CHEMICAL DYNAMICS

Quantum interference between spin-orbit split partial waves in the F + HD → HF + D reaction

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The effect of electron spin-orbit interactions on chemical reaction dynamics has been a topic of much research interest. Here we report a combined experimental and theoretical study on the effect of electron spin and orbital angular momentum in the F + HD → HF + D reaction. Using a high-resolution imaging technique, we observed a peculiar horseshoe-shaped pattern in the product rotational-state resolved differential cross sections around the forward-scattering direction. The unusual dynamics pattern could only be explained properly by highly accurate quantum dynamics theory when full spin-orbit characteristics were considered. Theoretical analysis revealed that the horseshoe pattern was largely the result of quantum interference between spin-orbit split–partial-wave resonances with positive and negative parities, providing a distinctive example of how spin-orbit interaction can effectively influence reaction dynamics.

In atomic and molecular collision processes, the inclusion of the coupling of electron spin and orbital angular momentum could also have a notable effect. For inelastic collisions such as that of NO(XI) with Ar, recent experimental studies have shown that differential cross sections depend sensitively on the change in total parity (9), suggesting that different spin-orbit states experience different potential interactions. In chemical reactions involving species with unpaired electron spins with orbital angular momentum, there are at least two spin-orbit states in the low-energy range: For halogen atoms such as F and Cl, these are 2P3/2 and 2P1/2. The relative reactivity of these two spin-orbit states with H2 has been a notable research topic (10–15). Owing to the breakdown of the Born-Oppenheimer approximation, which is caused mainly by the electrostatic spin-orbit coupling (SOC) between different electronic states, the excited state (2P1/2) was more reactive than the ground state (2P3/2) at low collision energy. Attention has also been devoted to chemical reactions with lambda-doublet products (16, 17).

In addition to the electrostatic SOC between different electronic states, couplings could also occur between electron spin and the angular momentum of nuclear orbital motions in chemical reactions, which leads to the splitting of partial waves, resulting in “fine” structures of the partial waves, similar to the fine structures in the spectra of the diatomic molecules. Yet how or whether the inclusion of the partial-wave splitting in a chemical reaction can affect the dynamics remains largely unknown.

The F + H2 → HF + H reaction is the most notable benchmark system for the study of quantum reaction resonances, which has attracted substantial attention over the past few decades. Reactive resonances were first predicted theoretically in 1973 for the F + H2 reaction by using a colinear reaction model (18, 19). In 1984, a landmark crossed-molecular-beam experiment was performed on the F + H2 reaction by Lee and co-workers, in which a peculiar forward-scattering peak for product HF(v′ = 3) was observed and attributed to reactive resonances (20). However, the dynamical origin of the forward-scattering peak remained unclarified (21, 22). In 2000, a steplike structure in the excitation function in the F + HD → HF + D reaction was observed by Liu and co-workers and was attributed to a quantum reactive resonance (23). Over the past two decades, the F + H2 and F + HD reactions have been extensively investigated using the high-resolution crossed-beams Rydberg H-tagging technique (24–28) and the negative-ion photodetachment spectroscopic method (29, 30), in association with accurate quantum dynamics calculations, and an accurate picture for reaction resonances in this benchmark system was established (31). The results of the molecular-crossed-beams experiment and the negative ion (FH−) photodetachment study on the cold reaction resonance in the F + H2 reaction were also found to be consistent (28). In all of these studies, the resonance signatures observed in the experimental results can be quite accurately accounted for by using the adiabatic theory without considering spin-orbit effects in these systems. Electron spin and orbital motions in these systems seemingly do not have a substantial effect on the dynamics of this resonance-mediated reaction, which occurs mostly in the adiabatic ground electronic state.

In this work, we have combined experimental and theoretical studies of the F(2P3/2) + HD → HF + D reaction at a collision energy of 2.10 kcal/mol, where the partial-wave resonances are substantial (32), to investigate the role of partial-wave splitting in the reaction by full consideration of the electron spin and orbit effects. Experimentally, we used a newly developed high-resolution velocity map imaging crossed-beams technique (33–35), in combination with near-threshold ionization of the D-atom product, to achieve the highest possible angular and translational energy resolution. This technique allowed us to accurately determine quantum-state–resolved angular distributions, which often carry the most detailed quantum dynamics information in chemical reactions. For example, this method has enabled detection of the geometric phase effect in the H + HD → H2 + D reaction (35). Theoretically, we performed the state-to-state time-dependent quantum wave-packet calculations using an adiabatic model and a full spin-orbit–coupled model, which included all angular momentum couplings between electronic spin, electron orbital angular momentum, and nuclear orbital angular...
momentum in this reaction. The model was initially developed by Alexander and co-workers (11, 12, 36). Our results conclusively show that the inclusion of fine structures of partial waves has a notable effect on the dynamics of this resonance-mediated \( \text{F}(^3\text{P}_{3/2}) + \text{HD} \rightarrow \text{HF} + \text{D} \) reaction.

Here we briefly describe our experimental procedures (see the supplementary materials for details; a schematic diagram of the experimental setup is provided in fig. S1). The F-atom beam was generated by discharge in the supersonic expansion of a gas mixture of 5% \( \text{F}_2 \) in helium through a pulsed valve (General Valve) with a stagnation pressure of 6 bar. The velocity \( v \) of the generated F-atom beam was determined to be 1.40 km/s with a speed ratio \( v/v_D \) of 15. To improve the beam quality, the electrode plates in the discharge area were cooled by liquid nitrogen. The HD molecular beam was produced by expanding the HD sample (97% purity) via a liquid nitrogen-cooled pulsed nozzle (Even-Lavie valve) with a stagnation pressure of 13 bar. The velocity of the HD molecular beam was 1.24 km/s with a speed ratio \( v/v_D \) of 30. Using the cryogenic expansion, we found that ~97% of the HD molecules in the HD molecular beam populated the \( \{v = 0, j = 0\} \) ground level. Both the pulsed F-atom beam and the HD molecular beam were collimated by double skimmers before entering the scattering chamber; the two beams were crossed in the reaction chamber with a 160° crossing angle. The collision energy of the current experiment was 2.10 kcal/mol, with an energy spread of 0.1 kcal/mol. The HD-atom molecules in the HD molecular beam populated the \( \{v = 0, j = 0\} \) ground level. Both the pulsed F-atom beam and the HD molecular beam were collimated by double skimmers before entering the scattering chamber; the two beams were crossed in the reaction chamber with a 160° crossing angle. The collision energy of the current experiment was 2.10 kcal/mol, with an energy spread of 0.1 kcal/mol. The D-atom products from the \( \text{F} + \text{HD} \rightarrow \text{HF} + \text{D} \) reaction in the beam-crossing region were detected by a two-color (1 + 1) laser threshold ionization, we were able to clearly resolve the rotational states of \( \text{HF}(v' = 2) \) product, and the \( j' = 3 \) rotational state is not immediately clear.

From the high-resolution D-atom product velocity map image in Fig. 1A, the differential cross section (DCS) for the HF product at different rotational states can be determined. For the forward-scattering direction, the rotational states of the HF\( (v' = 2) \) product were clearly resolved, which allowed us to extract the rotational-state-resolved DCS with high accuracy. The experimental angular distributions obtained for HF\( (v' = 2) \) in the \( j' = 3 \) and 5 rotational states from Fig. 1A are shown in Fig. 2. The angular distributions for other rotational states of HF\( (v' = 2) \) are plotted in fig. S4. Angular distributions for different \( j' \) states were all peaked at angles off of the exact center-of-mass forward-scattering direction (\( \theta = 0° \)), with a double-peak structure in the full DCS. The horseshoe structure in the image was due to the double-peak structure in the DCS for different rotational states of HF\( (v' = 2) \) in the forward-scattering direction (Fig. 2 and fig. S4), with increased spacing as the rotational quantum number \( j' \) increased.

To understand the dynamical origin of the horseshoe pattern in the DCS shown in Fig. 1A, we carried out theoretical investigations using different models with the time-dependent quantum reactive scattering theory. We first

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**Fig. 1.** The D-atom product from the \( \text{F} + \text{HD} \rightarrow \text{HF} + \text{D} \) reaction at a collision energy of 2.10 kcal/mol. (A) Experimental results; (B) theoretical results. The crossing angle of the two beams is 160°. \( \theta = 0° \) and 180° denote the forward- and the backward-scattering direction, respectively, for the HF coproduct in the center-of-mass frame relative to the F-atom beam direction. A peculiar horseshoe-like feature in the forward-scattering direction can be clearly seen in the scattering pattern. The D-atom product velocity map image from the \( \text{F}(^3\text{P}_{3/2}) + \text{HD} \rightarrow \text{HF} + \text{D} \) reaction at a collision energy of 2.10 kcal/mol was obtained for HF\( (v' = 2) \) products in different \( j' \) states in the forward-scattering hemisphere. However, the mechanism that causes this distinctive feature in the angular distribution is not immediately clear.

From the high-resolution D-atom product velocity map image in Fig. 1A, the differential cross section (DCS) for the HF product at different rotational states can be determined. For the forward-scattering direction, the rotational states of the HF\( (v' = 2) \) product were clearly resolved, which allowed us to extract the rotational-state-resolved DCS with high accuracy. The experimental angular distributions obtained for HF\( (v' = 2) \) in the \( j' = 3 \) and 5 rotational states from Fig. 1A are shown in Fig. 2. The angular distributions for other rotational states of HF\( (v' = 2) \) are plotted in fig. S4. Angular distributions for different \( j' \) states were all peaked at angles off of the exact center-of-mass forward-scattering direction (\( \theta = 0° \)), with a double-peak structure in the full DCS. The horseshoe structure in the image was due to the double-peak structure in the DCS for different rotational states of HF\( (v' = 2) \) in the forward-scattering direction (Fig. 2 and fig. S4), with increased spacing as the rotational quantum number \( j' \) increased.
performed adiabatic dynamics calculations on the single potential energy surface of the lowest adiabatic electronic state (28, 37). In this adiabatic model, the F atom was regarded as a structureless atom, whose electron spin (S) and electron orbital angular momentum (L) were neglected; only rotational quantum number \( J \) and orbital angular momentum of nuclei motions (L) were taken into consideration. Thus, the splitting of the partial waves did not arise. The recently developed interaction-asymptotic region decomposition method was applied to extract state-to-state reactive scattering information (38).

Using the adiabatic model, we calculated the opacity function for the HF(\( v' = 2, J = 3 \)) product channel (Fig. 3, blue curve with squares). The plot shows that two components—a main broad peak from \( J = 0 \) to 17 partial waves and a sharp peak at \( J = 18 \) partial waves—contributed to this product channel. Theoretical analysis indicated that the sharp peak at \( J = 18 \) was due to a reactive resonance via a single partial wave of \( J = 18 \), and the main broad peak was due to the direct reaction mechanism. The \( J = 18 \) partial-wave resonance was identified as the rotationally excited state of the quasi-bound (003) resonance, trapped in the HF(\( v' = 3 \))—D vibrational adiabatic potential well (Fig. 4) (24). At \( J = 18 \), the excited resonance state, (003), did not exist anymore, and the ground resonance state, (003), was supported by a centrifugal barrier. Therefore, the resonance at \( J = 18 \) is a Feshbach resonance for the HF(\( v' = 2 \)) channel and a shape resonance for the HF(\( v' = 3 \)) channel (39). Theoretical results also showed that the \( J = 18 \) single partial-wave resonance was mostly responsible for the forward-scattering products in this reaction, and the direct reaction component was largely backward-scattered (fig. S5).

We further computed the state-specific DCSs using the adiabatic model for HF(\( v' = 2, J \)) in the forward-scattering direction. The calculated adiabatic DCSs for HF(\( v' = 2, J = 3 \) and 5) are shown in Fig. 2, A and C, respectively, for comparison with the experimental results. The adiabatic DCSs for other rotational states of HF(\( v' = 2, J \)) are plotted in fig. S4, A, C, and E. For better comparison with the experiment, all of the calculated DCSs in Fig. 2 and fig. S4 have been convoluted with an estimated experimental angular resolution of 4°. No convolution was performed for the DCS with the collision energy spread. From the comparison in Fig. 2, A and C, and fig. S4, A, C, and E, we can see clearly that the adiabatic theoretical results were not in good agreement with the experimental results, especially in the exact forward-scattering direction. For the HF(\( v' = 2, J = 5 \)) DCS results, the two theoretical peaks off of 0° matched quite well with the experimental ones. However, there was an extra theoretical peak at \( \theta = 0° \), which did not arise in the experimental results. For HF(\( v' = 2, J = 3 \)), the deep dip in the adiabatic DCS shown at \( \theta = 0° \) was also not in good agreement with the experiment. Similarly, the adiabatic calculations were not able to reproduce the experimental findings for other \( j' \) values (fig. S4, A, C, and E). From these comparisons, it seems quite clear that the experimentally observed horseshoe pattern in the forward scattering cannot be accurately accounted for using the adiabatic dynamics model, in which the electron spin and electron orbital angular
magnetic quantum numbers were included. Thus, the question becomes whether the discrepancies between the adiabatic model and the experiment were caused by neglecting the electron spin and orbital motion in the adiabatic model—i.e., caused by neglecting the fine structure of partial waves.

We then carried out the time-dependent quantum wave-packet dynamics calculations using a full six-state diabatic model (11, 12, 36), which was developed by Alexander and coworkers. This model included all angular momentum couplings between the electron spin, electron orbital angular momentum, and angular momenta of the nuclear motions. A brief description of the full six-state diabatic model can be found in the supplementary materials. The calculated DCSs for the HF($v' = 2, j' = 3$ and 5) product using the full open-shell model are shown in Fig. 2, B and D, along with the experimental results. Notably, the theoretical DCSs using the full open-shell model were in near-perfect agreement with the experimental observations. The agreement for other $j'$ states of HF($v' = 2$) between theory and experiment was also excellent (fig. S4, B, D, and F). These results strongly suggest that the inclusion of the electron spin and electron orbital motions in the model had a marked effect on the dynamics of the resonance-mediated $F + HD$ reaction. The fine structures of partial waves in this reaction at this collision energy for reproducing the experimental DCSs of such high resolution cannot be ignored.

To elucidate the underlying dynamics of this phenomenon, we also used the full six-state diabatic model to calculate the opacity functions. The opacity function for the HF($v' = 2, j' = 3$) product is shown in Fig. 3, in comparison with that for the adiabatic model. In contrast to the case of a single partial-wave resonance ($J = 18$) in the adiabatic model, it appears that two partial-wave resonances, $J = 17.5$ and 18.5, were responsible for the resonance peak in the opacity function at a collision energy of 2.10 kcal/mol (Fig. 3), which refers to $F$(2$P_{3/2}$) + HD($v = 0, j = 0$) at infinite separation. This finding suggests that electron spin and orbital angular momenta were coupled to the angular momentum of the nuclear motion during the chemical reaction, which split the partial waves and substantially influenced the dynamics of this reaction. More detailed analysis showed that there were actually four partial waves contributing to that peak in the opacity function at a collision energy around 2.10 kcal/mol: two with $J = 17.5$ and two with $J = 18.5$ but with different total parities (fig. S6). In addition, theoretical analysis showed that the forward-scattering products in this reaction were mainly caused by the $J = 17.5$ and 18.5 partial-wave resonances, and the direct reaction component was dominantly backward scattered (fig. S5), similar to that predicted in the adiabatic model without considering all spin-orbit interactions.

The appearance of four partial waves in the full six-state diabatic model, instead of a single partial wave in the adiabatic model, deserves more explanation. In the adiabatic model, electron spin and orbital angular momentum were neglected, and the total angular momentum $J$ was the summation of the nuclear orbital angular momentum $L$ and the diatomic rotational angular momentum $J_a$ (i.e., $J = L + J_a$). For the reactant HD molecule in the $j = 0$ state, $J = L$. In the full six-state diabatic model, the electron spin ($S$) and electron orbital angular momentum ($I$) were included. The total angular momentum $J$ was thus the summation of the nuclear orbital angular moment $L$, the diatomic angular momentum $J_a$, and the total electronic angular momentum $J_e$, (i.e., $J = L + J_a + J_e$). Here, $J_e = S + I$, according to Hund’s case a (7). As in the experimental condition, the reactant HD molecule was in the $j = 0$ state, and we then have $J_a = L + j_a$. In the $F$(2$P_{3/2}$) + HD reaction, the initial $2P_{3/2}$ state is with $s = 1/2$ and $I = 1$, and thus $J_a$ could have four different values: 1.5, 0.5, -0.5, and -1.5. Consequently, for each $L$ quantum number, there are four $J$ values: $L = 1.5, L = 0.5, L = 0.5,$ and $L = 1.5$. For example, when $L = 18, J$ can have four possible values (16.5, 17.5, 18.5, and 19.5) in the

**Fig. 4. Schematic of the resonance-mediated reaction mechanism.** With inclusion of the full spin-orbit effects, a single $J = 18$ partial wave in the adiabatic picture is split into four partial waves (two with $J = 17.5$ of negative parity and two with $J = 18.5$ of positive parity). $E_{coll}$ collision energy.

**Fig. 5. Calculated DCSs for the HF($v' = 2, j' = 3$ and 5) channel.** (A) and (B) Interference between partial waves of positive and negative parities enhances the double-peak structure in the forward angular distribution and creates the slight oscillatory angular structures in the resonance-mediated $F + HD \rightarrow HF + D$ reaction. The comparison demonstrates that the double-peak structure is due to the interference between spin-orbit split-resonance partial waves of different parities.
we calculated the DCSs for the HF(1σg) entrance channel (fig. S7). These variations imply that a single J partial wave in the adiabatic model would split into four partial waves in the full six-state diabatic model (Fig. 4) when electron spin and orbital angular momenta of both electron and nuclei motions are included.

More notably, among these four partial waves accounting for the resonances at a collision energy of ~2.10 kcal/mol, two of them with J = 17.5 are of negative total parity (−), and the other two with J = 18.5 are of positive parity (+). From the calculated reaction probabilities, these four spin-orbit fine-structure partial waves should have similar potential energy surfaces so that resonance states transiently trapped on these surfaces all have similar energies (fig. S6). To determine whether spin-orbit split partial waves with different parities have any effect on the reaction dynamics, we calculated the DCSs for the HF(1σg) product with partial waves of pure negative or positive parity. Figure 5 displays the calculated DCS for HF(1σg) with partial waves with pure negative and positive parities. It appears that the double-peak structure in the calculated DCS for partial waves with pure negative or positive parity was substantially underestimated (Fig. 5), and the summation of these structures is clearly not in good agreement with the experimental results. However, when all partial waves with both negative and positive parities were included, the double-peak structure in the calculated DCSs became much more pronounced and was in excellent agreement with the experiment. A similar conclusion was reached for the other rotational states of product HF(1σg) (fig. 5). These findings suggest that the enhanced forward-scattering double-peak structure, the observed horseshoe pattern, originated from quantum interference between spin-orbit split partial waves of different total parities.

With respect to previous studies (28, 32), it is noteworthy that even though the inclusion of electron spin and orbit can substantially affect the detailed structures of the DCSs for the F + HD → HF + D reaction, the picture of reactive resonances in the full six-state diabatic model is quite similar to that in the adiabatic model, except that a single adiabatic partial resonance state is now split into four spin-orbit split–partial-wave resonances. From detailed theoretical dynamics calculations, we found that the positions of the four spin-orbit split–partial-wave resonances are almost exactly the same as those in the original adiabatic partial-wave resonance state (fig. S8).

In this combined experimental and theoretical study, we have shown that electron spin and orbital angular momenta can have profound effects on the dynamics of the resonance-mediated F + HD → HF + D reaction through spin-orbit partial-wave splitting. The strong effect of spin-orbit split partial waves on chemical reactivity manifested in the state-resolved DCSs is especially noteworthy, although the effect of the SOC on rotational energy levels has been well established for a long time in diatomic molecules and radicals (e.g., NO and OH). The experimental detection of the horseshoe-shaped DCS structure in the title reaction has demonstrated the power of the D-atom velocity map imaging method, in combination with threshold ionization, for accurately measuring the fine angular features in the state-resolved DCS. This finding allowed us to probe the hidden effects of spin-orbit interactions on the dynamics of this resonance-mediated chemical reaction.

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Materials and Methods

Figs. S1 to S9
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