The Triplet State in Chemistry and Physics

It is now about 23 years since the identification of the long-lived luminescence from organic molecules as triplet-state-to-ground-state emission. In intervening years we have seen development of a relatively sophisticated understanding of these excited triplet states. Much recent progress in triplet-state studies stems from applications of flash spectroscopy, electron paramagnetic resonance, optical spectra in high magnetic fields, studies of triplet excitons in molecular and ionic crystals and from theoretical models for spin-orbit and exchange coupling.

Notwithstanding recent advances and continuing exploitation of new techniques, many of the essential problems of 23 years ago are still unresolved. A prominent difficulty is understanding the nonradiative population and decay of triplet excited states and the nature of the participation of molecular and environmental vibrations in these processes. Another difficulty is understanding how the vibrational degrees of freedom influence the spin-orbit coupling, and still another problem concerns the differences in the electronic and nuclear structures of ground and excited states. Development of these and other questions has become as important to organic photochemistry as to solid-state physics; as important to the study of electronic properties of organic liquids as to the study of excitations in rare-gas solids. The recent International Symposium on the Triplet State (Beirut, 14–18 Feb.) therefore, was not only timely; it provided an appropriate stamping ground for both physicists and chemists whose interests lay not so much in a particular state of matter or in a particular technology, as in the common factor of metastable excited triplet states.

With this focus in mind the American University of Beirut was host to the symposium on the occasion of its 100th anniversary. The symposium was organized by members of the department of physics at the university under the able chairmanship of A. B. Zahlan.

Spin-orbit coupling. The symposium began with the theme of spin-orbit coupling in aromatic molecules, in which Hendrik F. Hameka (Pennsylvania) discussed the reliability of the spin-orbit Hamiltonian in systems having many electrons and nuclei. Hameka showed that contrary to often expressed views there is an exact form for the spin-orbit operator in a molecule; the operator contains one-electron and two-electron parts referring to the spin-orbit and spin–other-orbit interactions although it is not yet known which of these terms would dominate a given situation. It did seem apparent that core-approximation wave functions could give fairly good values for spin-orbit matrix elements—an encouraging situation.

Some of the actual spin-orbit mechanisms were discussed by Robin M. Hochstrasser (Pennsylvania) on the basis of high-field, Zeeman-effect studies of singlet-triplet transitions in organic crystals. An interesting feature was the suggestion that molecular spin-orbit coupling frequently occurs by higher-order mixing that involves the zero-point nuclear motions.

The selection rules associated with spin-orbit interaction leading to nonradiative crossing between excited singlet and triplet states were outlined by J. H. van der Waals and M. S. de Groot (Shell, Amsterdam) who concluded that in general this process would be accompanied by spin polarization, leading ultimately to a preferential population of one of the three spin states of the lowest triplet state. These ideas lead into a myriad of interesting experimental phenomena as yet untapped.

Along these lines the EPR-produced (electron paramagnetic resonance) modulation of the phosphorescence of perdeuteronaphthalene was described by M. Sharnoff (Delaware). Sharnoff spoke about how the phosphorescence of oriented molecules becomes modulated by alternately saturating and relaxing the EPR ($\Delta m = \pm 2$) transition. The results clearly demonstrate that the radiative matrix elements connecting the triplet sublevels with the ground state depend on the magnetic quantum numbers for the substates. The success of this experiment is a milestone in understanding metastable states of large molecules. A spin polarization caused by strong selection rules within the intersystem crossing and subsequent radiationless processes was also noted by M. Schwoerer and H. C. Wolf (Stuttgart) in reference to their studies of isotopically mixed naphthalene crystals.

Clyde Hutchison (Chicago) described the uses of EPR and ENDOR electron nuclear double resonance in studying the magnetic properties of organic molecules and crystals. Of particular interest was the story of how one can use ENDOR to examine the detailed protonic environment of a molecule in a magnetically active state. The zero-field splitting parameters for tetramethylpyrazine were reported by J. S. Vincent (University of California, Davis) to be characteristic of a $^3\pi\pi^*$ state, the indication being that the $^3\pi\pi^*$ and $^3n\pi^*$ states are inverted compared with the parent compound pyrazine. The other EPR work presented related to molecules of immediate biological interest such as hematoporphyrin, for which revealing zero-field splittings were reported by M. Ptak, C. Helene and J. M. Lhoste (Florida State).

Gas phase. Some of the symposium's liveliest discussion arose in connection with triplet states in the gas phase. In a number of experimental papers it was agreed that the gas-phase lifetimes of the lowest triplet states of aromatic hydrocarbons are measured (indirectly) to be many orders of magnitude less than the lifetimes known from condensed-phase measurements. It would appear that the change to the gas phase for benzene introduces quite new relaxation paths, for C. S. Parmenter and B. L. Ring (Indiana) demonstrated that this

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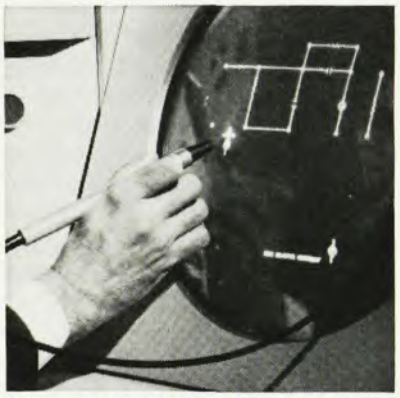
Programming Complex Problems Simply

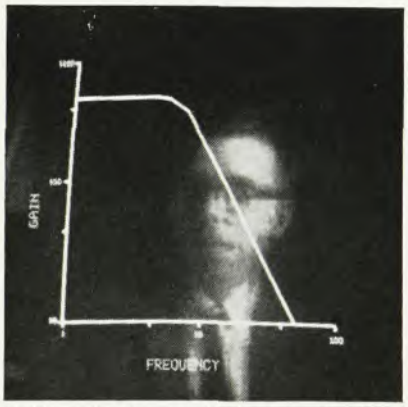
1. A program for GRAPHIC I lets engineer W. H. Ninke draw a circuit diagram on a cathode ray tube, using familiar component symbols.

2. In describing a circuit problem to the computer, he guides nodes (circuit junction points) into place with a light pen.



3. He next guides components into place. Where necessary, he can mark certain ones "variable" by placing a slant arrow across each.

4. With a keyboard, which resembles a typewriter, he inserts the values of the various components and the operating conditions of the circuit.



5. He asks the central computer to use this information to calculate and display a curve of gain vs. frequency response for the circuit.

6. Seeing the curve, he may modify the circuit, insert new values for variable components, request the computer to recalculate performance.

Scientists at Bell Telephone Laboratories have improved communications between engineers studying circuits and the computer that helps them. The key is an experimental console on which the engineer works with familiar graphics: component symbols, performance curves, and so on.

The engineer composes a circuit on a cathode-ray tube, inserts component values, makes certain components variable, as required. The display equipment responds immediately to his commands. As he proceeds, the console displays appropriate operating instructions. At his request, the computer calculates and displays circuit performance. He may adjust the variable components or revise the circuit and call for performance calculation again.

This sophisticated tool is not needed in routine circuit design. Its principal use will be where well established, highly automated design procedures do not exist—for example, when investigating effects of temperature, component tolerances, and stray coupling. The "conversational" ability promises to make this hardware-software system a valuable laboratory tool.

The console itself is GRAPHIC I, a man/machine computer terminal developed at Bell Laboratories. It includes a cathode-ray display, a keyboard for inserting letters or numbers, a light pen for selecting and positioning symbols on the tube, and a small display-control computer. Network analysis is handled by a separate large digital computer on a shared-time basis.

The circuit-analysis program is only one of several compiled for GRAPHIC I at Bell Laboratories. Others help generate integrated-circuit masks, design wiring patterns for magnetic-core logic devices, or retrieve documents. A special compiler (program for making programs) has been developed for GRAPHIC I. It is GRIN—for GRaphic INput.

Based on GRAPHIC I, a new generation of graphic terminals will be installed as part of an overall computer facility at Bell Laboratories.

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lifetime is 2.5×10^{-6} sec at 300° K and 20 torr, under conditions such that diffusion to the walls took much longer than this time. In general these conclusions were supported by the work of R. B. Cundall and A. S. Davies (Nottingham) and B. Stevens, M. S. Walker and E. Hutton (Sheffield).

A rather detailed account of molecular relaxation processes was presented by W. G. Robinson in which he examined the analogy between a solid and a large molecule in which electronic relaxation is efficient as compared with a vibrationally deficient smaller molecule in which electronic relaxation does not readily occur without the intervention of an environment. Benzene was considered as being intermediate between these extremes although the theory does not admit the lifetime anomaly mentioned above. Some general expressions for the vibrational overlap factors that are the crucial portion of the electronic relaxation matrix elements were presented by W. Siebrand (NRC, Ottawa) who was able to derive a simple isotope rule for radiationless transitions involving a change of multiplicity as well as demonstrate the involvement of C-H and C-D stretching.

David L. Dexter (Rochester) and W. B. Fowler (Lehigh) showed radiative lifetimes are influenced by the relaxation processes involving environmental states. Determinations of the quantum yields of intersystem crossing in isolated molecules is a most important endeavor, and a technique dependent on a kinetic analysis of triplet-triplet annihilation processes gave a value of 0.8 for this yield in phenanthrene vapor (G. L. Powell, R. C. Janagin and M. Silver; North Carolina). G. Finger, O. Z. Khamiri, J. Olmstead and A. B. Zahlan (American University, Beirut) presented a new method for measuring the fractional yield of excited singlet states produced by triplet-triplet encounters in the gas phase; they obtained a most interesting result for anthracene vapor in which the fractional yield was found to increase with increasing pressure.

Energy-transfer details for triplet states in rigid solutions and solids represented a significant portion of the symposium. R. E. Kellogg (DuPont) presented some elegant results on the interaction potential linking donor and acceptor molecules involved in triplet-singlet energy transfer; he demonstrated that the transfer efficiency showed no measurable deviation from an inverse-sixth dependence on the distance transferred, indicating the exact behavior predicted by T. Forster some years ago.

Some new notions regarding energy transfer studies arose from the theoretical work presented by J. S. Avery and J. C. Packer (Imperial College) who used a Green's function method to analyze the time-dependent luminescence of a random collection of donor and acceptor molecules. The general area of energy transfer in fluid media was reviewed by C. A. Parker (Admiralty Materials Laboratory), and in crystals—from rare gases to anthracene—by Stuart A. Rice (Chicago).

Since the spin-orbit coupling mechanisms in molecules are complex and not yet subject to confirmation, it is vital to find other methods of knowing properties of triplet state wave functions to test theoretical predictions. One such way is triplet-triplet absorption spectroscopy in which an effective ground triplet level is maintained by external radiation. Careful measurements of intensities and band structure over wide energy ranges are required and such results were in fact presented by Maurice W. Windsor and J. R. Novak (TRW Systems) on molecules in plastics. Some beautiful T-T absorption spectra of anthracene were presented and discussed by R. Astier and Y. H. Meyer (École Polytechnique), who found a reasonably good correlation with known theory in regard to energy and intensity. The polarization of the naphthalene T-T transitions in different solvents was determined by S. Seigel and H. S. Judeikis (Aerospace).

In the realm of new kinds of triplet states, J. Tanaka (Nagoya) demonstrated the presence of strong, localized-triplet-state-electron-transfer-state interactions in certain charge-transfer complexes.

What is the status of the triplet state? It is clear that a decent documentation of properties, especially of dynamic properties now exists. Many new characteristics have become predictable, at least on a semiempirical basis, even though there still exists a great deal of uncertainty with respect to the radiative transition mechanisms: No lifetime calculation has yet been successful. The microscopic theories of radiationless transitions tend to explain only selected phenomena—and whether the unexplained phenomena even relate to the question is not yet certain. We know the triplet skeleton fairly well; only the body remains to be built.

The proceedings of the symposium will be published as: *Proceedings of the International Symposium on the Triplet State,* Cambridge University Press (1 Sept. 1967).

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High-Energy Symmetry Principles at Coral Gables

Participants at this year's Coral Gables conference on Symmetry Principles at High Energy placed their bets on current algebra and superconvergence with Regge poles making a good recovery. Several papers were devoted to obtaining mass spectra with infinite representations of noncompact groups. The useful though reluctant quarks that have been discussed at previous conferences of this series, provide a more easily visualized realization of the abstract hadron symmetries, but they failed to appear explicitly at this conference. Nevertheless the apparitions of these ghost-like creatures could be seen to walk in the famous current-commutation relations proposed by Murray Gell-Mann.

The conference, which was held last January for the fourth successive year, was under the auspices of the University of Miami Center for Theoretical Studies and also had sponsorship from five government organizations.

The current-commutation relations are algebraic equations, postulated to hold at a given time among a set of generalized currents—namely, an octet of four-vector currents and an octet of axial four-vector currents that are assumed to have SU(3) transformation properties. (In a more conservative version, the equations are postulated