

Observation of Predicted Resonance Structure in the $\text{H} + \text{D}_2 \rightarrow \text{HD}(v' = 0, j' = 7) + \text{D}$ Reaction at a Collision Energy of 0.94 eV

Brian K. Kendrick

Theoretical Division (T-12, MS-B268), Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Lalith Jayasinghe, Steven Moser, Marcis Auzinsh, and Neil Shafer-Ray

Department of Physics and Astronomy, The University of Oklahoma, Norman, Oklahoma 73019

(Received 28 January 2000)

We present experimental verification of predicted resonance structure in the energy dependence of the $\text{H} + \text{D}_2$ reaction. Specifically we predict and observe a broad resonance in the $\text{H} + \text{D}_2 \rightarrow \text{HD}(v' = 0, j' = 7) + \text{D}$ reaction at a collision energy of 0.94 eV. This resonance structure is roughly Gaussian with a full width at half maximum of 0.1 eV. These results represent the first experimentally observed resonance structure in the fundamental $\text{H} + \text{H}_2$ reaction system.

PACS numbers: 34.50.Pi, 82.20.Pm

Understanding the role that dynamical scattering 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. 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. The prediction of resonance structure in the $\text{H} + \text{H}_2$ reaction system dates back to the 1D collinear calculations by Kuppermann and co-workers [1] and by Wu and Levine [2]. They were later found in the full 3D calculations of Schatz and Kuppermann [3] for $J = 0$ and 1 partial scattering waves, where J is the total angular momentum. The pioneering work of Schatz and Kuppermann showed that resonances were present even when the full 3D space of the internal nuclear degrees of freedom were treated correctly. These early theoretical predictions inspired many theoretical [4–14] and experimental [15–17] studies. 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 (DCSs). This concern was temporarily damped when the first experimental observation of resonance structure was reported by Nieh and Valentini in 1988 [15]. However, subsequent theoretical studies by several independent groups [5–7,10–13] were unable to reproduce the experimental observations. In particular, the fully converged results of Zhang and Miller [7,10] and Manolopoulos and Wyatt [11] showed that the resonance structure did indeed wash out as the sum over partial waves was extended to include more values of J . Their fully converged integral cross sections exhibited a smooth energy dependence in disagreement with the experiments of Nieh and Valentini [15], but consistent with a later experiment by Klinner, Adelman, and Zare [16]. Resonance structure due to geometric phase effects was reported by Kuppermann and Wu [14] for the $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$

reaction. However, recent high resolution molecular beam experiments by Wrede and Schnieder [17] found no evidence for this structure. Thus, until now, no theoretical evidence for resonant structure in the fundamental $\text{H} + \text{H}_2$ 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 $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$ reaction can now be measured experimentally as a function of energy with unprecedented resolution [18]. Theoretical evidence exists for resonance structure in the DCSs for rotationally resolved HD products for the $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$ reaction [11–13]. This structure appears to survive the sum over all partial waves but only for DCSs with rotationally resolved HD products. The sum over the rotational states of HD causes the structure to wash out. Recent theoretical calculations for the $\text{H} + \text{D}_2$ reaction predict resonance structure in *both* the integral and DCSs for rotationally resolved HD products [19]. We present results of uniquely accurate quantum scattering calculations and experimental data that provide strong evidence for resonance structure in the $\text{H} + \text{D}_2 \rightarrow \text{HD}(v', j') + \text{D}$ reaction.

Theory.—For the scattering energies considered in this study, the Born-Oppenheimer approximation is valid and the reaction occurs on the ground-state electronically adiabatic potential energy surface (PES) of H_3 . This PES is a function of the three internal nuclear degrees of freedom and is represented by the state-of-the-art Boothroyd-Keogh-Martin-Peterson fit to *ab initio* data [20]. 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 [19,21]. The calculations are computationally intensive and require extensive computer time on massively parallel supercomputers. Details of the coordinate system,

numerical techniques, parallelization, and convergence studies are described in Refs. [19,21].

Figure 1 plots the DCS for the $\text{H} + \text{D}_2(v = 0, j = 0) \rightarrow \text{HD}(v' = 0, j' = 7) + \text{D}$ reaction as a function of collision energy for 70 energies between 0.5 and 2.1 eV. The scattering angle (θ) 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. In order to reduce the computational effort, the current calculations *do not* include geometric phase effects. Recent calculations show that the geometric phase effects cancel out when contributions from even and odd values of total angular momentum (J) are added together [19]. The most striking feature is the prominent resonance near 0.94 eV which exhibits a large backwards scattering peak. The current results in Fig. 1 correspond to summing over the first 7 partial waves (i.e., all values of total angular momentum $J \leq 6$). We expect that another 20 partial waves will be required in order to obtain fully converged results up to 1.3 eV. However, the qualitative shape of the pronounced resonance near 0.94 eV appears to be independent of the number of partial waves which are included. Resonance structure very similar to that in Fig. 1 is also seen for all of the $v = 0, j = 1-4$ states of D_2 . Thus, the resonance structure is still present even when we add up the contributions for each $j \leq 4$ which correspond to a Boltzmann rotational distribution of the D_2 at $T = 230$ K. The persistent nature of this resonance suggests that it is “real” and provided the motivation for the experimental work described below.

Experiment.—The experimental apparatus has been explained in a previous work [18]. In brief, a single molecu-

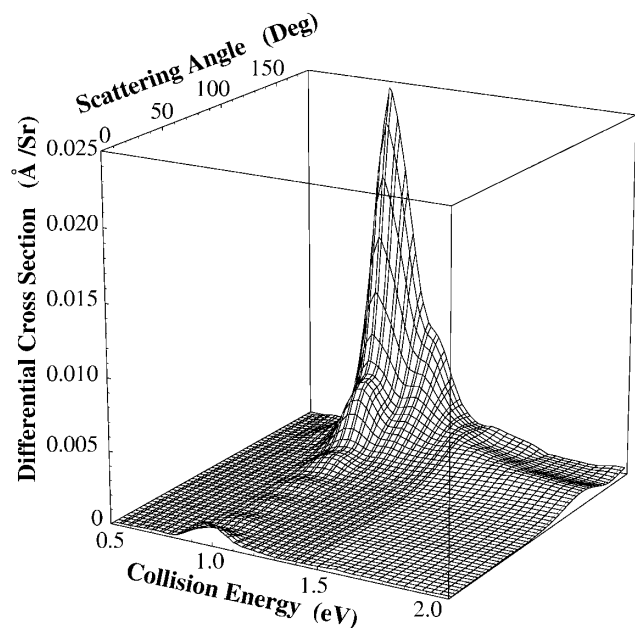
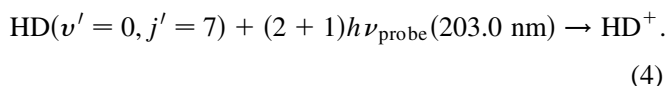
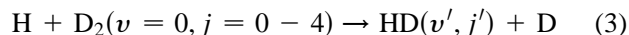
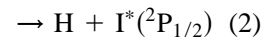
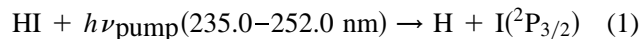


FIG. 1. Partial differential cross section for $\text{H} + \text{D}_2(v = 0, j = 0) \rightarrow \text{HD}(v' = 0, j' = 7) + \text{D}$ is plotted as a function of energy. The resonance feature at 0.94 eV is clearly visible.

lar beam mixture of 10% HI and 90% D_2 copropagates with two sources of 7.0 ns pulsed-laser radiation. One of these sources dissociates the HI, whereas the other selectively ionizes the $\text{HD}(v' = 0, j' = 7)$ product of the following reaction sequence:



As the pump laser radiation responsible for the photodissociation of step (1) is tuned, the collision energy of the reaction corresponding to the production of slow H atoms and I^* varies from 0.73 to 1.02 eV, whereas the collision energy of the reaction corresponding to the production of fast H atoms and I varies from 1.48 to 1.76 eV. The experimental apparatus has been designed to achieve a collision energy resolution of ± 0.015 eV.

The HD^+ ions produced by the probe laser radiation responsible for the ionization of step (4) are selected from a large background using a linear time-of-flight-mass spectrometer. Further discrimination is achieved by taking advantage of the high speed of the $\text{HD}(v', j')$ reaction product as compared to a background caused of thermal D_2 and HD ions. To accomplish this second level of discrimination, the ions are imaged onto a 25.0 nm diameter microchannel plate with a 9.0 mm wide rectangular mask placed in front of it (see Ref. [18]). Only those HD^+ ions that move with sufficient radial velocity to pass the mask are detected. To further discriminate against background, data are collected by measuring the increase in the yield of HD^+ as the delay between the pump and probe laser is switched from 10.0 to 50.0 ns. The raw experimental data are taken to be this increase in ionization yield divided by the following four measured quantities: (1) The average energy per pulse of the pump laser, as measured after the reaction chamber. (2) The average energy of the probe laser to the third power, as measured after the reaction chamber. (3) The base pressure behind the pulsed nozzle source. (4) The known HI absorption coefficient at the dissociation wavelength [22]. The data presented represent approximately 40 sweeps of the dissociation wavelengths. The error bars are taken to be 1 standard deviation of the mean of this set of measurements.

In addition to increasing the discrimination (and hence sensitivity) of the measurement, the mask in front of the microchannel plate detector creates a sensitivity to scattering angle. This sensitivity results from the well documented [23] one-to-one correspondence between the laboratory-frame speed of the state selected product of a photoinitiated reaction and the center-of-mass frame

scattering angle. This sensitivity to scattering angle can be accurately modeled using Monte Carlo simulation techniques [18], allowing our energy dependent measurement $S(E^*)$ to be compared to the energy dependent state-to-state DCS by the forward convolution

$$S(E^*) = N \left(\Gamma(E^*) \int_{-1}^1 \frac{d\sigma(E^*)}{d\Omega} G^*(E^*, x) dx + [1 - \Gamma(E^*)] \int_{-1}^1 \frac{d\sigma(E)}{d\Omega} G(E, x) dx \right). \quad (5)$$

Here E^* is the collision energy corresponding to slow H atoms, whereas $E = E^* + 0.748$ eV is the collision energy for reactions corresponding to fast H atoms. The parameter N is an arbitrary normalization factor, $d\sigma_E/d\Omega$ is the state-to-state DCS, $x = \cos\theta$, and $\Gamma(E^*)$ is the fractional yield of I^* in the photodissociation of HI found from a fit to the data of Regan *et al.* [24]. The instrument functions G and G^* are found from detailed Monte Carlo simulation of the experiment [18].

Figure 2 plots the DCS for collision energies of $E^* = 1.0$ eV and $E = 1.748$ eV. Also plotted are the sensitivity functions G^* (1.0 eV) and G (1.748 eV). The convolution of the DCS and sensitivity function is repeated at each point on our energy grid and for each value of $j = 0-4$. The contributions for each j are added together with the appropriate Boltzmann weights for a D_2 rotational distribution at $T = 230$ K. The normalization is chosen to give unit signal at $E = 0.89$ eV.

To obtain a quantitative agreement of theory with experiment, a parameter d is adjusted in the Monte Carlo determination of the instrument functions G^* and G . This parameter is an effective misalignment of the laser beams with respect to the time-of-flight detector. The best agreement between experiment and theory occurs when this

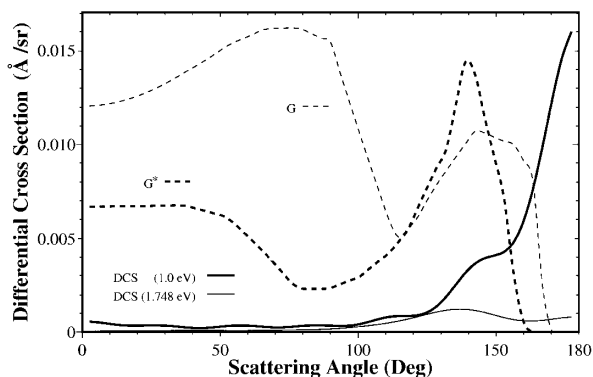


FIG. 2. The differential cross sections at 1.0 eV (thick solid curve) and 1.748 eV (thin solid curve) are plotted. The sensitivity functions G^* (1.0 eV) (thick dashed curve) and G (1.748 eV) (thin dashed curve) are also plotted. In order to make direct comparison with the experimental results, the theoretical results must be convoluted with the G^* and G (see text for discussion).

parameter corresponds to a $d = 2.5$ mm off-axis drift of the HD^+ ions as they travel 88 mm from the ionization point to the detector. Contributions to this nonideal behavior include actual misalignment of the laser beams, stray magnetic and electric fields, and imperfect mechanical alignment of the ion optics used to accelerate the HD^+ . Figure 3 compares the experimental measurements to the theoretical predictions for $d = 2.5$ mm and $d = 2.0$ mm. The d dependence of the forward-convoluted prediction of theory represents an uncertainty in the instrument function. This uncertainty prevents us from evaluating details of the energy-dependent shape of the DCS. However, the results of Fig. 3 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.

The theoretical work was done under the auspices of the U.S. Department of Energy under Project No. 990015 of the Laboratory Directed Research and Development program at Los Alamos under Contract No. W-7405-ENG-36. Computer time on the Cray-T3E was provided by a grant from the Ohio State Supercomputer Center and the National Partnership for Advanced Computational Infrastructure at the San Diego Supercomputer Center through the NSF cooperative agreement No. ACI-9619020. Computer time on an SGI Origin 2000 at the Advanced Computing Laboratory at Los Alamos was provided by the Institutional High Performance Computing Initiative at Los Alamos. The experimental work was supported by the donors of the Petroleum Research Fund administered by the American Chemical Society (PRF-32187-G6), the National Research Council (NRC-6224), the National Science Foundation (CHE-9875456), and the University of Oklahoma.

Note added.—The theoretical calculations have been extended to include 16 partial waves (i.e., all $J \leq 15$) and the conclusions of this paper are unchanged.

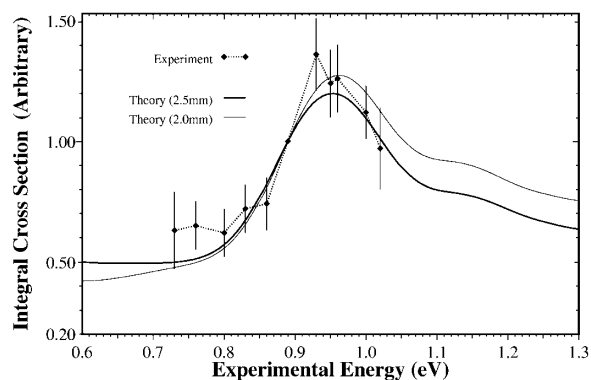


FIG. 3. Comparison of the experimental measurements (solid diamonds) and theoretical predictions for a misalignment parameter of $d = 2.5$ mm (thick solid curve) and $d = 2.0$ mm (thin solid curve). Excellent agreement is observed between theory and experiment.

- [1] D. G. Truhlar and A. Kuppermann, *J. Chem. Phys.* **52**, 3841 (1970); **56**, 2232 (1972); G. C. Schatz and A. Kuppermann, *ibid.* **59**, 964 (1973).
- [2] S.-F. Wu and R. D. Levine, *Chem. Phys. Lett.* **11**, 557 (1971); *Mol. Phys.* **22**, 881 (1971).
- [3] G. C. Schatz and A. Kuppermann, *Phys. Rev. Lett.* **35**, 1266 (1975).
- [4] P. G. Hipes and A. Kuppermann, *Chem. Phys. Lett.* **133**, 1 (1987).
- [5] M. Mladenovic, M. Zhao, D. G. Truhlar, D. W. Schwenke, Y. Sun, and D. J. Kouri, *Chem. Phys. Lett.* **146**, 358 (1988).
- [6] M. Mladenovic, M. Zhao, D. G. Truhlar, D. W. Schwenke, Y. Sun, and D. J. Kouri, *J. Phys. Chem.* **92**, 7035 (1988).
- [7] J. Z. H. Zhang and W. H. Miller, *Chem. Phys. Lett.* **153**, 465 (1988).
- [8] G. C. Schatz, *Annu. Rev. Phys. Chem.* **39**, 317 (1988).
- [9] F. Webster and J. C. Light, *J. Chem. Phys.* **90**, 300 (1989).
- [10] J. Z. H. Zhang and W. H. Miller, *J. Chem. Phys.* **91**, 1528 (1989).
- [11] D. E. Manolopoulos and R. E. Wyatt, *Chem. Phys. Lett.* **159**, 123 (1989).
- [12] R. E. Continetti, J. Z. H. Zhang, and W. H. Miller, *J. Chem. Phys.* **93**, 5356 (1990).
- [13] W. H. Miller and J. Z. H. Zhang, *J. Phys. Chem.* **95**, 12 (1991).
- [14] A. Kuppermann and Y. S. M. Wu, *Chem. Phys. Lett.* **241**, 229 (1995).
- [15] J. C. Nieh and J. J. Valentini, *Phys. Rev. Lett.* **60**, 519 (1988).
- [16] D. A. V. Kliner, D. E. Adelman, and R. N. Zare, *J. Chem. Phys.* **94**, 1069 (1990).
- [17] E. Wrede and L. Schnieder, *J. Chem. Phys.* **107**, 786 (1997).
- [18] S. Kennedy, K. Dharmesena, S. Moser, M. Auzinsh, and N. E. ShaferRay, *Chem. Phys.* **244**, 449 (1999).
- [19] B. K. Kendrick, *J. Chem. Phys.* **112**, 5679 (2000).
- [20] A. I. Boothroyd, W. J. Keogh, P. G. Martin, and M. R. Peterson, *J. Chem. Phys.* **104**, 7139 (1996).
- [21] B. K. Kendrick, R. T. Pack, R. B. Walker, and E. F. Hayes, *J. Chem. Phys.* **110**, 6673 (1999).
- [22] R. M. Martin and B. J. Huebert, *J. Phys. Chem.* **72**, 3946 (1968).
- [23] R. J. Gordon and G. E. Hall, *Adv. Chem. Phys.* **96**, 1 (1996).
- [24] P. M. Regan, D. Ascenzi, C. Clementi, M. N. R. Ashfold, and A. J. Orr-Ewing, *Chem. Phys. Lett.* **315**, 187 (1999).