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An integrated view of charge-transfer complexes

In the centenary year of the discovery of the electron by J. J. Thomson, it is perhaps appropriate to reminisce about R. S. Mulliken, one of the giants who contributed to molecular electronic structure theory.

Mulliken was born in 1896, just one year before the spectacular experiment of 'JJ'. Even as a school-boy, Mulliken was aware of the significance of the discovery, as can be seen from the title of his graduation oration: 'The Electron, What It Is and What It Does'. Since his father was a professor of organic chemistry at MIT, it was but natural that the young Mulliken took his early training in experimental chemistry. He went to Chicago for his doctoral work and had a few post-doctoral stints in Europe and at Harvard. In 1928, he joined the Chicago faculty in the Ryerson Physics Laboratories. With the insight of chemists and the rigour of physicists, he developed the field of Molecular Physics.

Mulliken's work has profoundly influenced the thinking of chemists. The coining of the term *orbital*, the generalization of the orbital description from atoms to molecules, and the formulation of molecular orbitals as linear combinations of atomic orbitals are some of his early contributions. His interpretations of electronic structures of diatomic and simple polyatomic molecules are textbook material. He worked out a new scale of electronegativity, which takes into account not only the affinity of an atom for an electron but also, in equal measure, its reluctance to lose an electron. He proposed the concept of hyperconjugation. He pointed out the importance of the

overlap integral and also suggested a simple scheme for partitioning electron densities over atomic and overlap regions. Mulliken was fittingly honoured with the Nobel Prize in Chemistry (1966) 'for his fundamental work concerning chemical bonds and the electronic structure of molecules by the molecular orbital method'.

Mulliken's contributions to molecular spectroscopy are equally important, as they have fundamentally shaped the course of research in this field. He emphasized the need to interpret the position of the bands, assign them to specific transitions, and quantify the intensity data. With his understanding of molecular orbitals and knowledge of group theory, assignments and selection rules were straightforward tasks. His formula for the oscillator strength forms the basis for all studies of absolute intensities. He also pointed out the importance of vibrational mixing, which contributes to the intensities of apparently forbidden transitions in electronic spectra.

A particularly interesting problem, which involves both bonding and spectroscopy, attracted the attention of Mulliken in 1950. When iodine is dissolved in benzene, an intense absorption band is observed at a wavelength quite different from the bands of the parent molecules. Mulliken suggested that the band was due to charge transfer from one species to the other. He proposed two idealized wave functions, one in which there was no transfer and another with a donor-acceptor bond. He argued that the ground electronic state was dominated by one of these functions, while a low lying excited state had the other character. With this qualitative model, he could explain the origin of the binding, dipole moment, and variation in band positions with

acidic and basic characters of the parent molecules for the general class of charge transfer complexes.

But the details were missing. For example, what are the precise structures of charge-transfer complexes? What happens to the energy levels of the filled and unfilled molecular orbitals of the constituent units? Can one examine species which do not necessarily have an absorption band in the uv-visible region?

Many of the above questions are now being answered. Charge-transfer complexes can be generated in the gas phase and studied using photoelectron spectroscopy and electron energy loss spectroscopy. The complementary procedures provide quantitative information about the orbital energies of filled and unoccupied levels, to a good approximation. By comparing with the peak positions of the parent species, changes in orbital energies due to complex formation can be precisely monitored. The data are best interpreted using the quantitative version of molecular orbital theory (proposed by Mulliken's student C. C. J. Roothaan). While such *ab initio* calculations are by no means exact, the results are extremely useful. Precise geometries, binding energies and trends in orbital energies can be obtained. Thus, the combined use of theory and experiment provides a comprehensive description of the nature of charge-transfer complexes.

M. S. Hegde provides an account of the work carried out in his group over the last few years along the above lines (page 747). Many new insights have been obtained. For example, in related halogen complexes, diethyl ether prefers to interact with its σ type lone pair, while the corresponding sulfide uses the

orthogonal p type lone pair. The computed structures have interesting parallels in the directionality of attractive intermolecular contacts found in the solid state for sulfur compounds. Complexes which do not have the characteristic charge-transfer band in the visible spectrum have also been studied. The results obtained for complexes with transition metal Lewis acids are of special interest.

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Loss of crop diversity in the Central Himalayas

Ironically, the very process of intensive agriculture or monoculture that saved the country from an almost certain famine during the early 1960s, has been one of major causes for a colossal reduction in the nation's crop biodiversity. Prior to the Green Revolution, over 30,000 indigenous varieties or landraces of rice were grown in the country. Today there are not more than fifty and it is estimated that by the year 2000, over 75 per cent of the area under rice cultivation will be covered by only 10 improved varieties. In wheat, over 90 per cent of the irrigated area is covered by a single variety. The situation is

nearly the same for many other crops such as cotton, sugarcane, pulses, etc. Monoculture has also led to a complete replacement and local extinction of many of our lesser known crops such as the minor millets, indigenous fibre crops and pulses. Thus in a typical village where one would have found about 30 to 40 crops under cultivation about 40 years ago, today only 6 to 10 exist.

While we have satiated on the fruits provided by modern agriculture, the concern over the loss of our native crop genetic resources is slowly but surely being echoed in different fora. Apart from the concerns of the 'purists', of 'conservation for the sake of conservation', the loss of crop biodiversity has been a major concern to the country at large also in ensuring a stable and secure food production system. The landraces and the traditional crops that have evolved in their native habitats are potential reservoirs of many useful genes. Literature is replete with instances of the wonders that have been churned out from these reservoirs. A wild plant of rice collected in 1963 from some part of Uttar Pradesh gave a gene that saved 30 million hectares of paddy from a disease, the grassy stunt virus. A wild melon from India provided genes for resistance to the fungal

disease, mildew, to melons in the United States of America.

Maikhuri *et al.* (page 777) present a poignant tale of the loss of crop biodiversity from the Central Himalayas, one of the 'cradles of crop biodiversity' in the country. Unlike the lower Indo-Gangetic Plains, the farming ecosystems of the Himalayas were relatively insulated from the syndromes of modern agriculture until about two decades ago. These sites have served as a rich storehouse of crop diversity, fostered in part by the tremendous heterogeneity of the landscapes as well as the innumerable cropping systems followed therein. However, in recent years, these storehouses are being rapidly undone with the advent of monoculture systems in the hills. Maikhuri *et al.* rightly lament that unless urgent measures are taken to stop this invasion and revive the traditional agroecosystems of the Central Himalayas, the region will be poorer of its immense crop genetic wealth. The consequences of the loss are, however, not going to be restricted to the Central Himalayas alone, but will certainly affect the rest of the country, for, the food security of a country can only be as good as the genetic diversity supporting it.

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