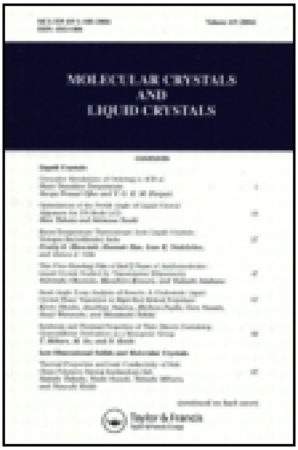

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photophysics of Charge Carrier Generation

Masahiro Kotani [a]
[a] Department of Chemistry, Gakushuin University, Tokyo, Japan

Version of record first published: 31 Jan 2007

To cite this article: Masahiro Kotani (2006): Photophysics of Charge Carrier Generation, Molecular Crystals and Liquid Crystals, 455:1, 183-191

To link to this article: http://dx.doi.org/10.1080/15421400600698352

Mol. Cryst. Liq. Cryst., Vol. 455, pp. 183–191, 2006
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400600698352

Photophysics of Charge Carrier Generation

Masahiro Kotani
Department of Chemistry, Gakushuin University, Tokyo, Japan

The role of highly excited states in charge carrier generation is experimentally surveyed. Fluorescence from highly excited states, electron emission from superexcited states, magnetic field effects on the luminescence under high-density excitation are presented and discussed in relation to charge carrier generation.

Keywords: charge carrier generation; exciton annihilation; organic photoconductors; photoconductivity; superexcited states

INTRODUCTION

Many insulators are insulators because of the low concentration of charge carriers under normal conditions. When a proper contact is attached, however, they can conduct electricity. In view of the advances in photoconductors, organic light emitting diodes and organic solar cells in recent years the importance of understanding electrical, optical and luminescent properties of such group of materials is clear.

Table 1 shows a few examples of insulators with their charge carrier mobility [1]. It is seen that charge carrier mobility can be very high in some of the typical insulators such as diamond and liquefied rare gases. Actually fast detectors using diamond have been fabricated which is sensitive only to ultraviolet radiation. Large volume radiation detectors made up of liquid xenon have also been constructed, in which

---

Much of the measurements presented in this talk were made in collaboration with former and present members of my laboratory at Gakushuin: E. Morikawa, R. Katoh, Y. Takeda, M. Ono, S. Fujiyoshi, and H. Kobayashi. We have learned much through the collaboration with Prof. K. Nakagawa. This work is supported in part by the High-Technology Research Center Promotion Project from the Ministry of Education, Culture, Sport, Science, and Technology (MEXT), of Japan.

Address correspondence to Masahiro Kotani, Department of Chemistry, Gakushuin University, Mejiro, Tokyo 171-8588, Japan. E-mail: masahiro.kotani@gakushuin.ac.jp

TABLE 1 Charge Carrier Mobility of Some Insulating Solids and Liquids [1]

	Electron mobility $cm^2 V^{-1} s^{-1}$	Hole mobility $cm^2 V^{-1} s^{-1}$	Band gap/eV
Diamond	1800	1200	5.4
Si	1300	500	1.14
Ge	4500	3500	0.67
Ar(Solid)	1000		14.2
Ar(liquid)	475		
Xe(solid)	4000	0.02	9.28
Xe(liquid)	1900		
CH_4(liquid)	300		
$Si(CH_3)_4$	90		
Anthracene	1	1	3

radiation induced ionization is utilized for detecting high-energy particles and cosmic rays.

Charge carriers can be generated in an insulator by various means. They can be classified into two categories: injection from surfaces and generation in the bulk. Let us discuss here a few examples.

INJECTION FROM SURFACES AND INTERFACES

Dye Sensitization

Carriers of either sign can be injected by exciting a molecule adsorbed on the surface of an insulator. A classical example is the dye sensitization of photographic emulsions [2]. In this case an electron is injected into a silver halide crystal when a dye molecule adsorbed on its surface is excited by absorption of a photon. The electron is transferred from the excited state of the dye to the conduction band of the crystal, which reduces a silver ion to give a neutral atom. A stable cluster of Ag_4 is formed in a micron-sized silver halide crystal when four silver ions are reduced which constitutes a latent image, a catalytic center which accelerates reduction of silver ions in the course of chemical development.

Dye sensitization has been known in organic crystals. In 1963 dye-sensitized hole injection into an anthracene crystal was first reported [3]. In this case an electronically excited dye molecule extracts an electron from the crystal, leaving a positive charge in the crystal. Energetics of carrier injection and spin-controlled recombination has been studied in detail [4].

Dye sensitized solar cells based on TiO_2 nanoparticles are being actively investigated [5].

Internal Photoemission

Electron spectroscopy has been applied with great success to the study of surfaces. The study of interfaces between organic solids and electrodes has suffered from the lack of appropriate means. There have been intensive studies of electronic states of ultrathin organic films on metal electrodes by UPS and XPS, with the hope that we may be able to understand a thin film system through this approach [6].

Internal photoemission is another possibility. It involves emission of electrons into a semiconductor by absorption of a photon in a metal. Less energy is needed for an electron to be emitted into the conduction band of a semiconductor, compared to the conventional photoemission of electrons, where electrons have to be excited above the vacuum level in order that they are emitted into vacuum. It is an established method for conventional semiconductors to investigate metal/semiconductor interfaces. This technique was first applied to organic solids in 1960s [7]. Recently it was applied successfully to conjugated polymers [8].

A very similar method has been known among the researchers investigating electronic properties of insulating liquids: measurements of a quantity called V_0 [9]. This is the negative of the electron affinity. A positive V_0 means a negative electron affinity. Experimentally one first measures the threshold photon energy for photoemission from a metal into vacuum. Then the metal is submerged into a liquid of interest and the measurement is repeated. This time the electrons are emitted into the liquid and the threshold can be larger or smaller than that for photoemission into vacuum, depending on the energy of the conduction state of the liquid. It has been found that there are indeed both cases: liquids such as methane and aliphatic hydrocarbons have positive V_0 (negative electron affinity), while many aromatic hydrocarbons have negative V_0 (positive electron affinity) (Table 2) [9].

CARRIER GENERATION IN THE BULK

The Role of the Superexcited States

Carrier injection from surfaces and interfaces are limited only to carriers of either sign i.e., either electron or holes. A pair of charge carriers, i.e., an electron and a hole, can be generated in a solid by absorption of light, if it has a proper energy. The absorption cross section of a solid depends on the photon energy and, as a result, the penetration depth of light changes as the excitation energy is varied. Two consequences have to be considered. One is that the excited states are generated close to the surface when the absorption is strong. In that case the excited states have more chance to interact with the surface,

TABLE 2 V_0 Values of Some Insulating Liquids

Liquids	T/K	V_0/eV
Helium	4.2	1.05
Hydrogen	13.5	1.5
Neon	25	0.67
Argon	84	– 0.2
Krypton	116	– 0.4
Xenon	161	– 0.67
Methane	100	– 0.25
Ethane	100	0.2
n-Pentane	296	0
n-Hexane	296	0.04
Neopentane	296	– 0.15
Tetramethyltin	296	– 0.7
Squalane	296	– 0.15

which may act as a dissociation center, or a quencher. The other is that the density of the excited states becomes larger when the absorption coefficient increases and the exciton–exciton interaction can then contribute to the eventual ionization in the bulk of the solid.

This complexity can be removed by adopting a two-step, two-color excitation. A spatially homogeneous distribution of excitons can be generated by weakly absorbed light and the excitons can be excited one step further with another photon, which is not absorbed by the solid in the ground state. By varying the energy of the second photon one can vary the excitation energy without introducing the difficulty associated with the changing penetration depth. Ionization of the highly excited states, if it occurs, can be detected by photoconductivity.

This technique has been applied to organic crystals such as anthracene, p-terphenyl and stilbene [10]. In all cases studied the results indicate that a superexcited state generated by successive absorption of two photons ionizes with a high efficiency. The efficiency does not, however, depend on the energy of the final state. Figure 1 shows that the quantum yield of the ionization follows closely that of photoabsorption (of the lowest excited state generated by the first step excitation in this case) and that the ratio of the two processes, which gives the ionization efficiency of the superexcited state, is hence independent of the energy of the state reached by the two-step excitation. This indicates that a rapid relaxation occurs to some lower-lying state which autoionizes.

Exciton–exciton annihilation is evidenced by the observation of fluorescence from highly excited states. Fluorescence from highly

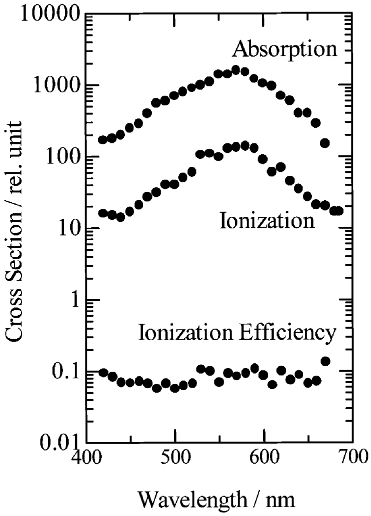

FIGURE 1 Ionization of highly excited states in a trans-stilbene single crystal [10]. The cross section for absorption (top), the cross section for ionization measured by photoconduction (middle). The ionization efficiency, given by the ratio of the two (bottom) is independent of the energy of the final state reached by two-step excitation, a fact that indicates autoionization after a fast relaxation.

excited states can be observed when an anthracene crystal is excited with a sufficiently intense light in the first absorption band around 3 eV. Fluorescence from states lying up to 6 eV is observed, although its intensity is many orders of magnitude smaller than that of the conventional fluorescence from the lowest singlet excited state [11].

Electron emission is also possible on exciton–exciton annihilation. Figure 3 shows that excitation of a pyrene crystal in the strong absorption band in the near UV leads to emission of electrons [12]. The remarkable feature of the emission is that it has a long lifetime, while the excitation is made with a short pulse of light. The lifetime of the electron emission is half as long as the fluorescence lifetime, a fact which clearly indicates that the annihilation of two fluorescent states is responsible for the generation of electrons which have a sufficient kinetic energy to be emitted into vacuum (Fig. 3).

Magnetic Field-Effects on Luminescence

Exciton annihilation can also be detected by measuring the intensity of fluorescence from an organic crystal. The intensity of fluorescence from an anthracene crystal is linearly proportional to the intensity

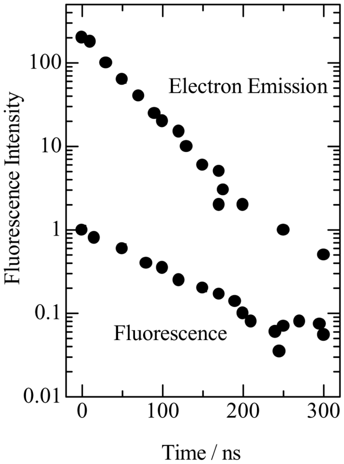

FIGURE 2 Decays of electron emission by annihilation of two singlet excitons (top) and of fluorescence (bottom) from a pyrene crystal, excited with a nanosecond laser pulse. The decay of the electron emission is twice as fast as compared to fluorescence, indicating that the emission is due to a bimolecular reaction.

of the exciting light and is not sensitive to the magnetic field. When, however, the intensity of the excitation exceeds a certain limit the dependence changes from a linear one to a square root one. This is because the decay of the fluorescent state is now dominated by exciton–exciton annihilation and not by the spontaneous decay. At the same time the fluorescence becomes sensitive to the magnetic field, as Figure 3 shows [13].

On applying a magnetic filed of several kilogauss the intensity of the fluorescence increases by a few tenths of a percent. The field dependence, as well as the dependence on the orientation of the magnetic field with respect to the crystallographic axes, clearly shows a close resemblance with the magnetic field effects on triplet–triplet annihilation. It has been established during 1970s that the annihilation is suppressed by a magnetic field [14]. Around the same time the reverse process, namely the fission of a singlet exciton into a pair of triplet excitons, has been found to be likewise sensitive to the magnetic field [15].

The magnetic field effect on the fluorescence intensity at high excitation densities can be interpreted as the result of the suppression of the fission process. The reduced rate, in a magnetic field, of fission of highly excited singlet states results in an increase of the density

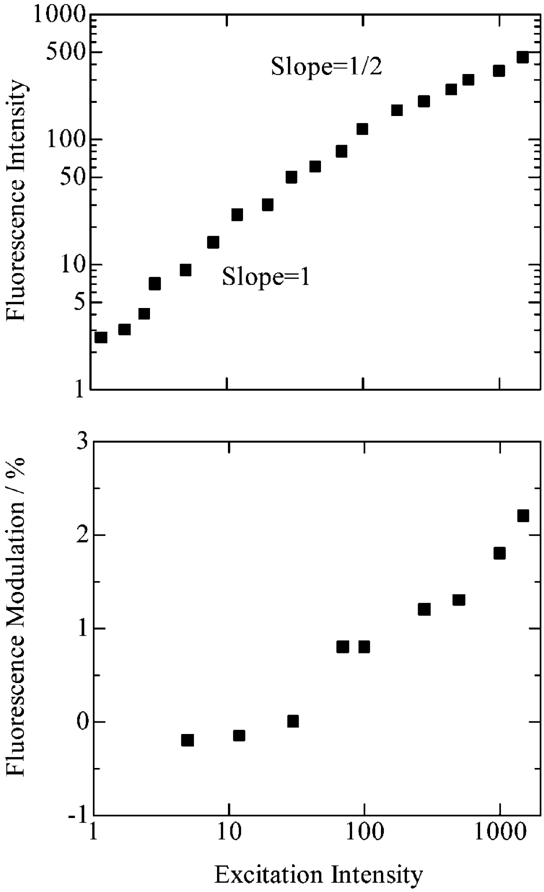

FIGURE 3 Magnetic field modulates the intensity of fluorescence of an anthracene crystal at high excitation intensities, where the bimolecular annihilation of singlet excitons is more important than the spontaneous monomolecular decay.

of the singlet excited state, and hence in an increase in the fluorescence intensity.

Magnetic field influences the intensity of the fluorescence excited by VUV photons [16]. Fluorescence excited by hard X-rays is also sensitive to magnetic field, but in a different way [17]. The results seem to indicate that, in the case of VUV excitation, fission of a highly excited singlet state into a pair of triplets is the main cause of the magnetic field effect. In the case of X-ray excitation the primary act is the ionization. The primary and secondary electrons lose their energy by creating many pairs of electrons and holes densely in the form of spurs along their tracks. Random recombination of the electrons and the holes in the spurs results in a high density of singlet and triplet excitons, with the ratio of 1:3. The magnetic field effect on the X-ray induced luminescence can be interpreted as due to the influence on the fusion of the triplets created in the charge recombination process.

Radiation Chemistry Region vs. Photochemistry Region

In photochemistry it is quite common that fluorescence quantum yield is a constant, irrespective of the photon energy for excitation. This is not the case in radiation chemistry, where fluorescence yield is counted per energy absorbed. The energy at which radiation chemistry region starts has been studied with anthracene [18]. It has been found that fluorescence quantum yield starts to increase at around 10 eV and increases linearly with photon energy at higher energies.

CONCLUSION

The basic principles of most of the phenomena discussed above have been well understood since 1980s, or even before. There is, however, renewed interest in these processes in the era of high brightness OLEDs and possible organic lasers, charge carriers and excitons coexist at high densities. Quantitative knowledge accumulated in the past may be quite useful in designing modern, high-performance organic devices.

REFERENCES

[1] Pope, M. & Swenberg, C. E. (1999). *Electronic Processes in Organic Crystals and Polymers*, Oxford University Press: New York, Oxford. Ref. [10] for data of insulating liquids.

[2] James, T. H. (1977). *Theory of Photographic Processes*, 4th Ed. MacMillan: New York.

[3] Steketee, J. W. & de Jonge, J. (1963). *Proc. Kon. Ned. Akad. Wet. Series*, *B66*, 76; Mulder, B. J. & de Jonge, J. (1963). *Proc. Kon. Ned. Akad. Wet. Series*, *B66*, 303.

[4] Nickel, B. (1972). *Mol. Cryst. Liq. Cryst.*, *18*, 227; Mueller, N., Papier, G., Charle, K.-P., & Willig, F. (1979). *Ber. Bunsenges. Phys. Chem.*, *83*, 130; Groff, R. P., Suna, A., Avakian, P., & Merrifield, R. E. (1974). *Phys. Rev.*, *9*, 2655.

[5] Hagfeldt, A. & Graetzel, M. (1995). *Chem. Rev.*, *95*, 49.

[6] Ishii, H., Sugiyama, K., Ito, E., & Seki, K. (1999). *Adv. Mater.*, *11*, 605 and references therein.

[7] Williams, R. & Dresner, J. (1967). *J. Chem. Phys.*, *46*, 2133; Caywood, J. M. (1970). *Mol. Cryst. Liq. Cryst.*, *12*, 1.

[8] Campbell, I. H., Hagler, T. W., Smith, D. L., & Ferrais, J. P. (1996). *Phys. Rev. Lett.*, *76*, 1900.

[9] Schmidt, W. F. (1997). *Liquid State Electronics of Insulating Liquids*, CRC Press: New York.

[10] Kotani, M., Morikawa, E., & Katoh, R. (1989). *Mol. Cryst. Liq. Cryst.*, *171*, 305; Kotani, M. & Katoh, R. (1992). In: *Dynamics and Mechanisms of Photoinduced Transfer and related Phenomena*, Mataga, N., Okada, T., & Masuhara, H. (Eds.), Elsevier Science Publishers: B. V. 425.

[11] Katoh, R. & Kotani, M. (1993). *Chem. Phys. Lett.*, *201*, 141.

[12] Ono, M., Katoh, R., & Kotani, M. (1995). SPIE Proceedings 2362 219; Ono, M. & Kotani, M. (1998). *Chem. Phys. Lett.*, *295*, 34.

[13] Katoh, R. & Kotan, M. (1992). *Chem. Phys. Lett.*, *196*, 108.

[14] Johnson, R. C., Merrifield, R. E., Avakian, P., & Flippen, R. P. (1967). *Phys. Rev. Lett.*, *19*, 285.

[15] Merrifield, R. E., Avakian, P., & Groff, R. P. (1969). *Chem. Phys. Lett.*, *3*, 155; Klein, G., Voltz, R., & Schott, M. (1972). *Chem. Phys. Lett.*, *16*, 340.

[16] Klein, J., Martin, P., & Volts, R. (1981). *J. Luminesc.*, *24/25*, 99.

[17] Takeda, Y., Katoh, R., Kobayashi, H., & Kotani, M. (1996). *J. Electron Spectrosc. Rel. Phenom.*, *78*, 423.

[18] Kimura, A., Nakagawa, K., Tanaka, K., Kotani, M., & Katoh, R. (1994). *Nuclear Instrum. Phys. Res. B*, *91*, 67.