A direct approach to study radiative emission from triplet excitations in molecular semiconductors and conjugated polymers

Jai Singh,[1,a)] H. Baessler,[2] and S. Kugler[3]

[1]*Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, USA and Hahn-Meitner-Institut-Berlin, Kekulestr. 5, 12489 Berlin, Germany*
[2]*Chemistry Department, Philipps-Universitaet Marburg, Hans Meerwein Strasse, D-35032 Marburg, Germany*
[3]*Department of Theoretical Physics, Budapest University of Technology and Economics, H-1521 Budapest, Hungary*

Using the recently discovered time-dependent spin-orbit-photon interaction operator and first order perturbation theory, the rate of spontaneous emission from triplet excitations is derived within the two-level approximation for organic molecular solids and conjugated polymers. The calculated rates and corresponding radiative lifetimes agree very well with the known experimental results. Present results are compared with those obtained through the traditional approach of the second order perturbation theory in some molecular crystals and found to be in better agreement with experiments. © 2008 American Institute of Physics. [DOI: 10.1063/1.2961010]

I. INTRODUCTION

Radiative emission from triplet excitations in organic solids and conjugated polymers has attracted much research interest recently[1–3] because of their commercial applications in flexible organic light emitting devices (LEDs). The problem with a triplet excitation is that its electron and hole (e-h) have parallel spins and hence their radiative recombination (phosphorescence) through dipolar transitions is spin forbidden. This is in contrast to the singlet excitations with antiparallel spins of e-h pairs; their radiative recombination (photoluminescence) is spin allowed through dipole transitions. A triplet radiative transition can occur only through the mediation of the spin-orbit interaction that can flip the spin to facilitate the recombination. It is so called well established that the spin-orbit interaction is proportional to the atomic number and hence it is weak in organic hydrocarbons and polymers. This results in inefficient radiative emission from a triplet exciton in such materials. Accordingly, in LEDs, one would like to have emissions only from singlet excitons. However, the operation of LEDs brings electrons and holes together from opposite electrodes and statistically should generate singlet and triplet excitons in the ratio of 1:3.[2] Thus, where triplet emission is not possible, LEDs are limited to only 25% efficiency at the most. It is therefore very important to understand the mechanism of triplet exciton emission very clearly in any material.

The well known spin-orbit interaction operator is a stationary interaction operator and hence it cannot cause any optical transition,[4] although it has been used to calculate the radiative lifetime of triplet excitons in benzene.[5] To the best of the authors' knowledge, no other interaction operator that can be used to calculate the transition matrix element between a triplet excited and a singlet ground state through the first order perturbation theory is known.

In the absence of a proper spin-orbit-photon transition operator, a very long standing tradition has been set up to calculate the transition matrix element between an excited triplet and a singlet ground state in two steps.[6–12] In the first step, the stationary spin-orbit interaction operator is used to calculate the energy splitting in a degenerate triplet state and the wave function of the triplet state is expanded as a linear combination of all singlet and triplet unperturbed wave functions. In the second step, then the dipole transition operator is used to calculate the transition matrix element between the first order triplet state and singlet ground state wave functions. In this way one gets fractional nonzero matrix element contributed by the singlet components in the expansion of triplet wave function. This approach has been used for inorganic[10] as well as organic solids and molecules.[6,7,12] Earlier attempts in some organic molecules and solids did not give good agreements with the observed lifetimes.[6,7] Some recent works, however, have applied this approach on conjugated polymers[8] and nonplanar aromatic heterocyclic molecules.[9] As the two-step process is equivalent to a second order perturbation theory, one wonders why there exists no spin-orbit-photon interaction operator for the triplet emission like the dipole transition operator for singlet emission.

Using the recently discovered time-dependent spin-orbit-photon interaction operator Singh[4] has calculated the rate of spontaneous emission from triplet excitons in noncrystalline inorganic semiconductors. The radiative lifetime of triplet excitons thus calculated for hydrogenated amorphous silicon agrees very well with the experimental results. The theory has also been extended to calculate the rates in amorphous chalcogenide glasses[13] and found to be in good agreement with experiments.

In this paper, using the new interaction operator the rates

a)Permanent address: School of Engineering and IT, B-41, Charles Darwin University, N.T. 0909, Australia. Electronic mail: jai.singh@cdu.edu.au.

of radiative recombination in a few molecular solids and conjugated polymers are calculated. The radiative lifetime of triplet excitations is also calculated and compared with the experimental results. The results agree very well with the recent experimental results in platinum containing molecular complexes, conjugated polymers, and organic crystals. The rate depends on the square of the atomic number of the constituting atoms, which explains clearly the observed enhancement of emission due to the incorporation of heavy atoms in polymers.[1–3,14–18] A theory for the constant separation between the singlet and triplet excitons recently observed in conjugated polymers[3,14,18] has also been presented here.

II. RATE OF SPONTANEOUS EMISSION FROM A TRIPLET MOLECULAR EXCITATION

It is considered that a pair of e-h is excited in a triplet spin configuration in a molecular semiconductor or conjugated polymer by an incident radiation of energy equal or greater than the band gap energy. As the triplet excitation state lies much below the conduction band, a two-level approximation is regarded to be valid for these materials. The recently derived time-dependent perturbation operator[4] for a molecular excitation in a molecule can be written as

$$\hat{H}_{so} = -\frac{eg}{2\mu_x^2 c^2}\left(-\frac{e}{c}\Sigma_n \mathbf{s}\cdot(\mathbf{A}\times\nabla V_n)\right), \quad (1)$$

where all symbols have their usual meanings as defined in Ref. 4. The spin-orbit-photon interaction given in Eq. (1) is such that in the presence of photons an electron gets attracted to a nucleus and the attractive force is proportional to the atomic number and inverse square of the distance between the electron and nucleus. Following earlier work by Hameka,[6] for $Z_n > 1$, the interaction between the excited electron and other valence electrons in an atom is considered to be negligible. As terms within the summation sign depend on the inverse square of the distance of the electron from a nucleus, the nearest nucleus is expected to have the dominant influence and the presence of other nuclei may then be neglected. Within this approximation, Z_n may be replaced by Z, an average site independent atomic number. However, this approximation is valid only for solids with atoms of not very different atomic numbers. In the case of hydrocarbons, only the atomic number of carbon is necessary to use. If a molecule contains heavier atoms, the atomic number of the heaviest atom should be used in the calculation. It may be noted that this approximation is not necessary for calculating the rates numerically. It is only used here to derive an approximate simple analytical expression for the rate of spontaneous emission. The rate of spontaneous emission from a triplet excitation thus derived within the two-level approximation is obtained as[4]

$$R_{sp} = \frac{e^6 Z^2 \kappa^2 \hbar \omega_{12}}{2\mu_x^4 c^7 \varepsilon^3 \varepsilon_0 |r|^4}, \quad k = (4\pi\varepsilon_0)^{-1} \quad (2)$$

where $\hbar\omega_{12} = E_2 - E_1$ is the emitted photon energy equal to $E_2 - E_1$. E_2 is the energy of the triplet and E_1 is that of the ground state or valence band.

$|r|^{-2} = \Sigma_{n=1}^N C_n^{H*} C_n^L \langle\varphi_{Hn}|r_{en}^{-2}|\varphi_{Ln}\rangle$, where $|r|$ is the average separation between the excited e-h before their radiative recombination, φ_{Hn} and φ_{Ln} are the atomic orbitals of the nth atom and C_n^H and C_n^L are the corresponding probability amplitude coefficients of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (triplet), respectively. However, for organic solids and polymers a simpler approach is to use $|r| = a_x/\varepsilon$, where a_x is the excitonic Bohr radius of a triplet exciton given by $a_x = (\mu\varepsilon/\mu_x)a_0$.[4,19] Substituting this in Eq. (1), we get the rate as

$$R_{sp} = \frac{e^6 Z^2 \kappa^2 \varepsilon \hbar \omega_{12}}{2\mu_x^4 c^7 \varepsilon_0 a_x^4}. \quad (3)$$

It may be noted that by substituting a_x as given above in R_{sp}, Eq. (3) becomes independent of μ_x. The radiative lifetime is calculated from the inverse of the rate, $\tau_R = 1/R_{sp}$.

III. EXCHANGE ENERGY BETWEEN SINGLET AND TRIPLET

The energy separation between the singlet and triplet exciton states in a solid depends on the magnitude of the exchange interaction between the excited e-h.[19,20] If the ratio of the Coulomb (C) interaction to the exchange (E) interaction between an excited pair of e-h is denoted by α ($C/E = \alpha$), then the exchange energy ΔE between a singlet and a triplet excitons is obtained as[19,20]

$$\Delta E = \left[1 - \frac{(\alpha-1)^2}{\alpha^2}\right]E_M, \quad E_M = \frac{\mu_x e^4 \kappa^2}{2\hbar^2 \varepsilon^2}. \quad (4)$$

If one knows α, then ΔE can be calculated and vice versa. In many conjugated polymers, the measured value of $\Delta E \approx 0.7$ eV,[2,3,14,16] and it is found to be nearly constant. Using $m_e^* = m_h^* = m_e$ (free electron mass) and $\varepsilon = 3$, one gets $E_M = 0.82$ eV from Eq. (4) and then substituting $\Delta E = 0.7$ eV, we get $\alpha = 1.619$. Most polymers have a dielectric constants of 3–4 (Refs. 21 and 22) and effective masses of electrons and holes also are not expected to vary much from one polymer to another. Therefore, E_M and α are expected to be the same for most polymers. As a result, one gets the same ΔE for most polymers. This is probably the simplest way of explaining constant ΔE observed in polymers.

IV. RESULTS

The rate in Eq. (3) is used to calculate the triplet radiative rates in benzene, naphthalene, anthracene, conjugated polymers containing platinum in the polymer chain, and platinum porphyrin.[18] For all polymers studied in Ref. 16, it is assumed that $m_e^* = m_h^* = m_e$ giving $\mu_x = 0.5m_e$ and $\varepsilon = 3$, and then the triplet excitonic Bohr radius becomes $a_x = (m_e\varepsilon/\mu_x)a_0 = 6a_0$. The rates are calculated for the first three polymers P$_1$, P$_2$, and P$_3$ from Ref. 16. We can calculate the rates for all the polymers studied in Ref. 16 but as they are all found to be of the same order of magnitude only the rates for the first three polymers are listed here. The triplet emission energy used in the calculation, calculated rates, and corresponding radiative lifetimes are listed in Table I along with their observed experimental rates and radiative lifetimes. For

TABLE I. Assuming $m_e^* = m_h^* = m_e$, which gives $\mu_x = 0.5 m_e$ and taking $\varepsilon = 3$, rates of spontaneous emission are calculated from Eq. (3) for a few molecular crystals, conjugated polymers, and platinum porphyrin [Pt(OEP)]. Using these values the triplet excitonic Bohr radius becomes $a_x = 6 a_0$ in these materials. For the first three solids $Z = 6$, and for the rest $Z = 78$ is used in the calculation.

Material	$\hbar\omega_{12}$ (eV)	R_{sp} (s^{-1}) [Eq. (4)]	R^{exp} (s^{-1})	$\tau_R = 1/R_{sp}$ (s)	τ^{exp} (s)
Benzene	3.66[a]	0.63	⋯	1.6	4–7[a]
Naphthalene	2.61[a]	0.45	⋯	2.2	2.5[a]
Anthracene	1.83[a]	0.31	⋯	3.19	0.1[a]
P1	2.40[b]	5.5×10^3	$(6 \pm 4) \times 10^{3}$[c]	1.82×10^{-4}	
P2	2.25[b]	5.1×10^3	$(1.8 \pm 0.9) \times 10^{3}$[c]	1.96×10^{-4}	
P3	2.05[b]	4.6×10^3	$(1 \pm 1) \times 10^{3}$[c]	2.17×10^{-4}	
Pt(OEP)	1.91[d]	4.9×10^3		2.03×10^{-4}	7.00×10^{-4}

[a]Reference 7.
[b]Reference 16.
[c]Reference 8.
[d]Reference 18.

conjugated polymers incorporated with platinum atoms, P_1, P_2, and P_3, the rates are found to be of the order of 10^3 s^{-1}, which agree very well with the experimental results.[16]

The excitonic reduced mass and average separation between the e-h have already been calculated[23] for some polymers such as polythiophene (PT). The values for PT are $\mu_x = 0.076 m_e$ and $|r| = 1.01$ nm. Using these and $\varepsilon = 3$, $Z = 6$ (carbon), and $\hbar\omega_{12} = 2.4$ eV in Eq. (1), we get $R_{sp} = 6.96$ s^{-1} and radiative lifetime $\tau_R = 1/R_{sp} = 0.14$ s (not listed in Table I). If we incorporate this with platinum and use $Z = 78$, we get $R_{sp} = 1.18 \times 10^3$ s^{-1} and $\tau_R = 0.85$ ms, which are also of the same order of magnitude as obtained from Eq. (3) with $\mu_x = 0.5 m_e$ and $a_x = 6 a_0$. This is because $\mu_x^4 a_x^4 = (m_e \varepsilon a_0)^4$ [Eq. (3)] $\approx \mu_x^4 |r|^4$ [Eq. (1)], which produces nearly the same rates from Eqs. (1) and (3). Hence, the calculated rates for all the five polymers studied in Ref. 23 are found to be of the same order of magnitude.

V. DISCUSSIONS

The rate in Eq. (3) is used to calculate the rates of radiative emission from triplet excitations in a few molecular solids and platinum incorporated conjugated polymers and phosphorescent dyes. The calculated rates agree very well with the observed rates in these materials (see Table I). The rate in Pt(OEP) dye is found to be 4.9×10^3 s^{-1}, which is of the same order of magnitude as in conjugated polymers considered above. Without the inclusion of Pt(OEP) dye in the host organic material, the rate with mainly carbon atoms is found to be about 46.0 s^{-1}, which is at least two orders of magnitude less. This enhancement in the recombination rate due to the doping of the organic LED matrix by Pt(OEP) agrees very well with the observed enhancement in electroluminescent devices.[17] The rate derived in Eq. (3) increases with the triplet state energy, which also agrees with the observed increase in several polymers.[16]

It may be argued that the traditional approach of calculating the radiative lifetime of triplet excitation, which goes back to many decades, is still valid. So what is the advantage of the present approach? To answer this question, we compare the present results with those calculated from the traditional approach in naphthalene and anthracene. Using the latter approach, the calculated radiative lifetimes for naphthalene and anthracene are found to be 10 and 55 s, respectively,[7] which are much longer than the experimental values as well as those obtained from the present theory (see Table I). Thus, the results of the present theory are in better agreement with experiments. However, the calculated radiative lifetime in anthracene given in Table I may not be considered in good agreement with the experimental result. This discrepancy can be attributed to the fact that experimentally only the total triplet lifetime (τ) has been measured, which is not the same as the radiative lifetime (τ_R) calculated here. The former depends also on the nonradiative decay rates of triplet excitons ($1/\tau = R_{sp} + R_{non-rad}$). In fact, this is true for benzene, naphthalene, and Pt(OEP) as well.

One may find the present approach to be oversimplified as it only considers the effect of the nearest atom and neglects the influences of molecular structure, electron-electron interaction, etc. As stated above, these approximations are used here only to derive a simple analytical expression for the rate of spontaneous emission [Eqs. (2) and (3)]. If one wants to compute these rates numerically then, of course, these approximations are not necessary. However, the important point is that even with these approximations the results are found to be in better agreement with the experimental results than those from the traditional approach (Table I). Using the traditional approach, the effect of molecular structures and molecular vibrations has recently[9] been incorporated in computing the rates in nonplanar heterocyclic molecules. These effects are probably important for molecules but for solids they are not expected to make a huge difference. For molecules, one may also have to calculate the separation between the excited e-h through HOMO and LUMO molecular orbitals [see Eq. (2)] as the use of excitonic Bohr radius may not be valid. In every other aspect, the theory can be applied to molecular structures as well.

The rates of radiative decay of triplet excitons have also been measured recently[24,25] in conjugated polymers with pendant phosphorescent iridium (Ir) complexes. The atomic number of Ir ($Z = 77$) is not very different from Pt ($Z = 78$) and hence according to the present theory, we should get similar rates as in Pt complexes. However, the observed rates

are found to be an order of magnitude higher in Ir complexes[25] than those in Pt complexes. This discrepancy may be attributed to the fact that in Ir complexes the excitation back transfer rate from iridium complexes to the polyfluorene backbone is much faster than the radiative rate from Ir calculated here. Then inverse of the triplet lifetime will depend on the sum of this nonradiative transfer and radiative rates. In that case, it may be necessary to consider the influence of the structure on the radiative rate in these materials. This requires further investigations.

[1] H. F. Wittman, R. H. Friend, M. S. Khan, and J. Lewis, J. Chem. Phys. **101**, 2693 (1994).
[2] V. Cleave, G. Yahioglu, P. L. Barny, R. H. Friend, and N. Tessler, Adv. Mater. (Weinheim, Ger.) **11**, 285 (1999).
[3] A. Köhler and D. Beljonne, Adv. Funct. Mater. **14**, 11 (2004).
[4] J. Singh, Phys. Rev. B **76**, 085205 (2007).
[5] D. S. McClure, J. Chem. Phys. **20**, 682 (1952).
[6] H. F. Hameka, *The Triplet State* (Cambridge University Press, Cambridge, 1967), pp. 1–30.
[7] J. B. Birks, *Photophysics of Aromatic Molecules* (Wiley, London, 1970).
[8] D. Beljonne, Z. Shuai, G. Pourtois, and J. L. Bredas, J. Chem. Phys. **105**, 3899 (2001).
[9] K. Schmidt, S. Brovelli, V. Coropceanu *et al.*, J. Chem. Phys. **111**, 10490 (2007).
[10] R. S. Knox, *Theory of Excitons* (Academic, New York, 1965).
[11] D. S. McClure, J. Chem. Phys. **17**, 905 (1949).
[12] B. R. Henry and W. Siebrand, J. Chem. Phys. **51**, 2396 (1969).
[13] J. Singh, J. Mater. Sci.: Mater. Electron. **9**, 3013 (2007).
[14] A. Köhler, J. S. Wilson, R. H. Friend, M. K. Al-Suti, M. S. Khan, A. Gerhard, and H. Baessler, J. Chem. Phys. **116**, 9457 (2002).
[15] D. Beljonne, H. F. Wittman, A. Köhler, S. Graham, M. Younus, J. Lewis, P. R. Raithby, M. S. Khan, R. H. Friend, and J. L. Bredas, J. Chem. Phys. **105**, 3868 (1996).
[16] J. S. Wilson, N. Chaudhury, R. A. Al-Mandhary, M. Younus, M. S. Khan, P. R. Raithby, A. Köhler, and R. H. Friend, J. Am. Chem. Soc. **123**, 9412 (2001).
[17] M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, Nature (London) **395**, 151 (1998).
[18] F. Laquai, C. Im, A. Kadashchuk, and H. Baessler, Chem. Phys. Lett. **375**, 286 (2003).
[19] J. Singh and K. Shimakawa, *Advances in Amorphous Semiconductors* (Taylor & Francis, London, 2003).
[20] J. Singh, T. Aoki, and K. Shimakawa, Philos. Mag. B **82**, 855 (2002).
[21] Low dielectric constant polymers, http://www..nrl.navy.mil/techtransfer/pdfs/M11.pdf
[22] Zeus Newsletter: Dielectric Properties of Polymers, http://www.zeusinc.com/newsletter/dielectric.html
[23] J. W. van der Horst, P. A. Bobbert, M. A. J. Michels, and H. Baessler, J. Chem. Phys. **114**, 6950 (2001).
[24] N. R. Evans, L. S. Devi, C. S. K. Mak, S. E. Watkins, S. I. Pascu, A. Köhler, R. H. Friend, C. K. Williams, and A. B. Holmes, J. Am. Chem. Soc. **128**, 6647 (2006).
[25] L. S. Devi, Ph.D. thesis, Cambridge University, 2008.