Coordination Chemistry Reviews, 125 (1993) 333–350

Redox, Fragmentation and Clustering Processes in the Excitation of Metal Complexes by Fast Atom Bombardment : Relationships with Photochemical Pathways

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(Received October 15 1992)

Abstract

Comparison is made between the variety of primary processes undergone by complexes of the transition metals on photochemical excitation in solution and those induced by fast atom bombardment (FAB) in a matrix of an involatile liquid. All of the well-established photochemical pathways (redox, dissociation, association, solvolysis, ligand fragmentation and clustering) have a counterpart in FAB, although the extent to which they occur can differ markedly.

A. INTRODUCTION

One of the earliest, but most valuable, contributions made by Professor V. Carassiti with Professor V. Balzani, to the community of inorganic photochemists was the systematisation of the variety of elementary processes undergone by inorganic molecules and ions on photo-excitation [1]. These same excited states, and therefore resulting chemical processes, are also achieved, of course, on excitation of inorganic species by other means, such as α- and β -particles, gamma and X-rays, sonochemical, electrochemical and mechanochemical excitation, processes frequently demonstrated by the appearance of the associated luminescence or the detection of derived free radicals.

Where the inorganic species in question is dissolved in a solvent, then these various means of excitation refer, in their initial stages of action, to transfer of energy from the fast particle, gamma-quantum, sound wave, etc. to the solvent (or matrix) which undergoes ionization and excitation. Transfer of solvent excitation to an inorganic solute can then result in the achievement by the latter of an excited state:

$$\text{Solvent}^{*} + \text{Solute} \rightarrow \text{Solvent} + \text{Solute}^{*} \tag{1}$$

Transfer of excitation-induced electrons and positive holes (the latter as solvent cation radicals) can also take place to the solute:

$$e^{-} + \text{Solute} \rightarrow \text{Solute}^{-\cdot} \tag{2}$$

$$\text{Solvent}^{+\cdot} + \text{Solute} \rightarrow \text{Solvent} + \text{Solute}^{+\cdot} \tag{3}$$

0010-8545/93/$24.00

and ion-recombination processes then generate further excited states:

$$\text{Solute}^{+\cdot} + \text{Solute}^{-\cdot} \rightarrow \text{Solute}^{*} + \text{Solute} \tag{4}$$

$$\text{Solvent}^{+\cdot} + \text{Solute}^{-\cdot} \rightarrow \text{Solvent} + \text{Solute}^{*}, \text{etc.} \tag{5}$$

Radiation-chemical energies are typically of the order of several MeV, which means that many thousands of acts of solvent excitation and ionization take place along the track of a single particle, or following absorption of a γ-ray to release a highly energetic secondary electron.

In mass spectrometry, one is dealing with energies of a hundred eV up to a few keV, which are intermediate in size between those of photochemical and radiation-chemical excitation. It is to be anticipated therefore that the results of excitation of inorganic species in the source of a mass spectrometer might perhaps reflect a character intermediate between photochemistry and radiation chemistry.

A nice parallel between the results of a metal centre photosensitising the decomposition of a ligand, and submitting the same ligand to electron impact in a mass spectrometer, is found in studies of the photodecomposition of complexes of organic ligands with Ce(IV) and U(VI) ions [2-5] in a low temperature matrix.

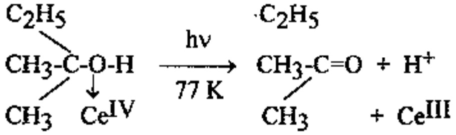
Fig. 1. E.s.r. spectrum of $\cdot C_2H_5$ radical obtained on photo-oxidation of 1,1-dimethylpropan-1-ol by Ce(IV) ammonium nitrate at 77 K [2].

Figure 1 shows the post-photolysis e.s.r. spectrum of a complex of Ce(IV) and tert-amyl alcohol at 77 K [2]. The detection of an ethyl radical indicates the route of ligand fragmentation to be

TABLE 1

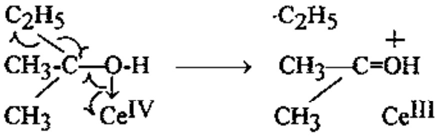
(a) Radicals detected in metal ion-photosensitized decomposition of ligands at 77 K and (b) major fragmentation species in electron-impact mass spectra of the respective ligand.

Ligand (metal ion)	Radical trapped on photosensitized decomposition	Major ion in mass spectrum	Neutral radical lost in electron impact	Refs.
$CH_3CH_2CH_2OH + U^{VI}$	$\cdot C_2H_5$	$\cdot CH_2OH^+$	$\cdot C_2H_5$	3,6
$(CH_3)_3COH + Ce^{IV}$	$\cdot CH_3$	$(CH_3)_2CHO^+$	$\cdot CH_3$	2,6
$C_2H_5(CH_3)_2COH + Ce^{IV}$	$\cdot C_2H_5$	$(CH_3)_2CHO^+$	$\cdot C_2H_5$	2,6
$(C_2H_5)_3COH + Ce^{IV}$	$\cdot C_2H_5$	$(C_2H_5)_2CO^+$	$\cdot C_2H_5$	2
$(PhCH_2)(Ph)CHOH + Ce^{IV}$	$PhCH_2\cdot$			2
$(CH_3)_2CHCO_2H + Ce^{IV}$	$(CH_3)_2CH\cdot$	$(CH_3)CO^+$	$\cdot CO_2H$	4,7
$CH_3CH(OH)CO_2H + Ce^{IV}$	$\cdot CH_3$			4
$CH_3COC_2H_5 + U^{VI}$	$\cdot C_2H_5$	CH_3CO^+	$\cdot C_2H_5$	5,8



(6)

The electron impact mass spectrum of tert-amyl alcohol shows the major positive ion to be that of acetone [6], signifying rapid loss of $\cdot C_2H_5$ from the parent ion. This suggests that the photofragmentation, eqn. (6), at 77 K may also occur from the radical cation of the tertiary alcohol even at 77 K, rather than by the concerted mechanism, eqn. (7)



(7)

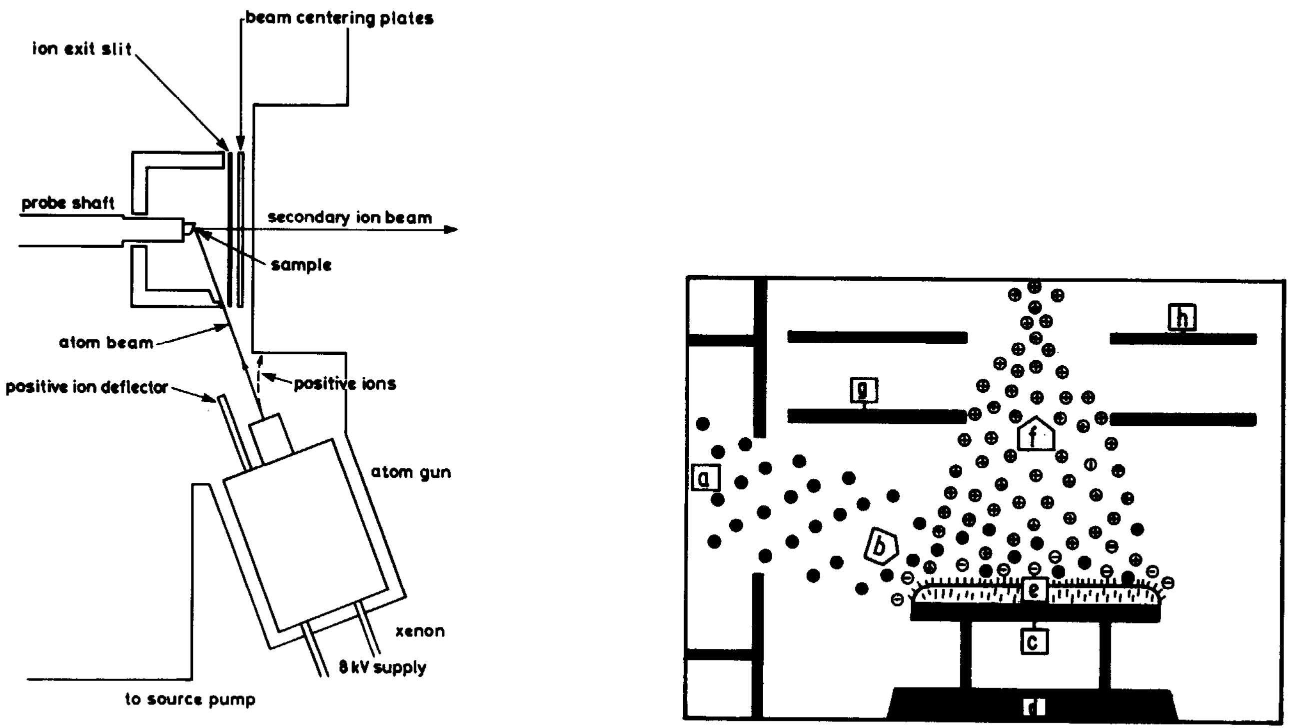
Some further illustrations of such parallel photochemical and mass spectroscopic behaviour, involving different organic ligands, are given in Table 1.

B FAB MASS SPECTROMETRY

The study of inorganic species by EI mass spectrometry goes back many years, [9,10] but it has been restricted by the problem of involatility of the substrate molecule. While EI spectra have been recorded for a number of organometallic compounds, the study of coordination compounds has accelerated dramatically since the development of fast atom bombardment (FAB) mass spectrometry in 1980 by Barber and colleagues [11], and several reviews and wide-ranging papers have appeared relating to coordination compounds [12,13], as have more general reviews of FAB [14].

This technique depends upon the sputtering of the inorganic molecule dissolved in an involatile matrix of an organic molecule, usually a viscous liquid, (typically glycerol or 3-nitrobenzyl alcohol), by a beam of fast neutral atoms of an inert gas (Ar, Kr, Xe) [Fig. 2(a)]. The act of sputtering is envisaged as the forcible ejection into the gas phase of a large cluster of the matrix together with any solute present in the cluster. The process of ion selection made immediately above the FAB source means that only species bearing a particular charge sign are conducted to the analysing magnetic and electric fields (Fig. 2(b)), and it is possible to examine both positive and negative ions derived from the solute in separate experiments by altering the polarity of the electric field.

A full and exact description of all the processes occurring during the FAB experiment is yet to be formulated, however the bulk of opinion favours the surface of the matrix as the site for most of the chemical transformations that occur [14]. The variety of processes found is considerable, as illustrated, with their photochemically-derived counterparts, in Table 2.



(a) (b)

Fig. 2. (a) Schematic picture of source layout for FAB experiment; (b) Close-up of events at FAB source: a-atom gun; b-fast atom beam; c-metal sample holder; d-end of probe; e-sample/solution in high viscosity, involatile solvent; f-ion beam; g-ion extraction plate; h-lens system leading to mass analyser. Adapted with permission from ref. [34].

TABLE 2

General types of process undergone by inorganic compounds (a) under photoirradiation and (b) under FAB

Process	Photochemical Example	Example from FAB	Refs.
Simple dissociation of one ligand	$W(CO)_6 \rightarrow W(CO)_5 + CO$	$K_4[Fe(CN)_6] \rightarrow \{K_4[Fe(CN)_5]\}^+ + \cdot CN + e^-$	15,16
Multiple dissociation of ligand to yield low coordination number	$Mo(CO)_6 \rightarrow Mo(CO)_3 + 3CO$	$K_4[Fe(CN)_6] \rightarrow \{K_4[Fe(CN)_2]\}^+ + 4\cdot CN + e^-$ $UO_2(gly)_4 \rightarrow UO_2^+ + 4gly^a + e^-$	16,17 18
Ligand fragmentation	(malonato) $Ce^{IV} \rightarrow \cdot CH_2CO_2H + H^+ + CO_2 + Ce^{III}$	$[RCH(NH_3^+)CO_2^-]UO_2 \rightarrow ([CH(NH_3^+)CO_2^-]UO_2)^+ + R\cdot$	4,18
Association of a ligand molecule	$Fe(CO)_4 + H_2 \rightarrow Fe(CO)_4H_2$	$[UO_2(alanine)_4]^+ \rightarrow [UO_2(alanine)_5]^+$	18,19
Association of a matrix molecule	$Cr(CO)_5 + CO \rightarrow Cr(CO)_6$	$FeSO_4 \rightarrow [FeSO_4glycH]^+, [FeSO_4glyc_2H]^+, [FeSO_4glyc_3H]^+$	13,20
Ligand solvolysis	$[W(CN)_8]^{4-} \rightarrow [W(CN)_7(H_2O)]^{3-} + CN^-$	$[Ag(bipy)_2]^+ClO_4^- \rightarrow [Ag(bipy)(glyc)]^+, [Ag(glyc)_n]^+$	21,22
Ligand exchange	$[Co(CN)_5(H_2O)]^{2-} + I^- \rightarrow [Co(CN)_5I]^{3-} + H_2O$	$[Th(NO_3)]_4 + PTSA \rightarrow [Th(PTSA\text{-}H)_2(glyc\text{-}H)]^+$	23
Reduction of metal centre	$[PtCl_6]^{2-} \rightarrow [Pt^{III}Cl_5]^{2-} + Cl^-$	$UCl_4 \rightarrow [U^{III}Cl_4]^-$	18,24
Oxidation of metal centre	$Fe(thionine)^{2+} \rightarrow Fe^{3+}$ + semithionine	$Rb_2[UO_2Cl_4] \rightarrow (Rb_2[U^{VII}O_2Cl_4])^+, (Rb_2[U^{VIII}O_2Cl_5])^+$	18,25
Cluster breakdown	$Ru_3(CO)_{12}/PPh_3/CO \rightarrow Ru(CO)_4PPh_3$	$[HSi_2W_{18}Zr_3O_{68}]^{7-} \rightarrow [H_7Si_2W_{14}O_{53}]^- + 4WO_3$	26,27
Cluster formation	$Re_2(CO)_{10}/H_2O \rightarrow [Re(CO)_3(OR)]_4$	$UO_2(NO_3)_2 \rightarrow (UO_2)_3^+, (UO_2)_2^+, (UO_2)O_5^+$, etc.	28,29

[a]gly = glycine, [b]glyc = glycerol, [c]PTSA = p-toluenesulphonic acid

TABLE 3

Masses and percentage relative abundances (normalised to base peak) in the complete negative FAB mass spectrum of $K_4[W(CN)_8]$. From ref. [16].

Ion (abundances)	Assignment	Ion (abundances)	Assignment
548(4)	$\{K_4[W(CN)_8\}^-$	432(3)	$\{K[W(CN)_8\}^-$
523(59)	$\{K_4[W(CN)_7\}^-$	407(13)	$\{K[W(CN)_7\}^-$
		379(38)	$\{K[W(CN)_6\}^-$
507(6)	$\{K_3[W(CN)_8\}^-$	355(65)	$\{K[W(CN)_5\}^-$
483(5)	$\{K_3[W(CN)_7\}^-$	327(37)	$\{K[W(CN)_4\}^-$
461(17)	$\{K_3[W(CN)_6\}^-$	302(35)	$\{K[W(CN)_3\}^-$
		276(46)	$\{K[W(CN)_2\}^-$
473(10)	$\{K_2[W(CN)_8\}^-$	250(25)	$\{K[W(CN)\}^-$
445(39)	$\{K_2[W(CN)_7\}^-$		
419(100)	$\{K_2[W(CN)_6\}^-$	393(33)	$\{[W(CN)_8\}^-$
		365(10)	$\{[W(CN)_7\}^-$
		341(19)	$\{[W(CN)_6\}^-$
		314(20)	$\{[W(CN)_5\}^-$
		288(49)	$\{[W(CN)_4\}^-$
		262(38)	$\{[W(CN)_3\}^-$
		236(7)	$\{[W(CN)_2\}^-$

TABLE 4

Species detected in positive FAB spectra of cyanometalate complexes featuring loss of a single ligand. From ref. [16].

$\{K_5[Fe(CN)_5]\}^+$	$\{K_4[Fe(CN)_5]\}^+$	$\{K_3[Fe(CN)_5]\}^+$
$\{K_4[Cr(CN)_5]\}^+$	$\{K_4[Cr(CN)_5]\}^+$	
$\{K_4[Ni(CN)_3]\}^+$	$\{K_3[Ni(CN)_3]\}^+$	
$\{K_5[Mo(CN)_7]\}^+$	$\{K_4[Mo(CN)_7]\}^+$	
$\{Na_5[W(CN)_7]\}^+$	$\{Na_4[W(CN)_7]\}^+$	$\{Na_3[W(CN)_7]\}^+$

C. PROCESSES IN FAB OF METAL COMPLEXES

(i) Simple dissociation of one ligand

The archetypal photochemical example of this process is the light-induced dissociation of CO from a metal carbonyl in a matrix to give a coordinately unsaturated species, [15], namely

$$M(CO)_n = M(CO)_{n-1} + CO \qquad (8)$$

as characterised by i.r. spectroscopy. This process is also achieved photochemically in the gas phase [30]. M refers to a considerable number of transition metals and the role of CO can be fulfilled by a variety of other ligands, e.g. PPh_3 and $CH_2{=}CH_2$. Metal carbonyls have been examined by electron-impact mass spectrometry [31] and found to undergo a sequence of ligand dissociations:

$$M(CO)_6^+ \rightarrow M(CO)_5^+ \rightarrow M(CO)_4^+ \rightarrow M(CO)_3^+ \rightarrow M(CO)_2^+ \rightarrow M(CO)^+ \rightarrow M^+ \qquad (9)$$

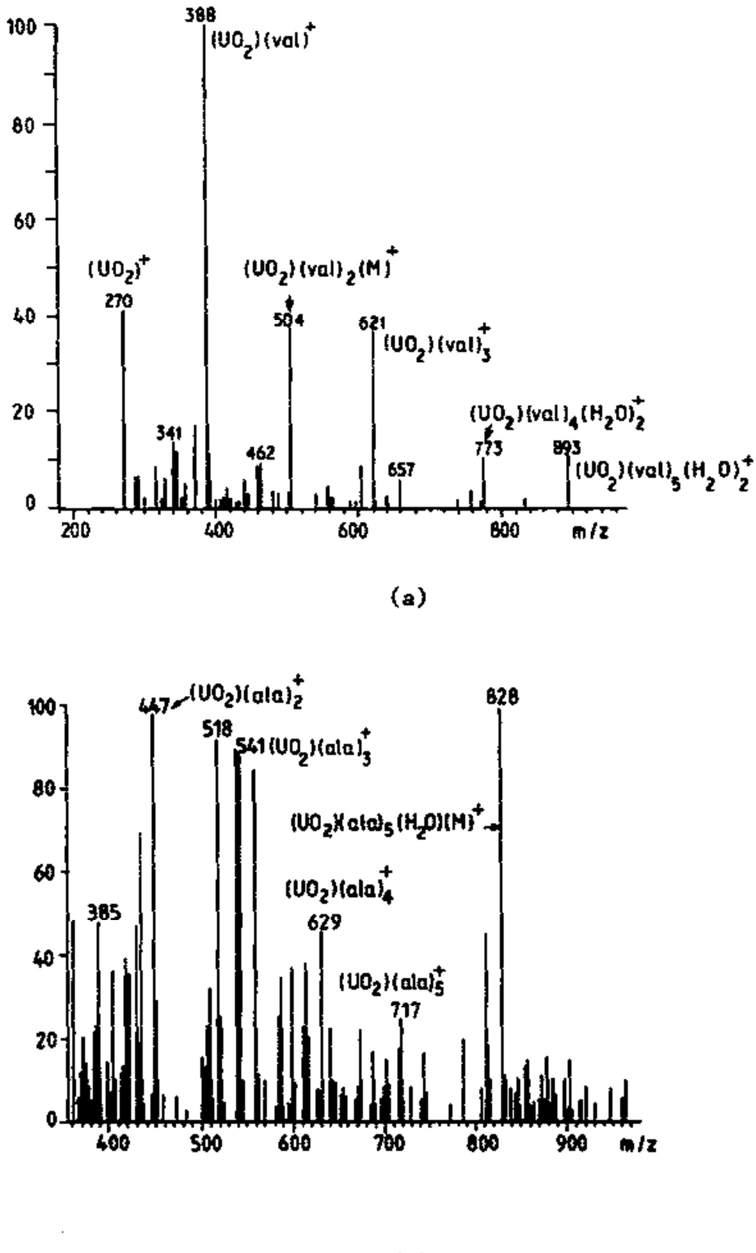
The most complete analogous sequence in FAB mass spectrometry refers to the cyanide complexes of Fe, W, Mo, Cr and Ni [16], especially as regards negative ions, thus $K_4[W(CN)_8]$ gave the mass peaks and assignments summarised in Table 3. These and related data indicate that the species presented in Table 4 are formed in the gas phase in the FAB experiment.

(ii) Multiple dissociation of ligand to yield low coordination number

This is well illustrated in Table 3 for $K_4[W(CN)_8]$, from which it can be seen that species with a very low coordination number are relatively abundant. The achievement of such low coordination numbers in the FAB experiment recalls the behaviour of metal carbonyls in matrices under prolonged photoirradiation [17] or in the gas phase under u.v. laser excitation [32]. The stepwise loss of the aminoacid valine (val) from the complex $[(UO_2)(val)_4(H_2O)_2](NO_3^-)_2$ is apparent from Fig. 3 [18]. All cyanometalates examined, both in positive and negative FAB, revealed stepwise loss of cyanide groups. CN^- as a ligand has similarities with CO, and stepwise loss of CO in electron impact experiments has been reported both for $[Cr(CO)_6]^+$ [31] and $[Cr(\eta^6\text{-}PhCH_3)(CO)_3]^+$ [33].

(iii) Ligand fragmentation

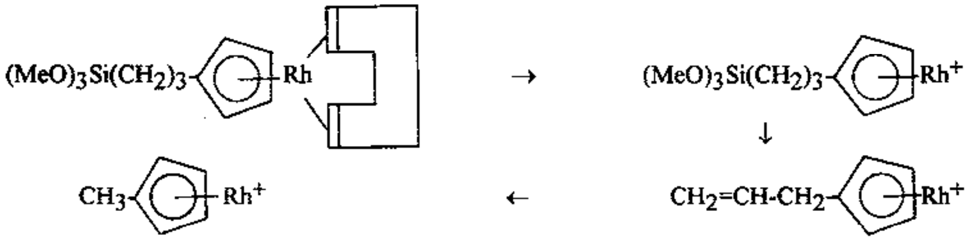
An early report by Barber et al. [34] pointed to a well-defined sequence:



(a)

(b)

Fig. 3 F.A.B. spectra of complexes of uranyl ion with (a) valine and (b) alanine. Matrix - glycerol.



Work in our laboratory [18] on FAB excitation of amino acid and peptide complexes of uranyl ion indicate fragmentation of the ligand to give the following sequence:

$$([UO_2][RCH(NH_3)^+CO_2^-]_n)^+$$

$$\downarrow$$

$$([UO_2][RCH(NH_3)^+CO_2^-]_{n-1}][CH(NH_3^+)CO_2^-])^+$$

$$\downarrow$$

$$([UO_2][RCH(NH_3^+)CO_2^-]_{n-1}[CO_2^-])^+$$

while L-glutamic acid and L-glutamine complexes of uranyl ion underwent ligand fragmentation as indicated below, as shown by the appearance of monopositive UO_2 ions coordinated to either one of the fragments indicated:

$$NH_3^+\text{-}CH(CO_2^-)\text{-}CH_2 \,\vert\, CH_2CO_2H$$

$$NH_3^+\text{-}CH(CO_2^-)\text{-}CH_2 \,\vert\, CH_2CO_2NH_2$$

(iv) Association of a ligand molecule

FAB excitation of glycerol solutions of aminoacid complexes of uranyl ion [18], exemplified by Fig. 3, induces ready expansion of the uranyl coordination sphere to accommodate one further ligand molecule, e.g.

$$[UO_2(ala)_4]^+ \rightarrow [UO_2(ala)_5]^+ \tag{10}$$

$$[UO_2(val)_4]^+ \rightarrow [UO_2(val)_5]^+ \tag{11}$$

Enhancement of coordination numbers in the mass spectra of coordination compounds is rare, and may be related to the exceptional ability of U^{VI} to achieve very high coordination [35].

(v) Association of a matrix molecule

Addition of one or more matrix molecules to a parent ion is not infrequent, thus $FeSO_4$ yields $[FeSO_4(glycH)]^+$ [13] and $[Iren_2Cl_2]ClO_4$ produces $\{[Iren_2Cl_2]glyc_n\}^+$ (n = 1,2) [36].

(vi) Ligand Solvolysis

Photosolvolysis is one of the best known photochemical processes of coordination compounds [1], and replacement of a ligand molecule by the matrix is also well-documented in FAB spectrometry (Table 5).

TABLE 5
Examples of ligand solvolysis

Substrate	Matrix	Ions Observed	Ref.
$[Ag(bipy)_2][ClO_4]$	glycerol	$[Ag(bipy)_n]^+$ (n = 1, 2) $[Ag(bipy)(glyc)]^+$, $[Ag(glyc)_n]^+$, (n = 1, 2)	22
$SnCl_4$	glycerol	$[SnCl_3(glyc)_2]^+$	37
$SbCl_3$	glycerol	$[SbCl_2(gly)_2]^+$	37

(vii) Ligand Exchange

Addition of p-toluenesulphonate acid (PTSA) to the glycerol matrix (glyc) results in the appearance of new sets of ions on FAB of thorium(IV) nitrate, including [13]

$[Th^{IV}(PTSA\text{-}H)(glyc\text{-}H)_2]^+$
$[Th^{IV}(PTSA\text{-}H)(glyc\text{-}H)_2G]^+$
$[Th^{IV}(PTSA\text{-}H)_2(glyc\text{-}H)]^+$
$[Th^{IV}(PTSA\text{-}H)(PTSA)(glyc\text{-}H)_2]^+$

(viii) Reduction of the metal centre

Studies of simple salts dissolved in glycerol media indicate that positive-ion FAB induces a one-electron reduction of the metal centre as shown in Table 6.

TABLE 6
One electron reduction processes in the positive FAB of simple inorganic species

Salt	Ions observed	Ref
$Cr(NO_3)_3$	$[Cr^{III}(G\text{-}2H)G]^+$, $[Cr^{II}(G\text{-}H)G]^+$, $[Cr^{III}(G\text{-}2H)]^+$	13
$CuCl_2$	$[Cu^{I}G_2]^+$, $[Cu^{II}(G\text{-}H)G]^+$, $[Cu^{I}G]^+$	13
$Fe_2(SO_4)_3$	$[Fe^{II}(G\text{-}H)G]^+$, $[Fe^{II}(G\text{-}H)]^+$	13
$Fe(acac)_3$	$[Fe^{II}(acac)G]^+$, $[Fe^{III}(acac)_2]^+$	13
$UO_2(NO_3)_2$	$[U^{V}O_2]^+$	29
$K_4[Fe^{II}(CN)_6]$	$\{K_4[Fe^{I}(CN)_4]\}^+$	16

G = glycerol

This conforms with the widely accepted view that FAB provides an essentially reducing environment, as indicated by the reduction of a number of organic species [38] during the FAB experiment. The species responsible for reduction have been variously attributed to electrons released by the photoionization process:

$$\text{Cs (10 keV)} + \text{solvent} \rightarrow \text{Cs (thermal)} + \text{solvent}^{+\cdot} + e^- \qquad (12)$$

to hydrogen atoms originating from the glycerol matrix [39] or by the *C*-centred glycerol radical produced on decomposition of the glycerol radical cation [40]. However, the evidence is that very low oxidation states of the metal centre can be achieved in the FAB of a number of cyanometalate complexes (Table 7), although it should be noted that the departure of each CN group as a neutral radical has the effect of reducing the oxidation state of the metal centre by one unit.

(ix) Cluster breakdown

Photochemical homolysis of metal-metal bonds in di- and tri-metal carbonyls is a well-established mode of behaviour [26,41,42]. An electron is promoted to a σ^* orbital of the M-M bond and it dissociates. The FAB of polynuclear metal carbonyls and triphenylphosphine and other complexes also features stepwise loss of mononuclear species [43], although this is not universally the case. The anion $[H_2Si_2W_8Nb_6O_{77}]^{6-}$ undergoes sequential loss of up to eight WO_3 fragments in negative FAB, but this tendency is much reduced in positive FAB [27]. The loss of WO_3 fragments from the anion is associated with entry of excess electrons into antibonding orbitals.

Cluster breakdown can also be induced by allowing a cluster ion to undergo impact with an inert gas in a collision cell to give a collision-induced decomposition spectrum. This process is illustrated in Fig. 6 in the next section for $[(LaO)_{10}O_5]^+$.

TABLE 7
Multi-electron reduction processes in the positive and negative FAB of cyanometalate complexes [16]

Substrate	FAB mode	Ion (m/z)	Assignment	Oxidation state of metal centre
$K_3[Cr(CN)_6]$	+	338	$\{K_4[Cr(CN)_5]\}^+$	+2
	+	311	$\{K_4[Cr(CN)_4]\}^+$	+1
	+	247	$\{K_3[Cr(CN)_3]\}^+$	+1
$K_4[Fe(CN)_6]$	+	380	$\{K_5[Fe(CN)_5]\}^+$	+1
	+	353	$\{K_5[Fe(CN)_4]\}^+$	0
	+	331	$\{K_5[Fe(CN)_3]\}^+$	-1
	+	303	$\{K_5[Fe(CN)_2]\}^+$	-2
	-	237	$\{K_2[Fe(CN)_4]\}^-$	+1
	-	212	$\{K_2[Fe(CN)_3]\}^-$	0
	-	187	$\{K_2[Fe(CN)_2]\}^-$	-1
	-	161	$\{K_2[Fe(CN)]\}^-$	-2
$K_4[W(CN)_8]$	+	496	$\{K_4[W(CN)_6]\}^+$	+3
	+	470	$\{K_4[W(CN)_5]\}^+$	+2
	+	444	$\{K_4[W(CN)_4]\}^+$	+1
	-	355	$\{K[W(CN)_5]\}^-$	+3
	-	327	$\{K[W(CN)_4]\}^-$	+2
	-	302	$\{K[W(CN)_3]\}^-$	+1
	-	276	$\{K[W(CN)_2]\}^-$	0
	-	250	$\{K[W(CN)]\}^-$	-1

(x) Cluster formation

The formation of metal clusters following photochemical irradiation is best-known for metals, e.g. the formation of finely divided platinum on the irradiation of hexachloroplatinate(IV) ion in solutions of alcohols [44]

$$[PtCl_6]^{2-} + RCH_2OH \xrightarrow{h\nu} Pt + RCHO + 6Cl^- + 2H^+ \tag{13}$$

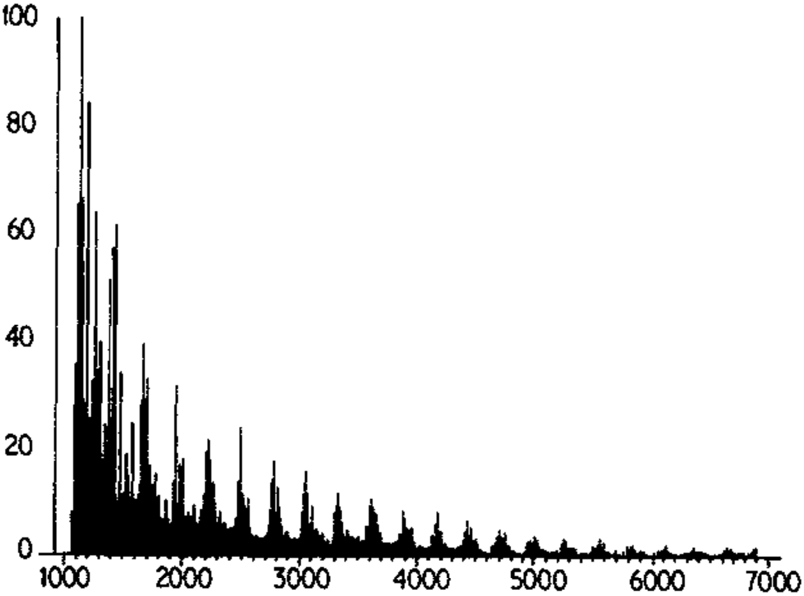


Fig. 4. FAB spectrum of uranyl nitrate (sulpholane matrix)

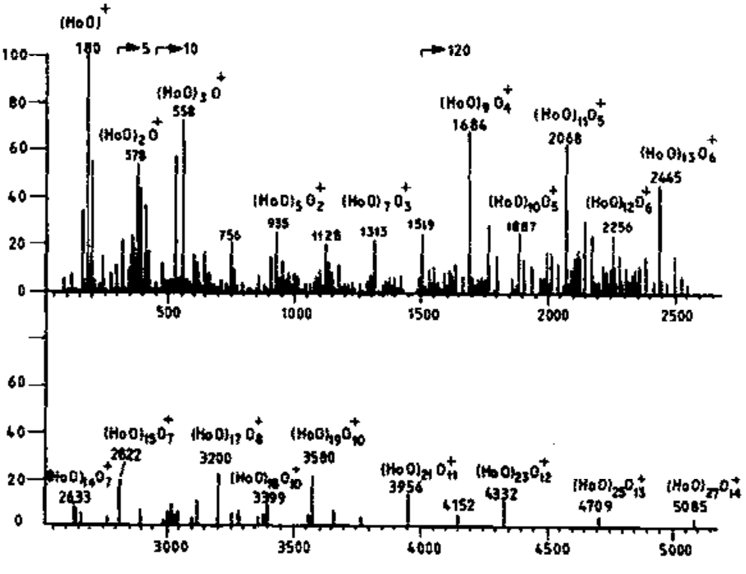


Fig. 5. FAB spectrum of glycerol solution of holmium nitrate

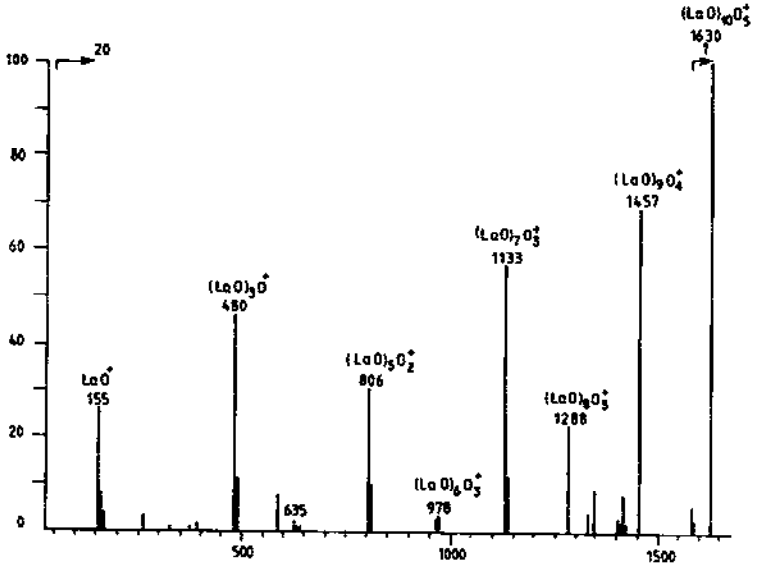


Fig. 6. Collision-induced decomposition spectrum of $(LaO)_{10}O_5^+$ cluster (collision gas - argon)

This proceeds presumably via aggregation of photogenerated single metal atoms.

The formation of small clusters of established structure is also known, e.g. the formation of $[Re(CO)_3(OH)_4$ on u.v. irradiation of $Re_3(CO)_{10}$ in water [28].

F.A.B. of metal salts is also known to be a series of large molecular clusters. Mass-spectral analogy is found in the precipitation of silver metal from a glycerol solution of silver acetate in a liquid SIMS experiment [45]. Thus Selbin and colleagues [46] showed salts of various lanthanides Ln to yield a series of oxolanthanide clusters up to $Ln_9O_{13}^+$ (for La, Ho, Y) and the collision-induced decomposition of yttrium oxide clusters to show strong odd-even effects attributed principally to the role of the formal oxidation state of Y [47].

Our laboratory [28] and also Brown [48] have reported salts of uranyl complexes to give clusters containing several U atoms and a variable number of oxygen atoms per U atom.

Recently, we have employed a four-sector tandem mass spectrometer to explore clusters of U and lanthanide oxides containing over 30 metal atoms (Fig. 4 and 5) and also the collision-induced decomposition of selected cluster species (Fig. 6) [18]. Evidently aggregation processes take place to give strong odd-even alternation effects in the peak intensities and in some instances there is strong evidence for the role of 'magic numbers' in determining cluster stoichiometry.

D CONCLUDING REMARKS

The clear exposition by Balzani and Carassiti [1] of the main photochemical pathways available to a metal complex on excitation have provided a valuable template on which it has been possible to make a systematisation of the wide variety of processes occurring in fast atom bombardment. As the F.A.B. techniques are refined to enable spectroscopic investigation of the many transient species present on the source, it should prove possible to delineate more precisely their modes of formation and the relationship between such species (and their mechanisms of formation) and those defined for analogous photochemical systems.

E ACKNOWLEDGEMENTS

I wish to acknowledge the sterling efforts by students and postdoctoral and visiting fellows over the years, especially D. Greatorex and R. J. Hill (e.s.r), B. Sieklucka (FAB of cyanometalates) and P. A. Read (FAB of uranium and lanthanide complexes). I acknowledge valuable discussion with Professors K. R. Jennings (Warwick) and D. A. Brown (University College, Dublin).

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