we wish that the experimentalists (of which we are) obtain useful informations on the complexes that it would be interesting to synthetize with the help of overlap density maps as those shown during the lecture. Such a map is schematized below for the case of a Cu(II) VO(II) heterobinuclear complex.

According to the available time, we intend to approach some of the following situations: (*i*) planar [1] and roof-shaped [2] hydroxo-bridged copper(II) dimers; (*ii*) heterobinuclear complexes in which the strict orthogonality of the magnetic orbitals is realized [3]; (*iii*) very strong antiferromagnetic coupling between transition ions far away from each other [4]; (*iv*) orbital reversal in copper(II) polynuclear complexes through the action of solvent molecules [5].

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Spin Crossover in Solid Solution

P. GÜTLICH

Institut für Anorganische und Analytische Chemie, Johannes Gutenberg-Universität, D-6500 Mainz, F.R.G.

The temperature dependent high spin (HS) $\rightleftharpoons$ low spin (LS) transition, otherwise called spin crossover, has been well established for many first-row transition metal complexes, particularly for complexes of iron(II) [1]. The phenomenon has been observed mostly in the crystalline state, but also in solution. The spin crossover characteristics have been found to depend on various chemical influences, such as ligand substitution, the nature of the non-coordinating anion and the crystallizing solvent.

It has been shown by ^{57}Fe Mössbauer spectroscopy that the spin crossover behaviour in the solid solutions of $[\mathrm{Fe}_x\mathrm{Zn}_{1-x}(2\text{-pic})_3]\mathrm{Cl}_2\cdot\mathrm{EtOH}$ (2-pic = 2-picolylamine) is also susceptible to metal dilution [2, 3]. At a given temperature, the HS state becomes favoured over the LS state with decreasing x. This may be qualitatively interpreted on the grounds of a cooperative domain model [2]. A phenomenological thermodynamic treatment [4] yields estimates of the changes of enthalpy and entropy as well as the domain size. A statistical model has also been successfully applied, which also allows to estimate the domain size and, in addition, an average effective frequency of the metal–ligand vibrational modes in each of the two spin states.

Mössbauer effect studies of the solid solution of $[\mathrm{Fe}_x\mathrm{Co}_{1-x}(2\text{-pic})_3]\mathrm{Cl}_2\cdot\mathrm{EtOH}$ show similar results. The relative stability of the HS state, at a given temperature, also increases with decreasing x. The $\mathrm{Fe}_x/\mathrm{Co}_{1-x}/2$-pic system, however, shows higher transition temperatures, at a given x, than the $\mathrm{Fe}_x/\mathrm{Zn}_{1-x}/2$-pic system, apparently due to the more rigid lattice of the former system.

The effect of metal dilution in solid solutions of $[\mathrm{Fe}_x\mathrm{M}_{1-x}(\mathrm{phen})_2(\mathrm{NCS})_2]$ (M = Co, Mn, Ni) as studied by Mössbauer spectroscopy [5] follows the same line: at a given temperature, the $^5T_2(O_h)$ state becomes favoured over the $^1A_1(O_h)$ state upon lowering x.

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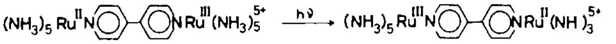
Electron Transfer in Mixed-Valence Compounds

T. J. MEYER

Department of Chemistry, University of North Carolina, Chapel Hill, N.C. 27514, U.S.A.

In mixed-valence compounds where electronic interactions between metal sites are relatively weak, 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