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The Förster, Dexter, and Inokuti-Hirayama Models of the Time Dependence of Fluorescence Amplitude: An Annotated Bibliography

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L. J. Dowell

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

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THE FÖRSTER, DEXTER, AND INOKUTI-HIRAYAMA MODELS OF THE TIME DEPENDENCE OF FLUORESCENCE AMPLITUDE: AN ANNOTATED BIBLIOGRAPHY

by

L. J. Dowell

ABSTRACT

This annotated bibliography reviews research in the fluorescence of systems described by the Förster model. Sixty-two papers, largely from research based on the work of Inokuti and Hirayama in 1965, are cited. The collection emphasizes the description of the time evolution of the fluorescence amplitude. This time evolution is important to the current research in thermal metrology that uses the temperature-dependent fluorescence of rare-earth-doped ceramic phosphors and in many other applications of fluorescent materials.

I. INTRODUCTION

The purpose of this bibliography is to review the development of models of nonexponential fluorescence. These models, for the time evolution of the fluorescence (here meaning photoluminescence) amplitude of various phosphors, are important in such fields as solid-state physics and organic chemistry, and in the engineering of phosphors for night vision, fluorescent lights, CRT displays, and laser crystals. Much of the recent interest in nonexponential fluorescence has grown from early works by Th. Förster, D. L. Dexter, M. Inokuti and F. Hirayama. The theories from these researchers have been applied to experimental results and in theoretical physics for over 40 years.

The model for the time evolution of the fluorescence amplitude S that results from the Förster, Dexter, and Inokuti-Hirayama theories is

$$S(t) = A \exp(-t/\tau) \exp\left[-\gamma (t/\tau)^{\theta}\right] , \tag{1}$$

where A is the initial amplitude of the fluorescence; τ is the characteristic lifetime of the exponential fluorescence decay that would result if there were no energy transfer between excited, atomic electron states in the phosphor; the dimensionless scaling factor γ and the exponent θ characterize the effect of such energy transfer with the resulting nonexponential fluorescence evolution; and t is time. This model results from energy transfer ("energy wandering" in Förster's original paper) between two excited-state populations during the time of the fluorescence. The transfer is an emission and absorption of a virtual photon and is modeled by the interaction between multipole components of the electron excited-state wave functions.

The mathematical model $S(t)$ for the fluorescence amplitude, as a function of time, is particularly important in the application of rare-earth-doped ceramic phosphors for precise, high-temperature thermometry. In this application, the parameters of the fluorescence waveform are functions of temperature. Thus, the temperature of surfaces can be determined remotely, by

optical means, with excellent accuracy and at high speeds on moving components. Los Alamos and Oak Ridge National Laboratories; the University of Virginia; and EG&G Energy Measurements, Santa Barbara Operations, are investigating this technique for remote thermometry of jet-engine components, the development of thermometry standards, and other applications.

The citations in this bibliography were selected from several previous compilations and from recent investigations as being representative of the current research in energy-transfer fluorescence physics. Special attention was given to papers describing results from experiments with the rare-earth-doped ceramics used in phosphor thermometry. Other papers were chosen to illustrate the status of energy-transfer theory and the conceded limitations of the theory. For a research project in progress at Los Alamos, consideration was given to theoretical and experimental treatments of energy cascade. In energy cascade, the fluorescence results from the decay of an excited state that becomes populated through the decay of some higher-energy, previously excited state. This phenomenon has been observed in certain excitation schemes used with the thermographic phosphors. The bibliography also gives attention to the sum-of-exponentials model for fluorescence. Because of the number of parameters involved, a simple sum of several single-exponential decays can provide a good empirical model for fluorescence amplitude. This technique has been used by some researchers, as is indicated in this bibliography. In another project in progress, Los Alamos is using hypothesis-testing analysis techniques to examine which of the different models are appropriate. Besides these topics, which motivated this bibliography, topics from energy transfer in the study of semiconductor and liquid phosphors are also included.

The bibliography is organized into three parts. In Section II, the bibliography cites the important papers that initiated the study of energy transfer in fluorescence physics. Section III cites selected papers from the current list of over 500 papers that were founded on the paper by Inokuti and Hirayama. Section IV lists other papers that have been useful in the Los Alamos investigations of energy-transfer luminescence.

The following is a list of publications documenting previous work in phosphor thermometry by Los Alamos and Oak Ridge National Laboratories; the University of Virginia; and EG&G, Santa Barbara Operations. This work has included previous bibliographic collections,[1–3] the application to thermal metrology,[4] and a variety of temperature-sensing applications in science and industry.[5–20]

1. L. J. Dowell, G. T. Gillies, S. W. Allison, and M. R. Cates, "Thermal Phosphor Research Survey," Martin Marietta Technical Report K/TS-11,771 (Oak Ridge, Tennessee: ORGDP, July 1986).

2. L. J. Dowell, G. T. Gillies, S. W. Allison, and M. R. Cates, "A Research Bibliography on the Temperature Dependencies of Thermographic Phosphors," *Journal of Luminescence* **36**, 375 (1987).

3. L. J. Dowell and G. T. Gillies, "Thermographic Phosphor Literature Catalog," University of Virginia Technical report UVA/640419/NEEP89/102, University of Virginia, Charlottesville, Virginia (April 1989).

4. L. J. Dowell, "Investigation and Development of Phosphor Thermometry," Ph.D. dissertation, University of Virginia, Charlottesville, Virginia (1989).

5. M. R. Cates, S. W. Allison, L. A. Franks, M. A. Nelson, T. J. Davies, and B. W. Noel, "Remote Thermometry of Moving Surfaces by Laser-Induced Fluorescence of Surface-Bonded Phosphor," Union Carbide Corporation report K/TS-11,232 (November 1983).

6. M. R. Cates, S. W. Allison, B. R. Marshall, L. A. Franks, T. J. Davies, M. A. Nelson, and B. W. Noel, "Applications of Pulsed-Laser Techniques and Thermographic Phosphors to Dynamic Thermometry of Rotating Surfaces," Martin Marietta report K/TS-11,504 (March 1985).

7. B. W. Noel, H. M. Borella, L. A. Franks, B. R. Marshall, S. W. Allison, M. R. Cates, and W. A. Stange, "Proposed Laser-Induced Fluorescence Method for Remote Thermometry in Turbine Engines," *Journal of Propulsion and Power* **2**, 565 (1986).

8. S. W. Allison, M. R. Cates, M. B. Scudiere, H. T. Bentley III, H. Borella, and B. Marshall, "Remote Thermometry in a Combustion Environment Using the Phosphor Technique," in "Proceedings of SPIE," **788**, 90 (1987).

9. B. W. Noel, S. W. Allison, D. L. Beshears, M. R. Cates, H. M. Borella, L. A. Franks, C. E. Iverson, S. S. Lutz, L. J. Dowell, G. T. Gillies, and W. N. Lutz, "Evaluating and Testing Thermographic Phosphors for Turbine-Engine Temperature Measurements," in "Proceedings of AIAA/SAE/ASME/ASEE 23rd Joint Propulsion Conference," AIAA-87-1761, San Diego, California (June 1987).

10. S. W. Allison, M. R. Cates, B. W. Noel, and G. T. Gillies, "Monitoring Permanent-Magnet Motor Heating with Phosphor Thermometry," *IEEE Transactions on Instrumentation and Measurement* **37**, 637 (1988).

11. D. L. Beshears, H. M. Henson, T. J. Henson, M. J. Bridges, R. M. Sadler, and M. A. Cyr, "Phosphor Bonding Studies—Burner-Rig Endurance Test," Martin Marietta Energy Systems report K/ETAC-59 (July 1988).

12. G. T. Gillies, L. J. Dowell, W. N. Lutz, S. W. Allison, M. R. Cates, B. W. Noel, L. A. Franks, and H. M. Borella, "Noncontact Thermometry via Laser Pumped, Thermographic Phosphors: Characterization of Systematic Errors and Industrial Applications," in "Proceedings of the Laser Institute of America," **62**, 15 (1988).

13. S. S. Lutz, W. D. Turley, H. M. Borella, B. W. Noel, M. R. Cates, and M. R. Probert, "Remote Temperature-Measurement Instrumentation for a Heated Rotating Turbine Disk," presented at the 34th International Instrumentation Symposium, Instrument Society of America, ISA paper 88-0725, Albuquerque, New Mexico (May 1988).

14. L. J. Dowell, G. T. Gillies, A. R. Bugos, and S. W. Allison, "High-Precision, Single-Crystal Fluorescence Thermometry: A Possible Temperature-Transfer Standard," in "Proceedings of the Laser Institute of America," **66**, 122 (1989).

15. A. R. Bugos, "Characterization of the Emission Properties of Thermographic Phosphors for Use in High Temperature Sensing Applications," M.S. Thesis, The University of Tennessee (May 1989).

16. B. W. Noel, M. C. Bibby, H. M. Borella, S. E. Woodruff, C. L. Hudson, S. S. Lutz, W. D. Turley, S. W. Allison, D. L. Beshears, M. R. Cates, J. J. Muhs, and K. W. Tobin, "Environmental Tests of Thermographic Phosphors for Turbine-Engine Temperature Measurements," in "Proceedings of AIAA/ASME/SAE/ASEE 25th Joint Propulsion Conference," AIAA 89-2913, Monterey, California (July 1989).

17. W. D. Turley, H. M. Borella, B. W. Noel, A. Beasley, W. K. Sartory, and M. R. Cates, "The Design and Characterization of a Prototype Optical Heat-Flux Gauge," Los Alamos National Laboratory report LA-11408-MS (January 1989).

18. W. Lewis, W. D. Turley, H. M. Borella, and B. W. Noel, "Noncontact Thermometry in Excess of 2500°F Using Thermographic Phosphors," in "Proceedings of ISA Conference," Denver, Colorado (May 1990).

19. B. W. Noel, H. M. Borella, W. Lewis, W. D. Turley, D. L. Beshears, G. J. Capps, M. R. Cates, J. D. Muhs, and K. W. Tobin, "Evaluating Thermographic Phosphors in an Operating Turbine Engine," presented at the Gas Turbine and Aeroengine Congress and Exposition, Brussels, Belgium. To be published in *Transactions of the ASME.*

20. B. W. Noel, W. D. Turley, M. R. Cates, and K. W. Tobin, "Two-Dimensional Temperature Mapping Using Thermographic Phosphors," presented at the 177th Meeting of the Electrochemical Society, Montreal, Canada (May 1990); Los Alamos National Laboratory report LA-UR-90-1534.

II. SEMINAL PAPERS

Th. Förster, "Zwischenmolekulare Energiewanderung und Fluoreszenz," *Annalen der Physik* **2**, 55 (1948).

This paper, in German, suggests the notion of de-excitation of an excited electron by exciting an unexcited neighbor through emission and absorption of a virtual photon. It discusses the time evolution of the excited-state population through the probability of transition of a single excited atom, the quantum-mechanical basis of this probability, the distance dependence of the transition probability, and the generalization of the model to a macroscopic number of excited atoms.

Th. Förster, "Exerimentelle und Theoretische Untersuchung des zwischenmolekularen Übergangs von Elektronenanregungsenergie," *Z. Naturforsch.* **4a**, 321 (1949).

Förster explicitly develops the square-root-of-time evolution of the fluorescence amplitude.

D. L. Dexter, "A Theory of Sensitized Luminescence in Solids," *Journal of Chemical Physics* **21**, 836 (1953).

Dexter develops quantum-mechanical models for higher-order multipole transitions that are applicable in Förster's model.

M. Inokuti and F. Hirayama, "Influence of Energy Transfer by the Exchange Mechanism on Donor Luminescence," *Journal of Chemical Physics* **43**, 1978 (1965).

In this important paper, the authors develop the model for the time evolution of the fluorescence amplitude using Förster's and Dexter's models. The *Science Citation Index* lists 528 citations of this paper.

III. REFERENCES TO THE INOKUTI-HIRAYAMA (I-H) PAPER: "DEVELOPMENT OF THE PHYSICAL AND MATHEMATICAL MODELS"

R. C. Dorfman, Y. Lin, and M. D. Fayer, "Experimental Investigation of Donor-Acceptor Electron Transfer and Back Transfer in Solid Solutions," *Journal of Physical Chemistry* **93**, 6388 (1989).

This paper discusses the chemical implications of ionization of the excited atom by electron transfer. The phenomenon is important in liquids, where the resultant ions can become separated by Brownian diffusion.

Y. Lin, R. C. Dorfman, and M. D. Fayer, "Time Dependence of Donor-Acceptor Electron Transfer and Back Transfer in Solid Solution," *Journal of Chemical Physics* **90**, 159 (1989).

The authors continue the discussion of the effect of electron transfer on fluorescence for the case of solids. Here, the electron transfer from an excited state is quite likely followed by a back transfer to the donor-atom's ground state.

S. R. Rotman, "Ambiguities in the Analysis of Non-Radiative Energy Transfer Data in Solid-State Laser Materials," *Applied Physics B* **49**, 59 (1989).

This paper is useful because it mentions the cascade of sensitized luminescence in Nd:Ce:YAG laser crystals. It does not discuss the time evolution of the acceptor fluorescence, although it points out that the time evolution is important in improved laser-crystal fluorescence efficiency due to sensitized fluorescence. Note that the donor lifetimes considered are much shorter than the acceptor lifetime, however.

S. R. Rotman, "Nonradiative Energy Transfer in Nd:YAG—Evidence for the Correlated Placement of Ions," *Applied Physics Letters* **54**, 2053 (1989).

In this paper, the I-H model is extended to consider the minimum separation between donor and acceptor in a crystalline solid solution. The paper mentions some abstractions used in the extension, refers to a paper by Rotman (1988) that presents the extension in greater generality, and refers to Blasse's article (*Progress in Solid State Chemistry* **18**, 79 (1988)) on the importance of codoped laser crystals.

A. Suchocki and J. M. Langer, "Auger Effect in the Mn^{2+} Luminescence of CdF_2:(Mn,Y) Crystals," *Physical Review B* **39**, 7905 (1989).

The authors describe quenching effects of impurities, giving several references. The Auger effect is exclusive to semiconductor crystals.

T. K. Anh *et al.*, "Energy Transfer Between Tb^{3+} and Eu^{3+} in Y_2O_3 Crystals," *Journal of Luminescence* **39**, 215 (1988).

This paper discusses energy transfer in co-doped yttrium oxide, but gives no evidence of time evolution through a cascade. A very short donor lifetime may explain this. Also, nonresonant charge-transfer excitation was studied.

R. C. Dorfman *et al.*, "Photoinduced Electron Transfer and Back Transfer in Systems of Randomly Distributed Donors and Acceptors: Picosecond Transient Grating Experiments," *Journal of Physical Chemistry* **92**, 4258 (1988).

Dorfman continues the discussion of electron-transfer ionization. This paper is not directly applicable to fluorescence time-evolution modeling.

I. Gersonde *et al.*, "Influence of Lattice Structure on Energy Transfer among Randomly Distributed Substitutional Impurities," *Chemical Physics Letters* **153**, 273 (1988).

The models presented are a little too general to be interpreted easily. This paper is similar in content to the Dornauf-Heber (1980) paper.

G. D. Gilliland, R. C. Powell, and L. Esterowitz, "Spectral and Up-Conversion Dynamics and Their Relationship to the Laser Properties of $BaYb_2F_8$:Ho^{3+}," *Physical Review B* **38**, 9958 (1988).

This papers describes an interesting application of the I-H model to an experiment, but there is no cascade or other model development.

M. Kaschke and K. Vogler, "Time-Resolved Studies of Intermolecular Electronic Energy Transfer Processes between Molecules in Solution," *Laser Chemistry* **8**, 19 (1988).

This paper reviews several of the transfer mechanisms and surveys some of the basic Förster-like fluorescence models.

I. Rips and J. Jortner, "Electronic Excitation Transport in a Substitutionally Disordered Medium," *Chemical Physics* **128**, 237 (1988).

This is a mathematical paper and is difficult to interpret in terms of engineering practicality in the modeling of fluorescence time-evolution.

S. R. Rotman and F. X. Hartmann, "Non-Radiative Energy Transfer in Non-Uniform Codoped Laser Crystals," *Chemical Physics Letters* **152**, 311 (1988).

The authors review the I-H theory. They assume the acceptors are not uniformly distributed around the donors but are concentrated nearby in a shell. This assumption may be a gross approximation of the Dornauf-Heber (1980) discrete location model.

D. Zambon *et al.*, "Fluorescence et Dynamique dans $LiNaY_2F_8$:Eu^{3+}," *Journal of Less-Common Metals* **143**, 345 (1988).

This paper is written in French. In it, Zambon uses a first-order cascade model.

A. G. Avanesov, V. F. Pisarenko, and E. N. Tumaev, "Acceptor Removal under Electron-Excitation Transfer in Disordered Media," *Optics and Spectroscopy* **62**, 337 (1987).

Here is an interesting mathematical model of what might be called a cascade process, but the authors never talk explicitly about populations as functions of time.

G. Blasse, "The Physics of New Luminescent Materials," *Materials Chemistry and Physics* **16**, 201 (1987).

Blasse reviews some of the physics of fluorescence. This is a good intermediate-level presentation.

G. Blasse and N. Sabbatini, "The Quenching of Rare-Earth Ion Luminescence in Molecular and Non-Molecular Solids," *Materials Chemistry and Physics* **16**, 237 (1987).

This paper continues the Blasse (1987) review. Europium is the featured special case. Multiphonon and charge-transfer quenching are discussed.

M. Buijs and G. Blasse, "Energy Migration in a Two-Dimensional Eu^{3+} Compound: $EuMgAl_{11}O_{19}$," *J. Solid State Chem.* **71**, 296 (1987).

These authors apply the I-H model. However, their waveforms are noisy, so that the fitted model is only a rough approximation of the waveform.

M. Buijs, A. Meyerink, and G. Blasse, "Energy Transfer between Eu^{3+} Ions in a Lattice with Two Different Crystallographic Sites: Y_2O_3:Eu^{3+}, Gd_2O_3:Eu^{3+}, and Eu_2O_3," *Journal of Luminescence* **37**, 9 (1987).

This paper considers resonance-excited europium fluorescence in three different materials. It applies the I-H model and incorporates several theories in its description of the experimental results.

P. A. M. Berdowski and G. Blasse, "Luminescence and Energy Transfer in a Highly Symmetrical System: $Eu_2Ti_2O_7$," *J. Solid State Chem.* **62**, 317 (1986).

This paper cites an interesting application of the I-H model in an analysis of an experiment. It includes a lot of spectroscopic data. Some of the waveforms shown exhibit cascade rise, but no cascade model is presented. Back-transfer is mentioned, as is the Yokota-Tanimoto (1967) paper.

J. Klafter and A. Blumen, "Models for Dynamically Controlled Relaxation," *Chemical Physics Letters* **119**, 377 (1985).

The I-H model is presented using a different mathematical technique.

Yu. S. Privis, V. A. Smirnov, and I. A. Shcherbakov, "Calculation of Time Evolution of Population of Excited Acceptor States in Multipole Static Interaction with Energy Donors," *Optics and Spectroscopy* (USSR) **58**, 478 (1985).

This is an important paper. It models the fluorescence of an acceptor after initial excitation and subsequent cascade of a donor. The paper assumes that the acceptor state is an exponential decay and that the donor state is modeled by the I-H analysis for dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions.

A. I. Burshtein, "Concentration Quenching of Noncoherent Excitation in Solutions," *Soviet Physics Uspekhi* **27**, 579 (1984).

Burshtein gives a comprehensive review of several theories and includes a big bibliography.

D. L. Huber, "Time Development of Trap Fluorescence Following Pulsed Excitation," *Journal of Luminescence* **28**, 475 (1983).

There is little difference between a trap and an acceptor. In this paper, the donors are excited, they transfer energy to the traps, and the traps fluoresce. Different assumptions are made about physics that apparently lead to different first-order cascade models.

S. Qiang *et al.*, "Luminescence and Energy Transfer in Y_2O_3 Co-Doped with Bi^{3+} and Eu^{3+}," *Journal of Luminescence* **28**, 1 (1983).

Mostly data, this paper is an example of sensitized fluorescence. The authors claim that 337-nm nitrogen laser excitation of bismuth leads to europium emission. This paper reminds us that sites can be excited selectively to study energy transfer between sites. The I-H model is mentioned, as is the Yokota-Tanimoto model.

A. Blumen and G. Zumofen, "Energy Transfer as a Continuous Time Random Walk," *Journal of Chemical Physics* **77**, 5127 (1982).

This paper reports on the numerical simulation of excited-state relaxation, in the presence of traps, by the random walk technique. Although it is an interesting exercise with realistic results, no parametric functions of time result.

C. M. Lawson, E. E. Freed, and R. C. Powell, "Models for Energy Transfer in Solids. II," *Journal of Chemical Physics* **76**, 4171 (1982).

The authors review the I-H theory for dipole-dipole interaction, the Yokota-Tanimoto theory (1967), and Burshtein's integral-equation theory (1972) for luminescence in the presence of traps. The authors point out that a good fit of the model to the data is not sufficient to justify the model; a sufficient justification would require that the parameters resulting from the fit must be within the range of validity for which the model was derived.

M. Loher and G. Zumofen, "Förster-Type Processes in Cascading Systems," *Chemical Physics Letters* **88**, 419 (1982).

The authors discuss Förster's processes and derive first-order cascade equations for an arbitrary number of higher excited states. They also show some graphs, but present no Förster/I-H cascade equations.

J. K. Tyminski, C. M. Lawson, and R. C. Powell, "Energy Transfer between Eu^{3+} Ions in $LiNbO_3$, $CaWO_4$, and $Eu_xY_{1-x}P_5O_{14}$ Crystals," *Journal of Chemical Physics* **77**, 4318 (1982).

This paper considers first-order cascade models. It suggests that discrete modeling of the crystal lattice would give more accurate results. It applies the model to measurements of the materials listed.

A. Blumen, "On the Anisotropic Energy Transfer to Random Acceptors," *Journal of Chemical Physics* **74**, 6926 (1981).

Blumen presents some interesting mathematics based on assumptions about the orientations and interactions between donors and acceptors. However, the results are given in terms of unspecified functions that characterize some of these assumptions, so that there is no practical extension of the I-H model.

J. Heber, H. Dornauf, and H. Siebold, "New Aspects in Energy Transfer in Inhomogeneous Systems," *Journal of Luminescence* **24–25**, 735 (1981).

These authors emphasize the necessity for discrete modeling of the lattice in the I-H model. They point out that an estimation error in lifetime parameters can lead to erroneous conclusions about energy transfer. The authors also recommend additional models for acceptor concentration. There is no explicit extension of the I-H model.

D. K. Sardar and R. C. Powell, "Time-Resolved Site-Selection Spectroscopy Studies of $NdAl_3(BO_3)_4$ Crystals," *Journal of Luminescence* **22**, 349 (1981).

The authors discuss an interesting cascade model that shows the effect of donor decay on the acceptor population for a case in which there is no transfer from the acceptor to the second-order acceptor. The discussion is especially nice because it gives the population evolution as a system of differential equations. However, the paper studies only the ratio of the intensities of the spectral lines from the decay from the two states.

H. Siebold and J. Heber, " 'Discrete Shell Model' for Analysing Time-Resolved Energy Transfer in Solids," *Journal of Luminescence* **22**, 297 (1981).

This paper gives a discrete-lattice model for excitation probability, starting basically from scratch. It includes the effect of temperature on transfer rates. However, the result is a sum-of-exponentials model for fluorescence.

J. C. Wright, "Probe Ion Techniques for Trace Analysis," *Modern Fluorescence Spectroscopy*, E. L. Wehry, ed. (New York: Plenum Press, 1981), p. 51.

This paper gives an example of the use of spectra to identify ions and energy-transfer effects.

K. Allinger and A. Blumen, "On the Direct Energy Transfer to Moving Acceptors," *Journal of Chemical Physics* **72**, 4608 (1980).

The authors generalize the I-H model to moving acceptors for which the donor-acceptor distance is not constant. This generalization may not be important if the velocity is small relative to the transition time. No time-evolution functions were presented.

A. Blumen, "On the Direct Energy Transfer via Exchange to Randomly Distributed Acceptors," *Journal of Chemical Physics* **72**, 2632 (1980).

This paper considers an exponential instead of an inverse-power law for energy transfer.

A. Blumen, J. Klafter, and R. Silbey, "Theoretical Studies of Energy Transfer in Disordered Condensed Media," *Journal of Chemical Physics* **72**, 5320 (1980).

This paper criticizes the I-H model for short times. It derives a limit expression for the Laplace transform of any fluorescence-amplitude function.

H. Dornauf and J. Heber, "Concentration-Dependent Fluorescence-Quenching in $La_{1-x}Pr_xP_5O_{14}$," *Journal of Luminescence* **22**, 1 (1980).

The authors rederive the I-H model, with a modification for discrete acceptor sites instead of continuum sites. They suggest that this significantly improves the description of fluorescence-amplitude time evolution. The derivation is easy to follow, making the paper a good tutorial.

K. Godzik and J. Jortner, "Electronic Energy Transport in Substitutionally Disordered Molecular Crystals," *Journal of Chemical Physics* **72**, 4471 (1980).

This paper, like some of A. Blumen's papers, is concerned with the physics of the energy transfer for the circumstance of high-impurity concentration and with the diffusion coefficient. See Yokota-Tanimoto (1967) for some insight into the diffusion constant. Their paper is concerned with the luminescence of semiconductors.

D. L. Huber, "Donor Fluorescence at High Trap Concentration," *Physical Review B* **20**, 5333 (1979).

This paper models traps, which act like acceptors. Energy is transferred between the donors and to the traps. The paper discusses asymptotic forms for the fluorescence but doesn't clearly describe time evolution.

D. L. Huber, "Fluorescence in the Presence of Traps," *Physical Review B* **20**, 2307 (1979).

Again, the traps act like acceptors. This paper is clear and probably is a good foundation for understanding later papers. The biggest effect discussed is that due to donor-donor energy transfer. In the limit of no transfer, the I-H model results. The rapid-transfer limit results in exponential fluorescence. This paper discusses the intermediate case, where the fluorescence becomes exponential asymptotically as time goes to infinity.

W. Y. Ching, D. L. Huber, and B. Barnett, "Models for the Time Development of Spectral Transfer in Disordered Systems," *Physical Review B* **17**, 5025 (1978).

The authors give an empirical evaluation of three different models of donor re-excitation in high-concentration phosphors.

D. L. Huber and W. Y. Ching, "Generalized Models for Spectral Transfer in Disordered Systems," *Physical Review B* **18**, 5320 (1978).

This paper repeats the findings of Ching (1978).

M. A. El-Sayed, A. Campion, and P. Avouris, "Temperature, Temporal and Concentration Dependence of the Laser-Narrowed $^5D_0 \rightarrow {}^7F_0$ Fluorescence Lineshape of Eu^{3+} in Glasses," *Journal of Molecular Structure* **46**, 355 (1978).

The authors suggest that phonon-coupled interactions become more important at higher donor concentrations. The I-H model is applied.

R. Reisfeld, "Excited States and Energy Transfer from Donor Cations to Rare Earths in the Condensed Phase," *Structure and Bonding* **30**, 65 (1976).

Reisfeld surveys theories of donor sensitization of acceptor luminescence. He defends the I-H model and discusses systems in which donor-donor transfer is important. A nice review.

J. C. Wright, "Up-Conversion and Excited State Energy Transfer in Rare-Earth Doped Materials," *Radiationless Processes in Molecules and Condensed Phases*, F. K. Fong, ed. (Berlin: Springer-Verlag, 1976).

Wright gives an excellent review of the rare-earth-fluorescence processes. Up-conversion is an inverted cascade model that achieves a higher energy state through two or more excitation phenomena. The technique is useful in making infrared night-vision devices. The I-H model and the diffusion model of Yokota-Tanimoto (1967) are discussed. The paper presents a variety of examples and a long bibliography.

C. Hsu and R. C. Powell, "Energy Transfer in Europium-Doped Yttrium Vanadate Crystals," *Journal of Luminescence* **10**, 273 (1975).

Besides data on the YVO_4:Eu thermographic phosphor, this paper yields an energy-state model from an analysis of the spectra, applies the I-H model, and refers to other fluorescence models examined by Powell (1972).

F. K. Fong and D. J. Diestler, "Many-Body Processes in Nonradiative Energy Transfer between Ions in Crystals," *Journal of Chemical Physics* **56**, 2875 (1972).

Transfer of energy from a donor to two or more acceptors is important in rare earth ions and whenever the donor emission doesn't closely overlap the acceptor absorption. Pair transfer leads to a linear dependence of the energy-transfer rate on acceptor concentration, while for transfer to two acceptors, the dependence is quadratic. The upshot is a criticism of the interpretation of s = 6,8,10 as dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole. This paper is thought provoking and is easily and intuitively understood.

N. Yamada, S. Shionoya, and T. Kushida, "Phonon-Assisted Energy Transfer between Trivalent Rare Earth Ions," *Journal of the Physical Society of Japan* **32**, 1577 (1972).

This paper mentions infrared up-conversion and measures energy-transfer rates for various rare earths doped in yttrium oxide. It applies the I-H theory and a theory proposed by Miyakawa-Dexter (1970).

W. J. C. Grant, "Role of Rate Equations in the Theory of Luminescent Energy Transfer," *Physical Review B* **4**, 648 (1971).

Grant examines the Pauli equation for energy-transfer rate and excited-state probability. The paper cites 119 references.

L. G. Van Uitert, "Characterization of Energy Transfer Interactions between Rare Earth Ions," *Journal of the Electrochemical Society* **114**, 1048 (1967).

This paper applies the I-H model. It includes a chart of energy levels for rare-earth ions and correlates it to transitions that are involved with either dipole-dipole or dipole-quadrupole energy transfer.

IV. OTHER REFERENCES

A. Blumen and J. Manz, "On the Concentration and Time Dependence of the Energy Transfer to Randomly Distributed Acceptors," *Journal of Chemical Physics* **71**, 4694 (1979).

This paper rederives the I-H model as a special case of a series-expansion solution of the initial mathematical model for energy transfer. It presents series representations of 'exact' solutions of the fluorescence model for different lattices. It also establishes limits on the applicability of the Förster/I-H model.

A. I. Burshtein, "Hopping Mechanism of Energy Transfer," *Soviet Physics JETP* **35**, 882 (1972).

This paper considers energy transfer among donors and yields different concentration-quenching dependence. It offers little development of the time-evolution functions.

U. Köbler, "Time Resolved Investigations of Energy Transfer in Eu^{3+}:Y_2O_3," *Zeitschrift für Physik* **250**, 217 (1972).

The discussion is specifically for yttrium oxide. Köbler uses the rate equations often used by Powell and others at Oklahoma State University (for instance, G. D. Gilliland, R. C. Powell, and L. Esterowitz, "Spectral and Up-Conversion Dynamics and Their Relationship to the Laser Properties of $BaYb_2F_8$:Ho^{3+}," *Physical Review B* **38**, 9958 (1988)). Köbler gets a sum of exponentials for the decay and does not use the I-H model.

R. C. Powell and Z. G. Soos, "Kinetic Models for Energy Transfer," *Physical Review B* **5**, 1547 (1972).

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J. Heber *et al.*, "Energy Levels and Interaction between Eu^{3+}-ions at Lattice Sites of Symmetry C_2 and Symmetry C_{3i} in Y_2O_3," *Zeitschrift für Physik* **237**, 189 (1970).

Using the site-selective excitation and fluorescence analysis suggested by Forest and Ban, the authors examine the spectra, energy levels, and energy transfer from the C_{3i} site. They make no mention of the I-H model.

T. Miyakawa and D. L. Dexter, "Phonon Sidebands, Multiphonon Relaxation of Excited States, and Phonon-Assisted Energy Transfer between Ions in Solids," *Physical Review B* **1**, 2961 (1970).

This is a theoretical development of phonon energy transfer. It makes no engineering models of the time evolution of the fluorescence amplitude.

M. Yokota and O. Tanimoto, "Effects of Diffusion on Energy Transfer by Resonance," *Journal of the Physical Society of Japan* **22**, 779 (1967).

This important paper doesn't refer to I-H directly but does draw the same result as I-H for dipole-dipole transfer. This paper is cited often. It seems to be concerned with diffusion by the physical movement of donors and acceptors in a liquid. It gives references to three other papers that had considered diffusion in fluorescence.

G. W. Robinson and R. P. Frosch, "Electronic Excitation Transfer and Relaxation," *Journal of Chemical Physics* **38**, 1187 (1963).

This paper was cited by Inokuti and Hirayama as evidence of the limited applicability of the Förster-Dexter model. It gives an explicit criticism of applying the F-D model in some circumstances.

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