LA-UR- 96-0236

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Photodissociation, and Recombination
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APR 01 1996

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Submitted to: DOE Office of Scientific and Technical
Information (OSTI)

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Quantum Resonance Effects in Exchange, Photodissociation, and Recombination Reactions

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Abstract

This is the final report of a three-year, Laboratory-Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). This project studied quantum resonance effects on chemical reactions. Our accurate reactive scattering calculations showed that quantum resonance phenomena dominate most chemical reactions and are essential to any real understanding of reactivity. It was found that, as long-lived metastable states of the colliding system, resonances can decay to reactants, products, or a mixture of both. Only the latter contribute to reaction. Conditions under which resonances can be neglected or treated statistically were studied. Important implications about the mechanism of recombination reactions were discovered, and some remarkable effects of geometric phases on the symmetries and energies of resonances were also discovered.

1. Background and Research Objectives

The reactive collisions that make and break chemical bonds are the very heart and soul of all chemistry, and a deeper understanding of chemical reactivity is key to progress. Early quantum model calculations showed resonances (long-lived collision complexes) in reactive collisions, but most people expected them to wash out in accurate three-dimensional (3D) physical space calculations. Now, with recent developments, it has become possible to do essentially exact 3D quantum calculations on triatomic systems of real chemical interest. To our surprise, it is found that there are now even more resonances! We have shown that the $\text{H} + \text{O}_2$ reaction discussed below displays a plethora of resonances. Such results throw confusion into the very foundations of chemistry. No reaction can now be truly understood until it is known what role quantum resonances are playing.

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Our objective was to calculate and interpret quantum resonances in three fundamental types of reactions; namely, exchange, photodissociation, and recombination. We have determined what resonance effects survive in experimental observables and classified the effects, so that the result ultimately will be general principles that can be used to interpret more complex systems.

2. Importance to LANL's Science and Technology Base and National R&D Needs

When the quantum resonances for a given reaction are known and understood, they can be accessed with lasers to achieve control over that reaction. This control is a key to the long-sought goal of bond-selective chemistry, which has many obvious scientific and technological applications. For example, a detailed understanding of the $H + O_2$ reaction is key to greater control of combustion, and more efficient combustion is a crucial national need. Likewise, until the isotopic composition of stratospheric ozone is understood, the ozone kinetics relating to the environment and climate are in question. Our reactive scattering computer codes have unique capabilities that enable study of reactions as complex as these. This project maintains and extends those capabilities.

3. Scientific Approach and Results

Our most general results obtained are the consequences of the fact that resonances are a state of the compound (colliding) system, not of either the reactants or products. This means that a given resonance can decay mostly to products, mostly to reactants, or to any mixture of the two. In some systems resonances provide the only pathway to reaction. However, in most systems that have many resonances, all three kinds are present, and the resonances can be ignored or treated statistically if all one wants is the rate coefficient. However, if one wants more detailed quantities, such as differential cross sections or the effects of lasers on the reaction, a detailed knowledge of the resonances is needed. Also, we proved that extremely narrow resonances contribute negligibly to rate constants.

We have reported some of the first accurate reaction probabilities for the exchange reactions

and

and showed that they are totally dominated by resonances. The kinetics are accurately described by simple statistical models, in agreement with the general principle discussed in the preceding paragraph. The first accurate calculations on the exchange reaction

have also been completed. Some very sharp resonances were found and it was shown that they come from trapping behind a low effective potential barrier in the reactant channel.

Likewise, the first accurate calculations of reaction probabilities were also completed for the reaction

which is the rate limiting step in the combustion of all hydrocarbons and the single most important reaction in all of combustion chemistry. Its deep potential well, bent intermediate, long-range forces, etc., make it the most complex and difficult reaction yet studied by accurate quantum methods. Its cumulative reaction probability, which is needed in calculating the rate constant, is dominated by resonances. Despite all these resonances, statistical models still fail for this reaction, indicating that there is something nonstatistical about it, but there was not time in the grant period to determine the source of the nonstatistical behavior.

We also generated the first accurate collision lifetimes for this reaction. They show that this reaction has many long-lived resonances with lifetimes of picoseconds at energies above the reaction threshold and lifetimes of tens of picoseconds at low energies. These low-energy resonances contribute to the recombination reaction that forms HO₂. Our results also show that the reaction probability increases basically linearly above threshold, that there is no enhancement of the reaction due to any vibrational or rotational excitation of the reactants, but that the reaction is enhanced when excited vibrational and rotational states of the products become accessible.

Also, it is known that there are conical intersections of the lowest potential energy surfaces (PES's) for this reaction, and most *ab initio* quantum chemistry methods do not give the coupling at these intersections. To determine the effects of coupling at these intersections and their associated geometric phases on the energies and widths of the resonances in this reaction, we have used the Diatomics in Molecules (DIM) model to fit *ab initio* data and have determined accurate new PES's.

Some very significant discoveries have been made concerning recombination reactions. The overall, net generic recombination reaction has the form

where A and B are any two atoms or molecules that can bind to each other and M is some third atom or molecule that carries off the excess energy. In all the standard textbooks and the

computer codes that are used to model chemical kinetics, these reactions are always assumed to go via a sequence of two-body collisions, such as

where AB^* is a metastable complex (resonance). We have found the first really solid evidence that pure, direct three-body collisions of the form given by the net reaction (5) contribute significantly to recombination reactions. Because the high-pressure dependence of the two mechanisms is different, current models are not giving the right high-pressure dependence of the effective rate coefficient.

We also have performed the first calculations of the effect of a geometric phase for the case when the atoms are chemically distinct. In earlier calculations, the atoms had been isotopically different at most, and could be treated with a simple approximation. We have applied the calculations to the system

which is important in combustion chemistry and atmospheric chemistry. Our results show clearly that the geometric phase, which is due to a conical intersection of low-lying potential energy surfaces in this system, causes drastic shifts and changes in the spectrum of resonances and high-lying bound vibrational states of this system.

In this connection, we have also found that the geometric phase gives the vibrational states of this system an anomalous symmetry that is impossible in systems without a conical intersection. This symmetry causes the states to be double-valued functions rather than the usual single-valued continuous functions and causes them to be symmetric on one side of the cone and antisymmetric on the other. This property must be understood by all who would assign the spectra of this and similar molecules.

Recent publications related to this LDRD project are listed below.

Publications

1. Pack, Russell T., "Conformally Euclidean Internal Coordinate Space in the Quantum Three-Body Problem," *Chemical Physics Letters* **230**, 223 (1994).
2. Parker, G. A., Lagana, A., Crocchianti, S., and Pack, R. T., "A Detailed 3D Quantum Study of the Li + FH Reaction," *Journal of Chemical Physics* **102**, 1238 (1995).
3. Kendrick, B. K. and Pack, R. T., "Potential Energy Surfaces for the Low-lying $2A''$ and $2A'$ States of HO_2 : Use of the DIM Model to Fit Ab Initio Data," *Journal of Chemical Physics* **102**, 1994 (1995).
4. Pack, Russell T., Butcher, Eric A., and Parker, Gregory A., "Accurate Three-Dimensional Quantum Probabilities and Collision Lifetimes of the $H + O_2$ Combustion Reaction," *Journal of Chemical Physics* **102**, 5998 (1995).
5. Kendrick, Brian K. and Pack, Russell T., "Recombination Resonances in Thermal $H + O_2$ Scattering," *Chemical Physics Letters* **235**, 291 (1995).

6. Barclay, V. J., Dateo, C. E., Hamilton, I. P., Kendrick, B., Pack, R. T., and Schwenke, D. W., "Anomalous Symmetries of the Rovibrational States of HO₂: Consequences of a Conical Intersection," *Journal of Chemical Physics* **103**, 3864 (1995).

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