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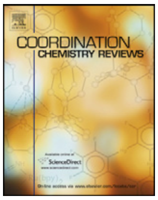

Review

Jahn–Teller coupling and the influence of strain in T_g and E_g ground and excited states – A ligand field and DFT study on halide $M^{III}X_6$ model complexes [$M = Ti^{III}–Cu^{III}$; $X = F^-, Cl^-$]

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ABSTRACT

In contrast to well established experimental results of vibronic coupling effects in octahedral d^n complexes with E_g ground states (Cu^{2+}, Ag^{2+}; Cr^{2+}, Mn^{3+} etc.), not much useful material is available for the Jahn–Teller (JT) effect in orbital triplet ground states. The present study is concerned with this deficiency, providing data for octahedral halide model complexes with $3d^n$ cations – in particular for Ti^{III}, V^{III} and high-spin Co^{III}, Ni^{III} with T_{2g} and T_{1g} ground states, which involve, to first-order, solely splitting of the π-antibonding t_{2g} MOs. Besides experimental results – structural and spectroscopic, mainly from d–d spectra – data from computations are needed for a quantitative treatment of the $T_g \otimes (\varepsilon_g + \tau_{2g})$ vibronic interaction as well as in the $E_g \otimes \varepsilon_g$ coupling case (Mn^{III}, low-spin Ni^{III}); DFT was the method of choice, if only critically selected outcomes are utilised. The theoretical bases of the treatment are the d^n ligand field matrices in O_h, extended by the inclusion of lower-symmetry distortion parameters, and the conventional theory of vibronic coupling. Caution is needed when classifying the effects of interelectronic repulsion; DFT does not reproduce the magnitudes of the Racah parameters B, C, as deduced from the d–d spectra, properly – the presumed reasons are analysed. DFT even allows one to deduce reliable vibronic coupling constants via the analysis of orbitally degenerate excited states (Cr^{III}, $^4A_{2g}$ ground state). The group-theoretical analysis of the interaction with the JT-active ε_g and τ_{2g} modes yields D_{4h}, D_{3d} and D_{2h} as the possible distortion symmetries in the case of a T_g ground state. The DFT-calculations give clear evidence, that the D_{4h} stationary points represent the absolute minima in the $T_g \otimes (\varepsilon_g + \tau_{2g})$ potential surface – in agreement with experiment, where available. For the first time, vibronic coupling constants, characterising JT splitting of ground and excited T_g states, can be presented for trivalent $3d^n$ cations in octahedral halide ligand fields. They turn out to be smaller by a factor of almost 3 in comparison to those, which determine the coupling in σ-antibonding e_g MOs.

The tetragonal splitting of T_g states is typically only small, around 0.1 eV, and suggests that strain influences from a specific ligand arrangement and/or the presence of different ligands may modify the potential surface considerably. We have studied such effects via compounds $A^IM^{III}F_4$, where an *elastic* strain induced by the host structure, and a *binding* strain, due to the simultaneous existence of (largely) terminal and of bridging ligands, are active. A novel strain model, in its interplay with JT coupling, is proposed and applied – using energies from the d–d spectra, structural results and data from DFT.

Chloride complexes are only known for Ti^{III} to Fe^{III}; the rather small electronegativity already of Co^{III} suggests a reducing ligand-to-metal ($3d^n$) electron transfer for $n \geq 6$. Similarly, the low-lying ligand-to-metal charge transfer bands in the d–d spectra of the $Cu^{III}F_6{}^{3-}$ complex and the reduced $T_g \otimes \varepsilon_g$ coupling strength suggest a pronounced covalency of the Cu^{III}–F, and, even more distinctly, of the Cu^{III}–O bond, which is of interest for superconductivity. The $Ni^{III}F_6{}^{3-}$ polyhedron possesses a low-spin configuration in the elpasolite structure. The spectroscopic evidence and the DFT data indicate, that the minimum positions of the alternative $_a{}^2A_{1g}(_a{}^2E_g)$ and $_a{}^4A_{2g}$ $(_a{}^4T_{1g})$ potential curves are only ≤0.02 eV apart, giving rise to interesting high-spin/low-spin phenomena. It is the strong $E_g \otimes \varepsilon_g$ as compared to the $T_{1g} \otimes \varepsilon_g$ coupling, which finally stabilises a spin-doublet ground state in D_{4h}.

We think, that the selected class of solids is unique particularly for the study of Jahn–Teller coupling in T ground states, with model character for other systems. In our overview a procedure is sketched, which uses reliable computational results (here from DFT) for supplementing incomplete experimental data, and presents – on a semiquantitative scale – convincing statements, consistent with chemical intuition. It is also a pleading for ligand field theory, which rationalises d-d spectra in terms of chemical bonding; though the latter spectra provide frequently only rather coarse information, their assistance in the energy analysis is crucial.