

Electron Photodetachment from Aqueous Anions. 1. Quantum Yields for Generation of Hydrated Electron by 193 and 248 nm Laser Photoexcitation of Miscellaneous Inorganic Anions[†]

Myran C. Sauer, Jr., Robert A. Crowell, and Ilya A. Shkrob*

Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

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Time-resolved transient absorption spectroscopy has been used to determine quantum yields for electron photodetachment in 193 nm and (where possible) 248 nm laser excitation of miscellaneous aqueous anions, including hexacyanoferrate(II), sulfate, halide anions (Cl^- , Br^- , and I^-), pseudohalide anions (OH^- , HS^- , and CNS^-), and several common inorganic anions for which no quantum yields have been reported heretofore: SO_3^{2-} , NO_2^- , NO_3^- , ClO_3^- , and ClO_4^- . Molar extinction coefficients for these anions and photoproducts of electron detachment from these anions at the excitation wavelengths were also determined. These results are discussed in the context of recent ultrafast kinetic studies and compared with the previous data obtained by product analyses. We suggest using electron photodetachment from the aqueous halide and pseudohalide anions as actinometric standards for time-resolved studies of aqueous photosystems in the UV.

1. Introduction: Background and Motivation

Photoinduced electron detachment from aqueous anions, such as halides and pseudohalides, is a rapid, efficient charge transfer reaction in which the solvent itself serves as an acceptor of the ejected electron (charge transfer to the solvent, CTTS).^{1,2} For any photoreaction, the quantum yield (QY) is one of the most important photophysical parameters, and electron detachment from the anions is no exception to this rule. Though many estimates for the quantum yields of hydrated electron generated in the course of CTTS photoreactions have been given in the literature, these estimates agree poorly with each other and depend strongly on the actinometric standards used. Furthermore, recent kinetic data (discussed below)^{3–14} suggest that the very approach used to obtain these quantum yields 20–40 years ago, by product analysis, was inherently inconsistent (as was realized by several authors in the 1960s).^{15,16} On the other hand, accurate QY measurements are necessary for understanding the photophysics of charge separation on short time scales.⁴ In this work, we report quantum yields and cross sections for 15 aqueous anions photoexcited at 193 and 248 nm. Due to unexpectedly complex photophysics and chemistry, these measurements turned out to be rather involved. This article deals mainly with these QY measurements per se and various complications encountered along the way. A meaningful interpretation of these QY data is possible only when these QY data on the free electron yield are combined with ultrafast kinetic measurements (as done in ref 4 for iodide); this task is deferred to another publication (part 3 of this series).¹⁷

In polar liquids, including aqueous solutions, some anions (X^-) exhibit absorption bands (CTTS bands) that are absent in their gas-phase spectra. Photoexcitation of these anions in their CTTS bands causes rapid (<180 fs for iodide,^{5a} <60 ^{5b} or <170

fs^{5c} for ferrocyanide), efficient (with the prompt QY approaching unity for halide anions)^{4,17} detachment of the electron from the photoexcited anion to the solvent. Solvated electrons generated in this reaction are observed on the time scale of 10^{-11} to 10^{-5} s.^{3–7,12–14} Because of the fundamental importance and perceived simplicity of this CTTS photoreaction, much effort has been devoted to studying the photophysics of electron detachment from halide anions. In particular, there have been several ultrafast studies in which the electron dynamics were studied on pico-^{3–7} and femtosecond⁵ time scales. These studies were complemented by state-of-the-art molecular dynamics^{18–20} and ab initio calculations² that shed light on the nature of the short-lived CTTS state and mechanistic aspects of the charge separation. Several other aqueous anions have been studied in addition to iodide, most significantly, ferrocyanide (hexacyanoferrate(II)),^{5b,c,13,14} which is a common source of hydrated electrons in photochemical studies. Interestingly, this polyvalent anion exhibited electron dynamics that were entirely different from those observed from the halide and pseudohalide anions.

For the majority of aqueous anions, fast kinetic studies of one-photon CTTS reactions were slow to come, because no convenient source of pulsed excitation in the UV (where these anions have their CTTS bands) was available. Recently, we used short 200 nm pulses (300 fs fwhm) to study the electron dynamics for several aqueous anions,^{12,17,21} including halides (I^- and Br^-), pseudohalides (HO^- , HS^- , and CNS^-), and divalent anions (SO_3^{2-} , CO_3^{2-}). These 200 nm studies, and complementary 250–220 nm studies carried out by Bradford and co-workers^{3–7} indicate the complexity of photoexcitation process in the CTTS systems. From these studies it appears that two different mechanisms operating in tandem are responsible for the electron detachment from the aqueous anions:

The first mechanism involves the dissociation of a short-lived CTTS state and results in a narrow distribution of the electrons around the parent species (X^\bullet radical or atom). Both the kinetic studies^{4,12,17} and molecular dynamics simulations²⁰ suggest the existence of a short-scale, attractive mean force potential

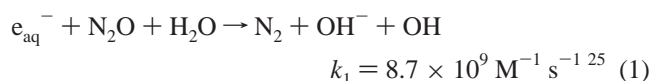
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* To whom correspondence should be addressed. Tel: 630-252-9516. Fax: 630-2524993. E-mail: shkrob@anl.gov.

between these electrons and the residual species (at least for halides and pseudohalides). The resulting kinetics exhibit a fast (10–50 ps) exponential component due to the recombination and escape of the electrons residing near the bottom of the mean force potential well. These fast kinetics are succeeded by a long-term $t^{-1/2}$ decay on subnanosecond (and longer) time scales;^{4,12,22} this decay is due to diffusional migration and recombination of the electrons that are thermally emitted from the potential well to the solvent bulk.

The second mechanism by which the hydrated electrons are generated is direct ionization of the anion by the UV photons. This competing process results in the formation of a mobile conduction band electron. This energetic electron localizes and thermalizes far from the parent species (>1 nm), and the resulting geminate decay kinetics are purely diffusional. According to our studies¹⁷ and work by Bradforth and co-workers,^{13,14} polyvalent anions yield this type of kinetics exclusively. Some polyatomic monovalent anions (e.g., thiocyanate) also seem to yield these kinetics only, even at low photoexcitation energy.¹⁷ For other monovalent anions, the direct ionization may or may not occur, depending on the excitation energy.^{10,11,17} E.g., for iodide, photoexcitation using light with wavelength > 220 nm yields decay kinetics that are independent of the excitation wavelength; however, 200 nm kinetics are very different from these 220–250 nm kinetics.^{11,17} In particular, the 200 nm kinetics exhibit higher escape yield of the electron and demonstrate other features that are consistent with broadening of the electron distribution around the iodine atom.¹⁷ Using two-photon excitation, Bradforth and co-workers¹¹ irradiated aqueous iodide at progressively higher energy and found that the escape yield systematically increased with the total excitation energy. These observations suggest a competition between the direct ionization and the CTTS process. Such a competition has been invoked previously to account for the observed increase in the quantum yield for electron detachment with an increase in photoexcitation energy (e.g., refs 23 and 24).

Most of the photophysical studies of anion CTTS were carried out in the 1960s, before the complexity of the electron dynamics was recognized. With few exceptions, the approach was to convert electrons to N₂ using 10 mM N₂O as a scavenger



and to measure the evolution of gaseous N₂. A high concentration of the scavenger was needed to prevent the loss of photogenerated free electrons to recombination.^{15,16} As a result, some geminate electrons were also scavenged, and this was recognized by Airey and Dainton (in their studies of ferrocyanide)¹⁵ and Jortner et al. (in their studies of iodide).²³ Picosecond kinetic studies justify the concerns of these authors because retrospective analysis of their data reveals many inconsistencies originating in the complexity of the electron dynamics.⁴ Although short-term exponential kinetics are too rapid to compete with the relatively slow reaction 1,^{4,12} long-term kinetics unfolding after this fast exponential decay are sufficiently slow, and some geminate electrons are scavenged by N₂O. Thus, a QY for N₂ evolution via reaction 1 provides an *upper limit* estimate for the QY of free electron formation. Because the relative weight of the fast (exponential) and slow (power law) kinetics varies for different photosystems (e.g., refs 4, 13, and 17) and depends on the relative efficiency of direct ionization and CTTS excitation for a given photon energy,^{10,11,17} even qualitative comparison between different photosystems is questionable.

Airey and Dainton¹⁵ pointed out another consequence of the geminate scavenging in N₂O-saturated aqueous solutions: In reaction 1, (geminate) electron is converted to a (geminate) hydroxyl radical. This radical rapidly reacts with the residual species X*, changing the product distribution. E.g., geminate OH radical can react with the cyanide ligand of ferricyanide that is formed in electron photodetachment from aqueous ferrocyanide; the resulting CN radical converts ferricyanide (hexacyanoferrate(III)) back to ferrocyanide.¹⁵ Consequently, the QY of the electron estimated from the ferricyanide yield is always *underestimated*. This conclusion pertains to other measurements in which the QY for the electron was estimated from the yield of a stable photoproduct derived from X* (e.g., I₃⁻ in the photoexcitation of iodide²⁶ and ferricyanide in the photoexcitation of ferrocyanide).²⁷

For higher excitation energies (180–200 nm), an additional source of uncertainty is actinometry. Dainton and Fowles^{28,29} based their measurements for OH⁻, SO₄²⁻, Cl⁻, and Br⁻ on the quantum yield of H₂ (0.3) in 185 nm photolysis of 0.01 M aqueous methanol (which, in turn, was estimated from the QYs of 0.3 and 0.46 for neat water and methanol, respectively, and the assumed QY of unity for photodissociation of aqueous N₂O),²⁸ whereas Jortner et al. assumed a QY of 0.65 for the same photosystem.³⁰ Such a discrepancy exists for other “standard” actinometers for the UV. E.g., the estimates for the QY of H₂ generation in the ethanol–water actinometer at 185 nm range from 0.4 to 0.8.³¹

It is apparent from the above that for the QY measurement to be reliable, (i) the electron yield should be determined directly, on a fast time scale, and (ii) precision photometry rather than actinometry should be used to determine the fluence of the UV photons. To our knowledge, only one previous study met these requirements. Iwata et al.²⁴ used pulsed UV light from an excimer laser and measured the absorbance of hydrated electron at 720 nm, ca. 50 ns after the end of the laser pulse. Photooxidation of water by Eu³⁺ was used for actinometry at 193 nm.³² For OH⁻, SO₄²⁻, Cl⁻, and Br⁻, the 193 nm measurement gave QYs that were not too far from the 185 nm yields obtained by Dainton and Fowles;²⁹ however, for I⁻, it gave a QY that was quite different from that obtained by Jortner et al.³⁰

In this work, we improve on these time-resolved measurements and extend the method to less common CTTS (and suspected CTTS) anions, such as carbonate, bicarbonate, nitrate, nitrite, chlorate, and perchlorate. We also give one-photon quantum yields for ionization of neat water by 193 nm light and dissociation of aqueous hydrogen peroxide by 248 nm light. In the course of this study, we realized that the QY data obtained by Iwata et al.²⁴ were compromised due to the absorption of the laser light by photoproducts generated within the duration of the laser pulse; our analysis includes corrections for this complicating effect. The correction is largest for anions that are efficient electron donors but absorb the excitation light poorly (e.g., SO₃²⁻ at 248 nm; Table 2) and anions that yield products that absorb strongly at the excitation wavelength (e.g., ferricyanide at 193 nm; Table 2). The absorptivity of these photoproducts can be estimated from the power dependence of the laser light transmittance, and we give such estimates for several species, including hydrated iodine atoms. Other complications included secondary chemistry, reactions of electrons with impurity (e.g., for hydrosulfide), competition between mono- and biphotonic excitation (for ClO₄⁻), protic equilibria (for HS⁻ and CO₃²⁻), ion pairing (for ferrocyanide), and the dependence of the QYs on the ionic strength of (concentrated)

TABLE 1: Decadic Molar Absorptivities (ϵ) of Selected Aqueous Anions and Absolute Quantum Yields (QY) for Generation of Free Hydrated Electrons from These Inorganic Anions by Single 193 and 248 nm Photon Excitation (Dilute Aqueous Solutions at 25 °C)^a

aqueous anion	248 nm (5 eV)		193 nm (6.43 eV)	
	QY	$\epsilon, \text{M}^{-1} \text{cm}^{-1}$	QY	$\epsilon, \text{M}^{-1} \text{cm}^{-1}$
[Fe(CN) ₆] ⁴⁻	0.674 ± 0.009	4273 ± 17 (+)	1.018 ± 0.050	7560 ± 43 (-)
SO ₃ ²⁻	0.108 ± 0.001	49 ± 1 (-)	0.391 ± 0.011	5990 ± 84 (+)
SO ₄ ²⁻			0.833 ± 0.023	46 ± 7 (-)
S ₂ O ₃ ²⁻	0.0252 ± 0.0003	412 ± 2 (-)	0.518 ± 0.016	3104 ± 36 (-)
CO ₃ ²⁻			0.453 ± 0.006	150 ± 20
HCO ₃ ⁻			0.070 ± 0.005	134 ± 2
Cl ⁻			0.463 ± 0.034	320 ± 12 (-)
Br ⁻			0.365 ± 0.011	11502 ± 154 (+)
I ⁻	0.286 ± 0.008	885 ± 3 (+)	0.497 ± 0.018	13250 ± 425 (+)
OH ⁻			0.112 ± 0.0015	3099 ± 15 (+)
CNS ⁻	0.0186 ± 0.005	60 ± 3 (-)	0.306 ± 0.003	10450 ± 3100 (+)
HS ⁻	0.0142 ± 0.0009	2170 ± 30 (0)	0.298 ± 0.015	5342 ± 73 (+)
NO ₃ ⁻			0.0064	7030
NO ₂ ⁻			0.066 ± 0.002	3517 ± 32 (+)
ClO ₃ ⁻			0.012 ± 0.001	424 ± 11 (-)
ClO ₄ ⁻			0.0043 ± 0.0001	0.565 ± 0.007

^a The signs of $\partial T/\partial Q|_{Q=0}$ (see eq 12) are given in the parentheses; the error limits indicate the standard deviation of least-squares fits, as explained in the text.

TABLE 2: Literature Data for Decadic Molar Extinction Coefficients ϵ of Aqueous Anions ($\text{M}^{-1} \text{cm}^{-1}$) at 193 and 248 nm Compared with the Values Obtained in This Work (Table 1)

anion	248 nm (5 eV)		193 nm (6.43 eV)	
	literature	this work	literature	this work
[Fe(CN) ₆] ⁴⁻	4480, ²³ 4730, ⁵⁰ 6000 ⁶⁷	4273	9170, ^a 8400 ⁵⁰	7560
SO ₃ ²⁻	30, ⁶⁸ 46 ⁶²	49		5990
SO ₄ ²⁻			125 ⁶⁸	46 ± 7
S ₂ O ₃ ²⁻	360 ⁶⁹	412		3104
CO ₃ ²⁻			630, ⁴⁹ 200 ⁵⁰	150
HCO ₃ ⁻			160 ⁴⁹	134
Cl ⁻			800, ⁶⁸ 470 ⁵⁰	320
Br ⁻			10 000, ⁶⁸ 12 000 ^{50,70}	11 502
I ⁻	400, ⁶⁸ 676, ⁶⁹ 900 ⁵⁰	885	14 000 ^{50,77}	13 250
OH ⁻			4000, ⁷⁹ 3000 ⁵⁰	3099
CNS ⁻	<100, ⁶⁸ 60–70 ⁵⁰	60	22 000, ^b 12 600 ⁵⁰	10 450
HS ⁻	1000 ⁶⁸	2170	10 000, ^c 6300 ⁵⁰	5342
NO ₃ ⁻			8000 ⁵⁰	7030
NO ₂ ⁻			3550 ⁵⁰	3517
ClO ₄ ⁻			<1 ⁷⁸	0.565

^a Calculated from the data of refs 14 and 23. ^b Calculated from the data of refs 72 and 73. ^c Calculated from the data of refs 68 and 71.

solutions. Because many of these anions exhibit one peculiarity or another, they are dealt with on a case to case basis (section 4). This survey is preceded by the analysis of pertinent photophysics given in section 3. To save space, some figures (Figures 1S–12S) are given in the Supporting Information.

2. Experimental Section

Setup. Unlike Iwata et al.,^{24,32} who used a 3 cm optical path cell and 90° detection at the cell midsection (where laser light was attenuated by the sample), a short optical path ($L = 1.36$ mm) cell and 30° detection were used in this work; i.e., all the electrons generated along the path of the excitation light were probed with the analyzing light. Another difference is our use of photometry instead of actinometry and direct measurement of the absorbed and transmitted laser power. These modifications

allowed us to deal with the complications introduced by the absorption of the laser light by photoreaction products.

Fifteen nanosecond fwhm, 1–20 mJ pulses from an ArF (193 nm) or KrF (248 nm) excimer laser (Lamda Physik LPX 120i) were used to photolyze N₂-saturated aqueous solutions of the anions. The optical cell had detachable 1 mm thick Suprasil windows sealed to the stainless steel body of the cell with Parafilm gaskets. Following the suggestion of Iwata et al.,²⁴ we used CaF₂ windows in some of the initial experiments; however, this material was found to be unsuitable due to rapid generation of color centers by 193 nm laser light and corrosion of these windows by photoexcited ions (such as thiocyanate). The refractive index for Suprasil is 1.508 at 248 nm and 1.56 at 193 nm,³³ and the calculated reflectivity of the window is 0.048 and 0.04, respectively. Typical transmittance of these windows at 193 nm was 90.6–91.5%. The reflection losses at the air–window boundary were factored into the QY calculation; the reflection losses at the glass–water boundary were ignored due to the similarity of the refraction indexes for the two media (for water, the refraction index is 1.4 at 193 nm and 1.35 at 248 nm,³⁴ so the reflection losses are <0.1%).

The laser beam was focused by a 50 cm focal length, 3 mm thick CaF₂ lens and uniformly illuminated a rectangular 3 mm × 6 mm, 130 μm thick brass aperture placed onto the front window. This laser beam was normal to the window. The beam energy was attenuated using a set of fine wire mesh filters placed 1.5 m away from the focusing lens (the pattern cast by these filters was destroyed by diffraction). The analyzing light from a superpulsed 75 W Xe lamp was passed through 4 cm of water (to reduce heat transfer to the sample) and a color glass filter (>500 nm) and crossed at 30° with the excitation beam. After traversing the sample, the analyzing light passed through another color glass filter and was focused on the detector using a 7 cm focal length achromat. The wavelength of the analyzing light (typically, 700 nm) was selected using a 10 nm fwhm band interference filter. With our beam and cell geometry, ca. 18% of the cell volume illuminated by the laser light was not probed by the analyzing light, and the effective mean path for the analyzing light was 1.29 mm. A correction was made to take this shadowing into account for the QY calculations.

A fast silicon photodiode (EG&G model FND100Q, biased at –90 V) with a 1.2 GHz video amplifier (Comlinear model

CLC449) terminated into a digital signal analyzer (Tektronix model DSA601) was used to sample the transient absorbance kinetics (3 ns response time). Two calibrated, NIST traceable, pyroelectric energy meters (Moletron model J25-080 with black oxide coating that provides flat spectral response in the UV) were used to measure the power of the incident and transmitted UV light. To this end, a small fraction of the excitation light was diverted to one of the meters using a thin Suprasil beam splitter before the sample cell; the second meter was placed ca. 50 cm behind the cell (where the beam is sufficiently expanded). The output signals from these energy meters were amplified using Gentec PRJ-D meters, terminated into 1 M Ω and sampled at 200 kHz using a 12-bit ADC board (National Instruments PCI-6064E). Eight to ten of these digitized waveforms were averaged, and the peak signals were converted to the laser energy using calibration values provided by the manufacturer. A series of 6–10 such measurements were collected and the energies given by the two detectors linearly correlated, to determine relative transmission of the laser light through the sample (this averaging and analysis was performed during kinetic sampling). Typical standard errors of the laser power and transmission measurements were 1–3% and 0.1–0.7%, respectively. Two power measurements, one for the cell filled with pure water and one for the aqueous solution being studied, were taken for each laser power. The difference between the measurements of transmitted energies (corrected by the window reflectivity) gave the number of absorbed photons, whereas their ratio (corrected by the ratio of incident laser energies) gave the transmission coefficient. To assess the reliability of the absolute power measurements, the readings from the J25-080 pyroelectric detector were compared with the readings from a thermopile detector (Gentec ED500 with EM-1 m). These two detectors were calibrated at 248 and 1064 nm, respectively. When the latter is corrected by 6% to take into account the reflectivity of the coating at 248 nm, the two readings were within 2% of each other.

Materials and the Flow System. An aqueous solution (0.2–0.5 L) of the salts was circulated through the cell using a peristaltic pump. The typical flow rate was 2–3 mL/min; the repetition rate of the laser was 1.7 Hz. ASTM Type I purified water (with conductivity <2 nS/cm) was used to prepare all of the aqueous solutions. The quality of water used to rinse the flow system was constantly monitored conductometrically (YSI model 35), and the optical cell was filled with a new sample only when the conductivity of the rinse water decreased to <1 μ S/cm. The UV spectra of the aqueous solutions were obtained using a generic spectrophotometer (OLIS/Cary 14).

Reagents of the highest purity available from Aldrich were used without further purification. For several reagents, purity was of special concern. Most brands of sodium chloride contain bromide and iodide impurity, and ultrapure 99.999% reagent was used. Sodium sulfite is oxidized by dissolved oxygen in water and the solutions were made using deaerated water and used immediately thereafter. *Ferrocyanide* typically contains *ferricyanide* impurity, and its aqueous solutions are not photo-stable; ultrapure 99.99+% reagent was used under anaerobic conditions, and the solutions were stored in the dark. Sodium hydrosulfide was available as a hydrate only (25 wt % of water was assumed from the specifications provided by the manufacturer) and contained traces of colloidal sulfur³⁵ that reacted with the electron ($k = 2 \times 10^9 \text{ s}^{-1}$ for 1 M HS⁻). Potassium thiocyanate (99.9+%) contained unidentified impurity that slowly reacted with the electron ($k = 4 \times 10^7 \text{ s}^{-1}$ for 1 M of CNS⁻). Hydrogen peroxide (1 M standard) was stabilized by

traces of tin; no absorbance from the stabilizer was apparent in the UV spectra. High-purity 0.989 N analytical standard KOH was used; the hydrosulfide and hydroxide solutions were purged by dry nitrogen and handled in a nitrogen box.

3. Quantum Yield Measurements: Analysis and Methodology

3.1. Analysis. In this section, we give basic equations needed for the determination of photophysical parameters. See the Appendix in the Supporting Information for derivation of these equations. Let us introduce x , the penetration depth of the excitation light, L , the sample thickness, $J(x,t)$, the laser radiance across the unit area of the sample at the delay time t (we assume uniform surface illumination), $J_0(t)$, the radiance of the light incident at the sample at $x = 0$, β , and β_{pr} , the molar absorptivities of the photolyzed species and the product, respectively, $c(x,t)$, the molar concentration of the photolyzate, $c_0 = c(x,t=-\infty)$, the initial concentration of this photolyzate, and ϕ , the quantum yield of the product. We will assume that (i) the absorption of the laser light by the photoproduct does not change the concentrations of this photoproduct and its precursor and (ii) the photoreactions are complete on a time scale that is much shorter than the duration of the laser pulse. With these assumptions, the absorption of the laser light obeys the following system of partial differential equations

$$\partial J(x,t)/\partial x = -([\beta - \beta_{\text{pr}}]c(x,t) + \beta_{\text{pr}}c_0)J(x,t) \quad (2)$$

$$\partial c(x,t)/\partial t = -\phi\beta c(x,t) J(x,t) \quad (3)$$

The sample-average photoconversion

$$\Phi = \langle c_{\text{pr}} \rangle / c_0 \quad (4)$$

is defined as the ratio of the end-of-pulse, mean-path product concentration

$$\langle c_{\text{pr}} \rangle = \frac{1}{L} \int_0^L dx (c_0 - c(x,t=\infty)) \quad (5)$$

and the initial photolyzate concentration c_0 . The mean concentration $\langle c_{\text{pr}} \rangle$ of the photoproduct may be determined from the optical density of this photoproduct at the probe wavelength (see below). For $\beta_{\text{pr}} = 0$, eqs 2 and 3 may be integrated analytically (see the Appendix) to obtain

$$\Phi = -D^{-1} \ln [1 - (1 - e^{-Q})(1 - T_0)] \quad (6)$$

where

$$Q = \phi\beta I_0 \quad (7)$$

is a dimensionless parameter, the quantity $I_0 = \int_{-\infty}^{+\infty} dt J_0(t)$ is the fluence of the excitation light at $x = 0$,

$$T_0 = \exp(-D) \quad (8)$$

is the laser transmittance at infinitely low light intensity ($Q \rightarrow 0$), and

$$D = \beta c_0 L \quad (9)$$

is the optical density of the sample. Note that the photoconversion Φ does not depend on the temporal profile $J_0(t)$ of the laser pulse; it depends only on the total photon fluence I_0 . The total number N_{abs} of photons absorbed by the sample per unit of area is given by

$$N_{\text{abs}} = I_0(1 - T) \quad (10)$$

where T is the transmittance of the laser pulse. For $\beta_{\text{pr}} = 0$ (see eq A24 in the Appendix),

$$\phi = L\langle c_{\text{pr}} \rangle / N_{\text{abs}} = (\Delta\text{OD}_{\lambda}^{\text{pr}} / \epsilon_{\lambda}^{\text{pr}}) / I_{\text{abs}} \quad (11)$$

where $\Delta\text{OD}_{\lambda}^{\text{pr}}$ is the (decadic) optical density of the photoproduct at wavelength λ of the analyzing light (assumed to be collinear with the excitation light), $\epsilon_{\lambda}^{\text{pr}}$ is the (decadic) molar absorptivity of this photoproduct, and I_{abs} is the total number of absorbed photons per unit area. The last quantity can be determined by subtracting the transmitted laser power from the incident power. Equation 11 provides a method for measuring a quantum yield from the initial slope of $\Delta\text{OD}_{\lambda}^{\text{pr}}$ vs I_{abs} (section 3.2).

As shown in the Appendix (see eqs A28 and A41 therein), for $Q \ll 1$ and any β_{pr}

$$\frac{T}{T_0} \approx 1 + \frac{1}{2}(1 - T_0) \left(1 - \frac{\beta_{\text{pr}}}{\beta}\right) Q \quad (12)$$

Formula 12 implies that the initial slope of the transmittance plotted as a function of the laser fluence has the same sign as the difference $\beta - \beta_{\text{pr}}$: at higher light fluence, the photolyzed species is converted to a product that is less (or more) absorptive and this makes the sample more (or less) transparent to the laser light. In the general case of $\beta_{\text{pr}} > 0$, eqs 2 and 3 cannot be solved analytically. However, the solution can be obtained numerically, using a finite-difference scheme. Figure 1Sb and 11Sa show typical results of this numerical integration. Because both the product and the substrate absorb laser light, eq 11 is no longer applicable, and for large Q , the quantum yield determined using eq 11 is smaller than the correct value. The first correction term for $Q \ll 1$ is given by

$$\phi \approx \frac{L\langle c_{\text{pr}} \rangle}{N_{\text{abs}}} \left[1 + \frac{\beta_{\text{pr}}}{4\beta}(1 + T_0)Q \right] \quad (13)$$

(see eq A44 in the Appendix). Note that eq 11 is *always* correct for $Q \rightarrow 0$; i.e., the quantum yield ϕ can always be determined from the *initial* slope of the plot of Φ vs N_{abs} . Numerical simulations suggest that for sufficiently small Q , the overall dependence of Φ on N_{abs} can be approximated by an exponential dependence (e.g., Figure 1S), which justifies the use of empirical eq 14 given below.

3.2. Methodology. The typical QY measurement included determination of four parameters: laser transmission T through the sample, the decadic transient absorbance (which was determined at the end of the laser pulse) $\Delta\text{OD}_{\lambda}$ of the photoproduct at wavelength λ of the analyzing light, the laser energy I_{abs} absorbed by the sample, and the incident beam energy I_0 . Several aqueous solutions of the salt were prepared so that the laser transmission through the sample varied between 0.1 and 0.8. The anion concentration and light fluence were chosen so that the decay half-time of this electron (due to cross recombination) was longer than 1 μs (for most photosystems, this time was 5–10 μs). For each of these solutions, the four parameters were determined and then $\Delta\text{OD}_{\lambda}$ was plotted as a function of I_{abs} . If the plots of $\Delta\text{OD}_{\lambda}$ vs I_{abs} were linear (or had a linear initial section), the initial slope of this dependence was determined by a least squares linear regression and QY was calculated using eq 11. This QY was then corrected for the window transparency and noncollinear beam geometry, as

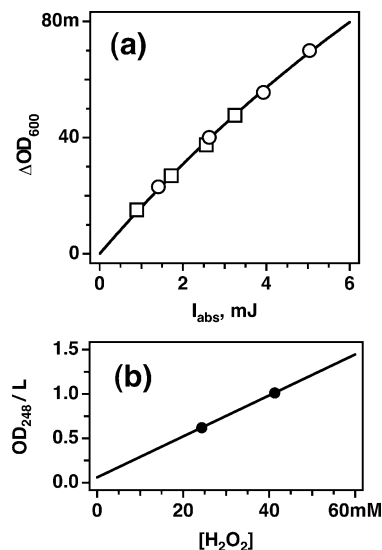


Figure 1. (a) Maximum transient absorbance of 600 nm analyzing light in 248 nm laser excitation of a solution containing 24.3 mM (open squares) and 41.3 mM (open circles) hydrogen peroxide and 1 M KHCO_3 plotted vs the absorbed laser power. The kinetic traces are shown in Figure 1Sa. This 600 nm absorbance signal is from carbonate radical formed by reaction 17; it is proportional to the yield of hydroxyl radicals photogenerated in reaction 16. The solid line is a least squares exponential fit using eq 14 (compare this plot with the simulated dependence given in Figure 1S). The negative curvature is due to the absorbance of 248 nm excitation light by photogenerated OH radicals (see Figure 2S and section 4.1.2). (b) Concentration dependence of OD_{248}/L ratio (hereafter, L is the optical path of the excitation light). The optical density OD_{248} of the solution was determined by extrapolation of the transmission data of Figure 2Sb to zero Q . The molar absorptivity of hydrogen peroxide at 248 nm can be determined from the slope of this plot.

explained in section 2. Some of the plots of $\Delta\text{OD}_{\lambda}$ vs I_{abs} were very curved (see section 4.2.2 and figures therein), even at low laser power. These dependencies were fit using an empirical formula

$$\Delta\text{OD}_{\lambda} \approx A[1 - \exp(-BI_{\text{abs}})] \quad (14)$$

where coefficients A and B were determined by least squares optimization. The initial slope was then estimated from the product AB . The use of eq 14 is justified by numerical simulations in section 3.1. If not stated otherwise, the absorption of hydrated electron at 700 nm ($\epsilon_{700} = 20\,560\text{ M}^{-1}\text{ s}^{-1}$)³⁶ at the end of the UV pulse (at 30 ns) was used to obtain the electron yield.

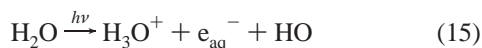
For all anion photosystems studied in this work, the plots of T vs I_0 (and, therefore, T vs Q) were fairly linear, and the molar extinction coefficients β for the anion and β_{pr} for the “photoproduct” (hydrated electron and radical X^*) were obtained as follows: The plot of T vs I_0 was fit using a least squares linear regression. The offset of the linear plot at $I_0 \rightarrow 0$ (i.e., $Q \rightarrow 0$) gave an estimate for T_0 (see eq 12). By plotting $D = -\ln(T_0)$ vs c_0 , an estimate for β was obtained (see eq 9). (In practice, we plotted the ratio OD_{λ^*}/L of the extrapolated decadic optical density at excitation wavelength λ^* and optical path L vs c_0 and determined the molar absorptivity ϵ of the anion from the slope of the plot; see Figure 1b). This estimate for β and the quantum yield ϕ (determined as stipulated in the previous paragraph) were used to calculate Q from I_0 and obtain $T_0^{-1}(\partial T/\partial Q)_{Q \rightarrow 0}$ from the slope of the linear plot. This quantity was plotted vs $(1 - T_0)/2$ for different concentrations c_0 , and the molar absorptivity β_{pr} of the product was determined from the

slope of this plot using eq 12. Where possible, we have justified this procedure by comparing the molar absorptivities determined from this procedure with the values determined spectrophotometrically (sections 4.1.2 and 4.4).

4. Results

This section is organized as follows: First, QY measurements for pure water at 193 nm and hydrogen peroxide at 248 nm are discussed. One-photon ionization of water at 193 nm is facile^{24,37} and its efficiency needs to be known to study electron detachment from anions that are poor absorbers of 193 nm light (e.g., chloride and perchlorate). Photodissociation of H₂O₂ by 248 nm light is a benchmark system to test the accuracy of our QY measurement (de facto providing an actinometric standard) as there have been very reliable QY measurements made by product analysis for this photosystem at 254 nm.³⁸ Second, we survey those photosystems for which the routine analysis outlined in sections 2 and 3 was insufficient. Third, the data on the anion absorptivities are summarized and compared with previous spectrophotometric data. Fourth, the discerned “photoproduct” absorptivities estimated by use of eq 12 are compared with the transient absorption data, where such data exist.

4.1. Benchmark Photosystems. *4.1.1. Photoionization of Water at 193 nm.* Absorption of 193 nm by water causes its ionization³⁷

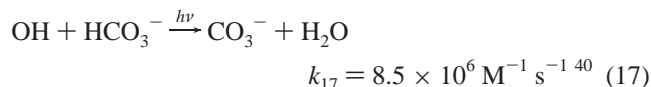


Taking into account the transmittance of the Suprasil windows, a decadic absorption coefficient of 1.4 m⁻¹ at 193 nm was estimated, in agreement with Quickenden and Irvin who gave 1.26 ± 0.03 m⁻¹ at 196 nm.³⁹ The absorbance of the electron at 700 nm induced by a 72 mJ/cm² pulse was ca. 1.75 × 10⁻³, and the QY was (1.40 ± 0.04) × 10⁻². A QY of (1.27 ± 0.17) × 10⁻² for hydrated electrons was obtained using a dc photoconductivity technique for an SF₆-saturated aqueous solution, by Bartels and Crowell, which also used an ArF excimer laser.³⁷

4.1.2. Photodissociation of Hydrogen Peroxide at 248 nm. Upon UV photoexcitation, hydrogen peroxide dissociates to two hydroxyl radicals,³⁸



These hydroxyl radicals can be rapidly reacted with bicarbonate



to yield carbonate radicals that absorb strongly at 600 nm (ε₆₀₀ = 1860 M⁻¹ cm⁻¹).⁴¹ We photolyzed 24.3 and 41.3 mM solutions of H₂O₂ in the presence of 1 M KHCO₃ (pH 8.33). Typical kinetics of 600 nm absorbance are shown in Figure 1Sa. The highest yield of the hydroxyl radicals estimated from our data was 300 μM (Figure 2Sa). As explained elsewhere,⁴² side reactions of hydroxyl radicals (e.g., with peroxide itself)⁴³ and cross recombination were too slow to compete with reaction 17 (carbonate radical was formed in 200 ns); the decay of the carbonate radicals was also too slow (5–15 μs) to deplete the concentration of these radicals at *t* = 200 ns (Figure 1Sa). The plot of the optical density at 600 nm vs absorbed laser power was slightly curved (Figure 1a), and the plot of the transmission vs the incident laser power exhibited a negative ∂*T*/∂*Q* slope

TABLE 3: Estimated Decadic Molar Absorptivity (M⁻¹ cm⁻¹) for Photoproduct(s) of 193 and 248 nm Laser Excitation of Selected Aqueous Anions (Obtained Using Eq 12)

anion	248 nm	193 nm
[Fe(CN) ₆] ⁴⁻	690 ± 120	14 320 ± 210
S ₂ O ₃ ²⁻	5046 ± 280	6640
SO ₃ ²⁻	1850 ± 190	
SO ₄ ²⁻		≈980
I ⁻		5565 ± 130
Br ⁻		2280 ± 310
Cl ⁻		≈1930

(Figure 2Sb). A quantum yield of 0.443 ± 0.01 for decomposition of H₂O₂ was obtained from the initial slope of the dependence shown in Figure 1b, and a molar extinction coefficient ε₂₄₈ of 24.8 ± 0.4 M⁻¹ cm⁻¹ was obtained at 248 nm. Our spectrophotometric measurement gave ε₂₄₈ = 26 M⁻¹ cm⁻¹ vs the reported 25 M⁻¹ cm⁻¹⁴⁴ (the absorbance of 248 nm light by bicarbonate was negligible, ca. 0.0206 M⁻¹ cm⁻¹). Our quantum yield compares well with the primary yield obtained by product analyses: 0.49 ± 0.07³⁸ and 0.47 ± 0.03⁴⁵ at 254 nm and 0.45 ± 0.06 at 222 nm.⁴⁶ Note that the accuracy of our measurement depends on the accuracy of the extinction coefficient for the carbonate radical, which is ±10%.⁴¹

The negative curvature of the ΔOD₆₀₀ plot in Figure 1a is accounted for by the absorption of 248 nm light by hydroxyl radicals generated by the laser pulse (as shown elsewhere, these radicals escape from the solvent cage in ca. 30 ps).⁴² Czapski and Bielski gave an estimate of ε₂₄₈(OH) = 500 M⁻¹ cm⁻¹.⁴⁷ Thus, under the conditions of our experiment, up to 20–40% of the 248 nm photons were absorbed by these radicals (Figure 2Sa, traces i and ii). Using our estimate for the molar absorptivity of peroxide and eq 12, ε₂₄₈ of 508 M⁻¹ cm⁻¹ was obtained for the hydroxyl radicals from the data of Figure 2Sb (this estimate neglects the conversion of OH radicals to CO₃⁻ radicals that occurred during the 248 nm pulse, which was less than 10%). Using this estimate and solving eqs 2 and 3 numerically, we were able to simulate the power dependence shown in Figure 1a (see Figure 1Sb). The estimates for the QY and the molar absorptivity of hydrogen peroxide and hydroxyl radicals obtained by our method agree very well with the estimates obtained by completely different techniques.

4.2. Special Cases. Most of the anion photosystems presented below were much like the benchmark system examined in the previous section: the ΔOD₇₀₀ plots of hydrated electron absorbance were linear or nearly linear with the absorbed laser power, the extrapolated absorbance at *Q* = 0 scaled with the anion concentration, etc. Some of the representative plots for these “perfect” systems are given in the Supporting Information (Figures 3S–7S), and the data are summarized in Tables 1–3; these results deserve little comment. Other systems exhibited more unusual features, and only those will be discussed below.

4.2.1. Carbonate (193 nm Photoexcitation). The peculiarity of the carbonate photosystem is the protic equilibria that involve the carbonate anion. The p*K*_a values for H₂CO₃ are 6.35 and 10.33 (at 25 °C),⁴⁸ and even dilute solutions of carbonate can be very basic. Let *c* be the molar concentration of the salt, *K*₂ be the second ionization constant, and *K*_w be the ionic product for water. For *c* > 1 mM, [OH⁻] ≈ [HCO₃⁻] ≈ 2*c*/(1 + [1 + 4*K*₂*c*/*K*_w]^{1/2}) and [OH⁻]/[CO₃²⁻] ≈ 0.0146/√*c*: the relative hydroxide concentration decreases with the carbonate concentration. Using accurate formulas, one can estimate that for 1.5 and 5.7 mM carbonate solutions (Figure 8S), the equilibrium concentrations of OH⁻ and CO₃²⁻ anions are 0.47 and 1.02 mM, respectively, and 1 and 4.7 mM, respectively. Because at 193

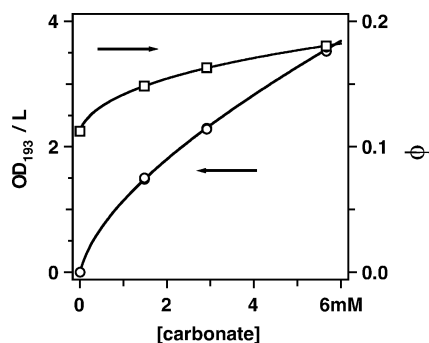


Figure 2. $[\text{Na}_2\text{CO}_3]$ dependence of the optical density of the carbonate solution at the laser wavelength (open squares) and “quantum yield” of photoelectron (open circles) in 193 nm laser photoexcitation of this solution. The concentration dependence of the “quantum yield” ϕ (given by eq 19) and the nonlinearity of the OD_{193} vs [carbonate] plot (see eq 18) originate through the photoexcitation of hydroxide, which is present in the carbonate solution due to (dark) protic equilibria. The solid lines were obtained by least-squares fit to the data using eqs 18 and 19.

nm hydroxide has 20.6 times higher molar absorptivity than carbonate (as shown below), the presence of hydroxide in the solution has significant implications. In particular, the often cited estimate for molar absorptivity by the carbonate at 193 nm, ca. $630 \text{ M}^{-1} \text{ cm}^{-1}$ (which can be traced back to the 1932 work by Ley and Arends)⁴⁹ is incorrect, as it does not take hydroxide into account. As demonstrated below, when the absorption of the UV light by the hydroxide is taken into account, carbonate and bicarbonate have very similar molar absorptivities at 193 nm.

The starting point of this analysis is the determination of ϕ and ϵ_{193} for hydroxide and bicarbonate at 193 nm. For the latter anion, the protic equilibria are inconsequential because the equilibrium concentration of hydroxide is maintained at ca. $2 \mu\text{M}$ due to buffering (Figure 9S). Both of these anions give linear ΔOD_{700} and OD_{193} plots (Figure 5S) and the corresponding data are given in Table 1. Figure 2 demonstrates the concentration dependence for the QY and 193 nm absorptivity for the carbonate system. Both of these quantities systematically increase with the carbonate concentration. Because the QY for electron detachment from bicarbonate is very low (0.07) this photoreaction may be neglected, and the dependencies shown in Figure 2 were interpreted in terms of competing absorbance of the 193 nm light by CO_3^{2-} and HO^- :

$$\text{OD}_{193}/L \approx \epsilon_{\text{OH}^-}[\text{OH}^-] + \epsilon_{\text{CO}_3^{2-}}[\text{CO}_3^{2-}] \quad (18)$$

$$\phi \approx \{\epsilon_{\text{OH}^-}[\text{OH}^-]\phi_{\text{OH}^-} + \epsilon_{\text{CO}_3^{2-}}[\text{CO}_3^{2-}]\phi_{\text{CO}_3^{2-}}\}/(\text{OD}_{193}/L) \quad (19)$$

The equilibrium concentrations of hydroxide and carbonate were estimated from the known ionization constants for carbonic acid,⁴⁸ so that only two parameters were unknown (the QY and molar absorptivity for the carbonate anion). Those were determined from the least-squares fit to eqs 18 and 19 which gave $\epsilon_{\text{CO}_3^{2-}}$ of $150 \pm 20 \text{ M}^{-1} \text{ cm}^{-1}$ (vs $134 \pm 2 \text{ M}^{-1} \text{ cm}^{-1}$ for bicarbonate) and a quantum yield $\phi_{\text{CO}_3^{2-}}$ of 0.453 (vs 0.112 for hydroxide). Note that in the above analysis we neglected the absorbance of carbonate radical that is formed in the course of the electron detachment. The latter has molar absorptivity of $685 \text{ M}^{-1} \text{ cm}^{-1}$ at 700 nm which is ca. 3% of that of the electron.

Though the hydrosulfide anion, HS^- , is also a strong base (H_2S has $\text{p}K_a$'s of 7.05 and 19),⁴⁸ the protic equilibria are unimportant because the deprotonation of HS^- is negligible. Even at the lowest hydrosulfide concentration used in this study

(0.23 mM), $[\text{HS}^-]/[\text{OH}^-] \approx 44$. Because the molar extinction coefficient for the hydrosulfide at 193 nm is 1.7 higher than that for the hydroxide, the contribution of the hydroxide to photolysis is negligible.

4.2.2. Ferrocyanide (248 and 193 nm Photoexcitation). At 193 nm, ferrocyanide exhibits a combination of a near unity quantum yield for electron photodetachment (Tables 1 and 4), a high molar absorptivity of the photolyzed anion,^{14,23,50} and an even higher molar absorptivity for one of the photoproducts (the reported ϵ_{193} for ferricyanide is $16\,300 \text{ M}^{-1} \text{ cm}^{-1}$)⁵⁰ As a consequence, the plots of ΔOD_{700} vs I_{abs} are strongly curved (Figure 3a) and photoconversion is extremely efficient (Figure 10S). The standard procedure used to extract the molar absorptivities using eq 12 gave $7560 \pm 40 \text{ M}^{-1} \text{ cm}^{-1}$ for ferrocyanide (Table 2) and $14\,300 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$ for the photoproduct (Table 3); see Figures 3b and 4b. Because the molar absorptivity of hydrated electron at 193 nm is ca. $2300 \text{ M}^{-1} \text{ cm}^{-1}$, the molar absorptivity for ferricyanide is estimated at $12\,000 \text{ M}^{-1} \text{ cm}^{-1}$, which is considerably lower than the value of $16\,300 \text{ M}^{-1} \text{ cm}^{-1}$ determined spectrophotometrically.⁵⁰ Furthermore, our estimate for ferrocyanide is also lower than the previously published values: 9170 ^{14,23} and $8400 \text{ M}^{-1} \text{ cm}^{-1}$.⁵⁰ Another peculiarity is that ΔOD_{700} vs I_{abs} plots obtained at different concentrations poorly match though all of these plots exhibit very similar initial slopes (Figure 3a, trace i). Numerical solution of eqs 2 and 3 using the obtained photophysical parameters reproduces the curvature of these plots but gives much less variation with the ferrocyanide concentration (Figure 11Sa).

The probable cause of these discrepancies is the considerable ion pairing that occurs in the ferrocyanide system.^{13,51,52} In the explored concentration range ($<0.7 \text{ mM}$) only single-cation association is important. Conductivity measurements of Davies⁵² suggest an association constant of 176 M^{-1} , whereas the optical measurements of Cohen and Plane⁵¹ suggest a somewhat lower value, $104 \pm 8 \text{ M}^{-1}$. Using the former value, we estimate that 30% of the anions are paired with a potassium cation in a 0.65 mM ferrocyanide solution. The $\text{KFe}(\text{CN})_6^{3-}$ anion is known to be a poorer absorber of the UV light than $\text{Fe}(\text{CN})_6^{4-}$.⁵¹ A closer examination of Figure 4a shows that absorption of the ferrocyanide solution at 193 nm is not exactly proportional to the concentration: there is a slight positive curvature. The latter can be explained by assuming the coexistence of free and associated anions that have slightly different molar absorptivities. Using the association constant given by Davies,⁵² we estimate that free ferrocyanide has ϵ_{193} of $7900 \pm 140 \text{ M}^{-1} \text{ cm}^{-1}$ whereas the associated anion has 17% lower absorptivity, $6580 \pm 400 \text{ M}^{-1} \text{ cm}^{-1}$. Progressive decrease in the absorptivity with the ferrocyanide concentration would account for the concentration dependence of the ΔOD_{700} vs I_{abs} plots in Figure 3a.

At 248 nm, ferricyanide is a much poorer light absorber than ferrocyanide (865 vs $4730 \text{ M}^{-1} \text{ cm}^{-1}$; Table 2) and the absorption of laser light causes photobleaching of the solution (Figure 12Sa). Both the QY and molar absorptivity of ferrocyanide at 248 nm are significantly lower than these quantities at 193 nm, and the behavior of this anion at 248 nm is much less extreme. Though the plot of ΔOD_{700} vs I_{abs} is curved, a single curve can be drawn through the data obtained for different ferrocyanide concentrations (Figure 12Sc). Spectrophotometric measurements suggest that the molar absorptivity of $\text{KFe}(\text{CN})_6^{3-}$ anion at 280 nm is just 2% lower than that of $\text{Fe}(\text{CN})_6^{4-}$;⁵¹ i.e., the ion pairing appears to be inconsequential for 248 nm photoexcitation. The estimated molar absorptivity of ferrocyanide at 248 nm, ca. $4300 \text{ M}^{-1} \text{ cm}^{-1}$, is close to values given in

TABLE 4: Absolute Quantum Yields of Free Hydrated Electrons for Photoexcitation of Inorganic Anions by 193 and 248 nm Light (25 °C Aqueous Solution)^a

aqueous anion	this work		ref 24			ref 17, 200 nm		product analyses (limiting yields) ^a
	248 nm	193 nm	248 nm	222 nm	193 nm	<i>t</i> = 0	<i>t</i> = ∞	
[Fe(CN) ₆] ⁴⁻	0.67	1.02				1.0	0.96	0.66 (254) ¹⁵ 0.65 (254) ²³ 0.45 (254) ²⁷ 0.66, 0.46 (254) ⁷⁴ 0.88 (214) ²³ 0.55 (254) ²³ 0.35 (254) ⁷⁵
SO ₃ ²⁻	0.11	0.39				0.35	0.23	0.71 (185) ²⁹ 0.43 (185) ²⁹ 0.49 (185) ^b 0.99 (185) ³⁰ 0.21 (229) ³⁰ 0.34 (185) ²⁹ 0.36 (185) ^b 0.68 (185) ³⁰ 0.22 (254) ²⁶ 0.29 (254) ¹⁶ 0.24 (229) ³⁰ 0.97 (185) ³⁰ 0.11 (185) ^{29,76}
SO ₄ ²⁻		0.83			0.73			
Cl ⁻		0.46			0.41			
Br ⁻		0.37			0.35	0.91	0.29	
I ⁻	0.29	0.50	0.22	0.27	0.47	0.90	0.42	
OH ⁻		0.11			0.11	0.38	0.09	
CNS ⁻	0.02	0.30	0.015	0.019	0.27	0.30	0.28	

^a Photolysis wavelengths (nm) are given in the parenthesis. ^b Calculated in ref 29 from the results of ref 30.

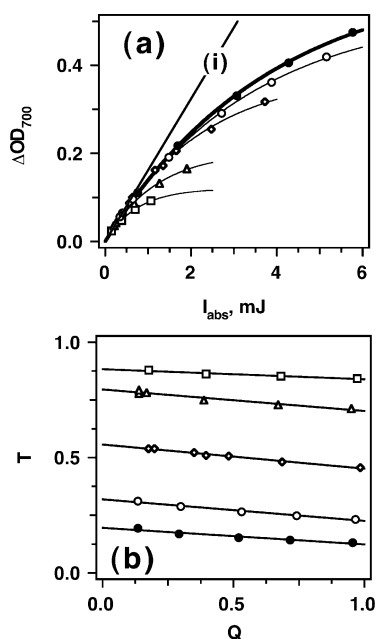


Figure 3. (a) End-of-pulse transient absorbance of photoelectron (observed at 700 nm) in 193 nm photoexcitation of aqueous potassium ferrocyanide plotted vs the absorbed laser power. The concentration of ferrocyanide was 50 μM (open squares), 100 μM (open triangles), 240 μM (open diamonds), 480 μM (open circles), and 695 μM (filled circles). The solid lines are least-squares fits to eq 14. The straight line (i) indicates the initial slope of these power dependencies; this slope does not depend on the ferrocyanide concentration. (b) Transmission of the 193 nm laser light in the same photosystem as a function of the dimensionless parameter $Q = \phi\beta I_0$ (the same symbols are used as in (a)). The negative slope indicates that $\beta_{pr} > \beta$ (eq 12). See Figure 4b for the plot of $1/T_0 (\partial T/\partial Q)_{Q=0}$ vs $(1 - T_0)/2$. Figure 11S exhibits a simulation of these plots using the formulas derived in section 3.

the literature (4480 M⁻¹ cm⁻¹,²³ 4730 M⁻¹ cm⁻¹⁵⁰). Our estimate for the “product” absorbance, 690 ± 120 M⁻¹ cm⁻¹ obtained using eq 12, is probably too low (the hydrated electron itself absorbs 248 nm light with a molar extinction coefficient of 600 M⁻¹ cm⁻¹).⁴⁴

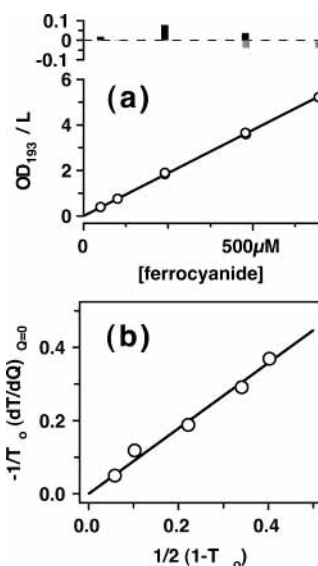


Figure 4. (a) Concentration dependence of path-scaled optical density OD_{193} (open circles) of ferrocyanide solution at the photoexcitation wavelength (see Figure 3). This density was determined by extrapolation of transmission T of 193 nm laser light to zero power (i.e., $Q = 0$) by linearization of the plots shown in Figure 3b. The solid line is a least squares line drawn through the experimental points; the residuals are given vide supra. (b) Plot of $-1/T_0 (\partial T/\partial Q)_{Q=0}$ vs $(1 - T_0)/2$ for five concentrations of ferrocyanide given in Figure 3b. A linear dependence is given by eq 12; the ratio β_{pr}/β can be determined from the slope of this plot.

4.2.3. Iodide: Secondary Chemistry. In the preceding analysis, it was implied that only a hydrated electron absorbs 700 nm analyzing light. For all halides and pseudohalides, with the exception of hydroxide, the residue X^* undergoes a hemicolli-gation reaction^{53–61}



(hydroxide undergoes a reversible deprotonation with the formation of O^- instead, with rate constant $(1.2–1.3) \times 10^{10}$

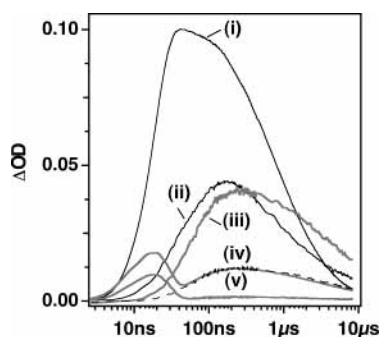


Figure 5. Formation and decay kinetics of transient absorbance in 248 nm laser photolysis of 2 mM sodium iodide solution (ca. 0.03 J/cm² flux of incident photons per pulse). Traces i and ii were obtained from N₂-saturated solution; traces iii–v were obtained from CO₂-saturated solution. Carbon dioxide served as a hydrated electron scavenger, traces ii and iii are of 400 nm absorbance, and traces iv and v are of 590 nm absorbance. The dashed line is scaled down trace iii. The delayed formation of transient absorbance in traces ii–iv is due to the generation of I₂⁻ in reaction 20. This reaction is faster in more concentrated iodide solutions (see Figure 3S). See section 4.2.3 for more detail.

M⁻¹ s⁻¹; see ref 12 for more detail). Most of the resulting X₂⁻ anions absorb in the near-UV and visible (see, for example, ref 56 for Cl₂⁻ and ref 59 for H₂S₂⁻) but only Br₂⁻ and I₂⁻ have absorbances at 700 nm. For Br₂⁻, the molar absorptivity at 700 nm is very low, ca. 380 M⁻¹ cm⁻¹ (2% of the electron absorbance)³⁶ and it can be safely neglected.^{57,58} For I₂⁻, this absorbance is not negligible because this anion has a strong absorption band centered at 720–750 nm.^{53–55,61} According to the survey by Elliot and Sopchyshyn,⁶¹ estimates for the molar absorptivity at the band maximum range from 2120 to 4000 M⁻¹ cm⁻¹, with 2560 M⁻¹ cm⁻¹ as the preferred value (which comprises 12.5% of the electron absorbance at 700 nm).³⁶ For iodine atoms, reaction 20 is rapid ($k_{20} = (0.88–1.2) \times 10^{10}$ M⁻¹ s⁻¹)^{53–55} and some I₂⁻ formation occurs by the end of the excitation pulse. To assess the degree to which this process interferes with the QY measurement, transient absorption kinetics in N₂ and CO₂ saturated solutions containing 2 mM iodide were obtained. Carbon dioxide served as an efficient electron scavenger²⁵ that removed the electron absorbance in ca. 40 ns; the residual absorbance was from I₂⁻. The progress of electron scavenging can be observed at 590 nm, where I₂⁻ does not absorb⁶¹ (see Figure 5, trace v). At 700 nm, the kinetics are composite: in the first 50 ns there is rapid decay of the electron absorbance; at later delay times there is the formation of I₂⁻, which is complete at 200 ns; after this initial growth, the signal slowly decays (Figure 5, trace iv). The formation kinetics of I₂⁻ can be observed with less interference from the electron at 400 nm, where I₂⁻ has a strong absorption band: $\epsilon = 10\,000$ M⁻¹ cm⁻¹⁶¹ vs 2300 M⁻¹ cm⁻¹ for the electron⁴⁴ (Figure 5, traces ii and iii). In Figure 5 we normalized this 400 nm trace iii so that the maximum signal at 200 ns matched that at 700 nm (dashed trace). It is seen from this plot that the end-of-pulse 700 nm signal from I₂⁻ comprises ca. 4% of the total signal in N₂ saturated solution (trace i in Figure 5). Our QY measurements for 193 nm were carried out using dilute iodide solutions (0.1–0.3 mM), and I₂⁻ formation was negligible. By contrast, the 248 nm measurements were done with more concentrated solutions (0.2–6 mM), and I₂⁻ formation was important at the higher end of this concentration range. For this reason, only 0.2–1 mM data were used for estimation of the QY; the 1–6 mM data were used for determination of the iodide absorptivity only.

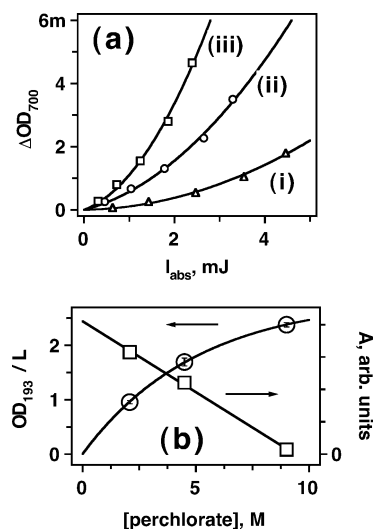


Figure 6. (a) Transient absorbance of 700 nm light at the end of the excitation pulse for 193 nm laser photolysis of (i) 9 M, (ii) 4.5 M, and (iii) 2.08 M NaClO₄ vs the absorbed laser power. All three power dependencies can be fit by a formula $\Delta OD_{700} \approx AI_{abs} + BI_{abs}^2$ (in which the first and the second term correspond to mono- and biphotonic excitation of the photosystem, respectively). (b) (Right, open squares) concentration plot of the optimum coefficient *A* thus obtained (which is proportional to ϕ) vs perchlorate concentration. The QY linearly decreases with [ClO₄⁻], the extrapolation of this plot to infinite dilution gives the photoelectron yield given in Table 1. (Left, open circles) concentration plot of the OD₁₉₃/L ratio for perchlorate. The observed nonlinearity is caused by a systematic blue shift of the absorption band of perchlorate with the ionic strength of the solution (see ref 21 for more detail).

For other photosystems studied in this work (with the exception of the carbonate and bicarbonate), no absorbances in the red from the corresponding radicals X* were found and reactions similar to reaction 20 are known not to occur for anions other than the halides and pseudohalides. Most of these radicals decay slowly by recombination and disproportionation in the bulk (e.g., refs 60 and 62). Given that the anion concentrations were low (typically, <2 mM), the effect of reaction 20 on the geminate recombination of (X*, e_{aq}⁻) pairs can be ignored.

4.2.4. Perchlorate: the Ionic Strength Effect. Perchlorate has very little absorbance at 193 nm, and to observe a signal, very concentrated (2–9 M) solutions were used (Figures 6a,b). As shown in part 2 of this series,²¹ for all anions, the addition of (chemically inert) salts, such as Na₂SO₄ and NaClO₄, causes a large decrease in the QY for electron photodetachment, ca. 6–10% per 1 M of ionic strength, and this pertains to the sulfate and perchlorate anions themselves. Though sulfate is a relatively strong absorber at 193 nm (46 ± 7 M⁻¹ cm⁻¹, Table 1), so that the QY can be determined in dilute solutions (4–20 mM) for which the ionic strength effect is minor, the extrapolated molar absorptivity for perchlorate (see below) is very low, ca. 0.57 M⁻¹ cm⁻¹, and the use of concentrated solutions is unavoidable. In such solutions, two other effects occur: the CTTS absorption band shifts to the blue¹ and the absorption band of the hydrated electron itself shifts to the blue (resulting in a 20% loss of 700 nm absorbance in 9 M NaClO₄ solution).^{21,63} Due to the anion band shift, the plot of OD₁₉₃ vs [ClO₄⁻] is nonlinear (Figure 6b), and the molar absorptivity given above was obtained from a polynomial fit to this plot and its extrapolation to zero concentration of the perchlorate. The plots of ΔOD_{700} vs I_{abs} exhibit a negative curvature, suggesting a competition between one- and two-photon excitation (Figure 6a). The plots were fit using the formula $\Delta OD_{700} \approx AI_{abs} + BI_{abs}^2$. Both of these coefficients linearly decrease with perchlorate concentration with

a slope of 11% per 1 M of ionic strength (Figure 6b). Similar slopes of 6–10% per M were observed for other anions in concentrated sulfate and perchlorate solutions (such as hydroxide, iodide, bromide, and sulfite).²¹ The extrapolated quantum yield for electron photodetachment from the perchlorate (at infinite dilution) is ca. 4×10^{-3} , which is 3 times lower than the QY for water itself. In 9 M perchlorate solution, almost no one-photon electron detachment occurs; the electron generation is completely biphotonic (Figure 6a).

For other anions, this biphotonic excitation was negligible. Furthermore, for all systems other than perchlorate, sufficiently high concentration of the anions can be used to avoid the photoexcitation of water at 193 nm (section 4.1.1). A more serious concern is the possibility that an impurity rather than the anion being studied yields electrons upon photoexcitation. Such a dilemma presents itself for all anions that exhibit low (<0.02) quantum yield for electron photodetachment. The presence of impurities in thiocyanate, chlorate, and hydrosulfide solutions can be discerned from the fact that electron half time was considerably shortened in these solutions. We believe that with the possible exception of thiocyanate at 248 nm and perchlorate at 193 nm, the involvement of impurity is unlikely because molar absorptivities of the low-QY anions (such as hydrosulfide, nitrite, nitrate, and chlorate; see Table 1) were actually quite large; moreover, these absorptivities compared well with the spectrophotometric data (Table 2). None of the impurity ions specified by the manufacturer (that are, typically, poor light absorbers such as sulfate, chloride, and transition metal cations) can account for the observed QYs at their expected concentrations.

4.3. Molar Absorptivities for Aqueous Anions. Table 2 provides a comparison between the molar absorptivities obtained in this study and those obtained spectrophotometrically, where such data are available. It must be stressed that for some of these anions, conflicting estimates of the absorptivities have been reported, especially at 193 nm, and it is not clear which values should be compared to ours. For most of these anions, at least one of the reported values was close to our estimate. For some anions (ferrocyanide, carbonate) there was a significant difference; the origin of these discrepancies has been addressed in section 4.2. A surprisingly large scatter exists in the literature for iodide at 248 nm (which is, after all, the benchmark system for CTTS studies): 400 to 900 $\text{M}^{-1} \text{cm}^{-1}$ (Table 2). We have carried out our own spectrophotometric measurement using 0.7 mM iodide solution and obtained $870 \pm 10 \text{ M}^{-1} \text{cm}^{-1}$ —in perfect agreement with the data of Tables 1 and 2.

4.4. Estimates for “Photoproduct” Absorptivities. Estimates for the molar absorptivity of “photoproducts” obtained using eq 12 are given in Table 3. Not all of the systems studied in this work provided good quality data for such a measurement, though the sign of $\partial T/\partial Q|_{Q=0}$ (and, therefore, the sign of $\beta - \beta_{\text{pr}}$) can be determined for all of these photosystems (these signs are given in Table 1). The analysis of these signs suggests that at 193 nm (248 nm) β was only greater than β_{pr} for anions whose absorptivities were greater than $3000 \text{ M}^{-1} \text{cm}^{-1}$ ($400 \text{ M}^{-1} \text{cm}^{-1}$, respectively). These values are not surprising because one of the “photoproducts”, hydrated electron, has an estimated molar absorptivity of $2300 \text{ M}^{-1} \text{cm}^{-1}$ at 193 nm and $600 \text{ M}^{-1} \text{cm}^{-1}$ at 248 nm.⁴⁴ To result in positive $\partial T/\partial Q|_{Q=0}$ slope, the absorptivity of the anion should be at least greater than that of the hydrated electron. For hydroxide excitation at 193 nm, this slope is only very slightly positive. Given the hydroxyl absorptivity of $500 \text{ M}^{-1} \text{cm}^{-1}$ at this wavelength,⁴⁷ one obtains that hydroxyl and electron in sum absorb 193 nm light with ϵ

$\approx 2800 \text{ M}^{-1} \text{cm}^{-1}$ —which is fairly close to the discerned “critical” value of $3000 \text{ M}^{-1} \text{cm}^{-1}$.

For sulfite radical, Hayon et al.⁶² give an estimate of $\epsilon_{280} = 630 \text{ M}^{-1} \text{cm}^{-1}$, from which $\epsilon_{248} \approx 1390 \text{ M}^{-1} \text{cm}^{-1}$ can be obtained using the spectrum of this radical given in the same work. Thus, at 248 nm $\epsilon(\text{SO}_3^-) + \epsilon(\text{e}_{\text{aq}}^-) \approx 1990 \text{ M}^{-1} \text{cm}^{-1}$ vs $1850 \pm 190 \text{ M}^{-1} \text{cm}^{-1}$ obtained from our data on electron detachment from sulfite (Table 3). For thiosulfate radical, Devonshire and Weiss⁵⁸ give $\epsilon_{375} \approx 1720 \text{ M}^{-1} \text{cm}^{-1}$, from which an estimate of $\epsilon_{248} \approx 5650 \text{ M}^{-1} \text{cm}^{-1}$ can be obtained using the spectrum of this radical given in the same work. Adding in the electron absorbance, one obtains $6250 \text{ M}^{-1} \text{cm}^{-1}$ vs $5046 \pm 280 \text{ M}^{-1} \text{cm}^{-1}$ in Table 3.

The extinction coefficients for halide atoms and sulfate radical at 193 nm are not known. From general considerations, one can expect that the absorptivity of SO_4^- , Cl, Br, and I increases with the polarizability. This trend is reflected in the data of Table 3. For iodide, the “photoproduct” (iodine atom and hydrated electron) has molar absorptivity that is much greater than $2300 \text{ M}^{-1} \text{cm}^{-1}$ (given by Nielsen et al. for the molar extinction coefficient of hydrated electron);⁴⁴ i.e., it is certain that the iodine atom absorbs 193 nm light. For bromide, the molar absorptivity of the “photoproduct” is close to that of the electron. For the other two anions, SO_4^{2-} and Cl^- , our estimates seem to be unrealistically low. This is not too surprising, because for these two anions even a relatively small error in the ratio β_{pr}/β estimated using eq 12 would cause large variation in the estimated “photoproduct” absorptivity (these ratios are, respectively, 21.2 and 6.1). Although these latter estimates may not be too reliable, it is clear that in many CTTS systems the absorption of the excitation light by the hydrated electron and the radical residue of the parent anion routinely occurs in the course of photoexcitation.

A pertinent question is, can this excitation change the QY? It is known from the kinetic studies of water ionization by Barbara and co-workers⁶⁴ that UV excitation of hydrated electron changes the escape yield of this electron due to the occurrence of geminate recombination suppression: the electron is excited into the conduction band and thermalizes further from the parent hole, so that the resulting solvated electron has a higher probability of escape. A similar decrease in the free electron yield after electron excitation has been observed for solvated electrons generated in sodide (Na^-) CTTS in tetrahydrofuran.⁸ According to Schwartz and co-workers,^{8–10} only electrons that are close to the residual sodium atom (and exhibit fast exponential kinetics) can be depleted via this photostimulated recombination. If that is also the case for aqueous CTTS photosystems, the UV excitation of electrons generated within the laser pulse is of little concern if this pulse is much longer than 10–20 ps, as is the case in this study.

5. Discussion

5.1. Comparison with the Previous Estimates. In Table 4, our estimates for the quantum efficiency of free hydrated electron generation in electron photodetachment from several anions (Table 1) are compared with (i) flash photolysis data of Iwata et al. for 193, 222, and 248 nm photoexcitation of the same anions,²⁴ (ii) ultrafast pump–probe kinetic and photometry data of Lian et al. for 200 nm photoexcitation (both the prompt and extrapolated free electron yields are given),¹⁷ and (iii) the estimates obtained using product analysis (mainly, using nitrogen evolution in reaction 1 for quantifying the electron yield) for 185, 229, and 254 nm (Hg line) photolysis. All in all, the quantitative agreement with the data of Iwata et al.²⁴ and the

product analyses of Dainton and Fowles²⁹ is quite reasonable. Reassuring as that may seem, this good correspondence is a result of error compensation (e.g., Iwata et al.²⁴ used a 10% lower estimate for the molar absorptivity of hydrated electron). It appears that Iwata et al.²⁴ systematically underestimated the QYs due to the occurrence of light absorbance by photoproduct(s). The good agreement between our 193 nm data for Br⁻ and HO⁻ and 185 nm data of Dainton and Fowles²⁹ is reassuring because it is known from the picosecond kinetic studies of Lian et al.¹⁷ that for these two anions, most of the geminate decay occurs in less than 50 ps and, therefore, geminate scavenging via reaction 1 is minimal. This is not the case for polyvalent anions such as sulfate, and QYs estimated from the N₂ evolution for such anions can be overestimated considerably. For ferrocyanide, almost no geminate decay was observed in the first 500 ps after 200 nm photoexcitation of this anion,¹⁷ and the closeness of the QY in 193 nm photoexcitation to the prompt (near unity) electron yield is not surprising. For 241 nm photoexcitation of ferrocyanide, Lenchenkov et al.^{13,14} observed a ca. 20% decrease in the electron concentration in the first 1.5 ns after the laser pulse; i.e., the geminate recombination is efficient and the QYs determined using the product analysis (in this case, N₂ and ferricyanide yields) depended strongly on the method used (Table 4).

For 254 nm photolysis of halide anions, especially iodide, the agreement between our QY estimates and those obtained by product analysis depends on which data sets are used (Table 4). As explained in section 1.1, the scatter in the latter estimates is traceable to corrections that were made to take into account scavenging of geminate electron in reaction 1. Most of the workers made no provision for such a reaction, and their results are suspect. Jortner et al.¹⁶ made the most consistent effort to make such a correction (without the benefit of knowing the geminate decay kinetics) and their best estimate for the QY (0.28–0.29) is close to ours. However, it should be stressed that some of their estimates were obtained by scavenging of the electron by sulfuric acid (with or without N₂O in the solution) and determining the electron yield from H₂ evolution; these particular sets of data are certainly incorrect because the QY for electron photodetachment depends on the ionic strength²¹ (this effect partially explains the inconsistencies noted by Bradforth and co-workers⁴).

5.2. Wavelength Dependence. For all aqueous anions studied in this work that yield hydrated electrons in the course of 248 nm photoexcitation, the QY of electron detachment in 193 nm photoexcitation is higher than in the 248 nm photoexcitation. When the QY data of Table 1 are complemented by 200 and 225 nm data obtained by Lian et al.¹⁷ and Iwata et al.,²⁴ respectively (see Table 4), the general trend of the increase of the free electron quantum yield with the excitation energy becomes apparent. As mentioned in the Introduction, a similar increase in the electron yield has been observed by Shirom and Stein²³ for photoexcitation of ferrocyanide and by Bradforth and co-workers for one- and two-photon excitation of iodide.¹¹

It is tempting to explain this behavior, in all of these cases, by an increase in the efficiency of direct ionization that is known to be more facile at higher excitation energy.¹¹ However, for some polyatomic anions, electron photodetachment is not the only photoreaction. From their kinetic studies, Lenchenkov et al.¹⁴ concluded that electron photodetachment from ferrocyanide by $\lambda > 224$ nm light (whose absorbance mainly facilitates metal-to-ligand transitions) is preceded by ultrafast internal conversion from the corresponding excited state to a dissociative CTTS state. It is not obvious that such a conversion is 100% efficient

for all wavelengths. At lower excitation energy, $\lambda > 250$ nm, ferrocyanide undergoes photoaquation (CN⁻/H₂O ligand exchange)⁶⁵ and thiocyanate photodissociates to sulfur and cyanide (for $\lambda > 236$ nm).⁶⁰ These photoreactions may occur, to a lesser degree, at higher excitation energies and compete with the electron detachment. In such a case, the increase in the electron yield with the photoexcitation energy may reflect a competition of the CTTS state dissociation with these side photoreactions rather than a competition between the latter and the direct ionization. Furthermore, for some of these anions the electron detachment could be concerted with other reactions. For example, photoexcitation of bicarbonate is likely to involve a concerted electron and proton transfer because the HCO₃ radical is extremely unstable in water.⁴⁰ This might account for a large difference between the QYs for electron detachment in 193 nm photoexcitation of bicarbonate and carbonate. Electron photodetachment from perchlorate is another possible example of electron transfer concerted with a rapid reaction of the residual radical, in this case, water oxidation (the ClO₄ radicals were observed in a low-temperature neon matrix only).⁶⁶

For several of the anions studied in this work (nitrate, nitrite, carbonate, bicarbonate, chlorate, and perchlorate) it is not settled whether their absorption bands in the UV actually involve a CTTS state, as their intramolecular transitions are known to occur in the same spectral region.¹ The occurrence of hydrated electrons does not settle the issue because these electrons can be generated via a direct ionization that does not involve a CTTS state. Nevertheless, relatively large QYs for bicarbonate, nitrite, and, especially, carbonate suggest that their CTTS states are indeed involved. For nitrite, this involvement has been suggested by Blandamer and Fox¹ who deduced it from the polarity effects on the position of high-energy, high-intensity subband.

5.3. Prompt vs Free Electron Yield. The QY for the free electron is given by a product of two quantities: the prompt QY of the electron and the fraction of photogenerated electrons that escape geminate recombination. Only ultrafast kinetic studies can give an estimate for these two quantities separately, and more detailed discussion of the prompt quantum yields will be given elsewhere. Combining the 220–250 nm results of Bradforth and co-workers^{3–7,11} and 200 nm results of Lian et al.¹⁷ (Table 4), it appears that the prompt QY for halide anions is near unity across the entire CTTS band whereas the prompt QY for pseudohalides is much lower, ca. 0.3–0.4 at the band maximum. The constancy of the prompt QY across the CTTS band is not a general property of the aqueous anions. For thiocyanate, the fraction of the escaped electrons increases by ca. 20% from 225 to 200 nm.¹⁷ It is unlikely that this fraction changes by an order of magnitude between 248 and 225 nm, as would be required to account for the QY of ca. 0.02 (at 248 nm, Table 1) if the prompt QY were constant between 200 and 248 nm (Table 4). The free electron QY for thiosulfate and hydrosulfide photoexcited by 248 nm light is more than 10 times less than that for 193 nm photoexcitation; again, it seems unlikely that a change in the escape fraction can be sufficiently great to account for this large decrease in the free electron yield.

6. Conclusion

Time-resolved transient absorption spectroscopy has been used to determine quantum yields for electron detachment in 193 and 248 nm laser photolysis of fifteen aqueous anions, including several anions for which no QYs have been reported (Table 1). Molar extinction coefficients for these anions at the laser wavelength were also determined (Tables 1 and 2) so that accurate cross sections for electron photodetachment can be

calculated from the data of Table 1. Furthermore, we have estimated the molar absorptivity of several photoproducts at these wavelengths; those estimates are given in Table 3. Our results for 193 nm photolysis of halide and pseudohalide anions correspond well with the previous estimates by Iwata et al.²⁴ and Dainton and Fowles,²⁹ and we suggest using these photo-systems as convenient short-wave actinometric standards for aqueous photochemistry. We also confirm the previous measurements of the quantum yields of water ionization (193 nm one-photon excitation)³⁷ and hydrogen peroxide dissociation (248 nm photoexcitation).^{38,45} The latter photosystem also provides a convenient actinometric standard for time-resolved studies.

It is shown that the QY for free electron formation systematically increases with the excitation energy, due to the increased efficiency of direct ionization at higher excitation energy and blocking of the alternative photoreaction routes. Relatively large QYs for electron generation in 193 nm photolysis of bicarbonate, nitrite, and carbonate suggest that their CTTS states are involved in the photoreaction, as was suggested by Blandamer and Fox.¹ Our data indicate that for polyatomic anions, both the free electron QY and the prompt electron QY increase with the photoexcitation energy, whereas for ferrocyanide and halides, the prompt electron QY is near unity across the whole CTTS band(s). Some of the anions were shown to be involved in thermal reactions (protic equilibria and ion pairing) that have significant implications for their photochemistry. Furthermore, as shown in part 2 of this series²¹ (and, for perchlorate, in this paper), the QY of electron detachment and the fraction of escaped electrons both decrease with an increase in the ionic strength when the latter is in the molar range. All of these observations point to the complexity of the primary photoprocess; there is little support for a popular claim that CTTS systems provide "simple" models for studying more involved electron transfer reactions.

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Supporting Information Available: An appendix giving the derivation of formulas in section 3 and captions to Figures 1S–12S and Figures 1S–12S. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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