Plenary and Session Lectures

B1

Experimental Access to the Electronic Structure of Organo-f-element Complexes

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(To be published later as a full paper)

B2

Optical and Magnetic Properties of Uranium and Neptunium Borohydrides and Tetrakismethylborohydrides

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B3

Spectroscopy and Nonradiative Phenomena of Rare Earths in Glasses: Future Applications

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The radiative transition probabilities of rare earth ions in glasses can be calculated from the measured intensity parameters and calculated transition matrix elements using the Judd–Ofelt theory. The Judd–Ofelt parameters in oxide, fluoride and chalcogenide glasses were obtained for a variety of rare earth ions. These intensity parameters depend on the chemical bonding between the rare earths and the glass matrix and the viscosity of the medium. The nonradiative transition probabilities are calculated using a phenomenological theory, experimentally measured fluorescence lifetimes and quantum efficiencies. The nonradiative transition probabilities show an exponential dependence of the phonon energy of the network forming material. Experimental results according to this theory show that Er^{3+} has the highest quantum efficiency in fluoride glasses. Technological implementation of the above theory will be discussed for glass lasers, sources for fiber waveguides and luminescent solar concentrators.

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B4

Photoelectron Spectroscopy of f-Element Complexes

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Although the chemical bonding of actinide complexes is far from being well understood and, hence, there is a high demand of details of their electronic structure, only few theoretical and/or experimental approaches are capable to probe deep insight into such aspects.

Today almost all informations on the bonding have been generally drawn from reactivity data [1] !

In fact, sophisticated MO calculations are hardly practicable with 5f-element complexes because of the very large basis set required while responses of most usual spectroscopic techniques are very hard to be rationalized and/or provide informations only on crystal field aspects.

By contrrast, gas-phase UV photoelectron spectroscopy is a well established spectroscopic technique which provides:

1) the energy ordering of 'valence' MOs,

2) the possible contribution of metal AOs to various MOs by using compared He–I *vs.* He–II relative intensity variations (this specially applies to spectra of 5f-element complexes).

3) and, finally, an adequate reference to test results of theoretical calculations at any level.

This discussion will be mainly limited to investigations carried out at the Chemistry Department of University of Catania on several classes of complexes of f-elements.

Organometallic Complexes

The wider group of complexes which attracted attention were cyclopentadienyl complexes of Th(IV), U(IV), and, where possible, of Zr(IV) because of their high vapour pressure at reasonable temperatures. Furthermore, the very intriguing series of complexes which can be prepared by stepwise substitution of cp rings by monodentate or bidentate ligands (namely the $U(C_5H_5)_3X$ and $U(C_5H_5)_2X_2$ series) allow to detect variations of electronic structures depending upon electronic prerequisites of the ligand as well as upon geometries.

The series which have been object of study are:

Cyclooctatetraene Complexes [2]
$U(C_8H_8R)_2$ R = $-Si(CH_3)_3$,$-P(t\text{-}but)_2$.

Cyclopentadienyl Complexes
i) $M(C_5H_4R)_4$ M = U, Th; R = H, CH_3 [3].
ii) $M(C_5H_5)_3X$ M = U, Th; X = F, Cl, Br, $-CH_3$, $-OC_2H_5$, –NCS, BH_4^- [4].
iii) $M(C_5R_5)_2X_2$ M = U, Th, Zr; R = H, CH_3; X = $-NH_2$, Cl, $-CH_3$, BH_4^- [5, 6].
iv) $M(C_9H_7)_3X$ M = U, Th; X = Cl, Br, $-CH_3$, $-OCH_3$ [7].

All these complexes are of pseudo-tetrahedral geometry.

v) $M(C_5H_5)_2X_2$ M = U; X = carboxylate and dithiocarbammate [8] anions.

These latter complexes are of 'pseudo-octahedral' geometry.

The spectra always show clearly identifiable bands attributable to $5f^{-1}$ ionizations, to suitable symmetry combinations of e_1'' MOs of various cp rings of D_{5h} symmetry and, finally, to ionizations of electrons mainly localized on the –X ligand (when present). As far as $5f^{-1}$ ionizations are concerned, the associated IE's span a wide range and they mostly depend upon the nature of the ligand X. Nevertheless, simple electronegativity arguments do not allow a straightforward correlation. The possible effects due to extra-atomic relaxation terms are also discussed. Finally, the energy dispersion of ionziations of symmetry combinations of cp based MOs seem to be greatly dominated by effects due to interligand repulsion. Furthermore, the trend of intensity variations upon switching from He–I to He–II radiations provides information on the nature of the metal-to-ligand bonding.

Classical Coordination Complexes

In the case of classical coordination complexes, studies spanned series of d and f transition element complexes with an identical ligand array:

i) $M(acac)_4$ M = U, Th, Zr; acac = acetylacetonate anion [9, 10].
ii) $UO_2(acac)_2$ [9, 10].
iii) M(trop) M = U, Th, Zr; trop = tropolonate anion [11].

The most striking result of this comparison is that the spectra, hence many of the bonding characteristics, are so similar.

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B5

Excited-state Properties of Cyclopentadienylytterbium Complexes

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The excited-state properties of species derived from tris(η^5-cyclopentadienyl)ytterbium(III), Cp_3Yb, and from bis(η^5-pentamethylcyclopentadienyl)ytterbium(II), $(Me_5C_5)_2Yb$, have been investigated. Electronic spectra of several adducts of Cp_3Yb have been examined in benzene solution. When added to solutions of this Lewis acid, bases such as Et_3P, pyrrolidine (pl), THF, and tetrahydrothiophene (THT) cause substantial changes in the rich Cp_3Yb absorption spectrum. Titrations reveal that these changes are consistent with the formation of 1:1 adducts whose formation constants, log K_f, range from ~3.5 for THF and THT to ~5.0 for Et_3P and pl. The magnitude of K_f roughly correlates with the position of a visible absorption band previously assigned as a ligand-to-metal charge-transfer (LMCT) transition, and with the gas-phase basicities of the bases employed. Luminescence is observed in the near-IR (~1000–1100 nm), f–f spectral region from Cp_3Yb and its adducts upon excitation into their LMCT bands. Spectral changes accompanying base addition are consistent with 1:1 adduct formation with apparent excited-state adduct formation constants, log K^*_{app}, equal to the corresponding log K_f values within experimental error. The coinci-