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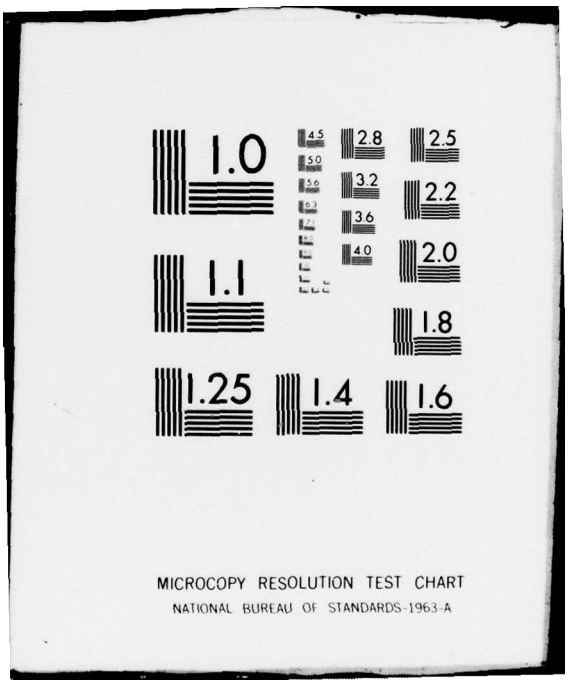
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Department of Chemistry

Progress Report

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STUDIES IN MOLECULAR COLLISION PHENOMENA

for the period

November 1, 1977 - November 30, 1978

Herschel Rabitz
Principal Investigator

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Molecular dynamics studies at Princeton are reviewed. The areas of research involved are:

1. inelastic molecular collisions
2. stochastic theory of molecular dynamics
3. inversion of relaxation data
4. sensitivity theory

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I. Contract Description

The research is concerned with molecular collisions and how they manifest themselves in a variety of physical phenomena. Emphasis is on attaining a better fundamental understanding of molecular dynamics as well as on the study of practical applications.

II. Scientific Problem

The aim of this research is to achieve a detailed understanding of the mechanism of energy transfer and chemical reaction dynamics at a molecular level. This information is essential for engineering design studies of many practical devices as well as being of fundamental concern to molecular physics and chemistry. The research is focused on discerning the fate of excited (particularly vibrationally and rotationally) molecules in a gaseous medium. Such excited 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. The basic computed quantities are rate constants for these processes. A vigorous effort is underway to map out the relationship between the temperature and quantum state behavior of these rate constants and the underlying input forces between the molecules. In addition to achieving a basic theoretical understanding of these processes, the research is being used to provide a framework for the analysis and inversion of appropriate laboratory measurements to yield detailed molecular rate information. Appropriate experimental data has been inverted to yield valuable excited state rate constants.

III. Scientific and Technical Approach

The varied nature of the research has necessitated a multi-faceted approach. For the ab initio calculation of collision dynamics fast and accurate state-of-the-art computational codes have been assembled. This work has been based on the use of effective Hamiltonian theory. In addition, an entirely new stochastic theory applied to molecular dynamics is being developed. This theory is designed to handle the commonly arising cases with many strongly coupled molecular levels. Both inter-molecular and intra-molecular situations are being treated. A general sensitivity theory is being developed to provide for critical parameter analyses in macroscopic kinetics as well as in microscopic molecular processes. The sensitivity theory is based on the use of special Green's function methods, and the method shows promise for application to a number of engineering and chemical physics problems.

IV. Research Progress

Outlined below are the specific areas of progress during the past year. The cited references are to the list of publications resulting from this contract.

1. Generalized effective Hamiltonians: Time scale separation within a semi-classical formalism.[1]

A theory for collision-induced transitions in the subset of quantum states $|a_e\rangle$ was developed, where the full molecular basis is $|a_e\, a_u\rangle$. The only assumption is that changes in a_u occur much more quickly than

those in a_e. The choice of a_e and a_u is in general arbitrary, and it was shown how to make this separation based on the type of experimental measurement under consideration. For example, an evaluation of an atom-vibrotor problem (i.e., $a_e = n$, $a_u = jm_j$) was considered. In conjunction with this illustration an analysis of the breathing sphere (BS) approximation was carried out. It was concluded that a modified BS method (i.e., use of the diagonal rotational potential) should be valid when the random phase approximation holds for the rotational scattering amplitude.

2. Rapid and accurate evaluation of inelastic molecular cross sections.[2]

An inexpensive and accurate technique for computing inelastic cross sections was developed by combining an exponential distorted wave (EDW) approximation and an effective Hamiltonian. This procedure was implemented through the use of uniformized WKB wavefunctions. It was shown to yield cross sections in semi-quantitative agreement with those from exact calculations representing a wide range of physical parameters. The EDW cross sections can be used to compute rate constants since good results are obtained even near threshold. The EDW procedure therefore provides a practical means for studying physical trends in cross sections, rate constants and relaxation.

3. On the use of various scaling theories in the deconvolution of rotational relaxation data: Application to pressure-broadened linewidth measurements.[3]

The inversion of pressure-broadened spectral linewidth data to yield

state-to-state rotationally inelastic rate constants was considered. Deconvolution procedures were presented based on the rate relationships given by information theory (IT), infinite order sudden (IOS), and dynamic coupling theory (DCT) formalisms. In addition, a statistical analysis for the IOS and DCT inversion methods was developed. The three scaling theories were applied to the inversion of experimental data for the CO-He, CO-Ne, HCl-He and HCl-Ne systems. The results indicated that the IT formalism is inappropriate for deconvoluting linewidth data. For the IOS method the extreme sensitivity of the rates to uncertainties in the measurements can often make the extracted rates unreliable. The DCT inversion procedure was shown to be stable and to yield reliable rates. The application of the DCT method to simulated linewidth data for the He-HCN system yielded rates in excellent agreement with ab initio calculated values and correctly predicted the propensity for even rotational changes in this near homonuclear system. The necessary input for an inversion is the width as a function of rotational level. We conclude that accurate linewidth measurements contain a wealth of detailed state-to-state collisional information which can now be obtained directly by use of the DCT inversion technique.

4. Direct inversion of pressure-broadened halfwidths to yield rotationally inelastic rate constants.[4]

The direct extraction of state-to-state rotationally inelastic rate constants $k_{j\to j'}$ from pressure-broadened halfwidth measurements has

generally been considered an intractable problem. In this work two new developments were presented which allow, for the first time, the deconvolution of experimental data to yield the individual rates $k_{j \to j'}$ without recourse to any dynamical calculations. The application of these developments provides for (a) the elimination of the redundancies in the rates, and (b) the assessment of the information content in the experimental data. From an experimental viewpoint the latter condition was shown to imply that the amount of experimental information is directly related to the dependence of the halfwidth on rotational quantum number. Data from the HCl-He, HF-He and HF-Ar systems was used to illustrate these points.

5. The effect of elastic and reorientation collisions on vibration-rotation lineshapes: A semi-empirical approach.[5]

Collisional broadening of rotation-vibration spectral lines was investigated. The contributions from inelastic and elastic-reorientation collisions were separated using a semi-empirical inversion procedure. The basis for this deconvolution was the derivation of a relationship between the inelastic W^{in} and elastic-reorientation W^{el-r} contributions to the width which depends on a single unknown parameter. It was shown that the experimental linewidth $W^{exp} = W^{el-r} + W^{in}$ suffices to uniquely determine this parameter which then is used to calculate the individual components W^{in} and W^{el-r}. Results of applications to the CO-, HF- and HCl-rare gas systems were presented.

6. On the correlation of relaxation data: A scaling theoretical analysis.[6]

The direct inversion of vibration-rotation linewidth data to yield detailed state-to-state information was demonstrated in 3 - 5 above. Central to this procedure is the existence of scaling theories or factorizations that relate different inelastic rates. This present extended work shows that such a scaling relationship has an important additional application as a means of data correlation, reduction and prediction. This method of data analysis has an extremely desirable property: the collisional information is contained in a single column of the physically measured rate matrix. This new methodology was successfully applied to the analysis of recent fluorescence data on the Xe-$Na_2(A\,^1\Sigma_u)$ system.

7. Multiple time scale stochastic formulation for collision problems with more than one degree of freedom.[7]

Individual molecular collisions have been described by non-equilibrium statistical mechanics in our previous work. The present research deals mainly with refinements and extensions of the theory for systems with more than one internal degree of freedom. For example, it was shown how quantum mechanics for one internal mode can be combined with stochastic equations for the other kinds of motion. A multiple time scale stochastic formulation which allows each degree of freedom its own natural time scale was also developed. It was shown, by an application to vibration-rotation inelasticity in the He-H_2

system, that this method gives results in good agreement with full quantum calculations and experimental measurements. A computationally simple technique for restoring microscopic reversibility to time-dependent quantum calculations that employ the classical path formulation was also described.

8. Stochastic theory of intramolecular energy transfer.[8]

The problem of internal energy redistribution in an isolated polyatomic molecule was treated by a stochastic theory approach. The fundamental assumption of this work is that a random phase approximation is valid at specific time intervals. This results in the replacement of the Schrödinger equation by a master equation that governs the evolution of a probability distribution in the quantum levels of the molecule. No assumptions regarding the strength of the coupling are made, and the problem of energy conservation is specifically considered. A stochastic variable is introduced in order to satisfy the requirement that the total energy remain fixed. The further approximation of the master equation by a Fokker-Planck diffusion-like equation was outlined. The latter approach is particularly attractive for treating large molecules. Finally, the master equation was applied to a model problem representing a linearly constrained tri-atomic molecule and the time evolution of an initially localized excitation was discussed.

9. The Green's function method for sensitivity analysis in quantum dynamics.[9]

The Green's function sensitivity method was applied to the Schrödinger equation in order to develop practical methods for calculating sensitivity information in quantum dynamical problems. From molecular collisions it was shown that no additional equations need to be solved in order to calculate sensitivities or partial derivatives of the observable cross sections with respect to input parameters in the Hamiltonian. A similar analysis was carried out for non-scattering systems having time-dependent Hamiltonians. The collision theory was illustrated by a sensitivity analysis on an atom-rigid rotor system. Sensitivity of the cross sections to the potential coupling parameters was studied. A second example considered a collision-free molecular beam entering a region containing arbitrary electric and magnetic fields. The sensitivity of the molecular transition probabilities to the field strengths was studied. Both of these examples yielded unique insight into the underlying dynamical processes.

10. Application and further development of the Green's function method of sensitivity analysis to chemical kinetics.[10]

An efficient numerical procedure was developed to implement the Green's function method of sensitivity analysis for chemical kinetics. The method was applied to three sets of chemical reactions: the Chapman mechanism for ozone kinetics, a mechanism for methane combustion,

and a mechanism for formaldehyde oxidation in the presence of carbon monoxide. Where possible, comparisons with alternative methods of sensitivity analysis were made. It was shown how carefully analyzed sensitivity profiles can be used in conjunction with experiments and/or models to obtain useful information about chemical kinetic behavior. A simple extension of the theory showed how to obtain an entire family of sensitivity coefficients each of which had a unique interpretation in terms of a particular laboratory measurement. A practical approximation was suggested for obtaining higher order sensitivity information. Finally the overall computational efficiency of the Green's function method was assessed and found to be quite promising.

11. The use of global wave functions in scattering theory.[11]

This work considered the potential savings associated with the use of global wave functions in scattering theory. The normal close coupling approach expands all variables except one in a chosen basis and thereby leads to coupled ordinary differential equations. The global approach expands all variables except two, and leads to fewer coupled partial differential equations. With the availability of efficient partial differential equation codes, the global approach has an important advantage in cases where the extra coordinate would require many basis functions by conventional close coupling. Within the global theory it was shown how to obtain state-to-state as well as total cross sections. The global approach has the attractive feature of allowing for the computation of total cross sections directly without recourse

to individual state-to-state cross sections. This aspect is particularly significant for complex systems. The use of the finite element method as a practical means for treating partial differential equations was also discussed. As an example, the results of a model colinear reactive scattering problem were shown to be in excellent agreement with exact solutions.

12. Finite element methods for reactive scattering.[12]

The finite element method was applied to collinear reactive scattering problems. In this way no basis set expansion of the wave function is required, and a direct solution of the two dimensional partial differential equation is achieved. It was shown how to generally formulate this approach and achieve fast and accurate results. As a test calculation, the method was applied to $H + H_2$ yielding excellent agreement with close coupling results. Since no basis sets are used in the finite element calculation, no question of basis set convergence or closed channel behavior arises. Some discussion on applications to higher dimensions was also included.

V. Publications Resulting from the Present Contract

1. "Generalized effective Hamiltonians: Time scale separation within a semi-classical formalism", A. DePristo and H. Rabitz, J. Chem. Phys. 68, 4017 (1978).

2. "Rapid and accurate evaluation of inelastic molecular cross sections", S. Tarr and H. Rabitz, J. Chem. Phys. 68, 642 (1978).

3. "On the use of various scaling theories in the deconvolution of rotational relaxation data: Application to pressure-broadened linewidth measurements", A. DePristo and H. Rabitz, J. Chem. Phys. 69, 902 (1978).

4. "Direct inversion of pressure-broadened halfwidths to yield rotationally inelastic rate constants", A. DePristo and H. Rabitz, J. Mol. Spec. 70, 476 (1978).

5. "The effect of elastic and reorientation collisions on vibration-rotation lineshapes: A semi-empirical approach", A. DePristo and H. Rabitz, J. Chem. Phys., in press.

6. "On the correlation of relaxation data: A scaling theoretical analysis", R. Ramaswamy, A. DePristo and H. Rabitz, Chem. Phys. Lett., in press.

7. "Multiple time scale stochastic formulation for collision problems with more than one degree of freedom", S. Augustin and H. Rabitz, J. Chem. Phys., in press.

8. "Stochastic theory of intramolecular energy transfer", R. Ramaswamy, S. Augustin and H. Rabitz, J. Chem. Phys., in press.

9. "The Green's function method for sensitivity analysis in quantum dynamics", J.-T. Hwang and H. Rabitz, J. Chem. Phys., in press.

10. "Application and further development of the Green's function method of sensitivity analysis to chemical kinetics", E. Dougherty, J.-T. Hwang, and H. Rabitz, J. Chem. Phys., in press.

11. "The use of global wave functions in scattering theory", H. Rabitz, A. Askar and A. Cakmak, Chem. Phys. 29, 61 (1978).

12. "Finite element methods for reactive scattering", A. Askar, A. Cakmak and H. Rabitz, Chem. Phys. 33, 267 (1978).

VI. Personnel Under the Contract

Dr. Stuart Augustin
Mr. Britton Chang
Dr. Andrew DePristo
Mr. Eugene Dougherty
Mr. Ramakrishna Ramaswamy*

* Mr. Ramaswamy received his Ph. D. on this contract in September 1978.