

Tanabe Y & Sugano S. On the absorption spectra of complex ions. I and II.
J. Phys. Soc. Jpn. 9:753-66; 766-79, 1954.
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Tokyo, Japan]

The first paper calculates energy matrices for 3d electrons in the octahedral complex ions, while the second attempts interpretation of the observed absorption spectra of these ions using the energy diagrams obtained by diagonalizing the matrices. [The SC1⁹ indicates that these papers have been cited over 1,745 times in 1,305 publications.]

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In the fall of 1951, S. Sugano and I read Racah's famous papers¹ on atomic spectra in a series of seminars for undergraduates held by M. Kotani in the Physics Department of Tokyo University. We were then given a problem to tackle as a related subject: calculating the multiplet-term energies of a d^4 system in a cubic field in the strong field scheme. This was because Kotani had long been interested in the electronic structures of the transition metal complexes through his celebrated work² on the paramagnetism of these ions.

Naturally, we were strongly impressed by Racah's work and therefore attempted to adapt his group theoretical technique to the case of the octahedral group. It took some time before we finished the calculation for d^4 because we had to redo the calculation for d^2 and d^3 by our method. By then, I had entered the graduate course and Sugano had obtained a post at the Institute of Broadcasting, NHK. At this

stage, we were mainly interested in obtaining the energy matrices for these systems, not in comparing directly the theoretical results with the observed spectra. I soon got involved in another problem and Sugano had his own subject at his institute, so that the problem was left behind intact for some time.

Our interest in the spectra of complex ions was revived by a stimulating book³ by R. Tsuchida of Osaka University on the color of complex salts. The book was full of the vivid imagination and ideas of a gifted chemist. We also had occasion to learn much from another chemist, Y. Kondo of the Tokyo Institute of Technology, who enlightened us on the experimental data. Then came Stevens's 1953 paper⁴ on the effect of covalent bonding in paramagnetic salts. With renewed interest, we started to calculate the energy matrices for the d^5 system. I remember my visits in the evening to Sugano's boarding house in the suburbs of Tokyo to check our results together after his work at the institute. We then went on to the intensity considerations for the d-d transitions and to the drawing of the energy diagrams using the eigenvalues obtained by the desk machines.

The energy diagrams turned out to be convenient in making assignments of the observed bands and lines of transition metal ions in a variety of environments, i.e., in solutions as well as in crystals, one of the reasons our paper has been so frequently cited. The most important reason, however, is probably its timeliness. The period 1955-1965 was the golden age in the development of the spectroscopic studies of the transition metal ions culminating in the realization of the ruby laser in 1960.

More recent work related to our 1954 paper can be found in reference 5.

1. Racah G. Theory of complex spectra. III. *Phys. Rev.* 63:367-82, 1943. (Cited 625 times since 1955.)
2. Kotani M. On the magnetic moment of complex ions. *J. Phys. Soc. Jpn.* 4:293-7, 1949. (Cited 155 times since 1955.)
3. Tsuchida R. *Kinzoku kagobutsu no iro to kōzō* (The structure and color of complex salts). Osaka: Zoshindo, 1944. 220 p. (Cited 40 times since 1955.)
4. Stevens K W H. On the magnetic properties of covalent XY_6 complexes. *Proc. Roy. Soc. London Ser. A* 219:542-55, 1953. (Cited 340 times since 1955.)
5. Lever A B P. *Inorganic electron spectroscopy*. Amsterdam: Elsevier, 1984. 863 p.