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Pressure Effects on Some Charge-Transfer and Transition Metal Ion Spectra in Aqueous Solution

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IN recent years there have been numerous studies of the effect of pressure on absorption spectra involving charge transfer processes and transition metal "*d*" electrons in solids. But there have been few studies involving similar species in solution. The purpose of this note is to report the magnitude of pressure shifts on spectra of some simple species in aqueous solution.

All measurements were made with a Cary model-14 spectrophotometer and a stainless-steel pressure cell with fused silica windows. On account of window thickness, measurements could not be made below 2100Å. Measurements were made at room temperature in the range 1–3000 atm and the results in Table I refer to the average shift for a pressure change of 2000 atm. Results are considered to indicate the directions of shifts and their magnitude within 25%.

We may note that the dielectric constant of water changes by similar amounts for a temperature change of 20°C and a pressure change of 2000 atm. A pressure change of this magnitude causes a much greater change in density than the 20° temperature change. In the case of transition metal spectra, the position of the first hydration shell is critical in determining the ligand-field splitting and with charge transfer it is probable that nearest-neighbor solvent molecules are involved as acceptors. In either case, one would not expect any direct correlation with bulk compressibility of the solvent. These changes should be more closely related to bond-length changes as in solids. Very generally, a pressure change of a thousand atmospheres results in shortening of similar magnitude to the expansion caused by a temperature change of 50°C.

The following conclusions may be drawn from the data in Table I. In the cases of "*d*" and "*f*" absorption, the direction and magnitude of shifts are similar to those observed in comparable solids.[1–3] The hydrated ion in a solvent cavity is thus as effectively compressed as the same ion in a crystalline solid. The shifts with the iodide and bromide ions are in the same direction and are of an order of magnitude which might be anticipated from studies of Stein and Treinin[4] on the effect of temperature. Little shift was observed with the planar nitrate ion. Strickler and Kasha[5] and Strickler (personal communication) observed small solvent effects with the nitrate ion. It appears reasonable to suppose that the initial ultraviolet absorption corresponds to an internal rearrangement rather than an ion-solvent transfer. The absorption edge of the thiosulphate ion moves to shorter wavelengths as with the simple halides but the magnitude appears to be greater. This again suggests a solvent transition with strong repulsion between two singly negative charged species in the excited state. In the case of the permanganate ion, the magnitude of changes in the bands around 5200Å is greater than changes observed in the solid by Bentley and Drickamer[6] and may reflect the influence of a hydrogen bonding medium.

TABLE I. Wavelengths and pressure shifts of absorption peaks and edges.

Specie	Position (Å)	Center	Edge	Shift	Magnitude (Å)
$Ni(H_2O)_6^{2+}$	3933	×		short	10
$Ni(C_5H_5N)_6^{2+}$	6100	×		short	12.5
	3700	×		short	12.5
$Co(H_2O)_6^{2+}$	5112	×		short	14
Sm_{aq}^{3+} as chloride		no significant shift in any lines in visible			
I^-	2250	×		short	12
Br^-	2250		×	short	12
NO_3^-	2975	×		indeterminate	
	2400		×	indeterminate	
$S_2O_3^{2-}$	2600		×	short	25
$C_2O_4^{2-}$	2850		×	long	25
$Ni(C_5H_5N)_6^{2+}$	3200		×	long	30
$Fe(CN)_6^{4-}$	3200	×		indeterminate	
	2800		×	short	25
$Fe(CN)_6^{3-}$	4200	×		long	25
MnO_4^-	5440	×		short	10
	5240	×		short	10
	5060	×		short	10
	2100		×	long?	small

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