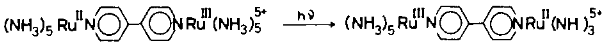
Intervalence Transfer (IT) absorption bands can appear (*e.g.* eqn. 1). The properties of IT absorption bands can be understood based on the early work of Hush and later theoretical developments. Perhaps most important is the information available in IT bands concerning related thermal electron transfer processes.



(1)

Experimentally, it has been possible to probe the role of molecular and solvent vibrations and of the distance between redox sites on the energy of the transition. Although a continuum model for the solvent has been successful in some cases, it is clear that specific solvent effects are important in others.

In more recent work, it has been possible to explore the relationship between IT and related, excited state transitions, to calculate thermal electron transfer rate constants from the properties of IT bands, and to extend the treatment involved to both metal–ligand and donor–acceptor charge transfer transitions.

Jahn–Teller Effect and Stereochemistry

M. BACCI

Istituto di Ricerca sulle Onde Elettromagnetiche of C.N.R., Florence, Italy

The main theoretical aspects of the Jahn–Teller effect (JTE) are outlined and particular attention is paid to a correct understanding of the related statements about the electronic degeneracy and the spontaneous distortion.

The 'static' and 'dynamic' limits and their connections by tunneling mechanism are considered. Moreover the role played by the JTE in quenching electronic operators (Ham effect) and in amplifying distorting perturbations is shown.

Successively the most significant results for the linear coupling in the 'static' approximation are summarized following Öpik and Pryce's analysis. On the other hand it is stressed how the introduction of second order and/or anharmonic terms can yield simultaneous stable distortions thus overcoming Öpik and Pryce's 'dichotomy'. Real systems, for which such a coexistence has been proved by experiments, are presented.

Finally, it is shown how a straightforward evaluation of the Jahn–Teller coupling constants is possible following the angular overlap model and some applications to molecules containing transition metal ions are reported.

Vibronic Model for Mixed Valence Compounds and Spin Crossover Systems

SUSAN B. PIEPHO

Department of Chemistry, Randolph-Macon Woman's College, Lynchburg, Va. 24503, U.S.A.

The vibronic coupling model for mixed valence systems recently proposed by Piepho, Krausz and Schatz [1] is described. Using the model, it is a simple process to obtain the vibronic energy levels and eigenfunctions relevant to an intervalence band. Calculations are essentially exact within the context of the model, and are not limited to the cases of very strong or very weak interactions. The eigenvalues and eigenvectors obtained may be used to determine properties associated with the mixed valence band. These include, for example, the absorption profile of the band, the degrees of delocalization and valence-trapping, and the electron transfer kinetics for the system.

Very similar formalism applies to both mixed valence and spin crossover systems. Thus the applicability of the model to single-center systems with two different spin states with intersecting potential surfaces is discussed.

Finally, the limitations of the mixed valence model are discussed, and methods of improving the model by more explicit consideration of the nature of the interacting centers are considered.

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Low Spin Co(II) Complexes in Various Solvents as Studied by ESR Spectroscopy

ALEX VON ZELEWSKY

Institute of Inorganic and Analytical Chemistry, University of Fribourg, CH-1700 Fribourg, Switzerland

Four-coordinated, low spin, Co(II)-complexes of the Co(salen) type, have a $^2A_2$ ground state, the unpaired electron being in a π-orbital of d_{yz} character. There are several excited states with the same (doublet) and with higher (quartet) spin multiplicity as the ground state within a range of only a few multiples or less of the spin–orbit coupling constant ($\lambda_{Co} \approx -400\ cm^{-1}$) [1, 2].

Upon dissolution of the complex Co(saphen) (which was chosen because of solubility reasons) in coordinating solvents a crossing of states is observed. The ground state of the complex changes from $^2A_2$ to $^2A_1$. This change is due to coordination of a solvent molecule in axial position. The a_1 (d_{z^2}) orbital is becoming stronger σ-antibonding and it is consequently raised above the d_{yz} orbital whose energy is little affected by the axial coordination. Near the 'crossing' point strong mixing of $^2A_2$ and $^2A_1$ occurs because both states belong to the same irreducible representation of the double group, the closest approach of the two states being $\sqrt{3}\lambda$. ESR Parameters change drastically near this 'crossing' point. The electronic rearrangement induced by solvent interaction in these complexes is due to an accidental near degeneracy of the ground state, which is typical for low spin d^7 systems with square planar structure.

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Variable Electronic Properties of High Spin Cobalt(II)

DANTE GATTESCHI

Istituto Chimica Generale, University of Florence, Florence, Italy

Octahedral high spin cobalt(II) is a well known example of electronic quasi degeneracy, since the ground $^4T_{1g}$ level of O_h symmetry is usually split to some extent by low symmetry components of the ligand field. ESR spectra are a very sensitive means for monitoring the nature of the distortions, because the g values are expected to vary dramatically according to which orbital component of $^4T_{1g}$ becomes the lowest energy state in the distorted field.

The theory necessary to understand the g and A values in octahedral and axial ligand fields was worked out by Abragam and Pryce [1], but it is an experimental result that often the actual symmetry is lower than axial and the principal directions of the spin hamiltonian tensors do not coincide with the 'molecular' axes [2].

Classic ligand field theory is not able to reproduce the experimental spin hamiltonian parameters which can be justified only using an Angular Overlap procedure we have developed [3], according to which both the principal values and directions of g and A can be obtained through a completely symmetry independent procedure. The main advantage of the Angular Overlap model, as compared to classic ligand field, is that it introduces parameters which reflect the σ and π nature of the bonding interaction. Further anisotropy in the π interaction is easily taken into account.

The versatility of the method has been checked on tetragonal octahedral complexes such as $Co(py)_4Cl_2$, $Co(pyz)_4Cl_2$, $Co(acac)_2L_2$ (py = pyridine; pyz = pyrazole; acac = 1,3-pentane-dione; L = pyridine, 6-methylquinoline, water). We were able to show that the g values and directions are mainly determined by the differences in the π ability of the axial and equatorial ligands.

The large variability of the electronic properties, as monitored by the spin hamiltonian parameters and their principal directions, is not a unique feature of octahedral complexes, and also tetrahedral and five-coordinate complexes show the same effects. In this case the ground orbital level is non degenerate. However spin–orbit coupling removes the spin degeneracy so that the two lowest Kramers doublets are quasi degenerate on the ESR experiment energy scale.

Examples will be provided for different geometrical distortions of the parent symmetries and attempts will be made to give general rules for using the ESR spectra as a structural tool for cobalt(II) complexes.

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Mixed Valence in Small and Big Polynuclear Entities having Metal–Oxygen–Metal-Bridges

Y. JEANNIN and J. P. LAUNAY

Laboratoire de Chimie des Métaux de Transition, Université Pierre et Marie Curie, Paris, France

As a part of a research program on mixed valence compounds of Mo, W and V with oxygen bridges, we