

EXCON '94: Inaugural address

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This conference has the unusual distinction that it is sponsored by two of the great international scientific unions, the International Unions of Pure & Applied Chemistry and of Pure & Applied Physics. The Australian Academy of Science, which is the Australian affiliating body to the International Council of Scientific Unions also warmly supports EXCON '94. One could expect that a conference in the field of solid state science should be sponsored by international bodies in both chemistry and physics, but joint support is not a common event. We have to thank EXCON '94 for arranging this happy and natural accommodation on the present occasion.

There has never before been a conference on excitons from a broad physics perspective in Australia. There have been, and there are, a number of scientists in exciton theory and experiment in Australian universities, but most have worked on excitons in molecular crystals, and they have been chemical physicists with a research emphasis on spectroscopic properties and photoconduction. That was certainly true until work began in the University of the Northern Territory that is more mainstream physics in character. The second unusual feature is the location of the meeting in Darwin. This is the first international conference in chemistry or physics in this city. In so large a country scientific activities tend to be concentrated in the big centres, particularly Sydney and Melbourne and, for special reasons, in Canberra. It requires a serious effort to promote research in science elsewhere. This conference is part of the move to hold scientific conferences in centres that are chosen not simply because they are large, but where there is a particular strength in the discipline.

Exciton theory is one of the oldest parts of our subjects. Frenkel's first paper appeared in 1931, just five years after the discovery of quantum mechanics. In the Russian literature his first paper came out in 1937. As I look back on the development of the subject with the perspective of a chemical physicist I see that we were drawn in at the start by the need to get an experimental lead on the properties of small molecules to overcome theoretical problems in molecular quantum mechanics. The goal was a theoretical description of the excited states of these molecules that would fit experiment. The theories were crude and had to be closely checked. One could calculate the energy intervals between the ground state and the excited states of a small molecule and test against measurements of spectroscopic intervals. The key problem was that it could not be claimed with assurance that the experimental quantity related to the same spectroscopic transition that the theory worked out.

One way of checking was to prove that the direction of transition moment agreed with the predictions of the calculations. There was therefore a strong interest in the directional properties of polarized light by molecules fixed rigidly in known positions and orientation in the crystal. There was much activity in this area.

The early experimental history also owes much to work in the former USSR. In 1936 Obreimov and Prikhotjko published in the *Physikalische Zeitschrift der Sowjetunion* an absorption spectrum of the three-ring aromatic hydrocarbon anthracene taken in polarized light. They gave the essential result that the absorption was much stronger in one crystalline direction. From that it is possible to deduce that the underlying transition is polarized along a particular molecular axial direction. At the same time there was the question of how this result, and others, was to be interpreted in the light of theories of molecular states. A molecular electronic transition in the vapour spectrum appears in the crystal spectrum as two or more transitions. A theoretical basis had to be found to calculate these changes and to relate them to experiment. This is the line of development that brought chemical physicists into the exciton field. My research group was active in this field in the 1940s and 1950s both in experiment and theory, the subject was substantially advanced by A.S. Davydov's work published earlier in the 1940s on the splitting of transitions in small molecules by crystal forces. In my group, then in London, we took up Davydov's theory, verified it experimentally in crystals of several aromatic molecular crystals, and extended the theory to include the influence of vibrational structure, which proved to be profound; the splitting of individual vibronic absorption bands was much smaller and the polarization of absorbed light modified.

The use of small aromatic molecules in this first phase of crystal studies was highly productive. The range of molecules grew to include angular and branched members, but the sizes have mostly been in the range of one to six benzene rings. It is easy to see the reason. They have electronic transitions easily studied in the visible and ultraviolet. Some transitions have dipole strengths that are very large with the result that the molecule-molecule dipole coupling supports excitons moving so quickly that neither molecular vibrations nor lattice motions can couple to them. They are excitons in a rigid molecule and a rigid lattice. In another case of weaker transitions the molecule-molecule transfer rate is slow enough to allow relaxation of the molecules but not of the lattice. And in a third class of very weak transitions the excitons are built on non-rigid molecules in a non-rigid lattice. The smaller coupling energies between molecules in this last case implies slower rates of excitation transfer, to the point where lattice relaxation can compete with transfer. Then the problems of exciton-phonon coupling have to be solved, and the associated self-trapping dealt with.

Theories have been proposed to deal with all three cases. In the last of them we have seen detailed analyses of exciton-phonon coupling, with associated self-trapping leading in some special cases to photochemical reactions as in the formation in the lattice of dimers of 9-cyanoanthracene.

At higher excitation energies certain examples from the same set of molecules show photoconduction. It is also of great practical importance that ultrapurification of these materials, while difficult, is possible in practice. This has provided for excitons generally a most important signpost to the profound effects of impurities even in minute concentrations. Impurities in amounts of one part per ten or a hundred million can confuse the interpretation of results in spectroscopy and electrical properties. Detection of such small amounts in molecular crystals is not difficult. We can readily observe impurity light emission in low temperature fluorescence.

All this is part of the ancient history of our conference topic. Things have moved on, not only in the organic crystal and polymer areas, but also in inorganic materials. We look forward to hearing about the current state of knowledge in all of these fields.

This account of 50 years of excitons in organic crystals prompts thoughts of the technical background of the progress in understanding. Scientists of my generation have lived through the entire history of computers. I can say that personally I started with a slide rule and ended with a supercomputer. The broad correctness of exciton theories had to be set in place by comparison of calculated and experimental band splittings and transition intensity ratios. The computations on which the prediction of crystal spectra depended were on the standards of the time extremely heavy. The key quantities were multipole-multipole electrostatic interactions between pairs of molecules summed over all pairs within a spherical volume, taken to convergence. The first comprehensive computations were begun in about 1952, at first limited to dipole coupling for a small selection of molecular crystals. There was the direct sum method, just mentioned, and the Ewald-Kornfeld method which converged more quickly; the sums were done by electric calculating machines. Everything had to be checked and re-checked. We can set the scale of the work by noting that my colleague, Dr. J.R. Walsh, spent about one year of a three-year doctorate program in getting reliable and precise dipole-dipole data for just a few crystals.

There was then a big step to the first generally available electronic computers. By 1956 Dr. S.H. Walmsley in University College London used the Ferranti Pegasus and IBM 650. Both were valve machines. They were not easy to program, and had memories that were counted in bytes rather than megabytes. By now the twelve months task was cut down to a few weeks if the programming time was included. The run times were just a few minutes.

And now ? The program might take a day or two to write and check, and the run time would be in the microsecond range. We have in one scientific lifetime seen a rate increase in computing of about thirteen orders of magnitude. It is intriguing to realize that experimenters who use light pulses to study fluorescence, trapping and photochemistry in crystals have done just as well: the rotating shutters of the early photochemists with their pulses of one hundredth of a second are replaced by femtosecond laser pulses, Again a thirteen orders of magnitude gain.

It is time to move from reminiscence to the here and now of 1994. I am delighted to open the proceedings.