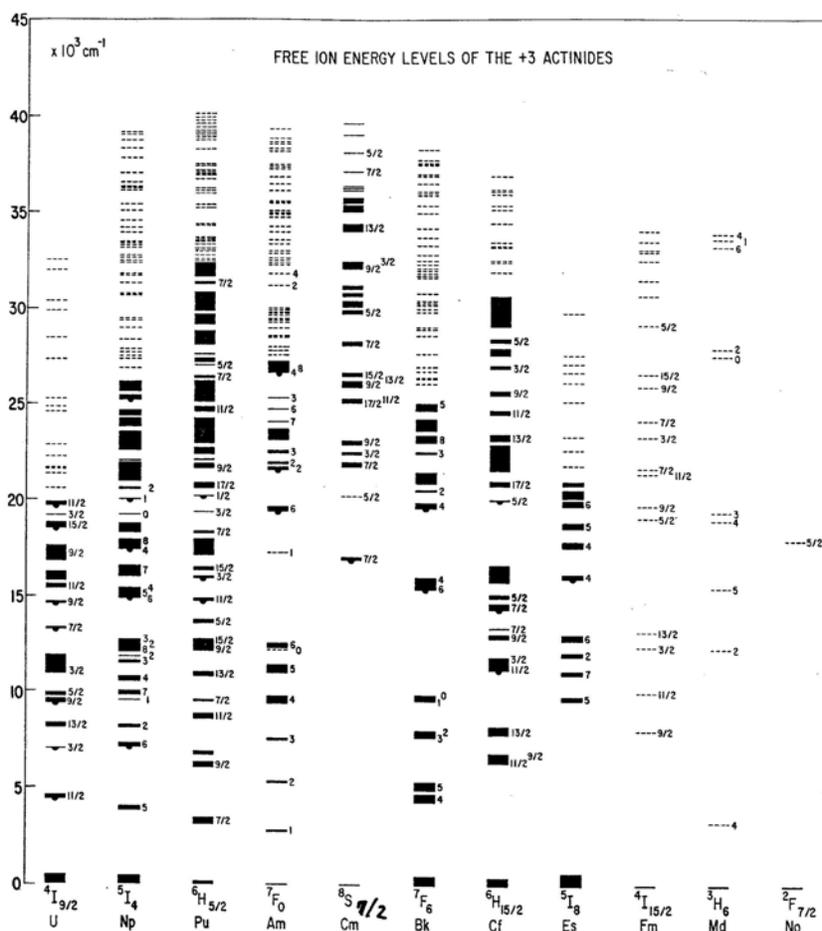


Free-ion Energy Level Structures for Trivalent Actinides



The above figure represents the terms of the lowest configuration of the trivalent actinide ions. The structure is due to the electrostatic repulsion between the f electrons of the ions and the coupling of their spin and orbital angular momentum. Calculations of the energies of the levels were performed by an approximate technique developed by K. Rajnak and B. G. Wybourne [1]. It includes, to second order, all the electrostatic interactions with configurations having two electrons excited from the ground configuration and effective three-body interactions to account for one-electron excitations. The actinide series of elements (Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, and Lr) has unique spectroscopic and chemical properties. The elements Ac, Th, Pa, U, ... Lr have electronic configurations denoted as $[Rn]6d^17s^2$, $[Rn]5f^16d^17s^2$, $[Rn]5f^26d^17s^2$, $[Rn]5f^36d^17s^2$, and $[Rn]5f^{14}6d^17s^2$, where [Rn] represents the electronic configuration of the closed shell radon atom with 86 electrons, the $6d^1$ denotes a single

electron with a principle quantum number, n , equal to 6 and an orbital angular momentum quantum number, ℓ , equal to 2, similarly $7s^2$ denotes two electrons with $n = 7$ and $\ell = 0$, and the notation $5f^1$, $5f^2$, $5f^3$, and $5f^{14}$ denotes 1, 2, 3, and 14 electrons with $n = 5$ and $\ell = 3$. Therefore, the actinide series is characterized by the sequential addition of electrons with a principle quantum number of 5 and an orbital angular momentum number of 3. The ions are produced by removing the 6d and and two 7s electrons from the atoms. Therefore, the electronic configuration of the trivalent uranium ion, U^{3+} is denoted $[Rn]5f^3$ and the trivalent curium ion, Cm^{3+} by $[Rn]5f^7$. The half circle below a level indicates that it fluoresces. The height of the solid black lines denotes the extent of the crystal or ligand field splitting of the terms.[2] Solid lines represent terms that have been identified by optical absorptive or fluorescent measurements and dashed lines indicate theoretical predictions. The X-axis denotes the sequence of trivalent actinide ions U^{3+} , Np^{3+} , Pu^{3+} , Am^{3+} , Cm^{3+} , Bk^{3+} , Cf^{3+} , Es^{3+} , Fm^{3+} , Md^{3+} , and No^{3+} . The notation just above the symbol for the element, for example $^4I_{9/2}$ above the U, denotes the approximate Russel-Saunders notation for the ground term, $(^{2S+1})L_J$. Therefore, for the trivalent uranium ion the ground term has a total orbital angular momentum, L , of 6, a total spin, S , of 3/2, and the total angular momentum, $|\vec{J}| = |\vec{L} + \vec{S}|$, is 9/2. Similarly, for Cm^{3+} , which has seven electrons beyond the closed radon shell, the lowest energy term $^8S_{7/2}$ denotes a spin of 7/2, an orbital angular momentum of 0, and a total angular momentum of 7/2. One of the complexities of the actinide ions stems from the fact that the Russel-Saunders coupling scheme[3] is not appropriate for all terms of the free-ion configurations. Therefore, the terms above the lowest term are only denoted by their total angular momentum, J . These values are given to the right of the solid lines. The actinides on the far right of the figure have short half lives. For example, the most abundant isotope of einsteinium, ^{253}Es , has a half life of only 20 days and the longest lived isotope, ^{252}Es , a half life of 471 days. It is the heaviest element that can be studied by conventional spectroscopic techniques. Therefore, the spectroscopy of the trivalent ions of the elements fermium, mendelevium, and nobelium have not been measured. The energies of the terms of the free-ions have been calculated by extrapolating parameters for the series and are shown as the dashed lines in the figure. The Y-axis represents energy. Expressing energy in the unit cm^{-1} , which is also called the wave number, is an old spectroscopic tradition (e.g. it was used by Johannes Rydberg in the 1880s). The fundamental relationship is $\Delta E = hc/\lambda$ where the energy difference between the initial and final level is ΔE , Plank's constant is h , the velocity of light in vacuum is c , and the wavelength of the light observed in the transition is λ . However, in this system of units $h = c = 1$ and energy is written $\Delta E = 1/\lambda$ where the wavelength is expressed in cm. Physically, it is the number of cycles per unit distance. For example, green light with a wavelength of 500 nm has an energy given by $(1/500 \text{ nm}) \times (10^7 \text{ nm}\cdot\text{cm}^{-1})$ or $20,000 \text{ cm}^{-1}$.

A Story Behind the Figure

Why did Katheryn Rajnak (B. A. Kalamazoo College, 1959, and Ph.D. University of California at Berkeley, 1963) have this figure in her office at the Physics Department of Kalamazoo College? Briefly, it represents Kathy's contribution to our understanding of the electronic structure of the f-elements, in particular, the actinides. The first part of the story began in 1898 when Marie Curie and Gerhard Schmidt showed that thorium ($Z=90$) was radioactive. The next year Andre Debienne extracted actinium ($Z=89$) from the uranium ore pitchblende, U_3O_8 . The element uranium ($Z=92$), the most abundant of the actinide elements, was used to add yellow color to ceramic glazes as early as 78 CE. The German chemist Martin Heinrich Klaproth is credited with discovering it in 1789. In 1917/1918 Otto Hahn and Lisa Meitner of Germany and Frederick Soddy and John Cranston of Great Britain independently discovered the long half-life 241 isotope of protactinium ($Z=91$). Perhaps the most significant event occurred in 1938/39 when Otto Hahn and Fritz Strassmann, at the Kaiser Wilhelm-Institut fuer Chemie in Berlin-Dahlem, discovered that one of the decay products of uranium was the light atom barium.[4][5] Lisa Meitner, who had fled Germany and was working at the Physical Institute of the Academy of Sciences in Stockholm, and her nephew, Otto R. Frish, who was at the Institute of Theoretical Physics in Copenhagen, used Bohr's "droplet" model of the nucleus and concluded that nuclear fission had been observed.[6] Shortly thereafter, the group at Berkeley, under the direction of Glen T. Seaborg, discovered the elements neptunium ($Z=93$) and plutonium ($Z=94$) by bombarding uranium atoms with high-energy alpha particles from the 60" cyclotron. These elements were created by the process of fusion. The discovery of the elements americium ($Z=95$) and curium ($Z=96$) was announced, shortly after the conclusion of World War II, in 1944. In both cases, the new elements resulted from bombarding plutonium with alpha particles. The same technique was used in 1949 to produce berkelium ($Z=97$) and in 1950 californium ($Z=98$). A study of the debris from the first hydrogen bomb in 1952 allowed scientists to identify the elements einsteinium ($Z=99$) and fermium ($Z=100$). In 1955 the bombardment of einsteinium with alpha particles produced mendelevium ($Z=101$). The discovery of nobelium ($Z=102$) was a contested issue that was, finally, resolved in 1966 when credit was given to scientists at the Joint Institute for Nuclear Research in Dubna in the former Soviet Union for a process that involved the fusion of uranium and neon to produce nobelium. The discovery of the final element, lawrencium ($Z=103$), not shown in the figure, was the most contentious. In 1961 a nuclear physics team at the Lawrence Radiation Laboratory at Berkeley bombarded californium with boron and in 1965 a similar team at Dubna bombarded americium with oxygen. Both claimed to have discovered element 103 and pointed out discrepancies in the other's work. Further experiments were performed in 1969 and 1970. Finally, in 1971 all previous results were confirmed and in 1976 and 1977 the energies of the X-ray emitted from ^{258}Lr were measured. The issue was finally laid to rest in 1997 when both groups were given credit for the discovery.

The second part of the story begins in 1953 when Gerhard H. Dieke (Johns Hopkins University), following a suggestion by Clyde A. Hutchinson, Jr. (University of Chicago), introduced trace amounts (0.2 to 2.0%) of the rare earth elements into the host lanthanum trichloride. Dieke and his students found, to their surprise, that the transitions were narrow and that some levels fluoresced.[7] This discovery led to intense interest in the optical properties of the trivalent rare earth ions and, ultimately, to the development of the Nd:YAG laser. The first publication of a similar figure for the rare earth ions appeared in the book *Spectra and Energy Levels of Rare Earth Ions in Crystals*. [8] In 1958, the U. S. Atomic Energy Commission decided to build a reactor specifically designed to produce significant quantities of the transuranium elements. Subsequently, in 1965, the High Flux Isotope Reactor at Oak Ridge National Laboratory was commissioned. Because all of these isotopes are radioactive, they can only be studied at laboratories specifically designed to safely handle radioactive materials such as the Lawrence Radiation Laboratory at Berkeley and the Chemistry Division at Argonne National Laboratory. In addition, the Atomic Spectroscopy group at Argonne, Mark Fred and Frank S. Tomkins ("K" class of 1937 and Ph.D. Michigan State University, 1942), had completed construction of a 9.15 m Paschen-Runge spectrograph that could be used to obtain high-resolution optical spectra from the ultraviolet (300 nm) to the infrared (1000 nm) in less than an hour. It was specifically designed to study the atomic spectroscopy of the actinide elements. Also, at this time, the leader of the heavy element research group, Paul R. Fields, in addition to studying the important separation process needed to isolate the heavy elements, decided, along with his protege, William T. Carnall, to study the optical properties of the actinide elements in solution. Having been trained as experimental chemists, they had little experience in theoretical physics. Therefore, they collaborated with Brian G. Wybourne and Kathy Rajnak and often interacted with Brian R. Judd (Johns Hopkins University).

Wybourne had completed his thesis in 1960 and did postdoctoral work first at Johns Hopkins University with Dieke and then at Argonne with Fields. In 1966 he returned to the University of Canterbury in New Zealand to become a professor of physics. While at Argonne, he wrote the book *Spectroscopic Properties of Rare Earths*, which was published in 1965 by John Wiley & Sons, Inc. After graduating from Kalamazoo College, Kathy went to the University of California at Berkeley to obtain a Ph.D. in chemistry. While a graduate student she published a paper on the excited eigenfunctions of the rare-earth ions that, for the first time, included the interaction between configurations.[9] This was followed, the next year, by the seminal paper on configuration interactions[1] that formed the foundation for parametric calculations of electronic energy levels and guided the search for new levels until computers became large and fast enough to couple the Slater-Rach method with Hartree-Fock evaluations of the radial integrals.[10] The importance of configuration interactions on crystal field theory was pointed out in a paper published in 1964[2] and applied to the energy levels of Nd^{3+} and Er^{3+} in 1965[11]. At about this time, she moved from Berkeley to her home town of Kalamazoo, Michigan, where she served

as an adjunct professor of physics at Kalamazoo College until her retirement in 1997. During her time in Kalamazoo she continued to consult with the scientists at Johns Hopkins, Argonne, Berkeley, and *Laboratoire Aime Cotton, Centre National de la Recherche Scientific* in France. She published over one hundred papers in peer-reviewed journals. Some of her more notable publications include the 1971 article with J. C. Morrison[12] that reported *ab initio* calculations of the phenomenological parameters[1] introduced in 1963. With Mark Fred she included the relativistic correction to improve predictions of the isotope shifts for Cm, Am, Pu, and U configurations.[13] A series of four papers was published in 1968 that reported calculations of the electronic energy levels in the trivalent lanthanide aquo ions.[14] The spectral intensities of the optical transitions were reported in a series of two papers.[15][16] Finally, her work on electronic structure culminated in 1989 with the publication of the article titled “A Systematic Analysis of the Spectra of the Lanthanides Doped into Single-Crystals LaF_3 ”.[17] The significance of this article is demonstrated by the fact that in the twenty-five years since its publication it has been referred to in over 630 peer-reviewed publications.

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