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Review

Absorption spectroscopy of octahedral nickel(II) complexes: A case study of interactions between multiple electronic excited states

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Contents

Abstract

Absorption spectra of octahedral nickel(II) complexes are used to illustrate that the limitation to only the initial and Born–Oppenheimer final states of an electronic transition is not adequate in order to rationalize the intensity and vibronic structure of the lowest-energy spin-forbidden transition of these compounds. Qualitative and quantitative models are applied and discussed for a series of absorption spectra measured in solution at room temperature and for the low-temperature single-crystal absorption spectra of nickel(II) ions doped into bromide host lattices. The spectra and models illustrate the influence of multiple allowed transitions on the lowest-energy spin-forbidden band.

Keywords: Nickel(II) complexes; Solution absorption spectra; Polarized single-crystal absorption spectroscopy; Vibronic structure; Theoretical models; Coupled electronic states; Interference effects

1. Introduction

The rich electronic structure of octahedral nickel(II) complexes has been explored over the past 50 years towards goals ranging from applying crystal field theory in inorganic coordination chemistry [1–3] to modern photophysical effects such as near-infrared to visible upconversion [4]. The d–d transitions observed in the absorption spectra provide the crucial experimental information needed to develop and test models and concepts for these areas. All electronic states arising from the d^8 electron configuration in O_h point group symmetry are shown in the Tanabe–Sugano diagram in Fig. 1. The most important excited states discussed in this review are the $^3T_{2g}$, $^3T_{1g}(^3F)$ and the ^1E_g states. The energy of the first singlet excited state, ^1E_g, is almost independent of ligand-field strength, as it arises from the same $t_{2g}{}^6e_g{}^2$ electron configuration as the electronic ground state. In contrast, the energies of the triplet excited states vary strongly with ligand field strength, due to their electron configurations with an increased population of the E_g orbitals. The d^8 configuration is particularly attractive for this review, as the $^3T_{2g}$ and $^3T_{1g}(^3F)$ excited states are close in energy at all ligand-field strengths. The main focus is on the electronic states in the oval zone in Fig. 1, containing only one singlet excited state and two nearby triplet excited states. Absorption

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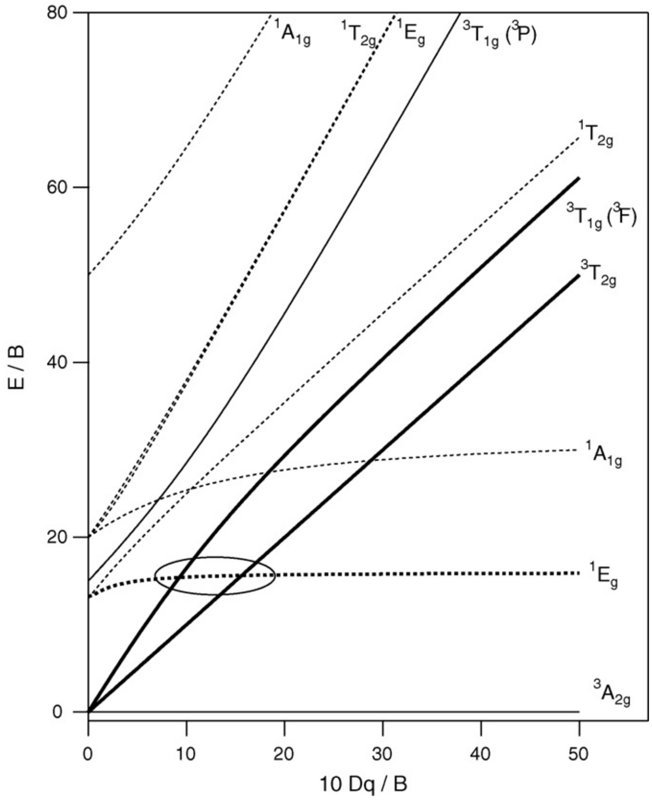

Fig. 1. Tanabe–Sugano diagram for the d^8 electron configuration in O_h point group symmetry. Triplet and singlet electronic states are given as solid and dotted traces, respectively, with excited states relevant to this review emphasized as thick traces. The oval denotes the energy and ligand-field strength range for which spectra are analyzed.

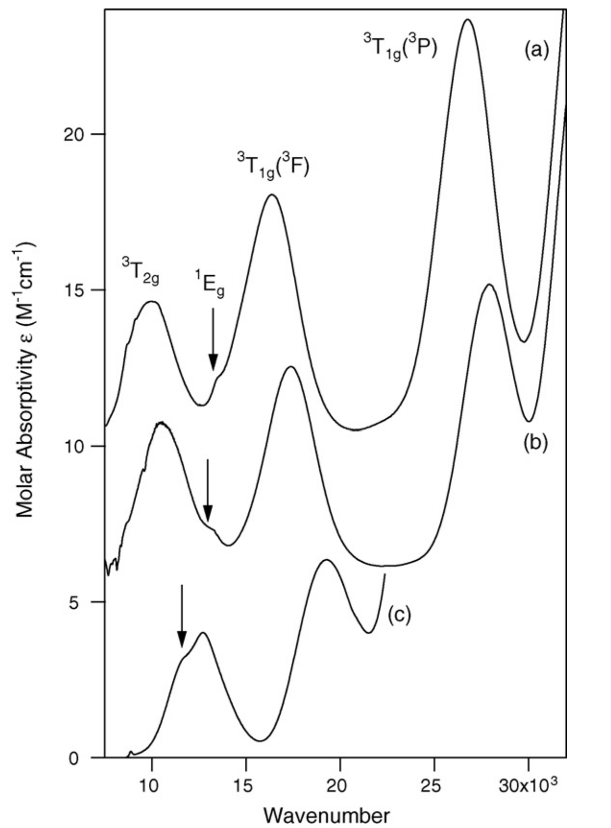

Fig. 2. Solution absorption spectra of: (a) $[Ni(imidazole)_6]^{2+}$, (b) $[Ni(NH_3)_6]^{2+}$, and (c) $[Ni(bipyridine)_3]^{2+}$. Traces (a) and (b) are offset along the ordinate for clarity. Vertical arrows denote the lowest-energy spin-forbidden transition to the ^1E_g excited state.

spectra covering this zone have been published and transition energies have been analyzed [1,3,5,6]. In the following, we discuss the intensity of the lowest-energy spin-forbidden transition, applying recently developed theoretical models [7,8]. The most important insight resulting from this review is that a forbidden transition close in energy to several allowed bands can lose or gain intensity compared to a situation where only a single allowed band is present and an intensity gain always occurs. The absorption spectra reviewed in the following show that intensity borrowing from several allowed bands is not additive, an effect often neglected when "mixed" wavefunctions of excited states are analyzed.

The transition to the lowest-energy singlet excited state in octahedral nickel(II) complexes can often be observed in solution spectra and it has been extensively discussed in literatures [1–3]. Both its intensity and unusual band shape, with resolved vibronic structure at low temperature, have been analyzed with detailed theoretical models [2,9–11]. All analyses are based on model potential energy surfaces, which are also the key ingredient to the approach discussed and applied in this review. It is important to point out that established electronic structure calculations are most often based on the adiabatic approximation and are not necessarily suitable to rationalize intensities of forbidden transitions, which are dominated by effects of coupling between potential energy surfaces, emphasizing the importance of detailed analyses of experimental spectra.

2. Intensity of a spin-forbidden transition: experimental overview and qualitative application of perturbation theory

The absorption spectra of many octahedral nickel(II) complexes can easily be interpreted using the Tanabe–Sugano diagram for the d^8 electron configuration given in Fig. 1. The electronic ground state is $^3A_{2g}$, and spin-allowed transitions to three triplet excited states are expected and easily observed in solution absorption spectra. One aspect of these spectra that has been discussed in detail is the lowest-energy spin-forbidden transition. Its intensity is often high enough to be observed in many solution absorption spectra, as illustrated in literatures [1,3,5,6,12] and for three representative complexes $[Ni(imidazole)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$ and $[Ni(bipyridine)_3]^{2+}$ in Fig. 2. These three homoleptic complexes all have six nitrogen ligator atoms, but the energies of their spin-allowed bands vary significantly. The position of the weak, spin-forbidden band can be either close to the lowest-energy spin-allowed transition to the $^3T_{2g}$ final state, illustrated by the bottom two spectra in Fig. 2, or close to the $^3T_{1g}$(^{3}F) band, as illustrated by the top trace in Fig. 2. For weak ligands, the transition can even be higher in energy than the $^3T_{1g}$(^{3}F) band, as has been observed and studied in detail for the $[Ni(H_2O)_6]^{2+}$ complex both in solution and in the solid state and for several solid chloride and bromide host lattices doped with nickel(II) ions [4,9–18]. The Tanabe–Sugano dia-