquantitative in calculating the ΔH of the proton transfer reaction under conditions that do not permit molecular rearrangement.

VII THE IMPLICATIONS OF PHOTOIONIZATION OF PROTONIC ASSOCIATED LIQUIDS TO PHOTOCHEMISTRY AND RADIATION CHEMISTRY

The rather unexpected general phenomenon of photoionization of protonic associated liquids, thoroughly investigated for the first time within the framework of this project, has important implications, both to the photochemistry and to the radiation chemistry of such systems. First, it is evident that a most reactive reducing species is readily produced photolytically in water and alcohols. The same phenomenon is expected to occur in glycols and other polyalcohols, as well as in various carbohydrates. If the photochemistry of amino acids or sugars involves photoionization, it could readily lead to intramolecular redox reduction, in which an electron extracted at one site is captured by the carbonylic entity at the other site of the same molecule.[87] The photoionization of glycine has been demonstrated, as has that of certain aromatic amines.[88]

From the photobiological standpoint it may be advisable to consider photoionization as an important pathway that involves long-range electron transfer rather than atom transfer. The notion that photoionization of simple neutral molecules may occur in the near uv or even in the visible has not yet reached the photochemist or photobiologist. In fact, the distinction between the "ionizing radiation" of the vacuum uv and the "nonionizing" radiation of lower energies, which has been the cornerstone of photochemistry to date,[89] seems to be outdated in view of our findings.

Not less important in our view is the impact of our findings on radiation chemistry in general and on that of water and aqueous solutions in particular. One of the most fundamental open questions in this field is the primary yield of electrons. Although the measured "primary" yield of electrons in radiolyzed water is about 3 per 100 eV,[90] the agreement between this value and the ion pair yield of water in the gas phase[35,91] may well be fortuitous, because it is expected that a considerable number of electrons recombine with H_2O^+ or OH radicals before having a chance to get out into the bulk of the solution. The argument that half the secondary electrons have energies below the ionization energy of water (12.6 eV)

and thus can get involved only in excitation processes,[92] which is valid for water vapor,[93,94] does not hold for liquid water if we know by now that quanta as low as 6.05 eV can induce ionization. The same revision is called for in the interpretation of the radiolytic behavior of alcohols.

It is evident that the "optical model,"[94] which is the most appropriate approach to the theoretical interpretation of the radiolytic behavior of materials, has to take into account the low-energy photoionization process at least in protonic associated liquids. In fact, low-energy ionization may be a major pathway in the radiolysis of such liquids. Although the energy absorption of photons is inhibited by the negligible absorption coefficient of associated molecules, these may still be excited by electrons carrying the same kinetic energies.[59] Further, as the energy spectrum of radiolyzed secondary electrons shows a maximum population in the 5 to 8 eV range,[95] the radiolytic energy deposition processes in associated liquids are expected to be more efficient than in the gas phase, except that they are counterbalanced by the "cage" effects. These eliminate many of the ion pairs and radical pairs before they have a chance to be detected by any chemical or physical means.

VIII GEOCHEMICAL AND COSMOCHEMICAL IMPLICATIONS OF THE PHOTOIONIZATION OF WATER

In this project we have demonstrated that water and other protonic associated liquids undergo photoionization by a single photon process at photon energies less than half those required for photoionization of the same molecules in the gas phase. This means that light of wavelengths as long as 200 nm, above the absorption band of oxygen, can induce photoionization in liquid water and produce hydrated electrons.

The photoionization of water at $\lambda > 190$ nm is of interest, not only from the theoretical standpoints of the photochemical and radiolytic behavior of associated protonic liquids (Part VII), but for its important geochemical and cosmochemical implications. Hydrated electrons, e^-_{aq}, the products of photoionization of water, are most potent reducing species ($E^o = 2.77$ volts)[46] superseded only by a few strongly electropositive metal atoms, i.e., the alkali metal and certain alkaline earths (excluding Mg). In any case, e^-_{aq} is by far a more reactive reducing agent than hydrogen atoms ($E^o = 2.0$ volts),[96] the "classical" products of photolysis of liquid water. Photoionization in a condensed state, unlike photodissociation, results in a product that may be ejected over considerable distances from the site of photon absorption. Unlike H + OH, which are formed in a solvent cage and tend to undergo very fast recombination,[40] the ejected electron may reach a distance of several molecular diameters from the site of ionization before undergoing solvation--a process that may take up to 5×10^{-11} sec.[97] At such a distance the probability of recombination with the parent ion is fairly low, and the electron may thus react with solutes at concentration of 10^{-6} M or less before being recaptured by a parent ion. The overall photolytic steady-state concentration of e^-_{aq} in the absence of scavengers may thus be significantly higher than that of the products of photodissociation.

When the light intensity is sufficiently high, the rate of reaction between the two e^-_{aq} to give H_2,[98]

$$2e^-_{aq} \rightarrow H_2 + 2OH$$

will efficiently compete with the removal of e^-_{aq} by reaction with OH and H_3O^+. Furthermore, the reaction of e^-_{aq} with H_3O^+, which is endemically present at 10^{-7} M concentration in neutral solution, will result in the formation of H atoms randomly distributed throughout the medium. This is in contrast to the photodissociatively generated H atoms, which are formed in the vicinity of OH radicals. These randomly produced H atoms have therefore a better chance to recombine to give H_2 than those produced by photodissociation in geminate pairs. The OH radicals formed simultaneously with the e^-_{aq} following the dissociation of H_2O^+,

$$H_2O^+ \xrightarrow{H_2O} H_3O^+ + OH$$

which also become randomly distributed, may now dimerize to give H_2O_2,[99] H_2O_2 may react with OH radicals to give HO_2 radicals

$$OH + H_2O_2 \rightarrow HO_2 + H_2O$$

which might be oxidized to O_2

$$OH + HO_2 \rightarrow O_2 + H_2O$$

Alternatively H_2O_2 may be photolyzed to give, in part, O atoms,[100]

$$H_2O_2 \xrightarrow{h\nu} 2OH$$
$$H_2O_2 \rightarrow H_2O + O$$

The latter will eventually dimerize to give O_2. In summary, the photoionization of liquid water significantly increases the probability of breaking up of the water to H_2 and $\frac{1}{2}O_2$.

In a closed system H_2 and O_2 will reach a steady-state concentration because of their reactions with H, e^-_{aq}, and OH radicals[98]

$$OH + H_2 \rightarrow H_2O + H$$
$$H + O_2 \rightarrow HO_2$$
$$e^-_{aq} + O_2 \rightarrow O_2^- \rightarrow HO_2$$

In an open system, however, the H_2 will diffuse out resulting in a net photolytic decomposition of liquid water far more extensive than would be caused by photodissociation.

Water can be photodissociated "irreversibly" to H_2 + O, but this process occurs only below 176 nm, in a region where most polyatomic species are strongly absorbing. Photoionization of liquid water thus provides a photolytic pathway leading to the formation of hydrogen and oxygen in a spectral region that is little obstructed by other simple molecular species. It should be remembered, however, that this unique pathway for the irreversible photolysis of water is available only to water in the liquid state or perhaps to water vapor at very high pressures.

The geochemical or cosmochemical implications of the preceding discussion is self-evident. We have demonstrated a plausible pathway for the planetary or interplanetary formation of molecular oxygen from liquid water, considering the relative ease of escape of hydrogen. Evidently the temperature and pressures have to be adequate to have water in the liquid state. In other words, liquid water is far more photosensitive than it would be if only photodissociation took place.

We have not investigated the photolysis of ice within the framework of this project. However, on the basis of our results in liquid water and in view of the available information on the behavior of electrons in ice,[101] we can make a few predictions. It is expected that ice will photoionize to the same or even higher degree than liquid water. The quantum yield of electrons measured in the presence of electron scavengers will be as high, if not higher, than in liquid water. The quantum yield of H atoms formed by photodissociation at the same concentrations of scavengers will be minimal because of the higher probability of geminate recombination of H + OH in the ice matrix. The net decomposition of ice in the absence of scavengers will be, however, by far lower than decomposition in liquid water. The reason is that the reaction

$$e^-_{aq} + e^-_{aq} \rightarrow H_2 + 2OH^-$$

which takes place in liquid water does not take place in ice, where two e^-_{aq} form a stable dimer, $(e^-_{aq})_2$, which is in equilibrium with e^-_{aq} and with nonhydrated electrons.[102] The latter, which are very short-lived in liquid water, are highly mobile in ice and will eventually recombine with OH radicals to give OH^-. A certain number of the labile electrons

will, however, encounter H_3O^+ ions, resulting in the formation of hydrogen atoms (hydrated or nonhydrated). The nonhydrated H atoms, which diffuse through the ice lattice if the temperature is not too low, may diffuse out of the surface either as atoms or, after recombining, as molecular hydrogen.

It should also be remembered that the absorption coefficient of ice in the 180 to 200 nm range is about three orders of magnitude lower than that of liquid water. This will result in a much more sparse distribution of the products of photodissociation and photoionization. The former products will have an extremely small chance for homorecombination (H + H or OH + OH) of adjacent radical pairs even at relatively high light intensities. The latter, which have a finite chance to escape recombination with the parent ion, will most probably become trapped electrons and bielectrons. In view of all that has been said on the photolysis of pure ice, it is expected that its rate of net photodecomposition in the same spectral region will be orders of magnitude lower than that of liquid water.

If water in a condensed state contains electron scavengers such as O_2, H_2O_2, N_2O, NO, NO_2, CO, and CO_2, these will be effectively reduced by the photolytic electrons, leaving an equivalent amount of OH radicals. Most of these scavengers are less reactive toward H atoms by many orders of magnitude, and in view of the effective geminate recombination of the H atoms, no effective reduction of dissolved scavengers would take place in the absence of photoionization. The OH radicals may now oxidize other simple molecules like CH_4 or NH_3 (to give CH_3 or NH_2) or add on to free radicals like CH_2, CH_3, NH_2, or CN. The products of these reactions, e.g., CH_2OH, NH_2OH, CNOH, and obviously CH_3OH, are undoubtedly of interest to chemical evolution. These products may subsequently react with each other or with e^-_{aq} and OH radicals and result in fairly complex chemical species.

The photoionization of condensed water at relatively long wavelengths, which produces dispersed OH and e^-_{aq}, allows effective scavenging by solutes present at concentrations low enough not to interfere with the

light absorption by water. The scavenging of the products of photodissociation, which are formed in geminate pairs, requires much higher concentrations of scavengers, which would, in most cases, absorb practically all of the incident light.

In brief, the photoionization of liquid water makes available a unique pathway for the formation of a large number of oxidized and reduced species in highly dilute aqueous solutions, the geochemical or cosmochemical importance of these processes is self-evident.

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