Electronic Rearrangements Induced by Solute–Solvent Interactions

Electronic Rearrangements Induced by Solute–Solvent Interactions

J. H. AMMETER

Institute of Inorganic Chemistry, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland

Molecules with low-lying excited electronic states tend to be 'electronically non-rigid', *i.e.* their electronic properties exhibit pronounced sensitivity to external perturbations. Often, drastic changes in various spectroscopic properties indicating substantial electronic rearrangements can be induced by relatively weak intermolecular forces as provided by nonpolar solvents or solid molecular host lattices. This behaviour can be explained by crossings of potential surfaces in the vicinity of the absolute minimum. Many physical properties of a given orbitally (near) degenerate system depend strongly on the relative magnitude of some characteristic parameters determining the shape of the ground Born–Oppenheimer potential surface(s) in the vicinity of the absolute minimum, *e.g.* Barrier height *versus* zero point energy, distance between minima *versus* zero point amplitude, energy difference between minima, *etc.* Typical examples are systems exhibiting Jahn–Teller activity, spin-crossovers, mixed valence, exchange couplings and other types of electronic near-degeneracies.

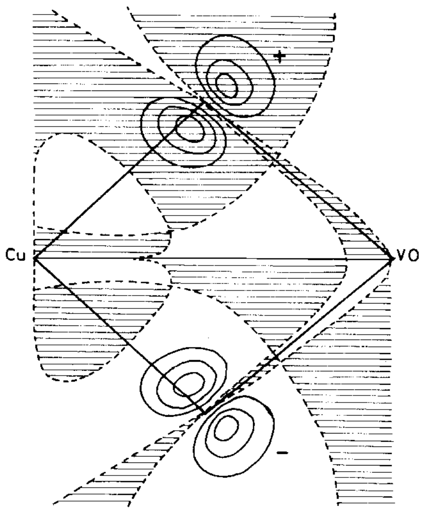
This microsymposium tries to join the theoreticians and spectroscopists working on systems exhibiting strongly variable electronic properties. One of the major purposes will be to confront both analogies and differences of the various cases of electronic lability, from the experimentalist's as well as from the theoretician's point of view. Whenever possible, the influence of intermolecular potentials ("solute–solvent-interactions") on the electronic properties of the particular systems under consideration will be discussed.

Exchange Coupled Systems. Overlap Density between Magnetic Orbitals and Molecular Structure

OLIVIER KAHN* and MARIE FRANCE CHARLOT

Laboratoire de Spectrochimie des Eléments de Transition, ERA No 672, Université de Paris Sud, 91405 Orsay Cedex, France

Although significant advancements have been achieved during the last years in the interpretation of the nature and the magnitude of the exchange interaction which occurs in polynuclear complexes with paramagnetic centers, a lot of problems remain to be solved in this field. For instance, in all the orbital models proposed so far to describe the exchange interaction in an A–B dimer, the J parameter of the phenomenological exchange Hamiltonian $-J\ \hat{S}_A \cdot \hat{S}_B$ is expressed as the sum of a negative antiferromagnetic contribution J_{AF} and a positive ferromagnetic contribution J_F. Whereas successful efforts have been spread out to understand how J_{AF} varied *versus* small structural changes in series of similar complexes, the influence of these structural modifications on J_F has never been investigated. And yet it is not doubtful that, as J_{AF}, J_F must depend on the geometry of the complex. In our lecture, we shall propose an approach of the exchange interaction grounded on the concepts of *magnetic orbitals* and of *overlap densities* between magnetic orbitals. It is important to specify here that we do not look for proposing, after many other authors, some new mathematical considerations on the exchange but, on the contrary, to extract from the existing theory a very small number of simple and essential ideas and to show how they can lead to a prevision of the variations of J_{AF} and J_F in closely related complexes. Our results will be presented under the form of overlap density maps. In the same manner as the walker finds his way with the help of the map of the region,



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].

References

1 V. N. Crawford, H. V. Richardson, J. R. Wasson, D. J. Hodgson and W. E. Hatfield, *Inorg. Chem.*, *15*, 2107 (1976).
2 M. F. Charlot, S. Jeannin, Y. Jeannin, O. Kahn, J. Lucrece Abaul and J. Martin Frere, *Inorg. Chem.*, *18*, 1675 (1979); M. F. Charlot, O. Kahn, S. Jeannin and Y. Jeannin, *Inorg. Chem.*, in press.
3 O. Kahn, J. Galy, P. Tola and H. Coudanne, *J. Am. Chem. Soc.*, *100*, 3931 (1978); O. Kahn, R. Claude and H. Coudanne, *N. J. Chim.*, in press.
4 J. J. Girerd, Y. Jeannin, O. Kahn and G. Lavigne, *Inorg. Chem.*, *18*, 3015 (1979).
5 J. J. Girerd, O. Kahn and M. Verdaguer, *Inorg. Chem.*, in press.

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) ⇌ 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 $[Fe_xZn_{1-x}(2\text{-pic})_3]Cl_2 \cdot EtOH$ (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 $[Fe_xCo_{1-x}(2\text{-pic})_3]Cl_2 \cdot EtOH$ show similar results. The relative stability of the HS state, at a given temperature, also increases with decreasing x. The $Fe_x/Co_{1-x}/2$-pic system, however, shows higher transition temperatures, at a given x, than the $Fe_x/Zn_{1-x}/2$-pic system, apparently due to the more rigid lattice of the former system.

The effect of metal dilution in solid solutions of $[Fe_xM_{1-x}(phen)_2(NCS)_2]$ (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.

References

1 H. A. Goodwin, *Coord. Chem. Rev.*, *18*, 293 (1976).
2 M. Sorai, J. Ensling and P. Gütlich, *Chem. Phys.*, *18*, 199 (1976).
3 P. Gütlich, R. Link and H.-G. Steinhäuser, *Inorg. Chem.*, *17*, 2509 (1978).
4 P. Gütlich, R. Link, H. Köppen and H.-G. Steinhäuser, *J. Chem. Phys.*, *70 (8)*, 3977 (1979).
5 P. Ganguli and P. Gütlich, to be published.

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,