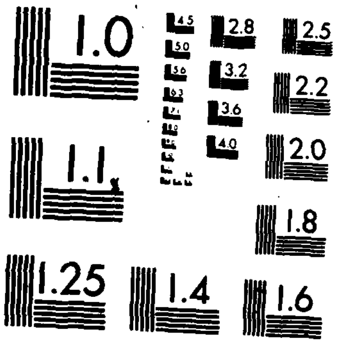
AD-A137 714 RATES AND MECHANISMS OF ENERGY DISSIPATION AND THE 1/1
STRUCTURE OF MOLECULAR SOLIDS(U) CALIFORNIA UNIV LOS
ANGELES DEPT OF CHEMISTRY AND BIOCHEMISTR..
UNCLASSIFIED M A EL-SAYED 31 JAN 84 N00014-75-C-0602 F/G 7/4 NL

END
FILMED
3-84
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

(12)

OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0602

Task No. NR 056-498

FINAL REPORT

Period: January 1, 1975 - March 31, 1983

Title: "Rates and Mechanisms of Energy Dissipation and the Structure of Molecular Solids"

Principal Investigator:

M. A. El-Sayed
Department of Chemistry and Biochemistry
University of California, Los Angeles
Los Angeles, CA 90024

January 1984

unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER FINAL REPORT	2. GOVT ACCESSION NO. [illegible]	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Rates and Mechanisms of Energy Dissipation and the Structure of Molecular Solids		5. TYPE OF REPORT & PERIOD COVERED FINAL REPORT (January 1,1975-March 31, 1983)
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) M. A. El-Sayed		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0602
9. PERFORMING ORGANIZATION NAME AND ADDRESS Regents of the University of California University of California, 405 Hilgard Ave. Los Angeles, CA 90024		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR-056-498
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Chemistry Branch Arlington, Virginia 22217		12. REPORT DATE January 31, 1984
		13. NUMBER OF PAGES 10
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office) Office of Naval Research Branch Office 1030 East Green Street Pasadena, CA 91106		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) This document has been approved for public release and sale; distribution of this document is unlimited		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) N/A		A1
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) N/A		

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

I. Support Period

This final report covers the period January 1, 1975 through March 31, 1983.

II. Summary of Accomplishments

In eight years of support, twenty-three publications in reviewed journals have resulted. Eight graduate students have received their Ph.D. degree and six postdoctoral fellows have received their postgraduate training with the ONR support. Five visiting professors have collaborated with us for different periods of time during the support period.

III. Details of Accomplishments

a. Research

The research carried out covered a number of research areas. The use of spins of the lowest triplet state was studied as a probe of intramolecular intersystem energy transfer in molecules. The interplay between singlet and triplet of different electronic nature (e.g., n,π^* and π,π^*) was quantitatively examined (publications 1-5, 8 and 13). Nonradiative processes in the gas phase and in solution were studied in publications 7,10,11 and 14. Spectral diffusion studies due to intermolecular energy transfer in solids were made for both spin transitions (publications 15 and 16), electronic transitions of rare earth ions in glasses (publications 6,17,18 and 20) and singlet-triplet electronic transitions in orientationally disordered solids (publications 19,21-23). In all these studies, the mechanisms of the energy transfer processes involved are investigated in terms of the interaction coupling involved.

b. Graduate Students

The names of the graduate students involved in the published work are:

Talal Akasheh (teaching at U. of Yarmouk, Jordan)
Alan Campion (teaching at U. of Texas, Austin)
Christina L. Gniazdowski (Industry)
William D. Hopewell (at IBM, San Jose)
Anne-Marie Merle (University of Bordeaux)
David H. Parker (teaching at UC Santa Cruz)
William M. Pitts (NBS)
Jack Morgan (postdoctoral fellow, UC Berkeley)

c. Postdoctoral Fellows

The names of the postdoctoral fellows involved in the published work are:

Phaedon Avouris (IBM, Yorktown)
Jacqueline O. Berg (TRW)
Alan R. Burns (Sandia Corp.)
Jai-Hyung Lee (teaching at U. of Seoul)
S. J. Sheng (industry)
Paul Zinsli (University of Bern)

d. The names of Visiting Professors involved in the published work are:

Paras Prasas (SUNY, Buffalo)
J. Prochorow (Polish Academy)
Ray Orbach (UCLA)
William M. Gelbart (UCLA)

e. The titles of the theses finished are:

1. Talal Akasheh, "Perturbation Effects on Molecular and Resonance Pair Triplet Excited States," 1977.

2. Alan Campion, "Energy Transfer in Inorganic, Organic and Biological Materials: Time-Resolved Laser Spectroscopy Studies," 1977.

3. William D. Hopewell, "Energy Transfer in Ionic and Molecular Systems," 1980.

4. Anne-Marie Merle, "The Origin of the Multiple Sites in a Shpol′skii Matrix," 1978.
5. David H. Parker, "Multiphoton Ionization in Polyatomic Molecules," 1979.
6. William M. Pitts, "Triplet-Spin Labels in Structural and Dunamic Studies of Mixed Aromatic Solids," 1978.

f. Publications

1. Paul E. Zinsli, "The Mechanism of $S_1 \rightsquigarrow T_1$ Nonradiative Process in Quinoxaline by Zeeman-PMDR Spectroscopy," Chem. Phys. Letters 34, 403 (1975).
2. Paul E. Zinsli, "Zeeman Effect on the PMDR Signal and the Mechanism of the Intersystem Crossing Process in Pyrazine at 1.6 K," Chem. Phys. Letters 36, 290 (1975).
3. Phaedon Avouris, Alan Campion and M. A. El-Sayed, "Luminescence and Intersystem Crossing Process in Camphorquinone Crystals," Chem. Phys. 19, 147 (1977).
4. S. J. Sheng and M. A. El-Sayed, "Electric Field Effect on the Spin Alignment of Triplet Traps of 4,4′-Dichlorobenzophenone Crystal," Chem. Phys. Letters 45, 6 (1977).
5. William M. Pitts and M. A. El-Sayed, "Cross Relaxation between the Spin Levels of Phosphorescent 1,2,4,5-Tetrachlorobenzene and Photochemical Products of the Durene Host," Chem. Phys. 25, 315 (1977).
6. Phaedon Avouris, Alan Campion and M. A. El-Sayed, "Variations in Homogeneous Fluorescence Linewidth and Electron-Phonon Coupling within an Inhomogeneous Spectral Profile," J. Chem. Phys. 67, 3397 (1977).
7. Phaedon Avouris, William M. Gelbart and M. A. El-Sayed, "Nonradiative Electronic Relaxation under Collision-Free Conditions," Chem. Revs. 77, 793 (1977).
8. A. M. Merle, W. M. Pitts and M. A. El-Sayed, "Distortion and Orientation for Triplet Coronene in Different n-Heptane Shpol′skii Sites Using Polarized Microwave MIDP Technique," Chem. Phys. Letters 54, 211 (1978).
9. Anne-Marie Merle, Alan Campion and M. A. El-Sayed, "The Two-Photon Excitation Spectrum of Triphenylene in n-Heptane Single Crystals," Chem. Phys. Letters 57, 496 (1978).

10. Talal Akasheh, "The Study of the Intramolecular Heavy Atom Effect in 9,10-Dichlorophenanthrene and 1,2,3,4-Tetrachloronaphthalene Using PMDR Techniques," Chem. Phys. Letters 59, 392 (1978).

11. Robert E. Turner, Veronica Vaida, Carol A. Molini, Jacqueline O. Berg and David H. Parker, "The Multiphoton Ionization Spectra of Pyridine and Pyrazine," Chem. Phys. 36, 437 (1979).

12. William M. Pitts, Anne-Marie Merle and M. A. El-Sayed, "Spectroscopic Investigation of the Origin of Distortion of Guest Coronene in Various Sites of n-Heptane Shpol′skii Matrix," Chem. Phys. 36, 437 (1979).

13. Christina L. Gniazdowski, William M. Pitts and M. A. El-Sayed, "Magnetic Field Induced Cross Relaxation Between Two Different Spin Transitions of Triplet Coumarin," Chem. Phys. 39, 123 (1979).

14. J. Prochorow, W. Hopewell and M. A. El-Sayed, "The α-Substitution Effect, Intramolecular or Medium Induced?" Chem. Phys. Letters 65, 410 (1979).

15. William M. Pitts and M. A. El-Sayed, "Optical Detection of Spectral Diffusion of the Triplet State Zerofield Transition Energy," Mol. Cryst. Liq. Cryst. 58, 19 (1980).

16. A. R. Burns, M. A. El-Sayed and J. C. Brock, "Analysis of Spectral Diffusion of Localized Triplet Spin Transitions within an Inhomogeneous Profile," Chem. Phys. Letters 75, 31 (1980).

17. J. R. Morgan, E. P. Chock, W. D. Hopewell, M. A. El-Sayed and R. Orbach, "Origins of Homogeneous and Inhomogeneous Line Widths of the $^5D_0-^7F_0$ Transition of Eu^{3+} in Amorphous Solids," J. Phys. Chem. 85, 747 (1981).

18. Jack R. Morgan and M. A.El-Sayed, "Temperature Dependence of the Homogeneous Linewidth of the $^5D_0-^7F_0$ Transition of Eu^{3+} in Amorphous Hosts at High Temperatures," Chem. Phys. Letters 84, 213 (1981).

19. Paras N. Prasad, Jack R. Morgan and Mostafa A. El-Sayed, "Spectral Diffusion in Orientationally Disordered Organic Solids," J. Phys. Chem. 85, 3569 (1981).

20. Jack R. Morgan and M. A. El-Sayed, "Temporal and Temperature Dependence of the Energy Transfer Process among Eu^{3+} in an Amorphous Solid," J. Phys. Chem. 85, 3566 (1981).

21. Jack R. Morgan and M. A. El-Sayed, "Low Temperature Energy Trapping and Emission Line Profile of Disordered Solid," J. Phys. Chem. 87, 383 (1983).

22. Jack R. Morgan and M. A. El-Sayed, "Energy Transfer Mechanism Switching in Disordered Solids," J. Phys. Chem. 87, 200 (1983).

23. Jack R. Morgan and M. A. El-Sayed, "Mechanism Switching and Trapping of Triplet-Triplet Energy Transfer in an Orientationally Disordered Molecular Solid," J. Phys. Chem. 87, 2178 (1983).

IV. Accomplishments of last year

a. Summary

During the last year, we have used laser phosphorescence line narrowing techniques to study the spectral diffusion in orientationally disordered solids at 4.2 K. At these temperatures, the increase in the laser wavelength results in a decrease in the concentration of the acceptor molecules to which the laser excitation energy is transferred within the inhomogeneous width of the 0,0 band. In this manner, we were able to change continuously the donor-acceptor distance and look for possible switching of the mechanism of the transfer from a short range exchange interaction to a long range dipolar mechanism at long wavelength of excitation. Indeed, a mechanism switching was observed when the acceptor fell below a few mole percent. The energy trapping in these orientationally disordered crystals has been examined and modeled. Three publications have resulted from this work:

1. Jack R. Morgan and M. A. El-Sayed, "Energy Transfer Mechanism Switching in Disordered Solids," J. Phys. Chem. 87, 200 (1983).

2. Jack R. Morgan and M. A. El-Sayed, "Low-Temperature Energy Trapping and Emission Line Profile of Disordered Solids," J. Phys. Chem. 87, 383 (1983).

3. Jack R. Morgan and M. A. El-Sayed, "Mechanism Switching and Trapping of Triplet-Triplet Energy Transfer in an Orientationally Disordered Molecular Solid," J. Phys. Chem. 87, 2178 (1983).

LIST A

TECHNICAL REPORTS

Technical Reports submitted to the Office of Naval Research for work supported by Contract No. N00014-75-C-0602, Task No. NR-056-498.

Report No.

22 Paul E. Zinsli, "The Mechanism of $S_1 \rightsquigarrow T_1$ Nonradiative Process in Quinoxaline by Zeeman-PMDR Spectroscopy," Chem. Phys. Letters 34, 403 (1975).

23 Paul E. Zinsli, "Zeeman Effect on the PMDR Signal and the Mechanism of the Intersystem Crossing in Pyrazine at 1.6 K," Chem. Phys. Letters 36, 290 (1975).

24 Phaedon Avouris, Alan Campion and M. A. El-Sayed, "Luminescence and Intersystem Crossing Processes in Camphorquinone Crystals," Chem. Phys. 19, 147 (1977).

25 S. J. Sheng and M. A. El-Sayed, "Electric Field Effect on the Spin Alignment of Triplet Traps of 4,4'-Dichlorobenzophenone Crystal," Chem. Phys. Letters 45, 6 (1977).

26 William M. Ptts and M. A. El-Sayed, "Cross Relaxation Between the Spin Levels of Phosphorescent 1,2,4,5-Tetrachlorobenzene and Photochemical Products of the Durene Host," Chem. Phys. 25, 315 (1977).

27 Phaedon Avouris, Alan Campion and M. A. El-Sayed, "Variations in Homogeneous Fluorescence Linewidth and Electron-Phonon Coupling within an Inhomogeneous Spectral Profile," J. Chem. Phys. 67, 3397 (1977).

28 A. M. Merle, W. M. Pitts and M. A. El-Sayed, "Distortion and Orientation for Triplet Coronene in Different n-Heptane Shpol'skii Sites Using Polarized Microwave MIDP Technique," Chem. Phys. Letters 54, 211 (1978).

29 Anne-Marie Merle, Alan Campion and M. A. El-Sayed, "The Two-Photon Excitation Spectrum of Triphenylene in n-Heptane Single Crystals," Chem. Phys. Letters 57, 496 (1978).

30 Talal Akasheh, "The Study of the Intramolecular Heavy Atom Effect in 9,10-Dichlorophenanthrene and 1,2,3,4-Tetrachloronaphthalene Using PMDR Techniques," Chem. Phys. Letters 59, 392 (1978).

31 Robert E. Turner, Veronica Vaida, Carol A. Molini, Jacqueline O. Berg and David H. Parker, "The Multiphoton Ionization Spectra of Pyridine and Pyrazine," Chem. Phys. 36, 437 (1979).

32 William M. Pitts, Anne-Marie Merle and M. A. El-Sayed, "Spectroscopic Investigation of the Origin of Distortion of Guest Coronene in Various Sites of n-Heptane Shpol'skii Matrix," Chem. Phys. 36, 437 (1979).

33 Christina L. Gniazdowski, William M. Pitts and M. A. El-Sayed, "Magnetic Field Induced Cross Relaxation Between Two Different Spin Transitions of Triplet Coumarin," Chem. Phys. 39, 123 (1979).

Report
No.

34 J. Prochorow, W. Hopewell and M. A. El-Sayed, "The α-Substitution Effect, Intramolecular or Medium Induced?," Chem. Phys. Letters 65, 410 (1979).

35 William M. Pitts and M. A. El-Sayed, "Optical Detection of Spectral Diffusion of the Triplet State Zerofield Transition Energy," Mol. Cryst. Liq. Cryst. 58, 19 (1980).

36 A. R. Burns, M. A. El-Sayed and J. C. Brock, "Analysis of Spectral Diffusion of Localized Triplet Spin Transitions within an Inhomogeneous Profile," Chem. Phys. Letters 75, 31 (1980).

37 J. R. Morgan, E. P. Chock, W. D. Hopewell, M. A. El-Sayed and R. Orbach, "Origins of Homogeneous and Inhomogeneous Line Widths of the $^5D_0$-$^7F_0$ Transition of Eu^{3+} in Amorphous Solids," J. Phys. Chem. 85, 747 (1981).

38 Jack R. Morgan and M. A. El-Sayed, "Temperature Dependence of the Homogeneous Linewidth of the $^5D_0$-$^7F_0$ Transition of Eu^{3+} in Amorphous Hosts at High Temperatures," Chem. Phys. Letters 84, 213 (1981).

39 Paras N. Prasad, Jack R. Morgan and Mostafa A. El-Sayed, "Spectral Diffusion in Orientationally Disordered Organic Solids," J. Phys. Chem. 85, 3569 (1981).

40 Jack R. Morgan and M. A. El-Sayed, "Temporal and Temperature Dependence of the Energy Transfer Process among Eu^{3+} in an Amorphous Solid," J. Phys. Chem. 85, 3566 (1981).

41 Jack R. Morgan and M. A. El-Sayed, "Low Temperature Energy Trapping and Emission Line Profile of Disordered Solids," J. Phys. Chem. 87, 383 (1983).

42 Jack R. Morgan and M. A. El-Sayed, "Energy Transfer Mechanism Switching in Disordered Solids," J. Phys. Chem. 87, 200 (1983).

43 Jack R. Morgan and M. A. El-Sayed, "Mechanism Switching and Trapping of Triplet-Triplet Energy Transfer in an Orientationally Disordered Molecular Solid," J. Phys. Chem. 87, 2178 (1983).

APPENDIX I

Reprints of papers that appeared in 1983.

Reprinted from The Journal of Physical Chemistry, 1983, 87, 383.

Low-Temperature Energy Trapping and Emission Line Profile of Disordered Solids

Jack R. Morgan and M. A. El-Sayed*

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024
(Received: October 22, 1982; In Final Form: December 13, 1982)

In a disordered solid, where random excitation energy and donor–acceptor separation are expected, low-temperature energy transfer between a high-energy excited molecule to a lower-energy acceptor might not be complete. As a result, the emission profile of the solid at low temperature is determined by the energy distribution of the emission of the trapping sites. Predictions based on these ideas are used and a fit is made to the 4.2 K observed phosphorescence profile of 1-bromo-4-chloronaphthalene (BCN), and orientationally disordered molecular solid. The theoretical fit to the observed emission profile is discussed in terms of the possible energy transfer mechanism(s) in this solid.

Introduction

The characteristics of phonon-assisted spectral diffusion in disordered materials have recently attracted considerable attention. Time-resolved fluorescence line narrowing (TRFLN) studies of spectral diffusion within an inhomogeneously broadened impurity transition in host glasses[1,2] and crystals[3] at high temperatures (i.e., $kT > \Gamma$, the inhomogeneous width observed in absorption) have shown that the narrowed component typically decays preserving its width while the remainder of the inhomogeneous profile emerges uniformly and at long times resembles the absorption profile. Recent TRFLN studies of the $T_1 \leftarrow S_0$ transition of neat 1-bromo-4-chloronaphthalene (BCN) have shown[4] that only exothermic energy transfer from *high- to low-energy sites is observed* at 4.2 K. The exothermic nature of the energy transfer in this system is manifested in the emission spectrum which is shifted to lower energy and is narrower than the corresponding absorption spectrum of the same transition,[5] suggesting only emission from the low-energy sites.

In this Letter we present the emission line-shape function for an inhomogeneously broadened absorption profile for $kT \ll \Gamma$ where only exothermic energy transfer occurs. An interaction radius is defined as the distance between donor and acceptor where the unimolecular radiative lifetime of the donor and the energy transfer time are equal.[6] An energetically excited site with no lower-energy sites within the interaction volume is considered trapped and will contribute to the emission profile. Those sites with lower-energy sites within the interaction volume will transfer the excitation before radiating and will not be observed in emission. The *emission profile in disordered solids at low temperatures will thus reflect the frequency distribution of the emission of the trapping sites.* The results of this model show that, as the number of sites contained in the interaction volume increases, the emission profile is shifted to lower energy and the emission width narrows. We find that from the emission and absorption profiles, along with the radiative lifetime in the absence of energy transfer, one can determine the microscopic energy transfer parameters if the coupling mechanism and dimensionality of the energy transfer are known. The fit to the observed emission profile of the $T_1 \rightarrow S_0$ transition of BCN is found to be good with only one adjustable parameter, the number of sites within the interaction volume.

Emission Line-Shape Function

In the model considered here, the inhomogeneously broadened absorption spectrum is assumed to be due to a random (uncorrelated) distribution of site energies. The effects of homogeneous broadening are taken to be much smaller than the absorption or emission line widths and the oscillator strength is assumed constant across the band such that the distribution of site energies is represented by the absorption profile. The microscopic transfer rate between sites is taken to be independent of the energy of the sites between which energy transfer takes place, *except that only exothermic energy transfer is allowed.* For temperatures where $kT \ll \Gamma$, energy transfer is only possible from high- to low-energy sites since transfer from a low-energy site to a high-energy site requires the population of phonons which will be small at this temperature. For an excitation at energy ν_{exc} in a single-component crystal one can describe the acceptor concentration as the mole fraction of sites having energy $\nu \leq \nu_{\text{exc}}$. Those sites with energy $\nu > \nu_{\text{exc}}$ will correspond to host sites since energy transfer from an excited site at energy ν_{exc} to higher-energy sites will be negligible at low temperatures.

The decay of an energetically excited donor site in the presence of acceptors can occur by radiative and nonradiative unimolecular processes or by the donor transferring its excitation nonradiatively to an acceptor. The radiative and nonradiative unimolecular processes are taken to be independent of the nature of the excited site and to occur with a rate of $1/\tau_0$, where τ_0 is the decay time of the excited state in the absence of acceptors. In the presence of acceptors the donor may transfer its energy nonradiatively through either multipolar or exchange interactions. The rate of energy transfer, $W(R)$, can be written as[6]

$$W(R) = (1/\tau)(d/R)^s \qquad (1)$$

for multipolar interactions where τ is the nearest-neighbor transfer time, d is the nearest-neighbor distance, R is the donor–acceptor pair distance, and $s = 6, 8, 10$ for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively, and for exchange interactions

$$W(R) = (1/\tau)\exp(\gamma(d - R)) \qquad (2)$$

where γ is a measure of the dependence of the transfer rate on distance. For both types of interactions, the transfer rate is strongly dependent on the donor–acceptor distance. One can define an interaction radius,[6] R', as the donor–acceptor distance for which the energy transfer rate is

---

[1] P. Avouris, A. Campion, and M. A. El-Sayed, *Chem. Phys. Lett.*, **50**, 9 (1977).

[2] M. J. Weber, J. A. Paisner, S. S. Sussman, W. M. Yen, L. A. Riseberg, and C. Brecher, *J. Lumin.*, **12/13**, 729 (1976).

[3] D. L. Huber, D. S. Hamilton, and B. Barnett, *Phys. Rev. B*, **16**, 4642 (1977).

[4] P. N. Prasad, J. R. Morgan, and M. A. El-Sayed, *J. Phys. Chem.*, **85**, 3569 (1981).

[5] J. C. Bellows and P. N. Prasad, *J. Phys. Chem.*, **86**, 328 (1982).

[6] D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).

0022-3654/83/2087-0383$01.50/0 © 1983 American Chemical Society

equal to the unimolecular decay rate. From eq 1 and 2 one finds

$$R_0 = R'/d = (\tau_0/\tau)^{1/s} \tag{3a}$$

$$R_0 = 1 + (1/\gamma d) \ln (\tau_0/\tau) \tag{3b}$$

for multipolar and exchange interactions, respectively, where R_0 is the interaction radius in units of the lattice spacing, d. The number of sites (excluding the one occupied by the donor) within the interaction volume, n, is given by

$$n = \tfrac{4}{3}\pi R_0^3 - 1 \tag{4a}$$

$$n = 2\pi R_0^2 - 1 \tag{4b}$$

$$n = 2R_0 - 1 \tag{4c}$$

for 3-D, 2-D, and 1-D interactions, respectively.

We now consider the steady-state excitation of sites on the high-energy side of the inhomogeneous profile where the probability of an acceptor site being in the interaction volume of the initially excited site is near unity. The initial excitation will thus transfer exothermally with unit probability. The exothermic energy transfer process continues until a site is reached for which no lower-energy acceptors lie within the interaction volume. The excitation is thus trapped and will then radiate. Assuming that the initial excitation finds these trapped sites with equal probability, the emission profile will represent the energetic distribution of sites for which no lower-energy acceptors lie within the interaction volume. The distribution of trapped sites can be obtained from calculating, as a function of ν, the product of the probability that a site at energy ν has no lower-energy acceptors within the interaction volume and the relative number of sites at energy ν.

The probability that an energetically excited site has no lower-energy acceptors within the interaction volume given by n is $(1 - \chi_\nu)^n$, where χ_ν is the mole fraction of acceptor sites and is dependent on the excitation energy, ν, of the site for the system considered here. For an inhomogeneously broadened single-component crystal with a Gaussian absorption profile centered at $\nu_{\max}$, the corresponding emission profile, $I(\nu)$, is given by

$$I(\nu) = (\text{constant})(1 - \chi_\nu)^n \exp(-\ln 2((\nu - \nu_{\max})/\Gamma)^2) \tag{5}$$

where Γ is the Gaussian width (hwhm), and

$$\chi_\nu = \Gamma^{-1}(\ln 2/\pi)^{1/2} \int^{\nu' \le \nu} \exp(-\ln 2((\nu' - \nu_{\max})/\Gamma)^2)\, d\nu' \tag{6}$$

For an optically active guest species in a spectrally inert host lattice where the guest species occupy the host lattice sites with probability p (given by the overall mole fraction of the guest), eq 5 holds with $\chi_\nu \rightarrow \chi'_\nu p$, where χ'_ν is determined from the guest absorption profile by using eq 6.

Results

In this section we present our results of the numerical evaluation of eq 5. The emission line shapes for several values of n in the range of 10–10 000 sites for a single-component disordered crystal are displayed in Figure 1, along with the Gaussian absorption profile. Figure 1 illustrates that, as the interaction volume gets larger, the emission profile is shifted further to lower energy and the emission line width narrows. These results can be understood with the physical model used here. For a particular energetically excited site, the probability of finding a lower-energy acceptor site within the interaction volume grows with the interaction volume. The distribution of the emission frequency of the trapping sites is thus shifted to lower energy where the concentration of possible lower-energy acceptors is smaller. The shift in the emission maximum from the absorption maximum and the emission line width vs. the interaction volume are plotted in Figures 2 and 3, respectively. From the absorption and emission spectra of a system, one can find n, the number of sites within the interaction volume, from the energy difference of the absorption and emission maximum using Figure 2. Similarly, one can also determine n using the emission line width and Figure 3. Knowing n, one can infer the microscopic energy transfer parameters in eq 1 and 2 from eq 3 and 4 assuming a particular coupling mechanism and dimensionality.

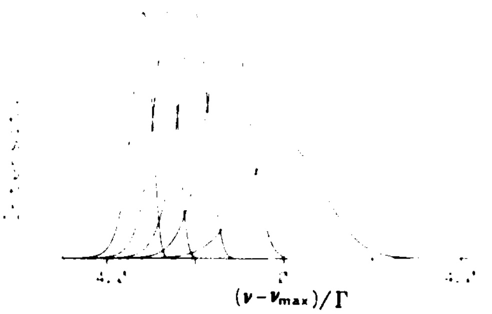


Figure 1. Emission profile $I(\nu)$ for a Gaussian absorption profile in a single-component crystal with an energy transfer interaction volume of n sites. Plotted from right to left are the Gaussian absorption profile and the emission profiles for n = 10^1, 10^2, 10^3, and 10^4 sites, respectively. The emission profile is found to shift to lower energy and to narrow in width with increasing n.

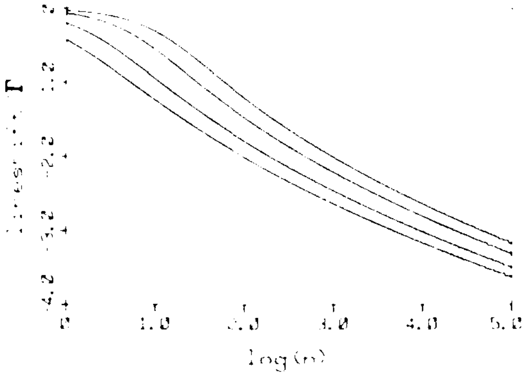


Figure 2. Shift in the guest emission maximum from the absorption maximum normalized by the Gaussian absorption width Γ (hwhm) vs. the interaction volume n. From bottom to top, these curves are for guest mole fractions p = 1.0, 0.5, 0.2, and 0.1, respectively.

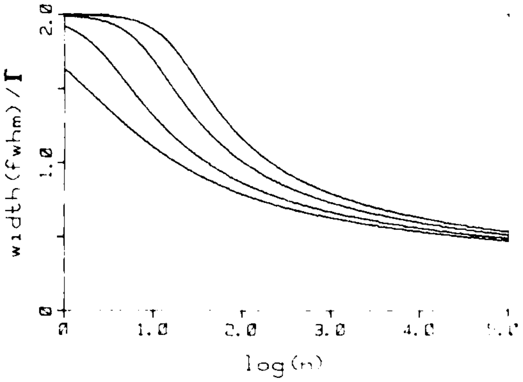


Figure 3. Guest emission line width (fwhm) normalized by Γ vs. the interaction volume n. From bottom to top, these curves are for guest mole fractions p = 1.0, 0.5, 0.2, and 0.1, respectively.

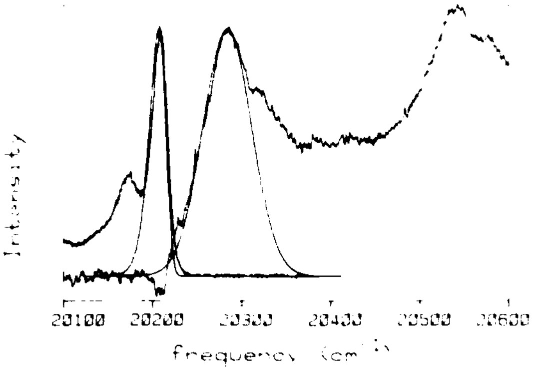


Figure 4. Emission and absorption spectra of the T_1–S_0 transition of 1-bromo-4-chloronaphthalene (BCN) at 4.2 K. The observed absorption profile of the zero phonon line of the 0,0 band is fitted to a Gaussian centered at 20 284 cm^{-1} with $\Gamma = 32$ cm^{-1} (solid line). The observed narrowed emission profile centered at 20 208 cm^{-1} along with the calculated emission line shape (solid line) using eq 5 with $n = 365$ sites.

Absorption and Emission Spectra of BCN. The absorption and emission spectra of the T_1–S_0 transition of BCN at 4.2 K are shown in Figure 4. The spectra were recorded in a similar manner to, and are in agreement with, those reported in ref 5. The absorption spectrum was fitted with a Gaussian profile centered at 20 284 cm^{-1} and with $\Gamma = 32$ cm^{-1}. The calculated trapped emission spectrum shown in Figure 4 is that for $n = 365$ sites and is found to be in good agreement with the observed spectrum. We now discuss this interaction volume in terms of the different energy transfer mechanisms which might be expected to be important for BCN.

The napthalene skeletons of the different BCN molecules are stacked along a one-dimensional array,[7] similar to the 1,4-dibromonaphthalene (DBN) crystal for which the triplet exciton dynamics are found to be one-dimensional and to occur through exchange coupling with a nearest-neighbor interaction, β, of 7.4 cm^{-1}.[8] The 365 sites contained in the interaction volume would yield an interaction radius, R_0, of 182 for a one-dimensional interaction. Using $\beta = 7.4$ cm^{-1}, $R_0 = 182$, and $\tau_0 = 20$ ms[9] for BCN, one obtains from eq 3b a value for γd for direct 1-D exchange of 0.1. Exchange interactions are usually of shorter range, i.e., $\gamma d \gg 1$, with $\gamma d \approx 5$ being typical for many aromatic systems.[10] At these relatively large donor–acceptor distances, superexchange, rather than the exchange, mechanism is expected to be dominant for the BCN system. For the superexchange mechanism the rate of energy transfer at a distance $(N + 1)d$ is given by[11]

$$W(R) \simeq (1/\tau) \exp(N \ln (\beta/\Delta E)) \qquad (7)$$

where ΔE is the separation between host and guest singlet–triplet transition energies. For BCN one can assume that ΔE in this disordered system is given by the energy separation between the absorption and emission maxima. Using $\Delta E = 76$ cm^{-1} and $N = 181$, one finds $\beta \approx 66$ cm^{-1}. This value of β is about 1 order of magnitude larger than the value determined for DBN.[8] This could be due to the following: (a) the assumption used for ΔE, (b) one-dimensional superexchange mechanism is not dominant, (c) eq 7 is not the correct one to use for a system in which ΔE is also a disorder parameter. This makes the transfer time between a particular donor–acceptor pair dependent not only on the donor–acceptor separation but also on the random energy barriers due to intervening molecules of higher triplet energy levels. A detailed theoretical development of this important problem is needed.

We now consider possible three-dimensional interactions. At low acceptor concentrations, which is the case for the region of observed emission in BCN (see Figure 4), energy transfer by weaker but more isotropic interactions may become important.[12] From $n = 365$ one obtains $R_0 = 4.5$ for a three-dimensional interaction. For direct exchange in three dimensions, using $\beta \leq 7.4$ cm^{-1} as an upper limit for the isotropic exchange interaction, one obtains $\gamma d \leq 7$ using eq 3b. For superexchange in three dimensions using an effective $\Delta E = 76$ cm^{-1} and eq 7 one obtains an isotropic $\beta = 0.6$ cm^{-1}. We also consider the isotropic dipole–dipole mechanism here. Using $R_0 = 4.5$ and eq 3a, one obtains a value for the nearest-neighbor dipolar transfer time $\tau = 2.6$ μs.

We have analyzed the emission spectrum of BCN in terms of one-dimensional exchange-type interactions, as observed for the triplet exciton in the analogous DBN system, and possible three-dimensional interactions. The results suggest that the energy transfer at low concentrations in this system is three-dimensional or that the approximate analysis of one-dimensional energy transfer in this system is inadequate. We could not, however, distinguish between three-dimensional exchange-type and dipole–dipole interactions. In this respect, we note that recent time-resolved phosphorescence line narrowing studies of the T_1–S_0 transition of BCN in the low-energy region where the BCN phosphorescence is observed indicate that the energy transfer is of a three-dimensional dipole–dipole nature.[9] From the data in ref 9, a value of τ for dipolar coupling on the order of 10 μs is obtained, in good agreement with the value of 2.6 μs obtained here from the absorption and emission spectra.

Conclusions

In this Letter we have presented a simple, but quite general, model explaining the observed emission profile from energy trapping sites in inhomogeneously broadened systems, where $kT \ll \Gamma$, i.e., when only exothermic energy transfer occurs. The competition between radiation and energy transfer is taken into account by the formulation of an interaction distance R_0 where the radiative and transfer times are equal. An energetically excited site with no lower-energy acceptor sites at a distance $R \leq R_0$ is considered trapped and will contribute to the observed emission. The emission profile is then calculated from the transition energy distribution of these trapping sites. From the absorption and emission profiles one can determine the microscopic energy transfer parameters in eq 1 and 2 knowing the radiative lifetime of the system in the absence of energy transfer and assuming a particular coupling mechanism and dimensionality.

Acknowledgment. We thank Dr. Paras Prasad for supplying us with the BCN sample. The support of the Office of Naval Research is greatly appreciated.

Registry No. BCN, 53220-82-9.

---

[7] J. C. Bellows, E. D. Stevens, and P. N. Prasad, *Acta Crystallogr., Sect. B*, **34**, 3256 (1978).

[8] R. M. Hochstrasser and J. D. Whiteman, *J. Chem. Phys.*, **56**, 5945 (1972).

[9] J. R. Morgan and M. A. El-Sayed, *J. Phys. Chem.*, **87**, 200 (1983).

[10] A. Blumen and R. Silbey, *J. Chem. Phys.*, **70**, 3707 (1979).

[11] G. C. Nieman and G. W. Robinson, *J. Chem. Phys.*, **37**, 2150 (1962).

[12] J. Klafter and R. Silbey, *J. Chem. Phys.*, **72**, 849 (1980).

Reprinted from The Journal of Physical Chemistry, 1983, 87, 200.

Energy Transfer Mechanism Switching in Disordered Solids

Jack R. Morgan and M. A. El-Sayed*

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024 *(Received: October 22, 1982)*

The excitation decay of the long wavelength portion of the inhomogeneously broadened 0,0 band of the $T_1 \leftarrow S_0$ transition due to triplet–triplet energy transfer in 1-bromo-4-chloronaphthalene (orientationally disordered solid) at 4.2 K is analyzed in terms of one-dimensional exchange and three-dimensional dipole–dipole mechanisms. The fit to a dipole–dipole mechanism is observed at long decay times and very long excitation wavelength (i.e., very low acceptor concentrations). As the excitation wavelength decreases (i.e., as the acceptor concentration increases), the one-dimensional exchange mechanism, which describes only the early portion of the decay at the longest wavelength, begins to dominate in describing the full decay range.

Introduction

Disordered solids have a number of properties not possessed by crystalline solids. For example, excitation energies of the different molecules in the disordered solid have a larger spread than in crystalline solids, resulting in a larger inhomogeneous line width for the former (100 cm^{-1} as compared to 1 cm^{-1} at 4.2 K). Furthermore, in disordered solids, the distance between molecules that can exchange excitation energy is not constant leading to an energy diffusion constant which changes with time[1] after a pulsed excitation of the donor in the system. Since the different energy transfer interactions may be of different dimensionality and are expected to be most effective at different ranges of donor–acceptor separation, i.e., at different time scales after the donor excitation, it is possible that, by selecting the proper disordered solid, a switch in the excitation transfer mechanism from a short range and less isotropic interaction to a long range and more isotropic interaction might be observed by analyzing the temporal dependence of an excited donor population at a certain acceptor concentration.[2] Such a behavior is not expected for crystalline materials.

Two different types of energy transfer studies have been carried out. The usual one is that in which the donor and acceptor are two different chemical species. In the second one, using lasers, a set of molecules or ions within the inhomogeneous profile ($\Delta\nu_{\text{inh}}$) can be excited, thus acting as the donors. Some of the species of the same chemical remaining unexcited can act as the acceptors. If $kT > \Delta\nu_{\text{inh}}$, then all the unexcited species are indeed acceptors and the energy transfer process occurs to species of higher or lower frequency than the donor by phonon-assisted processes,[3] e.g., Eu^{3+} in phosphate glasses.[4] If, however, $kT << \Delta\nu_{\text{inh}}$, only those species with absorption frequencies equal to or lower than those excited with the laser are potential acceptors, e.g., the transfer in orientationally disordered 1-bromo-4-chloronaphthalene[5] (BCN) at 4.2 K.

In BCN, the naphthalene skeletal of the different BCN molecules are stacked along a one-dimensional array,[6] similar to the 1,4-dibromonaphthalene crystal for which the energy transfer is found to be one dimensional and to occur by exchange coupling.[7] The disorder, however, arises from the relative orientation of the chlorine and bromine atoms in the solid. The disorder changes the inhomogeneous line width at 4.2 K from 1 cm^{-1} for 1,4-dibromonaphthalene to over 80 cm^{-1} in BCN.[8] Steady-state excitation of the singlet manifold of this system results in phosphorescence[8] with a 20-cm^{-1} half-width appearing at the long wavelength edge of the 0,0 band of the T_1–S_0 absorption.[8] Time-resolved spectral diffusion results at 4.2 K following excitation in the 0,0 band of the T_1–S_0 transition of the BCN solid have recently been published.[5] These studies[5] showed that the rate of the triplet energy transfer increased as the wavelength of the laser (the donor absorption) decreases. As the laser excites molecules of higher triplet energy within the inhomogeneous line width, the mole fraction of molecules within the BCN solid to which the excitation can be transferred increases. This leads to an increase in the transfer rate.

The BCN system seems to be the appropriate solid for these studies. At 4.2 K pulsed laser excitation produces a set of donors of a certain energy. The emission intensity from these molecules, after correcting for first-order decay, monitors the population of the donor decay due to the energy transfer process to molecules having equal or lower T_1–S_0 transition energy. Analysis of this decay in terms of available theoretical expressions for different transfer mechanisms could examine the possibility of energy transfer mechanism switching. Such a possibility has previously been discussed.

The results show that, at low acceptor concentrations (i.e., when exciting at the very long wavelength edge of the 0,0 band), the decay curve could not be fitted to a single mechanism. It could, however, be fitted to a one-dimensional electron exchange expression[9] at short times and a three-dimensional dipole–dipole expression[10,11] at long times. The range of the fit of the exchange mechanism increases and that for dipole–dipole decreases as the excitation wavelength decreases (i.e., as the acceptor concentration increases). These results are explained as follows: At low acceptor concentrations the probability of finding a BCN molecule with triplet energy equal to or less than the donor energy and which is located nearby on the linear chain for electron exchange coupling is very small. This freezes the short-range exchange mechanism and allows for the long-range three-dimensional dipole–dipole mechanism to take over. Of course, as the excitation wavelength decreases and the acceptor concentration in-

---

(1) S. W. Haan and R. Zwanzig, *J. Chem. Phys.*, **68**, 1879 (1978).

(2) J. Klafter and R. Silbey, *J. Chem. Phys.*, **72**, 849 (1980).

(3) T. Holstein, S. K. Lyo, and R. Orbach, *Phys. Rev. Lett.*, **36**, 891 (1976).

(4) (a) P. Avouris, A. Campion, and M. A. El-Sayed, *Chem. Phys. Lett.*, **50**, 9 (1977); (b) J. R. Morgan and M. A. El-Sayed, *J. Phys. Chem.*, **85**, 3566 (1981).

(5) P. N. Prasad, J. R. Morgan, and M. A. El-Sayed, *J. Phys. Chem.*, **85**, 3569 (1981).

(6) J. C. Bellows, E. D. Stevens, and P. N. Prasad, *Acta Crystallogr., Sect. B*, **34**, 3256 (1978).

(7) R. M. Hochstrasser and J. D. Whiteman, *J. Chem. Phys.*, **56**, 5945 (1972).

(8) J. C. Bellows and P. N. Prasad, *J. Phys. Chem.*, **86**, 328 (1982).

(9) A. Blumen, *J. Chem. Phys.*, **72**, 2632 (1980).

(10) M. Inokuti and F. Hirayama, *J. Chem. Phys.*, **43**, 1978 (1965).

(11) A. Blumen and J. Manz, *J. Chem. Phys.*, **71**, 4694 (1979).

0022-3654/83/2087-0200$01.50/0

creases, the probability of finding a nearby BCN molecule which satisfies the energy conservation condition during the transfer process also increases, leading to the dominance of the exchange mechanism.

Experimental Section

The 1-bromo-4-chloronaphthalene was supplied by Professor P. Prasad. It was extensively zone refined. Crystals were grown from the melt in a Bridgmann furnace. Samples were immersed in liquid helium at 4.2 K. A Quanta-Ray Nd:YAG pumped PDL-1 pulsed dye laser with a spectral width of ~0.3 cm^{-1} and a pulse width of 6 ns was used as the T_1–S_0 excitation source at ~0.5 mJ/pulse. Front surface excitation was used throughout. The emission was dispersed with a 1-m Jarrell-Ash monochromator with a 2-cm^{-1} slit width. The monochromator was carefully tuned to the donor 0,0 −321 cm^{-1} vibronic band so as to follow the donor phosphorescence. A gated phototube[12] was used in order to reject the intense scattered laser light. The first 8 μs of signal following the laser pulse was rejected due to interference from switching the focus electrode. The signal was fed into a Biomation 805 waveform recorder. The digitized signal was averaged by a homebuilt signal-averaging computer and analyzed on a PDP 11/45 computer.

Results and Discussion

The physical quantity of interest in these experiments is the donor excitation probability after correcting for the population loss due to unimolecular decay processes, $P(t)$, and is given by $(I(t)/I_0)\exp(t/\tau_0)$, where $I(t)$ is the phosphorescence intensity at time t, I_0 is the intensity at $t = 0$, and τ_0 is the first-order lifetime of the $T_1 \leftrightarrow S_0$ transition. I_0 was determined by extrapolating a log I vs. t fit to the first 10–50 μs of signal to $t = 0$. We estimate I_0 determined in this manner to be accurate to ±20%. τ_0 was determined by fitting the decay at long wavelength and time, where the unimolecular decay dominates, to the first-order decay law and found to be 20 ms.

Fit of Donor Excitation Decay to One-Dimensional Exchange Mechanism. It is generally accepted that triplet–triplet energy transfer between organic molecules occurs via an electron exchange mechanism. Though the nature of the exchange interaction is of short range, even trap-to-trap migration of triplet excitations over an order of ten intervening host molecules in mixed organic crystals has been interpreted in terms of exchange or superexchange.[13] For a single donor–accepter pair, the energy transfer rate $W(R)$, where R is the position of the acceptor relative to the donor position, can be written for the exchange coupling as[14]

$$W(R) = 1/\tau \exp[\alpha(d - R)] \tag{1}$$

where d is the nearest neighbor distance, τ is the transfer time at the nearest neighbor distance, and α is a measure of the dependence of the transfer rate on distance. For superexchange[13]

$$W(R) = 1/\tau \exp[n \ln (\beta/\Delta E)] \tag{2}$$

where τ is the nearest-neighbor transfer time via direct exchange, β is the near-neighbor energy transfer matrix, ΔE is the energy difference between host and guest bands and is $>>\beta$, and n is the number of host molecules over which guest–guest transfer occurs.

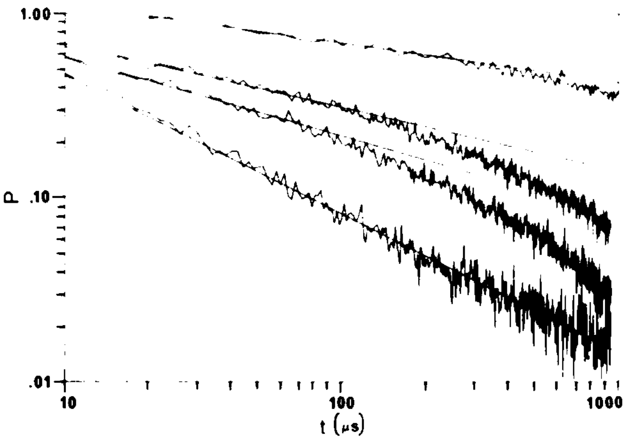


Figure 1. The fit of the early portion of the decay of the triplet excitation due to triplet–triplet energy transfer to an exchange mechanism for different excitation wavelengths (4947, 4943, 4942, and 4940 Å from top to bottom, respectively) within the 0,0 band of the $T_1 \leftarrow S_0$ transition in 1-bromo-4-chloronaphthalene at 4.2 K. The range of the fit increases as the excitation wavelength decreases, i.e., as the acceptor concentration increases.

TABLE I: A Comparison of the Value of the Excitation Probability (P) for Which the One-Dimensional Exchange Fit Ends and the Three-Dimensional Dipolar Mechanism Begins for Different Excitation Wavelengths (λ_{exc})

	P^a	
λ_{exc}, Å	at *end* of 1-D exchange fit	at *start* of 3-D dipolar fit
4947	0.55	0.66
4946	0.56	0.62
4945	0.49	0.57
4944	0.28	0.34
4943	0.28	0.24
4942	0.19	0.17
4941	0.08	0.10
4940	0.015	
4939	0.015	

[a] These values are obtained from one set of data. A least-squares fit was made with a value for χ^2 of 10^{-3}–10^{-4}. These values are the point where the data begin to deviate from the fitted line and should be good to ±10–20%.

The theory of the time dependence of the donor luminescence for direct energy transfer via exchange to randomly distributed acceptors has been worked out for all dimensions.[9] Triplet–triplet exchange interactions in 1,4-dihalonaphthalenes have been shown to be highly anisotropic, with the dominant interaction along the direction almost perpendicular to the plane leading to a one-dimensional character for the exchange interaction.[6] For one-dimensional exchange, Blumen[9] finds that the time dependence of the donor excitation probability, $P(t)$, after subtracting out the first-order decay, can be described by

$$\ln P(t) = -(\alpha d)^{-1} C_a \left(\ln \left(\frac{t}{\tau} e^{\alpha d} \right) + 0.57722 \right) \tag{3}$$

where C_a is the mole fraction of sites occupied by acceptor molecules. For superexchange interactions, eq 3 describes the decay with $-\ln(B/\Delta E)$ substituted for αd.[15]

Figure 1 shows the fit at early times to eq 3 for several excitation frequencies (ν_{exc}) on the low-energy side of the 0,0 absorption band of the $T_1 \leftarrow S_0$ transition. We plot log P vs. log t. On this choice of scales, the decay should be linear for transfer to randomly distributed acceptors

---

[12] W. D. Hopewell, Thesis, University of California, Los Angeles, 1980.

[13] G. C. Nieman and G. W. Robinson, *J. Chem. Phys.*, 37, 2150 (1962).

[14] D. L. Dexter, *J. Chem. Phys.*, 21, 836 (1953).

[15] A. Blumen and R. Silbey, *J. Chem. Phys.*, 70, 3707 (1979).

by the exchange mechanism with a slope of $-C_a/(\alpha d)$. Table I gives the value of P for each excitation wavelength at which the observed decay curve starts to deviate from the fit. It is clear from these values that, although the fit is poor at long excitation wavelengths (4947–4945 Å) (low acceptor concentrations), the fit describes almost the entire decay at the lowest excitation wavelength used (4939 Å) (i.e., higher acceptor concentrations). At shorter than 4939 Å, the expected exchange mechanism must then be the sole transfer mechanism in this crystal.

Fit to a Dipole–Dipole Mechanism. Could the deviation from the fit to an exchange mechanism at long times and excitation wavelengths (low acceptor concentrations) be a result of competition with the long-range dipole–dipole mechanism? In order to test this possibility, we examine the fit of the long time of the decay to theoretical expressions derived for dipolar three-dimensional transfer in disordered systems.

For a single donor–acceptor pair, the energy transfer rate for multipolar interactions can be written as[14]

$$W(R) = 1/\tau(d/R)^S \qquad (4)$$

where $S = 6$, 8, and 10 for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. The time dependence of the donor excitation probability for transfer to randomly distributed acceptors by multipolar interactions has been worked out in three dimensions[10] and later generalized to all dimensions.[11] For dipole–dipole transfer in three dimensions, neglecting back transfer, the decay of the donor can be described by[11]

$$\ln P(t) = -4/3\pi\Gamma(1/2)C_a(t/\tau)^{1/2} \qquad (5)$$

where Γ is the gamma function.

The fit of the long-time donor decay to eq 5 is shown in Figure 2 where we plot log P vs. $t^{1/2}$. It is interesting to observe that the fit covered a larger portion of the decay for long excitation wavelength (low acceptor concentrations). Table I shows this clearly. It gives the maximum value of P at which the observed decay data begins to deviate for the dipole–dipole equation for the different excitation wavelengths used. $P_{\max}$ is highest for longer wavelengths of excitation (lowest acceptor concentrations).

The above results shown in Figures 1 and 2 as well as in Table I can be summarized as follows: At short times of decay, the exchange mechanism seems to fit the data. This fit continues for longer times as the acceptor concentration increases (i.e., donor excitation wavelength decreases). A three-dimensional dipolar mechanism might be involved at very low acceptor concentrations at longer decay times. If this is true, the above data demonstrate for the first time that a switch of the transfer mechanism is taking place during the energy transfer for low acceptor concentrations. At short times, donor molecules lose their energy to nearby molecules with triplet energies equal or lower than their own. As time goes on, the probability of finding this type of molecule decreases and the long-range three-dimensional dipole-dipole mechanism takes over. As the excitation energy increases, i.e., the acceptor concentration increases, the probability of finding molecules with equal or lower energy at close distances becomes nonvanishing even at long decay times and the exchange mechanism becomes dominant, as expected for triplet–triplet energy migration in crystalline solids. As support for possible competition between two mechanisms at low acceptor concentrations, Table I shows that the value of P at which the exchange mechanism begins to fail in describing the decay data (taken from Figure 1) is similar to that at which the dipole–dipole mechanism begins to describe the transfer decay process at long times (taken from Figure 2). Detailed concentration dependence of the transfer in both mechanisms is now under examination and will be published soon.

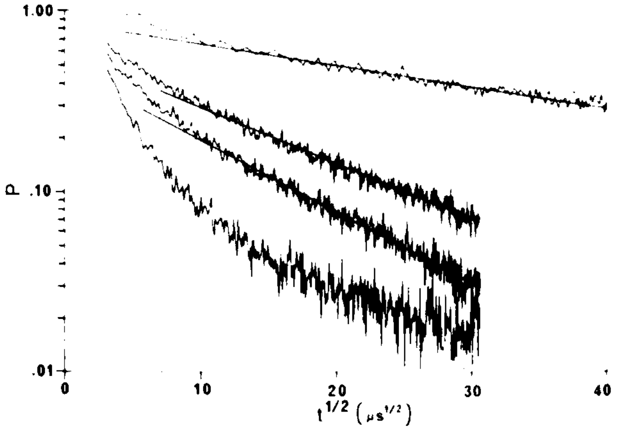


Figure 2. The fit of the long time portion of the decay of the triplet excitation of the 0,0 band of the $T_1 \leftarrow S_0$ transition of 1-bromo-4-chloronaphthalene at 4.2 K due to triplet–triplet energy transfer to a three-dimensional dipolar mechanism for the excitation wavelengths given in Figure 1. The range of the fit is better at longer excitation wavelengths, i.e., at low acceptor concentrations.

Acknowledgment. The authors thank Professor P. Prasad for supplying us with the samples and for fruitful discussions. M.A.E. thanks Dr. Abe Blumen of the Technical University of Munich for useful discussions. M.A.E. also thanks the Alexander von Humboldt Foundation for a Senior U.S. Scientist Award during which some of the thought and writing of this manuscript took place. The financial support of the Office of Naval Research is gratefully acknowledged.

Registry No. 1-Bromo-4-chloronaphthalene, 53220-82-9.

Reprinted from The Journal of Physical Chemistry, 1983, 87, 2178.

Mechanism Switching and Trapping of Triplet–Triplet Energy Transfer in an Orientationally Disordered Molecular Solid

Jack R. Morgan and M. A. El Sayed*

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024 *(Received: December 29, 1982)*

The separation between the ions or molecules in disordered solids varies at random. The optical transition energy could also vary over a wide range for the different molecules or ions in the solid resulting in a large inhomogeneous line width ($\Delta\upsilon_{\mathrm{inh}}$). This allows energy transfer and spectral diffusion studies to be carried out between the same chemical species but at different local environments in these solids by using lasers for excitation. Furthermore, when carried out at temperatures at which $kT << \Delta\upsilon_{\mathrm{inh}}$, energy transfer becomes unidirectional, i.e., to molecules or ions having transition energies equal to or lower than the laser-excited donors within the inhomogeneous profile. This allows studies on the dependence of the rate and mechanism of the energy transfer on the acceptor concentration (i.e., on donor–acceptor separation) to be carried out by simply changing the laser wavelength within the inhomogeneous profile. By analyzing the temporal behavior of the emission intensity of the pulsed-laser-excited set of molecules or ions (donors), the mechanism of the excitation transfer can be elucidated. These types of studies are carried out on the triplet–triplet energy transfer in a unique type of disordered solid, orientationally disordered molecular solids, e.g., 1-bromo-4-chloronaphthalene (BCN) neat solid. In this solid, the T_1–S_0 transition energy is inhomogeneously broadened with $\Delta\upsilon_{\mathrm{inh}} = 64$ cm^{-1}. The temporal behavior of the donor emission intensity can be described by a one-dimensional electronic exchange mechanism, expected for triplet–triplet energy transfer in this system, at laser wavelengths for which the mole fraction of acceptors is >0.1. At longer wavelengths, i.e., for acceptor mole fractions <0.1, the lower energy acceptors are on the average at distances for which the exchange mechanism becomes inefficient. This might explain the observation that, at these wavelengths, the intensity temporal behavior can be described by the long-range, three-dimensional electric dipole–dipole mechanism. Not only the observed temporal behavior but also the quantitative acceptor concentration dependence results point to the possibility of the mechanism switching for the triplet–triplet energy transfer process in this system. At still larger donor-acceptor separation, the dipole–dipole mechanism becomes inefficient and the excitation energy becomes trapped on some of these randomly distributed sites. This allows radiative processes to be observed from these sites. As a result, the observed emission profile of the solid at low temperature is determined by the energy distribution of the emission of the trapping sites. Predictions based on these ideas are used and a fit is made to the 4.2 K observed phosphorescence profile of the BCN solid. The theoretical fit to the observed emission profile is discussed in terms of the possible energy transfer mechanism(s) discussed above.

Introduction

In recent years, considerable interest has been shown in the optical properties of disordered solids, where the disorder can affect both the static and dynamic properties of electronic excitations. Research activities have been on three different types of these systems: the first is rare-earth ions in inorganic glasses,[1-5] the second is protonated and deuterated isotopically mixed aromatic crystals,[6,7] and the third (more recently) is orientationally disordered solids[8-10] (ODS). The latter are molecular crystals which retain a high degree of translational correlation in terms of lattice positions of the center of mass and general molecular orientation but show a distribution of orientations with respect to substituent groups.[11] An example of this type of disorder is the 1-bromo-4-chloronaphthalene (BCN) crystal.[12]

In all of the above systems, the disorder results from a random distribution of the separation between the different molecules or ions being studied. In the first and third systems, the separation as well as the transition energy of the molecules or ions of interest can also vary over a reasonably wide range. This gives rise to a relatively large inhomogeneous line width ($\Delta\upsilon_{\mathrm{inh}}$) for these systems than for crystalline materials. In these solids, where the long-range structural order of simple crystals is absent, not only the inhomogeneous width but also the homogeneous line width is found to be broader than in crystalline materials.[13,14] The homogeneous broadening in glasses has been interpreted[13-18] in terms of the "two-level system" model[19,20] which postulates the existence of a tunneling-type motion of atoms or molecules between two inequivalent minima. Both the inhomogeneous and homogeneous line widths of Eu^{3+} in B_2O_3 glasses have been found[21] to be sensitive to,

---

(1) Motegi, N.; Shionoya, S. *J. Lumin.* **1973**, *8*, 1.
(2) El Sayed, M. A.; Campion, A.; Avouris, P. *J. Mol. Struct.* **1978**, *46*, 355.
(3) Avouris, P.; Campion, A.; El Sayed, M. A. *Chem. Phys. Lett.* **1977** *50*, 9.
(4) Chu, S.; Gibbs, H. M.; McCall, S. L.; Passner, A. *Phys. Rev. Lett.* **1980**, *45*, 1715.
(5) Morgan, J. R.; El Sayed, M. A. *J. Phys. Chem.* **1981**, *85*, 3566.
(6) Kopelman, R.; Monberg, E. M.; Ochs, W. *Chem. Phys.* **1977**, *19*, 413.
(7) Smith, D. D.; Mead, R. D.; Zewail, A. H. *Chem. Phys. Lett.* **1977**, *50*, 358.
(8) Prasad, P. N.; Morgan, J. R.; El Sayed, M. A. *J. Phys. Chem.* **1981**, *85*, 3569.
(9) Morgan, J. R.; El Sayed, M. A. *J. Phys. Chem.* **1983**, *87*, 200.
(10) Morgan, J. R.; El Sayed, M. A. *J. Phys. Chem.* **1983**, *87*, 383.
(11) Kitaigorodsky, A. I. "Molecular Crystals and Molecules"; Academic Press: New York, 1973.
(12) Bellows, J. C.; Prasad, P. N. *J. Phys. Chem.* **1982**, *86*, 328.
(13) Selzer, P. M.; Huber, D. L.; Hamilton, D. S.; Yen, W. M.; Weber, M. J. *Phys Rev. Lett.* **1976**, *36*, 813.
(14) Hegarty, J.; Yen, W. M. *Phys. Rev. Lett.* **1979**, *43*, 1126.
(15) Reinecke, T. L. *Solid State Commun.* **1979**, *32*, 1103.
(16) Lyo, S. K.; Orbach, R. *Phys. Rev. B* **1980**, *22*, 4223.
(17) Lyo, S. K. *Phys. Rev. Lett.* **1982**, *48*, 688.
(18) Reineker, P.; Morawitz, H. *Chem. Phys. Lett.* **1982**, *86*, 359.
(19) Anderson, P. W.; Halperin, B. I.; Varma, C. M. *Phil. Mag.* **1972**, *25*, 1.
(20) Phillips, W. A. *J. Low Temp. Phys.* **1972**, *7*, 351.
(21) Morgan, J. R.; Chock, E. P.; Hopewell, W. D.; El Sayed, M. A.; Orbach, R. *J. Phys. Chem.* **1981**, *85*, 747.

0022-3654/83/2087-2178$01.50/0

and well correlated with, chemical structural changes induced by the addition of Na_2O.

At higher impurity concentrations in glasses, spectral diffusion among the impurity sites due to the nonradiative exchange of electronic excitation at temperatures where $kT > \Delta\upsilon_{inh}$ has been studied by using time-resolved fluorescence line-narrowing techniques.[1-5] The time dependence of the donor emission, which is sensitive to the coupling mechanism and disorder in donor–acceptor distances,[1,22-24] has been used[2,3,5] to show that the transfer is dipolar in nature. Similar results are obtained with crystalline hosts, where a dipolar mechanism has also been found.[25]

In the case of molecular crystals, it is now accepted that triplet exciton transfer results from the electron exchange interaction.[26] Energy transfer in pure crystals is well-understood in terms of the exciton model,[26] where the electronic energy levels of the molecules become bands in the crystal. In the isotopic mixed molecular (disordered) crystals, the large increase in the energy transfer efficiency at some critical trap concentration[6,7] has been interpreted in terms of a percolation model,[6] a model in which a transition from localized to extended states is important[27] (as in the Anderson transition[28] model), and a model based on a hopping mechanism of excitation transfer.[29]

Disordered solids in which both the transition energy and the separation changes over a wide range have a number of properties not possessed by crystalline solids. First, the excitation energies of the different molecules in the disordered solid have a larger spread in excitation energy than in crystalline solids, resulting in a larger inhomogeneous line width for the former (100 cm^{-1} as compared to 1 cm^{-1} at 4.2 K). Second, in disordered solids, the distance between molecules that can exchange excitation energy is not constant, leading to a diffusion coefficient which changes in time[30] after a pulsed excitation of the donor in the system. Third, with the use of lasers, a set of molecules or ions within the inhomogeneous profile can be excited, thus acting as the donors. Some of the species of the same chemical remaining unexcited can act as the acceptors. If $kT > \Delta\upsilon_{inh}$, then all the unexcited species are indeed potential acceptors and the energy transfer process occurs to species of higher or lower frequency than the donor by phonon-assisted processes,[31] e.g., between Eu^{3+} ions in phosphate glasses.[2,3] If, however, $kT << \Delta\upsilon_{inh}$, only those species with transition frequencies equal to or lower than those excited with the laser are potential acceptors, e.g., the transfer in ODS like BCN[8-10] at 4.2 K. In these systems, the concentration of the potential acceptors can be changed continuously by simply changing the wavelength of the tunable laser used for excitation. Since the different energy transfer mechanisms may be of different dimensionality and are expected to be most effective at different ranges of donor–acceptor separation, i.e., at different time scales after the donor excitation, a switch in the excitation transfer mechanism from a shorter range and less isotropic interaction to a long range and more isotropic interaction might be observed by analyzing the temporal dependence of an excited donor population at a certain acceptor concentration,[32] e.g., by adjusting the laser excitation wavelength at low temperatures. Such a behavior is not expected for crystalline materials.

The T_1–S_0 transition of BCN at low temperatures has an inhomogeneous width on the order of 100 cm^{-1}. This line width is about two orders of magnitude larger than the line width observed for the corresponding transition in 1,4-dichloronaphthalene (DCN) and 1,4-dibromonaphthalene (DBN), suggesting that the width in BCN is due to the static orientational disorder in the halogen positions in the crystal.[12] Comparative studies of the crystal structures[33] and Raman spectra[34] of this 1,4-dihalonaphthalene series show that the one-dimensional stacking feature and intermolecular interactions in BCN are similar to DBN for which one-dimensional exchange-type triplet excitons have been observed.[35]

Recent results on the time-resolved phosphorescence line-narrowing (TRPLN) studies at 4.2 K ($kT << \Delta\upsilon_{inh}$) have shown[8] that following pulsed narrow-band excitation on the low-energy side of the absorption profile the line-narrowed component (donor) decays with time while the emission from lower-energy sites emerges uniformly. This is interpreted in terms of a unidirectional high to low energy transfer. The increase in the donor decay rate with increasing donor site energy is interpreted as arising from the increase in the mole fraction of lower energy acceptor sites as one moves to higher energies within the inhomogeneous profile.

In this paper, we present the temporal behavior of the phosphorescence emission intensity of laser-excited triplet energy donors in BCN at 4.2 K. From the analysis of the donor emission decay, the coupling mechanism can be inferred. This analysis is carried out as a function of the acceptor concentration (i.e., the excitation laser wavelength). The aim of these studies is to look for possible switching of the energy transfer mechanism in a disordered solid like BCN as the donor–acceptor separation (i.e., acceptor concentration) is changed. The results suggest that a possible switching from a one-dimensional exchange to a three-dimensional electric dipole–dipole mechanism takes place as the acceptor concentration is reduced below 10 mol %. At still larger donor–acceptor separation, none of the coupling mechanims can compete with radiative processes, leading to excitation trapping. On the basis of this simple idea, a phenomenological description of the trapping process in these disordered solids is given which is found to account for the observed trapped emission in BCN and to give energy transfer parameters which are in reasonable agreement with the results obtained from the decay analysis of the temporal behavior discussed above. Preliminary reports of this work have recently been communicated.[9,10]

Experimental Section

The BCN was synthesized from 1-amino-4-chloronaphthalene by means of a procedure described elsewhere.[12] The material was extensively zone refined. Crystals were grown from the melt in a Bridgemann furnace. The 4.2 K measurements were carried out with the sample immersed in liquid helium.

---

(22) Inokuti, M.; Hirayama, F. *J. Chem. Phys.* 1965, *43*, 1978.

(23) Blumen, A.; Manz, J. *J. Chem. Phys.* 1979, *71*, 4694.

(24) Blumen, A. *J. Chem. Phys.* 1980, *72*, 2632.

(25) Selzer, P. M.; In "Topics in Applied Physics"; Yen, W. M.; Selzer, P. M., Ed.; Springer: Berlin, 1981; Vol. 49, Chapter 4, and references therein.

(26) Craig, D. P.; Walmsley, S. H. "Excitons in Molecular Crystals"; W. A. Benjamin: Amsterdam, 1968.

(27) Klafter, J.; Jortner, J. *Chem. Phys. Lett.* 1977, *49*, 410.

(28) Anderson, P. W. *Phys. Rev.* 1958, *109*, 1492.

(29) Blumen, A.; Silbey, R. *J. Chem. Phys.* 1979, *70*, 3707.

(30) Haan, S. W.; Zwanzig, R. *J. Chem. Phys.* 1978, *68*, 1879.

(31) Holstein, T.; Lyo, S. K.; Orbach, R. *Phys. Rev. Lett.* 1976, *36*, 891.

(32) Klafter, J.; Silbey, R. *J. Chem. Phys.* 1980, *72*, 849.

(33) Bellows, J. C.; Stevens, E. D.; Prasad, P. N. *Acta Crystallogr., Sect. B* 1978, *34*, 3256.

(34) Bellow, J. C.; Prasad, P. N. *J. Chem. Phys.* 1978, *67*, 5802.

(35) Hochstrasser, R. M.; Whiteman, J. D. *J. Chem. Phys.* 1972, *56*, 5945.

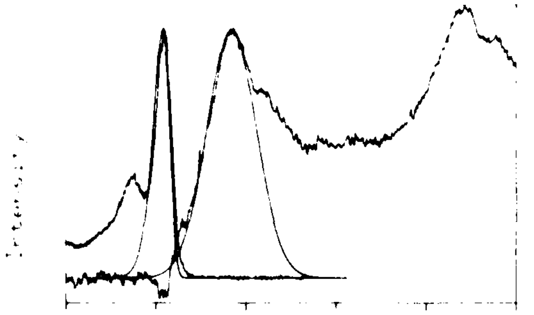


Figure 1. The emission and absorption spectra of the T_1–S_0 transition of 1-bromo-4-chloronaphthalene (BCN) at 4.2 K. The observed absorption profile of the zero phonon line of the 0,0 band is fitted to a Gaussian centered at 20 284 cm^{-1} with Γ = 32 cm^{-1} (solid line). The observed narrowed emission profile centered at 20 208 cm^{-1} along with the calculated emission line shape (solid line) by using eq 12 with n = 365 sites.

Spectra were recorded with a 1-m Jarrell-Ash monochromator with 2-cm^{-1} resolution used throughout. Steady-state phosphorescence spectra were obtained by excitation with the 3300-Å region of a 100-W mercury–xenon lamp. Absorption spectra were obtained with a 80-W quartz–halogen lamp. The signal was averaged with a PAR Model 162 boxcar averager, recorded on a Tracor-Northern NS-570A multichannel digitizer, and analyzed on a PDP-11/45 computer.

For time-resolved measurements, a Quanta-Ray DCR-1 Nd:YAG pumped pulsed dye laser at a repetition rate of 10 Hz with a spectral width of 0.3 cm^{-1} and a pulse width of 6 ns was used as the T_1–S_0 excitation source. Time-resolved spectra of the T_1–S_0 phosphorescence of the 0,0 321-cm^{-1} band in the wavelength domain were recorded with the PAR boxcar averager. The temporal dependence of the donor phosphorescence was performed by carefully tuning the monochromator to the donor 0,0 321-cm^{-1} band so as to follow the donor intensity. Spectra were recorded with a Biomation 805 waveform digitizer, averaged with a homebuilt signal-averaging computer, and analyzed on a PDP-11/45 computer. A special gated phototube was used in order to reject scattered laser light. Due to interference from switching the focus electrode, the first 10 μs of signal following the laser pulse was rejected. In order to estimate I_0, the intensity at time t = 0, I_0 was determined by extrapolating a log I vs. log t fit to the first 10–50 μs of signal to t = 0.

Absorption and Emission Spectra of BCN

The broad features observed in the T_1–S_0 absorption spectrum of BCN indicate that the singlet–triplet absorption in this system is inhomogeneously broadened. The nature of the inhomogeneous broadening most likely arises from the static orientational disorder in the bromine and chlorine positions in the crystal. The orientational disorder leads to an inhomogeneous distribution of the site energy due to the disorder in the static crystal shift from the gaseous excitation energy. The absorption profile of the 0,0 band of the singlet–triplet transition of neat BCN at 4.2 K is shown in Figure 1. The general characteristics are in agreement with the spectrum reported in the literature.[12] Shown in Figure 1 is a fit of the absorption profile to a Gaussian with a 32-cm^{-1} width (hwhm), suggesting an inhomogeneous type of broadening. A temperature-dependent study of the absorption line shape for BCN has shown that the homogeneous broadening due to interactions with phonons is much smaller than that due to the disorder.[12] The broad, structureless, and nearly Gaussian absorption profile lend support to the interpretation that the inhomogeneous profile is determined by the static structural disorder.

The phosphorescence profile of the 0,0 band of the T_1–S_0 transition of neat BCN is also shown in Figure 1, which agrees with that previously reported.[12] The phosphorescence profile is observed to be narrower than the absorption profile and to originate from the low-energy sites observed in absorption. These results indicate that at 4.2 K a rapid phonon-assisted energy cascade from high to low energy sites occurs in neat BCN at 4.2 K. At temperatures where $kT <<$ inhomogeneous width, energy transfer from low to high energy sites will be negligible since energy transfer from low to high energy sites requires the population of phonons which will be small in this temperature regime. We will return to the origin of the phosphorescence profile after describing the results of the time-resolved phosphorescence line-narrowing (TRPLN) studies in this system.

Dynamics of Spectral Diffusion in BCN

The results of the TRPLN studies reported in ref 8 show that spectral diffusion of the T_1–S_0 transition energy occurs in BCN, where the band shape of the first vibronic band was monitored as a function of delay time. The results show that the line-narrowed component decreases in intensity preserving its width, while phosphorescence from the lower energy acceptors increases in intensity. The acceptor phosphorescence is observed to increase uniformly in time and at long times resembles the steady-state phosphorescence of the 0,0 321-cm^{-1} band.

The results of the dependence of the rate of spectral diffusion on the donor site excitation energy reported in ref 8 show that the energy transfer rate is strongly dependent on the donor excitation energy. Excitation at lower energies within the absorption profile result in phosphorescence mainly from the initially excited sites. With excitation at higher energies within the absorption profile the relative donor to lower energy acceptor phosphorescence decreases uniformly. For excitation at 4937 Å only the acceptor emission is observed on the time scale used. Excitation at higher energies within the inhomogeneous profile results in emission only from the lower energy sites. The phosphorescence from the low-energy acceptors following pulsed excitation within the 0,0 absorption profile at energies higher than 4937 Å is similar in both width and position to the phosphorescence profile observed with steady-state broad-band excitation of the S_1–S_0 transition. These results show that the energy cascades down to the same energetic distribution of sites regardless of the initially excited site energy for energies higher than the phosphorescence profile.

The TRPLN results confirm that the absorption profile is inhomogeneously broadened and that a one-way energy transfer from high to low energy sites occurs in this system. In the BCN system at 4.2 K, $kT \sim 3$ cm^{-1} while the inhomogeneous width is 64 cm^{-1} (fwhm). At this temperature, transfer from low-energy sites to higher-energy sites by the absorption of one phonon is negligible since this process requires the population of phonons of energy $\Delta E_{12} >> kT$, where ΔE_{12} is the energy mismatch between the donor and acceptor sites, which will be very small. For the same reason, the higher-order Raman and Orbach type phonon-assisted processes[31] for transfer from low to high energy sites will also be unimportant at this temperature.

The time development of the low-energy acceptor phosphorescence reported in ref 8 shows that the initially excited line-narrowed component decreases in time preserving its width while the low-energy acceptor phosphorescence emerges uniformly resembling the steady-state phosphorescence profile at all times. The acceptor phosphorescence does not simply reflect the energetic distribution of all of the lower energy acceptors which is given by the tail of the Gaussian for $E < E_1$, where E_1 is the energy of the initially excited donors. For symmetric energy transfer, where transfer to higher or lower energy sites occurs with a similar probability, the details of the emergence of the acceptor profile and the wavelength dependence of the energy transfer rate can be used to determine the dependence of the energy transfer rate on the donor–acceptor energy mismatch.[25,31] The interpretation of the energy mismatch dependence when energy transfer is observed to take place only to lower energy acceptor sites is complicated by the increase in the density of lower energy acceptors as the energy of the donor is increased. This could explain the increase in the energy transfer rate with increasing donor site energy. The analysis of the temporal development of the low-energy acceptor phosphorescence is thus complicated by spectral diffusion within the acceptor system. For an initial transfer step from the initially excited donor at energy E_1 to an acceptor at energy E_2 where ΔE_{12} is small on the scale of the average donor–acceptor energy mismatch, the time scale of a second transfer step from E_2 to a still lower energy acceptor will be comparable to the initial transfer from E_1 to E_2. The occurrence of multiple transfer steps for a single excitation will prevent the observation of phosphorescence from the full acceptor density at higher acceptor energies. The emergence of the phosphorescence from the full spectrum of lower energy acceptors resembling the steady-state phosphorescence profile regardless of the initial excitation energy indicates that the energy transfer process is only weakly dependent on the energy mismatch. The increase in the energy transfer rate with increasing donor excitation energy is then predominantly due to the increase in the density of acceptors. We now turn to the temporal dependence of the donor intensity and assume that the acceptor concentration can be described by the mole fraction of sites with energies equal to or less than the initial donor excitation energy.

Temporal Behavior of the Donor Excitation Probability

The inhomogeneous broadening of the T_1–S_0 transition energy in BCN is assumed to be microscopic in nature with a random spatial distribution of transition energies. A high degree of correlation in site energies would most likely result in a distortion of the low-energy acceptor phosphorescence profile with different excitation wavelengths due to preferential energy transfer to a particular type of acceptor. The uniformity of the acceptor phosphorescence with time and donor excitation wavelength suggests that the site energies are to a good degree uncorrelated, at least on the low-energy tail of the absorption profile where all of our measurements have been made. The random nature of the site energies at the low-energy side of the absorption profile results in a distribution of the distances between donor and lower energy acceptors. For a single donor–acceptor pair the energy transfer rate $W(R)$, where R is the position of the acceptor, can be written as[36,37]

$$W(R) = \frac{1}{\tau}\exp[\gamma(d - \mathrm{R})] \qquad (1)$$

for isotropic exchange coupling, and

$$W(R) = \frac{1}{\tau}(d/R)^s \qquad (2)$$

for isotropic multipolar interactions. Equations 1 and 2 are expressed in terms of d, the nearest-neighbor distance, and τ, the transfer time from a donor to an acceptor at a distance d. In eq 1, γ is a measure of the dependence of the transfer rate on distance for exchange coupling. The exponent s in eq 2 is 6, 8, or 10 for electrostatic dipole–dipole, dipole–quadrupole, or quadrupole–quadrupole interactions, respectively.

So that the time dependence of the donor excitation probability, $P(t)$, in a macroscopic system can be described, a statistical averaging of the distances R is necessary. The distance averaging was first treated by Inokuti and Hirayama[22] for exchange and multipolar interactions in three dimensions and later generalized to all dimensions for both exchange[24] and multipolar[23] interactions. The time dependence of the donor excitation probability, after correcting for the first-order radiative decay, for exchange can be described by[24]

$$\ln\,[P(t)] = -aV_\Delta(\gamma d)^{-\Delta}cg_\Delta\left(\frac{t}{\tau}e^{\gamma d}\right) \qquad (3)$$

where V_Δ is the volume of a unit sphere in a space of Δ dimensions, a is a constant ~ 1 whose exact value depends on the lattice geometry, and c is the acceptor concentration. The function $g_\Delta((t/\tau)e^{\gamma d})$ is given by[24]

$$g_1\left(\frac{t}{\tau}e^{\gamma d}\right) = \ln\left[\frac{t}{\tau}e^{\gamma d}\right] + 0.57722 \qquad (4a)$$

$$g_2\left(\frac{t}{\tau}e^{\gamma d}\right) = \left(\ln\left[\frac{t}{\tau}e^{\gamma d}\right]\right)^2 + 1.15443\ln\left[\frac{t}{\tau}e^{\gamma d}\right] + 1.97811 \qquad (4b)$$

$$g_3\left(\frac{t}{*\mathrm{au}}e^{\gamma d}\right) = \left(\ln\left[\frac{t}{\tau}e^{\gamma d}\right]\right)^3 + 1.73165\left(\ln\left[\frac{t}{\tau}e^{\gamma d}\right]\right)^2 + 5.93434\ln\left[\frac{t}{\tau}e^{\gamma d}\right] + 5.44487 \qquad (4c)$$

For multipolar interactions, the time dependence of the donor excitation probability, after correcting for the first-order radiative decay, can be described by[23]

$$\ln\,[P(t)] = -V_\Delta\Gamma\left(1 - \frac{\Delta}{s}\right)c(t/\tau)^{\Delta/s} \qquad (5)$$

where $\Gamma(1 - \Delta/s)$ is the gamma function. The above results were obtained for low acceptor concentrations and neglecting back transfer from acceptor to donor.

It is generally accepted that triplet–triplet energy transfer in organic molecular crystals is of the exchange type. Though the nature of the exchange interaction is of short range, even trap-to-trap migration of triplet excitations over an order of 10 intervening host molecules in mixed organic crystals has been interpreted in terms of exchange or superexchange.[38] In a study of the exciton dynamics in DBN,[35] it was found that the exciton could well be described by a one-dimensional behavior along the DBN stack with a nearest-neighbor exchange coupling β of 7.4 cm^{-1}, where $\tau = h/\beta$. The one-dimensional behavior was attributed to the strong pπ orbital overlap between nearest neighbors in a direction almost perpendicular to the molecular plane. In a comparative study of the crystal structures of the 1,4-dihalonaphthalenes it was found that,

---

(36) Forster, T. *Z. Naturforsch. A* 1949, *4*, 321.
(37) Dexter, D. L. *J. Chem. Phys.* 1953, *21*, 836.
(38) Niemann, G. G.; Robinson, G. W. *J. Chem. Phys.* 1962, *37*, 2150.

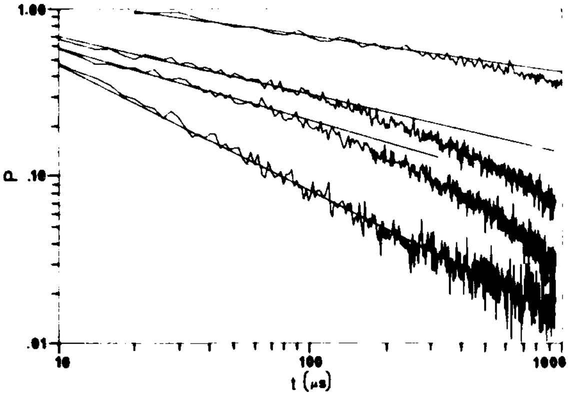


Figure 2. The fit of the early portion of the decay of the triplet excitation due to triplet–triplet energy transfer to an exchange mechanism for different excitation wavelengths (4947, 4943, 4942, and 4940 Å from top to bottom, respectively) within the 0,0 band of the T_1–S_0 transition in 1-bromo-4-chloronaphthalene at 4.2 K. The range of the fit increases as the excitation wavelength decreases, i.e., as the acceptor concentration increases.

although DCN and BCN crystallize in a somewhat different structure ($P2_1/c$, $Z = 4$) than DBN ($P2_1/c$, $Z = 8$), both structures show a very similar stacking feature suggesting that the BCN structure should also show a one-dimensional intermolecular interaction.[33] The study of the Raman spectra in the neat and mixed crystals has suggested that the intermolecular interactions in the 1,4-dihalonaphthalenes are similar.[34]

Because of the similarities of the interactions in the BCN crystal, to those in the DBN crystal, where one-dimensional exchange-type excitons are observed, we will first examine the temporal dependence of the donor phosphorescence intensity in terms of one-dimensional exchange interactions in order to test if this dimensionality and type of interaction is preserved for the long-range (greater than nearest neighbor at low acceptor concentrations), nonresonant energy transfer that results from the inhomogeneity of the T_1–S_0 transition in BCN. The fit of the donor excitation probability after correcting for the first-order radiative decay, $P(t)$, to the one-dimensional exchange mechanism by using eq 3 and 4a for several excitation wavelengths on the low-energy tail of the 0,0 band of the T_1–S_0 transition of BCN is shown in Figure 2 where we plot log [$P(t)$] vs. log t. The quantity $P(t) = I(t) \exp(t/\tau_0)$, where $I(t)$ is the phosphorescence intensity normalized to one at $t = 0$ and τ_0 is the radiative lifetime in the absence of energy transfer. On this choice of scales, the decay should be linear for energy transfer to randomly distributed acceptors in one dimension by the exchange mechanism with a slope of $-c/\gamma d$. The fit to this mechanism and dimensionally at short times, although poor at longer wavelengths (lower acceptor concentrations), is very good at shorter wavelengths (4940 Å) where the acceptor concentration is higher.

We now discuss the acceptor concentration dependence of the slopes of the fit to the one-dimensional (1-D) exchange mechanism above in Figure 2. We have previously described the acceptor concentration in the BCN system at 4.2 K as the mole fraction of BCN molecules whose T_1–S_0 transition frequencies, υ, are less than the donor transition frequency, υ_{exc}. For a Gaussian distribution of site energies, the mole fraction of sites having transition frequencies less than υ, X_υ, is given by

$$X_\upsilon = \Gamma^{-1}\left(\frac{\ln 2}{\pi}\right)^{1/2} \int^{\upsilon<\upsilon'} \exp[-(\ln 2)((\upsilon' - \upsilon_{\max})/\Gamma)^2]\, d\upsilon' \tag{6}$$

Figure 3. The magnitude of the slope of the 1-D exchange fit ($-m_{1\text{-D},E}$) to the early portion of the decay of the triplet excitation shown in Figure 2 vs. the mole fraction of lower energy acceptors (X_ν) determined from eq 6 for BCN at 4.2 K. The solid line is the graph of $-m_{1\text{-D},E} = X_\nu/\gamma d$ where $\gamma d = 0.1$. The dashed line is for $\gamma d = 5$, a value typical for many aromatic systems.[29]

where Γ is the Gaussian width (hwhm) centered at $\upsilon_{\max}$. From Figure 1 we find $\Gamma = 32$ cm^{-1} and $\upsilon_{\max} = 20284$ cm^{-1} for the 0,0 band of the T_1–S_0 transition of BCN at 4.2 K. The magnitude of the slope of the (1-D) exchange fit, $-m_{1\text{-D},E}$ vs. X_υ is shown in Figure 3. The solid line is the graph of $-m_{1\text{-D},E} = X_\upsilon/\gamma d$ where $\gamma d = 0.1$. Exchange interactions are usually of shorter range, i.e., $\gamma d >> 1$, with $\gamma d = 5$ being typical for many aromatic systems.[29] For illustrative purposes, the expected concentration dependence of $-m_{1\text{-D},E}$ for γd equal to 5 is also displayed in Figure 3. From the poor fit of the 1-D exchange mechanism we conclude that this mechanism is not the dominant energy transfer mechanism for the excitation energies used here. At these relatively low acceptor concentrations, superexchange, rather than the exchange mechanism, may be expected to be dominant. For the supperexchange mechanism the rate of energy transfer at a distance $(N + 1)d$ is given by[38]

$$W(R) = \frac{1}{\tau} \exp(N \ln (\beta/\Delta E)) \tag{7}$$

where ΔE is the separation between host and donor singlet–triplet transition energies and is $>> \beta$. From the similarity of eq 1 and 7 one can see that the form of the superexchange interaction is the same as the exchange interaction with $-\ln (\beta/\Delta E)$ equivalent to γd.[29] Equation 3 may then describe the donor excitation probability with $\gamma d = -\ln(\beta/\Delta E)$. We define the host species in BCN as those molecules with transition frequencies $\upsilon > \upsilon_{\text{exc}}$. Taking the absorption maximum as an effective host energy level one obtains $\Delta E = 37$–70 cm^{-1} for the excitation energies used here. For $\beta << 37$ cm^{-1} the temporal decay of the donor excitation probability should be linear on a log [$P(t)$] vs. log t scale for the superexchange mechanism. The poor fit at the longer excitation wavelengths shown in Figure 2 indicate that the superexchange mechanism is also not important at low acceptor concentrations. For excitation at 4940 Å, the decay appears to fit the superexchange mechanism with $-m_{1\text{-D},E} = 0.78$. Taking $-m_{1\text{-D},E} = c/[-\ln (\beta/\Delta E)]$ with $c = 0.066$ from eq 6 and $\Delta E = 41$ cm^{-1} for excitation at 4940 Å, one obtains $\beta = 38$ cm^{-1} for BCN. This value is much greater than the 7.4-cm^{-1} value observed for β in the DBN crystal which should show a similar exchange coupling. It also yields a value for $\Delta E/\beta$ of about unity for which the description of the superexchange coupling in eq 7 may not be entirely valid. In addition, the description of the superexchange coupling given in eq 7 assumes constant energy separation ΔE. In the BCN system, however, the individual host energy levels

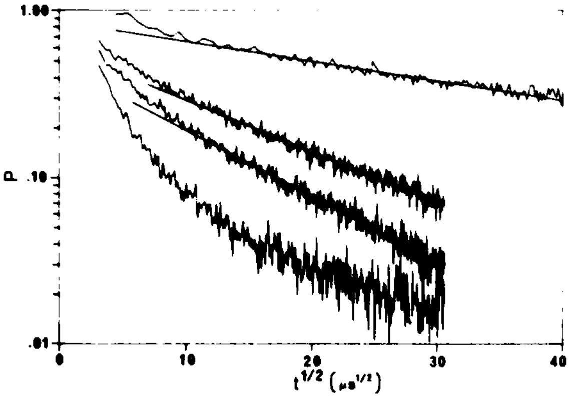


Figure 4. The fit of the long time portion of the decay of the triplet excitation of the 0,0 band of the T_1–S_0 transition of 1-bromo-4-chloronaphthalene at 4.2 K due to triplet–triplet energy transfer to a three-dimensional dipolar mechanism for the excitation wavelengths given in Figure 2. The range of the fit is better at longer excitation wavelengths, i.e., at low acceptor concentrations.

are not constant, with a spread of transition frequencies given by $\Delta\nu_{\rm inh}$. The use of eq 7 for the description of the superexchange coupling with an effective ΔE, and the subsequent analysis with eq 3, may not be adequate for this system, where the disorder in host energy levels is comparable to ΔE. A theoretical examination of the superexchange mechanism for energy transfer in a disordered host is indeed needed.

We now consider the possibility that the energy transfer in the BCN system at the long wavelength region of the absorption band where the acceptor concentration is low may arise from more isotropic interactions. One-dimensional exchange-type interactions have been found to be unable to account for the temporal dependence of the donor excitation probability. At low acceptor concentrations, where energy transfer to acceptor sites at distances greater than the nearest-neighbor distance is important, more isotropic interactions may dominate over a one-dimensional interaction. We now examine the temporal dependence of the donor excitation probability in terms of the dipole–dipole interaction in three dimensions since this interaction is more isotropic and also has a slower distance dependence than the exchange interaction in this crystal.

The fit of $P(t)$ to the three-dimensional dipolar interaction with eq 5 for the same excitation wavelengths used in Figure 2 is shown in Figure 4 where we plot log $[P(t)]$ vs. $t^{1/2}$. On this choice of scales the decay should be linear with a slope proportional to the acceptor concentration. At the longest wavelength (4947 Å) the decay is well described by the three-dimensional (3-D) dipole–dipole form, while at shorter wavelengths deviations from the fit are observed at early times. At 4940 Å we were unable to fit any sizable portion of the decay to the dipolar form. These results suggest that at long excitation wavelengths (low acceptor concentration) and at long times the dipolar interaction dominates the energy transfer in this system. At short times and short excitation wavelengths (corresponding to shorter donor–acceptor distances) other interactions become important and the decay curve deviates from the dipolar form. At shorter donor–acceptor distances the one-dimensional exchange or possibly three-dimensional exchange interactions most likely become important also. For excitation at 4940 Å, which correspond to relatively high acceptor concentration, both exchange and dipolar interactions may be active, which could account for our inability to interpret the decay in terms of only one mechanism.

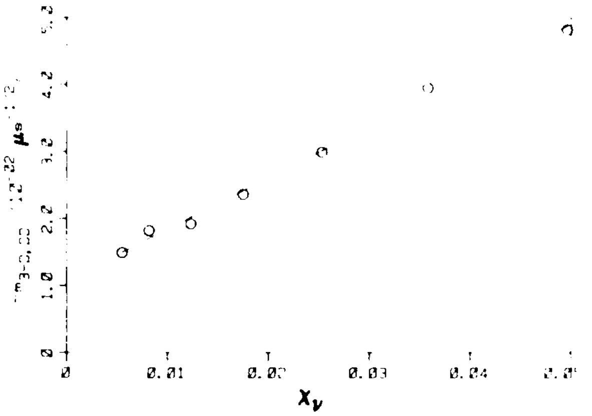


Figure 5. The magnitude of the slope of the 3-D dipole–dipole fit ($-m_{3\text{-D,DD}}$) to the long-time portion of the triplet excitation shown in Figure 4 vs. the mole fraction of lower energy acceptors (X_ν) for BCN at 4.2 K. $m_{3\text{-D,DD}}$ shows the predicted linear dependence on acceptor concentration for dipole–dipole coupling.

As further evidence of the dipolar nature of the decay, we show in Figure 5 the acceptor concentration dependence of $-m_{\rm 3D,D\text{-}D}$, where $m_{\rm 3D,D\text{-}D}$ is the slope of the fitted line in the log $[P(t)]$ vs. $t^{1/2}$ plot. $m_{\rm 3D,D\text{-}D}$ shows the predicted linear dependence on concentration according to eq 5. The solid line in Figure 5 is the best-fit line with $-m_{\rm 3D,D\text{-}D} = 1.8\ \mu s^{-1/2}(c + 0.013)$. Although $m_{\rm 3D,D\text{-}D}$ does not extrapolate to zero at zero acceptor concentration, this may be due to either errors in our estimation of the acceptor concentration from the assumption of a Gaussian absorption profile (see Figure 1) or from contributions to the decay from exchange coupling. For $-m_{\rm 3D,D\text{-}D} = 1.8\ \mu s^{-1/2}c$, one obtains from eq 5 a value for the transfer time at the nearest-neighbor distance for dipolar coupling of 17 μs.

Trap Phosphorescence Profile of BCN at 4.2 K

In the previous sections we have described the spectral diffusion in the BCN system at 4.2 K in terms of a one-way high to low energy transfer process in which the increasing mole fraction of lower energy acceptors as one goes to higher energies within the inhomogeneously broadened T_1–S_0 absorption profile plays an important role. These features are manifested in the phosphorescence profile of the same transition which is narrower than the absorption profile and originates from the lower-energy sites. In this section we develop a simple model for the phosphorescence profile in which the energy cascades down from higher to lower energy sites until sites are reached for which the transfer rate becomes slower than the radiative decay rate.

The decay of an energetically excited donor site in the presence of acceptors can occur by radiative and nonradiative unimolecular process or by the donor transfering its excitation nonradiatively to an acceptor. The radiative and nonradiative unimolecular processes are taken to be independent of the nature of the excited site and to occur with a rate of $1/\tau_0$, where τ_0 is the decay time in the absence of acceptors. In the presence of acceptors the donor may transfer its energy nonradiatively through either multipolar or exchange-type interactions where $W(R)$ is given in eq 1, 2, and 7 for exchange, multipolar, and superexchange interactions, respectively. One can define an interaction radius, R', as the donor–acceptor distance for which the energy transfer rate is equal to the unimolecular decay rate.[37] From eq 1, 2, and 7 one finds

$$R_0 = R'/d = (\tau_0/\tau)^{1/s} \tag{8a}$$

$$R_0 = 1 + \frac{1}{\gamma d} \ln (\tau_0/\tau) \tag{8b}$$

$$R_0 = 1 + \frac{1}{-\ln (\beta/\Delta E)} \ln (\tau_0\beta/h) \qquad (8c)$$

for multipolar, exchange, and superexchange interactions, respectively, where R_0 is the interaction radius in units of the lattice spacing, d. The radiative quantum yield, $\Phi(R)$, for a donor with an acceptor at distance R is given by

$$\Phi(R) = \frac{\tau_0^{-1}}{\tau_0^{-1} + W(R)} \qquad (9)$$

where τ^0 is the radiative decay rate. Using eq 8a and 8b one can write the quantum yield in terms of R' as

$$\Phi(R) = [1 + (R'/R)^s]^{-1} \qquad (10a)$$

$$\Phi(R) = [1 + \exp(\gamma d(R'/d - R/d))]^{-1} \qquad (10b)$$

for multipolar and exchange interactions, respectively. A form similar to eq 10b exists for the superexchange interaction. Equations 10a and 10b yield sigmoid type curves with $\Phi(R) = 1/2$ at $R = R'$. We now approximate eq 10a and 10b with a step function where $\Phi(R) = 0$ if $R < R'$ and $\Phi(R) = 1$ if $R > R'$. An electronically excited molecule with no lower energy acceptors at a distance $R < R'$ is then assumed to emit radiation while a molecule with a lower energy acceptor at $R < R'$ will transfer its excitation before emitting and will not be seen in emission. The number of sites (excluding the one occupied by the donor) within the interaction volume, n, is given by

$$n = 4/3\pi R_0^3 - 1 \qquad (11a)$$

$$n = 2\pi R_0^2 - 1 \qquad (11b)$$

$$n = 2R_0 - 1 \qquad (11c)$$

for 3-D, 2-D, and 1-D interactions, respectively.

We now consider the steady-state excitation of sites on the high-energy side of the inhomogeneous profile where the probability of an acceptor site being in the interaction volume of the initially excited site is near unity. The initial excitation will thus transfer exothermally with unit probability. The exothermic energy transfer process continues until a site is reached for which no lower energy acceptors lie within the interaction volume. The excitation is thus trapped and will then radiate. If we assume that the initial excitation finds these trapping sites with equal probability, the emission profile will represent the energetic distribution of sites for which no lower energy acceptors lie within the interaction volume. The distribution of trapping sites, $I(\upsilon)$, can be obtained from calculating, as a function of υ, the product of the probability that a site at energy υ has no lower energy acceptors within the interaction volume, $Pr(\upsilon)$, and the relative number of sites at energy υ, $N(\upsilon)$, i.e.

$$I(\upsilon) = \text{constant} \times Pr(\upsilon)\, N(\upsilon) \qquad (12)$$

The probability, $Pr(\upsilon)$, that an energetically excited site has no lower energy acceptors within the interaction volume given by n is $(1 - X_\upsilon)^n$. For an inhomogeneously broadened single component (i.e., neat crystal with a Gaussian absorption profile, the corresponding emission profile, $I(\upsilon)$, is given by

$$I(\upsilon) = \text{constant} \times (1 - X_\upsilon)^n \exp(-(\ln 2)((\upsilon - \upsilon_{\max})/\Gamma)^2) \qquad (13)$$

where X_υ is given by eq 6. For an optically active guest species in a spectrally inert host lattice where the guest species occupy the host lattice with probability p (given by the overall mole fraction of the guest), eq 12 still holds with $X_\upsilon = X_\upsilon'p$, where X_υ' is determined from the guest absorption profile by using eq 6.

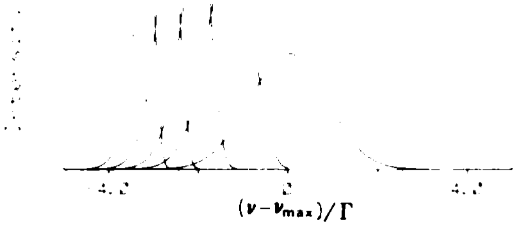


Figure 6. The emission profile $I(v)$ for a Gaussian absorption profile in a single-component crystal with an energy transfer interaction volume of n sites. Plotted from right to left are the Gaussian absorption profile and the emission profiles for $n = 10^1, 10^2, 10^3$, and 10^4 sites, respectively. The emission profile is found to shift to lower energy and to narrow in width with increasing n.

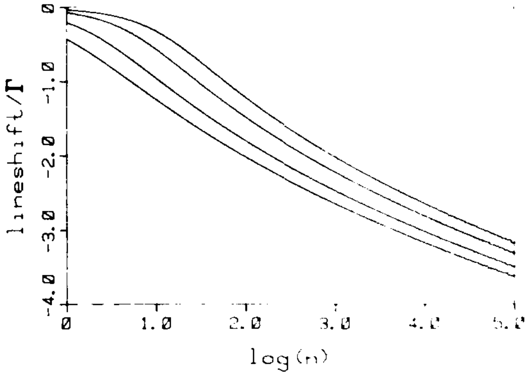


Figure 7. The shift in the guest emission maximum from the absorption maximum normalized by the Gaussian absorption width Γ (hwhm) vs. the interaction volume n. From bottom to top, these curves are for guest mole fractions p = 1.0, 0.5, 0.2, and 0.1, respectively.

The emission line shape for several values of n in the range of 10 to 10000 sites for a single-component disordered crystal are displayed in Figure 6, along with the Gaussian absorption profile. Figure 6 illustrates that, as the interaction volume gets larger, the emission profile is shifted further to lower energy and the emission line width narrows. These results can be understood with the physical model used here. For a particular energetically excited site, the probability of finding a lower-energy acceptor site within the interaction volume grows with the interaction volume. The energetic distribution of trapped sites is thus shifted to lower energy where the concentration of possible lower energy acceptors is smaller. The shift in the emission maximum from the absorption maximum and the emission line width vs. the interaction volume are plotted in Figures 7 and 8, respectively. From the absorption and emission spectra of a system, one can find n from the energy difference of the absorption and emission maxima using Figure 7. Similarly, one can also determine n using the emission line width and Figure 8. Knowing n, one can infer the microscopic energy transfer parameters in eq 1, 2, or 7 from eq 8 assuming a particular coupling mechanism and dimensionality.

The phosphorescence profile of the 0,0 band of BCN at 4.2 K along with the emission spectrum calculated from eq 13 with $n = 365$ sites is shown in Figure 1, where the calculated and observed spectra are found to be in good agreement. We now discuss this interaction volume in terms of the different energy transfer mechanisms which

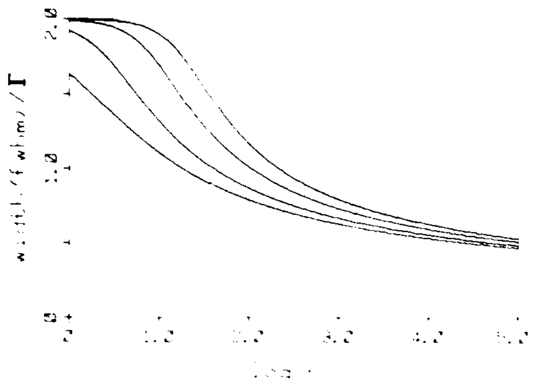


Figure 8. The guest emission line width (fwhm) normalized by Γ vs. the interaction volume *n*. From bottom to top, these curves are for guest mole fractions p = 1.0, 0.5, 0.2, and 0.1, respectively.

might be expected to be important in BCN. The 365 sites contained in the interaction volume would yield an interaction radius, R_0, of 182 for a one-dimensional interaction. Using β = 7.4 cm^{-1}, τ_0 = 20 ms for BCN, one obtains form eq 8b a value for direct exchange of γd = 0.1. Exchange interactions are usually of shorter range, i.e., γd >> 1, with γd = 5 being typical for many aromatic systems. For superexchange, one can estimate ΔE in this system as the energy separation between absorption and emission maxima. Using ΔE = 76 cm^{-1}, one finds β = 66 cm^{-1} for the 1-D superexchange mechanism. This value of β is about an order of magnitude larger than the value determined for DBN. Considering three-dimensional interactions with n = 365 sites, one obtains R_0 = 4.5. For direct exchange in three dimensions, using β = 7.4 cm^{-1} as an upper limit for the isotropic exchange interaction, one obtains γd < 7 using eq 8b. For superexchange with ΔE = 76 cm^{-1} one obtains an isotropic β = 0.6 cm^{-1} from eq 8c. For dipole–dipole coupling in three dimensions one obtains from eq 8a a value for the nearest-neighbor transfer time τ = 2.6 μs. The results of this analysis of the phosphorescence profile provide further support to the conclusion that the energy transfer is three dimensional for excitations on the low-energy side of the absorption profile. At higher excitation energies where nearest-neighbor transfer is important, the energy transfer may be one dimensional. The fit of the emission profile to eq 13 gives the interaction volume for the interaction with the largest range. An interaction with a smaller range, even with a stronger coupling within that range, would be unimportant in determining the emission profile.

Acknowledgment. The authors thank Prof. P. Prasad for our initial collaboration on this work and for supplying us with the sample. M.A.E. thanks Drs. A. Blumen, S. Fischer, and E. Knapp of the theoretical group of the Technical University of Munich for many helpful discussions. M.A.E. thanks the Alexander von Humbolt foundation for a Senior Humbolt Award spent in Munich (Feb–Aug 1982). The financial support of the Office of Naval Research is greatly appreciated.

Registry No. BCN, 53220-82-9.

FINAL REPORT DISTRIBUTION LIST

ONR Pasadena Detachment
Attn: Scientific Officer
1030 East Green St.
Pasadena, CA 91106 2 copies

ONR Pasadena Detachment
Attn: Carlena Leufroy
1030 East Green Street
Pasadena, CA 91106 1 copy

Naval Research Laboratory
Code 2627
Washington, D.C. 20375 6 copies

Defense Technical Information Center
Building 5, Cameron Station
Alexandria, Virginia 22314 12 copies

Office of Naval Research
Attn: Chief of Naval Research
Code 1021P
800 N. Quincy St.
Arlington, VA 22217 6 copies

END

FILMED

3-84

DTIC