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D.M. Neumark, A.M. Wodtke, G.N. Robinson,
C.C. Hayden, and Y.T. Lee

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EXPERIMENTAL INVESTIGATION OF RESONANCES IN
REACTIVE SCATTERING: THE F+H₂ REACTIOND.M. Neumark, A.M. Wodtke, G.N. Robinson, C.C. Hayden,^{a)} and Y.T.Lee^{b)}Materials and Molecular Research Division
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ABSTRACT:

The F+para-H₂→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, in contrast to the backward scattering of all DF product vibrational states from F+D₂ at the same collision energy, 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 hypersurface in the neighborhood of the transition state determines several important properties for a reaction such as the rate constant and the partitioning of excess energy among product degrees of freedom. The experimental techniques to measure these properties of a reaction have developed considerably in recent years, and 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 potential energy surface near the transition state based on these results. One promising approach to this problem derives from quantum mechanical reactive scattering calculations in which resonances are shown to 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 potential energy surface near the transition state.³ The experimental observation of effects attributable to resonances should therefore provide a far more sensitive probe of the transition state than has been previously available. 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. This highly exoergic reaction produces an inverted HF vibrational distribution populating mainly $v=2$ and $v=3$ at thermal collision energies.^{4,5}

Reactive scattering calculations on model potential energy surfaces for $F+H_2$, of which the Muckerman 5 (M5) surface⁶ is the most popular, indicate what type of experiment is necessary to observe resonance

effects. Collinear quantal scattering calculations on M5 of the reaction probability vs. collision energy show sharp resonance features with typical widths of 0.01 eV.^{7,8} These features result from the ability of the potential energy surface to support quasi-bound FH_2 states which live for several vibrational periods before decomposing to products.^{8,9} However, 3-dimensional quantal calculations of the total reaction cross section vs. energy do not show any sharp structure.^{10,11} This is due to the contribution of collisions with nonzero orbital angular momentum to the reaction.¹⁰ A quasi-bound state formed by a collision of orbital angular momentum $\underline{L}\hbar$ will have a rotational energy on the order of $B\underline{L}(\underline{L}+1)$, where B is the rotational constant of the reaction intermediate. If an $\underline{L}=0$ resonance occurs at energy E_0 , then at approximately $E_0 + B\underline{L}(\underline{L}+1)$ a quasi-bound state can be formed by a collision of orbital angular momentum $\underline{L}\hbar$. 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 the experimental observation of reactive resonances will not come from the measurement of state-resolved total reaction cross sections as a function of reactant translational energy.

On the other hand, the three-dimensional quantal calculations¹⁰ suggest that resonances can be observed in an experiment which is sensitive

to the opacity function, that is, the reaction probability as a function of reactant translational energy. To observe the effect of orbital angular momentum at a particular collision energy the angular distribution of products from reactive scattering must be determined. In the $F+H_2$ reaction the angular distributions of various HF product vibrational states will respond differently to the occurrence of a resonance. It appears that the only experiment which is likely to show the existence of dynamical resonances in $F+H_2$ is the measurement of vibrationally state-resolved differential cross sections of the HF product at appropriate translational energies.

Scattering calculations show specific kinds of changes in product angular distributions as a function of energy that can occur as the result of a resonance. The barrier in the entrance channel for the $F+H_2$ reaction is lowest for collinear approach of the reactants and rises rapidly for noncollinear approach as the F-H-H bending angle increases, as shown on the M5 surface. The consequences of this are evident in quasi-classical trajectory studies on M5 which show that at collision energies as high as 5.0 kcal/mole, the opacity functions for the formation of the $v=2$ and $v=3$ products decrease monotonically with increasing orbital angular momentum.¹² The resulting differential cross sections are backward-peaked at 180° with respect to the incident F beam.^{12,13} The 3-dimensional quantal results are quite different.¹⁰ When the collision energy is raised from 2 to 3 kcal/mole, the peak in the $v=2$ opacity function shifts to nonzero orbital angular momentum whereas the $v=3$ opacity function 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. The shift in the $v=2$ angular distribution will be even more pronounced if the lifetime of the quasi-bound state is an appreciable fraction of the rotational period of the complex.

Our previous experimental studies on this reaction which 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 which limited the range of the angular scan.^{14,15} The significance of this limitation is apparent in the new results reported here, for the $F+\text{para-H}_2$ reaction at 1.84 kcal/mole collision energy. These were obtained using a new experimental arrangement which included a different configuration for the F source and several other modifications, all of which served to improve the collision energy resolution and reduce the HF background. This permitted the observation of all the $v=3$ product as well as the unambiguous identification of the product vibrational states at any angle.

The major features of the crossed molecular beams apparatus used in these studies have been described elsewhere.^{16,17} 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.¹⁸ The para-H₂ beam was produced by a supersonic expansion of 80 psig through a 70 μ orifice at 304°K. The peak velocity was 2.79×10^5 cm/sec with a FWHM spread of 3 per cent. The FWHM reactant kinetic energy spread in the center-of-mass was only 0.1 kcal/mole. Photoelectron spectroscopy on supersonic p-H₂ beams indicates that about 80 per cent of the p-H₂ will be in J=0 under these conditions.¹⁹ The HF product was detected with a rotatable ultrahigh vacuum mass spectrometer. Angular scans were taken by modulating the H₂ beam at 150 Hz with a tuning fork chopper and recording the modulated HF signal as a function of angle. Product velocity distributions were obtained at 19 angles between 8° and 54° from the F beam by the cross-correlation time-of-flight technique.²⁰ The flight length was nominally 30 cm.

The angular distribution for the HF product is shown in fig. 1. The LAB angle θ is measured from the F beam. The Newton diagram below the figure aids in relating features in the laboratory angular distribution to the center-of-mass(CM) distributions. (v_F , v_{H_2}) and (u_F , u_{H_2}) are the LAB and CM velocities, respectively, of the reactants. θ_{CM} is the LAB angle of the velocity vector for the center-of-mass in the LAB frame. The tip of this vector defines the origin of the center-of-mass coordinate system. In the CM coordinate system, $\theta=0^\circ$ is defined as the direction of the incident F beam, 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 $v=3$. This prominent feature was obscured by high $m/e=20$ background near the F beam in the earlier studies. We searched on the other side of the F beam for forward-scattered $v=2$ product but no signal was detected.

The LAB product angular distribution alone yields only a qualitative picture of the reaction. The time-of-flight measurements of the product velocity distributions allow the quantitative determination of the contribution from each vibrational state to the total signal at a LAB angle. The high angular and velocity resolution combined with the small amount of product rotational excitation⁴ relative to the HF vibrational spacing results in discrete peaks in the TOF spectra from the various product vibrational states. Three sample TOF spectra with their vibrational state assignments are shown in figure 2. The spectrum at $\theta=18^\circ$ 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 $\theta=30^\circ$ and at other LAB angles which are nearly tangent to the $v=3$ Newton circle. The spectrum at $\theta=8^\circ$ confirms that the forward peak in the angular scan is from $v=3$ product.

The translational energy and angular distributions in the CM coordinate system were determined for each product vibrational state by forward convolution. A trial CM distribution for each state was input to a computer program which averaged over beam velocity spreads and detector resolution. The program generated a LAB angular distribution and TOF spectra, and the trial distributions were adjusted until the computer-generated results matched the data. The lines in figs. 1 and 2 are the LAB distributions generated by the best-fit CM parameters.

The slow peak at $\theta=30^\circ$ has a fast shoulder. A similar feature appears in other TOF spectra that sample $v=3$ product near $\theta=180^\circ$, and this could be fit only by assuming it was due to HF($v=3$) from reactants with approximately 1 kcal/mole internal excitation. This product, designated as $v=3'$, could originate from spin-orbit excited $F(^2P_{1/2})$ which lies 1.16 kcal/mole above the $^2P_{3/2}$ ground state and constitutes 21 per cent of the F beam at 920°K, but the reaction between $F(^2P_{1/2})$ and H_2 can only occur by an electronically non-adiabatic process and is expected to be inefficient.²¹ The more likely possibility is that the $v=3'$ product is 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 per cent of the para- H_2 beam.¹⁹

The CM distributions for the HF products are summarized graphically in fig. 3, a contour map of the velocity flux distribution as a function of the CM scattering angle θ . The $v=1$ contours are not reliable due to the low intensity of that state. The $v=2$ state is backward-peaked and drops off slowly for $\theta < 180^\circ$. The $v=3$ state has a broad maximum around $\theta=80^\circ$ and, in contrast to the $v=2$ state, has a sharp, intense peak at $\theta=0^\circ$. The $v=3'$ state is scattered entirely into the backward hemisphere. The relative total cross sections into each vibrational state are as follows:

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

The sharp forward peak and pronounced sideways scattering in the $v=3$ angular distribution, in contrast to the strong backward-scattering observed for $v=2$, 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 quasi-bound state followed by selective decay to $v=3$ products. It seems highly unlikely that a potential energy surface could be constructed which would exhibit such state-specific behavior in a quasi-classical trajectory calculation. The intense forward peak results from the strong correlation between the direction of \underline{L} and \underline{L}' , the final orbital angular momentum vector, for the collisions that form the quasi-bound state. In true long-lived complexes that survive for several rotational periods, this correlation results in a symmetric angular distribution peaking at 0° and 180° in the center-of-mass.²² The much weaker intensity at 180° in this experiment shows that the quasi-bound state only lives 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. Quasi-classical trajectory calculations do not show such state specific behavior for this reaction. Further support for our identification of the $v=3$ forward peak as a resonance effect comes from our studies on the effect of isotopic substitution on this reaction. Dynamical resonances are predicted to be highly isotope-dependent, and should, for example, be much weaker in $F+D_2$ than $F+H_2$.²³ The contour map for $F+D_2$ at 1.82 kcal/mole displayed in fig. 4 shows no forward peak, although the $v=4$ product is slightly sideways-peaked.

Our results indicate that the quasi-bound 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^{6,24} suggest

that the M5 surface is an inadequate representation of the $F+H_2$ potential energy surface. The exact nature of the modifications to be made is beyond the scope of this letter and will be discussed in a later article.

However, it should be noted that quantal collinear calculations on other model surfaces did 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 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 and represent an important step in the ability to experimentally characterize a chemical reaction. A 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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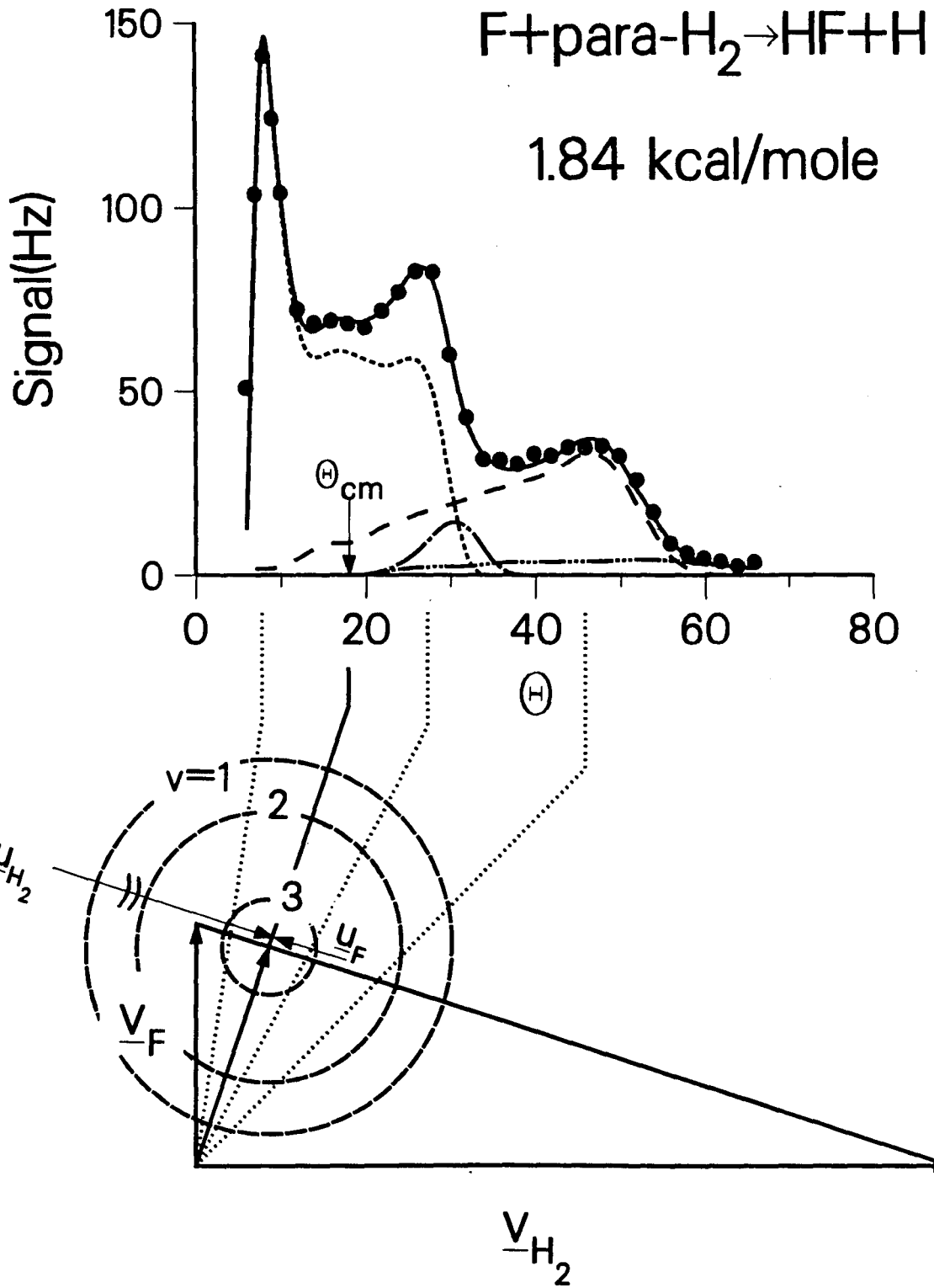


Fig. 1

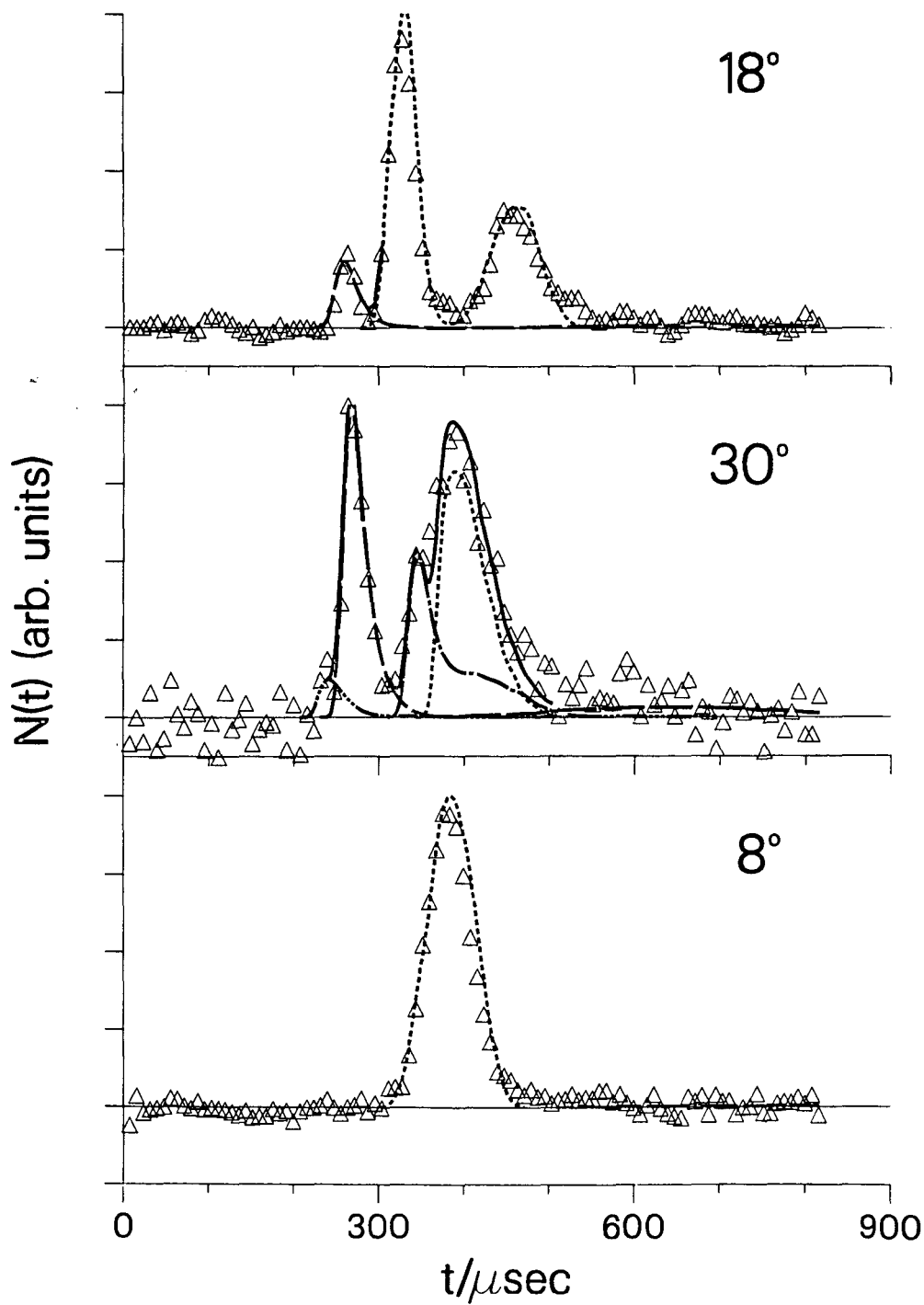
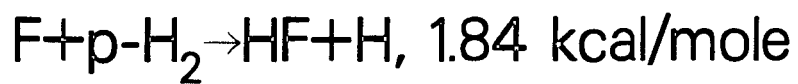
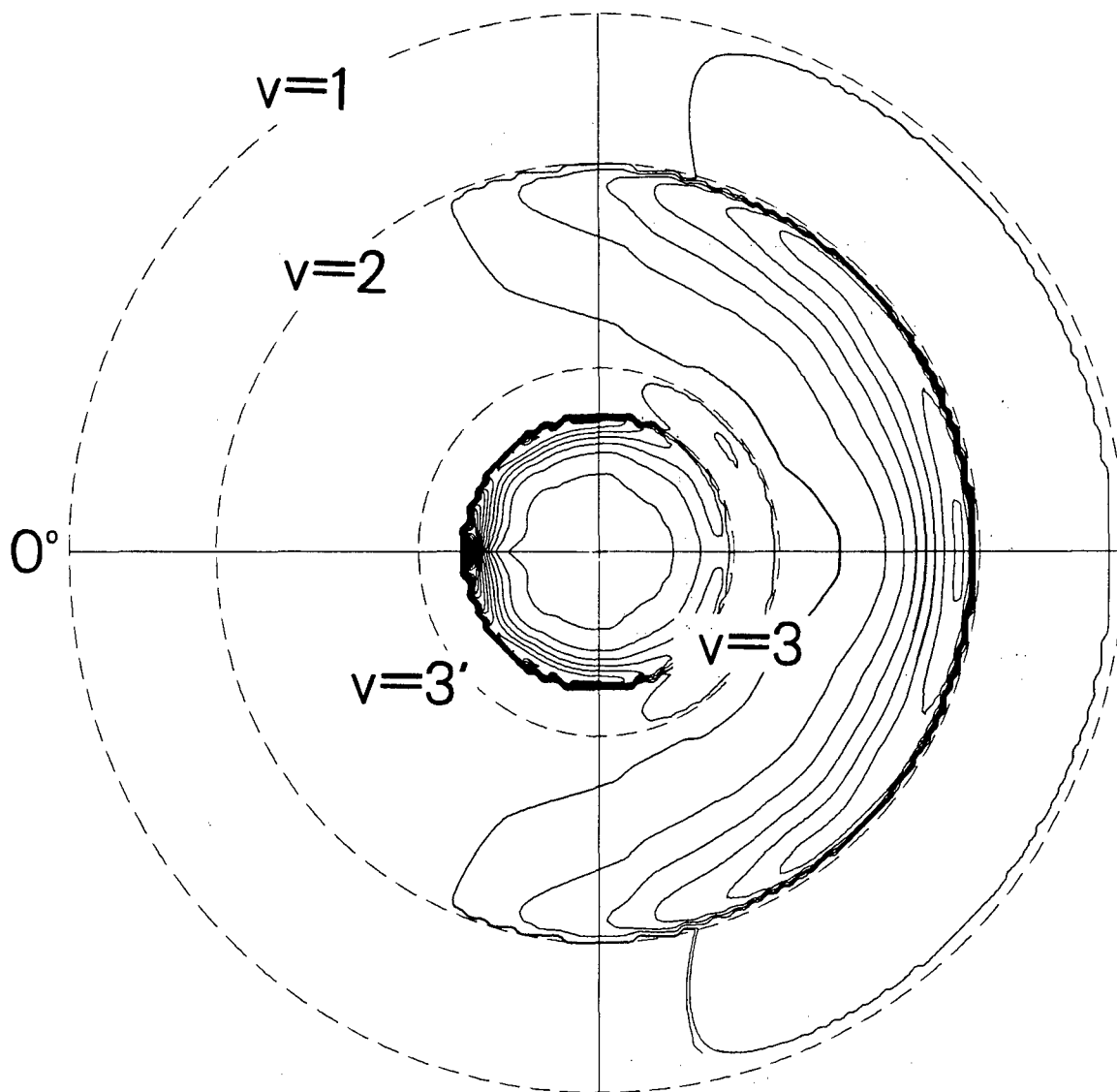
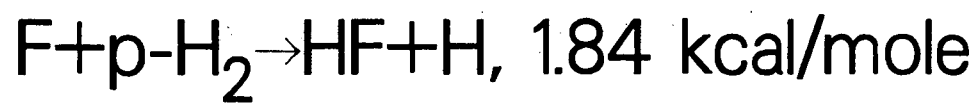


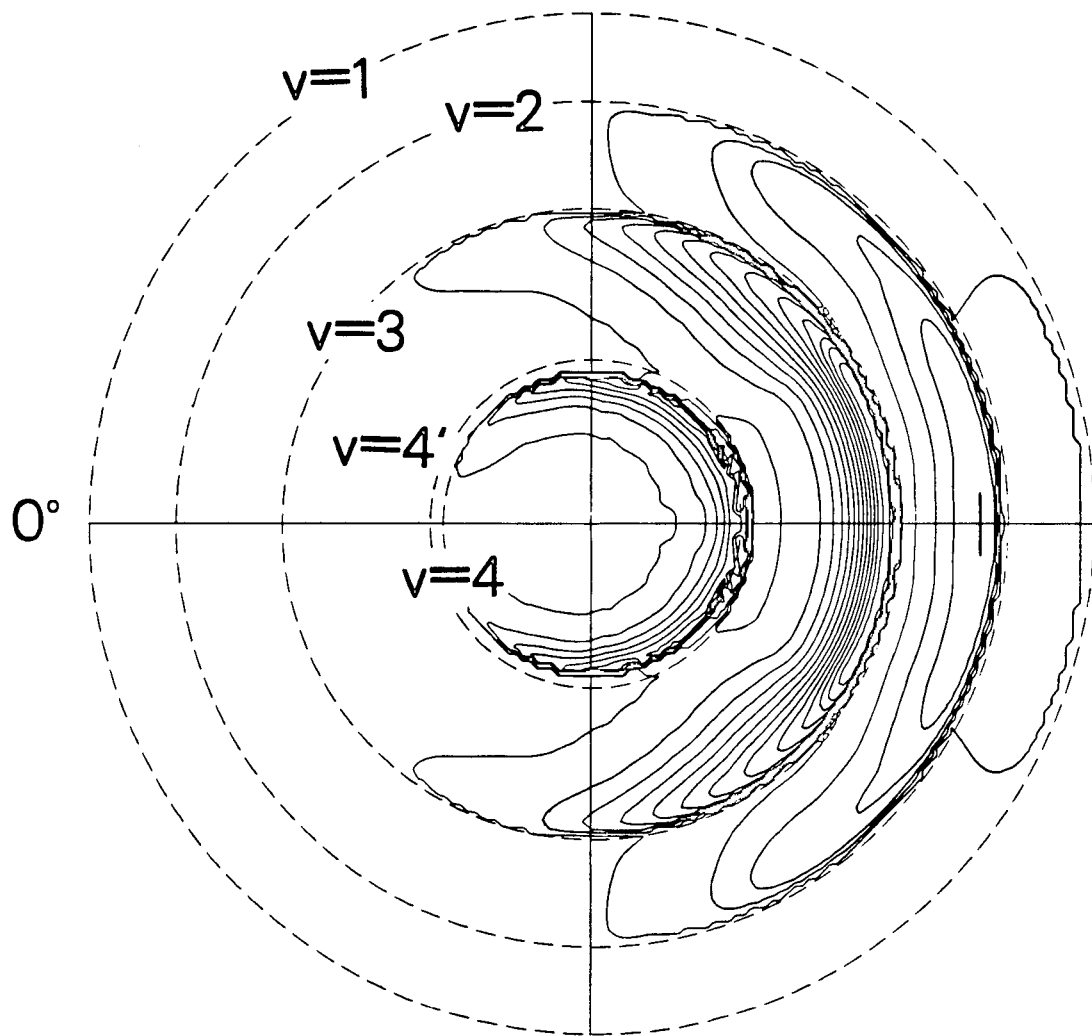
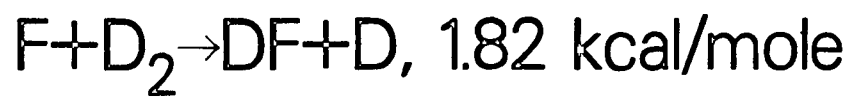
Fig. 2

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Fig. 3



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Fig. 4

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