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SPECTROSCOPIC STUDIES OF THE TRANSPLUTONIUM ELEMENTS*

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1. Introduction

The challenging opportunity to develop insights into both atomic structure and the effects of bonding in compounds makes the study of actinide spectroscopy a particularly fruitful and exciting area of scientific endeavor. It is also the interpretation of f-element spectra that has stimulated the development of the most sophisticated theoretical modeling attempted for any elements in the periodic table. The unique nature of the spectra and the wealth of fine detail revealed make possible sensitive tests of both physical models and the results of Hartree-Fock type ab initio calculations.

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In many respects there is a similarity between the spectra of the lanthanides and those of the actinides, but in the 5f-series, the f-electrons are less well shielded from potential interaction with ligands. There is consequently a discernable approach to the character of the d-transition elements in certain actinide compounds. Nevertheless, the essential f-element character of sharply-defined transition energies is retained, so that the interplay between the electrostatic and spin-orbit interaction of the non-bonding f-electrons, and the nature of the bonding and site symmetry can be explored in detail. In contrast to the atomic spectra of the lanthanides, the actinides exhibit an even more complex and scientifically challenging spectra because energy levels characteristic of many more electronic configurations occur at relatively low energies.

What then can be said about the unique character of heavy-actinide spectroscopy, which is the focus of the present discussion? How does it differ from that of the lighter members of the series, and what are the special properties that are manifest? What properties particularly recommend study of the heavier members of the series?

When one has available a large number of levels of a given configuration then these levels may be used as input to calculations that yield the model Slater (electrostatic) and spin-orbit interaction parameters for the configuration. If several configurations are known then interactions between configurations can be calculated. These data and calculations for the lighter actinides together with Hartree-Fock calculations are significantly increasing our insight into the structure of the atoms. The transplutonium elements provide a unique area to test atomic theory because the coupling of electrons is not pure and because relativistic effects are so important.

The distinct changes that occur in the character of actinide spectra in condensed phases as atomic number is increased are related to the increasing stabilization of lower-valence states. The higher multiple valence states that are characteristic of the light half of the series provide an as yet almost untapped and challenging area for theoretical interpretation. In contrast, the increased stability of lower oxidation states in the heavy members of the series provides an experimental basis for exploring the character of the electronic structure resulting from a quite different hierarchy of interactions. As a result the spectra of the light and heavy actinides provide complementary opportunities for theoretical analysis. The spectra of divalent compounds of Cf and Es are just beginning to be interpreted, but predictions regarding the nature of similar spectra for the lighter actinides where no experimental data exist can already be made based on the limited available information. These predictions confirm the potential importance of spectroscopic observations in the ongoing attempts to synthesize such compounds as PuCl_2 . Of course the position can also be taken that one of the very interesting aspects of heavy actinide chemistry lies in the challenge of stabilizing the elements in higher-valence states.

Spectroscopic studies that are part of attempts to synthesize compounds with unusual actinide-ion oxidation states provide potential high detection sensitivity and the basis for definitive valence state characterization. In this connection it is useful to point out that spectroscopic data have also been used as the sole basis of identifying valence states in some instances. In a recent series of innovative experiments, changes in the crystallographic structure and oxidation state of heavy actinide compounds (EsCl_3 , BkCl_3) induced by radioactive decay were sensitively monitored by spectroscopic techniques. This work showed that while the absence of long range order in a

crystalline environment precluded obtaining structural information from x-ray patterns, the shorter range order determined by the arrangement of nearest neighbor ions about the central actinide ion yielded spectra that could be uniquely interpreted.

2. The Role of Systematic Studies and the Relationship of Heavy-Actinide Spectroscopy to Ongoing Spectroscopic Investigations of the Lighter Members of the Series

The importance of a systematic theoretical analysis of the atomic spectra across a series of elements such as the actinides is well established. One result can be the essential insight provided into the special interpretive problems encountered for an individual element. The importance of the systematic approach is somewhat less clearly documented for the spectra of actinide compounds. Indeed, the only relatively well-established analysis of the latter type involves the trivalent series. However, even here the guidance provided by averaged theoretical-model parameter values can be clearly demonstrated. In part this is because the spectra of the trivalent actinides have been found to exhibit an increasingly lanthanide-type character with increasing atomic number. It is instructive to point out that it was more difficult to interpret the spectrum of $U^{3+}:\text{LaCl}_3$ than of $\text{Np}^{3+}:\text{LaCl}_3$ or $\text{Pu}^{3+}:\text{LaCl}_3$ and important insights into the nature of the appropriate physical model for the actinide series as a whole were gained in the analysis of $\text{Cm}^{3+}:\text{LaCl}_3$, BkCl_3 and CfCl_3 . In part our interest in heavy-actinide spectra also derives from special situations. For example, a great deal of interest continues to center on the chemistry of Pu^{4+} in neutral to basic solutions.

To the extent that any comparisons can be made on the basis of spectroscopic studies, Bk is the first heavier actinide after Pu to exhibit a stable 4+ oxidation state in neutral-to-basic solution.

The importance of systematic investigations of energy-level structure is also apparent as we attempt to extrapolate into uncharted, and perhaps experimentally unchartable, areas of heavy-element spectroscopy. Einsteinium is the last element in the periodic table that can be studied by conventional techniques. It is thus the springboard from which predictions of structure of yet heavier actinides will be launched. Its spectral properties and characteristics consequently take on a special significance as we model the spectra of Fm and No and examine the potential use of the highest-sensitivity techniques that might permit experimental detection of selected states.

One of the important applications of actinide spectroscopy has come in connection with the development of isotope-separation processes. Both in the case of uranium and plutonium, ongoing experimental and interpretive investigations of atomic spectra have been directly instrumental in the development of new concepts for separations that are progressing toward commercialization. Part of the longer-range research effort in heavy element spectroscopy is devoted to exploring the photophysics and photochemistry of PuF_6 based on the observation of isotope shifts in the vibronic structure which accompanies electronic transitions. The latter investigation takes advantage of the volatility of the higher fluorides of the light actinides. Analogous studies of the most volatile compounds available for lower valence states will also be of interest. While higher-valent, volatile heavy actinide compounds have not yet been prepared, they may exist. Certainly with 3+ and 4+ compounds analogous examination for isotope separation potential will be important over the whole series. While the present practical application lies

in the light end of the series, insights into mechanisms or the role of a particular variable may come from investigations involving the heavier actinides.

Similarly, the development of sensitive methods of detection of actinides in waste streams, in the environment, and as part of waste-management scenarios (primarily associated with the light actinides at present) is an area to which actinide spectroscopy is making very important contributions. The question of detection sensitivity is strongly dependent upon a knowledge of the details of the electronic energy levels.

3. Atomic (free-ion) Spectra

A. Summary of the Present Status of Spectroscopic Studies with the Transplutonium Elements.

While americium is the first transplutonium element, its production is not associated with the HFIR-TRU facility. Its early availability resulted in some work being done on its atomic spectra and the publication of a partial term analysis, Fred and Tomkins (1957). In large part, the previous statement regarding availability not associated with HFIR-TRU also applies to Cm. Much of the published spectroscopic data, both atomic and that involving compounds, was obtained using ^{244}Cm . The longer-lived ^{248}Cm isotope, a product of the TRU-facility, can be useful for spectroscopic studies in connection with isotope-shift determinations and where marginal phase or valence stability is expected to be a controlling factor. The status of the energy level analysis in Cm I was recently given by Worden and Conway (1976). The literature prior to ~1970 for all transuranium element atomic spectra was surveyed by Carnall (1971).

Atomic spectra data and the current status of the analysis in terms of levels and configurations is for the most part unpublished. The extensive nature of the line lists makes it difficult to find suitable avenues for publication, especially since there are revisions as new information is developed. Publications of transcurium atomic spectra data include: for Bk, Worden and Conway (1978); for Cf, Worden and Conway (1970); and for Es, Worden et al. (1970). Extensive experimental data, primarily for Es I, was obtained subsequently in a cooperative effort between groups at ANL, LBL, and LLL and is presently being analyzed.

B. Future Needs and Directions in Atomic Spectroscopy.

Free-ion spectroscopy of the actinides has provided the basis for present understanding of the electronic structure of that group of elements. The problem is complicated by the fact that there are electrons formally belonging to four different orbitals that can combine in various ways to produce a given configuration (5f,6d,7s,7p). Table I lists the pertinent configurations, most of which were derived from free-ion work. The results given in Table II indicate the present state of affairs with respect to the classification of the spectral lines in terms of levels. The best-studied and understood are uranium and plutonium; for einsteinium there are only a few hundred lines that have been measured and a mere tens of levels. A need for more work on americium, berkelium, californium and einsteinium is apparent in order to even begin to appreciate the unique challenges and insights that will develop in the study of these elements. It should be emphasized again that work on one spectrum is greatly aided by the results for others and that for maximum productivity there should be closely-correlated studies of many spectra by different research groups. Fourteen configurations have been identified in

the neutral spectrum of plutonium and nine configurations in the first ion. The requirements for the analysis are at the limits of present theoretical understanding and computational abilities and stimulate both new approaches and methods. Similar results could be obtained for other members of the series.

Experimentally, Fourier Transform Spectroscopy which has been developed in the last five to eight years, has made it possible to improve measurement accuracy by a factor of ten, and for the first time to obtain meaningful intensity information. Improved accuracy reduces the statistical errors in coincidence searches among wavelength lists that can typically contain 20,000 entries. There are now only two instruments in the world, one at Kitt Peak National Observatory and one at Orsay, France, capable of the required precision. In addition to the instrumental needs, there is also a great need for source development to produce the spectra. A source which produces a rich spectrum but uses one to ten micrograms of material and which lasts a very long time is needed. Practical sources must also produce the spectra of the higher ionization states using microgram size samples.

The atomic spectra of the higher ions, i.e. An^{2+} , An^{3+} , etc. have not been produced for the transplutonium elements; in fact only in the cases of thorium and uranium have experimental studies been reported. These ions are the species that occur in solids and solutions. Consequently, insights gained from analysis of such spectra are of particular interest to chemistry.

Studies of the hyperfine structure and isotope-shift of the spectral lines provide an insight as to the size and structure of the nucleus. Nuclear moments and spin are derived from such studies. It is possible to conceive of the day when laser isotopic separation methods will be used to prepare small samples for nuclear experiment targets as well as for other studies. Such

methods can enrich a given isotope or remove an isotope thus making the sample more suitable to the scientific purposes of the experimenter. The basic data comes from measurements of the isotope shift of spectra lines some of which have already been observed. Laser spectroscopy methods for achieving separation have already been perfected in programs relevant to uranium. If this separation equipment were properly configured it would be possible to measure the first and second ionization potentials of all the transplutonium elements.

Analytical chemists and astrophysicists are also users of wavelength data. There are a number of papers dealing with the spectrochemical analysis of americium and curium and in a few cases the other elements have also been analyzed both as an impurity in a sample or to determine the purity of the elemental sample. Astrophysicists have looked for the presence of the actinides in the sun and stars. There are certain types of stars which contain rare earths and a few of these stars have been looked at to see if actinides occur. The stellar line lists used contained spectral lines of the neutral and first ion whereas the stars usually have lines of the first and second ion, so without good data on the second ion not many firm conclusions may be drawn. Curium-247 because of its halflife ($\sim 10^7$ y) is a likely candidate to be found in stars.

4. The Spectra of Actinide Compounds

A. Summary of the Present Status of Spectroscopic Studies with Compounds of the Transplutonium Elements

Because of its long and widespread availability, a great deal of spectroscopic information relative to Am compounds is available. In much of this spectroscopy, there is a pronounced similarity to that of the light actinides U, Np, Pu. Only reference to divalent compound spectra will be made here. In contrast to the case for the lighter actinides, published data relative to the optical spectra of Cm and the heavier actinides is essentially limited to the lower oxidation states, as indicated below:

Valence States for which Characteristic Optical Absorption Spectra have been Reported

<u>Cm</u>	<u>Bk</u>	<u>Cf</u>	<u>Es</u>
4	4		
3	3	3	3
		2	2

While only tracer-scale studies with Fm have been carried out, the 3+ and 2+ valence states are well characterized. Available sensitive methods of detection make it highly probable that the energies of at least one or two of the excited states in the energy level schemes could be established for both the indicated valencies.

Absorption spectra for $\text{Am}^{2+}:\text{CaF}_2$ have been published by Edelstein et al. (1967) and for $\text{Es}^{2+}:\text{CaF}_2$ by Edelstein et al. (1970). Characteristics of the pure dihalide spectra of Cf and Es have been reported in a number of communications, for example see Haire and Young (1978).

Spectra of the trivalent state for each actinide from U^{3+} through Es^{3+} have been reported, and systematic theoretical analyses of the crystal-field states in D_{3h} -symmetry, while not complete, are well advanced, Hessler and Carnall (1980); more recent studies have addressed investigations of transition probabilities, Carnall et al. (1982), and the mechanisms of excited-state relaxation, Hessler et al. (1980).

While spectra characteristic of Cm(IV) both as solid CmF_4 and in solution in 15 M HF were measured some years ago, Keenan (1961), the solid state spectrum of BkF_4 , Ensor et al. (1981) has just recently been published. This extends the data previously limited to observations of Bk(IV) solution spectra in 0.4 M D_2SO_4 , Carnall et al. (1971). Absorption bands attributed to Am^{4+} stabilized in solutions of unsaturated heteropoly tungstates $\text{K}_7\text{PW}_{11}\text{O}_{39}$ or $\text{K}_{10}\text{P}_2\text{W}_{17}\text{O}_{61}$ have also been reported for Am^{4+} and Cm^{4+} , Saprykin et al. (1976), and for Cf^{4+} , (Kosyakov et al. (1977), but no clearly defined spectra of Cf^{4+} (or Es^{4+}) showing characteristic sharp f→f bands appear to be available. The only report involving Es^{4+} was made on the basis of thermochromatographic experiments. EsF_4 was postulated to have been formed in the gas phase, Boussieres et al. (1980).

Interesting reports of the stabilization of unusual oxidation states; Am(VII), Krot et al. (1974), and Cm(VI), Peretruchin et al. (1978), have been made.

B. Future Directions

One of the aspects of heavy-actinide spectroscopy that can be identified as having significant potential for rewarding future work is illustrated in Fig. 1. Although based on model calculations for both the $5f^N$, Carnall and Crosswhite (1982) and higher-lying configurations, Brewer (1971), the level energies shown in the figure indicate that experimental data on the energy level structure for a number of different configurations should be accessible in the optical range in divalent actinide spectra; however, based on work done to date, the most productive experiments will be those involving the heavy actinides. Since in comparison to similar spectra of the lanthanides, the An(II) excited configurations lie much lower in energy, characterization of the An(II) spectra should lead to valuable additions to our understanding of configuration interaction. There is a similar tabulation for Ln(II) in Dieke (1968).

Figure 1 also suggests that spectroscopic methods of detection should be suitable for establishing the existence of the elusive Bk(II) species. One of the interesting facets of recent work has been the inability to observe absorption bands characteristic of Bk^{2+} , even in the decay chain of $EsCl_2 \rightarrow (BkCl_x) \rightarrow CfCl_2$ where both the Es^{2+} and Cf^{2+} spectra were well characterized, Young et al. (1981). In well-characterized Am^{2+} , Cf^{2+} and Es^{2+} samples, the ability to detect fluorescence in the near-infrared range should make it possible to explore excited-state relaxation phenomena in a class of compounds that is unique, since available experimental evidence indicates that the crystal-field splitting of the free-ion manifolds is relatively small, comparable to that for Ln^{3+} .

The broad outlines of the energy level structure for An^{3+} appear to be well established. Consequently, we have the required basis for future work

devoted to exploring both the models for computing transition intensities as well as relaxation and energy transfer mechanisms. The latter type of study has exciting potential for new-frontier science. The degree of agreement attained in the comparison between experimental and model-computed intensities for the An^{3+} aquo ion, Carnall et al. (1982), was sufficient to encourage refinement of the model and to suggest that it would be appropriate to devote considerable effort to the next step in the analysis, namely the computation of oscillator strengths for the crystal-field components for An^{3+} and Ln^{3+} in appropriate matrices.

Attempts to observe fluorescence in the aqueous solution spectra of the actinides have only been successful for the heavy actinides where the energy gaps between the ground and first excited states are sufficiently large to permit fluorescence to compete with non-radiative modes of decay, Beitz et al. (1981). Since sensitive laser-based methods exist for determining the extent of non-radiative decay in such systems, both radiative and non-radiative relaxation can be monitored to probe the mechanisms involved.

The spectra of organometallic compounds of a number of An^{3+} ions are known, but this area of spectroscopy merits further exploitation. There are many opportunities here to examine and characterize the relative influences of structure and bonding on the spectra. The somewhat greater isolation of free-ion groups in the heavy members of the trivalent series provides added opportunity for developing the interpretation. The large organo-ligands are also of interest because they make it possible to insulate one actinide ion center from the influence of other neighboring actinide-ion centers and this in principle gives rise to narrow-band spectroscopic structure.

The spectra of quadrivalent Am, Cm, Bk, and Cf can play an important role in the development of a systematic interpretation of the spectra of An^{4+} if,

as seems to be the case, the observed absorption bands are relatively more isolated in energy and there is less overlap of different free-ion manifolds than for the light actinides. The theoretical treatment of An^{4+} spectra has long been a source of contradictory interpretations. Little progress has been made in the last 20 years toward a unified and consistent analysis of $An(IV)$ spectra compared to the successful and increasingly detailed analysis of An^{3+} spectra that has developed. The indicated heavier actinides may well contribute the type of experimental data that is necessary for progress in this area. Since the +4 compounds in question are all powerful oxidants, the conditions under which stable compounds can be prepared will be limited, and little if any opportunity to stabilize quadrivalent actinide organometallic compounds would be expected. Interest does focus on development of a detailed interpretation of the ligand- (or crystal-) field interaction which is at present poorly understood. Part of the long-term problem of interpretation lies in the lack of well-characterized spectroscopic data for which the quantum description of each state has been established by model independent methods such as spectroscopic polarization or Zeeman studies.

As indicated earlier, evidence for the existence of some heavier actinide compounds with oxidation number >4 has been presented. There is little doubt that under the proper stabilizing conditions, such compounds can be prepared and that their spectra would offer exciting insights into the type and nature of bonding involved. In such work it is clear that spectroscopy can provide evidence for the stabilization of a new valence state, in some cases the only reliable evidence if x-ray patterns are not clear; and can also provide evidence for changes in the symmetry of the actinide site where more than one phase can be stabilized.

Important chemical information concerning the heavier actinides can be derived from spectral studies in complexing solutions or molten salts, particularly when spectroelectrochemical techniques are employed. The monitoring of oxidation state changes as a function of applied potential can yield information on quantities characterizing the nature of the species formed: the oxidation states, stabilities and redox potentials. The spectroelectrochemical technique is particularly well suited to exploring the possible production of unusual valence states in the heavier actinides, Hobart et al. (1981).

Along a quite different line of spectroscopic research it should be noted that heavy-ion-induced x-ray fluorescence is a technique which may provide new insight into the valence states of actinide metals, particularly the transplutonium metals, and their alloys. The metallic valence state of the transplutonium metals has been a subject of debate over a number of years.

Another potential area for study would involve determining the variation in spectral properties of transplutonium compounds as a function of pressure. Examination of transplutonium metals under high-pressures using x-ray diffraction techniques suggests a discernable influence on the 5f electron orbitals. The effect of pressure on the optical spectra of transplutonium compounds is also a new area that has exciting possibilities for providing information about bonding and structure relationships.

Resonance ionization Spectroscopy (RIS) or Resonance Ionization Mass Spectrometry (RIMS) are two new laser ionization techniques that can be applied to the transplutonium elements to further our knowledge of these materials. One interesting application of RIMS would be in differentiating between Bk-249 and Cf-249 in vapor species/reaction mechanism studies, where the Cf-249 daughter signal cannot be differentiated from its parent by conventional mass spectroscopy.

Most of the spectroscopic investigations cited here involve application of more or less conventional spectroscopic techniques. However, the past decade has seen the development of (1) greatly-improved Fourier-Transform instrumentation, which improves the precision of atomic-spectra data by an order of magnitude; (2) laser spectroscopy, which not only is capable of higher precision for both vapor- and condensed-phase spectroscopic studies, but also introduces a broad range of new methods for analysis; (3) accelerator technology, which combined with laser techniques permits nuclear spin and moment studies of short-lived isotopes, and which should be particularly interesting for isotopes in the transplutonium region which are far from stability; and, of course (4) the great extensions that have been made in computer capabilities. It is clear that the extent to which advantage can be taken of these opportunities depends on the extent to which the laboratories developing these methods are also properly equipped to handle the whole complement of these highly-radioactive samples. There is therefore a special need for the national laboratories engaging in this critical research to be as well appointed as possible to conduct these experiments, which by their very nature require efficient and tightly-controlled timing. Production of large quantities of the heavier actinides will have no purpose unless both equipment and personnel are available to insure efficient and creative use.

5. Other Spectroscopies

Mössbauer--see The Actinides, Electronic Structure and Nuclear Properties. Freeman and Darby, Es. Vol. 1, Chapter 5, p. 237 (Academic Press, 1974). There are serious problems arising with the potential use of Mössbauer

spectroscopy in work with the heavier actinides. Line broadening can be expected to be a problem. It is doubtful if the Mössbauer technique would yield useful information even if suitable source - sample couples could be identified.

Neutron Spectroscopy--The ability to explore higher energy ranges--for example to $\sim 2000 \text{ cm}^{-1}$ in some cases of crystal-field split levels, makes the neutron a useful tool where photons cannot yield the desired information. The problem is sample size and type--single crystals are greatly to be desired.

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TABLE I.

Ground-State Configurations for the Actinides in Various Charge States.

		I	II	III	IV
Actinium	Ac	$6d7s^2$	$7s^2$	$7s$	
Thorium	Th	$6d^27s^2$	$6d7s^2$	$5f6d$	$5f$
Protactinium	Pa	$5f^26d7s^2$	$5f^27s^2$		
Uranium**	U	$5f^36d7s^2$	$5f^37s^2$		$5f^3*$
Neptunium	Np	$5f^46d7s^2$	$5f^46d7s$		$5f^4*$
Plutonium	Pu	$5f^6 7s^2$	$5f^67s$		$5f^5*$
Americium	Am	$5f^7 7s^2$	$5f^77s$	$5f^7*$	$5f^6*$
Curium	Cm	$5f^76d7s^2$	$5f^77s^2$		$5f^7*$
Berkelium	Bk	$5f^9 7s^2$	$5f^97s$		$5f^8*$
Californium	Cf	$5f^{10} 7s^2$	$5f^{10}7s$		$5f^9*$
Einsteinium	Es	$5f^{11} 7s^2$	$5f^{11}7s$	$5f^{11}*$	$5f^{10}*$
Fermium	Fm	$5f^{12} 7s^2$			

*From crystal work.

**U V $5f^2$ and U VI $5f$ free-ion analyses have also been completed.

TABLE II.

Status of the Number of Lines Measured and Levels Assigned
for the First and Second Spectra of the Actinides.

		<u>Number of Levels</u>					
		U	Np	Pu	Am	Cm	Bk
I	Even	1307	181	601	39	348	186
	Odd	405	284	585	12	335	166
II	Even	518	30	239	63	415	97
	Odd	178	46	743	5	441	38
#	Lines	100000	6000	20000	3000	13000	5000

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FIGURE 1

ESTIMATED RANGES OF ENERGY IN WHICH $f \rightarrow f$ TRANSITIONS IN An^{2+} IONS MAY BE OBSERVED

