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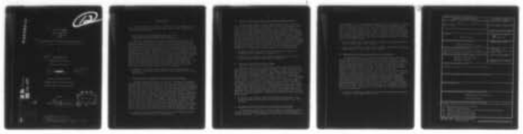

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(6) COLLISION STUDIES OF GASEOUS MOLECULAR LASERS.

by

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REPORT SUMMARY

Research under the contract has progressed in several different areas. The principal activities are outlined below along with the publications resulting from the research.

I. Inversion of Pressure-Broadened Spectral Line Shapes to Yield Rotationally Inelastic Rate Constants

The direct extraction of state-to-state rotationally inelastic rate constants ($k_{jj'}$) from bulk relaxation measurements has generally been considered an intractable problem. However, we have now shown that two new developments allow for the first time the deconvolution of experimental data to yield the individual rates without recourse to any dynamical calculations. The implication of these developments provides for (1) the elimination of the redundancies in the rates, and (2) the assessment of the information content in the experimental data. We have focused on spectral line shape measurements since a large body of experimental data is already available. The new inversion theory has allowed us to extract state-to-state rate constants from numerous rare gas - molecule systems. The extracted rate constants are extremely valuable and can be immediately applied to other observables. We believe this new inversion theory should revitalize the usefulness and interest in further bulk relaxation measurements. Continuing research on this subject will be vigorously pursued in the coming year.

1. A. DePristo and H. Rabitz, Direct Inversion of Pressure-Broadened Halfwidths to Yield Rotationally Inelastic Rate Constants, J. Mol. Spec., 1978, in press.

II. The Use of Global Wavefunctions in Chemical Reaction Dynamics

The understanding of chemical reactions at a fundamental microscopic level has been a long-sought-after goal. However, the extreme complexities involved with the theory have severely limited progress in this area; only in the past few years has the simplest system $H + H_2$ been treated at a realistic level by normal close coupling methods. The close coupling approach expands all variables except one in a chosen basis and thereby leads to coupled ordinary differential equations. The prime difficulty involved is associated with the large number of equations that must be solved. Rather than follow this approach, we have formulated the problem in terms of fewer coupled partial differential equations. For example, in this case all variables except two are expanded in a basis set. With the availability of efficient finite element partial differential equation codes, the global approach can have important advantages. We have set forth the basic theory behind this method and applied it to model collinear reactive scattering problems. These calculations demonstrated that the method is both accurate and efficient. The theory is presently being scaled up to treat full three-dimensional problems.

1. H. Rabitz, A. Askar, and A. Cakmak, The Use of Global Wavefunctions in Scattering Theory, Chem. Phys., 1978, in press.

III. Stochastic Theory for Inter- and Intramolecular Energy Transfer

Energy transfer studies in large complex molecules have always been hampered by the large number of energy levels involved. Although such problems could be treated by classical mechanics, it is always desirable to retain as much of the quantum aspects as possible. Due to the large multilevel nature of these problems, we have naturally introduced the concept of using non-equilibrium statistical mechanics at the molecular level. Up until the present time this theory, which was initiated under the present contract, has been concerned with intermolecular energy transfer. The methodology is now quite well developed with successful application to situations heretofore impossible to treat by conventional methods. We have now turned our attention to application of these ideas to intramolecular energy transfer where special concern is being given to the basic foundations of unimolecular rate theory. An important question we plan to address is the factors controlling the achievement of a statistical energy distribution in an excited molecule.

1. S. Augustin and H. Rabitz, Multi-Time Scale Approach to Molecular Stochastic Theory, manuscript in preparation.

2. R. Ramaswamy, S. Augustin, and H. Rabitz, Stochastic Theory of Intramolecular Energy Transfer, manuscript in preparation.

IV. Generalized Effective Hamiltonian Theory

Molecular collision theory inherently involves treating systems with more than one internal mode or degree of freedom. It often occurs that the different modes can exhibit different time responses during a collision. We have used this observation to develop a generalized effective Hamiltonian for treating collisional-induced transitions. In this formulation the molecular states are divided into two subsets a_e and a_u. The 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 we have shown how to make the separation based on the type of experimental measurement under consideration. For example, an evaluation of an atom-vibrotor problem (*i.e.*, $a_e = n$, $a_u = j$) was considered in the initial work. In conjunction with this illustration an analysis of the breathing sphere (BS) approximation was considered. 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. Numerical calculations with this theory are being pursued.

1. A. DePristo and H. Rabitz, Generalized Effective Hamiltonians: Time Scale Separation Within a Semiclassical Formulation, Chem. Phys., 1978, in press.

V. The Extraction of VV and VT Rates from CO Electric Discharges

In collaboration with Prof. E. Fisher, Wayne State University, we have analyzed excited vibrational population distributions in carbon monoxide electric discharges. All too often past work in this area has resulted in an over-analysis of the actual information contained in the experiments. Special care is needed so as not to build in self-fulfilling assumptions about the trends or magnitudes of the rates. With this important concern in mind, we have shown that the available experiments can yield a ratio of the VV to VT rates at high quantum numbers (i.e., $n \approx 25$). A careful analysis of this data shows that it is in semiquantitative agreement with theoretical rate information determined at an earlier time under this contract. As a result of the analysis new experiments are being planned to precisely pin down the relevant rates at high quantum numbers.

1. S. H. Lam and H. Rabitz, Correlation of Vibration-Translation Rates for CO-He, J. Chem. Phys., 1978, in press.

2. S. H. Lam, H. Rabitz, E. Fisher, and A. Lightman, CO-He VT Rates at High Quantum Numbers, J. Chem. Phys., 1978, in press.

VI. High-Temperature Vibration-Rotation Relaxation Behavior

An ongoing part of our research has always been concerned with the general behavior of vibrationally-rotationally excited molecules. In order to implement this work, sophisticated state-of-the-art computational methods have been developed and they are described in our earlier reports. As an initial fundamental application of the new program, a detailed treatment of $He\text{-}H_2$ at high temperatures was pursued. Collision energies up to several electron volts were considered and rate constants over the range $1000^0 K \leq T \leq 3000^0 K$ were calculated. The rate constants were then used in a kinetic relaxation calculation to simulate shock tube behavior. The eigenvalues and eigenvectors of the relaxation rate matrix showed that a rich variety of complex vibration-rotation energy transfer pathways existed. Nevertheless, it was shown that experiments corresponding to normal shock tube conditions would yield simple exponential energy decay. Conditions widely differing from normal shock behavior were shown to yield strong deviations from exponential decay. These calculations are of interest in their own right, but they also serve to just illustrate the capability of our state-of-the-art program. At the present time applications to symmetric top molecules are being pursued.

1. S. Tarr and H. Rabitz, High-Temperature Vibrational-Rotational Relaxation in $He\text{-}H_2$, J. Chem. Phys., 1977, in press.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
Molecular collision research at Princeton is reviewed. The topics covered are:

I. Inversion of Spectral Line Shapes,
II. Chemical Reaction Dynamics,
III. Stochastic Theory of Intra- and Intermolecular Energy Transfer,
IV. Effective Hamiltonian Theory,
V. CO-He Electric Discharges, and
VI. Vibration-Rotation Relaxation.

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