



Two-photon spectroscopy of inductively perturbed naphthalenes
by Richard Dwight Jones

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry

Montana State University

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Abstract:

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Polarized two-photon fluorescence excitation spectra in the laser wavelength range 450-650 nm are compared to one-photon absorption spectra for solution-phase naphthalene, 1- and 2 - fluoronaphthalenes, 1- and 2-chloronaphthalenes, isoquinoline and its cation. Results of INDO/S calculations using singly as well as singly and doubly excited configuration interaction are presented for naphthalene, vibrationally distorted naphthalenes, the fluoronaphthalenes, the azanaphthalenes and their cations. The calculations underestimate the inductive effect of fluorine, especially in the 2- position.

A method is developed for properly normalizing two-photon spectral data which greatly reduces the uncertainties involved in matching spectral segments from different laser dyes. The usual linear reference detector is replaced with a quadratic detector based on powders of nonlinear optical materials such as potassium dihydrogen phosphate (KDP). The source of the uncertainties resulting from normalizing two-photon excited fluorescence to the square of a linear reference is due primarily to changes in laser temporal pulse widths as the dye laser is scanned.

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by

Richard Dwight Jones

A thesis submitted in partial fulfillment
of the requirements for the degree

of

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in

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Richard Dwight Jones

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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Date 14 December 1987

This work is dedicated to the memory of Professor Ray Woodriff whose encouragement and inspiring example led the author to graduate studies.

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ABSTRACT

Perturbative effects on the one- and two-photon spectra of naphthalene caused by fluorine, chlorine and aza (nitrogen in the place of carbon) substitution are investigated. The results are in general accord with the pseudoparity selection rules of Callis, Scott and Albrecht *J. Chem. Phys.* 78, 16 (1983). Enhancement of two-photon absorptivity in the second excited singlet state (L_a) by fluorine substitution is not as dramatic in the fluoronaphthalenes, as it is in fluorobenzene. As seen in the one-photon spectra, fluorine substitution has a greater inductive effect in the 2- position of naphthalene, but has less than aza substitution.

Polarized two-photon fluorescence excitation spectra in the laser wavelength range 450-650 nm are compared to one-photon absorption spectra for solution-phase naphthalene, 1- and 2-fluoronaphthalenes, 1- and 2-chloronaphthalenes, isoquinoline and its cation. Results of INDO/S calculations using singly as well as singly and doubly excited configuration interaction are presented for naphthalene, vibrationally distorted naphthalenes, the fluoronaphthalenes, the azanaphthalenes and their cations. The calculations underestimate the inductive effect of fluorine, especially in the 2- position.

A method is developed for properly normalizing two-photon spectral data which greatly reduces the uncertainties involved in matching spectral segments from different laser dyes. The usual linear reference detector is replaced with a quadratic detector based on powders of nonlinear optical materials such as potassium dihydrogen phosphate (KDP). The source of the uncertainties resulting from normalizing two-photon excited fluorescence to the square of a linear reference is due primarily to changes in laser temporal pulse widths as the dye laser is scanned.

OVERVIEW

The initial goal of the research described in this two part thesis was to use one-photon and two-photon spectroscopies to compare the absorption strengths of the two lowest excited singlet states of substituted naphthalenes. The major scientific contribution from this work resides in the two-photon spectra of these molecules, which are presented with their respective one-photon spectra in Part I. Also included in Part I are results of semiempirical molecular orbital calculations on species pertinent to this study.

To confidently compare two-photon absorptivities of the lowest excited states, a new method of normalizing two-photon excited fluorescence was developed. Most of the uncertainty heretofore involved in constructing long-range spectra was eliminated by using a reference detector based upon second harmonic of the excitation frequency which was generated from powders of nonlinear optical materials. Part II describes this method and the insights revealed by temporal and spatial beam profiles concerning the causes of the uncertainty which has previously plagued two-photon spectroscopy.

PART I
SPECTRA OF PERTURBED NAPHTHALENES

INTRODUCTION

Two-photon (TP) absorption is a nonlinear optical phenomenon in which two quanta of light are simultaneously absorbed to excite an atom or molecule to a state whose transition energy is the sum of the single photon energies. The probability for such a process is quadratically dependent upon the intensity of the excitation light, whereas for one-photon (OP) absorption it is linearly dependent. Moreover, cross-sections for TP absorption are some thirty orders of magnitude smaller than those for OP absorption. Consequently moderately powerful lasers are required to induce observable TP absorption.

TP spectroscopy provides information which is complementary or inaccessible to common OP experiments, just as Raman spectroscopy does to infrared absorption. In centrosymmetric molecules the selection rules for TP absorption, $g \leftrightarrow g$ or $u \leftrightarrow u$, are opposite those for OP transitions, $g \leftrightarrow u$, which allow different sets of states to be probed. Even for molecules without a center of symmetry, states which are weak OP absorbers are often strong TP absorbers, so information absent or hidden in one spectrum is revealed by the other. In addition, the dependence of TP absorption upon the polarization of the

excitation light provides knowledge about the symmetry of the excited state.

Benzene and naphthalene were among the first organic molecules to be investigated by TP spectroscopy - the reason being to examine theories of their electronic structure which had been built upon OP spectroscopic data. The following section recounts the historical development of theories explaining the spectral features of these and related molecules.

Historical Background

In the early 1940's, patterns began to appear in the OP electronic absorption spectra of aromatic hydrocarbons and their substituted derivatives (1 - 3). Three types of bands were observed in most of these ultraviolet absorption spectra:

- 1) weak bands, usually of lowest energy, with complex vibrational structure, having intensities and positions sensitive to substituents,
- 2) moderately intense bands unchanged by substituents, with regular vibrational structure, and
- 3) strong bands of highest energy with little vibrational structure.

Theoretical descriptions of benzene's excited states (4,5) and the effects of substituents on its least intense band (6,7) were complex and could not be applied to larger molecules. Not until a simple unified theory was developed could these spectral features be understood.

Platt (8), in 1949, introduced an elegant method of describing and classifying the electronic states of benzene-like hydrocarbons, which forms the basis of the present understanding. The idea of π electrons in an unsaturated system being "mobile" (9), delocalized or free had been used to describe those electrons as quantum mechanical particles in a box (10) and applied to explain the spectra of linear polyenes (11). Platt postulated that the π and π^* orbitals in cata-condensed hydrocarbons (those polyacenes in which all carbon atoms lie on a perimeter) are like those of a free electron moving on a one-dimensional loop of constant potential around the perimeter. Such orbitals are described by wavefunctions of the form $e^{im\phi}$, where m is the quantum number for the z component of angular momentum and ϕ is the azimuthal angle. For the orbitals of cyclic polyenes,

$$-(2n + 1) \leq m \leq +(2n + 1)$$

where $2(2n + 2)$ is the number of carbon atoms in the ring.

Orbitals with the same absolute value of m are degenerate in energy, but along with this energy pairing

there is also a mirror image pseudo-pairing across the barycenter of energy.

These properties are illustrated in Figure 1 by the π molecular orbitals of cyclodecapentaene in the atomic orbital representation. The size of a circle is proportional to the coefficient of the respective $2p\pi$ atomic orbital and the filled and unfilled circles are negative and positive coefficients, respectively. In this form, or representation, the molecular orbitals are not necessarily eigenfunctions of the angular momentum operator, but they do retain the nodal patterns of the $e^{im\phi}$ eigenfunctions of this operator.

The mirror image pseudo-pairing alluded to above is present in each primed and unprimed molecular orbital pair. For example, in molecular orbital 1 all of the coefficients have the same magnitude and sign. In molecular orbital 1' the coefficients are the same as in 1, but the sign of alternate coefficients has changed. It would soon be discovered that this pseudo-pairing property resulted in configuration interaction states which fell into two distinct subsets, and that these two types of states behaved differently under the influence of different perturbations.

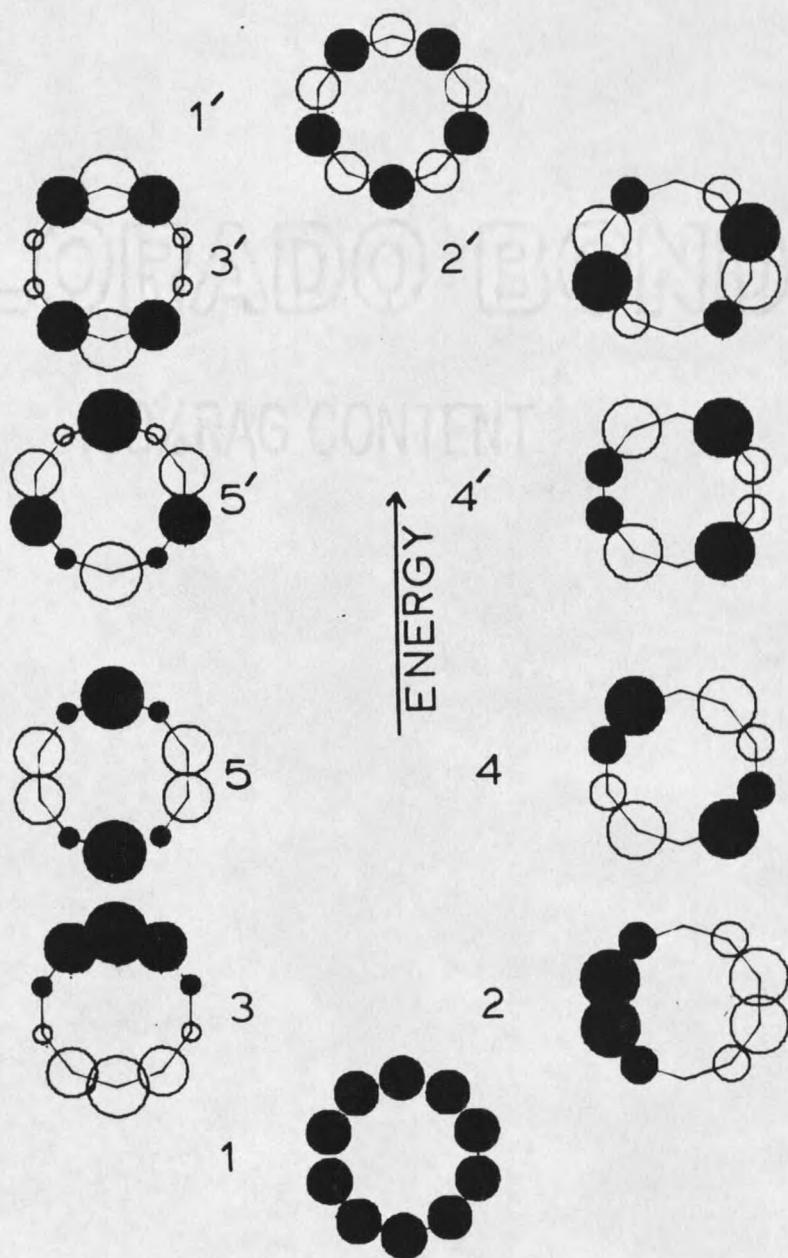


Figure 1. Pi molecular orbitals of cyclodecapentaene in the atomic orbital basis

If the carbon atoms of cyclodecapentaene are numbered sequentially, starting at the top, then naphthalene is formed by removing the hydrogen atoms bonded to carbons one and six and bonding these carbons together. This cross-linking process has no effect on the energies of the even numbered cyclodecapentaene molecular orbitals which contain no contributions from $2p\pi$ orbitals on atoms one and six. However, the odd numbered molecular orbitals do have nonvanishing coefficients at atoms one and six and the energies of these molecular orbitals are decreased if the two coefficients have the same sign or increased if they have opposite sign. This is illustrated in Figure 2 which shows the molecular orbitals of naphthalene, again in the atomic orbital representation.

As Huckel had done in the case of benzene (12), Platt summed the orbital angular momenta of all the π (free) electrons to obtain the total ring quantum number for a particular electronic state. His model identified the three absorption bands in the cata-condensed hydrocarbons. In his nomenclature, based on changes in total ring quantum number upon excitation, the weak band is labeled L_b , the moderate band L_a , and the strong band (degenerate in the cyclic polyenes) B_a or B_b . Although Platt's description included triplet as well as singlet states, this work is only concerned with the latter and will not label states by their multiplicity.

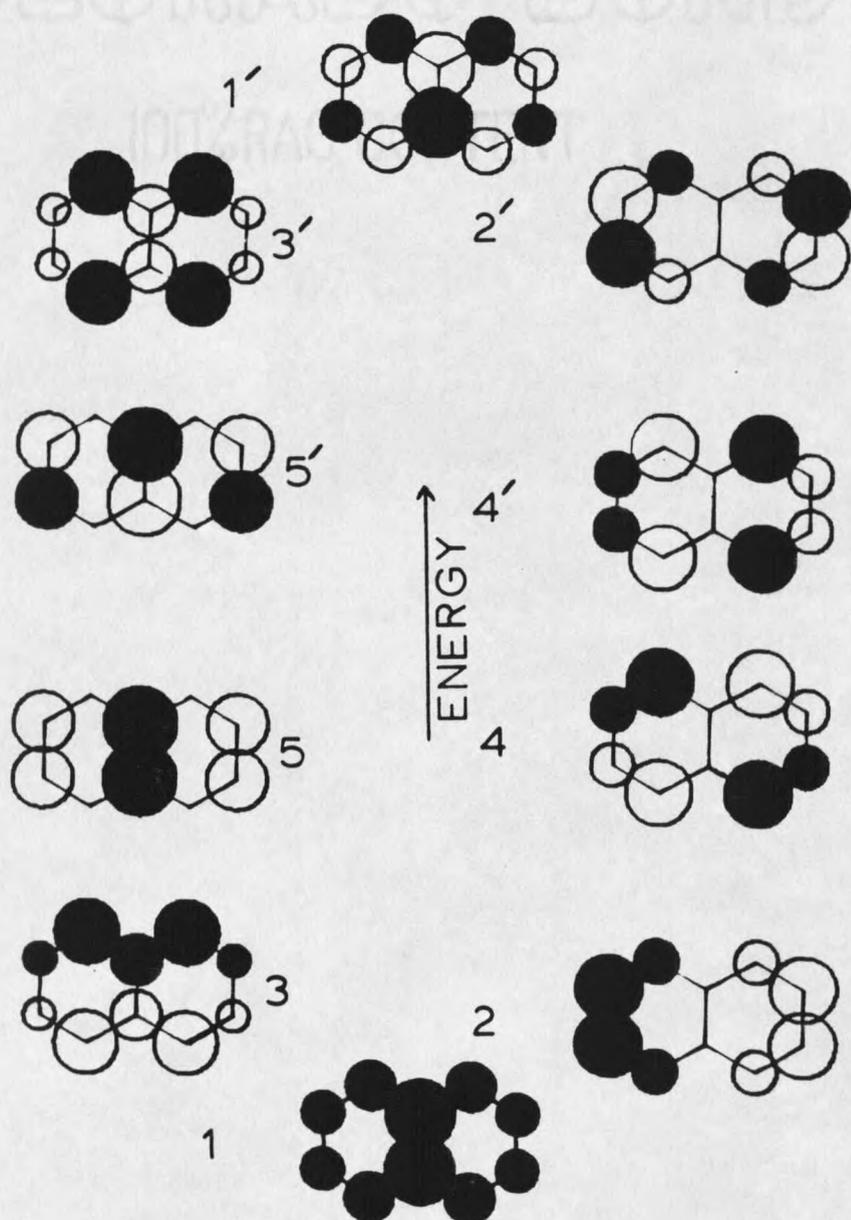


Figure 2. Pi molecular orbitals of naphthalene in the atomic orbital basis

In a later work extending the treatments of Sklar (6) and Forster (7), Platt presented a semi-quantitative model for the intensity induced in the L_b (lowest energy) bands of mono-, di- and tri-substituted polyacenes (13). He determined relative "spectroscopic moments" for 25 different substituents including fluorine, chlorine and aza (nitrogen in the place of carbon). It should be noted here for future reference that in this vector model the signs of the moments induced by fluorine and chlorine were taken as positive and that of aza was negative.

A more quantitative and complete model of the OP spectra of cata-condensed hydrocarbons was formulated by Moffitt (14). To Platt's perimeter model he applied the linear combination of atomic orbitals (LCAO) instead of the free-electron orbitals. Starting with the known spectrum of benzene, he estimated the properties of the hypothetical cyclic polyene molecules, which he then perturbed by cross-linking, to form the cata-condensed molecules, such as naphthalene, azulene, anthracene, and phenanthrene.

One of the most revealing discoveries of Moffitt's treatment was his bisection of the perturbation matrix into "odd" and "even" parts. The following equation illustrates the division of a 3 x 3 matrix into odd and even matrices:

$$\begin{bmatrix} 1 & 2 & 3 \\ 4 & 5 & 6 \\ 7 & 8 & 9 \end{bmatrix} = \begin{bmatrix} 0 & 2 & 0 \\ 4 & 0 & 6 \\ 0 & 8 & 0 \end{bmatrix} + \begin{bmatrix} 1 & 0 & 3 \\ 0 & 5 & 0 \\ 7 & 0 & 9 \end{bmatrix}$$

Although the elements of the first matrix on the right are even numbers the matrix is "odd", by Moffitt's definition, because the sum of the indices of every non-zero element is an odd number. Moffitt also realized that each of the cyclic polyene states possessed an even or odd character, and of the two lower energy, dipole-forbidden states, one (L_b) would be coupled to the dipole-allowed states only by even perturbations and the other (L_a) only by odd perturbations. Cross-linking - forming polyacenes from their respective cyclic polyenes (such as naphthalene from cyclodecapentaene) - is an odd perturbation since the new matrix element is in the 1,6 position. This odd perturbation couples the otherwise forbidden L_a state of naphthalene to the allowed B state thereby inducing OP absorptivity.

He continued by considering the effect of inductive substituents as being "even" perturbations since they are associated with changes in the diagonal (even) elements of the Coulomb matrix. This analysis resulted in excellent agreement with experimental intensities of the L_b bands of ortho-, meta- and para- disubstituted benzenes. Likewise he demonstrated that stretching vibrations, as odd

perturbations, could couple L_a to a dipole-allowed state, provided they have the proper symmetry as dictated by group theory.

McLachlan (15) and Donath (16) explained the even or odd character Moffitt had utilized. Configurations involving promotion of a π electron from a bonding molecular orbital j , for example, into its corresponding antibonding orbital j' , are termed symmetrically excited configurations. Any nonsymmetric configuration $j \rightarrow k'$, for example, has a related (degenerate in the cyclic polyenes) configuration $k \rightarrow j'$. Linear combinations of nonsymmetric configuration pairs are divided into two distinct classes: the additive combinations, termed plus, and the subtractive combinations, termed minus. Symmetric and plus configurations may mix through configuration interaction to produce plus states. Likewise, minus configurations (including the ground state configuration) interact only among themselves resulting in minus states. L_b is a minus state and L_a is a plus state. Pariser (17) showed that pseudoparity, as this even or odd character is now called, dictates electric dipole selection rules, plus \leftrightarrow minus (even \leftrightarrow odd), in addition to those of group theory. Further refinements were made in the analysis of vibronic effects by Albrecht (18) and of inductive and mesomeric (substituent) effects by Petruska (19).

Modern computers have obviated pencil-and-paper calculations of molecular spectroscopic information, but the simplicity and qualitative accuracy of the Platt - Moffitt model have proven it to be a useful tool in interpreting recent experimental results. In particular, the TP spectra of aromatic molecules have been explained on the basis of this model.

In 1931 Goeppert-Mayer predicted the possibility of simultaneous absorption of two photons (20). Not until 1961, after the laser was invented was this phenomenon observed (21). The first organic molecule used as a TP sample was 1-chloronaphthalene (22) which initiated a flurry of spectroscopic activity. By the beginning of this decade, TP spectra of more than one hundred aromatic compounds had been gathered and once again patterns became apparent.

Goodman and coworkers produced many vapor-phase TP spectra of substituted benzenes (23-25), and extended the work of Sklar (6), Forster (7), Moffitt (14) and Petruska (19) to explain the intensity regularities in the L_b bands of polysubstituted benzenes. Their work entitled "Two-Photon Spectroscopy of Perturbed Benzenes" is an excellent review (26). Pertinent to the present work is their finding that inductive substituents have little effect on the TP absorption strength of the L_b band, which is formally TP-forbidden but gains absorptivity through

vibrational perturbation of the hexagonal D_{6h} symmetry. This was also seen by Callis, Scott and Albrecht in their solution-phase TP spectrum of pyrimidine (27).

Coupling this observation with the pseudoparity selection rules in OP spectroscopy, Callis, Scott and Albrecht (28,29) formulated selection rules for OP,TP and three-photon spectroscopies of alternant hydrocarbons. By extending the TP spectra of benzene and fluorobenzene into the L_a region the latter group saw that, while L_b is unaffected by inductive substitution, L_a is substantially enhanced (28).

The selection rules combine restrictions imposed by group theory with those imposed by the pseudoparity properties of alternant hydrocarbon electronic states. They showed that transition bond order matrices between these states fall into the even and odd matrix categories Moffitt had seen in the perturbation Hamiltonian matrices. Transition bond order matrices between states having the same pseudoparity are odd matrices while those between states of different pseudoparity are even.

To determine if a perturbation, \mathcal{H}' , can couple two states, Ψ_1 and Ψ_2 , the matrix element $\langle \Psi_1 | \mathcal{H}' | \Psi_2 \rangle$ must be evaluated. Another way to write this is:

$$\text{tr} (\mathcal{H}' | \Psi_2 \rangle \langle \Psi_1 |) = \text{tr} (\mathcal{H}' \rho^{12}),$$

where ρ^{12} is a first-order reduced density matrix (applicable in this case since \mathcal{H}' is a one-electron operator)

and tr means the trace of the matrix product. The symmetrized density matrix or transition bond order matrix, B , is given by $B^{12} = 1/2(\rho^{12} + \rho^{21})$. Finally they demonstrated as Donath (16) had, that if the perturbation matrix is odd (even) it can only couple states whose transition bond order matrix is odd (even).

In the OP spectra of benzene and naphthalene, only perturbed by vibrations (odd perturbations), the selection rules predict a weak L_b (minus) band since its transition bond order with the ground state (minus) is an even matrix. However, L_a has plus pseudoparity and its transition bond order with the ground state is an odd matrix. Its contraction with the vibrational or cross-link perturbation matrix (also odd in the polyacenes, but even in the case of azulene, for example) does not vanish, resulting in moderate absorptivity in the L_a . On the other hand, fluoro- and aza- benzenes and naphthalenes are inductively perturbed (odd perturbation matrix) resulting in enhancement of L_b absorptivity with little effect upon L_a . These predictions are confirmed in the OP spectra of benzene, fluorobenzene and pyridine (azabenzene) and naphthalene, quinoline and isoquinoline (azanaphthalenes).

Callis, Scott and Albrecht realized that in the TP spectra of these compounds the roles of inductive and vibrational perturbations are reversed, since in a TP process plus-to-plus or minus-to-minus transitions are

induced. According to the selection rules the L_b state gains intensity through vibrational perturbations and should be unaffected by inductive effects. However inductive perturbations will enhance the L_a band. These predictions are verified in the TP spectra of benzene and fluorobenzene (28), which are shown in Figure 3 with their OP spectra.

Statement of Problem

As the present project began, TP spectra of naphthalene - the aromatic alternant hydrocarbon most similar to benzene - had been published (30,31). TP spectra of only two substituted naphthalenes, 1-chloronaphthalene (32,22) and acenaphthene (31) were available. To further test the pseudoparity selection rules regarding inductive perturbations which appeared to hold in these cases, this work undertook the task of obtaining TP spectra of fluoro- and aza- naphthalenes.

During the early part of this research, Rava and Goodman (33) published vapor-phase TP spectra of 1- and 2-fluoronaphthalenes. Their spectra of the L_b bands of these compounds display totals of 7 and 5 nm respectively. Their finding that the inductive perturbation of fluorine especially in the 2- position greatly enhanced the L_b origin is in sharp contrast to the predictions of the pseudoparity selection rules.

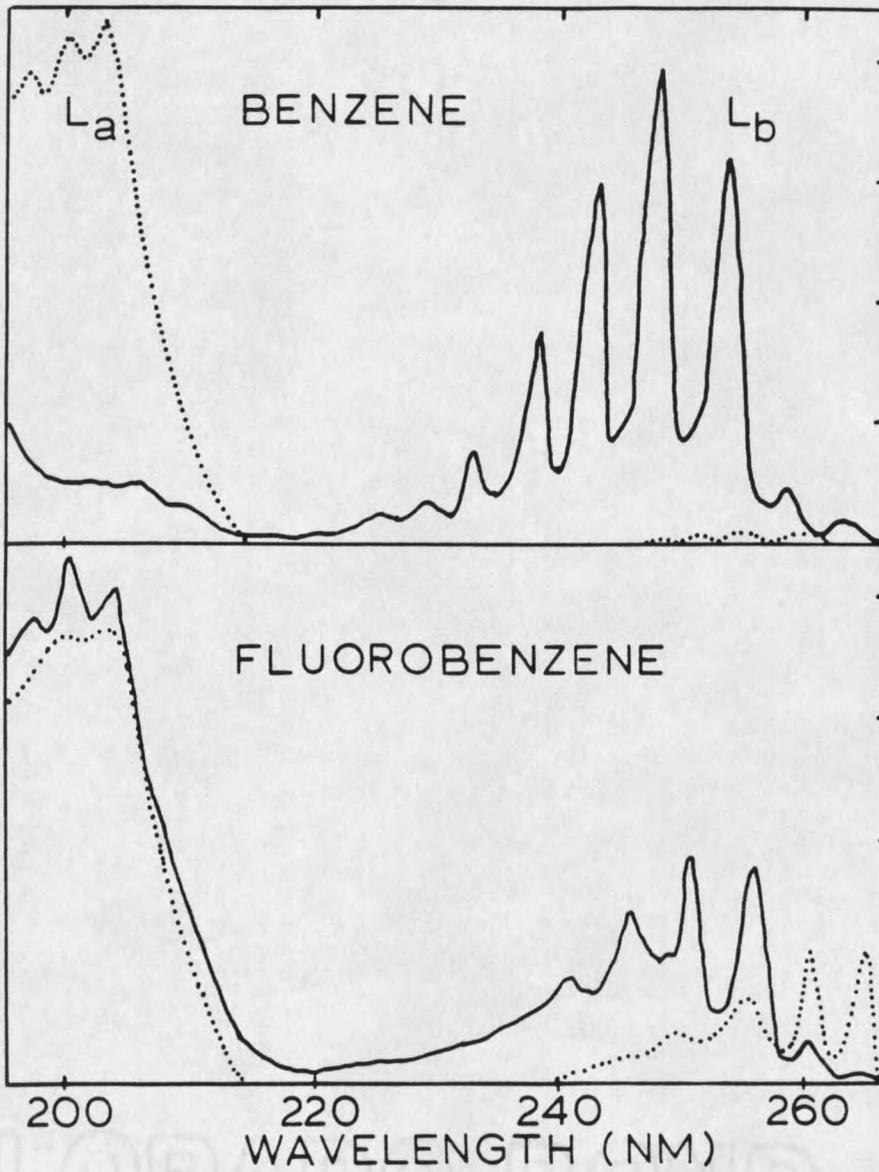


Figure 3. One-Photon (dotted line) and Two-Photon (solid line) spectra of benzene (upper) and fluoro-benzene (lower) from reference 28 with author's (P.R. Callis) permission

At the time these results appeared, the present work had produced preliminary TP spectra of 1- and 2- fluoronaphthalenes which agreed not with the results of Rava and Goodman but with the predictions of Callis, Scott and Albrecht. In order to challenge the vapor-phase results of Rava and Goodman, it was essential to be confident in the relative peak heights of these solution-phase spectra. The joining of TP fluorescence excitation data obtained with different dyes was, at that time, known as a "black art" (34). Development of the technique described in Part II has reduced the uncertainty in the TP experiment and resulted in reliable spectra of inductively perturbed naphthalenes which are presented in the following sections.

PROCEDURES

Two-Photon Experiments

The chemicals used as samples in this work are listed in Table 1. All were fractionally distilled under 0.1-1.0 mm Hg vacuum with the help of Richard R. Copp, Jr. to whom the author is most grateful. Purities were confirmed by fluorescence emission spectra taken at three different excitation wavelengths and by chromatographic/mass spectral analysis performed by L. Joseph Sears at the M.S.U. mass spectrometry facility.

Table 1. Sources of chemicals used in spectroscopic experiments

<u>Chemical</u>	<u>Source</u>
naphthalene	Chem Service
1-fluoronaphthalene	Aldrich
2-fluoronaphthalene	Pfaltz and Bauer
isoquinoline	Aldrich
1-chloronaphthalene	Chem Service
2-chloronaphthalene	Eastman
1,2,3,4-tetrafluoronaphthalene	research sample donated by Dr. Robert Filler Dept. of Chemistry Ill. Inst. of Tech.

Solutions of naphthalene and the fluoro- and chloro-naphthalenes were made at 0.100 M in Aldrich Gold Label spectrophotometric grade cyclohexane. Isoquinoline was dissolved in spectroscopic grade ethanol at a concentration of 0.200 M. A 0.20 M solution of isoquinolinium cation was prepared by using 0.2 M hydrochloric acid in ethanol as the solvent.

The polarized TP fluorescence excitation apparatus was designed by Bruce E. Anderson and is described in detail in his doctoral thesis (35). Changes in his apparatus made during the course of this work include replacing the homebuilt stepping motor drivers and signal amplifiers with commercial units, use of a monochromator and thermoelectrically cooled photomultiplier in the fluorescence detection channel, and use of a photodiode as the detector of quantum counter fluorescence. The quadratic reference detector based on KDP powder is described in Part II. A diagram of the apparatus is shown in Figure 4, in which M is a monochromator, F is a visible-absorbing/ultraviolet-transmitting filter, PMT is a Hamamatsu R955 photomultiplier tube configured for fast response, IS is a diffusing integrating sphere, QC is a quantum counter solution of Rhodamine B or Nile Blue A, PD is a fast response (back biased) PIN photodiode and X is the 2 mm cell containing 75-150 μm particle size KDP (potassium dihydrogen phosphate) powder in decalin.

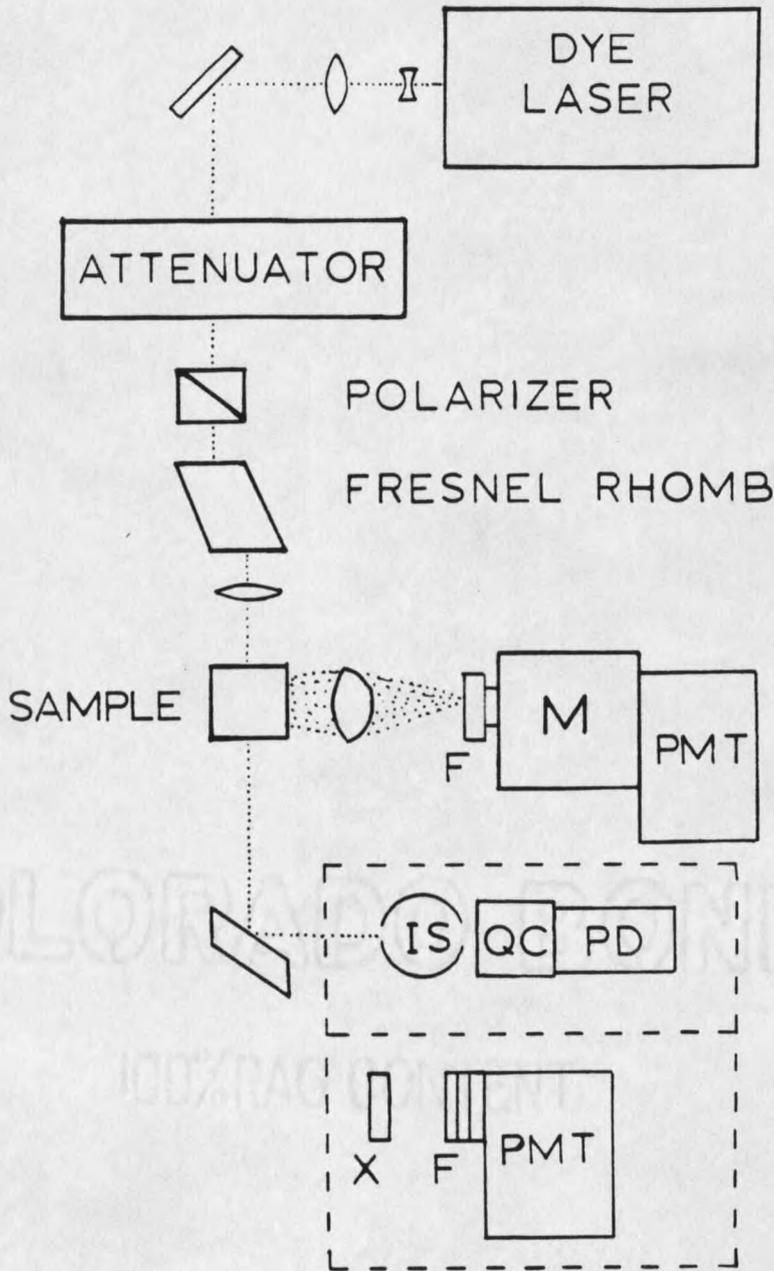


Figure 4. Polarized two-photon fluorescence excitation apparatus

The one major improvement in the apparatus was the replacement of the troublesome NRG nitrogen-pumped dye laser with a Lumonics Nd:YAG-pumped dye laser. Adaptation of existing data acquisition software to the new dye laser was done by David Theiste and the author.

The first step in collecting meaningful TP spectral data is to confirm the quadratic dependence of TP excited fluorescence on the laser intensity. This was done for each sample at the maximum intensity wavelength of each dye and/or at a maximum in the TP fluorescence excitation spectrum. Two methods were used to test for this: crossed polarizer and neutral density filter attenuation of the laser light. Reducing the laser intensity to 50% should reduce the fluorescence to 25%.

A criterion for acceptable data in this work was that Q , as defined below, should be within the range 1.9-2.0.

$$Q = \log \left(\frac{\langle F \rangle}{\langle F' \rangle} \right) \quad \log \left(\frac{\langle I \rangle}{\langle I' \rangle} \right)$$

$\langle F \rangle$ is the average integrated fluorescence intensity, $\langle I \rangle$ is the average integrated laser intensity and the primed quantities are those measured when the beam is attenuated. Most Q values were in the 1.95-2.00 range except those for isoquinoline and its cation which both have fluorescence quantum yields approximately a tenth that of naphthalene, resulting in weak fluorescence signals and lower signal-to-noise ratios. If the Q value was unacceptable, photon

flux in the sample was reduced by either defocusing the beam or decreasing the laser power.

Once this criterion was satisfied, a software option could be used to insert three neutral density filters (79, 63 and 50 %T) into the beam and step the laser wavelength. At several wavelengths in the lasing region of a dye, four values of $\langle F \rangle / \langle I \rangle^2$ were calculated. At a particular wavelength the relative standard deviation among these (using $n - 1 = 3$ weighting) was commonly less than 5%. These tests insured that stationary states excited by TP absorption did fluoresce instead of undergoing further excitation into non-fluorescing states.

After it was confirmed that fluorescence intensity depended quadratically on laser intensity, data were collected at 0.5 nm increments from 550 to 650 nm and at 1.0 nm increments from 450 to 550 nm. Dyes were diluted, mixed or solvent shifted to produce scan ranges which overlapped by at least 5 nm or 10 data points. Dyes used, their scan ranges and maximum pulse energies (at the sample) are listed in Table 2.

The signal-to-noise ratio, limited by linearity of the signal amplifiers and integrators, was optimized by changing the photomultiplier voltages or amplifier gains. The consequence of these adjustments is that TP data segments must be fit together by multiplying an entire

