THEORY AND APPLICATIONS OF CHARGE-TRANSFER-TO-SOLVENT SPECTRA

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Contents

I. Introduction

The purpose of this review is to outline the general features of a particular class of electronic absorption spectra called charge-transfer-to-solvent (ctts) spectra[1-4] and to examine recent theoretical treatments of these spectra. It will also be shown how absorption bands in the spectra of ions in solution can be assigned to this class of transition and how ctts spectra provide information concerning both ion–ion and ion–solvent interactions.

The important symbols used in the review are as follows:

c	velocity of light
cm^{-1}	wave number
ΔC_p°	standard heat capacity
D	Debye unit of dipole moment
E_A	electron affinity of radical
E_{max}	energy of absorption band maximum
eV	electron volt ($1.0\ eV \equiv 8063\ cm^{-1} \equiv 23.063$ kcal $mole^{-1}$)
e	electronic charge
h	Planck's constant
IP	ionization potential
ΔH_s°	standard enthalpy of solvation
$\Delta' H_s^\circ$	standard enthalpy of solvation in preformed solvent cavity
m	mass of electron
R_c	radius of excited-state orbital for electron: confined model
R_D	radius of excited-state orbital for electron: diffuse model
r_i	crystallographic radius of ion
ΔS°	standard entropy of solvation
Z	charge on anion
ϵ	molar decadic absorption coefficient at $\bar{\nu}$
ϵ_{max}	molar decadic absorption coefficient at $\bar{\nu}_{max}$
ϵ_s	static dielectric constant
ϵ_{op}	optical dielectric constant
μ	dipole moment
$\bar{\nu}$	wave number of *e–m* radiation
$\bar{\nu}_{max}$	wave number of absorption maximum
α	ratio of radii R_D to r_i (diffuse model)

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Generally, the absorption spectra of molecules and molecular ions in the visible and ultraviolet region of the electromagnetic spectrum involve excitation of an electron from molecular ground to molecular excited states,[5] *i.e.*, intramolecular transitions. Here the excited orbital is a property of the molecule, the electron remaining essentially bound to the molecule. The energy of absorption maximum, $E_{\max}$ ($= hc\bar{\nu}_{\max}$, where $\bar{\nu}_{\max}$ is the wave number at the absorption maximum) measures the energy difference between ground and molecular electronic states. The absorption spectra may also show vibrational fine structure. Analysis of solvent effects on $\bar{\nu}_{\max}$ (and also on band shape and intensity) requires examination of these effects on both energy states.[5–8] These few comments serve to contrast intramolecular transitions with those which are the subject of this review. Here, the solvent plays a much more integral role in defining the energies of electronic excited states, illustrated with reference to iodide in aqueous solution.

The ionization potential of iodide is close to 70 kcal mole^{-1} (Table I). There are no stable binding atomic levels for halide ions in the gas phase above the ground state, the energy associated with a $5p^6 \rightarrow 5p^5 6s^1$ transition being greater than the ionization potential.[9] In aqueous solution at 20°, the absorption spectra show two well-resolved bands at much high energies, 126.6 and 147.8 kcal mole^{-1}, and the energy separation of these band maxima is close to the energy difference between the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ states of the iodine atom (Table I). Thus, the process of light absorption leads to an iodine atom and an electron, *i.e.*, $I_{aq}^- \rightarrow (I + e^-)_{aq}$, the electron bound within a stationary state approximately 50 kcal mole^{-1} above that required for ionization of the iodide and the excited state being essentially defined by the environment of the ion. This class of transition is therefore called charge-transfer-to-solvent spectra,[1] being a special example of electron-transfer spectra.[9] Absorption spectra of molecular anions, *e.g.*, dihydrogen phosphate and thiosulfate, in solution show bands due to both intramolecular and ctts transitions (section V).

Table I

Properties of Halide Ions Relevant to Ctts Spectroscopy

Ion	*IP*, *kcal/mole*	*Doublet splitting* *kcal/mole*	*cm^{-1}*	*Ionic radius, Å*
Iodide	70.99[a]	21.73[a]	7600[a]	2.05[e]
	74.6 ± 1.5[b]	21.74[d]	7603[d]	2.16[f]
	74.5[c]			
Bromide	77.91[a]	10.54[a]	3690[a]	1.80[e]
	81.6 ± 1.5[b]	10.53[d]	3685[d]	1.95[f]
	80[c]			
Chloride	83.67[a]	2.52[a]	880[a]	1.64[e]
	88.2 ± 1.5	2.49[d]	871[d]	1.81[f]
	87[c]			
Fluoride	83.5[b]			1.16[e]
	79.52[e]			1.36[f]

[a] Reference 537. [b] Reference 500. [c] Reference 515. [d] Landolt–Börnstein, "Physikalisch-Chemische Tabellen," Springer-Verlag, Berlin, 1950. [e] Reference 567. [f] L. Pauling, "The Nature of the Chemical Bond and the Structure of Molecules and Crystals," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

Charge-transfer-to-solvent spectra are smooth, structureless, absorption bands in the ultraviolet region. The bands are intense, oscillator strengths of the order of 0.1 and greater being common. Since the solvent plays such an integral part in defining the excited state, the spectra provide information concerning the structure of the medium surrounding the ion. This feature has been used to study ion-pair formation (section VI) and hydration of ions in aqueous solution (section IV), the latter being a relatively new development. Properties and structure of water are reviewed elsewhere.[10–26] An important advantage in the study of ctts spectra of ions is that information is obtained for a single ionic species. In contrast, many studies of salt solutions are often bedeviled with problems associated with the assignment of separate contributions to an observable by both cation and anion. This difficulty is encountered, for example, in analyzing trends in Gibbs free energies, enthalpies, and entropies of solvation,[27–29] ionic activity coefficients,[30, 31] *B* viscosity coefficients,[32] and proton and ^{17}O magnetic resonance spectra of aqueous solutions.[33–36] Thus, ctts spectra of ions fall into a class of experiments which contains relatively few other techniques, *e.g.*, ionic conductances derived from equivalent conductivities and transport numbers, electron spin resonance spectra of radical ions,[37] magnetic resonance spectra of ions,[33–35] and nmr spectra of solvent molecules in ionic solvation shells.[38,39] Previous reviews[9,40] of ctts

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absorption spectra were mainly concerned with spectra in aqueous solutions, and the discussions were confined to E_{max}, band shapes, and intensities at one temperature. The models outlined[9,40] for ctts spectra have been largely supplanted by the treatments discussed in section III of this review. An important feature in these new treatments of ctts spectra is comparison between the spectra of ions in solution and in crystals and cross reference to the photochemistry of ionic solutions.

Advances in the chemistry of ctts spectra are closely related to technical advances in spectrophotometry which have led to the development of single- or double-beam spectrophotometers with a working range up to 54,000 cm^{-1}. If spectra are recorded above 51,000 cm^{-1}, then the optical path should be flushed with dry nitrogen to remove the Schumann–Runge absorption bands of oxygen.[41] Serveral double-beam spectrophotometers having synthetic silica optical components are available for spectra up to 62,500 cm^{-1}.

In general, ctts spectra in aqueous solution have absorption maxima above 40,000 cm^{-1}. A troublesome feature in this region of the spectrum is scattered light, *i.e.*, white, or unmonochromated, radiation present in most optical systems.[41, 42]

II. General Properties of Charge-Transfer-to-Solvent Spectra

Since their absorption spectra are relatively simple and do not involve bands due to intramolecular transitions, the ctts spectra of halide ions, particularly iodide, have received detailed attention. (Work prior to 1942 is summarized in ref 9.) This is due to the simplicity of the absorption spectra and the good resolution of the iodide doublet, changes in $\bar{\nu}_{max}$ following changes in solvent, temperature, pressure, and concentration of added salt being easily studied. Such changes lead to a set of generalizations for all ctts spectra which are now briefly reviewed. Attention is confined to spectra where iodide in solution can be regarded as essentially free. Thus if iodide is part of a complex ion,[43–46] *e.g.*, ZnI_4^{2-} and AgI_2^- in aqueous solution, $CaI_2 \cdot 4NH_3$ in ammonia, the characteristic features of ctts spectra are lost,[3] the spectra of these complex ions being outside the scope of this review. Characteristic features of ctts spectra are also lost when iodide becomes part of a donor–acceptor charge-transfer complex in, *e.g.*, pyridinium iodide,[47] and complexes between iodide and powerful acceptors, *e.g.*, trinitrobenzene.[48] Ion-pair formation also produces some modifications in ctts spectra (section VI), but this can generally be ruled out if the spectra are unaltered when the cation is changed, *e.g.*, sodium to tetra-*n*-butylammonium.[49] Indeed, cation independence of $\bar{\nu}_{max}$ at low salt concentrations, *e.g.*, 1×10^{-4} *M*, is one criterion of a simple ctts transition.[3]

A. ABSORPTION SPECTRA AT FIXED TEMPERATURE AND PRESSURE

The ultraviolet absorption spectrum of iodide in water at room temperature (~20°) shows a well-resolved doublet,[2,3,42,50,51] having maxima at 44,300 and 51,700 cm^{-1}. The observed differences between the energies of the two maxima, while close to that between the $^2P_{1/2}$ and $^2P_{3/2}$ states of the iodine atom, is not exactly equal because of overlap of the two bands. This band overlap shifts the observed band maxima closer together, the extent of this shift depending on the separation and relative intensities of the two bands.[52] The low-energy absorption band is otherwise quite symmetric[53] about the absorption maximum, and the energy of the absorption maximum can be accurately determined using a method of midpoint analysis.[54] An important limiting factor in estimating $\bar{\nu}_{max}$ is the quality of the thermostating of the solution in the spectrophotometer.[54] In nearly all experimental investigations of the ctts spectra of iodide, $\bar{\nu}_{max}$ for the low-energy component of the doublet has been monitored, it being generally assumed that $\bar{\nu}_{max}$ for the high-energy component behaves in a similar manner. Where this has been tested, the assumption is generally valid although in some instances the high-energy band is slightly more intense. This may be due to overlap with other absorption bands at higher energies, the nature of which are unknown.

On going from iodide to bromide, the absorption maxima move to higher frequencies, and the bromide doublet is not so well resolved.[50,54,55] Indeed, for some solutions, the spectra simply comprise a very broad band because of poor resolution. Here $\bar{\nu}_{max}$ for the low-energy band has been estimated from the over-all band shape using either geometric or computer analytical techniques.[54] Within experimental error, the two bands are separated by the difference between the $^2P_{1/2}$ and $^2P_{3/2}$ energy states of the bromine atom in the gas phase (Table I). The ctts spectra of choloride is at higher energies, and $\bar{\nu}_{max}$ has been observed in relatively few systems, *e.g.*, water[56] and acetonitrile.[54,55] Only a single absorption band is recorded since the two component bands are too broad, and the doublet splitting, Δ, is too small for the bands to be resolved. The absorption maxima for the two bands can be estimated by adding and subtracting $\Delta/2$ cm^{-1} from the observed $\bar{\nu}_{max}$.

B. SOLVENT EFFECTS

The energies of absorption maxima, E_{max}, for iodide in a range of solvents (Table II) show the extreme solvent sensitivity of ctts spectra.[3] In fact, the sensitivity is generally more marked than for intramolecular transitions with the possible exception of certain dyes[57–59] and some charge-transfer complexes, *e.g.*, pyridinium iodides.[47] There is no clear-cut cor-

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Table II

Values of E_{max} and dE_{max}/dT for Halide Ions in Pure Solvents at 20°

	Solvent	E_{max}, *kcal mole*$^{-1}$	dE_{max}/dT, *cal mole deg*$^{-1}$	*Temp range, °C*	*Ref*
		For Iodide			
1.	Water	126.40	32.8	1–91	445
			33	4–96	2–4
			32	4–54	51
			35.7	20–55	426
2.	KI crystals	129.91	26	−250–25	3, 4
3.	Methyl alcohol	130.00	10		3, 4
4.	Ethyl alcohol	130.50	10		3, 4
5.	Ammonia (liquid)	110.10	61.5	−78– −33	45
		108.1	67	−34–54	77
6.	Acetone	112.4	75		74
7.	Acetonitrile	116.50	50		3, 4
8.	Propionitrile	112.4	47		3, 4
9.	Dimethoxyethane	121.4	55	−23–35	78
10.	Isobutyl alcohol	129.95	42	1–63	78
11.	*n*-Heptyl alcohol	128.0	24	−25–69	78
12.	Ethanediol	132.96	29.1	16–189	78
13.	Glycerol	134.12	29.7	0–234	78
14.	*t*-Butyl alcohol	127.88	45	21–59	78
15.	Isoamyl alcohol	130.40	41	18–75	78
16.	1,2-Dichloroethane	118.78	34	32–74	78
17.	Propanediol	131.6	16	4–66	78
18.	Diethylene glycol dimethyl ether	118.2	40	3–66	78
19.	Diethylene glycol monobutyl ether	127.1	32	3–66	78
20.	3,5,5-Trimethylhexanol	129.95	27	19–68	78
21.	2-Methoxyethanol	127.75	27	3–65	78
22.	Propylene carbonate	122.71	51	21–77	78
23.	Ethylene carbonate	123.67	33	48–70	78
24.	Dimethyl carbonate	120.4	58	37–66	78
25.	2-Methylpentane-2,4-diol	127.7	20	20–50	78
26.	Isopropyl alcohol	129.91	45.5	29–72	78
27.	Dimethyl sulfone	123.25	45.0	124–218	78
28.	2-Butoxyethanol	130.57	27.6	51–148	78
29.	Ethylene glycol monomethyl ether	128.59	34	28–133	78
30.	Triethylene glycol	130.06	33.7	29–232	78
31.	Cyanoethanol	130.5	20.5	5–65	*a*
32.	Methylene dichloride	116.3	28	Tetra-*n*-hexylammonium salt	3, 4
33.	Tetrahydrofuran	116.4	30	Tetra-*n*-hexylammonium salt	49
		122.3	19	Sodium salt	49
34.	2-Methyltetrahydrofuran	124.0		Sodium salt	49
		117.3		Tetra-*n*-hexylammonium salt	49
35.	1,3-Dioxalone	121.2	36	Tetra-*n*-hexylammonium salt	49
		131.6	54	Sodium salt	49
36.	*t*-Butyl alcohol	128.2	56	Tetra-*n*-hexylammonium salt	49
37.	1,4-Dioxane	121.4	14	Tetra-*n*-hexylammonium salt	49
38.	*t*-Pentyl alcohol	129.7	53	Tetra-*n*-hexylammonium salt	49
		134.6	50	Sodium salt	49
		For Bromide			
	Water	143.7	33.0	23–73	54
		145.8			50
		141.5			55
	Acetonitrile	130.3	65	26–69	54
		130.2	64		
		131.3			55
		131.7			50
	1,3-Dioxalane	135.8			54
	Methylene dichloride	130.3	16		54
	Carbon tetrachloride	110.5	0		54
		For Chloride			
	Water	155.8			9
		163.3			56
	Acetonitrile	144.8	58.6		54
		145.1			55
		146.2			50

[a] M. J. Blandamer, P. W. Mynott, and M. C. R. Symons, unpublished data.

relation between E_{max} and the dielectric constant of the solvent, for on going from water to methyl alcohol to acetone the dielectric constant decreases but E_{max} first increases, then decreases. Indeed, E_{max} values for iodide in alcohols (and water, the "zeroth" alcohol) are closely grouped together. These features suggest that simple correlations for E_{max} based on the Born equation[60] for the Gibbs free energy and enthalpy of ionic solvation are incorrect.

The simple Born equation is quite inadequate in dealing with trends in solvation energies and repeated tests have shown that it fails quantitatively[61] and qualitatively.[62] A consequence of this failure has led to alternative methods of defining the "polarity" of the solvent. Since the Born equation for the free energy of solvation of an ion and the Kirkwood expression for the free energy of solvation for a dipole[63] require a similar trend when the solvent dielectric constant is greater than 5,[64,65] a common measure of solvent polarity[59]

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can be introduced for both classes of solutes. Particularly useful have been Y values, based originally on rate constants for solvolytic reactions[65, 66] and Z values.[67–72] The latter are spectroscopic values defined by E_{max} (expressed in kcal mole^{-1}) for the charge-transfer complex 1-ethyl-4-carbomethoxypyridinium iodide and are extremely valuable in discussing the effect of solvent on spectra of other solutes,[68,69] kinetic data,[70] and molecular shape.[71] Further, Y and Z values also link in a consistent manner[72, 73] However, despite claims to the contrary, E_{max} for iodide in a range of solvents shows no simple correlation with Z.[74] This shows that a ctts transition does not involve a linear movement of charge and, since no simple correlation exists between E_{max} and Z (and Y) values, then E_{max} for iodide defines another scale for solvents.[3,75] Each solvent is characterized by a ctts value, *i.e.*, E_{max} for iodide at 20°, and this scale has been used in assigning bands in the spectra of other ions to ctts transitions. A similar proposal has been made[76] for the effect on E_{max} of replacing water by deuterium oxide, the ctts bands being shifted to higher energies by 400 cm^{-1} while E_{max} values for intramolecular transitions are relatively unaffected. This solvent isotope effect is diagnostic of ctts transitions.[76]

The lowest energy ctts value is found for ammonia, *i.e.*, 108.1 kcal mole^{-1} (actually measured above atmospheric pressure[77]) and the highest for glycerol, 134.12 kcal mole^{-1} [78] (Table II). There is, despite claims to the contrary,[79] no simple distinction between E_{max} values in protic and aprotic solvents. Ctts values have the advantage that they are readily determined, particularly for those solvent systems, *e.g.*, water-rich mixtures, where the determination of either Z or Y values is difficult.

C. BAND SHAPE AND INTENSITY

Ctts absorption bands of iodide obey Beer's law. The extinction coefficient, ϵ_{max}, for the low-energy band of iodide in water at 20° is 1.35×10^4 M^{-1} cm^{-1}, and the oscillator strength is 0.25.[80] The absorption band is, within experimental error, gaussian in shape,[54,74,80] the band width, $\Delta\bar{\nu}_{1/2}$, being 4250 cm^{-1}.[55] At 20°, ϵ_{max} and the extinction coefficient at $\bar{\nu}$ are given by $\log (\epsilon_{max}/\epsilon) = -7.126 + 2 \log (\bar{\nu}_{max} - \bar{\nu})$. The high-energy band, as far as can be observed, is also symmetric about the maximum[51] and has approximately the same oscillator strength.

The absorption spectra of both bromide and chloride in water at 20° are over-all less intense than that of iodide and, since overlap of the two component bands has the order $I^- < Br^- < Cl^-$, the intensities of the components must decrease more markedly.[54–56] Nevertheless, the extinction coefficients remain very high, being, for example, an order of magnitude greater than that for the absorption bands of permanganate in the visible region.[9]

The ratio of the oscillator strength to $\bar{\nu}_{max}$ for iodide in water, alcohols, acetonitrile, and salt solutions is essentially constant.[55] In water, the oscillator strength is independent of temperature,[53,55] but with increasing temperature $\bar{\nu}_{max}$ decreases, the band broadens, and the doublet becomes less resolved. In nonaqueous solvents the observed high-energy component of the iodide spectrum is generally more intense than the low-energy component,[55] probably because of overlap with higher energy absorption bands.

D. TEMPERATURE DEPENDENCE

The energy of the absorption maximum, E_{max}, for a ctts absorption band is very sensitive to temperature,[2, 3, 53, 54, 74, 80–82] the band shifting to lower energies with increase in temperature; *i.e.*, dE_{max}/dT is negative. A striking feature of these trends is the rectilinear interdependence of E_{max} and temperature (Figure 1) such that the ctts spectra for a given ion in a given solvent can be characterized[2,74] by the slope, dE_{max}/dT. As before, it is assumed that this value of dE_{max}/dT characterizes the behavior of both low- and high-energy components of the doublet. This assumption has been checked for iodide in water and the difference is small.[51] Indeed, the small difference observed could arise from varying effects of overlapping high-energy bands. Generally, where E_{max} is independent of cation, then so is dE_{max}/dT. Some slight dependence of dE_{max}/dT on cation is observed for alkali iodides in ammonia,[45] but the differences are small. By far the greater change is observed when alkali metal cation is replaced by barium or strontium, when dE_{max}/dT is halved. This may be due to the formation of solvent-shared ion pairs[45] (section VI).

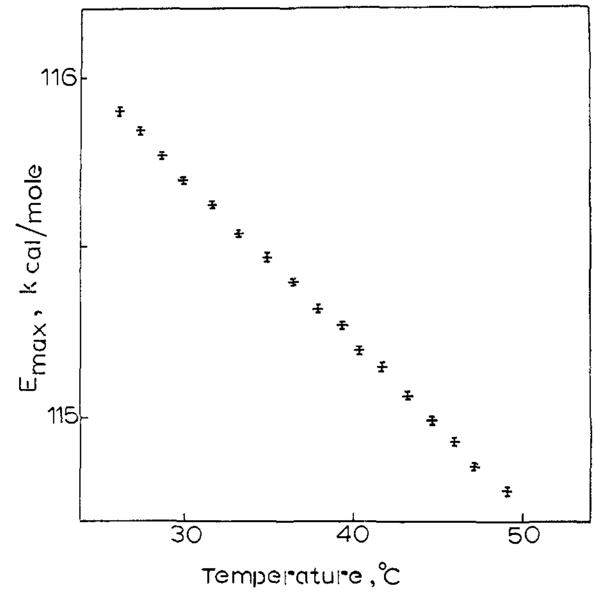

Figure 1. E_{max} as a function of temperature for iodide (5×10^{-5} M) in acetonitrile (from ref 445).

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Another correlation[2,4,74] (the Smith–Symons correlation) for iodide in many solvent systems is the linear interdependence of dE_{max}/dT and E_{max} at constant temperature (generally 20°). The data points are scattered about a straight line having slope $-T$°K, *i.e.*, −293°K (Figure 2). A similar trend seems to hold for bromide although the data are not so extensive.[54] This linear interdependence can be written as

$$(E_{max})_{T,S} = T(dE_{max}/dT)_S + \text{constant} \qquad (1)$$

A best fit analysis of the data (Table II) to eq 1 gave a slope of −236°K with an intercept of 134.101 kcal/mole^{-1}. No solvent has been found where E_{max} for iodide at 20° is significantly greater than 134.1 kcal mole^{-1}. Equation 1 would require $(dE_{max}/dT)_S$ for such a system to be positive. In general, hydrogen-bonded solvents have low values for dE_{max}/dT and, over-all, the lower E_{max}, the greater is the temperature dependence. E_{max} for iodide in ammonia is very sensitive to temperature, and three values[45,74,77] of dE_{max}/dT have been reported (Table II), the differences being possibly due to different pressures operating on the solution. Thus in one determination E_{max} was measured to 55° requiring a pressure greater than atmospheric.[77] If E_{max} for iodide is as sensitive to pressure as it is to temperature, the different values of dE_{max}/dT are accounted for.

The marked low-energy shift following an increase in temperature is diagnostic of ctts transitions since in systems where iodide is part of a complex the shift of the low-energy absorption band is very small and sometimes zero.[43]

E. PRESSURE DEPENDENCE

At a fixed temperature, E_{max} for iodide in water shifts to higher energies with increase in pressure, and the pressure sensitivity is generally greater than that for intramolecular transitions.[83,84] In acetonitrile, E_{max} for iodide is a linear function of pressure over the range 0–1400 bars, and a similar trend occurs for iodide in water at the higher pressure end of this range. At low pressures, E_{max} is more sensitive, but when potassium fluoride (2.5 *M*) or dioxane (mole fraction $x_2 = 0.02$) is added, E_{max} is again a linear function of pressure.

F. SPECTRA IN MIXED SOLVENTS

In general, the absorption spectra of solutes in mixed solvents fall into one of two classes which can be referred to as "band shift" or "band change."[85] When a second solvent is added to a solution, the intensity of the absorption band may decrease accompanied by an increase in intensity of a new absorption at a frequency characteristic of the solute in the added solvent, often with the generation of isobestic points, *i.e.*, a band change. Alternatively, the absorption band may shift, without major change in intensity, ultimately reaching the position of the absorption band in the pure cosolvent, *i.e.*, a band shift. The latter situation is observed for ctts spectra of iodide in mixed solvents.[71,74] The plot of E_{max} against mole fraction for binary solvent mixtures is not a straight line, and the pattern of behavior generally shows that iodide prefers an environment having a different composition than that of the bulk mixture.

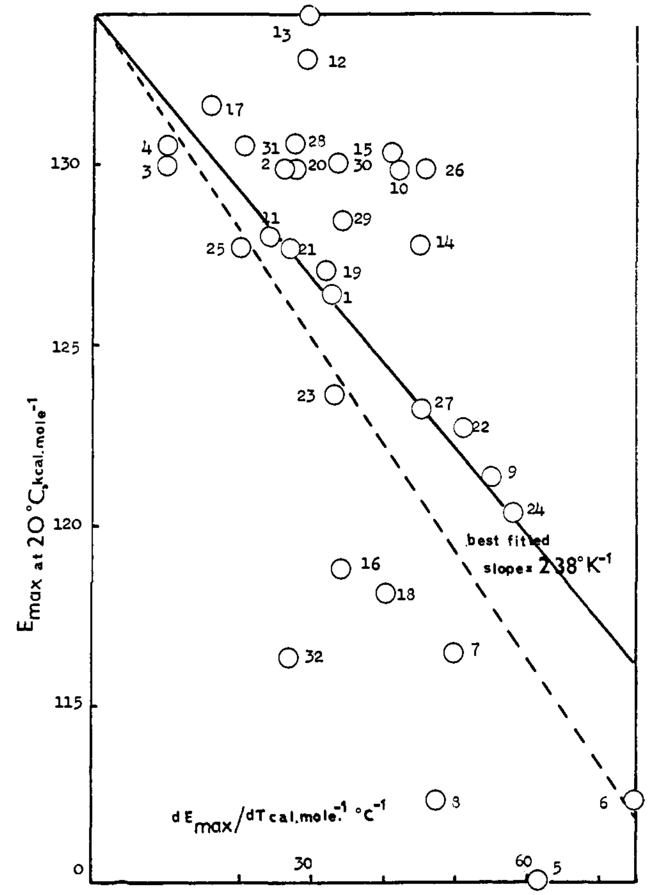

Figure 2. E_{max} as a function of dE_{max}/dT for iodide in a range of solvents (the key to solvents is given in Table II): best fitted line, slope −236°K, ———; Smith–Symons correlation, slope −298°K, — — —. Intercept = 134.10 kcal/mole.

The pattern of behavior for aqueous mixtures is more complex, but again the bands shift (Figure 3) when nonaqueous solvents, *e.g.*, alcohols, dioxane, acetonitrile, are added (section IV). This similarity in the pattern of behavior rules out (as do other trends) the model[86] in which iodide in acetonitrile is involved in specific complex formation with a solvent molecule. Thus, if the transition were due to a specific charge transfer to one solvent molecule, S, *i.e.*, $I^- S \rightsquigarrow I \cdot S^-$, then addition of another solvent, S′, would show a band change arising from the equilibrium $I^-S + S' \rightleftharpoons I^-S' + S$. Further, this model does not seem to hold in any solvent system where iodide shows ctts spectra.

G. EFFECT OF ADDED SOLUTE

The energy of the absorption maximum, E_{max}, for iodide in water is sensitive to added salt (Figure 4). When alkali halides and other metal salts (Figure 4a) are added, the band shifts to higher energies with increase in salt concentration.[3,9,80,87,88] These large high-energy shifts are also diagnostic of ctts transitions.[3] A similar high-energy shift occurs when sucrose, glucose, and urea, $0 < M < 1.0$, are added, which again can

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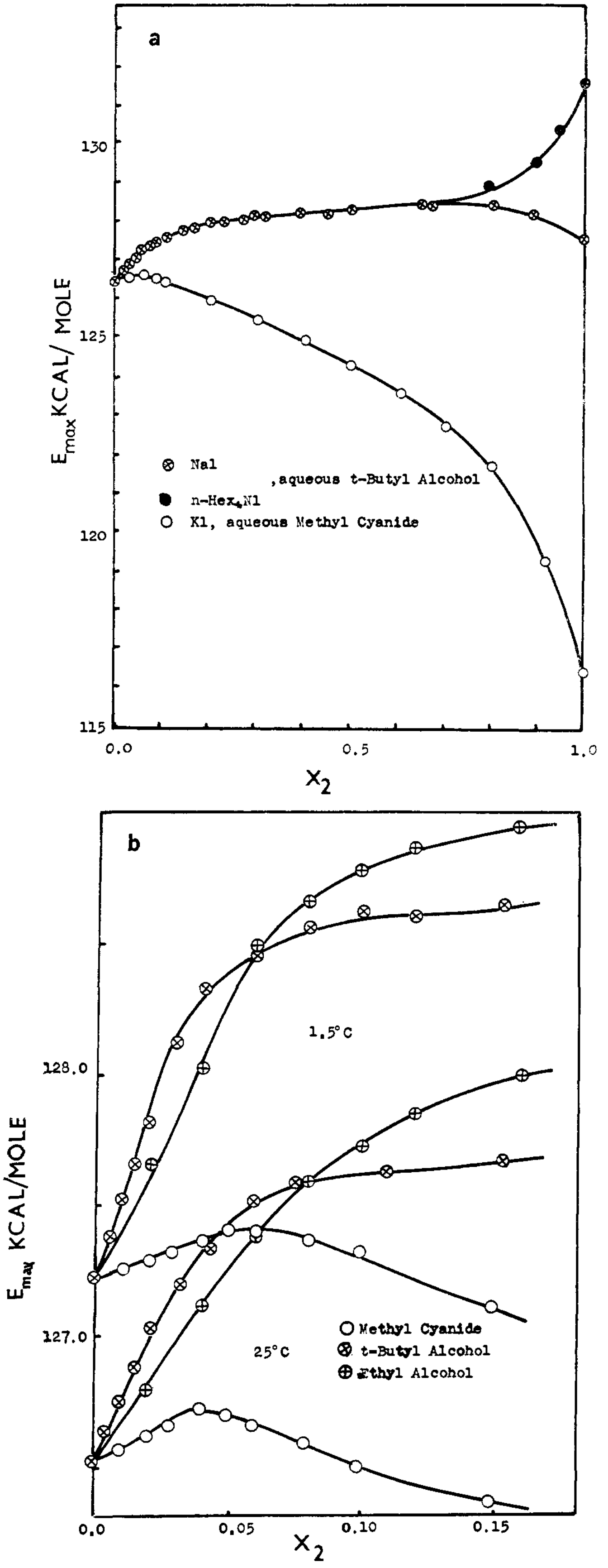

Figure 3. (a) E_{max} as a function of solvent system composition at 1.5 and 25°, for iodide (5×10^{-5} *M*) (from ref 374). (b) E_{max} as a function of solvent system composition in the highly aqueous region $0.0 < x_2 < 0.15$.

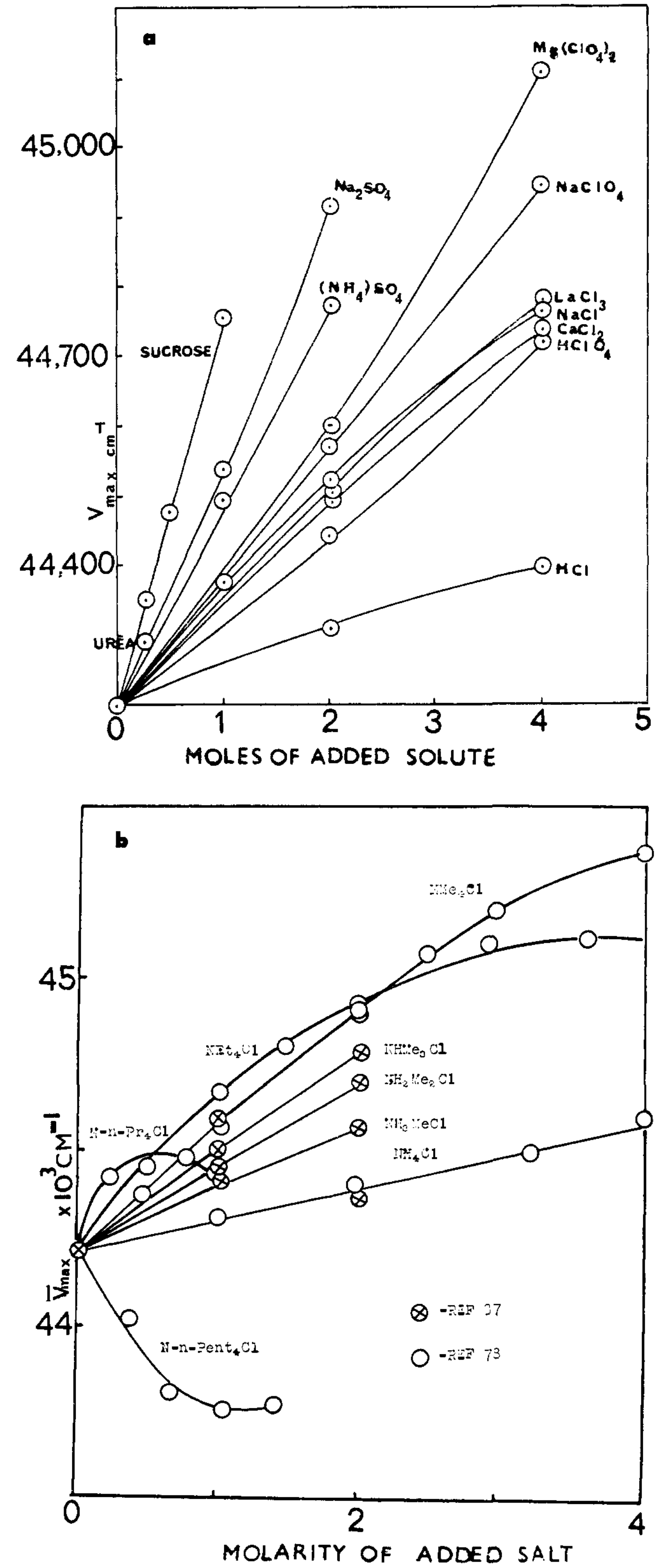

Figure 4. E_{max} as a function of added salt in water for iodide $\sim 5 \times 10^5$ *M*) for (a) simple inorganic salts, and (b) alkylammonium salts (from ref 78 and 87).

be used as diagnostic of ctts transitions.[89] A similar high-energy shift is observed for iodide in propanol[8] and ammonia[45] when salts are added.

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III. Theoretical Treatments of Ctts Spectra

Quantitative treatments of ctts absorption spectra have, in the main, attempted to correlate the variation of E_{max} with changes in temperature and solvent. The former has proved a particularly important criterion for the models proposed. Earlier unsuccessful, and perhaps unjustifiable,[53] attempts were made to correlate dE_{max}/dT with entropies of electrode reactions[90] and of solvation.[82] On the other hand, relatively little attention has been given to analyses of intensity, band width, and oscillator strength.[55] The problems encountered in the interpretation of ctts spectra are not uncommon in the analysis of solvent effects in electronic absorption spectra.[5-8] Thus E_{max} measures the difference between the energies of electronic excited and ground states, and a change in E_{max} following, *e.g.*, a change in temperature, may reflect changes in the energies of the ground state, excited state, or both. In the absence of other evidence, changes in both energy states must be considered. These problems present difficulties if ctts absorption spectra are to be used in studies of ion–solvent and ion–ion interactions. Similar difficulties are not encountered in nuclear magnetic[33-35] and electron spin resonance spectroscopy[35,37] since here only electronic ground states are involved. Quantitative analysis of ctts spectra is made more manageable if the Franck–Condon principle is extended to include the solvent molecules around the anion. Consequently, the arrangement of solvent molecules in the excited state is identical with the ground state, and information concerning ground-state ion–solvent interactions can be carried over to formulating structures for the excited state. Important details concerning the nature of the excited state have also been gained from studies of the photochemistry of salt solutions, and, in view of the close link with this subject, some of the important developments in this field are briefly reviewed.

The two subjects, spectroscopy and photochemical kinetics of aqueous anions, have developed along interdependent and parallel courses. The over-all photochemical reaction has been summarized initially as[91,92]

$$2X_{aq}^- + 2H^+ \xrightarrow{h\nu} H_2 + X_2 \qquad (2)$$

preceding *via*[93]

$$X^-(H_2O) \xrightarrow{h\nu} X\cdot + H\cdot + OH^- \qquad (3)$$

However, the observed dependence of the quantum yield, $\phi_{H_2} = 0$ at pH >3, did not agree with this model,[94] and the primary photochemical process for aqueous anions, by analogy to the photochemistry and spectra of gaseous and crystalline alkali halides, involves transfer of an electron to a water molecule[94,95]

$$X^-\cdot H_2O \longrightarrow X\cdot\ (H_2O)^- \qquad (4)$$

followed either by thermal degradation to the ground state (eq 5a) or the transfer diffusion of the electron from the hydration sphere of the anion to a hydrogen ion, giving a hydrogen atom (eq 5b). This mechanism has been

$$X\cdot\ (H_2O)^- \longrightarrow X^-(H_2O) \qquad (5a)$$

$$\longrightarrow X\cdot + H\cdot + H_2O \qquad (5b)$$

modified by including intermediate formation of an excited complex[96] (eq 6 and 7), where the hydrogen atom is scavenged

$$X^-(H_2O) \xrightleftharpoons{h\nu} (X^-\cdot H_2O)^* \qquad (6)$$

$$(X^-\cdot H_2O)^* \longrightarrow X\cdot + H\cdot + OH^- \qquad (7)$$

by hydrogen ion to give H_2^+.

$$H\cdot + H^+ \longrightarrow H_2^+ \qquad (8)$$

$$H_2^+ + I^- \longrightarrow I\cdot + H_2 \qquad (9)$$

This scheme accounted for the dependence of ϕ_{H_2} upon pH and halide concentration and ascribed the low quantum yield to competing scavenging–recombination reactions. However, hydrogen ions are not essential and photolysis of aqueous iodide in neutral and alkaline solution yields iodine in the presence of solutes which scavenge hydrogen or solvated electrons.[97,98] The latter species was considered following advances in the interpretation of the radiolysis of aqueous solutions.[99-105] Previously the solvated electron had been generally discounted as an intermediate[92] after it had been proposed in 1928.[106]

The initial photochemical act (equivalent to the spectroscopic absorption process) leads to either (a) formation of an excited, bound state of the electron around the parent anion site

$$X_{aq}^- \xrightarrow{h\nu} X_{aq}^{-*} \longrightarrow (X_{aq}\cdot + e^-)_{aq} \qquad (10)$$

where the parentheses indicate the original solvation shell of the parent ion, or, (b) a direct photoionization

$$X_{aq}^- \xrightarrow{h\nu} X_{aq}\cdot + e_{aq}^- \qquad (11)$$

A series of investigations[107-113] using specific scavengers for solvated electrons and hydrogen atoms have established that the initial act involves formation of an excited state which then decays either *via* a radiationless transition to the ground state or into a radical and solvated electron in close proximity (eq 10). This work separated the initial reactions from competing, secondary reactions. The quantum yield of electrons, ϕ_e, was finite but low (0.03) in solutions of pH >2 (with alcohols as hydrogen atom scavengers, at pH >5–6) rising to $\phi_e = 0.29$ at pH <2.

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The radicals formed in a solvent cage, $X_{aq}\cdot + e_{aq}^-$, may either recombine or diffuse to the bulk solvent and then recombine with either original or other partners.[112] The latter bulk diffusion-recombination gives low quantum yields in the absence of scavenging solutes. Addition of the latter gives a limiting value for the production of radical pairs which is much less than unity. This reaction scheme also accounts for the independence of ϕ_e upon irradiation intensity, which is not predicted if the electron is ejected directly into the solvent. The over-all reaction scheme is therefore

$$\begin{tikzcd} I_{aq}^- \arrow[r, "h\nu"] & I_{aq}^- \arrow[r] & (I + e^-)_{aq} \arrow[r, "H^+"] \arrow[ll, bend left] & {} \end{tikzcd}$$

original *or* unoriginal partners

$$(I\cdot + H\cdot) \xrightarrow{RH} I\cdot + R\cdot + H_2 \quad (12)$$

(or Brønsted acids)

where RH is generally an alcohol. The mechanism has been extended to iodide in other solvents[109] and to other ions in water.[110]

The detailed processes leading to formation of radical pairs has been questioned.[114] Using specific scavengers for solvated electrons produced in the photolysis of iodide in solutions of varying ionic strength, the process governing the translation of the electron in the excited state when not deactivated (eq 10) is attributed[114] to rotation of water molecules. The distance of separation between the radicals in the latter process of eq 10 is close to 10 Å. There are, however, still discrepancies in the values of ϕ_e for iodide photolysis at 39,780 cm^{-1} (ϕ_e = 0.16,[97,114] 0.23,[114] and 0.29[107]) and at 43,710 cm^{-1} (ϕ_e = 0.23[110] and 0.32[114]).

There is, therefore, strong support for a model of the iodide excited state in which the electron is closely confined to the anion site. Further evidence for an over-all charge-transfer process, but not the detailed processes discussed previously, is given by the production of solvated electrons in the flash photolysis of aqueous chloride, bromide, hydroxide, thiocyanate, and ferrocyanide solutions.[115] Supporting evidence from photochemistry is important in the assignment of ctts spectra when other criteria are not conclusive, particularly where the absorption band maxima are greater than 55,000 cm^{-1} (section V). Transient radicals formed from dissociation of the excited state (eq 10) may also be observed.

Another closely linked subject is the chemistry of the solvated electron.[116–121] Formerly, attention was confined to solvated electrons produced by dissolution of metals in ammonia and amine solvents. However, added interest has come from the detection of solvated electrons produced by irradiation techniques in fluid aqueous and other polar media[104,105,122–180] and of solvated electrons produced by irradiation of related frozen systems.[131–140] In these subjects, a major problem is describing a satisfactory model for the solvated electron in terms of the various factors responsible for the stabilization of the electron. There is a close link between the ground-state orbital for solvated electrons and the ctts excited state for halides in solution, and for many purposes, *e.g.*, salt effects on rate constants, the solvated electron can be treated as the zeroth halide.[141]

The important step forward, particularly for ctts spectra, came in 1952 when a new model was proposed[142] which, despite some important shortcomings, has provided the basis of later treatments.

A. PLATZMAN AND FRANCK'S MODEL[142]

The important feature of this model is the treatment of the excited state. The discrete orbital for the electron in the excited state is spherically symmetric having its center coinciding with the center of the cavity which contains the ion. The treatment was confined to the spectra of anions in aqueous solution, the solvent being treated for the most part as a dielectric continuum characterized by static, ϵ_s, and optical, ϵ_{op}, dielectric constants. The final expression for the energy of absorption maximum was derived using essentially the following cycle.

$$\begin{tikzcd} X_g^- + aq \arrow[r, "B"] & X_g\cdot + e^- + aq \arrow[d, "C"] \\ X_{aq}^-(aq) \arrow[u, "A"] \arrow[r, "E_{max}"] & X\cdot(aq)^- \end{tikzcd}$$

[The original analysis also considered an inner potential of water, being the average potential (ignoring electric polarization effects) of an infinitesimal point charge for all positions in the liquid; this potential contribution cancels in the cycle.]

Process A involves removal of the hydrated anion, $X^-(H_2O)$, from the solution, aq, to form the anion in the gas phase, the

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energy change being equal but opposite to the enthalpy of solvation of the anion.[143] The nearest neighbor water molecules in the model[143] used to calculate $\Delta H_s°$ are positioned such that the water molecule is coplanar with the ion, with O–H···X⁻ colinear, the second hydrogen being available for hydrogen bonding to the water structure. Included in this enthalpy change is the contribution associated with the rearrangement of solvent structure from that around the ion to that of the bulk solvent. This introduces complications in the calculation of energy changes associated with process C, for part of the energy change involved here arises from replacement of atom, X, into the solvent, *i.e.*, the enthalpy of solvation, $\Delta H_s°(X\cdot)$. This was taken to be one-half the heat of solution of the corresponding halogen molecule, namely 4.6 kcal mole^{-1}, for Cl·, Br·, and I· in water at 25°. In addition, there is a corresponding energy change, ΔR, associated with reproducing the same degree of solvent polarization around this atom as for the ion in the ground state (Franck–Condon principle). This positive energy contribution, ΔR, was calculated for six water molecules in the hydration shell surrounded by bulk solvent.[143] The energy is of the order of 18.4 kcal mole^{-1}, depending only slightly on the halide. Also involved in process C is the energy change, binding energy B, associated with transferring the electron from the gas phase into a centrosymmetric excited state.

The energy change associated with process B equals the ionization potential (IP) and hence E_{max} for a univalent anion in water is given by

$$E_{\text{max}} = h\nu_{\text{max}} = \Delta H_s°(\text{X}^-) + \text{IP} + \Delta R - \Delta H_s°(\text{X}\cdot) - B \quad (13)$$

As noted above, the important step in this theory is calculating B, the binding energy. Here a close link with treatments of solvated electrons is firmly established, the ctts excited state being treated in similar terms to that of the Polaron model for solvated electrons.[144–149]

This Polaron treatment recognizes that an electron can be trapped by the self-polarization of the polar medium;[150,151] *i.e.*, the electron digs its own hole. Within this shallow potential energy well there exists a number of defined stationary states. For an electron within a polarizable medium, the electrostatic potential, $V(r)$, distance r from the electron equals $-(\epsilon/r)[(1/\epsilon_{\text{op}}) - (1/\epsilon_s)]$. The ctts excited state can be treated in a like manner such that the excited states are hydrogen-like with effective atomic number, Z_{eff}, equal to $(1/\epsilon_{\text{op}}) - (1/\epsilon_s)$, and the energies of these levels with quantum numbers n are given by

$$E_e = 2\pi^2 me^4 Z_{\text{eff}}/h^2n^2 \quad (14)$$

The lowest energy state which has sufficient penetration by the electron into water is the 2s state for which E_e is 1.0 eV with a mean radius, $\bar{R}_e$, 5.8 Å, for the electron. This penetration is demanded by the model since stabilization only occurs through long-range interactions. In contrast any short range interactions are possibly repulsive and cannot lead to stabilization. Both E_e and $\bar{R}_e$ are derived independently of the nature of the anion and comparison of $\bar{R}_e$ with ionic radius, Table I, shows that the electron is extensively delocalized into the solvent.

For this reason the use of bulk dielectric parameters is acceptable. The extent of this delocalization can be compared, for example, to delocalization of the electron centered on P$^+$ in phosphorus-doped silicon.[152] In addition to the stabilization measured by E_e, there is a further stabilizing influence of the electron in the ctts excited state arising from the electronic polarization of the solvent. For aqueous solutions at 25° and a 2s orbital, this is approximately 11.5 kcal mole^{-1} so that the total binding energy is 34.6 kcal mole^{-1}.

All the terms in eq 13 are now known, so that for iodide in water at 25°

$$E_{\text{max}} = 72.3 + 73.5 + 16.1 - 4.6 - 34.5 = 122.7$$

which is close to that observed, 124.1 kcal mole^{-1}. For the halides in water at 25°, eq 13 can be approximated to $E_{\text{max}} = \text{IP} + \Delta H_s°(\text{X}^-) - 20.7$ kcal mole^{-1}.

This treatment does not account for the marked variation of E_{max} with temperature. Indeed, the small shift which comes out of this analysis is opposite to that observed.[4,53,153]

The arguments for the adoption of a 2s excited state are qualitatively rather than quantitatively convincing. The method of calculating Δ_{pol} has also been criticized.[153] The model cannot account for the relative constancy of the ratio of oscillator strength to $\bar{\nu}_{\text{max}}$ for iodide in various media.[55] The observed trends in E_{max} for iodide in different solvents do not follow predicted trends.[4] The mean radius $\bar{R}$ corresponds roughly to the distance of the lone pair of electrons in the oriented water molecules,[4] which seems an unlikely situation. The major difficulty in computing E_{max} using this model can be traced to the calculation of the energy change for X· + aq → X·(aq), where (aq) is polarized solvent. This difficulty was overcome[2] in the two models described below by leaving the polarized cavity, (aq), intact throughout the cycle. The models differ in the extent to which the electron in the excited state extends into the solvent. They are generally distinguished by referring to the diffuse[153] and confined[2–4] models. The latter preceded the diffuse model, but the diffuse model will be treated first since it has close similarity to that given by Platzman and Franck.

In an attempted extension[154] of the Platzman and Franck model, $\text{d}E_{\text{max}}/\text{d}T$ was related to $-Rn$, where R is the gas constant and n the number of solvating molecules around iodide.

For aqueous solution n was taken as 10, but this predicts a lower $\text{d}E_{\text{max}}/\text{d}T$ than observed (Table III).

B. DIFFUSE MODEL[153]

This treatment will first be outlined for univalent anions. The following cycle is employed.

$$\begin{tikzcd}
\text{X}_g^- + (\text{aq}) \arrow[r, "\text{B}"] & \text{X}_g\cdot + \text{e}_g^- + (\text{aq}) \arrow[d, "\text{C}"'] \\
\text{X}^-(\text{aq}) \arrow[u, "\text{A}"] \arrow[r, "E_{\text{max}}"] & \text{X}\cdot(\text{aq})^-
\end{tikzcd}$$

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As before, the energy change involved in B is the ionization potential which for polyatomic anions refers to the vertical ionization potential from the Franck–Condon principle. The solvent cavity, (aq), having radius R_d is carried through the cycle. The energy change accompanying process A is not equal to the enthalpy of hydration, $\Delta H_s°(X^-)$, since the cavity remains intact when the ion is removed. Rather, $\Delta' H_s°(X^-)$ is calculated from the interaction energies of the ion with the cavity, both atomic and dipolar polarization, E_i, and electric polarization, S_i, energies being involved with reference to an ion occupying a cavity radius R_d. Thus

$$S_i = (e^2/2R_d)\,[1 - (1/\epsilon_{op})] \tag{15a}$$

$$E_i = (e^2/2R_d)\,[(1/\epsilon_{op}) - (1/\epsilon_s)] \tag{15b}$$

Process C includes an energy change accompanying replacement of X· into the preformed cavity. This energy $\Delta' H_s°$-(X·) was equated to the enthalpy of solvation of the radical,[155] $\Delta H_s°(X\cdot)$. The latter was estimated[155] using the hydration energies of gases.[156] The values for the halogens were obtained from the data[156] for adjacent noble gas; OH· like HF in 1.0 *M* aqueous potassium fluoride, ClO· like NO, and CN· like CO. Values for SH·, $ClO_3\cdot$, and $NO_3\cdot$ were guessed.[155] This contribution, $\Delta H_s°(X\cdot)$, is small, being approximately 4.6 kcal mole^{-1} for the iodine atom.[153] This is fortunate since the enthalpy for solvation, $\Delta H_s°(X\cdot)$, refers to a dissolution process in which the cavity must be formed. Indeed, the structure of water around an atom in water is generally thought to differ from that around a halide, as represented by (aq) in this cycle.[12,15,156–162] The thermodynamics of dissolution of a neutral species are dominated by changes in water–water interactions rather than water–solute interactions.

With these modifications to the Platzman and Franck model, and accepting the previously proposed expressions for the binding energy for the excited state, the final equation is

$$\begin{aligned}E_{max} = \mathrm{IP} - \Delta H_s°(X\cdot) + (e^2/R_d)[(1/2) - \\ ({}^1/{}_2\epsilon_{op}) - (1/\epsilon_s)] - (e^2/2R_d)[1 - (1/\epsilon_{op})] - \\ (\pi^2 mc^4/2h^2)[(1/\epsilon_{op}) - (1/\epsilon_s)]^2\end{aligned}$$

For aqueous solutions at 25° this equation becomes

$$E_{max}\,(\mathrm{eV}) = \mathrm{IP} - \Delta H_s°(X\cdot) + (17.8e^2/R_d) - 36.4$$

The important term in the above equations is the third on the right-hand side which contains a radius parameter characterizing the ionic cavity. From measured values of E_{max} for a series of anions in water, *e.g.*, halides, OH^-, SH^-, NO_2^-, NO_2^-, ClO_3^-, and CN^- (N.B.: no other justification was given to confirm that the quoted bands were due to ctts transitions; see section V), and using published values[155] for $\Delta H_s°(X\cdot)$, R_d was calculated. These values are close to the product $1.25r_i$, where r_i is the ionic radius as given by Pauling for the halides (Table I) and Yatsimirskii[163] for the others. Although the significance of ionic radii is not always clear,[164–166] especially when applied to ions in solution,[164] the R_d values are close to those predicted from an analysis of partial molar ionic volumes[167,168] and of electrostriction effects.[169] The factor 1.25 agrees with that found in analysis of partial molar volumes, *i.e.*, 1.21.[170] The constancy of this ratio might reflect a common mode of packing water molecules around an ion.[75] As a consequence there is probably some dead space around an ion in solution, a possibility also discussed with reference to ionic partial molar volumes in water.[171–174] If this factor is accepted, then R_d can be calculated from crystal radii, and, since all the terms in eq 16 are known or can be estimated, E_{max} can be calculated.

The diffuse model can be extended to predict E_{max} for the high-energy component of the halide doublet.[51] An additional term, Δ, in eq 16 represents the difference between energies of the $^2P_{1/2}$ and $^2P_{3/2}$ states of the halogen atom. The difference between the observed doublet splitting from spectra in aqueous solution and *in vacuo*, 0.8 kcal mole^{-1}, for iodide has been attributed to the difference in the heats of solution of the different atomic states of the iodine radicals.[51] Alternatively, this slight difference might be due to overlap of the absorption bands.[52]

Polyvalent Ions.[175] In these systems the transition corresponds to the process $(X^z)_{aq} \rightarrow (X^{(z-1)} + e^-)_{aq}$. Process C now involves placing an anion, $X^{(z-1)}$, into the cavity. The expression for $\Delta H_s°(X^-)$ is recast for a polvalent anion, but expressions for the energy change in replacing $X^{(z-1)}$ into the cavity, $\Delta H_s°(X^{(z-1)})$ (the radical ion is presumably in a vibrationally excited state), recognize that the solvent molecules have the same positions as in the ground state.

$$\begin{aligned}\Delta' H_s°(X^{(z-1)}) = [(z-1)\,ze^2/R_d]\,[(1/\epsilon_{op}) - (1/\epsilon_s)] + \\ [(z-1)^2e^2/2R_d]\,[1 - (1/\epsilon_{op})]\end{aligned}$$

In addition, the calculation takes account of dielectric saturation near the polyvalent ion[176,177] which in aqueous solution diminishes $\Delta' H_s°(X^z)$ by $11z^3/R_d^5$. If the previously derived relation between ionic radii, r_i, and cavity radius is accepted[175,176] for all anions, *i.e.*, $R_d/r_i = 1.25$, then for divalent anions in aqueous solution at 25°, $E_{max} = \mathrm{IP} + (465/r_i) - (29/r_i^3) - 35$ (in kcal mole^{-1}) where IP is the (vertical) ionization potential.

C. CONFINED MODEL[2–4]

This treatment, which preceded the diffuse model, employs the same cycle, but the final expression is much simpler. However, before reviewing this model, some interesting similarities between ctts spectra of halide ions in solution and absorption spectra of other systems are reviewed. For example, E_{max} for

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the exciton band of iodide in potassium iodide[9,40,74,178] is close to that for iodide in water. Further, exciton bands for alkali halides show two low-energy bands where the splitting in many cases is close to that expected for iodine and bromine atoms in iodides and bromides, respectively, while the chlorine doublet is unresolved[9,40] except at low temperatures.[178]

Exciton bands also shift to higher energy with increase in ionization potential of the halide and the oscillator strengths of iodide in water (0.25), potassium iodide (0.28), molten alkali chlorides (0.24), and cesium iodide (0.23) are very similar.[74] The exciton bands shift to lower energies with increase in temperature and, apart from temperatures near 0 °K, E_{max} is a rectilinear function of temperature, and dE_{max}/dT for iodide crystals is similar to that found for iodide in water.[74] Further, E_{max} is more closely a function of the lattice parameter[179] than a function of the nature or composition of the lattice as shown in comparison of E_{max} for iodide in different hosts, *e.g.*, potassium iodide, potassium bromide,[180] and potassium chloride,[181] where E_{max} shifts to higher energies with decrease in lattice parameter.

Exciton spectra show a series of high-energy bands which may be linked in some way to the high-energy absorption bands in the ctts spectra of ions in solution. There are detailed differences between ctts and exciton spectra.[55] Thus, oscillator strengths are generally smaller in the crystal and also depend on the cation.[55] The link between ctts and exciton spectra has also been criticized[55] on the grounds that oscillator strengths for exciton bands decrease on melting[182] and are very dependent on temperature[183] in contrast to ctts transitions.

Another closely linked system to exciton spectra is the absorption spectra of F-centers, *i.e.*, electrons occupying anion vacancies in a crystal.[184–186] The energies of absorption band maxima [184–185] for F-centers are more closely related to the lattice parameter[187,188] than to the nature or composition of the lattice; this relationship has been generalized[187] by the equation λ_{max} (Å) = $703a^{1.84}$ (Ivey's rule for face-centered cubic lattices). Although the precise details of the structure for F-centers are not completely understood, magnetic resonance experiments[189,190] indicate that the electron is closely confined within the anion vacancy and first shell of cations.[191] A model in which the electron is contained in an orbital formed by the six surrounding cations satisfactorily accommodates electron spin resonance data, the apparent spin density being a simple rectilinear function of lattice parameter.[191] There is, therefore, a clear contrast between the F-center and the extensive delocalization of the electron in P^+ in phosphorus doped silicon.[152] A simple model for an F center is a spherical potential energy well having radius R_c, the potential energy, V, being zero where $r < R_o$ and infinity when $r > R_c$. The lowest energy stationary state for an electron trapped within such a square-well cavity[192] equals $h^2/8mR_c^2$, corresponding to a 1s type orbital. The energy of a 2p state equals $2.04h^2/8mR_o^2$, and therefore E_{max} for the 1s → 2p transition equals $1.04h^2/8mR_c^2$. The radius of the square well and the lattice parameter are rectilinearly interdependent,[193] *i.e.*, $1.243a + 0.353 = R_c$. Also noteworthy is the low-energy shift of the *F* bands with increase in temperature, together with an associated broadening of the absorption band.

A similar confined model to that used for F-centers is also successful in interpreting data for solvated electrons in hydroxide glasses[135,193] and in ammonia, water, alcohol, and other fluid media.[193] For the solvated electron in ammonia, the cavity is formed by the walls of the potential energy barrier associated with the high electron density on the doubly filled n electrons on nitrogen.

In this diversion to consider the spectra of other systems a chain has been built up: iodide in solution, to iodide in crystals, to F-centers in crystals, to solvated electrons in glasses and fluid media. The final link back from the spectra of solvated electrons to the ctts spectra of ions is now made, and indeed the spectra again show close parallelisms in behavior. The shift, dE_{max}, on going from solutions in water to solutions in ammonia is 20.6 kcal mole^{-1} for iodide and 20.2 kcal mole^{-1} for the solvated electron, even though the bands occur in different energy regions of the spectrum.[193] Another common feature is that E_{max} values are slightly higher in methanol than in water, a trend which is contrary to that expected from differences in dielectric properties. E_{max} for iodide and solvated electrons in ethanol, water, aqueous ammonia, ethylenediamine, crystalline KI, and aqueous salt solutions are rectilinearly interdependent[193,194] (Figure 5). Indeed, E_{max} for a solvated electron in a given solvent can be predicted[194] from the ctts value for that solvent.[75] As for iodide, the absorption bands for solvated electrons shift to higher energies when electrolyte is added[194–196] and, further, the absorption coefficient is only slightly affected.[194] Again, as for iodide, the band maximum for solvated electron shifts to higher energies when water is replaced by deuterium oxide. Similarly with increase in temperature, the band maximum for the solvated electron shifts to lower energies in water[197] and in ammonia.[198–200]

This final link is carried over in a treatment of the ctts excited state using the confined model for the ground state of the F-center. Here the potential energy well is formed by neighboring solvent molecules. The energy change associated with steps A and B are, as before, IP + $\Delta' H_s°(X^-)$. In the next step, the change associated with replacing the neutral atom within the cavity is taken as zero since the cavity can easily accommodate the atom, being smaller than the ion.

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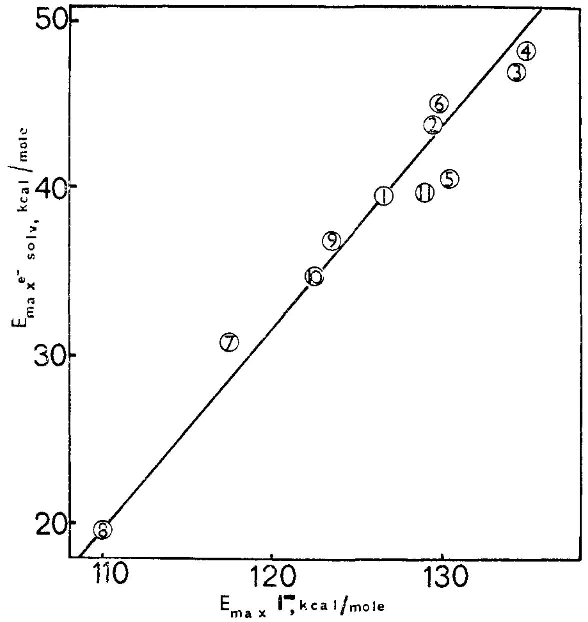

Figure 5. Plot of E_{max} for iodide against E_{max} for solvated electrons in a given solvent (data from ref 194 and 196). Key: (1) H_2O; (2) $MgCl_2$, 4.6 *M;* (3) KF, 12 *M;* (4) LiCl, 15 *M;* (5) MeOH; (6) EtOH; (7) ethylenediamine; (8) liquid ammonia (E_{max} for iodide extrapolated to 20°); (9) 25% NH_3 in H_2O; (10) 12 *M* NH_3 in H_2O; (11) KI crystal.

The energy change associated with transferring an electron from a state at zero potential and zero kinetic energy into the cavity is divided into two contributions. Since the size of the cavity is constant, the energy of interaction between an electron within the cavity with the solvent environment, $\Delta' H_s°(e^-)$, exactly counterbalances the enthalpy of hydration of the univalent anion, $\Delta' H_s°(X^-)$. There is a gain in energy of the electron arising from the kinetic energy of the electron within the potential energy well, equal to $+h^2/8mR_0^2$. It is assumed that the potential energy walls are infinitely steep, an assumption which is probably unjustified. Therefore

$$E_{max} = \Delta' H_s°(X^-) + IP - \Delta' H_s°(e^-) + h^2/8mR_c^2 \quad (16)$$

or

$$E_{max} = IP + h^2/8mR_0^2 \quad (17)$$

Thus, E_{max} depends on the radius of the potential energy well defining the excited state, and the ionization potential. There are no terms in the final expression for E_{max} which directly refer to the ground state, these being cancelled out in the cycle. For this reason, changes in E_{max} due to changes in, for example, solvent, temperature, and pressure, arise from changes in the energy of the excited state. The solvation energy of the ion may, of course, vary with changes in solvent but this change cancels in the cycle used in calculating the difference between ground- and excited-state energies. According to the Franck–Condon principle, the dimensions of the cavity are defined by ground-state ion–solvent interactions. The major disadvantage of the confined model is that R_0 cannot be calculated *a priori.* Thus R_0 is not equal to the radius parameter introduced into the diffuse model. The latter is the distance between ion center to the near-inside edge of the solvent molecules, while in the confined model R_0 is the distance between ion center and the inner surface of the potential energy well.

The confined and diffuse models differ in the extent to which the ctts excited state is constrained. The models represent two limiting cases, and both are gross simplifications. Both treatments basically use a radius parameter which is sensitive to constraints applied to the system. Indeed, there has been no experimental result or calculation to show convincingly the superiority of either model.

D. JORGENSON'S MODEL

Since there appears to be only one acceptor orbital in water and in methanol, it is proposed that this orbital is preponderantly the $(n + 1)$s orbital of the halogen with the radial function somewhat changed by its environment.[201–205] Such a model is attractive in that a similar model has been proposed for the ultraviolet spectra of alkali halide crystals and accounts for the exciton and higher energy absorption bands by $np^6 \rightarrow np^5(n + 1)s$ and $\rightarrow np^5(n + 1)d$ transitions.[178] The marked similarities between halide solution spectra and alkali halide spectra lend support to this model.

The model has not been developed in detail and comparison with the confined and diffuse models is difficult. A study of intensities for the ctts spectra of halide ions comparing the diffuse, confined, and $(n + 1)$s acceptor orbital (Rydberg) models shows poor agreement between predicted and observed intensities for the Rydberg transition model.[55] Such conclusions have been countered by the proposal that it is the detailed interaction between the $(n + 1)$s orbital and its environment which must be taken into account.[204]

IV. *Charge-Transfer-to-Solvent Spectra of Halide Ions*

In this section, the ctts spectra of halide ions in a variety of solvent media are reviewed, and, where appropriate, application of theoretical models will be described.

A. DEPENDENCE OF E_{max} ON TEMPERATURE

This is the most notable feature of ctts spectra. Two major effects must be explained: the decrease in E_{max} with increase in temperature and the rectilinear interdependence of E_{max} and temperature (Figure 1). The first has been accounted for, but the second is not completely understood.

1. Confined Model

The dependence of E_{max} on temperature is most readily understood in terms of an increase in R_c with increase in temperature. Thus it follows from eq 16 that

$$dE_{max}/dT = -(h^2/4mR_c^3)\, dR_c/dT \quad (18)$$

For example, R_c for iodide in water at 25° is approximately 4 Å, increasing by 0.1 Å over the range 25–50°. Since dR_c/dT is positive, then dE_{max}/dT is negative. For a given ion it is possible to adjust the temperature of two solvents such that E_{max} is the same. Since dE_{max}/dT is usually different for two

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solvents, then the two systems must differ in the way in which R_o is affected by a change in temperature. It is not clear from the model (or diffuse model; see below) why $E_{\max}$ is a linear function of temperature although the integrated form of eq 18 requires a dependence of R_c on temperature which is similar to that for the thermal expansion of alkali halide crystals.[4] The different values of $\mathrm{d}E_{\max}/\mathrm{d}T$ represent the differing sensitivities of R_o in different solvents to a change in temperature.[4] The factors which contribute to $\mathrm{d}E_{\max}/\mathrm{d}T$ are not clearly understood. If it were a simple function of the expansibility of the solvent, then for water at 4° $\mathrm{d}E_{\max}/\mathrm{d}T$ would be zero. This is not observed. Further, $\mathrm{d}E_{\max}/\mathrm{d}T$ is not a simple function of ion size. Thus, in acetonitrile, $\mathrm{d}E_{\max}/\mathrm{d}T$ values for chloride, bromide, and iodide are essentially the same.

2. *Diffuse Model*

The idea of the radius parameter being temperature dependent was carried over from the confined model.[53] If only changes in ϵ_s and ϵ_{op} are considered, then for iodide in water, $\mathrm{d}E_{\max}/\mathrm{d}T$ is less than 10% of that observed. Changes in R_d are therefore dominant. Since R_d is the cavity radius as defined by the anion in the ground state, then $\mathrm{d}E_{\max}/\mathrm{d}T$ reflects to a large degree the variation of the ground-state energy with temperature. This gives a way of linking spectroscopic and thermodynamic data. For iodide in water at 25°, $\mathrm{d}R_d/\mathrm{d}T = 9.3 \times 10^{-4}$ Å deg^{-1}.[53] As expected, the cavity radius increases with increase in temperature, and this variation is between that estimated[53] from entropies of hydration and partial molar volumes.

For both models, the steady change in $E_{\max}$ with increase in temperature shows that, over the limited temperature ranges employed, there are no dramatic changes in the constitution of the solvation shell, as would be expected if the solvation numbers changed suddenly at a particular temperature.

Analysis of experimental data for salt solutions, especially spectroscopic data, requires molecular models for these solutions. Unfortunately, structural data are sparse. Some information comes from X-ray studies of alkylammonium salt hydrates,[206,207] although here interest is usually directed toward the role of the alkylammonium ion. In tetraisoamylammonium fluoride hydrate,[208] $(i\text{-}C_5H_{11})_4N^+F^- \cdot 38H_2O$, fluoride occupies a water lattice site having tetrahedral coordination with four water molecules, where the F^-–(H)–O distance is between 3.0 and 3.2 Å. Since this crystal has the same general formula as the chloride,[209–211] it may have a similar hydrated structure. Similarly, in tetra-*n*-butylammonium fluoride hydrate, $(n\text{-}C_4H_9)_4N^+F^- \cdot 32.8H_2O$, the anion occupies a similar site, the F^-–(H)–O distance being between 2.80 and 2.87 Å. This salt has the same structure as the chloride and bromide,[209] and again the structures of water next to the anions are probably similar. These structures agree in principle with the model[143] of ionic solvation adopted in the Platzman and Franck model. However, these substituted ammonium hydrates are probably special cases, and it may be significant that no comparable iodide hydrate is known.[210] Potassium fluoride tetrahydrate, $KF \cdot 4H_2O$, is built from edge and corner sharing octahedra, $K^+(H_2O)_6$ and $F^-(H_2O)_6$, the F^-–O distance varying between 2.71 and 2.78 Å, with two close oxygens and two further away.[211]

X-Ray diffraction studies of solutions have been made, but are limited to concentrated solutions and even then interpretation of the data is difficult.[212–214] In potassium chloride (20% by weight) in water, K^+ has a hydration number of 4 and Cl^- of 6 where $r(Cl^-) + r(H_2O) = 3.2$ Å, the water molecules nearest the ion being significantly oriented toward it, thereby disrupting the water structure.[213] In lithium chloride solutions[214] the hydration number of chloride is between 8 and 9.

However, it is difficult to separate out from this structural information the various contributing influences of ion–ion, ion–solvent, and solvent–solvent interactions. A more general method is to start with an examination of ion–solvent interactions, ion–ion interactions being absent, *i.e.*, in a hypothetical standard state. Here the effects of added solute on the structure (albeit unknown[11–26]) of water are considered under two headings. Thus some solutes are called "structure breakers" since the structure of water in solution is thought to resemble that of pure water at a higher temperature.[215] Similarly, some solutes are called "structure formers," the water structure resembling that of water at a lower temperature.[215] For closed-shell anions, these effects are conveniently rationalized in terms of a simple model in which the structure of water around an ion is divided into three zones.[156,216,217] In zone A, closest to the ion, nearest neighbor water molecules have their dipoles directed toward the ion and are immobilized by the local intense electric field. In zone C, furthest from the ion, the water structure is similar to that in pure water at the same temperature except that it is under the influence of the field due to the ion. Between these two zones, A and C, there is a zone B where the water structure is "broken-down" to a more random structure; *cf.*, a fault zone.[16]

Thus, fluoride is thought to be a structure former, zone B being absent, with the hydrated ion fitting into the water structure. With increase in ion size, *e.g.*, through the series chloride, bromide, and iodide, the mismatch between the arrangement of water molecules in zone A and zone C produces zone B, the last increasing through this series to produce increase in the "structure-breaking" role.

The order of structure breaking for alkali metal and halide ions is generally written as $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$ and $F^- < Cl^- < Br^- < I^-$. This simple model has been used in correlating experimental data for aqueous solutions. It accounts for trends in heat capacities,[16,216] dielectric relaxation,[216,218] self-diffusion coefficients,[216,219,220] viscosities,[216,217,221] entropies, and enthalpies of hydration,[216] diffusion of ions,[222] entropies of transfer between water and

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deuterium oxide,[223,224] and near-infrared spectra of water in aqueous solutions.[225]

In some instances zone B may swamp zone A such that the nearest neighbor water molecules are disordered, *i.e.*, neither fully oriented toward the ion nor part of the bulk water structure.[217] This may occur for iodide in water.[16,217,226] Alternatively, iodide may interact with one hydrogen of each water molecule, thereby allowing the other to interact with the bulk solvent,[143,227] a model comparable to that found for the hydrates of the other halides. There are no marked differences between the ctts spectra of iodide, bromide, and chloride and so their mode of solvation must be similar.

B. BAND SHAPES AND INTENSITIES

1. *Diffuse Model*

The breadth of the absorption band is due to a distribution of cavity radii about the most probable value, the latter corresponding to $E_{\max}$. The lowest value of R_d is fixed at the ionic radius, r_i, and the highest value corresponds to the onset of absorption on the low-energy side. With decrease in temperature, the most probable value of R_d decreases, the band narrows, and $\epsilon_{\max}$ increases since the range of cavity size decreases, *i.e.*, $r_i \leqslant R_d \leqslant R_d(\max)$. Oscillator strengths have been calculated[55] using a nodeless 2s Slater wave function for the hydrogen-like excited state. The derived oscillator strengths were in fair agreement with experiment, *e.g.*, for iodide in water 0.33 (calculated) and 0.47 (observed).

2. *Confined Model*

The absorption band arises from a distribution of R_c values about the most probable, which corresponds to $E_{\max}$. However, no lower limit is envisaged for R_c, the onset of absorption at both high- and low-energy edges being therefore symmetrical about the absorption maximum. Theoretical calculation of oscillator strengths using this model have not been too successful, and it may be that this model treats the electron in the excited state as overconfined. Indeed, the confined model has its major success in correlating $E_{\max}$. The 1s-type wave function is far less satisfactory for those regions within the potential energy well where overlap occurs with the ground-state wave function[74] and higher orbitals of the iodine atoms, *e.g.*, 6s, whereas it is satisfactory for the extremes of the potential energy well, *i.e.*, as $r \rightarrow R_c$, and it is these conditions which are important in determining $E_{\max}$. The 1s wave function places a substantial part of the charge within the radius of the halogen atom.

C. DEPENDENCE OF $E_{\max}$ ON SOLVENT

1. *Confined Model*

At a given temperature, different $E_{\max}$ values for a given ion in a range of solvents reflect differences in the most probable value of the square-well radius, R_c. As expected this radius is larger than the ionic radius, *e.g.*, 3.9 Å for iodide in water at 25°. R_c may be broken down into three different contributions, *e.g.*, ionic radius plus penetration of the electron into the solvent molecule, r_p, plus the dead space between ion and solvent molecule.[54] If the latter is zero at 0°K, then r_p may be calculated from $E_{\max}$ at 0°K, obtained from the linear interdependence of $E_{\max}$ on temperature. For iodide, bromide, and chloride in acetonitrile, r_p is 1.68 ± 0.01 Å.[54]

Although R_c cannot be calculated for a solvent *a priori* some rationalization is possible. It is envisaged that the nearest neighbor solvent molecules around the ion are oriented with their dipoles toward the ion, the potential energy well for an ion in water being formed by regions of high electron density in the nonbonding orbitals on oxygen. In ammonia the potential energy well is formed by nonbonding orbitals on nitrogen. Here, $E_{\max}$ is at low energies and R_c is large. It is reasonable that for such a large "floppy" cavity dR_c/dT and $dE_{\max}/dT$ should also be large (Table III) and R_c links with the properties of liquid ammonia.[45]

2. *Diffuse Model*

The variation of $E_{\max}$ with solvent is dependent on change in the solvent dielectric constant and also with R_d,[87] although the relationship between r_i and R_d is not known for nonaqueous solvents.[175,176] The change in $E_{\max}$ is dominated by changes in the ground state, the binding energy of the electron in the excited state being relatively independent of solvent.[175]

3. *Deuterium Oxide*

The high-energy shift on $E_{\max}$ on replacing water by deuterium oxide and the increase in $dE_{\max}/dT$ are in agreement with the generally accepted viewpoint that water and deuterium oxide are very similar[228] in their properties, except that those of deuterium oxide[229–231] are comparable to water at a lower temperature; *i.e.*, more structural order exists in deuterium oxide.[232] The same structural models reproduce the properties of both solvents,[157,158,233–236] and this structural contrast accounts for trends in near-infrared spectra,[237] Walden products of ions,[238] Arrhenius activation parameters for conductivity,[239] kinetic solvent isotope effects,[240–242] entropies of transfer of salts between the two solvents,[223] and thermal diffusion[243] of salts.

4. *Acetonitrile*

The low value of $E_{\max}$ for halides in acetonitrile and the correspondingly large value of $dE_{\max}/dT$ point to the conclusion that the ion is contained in a large "floppy" cavity. Acetonitrile

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has a relatively large dipole moment, $\mu = 3.37$ D, but the positive charge is on the carbon of the CN group and solvation of an anion is impeded by the methyl group, halide ions favoring water over acetonitrile as a solvent.[244]

5. Propylene Carbonate

This is an interesting solvent since its dielectric constant at 25°, 65.1,[245] is close to that for water and provides a useful contrasting solvent in which to compare properties of solutes.[246-248] The enthalpies of transfer, ΔH_{tr}, from water to propylene carbonate have been analyzed assuming that ΔH_{tr}'s for Cs^+ and Cl^- are essentially equal, *i.e.*, -3.6 kcal mole^{-1}. For iodide the transfer is exothermic which means that the ground state for iodide in propylene carbonate is lower than in water. However, the shift in E_{max} is to lower energies by 3.9 kcal mole^{-1} which means that the energy of the excited state must decrease to an even greater extent, by approximately 7.5 kcal mole^{-1}. This pattern of behavior is contrary to that predicted by the diffuse model.

D. EFFECT OF ADDED SOLUTE

The effects of added salt on ctts spectra (Figure 4) have been extensively investigated (section II) but these effects are not well understood. In nearly all systems addition of a solute or cosolvent (section IV.E) shifts the iodide band to higher energies. Nevertheless, the shifts have been interpreted in several ways. Here the problems are briefly reviewed with particular reference to the spectra of halide in aqueous solution containing metallic salts and, later, alkylammonium salts.

For iodide in water, E_{max} generally increases when salts are added, and, over the range 1–10 equiv l.$^{-1}$, E_{max} is nearly a linear function of concentration. However, below 1 equiv l.$^{-1}$, E_{max} is slightly more sensitive to salt concentration.[3] The over-all shifts in E_{max} are relatively small, but within the above general pattern several specific salt effects are observed.[87] Initially, these specific effects were noted for different anions, different cations having, it was thought, the same effect at the same concentration (in equiv l.$^{-1}$, C^*). However, the detailed pattern which emerges is quite complex.[80,87]

In these investigations, the iodide concentration is low, *e.g.*, 10^{-4} *M* potassium iodide in a 10-mm path-length cell. If significantly more iodide is added, the absorbance is so large that it is difficult to measure E_{max} accurately. Added potassium iodide shifts the band edge to lower energies[80] and a similar shift occurs for bromide when potassium or sodium bromide is added, but these shifts are probably a consequence of concentration broadening. In contrast, addition of potassium chloride shifts the chloride band edge to higher energies.[80]

The most notable feature of the effect of salt on the spectra of iodide in water is the relative insensitivity of the band shape to added salt. The extinction coefficient, ϵ_{max}, and band width for iodide is the same in water and 12 *M* aqueous lithium chloride.[87] There is, however, a slight broadening when 3 *M* sodium bromide is added.[80]

At low concentration, $0 < C < 4$, the shift in E_{max} is not a linear function of salt concentration and, moreover, different salts shift the band by differing amounts. In these solutions, E_{max} shifts to lower energy with increase in temperature and is rectilinearly dependent upon temperature for each solution. The slope, dE_{max}/dT, is generally less than in water (Figure 6). One report indicates that the changes in dE_{max}/dT do not follow a simple pattern, dE_{max}/dT decreasing when C^* is 1, increasing when C^* is 2, and decreasing when C^* is 3 in aqueous solutions.[87] Another report[78] shows that dE_{max}/dT decreases with increase in potassium chloride concentration. The changes are nevertheless small. Similarly, for iodide in ammonia, dE_{max}/dT increases when 100-fold excess potassium perchlorate is added and the band moves to higher energies.[45] These shifts can be understood using both confined and diffuse models in terms of changes in radius parameters as a result of the action of added salt. Although no direct evidence for this postulate is available, the ratio, α, of solvent cavity radius to crystallographic radius, decreases with increase in salt concentration.[80] This was computed using a modified Hepler equation derived from the partial molar volume variation of both potassium chloride and bromide with added sodium chloride.[249-251] The predicted trend, according to the diffuse model, is in the right direction *i.e.*, $+350$ cm^{-1}, but this is greater than the observed shift, $+100$ cm^{-1}. This is an example of the way in which spectroscopic and thermodynamic data can be linked using the diffuse model.

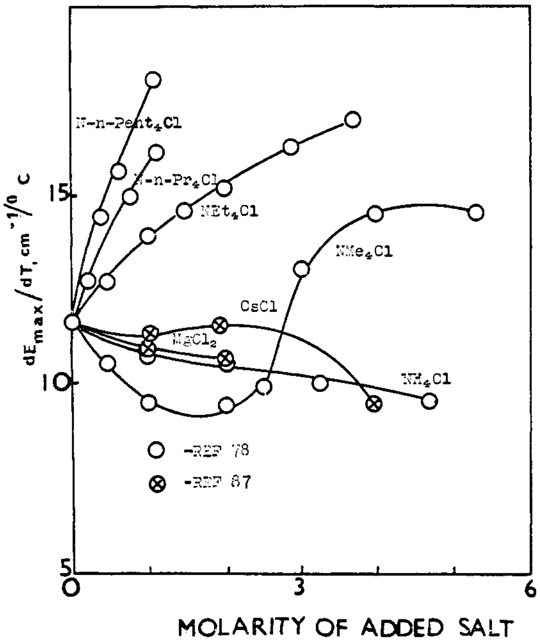

Figure 6. dE_{max}/dT as a function of added salt for iodide ($\sim 5 \times 10^{-5}$ *M*) (from ref 78 and 87).

In more qualitative terms, E_{max} will increase if molecules are removed from the solvent shell of the anion since, in the first limit, E_{max} is governed by the radius of this shell and thereby the number of molecules in this shell.[3,87] In this analysis it is assumed that both protons of each nearest neighbor water molecule are directed toward the ion. One

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approach[87] considers the effect of added salt on the number of single water molecules in solution,[252] but there is considerable discussion whether such species exist even in pure water. Analysis of the ultraviolet spectrum of water shows that their concentration is very low or zero.[253] Former persuasive arguments in favor of monomer based on the detection of a low-energy peak[254,255] in the inelastic neutron-scattering spectrum of water now seem out of favor.[256] However, the near-infrared spectra of water over the temperature range 30–374° shows that the possibility that monomers exist cannot be completely ruled out.[257] A more useful approach in the analysis of ctts spectra, and one which does not introduce these difficulties, is to consider only the number of nonhydrogen-bonded hydrogen atoms. Such a hydrogen atom may still be part of a water molecule which is involved in three other hydrogen bonds. There is good spectroscopic evidence for such nonhydrogen bonded groups both from near-infrared spectra of HOD in D_2O[258] and Raman spectra of HOD in H_2O.[259] Thus, when anions are added to water, the number of such protons available to iodide decreases[87] by virtue of the "proton affinity" of the added anions. In contrast, added cations, in bonding to water molecules through the oxygen atom, only slightly affect the number of hydrogen atoms available to iodide. In the limit, solvent sharing between a cation and iodide satisfies the hydration demands of both ions. This model accounts for the more marked effects of added anions than cations on the spectra.[87] Added anions also affect the Raman spectra of water more than added cations,[256,260–265] where presumably the dominant change is replacement of $H\text{-}OH \cdots OH_2$ by $H\text{-}O\text{-}H \cdots X^-$ interactions, the change to $M^+ \cdots OH_2$ being less important on the spectra of water. A similar trend is observed in the effect of added salt on the OH stretch in methanol.[266] A similar model also accounts for the effect of added salt on the spectra of iodide in ammonia.[45]

Although division of salt effects into separate effects of anions and cations is necessarily arbitrary, some interesting trends emerge for spectra in aqueous solution.

1. Anions

For a series of sodium salts, the spectra show two groups of anions with respect to their effect on E_{max} for iodide.[80] In the first group, the shifts to high energy are small and in the order $I^- < Br^- < Cl^-$ ($< OH^-$) $< F^-$. In the second group,[80] the shifts to high energy are much larger, the order being $HSO_4^- < ClO_4^- < ClO_3^- < H_2PO_4^- < HCO_2^- < CH_3CO_2^- < CN^- < SO_4^{2-} < HPO_4^{2-} < PO_4^{3-} <$ tartrate $<$ citrate. A similar series is observed for the effect of added salts on the O–H stretching frequency of HOD in D_2O,[267] *e.g.*, $ClO_4^- < ClO_3^- < I^- < Br^- < Cl^- \ll RCO_2^-$, although in methanol the effect of added salt on the O–H stretching frequency is the reverse, *e.g.*, $F^- < Cl^- < SO_4^{2-} < ClO_4^-$. A good correlation exists between these shifts, *i.e.*, ΔE_{max}, due to added oxyanions and the order in the lyotropic or Hofmeister series, *i.e.*, the lyotropic number.[268–270] The latter number measures the extent to which an ion binds water to itself and thereby precipitates a colloid. Here E_{max} decreases with increase in lyotropic number; *e.g.*, the lyotropic number at 0.5 M has the order $ClO_4^- > ClO_3^- > CH_3CO_2^- > HCO_2^- > SO_4^{2-}$. This correlation is in agreement with the proposal that the shift is a result of impoverishment by added anions of the hydration layer around iodide. A similar correlation is found for the "chaotropic order" for anions[271] and for surface potentials of aqueous solutions.[272] However, the correlation is not as good for halide ions although the same general trend is observed.[80] This may be due to the effects of these added anions on the structure of water in iodide solution. Thus, at fixed temperature, the size of the solvent cavity represents a balance between the effects of iodide–water interactions, water–water interactions, and added salt–water interactions. Since the added salt concentration greatly exceeds the concentration of iodide, the effect of added salt is dominant. Fluoride has a dominant high-energy shift since by enhancing the structure of water, *i.e.*, water–water interactions, iodide ion is impoverished of water; the cavity contracts and the band shifts to higher energies.[87] However, this model is by no means convincing (see below).

2. Alkali Metal Cations

For iodide in water, the relative high-energy shifts of E_{max} when chlorides are added have the order[87] $H_3^+O < NH_4^+ < Na^+ < Li^+ < K^+ < Rb^+ < Cs^+$. To a first approximation, the order for the alkali metal cations may again be rationalized in terms of structural changes induced in the water. This is not, however, consistent with the order for the anions, the largest energy shifts being due to structure-making fluoride and the structure-breaking cesium. Further, the position of lithium in this series is somewhat unexpected, both on these grounds and on the basis of ion size. In addition, it might have been anticipated that the changes in band intensity would accompany these structural changes, the latter being compared to the effect temperature. In fact, the extinction coefficients and band shapes are relatively unaffected by added salts. Again, the high-energy shift of, for example, added potassium chloride is not that expected of a structure-breaking salt and the observed shift is in the same direction as when *t*-butyl alcohol is added at low concentration (see below), this solute being generally thought to be a structure former. Similarly, the partial molal entropy of water in aqueous solution for chlorides, bromides, and iodides[273] up to salt concentrations of 3 M have the order $Li^+ < K^+ < Na^+$, and the same order exists for the Despretz constants.[274]

To a large part the difficulties in interpreting the effect of added salt on E_{max} are typical of those encountered in many other studies of salt solutions.

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The ideas of structure breaking and structure making are directly appropriate to analysis of ion–solvent interactions and thereby analysis of standard-state thermodynamic properties of solutes, *e.g.*, entropies, $\bar{S}_s°$, heat capacities, $\bar{C}_p°$, and limiting ionic mobilities, $\lambda_i°$. However, in real solutions, the effects of competing influences of anion–water, cation–water, interionic intreractions must be considered. In extremely dilute solutions these effects can be quantitatively treated using the Debye–Hückel equations. At slightly higher concentrations, *e.g.*, 0.001 to about 0.05 *M*, an analysis using a pseudo-lattice model is indicated.[275–278] These properties may also be reviewed in terms of effects of overlap between cospheres of the ions.[217,277,279–282] Certainly, discussion of experimental data for salt solutions in terms of excess functions[283] comparable to excess functions used to analyze thermodynamics of mixing for liquids has proved a useful advance.[284–290] These excess functions for concentrated salt solutions disclose patterns of behavior which can be related to the structure-making–structure-breaking action of the ions. Qualitatively, two similar "structure acting" ions salt each other in, while two differently acting ions salt each other out. An interesting point from these studies is that in mixed aqueous salt solutions interactions between ions of like charge appear to be more important than interactions between oppositely charged ions. In the context of ctts spectra of anions, this may be linked with the more marked specificity of effect of added anion. It is recalled that in a 1 *M* solution of 1:1 electrolyte the ion centers are, on average, only 9.4 Å apart,[291] and many water molecules will be mutually shared by the ions.[87]

The trends in ionic effects on ctts spectra can be compared with other spectroscopic data obtained in comparable concentration ranges. In an ^{17}O nmr study of aqueous salt solutions,[292] the ionic molal shifts (relative to that for ammonium[293]) have the order $Cs^+ < Rb^+ < K^+ < Li^+ < Na^+$ where the position of sodium is anomalous and the similarity in the cation effect on ctts spectra is striking. This trend is found for many systems, even to the extent of sodium being further along the series, near to rubidium. Examples include the effect of alkali chlorides on the proton magnetic resonance in aqueous solutions[294] and the bromine nmr resonance in aqueous solutions[295] and in the plot of the ratio of line width to viscosity against salt concentration for ^{127}I, where the order is $K^+ < Na^+ < Rb^+ < Cs^+$.[296] Similar anomalous orders for the cations are also found for the chlorine and bromine resonances in solid halides.[297]

The same order for the anions is also found for Rb and Cs resonances in solid halides[298] and for Na, K, Rb, and Cs resonances in aqueous solution.[299]

This pattern of behavior[292] suggests that these salt shifts have a common origin. The nmr studies of solids attributes the shifts to deviations from spherical symmetry of the ionic electron shells due to overlap of atomic wave functions of nearest neighbor ions,[300] and this treatment has been invoked in analysis of chemical shifts for cations in alkali halides[297] and in aqueous solutions.[296] It has not been applied to trends in E_{max}, and, while these links may provide the solution to the problem, the possibility that the shift was due to assymetric forces has been ruled out previously on the basis of line shapes in the nmr for chloride ions.[301]

In view of the previously noted links between ctts spectra and spectra of solvated electrons, a comparison of salt shifts for the two systems is rewarding. While the effect of added salt on the solvated electron band is small, there is nevertheless a detectable change in the electron spin resonance spectra for electrons in ammonia when 0.5 *M* salt is added.[302] Here the effect of added cation is small, the dominant effect being due to the anion.[303,304] The negative shift in the *g* factor for the solvated electron is $Cl^- < Br^- < I^-$. Although this is formally a reverse trend to that for the ctts shift in water, the dependence on anion is consistent with an interaction between the solvated electron ground state (*cf.* ctts excited state) and, *e.g.*, the outer 5p level of added iodide.

3. Alkylammonium Cations[78]

Addition of ammonium and tetramethylammonium chlorides $0 < C < 3$ *M* to iodide in water results in a shift of E_{max} to higher energies, the effect of tetramethylammonium chloride being more marked (Figure 4b). In contrast, tetra-*n*-amylammonium chloride shifts the band initially to lower energies, while tetra-*n*-propylammonium shifts the band to higher and then to lower energies. These effects do not fit a pattern expected from the relative sizes of the cations, and a similar contrast occurs for dE_{max}/dT for iodide in these solutions (Figure 6). Here, addition of ammonium chloride decreases dE_{max}/dT while addition of ethyl, *n*-propyl, and *n*-amyl salts shows a reverse trend.

The physicochemical properties of alkylammonium salt solutions, especially aqueous solutions, have attracted much detailed attention. In the development of electrochemistry they have been used extensively since they are soluble in most solvents and, by changing the alkyl group, effects due to

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change in size and shape of ions are easily probed.[305] It was apparent quite early that the properties of their aqueous solutions are not straightforward; *e.g.*, the mobilities of alkali metal cations in water at 25° increase with increase in size, whereas the reverse trend occurs for the symmetrical tetra-*n*-alkylammonium ions.[306–311] The properties of alkylammonium ions in their standard states indicate that cations larger than tetraethylammonium are structure makers.[312] In real solutions, interactions between these ions lead to a net enhancement of water structure due to cation–cation interactions.[313–317] Indeed, following the important discovery that these salts formed low-melting hydrates,[318,319] detailed structural data[207] for these hydrates have shown how closely they resemble rare gas hydrates, the alkyl chains being guests in an essentially water lattice. This knowledge has aided the interpretation of the properties of their aqueous solutions, *e.g.*, heats of dilution,[320] compressibility,[321] partial molar volumes,[322–324] and activity coefficients,[280] and has been extended to aqueous solutions of tri-*n*-alkylsulfonium salts.[325,326] Tetramethylammonium is structure breaking although not as effective as cesium.[309,312,313,327–331] Further, while the fluoride and hydroxide form hydrates, their structures are very different from the other alkylammonium ions, the whole cation occupying voids in the lattice.[332,333] Ammonium is generally thought to fit into the water lattice, being neither structure forming nor breaking,[312,334] although both alternatives have been proposed.[273,335] Structure-breaking and structure-making effects seem also to balance out in tetraethylammonium ions.[312,321,330] The extensive cation dependence on $E_{\max}$ for iodide when these salts are added is therefore not unexpected. Iodides do not form these solid clathrate hydrates, and the iodides show least deviation from classical behavior.

The properties of concentrated solutions show further changes in properties in the region where the ctts spectra are measured. For example, the solubility of benzene in aqueous tetramethylammonium bromide solutions increases linearly with salt concentration.[336,337] The solubility of benzene in aqueous solutions of tetraethylammonium bromide increases markedly above 5 *M*, of tetra-*n*-propylammonium bromide above 2–3 *M*, and of tetra-*n*-butylammonium bromide above 1 *M*.[338] This pattern resembles the solubility of benzene in aqueous detergent solutions[339] and may indicate micelle formation by these ammonium salts in aqueous solutions.[338,340] Interestingly, when tetra-*n*-butylammonium salts are recrystallized from benzene, large flocculent crystals are produced which contain large amounts of benzene.[341] The solubility patterns also resemble plots of ultrasonic absorption (α/f^2, where α is the amplitude absorption coefficient and f the frequency, 70 MHz) against alkylammonium salt concentration.[342] Here the controlling factor is associated with equilibria involving different rotational isomers.[343,344] It would be interesting to compare these effects with the shift in $E_{\max}$ when tetraethanolammonium salt is added since the insertion of the hydrophilic group is accompanied by dramatic changes in the properties of the salt.[345–347]

4. *Urea*

The high-energy shift of $E_{\max}$ for iodide in water when urea is added can, in the first limit, be interpreted in terms of an effective decrease in temperature as a consequence of an unexpected structure-forming action by urea. The effect of added urea on water structure is particularly interesting in view of links with biochemical studies. The denaturing effect of added urea on proteins is attributed to an ability to weaken hydrophobic bonds[348–360] which are thought to be responsible for their

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structure and stability in aqueous solutions (but there are alternative views[361] although urea is still envisaged as operating by water structure breaking). These effects may be rationalized in terms of a structure-breaking action of urea on water;[362–364] *cf.* the decrease in ultrasonic abosrption due to structural effects, *e.g.*, $(\alpha/f^2)_{\text{struct}}$, when urea is added to water.[365,366] This simple model for urea–water solutions is not completely satisfactory.[367–370] For example, the transfer of hydrocarbons from water to aqueous urea is accompanied by a decrease in free energy although the enthalpy change is unfavorable.[367] The high-energy shift may arise because urea dissolves preferentially in the B zone, thereby insulating the hydrated ion, which contracts with associated high-energy shift. This model is very similar to that proposed for urea–water mixtures,[371] where in a mixture model for water the urea is envisaged as dissolving preferentially in the broken-down water structure. As a consequence of this dilution, structured water breaks down to form a new equilibrium situation.

E. EFFECT OF ADDED COSOLVENT

The discussion is extended in this section to include the spectra of iodide in binary solvent mixtures where one component is water. The spectra show band shifts and $dE_{\max}/dT$ values in the mixtures are usually greater[8] than predicted from the Smith–Symons correlation (eq 18). The trends in $E_{\max}$ for these aqueous mixtures show interesting features which are attributed to changes in water structure due to the added cosolvent. Not all effects are understood, *e.g.*, the linear interdependence of $E_{\max}$ and temperature in each solvent mixture. The first report of these shifts concerned addition of dioxane. However, the effect of added alcohol, particularly added *t*-butyl alcohol, has been more extensively examined (Figure 3).

1. Alcohols

The absorption spectra of iodide in *t*-butyl alcohol shows that iodide is essentially ion-paired[49] (section VI). Consequently, addition of this alcohol to iodide in water would be expected to produce little or no initial shift, the ion preferring a water-rich environment. $E_{\max}$ for iodide is rapidly shifted to higher energies,[3,85,372–375] $E_{\max}$ at 25° being a rectilinear function of alcohol mole fraction, x_2, over the range $0 < x_2 < 0.03$. The changes when *t*-butyl alcohol is added are most marked although a similar pattern is observed when *n*-propyl and ethyl alcohols are added.[376]

Interpretation of the effect of added cosolvents on the structure of water must be made cautiously. There are sets of experimental data which refer essentially to the infinitely dilute solution of the alcohol in water. Other sets refer to real solutions and, at its simplest, the effect of overlap between cospheres of added solute must be considered.[377] At low alcohol concentrations, the effect of a monohydric alcohol on water structure can be compared to that of a substituted paraffin.[158] The alcohol molecule is regarded as a guest in the water host, the structure resembling a water clathrate[207,378] such that water structure around the paraffin group is enhanced, the hydroxyl group being probably hydrogen bonded and incorporated into the water lattice.[379–385] This model accounts, for example, for the negative relative partial molar volume, $\bar{V}_2{}^0 - V_2{}^0$. When real solutions are examined, the continued decrease in $\bar{V}_2 - V_2{}^0$ with increase in alcohol concentration[386] is attributed to a mutual reinforcement of clathrate cages,[381,382,387] the water structure being steadily enhanced. This model also satisfactorily accounts for spectroscopic, thermodynamic, and ultrasonic properties of these dilute alcohol solutions.[375,386–396] The same clathrate model also accounts for the variation in the properties of solutes in these alcohol mixtures. Indeed, the changes can be quite dramatic for ionic and dipolar solutes.[372,373,375,397,398] Particularly important in this respect are the studies of heats of solution for solutes in aqueous mixtures.[399,400] Thus, the free energies of activation, $\Delta G^{\ddagger}$ (and hence Y values[65,66]) change gradually with solvent composition for S_N1 solvolytic reactions. The gradual change is a consequence of compensation

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effects,[66,401] the enthalpies of activation, $\Delta H^{\ddagger}$, passing through minima in the highly aqueous region.[402–406]

The heats of solution of the solute (at essentially infinite dilution) become more endothermic with added ethyl alcohol, reaching a maximum near $x_2 = 0.15$ in the region where $\Delta H^{\ddagger}$ is a minimum. A similar pattern emerges for salts, *e.g.*, for potassium[407,408] and sodium chlorides, the enthalpy of transfer from water to dilute alcohol solution being endothermic. For sodium tetraphenylborate in *t*-butyl alcohol mixtures, the trend is more marked, ΔH_s being a maximum at lower alcohol mole fraction, $x_2 = 0.04$ at 25°.[409] Here the changes become marked with decrease in temperature, the endothermic maxima increasing and shifting slightly to lower alcohol mole fractions.[410] These studies have assisted interpretation of kinetic data for solvolytic reactions in these aqueous mixtures,[411–413] and they are also important in analysis of changes in E_{max} for iodide in water when *t*-butyl alcohol is added. The initial high-energy shift is in the direction expected if the alcohol effectively "cools" the system by enhancing water–water interactions, but this does not account for such features as the linear interdependence of E_{max} on x_2[372–374] which requires that the smallest amount of added alcohol is effective in shifting E_{max}. This can occur in one of two ways. The added alcohol may dissolve preferentially close to the iodide ion, the latter concentration being $\sim 10^{-4}\,M$. This seems unlikely in view of the close link between trends in E_{max} and properties of the aqueous mixtures. Also, added alcohol may have extremely long-range effects on water structure. This model seems more satisfactory in view of the accepted cooperative nature of hydrogen bonding in water. This effect could not occur if the structure-broken B-zone[216] around iodide is a time-independent property since this zone would insulate the ion from these effects. This suggests that the simple model of ionic solvation which identifies A, B, and C zones is essentially a time-averaged model, at any one instant zones A and C being partially linked.

The high-energy shift for E_{max} for iodide (difference between ground and excited states) can be compared with the increasing endothermic change in the heat of dissolution for potassium iodide (and sodium chloride) with added alcohol. If it is assumed that the enthalpy of solution for iodide is also positive, the shift in E_{max} cannot simply result from a change in ground-state solvation energy since this shifts in the wrong direction. If the energy of the ground state is raised, then for E_{max} to increase the energy of the excited state must be raised to a greater extent. These trends do not fit the pattern required by the diffuse model but agree with that expected from the confined model.

Through the series *t*-butyl, *n*-propyl, ethyl, and methyl alcohols the initial high-energy shift becomes less marked.[3,376] This trend is consistent with the order predicted from the properties of these mixtures.[378] In contrast, the trends in E_{max} and band width for the solvated electron in these systems follow a normal pattern, E_{max} in water–isopropyl alcohol mixtures being more sensitive to composition in the alcohol-rich region.[414]

Many properties of alcohol–water mixtures and solutes in these solvent systems show marked changes in the region of a critical mole fraction. Thus, near $x_2 = 0.04$ in *t*-butyl alcohol–water mixtures at 25°, E_{max} becomes less sensitive to added alcohol,[372–375] while, for example, the ultrasonic absorption becomes more sensitive.[394] This changeover is also noted in the maximum in heats of solution for the solutes.[399,400] Other properties which show points of inflection, maxima, or minima include molar volumes,[386–389] Walden products for ionic mobility,[415] and sound velocity.[416–418]

At higher mole fractions, $0.04 < x_2 < 0.5$, E_{max} is relatively insensitive to added *t*-butyl alcohol. No structural models have been proposed for this region. The maxima in the ultrasonic absorption for these mixtures[394,395] (as is also found in other alcohol and amine mixtures[419–424]) together with at least two well-defined relaxation frequencies[395,425] show that there are a series of equilibria in these systems which may involve different clathrate structures and different hydrophobically stabilized alcohol polymers.[375,395] It is not clear why E_{max} for iodide remains so insensitive to composition in the presence of such equilibria.

The initial high-energy shift, dE_{max}/dx_2, decreases over-all with increase in temperature, but a detailed examination[373,374] shows that, despite claims to the contrary,[426] dE_{max}/dx_2 is relatively insensitive to temperature over the range 30–50° (Figure 7). In addition, there are indications that dE_{max}/dx_2 is a maximum near 4°. A similar trend is also observed[374] for iodide in deuterium oxide when *t*-butyl alcohol-d_1 is added, a maximum being indicated near 10°.

In these analyses the linear plot of E_{max} *vs.* added alcohol mole fraction at a fixed temperature passes through the data point for water (or deuterium oxide). These trends must stem from the properties of iodide in water, and, indeed, there are many reports of maxima, minima, and points of inflection in the properties of water and aqueous solutions near 30–50°; *e.g.*, the activation barrier for flocculation of polyvinyl acetate sols in water[427] changes near 35°. The plot of dE_{max}/dx_2 against temperature resembles that for the differences in intensities of the absorption maximum at 2100 cm^{-1} and minimum

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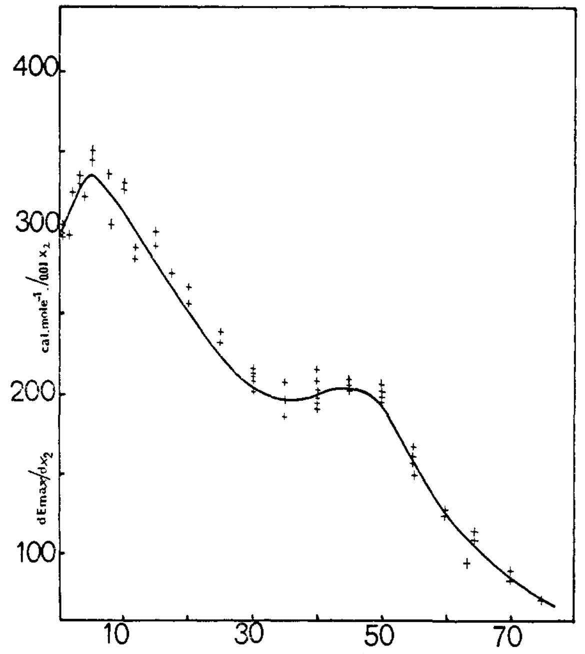

Figure 7. dE_{max}/dx_2 as a function of temperature, from ref 368, for iodide (5 × 10^{-5} *M*) in aqueous *t*-butyl alcohol mixtures.

at 1900 cm^{-1} against temperature in the absorption spectrum of water.[428] The heat capacity of pure water at constant pressure[429] has a minimum near 35°. The minima in the plots of viscosity at constant temperature against pressure are lost both for water[430–433] and deuterium oxide[434] above 30 and 30–40°, respectively. A minimum near 30° in the heat capacity at constant pressure for the dissociation of aqueous cyanoacetic acid is also observed[20] and, even after a more detailed analysis, this minimum is still indicated.[401]

Other anomalous temperature effects in this temperature region have been reported[10] including trends in ^{17}O nmr relaxation times.[435] However, the maximum in ΔH and ΔS for the interfacial tension between *n*-hexane and water near 30°[436,437] may be due to internal changes in the hydrocarbon phase.[438]

These changes in the region of 30–40° have been interpreted in terms of a "structural melting" of water[401] although the trends in dE_{max}/dx_2 have been interpreted to indicate that, if such a melting occurs, then it takes place nearer 50°.[374] This "melting" may be modified by the added alcohol, as indicated by the irregular pattern for the partial molar enthalpy of water in ethanol–water mixtures at 20, 30, and 40°[439] (compare, however, smooth curves for the heats of mixing at 25°).[387,440,441]

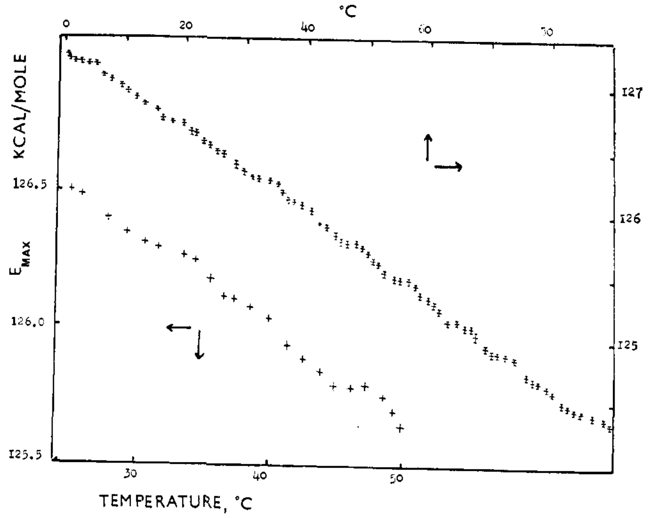

Figure 8. E_{max} as a function of temperature for iodide (5 × 10^{-5} *M*) in water from 1 to 91° (from ref 446).

Maxima for dE_{max}/dx_2 occur near the temperatures of maximum density for water and deuterium oxide, which is surprising since these temperatures are not associated with any structural changes. However, maxima in Arrhenius activation energies for conductivity of 1:1 salts in water[442,443] and deuterium oxide[239] show that ionic properties can be modified in this temperature region. This effect is not shown by 2:2 electrolytes.[444]

Trends in dE_{max}/dx_2 with change in temperature show a pattern which can be linked with the properties of water and other aqueous solutions although the changes are often small and close to experimental error. Nevertheless, these are gross features compared to other properties of water which are taken as indicating a further "fine structure" in the properties of water. This highly contentious subject concerns the claim that water shows "kinks" in plots of properties against temperature.

Previously reference was made to the linear interdependence of E_{max} and temperature for a given solvent system. In general, these conclusions are based on spectra measured at not less than 5° intervals. A check of this assumption[445] for iodide in acetonitrile shows that, with data at much closer temperature intervals, E_{max} is almost exactly a rectilinear function of temperature. However, similar plots for iodide in water do not have such a good fit, and the plots show a number of kinks (or thermal anomalies) superimposed on a general decrease in E_{max} with increase in temperature[445] (Figure 8). A similar pattern emerges for iodide in deuterium oxide for E_{max} values recorded at 1.2° intervals.[446]

The case for considering these features in properties of

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water has been reviewed in detail[18,447–449] both with reference to chemical and biochemical systems.[450] As a nmemonic (and only a nmemonic) these kinks are thought to occur at 15° intervals, *e.g.*, 15, 30, 45, and 60°. However, claims for "kinks" are not confirmed on reanalysis or reinvestigation,[451–455] and many properties of water show smooth and gradual changes with increase in temperature.[456,457] The subject is still in a state of acute controversy with claims and counterclaims.

The trends in E_{max} favor the viewpoint that the kinks are real. Analyses of the viscosities of other systems, *e.g.*, alcohols[458] and aqueous mixtures,[459] indicate that the phenomenon may be more common than originally envisaged.

2. *Acetonitrile*

Although aqueous mixtures of acetonitrile have only rarely been used as a solvent,[3,54,460] the contrast in the properties of this mixture with aqueous alcohols[392] could provide a useful guide to the role of the solvent in physico-chemical processes. The relative partial molar volume of acetonitrile shows no minimum in the aqueous-rich region,[392,461–464] and the mixture has an upper critical solution temperature at approximately $-1.0°$ and $x_2 = 0.40$ indicating that at 25°, the mixing is essentially enthalpy rather than entropy controlled.[465] Consistent with this is the failure to prepare a hydrate of acetonitrile.[388] The change in the near-infrared spectra of HOD in deuterium oxide[258] when acetonitrile is added shows that the water structure is not simply enhanced (*cf.* addition of *t*-butyl alcohol[392]). E_{max} for iodide shifts to higher energies,[376] but the shift is small in magnitude although quite significant when set against the extent of the over-all shift between pure water and pure acetonitrile. The thermodynamics[392,464] and spectra[392] of the mixture indicate extensive intercomponent hydrogen bonding followed by rapid breakdown of watery structure. This intercomponent interaction appears to initially deplete the iodide solvation shell, but the ensuing breakdown of the water structure when more acetonitrile is added releases the water molecules, and the tendency to a high-energy shift is quickly counteracted.

3. *Dioxane*

In contrast to acetonitrile mixtures, water–dioxane mixtures have been used extensively as solvent media, particularly in conductivity studies of salt solutions.[466] The two liquids are completely miscible at room temperature, and the mixtures provide a wide range of solvent dielectric constants.

Although the properties of these liquid mixtures have been extensively investigated, there is as yet no clear-cut evidence concerning the manner in which added dioxane affects water. Dioxane forms a 17-Å cubic hydrate, 8(dioxane)·$136H_2O$,[207] and the thermodynamics of mixing for the liquid mixtures are close to those required for a lower critical solution temperature.[467] The heat of solution for sodium tetraphenylborate in water becomes more endothermic when small amounts of dioxane, $x_2 < 0.05$, are added, although the trend is less marked than for ethyl alcohol.[399] Further, though there is no large excess ultrasonic absorption, 2:1 and 2:2 water–dioxane complexes are formed,[468–470] their stability being due to formation of hydrophobic clusters around the hydrocarbon part of dioxane.[468]

The relative partial molar volumes of dioxane show that if there is a minimum, it is very weak.[471,472] Direct density measurements show that the partial molar volume of dioxane in the extremely water-rich mixtures decreases slowly with increase in dioxane concentration.[473] The variation in the solubilities of argon in water when dioxane is added[474] is quite different than when ethyl alcohol is added[475] (*cf.* methyl alcohol[476]), the dioxane appearing to act as a structure breaker.[474,477]

The small high-energy shift for E_{max} of iodide when dioxane is added follows the same trend as for ethyl alcohol, and the heat of solution of sodium tetraphenylborate shows the same initial trend in both systems. The shift is opposite to that expected if ion–dioxane interactions are involved. Nuclear magnetic resonance and diffusion data show that there is no specific interaction of this form in 50% v/v mixtures,[478] and the Walden product for cesium iodide in dioxane–water mixtures changes gradually with composition.[479] These features can be reconciled if small amounts of dioxane structurally enhance the water, but this is gradually offset by strong intercomponent interaction, the latter, in the limit breaking down the water structure. Thus, addition of 60% v/v of dioxane to deuterium oxide and water results in a kinetic solvent isotope effect of close to unity for hydrolysis of *t*-butyl chloride.[480]

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4. *Acetone*

Acetone forms a hydrate[481–484] and the heats of solution of sodium tetraphenylborate in these mixtures are most endothermic near $x_2 = 0.1$, the change being not so marked as that for ethyl alcohol mixtures but more marked than the dioxane system.[400] Similar trends are seen in the viscosities of these mixtures.[485,486] The activation enthalpies for solvolysis reactions in these mixtures show minima near these compositions at 25°,[487,488] and the ultrasonic absorption plots have intense maxima.[489] Consistent with these trends is the high-energy shift in $E_{\max}$ when acetone is added to iodide in water.[3]

F. EFFECT OF APPLIED PRESSURE

The high-energy shift of $E_{\max}$ at approximately 25°[83,84] can be understood in terms of a decrease in the size of the cavity, R, with increase in pressure, and this is the basis of interpretation for both the confined and diffuse models. Attempts to correlate the high-energy shift with changes in bulk solvent properties, such as dielectric constant and compressibility, have not succeeded, the former being small enough to be ignored.[175] The pressure dependence of $E_{\max}$ is proportional to $d\alpha/dP$ in the diffuse model. The confined model correlated a constant value of $dE_{\max}/dP$ and $dE_{\max}/dT$ with a given solvent cavity of constant composition. The pressure dependence of the onset of absorption for thiosulfate is twice that for I^- at $\bar{\nu}_{\max}$.[175] As dE/dT for iodide at the onset of absorption is twice that at the peak, the same pressure dependence on the peaks of I^- and $S_2O_3^{2-}$ are predicted.[175]

The linear pressure dependence of $E_{\max}$ for iodide in 0.02 mole fraction aqueous dioxane, 2.5 and 4 M aqueous KF, and acetonitrile[84] is defined as "normal," with the solvent cavity being uniformly compressed with increase in pressure. These results contrast with the initial, nonlinear, pressure dependence of $E_{\max}$ for iodide in aqueous solution for the range 0–400 bars (at 25°). The transition to a linear dependence of $E_{\max}$ on pressure is not clear-cut but certainly is in the region of 4–800 bars. This initial, nonlinear, shift may reflect a breakdown of water structure with applied pressure.

The response of open, hydrogen-bonded, structures toward applied pressure may take several forms.[430,490] Above *ca.* 1000 bars the dominant effect at all temperatures is an increase in relative viscosity, the "normal" effect. Below 30°, and particularly below 4°, the applied pressure up to $\sim$1000 bars destroys water structure. A similar effect has been noted in the relative viscosity of D_2O as a function of pressure, the minimum disappearing in the region of 35–40°.[434] An interesting link back to the pressure dependence of $E_{\max}$ in aqueous 2.5 M potassium fluoride is the decrease in the depth of the minimum in relative viscosity at a given temperature following addition of electrolyte.[491,492] Thus, following addition of organic and inorganic solutes, the pressure dependence of $E_{\max}$ and relative viscosity in the low-pressure region become more "normal." Addition of solutes to aqueous iodide increases $dE_{\max}/dP$ in the same sense as $dE_{\max}/dT$ is affected.[84] Similarly, $dE_{\max}/dP$ and $dE_{\max}/dT$ values are higher for iodide in methyl cyanide than in water.[84] Undoubtedly, the behavior of $E_{\max}$ for iodide,[84] relative viscosity,[430,434] activation energy of conduction,[493] and cmc[494,495] under applied pressure point to a change in water structure below 1000 bars, the details of which are as yet imperfectly understood. The effect of pressure of ionic hydration is different from that of temperature in that the former breaks down the ordered region about the ion in addition to breaking down the bulk structure.[496] A combination of these two effects is therefore of particular interest. Preliminary results[497] indicate that the plot of $E_{\max}$ for aqueous iodide against pressure becomes more linear with increase in temperature, the initial nonlinear region being gradually lost. This is in accord with extrapolation from trends in relative viscosities.

V. *Charge-Transfer-to-Solvent Spectra of Other Anions*

The purpose of this section is to review the solution spectra of (generally) polyatomic anions (Table III). Problems arise in assigning values to the ionization potential[498] and ionic radius for an anion. The ionization potential value of an anion equals the electron affinity of the related radical only when the anion is monatomic. The vertical excitation–ionization process (Franck–Condon principle) will generally produce a vibrationally excited or strained anion radical. In some cases, such as azide radical,[499] the difference between the vertical and equilibrium values of the ionization potential is small, but this may not always be the case. Measurement of electron affinity by addition of an electron to an equilibrated radical will tend to give a vibrationally excited electronic ground-state anion. The approximation is generally made that the ionization potential of the anion is equal but opposite to the electron affinity of the radical. Differences between independent and ctts ionization potential values are generally ascribed to the breakdown of this approximation.

Electron affinities are much more readily available.[498,500] An important development is calculation of electron affinities,[501] in very good agreement with observed values.[502,503]

If $E_{\max}$(calcd) is to be compared to $E_{\max}$(obsd), a value of r_1 is required. It is important that sets of radii for anions are internally consistent and the values for anions reviewed are generally those given by Yatsimirskii.[163]

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A. PSEUDO-HALIDES

This term includes XH$^-$ (where X is O and S), CNX$^-$ (where X is O, S, Se, and Te), cyanide, and azide.

1. XH$^-$

Both O$^-$ and SH$^-$ have intense absorption spectra in the ultraviolet region.[9] Different values of ν_{max} for aqueous hydroxide ion have been reported,[9,504–506] three values agreeing that $\bar{\nu}_{max}$ is at 53,500 cm^{-1}, [9,504,505] and the other at 52,300 cm^{-1} at 20°. In the last report ϵ_{max} is approximately equal to ϵ at this frequency in the other reports, pointing to the possible role of errors due to scattered light. The extinction coefficients are 3.9,[9] 3.85[504], and 2.9[505] × 10^3 M^{-1} cm^{-1}, being approximately 25% of that for iodide. Extinction coefficients for polyatomic anions are generally less than those for halides and the intensities also appear to decrease with increase in the number of atoms in the ion. Oscillator strengths are infrequently reported for ctts spectra of polyatomic anions, one difficulty being that bands generally overlap and half-band widths cannot readily be determined.

The effect of temperature on spectra of aqueous hydroxide has been reported but these results are possibly affected by scattered light.[506] The apparent $\bar{\nu}_{max}$ shifted to lower energies with increase in temperature. The diffuse model gave an ionic radius, 1.78 Å, for OH$^-$ in aqueous solution at 20°.[506] The hydroxyl radical electron affinity was taken as 50 kcal mole^{-1},[500] while recent theoretical and experimental work favor 40 kcal mole^{-1},[501,502] and the magnetron technique gives 43.45 kcal mole^{-1}.[507] The derived r_i, 1.78 Å, lies within the (cation dependent) value of r_i for OH$^-$ in crystalline hydroxides, 1.32–1.84 Å,[508] and is greater than that derived from heats of transfer from water to aqueous dioxane,[509] r_i = 1.53 Å. If $\bar{\nu}_{max}$ = 53,500 cm^{-1} and E_A(OH) = 40 kcal mole^{-1}, the diffuse model gives 1.62 Å for r_i.

Further evidence that this absorption band of hydroxide is due to a ctts transition is sparse. The assignment rests primarily upon the intensity of the absorption and the absence of vibrational fine structure. Since hydroxide is generally classed as a pseudo-halide, a ctts absorption is expected. Measurements of spectra in nonhydroxylic solvents are complicated by chemical reaction.

More convincing evidence comes from steady-state and flash photolysis studies. Two detailed photochemical studies using the mercury excitation line at 54,090 cm^{-1} gave ϕ_e values of 0.105[510] and 0.11[511] using specific scavengers for solvated electrons and hydrogen atoms. A report[110] that ϕ_e = 0.50 has not been substantiated. Flash photolysis of aqueous hydroxide gives the well-characterized spectrum of solvated electrons[115] which is suppressed by specific scavengers for this species.

There is more spectroscopic evidence for the nature of hydrosulfide absorption in aqueous,[512,513] aqueous binary,[513] and liquid ammonia solution.[514] Changes in E_{max} of hydrosulfide following changes in temperature and solvent system are similar to those observed for halides. The spectra of hydrosulfide was assigned to a ctts process and the asymmetry of the ion ignored.[513] In contrast to an earlier analogy drawn with chloride,[153] a better correlation is claimed between hydrosulfide and bromide, as expected from their very similar crystallographic radii.[513]

Using 52 kcal mole^{-1},[501] for E_A(HS$^-$), in good agreement with the magnetron value of 53 kcal mole^{-1},[515] the difference E_{max}(Br$^-$) − E_{max}(HS$^-$) should equal the difference between the ionization potentials (or electron affinities), *i.e.*, 24.9 kcal mole^{-1}. The observed difference is 17.2 kcal mole^{-1}, the discrepancy of 7.7 kcal mole^{-1} being significant but difficult to explain in view of the close correlations reported for other properties of these two ions.

Plots of E_{max} against mole fraction in aqueous acetonitrile and aqueous methanol solution for iodide and hydrosulfide indicate a greater selectivity for the aqueous component of the solvent systems by hydrosulfide.[513]

The spectra of hydrosulfide in aqueous solutions of pH 1–10.5 give pK_{H_2S} (7.05) and pK_{HS^-} (13.8) at 25°[516] and over a range of temperatures up to 90°.[512] There is a clear-cut difference between the reported spectra, the spectra in the region of 44,000 cm^{-1} being seen as a shoulder[9] and as a well-resolved symmetrical peak.[513]

The spectra of hydrosulfide in liquid ammonia, ν_{max} at 35,910 cm^{-1} (238°K), derived from hydrogen sulfide differs from that obtained by the dissolution of alkali sulfides, where d$\bar{\nu}$/dT is 26.9 cm^{-1} deg^{-1}, the former not obeying Beers law and having a different value of d$\bar{\nu}$/dT, 23.6 cm^{-1} deg^{-1}. Potentiometric and conductometric data, together with the spectra of solutions containing hydrogen sulfide and potassium metal, assigned the species responsible for the absorption at 36,000 cm^{-1} not to hydrosulfide but to an equilibrium between $S^{2-}\cdots NH_4^+$ and $HS^-\cdots NH_3$ with an equilibrium constant of 1.04×10^{-2}. The increase in K_1 parallels the increase in basicity of the solvent from water to liquid ammonia. The spectra of both OH$^-$(aq) and $S^{2-}\cdots HNH_3^+/HS^-\cdots NH_3$ in liquid ammonia show higher energy transitions whose nature has not been determined.[9,514]

In the absorption spectra of sulfide in aqueous solutions of pH 15, $\bar{\nu}_{max}$ is 27,300 cm^{-1}.[512] An increase in temperature shifts $\bar{\nu}_{max}$ to lower energies (−3 cm^{-1} deg^{-1}), and by analogy to the spectra of alkaline earth sulfides,[517] the absorption was assigned to a ctts process. The value of d$\bar{\nu}$/dT is less than that for iodide, −11 cm^{-1} deg^{-1}, but a dinegative ion is expected to have a more tightly bound solvation shell. The diffuse model predicts that d$\bar{\nu}$/dT should be nearly independent of the ionic potential,[175] but the spectra of sulfide does not support this. The negative ionization potential of sulfide in the

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Table III

Absorption Bands of Anions in Solution (Omitting Halides)

Anion	*Solvent*	*$10^{-3}\ \bar{\nu}_{\max}$ at 20°*	$\epsilon_{\max}$, *$M^{-1}\ cm^{-1}$*	*Assignment*	*Ref*
OH^-	Aq	53.5	3.9×10^3	Ctts	9
		53.5	3.85×10^3	Ctts	504
		53.5	2.9×10^3	Ctts	505
		52.3	2×10^3	Ctts	506
SH^-	Aq	43.5	7.94×10^3	Ctts	9, 513
	0.5 *M* NaOH	43.5	7×10^3	Ctts	512
	Liq NH_3 (−77°)	37.0	6×10^3	Ctts	514
S^{2-}	pH 15, aq soln	27.8	Weak	Ctts	513
Se^{2-}	Aq H_2Se	24.0	Unknown	Unknown	518
CN^-	Aq	>55.0			519
CNO^-	Aq				
CNS^-	Aq	45.0	3.5×10^3	Ctts	89
	MeCN	41.4	3.5×10^3	Ctts	89
	Aq, MeCN	>45.0	$>1 \times 10^4$	Unknown	89
	Liq NH_3	40.5	$\sim 4 \times 10^3$	Ctts	77
$CNSe^-$	Aq	42.5	3×10^3	Ctts	89
	MeCN	38.9	3.5×10^3	Ctts	89
	Aq MeCN	>45.0	$>1 \times 10^4$	Unknown	89
$CNTe^-$	Aq	37.0	$\sim 3 \times 10^3$	Ctts	89
		42.5	$\sim 7 \times 10^3$	Ctts	89
		>45.0	$>1 \times 10^4$	Ctts	89
N_3^-	Aq	53.0	$>1 \times 10^4$	Intramolecular	499
		49.3	$\sim 4 \times 10^3$	Ctts	499
		43.0	4×10^2	$^1\Sigma_g{}^+ \rightarrow {}^1\Delta_u$	499
HCO_3^-	Aq	45.0	<1	Forbidden n–π*	527
		>52.0	$>4 \times 10^2$	Unknown	9
CO_3^{2-}	Aq	37.0	<1	Forbidden n–π*	526
		~50.0	$\sim 2 \times 10^2$	Forbidden n–π*	9, 526
		46.1		Intramolecular	528
CS_3^{2-}	Aq	20.0	3×10^1	Intramolecular	528
		29.8	1×10^4		
		~44.8	$\sim 1 \times 10^4$		
CSe_3^{2-}	Aq	15.8	8×10^1	Intramolecular	528
		21.3	8×10^2		
		26.3	2×10^4		
		41.5	1×10^4		
NO_2^-	Aq	28.2	22.5	$n_0 \rightarrow \pi^*$	532
		~34.8	9.4	$n_0 \rightarrow \pi^*$	532
		47.62	5.38×10^3	$\pi \rightarrow \pi^*$	532
		52,000	$\sim 5 \times 10^3$	Ctts?	532
NO_3^-	Aq	33.0	7	$n \rightarrow \pi^*$	533
		49.5	9.9×10^3	$\pi \rightarrow \pi^*$	530
HPO_4^{2-}	Aq	56.0 (extrapd)	$\sim 16^3$	Ctts	536
$H_2PO_4^-$	Aq	59.0 (extrap)	$>10^2$	Ctts	536
		48.0	<1	Intramolecular	536
		37.0	<1		
HSO_3^-	Aq	>55.0	Weak	Unknown	9
SO_3^{2-}	Aq	44,000	$>10^3$	Ctts	521
HSO_4^-	Aq	>60,000	$>10^2$	Ctts	539
SO_4^{2-}	Aq	57,140	3×10^2	Ctts	56
	D_2O	58,600	3×10^3	Ctts	56
$S_2O_3^{2-}$	Aq	>50.0	$>4 \times 10^3$	Intramolecular	546
		46.5	4×10^3	Ctts	546
		41.0	2×10^2	Intramolecular	546
ClO^-	Aq	34.4	310	Intramolecular	155
		34.4	360		549
		34.4	360		550
BrO^-	Aq	30.0	326	Intramolecular	551
IO^-	Aq	27.4	31	Intramolecular	553
		39.2	400		553
		>42.0	$>10^3$		553

Table III (Continued)

Anion	*Solvent*	*10^{-3} $\tilde{\nu}_{max}$ at 20°*	*ϵ_{max} M^{-1} cm^{-1}*	*Assignment*	*Ref*
ClO_2^-	Aq	~38.0	1.5×10^2	Intramolecular	155
		~47.0	2×10^2	Unknown	155
		>50.0	$>5 \times 10^2$	Unknown	155
ClO_3^-	Aq	>50.0	$>10^3$	Intramolecular	555
BrO_3^-		>50.0	$>10^3$	Intramolecular	555
IO_3^-		>50.0	$>10^3$	Intramolecular	555
ClO_4^-	Aq	>55.5	>20	Intramolecular	556
IO_4^-	Aq	~46.0	$\sim 10^4$	Intramolecular	557
XeO_4^{2-}	Aq	40.0	6×10^3	Unknown	558
NH_2^-	Liq NH_3	30.12	3.48×10^3 (−49.1)	Ctts	559
$NHEt^-$	Ethylamine–liq NH_3	31.5	$2.7 \pm 0.4 \times 10^3$	Ctts	562
Ferrocyanide	Aq	39.0		Ctts	563

gas phase (−104 kcal mole^{-1})[500] introduces complications into the thermodynamic cycles described in section III. A band with ν_{max} at 24,000 cm^{-1} [518] in the spectra of aqueous hydrogen selenide has been assigned to selenide.

2. CN^- and CNX^-

The absorptions of cyanide and cyanate in aqueous solution are intense near 55,000 cm^{-1},[519] but the maxima have not been determined. On going from CNS^- to $CNTe^-$ the maxima shift from 45,000 to 38,000 cm^{-1} [89] in aqueous solution with a higher intensity absorption edge at higher frequencies. The higher energy bands have not been investigated but changes in temperature and solvent, used to characterize the lower energy bands, result in greater resolution, implying that the former bands are internal transitions.

The bands are intense and effectively unchanged in character by X changing from S to Te. There are no intramolecular transitions underlying these bands. The shoulder at 45,000 cm^{-1} in the spectrum of CNS^- was assigned, without evidence, to a ctts process.[9] Later, $\tilde{\nu}_{max}$ was stated to be in the region 50,000 cm^{-1}.[520] The low-energy absorption bands in the spectra of CNX^- ions in water, aqueous acetonitrile, anhydrous acetonitrile, and liquid ammonia (for CNS^-[77]) are due to ctts processes. This conclusion is supported by formation of solvated electrons when aqueous CNS^- is irradiated at 43,860 cm^{-1} [89] and by the detection of solvated electrons in flash photolyses of CNS^- solutions.[521] Two decay schemes are proposed[521] consistent with simultaneous ctts and intramolecular excitation. If a filter cuts off radiation above 42,200 cm^{-1}, solvated electrons are not formed, but sulfur and hydrogen sulfide are, implying an underlying intramolecular transition as yet undetected.

There is a discrepancy between ionization potentials derived *via* the diffuse model (r_i being known)[163] (69 kcal mole^{-1}) and the electron affinity of CNS radical (49.9 kcal mole^{-1}).[515] The Franck–Condon strain produced in the vertical ionization process cannot account for a difference of this magnitude.[89] A similar discrepancy occurs for selenocyanate, $CNSe^-$, where the electron affinity of the radical is 66 ± 6 kcal mole^{-1}.[515] An almost linear relationship exists between E_{max} for CNX^- in aqueous solution and the decomposition voltage of 0.1 *M* KCNX solution (Figure 9). Analysis of this link in terms of the dissociation energy of A_2, solvation energy, and entropy of A· (where A· is a halogen atom) requires a slope of unity.[522] The empirical correlation has a slope greater than unity, but predicts $\tilde{\nu}_{max}$ of other aqueous anions.[89]

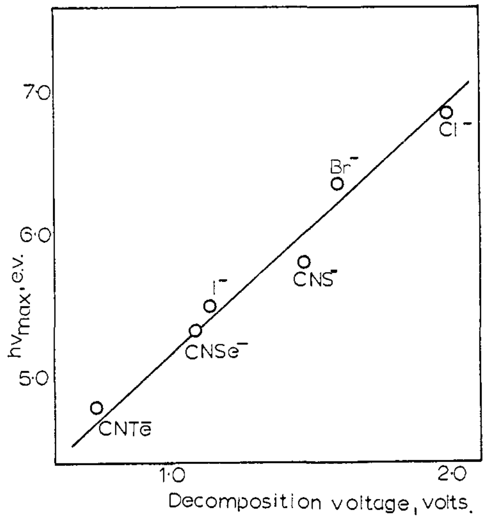

Figure 9. E_{max} (in electron volts) as a function of the decomposition voltage of halide and pseudo-halide ions in 0.1 *M* salt solution (from ref 89 by kind permission of the authors).

B. AZIDE

The ultraviolet absorption spectra of aqueous azide includes absorptions due to a ctts process.[523] The spectrum[499] comprises three over-lapping bands, labeled A, B, and C, progressing to higher energies in that order. Bands A ($\tilde{\nu}_{max}$ >53,000 cm^{-1}) and C ($\tilde{\nu}_{max}$ 43,000 cm^{-1}, ϵ_{max} 400 M^{-1} cm^{-1}) were assigned to intramolecular transitions, comparison being made with azide crystal low-temperature spectra and similar molecules such as CO_2 and CS_2. This assignment agrees with a theoretical study of azide and alkyl azides,[523] although the possibility of a ctts transition was not considered. Analysis[499] of changes in spectra with change in solvent and temperature assigned band B ($\tilde{\nu}_{max}$ ~49,300 cm^{-1}, ϵ_{max} 4 × 10^3 M^{-1} cm^{-1}) to a ctts process. This band is not immediately apparent from the re-

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corded spectra, and overlap of bands inhibits measurement of d$\bar{\nu}$/dT. The electron affinity of the azide radical, following a study of the iodine–azide ion complex, equals 82 kcal mole^{-1}. Allowing for the Franck–Condon principle in the production of a strained radical gives a correction of -0.75 kcal/mole and thus $E_A(N_3)$ is 81 kcal/mole.

This value differs from the result of an electron-impact study, where $E_A(N_3) = 69 \pm 7$ kcal mole^{-1}.[524] Assignment of band A to ctts transition gave $E_A(N_3)$ as 54 kcal mole^{-1}.[525] The spectra of azide are clearly complex and only partially ctts in character, and assignments of ctts spectra "by analogy" to the halides must henceforth be made cautiously.

C. GROUP IV ANIONS

There is less information on the absorption spectra of oxyanions of group IV. Aqueous carbonate and bicarbonate show broad low-energy bands at $\bar{\nu}_{max}$ 37,000 and 46,500 cm^{-1}, respectively.[526,527] These bands have very low intensity, $\epsilon_{max} < 1$, and are assigned to forbidden n-σ^* and n-π^* intramolecular transitions. The oscillator strengths vary with concentration and cation. These bands were not reported in an earlier study of carbonate–bicarbonate aqueous solution spectra,[9] due to their low intensity, this work concentrating on higher energy, high-intensity bands, $\bar{\nu}_{max}$ 40,000 cm^{-1}. The absorption maximum for carbonate at 50,000 cm^{-1} has been tentatively assigned to a forbidden intramolecular transition.[526] This assignment is supported by a study of trichalcogen carbonate ions.[528] For carbonate, trithiocarbonate, and triselenocarbonate, weak bands (ϵ_{max} 1, 30, and 80 M^{-1} cm^{-1}) shifting progressively to lower energies are found and theoretically predicted.[528] For the trithio- and triselenocarbonates high-intensity bands are observed at 29,800 and 44,800 cm^{-1} ($\epsilon_{max} \sim 1 \times 10^4 M^{-1}$ cm^{-1}) and 21,300, 26,300, and 41,500 cm^{-1} (ϵ_{max} 8×10^2, 2×10^4, and 1×10^4 M^{-1} cm^{-1}), respectively. A molecular orbital approach predicts the high-intensity bands quite well, giving 51,300, 29,360, and 26,730 cm^{-1} for $\bar{\nu}_{max}$ of the series CO_3^{2-}, CS_3^{2-}, and CSe_3^{2-}, the low-intensity bands being described as either forbidden or forbidden with vibronic interaction.[528] The possibility of ctts bands was not considered. The existence of carbonate radical anion is established[529] and a ctts band for carbonate is expected above 50,000 cm^{-1}.

D. GROUP V ANIONS

The spectra of group V anions in solution have been investigated more intensively. Both nitrate[530–532] and nitrite[533] have low-energy, low-intensity, and high-energy, high-intensity absorption bands. For nitrate, band A at 33,000 cm^{-1} (ϵ_{max} 7 M^{-1} cm^{-1})[532] and band B at 49,500 cm^{-1} (ϵ_{max} 9.9×10^3 M^{-1} cm^{-1})[530] are assigned to internal transitions. Band A is at higher energies in low polarity solvents,[534] which would be consistent with a ctts process but is in fact due to the polarizing effect of cations in ion pairs formed in these solvents at the high concentrations necessary to observe spectra.[532] The band is assigned[532] to an intramolecular transition and its intensity is dependent upon the hydrogen-bonding properties of the solvent. (Tetraalkylammonium salts were used to avoid changes in spectra due to ion-pairing effects.) An approximate isosbestic point in the spectra of nitrate is observed when the solvent is varied gradually from acetonitrile to methanol. Although the effects are not exactly comparable with results for carbonate and bicarbonate, a pattern emerges for changes in the low-energy, low-intensity bands which are clearly opposite in sense to those observed for ctts transitions. Increase in hydrogen-bonding effects, either by concentration variation or solvent change, alters the forbiddenness of the intramolecular transition. The interaction of solute and solvent is important[530,532] in determining the intensity of the transition. The assignment of the absorption to an internal transition is supported by the photochemistry, the kinetics of product formation favoring this interpretation and not solvated electron formation from a ctts process.[535]

The high-energy transition is assigned to an allowed π-π^* transition. Nitrate is a good example of the response of both allowed and forbidden intramolecular transitions toward temperature and solvent. This is further illustrated by comparing the very small shift for E_{max} of the low-energy band of nitrate from water at 20° to liquid ammonia at $-33°$ (<1 kcal mole^{-1}) with that for iodide ($\sim$18 kcal mole^{-1}).[77] Vibrational structure is seen in the low-temperature spectra of nitrate in liquid ammonia.[77]

Nitrite has been studied theoretically,[334,533] and conflicting assignments have been made both for observed and predicted transitions. The possibility of ctts transitions has not been considered theoretically, but the high-energy, high-intensity band has been assigned, without evidence, to a ctts process.[53,155] A detailed study of nitrite spectra from 28,000 to 52,000 cm^{-1} in a range of solvents of varying polarity identified one possible and three definite overlapping bands.[533] The two lowest energy bands were of low intensity and were assigned to forbidden intramolecular transitions, n_0-π^*, of different symmetry. The high-intensity band[155] at 47,000 cm^{-1} is attributed to an allowed π-π^* transition. For solution in acetonitrile there is evidence for another intense band at even higher energies which is not observed in water or ethanol. The solvent sensitivity of this band shows that it may be a ctts transition with $\bar{\nu}_{max} > 52{,}000$ cm^{-1} in water.

The phosphorus oxyanions have proved more fruitful in the search for ctts solution spectra. Spectra of phosphate have not been observed, spectra in aqueous solution being composites of the spectra of hydrogen phosphate and hydroxide ions,[536] in agreement with the acid–base reaction

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + OH^- \qquad (19)$$

where K_3 is 4.8×10^{-13} at 25°.

Aqueous hydrogen phosphate, HPO_4^{2-}, has a high intensity absorption band with onset of absorption in the region of 45,000 cm^{-1}.[536] No low-intensity bands are observed and the changes in spectra due to the addition of acetonitrile, deuterium

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oxide, and methanol to the solution are consistent with a ctts process.

Extrapolation of a plot of d$\bar{\nu}$/dT at $\bar{\nu}$ against $\bar{\nu}$[53,153,506] gives $\bar{\nu}_{\max}$ as 56,000 cm^{-1}, just beyond the range of measurements. (This analytical procedure is developed from the diffuse model.[53,153,506]) The ionization potential for this ion is 3 kcal mole^{-1} from the diffuse model, but another approach using values of d$\bar{\nu}$/dT at $\bar{\nu}$ in aqueous mixed solvents gave +50 kcal mole^{-1}. The complexity of d$\bar{\nu}$/dT in aqueous organic binary solvent systems is stressed in sections II and IV. Ionization potentials for such anions in the gas phase should be negative.[175]

Spectra of dihydrogen phosphate, $H_2PO_4^-$, in aqueous solution show evidence for three bands.[536] Two broad, low-energy, bands of low intensity, ($\epsilon < 1$ M^{-1} cm^{-1}) occur at 37,000 and 48,000 cm^{-1}. A change in temperature does not affect these bands but shifts the high-energy absorption edge (ϵ 100 M^{-1} cm^{-1} at 55,000 cm^{-1}, 1°) to higher energies. Similar shifts were observed on changing to aqueous methanol and deuterium oxide solutions. Extrapolation techniques[53,153,506] gave $\bar{\nu}_{\max}$ as 59,000 cm^{-1} and the diffuse model gives a vertical ionization potential for $H_2PO_4^-$ of ~132 kcal mole^{-1}. This is much higher than those for halides, ~71–84 kcal mole^{-1}, but comparable to $E_A(ClO_4)$, 134 kcal mole^{-1}.[500]

Polymeric phosphates, pyrophosphate, and tripolyphosphate and the cyclic trimer, trimetaphosphate, show absorption spectra in aqueous solution which are similar to hydrogen phosphate and dihydrogen phosphate, respectively.[537] Pyrophosphate has absorbance values per phosphorus atom approximately equal to that for hydrogen phosphate. Release of solvated electrons to the solvent following irradiation at 54,090 cm^{-1} supports the assignment of the absorption edges to ctts processes.[538] When alcohols are used as scavengers the photochemical kinetics are not readily understood (*cf.* sulfate ion photolysis[539]), but when specific scavengers for solvated electrons are used,[538] unequivocal evidence for this species is obtained. Flash photolysis studies have shown that solvated electrons are produced when hydrogen phosphate, dihydrogen phosphate, and pyrophosphate are irradiated.[540]

E. GROUP VI ANIONS

Group VI anions considered here are principally those of sulfur. Spectra of aqueous selenate and tellurate have not been reported.

Aqueous bisulfite shows only a weak, unresolved, absorption below 55,000 cm^{-1},[9] whereas sulfite has a fairly intense absorption with ϵ 10^3 M^{-1} cm^{-1} at 44,000 cm^{-1}, but $\bar{\nu}_{\max}$ has not been determined.[9] Flash photolysis of sulfite solutions gives solvated electrons,[521] and the transition may be assigned to a ctts process.

Sulfate and bisulfate in aqueous solution absorb at higher energies, above 50,000 cm^{-1},[9] but analysis of the absorption spectra of bisulfate is complicated by acid dissociation.[505] The dissociation constant is 1×10^{-2},[541] and as sulfuric acid is transparent below 55,000 cm^{-1}, $\epsilon_{54.090}$ is 49 M^{-1} cm^{-1}.[504] This is on the long-wavelength edge of the absorption band and is principally used in photochemical studies but also demonstrates an absorption unique to bisulfate at this frequency. Irradiation into this band gives photochemical kinetics and products consistent with solvated electron formation and thus a ctts process is indicated.[539] Further confirmation of this assignment has not been reported, $\bar{\nu}_{\max}$ probably being above 60,000 cm^{-1}.

The absorption spectra of aqueous sulfate has been characterized to 62,500 cm^{-1} [56] with $\bar{\nu}_{\max}$ at 57,140 cm^{-1}, shifted in deuterium oxide to 58,500 cm^{-1}.[76] This maximum is superimposed on a steeply rising absorption edge which is shifted in deuterium oxide at equivalent absorbance values by approximately 1460 cm^{-1}. Thus, the first maximum is better resolved in deuterium oxide. The first band is assigned to a ctts process,[76] and there are two independent reports of solvated electron formation when aqueous sulfate solutions are irradiated at 54,090 cm^{-1}.[510,539] An absorption attributed to sulfate radical ion is observed following flash photolysis.[542] There is a discrepancy between the values of ϵ reported for the complete spectra down to 62,500 cm^{-1} [56] and down to 55,000 cm^{-1}.[9,505,510] Whereas the three reports agree well, *e.g.*, $\epsilon_{54.090} = 200 \pm 2$ M^{-1} cm^{-1}, in another report[56] $\epsilon_{54,090} = 100$ M^{-1} cm^{-1}. This discrepancy was confirmed at lower energies.[56] Cells having path lengths of approximately 4–5 × 10^{-4} cm reduced the water background absorption,[56] and thus high salt concentrations of approximately 1.0 M were necessary. The consequent shift of these bands to higher energies can account for the discrepancy. Alternatively, the discrepancy may be due to the dependence of the band intensity ($\bar{\nu}_{\max}$ 57,140 cm^{-1}) on concentration; *cf.* carbonate,[526] bicarbonate,[527] and nitrate.[530,532] Such dependence conflicts with the bands' proven ctts character; on the other hand, the intensity dependence of ctts spectra in aqueous solution has not been determined, certainly not for anions of this complexity. The intensity of the sulfate absorption at $\bar{\nu}_{\max}$, $\epsilon_{\max}$ 3×10^2 M^{-1} cm^{-1}, is also much lower than that for a typical ctts absorption, *e.g.*, iodide where $\epsilon_{\max}$ is 1.35×10^4 M^{-1} cm^{-1}.[55]

The high-intensity absorption edge has been attributed to another ctts transition of sulfate ion.[55] Alternatively, it may be due to an imbalance of solvent absorption in the reference and sample cells. The marked effect of temperature on absorption spectra of water[543] is due to an increase in the concentration of unbonded OH groups,[258,362] and it is possible that the high concentrations of salt necessary (sulfate is a structure-breaking ion[258]) cause the absorbance of sample solvent to differ from that of reference solvent. This would produce a sharp absorption near 60,000 cm^{-1}. A theoretical study of sulfate and sulfate radical ion does not predict an intramolecular transition in the region of 60,000 cm^{-1},[544] but this treatment has been questioned.[545] The spectra of thiosulfate has been studied in a variety of solvents.[546] The single absorption band was assigned[1] to a ctts transition, but a detailed examination[546] shows the accessible spectra consist of three absorption bands, A, B, and C, progressing to higher energies. Bands A and C at 41,000

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$\mathrm{cm^{-1}}$ ($\epsilon_{\max}$ 200 $M^{-1}\ \mathrm{cm^{-1}}$) and 50,000 $\mathrm{cm^{-1}}$ ($\epsilon_{\max}$ 4 × 10^3 M^{-1} $\mathrm{cm^{-1}}$), respectively, were assigned[547] to internal transitions.

A molecular orbital scheme for thiosulfate[544] predicted bands A and C reasonably well, but this scheme has been criticized.[545] No provision was made for a ctts process. Band B, $\bar{\nu}_{\max}$ 46,500 $\mathrm{cm^{-1}}$ and $\epsilon_{\max}$ 4 × 10^3 $M^{-1}\ \mathrm{cm^{-1}}$, is assigned to a ctts process. Photolysis at 43,750 $\mathrm{cm^{-1}}$ gives solvated electrons,[546] $\phi_e = 0.075$, supporting the ctts assignment. This has been confirmed by flash photolysis[521] which also shows that thiosulfate decomposes by two processes. These processes may be related to the intramolecular and ctts transitions in the absorption spectra of thiosulfate and confirm the partial ctts character of the spectra.

The diffuse model gives −26 kcal $\mathrm{mole^{-1}}$ for the ionization potential of thiosulfate. The negative ionization potentials obtained for dinegative ions have been questioned,[547] and inclusion of terms arising from the interaction of thiosulfate and the solvent molecules gives 43 kcal $\mathrm{mole^{-1}}$.[548]

F. GROUP VII ANIONS

Halogen anions range from the hypohalites to the perhalates, and for the former the chloro, bromo, and iodo derivatives have been observed spectroscopically. Hypochlorite in aqueous solution has $\bar{\nu}_{\max}$ at 34,000 ± 100 $\mathrm{cm^{-1}}$ and $\epsilon_{\max}$ 300,310[155,549] and 360 $M^{-1}\ \mathrm{cm^{-1}}$.[550] The low $\epsilon_{\max}$, together with the temperature insensitivity from 5 to 35°, indicates an intramolecular transition. A higher energy absorption band has $\bar{\nu}_{\max}$ 50,000 $\mathrm{cm^{-1}}$,[155] but no assignments have been made.

Aqueous hypobromite has $\bar{\nu}_{\max}$ at 30,000 $\mathrm{cm^{-1}}$ and $\epsilon_{\max}$ 326 $M^{-1}\ \mathrm{cm^{-1}}$.[551] The radical BrO· has been produced in pulse radiolysis studies, no evidence for solvated electrons formed from hypobromite being reported.[552] A ctts transition may occur at higher energies. Hypoiodite is unstable in aqueous solution, and spectra were reconstructed by extrapolation to zero time.[553] Three bands were observed: a low-intensity band at 27,400 $\mathrm{cm^{-1}}$ ($\epsilon_{\max}$ 31 $M^{-1}\ \mathrm{cm^{-1}}$), a shoulder at 39,200 $\mathrm{cm^{-1}}$ ($\epsilon_{\max}$ 400 $M^{-1}\ \mathrm{cm^{-1}}$), and a high-intensity band, $\bar{\nu}_{\max}$ >42,000 $\mathrm{cm^{-1}}$ ($\epsilon_{\max}$ >1 × 10^3 $M^{-1}\ \mathrm{cm^{-1}}$). The low-intensity, low-energy bands of the hypohalites have been assigned to internal transitions.[554]

The spectra of aqueous chlorite has a maximum at approximately 38,000 $\mathrm{cm^{-1}}$ ($\epsilon_{\max}$ 150 $M^{-1}\ \mathrm{cm^{-1}}$), a shoulder at 47,000 $\mathrm{cm^{-1}}$, and an intense absorption edge beyond 50,000 $\mathrm{cm^{-1}}$.[155] The two higher energy bands have been assumed to be ctts transitions, and the lowest band, fitting Mulliken's correlation for AO_2 molecules,[554] is an intramolecular transition.

The spectra of halate anions in aqueous and aqueous organic mixtures show that the intense bands $\nu_{\max}$ >50,000 $\mathrm{cm^{-1}}$ for XO_3^- (where X is Cl, Br, and I) are due to allowed, intramolecular, transitions,[555] whereas previously these bands have been treated as ctts transitions.[555] Photolysis of aqueous bromate in the presence of specific electron scavengers gave a very low quantum yield, $\phi_e = 5 \times 10^{-4}$, attributed to thermal ionization of the excited state. In contrast, the main photochemical reaction is evolution of oxygen, $\phi_{O_2} = 0.15$, from

$$\mathrm{BrO_3} \xrightarrow{h\nu} \mathrm{BrO^-} + \mathrm{O_2} \qquad (20)$$

This implies that there are no important ctts bands masked by the intense intramolecular absorption bands.

The spectrum of aqueous perchlorate has a very low absorption below 55,000 $\mathrm{cm^{-1}}$ (ϵ at 55,000 $\mathrm{cm^{-1}}$ is 20 $M^{-1}\ \mathrm{cm^{-1}}$).[505] Photolysis at 54,090 $\mathrm{cm^{-1}}$ gives oxygen as the main product.[556] This work was concluded prior to the recognition of the solvated electron as a possible intermediate, and consequently this species was not searched for. The formation of oxygen as main product is inconsistent with a ctts process.

The spectra of aqueous periodates are more complicated due to the possible presence of condensed species.[557] However, the spectra of periodate is isolated under certain conditions and has a broad absorption centered on 46,000 $\mathrm{cm^{-1}}$ due to an intramolecular transition. Irradiation into this band gave oxygen, analogous to the photochemistry of perchlorate ion. The spectra of aqueous perxenate solutions are similar to periodate, several species being formed which have as yet not been unequivocally assigned.[558]

G. AMIDE AND FERROCYANIDE

There are several anions of interest outside the foregoing survey, the most important being amide and ferrocyanide. Amide has only been studied in liquid ammonia, being unstable in aqueous solutions.[559] At a given temperature $\bar{\nu}_{\max}$ for a series of alkali amides decrease from Li to K and is independent of cation at 30,120 $\mathrm{cm^{-1}}$ for K to Cs amides. The latter species are interpreted in terms of solvent-separated ion pairs and the former in terms of appreciable cation–anion interaction.

Amide in ammonia solution, $\bar{\nu}_{\max}$ being 28,000 $\mathrm{cm^{-1}}$ at 20°,[560] is of particular interest since it is the analog of hydroxide in aqueous solution. The solution must be pressurized to maintain ammonia as a liquid at 20° and here $\mathrm{d}\bar{\nu}/\mathrm{d}T$ is 30 $\mathrm{cm^{-1}\ deg^{-1}}$. However, in ammonia under its own vapor pressure and at low temperatures, $\mathrm{d}\bar{\nu}/\mathrm{d}T$[561] is 17 $\mathrm{cm^{-1}\ deg^{-1}}$, the discrepancy probably being a consequence of the pressure difference. The variation of $\bar{\nu}_{\max}$ and the (density corrected) variation of $\epsilon_{\max}$ with temperature are consistent with a ctts process for amide. The nearest neighbor distance in the solvent is linked with the radius of the excited-state orbital (confined model) for amide in ammonia. The spectra of amide in liquid ammonia provides an important method for studying acid–base equilibria in this solvent, particularly for weak acids.

Amide is prepared *in situ* by the decomposition of metal–ammonia solutions and the analogous monoethylamide, $\mathrm{NHEt^-}$, has been prepared in metal–ethylamine solutions,[562] $\bar{\nu}_{\max}$ 31,500 $\mathrm{cm^1}$ (at room temperature) with $\mathrm{d}\bar{\nu}/\mathrm{d}T = -15$ $\mathrm{cm^{-1}\ deg^{-1}}$. The large value of $\mathrm{d}\bar{\nu}/\mathrm{d}T$ and the intensity ($\epsilon_{\max}$ 2.7 ± 0.4 × 10^3 at 31,500 $\mathrm{cm^{-1}}$ and room temperature) support the assignment of the band to a ctts process.

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Ferrocyanide has been studied both spectroscopically and photochemically and shows a ctts band, $\bar{\nu}_{max}$ 39,000 cm^{-1}, in the presence of two ligand field bands.[563] When irradiated at frequencies over the band, solvated electrons are formed, while irradiation into the ligand field bands below 33,000 cm^{-1} gave no solvated electrons. This interpretation of ferrocyanide photochemistry has been confirmed using both hydrogen atom and solvated electron scavengers.[564] Thus a ctts band can exist in the presence of ligand field bands. Further details of ligand field band spectra and photochemistry are given in a recent review.[565]

It is clear that ctts transitions occur in many anions other than halides, the spectra becoming more complex because of the occurrence of intramolecular transitions as the number of atoms in the anion increases. In several cases, such as hydroxide, hydrosulfide, thiocyanate, and thioselenate, there is a discrepancy between ionization potentials derived from application of the models (section III) and values derived from the free ion. These ions all have lower ionization potentials than the halides; in the latter case, the ionization potential contributes 60% of E_{max}. The former ions have a much lower contribution from this source and in the limit, E_A(OH) is less than 30% of E_{max} for hydroxide ion. Thus, an increasingly large contribution to E_{max} is assigned to the energy term of the electron in the excited state, which is expected from both models when r_i is small. But the crystallographic radii are fully comparable to those for the halides. Clearly, as the theories for ctts transitions are extrapolated from the halides to polyatomic anions, discrepancies arise and the simple models are incomplete.

Not yet incorporated in current theories is the overlap contribution between the orbitals of, say, an oxyanion and the solvent molecules. This contribution has been mentioned several times as a possible cause of discrepancy.[175,499,548] For some polyatomic anions ctts processes exist in the same energy range as internal transitions of the anion. In other anions it is possible and, indeed, probable that ctts bands occur at higher energies. A situation occurs where the anion, excited by radiation $\bar{\nu}$ (cm^{-1}), has an equal probability of going either to an intramolecular or ctts excited state. The transitions possess a common ground state yet totally different excited states, defined by the anion and the solvent, respectively. The former transition may be described by a molecular orbital study but with no reference to the ctts state, and *vice versa*. A possible way forward is to widen the terms of reference of the theoretical studies and take the solvated ion as the basic unit.

The ctts spectra of polyatomic anions are more complex than those of the halides and can be examined over-all in terms of (i) valency change, and (ii) increase in the number of oxygen atoms attached (for the oxyanions) to the central atom.

(i) There is a definite trend for a protonated, mononegative anion to have $\bar{\nu}_{max}$ at higher energies than a dinegative anion. This is shown by the pairs HSO_4^-/SO_4^{2-}, and $H_2PO_4^-/HPO_4^{2-}$ and possibly, as both spectra have not been assigned to ctts processes, by HSO_3^-/SO_3^{2-} and HCO_3^-/CO_3^{2-}. This shift arises since the ionization potential of the first electron is less than that of the second, despite the effect of protonation; *cf.* the identical electron affinities of O· and OH·,[500] but note the difference of 40–50 kcal mole^{-1} for O_2 and HO_2.[500]

It is reasonable to extrapolate the estimated $\bar{\nu}_{max}$ for phosphate to the region of 50,000–53,000 cm^{-1} from the values of dihydrogen and monohydrogen phosphates (59,000 and 56,000 cm^{-1}, respectively),[536] and in an aqueous solution at pH 13 it should be possible to observe an absorption due to phosphate.

(ii) The effect of stepwise addition of oxygen to an atom may be seen with reference to the sulfide and sulfur oxyanions. There is a steady progression to higher energies for E_{max} from S^{2-} through SO_3^{2-} to SO_4^{2-}. A weaker parallel occurs for nitrite–nitrate in that a possible ctts transition has been observed for nitrite and not for nitrate below 54,000 cm^{-1}. This assumes a high-energy ctts transition for nitrate at frequencies >54,000 cm^{-1}, a not unreasonable assumption given E_A (NO_3) = 89.5 kcal mole^{-1}; *cf.* E_A(Cl) = 83.5 kcal mole^{-1}. The trend stems from two opposing effects: first, the increasing size of the ion and, second, the change in the ionization potential as x increases in MO_X^{2-} from 0 to 4 for sulfur anions (or 2 to 3 for nitrogen anions).

The values of $\bar{\nu}_{max}$ for the ctts spectra of this series would be shifted to lower energies as r increases in both the confined and diffuse models, due to the r^{-n} dependence. On the other hand, little is known of the ionization potentials–electron affinities of dinegative ions since very few doubly charged anions are stable in the gas phase,[566] and their stability[566] in crystals or solution is dependent upon interaction with their environment. The apparent electron affinity of an anion will therefore be increased for both mono- and dinegative ions relative to their gas-phase values. This effect is eliminated by the description of the cycles for ctts processes (section III). The first electron affinity increases from chlorine to perchlorate radical (84 through 67, 79–134 kcal mole^{-1}), for NO, NO_2, and NO_3, and also for O_2 and O_3.[500,537] The second electron affinity of such radicals is not known except for O^-, O_2^-, and S^- and Se^- where the addition of a second electron is strongly endothermic. It is inferred that as $O^- + e \rightarrow O^{2-}$ is more endothermic than $O_2^- + e^- \rightarrow O_2^{2-}$,[500] then the series of anions described would (tentatively) have electron affinities which are increased, that is, less endothermic, as the anion contains more oxygen atoms. This phenomenon is complex in that there are several effects which can explain the shift of $\bar{\nu}_{max}$ from 27,000 to 57,000 cm^{-1} for $S^{2-} \rightarrow SO_4^{2-}$, *e.g.*, the increased overlap between anion and solvent orbitals.

The extended diffuse theory[175] predicts the same dependence of $\bar{\nu}_{max}$ upon temperature or pressure, presumably in the same solvent, for different anions of different charge. The data for the dinegative anion, sulfide, does not agree with this prediction, but $d\bar{\nu}/dT$ is measured in solutions of pH 15, *i.e.*, 10 *M* hydroxide.[512] It is claimed that $\bar{\nu}_{max}$ for aqueous thiosulfate has the same temperature dependence as aqueous iodide[175] though it is difficult in the presence of overlapping bands to assign accurate values of $d\bar{\nu}/dT$, and this claim has not been substantiated.

The survey shows an incomplete study of the ctts spectra of polyatomic anions in solution. The few anions investigated in depth, both spectroscopically and photochemically, are in themselves paradoxes. Aqueous sulfate and phosphate have clearly defined ctts spectra, yet in both the absorption

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intensity is of the order of intramolecular transitions and, for sulfate, is possibly dependent upon concentration. The quantum yield of solvated electrons is much higher (0.64 for sulfate, 0.50 for hydrogen phosphate) than for aqueous iodide (0.23 or 0.29).

The ctts spectra of fluoride and astatide have not been observed for different practical reasons.

The ionization potential of fluoride lies between those for chloride and bromide, and therefore the ctts spectrum should be observable. This conclusion is underlined by the link between the halide spectra in crystals and halide spectra in solution. The spectra of alkali fluoride crystals occur at high energies and are assigned to exciton processes as in the other alkali halide crystal spectra.[178] On the other hand, both current theories of ctts transitions have a term or terms which are dependent upon higher powers of r_i, the ionic radius. Since the radius of fluoride is much smaller than the other halides[567] both models, diffuse and confined, require that the ctts band is at very high energies. The predicted value of $\bar{\nu}_{max}$ is 67,000 cm^{-1} from the Franck–Platzman model.[142] Determined efforts have been made to observe the fluoride ion absorption. In a 4–5 × 10^{-4} cm cell the background absorption at high energies is very intense and the spectra derived from the difference of two large absorbance values.[56] However, no positive conclusion was reached as to whether the fluoride ion absorption had been observed. The difficulty lies primarily in reducing the solvent background absorption.

The most stable isotope of astatine, ^{210}At,[568] has a half-life of approximately 8 hr. Consequently, the solution chemistry of astatine is difficult (and hazardous!) but −1, 0, and +5 oxidation states and some photochemical effects have been reported.[568] Aqueous astatide is predicted to be slightly yellow due to the low-energy tail of the absorption extending into the visible.[142] The most concentrated solutions handled appear to be of the order 10^{-8} *M*, too low for conventional spectrophotometry.[568] Nevertheless, the spectrum of gaseous astatine has been investigated and the transitions assigned to $^4P_{5/2}$ and and $^4\mathrm{P}_{7/2}$ states of astatine.[569]

VI. Ion-Pair Formation

A. DISCUSSION

The Bjerrum treatment of ion-pair formation has been particularly successful in correlating the properties of salts in solvents of low dielectric constant.[307,570–578] Here the distinction between free ions and ion pairs is based upon a minimum in a plot of probability distribution against interionic distance. If two counterions are less than this critical distance apart, they constitute an ion pair. However, with the development of the subject, the concept of particular ion-pair structural units was introduced. Conductivity data for solutions containing tetra-*n*-butylammonium bromide were analyzed in terms of two equilibria, one involving free ions and solvent-shared ion pairs, *e.g.*, $R_4N^+SX^-$, where S is a solvent molecule, and another equilibrium involving solvent-shared and contact ion pairs.[574] However, this model was not initially exploited, at least in analysis of conductivity data, in contrast to treatments of kinetic data.[575,576] Rather, a more rigid definition,[577] ions being either "free" or part of contact ion pairs, has formed the basis of other quantitative treatments of ion-pair equilibrium constants,[578–580] although in applying these equations dimensions of equilibrium constants must be compatible.[581,582]

This model has been used[583] extensively in the analysis of conductivity data.[310,584] However, a reappraisal of conductivity data for alkali halides in water suggests that conductance measures the association constant for solvent separated ion pairs.[466] This highlights a major problem in conductivity work in that the measured quantity is the mobility of free ions, and structures of ion pairs have to be derived indirectly. Common to these treatments is the characterization of the solvent by its dielectric constant. In some instances, equations relating association constants and solvent properties have been modified to take account of interaction energies[578] and effective dielectric constants.[585,586] There is also good evidence in other systems for specific ion–solvent interactions,[587] although the need for this interaction to account for trends in other systems[588] is not necessarily confirmed in a reanalysis.[589,590] In mixed solvents the two components may interact and thereby modify the ion-pair equilibrium,[591,592] the trends in equilibrium constant with solvent composition being sometimes a closer function of composition than of dielectric constant.[593,594]

Despite these latter developments, it is clear that the conductivity studies[595,596] have provided the largest single contribution to the understanding of ion-pair equilibria. However, developments in other fields have had a major impact in the formulation of structural models for ion pairs. These developments have occurred particularly in the analysis of kinetic data,[575,576] electron spin resonance spectra of radical anions,[37] and ultrasonic relaxation data. The latter subject has possibly made the largest impact, the major breakthrough being in analysis of ultrasonic relaxation curves for 2:2 elec-

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trolytes in water. Here the relaxation frequencies are attributed to different equilibria characterizing the association (and dissociation) steps from separated ions through intermediate separation of one and two solvent molecules to form the undissociated salt.[597–605] Similar models have been employed in analysis of dielectric data for manganese sulfate solutions[606] and ultrasonic relaxation data for aqueous solutions of lanthanide salts.[607] This treatment has been extended to analysis of relaxation curves for solutions in nonaqueous solvents containing alkylammonium salts,[608–610] although one of the relaxations may be a property of the alkylammonium ion itself, *i.e.*, a form of rotational isomerism.[343]

These observations provide convincing evidence for adopting structural models for ions and ion pairs in solution. The following four classes of species are predefined.[611]

1. *Free Ions*

The properties of these ions are essentially independent of all other ions except for long-range spherically symmetric electrostatic interactions. In solvents of low polarity, these species are in equilibrium with ion pairs (see below), but other than this restriction they are still independent in the manner described. This assumption is implicit in analyses of conductivity data where it is assumed that the ionic mobility of free ions is unaffected by the presence of ion pairs.[612]

2. *Contact Ion Pairs*

Contact ion pairs are two ions, anion and cation, in contact, with no other intervening solvent molecules. The stability of this species is *defined* as due to electrostatic interaction only, and this is probably a good approximation where closed-shell ions are involved, *e.g*, alkali metal, alkylammonium, and halide ions. Within this ion pair, the two ions may have preferred positions, as shown by the electron spin resonance spectra of systems where the counterion has two low-energy positions, this ion hopping between the two sites within the ion pair.[37,613–617]

The possibility has been discussed where the ions are either tight ion pairs or loose ion pairs, the latter having a more intense interaction between the ions and the nearest neighbor solvent molecules.[618,619]

3. *Solvent-Shared Ion Pairs*

Solvent-shared ion pairs are two ions, cation and anion, linked electrostatically through a solvent molecule, this molecule being part of the primary solvation shell of both ions.[620] There may also be a case for considering here structures where two solvent molecules are both part of the solvation shell of both ions. In some systems, the two states, contact and solvent-shared ion pairs, may coexist.[621] This was envisaged in the model discussed above,[574] with reference to conductivity data, and this approach has now been extensively employed.[622–624]

4. *Solvent-Separated Ion Pairs*

Solvent-separated ion pairs are pairs of ions linked electrostatically but separated by more than one solvent molecule. By introducing this class of ion pairs it is possible to reconcile evidence, *e.g.*, conductivity and spectroscopy, which give different estimates of the degree of ion association.[625] Thus, for some solvent media, ctts spectra show unequivocal evidence for ion pairs (see below). However, in some solvents no evidence can be found while conductivity data have indicated some degree of ion association. Such systems where the evidence is not complimentary include acetone,[626] acetonitrile,[627,628] methanol,[629] and *n*-butyl alcohol,[630] although the association constants are generally small.

These are limiting, formalized, models, the contact and solvent shared ion-pairs being regarded as specific entities with appropriate minima in potential energy. In some systems, the distinction may be lost if the potential energy well for ion pairs is shallow and wide, the energy changing gradually with distance apart.[631]

Evidence for ion association as deduced from analysis of visible and ultraviolet spectroscopy has sometimes been contradictory, and here discussion is confined to investigations other than where the absorbance at only one frequency is used to evaluate equilibrium constants.[632,633] This latter procedure can lead to spurious results if the band(s) shifts when the concentration is changed.[634] This latter problem can be partly overcome if the solution is maintained at constant ionic strength, but even then the interpretation is not straightforward.[635] In most attempts to probe ion-pair formation

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using spectroscopic techniques, the starting point is to expect that the absorption spectra of a free ion should differ from that of the same ion within an ion pair since the environments are different. There have been a number of investigations to link changes in the absorption spectra of a solute with the changes in association constant derived from conductivity data, but the results have sometimes been disappointing.[636–640] For example, the conductivity of tetraphenylarsonium chloride shows a marked increase in association through the series of solvents, water, 70% dioxane–water, ethylene dichloride, and 95% dioxane–water, but the absorption spectra are relatively unaffected, Beer's law being obeyed.[636] Similarly, no link is found between association constants derived from conductivity data[641] and absorption spectra[42] for sodium and potassium tetraphenylborates in dioxane–water mixtures. These trends may arise if the intramolecular transitions of the molecular anions are not sufficiently sensitive to the environment for the change in ion-pairing to be detected. Thus, replacement of one or more dipolar solvent molecules around the chromophore ion by a counterion may, in effect, be only a very small change. In addition, ion pairs characterized by conductivity may be still separated by one or more solvent molecules, and, while there may be a consequent change in ionic mobility, it does not follow that there should be a change in the absorption spectra. However, detailed spectrophotometric studies of solutions containing, for example, the sodium salt of biphenyl,[642] nitrobenzene anion,[643] 9-fluorenyl salts,[623,644] and 9,10-dihydroanthracene,[645a] have shown good evidence for ion-pairing, as also have recent infrared data.[645b,c]

The very nature of the ctts absorption spectra would suggest that E_{max} for free iodide would be different for iodide within an ion pair. One possibility is that a specific charge transfer to cation within an ion pair might occur, comparable to the spectra of alkali halides in the gas phase.[9] However, such bands have not been observed and claims that an absorption band at 34,500 cm^{-1} for alkylammonium iodides in both carbon tetrachloride and benzene are due to such transitions[611] have been withdrawn.[49]

The absorption maximum for iodide in benzene is at higher energies,[49] and the transition in carbon tetrachloride is reassigned to a charge-transfer band involving one solvent molecule rather than the cation as electron acceptor.[646] A similar model would seem likely for the comparable band observed for alkylammonium bromides in carbon tetrachloride.[54]

In spite of these limitations, the spectra of iodides in solvents of low polarity, *e.g.*, methylene dichloride, 1,4-dioxane, tetrahydrofuran, *t*-pentyl alcohol, and *t*-butyl alcohol, show good evidence for ion pairs.[49,85]

Evidence for ion pairs in these systems is based in the first instance, on contrasting the spectra with the ctts spectra of iodide in polar solvents (section II). For example, in these solvents, the position of the absorption maximum for iodide is dependent on both cation and solvent.[49] In a given solvent, E_{max} generally decreases with increase in cation size, being smaller for substituted alkylammonium salts than alkali-metal iodides.[49] However, for tetra-*n*-alkylammonium ions, RN_4^+, E_{max} is independent of the size of the cation for R > *n*-propyl, which indicates that the alkyl chains are sufficiently flexible to maintain nearly constant distance of separation between iodide and the nitrogen charge center. Therefore, in general, the greater the stabilization of the ion pair due to electrostatic interaction, the greater is E_{max}. For alkylammonium ions containing a methyl group, *e.g.*, R_3N^+–Me, E_{max} is not dependent on R, which indicates that these ion pairs have structures where the charge centers are closest, *e.g.*, R_3N^+–MeI$^-$.[647,648] This preference is borne out by a competition experiment between tetra-*n*-hexylammonium and dicyclohexylammonium cations for added iodide. The latter cation has at least a tenfold greater affinity for iodide. The changes in absorbance at a fixed frequency following changes in the relative amounts of these two cations show that only ion-paired species are involved. Solutions of tetra-*n*-hexylammonium iodide in methylene dichloride do not obey Beer's law, but estimates of association constants[49] are not straightforward because of the difficulties in predicting trends in ionic activity coefficients.[649] In contrast to the above cation dependence, E_{max} remains the same for tetramethylammonium and trimethylsulfonium iodides.[49] The influence of size and shape of the cation of E_{max} and the relative unimportance of the nature of the cation shows that the cation is not acting as an electron acceptor. The good correlation[49] between E_{max} for iodide in tetrahydrofuran and the sum of ionic radii plus 3 Å points to the presence of a solvent-shared ion pair.

For these systems, *e.g.*, tetra-*n*-hexylammonium iodide, E_{max} is rectilinearly dependent upon the solvent *Z* value,[67] E_{max} increasing with increase in *Z*. This requires that within the ion pair there is a linear movement of charge toward the cation, thereby diminishing the dipole moment. Further, dE_{max}/dT is dependent both on the cation and solvent such that dE_{max}/dT for a given cation increases with increase in E_{max} at 20°. The spectra in mixed solvents[85] shows both band changes and band shifts. When a small amount of *t*-pentyl alcohol is added to iodide in methylene dichloride, the spectra show isosbestic points[85] due to specific interaction between added solvent and iodide within the ion pair (but compare behavior at much higher concentrations[650,651]). Further addition results in a band shift, E_{max} being essentially a linear function of solvent composition. When a small amount of polar solvent, *e.g.*, methanol, is added, the change in E_{max} shows a preferential solvation by the more polar component, but there is no abrupt change in the spectra. At low concentration of added polar solvent, E_{max} depends on the cation until at a certain composition, it becomes independent of cation, the band shifting further when more polar solvent is added (section IV). Since there is no abrupt band change, the transi-

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tion within the ion pair must be smoothly transformed into the normal ctts transition of the free ions.

B. A MODEL FOR CTTS TRANSITIONS WITHIN SOLVENT-SHARED ION PAIRS

The iodide excited state is envisaged as an asymmetric ellipsoid, which is distorted toward the charge center of the cation within a solvent-shared ion pair. At higher salt concentration, *i.e.*, 0.2 *M*, contact ion pairs may also be formed, two types being then present.[652]

Although this model accounts for the experimental data, in no pure solvent have two bands been observed which can be separately identified with iodide ion in an ion pair and in the free state. In contrast, conductivity data show that the methyltriethylammonium iodide in methylene dichloride is not completely associated over the temperature range 0 to −95°.[653] There is, therefore, a remarkable coincidence of cation-dependent and solvent-dependent $E_{\max}$ for free and associated iodide. The gradual band shift of $E_{\max}$ with added polar solvents shows that the difference in energies between free and associated iodide is small.

C. IODIDE IN CARBON TETRACHLORIDE

The lack of measurable variation of $E_{\max}$ of the low-energy absorption band when either temperature[611] or pressure is changed was interpreted in terms of contact ion-pair formation.[611] The analogy was drawn with the low-energy absorption bands of iodide ion pairs in the gas phase.[9] An alternative explanation[654] that the ions were in clusters was ruled out since the absorbance obeyed Beer's law and was in a different part of the spectrum to that expected if iodide were in such clusters.[655] The dependence of $E_{\max}$ on cation was in agreement with an ion-pair system. However, the changes in spectra when other solvents were added were not entirely consistent with the model in which the cation acted as the electron acceptor.[611] Since there are other grounds[646] for treating carbon tetrachloride as an electron acceptor, the transition for iodide was assigned to specific charge transfer to a solvent molecule.[646] The dependence of $E_{\max}$ on cation requires that iodide is present as a contact ion pair. When acetonitrile is added, the ion pair dissociates initially, but the iodide remains complexed with the carbon tetrachloride. When an alcohol is added, an equilibrium is set up which involves as one component a system where the alcohol is hydrogen bonded to iodide,[656–658] the iodide remaining part of the contact ion pair.

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