

Ultraviolet Spectra of Tl^+ , Pb^{2+} and Bi^{3+} Probe Ions in Molten Fluoride Media

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Although the orbital-expansion (nephelauxetic) parameter, h , for fluoride is usually assigned a value of 0.8, frequencies of the $^1S_0 \rightarrow ^3P_1$ transition obtained from the ultraviolet absorption spectra of Tl^+ , Pb^{2+} and Bi^{3+} probe ions in molten $LiF-NaF-KF$ (46.5:11.5:42) indicate values of 1.38, 1.33 and 1.09, respectively. These are consistent with the absorption spectra of thin films of the four halides of each of the metal ions. It is shown that Tl^+ , Pb^{2+} and Bi^{3+} are capable of detecting the reduction in electron-donor power of fluoride when it is modified by polarising cations such as boron(III) or phosphorus(V) as in molten alkali-metal tetrafluoroborate or hexafluorophosphate. Addition of KF to molten alkali-metal tetrafluoroborate results in a gradual replacement of the polarised fluorides by F^- ions in the coordination sphere of the probe ion rather than the direct formation of the discrete fluoro-complex of Tl^+ , Pb^{2+} or Bi^{3+} ; substitution is virtually complete at KF contents $< 20\%$.

The application of 'probe-ion spectroscopy' to structural problems in molten salts and glasses is well-known. Often the probes are transition-metal ions, and electronic spectroscopy reveals the stereochemistries which can be adopted in the medium, usually by comparison with documented $d-d$ absorption envelopes. Probe-ion spectroscopy which utilises electron-transfer absorption or orbital-expansion (nephelauxetic¹) effects is less straightforward and has received far less attention. However, the information which can be gleaned from this type of spectroscopy is valuable for assessing the electron-donor power in sites provided by anions, and for oxide systems lends itself to the quantitative measurement of basicity.²⁻⁵ The study of probe ions in borates, phosphates, *etc.* indicates that the oxide ($-II$) species can exist over a wide range of 'states' (*i.e.* predominantly ionic, covalent or metallic) and still be capable of donating electrons to an acidic particle (such as a probe cation).

Electronic spectroscopy in oxide systems has been discussed previously⁶ in terms of its application to molten fluoride media, and the important question emerged: can the effect of bonding interactions with polarising cations be detected in fluoride? In other words, when fluoride is present in complex ions such as $[BF_4]^-$ or $[SiF_6]^{2-}$, can probe ions detect the changes brought about by the covalent interaction of the fluoride with the boron(III), silicon(IV), *etc.*? Being able to answer this question is important not only for media where fluoride is the sole anionic species (either in monatomic or complexed form) but also in the longer term for deciding whether or not mixed-oxide-fluoride systems are amenable to probe-ion spectroscopy, especially since these two anions occur in a number of technologically important media, for example, the bauxite-cryolite melts for aluminium extraction and fluorophosphate laser glasses.

ORBITAL-EXPANSION SPECTROSCOPY

Although it is desirable to include electron-transfer spectra in this study, from a practical point of view it is hardly possible owing to the very high optical electro-negativity of fluoride (3.9) which places the first Laporte-allowed electron-transfer band in the vacuum ultraviolet region for many metal fluoro-complexes. Therefore, we concentrate on the orbital-expansion effect and consider first of all the nephelauxetic h parameter of conventional fluoro-metallate complexes. h is obtained from $d-d$ spectra using eqn (1):

$$B(\text{free ion}) - B(\text{complex}) = B(\text{free ion})hk \quad (1)$$

where $B(\text{free ion})$ is the Racah parameter of the gaseous, free metal ion (15 B separates the ground-state F term from the P term of the same multiplicity) and $B(\text{complex})$ is the Racah parameter in the fluoro-complex; k is a constant peculiar to the metal ion, and has been assigned on the basis of spectral data of its complexes [the validity of eqn (1) is discussed in ref. (1)]. Existing spectroscopic data allow h to be evaluated for fluoride in several fluoro-metallate complexes, and, as seen from table 1, h varies

TABLE 1.—ORBITAL-EXPANSION DATA FROM $d-d$ SPECTRA OF HEXAFLUOROCOMPLEXES

ion	$\frac{B(\text{complex})^a}{B(\text{free ion})}$	k^b	$h(\text{fluoride})$
V ³⁺	0.78	0.28	0.79
Cr ³⁺	0.80	0.20	1.00
Fe ³⁺	0.77	0.24	0.96
Mo ³⁺	0.90	0.15	0.67
Rh ³⁺	0.64	0.28	1.29
Ni ²⁺	0.88 ^c	0.12	1.00

^a Values taken from G. C. Allen and K. D. Warren, *Struct. Bonding (Berlin)*, 1974, **19**, 105 (except for Ni²⁺); ^b values from ref. (1) except for V³⁺ for which is based upon data for the hexa-aquo ion; ^c calculated from data for Ni²⁺ in molten 'FLiNaK' taken from J. P. Young and G. P. Smith, *J. Chem. Phys.*, 1964, **40**, 913.

from 0.7 to 1.3. Usually h for an anion is more or less fixed, the principal exception being oxide (—II). In the past, a value of 0.8 has been assigned to $h(\text{fluoride})$,¹ but in the light of table 1 it is probably best to regard this as a nominal value. The values of h for the other halide ions are: Cl[−], 2.0; Br[−], 2.3; I[−], 2.7.¹

The h parameter can also be measured using p block s^2 ions such as Tl⁺, Pb²⁺ and Bi³⁺. The $6s^2 \rightarrow 6s6p$ transition, $^1S_0 \rightarrow ^3P_1$, gives rise to a strongly absorbing band in the ultraviolet region, and an expression analogous to eqn (1) holds:

$$\nu(\text{free ion}) - \nu(\text{complex}) = \nu(\text{free ion})hm \quad (2)$$

where $\nu(\text{complex})$ is the $^1S_0 \rightarrow ^3P_1$ frequency of the complexed metal ion and $\nu(\text{free ion})$ the (corrected) free-ion frequency; m is a constant specific to the metal ion and its values, and also those of $\nu(\text{free ion})$, are in table 2.⁷ Thus the h parameter is obtained directly from the frequency maximum, ν , and, since this is very sensitive to the electron-donor power of the anions, the s^2 ions are especially suited to the purpose

of detecting changes in the state of the fluoride ion when it is influenced by polarising cations (see above).

First, however, it is necessary to discover what h value is signalled by Tl^+ , Pb^{2+} and Bi^{3+} when they are coordinated by uncomplexed F^- ions, as in an alkali-metal fluoride melt for example. In the present study, molten LiF-NaF-KF (46.5:11.5:42), 'FLiNaK', was used (melting point 439°C).

RESULTS AND DISCUSSIONS

Thallium(I) fluoride, lead(II) fluoride and bismuth(III) fluoride dissolved in 'FLiNaK' and the absorption spectra of the resulting solutions revealed the $^1S_0 \rightarrow ^3P_1$ band for each ion (see fig. 1). The h values calculated from the absorption maximum,

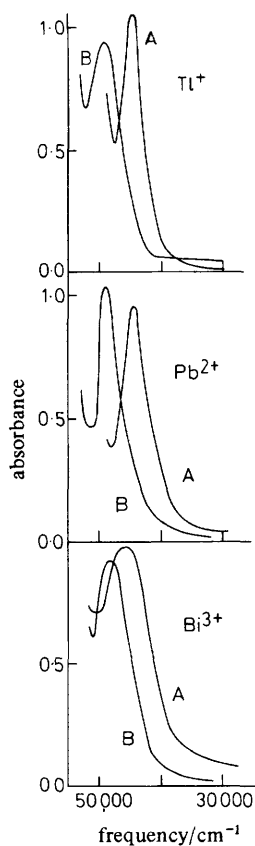


FIG. 1.—Absorption spectra of Tl^+ , Pb^{2+} and Bi^{3+} in (A) molten 'FLiNaK', and (B) molten $\text{Na}[\text{BF}_4]\text{-K}[\text{BF}_4]$ (1:1) just above the melting point. Pathlength is *ca.* 0.8 mm and concentration of s^2 ion is $10^{-2}\text{-}10^{-3} \text{ mol dm}^{-3}$.

using eqn (2), show some variation (table 2) but are consistent with the formation of fluoro-complexes. As is the case for the data in table 1, it is again necessary to specify the metal ion of the fluoro-complex when quoting the h parameter for fluoride. The variation revealed by Tl^+ , Pb^{2+} and Bi^{3+} , however, is only slightly worse than that

TABLE 2.—ABSORPTION MAXIMA (cm^{-1}) OF $^1S_0 \rightarrow ^3P_1$ BAND OF Tl^+ , Pb^{2+} AND Bi^{3+} AND VALUES OF h^a IN MOLTEN-HALIDE MEDIA

ion	spectral parameters		LiCl-KCl^b		'FLiNaK' ^c		$\text{Na}[\text{BF}_4]\text{-K}[\text{BF}_4]^d$		$\text{K}[\text{PF}_6]^e$	
	$\nu(\text{free ion})$	m	ν	h	ν	h	ν	h	ν	h
Tl^+	55 300	0.14	40 500	1.91	44 600	1.38	48 500	0.88	46 500	1.14
Pb^{2+}	60 700	0.20	36 200	2.02	44 600	1.33	48 800	0.98	47 500	1.09
Bi^{3+}	56 000	0.21	30 200	2.19	43 200	1.09	47 300	0.74	44 000 ^{sh} ^f	

^a Calculated from eqn (2); ^b 59:41 molar ratio, 440 °C; values of ν from G. P. Smith, D. W. James and C. R. Boston, *J. Chem. Phys.*, 1965, **42**, 2249; ^c 460 °C ($\pm 15^\circ$); ^d 50:50 molar ratio, 570 °C ($\pm 15^\circ$); ^e 580 °C ($\pm 15^\circ$); ^f sh = shoulder. Concentration of probe ion was 10^{-2} – 10^{-3} mol dm^{-3} .

for chloride, for example, where data in molten LiCl-KCl indicate a value for h which is also not constant (see table 2).

Some check on these values for $h(\text{fluoride})$ is possible by considering the $^1S_0 \rightarrow ^3P_1$ frequencies for the simple binary fluorides of the probe ions, namely TlF , PbF_2 and BiF_3 , and comparing them with the frequencies of the other binary halides. This can be done by recording absorption spectra of thin films of thallium(I), lead(II) and bismuth(III) halides deposited on to u.v.-transparent substrates. Some of these spectra have been previously recorded and the $^1S_0 \rightarrow ^3P_1$ transition identified as the lowest-energy band [see ref. (8) for example]. When present in a binary salt, the probe ion is in a very high concentration and forms part of a continuous system rather than part of a discrete halogeno-complex. Nevertheless, it is still possible to treat the cation-anion interaction on a localised basis, although cooperative effects modify the energies of the excited states.⁹ Therefore, eqn (2) might be expected still to apply but possibly with different values for the various parameters compared with those applicable to the discrete complexes. If the four halides of each metal are considered, and the h parameters are chosen as those applicable to halogeno-complexes, then it is anticipated that the plot of $^1S_0 \rightarrow ^3P_1$ frequency against h should be linear, but of different slope and $\nu(\text{free ion})$ compared with the same type of plot for the halogeno-complexes. This indeed is found to be the case (fig. 2), and it is noteworthy that the intercepts when h is zero yield values of $\nu(\text{free ion})$ that are very close to the experimental $^1S_0 \rightarrow ^3P_1$ frequency of the gaseous metal ion rather than a corrected value; this is especially so for bismuth, where the difference between $\nu(\text{free ion})$ for complexes and the experimental free-ion value is very large (19900 cm^{-1}). More important in the present context is the good fit in fig. 2 of the h parameter for the metal fluorides, thereby substantiating the h values found in 'FLiNaK' (table 2).

Returning now to 'complexed' probe ions, next it is necessary to determine whether or not the modification of the electron-donor power of the fluoride ion, due to the influence of highly polarising cations, can be detected by the s^2 probe ions. In oxide systems it is observed that $h(\text{oxide})$ is dramatically reduced when oxide is polarised by species such as boron(III), silicon(IV), etc. For example, whereas $h = 2.9$ for Na_2O (based upon Pb^{2+} data¹⁰), in $\text{Na}_2\text{B}_4\text{O}_7$ glass $h = 1.50$, and in NaPO_3 glass $h = 1.17$. Thus, it is expected that in analogous media, e.g. $\text{Na}[\text{BF}_4]$ or $\text{Na}[\text{PF}_6]$, $h(\text{fluoride})$ would undergo a pronounced decrease compared with the 'FLiNaK' value. However, there is an important difference between fluoride and oxide, which is that F^- forms discrete fluoro-complexes readily with cations of 'medium' oxidation number (such as the probe ions Tl^+ , Pb^{2+} and Bi^{3+}), whereas O^{2-} forms discrete oxo-complexes

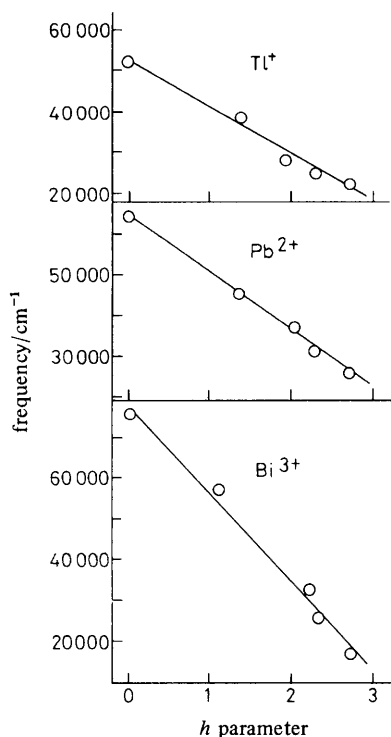


FIG. 2.—Plot of nephelauxetic parameter, h , against $^1S_0 \rightarrow ^3P_1$ frequency of Tl^+ , Pb^{2+} and Bi^{3+} for the gaseous ions ($h = 0$) and in thin films of their halides; h is taken as 2.3 for bromides, 2.7 for iodides¹ and the values indicated in table 2 for fluorides and chlorides. Frequencies are from C. E. Moore, *Atomic Energy Levels* (National Bureau of Standards, Washington, D.C., 1952) for the gaseous ions, and the present work for the metal halides except PbI_2 , which is from A. I. Rybalka and V. Miloslavskii, *Sov. Phys. Solid State*, 1976, 18, 1813 and refers to PbI_2 with the $PbCl_2$ structure.

usually only with cations having a 'high' oxidation number, *e.g.* Cr^{6+} or Mn^{7+} . Thus a second possibility must be considered when the probe ions are introduced into fluoroborate, fluorophosphate, *etc.* media: they could remove fluoride ions from the $[BF_4]^-$, $[PF_6]^-$, *etc.* anions and produce discrete fluoro-complexes. If this occurred, then the $^1S_0 \rightarrow ^3P_1$ frequency would be virtually the 'FLiNaK' value and there would be no significant change in h .

The most amenable of the fluoro-complex media (from the point of view of melting point and thermal stability) are the alkali-metal tetrafluoroborates. For use on the spectrophotometer hot-stage, $K[BF_4]$ or $Na[BF_4]$ — $K[BF_4]$ mixtures were found to be satisfactory, and good absorption spectra of Tl^+ , Pb^{2+} and Bi^{3+} were obtained (fig. 1). The $^1S_0 \rightarrow ^3P_1$ frequencies, and the h parameters calculated from them, are in table 2. Compared with 'FLiNaK' values, h has decreased markedly (by 36% for Tl^+ , 26% for Pb^{2+} , 32% for Bi^{3+}), indicating that the probe ions have indeed responded to the reduction of the electron-donor power of the fluorides which has resulted from the boron-fluorine covalent interaction. Furthermore, discrete fluoro-complexes ($[MF_x]^{(x-n)-}$, $M^{n+} = Tl^+$, Pb^{2+} , Bi^{3+}) are not formed to any significant extent.

The $^1S_0 \rightarrow ^3P_1$ frequency difference between $Na[BF_4]$ — $K[BF_4]$ and 'FLiNaK' is *ca.* 4000 cm^{-1} for all three probe ions. The effect of adding NaF or KF to the

$\text{Na}[\text{BF}_4]\text{--K}[\text{BF}_4]$ melt should therefore be readily discernible from the absorption envelope. Experimentally, a gradual red-shift of the $^1S_0 \rightarrow ^3P_1$ band was observed and, as seen from fig. 3, the h parameter became approximately the 'FLiNaK' value at low KF contents, especially in the case of Ti^+ , indicating formation of the discrete

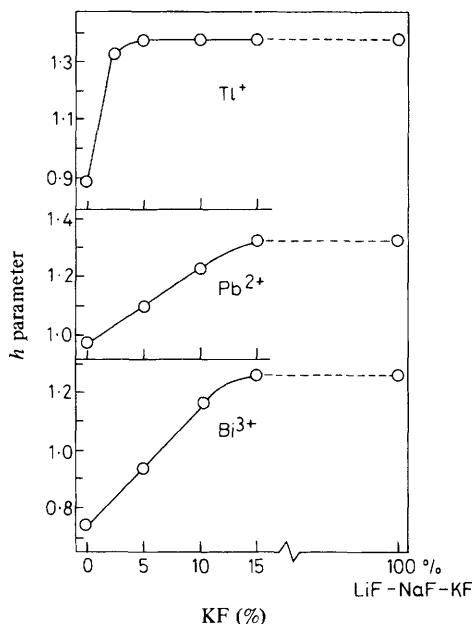
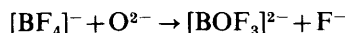


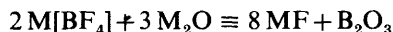
FIG. 3.—Plot of h parameter registered by Ti^+ , Pb^{2+} and Bi^{3+} in $\text{NaBF}_4\text{--KBF}_4$ (1:1)–potassium fluoride melts against molar percentage of KF. The trends are compared with the h parameter in molten 'FLiNaK'.

fluoro-complex of the probe ion. In the mixed fluoride–fluoroborate melt system, the probe ions have the choice between two distinct fluoride species, and it is apparent that they favour the more basic (uncomplexed) fluoride ions. (This aspect of the solvent behaviour of molten salts has been discussed previously.¹⁰) The red-shift of the $^1S_0 \rightarrow ^3P_1$ band, rather than the generation of a new band in the 'FLiNaK' position, indicates that the coordination sphere continuously gains F^- ions and loses fluorides attached to boron(III) atoms as the KF content is increased. It is not clear why Ti^+ shows the greatest affinity for the more basic F^- ions, but it is possible that this behaviour is related to the observation in high alkali-metal borate glasses that, of the three s^2 ions, Ti^+ has the greatest tendency for seeking sites of higher than average basicity.³

It is possible to calculate the h parameter for the $[\text{BF}_4]^-$ ion from the values of h for B_2O_3 (1.12), Na_2O (2.9) and NaF (1.33) (figures quoted are based upon Pb^{2+} data). Since $[\text{BF}_4]^-$ ions react with oxide ions through reactions of the type



it follows that



(we are not distinguishing here between Na and K, either being denoted by M). Thus, if a 'law of average environment'¹ is envisaged for the nephelauxetic effect, then it follows from the above equivalence that

$$\frac{8}{11}h(\text{M}[\text{BF}_4]) + \frac{3}{11}h(\text{M}_2\text{O}) = \frac{8}{11}h(\text{MF}) + \frac{3}{11}h(\text{B}_2\text{O}_3).$$

Substituting the values of h quoted above, $h(\text{M}[\text{BF}_4]) = 0.7$, a value below that determined experimentally, 0.98 (table 2). The discrepancy, however, is not too serious since in part it can be accounted for by (i) temperature, the h parameters for B_2O_3 , Na_2O and NaF being quoted for the solids at ambient temperature, and (ii) the probable presence of small quantities of F^- ions in the $\text{Na}[\text{BF}_4]\text{--K}[\text{BF}_4]$ melt which red-shift the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ frequency (see fig. 3).

Other melts containing complex fluoro-species, for example hexafluorosilicate, have high melting points and decompose to various extents. Of these experimentally more difficult media, absorption spectra were obtained only in molten potassium hexafluorophosphate (which had a tendency to turn yellow after a short time). The h values (table 2) are greater than those for the fluoroborate medium, but are significantly lower than the 'FLiNaK' values, again indicating the polarisation of the fluoride species [by the phosphorus(V)]. The data obtained in $\text{K}[\text{PF}_6]$ should be regarded with caution since it is not known what proportion of free fluoride ions are present (arising from thermal decomposition of the melt); their presence would increase the apparent h value similarly to their action in fluoroborate media (fig. 3). Nevertheless, the data provide another instance of how polarisation of fluoride is detectable by probe ions.

EXPERIMENTAL

Materials were as follows: AnalaR NaF, KF, 'very pure' LiF, G.P.R. TiCl_3 , TiBr_3 , PbF_2 , PbCl_2 , PbBr_2 and KBF_4 from B.D.H.; BiCl_3 , BiBr_3 , BiI_3 and NaBF_4 from Hopkins and Williams; TlF and KBF_6 from Alfa Products; BiF_3 from Pfaltz and Bauer; TlI from Koch-Light. All were used without further purification apart from drying, and this was done before mixing in the preparation of 'FLiNaK'.

Absorption spectra were recorded on a Unicam SP700 C instrument. Molten materials were held on a platinum gauze hot-stage, heated electrically, which was encapsulated by a glass dome fitted with u.v.-transparent silica-disc windows. Melting was in dry nitrogen rather than under vacuum to minimise decomposition. Masks were arranged so that the 'sample' beam impinged on the centre of the melt and also so that the 'reference' beam was suitably attenuated. The concentration of probe ion in the melt was between 10^{-2} and 10^{-3} mol dm^{-3} and was roughly determined by dissolving a known weight of doped melt in 6 mol dm^{-3} hydrochloric acid and measuring the u.v. absorption of the chloro-complex.

Thin films were prepared as follows. Halides of Tl^+ , Pb^{2+} and Bi^{3+} were coated on to vitreous silica substrates by vacuum deposition, and spectra were recorded at ambient temperature. Frequency maxima of the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ absorption were found to be close to literature values (where these existed).

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