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TECHNICAL FINAL REPORT

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(with continuing publications to 1997)

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TECHNICAL FINAL REPORT Contract DE-FG05-87ER-60517
Research Project
ENERGY TRANSFORMATION IN MOLECULAR ELECTRONIC SYSTEMS

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Background of the Report. This report covers the contract period 1993-1995. A number of the projects were completed in 1996, and those papers are included in the report. The DOE contract was terminated at the end of 1995 owing to a reorganizational change eliminating nationally the projects under the Office of Health and Environmental Research, U. S. Department of Energy.

Personnel

Principal Investigator: M. Kasha, Distinguished University Professor
Graduate Students: Dimitri Parthenopoulos, Barry Dellinger, David Gormin, Igor Litviniuk
Post-Doctorate Associates: Alexander Sytnik, Jozef Heldt, Ahsan Khan, Juan-Carlos del Valle
International Collaborators: Jozef Heldt (Poland), Javier Catalán (Spain)

Research Summary

This laboratory has developed many new ideas and methods in the electronic spectroscopy of molecules. The support of the Department of Energy and its predecessors goes back to 1960, when the Institute of Molecular Biophysics was established by the Atomic Energy Commission. Many of the research projects described here have their origins in earlier research under DOE, ERDA and now DOE sponsorship.

Attached is the list of 15 publications for the current report, followed by abstracts of the numbered papers, and an Appendix of two examples. The main topics can be summarized as follows.

A. *Solvent Cage Spectroscopy* (Papers 1,3) (Appendix I).

One of the fundamental needs in condensed matter research, whether liquids, glasses or crystalline solids is a bridge connecting observations of electronic excitation modes in the gas phase with the more complex behavior of condensed matter systems.

We have developed in a series of papers a quantum mechanical theory based on Born-Oppenheimer separability of rate of intra-molecular and inter-molecular solute *vs.* solvent matrix motions. This we have applied to more than six different molecular potentials. The current papers summarize the applications.

B. *Spectroscopic Electronic Theory* (Papers 1,2,10,11,15)

In addition to the solvent cage theory, we have explored a wide variation of electronic modes of excitation, especially those connected with molecular framework distortion: intra-molecular torsion, proton-transfer tautomerization, *etc.* For example, paper 10 analyzes the several possible types of lowest triplet-state potentials which could exist in proton-transfer excitation. This has led to a real break-through in observability of the difficultly observable triplet state of the proton transfer tautomer. Thus J. Catalán (Madrid) has published the first observed, clearly defined triplet-singlet emissions in a proton-transfer tautomer (J. Catalán and C. Diaz, J. Phys. Chem., **102**, 323 (1998)). We have applied our ideas to various cases, including the development of new scintillator materials for radiation detection, and protein structural fluorescence probes.

C. *Singlet Molecular Oxygen Research* (Papers 4,5) (Appendix III)

This laboratory discovered the chemical reaction production of singlet molecular oxygen in our original 1963 J. Chem. Physics papers by Khan and Kasha under our AEC contract. This was followed by a

decade or more of research applications. Singlet molecular oxygen is the electronically excited form of O_2 , which is highly reactive and 'long lived,' was totally neglected by chemists and biologists until its renaissance. Since 1963, a dozen monographs and collected volumes have appeared, including the four volume CRC Press Handbook edited by Aryeh A. Frimer in 1986 (Cf. Appendix II).

Our new papers (4,5) present a remarkable observation that the evolution of Cl_2 gas upon *mere acidification* of alkaline hypochlorite solutions is preceded by a burst of singlet O_2 . This we connected with epidemiological research on cancer deaths appraised for the drinking of chlorinated city water. The acidity of stomach fluids could cause singlet O_2 evolution which could initiate radical chain chemistry with its chemical and biological consequences.

D. *Proton Transfer Fluorescence Probes for Proteins* (Papers 6,7,8,9)

A considerable effort has been expended in this laboratory to show the power of proton-transfer fluorescences as protein binding-site probes. The enormous wavelength shift ($5000-10000\text{ cm}^{-1}$) from the first UV absorption bond of the probe molecule separates their proton-transfer fluorescence from normal UV to blue region interferences. Various probes are described which can characterize the binding site of the several serum albumens studied.

Flavonols are the dominant species studied in our proton-transfer spectroscopy. They prove to be powerful anti-oxidants, and powerful radical quenchers in radiobiology. Our studies were carried out in order to provide the photophysical background for this work. It has not escaped our attention that the new emphasis on flavonol health benefits of the vegetarian diet could be reinforced by such studies.

E. *Proton-Transfer Dynamics Mechanisms via Laser Spike Spectroscopy* (Papers 12,13,14)

The studies on amplified spontaneous emission (ASE) laser spike spectroscopy (mirror-less lasing) were carried out not in order to find new laser materials, but to characterize their special electronic structure and excitation modes, especially in the dynamics of excitation. Our work has shown four diverse mechanisms of excitation, with unique requirements on dynamical aspects. Three of these modes have never been observed previously, and will be studied in future research via femtosecond laser spectroscopy which our laboratory is preparing to do.

Appendix I

In this Appendix, paper (1) is presented in full to expand on our solvent-cage potential energy curve perturbation model, and to illustrate various new excitation concepts.

Appendix II Chemical Production of Singlet Molecular Oxygen.

This page succinctly presents the chemiluminescence red-orange glow at 634 nm of the aqueous hydrogen-peroxide (sodium) hypochlorite reaction at 298K reported in A. U. Khan and M. Kasha, J. Chem. Phys. 39, 2105 (1969).

The red-orange chemiluminescence arises from the *simultaneous transition* of two excited singlet oxygen molecules yielding *one photon* at 634 nm excitation from the *two* $1268\text{ nm }^1\Delta_g$ excited molecules.

The book shelf pictures some of the main books which have appeared since the first communication.

Appendix III (Papers 4,5)

A single combined page presents the spectroscopic evidence succinctly of the two new observations made in our current singlet oxygen research.

Reprints removed for separate processing —

PUBLICATIONS

1. Challenges to Computational Quantum Chemistry from Contemporary Advances in Polyatomic Molecular Electronic Spectroscopy, M. Kasha, D. Parthenopoulos and B. Dellinger, *Int. J. Quantum Chem.*, **45**, pp. 689-708 (1993).
2. Spectroscopic Criteria for Wavelength Shifting, Fast, and Red-infrared Scintillators, A. Sytnik and M. Kasha, *Radiation Physics and Chemistry*, **41**, No. 1/2, 331-349 (1993).
3. Solvent Cage Spectroscopy, M. Kasha, A. Sytnik and B. Dellinger, *Pure and Appl. Chem.*, **65**, 1641-1646 (1993).
4. Singlet Molecular Oxygen Evolution upon Simple Acidification of Aqueous Hypochlorite: Application to Studies on the Deleterious Health Effects of Chlorinated Drinking Water, A. U. Khan and M. Kasha, *Proc. Natl. Acad. Sci., USA*, **91**, 12362-12364 (1994);
5. Singlet Molecular Oxygen in the Haber-Weiss Reaction, A. U. Khan and M. Kasha, *Proc. Natl. Acad. Sci. USA*, **91**, 12365-12367 (1994).
6. Excited-State Intramolecular Proton Transfer as a Fluorescence Probe for Protein Binding-site Static Polarity, A. Sytnik and M. Kasha, *Proc. Natl. Acad. Sci. USA*, **91**, 8627-8630 (1994).
7. Interplay Between Excited-State Intramolecular Proton Transfer and Charge Transfer in Flavonols and Their Use as Protein-Binding-Site Fluorescence Probes, A. Sytnik, D. Gormin and M. Kasha, *Proc. Natl. Acad. Sci. USA*, **91**, 11968-11972 (1994).
8. Steady-State and Time-Resolved Study of the Proton-Transfer Fluorescence of 4-Hydroxy-5-azaphenanthrene in Model Solvents and in Complexes with Human Serum Albumin, A. Sytnik and J.-C. Del Valle, *J. Phys. Chem.*, **99**, 13028-13032 (1995).
9. Energy Transfer to a Proton-Transfer Fluorescence Probe: Tryptophan to a Flavonol in Human Serum Albumin, A. Sytnik and I. Litvinyuk, *Proc. Natl. Acad. Sci. USA*, **93**, 12959-12963 (1996).
10. Triplet State Potentials in the Competitive Excitation Mechanisms of Intramolecular Proton Transfer, D. Gormin, J. Heldt and M. Kasha, *J. Phys. Chem.*, **99**, 7281-7284 (1995).
11. Chemical Physics of Excitation Dynamics via Amplified Spontaneous Emission (ASE) Laser Spike Spectroscopy in Substituted Phenyloxazoles, J.-C. del Valle, M. Kasha and J. Catalán, *Chem. Phys. Lett.*, **263**, 154 (1996).
12. Spectroscopy of Amplified Spontaneous Emission Laser Spikes in Polyhydroxyflavones, D. Gormin, A. Sytnik and M. Kasha, *J. Phys. Chem.*, **101**, 672-677 (1997).
13. Spectroscopy of Amplified Spontaneous Emission Laser Spikes in Phenyloxazoles. Prototype Classes, J.-C. del Valle and M. Kasha, *J. Phys. Chem.*, **101**, 3260-3272 (1997).
14. Inter-ring Torsional Modulation in Molecular Lasers. Ultraviolet Lasing via Amplified Spontaneous Emission Spectroscopy of Phenylimidazoles, J. Catalan, J. L. G. de Paz, J.-C. del Valle and M. Kasha, *J. Phys. Chem.*, **101**, 5284-5291 (1997).
15. A Method for Separation of Homogeneous and Inhomogeneous Components of Spectral Broadening of Rigid Systems, I. V. Litvinyuk, *J. Phys. Chem.*, **101**, 813-316.