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Sean P. McGlynn
Boyd Professor of Chemistry

Organization

Louisiana State University
Chemistry Department
Baton Rouge, Louisiana 70803

Signature Seán P. McGlynn	Date 4/10/76

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E-(40-1)-3018

ANNUAL REPORT

1975 - 1976

UNITED STATES ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

BIOMEDICAL AND ENVIRONMENTAL RESEARCH PHYSICS PROGRAM

E-(40-1)-3018

"A PHYSICO-CHEMICAL STUDY OF SOME AREAS OF FUNDAMENTAL SIGNIFICANCE TO BIOPHYSICS"

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May 15, 1976

S. P. McGlynn
Principal Investigator
Boyd Professor of Chemistry

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INTRODUCTION

The ten (10) Bibliographic Titles of Section 1A(5) (No.'s 144 - 153 of the Bibliography of 1975 - 1976) constitute the gist of this Report. These entities represent work completed and published (or in process of publication). Apart from this listing and the provision of reprints/preprints, no further discussion of such works are available in this Report.

The reports presented in Section 2 (Research Accomplished or in Process) contain short descriptions written by postdoctoral fellows and graduate students summarizing that part of their research effort which is not discussed elsewhere nor listed among the ten (10) Bibliographic Titles (No.'s 144 - 153) for 1975 - 1976. These reports are unedited. Because of this, these reports should provide personnel insights not otherwise available. Additionally, these reports constitute reminders to graduate students and postdoctoral fellows of the quality and quantity of their individual research efforts.

It should be emphasized that the reports of Section 2 constitute remnant material left over from the Bibliography of Section 1A(4). These reports are included for the sake of completeness and not because of their importance. Finally, these individual reports may not agree among themselves; the enforcement of such agreement would have constituted improper editorial intrusion at this stage of the various research efforts.

ITEM 1.

BIBLIOGRAPHY OF TITLES PUBLISHED, SYMPOSIA ATTENDED, LABORATORY GUESTS, EXITING PERSONNEL AND EQUIPMENT PURCHASED

A. BIBLIOGRAPHY OF TITLES

The bibliography of twenty-three (23) titles constitutes the bulk of this Report. These are separated into five (5) categories. The first of these consists of one (1) title and provides information pertaining to the 1971 - 1972 Annual Report; the second of these consists of one (1) title and provides information pertaining to the 1972 - 1973 Annual Report; the third of these consists of three titles and provides reprints and information pertaining to the 1973 - 1974 Annual Report; the fourth of these consists of eight (8) titles and provides reprints and information pertaining to the 1974 - 1975 Annual Report; the fifth of these consists of ten (10) titles and provides reprints and/or preprints pertinent to the present reporting period (1975 - 1976).

1. Completion of the 1971 - 1972 Annual Report

The index number used in this section is that which was assigned to the work in question in the 1971 - 1972 Annual Report.

90. Hochmann, P., Foster, S. I. and McGlynn, S. P., "Geiometry of Excited Molecules."
(7 preprints provided in the 1971 - 1972 Annual Report; not yet submitted for publication).

The 1971 - 1972 Annual Report remains incomplete.

2. Completion of the 1972 - 1973 Annual Report

The index number used in this section is that which was assigned to the work in question in the 1972 - 1973 Annual Report.

110. Maria, H. J. and McGlynn, S. P., "Photoelectron Spectra of Molecules Isoelectronic With Acetone."
(7 preprints provided in the 1972 - 1973 Annual Report; not yet submitted for publication).

The 1972 - 1973 Annual Report remains incomplete.

Reprints + preprints removed

3. Completion of the 1973 - 1974 Annual Report

122. Meeks, J. L., Maria, H. J., Brint, P. and McGlynn, S. P., "Photoelectron Band Assignments in Monocarbonyls and α-Dicarbonyls," Chem. Reviews, 75, 603(1975).
(7 reprints appended to this Report)

125. Hochmann, P., Templet, P. H. and McGlynn, S. P., "The Assignment of Molecular Rydberg Transitions. Energy Separations of the 1s Rydberg Levels of Monohalides," not yet submitted for publication.
(7 preprints appended to the 1973 - 1974 Annual Report)

126. Templet, P. H., Hochmann, P. and McGlynn, S. P., "The Assignment of Molecular Rydberg Transitions. Low-Energy Rydberg Transitions in Mercury Halides," not yet submitted for publication.
(7 preprints appended to the 1973 - 1974 Annual Report)

The 1973 - 1974 Annual Report remains incomplete.

4. Completion of the 1974 - 1975 Annual Report

135. Lui, Y. H. and McGlynn, S. P., "Electronic Spectroscopy of Highly-Polar Aromatics. XI. Luminescence of the Cyanoanilines," J. Luminescence, 10, 113(1975).
(7 reprints appended to this Report)

136. Lui, Y. H. and McGlynn, S. P., "Electronic Spectroscopy of Highly-Polar Aromatics. XII. Luminescence of the Aminoacetophenones," not yet submitted for publication.
(7 preprints appended to the 1974 - 1975 Annual Report)

137. Meeks, J. L., Arnett, J. F., Larson, D. B. and McGlynn, S. P., "Photoelectron Spectroscopy of Carbonyls. Urea, Oxamide, Oxalic Acid and Oxamic Acid, J. Amer. Chem. Soc., 97, 3905(1975).
(7 reprints appended to this Report)

138. Meeks, J. L. and McGlynn, S. P., "Photoelectron Spectroscopy of Carbonyls. Oxamide, Parabanic Acid and Their N-Methyl Derivatives," J. Amer. Chem. Soc., 97, 5079(1975).
(7 reprints appended to this Report)

139. Meeks, J. L. and McGlynn, S. P., "Photoelectron Spectroscopy of Carbonyls. Oxalyl Chloride, Ethyl Oxalyl Chloride, Ethyl Oxamate and N,N-Dimethyl Ethyl Oxamate," Spectrosc. Letters, 8(7), 439(1975). Corrigenda, Spectrosc. Letters, 8(11), 941(1975).
(7 reprints appended to this Report)

140. Meeks, J. L. and McGlynn, S. P., "Photoelectron Spectroscopy of Carbonyls. Carbonates, Oxalates and Esterification Effects," J. Electron Spectrosc. Relat. Phenom., 8, 85(1976).
(7 reprints appended to this Report)

141. Khalil, O. S. and McGlynn, S. P., "Electronic Spectroscopy of Highly-Polar Aromatics. XIII. Absorption and Luminescence of Nitroanilines," J. Luminescence, 11, 185(1976).
(7 reprints appended to this Report)

142. Hochmann, P. and McGlynn, S. P., "Rydberg States. II. A Correlation Algorithm," in VACUUM ULTRAVIOLET RADIATION PHYSICS, E. -E. Koch, R. Haensel and C. Kunz, Eds., Pergamon/Vieweg, Braunschweig, Germany, 1975.
(7 reprints appended to this Report)

Apart from item 136, the 1974 - 1975 Annual Report is now complete.

5. Bibliography for 1975 - 1976

144. Felps, S., Hochmann, P., Brint, P. and McGlynn, S. P., "Molecular Rydberg Transitions. The Lowest-Energy Rydberg Transitions of s-Type in CH_3X and CD_3X, X = Cl, Br and I," J. Mol. Spectrosc., 59, 355(1976).
(7 reprints appended to this Report)

145. Dougherty, D., Wittel, K., Meeks, J. L. and McGlynn, S. P., "Photoelectron Spectroscopy of Carbonyls. Ureas, Uracils and Thymine," submitted to J. Amer. Chem. Soc.
(7 preprints appended to this Report)

146. Khalil, O. S., Meeks, J. L. and McGlynn, S. P., 'Electronic States and "Geometric Isomerism" of p-Disubstituted Cyanoanilines," submitted to Chem. Phys. Letters.
(7 preprints appended to this Report)

147. Wittel, K., Meeks, J. L. and McGlynn, S. P., "Electronic Structure of the Cyanato and Thiocyanato Groups. Ground State and Excited States," in THE CHEMISTRY OF CYANATES AND THEIR THIO DERIVATIVES, S. Patai, Ed., in press.
(7 preprints appended to this Report)

148. Chattopadhyay, S., Hochmann, P. and McGlynn S. P., "Molecular Rydberg Transitions. V. Atomic Correlation Lines," submitted to J. Chem. Phys.
(7 preprints appended to this Report)

149. Dougherty, D., Arnett, J. F., Bloomfield, J. G., Newkome, G. R. and McGlynn, S. P., "Photoelectron Spectra of Carbonyls. Propella-enes and Propella-ones," submitted to *J. Phys. Chem.*
(7 preprints appended to this Report)

150. Brint, P., Dougherty, D. and McGlynn, S. P., "Photoelectron Spectra of Carbonyls. The Non-bonding n-MO's of Dicarbonyl Compounds," in preparation.
(7 preprints appended to this Report)

151. Brint, P. and McGlynn, S. P., "The Low-Energy $^1\Gamma_{n\pi*}$ Excited States of Tetramethyl-1,3-cyclobutanedione," submitted to *J. Amer. Chem. Soc.*
(7 preprints appended to this Report)

152. Brint, P., Wittel, K., Felps, W. S. and McGlynn, S. P., "Molecular Rydberg Transitions. III. A Linear Combination of Rydberg Orbitals (LCRO) Model for the Two-Chromophoric System 2,2,4,4-Tetramethylcyclobutane-1,3-dione (TMCBD)," submitted to J. Amer. Chem. Soc.
(7 preprints appended to this Report)

153. Annual Report 1975 - 1976. A Bibliography of Titles and Reports of Research Accomplished or in Progress (Incomplete Work) for the period 1975 - 1976 of Research Contract No. AT-(40-1)-3018.
(7 copies submitted to the U. S. Energy Research and Development Administration on May 15,1976)

B. SYMPOSIA ATTENDED

1975 - 1976

1. S. P. McGlynn, "Excited Electronic States of α-, β-, and γ-Dicarbonyls," VIII international Conference on Photochemistry, The University of Alberta, Alberta, Edmonton, Canada, August 7-12, 1975.

   --Invited Lecture

2. S. P. McGlynn, "Analytical Applications of Fluorescence, "The Louisiana State University, Baton Rouge, Louisiana, October 1, 1975.

   --Invited Lecture

3. The 27th Southeast-31st Southwest Combined Regional Meeting of The American Chemical Society, Memphis, Tennessee, October 29-31, 1975.

   S. P. McGlynn, "Photoelectron Band Assignments in Monocarbonyls and α-Dicarbonyls."

   --Invited Lecture

   S. P. McGlynn, "Photoelectron Spectra of Urea and Uracils."

   --Invited Lecture

   S. P. McGlynn, "Photoelectron Spectra of Benzoic Acid and Related Molecules."

   --Invited Lecture

4. S. P. McGlynn, "Molecular Rydberg States," The Florida State University, Tallahassee, Florida, November 14, 1975.

   --Invited Lecture

5. S. P. McGlynn, "The Excitement of Science," Omicron Delta Kappa National Leadership Honorary, The Florida State University, Tallahassee, Florida, November 15, 1975.

   --Invited Lecture

6. S. P. McGlynn, "The Color of Inorganic Ions," Michael Kasha Symposium on Energy Transfer in Organic, Inorganic, and Biological Systems, The Florida State University, Tallahassee, Florida, January 8-10, 1976.

   --Invited Lecture

7. S. P. McGlynn, "Colors of Simple Polyatomic Anions," The University of Miami, Miami, Florida, January 12, 1976.

--Invited Lecture

8. S. P. McGlynn, "The Price of Precision," Planetarium Chamber, Louisiana Arts and Sciences Center, Baton Rouge, Louisiana, February 4, 1976.

--Invited Lecture

9. S. P. McGlynn, "The Need for Work," Louisiana State University Alumni Federation Scholars Program, Louisiana State University, Baton Rouge, Louisiana, February 10, 1976.

--Invited Lecture

10. S. P. McGlynn, "Molecular Rydberg Transitions," Department of Chemistry, The University of Houston, Houston, Texas, March 19, 1976.

--Invited Lecture

C. LABORATORY GUESTS

1. Professor Hans Bock
   Chemische Institute der Universität
   6 Frankfurt/Main 70
   Theodor Stern Kai 7
   West Germany
   May, 1975

2. Professor J. Wayne Rabalais
   Department of Chemistry
   University of Houston
   Houston, Texas 77004
   June, 1975

3. Dr. Haim Levanon
   Department of Physical Chemistry
   The Hebrew University of Jerusalem
   Jerusalem, Israel
   July, 1975

4. Dr. Fred Watson
   Department of Chemistry
   University of Arkansas
   Little Rock, Arkansas
   November, 1975

5. Dr. Loucas G. Christophorou
   Oak Ridge National Laboratory
   Post Office Box X
   Oak Ridge, Tennessee 37830
   February, 1976

6. Professor B. V. McKoy
   Department of Chemistry
   California Institute of Technology
   Pasadena, California
   March, 1976

7. Mr. T. Overton
   Deputy Director SCRDE
   Ministry of Defense
   Flagstaff Road
   Colchester Essex
   England
   April, 1976

8. Professor L. Vanquickenborne
Université Te Leuven
Department Scheikunde
Delestijnenlaan 200F
3030 Heverlee
Belgium
April, 1976

9. Professor L. Klasinc
Institut Ruder Boskovic
41001 Zagreb
Yugoslavia
Bijenecka cesta 54
Post pretinac 1016
April, 1976

D. PERSONNEL DEPARTING LABORATORY, 1975 - 1976

Postdoctoral Fellow

Brint, Paul	1973 - 1975	Department of Physics Schuster Laboratories The University Manchester M13 9PL England
Wittel, Klaus	1975 - 1976	Chemische Institute der Universität 6 Frankfurt/Main 70 Theodor Stern Kai 7 West Germany

E. EQUIPMENT PURCHASED

We have requested a budget readjustment since our replacement costs have been greater than expected. A considerable amount of this has involved the vacuum ultraviolet spectrophotometer. The accompanying letter, submitted to your department April 29, 1976, provides the details of this budget readjustment.

April 29, 1976

A. H. Frost, Jr., Chief
Research Contracts, Procedures and Reports Brance
Contract Division
P. O. Box E
Oak Ridge, Tennessee 37830

Re: ERDA Contract AT-(40-1)-3018 with the Louisiana State University
LSU Account No. 115-20-5152

Dear Mr. Frost:

I wish a budget readjustment for 1975-76 for the contract specified above. The readjustment requested is as follows:

	From	To
Salaries	58055.00	59055.00
Wages	-----	-----
Travel	3000.00	3700.00
Supplies	8764.00	14764.00
Equipment	10000.00	1694.00
Indirect Costs	26705.00	27165.00
Employee Benefits	8476.00	8622.00
	$115000.00	$115000.00

This readjustment does not alter the amount of committed ERDA funds nor does it require any further ERDA funds.

The reasons for this readjustment request are three fold:

(i) Dr. Klaus Wittel (Deutsche Forschungsgemeinschaft and University of Frankfurt) decided to stay here an extra two months in order to complete his research project. Dr. John Scott, who had been here approximately 1 year was given a small salary increment in March 1976 in order to bring his salary into line with other post-doctoral personnel in this department. Finally, a Mr. David Bouler and a Mr. Sihi will be joining this group as graduate students a few months prior to their going on Departmentally-funded graduate assistantships and we wish to make provision for their support for that period ... The requested adjustment is quite moderate.

(ii) We ran into considerable replacement costs, all of which came from our supplies budget. Some of these costs are:

Replacements	Cost
Slave multimeter	311.12
Diffusion pump heater	37.85
Thermocouple gauge	71.82
Parts for Hinteregger Lamp	718.91
Replacement Grating	3744.05
Heated probe for PES	517.75
Dewar, graded seals	450.57
	$5852.07

In addition to the above, we ran into considerable costs for simple optics. An example, embondying only cells, windows and optical flats is given:

VUV windows	467.64
Optical flats	169.60
LiF windows	368.70
UV cells	666.41
Quartz discs	36.46
	$1708.81

These expenditures, coupled with normal purchases of chemicals and publication costs have produced a serious over-run in our Supplies budget.

(iii) We have spent virtually none of our Equipment allotment. We reserved this money for the purchase of a McPherson 2 meter VUV monochromator. This instrument was for sale by the Department of Chemistry at the University of Arizona. Upon detailed investigation, it turned out that the configuration of this instrument was not adaptable to our needs and that the UA people really wanted ~ $20,000.00. (The original cost was $64,000.00!) At this point, we decided to go to our second priority equipment item, namely a Super-dewar Cryogenic-magnet system (85 kG). However, the Louisiana State University has decided to purchase this item for us at a cost of ~ $19,000.00. Hence, we never made a request for a budget change in this regard. We then thought of moving to 3rd priority. But, again, LSU is buying us a tunable dye laser for ~ $25,000.00.

Hence the ~ $10,000.00 in Equipment remains unused.

The budget change we seek concerns a movement of funds from Equipment into Salaries ($1000.00), Travel ($700.00), Supplies ($6000.00), Indirect costs ($460.00) and Employee Benefits ($146.00).

We also seek to have the $1694.00 remaining in Equipment reclassified so that the item to be purchased in this category remains unspecified. The item to be purchased will be either an X-Y recorder or a phase-sensitive amplification system ... As yet, we cannot specify which. However, when and if we reach a decision, we will inform you prior to purchase.

I enclose a status report on Grant Expenditures complete to 4/14/76, and the most recent appointment forms for Dr.'s Klaus Wittel and John Scott. I trust you will find the information given to be adequate and our request to be moderate. Should you desire any further details, we will be glad to supply them.

In the meantime, we would appreciate your consideration.

Sincerely,

S. P. McGlynn
Boyd Professor of Chemistry
Research Director

SPM:cy

ITEM 2.

REPORTS OF RESEARCH ACCOMPLISHED OR IN PROGRESS
(Incomplete Work)

RYDBERG SPECTROSCOPY

by

Klaus Wittel

Postdoctoral Research Associate

Since I was familiar with photoelectron spectroscopy, I directed my efforts toward an understanding of Rydberg Spectroscopy: Rydberg states, after all, are precursors to the cationic states investigated in photoelectron spectroscopy. This effort led to the investigation of several quite distinct aspects of vacuum ultraviolet spectroscopy. These are discussed briefly in the following:

1. Theoretical Investigation of the Applicability of the MO-Approximation.

Rydberg spectra are usually analyzed in terms of the Rydberg equation

$$\tilde{\nu}_{\underline{n}} = \mathrm{IE} - R/(\underline{n}+\delta_{\ell})^2; \quad \underline{n} = 1,2,3,.......$$

where $\tilde{\nu}_{\underline{n}}$ is the transition energy; IE is the ionization energy to which the series converges; and δ_{ℓ}, the quantum defect, often carries an ancillary orbital angular momentum quantum number index ℓ. Intravalence excitations, on the other hand, are usually discussed using MO or VB ideas. Consequently, it was of some interest to investigate the interrelations of extravalence and intravalence transitions.

The detailed discussion of these interrelationships is available in Reference 1. However, the primary result of that work was the determination that Rydberg states should be very amenable to an MO description.

Particular attention was paid to the approximations involved in the

MO concept and the manner in which they affected the application of orbital ideas to different physical observables. This is also contained in Reference 1. Reference 2 consists of an effort to apply these ideas to a particular system, namely, the _iso_cyanato and _iso_thiocyanato substituents.

2. Selection Rules in Rydberg Spectroscopy.

The g $\leftrightarrow$ u selection rules must apply to the optical transitions of any centrosymmetric molecule. Even if a molecule is not centrosymmetric, the ℓ labelling of δ_ℓ implies that molecular Rydberg orbitals are nearly atomic and, hence, approximately centrosymmetric. It was of interest to investigate the extent to which this might be true.

The molecule chosen for study was 2,2,4,4-tetramethylcyclobutane-1,3-dione. This molecule is centrosymmetric. It was found that the g/u selection rule was violated by experiment when the Rydberg orbital was supposed to be situated on the inversion center. The only resolution of the resultant dilemma led to the supposition that the Rydberg orbital was delocalized, and that it consisted of a Linear Combination of Rydberg Orbitals (LCRO) from different atomic centers in the molecule. This, in turn, implies that the ℓ-labelling should be discarded.

As a result of this work, certain experiments, one specifically designed to test the proposed LCRO-approach, have been suggested. In addition, the need for computations, possibly in a pseudopotential format, become imperative in order to gain a feeling for relative intensities of Rydberg transitions and for the occurrence criteria which determine whether or not a given series will be observed (Reference 3).

These ideas have been investigated further for the series of bromoethylenes. It turns out that those molecules which possess a center of symmetry display a simple spectrum, indicating that a g ↔ u selection rule is, in fact, operative. A closer investigation of *trans*-dibromoethylene, however, leads to the conclusion that the localization properties of the initial (i.e., core) orbitals determines whether or not a strict *g*-labelling of Rydberg orbitals will apply (Reference 4).

3. Upper State Geometries from Vibrational Intensities.

The theory of internal rotation (internal-axis method) was applied to the first Rydberg state of 1,1-dideuteroethylene. The purpose of this work was to settle an argument about the geometry of the excited state. For a complete account of this work, see Reference 5.

4. Intermediate Coupling in Linear Molecules.

A program (FORTAN IV) was written to do intermediate coupling calculations on the $\pi^3\pi^*$, $\pi^3\sigma^*$, $\sigma\pi^*$ and $\sigma\sigma^*$ excited states of linear molecules. Parameters were taken from atomic spectral data. The computational output which is now available consists of the intensities and the energies of valence and Rydberg transitions for the mercury halides and the s- and p-Rydberg transitions of the hydrogen- and methylhalides. The program has also been extended to obtain estimates of the MCD effects to be expected in these molecules. This work is still in progress. A preliminary account of it is contained in Reference VI.

5. Search for Regularities in the Vacuum Ultraviolet Spectra of Haloethylenes.

The VUV spectra of nine haloethylenes (monochloro-, monobromo-, *cis*-

dibromo-, trans-dibromo, 1,1-dibromo-, tribromo-, tetrafluoro-, tetrachloro-, and tetrabromo-) were obtained in order to serve as the data base with which to answer the following questions:

1. What is the numerical reliability of VUV data when translated into quantum defect values?

2. Does an inverted ligand field approach work? Or does an LCRO model (Reference 3) provide the superior description?

3. Are there any meaningful correlations between transition energies and ionization potentials besides the Rydberg equation?

Since the information content of the spectra is extremely large, much of this effort consists of making assignments of electronic transitions. This work is still in progress. The analysis of the VUV spectrum of trans-dibromoethylene is contained in Reference 4.

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Having worked on a number of different aspects of Rydberg spectroscopy, those areas where further research would be of value can now be specified. So far, transition energies have provided the dominant information input for the assignment and interpretation of Rydberg spectra. Intensities, which have provided extremely useful information for valence transitions, should be exploited further, if for no other reason than to provide independent assignment criteria. In addition, any measurement of properties of Rydberg states other than from their energies will provide an extremely powerful tool for assigning and, subsequently, discussing Rydberg transitions in a more physical way.

REFERENCES

1. K. Wittel and S. P. McGlynn, "The Molecular Orbital Approach to Electron and Electronic Spectra," Chem. Revs., submitted for publication.
2. K. Wittel, James L. Meeks and S. P. McGlynn, "Electronic Structure of the Cyanato and Thiocyanato Groups. Ground State and Excited States," in THE CHEMISTRY OF THE CYANATO AND THIOCYANATO GROUPS, Saul Patai, Ed., in press.
3. P. Brint, K. Wittel, W. S. Felps and S. P. McGlynn, "Molecular Rydberg Transitions. III. A Linear Combination of Rydberg Orbitals (LCRO) Model for the Two-Chromophoric System 2,2,4,4-Tetramethylcyclobutane-1,3-dione (TMCBD)," J. Amer. Chem. Soc., submitted for publication.
4. K. Wittel, W. S. Felps and S. P. McGlynn, "The VUV Spectrum of trans-$C_2H_2Br_2$," in preparation.
5. G. Findley, K. Wittel, W. S. Felps and S. P. McGlynn, "The VUV Spectrum of $C_2H_2D_2$," in preparation.
6. K. Wittel, W. S. Felps and S. P. McGlynn, "The Rydberg Spectra of Linear HgX_2 molecules (X = Cl, Br and I)," in preparation.

INTERMEDIATE COUPLING MODEL FOR LINEAR MOLECULES

by

Klaus Wittel
Postdoctoral Fellow

1. INTRODUCTION

This is a highly technical description of a program which should provide a basis for the understanding of

a) How the basic formulae were obtained.

b) How they were implemented in a FORTRAN IV program.

Thus, the reader should be in a position to understand the theory and to check the different parts of the program. A listing and input instructions are provided at the end.

2. DEFINITION OF THE MODEL

Although the model is fully defined only when every single step has been specified, we will give a coarse definition which is essentially correct and nearly complete.

This intermediate-coupling model consists of a configuration interaction of all states arising from the atomic np → n'p excitations. It treats spin-orbit as well as coulombic electron-electron interactions. Thus, all states arising from the configurations

$$\sigma\pi^4\pi^* \qquad \sigma^2\pi^3\pi^*$$

$$\sigma\pi^4\sigma^* \qquad \sigma^2\pi^3\sigma^*$$

are included. The excitations may be intravalence (n = n') or extravalence (RYDBERG) (n ≠ n') in nature. In the former case, an s/p mixing is allowed for $m_\ell = 0$ orbitals (i.e., for σ and σ* spin orbitals). The program essentially sets up the configuration interaction matrices for each M_J value and diagonalizes, in order to get the energies and wavefunctions. Thereafter, relative transition intensities are calculated for nominal "singlet" and "triplet" states.

The LCAO exapnsion may, or may not be used. If used, the zero-differential overlap normalization

$$\sum_\mu c_{i\mu}\, c_{j\mu} = c_{ij}$$

should be used, in line with the NDDO (No Diatomic Differential Overlap) approximation for the two electron integrals.

3. MOLECULAR ORBITALS

Molecular orbitals with the following quantum numbers are considered.

# of MO	m_ℓ	orbital energy
1	0	ϵ_1
2	1	ϵ_2
3	-1	ϵ_2
4	1	ϵ_3
5	-1	ϵ_3
6	0	ϵ_4

a. LCAO expansion

If the LCAO expansion is used, coefficients are stored in one array CMO (10, 4), This array is subsequently equivalenced.

			MO	AO
CS	CSP	CMO(1,1) - CMO(5,1)	σ	p
	CSS	CMO(6,1) - CMO(10,1)	σ	s
	CP	CMO(1,2) - CMO(5,2)	π	p
	CPE	CMO(1,3) - CMO(5,3)	π*	p
CSE	CSEP	CMO(1,4) - CMO(5,4)	σ*	p
	CSES	CMO(6,4) - CMO(10,4)	σ*	s

For instance, CSES means Coefficient, Sigma Excited s-type.

For Rydberg excitation, either CSES is zero, or CPE and CSEP are zero, i.e. only p_π, p_σ or s-Rydberg orbitals are allowed. The LCAO expansion coefficients are considered as basic input, as are the four molecular SCF-orbital energies ϵ.

4. MOLECULAR SPINORBITALS

Molecular spinorbitals φ are generated and are classified by the quantum numbers $\{ m_{\ell}, m_s, m_j \}$, where

$$m_j = m_{\ell} + m_s$$

and by a spinorbital energy $\tilde{\epsilon}$

$$\underline{F}\varphi_i = \tilde{\epsilon}_i \varphi_i$$

where

$$\underline{F}(1) = \underline{F}^{o}(1) + \underline{H}_{SO}(1)$$

is the FOCK-operator of the ground configuration $\sigma^2\pi^4$,

List of spinorbitals

#	m_{ℓ}	m_s	m_j	#MO	Designation
1	0	0.5	0.5	1	$\sigma_{\frac{1}{2}}$
2	0	-0.5	-0.5	1	$\sigma_{-\frac{1}{2}}$
3	1	0.5	1.5	2	$\pi_{3/2}$
4	1	-0.5	0.5	2	$\pi_{\frac{1}{2}}$
5	-1	0.5	-0.5	3	$\pi_{-\frac{1}{2}}$
6	-1	-0.5	-1.5	3	$\pi_{-3/2}$
7	1	0.5	1.5	4	$\pi^*_{3/2}$
8	1	-0.5	0.5	4	$\pi^*_{\frac{1}{2}}$
9	-1	0.5	-0.5	5	$\pi^*_{-\frac{1}{2}}$
10	-1	-0.5	-1.5	5	$\pi^*_{-3/2}$
11	0	0.5	0.5	6	$\sigma^*_{\frac{1}{2}}$
12	0	-0.5	-0.5	6	$\sigma^*_{-\frac{1}{2}}$

a. Spin-orbit interaction

Spinorbital energies are related to orbital energies by

$$\tilde{\epsilon} = \epsilon_i + m_s \cdot m_\ell \cdot A(i,i)$$

where A(i,i) is the appropriate effective spin-orbit parameter, characteristic of the orbital i.

$A(\pi,\pi)$ and $A(\pi^*,\pi^*)$, and two non-diagonal terms $A(\pi,\sigma)$ and $A(\pi^*,\sigma^*)$ are either read in as such, or calculated using LCAO coefficients and atomic parameters. As an approximation, the off-diagonals $A(\pi,\sigma^*)$ and $A(\sigma,\pi^*)$ are set equal to zero. This is justified not so much by actual magnitudes, as by the small effect on energies which are given, as an example, by

$$\Delta E_{is}(\sigma,\pi^*) = \frac{A(\sigma,\pi^*)^2}{\epsilon_\sigma - \epsilon_{\pi^*}} \cdot \frac{1}{2}$$

where $\epsilon_\sigma - \epsilon_{\pi^*}$ is large.

LCAO expansion

The effective spin-orbit operator is assumed to be

$$H_{SO}(1) = \sum_A \zeta_A(r_{A1}) \cdot \vec{\ell}_{A1} \cdot \vec{s}_1$$

where $\zeta_A(r_{A1})$ is only defined through its integrals over atomic orbitals

i) One center radial integrals

$$\langle A | \zeta_A(r_A) | A \rangle \equiv \zeta_A$$

are set equal to some constant, obtained from the intermediate coupling model and atomic spectral data (e.g., K. Wittel and R. Manne, Theor. Chim. Acta, 33, 397(1974))

ii) All two and three center integrals are set to zero, in line with the ZDO-approximation.

iii) The angular part of one center integrals is evaluated exactly.

The effective spin-orbit parameter A(i,j) is now defined as the radial part of the integral

$$A(i,j) = \langle \phi_i | H_{SO} | \phi_j \rangle$$

To be specific

$$A(\pi,\pi) = \sum_{i=1}^{5} \zeta_i \cdot CP_i^2$$

$$A(\pi^*,\pi^*) = \sum_{i=1}^{5} \zeta_i \cdot CPE_i^2$$

$$A(\sigma,\pi) = \sum_{i=1}^{5} \zeta_i \cdot CSP_i \cdot CP_i$$

$$A(\sigma^*,\pi^*) = \sum_{i=1}^{5} \zeta_i \cdot CSEP_i \cdot CPE_i$$

The angular part is considered separately.

For valence orbitals, ζ_i is read into ZETAA (i), i = 1-5; for Rydberg orbitals, if needed, the additional ζ_i are read into ZETAA (i), i = 6-10.

Angular part of spin-orbit integrals

Using $|m_\ell\, m_s\rangle$ notation, all are zero except the off-diagonal elements

$$\langle -1\alpha | \vec{\ell} \cdot \vec{s} | 0\beta \rangle = \frac{1}{\sqrt{2}}$$

$$\langle 0\alpha | \vec{\ell} \cdot \vec{s} | 1\beta \rangle = \frac{1}{\sqrt{2}}$$

and the diagonals are given by

$$\langle m_\ell m_s | \vec{\ell} \cdot \vec{s} | m_\ell m_s \rangle = m_\ell \cdot m_s$$

5. BASIS CONFIGURATIONS

The following basis configurations were considered:

Config. No.	i→j		Spinorbitals						M_L	M_S	M_J	Type	Symmetry
1	6	7	1	2	3	4	5	7	2.	1.	3.	$\pi\to\pi^*$	Φ
2	6	8	1	2	3	4	5	8	2.	0.	2.	$\pi\to\pi^*$	Δ
3	5	7	1	2	3	4	7	6	2.	0.	2.	$\pi\to\pi^*$	
4	6	11	1	2	3	4	5	11	1.	1.	2.	$\pi\to\sigma^*$	
5	2	7	1	7	3	4	5	6	1.	1.	2.	$\sigma\to\pi^*$	
6	5	8	1	2	3	4	8	6	2.	-1.	1.	$\pi\to\pi^*$	Π
7	4	7	1	2	3	7	5	6	0.	1.	1.	$\pi\to\pi^*$	
8	6	9	1	2	3	4	5	9	0.	1.	1.	$\pi\to\pi^*$	
9	5	11	1	2	3	4	11	6	1.	0.	1.	$\pi\to\sigma^*$	
10	6	12	1	2	3	4	5	12	1.	0.	1.	$\pi\to\sigma^*$	
11	1	7	7	2	3	4	5	6	1.	0.	1.	$\sigma\to\pi^*$	
12	2	8	1	8	3	4	5	6	1.	0.	1.	$\sigma\to\pi^*$	
13	2	11	1	11	3	4	5	6	0.	1.	1.	$\sigma\to\sigma^*$	
14	3	7	1	2	7	4	5	6	0.	0.	0.	$\pi\to\pi^*$	Σ^+/Σ^-
15	4	8	1	2	3	8	5	6	0.	0.	0.	$\pi\to\pi^*$	
16	5	9	1	2	3	4	9	6	0.	0.	0.	$\pi\to\pi^*$	
17	6	10	1	2	3	4	5	10	0.	0.	0.	$\pi\to\pi^*$	
18	5	12	1	2	3	4	12	6	1.	-1.	0.	$\pi\to\sigma^*$	
19	4	11	1	2	3	11	5	6	-1.	1.	0.	$\pi\to\sigma^*$	
20	1	8	8	2	3	4	5	6	1.	-1.	0.	$\sigma\to\pi^*$	
21	2	9	1	9	3	4	5	6	-1.	1.	0.	$\sigma\to\pi^*$	
22	1	11	11	2	3	4	5	6	0.	0.	0.	$\sigma\to\sigma^*$	
23	2	12	1	12	3	4	5	6	0.	0.	0.	$\sigma\to\sigma^*$	

They are characterized by their

i) orbital angular momentum quantum number

$$M_L = \Sigma\, m_\ell$$

ii) spin angular momentum quantum number

$$M_S = \Sigma\, m_s$$

iii) total angular momentum quantum number

$$\begin{aligned} M_J &= M_L + M_S \\ &= \Sigma\, m_j \end{aligned}$$

All three are the projections on the molecular axis; M_J is always a good quantum number (we neglect any vibrational and rotational effects), M_L and M_S are only so, if we neglect off-diagonal spin-orbit interaction, i.e., set $A(i,j) = 0$ for $i \neq j$.

Consequently, there are no interaction matrix elements between configurations with differing M_J; furthermore, electrostatic matrix elements $\langle \psi_i | \frac{1-P_{12}}{r_{12}} | \psi_j \rangle$ are zero unless

$$M_S(i) = M_S(j)$$

and

$$M_L(i) = M_L(j)$$

The set of $M_J = 0$ configurations can be transformed so that it decomposes into two subsets, each transforming according to Σ^+ or Σ^-. This induces the following symmetry decomposition of the CI matrix:

Φ (1 by 1) Δ (4 by 4) Π (8 by 8)

Σ^+ (5 by 5) Σ^- (5 by 5)

For $M_J \neq 0$, there is an additional configuration with

$$M_J' = -M_J, \qquad M_S' = -M_S, \qquad M_L' = -M_L$$

which is degenerate with the original one and therefore not considered here.

6. CONFIGURATION INTERACTION MATRICES*

The following presents CI-matrices for the different irreducible representations (space and spin). Diagonal elements are with respect to the energy of the ground $\sigma^2\pi^4$ configuration. All matrix elements are real.

Φ state: $M_J = 3$

	$\|1\rangle$
$\langle 1\|$	$\epsilon_3-\epsilon_2 + \frac{1}{2}(\zeta^* - \zeta) - C1$

Δ STATES: $M_J = 2$

	$\|2\rangle$	$\|3\rangle$	$\|4\rangle$	$\|5\rangle$
$\langle 2\|$	$\epsilon_3-\epsilon_2+(\zeta-\zeta^*)$ $-C1+L1$	$L1$	$\frac{1}{\sqrt{2}}\zeta'^*$	
$\langle 3\|$		$\epsilon_3-\epsilon_2+\frac{1}{2}(\zeta^*-\zeta)$ $-C1+L1$		$-\frac{1}{\sqrt{2}}\zeta'$
$\langle 4\|$			$\epsilon_4-\epsilon_2-\frac{1}{2}\zeta-C3$	$M2$
$\langle 5\|$				$\epsilon_3-\epsilon_1+\zeta^*-C2$

*Due to a transcription error ζ and ξ are used interchangeably in this work.

π STATES: $M_J = 1$

	$\vert 6\rangle$	$\vert 7\rangle$	$\vert 8\rangle$	$\vert 9\rangle$	$\vert 10\rangle$	$\vert 11\rangle$	$\vert 12\rangle$	$\vert 13\rangle$
$\langle 6\vert$	$\epsilon_3-\epsilon_2-\frac{1}{2}(\xi^*+\xi)$ $-C1$			$\frac{1}{\sqrt{2}}\xi'^*$			$-\frac{1}{\sqrt{2}}\xi'$	
$\langle 7\vert$		$\epsilon_3-\epsilon_2+\frac{1}{2}(\xi^*+\xi)$ $-C1$	$-M1$			$-\frac{1}{\sqrt{2}}\xi'$		$-M2$
$\langle 8\vert$			$\epsilon_3-\epsilon_2-\frac{1}{2}(\xi^*+\xi)$ $-C1$		$\frac{1}{\sqrt{2}}\xi'^*$			$-M2$
$\langle 9\vert$				$\epsilon_4-\epsilon_2+\frac{1}{2}\xi$ $-C3+L3$	$L3$	$-M3+M2$	$-M3$	$-\frac{1}{\sqrt{2}}\xi'$
$\langle 10\vert$					$\epsilon_4-\epsilon_2-\frac{1}{2}\xi$ $-C3+L3$	$-M3$	$-M3+M2$	
$\langle 11\vert$						$\epsilon_3-\epsilon_1+\frac{1}{2}\xi^*$ $-C2+L2$	$L2$	
$\langle 12\vert$							$\epsilon_3-\epsilon_1-\frac{1}{2}\xi^*$ $-C2+L2$	$\frac{1}{\sqrt{2}}\xi'^*$
$\langle 13\vert$								$\epsilon_4-\epsilon_1-C4$

Σ^+ STATES: $M_J = 0^+$

	$\frac{1}{\sqrt{2}}\{\|14\rangle+\|17\rangle\}$	$\frac{1}{\sqrt{2}}\{\|15\rangle+\|16\rangle\}$	$\frac{1}{\sqrt{2}}\{\|18\rangle+\|19\rangle\}$	$\frac{1}{\sqrt{2}}\{\|20\rangle+\|21\rangle$	$\frac{1}{\sqrt{2}}\{\|22\rangle+\|23\rangle\}$
$\frac{1}{\sqrt{2}}\{\langle 14\|+\langle 17\|\}$	$\epsilon_3-\epsilon_2+\frac{1}{2}(\xi^*-\xi)$ $-C1+2K1$	$2K1-M1$			$2M4-M2$
$\frac{1}{\sqrt{2}}\{\langle 15\|+\langle 16\|\}$		$\epsilon_3-\epsilon_2-\frac{1}{2}(\xi^*-\xi)$ $-C1+2K1$	$\frac{1}{\sqrt{2}}\xi'^*$	$-\frac{1}{\sqrt{2}}\xi'$	$2M4-M2$
$\frac{1}{\sqrt{2}}\{\langle 18\|+\langle 19\|\}$			$\epsilon_4-\epsilon_2+\frac{1}{2}\xi$ $-C3$	$M2$	$\frac{1}{\sqrt{2}}\xi'^*$
$\frac{1}{\sqrt{2}}\{\langle 20\|+\langle 21\|\}$				$\epsilon_3-\epsilon_1-\frac{1}{2}\xi^*$ $-C2$	$\frac{1}{\sqrt{2}}\xi'^*$
$\frac{1}{\sqrt{2}}\{\langle 22\|+\langle 23\|\}$					$\epsilon_4-\epsilon_1$ $-C4+2K2$

Σ^- STATE: $M_J = 0^-$

	$\frac{1}{\sqrt{2}}\{\lvert 14\rangle - \lvert 17\rangle\}$	$\frac{1}{\sqrt{2}}\{\lvert 15\rangle - \lvert 16\rangle\}$	$\frac{1}{\sqrt{2}}\{\lvert 18\rangle - \lvert 19\rangle\}$	$\frac{1}{\sqrt{2}}\{\lvert 20\rangle - \lvert 21\rangle\}$	$\frac{1}{\sqrt{2}}\{\lvert 22\rangle - \lvert 23\rangle\}$
$\frac{1}{\sqrt{2}}\{\langle 14\rvert - \langle 17\rvert\}$	$\epsilon_3-\epsilon_2+\frac{1}{2}(\xi^*-\xi)$ $-C1$	$M1$			$-M2$
$\frac{1}{\sqrt{2}}\{\langle 15\rvert - \langle 16\rvert\}$		$\epsilon_3-\epsilon_2-\frac{1}{2}(\xi^*-\xi)$ $-C1$	$-\frac{1}{\sqrt{2}}\xi'^*$	$-\frac{1}{\sqrt{2}}\xi'$	$M2$
$\frac{1}{\sqrt{2}}\{\langle 18\rvert - \langle 19\rvert\}$			$\epsilon_4-\epsilon_2+\frac{1}{2}\xi$ $-C3$	$M2$	$\frac{1}{\sqrt{2}}\xi'$
$\frac{1}{\sqrt{2}}\{\langle 20\rvert - \langle 21\rvert\}$				$\epsilon_3-\epsilon_1-\frac{1}{2}\xi^*$ $-C2$	$\frac{1}{\sqrt{2}}\xi'^*$
$\frac{1}{\sqrt{2}}\{\langle 22\rvert - \langle 23\rvert\}$					$\epsilon_4-\epsilon_1$ $-C4$

A slight change of notation is contained in these matrices:

$$\zeta = A(\pi,\pi) \qquad \zeta^* = A(\pi^*,\pi^*)$$

$$\zeta' = A(\sigma,\pi) \qquad \zeta'^* = A(\sigma^*,\pi^*)$$

The two electron integrals are described in the following sections.

7. TWO ELECTRON INTEGRALS: MOLECULAR BASIS

Two electron integrals are defined as follows:

$C1 = (1^* \ 1^* | \ 1 \ 1)$

$\quad = (1^* \ 1^* \ 1 \ -1 \ -1) = (-1^* \ -1^* | \ -1 \ -1)$

$C2 = (1^* \ 1^* | \ 0 \ 0)$

$\quad = (-1^* \ -1^* | \ 00)$

$C3 = (0^* \ 0^* | \ 1 \ 1)$

$\quad = (0^* \ 0^* | \ -1 \ -1)$

$C4 = (0^* \ 0^* | \ 0 \ 0)$

$K1 = (1^* \ 1 | \ 1 \ 1^*)$

$\quad = (-1^* \ -1 \ | \ -1 \ -1^*) = (1^* \ 1 | \ -1 \ -1^*)$

$K2 = (0^* \ 0 | 0 \ 0^*)$

$L1 = (1^* \ -1 | \ -1 \ 1^*)$

$\quad = (-1 \ 1^* | \ 1^* \ -1)$

$L2 = (1^* \ 0 | \ 0 \ 1^*)$

$L3 = (0^* \ 1 | \ 1 \ 0^*)$

$\quad = (0^* \ -1 | \ -1 \ 0^*)$

$M1 = (1^* \ -1^* | \ -1 \ 1)$

$M2 = (1^* \ 0^* | \ 0 \ 1)$

$\quad = -(0 \ 1 | \ 0^* \ -1^*)$

$\quad = (0 \ -1 | \ -1^* \ 0^*)$

$\quad = (0 \ 1 | \ 1^* \ 0^*)$

$\quad = -(0 \ -1 | \ 0^* \ 1^*)$

$$M3 = (1^* \; 0 | 0^* \; 1)$$

$$= -(0 \; 1^* | 0^* \; -1)$$

$$M4 = (1^* \; 1 | \; 0 \; 0^*)$$

$$= (0 \; 0^* | \; -1^* \; -1) = (0 \; 0^* | \; 1^* \; 1)$$

The phase convention of CONDON-SHORTLEY is used, i.e.

$$Y_{11} = -\frac{1}{2}\sqrt{\frac{3}{2\pi}}\; e^{i\varphi}\sin\theta$$

$$Y_{10} = \sqrt{\frac{3}{2\pi}}\;\cos\theta$$

$$Y_{1-1} = +\frac{1}{2}\sqrt{\frac{3}{2\pi}}\; e^{-i\varphi}\sin\theta$$

The $e^{im\varphi}$ part is the only complex part

$$Y_{11}^{*} = -Y_{1-1} \qquad\qquad Y_{1-1}^{*} = -Y_{11}$$

The other equalities used are very basic ones.

8. LCAO EXPANSION OF TWO ELECTRON INTEGRALS

We write

$$\varphi_i = \sum_k \chi_k c_{ki}$$

$$\varphi_j = \sum_\ell \chi_\ell c_{\ell j}$$

$$\varphi_h = \sum_m \chi_m c_{mh}$$

$$\varphi_g = \sum_n \chi_n c_{ng}$$

The two-electron integrals of the previous section are expanded as

$$(\varphi_i(1)\varphi_j(1)|\varphi_h(2)\varphi_g(2)) = \sum_k \sum_\ell \sum_m \sum_n c_{ki}c_{\ell j}c_{mh}c_{ng}(\chi_k(1)\chi_\ell(1)|\chi_m(2)\chi_n(2))$$

where $(\chi_k(1)\chi_\ell(1)|\chi_m(2)\chi_n(2))$ is set to zero, whenever χ_k and χ_ℓ or χ_m and χ_n are located on different atoms: No Diatomic Differential Overlap.

a. One center integrals

For intravalence excitations, the necessary one-center terms are expressed in terms of Slater-Condon parameters F_k and G_k ('F sub k")

$Q1\ (A,A) = (1\ 1|1\ 1) = F_0(A) + F_2(A)$

$Q2\ (A,A) = (1\ 1|0\ 0) = F_0(A) - 2F_2(A)$

$Q3\ (A,A) = (p\ p|s\ s) = F_0(A)$

$Q4\ (A,A) = (0\ 0|0\ 0) = F_0(A) + 4F_2(A)$

$Q5\ (A,A) = (s\ s|s\ s) = F_0(A) = Q3(A,A)$

$Q6\ (A,A) = (1\ {-1}|{-1}\ 1) = 6\ G_2(A) = 6F_2(A)$

$Q7\ (A,A) = (1\ 0|0\ 1) = 3G_2(A) = 3F_2(A)$

$Q8\ (A,A) = (p\ s|s\ p) = G_1(A) = F_1(A)$

s and p orbital are assumed to have identical radial dependence, thus the

F_k's depend not on ℓ.

For extravalence excitations, the necessary integrals are (R and v stand for Rydberg and valence, respectively):

$Q1(A,A) = (1^R\ 1^R|1^v\ 1^v) = F_0(A) + F_2(A)$

$Q2(A,A) = (1^R\ 1^R|0^v\ 0^v) = F_0(A) - 2F_2(A)$

$Q3(A,A) = (1^R\ 1^R|s^v\ s^v) = F_0(A)$

$Q4(A,A) = (0^R\ 0^R|0^v\ 0^v) = F_0(A) + 4F_2(A)$

$Q5(A,A) = (1^R\ 1^v|1^v\ 1^R) = G_0(A) + G_2(A)$

$Q6(A,A) = (0^R\ 0^v|0^v\ 0^R) = G_0(A) + 4G_2(A)$

$Q7(A,A) = (p^R\ s^v|s^v\ p^R) = G_1(A)$

$Q8(A,A) = (s^R\ s^v|s^v\ s^R) = G_0(A)$

$Q9(A,A) = (1^R\ 0^v|0^v\ 1^R) = 3G_2(A)$

$Q10(A,A) = (1^R\ {-1}^v|{-1}^v\ 1^R) = 6G_2(A)$

$Q11(A,A) = (1^R\ {-1}^R|{-1}^v\ 1^v) = 6F_2(A)$

$Q12(A,A) = (1^R\ 0^R|0^v\ 1^v) = 3F_2(A)$

$Q13(A,A) = (1^R\ 1^v|0^v\ 0^R) = G_0 - 2G_2$

These formulas imply that one considers either

a) valence to valence excitations

$\pi \rightarrow \pi^*$ $\quad$ $\pi \rightarrow \sigma^*$ $\quad$ $\sigma \rightarrow \pi^*$ $\quad$ $\sigma \rightarrow \sigma^*$

or any part of these

b) valence to Rydberg

$\pi \rightarrow p_\pi$ $\quad$ $\pi \rightarrow p_\sigma$ $\quad$ $\sigma \rightarrow p_\pi$ $\quad$ $\sigma \rightarrow p_\sigma$

or any part of these

c) valence to Rydberg

$\pi \rightarrow s$ $\quad$ $\sigma \rightarrow s$

or one of these

but one must not consider either Rydberg/valence mixing or p_σ/s mixing of Rydberg orbitals.

For p-Rydberg excitation, one needs a total of four atomic parameters

F_o F_2 G_o G_2

for s-Rydberg excitation, one need a total of three atomic parameters

F_o G_o G_1

for valence excitation, one needs a total of three parameters

F_o F_1 F_2

Some of the calculated integrals (valence orbitals) (J. B. Mann, Los Alamos Scientific Laboratory, Report LA-3690) are listed below (kk):

Element	$\langle F_o \rangle^a$	G_1=F_1	F_2
H	137.2	-	-
Li	70.8	-	-
Be	75.4	-	-
B	96.2	20.0	1.67
C	121.1	24.9	2.10
N	145.6	29.7	2.52
O	169.9	34.4	2.93
F	194.0	39.1	3.34
Ne	218.1	43.8	3.75
Cl	117.5	25.5	2.14
Br	103.7	22.6	1.95
I	86.5	19.1	1.69
Ar	129.4	28.2	2.39
Kr	111.3	24.5	2.11
Xe	92.0	20.5	1.81
Zn	68.7	-	-
Cd	61.5	-	-
Hg	59.7	-	-

$^a\langle F_o \rangle = {}^1/_3 \{F_o(s,s) + F_o(p,p) + F_o(s,p)\}$ when all three are available.

b. Two center integrals

Three basic approximations were found to yield very similar results

a) Mataga-Nishimoto

$$(AA|BB) = \left(r_{AB} + \frac{2}{(AA|AA) + (BB|BB)}\right)^{-1}$$

b) Klopman

$$(AA|BB) = \left(r_{AB}^2 + \left(\frac{1}{2(AA|AA)} + \frac{1}{2(BB|BB)}\right)^2\right)^{-\frac{1}{2}}$$

c) Ohno

$$(AA|BB) = (r_{AB}^2 + 2/((AA|AA) + (BB|BB)))^{-\frac{1}{2}}$$

For no particular reason, the Ohno approximation was used.

Note: At the time of writing, it was obvious that certain of the Q-Matrices may not be approximated by any of these formulas, but that they should be considered as diagonal matrices.

c. Expansion formulas

This collection is fairly lengthy, but necessary in case errors should be found.

Valence excitations

$$C1 = \sum_A \sum_B CPE(A)^2 \cdot CP(B)^2 \cdot Q1(A,B)$$

$$\begin{aligned} C2 = \sum_A \sum_B CPE(A)^2 \cdot \{&CSP(B)^2 \cdot Q2(A,B) \\ &+ CSS(B)^2 \cdot Q3(A,B)\} \end{aligned}$$

$$\begin{aligned} C3 = \sum_A \sum_B CP(B)^2 \cdot \{&CSEP(A)^2 \cdot Q2(A,B) \\ &+ CSES(A)^2 \cdot Q3(A,B)\} \end{aligned}$$

$$\begin{aligned} C4 = \sum_A \sum_B\ & CSEP(A)^2 \cdot CSP(B)^2 \cdot Q4(A,B) \\ &+ \{CSEP(A)^2 \cdot CSS(B)^2 + CSES(A)^2 \cdot CSP(B)^2\} \\ &\qquad \cdot Q3(A,B) \\ &+ CSES(A)^2 \cdot CSS(B)^2 \cdot Q5(A,B) \\ &+ 4\,\{CSES(A)\ CSEP(A)\ CSS(B)\ CSP(B)\} \cdot Q8(A,B) \end{aligned}$$

$$K1 = \sum_{A}\sum_{B} \mathrm{CPE}(A)\ \mathrm{CP}(A)\ \mathrm{CP}(B)\ \mathrm{CPE}(B)\ Q1(A,B)$$

$$\begin{aligned}
K2 = \sum_{A}\sum_{B} & \mathrm{CSEP}(A)\ \mathrm{CSP}(A)\ \mathrm{CSP}(B)\ \mathrm{CSEP}(B)\ Q4(A,B) \\
& + Q8(A,B)\ \{\mathrm{CSES}(A)\ \mathrm{CSP}(A)\ \mathrm{CSP}(B)\ \mathrm{CSES}(B) \\
& \qquad + \mathrm{CSES}(A)\ \mathrm{CSP}(A)\ \mathrm{CSS}(B)\ \mathrm{CSEP}(B) \\
& \qquad + \mathrm{CSEP}(A)\ \mathrm{CSS}(A)\ \mathrm{CSP}(B)\ \mathrm{CSES}(B) \\
& \qquad + \mathrm{CSEP}(A)\ \mathrm{CSS}(A)\ \mathrm{CSS}(B)\ \mathrm{CSEP}(B)\} \\
& + Q3(A,B)\ \{\mathrm{CSEP}(A)\ \mathrm{CSP}(A)\ \mathrm{CSS}(B)\ \mathrm{CSES}(B) \\
& \qquad + \mathrm{CSES}(A)\ \mathrm{CSS}(A)\ \mathrm{CSP}(B)\ \mathrm{CSEP}(B)\} \\
& + Q5(A,B)\ .\ \mathrm{CSES}(A)\ .\ \mathrm{CSS}(A)\ .\ \mathrm{CSS}(B)\ \mathrm{CSES}(B)
\end{aligned}$$

$$L1 = \sum_{A}\sum_{B} \mathrm{CPE}(A)\ \mathrm{CP}(A)\ \mathrm{CP}(B)\ \mathrm{CPE}(B)\ .\ Q6(A,B)$$

$$\begin{aligned}
L2 = \sum_{A}\sum_{B} & \mathrm{CPE}(A)\ \mathrm{CSP}(A)\ \mathrm{CSP}(B)\ \mathrm{CPE}(B)\ Q7(A,B) \\
& + \mathrm{CPE}(A)\ \mathrm{CSS}(A)\ \mathrm{CSS}(B)\ \mathrm{CPE}(B)\ Q8(A,B)
\end{aligned}$$

$$\begin{aligned}
L3 = \sum_{A}\sum_{B} & \mathrm{CSEP}(A)\ \mathrm{CP}(A)\ \mathrm{CP}(B)\ \mathrm{CSEP}(B)\ Q7(A,B) \\
& + \mathrm{CSES}(A)\ \mathrm{CP}(A)\ \mathrm{CP}(B)\ \mathrm{CSES}(B)\ Q8\ (A,B)
\end{aligned}$$

$$M1 = \sum_{A}\sum_{B} \mathrm{CPE}(A)^2\ \mathrm{CP}(B)^2\ Q6(A,B)$$

$$\begin{aligned}
M2 = \sum_{A}\sum_{B} & \mathrm{CPE}(A)\ \mathrm{CSEP}(A)\ \mathrm{CSP}(B)\ \mathrm{CP}(B)\ Q7 \\
& + \mathrm{CPE}(A)\ \mathrm{CSES}(A)\ \mathrm{CSS}(B)\ \mathrm{CP}(B)\ Q8
\end{aligned}$$

$$\begin{aligned}
M3 = \sum_{A}\sum_{B} & \mathrm{CPE}(A)\ \mathrm{CSP}(A)\ \mathrm{CSEP}(B)\ \mathrm{CP}(B)\ Q7(A,B) \\
& + \mathrm{CPE}(A)\ \mathrm{CSS}(A)\ \mathrm{CSES}(B)\ \mathrm{CP}(B)\ Q8(A,B)
\end{aligned}$$

$$\begin{aligned}
M4 = \sum_{A}\sum_{B} & \mathrm{CPE}(A)\ \mathrm{CP}(A)\ \mathrm{CSP}(B)\ \mathrm{CSEP}(B)\ Q2(A,B) \\
& + \mathrm{CPE}(A)\ \mathrm{CP}(A)\ \mathrm{CSS}(B)\ \mathrm{CSES}(B)\ Q3(A,B)
\end{aligned}$$

Rydberg excitations

C1 as for valence

C2 as for valence

C3 as for valence

$$\begin{aligned} C4 = \sum_A \sum_B & \mathrm{CSEP}(A)^2\ \mathrm{CSP}(B)^2\ Q4(A,B) \\ & + Q3(A,B)\ \{\mathrm{CSES}(A)^2 .\ \mathrm{CSP}(B)^2 + \mathrm{CSEP}(A)\ .\ \mathrm{CSS}(B)^2 \\ & + \mathrm{CSES}(A)^2\ \mathrm{CSS}(B)^2\} \end{aligned}$$

$$K1 = \sum_A \sum_B \mathrm{CPE}(A)\ \mathrm{CP}(A)\ \mathrm{CP}(B)\ \mathrm{CPE}(B)\ Q5(A,B)$$

$$\begin{aligned} K2 = \sum_A \sum_B & \mathrm{CSEP}(A)\ \mathrm{CSP}(A)\ \mathrm{CSP}(B)\ \mathrm{CSEP}(B)\ .\ Q6(A,B) \\ & + \mathrm{CSEP}(A)\ \mathrm{CSS}(A)\ \mathrm{CSS}(B)\ \mathrm{CSEP}(B)\ Q7(A,B) \\ & + \mathrm{CSES}(A)\ \mathrm{CSP}(A)\ \mathrm{CSP}(B)\ \mathrm{CSES}(B)\ Q7(A,B) \\ & + \mathrm{CSES}(A)\ \mathrm{CSS}(A)\ \mathrm{CSS}(B)\ \mathrm{CSES}(B)\ Q8(A,B) \end{aligned}$$

$$L1 = \sum_A \sum_B \mathrm{CPE}(A)\ \mathrm{CP}(A)\ \mathrm{CP}(B)\ \mathrm{CPE}(B)\ Q10(A,B)$$

$$\begin{aligned} L2 = \sum_A \sum_B & \mathrm{CPE}(A)\ \mathrm{CSP}(A)\ \mathrm{CSP}(B)\ \mathrm{CPE}(B)\ Q9(A,B) \\ & + \mathrm{CPE}(A)\ \mathrm{CSS}(A)\ \mathrm{CSS}(B)\ \mathrm{CPE}(B)\ Q7(A,B) \end{aligned}$$

$$\begin{aligned} L3 = \sum_A \sum_B & \mathrm{CSEP}(A)\ \mathrm{CP}(A)\ \mathrm{CP}(B)\ \mathrm{CSEP}(B)\ Q9(A,B) \\ & + \mathrm{CSES}(A)\ \mathrm{CP}(A)\ \mathrm{CP}(B)\ \mathrm{CSES}(B)\ Q7(A,B) \end{aligned}$$

$$M1 = \sum_A \sum_B \mathrm{CPE}(A)^2\ \mathrm{CP}(B)^2\ Q11(A,B)$$

$$M2 = \sum_A \sum_B \mathrm{CPE}(A)\ \mathrm{CSEP}(A)\ \mathrm{CSP}(B)\ \mathrm{CP}(B)\ Q12(A,B)$$

$$M3 = \sum_A \sum_B \mathrm{CPE}(A)\ \mathrm{CSP}(A)\ \mathrm{CSEP}(B)\ \mathrm{CP}(B)\ Q9(A,B)$$

$$M4 = \sum_A \sum_B \mathrm{CPE}(A)\ \mathrm{CP}(A)\ \mathrm{CSP}(B)\ \mathrm{CSEP}(B)\ Q13(A,B)$$

Note: At the time of writing, it was not yet obvious whether the LCRO expansion is a useful one or not from a computational point of view.

g. Relative Transition Intensities

Intensity borrowing is calculated by transforming to a ${}^{2S+1}\Gamma$ basis and calculating the expansion coefficient of each CI-wavefunction in terms of the following singlet configurations:

$^1\Sigma^+(\sigma \rightarrow \sigma^*)$: $\frac{1}{\sqrt{2}}\{|22\rangle + |23\rangle\}$

$^1\Pi\ (\sigma \rightarrow \pi^*)$: $\frac{1}{\sqrt{2}}\{|11\rangle + |12\rangle\}$

$^1\Pi(\pi \rightarrow \sigma^*)$: $\frac{1}{\sqrt{2}}\{|9\rangle + |10\rangle\}$

$^1\Delta(\pi \rightarrow \pi^*)$: $\frac{1}{\sqrt{2}}\{|12\rangle + |3\rangle\}$

$^1\Sigma^+(\pi \rightarrow \pi^*)$: $\frac{1}{2}\{|14\rangle + |15\rangle + |16\rangle + |17\rangle\}$

$^1\Sigma^-(\pi \rightarrow \pi^*)$: $\frac{1}{2}\{|14\rangle + |15\rangle - |16\rangle - |17\rangle\}$

10. INPUT INSTRUCTION

1 card (20A4)	any text (title)
1 card (20I3)	List of parameters IP(i) which control the program.
IP(1) = 0	no spin orbit
= 1	include spin orbit
IP(2) = 0	no LCAO expansion used
= 1	LCAO expansion used
IP(3)	dummy
IP(4) = 0	read in effective spin-orbit-parameters
= 1	calculate those from atomic data; read in those
IP(5) = 0	read in molceular two electron integrals
= 1	use LCAO expansion, read in Slater Condon parameters
IP(6) = 0	no off-diagonal spin-orbit matrix element considered
= 1	off-diagonal spin-orbit matrix elements considered
IP(7) = 0	valence excitation
= 1	Rydberg excitation
IP(8-11) = 0	all configurations included
IP(8) = 1	no $\pi \rightarrow \pi^*$ excitation
IP(9) = 1	no $\pi \rightarrow \sigma^*$ excitation
IP(10) = 1	no $\sigma \rightarrow \pi^*$ excitation
IP(11) = 1	no $\sigma \rightarrow \sigma^*$ excitation
IP(12) = 1	must be 1 at the moment

If IP(2) = 1 read LCAO coefficients

1) σ-orbital (8F10.4) first all p_σ, then s
   (2 cards)

2) π-orbital (5F10.4) (1 card)
   blank card

3) π*-orbital (5F10.4) (1 card)

blank card

4) σ*-orbital (8F10.4) first all p_0, then s

2 cards

Five atoms allowed

Read orbital energies (6F10.4) (0,1,-1,1*,-1*,0*) (1 card)

If IP(1) = 1 and IP(4) = 0:

1 card read effective spin orbit parameters (4F10.4)

or If IP(1) = 1 and IP(4) = 1

read atomic spin orbit coupling constants (8F10.4) first for valence, then for Rydberg orbitals, if any (2 cards)

If IP(5) = 0 Read C1, C2, C3, C4, K1, K2, L1, L2, L3, M1, M2, M3, M4 (8F10.4) (2 cards)

or If IP(5) = 1 Read F_0, F_1, F_2, G_0, G_1, G_2 (6F10.4) one card per atom.

blank card.

(4F10.4) Read coordinates of atoms (2 - 5), only if IP(5) = 1 (1 card).

Continue with next molecule, or not.

ATOMIC CORRELATION LINES

by

Swapan Chattopadhyay

Graduate Student

The one-electron model of Rydberg states leads to the following expressions for the energies of atomic Rydberg transitions:

(i) For a group of atoms with isoelectronic valence shells and variable core charge, first-order perturbation theory yields the equation

$$T_{\underline{n}\ell}/Z^2 = c_{\underline{n}\ell}I_\mu/Z^2 + d_{\underline{n}\ell} + f_{\underline{n}\ell}(Z-1)/Z^2 \qquad \ldots (1)$$

where $T_{\underline{n}\ell}(I_\mu)$ is the term value; Z is the core charge; and the parameters $c_{\underline{n}\ell}$, $d_{\underline{n}\ell}$ and $f_{\underline{n}\ell}$ for a particular group of atoms depend on both $\underline{n}$ and ℓ (i.e., on the terminating Rydberg orbital).

(ii) For the same group of atoms, second-order perturbation theory yields the equation

$$T_{\underline{n}\ell}/Z^2 = g_{\underline{n}\ell}(I_\mu/Z^2)^2 + h_{\underline{n}\ell}(I_\mu/Z^2) + j_{\underline{n}\ell} + k_{\underline{n}\ell}(Z-1)/Z^2 \qquad \ldots (2)$$

where $g_{\underline{n}\ell}$, $h_{\underline{n}\ell}$, $j_{\underline{n}\ell}$ and $k_{\underline{n}\ell}$ are constants which characterize the particular Rydberg series and the particular group of atoms. The second-order model predicts that $|g_{\underline{n}\ell}/h_{\underline{n}\ell}| \ll 1$, $|k_{\underline{n}\ell}/j_{\underline{n}\ell}| \ll 1$, $h_{\underline{n}\ell} \cong c_{\underline{n}\ell}$ and $j_{\underline{n}\ell} \cong d_{\underline{n}\ell}$.

Thus, for constant Z and when second order effects are unimportant, one will expect a correlation between $T_{\underline{n}\ell}$ and I_μ of the form

$$T_{\underline{n}\ell}/Z^2 = a_{\underline{n}\ell}I_\mu/Z^2 + b_{\underline{n}\ell} \qquad \ldots (3)$$

where $a_{n\ell}$ and $b_{n\ell}$ are constants.

The present work describes the extent to which equations 1-3 apply to atomic systems.

Three groups of atoms have been studied. Group I consists of rare gases with electronic configuration ns^2np^6; Group II consists of neutral alkaline earth metals having electronic configuration $np^6(n+1)s^2$. Group III consists of ZnI, CdI, HgI, GaII, InII, TℓII, GeIII, SnIII, PbIII, AsIV, SbIV and BiIV and has the electronic configuration $nd^{10}(n+1)s^2$.

The least-square technique has been used to fit the experimental data to the equations. A comparison of the results obtained from the least-square fit technique brings up the following points:

(1) The standard deviation for the total fit is less for Equation 1 than for Equation 3. This is as it should be. However, the difference in standard deviations is physically insignificant relative to the breadth of $n\ell$ levels.

(2) The magnitudes of $f_{n\ell}$ and σ_f are comparable. Consequently, $f_{n\ell}$ is not a statistically good parameter.

(3) $|\sigma_d/d_{n\ell}| \gg |\sigma_b/b_{n\ell}|$. In other words, parameter $b_{n\ell}$ of Equation 3 is less uncertain than the corresponding parameter $d_{n\ell}$ of Equation 1.

(4) Application of Student's t-test for the parameter $f_{n\ell}$ indicates that t does not deviate appreciably from unity. Thus, Equation 1 does not provide a significantly better correlation than Equation 3.

Equations 2 and 3 have been applied to all three groups of atoms in order to decide whether or not a term quadratic in I_μ should be included in the correlation alogarithm. It appears that the inclusion of the quadratic term does not contribute significant improvement. The reasons for this conclusion are as follows:

(1) The standard deviation of the total fit as obtained by least-square fitting of the experimental data to Equation 2 does not show a significant change when compared to the corresponding quantity for Equation 1.

(2) The quantity $g_{\underline{n}\ell}$ is small relative to $h_{\underline{n}\ell}$ and $j_{\underline{n}\ell}$.

(3) The magnitudes of $g_{\underline{n}\ell}$ and σ_g are comparable.

(4) The quantities $h_{\underline{n}\ell}/\sigma_h$ and $g_{\underline{n}\ell}/\sigma_g$ of Equation 2 are consistently larger than the corresponding ratios $a_{\underline{n}\ell}/\sigma_a$ and $b_{\underline{n}\ell}/\sigma_b$ of Equation 1.

(5) Student's t-test for the parameter $g_{\underline{n}\ell}$ produces t-values which do not differ significantly from unity.

In those instances where Equation 2 yields a better fit, statistically speaking, this betterment may not be physically significant. Thus, Equation 3 provides an excellent fit to the atomic data and Equations 1 and 2, while providing somewhat better fits, do not do so in physically and/or statistically meaningful ways.

Finally, a similar linear relationship between configurational ionization energies and configurational excitation energies has been found.

The standard deviation of the total fit for any $\underline{n}\ell$ series decreases rapidly with increasing $\underline{n}$. The standard deviations are always largest for the 1ℓ series, when ℓ = s, p, d or f. The cause of the larger deviations of the 1ℓ series is the larger energetic spread of levels which, because of large exchange integrals $K(1\ell)$, are found for 1ℓ-configurations. The validity of the one-electron model depends on the assumed separability of core and Rydberg orbitals as measured by (i), small magnitudes of the exchange integral between core and Rydberg electron; and (ii), the fact that the spin-orbit coupling constants are very close to those for the cationic core. These conditions are least well satisfied by the 1ℓ series.

A concept of the average member of a group emerges from the discussion of the dependencies of $b_{n\ell}$ on n. The explicit expression is as follows

$$\bar{n}^*_{n\ell} = (R/\bar{T}_{n\ell})^{\frac{1}{2}} \qquad \ldots (4)$$

where $\bar{n}^*$ is the average effective principal quantum number and $\bar{T}_{n\ell}$ is the average term value. $\bar{T}_{n\ell}$ is related to the ionization potential of the average member by

$$\bar{T}_{n\ell} = a_{n\ell}\bar{I} + b_{n\ell}Z^2 \qquad \ldots (5)$$

Thus, $\bar{I}$ turns out to be a characteristic property of any group and its optimal value is such that the resulting values of $\bar{n}^*$ for fixed ℓ when plotting n against $(n + \ell)$ gives a slope of unity.

The dependencies of $a_{n\ell}$ on n have been studied. The values of $a_{n\ell}$ decrease with increasing n and the limiting value of $a_{n\ell}$ tends toward zero as n tends toward infinity. This behavior of $a_{n\ell}$ is completely in conformity with the requirements of the one-electron model.

The explicit relationship between $a_{n\ell}$ and n is expressed as follows

$$|a_{n\ell}| = P_\ell/(\bar{n}^*)^{\gamma_\ell}$$

where P_ℓ and γ_ℓ are constants.

Future Developments.

An extension of this correlative approach to Group 1A and Group 2A (singly charged atoms) as well as to each of the Groups 5A, 6A and 7A is planned. Computations of exchange integrals and spin-orbit coupling constants involving least-square procedures for systems (d^9,ns) (d,ns), (s,np), (s,nd), (s,nf), etc. have been initiated.

RYDBERG SPECTROSCOPY.
MAGNETIC CIRCULAR DICHROISM AND STARK EFFECT SPECTROSCOPY IN THE VACUUM ULTRAVIOLET

by

John D. Scott

Postdoctoral Research Associate

INTRODUCTION

Our knowledge of VUV excited electronic states of molecules has been limited to that which can be inferred from conventional absorption spectroscopy. In other words, the transition energy, the shape and structure of absorption bands, and the effects of condensing the phase and solvating the sample are the principal data available. It is surprising, at first glance anyway, that the investigation of other properties of these VUV excited states has not been pursued. However, when one considers the optical problems associated with this spectral region, the reasons for experimental limitations become apparent.

The recent developments of various optical components and electronic detection systems have made techniques such as the measurements of magnetic and electric-field effects feasible in the VUV. At the present time, two groups outside of this Laboratory are known to be making such measurements on gas-phase molecules -- one involved with MCD spectroscopy[1,2], the other with electrochromism (Stark) studies[3]. At the present time, we are investigating both effects, the primary emphasis being on VUV Rydberg transitions. Before discussing the experimental aspects of this research, a brief review of the present status of Rydberg information is presented.

PRESENT STATUS OF RYDBERG INFORMATION

The fact that the term values of complex atoms and ions are similar to the eigenvalues of a hydrogenic atom has provided the basis for a number of mathematical models of these multi-electron systems. In fact, the most widely used analytical expression for the term value T_n is

$$T_n = \frac{z_c^2 R}{(n-\delta)^2} \qquad \ldots (1)$$

The similarity of this expression to that for the hydrogenic atom, namely

$$E_n = \frac{z_c^2 R}{n^2} \qquad \ldots (2)$$

suggests that the former is perturbatively derivable from the latter. In Equations 1 and 2, the nuclear charge is z_c, $\underline{n}$ is an integer, $\underline{R}$ is the Rydberg constant, and $\underline{\delta}$ is the quantum defect. It is thought that the simple coulombic potential well, whose quantum mechanical solution is equation (2), leads, when perturbed by the presence of "core" electrons, to equation (1). The perturbations produced by the core electrons have been viewed variously -- from simple shielding effects to the more complex treatments which attempt to account for relativistic effects.

The formation of a molecule introduces a strong internal field with a symmetry which is determined by the nuclear distribution. Even so, the molecular term values can be represented by equation (1). Even the phenomena of moment coupling (i.e., spin-orbital, spin-spin, etc.) appear to revert smoothly from atom to molecule. The Rydberg absorption bands of linear and symmetric-top molecules which contain heavy atoms (e.g., Cl, Br and I)[4,5] are assigned in terms of spin-orbit coupling[6] and the molecular term values are often compared with those of some appropriate united atom. In fact, the use of the united-atom approach has led to correlative techniques that quantitatively relate atomic and molecular data[7].

One is made aware of the gaps that exist in present knowledge of Rydberg states upon reading the recent books[8,9] and reviews[10] devoted to the subject. In these publications, detailed descriptions of the present status of the theory, data, and interpretations are given. Briefly, the data on which Rydberg assignments are based consists of the following:

(1) <u>The energy of the transition with respect to the ionization potential of interest</u>. This energy is the molecular term value. The usual criteria may be formulated as questions:

(a) Does the term value fit into a mathematical progression of values which differ by the integer <u>n</u> and which have a limit of zero?

(b) Does the term value lie in that rather broad region in which empirical considerations dictate it should?

(2) <u>The intensity and shape of the band in question</u>. The relative intensities of the members of a particular Rydberg series are expected to diminish rapidly with increasing <u>n</u>. This is not a quantitative criterion: The presence of many bands in the higher-energy region makes the determination of intensities, to say the least, difficult. The shape of the bands in photoelectron spectra (PES) can be helpful in assigning the initial members of Rydberg series since the shapes of PES bands and corresponding Rydberg bands are sometimes strikingly similar.

(3) The effect of pressure. Since Rydberg orbitals are large, Rydberg states are "big-orbit states". As such, they are sensitive to environment. Therefore a primary criterion in assigning a band as "Rydberg" is the rapidly increasing diffuseness of the band with increasing pressure[11].

The existing data set is very limited. It would be of fundamental importance to add further criteria to those listed above. Also, the determination of various physical properties of Rydberg states would enable one to test and/or develop models of Rydberg states and, therefore, cationic molecular cores.

OUTLINE OF RESEARCH PROGRAM

The general philosophy of the research involves the perturbation of molecules with external fiels and the determination of the effects of these perturbations. The nature of this study is two-fold:

(1) The study of the magnetic circular dichroism (MCD) spectra of gas-phase compounds in the VUV spectral region, with particular emphasis on bands thought to originate from Rydberg transitions, and

(2) The study of the effects of strong electric fields on Rydberg bands.

MCD SPECTROSCOPY.

In principle, the MCD spectrum is the difference in the absorption of left and right circularly polarized radiation by a compound which is situated in an external magnetic field that is parallel to the propagation vector of the radiation. In practice, this determination is usually carried-out by alternately producing right and left circularly polarized light at a given frequency and determining the degree to which the transmitted radiation is modulated at this frequency. There are several excellent reviews[12,13,14] concerning the basics of MCD spectroscopy. The following is a qualitative description of the effects involved.

There are three independent effects produced by the field, all of them proportional to the first power of the field strength.

(1) The first of these effects is observed for molecules which possess degenerate states. The diatomic molecule serves as an example. In the linear molecule, excitation to a degenerate state (i.e., $\Lambda > 0$) can be accomplished by either left or right circularly polarized radiation; however, the projection of the angular momentum vector on the internuclear axis will be equal in magnitude but opposite in sign with respect to the propagation vector for the two different polarizations. Thus, the application of the magnetic field removes the degeneracy.

The shape of the MCD band is the derivative with respect to energy of the corresponding absorption band and is scaled by the magnetic moment of the excited state. Since this moment can be related to Λ, determination of the MCD spectrum leads to a measure of this quantum number and, hence, to the assignment of the state.

(2) The second effect is caused by the magnetic-field induced mixing of the ground and excited states with each other and with other states. The result of this mixing is an overall increase or decrease in band intensity and the effect is, therefore, proportional to absorbance. From an analysis of this effect one can infer the extent of configuration mixing brought about by the spin-orbit Hamiltonian. This information is of value in the study of band components which are spin-orbitally allowed.

(3) The third effect occurs for molecules that have non-zero magnetic moments in their ground state. Since the majority of molecules to be studied have closed-shell ground states, this effect is of little importance. Briefly, it results from a preferential orientation of the ground state molecules and, therefore, produces an overall intensity change. It is directly proportional to the absorbance and inversely proportional to temperature.

- - - - - - - - - - -

The utility of MCD spectroscopy follows from items 1, 2 and 3, above. The value of the projection of the angular momentum on the inter-nuclear axis may be determined, thereby establishing the symmetry of the excited state. In addition, spin-orbital interactions may be inferred and measured. If analogous parameters were available for the corresponding united atom, a first approximation to the nature of the molecular states might be possible.

ELECTRIC-FIELD EFFECTS.

These effects are concerned with the change of shape of molecular absorption bands produced by an external electric field. In practice, the effects are measured by applying an alternating electric field perpendicular to the propagation vector of a beam of linearly polarized radiation. That portion of the transmitted radiation that is modulated at the frequency of the alternating external field is then determined.

For moderate field strengths (up to ca. 2.5×10^5 volts cm^{-1}), the effect is dependent on the square of the field strength. A number of papers[15,16,17] deal with the theoretical and experimental aspects of this field. The following is a brief discussion of the effects encountered. These phenomena are:

---If the molecule under investigation has a ground-state dipole moment, there is a preferred orientation of the sample in the electric field. This gives rise to an overall increase or decrease of intensity. The effect is directly proportional to the absorbance and the square of the dipole moment and is inversely proportional to the square of the temperature.

---A second effect, also proportional to absorbance, results from the electric field mixings of various excited states with the ground state and the particular excited state in question. A small part of this mixing is orientation dependent and is proportional to both the permanent dipole moment and the first energy derivative of the absorbance.

---Changes in the polarizability between the ground and excited states account for an effect that is also first derivative dependent.

---An important effect is caused by the difference in permanent dipole moment between the ground and excited states. This difference is expressed as both a first derivative (absorbance) and a second derivative.

The molecular parameters that can be determined from the electric field study are:

(a) The orientation of the transition moment with respect to the permanent dipole moment of the ground state. Therefore, a well-supported inference of the electronic symmetry of the excited state may be made.

(b) The difference between the permanent dipole moments of the ground and excited states. This information might provide a fairly sensitive probe of the electron-transfer character of the transition.

(c) The change in electric polarizability upon excitation. This change, when compared with that of the analogous transition in the corresponding inert gas should aid in the characterization of the excited state.

PRESENT STATUS OF EXPERIMENTAL WORK

The MCD data obtained in this Laboratory for methyl iodide is shown in Figure 1. This band has been assigned to the singlet (Λ=1) first s Rydberg transition[3]. The corresponding state would be doubly degenerate and would possess a magnetic moment. The MCD spectrum validates this assignment.

More important than the above mentioned proof of the degenerate nature of an electronic state is the fact that this MCD spectrum proves that this Laboratory is capable of doing MCD in the vacuum ultraviolet. The data gathering and analyzing system allows a direct analog output of the MCD spectrum [i.e., $(I_t^+ - I_t^-)/I_t$, where I_t is the transmitted radiation and the superscripts (+) and (-) are for right and left circularly polarized radiation, respectively]; an output of the log of the transmitted radiation for measurement of absorbance; the first and second derivatives and the integral with respect to wavelength of absorbance and of $(I_t^+ - I_t^-)/I_t$; and an output of wavenumber so that plots of the data may be made on an energy scale. Schematic diagrams of the electronics that handle these different tasks are given in Figures 2-5.

Figure 1. Absorbance (•) and MCD (+) Spectra of the 1830Å Band of Methyl Iodide.

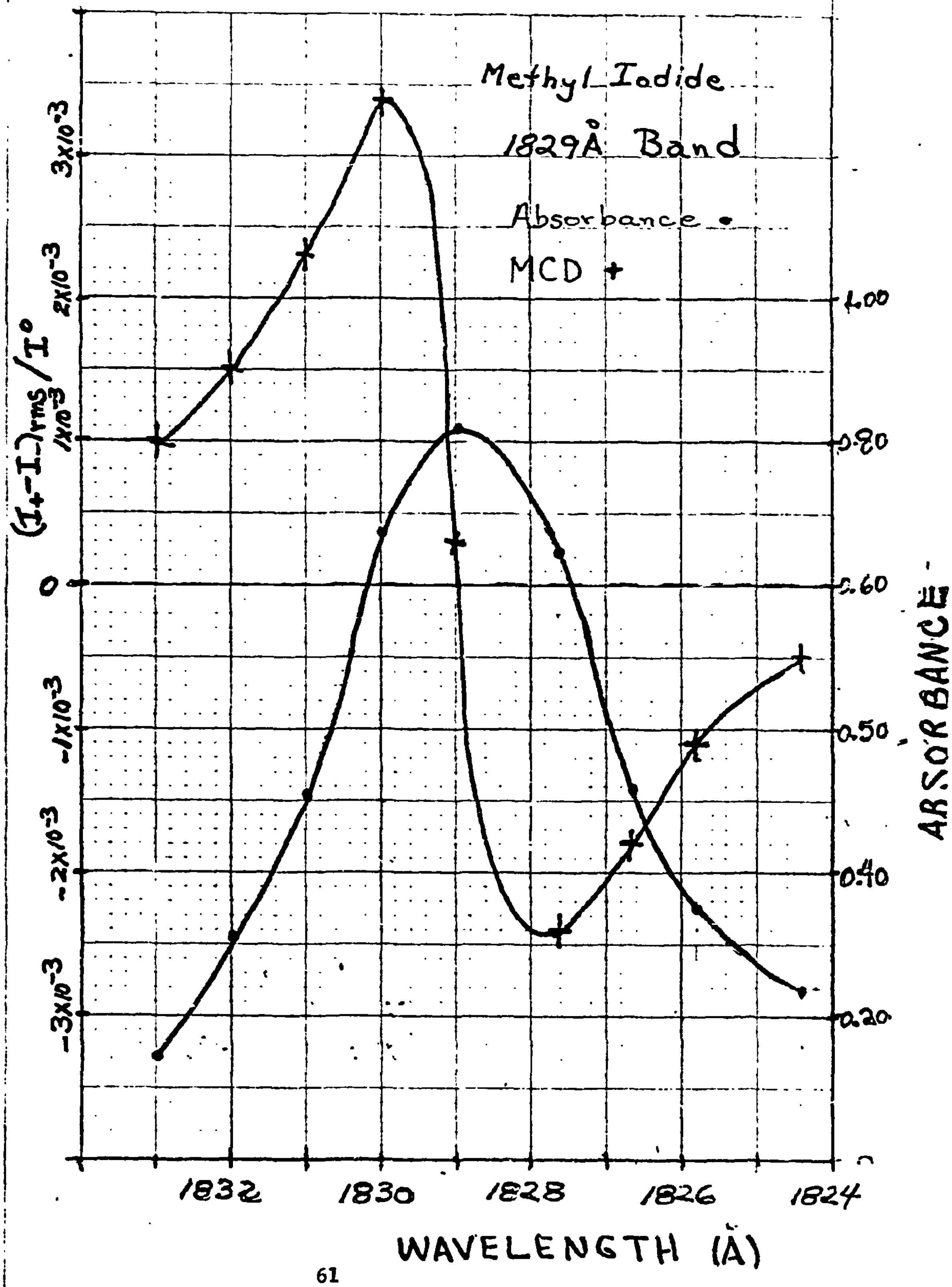

Methyl Iodide
1829Å Band
Absorbance •
MCD +
$(I_+ - I_-)_{rms}/I^0$
3x10⁻³
2x10⁻³
1x10⁻³
0
-1x10⁻³
-2x10⁻³
-3x10⁻³
1.00
0.80
0.60
0.50
0.40
0.20
ABSORBANCE
1832
1830
1828
1826
1824
WAVELENGTH (Å)

Figure 2. Schematic of Signal Detection System.

$h\nu$ = monochromatic radiation

P = polarizing prism

M = photoelastic modulator

S = sample cell

H = magnet

PMT = photomultiplier tube

MPS = modulator power supply (produces voltage for stress of photoelastic modulator at its resonant frequency f_m)

HV = high voltage power supply for PMT. Programed by current to maintain a constant output signal.

E = operational amplifier of electrometer quality, also responsive to high frequency of photoelastic modulator.

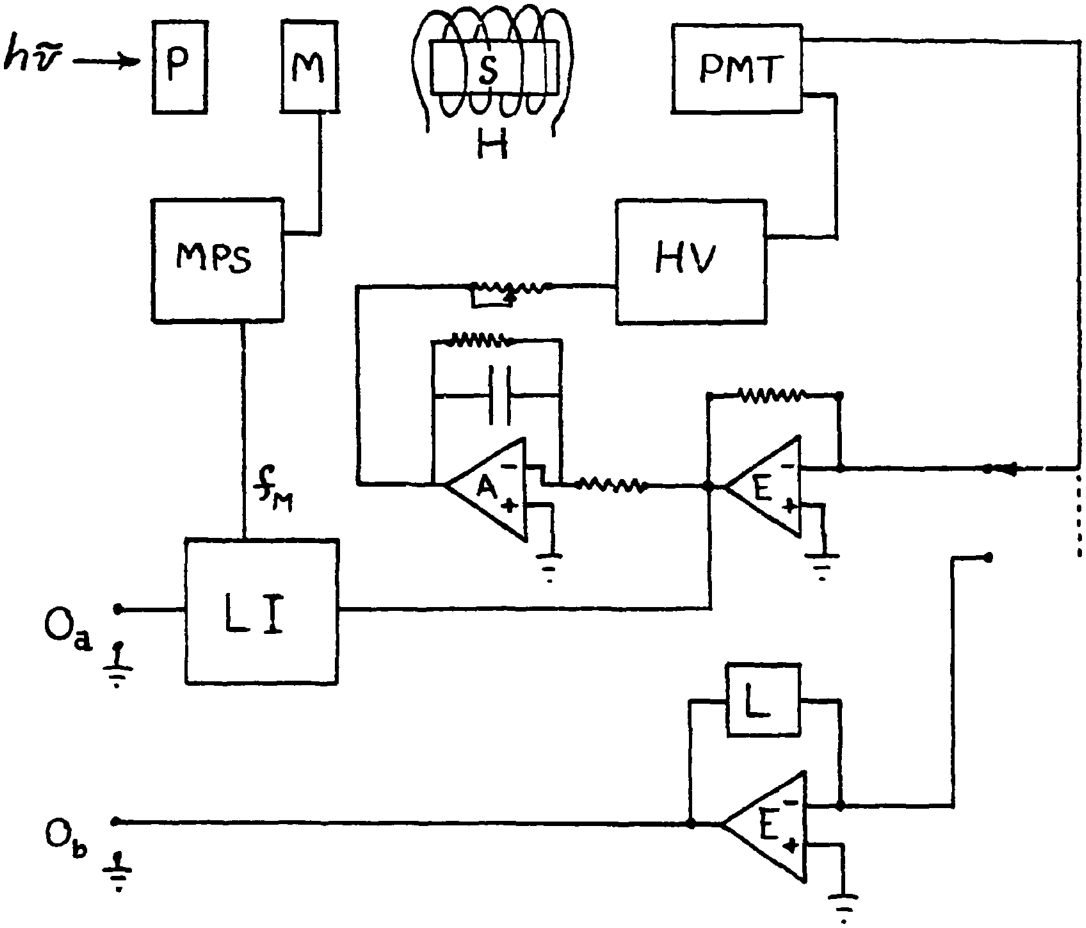
A = negative-unity gain amplifier

LI = lock-in amplifier

L = logarithmic element

0_a = output that is proportional to $(I_t^+ - I_t^-)/I_t$

0_b = output that is proportional to $\log I_t$



$h\tilde{\nu}$
P
M
S
H
PMT
MPS
HV
A
E
f_M
LI
O_a
L
E
O_b

Figure 3. Schematic of Wavenumber Generator.

P = adjustable D.C. voltage supply (low output impedance, ($< 75\Omega$) that produces V_p.

R_λ = resistor series that is driven by monochromator and is proportional to wavelength.

R_f = fixed feed-back resistance.

O_c = $-V_p R_f/R_\lambda$, which is proportional to wavenumber.

O_d = $V_p R_f/R_\lambda$ + off-set voltage.

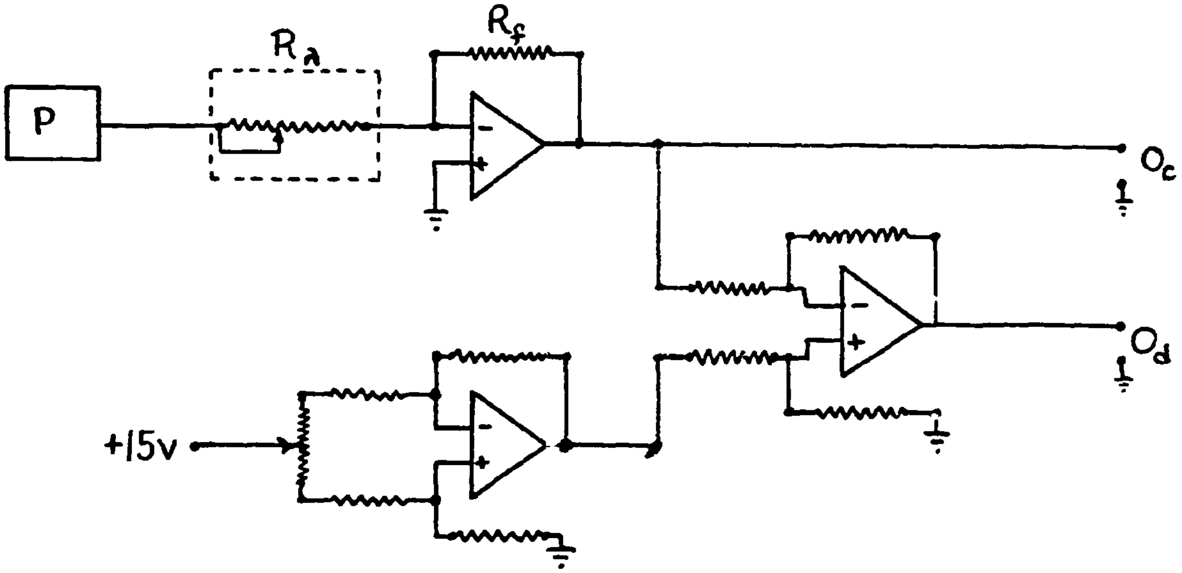

R_f
R_a
P
O_c
O_d
+15v

Figure 4. Schematic of Signal Processor.

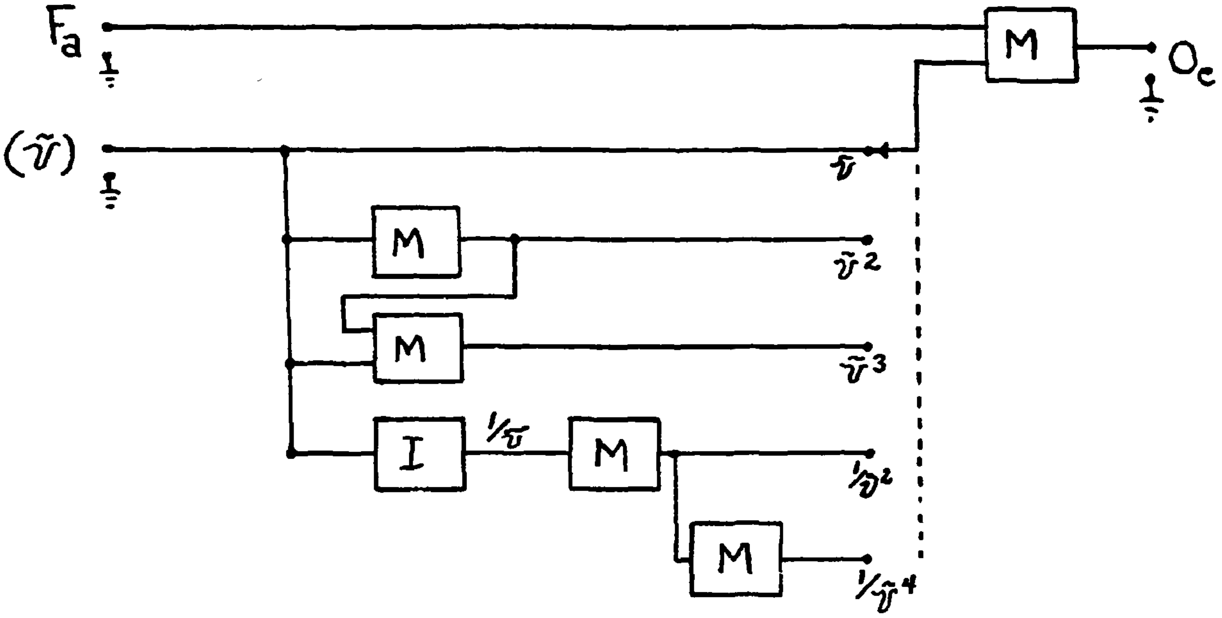
M = multiplier

I = invertor

F_a = input signal, usually O_a, O_b (see Figure 2), O_f, or O_g (Figure 5).

$(\tilde{\nu})$ = signal that is proportional to spectral energy $\tilde{\nu}$, this is O_c (see Figure 3).

$O_e = F_a \cdot (\tilde{\nu})^n$, where n = -4, -2, 1, 2 or 3.



F_a
O_c
$(\tilde{v})$
M
M
M
I
$1/\tilde{v}$
M
M
$\tilde{v}$
$\tilde{v}^2$
$\tilde{v}^3$
$1/\tilde{v}^2$
$1/\tilde{v}^4$

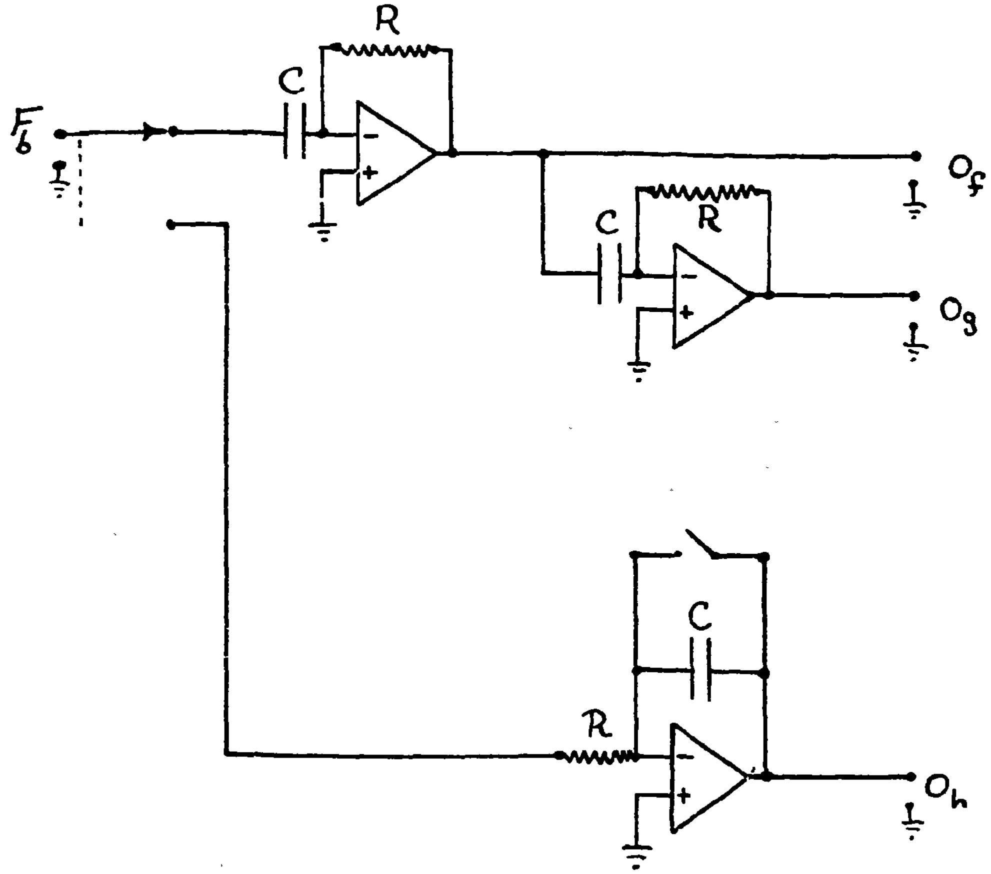
Figure 5. Differentiator-and-Integrator Schematic.

F_b = input signal that varies in time (t), usually O_b(Figure 2).

$O_f = -\frac{RCdF_b}{dt}$; therefore, after transformation to λ utilizing $\underline{S}$ the scan speed in Å/sec, $\frac{dF_b}{d\lambda} = -\frac{O_f}{RCS}$

$O_g = (RC)^2 \frac{d^2F_b}{dt^2}$; therefore, $\frac{d^2A}{d\lambda^2} = \frac{O_g}{(RCS)^2}$

$O_h = -\frac{1}{RC} \int F_b dt$; therefore, $\int F_b d\lambda = -SRCO_h$


R
C
F_b
O_f
C
R
O_g
C
R
O_h

The status of the electrochromism instrumentation is that the optics, being the same as for the MCD, are operational and that the Stark cell is in the final stage of construction. The data processing electronics are the same as for the MCD work. The high voltage power supply is also in working order. (See Reference 3 for a description of the experimental apparatus).

In both the MCD and electrochromism experiments the method of moment analysis will be utilized when possible. The following is a brief description of this method and the technique that will be utilized in this Laboratory to accomplish this analysis. The data can be fitted to an equation of the form

$$F(\tilde{\nu}) = c_1 A(\tilde{\nu}) + c_2\left(\frac{dA(\tilde{\nu})}{d\tilde{\nu}} - \frac{A(\tilde{\nu})}{\tilde{\nu}}\right) + c_3\left(\frac{d^2A(\tilde{\nu})}{d\tilde{\nu}^2} - \frac{2}{\tilde{\nu}}\frac{dA(\tilde{\nu})}{d\tilde{\nu}} + \frac{2}{\tilde{\nu}^2}A(\tilde{\nu})\right) \qquad \ldots (3)$$

where $F(\tilde{\nu})$ is the MCD or electrochromism effect at energy $\tilde{\nu}$, $A(\tilde{\nu})$ is the zero-field absorbance at $\tilde{\nu}$, and c_1, c_2, and c_3 are coefficients that are intrinsic to the molecule under investigation. (For MCD, c_3 is equal to zero). For an isolated absorption band the following integrals may be measured (All integrations are over the total absorption band).

$$M_o \equiv \int \frac{A(\tilde{\nu})}{\tilde{\nu}}\, d\tilde{\nu} \qquad \ldots (4)$$

$$M_1 \equiv \int A(\tilde{\nu})\, d\tilde{\nu} \qquad \ldots (5)$$

$$M_2 \equiv \int \tilde{\nu} A(\tilde{\nu})\, d\tilde{\nu} \qquad \ldots (6)$$

$$\int \frac{1}{\tilde{\nu}}\left(\frac{dA(\tilde{\nu})}{d\tilde{\nu}} - \frac{A(\tilde{\nu})}{\tilde{\nu}}\right) d\tilde{\nu} = 0 \qquad \ldots (7)$$

$$\int \left(\frac{dA(\tilde{\nu})}{d\tilde{\nu}} - \frac{A(\tilde{\nu})}{\tilde{\nu}} \right) d\tilde{\nu} = -M_o \qquad \ldots (8)$$

$$\int \tilde{\nu} \left(\frac{dA(\tilde{\nu})}{d\tilde{\nu}} - \frac{A(\tilde{\nu})}{\tilde{\nu}} \right) d\tilde{\nu} = -2M_1 \qquad \ldots (9)$$

$$\int \frac{1}{\tilde{\nu}} \left(\frac{d^2A(\tilde{\nu})}{d\tilde{\nu}^2} - \frac{2}{\tilde{\nu}} \frac{dA(\tilde{\nu})}{d\tilde{\nu}} + \frac{2}{\tilde{\nu}^2} A(\tilde{\nu}) \right) d\tilde{\nu} = 0 \qquad \ldots (10)$$

$$\int \left(\frac{d^2A(\tilde{\nu})}{d\tilde{\nu}^2} - \frac{2}{\tilde{\nu}} \frac{dA}{d\tilde{\nu}} + \frac{2}{\tilde{\nu}^2} A(\tilde{\nu}) \right) d\tilde{\nu} = 0 \qquad \ldots (11)$$

$$\int \tilde{\nu} \left(\frac{d^2A(\tilde{\nu})}{d\tilde{\nu}^2} - \frac{2}{\tilde{\nu}} \frac{dA}{d\tilde{\nu}} + \frac{2}{\tilde{\nu}^2} A(\tilde{\nu}) \right) d\tilde{\nu} = 2M_o \qquad \ldots (12)$$

Integration of $F(\tilde{\nu})$ in a manner analogous to the integration of $A(\tilde{\nu})$ in equations 4-6 yields a set of equations

$$\int \frac{F(\tilde{\nu})}{\tilde{\nu}} d\tilde{\nu} = c_1 M_o \qquad \ldots (13)$$

$$\int F(\tilde{\nu}) d\tilde{\nu} = c_1 M_1 - c_2 M_o \qquad \ldots (14)$$

$$\int \tilde{\nu} F(\tilde{\nu}) d\tilde{\nu} = c_1 M_2 - 2c_2 M_1 + 2c_3 M_o \qquad \ldots (15)$$

Simultaneous solution of these three equations yields c_1, c_2 and c_3, the coefficients that contain the molecular information. The values of the six integrals necessary for the analysis will be obtained electronically -- directly from the output signal of the photomultiplier tube. In this way no data transposition error can be introduced.

PRESENT STATUS OF THEORETICAL WORK

The current status of the interpretive abilities of this Laboratory can be described as follows:

---Both the apparatus and ability are present for the calculation of parameters by standard molecular orbital techniques such as simple Huckel, extended Huckel, and a number of CNDO versions. An IBM 360-65 computing system is available for these calculations.

---Two perturbative models for Rydberg states are currently in development. Both models are based on the electrostatic perturbation of spherically symmetric atoms by the presence of the additional nuclei of the same molecule. By choosing appropriate basis sets, various molecular properties can be calculated. These include electric and magnetic transition moments and permanent dipole moments. The resulting perturbation wave functions should answer many questions dealing with the electron distribution in these states. This research will enrich the data set for Rydbergs and will provide "checks" of the theoretical results that the energy and intensity data do not provide.

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THE LOWEST-ENERGY RYDBERG TRANSITIONS
OF s-TYPE IN THE ALKYL HALIDES

by

Sidney Felps
Postdoctoral Research Associate

An analysis of the absorption spectra associated with transition to the lowest-energy s-type Rydberg states of CH_3X and CD_3X ($X = Cl$, Br and I) has been presented previously[1]. The spectra of the bromides and iodides were shown to consist, individually, of four electronic origins of s-excitation type. However, the spectra of the chlorides were amenable to a number of different vibronic analyses, none of them unique. In order of increasing energy, these electronic origins of the alkyl halides are associated with the transition from the A_1 ground state to (1) and E state, (2) and E state, (3) and A_1 and A_2 state which are nearly degenerate and (4) and E state. The relative separations of these states are a function of the degree of spin-orbit interaction and can be expressed explicitly[2,3] in terms of a single electronic parameter K and a single spin-orbit parameter ξ.

Chapter III of Reference 4 contains a discussion of the energy separation of the levels which arise from this s-type Rydberg excitation in terms of the pertinent spin-orbit and exchange interaction parameters. The methyl halide data was used together with the available data for the hydrogen halides, cyanogen halides and some normal alkyl iodides. The energy separations between the origin bands of these monohalides are accurately predicted by this intermediate spin-orbit coupling scheme and leads to our reassignment of the methyl chloride spectrum.

I have measured the absorption spectra associated with transitions to the lowest-energy s-types Rydberg states of several normal-alkyl halides. The room temperature spectra of some of these are presented in Figures 1-12 along with the spectra of the methyl halides. A vibrational analysis of these spectra leads to an assignment of electronic origins and these are denoted in the figures. As is evident, the origin bands have undergone splittings which are most reasonably attributed to a lowering of point group symmetry from C_{3v} to C_s upon lengthening the alkyl chain.

In ethyl iodide, states 1, 2 and 4 are split. This is as expected since these are all E states and should split upon lowering of the point group symmetry. It should be noted that similar splittings are observed for n-propyl iodide. In the higher alkyl bromides states 1 and 2 are not apparently split though this may be due to the lack of spectral resolution.

The higher alkyl chlorides behave similarly. These spectra would seem to confirm our reassignment of the methyl chloride spectrum. To further support these assignments, I am now obtaining the integrated intensities associated with the transitions to states 2 and 4. These intensity ratios should be in agreement with that predicted using Mulliken's expression and the observed energy separations of states 2 and 4 of the alkyl halides.

I also plan to evaluate the spin-orbit integral ξ and the exchange integral K for the higher alkyl halides from the energy level separations which have been obtained. These results will be included with the molecular data of Reference 4 for publication in the near future.

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FIGURE CAPTIONS

Figure 1. The absorption spectrum of methyl iodide vapor, ~90μ pressure.

Figure 2. The longer wavelength absorption spectrum of ethyl iodide vapor, ~85μ pressure.

Figure 3. The shorter wavelength absorption spectrum of ethyl iodide vapor, ~85μ pressure.

Figure 4. The longer wavelength absorption spectrum of ethyl iodide vapor, ~700μ pressure.

Figure 5. The shorter wavelength absorption spectrum of ethyl iodide vapor, ~700μ pressure.

Figure 6. The absorption spectrum of methyl bromide vapor at various pressures: (a), ~90μ; (b) ~165μ; (c) ~300μ; (d) ~2mm.

Figure 7. The aborption spectrum of ethyl bromide vapor, ~135μ pressure.

Figure 8. The absorption spectrum of n-propyl bromide vapor, ~200μ pressure.

Figure 9. The absorption spectrum of methyl chloride vapor, ~330μ pressure.

Figure 10. The absorption spectrum of ethyl chloride vapor, ~600μ pressure.

Figure 11. The absorption spectrum of n-propyl chloride vapor, ~1100μ pressure.

Figure 12. The absorption spectrum of n-butyl chloride vapor, ~1100μ pressure.

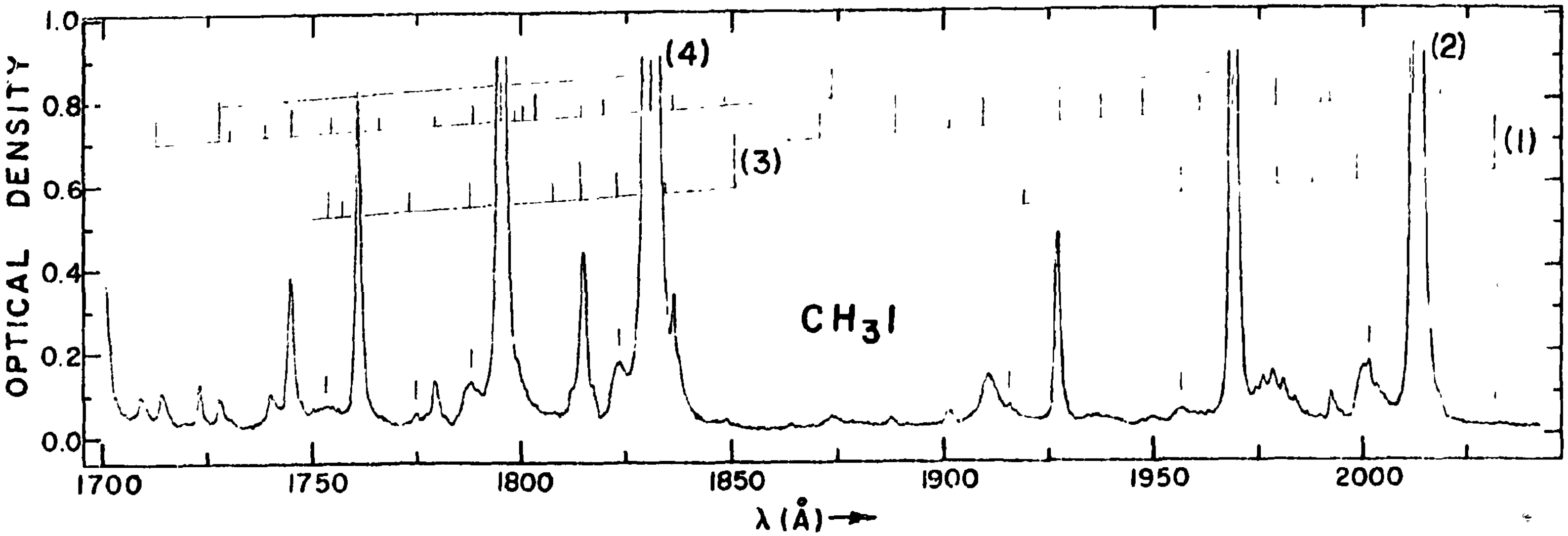

OPTICAL DENSITY
1.0
0.8
0.6
0.4
0.2
0.0
1700
1750
1800
1850
1900
1950
2000
λ (Å) →
CH₃I
(1)
(2)
(3)
(4)

Figure 1

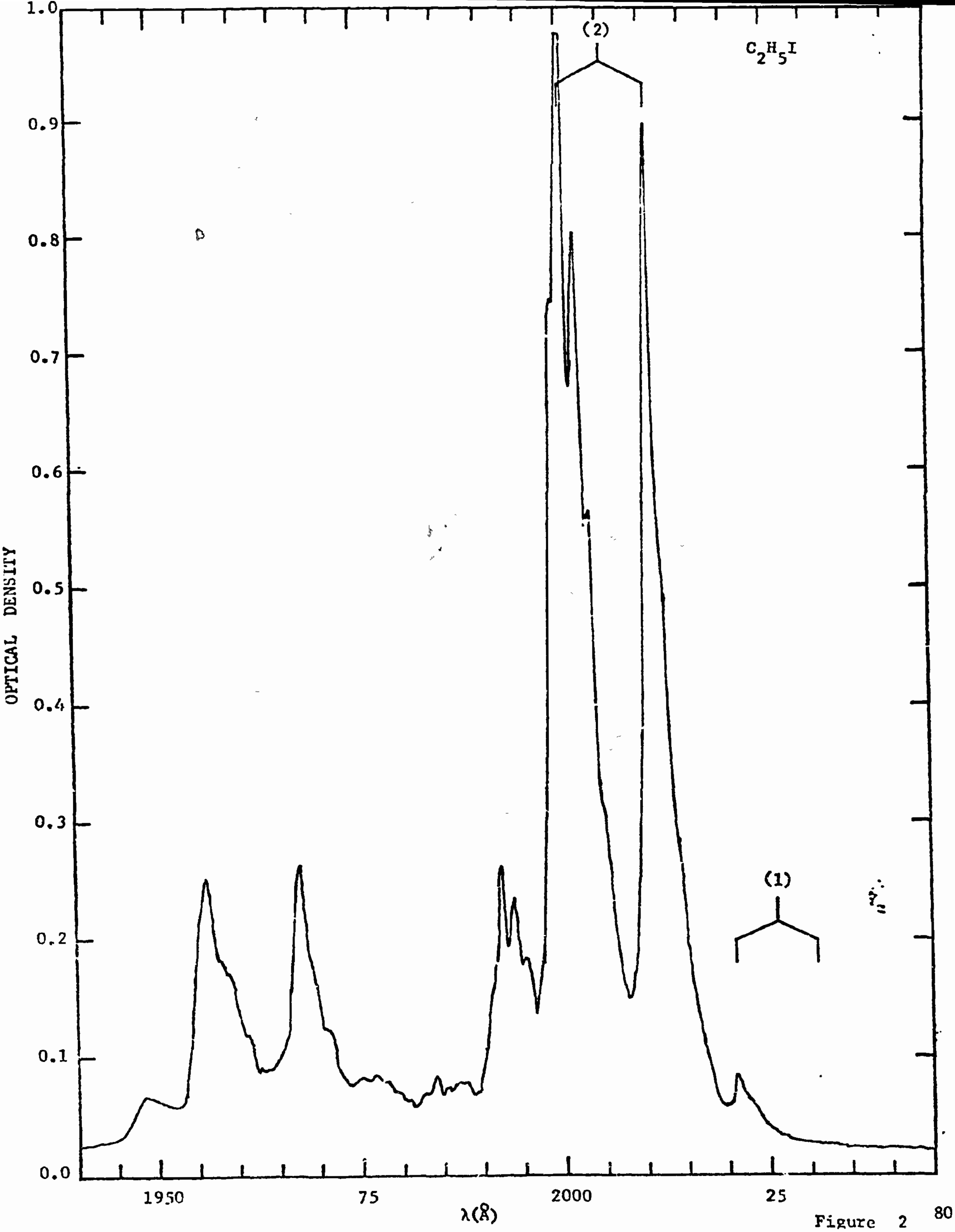
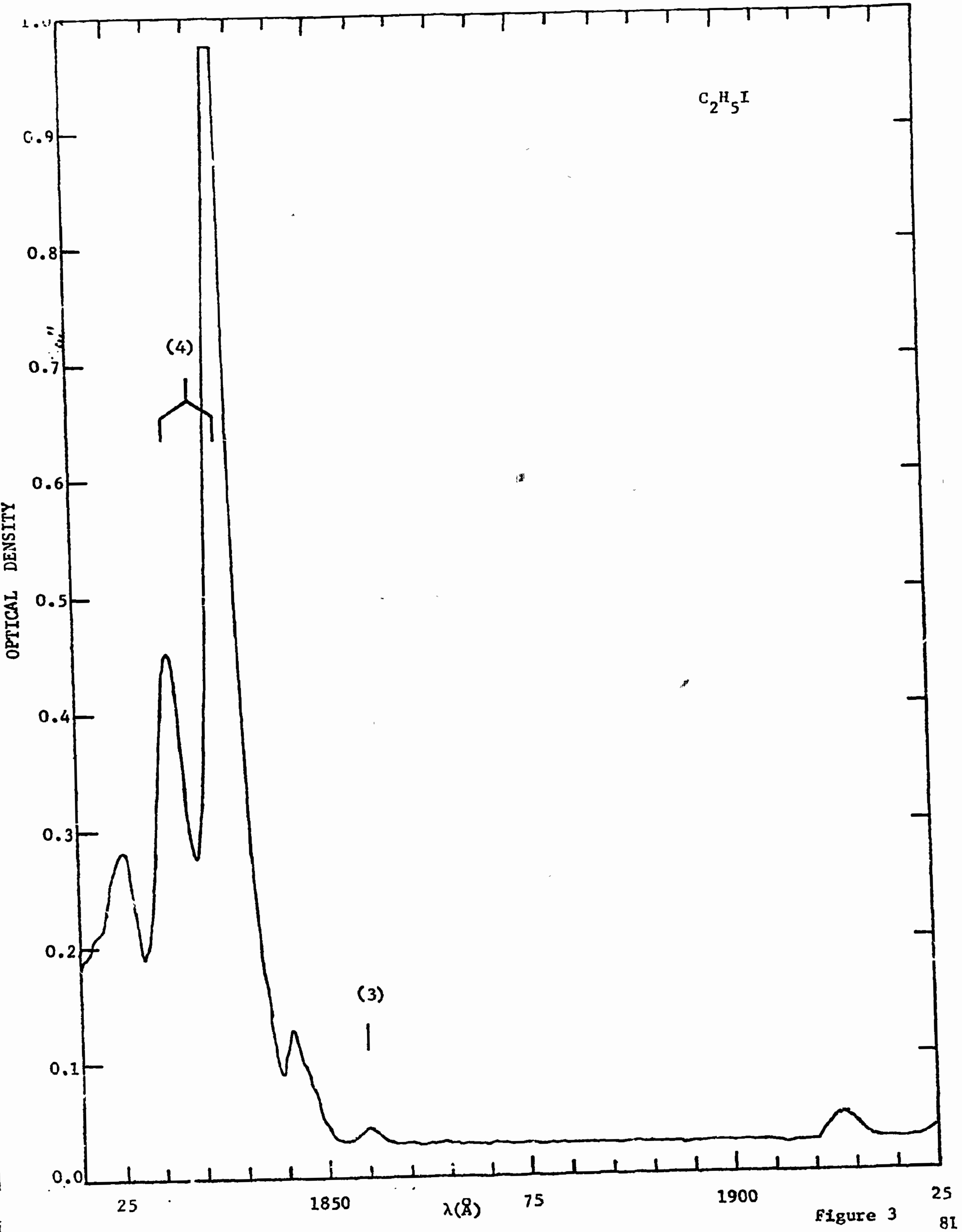

C$_2$H$_5$I
(2)
(1)
OPTICAL DENSITY
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1950
75
2000
25
λ(Å)

Figure 2



C$_2$H$_5$I
OPTICAL DENSITY
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
(4)
(3)
25
1850
λ(Å)
75
1900
25

Figure 3

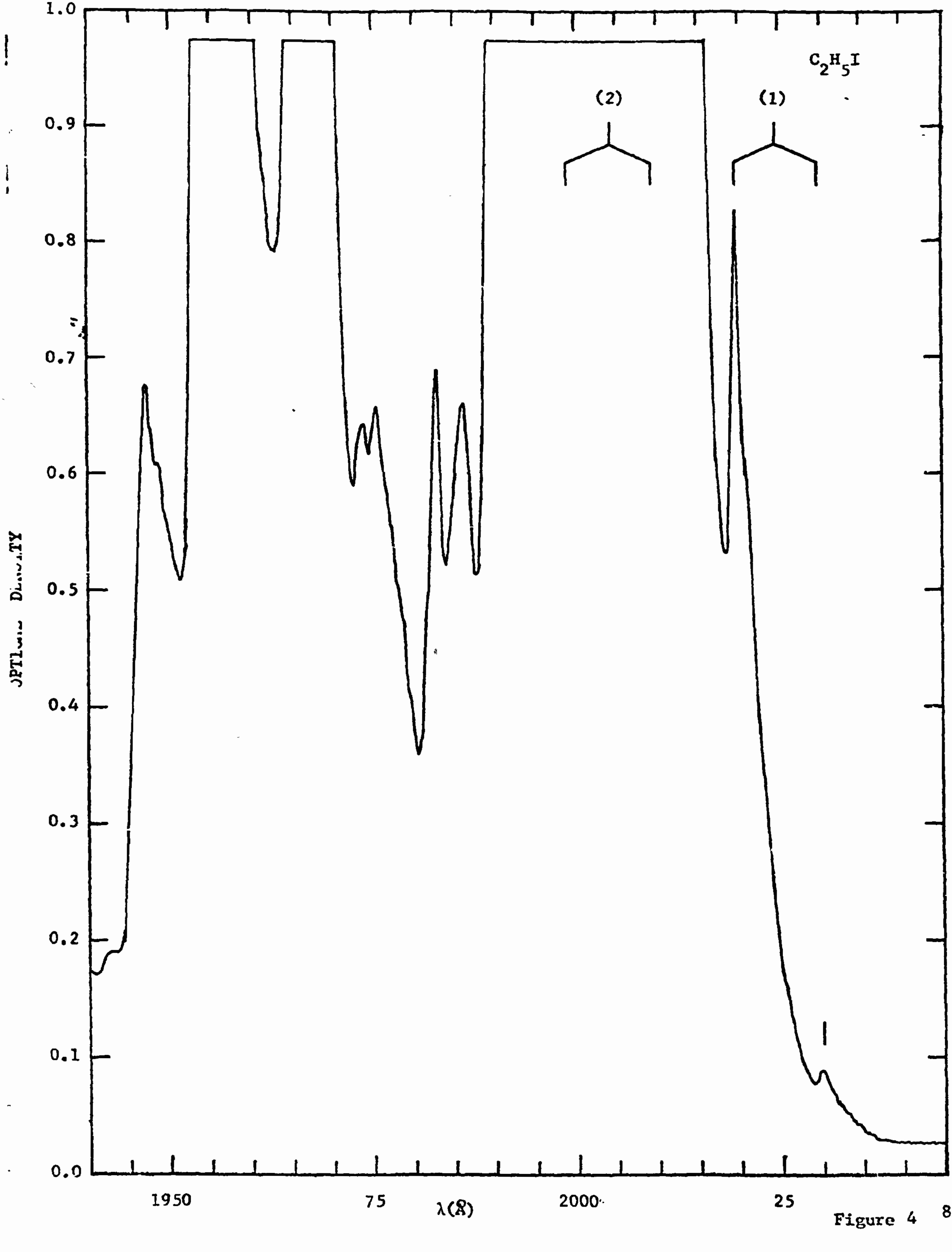
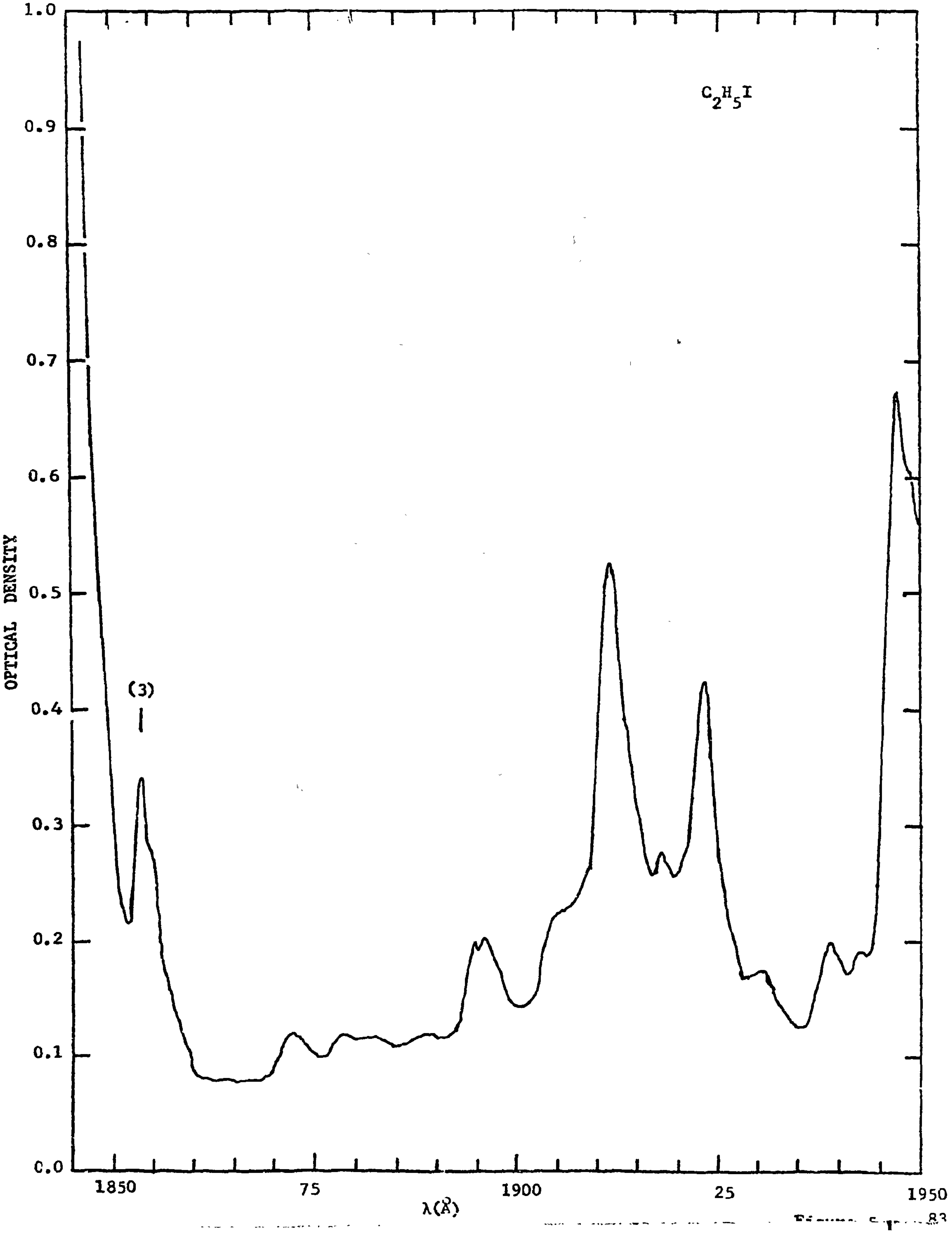

1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
OPTICAL DENSITY
1950
75
λ(Å)
2000
25
C_2H_5I
(2)
(1)

Figure 4


1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
OPTICAL DENSITY
C_2H_5I
(3)
1850
75
1900
25
1950
λ(Å)

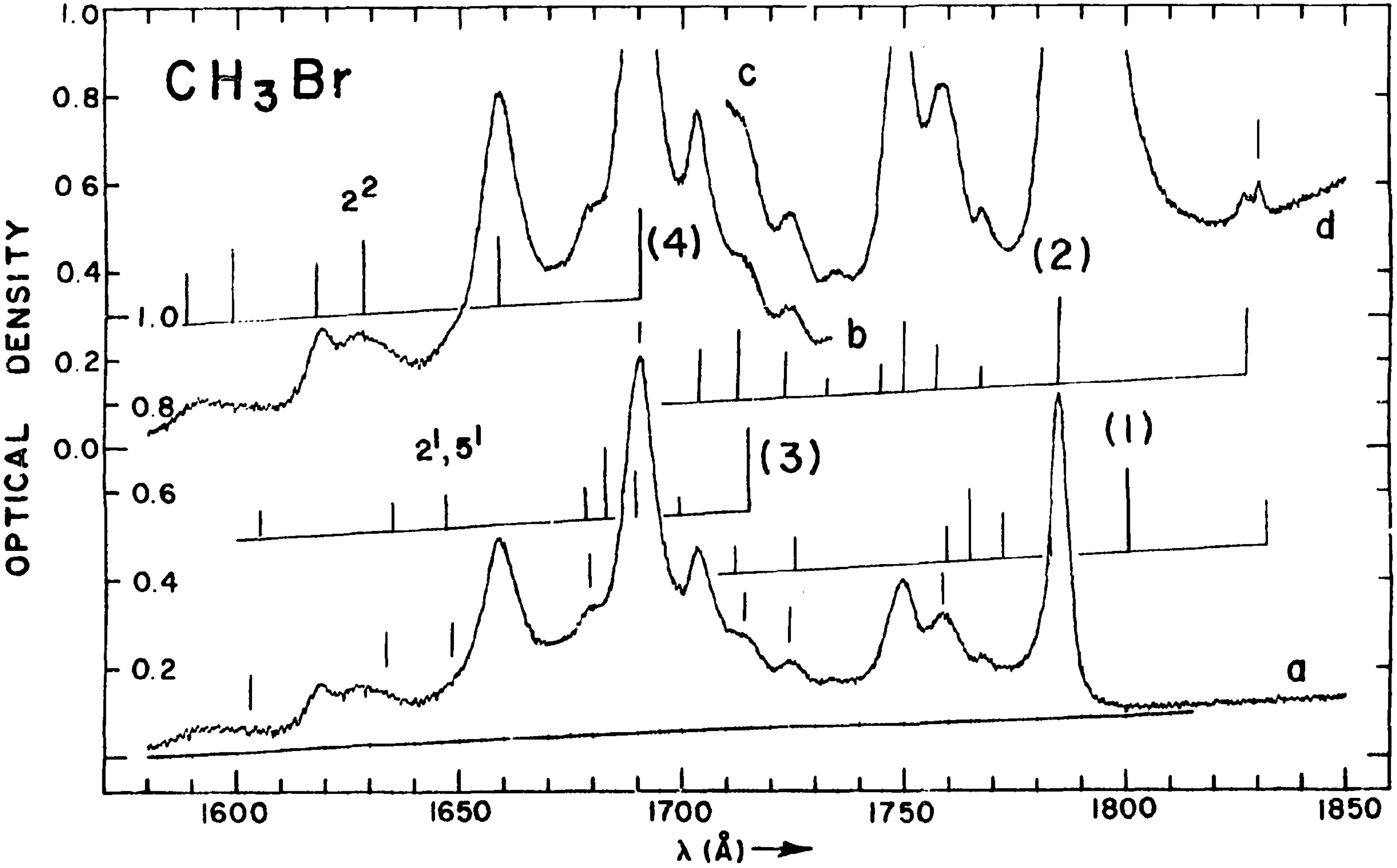
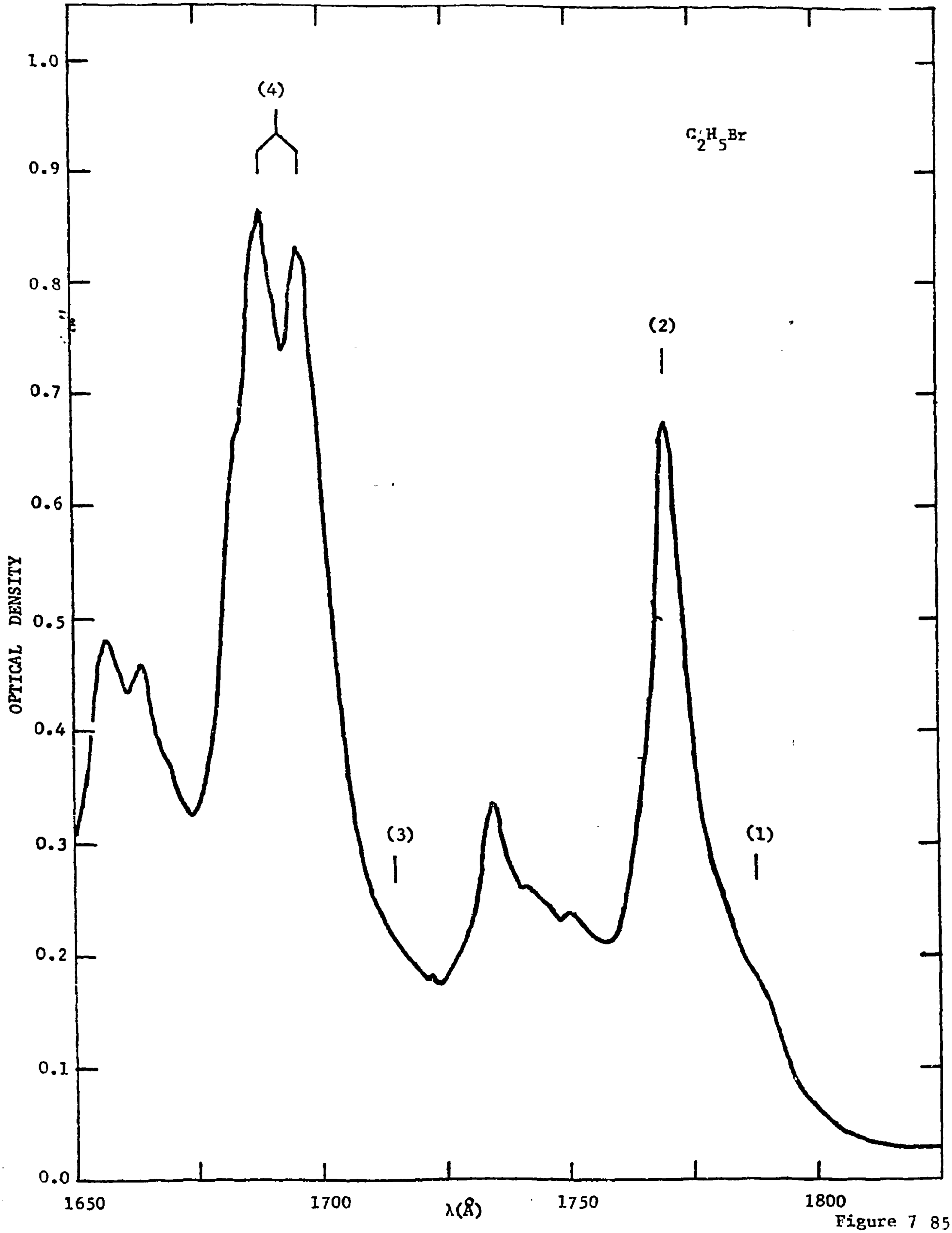

CH_3Br
OPTICAL DENSITY
1.0
0.8
0.6
0.4
0.2
0.0
1.0
0.8
0.6
0.4
0.2
2^2
$2^1,5^1$
(4)
(3)
(2)
(1)
a
b
c
d
1600
1650
1700
1750
1800
1850
λ (Å) →

Figure 6



1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
OPTICAL DENSITY
(4)
(3)
(2)
(1)
C_2H_5Br
1650
1700
1750
1800
λ(Å)

Figure 7

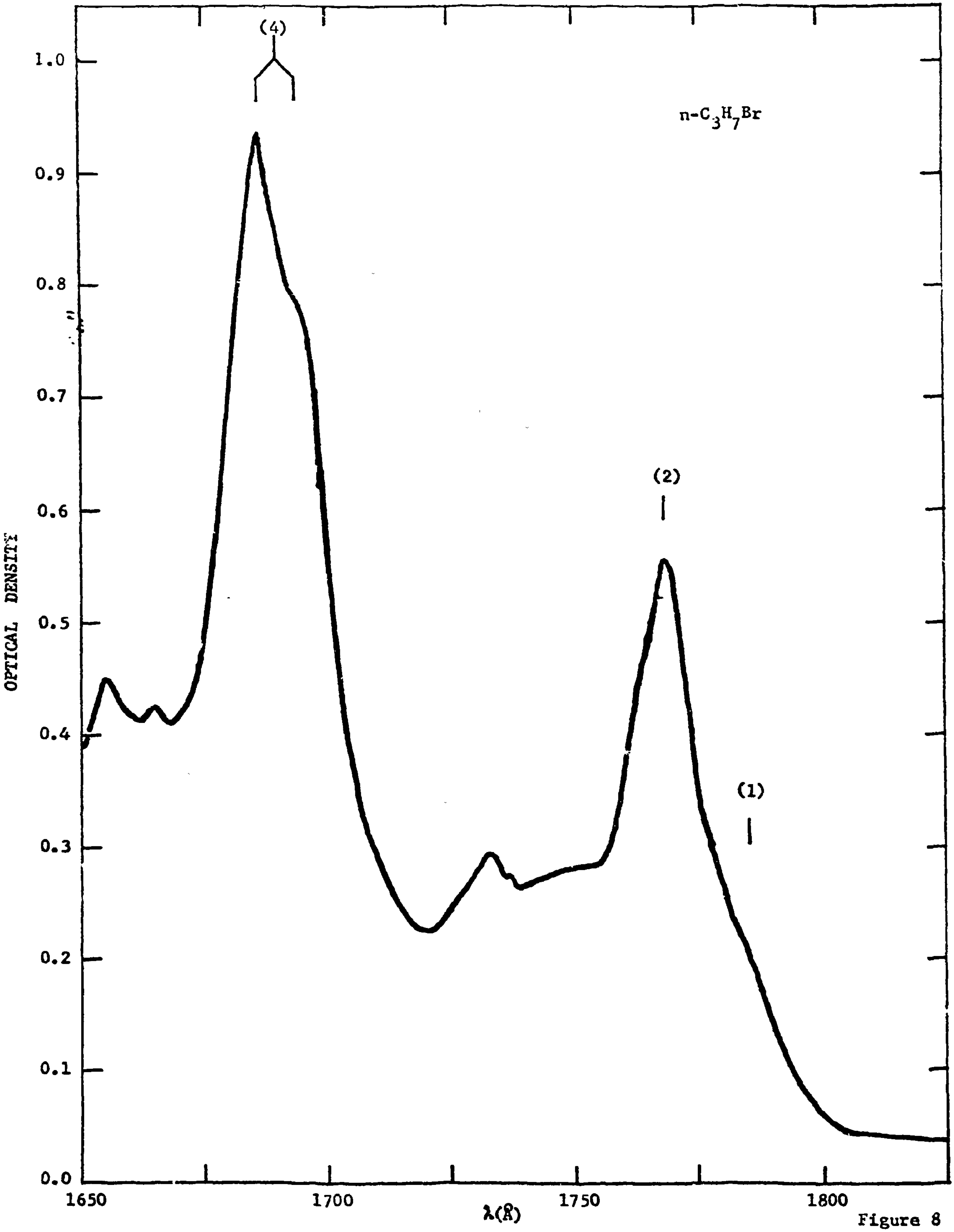
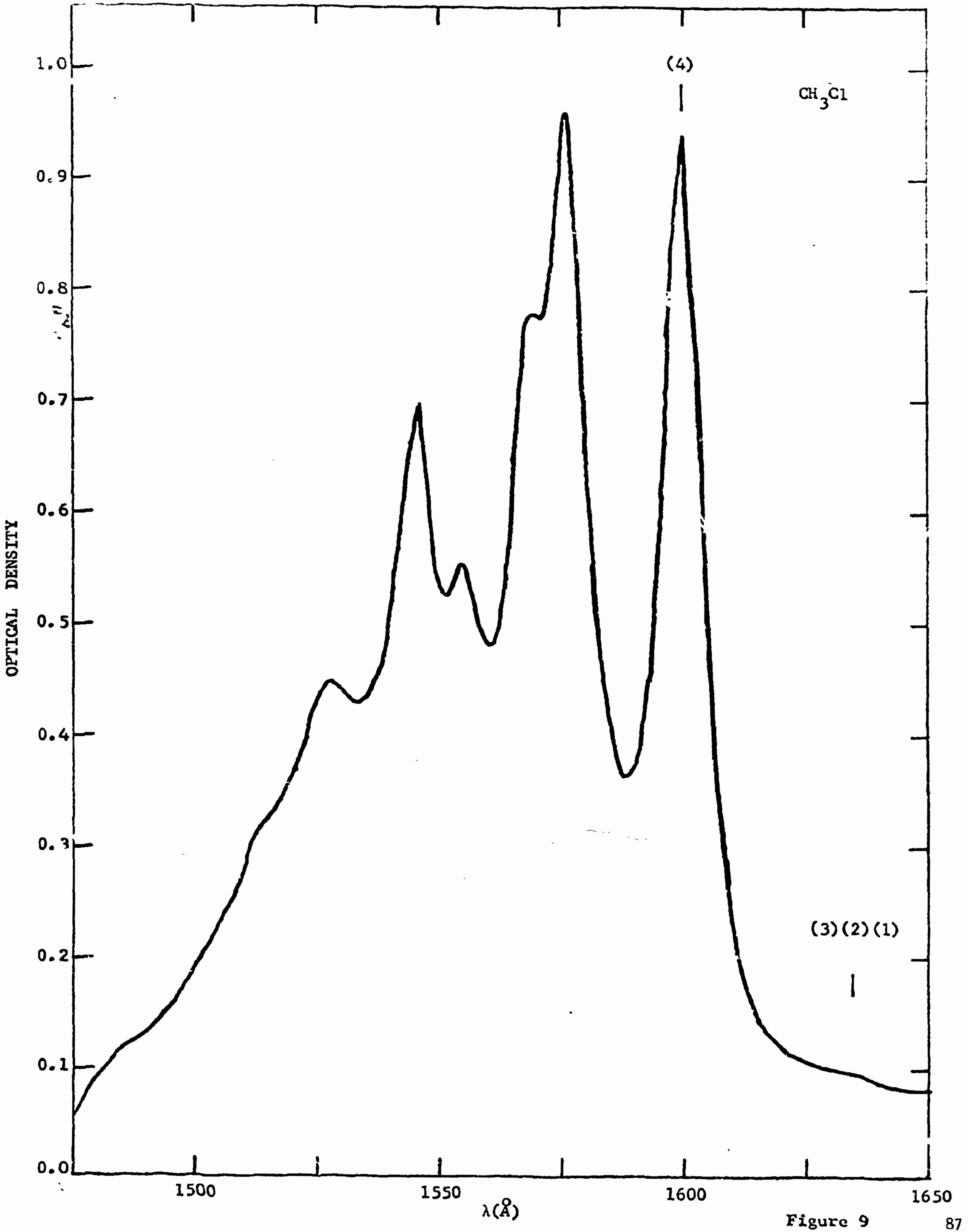

(4)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
OPTICAL DENSITY
$n-C_3H_7Br$
(2)
(1)
1650
1700
1750
1800
λ(Å)

Figure 8



OPTICAL DENSITY
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1500
1550
1600
1650
λ(Å)
(4)
CH$_3$Cl
(3)(2)(1)

Figure 9

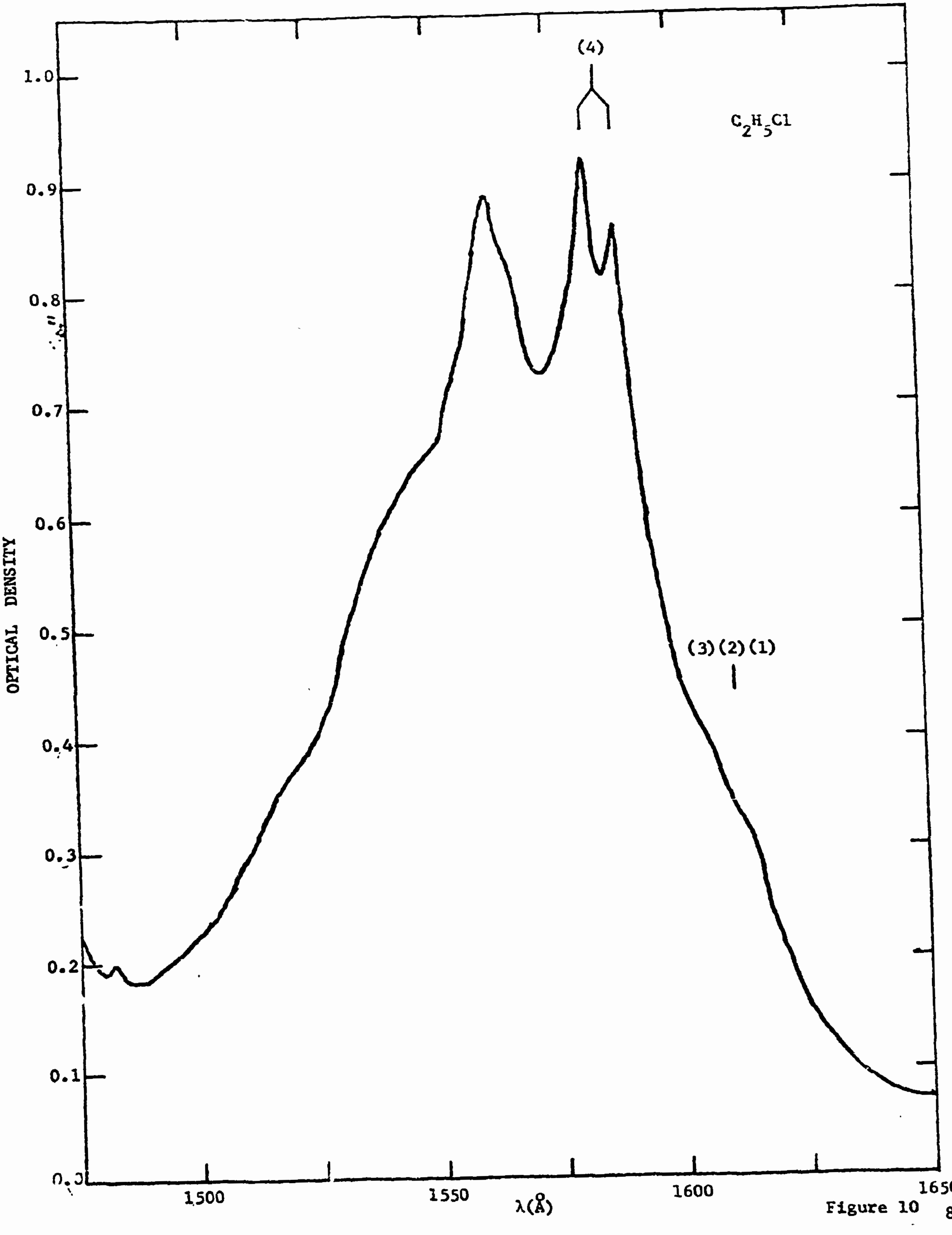

(4)
C_2H_5Cl
(3) (2) (1)
OPTICAL DENSITY
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1500
1550
1600
1650
λ(Å)

Figure 10

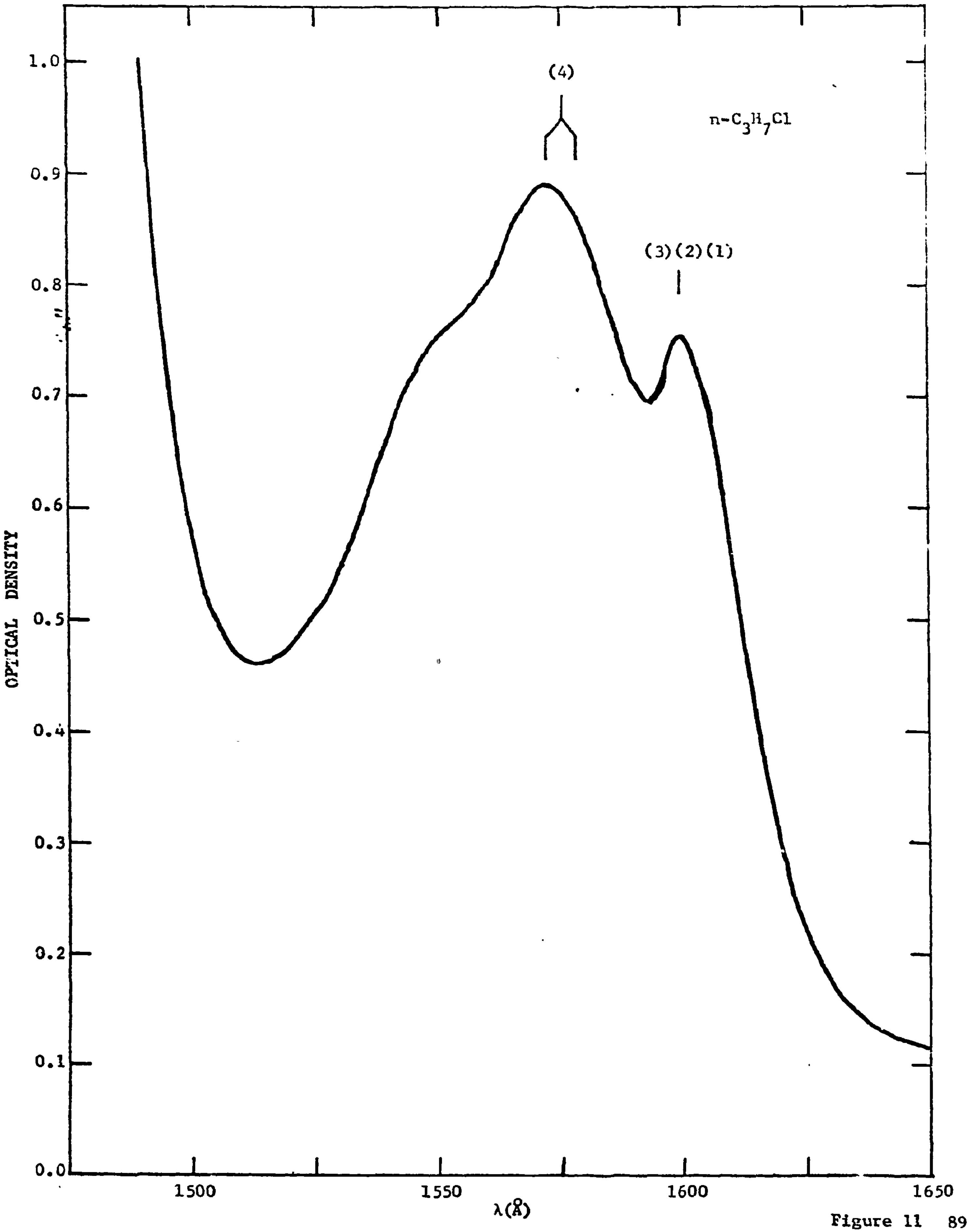
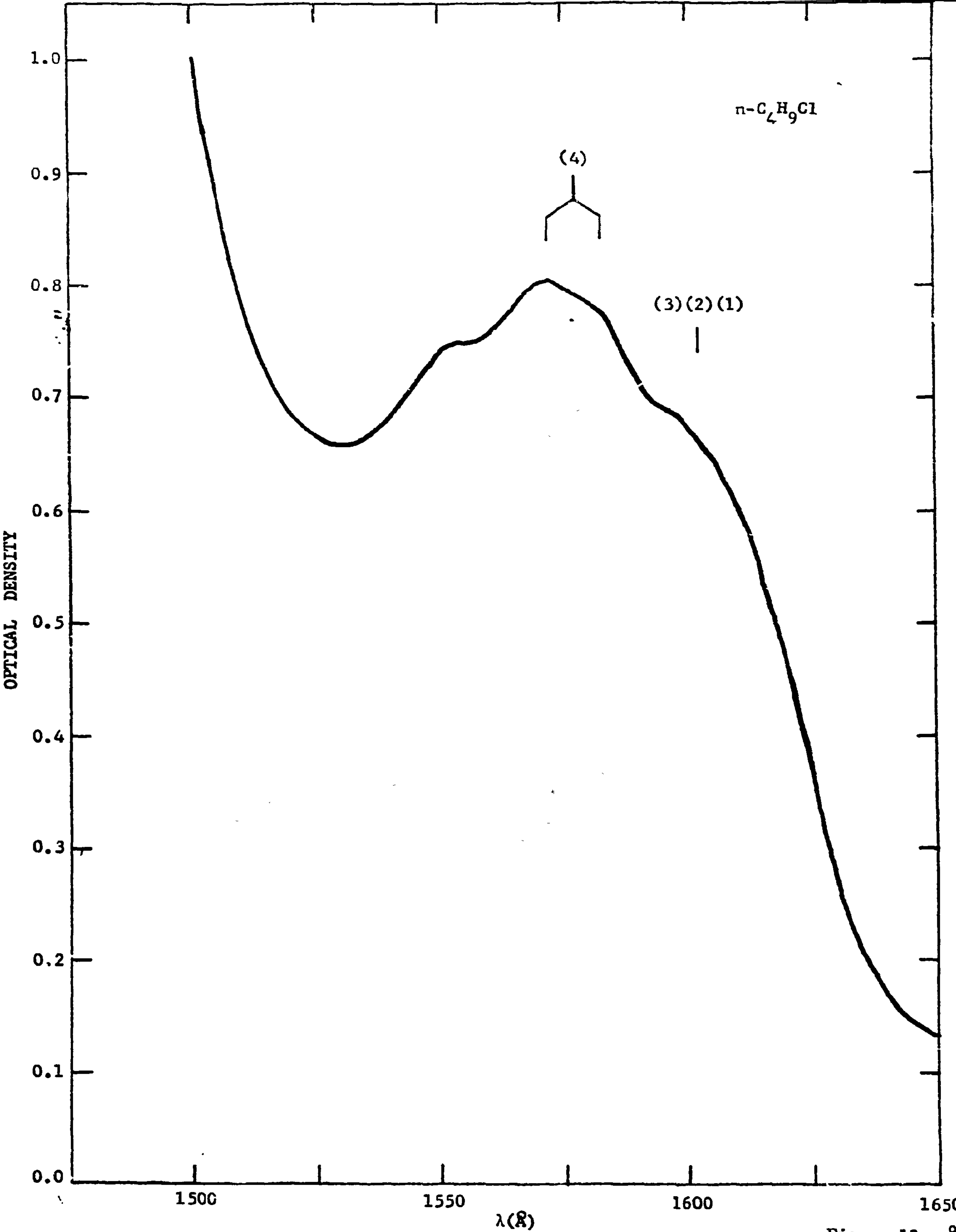

(4)
n-C_3H_7Cl
(3)(2)(1)
OPTICAL DENSITY
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1500
1550
1600
1650
λ(Å)

Figure 11



n-C_4H_9Cl
(4)
(3)(2)(1)
OPTICAL DENSITY
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
1500
1550
1600
1650
λ(Å)

Figure 12

THE ELECTRONIC STRUCTURE OF DICARBONYL COMPOUNDS

by

David Dougherty

Graduate Student

The aims of my research are the following: (i), To continue studying the effects of substituting N-H, O and S units (heteroatoms) between and/or beside the carbonyl groups of α, β and γ dicarbonyl ring system; (ii), To study the effect on the electronic spectrum of varying the dihedral angle between the carbonyl units of α-dicarbonyls; and (iii), To attempt the empirical assignment of the photoelectron spectra (PES) of *para*-benzoquinone and some of its methyl and halogen derivatives.

HETEROATOM EFFECT.

The study of the PES of a great many simple dicarbonyls has indicated a general relationship[1] between the separation of the carbonyl centers, and the energy splitting of the n_+/n_- as n_s/n_a lone pair molecular orbitals (MO's). The term simple dicarbonyls denotes saturated hydrocarbon molecules containing two carbonyl groups. The designation n_+/n_- or n_s/n_a denote the symmetric and antisymmetric linear combination of the carbonyl oxygen n orbitals with respect to some symmetry operation--usually a rotation. This relationship says that the energy splitting between n_+ and n_- is ~2.0eV for α-dicarbonyls, ~0.8eV for β-carbonyls and ~0.3eV for γ-dicarbonyls.

The introduction of heteroatoms -- nitrogen or oxygen -- and/or unsaturation into a dicarbonyl will affect the MO structure because of changes in bond length, electronegativity (e.g., inductive effect) and the presence of other "lone pair" and/or π orbitals of the heteroatom(s) which interact with the n_+/n_- set of MO's. Examples[2,3] which suggest that the α, β, γ-splitting interval rules also hold for molecules containing heteroatoms are available. The trend observed in the data of Figure 1a-d indicates that the n_+/n_- splitting rules are independent of the groups which are interposed between the β-dicarbonyl units. The splitting, however, does appear to be dependent on ring size (e.g., the splitting in the 5-member β-dicarbonyl is greater than in the 6-member ring).

Ultimate interest in these molecules lies in the fact that many biological molecules have structures consisting of carbonyl units with "nearby" amine and imine groups. One particularly large class of this type is the barbiturates. The PES of barbituric acid has been obtained but has not been analyzed yet. Quantum chemical studies of several barbiturates are in process.

DIHEDRAL ANGLE EFFECT IN α-DICARBONYLS.

The ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ transition energies are quite variable in α-dicarbonyls. This variability is usually attributed to changes in the CO/CO dihedral angles[4,5]. It is known from the PES of α-dicarbonyls that the energy of the n_+ MO -- which is also the highest occupied MO in these molecules -- is very insensitive to changes in dihedral angle. However, the $\pi^*_\pm$ virtual MO's, which are degenerate when the dihedral angle is 90°, diverge and achieve a maximum separation at a dihedral angle of 0° or 180°. Thus, one expects that as the CO/CO angle increases from 0° to 90° to 180°, the ${}^1\Gamma_{n\pi^*} \leftarrow {}^1\Gamma_1$ energy will start out small, go through a maximum, and then decrease again.

In order to investigate this hypothesis, all of the cyclic α-dicarbonyls with ring sizes 4 through 14 bonds are being synthesized. The objective is to run the absorption spectra, the PES, and possibly the luminescence of all these molecules. It is expected that the small, rigid, ring systems in which the carbonyl units are planar, or very nearly planar, will have absorption in the visible or near UV; the larger ring systems will have transitions further into the UV region. The largest rings should allow the carbonyls to assume a <u>trans</u>-planar configuration and, thus, move the absorption band back toward the near UV and visivle. The PES measurements will show the energy level for the n_+ MO for each of these molecules, and this is not expected to change significantly. The luminescence of these molecules will provide information on the ground state geometry since the ${}^1\Gamma_1 \leftarrow {}^1\Gamma_{n\pi*}$ fluorescence occurs only from a CO/CO coplanar configuration. Thus, if the vertical transitions for both absorption and emission are nearly coincident, the ground state geometry should be CO/CO coplanar. If there is a large separation between the absorption maximum and the emission maximum, then the molecule in the ground state will not have coplanar carbonyl units.

In sum, I expect that, for α-dicarbonyls with CO/CO coplanarity, the ${}^1\Gamma_{n\pi*} \leftarrow {}^1\Gamma_1$ absorption will occur at longer wavelengths than it will for non-coplanar α-dicarbonyl systems. I also expect that the Stokes shift between emission and absorption in the coplanar case will be small for the vertical event, while it will be large for the non-coplanar case. The PES of these molecules will give the energy of the n_+ MO, within the limits of Koopmans' theorem, and thus some idea of the change in energy of the π_+^* virtual MO energy can be obtained. These data should also validate the Stokes shift between absorption and emission bands as a tool for determining the coplanarity of α-dicarbonyls in the ground state[3].

PARA-BENZOQUINONE.

The PES of p-benzoquinone and tetrafluoro-p-benzoquinone, despite several attempts[6,7,8,9], are not convincingly assigned. I have studied the PES of numerous substituted p-benzoquinones in an attempt to assign the spectra using the various empirical assignment rules available: the perfluoro effect; ~0.3eV separation for n_+ and n_- ionization energies of γ-dicarbonyls; progressive methylation, which should decrease the energy of the π MO's faster than that of the n MO's; and vibronic similarities between the same PES bands in different molecules. The result is the tentative correlation diagram shown in Figure 2. The results of CNDO/s MO calculations are shown in Figure 3. The nomenclature used in Figures 2 and 3 is elaborated in Figure 4.

The general behavior of the p-benzoquinone moiety, as evidenced in these correlation diagrams, encompasses the following characteristics: (i), Substituents which supply electron density to the ring increase the n_-/n_+ splitting and destabilize the π_- MO more than the π_+ MO; (ii), Substituents which remove electron density from the ring stabilize the n_- MO relatively more than the n_+ MO.

The shift of the π_+ MO to higher ionization potential is, however, not readily explained. One possible explanation is that the nodes between the carbonyl π's and the ring π's prevent effective "back-bonding" from the fluorine and other highly electronegative -- but known π back-bonding --

groups such as C≡N. This would help explain why the π_- band does not shift downfield as much as might be expected.

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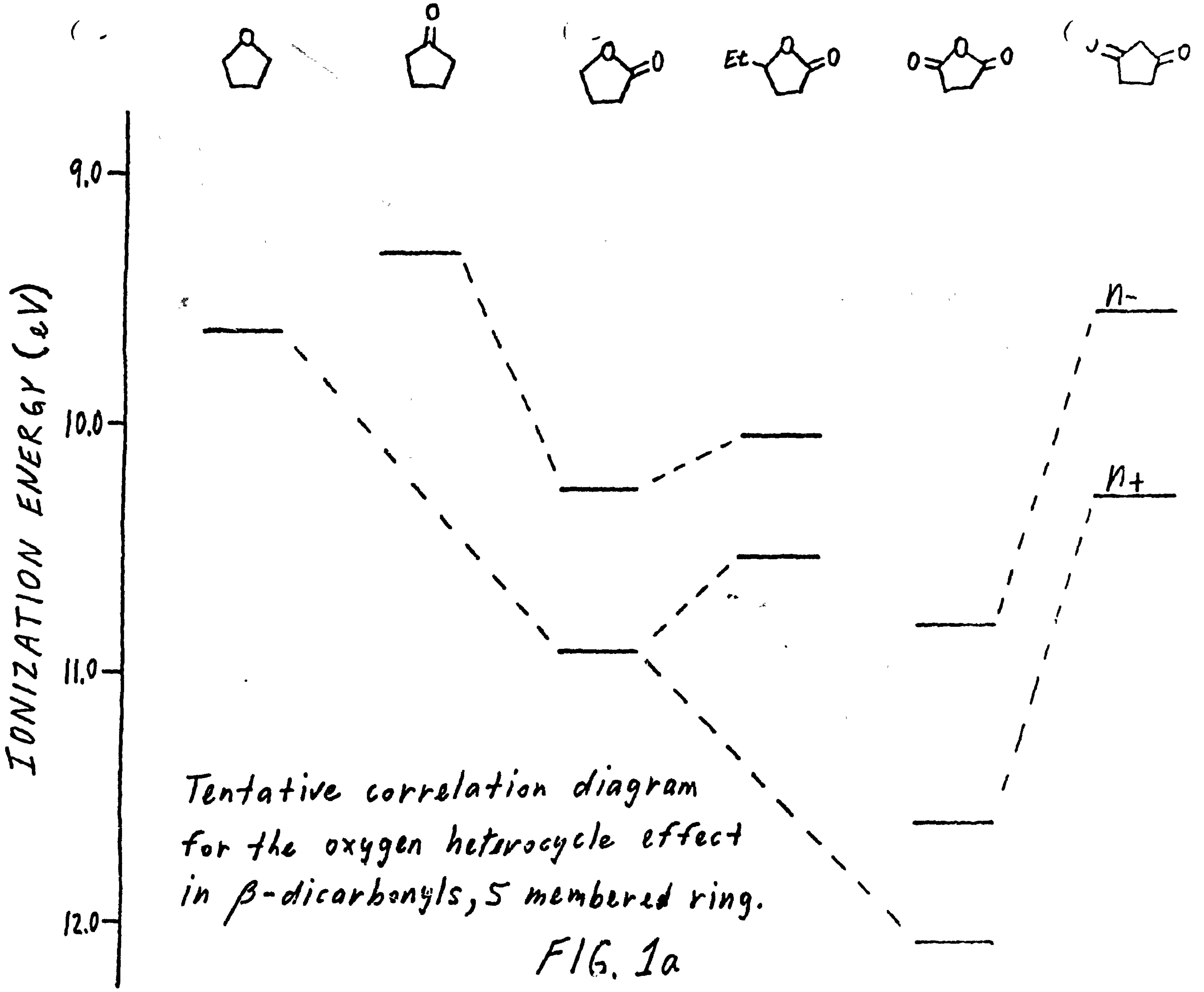
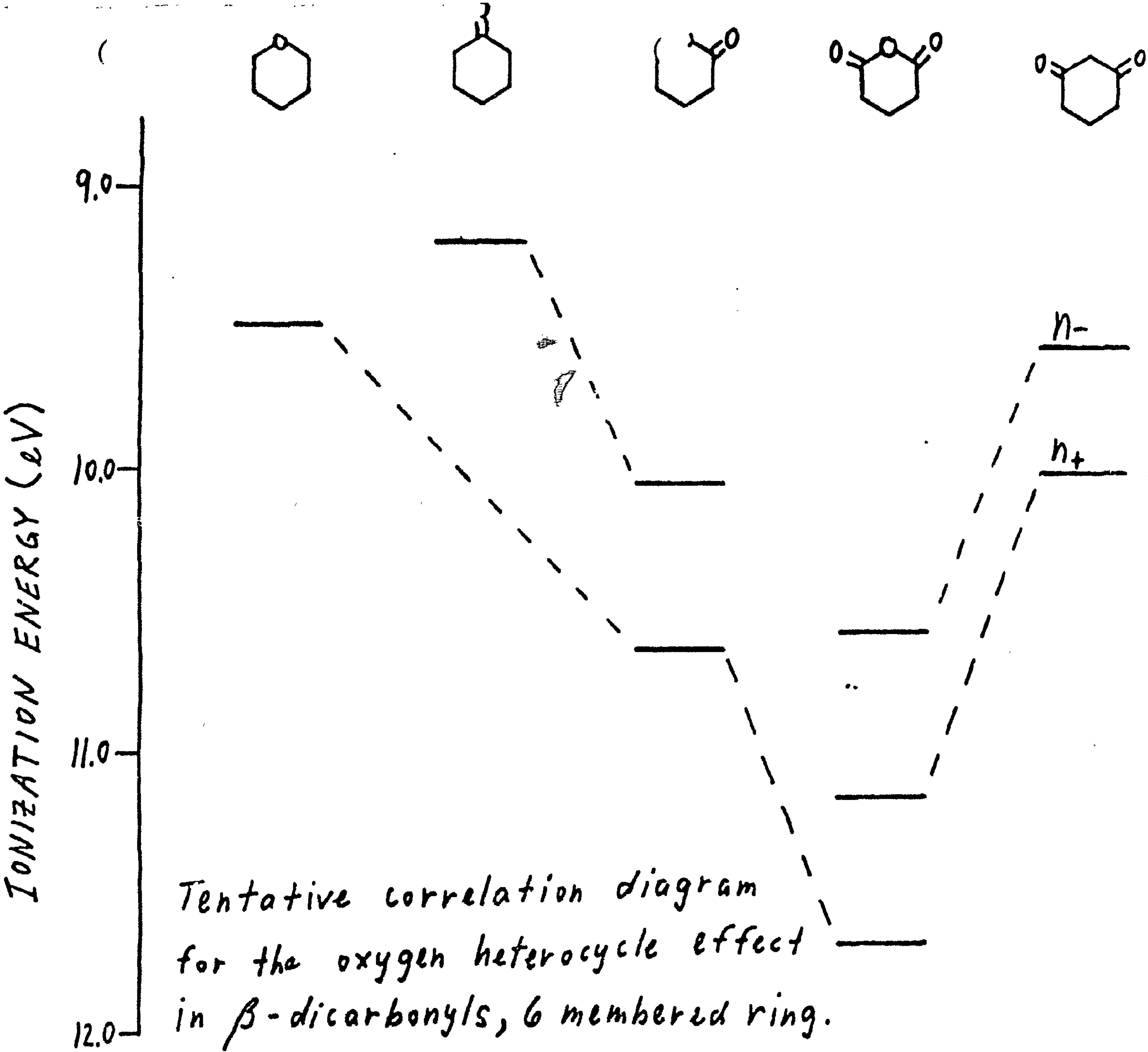


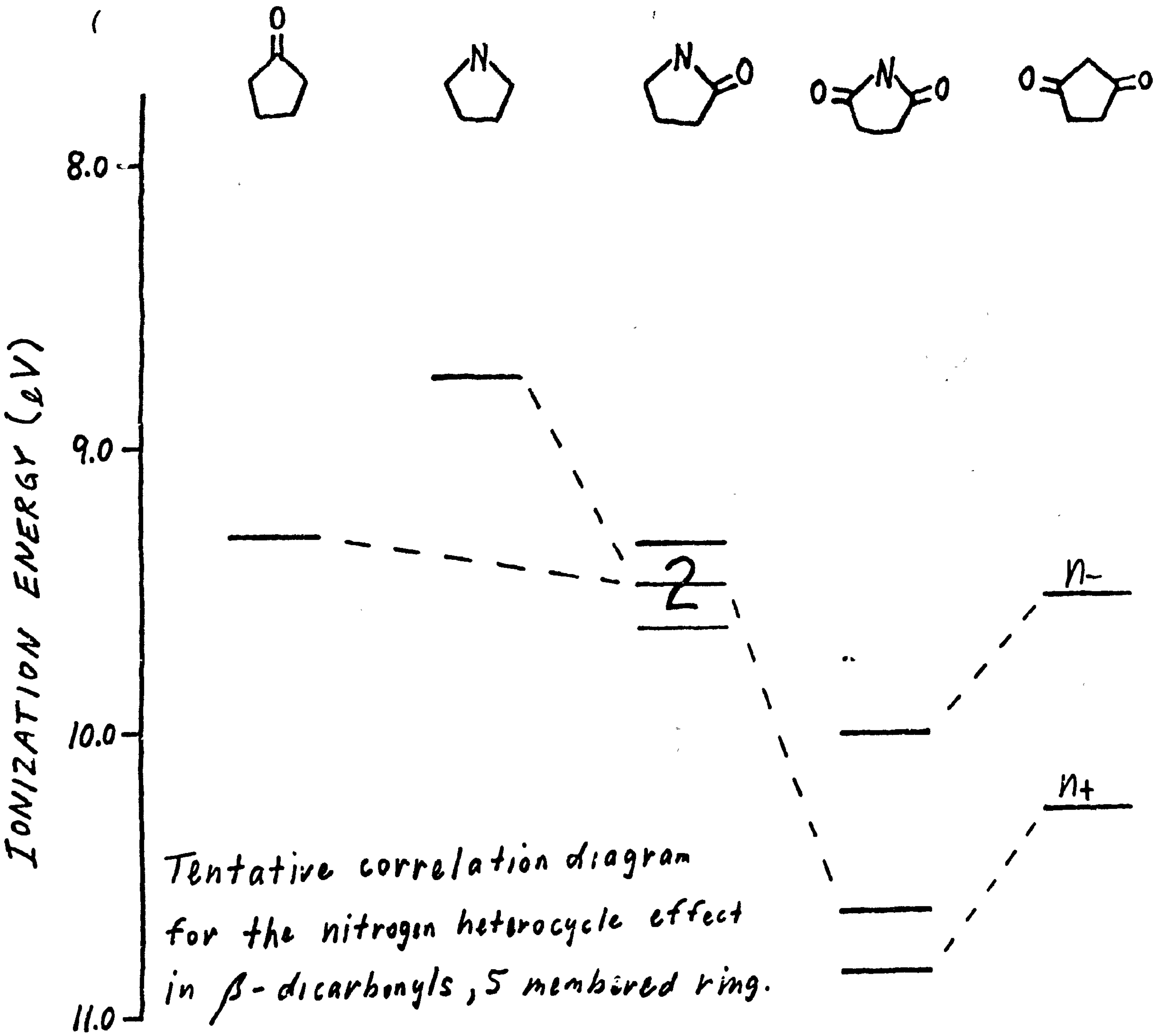
Tentative correlation diagram for the oxygen heterocycle effect in β-dicarbonyls, 5 membered ring.

FIG. 1a



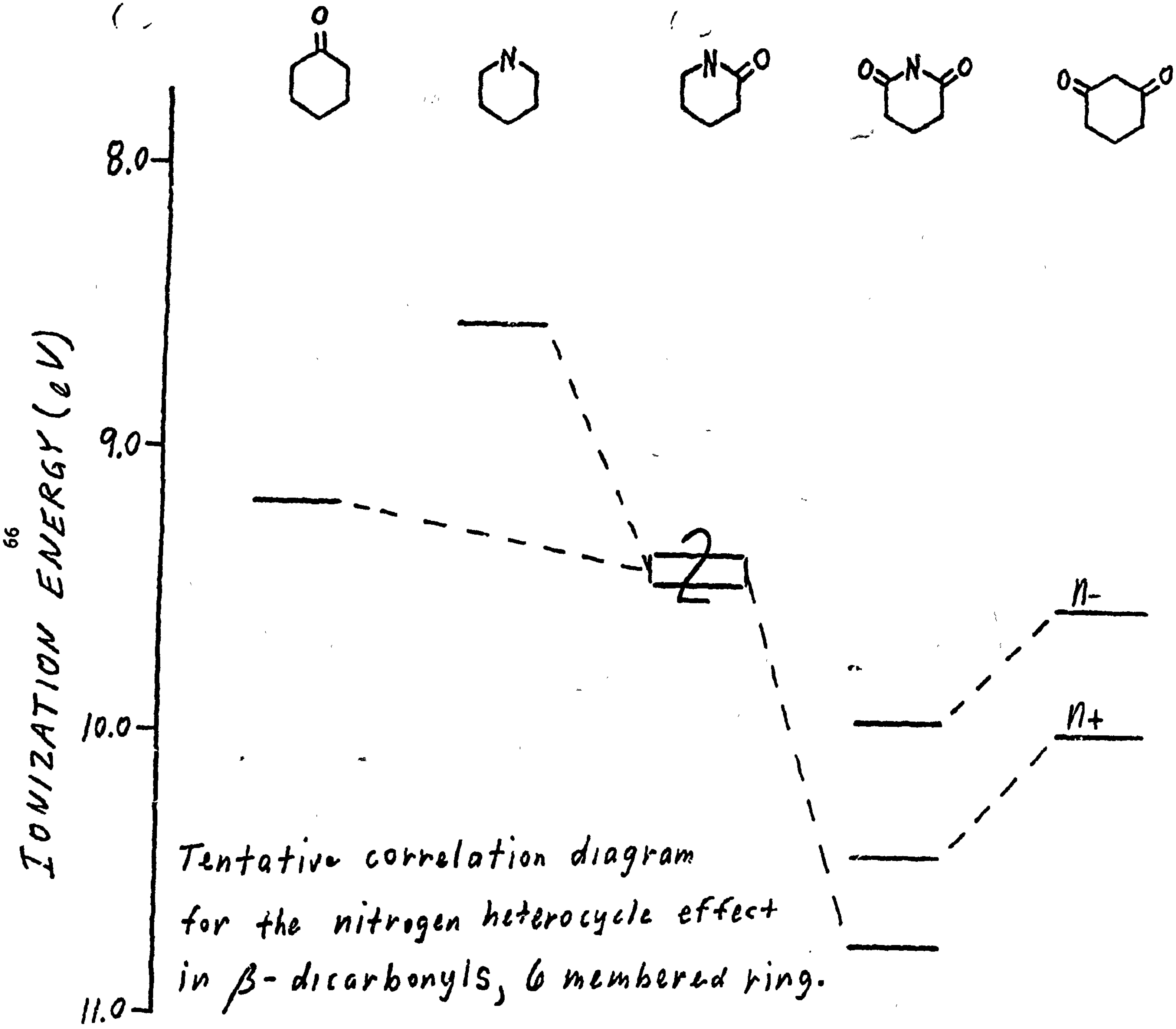
Tentative correlation diagram for the oxygen heterocycle effect in β-dicarbonyls, 6 membered ring.

FIG. 1b



Tentative correlation diagram for the nitrogen heterocycle effect in β-dicarbonyls, 5 membered ring.

FIG. 1c



Tentative correlation diagram for the nitrogen heterocycle effect in β-dicarbonyls, 6 membered ring.

FIG. 1d

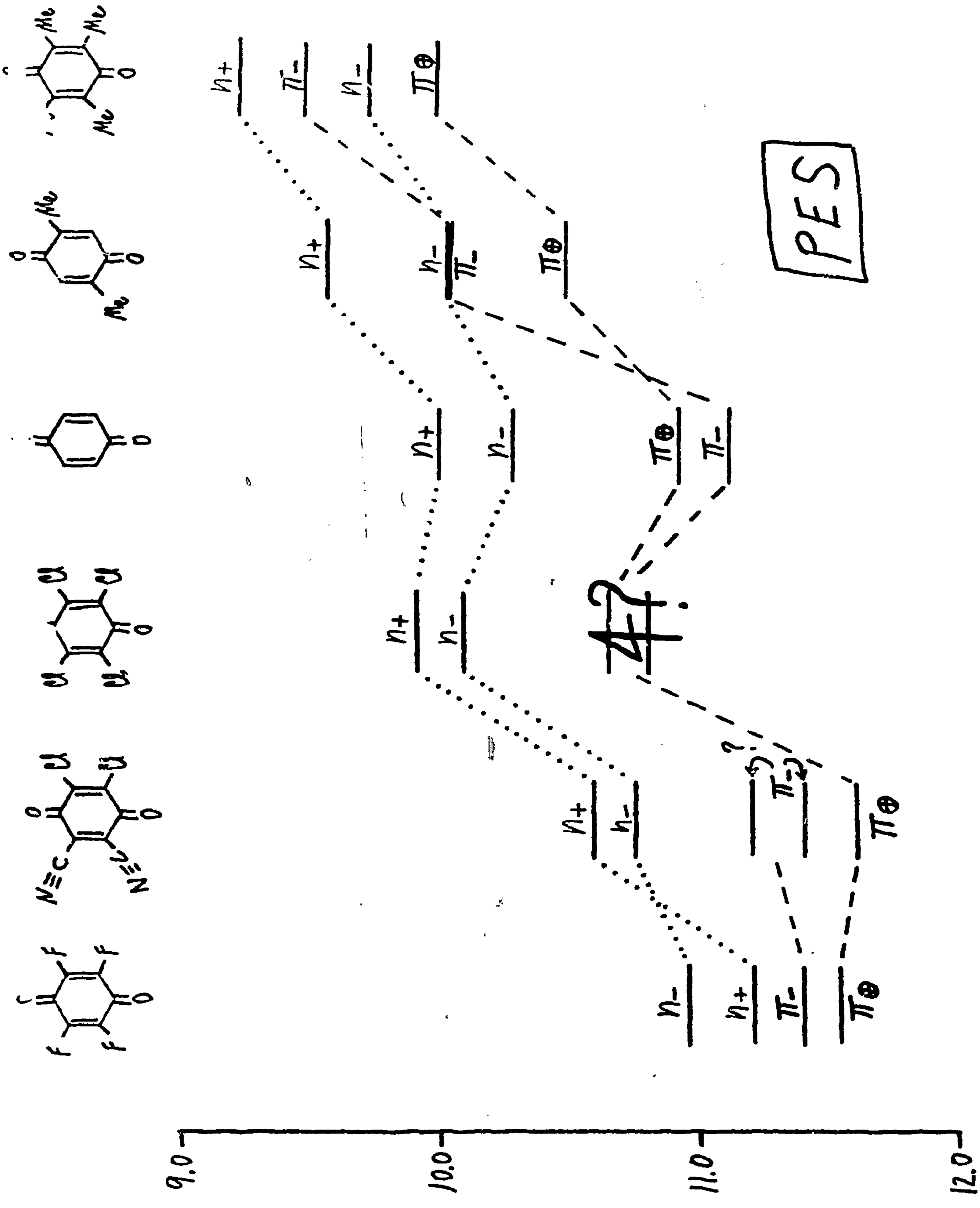
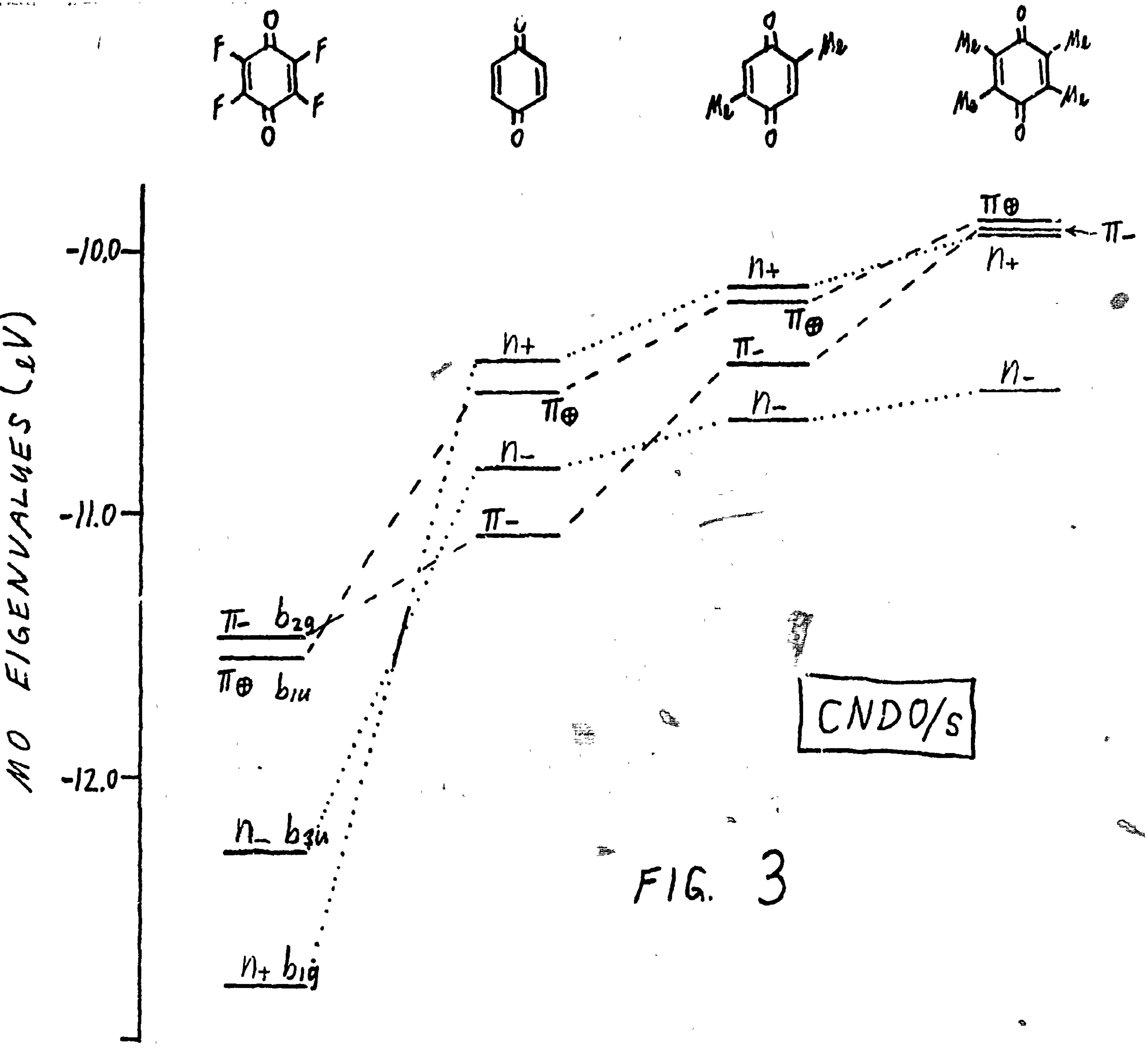


FIG. 2


MO EIGENVALUES (eV)
-10.0
-11.0
-12.0
F
O
Me
π− b_{2g}
π⊕ b_{1u}
n− b_{3u}
n+ b_{1g}
n+
π⊕
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n+
n−
CNDO/s

FIG. 3

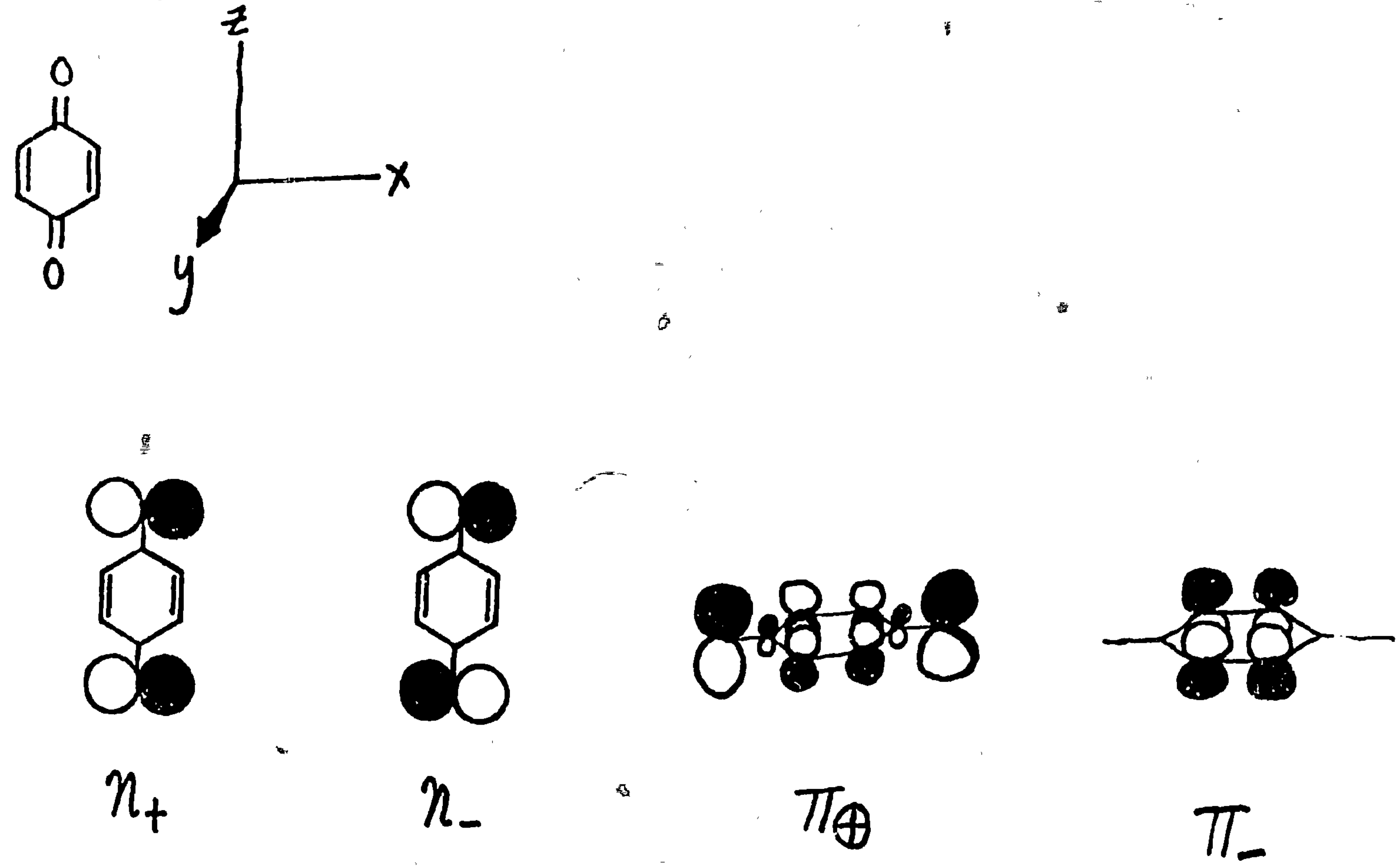


FIG. 4

THE ABSORPTION AND EMISSION CHARACTERISTICS OF HIGHLY-POLAR AROMATICS

by

Thomas P. Carsey and Gary L. Findley
Graduate Students

INTRODUCTION

The perturbative effect of substituents on the electronic structure of benzene has been a subject of investigation for many years. In view of the ubiquity of substituted benzenes in nature (for example, the amino acids tyrosine and phenylalanine), the study of the electronic structure of these types of compounds has the potential of generating new insights into the structures and reactions of certain biologic molecules.

A subgroup of substituted benzenes which has received much attention in this laboratory are those in which an electron donor and an electron acceptor are substituted onto the benzene ring. This subgroup is particularly interesting since the polarity of a series of these molecules can be smoothly varied from essentially non-polar (benzene-like) molecules to highly-polar molecules by varying the benzene substituents within the series. If the polarity of the different substituents is ordered in some fashion within the series, then overall trends in the absorption and emission spectra may be discerned, and correlations may be made between the polarity of the substituents and the electronic structure of these Donor-Benzene-Acceptor (D-ϕ-A) molecules.

With this in mind we have undertaken to study the absorption and emission characteristics of a large number of D-ϕ-A molecules (in ortho, meta and para forms). In addition we have utilized the CNDO/s-CI approximation to perform quantum chemical computations on these molecules in an attempt to reproduce experiment and as a means of correlating changes in specific energy states as a function of substituent polarity.

EXPERIMENTAL DATA

So that we may have an independent criterion with which to order a series of substituents according to their polarity, we have utilized substituent activation of the benzene ring toward electrophilic substitution as a ranking device. This classification orders the substituents by the direction and the increasing degree of induced electron migration[1].

Electron Donors

$-CH_3$
$-F$
$-C\ell$
$-Br$
$-OH$
$-OCH_3$
$-NH_2$
$-O^-$
$-N(CH_3)_2$

Electron Acceptors

$-CN$
$-COOH\ (-COOR)$
$-COCH_3$
$-CHO$
$-NO_2$

Use of the above substituents allows one to study seven distinct types of series:

1. The electron donor is held constant while the electron acceptor is varied. This series generates three subseries, one for each of the ortho, meta and para substituent positions.

2. The electron acceptor is held constant while the electron donor is varied. This series also generates three subseries.

3. The electron donor and the electron acceptor are both held constant while the position of substitution is varied.

In order to present an overview of the absorption and emission characteristics of these molecules, a description of series (3), the ortho, meta and para (OMP) triads, is advantageous. We will therefore consider, in some detail, three triads: fluorobenzonitrile (weakly polar), cyanoaniline (moderately polar) and nitroaniline (highly polar).

Fluorobenzonitrile

The absorption and emission spectra of the ortho, meta and para isomers of the weakly polar fluorobenzonitrile are presented in Figure 1. The following general observations may be made:

1. All three members of the triad have almost identical absorption spectra, resembling the absorption spectrum of benzene and that of benzonitrile in general characteristics. This indicates that the perturbation of the electronic structures of the fluorobenzonitriles by substituent effects is quite small. If these molecules were highly polar, one would expect to see much less correlation between their absorption spectra and the absorption spectrum of benzene than is actually observed.

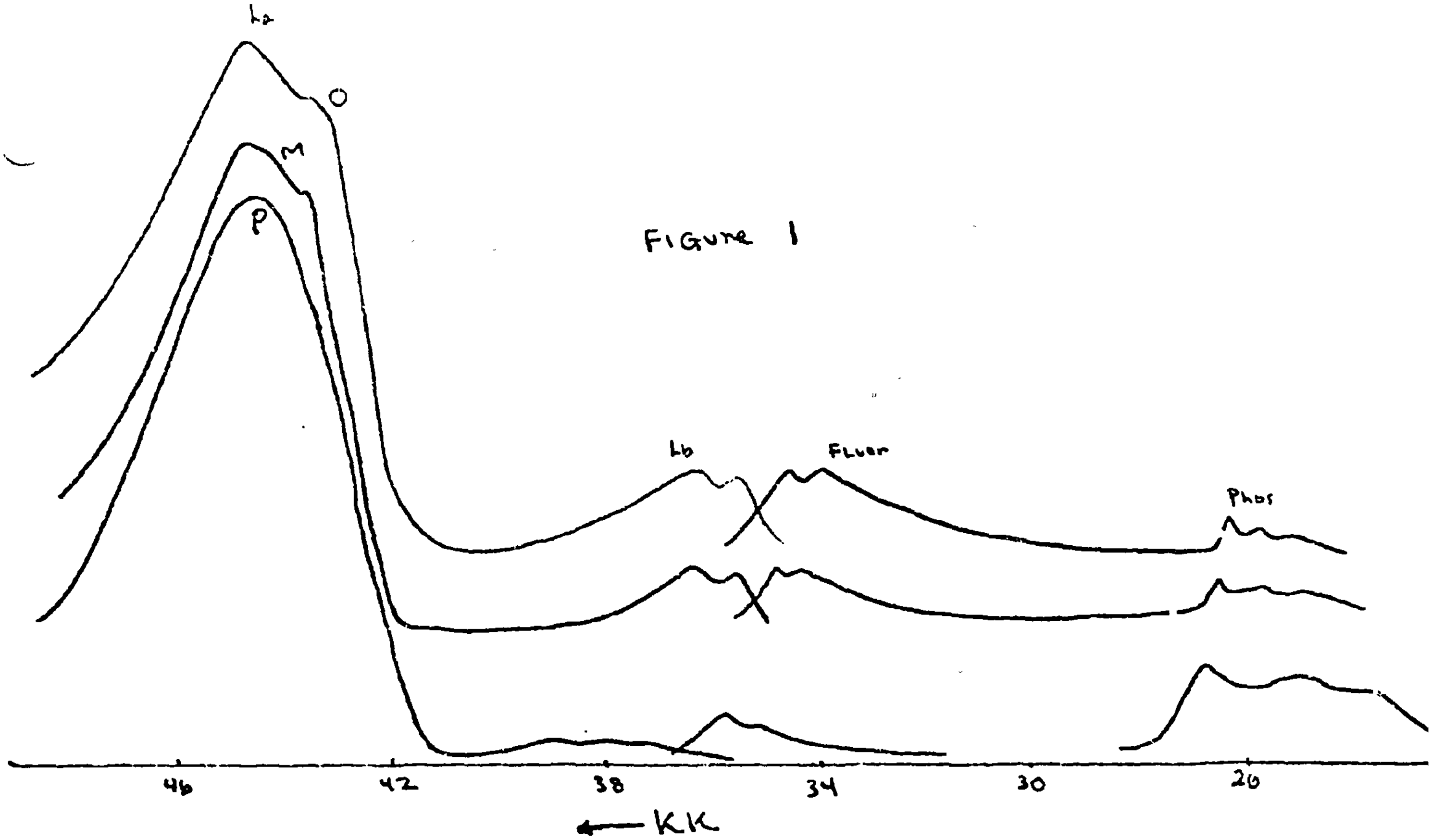


Figure 1

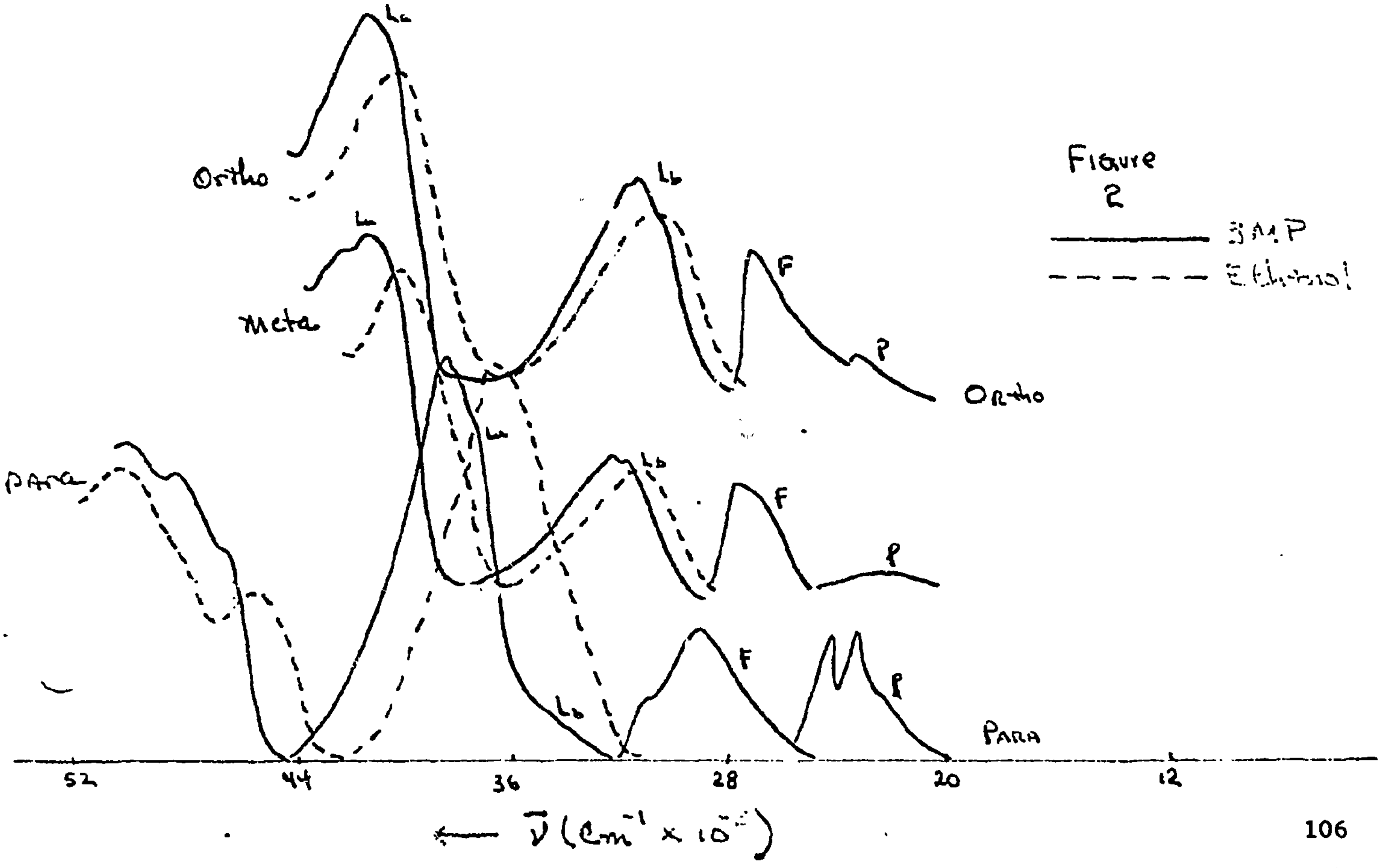


Figure 2

2. The 36000cm^{-1} band ($^1L_b \leftarrow {}^1A$) is reduced in intensity and lies at a slightly higher energy in the para isomer, whereas the 44000cm^{-1} band ($^1L_a \leftarrow {}^1A$) lies at a slightly lower energy[2]. (Table 1)

3. The L_a - L_b band gap is quite large (~7000cm^{-1}) for all three isomers, but is smallest for the para isomer.

4. Fluorescence is structured and is the mirror image of the 36000cm^{-1} band ($^1L_b \leftarrow {}^1A$) in every case. The lifetimes and quantum yield data for the fluorobenzonitrile isomers are presented in Table 2. The conclusion from the emissive lifetimes and the mirror imaging of the fluorescence and absorption spectra is that fluorescence is $^1L_b \rightarrow {}^1A$ in nature.

5. The phosphorescence spectra are observed to be more structured that the fluorescence spectra in all cases. An analysis of isomer energies indicates that the T_1 state is energetically similar to the ^1L_b state[2]. The increased structure of phosphorescence suggests that the T_1 state is less polar, and therefore contains less charge-transfer configurations, than does the ^1L_a state[2].

6. The greater ϕ_P/ϕ_F value for p-fluorobenzonitrile indicates a greater rate constant for intersystem crossing (k_{ISC}) and a smaller rate constant for fluorescence (k_F) - both of which act to decrease ϕ_F - in the para isomer as compared to the other two isomers[2].

Cyanoaniline

The absorption spectra and the emission spectra of the ortho, meta and para isomers of the moderately polar cyanoaniline are presented in Figure 2[3]. The following general observations may be made:

TABLE 1[a]

ABSORPTION AND EMISSION DATA FOR FLUOROBENZONITRILE[b]

(A) ${}^{1}L_{b} \leftrightarrow {}^{1}A$

Molecule	Absorption 0,0 energy (cm^{-1})	Emission 0,0 energy (cm^{-1})	Absorption ε(f)
Benzonitrile	36,200	35,500	800(0.0093)
o-Fluorobenzonitrile	35,590	35,000	1670(0.020)
m-Fluorobenzonitrile	35,520	34,900	1700(0.020)
p-Fluorobenzonitrile	36,540	35,750	310(0.005)

(B) ${}^{1}L_{a} \leftrightarrow {}^{1}A$

Molecule	Absorption 0,0 energy (cm^{-1})	Absorption ε(f)
Benzonitrile	43,390	10,160(0.21)
o-Fluorobenzonitrile	43,570	8,930(0.18)
m-Fluorobenzonitrile	43,670	9,860(0.15)
p-Fluorobenzonitrile	43,300	9,000(0.19)

---

[a] Adapted from Reference 2.

[b] Absorption measurements were made in ethanol at 298°K; emission studies were made in ethanol at 77°K. The experimental error is ±50cm^{-1}. The symbol ε refers to extinction coefficient (in ℓ $mole^{-1}$ cm^{-1}) and the symbol f refers to oscillator strength.

TABLE 2

LIFETIME (τ) AND QUANTUM YIELD (ϕ) DATA FOR FLUOROBENZONITRILE[a]

Compound	τ_F(ns)	τ_P(s)	ϕ_P	ϕ_F	ϕ_P/ϕ_F
o-Fluorobenzonitrile	25.3	2.43	0.093	0.51	0.18
m-Fluorobenzonitrile	24.7	2.60	0.082	0.54	0.15
p-Fluorobenzonitrile	33.9	2.05	0.23	0.24	0.96

[a] Determined in ethanol glass at 77°K. The subscripts P and F refer to phosporescence and fluorescence, respectively.

Figure 3

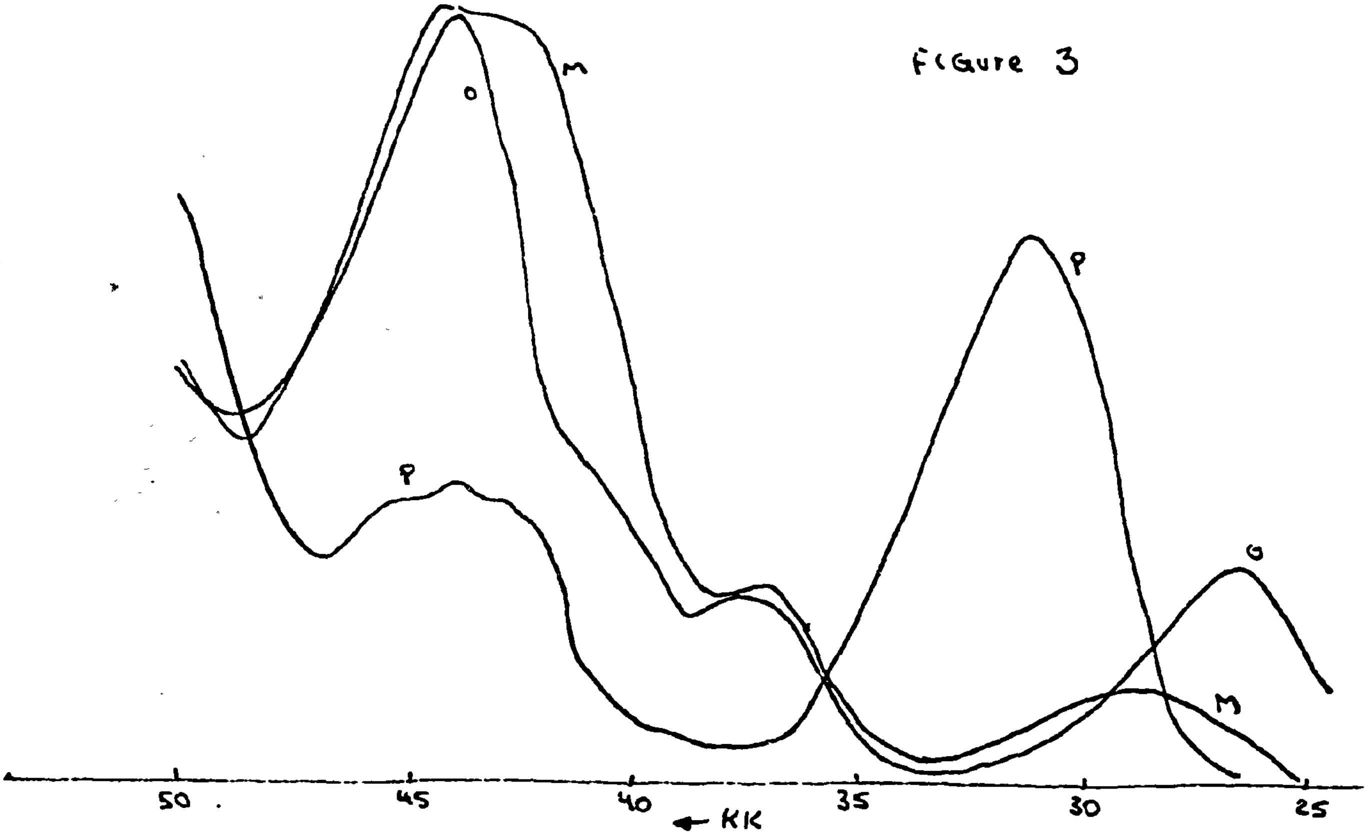
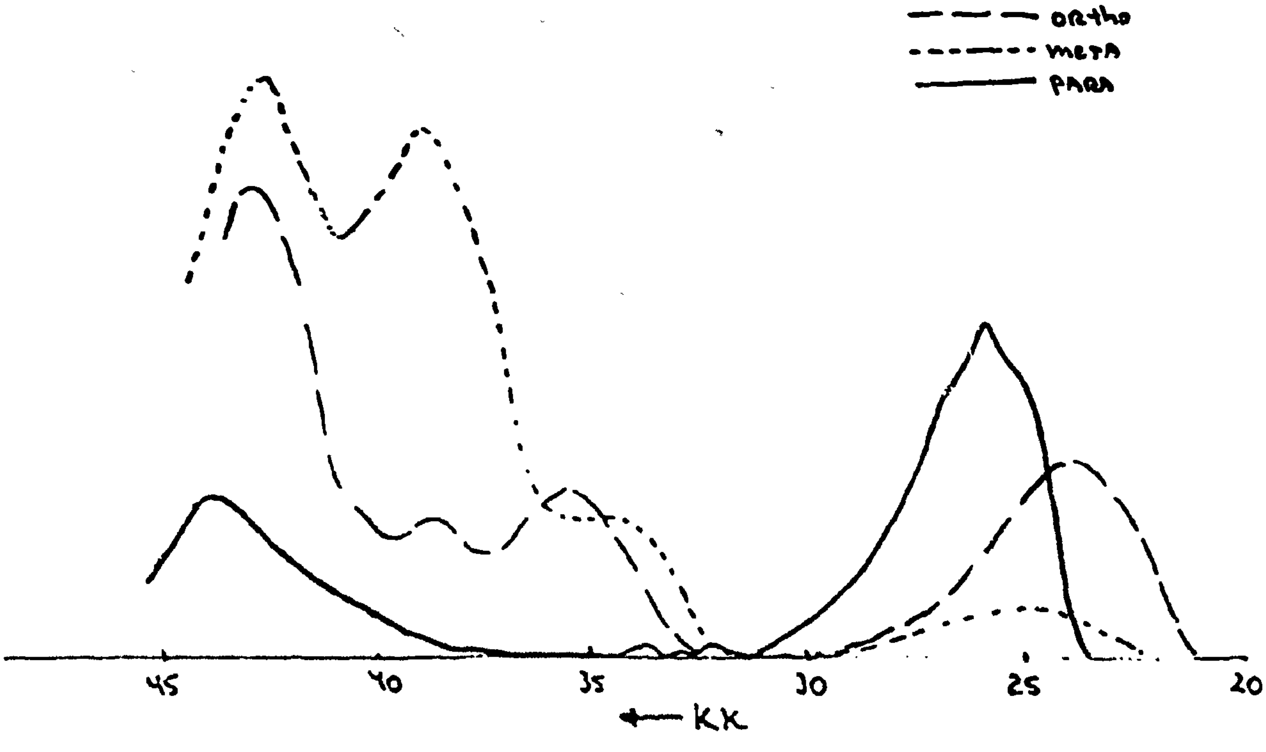


Figure 4



1. The absorption spectra of the ortho and meta isomers are similar and are not much affected in going from a non-polar to a polar solvent except for a slight energy decrement of 1000cm^{-1}. In contrast, however, the absorption spectrum of the para isomer is distinct from the ortho and meta isomers and is more affected by solvent polarity.

2. The low energy absorption band of the para isomer consists of at least two separate electronic transitions which are partially resolved in the non-polar solvent. In 3-methyl pentane (3MP) the lowest energy band maximizes at ~34500cm^{-1} and consists primarily of the ^1L_b electronic excitation ($^1L_b \leftarrow {}^1A$), while the band that maximizes at 38000cm^{-1} corresponds to the ^1L_a electronic excitation ($^1L_a \leftarrow {}^1A$) into which is mixed a large number of "charge-transfer" excitations of the type $D^+\text{-}\phi^-\text{-}A$, $D\text{-}\phi^+\text{-}A^-$, and $D^-\text{-}\phi\text{-}A^-$ [3]. The details of these two transitions for all three isomers are presented in Table 3.

3. The primary difference between the spectra of the ortho and meta isomers and the spectrum of the para isomer is a decrease in energy and increase in intensity of the ^1L_a related transition in the para isomer along with an increase in energy and decrease in intensity of the ^1L_b related transition in the para isomer[3]. Thus, in comparison to the weakly polar p-fluorobenzonitrile in which the ^1L_b transition is still distinct, the ^1L_b-related transition of p-cyanoaniline in a polar solvent is completely occluded by the ^1L_a-related transition.

4. As a result of the large charge-transfer character of the ^1L_a-related transition of the p-isomer, the ($^1L_a \leftarrow {}^1A$) excitation is greatly affected by solvent polarity. Thus, the ^1L_a-related transition

TABLE 3[a]

ABSORPTION AND EMISSION DATA FOR CYANOANILINE[b]

(A) $^1L_b \leftarrow {}^1A$

Molecule	Absorption Energy (cm^{-1})		Emission Energy (cm^{-1})	Absorption Intensity	
	0,0	Maximum	Maximum	$\epsilon_{max}(f)$	
	3MP	Ethanol	Ethanol	3MP	Ethanol
o-Cyanoaniline	~30,440	30,750	27,600	4,330(0.062)	3,450(0.055)
m-Cyanoaniline	30,900	31,200	27,500	2,860(0.042)	2,350(0.042)
p-Cyanoaniline	33,000	---	30,000	2,350(0.038)	---

(B) $^1L_a \leftarrow {}^1A$

	Absorption Energy (cm^{-1})		Absorption Intensity	
	Band Maximum		$\epsilon_{max}(f)$	
	3MP	Ethanol	3MP	Ethanol
o-Cyanoaniline	41,200	40,300	7,460(0.17)	6,110(0.11)
m-Cyanoaniline	41,200	39,700	7,050(0.20)	6,220(0.16)
p-Cyanoaniline	38,200	36,200	19,900(0.30)	19,600(0.37)

---

[a] Taken from Reference 3.

[b] Absorption measurements were made at 298°K; emission studies were made at 77°K. The experimental error is $\pm 50 cm^{-1}$. The symbol ϵ denotes the extinction coefficient (in $\ell\ mole^{-1}\ cm^{-1}$) and f denotes oscillator strength.

exhibits a larger energy decrement than the ^1L_b-related transition in a polar solvent.

5. The fluorescence spectra of all three isomers exhibit little structure as compared to the fluorescence spectra of the weakly polar fluorobenzonitriles. This may be attributed to the near degeneracy of the ^1L_a and ^1L_b states in these more polar D-ϕ-A molecules, but it probably reflects the increased solvent-solute arrangements and solute-solute interactions in these systems[3].

6. The absorption and fluorescence spectra of p-cyanoaniline do not exhibit a mirror image relationship. The vibronic intervals (800 and 1200cm^{-1}) of the fluorescence spectrum, however, are the same as those of the low energy "tail" of the lowest energy absorption band[3]. This suggests that the fluorescence emission is the inverse of the ($^1L_b \leftarrow {}^1A$) transition. This conclusion is further substantiated by the large half-width of the lowest energy absorption band (~4500cm^{-1}) in comparison to that of the fluorescence band (~3000cm^{-1})[3]. Also, the intrinsic radiative lifetime of the fluorescence calculated from the absorption oscillator strength data, assuming the fluorescence to be the inverse of the low energy "tail", is 27ns, which agrees well with the observed intrinsic radiative lifetime of 33ns[3]. In contrast, however, the intrinsic radiative lifetime calculated assuming that the fluorescence is the inverse of the entire lowest energy band is ~2ns[3]. The luminescence lifetimes and quantum yield data for the cyanoaniline triad are presented in Table 4.

7. Even though the diffuseness of the fluorescence spectra prohibit any mirror image correlation for the ortho and meta isomers, the half-

TABLE 4[a]

LUMINESCENCE LIFETIME (τ) AND QUANTUM YIELD (ϕ) DATA FOR CYANOANILINE[b]

Molecule	τ_F(ns)	τ_F^o(ns)		τ_P(s)	ϕ_F	ϕ_P	ϕ_P/ϕ_F
		Abs.[c]	Em.				
<u>o</u>-Cyanoaniline	6.9	22	22	3.65	0.31	0.096	0.31
<u>m</u>-Cyanoaniline	12.9	22	15	2.65	0.87	0.047	0.054
<u>p</u>-Cyanoaniline	3.3	27	33	2.45	0.15	0.11	0.73

[a] Taken from Reference 3.

[b] In ethanol glass at 77°K; the subscripts P and F refer to phosphorescence and fluorescence, respectively.

[c] The absorption data refer to glassy ethanol solutions at 77°K.

widths of the fluorescence and the lowest energy absorption band ($^1L_b \leftarrow {}^1A$) are almost identical (~3000cm^{-1})[3]. In addition, the observed intrinsic emissive lifetimes (22 and 15ns, respectively) agree well with those calculated from the absorption oscillator strength data (~22ns in both cases), assuming the fluorescence to be the inverse of the lowest energy absorption ($^1L_b \leftarrow {}^1A$)[3].

8. The increased structure of the phosphorescence spectra as compared to the fluorescence spectra indicates that the T_1 state is less polar, and consequently contains a smaller admixture of charge-transfer configurations than either ^1L_a-related or the ^1L_b-related states[3].

9. As is the case for the fluorobenzonitriles, the ϕ_P/ϕ_F ratio is largest for the para isomer. This is again attributed to a larger k_{ISC} and a smaller k_F for the para isomer as compared to the other two isomers.

Nitroaniline

The absorption spectra of the ortho, meta and para isomers of the highly-polar nitroaniline are presented in Figures 3 and 4. Luminescence spectra are presented in Figure 5[4]. The following general characteristics may be discerned:

1. The lowest energy band is distinct for all three isomers while the higher energy bands exhibit considerable overlapping.

2. An increase in structure, accompanied by significant band shifts, occurs in going from a non-polar solvent at 300°K to a polar, glassy medium at 77°K. The lowest energy absorption band suffers the largest energy decrease; the energy decrements are ortho, 2700cm^{-1}; meta, 3700cm^{-1}; and para, 5200cm^{-1}. The data for all excitations are collected in Table 5.

Figure 5

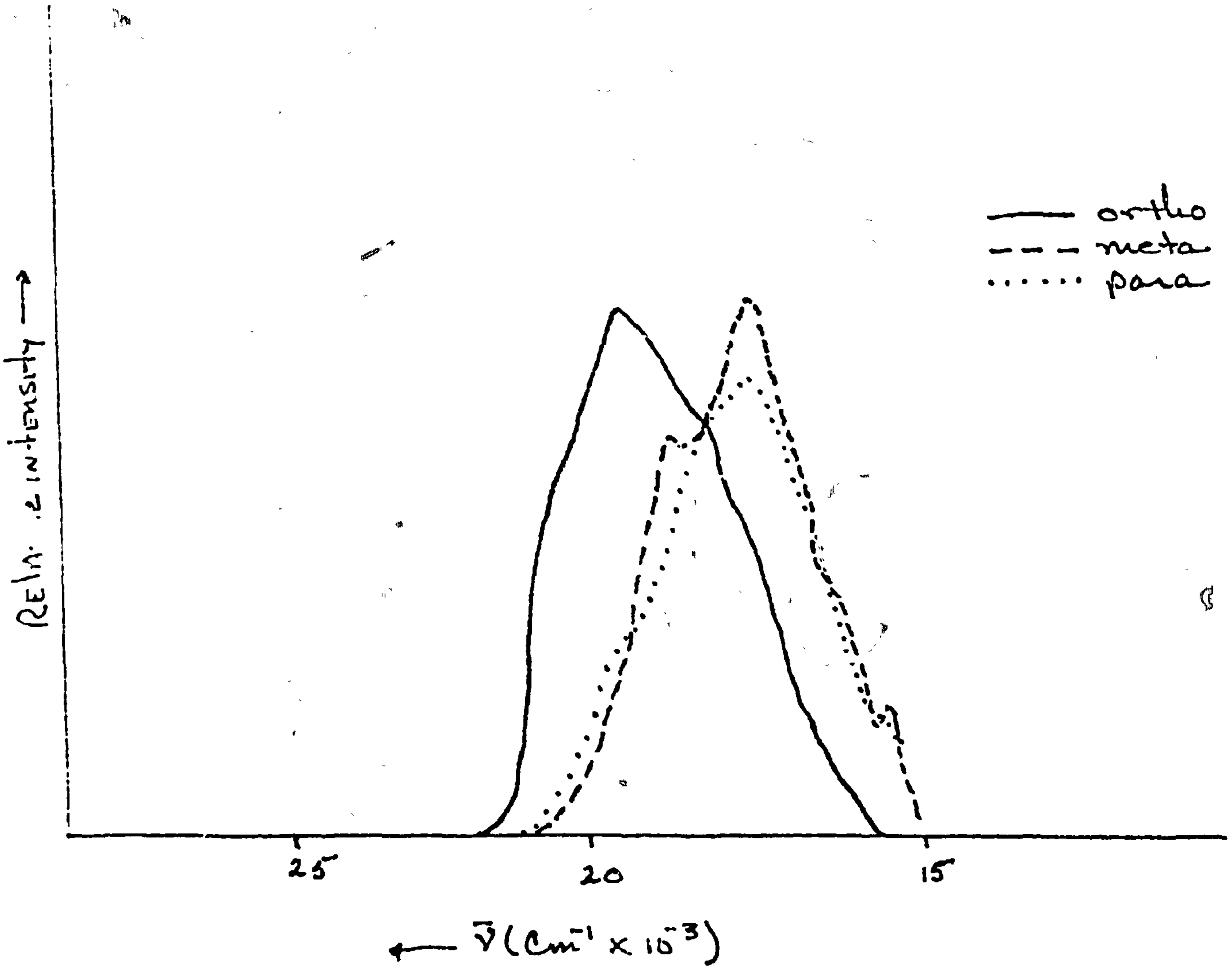


TABLE 5

ABSORPTION DATA FOR NITROANILINE[a]

	Absorption Energy (cm^{-1})		Absorption Intensity
	Band Maximum		ϵ_{max}(f)
	MCH	EPA Glass	MCH
o-Nitroaniline	26,500	23,800	4,800(0.11)
	37,000	35,500	4,600(0.1)
	40,500	38,700	7,000
	43,800	42,700	17,750
m-Nitroaniline	28,700	25,000	2,200(0.04)
	37,200	34,500	4,200(0.08)
	42,000	38,700	17,250
	44,000	42,600	18,200
p-Nitroaniline	31,000	25,970	12,600(0.32)
	33,000- 36,000	32,520	1,500
	41,000	40,000	2,500
	45,500	43,700	6,500

---

[a] The extinction coefficient is denoted ϵ and is cited in units of ℓ mole^{-1} cm^{-1}; the oscillator strengths are denoted f and are taken from reference 6; no attempt was made to estimate f in this work because of severe band overlapping; EPA spectra were run at 77°K; methylcyclohexane spectra were run at 300°K. EPA is an ether, isopentane, alcohol mix in a 5/5/2 (by volume) ratio.

3. The large red-shift of the lowest energy absorption band of the para isomer, which takes place in polar media, uncovers a structured region with apparent origin at 33000cm^{-1}. In addition, the solvatochroism[5] of the 31000cm^{-1} component suggests the existence of at least two other electronic transitions within the lowest energy absorption envelope.

4. The luminescence of the nitroanilines may be summarized as[4]:

--- The ortho and meta isomers do not phosphoresce, regardless of the polarity of the medium or of the excitation energy.

--- The para isomers do not fluoresce in non-polar media, regardless of the excitation energy.

--- A fluorescence of the para isomer is induced in polar media, and its intensity increases upon increasing the solvent polarity.

--- The ratio ϕ_P/ϕ_F for the para isomer depends, in certain polar media, on the excitation energy.

Summary

The study of the above three triads shows certain general trends that are typical of the D-ϕ-A class of molecules:

--- As the polarity of the molecule increases, the L_a-related transition decreases in energy. This is evident in going from fluorobenzonitrile to cyanoaniline (ortho energy decrement - 3270cm^{-1}; meta, 3970cm^{-1}; para, 7100cm^{-1}; all in polar solvent). This phenomenon is also observed within each series, with the energies of the isomers being ordered: $c \approx m > p$. Since the high polarity of p-nitroaniline would be expected to cause a large red-shift of the L_a band, entirely obscuring the L_b band, we feel justified in calling the lowest energy transition of these moledules "L_a-like" in our attempts to correlate polarity with the decrease in the L_a band energy. With this in mind, we find that the L_a-like band of *p*-nitroaniline does indeed lie lower in energy than the corresponding band in *p*-cyanoaniline.

--- If we consider the para isomers from all three triads (Figures 1, 2 and 3), we see that as the polarity of the molecules increases the L_a and L_b bands become less distinct, and finally merge into one absorption envelope in *p*-nitroaniline.

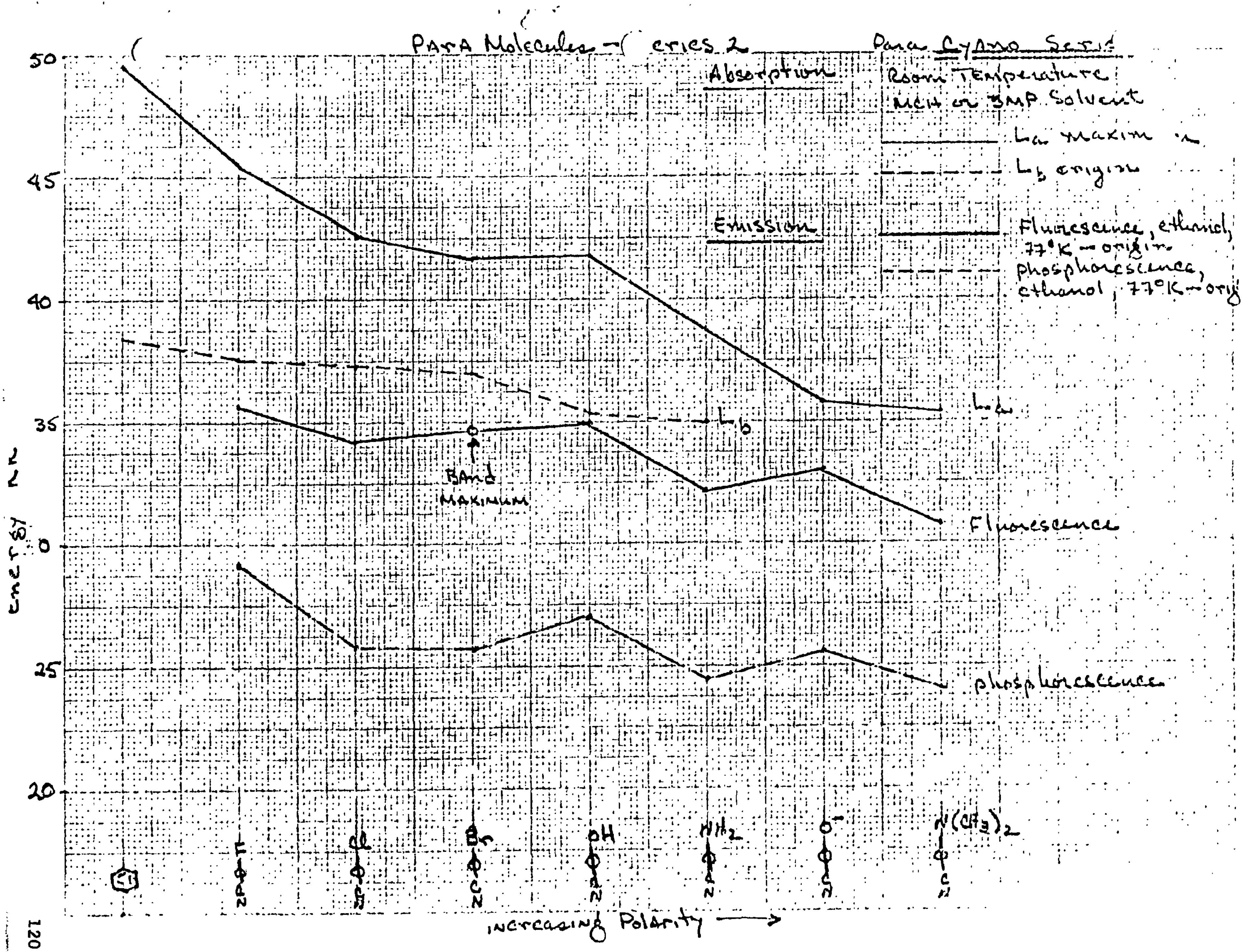
--- In the less polar fluorobenzonitriles and cyanoanilines, fluorescence is from the L_b state, while in the highly-polar nitroanilines, fluorescence is weak or disappears entirely. In this last case, phosphorescence dominates. Also, as the polarity of the molecules increases, ϕ_P/ϕ_F increases.

--- Solvent effects are greater for the para compounds, indicating their greater polarity due to an increased mixing-in of charge-transfer states.

Para Molecules

With this over-view of the general characteristics and trends of D-ϕ-A molecules in mind, we will begin the discussion of Series 1 and 2, considering first the para molecules.

An example of series 2 is the para-cyano series, in which the cyano grouping is held constant while the other substituent is varied in the order of increasing polarity according to our criterion. The absorption and emission data for this series are presented in Figure 6. A most

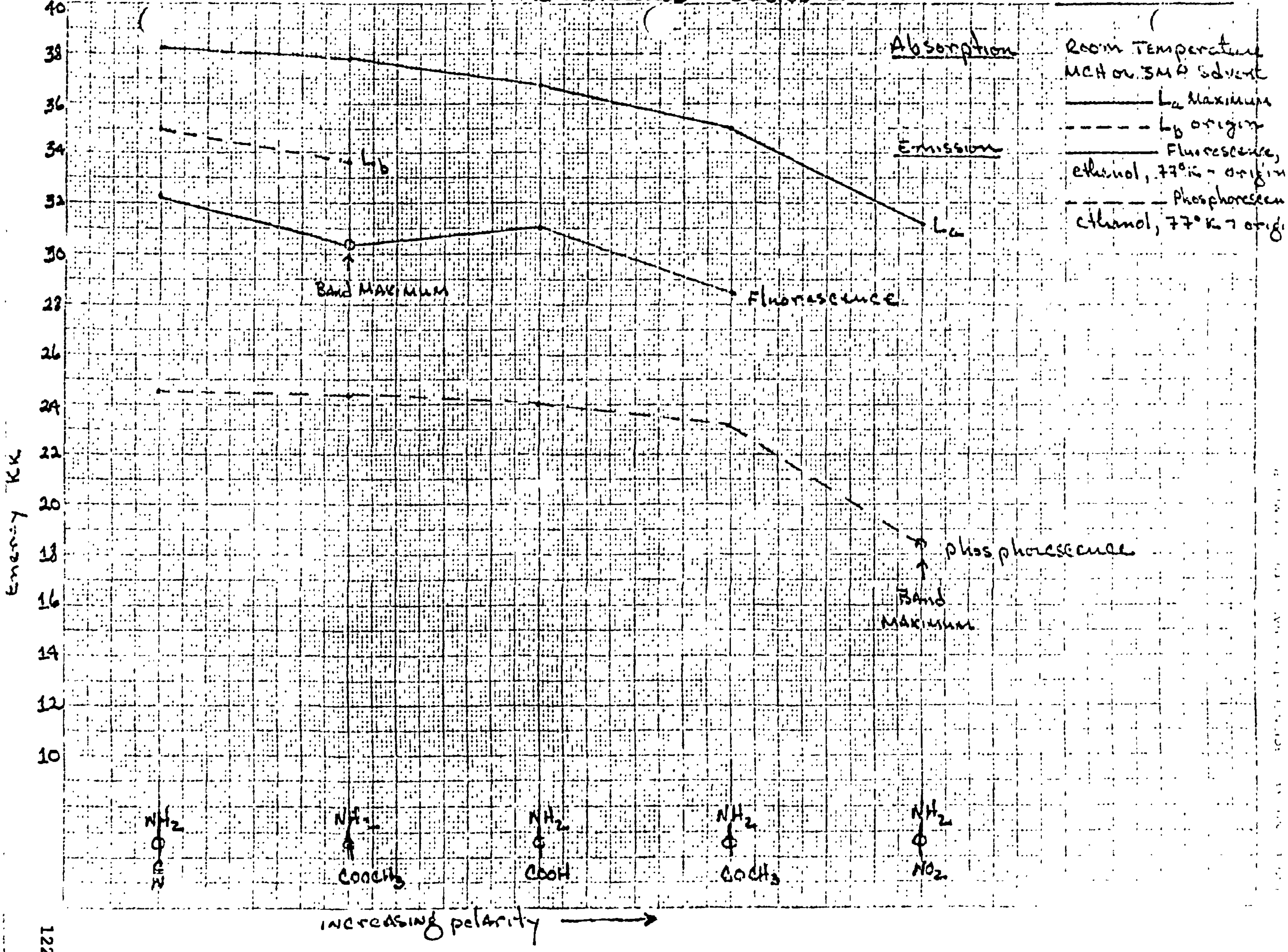

PArA Molecules – (eries 2
Para Cyano Series
Absorption
Room Temperature
MCH or 3MP Solvent
La maxim
Lb origin
Emission
Fluorescence, ethanol, 77°K – origin
phosphorescence, ethanol, 77°K – orig
La
Lb
Fluorescence
phosphorescence
BAnd MAXIMUM
50
45
40
35
30
25
20
energy kK
Cl
Br
OH
NH2
O⁻
N(CH3)2
CN
Increasing Polarity →

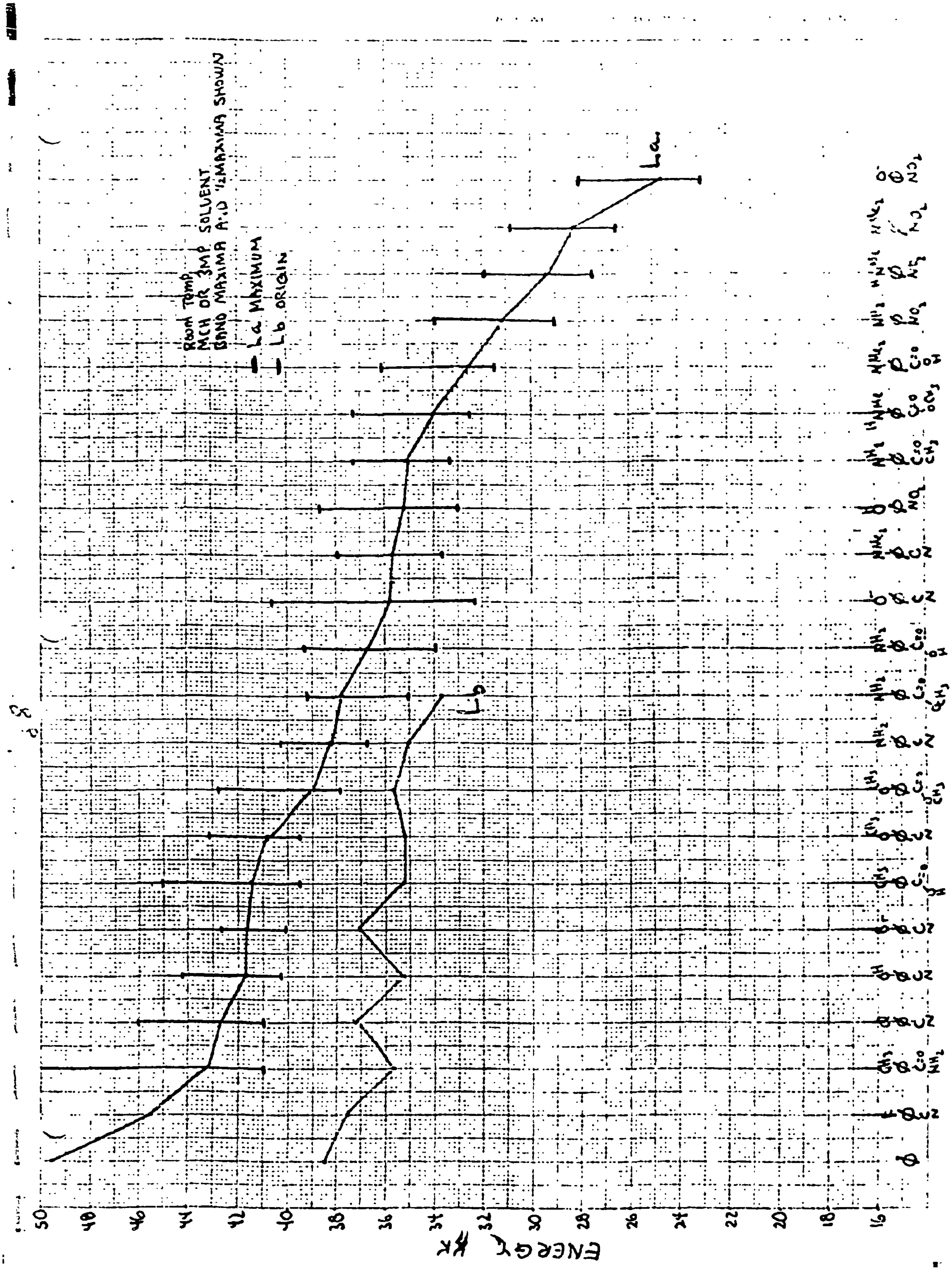
striking feature of this graph is the smooth decrease in energy of the L_a-related band as the polarity of the molecule increases. A similar phenomenon is observed for the energy of the L_b-related band, fluorescence energy, and phosphorescence energy. It is instructive to note that when the polarity increases to the point of p-cyanophenoxide, the L_b band is no longer observed but has been overtaken by the L_a-related band.

The absorption and emission data for the para-amino series, an example of series 1, are presented in Figure 7. This series represents a variation of the second substituent in order of increasing polarity while the amino grouping is held constant. Again, the L_a-related band smoothly decreases in energy as the polarity of the molecule increases. A similar trend is observed for the energy of the L_b-related band, fluorescence energy and phosphorescence energy.

On the basis of the decline in the energy of the L_a band as molecule polarity increases, we feel confident in reversing our criterion: a decline in the energy of the L_a band can be used as a ranking device to construct a series of molecules of increasing polarity. The absorption and emission data for 22 para D-ϕ-A molecules ordered according to decreasing energy of the L_a band are collected in Figures 8 and 9, respectively. The L_a band maxima and half-widths and the L_b origins from the room temperature spectra of molecules in non-polar solvents are plotted in Figure 8. The (0,0) energies (except where denoted by M, in which case band maxima are plotted) of fluorescence and phosphorescence are presented in Figure 9. When the energy of the L_a band has

Para Molecules - Series 1




ROOM TEMP
MCH OR 3MP SOLVENT
BAND MAXIMA AND ½ MAXIMA SHOWN
La MAXIMUM
Lb ORIGIN
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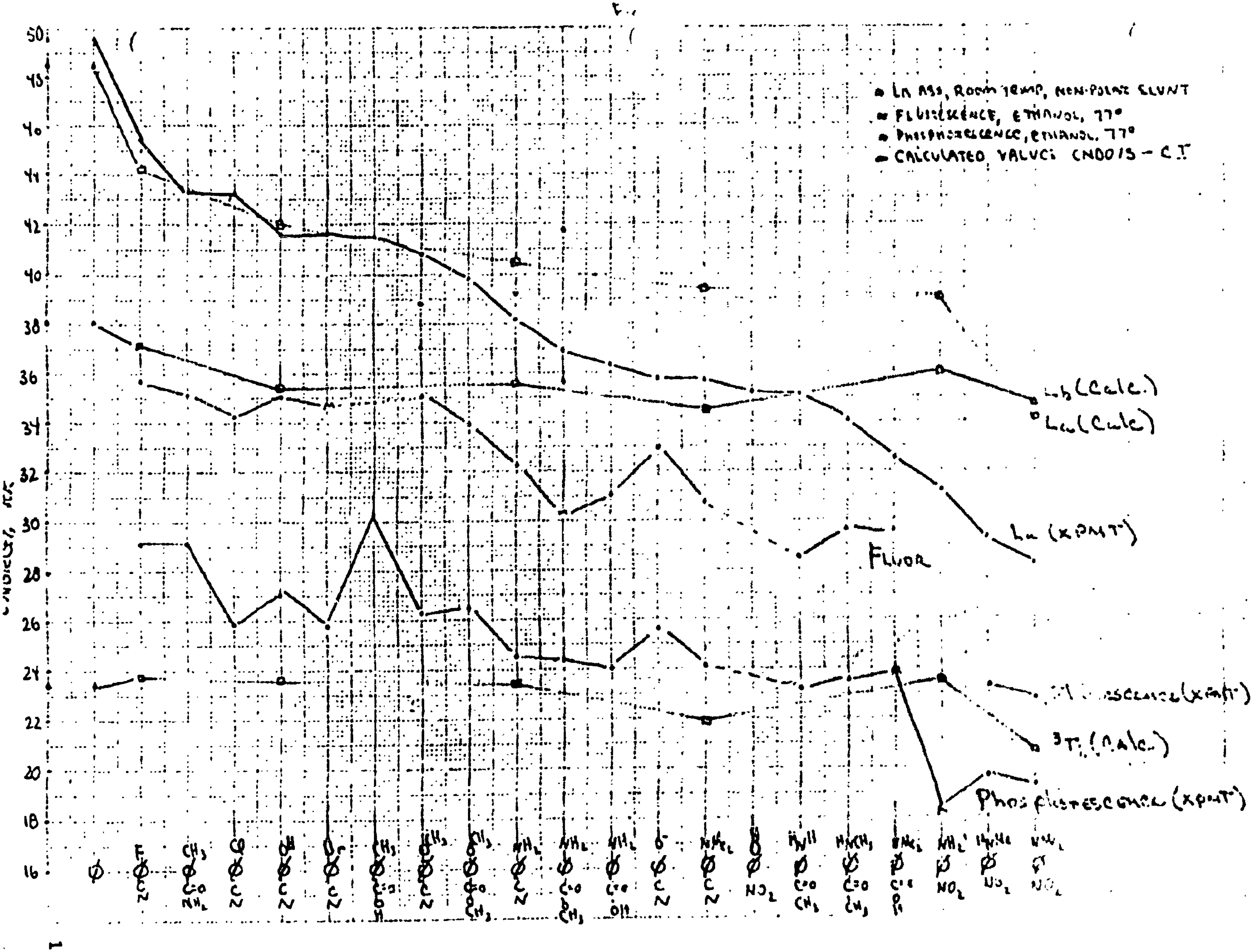

Ln Abs, Room Temp, Non-Polar Solvent
Fluorescence, Ethanol, 77°
Phosphorescence, Ethanol, 77°
Calculated Values CNDO/S – C.I.
Lb (Calc.)
La (Calc.)
La (XPMT)
Fluor
Fluorescence (XPMT)
³T₁ (Calc.)
Phosphorescence (XPMT)
50
48
46
44
42
40
38
36
34
32
30
28
26
24
22
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18
16

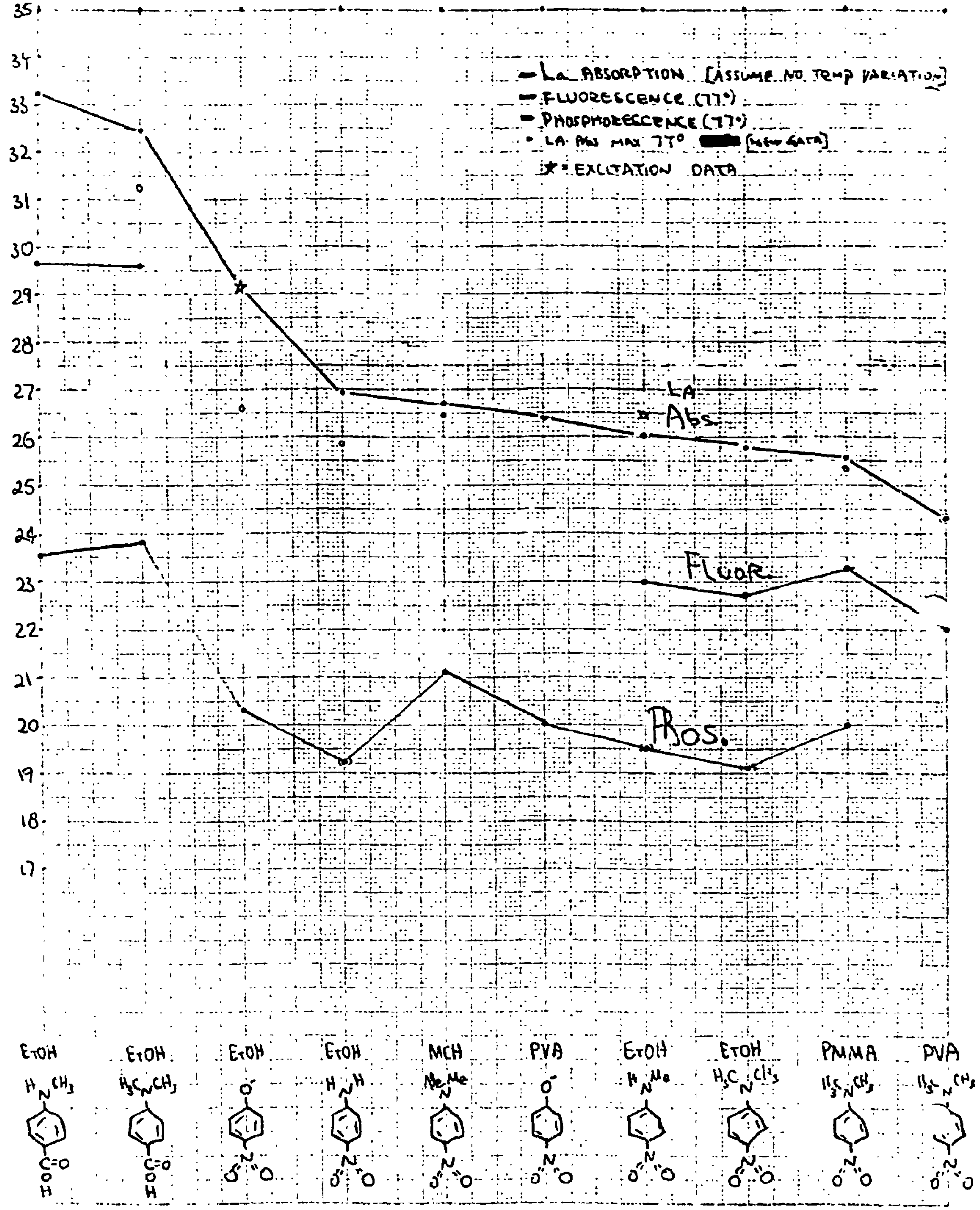
decreased to that found for p-aminobenzoic acid, the L_b band is no longer observed. It is of great interest to investigate those molecules in which the L_a transition may have overtaken the L_b transition as the former decreased in energy. In these molecules we expect that:

1. If the L_a band is lower in energy than the L_b band, an efficient fluorescence pathway ($L_a \rightarrow {}^1A$) is provided, and phosphorescence should decrease in intensity or disappear altogether; and

2. Solvent effects will become more important because of the increased polarity of the ground electronic state and, particularly, the excited electronic state.

In order to utilize point 2, it is useful to view the molecule and its surrounding solvent cage as one distinct absorbing and emitting entity: a particular molecule imbedded in two different solvent cages will become, in effect, two different "molecules". If the energy of the L_a band is then used to order a series of these molecule-solvent species, certain generalizations about fluorescence and phosphorescence may be noted. The absorption and emission data for such a series are presented in Figure 10. As the energy of the L_a band decreases, fluorescence disappears and phosphorescence dominates the emission spectra. According to point 1 above, in these systems the L_a band is lower in energy than the L_b band. Since the L_a state is long-axis polarized and the L_b state is short-axis polarized, it is possible to determine from which state the fluorescence arises by determining the polarization of the emitted light. This is substantiated by our polarization studies: when exciting into the L_a absorption band, the (0,0) fluorescence polarization for p-cyanoaniline is out-of-plane (indicating that fluorescence originates from

Fig. 10



SQUARES TO CENTIMETER

the L_b band), while that for N,N-dimethyl-p-nitroaniline is in-plane (indicating that fluorescence originates from the L_a band).

Ortho and Meta Molecules

A major complication in the analysis of the ortho and meta isomers is the loss of the L_a and L_b designations necessitated by the reduction of symmetry.

The absorption and emission data for four ortho isomers, ranked according to the energy of the first and second absorption bands, are presented in Figure 11. The ϕ_P/ϕ_F ratios decrease across the series. The first absorption band undergoes an intensity increase while the second undergoes an intensity decrease. The absorption and emission for several meta isomers are presented in Figure 12. The overall trends are the same as for the ortho isomers.

Further work in this area will be concentrated on increasing our data base for the ortho and meta isomers so that series 1 and series 2 plots may be made.

COMPUTATIONS

CNDO/s-CI computations were performed for representative D-ϕ-A molecules. The program was obtained from the Quantum Chemistry Program Exchange (QCPE 174) and uses the Mataga-Nishimoto approximation[7] to calculate the two-center repulsion integrals. The thirty lowest mono-excited configurations were included. Molecular geometries were taken from published crystal structures or were generated from similar molecules if the crystal structures were not available.

CK IHO (MAXIMA), EtOH

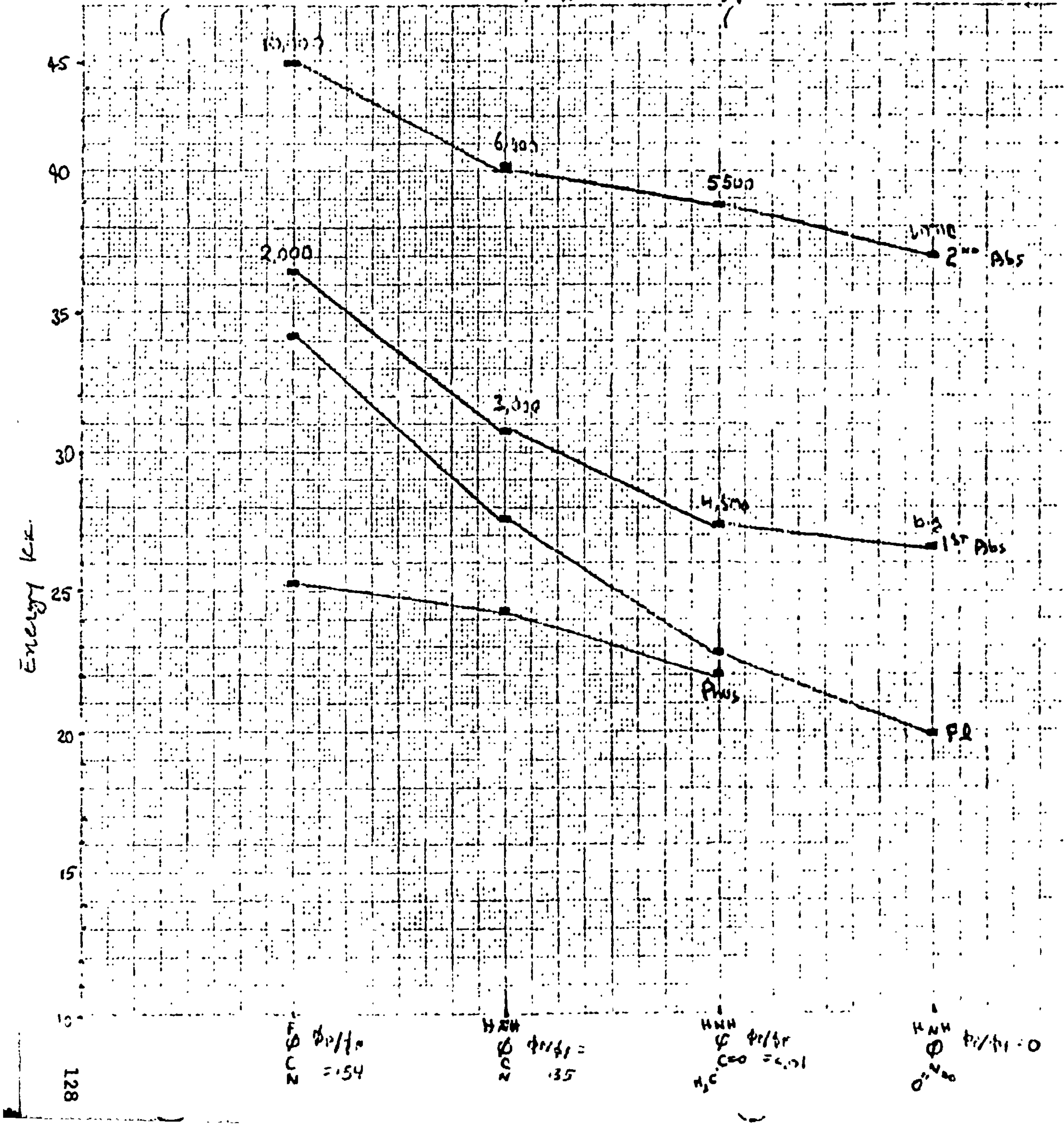
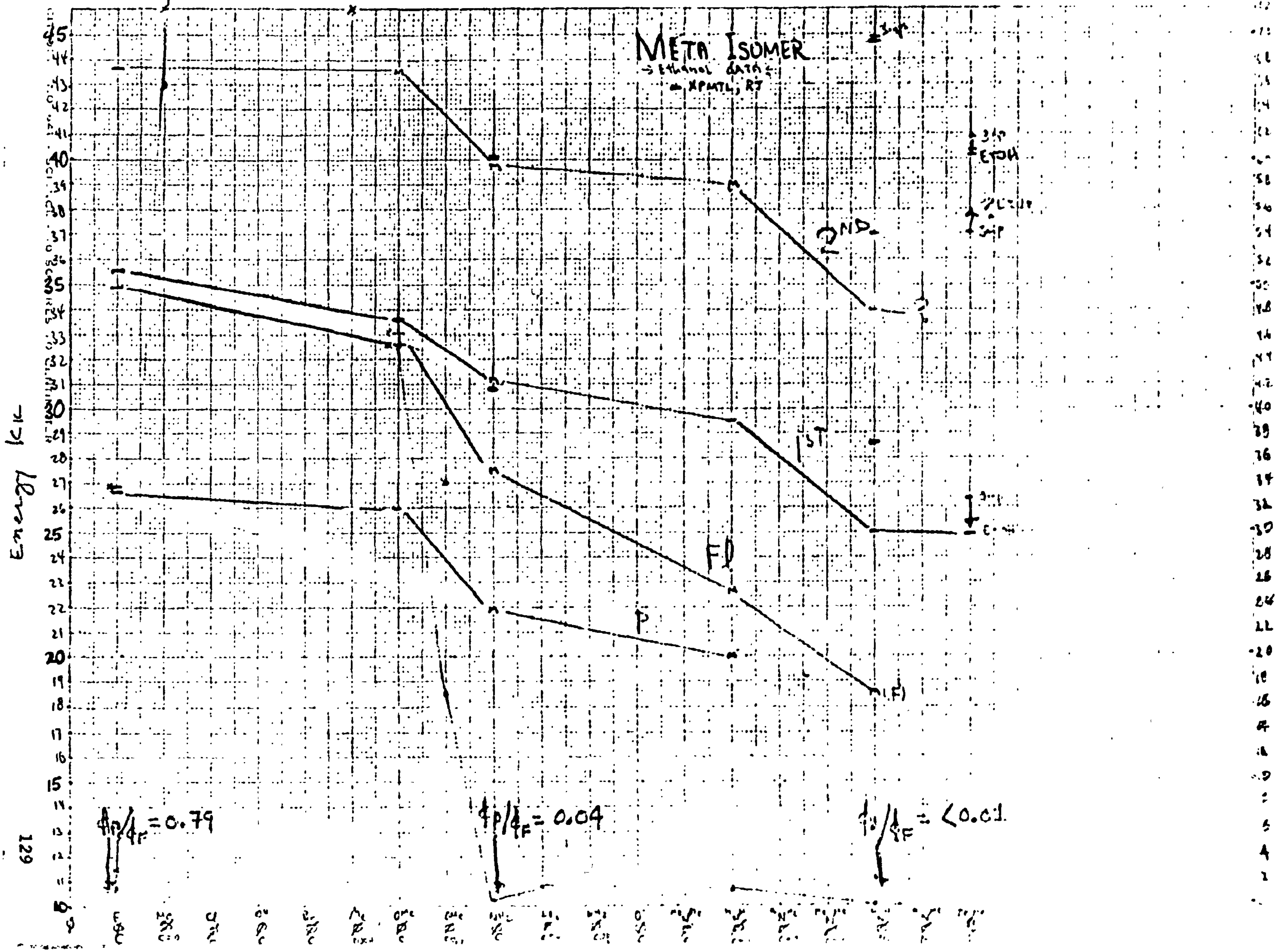


Figure 12



META ISOMER
→ Ethanol data ←
XPMTL; RT
2ND
1ST
FD
P
(F)
EtOH
Energy Kk
45
40
35
30
25
20
15
10
φp/φF = 0.79
φp/φF = 0.04
φp/φF = <0.01

Para Molecules

The calculated maxima of absorption and emission are presented in Figure 9. It is observed that all general characteristics of the experimental data are reproduced. The energy decrements, however, are underestimated. Crossing of the ^1L_a transition over the ^1L_b transition is predicted to occur when molecule polarity has increased to that of N,N-dimethyl-p-nitroaniline.

The existence and characterization of a charge-transfer (CT) transition in D-ϕ-A molecules has been the subject of controversy. According to some authors[8,9,10], the benzene ^1L_a and ^1L_b transitions are essentially undisturbed by the addition of substituents to the benzene ring. Further, as the polarity of the molecules increases, various CT transition (substituent → substituent, and/or ring → substituent) are mixed into the benzene-like transitions. These authors have assigned the intense transition dominating the ultraviolet spectra of most polar D-ϕ-A molecules as primarily charge-transfer in nature.

In order to investigate this problem, we have addressed ourselves to the following two questions:

1. Is there a consistency in the molecular orbital symmetry throughout the series which would allow the above assignment to be unequivocably made?

2. Is there a suitable computational and/or experimental parameter which would indicate clearly the degree of charge-transfer character in a transition?

The symmetries of the molecular orbitals involved in a transition can easily be obtained from the sign of the summed atomic orbital (AO) coefficients contributing to a particular molecular orbital since:

$$\psi = \sum_i c_i \chi_i$$

where ψ = molecular orbital wavefunction, χ_i = ith atomic orbital and c_i = coefficient of the ith atomic orbital.

The molecular orbital symmetries have been found to display a consistent nodal pattern throughout the series, allowing for additional nodes between the ring and substituents. A correlation of the molecular orbital symmetries for these molecules with the molecular orbital symmetries of benzene is shown in Figure 13.

In order to apply the molecular orbital description to a particular electronic transition, the extent of configuration interaction must be examined since CI will mix transitions having different c_i values. We are fortunate to find no significant CI mixing in the ^1L_a transition and little in the ^1L_b transition (see Table 6). We therefore use the nodal description of the molecular orbital exhibiting the maximum contribution to the CI state of interest. This permits an assignment of the bands across the series by molecular orbital symmetry as is presented in Figure 14.

The extent of charge-transfer in a transition can be derived computationally by equating charge-transfer to a movement of electron density -- a movement from the vicinity of the donor to the vicinity of the acceptor. Since electron density in a molecular orbital is equivalent to the square of the AO coefficient, then the amount of electron density lost by the donor substituent in the transition (2 ← 1) may be expressed as:

Fig 13

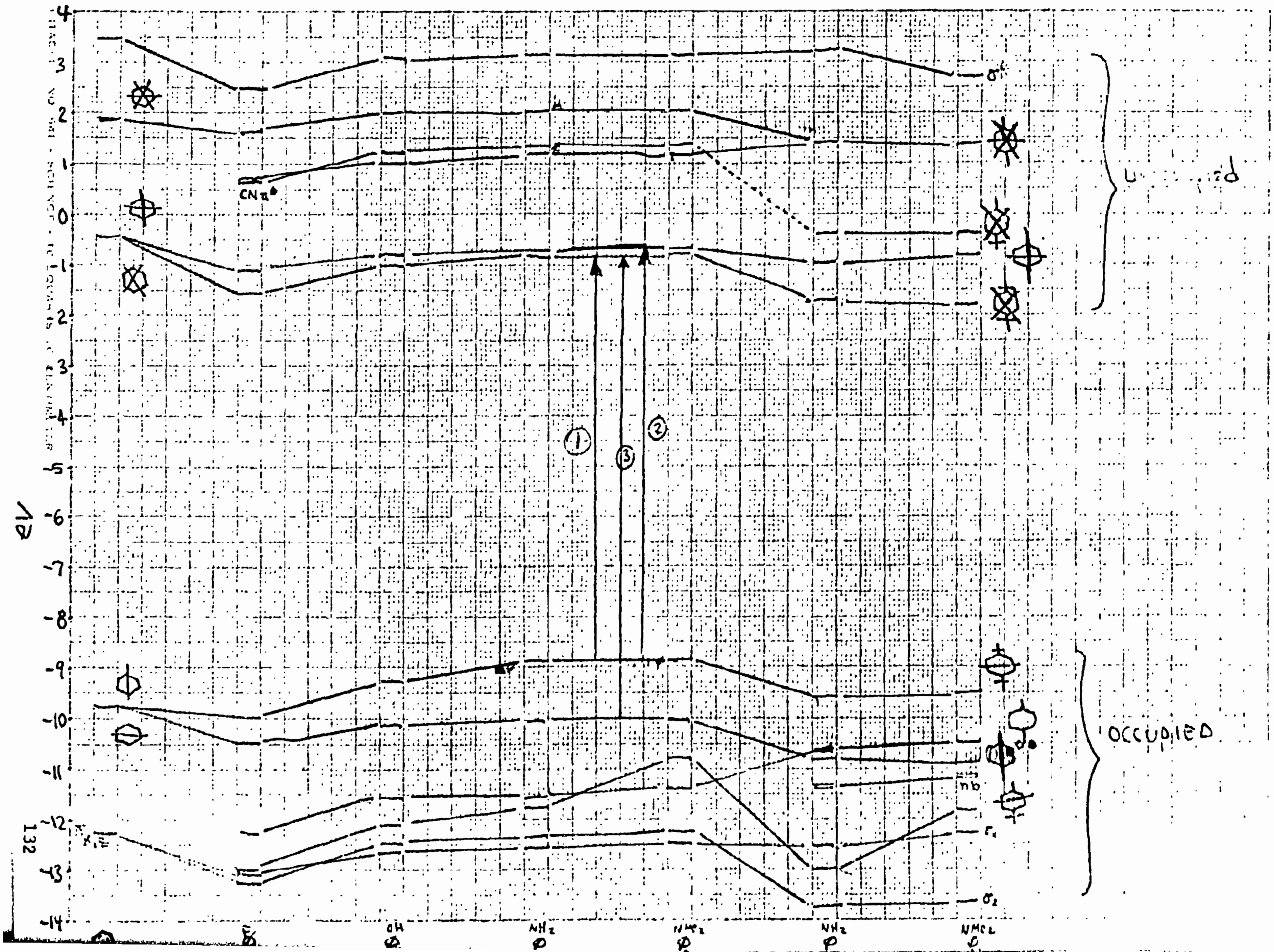

eV
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
CNπ*
σ*
①
③
②
Unoccupied
OCCUPIED
nb
σ₁
σ₂
OH
NH₂
NMe₂
NH₂
NMe₂

TABLE 6

PERCENT CONTRIBUTION OF SCF STATES TO CI STATES[a]

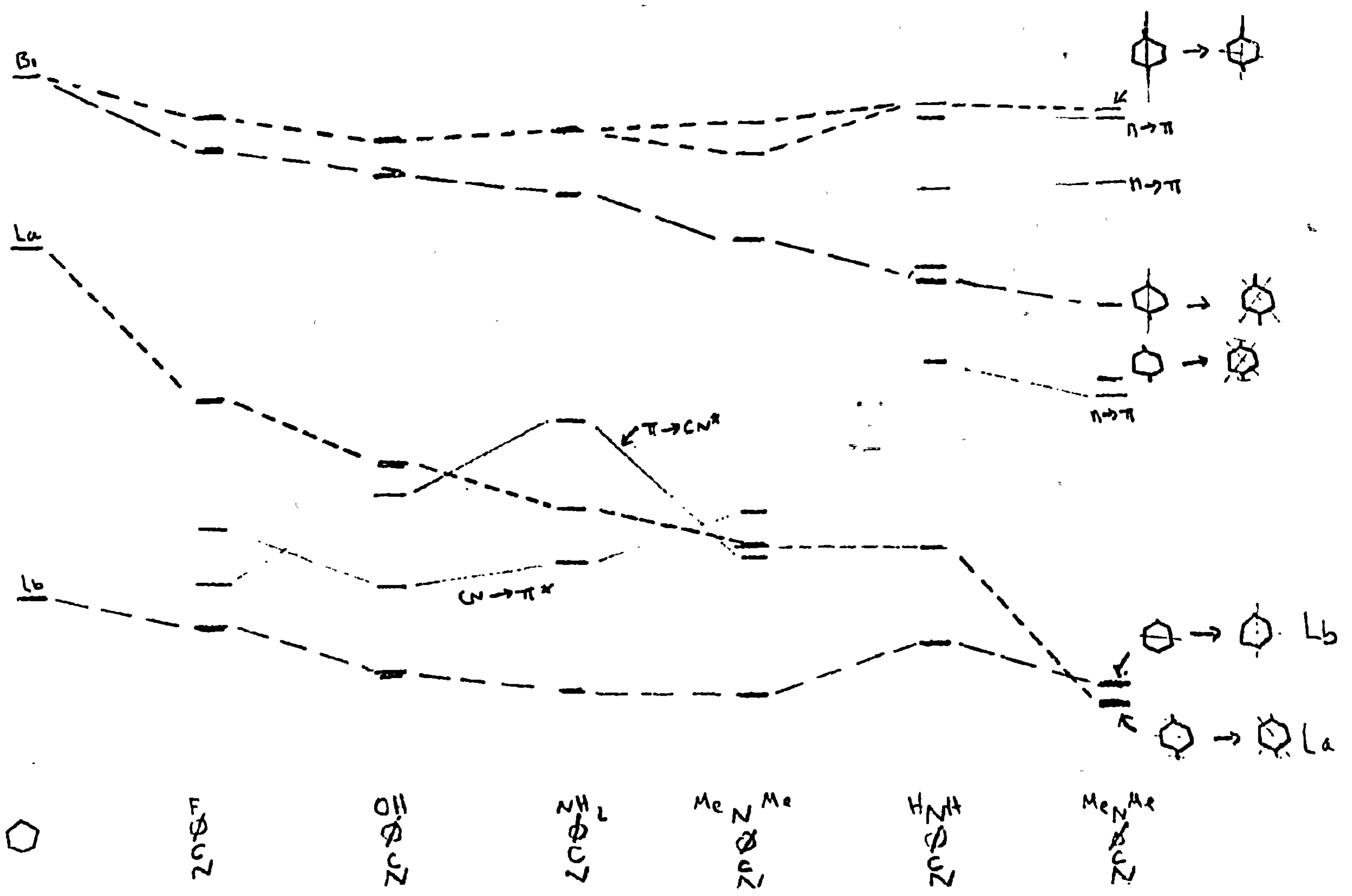
Molecule	${}^1L_a \leftarrow {}^1A$(CI State)	${}^1L_b \leftarrow {}^1A$(CI State)
	% Contribution of a Major Contributing SCF State	
$\mathrm{F\phi CN}$	90.04	52.24
$\mathrm{HO\phi CN}$	92.33	64.85
$\mathrm{H_2N\phi CN}$	93.97	72.00
$\mathrm{Me_2N\phi CN}$	95.01	67.99
$\mathrm{H_2N\phi NO_2}$	95.39	54.09
$\mathrm{Me_2N\phi NO_2}$	97.60	63.34

---

[a] ${}^1L_a \leftarrow {}^1A$ refers to transition #1 of Figure 13.

[b] ${}^1L_b \leftarrow {}^1A$ refers to transition #2 of Figure 13.

Fig. 19


B1
La
Lb
n→π
n→π
n→π
π→CN*
CN→π*
Lb
La
F ø CN
O ø CN
NH2 ø CN
Me N Me ø CN
H N H ø CN
Me N Me ø CN

$$F_D = (\sum_i c_i^2)_{D,1} - (\sum_i c_i^2)_{D,2}$$

$$= X_{D_1} - X_{D_2}$$

where, $(\sum_i c_i^2)_{D,1}$ = sum of the squared AO coefficients of the donor in state 1 and X_{D_1} = electron density of the donor in state 1. Analogously, the amount of electron density gained by the acceptor in the transition (2 ← 1) may be expressed as:

$$F_A = (\sum_i c_i^2)_{A,2} - (\sum_i c_i^2)_{A,1}$$

$$= X_{A_2} - X_{A_1}$$

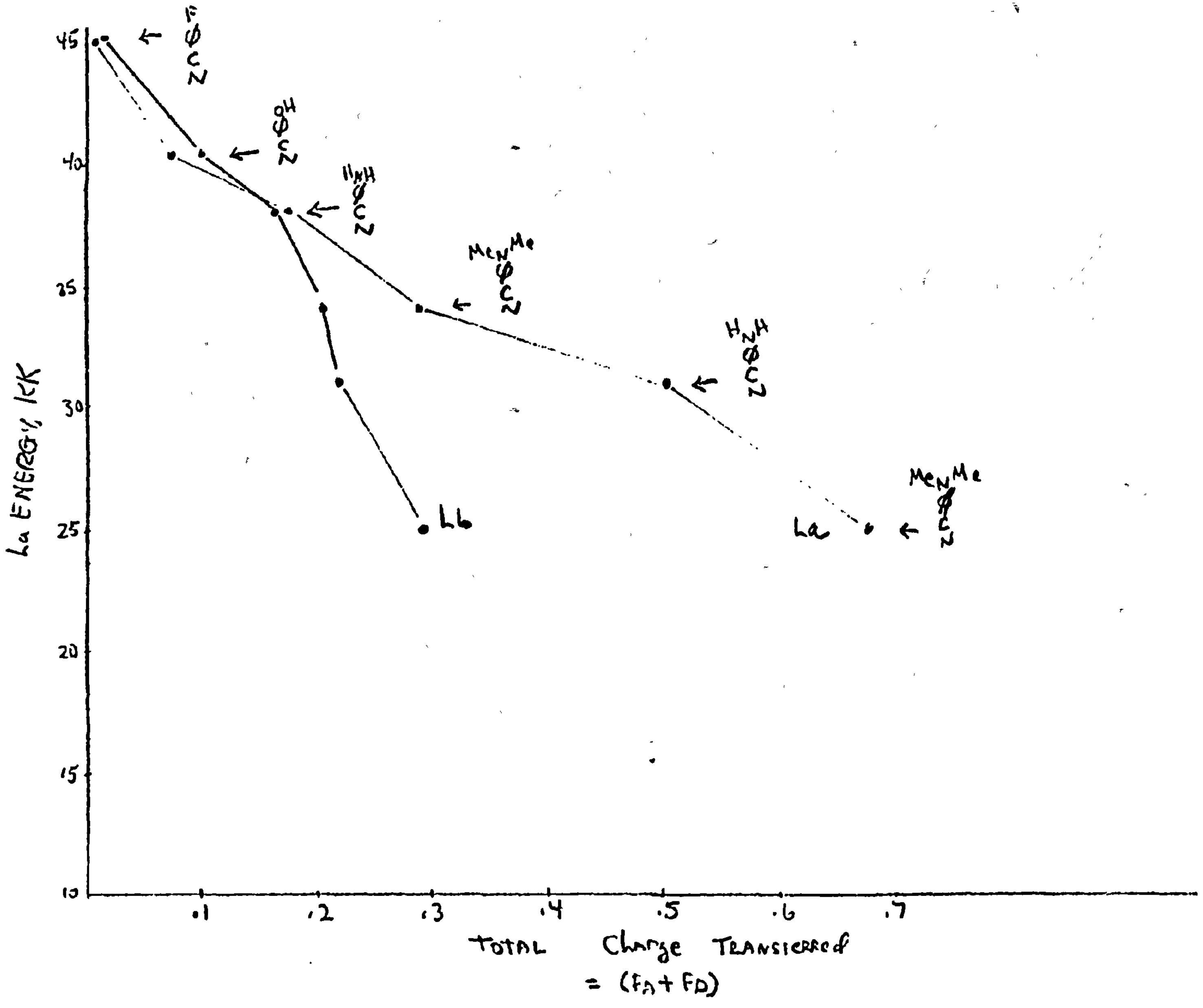
We define $(F_A + F_B)$ as the extent of charge-transfer in the transition (2 ← 1). In Figure 15 we have plotted $(F_A + F_B)$ versus L_a and L_b energies for a number of para isomers. If X_D and X_A for the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) are plotted versus molecule polarity (Figure 16), it is observed that the HOMO is affected more by the donor substituent than the acceptor substituent while the opposite is true for the LUMO.

We conclude that the L_a transition is essentially a Donor → Acceptor charge-transfer transition in the case of highly-polar molecules, and that phosphorescence arises from the ^3L_a state.

Ortho and Meta Molecules

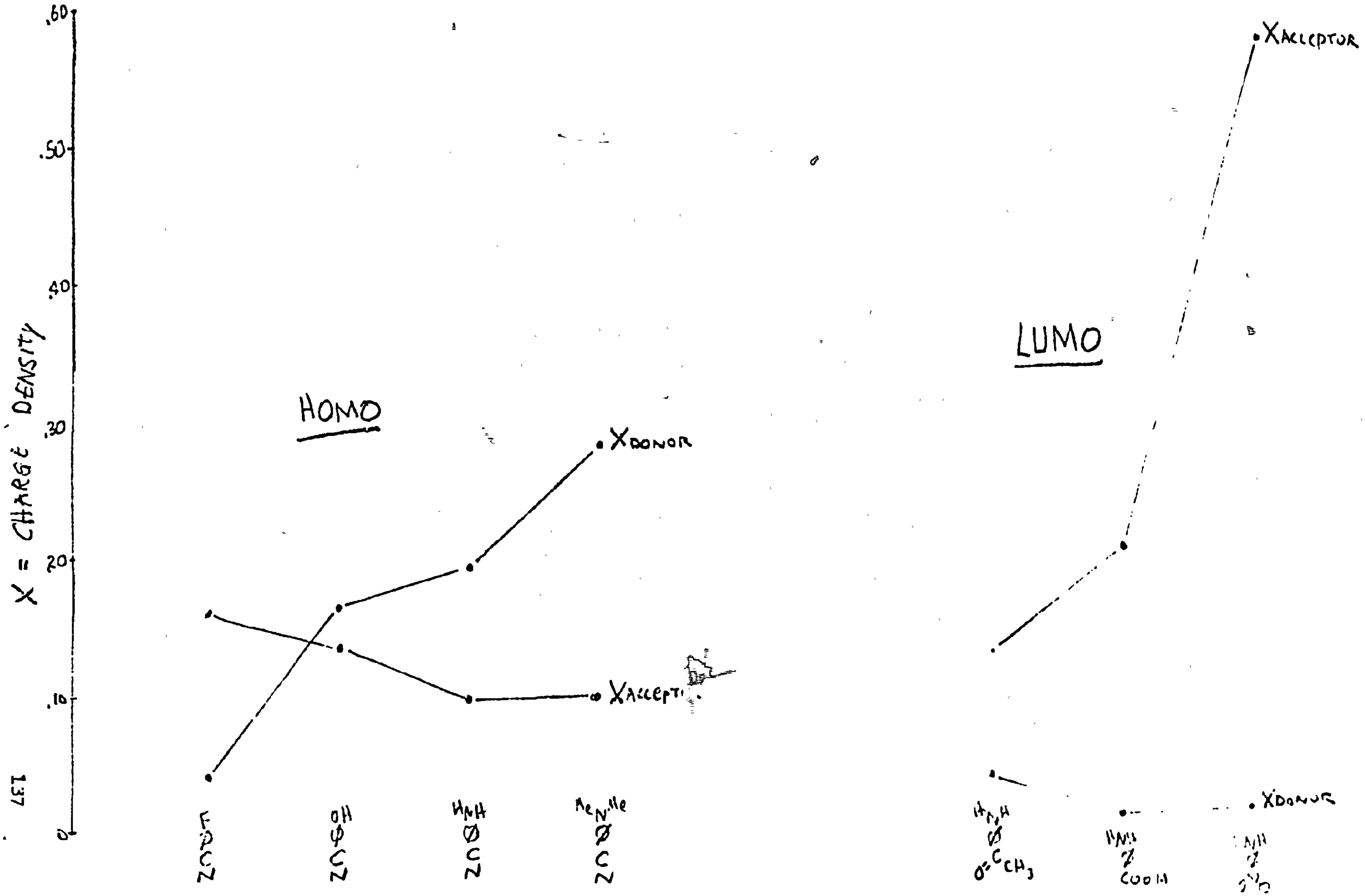
The decrease in symmetry to C_s mixes the L_a and L_b designations to the point that both assignments become meaningless. However, two strong transitions do dominate the ultraviolet region of the spectrum with phosphorescence arising from the second (higher energy) transition as

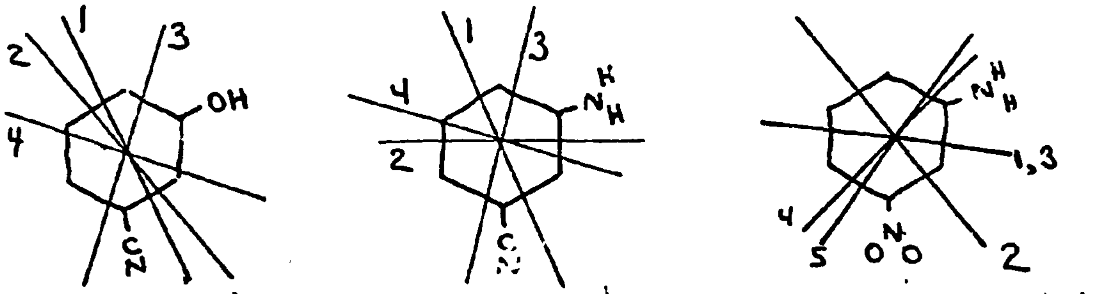
Fig 15



F ϕ CN
OH ϕ CN
HNH ϕ CN
MeNMe ϕ CN
HNH ϕ CN
MeNMe ϕ CN
Lb
La
La ENERGY, KK
45
40
35
30
25
20
15
10
.1
.2
.3
.4
.5
.6
.7
TOTAL Charge TRANSferred
= (fA + fD)

Fig 16


X = CHARGE DENSITY
.60
.50
.40
.30
.20
.10
0
HOMO
LUMO
X DONOR
X ACCEPTOR
X ACCEPTOR
X DONOR
F Ø CN
OH Ø CN
H N H Ø CN
Me N Me Ø CN
COOH



POLARIZATION OF TRANSITIONS

calculated

is the case for the para isomers. The transition dipole moment vectors point in various directions and show no particular order (Figure 17) as expected for these molecules since there are no two completely perpendicular transitions as there are for the para molecules.

A further computational effort is underway to provide examples of series 1 and 2 in the hope that some correlations may be made for the ortho and meta isomers.

EXPERIMENTAL

All compounds were vacuum sublimed and/or recrystallized until further purification did not change the spectra. Solvents did not emit under the conditions used in emission studies. Absorption data were recorded on an Aminco-Bowman Spectrophosphorimeter or a total emission spectrometer built at LSU. Emission spectra were recorded at -77^{o}, with solute concentrations not exceeding 10^{-4} and usually around 10^{-6}, to avoid inner-filter and dimerization effects. All spectra are corrected unless noted otherwise.

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VALENCE-BOND DESCRIPTION OF METAL-ANION INTERACTION

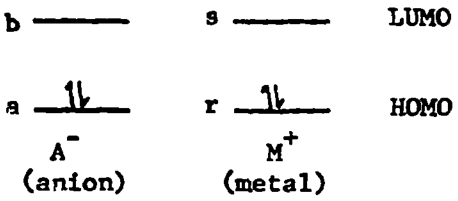
by

Tom Carsey

Graduate Student

The aim is the quantum-mechanical description of partially covalent complexes of metal cations and ordinary inorganic anions, many of which show unusual colors, solubilities, melting points, etc.[1,2]

We begin by assuming that the interaction is restricted to the Highest Occupied Molecular Orbital (HOMO) and the Lowest Unoccupied Molecular Orbital (LUMO) of the metal and the anion. These molecular orbitals are designated



We assume the existance of both substantial spin-orbit coupling and of interelectron repulsion perturbations. We seek the new electric dipole transition moments which are present in the complex, above those found in the isolated species, and the increases in transition probability for excitations which remain primarily localized on the individual ions.

The states and wave functions which we will investigate are given in Figure 1 and Table 1.

Figure 1

VALENCE BOND "STATES"

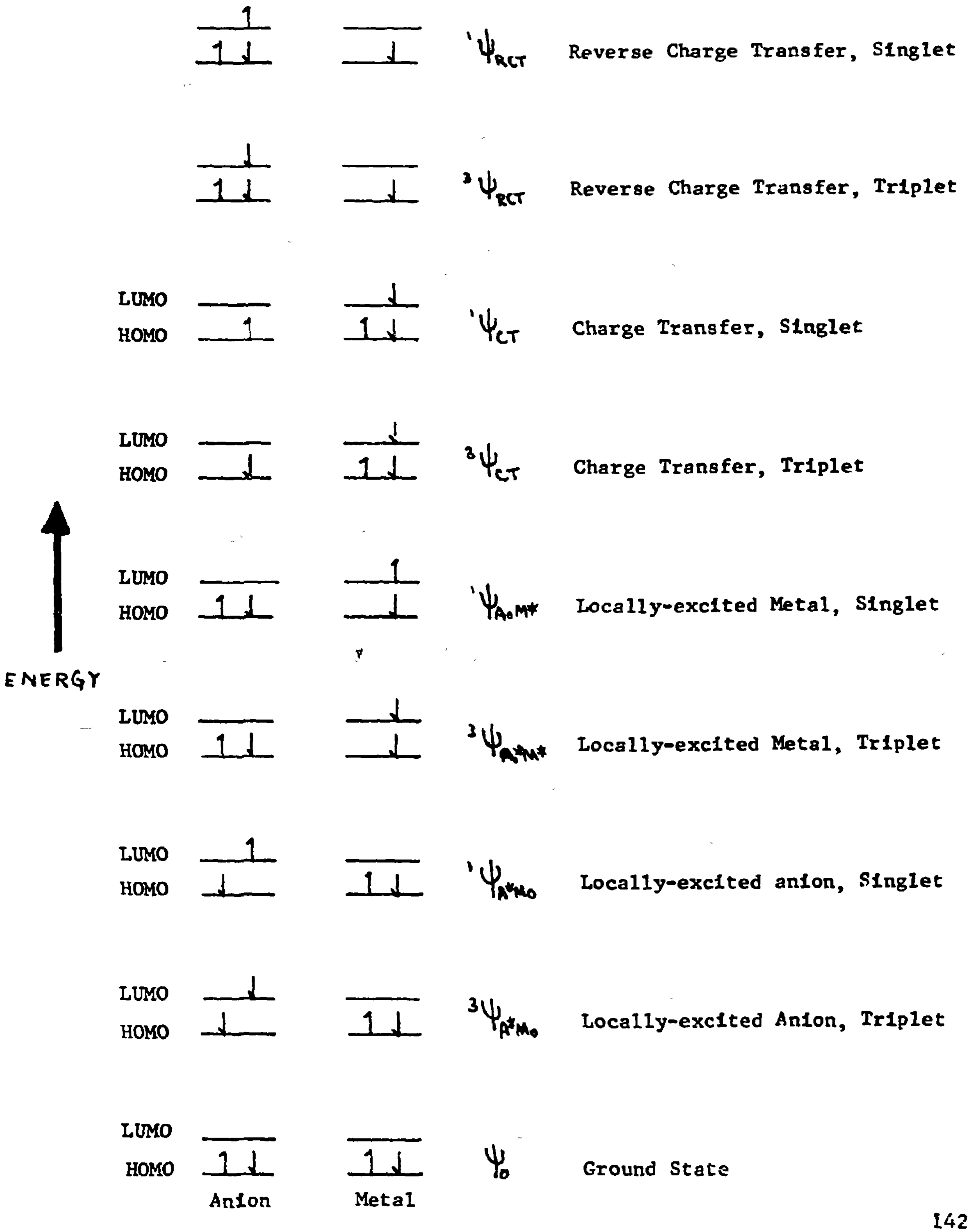


TABLE 1

WAVE FUNCTIONS[a]

VALENCE BOND "STATE"	SINGLETS	TRIPLETS	M_S
Ground State	$\|a\bar{a}r\bar{r}\|$		
$^{\psi}A^{*}_{1}M_{o}$	$\|a\bar{b}r\bar{r}\| + \|\bar{a}b\bar{r}r\|$	$\|abr\bar{r}\|$	+1
		$\|\bar{a}\bar{b}r\bar{r}\|$	-1
		$\|a\bar{b}r\bar{r}\| - \|\bar{a}b\bar{r}r\|$	0
$^{\psi}A_{o}M^{*}_{1}$	$\|a\bar{a}r\bar{s}\| + \|\bar{a}a\bar{r}s\|$	$\|a\bar{a}rs\|$	+1
		$\|a\bar{a}\bar{r}\bar{s}\|$	-1
		$\|a\bar{a}r\bar{s}\| - \|\bar{a}a\bar{r}s\|$	0
$^{\psi}A^{o}M^{o}$ CT	$\|a\bar{r}r\bar{s}\| + \|\bar{a}r\bar{r}s\|$	$\|a\bar{r}rs\|$	+1
		$\|\bar{a}r\bar{r}\bar{s}\|$	-1
		$\|a\bar{r}r\bar{s}\| - \|\bar{a}r\bar{r}s\|$	0
$^{\psi}A^{=}M^{++}$ RCT	$\|a\bar{a}b\bar{r}\| + \|\bar{a}a\bar{b}r\|$	$\|a\bar{a}br\|$	+1
		$\|a\bar{a}\bar{b}\bar{r}\|$	-1
		$\|a\bar{a}b\bar{r}\| - \|\bar{a}a\bar{b}r\|$	0

---

[a] The determinant $|a\bar{a}r\bar{r}|$, for example, represents

$$\frac{1}{4!}\begin{vmatrix} \varphi_a(1)\alpha(1) & \varphi_a(1)\beta(1) & \varphi_r(1)\alpha(1) & \varphi_r(1)\beta(1) \\ \varphi_a(2)\alpha(2) & \varphi_a(2)\beta(2) & \varphi_r(2)\alpha(2) & \varphi_r(2)\beta(2) \\ \varphi_a(3)\alpha(3) & \varphi_a(3)\beta(3) & \varphi_r(3)\alpha(3) & \varphi_r(3)\beta(3) \\ \varphi_a(4)\alpha(4) & \varphi_a(4)\beta(4) & \varphi_r(4)\alpha(4) & \varphi_r(4)\beta(4) \end{vmatrix}$$

where φ_a, φ_r are the highest occupied molecular orbitals of the anion and the metal, respectively. All molecular arbitals are assumed to be orthonormal.

The interactions investigated are

I. Mixing by $1/r_{ij}$ of triplet states into lowest triplet ${}^3\psi_{A*,M_o}$

II. Mixing by $1/r_{ij}$ of singlet states into ground state ψ_o

III. Mixing by spin-orbit coupling of triplet states into ψ_o

IV. Mixing by spin-orbit coupling of singlet states into ${}^3\psi_{A*,M_o}$

V. Transition moment for $\psi_o \rightarrow {}^3\psi_{A*}$ with above perturbations

- - - - - - - - - - -

I. Assume ${}^3\psi_{A*} = a\,{}^3\psi_{A*} + b\,{}^3\psi_{M*} + c\,{}^3\psi_{CT} + d\,{}^3\psi_{RCT}$

where, by first order perturbation theory

$$b = \frac{\int {}^3\psi_{A*}(1/r_{ij})\,{}^3\psi_{M*}}{{}^3E_{A*} - {}^3E_{M*}}$$

We find that b, for any of the three M_s components, is

$$b = \frac{-(bs/ra)}{{}^3E_{A*,M_o} - {}^3E_{A_o,M*}}$$

where

$$(bs/ra) = \iint \varphi_b^*(1)\varphi_s(1)(1/r_{12})\varphi_r^*(2)\varphi_a(2)\,d\tau_1 d\tau_2$$

and

$$c = \frac{H_{bs}^c + 2(bs|rr) - (br|rs) + (aa|bs) - (as|cb)}{{}^3E_{A*,M_o} - {}^3E_{CT}}$$

where

$$H_{bs}^c = \int \varphi_b^*(1)\hat{H}_{(1)}^c\varphi_s(1)\,d\tau(1)$$

and

$$\hat{H}^{c}_{(1)} = \tfrac{1}{2}\nabla^{2}_{(1)} - \frac{Z_{anion}}{r_{1A}} - \frac{Z_{metal}}{r_{1M}}$$

and, finally,

$$d = \frac{H^{c}_{ar} + (rr\,|ar) + (bb\,|ra) + (aa\,|ra)}{{}^{3}E_{A*,M_{o}} - {}^{3}E_{RCT}}$$

II. Assume $\psi'_{o} = a'\psi_{o} + b'\psi_{A*,M_{o}} + c'\psi_{A_{o},M*} + d\psi_{CT} + e\psi_{RCT}$. Then

$$b' = \frac{\int {}^{1}\psi_{o}\,|1/r_{ij}|\,{}^{1}\psi_{A*}\,d\tau}{E_{o} - {}^{1}E_{A*}} = \frac{1}{\sqrt{2}}\frac{(4(ab\,|rr) + 2(aa\,|as) - 2(ar\,|br) + 2H^{c}_{ab})}{E_{o} - {}^{1}E_{A*}}$$

$$c' = \frac{1}{\sqrt{2}}\frac{(4(aa\,|rs) + 2(rr\,|rs) - 2(as\,|ra) + 2H^{c}_{rs}}{E_{o} - {}^{1}E_{M*}}$$

$$d' = \frac{1}{\sqrt{2}}\frac{(2(ar\,|rs) - 4(as\,|rr) - 2(aa\,|sa) + 2H^{c}_{ab}}{E_{o} - {}^{1}E_{CT}}$$

$$e' = \frac{1}{\sqrt{2}}\frac{(4(aa\,|rb) - 2(ab\,|ra) - 2(rr\,|rb) + 2H^{c}_{rb}}{E_{o} - {}^{1}E_{RCT}}$$

III. Assume that $\psi'_{o} = a'\psi_{o} + b''\,{}^{3}\psi_{A*} + c''\,{}^{3}\psi_{M*} + d''\,{}^{3}\psi_{CT} + e''\,{}^{3}\psi_{RCT}$. Then, we find

$$b'' = \frac{\langle {}^{3}\psi_{A*}\hat{H}_{so}\psi_{o}\rangle}{E_{o} - {}^{3}E_{A*}}$$

where the components for $M_{s} = 1, -1$, and 0, in the x, y, and z directions (numerators) are given by:

	$M_S=-1$	$M_S=0$	$M_S=+1$
x	$-\langle a \lvert H'_x \rvert b\rangle$	0	$\langle a \lvert H'_x \rvert b\rangle$
y	$i\langle a \lvert H'_y \rvert b\rangle$	0	$i\langle a \lvert H'_y \rvert b\rangle$
z	0	$-\sqrt{2}\langle a \lvert H'_z \rvert b\rangle$	0

where

$$H'_z = \frac{1}{\sqrt{2}} \hbar A_z \hat{\ell}_z$$

$$iH'_y = \frac{i}{\sqrt{2}} \hbar A_y \hat{\ell}_y$$

$$iH'_x = \frac{i}{\sqrt{2}} \hbar A_x \hat{\ell}_x$$

Similarly, we find the components of the numerator of c" to be

	$M_S=-1$	$M_S=0$	$M_S=+1$
x	$-\langle r \lvert H'_x \rvert s\rangle$	0	$\langle r \lvert H'_x \rvert s\rangle$
y	$i\langle r \lvert H'_y \rvert s\rangle$	0	$i\langle r \lvert H'_y \rvert s\rangle$
z	0	$\frac{1}{\sqrt{2}}\langle r \lvert H'_z \rvert s\rangle$	0

The components of the numerator d" are

	$M_S=-1$	$M_S=0$	$M_S=+1$
x	$-\langle a \lvert H'_x \rvert s\rangle$	0	$-\langle a \lvert H'_x \rvert s\rangle$
y	$i\langle a \lvert H'_y \rvert s\rangle$	0	$-i\langle a \lvert H'_y \rvert s\rangle$
z	0	$\frac{1}{\sqrt{2}}\langle a \lvert H'_z \rvert s\rangle$	0

The components of the numerator of e" are

	$M_S=-1$	$M_S=0$	$M_S=+1$
x	$\langle r \vert H'_x \vert b\rangle$	0	$-\langle r \vert H'_x \vert b\rangle$
y	$-i\langle r \vert H'_y \vert b\rangle$	0	$-i\langle r \vert H'_y \vert b\rangle$
z	0	$\frac{1}{\sqrt{2}}\langle r \vert H'_z \vert b\rangle$	0

IV. Assume that ${}^3\psi'_{A*}= a''''\,{}^3\psi_{A*}+b''''\,{}^1\psi_o+c''''\,{}^1\psi_{A*}+d''''\,{}^1\psi_{M*}+e''''\,{}^1\psi_{CT}+f''''\,{}^1\psi_{RCT}$

$$b'''' = b'' = \frac{\langle {}^3\psi_{A*}H_{so}\,{}^1\psi_o\rangle}{E_o-{}^3E_{A*}}$$

		$M_S=-1$	$M_S=0$	$M_S=+1$
	x	$\frac{1}{\sqrt{2}}(\langle a \vert H_x \vert a\rangle-\langle b \vert H_x \vert b\rangle)$	0	$\frac{1}{\sqrt{2}}(\langle b \vert H_x \vert b\rangle-\langle a \vert H_x \vert a\rangle)$
a'''	y	$\frac{i}{\sqrt{2}}(\langle a \vert H_y \vert a\rangle-\langle b \vert H_y \vert b\rangle)$	0	$\frac{i}{\sqrt{2}}(-\langle b \vert H_x \vert b\rangle+\langle a \vert H_y \vert a\rangle)$
	z	0	$\langle a \vert H_z \vert a\rangle-\langle b \vert H_z \vert b\rangle$	0

d'''' 0

		$M_S=-1$	$M_S=0$	$M_S=+1$
	x	$\frac{1}{\sqrt{2}}\langle b \vert H_x \vert s\rangle$	0	$\frac{1}{\sqrt{2}}\langle b \vert H_x \vert s\rangle$
e''''	y	$\frac{i}{\sqrt{2}}\langle b \vert H_y \vert s\rangle$	0	$-\frac{i}{\sqrt{2}}\langle b \vert H_y \vert s\rangle$
	z	0	$-\langle b \vert H_z \vert s\rangle$	0

		$M_S=-1$	$M_S=0$	$M_S=+1$
	x	$\frac{1}{\sqrt{2}}\langle r \vert H_x \vert a \rangle$	0	$\frac{-1}{\sqrt{2}}\langle r \vert H_x \vert a \rangle$
f''''	y	$\frac{i}{\sqrt{2}}\langle r \vert H_y \vert a \rangle$	0	$\frac{i}{\sqrt{2}}\langle r \vert H_y \vert a \rangle$
	z	0	$\langle r \vert H_z \vert a \rangle$	0

V. Transition Dipole Moments

The oscilator strength f for a transition $\psi_2 \leftarrow \psi_1$ is related to the transition dipole moment by

$$f \propto \bar{M} = \int \psi_1 \sum_i e\bar{r}\psi_2 d\tau$$

We evaluate $\bar{M}$ for the transition ${}^3\psi_{A*,M_o} \leftarrow {}^1\psi_o$ which obtains intensity by mixing into the ground or excited states. We investigate:

1. Mixing of triplets into ψ_o by spin-orbit coupling.
2. Mixing of singlets into ψ_o by interelectron repulsions.

The resulting integrals $\bar{M}$, for each case, are interpreted with respect to first or second order nature and whether they represent added intensity conferred, by the effects of complexing, on a localized transition. "First-order" means that a single perturbation is required for the transition to occur; "second-order" means that both $1/r_{ij}$ and spin-orbit coupling must be present. (The list, as given, contains some redundancies but is presented complete in order to provide ground state or excited state referencing). We have neglected static dipole moments. The results are given in Tables 2 and 3.

TABLE 2

INVESTIGATION OF GROUND STATE MIXING

(a) TRIPLETS

1. Mixing of ($^3A_1^*, M_o$) into $^1\psi_o$	Value, Order of $\overline{M}$
$^1\psi_o + {}^3\psi_{A*} \rightarrow {}^3\psi_{A*}$	0
" → " $+{}^3\psi_{M*}$	0
" → " $+{}^3\psi_{CT}$	2nd order
" → " $+{}^3\psi_{RCT}$	2nd order
2. Mixing of ($A_o, {}^3M_1^*$) into $^1\psi_o$	
$^1\psi_o + {}^3\psi_{M*} \rightarrow {}^3\psi_{A*}$	0
" + " → " $+{}^3\psi_{M*}$	0
" + " → " $+{}^3\psi_{CT}$	2nd order
" + " → " $+{}^3\psi_{RCT}$	2nd order
3. Mixing of $^3\psi_{CT}$ into $^1\psi_o$	
$^1\psi_o \div {}^3\psi_{CT} \rightarrow {}^3\psi_{A*}$	1st order, =§
" + " → " $+\psi_{M_1^*}$	1st & 2nd order
" + " → " $+{}^3\psi_{CT}$	1st order, same as §
" + " → " $+{}^3\psi_{RCT}$	1st order, same as §

TABLE 2 cont.

(a) TRIPLETS
(cont.)

4. Mixing of $^3\psi_{RCT}$ into $^1\psi_o$	Value, Order of $\overline{M}$
$^1\psi_o + {}^3\psi_{RCT} \rightarrow {}^3\psi_{A*}$	1st order = ‡
" + " → " $+\psi_{M*}$	1st & 2nd order
" + " → " $+{}^3\psi_{CT}$	1st order, same as ‡
" + " → " $+{}^3\psi_{RCT}$	1st order, same as ‡

(b) SINGLETS

5. Mixing of $^1\psi_{A*,M_o}$ into $^1\psi_o$	Value, Order of $\overline{M}$
$^1\psi_o + {}^1\psi_{A*} \rightarrow {}^3\psi_{A*}$	0
" + " → " $+{}^1\psi_o$	2nd order
" + " → " $+{}^1\psi_{A*}$	a,b only*, 1st order
" + " → " $+{}^1\psi_{M*}$	0
" + " → " $+{}^1\psi_{CT}$	1st & 2nd order
" + " → " $+{}^1\psi_{RCT}$	1st & 2nd order

6. Mixing of $^1\psi_{A_o,M_1^*}$ into $^1\psi_o$	
$^1\psi_o + {}^1\psi_{A_o,M_1^{**}} \rightarrow {}^3\psi_{A*}$	0
" + " → " $+{}^1\psi_o$	2nd order
" + " → " $+{}^1\psi_{A*}$	a,b only*, 1st order
" + " → " $+{}^1\psi_{M_1^*}$	0
" + " → " $+{}^1\psi_{CT}$	2nd order
" + " → " $+{}^1\psi_{RCT}$	2nd order

TABLE 2 cont.

(b) SINGLETS
(cont.)

7. Mixing of $^1\psi_{CT}$ into $^1\psi_o$	Value, Order of $\overline{M}$
$^1\psi_o + {}^1\psi_{CT} \rightarrow {}^3\psi_{A*}$	0
" + " → " $+ {}^1\psi_{A*}$	a,b only[a], 1st order
" + " → " $+ {}^1\psi_{M_1^*}$	0
" + " → " $+ {}^1\psi_{CT}$	no added intensity due to $^1\psi_{CT}$ in ψ_o
" + " → " $+ {}^1\psi_{RCT}$	"
8. Mixing of $^1\psi_{RCT}$ into $^1\psi_o$	
Similar to 7.	

[a] "a,b only" means that this transition is localized on anion.

TABLE 3

INVESTIGATION OF EXCITED STATE MIXING

(a) TRIPLETS

9. Mixing of $^3\psi_{A_o,M_1^*}$ into Excited State	Value, Order of $\bar{M}$
$^1\psi_o \rightarrow {}^3\psi_{A^*} + {}^3\psi_{M_1^*}$	0
" $+{}^3\psi_{A^*} \rightarrow {}^3\psi_{A^*} + {}^3\psi_{M_1^*}$	0
" $+{}^3\psi_{M_1^*} \rightarrow$ " + "	0
" $+{}^3\psi_{CT} \rightarrow$ " + "	1st & 2nd order increase
" $+{}^3\psi_{RCT} \rightarrow$ " + "	1st & 2nd order increase
10. Mixing of $^3\psi_{CT}$ into Excited State	
$^1\psi_o \rightarrow {}^3\psi_{A^*} + {}^3\psi_{CT}$	0
" $+{}^3\psi_{A^*} \rightarrow {}^3\psi_{A^*} + {}^3\psi_{CT}$	2nd order effect only
" $+{}^3\psi_{M_1^*} \rightarrow$ " + "	2nd order effect only
" $+{}^3\psi_{CT} \rightarrow$ " + "	no add. intensity due to $^3\psi_{CT}$ in excited state
" $+{}^3\psi_{RCT} \rightarrow$ " + "	"

TABLE 3 cont.

(a) TRIPLETS
(cont.)

11. Mixing of $^3\psi_{RCT}$ into Excited State		Value, Order of $\overline{M}$
$^1\psi_o$	$\rightarrow {}^3\psi_{A*}+{}^3\psi_{RCT}$	0
$^1\psi_o+{}^3\psi_{A*}$	$\rightarrow$ " + "	2nd order effect only
$^1\psi_o+{}^3\psi_{M^*_1}$	$\rightarrow$ " + "	2nd order effect only
$^1\psi_o+{}^3\psi_{CT}$	$\rightarrow$ " + "	no add. intens. due to $^3\psi_{RCT}$ in ψ_o
$^1\psi_o+{}^3\psi_{RCT}$	$\rightarrow$ " + "	"

(b) SINGLETS

12. Mixing of $^1\psi_o$ into $^3\psi_1$		Value, Order of $\overline{M}$
$^1\psi_o$	$\rightarrow {}^3\psi_{A*}+{}^1\psi_o$	0
$^1\psi_o+{}^1\psi_{A*}$	$\rightarrow {}^3\psi_{A*}+{}^1\psi_o$	2nd order increase
" $+{}^1\psi_{M^*_1}$	$\rightarrow$ " + "	2nd order increase
" $+{}^3\psi_{CT}$	$\rightarrow$ " + "	2nd order increase
" $+{}^1\psi_{RCT}$	$\rightarrow$ " + "	2nd order increase

TABLE 3 cont.

(b) SINGLETS
(cont.)

13. Mixing of $^1\psi_{A*}$ into Excited State ($^1\psi_{M*}$ will not mix into ψ_o)	Value, Order of $\overline{M}$
$^1\psi_o \rightarrow {}^3\psi_{A*} + {}^1\psi_{A*}$	1st order = a,b only
$^1\psi_o + {}^1\psi_{A*} \rightarrow$ " + "	1st order = a,b only
$^1\psi_o + {}^1\psi_{M^*_1} \rightarrow$ " + "	1st order = a,b only
$^1\psi_o + {}^1\psi_{CT} \rightarrow$ " + "	1st & 2nd order
$^1\psi_o + {}^1\psi_{RCT} \rightarrow$ " + "	1st & 2nd order

14. Mixing of $^1\psi_{CT}$ into Excited State	
$^1\psi_o \rightarrow {}^3\psi_{A*} + {}^1\psi_{CT}$	1st order = 0
$^1\psi_o + {}^1\psi_{A*} \rightarrow$ " + "	1st & 2nd order
$^1\psi_o + {}^1\psi_{M^*_1} \rightarrow$ " + "	1st & 2nd order
$^1\psi_o + {}^1\psi_{CT} \rightarrow$ " + "	1st order = 0
$^1\psi_o + {}^1\psi_{RCT} \rightarrow$ " + "	1st order = 0

TABLE 3 cont.

(b) SINGLETS
(cont.)

15. Mixing of ${}^1\psi_{RCT}$ into Excited State	Value, Order of $\bar{M}$
${}^1\psi_o \rightarrow {}^3\psi_{A*} + {}^1\psi_{CT}$	1st order increase = #
${}^1\psi_o + {}^1\psi_{A*} \rightarrow$ " + "	1st & 2nd order
${}^1\psi_o + {}^1\psi_{M^*_1} \rightarrow$ " + "	1st & 2nd order
${}^1\psi_o + {}^1\psi_{CT} \rightarrow$ " + "	1st order = #
${}^1\psi_o + {}^1\psi_{RCT} \rightarrow$ " + "	1st order = #

The preliminary results are

1. Covalency (mixing of $^3\psi_{CT}$ into ψ_o) will tend to enhance the singlet → triplet transition dipole moment.

2. Triplet states which acquire some charge transfer (mixing of $^1\psi_{CT}$ into $^3\psi_{A*,M_o}$) will have a higher singlet → triplet transition dipole moment.

Aside from second order perturbations (transitions 5 and 6 of Table 3, for example), the only mechanism for the enhancement of the singlet → triplet transition moment is the existence of nearby charge-transfer states. A system which contains such states as well as a heavy metal will be the best systems for the observation of the enhanced singlet → triplet transition.

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MATRIX ELEMENTS OF MONO-EXCITED SLATER DETERMINANTS CONSTRUCTED FROM AXIAL SPIN-ORBITALS

by

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The following is a compilation of matrix elements of zero-, one-, and two-electron operators between various Slater determinantal wavefunctions. It is an initial effort in the process of generating such elements for molecules of any symmetry whatsoever. When complete, it should lead to a general formalism, independent of coupling scheme, for any molecule regardless of how complex it might be.

Matrix Elements of Mono-Excited Slater Determinants Constructed from Axial Spin-Orbitals.

A. Spin-orbitals:

$\zeta(\mu,\lambda,s;x) = \chi(\mu,|\lambda|;r,\theta)\exp[i\lambda\varphi]\eta(s;\sigma)$ 1

where: μ ---- one electron energy quantum no.

λ ---- azimuthal quantum no., $\lambda = \pm|\lambda|$

s ---- spin quantum no., $s = \pm 1$

x ---- set of spin, space variables

B. Configurations and Slater Determinantes:

Ground state closed shell configuration (0), and its Slater determinant:

Config. (0) $\equiv \left\{(\mu_1,\lambda_1,s_1).\ .\ .\ (\mu_I,\lambda_I,s_I).\ .\ .\ .\ (\mu_N,\lambda_N,s_N)\right\}$

where: N is even. For every set (μ_P,λ_P,s_P) the sets $(\mu_P,\lambda_P,-s_P)$, $(\mu_P,-\lambda_P,s_P)$ and $(\mu_P,-\lambda_P,-s_P)$ also appear in (0).

Det. $|(0)\rangle = \hat{\mathcal{A}}\prod_{P=1}^{N}\zeta(\mu_P,\lambda_P,s_P;x_P)$ 2

Monoexcited configurations and their Slater determinants are derived from (0) as follows:

Config.(I,J) $\equiv \{(\mu_1,\lambda_1,s_1),\ ....\ (\mu_J,\lambda_J,s_J),\ ....\ (\mu_N,\lambda_N,s_N)\}$

$\equiv (\mu_I,\lambda_I,s_I;\ \mu_J,\lambda_J,s_J)$, where (μ_J,λ_J,s_J) is not $\epsilon(0)$ and stands in the Ith position of (0).

Config.(K,L) $\equiv \{(\mu_1,\lambda_1,s_1),\ ....\ (\mu_L,\lambda_L,s_L),\ ....\ (\mu_N,\lambda_N,s_N)\}$

$\equiv (\mu_K,\lambda_K,s_K;\ \mu_L,\lambda_L,s_L)$, where (μ_L,λ_L,s_L) is not $\epsilon(0)$ and stands in the Kth position of (0).

$$\text{Det. } |(I,J)\rangle = \hat{\mathcal{A}}\Big[\prod_{P=1}^{I-1}\xi(\mu_P,\lambda_P,s_P;x_P)\Big]\xi(\mu_J,\lambda_J,s_J;x_J)\Big[\prod_{P=I+1}^{N}\xi(\mu_P,\lambda_P,s_P;x_P)\Big]$$

$$\text{Det. } |(K,L)\rangle = \hat{\mathcal{A}}\Big[\prod_{P=1}^{K-1}\xi(\mu_P,\lambda_P,s_P;x_P)\Big]\xi(\mu_L,\lambda_L,s_L;x_L)\Big[\prod_{P=K+1}^{N}\xi(\mu_P,\lambda_P,s_P;x_P)\Big] \quad .....3$$

Mono-excited configurations:

$\{(\mu_I, |\lambda_I|;\mu_J |\lambda_J|\} \equiv$ set of all $(\mu_I,\lambda_I,s_I;\mu_J,\lambda_J,s_J)$ with fixed μ_I, $|\lambda|$, and μ_J, $|\lambda_J|$.

C. Matrix elements of $\hat{\mathcal{H}}(x_1,\ldots x_N)$ in the basis of $|(I,J)\rangle$.

Properties of $\hat{\mathcal{H}}(x_1,\ldots x_N)$:

$$\hat{\mathcal{H}}(x_1,\ldots.x_N) = \sum_{i=1}^{N}\hat{\mathcal{H}}(x_i) + \tfrac{1}{2}\sum_{i\neq j}^{NN}\hat{\mathcal{H}}(x_i,x_j) \text{ where } \hat{\mathcal{H}}(x_i,x_j) = \hat{\mathcal{H}}(x_j,x_i).$$

Writing $A_1 = \sum_{i}^{N}\hat{\mathcal{H}}(x_i)$, $A_2 = \frac{1}{2}\sum_{i\neq j}^{NN}\hat{\mathcal{H}}(x_i,x_j)$

and $|(0)\rangle = 1.....I.....K.....N$

$|(I,J)\rangle = 1.....J.....K.....N$

$|(I,L)\rangle = 1.....L.....K.....N$

$|(K,J)\rangle = 1.....I.....J.....N$

$|(K,L)\rangle = 1.....I.....L.....N$

and apply Slater Rules to:

$$\langle(I,J)|A_1|(I,J)\rangle = \sum_{P\neq I}^{N}\langle P|A_1|P\rangle + \langle J|A_1|J\rangle = \sum_{P=1}^{N}\langle P|A_1|P\rangle + \langle J|A_1|J\rangle - \langle I|A_1|I\rangle.$$

$$\langle(I,J)|A_1|(I,L)\rangle = \langle J|A_1|L\rangle = \langle J|A_1|L\rangle$$

$$\langle(I,J)|A_1|(K,L)\rangle = -\langle I|A_1|K\rangle = -\langle I|A_1|K\rangle$$

$$\langle(I,J)|A_1|(K,J)\rangle = \quad 0 \quad = \quad 0$$

Therefore:

$$\langle(I,J)|A_1|(K,J)\rangle = \langle(0)|A_1|(0)\rangle\delta_{IK}\delta_{JL} + \langle J|A_1|L\rangle\delta_{IK} - \langle I|A_1|K\rangle\delta_{JL} \quad .....4$$

$$\langle (I,J)\,|A_2|\,(I,J)\rangle = \langle (0)\,|A_2|\,(0)\rangle + 2\sum_{P=1}^{N}\langle JP|A_2|JP\rangle - 2\sum_{P=1}^{N}\langle IP|A_2|IP\rangle - 2\langle IJ|A_2|IJ\rangle$$

$$\langle (I,J)\,|A_2|\,(I,L)\rangle = + 2\sum_{P=1}^{N}\langle JP|A_2|LP\rangle \qquad - 2\langle IJ|A_2|IL\rangle$$

$$\langle (I,J)\,|A_2|\,(K,L)\rangle = - 2\sum_{P=1}^{N}\langle KP|A_2|IP\rangle - 2\langle KJ|A_2|IJ\rangle$$

$$\langle (I,J)\,|A_2|\,(K,L)\rangle = - 2\langle KJ|A_2|IL\rangle$$

$$\langle (I,J)\,|A_2|\,(K,L)\rangle = \langle (0)\,|A_2|\,(0)\rangle\delta_{IK}\delta_{JL} + 2\sum_{P=1}^{N}\langle JP|A_2|LP\rangle\delta_{IK} - 2\sum_{P=1}^{N}\langle KP|A_2|IP\rangle\delta_{JL}$$
$$- 2\langle KJ|A_2|IL\rangle$$

D. Using symbols for integrals:

$$[\mu_1\ \lambda_1\ s_1\,|\,\mu_2\ \lambda_2\ s_2] = \langle \xi(\mu_1,\lambda_1,s_1;x_i)\,\hat{\mathcal{H}}(x_i)\,|\,\xi(\mu_2,\lambda_2,s_2;x_i)\rangle \ldots\ldots\ldots 6$$

$$\left[\begin{matrix}\mu_1 & \lambda_1 & s_1\\ \mu_3 & \lambda_3 & s_3\end{matrix}\,\middle|\,\begin{matrix}\mu_2 & \lambda_2 & s_2\\ \mu_4 & \lambda_4 & s_4\end{matrix}\right] =$$

$$\langle \xi(\mu_1,\lambda_1,s_1;x_i)\,\xi(\mu_3,\lambda_3,s_3;x_j)\,\hat{\mathcal{H}}(x_i,x_j)(\hat{I} - \hat{T}_{ij})\,|\,\xi(\mu_2,\lambda_2,s_2;x_i)\,\xi(\mu_4,\lambda_4,s_4;x_j)\rangle$$

$$\ldots\ldots\ldots\ldots 7$$

$$\{\mu_1\ \lambda_1\ s_1\,|\,\mu_2\ \lambda_2\ s_2\} = [\mu_1\ \lambda_1\ s_1\,|\,\mu_2\ \lambda_2\ s_2] + \sum_{P=1}^{N}\left[\begin{matrix}\mu_1 & \lambda_1 & s_1\\ \mu_P & \lambda_P & s_P\end{matrix}\,\middle|\,\begin{matrix}\mu_2 & \lambda_2 & s_2\\ \mu_P & \lambda_P & s_P\end{matrix}\right] \ldots\ldots\ldots 8$$

Then, using 4, 5, 6, 7 and 8:

$$\langle (I,J)\,\hat{\mathcal{H}}(x_1,\ldots x_N)\,|\,(K,L)\rangle = \langle (\mu_I,\lambda_I,s_I;\mu_J,\lambda_J,s_J)\,\hat{\mathcal{H}}(x_1\ldots x_N)\,|\,(\mu_K,\lambda_K,s_K;\mu_J,\lambda_L,s_L)\rangle$$

$$= \langle (0)\,\hat{\mathcal{H}}(x_1\ldots x_N)\,|\,(0)\rangle\delta\begin{pmatrix}\mu_I & \lambda_I & s_I\\ \mu_K & \lambda_K & s_K\end{pmatrix}\delta\begin{pmatrix}\mu_J & \lambda_J & s_J\\ \mu_K & \lambda_K & s_K\end{pmatrix} + \{\mu_J\ \lambda_J\ s_J\,|\,\mu_L\ \lambda_L\ s_L\}\delta\begin{pmatrix}\mu_I & \lambda_I & s_I\\ \mu_K & \lambda_K & s_K\end{pmatrix}$$

$$-\{\mu_K\ \lambda_K\ s_K\,|\,\mu_J\ \lambda_J\ s_J\}\delta\begin{pmatrix}\mu_J & \lambda_J & s_J\\ \mu_L & \lambda_L & s_L\end{pmatrix} - \left[\begin{matrix}\mu_K & \lambda_K & s_K\\ \mu_J & \lambda_J & s_J\end{matrix}\,\middle|\,\begin{matrix}\mu_I & \lambda_I & s_I\\ \mu_I & \lambda_I & s_I\end{matrix}\right]$$

Spin-Less Hamiltonian.

A. Definition of the operator:

$$\hat{\mathcal{H}}(\vec{r}_1 \ldots\ldots \vec{r}_N) = \sum_{i=1}^{N} \hat{\mathcal{H}}(\vec{r}_i) + \tfrac{1}{2} \sum_{i \neq j}^{NN} \hat{\mathcal{H}}(\vec{r}_i, \vec{r}_j) \ldots\ldots\ldots\ldots 9$$

where:

$$\hat{\mathcal{H}}(\vec{r}_i) = \frac{-\hbar^2}{2m_e} \nabla^2(r_i, \theta_i, \varphi_i) - \sum_{\alpha=1}^{K} \frac{Z_\alpha e^2}{|\vec{r} - \vec{R}_\alpha|}$$

$$= \frac{-\hbar^2}{2m_e} \frac{1}{r_i^2} \frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i} + \frac{1}{\sin\theta_i} \frac{\partial}{\partial \theta_i} \sin\theta_i \frac{\partial}{\partial \theta_i} + \frac{1}{\sin^2\varphi} \frac{\partial^2}{\partial\varphi^2} + V(r_i \theta_i) \ldots . 10$$

where $V(r_i \theta_i) = -\sum_{\alpha=1}^{K} \frac{Z_\alpha e^2}{|\vec{r} - \vec{R}_\alpha|} = -\sum_{\alpha=1}^{K} Z_\alpha e^2 \sum_{n=0}^{\infty} \frac{r_<^n}{r_>^n} P_n^0(\cos\theta_i)$

$$\hat{\mathcal{H}}(\vec{r}_i, \vec{r}_j) = \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

$$= e^2 \sum_{n=0}^{\infty} \sum_{m=-n}^{n} \frac{(n-|m|)!}{(n+|m|)!} \frac{r_<^n}{r_>^{n+1}} P_n^{|m|}(\cos\theta_i) P_n^{|m|}(\cos\theta_j) \exp[im(\varphi_i - \varphi_j)]$$

$$= \sum_{m=-\infty}^{\infty} e^2 \left\{ \sum_{n=-m}^{m} \frac{(n-|m|)!}{(n+|m|)!} \frac{r_<^n}{r_>^{n+1}} P_n^{|m|}(\cos\theta_i) P_n^{|m|}(\cos\theta_j) \right\} \exp[im(\varphi_i - \varphi_j)]$$

$$= \sum_{m=-\infty}^{\infty} e^2 C_{|m|}(r_i \theta_i, r_j \theta_j) \exp[im(\varphi_i - \varphi_j)]$$

where:

$$C_{|m|}(r_i \theta_i, r_j \theta_j) = C_{|m|}(r_j \theta_j, r_i \theta_i)$$

B. Action of $\nabla^2(\vec{r})$ on axial spin-orbital.

Denote:

$$\hat{T}_1(r_i, \theta_i) = \frac{-\hbar^2}{2m_e} \frac{1}{r_i^2} \left[\frac{\partial}{\partial r_i} r_i^2 \frac{\partial}{\partial r_i} + \frac{1}{\sin\theta_i} \frac{\partial}{\partial \theta_i} \sin\theta_i \frac{\partial}{\partial \theta_i} \right]$$

$$f(r_i\theta_i) = \frac{-\hbar^2}{2m_e}\frac{1}{r_i^2}\frac{1}{\sin^2\theta_i}$$

Then:

$$\frac{-\hbar^2}{2m_e}\nabla^2(r_i,\theta_i,\varphi_i) = \hat{T}_1(r_i,\theta_i) + f(r_i,\theta_i)\frac{\partial^2}{\partial\varphi_i^2}$$

Now:

$$\{\frac{-\hbar^2}{2m_e}\nabla^2(r_i,\theta_i,\varphi_i)\}\xi(\mu,\lambda,s;x_i)$$

$$= \{\hat{\hat{T}}_1(r_i,\theta_i) + f(r_i,\theta_i)\frac{\partial^2}{\partial\varphi_i^2}\}\chi(\mu,|\lambda|;r_i,\theta_i)\exp[i\lambda\varphi_i]\eta(s;\sigma_i)$$

$$= \{\hat{T}_1(r_i,\theta_i) - \lambda^2 f(r_i,\theta_i)\}\chi(\mu,|\lambda|;r_i,\theta_i)\exp[i\lambda\varphi_i]\eta(s;\sigma_i)$$

$$= \hat{T}_{|\lambda|}(r_i,\theta_i)\xi(\mu,\lambda,s;x_i)$$

and

$$\hat{\mathcal{H}}(\vec{r}_i)\,\xi(\mu,\lambda,s;x_i) = \hat{h}_{|\lambda|}(r_i,\theta_i)\xi(\mu,\lambda,s;x_i)$$

where

$$\hat{h}_{|\lambda|}(r_i,\theta_i) = \hat{T}_{|\lambda|}(r_i,\theta_i) + V(r_i,\theta_i)$$

Integrals of $\hat{\mathcal{H}}(\vec{r}_i)$:

$$[\mu_1\ \lambda_1\ s_1|\mu_2\ \lambda_2\ s_2] \equiv \langle\xi(\mu_1,\lambda_1,s_1;x_i)|\hat{\mathcal{H}}(\vec{r}_i)|\xi(\mu_2,\lambda_2,s_2;x_i)\rangle$$

$$= \langle\xi(\mu_1,\lambda_1,s_1;x_i)|\hat{h}_{|\lambda_2|}(r_i,\theta_i)|\xi(\mu_2,\lambda_2,s_2;x_i)\rangle$$

$$= \langle\chi(\mu_1,|\lambda_1|;r_i,\theta_i)|\hat{h}_{|\lambda_2|}(r_i,\theta_i)|\chi(\mu_2,|\lambda_2|;r_i,\theta_i)\rangle$$

$$\langle\exp[i\lambda_1\varphi_i]|\exp[i\lambda_2\varphi_i]\rangle\langle\eta(s_1,\sigma_i)|\eta(s_2,\sigma_i)\rangle$$

$$= \delta(s_1,s_2)\delta(\lambda_1,\lambda_2)\langle\chi(\mu_1,|\lambda_1|;r_i\theta_i)|\hat{h}_{|\lambda_2|}(r_i\theta_i)|\chi(\mu_2|\lambda_2|;r_i\theta_i)\rangle$$

$$= \delta\begin{pmatrix}s_1\\s_2\end{pmatrix}\delta\begin{pmatrix}\lambda_1\\\lambda_2\end{pmatrix}(\mu_1|\lambda_1|\,|\mu_2|\lambda_2|) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 12$$

Writing:

$$\left\{\begin{matrix}\mu_1 & \lambda_1 & s_1\\ \mu_2 & \lambda_2 & s_2\end{matrix}\,\middle|\,\begin{matrix}\mu_3 & \lambda_3 & s_3\\ \mu_4 & \lambda_4 & s_4\end{matrix}\right\}$$

$$\equiv \langle\xi(\mu_1,\lambda_1,s_1;x_i)\xi(\mu_2,\lambda_2,s_2;x_j)|\hat{\beta}(\vec{r}_i,\vec{r}_j)|\xi(\mu_3,\lambda_3,s_3;x_i)\xi(\mu_4,\lambda_4,s_4;x_j)\rangle$$

From 1 and 11:

$$= \langle n(s_1;\sigma_i)|n(s_3;\sigma_i)\rangle\langle n(s_2;\sigma_j)|n(s_4;\sigma_j)\rangle$$

$$\times\sum_{m=-\infty}^{\infty}\int_0^{2\pi}d\varphi_i\int_0^{2\pi}d\varphi_j\exp(-i\lambda_1\varphi_i)\exp(-i\lambda_2\varphi_j)\exp(i\lambda_3\varphi_i)\exp(i\lambda_4\varphi_j)\exp[im(\varphi_i-\varphi_j)]$$

$$\times\int_0^{\infty}r_i^2dr_i\int_0^{\infty}r_j^2dr_j\int_0^{\pi}\sin\theta_i d\theta_i\int_0^{\pi}\sin\theta_j d\theta_j\chi^*(\mu_1|\lambda_1|;r_i\theta_i)\chi^*(\mu_2|\lambda_2|;r_j\theta_j)e^2C_{|m|}(r_i\theta_i,r_j\theta_j)$$

$$\chi(\mu_3|\lambda_3|;r_i\theta_i)\chi(\mu_4|\lambda_4|;r_j\theta_j)$$

$$= \delta(s_1,s_3)\delta(s_2,s_4)\sum_{m=-\infty}^{\infty}\delta(m,\lambda_3-\lambda_1)\delta(m,\lambda_2-\lambda_4)\left(\begin{matrix}\mu_1 & |\lambda_1|\\ \mu_2 & |\lambda_2|\end{matrix}\,\middle|\,\begin{matrix}\mu_3 & |\lambda_3|\\ \mu_4 & |\lambda_4|\end{matrix}\right)_{|m|}$$

Then from 7:

$$\left[\begin{matrix}\mu_1 & \lambda_1 & s_1\\ \mu_3 & \lambda_3 & s_3\end{matrix}\,\middle|\,\begin{matrix}\mu_2 & \lambda_2 & s_2\\ \mu_4 & \lambda_4 & s_4\end{matrix}\right] = \left\{\begin{matrix}\mu_1 & \lambda_1 & s_1\\ \mu_3 & \lambda_3 & s_3\end{matrix}\,\middle|\,\begin{matrix}\mu_2 & \lambda_2 & s_2\\ \mu_4 & \lambda_4 & s_4\end{matrix}\right\} - \left\{\begin{matrix}\mu_1 & \lambda_1 & s_1\\ \mu_3 & \lambda_3 & s_3\end{matrix}\,\middle|\,\begin{matrix}\mu_4 & \lambda_4 & s_4\\ \mu_2 & \lambda_2 & s_2\end{matrix}\right\}$$

$$= \delta(s_1,s_2)\delta(s_3,s_4)\sum_m \delta(m,\lambda_2-\lambda_1)\delta(m,\lambda_3-\lambda_4)\left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_2 & |\lambda_2| \\ \mu_3 & |\lambda_3| & \mu_4 & |\lambda_4| \end{array}\right)_{|m|}$$

$$- \delta(s_1,s_4)\delta(s_2,s_3)\sum_m \delta(m,\lambda_4-\lambda_1)\delta(m,\lambda_3-\lambda_2)\left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_4 & |\lambda_4| \\ \mu_3 & |\lambda_3| & \mu_2 & |\lambda_2| \end{array}\right)_{|m|}$$

$$= \delta\begin{pmatrix} s_1,s_3 \\ s_2,s_4 \end{pmatrix}\delta\begin{pmatrix} \lambda_2-\lambda_1 \\ \lambda_3-\lambda_4 \end{pmatrix}\left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_2 & |\lambda_2| \\ \mu_3 & |\lambda_3| & \mu_4 & |\lambda_4| \end{array}\right)_{|\lambda_3-\lambda_4|}$$

$$- \delta\begin{pmatrix} s_1,s_2 \\ s_4,s_3 \end{pmatrix}\delta\begin{pmatrix} \lambda_4-\lambda_1 \\ \lambda_3-\lambda_2 \end{pmatrix}\left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_4 & |\lambda_4| \\ \mu_3 & |\lambda_3| & \mu_2 & |\lambda_2| \end{array}\right)_{|\lambda_3-\lambda_2|}$$

$$= \left\{\left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_2 & |\lambda_2| \\ \mu_3 & |\lambda_3| & \mu_4 & |\lambda_4| \end{array}\right)_{|\lambda_3-\lambda_4|}\delta\begin{pmatrix} s_1,s_3 \\ s_2,s_4 \end{pmatrix} - \left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_4 & |\lambda_4| \\ \mu_3 & |\lambda_3| & \mu_2 & |\lambda_2| \end{array}\right)_{|\lambda_3-\lambda_2|}\delta\begin{pmatrix} s_1,s_3 \\ s_4,s_2 \end{pmatrix}\right\}\delta\begin{pmatrix} \lambda_2-\lambda_1 \\ \lambda_3-\lambda_4 \end{pmatrix}$$

Also, see 8:

$$\sum_{P=1}^{N}\left[\begin{array}{ccc|ccc} \mu_1 & \lambda_1 & s_1 & \mu_2 & \lambda_2 & s_2 \\ \mu_P & \lambda_P & s_P & \mu_P & \lambda_P & s_P \end{array}\right]$$

$$= \sum_{P=1}^{N}\left\{\left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_2 & |\lambda_2| \\ \mu_P & |\lambda_P| & \mu_P & |\lambda_P| \end{array}\right)_{|\lambda_P-\lambda_P|}\delta\begin{pmatrix} s_1,s_P \\ s_2,s_P \end{pmatrix} - \left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_P & |\lambda_P| \\ \mu_P & |\lambda_P| & \mu_2 & |\lambda_2| \end{array}\right)_{|\lambda_P-\lambda_2|}\delta\begin{pmatrix} s_1,s_P \\ s_P,s_2 \end{pmatrix}\right\}\delta\begin{pmatrix} \lambda_2-\lambda_1 \\ \lambda_P-\lambda_P \end{pmatrix}$$

$$= \sum_{P=1}^{N} \left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_2 & |\lambda_2| \\ \mu_P & |\lambda_P| & \mu_P & |\lambda_P| \end{array}\right)_0 - \left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_P & |\lambda_P| \\ \mu_P & |\lambda_P| & \mu_2 & |\lambda_2| \end{array}\right)_{|\lambda_P-\lambda_2|} \delta\begin{pmatrix} s_1 \\ s_P \end{pmatrix} \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ 0 \end{pmatrix}$$

But:

$$\sum_{P=1}^{N} \left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_2 & |\lambda_2| \\ \mu_P & |\lambda_P| & \mu_P & |\lambda_P| \end{array}\right) = \sum_{\mu_P, \lambda_P} 2 \left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_2 & |\lambda_2| \\ \mu_P & |\lambda_P| & \mu_P & |\lambda_P| \end{array}\right)$$

as for every value of λ_P, $s_P = \pm\frac{1}{2}$. This removes sum over s_P implied in $\sum\limits_{P}$

Also:

$$\sum_{P=1}^{N} \left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_P & |\lambda_P| \\ \mu_P & |\lambda_P| & \mu_2 & |\lambda_2| \end{array}\right) \delta\begin{pmatrix} s_2 \\ s_P \end{pmatrix} = \sum_{\mu_P, \lambda_P} \left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_P & |\lambda_P| \\ \mu_P & |\lambda_P| & \mu_2 & |\lambda_2| \end{array}\right)$$

as for every value of λ_P, $s_P = \pm\frac{1}{2}$, $=s_2$ in one case

$\neq s_2$ in the other.

Hence:

$$\sum_{P=1}^{N} \left[\begin{array}{ccc|ccc} \mu_1 & \lambda_1 & s_1 & \mu_2 & \lambda_2 & s_2 \\ \mu_P & \lambda_P & s_P & \mu_P & \lambda_P & s_P \end{array}\right]$$

$$= \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_1 \\ \lambda_2 \end{pmatrix} \underbrace{\sum_{\mu_P, \lambda_P} \left\{ 2 \left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_2 & |\lambda_2| \\ \mu_P & |\lambda_P| & \mu_P & |\lambda_P| \end{array}\right)_0 - \left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_P & |\lambda_P| \\ \mu_P & |\lambda_P| & \mu_2 & |\lambda_2| \end{array}\right)_{|\lambda_P-\lambda_2|} \right.}_{\text{depends only on } |\lambda_2|} \quad \ldots 13$$

Proof that the above quantity depends only on $|\lambda_2|$:

$$\text{let, } f(\lambda_2) = \sum_{\mu_P, \lambda_P} \left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_P & |\lambda_P| \\ \mu_P & |\lambda_P| & \mu_2 & |\lambda_2| \end{array}\right)_{|\lambda_2-\lambda_P|}$$

$$= \sum_{\mu_P, \lambda_P=0} \left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_P & |\lambda_P| \\ \mu_P & |\lambda_P| & \mu_2 & |\lambda_2| \end{array}\right)_0 + \sum_{\mu_P, \lambda_P=|\lambda_P|} \left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_P & |\lambda_P| \\ \mu_P & |\lambda_P| & \mu_2 & |\lambda_2| \end{array}\right)_{|(\lambda_2-|\lambda_P|)|}$$

$$+ \sum_{\mu_P, \lambda_P=-|\lambda_P|} \left(\begin{array}{cc|cc} \mu_1 & |\lambda_1| & \mu_P & |\lambda_P| \\ \mu_P & |\lambda_P| & \mu_2 & |\lambda_2| \end{array}\right)_{|(\lambda_2+|\lambda_P|)|}$$

$$= f(-\lambda_2)$$

Then from 8, 12 and 13:

$$\{\mu_1\ \lambda_1\ s_1 \mid \mu_2\ \lambda_2\ s_2\} = \Bigg\{ (\mu_1\ |\lambda_1|\ |\mu_2\ |\lambda_2|)$$

$$+ \sum_{\mu_P, \lambda_P} 2 \begin{pmatrix} \mu_1 & |\lambda_1| & | & \mu_2 & |\lambda_2| \\ \mu_P & |\lambda_P| & | & \mu_P & |\lambda_P| \end{pmatrix}_0 - \sum_{\mu_P, \lambda_P} \begin{pmatrix} \mu_1 & |\lambda_1| & | & \mu_P & |\lambda_P| \\ \mu_P & |\lambda_P| & | & \mu_2 & |\lambda_2| \end{pmatrix}_{|\lambda_P - \lambda_2|}$$

$$\delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_1 \\ \lambda_2 \end{pmatrix}$$

$$= \langle \chi(\mu_1, |\lambda_1|; r_i, \theta_i)\, |\hat{h}_{|\lambda_2|}(r_i, \theta_i)\, |\chi(\mu_2, |\lambda_2|; r_i, \theta_i)\rangle$$

$$+ \sum_{P=1}^{N} \langle \chi(\mu_1, |\lambda_1|; r_i, \theta_i)\chi(\mu_P, |\lambda_P|; r_j, \theta_j)\, |\frac{e^2}{4\pi^2} C_0(r_i\theta_i, r_j\theta_j)\, |\chi(\mu_P, |\lambda_P|; r_j, \theta_j)$$

$$\chi(\mu_2, |\lambda_2|; r_i, \theta_i)\rangle$$

$$- \sum_{P=1}^{N} \langle \chi(\mu_1, |\lambda_1|; r_i, \theta_i)\chi(\mu_P, |\lambda_P|; r_j\theta_j)\, |\frac{e^2}{4\pi^2} C_{|\lambda_P - \lambda_2|}(r_i\theta_i, r_j\theta_j)\hat{T}_{ij}\, |$$

$$\chi(\mu_P, |\lambda_P|; r_j, \theta_j)\chi(\mu_2, |\lambda_2|; r_i\theta_i)\rangle$$

$$= \langle \chi(\mu_1 |\lambda_1|; r_i\theta_i)\, |[\hat{h}_{|\lambda_2|}(r_i\theta_i) + \sum_{P=1}^{N} \langle \chi(\mu_P |\lambda_P|; r_j\theta_j)\, |\frac{e^2}{4\pi^2} C_0(r_i\theta_i, r_j\theta_j)$$

$$- \frac{e^2}{4\pi^2} C_{|\lambda_P - \lambda_2|}\, \hat{T}_{ij}\, |\chi(\mu_P |\lambda_P|; r_j\theta_j)\rangle]\, |\chi(\mu_2 |\lambda_2|; r_i\theta_i)\rangle$$

$$= \langle \chi(\mu_1 |\lambda_1|; r_i\theta_i)\, |\hat{\mathcal{H}}_{|\lambda_2|}(r_i\theta_i)\, |\chi(\mu_2 |\lambda_2|; r_i\theta_i)\rangle$$

Spin-Orbit Hamiltonian

A. N-electron spin-orbit hamiltonian $\hat{\mathcal{H}}_{so}$ and its components.

$$\hat{\mathcal{H}}_{so}(\vec{x}_1\ldots\vec{x}_N) = \sum_{i=1}^{N}\frac{g\beta^2}{\hbar}\,\hat{s}(i).\left\{\sum_{\alpha=1}^{K} Z_\alpha\,\frac{\vec{R}_{\alpha i}}{|\vec{R}_{\alpha i}|^3}\right\}\times\hat{p}(i)$$

$$-\sum_{i\neq j}^{NN}\frac{g\beta^2}{\hbar}\,\hat{s}(i)\cdot\frac{\vec{r}_{ji}}{|\vec{r}_{ij}|^3}\times\hat{p}(i) - 2\sum_{i\neq j}^{NN}\frac{g\beta^2}{\hbar}\,\hat{s}(j)\,\frac{\vec{r}_{ji}}{|\vec{r}_{ji}|^3}\times\hat{p}(i) \quad \ldots 15$$

where:

$\vec{R}_{\alpha i} = \vec{r}_i - \vec{R}_\alpha$

$\vec{r}_{ji} = \vec{r}_i - \vec{r}_j$

Components of $\vec{r}_i, \hat{p}(i), \hat{s}(i), \vec{R}_\alpha$ in the cartesian axes $\vec{k}_1, \vec{k}_2, \vec{k}_3$.

$$\vec{r}_i = \sum_{t=1}^{3}\vec{k}_t\,x_t(i)$$

$$\hat{p}(i) = \sum_{t=1}^{3}\vec{k}_t\hat{p}_t(i)\ , \quad p_t(i) = i\hbar\,\frac{\partial}{\partial x_t(i)}$$

$$\hat{s}(i) = \sum_{t=1}^{3}\vec{k}_t\hat{s}_t(i)$$

$$\vec{R}_\alpha = \sum_{t=1}^{3}\vec{k}_t X_t(\alpha)\ , \quad X_t(\alpha) = \delta_{3t}X_3(\alpha) \text{ - all nuclei are on } \vec{k}_3 \text{ axis}$$

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Components of $\hat{\mathcal{H}}_{so}$.

$$\hat{\mathcal{H}}_{so}(\vec{x}_1\ldots\vec{x}_N) = \sum_{i=1}^{N}\hat{\mathcal{H}}(\vec{x}_i) + \sum_{i\neq j}\hat{\mathcal{H}}(\vec{x}_i/\vec{r}_j) + \sum_{i\neq j}\hat{\mathcal{H}}(\vec{x}_i,\vec{x}_j)$$

$$\hat{\mathcal{H}}(\vec{x}_i) = \frac{g\beta^2}{\hbar}\,\hat{s}(i)\,.\left\{\sum_\alpha Z_\alpha \frac{\vec{R}_{\alpha i}}{|\vec{R}_{\alpha i}|^3}\right\} \times \hat{p}(i)$$

$$\hat{\mathcal{H}}(\vec{x}_i/\vec{r}_j) = \frac{-g\beta^2}{\hbar}\,\hat{s}(i)\,.\,\frac{\vec{r}_{ji}}{|\vec{r}_{ji}|^3} \times \hat{p}(j)$$

$$\hat{\mathcal{H}}(\vec{x}_i,\vec{x}_j) = \frac{-2g\beta^2}{\hbar}\,\hat{s}(j)\,.\,\frac{\vec{r}_{ji}}{|\vec{r}_{ji}|^3} \times \hat{p}(i)$$

$$\doteq \frac{-g\beta^2}{\hbar}\;\frac{\hat{s}(j)\,.\,\vec{r}_{ji}\times\hat{p}(j) + \hat{s}(i)\,.\,\vec{r}_{ij}\times\hat{p}(j)}{|\vec{r}_{ji}|^3} \qquad \ldots\ldots\ldots\ldots\ldots 15'$$

Expanding over spherical harmonics:

$$|\vec{R}_{\alpha i}|^{-3} = |\vec{r}_1-\vec{R}_\alpha|^{-3} = \left\{\sum_{n=0}^{\infty}\frac{r_<^{\,n}}{r_>^{\,n+1}}\,P_n\,(\cos\theta_1)\right\}^3 = V(r_1,\theta_1;R_\alpha)$$

$$|\vec{r}_{21}|^{-3} = |\vec{r}_1-\vec{r}_2|^{-3} = \left(\sum_{m=-\infty}^{\infty} C_{|m|}(r_1\theta_1;r_2\theta_2)\exp[im(\varphi_1-\varphi_2)]\right)^3$$

$$= \sum_{m_1=-\infty}^{\infty}\;\sum_{m_2=-\infty}^{\infty}\;\sum_{m_3=-\infty}^{\infty} C_{|m_1|}C_{|m_2|}C_{|m_3|}\exp[i(m_1+m_2+m_3)(\varphi_1-\varphi_2)]$$

define: $m = m_1+m_2+m_3$

$m' = m_2+m_3$

$m'' = m_3$

$$|\vec{r}_{21}|^3 = \sum_{m=-\infty}^{\infty}\left\{\underbrace{\sum_{m'}\sum_{m''} C_{|m-m'|}C_{|m'-m''|}C_{|m''|}}_{D_{|m|}(r_1\theta_1;r_2\theta_2)}\right\}\exp[im(\varphi_1-\varphi_2)]$$

Therefore:

$$|\vec{R}_{\alpha 1}| = V(r_1\theta_1;R_\alpha) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 17$$

$$|\vec{r}_{21}| = \sum_{m=-\infty}^{\infty} D_{|m|}(r_1\theta_1;r_2\theta_2)\exp[im(\varphi_1-\varphi_2)]$$

Expansion for $\sum_\alpha Z_\alpha \dfrac{\vec{R}_{\alpha 1}}{|\vec{R}_{\alpha 1}|^3}$

From 16 and 17

$$= \sum_t \vec{k}_t \sum_\alpha Z_\alpha [x_t(1) - X_t(\alpha)] V(r_1\theta_1;R_\alpha)$$

$$= \sum_t \vec{k}_t \left\{ x_t(1) \underbrace{\sum_\alpha Z_\alpha V(r_1\theta_1;R_\alpha)}_{d_1(r_1,\theta_1)} - \delta_{3t} \underbrace{\sum_\alpha Z_\alpha R_\alpha V(r_1\theta_1;R_\alpha)}_{d_2(r_1,\theta_1)} \right\}$$

$$= \sum_{t=1}^{3} \vec{k}_t \{x_t(1) d_1(r_1\theta_1) - \delta_{3t} d_2(r_1\theta_1)\} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 18$$

Expansion for $\vec{r}_{21}/|\vec{r}_{21}|^3$

From 16 and 17

$$= \sum_t \vec{k}_t [x_t(1) - x_t(2)] \sum_m D_{|m|}(r_1\theta_1;r_2\theta_2)\exp[im(\varphi_1-\varphi_2)]$$

$$= \sum_{m=-\infty}^{\infty} \sum_{t=1}^{3} \vec{k}_t [x_t(1) - x_t(2)] D_{|m|}(r_1\theta_1;r_2\theta_2)\exp[m(\varphi_1-\varphi_2)] \quad \ldots\ldots\ldots 19$$

Then:

$$\frac{\hbar}{g\beta^2}\hat{\mathcal{H}}(\vec{x}_1) = \hat{s}(1) \cdot \left\{ \sum_\alpha \frac{\vec{R}_{\alpha 1}}{|\vec{R}_{\alpha 1}|^3} \right\} \times \hat{p}(1)$$

$$= \sum_{r=1}^{3} \vec{k}_r\, \hat{s}_r(1) \cdot \sum_{s=1}^{3} \vec{k}_s \{x_s(1) d_1(r_1\theta_1) - \delta_{3s} d_2(r_1\theta_1)\} \times \sum_{t=1}^{3} \vec{k}_t\, \hat{p}_t(1)$$

From 15' and 18:

$$= \sum_r \vec{k}_r\, \hat{s}_r(1) \cdot \{d_1(r_1\theta_1) \sum_s \vec{k}_s\, x_s(1) - d_2(r_1\theta_1) \sum_s \vec{k}_s\, \delta_{3s}\} \times \sum_t \vec{k}_t\, \hat{p}_t(1)$$

$$= d_1(r_1\theta_1) \underbrace{\begin{vmatrix} \hat{s}_1(1) & x_1(1) & \hat{p}_1(1) \\ \hat{s}_2(1) & x_2(1) & \hat{p}_2(1) \\ \hat{s}_3(1) & x_3(1) & \hat{p}_3(1) \end{vmatrix}}_{\equiv \text{Det} |\hat{s}(1), x(1), \hat{p}(1)|} - d_2(r_1\theta_1) \underbrace{\begin{vmatrix} \hat{s}_1(1) & 0 & \hat{p}_1(1) \\ \hat{s}_2(1) & 0 & \hat{p}_2(1) \\ \hat{s}_3(1) & 1 & \hat{p}_3(1) \end{vmatrix}}_{\equiv \text{Det} |\hat{s}(1), \delta, \hat{p}(1)|}$$

and:

$$\frac{h}{g\beta^2} \hat{\mathcal{H}}(\vec{x}_1/\vec{r}_2) = \hat{s}(1) \cdot \frac{\vec{r}_{21}}{|\vec{r}_{21}|^3} \times \hat{p}(1)$$

from 15' and 19

$$= \sum_r \vec{k}_r\, \hat{s}_r(1) \cdot \left\{ \sum_s \vec{k}_s [x_s(1) - x_s(2)] \sum_m D_{|m|}(r_1\theta_1; r_2\theta_2) \exp[im(\varphi_1 - \varphi_2)] \right\}$$
$$\times \sum_t \vec{k}_t\, \hat{p}_t(1)$$

$$= \sum_{m=-\infty}^{\infty} D_{|m|}(r_1\theta_1; r_2\theta_2) \exp[im(\varphi_1 - \varphi_2)] \sum_{r=1}^{3} \vec{k}_r\, \hat{s}_r(1) \cdot \left\{ \sum_{s=1}^{3} \vec{k}_s\, x_s(1) - \sum_{s=1}^{3} \vec{k}_s\, x_s(2) \right\}$$
$$\times \sum_{t=1}^{3} \vec{k}_t\, \hat{p}_t(1)$$

$$= \sum_{m=-\infty}^{\infty} D_{|m|}(r_1\theta_1;r_2\theta_2)\exp[im(\varphi_1-\varphi_2)]$$

$$\left\{ \underbrace{\begin{vmatrix} \hat{s}_1(1) & x_1(1) & \hat{p}_1(1) \\ \hat{s}_2(1) & x_2(1) & \hat{p}_2(1) \\ \hat{s}_3(1) & x_3(1) & \hat{p}_3(1) \end{vmatrix}}_{\equiv \text{Det}\,|\hat{s}(1),x(1),\hat{p}(1)|} - \underbrace{\begin{vmatrix} \hat{s}_1(1) & x_1(2) & \hat{p}_1(1) \\ \hat{s}_2(1) & x_2(2) & \hat{p}_2(1) \\ \hat{s}_3(1) & x_3(2) & \hat{p}_3(1) \end{vmatrix}}_{\equiv \text{Det}\,|\hat{s}(1),x(2),\hat{p}(1)|} \right\}$$

and:

$$\frac{-\hbar}{2g\beta^2}\,\hat{\mathcal{H}}(\vec{x}_i,\vec{x}_j) = \hat{s}(2)\cdot\frac{\vec{r}_{21}}{|\vec{r}_{21}|^3}\times\hat{p}(1)$$

$$= \sum_{m=-\infty}^{\infty} D_{|m|}(r_1\theta_1;r_2\theta_2)\exp[im(\varphi_1-\varphi_2)]$$

$$\underbrace{\begin{vmatrix} \hat{s}_1(2) & x_1(1) & \hat{p}_1(1) \\ \hat{s}_2(2) & x_2(1) & \hat{p}_2(1) \\ \hat{s}_3(2) & x_3(1) & \hat{p}_3(1) \end{vmatrix}}_{\equiv \text{Det}\,|\hat{s}(2),x(1),\hat{p}(1)|} - \underbrace{\begin{vmatrix} \hat{s}_1(2) & x_1(2) & \hat{p}_1(1) \\ \hat{s}_2(2) & x_2(2) & \hat{p}_2(1) \\ \hat{s}_3(2) & x_3(2) & \hat{p}_3(1) \end{vmatrix}}_{\equiv \text{Det}\,|\hat{s}(2),x(2),\hat{p}(1)|}$$

Evaluation of determinants:

$$\text{Det}\,|\hat{s}(1),x(1),\hat{p}(1)|$$

$$= \hat{s}_1(1)\underbrace{\{x_2(1)\hat{p}_3(1)-x_3(1)\hat{p}_2(1)\}}_{\hat{L}_1(1)}+\hat{s}_2(1)\underbrace{\{x_3(1)\hat{p}_1(1)-x_1(1)\hat{p}_3(1)\}}_{\hat{L}_2(1)}$$

$$+\hat{s}_3(1)\underbrace{\{x_1(1)\hat{p}_2(1)-x_2(1)\hat{p}_1(1)\}}_{\hat{L}_3(1)}$$

$$= \sum_{t=1}^{3} \hat{s}_t(1)\hat{L}_t(1)$$

Similarly:

$$\mathrm{Det}\,|\hat{s}(2),x(1),\hat{p}(1)| = \sum_{t=1}^{3} \hat{s}_t(2)\hat{L}_t(1) \quad \text{and}$$

$$-\mathrm{Det}\,|\hat{s}(1),\delta,\hat{p}(1)| = \begin{vmatrix} \hat{s}_1(1) & \hat{p}_1(1) \\ \hat{s}_2(1) & \hat{p}_2(1) \end{vmatrix} = \hat{s}_1(1)\hat{p}_2(1) - \hat{s}_2(1)\hat{p}_1(1)$$

$$\mathrm{Det}\,|\hat{s}(1),x(2),\hat{p}(1)| = \begin{vmatrix} x_1(2) & \hat{s}_1(1) & \hat{p}_1(1) \\ x_2(2) & \hat{s}_2(1) & \hat{p}_2(1) \\ x_3(2) & \hat{s}_3(1) & \hat{p}_3(1) \end{vmatrix}$$

$$= x_1(2)\{\hat{s}_2(1)\hat{p}_3(1)-\hat{s}_3(1)\hat{p}_2(1)\} + x_2(2)\{\hat{s}_3(1)\hat{p}_1(1)-\hat{s}_1(1)\hat{p}_3(1)\}$$
$$+ x_3(2)\{\hat{s}_1(1)\hat{p}_2(1)-\hat{s}_2(1)\hat{p}_1(1)\}$$

Similarly:

$$\mathrm{Det}\,|\hat{s}(2),x(2),\hat{p}(1)| = x_1(2)\{\hat{s}_2(2)\hat{p}_3(1)-\hat{s}_3(2)\hat{p}_2(1)\} + x_2(2)\{\hat{s}_3(2)\hat{p}_1(1)$$
$$-\hat{s}_1(2)\hat{p}_3(1)\} + x_3(2)\{\hat{s}_1(2)\hat{p}_2(1)-\hat{s}_2(2)\hat{p}_1(1)\}$$

Combining the above:

$$\hat{\mathcal{H}}(\vec{x}_1) = \{\frac{g\beta^2}{\hbar} d_1(r_1\theta_1)\}\sum_{t=1}^{3} \hat{s}_t(1)\hat{L}_t(1) + \{\frac{g\beta^2}{\hbar} d_2(r_1\theta_1)\}[\hat{s}_1(1)\hat{p}_2(1)-\hat{s}_2(1)\hat{p}_1(1)] \qquad \ldots\ldots\ldots 20$$

$$\hat{\mathcal{H}}(\vec{x}_1/\vec{r}_2) = -\{\sum_{m=-\infty}^{\infty} \frac{g\beta^2}{\hbar} D_{|m|}(r_1\theta_1;r_2\theta_2)\exp[im(\varphi_1-\varphi_2)]\sum_{t=1}^{3}\hat{s}_t(1)\hat{L}_t(1)$$
$$+ \{\sum_{m=-\infty}^{\infty} \frac{g\beta^2}{\hbar} D_{|m|}(r_1\theta_1;r_2\theta_2)\exp[im(\varphi_1-\varphi_2)]\}\{x_1(2)[\hat{s}_2(1)\hat{p}_3(1)-\hat{s}_3(1)\hat{p}_3(1)]$$
$$+ x_2(2)[\hat{s}_3(1)\hat{p}_1(1)-\hat{s}_1(1)\hat{p}_3(1)] + x_3(2)[\hat{s}_1(1)\hat{p}_2(1)-\hat{s}_2(1)\hat{p}_1(1)]\} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 21$$

$$\hat{\mathcal{H}}(\vec{x}_1,\vec{x}_2) = -2\{\sum_{m=-\infty}^{\infty} \frac{g\beta^2}{\hbar} D_{|m|}(r_1\theta_1;r_2\theta_2)\exp[im(\varphi_1-\varphi_2)]\} \sum_{t=1}^{3} \hat{s}_t(2)\hat{L}_t(1)$$

$$+ 2\{\sum_{m=-\infty}^{\infty} \frac{g\beta^2}{\hbar} D_{|m|}(r_1\theta_1;r_2\theta_2)\exp[im(\varphi_1-\varphi_2)]\}\{x_1(2)[\hat{s}_2(2)\hat{p}_3(1)$$

$$-\hat{s}_3(2)\hat{p}_2(1)] + x_2(2)[\hat{s}_3(2)\hat{p}_1(1)-\hat{s}_1(2)\hat{p}_3(1)] + x_3(2)[\hat{s}_1(2)\hat{p}_2(1)-\hat{s}_2(2)\hat{p}_1(1)]\}$$

..............................22

For all quantities, $\hat{L}$, $\hat{S}$, $\hat{p}$, x

introduce: $\hat{A}^+ = \hat{A}_1 + i\hat{A}_2$; $\hat{A}_1 = \frac{1}{2}(\hat{A}^+ + \hat{A}^-)$

$\hat{A}^- = \hat{A}_1 - i\hat{A}_2$; $\hat{A}_2 = -i/2(\hat{A}^+ - \hat{A}^-)$

See 20, 21 and 22; then:

$\{\hat{s}_1(j)\hat{p}_2(1)-\hat{s}_2(j)\hat{p}_1(1)\} = i/2\{\hat{s}^+(j)\hat{p}^-(1)- \hat{s}^-(j)\hat{p}^+(1)\}$ 23

and: $x_1(2)\{\hat{s}_2(j)\hat{p}_3(1)-\hat{s}_3(j)\hat{p}_2(1)\} - x_2(2)\{\hat{s}_1(j)\hat{p}_3(1)-\hat{s}_3(j)\hat{p}_1(1)\}$

$= \{x_1(2)\hat{s}_2(j)-x_2(2)\hat{s}_1(j)\}\hat{p}_3(1) - \{x_1(2)\hat{p}_2(1)-x_2(2)\hat{p}_1(1)\}\hat{s}_3(j)$

$= i/2\{x^+(2)\hat{s}^-(j)-x^-(2)\hat{s}^+(j)\}\hat{p}_3(1) - i/2\{x^+(2)\hat{p}^-(1)-x^-(2)\hat{p}^+(1)\}\hat{s}_3(j)$

.................24

Introduction of spherical coordinates:

$$x_1 = r \sin\theta \cos\varphi \qquad r = (\sum_{j=1}^{3} x_j^2)^{\frac{1}{2}}$$

$$x_2 = r \sin\theta \sin\varphi \qquad \theta = \cos^{-1}[x_3/\sum_{j=1}^{3} x_j^2)^{\frac{1}{2}}]$$

$$x_3 = r \cos\theta \qquad \varphi = \tan^{-1}(x_2/x_1)$$

$$\frac{\partial r}{\partial x_1} = \sin\theta \cos\varphi \qquad \frac{\partial\theta}{\partial x_1} = \frac{1}{r} \cos\theta \cos\varphi \qquad \frac{\partial\varphi}{\partial x_1} = -\frac{1}{r} \frac{\sin\varphi}{\sin\theta}$$

$$\frac{\partial r}{\partial x_2} = \sin\theta \sin\varphi \qquad \frac{\partial\theta}{\partial x_2} = \frac{1}{r} \cos\theta \sin\varphi \qquad \frac{\partial\varphi}{\partial x_2} = \frac{1}{r} \frac{\cos\varphi}{\sin\theta}$$

$$\frac{\partial r}{\partial x_3} = \cos\theta \qquad \frac{\partial\theta}{\partial x_3} = -\frac{1}{r} \sin\theta \qquad \frac{\partial\varphi}{\partial x_3} = 0$$

$$\frac{\partial x_1}{\partial r} = \sin\theta \cos\varphi \qquad \frac{\partial x_1}{\partial\theta} = r \cos\theta \cos\varphi \qquad \frac{\partial x_1}{\partial\varphi} = -r \sin\theta \sin\varphi$$

$$\frac{\partial x_2}{\partial r} = \sin\theta \sin\varphi \qquad \frac{\partial x_2}{\partial\theta} = r \cos\theta \sin\varphi \qquad \frac{\partial x_2}{\partial\varphi} = r \sin\theta \cos\varphi$$

$$\frac{\partial x_3}{\partial r} = \cos\theta \qquad \frac{\partial x_3}{\partial\theta} = -r \sin\theta \qquad \frac{\partial x_3}{\partial \varphi} = 0$$

Operators $(i\hbar\partial/\partial\theta)$ and $(i\hbar\partial/\partial\varphi)$ in terms of $\hat{L}_1, \hat{L}_2$ and $\hat{L}^+, \hat{L}^-$.

$$\hat{L}_1 = i\hbar(\sin\varphi\ \partial/\partial\theta + \cot\theta \cos\varphi\ \partial/\partial\varphi)$$

$$\hat{L}_2 = -i\hbar(\cos\varphi\ \partial/\partial\theta - \cot\theta \sin\varphi\ \partial/\partial\varphi)$$

$$\sin\varphi\ \hat{L}_1 = \sin^2\varphi(i\hbar\ \partial/\partial\theta) + \cot\theta \sin\varphi \cos\varphi(i\hbar\ \partial/\partial\varphi)$$

$$\cos\varphi\ \hat{L}_2 = -\cos^2\varphi(i\hbar\ \partial/\partial\theta) + \cot\theta \sin\varphi \cos\varphi(i\hbar\ \partial/\partial\theta)$$

$$i\hbar\ \partial/\partial\theta = (\sin\varphi\ \hat{L}_1 - \cos\varphi\ \hat{L}_2)$$

$$\cos\varphi\ \hat{L}_1 = \sin\varphi\ \cos\varphi(i\hbar\ \partial/\partial\theta) + \cot\theta\ \cos^2\varphi(i\hbar\ \partial/\partial\varphi)$$

$$\sin\varphi\ \hat{L}_2 = -\sin\varphi\ \cos\varphi(i\hbar\ \partial/\partial\theta + \cot\theta\ \sin^2\varphi(i\hbar\ \partial/\partial\varphi)$$

$$i\hbar\ \partial/\partial\varphi = \frac{1}{\cot\theta}(\cos\varphi\ \hat{L}_1 + \sin\varphi\ \hat{L}_2) = \frac{\sin\theta}{\cos\theta}(\cos\varphi\ \hat{L}_1 + \sin\varphi\ \hat{L}_2)$$

thus:

$$i\hbar\ \partial/\partial\theta = [\sin\varphi\ \tfrac{1}{2}(\hat{L}^+ + \hat{L}^-) + i\cos\varphi\ \tfrac{1}{2}(\hat{L}^+ - \hat{L}^-)]$$

$$= i/2[(\cos\varphi - i\sin\varphi)\hat{L}^+ - (\cos\varphi + i\sin\varphi)\hat{L}^-]$$

$$= i/2[e^{-i\varphi}\hat{L}^+ - e^{i\varphi}\hat{L}^-]$$

$$i\hbar\ \partial/\partial\varphi = \frac{\sin\theta}{\cos\theta}[\cos\varphi\ \tfrac{1}{2}(\hat{L}^+ + \hat{L}^-) - i\sin\varphi\ \tfrac{1}{2}(\hat{L}^+ - \hat{L}^-)]$$

$$= \tfrac{1}{2}\ \frac{\sin\theta}{\cos\theta}[(\cos\varphi - i\sin\varphi)\hat{L}^+ + (\cos\varphi + i\sin\varphi)\hat{L}^-]$$

$$= \tfrac{1}{2}\ \frac{\sin\theta}{\cos\theta}[\ e^{-i\varphi}\hat{L}^+ + e^{i\varphi}\hat{L}^-]$$

Operator $\hat{p}_1, \hat{p}_2, \hat{p}_3$ and $\hat{p}^+, \hat{p}^-$ in spherical coordinates.

$$\hat{p}_1 = i\hbar\ \partial/\partial x_1 = \frac{\partial r}{\partial x_1}(i\hbar\ \partial/\partial r) + \frac{\partial\theta}{\partial x_1}(i\hbar\ \partial/\partial\theta) + \frac{\partial\varphi}{\partial x_1}(i\hbar\ \partial/\partial\varphi)$$

thus:

$$\hat{p}_1 = \sin\theta\ \cos\varphi\ (i\hbar\ \partial/\partial r) + \frac{1}{r}[\cos\theta\ \cos\varphi\ (i\hbar\ \partial/\partial\theta) - \frac{\sin\varphi}{\sin\theta}(i\hbar\ \partial/\partial\varphi)]$$

$$\hat{p}_2 = \sin\theta\ \sin\varphi(i\hbar\ \partial/\partial r) + \frac{1}{r}[\cos\theta\ \sin\varphi(i\hbar\ \partial/\partial\theta) + \frac{\cos\varphi}{\sin\theta}(i\hbar\ \partial/\partial\varphi)]$$

$$\hat{p}_3 = \cos\theta(i\hbar\ \partial/\partial r) - \frac{1}{r}\ \sin\theta\ (i\hbar\ \partial/\partial\theta)$$

$$\hat{p}^{\pm} = \sin\theta\ e^{\pm i\varphi}(i\hbar\ \partial/\partial r) + \frac{\cos\theta}{r}\ e^{\pm i\varphi}(i\hbar\ \partial/\partial\theta) \pm \frac{i}{r\sin\theta}\ e^{\pm i\varphi}(i\hbar\ \partial/\partial\varphi)$$

$\hat{p}^+, \hat{p}^-, \hat{p}_3$ in terms of $\hat{L}^+$ and $\hat{L}^-$.

First note that:

$$\frac{\cos\theta}{r} e^{i\varphi}(i\hbar\ \partial/\partial\theta) + \frac{i}{r\sin\theta} e^{i\varphi}(i\hbar\ \partial/\partial\varphi)\ .$$

$$= \frac{\cos\theta}{r} e^{i\varphi}[e^{-i\varphi}\hat{L}^+ - e^{i\varphi}\hat{L}^-] + \frac{i}{r\sin\theta} e^{i\varphi}\ \tfrac{1}{2}\frac{\sin\theta}{\cos\theta}[e^{-i\varphi}\hat{L}^+ + e^{i\varphi}\hat{L}^-]$$

$$= \frac{i}{2r\cos\theta}\{(1+\cos^2\theta)\hat{L}^+ + \sin^2\theta\ e^{i2\varphi}\hat{L}^-\}$$

and

$$\frac{\cos\theta}{r} e^{-i\varphi}(i\hbar\ \partial/\partial\theta) - \frac{i}{r\sin\theta} e^{-i\varphi}(i\hbar\ \partial/\partial\varphi)$$

$$= \frac{\cos\theta}{r} e^{-i\varphi}\ \frac{i}{2}[e^{-i\varphi}\hat{L}^+ - e^{i\varphi}\hat{L}^-] - \frac{i}{r\sin\theta} e^{-i\varphi}\ \tfrac{1}{2}\frac{\sin\theta}{\cos\theta}[e^{-i\varphi}\hat{L}^+ + e^{i\varphi}\hat{L}^-]$$

$$= -\frac{i}{2r\cos\theta}\{\sin^2\theta\ e^{-i2\varphi}\hat{L}^+ + (1 + \cos^2\theta)\hat{L}^-\}$$

also:

$$\frac{\sin\theta}{r}(i\hbar\ \partial/\partial\theta) = \frac{i\sin\theta}{r}[e^{-i\varphi}\hat{L}^+ - e^{i\varphi}\hat{L}^-]$$

therefore:

$$\hat{p}^+ = \sin\theta\ e^{i\varphi}(i\hbar\ \partial/\partial r) + \frac{i}{2r\cos\theta}\{(1+\cos^2\theta)\hat{L}^+ + \sin^2\theta\ e^{i2\varphi}\hat{L}^-\}$$

$$\hat{p}^- = \sin\theta\ e^{-i\varphi}(i\hbar\ \partial/\partial r) - \frac{i}{2r\cos\theta}\{\sin^2\theta\ e^{-i2\varphi}\hat{L}^+ + (1+\cos^2\theta)\hat{L}^-\}$$

$$\hat{p}_3 = \cos\theta(i\hbar\ \partial/\partial r) - \frac{i\sin\theta}{2r}\{e^{-i\varphi}\hat{L}^+ - e^{i\varphi}\hat{L}^-\}$$

NB: $x^+ = x_1 + ix_2 = r\sin\theta(\cos\varphi + i\sin\varphi) = r\sin\theta\ e^{i\varphi}$

$x^- = x_1 - ix_2 = r\sin\theta(\cos\varphi - i\sin\varphi) = r\sin\theta\ e^{-i\varphi}$

substituting into 23 and 24:

$$i/2\{\hat{s}^{+}(j)\hat{p}^{-}(1) - \hat{s}^{-}(j)\hat{p}^{+}(1)$$

$$= i/2\{\hat{s}^{+}(j)\sin\theta_1 e^{-i\varphi_1} - \hat{s}^{-}(j)\sin\theta_1 e^{i\varphi_1}\}(i\hbar\ \partial/\partial r_1) + i/2\ \hat{s}^{+}(j)\frac{-i}{2r_1\ \cos\theta_1}$$

$$\{\sin^2\theta_1 e^{-i2\varphi_1}\hat{L}^{+}(1) + (1 + \cos^2\theta_1)\hat{L}^{-}(1)\} - i/2\ \hat{s}^{-}(j)\ \frac{i}{2r_1\ \cos\theta_1}$$

$$\{(1 + \cos^2\theta_1)\hat{L}^{+}(1) + \sin^2\theta_1\ e^{i2\varphi_1}\hat{L}^{-}(1)\}$$

$$= -\frac{\hbar}{2}\sin\theta_1\{e^{-i\varphi_1}\hat{s}^{+}(j) - e^{i\varphi_1}\hat{s}^{-}(j)\}(\partial/\partial r_1) + \frac{\sin^2\theta_1}{4r_1\ \cos\theta_1}\{e^{-i2\varphi_1}\hat{s}^{+}(j)\hat{L}^{+}(1)$$

$$+e^{i2\varphi_1}\hat{s}^{-}(j)L^{-}(1)\} + \frac{(1 + \cos^2\theta)}{4r_1\ \cos\theta_1}\{\hat{s}^{+}(j)\hat{L}^{-}(1) + s^{-}(j)\hat{L}^{+}(1)\}$$

and:

$$i/2\{x^{+}(2)\hat{s}^{-}(j) - x^{-}(2)\hat{s}^{+}(j)\}\hat{p}_3(1)$$

$$= i/2\{r_2\ \sin\theta_2 e^{i\varphi_2}\hat{s}^{-}(j) - r_2\ \sin\theta_2 e^{-i\varphi_2}\hat{s}^{+}(j)\}\{\cos\theta_1(i\hbar\ \partial/\partial r_1)$$

$$- \frac{i\ \sin\theta_1}{2r_1}[e^{-i\varphi_1}\hat{L}^{+}(1) - e^{i\varphi_1}\hat{L}^{-}(1)]\}$$

$$= \frac{\hbar}{2}\ r_2\ \sin\theta_2\cos\theta_1\{e^{-i\varphi_2}\hat{s}^{+}(j) - e^{i\varphi_2}\hat{s}^{-}(j)\}(\partial/\partial r_1) + \frac{r_2\ \sin\theta_2\sin\theta_1}{4r_1}$$

$$[e^{i\varphi_2}\hat{s}^{-}(j) - e^{-i\varphi_2}\hat{s}^{+}(j)][e^{-i\varphi_1}\hat{L}^{+}(1) - e^{i\varphi_1}\hat{L}^{-}(1)]$$

$$= \frac{\hbar}{2} r^2 \sin\theta_2 \cos\theta_1 \{e^{-i\varphi_2}\hat{s}^+(j) - e^{i\varphi_2}\hat{s}^-(j)\}(\partial/\partial r_1) - \frac{r_2 \sin\theta_2 \sin\theta_1}{4r_1}$$

$$\{e^{-i(\varphi_2+\varphi_1)}\hat{s}^+(j)\hat{L}^+(1) + e^{i(\varphi_2+\varphi_1)}\hat{s}^-(j)\hat{L}^-(1)\} + \frac{r_2 \sin\theta_2 \sin\theta_1}{4r_1}$$

$$\{e^{-i(\varphi_2-\varphi_1)}\hat{s}^+(j)\hat{L}^-(1) + e^{i(\varphi_2-\varphi_1)}\hat{s}^-(j)\hat{L}^+(1)\}$$

also:

$$-i/2\{x^+(2)\hat{p}^-(1) - x^-(2)\hat{p}^+(1)\}\hat{s}_3(j) = -i/2\ r_2 \sin\theta_2\{e^{i\varphi_2}\hat{p}^-(1) - e^{-i\varphi_2}\hat{p}^+(1)\}\hat{s}_3(j)$$

$$= \frac{\hbar}{2} r_2 \sin\theta_2 \sin\theta_1\{e^{i\varphi_2}e^{-i\varphi_1} - e^{-i\varphi_2}e^{i\varphi_1}\}\hat{s}_3(j)(\partial/\partial r_1)$$

$$- \frac{r_2 \sin\theta_2}{4r_1 \cos\theta_1} \{e^{i\varphi_2}e^{-i2\varphi_1}\sin^2\theta_1\hat{L}^+(1) + e^{i\varphi_2}(1 + \cos^2\theta_1)\hat{L}^-(1)$$

$$+ e^{-i\varphi_2}(1 + \cos^2\theta_1)\hat{L}^+(1) + e^{-i\varphi_2}e^{i2\varphi_1}\sin^2\theta_1\hat{L}^-(1)\}\hat{s}_3(j)$$

$$= \frac{\hbar}{2} r_2 \sin\theta_2 \sin\theta_1\{e^{i(\varphi_2-\varphi_1)} - e^{-i(\varphi_2-\varphi_1)}\}\hat{s}_3(j)(\partial/\partial r_1)$$

$$- \frac{r_2 \sin\theta_2}{4r_1 \cos\theta_1}\{[e^{i(\varphi_2-2\varphi_1)}\sin^2\theta_1 + e^{-i\varphi_2}(1 - \cos^2\theta_1)]\hat{s}_3(j)\hat{L}^+(1)$$

$$+ [e^{-i(\varphi_2-2\varphi_1)}\sin^2\theta_1 + e^{i\varphi_2}(1 + \cos^2\theta_1)]\hat{s}_3(j)\hat{L}^-(1)\}$$

Substituting 25 for 23 in 20:

$$\frac{\hbar}{g\beta^2}\hat{\mathcal{H}}(\vec{x}_1) = d_1(r_1\theta_1)\{\tfrac{1}{2}[\hat{s}^+(1)\hat{L}^-(1) + \hat{s}^-(1)\hat{L}^+(1)] + \hat{s}_3(1)\hat{L}_3(1)\}$$

$$-d_2(r_1\theta_1)\,\frac{\sin\theta_1}{2}(\hbar\,\partial/\partial r_1)\{e^{-i\varphi_1}\hat{s}^+(1) - e^{i\varphi_1}\hat{s}^-(1)\}$$

$$+d_2(r_1\theta_1)\frac{\sin^2\theta_1}{4r_1\cos\theta_1}\{e^{-i2\varphi_1}\hat{s}^+(1)\hat{L}^+(1) + e^{i2\varphi_1}\hat{s}^-(1)\hat{L}^-(1)$$

$$+d_2(r_1\theta_1)\frac{1+\cos^2\theta_1}{4r_1\cos\theta_1}\{\hat{s}^+(1)\hat{L}^-(1) + \hat{s}^-(1)\hat{L}^+(1)\}$$

$$= d_1(r_1\theta_1)\hat{s}_3(1)\hat{L}_3(1) + \tfrac{1}{4}[2d_1(r_1\theta_1) + d_2(r_1\theta_1)\frac{1+\cos^2\theta_1}{r_1\cos\theta_1}]$$

$$\{\hat{s}^+(1)\hat{L}^-(1) + \hat{s}^-(1)\hat{L}^+(1)\} + \tfrac{1}{4}[d_2(r_1\theta_1)\frac{\sin^2\theta_1}{r_1\cos\theta_1}]$$

$$\{e^{-i2\varphi_1}\hat{s}^+(1)\hat{L}^+(1) + e^{i2\varphi_1}\hat{s}^-(1)\hat{L}^-(1)\} - \tfrac{1}{2}[d_2(r_1\theta_1)\sin\theta_1]$$

$$\{e^{-i\varphi_1}\hat{s}^+(1) - e^{i\varphi_2}\hat{s}^-(1)\}$$

Substituting 26 & 27 for 24 in 21:

$$\frac{\hbar}{g\beta^2}\hat{\mathcal{K}}(\vec{x}_1/\vec{r}_2) =$$

$$-\sum_m D_{|m|}(1,2)\,e^{im(\varphi_2-\varphi_1)}\{\tfrac{1}{2}[\hat{s}^+(1)\hat{L}^-(1) + \hat{s}^-(1)\hat{L}^+(1)] + \hat{s}_3(1)\hat{L}_3(1)\}$$

$$-\sum_m D_{|m|}(1,2)\,e^{im(\varphi_2-\varphi_1)}\,\frac{r_2\cos\theta_2\sin\theta_1}{2}(\hbar\,\partial/\partial r_1)\,\{e^{-i\varphi_1}\hat{s}^+(1) - e^{i\varphi_1}\hat{s}^-(1)\}$$

$$+\sum_m D_{|m|}(1,2)e^{im(\varphi_2-\varphi_1)}\,\frac{r_2\cos\theta_2\sin^2\theta_1}{4r_1\cos\theta_1}\,\{e^{-i2\varphi_1}\hat{s}^+(1)\hat{L}^+(1) + e^{i2\varphi_1}\hat{s}^-(1)\hat{L}^-(1)\}$$

$$+\sum_m D_{|m|}(1,2)e^{im(\varphi_2-\varphi_1)}\ \frac{r_2\ \cos\theta_2(1+\cos^2\theta_1}{4r_1\ \cos\theta_1}\ \{\hat{s}^+(1)\hat{L}^-(1)+\hat{s}^-(1)\hat{L}^+(1)\}$$

$$+\sum_m D_{|m|}(1,2)e^{im(\varphi_2-\varphi_1)}\ \frac{r_2\ \sin\theta_2\cos\theta_1}{2}(\hbar\ \partial/\partial r_1)\{e^{-i\varphi_2}\hat{s}^+(1)-e^{-i\varphi_2}\hat{s}^-(1)\}$$

$$+\sum_m D_{|m|}(1,2)e^{im(\varphi_2-\varphi_1)}\ \frac{r_2\ \sin\theta_2\sin\theta_1}{2}\ (\hbar\ \partial/\partial r_1)\ \{e^{i(\varphi_2-\varphi_1)}-e^{-i(\varphi_2-\varphi_1)}\}\hat{s}_3(1)$$

$$-\sum_m D_{|m|}(1,2)\ e^{im(\varphi_2-\varphi_1)}\ \frac{r_2\ \sin\theta_2\sin^2\theta_1}{4r_1\ \cos\theta_1}\{e^{i(\varphi_2-2\varphi_1)}\hat{L}^+(1)+e^{-i(\varphi_2-2\varphi_1)}\hat{L}^-(1)\}\hat{s}_3(1)$$

$$-\sum_m D_{|m|}(1,2)e^{im(\varphi_2-\varphi_1)}\ \frac{r_2\ \sin\theta_2(1+\cos^2\theta_1)}{4r_1\ \cos\theta_1}\ \{e^{-i\varphi_2}L^+(1)+e^{i\varphi_2}L^-(1)\}\hat{s}_3(1)$$

$$-\sum_m D_{|m|}(1,2)e^{im(\varphi_2-\varphi_1)}\ \frac{r_2\ \sin\theta_2\sin\theta_1}{4r_1}\ \{e^{-i(\varphi_2+\varphi_1)}\hat{s}^+(1)\hat{L}^+(1)+e^{i(\varphi_2+\varphi_1)}\hat{s}^-(1)\hat{L}^-(1)\}$$

$$+\sum_m D_{|m|}(1,2)e^{im(\varphi_2-\varphi_1)}\ \frac{r_2\ \sin\theta_2\sin\theta_1}{4r_1}\ \{e^{-i(\varphi_2-\varphi_1)}\hat{s}^+(1)\hat{L}^-(1)+e^{i(\varphi_2-\varphi_1)}\hat{s}^-(1)\hat{L}^+(1)\}$$

$$\frac{h}{g\beta^2}\hat{\mathcal{H}}(\vec{x}_1/\vec{r}_2) =$$

$$- \sum_m D_{|m|}(1,2)\{e^{im(\varphi_2-\varphi_1)}\hat{s}_3(1)\hat{L}_3(1)\}$$

$$- \sum_m \frac{1}{4} D_{|m|}(1,2)\left[2-\frac{r_2 \cos\theta_2(1+\cos^2\theta_1}{r_1 \cos\theta_1}\right] e^{im(\varphi_2-\varphi_1)} \{\hat{s}^+(1)\hat{L}^-(1) + \hat{s}^-(1)\hat{L}^+(1)\}$$

$$+ \sum_m \frac{1}{4} D_{|m|}(1,2)\left[\frac{r_2 \sin\theta_2 \sin\theta_1}{r_1}\right] e^{im(\varphi_2-\varphi_1)}\{e^{-i(\varphi_2-\varphi_1)}\hat{s}^+(1)\hat{L}^-(1) + e^{i(\varphi_2-\varphi_1)}\hat{s}^-(1)\hat{L}^+(1)\}$$

$$+ \sum_m \frac{1}{4} D_{|m|}(1,2)\left[\frac{r_2 \cos\theta_2 \sin^2\theta_1}{r_1 \cos\theta_1}\right] e^{im(\varphi_2-\varphi_1)} \{e^{-i2\varphi_1}\hat{s}^+(1)\hat{L}^+(1) + e^{i2\varphi_1}\hat{s}^-(1)\hat{L}^-(1)\}$$

$$- \sum_m \frac{1}{4} D_{|m|}(1,2)\left[\frac{r_2 \sin\theta_2 \sin\theta_1}{r_1}\right] e^{im(\varphi_2-\varphi_1)}\{e^{-i(\varphi_2+\varphi_1)}\hat{s}^+(1)\hat{L}^+(1) + e^{i(\varphi_2+\varphi_1)}\hat{s}^-(1)\hat{L}^-(1)\}$$

$$- \sum_m \frac{1}{4} D_{|m|}(1,2)\left[\frac{r_2 \sin\theta_2(1+\cos^2\theta_1}{r_1 \cos\theta_1}\right] e^{im(\varphi_2-\varphi_1)}\{e^{-i\varphi_2}\hat{s}_3(1)\hat{L}^+(1) + e^{i\varphi_2}\hat{s}_3(1)\hat{L}^-(1)\}$$

$$- \sum_m \frac{1}{4} D_{|m|}(1,2)\left[-\frac{r_2 \sin\theta_2 \sin^2\theta_1}{r_1 \cos\theta_1}\right] e^{im(\varphi_2-\varphi_1)} \{e^{i(\varphi_2-2\varphi_1)}\hat{s}_3(1)\hat{L}^+(1) + e^{-i(\varphi_2-2\varphi_1)}\hat{s}_3(1)\hat{L}^-(1)\}$$

$$- \sum_m \frac{1}{2} D_{|m|}(1,2)[r_2 \cos\theta_2 \sin\theta_1]\, e^{im(\varphi_2-\varphi_1)}(h\, \partial/\partial r_1) \{e^{-i\varphi_1}s^+(1) - e^{i\varphi_1}s^-(1)$$

$$+ \sum_m \frac{1}{2} D_{|m|}(1,2)[r_2 \sin\theta_2 \cos\theta_1]\, e^{im(\varphi_2-\varphi_1)}(h\, \partial/\partial r_1)\{e^{-i\varphi_2}s^+(1) - e^{i\varphi_1} s^-(1)\}$$

$$+\sum_m \tfrac{1}{2} D_{|m|}(1,2)[r_2 \sin\theta_2 \sin\theta_1]\, e^{im(\varphi_2-\varphi_1)}(\hbar\, \partial/\partial r_1)\ \{e^{i(\varphi_2-\varphi_1)} s_3(1) - e^{-i(\varphi_2-\varphi_1)} s_3(1)\}.$$

Similarly:

$$\frac{\hbar}{2g\beta^2}\,\hat{\mathcal{H}}(\vec{x}_1,\vec{x}_2) =$$

$$-\sum_m D_{|m|}(1,2)\{e^{im(\varphi_2-\varphi_1)}\hat{s}_3(2)\hat{L}_3(1)\}$$

$$-\sum_m \tfrac{1}{4} D_{|m|}(1,2)\Big[2-\frac{r_2 \cos\theta_2(1+\cos^2\theta_1}{r_1 \cos\theta_1}\Big]\, e^{im(\varphi_2-\varphi_1)}\ \{\hat{s}^+(2)\hat{L}^-(1) + \hat{s}^-(2)\hat{L}^+(1)\}$$

$$+\sum_m \tfrac{1}{4} D_{|m|}(1,2)\Big[\frac{r_2 \sin\theta_2 \sin\theta_1}{r_1}\Big]\ e^{im(\varphi_2-\varphi_1)}\{e^{-i(\varphi_2-\varphi_1)}\hat{s}^+(2)\hat{L}^-(1) + e^{i(\varphi_2-\varphi_1)}\hat{s}^-(2)\hat{L}^+(1)\}$$

$$+\sum_m \tfrac{1}{4} D_{|m|}(1,2)\Big[\frac{r_2 \cos\theta_2 \sin^2\theta_1}{r_1 \cos\theta_1}\Big]\, e^{im(\varphi_2-\varphi_1)}\ \{e^{-i2\varphi_1}\hat{s}^+(2)\hat{L}^+(1) + e^{i2\varphi_1}\hat{s}^-(2)\hat{L}^-(1)\}$$

$$-\sum_m \tfrac{1}{4} D_{|m|}(1,2)\ \Big[\frac{r_2 \sin\theta_2 \sin\theta_1}{r_1}\Big]\, e^{im(\varphi_2-\varphi_1)}\{e^{-i(\varphi_2+\varphi_1)}\hat{s}^+(2)\hat{L}^+(1) + e^{i(\varphi_2+\varphi_1)}\hat{s}^-(2)\hat{L}^-(1)\}$$

$$-\sum_m \tfrac{1}{4} D_{|m|}(1,2)\Big[\frac{r_2 \sin\theta_2(1+\cos^2\theta_1}{r_1 \cos\theta_1}\Big]\ e^{im(\varphi_2-\varphi_1)}\{e^{-i\varphi_2}\hat{s}_3(2)\hat{L}^+(1) + e^{i\varphi_2}\hat{s}_3(2)\hat{L}^-(1)\}$$

$$- \sum_{m} \frac{1}{4} D_{|m|}(1,2)\left[\frac{r_2 \sin\theta_2 \sin^2\theta_1}{r_1 \cos\theta_1}\right] e^{im(\varphi_2-\varphi_1)} \{e^{i(\varphi_2-2\varphi_1)} \hat{s}_3(2)\hat{L}^+(1) + e^{-i(\varphi_2-2\varphi_1)} \hat{s}_3(2)\hat{L}^-(1)\}$$

$$- \sum_{m} \tfrac{1}{2} D_{|m|}(1,2)[r_2 \cos\theta_2 \sin\theta_1] e^{im(\varphi_2-\varphi_1)} (\hbar\, \partial/\partial r_1) \{e^{-i\varphi_1} s^+(2) - e^{i\varphi_1} s^-(2)$$

$$\sum_{m} \tfrac{1}{2} D_{|m|}(1,2)[r_2 \sin\theta_2 \cos\theta_1] \quad e^{im(\varphi_2-\varphi_1)} (\hbar\, \partial/\partial r_1)\{e^{-i\varphi_2} s^+(2) - e^{i\varphi_1} s^-(2)\}$$

$$- \sum_{m} \tfrac{1}{2} D_{|m|}(1,2)[r_2 \sin\theta_2 \sin\theta_1] e^{im(\varphi_2-\varphi_1)} (\hbar\, \partial/\partial r_1) \{e^{i(\varphi_2-\varphi_1)} s_3(2) - e^{-i(\varphi_2-\varphi_1)} s_3(2)\}.$$

Definitions:

$$\Delta^{(o)}(1) = d_1(r_1\theta_1)$$

$$\Delta^{(1)}(1) = \tfrac{1}{4}[2d_1(r_1\theta_1) + d_2(r_1\theta_1)\frac{1+\cos^2\theta_1}{r_1\ \cos\theta_1}$$

$$\Delta^{(2)}(1) = \frac{1}{4}\ d_2(r_1\theta_1)\frac{\sin^2\theta_1}{r_1\ \cos\theta_1}$$

$$\Delta^{(3)}(1) = -\tfrac{1}{2}d_2(r_1\theta_1)\ \sin\theta_1$$

$$\Delta^{(o)}_{|m|}(1,2) = -D_{|m|}(r_1\theta_1;r_2\theta_2)$$

$$\Delta^{(1)}_{|m|}(1,2) = -\frac{1}{4}\ D_{|m|}(r_1\theta_1;r_2\theta_2)[\ 2-\frac{r_2\ \cos\theta_2(1+\cos^2\theta_1}{r_1\ \cos\theta_1}]$$

$$\Delta^{(2)}_{|m|}(1,2) = \frac{1}{4}\ D_{|m|}(r_1\theta_1;r_2\theta_2)\frac{r_2\ \sin\theta_2\sin\theta_1}{r_1}$$

$$\Delta^{(3)}_{|m|}(1,2) = \frac{1}{4}\ D_{|m|}(r_1\theta_1;r_2\theta_2)\frac{r_2\ \cos\theta_2\sin^2\theta_1}{r_1\ \cos\theta_1}$$

$$-\Delta^{(2)}_{|m|}(1,2) = \Delta^{(4)}_{|m|}(1,2) = -\frac{1}{4}\ D_{|m|}(r_1\theta_1;r_2\theta_2)\frac{r_2\ \sin\theta_2\sin\theta_1}{r_1}$$

$$\Delta^{(5)}_{|m|}(1,2) = -\frac{1}{4}\ D_{|m|}(r_1\theta_1;r_2\theta_2)\frac{r_2\ \sin\theta_2(1+\cos^2\theta_1)}{r_1\ \cos\theta_1}$$

$$\Delta^{(6)}_{|m|}(1,2) = -\ \frac{1}{4}\ D_{|m|}(r_1\theta_1;r_2\theta_2)\frac{r_2\ \sin\theta_2\sin^2\theta_1}{r\ \cos\theta_1}$$

$$\Delta^{(7)}_{|m|}(1,2) = -\tfrac{1}{2}\ D_{|m|}(r_1\theta_1;r_2\theta_2)\ r_2\ \cos\theta_2\sin\theta_1$$

$$\Delta^{(8)}_{|m|}(1,2) = \tfrac{1}{2}\, D_{|m|}(r_1\theta_1; r_2\theta_2)\; r_2\, \sin\theta_2 \cos\theta_1$$

$$\Delta^{(9)}_{|m|}(1,2) = \tfrac{1}{2}\, D_{|m|}(r_1\theta_1; r_2\theta_2)\; r_2\, \sin\theta_2 \sin\theta_1$$

<u>NB</u>. $\Delta^{(n)}(1,2) \neq \Delta^{(n)}(2,1)$ generally.

then:

$$\begin{aligned}\hat{\mathcal{H}}(\vec{x}_1) = {} & \Delta^{(o)}(1)\hat{s}_3(1)\hat{L}_3(1) + \Delta^{(1)}(1)\{\hat{s}^+(1)\hat{L}^-(1) + \hat{s}^-(1)\hat{L}^+(1)\} \\ & + \Delta^{(2)}(1)\{e^{-i2\varphi_1}\hat{s}^+(1)\hat{L}^+(1) + e^{i2\varphi_1}\hat{s}^-(1)\hat{L}^-(1)\} \\ & + \Delta^{(3)}(1)(\hbar\, \partial/\partial r_1)\{e^{-i\varphi_1}\hat{s}^+(1) - e^{-i\varphi_1}\hat{s}^-(1)\}\end{aligned}$$

$$\hat{\mathcal{H}}(\vec{x}_1/\vec{r}_2) =$$

$$\begin{aligned}& \sum_m \Delta^{(o)}_{|m|}(1,2)\; e^{im(\varphi_2-\varphi_1)}\hat{s}_3(1)\hat{L}_3(1) \\ & + \sum_m \Delta^{(1)}_{|m|}(1,2)\; e^{im(\varphi_2-\varphi_1)}\{\hat{s}^+(1)\hat{L}^-(1) + \hat{s}^-(1)\hat{L}^+(1)\} + e^{i(\varphi_2-\varphi_1)}\hat{s}^-(1)\hat{L}^+(1)\} \\ & + \sum_m \Delta^{(2)}_{|m|}(1,2)\; e^{im(\varphi_2-\varphi_1)}\hat{s}^+(1)\hat{L}^-(1)\;\{e^{-i2\varphi_1}\hat{s}^+(1)\hat{L}^+(1) + e^{i2\varphi_1}\hat{s}^-(1)\hat{L}^-(1)\} \\ & + \sum_m \Delta^{(4)}_{|m|}(1,2)\; e^{im(\varphi_2-\varphi_1)}\;\{e^{-i(\varphi_2+\varphi_1)}\hat{s}^+(1)\hat{L}^+(1) + e^{i(\varphi_2+\varphi_1)}\hat{s}^-(1)\hat{L}^-(1)\} \\ & - \sum_m \Delta^{(5)}_{|m|}(1,2)\; e^{im(\varphi_2-\varphi_1)}\{e^{-i\varphi_2}\hat{s}_3(1)\hat{L}^+(1) + e^{i\varphi_2}\hat{s}_3(1)\hat{L}^-(1)\} \\ & + \sum_m \Delta^{(6)}_{|m|}(1,2)\; e^{im(\varphi_2-\varphi_1)}\{e^{i(\varphi_2-2\varphi_1)}\hat{s}_3(1)\hat{L}^+(1) + e^{-i(\varphi_2-2\varphi_1)}\hat{s}_3(1)\hat{L}^-(1)\} \\ & + \sum_m \Delta^{(7)}_{|m|}(1,2)\; e^{im(\varphi_2-\varphi_1)}(\hbar\, \partial/\partial r_1)\{e^{i\varphi_1}\hat{s}^+(1) - e^{i\varphi_1}\hat{s}^-(1)\} \\ & + \sum_m \Delta^{(8)}_{|m|}(1,2)\; e^{im(\varphi_2-\varphi_1)}(\hbar\, \partial/\partial r_1)\{e^{-i\varphi_2}\hat{s}^+(1) - e^{i\varphi_2}\hat{s}^-(1)\}\end{aligned}$$

$$+ \sum_m \Delta^{(9)}_{|m|}(1,2)\ e^{im(\varphi_2-\varphi_1)}(\hbar\ \partial/\partial r_1)\{e^{i(\varphi_2-\varphi_1)}\hat{s}_3(1) - e^{-i(\varphi_2-\varphi_1)}\hat{s}_3(1)\}$$

$$\hat{\mathcal{H}}(\vec{x}_1,\vec{x}_2) =$$

$$2\sum_m \Delta^{(0)}_{|m|}(1,2)\ e^{im(\varphi_2-\varphi_1)}\hat{s}_3(2)\hat{L}_3(1)$$

$$+ 2\sum_m \Delta^{(1)}_{|m|}(1,2)\ e^{im(\varphi_2-\varphi_1)}\ \{\hat{s}^+(2)\hat{L}^-(1) + \hat{s}^-(2)\hat{L}^+(1)\}$$

$$+ 2\sum_m \Delta^{(2)}_{|m|}(1,2)\ e^{im(\varphi_2-\varphi_1)}\ \{e^{-i(\varphi_2-\varphi_1)}\hat{s}^+(2)\hat{L}^-(1) + e^{i(\varphi_2-\varphi_1)}\hat{s}^-(2)\hat{L}^+(1)\}$$

$$+ 2\sum_m \Delta^{(3)}_{|m|}(1,2)\ e^{im(\varphi_2-\varphi_1)}\{e^{-i2\varphi_1}\hat{s}^+(2)\hat{L}^+(1) + e^{i2\varphi_1}\hat{s}^-(2)\hat{L}^-(1)\}$$

$$+ 2\sum_m \Delta^{(4)}_{|m|}(1,2)\ e^{im(\varphi_2-\varphi_1)}\{e^{-i(\varphi_2+\varphi_1)}\hat{s}^+(2)\hat{L}^+(1) + e^{i(\varphi_2+\varphi_1)}\hat{s}^-(2)\hat{L}^+(1)\}$$

$$+ 2\sum_m \Delta^{(5)}_{|m|}(1,2)\ e^{im(\varphi_2-\varphi_1)}\{e^{-i\varphi_2}\hat{s}_3(2)\hat{L}^+(1) + e^{i\varphi_2}\hat{s}_3(2)\hat{L}^-(1)\}$$

$$+ 2\sum_m \Delta^{(6)}_{|m|}(1,2)\ e^{im(\varphi_2-\varphi_1)}\{e^{i(\varphi_2-2\varphi_1)}\hat{s}_3(2)\hat{L}^+(1) + e^{-i(\varphi_2-2\varphi_1)}\hat{s}_3(2)\hat{L}^-(1)\}$$

$$+ 2\sum_m \Delta^{(7)}_{|m|}(1,2)\ e^{im(\varphi_2-\varphi_1)}(\hbar\ \partial/\partial r_1)\{e^{-i\varphi_1}\hat{s}^+(2) - e^{i\varphi_1}\hat{s}^-(2)\}$$

$$+ 2\sum_m \Delta^{(8)}_{|m|}(1,2)\ e^{im(\varphi_1-\varphi_2)}(\hbar\ \partial/\partial r_1)\{e^{-i\varphi_2}\hat{s}^+(2) - e^{i\varphi_2}\hat{s}^-(2)\}$$

$$+ 2\sum_m \Delta^{(9)}_{|m|}(1,2)\ e^{im(\varphi_1-\varphi_2)}(\hbar\ \partial/\partial r_1)\{e^{i(\varphi_2-\varphi_1)}\hat{s}_3(2) - e^{-i(\varphi_2-\varphi_1)}\hat{s}_3(2)\}$$

5. Spin-Orbit Coupling Operator of $\hat{L}_3\ \hat{s}_3$ Type:

Definition of operator:

$$\hat{\mathcal{H}}^{(o)}(\vec{x}_1 \ldots\ldots \vec{x}_N) = \sum_{i=1}^{N} \hat{\mathcal{H}}^{(o)}(\vec{x}_i) + \tfrac{1}{2}\sum_{i \neq j}^{NN} \hat{\mathcal{H}}^{(o)}(\vec{x}_i, \vec{x}_j)$$

where:

$$\hat{\mathcal{H}}^{(o)}(\vec{x}_i) = \Delta^{(o)}(i)\hat{s}_3(i)\hat{L}_3(i)$$

$$\hat{\mathcal{H}}^{(o)}(\vec{x}_i, \vec{x}_j) = \sum_{m=-\infty}^{\infty} \Delta^{(o)}_{|m|}(i,j)\{e^{im(\varphi_j-\varphi_i)}\hat{s}_3(i)\hat{L}_3(i) + e^{im(\varphi_i-\varphi_j)}\hat{s}_3(j)\hat{L}_3(j)$$

$$+ 2e^{im(\varphi_j-\varphi_i)}\hat{s}_3(j)\hat{L}_3(i) + 2e^{im(\varphi_i-\varphi_j)}\hat{s}_3(i)\hat{L}_3(j)\}$$

$$= \sum_{m=-\infty}^{\infty} \Delta^{(o)}_{|m|}(i,j)\{e^{im(\varphi_j-\varphi_i)}[\hat{s}_3(i) + 2\hat{s}_3(j)]\hat{L}_3(i)$$

$$+ e^{im(\varphi_j-\varphi_i)}[\hat{s}_3(j) + 2\hat{s}_3(i)]\hat{L}_3(j)\}$$

where $\Delta^{(o)}_{(i)} = \Delta^{(o)}(r_i\theta_i)$

$$\Delta^{(o)}_{|m|}(i,j) = \Delta^{(o)}(r_i\theta_i;r_j\theta_j) = \Delta^{(o)}_{|m|}(j,i)$$

Action of $\hat{L}_3$ and $\hat{s}_3$ on spin-orbitals defined in (1).

$$\hat{L}_3(i)\xi(\mu,\lambda,s;x_i) = \hbar\lambda\xi(\mu,\lambda,s;x_i)$$

$$\hat{s}_3(i)\xi(\mu,\lambda,s;x_i) = \frac{\hbar}{2}\, s\xi(\mu,\lambda,s;x_i)$$

Symbols for relevant integrals:

$$[\mu_1, \lambda_1, s_1 || \mu_2, \lambda_2, s_2] = \langle \xi(\mu_1 . \lambda_1 , s_1 ; x_i \, \hat{\mathcal{H}}^{(o)}(x_i) \, | \mu_2, \lambda_2 . s_2 ; x_i) \rangle$$

$$\left\{ \begin{matrix} \mu_1 & \lambda_1 & s_1 \\ \mu_2 & \lambda_2 & s_2 \end{matrix} \middle\| \begin{matrix} \mu_3 & \lambda_3 & s_3 \\ \mu_4 & \lambda_4 & s_4 \end{matrix} \right\} \equiv \langle \xi(\mu_1, \lambda_1, s_1 ; x_i) \xi(\mu_2, \lambda_2, s_2 ; x_j) \, \hat{\mathcal{H}}^{(o)}(x_i, x_j) \, | \; \xi(\mu_3, \lambda_3, s_3 ; x_i) \xi(\mu_4, \lambda_4, s_4 ; x_j) \rangle$$

then:

$$\begin{aligned} [\mu_1, \lambda_1, s_1 || \mu_2, \lambda_2, s_2] &= \langle \xi(\mu_1, \lambda_1, s_1 ; x_i \, | \Delta^{(o)}(i) s_3(i) L_3(i) \, | \xi(\mu_2, \lambda_2, s_2 ; x_i) \rangle \\ &= \frac{\hbar^2}{2} \lambda_2 s_2 \langle n(s_1, \sigma_i \, | n(s_2, \sigma_i) \rangle \langle \exp[i\lambda_1 \varphi_i] \, | \exp[i\lambda_2 \varphi_i] \rangle \\ &\quad \langle \chi(\mu_1, |\lambda_1| ; r_i \theta_i) \, | \Delta^{(o)}(r_i \theta_i) \, | \chi(\mu_2, |\lambda_2| ; r_i \theta_i) \rangle \\ &= \frac{\hbar^2}{2} \lambda_2 s_2 \delta(s_1, s_2) 2\pi \delta(0, \lambda_2 - \lambda_1) \frac{1}{\hbar^2 \pi} (\mu_1, |\lambda_1| || \mu_2, |\lambda_2|) \\ &= \lambda_2 s_2 \delta(s_1, s_2) \delta(0, \lambda_2 - \lambda_1) (\mu_1, |\lambda_1| || \mu_2, |\lambda_2|) \end{aligned}$$

and:

$$\begin{aligned} \left\{ \begin{matrix} \mu_1 & \lambda_1 & s_1 \\ \mu_2 & \lambda_2 & s_2 \end{matrix} \middle\| \begin{matrix} \mu_3 & \lambda_3 & s_3 \\ \mu_4 & \lambda_4 & s_4 \end{matrix} \right\} &= \sum_{m=-\infty}^{\infty} \langle \xi(\mu_1, \lambda_1, s_1 ; x_i) \xi(\mu_2, \lambda_2, s_2 ; x_j) \, | \\ &\quad \Delta^{(o)}_{|m|}(i, j) \{ e^{im(\varphi_j - \varphi_i)} [\hat{s}_3(i) + 2\hat{s}_3(j)] \hat{L}_3(i) \\ &\quad + e^{im(\varphi_i - \varphi_j)} [\hat{s}_3(j) + 2\hat{s}_3(i)] \hat{L}_3(j) \} \, | \\ &\quad \xi(\mu_3, \lambda_3, s_3 ; x_i) \xi(\mu_4, \lambda_4, s_4 ; x_j) \rangle \end{aligned}$$

$$= \frac{\hbar^2}{2} \sum_m \langle \xi(\mu_1, \lambda_1, s_1; x_i)\, \xi(\mu_2, \lambda_2, s_2; x_j)\, \Big| \Delta^{(o)}_{|m|}(i, j) \{ e^{im(\varphi_j - \varphi_i)}$$

$$[s_3 + 2s_4]\lambda_3 + e^{im(\varphi_j - \varphi_i)} [s_4 + 2s_3]\lambda_4 \} \Big|$$

$$\xi(\mu_3, \lambda_3, s_3; x_i)\, \xi(\mu_4, \lambda_4, s_4; x_j) \rangle$$

$$= \frac{\hbar^2}{2} \underbrace{\langle n(s_1, \sigma_i) | n(s_3; \sigma_i) \rangle}_{\delta(s_1, s_3)} \underbrace{\langle n(s_2, \sigma_j) | n(s_4, \sigma_j) \rangle}_{\delta(s_2, s_4)}$$

$$\underbrace{\sum_m \langle \chi(\mu_1, |\lambda_1|; r_i\theta_i)\, \chi(\mu_2 |\lambda_2|; r_j\theta_j)\, \Big| \Delta^{(o)}_{|m|}(r_i\theta_i; r_j\theta_j \Big| \;\; \xi(\mu_3, |\lambda_3|; r_i\theta_i)\, \xi(\mu_4 |\lambda_4|; r_j\theta_j) \rangle}_{\frac{1}{2\hbar^2\pi^2} \left(\begin{matrix} \mu_1 & |\lambda_1| \\ \mu_2 & |\lambda_2| \end{matrix} \middle\| \begin{matrix} \mu_3 & |\lambda_3| \\ \mu_4 & |\lambda_4| \end{matrix} \right)_{|m|}}$$

$$\{ [s_3 + 2s_4]\lambda_3 \underbrace{\langle e^{i\lambda_1\varphi_i} | e^{-im\varphi_i} | e^{i\lambda_3\varphi_i} \rangle}_{2\pi\delta(m, \lambda_3 - \lambda_1)} \underbrace{\langle e^{i\lambda_2\varphi_j} | e^{im\varphi_j} | e^{i\lambda_4\varphi_j} \rangle}_{2\pi\delta(m, \lambda_2 - \lambda_4)}$$

$$+ [s_4 + 2s_3]\lambda_4 \underbrace{\langle e^{i\lambda_1\varphi_i} | e^{im\varphi_i} | e^{i\lambda_3\varphi_i} \rangle}_{2\pi\delta(m, \lambda_1 - \lambda_3)} \underbrace{\langle e^{i\lambda_2\varphi_j} | e^{-im\varphi_j} | e^{i\lambda_4\varphi_j} \rangle}_{2\pi\delta(m, \lambda_4 - \lambda_2)} \}$$

$$= \delta(s_1, s_3)\, \delta(s_2, s_4) \sum_{m=-\infty}^{\infty} \{ [s_3 + 2s_4]\lambda_3\, \delta(m, \lambda_3 - \lambda_1)\, \delta(m, \lambda_2 - \lambda_4)$$

$$+ [s_4 + 2s_3]\lambda_4\, \delta(m, \lambda_1 - \lambda_3)\, \delta(m, \lambda_4 - \lambda_2) \} \left(\begin{matrix} \mu_1 & |\lambda_1| \\ \mu_2 & |\lambda_2| \end{matrix} \middle\| \begin{matrix} \mu_3 & |\lambda_3| \\ \mu_4 & |\lambda_4| \end{matrix} \right)_{|m|}$$

$$= \delta(s_1,s_3)\delta(s_2,s_4)\sum_{m=-\infty}^{\infty}\{[s_3+2s_4]\lambda_3+[s_4+2s_3]\lambda_4\}$$

$$\delta(m,\lambda_3-\lambda_1)\delta(m,\lambda_2-\lambda_4)\left(\begin{array}{cc||cc} \mu_1 & |\lambda_1| & \mu_3 & |\lambda_3| \\ \mu_2 & |\lambda_2| & \mu_4 & |\lambda_4| \end{array}\right)_{|m|}$$

$$= \{[s_3+2s_4]\lambda_3+[s_4+2s_3]\lambda_4\}\delta(s_1,s_3)\delta(s_2,s_4)$$

$$\sum_{m=-\infty}^{\infty}\delta(m,\lambda_3-\lambda_1)\delta(m,\lambda_2-\lambda_4)\left(\begin{array}{cc||cc} \mu_1 & |\lambda_1| & \mu_3 & |\lambda_3| \\ \mu_2 & |\lambda_2| & \mu_4 & |\lambda_4| \end{array}\right)_{|m|}$$

then

$$\left[\begin{array}{ccc||ccc} \mu_1 & \lambda_1 & s_1 & \mu_2 & \lambda_2 & s_2 \\ \mu_3 & \lambda_3 & s_3 & \mu_4 & \lambda_4 & s_4 \end{array}\right] = \left\{\begin{array}{ccc||ccc} \mu_1 & \lambda_1 & s_1 & \mu_2 & \lambda_2 & s_2 \\ \mu_3 & \lambda_3 & s_3 & \mu_4 & \lambda_4 & s_4 \end{array}\right\} - \left\{\begin{array}{ccc||ccc} \mu_1 & \lambda_1 & s_1 & \mu_4 & \lambda_4 & s_4 \\ \mu_3 & \lambda_3 & s_3 & \mu_2 & \lambda_2 & s_2 \end{array}\right\}$$

$$= \{[s_2+2s_4]\lambda_2 + [s_4+2s_2]\lambda_4\}\delta(s_1,s_2)\delta(s_3,s_4)$$

$$\sum_{m}\delta(m,\lambda_2-\lambda_1)\delta(m,\lambda_3-\lambda_4)\left(\begin{array}{cc||cc} \mu_1 & |\lambda_1| & \mu_2 & |\lambda_2| \\ \mu_3 & |\lambda_3| & \mu_4 & |\lambda_4| \end{array}\right)_{|m|}$$

$$- \{[s_4+2s_2]\lambda_4 + [s_2+2s_4]\lambda_2\}\delta(s_1,s_4)\delta(s_2,s_3)$$

$$\sum_{m}\delta(m,\lambda_4-\lambda_1)\delta(m,\lambda_3-\lambda_2)\left(\begin{array}{cc||cc} \mu_1 & |\lambda_1| & \mu_4 & |\lambda_4| \\ \mu_3 & |\lambda_3| & \mu_2 & |\lambda_2| \end{array}\right)_{|m|}$$

$$= \{[s_2+2s_4]\lambda_2 + [s_4+2s_2]\lambda_4\}\, \delta\begin{pmatrix} s_1, s_3 \\ s_2, s_4 \end{pmatrix} \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ \lambda_3-\lambda_4 \end{pmatrix}$$

$$\left(\begin{matrix} \mu_1 & |\lambda_1| \\ \mu_3 & |\lambda_3| \end{matrix}\middle\|\begin{matrix} \mu_2 & |\lambda_2| \\ \mu_4 & |\lambda_4| \end{matrix}\right)_{|\lambda_3-\lambda_4|} - \delta\begin{pmatrix} s_1, s_3 \\ s_4, s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_4-\lambda_1 \\ \lambda_3-\lambda_2 \end{pmatrix}$$

$$\left(\begin{matrix} \mu_1 & |\lambda_1| \\ \mu_3 & |\lambda_3| \end{matrix}\middle\|\begin{matrix} \mu_4 & |\lambda_4| \\ \mu_2 & |\lambda_2| \end{matrix}\right)_{|\lambda_3-\lambda_2|}$$

now,

$$\left.\begin{aligned} &\lambda_2-\lambda_1 = \lambda_3-\lambda_4 = \Delta \\ &\lambda_4-\lambda_1+\lambda_2 = \lambda_3 = \Delta + \lambda_4 \\ &\lambda_4-\lambda_1 = \lambda_3-\lambda_2 = \Delta + \lambda_4-\lambda_2 \end{aligned}\right\} \quad \delta\begin{pmatrix} \lambda_4-\lambda_1 \\ \lambda_3-\lambda_2 \end{pmatrix} = \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ \lambda_3-\lambda_4 \end{pmatrix}$$

Hence:

$$\left[\begin{matrix} \mu_1 & \lambda_1 & s_1 \\ \mu_3 & \lambda_3 & s_3 \end{matrix}\middle\|\begin{matrix} \mu_2 & \lambda_2 & s_2 \\ \mu_4 & \lambda_4 & s_4 \end{matrix}\right] = \{[s_2+2s_4]\lambda_2+[s_4+2s_2]\lambda_2\}\left\{\left(\begin{matrix} \mu_1 & |\lambda_1| \\ \mu_3 & |\lambda_3| \end{matrix}\middle\|\begin{matrix} \mu_2 & |\lambda_2| \\ \mu_4 & |\lambda_4| \end{matrix}\right)_{|\lambda_3-\lambda_4|}\right.$$

$$\left.\delta\begin{pmatrix} s_1, s_3 \\ s_2, s_4 \end{pmatrix} - \left(\begin{matrix} \mu_1 & |\lambda_1| \\ \mu_3 & |\lambda_3| \end{matrix}\middle\|\begin{matrix} \mu_4 & |\lambda_4| \\ \mu_2 & |\lambda_2| \end{matrix}\right)_{|\lambda_3-\lambda_2|} \delta\begin{pmatrix} s_1, s_3 \\ s_4, s_2 \end{pmatrix}\right\} \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ \lambda_3-\lambda_4 \end{pmatrix}$$

Therefore:

$$\begin{bmatrix} \mu_K & \lambda_K & s_K \\ \mu_J & \lambda_J & s_J \end{bmatrix}\!\!\left|\!\left| \begin{matrix} \mu_I & \lambda_I & s_I \\ \mu_L & \lambda_L & s_L \end{matrix} \right.\right] = \left[s_I\lambda_I + s_L\lambda_L + 2(s_L\lambda_I + s_I\lambda_L) \right] \delta\begin{pmatrix} \lambda_I - \lambda_K \\ \lambda_J - \lambda_L \end{pmatrix}$$

$$\left\{ \begin{pmatrix} \mu_K & |\lambda_K| & \mu_I & |\lambda_I| \\ \mu_J & |\lambda_J| & \mu_L & |\lambda_L| \end{pmatrix}_{|\lambda_J - \lambda_L|} \delta\begin{pmatrix} s_I, s_J \\ s_K, s_L \end{pmatrix} \right.$$

$$\left. - \begin{pmatrix} \mu_K & |\lambda_K| & \mu_L & |\lambda_L| \\ \mu_J & |\lambda_J| & \mu_I & |\lambda_I| \end{pmatrix}_{|\lambda_J - \lambda_I|} \delta\begin{pmatrix} s_I, s_K \\ s_J, s_L \end{pmatrix} \right\}$$

Thus expanding:

$$\sum_{p=1}^{N} \begin{bmatrix} \mu_1 & \lambda_1 & s_1 \\ \mu_p & \lambda_p & s_p \end{bmatrix}\!\!\left|\!\left| \begin{matrix} \mu_2 & \lambda_2 & s_2 \\ \mu_p & \lambda_p & s_p \end{matrix} \right.\right] = \sum_{p=1}^{N} \left[\lambda_2 s_2 + \lambda_p s_p + 2(\lambda_2 s_p + \lambda_p s_2) \right] \left\{ \begin{pmatrix} \mu_1 & |\lambda_1| & \mu_2 & |\lambda_2| \\ \mu_p & |\lambda_p| & \mu_p & |\lambda_p| \end{pmatrix}_{|\lambda_p - \lambda_p|} \right.$$

$$\left. \delta\begin{pmatrix} s_1, s_p \\ s_2, s_p \end{pmatrix} - \begin{pmatrix} \mu_1 & |\lambda_1| & \mu_p & |\lambda_p| \\ \mu_p & |\lambda_p| & \mu_2 & |\lambda_2| \end{pmatrix}_{|\lambda_p - \lambda_2|} \delta\begin{pmatrix} s_1, s_p \\ s_p, s_2 \end{pmatrix} \right\} \delta\begin{pmatrix} \lambda_2 - \lambda_1 \\ \lambda_p - \lambda_p \end{pmatrix}$$

Consider Terms:

$$\sum_{p=1}^{N} \lambda_p s_p \left(\quad \| \quad \right) \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2 - \lambda_1 \\ 0 \end{pmatrix} = 0, \text{ for every } s_p, \lambda_p = \pm|\lambda_p|$$

$$\sum_{p=1}^{N} 2\lambda_2 s_p \left(\quad \| \quad \right) \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2 - \lambda_1 \\ 0 \end{pmatrix} = 0, \text{ for every value of } \lambda_2, s_p = \pm\tfrac{1}{2}$$

$$\sum_{p=1}^{N} 2\lambda_p s_2 \left(\quad \| \quad \right) \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2 - \lambda_1 \\ 0 \end{pmatrix} = 0, \text{ for every value of } s_2, \lambda_p = \pm|\lambda_p|$$

$$\sum_{p=1}^{N} \lambda_2 s_2 \left(\qquad \middle\| \qquad \right) \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ 0 \end{pmatrix} = \sum_{\mu_p,\lambda_p} 2\lambda_2 s_2 \left(\qquad \middle\| \qquad \right) \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ 0 \end{pmatrix}$$

removing sum over s_p implied in $\sum\limits_{p}$; for every $\lambda_p, s_p = \pm\frac{1}{2}$.

$$-\sum_{p=1}^{N} \lambda_2 s_2 \left(\qquad \middle\| \qquad \right)_{|\lambda_p-\lambda_2|} \delta\begin{pmatrix} s_p \\ s_2 \end{pmatrix} \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ 0 \end{pmatrix}$$

$$= -\sum_{\mu_p,\lambda_p} \lambda_2 s_2 \left(\qquad \middle\| \qquad \right)_{|\lambda_p-\lambda_2|} \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ 0 \end{pmatrix}$$

for every value of $\lambda_p, s_p = \pm\frac{1}{2}$ $= s_2$ in one case;
$\neq s_2$ in the other.

$$-\sum_{p=1}^{N} \lambda_p s_p \left(\qquad \middle\| \qquad \right)_{|\lambda_p-\lambda_2|} \delta\begin{pmatrix} s_p \\ s_2 \end{pmatrix} \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ 0 \end{pmatrix}$$

$$= -\sum_{\mu_p,\lambda_p}^{N} \lambda_p s_2 \left(\qquad \middle\| \qquad \right)_{|\lambda_p-\lambda_2|} \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ 0 \end{pmatrix}$$

and

$$-\sum_{p=1}^{N} 2\lambda_2 s_p \left(\qquad \middle\| \qquad \right)_{|\lambda_p-\lambda_2|} \delta\begin{pmatrix} s_p \\ s_2 \end{pmatrix} \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ 0 \end{pmatrix}$$

$$= -\sum_{\mu_p,\lambda_p} 2\lambda_2 s_2 \left(\qquad \middle\| \qquad \right)_{|\lambda_p-\lambda_2|} \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ 0 \end{pmatrix}$$

and

$$-\sum_{p=1}^{N} 2\lambda_p s_2 \left(\begin{array}{c||c} \quad & \quad \end{array} \right)_{|\lambda_p-\lambda_2|} \delta\begin{pmatrix} s_p \\ s_2 \end{pmatrix} \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ 0 \end{pmatrix}$$

$$= -\sum_{\mu_p,\lambda_p} 2\lambda_p s_2 \left(\begin{array}{c||c} \quad & \quad \end{array} \right)_{|\lambda_p-\lambda_2|} \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ 0 \end{pmatrix}$$

Hence:

$$\sum_{p=1}^{N} \left[\begin{array}{ccc||ccc} \mu_1 & \lambda_1 & s_1 & \mu_2 & \lambda_2 & s_2 \\ \mu_p & \lambda_p & s_p & \mu_p & \lambda_p & s_p \end{array} \right] = \sum_{\mu_p,\lambda_p} 2\lambda_2 s_2 \left(\begin{array}{cc||cc} \mu_1 & |\lambda_1| & \mu_2 & |\lambda_2| \\ \mu_p & |\lambda_p| & \mu_p & |\lambda_p| \end{array} \right)_0 \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ 0 \end{pmatrix}$$

$$-\sum_{\mu_p,\lambda_p} 3\lambda_2 s_2 \left(\begin{array}{cc||cc} \mu_1 & |\lambda_1| & \mu_p & |\lambda_p| \\ \mu_p & |\lambda_p| & \mu_2 & |\lambda_2| \end{array} \right)_{|\lambda_p-\lambda_2|} \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ 0 \end{pmatrix}$$

$$-\sum_{\mu_p,\lambda_p} 3\lambda_p s_2 \begin{pmatrix} \mu_1 & |\lambda_1| & \mu_p & |\lambda_p| \\ \mu_p & |\lambda_p| & \mu_2 & |\lambda_2| \end{pmatrix}_{|\lambda_p-\lambda_2|} \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ 0 \end{pmatrix}$$

$$= \lambda_2 s_2 \sum_{\mu_p,\lambda_p} \left\{ 2 \begin{pmatrix} \mu_1 & |\lambda_1| & \mu_2 & |\lambda_2| \\ \mu_p & |\lambda_p| & \mu_p & |\lambda_p| \end{pmatrix}_0 - 3\left(1+\frac{\lambda_p}{\lambda_2}\right) \begin{pmatrix} \mu_1 & |\lambda_1| & \mu_p & |\lambda_p| \\ \mu_p & |\lambda_p| & \mu_2 & |\lambda_2| \end{pmatrix}_{|\lambda_p-\lambda_2|} \right\}$$

$$\delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2-\lambda_1 \\ 0 \end{pmatrix}$$

depends only on $|\lambda_2|$

Proof that above quantity depends only on $|\lambda_2|$.

a. $\lambda_2 = 0; \sum_{p=1}^{N} \left[\begin{array}{ccc||ccc} \mu_1 & \lambda_1 & s_1 & \mu_2 & \lambda_2 & s_2 \\ \mu_p & \lambda_p & s_p & \mu_p & \lambda_p & s_p \end{array}\right] = 0.$

b. $\sum_{\mu_p,\lambda_p=0}$; $3\left(1+\frac{\lambda_p}{\lambda_2}\right)\left(\begin{array}{cc||cc} \mu_1 & |\lambda_1| & \mu_p & |\lambda_p| \\ \mu_p & |\lambda_p| & \mu_2 & |\lambda_2| \end{array}\right)_{|\lambda_p-\lambda_2|}$

$$\Longrightarrow 3\left(\begin{array}{cc||cc} \mu_1 & |\lambda_1| & \mu_p & |\lambda_p| \\ \mu_p & |\lambda_p| & \mu_2 & |\lambda_2| \end{array}\right)_{|-\lambda_2|} = 3\left(\begin{array}{cc||cc} \mu_1 & |\lambda_1| & \mu_p & |\lambda_p| \\ \mu_p & |\lambda_p| & \mu_2 & |\lambda_2| \end{array}\right)_{|\lambda_2|}$$

c. $\sum_{\mu_p,\lambda_p\neq 0}$, $f(\lambda_2) = \sum_{\mu_p,\lambda_p\neq 0} 3\left(1+\frac{\lambda_p}{\lambda_2}\right)\left(\begin{array}{cc||cc} \mu_1 & |\lambda_1| & \mu_p & |\lambda_p| \\ \mu_p & |\lambda_p| & \mu_2 & |\lambda_2| \end{array}\right)_{|\lambda_2-\lambda_p|}$

$$f(\lambda_2) = \sum_{\mu_p,\lambda_p\neq 0} 3\left(1 \div \frac{|\lambda_p|}{\lambda_2}\right)\left(\begin{array}{cc||cc} \mu_1 & |\lambda_1| & \mu_p & |\lambda_p| \\ \mu_p & |\lambda_p| & \mu_2 & |\lambda_2| \end{array}\right)_{|\lambda_2-|\lambda_p||}$$

$$+ \; 3\left(1 - \frac{|\lambda_p|}{\lambda_2}\right)\left(\begin{array}{cc||cc} \mu_1 & |\lambda_1| & \mu_p & |\lambda_p| \\ \mu_p & |\lambda_p| & \mu_2 & |\lambda_2| \end{array}\right)_{|\lambda_2+|\lambda_p||}$$

$$= f(-\lambda_2)$$

Thus for all values of λ_2, λ_p above quantity depends only on $|\lambda_2|$

Thus:

$$\{\mu_1\ \lambda_1\ s_1\ ||\ \mu_2\ \lambda_2\ s_2\} = \lambda_2 s_2 \left\{ (\mu_1\ |\lambda_1|\ ||\ \mu_2\ |\lambda_2|) + \sum_{\mu_p, \lambda_p} 2 \begin{pmatrix} \mu_1 & |\lambda_1| & \mu_2 & |\lambda_2| \\ \mu_p & |\lambda_p| & \mu_p & |\lambda_p| \end{pmatrix}_0 \right.$$

$$\left. - \sum_{\mu_p, \lambda_p} 3\ (1 + \frac{\lambda_p}{\lambda_2}) \begin{pmatrix} \mu_1 & |\lambda_1| & \mu_p & |\lambda_p| \\ \mu_p & |\lambda_p| & \mu_2 & |\lambda_2| \end{pmatrix}_{|\lambda_p - \lambda_2|} \right\} \delta\begin{pmatrix} s_1 \\ s_2 \end{pmatrix} \delta\begin{pmatrix} \lambda_2 - \lambda_1 \\ 0 \end{pmatrix}$$

Term in { } above :

$$= \langle \chi(\mu_1, |\lambda_1|; r_i, \theta_i) \Big| \frac{1}{\hbar^2 \pi} \Delta^{(o)}(r_i \theta_i) \Big| \chi(\mu_2, |\lambda_2|; r_i, \theta_i) \rangle$$

$$+ \sum_{\mu_p, \lambda_p} \langle \chi(\mu_1, |\lambda_1|; r_i, \theta_i) \chi(\mu_p, |\lambda_p|; r_j, \theta_j) \Big| \frac{2}{\hbar^2 2\pi^2} \Delta_o^{(o)}(r_i, \theta_i; r_j, \theta_j) \Big|$$

$$\chi(\mu_p, |\lambda_p|; r_j, \theta_j) \chi(\mu_2, |\lambda_2|; r_i, \theta_i) \rangle$$

$$- \sum_{\mu_p, \lambda_p} \langle \chi(\mu_1, |\lambda_1|; r_i, \theta_i) \chi(\mu_p, |\lambda_p|; r_j, \theta_j) \Big| 3(1 + \frac{\lambda_p}{\lambda_2}) \frac{1}{\hbar^2 2\pi^2} \Delta^o_{|\lambda_p - \lambda_2|}(r_i \theta_i; r_j \theta_j) T_{ij} \Big|$$

$$\chi(\mu_p, |\lambda_p|; r_j, \theta_j) \chi(\mu_2, |\lambda_2|; r_i, \theta_i) \rangle$$

T_{ij} introduced to get ket pair in same order as Coulombic term.

$$= \langle \chi(\mu_1, |\lambda_1|; r_i, \theta_i) \Big| \frac{1}{\hbar^2 \pi} \Delta^{(o)}(r_i, \theta_i) + \sum_{\mu_p, \lambda_p} \langle \chi(\mu_p, |\lambda_p|; r_j, \theta_j) \Big|$$

$$\frac{1}{\hbar^2 2\pi^2} \{ \Delta_o^{(o)}(r_i, \theta_i; r_j, \theta_j) - 3(1 + \frac{\lambda_p}{\lambda_2}) \Delta^{(o)}_{|\lambda_p - \lambda_2|}(r_i, \theta_i; r_j, \theta_j) T_{ij} \} \Big| \chi(\mu_p, |\lambda_p|; r_j, \theta_j) \rangle \Big|$$

$$\chi(\mu_2, |\lambda_2|; r_i, \theta_i) \rangle$$

$$= \langle \chi(\mu_1, |\lambda_1|; r_i, \theta_i) | \xi_{|\lambda_2|}(r_i, \theta_i) | \chi(\mu_2, |\mu_2|; r_i, \theta_i) \rangle$$