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Theory of Spin Triplet Ground States in d^6 Transition Metal Compounds and the Effect of High-Energy States on the Nature of the Ground State

E. König and R. Schnakig

Institut für Physikalische Chemie II, Universität Erlangen-Nürnberg, D-8520 Erlangen, Germany

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The formation of spin triplet, quintet, and singlet ground states within the $3d^6$ electron configuration is investigated in D_{4h} and D_{3d} symmetries employing irreducible tensor operator methods. Significant differences in the possible ground states are encountered between a complete CI and spin-orbit interaction treatment and an approximate calculation within the cubic ${}^5T_2$, ${}^1A_1$, ${}^3T_1$, and ${}^3T_2$ parents.

Key words: d^6 configuration – Ligand Field Theory

The stabilization of spin triplet ground states in compounds of the electronic configuration d^6 has been a matter of considerable interest and of some speculation in recent years. On the basis of experimental investigations, $S=1$ ground states are definitely established in the planar iron(II) phthalocyanine [1], in certain distorted octahedral bis(diimine) iron(II) complexes, a representative example being $\mathrm{Fe(phen)_2ox \cdot 5\,H_2O}$ [2–4], and in the planar bis(biuretato) cobalt(III) complexes [5, 6]. Triplet ground states are likewise formed on reduction from iron(III) to iron(II) under high pressure in biological compounds like hemin, hematin, and imidazole protohemichrome [7]. Finally, the apparent function of a triplet state in the biologically essential oxygenation of hemoglobin should not be overlooked [8].

At the beginning, the results of physical measurements (e.g. the effective magnetic moments) have not been understood, since, within the parent octahedral symmetry, only ${}^5T_{2g}(t_{2g}^4e_g^2)$ and ${}^1A_{1g}(t_{2g}^6)$ ground states are formed. Under the same conditions, the lowest triplet state ${}^3T_{1g}(t_{2g}^5e_g)$ is at least $5000\,\mathrm{cm}^{-1}$ higher in energy [9]. However, if tetragonal (D_{4h}) or trigonal (D_{3d}) symmetry is assumed, ligand field calculations based on a limited set of basis functions demonstrate that spin triplet states as well as various spin-mixed states may be stabilized in addition [10]. Recently, completely computerized methods have been developed which use the irreducible tensor operators of Racah in several different coupling schemes [11]. These methods may be applied in a straightforward way to any incompletely filled p^n, d^n or f^n configuration and to any symmetry. On the basis of this method, complete configuration interaction calculations were performed within the d^6 configuration in D_{4h} and D_{3d} symmetries both without and with spin-orbit coupling included. A subsequent search program determined the boundaries for the various electronic ground states in

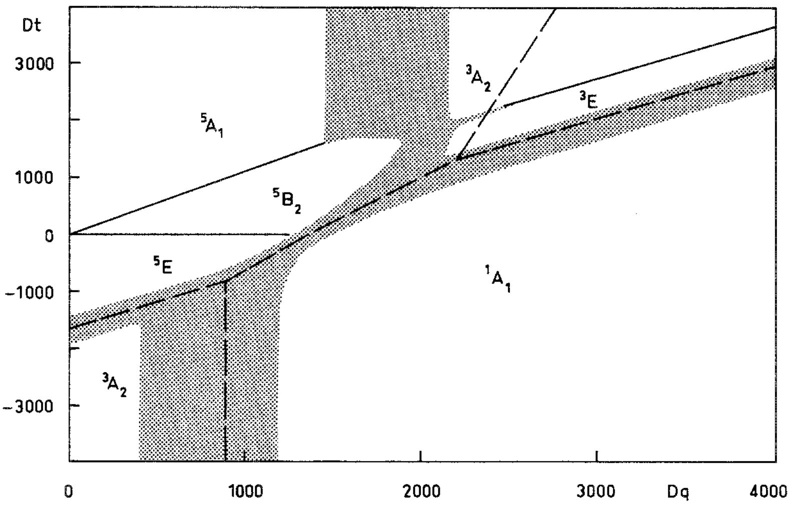

Fig. 1. Ground state boundary regions for the d^6 configuration in D_{4h} symmetry including complete CI and spin-orbit coupling ($B = 730\ \mathrm{cm}^{-1}$, $C = 4B$, $\zeta = 420\ \mathrm{cm}^{-1}$) assuming $\kappa = Ds/Dt = 1.0$. Results of a limited calculation are indicated by broken lines

parameter space. The results have interesting consequences with respect to the effect of high-energy levels in general.

Figure 1 shows the ground states which result from a complete configuration interaction calculation within a space spanned by the parameters [12] Dq of the parent octahedral (O_h) field and Dt of the tetragonal (D_{4h}) field, whereas Ds has been fixed by the requirement $\kappa = Ds/Dt = 1.0$. In addition, the Racah parameters of interelectronic repulsion have been taken as $B = 730\ \mathrm{cm}^{-1}$ and $C = 4B$ and the spin-orbit coupling constant $\zeta = 420\ \mathrm{cm}^{-1}$. When spin-orbit interaction is taken into account, there may be non-zero contributions of various spin multiplicities to each state in question. In addition to (almost) pure spin singlet, triplet, and quintet ground states, substantially spin-mixed ground states are expected. For the purpose of demonstration, we arbitrarily define a pure spin ground state as one having less than 2% admixture of any other spin multiplicity (blank areas in Fig. 1 separated by full lines) and all other ground states are considered as spin-mixed (shaded areas in Fig. 1). For comparison, the results obtained from a limited basis set calculation comprising the four lowest energy multiplets of the octahedral field, i.e. $^5T_{2g}(t_{2g}^4e_g^2)$, $^1A_{1g}(t_{2g}^6)$, $^3T_{1g}(t_{2g}^5e_g)$ and $^3T_{2g}(t_{2g}^5e_g)$, are shown by a broken line [10]. These states are all which occur up to an energy of at least $10000\ \mathrm{cm}^{-1}$. The approximation is reasonable for $Dt < 0$ and for small positive Dt in conjunction with reasonably large Dq. On the other hand, significant differences are clearly evident for large and positive values of both Dt and Dq. In particular, a new $^3A_2$ ground state arises for large Dq and a new $^5A_1$ ground state for small Dq, both at $Dt > 0$. A large spin-mixed area separates the two states. Additional differences comprise a broadening of all spin-mixed state areas in the complete CI calculation as compared to the limited calculation including spin-orbit coupling. In addition, the spin-mixed regions are larger in tetragonal symmetry than if the symmetry is O_h, viz. $Dt = 0$,

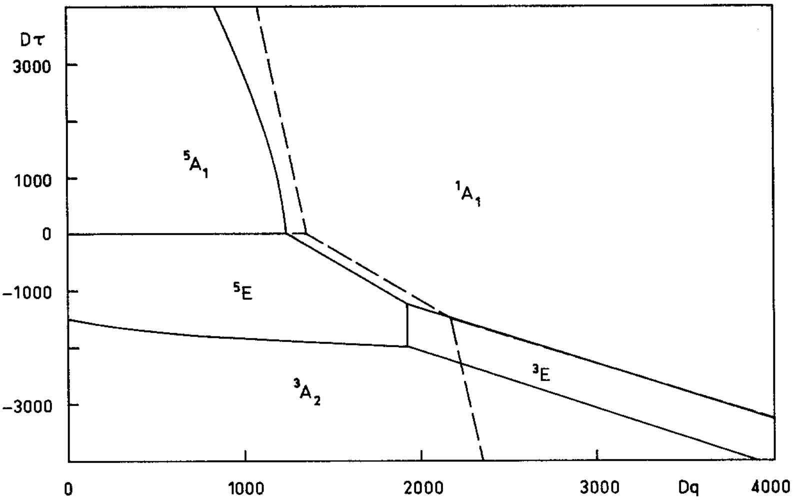

Fig. 2. Ground state boundary regions for the d^6 configuration in D_{3d} symmetry including complete CI and spin-orbit coupling ($B = 730\,\mathrm{cm}^{-1}$, $C = 4B$, $\zeta = 420\,\mathrm{cm}^{-1}$) assuming $\kappa = D\sigma/D\tau = 1.0$. Results of a limited calculation are indicated by broken lines

$Dq \sim 1400\,\mathrm{cm}^{-1}$ in Fig. 1. These areas on both sides of the actual cross-over are important in that various physical properties are determined by the actual distribution of low-lying levels and by their mixing [13].

In a separate study, we investigated the origin of the $^3A_2$ ground state at high and positive values of Dt and Dq. It is well known that, in an O_h field, altogether seven different excited $^3T_{1g}$ states exist [14]. All of these states could be parents to the $^3A_2$ state in question since, in a D_{4h} field, $^3T_1 \rightarrow {}^3A_2 + {}^3E$, whereas $^3A_2(O_h) \rightarrow {}^3B_1(D_{4h})$. The investigation shows the $^3A_2$ state to consist of $\sim 50\%$ contribution from the parent $^3T_1[t_2^4(^3T_1)\,e^2(^1A_1)]$ which is known to occur at an energy $> 30000\,\mathrm{cm}^{-1}$ and $\sim 40\%$ contribution from $^3T_1[t_2^4(^3T_1)\,e^2(^1E)]$ at an energy $> 21000\,\mathrm{cm}^{-1}$. Neither one of the two states can become ground state alone, and no effect of the remaining $^3A_2(^3T_1)$ states on the ground state is apparent.

Figure 2 shows the ground states resulting from a complete CI calculation within a space spanned by the parameters [12] Dq of O_h and $D\tau$ of trigonal (D_{3d}) symmetry in the limit of zero spin-orbit interaction. The parameter $D\sigma$ is fixed by $\kappa = D\sigma/D\tau = 1.0$. Again, the results of a limited basis set calculation employing the same multiplets as above have been indicated by a broken line. It is evident that the approximation is applicable for $D\tau > 0$ and if $D\tau$ assumes negative though small values. As in D_{4h} symmetry, a $^3A_2$ ground state is formed if $D\tau < -1500\,\mathrm{cm}^{-1}$ or less. It should be observed that, in D_{3d} symmetry, $^3T_1 \rightarrow {}^3A_2 + {}^3E$, whereas the $^3A_2$ is not changed. A detailed study shows that the $^3A_2$ ground state encountered is composed of $\sim 70\%$ $^3T_1[t_2^4(^1T_2)\,e^2(^3A_2)]$ (at $> 25000\,\mathrm{cm}^{-1}$) and $\sim 20\%$ $^3A_2[t_2^4(^1A_1)\,e^2(^3A_2)]$ (at $> 30000\,\mathrm{cm}^{-1}$) parents. Additional contributions ($\sim 5\%$ each) derive from $^3A_2[t_2^3(^2E)\,e^3]$ and $^3T_1[t_2^3(^2T_2)\,e^3]$, these states occurring normally at an energy above 30000 and $45000\,\mathrm{cm}^{-1}$, respectively. For small values of Dq and $D\sigma = D\tau < -1500\,\mathrm{cm}^{-1}$, another $^3A_2$ state is formed, its parent being almost exclusively (to ~95%) $^3T_1(t_2^2e^4)$. The accurate boundaries between the two $^3A_2$ states were not studied.

Complications similar to those discussed above are encountered if values different from $\kappa = Ds/Dt = 1.0$ are investigated. Thus, if $\kappa = 3.0$ and D_{4h} symmetry are assumed, $^3B_2$, $^3A_2$, and ^3E ground states arise for $Dt > 0$ in the region of the $^3A_2$ and ^3E states of Fig. 1. Compared to a limited basis set study, the additional terms $^3A_2$, ^3E, and $^5A_1$ are formed. If $\kappa = -3.0$, the ground state boundaries are similar in both the limited and the complete CI calculation, while the $^3B_2$ state region is replaced by that of the ^3E state. Turning our attention to D_{3d} symmetry and assuming $\kappa = 3.0$, the CI calculation differs from the limited study [10] in that an additional region of $^3A_2$ state stabilization is formed for $D\tau < -1500\,\mathrm{cm}^{-1}$ and $Dq < 2500\,\mathrm{cm}^{-1}$. Finally, if $\kappa = -3.0$, a ^3E ground state arises in the CI treatment for $D\tau < -1500\,\mathrm{cm}^{-1}$ and $Dq < 1500\,\mathrm{cm}^{-1}$, whereas no such state is formed within the limited approach.

In conclusion, limited basis set calculations comprising the low-energy octahedral terms $^5T_2$, $^1A_1$, $^3T_1$, and $^3T_2$ reasonably describe the electronic ground state in D_{4h} and D_{3d} symmetries close to O_h within large regions of parameter space (Dt, Ds or $D\tau$, $D\sigma$ and Dq). However, if significant departures from octahedral symmetry are considered, *an incorrect ground state may result.* The possible conclusions concerning the excited states are even more restrictive. Therefore, great caution should be exercised in applications of any limited basis set treatment in ligand field theory.

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Dr. E. König
Institut für Physikalische Chemie II
Universität Erlangen-Nürnberg
D-8520 Erlangen
Egerlandstraße 3
Federal Republic of Germany