Commentary

Reactive resonance and the role of electron angular momentum

Mingfei Zhou^{1,*} and Kopin Liu^{2,*}

¹Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysts and Innovative Materials, Fudan University, Shanghai 200438, China ²State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China *Correspondence: mfzhou@fudan.edu.cn (M.Z.); kpliu@gate.sinica.edu.tw (K.L.)

Received: April 7, 2021; Accepted: June 15, 2021; Published Online: June 18, 2021; https://doi.org/10.1016/j.xinn.2021.100136

© 2021 The Author(s). This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

Citation: Zhou M. and Liu K. (2021). Reactive resonance and the role of electron angular momentum. The Innovation 2(3), 100136.

Understanding the reaction mechanism at the atomic and molecular level is a central task of chemistry. Within the Born-Oppenheimer approximation, a chemical reaction is envisioned as nuclear dynamics evolving from reactants to products on a potential energy surface (PES). To reveal the detailed mechanistic origin of such an old bond-breaking and new bond-forming process, a measurement of state-to-state differential cross-sections (DCSs) is essential. Its fine structure often serves as a fingerprint to identify quantum dynamics phenomena in a bimolecular reactive encounter. Observation of these fine structures is, however, difficult, because the interference feature may appear in the state-to-state DCSs only with very high angular resolution.

Recently, Chen et al. observed a peculiar "horseshoe" structure in the DCSs of the F + HD \rightarrow HF ($\sqrt{2}$ = 2) + D reaction (Figure 1).¹ The combined study of molecular crossed beam experiments and theoretical quantum dynamics simulations uncovered the pivotal role of the angular momenta of the unpaired electron of the F atom in the chemical reaction for the first time, fully making use of the significant partial wave resonances in the reaction. The finding marks a significant breakthrough in the study of chemical dynamics.

Quantum resonance is a ubiquitous phenomenon in physics and chemistry. For example, the peaks in the atomic and molecular spectroscopy are perhaps the most familiar phenomena that manifest quantum resonance behavior. When photon energy is tuned to match the energy difference of two levels of a species, a sharp peak (resonance) appears provided that the optical selection rules permit the transition. The resulting spectrum, the intensity versus photon energy, then gives the fingerprint of the species, and the energy width of the spectral peak provides the information of the lifetime of the corresponding excited state. Similar quantum resonance behaviors have also been observed in the scattering processes of many particles, such as the inelastic atomic and molecular collisions and electron-heavy particle scattering processes. Historically, $F + H_2$ and its isotopic reactions have been the benchmark for developing the concept of the elusive reactive resonance or quantum dynamical resonance. A reactive resonance here refers to a transiently formed compound state of the reacting system, which is temporally trapped (with a typical lifetime of a few tens to hundreds of femtoseconds) in the vicinity of the transition state region even on a totally repulsive PES. Thus, reactive resonance is a quasi-bounded state along the reaction coordinate and an approximate quantum number can be assigned to it.

Due to the elusive nature of the reactive resonance, there is long history for identifying their existence in a chemical reaction. In the 1970s, theorists predicted that reaction resonances exist in the F + H₂ reaction. The signature of theoretical resonance manifests itself as a sharp Lorentzian-like peak in the computed reaction probabilities as a function of collision energies. However, at that time, the PES used was empirical and the scattering calculation was restricted to one-dimensional (collinear) dynamics. Therefore, it was not totally clear whether the predicted resonance was a real physical phenomenon or just a theoretical construct from the approximation used. In 1985, a landmark crossed molecular beams study on the F + H₂ reaction was reported.² An anomalous forward-scattered HF (v' = 3) + H product was observed in the DCS and was regarded as a resonance feature for a time. However, detailed analysis of the classical trajectory theory (QCT) revealed that the forward-scattering results from the large impact parameter collision, in which the centrifugally shifted barrier slows down the trajectory, leading to the forward-scattered products-a classical mechanism-other than guantum resonance.

The first unambiguous reactive resonance was instead sighted and identified in the F + HD \rightarrow HF + D reaction in 2000.³ A prominent step-like structure near the collision energy of 0.5 kcal/mol was observed in the excitation

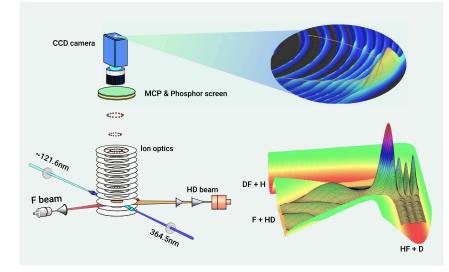


Figure 1. Schematic of experimental setup (left panel) Image of products in forward-scattering direction showing the "horseshoe" structure (upper right). Schematic of the potential energy surface of the F + HD reaction (low right).

Commentary

function (the reaction cross-section as the function of the collisional energy), which was entirely absent in the QCT simulation using the Stark-Werner PES as well as in the alternative DF + H product channel. Resonance signatures in the vibrationally resolved DCSs were also elucidated by contrasting the two isotopic product channels. Concurrent quantum dynamics calculations and analysis on the same PES proved the step being the result of a Feshbach resonance in the F + HD reaction. Since then, great progresses have been made on the resonances in the F + HD and H₂ reactions with refined experimental techniques and more accurate PESs.

However, the excitation function of the F + H₂ reaction is monotonic, which makes the observation of its reaction resonances more challenging. In 2006, using the Rydberg state H atom time-of-flight technique, a peculiar forward peak was observed in the HF(v' = 2) products.⁴ Theoretical analysis suggested that the forward peak results from the interference between two quasi-bound resonance states. More recently, using negative-ion photode-tachment spectroscopy, the resonance-related structures of the F + H₂ reaction were also observed as sharp peaks.⁵ Scattering resonances involving vibrationally excited reactants and resonances in more complex polyatomic reaction systems have also been experimentally explored. These findings on the reaction resonances have served as important benchmarks in the development of chemical dynamics.

In the F + HD reaction, the F atom is characterized by an unpaired *p* electron with the orbital angular momentum I = 1 and the spin angular momentum s = 1/2; the coupling of *I* and *s* yields the total electronic angular momentum j = I + s and results in two spin-orbit electronic states j = 3/2 and 1/2. How the angular momenta of the unpaired electron play their role in the reaction is unclear. As the electron angular momentum couplings of the F atom are fully considered, the previous single partial wave *L* will split into 4-fold partial waves, with total angular momentum quantum numbers $L \pm 1/2$ and $L \pm 3/2$, as the result of the coupling of *s* and *I* to the nuclear orbital angular momentum *L*. The inclusion of the interference between these four spin-orbit split resonance pathways should then be considered, which is challenging both theoretically and experimentally.

All previous product quantum state-resolved theoretical investigations invoke electronic adiabatic approximation, which neglects the spin-orbit effects. If the role of the electronic angular momenta could be revealed is not altogether clear, because the associated energy splitting is so small. Usually the DCSs are contributed by many partial waves that may smear out the fine structures caused by the electronic angular momenta. Notably, the reactive resonance in the F + HD reaction is very special, which is well separated and of long lifetime, exhibiting as a sharp peak in the excitation function of a

single partial wave. This reaction provides the chance to magnify the sighting of the role of electronic angular momenta. With high-resolution crossed molecular beam experiments, the scattering patterns of quantum state-resolved products over the full angular range can be captured. In the work by Chen et al., a more sensitive technique called near-threshold ionization was developed and employed in the crossed molecular beams velocity map ion imaging measurement.¹ The angular structures observed in the work by Chen et al. turn out to be beneficial in sighting the oscillations of the quantum interferences between the spin-orbit split partial wave reactive resonances. New quantum reactive scattering theory was also developed with the characteristics of the electron angular momenta being fully accounted for. The combined experimental and theoretical study clearly demonstrates that the experimentally observed "horseshoe-shaped" angular feature could only be explained using the accurate calculations with the spin-orbit coupling being fully included.

Scientists are now able to study the reactive scattering dynamics at much finer level. With the state-of-the-art experimental techniques and highly accurate theoretical calculations, one would anticipate to further discover interesting quantum dynamics in chemical reactions. For example, future study might involve the control of the magnetic quantum number of the angular momentum associated with either the *p*-orbital electron of F atoms or the rotational state of HD (H₂), or both, in the laboratory. Such spatial control portrays the steric effect of reactivity, which could provide a more intuitive and fine picture of the atomic rearrangement in a reactive scattering event.

REFERENCES

- 1. Chen, W., Wang, R., Yuan, D., et al. (2021). Quantum interference between spin-orbit split partial waves in the F + HD \rightarrow HF + D reaction. Science **371**, 936–940.
- Neumark, D.M., Wodtke, A.M., Robinson, G.N., et al. (1985). Molecular beam studies of the F + H₂ reaction. J. Chem. Phys. 82, 3045–3066.
- Skodje, R.T., Skouteris, D., Manolopoulos, D.E., et al. (2000). Resonance-mediated chemical reaction: F + HD→HF + D. Phys. Rev. Let. 85, 1206–1209.
- Qiu, M., Ren, Z., Che, L., et al. (2006). Observation of Feshbach resonances in the F + H₂ → HF + H reaction. Science 311, 1440–1443.
- Kim, J.B., Weichman, M.L., Sjolander, T.F., et al. (2015). Spectroscopic observation of resonances in the F + H₂ reaction. Science 349, 510–513.

ACKNOWLEDGMENTS

We thank an anonymous reviewer for the constructive suggestions.

DECLARATION OF INTERESTS

The authors declare no conflict of interest.

2