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DYNAMICAL STUDIES OF MOLECULAR SYSTEMS

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SUMMARY

During the past year the research under the contract has evolved along several lines consistent with our goal of achieving a better understanding of the interaction of molecules. First, we have developed appropriate theoretical collision techniques and implemented them for practical systems of interest. This activity emphasized the determination of key physical factors controlling inelastic collision behavior. We have also developed new methods for inverting experimental relaxation data to yield detailed state-to-state rate constants. In addition a new effort was undertaken to develop efficient sensitivity analysis techniques for probing parameter dependencies in chemical kinetics systems. In summary, research on the following topics was pursued:

- I. Physical Analysis of Atom-Symmetric Top Collisions
- II. Vibration-Rotation Inelastic Collisions in the CO-He System
- III. Collisional Excitation of Interstellar Molecules: H_2
- IV. Sensitivity Analysis in Quantum Dynamics
- V. Correlation of Relaxation Data: Application to $(A^1\Sigma_u)Na_2^*-Xe$
- VI. Vibrational-Rotational Relaxation from High Vibrational States in He-HD
- VII. The Green's Function Method of Sensitivity Analysis in Chemical Kinetics
- VIII. The Classical Path Approximation in Time-Dependent Quantum Collision Theory

The essence of these various activities is described in the body of this report. The publications resulting from this research contain further detailed information, and these papers are listed at the end of the report.

DETAILS OF RESEARCH PROGRESS

I. Physical Analysis of Atom-Symmetric Top Collisions¹

This study focussed on the general features of rotationally-inelastic atom-symmetric top collision systems. It was demonstrated that consideration of symmetry properties of symmetric tops leads to a significant reduction in the dimensionality of scattering equations and significant labor savings. Physical trends observed in cross sections and rate constants were shown to be understandable in terms of energetic and coupling concepts. Figure 1 illustrates a polar plot of some intermolecular potentials used in the calculations. Figure 2 shows some typical collision rates for an oblate and prolate symmetric top. Rate constants were calculated for various systems and subsequently used to analyze relaxation behavior. Symmetric top molecules represent the simplest class of non-linear polyatomic molecules of experimental and theoretical interest for dynamical purposes. Heretofore studies of such polyatomics have largely been relegated to perturbation theory methods. However the present work illustrates that a combination of effective Hamiltonian theory and exponential distorted wave dynamics can yield an efficient procedure for studying these systems.

II. Vibration-Rotation Inelasticity in the CO-He System²

The CO vibration-rotation system is of considerable practical interest for laser purposes, and it also represents a rather typical molecule with many densely packed rotational states between each vibrational level. For these reasons we undertook an elaborate study of the CO-He problem based on the use

of new stochastic theory methods. Cross sections were obtained for purely rotational transitions using a modified electron gas potential. Vibration-rotation cross sections were calculated in the energy range $2,200 \text{ cm}^{-1} < E < 4,000 \text{ cm}^{-1}$. At the highest energy a total of 76 molecular states are energetically accessible. A comparison with earlier results was made and coarse graining techniques for the treatment of large problems were utilized. Strong participation of rotational states in the overall relaxation was observed.

III. Collisional Excitation of Interstellar Molecules: H_2 ³

Hydrogen is the most ubiquitous molecule in the interstellar medium, and therefore hydrogenic collision information is needed for a number of astrophysical models. In addition, $\text{H}_2\text{-H}_2$ is of fundamental experimental and theoretical concern as a prototype molecular collision system. We therefore undertook an elaborate study of this problem for collisional energies up to $20,000^\circ\text{K}$ including states up to $j=11$ in both molecules. Extensive rates and cross sections were generated and analyzed for their general behavior. A sample of similar He-H_2 rates $j \rightarrow j+2$ and $j \rightarrow j+4$ are shown in Figure 3. These latter calculations were run to contrast H_2 and He as collision partners. The vast amount of collisional data generated in this study could be conveniently correlated in terms of a diffusion-like picture in quantum number space. This is in accord with our previous work on stochastic collision theory.

IV. Sensitivity Analysis in Quantum Dynamics⁴

A central role of quantum dynamics is the understanding of how the structure of the Hamiltonian manifests itself in observable properties. For example, in molecular collision theory the role of well-depth repulsive walls or of coupling strengths is of fundamental concern. Information on the role of these factors has been difficult to obtain except by laborious, repeated calculation. Fortunately this problem is ideally suited to the same techniques of sensitivity analysis we have developed for chemical kinetics (see VII below). This work represents initial research into the extension of these latter procedures for the treatment of quantum dynamics problems. Two simple examples were studied to illustrate the procedure: (1) the collision of an atom with a rigid-rotor where the anisotropic potential coupling strengths were treated as parameters, and the sensitivity of the cross sections to these parameters was sought, and (2) a collision-free molecular beam was studied in the presence of an arbitrary electric and magnetic field where the sensitivity of the molecular transition amplitudes to the field strengths was sought. Figure 4 illustrates a portion of the collisional results where cross sections $\sigma(0 \rightarrow j)$ and normalized sensitivity coefficients $\frac{\partial}{\partial \alpha_1} \ln \sigma(0 \rightarrow j)$ are presented. Detailed and unique insight into the role of the potential parameters was obtained by a careful analysis of such plots. We plan to vigorously pursue this area in the coming year.

V. Correlation of Relaxation Data: Application to $(A^1\Sigma_u)Na_2^*-Xe$ ⁵

As a necessary part of our research on the inversion of relaxation data we have developed scaling relations for rates and collision cross sections. By means of these relations it has proved possible to express all the elements of the rotational rate constant matrix $k_{j \rightarrow j'}$ in terms of the first column of the matrix $k_{0 \rightarrow j}$. This compaction of the information in the rate matrix is an essential step for the extraction of detailed state-to-state rate constants from experimental data. Thus far only rotational line-shape data has been treated, and the present paper presents an illustration handling fluorescence data on the $(A^1\Sigma_u)Na_2^*-Xe$ system. Figure 5 shows the experimental results of Pritchard, et al. (private communication) and the theoretical correlation. The new planned research for the coming year will extend the scaling theory to include vibrational degrees of freedom, and thereby expand the type of experiments that may be treated.

VI. Vibrational-Rotational Relaxation from High Vibrational States in He-HD⁶

Relaxation behavior of highly excited vibrational states is a problem of current concern to the kinetics community. The hydrogen system has received much attention due to its fundamental role, and the present work contributes to this understanding in the HD system. This theoretical study was also undertaken because we are in preparation for performing vibrational-relaxation experiments on highly excited HD. The relaxation behavior of He-HD was treated by applying an exponential distorted wave procedure to calculate the cross sections and the rate constants for vibrational-rotational energy transfer. In

the vibrational manifolds $0 \leq n \leq 5$ the rotational states were shown to play an important role in vibrational-relaxation by providing many pathways for vibrational-rotational-translational energy exchange. By comparison with breathing sphere calculations it was demonstrated that the near exponential growth in the $n \rightarrow n-1$ rates from vibrational calculations can be attributed not only to the vibrational anharmonicity, but also to the decreasing rotational energy spacings as n increases. As an illustration of the relaxation process Figure 6 shows a cascade of vibrational population ($\rho_n = \sum_j P_{nj}$) for the HD system initially prepared in state $n=5$. The theoretical work in this paper should provide a valuable guide to our planned experiments.

VII. The Green's Function Method of Sensitivity Analysis in Chemical Kinetics⁷

The need for sensitivity analysis of complex kinetic systems is well known. The chief problem in this area is obtaining an efficient and accurate algorithm for calculating the sensitivities. A new approach to this sensitivity analysis of large computational models was presented in this work. The basis for the method is the well-known Green's function technique. By working with the same differential equations as the conventional direct method this new approach reduces a number of differential equations to be solved and replaces them by a set of integrals. Altogether there is only one set of differential equations in the Green's function method regardless of the number of parameters m . The sensitivity coefficients of all orders are expressed in integral form and evaluated in a recursive manner. Since evaluating well behaved integrals is

usually much easier than solving stiff differential equations. Substantial savings can be achieved by the method when the number of system parameters is large. It is estimated that if only linear sensitivity coefficients are desired then the Green's function method could be advantageous for the case $m > n$, where n is the number of dependent variables. However if both linear and higher order sensitivity coefficients are to be computed the method could be competitive with other approaches even when $m < n$. A numerical calculation on a simple linear system is presented to provide a brief illustration of the method.

VIII. The Classical Path Approximation in Time-Dependent Quantum Collision Theory⁸

Time-dependent treatments of molecular collisions have frequently employed the combination of quantum equations for the internal degrees of freedom (i.e., vibration, rotation) with a classical description of the translational motion. In this work we showed how energy conserving classical path equations could be derived from first principals thereby obtaining quantum correction terms of arbitrary order. These expressions have interesting implications for the question of how the classical limit is approached. If the translational degree of freedom is assumed to be described by a very narrow wave packet the correction term to first order in $\hbar$ is purely imaginary and therefore non-hermitian. These techniques can be generalized to a classical treatment of other degrees of freedom and the case of rotation in an atom-vibrotor collision was explicitly considered. For both the translational and rotational examples the full series of corrections takes on an interesting and suggestive exponential

form. This work opens up some new and basic questions concerning the connection of classical and quantum dynamics. It is strongly suggested that quantum tunneling corrections to the ordinary classical trajectories are being introduced by the new terms in the Hamiltonian. We plan to analyze this theory further in order to better understand its meaning as well as implement it for real trajectory calculations.

PUBLICATIONS RESULTING FROM RESEARCH UNDER THE CONTRACT

1. S. Tarr and H. Rabitz, "Physical Analysis of Atom-Symmetric Top Collisions", Chem. Phys., in press.
2. R. Ramaswamy, S. Augustin and H. Rabitz, "Vibration-Rotation Inelasticity in the CO-He System", J. Chem. Phys., in press.
3. S. Green, R. Ramaswamy and H. Rabitz, "Collisional Excitation of Interstellar Molecules: H_2 ", Ap. J. 36, 483 (1978).
4. J.-T. Hwang and H. Rabitz, "Sensitivity Analysis in Quantum Dynamics", J. Chem. Phys., in press.
5. R. Ramaswamy, A. DePristo and H. Rabitz, "Correlation of Relaxation Data: Application to $(A^1\Sigma_u)Na_2^*-Xe$, in preparation.
6. S. Tarr and H. Rabitz, "Vibrational-Rotational Relaxation from High Vibrational States in He-HD", J. Chem. Phys., in press.
7. J.-T. Hwang, E. P. Dougherty, S. Rabitz and H. Rabitz, "The Green's Function Method of Sensitivity Analysis in Chemical Kinetics", J. Chem. Phys., in press.
8. S. Augustin and H. Rabitz, "The Classical Path Approximation in Time-Dependent Quantum Collision Theory", J. Chem. Phys., in press.

FIGURE CAPTIONS

Figure 1. Polar plots of the atom-symmetric top intermolecular potentials.

In all cases the radial distance represents the value of the potential. In the lower plots, the potential is given as a function of the twist angle χ ($0 \leq \chi \leq 360^\circ$) for fixed polar angle θ . In the upper plots, since θ varies only from $0^\circ \rightarrow 180^\circ$, an equivalent type of plot is obtained by setting $\chi = 180^\circ$ on the r.h.s. and $\chi = 0^\circ$ on the l.h.s. A variation in θ over the range $0 \leq \theta \leq 180^\circ$ occurs on each side of the upper plots.

Figure 2. Rates $k_{j \rightarrow j'}$ for (a) an oblate D_3 molecule and (b) a prolate D_3 molecule. Encircled points represent those transitions for which the energy transfer is minimum. The lines are labelled by j , and the rates are in dimensionless units.

Figure 3. Excitation rates for $j \rightarrow j+2$ and $j \rightarrow j+4$ are presented for $H_2 + He$. The results are very similar to the extensive $H_2 + H_2$ calculations in ref. 3, and He- H_2 runs were performed for comparative purposes.

Figure 4. Plot (a) shows the cross section $\sigma(0 \rightarrow j)$ and (b) shows the normalized sensitivity coefficient $\frac{\partial}{\partial \alpha_1} \ln \sigma(0 \rightarrow j)$. The parameter α_1 is the anisotropy parameter ($\alpha_1 = \alpha_2 = 0.1$) for the $P_1(\cos \theta)$ term is the atom-rigid rotor potential $V = \epsilon [(\sigma/R)^{12} - (\sigma/R)^6]$ $\times [1 + \alpha_1 P_1(\cos \theta) + \alpha_2 P_2(\cos \theta)]$.

Figure 5. Scaling predicted and experimental rates: The rates $k_{16\ 16+\Delta}$ (o) are used to determine the k_{L0} from the new scaling theory. These elementary rates k_{L0} are then used to predict the rates $k_{54\ j'}$ (Δ) and $k_{16\ 16-\Delta}$ ($\bullet$) which agree with the corresponding experimental values $k_{54\ j'}$ (+) and $k_{16\ 16-\Delta}$ (-) within the experimental uncertainty. The experimental data is by D. E. Pritchard, MIT, private communication.

Figure 6. Semi-logarithmic plot of the vibrational populations $\rho_n(t)$ vs time for $\rho_n(0) = \delta_{n,5}$ at $T = 300^\circ\text{K}$. Time is in units of mole-sec/cm³.

(a) D_3 - PROLATE

(b) D_3 - OBLATE

(c) C_3 - OBLATE

FIGURE 1

FIGURE 2

Figure 3

Figure 4

Figure 5

Figure 6