DESTRUCTION OF TRIPLET EXCITONS IN ANTHRACENE BY INJECTED ELECTRONS*

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It is well known that triplet-singlet intersystem crossing rates can be greatly enhanced by the presence of paramagnetic impurities such as oxygen molecules. Free charge carriers may be anticipated to act similarly. The present note demonstrates the destruction of triplet excitons in anthracene crystals by interaction with electrons. The electrons were introduced by means of space-charge-limited (SCL) currents, and caused a decrease of the triplet exciton lifetime.

Triplet excitons in anthracene are known to decay at low concentrations by a radiationless monomolecular process with a lifetime of about 20 msec.[1,2] Concentration and lifetime are measured via the delayed fluorescence, an emission that is due to singlet excitons (3.1 eV) which are generated by bimolecular recombination of a few of the triplets (1.8 eV). Let us assume that SCL electron currents are injected into the sample and that the carriers are not trapped. Then the triplet lifetime τ should obey the relation

$$\frac{1}{\tau}-\frac{1}{\tau_0}=\kappa n_e, \tag{1}$$

with

$$n_e=\epsilon\epsilon_0 V/eL^2. \tag{2}$$

Here τ_0 is the lifetime without injected electrons,[3] κ is the rate constant of the bimolecular exciton-electron reaction destroying triplets, n_e is the electron density,[4] ϵ is the dielectric constant ($=3.4 \parallel c'$ axis which was the direction of current flow[5]), e is the elementary charge, V is the applied voltage, and L is the crystal thickness.

Crystal growth and the method used for electron injection have been described elsewhere.[5] The triplet excitons were generated[6] by the intermittent light[7] of a continuous laser (6328 Å, circa 0.03 W, beam cross section roughly 0.1 cm^2). The beam shone through a fused-quartz plate, an aqueous solution of NaOH serving as noninjecting electrode, and the crystal. It was absorbed by the dark blue injecting contact.[5] In the crystal the beam was parallel to and within the current path, the cross section of the latter being about 0.3 cm^2. The photomultiplier serving as detector had a blue filter in front of it in order to keep off a weak red or infrared phosphorescence of materials hit by stray light from the laser beam. The decay of the fluorescence intensity I with time t after a pulse of exciting light fitted satisfactorily an exponential law and the relation $I\propto\exp(-2t/\tau)$ was used to determine the triplet lifetime.

The dependence of $1/\tau$ on V is shown for four different crystals (out of eight) in Fig. 1.

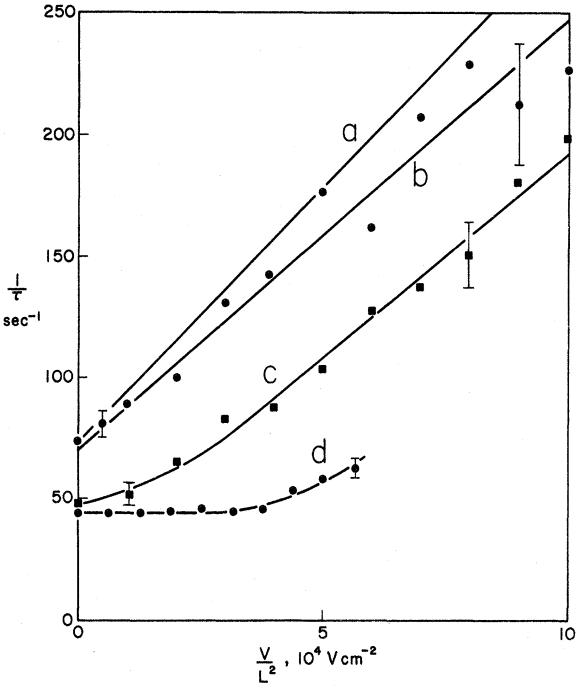

FIG. 1. Reciprocal triplet lifetime versus applied voltage for four crystals. The thicknesses were for *a*, *b*, and *c*, 1.4 mm; for *d*, 4.0 mm. As curves *a* and *b* almost coincide, the data of crystal *a* are not shown. (The limits of error of the data of crystal *a* are comparable to those of crystal *c*.) V/L^2 is used instead of V as abscissa. It is proportional to the carrier concentration which is the physically relevant variable. 1×10^5 V cm^{-2} corresponds to roughly[4] 2×10^{11} electrons per cm^3.

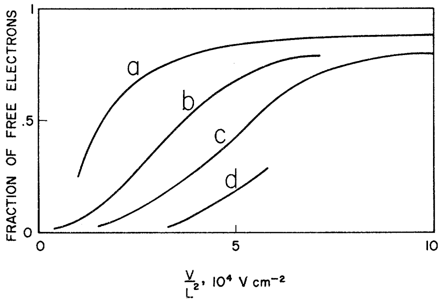

FIG. 2. Fraction of free electrons. The crystals were the same as in Fig. 1.

The fraction of free electrons is plotted for the same crystals in Fig. 2. It was taken to be the ratio of the actual current (as observed when a lifetime was measured) to the theoretical current that would flow without trapping (taking the electron mobility to be 0.4 cm^2 V^{-1} sec^{-1}).[5,8] The ratio could be determined with an accuracy of about ±15%. With seven crystals a linear rise of $1/\tau$ with V was observed at high voltages where most of the electrons were free. (It was not obtained with crystal d where apparently the voltage range was too short.) The slope of this portion, when plotted versus V/L^2, did not scatter by more than ±15% though L varied from 1.2 to 2.9 mm. κ may be derived from the *slope* after replacing $(1/\tau - 1/\tau_0)$, n_e, and V by $\Delta(1/\tau)$, Δn_e, and ΔV in Eqs. (1) and (2). The result is

$$\kappa = 1.1 \times 10^{-9}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}\ (\pm 30\%).$$

Since at the higher charge densities most of the electrons were free this value should be the rate constant of triplet destruction by free electrons. It was not possible to extend the measurements to higher values of V/L^2. There the lifetimes were too short to be determined with reasonable accuracy and the crystals warmed up because of the high voltages and currents required.

Theory indicates that the thermal velocity of electrons[9] is much larger than that of triplet excitons[10] in anthracene crystals. In conjunction with our large value of κ this suggests that the electron velocity may be the rate-determining quantity in triplet destruction.[11] Consistent with such a picture, trapped electrons are apparently less efficient than free electrons in destroying triplets. (See left half of Figs. 1 and 2.) This effect is clearly displayed by crystal d; it seems, however, weak or absent with crystals c, b, and a where perhaps extended structural defects[12] trap but do not completely immobilize the electrons.

Applying a voltage did not change the triplet lifetime when the electron-injecting contact was positive or when both contacts were noninjecting.

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[1] R. G. Kepler, J. C. Caris, P. Avakian, and E. Abramson, Phys. Rev. Letters 10, 400 (1963).

[2] S. Singh, W. J. Jones, W. Siebrand, B. P. Stoicheff, and W. G. Schneider, J. Chem. Phys. 42, 330 (1965).

[3] Part of the triplet excitons may diffuse to and decay at the crystal surface [R. G. Kepler and A. C. Switendick, Phys. Rev. Letters 15, 56 (1965)]. Simple considerations show that this could lead to a τ_0 smaller than the intrinsic value but would not affect the dependence of $1/\tau - 1/\tau_0$ on n_e.

[4] It can easily be shown that without trapping the average carrier density under SCL current flow is $(\frac{3}{2})\epsilon\epsilon_0 V/L^2 e$ [see, e.g., N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, England, 1940), p. 172]. The density varies as $(x/L)^{-1/2}$, where x is the distance from the injecting electrode. While the concentration is infinitely large at the injecting electrode (idealized boundary conditions are used), it is only $\frac{1}{2}$ of the average value at the exit electrode. Triplets generated near the injecting contact may be neglected, as they decay much faster than the other excitons because of a larger electron concentration. For this reason the density adopted in Eq. (2) seemed a more realistic average than the theoretical value.

[5] W. Helfrich and W. G. Schneider, Phys. Rev. Letters 14, 229 (1965); and to be published. In the second paper it is shown that at least several percent of the injected electrons are always trapped in steady-state current flow (possibly by structural defects).

[6] For the excitation spectrum of anthracene see P. Avakian, E. Abramson, R. G. Kepler, and T. C. Caris, J. Chem. Phys. 39, 1127 (1963).

[7] The apparatus, a "phosphoroscope" similar to that described in Ref. 2, was designed by F. R. Lipsett, who kindly lent it to the author.

[8] R. G. Kepler, in *Organic Semiconductors: Proceedings of an Inter-Industry Conference*, edited by J. J. Brophy and John W. Buttrey (The Macmillan Company, New York, 1962), p. 1.

[9] R. Silbey, J. Jortner, S. A. Rice, and M. T. Vala, J. Chem. Phys. 42, 733 (1965).

[10] J. Jortner, S. A. Rice, J. L. Katz, and S.-I. Choi,

J. Chem. Phys. 42, 309 (1965).

[11] Assuming a diffusion-controlled process one may write $\kappa = (\frac{1}{3})vz\sigma$. $\sigma \approx 2.5\times10^{-15}$ cm^2 is the geometric cross section of an anthracene molecule. The factor $\frac{1}{3}$ is needed because only encounters where the total spin is $\frac{1}{2}$ (atomic units) can lead to triplet destruction. z, which we may assume to be 8, is the number of configurations of two neighboring molecules (one occupied by a triplet exciton, the other by an electron) which allow reaction. Insertion yields a thermal electron velocity $v \approx 1\times10^6$ cm sec^{-1}. This agrees well with the theoretical value.[9]

[12] W. Helfrich and F. R. Lipsett, J. Chem. Phys. 43, 4368 (1965).

FOUNDATIONS FOR HARTREE-FOCK CALCULATIONS WITH SINGULAR POTENTIALS*

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It has been clear for some time that the application of the Hartree-Fock method to the problems of nuclear structure would provide a natural foundation for the discussion of most nuclear properties. The fact that two-body forces which fit the scattering data are strongly repulsive at short distances has made a direct application of the Hartree-Fock method impossible and thus various groups have tried to construct velocity-dependent or nonlocal potentials for which the Hartree-Fock method may be applied. These potentials have only had a qualitative success when applied to nuclear structure problems. Also, calculations using reaction matrices taken from infinite nuclear matter calculations have had rather limited success and are also computationally difficult.

Recently, investigations of the effective interaction in finite nuclei using realistic forces have been performed using a unitary model-operator approach.[1] Using this approach we, in this paper, try to provide a theoretical foundation for the application of effective interaction in the nuclear Hartree-Fock calculations. Two important advantages of this method over a reaction-matrix approach are (1) the fundamentally Hermitian character of the effective Hamiltonian generated and (2) the absence of rearrangement terms in the calculational procedure.

It has been shown previously[1] that the application of a unitary operator, e^{iS}, to a set of uncorrelated basis states leads to an effective Hamiltonian of the form

$$\tilde{H} = e^{-iS}He^{iS} = \sum t_{\alpha\beta}a_\alpha^\dagger a_\beta + \tfrac{1}{2}\sum a_\alpha^\dagger a_\beta(\alpha\beta|e^{-iS}(t_1+t_2+v_{12})e^{iS}-(t_1+t_2)|\gamma\delta)a_\delta a_\gamma + \cdots. \tag{1}$$

The highest order terms in the cluster expansion implied in Eq. (1) can be shown to be quite small if the correlations induced by e^{iS} are of sufficiently short range. Indeed, the requirement of convergence of the cluster expansion leads directly to the introduction of a generalized separation method[2] approach for defining the short-range correlation structure.

It is useful at this point to add the following expression[1] to the matrix element in Eq. (1):

$$(\alpha\beta|e^{-iS}(U_1+U_2)e^{iS}-(U_1+U_2)|\gamma\delta). \tag{2}$$

It is easily seen that for the short-range correlations we define below, the added term makes a negligibly small contribution to the energy. We require the single-particle potentials U_1 and U_2 to have the harmonic-oscillator form: $U_1 = \frac{1}{2}kr_1^2$, $U_2 = \frac{1}{2}kr_2^2$.

We introduce the solutions of the following problem:

$$(t_1+t_2+U_1+U_2+v_{12}^{S})\Psi_{n_1n_2}(\vec{r}_1,\vec{r}_2) = (\epsilon_{n_1}+\epsilon_{n_2})\Psi_{n_1n_2}(\vec{r}_1,\vec{r}_2),$$

$$(t_1+t_2+U_1+U_2)\Phi_{n_1n_2}(\vec{r}_1,\vec{r}_2) = (\epsilon_{n_1}+\epsilon_{n_2})\Phi_{n_1n_2}(\vec{r}_1,\vec{r}_2), \tag{3}$$