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Electron Transfer Spectra and Their Photochemical Effects*

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I. INTRODUCTION

THE spectra discussed in this paper are often referred to as Electron Affinity Spectra. The designation Electron Transfer Spectra is more appropriate, since the common characteristic of these spectra is the transfer of an electron from one atom to another. In order that such a process may occur with considerable probability, the two atoms must be bound together by comparatively strong forces. However, the bonding must not interfere with the assignment of the electrons to individual atoms—in other words, the bond must be of an ionic or ion-dipole character, rather than a true atomic (electron-pair) bond.

The absorption bands which fall into this class include those of gaseous ionic molecules, ionic crystals, and simple and complex ions in solution. In the case of complexes, certain difficulties arise in connection with the interpretation of the chemical bonds. Complexes of the type of $Fe(CN)_6^{3-}$, which are characterized by high stability and a partial or complete compensation of the spin magnetism of the central ion, are customarily interpreted as containing true electron-pair bonds. For example, in the ferricyanide ion, six cyanogen ions are supposed to donate six electrons to the central ferric ion, so that six electron-pair bonds can be formed between Fe^{3-} and six CN radicals. The application of the magnetic criterion often leads to a qualitative distinction between otherwise similar compounds —e.g., between the complex amines of nickel and of cobalt—some being classified as "true" atomic complexes ("penetration complexes" according to Klemm's terminology), others as "ion-dipole" complexes (Klemm's "association complexes"). If this distinction is valid, the same criterion should also be used in the interpretation of the spectra of these complexes, since only ionic complexes can be expected to show typical electron-transfer bands. The known absorption bands of true atomic compounds correspond either to an excitation of their bonding electrons or to an excitation of individual non-bonding electrons, without their transfer from atom to atom. (For examples, see Mulliken[1, 1a] and McMurry and Mulliken.[1b])

However, it may be asked whether the distinction between "atomic" and "ionic" complexes does not imply a *qualitative* difference where only a *quantitative* difference exists. A comparatively small contribution of atomic (electron-pair) bonding to an essentially ionic (or ion-dipole) bond may be sufficient to "freeze" the spins and to prevent their orientation in an external magnetic field (whose orienting force is very weak compared to the strength of a chemical bond). If this suggestion is correct, the distinction between complexes with compensated paramagnetism and those with the full paramagnetism of the central atom reduces itself to differences in the proportional contribution of the electron-pair bonding, and even such diamagnetic complexes as $Fe(CN)_6^{4-}$ could perhaps be considered as associations of Fe^{2+} ions with CN^- ions, held together mainly by electrostatic forces. No qualitative distinction would then be necessary also between the spectra of "penetration" and "association" complexes.

As a matter of fact, the spectra of all complex ions which have been investigated far enough in the ultraviolet, contain bands whose position and intensity make their interpretation as "electron transfer bands" plausible. The extinction coefficients in the maxima of these bands reach or exceed 10^4—i.e., they approach the intensity of the absorption bands of organic dyes. These absorption maxima are much higher than those which some simple inorganic ions—and most complex ions—possess in the visible and near ultraviolet. For example, the maximum molar extinction coefficient of such an intensely colored ion as MnO_4^- is only of the order of $\epsilon = 2000$; that of CrO_4^{2-} (situated in the near ultraviolet), of the order of 4000. The absorption bands

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of colored cations, e.g., Ni^{2+} or Co^{2+}, are even much weaker —$\epsilon_{max} = 0.1$ or 1. These bands correspond to "prohibited" electron transitions in the metallic ions, made possible by the electric fields of oxygen ions (in MnO_4^- or CrO_4^{2-}) or water dipoles (in Ni_{aq}^{2+}). The "electron transfer bands" differ from these "electron excitation bands" by their much higher intensity, and are in general situated much further towards shorter waves, usually slightly above or even below 200 mμ.

II. ELECTRON TRANSFER SPECTRA OF GASEOUS MOLECULES

The electron transfer spectra of gaseous salt molecules have been identified by Franck and his co-workers in 1926. In a first step, Kondratjew,[2] working in Franck's laboratory, interpreted the fluorescence of alkali halide vapors, excited by extreme ultraviolet light, and first observed by Terenin[2a] as a consequence of the electron transfer process

$$A^+X^- \xrightarrow{h\nu} A^* + X.$$

(A^+X^- = ionic salt molecule, A^* = excited alkali atom, capable of emitting visible fluorescence, X = halogen atom.) In the process cited, the electron transfer from X^- to A^+ is supposed to lead to the dissociation of the molecule into an excited metal atom and a normal halogen atom.

Subsequent direct investigations of the absorption spectra of the alkali halide vapors by Müller[3] and particularly by Franck, Kuhn, and Rollefson[4] led to the conclusion that other electron transfer processes, similar to (1), but requiring less energy, result in the dissociation of A^+X^- into two normal atoms, A and X, or into a normal metal atom A and an excited halogen atom X^*. Figure 1 shows, as an example, the absorption curves of NaCl, NaBr, and NaI (in arbitrary units). Their interpretation as electron transfer spectra is supported by the frequency differences between the two peaks in NaBr and NaI (3300 and 7200 cm^{-1}) which correspond closely to the frequency differences between the two components of the ground multiplet ^2P in the atoms Br and I (3700 and 7600 cm^{-1}), and indicate a dissociation of Na^+X^- into $Na(^2S)+X(^2P_{1/2})$ and $Na(^2S)+X(^2P_{3/2})$, respectively. The corresponding distance in the Cl-spectrum is only 880 cm^{-1} and this accounts for the absence of doublet structure in the NaCl absorption spectrum.

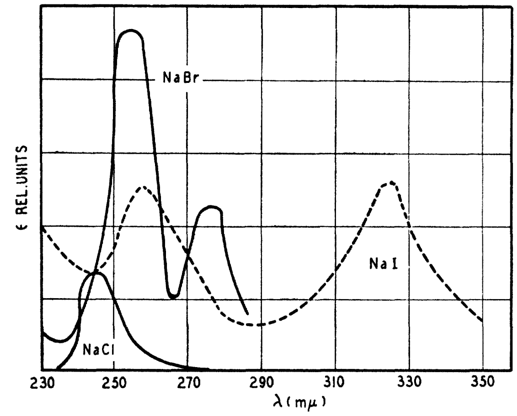

FIG. 1. Absorption curves of gaseous sodium halides (Franck, Kuhn, and Rollefson).

TABLE I. Absorption bands of cesium iodide vapor.

Band maxima (mμ)	Dissociation Products I	Cs	Δν (molecule) cm^{-1}	Δν (atom) cm^{-1}
324	$^2P_{3/2}$	6^2S	0	0
258	$^2P_{1/2}$	6^2S	7900	7600
239.5	$^2P_{3/2}$	6^2P	10900	11450
212.5	$^2P_{3/2}$	6^2D	16200	14550
199	$^2P_{1/2,3/2}$	6^2P or 7^2S	19400	18550
185	$^2P_{1/2,3/2}$	6^2D or 7^2P	23200	21850

Additional alkali halide absorption bands, situated further towards shorter waves, and responsible for the fluorescence of the alkali atoms, have been identified in an extension of the measurements of Franck, Kuhn and Rollefson[4] by Schmidt-Ott[5] in Franck's laboratory. Table I shows, as an example, the six absorption peaks measured by Schmidt-Ott in the spectrum of cesium iodide. The first band leads to the dissociation into two normal atoms; the second to the dissociation into a normal cesium atom and a iodine atom in the upper state of the ground doublet, $^2P_{1/2}$. The remaining four bands, however, lead to the formation of excited cesium atoms (in the states 6^2P, 6^2D, 7^2S, and 7^2P) which emit visible fluorescence by their return into the ground state 6^2S. This assignment of the bands is confirmed by the approximate equality of the distances Δν (molecule) between the band peaks, and the differences Δν (atom) between the corresponding terms in the spectra of atomic cesium and iodine.

The correspondence between $\Delta\nu$ (molecule) and $\Delta\nu$ (atom) is not exact, because the potential curves of the various upper states reached by light absorption are not exactly parallel. Figure 2 shows that the energy of the quantum corresponding to the maximum of absorption is determined by the energy of the corresponding dissociation products and by the difference Δ between the potential energies of the systems A^+X^- and AX, determined for *equal nuclear distances* (according to the Franck-Condon principle):

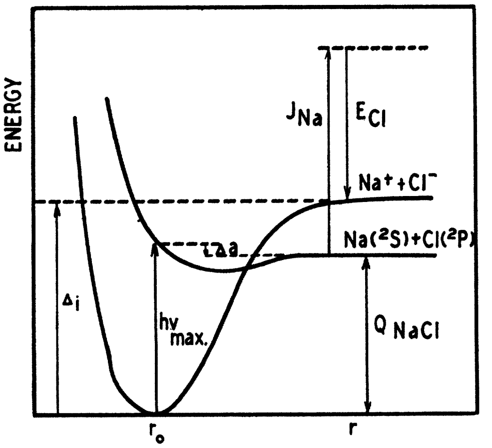

FIG. 2. Potential curves of NaCl. $h\nu_{max}=E_{Cl}-J_{Na}+\Delta$. $\Delta=\Delta_i-\Delta_a$.

$$h\nu_{max}=E_X-J_A+W_X+W_A+\Delta. \quad (1)$$

E_X is the electron affinity of the halogen E, J_A the ionization energy of the metal A, and W_X and W_A the excitation energies of the dissociation products. The first four terms in (1) determine the energy of the dissociation products relative to that of the free atoms A and X in their ground states. The meaning of Δ is obvious from the construction in Fig. 2—it is the difference between the energy of formation of the ionic molecule from free ions, and the energy of formation of the atomic molecule from (normal or excited) free atoms. The first term is large, the second small and usually becomes negative if determined for a nuclear separation equal to the normal A–X distance r_0 in the ionic molecule.

Variations in Δ, as well as those in E_X and J_A, contribute to differences in the positions of the corresponding bands in the spectra of alkali halides containing different cations or anions. In the anion series, the electron affinities decrease from Cl to I (86.5 kcal. for Cl, 81.5 kcal. for Br, and 74.2 kcal. for I, according to Mayer and Helmholz[6]) and the Δ values change in the same direction, because the main component of Δ is the electrostatic energy of formation of the ionic molecule from free ions, and this energy becomes smaller with the increasing size of the anion. Consequently, the corresponding bands shift regularly towards longer waves from chloride to bromide and iodide (e.g., the peaks of the first bands of CsCl, CsBr, and CsI lie at 247, 275, and 324 mμ, respectively). On the other hand, the exchange of a lighter alkali metal A in AX for a heavier one causes two antagonistic effects: the decrease in ionization energy tends to shift the bands towards shorter waves (because less energy is gained by the neutralization of a cation with a lower ionization potential), while the simultaneous increase in the radius of the cation leads to a decrease in the energy of formation of A^+X^-, thus making the term Δ in (1) smaller, and tends to shift the bands towards longer waves. The two effects compensate each other—sometimes so completely that, for example, the maxima of the first absorption bands of NaI, RbI, and CsI are all situated at the same wave-length—324 mμ.

TABLE II. Energies of dissociation of alkali halide molecules into normal atoms (at 0° abs. after Beutler and Levi).

	Thermochemical	Optical
NaCl	97.5	97.4
NaBr	87.7	88.2
NaI	70.7	72.3
KCl	101.2	101.2
KBr	90.3	90.6
KI	76.0	76.4

At the higher temperatures and densities, the absorption spectrum of alkali halide vapors spreads towards longer waves and a long series of diffuse bands appears, which correspond to transitions from different vibrational states of the ionic molecule into the shallow minimum of the atomic potential curve. The study of these band series, measured by Beutler and Josephy[7] and Sommermeyer,[8] permit the determination

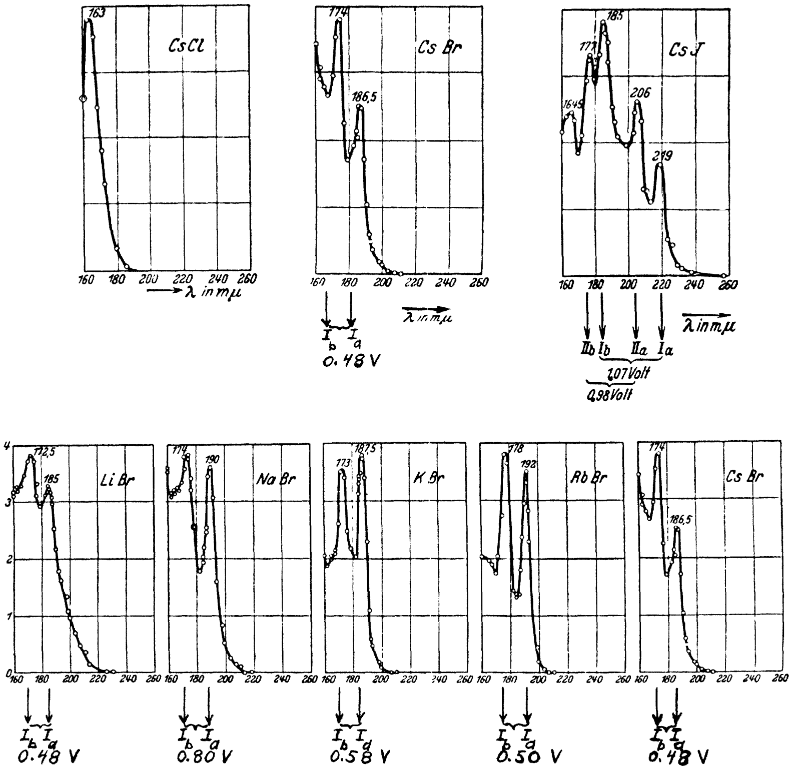

FIG. 3. Absorption curves of alkali halide crystals (Hilsch and Pohl).
Note: For Na Br, 0.80v should be 0.60v.

of the energy of dissociation of A^+X^- into the normal atoms A and X, and the results obtained in this way (Table II) are found to be in good agreement with figures calculated from thermochemical cycles (cf. Beutler and Levi[9]).

The theoretical calculation of Δ, and thus of the position of the absorption bands of alkali halide vapors, which must involve estimates of electrostatic attraction, molecular repulsion, van der Waals forces, and polarization forces in the ground state, and of repulsion, van der Waals attraction, and exchange forces in the upper state, although feasible, has not yet been pushed so far as the corresponding calculations for alkali halide *crystals* (cf. Section III). A semi-theoretical diagram of the ionic and atomic potential curves of sodium iodide has been given by Mulliken.[1]

III. ELECTRON TRANSFER SPECTRA OF CRYSTALS

The concept of electron transfer spectra has arisen in the theory of ionic crystals even earlier than in the spectroscopy of gases. Goldstein[10] discovered in 1896 the coloration of alkali halide crystals by ultraviolet light, and Pržibram[11] interpreted the "color centers" in these crystals as neutral alkali atoms formed by a photoelectric electron transfer from anion to cation. Pohl stressed the analogy between this phenomenon and the "photographic primary process" in silver halide crystals, which leads to the formation of the latent image. He and his co-workers (cf., for example, Hilsch and Pohl[12–14] and Pohl[15–17]) have investigated systematically the ultraviolet absorption spectra of numerous halide crystals and have also measured the "secondary" absorption spectra of the color centers, formed in these crystals by ultraviolet illumination.

Figure 3 shows the absorption curves of a number of alkali halide crystals, as measured by Hilsch and Pohl. The qualitative similarity with the spectra of the corresponding vapors is easily recognized. We find again the single band of the chlorides and the double bands of the bromides and iodides, with the corresponding peaks shifted towards longer waves in the progression ACl-ABr-AI. Again, no definite trend is observed in the series LiX-NaX-KX-RbX-CsX. The distances between the double peaks of the bromides vary between 0.48 and 0.60 ev, corresponding to 3900 to 4850 cm^{-1}, and these values are not very different from the doublet splitting of the ground term of Br (3700 cm^{-1}). The corresponding distances in the iodide spectrum vary between 0.95 and 1.19 ev, or 7700 and 9650 cm^{-1}, which is close to the doublet splitting of the ^2P term of iodine (7600 cm^{-1}).

These features of the spectra of alkali halide crystals are consistent with the assumption that the primary absorption process is the transfer of an electron from a lattice anion to an adjoining lattice cation, leaving the halogen atom either in the ground state $^2P_{3/2}$, or in the first excited state $^2P_{1/2}$. However, several problems arise in connection with the more detailed and quantitative interpretation of the spectrum. They concern, first, the absolute magnitude of the absorbed quanta; second, the interpretation of the multitude of peaks which exceeds simple doublet structure (particularly in the spectra of the iodides), and third, the photochemical consequences of the absorption, as revealed by the formation of color centers and of the photographic latent image. Connected with the last problem is the interpretation of the absorption bands of the color centers.

The electron transfer bands of the crystals are situated on the short wave side of the bands of the corresponding free molecules. This relationship is natural, since the symmetric arrangement of ions in the lattice decreases the electrostatic energy and makes the electron transfer from anion to cation more difficult. When Born[18] and Wolf and Herzfeld[19] first calculated the absorption frequencies from the electrostatic energy of the lattice, they arrived at figures even much larger than the observed ones—e.g., the calculated position of the first peak of NaCl was 109 mμ, as against an observed value of 158 mμ. Klemm[20] and von Hippel[21] showed that this discrepancy is due not to an error in the assignment of the bands, but to approximations involved in the calculations of Born[18] and of Wolf and Herzfeld.[19] The expression for the frequency of the first absorption peak in the crystal is, in analogy to (1),

$$h\nu = E_{\mathrm{X}} - J_{\mathrm{A}} + \Delta, \qquad (2)$$

where Δ represents the difference in energy between the normal ionic crystal, and the same crystal in which two adjoining lattice ions have been neutralized, *without changing the positions of the nuclei.* In the above-mentioned first calculations, electrostatic attraction only was considered in the determination of Δ. According to von Hippel,[21] the values calculated in this way have to be corrected (a) for the repulsive forces between the ions, (b) for the thermal energy and dilatation of the lattice, (c) for the energy of attraction of the lattice for the neutral atoms, and (d) for the polarization energy of the ions, whose neighbors have been neutralized and which are therefore situated in a field lacking the high symmetry of a complete cubic lattice. By means of reasonable assumptions concerning these correction terms, Klemm and von Hippel arrived at a satisfactory interpretation of the absorption frequencies. Correction (b) allows an explanation of the "red shift" of the absorption bands with increasing temperature, as observed by Fesefeldt.[22] (For example, in the case of rubidium bromide, the first absorption peak is shifted from 187 mμ at −186°C to 198 mμ at +220°C.)

The increase in electrostatic energy, caused by mutual neutralization of two ions in the lattice, is largest for two nearest neighbors in the lattice, and smaller for ions which are situated further apart—e.g., neighbors on the diagonal of the elementary cube, instead of its edge. On the other hand, the polarization energy gained in consequence of neutralization, is larger for a more distant ion pair. Von Hippel[21] attributed the complex structure of the absorption spectra, as shown by the iodides in Fig. 2, to the occurrence of electron transfers between ions which are not nearest neighbors. He suggested, in particular, that "diagonal" transfers are responsible for the occurrence of the second pair of absorption maxima (marked IIa and IIb in Fig. 3) with the same separation (about 1 ev) as shown by the main peaks Ia and Ib. The alternative interpretation of the short wave maxima as due to the formation of excited alkali atoms (similar to the explanations adopted in Table I) was opposed by von Hippel because he argued that excited levels of the ions (except those which, like the $^2P_{1/2}$ level of the halogens, do not increase the volume of the electron cloud) cannot be accommodated in the tightly packed ionic lattice. Excited cation terms are replaced, upon the formation of the lattice, by "energy bands" stretching over the whole of the crystal. Electrons transferred into these levels become free conductance electrons. The absence of photoelectric conductivity of alkali halides in the wavelength region represented in Fig. 3 argues against the assumption that any of the absorption peaks included in this figure correspond to electron jumps to such conductance levels.

The last of the three above-mentioned questions—that of the mechanism of the formation of color centers by ultraviolet absorption—has caused much discussion. As pointed out, among others, by Smekal,[23] the presence of two neutral atoms side by side in the lattice cannot represent a stable (or even metastable) state, since the electron will immediately return from the halogen to the metal. In order to produce long-living color centers, the electrons must either diffuse away from the original site of absorption (by jumping from one cation to another), until they are trapped in a "disturbed" lattice point, or they must be produced in the direct neighborhood of such a disturbance. The study of the quantum yield of the production of color centers by Smakula[24] and Hilsch and Pohl[25] shows that it increases with temperature (in the case of KBr, from 0 at −100°C to 1 at +400°C). This change is attributed by von Hippel to the increased probability of the diffusion of the electron away from the originally neutralized cation, brought about by thermal vibrations. Smekal,[23] on the other hand, has stressed the second possible mechanism of production of stable color centers—the absorption in already disturbed lattice points; he attributed to this phenomenon the observed extension of the first absorption band towards longer waves—a "tail," whose shape and intensity depends on the degree of imperfection of the crystal.

Smekal considered elastic stresses caused by the presence of impurities as the main cause of the trapping of electrons. Cations adjoining such imperfections have a higher electrostatic energy, and therefore a larger electron affinity than normal lattice cations; and once the electron has become attached to one of them it cannot continue its diffusion without the supply of additional energy. However, de Boer[26] pointed out that unoccupied lattice points also can function as electron traps. The existence of such empty lattice points in a perfect lattice is required by thermodynamic equilibrium conditions (cf., for example, Schottky,[27] Jost,[28] and Rabinowitch[29]). Gurney and Mott[30] discussed the possibility of electron trapping in a complete lattice by accidental sojourn of the diffusing electron in one elementary cell for a period sufficient for the readjustment of the heavy nuclei, but Mott[31, 32] acknowledged that de Boer's mechanism has the greatest probability. He pointed out that the electron is trapped not by a single cation adjoining the site of a missing anion, but by the "hole as a whole," i.e., by the combined field of the six cations surrounding the empty place Consequently, the greatest electron density occurs in the center of the hole, as if the electron would simply replace the missing anion.

The absorption bands of the "color centers" can originate either in neutral metal atoms, or in neutral halogen atoms imbedded in the lattice in consequence of absorption of ultraviolet light. Because of the non-existence of electronic excitation states of individual ions in the lattice, these bands too must be interpreted as electron transfer bands. In the case of electrons trapped in lattice holes or imperfections, these bands must correspond to an electron transfer to the nearest "normal" cation. From this cation, the electron can diffuse away by jumping from cation to cation, until it meets a halogen atom and recombines with it. The final photochemical effect is thus the disappearance of the color center and the restoration of the normal lattice. The interesting details of this photochemical "back reaction," cannot be discussed here.

The conditions in silver halide crystals are somewhat different from those in alkali halides. The wide extension of the photochemically efficient absorption band, the absence of pronounced extinction peaks, and the large photoelectric conductivity, first established by Lehfeldt,[33] make it probable that light absorption brings

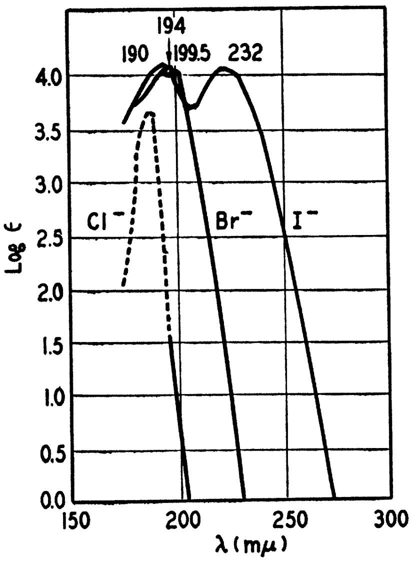

FIG. 4A. Absorption curves of halogen ions in aqueous solutions (Scheibe; and Fromherz and Menschik). (Cl⁻ curve in arbitrary units.)

the electron directly into a conductance level, without primary attachment to an adjoining cation (cf. Gurney and Mott[34]). In dye-sensitized plates, electrons must be ejected by light from the adsorbed dye molecules into the same conductance level. Because of the practical importance of the photographic process, a very large number of papers has been devoted to the elementary processes in silver halide crystals and emulsions, and we cannot enter here into the details concerning this special system. We may only mention that the decolorizing effect of light absorption by the "color centers" in alkali halides has its analogy in the destruction of the latent image by long wave radiation (so-called Herschel effect).

IV. THE SPECTRA OF ANIONS IN SOLUTION

The absorption bands of free hydrated anions in aqueous solution have been attributed to the electron transfer from the anion to water and designated as "electron affinity spectra" by Franck and Scheibe.[35] The bands of halogen anions have been observed and measured by Hantzsch,[36] Scheibe,[37,38] Fromherz and co-workers,[39–41] and Lederle,[42] those of OH^- and SH^- ions by Ley and Arends.[43,44] Figures 4 show the extinction curves of these five anions. The splitting of the Br^- and I^- spectra into two bands again suggests the formation of halogen atoms in the two states $^2P_{3/2}$ and $^2P_{1/2}$, although the distance between the two Br^- peaks ($\sim$2000 cm^{-1}) is somewhat too small compared to the doublet splitting of the term Br(^2P) (3700 cm^{-1}). The agreement is better in the case of I^- ($\Delta\nu$ (molecule) = 7300 cm^{-1} against $\Delta\nu$ (atom) = 7600 cm^{-1}). The origin of the two bands of SH^- is not clear, because their distance (10,000 cm^{-1}) appears too large to be explained by doublet splitting, and too small to be identified with the distance between the terms $3p\sigma^2\, 3p\pi^3\, {}^2\Pi$ and $3p\sigma\, 3p\pi^4\, {}^2\Sigma$ in the spectrum of the SH molecule.

Although, according to Eq. (2), the electron affinity E_X represents only one term in the expression for the energy quantum of the electron transfer, the general parallelism between the positions of the absorption maxima and the electron affinities of the anions can be quoted in support of the interpretation of the spectra in Figs. 4 as electron transfer spectra. This parallelism is illustrated by the values in Table III.

As to the anions other than the abovementioned halogens and "pseudo halogens," their absorption spectra have not been investigated far enough into the ultraviolet to reveal the location of the maxima of the electron transfer bands. An exception is the nitrate ion, NO_3^-, whose absorption spectrum, investigated by Scheibe,[46] shows an intense band (log ϵ_{max}

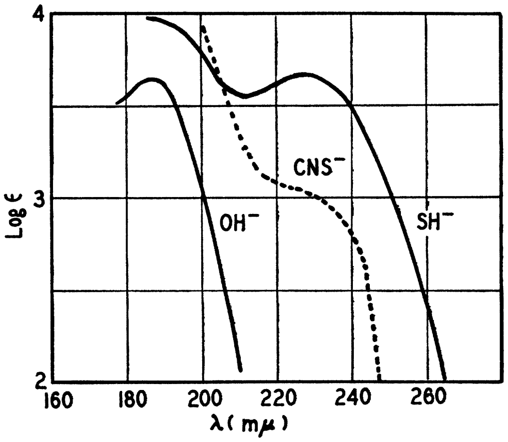

FIG. 4B. Absorption curves of pseudohalogen ions in aqueous solution (Ley and Arends, and von Kiss, Abraham, and Hegedüs). (CNS⁻ curve is approximate.)

=4.05) at 198 mμ. The steep rise in absorption towards shorter waves, which probably indicates the beginning of the electron-transfer absorption band system, was observed by Ley and Arends[47] for a number of monovalent organic anions, and is illustrated by Fig. 5. The monovalent, oxygen-containing inorganic anions ClO_4^-, HSO_4^-, HSO_3^-, are transparent down to 200 mμ, and the weak absorption which sets in below 200 mμ does not allow any conclusions as to the position of their electron transfer bands (cf. Ley and Arends,[44] Lorenz and Samuel,[48] Fromherz and Menschik,[39] Albu and Goldfinger[49]). The divalent ions CO_3^{2-}, $(COO)_2^{2-}$, SO_4^{2-} and SO_3^{2-}, absorb at longer waves than the corresponding monovalent ions, as shown by Fig. 6 (probably because the affinity for the second electron is smaller than for the first one).

The interpretation of the bands whose ascending parts are shown in Fig. 6 as electron transfer bands appears plausible because of their similarity (in respect to position and intensity) with the bands of the halogen anions. Many polyatomic anions possess additional bands in the medium and near ultraviolet, or in the visible, but these are considerably weaker, as shown by the example of the NO_3^- ion in Fig. 7. Even the absorption peaks of such intensely colored anions as CrO_4^{2-} and MnO_4^- are considerably lower than the typical electron transfer bands ($\log \epsilon_{max} = 3.6$ for CrO_4^{2-} at 370 mμ, cf. Rössler[50] and von Halban and Eisenbrand,[51] and $\log \epsilon_{max} = 3.3$ for MnO_4^- at 547 mμ, according to Hagenbach and Percy[52]). As mentioned in Section I, these bands are probably due to the electronic excitation of the central metal atom, rather than to an electron transfer process. In the case of organic anions, the absorption on the long wave side of the electron transfer bands may be due to weak chromophoric properties of the organic radicals—e.g. in the case of the ion HOOC·COO⁻ (Fig. 5)—of the second carboxyl.

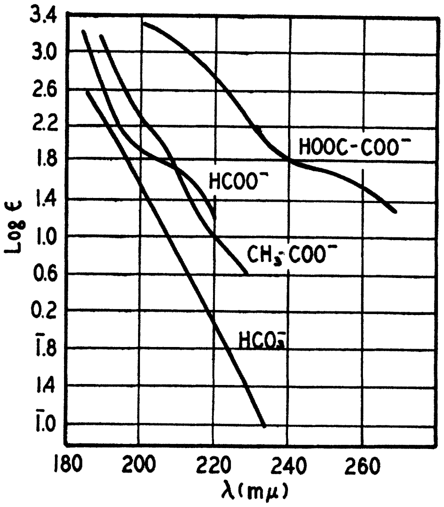

FIG. 5. Absorption curves of some organic anions (Ley and Arends).

TABLE III. Absorption maxima of hydrated anions.

	λ_{max}* (mμ)	ν_{max}* (cm^{-1})	E_X (kcal.)
Cl^-	181	55300	86.5
OH^-	187	53500	85†
Br^-	200	50000	81.5
CNS^-	224‡	44700	
I^-	226	44300	74.2
SH^-	227	44000	

* First band on the long wave end of the spectrum.
† Cf. Weiss, reference 45.
‡ Own observations.

The extremely weak bands observed by Brannigan and Macbeth,[53] Hüttig and Keller,[54] and Müller[4] in the near ultraviolet, in the absorption spectra of alkali and alkaline earth halides, were attributed by Hantzsch[36] and Fromherz and Menschik[39, 40] to impurities. A band at 355 mμ, often observed in iodide solutions, is due to the ion I_3^-, produced by oxidation of the iodide by atmospheric oxygen (cf. Wintner[55] and Job[56]). The existence of weak absorption bands, found by Lorenz and Samuel[48] in the spectrum of $NaHSO_4$ at 250 and 310 mμ, was denied by Ley and Arends;[44] these bands, too, must have been due to impurities.

The frequency of the electron transfer process in solution must be determined by an equation similar to (2), in which E_X now stands for the electron affinity of water and Δ for the electrostatic energy of the hydrated system before and after the electron transfer, with all nuclei in unchanged positions (according to the Franck-Condon principle), and therefore with the water dipoles still oriented towards the original site of the electric charge.

Franck and Scheibe[35] at first assumed that the electron, ejected from the anion, becomes a free "solution electron," and wrote down an

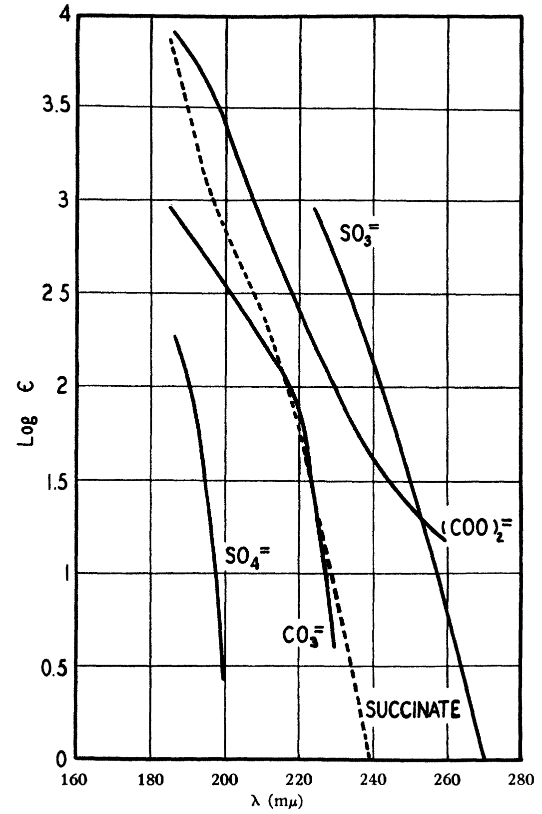

FIG. 6. Absorption curves of divalent anions (Ley and Arends).

energy equation which included the "solvation energy of a free electron." The existence of free electrons in water is, however, contradicted by experience, and Franck and Haber[57] substituted, for the original hypothesis of Franck and Scheibe, the assumption that the electron is transferred from the anion to a specific water molecule in the hydration sphere. To account for the photochemical effects of the light absorbed, e.g., by I^- or SO_3^{2-} anions (photodecomposition of hydroiodic acid and oxidation of sulfite to sulfate), they suggested that the electron transfer to a water molecule causes an immediate dissociation of the latter into OH^- and H, so that the primary light absorption act becomes, for example, in the case of the iodide

$$I^- \cdot (H_2O) \xrightarrow{h\nu} I + H + OH^-. \quad (3)$$

The corresponding equation for the absorption frequency is

$$h\nu = D + (E_I - E_{OH}) + \Delta, \quad (4)$$

where D is the energy of dissociation of H_2O into H and OH, E_I and E_{OH} the electron affinities of the two anions, and Δ, as usual, the change in the potential energy of the system caused by the electron transfer with unchanged positions of the atomic nuclei. L. and A. Farkas[58] pointed out that the dependence of the quantum yield of hydroiodic acid decomposition on concentration, observed by Warburg and Rump[59] as well as the effect of acidity observed by themselves[60] cannot be explained by the primary process (3) and suggested that the primary photochemical process in hydrated anions is analogous to that in gaseous and solid alkali halides and consists of an electron transfer from the anion to a water molecule

$$X^-(H_2O) \xrightarrow{h\nu} X(H_2O)^-. \quad (5)$$

This primary spectroscopic transition can be followed either by restitution of the original state, or by a further migration of the electron, e.g., by the secondary reaction

$$H_2O^- + H^+ \rightarrow H_2O + H. \quad (6)$$

This secondary reaction leads to the photodecomposition of HI in solution, and explains why the quantum yield of this process is dependent on hydrogen ion concentration.

If (5) is the elementary process, Eq. (4) for the band frequency can be replaced by Eq. (2), in which the electron affinity of a free water molecule, E_{H_2O}, is substituted for that of the metal ion, $-J_A$:

$$h\nu = E_X - E_{H_2O} + \Delta. \quad (7)$$

L. and A. Farkas[58] derived another equation:

$$h\nu = E_X + H_X - E'_{H_2O}. \quad (8)$$

Here, H_X means the hydration energy of the anion, so that $E_X + H_X$ is equal to the energy required for the removal of the anion from the solution, and its dissociation into X and an electron in the gas phase. The energy gained by bringing the neutral atom X back into the solution apparently is neglected in (8). E'_{H_2O} is designated as "electron affinity of water," but what it actually means is the energy gained by bringing an electron from vacuum into liquid water, associating it with a water molecule and building up, around this molecule, an unstable system of oriented water dipoles identical with the one which existed prior to the removal of the X^- ion (because the energy gained by the disintegration of this system was included in the term H_X). Consequently, the magnitude E'_{H_2O} (for which the authors calculated a value of 18 kcal. per mole) is not identical with the true electron affinity of free water molecules, and can be expected to vary from ion to ion. L. and A. Farkas quote the distances between the absorption bands of the anions Cl^-, Br^-, and I^- as a proof of the approximate constancy of E'_{H_2O}. They use the wave-lengths 206 mμ, 231 mμ, and 272 mμ, at which the extinction coefficients reach unity for the three halide ions, and compare the differences between the corresponding $h\nu$-values with the differences between the sums E_X+H_X:

	$\Delta h\nu$ (kcal.)	$\Delta(E_X+H_X)$
$Br^- - I^-$	18.6	17.3
$Cl^- - Br^-$	14.7	12.0

V. THE SPECTRA OF CATIONS IN SOLUTION

The "closed shell" type cations (Na^+, Mg^{++}, etc.) are so stable in solution that their electron transfer bands are situated beyond the spectroscopically accessible range. (A limitation of measurements to wave-lengths above 180 mμ is imposed by the absorption of water.) Heavy metal cations usually have absorption bands in the visible (Cr^{3+}, Ni^{2+}, Co^{2+}, etc.) or in the near ultraviolet, which correspond to transitions between different terms belonging to the same electron configuration. Such transitions are prohibited in free ions, but the Stark effect of the water dipoles transforms the multiplet structure of the spectrum, and makes some transitions permissible, although their intensity remains comparatively small, e.g., $\epsilon_{max} \leq 1$ for the colored ions of nickel, iron (compare Fig. 12), cobalt, and chromium. In *complex* ions, the effect of the surrounding atoms or ions on the energy levels of the central ion is even stronger, and the visible and near ultraviolet bands of such complexes are more intense, with ϵ_{max} values of the order of 100 or 1000.

Whenever the absorption spectrum of simple or complex cations has been followed far enough into the ultraviolet, much more intense bands have appeared, with peak values of the extinction coefficient reaching or exceeding 10^4. These bands may correspond to fully permitted transitions in the term system of the cation, but they may also be interpreted as electron transfer spectra, similar to those described above for the anions. (The energy of coupling with the water dipoles is, at least to the first approximation, the same for positive and negative ions of equal valency.)

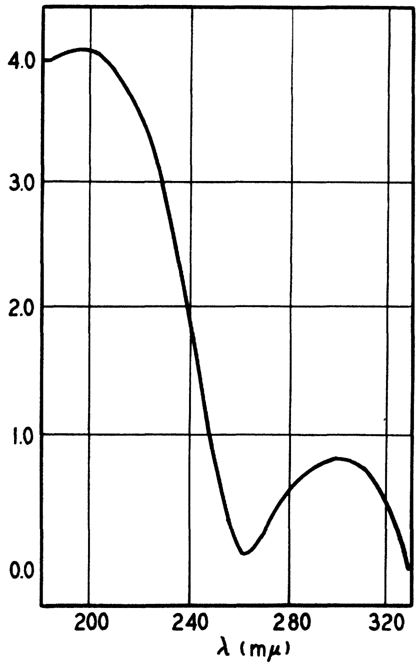

FIG. 7. Absorption curve of the nitrate ion (Scheibe).

In the study of the absorption spectra of simple heavy metal salts in solution, one has to contend with the tendency of their cations to associate themselves with the available anions (including the OH^- ions of water) forming different complex species. Similarly, the dissolution of a complex salt may lead to a variety of ionic species, formed either by dissociation or higher association of the original ions. This mixed nature of the heavy metal salt solutions makes a large number of published extinction curves almost valueless. The strongest observed bands can usually be safely attributed to one of the main ionic species, but medium and weak bands may often belong to some entirely neglected minor constituents, present only to the

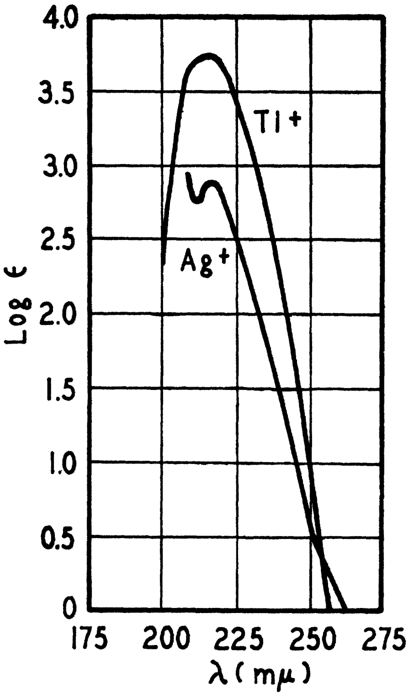

FIG. 8. Absorption curves of monovalent cations in aqueous solution (Fromherz, Menschik and Lih).

extent of 1 percent or 0.1 percent of the main component. For example, Samuel[61] and von Kiss, Ābrahām, and Hegedüs[62] observed, in ferric salt solutions, a rather strong band in the region of 330 mμ, which they attributed to free hydrated Fe^{3+} ions, but which was later found[63] to belong to the associated species $FeOH^{2+}$. Von Kiss and co-workers used for these experiments ferric perchlorate dissolved in 2.55 molar perchloric acid; but even this precaution proved to be insufficient. True, the capacity of perchlorate ions for association is so small that these ions do not interfere with the freedom of the Fe^{3+} ions; but the concentration of OH^- ions in 2.55 normal perchloric acid is large enough to produce appreciable quantities of associated ions $FeOH^{2+}$. The true extinction curves of non-associated polyvalent cations can be determined only by systematic investigations, using varying concentrations and acidities. The curves obtained by Fromherz and Menschik[39, 40] for the ions Ag^+ and Cu^{2+}, by Fromherz and Lih[64] for Tl^+ and Pb^{2+}, and later[65] for Hg^{2+}, by Doehlemann and Fromherz[66] for Cd^{2+} and Zn^{2+}, and by Fromherz and Walls[67] for Sn^{2+}, can be attributed to free (hydrated) ions. (In all these experiments, perchlorate solutions were used to eliminate associations with the acid anions). However, a partial association with OH^- ions cannot be considered as excluded even in these careful investigations. The extinction curve of the Fe^{3+} ion was constructed by Rabinowitch and Stockmayer[63] by combination of their own measurements with those of von Kiss, Ābrahām, and Hegedüs.[62] Potteril, Walker, and Weiss[68] determined the extinction curve of Fe^{2+} ions in the far ultraviolet; but this curve was obtained by using $FeCl_2$ and $FeSO_4$ solutions, and is therefore not reliable (nothing being known about the association of ferrous ions with Cl^-, SO_4^{2-} and OH^- ions). Weiss and Porret[69] determined the extinction curve of $Ce(ClO_4)_4$ solutions, but the influence of OH^- ions was not investigated, and much of the observed extinction may have been due to $CeOH^{3+}$ or similar associated ions.

Figures 8 and 9 show the extinction curves of some of the above-mentioned cations. The ions Zn^{2+} and Cd^{2+} approach the stability of the alkaline earth ions, and their absorption peaks must be situated far below 180 mμ.

If one decides tentatively to attribute the intense cation bands in the far ultraviolet, shown in these figures, to electron transfer processes, one has the alternative of postulating an electron transfer from ion to water (as assumed in the interpretation of anionic bands) or from water to the ion. Photochemically, the first process is equivalent to a photoreduction and the second to a photooxidation of water. We can surmise that ions of the oxidizing type (e.g., Fe^{3+} or Ce^{4+}) act as electron acceptors rather than electron donors; whereas ions of the reducing type (e.g., Fe^{2+} or Tl^+) may be expected to behave in the opposite way; but definite predictions as to the direction of electron transfer appear impossible in absence of the necessary thermochemical data. No attempts have been as yet made to calculate the terms Δ and E_{H_2O} in (7) and thus to provide a qualitative justification for the assignment of the ultraviolet bands of anions and cations in solution to electron transfers from and to water.

Potteril, Walker, and Weiss[68] interpreted the Fe^{2+} spectrum shown in Fig. 9 as an electron transfer spectrum. They formulated the primary process, according to the mechanism (3) of Franck and Haber, as

$$Fe^{2+}(H_2O)\xrightarrow{h\nu}Fe^{3+}+OH^-+H \qquad (9)$$

followed by

$$H+H\rightarrow H_2. \qquad (10)$$

This mechanism was postulated to account for the observation of Weiss[70] who found that ferrous sulfate solutions, illuminated by the light of a powerful mercury arc, evolve hydrogen. The quantum yield of this reaction was determined by Potteril, Walker, and Weiss to $\gamma=0.02-0.05$.

L. and A. Farkas,[58] who in the case of iodide decomposition, suggested the substitution of the pure electron transfer mechanism (5) for the transfer-and-dissociation mechanism of Franck and Haber, gave a similar re-interpretation of the primary photochemical process in ferrous salt solutions. The suggested primary reaction is

$$Fe^{2+}(H_2O)\xrightarrow{h\nu}Fe^{3+}(H_2O)^-. \qquad (11)$$

In the case of iodide decomposition, the subsequent reaction was assumed to take place between H_2O^- and H^+—cf. Eq. (6). Because the electron transfer from H_2O^- back to I (or Fe^{3+}) can occur almost instantaneously, L. and A. Farkas assumed that the secondary reaction (6) takes place by interaction with H^+ ions present in the immediate neighborhood of the $I(H_2O)^-$ complex at the very moment of absorption, rather than by a subsequent encounter. The probability of finding an H^+ ion close to the absorbing $I^-(H_2O)$ complex is enhanced by electrostatic attraction (Debye-Hückel's ionic cloud!). In the case of the $Fe^{3+}(H_2O)$ system, on the other hand, the H^+ ion is repulsed by the positive charge of the complex; the authors therefore considered the secondary reaction

$$Fe^{3+}(H_2O)^-+H^+\rightarrow Fe^{3+}(H_2O)+H \qquad (12)$$

as improbable, and suggested a different mechanism of hydrogen liberation, namely

$$Fe^{3+}(H_2O)^-\rightarrow FeOH^{2+}+H. \qquad (13)$$

In contrast to the photo-decomposition of hydroiodic acid and photo-autoxidation of sulfite, the photo-reduction of water by ferrous ions proceeds against the gradient of chemical potential (as shown by the fact that the normal potential of the ferro-ferri system is more

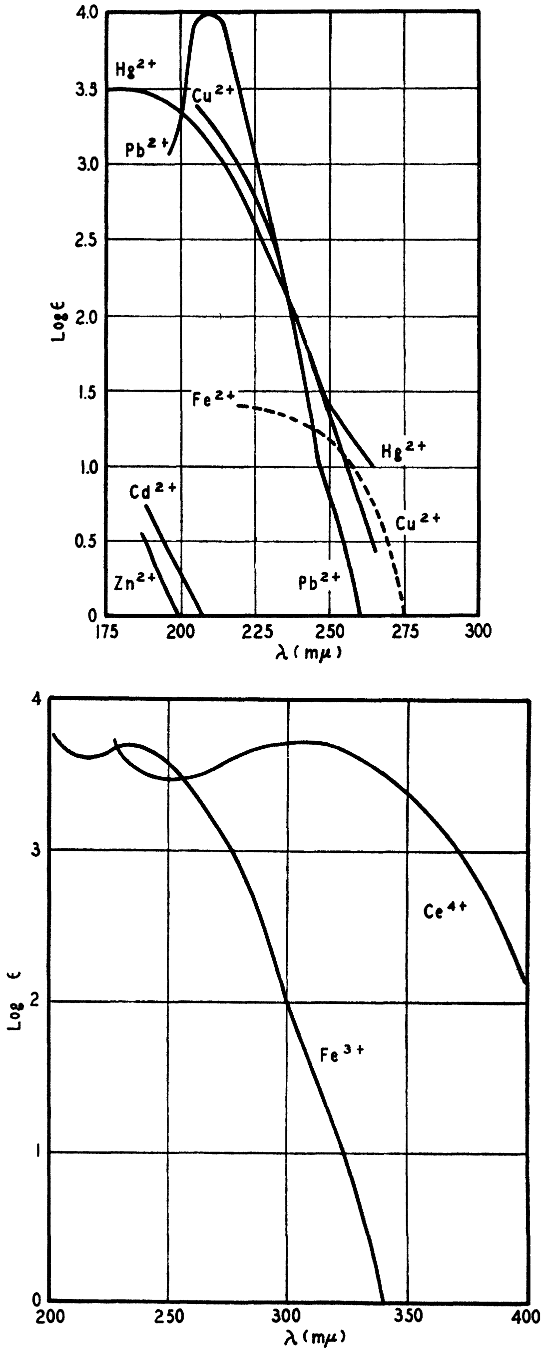

FIG. 9. Absorption curves of polyvalent cations in aqueous solution (Fromherz, and co-workers; Potteril, Walker, and Weiss; Weiss and Porret; and Rabinowitch and Stockmayer).

positive than that of the hydrogen electrode) and also against the gradient of total energy—i.e., with the conversion of a part of light energy into chemical energy. L. and A. Farkas[58] constructed an energy diagram which showed that, while the intermediate state $Fe^{3+}(H_2O)^-$ may lie 104 kcal. above the initial state $Fe^{2+}(H_2O)$, the final state of reaction (13), $FeOH^{2+}+H$, is situated only 67 kcal. above the initial state, and thus 37 kcal. below the intermediate state. Thus, the system in the intermediate state $Fe^{3+}(H_2O)^-$ has a choice of either returning back into the initial state, dissipating all the absorbed light energy, or sliding into the new, although comparatively shallow, energy trough and retaining about $\frac{1}{3}$ of absorbed energy. The small quantum yield ($\gamma=0.02$ to 0.05) observed by Potteril, Walker, and Weiss[68] may be looked upon as the measure of the relative probability of the two competing secondary reactions. However, the low quantum yield may be caused, in addition to the "primary" return of the electron, also by a "secondary" back reaction: $H+Fe^{3+}\rightarrow Fe^{2+}+H^+$ intervening between (13) and (10). This possibility was suggested by Potteril, Walker, and Weiss and confirmed by the observation that the quantum yield is further reduced by the addition of excess ferrous salt.

The energy calculations of L. and A. Farkas can be corrected for the neglected difference between free energy and total energy of the ferri-ferro system, and for the heat of formation of $FeOH^{2+}$ from Fe^{3+} and H_2O. The first correction lowers the energy of the final state, $(FeOH^{2+}+H)$, by about 7 kcal., because the oxidizing power of ferric ions is due not only to their higher energy but also to their smaller entropy. The second correction increases the energy of the final level by 12.3 kcal., because the first step in the hydrolysis of Fe^{3+} is endothermal to this extent (cf. Rabinowitch and Stockmayer[63]). Thus, the final state of reaction (13) must be at least 75 kcal. above the initial level, and probably somewhat higher (because of the potential energy of water dipoles, which have no time to re-orient themselves). These corrections do not affect the qualitative conclusion that the final state of (13) represents a drop in energy compared to the intermediate state $Fe^{3+}(H_2O)^-$. It may be argued, on the basis of the above-mentioned negative heat of formation of $FeOH^{2+}$, that the formation of this complex, as assumed in (13), does not give any advantage in energy compared to the straightforward dissociation $Fe^{3+}(H_2O)^-\rightarrow Fe^{3+}+OH^-+H$, and is distinctly less advantageous than the reaction $Fe^{3+}(H_2O)^-+H^+\rightarrow Fe^{3+}+H_2O+H$; but this applies only to the states reached after the separation and complete hydration of the ions; as far as the instantaneous electronic reaction with unchanged relative positions of the nuclei is concerned, the dissociation according to (13), which makes use of the electrostatic attraction between Fe^{3+} and OH^-, probably represents the easiest step towards hydrogen liberation.

The possibility of a photochemical electron transfer from water to the cation has been indicated by Weiss and Porret[69] in the study of ceric ions. They found that ceric perchlorate solutions, illuminated by the light of a strong mercury arc, evolve oxygen, and interpreted this effect by the equations:

$$Ce^{4+}\cdot H_2O\xrightarrow{h\nu}Ce^{3+}+H^++OH, \qquad (14)$$

$$OH\rightarrow \tfrac{1}{4}O_2+\tfrac{1}{2}H_2O. \qquad (15)$$

The primary process (14), which is analogous to Franck and Haber's process (3), should be replaced, according to the general concept of L. and A. Farkas[58] by the electron transfer process

$$Ce^{4+}(H_2O)\xrightarrow{h\nu}Ce^{3+}(H_2O)^+. \qquad (16)$$

The subsequent reaction can be written, in analogy to (6), in the form

$$Ce^{3+}(H_2O)^++OH^-\rightarrow Ce^{3+}(H_2O)+OH, \quad (17)$$

followed in its turn by the irreversible transformation (15). Reaction (14, 15) leads to a decrease in chemical potential. (The normal potential of the ceri-cero system, +1.6 volt, is higher than that of the oxygen electrode at *p*H 0.) Thus, it is probable that the transformation (17) is strongly exothermal, and the liberation of oxygen can occur with a substantial quantum yield. (However, even if the probability of the primary back reaction—i.e., of an immediate reversal of (16)—is not high, there remains the possibility of a secondary back reaction, $Ce^{3+}+OH\rightarrow Ce^{4+}+OH^-$, intervening between (17) and (15).

The occurrence of this back reaction is made plausible by the observation of Weiss and Porret that the presence of excess cerous salt has a depressing effect on the yield of oxygen liberation.)

The oxidation potential of ferric ions is considerably lower than that of ceric ions (0.75 against 1.6 volt), and a photoxidation of water by ferric ions would represent a photochemical reaction against the gradient of chemical potential, and a conversion of light into chemical energy. However, an approximate estimate of the energies involved in this reaction makes it appear less endothermal than the experimentally known photo-reduction of water by ferrous ions. (The ferri-ferro potential is closer to that of the oxygen electrode than to that of the hydrogen electrode.) There is therefore no obvious reason why ferric salt solutions—e.g., a solution of ferric perchlorate—illuminated by ultraviolet light in the region of 200–250 mμ, should not liberate oxygen—although, of course, the quantum yield of this reaction must depend on ionic radii, potential curves, and other specific factors which affect the competition between dissociation and primary back reaction, and probably will be found to be much smaller than the yield of oxidation of water by ceric ions.

The subject of the photochemical effects caused by the ultraviolet electron transfer bands of anions and cations in solution has only been tapped by the investigations of Warburg, Franck, Haber, and Weiss, and certainly deserves a more extensive study.

VI. THE SPECTRA OF CATION-ANION COMPLEXES

The absorption spectra of complex ions have been the subject of considerable study and discussion. However, the results have not been entirely satisfactory. On the experimental side, the above-mentioned difficulty of isolation of the absorption bands of single ionic species in the composite empirical extinction curves can be solved only by systematic study of the spectra under different conditions, whereas most authors were satisfied with the determination of one extinction curve for each compound, rapidly scanning in this way a long series of complexes. On the theoretical side, attempts to correlate the observed bands with transitions between known terms of the central ion, made, e.g., by Bose and Datta[71] and Karim and Samuel[72] were carried out without the realization of the extent of changes in the multiplet structure, caused by the electrical fields of the surrounding ions and dipoles. The analysis of the term systems of ions in electric fields of different symmetry has been developed recently for ionic crystals, but no calculations have been made for hydrated and associated ions.

Whenever the spectra of complex ions have been studied down to 200 mμ or lower, very intense bands have been observed whose positions and intensities are similar to those of the electron transfer bands of simple anions and cations. Bands of this type can be found, e.g., in the extinction curves given by von Kiss and von Szegledy[73] for cobaltic complexes, and by Samuel and co-workers[61, 74–76] for the complexes of Fe, Ni, Co; Ru, Rh, Pd; Os, Ir, Pt; Cr, Mn, Pb, and Re.

Because of doubtful identification and interpretation of these complex spectra, we will not speak of them here, but shall be satisfied with the discussion of the absorption spectra of simpler complexes, formed by the association of cations and anions in pairs or other simple, small groups. These spectra can be determined by systematic analysis of the extinction curves of polyvalent cations with a moderate tendency for association. Fromherz and Lih[64] analyzed the spectra of diluted solutions of lead halides in terms of superimposed bands of Pb_{aq}^{2+} and PbX_{aq}^{+}. Figure 10 shows such an analysis of the $PbCl_2$ spectrum. The fact that all extinction curves cross in one point confirms the assumption that only two species are involved. The same authors analyzed also the absorption spectra of $PbBr_2$ and PbI_2, and Fromherz[77] determined, from the changes in the relative intensity of the two bands with concentration, the corresponding association constants K, given in Table IV:

$$K = [\mathrm{PbX}^+]/[(\mathrm{Pb}^{2+})(\mathrm{X}^-)]. \qquad (18)$$

The assignment of the short wave band to free Pb^{2+} ions (in contrast to a previous suggestion of Koch and Pohl,[78, 79] who attributed it to undissociated PbX_2 molecules), is confirmed by its identity with the only absorption band

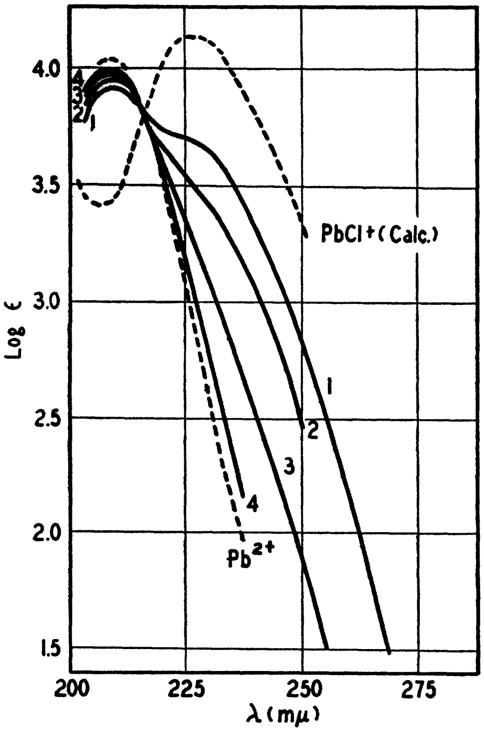

FIG. 10. Absorption curves of $PbCl_2$ solutions. $[PbCl_2]=0.028$ (1), 0.011 (2), 0.0028 (3) and 0.000092 (4) mole/l. Pb^{2+} curve from measurements on $Pb(ClO_4)_2$. $PbCl^+$ curve calculated (Fromherz and Lih).

observed in lead perchlorate solutions; while the assignment of the long wave bands to the ion-pairs PbX^+ (rather than to higher associates) is confirmed by experiments on $PbBr_2$ and PbI_2 in presence of a large excess of $Pb(ClO_4)_2$. (A large excess of Pb^{2+} ions must prevent any single one of them from associating with more than one anion, because of the equilibrium equation $Pb^{2+}(X^-)_n+(n-1)Pb^{2+}\rightleftharpoons n(PbX^+)$.)

The differences between the $\nu_{\max}$ of the bands of the three halides are 1900 and 4600 cm^{-1}, respectively. Assuming that these bands are due to the electron transfer

$$Pb^{2+}X^-\xrightarrow{h\nu}Pb^+X,$$

we can apply Eq. (2), and compare the $\Delta\nu$ values with the differences ΔE_X in the electron affinities of the three halogens (2300 and 3300 cm^{-1}, respectively). The shifts are in the expected direction and of the expected order of magnitude; as mentioned above changes in the term Δ may account for the absence of an exact parallelism between $\Delta\nu$ and ΔE_X.

As mentioned above, Fromherz and Lih were not disturbed, in their measurements in dilute lead halide solutions, by the occurrence of higher associates, e.g., of the neutral molecules $PbCl_2$, $PbBr_2$, and PbI_2. However, when they investigated the absorption spectra of the same compounds in concentrated alkali halide solutions, they found a predominance of a highly associated species which they surmised to be PbX_4^{2-}. Upon dilution, the bands attributed to these complex anions, suffered a diminution in intensity and a shift in position, but no new bands developed until the spectrum was gradually transformed into that of a (PbX^++Pb^{2+}) mixture. The authors acknowledged that this continuous transformation may indicate a gradual dissociation of the PbX_4^{2-} complexes into PbX_3^-, PbX_2, PbX^+, and Pb^{2+} but they considered the intermediate species as "unstable" and not possessed of characteristic absorption bands. It is, however, more probable that the forms PbX_3^- and PbX_2 have their own characteristic absorption peaks, but that their bands are situated in the same general region as the bands of the two extreme forms, and that the association constants are spaced so closely that the intermediary species can never be obtained except in a mixture with at least one of the extreme forms. This explains why the bands of the intermediates do not appear as distinct peaks at any stage of dilution. The continuous change in shape and position of the absorption bands, caused by dilution, probably results from the superposition of the bands of the intermediates in variable proportions. The only way to obtain the extinction curves of the intermediates is by mathematical analysis of the composite extinction curves.

The assumption that the "coordinatively saturated" complexes are favored by nature at the expense of the intermediary "non-saturated".

TABLE IV. Association constants and absorption peaks of lead halide complexes PbX^+.

	K $(\mu=0)$	$\lambda_{\max}$ mμ	$\log \epsilon_{\max}$	$\nu_{\max}$	$\Delta\nu$
$PbCl^+$	12.9	226	4.07	44300	
					1900
$PbBr^+$	14.1	235.8	4.29	42400	
					4600
PbI^+	29.0	264.5	4.33	37800	

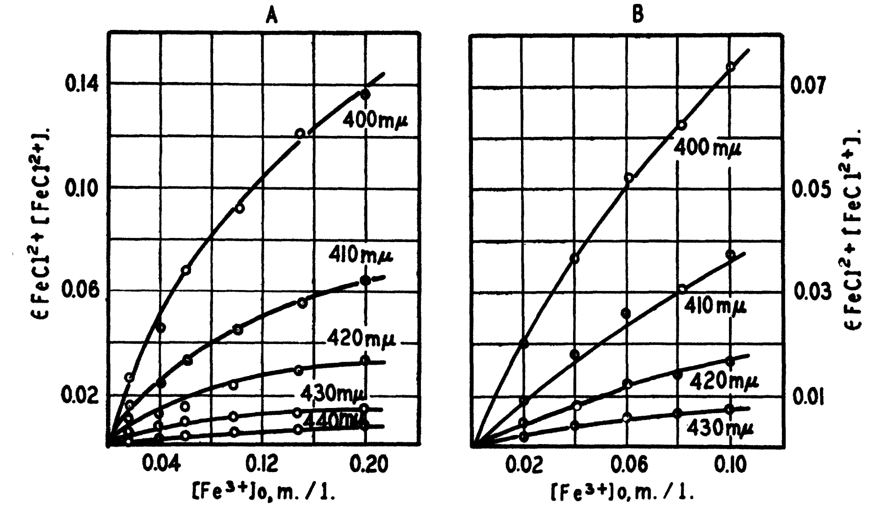

FIG. 11. Increase in absorption of an HCl solution with the addition of $Fe(ClO_4)_3$, due to the formation of $FeCl^2$ ions: (*A*) at $\mu=2.186$, $[HCl]=0.002$ mole/l, $[HClO_4]=0.986$ mole/l, $[Fe(ClO_4)_3=0.02$ to 0.20 mole/l, $[NaClO_4]=1.08$ to 0 mole/l; (*B*) at $\mu=1.094$, $[HCl]=0.002$ mole/l, $[HClO_4]=0.492$ mole/l, $[Fe(ClO_4)_3]=0.01$ to 0.1 mole/l, $[NaClO_4]=0.54$ to 0 mole/l. Curves calculated for single association. (*A*) $K_1=6.0$, (*B*) $K_1=4.2$ (Rabinowitch and Stockmayer).

forms—not only in the crystalline state, but also in solution—has often been made, but cannot be accepted as a general rule. In the case of FeX_3 solutions, for example, the intermediate forms FeX^{2+}, $FeX_2{}^+$, and FeX_3 predominate over the extreme forms Fe^{3+} and $FeX_6{}^{3-}$, over a wide range of concentrations. This result was obtained by Rabinowitch and Stockmayer[63] by a systematic study of the spectrum of ferric perchlorate, chloride and bromide in the visible region, at different acidities, ionic strengths, concentrations, and temperatures. From these observations the authors calculated the extinction curves and the association constants for the first three associated species $FeCl^{2+}$, $FeCl_2{}^+$, and $FeCl_3$. All these species possess intense bands in the ultraviolet, which extend into the visible and contribute to the yellow or orange color of ferric chloride solutions. The successive association constants are so close ($K_1=4.2$, $K_2=1.3$ and $K_3=0.04$, at an ionic strength of $\mu=1$), that all solutions of ferric chloride contain at least two or three species in comparable quantities, and their empirical extinction curves contain contributions by all of them—as well as by the unavoidable intermediary products of hydrolysis, $FeOH^{2+}$ and $Fe(OH)_2{}^+$.

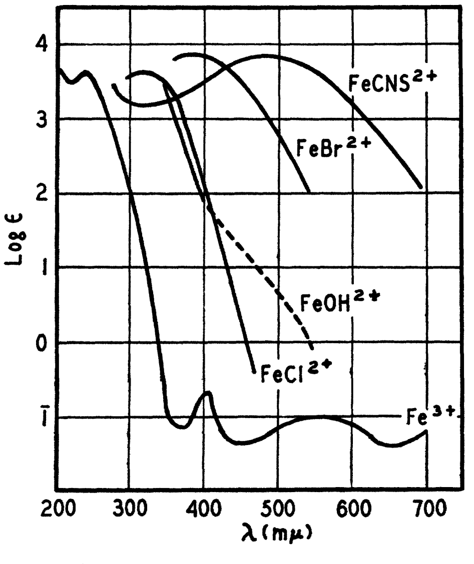

FIG. 12. Absorption curves of Fe^{3+} and of $Fe^{3+}X^-$ complexes in aqueous solution (Rabinowitch and Stockmayer).

The absorption curve of the first associate, FeX^{2+} can be obtained free from those of the higher associates, $FeX_2{}^+$, $FeX_3 \cdots$ (although contaminated by the extinction due to the products of hydrolysis), by using a low constant concentration of HCl and a comparatively large and gradually increasing concentration of $Fe(ClO_4)_3$. If $HClO_4$ and $NaClO_4$ are added in

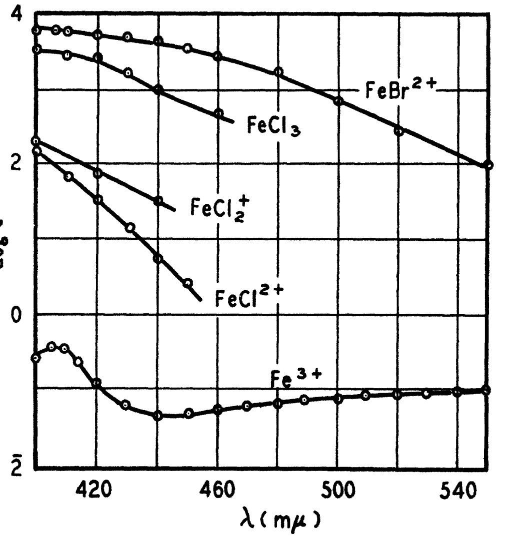

FIG. 13. Absorption curves of Fe^{3+} complexes (Rabinowitch and Stockmayer).

quantities required for the maintenance of constant acidity and ionic strength, the resulting curves (Fig. 11), showing the average extinction coefficient $\bar{\epsilon}$ as a function of $[Fe^{3+}]$, conform to the formula derived for a single association equilibrium, and thus allow the calculation of the association constant K_1 and of the extinction coefficients of the first associates, $\epsilon_{FeX^{2+}}$.

Figure 12 shows the extinction curves of several first associates of ferric ions, together with the extinction curve of the free hydrated Fe^{3+} ion. The latter curve can serve to illustrate the difference in intensity between the weak bands due to prohibited electron excitations in the cation (Fe^{3+} bands at 407, 560, and 700 mμ), and the strong electron transfer bands.

The interpretation of the bands represented in Fig. 12 as electron transfer bands is supported by the relative positions of the $FeOH^{2+}$, $FeCl^{2+}$, and $FeBr^{2+}$ bands, which correspond to the order of electron affinities. If, as sometimes suggested, the bands of the associate ions were absorption bands of the metal ion shifted towards longer waves by the electric field of the associated anion, one would expect a relationship between the strength of the association and the position of the band. In fact, however, the energies of association increase from $FeCl^{2+}$ (−8.5 kcal.) through $FeBr^{2+}$ (−6.1 kcal.) to $FeOH^{2+}$ (+1.2 kcal.), whereas the "red shift" is greatest in the case of $FeBr^{2+}$.

A none too reliable extinction curve of $FeCNS^{2+}$ has been included in Fig. 12 for the sake of comparison. It was taken from the measurement of von Kiss, Abraham, and Hegedüs,[62] in which 0.0218 mole/l KCNS were dissolved in 0.37 molar $HClO_4$. Under these conditions, at least 75 percent of the Fe^{3+} ions must be associated with CNS^- ions to $FeCNS^{2+}$ (cf. Edmonds and Birnbaum[80] and Bent and French[81]), but the solution may contain considerable quantities of higher associates, also contributing to the extinction curve.

Rabinowitch and Stockmayer have also determined the absorption curves of $FeCl_2^+$ and $FeCl_3$ in the visible region (Fig. 13). These curves generally run above the corresponding curve for $FeCl^2$; the extinction coefficient of $FeCl_3$ at 400 mμ reaches 3400, as against 128 for $FeCl^{2+}$. It would be interesting to know whether the extinction curves of the higher associates have higher maxima than those of the binary complexes. This seems possible because of the presence of several anions, each of whom can transfer an electron to the central cation. The existence of such a relationship is indicated by the results of Fromherz and co-workers. It was mentioned above that Fromherz and Lih[64] have attributed the absorption bands found in the solutions of lead halides in concentrated alkali halide solutions to the "coordinatively saturated" anions $PbCl_4^{2-}$, etc. A similar

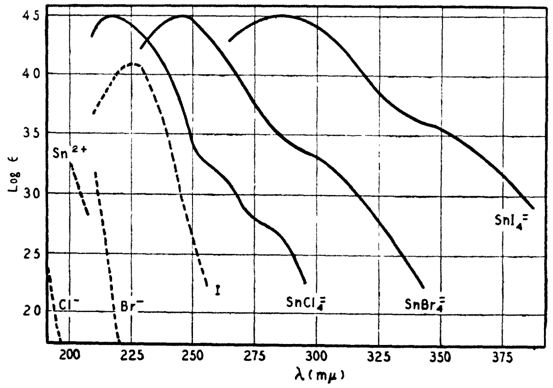

FIG. 14. Absorption curves of SnX_4^{2-} complexes. $SnI_4^{=}$-curve: 2.7×10^{-3} mole/l SnI_2 in 1.32 mole/l KI. $SnBr_4^{=}$-curve: 9.8×10^{-2} mole/l $SnBr_2$ in 6.55 mole/l KBr. $SnCl_4^{=}$-curve: 7.5×10^{-2} mole/l $SnCl_2$ in 7.64 mole/l KCl (Fromherz and Walls).

explanation was given by Fromherz and coworkers to the bands of Ag^+, Cu^{2+},[39] Tl^+,[64] Hg^{2+},[65] Zn^{2+}, Cd^{2+},[66] and Sn^{2+} [67] observed in concentrated alkali halide solutions. It is interesting that in many of these spectra, the extinction curve in the far ultraviolet rises to extraordinary high values, not encountered in the spectra of free anions or binary associates. Figure 14 shows as an example, the extinction curves of Sn^{2+} halides in concentrated alkali halide solution, with bands attributed to the ions SnX_4^{2-}. They all rise to $\log \epsilon = 4.5$. The maximum extinction coefficient of $PbBr_4^{2-}$ (as observed in 4.2 molar KCl) is even higher $-\log \epsilon = 4.9$ (at 225 mμ)—i.e., a whole order of magnitude above the maximum extinction coefficient of most binary complexes, and equal to that of the strongest known organic dyes. Figure 15 shows that this spectrum also contains a second band, at 304 mμ, with a maximum extinction coefficient of $\log \epsilon = 4.3$. Two bands (λ200 and λ272 mμ, $\log \epsilon = 4.3$) are present also in the spectrum of $PbCl_4^{2-}$ ($PbCl_2$ in concentrated KCl solution), as well as in those of the complex halides of thallium. The two bands are too far apart to be attributed to the doublet structure of the halogen. The second band may be due to an excited state of the Pb^+ ion; but one has also to consider the possibility that the electron transfer to the central cation may take place not from one definite X^- ion, but from the anion shell as a whole. (In other words, the remaining three electrons in $Pb^+Cl_4^{3-}$ may be able to exchange rapidly between all four Cl atoms.) This may lead to a band structure which can be interpreted only in terms of the electronic configuration of the complex Cl_4^{3-}, as a whole, rather than of a single Cl atom.

The regular "red shift" of the bands in the series chloride-bromide-iodide, which we have encountered in dealing with gaseous and solid halides, free anions and binary cation-anion complexes, is found also in the spectra of the "coordinatively saturated" complexes. Table V is based on figures given by Fromherz and Walls.[67] The bands of the saturated complexes with a given anion and variable cation shift in the same way as the absorption bands of the free cations. The comparison of this order with the order of the second ionization potentials J'' (i.e. with the energies of transition from A^+ to A^{2+} in the gas phase) reveals no significant parallelism, comparable to that existing between the electron affinity of the halogen and the position of the bands. (The cause is probably the same as was discussed in Section II for gas molecules. In the case of the halogens, the increase in electron affinity goes parallel with the decrease in ionic radius, and thus the two terms E and Δ in Eq. (2) change in the same direction; in the case of the cations, the ionization potential decreases with increasing ionic radius, and the terms $-J$ and Δ change in opposite directions, so that the changes in $h\nu_{\max}$ values become erratic.)

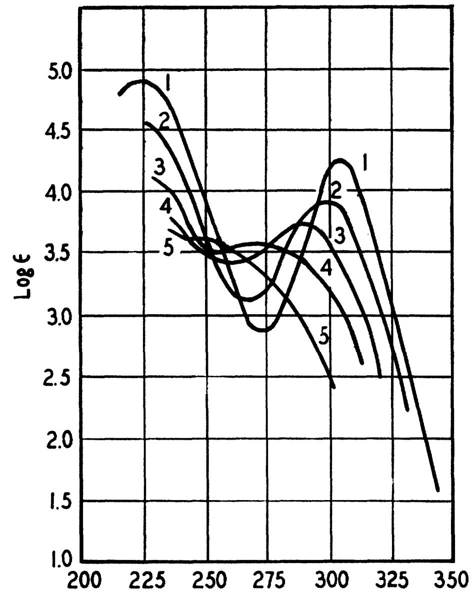

FIG. 15. Absorption curve of $PbBr_4^{2-}$ and its transformation upon dilution into the absorption curve of Pb^{2+} and $PbBr^+$. 1. 6.3×10^{-3} mole/l $PbBr_2$, 4.2 mole/l KBr. 2. 4.7×10^{-4} mole/l $PbBr_2$, 2.1 mole/l KBr. 3. 1.88×10^{-4} mole/l $PbBr_2$, 0.84 mole/l KBr. 4. 9.4×10^{-5} mole/l $PbBr_2$, 0.42 mole/l KBr. 5. 3.13×10^{-5} mole/l $PbBr_2$, 0.14 mole/l KBr.

TABLE V. Wave-lengths in mμ of band maxima of saturated complexes $AX^{2-}{}_4$.

Electron donor	Zn^{2+}	Cd^{2+}	Sn^{2+}	Hg^{2+}	Cu^{2+}	Pb^{2+}
H_2O	$\ll 180$	$\ll 180$	< 180	180	200	208.5
Cl_4^{2-}		187.5	218.5	228.5	250	272
Br_4^{2-}		215.5	245	250	281	304
I_4^{2-}	238.5	257	290	323		363.3
J''_A (ev)	17.9	16.8	14.5	18.6	20.5	15.0

If the interpretation of the intense absorption bands of anion-cation complexes as electron transfer bands is correct, all these bands must be "photochemically active," and the primary process must be the reduction of the cation and the oxidation of the anion. Whether the photochemical effect becomes apparent, e.g., by the liberation of free halogen (or other irreversible changes), or remains hidden, must depend on special circumstances, which determine whether the electron returns from the oxidized anion to the reduced cation, by a "primary back reaction," or whether it has a chance of escaping recombination. However, even if the separation succeeds with a fair quantum yield, the process still may be reversed by a "secondary" back reaction, as in the sequence:

$FeCl^{2+}\overset{h\nu}{\rightleftharpoons}Fe^{2+}Cl$ (photoxidation of Cl^- and primary back reaction),

$Fe^{2+}Cl \rightarrow Fe^{2}+Cl$ (separation of primary products),

$Cl+Fe^{2+}\rightarrow Fe^{3+}+Cl^-$ (secondary back reaction).

Some photochemical processes are known in which ferric ions play the part of the photosensitive component (e.g., the well-known photochemical oxidation of organic acids by ferric salts). In the above-discussed simpler cases—e.g., those of pure ferric halide or lead halide solutions—no photochemical changes have been reported; but perhaps nobody has looked for them closely enough.

In studying the photochemistry of solutions, one comes to the realization that the analytically observable transformations are only a small part of the chemical changes which actually occur in solutions under the influence of light, and which are either too slow or too easily reversible to be detected by ordinary analytical methods. If the interpretation of the intense cation and anion bands as electron transfer spectra is correct, ultraviolet-illuminated solutions of all common acids, alkalis, and salts must contain unstable oxidation and reduction products, free atoms and radicals, which only wait for the opportunity to be converted into stable products by secondary reactions. This picture of "hidden" chemical transformations in illuminated solutions (cf. Baur[82]) can help to understand some otherwise puzzling phenomena—e.g., the strong photogalvanic potentials ("Becquerel effects") which have been observed (for example, by Svensson[83] and Lifschitz and Hooghoudt[84]) in solutions of (supposedly) photostable inorganic acids, alkalis, and salts.

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