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EXPERIMENTAL AND THEORETICAL STUDIES IN PHOTOCHEMISTRY. (U)
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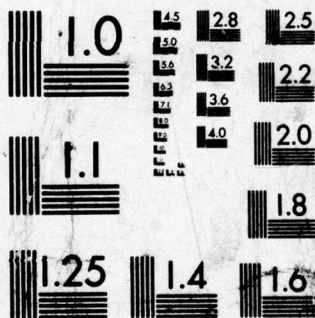
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FINAL REPORT

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CONTRACT AFOSR F 44620-73-C-0005

Stuart A. Rice

The James Franck Institute

The University of Chicago

Chiccco, Illinois 60637

September 30, 1976

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FINAL REPORT

Experimental and Theoretical Studies in Photochemistry

September 1, 1972 to August 31, 1976

This report summarizes the results of research supported by the Air Force Office of Scientific Research at the University of Chicago from September 1, 1972 through August 31, 1976 under Contract AFOSR F 44620-73-C-0005 entitled "Experimental and Theoretical Studies in Photochemistry." Progress reports have been incorporated in each of the annual requests for support during that time interval.

The goal of the research under discussion is the elucidation of the primary physical and chemical processes following photo-excitation of a molecule. As will be made evident, a variety of approaches has been used, all addressed to answering one or more of the following questions:

- 1) What general principles determine the nature of the primary products of a photochemical reaction?
- 2) How does the excitation process, e.g. the initial state selected, the use of coherent versus incoherent light, etc., influence the reaction products?
- 3) Does internal energy transfer compete with bond-breaking or isomerization? When and under what conditions is this important?
- 4) Can reaction pathways be selected or optimized by controlled excitation of selected initial states?

For several years before the contract period under discussion, I participated in the development of a general theory of radiationless processes and initiated the application of that theory to photochemical reactions. The central theme of the theory is deceptively simple, namely that an initially prepared state of a molecule is, in general, nonstationary. The kind of nonstationary state prepared depends both on details

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of the molecular spectrum of states and on the nature of the excitation. The evolution of the prepared nonstationary state, which determines the nature of the reaction, is also influenced by the character of the spectrum of the molecule, the intramolecular couplings and rates of relaxation, the absence or presence of collisions, etc. Reduction of the general theory by application to specific problems has been one of the principle activities during the contract period. There has been fruitful exchange of insights as the theory and the experimental work developed side by side. Practical application of the findings of this research will depend on whether or not we can learn to control the coupled excitation and evolution of nonstationary molecular states and thereby develop a selective photochemistry.

A schematic diagram of the way my research program has evolved is displayed on the next page. The numbers next to each subject grouping identify papers in the appended list of publications. Included with each reference in that list is an abstract. In this portion of the report I will, therefore, deal only with the overall scope of the research effort and the relations between its parts.

Given that I had participated in the development of the general theory of radiationless processes, it was natural that my laboratory play a role in testing that theory. Because of the influence of the initial state on the rate emphasized in the theoretical analysis, attention was focussed on determining the roles of the extent of vibrational excitation, amplitude, frequency and origin shifts, and symmetry, for a typical radiationless process. The method selected, nanosecond time resolved single vibronic level fluorescence spectroscopy, has also been used to study some photochemical reactions. That this is possible is testimony to the value of information obtained for photophysical radiationless processes, and the transferability of concepts for the description of photochemical reactions. As of this writing a rather extensive test of the theory,

General Theory of Radiationless Processes

photophysical
processes

photochemical
processes

tests and extensions of theory focussed on the influence on the rate of: frequency shifts, origin shifts, amplitude of motion and symmetry of vibrational modes of the molecule.
222 (71), 227 (72), 256, 258, 262, 263

further tests focussed on: rotational effects, isolation of influence of mixed vibrational excitation, large changes in molecular geometry.

collision induced intramolecular energy exchange

nanosecond single vibronic level fluorescence

theory; transfer of background information

pulsed supersonic molecular beam source

extensions of theory 239 (72), 257, 268, 285

studies of influence of geometry change on reaction rate 233 (72), 242, 279, 285

studies of intramolecular energy exchange 224 (72), 241 (72), 244, 245, 246, 247, 248, 249, 251, 260, 261, 270, 274, 286

picosecond spectroscopy for study of energy exchange 277, 290

study of single vibronic level photochemistry, influence on product energy distribution of nature of prepared state, etc.

for the case of intersystem crossing, has been completed, using as test cases benzene, several partially deuterated benzenes, aniline and deuterated anilines, and others (222 (71), 227 (72), 256, 258, 262, 263). These investigations confirm many of the predictions of the general theory, and the utility of algorithms developed by my colleague Karl Freed. They are, however, not complete. In particular, we do not yet know very much about the influence on the rate of radiationless processes of coupling of rotational and vibrational motion in an isolated molecule. This form of coupling is known to be extremely important in the case of photochemical reactions (one such case is reported in Ref. 242); by inference it should play an important role in those radiationless processes coupling molecular states with very different geometries (hence moments of inertia). Furthermore, at present little is known of the specific consequences of exciting several vibrations in the prepared state. The investigation of the effects of excitation of a mixture of vibrations is important for practical applications since, at ordinary temperatures, even a narrow band laser applied to the excitation of a typical organic molecule (e.g. benzophenone) will generate a mixture of states by virtue of hot band and sequence congestion in the spectrum. To further test and provide data for the extension of the theory, I have started several investigations using a pulsed supersonic molecular beam source. By virtue of isentropic expansion, as the beam flows through the nozzle, the translational temperature in the beam can be reduced to less than 1 K, the rotational temperature to 1 - 10 K and the vibrational temperature to 10 - 100 K. Such a beam source is suitable, with excitation by a pulsed narrow band laser, for investigation of the rotational effects mentioned, as well as for eliminating the effects on preparation of the initial state of hot band and sequence congestion in the spectra of fairly large molecules.

Having studied radiationless processes in isolated molecules (on a time scale shorter than the time between collisions) it is natural to use the information obtained to learn how collisions lead to intramolecular energy exchange. Such processes are of great

importance in unimolecular reactions, both those which are thermally induced and those induced by multiphoton absorption and putatively of use for isotope separation. As one example, I note that a direct benefit of my visit to Laboratoire d'Optique Quantique, CNRS, in June and July, 1976, was the development of a theory of laser induced photochemical reaction for the case of incoherent excitation (294). This class of reactions has just been discovered and reported by Grunwald (D. F. Dever and E. Grunwald, J. Am. Chem. Soc. 98, 5055 (1976)). The characteristic features of technical interest are the use of low intensity CO₂ laser irradiation ($\sim 1 - 2 \text{ MW/cm}^2$) and high sample pressure (60 Torr), so practical chemistry can be carried out (i.e. with yields of measurable size). The Grunwald experiments are amongst the first to be reported for which it seems that one has some control over the competition between excitation and relaxation processes. A preprint of my theoretical analysis is attached to this report.

Since most reactions occur under conditions where many collisions occur prior to reaction, an understanding of how collisions alter the distribution of vibrational energy of a polyatomic molecule is of obvious value. Studies of collision induced intramolecular vibrational relaxation in benzene have been started, using as background the information already available on the properties of the isolated molecule.

The first stage in my studies of photochemical primary processes consisted of developing extensions of the theory with respect to the influence of changes in molecular geometry and the distribution of internal coupling strengths (233 (72), 242, 279, 285). Simultaneously, the application of the theory of radiationless processes to various photochemical reactions led me to study intramolecular vibrational relaxation in an isolated molecule (224 (72), 241 (72), 244, 245, 246, 247, 248, 249, 251, 260, 261, 270, 274, 286). As a result of work in Chicago and elsewhere, it is now apparent that this kind of

relaxation can be slower than reaction in a number of cases, a finding likely to be of profound importance for the development of practical selective photochemistry. For, selectivity in a photochemical reaction will depend upon memory effects, that is, on being able to use a specific prepared vibronic state to produce specific reaction products. If intramolecular energy exchange is rapid so that the excitation energy placed in a molecule is scrambled rapidly, product selectivity is unlikely to occur. If, on the other hand, intramolecular energy exchange is slow, it is in principle possible (though not necessarily easy or efficient) to produce both different yields and different products by selective excitation of different initial states.

The theoretical contributions to this problem which I have made largely focus on the analysis of the behavior of simple models of dynamical processes. The studies completed to date confirm, on the whole, that it is possible that intramolecular energy exchange can be slow, but as of this writing the theory is very incomplete and has not yet yielded detailed understanding of when and why intramolecular energy exchange is fast or slow. The next stage in the evolution of this research is the direct examination of the intramolecular relaxation process. I initiated said direct examination three years ago, but it is far from complete. Briefly put, the goal is to use picosecond spectroscopy to observe directly the evolution of a prepared vibronic state in a molecule. Thus far, we have developed a tunable infrared picosecond source (277, 290) and have learned much about the vagaries of working at the very edge (perhaps somewhat beyond the edge) of technology. Although there are day to day improvements, we do not yet have results, and work will continue well into the new contract period before results are obtained.

The two research lines sketched, namely investigation of photophysical and of photochemical processes, join at several points, as shown in the diagram. Consider one example: the use of pulsed supersonic molecular beam technology. I have already

mentioned how it is intended to use a pulsed supersonic molecular beam source to cool molecules so that the effects of rotation on radiationless processes can be investigated. The same source will also be used to investigate how a collision induces intramolecular vibrational energy exchange and, in the near future, for how the energy of an excited molecule is partitioned between and within the products of a photochemical reaction.

In summary, considerable progress has been made in answering the questions which defined the research efforts of the last four years. As is to be expected, increased understanding of some phenomena showed relationships and analogies previously unexpected, but also raised new questions and posed new problems in the quest for development of practical applications of controlled molecular dynamics.

Abstracts of Publications

Contract AF.OSR F 44620-73-C-0005

Please note that the numbering used corresponds to the numbering in my publication list. This numbering is also used in the text.

- 222.* A Study of the Lifetimes of Individual Vibronic States of the Isolated Benzene Molecule. With Kenneth G. Spears, J. Chem. Phys. 55, 5561 (1971)
- 224.* Random Matrix Theory and the Master Equation for Finite Systems. With William Gelbart and Karl Freed. J. Chem. Phys. 57, 4699 (1972).
- 227.* Lifetimes and Quantum Yields of Individual Vibronic States of C_6D_6 and C_6H_5D . With Allan Abramson and Kenneth Spears. J. Chem. Phys. 56, 2291 (1972).
- 233.* Competition Between Photon Emission and Photodissociation in Electronically excited Chloro- and Bromoacetylene. With Keith Evans. Chem. Phys. Letters 14, 8 (1972).
- 241.* Decay of Fluorescence From Single Vibronic States of SO_2 . With Man Him Hui. Chemical Physics Letters 17, 474 (1972).
242. Primary Photochemical and Photophysical Processes in Chloro- and Bromo-Acetylene. With Keith Evans, Donald Heller, and Richard Scheps. Faraday Society II. 69, 856 (1973).

Measurements of the fluorescence lifetimes and quantum yields of fluorescence from selected individual vibronic states of chloro- and bromoacetylene are reported and the data analyzed in terms of the coupling of photon emission to the photodissociation reaction $HCCX \rightarrow HCC \cdot (^2\Pi) + X \cdot (^2P)$ where $X = Cl, Br$. It is suggested that the reaction involves a slow internal conversion from the first excited singlet state to the ground electronic state, and that vibrational relaxation in the ground electronic state is sufficiently slow that randomization of the excitation energy does not occur before dissociation. Consequent competition between vibrational relaxation and resonance amongst quasi isolated groups of states leads to a departure from RRKM type behavior.

An unusual variation with energy of the nonradiative lifetimes of vibronic states is found. This observation is interpreted by taking note of the constraints imposed on the dissociation rate by the simultaneous conservation of energy, linear and angular momentum.

* These papers cited for continuity of research line.

The i.r. and u.v. spectra of chloro- and bromo-acetylene are re-investigated and differences between our findings and those of others are discussed in terms of the electronic structure of these molecules.

244. Substitution Reactions of Fluorine Atoms with Unsaturated Hydrocarbons: Crossed Molecular Beam Studies of Unimolecular Decomposition. With John M. Parson, Kosuke Shobatake and Yuan T. Lee. *Disc. Far. Soc.* 55, 344 (1973). •

This paper briefly reviews an extensive set of studies of the reactions of fluorine atoms with olefins, dienes, aromatic and heterocyclic molecules by the method of crossed molecular beams. From measurements of the angular distribution of products and the recoil energy spectrum of products it is inferred that the statistical theories of reaction are inadequate. Although RRKM theory seems capable of predicting the ratios of cross sections for pairs of products, the same theory is incapable of accounting for the internal energy distribution of the products. The failure of the hypothesis that internal energy exchange is more rapid than chemical reaction is discussed and a proposal advanced to explain the origin of the failure.

245. Unimolecular Decomposition of the Long-Lived Complex Formed in the Reaction $F + C_4H_8$. With John M. Parson, Kosuke Shobatake and Yuan T. Lee. *J. Chem. Phys.* 59, 1402 (1973).

The reactions of fluorine atoms with four butene isomers have been studied by the method of crossed molecular beams. Angular distributions and velocity spectra of products formed by substitution of F for CH_3 and H have been measured. Relative rates for CH_3 and H substitution are in qualitative agreement with RRKM predictions for competitive rates of dissociation of a fluorobutyl complex. Quantitative agreement is possible with minor adjustments in the exothermicities or barriers to dissociation. The kinetic energy distributions of the products, on the other hand, are not in accord with those predicted by statistical theories of unimolecular reactions. The results suggest that the assumption of randomization of internal energy breaks down at least for complex configurations close to the transition state where coupling between separating fragments is still strong enough to allow appreciable nonrandom mixing of translational energy with rotations and vibrations of the larger fragment.

246. The Unimolecular Decomposition of Long-Lived Complexes of Fluorine and Substituted Mono-Olefins, Cyclic Olefins and Dienes. With Kosuke Shobatake, John M. Parson and Yuan T. Lee. *J. Chem. Phys.* 59, 1416 (1973).

The reactions of fluorine atoms and substituted mono-olefins, cyclic olefins, and dienes have been studied by the technique of crossed molecular beams. In each case the experimental evidence suggests the existence of a long-lived intermediate complex. Analysis of the angular distribution of products then permits a test of the energy randomization hypothesis of the statistical theories of unimolecular reaction rate. The data obtained strongly imply that for the class of reactions studied energy randomization is not faster than decomposition of the complex.

247. The Laboratory Angular Dependence and the Recoil Energy Spectrum of the Products of the Reaction $F + C_6D_6 \rightarrow D + C_6D_5F$. With Kosuke Shobatake, John M. Parson and Yuan T. Lee. *J. Chem. Phys.* 59, 1427 (1973).

The reaction of fluorine atoms with perdeuterobenzene has been studied by the method of crossed molecular beams. In this reaction a long-lived intermediate complex is formed. Analysis of the kinetic energy distribution of the products and their angular distribution in space cannot be satisfactorily accounted for by the available statistical theories of unimolecular decomposition. The results of this study can be used to infer that randomization of the internal energy of a molecule is not necessarily rapid relative to chemical reaction.

248. The Reaction of F Atoms and Aromatic and Heterocyclic Molecules: Energy Distribution in the Reaction Complex. With Kosuke Shobatake and Yuan Lee. *J. Chem. Phys.* 59, 1435 (1973).

This paper reports studies of the reactions of fluorine atoms and several aromatic and heterocyclic molecules. As in earlier work we have used the method of crossed molecular beams to create long-lived reaction intermediates and to deduce from the angular distribution of the product molecules information about the energy distribution in the reaction complex. The data reported in this paper complement those collected earlier. They show that when a light group is emitted from a reaction complex randomization of the internal energy of the complex is not more rapid than reaction. When a heavy atom is emitted from the reaction complex the limited data available indicate that almost all vibrational degrees of freedom of the complex participate in the reaction. This

latter observation provides an interesting connection between vibration-translation energy exchange and the mechanism of chemical reaction.

249. Intramolecular Vibrational Energy Transfer: A Study of Representations. With Kenneth G. Kay. *J. Chem. Phys.* 58, 4852 (1973).

In this paper we report a study of possible representations for the description of intramolecular energy transfer. Our ultimate goal is the definition of a scheme suitable to the description of a molecule undergoing dissociation which is valid everywhere along the reaction path. For this reason we study three sets of basis functions for dynamical calculations of intramolecular vibrational energy transfer in one-dimensional, bound or metastable, triatomic molecules having one harmonic and one Morse bond. The different sets result from different definitions of bond coordinates and different methods for separating the bond motions. For Basis Set 1, the two bond coordinates are internuclear distances between adjacent atoms and the interbond coupling is caused by kinetic energy cross-terms. For Basis Sets 2 and 3 the coordinates are the distance between adjacent atoms in the harmonic bond and the distance between the dissociable atom and the remaining diatomic. The separation of coordinates for Basis Set 2 is analogous to the "static" resolution of bond motions in collision theory while the separation of coordinates for Basis Set 3 is an adiabatic separation. The nature and mechanism of bond coupling in the adiabatic approximation is analyzed in detail and dominant contributions are identified. We find that the relative merits of the basis functions depend strongly on the masses of the atoms and the harmonic frequencies of the bond. When the vibrational frequency of the harmonic bond exceeds the frequency for small oscillations of the Morse Bond, Basis 3 is usually superior to both Bases 1 and 2. When the opposite condition holds and the mass of the central atom is (modestly) large relative to the masses of the other atoms, Basis 1 is usually superior. The conditions which favor the adiabatic separation are similar to those which favor the "perturbed stationary states" approximation in collision theory. The weak energy-dependence of the basis sets is explained in terms of a strong dependence of the optimal bond coordinates upon the interatomic distances.

250. Comment on "Decay of Fluorescence from Single Vibronic Levels of SO_2 ." With Man Him Hui. *Chem. Phys. Letters*, 20, 411 (1973).

In response to a personal inquiry we have reexamined the pressure dependence of the lifetime of three excited vibronic states of SO_2 . The new measurements confirm the old ones, in particular the observation that the cross section for self-quenching is very large. A possible interpretation of the observation is suggested.

251. An ITFITS Model for Vibration-Translation Energy Partitioning in Atom-Polyatomic Molecule Collision. With K. Shobatake and Yuan T. Lee. *J. Chem. Phys.* 59, 2483 (1973).

A model for vibration-translation energy partitioning in the collinear collision of an atom and an axially symmetric polyatomic molecule is proposed. The model is based on an extension of the ideas of Mahan and Heidrich, Wilson and Rapp. Comparison of energy transfers computed from classical trajectory calculations and the model proposed indicate good agreement when the mass of the free atom is small relative to the mass of the bound atom it strikes. The agreement is less satisfactory when that mass ratio becomes large.

252. A Crossed Molecular Beams Study of the Reaction $\text{F} + \text{C}_2\text{H}_2\text{Cl}_2 \rightarrow \text{Cl} + \text{C}_2\text{H}_2\text{ClF}$. With Kosuke Shobatake and Yuan T. Lee, *J. Chem. Phys.* 59, 6104 (1973).

We report studies of the reactions of F atoms with cis-1,2-, trans-1,2- and 1,1-dichloroethylene by the method of crossed molecular beams. We find that for the products of Cl emission the recoil energy distributions, deduced from product laboratory angular distributions, are consistent with existence of a reaction complex in which almost all vibrations participate in the partitioning of energy.

256. Influence of Large Amplitude Vibrational Motion on the Rate of Intersystem Crossing: A Study of Single Vibronic Level Fluorescence From Aniline- h_7 , Aniline-N, N- d_2 and Aniline- d_5 . With Richard Scheps and Donald Florida. *J. Chem. Phys.* 61, 1730 (1974).

Results of single vibronic level fluorescence measurements in aniline- h_7 , aniline-N, N- d_2 , aniline- d_5 , and aniline- d_7 are reported. For each excited level the radiative and nonradiative lifetimes and fluorescence yields have been obtained. The dependence of the nonradiative lifetime of the excited level on the excess energy in aniline- h_7 is seen to behave similarly to that in benzene

for states independent of inversion mode excitation. Levels involving inversion amplitude must be treated separately; we interpret their lifetimes by postulating that a nonplanar triplet state is involved in the intersystem crossing. Deuteration in the ring and amino positions affects the nonradiative lifetimes to different degrees and leads to the rejection of crossing to the 3B_2 state as the rate determining step. A detailed study of the dependence of the nonradiative process on excitation of the inversion mode was carried out using the methods of Heller, Freed, and Gelbart. The numerical calculations were based on Franck-Condon overlap factors appropriate for transitions from a near planar initial state to a significantly bent final state. The experimental trends observed with excitation of inversion mode were qualitatively reproduced for all the molecules studied except aniline N, N-d₂.

257. Some Comments on the Dynamics of Primary Photochemical Processes. In *Advances in Electronic Excitation and Relaxation*, Volume 11, edited by Edward C. Lim (Academic Press, New York) pp 111-320 (1975).

Within the last decade a combination of new experimental techniques and new theoretical analyses has considerably altered our understanding of the kinetics of chemical reactions. It is the purpose of this review to survey those aspects of these developments that are pertinent to the understanding of primary processes. The subject matter discussed has been organized around the following questions:

- (i) In what fashion does the reaction pathway followed depend on the nature of the initially excited state?
- (ii) Do the conservation of energy and momentum lead to any unusual restrictions on photochemical reactions?
- (iii) Under what conditions is intramolecular energy mixing rapid relative to chemical reaction?

Experimental data are surveyed along with theoretical developments where pertinent.

258. Comments on the Spectrum and Photophysical Properties of Trimethylene-Cyclopropane. With Ernest A. Dorko and Richard Scheps. *J. Phys. Chem.* 78, 568 (1974).

The spectrum and fluorescence of TMCP are analyzed with respect to possible photoproducts.

260. Quantum Ergodicity and Vibrational Relaxation in Isolated Molecules.

With K. Sture J. Nordholm. *J. Chem. Phys.* 61, 203 (1974).

Recent advances in classical ergodic theory have produced qualitative information about the dynamics of anharmonic systems that is relevant to internal molecular dynamics and to unimolecular reaction rate theories. We describe here the results of an attempt to translate this progress into quantum molecular dynamics. Existing theories of quantum ergodicity are found to be ill suited to our task, so an extended concept of quantum ergodicity closely adhering to the well established classical concept is suggested. The new concept has the desired relevance to relaxation processes in isolated molecules, and it allows straightforward numerical investigation of molecular models. We report results for several triatomic models and one model of a linear molecule with four atoms. A prevalence of nonergodic behavior is observed for energies below the minimum required for dissociation.

261. Intramolecular Energy Transfer in Cis-Trans Isomerization: A Study of Fluorescence from Single Vibronic Levels of Styrene, trans- β -Styrene- d_1 , Styrene- d_8 , and Ethynlbenzene. With Man Him Hui. *J. Chem. Phys.* 61, 833 (1974).

The fluorescence lifetimes of, and quantum yields of emission from, individual vibronic levels of isolated molecules of styrene, trans - β -styrene- d_1 , styrene- d_8 , and ethynlbenzene have been measured. These data are subjected to a decomposition, under a plausible hypothesis, into parameters descriptive of an isomerization process and an intersystem crossing process. It is argued that the two processes proceed independently in parallel. The rate of isomerization is found to be independent of the vibrational energy content of the isolated molecule and to have a dependence on isotopic mass consistent with the prediction that the torsional mode is the best ground state acceptor in the reaction channel. A plausible schematic potential energy surface is constructed from a combination of spectroscopic observations and analogies with theoretically derived surfaces for similar molecules. Analysis of the experimental data, and deductions from those data, in terms of the properties of the potential surface, leads to the inference that intramolecular vibrational relaxation is slower than chemical reaction for excess vibrational energy up to $\sim 2500 \text{ cm}^{-1}$.

262. Nonradiative Processes in $p\text{-C}_6\text{H}_4\text{F}_2$ and $m\text{-C}_6\text{H}_4\text{F}_2$. With Charles Guttman. J. Chem. Phys. 61, 661 (1974).

The nonradiative lifetimes and quantum yields of individual vibronic levels of m - and $p\text{-C}_6\text{H}_4\text{F}_2$ have been experimentally determined. The data collected for the difluorobenzenes show great differences between the non-radiative decay processes in the para and meta compounds and similarity between these processes in meta-difluorobenzene and monofluorobenzene. It is suggested that the differences cited are a consequence of the different molecular symmetries and, as a result, the different possible accepting modes and the manner in which the excess energy distributes itself in the triplet manifold.

263. Fluorescence Lifetimes of Individual Vibronic Levels of Partially Deuterated Benzenes: A Further Test of the Theory of Radiationless Processes. With Charles Guttman. J. Chem. Phys. 61, 651; (1974).

This paper reports experimental studies of the nonradiative lifetimes of individual vibronic levels of several partially deuterated benzenes. The different deuterated species transform according to different symmetries, and therefore *the number of totally symmetric modes differs from molecule to molecule*. The observed rates of nonradiative decay fall into a regular pattern as a function of increasing deuteration. This observation, together with theoretical arguments, suggests that the accepting modes are, to a good approximation, local modes. Comparison of the predicted relative nonradiative rates with those observed is generally good, but not as accurate as for C_6H_6 and C_6D_6 . The likely source of the discrepancy is discussed.

267. 2,3-Naphtho-2,5-bicyclo[2.2.0] hexadiene. With N. C. Yang, Richard V. Carr, Ellen Li, Jeffrey K. McVey. J. A. C. S. 96, 2297 (1974).

2,3-Naphtho-2,5-bicyclo[2.2.0] hexadiene (1) decomposes thermally and photochemically ($\phi = 0.41$) to give anthracene. The amount of energy available in the adiabatic conversion of 1 to anthracene is sufficient to populate anthracene either in its triplet state or, possibly, its singlet excited state. Although thermal decomposition of dewar benzenes can yield benzenes in their triplet states, thermal decomposition of 1 does not give an appreciable yield of excited anthracene. The failure of thermal conversion of 1 to yield excited anthracene has been

attributed to the lack of orbital symmetry in said conversion. 1 does undergo photorearrangement to give anthracene in its singlet excited state ($\phi = 0.1$). This constitutes the first example known to us of the rearrangement of one excited molecule to another in their respective singlet excited states. The probability of such a transition is enhanced in this case by the similarity between the molecular orbitals, X_e of anthracene (2) and the MO of 1 constructed from X_e of naphthalene and those of cyclobutene after a disrotatory ring opening (3).

268. Random Coupling Model for Molecular Dissociation. With Eric J. Heller
J. Chem. Phys. 61, 936 (1974).

In this paper, we propose and solve sequential coupling models for molecular dissociation of the Rice-McLaughlin-Jortner (RMJ) type in which the usual assumption of constant coupling among the states is replaced by an assumption of random coupling. The counter-intuitive nonsequential branching behavior found previously for constant coupling is eliminated and we find completely sequential time dependence which obeys the phenomenological rate equations. We isolate the features of constant vs random coupling which give rise to the branching vs sequential behavior in terms of simple physical models and considerations of the coherence properties of the wavefunction. It is concluded that constant coupling is inappropriate for most molecules, and that the random coupling assumption has the effect of validating the use of a random phase approximation which in turn causes the molecule to decay as if each quasibound molecular level is coupled to its own continuum. Our conclusions do not change when we solve an extended model with many continua, with each molecular level coupled to each continuum.

270. Quantum Ergodicity and Vibrational Relaxation in Isolated Molecules II-
 λ -Independent Effects and Relaxation to the Asymptotic Limit. With
Sture Nordholm. J. Chem. Phys. 61, 768 (1974).

In this second article on quantum ergodic properties of simple anharmonic molecular models, we present further numerical calculations for the Barbanis and Henon-Heiles models. For the cases studied herein, the density of energy eigenstates is larger by about a factor of five than that used earlier. We show that the character of the low lying states of the model Hamiltonians is dominated by λ -independent effects which can be obtained by second order degenerate perturbation theory. Nondegenerate modifications of the above systems are

again found to be highly nonergodic. We also discuss estimates of the time scale upon which the dynamics takes place. Two simple estimates are obtained on the basis of the ergodic properties and found to be reasonably accurate for the Barbanis system.

274. A Quantum Ergodic Theory Approach to Unimolecular Fragmentation. With Sture Nordholm. *J. Chem. Phys.* 62, 157 (1975).

Projection operator techniques are used to separate the complete Hilbert space of a molecular system into parts corresponding to bound and continuum states. The equation of motion of the amplitude associated with an initial excitation of the molecule is then formulated; this equation of motion contains memory effects. Although formally exact, its utility lies in the approximations suggested by its structure. Drawing on recent studies of intramolecular relaxation, a Markovian approximation is formulated and the properties of the model so defined investigated by numerical solution. The decay rate for the model is found to depend strongly upon the nature of the initial excitation, and to correlate with the ergodicity or lack of ergodicity of the initial excitation. When the prepared state is nonergodic, or nearly so, there is a delay in the decay of the molecule. When the state initially prepared is ergodic, there is not such delay. Intermediate cases are also found. It is argued that the formal analysis permits the development of better models and of more sophisticated treatments of the competition between intramolecular relaxation and molecular fragmentation, but that the simple model discussed contains the qualitative elements of importance in such processes.

277. Stabilization of a Mode-Locked Nd: Glass Laser by Intracavity Second-Harmonic Generation. With R. Bruce Weisman. *Spectroscopy Letters*, 8(5) 329 (1975).

A method is described for generating stabilized, intensity-limited pulse-trains from a mode-locked Nd:glass laser with internal second-harmonic generation.

279. Angular Momentum Conservation in Photochemical Fragmentation: A Simple Model. With Donald Florida. *Chem. Phys. Letters* 33, 207 (1975).

The role of conservation of angular momentum in a photofragmentation reaction involving a large change in molecular geometry between reactants and products is discussed in terms of a simple model.

286. Nonlinear Resonance and Stochasticity in Intramolecular Energy Exchange. With David W. Oxtoby. *J. Chem. Phys.* In press.

The dynamics of intramolecular vibrational energy transfer is studied, with particular reference to its effect on the unimolecular dissociation rates of isolated molecules. The molecule is represented as a set of classical, coupled, nonlinear (anharmonic) oscillators which transfer energy through resonant interactions. We suggest that isolated nonlinear resonances (which predominate at low energies) lead to trapping of the vibrational energy of the system, hence to slow vibrational relaxation, while resonance overlap at higher energies leads to rapid energy exchange and the random lifetime distribution assumed by RRKM theory. Results are presented for some simple model systems, and the approach is compared with other recent theoretical descriptions of vibrational relaxation in isolated molecules.

290. Tunable Infrared Ultrashort Pulses From a Mode-Locked Parametric Oscillator. With R. Bruce Weisman. *Optics Communications*, in press.

Mode-locked parametric oscillation has been achieved. A single resonant non-collinear LiIO_3 oscillator is synchronously pumped by the second-harmonic from a passively mode-locked, amplified Nd:glass laser. We observed conversion efficiencies in the range of several percent. The intense picosecond infrared output of this device is tunable from 1.4 to 3.8 μm and surpasses single-pass parametric generators in spectral and spatial purity.

294.* Reactions Induced by Incoherent Multiphoton Absorption. With Joshua Jortner.

A mechanism is proposed for the multiphoton induced photochemical reactions described by Dever and Grunwald. The mechanism relies on destruction of phase coherence by collisions such that multiphoton absorption becomes incoherent. When this conditions is satisfied, off-diagonal elements of the Master Equation can be neglected, and it is shown that the conversion to products per laser pulse has the form

$$\ln(CPF) = \ln A - E_{act} / E_{abs}$$

with E_{abs} the energy absorbed per molecule and E_{act} the activation energy. This result implies localization of the excitation energy in the oscillator pumped for the duration of the laser pulse. The form shown is in agreement with the observations by Dever and Grunwald.

243.** Spectroscopic Properties of Polyenes I. The Lowest Energy Allowed Singlet-Singlet Transition for Cis and Trans-1,3,5-Hexatriene. With R. M. Gavin, Jr., and Salomon Risemberg. J. Chem. Phys. 58, 3160 (1973).

The absorption spectra of cis- and trans-1,3,5-hexatriene are reported for the region of the first allowed singlet-singlet electronic transition, 2600 to 2100 Å.

A least squares procedure in which a Lorentzian line shape is assumed for each band was used to fit the spectra. Progressions are found of 408, 1262 and 1626 cm^{-1} for the cis isomer and of 350, 1232, and 1628 cm^{-1} for the trans isomer. The 0-0 transition for the cis compound, 39668 cm^{-1} , lies about 130 cm^{-1} lower than that for the trans, 39800 cm^{-1} . The fact that the 0-0 transition energy for cis is less than that for trans is interpreted as evidence that the cis isomer has a non-planar geometry in the electronic ground state. The extinction coefficient for the 0-0 band of the trans isomer is about 1.5 times that for the cis.

* to be submitted to J. Chem. Phys. ** This listing is out of order through an oversight.

Papers by Postdoctoral Research Associate Eric J. Heller.

1. Time Dependent Approach to Semiclassical Dynamics. *J. Chem. Phys.* 62, 1544 (1975)

In this paper we develop a new approach to semiclassical dynamics which exploits the fact that extended wavefunctions for heavy particles (or particles in harmonic potentials) may be decomposed into time-dependent wave packets, which spread minimally and which execute classical or nearly classical trajectories. A Gaussian form for the wave packets is assumed and equations of motion are derived for the parameters characterizing the Gaussians. If the potential (which may be nonseparable in many coordinates) is expanded in a Taylor series about the instantaneous center of the (many-particle) wave packet, and up to quadratic terms are kept, we find the classical parameters of the wave packet (positions, momenta) obey Hamilton's equation of motion. Quantum parameters (wave packet spread, phase factor, correlation terms, etc.) obey similar first order quantum equations. The center of the wave packet is shown to acquire a phase equal to the action integral along the classical path. *State-specific quantum information is obtained from the wave packet trajectories* by use of the superposition principle and projection techniques. Successful numerical application is made to the collinear He + H₂ system widely used as a test case. Classically forbidden transitions are accounted for and obtained in the same manner as the classically allowed transitions; turning points present no difficulties and flux is very nearly conserved.

2. Variational Correction to Wigner R-Matrix Theory of Scattering. With David J. Zvijac, and John C. Light. *J. Phys. B: Atom. Molec. Phys* 8, 1016 (1975).

Three stages in the development of R-matrix scattering theory are discussed. The standard calculation using N basis functions is variationally stable in the N -dimensional basis space, yet results often converge slowly with increasing N . As an improvement the Hamiltonian is separated into two parts, a soluble H^0 and a potential V . The Buttle correction is used to account for H^0 exactly. This is equivalent to solving the approximate Hamiltonian $H^0 + V^N$ where V^N is an $N \times N$ matrix approximation to V . The exact solution to the approximate Hamiltonian The exact solution to the approximate Hamiltonian may be considered as a trial wavefunction for the full Hamiltonian H . The major topic of this paper deals with the problem of obtaining scattering information from this

trial wavefunction which is variationally stable against arbitrary variations, as opposed to variations in a finite trial space. Using the variational procedure given here, significant improvement over the N-term variational and Buttle corrected R-matrix results is found for a model inelastic system studied by Secrest and Johnson.

3. Wavepacket Path Integral Formulation of Semiclassical Dynamics. *Chemical Physics Letters* 34, 321 (1975).

The "quantum trajectory" wavepacket approach to semiclassical collision dynamics is generalized to include effects which cause distortion of initially gaussian wavepackets. The generalization takes the form of a discrete phase space path "integral" or sum. A complete set of gaussian phase space localized basis functions is proposed, and in the semiclassical limit, each basis function time develops in a simple classical-like fashion. Thus, the formulation conveniently builds in the correct limiting semiclassical behavior.

4. Theory of J-Matrix Green's Functions with Applications to Atomic Polarizability and Phase Shift Error Bounds. *Phys. Rev. A* 12, 1222 (1975).

The recently introduced Jacobi or J-matrix techniques for quantum scattering are developed to include the construction of exact analytic matrix elements of regular and Coulomb partial wave zeroth order and full Green's functions. Very simple results obtain for the unperturbed Green's functions, while full Green's functions require a single diagonalization of an $N \times N$ Hamiltonian matrix, where N is the number of basis functions coupled by the matrix truncated potential. In an application of the J-matrix Green's functions to the theory of atomic dynamic polarizabilities, the analytic result for hydrogen is derived, and it is shown how more general systems may be treated in a way which is superior to the usual N-term variational approach. In an application to error bounds for phase shifts, we show how the full Green's functions can be used to demonstrate the absence of false pseudoresonances in J-matrix scattering calculations, and bound the possible errors in computed phase shifts.

Publications

- 1.* A Study of Primary Photochemical and Photophysical Processes in Chloro- and Bromoacetylene. With Keith Evans, Richard Scheps and Donald Heller. *Faraday Society II*, 69, 856 (1973).
- 2.* Spectroscopic Properties of Polyenes I. The Lowest Energy Allowed Singlet-Singlet Transition for Cis and Trans-1,3,5-Hexatriene. With R. M. Gavin, Jr., and Salomon Risemberg. *J. Chem. Phys.* 58, 3160 (1973).
- 3.* Substitution Reactions of Fluorine Atoms with Unsaturated Hydrocarbons: Crossed Molecular Beam Studies of Unimolecular Decomposition. With John M. Parson, Kosuke Shobatake and Yuan T. Lee. *Disc. Far. Soc.* 55, 344 (1973).
- 4.* Unimolecular Decomposition of the Long-Lived Complex Formed in the Reaction $F + C_4H_8$. With John M. Parson, Kosuke Shobatake and Yuan T. Lee. *J. Chem. Phys.* 59, 1402 (1973).
- 5.* The Unimolecular Decomposition of Long-Lived Complexes of Fluorine and Substituted Mono-Olefins, Cyclic Olefins and Dienes. With Kosuke Shobatake, Yuan T. Lee and John M. Parson, *J. Chem. Phys.* 59, 1416 (1973).
- 6.* The Laboratory Angular Dependence and the Recoil Energy Spectrum of the Products of the Reaction $F + C_6D_6 \rightarrow D + C_6D_5F$. With Kosuke Shobatake, John M. Parson and Yuan T. Lee. *J. Chem. Phys.* 59, 1427 (1973).
- 7.* The Reactions of F Atoms and Aromatic and Heterocyclic Molecules: Energy Distribution in the Reaction Complex. With Kosuke Shobatake and Yuan Lee. *J. Chem. Phys.* 59, 1435 (1973).
- 8.* Intramolecular Vibrational Energy Transfer: A Study of Representations. With Kenneth G. Kay. *J. Chem. Phys.* 58, 4852 (1973).
- 9.* Comment on "Decay of Fluorescence from Single Vibronic Levels of SO_2 ." With Man Him Hui. *Chem. Phys. Letters*, 20, 411 (1973).
- 10.* An ITFITS Model for Vibration-Translation Energy Partitioning in Atom-Polyatomic Molecule Collision. With K. Shobatake and Yuan T. Lee. *J. Chem. Phys.* 59, 2483 (1973).
- 11.* A Crossed Molecular Beams Study of the Reaction $F + C_2H_2Cl_2 \rightarrow Cl + C_2H_2ClF$. With Kosuke Shobatake and Yuan T. Lee, *J. Chem. Phys.* 59, 6104 (1973).

- 12.* Influence of Large Amplitude Vibrational Motion on the Rate of Intersystem Crossing: A study of Single Vibronic Level Fluorescence From Aniline- h_7 , Aniline-N, N- d_2 and Aniline- d_5 . With Richard Scheps and Donald Florida. *J. Chem. Phys.* 61, 1730 (1974).
- 13.* Some Comments on the Dynamics of Primary Photochemical Processes. In *Advances in Electronic Excitation and Relaxation, Volume II*, edited by Edward C. Lim (Academic Press, New York) pp 111 - 320 (1975).
- 14.* Comments on the Spectrum and Photophysical Properties of Trimethylene-Cyclopropane. With Ernest A. Dorko and Richard Scheps. *J. Phys. Chem.* 78, 568 (1974).
- 15.* Quantum Ergodicity and Vibrational Relaxation in Isolated Molecules. With K. Sture J. Nordholm. *J. Chem. Phys.* 61, 203 (1974).
- 16.* Intramolecular Energy Transfer in Cis-Trans Isomerization: A Study of Fluorescence from Single Vibronic Levels of Styrene, trans - Styrene- d_1 , Styrene- d_8 , and Ethynlbenzene. With Man Him Hui. *J. Chem. Phys.* 61, 833 (1974).
- 17.* Nonradiative Processes in p- $C_6H_4F_2$ and m- $C_6H_4F_2$. With Charles Guttman. *J. Chem. Phys.* 61, 661 (1974).
- 18.* Fluorescence Lifetimes of Individual Vibronic Levels of Partially Deuterated Benzenes: A Further Test of the Theory of Radiationless Processes. With Charles Guttman. *J. Chem. Phys.* 61, 651, (1974).
- 19.* 2,3-Naphtho-2,5-bicyclo [2.20] hexadiene. With N. C. Yang, Richard V. Carr, Ellen Li, Jeffrey K. McVey. *J. A. C. S.* 96, 2297 (1974).
- 20.* Random Coupling Model for Molecular Dissociation. With Eric J. Heller. *J. Chem. Phys.* 61, 936 (1974).
- 21.* Quantum Ergodicity and Vibrational Relaxation in Isolated Molecules II - Independent Effects and Relaxation to the Asymptotic Limit. With Sture Nordholm. *J. Chem. Phys.* 61, 768 (1974).
- 22.* A Quantum Ergodic Theory Approach to Unimolecular Fragmentation. With Sture Nordholm. *J. Chem. Phys.* 62, 157 (1975).
- 23.* Stabilization of a Mode-Locked Nd: Glass Laser by Intracavity Second-Harmonic Generation. With R. Bruce Weisman. *Spectroscopy Letters*, 8(5) 329 (1975).
- 24.* Angular Momentum Conservation in Photochemical Fragmentation: A Simple Model. With Donald Florida. *Chem. Phys. Letters.* 33, 207 (1975).

25. Nonlinear Resonance and Stochasticity in Intramolecular Energy Exchange. With David W. Oxtoby. *J. Chem. Phys.* (submitted).
26. Tunable Infrared Ultrashort Pulses From a Mode-Locked Parametric Oscillator. With R. Bruce Weisman. Submitted to *Optics Communications*.
27. Reactions Induced by Incoherent Multiphoton Absorption. With Joshua Jortner. (to be submitt to *J. Chem. Phys.*)

Papers by Postdoctoral Research Associate Eric J. Heller.

1. * Time Dependent Approach to Semiclassical Dynamics. *J. Chem. Phys.* 62, 1544 (1975).
2. * Variational Correction to Wigner R-Matrix Theory of Scattering. With David J. Zviljac and John C. Light. *J. Phys. B: Atom. Molec. Phys.* 8, 1016 (1975).
- 3.* Wavepacket Path Integral Formulation of Semiclassical Dynamics. *Chemical Physics Letters* 34, 321 (1975).
4. Theory of J-Matrix Green's Functions with Applications to Atomic Polarizability and Phase Shift Error Bounds. *Phys. Rev. A.* 12, 1222 (1975).

* Copies of reprints have been sent. Others will be sent when available.

COMPLETED PROJECT SUMMARY

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1. TITLE: Experimental and Theoretical Studies in Photochemistry
2. PRINCIPAL INVESTIGATOR: Stuart A. Rice
3. SENIOR RESEARCH PERSONNEL

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