Electroluminescence and Band Gap in Anthracene

MIZUKA SANO, MARTIN POPE, AND HARTMUT KALLMANN
Department of Physics, Radiation and Solid State Laboratory
New York University, New York, New York

(Received 14 December 1964)

IN this paper, we describe the occurrence of delayed electroluminescence (EL) and give evidence that $E_{c'}$, the energy of the lowest state that is conducting in anthracene, is greater than 3.1 eV.[1]

The electrodes consisted of a silver–epoxy-paste electrode (called the point electrode), about 2 mm in diameter, on one side of a crystal (typically 20 μ thick) and a transparent vacuum-evaporated silver electrode on the opposite side.

There was a voltage range in which light was emitted from the point electrode regardless of its polarity.[2] At a lower voltage range, light was emitted only when the point was negative. We worked only in the lower voltage range.

Upon application of a (1-cps) ac voltage to the crystal, EL appeared as small bright spots at the cathode. Upon application of a negative voltage pulse 10^{-7} sec in duration a delayed EL was observed, in which an appreciable fraction of the total light output appeared after the applied voltage disappeared, sometimes in the form of a second peak. The spectrum of the delayed EL was checked only at 421 and 444 mμ, and there were EL maxima at both wavelengths. We assume from this that the energy origin of the delayed EL is at least as high as the excited singlet state.

The appearance of the second peak led us to the conclusion that the delayed EL was caused by the recombination of carriers. In order to show that charge-carrier recombination produced delayed EL also in those crystals that were without the second peak, the following experiment was performed.[3]

A second voltage pulse (V_2) of variable duration was applied (within 1 μsec) after the first voltage pulse (V_1). In one case, V_2 had the same polarity as V_1 ($+V_2$), and in the other case, V_2 was of opposite polarity to V_1 ($-V_2$). The voltage V_2 produced no EL in the absence of V_1. The results are shown in Fig. 1.

The electric field of V_2 strongly modified the delayed EL; the delayed EL decreased during the duration of ($+V_2$), and a new EL peak appeared upon the disappearance of ($+V_2$). At the onset of the application of ($-V_2$), the delayed EL was enhanced and dropped eventually to a level below that produced by V_1 alone.

We take these results as evidence that an appreciable part of the delayed EL is caused by carrier recombination; singlet formation by triplet–triplet annihilation can occur in addition. The first voltage pulse (with point electrode negative) is responsible for the creation of pairs of free carriers, not all of which are discharged during the duration of V_1. The separated carriers set up an opposing polarization field, producing the polarization voltage V_p, and, on the disappearance of V_1, carrier recombination takes place. The second pulse ($+V_2$) prevents this recombination ($\therefore V_2 > V_p$), transposing the delayed EL peak to the end of V_2, but the pulse ($-V_2$) together with V_p, assists in the recombination. We conclude that the electrons are in the normal conduction level because V_p is the only voltage present during the delayed EL produced by V_1. Since V_2 alone produces a current equal to the normal dark current, and $V_2 > V_p$, V_p cannot accelerate an electron. Thus, recombination occurs between holes and electrons that are either in the lowest conduction level or were released from traps. Since the spectral maxima of the delayed EL were those of the normal fluorescence, $E_{c'} > 3.1$ eV. Thus, photoconductivity observed at an energy less than 3.1 eV[1] is not due to an intrinsic monomolecular process.

This conclusion in regard to $E_{c'}$ is independent of the mechanism of carrier generation; however, the holes are not produced by injection because EL occurs only with point negative, and close to the cathode. Also, the

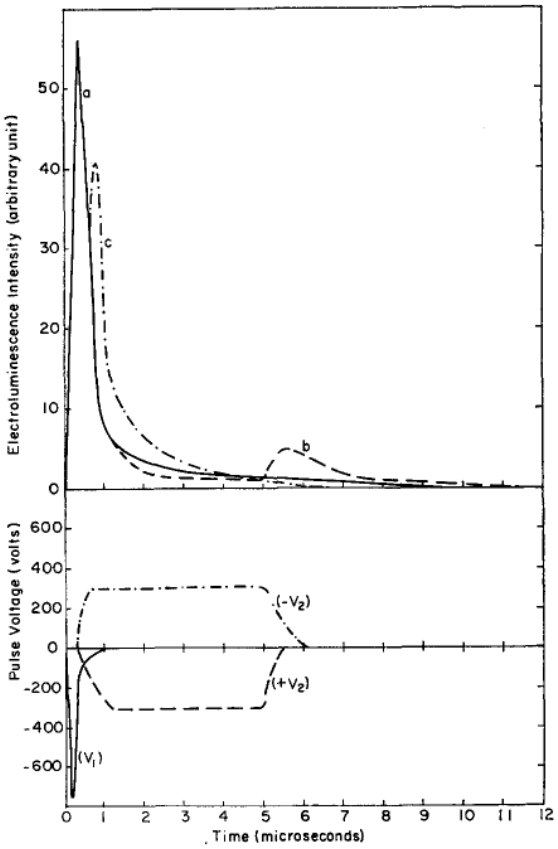


FIG. 1. Effect of electric field on delayed electroluminesecnce in anthracene crystal. Top: a, $(V_1) = 780$ V, $(V_2) = 0$ V; b, $(V_1) = 780$ V, $(+V_2) = 320$ V; c, $(V_1) = 780$ V, $(-V_2) = 320$ V. Crystal thickness: 20 μ; temperature: -67°C; pressure: 10^{-6} mm Hg. Bottom: Pulse (V_1) width: 0.1 μsec; pulse (V_2) width: 4.4 μsec.

Downloaded 09 Aug 2013 to 128.104.1.219. This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://jcp.aip.org/about/rights_and_permissions

BOE v. Samsung IPR2025-01479
Ex-1023

thermal equilibrium density of holes is practically zero at these temperatures; furthermore, holes cannot gain energy in the field due to the narrowness of the hole band.[4] Thus, the only possibility of producing holes is from accelerated electrons. Since the normal electron band is narrow[4] (~0.1 eV), no effective acceleration can take place in this band. We conclude that the acceleration takes place by injection of the electrons into an upper and broad electron conduction band, where they can gain energy.

We wish to acknowledge the valuable contribution of Robert Laupheimer in designing our electronic equipment and for stimulating discussions.

This work was supported by the U.S. Office of Naval Research, using materials prepared with U.S. Army Research Office support.

[1] (a) For a review of band gap studied, see L. E. Lyons, in *Physics and Chemistry of the Organic Solid State*, edited by D. Fox, M. M. Labes, and A. Weissberger (John Wiley & Sons, Inc., New York, 1963). (b) R. G. Kepler, Phys. Rev. **119**, 1226 (1960).
[2] M. Pope, H. Kallmann, and P. Magnante, J. Chem. Phys. **38**, 2042 (1963).
[3] This experiment was performed after submission of this paper.
[4] J. L. Katz, S. A. Rice, S. Choi, and J. Jortner, J. Chem. Phys. **39**, 1683 (1963).

Electron Spin Resonance Transitions Involving Simultaneous Changes in Spin States of Two Neighboring Protons*

WALLACE SNIPES AND WILLIAM BERNHARD
Department of Biophysics, The Pennsylvania State University University Park, Pennsylvania

(Received 6 July 1965)

SATELLITE lines arising from simultaneous changes in the spin state of a single proton and the spin state of the unpaired electron are occasionally seen in electron spin resonance spectra. These transitions, first detected in irradiated frozen acids,[1] are induced by a weak dipole–dipole coupling between the electron magnetic moment and the magnetic moment of the neighboring proton. During the investigation of the ESR of an irradiated single crystal of barbituric acid dihydrate, we have observed an additional set of satellite lines which arise from changes in the spin states of two neighboring protons concurrent with the change in spin state of the unpaired electron. These transitions have been predicted by Trammell *et al.*[2] but to our knowledge have not been observed in ESR spectra of free radicals.

Gamma irradiation of barbituric acid dihydrate produces a free radical having an unpaired electron localized mainly in a $2p\pi$ orbital on a carbon atom.[3] Hyperfine interaction with a single proton splits the absorption into a doublet. This doublet is shown in Fig. 1(a) for an orientation of the crystal in the magnetic field for which all four molecules per unit cell[4] are magnetically equivalent. At higher spectrometer sensitivity [Fig. 1(b)], satellite lines appear corresponding to a change in spin state of a single proton along with the change in spin state of the electron. The separation of these satellite lines from the main hyperfine lines, in frequency units, is close to the proton resonance frequency for the particular magnetic-field strength at which the observation is made.[2] Calculated values of this separation for magnetic-field strengths of 3030 and 3390 G are 4.6 and 5.2 G; our observed values for these splittings are 5.3 and 5.8 G. The separation of the satellite lines from the main hyperfine lines is independent of the orientation of the crystal in the external magnetic field.

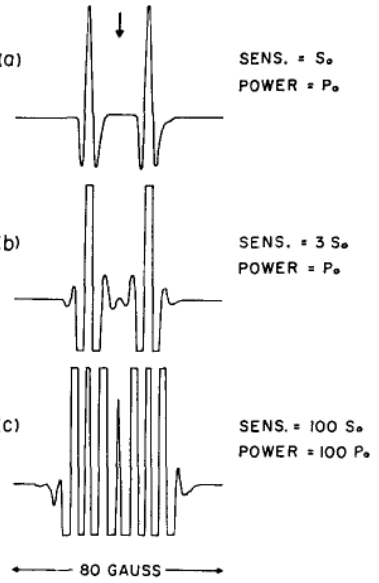


FIG. 1. Second-derivative ESR tracing of an irradiated single crystal of barbituric acid dihydrate with the external magnetic field in the crystallographic *bc* plane. The magnetic-field intensity increases from left to right, with the arrow indicating the field position of the resonance of DPPH for which $g=2.0036$. Relative spectrometer sensitivities and microwave power levels are indicated for each tracing. Observations were made at a microwave frequency of 9510 Mc/sec.

Figure 1(c) shows a spectrum taken at an even higher spectrometer sensitivity so that the set of satellite lines shown in Fig. 1(b) is now off scale. Within experimental error, the additional satellite lines which now appear are separated from the original satellite lines by exactly the same amount that the original satellite lines are separated from the main hyperfine lines. This was observed at magnetic-field strengths of both 3030 and 3390 G. Although there should be eight of these satellite lines corresponding to changes in spin states of two protons, four of them fall identically under the main hyperfine lines. While the most clearly resolved of these lines are those which lie outside the remainder of the spectrum, the line at the center of the spectrum is actually a superposition of two of these satellite lines. If it were possible to make observations at crystal orientations for which

Downloaded 09 Aug 2013 to 128.104.1.219. This article is copyrighted as indicated in the abstract. Reuse of AIP content is subject to the terms at: http://jcp.aip.org/about/rights_and_permissions

BOE v. Samsung IPR2025-01479
Ex-1023