MASTER

ANNUAL REPORT

1979 - 1980

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MASTER

DE-AS05-76EV03018/213

ANNUAL REPORT

1979-1980

UNITED STATES DEPARTMENT OF ENERGY

DE-AS05-76EV03018

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

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July 7, 1980

S. P. McGlynn

S. P. McGlynn
Principal Investigator
Boyd Professor of Chemistry

by

G. L. Findley

G. L. Findley
Co-Director of Research
Visiting Assistant Professor
of Chemistry

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INTRODUCTION

The eleven (11) Bibliographic Titles of Section 1A(6) (No.'s 203-213 of the Bibliography of 1979 - 1980) constitute the gist of this Report. These entities represent work completed and published (or in the process of publication). Apart from this listing and the provision of reprints/pre-prints, no further discussion of such works is available in this Report.

The reports presented in Section 2 (Individual Evaluations) contain short descriptions written by postdoctoral fellows and graduate students summarizing their research efforts for the period 1979 - 1980. 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.

The individual evaluations of Section 2 may not agree among themselves. Enforcement of 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,
IN-HOUSE SYMPOSIUM AND
EQUIPMENT PURCHASED AND/OR FABRICATED

A. BIBLIOGRAPHY OF TITLES

The bibliography of twenty-six (26) titles constitutes the bulk of this Report. These are separated into six (6) 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 1975 - 1976 Annual Report; the third of these consists of three (3) titles and provides information pertaining to the 1976 - 1977 Annual Report; the fourth of these consists of five (5) titles and provides information pertaining to the 1977 - 1978 Annual Report; the fifth of these consists of five (5) titles and provides information pertaining to the 1978 - 1979 Annual Report; the sixth of these consists of eleven (11) titles and provides reprints or preprints pertinent to the present reporting period (1979 - 1980)

The index numbers used in this section are those which were assigned to the works in question in previous Reports.

1. Completion of the 1971 - 1972 Annual Report

90. Hochmann, P., Foster, S. I. and McGlynn, S. P., "Geometry of Excited Molecules."
(7 preprints provided in the 1971 - 1972 Annual Report; amended version in preparation)

Apart from item 90, the 1971 - 1972 Annual Report is now complete.

2. Completion of the 1975 - 1976 Annual Report

151. Brint, P. and McGlynn, S. P., "The Low-Energy ${}^1\Gamma_{n\pi^*}$ Excited States of Tetramethyl-1,3-cyclobutanedione."
(7 preprints provided in the 1975 - 1976 Annual Report; amended version in preparation)

Apart from item 151, the 1975 - 1976 Annual Report is now complete.

3. Completion of the 1976 - 1977 Annual Report

164. Hochmann, P., Findley, G. L. and McGlynn, S. P., "Molecular Rydberg Transitions. X. Correlation Algorithms for Rydberg Term Values," Z. Naturforsch., **35a**, 000 (1980).
(7 reprints appended to this Report)
173. McGlynn, S. P., Wang, H. -t., Findley, G. L., Felps, W. S. and Rau, A. R. P., "Applications of Quantum Defect Theory to Molecular Rydberg States," Spectrosc. Lett., **12**, 631 (1979).
(7 reprints appended to this Report)

177. Felps, W. S., Scott, J. D. and McGlynn, S. P., "The $\sigma \rightarrow \sigma^*$ Excitation in CH_3I ."
(7 preprints appended to 1976 - 1977 Report; amended version in preparation)

Apart from items 164 and 177, the 1976 - 1977 Annual Report is now complete.

4. Completion of the 1977 - 1978 Annual Report

187. Findley, G. L. and McGlynn, S. P., "Applications of Differential Geometry to Molecular Genetics," Phys. Scr., submitted for publication.
(7 amended preprints provided in the 1978 - 1979 Annual Report)
189. Carsey, T. P., Findley, G. L. and McGlynn, S. P., "Systematics in the Electronic Spectra of Polar Molecules. I. Para Disubstituted Benzenes," J. Amer. Chem. Soc., 101, 4502 (1979).
(7 reprints appended to this Report)
190. Meeks, J. L., Wahlborg, A. and McGlynn, S. P., "Photoelectron Spectroscopy of Carbonyls. Benzoic Acid and its Derivatives," J. Electron Spectrosc., submitted for publication.
(7 amended preprints provided in the 1978 - 1979 Annual Report)
191. Dougherty, D., Lewis, J., Nauman, R. V. and McGlynn, S. P., "Photoelectron Spectroscopy of Azulenes," J. Electron Spectrosc., 19, 21 (1980).
(7 reprints appended to this Report)
193. Findley, G. L. and McGlynn, S. P., "Symmetry Characteristics of the Genetic Code," Proc. Natl. Acad. Sci. USA, submitted for publication.
(7 preprints provided in the 1977 - 1978 Annual Report)

Apart from items 187, 190 and 193, the 1977 - 1978 Annual Report is now complete.

5. Completion of the 1978 - 1979 Annual Report

196. Findley, G. L., Carsey, T. P. and McGlynn, S. P., "Systematics in the Electronic Spectra of Polar Molecules. II. Ortho and Meta Disubstituted Benzenes," J. Amer. Chem. Soc., 101, 4511 (1979).
(7 reprints appended to this Report)
197. (a) Findley, G. L. and McGlynn, S. P., "A Generalized Genetic Code," Int. J. Quantum Chem., Quantum Biol. Symp. 6, 313 (1979).
(7 reprints appended to this Report)

197. (b) Findley, G. L. and McGlynn, S. P., "A Generalized Genetic Code," in: ORIGIN OF THE GENETIC CODE, J. R. Jungck, ed. (BENCHMARK PAPERS IN SYSTEMATIC AND EVOLUTIONARY BIOLOGY, Dowden, Hutchinson and Ross, Inc., Stroudsburg, Pennsylvania, in press). A reprint of Paper No. 197 (a)
(7 preprints provided in the 1978 - 1979 Annual Report)
198. Boulter, D., Felps, W. S., Lewis, J., Nauman, R. V. and McGlynn, S. P., "Molecular Rydberg States. Azulene and 4,6,8-Trimethylazulene," Chem. Phys. Lett., 67, 420 (1979).
(7 reprints appended to this Report)
199. Felps, W. S., McGlynn, S. P. and Findley, G. L., "Molecular Rydberg Transitions. Cyanogen Chloride," J. Mol. Spectrosc., in press.
(7 amended preprints appended to this Report)
201. McGlynn, S. P., Scott, J. D., Felps, W. S. and Findley, G. L., "Molecular Rydberg Transitions. XVI. MCD of CH₃Br," J. Chem. Phys., 72, 421 (1980).
(7 reprints appended to this Report)

Apart from items 197(b) and 199, the 1978 - 1979 Annual Report is now complete.

6. Bibliography for the 1979 - 1980 Annual Report

203. McGlynn, S. P., Felps, W. S. and Scott, J. D., "Molecular Rydberg Transitions. XVIII. Vibronic Doubling in Methyl Iodide," J. Chem. Phys., submitted for publication.
(7 preprints appended to this Report)
204. Findley, G. L. and McGlynn, S. P., "The Generalized Genetic Code. A Modification of Code Universality," Int. J. Quantum Chem., Quantum Biol. Symp. 7, in press.
(7 preprints appended to this Report)
205. Findley, G. L. and McGlynn, S. P., Fundamental Spectroscopic Studies of Some Atmospheric Pollutants," in: PROCEEDINGS OF THE UNITED STATES DEPARTMENT OF ENERGY PROGRAM REVIEW ON THE PHYSICS AND CHEMISTRY OF ENERGY-RELATED ATMOSPHERIC POLLUTION (USDoe, in press).
(7 preprints appended to this Report)
206. McGlynn, S. P., Azumi, T. and Kumar, D., "The Colors of Post-Transition-Metal Salts," Accts. Chem. Res., submitted for publication
(7 preprints appended to this Report)

207. Lewis, J. W., Nauman, R. V., Bouler, D. B., Jr. and McGlynn, S. P., "Molecular Rydberg Transitions. XIX. Low-Energy Rydberg States of Azulene," J. Chem. Phys., to be submitted.
(7 preprints appended to this Report)
208. Felps, W. S., Scott, J. D., and McGlynn, S. P., "Molecular Rydberg Transitions. XX. Vibronic Doubling in Alkyl Bromides," J. Chem. Phys., to be submitted.
(7 preprints appended to this Report)
209. Felps, W. S. and McGlynn, S. P., "Molecular Rydberg Transitions. XXI. Intermediate Coupling in Simple Bromides," J. Chem. Phys., to be submitted.
(7 preprints appended to this Report)
210. McGlynn, S. P. and Felps, W. S., "Molecular Rydberg Transitions. XXII. The $\pi \rightarrow 4s$ Transition of C₆CN," J. Chem. Phys., to be submitted.
(7 preprints appended to this Report)
211. Chattopadhyay, S., McGlynn, S. P. and Findley, G. L., "Photoelectron Spectroscopy of Phosphites, Phosphates and Substituted Phosphates," J. Electron Spectrosc., to be submitted.
(7 preprints appended to this Report)
212. Scott, John D., "A Perturbed Linear Molecule Model for the Spectroscopy of Almost Linear Molecules," a preliminary manuscript.
(7 preprints appended to this Report)
213. Annual Report 1979 - 1980. A Bibliography of Titles, Reports of Works in Progress and Works Completed (Items 203 - 212) for the period 1979 - 1980 of Research Contract No. DE-AS05-76EV03018.
(7 copies of the United States Department of Energy - Division of Biomedical and Environmental Research - Physics and Technological Program on July 7, 1980)

*Reprints + Reprints
Removed 2/18/81*

B. SYMPOSIA ATTENDED

1979 - 1980

Invited Lectures

1. S. P. McGlynn, participant at the Jahrestagung of the Alexander von Humboldt Foundation, Bonn, West Germany, September 17-19, 1979.

---By Invitation

2. G. L. Findley, "The Myth of Scientific Induction," Enrichment Program of East Feliciana Parish Science Teachers, Clinton High School, Clinton, Louisiana, November 16, 1979.

---Invited Philosophy
Lecture

3. S. P. McGlynn, "Field-Effect Phenomena," Department of Physics, The University of Bonn, Bonn, West Germany, January 15, 1980.

---Invited Lecture

4. S. P. McGlynn, "Vibronic Effects in Rydberg Spectra," Department of Physical Chemistry, The University of Bonn, Bonn, West Germany, January 15, 1980.

---Invited Lecture

5. S. P. McGlynn, "Molecular Rydberg States," Department of Chemistry, The University of Munich, Munich, West Germany, January 17, 1980.

---Invited Lecture

6. S. P. McGlynn, "Optical Field-Effect Phenomena without Transmitting Optics," Department of Physics, The University of Bonn, Bonn, West Germany, January 22, 1980.

---Invited Lecture

7. G. L. Findley, participant at 13th Annual Radiological and Chemical Physics Contractors' Meeting of the United States Department of Energy, Battelle Seattle Research Center, Seattle, Washington, March 17-18, 1980.

---By Invitation

8. G. L. Findley, "Multi-Channel Quantum Defect Theory for Molecular Rydberg States," Department of Chemistry, The University of Montana, Missoula, Montana, March 20, 1980.

---Invited Lecture

9. G. L. Findley, "Group Theory and the Genetic Code," Department of Pure and Applied Mathematics, The Washington State University, Pullman, Washington, March 24, 1980.

---Invited Lecture

10. G. L. Findley, "Quantum Defect Theory. Single-Channel and Multi-Channel Studies," Department of Chemistry, The Washington State University, Pullman, Washington, March 25, 1980.

---Invited Lecture

11. G. L. Findley, "A Scattering Theory Approach for Molecular Rydberg States," Department of Radiological Physics, Battelle Pacific Northwest Laboratories, Richland, Washington, March 27, 1980.

---Invited Lecture

12. G. L. Findley, "Applications of Group Theory to Molecular Biology," Department of Chemistry, The University of Texas at San Antonio, San Antonio, Texas, April 17, 1980.

---Invited Lecture

13. S. P. McGlynn, "The Colors of Post-Transition-Metal Salts," presented at the following universities:

(a) Department of Chemistry, University College, Galway, Ireland, April 30, 1980.

(b) Department of Chemistry, New University of Ulster, Ulster, Ireland, May 7, 1980.

(c) Department of Chemistry, Queens University, Belfast, Ireland, May 8, 1980.

---Invited Lectures

14. S. P. McGlynn, "Photochemistry in the Vacuum Ultraviolet," Department of Chemistry, University College, Galway, Ireland, May 1, 1980.

---Invited Lecture

15. S. P. McGlynn, "Molecular Rydberg States," Department of Chemistry, University College, Cork, Ireland, May 2, 1980.

---Invited Lecture

16. S. P. McGlynn, "Molecular Spectroscopy in the Vacuum Ultraviolet," Department of Chemistry, University College, Dublin, Ireland, May 5, 1980.

---Invited Lecture

17. G. L. Findley, "Fundamental Spectroscopic Studies of Some Atmospheric Pollutants," United States Department of Energy Program Review: The Physics and Chemistry of Energy-Related Atmospheric Pollution, Harper's Ferry, West Virginia, May 28-30, 1980.

---Invited Lecture

18. G. L. Findley, "Non-Universality of the Genetic Code," Symposium on the Biochemical Evolution of the Genetic Apparatus, 10th American Chemical Society Northeast Regional Meeting, Clarkson College, Potsdam, New York, July 2-3, 1980.

---Invited Lecture

Contributed Papers

1. G. L. Findley and S. P. McGlynn, "The Generalized Genetic Code: Recent Results," 7th International Symposium on Quantum Biology and Quantum Pharmacology, Palm Coast, Florida, March 5-8, 1980.

---Contributed Paper

2. J. L. Meeks, T. J. Melton, A. Wahlborg and S. P. McGlynn, "Photoelectron Spectra of Monothio and Dithiooxamides," 179th American Chemical Society National Meeting, Houston, Texas, March 26, 1980.

---Contributed Paper

3. S. P. McGlynn and T. L. Mathers, "VUV Photolytic Effects: H_2O , OH^- and Aqueous Systems," VIIIth IUPAC Symposium on Photochemistry, Seefeld, Austria, July 20-26, 1980.

---Contributed Paper

C. LABORATORY GUESTS

1. Dr. R. Mohanty
Physics Department
Southern University
Baton Rouge, Louisiana
Weekly, throughout 1979-1980
2. Dr. P. R. LeBreton
Department of Chemistry
University of Illinois
at Chicago Circle
Chicago, Illinois
August, 1979
3. Dr. H. Aldrich
Department of Chemistry
Loyola University
New Orleans, Louisiana
August, 1979
4. Dr. J. Orban
Department of Physics
Free University of Brussels
Brussels, Belgium
December, 1979
5. Dr. J. D. Scott
Department of Chemistry
University of Montana
Missoula, Montana
December, 1979
6. Dr. W. S. Felps
Ames Laboratory USDOE
Iowa State University
Ames, Iowa
December, 1979
7. Dr. L. Klasinc
Department of Physical Chemistry
Ruder-Boskovic Institute
Zagreb, Yugoslavia
March, 1980
8. Dr. A. J. Stone
University Chemistry Laboratory
Cambridge University
Cambridge, England
April, 1980

9. Dr. H. F. Schaeffer, III
Department of Chemistry
University of California
Berkeley, California
May, 1980
10. Dr. P. Hochmann
Department of Chemistry
University of Texas at San Antonio
San Antonio, Texas
May-August, 1980
11. Dr. H. B. Silber
Department of Chemistry
University of Texas at San Antonio
San Antonio, Texas
June, 1980

D. IN-HOUSE SYMPOSIUM

The following seven pages are in the program for the 8th Annual Symposium on Molecular Electronic Structure and Spectroscopy. This Symposium is organized by members of Professor McGlynn's research group and participation, which was previously restricted to members of this research group, has been opened to limited outside participation.

8th ANNUAL
SYMPOSIUM ON MOLECULAR ELECTRONIC
STRUCTURE AND SPECTROSCOPY

VIEUX CARRE ROOM
UNION BUILDING
LOUISIANA STATE UNIVERSITY
BATON ROUGE, LOUISIANA

May 22 & 23, 1980

8th ANNUAL
SYMPOSIUM ON MOLECULAR ELECTRONIC
STRUCTURE AND SPECTROSCOPY

D. B. Boulter - Director

Participants*

D. Boulter, Graduate Student
J. Daigneault, Graduate Student
G. L. Findley, Postdoctoral Fellow
T. L. Mathers, Graduate Student
R. Maroun, Graduate Student
V. Shirley, Graduate Student
R. V. Nauman, Professor of Chemistry
F. Pascal, Graduate Student

* All participants are associated with LSU-BR
Department of Chemistry

INVITED SPEAKER

P. Hochmann

Department of Chemistry

University of Texas at San Antonio

THURSDAY MORNING - D. Boulter, CHAIRMAN

9:00-9:15 G. L. Findley, "Opening Remarks."

RYDBERG STATES

9:15-9:45 D. Boulter, "Low-Energy Rydberg States in Azulenes."

9:45-10:30 J. Daigneault, "Vibronic Coupling Effects in the Hydrogen Halides."

10:30-10:45 BREAK

10:45-11:30 J. Dagata, "Multi-Channel Quantum Defect Theory Applied to Molecular Rydberg States."

11:30-12:15 V. Shirley, "Similarities in the Rydberg States of Hydrogen Sulfide and Water."

12:15-1:45 LUNCH, DINING ROOM B

THURSDAY AFTERNOON - R. V. Nauman, CHAIRMAN

SPECTROSCOPY AND PHOTOCHEMISTRY

- 1:45-2:30 R. V. Nauman, "Spectroscopy and Photo-chemistry of Salicylaldehyde and Related Beta-Dicarbonyls."
- 2:30-3:15 F. Pascal, "Spectrosocpy and Photochemistry of Beta-Diketones."
- 3:15-3:30 BREAK
- 3:30-4:00 R. V. Nauman, "Absorption and Luminescence Spectroscopy of Positive Ions of Derivatives of Azulene."

FRIDAY MORNING - V. Shirley, CHAIRMAN

THEORETICAL AND BIOLOGICAL STUDIES

- 9:00-9:30 T. Mathers, "The 4.5eV Energy Absorption in Aqueous Systems."
- 9:30-10:00 V. Shirley, "Chemically Induced Luminescence of Chick Embryo Fibroblast-Windfall or Windmill?"
- 10:00-10:15 BREAK
- 10:15-10:45 P. Hochmann, "Variation of the Lowest Ionization Energies of Mono Substituted Alkanes with the Structures of Chromophores and Substituents."
- 10:45-11:15 R. Maroun, "Contributions to the Study of Electronic Term Values of Linear Molecules within an Intermediate Coupling Scheme."
- 11:15-11:45 P. Hochmann, "Contribution of Non-Coulombic Interactions and Correlative Effects on Electronic Term Values."
- 11:45-1:15 LUNCH, DINING ROOM B

FRIDAY AFTERNOON - J. Daigneault, CHAIRMAN

SUMMARY

1:15-2:15 Free Discussion

2:15-2:30 G. L. Findley, "Closing Remarks."

E. EQUIPMENT PURCHASED AND/OR FABRICATED

1. Dual Pen X-Y Recorder with Marker, Time Base, Remote TTL Logic Control and Consummable Starter Kit (Hewlett-Packard)	\$ 4,130.00
2. Dye Pump Module for CMX-4 Laser (Chromatix)	1,050.00
3. Five Sets of Dye Flow Lines (Chromatix)	650.00
4. Clamping Ring for CMX-4 Laser Mirror Holder (Chromatix)	7.15
5. Three Piezoelectric Transducers (Transducer Products, Ltd.)	69.00
6. Low-Noise, Chopper-Stabilized Amplifier Module with Socket (Analog Devices)	90.50
7. One-Quadrant, Programmable-Gain Analog Divider with Socket (Analog Devices)	108.50
8. Miscellaneous Pots and Op-Amps (Analog Devices)	50.30
9. Laser Dyes: (a) Exiton Chemical Co.	50.00
(b) Eastman-Kodak Co.	52.50
10. Optoacoustic Cell with Detector (Constructed at LSU)	NC
11. Wide-Band (~1MHz), Low-Noise Pre-Amp (Constructed at LSU)	NC
12. Shelf Assembly and Dust Cover for Laser Table (Constructed at LSU)	NC

TOTAL \$ 6,257.95

Approximately 34% of these expenditures were made with DOE funds. The balance of 66% was provided by The Chemistry Department, The Louisiana State University, Baton Rouge, Louisiana.

ITEM 2.

INDIVIDUAL REPORTS

(Complete and in Progress)

G. L. FINDLEY
VISITING ASSISTANT PROFESSOR OF CHEMISTRY
CO-DIRECTOR OF RESEARCH

I. PUBLICATIONS

A. Completion of the 1976 - 1977 Annual Report

164. Hochmann, P., Findley, G. L. and McGlynn, S. P., "Molecular Rydberg Transitions. X. Correlation Algorithms for Rydberg Term Values," Z. Naturforsch., 35a, 000 (1980).
(7 reprints appended to this Report)
173. McGlynn, S. P., Wang, H. -t., Findley, G. L., Felps, W. S. and Rau, A. R. P., "Applications of Quantum Defect Theory to Molecular Rydberg States," Spectrosc. Lett., 12, 631 (1979).
(7 reprints appended to this Report)

B. Completion of the 1977-1978 Annual Report

187. Findley, G. L. and McGlynn, S. P., "Applications of Differential Geometry to Molecular Genetics," Phys. Scr., submitted for publication.
(7 amended preprints provided in the 1978-1979 Annual Report)
189. Carsey, T. P., Findley, G. L. and McGlynn, S. P., "Systematics in the Electronic Spectra of Polar Molecules. I. Para Disubstituted Benzenes," J. Amer. Chem. Soc., 101, 4502 (1979).
(7 reprints appended to this Report)
193. Findley, G. L. and McGlynn, S. P., "Symmetry Characteristics of the Genetic Code," Proc. Natl. Acad. Sci. USA, submitted for publication.
(7 preprints provided in the 1977-1978 Annual Report)

C. Completion of the 1978-1979 Annual Report

196. Findley, G. L., Carsey, T. P. and McGlynn, S. P., "Systematics in the Electronic Spectra of Polar Molecules. II. Ortho and Meta Disubstituted Benzenes," J. Amer. Chem. Soc., 101, 4511 (1979).
(7 reprints appended to this Report)

197. (a) Findley, G. L. and McGlynn, S. P., "A Generalized Genetic Code," Int. J. Quantum Chem., Quantum Biol. Symp. 6, 313 (1979)
(7 reprints appended to this Report)

(b) Findley, G. L. and McGlynn, S. P., "A Generalized Genetic Code," in: ORIGIN OF THE GENETIC CODE, J. R. Jungck, ed. (BENCHMARK PAPERS IN SYSTEMATIC AND EVOLUTIONARY BIOLOGY, Dowden, Hutchinson and Ross, Inc., Stroudsburg, Pennsylvania, in press).

A reprint of Paper No. 197 (a)

(7 preprints provided in the 1978-1979 Annual Report)

199. Felps, W. S., McGlynn, S. P. and Findley, G. L., "Molecular Rydberg Transitions. Cyanogen Chloride, J. Mol. Spectrosc., in press.

(7 amended preprints appended to this Report)

201. McGlynn, S. P., Scott, J. D., Felps, W. S. and Findley, G. L., "Molecular Rydberg Transitions. XVI. MCD of CH_3Br ," J. Chem. Phys., 72, 421 (1980).

(7 reprints appended to this Report)

D. Bibliography for 1979 - 1980

1. Findley, G. L. and McGlynn, S. P., "The Generalized Genetic Code. A Modification of Code Universality," Int. J. Quantum Chem., Quantum Biol. Symp. 7, in press.
(7 preprints appended to this Report)

ABSTRACT: The generalized genetic code [G. L. Findley and S. P. McGlynn, Int. J. Quantum Chem., Quantum Biol. Symp. 6, 313 (1979)] is reviewed from the perspective of recently published empirical evidence which indicates the nonuniversality of the standard genetic code. It is shown how a modified form of universality is retained in the generalized genetic code. In addition, the nature of biological contexts and their relation to the generalized genetic code are discussed.

2. Findley, G. L. and McGlynn, S. P., "Fundamental Spectroscopic Studies of Some Atmospheric Pollutants," in: PROCEEDINGS OF THE UNITED STATES DEPARTMENT OF ENERGY PROGRAM REVIEW ON THE PHYSICS AND CHEMISTRY OF ENERGY-RELATED ATMOSPHERIC POLLUTION (USDOE, in press).

(7 preprints appended to this Report)

ABSTRACT: A short review of the LSU program for the study of molecular Rydberg states of atmospheric pollutant molecules is presented. Assignment techniques, quantum defect theory, vibronic coupling and field-effect spectroscopy are discussed.

3. Chattopadhyay, S., McGlynn, S. P. and Findley, G. L., "Photoelectron Spectroscopy of Phosphites, Phosphates and Substituted Phosphates," J. Electron Spectrosc., to be submitted. (7 preprints appended to this Report)

ABSTRACT: The photoelectron spectra of trimethyl and triethyl phosphite, trimethyl and triethyl phosphate and four substituted phosphates are presented and assigned. Assignments based on analogies to available data on phosphorous trichloride and phosphoryl trichloride are substantiated by CNDO/2 computations and a consistent set of assignments is achieved. The mechanism of P-O (axial) bond formation is discussed in terms of σ -donation/ π -acceptance properties of the phosphites. Photoelectron spectral data of the substituted phosphates are rationalized from the basis of symmetry-lowering effects.

II. LECTURES

1. "The Myth of Scientific Induction," Enrichment Program of East Feliciana Parish Science Teachers, Clinton High School, Clinton, Louisiana, November 16, 1979.

---Invited Philosophy
Lecture
2. G. L. Findley and S. P. McGlynn, "The Generalized Genetic Code: Recent Results," 7th International Symposium on Quantum Biology and Quantum Pharmacology, Palm Coast, Florida, March 5-8, 1980.

---Contributed Paper

3. Participant at 13th Annual Radiological and Chemical Physics Contractors' Meeting of the United States Department of Energy Battelle Seattle Research Center, Seattle, Washington, March 17-18, 1980

---By Invitation

4. "Multi-Channel Quantum Defect Theory for Molecular Rydberg States," Department of Chemistry, The University of Montana, Missoula, Montana, March 20, 1980.

---Invited Lecture

5. "Group Theory and the Genetic Code," Department of Pure and Applied Mathematics, The Washington State University, Pullman, Washington, March 24, 1980.

---Invited Lecture

6. "Quantum Defect Theory. Single-Channel and Multi-Channel Studies," Department of Chemistry, The Washington State University, Pullman, Washington, March 25, 1980.

---Invited Lecture

7. "A Scattering Theory Approach for Molecular Rydberg States," Department of Radiological Physics, Battelle Pacific Northwest Laboratories, Richland, Washington, March 27, 1980.

---Invited Lecture

8. "Applications of Group Theory to Molecular Biology," Department of Chemistry, The University of Texas at San Antonio, San Antonio, Texas, April 17, 1980.

---Invited Lecture

9. "Opening Remarks," 8th Annual Symposium on Molecular Electronic Structure and Spectroscopy, The Louisiana State University, Baton Rouge, Louisiana, May 22-23, 1980.

---Invited Lecture

10. "Fundamental Spectroscopic Studies of Some Atmospheric Pollutants," United States Department of Energy Program Review: The Physics and Chemistry of Energy-Related Atmospheric Pollution, Harper's Ferry, West Virginia, May 28-30, 1980.

Invited Lecture

11. "Non-Universality of the Genetic Code," Symposium on Biochemical Evolution of the Genetic Apparatus, 10th American Chemical Society Northwest Regional Meeting, Clarkson College, Postdam, New York, July 2-3, 1980.

---Invited Lecture

III. WORK IN PROGRESS

Work on the following topics continues:

---Multi-channel quantum defect theory applied to atomic and molecular Rydberg states (with J. Dagata).

---Correlation algorithms for atomic and molecular Rydberg term values (with P. Hochmann).

---Hilbert spaces over an algebraic field of functions (with P. Hochmann).

---Group order-isomorphism classifications for finite sets (with P. Hochmann).

---Partitions on free monoids: generation by finite groups.

---A differential-geometric interpretation of Roothaan's equations.

---Nonuniversality of the genetic code.

---Differential geometry applied to molecular genetics.

R. V. NAUMAN
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I. PUBLICATIONS

A. Completion of the 1977 - 1978 Annual Report

191. Dougherty, D., Lewis, J., Nauman, R. V. and McGlynn, S. P.,
"Photoelectron Spectroscopy of Azulenes," J. Electron Spectrosc.,
19, 21 (1980).
(7 reprints appended to this Report)

B. Completion of the 1978 - 1979 Annual Report

198. Bouler, D., Felps, W. S., Lewis, J., Nauman, R. V. and McGlynn,
S. P., "Molecular Rydberg States. Azulene and 4,6,8-Trimethyl-
azulene," Chem. Phys. Lett., 67, 420 (1979).
(7 reprints appended to this Report)

C. Bibliography for 1979 - 1980

1. Lewis, J. W., Nauman, R. V., Bouler, D. B., Jr. and McGlynn,
S. P., "Molecular Rydberg Transitions. XIX. Low-Energy Rydberg
States of Azulene," J. Chem. Phys., to be submitted.
(7 preprints appended to this Report)

ABSTRACT: Various electronic spectra (absorption, emission, ELD and MCD) of azulene and six of its derivatives are discussed. The focus of the work is the low-energy Rydberg states of azulene and their spectroscopic and photophysical consequences. It is shown that the 3d Rydberg states lie in the $45000\text{--}50000\text{cm}^{-1}$ range, that they are partially quenched by affixing chemical substituents, and totally quenched in condensed media. The 3p Rydberg states lie at $\sim 40000\text{cm}^{-1}$ in azulene but are largely quenched in all derivatives. It is

shown that the quenching of the 3p Rydbergs of azulene in condensed media is responsible for much of the gross alterations which occur in the $S_4 \leftarrow S_0$ absorption region upon going from gaseous to condensed phases. It is shown that the 3s Rydberg state should lie in the vicinity of the $S_2 \leftarrow S_0$ absorption region. Our investigations of this region demonstrate the presence of only one origin band α in the $S_2 \leftarrow S_0$ emission whereas two, α and β , exist in the $S_2 \leftarrow S_0$ absorption spectrum. It is shown that the lack of mirror symmetry of $S_2 \leftrightarrow S_0$ absorption and emission and the gross variations of the $S_2 \leftarrow S_0$ absorption which occur in different media are associable with the presence of the β -origin. It is suggested that the β -origin may be of 3s Rydberg nature.

II. LECTURES

1. "Overview of Photoacoustic Spectroscopy," Department of Chemistry, The Louisiana State University, Baton Rouge, Louisiana, August 27, 1979.

---Invited Lecture

2. "Rydberg States of Azulenes," Department of Chemistry, The Louisiana State University, Baton Rouge, Louisiana, January 21, 1980.

---Invited Lecture

3. "Spectroscopy and Photochemistry of Salicylaldehyde and Related β -Dicarbonyls," 8th Annual Symposium on Molecular Electronic Structure and Spectroscopy, The Louisiana State University, Baton Rouge, Louisiana, May 22-23, 1980.

---Invited Lecture

4. Chairman of "Spectroscopy and Photochemistry" Session, 8th Annual Symposium on Molecular Electronic Structure and Spectroscopy, The Louisiana State University, Baton Rouge, Louisiana, May 22-23, 1980.

---Session Chaired

III. WORK IN PROGRESS

A. Photochemistry and Spectroscopy of β -Diketones:

Prior work on the photochemistry and spectroscopy of β -diketones is being prepared currently for publication. This work has shown the importance of hydrogen-bond breaking in the chelated enol form of β -diketones. The photoproducts that result from excitation and H-bond breaking vary from molecule to molecule. In some cases luminescence from a neutral keto form results; in other cases luminescence from a negative ion results.

B. Negative-Ion Luminescence:

We recently have begun a preliminary investigation of the luminescence of aromatic molecules adsorbed on metal surfaces. By adsorbing these molecules on metals that have a very low ionization potential (e.g., sodium), it is hoped that the negative ions of the adsorbed species can be observed and that their spectra can be compared with negative-ion spectra obtained by conventional procedures.

C. Effects of Excitation on Luminescence Contours:

We are continuing a study of excitation effects on the contours of luminescence spectra. Equipment for picosecond, Fourier-transform, luminescence spectroscopy is being developed slowly. This work is an extension of spectroscopic studies that demonstrate the effects of conformational and geometrical isomerization on electronic transitions [see, e.g., E. Hughes, J. W. Wharton and R. V. Nauman, J. Phys. Chem., **75**, 3097 (1971)].

* * * * *

R. V. Nauman is also associated with the work of D. Kumar, D. Boulter and T. L. Mathers.

P. HOCHMANN

VISITING ASSOCIATE PROFESSOR OF CHEMISTRY

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I. PUBLICATIONS

A. Completion of the 1976 - 1977 Annual Report

164. Hochmann, P., Findley, G. L. And McGlynn, S. P., "Molecular Rydberg Transitions. X. Correlation Algorithms for Rydberg Term Values," Z. Naturforsch., 35a, 000 (1980).
(7 reprints appended to this Report)

II. LECTURES

1. 8th Annual Symposium on Molecular Electronic Structure and Spectroscopy, The Louisiana State University, Baton Rouge, Louisiana, May 22-23, 1980.
- (a) "Variation of the Lowest Ionization Energies of Mono-Substituted Alkanes with the Structures of Chromophores and Substituents."
- (b) "Contribution of Non-Coulombic Interactions and Correlative Effects on Electronic Term Values."

---Invited Lectures

III. WORK IN PROGRESS

A. Algorithms for Band Deconvolution:

The present status of this investigation is described in the following Note.

DECOMPOSITION OF A SPECTROSCOPIC SIGNAL INTO A SYSTEM OF BANDS.

PRELIMINARY DESIDERATA

FOR ALGORITHMIC IMPLEMENTATION

by

P. Hochmann

1. Introduction:

The purpose of this Note is to provide background information for the construction and reliable application of our band decomposition algorithms (DECAY). These programs are primarily designed to decompose the measured frequency distribution $S(\nu)$ of a spectroscopic signal S into a system of "spectral bands".

Sections 2 and 3 provide the basic definitions and describe the technique of Least Squares (LSQ) as it will be used for signal decomposition; Section 4 is concerned with data organization; and Section 5 describes a particular mathematical model for $S(\nu)$ which will be incorporated into the first version of the DECAY program, DECAY I.

Since it is our intention to extend this Note after additional models are formulated, we do not offer any concluding section.

We have attempted to make this Note as self-contained as possible and, therefore, very few references are provided. To the reader interested in additional information on the Least Squares Method, we recommend Refs. 1-3. Ref. 3 also may be consulted for sources on bilinear forms, some properties of which are used in Section 3.

2. Basic Assumptions and Definitions:

Let $S(\nu)$ be the observed frequency distribution of a spectroscopic signal S . For our purposes we will distinguish between signals of the first and second kinds as follows: (1), Signals of the first kind are

represented by distributions $S(\nu)$ which are non-negative over the entire frequency range. The most important examples are intensity distributions in absorption, emission and photoelectron spectra; (ii), Signals of the second kind are represented by distributions which may have both positive and negative values over the frequency range of interest. Examples are differential absorption, emission and photoelectron spectra; difference absorption spectra; magnetic circular dichroism and electric linear dichroism spectra; etc.⁴

It is assumed that the value of $S(\nu)$ for every ν within the frequency interval $\langle \nu_L, \nu_U \rangle$ (where $\nu_L < \nu_U$) can be determined experimentally. In addition, it is assumed that $S(\nu)$ is a sum of signal distributions for the "background" and L "spectral bands" ($L \geq 1$).

The signal distribution within an i th spectral band is modeled by some suitably chosen band shape function $\epsilon_i(\nu; P_i)$, where $P_i \equiv \{P_{i1}, \dots, P_{im_i}\}$ is a set of m_i parameters which specify the shape of this band (e.g., amplitude, positions of maxima and minima, width, asymmetry, etc.). The background signal distribution is modeled by some chosen baseline shape function $\epsilon_0(\nu; P_0)$, where $P_0 \equiv \{P_{01}, \dots, P_{0m_0}\}$ is the set of background shape parameters. Thus, the spectral distribution $S(\nu)$ is modeled by the function $S(\nu, Q)$:

$$S(\nu, Q) = \sum_{i=0}^L \epsilon_i(\nu; P_i), \quad (1)$$

where $Q = \bigcup_{i=0}^L P_i$ is the combined set of band and baseline shape parameters and consists of $M = \sum_{i=0}^L m_i$ parameters. Within Q , the parameters P_{ij} ($i=0, 1, \dots, L; j=1, \dots, m_i$) are ordered in the following manner $\{P_{01}, \dots, P_{0m_0}, P_{11}, \dots, P_{1m_1}, \dots, P_{L1}, \dots, P_{Lm_L}\}$ and, for the sake of brevity, denoted Q_ℓ . The correspondence between Q_ℓ and P_{ij} is specified by

$$l = \begin{cases} j & \text{if } i=0 \\ \sum_{k=0}^{i-1} m_k + j & \text{if } 1 \leq i \leq m \end{cases}$$

A particular model for the distribution $S(v)$ is fixed when the choice of a particular model function $S(v;Q)$ is made. In turn, the choice of $S(v;Q)$ is determined by the number of bands L and the selection of particular shape functions. As a rule, such a model also includes certain restrictions imposed on the ranges within which the Q parameters are allowed to vary. In the following discussion, P_1 and Q denote the sets of parametric variables, or the set of some fixed (but further unspecified) values of these parameters. The sets of particular values of these parameters are labeled by superscripts.

For a given model, the decomposition of a specific, measured signal distribution $S(v)$ into a system of L spectral bands with baseline consists of the determination of a set $Q^{(S)}$ such that the model function $S(v;Q^{(S)})$ represents a "best fit" of $S(v)$. Two comments on the meaning of "best fit" are necessary:

First, the concept of a "best fit" is meaningful only in connection with some criteria designed to evaluate the degree with which the model function $S(v;Q)$ approximates the distribution $S(v)$. The most frequently used criteria are based on "pointwise" and "integral" comparisons of $S(v)$ and $S(v;Q)$

Pointwise comparisons usually introduce some simple, non-negative function $\Delta(v,Q)$ of the difference $S(v) - S(v,Q)$ (such as, $\Delta(v,Q) = |S(v) - S(v,Q)|$ or $\Delta(v,Q) = [S(v) - S(v,Q)]^2$) and define the quantity $\Delta(Q)$ as the largest value of $\Delta(v,Q)$ on the interval $\langle v_L, v_U \rangle$. Since $0 \leq \Delta(v,Q) \leq \Delta(Q)$, the value of $\Delta(Q)$ gives a measure of the "fit" of $S(v)$ by $S(v,Q)$. The

best possible fit is then given by the model function $S(v; Q^{(S)})$, where the set $Q^{(S)}$ minimizes the value of $\Delta(Q)$ over the range of parameters Q . An appealing feature of pointwise comparisons and the associated fitting criteria is the simple relation between the measure $\Delta(Q)$ of the fit and the largest deviation of $S(v; Q)$ from $S(v)$. Unfortunately, the same criteria lead to very unruly algorithms for the evaluation of $Q^{(S)}$ and, therefore, are unsuitable for decompositions.

The most favored integral comparison uses the residual quadratic error $D(Q)$ as the measure of the fit:

$$D(Q) = \int_{v_L}^{v_U} dv W(v) \{S(v; Q) - S(v)\}^2, \quad (2)$$

where the weight function $W(v)$ is, in general, a non-negative, bounded function on the interval $\langle v_L, v_U \rangle$. When used to weight the spectral signal distributions $S(v)$, it is advantageous to make $W(v)$ proportional to the signal-to-noise ratio of the $S(v)$ measurements.

With $D(Q)$ as the measure of the fit of $S(v)$ by $S(v; Q)$, the best fit is again given by the model function $S(v; Q^{(S)})$, where the set $Q^{(S)}$ is chosen such that $D(Q^{(S)})$ is the absolute minimum of $D(Q)$ over the allowed range of Q :

$$D(Q^{(S)}) = [D(Q)]_{\text{abs. min.}} \quad (3)$$

The error measure and fitting criterion of Eqs. 2 and 3, respectively, constitute the core of the Least Squares (LSQ) Method. Since the LSQ method leads to relatively simple algorithms for the evaluation of $Q^{(S)}$, it will be adopted here. From Eq. 2 it follows that if $W(v) = 1$ over the entire interval $\langle v_L, v_U \rangle$, the largest pointwise deviation of $S(v; Q^{(S)})$ from $S(v)$ is,

$$|S(v) - S(v; Q^{(S)})| \leq D(Q^{(S)})^{1/2}.$$

However, since $D(Q)$ is an integral measure, the above criterion is rather weak in the sense that the actual largest error $\Delta(Q^{(S)})$ is usually considerably smaller than $D(Q^{(S)})^{1/2}$ or $D(Q^{(S)})$. If $W(v)$ is not a constant over $\langle v_L, v_U \rangle$, the relations between $D(Q^{(S)})$ and the pointwise measures $\Delta(Q^{(S)})$ are too complex to be useful and, therefore, are not discussed here.

Second, the best possible fit which can be achieved within some particular model may yield a function $S(v; Q^{(S)})$ which is still a poor representation of a given $S(v)$. In this case a more flexible model, allowing for a larger number of bands or for a more flexible shape function, must be chosen.

Our strategy in the evaluation of a particular model and in the comparison of different models will be the optimization of $Q^{(S)}$ by LSQ techniques, followed by an analysis of quantities such as $|S(v) - S(v; Q^{(S)})|$ or $W(v)|S(v) - S(v; Q^{(S)})|$ over the entire interval $\langle v_L, v_U \rangle$.

3. LSQ Evaluation of $Q^{(S)}$ Parameters:

For a given distribution $S(v)$, weight function $W(v)$, interval $\langle v_L, v_U \rangle$, and model function $S(v; Q)$, the residual quadratic error $D(Q)$ is a non-negative function of M variables $Q_1, \dots, Q_M$. The shape functions $c_i(v, P_i)$ are usually chosen to be continuous functions of the parameters P_{ij} and, consequently, $S(v; Q)$ and $D(Q)$ are continuous functions of the Q parameters.

At the point $Q^{(S)}$, the following conditions are necessary for a minimum of $D(Q)$:

$$\left[\frac{\partial D(Q)}{\partial Q_i} \right]_S = 0, \text{ for } i=1, \dots, M \quad (4a)$$

where the subscript S indicates that the derivatives are evaluated at $Q = Q^{(S)}$. Substitution of Eq. 2 into 4a yields a more explicit form of the minimum conditions:

$$\int_{v_L}^{v_U} dv W(v) [S(v) - S(v; Q^{(S)})] \left[\frac{\partial S(v; Q)}{\partial Q_i} \right]_S = 0, \text{ for } i=1, \dots, M \quad (4b)$$

From Eq. 4b we infer the following set of equations for the determination of $Q^{(S)}$:

$$\int_{v_L}^{v_U} dv W(v) [S(v) - S(v; Q)] \left[\frac{\partial S(v; Q)}{\partial Q_i} \right] = 0, \text{ for } i=1, \dots, M$$

The solution of Eq. 5 for the unknown $Q^{(S)}$ poses several problems. One of these, perhaps the least critical, is the evaluation of the integrals in Eq. 5, a point to which we shall return later. More severe problems arise from the fact that, for the majority of interesting model functions $S(v; Q)$, Eq. 5 is non-linear. In order to appreciate the extent and nature of the difficulties caused by this non-linearity, we shall first analyze the linear case.

Suppose that $S(v; Q)$ is a linear function of the parameters $Q_1, \dots, Q_M$. That is:

$$S(v; Q) = \sum_{j=1}^M S_j(v) Q_j + S_0(v) \quad (6)$$

In Eq. 6 it is assumed that the functions $S_j(v)$ ($j=0, 1, \dots, M$) are independent of the parameters Q and, for $j=1, \dots, M$ form a linearly independent set.

The substitution of Eq. 6 into Eq. 5 yields the following set of equations:

$$\sum_{j=1}^M A_{ij} Q_j = B_i, \text{ for } i=1, \dots, M \quad (7a)$$

where A_{ij} and B_i are given by:

$$A_{ij} = \int_{v_L}^{v_U} dv W(v) S_i(v) S_j(v) \quad (8)$$

$$B_i = \int_{v_L}^{v_U} dv W(v) [S(v) - S_0(v)] S_i(v) \quad (9)$$

It will be convenient to regard the coefficients A_{ij} and B_i as the elements of an $M \times M$ matrix A and an $M \times 1$ matrix B , respectively. Then, viewing the set Q as an $M \times 1$ matrix, Eq. 7 can be written as

$$A Q = B \quad (7b)$$

The assumed linear independence of the function $S_j(v)$ ($j=1, \dots, M$) ensures that A is a non-singular, positive-definite matrix and, therefore, that Eqs. 7a or 7b have a unique solution $Q^{(S)}$ given by

$$Q^{(S)} = A^{-1}B \quad (10)$$

The uniqueness of the solution of Eq. 7b for linear model functions follows from the form of $D(Q)$. Substitution of $S(v;Q)$ from Eq. 6 into Eq. 2 yields

$$D(Q) = \sum_{i=1}^M \sum_{j=1}^M A_{ij} Q_i Q_j - 2 \sum_{i=1}^M B_i Q_i + C_0 \quad (11)$$

where A_{ij} and B_i are given by Eqs. 8 and 9, and C_0 is given by:

$$C_0 = \int_{v_L}^{v_U} dv W(v) [S(v) - S_0(v)]^2 \quad (12)$$

Eq. 11 shows that, for a linear model function, $D(Q)$ can be viewed as a parabolic hypersurface in $(M+1)$ -dimensional space, with the only extremum at

the point $[Q^{(S)}, D(Q^{(S)})]$. Since A is assumed to be positive-definite, this extremum corresponds to the absolute minimum of $D(Q)$. In other words, for a linear model function in which $S_1(v), \dots, S_M(v)$ are linearly independent, Eq. 4a represents the sufficient conditions for the absolute minimum of $D(Q)$.

The quadratic residual error $D(Q)$ of the non-linear model functions can also be viewed as a hypersurface in $(M+1)$ -dimensional space. However, depending on the degree of non-linearity of the model functions, such a hypersurface may differ significantly from the parabolic one and may display a number of extrema (such as various local minima, maxima and inflection points). Consequently, in the case of non-linear model functions, Eq. 4a represents only necessary conditions for a minimum, and Eq. 5 may have a number of solutions. In principle, the search for $Q^{(S)}$ requires finding all these solutions and investigating each of them as to its correspondence to the absolute minimum. A possible multitude of solutions of Eq. 5, combined with the considerable difficulty of solving these systems of non-linear equations, makes the use of the non-linear LSQ method very difficult.

From a large variety of techniques designed to evaluate positions of extremal points on multidimensional surfaces (such as $D(Q)$) we shall discuss only two. The first of these, usually termed the discrete mesh technique, starts with the selection of a finite number, say k_i , of values of each parameter Q_i ($i=1, \dots, M$). These values are selected in such a way that they cover that range $\langle Q_{iL}, Q_{iU} \rangle$ of Q_i which is suspected of containing i th coordinates $Q_i^{(e)}$ of all extrema e . The array $\{Q_i\}$, comprised of the selected values k_i of Q_i and ordered according to increasing (or decreasing) magnitude, is termed the i th one-dimensional mesh. From these one-dimensional meshes $\{Q_i\}$ ($i=1, \dots, M$) is constructed an M -dimensional mesh $\{Q\}$, which is essentially the cartesian product $\{Q_1\} \times \{Q_2\} \times \dots \times \{Q_M\}$ of one-dimensional meshes

$\{Q_i\}$. The mesh $\{Q\}$ consists of $K = \sum_{i=1}^M k_i$ "points" $Q^{(\alpha)}$, where α denotes a selection of M elements, one from each of the $\{Q_i\}$. The values $D(Q^{(\alpha)})$ are evaluated for each point $Q^{(\alpha)}$ and arrayed in $\{D(Q^{(\alpha)})\}$ in the same order as the points $Q^{(\alpha)}$ are arrayed in $\{Q\}$. A comparison of the values of $D(Q^{(\alpha)})$ in the neighborhood of each point $Q^{(\beta)}$ allows the identification of the regions of Q which contain coordinates of the individual extrema. Consecutive refinements of the mesh $\{Q\}$ in these regions, and the narrowing of these regions yields the sets $Q^{(e)}$ and, in particular, the set $Q^{(S)}$.

The major advantage of this mesh technique is the global nature of the search for extrema. Such a search highly facilitates the identification of the absolute minimum of $D(Q)$ from among the possible varieties of local minima. The mesh technique is also free from divergence and numerical instability problems. In addition, because of algorithmic simplicity the corresponding computer programs are rather compact. However, while convergence toward the points $Q^{(e)}$ is, in principle, guaranteed, it may be very slow if the initial ranges $\langle Q_{iL}, Q_{iU} \rangle$ are large, and if the final estimates of $Q_i^{(e)}$ are sought to high precision. Finally, with an increasing number of parameters to be determined, computer storage demands become exceedingly high. For example, for $M = 10$ and $k_i = 10$, the storage of at least 2×10^{10} bits is required. In practice, the mesh technique is seldom used for M larger than three or four.

The second technique (the one of preference for the present research) belongs to the category of local search techniques. These methods search for the location of single extrema, one at a time, and require an a priori knowledge of the approximate locations of these extrema. The particular technique discussed here is based on an approximate linearization of Eq. 5.

Let $Q^{(n)}$ be a point located in the vicinity of some extremum $Q^{(e)}$.

For a given model function $S(v; Q)$ and point $Q^{(n)}$, we define the auxiliary function $S(v; Q)_n$:

$$S(v; Q)_n = S(v; Q^{(n)}) + \sum_{j=1}^M \left[\frac{\partial S(v; Q)}{\partial Q_j} \right]_n \Delta Q_j \quad (13)$$

where $\Delta Q_j = Q_j - Q_j^{(n)}$ and the derivatives are evaluated at $Q^{(n)}$. The function $S(v; Q)_n$ given by Eq. 13 is, obviously, a leading part of the Taylor expansion of $S(v; Q)$ around the point $Q^{(n)}$.

We will denote by $D(Q)_n$ the residual quadratic error of Eq. 2, evaluated from the model function $S(v; Q)_n$. Since $S(v; Q)_n$ is a linear function of variables ΔQ_i ($i=1, \dots, M$) it is possible to evaluate the set $Q^{(n+1)}$ (which minimizes the value of $D(Q)_n$) in a fashion analogous to that for the function of Eq. 6. The substitution of Eq. 13 into Eq. 5 results in the following set of equations:

$$\sum_{j=1}^M A_{ij}(Q^{(n)}) \Delta Q_j = B_i(Q^{(n)}), \text{ for } i=1, \dots, M \quad (14a)$$

The coefficients $A_{ij}(Q^{(n)})$ and $B_i(Q^{(n)})$ are given by

$$A_{ij}(Q^{(n)}) = \int_{v_L}^{v_U} dv W(v) \left[\frac{\partial S(v; Q)}{\partial Q_i} \right]_n \left[\frac{\partial S(v; Q)}{\partial Q_j} \right]_n \quad (15)$$

and

$$B_i(Q^{(n)}) = \int_{v_L}^{v_U} dv W(v) [S(v) - S(v; Q^{(n)})] \left[\frac{\partial S(v; Q)}{\partial Q_i} \right]_n \quad (16)$$

Introducing the $M \times M$ matrix $A(Q^{(n)})$, whose elements are the coefficients $A_{ij}(Q^{(n)})$, and $M \times 1$ -matrices $B(Q^{(n)})$ and ΔQ with elements $B_i(Q^{(n)})$ and ΔQ_i , respectively, Eq. 14a can be rewritten as

$$A(Q^{(n)}) \Delta Q = B(Q^{(n)}) \quad (14b)$$

If the M derivatives $\left[\frac{\partial S(v; Q)}{\partial Q_i} \right]_n$ ($i=1, \dots, M$) form a system of linearly independent functions of the variable v , the matrix $A(Q^{(n)})$ is non-singular, positive-definite matrix. In such a case, Eq. 14b has the unique solution $\Delta Q^{(n+1)}$ given by

$$\Delta Q^{(n+1)} = A(Q^{(n)})^{-1} B(Q^{(n)}) \quad (17)$$

The relevance of Eq. 14b and the solutions given in Eq. 17 to the problem of finding the minima of $D(Q)$ can be seen from the analysis of an explicit form of $D(Q)_n$. Substitution of Eq. 13 into Eq. 2 gives:

$$D(Q)_n = \sum_{i=1}^M \sum_{j=1}^M A_{ij}(Q^{(n)}) \Delta Q_i \Delta Q_j - 2 \sum_{i=1}^M B_i(Q^{(n)}) \Delta Q_i + C_0(Q^{(n)}) \quad (18)$$

where $C_0(Q^{(n)})$ is the following integral:

$$C_0(Q^{(n)}) = \int_{v_L}^{v_U} dv W(v) [S(v) - S(v; Q^{(n)})]^2 \quad (19)$$

Eq. 18 shows that $D(Q)_n$ is a parabolic type of hypersurface and, if $A(Q^{(n)})$ is positive-definite, $D(Q)_n$ has only one extremum which is the minimum.

It is also easy to show that

$$D(Q^{(n)})_n = D(Q^{(n)}) \quad (20a)$$

and

$$\left[\frac{\partial D(Q)_n}{\partial Q_i} \right]_n = \left[\frac{\partial D(Q)}{\partial Q_i} \right]_n, \quad \text{for all } i=1, \dots, M \quad (20b)$$

Consequently, the parabolic surfaces $D(Q)_n$ is tangential to the surface $D(Q)$ at $Q = Q^{(n)}$.

The set $Q^{(n+1)}$ which minimizes the value $D(Q)_n$ relates to $Q^{(n)}$ and to $\Delta Q^{(n+1)}$ as $Q^{(n+1)} = Q^{(n)} + \Delta Q^{(n+1)}$. If the surface $D(Q)$ has a favorable shape in the vicinity of one of its minima, the sequence $Q^{(n)}, Q^{(n+1)}, Q^{(n+2)}, \dots$ converges to the value $Q^{(e)}$ at this minimum:

$$\lim_{n \rightarrow \infty} Q^{(n)} = Q^{(e)} \quad (21)$$

A necessary but not sufficient condition of the convergence of Eq. 21 is the positive-definiteness of the matrix $A(Q^{(n)})$ for all the members of the $Q^{(n)}$ -sequences. Rather than discussing the technical details of the convergence or divergence conditions of the $Q^{(n)}$ -sequences, several characteristic situations are illustrated in Figures 1-3.

In these figures the horizontal axis schematizes the M -dimensional manifold of Q -variables and the solid curves schematize segments of the hypersurface $D(Q)$. The dashed curves labeled $n, n+1$ and $n+2$ represent parabolic hypersurfaces $D(Q)_n, D(Q)_{n+1}$ and $D(Q)_{n+2}$. The circles indicate the tangential points between $D(Q)$ and the respective parabolic hypersurfaces. The labels $n, n+1, n+2, e$ and e' denote the positions of $Q^{(n)}, Q^{(n+1)}, Q^{(n+2)}, Q^{(e)}$, and $Q^{(e')}$ on the " Q -axis". Figure 1 illustrates a situation in which $D(Q^{(n)}) > D(Q^{(n+1)}) > D(Q^{(n+2)}) > \dots$, and in which the $Q^{(n)}$ -sequence converges to $Q^{(e)}$.

Figures 2 and 3 illustrate situations in which the sequence $Q^{(n)}$ might be divergent even though the matrix $A(Q^{(n)})$ is positive-definite. In Figure 2 the sequence oscillates around $Q^{(e)}$ while diverging. In Figure 3 the $D(Q)$ surface is, on the right of the maximum $D(Q^{(e')})$, decreasing up to the upper limit of the Q range. In this case the $Q^{(n)}$ -sequence "jumps" over the narrow minimum and diverges toward the limit of the Q range.

Unless the $D(Q)$ hypersurface has an unusually pathological form, the above mentioned divergencies can be avoided by building into the algorithm suitable safeguards, combined with procedures for bypassing the troublesome parts of the $D(Q)$ surface.

FIGURE 1

FIGURE 2

FIGURE 3

The above procedure for the minimization of $D(Q)$ can be summarized into the following basic steps:

---A trial set $Q^{(1)}$, which is thought to be a close estimate of $Q^{(S)}$, is found. The index n in Eqs. 14-17 is set equal to 1 and the next step is initiated.

---The matrices $A(Q^{(n)})$ and $B(Q^{(n)})$ are evaluated and, providing $A(Q^{(n)})$ is positive-definite, Eq. 14b is solved.

---The set $Q^{(n+1)} = Q^{(n)} + \Delta Q^{(n+1)}$ is constructed and checked against some suitable convergence criteria. If these criteria are met, the procedure is terminated. Otherwise, the value of the index n is reset to $n+1$ and the second step is repeated.

It should be emphasized that even if the above iterative procedure converges and a minimum of $D(Q)$ is found, the technique itself does not provide any means for ascertaining whether this minimum is absolute or local. If it is suspected that the found minimum is not absolute, the minimization procedure must be repeated with a different trial set $Q^{(1)}$:

4. The Model Design Matrix and Evaluation of $A_{ij}(Q)$, $B_i(Q)$ and $C_0(Q)$:

Eqs. 14, 17 and 18 require the evaluation of integrals of Eqs. 15, 16 and 19. In all practical cases, the distribution $S(v)$ and the weight function $W(v)$ are specified by sets of their values $S(v_i)$ and $W(v_i)$ at selected frequencies $v_i (i=1, \dots, N)$ and, consequently, numerical estimates of these integrals are used.

In order to facilitate programming for the evaluation of these integrals, the following arrays are defined. The first of them, the F array, is defined as

$$F = \{v_i | i=1, \dots, N; v_L \leq v_i \leq v_U; v_i < v_j \text{ if } i < j\} \quad (22)$$

The F array represents a discrete mesh superimposed on the frequency interval $\langle v_L, v_U \rangle$. It is assumed that $M < N$ and that every sub-interval $\langle v_i, v_{i+1} \rangle$ is narrow enough so that the integrands in the integrals of Eq. 15, 16 and 19 may be treated as linear functions of v within each of the sub-intervals $\langle v_i, v_{i+1} \rangle$. This piecewise linearity of the integrands will allow the use of the trapezoidal rule for integration. In practice, the mesh F is chosen in such a way that only a piecewise linearity of $S(v)$ is secured.

For a given function $\phi(v)$ defined over the interval $\langle v_L, v_U \rangle$, we introduce the array ϕ of values of $\phi(v)$ over the mesh F :

$$\phi = \{\phi_i | i=1, \dots, N; \phi_i = \phi(v_i); v_i \in F\} \quad (23)$$

The notation which will be used for the array ϕ when $\phi(v)$ is represented by $S(v)$, $W(v)$, $S(v;Q)$, $S(v) - S(v;Q)$ or $\left[\frac{\partial S(v;Q)}{\partial Q_i} \right]$ is given in Table 1.

It is implied that the arrays SQ , SSQ and DSW_j are evaluated for some fixed set of Q values.

It will be convenient to view the array W as the diagonal of an $N \times N$ diagonal matrix, which also is denoted by W . The arrays F , S , SQ , SSQ and DSQ_j are, alternatively, interpreted as $N \times 1$ matrices. We will also introduce an $N \times M$ matrix RM , in which the j th column is the array DSQ_j ($j=1, \dots, M$). This matrix is termed the model design or regression matrix.

Oftentime only some of the Q -parameters, say P of them, $P < M$, are allowed to vary during the minimization of $D(Q)$, while the remaining $M - P$ parameters are kept fixed at some estimated values. Such a partial minimization might improve the convergency in the search for minima of $D(Q)$. The $N \times P$ matrix obtained from RM by deletion of columns which correspond to parameters not being optimized is sometimes termed the contracted design matrix.

TABLE 1

NOTATION FOR ARRAYS OF EQUATION 23

Function	Array Symbol	Element Definition
$S(v)$	S	$S_i = (v_i)$
$W(v)$	W	$W_i = W(v_i)$
$S(v;Q)$	SQ	$SQ_i = S(v_i;Q)$
$S(v) - S(v;Q)$	SSQ	$SSQ_i = S(v_i) - S(v_i;Q)$
$\left[\frac{\partial S(v;Q)}{\partial Q_j} \right]$	DSQ_j	$DSQ_{ji} = \left[\frac{\partial S(v_i;Q)}{\partial Q_j} \right]$

We also introduce the arrays DF ($DF_i = \Delta_i$) and DW ($DW_i = \Delta_i W_i$) where the Δ_i are defined as

$$\begin{aligned}\Delta_i &= (v_{i+1} - v_{i-1})/2, \text{ for } i=2, \dots, N-1 \\ \Delta_1 &= (v_2 - v_1)/2 \\ \Delta_N &= (v_N - v_{N-1})/2\end{aligned}\tag{24}$$

When the integrals of Eqs. 15 and 16 are repeatedly evaluated for various sets Q , the array DW offers considerable programmatic and time-saving advantages.

Let $f(v)$ denote the integrand in the in the integrals of Eqs. 15, 16 and 19, and let $f_i = f(v_i)$, where $v_i \in F$. If the mesh F is such that $f(v)$ is nearly linear over each of the subintervals $\langle v_i, v_{i+1} \rangle$, then the integral

$\int_{v_L}^{v_U} dv f(v)$ can be estimated by means of the trapezoidal rule:

$$\int_{v_L}^{v_U} dv f(v) \approx \frac{1}{2} \sum_{i=1}^{N-1} (f_i + f_{i+1})(v_{i+1} - v_i)\tag{25}$$

A slight rearrangement of the sum in Eq. 25 allows the trapezoidal-rule estimate to be written as

$$\int_{v_L}^{v_U} dv f(v) \approx \sum_{i=1}^N f_i \Delta_i\tag{26}$$

where Δ_i are the elements of the DF array, defined by Eq. 24. Eq. 26 allows the integrals $A_{ij}(Q)$, $B_i(Q)$ and $C_0(Q)$ to be written as

$$A_{ij}(Q) = \sum_{k=1}^N W_k \cdot \Delta_k \cdot DSQ_{ik} \cdot DSQ_{jk} \quad (27a)$$

$$B_i(Q) = \sum_{k=1}^N W_k \cdot \Delta_k \cdot SSQ_k \cdot DSQ_{ik} \quad (28a)$$

$$C_0(Q) = \sum_{k=1}^N W_k \cdot \Delta_k \cdot (SSQ_k)^2 \quad (29a)$$

Interpreting the array DW as the diagonal of the N x N diagonal matrix DW, Eqs. 27a-29a can be written in compact matrix form:

$$A_{ij}(Q) = \widetilde{DSQ_i} \cdot DW \cdot DSQ_j \quad (27b)$$

$$B_i(Q) = \widetilde{DSQ_i} \cdot DW \cdot SSQ \quad (28b)$$

$$C_0(Q) = \widetilde{SSQ} \cdot DW \cdot SSQ \quad (29b)$$

where the tilde denotes matrix transposition. By means of the design matrix RM an even more compact notation can be achieved:

$$A(Q) = \widetilde{RM} \cdot DW \cdot RM \quad (30)$$

$$B(Q) = \widetilde{RM} \cdot DW \cdot SSQ \quad (31)$$

where the M x M and M x 1 matrices A(Q) and B(Q) are those of Eq. 14b.

5. Shape Functions $\epsilon_1(v; P_1)$:

In this section we specify those particular baseline and band shape functions which are built into the program DECAY I.

It is assumed that the baseline shape function $\epsilon_0(v; P_0)$ has the form:

$$\epsilon_0(v; P_0) = E_0 + E_1 v + E_2 v^2 \quad (32)$$

and, therefore, that $P_0 = \{E_0, E_1, E_2\}$.

The form of the band shape functions $\epsilon_i(v; P_i)$ is specified as follows:

$$\epsilon_i(v; P_i) = \epsilon_1(v; a_i, b_i, c_i, d_i) \cdot \epsilon_2(v; d_i, f_i, g_i, \delta_i, m_i, n_i) \quad (33)$$

where $i=1, \dots, L$; and where (i-index suppressed for convenience):

$$\epsilon_1(v; a, b, c, d) = a \frac{e^{-b(v-d)^2}}{1 + c(v-d)^2} \quad (34)$$

$$\epsilon_2(v; d, f, g, \delta, m, n) = \delta + f \frac{(v-d)^m}{1 + g(v-d)^n} \quad (35)$$

The parameters $a_i, b_i, c_i, d_i, e_i, f_i$ and g_i will be optimized during the minimization of $D(Q)$. The parameters δ_i, m_i and n_i are not optimized and their values for each band have to be chosen during the specification of the model.

For an analysis of those band shapes which are allowed by the shape functions of Eqs. 33-35, the derivatives of $\epsilon_i(v; P_i)$ over the frequency v and parameters a, b, c, d, f and g are needed. In order to abbreviate the notation in the expressions to follow, the functions of Eqs. 33-35 are denoted by ϵ, ϵ_1 and ϵ_2 , respectively. Also, the substitution $x = v - d$ is introduced. First, we observe that:

$$\frac{\partial \epsilon}{\partial v} = \frac{\partial \epsilon}{\partial x} = \epsilon_1 \frac{\partial \epsilon_2}{\partial x} + \epsilon_2 \frac{\partial \epsilon_1}{\partial x} \quad (36)$$

$$\frac{\partial^2 \epsilon}{\partial x} = \frac{\partial^2 \epsilon}{\partial v^2} = \epsilon_1 \frac{\partial^2 \epsilon_2}{\partial x^2} + 2 \frac{\partial \epsilon_1}{\partial x} \frac{\partial \epsilon_2}{\partial x} + \epsilon_2 \frac{\partial^2 \epsilon_1}{\partial x^2} \quad (37)$$

The expressions for the first and second derivatives of ϵ_1 and ϵ_2 are given by

$$\frac{\partial \epsilon_1}{\partial x} = a \frac{e^{-bx^2}}{[1 + cx^2]^2} (-2x) [(b+c) + bcx^2] \quad (38)$$

$$\frac{\partial \epsilon_2}{\partial x} = f \frac{x^{m-1}}{[1 + gx^n]^2} [m + (m-n)gx^n] \quad (39)$$

$$\begin{aligned} \frac{\partial^2 \epsilon_1}{\partial x^2} = a \frac{e^{-bx^2}}{[1 + cx^2]^3} \cdot \{ 2\{2x^2[(b+c) + bcx^2]^2 - (3+cx^2)[(b+c) + bcx^2] \\ + 2(b+c)[1 + cx^2]\} \end{aligned} \quad (40)$$

$$\begin{aligned} \frac{\partial^2 \epsilon_2}{\partial x^2} = f \frac{x^{m-2}}{[1 + gx^n]^3} \{ m(m-1) + [(2m+1)(m-n) - n^2 - m] gx^n \\ + (m-n+1)(m-n) g^2 x^{2n} \} \end{aligned} \quad (41)$$

The explicit form of $\frac{\partial \epsilon}{\partial x}$ follows from Eqs. 36, 38 and 39:

$$\frac{\partial \epsilon}{\partial x} = \frac{ae^{-b^2 x^2}}{[1 + cx^2]^2 [1 + gx^n]^2} F(x)_{mn} \quad (42)$$

where

$$F(x)_{mn} = fx^{m-1}R(x)_{n+4} - 2\delta x R(x)_{2n+2} \quad (43)$$

$$R(x)_{n+4} = [1 + cx^2] [m + (m-n) gx^n] - 2x^2[1 + gx^n] [(b+c) + bcx^2] \quad (44a)$$

$$R(x)_{2n+2} = [1 + gx^n]^2 [(b+c) + bcx^2] \quad (45a)$$

The functions $R(x)_{n+4}$ and $R(x)_{2n+2}$ are polynomials of degree $n+4$ and $2n+2$, respectively:

$$R(x)_{n+4} = \sum_{k=0}^{n+4} R_{n+4,k} (x^k) \quad (44b)$$

$$R(x)_{2n+2} = \sum_{k=0}^{2n+2} R_{2n+2,k} (x^k) \quad (45b)$$

However, the only non-zero coefficients of $R_{n+4,k}$ and $R_{2n+2,k}$ are those with $k = 0, 2, 2, n, n+2, n+4$ and $k = 0, 2, n, n+2, 2n, 2n+2$, respectively. The explicit expressions for these coefficients are given in Table 2. Table 3 gives these coefficients for $n = 2, 4$ and 6 . It can be seen from Table 2 that, for even values of n , the polynomials $R(x)_{n+4}$ and $R(x)_{2n+2}$ are even functions of x . The function $F(x)_{mn}$ of Eq. 43 is also a polynomial in x and, for $m > n$, its order is $(m+n+3)$. For $m \leq n$, the order of $F(x)_{mn}$ is $(2n+3)$ when $\delta \neq 0$ and $(m+n+3)$ when $\delta = 0$. The first derivatives of ε over the parameters a, b, e, d, f and g are:

TABLE 2

COEFFICIENTS OF $R(x)_{n+4}$ AND $R(x)_{2n+2}$

k	$R_{n+4,k}$	$R_{2n+2,k}$
0	m	$(b+c)$
2	$mc - 2(b+c)$	bc
4	$-2bc$	0
n	$(m-n)g$	$2(b+c)g$
$n+2$	$(m-n)cg - 2(b+c)g$	$2bcg$
$n+4$	$-2bcg$	0
$2n$	0	$(b+c)g^2$
$2n+2$	0	bcg^2

TABLE 3

COEFFICIENTS OF $R(x)_{n+4}$ AND $R(x)_{2n+2}$ FOR $n = 2, 4, 6$

k	n=2		n=4		n=6	
	$R_{n+4,k}$	$R_{2n+2,k}$	$R_{n+4,k}$	$R_{2n+2,k}$	$R_{n+4,k}$	$R_{2n+2,k}$
0	m	b+c	m	b+c	m	b+c
2	$mc - 2(b+c) + (m-2)g$	$bc + 2(b+c)g$	$mc - 2(b+c)$	bc	$mc - 2(b+c)$	bc
4	$(m-2)cg - 2(b+c)g - 2bc$	$2bcg + (b+c)g^2$	$(m-4)g - 2bc$	$2(b+c)g$	-2bc	0
6	-2bcg	bcg^2	$(m-4)cg - 2(b+c)g$	2bcg	$(m-6)g$	$2(b+c)g$
8			-2bcg	$(b+c)g^2$	$(m-6)cg - 2(b+c)g$	2bcg
10				bcg^2	-2bcg	0
12						$(b+c)g^2$
14						bcg^2

$$\frac{\partial \epsilon}{\partial a} = \frac{1}{a} \epsilon_1 \epsilon_2 \quad (46)$$

$$\frac{\partial \epsilon}{\partial b} = \epsilon_1 \epsilon_2 [-x^2] \quad (47)$$

$$\frac{\partial \epsilon}{\partial c} = \epsilon_1 \epsilon_2 \left[-\frac{x^2}{1+cx^2} \right] \quad (48)$$

$$\frac{\partial \epsilon}{\partial} = \epsilon_1 \epsilon_2 2x \frac{(b+c) + bcx^2}{1 + cx^2} - \epsilon_1 \frac{fx^{m-1}}{(1+gx^n)^2} [m + (m-n) gx^n] \quad (49)$$

$$\frac{\partial \epsilon}{\partial f} = \epsilon_1 \frac{x^m}{1 + gx^n} \quad (50)$$

$$\frac{\partial \epsilon}{\partial g} = \epsilon_1 \left[-\frac{fx^{m+n}}{(1 + gx^n)^2} \right] \quad (51)$$

REFERENCES

1. J. Mandel, The Statistical Analysis of Experimental Data (Interscience, New York, 1964); Chs. 7, 11 and 12.
2. W. C. Hamilton, Statistics in Physical Science (Ronald Press, 1964); Chs. 4-6.
3. G. A. F. Seber, Linear Regression Analysis (Wiley New York, 1977)
4. The fact that the signal S is distributed over the frequency ν of electromagnetic radiation is completely irrelevant to the problem of signal decomposition. Thus, for example, in proton NMR the signal can be distributed over the intensity of the magnetic field, while in gas or liquid chromatography the signal is distributed over time. The method described in this Note is applicable to these types of signal without any modifications.

D. KUMAR

VISITING ASSISTANT PROFESSOR OF CHEMISTRY

RESEARCH ASSOCIATE

I. PUBLICATIONS

A. Bibliography for 1979 - 1980

1. McGlynn, S. P., Azumi, T. and Kumar, D., "The Colors of Post-Transition-Metal Salts," Accts. Chem. Res., submitted for Publication.
(7 preprints appended to this Report)

ABSTRACT: Certain post-transition heavy metal salts [e.g., $\text{Pb}(\text{NO}_2)_2$], of which neither the anion nor the cation are separately colored, exhibit striking colorations. It is shown that the existing experimental data is interpretable along simple theoretical lines. Primary among these lines are (i), the spin-orbit intensification of low energy spin-forbidden transitions of the anion; (ii), the enhancement of forbidden spin-allowed transitions of the anion by symmetry decrements in the heavy metal salt; and (iii), the occurrence of low energy charge-transfer, cation $\leftrightarrow$ anion electronic transitions. These considerations are applied specifically to nitrite, chlorite, cyanate, thiocyanate, azide, nitrate, carbonate, borate, chlorate, bromate, iodate, permanganate, perrhenate, tungstate, molybdate, phosphate, sulfate, formate, acetate, benzoate and phenylacetate salts -- and, by extension, to all other oxyanion salts. It is found that the process (i) provides the most common route to post-transition-metal salts.

II. LECTURES

None

III. WORK IN PROGRESS

A. Two-Photon Optoacoustic Spectroscopy:

Our laser-based spectroscopic system is now operational. We are currently using the optoacoustic technique as a detection mechanism and hope to increase time resolution into the nanosecond range by suitable modifications. The high sensitivity of the optoacoustic technique will be employed to study weak two-photon processes. We also intend to interface the automatic laser scanner with a mini computer to facilitate data collection and processing.

T. L. MATHERS
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RESEARCH ASSISTANT

I. PUBLICATIONS

None

II. LECTURES

1. "4.5eV Absorption in Water Systems," 8th Annual Symposium on Molecular Electronic Structure and Spectroscopy, The Louisiana State University, Baton Rouge, Louisiana, May 22-23, 1980.

---Invited Lecture

III. WORK IN PROGRESS

A. Luminescence of Aqueous Systems:

Luminescence of the hydroxide ion [See, for example, H. J. Maria and S. P. McGlynn, J. Chem. Phys., 52, 3402 (1970)], as well as that of various salts in water matrices is being investigated. Those salts which exhibit a luminescence similar to that of the hydroxide ion generally have had assigned a charge-transfer-to-solvent (CTTS) absorption band in the vicinity of the luminescence excitation. One possible model for this luminescence invokes production of hydrogen atoms which then react with water to form a transient species $\text{H}_3\text{O}^\cdot$. It is suspected that this transient is responsible for the above luminescence. More complicated analogs, such as $\text{LiH}_2\text{O}^\cdot$ and BeH_2O^+ , may also exist.

This work is both theoretical and experimental:

---Extensive calculations of hydrogen atoms in ice matrices will be performed using GAUSSIAN 76. Previous work with GAUSSIAN 70 was inconclusive.

---Experimentally, we plan to investigate the luminescence from non-aqueous solutions of ions exhibiting CTTS transitions (e.g., hydroxide and hydrosulfide ions, among others). Our previous attempts have been unsuccessful because of self-luminescence of the solvents.

Finally, we plan to extend studies currently available in the literature by measurement of absorption of the hydronium radical in low-temperature, glassy matrices. We hope to answer not only the question of the origin of aqueous-salt luminescence, but also that of the nature of the 4.5eV absorption in aqueous systems.

B. Two-Photon Optoacoustic Spectroscopy:

With D. Kumar, See p. 55.

D. B. BOULER
GRADUATE STUDENT
TEACHING ASSISTANT

I. PUBLICATIONS

A. Completion of the 1978 - 1979 Annual Report

198. Boulter, D., Felps, W. S., Lewis, J., Nauman, R. V. and McGlynn, S. P., "Molecular Rydberg States. Azulene and 4,6,8-Trimethylazulene," Chem. Phys. Lett., **67**, 420 (1979).
(7 reprints appended to this Report)

B. Bibliography for 1979 - 1980

1. Lewis, J. W., Nauman, R. V., Boulter, D. B., Jr. and McGlynn, S. P., "Molecular Rydberg Transitions. XIX. Low-Energy Rydberg States of Azulene," J. Chem. Phys., to be submitted.
(7 reprints appended to this Report)

ABSTRACT: Various electronic spectra (absorption, emission, ELD and MCD) of azulene and six of its derivatives are discussed. The focus of the work is the low-energy Rydberg states of azulene and their spectroscopic and photophysical consequences. It is shown that the 3d Rydberg states lie in the $45000\text{--}50000\text{cm}^{-1}$ range, that they are partially quenched by affixing chemical substituents, and totally quenched in condensed media. The 3p Rydberg states lie at $\sim 40000\text{cm}^{-1}$ in azulene but are largely quenched in all derivatives. It is shown that the quenching of the 3p Rydbergs of azulene in condensed media is responsible for much of the gross alterations which occur in the $S_4 \leftarrow S_0$ absorption region of azulene upon going from gaseous to condensed phases. It is shown that the 3s Rydberg state should lie in the vicinity of the $S_2 \leftarrow S_0$ absorption region. Our investigations of this region demonstrate the presence of only

one origin band α in the $S_2 \leftarrow S_0$ emission whereas two, α and β , exist in the $S_2 \leftarrow S_0$ absorption spectrum. It is shown that the lack of mirror symmetry of $S_2 \leftrightarrow S_0$ absorption and emission and the gross variations of the $S_2 \leftarrow S_0$ absorption which occur in different media are associable with the presence of the β -origin. It is suggested that the β -origin may be of $3s$ Rydberg nature

II. LECTURES

1. Organizer of the 8th Annual Symposium on Molecular Electronic Structure and Spectroscopy, The Louisiana State University, Baton Rouge, Louisiana, May 22-23, 1980.

---Symposium Organized

2. "Low-Energy Rydberg States in Azulenes," 8th Annual Symposium on Molecular Electronic Structure and Spectroscopy, The Louisiana State University, Baton Rouge, Louisiana, May 22-23, 1980.

---Invited Lecture

III. WORK IN PROGRESS

None

(Mr. Bouler is currently in the final stages of writing his MS Thesis.)

J. DAGATA
GRADUATE STUDENT
TEACHING ASSISTANT

I. PUBLICATIONS

None

II. LECTURES

1. "Multi-Channel Quantum Defect Theory Applied to Molecular Rydberg States," 8th Annual Symposium on Molecular Electronic Structure and Spectroscopy, The Louisiana State University, Baton Rouge, Louisiana, May 22-23, 1980.

---Invited Lecture

III. WORK IN PROGRESS

A. Quantum Defect Theory and Molecular Rydberg States:

This study is described in the following Preliminary Report.

MULTI-CHANNEL QUANTUM DEFECT THEORY
APPLIED TO MOLECULAR RYDBERG STATES.

A PRELIMINARY REPORT

by

J. Dagata

1. Introduction:

Our current efforts in the study of molecular Rydberg states involve three diverse, although complementary, approaches. First, systematic methods of assignment of spectra are being developed further. These procedures must be designed such that several reliable energy levels can be used to extend a series assignment, thereby locating levels in energy regions in which overlapping bands and perturbations induce spectral complications. Second, algorithms appropriate for parameter optimization and subsequent correlation to related experimental data are being constructed. Third, studies which attempt to achieve a deeper understanding of molecular quantum defects are being pursued.

In a given energy region, atoms and molecules exhibit overlapping series which are coupled more or less strongly by the angular momentum components of the optical electron and the molecular core. Properties ascribed to the quantum defect are dependent on how the individual series and their interactions are represented. In particular, it is necessary to understand how quantum defects in the single-channel scheme relate to those in the multi-channel scheme since, in the latter case, individual series can no longer be labeled by the orbital angular momentum of the optical electron. This question will be seen to bear on the methods

available for spectral analysis of molecular systems.

Multi-channel quantum defect theory (MQDT) was originally developed by Seaton¹ as an ab initio method of calculating wavefunctions from quantum defects. It has since been extended by Fano and co-workers^{2,3} to include semi-empirical determinations of quantum defects, oscillator strengths and Landé g-factors.

MQDT has its origins in collision theory, which provides the required energy-momentum conservation for configurational interactions. By virtue of the connection MQDT makes between series levels in the discrete region and scattering channels in the continuum, information from these quite different sources can be correlated and this, in turn, decreases the sometimes arbitrary nature of assignments of energy levels and quantum defects.

The systems which we are studying are CH₃I, HI and their atomic analogue, Xe. There is sufficient evidence that Xe forms an excellent zero-order model for these molecular systems and this has led to a single-channel assignment of their Rydberg spectra.⁴ Preliminary results for the coupling parameters of MQDT for CH₃I strengthen this model assumption (vide infra).

Section 2 of this report briefly develops the connection between scattering theory and QDT; presents in part the equations derived by Lu⁵ in his analysis of Xe; and discusses preliminary results for CH₃I. (Adequate data for HI is not available at present.) Section 3 outlines the strategy for a systematic analysis of Rydberg series data that currently seems feasible.

2. Scattering and Quantum Defect Theory:

Quantum defect theory proceeds through the construction of a "channel", which is comprised of a set of scattering states and a set of bound states (Rydberg series), all having the same total angular momentum, J. The coupling of channels

of different L but with the same J is not allowed in single-channel quantum defect theory (SQDT). For the purposes of obtaining initial assignments and quantum defects, this neglect is convenient for molecular systems exhibiting complicated spectra. MQDT removes this restriction, however.

The channel described above may be seen to be less artificial than it appears initially. That a Rydberg series can be found for a molecule implies that, for these states, the system is nearly hydrogenic. As the series levels converge to the ionization limit, then, very little non-Coulombic potential remains, and, in the limit, the potential becomes essentially Coulombic. The way in which this viewpoint relates phase shifts to quantum defects will be discussed next.

A. The Phase Amplitude Method: An N electron atom or molecule may be viewed as an $(N-1)$ -electron core and an associated optical electron. In the case of a neutral species, there will exist an attractive Coulomb potential and various short-ranged/long-ranged, attractive/repulsive forces due to coupling and anisotropic molecular effects. Since the excitation energies are relatively large, the radii of the Rydberg orbitals are large enough to justify the assumption that the effective potential is spherically symmetric beyond some finite radius, r_0 . For electron/core scattering under these assumptions, the radial Hamiltonian can be written as

$$H\psi = (H_0 + U(\vec{r}))\psi = E\psi \quad (1)$$

where

$$H_0 = -\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2} - V_{\text{coulomb}}$$

$$\begin{aligned} U(\vec{r}) &= V_{\text{atomic}}(r) + V_{\text{molecular}}(\vec{r}) & r < r_0 \\ &= 0 & r \geq r_0 \end{aligned}$$

The solution has the form of a superposition of an incoming plane wave and an outgoing scattered wave. All effects of the short-ranged potentials are manifested in the phase shift. Thus,²

$$\psi(r) = A(r)\{f\cos[\delta(r)] - g\sin[\delta(r)]\} \quad (2)$$

where

$A(r)$ --- amplitude function

$\delta(r)$ --- phase function

f, g --- regular and irregular Coulomb functions, respectively.

Boundary conditions require that the wavefunction remain finite at $r=0$ and $r=\infty$. Hence,

$$\delta(r) = \begin{cases} 0, & r=0 \\ \text{constant}, & r \geq r_0 \end{cases} \quad (3)$$

The amplitude function is determined once the phase shift at r_0 is known.

Before and after a collision the system is in an eigenstate. However, no such restriction applies when the electron is in close approach to the core: The state of the system has components in all eigenstates, gauged with probability given by the squares of the eigenvalues of the S-matrix (which are parameterized by the phase shifts),⁶ Thus, the S-matrix contains all information on channel interactions arising from the non-Coulombic potentials.

B. Quantum Defect Theory: From the empirical definition of a Rydberg series:

$$E_{i\alpha} = I - T_{i\alpha} = I - \frac{1}{(v_{i\alpha})^2}, \text{ in Rydberg units} \quad (4)$$

where

$E_{i\alpha}$ --- excitation energy to the i th level of the α th channel ($\alpha=1$ in SQDT)

I --- ionization potential

$T_{i\alpha}$ --- term value

$\nu_{i\alpha} = (n_i - \mu_\alpha)$ --- effective quantum number ($n_i = 1, 2, \dots$ in SQDT)

it is clear that the quantum defect provides a measure of the deviation from hydrogenicity of atomic and molecular systems. By replacing f and g in Eq. 2 by independent, asymptotic solutions to the radial equation,

$$\begin{aligned} f u(r) \sin \pi \nu - v(r) e^{i\pi \nu}, \quad r \rightarrow \infty \\ g u(r) \cos \pi \nu + v(r) e^{i\pi(\nu + \frac{1}{2})}, \quad r \rightarrow \infty \end{aligned} \quad (5)$$

where $u(r)$ and $v(r)$ are rising and falling exponentials, respectively,

Seaton has shown¹ that the phase shift is related to the quantum defect by

$$\delta = \pi \mu. \quad (6)$$

From (5) one sees that the $r \rightarrow \infty$ boundary conditions for a bound state require that

$$\sin \pi(\nu + \mu) = 0, \quad r \rightarrow \infty \quad (7)$$

Thus,

$$\nu = (n - \mu); \quad n = 1, 2, \dots \quad (8)$$

Eq.'s 7, 8 not only provide a connection between scattering theory and QDT, but establish a theoretical insight into the Rydberg equation.

C. Multi-Channel Quantum Defect Theory: For each channel, when the energy of the system is less than the ionization potential, Eq. 7 must be satisfied: That is, a quantum defect must be determined for each series. This leads to a representation of the S-matrix in terms of quantum defects and a unitary matrix U :³

$$e^{2i\pi\mu} \delta_{\alpha\beta} = \sum_{i,j} U_{\alpha i}^\dagger S_{ij} U_{j\beta} \quad (9)$$

where $\delta_{\alpha\beta}$ is the Kronecker delta; or, equivalently,

$$S_{ij} = \sum_{\alpha} U_{i\alpha} e^{2i\pi\mu} U_{\alpha j}^\dagger \quad (10)$$

(Note: In Eq.'s 9, 10, roman indices refer to the scattering channels, while

greek indices refer to linear combinations of all of these channels, each with the same eigenphase-shift $\pi\mu_\alpha$. These linear combinations are termed close-coupling channels.)

The total electronic wavefunction in the many-channel case is a superposition of all α , N-electron, close-coupling eigenfunctions:

$$\psi = \sum_{\alpha} \psi_{\alpha} A_{\alpha} \quad (11)$$

$$= \sum_i \phi_i \{ f \sum_{\alpha} U_{i\alpha} \cos \pi \mu_{\alpha} A_{\alpha} - g \sum_{\alpha} U_{i\alpha} \sin \pi \mu_{\alpha} A_{\alpha} \} \quad (12)$$

where ϕ_i is the i th core-electron wavefunction.

As in the single channel case, application of the boundary conditions for the bound states leads to

$$\sum_{\alpha} U_{i\alpha} \sin \pi (\nu_i + \mu_{\alpha}) A_{\alpha} = 0 \quad (13)$$

D. MQDT Applied to Xenon: Based on the remarkable similarities of the spectra of Xe, HI, and CH₃I and the evidence from a SQDT study,⁴ it is expected that the MQDT analyses of HI and CH₃I should correlate with that for Xe.

For Xe there are five channels ($J=1$) for the allowed s and d transitions converging on core states with $J_c=1/2, 3/2$. These are given in Table 1.

Lu's graphical representation of Rydberg states⁵ utilizes two analytical functions which will be derived for Xe. First, in the discrete region, each excitation energy is associated with term values for either ionization limit:

$$\begin{aligned} E_i &= I_{3/2} - \frac{1}{(\nu_{3/2,1})^2} \\ &= I_{1/2} - \frac{1}{(\nu_{1/2,1})^2} \end{aligned} \quad (14)$$

From this a functional relationship between the effective quantum numbers is given by

TABLE 1

Xe, J=1 CHANNELS ARISING FROM THE
 CONFIGURATIONAL EXCITATIONS $\dots 5p^6; 1s_0 \rightarrow$
 $\dots 5p^5(2p_{3/2,1/2})n_j \ell, \ell=\bar{s} \text{ or } d.$

Channel Index	Channels	
	$2p_{3/2}$	$2p_{1/2}$
i=1	$d_{5/2} \equiv \bar{d}$	
2	$d_{3/2} \equiv d$	
3	$s_{1/2} \equiv s$	
4		$d_{3/2} \equiv d'$
5		$s_{1/2} \equiv s'$

$$v_{3/2} = \frac{v_{1/2}}{[1 - (I_{1/2} - I_{3/2})v_{1/2}^2]^{1/2}} \quad (15)$$

The shape of this function depends on the difference of IP's.

Second, Eq. 13 constitutes five equations, one for each of the five channels, for which the coefficients must be determined.

Lu⁵ reduces this to a set of two equations by the substitution

$$A_\alpha = \frac{1}{\sin(v_{3/2} + \mu_\alpha)} \sum_{j=4}^5 U_{\alpha j}^+ B_j \quad (16)$$

from which is obtained

$$\sum_{j=4}^5 \sum_{\alpha} (\sum_{i\alpha} U_{\alpha j}^+) B_j = \sum_{j=4}^5 \delta_{ij} B_j = 0; i=1,2,3 \quad (17)$$

and

$$\sum_{j=4}^5 \left[\sum_{\alpha} U_{i\alpha} \frac{\sin\pi(v_{1/2} + \mu_\alpha)}{\sin\pi(v_{3/2} + \mu_\alpha)} U_{\alpha j}^+ \right] B_j = 0; i=4,5 \quad (18)$$

Eq. 18 may be rewritten

$$\sum_{j=4}^5 [\cot\pi(v_{1/2} - v_{3/2}) \delta_{ij} + M_{ij}] B_j = 0; i=4,5 \quad (19)$$

where $M_{ij} = \sum_{\alpha} U_{i\alpha} \cot\pi(v_{3/2} + \mu_\alpha) U_{\alpha j}^+$

Setting the determinant of the coefficients of B_j in Eq. 19 equal to zero gives a quadratic expression in $\cot(v_{1/2} - v_{3/2})$:

$$F = \cot^2\pi(v_{1/2} - v_{3/2}) + G \cot\pi(v_{1/2} - v_{3/2}) + H = 0 \quad (20)$$

where

$$G = \sum_{\alpha} (U_{4\alpha}^2 + U_{5\alpha}^2) \cot\pi(v_{3/2} + \mu_\alpha)$$

$$H = \sum_{\alpha\beta} (U_{4\alpha} U_{5\alpha} - U_{5\alpha} U_{4\beta}) U_{4\alpha} U_{5\beta} \cot\pi(\nu_{3/2} + \mu_{\alpha}) \cot\pi(\nu_{3/2} + \mu_{\beta})$$

The function $F(\nu_{1/2}, \nu_{3/2}) = 0$ is shown for Xe in Figure 1. Since the cotangent function has period 1, the data are plotted modulo 1. The function exhibits strongly perturbing regions in the form of avoided crossings or jumps. The parameters control this function in the following ways: (i), the quantum defect is the value of $\nu_{3/2} \pmod{1}$ as $F(\nu_{1/2}, \nu_{3/2}) = 0$ crosses the diagonal and it is at these points that the series become uncoupled; and (ii), the elements of the U-matrix determine the slope of $F(\nu_{1/2}, \nu_{3/2}) = 0$ at the points of uncoupling. There are also additional constraints that limit the values that the U-matrix parameters may take on.

E. Methyl Iodide: Preliminary results for CH_3I are shown in Figure 2 and Table 2. While it is evident that further fitting is necessary, an initial comment can still be made: All parameters for Xe are roughly similar to those of CH_3I . However, the coupling parameters $U_{i\alpha}$ appear to show less variation than the quantum defects in comparing the atomic case with the molecular case. That a trend of any sort emerges at this stage reinforces the claim that this technique will prove to be useful in the analysis of molecular Rydberg states, both in terms of the assignments of bands and the determination of quantum defects and coupling parameters.

3. Further Applications to Molecular Systems:

Figure 3 gives a scheme that appears suitable for the systematic analysis of molecular Rydberg series. For any system, the series must be identified and the appropriate form of $F(\nu_{1/2}, \nu_{3/2})$ must be found. If an atomic system can be used as a model, the task is then simplified. Agreement of photoionization cross-sections with those calculated using the phase shifts and coupling parameters will provide a consistency check for

Xe, DISCRETE REGION

FIGURE 1

CH₃I, DISCRETE REGION

FIGURE 2

TABLE 2

COMPARISON OF MQDT PARAMETERS
FOR XENON AND METHYL IODIDE^a

α	1	2	3	4	5
Xenon					
μ_α	0.57	0.36	0.13	0.05	-0.01
$U_{4\alpha}^2$	0.13	0.48	0.37	0	0
$U_{5\alpha}^2$	0	0	0	0.80	0.17
METHYL IODIDE					
FIT I					
μ_α	0.85	0.22	0.17	0.09	-0.06
$U_{4\alpha}^2$	0.17	0.40	0.25	0	0
$U_{5\alpha}^2$	0	0	0	0.90	0.30
FIT II					
μ_α	0.86	0.21	0.15	0.08	-0.06
$U_{4\alpha}^2$	0.18	0.40	0.25	0	0
$U_{5\alpha}^2$	0	0	0	0.90	0.30

^aFor preliminary fitting, s/d uncoupling is presumed. Thus, $\alpha=1,2,3$ are primary due to d excitation, while $\alpha=4,5$ are primarily due to s excitation.

FIGURE 3

the determined values of these parameters. Additionally, such a scheme should aid in the exploration of the properties of the quantum defect and its variation with energy and environment.

REFERENCES

1. M. J. Seaton, Proc. Phys. Soc. (Lond.), 88, 801, 815 (1966).
2. U. Fano and J. L. Dehmer, Phys. Rev., A2, 304 (1970).
3. U. Fano, Phys. Rev., A2, 353 (1970); K. T. Lu and U. Fano, Phys. Rev., A2, 81 (1970); and U. Fano, J. Opt. Soc. Am., 65, 979 (1975).
4. H. -t. Wang, W. S. Felps, G. L. Findley, A. R. P. Rau and S. P. McGlynn, J. Chem. Phys., 67, 3940 (1977).
5. K. T. Lu, Phys. Rev., A4, 579 (1971).
6. L. S. Rodberg and R. M. Thaler, Introduction to the Quantum Theory of Scattering (Academic Press, New York, 1967).

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I. PUBLICATIONS

None

II. LECTURES

1. "Vibronic Coupling Effects in the Hydrogen Halides," 8th Annual Symposium on Molecular Electronic Structure and Spectroscopy, The Louisiana State University, Baton Rouge, Louisiana, May 22-23, 1980.

---Invited Lecture

III. WORK IN PROGRESS

A. Vibronic Coupling in the Hydrogen Halides:

Certain anomalies in the VUV spectra of methyl iodide (S. P. McGlynn, W. S. Felps and J. D. Scott, "Molecular Rydberg Transitions. XVIII. Vibronic Coupling in Methyl Iodide," J. Chem. Phys., submitted) and cyanogen chloride (W. S. Felps, S. P. McGlynn and G. L. Findley, "Molecular Rydberg Transitions. Cyanogen Chloride," J. Mol. Spectrosc., in press) have been observed which can be interpreted by invoking vibronic coupling and treating it within a first-order perturbation-theoretic format. In this fashion it is possible to explain energy-spacing and intensity aberrations of some Rydberg transitions which had previously defied analysis. Our present work concerns an extension of this method to an analysis of possible vibronic-coupling effects in the hydrogen halides.

The VUV spectra of HBr, DBr and DI have been obtained on an energy scale. At present, there is evidence that vibronic coupling does occur in the Rydberg region of DI and the analogous spectrum of HI is being measured to substantiate this result.

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I. PUBLICATIONS

None

II. LECTURES

1. "Contributions to the Study of Electronic Term Values of Linear Molecules within an Intermediate Coupling Scheme," 8th Annual Symposium on Molecular Electronic Structure and Spectroscopy, The Louisiana State University, Baton Rouge, Louisiana, May 22-23, 1980.

---Invited Lecture

III. WORK IN PROGRESS

A. Algorithms for Band Deconvolution:

This work is being done jointly with P. Hochmann (See p.29 for background).

We are presently studying the local and nonlocal behavior of a new model band shape function, $\epsilon_i(\nu; P_i)$:

$$\begin{aligned}\epsilon_i(\nu; P_i) &= \epsilon_1(\nu; a_i, b_i, f_i) \cdot \epsilon_2(\nu; c_i, d_i, f_i) \\ &\cdot \epsilon_3(\nu; e_i, f_i)\end{aligned}$$

where

$$\epsilon_1(\nu; a_i, b_i, f_i) = a_i \exp[-b_i(\nu - f_i)^2]$$

$$\epsilon_2(\nu; c_i, d_i, f_i) = [1 + c_i(\nu - f_i)^2 + d_i(\nu - f_i)]^{-1}$$

$$\epsilon_3(\nu; e_i, f_i) = \exp[e_i(\nu - f_i)]$$

and where i is a band index. For suitable choices of the parameter set P_i , this model function is strictly positive and, thus, is suitable only for bands of the first kind. Further, it can be shown that $\epsilon_i(v; P_i)$ possesses a single extremum which, in this case, is a maximum.

Extremal conditions imposed on $\epsilon_i(v; P_i)$ yield a 3rd order polynomial which can be shown to possess only one real root, the maximum of $\epsilon_i(v; P_i)$. We are in the process of coding these conditions in order to modify our LSQ method.

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I. PUBLICATIONS

None

II. LECTURES

1. 8th Annual Symposium on Molecular Electronic Structure and Spectroscopy, The Louisiana State University, Baton Rouge, Louisiana, May 22-23, 1980.
 - (a) "Similarities in the Rydberg States of Hydrogen Sulfide and Water."
 - (b) "Chemically Induced Luminescence of Chick Embryo Fibroblasts - Windfall or Windmill?"

---Invited Lectures

III. WORK IN PROGRESS

A. Electronic Structure of H_2S_n :

Work is underway to synthesize and measure the UV, VUV and photoelectron spectra of the hydrosulfanes. Our primary intention is to generate data for use in an analysis of the electronic structure of sulfur-sulfur bonds. For background purposes, we are also in the process of generating the VUV spectra of H_2S and D_2S and plan to make an extensive comparison of this data with the analogous data for H_2O/D_2O [H. -t. Wang, W. S. Felps and S. P. McGlynn, J. Chem. Phys., **67**, 2614 (1977)]. Eventually, we hope to achieve a consistent Rydberg analysis of H_2S and D_2S .

B. UV Chemiluminescence from Virus-Infected Chick Embryo Fibroblast Cells:

V. P. Kaznacheev, S. P. Schurin, L. P. Mikhailova and N. V. Ignastovitch (in ULTRAWEAK LUMINESCENCES IN BIOLOGY, Moscow Publishing House, 1972) have reported the following results: When a chick embryo fibroblast is infected with a virus, it chemiluminesces. Our efforts to duplicate this result are continuing.