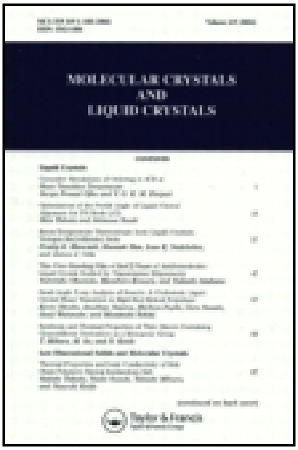

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
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The Scientific Contributions of Martin Pope

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Martin Pope is one of the founding fathers in the field of organic conductivity. He entered the field in 1956 and has made seminal contributions in almost every area. In reviewing these contributions, one is struck by the simplicity and the elegance of his experimental techniques and the broad range of phenomena that have either been discovered or explained by him and his co-workers. Rather than providing a chronological account of Professor Pope's contributions, we decided to summarize his work in terms of the different research areas to which he has contributed.

A. EXPERIMENTAL TECHNIQUES

1. Crystal growth

Though it was evident even in the earliest days that more reproducible conductivity measurements could be made by using pure single crystals of anthracene rather than compressed powder pellets or melts, no easy method had been developed to grow these crystals. In addition, since anthracene is an insulator, the task of measuring small currents using a modest voltage supply would be simpler if the crystals were thin. It was therefore noteworthy when in 1958, Pope and Kallmann[1] developed a novel and simple technique for growing thin (5–50 μ thick) crystals with an area of 0.5 cm^2 or more. This method involved crystal growth in solution in a density gradient made up of a solution of anthracene in ethylene dichloride, covered by a blanketing layer of xylene. The density gradient was centered around the density of anthracene, so minute convection currents made it possible for crystals of different sizes to become separated from each other. This made it easy to pick out each crystal. This method is still in use.[2]

2. Electrolytic contacts

Another obstacle to making conductivity measurements was that of making good transparent conducting contacts to the crystal. Pope solved this problem by developing the Pope-Kallmann Cell,[3] in which electrolyte solutions were used as contacts for the first time. This was done[2] by mounting a crystal so that it covered a hole in a piece of thin plastic. The crystal was fastened securely by a thin film of grease that surrounded the hole; the plastic sheet bearing the crystal was then used as a separator between two compartments that contained electrolyte solutions. With this Pope-Kallmann Cell, the modern study of the electrochemistry of organic crystal and polymer electrodes began.[3]

3. Photoemission

Perhaps his most elegant contribution to experimental techniques was in the adaptation of the Millikan oil-drop apparatus to elaborate the ionized energy level structure and other properties of small single organic crystals in the size range 5–50 μ. This is now an active field, and its origins can be traced to the papers of Pope *et al.*[4] in which he described how the extremely sensitive Millikan capacitor technique could be used to determine essentially all of the ionic energy levels in organic crystals, and even the dynamics of exciton motion.[5] The original Millikan-Pope apparatus was later modified (Millikan-Pope-Arnold apparatus[6]) to enable the suspended particle to be held in place by a feed-back servo-mechanism.

4. Photophoretic spectroscopy

Pope, Arnold and Rozenshtein,[7] using the MPA apparatus, made the seminal discovery of Photophoretic Spectroscopy, a new method for obtaining the absorption spectrum and hence determining the identity of a single particulate. With this technique, the radiationless absorption spectrum of single particulates, weighing less than 1 ng could be obtained. The principle of photophoretic spectroscopy was characteristically simple. When a particulate is suspended in the MPA apparatus in a N_2 atmosphere at a pressure of about 0.2 atm. it essentially becomes a radiometer. Thus, if the top surface of a suspended particle is exposed to light of varying photon energy, this surface will be heated to a degree determined by the amount of energy absorbed at each wavelength. The heated surface imparts additional reflecting momentum to impacting gas molecules, causing in turn a transfer of momentum to the particle, forcing it out of its equilibrium position. The particle is automatically restored to its new equilibrium position by the feed-back mechanism, and the force (electric field) necessary to accomplish this maps out the radiationless absorption spectrum of the material.

B. PHOTOCONDUCTIVITY

Using the Pope-Kallmann cell[3] and the thin anthracene crystals, Pope and his colleagues made a series of basic discoveries in the field of photoconductivity. First was that of the photovoltaic effect in organic crystals[4]; this was an example of the

Dember effect, in which a plasma of holes (created by light on one side of the crystal) diffused into the dark region of the crystal. The diffusion is eventually halted by the build-up of an internal field that opposes the further diffusion of the holes. This field is measured as the photovoltage. In view of present day energy needs, the importance of photovoltaic studies is obvious.

A classic paper by Kallmann and Pope[8] in 1960 marked the discovery of charge injection into organic crystals in particular and into organic insulators in general. This discovery made possible the beginning of the systematic study of space charge limited currents in organic materials by Mark and Helfrich.[9] It also marked the discovery of sensitized charge injection in which a thin layer of solution (an I_3^- solution) in contact with the anthracene crystal became the source of holes that were injected into the anthracene crystal. The I_3^- solution was activated by light to which the anthracene was completely transparent. This development foreshadowed the modern electrophotography technique in which a two-layer photoconductor is used[10]; the top layer is the charge-generating layer and the bottom layer is the charge-transport layer. In a recent review of electrically conducting polymers,[11] this 1960 paper by Kallmann and Pope was singled out as the classic paper that stands at the base of attempts to use organic materials as conducting electrodes in the course of preparing highly conducting polymers and superconductors.

Also in 1960, the theory of the energetics of charge injection was first described by Kallmann and Pope,[12] and dark-injecting electrolytic contacts were discovered.[13] The dark-injecting contact consisted of a solution of the oxidizing agent Ce^{4+} (aq) and it was immediately evident that contacts with a wide range of work functions could be made, simply by choosing well-known electrolytic redox systems, using the energetic principles already outlined.[12]

C. PHOTOEMISSION

In 1962, Pope *et al.* introduced the use of the Millikan-Pope capacitor technique[4] for studying photoemission from organic crystals. The significant and original step taken by Pope was to combine the Einstein photoelectric equation and the Millikan equation, which made possible the discovery of a two-quantum process for photoemission in organic solids.[14] This was the first such observation in organic solids. The two-quantum process (referred to as the double-quantum external photoelectric effect (DQEPE)) first seen in anthracene was the first unequivocal demonstration of the fusion of two singlet excitons to create free charge carriers.

D. CARRIER GENERATION

In the early 1960's there was still uncertainty as to whether the bandgap energy of anthracene was greater than or less than that of the singlet exciton.[15] This uncertainty was removed by the discovery of electroluminescence in anthracene by Pope *et al.*[16a,16b] In the latter paper,[16b] Sano and Pope demonstrated that the electroluminescence (which was identical to the fluorescence) was produced by the recombination of holes and electrons; it could therefore definitely be concluded that the band gap energy was greater than 3.1 eV.

As for the basic mechanism of the intrinsic carrier generation in anthracene, it was assumed at that time to be the same as it was in inorganic solids, namely a band-to-band transition.[17] However, in a series of experiments making use of the DQEPE (Pope and Burgos[18]) and the lack of dependence of the intrinsic carrier generation process on the absorption coefficient of light (Geacintov and Pope[19]), it was shown that the band-to-band theory was untenable and that for energies greater than the band-gap, an autoionization of a super-excited Frenkel state was the more appropriate model for the initial step in the intrinsic ionization process. This is the most widely accepted theory of the ionization process in anthracene for photon energies greater than the band gap energy.

E. EXCITONS

A dominant feature of organic van der Waals solids is the prevalence of excitonic phenomena. Excitons make possible the temporary storage and transfer over relatively large distances of electronic excitation in the eV range. The vital process of photosynthesis depends on excitons to transport the photon energy within the antenna chlorophyll system to the active center.

In the 1960's, in keeping with the then current intense interest in the theory of excitons in organic crystals, the existence of a metastable nearest-neighbor hole-electron pair, referred to as a charge-transfer (CT) exciton was postulated.[20] According to theory, the existence of the CT exciton would be difficult to verify because the absorption coefficient for this state was anticipated to be about 10^{-5}cm^{-1} and the lifetime of this state was predicted to be less than 1 ns. However, in 1965, Pope, Burgos and Giachino[21] announced the discovery of a CT exciton in tetracene, using the DQEPE. The experiment was simple; a DQEPE was observed in tetracene only when the photon energy exceeded 2.9 eV, and the photoemission yield (Y) varied as the square of the light intensity (I^2). Since the fusion of two singlet excitons produced an energy of only 4.6 eV, and the ionization energy of tetracene was 5.3 eV, this singlet exciton mechanism for photoemission was ruled out. The photons of energy greater than 2.9 eV could however produce hole-electron pairs, so in principle, ionized states could be involved in the photoemission. The interaction of a photon or an exciton with a free or trapped carrier could be ruled out because this would result in $Y \rightarrow I^{1.5}$, which was not observed. Furthermore, the maximum kinetic energy of the emitted electron in tetracene was constant and independent of photon energy, so photon involvement in general was ruled out.

Energetically, only a CT exciton at about 2.9 eV fusing with another CT exciton would satisfactorily explain the observed results, and it wasn't until Sebastian, Weiser and Bassler[21] perfected the technique of electroabsorption sixteen years later that the CT state was observed by a means other than the DQEPE. The CT state is now presumed to precede all ionization processes near the threshold energy, and all processes of carrier-pair recombination.

In the years following 1967, Pope maintained his interest in excitons and in their interactions with each other and with carriers. Some of his notable contributions in this period were the following: in 1969, the fission of a singlet exciton into two triplet excitons was discovered (Geacintov, Pope, and Vogel[23]; Pope, Geacintov and Vogel[24]). This marked the confirmation of the brilliant prediction by Swenberg and Stacy[25] that the low fluorescence efficiency of tetracene crystals was due to a spin-allowed decay of a singlet exciton into two triplet excitons. The fusion of two triplets to form a singlet exciton in anthracene had been discovered previously by Sternlicht, Nieman and Robinson.[26] In addition, a seminal discovery was made by du Pont scientists[27] that a modest magnetic field would alter the efficiency of reactions involving triplet excitons and other paramagnetic species. Using the magnetic field technique, Geacintov, Pope and Fox[28] showed that the triplet exciton detrapping of charge carriers could be modified by means of the magnetic field.

Again using the magnetic field technique, Geacintov *et al.*[29] discovered another channel for the decay of an exciton, namely heterofission of a singlet exciton into two different triplet excitons in doped organic crystals. In a pentacene-doped tetracene crystal, a singlet exciton in the tetracene lattice dissociated into a tetracene triplet exciton and a pentacene triplet state upon coming in contact with the pentacene impurity.

The discovery of singlet exciton fission was made use of in an ingenious experiment that anticipated much of the present interest in the kinetics of excitonic reactions in restricted domains. Such domains exist in biological systems such as cells and cell nuclei. Pope conceived of a plan to create fenced-in domains, or cages, of molecular dimensions, in which pairs of triplet excitons would be created. This was accomplished by Arnold *et al.*[30,31] who discovered that the rate constant of exciton-exciton reactions could be increased if the excitons were confined in the lattice cage. The cages were generated by preparing mixed crystals of tetracene and 2,3-benzocarbazole (BC). The BC molecules acted as tetracene exciton reflectors by virtue of the higher energy BC exciton levels. By illuminating the mixed crystal with tetracene singlet-generating light, singlet exciton fission ensued, producing a pair of triplet excitons in the domains that were partially caged by BC molecules. Making use of one of the first applications of computer simulation to model a kinetic experiment in organic crystals, it was shown that exciton recombination was enhanced.

In his most recent work involving excitonic states, Pope postulated the existence in tetracene crystals of a metastable excitonic ion, consisting of a complex of a charge-transfer (CT) exciton and an electron.[32,33] The experimental evidence consisted of a DQEPE that occurred only when the photon energy exceeded the band gap energy, did not involve Frenkel excitons or photons as reactive mobile species, depended on the light intensity I according to a $I^{1.5}$ dependence, and produced a photoelectron with a maximum kinetic energy that corresponded to the Auger ejection of a conduction electron by the recombining hole-electron pair in an exciton ion complex. Theoretical calculations have been made by Andreev and Pope[34] and by Munn, Mabbot, and Pope[35] that support the existence of a metastable excitonic ion.

F. CARRIER RECOMBINATION

Unlike the situation in silicon and germanium, the efficiency of photogeneration of carriers in anthracene and other polyacenes is small (10^{-4}). It eventually was shown that rapid carrier recombination was the main reason for this low efficiency. Geacintov, Pope and Kallmann[36] were the first to conclude from their photoconductivity experiments that the dominant reason for a low-efficiency of bulk carrier-generation in tetracene was carrier recombination that was kinetically first-order and strongly field-dependent, due to the close proximity of newly created carrier pairs. As it turned out, Onsager[37] in 1938 published a theory of ion-recombination in insulating liquids called geminate or kinetically first-order recombination that was shown conclusively by Chance and Braun[38] to be the correct theory to be used to describe carrier-generation in anthracene, and in similar organic insulating solids.

A key boundary condition for the Onsager 1938 theory was the requirement for instantaneous recombination of the geminate pair at the origin. In 1934, Onsager also considered the effect of an external field on the ionization constant of a weakly dissociating compound, such as acetic acid.[39] Recently, this 1934 Onsager theory has been used to explain the field dependence of the carrier yield when the final state of recombination was a small radius charge transfer exciton or exciplex with a relatively long lifetime.[40] The importance of using the Onsager 1934 theory instead of the 1938 theory in such cases was first pointed out by Geacintov and Pope,[41] and by Pope and Swenberg.[42] However, the definitive application of the Onsager 1934 theory to this problem was made by Braun.[40] This has cleared up the apparent paradox in which the electron-hole thermalization distance in donor-acceptor (DA) crystals was calculated to be 2 to 3 nm (using the Onsager 1938 theory) when it was known that the nearest neighbor separation of the initial optically excited CT state was only 0.5 nm; the 1934 theory was able to justify the observed ionization efficiency of the DA crystals without invoking large thermalization distances.

G. PHOTOSYNTHESIS

Since exciton phenomena played an important role in the chlorophyll photosynthetic unit, an external magnetic field was used by Geacintov *et al.*[43] on Chlorella in aqueous suspension. The fascinating result was the discovery of a new mechanical effect of the magnetic field, in that the Chlorella organism was rotated so that the planes of the chlorophyl molecules were perpendicular to the external magnetic field. This confirmed that the chlorophyll molecules were oriented in a specific direction in the thylakoid membrane.

Further work by Swenberg, Geacintov and Pope[44] on the behavior of excitons in the photosynthetic unit showed for the first time that singlet excitons could be quenched by other singlet excitons at incident light intensities that could be generated by bright sunlight.

H. ELECTROCHEMISTRY

The first attempt at a quantitative treatment of the dynamics of charge exchange at the electrolyte organic crystal interface was made by Kallmann and Pope in 1962.[45] In this paper, two important concepts were introduced, namely, the existence of an image potential well inside the anthracene crystal, and the subsequent enhancement of the recombination velocity of the injected hole with the solution electrode. These properties were major reasons for the differences between organic crystals and metal electrodes. These ideas were more completely developed by Willig and Charle, and Willig *et al.*[46]

The all-important development of electrolytic electrodes for the organic crystals, with the further discovery of dark and photo injection of carriers, and of sensitized photoinjection have already been described. More recently, Pope turned his attention to the chemical reactions that occurred during the passage of current across the crystal/aqueous solution interface. According to Faraday's Laws, at the boundary where the current flow changes from electronic to ionic, there must be an oxidation-reduction reaction. Thus at a crystal/water interface where holes are discharged, there must be an oxidation reaction. This oxidation takes place on the crystal surface or in the aqueous phase, producing in the former case various oxidation products of anthracene, and in the latter case, H_2O_2 and/or O_2. In an early study by Jarnagin *et al.*,[47] no generation of O_2 was found, but there was ample evidence of surface oxidation to produce anthraquinone and other products. However, by increasing the current flow, Pope and Slotnick[48] demonstrated that H_2O_2 and O_2 were indeed generated in the aqueous phase. These electrolytic reactions will have to be taken into account in designing stable conducting polymers, particularly those intended for use in batteries.

I. LITERATURE

In 1982, the book "Electronic Processes in Organic Crystals" by Pope and Swenberg was published by Clarendon Press of Oxford University. In the words of C. B. Duke who reviewed this book,[49]

> "[it] sets the standard for reference texts in the field . . . Its unique combination of broad scope, together with detailed treatments of modern topics and recent data, renders it a singular contribution to organic solid state physics."

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