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DISCLAIMER

EXPERIMENTAL INVESTIGATION OF RESONANCES IN REACTIVE SCATTERING: THE $F+H_2$ REACTION

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ABSTRACT:

The $F+para\text{-}H_2 \rightarrow HF+H$ reaction 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 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 $F+H_2 \rightarrow HF+H$ reaction 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 vs. 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 quasi-bound FH_2 states which live for several vibrational periods before decomposing to products.[6,7] However, 3-dimensional quantal calculations of the total

reaction cross section vs. energy do not show any sharp structure,[9,10] because collisions with nonzero orbital angular momentum contribute to the reaction.[8] A quasi-bound 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 quasi-bound 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 progressively 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[8] 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, non-resonant processes. Thus, resonances will be most prominent in an experiment which determines vibrational state-resolved

angular distributions. Quasi-classical 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.[10] The resulting differential cross sections are backward-peaked at 180° with respect to the incident F beam.[10,11] The 3-dimensional quantal results are quite different.[8] 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 $\underline{L}$ 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 2-3 kcal/mole. The results for the v=3 state were inconclusive, however, because of experimental difficulties that limited the range of the angular scan.[11]

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 FWHM velocity spread of 11 per cent. The para-H_2 beam was produced by a supersonic expansion of 80 psig through a 70μ orifice at 304°K. The peak velocity was 2.79×10^5 cm/sec with a FWHM spread of 3 per cent. About 80 percent of p-H_2 in J=0 under these conditions.[15] The FWHM reactant kinetic energy spread in the center-of-mass was only 0.1 kcal/mole. The HF product was detected with a rotatatable 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 19 angles by the cross-correlation time-of-flight technique.

The angular distribution for the HF product is shown in Fig. 1. The LAB angle Θ is measured from the F beam. ($\underset{\sim}{v}_F$, $\underset{\sim}{v}_{H2}$) and ($\underset{\sim}{u}_F$, $\underset{\sim}{u}_{H2}$) in the Newton diagram below are the LAB and CM velocities, respectively, of the reactants. In the CM coordinate system, $\theta=0°$ is defined as the direction of the incident F beam, $\underset{\sim}{u}_F$. 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 product, respectively. The sharp peak at 8° is from forward-scattered v=3. No product signal was detected on the other side of the beam.

Time-of-flight measurements of the product velocity distributions allow one to quantitatively determine the contribution from each

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 show a dramatic effect from dynamical resonance phenomena; 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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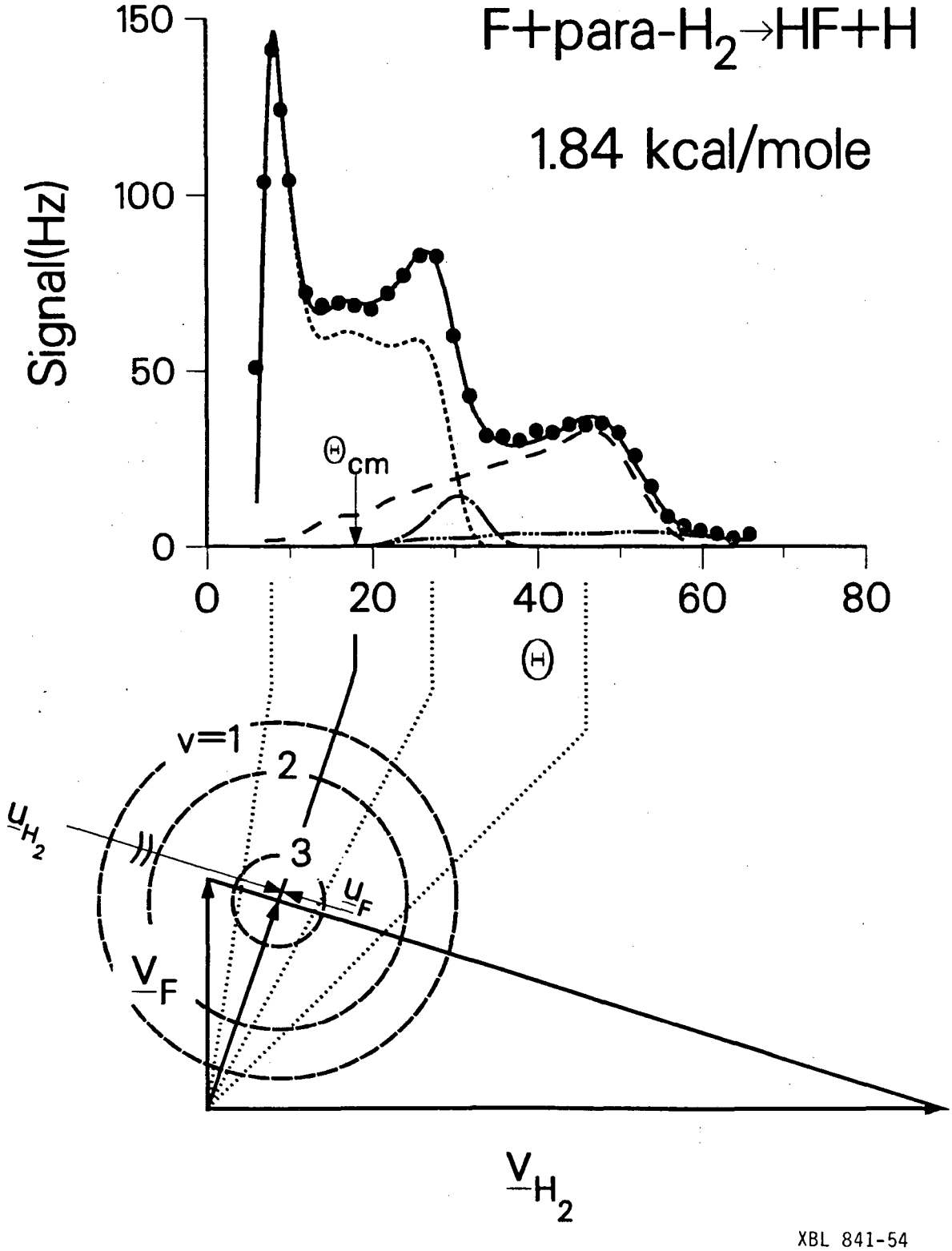
List of Figures

Fig. 1. Angular scan and Newton diagram for F+para-H_2→HF+H at 1.84 kcal/mole collision energy showing contributions from each HF vibrational state (data ●, total calculated distribution ————— , v=1 —— ··· ——, v=2 — — — , v=3 - - - - - -, v=3' —— - —— - ——)

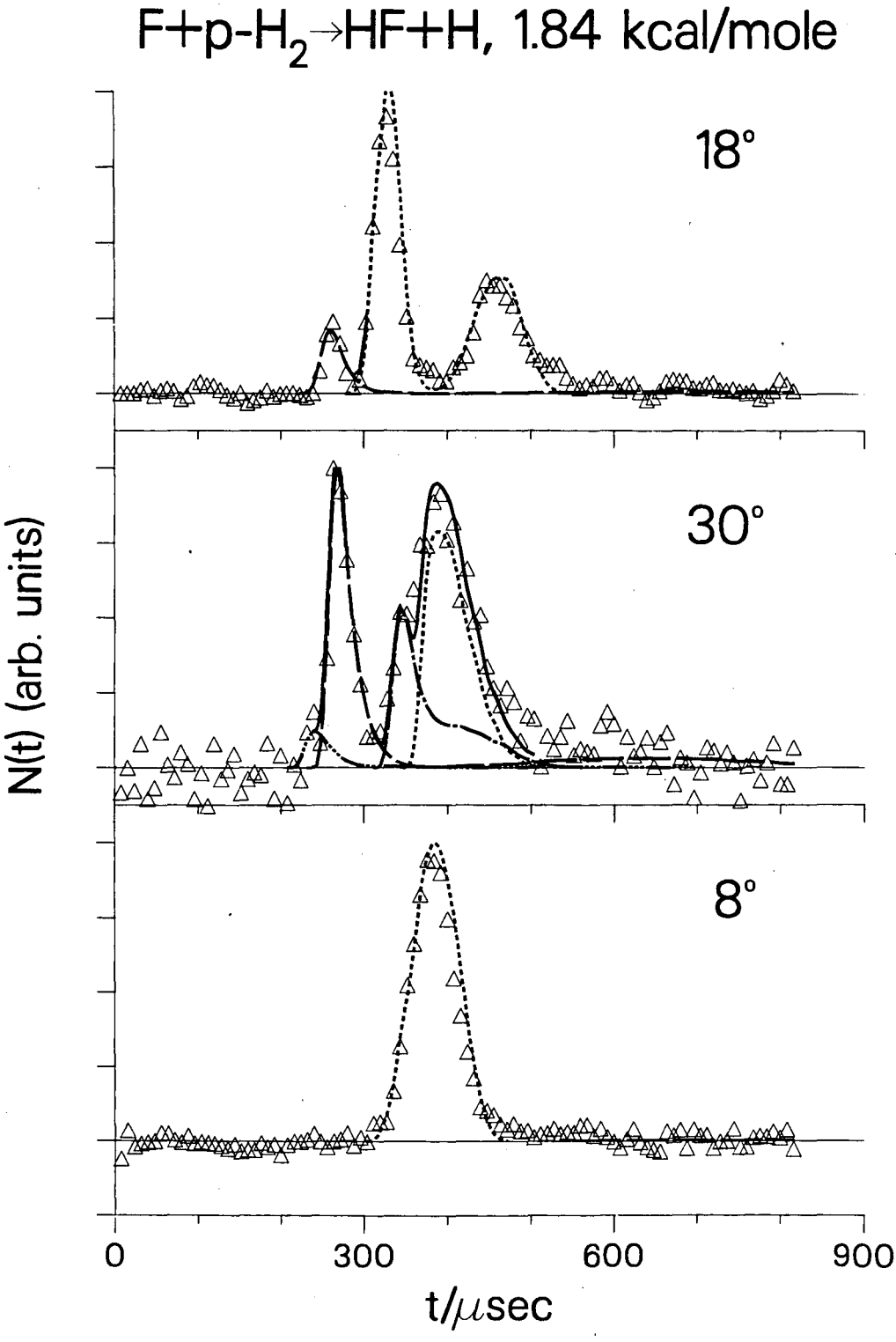
Fig. 2. Time-of-flight spectra at LAB angles 18°, 30°, and 8° with vibrational state assignments(data Δ,total calculated dist. ———, vibrational states same as Figure 1, solid line not shown when it obscures a vibrational state)

Fig. 3. Center-of-mass velocity flux contour map for F+para-H_2. The dashed lines are the Newton circles. The F beam velocity vector goes from right to left.



XBL 841-54

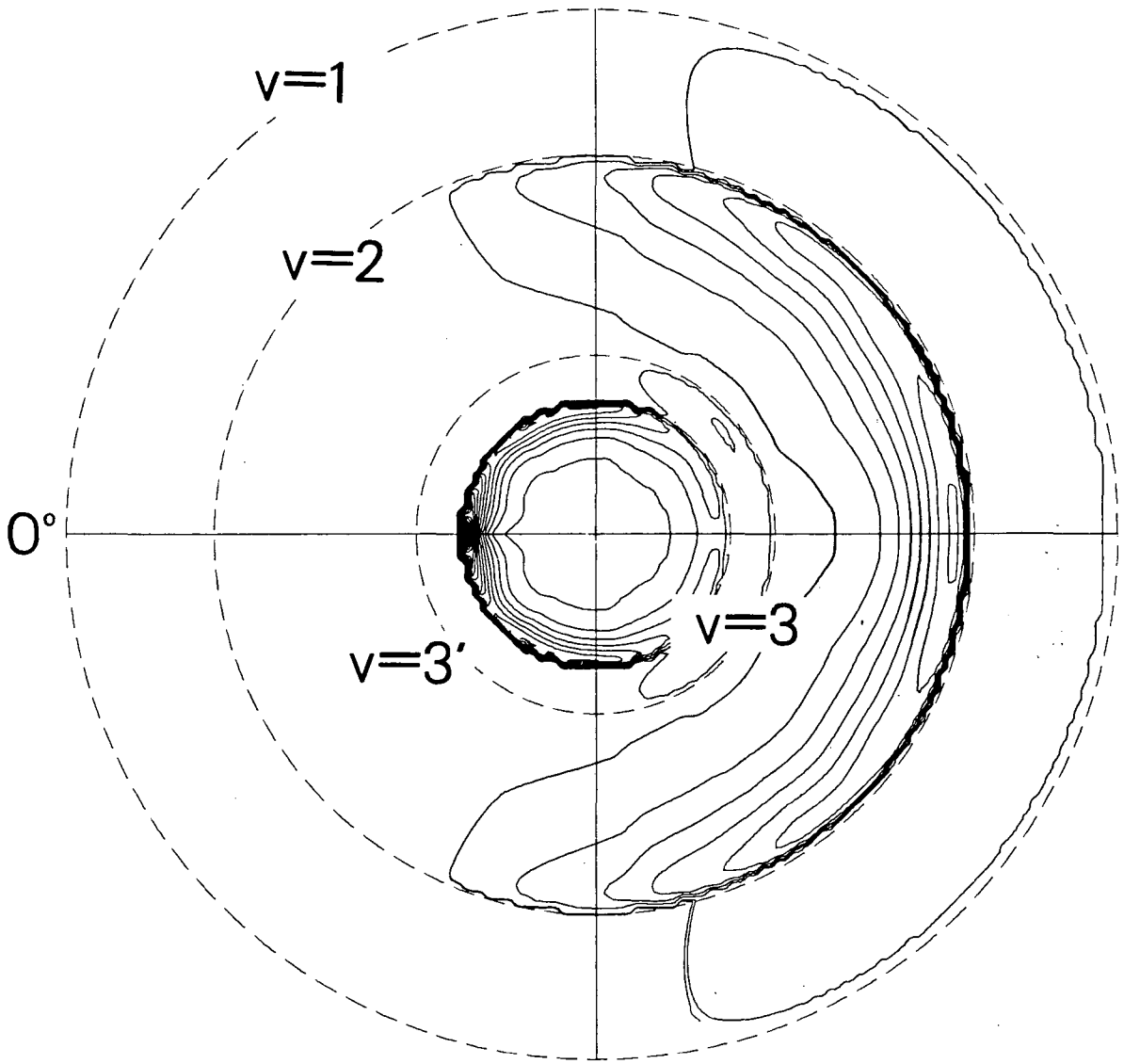
Fig. 1



XBL 841-438

Fig. 2

$F+p\text{-}H_2 \rightarrow HF+H$, 1.84 kcal/mole



XBL 841-21

Fig. 3

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