Experimental Investigation of Resonances in Reactive Scattering: The $F+H_2$ Reaction

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The reaction $F+p\text{-}H_2 \rightarrow HF+H$ was studied in a high-resolution crossed-molecular-beams experiment at a collision energy of 1.84 kcal/mole. Center-of-mass translational energy and angular distributions were determined for each product vibrational state. The $v=3$ product showed intense forward scattering while the $v=2$ product was backward peaked. These results suggest that dynamical resonances play an important role in the reaction dynamics of this system.

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A direct probe of the transition state in chemical reactions has been one of the more elusive goals of experimental studies in reaction dynamics. The region of the potential energy surface (PES) near the transition state determines several important properties of a reaction such as the rate constant and the partitioning of excess energy among product degrees of freedom. The techniques necessary to measure these properties of a reaction have developed considerably in recent years. Attempts to study the transition state by photon emission and absorption have been carried out,[1] but it has proved difficult to work backwards and characterize the critical region of the PES near the transition state based on these results. One promising approach to this problem derives from quantum mechanical reactive-scattering calculations which show that the resonances play a significant role in the reaction dynamics of simple systems.[2] The exact nature of these reactive resonances depends strongly on the details of the PES near the transition state.[3] Observing the effects of such resonances should provide greater insight into the transition state than has previously been possible. To this end we have performed a high-resolution reactive-scattering study of the reaction $F+H_2 \rightarrow HF+H$ with the crossed-molecular-beams technique.

Collinear quantal scattering calculations on the Muckerman 5 (M5)[4] PES for $F+H_2$ of the reaction probability versus collision energy show sharp resonance features with typical widths of 0.01 eV.[5,6] These features result from the ability of the PES to support quasibound FH_2 states which live for several vibrational periods before decomposing to products.[6,7] However, three-dimensional quantal calculations of the total reaction cross section versus energy do *not* show any sharp structure,[8,9] because collisions with nonzero orbital angular momentum contribute to the reaction.[10] A quasibound state formed by a collision of orbital angular momentum $L\hbar$ will have a rotational energy on the order of $BL(L+1)$, where B is the rotational constant of the reaction intermediate. If an $L=0$ resonance occurs at energy E_0, then at approximately $E_0+BL(L+1)$ a quasibound state can be formed by a collision of orbital angular momentum $L\hbar$. Consequently, as the collision energy is increased beyond E_0, collisions with progressivley larger values of orbital angular momentum will be brought into resonance. The large number of partial waves involved in reactive scattering allows the resonance to be accessed over a wide energy range, and resonances appear as broad, smooth features in the collision energy dependence of the reactive cross section which are difficult to distinguish from the substantial contribution from direct reaction. Thus resonances will not be observed by measuring state-resolved total reaction cross sections as a function of reactant translational energy.

On the other hand, the three-dimensional quantal calculations[10] on $F+H_2$ suggest that resonances can be observed in an experiment which is sensitive to the reaction probability as a function of orbital angular momentum, $P(L)$, for each product vibrational state. The angular distribution of products from reactive scattering is closely related to $P(L)$. The HF product vibrational states resulting from decay of a resonance should have a different angular distribution than those formed primarily via direct, nonresonant processes. Thus, resonances will be most prominent in an experiment which determines vibrational-state–resolved angular distributions. Quasiclassical trajectory studies on M5 show that at collision energies as high as 5.0 kcal/mole, $P(L)$ for the formation of the $v=2$ and $v=3$ products decreases monotonically with increasing orbital angular momentum.[9] The resulting differential cross sections are backward peaked at

180° with respect to the incident F beam.[9,11] The three-dimensional quantal results are quite different.[10] When the collision energy is raised from 2 to 3 kcal/mole, the peak in the $P(L)$ of $v=2$ shifts to nonzero orbital angular momentum whereas the $P(L)$ of $v=3$ remains monotonically decreasing. This occurs because the resonance on M5 decays specifically to $v=2$ product, and, for a given collision energy, the resonance is accessible only over a relatively narrow range of L which is centered at progressively higher values of orbital angular momentum as the collision energy is raised. At 3 kcal/mole, the resonance-enhanced contribution from the high–impact-parameter collisions should lead to increased sideways and possibly forward scattering for the $v=2$ product while the $v=3$ product remains backward peaked.

Our previous experimental studies on this reaction showed that the $v=2$ angular distribution did indeed broaden and exhibit slight sideways peaking as the collision energy was raised from 2 to 3 kcal/mole. The results for the $v=3$ state were inconclusive, however, because of experimental difficulties that limited the range of the angular scan.[12]

The major features of the crossed–molecular-beams apparatus have been described elsewhere.[13,14] Modifications were made on the apparatus to improve the velocity resolution and to reduce the HF background. An effusive beam of F atoms was produced by thermally dissociating F_2 at 2.0 Torr and 920 K in a resistively heated nickel oven. The F beam was velocity selected to give a peak velocity of 8.7×10^4 cm/sec with a full width at half maximum (FWHM) velocity spread of 11%. The p-H_2 beam was produced by a supersonic expansion of 80 psi (gauge) through a 70-μm orifice at 304 K. The peak velocity was 2.79×10^5 cm/sec with a FWHM spread of 3%. About 80 percent of p-H_2 was $J=0$ under these conditions.[15] The FWHM reactant kinetic energy spread in the center-of-mass frame was only 0.1 kcal/mole. The HF product was detected with a rotatable ultrahigh-vacuum mass spectrometer. Angular scans were taken by modulating the H_2 beam at 150 Hz and recording the modulated HF signal as a function of angle. Product velocity distributions were obtained at nineteen angles by the cross-correlation time-of-flight technique.

The angular distribution for the HF product is shown in Fig. 1. The laboratory angle Θ is measured from the F beam. $(\vec{v}_F, \vec{v}_{H2})$ and $(\vec{u}_F, \vec{u}_{H2})$ in the Newton diagram below are the laboratory and c.m.s. velocities, respectively, of the reactants. In the c.m. coordinate system, $\theta=0°$ is defined as the direction of the incident F beam, $\vec{u}_F$. The "Newton circles" represent the maximum center-of-mass speed for HF product formed in the indicated vibrational state. The broad peaks in the angular distribution around 28° and 45° are from back-scattered $v=3$ and $v=2$ products, respectively. The sharp peak at 8° is from forward-scattered $v=3$. No product signal was detected on the other side of the beam.

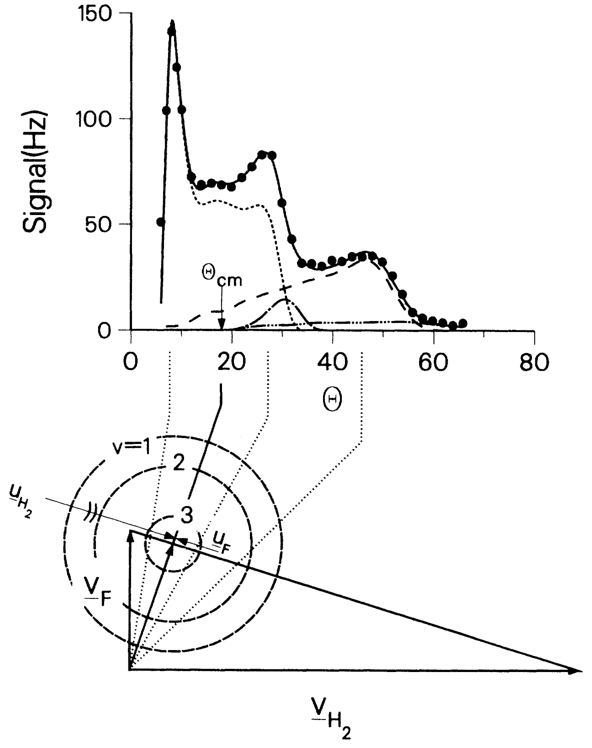

FIG. 1. Angular scan and Newton diagram for $F+p\text{-}H_2 \rightarrow HF+H$ at 1.84 kcal/mole collision energy showing contributions from each HF vibrational state (data, circles; total calculated distribution, solid line; $v=1$, dash-dotted line; $v=2$, long-dashed line; $v=3$, short-dashed line; $v=3'$, long- and short-dashed line.

Time-of-flight measurements of the product velocity distributions allow one to determine quantitatively the contribution from each vibrational state to the total signal at laboratory angle. Sample TOF spectra with their vibrational-state assignments are shown in Fig. 2. The spectrum at $\Theta=18°$ shows three distinct peaks. The fastest peak is from $v=2$ product, and the two slower peaks are from $v=3$. The two $v=3$ peaks merge at $\Theta=30°$ and at other laboratory angles which are nearly tangent to the $v=3$ Newton circle. The spectrum at $\Theta=8°$ confirms that the forward peak in the angular scan is from $v=3$ product.

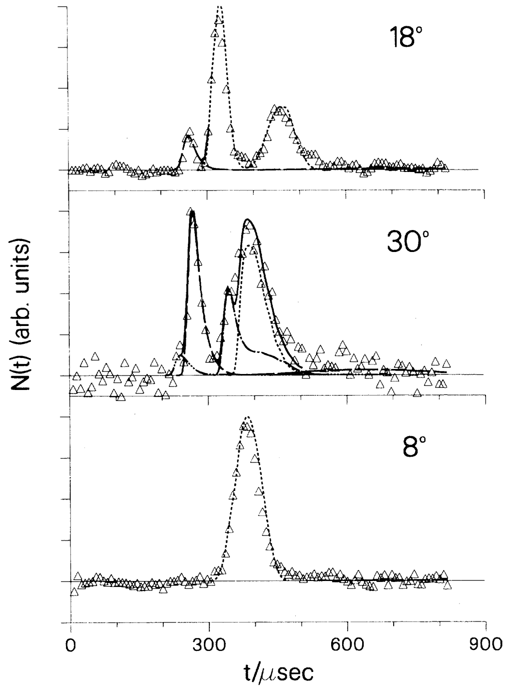

FIG. 2. Time-of-flight spectra at laboratory angles 18°, 30°, and 8° with vibrational state assignments (data, triangles; total calculated distribution, solid line; vibrational states same as Fig. 1; solid line not shown when it obscures a vibrational state).

The translational energy and angular distributions in the c.m. coordinate system were determined for each product vibrational state by forward convolution of trial distributions. The lines in Figs. 1 and 2 are the laboratory distributions generated by the best-fit c.m.s. parameters.

The slow peak at $\Theta = 30°$ has a fast shoulder. A similar feature appears in other TOF spectra that sample $v = 3$ product near $\theta = 180°$, and this could be fitted only by assuming it was due to HF($v = 3$) from reactants with approximately 1 kcal/mole internal excitation. This product, designated as $v = 3'$, is most probably from the reaction of $F(^2P_{3/2})$ with $H_2(J = 2)$ which is 1.03 kcal/mole above $H_2(J = 0)$ and makes up about 20% of the p-H_2 beam.[15]

The c.m.s. distributions for the HF products are illustrated in Fig. 3. The $v = 2$ state is backward-peaked and drops off slowly for $\theta < 180°$. The $v = 3$ state has a broad maximum around $\theta = 80°$ and, in contrast to the $v = 2$ state, has a sharp, intense peak at $\theta = 0°$. The $v = 3'$ state is scattered entirely into the backward hemisphere. The relative total cross sections into each vibrational state

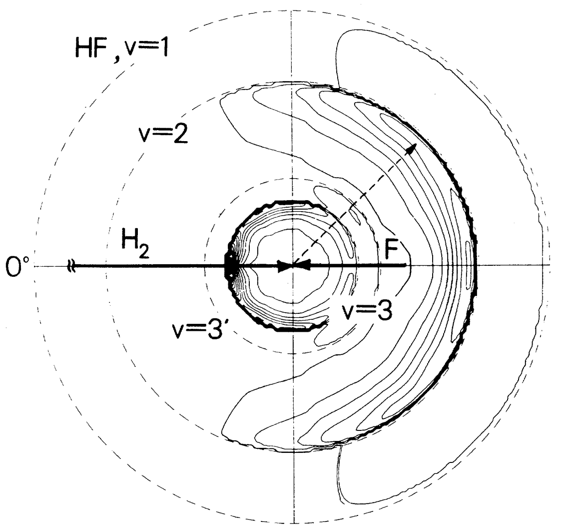

FIG. 3. Center-of-mass system velocity contour map for HF product from the reaction of $F + p$-H_2. Contours of constant product flux are plotted as a function of both center-of-mass system velocity and scattering angle. the c.m.s. scattering angle is measured from the F beam velocity vector. The dashed lines indicate the maximum velocities allowed for HF in different vibrational states.

are as follows: $\sigma_1 = 0.20$, $\sigma_2 = 1.00$, $\sigma_3 = 0.68$, $\sigma_{3'} = 0.05$.

When contrasted with the strong backward scattering observed for $v = 2$, the sharp forward peak and pronounced sideways scattering in the $v = 3$ angular distribution is the most compelling evidence to date for quantum mechanical dynamic resonance effects in reactive scattering. The shape of the distribution is consistent with what one expects when collisions at relatively high impact parameters contribute to the formation of a quasibound state followed by selective decay to $v = 3$ products. The intense forward peak results from the strong correlation between the directions of L and L^1, the final orbital angular momentum vector, for the collisions that form the quasibound state. In complexes that survive for several rotational periods, this correlation leads to a symmetric angular distribution peaking at 0° and 180° in the center-of-mass system.[16] The much weaker intensity at 180° in this experiment shows that the quasibound state lives only a fraction of a rotational period. The contrast between the $v = 2$ and $v = 3$ product distributions lends support to the interpretation of the results in terms of quantum mechanical resonances. Quasiclassical trajectory calculations do not show such state-specific behavior for this reaction.

Our results indicate that the quasibound state decays to $v=3$ product in contrast to the calculations on M5 which predict decay exclusively to $v=2$. This discrepancy as well as other recent developments[4] suggest that the M5 surface is an inadequate representation of the $F+H_2$ PES. Quantal collinear calculations on other model surfaces show the corresponding resonance decaying to $v=3$.[3] While these surfaces are inferior to M5 in terms of exothermicity and entrance-channel barrier height, the calculations illustrate that small changes in the interaction region markedly affect the predicted role of resonances in this reaction.

The vibrationally state-resolved differential cross sections obtained in this experiment point to resonances playing a part in the dynamics of the $F+H_2$ reaction; comparison of these results with future scattering calculations should be of great utility in the development of an accurate potential energy surface for this reaction.

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