

FINAL REPORT

11/15/86 - 11/14/95

UNITED STATES DEPARTMENT OF ENERGY


DE-FG05-87ER60503


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

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FOREWORD

This Final Report (DOE/ER/60503-367) also constitutes a 3-year Comprehensive Report for the period 11/15/92 - 11/14/95. This Report (DOE/ER/60503-367) together with two other 3-year Comprehensive Reports

DOE/ER/60503-314 for 11/15/86 - 11/14/89

DOE/ER/60503-353 for 11/15/89 - 11/14/92

(which are already in your possession) constitute the entirety of the Final Report for the period 11/15/86 - 11/14/95.

I. STATEMENT OF OTHER SUPPORT

The work described in this Final Report was also supported by the following agencies:

LEQSF Enhancement Proposal, "Lesion Spectra:
Radiation Signature" awarded to S. P. McGynn,
J. Battista, K. Rupnik, et al. 61,100.

LSU, Office of Research and Economic Development
Faculty Pass-Through Program, "Advancement
of Gas Sensors Fabrication Technology and Testing
in Simulated Chemical Environments," 2,917.

II. LIST OF TITLES , SYMPOSIA AND PERSONNEL

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A. BIBLIOGRAPHY OF TITLES PUBLISHED

1992 - 1995

(serial numbers refer to the numbers allotted in previous reports)

354. L. Klasinc, L. Pasa-Tolic', H. Spiegl, J. V. Knop and S. P. McGlynn, "Long-Range Interactions of Substituents in Steroidal Molecules," *Int. J. Quant. Chem.; Quant. Biol. Symp.* 20, 191 (1993).
355. S. P. McGlynn, K. Rupnik, M. N. Varma and L. Klasinc, "Radiation Signatures and Radiation Markers," *Radiation Protection Dosimetry* 52 (1-4), 155 (1994).
356. W. H. Koppenol and L. Klasinc, "Ab Initio Calculations on ONOOH and ONOO⁻," *Int. J. Quant. Chem.; Quant. Biol. Symp.* 20, 1-6 (1993).
357. I. Novak, L. Klasinc, B. Kovac, S. P. McGlynn, "Electronic Structure of Haloalkanes: A high Resolution Photoelectron Spectroscopic Study," *J. Mol. Struct.* 297, 383 (1993).
358. D. Kumar, P. L. Clancy, L. Klasinc and S. P. McGlynn "Laser Optogalvanic Spectrum of Cesium in a Radiofrequency Discharge," *Croat. Chem. Acta*, CCACAA 66, 217 (1993).
359. D. Kumar, R. R. Zinn, and S. P. McGlynn, "Optogalvanic Transients in a Neon RF Discharge," *J. Chem. Phys.* 101 3, 1959 (1994).
360. L. Klasinc, L. Pasa-Tolic, D. Vikic-Topic, J. Knop and S. P. McGlynn, "Long Range Electronic Interaction in Androstanediones," in revision.
361. Annual Report for 1992-93. A Bibliography of Titles. report of Work in Progress and Work Completed (Items 340-361) for the Period of 1992-93 of Research Grant Number DE-FG05-87ER60503.
362. A. Srivastava, J. Cherukuri, S. P. McGlynn and D. Kumar, "Hydrogen Gas Sensing with Silicon Microsensors and the Monitoring Microchip Design," *Proceedings of the 1994 Federal Environmental Restoration III & Waste Minimization II Conference and Exhibition, Hazardous Materials and Control Resource Institute Press, Rockville, MD, 1994*, p.p. 1520-1527.

363. K. Rupnik, L. Klasinc, M. N. Varma, J. Battista and S. P. McGlynn, "Lesion Spectra: Radiation Signatures and Biological Gateways," J. Chem. Information and Computer Sciences 34, 1054 (1994).
364. L. Klasinc, A. Mannschreck, M. Mintas and S. P. McGlynn, "Photoelectron Spectra of Alkyl Diaziridines," J. Chem. Soc. Perkin Trans. II, 2, 2059 (1994).
365. K. Rupnik, U. Asaf and S. P. McGlynn, "Pressure Shifts and Electron Scattering in Atomic and Molecular Gases," Proceedings of VIIIth International Symposium on Gaseous Dielectrics, 87, Plenum Publishing Co.; NY; 1994.
366. D. Kumar, R. R. Zinn, T. D. Armstrong, S. P. McGlynn, "The Optogalvanic Effect as a Probe of Plasma Processes," J. Phy. Chem. (M.F.A. El-Sayed Festschrift), April, 1995.
367. Annual Report for 1993-1994. A Bibliography of Titles, Report of Work in Progress and Work Completed (Items 341-368) for the period 1993-1994 of Research Grant Number DE-FG05-87ER60503.
(3 copies submitted to the United States Department of Energy, Office of Health and Environmental Research, on August 12, 1994)

354. L. Klasinc, L. Pasa-Tolic', H. Spiegl, J. V. Knop and S. P. McGlynn, "Long-Range Interactions of Substituents in Steroidal Molecules," *Int. J. Quant. Chem.; Quant. Biol. Symp.* 20, 191 (1993).

The results of semiempirical MNDO calculations with full geometry optimization are reported for carbonyl and hydroxy derivatives of sterane (perhydrocyclopentano-phenanthrene) and perhydrochrysene the substituent(s) being located in ring(s) A and/or D of the parent molecules. Emphasis is placed on the long-range effects of substituents located at the biologically important 3- and 17-position of the steroid skeleton and on the dependence of these effects on the basic structure, location and presence of interpolated localized double bonds which are usually found in steroid hormones. Such long-range effects seem to exert considerable influence on conformation, on activity and particularly on fast intramolecular electron transfer that has been observed recently in steroid solutions.

355. S. P. McGlynn, K. Rupnik, M. N. Varma and L. Klasinc, "Radiation Signatures and Radiation Markers," *Radiation Protection Dosimetry* 52 (1-4), 155 (1994).

The distribution of DNA molecular lesions is defined as the histogram of lesion occurrence probability versus lesion type and is termed a molecular lesion spectrum (MLS). The MLS's for 405nm, 254nm and γ -ray electromagnetic radiations are investigated here, and it is shown that 8-, 5-, 4-, 3- and 2- lesion sets function as very good radiation signatures: that is, MLS's based upon these lesion sets can be used to identify the causal electromagnetic radiation. The approach we have adopted is based on pattern recognition techniques couched in neural network formalism, the patterns being defined as vectors and their uniqueness described as a degree of vector orthogonality. The minimal lesion set for signature of the three radiations is found to consist of two lesions, thymine dimer (d) and locally multiply damaged site (lmds) lesions. This is a surprising finding, and it works only because the d-lesion turns out to be a radiation marker for 254nm radiation and the lmds-lesion to be a radiation marker for γ -rays. Since these findings about signatures and markers are important from safety, insurance and medical aspects, it is well to caution that only three radiations, all electromagnetic, have been investigated here. Work on particulate and other electromagnetic radiations is underway.

356. W. H. Koppenol and L. Klasinc, "Ab Initio Calculations on ONOOH and ONOO⁻, Int. J. Quant. Chem.; Quant. Biol. Symp. 20,1-6 (1993).

The geometry and electronic structure of peroxyntrous acid (O=NOOH) and peroxyntrite ion (O=NOO⁻) were studied at the 6-31G**level. The *cis*-configuration of peroxyntrous acid was found to be more stable by 3.9 kJ/mol than the *trans*-form, whereas peroxyntrite is more stable by 4.6 kJ/mol in the *trans*-form. Calculations of the skew forms, which are as defined by an angle of 90° between the ONO/NOO planes, yield energies larger than those of the most stable forms of the acid or anion by 51.4 and 68.1 kJ/mol, respectively, thus providing an estimate of the gas phase energy barrier. The electronic structure is discussed from the point of view of the reactivities and transformation processes of ONOOH and ONOO⁻.

357. I. Novak, L. Klasinc, B. Kovac, S. P. McGlynn, "Electronic Structure of Haloalkanes: A high Resolution Photoelectron Spectroscopic Study," *J. Mol. Struct.* 297, 383 (1993).

High resolution He I photoelectron spectra (PES) of a number of iodo- and bromoalkanes have been measured. Linear relationships between ionization energies (E_i) and $1/n$ (n =number of carbon atoms in the chain) describe the trends reasonably well if $n=1$ is excluded for dihaloalkanes. This property (i.e., line slopes), when joined with the alternation of halogen lone pair bandwidths within a given spin-orbit doublet, can be used to provide a fully empirical assignment of the four non-bonding orbital ionizations of the dihaloalkanes. The interactions between the halogen lone pair orbitals and the alkane σ -orbitals dominate in those dihaloalkanes for which $n \geq 2$, and the through space interaction is important only for the case $n=1$. Vibrational fine structures are used to infer the existence of hyperconjugative effects.

358. D. Kumar, P. L. Clancy, L. Klasinc and S. P. McGlynn "Laser Optogalvanic Spectrum of Cesium in a Radiofrequency Discharge," *Croat. Chem. Acta*, CCACAA 66, 217 (1993).

The laser optogalvanic (LOG) spectrum of cesium vapor at ~50 mTorr in a low power (≤ 1 W), ~30MHz radiofrequency discharge has been recorded in the range 16,250 to 16,860 cm^{-1} . Members of several Rydberg series ($6p \rightarrow ns$, $6p \rightarrow nd$, $5d \rightarrow np$ and $5d \rightarrow nf$) which terminate on the first ionization limit have been observed. The line broadening of high- n ($n \geq 30$) f- levels in cesium is considerably less than that for xenon. The excessive broadening in xenon is attributed in part to interactions of the Rydberg electron with the open-shell core.

359. D. Kumar, R. R. Zinn, and S. P. McGlynn, "Optogalvanic Transients in a Neon RF Discharge," J. Chem. Phys. 101 3, 1959 (1994).

The time dependence of the optogalvanic signals induced by $1s_j \rightarrow 2p_k$ (Paschen notation) pulsed laser excitations of neon in a low power ~ 30 MHz rf discharge at ~ 5 torr has been investigated. The method of Kumar and McGlynn [Chem. Phys. Lett. 176, 536 (1991)] has been improved and is used to separate the temporal profiles of the optogalvanic signals into two components: one attributable to ionization rate changes and the other to acoustic effects. This separation simplifies the identification of the kinetic processes which produce optogalvanic signals. Selective laser excitation of $2p_k$ states, ones which possess quite different decay branching ratios to the metastable and non-metastable $1s_j$ states, reveals time dependencies due to unique perturbations of specific $1s_j$ populations. No dimer-mediated nor, indeed, any effects associable with $2p_k$ state populations contribute to the profiles. Competitive processes which increase or decrease the ionization rates are identified at $t \geq 1\mu s$. The extensive broadening of the acoustic and ionization components is caused by radiation trapping of $1s_2 \rightarrow 1S_0$ and $1s_4 \rightarrow 1S_0$ photons.

360. L. Klasinc, L. Pasa-Tolic, D. Vikić-Topić, J. Knop and S. P. McGlynn, "Long Range Electronic Interaction in Androstenediones," in revision.

We have become interested in electronic structure of steroids for some time. In particular, the possibility of long-range interactions between substituents located at both ends of the basic skeleton, interactions too weak to be observed in our photoelectron (PE) spectra but suggested by other methods (e.g. fast intramolecular electron transfer), have remained intriguing.

362. A. Srivastava, J. Cherukuri, S. P. McGlynn and D. Kumar, "Hydrogen Gas Sensing with Silicon Microsensors and the Monitoring Microchip Design," Proceedings of the 1994 Federal Environmental Restoration III & Waste Minimization II Conference and Exhibition, Hazardous Materials and Control Resource Institute Press, Rockville, MD, 1994, p.p. 1520-1527.

The economy of the State of Louisiana is largely dependent on the agricultural and petrochemical industrial sectors. Most petrochemical industries in the United States are in fact located within the State of Louisiana. The environmental pollution by the chemical fumes has reached crisis proportions. Therefore, there is an urgent need for highly sensitive sensors for explosive as well as toxic gases. Indeed, hydrogen has been identified as a leading air-contaminant because of its extensive commercial and domestic use. Thus, a hydrogen gas sensor with high selectivity and sensitivity will find extensive use in the control of H₂ gas leakage into the environment.

It is well established that palladium adsorbs, dissolves, and catalytically dissociates hydrogen, giving rise to reversible changes in bulk and surface properties of the various hydrogen-induced changes in palladium. The significant lowering of the work-function (by upto 1eV) results in a remarkable change in the performance of palladium gate MOSFETS, MOS capacitors and Schottky barrier diodes. In the present work, we report the work being done on the development of hydrogen sensitive palladium-oxide-silicon (Pd-SiO₂-Si) sensors, including design of readout electronics using silicon integrated circuit technology.

At present we are working on the design of an environmental chamber to test hydrogen sensors with readout electronics under simulate chemical environments. The results will be reported at the conference.

363. K. Rupnik, L. Klasinc, M. N. Varma, J. Battista and S. P. McGlynn, "Lesion Spectra: Radiation Signatures and Biological Gateways," J. Chem. Information and Computer Sciences 34, 1054 (1994).

We have proposed and, in part, justified that the distribution (spectrum) of molecular lesions generated in DNA by exposure to a particular radiation is a characteristic of (i.e, is a signature for) the causal radiation. The research involves construction, for both *in vivo* and *in vitro* systems, of molecular lesion spectra for a variety of radiations, particulate and electromagnetic; assay for a variety of lesions (i.e., breaks, adducts, multiple locally-damaged sites, etc.); and a neural network processing of the lesion distributions (i.e., patterns) to establish distinctiveness (i. e., orthogonality) of lesion spectra.

The radiation signature possesses a number of advantages, namely (1), high fidelity; (2) a persistence time at least ten orders of magnitude greater than track structures; and (3), a space-time cellular position which is an ideal gateway to ultimate biological (dys)function, such as mutagenesis or carcinogenesis. It is important to note that molecular lesion spectra, as defined, occur after the physics and chemistry is completed and at the point where biology onsets.

Radiation signatures are located, in a decadic temporal sense, halfway between radiation track and carcinogenesis. Thus, previous inability to correlate carcinogenesis with track structures should be reinvestigated, because the correlative length from malignancy to the molecular lesion spectrum is one half of that to the track, in both temporal and spatial senses.

Signature fidelity will be enhanced by discovery of new lesion sets, and new assay procedures for old assay sets. Fidelity may also be a function of fluence and fluence delivery rate of the radiation. These four topics will be discussed.

364. L. Klasinc, A. Mannschreck, M. Mintas and S. P. McGlynn, "Photoelectron Spectra of Alkyl Diaziridines," J. Chem. Soc. Perkin Trans. II, **2**, 2059 (1994).

He I photoelectron (PES) spectra were obtained for six trisubstituted and three tetrasubstituted diaziridines: 1,3,3-trimethyldiaziridine (1), 1-isopropyl-3,3-dimethyldiaziridine (2), 1-methyl-3,3-cyclohexyldenediaziridine (3), 1-benzyl-3,3-dimethyldiaziridine (4), 1,3-dimethyl-3-benzilyldiaziridine (5), 1-methyl-3,3-dibenzilyldiaziridine (6), tetramethyldiaziridine (7 or Me-1), 1-benzyl-2,3,3-trimethyldiaziridine (8 or Me-4) and 1,2,3-trimethyl-3-benzilyldiaziridine (9 or Me-5). Analysis provided information about the outer valence electronic structures and geometric conformations. The observed splitting of the n^+ and n^- ionization events indicates that all compounds exist in *trans* configurations; the lone pair - lone pair dihedral angle is $100^\circ \leq \theta \leq 110^\circ$; and θ decreases with substitution. The center of gravity of the two lone-pair ionizations remains fairly constant at $E = 9.5$ (9.15)eV for trialkyl (tetraalkyl) substitution. N-alkylation has a much greater effect on the electronic structure of diaziridine than does C-alkylation. The additional phenyl group of benzyl substituents and the *p*-methoxyphenyl group of 1-(*p*-methoxybenzyl)-3,3-dimethyldiaziridine (10) exert negligible influences. The 1,3-trisubstituted diaziridine (10) decomposes thermally to form NH_3 , a reaction described previously only for 3,3-dialkyl- and 1,2,3-trialkyl-diaziridines.

365. K. Rupnik, U. Asaf and S. P. McGlynn, "Pressure Shifts and Electron Scattering in Atomic and Molecular Gases," Proceedings of VIIth International Symposium on Gaseous Dielectrics, 87, Plenum Publishing Co.; NY; 1994.

Photoabsorption or photoionization spectra of CH_3I are discussed as a function of perturber pressure for 11 different binary gas mixtures consisting of CH_3I and each one of eleven different gaseous perturbers. Five of the perturbers were rare gases and six were non-dipolar molecules. The energy shifts of CH_3I Rydberg states become independent of n , the principal quantum number, for $n \geq 10$. The energy shifts for $n \geq 10$ vary in a linear fashion with perturber number density. The electron scattering lengths for the perturbers are extracted from the shifts using Fermi theory in which the polarization term is that of Alekseev and Sobel'man. These scattering lengths are compared with those from swarm and time-of-flight experiments. It is found that the uncorrected shift scattering lengths correspond to the zero energy or near-zero energy scattering lengths obtained from extrapolated swarm and time-of-flight data. It is found that plots of scattering length versus polarizability α ($\bar{\alpha}$ for molecules) define two linearities, one for the rare gases and one for molecules, CO_2 being an exception to the latter linearity (presumably because of its large quadrupole moment). For a given polarizability, it is also found that molecules exhibit a larger scattering length than the rare gases. These results are discussed and consequences for scattering cross-sections are elaborated.

366. D. Kumar, R. R. Zinn, T. D. Armstrong, S. P. McGlynn, "The Optogalvanic Effect as a Probe of Plasma Processes," J. Phy. Chem. (M.F.A. El-Sayed Festschrift), April, 1995.

The time dependence of the optogalvanic signals induced by $1s_j \rightarrow 2p_k$ (Paschen notation) pulsed laser excitations of neon in a low power ~ 30 MHz rf discharge at ~ 5 torr has been investigated. The method of Kumar and McGlynn [Chem. Phys. Lett. 176, 536 (1991)] has been improved and is used to separate the temporal profiles of the optogalvanic signals into two components: one attributable to ionization rate changes and the other to acoustic effects. This separation simplifies the identification of the kinetic processes which produce optogalvanic signals. Selective laser excitation of $2p_k$ states, ones which possess quite different decay branching ratios to the metastable and non-metastable $1s_j$ states, reveals time dependencies due to unique perturbations of specific $1s_j$ populations. No dimer-mediated nor, indeed, any effects associable with $2p_k$ state populations contribute to the profiles. Competitive processes which increase or decrease the ionization rates are identified at $t \geq 1\mu s$. The extensive broadening of the acoustic and ionization components is caused by radiation trapping of $1s_2 \rightarrow 1S_0$ and $1s_4 \rightarrow 1S_0$ photons.

368. FINAL REPORT (1986 - 95) and Three Year Comprehensive Report (1992 - 95) to the U. S. Department of Energy on Contract DE-FG05-87ER60503 entitled "A Physico-Chemical Study of Some Areas of Fundamental Significance to Biophysics." (This Report)

COMMENTS

The bibliography of titles consists of 84 titles. These may be divided as follows:

	1986 - 89	1989 - 92	1992 - 95	TOTAL
Articles	28	32	12	72
Patents	0	0	1	1
DOE Reports	4	4	3	11
TOTAL	32	36	16	84

Disregarding Dissertations and Reports, the average cost per publication was ~ \$17,000.00. This number takes no account of the extent to which grant expenditures contributed to the training and education of the persons employed on DOE monies.

The above numbers do not take into account the extent to which grant expenditures contributed to the caliber of the Undergraduate Programs in this Department. This contribution was so pervasive, yet so ill-defined, that it cannot be categorized. However, such effects did occur and they were important.

B. SYMPOSIA ATTENDED

1992 - 1995

4. K. Rupnik attended a two day DOE/EPSCOR workshop held at Tulane University, New Orleans, Louisiana, March 21-22, 1992.
-- -Contributed work
1. S. P. McGlynn, attendee at the Von Humbolt Foundation Luncheon Meeting, New Orleans, Louisiana, March 31, 1992.
-- -Invited participant
2. S. P. McGlynn attended and participated in the awards ceremony at the 25th DOE Radiological and Chemical Physics Contractor's Meeting, Wakulla Springs, Florida, June 8-10, 1992.
-- -Invited participant
3. S. P. McGlynn and D. Kumar, "Laser Optogalvanic (LOG) Effect in a Capacitively Coupled Plasma," 14th IUPAC Symposium Photochemistry, K. U. Leuven, Belgium, July 19-25, 1992.
-- -Invited Paper
7. D. Kumar, R. R. Zinn and S. P. McGlynn, "Optogalvanic Effect as a Probe for Plasma Processes," 45th Annual Gaseous Electronics Conference, Boston, October 27 - 30, 1992.
-- -Contributed Paper
8. D. Kumar, R. R. Zinn and S. P. McGlynn, "Temporal and Spectral Characteristics of Laser Optogalvanic Signals in an Argon RF Discharge," 45th Annual Gaseous Electronics Conference, Boston, October 27 - 30, 1992.
-- -Contributed Paper
5. S. P. McGlynn and K. Rupnik, "Lesion Spectra: Radiation Signature and Biological Gateway," at 11th Symposium on Microdosimetry, Gatlinburg, Tennessee, September, 3-17, 1993.
-- -Invited Paper
6. S. P. McGlynn and K. Rupnik attended a DOE/CEC workshop organized by the Office of Health and Environmental Research of the U. S. Department of Energy and the Radiation Protection Program of the Commission of European Committees, Gatlinburg, Tennessee, September, 18th, 1993.
9. S. P. McGlynn, Uri Asaf, K. Rupnik, G. Reisfeld and S. Felps, "Scattering of Rydberg Electrons in Multi Component Systems," Big Muddy Quantum Fest II Symposium, Louisiana State University, Baton Rouge, Louisiana, February 13th, 1993.
-- -Invited Lecture

10. S. P. McGlynn, K. Rupnik, M. Varma and L. Klasinc, "Radiation Signatures and Markers," Sanibel Symposium on Atomic, Molecular and Condensed Matter Theory in St. Augustine, Florida, March 13-20, 1993.
S. P. McGlynn was a symposia leader.
- - - Invited Lecture

11. L. Klasinc, L. Pasa-Tolic, H. Spiegl, J. V. Knop and S. P. McGlynn, "Long-Range Interactions of Substituents in Steroidal Molecules", Sanibel Symposium on Atomic, Molecular and Condensed Matter Theory, St. Augustine, Florida, March 13-20, 1993. Dr. S. P. McGlynn was also a discussion leader at this conference.
- - -Invited Paper
- - -Discussion Leader

12. Sean P. McGlynn, "Environmental Science and Environmental Law", the Prosecuting Environmental Crimes Seminar, Louisiana State Police Training Academy, Baton Rouge, LA, March, 1993.
- - -Invited Lecture

13. S. P. McGlynn, K. Rupnik, N. N. Varma and L. Klasinc, "Radiation Signatures and Radiation Markers, " International Symposium on Environmental UV Radiation Health Effects, Bundesamt fur Strahlenschutz, Munich, Germany, May, 1993.
- - -Poster

14. K. Rupnik, Seminar on *Neural Networks* Computing Applications in Pittsburgh, PA on May 22-27, 1993.
- - -Contributed work

15. S. P. McGlynn, K. Rupnik, M. Varma and L. Klasinc, " Radiation Signatures and Markers," *Neural Networks* Computing Applications, Pittsburgh, PA, May 22-27, 1993.
- - -Contributed work

16. S. P. McGlynn, "Scattering of Rydberg Electrons," 1993 DOE Contractor's meeting on Fundamental Physical Processes and Interactions in Condensed Phase: Implications for Understanding Mechanisms of Biological Action, Argonne National Laboratory, Chicago, Illinois, June 1-2, 1993.
- - -Invited Lecture

17. L. Klasinc, S. P. McGlynn, K. Rupnik and M. N. Varma, "Lesion Spectra: Radiation Signatures and Biological Gateway," Math/Chem/Comp '93, Rovinj, Croatia, June 12, 1993.
- - -Invited Lecture

18. S. P. McGlynn, "Scattering of Rydberg Electrons", 1993 International Society of Theoretical Chemical Physics, Girona, Spain, June 1993.
- - -Invited Lecture

- -Session Chairman
19. D. Kumar and R. Zinn attended a National Instruments Workshop in New Orleans, LA. September 14, 1993.
- Attendance
20. D. Kumar, R. Zinn and S. P. McGlynn, "The Optogalvanic Effect in Radiofrequency Plasmas," El-Sayed Symposium, UCLA, November 5-6, 1993.
- -Invited Lecture
21. D. Kumar, "The Optogalvanic Effect," presented under the auspices of "The Newtonian Program," K. M. College, University of Delhi, January 25-28, 1994
- Invited Lecture
22. D. Kumar, L. Klasinc and S. P. McGlynn, "Spectroscopic Applications of Optogalvanic Effect," Microwave Spectroscopy Laboratory, Department of Physics, University of Delhi, February 14, 1994.
- Invited Lecture
23. D. Kumar, R. R. Zinn, and S. P. McGlynn, "Optogalvanic Study of Some Plasma Processes," Microwave Spectroscopy Laboratory, Department of Physics, University of Delhi, March 2, 1994.
- Invited Lecture
24. D. Kumar, R. R. Zinn and S. P. McGlynn, "Optogalvanic Effect in a Capacitively Coupled RF Plasma," Department of Electronic Science, University of Delhi-South Campus, March 8, 1994.
- Invited Lecture
25. K. Rupnik, U. Asaf and S. P. McGlynn, "Pressure Shifts and Electron Scattering in Atomic and Molecular Gases," VIIth International Symposium on Gaseous Dielectrics, Knoxville, Tennessee, April 24-28, 1994.
- Submitted paper
26. A. Srivastava, J. Cherukuri, S. P. McGlynn and D. Kumar, "Hydrogen Gas Sensing with Silicon Microprocessors and the Monitoring Microchip Design," 1994 Federal Environmental Restoration III and Waste Minimization II Conference and Exhibition, New Orleans, April 27-29, 1994.
- Submitted Paper
27. S. P. McGlynn and K. Rupnik, "Lesion Spectra: Radiation Signatures and Biological Gateway," XVth IUPAC Symposium on Photochemistry, Prague, Czechia, July 17-24, 1994.
- -Submitted Paper

28. S. P. McGlynn and K. Rupnik, "Lesion Spectra: Radiation Signatures and Biological Gateway," 10th International Conference on Photochemical Conversion and Storage of Solar Energy (IPS-10), Interlaken, Switzerland, July 24-29, 1994.

- - - Submitted Paper

III. SCIENTIFIC REPORT

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A. RADIATION SIGNATURES

A major goal of biophysical modelling is to relate physical events such as ionization, excitation, etc. to the production of radiation carcinogenesis. All types of radiations are of concern since each one is potentially carcinogenic. A description of the physical events is provided by track or ion distribution structures. The track structure is determined by radiation quality, and it can be considered to be the "physical signature" of the radiation. Unfortunately, the uniqueness characteristics of these signature are dissipated in biological systems in $\sim 10^{-9}$ s. Nonetheless, it is our contention that this physical disturbance of the biological system eventuates later, at 10^0 - 10^2 s or greater, in molecular lesion spectra, which we dub the "lesion signature" or "radiation signature" and which also characterize the causal radiation.

The best way to understand the radiation signature paradigm is by a representation of a spatio-temporal path from a normal , just insulted cell to a fully transformed carcinogenic cell. Much radiation physics work has been concentrated on the track structures at the $\leq 10^{-11}$ s level and ion distribution at the 10^{-7} s level. Unfortunately, the observed tracks are too far removed, in a spatio-temporal sense, from clinical manifestations of cancer. Clinical manifestations of cancer may take more than 20 years to develop, which places any possible radiation signature based on malignancy or mutation type at 10^8 to 10^9 s . Thus it becomes necessary to follow the radiation track through a whole host of chemical, biochemical, biological repair and emergent cellular happenings before its manifestation as cancer. The radiation signature paradigm is aimed at finding an intermediate point on the spatio-temporal path. We suggest that the most appropriate place to seek such a "signature" is at the junction of the chemical and biological regimes. If such a signature exists at a point which provides identification capability for the causal radiation, it should

also serve as a gateway point for the bioprocessing which ultimately ends in malignancy. The correlation of the two ends of the spatio-temporal path might then be significantly facilitated by relating both ends to the midway point.

It is our contention that such a signature is provided by the spectrum (or histogram) of DNA molecular lesions. These signatures have the advantages of (1) high fidelity, (2) persistence times some ten orders of magnitude greater than track structures, and (3) a space-time cellular position which is approximately half way between initial insult and ultimate biological dysfunction.

Molecular lesion spectra contain information about the mechanism of radiation damage at the molecular level. That is, the types of lesions produced by a given radiation surely reflect the variety of different physico-chemical-biological processes that take place after radiation insult. In fact, some lesions may be a result of some particular radiation: for example, double strand breaks and multiply locally damaged sites that are mainly (but not solely) associated with high density radiations.

In this work, in order to clarify terminology in radiation signature research we introduce certain definitions:

- (i) Molecular Lesion: A molecular lesion in DNA is defined differently in different fields. For example, definitions at the organismal, cellular and sub-cellular levels vary widely. We shall adopt an operational definition, and take a molecular lesion in DNA to be any damage, whether constitutional or conformational, that can be measured reproducibly by different investigators. It is implied, then, that a good assay method exists for the lesion. It is also implied, for now anyway, that irradiations and measurements be done in the vicinity of 0°C since, otherwise, differential repair rates might vitiate reproducibility.
- (ii) Sub-lesion: We suppose sub-lesions to be post-radiative damage usually consisting of loci at which energy has been deposited or ionizations have occurred. We suppose them to lie in the time domain in which physics has

terminated and chemistry (but not biology) has initiated. The important point is that they are unstable and that processing of them may produce more than one type of molecular lesion. That is, branching may take place.

(iii) Molecular Lesion Spectra: We define a molecular lesion spectrum (MLS) as a plot of lesion frequency (or probability), usually in bar graph form, versus lesion type (categorized, for example, by indices 1,2,3,...). The sum of bars is normalized to 100. The set of lesions should be complete; that is, every lesion, regardless of how low its frequency, should be represented. Reality, however, intrudes: we have neither detected all possible lesions produced by a particular radiation nor learned to perform reliable assay for the limited set that has been detected. Thus, we must make do with a constrained definition which replaces "complete set" with "maximal detected set that can be reliably assayed".

(iv) Radiation Signature: The term radiation signature implies the existence of a set of post-irradiation properties of DNA that can be used to identify the radiation which caused them. The search for such a property set is an urgent desideratum of the radiation safety, insurance and environmental fields. It is our contention that molecular lesion spectra provide such a signature. Any individual possesses a variety of signatures: the "name" signature is used to validate a contract; the bank card microchip to obtain money from an automatic teller; the metallized parking card to gain entry to an automobile lot; or a voice recognition system to open a pension door. In any event, signature and purpose must be related. The purpose of this work is to define a radiation signature in DNA which not only serves as an identifier of the radiation which produced the signature but also functions as an appropriate gateway to the cellular processings which ultimately result in cell carcinogenesis. We contend that molecular lesion spectra serve as such a nexus.

(v) The Spatio-Temporal Pathway: There is a path (perhaps many paths) from normal to carcinogenic cell. The point of reference for a signature based on track

structure is $\leq 10^{-10}$ s, at the lower left of the curve. The point of reference for a signature based on carcinogenesis (i. e., on medicine) is years. These two points are too far removed in both organismal (or cellular) space and in time to permit other than an allusive correlation of one with the other. It is our contention that an intermediate point provides signature for one end (i. e., radiation) and gateway to the other (i. e., cancer), and permits a real two-fold correlation which, in a single end-to-end correlation, might forever remain suppositional. We contend that molecular lesion spectra fit those requirements.

In this work, which is part of a long-term radiation signature study, the focus is on molecular lesion spectra as radiation identifiers. The objects of the research are: (1) to demonstrate that MLS can serve as radiation signatures for various radiations and to study the "sensitivity" and precision of these signatures; (2) to expand the data bases for such research; and (3) to develop tools for feature recognition and extraction. We have shown that these goals are realistic and we have made much progress with respect to items 1 & 3. However, those goals that involve any relationship between signatures and carcinogenesis, if any, are still in process of formulation. Indeed, we intend, at least for now, to keep the accent solely on molecular lesion spectra as signatures of a causative radiation.

The experimental data bases for the great majority of radiations (i. e., item 2) are very fragmented, so much so that a systematic study of radiation signatures is largely inhibited. The situation would improve enormously if more and better data were available. However, the advent of new experimental techniques, such as the polymerase chain reaction or laser technology promise much in unraveling the difference between high and low intensity radiation effects, in generating new data on the intensity-dependent photochemistry of DNA, in elucidating the effects of biphotonic processes, etc. In sum, the systematic elucidation of lesion types and frequencies, with proper regard paid to dosimetry

(e.g., energy absorbed, cell concentration of insult, etc.) and biology (e.g., *in vitro*, *in vivo*, cell cycle stage, etc.), is a massive task that must be engaged in order to put the concept of spectrum as signature on a firm footing.

The concept of a signature (i.e., feature recognition) implies the existence of a set of object characteristics that can discriminate between different objects and /or classes of objects. A signature should possess such characteristics as repeatability (i.e., confidence) and ease of recognition (i.e., ease of discrimination from threshold "noise"). However, since the characteristics of a signature need not always be explicitly circumscribed by rules, some element of adaptability in the models used for feature extraction, particularly when the experimental data are collected under conditions that are exceedingly difficult to standardize, appears to be mandatory. For that reason, we have also introduced methods for the extraction of radiation signatures from diverse data sets: that is, an adaptive lesion model , which originates in parallel distributed processing (PDP) methods and which is related to adaptive nonlinear (neural) networks (ANN) and/or genetic algorithms (GA). It might be argued that that the use of feature (or pattern) recognition techniques in the present instance is redundant in the cases where the MLS are visually different. One answer is that visual differentiation is a qualitative sorting, and that one should make the sorting quantitative. To that end, each of the MLS is viewed as a "vector" in a space spanned by the MLS (or patterns), and the distinctiveness of patterns is quantified as the degree of orthogonality of the representative vectors. A second, and more relevant answer is that feature recognition techniques become necessary when one deals with data bases that are less than optimal, when one queries the minimum number of lesions adequate for a signature,

or when one pursues any presumptive connection of a causal radiation and clinical outcome.

There are a variety of network architectures available. The counter-propagating network used here happens to be particularly advantageous for handling data sets that are either restricted in the number of lesions for which frequency data are available or of mixed quality because of lesion assay methods. Other network architectures, such as the backpropagating network, are also under study. The results of this study, indicate that the radiation signature approach can indeed identify the causative radiation and also provide valuable information on the role that specific lesion types play in the radiation signature. As a result, we expect to be able to limit molecular lesion spectra to a "minimum set" of lesions and to define those lesions which are the crucial identifiers for a given radiation.

THE SPECTRUM OF MOLECULAR LESIONS: AN EXAMPLE

Somewhat complete assays exist for only three different electromagnetic radiations, namely

Radiation	Energy	Source of data
VIS (limit of UV-A)	405 nm	Peak and Peak, (1987)
UV-C	254 nm	Setlow and Setlow, (1972)
γ -RAY	^{137}Cs (~0.6 MeV) ^{60}Co (~1.1 MeV)	Ward, (1988)

The molecular lesion spectra (or histograms) for these three radiations have been constructed as bar graphs of lesion frequency versus lesion type. The bar sum in any one graph is arbitrarily normalized to 100.

The molecular lesions assayed in the three data sets are

Index	Name	Abbreviation
1	cytidine hydrate	ch
2	thymine dimer	d
3	pyrimidine adduct	pa
4	DNA-protein cross-link	dpc
5	DNA-DNA cross-link	ddc
6	single strand break	ssb
7	double strand break	dsb
8	locally multiply damaged sites	lmbs

Indeed, these eight lesions are those for which assay data are most generally available.

The three data sets refer to the DNA of various cells and of different biological entities. All data refer to the number of lesions produced by an F37 (D37) radiation fluence. Intercomparison of the three data sets must be accompanied with certain reservations:

- - Peak and Peak studied DNA lesions in mammalian cells at 405 nm . The F37 fluence was equivalent to $\sim 4\text{MJ}/\text{m}^2$. The cell line was a cultured P3 teratocarcinoma strain.

- - The Setlow and Setlow data for 254nm refer to vegetative mammalian cells at room temperature, again at an F37 fluence which , in this case , corresponded to $10\text{J}/\text{m}^2$.

- - The Ward data also refer to mammalian cells at an F37 dose. However, in this instance of ionizing radiation, the kill efficiency was much higher than for either 405 or 254nm. That is, in a relative sense, the γ -rays produced low levels of DNA damage. The high mortality level is apparently attributable to the ability of γ -rays to produce damage in which more than one moiety in a localized region of the DNA suffers damage, the so-called "locally multiply-damaged sites" (LMDS). It is important to point out that the LMDS category, index 8,

encompasses a large variety of lesions, many of them categorizable under indices 1 through 7.

The defects then, are: (i), the supposition that F37 is an appropriate standard for radiation dosage; (ii), the use of different cell lines under different experimental conditions, both physical and biological; (iii), the lack of fluence considerations, and a disregard for the manner in which lesion interactions relate to fluence and fluence rate on the one hand and mortality and lesion production on the other.

The 405nm distribution is quite similar to the γ -ray distributions if the lmds lesion category, category 8, of the latter is disregarded; and both the 405nm and γ -ray distributions are markedly different from the 254nm spectrum.

According to radiation quality considerations, on the other hand, it is the 405 and 254nm distributions which should exhibit similarity, and both should be quite different from the γ -ray distribution. It is clear, then, that radiation quality does not provide an apt classification of DNA damage at the molecular level, and that the nature and loci of the energy deposition events is the significant descriptor. In specific, the 254nm distribution reflects direct absorption by, and deposition in the DNA bases, events which are totally impossible at 405nm and statistically improbable at $\sim 1\text{MeV}$; the similarity of the 405nm and γ -ray spectra, the lmds category of the latter excepted, is probably a consequence of energy deposition in the aqueous environment, directly for γ -rays and through the intermediacy of some third-party-chromophore for 405nm.

The construction of a portfolio of trustworthy radiation signatures is inseparable from the existence of reliable, quantitative data sets of molecular lesions. The imposition of the reliability consideration probably implies that repair processes be inoperable. That is, irradiation must be made at temperature near 0°C in order to inhibit repair. Enzymatic repair rates are functions of lesion type and, hence, the relative concentrations of lesions types may change

with post-irradiation time. Should that be the case, the fidelity of radiation signatures would be diminished.

Apart from a subcategorization of existing lesion sets (e.g., the dimer set), the signature fidelity would also be enhanced by the discovery and assay of new lesion sets. In view of the importance of the $\text{OH}\cdot$ radical and other oxygen-hydrogen entities, it is surprising, for example, that nitrogenous species are not implicated in the indirect production of molecular lesions. It is known that irradiation of protein produces generous amounts of $\text{NH}_2\cdot$, a radical isoelectronic with and no less reactive than $\text{OH}\cdot$, yet lesions produced by $\text{NH}_2\cdot$ seem not to occur or, at least, not to have been detected.

At this time, there is no unique, generally acceptable standard for biological dose. The data used in this work are based on a biological normalization related to the "efficiency of killing", namely the dose (D37) or fluence (F37) which permits a survivor fraction of 37%. This type of normalization presents at least two difficulties. Firstly, it appears that the ratio of lesion production to cell mortality may be a function of the radiation. For example, if 405nm is, as it appears to be, inefficient in killing, a D37 dose at 405nm implies measurement of the lesion production at very high fluence. That is (D37/F37) for the γ -ray region may well be more than 10^6 times larger than (D37/F37) for the 405nm region. This question, in turn, generates the second difficulty: if the quadratic component in the linear-quadratic dependence of effect on dose is dominant, or merely important, the distribution of lesion intensity in the lesion spectra will vary with dose (and fluence), and the concept of a signature will run into difficulty. Thus, it is imperative that the effects of fluence on lesion distribution be investigated in detail. If it is found that lesion distributions are dose dependent, this will require an extension of the concept of a signature promulgated here to one which acquires multidimensionality in the sense that, for electromagnetic radiation of wavelength λ , the signature $S = S(F)$ will have

to be replaced by $S \equiv S(\lambda, F)$. In terms of the adaptive PDP approach advocated here, such a change poses no problem. In fact, it should produce better signature discrimination characteristics. However, it surely would increase the experimental workload, and reasons of economy alone could cause the signature concept, even if fully validated in a multidimensional sense, to lose utility.

B. ELECTRONIC STRUCTURE

1. Steroids

Investigations of the electronic structure of steroids were continued experimentally (PES, NMR, FTMS, Synthesis of model compounds) and theoretically (SCF, MNDO, MM2, *ab initio* STO-3G and 3-21G calculations), the emphasis being the determination of the electronic distributions within the frontier ("ribbon-like") orbitals of the steroid hydrocarbon androstane and, the role of these orbitals in coupling substituents, particularly those in the 3-and/or 11- and/or 16- and/or 17- positions. The 3-, 11- and 17- positions are those which are usually found to be substituted in biologically-active steroids. The theoretical and experimental evidences suggest that the coupling between substituents in steroidal systems is provided by interactions with the frontier orbitals of the intervening molecular fragments. Efficient intramolecular electron transfer has been found for 3,16-disubstituted androstanes. It follows that the "ribbon-like" orbitals of saturated polycyclic hydrocarbons can "conduct" electrons over ten or even more single CC bonds.

According to its photoelectron (PE) spectrum 5 α -androstane has two characteristic low energy ionizations of 9.21 eV and 9.49 eV which, assuming Koopmans' theorem, correspond to the release of electrons from the two highest occupied MO's of the molecule. These energies, both absolutely and relatively, are in excellent accord with the STO-3G results.

The 3-21G calculations are still underway because of the extensive optimization procedures that are required. Qualitative arguments indicate that these two topmost orbitals contain C2p AO's aligned somewhat in the molecular plane. Indeed, MNDO calculation yields a HOMO with constituent C2p AO's aligned along the short molecular axis (T-type MO) and a SHOMO in which the

C2p AO's are aligned along the long molecular axis (L-type MO). It is believed that such MO's, best described as a mixture of σ_{CC} and π_{CH_2} orbitals and colloquially termed "ribbon orbitals," are essential for the transmission of electronic effects in large saturated polycyclic hydrocarbon molecules.

According to MNDO calculations for the androstanones, the T-type MO interacts with 3-substituents, while the L-type MO interacts with 17-substituents, the same exclusivity being retained for 3,17-disubstitution. The 16-substituent, however, interacts with both types of MO and, as a consequence, so also do dual substituents, one each in the 3 and 16 positions. This behavior leads one to assume that, in 3,16-disubstitution, long range electronic interaction should be heavily promoted. In the STO-3G calculation the order of the two orbitals is reversed relative to the MNDO situation: that is, the HOMO is now L-type and the SHOMO is T-type. The electron distribution of these L-and T-type MO's is somewhat lumped on the inner B and C ring carbons according to MNDO results, but is more evenly distributed over all four rings in the STO-3G calculation. In particular, the electron density at C3 of the L-type HOMO and C16 of the T-type SHOMO is considerably higher in STO-3G than in MNDO. Thus, the STO-3G calculations suggest ribbon-like MO's that are better suited for the transmission of electronic effects. They also suggest that such transmissions will be particularly effective in the case of 3,16-disubstitution. The energy inversion of L-and T-type MO's that occurs in the two computations is not really discriminatory because of the near accidental degeneracy of these ribbon-like MO's ($\Delta_{MNDO} = 0.117\text{eV}$ and $\Delta_{STO-3G} = -0.154\text{eV}$). The salient point is that the STO-3G computation both validates and enhances the concept of ribbon-like MO's for both the SHOMO and HOMO of 5 α -androsterane and, by extension, for steroids generally.

2. Vitamins

This work continues the study of solid-state binding energy shifts of inner-shell levels in biologically-important molecules. In these processes, energy is deposited in volumes of the order of nanometers³, and the specific atomic characteristics, which are dependent on the atomic environment, may be elucidated. Indeed, these processes serve as very precise probes of energy transfer and deposition. As a result, we are able to probe the positions of potentially sensitive sites in biomolecular structures exposed to radiation insult. In this work, the inner shell levels of ascorbic acid (AA) and some related model compounds were examined. The intramolecular and extramolecular electronic structures and electronic redistributions occurring during the process of radiation insult were investigated. *Ab initio* and semiempirical (SCC-MO) models were used to interpret the observed phenomena.

We plan to continue the present study of binding energy shifts in the X-ray energy region. However, we will now focus on radiation-induced damage in DNA, which fits well with our concerns in the radiation signature field and in the valence photoelectron spectroscopy of the DNA bases.

The major goal is the development of biophysical/biochemical models of radiation damage in DNA. The photoelectron spectroscopic data will be used to test the assumptions of current models of biophysical/biochemical mechanisms of radiation damage. For example, we believe that theoretical research in this area can model or distinguish between models of the mechanisms of sub-lesion to lesion branching and lesion-lesion interactions.

Following Siegbahn's development of ESCA, we were among the first to develop and apply an effective computational technique to the study of X-ray induced electronic processes (ionization, excitation, Auger, etc.,) in biologically-important molecules. However, the whole area needs reinvestigation. It is

expected that the use of synchrotron radiation and VUV lasers the last of which are still being developed, could add much to this area.

In sum, the present theoretical work and the potential for more precise experimental data suggest that we have opened up a very fertile, very important area.

3. General

Much of the attraction of photoelectron spectroscopy (PES), in its early years at least, was vested in the belief that one of the most basic concepts of modern chemistry, namely the orbital concept, would be interpretively sufficient and, further, that this belief was experimentally vindicated by the existing PES data. Now, after a quarter of a century, it is clear that PES has outgrown this convenient, but naive expectation, that the whole area has become much less transparent and quite multilayered, and that a particular interpretive mode will often be determined by the viewpoint, intention and purpose of the modern investigator. None the less, while the "now" investigator tends to move away centrifugally from the familiar picture of photoejection of electrons from orbitals and photo-creation of holes in these orbital levels, and while he may, for example, present his story as time-dependent scattering process, he and/or the users of his results will invariably refer the conclusion back to the orbital concept because of the simplicity and utility which this referral confers. Indeed, if the orbital concept were to lose such utility vis-a-vis PES data, it is quite sure that the PES technique would lose its somewhat special status and become no more than another physical method for the investigation of matter.

In the work performed during this 3-year period we have used the orbital interpretive model to combine PES experimental results with quantum chemical calculations. We have elucidated the electronic structure of numerous biologically active or otherwise important molecules: nitroethene, p-quinones, semiquinones, aromatic ketones, thiooxamides, numerous lignin model compounds, halogenofurans and methyl pseudohalides. We have been particularly interested in the assignment of lone-pair ionizations, which, because of a lack of HeII/HeI intensity ratios and sufficient spectral resolution have been

often incorrectly assigned in previous works. The lone pair electrons play a crucial role in determining the properties of biologically active molecules.

A continuation of work along these lines on biologically active molecules is important for a number of reasons:

- (i) It provides chemists and biologists an interpretive mode that is a part of their existing theoretical armamentarium.
- (ii) Increased computer power brings high quality *ab initio* methods more and more into the range of big biomolecules. In addition many of the existing semiempirical many- and one-electron-methods have been specifically parametrized for PES, and they provide a convenient, first-run interpretive approach that can be refined using various correlative techniques.
- (iii) It is a technique which, when wedded to experience, is usually pretty much on target relative to ion-state assignments.

C. LASER OPTOGALVANIC EFFECT

The laser optogalvanic (LOG) technique is an extremely versatile and sensitive detection/spectroscopic tool. It has found important applications in such diverse areas as combustion diagnostics, plasma studies, atomic and molecular spectroscopy, gas laser stabilization, environmental monitoring, etc. Despite these applications, the exact mechanism(s) for the generation of LOG signals were not clearly understood. Obviously, full exploitation of this technique requires a better understanding of these mechanisms.

The LOG effect is the change of electrical impedance of a plasma produced by resonant absorption of laser radiation by a plasma moiety. This effect was discovered by Penning in 1928. However, the technique remained dormant until after the development of tunable dye-lasers and gained prominence in early eighties.

Our initial objective in the LOG area was to understand the mechanisms involved in the generation of LOG signals, to find the optimum experimental configuration for a particular application, and to develop it as a sensitive analytic and spectroscopic tool. We discovered rather rapidly that the optogalvanic effect was not properly understood, and that the comprehension of the basic physics underlying the phenomenon was in part wrong and/or incomplete. Thus, we had to devote ourselves to extensive investigations into the characteristics and mechanisms of production of LOG signals. These attempts have been largely successful and, as a result, we have shown that:

- (i) The temporal profile of a LOG signal contains two physically distinct components: one attributable to ionization rate changes, the other to an optoacoustic effect.
- (ii) Under suitable conditions, these two components are uniquely separable, even when they exhibit extensive temporal overlap, by an experimental method which treats the plasma as an integral rf circuit component.

- (iii) The physical origins of these two components may be understood using simple term diagrams for the laser excited species. In this regard, we have emphasized some halogens and rare gases (I₂, Br₂, Ne, Ar).
- (iv) The plasma, as sensed by the LOG effect, is a very sensitive optoacoustic detector.
- (v) The physical processes, underlying the LOG effect, whether produced by radiative or collisional ionization, or by the movement of bulk positive ions, can be disentangled.
- (vi) Capacitively (or inductively) coupled rf discharge (with no internal electrodes) in conjunction with transverse laser (pulsed) excitation provides an excellent experimental configuration.

These are significant findings. Plasma is a complex mixture of different species (neutrals, ions, etc.) in various states of excitation. In addition, lack of knowledge about various rates/cross-sections prohibits accurate quantitative modeling. The separation and identification of the IRC and OA components in the temporal profile of a LOG signal can provide important information about various excited states and plasma processes. Our patent application regarding these findings has recently been approved by the U. S. Patent Office.

Our interpretation of the various components in the temporal profile of a LOG signal provides a simple and accurate procedure for investigation of radiation trapping of strongly self-absorbed atomic emission lines. Our initial attempts to investigate OH⁻ generated in an rf discharge in water were not successful, primarily because of the lack of a tunable IR laser. This experimental apparatus we hope, will be acquired in the near future.

Since the LOG signal is generated either by one or both of ionization rate changes and optoacoustic effects, both of which are inherently sensitive processes, the detectivity limits for plasma species can be extremely low. For example, detectivity limits for Xenon can readily approach the fmole range. This suggests an important application for low-level monitoring of environmental Radon. This will, of course, involve some developmental work involving two and multi-component mixtures. This specific application will

form the basis of a separate research proposal which will be submitted to the Department of Energy in the near future.

Our ability to disentangle and identify the individual IRC and OA components in the temporal profiles of pulsed LOG signals will permit us to discriminate between two interfering species. This is a serious problem which besets some prominent detection/analysis technologies (e.g., Inductively-coupled Plasma (ICP)). Thus, the LOG technique can evolve as a sensitive environmental monitoring tool, either as a complementary adjunct to ICP fluorescence or as a real time monitor for simultaneous maximizing burn energy production and minimizing burn pollutant generation. It will also evolve into a superb probe of plasma characteristics, particularly as these relate to etching/deposition applications in microelectronics.

The full impact of our contribution to this area of research can only to be assessed in the future. We believe it will be large.

D. VACUUM ULTRAVIOLET SPECTROSCOPY

1. Electron Scattering

Most of our spectroscopic work has been confined to the measurement of electron scattering cross sections for a number of reasons, all of them derivative of our own work. These are:

- - -The spectroscopic method is much quicker than either time-of-flight (TOF) or swarm measurements (days as opposed to weeks or months).

- - -The spectroscopic method appears to yield zero-energy cross-sections, whereas a MERT extrapolation must be used to remove residual energy effects in both TOF and swarm experiments before zero-energy cross-sections become available. MERT extrapolations are neither easy nor accurate, and sometimes they can be wrong.

- - -We have performed spectroscopic density effect measurements at 70atm and see no reason why we cannot go to even higher pressures. Thus, the ability to cross the gas/liquid boundary is at hand. Consequently, we are in a position to study band development, scattering changes, etc. as we cross the pressure boundary between gas and liquid. This capability is not inherent in either the TOF or swarm methods.

- - -Since data can be generated quickly, we are in a position to investigate many scatterer entities and, hence, to delineate empirically the dependence of scattering length on scatterer polarizability. Indeed, we have already generated some very salient insights on this dependency.

- - -The spectroscopic method provides a direct measure of scattering length. The other methods do not. The scattering length can be either negative or positive, and provides some direct insights into the scattering potential.

Indeed, one could say that our work has directed attention to the lengths, and away from the cross-sections where, unfortunately, it should not have focussed.

--The plus/minus nature of lengths provides a very simple means of devising mixtures with tailored scattering lengths and, hence, cross-sections.

--The demonstration that autoionization effects may be used in the same way as found Rydberg absorptivities opens up the ability to study opaque perturbers, and hence to greatly expand the data base.

In view of the above, it is clear that this is an important research venture. Hence, we now provide a more rambling and , therefore, more informative discussion.

We have shown that spectroscopic studies of perturber number density effects for both atomic and molecular perturbers is the most efficient approach to a study of the mechanisms of momentum and energy transfer and energy deposition in density dependent, highly-energetic electronic processes. Indeed, our recent VUV study of CH_3I and C_6H_6 and H_2 was the first measurement of the effects of a molecular perturber on the high- n Rydberg transitions of molecular absorbers.

The measured spectral shifts may be used to generate scattering cross-sections and electronic scattering lengths for perturbers. The shifts of molecular absorbers, even in the large number density range (~ 70 atm), have been found to vary linearly with densities for both atomic (Ar) and molecular (H_2) perturbers. The results indicate that this sort of experiment can approach perturber densities comparable to those of liquids. In view of these results, well-known criteria, which suppose that Rydberg series should be broadened or disappear in highly dense and liquid media whereas valence transitions should not, demand further examination.

A new experimental method, using autoionization spectra for the determination of pressure shifts, was also developed. All in all, photoabsorption

and autoionization spectra of CH_3I have generated pressure shift data for 11 perturber gases. The perturbers include molecules such as CO_2 , CH_4 , C_2H_6 and C_3H_8 . As a result, electron scattering lengths have been obtained for these perturber gases, some for the first time.

Recent experiments on the CH_3I /nitrogen systems have addressed the role of polarizability in electronic scattering processes and, in particular, have used the Alekseev-Sobel'mann polarizability dependence.

We have compared three sets of scattering length data: one from density effects on high- n Rydberg states of CH_3I , a second from TOF data, and a third from the drift of electron swarms. The latter two data sets yield a scattering length A only after a MERT extrapolation to zero energy.

The primary adjustable parameter in the MERT expression is the electron scattering length. A comparison of scattering lengths from pressure shift data for the Rydberg states $n=10-16$ (0.13-0.05eV) with those from MERT expansions yields generally good agreement.

We have investigated mixtures of rare gases of different signs in order to make mixtures with an effective, net scattering length of zero. Perturber gases of positive scattering length (He, Ne, H_2) exhibit a blue spectral shift, while those of negative scattering length (Ar, Kr, Xe, CH_4 , CO_2 , C_2H_6 , etc.) produce a red shift. The observed "additivity" in mixtures of gases provides the ability to tailor any value, including zero, for an effective cross-section.

We have investigated the role of atomic and molecular polarizabilities in scattering. For example, following atomic effective-range theory, which applies to neutral electron scatterers, we find that a simple linear correlation brings the rare gases into a common frame: that is, a linear correlation exists between the electron scattering length, A , of the atomic perturbers and the polarizability of the rare gases. This correlation, evades any MERT extrapolation, in the sense that the direct results of measurement provide scattering lengths at the low-

energy limit. Finally, it also illumines the nature of the scattering potential, whether repulsive or attractive, since the correlative behavior predicts both the size and sign of the electron scattering length.

Our recent work has begun to focus in on the polarizability. We find two separate correlations: one for the rare gases and CH_4 which uses α , the other for H_2 , N_2 , C_2H_6 and C_3H_8 which uses α , the average polarizability. The two lines have essentially the same intercept of ~ 1.23 but quite different slopes. The results indicate that the more anisotropic molecular systems "see" electrons in a different way than do isotropic systems. This behavior is the subject of much of our present work.

These correlations between electron scattering lengths and polarizabilities indicates that Rydberg electron scattering by atomic and molecular perturbers should be described in terms of spatio-temporal response functions for the perturbers.

2. Photochemistry

We have analyzed the electronic absorption spectra of the cyanogen halides in a way that accounts for their electronic molecular spectroscopy and photochemistry. We have shown that intravalence excitations may not be ignored in the analysis of the electronic spectra of those polyatomic molecules in the VUV. We have discussed the relevance of our analysis to the photochemistry of the cyanogen halides. Specific predictions are presented for the production, as primaries, of various states of the CN radical and halogen atoms fragments. These predictions, in most instances, are verifiable by further photochemical investigations.

3. Magnetic Circular Dichroism

In this work, the emphasis is on the VUV MCD of HI. Experimental MCD work in this Laboratory has always focussed on the VUV region and on particular groups of molecules and atoms: simple gaseous molecular systems such as CH_3I which exhibit both Rydberg and valence electronic spectral structures. Our aim has been to develop an MCD VUV technique which is both easy to use and for which the results are easy to interpret.

MCD is a spectroscopic method that probes the earliest, electronic events in photophysics/photochemistry. In MCD spectroscopy, which measures the difference of absorptivity of right and left circularly polarized light, one applies a static magnetic field parallel to the incidence direction of a polarized light beam. In Circular Dichroism (CD) spectroscopy, on the other hand, one measures the difference of absorption of left and right circularly polarized light caused by the torques exerted on the molecular constituents by the electromagnetic field. Consequently, CD measurements are dependent on the molecular structure as well as on the changes that occur during interactions with the field and/or with the molecular environment. In MCD measurement the two forces, circularly polarized light and (static) magnetic field, are coupled.

Circular dichroism spectroscopy has been applied to a great variety of structures ranging from small chiral molecules to larger structures such as eukaryotic cells in solutions. MCD spectra are not so readily available. Indeed, MCD spectra are very scarce even for small molecules and are virtually non-existent in the VUV. . .this, despite the fact that all molecular systems must exhibit electronic MCD spectra whereas chirality is a prerequisite for CD spectra. Because of its general presence, MCD could

become the spectroscopy of choice for the study of molecular DNA damage, in particular local DNA molecular lesions.

The VUV absorption and MCD spectra of the first Rydberg transitions of gaseous HI have been studied at $\lambda > 140\text{nm}$, at various pressures below 1 Torr . This molecule is a simple diatomic with resolved rotational and vibrational electronic structures above the CaF_2 cutoff at 140nm. Progress in MCD measurements beyond the 140nm limit requires optics that are not presently available. An expansion of MCD spectroscopy below this limit was one of the subjects discussed at a recent Synchrotron Workshop on MCD. Analysis of the MCD spectra provides quantitative information concerning the large spin-orbit parameters ($>5000\text{ cm}^{-1}$) of the HI molecule. Indeed, the observed MCD spectra encompass the two most intense absorption bands which are the result of a spin-orbit splitting. A small shift of $\sim 20\text{ cm}^{-1}$ is observed at the center of the 62320 cm^{-1} line. The interpretation of this shift demands a quantitative interpretation of high resolution rotational and vibrational electronic spectra. Secondly, unexpectedly strong MCD signals are observed in the region of all absorption bands, some of which appear to be in complete discord with some existing state assignments, s, d or p . Thirdly, many of the observed (low resolution) MCD spectral structures do not meet either of the two specifications for A (derivative) or B (absorption) signal types, a simple typing which frequently is used for the analysis of low-resolution MCD spectra. Thus, the need for a model, which incorporates explicit rotational and vibrational structures is established.

Magnetic field strength effects are observed in the MCD spectrum: the intensity of the MCD lines is linear, as expected, with field, and no peak to peak shifts are observed in the A signatures. An analysis of the observed spectra as a combination of A structures, an approach similar to that used in earlier studies of opto-magnetic activity, indicates that a field induced

"mixing" of electronic states may be taking place. The observed MCD spectra may be fitted extremely well with two derivative functions, extracted from the MCD spectra in the energy region around 56740 cm^{-1} , the separation (or splitting) between the pairs of "doublets" for the first four MCD bands being in the range 20 to 90 cm^{-1} . We do not yet know the nature of the "states" implied by this analysis.

The magnetic momentum ratio obtained from the MCD spectra for the first (around 55830 cm^{-1}) and second (around 56790 cm^{-1}) bands is: $m_1/m_2 \sim 2.25$, and the ratio between the first and fourth (around 67330 cm^{-1}) bands is $m_1/m_4 \sim 2$. The magnetic moment of from the MCD spectrum in the region of the third band (around 60840 cm^{-1}) is difficult to estimate.

The MCD results call attention to the coupling mechanisms of electronic and nuclear motions in the rovibronic levels of Rydberg states. Thus we have begun an analysis based on a previously - developed spin-uncoupling model. This model was recently applied to a study of the VUV spectra of CH_3I . It was shown that uncoupling of the spin angular momentum of the optical electron from the molecular axis was essentially complete in some s- Rydberg states. We believe that this same model can account for the main MCD characteristics found in the HI spectra.

We have also initiated a computational analysis of the observed spectra, using Fourier convolution and deconvolution procedures. The results of the analysis indicate that the observed roelectronic envelope of the first electronic transition can be correlated directly to the observed MCD spectra. If successful, this study will provide direct and very specific information about low-n Rydberg electrons in magnetic fields.

E. OZONE

Ozone is one of the most important microconstituents of Earth's atmosphere. In the stratosphere it acts as a shield against harmful UV radiation; however, in the troposphere it enters numerous reactions some of which are harmful and of considerable environmental importance. Within the report period we here investigated the rate of destruction of ozone on various powder materials and the heterogeneous reaction of ozone with polycyclic aromatic hydrocarbons (PAH's) adsorbed on the surface of a (silica-gel) carrier.

As adjunct to an earlier work on the correlation of ozone reaction rates with the ionization potentials of conjugated molecules (e.g., L. Klasinc, H. Güsten, S. P. McGlynn, Title 272 in Comprehensive Report 1983-86) we have extended the correlation almost to the diffusion controlled limit by including new results for 10,10-dimethyl-9,9' biacridylidene.