Differentiation of Spectra as a Means of Resolving Spin-forbidden Bands: Iron(III) Complexes

By TREVOR R. GRIFFITHS*
(*Department of Inorganic and Structural Chemistry, University of Leeds, Leeds* LS2 9JT)
and KEITH KING
(*Shell Research Ltd., Thornton Research Centre, P.O. Box* 1, *Chester* CH1 3SH)

Summary Calculated second and fourth differentials of iron(III) spectra in molten salts (an extreme case, where temperature-broadened spin-forbidden transitions barely show up on an intense charge-transfer band edge) have resolved out expected transitions, plus some more which are tentatively assigned; this approach, which requires no prior knowledge of the correct number of bands present or their mathematical shape, is thus capable of resolving and subsequently assigning ligand-field spectra, but cannot be directly performed on modern spectrophotometers without due care being taken.

IN order to resolve a spectrum by curve-fitting, all procedures currently in use require the prior knowledge of the correct number of bands under the envelope, estimates (generally good estimates) of their peak maxima, peak heights and half-widths, and a knowledge of the mathematical descriptions of their band shapes (Gaussian, Lorentzian, *etc.*).[1,2] The process of smoothing and differentiating spectra using convolution coefficients[3] is an exact, least-squares fitted procedure which allows the correct number of bands and their peak maxima to be determined, and this is the main information sought when attempting curve-fitting. The convolution procedure has the crucial advantage that no assumptions need to be made regarding band positions, heights, half-widths, mathematical functions, or indeed, the number of component bands. In practice, absorption edges and the largest and broadest band are lost, and smaller, narrower bands enhanced, their heights increased inversely in a power relationship to their width.

As part of the development of a new spectroscopic technique to determine the rate of corrosion of metals by molten salts we calculated the even-order differentials of the (digitized) electronic absorption spectra of nickel(II), chromium(III), and iron(III) complexes in fused sulphates and chlorides. It was found that spin-allowed transitions became clearly identified, and spin-forbidden bands appeared with approximately the same heights as the spin-allowed bands. The latter are absent in iron(III) complexes, and to date only some of the theoretically possible transitions have been determined by eye from the small ripples on the charge-transfer edge of spectra taken at ambient[4] and liquid hydrogen temperatures:[5] our studies, at nearly 1000 °C higher, and thus with spin-forbidden bands considerably

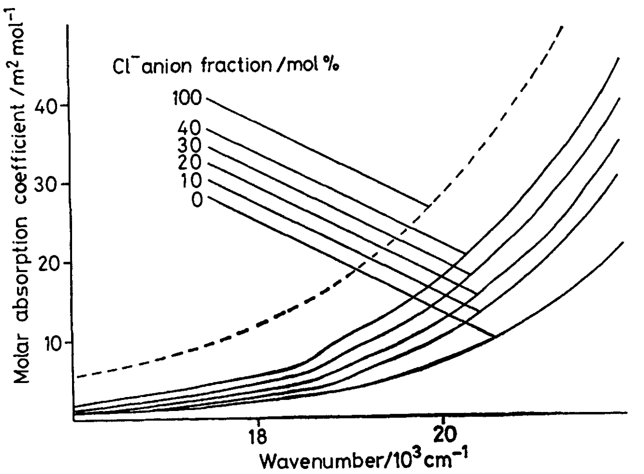

FIGURE 1. Spectrum of iron(III) in (Na, K, Al)SO_4 melt at 972 K showing the effect of added chloride. Dashed line, pure chloride melt. Spectra subjected to 47-point smoothing, fifth-order polynomial.

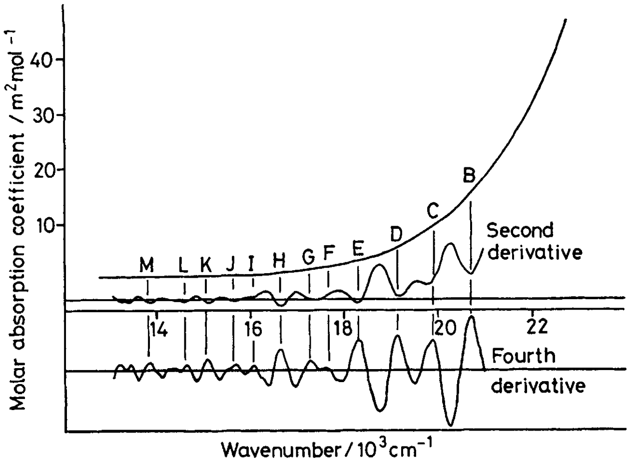

FIGURE 2. Zeroth-, second- and fourth-derivative spectra (35-point derivative of 35-point smoothed spectrum, fifth-order polynomial) of iron(III) in (Na, K, Al)(SO_4, Cl) melts containing 20 mol anion % chloride at 913 K. Note resolved spin-forbidden transitions (for assignments of B—M see Table) and correspondence of second-derivative minima with fourth-derivative maxima.

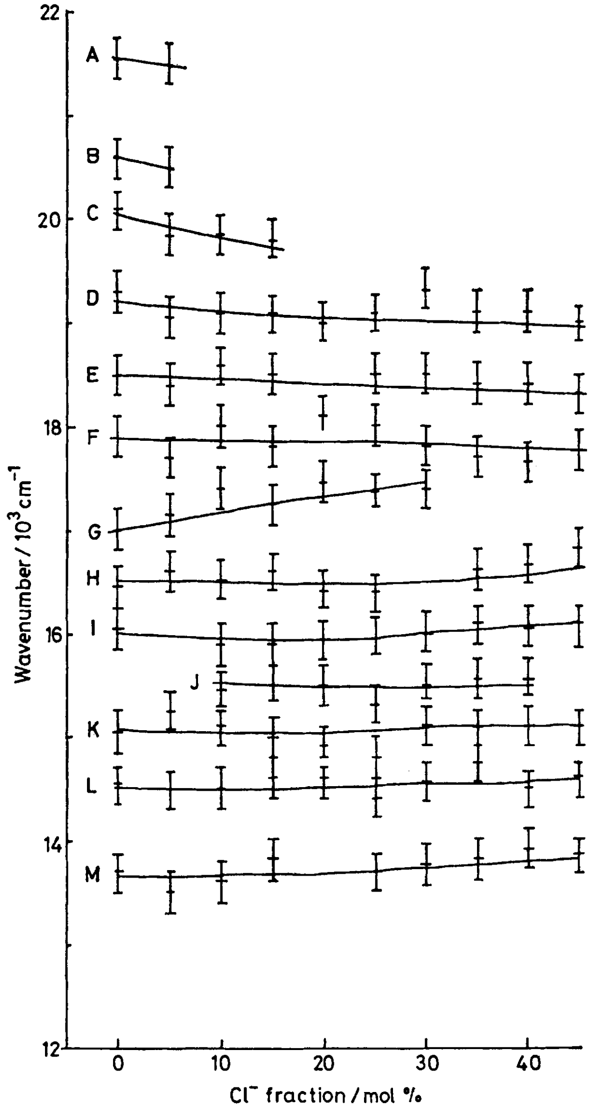

FIGURE 3. Variations of the energies of resolved bands of the iron(III) spectrum in (Na, K, Al)(SO_4, Cl) melts with chloride content at 913 K.

broadened, would therefore provide a severe test of the differentiation technique, and be of general interest, since many commercial spectrophotometers are now provided with differentiation facilities. Further, visual examination of iron(III) spectra has not the slightest possibility of providing the information necessary for curve-fitting procedures.

The spectrum of iron(III) in an (Na, K, Al)SO_4 melt (cation proportions 17 : 17 : 6, respectively) and the effects of chloride addition, which shifts the strong ligand-to-metal charge-transfer edge to lower energy, are shown in Figure 1. Since noise fluctuations would be enhanced by differentiation the spectra were subjected to a 47-point smoothing, fitted to a fifth-order polynominal. This improves the original signal-to-noise ratio by a factor of around 14. Figure 2 shows typical second and fourth differential spectra (and their original spectrum), and the resultant minima and maxima, respectively. To ensure further that the peaks resolved were not due to random noise the differentials were calculated using various convolution coefficients for each spectrum, and regular patterns among some 60 spectra were established as a function of both temperature and chloride content (Figure 3).

The geometry of the complex and band assignments can now be made. The pattern of crystal-field splitting for a d^5 ion is the same in both octahedral and tetrahedral fields, and the only changes expected upon co-ordination change result from a variation in the splitting parameter Δ. Since chloride and sulphate have adjacent positions in the spectrochemical series for molten salts,[6] and the energies of the resolved bands are virtually independent of chloride concentration, no co-ordination change takes place here with increase in chloride content. Also, for a d^5 ion there is no net change in crystal-field stabilisation energy on going from octahedral to tetrahedral co-ordination. Electrostatic factors will favour four-fold co-ordination. We therefore assume $FeCl_4^-$ ions to be present in the (Na, K, Al)Cl melt, and in the pure sulphate melt a tetrahedral complex, *viz.* $[Fe(SO_4)_4]^{5-}$, since it is unlikely that a bidentate sulphate could span two adjacent tetrahedral sites.

Our resolved bands may be assigned with reference to the spectrum of the $[FeCl_4]^-$ species in acetone[4] and in the solid pyridinium (PyH) salt $(PyH)_3Fe_2Cl_9$ at 20 K.[5] The assignments for $[FeCl_4]^-$ are complex. Balt[4] has discussed possible assignments of his bands: our bands are now identified using the basis of his assignments (Table).

TABLE. Comparison of maxima (cm^{-1}) of the resolved bands from the iron(III) spectrum in (Na, K, Al)SO_4 and (Na, K, Al)Cl melts with the reported maxima of $[FeCl_4]^-$.

Band	Assignment	$[FeCl_4]^-$ in acetone at 300 K	$[FeCl_4]^-$ in $(PyH)_3Fe_2Cl_9$ at 20 K	Fe^{III} in (Na, K, Al)Cl at 972 K	Fe^{III} in (Na, K, Al)SO_4 at 1003 K
A	$^4T_1(^4P)$	22,000[a]	22,100	n.f.[b]	21,500
B		n.f.	n.f.	n.f.	20,900
C		n.f.	n.f.	n.f.	20,000
D	$^2\Gamma$	n.f.	19,750	n.f.	19,500
E	$^4E(^4D)$	18,760	18,800	18,800	18,700
F		n.f.	n.f.	18,300	18,300
G	$^2\Gamma$	n.f.	17,800	17,700	17,600
H	$^4T_2(^4D)$	16,700	16,500	16,900	16,700
I	$^4A_1(^4G)$	16,150	16,150	15,900	16,200
J	$^4E(^4G)$	n.f.	15,650	n.f.	15,600[c]
K		n.f.	n.f.	15,100	15,100
L	$^4T_2(^4G)$	14,600	14,600	n.f.	14,400
M	$^4T_1(^4G)$	13,700	13,700	13,200	13,400

[a] 883 K. [b] n.f. = not found. [c] 943 K.

Assignments designated $^2\Gamma$ by Balt represent transitions to unspecified doublet terms, arising from the ^2I free ion state, and are observed in the solid-state $[FeCl_4]^-$ spectrum but not in solution. Bands B, C, F, and K observed in this study have not previously been detected, and may be assigned to further sextet–doublet transitions, or possibly to splitting of the quartet-term states.

It was expected that the $[FeCl_4]^-$ spectrum at 20 K would reveal more bands than at ambient temperature: we note that from our melt spectra these low-temperature bands were identified, and other bands as well. Examination of the Table shows general consistency, and the close similarity of the peak maxima identified in the chloride and sulphate melts reveals that these ligands have essentially identical, rather than adjacent, positions in the spectrochemical series for molten salts[6] when co-ordinated to iron(III). We expect that differentiation of the spectrum of $[FeCl_4]^-$ at 20 K will reveal the additional bands we report, and possibly some more, and hence facilitate further assignments.

Thus, differentiation of ligand-field spectra at ambient temperatures has the ready potential for enhancing spin-forbidden bands so that many of them may be now appropriately assigned, and yield further information concerning iron(III) complexes in particular. However, we caution the reader that we know of no current commercial spectrophotometer which has the flexibility to differentiate spectra with the same authority as these results. To ensure elimination of enhanced spurious noise bands spectra must first be smoothed. Differential spectra must then be calculated using various numbers of convolution coefficients. At present this requires the transference of spectra to a computer, either by direct interfacing or *via* punched tape, in order that a comparison and consistency check can be made on various differentiations of the same spectrum.

This approach has also been used to resolve the spectra of nickel(II) and chromium(III) in molten salts: the expected number, and no more, of spin-allowed and spin-forbidden bands were found. This will be published, with the iron(III) work, when the project is completed.

We thank the S.R.C. for a Cary 14H spectrophotometer and a CASE Studentship, in co-operation with Dr. D. Mortimer, Head of the Corrosion and Combustion Division, Central Electricity Generating Board, Harrogate, North Yorkshire, to K. K. We also thank Dr. P. Gans for valuable discussions and computing assistance.

(*Received*, 22*nd January* 1981; *Com.* 074.)

[1] B. E. Barker and M. F. Fox, *Chem. Soc. Rev.*, 1980, **9**, 143.
[2] W. F. Maddams, *Appl. Spectrosc.*, 1980, **34**, 245.
[3] A. Savitsky and M. J. E. Golay, *Anal. Chem.*, 1964, **36**, 1627.
[4] S. Balt, *Recl. Trav. Chim. Pays-Bas*, 1967, **86**, 1025.
[5] A. P. Ginsberg and M. B. Robin, *Inorg. Chem.*, 1963, **2**, 817.
[6] K. E. Johnson, *Electrochim. Acta*, 1966, **11**, 129.