

Resonance Structure in Chemical Reactions

Brian K. Kendrick

Dynamical scattering resonances are one of the most intriguing quantum mechanical effects in a bimolecular chemical reaction. Understanding the role that these resonances play in chemical reactions is crucial to our basic understanding of all chemical reactivity. This understanding is key to laser control of reactions and the long-sought bond selective chemistry. A resonance refers to a metastable collision complex that is formed when reagents collide with the appropriate energy to excite a vibration of the complex. The excited complex subsequently decays either into reactants or products. The outcome of the scattering event can be significantly influenced by accessing a resonance state. Interference between resonant and direct scattering waves produces oscillations in the reaction probability. Thus, resonances are associated with increases in reaction times in comparison with direct reactions, and they appear as sharp variations in differential reaction cross sections as a function of collision energy. The identification of dynamical scattering resonances is a “spectroscopy of the transition state” of a bimolecular chemical reaction and intense interest has been focused on their calculation and observation.

1 partial scattering waves, where J is the total angular momentum. The pioneering three-dimensional work showed that resonances were present even when all of the internal nuclear degrees of freedom were treated correctly.

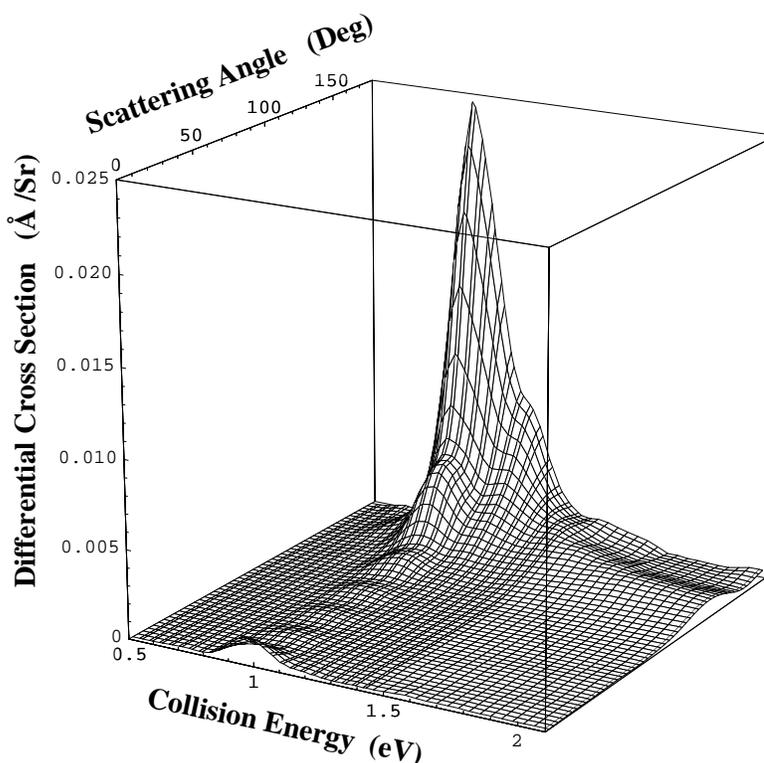


Figure 1: Differential cross section for the $H + D_2(v=0, j=0) \rightarrow HD(v'=0, j'=7) + D$ reaction. The resonance “bump” is clearly visible.

The prediction of resonance structure in the fundamental $H + H_2$ reaction system dates back to the one-dimensional

Understanding the role that these resonances play in chemical reactions is crucial to our basic understanding of all chemical reactivity.

collinear calculations of the early 1970s. They were later found in full three-dimensional calculations for $J = 0$ and

These early theoretical predictions inspired many theoretical and experimental studies which continue to this day. One of the main concerns of the early theoretical studies was if the resonance structure would “wash out” by the summation over J required to calculate the fully converged integral and differential cross sections. This concern was temporarily damped when the first experimental observation of resonance structure was reported in 1988. However, subsequent theoretical studies by several independent groups were unable to reproduce the experimental observations. These fully converged theoretical studies showed that the resonance structure did

indeed “wash out” as the sum over partial waves was extended to include more values of J . The fully converged integral cross sections exhibited a smooth energy dependence in disagreement with the first experiment. A later experiment in 1990 was consistent with the theoretical studies. Thus, until now, no theoretical evidence for resonant structure in the fundamental $H + H_2$ reaction system has been conclusively verified experimentally.

Recent advances in both theory and experiment have made the accurate calculation and observation of quantum resonances in chemical reactions possible. In particular, integral cross sections for rotationally resolved HD products in the $H + D_2 \rightarrow HD + D$ reaction can now be measured experimentally as a function of energy with unprecedented resolution. Theoretical evidence exists for resonance structure in the differential cross sections for rotationally resolved HD products for the $D + H_2 \rightarrow HD + H$ reaction. This structure appears to survive the sum over all partial waves but only for differential cross sections with rotationally resolved HD products. The sum over the rotational states of HD causes the structure to wash out. Our recent theoretical calculations for the $H + D_2$ reaction predict resonance structure in *both* the integral and differential cross sections for rotationally resolved HD products.

In the Born-Oppenheimer method for molecules, the center of mass motion is removed and the total molecular wavefunction is written as a product of three wavefunctions: nuclear, electronic and nuclear spin. The nuclear wavefunction is a function of the nuclear coordinates. The electronic wavefunction is a function of the electronic coordinates and it also depends parametrically on the nuclear coordinates. For low enough energies (which we are considering) the coupling to excited electronic states can be ignored and only one electronic wavefunction (the ground state) need be considered. Thus, in the current study the reaction occurs on the ground-state electronic potential energy surface of H_3 . This surface is a function of the three internal nuclear degrees of freedom and is represented by the state-of-the-art fit to *ab initio* data. The nuclear spin wavefunction is the total nuclear spin wavefunction. The relevant nuclear Schrödinger equation is solved using symmetrized hyperspherical coordinates and a newly developed hybrid numerical technique based on a Discrete Variable Representation and Finite Basis Representation. The calculations are computationally intensive and require extensive computer time on massively parallel supercomputers.

Figure 1 plots the differential cross section for the $H + D_2 \rightarrow HD + D$ reaction as a function of collision energy for 70 energies between 0.5 eV and 2.1 eV. The scattering angle is the angle between the center-of-mass velocity vector of the final HD product and the center-of-mass velocity vector of the initial H atom. The most striking feature is the prominent resonance near 0.94 eV which exhibits a large backwards scattering peak.

Figure 2 compares the recent experimental measurements of Shafer-Ray and coworkers at the University of Oklahoma to our theoretical predictions. The experiment is based on both molecular beam and photoinitiated (laser) techniques. The product is state-selected via multiphoton ionization and the sensitivity to scattering angle is obtained by measuring the time-of-flight of the HD^+ ions. In order to compare our theoretical predictions to their experimental measurements, we must account for the misalignment between the molecular beam and time-of-flight detector. The best agreement between experiment and theory occurs for a 2.5 mm off-axis drift of the HD^+ ions as they travel 88 mm from the ionization point to the detector. The results of Figure 2 clearly show that a quantum resonance has been predicted and observed in the $H + D_2 \rightarrow HD(v', j') + D$ reaction. This agreement confirms the validity of the scattering calculation and the existence of dynamical resonances in the $H+H_2$ reaction system for the first time.

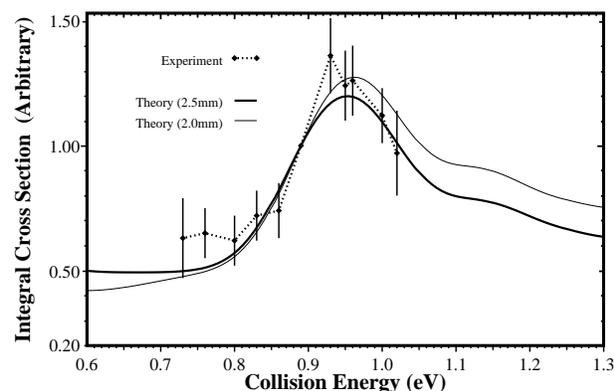


Figure 2: Comparison of the experimental measurements and theoretical predictions.

B. K. Kendrick, L. Jayasinghe, S. Moser, M. Auzinsh, and N. Shafer-Ray, *Phys. Rev. Lett.*, in press.

A U. S. Department of Energy Laboratory

This paper is a portion of LA-UR-00-1.

bkendric@lanl.gov
Los Alamos