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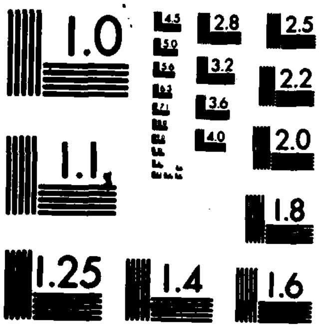

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Princeton University

Department of Chemistry

Herschel Rabitz

Final Technical Report

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STUDIES IN NON-EQUILIBRIUM STATISTICAL MECHANICS

for the period 30 Sep 1978 - September 29, 1982

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The research accomplished under the stated contract is summarized with work performed in the following primary areas.

1. Stochastic dynamics;
2. Sensitivity analysis
3. Collisional scaling theories;
4. Quantum collision dynamics.

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I. Background of Accomplished Research

The research aimed to study a closely related set of techniques and problems in the area of molecular dynamics at both the microscopic and macroscopic scales. The aim of the research was to achieve a fundamental understanding of reactive and non-reactive chemical dynamics. This information is of fundamental importance in molecular physics and chemistry as well as being central to engineering design studies of many practical devices. The research was focused on discerning the fate of excited molecules, particularly in the gaseous medium. Such molecules could react or transfer their excitation to other molecules upon collisional impact. In addition, an excited polyatomic molecule could undergo self-relaxation or scrambling of its internal energy even without a collision. Recognizing these needs the theoretical research consisted of two broad classes of approach to these problems. First, ab initio or first principles techniques were developed and exploited to calculate observable dynamic and kinetic phenomena ultimately starting with a system hamiltonian. Secondly, appropriate theoretical techniques were developed to aid in the inversion of laboratory data back to more fundamental dynamical information. The research in these two distinct approaches benefited from accomplishments in each area. The varied nature of the research necessitated a multi-faceted approach involving quantum dynamics, stochastic theory, phenomenological kinetics, sensitivity analysis, scaling theoretical techniques and general quantum methodology. The overall research consisted of developmental effort as well as implementation of the theory for practical problems. Outlined below are the specific areas of research and progress in this contract.

II. Itemized Research Summary.

A. Stochastic Theory.

1. Stochastic Theory for Molecular Collisions: Application to the CO-He System[1].

Vibration-rotation inelasticity in the CO-He collision system is studied within the stochastic formulation. Cross sections are obtained for purely rotational transitions using a modified electron gas potential. Vibration-rotation cross sections have been calculated in the energy range $2200\ \mathrm{cm}^{-1} < E < 4000\ \mathrm{cm}^{-1}$. At the higher energy, a total of 76 molecular states are energetically accessible. A comparision with earlier result is made, and coarse graining techniques for the treatment of large problems are utilized.

2. Stochastic Theory of Intramolecular Energy Transfer in the Presence of Radiation[2].

A theory for internal energy redistribution in polyatomic molecules perturbed by strong radiation fields was constructed. Use was made of stochastic theory, which assumes that a random phase approximation is valid after appropriate time intervals. This approximation permits the Schrodinger equation to be replaced with a finite-difference master equation for the probabilities of occupying the various quantum levels. The semiclassical theory of the radiation-molecule interaction is employed in this work. A laser line profile is incorporated in the formalism, and this is used to simulate the effects of rotational states and collisions. At each stochastic step the energy changes in the molecules due to radiation are estimated. Thus, energy conservation is explicitly taken into account. Model calculations for SO_2, whose transition dipole moment matrix elements and anharmonic force constants have been determined, indicate a complex interplay of anharmonic and radiative coupling. Power density, laser linewidth, and detuning from resonance are observed to play a significant role in energy redistribution.

3. Stochastic Theory of Intramolecular Vibrational Energy Redistribution and Dissociation in the Presence of Radiation[3].

A theory for internal vibrational energy redistribution and dissociation in polyatomic molecules in the presence of a strong radiation field is formulated. The fundamental assumption is that a random phase approximation is valid at specific time intervals. This results in the replacement of the Schrodinger equation by a master-type equation, which is further approximated by a Fokker-Planck diffusion like equation. Energy transfer is described as a flow of probability among the quantum states, and the dissociation dynamics are embodied in the boundary conditions. By virtue of the continuous character of the Fokker-Planck equation, the computational difficulty of its numberical solution depends only on the number of degrees of freedom and not on the number of states. Due to the high density of levels encountered in a polyatomic molecule, this is of paramount importance in reducing the problem to a manageable size. A multiple time scale stochastic formulation, which allows for a mixed quantum-stochastic approach, is also described. No assumptions regarding the strength of the intramolecular coupling are made, and energy conservation is specifically enforced. The coefficients of the Fokker-Planck equation are shown to be expressible in terms of simple functions of the molecular potential, which involve raising and lowering operators. Finally, the coefficients of the Fokker-Planck equation are calculated using the best available potential information for the case of the ozone molecule in a strong infrared laser field, and their physical significance is discussed. Figures (1) and (2) depict, respectively, the two convective and diffusive coefficients for ozone.

B. Sensitivity Analysis

4. Chemical Sensitivity Analysis Theory with Applications to Molecular Dynamics and Kinetics[4].

This paper presents an overview of sensitivity analysis theory for application to chemical problems. The generality of the concept is emphasized with illustrative examples from molecular collision dynamics and chemical kinetics. The article aims to bring sensitivity concepts to the attention of the chemical community, and in this regard, the paper does not cover extensive algorithmic

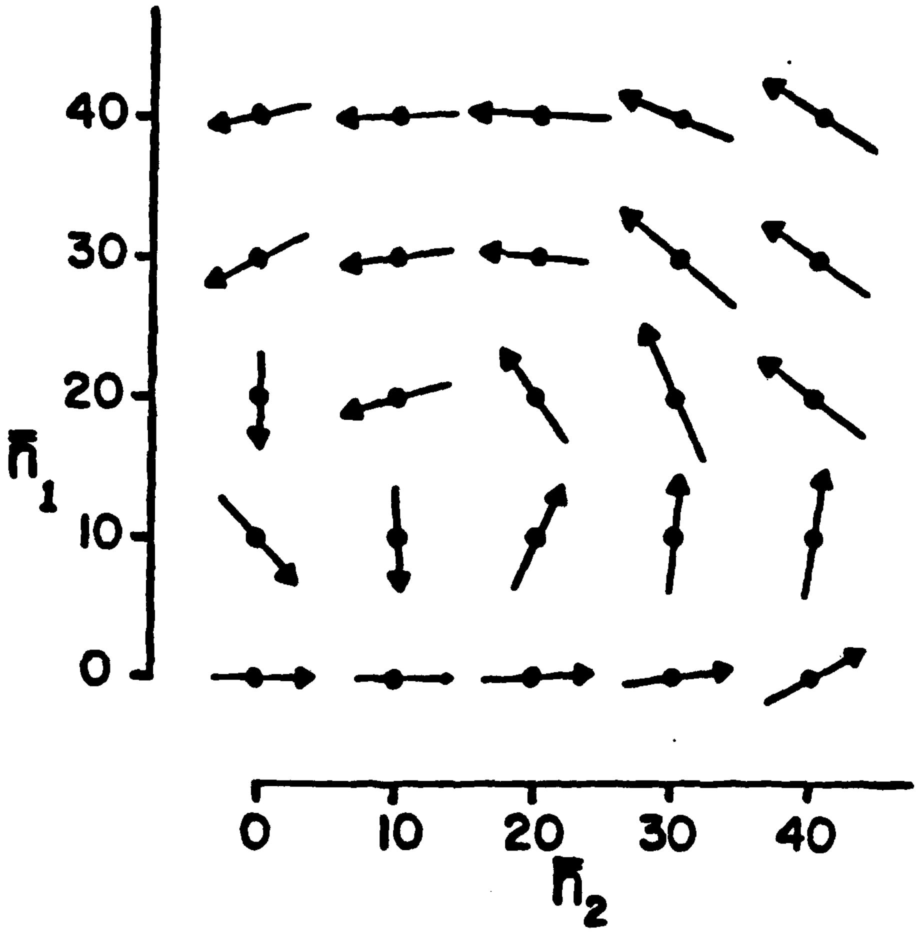

FIGURE 1.

Vector field plot of the negative of the first convective Fokker-Planck coefficient for the *ozone* molecule as a function of the degree of excitation in the first and second modes, $\bar{n}_1$ and $\bar{n}_2$. The third mode is kept at the local direction of convective flow of probability. The length of the arrows indicates their relative logarithmic magnitude. The numbers on the axes are normal mode quantum numbers, and the grid points are every ten quantum numbers. The laser width is 20 cm^{-1}, the intensity 8 GW/cm^2, and the frequency 700 cm^{-1}.

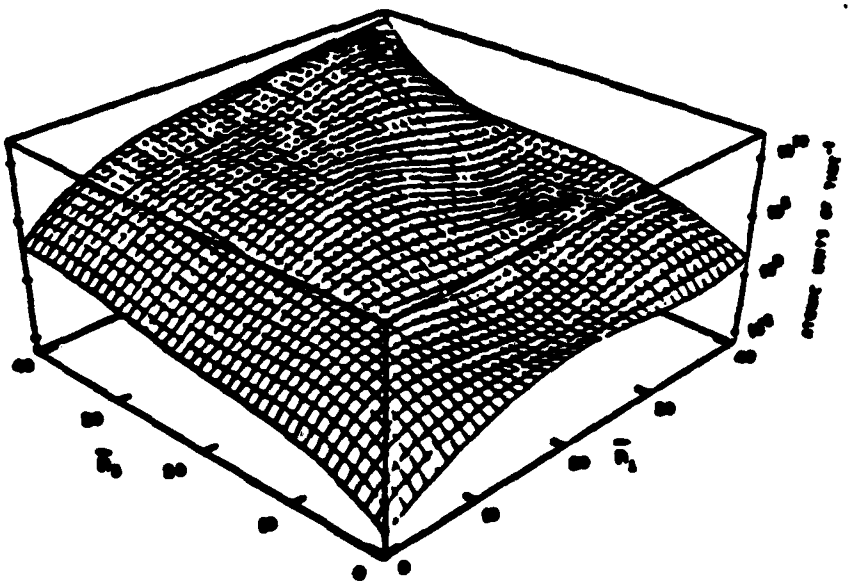

FIGURE 2

The magnitude of the probability diffusion coefficient for the ozone molecule as a function of degree of excitation for two degrees of freedom. The other degree of freedom is kept at the ground state. A biquadratic interpolation was done between grid points. The laser width is 20 cm^{-1}, the intensity 8 GW/cm^2, and the frequency 1150 cm^{-1}.

details which are available in the cited literature. It is shown that sensitivity methods have wide application in fundamental as well as practical problems in numerical modelling and the theory can quantitatively address a host of physical and chemical questions heretofore difficult to treat. Figure (3) depicts the general relationship of sensitivity analysis, modelling and laboratory measurement.

5. Chemical Kinetic Functional Sensitivity Analysis: Elementary Sensitivities[5].

Sensitivity analysis is considered for kinetics problems defined in the space-time domain. This extends an earlier temporal Green's function method to handle calculations of elementary functional sensitivities $\delta u_i/\delta\alpha_j$ where u_i is the i-th species concentration and α_j is the j-th system parameter. The system parameters include rate constants, diffusion coefficients, initial conditions, boundary conditions, or any other well-defined variables in the kinetic equations. These parameters are generally considered to be functions of position and/or time. Derivation of the governing equations for the sensitivities and the Green's function are presented. The physical interpretation of the Green's function and sensitivities is given along with a discussion of the relation of this work to earlier research.

6. Computational Kinetics and Sensitivity Analysis of Hydrogen-Oxygen Combustion[6].

Kinetic modelling calculations on the H_2-O_2 system have been carried out with an extensive reaction set to probe the vicinity of the three explosion limits. Sensitivity analysis is used throughout this investigation to study system behavior, in particular, to elucidate mechanistic details. The concentrations and sensitivity profiles are discussed in light of the appropriate experimental results and existing theories of hydrogen combustion. The results indicate the present model to be useful over a wide pressure-temperature range. The reaction set is also used to probe the sensitivities for an experimental

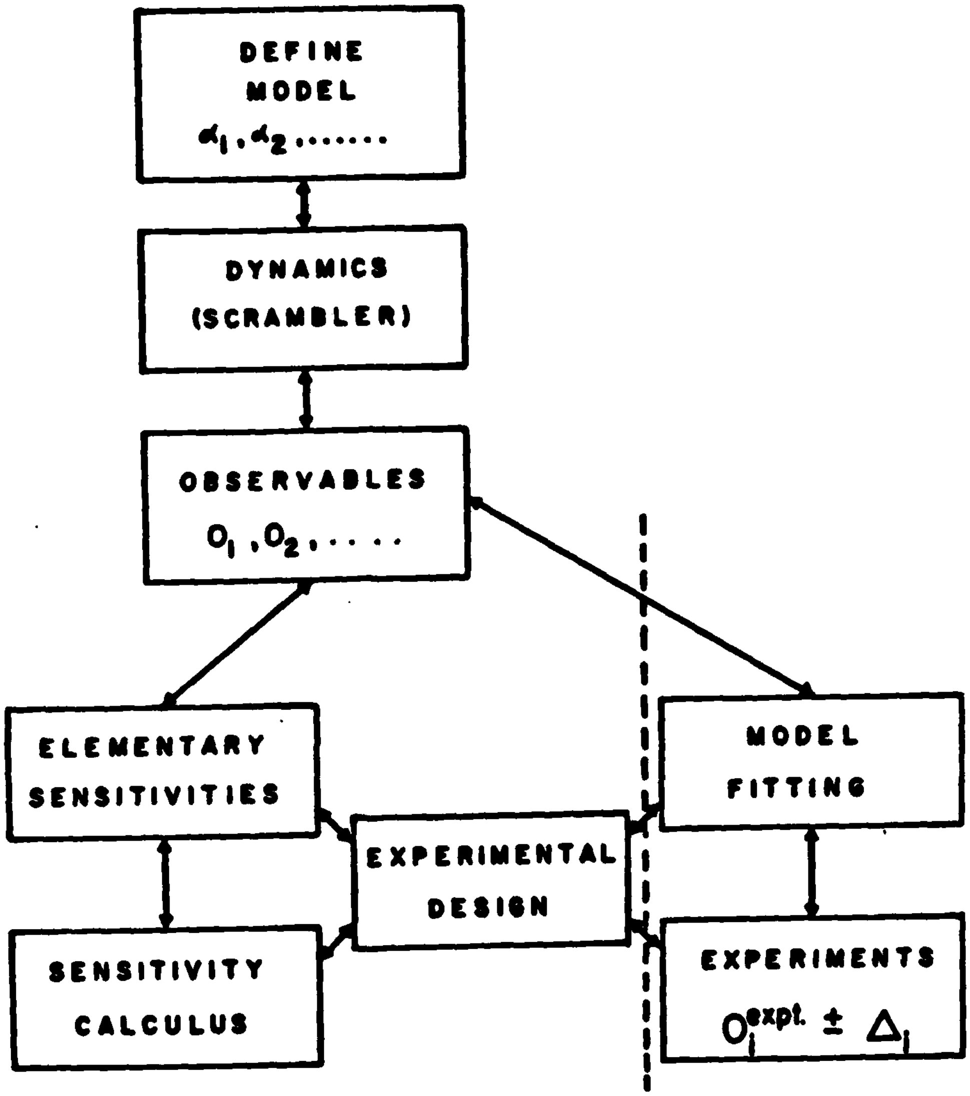

FIGURE 3

Block diagrammatic representation of the relationship bewteen modelling, sensitivity analysis and laboratory measurements. The vertical line indicates a separation between the experimental and theoretical aspects of a problem.

study designed to measure the rate constant of an important elementary reaction, $H + O_2 + M \rightarrow HO_2 + M$, involved in this system. The versatility of the reaction set is also demonstrated by a study of a related chemical reaction, the decomposition of hydrogen peroxide. Finally, prospects for utilizing the methods and results of this study to examine other complex kinetic schemes are discussed.

7. Further Developments and Applications of the Green's Function Method of Sensitivity Analysis in Chemical Kinetics[7].

A numerical procedure is presented for implementing the Green's function method of sensitivity analysis in chemical kinetics. The procedure is applied to three sets of chemical reactions: the Chapman mechanism for ozone kinetics, a mechanism for methane combustion and a model for formaldehyde oxidation in the presence of carbon monoxide. Whenever possible, comparisons with alternative methods of sensitivity analysis are made. It is shown that carefully analyzed sensitivity profiles can be used in conjunction with experiments and/or models to obtain useful information about chemical kinetic behavior. By using methods from multivariable calculus an entire family of sensitivity coefficients may be derived from the elementary sensitivities obtained by solving differential equations. Each elementary or derived sensitivity coefficient has a unique physical interpretation in terms of an experiment or modelling calculation. A simple non-linear interpolation formula is suggested for easily estimating higher-order sensitivity information. Finally, the overall computational efficacy of the Green's function method of sensitivity analysis is assessed.

C. Collisional Scaling Theory

8. A Further Analysis of V-V Transfer Rates for High-Lying States of CO[8].

This paper was a note concerning a comment of Brechignac about the importance of multi-quanta V-V rates [illegible] O. [illegible] argue that the presently available data are inconclusive about the issue, but such processes will certainly play a role at sufficiently high quantum levels.

9. A Rapidly Convergent Expansion Technique for Local Quantum Mechanical Operators[9].

A general technique is described for efficiently expanding quantum mechanical operators. The basis is a particular set of wave functions and the expansion coefficients are physically meaningful matrix elements of the operator. Two applications to molecular properties, the transition dipole operator and the anharmonic force field, are discussed. We demonstrate that the entire force field can be expressed exactly in terms of anharmonic perturbations of the ground state, and that a great deal of information can be easily obtained from the spectroscopic frequencies. Similarly, the dipole moment matrix elements in any vibrational band are shown to be given in terms of a sum of only the R(1) matrix elements for various vibrational levels. Numerical results are presented for HCl rotational line strengths. These applications are only two examples of the potential experimental and theoretical uses of this method.

10. A Scaling Theoretical Analysis of Vibrational Relaxation Experiments: Rotational Effects and Long-Range Collisions[10].

Expressions for the quantum number scaling of vibration-translation (V-T) and vibration-vibration (V-V) rates are derived. The derivation uses the recently developed scaling theory of non-reactive processes and invokes the assumption of rotational equilibrium. However, the V-V and V-T scaling relationships include rotational effects through the rotational energy gaps and the rotational distributions. The variables in this theory are a fundamental set of rates and the average collision range, ℓ_c, for the particular inelastic process. The physically transparent meaning of these variables, combined with the a priori nature of the scaling coefficients, allows one to investigate actual dynamical effects and not just merely fit data. A detailed analysis of V-V energy transfer in the CO-CO system is presented. Three conclusions are drawn: (1) rotational effects are crucially important in the scaling of the rates (2) the process is predominantly long-range with $\ell_c = 5.5 \pm 0.5$ au and, (3) the available experimental data is consistent with single quanta vibrational changes in the V-V rates.

11. On the Correlation of Rotationally Inelastic Rates: A Scaling Theoretical Analysis[11].

The recently measured rates for the rotationally inelastic process $(A^1\Sigma_u)Na_2(j) + Xe \rightarrow (A^1\Sigma_u)Na_2(j') + Xe$ are analyzed and correlated with a scaling theory that explicitly accounts for the adiabaticity of the collision. A brief discussion of previous scaling theories (which neglect this effect) is presented. Figure (4) shows the excellent quality of the scaling results in relation to available experimental data.

12. The Initial Value Representation (IVR) for Three-Dimensional Scattering Problems[12].

In this paper, we describe a new family of local integral representations for S-matrix elements. Although the historical origins of the IVR are in stationary phase semiclassical mechanics, we will show that it can be valid when the stationary phase approximation is inappropriate. Quantum mechanical corrections to the original form of IVR are included by transforming to a representation in terms of conventional coordinates. For a simple collinear model problem, we demonstrate that this new conventional coordinate IVR is in exact agreement with the known quantum mechanical results. In the case of atom-rigid rotor scattering, the IVR can be cast as a one-dimensional integral analogous to the infinite order sudden (IOS) result. Calculations of rotational inelasticity for the $He\text{-}H_2$ system are presented. The IVR cross sections are significantly better than the IOS values at low collision energies without requiring a substantial increase in computational effort.

13. Scaling Relations for Inelastic Collision Data Obtained from the Initial Value Representation (IVR)[13].

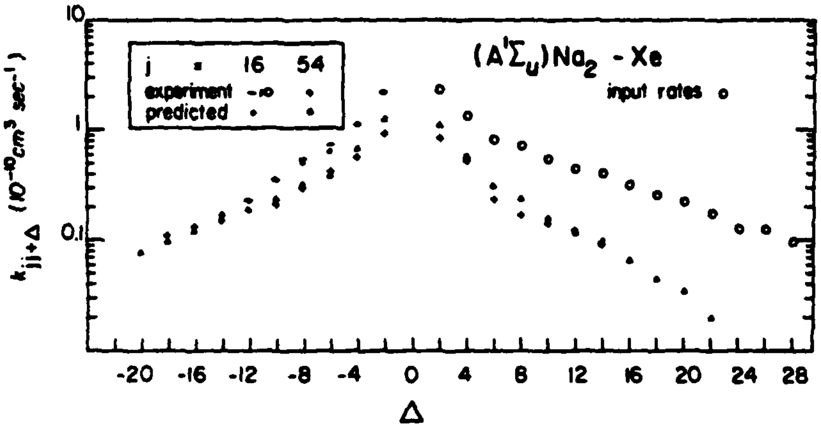

FIGURE 4

Scaling predicted and experimental rates: The rates $k_{16\ 16+\Delta}$(○) are used to determine the scaling coefficients. The resultant scaling predicted rates $k_{54j'}$(▲) and $k_{16\ 16-\Delta}$(●) agree with the corresponding experimental values $k_{54j'}$(+) and $k_{16\ 16-\Delta}$(-) within the experimental uncertainty.

In this paper we have developed scaling relations for inelastic collision data based upon the IVR, an approximation which is accurate in both the sudden and adiabatic limits. We have used this to obtain connections between S-matrix elements at either the same kinetic energy or the same total energy. The constant kinetic energy scaling has the same overall form as the earlier energy corrected sudden (ECS) theory, but with different adiabaticity factors. In a practical application these factors may be obtained from a knowledge of the scattering potential or else from model collision lifetime functions, examples of which are presented in this work. The IVR scaling theory reduces the importance of multiquanta transitions relative to the ECS result, and it also provides an adiabatic correction to the phases of the S-matrix elements. Numerical calculations for a collinear oscillator problem are given as a test of the total energy scaling relations.

D. Quantum Collision Dynamics

14. Action-angle Variables for the Quantum Three Particle System[14].

This paper uses the newly developed quantum action-angle variable formalism to reduce the Schrodinger equation for the three atom system to a minimum number of coordinates. A transformation is also presented which converts the operator to a form amenable to conventional direct numerical integration techniques. Computational considerations relevant to the application of finite elements are discussed, and these are illustrated with a numerical calculation of the quantum energy levels of a rigid asymmetric rotor. The ordinary differential equation which is derived for the last problem permits an unambiguous assignment of the correct expression for the total angular momentum, and the result is different from that used in previous semiclassical calculations.

15. Action-angle Variables in Quantum Mechanics[15].

Conventional quantum mechanical treatments of many systems have worked with coordinates and moments that are not canonically conjugate. In this work it is shown how the quantum expressions may be reformulated in terms of the canonical set of action-angle variables, and specific examples of the harmonic oscillator, linear rotor, and triaxial rotor are presented. When expressed in these terms, the quantum mechanics take on a form which can be directly related to analogous results from classical mechanics. In addition, it becomes possible to express the Hamiltonian in the minimum number of coordinates. It is also shown that the common assumption of an exponential form for the overlap of canonical coordinate and momentum eigenstates is false for an asymmetric rotor. This has important implications for the quantization rules applicable to nonseparable systems.

16. Vibrational and Rotational Collision Processes[16].

This paper was a review article covering recent work on inelastic molecular collisions. The emphasis was on new techniques and wherever possible we projected ahead to new directions for active research.

17. Numerical Methods for Solving Time-Dependent Quantum-Mechanical Problems with Applications[17].

Two numerical techniques which can be applied to time-dependent quantum-mechanical problems are described and compared with a predictor-corrector-type method. The first method, the piecewise Magnus solution, provides an approximate solution with the exact Hamiltonian by using the first Magnus approximation over many time intervals. The second approach, the piecewise analytical solution, produces the analytical solution to an approximate Hamiltonian obtained by ignoring off-diagonal elements within each small time interval. Several illustrative model problems are reported in which the speed and accuracy of these procedures were compared with a standard Gear package. Included in these examples is the physically interesting problem of using the stimulated Raman effect to produce selectively excited molecules. Within this problem the quality of the rotating wave approximation is tested. In cases with highly oscillatory wavefunctions, it was found that the piecewise solution methods performed well while the Gear program was incapable of providing a reliable solution. Figure (5) shows the Raman arrangement, and the predictions from the theory have formed the basis of a set of experiments underway at Princeton to see their effect in O_2. The excited $O_2(v >> 1)$ will be used to react with various hydrocarbons.

18. A Localized Integral Equation Formulation of Molecular Scattering[18].

A new integral equation formulation is presented for molecular scattering. This is obtained by exactly transforming the common close-coupling theory into an equivalent nonlocal integral equation form which is not a set of coupled discrete basis equations. The integral equation if formally localized by the introduction of a translation operator, thereby leading to a Hamiltonian (or portion of it) that is a Fourier transform of the original kernel. The theory makes no use of Green's functions and this overall approach has two attractive features. Firstly, an examination of the integral kernels allows the development of optimal quadrature schemes for each problem and, secondly, judicious approximations of the localized Hamiltonian operator lead to very attractive practical equations. As an illustration of the latter point, the method is applied to replace the differential internal Hamiltonian operator by an effective local function which can act to correct the usual sudden approximation without excess computational effort. Various asymptotic limits of the theory are also discussed.

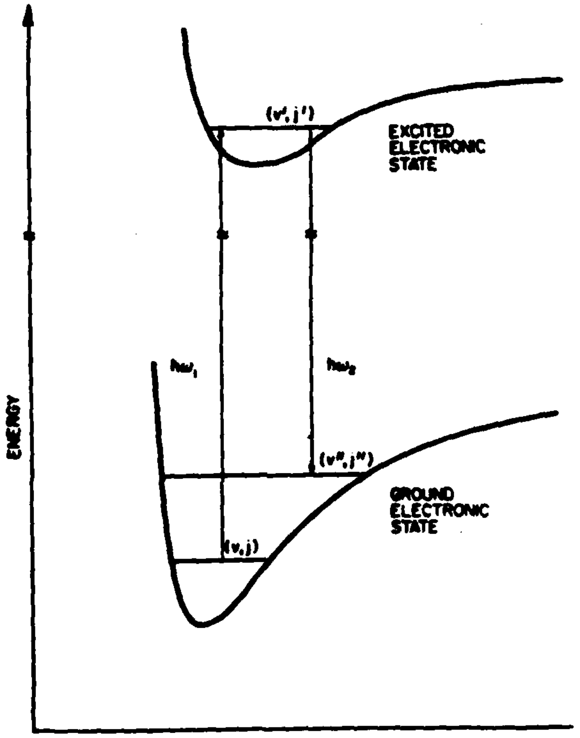

FIGURE 5

Schematic representation of the stimulated resonance Raman process with two lasers of frequency ω_1 and ω_2. Specific resonant vibration-rotation levels are shown.

III. Publications Resulting from this Research.

1. R. Ramaswamy, S. Augustin and H. Rabitz, "Stochastic Theory of Molecular Collisions: Application to the CO-He System", J. Chem. Phys. 70, 2455 (1979).

2. E. Dougherty, S. Augustin and H. Rabitz, "Stochastic Theory of Intramolecular Energy Transfer in the Presence of Radiation", J. Chem. Phys. 74, 1175 (1981).

3. L. Eslava, S. Augustin and H. Rabitz, "Stochastic Theory of Intramolecular Vibrational Energy Redistribution and Dissociation in the Presence of Radiation", J. Chem. Phys., submitted.

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8. A. DePristo and H. Rabitz, "A Further Analysis of V-V Transfer Rates for High-Lying States of CO", Chem. Phys. 62, 243 (1981).

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10. A. DePristo and H. Rabitz, "A Scaling Theoretical Analysis of Vibrational Relaxation Experiments: Rotational Effects and Long Range Collisions", Chem. Phys. 44, 171 (1979).

11. R. Ramaswamy, A. DePristo and H. Rabitz, "On the Correlation of Rotationally Inelastic Rates: A Scaling Theoretical Analysis", Chem. Phys. Lett. 61, 495 (1979).

12. S. Augustin, "The Initial Value Representation (IVR) for Three Dimensional Scattering Problems", J. Chem. Phys. 77, 3953 (1982).

13. S. Augustin, "Scaling Relations for Inelastic Collision Data Obtained from the Initial Value Representation (IVR)", J. Chem. Phys. 78, 206 (1983).

14. S. Augustin, M. Demiralp, H. Rabitz and A. Askar, "Action-angle Variables for the Quantum Three Particle System", J. Chem. Phys. 73, 268 (1980).

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18. S. Saha and H. Rabitz, "A Localized Integral Equation Formulation of Molecular Scattering", J. Chem. Phys. 76, 417 (1982).