AMES GRANT
IN-72
CR
12360
P·10

Final Report on NASA Grant NASA-Ames NAG2-503

"Theoretical Studies of Molecular Collisions"

Donald J. Kouri, P.I.
Dept. of Chemistry
University of Houston
Houston, TX 77204-5641

TO STIF

1

I. Summary of Results and Publications

Although we were unable to complete all the research we had hoped to due to the unforeseen budgetary problems which prevented our continuing for the third year of this grant, tremendous progress was made in the development of new methods and their applications to the calculation of converged three-dimensional quantum scattering information. This has enabled us to make detailed comparisons of converged 3-D quantum results to analogous quasi-classical trajectory (QCT) results obtained by Dr. Rich Jaffe, in order to assess the accuracy and reliability of the latter. Of greatest significance is the fact that the first fully converged 3-D quantum cross sections over a wide range of energies for the $F + H_2 \rightarrow HF + H$ reaction were obtained, and the results compared with QCT and experimental cross sections. This is a landmark achievement, and it was found that there are very significant quantum effects! These quantum effects are manifested in the threshold energy regime, and in the dependence of the reactive cross sections on the initial rotational state of the H_2 molecule. It appears therefore that considerable care must be exercised in simulating reactive scattering processes by the QCT method, especially under threshold conditions, and when the experiment is probing low initial rotational states of the reactant molecules.

In a related study of vibration-rotational inelastic scattering of N_2 by oxygen atoms, O, over a very large energy range we found very large quantum effects in the thresholds for producing vibrationally excited N_2. The results showed that the QCT leads to vibrational excitation at substantially lower total energies than the quantum results. This will have

a <u>major</u> effect on the energy transfer rates and the collisional line broadening of the N_2 under the conditions expected in the shock produced by the AOTV. Again, this indicates that great care must be exercised in simulating molecular collision processes in the shock wave associated with the AOTV.

We anticipate continuing this program of research in collaboration with Dr. Rich Jaffe of NASA-Ames. For example, several powerful new methods for propagating quantum wavepackets and for obtaining the most detailed state-to-state reactive scattering amplitudes have been developed. We will continue to carry out calculations for the $O + N_2$ and $F + H_2$ systems in order to complete the comparisons of exact quantum results with Dr. Rich Jaffe's QCT results. In addition, we still expect to be able to compute reactive scattering results for the extremely difficult, highly exoergic $N + O_2 \rightarrow NO + O$ reaction for comparison to QCT results.

We turn now to a brief summary of the detailed results obtained under support of NAG2-503. It is convenient to frame this in terms of the refereed publications resulting from the grant support. There are a total of fourteen such papers.

1. Total Integral Reactive Cross Sections for $F + H_2 \rightarrow HF + H$: Comparison of Converged Quantum, Quasiclassical Trajectory and Experimental Results, D. Neuhauser, R. S. Judson, R. L. Jaffe, M. Baer, and D. J. Kouri, Chem. Phys. Lett. <u>176</u>, 546 (1991).

This paper reports a major breakthrough in the quantum theory of reactive scattering. The first converged 3-D quantum complete reactive cross sections for this prototype of an exoergic reaction yielding a population inversion are reported, both for H_2 in the $v = 0$, $j = 0$ and $v = 0, j = 1$ initial (reactant) states. The comparison to QCT results shows very

strong quantum effects in the threshold behavior and the dependence on initial rotational state of the reactant H_2 molecule. The comparison to experiment (combined with the comparison to the QCT results) demonstrates that the potential (T5A due to Truhlar and collaborators) is not sufficiently accurate to correctly describe the system. This is by far the most important paper published under the grant, and a much more complete paper will be prepared for submission in the coming months.

2. A Theoretical Study of Inelastic $O + N_2$ Collisions: Comparison of Classical with Exact Quantum Results for Energies up to 2.6 eV and Selected Total Angular Momenta, R. S. Judson, C.-K. Zhang, D. J. Kouri, and R. L. Jaffe, in preparation.

This paper is almost ready for submission to the Journal of Chemical Physics. Because of the large masses of the O atom and N_2 molecule, and the high collision energies considered, one would have expected very good agreement between QCT and accurate 3-D quantum results. In fact, due to the very stiff N_2 bond, there are large quantum effects in the vibrational excitation probabilities. Thus, the QCT threshold for vibrationally exciting the N_2 occurs much lower in energy that the quantum threshold. The energy difference in the threshold is such that the QCT vibrational excitation rate constant should be orders of magnitude larger than the quantum rate. It is found in both quantum and QCT results that very large changes in N_2-rotational angular momentum occur, both for $\Delta v = 0$ and $\Delta v \neq 0$ vibrational transitions. As would be expected from the repulsive nature of the potential, rotational rainbow structure occurs in the final N_2-rotational state distributions. This is seen in both the quantal and the QCT results. The peak of the rotational rainbow typically occurs at a slightly larger final j-state in the quantum results than in the QCT

4

results.

3. Time Dependent (Wavepacket) Quantum Approach to Reactive Scattering: Vibrationally Resolved Reaction Probabilities for $F + H_2 \rightarrow HF + H$, D. Neuhauser, M. Baer, R. S. Judson, and D. J. Kouri, Chem. Phys. Lett. $\underline{169}$, 372 (1990).

This paper presents the first detailed state-to-state converged 3-D quantum reactive scattering transition probabilities for the extremely difficult $F + H_2 \rightarrow HF + H$ reaction, obtained with wavepackets. The results demonstrated that such state-to-state reactive probabilities for such a system could be obtained at many collision energies from a single wavepacket propagation.

4. Body Frame Close Coupling Wave Packet Approach to Gas Phase Atom-Rigid Rotor Inelastic Collisions, Y. Sun, R. S. Judson, and D. J. Kouri, J. Chem. Phys. $\underline{90}$, 241 (1989).

This paper provided the foundation of the wavepacket propagation for inelastic scattering in 3-D in a rotating frame of reference, as well as the detailed proofs that one could obtain the state-to-state S-matrix at many energies. This is one of the papers that provided tools for developing the general 3-D quantum wavepacket method for reactive scattering.

5. Wavepacket Study of Gas Phase Atom-Rigid Rotor Scattering, Y. Sun and D. J. Kouri, J. Chem. Phys. $\underline{89}$, 2958 (1988).

This paper was the demonstration calculation that accurate 3-D quantum S-matrix results for atom-diatom could be obtained by wavepacket methods. The formulation was in a space fixed, center of mass reference frame, which was extended in paper 4 above to a rotating frame.

5

6. The Application of Optical Potentials for Reactive Scattering: A Case Study, D. Neuhauser, M. Baer, and D. J. Kouri, J. Chem. Phys. $\underline{93}$, 2499 (1990).

This paper gives a numerical study of the optical (absorbing) potential idea which was used to enable converged quantum reactive scattering calculations to be done using much smaller grid sizes. This greatly reduces the computational labor required. It also enables one to decouple arrangements in such a way that nonreactive scattering coordinates can be used.

7. Time Dependent, Three Dimensional Body Frame Quantal Wavepacket Treatment of the $H + H_2$ Exchange Reaction on the Liu-Siegbahn-Truhlar-Horowitz (LSTH) Surface, D. Neuhauser, M. Baer, R. S. Judson, and D. J. Kouri, J. Chem. Phys. $\underline{90}$, 5882 (1989).

The first full 3-D time dependent quantum wavepacket calculations for a chemical reaction were reported in this paper. It used the crudest form of the method. Thus, each single energy required a separate wavepacket propagation, and the results really represented scattering of a spread of energies peaked at the nominal energy of interest. However, state-to-state probabilities were obtained and the general ideas of the method were shown to be sound. The system studied was the $H + H_2$ exchange reaction (chosen because accurate results were available for comparison to be sure our codes were working correctly).

8. A Time-Dependent Wavepacket Approach to Atom-Diatom Reactive Collision Probabilities: Theory and Application to the $H + H_2(J = 0)$ System, D. Neuhauser, M. Baer, R. S. Judson, and D. J. Kouri, J. Chem. Phys. $\underline{93}$, 312 (1990).

The basic theory of the version of the wavepacket method to be used in the subsequent

study of the $F + H_2 \rightarrow HF + H$ reaction was given in this paper, along with example calculation results for the standard $H + H_2$ exchange reaction. The paper is a synthesis of the CCWP propagation method of paper 4, the absorbing potential of paper 6, new flux methods for the final state analysis, and a projection operator procedure for reducing the grid size in the reactant entrance channel. Only reaction probabilities could be gotten by this method.

9. Time-Dependent Wavepacket for the Complete Determination of S-matrix Elements for Reactive Molecular Collisions in Three Dimensions, R. S. Judson, D. J. Kouri, D. Neuhauser, and M. Baer, Phys. Rev. A 42, 351 (1990).

A more general method for 3-D reactive quantum wavepacket propagation is given that is able to determine an entire column of the S-matrix both for reactive and the accompanying nonreactive scattering. The method uses the body frame propagation, complex absorbing potentials to reduce grid size, and interpolation method to change from the reactant to a product space grid, and a final state analysis yielding the most detailed S-matrix elements. It was shown to work by application to the standard $H + H_2$ exchange reaction.

10. The Application of Time-Dependent Wavepacket Methods to Reactive Scattering, D. Neuhauser, M. Baer, R. S. Judson, and D. J. Kouri, Computer Phys. Commun. 63, 460 (1991).

A summary of the various methodologies in reactive scattering wavepacket calculations is given. It combines essentially all the ideas of papers 8 and 9.

11. Time Dependent Treatment of Scattering: Integral Equation Approaches Using the Time-Dependent Amplitude Density, D. K. Hoffman, O. Sharafeddin, R. S. Judson, and

D. J. Kouri, J. Chem. Phys. 92, 4167 (1990).

A totally new way to propagate wavepackets is developed making use of the time dependent Lippmann-Schwinger integral equation. The objective is to develop a new class of propagation schemes which may make the quantum wavepacket method even more powerful for treating reactive scattering. An auxiliary function, the time dependent amplitude density, is introduced and shown to enable one to restrict consideration solely to the region in space where the potential is nonzero. This can lead to smaller grid sizes.

12. Time Dependent Treatment of Scattering. II. Novel Integral Equation Approach to Quantum Wavepackets, O. A. Sharafeddin, R. S. Judson, D. J. Kouri, and D. K. Hoffman, J. Chem. Phys. 93, 5580 (1990).

Work on the integral equation based schemes for propagating quantum wavepackets is continued by exploring novel ways to define reference and interaction Hamiltonians. The radical choice of the potential as H_0 and the kinetic energy as the perturbation is shown to work and yield identical results to more standard choices!

13. A Comparison of Three Time Dependent Wavepacket Methods for Calculating Electron-Atom Elastic Scattering Cross Sections, R. S. Judson, D. B. McGarrah, O. A. Sharafeddin, D. J. Kouri, and D. K. Hoffman, J. Chem. Phys. 94, 3577 (1991).

The Chebychev propagation, Amplitude Density propagation (see paper 11), and a new integral equation based method called the Modified Cayley propagation were compared by calculating complete elastic scattering of an electron off a spherically symmetric target (atom). All three methods worked well, with the Modified Cayley being the most efficient, as well as stable.

14. A Numerically Exact Full Wavepacket Approach to Molecule-Surface Scattering, R. C. Mowrey, Y. Sun, and D. J. Kouri, J. Chem. Phys. <u>91</u>, 6519 (1989).

Wavepacket propagation involving the polar angle, θ, is problematic due to the fact that the kinetic energy operator involves terms containing the factor $(1/\sin\theta)$. This leads to roundoff errors in the computer that produce instability after a number of time steps or applications of the Hamiltonian to a wavepacket. However, wavepacket propagation on a grid for all variables is very desirable if one wants to take maximum advantage of the $N\log_2 N$ scaling of Fast Fourier Transforms with the number of grid points, N. This paper presents such a method which is stable and accurate. Although applied here to molecule-surface collisions, the same method can be applied to any 3-D quantum scattering problem.

II. Personnel Supported Under NAG2-503

1. Donald J. Kouri (PI)
2. Danny Neuhauser (postdoc)
3. Ching-Kuang Zhang (graduate student)
4. Richard S. Judson (postdoc)
5. Bernard Chang (postdoc)
6. Omar A. Sharafeddin (graduate student)
7. Ferrel Bowen (graduate student)

III. Enclosures
Reprints of thirteen refereed publications are included.

IV. Funds
All funds were expended.