

Resonance-Mediated Chemical Reaction: $F + HD \rightarrow HF + D$

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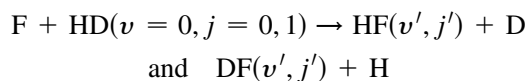
Conclusive evidence is presented for the existence of a reactive resonance in the $F + HD$ reaction. In a molecular beam experiment, the resonance appears in the integral cross section as a distinct steplike feature, while in the differential cross section it is manifested as sharply varying forward-backward peaks in the product distribution. A detailed analysis of the quantum dynamics establishes that a reactive resonance localized in the transition-state region is responsible for these remarkable observations. At collision energies below 1 kcal/mol, the reaction proceeds almost exclusively through resonant tunneling with very little contribution from the more conventional direct mechanism.

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The existence of short-lived resonance states trapped in the vicinity of the transition state of chemical reactions has been long predicted on the basis of quantum dynamics simulations [1]. Unfortunately, the experimental search for these intermediate complexes has shown that they are particularly elusive to direct observation. Unlike resonance observed in other collision processes, such as nuclear scattering, chemical reactive resonances generally do not yield characteristic Lorentzian signatures in the integral cross section (ICS). In simple terms, this is because a reactive resonance tends to exist over a broad range of total angular momenta, J , which tend to overlap, thereby obscuring the resonance fingerprints in the ICS. Experimentalists have been thus forced to probe the details of state-resolved differential cross sections (DCS) for manifestations of resonance phenomena. Despite considerable effort devoted to such studies, at this point it is not totally clear how the resonance would be detected in a full collision experiment, and thus far no scattering data exist that prove the existence of reactive resonances in any known chemical reaction.

The $F + H_2$ reaction, along with its isotopic partners, has served as a focal point in the search for reactive resonances. Theoretical calculations employing empirical potential energy surfaces predicted the existence of reactive resonances as early as 1973 [2]. In 1985, a molecular beam study by Lee and co-workers [3] revealed an anomalous forward scattering peak in the vibrationally state-resolved angular distribution which was attributed to a resonant mechanism. However, the evidence for reactive resonance in the beam experiments was not conclusive since there are other possible dynamical explanations for the forward scattering peak that could not be ruled out [4]. More recent attempts [5] to locate resonances have employed the techniques of transition-state spectroscopy to probe the dynamics near the transition state via the photodetachment spectrum of FH_2^- . While spectral peaks were observed, the available level of energy resolution was not sufficient to distinguish reactive resonance peaks from other phenomena.

In this study, we focus on the reaction



at collision energies, $E_C = 0.2\text{--}5$ kcal/mol. The unique feature in the reaction of this molecule is that a resonance appears to survive the partial-wave averaging and manifests itself as a distinctive feature in the ICS [6]. To our knowledge, this is the first conclusive observation of a reactive resonance in any molecular scattering experiment. Here, we present the DCS, which not only supports this conclusion but also reveals the resonance fingerprints in the product angular distribution.

The experimental observations were made using a crossed-molecular beam apparatus discussed previously [7,8]. The H- and D-atom reaction products were interrogated using a $(1 + 1)$ resonance-enhanced multiphoton ionization detection scheme combined with time-of-flight (TOF) spectrometry. The TOF spectrometer can be operated either in the mass mode for the ICS measurement [7] or in the velocity mode for a direct mapping of the center-of-mass DCS [8].

As a prelude to the angular distribution, in Fig. 1, we replot from Ref. [6] the experimental $\sigma(E)$, summed over $HF(v', j')$ states, along with the prediction of a quasiclassical trajectory (QCT) simulation [9], quantum mechanical (QM) scattering theory [6], and a resonance model. Quite apparent is a distinct step near $E_C = 0.5$ kcal/mol. This feature is not reproduced by QCT and, hence, is suspected to be of quantum mechanical origin. Indeed, the dynamical barrier to reaction lies in the range 1.1–1.5 kcal/mol, which situates this peak in the tunneling energy regime. A much more gradual increase in $\sigma(E)$ is observed between 1.1–1.8 kcal/mol, which is consistent with the onset of direct, over-the-barrier reaction. In contrast, there is no analogous steplike feature in the $F + HD \rightarrow DF + H$ excitation function (see Ref. [6]) which, instead, is apparently dominated by direct reaction.

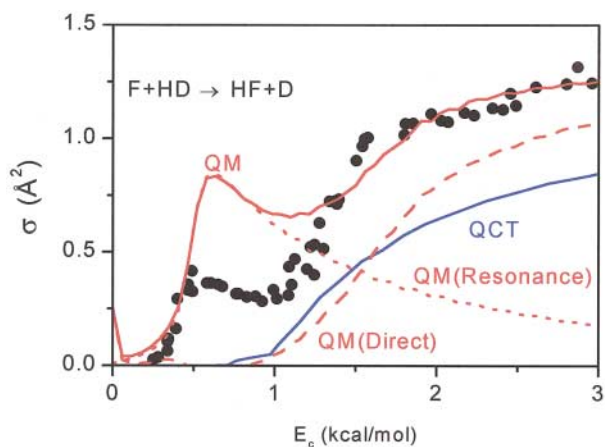


FIG. 1 (color). The excitation functions for $F + HD \rightarrow HF + D$. The experimental results are shown with solid dots, the QCT simulations [9] with a blue line, and the QM results with a red line. The resonance contribution is depicted with a dotted red line, and the direct reaction contribution with a dashed red line. A multisurface factor of $\frac{1}{2}$ has been used to scale the ICS.

Using the accurate Stark-Werner potential energy surface (SE-PES) [10], the QM simulations were carried out using a convergent numerical procedure described in depth elsewhere [11]. In Fig. 1, we show the theoretically simulated excitation function. The steplike peak in the $HF + D$ channel is well reproduced in position and shape, but the absolute magnitude is too high by about a factor of 2; theory and experiment are in good agreement for the barrier region, 1.1–1.5 kcal/mol and above. As argued in Ref. [6], we suspect that the difference in the resonance peak heights is due to a slight error in the barrier width predicted by the SW-PES, or possibly to the neglect of spin-orbit coupling.

The DCS obtained by experiment and theory are shown in Figs. 2–4. In Fig. 2 we show the experimental total angular distributions, $d\sigma/d\Omega$, around the 0.5 kcal/mol feature obtained by summing over all (v', j') states of the HF products. (The resolution was sufficiently high to resolve most of the product rovibrational states for $j' \geq 4$ in the DCS.) The product angular distribution starts as backward peaked near threshold. With increasing collision energy, a dramatic and systematic shift toward the sideways direction is observed. At the same time, a forward peak starts to develop. By 1.18 kcal/mol, it evolves into a predominantly forward-backward peaked distribution. As a result, a ridge which starts at $\theta = 180^\circ$ at 0.4 kcal/mol and moves to about 90° at 1 kcal/mol was clearly visible in the angle-energy plot. Based on theoretical considerations, Zhang and Miller [12] have predicted such a ridge to be the signature of a resonance. However, Aoiz *et al.* [13] subsequently found a similar ridge in a QCT simulation of the $D + H_2$ reaction, and thus it was not conclusive evidence of a resonance. In any event, the striking variation of the angular distributions of

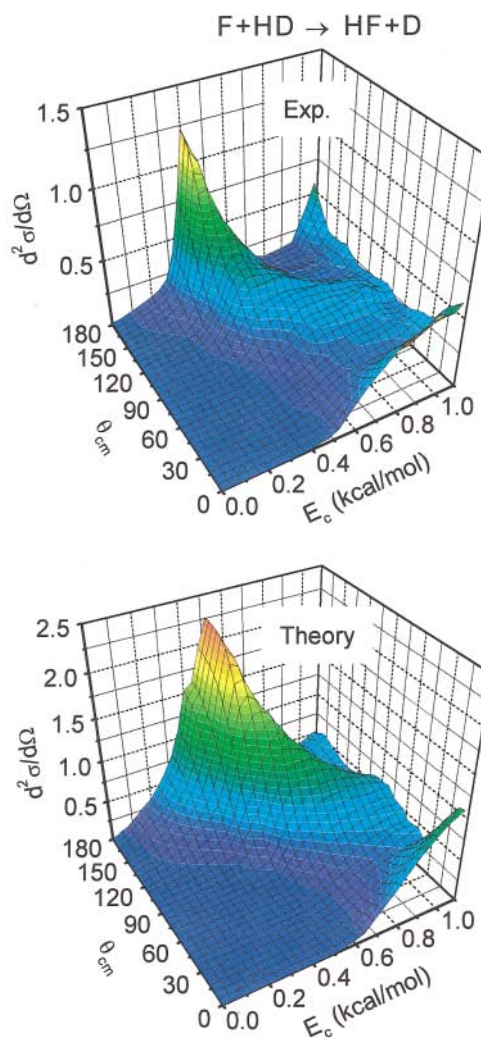


FIG. 2 (color). The low energy total differential cross section in $\text{Å}^2/\text{sr}$ for the $HF + D$ reactive channel. The upper panel shows the experimental results while the lower panel presents QM. An angular scaling factor of 2π has been included in the DCS shown in this figure and Fig. 3, but not in the DCS shown in Fig. 4.

reaction products over such a narrow energy range is unprecedented in any previous molecular beam experiment, and is entirely consistent with what we would expect from a resonant mechanism [3].

In Fig. 3, we plot $d\sigma/d\Omega$ over an expanded energy range for both isotopic channels. A forward-backward peaking in the $HF + D$ distribution is quite apparent at energies between 1 and 3 kcal/mol, and these peaks show a rapid “exchange” of flux as a function of collision energy. In the $DF + H$ channel, the distribution is smoother and localized in a broad swath in the backward hemisphere. The angular product distribution for $HF + D$ also shows an analogous swath although extending somewhat into the forward hemisphere.

From the ICS results, the presumed resonance is manifested only in the $HF + D$ channel [6]. Thus, the scattering into the $DF + H$ channel is predominantly direct

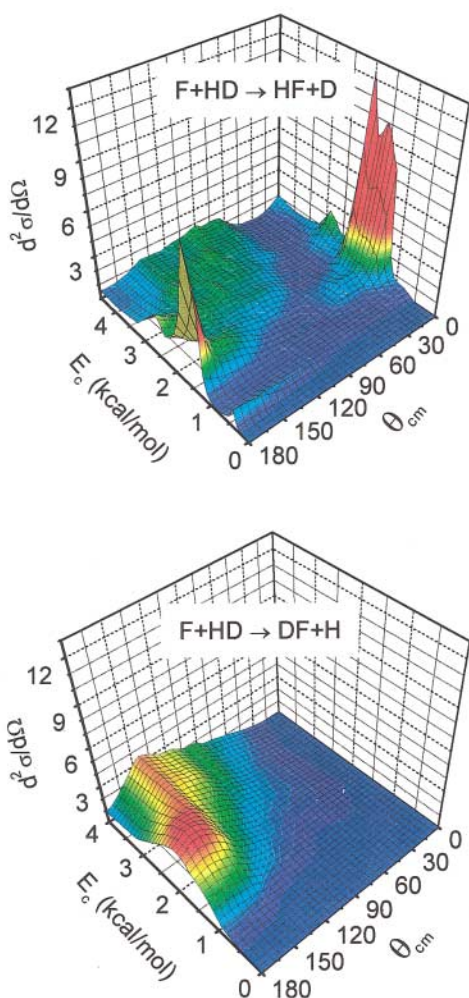


FIG. 3 (color). The experimental total differential cross section in A^2/sr over the full range of collision energies.

reaction. In terms of the DCS, therefore, it is reasonable to conclude that the broad swath is characteristic of direct reaction. If this conclusion is extended to the HF + D channel, and the swath in this channel is also direct, it is conjectured that the remaining ridge structure, at low energy, and the forward-backward peaking, at higher energy, is the result of the resonance scattering.

In Figs. 2 and 4, we plot the QM simulation for $d\sigma/d\Omega$ over the narrow and expanded energy ranges, respectively. The agreement with experiment is seen to be quantitatively good at low energy, i.e., <1 kcal/mol [14], but only qualitatively reasonable at higher energies. The “resonance ridge” starting at 0.5 kcal/mol is quite apparent in the calculation. The forward-backward peaking and direction reaction swath seen in the experiment at higher energy also occur in the QM results, although the relative magnitudes are not correct. Since the dynamics calculations are converged, the quantitative differences between theory and experiment presumably trace back to errors in the SW-PES.

The remaining question is the physical origin of the steplike feature in $\sigma(E)$ and the unusual peaking in

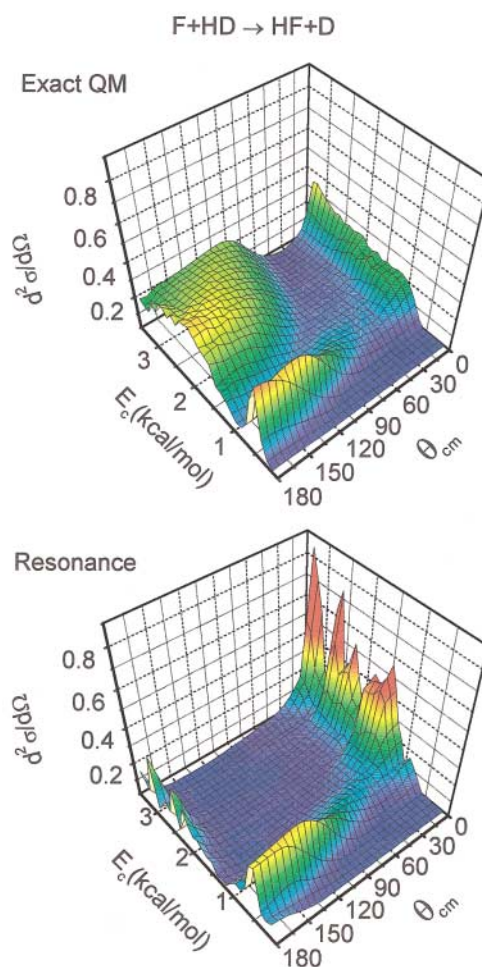


FIG. 4 (color). The computed $d\sigma/d\Omega$ for F + HD in A^2/sr . The upper panel is the result of QM while the bottom panel is the pure resonance contribution.

$d\sigma/d\Omega$, seen in the experiment and predicted by QM. Using time-dependent quantum wave packets and the spectral quantization method described previously [6,15], we identified a resonance state at $E_C = 0.52$ kcal/mol, precisely the location of the steplike feature observed in the experiment and scattering calculations. The resonance was assigned with normal modes of a linear FHD triatomic as $(\nu_{ss}, \nu_{bend}, \nu_{as}) = (0, 0, 3)$. The lifetime of the state was 109 fs and the B constant for rotation of the complex was found to be 1.8 cm^{-1} . The resonance contribution to the excitation function is then computed by superimposing Lorentzian profiles for each total angular momentum, J , using the “ J -shifting” algorithm with a slight modification for the nearby threshold [6]. The inputs into this calculation are the resonance energies and widths as functions of J . From a fitting of the quantum results, we obtained $E(J) = 0.52 + 0.00051J(J+1)$ and $\Gamma(J) = 0.148 + 0.00127[\exp(0.2635J) - 1]$, in kcal/mol. In Fig. 1, we show the resonance contribution to the excitation function obtained in this way. Clearly, below about $E_C = 1$ kcal/mol, the QM result is well

reproduced confirming that the steplike feature is, in fact, a resonance signature. The difference between the total cross section and the resonance component, also shown in Fig. 1, can be viewed as the contribution from direct reaction and shows the typical threshold behavior.

The resonance contribution to the DCS requires a more detailed calculation since the partial wave contributions add as amplitudes (i.e., with phases) in this case rather than as probabilities. Thus, we have extracted from the QM results the partial widths and the local energy dependence of the phase for each scattering matrix element at each total angular momentum. Having done this, and replaced the scattering matrix with the resonance contribution in the usual formulas [16], we obtain the resonance contribution to $d\sigma/d\Omega$. The result, also shown in Fig. 4, is in good agreement with the full QM result at low energies where the resonance contribution dominates. At higher energy, the resonance contribution shows a highly localized forward-backward distribution. The direct scattering swath is seen to completely disappear. This tends to confirm the earlier conjecture that forward-backward peaking is a signature of the resonance.

One property of the F + HD reaction which is particularly unique is the nearly complete absence of direct reaction background at energies below about $E_C = 1$ kcal/mol. At these low energies the reaction, and all of its observable characteristics, is mediated through a reactive resonance. Wave packets, started in the entrance channel HD($\nu = 0, j = 0$) + F to simulate collisions, clearly reveal that nearly all of the reactive flux at low energies must pass through the resonance state (via resonant tunneling) which therefore serves as a "gateway state" to the product channels. This resonance mediation reaction mechanism stands in contrast to the usual over-the-barrier mechanism that has been applied ubiquitously to chemical reactions. The mechanism has predictive power, since effectively all the reaction attributes can be ascribed to particular properties of the resonance state. In addition to the cross sections, discussed above, we can add the product branching ratios and the low temperature rate constant.

In summary, the present study of the F + HD reaction has provided the first unequivocal evidence for a reactive resonance in a molecular beam experiment. The accompanying theoretical simulations have established the characteristics of the resonance in both the ICS and the DCS.

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