

**Lever A B P.** The electronic spectra of tetragonal metal complexes: analysis and significance. *Coord. Chem. Rev.* 3:119-40, 1968.

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This article presents the matrices for solving the high-spin electronic spectra of tetragonal  $d^n$  complexes within the crystal field, in the McClure Model, and in the Orbital Angular Overlap Model. It also demonstrates that a zero-order analysis omitting configurational interaction is generally grossly inadequate. [The SCT® indicates that this paper has been cited in over 245 publications.]

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In the early 1960s, inorganic coordination chemistry was growing rapidly, while, at the same time, scanning UV/VIS (ultraviolet/visible) spectrometers (as distinct from manual point-by-point spectrographs) were becoming more widely available. Inorganic chemists were reporting (crystal field)  $Dq$  and (Racah)  $B$  values for a myriad of octahedral ( $x=y=z$ ) and pseudo-octahedral coordination complexes.

However, many tetragonal ( $x=y \neq z$ ) complexes were also being prepared, and obviously there was interest in reporting and analysing their spectra. In this lower symmetry, additional splitting of the absorption peaks was observed. Some workers averaged these data and treated the species as octahedral. Many others used a very simple zero-order treatment that was easy to calculate but neglected configurational interaction between states of the same symmetry. In this way, one readily obtained values for the equatorial and axial crystal field strengths ( $Dq_{eq}$  and  $Dq_{ax}$ , respectively). By deriving such field strengths along different axes, it was hoped to understand how the bonding differed along different directions in these species. Electronic spectroscopy

appeared to offer a facile procedure for obtaining such information.

I was also interested in preparing tetragonal complexes and obtaining high-quality spectroscopic data, where possible at cryogenic temperatures. I used a more detailed and, necessarily, more complex analysis, which included configurational interaction. This involved (for example) for  $F$  and  $P$  terms, the solution of  $3 \times 3$  secular determinants. Today, such a calculation would be deemed trivial, but 20 years ago, many chemists showed some reticence in getting so mathematically involved.

It was evident through comparison of the resulting crystal field parameters that use of the zero-order analysis was grossly inadequate and that, despite the added complexity, a full treatment with configurational interaction was not just desirable but essential.

In 1967 I was honoured to present a plenary lecture to the International Symposium on the Synthetic and Stereochemical Aspects of the Chemistry of Coordination Compounds held at Nara, Japan, following the Xth International Conference on Coordination Chemistry. This provided an opportunity to write what was one of the first review articles to deal with the electronic spectra of low symmetry, especially tetragonal, complexes.

I considered the spectra arising from tetragonal complexes of all the  $d^n$  configurations, reviewing all the available high-quality data. These were analysed with inclusion of configurational interaction and the results compared, for specific cases, with the zero-order analysis. It was evident in this presentation that a zero-order analysis was inappropriate.

The review article provided the relevant equations for dealing with tetragonal  $d^n$  species in the crystal field, in the older McClure LCAO model approach,<sup>1</sup> and in the then newly introduced (by Schäffer and Jørgensen<sup>2</sup>) Orbital Angular Overlap Model.

Providing this body of information in one place evidently proved of considerable value to those who studied the spectra of tetragonal complexes. It is gratifying that this review article has played such an important role in developing the use of electronic spectroscopy in coordination chemistry.<sup>3-5</sup>

1. McClure D S. Energy level splittings in non-cubic ions, and the two-dimensional spectrochemical series. (Kirschner S, ed.) *Advances in the chemistry of the coordination compounds*. New York: Macmillan, 1961. p. 498-508.
2. Schäffer C E & Jørgensen C K. The angular overlap model, an attempt to revive the ligand field approaches. *Mol. Phys.* 9:401-12, 1965. (Cited 205 times.)
3. Lever A B P. Analytical treatment of the electronic spectra of some low-symmetry transition metal complexes. *Coord. Chem. Rev.* 43:63-85, 1982.
4. ———. *Inorganic electronic spectroscopy*. Amsterdam: Elsevier, 1968. 420 p. (Cited 975 times.)
5. ———. *Inorganic electronic spectroscopy*. Amsterdam: Elsevier, 1984. 862 p.