HANDBOOK OF FLUORESCENCE SPECTRA OF AROMATIC MOLECULES

SECOND EDITION

ISADORE B. BERLMAN

Handbook of
FLUORESCENCE SPECTRA OF AROMATIC MOLECULES

SECOND EDITION

Isadore B. Berlman

RADIOLOGICAL PHYSICS DIVISION
ARGONNE NATIONAL LABORATORY
ARGONNE, ILLINOIS

PHYSICS DEPARTMENT
HEBREW UNIVERSITY
JERUSALEM, ISRAEL

ACADEMIC PRESS New York and London 1971

COPYRIGHT © 1971, BY ACADEMIC PRESS, INC.

COPYRIGHT ASSIGNED TO THE GENERAL MANAGER OF THE UNITED STATES ATOMIC ENERGY COMMISSION.

ALL RIGHTS RESERVED
NO PART OF THIS BOOK MAY BE REPRODUCED IN ANY FORM, BY PHOTOSTAT, MICROFILM, RETRIEVAL SYSTEM, OR ANY OTHER MEANS, WITHOUT WRITTEN PERMISSION FROM THE PUBLISHERS.

ACADEMIC PRESS, INC.
111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
Berkeley Square House, London W1X 6BA

LIBRARY OF CONGRESS CATALOG CARD NUMBER: 79-154388

PRINTED IN THE UNITED STATES OF AMERICA

PREFACE TO SECOND EDITION

The fluorescence and absorption characteristics of about two hundred compounds have been included in the present edition, about twice the number in the previous edition. Most of the "new" compounds added to this work fall into the following classes: (1) *p*-oligophenylenes, (2) indole derivatives, (3) fluoranthene derivatives, (4) napthalene derivatives, (5) biphenyl derivatives, and (6) biological stains. We have continued to employ an inductive process of accumulating and tabulating data, and looking for rule-of-thumb regularities. By this method, qualitative inferences of wide generality as well as anomalies have been found.

The present text is more than twice the size of the earlier edition. Two chapters have been added and the others have been enlarged. Many recent developments, such as experiments with lasers and their relevance to fluorescence studies, are included in a chapter on Uses of Fluorescent Compounds. Three sections have been added to the appendix. In one section some additional computations derived from the data contained in the graphs are presented. These computations are values of (1) R_0, a mean radiative transfer distance between two dissimilar molecules, (2) C_0, a reference concentration derived from R_0, and (3) the overlap integral

used in computing R_0. In the second section, data culled from the literature and pertinent to phosphorescence, such as values of phosphorescence decay time and energy of the phosphorescence transition, have been added. In the third section, data on spectral width are collected. To reduce the number of pages, the section containing conversion tables has been eliminated. Of no little importance, a reprinting of this handbook has made it possible to correct errors present in the original edition.

The revised text was written in the main during the period from September, 1967, through November, 1968, when the author served as a visiting scientist at the Hebrew University in Jerusalem, Israel. He would like to thank Dr. Arye Weinreb for his assistance in making the assignment at the Hebrew University productive.

In addition to the people mentioned in the previous edition, the author wishes to thank Dr. Robert E. Rowland, Director of the Radiological Physics Division, for his support of this work, Dr. Hermann O. Wirth for providing most of the indole, *p*-oligophenylene, and fluoranthene derivatives and for his assistance in correcting graphical errors, Dr. Jochanan Blum for purifying compound #179C, Dr. Hanna Feilchenfeld for #169B, Prof. Dr. W. Ried for #85C, Dr. J. B. Gallivan for #152C, #153C, #154C, and #155C, Dr. Weldon G. Brown for #40C, Dr. Arnon Shani for #177A Dr. Guy Meyer for #171C, Mr. Joseph J. Bauer for his assistance in drawing the chemical symbols in the graphs, Mrs. Frances R. Clark for her assistance in typing the manuscript, Mr. W. R. Anderson for his valuable assistance in editing the manuscript, and Mr. Yong-Ki Kim and Mr. Burton S. Garbo for their kind assistance in programming the tables in Appendix 7.1.

此为试读,需要完整PDF请访问: www.ertongbook.com

PREFACE TO FIRST EDITION

Is radiation detection by fluorescent materials an art or a science? To help make it the latter this handbook has been compiled to provide answers to some basic questions concerning the fluorescence characteristics of aromatic molecules. Hopefully, it will also provide a stimulus for further investigations.

The usefulness of fluorescence and absorption spectra of organic molecules is universally recognized and much progress has been made in investigating these molecules. Although numerous articles on fluorescent organic molecules illustrate various specific characteristics such as the influence of position and type of substituent on a fluorescence spectrum, the effect of a particular solvent on the shape and position of an emission spectrum, the measurement of fluorescence decay times, etc., the author knows of no major collection of fluorescence data assembled in one volume. A unique feature of this handbook is that all of the measurements were made in one laboratory—not culled from the literature. Many of the results of research appear here in print for the first time.

Spectra of approximately 100 aromatic molecules, varying in size, shape, and structure, are assembled in this handbook. The list of molecules begins

with the simple aromatic molecule benzene and includes progressively larger and more complicated systems. Although a special effort has been made to include practically all of the currently popular organic scintillators, the choice of the other molecules has been rather arbitrary.

The luminescence characteristics of each aromatic molecule have been measured in a systematic fashion. Fluorescence and absorption spectra are plotted for each molecule and additional data related to the fluorescence process are given in each graph. The additional data include the fluorescence decay time, the fluorescence quantum yield, the natural lifetime as computed from the absorption spectrum, the Stokes loss, the wavelength of the center of gravity of the fluorescence spectrum, and the average wavelength of the fluorescence spectrum. Such supplementary material as topical bibliographies, tables to convert wavelength to wave number and energy, a table of values of the index of refraction of cyclohexane as a function of wave number, and a table of values of oscillator strengths have been placed in the Appendix.

The text is an experimentalist's approach to the understanding of luminescence phenomena. It is hoped that it will facilitate the entry of a newcomer into the field. To aid students specializing in certain areas of research, selective topical bibliographies are included.

These bibliogarphies have been compiled for the purpose of illustration and representation and not for completeness. This means that some contributions have been unavoidably omitted.

I wish to express my thanks to Mr. L. D. Marinelli for his many valuable suggestions, to Miss J. M. Prince for her generous assistance in transforming the graphs into digital form for use in the computer, to Mr. O. J. Steingraber for his able assistance in measuring the fluorescence decay times, to Mr. W. L. Hafner for his capable programming of our data, to Dr. F. Hirayama for his many valuable suggestions concerning the presentation of this work, to Dr. M. Inokuti for many stimulating discussions and for his aid in preparing the computer program for computing the table in the Appendix (Section 4.1a), to Mr. W. R. Anderson for calibrating the spectrophototometer and the monochromator and also for his many valuable suggestions on the preparation of the manuscript, to Mr. N. P. Zaichick for tracking down some of the early publications on luminescence, to Miss S. Katilavas for her willing assistance in the handling of the data cards and the computer-output data, to Mr. J. E. Guderian for his aid in organizing the bibliography, to Mr. F. M. Gentille for his cooperation in the completion of the graphs, and to the many members of the laboratory who cooperated so willingly when needed.

CONTENTS

PREFACE TO SECOND EDITION xi
PREFACE TO FIRST EDITION xiii

1. Introduction

1.1 Preliminary Remarks 1
1.2 Historical Development 2
a. Compounds 2
b. Methods and Processes 4
c. Equipment 5
1.3 Elementary Considerations 7
a. Luminescence—The Many Modes of Excitation 7
b. Excitation of Electronic States and Attendant Processes . . . 8
c. Definitions 16
1.4 Data Presentation 21
a. Graphs 21
b. Natural Fluorescence Lifetime 23
c. Quantum Yield 24
d. Additional Information 27
e. Error Estimation 28

1.5 Materials 29
a. Purity Considerations 29
b. Photochemical Effects and Molecules Omitted 30
1.6 Equipment 32

2. The Free Electron Model

2.1 General 39
2.2 ^1L_a and ^1L_b States 39
2.3 Phosphorescence and the ^3L_a State 41
2.4 The $4n + 2$ Rule of Aromaticity 45

3. General Information

3.1 Chromophores 47
3.2 Planar and Nonplanar Molecules 48
a. Steric Hindrance 48
b. Effects of Planarity on Fluorescence 49
c. Rigidity of Molecules 50
d. A Spectroscopic "Straightedge" 50
3.3 Solvent Effects 52
3.4 Concentration Effects 54
3.5 Stokes Loss 57
3.6 L_0/L Ratios 58
3.7 Hidden Transitions and Submerged Bands 61
3.8 Polarization 62
3.9 FWRE Values 65

4. Compounds

4.1 General Information 67
4.2 Benzene 68
a. General 68
b. Effect of Substituents on the Aromatic Ring 69
1. Introduction 69
2. Isotopic Replacement 70
3. Alkyl Substituents 70
4. Substitution of Unsaturated Groups 71

4.3 Intermediate Compounds 72
a. Naphthalene 72
b. Biphenyl 74
4.4 Polycyclic Hydrocarbons 77
a. Catacondensed Aromatics 77
1. Linear Systems 77
2. Bent Systems 80
b. Pericondensed Systems 81
c. *p*- and *m*-Oligophenylenes 82
4.5 Heterocyclics and Five-Membered Rings 87
a. General 87
b. Indoles 88
c. Oxasoles, Oxadiazoles, and Furan Derivatives 88
d. Biological Stains 90
4.6 Ring–Chain Systems 91
a. General 91
b. Photoisomerism 91
4.7 Nonalternants 93
a. General 93
b. Fluoranthene and Its Derivatives 94
c. Azulene and Its Derivatives 94

5. Uses of Fluorescent Compounds

5.1 Scintillation Solutions 96
a. General 96
b. Fast-Coincidence Experiments 97
c. Neutron Detection 97
5.2 Lasers Experiments 98
a. General 98
b. Intermolecular Interactions at High Excitation Intensities . . . 99
c. Holograms and Luminescent Materials 99
References 100

6. Graphs 107

7. Appendix 417

7.1 R_e, C_e, and Overlap Integral Data 417
7.2 Index of Refraction of Cyclohexane versus Wave Number 422

7.3 Oscillator Strength (f) and Natural Fluorescence Lifetime (τ_0) . . . 423
7.4 Phosphorescence Data . . . 425
7.5 Spectral Width Data . . . 427
7.6 Selected Bibliographies . . . 432

NAME INDEX OF SPECTRA . . . 461
FORMULA INDEX OF SPECTRA . . . 467

此为试读,需要完整PDF请访问: www.ertongbook.com

1

INTRODUCTION

1.1 Preliminary Remarks

Scintillators under certain favorable conditions afford the highest possible sensitivity in detecting physical and chemical processes (events). Each scintillation pulse is caused by at least one event, and every scintillation pulse is capable of being detected. Therefore, in many experiments single events can be detected.

Scintillation materials have played an important role in numerous scientific experiments. Roentgen in 1895 became aware of the existence of X rays when he noticed that a plate coated with barium platinocyanide would fluoresce whenever he turned on a gas discharge tube. Rutherford was able to detect and count α particles impinging on a ZnS screen. Today, experiments with large accelerators often use scintillation detectors in one form or another. In their study of mesic X rays, Björkland *et al.*[1] employed as many as eight scintillators. In their neutrino experiment, Cowan *et al.*[2] used over ten cubic feet of liquid scintillating solution. Anderson,[3] in his "whole-body counter," used 100 gallons of liquid scintillator. Nuclear and neutron physicists[4,5] have been using liquid organic scintillators to detect neutrons in the presence of γ rays.

Many disciplines are interested in the *mechanisms* of the scintillation

process. Biologists[6] have been able to explain photosynthesis by an energy transfer process. Radiation chemists[7-9] have recently been using the mechanism of energy transfer to explain some of their results. Theoretical scientists[10] have obtained the lifetimes of stable and metastable states by determining oscillator strengths. For scientists in all of these disciplines this publication is a modest attempt at being a "Who's Who" and "What's What" of the aromatic molecules which scintillate when in liquid solution.

Because everyone wishes to obtain the optimum performance from his equipment, a complete understanding of the many factors affecting the scintillation process would obviously aid those scientists who work with organic liquid scintillation detectors. Unfortunately, many of the basic questions concerning the scintillation process still have not been quantitatively answered. For example, the general question of where the energy goes when a scintillation solution is excited by a 1-MeV β particle remains essentially unresolved. A few percent of the energy of the β particle is known to be emitted as fluorescence radiation, but how the remaining energy is dissipated is not known accurately. The present handbook is but one step in the direction of answering the question: Where does the energy go? In the studies presented here, aromatic molecules in a transparent solvent were excited directly by monochromatic uv radiation with just enough energy to raise one of the π electrons to the first excited singlet level. Thus the fluorescence quantum yield of the molecules could be studied in the absence of secondary competing reactions. Although many articles have been written on energy transfer and radiation damage, some of which are tabulated in the topical bibliography in the Appendix (Section 7.6), much remains to be learned. The area involving excitation by radiation with energy between ~5 eV and 10 keV still remains comparatively unexplored, and since many of the answers lie precisely here, equipment and techniques for use at these energies are presently being developed in many laboratories.

For the past 15 years solid state physics has been one of the attractive fields of research. It is the author's belief that in the immediate future attention will also be directed toward investigating more fully the properties of liquids. We endorse the sentiments of Vavilov,[11] who maintained that a scintillation solution forms an ideal system for studying the *liquid* state.

1.2 Historical Development

a. Compounds

That certain compounds emit visible radiation when exposed to the rays from the sun has been known for several centuries. In 1565 a doctor,

Nicolas Monardes, reported[12] that water containing a certain kind of wood then popularly known as *lignum nephriticum* would glow in the sunlight. The luminescent liquid was believed to be of therapeutic value as a cure for kidney stones—thus the name *lignum nephriticum*, Latin meaning "kidney wood." So popular was this wood that chalices were made from it and presented to nobility. After 1732 the medical value of the solution was discounted and little attention was thereafter paid to it. A picture of a cup from that period and a flask containing the luminescent liquid may be found in a comprehensive article on the wood, Reference 13.

One of the first references to phosphorescence was made in 1603. A shoemaker in Bologna found that a local stone when exposed to sunlight and then removed to a darkened area would continue to emit light—in more scientific terms, to phosphoresce. This mineral, which probably contained barium sulfate, became known in the literature as the Bologna stone. In a monograph on phosphorescence written by F. Liceti entitled "Litheosporous" and published in 1640, the effect was explained as follows: The stone was impregnated by the sun and an interval of time was needed for the light to be born.

Several centuries later, in the middle of the nineteenth century, limited advances were made in the understanding of the luminescence process. Herschel,[14] in 1845, reported that a solution containing sulfate of quinine emitted a strong luminescence radiation when held in sunlight. His purpose in the report was to point out the difference between this type of radiation and ordinary scattered light. Stokes,[15] in 1852, studying the same compound, found that the emitted light was composed of wavelengths longer than those of the absorbed light—a phenomenon now called Stokes shift. In his report, Stokes also discusses photochemical changes produced by sunlight.

Wiedemann and Schmidt[16] appear to be the first to have reported, in 1895, observing radiation from anthracene (vapor). Stark,[17] in 1907, measured the photoluminescence in liquid benzene, and Stark and Mayer[18] made similar measurements on benzene derivatives. Luminescence from frozen aromatic compounds, such as benzene and xylene, was reported by E. Goldstein[19] in 1910. The first studies of sensitized fluorescence of gases were made by Franck[20] and Cario.[21]

Although it is tacitly assumed that currently popular scintillators are rather recent achievements, it is surprising to learn how long ago they were first synthesized. The compound 2,5-diphenyloxazole (PPO), recognized today as an efficient solute in scintillation solutions, was first compounded by Emil Fisher[22] in 1896. Fluorene was made by Berthelot[23] in 1867, and

fluorescein was synthesized by Baeyer[24] in 1871. Michael Faraday, known best for his work in the field of electricity, is given credit for the discovery of benzene in 1825.

The following experiment performed in 1877 illustrates the sensitivity of the luminescence process: In the Alps there is a large limestone region honey-combed with water-filled caverns. It was believed that in this region there was a subterranean connection between the Danube and the Rhine Rivers. To verify this hypothesis, a suggestion by Baeyer, who had synthesized fluorescein and was well aware of its great sensitivity as a dye, was followed, and 10 kg of fluorescein were thrown into the headwaters of the Danube River. Sixty hours later the characteristic fluorescence of the dye appeared in a small river having no visible connection with the Danube but emptying into Lake Constance and hence into the Rhine. Thus the connection between the two major rivers was unequivocally established.

b. Methods and Processes

The law of the exponential attenuation of visible and ultraviolet radiation by an absorbing medium was independently studied first by Bouger in 1729 and then by Lambert in 1760 and the reciprocal relationship between sample thickness and concentration was found by Beer in 1852. In the literature the attenuation law is called by the names of the above three scientists, taken in some combination of one, two, or three at a time. The reader is referred to Reference 25 for further historical details.

Concentration quenching, a process whereby the luminescence efficiency of a scintillation solution decreases with an increase in solute concentration, has received a good deal of attention recently (see Section 3.4). What is not well known is the fact that Walter[26] studied concentration quenching of the luminescence in fluorescein solutions as early as 1888. Surprisingly, even he was not the first to study the effect, for he wrote[27] in 1889 that he had just become aware of Lommel's work[28] in this area in 1877, 12 years earlier.

Concentration depolarization, the decrease in polarisation of the fluorescence with increasing solute concentration, was first reported by Gaviola and Pringsheim[29] in 1924. This effect arises from the fact that excitation transfer takes place between like molecules and furthermore that this can occur in repeating steps, so that the energy is capable of migrating over long distances.

Mirror symmetry between an absorption curve and a fluorescence curve was first observed by Nicols and Merrit[30] in 1907, in eosin and resorufin solutions. The topic of mirror symmetry was seriously pursued by Levshin,[31] beginning in 1931, for many compounds.

Fluorescence quantum yields were being measured at least as early as 1910, when determinations were made for substituted benzene derivatives by Ley and Engelhardt.[32] These values were still quoted as late as 1956.[33] Vavilov,[34] in 1926, was the first to find that the fluorescence yield was generally independent of the wavelength of the exciting radiation. (It is presently believed that this observation is true only if the exciting radiation is composed of wavelengths absorbed by the longest wavelength absorption bands, but if shorter wavelengths are employed the contention may not be true.) Many quantum-yield determinations have since been made, as noted in the bibliography in the Appendix (Section 7.6).

In the early literature there was some discussion as to the type of radiation involved in the fluorescence process. It was generally assumed to be electric-dipole radiation. Selenyi,[35] by studying the angular distribution of the fluorescence radiation from fluorescein by means of a wide-angle interference technique which he[36] had developed in 1911, was able to demonstrate unequivocally that this is electric-dipole radiation. Weissman and Lipkin,[37] using the same technique, were able to conclude that β phosphorescence from fluorescein could also be classified as electric-dipole radiation. More recently, Bücher *et al.*[38] used a monomolecular-layer technique to illustrate the electric-dipole character of fluorescence radiation.

c. EQUIPMENT

In 1672, Newton reported to the Royal Society on his discovery and investigation of the dispersion of light by a prism. More than a century passed before the discovery of the infrared and uv parts of the spectrum, the infrared by F. W. Herschel in 1800 and the ultraviolet by J. W. Ritter in 1801. The invention of the diffraction grating was reported by J. Fraunhofer in 1821. By the use of a grating instead of a lens, certain problems of aberration were eliminated and work in the ultraviolet region was made feasible.

The first phosphoroscope was built by E. Becquerel in 1858. With it he could measure phosphorescence decay times as short as 10^{-3} sec. Another early measurement of luminescence decay time was that by Wood[39] in 1905. A phosphor was placed on the rim of a wheel and mechanically excited at a point as the wheel was rapidly rotated. Wood was able to follow the luminescence along the wheel as it was displaced from the point of excitation. Another technique, which he[40] described in 1921, was to use a jet of liquid scintillating solution, excite the solution along a small area, and observe the jet along its path of travel beyond the point of excitation. Not being able to observe any fluorescence along the jet, he concluded that the fluorescence decay time was less than 0.5 μsec.

This spatial tracking of radiation, although seemingly not very effective in the experiments just mentioned, is today one of the most sensitive methods of recording short lifetimes. For example, the lifetime of π^0 mesons was determined by measuring minute track gaps (the distance between tracks formed by parent and daughter nuclei) left in a nuclear emulsion in which they were created. From a gap length of about 10^{-7} m and a velocity approximately that of light, a lifetime of 10^{-16} sec was estimated. As another example, Giordmaine *et al.*[41] were able to determine the coincidence time of a picosecond (10^{-12} sec) laser pulse by measuring the size of darkened areas on a photographic emulsion.

Gottling,[42] in 1923, adopting a technique developed by Abraham and Lemoine,[43] was able to give the decay time of rhodamine the value of 21 nsec. In his method, a spark was used to excite a solution, and then the double refractive property of a Kerr cell was used to measure the time delay of the fluorescence. A very accurate apparatus was assembled by Gaviola[44] in 1926. He used a phase-shift method based on the technique of Abraham and Lemoine and reported the fluorescence decay time of rhodamine B in water to be approximately 2.5 nsec. For several years thereafter this phase-shift technique received only sporadic attention. It was used by Tumerman[45] in 1941, and by Bailey and Rollefson[46] in 1953. However, since 1958 the number of people using this type of apparatus has become much larger.

Wood and Ellett[47] found, and the idea was developed further by Hanle,[48] that a weak magnetic field (only a few gauss) produces depolarization by causing the dipole oscillators to precess around the direction of the field. The depolarization is a function of the field strength and the decay time of the excited state. Since the magnitude of the applied field is a measurable quantity, the decay time can be readily determined. This technique, beautifully simple and capable of nanosecond measurements, while investigated in the early 1930s, has since then not been adequately exploited.

Other techniques for measuring fluorescence decay times have been used. Post and Shiren[49] used a short-stub technique. Phillips and Swank[50] first used pulsed X rays to excite their phosphors and later, in collaboration with others,[51] modified their original technique to use a pulsed beam of 75-keV electrons. With the advent of pulse-sampling oscilloscopes and multichannel analyzers with large storage capacity, decay times can now be measured in the subnanosecond region.

A pulse sampling technique for measuring fluorescence decay times was developed by Steingraber and Berlman[52] and a photon sampling technique by Bollinger and Thomas.[53] Both methods allow one to make measurements to below 1 nsec. A more complete list of references on decay-time measurements is given in the topical bibliography in the Appendix (Section 7.6).

此为试读,需要完整PDF请访问: www.ertongbook.com