UCRL-11401

University of California

Ernest O. Lawrence Radiation Laboratory

A MISSING BAND IN THE SPECTRUM OF THE TRIPOSITIVE AMERICIUM ION

Berkeley, California

Rept. submitted for pub. as note
in the Journal of Chemical Phys.

UCRL-11401

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

A MISSING BAND IN THE SPECTRUM OF THE TRIPOSITIVE AMERICIUM ION

John G. Conway and B. R. Judd

April, 1964

A MISSING BAND IN THE SPECTRUM OF THE TRIPOSITIVE AMERICIUM ION*

John G. Conway
Lawrence Radiation Laboratory, Berkeley, California

and

B. R. Judd
Laboratoires de Bellevue, Bellevue, Seine-et-Oise, France

April 1964

In a recent article, a comparison has been made between the theoretical and experimental levels of the ion Am^{3+} substituted for La^{3+} in $LaCl_3$.[1] Good agreement is obtained for all the levels of the ground multiplet, ^7F, and for three higher levels for which $J = 2$ (twice) and $J = 6$. There is, however, no experimental evidence for the transition $^7F_0 \longleftrightarrow {}^5D_1$, which should lie at 17500 cm^{-1}. The absence of this expected band forms the subject of this note.

There are two alternative explanations. Either the calculation is inadequate, and there is in fact no level in the vicinity of 17500 cm^{-1} above $^7F_0$; or else the transition probability for $^7F_0 \longleftrightarrow {}^5D_1$ is exceptionally small. The good agreement between experiment and theory that has been obtained[2] for Pu^{3+} and Cm^{3+}, the ions immediately lighter and heavier than Am^{3+}, suggests that the second alternative should be taken seriously. Now, an electric-dipole transition between $^7F_0$ and $^5D_1$ is expected to be much weaker than the average transition within the 5f shell, because, independent of the extent of the breakdown of Russell-Saunders coupling, no tensors of even rank can have matrix elements between levels for which $J = 0$ and $J = 1$.[3] Indeed, for the lanthanide analog, namely Eu^{3+}, the transition $^7F_0 \rightarrow {}^5D_1$ has been observed to be almost entirely magnetic-dipole in character.[4] The much larger deviations from Russell-Saunders coupling for ions of the actinide series indicate that magnetic-dipole transitions should be no less intense in these cases. However, a detailed calculation reveals a remarkable fact: The reduced matrix element of the magnetic-dipole operator $L + 2S$ between states corresponding to $^7F_0$ and $^5D_1$ comprises positive and negative parts that almost exactly cancel. This is strongly brought out if we make a comparison with the reduced matrix element between $^7F_1$ and $^5D_0$, which has a typical value:

$$([^7F_0]\|L + 2S\|[^5D_1])/([^7F_1]\|L + 2S\|[^5D_0]) = 0.023 \quad .$$

Brackets denote the use of the correct states, calculated in intermediate coupling with the aid of the programme of Koster and Nielson for the configuration f^6.[5] Thus magnetic-dipole transitions between $^7F_0$ and $^5D_1$ will be depressed, apparently accidentally, by a factor of the order of $(0.023)^2$, or roughly 10^{-3}, below an intensity that we would otherwise anticipate. We feel that this is the reason for the absence of the band at 17500 cm^{-1}. But even if $^5D_1$ does not lie close to its predicted position, the above demonstration of the anomalously weak magnetic-dipole character of the transition $^7F_0 \leftrightarrow {}^5D_1$ will remain valid.

We wish to thank Dr. Chr. Klixbüll Jørgensen for several stimulating discussions.

FOOTNOTES AND REFERENCES

*Work done under the auspices of the U. S. Atomic Energy Commission and Centre National de la Recherche Scientifique.

1. J. G. Conway, J. Chem. Phys. 40, , (1964).
2. H. Lämmermann and J. G. Conway, J. Chem. Phys. 38, 259 (1963); B. G. Wybourne, J. Chem. Phys. 40, 1456, (1964).
3. G. S. Ofelt, J. Chem. Phys. 37, 511 (1962); B. R. Judd, Phys. Rev. 127, 750 (1962).
4. K. H. Hellwege and H. G. Kahle, Z. Physik 129, 62 and 85 (1951); E. V. Sayre and S. Reeed, J. Chem. Phys. 24, 1213 (1956).
5. G. F. Koster and C. W. Nielson, Energy Matrices for All Configurations of Equivalent f Electrons (Magnetic Tape), Massachusetts Institute of Technology, Cambridge, Mass.