

Experimental Observation of Dynamical Resonances in the $\text{H} + \text{H}_2$ Reaction

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We report observation of dynamical resonances in the reaction $\text{H} + \text{H}_2(v=0, j=0, 2) \rightarrow \text{H}_2(v', j') + \text{H}$. The reactive cross section as a function of v' and j' is determined under single-collision conditions for 22 total energies between 0.95 and 1.37 eV. Resonances appear as sharp increases in the $v'=1$ cross section at 0.97, 1.20, and 1.26 eV, and possibly 1.11 eV. These energies are in excellent agreement with the energies of theoretically predicted Feshbach resonances in the reaction.

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The hydrogen exchange reaction, $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$, has been the prototype chemical reaction employed in the testing and development of quantum mechanical descriptions of chemical reactions ever since the development of quantum theory.¹⁻⁵ Perhaps the most intriguing aspect of quantum calculations on the $\text{H} + \text{H}_2$ reaction is the prediction of resonances in the reaction.⁵⁻¹¹ The resonances were first revealed in collinear quantum calculations^{6,7} but have been found in three-dimensional calculations as well.^{5,8-10} The resonances appear as a sharp variation of the partial cross sections, the cross sections into particular final vibrational and rotational states, v' and j' , as functions of collision energy. The sharp maxima and minima in the partial cross sections reflect the interference between two scattering amplitudes, a direct one and a resonant one. The latter arises because of nonadiabatic coupling between the relative motion and the internal degrees of freedom, leading to the formation of quasibound excited states.⁷ The binding force that holds the resonant states is dynamic and these resonances are Feshbach resonances.

The nature of the dynamical binding of the resonant states makes them of particular significance. The internal degrees of freedom that provide the resonant states are the vibrational degrees of freedom of the H_3 transition state, that is, the vibrational motions perpendicular to the relative motion in the vicinity of the "transition" from reactants to products. Thus the spectrum of resonant states is the spectrum of vibrational eigenstates of the transition state, and mapping out the dynamical resonances in the reaction is tantamount to vibrational spectroscopy of the transition state.¹¹ The resonance features thus are a very sensitive probe of the structure of the transition state.¹²

Since the resonances are associated with nonadiabatic coupling to particular vibrational states of the H_3 transition state, it is convenient to label them by vibrational quantum numbers to indicate the excited vibrational state responsible for the resonance. The labeling^{10,13,14} is (v_1, v_2^a, v_3) , where v_1 is the number of symmetric stretch quanta and v_2 the number of bending quanta. The superscript Ω gives the component of vibrational angular

momentum along the molecular axis. At the transition state the antisymmetric stretch is the $\text{H} + \text{H}_2$ relative motion, an unbound motion, so that v_3 is undefined. By convention it is written as 0.

Calculations that predict the energies of the Feshbach resonances in $\text{H} + \text{H}_2$ have been carried out not only by exact quantum methods,⁵⁻¹⁰ but also by approximate quantum methods,¹³⁻¹⁵ and by semiclassical approaches.^{16,17} At total energies (collision energy plus H_2 vibrational energy) between 0.95 and 1.3 eV, these calculations predict the resonances (1,0,0), (1,1¹,0), (1,2⁰,0), and (1,2²,0) at total energies 0.98, 1.10, 1.20, and 1.23 eV, respectively.^{5,8-11,13-17} The common feature shared by these particular resonances is that each appears as an increase in the $v'=1$ reactive cross section and a corresponding decrease in the $v'=0$ reactive cross section in a narrow energy region around the resonance energy. This behavior comes about because the $\text{H} + \text{H}_2$ reaction dynamics favor formation of a $v'=1$ product if an H_3 vibrational state having one quantum of symmetric stretch is accessed.

In this Letter we report experimental observation of the (1,0,0), (1,2⁰,0), and (1,2²,0) resonances, and possibly the (1,1¹,0) resonance, in the reaction $\text{H} + \text{H}_2(v=0, j=0, 2) \rightarrow \text{H}_2(v', j') + \text{H}$, at total energies of 0.97, 1.11, 1.20, and 1.26 eV. The partial cross sections, $\sigma(v', j')$, for the reaction are determined from coherent anti-Stokes Raman-scattering (CARS) spectroscopy of the $\text{H}_2(v', j')$. uv photolysis of HI at wavelengths between 266 and 308 nm yields H atoms with well-defined translational energies, giving $\text{H} + \text{H}_2$ collision energies of 0.68 to 1.1 eV and total energies of 0.95 to 1.37 eV. Pulsed lasers of ≈ 5 -ns pulse duration are used both for production of the H atoms and for the CARS probing of the H_2 product, in a gas cell through which a mixture of HI and H_2 flows, at total pressures of a few Torr. The time delay between the photolysis and probe laser pulses is ≈ 4 ns, a time sufficiently short that the H_2 product is formed and detected under single-collision conditions. The experimental approach and apparatus have been used previously in our related experiments on the $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$ reaction.¹⁸

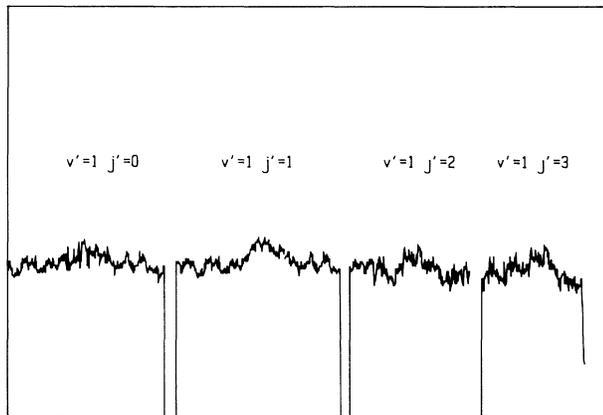


FIG. 1. Part of the vibrational Q -branch CARS spectrum of H_2 from the $H + p\text{-}H_2$ reaction at a total energy of 1.37 eV.

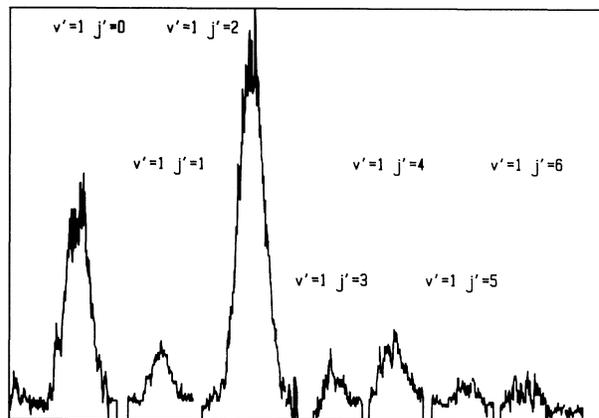


FIG. 2. Part of the vibrational Q -branch CARS spectrum of H_2 from the $H + p\text{-}H_2$ reaction at a total energy of 1.20 eV.

In the present experiments the reactant molecule is pure ($\geq 99\%$) parahydrogen, which at the ambient temperature of our gas cell contains almost equal populations of the rotational levels $j=0$ and $j=2$, with a very small ($\approx 1\%$) amount of $j=4$, and only the ground vibrational state, $v=0$. The use of parahydrogen allows us to distinguish the reactive $H_2(v',j')$ product from the inelastic $H_2(v',j')$ product. Since inelastic collisions do not convert para states to ortho states, the inelastic $H_2(v',j')$ is limited to $j'=0,2,4,\dots$ while reactive collisions do lead to para-to-ortho conversion and hence populate all energetically accessible j' .² All $H_2(v',j')$ detected in $j'=1,3,5,\dots$ is unambiguously reactive product, while the $H_2(v',j')$ in $j'=0,2,4,\dots$ is due to both inelastic and reactive encounters. Separation of the reactive and inelastic processes is desirable because the Feshbach resonances are predicted to influence the inelastic and reactive scattering differently.¹⁰

Figures 1 and 2 show part of the vibrational Q -branch CARS spectra of H_2 formed in the $H + H_2(v=0, j=0,2)$ reaction at total energies of 1.20 and 1.37 eV. At the higher energy there is only a barely detectable signal from the product in $v'=1$ while at 1.20 eV the $v'=1$ yield is much greater. Throughout most of the 0.95- to 1.37-eV total energy range the CARS spectra indicate very small production of $v'=1$. However, there are narrow energy ranges, such as around 1.20 eV, in which the yield of the vibrationally excited product is greatly enhanced. This behavior is shown in Fig. 3, which presents the partial reactive cross sections $\sigma(v',j')$, for $v'=1, j'=1$ and 3. Note that the threshold for $v'=2$ production occurs at about 1.36 eV,^{9,10} and so for all but the highest energy studied here the only available product vibrational channels are $v'=0$ and 1.

These partial cross sections are obtained from the H_2 -product quantum-state number densities, extracted by analysis^{18,19} of CARS spectra which are averages over five to ten single scans like those shown in Figs. 1 and 2.

The densities of the reactants H and H_2 are also determined from CARS spectra: for the reactant $H_2(v=0, j=0,2)$ from spectra taken in the absence of H atom generation, and for the reactant H atom from the difference between spectra of the precursor HI with and without uv photodissociation. The relative density measurements of reactants and product are converted to absolute densities through calibration of the CARS spectra by reference to H_2 and HI spectra taken at known number density. These product number densities yield partial cross sections through the relation $\sigma(v',j') = n(v',j') / [n_H n_{H_2} v_{rel} \langle \Delta t \rangle]$, where $n(v',j')$ is the product number density in v',j' , n_{H_2} is the number density of the H_2 reactant, n_H is the number density of the H -atom reactant, v_{rel} is the relative (collision) velocity of $H + H_2$, and $\langle \Delta t \rangle$ is the average time delay between creation of the H atom and detection of $H_2(v',j')$. An average over Δt is necessary, because of the finite pulse widths of the lasers used to create the H -atom reactant and to detect the H_2 product. This method of absolute cross section determination leads to uncertainties (estimated one standard

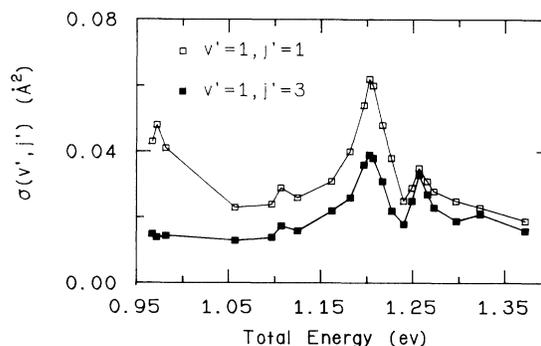


FIG. 3. Product partial cross sections for the $H + H_2(v=0, j=0.2) \rightarrow H_2(v', j') + H$ reaction as a function of total energy. Error bars are not shown; see text.

deviation) ranging from $\pm 20\%$ for the largest $\sigma(v',j')$ in Fig. 3 to $\pm 50\%$ for values less than 0.02 \AA^2 .

There are clear maxima in the $\sigma(v'=1,j')$ shown in Fig. 3, and in $\sigma(v'=1)$, the sum over odd j' of $\sigma(v'=1,j')$, at 0.97, 1.20, and 1.26 eV, in excellent agreement with the energies at which maxima in the $\sigma(v'=1)$ are theoretically predicted as a consequence of the (1,0,0), (1,2⁰,0), and (1,2²,0) Feshbach resonances. There is a weaker maximum at 1.11 eV, in agreement with the energy at which the (1,1¹,0) resonance is predicted. As discussed above, the $\sigma(v'=1,j')$ for odd j' (ortho-hydrogen) are purely reactive while the $\sigma(v'=1,j')$ for even j' (para-hydrogen) contain contributions from both reactive and inelastic collisions because the reactant is pure para-hydrogen. Of the ortho-hydrogen rotational levels $j=1$ and 3 carry most of the population in $v'=1$, and the only other ortho level with detectable population ($\sigma > 0.005 \text{ \AA}^2$) is $j=5$. The limited energy resolution ($\approx 0.1 \text{ eV}$) of these experiments with a thermal H_2 gas sample and the limited number of energies at which the experiments have been carried out make it difficult to determine the energy widths of the resonance features and use these widths to measure the lifetimes of the resonant states. However, the lifetimes must not be less than about 15 fs. For the same reasons the accuracy of the specification of the resonance energies is limited to $\pm 0.01 \text{ eV}$.

An alternative way to locate the resonance energies is to determine the ratio of the $\sigma(v'=1)$ and $\sigma(v'=0)$ cross sections. This ratio should perhaps even more clearly reveal the resonances because of the predicted^{5,8-11} depletion of $v'=0$ product that accompanies the enhancement of $v'=1$ production at these resonances. Figure 4 presents a plot of $\sigma(v'=1)/\sigma(v'=0)$ versus energy, and the resonances are observed in it as well. The cross-section ratio plotted here is the ratio of the reactive partial cross sections into $v'=1$ and $v'=0$, obtained by summation over odd j' . The error bars represent the one-standard-deviation uncertainty. Like $\sigma(v'=1,j')$

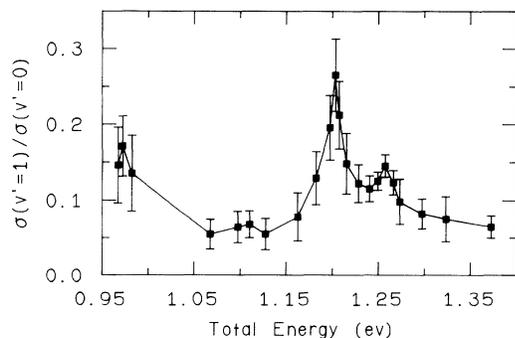


FIG. 4. The $\sigma(v'=1)/\sigma(v'=0)$ partial cross-section ratio for the reaction $\text{H} + \text{H}_2(v=0, j=0.2) \rightarrow \text{H}_2(v', j') + \text{H}$ as a function of total energy. Error bars represent one standard deviation.

and $\sigma(v'=1)$, $\sigma(v'=1)/\sigma(v'=0)$ has strong maxima at 0.97, 1.20, and 1.26 eV and a weak maximum at 1.11 eV.

The results reported here represent the first experimental observation of the theoretically predicted Feshbach resonances in the reaction $\text{H} + \text{H}_2$. These observations confirm theoretical predictions about the energies at which the resonances should be observed. The resonance effects are even stronger than might be expected.¹¹ For different partial waves (orbital angular momentum states, l) the resonances occur at slightly different energies, and it is not possible to select partial waves experimentally. The effect of having many partial waves contributing to the reaction, each with a slightly different resonance energy, will be to damp the magnitude of the resonance effects, making them less observable. Whatever the extent of such damping, our experiments indicate that it is not severe enough to eliminate the resonance features.

The small magnitudes of the $\sigma(v'=1,j')$ and $\sigma(v'=1)$ suggest that only partial waves of small l are important and that only a few such partial waves contribute. For $\sigma(v'=1) = 0.1 \text{ \AA}^2$ it seems unlikely that partial waves much greater than $l=4$ are important. The full partial-wave expansion, exact quantum calculations of Schatz and Kuppermann,³ show that when the reactive cross section into $v'=0$ is 0.1 \AA^2 , only partial waves of $l \leq 5$ are important. These are, however, calculations done at energies far removed from the resonance energies and so their use to suggest the extent of contributions from different partial waves near resonance is not without question. If only four or five partial waves contribute to $\sigma(v'=1)$ then the resonance effects are not likely to be averaged out. Contributions from such a range of partial waves would be expected to shift the $\sigma(v'=1)$ maxima by $\approx 0.008 \text{ eV}$ to higher energy from the values for $l=0$, because of the resonance energy dependence on l ,¹⁷ but such a small shift is within the uncertainty of our measurements.

The influence on the partial cross sections is not the only observable consequence of dynamical resonances. The first observation of a resonance effect in a chemical reaction was a change in the product angular distribution for specific v' in the reaction $\text{F} + \text{H}_2 \rightarrow \text{HF} + \text{H}$.²⁰ A resonance for this reaction was predicted theoretically,^{12,21-23} and the observed²⁰ shift in the differential cross section to forward peaked at the resonance is the expected behavior.²³

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