Dynamical resonances in chemical reactions

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The transition state is a key concept in the field of chemistry and is important in the study of chemical kinetics and reaction dynamics. Chemical reactions in the gas phase are essentially molecular scattering processes, which are quantum mechanical in nature. Thus probing and understanding detailed quantum structure in the transition state region of chemical reactions, such as reactive resonances, is a central topic in this field. In this article, we focus on recent progress in the study of resonances in elementary bimolecular reactions using state-of-the-art transition state spectroscopy methods: high-resolution photoelectron spectroscopy and quantum state specific backward scattering spectroscopy. The experimental results are compared with high-level quantum dynamics calculations based on highly accurate potential energy surfaces. The dynamics of reactive resonances are also interpreted based on scattering wavefunctions obtained by time-dependent wavepacket calculations. Here, we review many systems that illustrate how reactive resonances can strongly influence the dynamics of elementary chemical reactions.

I. Introduction

Resonances are ubiquitous in both classical and quantum systems. In atomic and molecular systems, when the energy of a photon equals the energy difference between two quantum mechanical states, the photon can be resonantly absorbed. The absorption spectrum correspondingly shows a resonance peak, and the width of this peak can be related to the lifetime of the states involved. Resonance phenomena have also been detected in particle scattering processes in nuclear physics. In the 1930s, Fermi and collaborators noticed elevated cross sections for slow

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neutron scattering at certain energies,\textsuperscript{1–4} which were interpreted by Bethe\textsuperscript{5} and Bohr\textsuperscript{6} as particle scattering resonances due to certain quasi-stable states of the collision complex. These elementary particle resonances have been crucial for the understanding of the fundamental forces of nature. Scattering resonances have also been discovered in electron-heavy particle scattering processes.\textsuperscript{7–9} Resonances also exist in inelastic atomic and molecular collisions. As gas-phase chemical reactions are in essence atomic and molecular scattering processes, resonant phenomena have been an important topic in the study of the dynamics of chemical reactions over the last few decades.

In a chemical reaction, reactants pass through a transition state region along the reaction coordinate between reactants and products, where chemical bonds are broken and reformed. This transition state, first proposed by Polanyi and Eyring in the early 1930s,\textsuperscript{10–12} dictates almost every aspect of a chemical reaction, and has played a central conceptual role in the development of chemistry as a branch of science. Therefore, observing and understanding the transition state have been regarded as the “Holy Grails” of chemistry.\textsuperscript{13,14}

In the transition state region of a chemical reaction, there can exist quantum resonance states which sometimes dominate reaction dynamics. We can use a one-dimensional model of a chemical reaction (Fig. 1) to illustrate the concept of the transition state and reactive resonances.\textsuperscript{15} In a typical chemical reaction with a simple energy barrier (Fig. 1a), the transition state is traditionally defined as the region near the top of the energy barrier. In this model system, the barrier simply acts as a bottleneck for chemical reaction, and the reaction probability increases monotonically to a plateau value as the reaction propagates through the transition state region. This process can be modeled by a one-dimensional reaction coordinate $r$, where the reaction probability $P(r)$ is given by the Boltzmann distribution:

$$P(r) = \frac{1}{Z} e^{-\frac{E_b - \mu}{kT}}$$

Here, $E_b$ is the energy barrier, $\mu$ is the chemical potential, $k$ is the Boltzmann constant, and $T$ is the temperature. The zero-point energy (ZPE) of the system is given by:

$$ZPE = \frac{1}{2} k T \ln \left( \frac{v}{v_0} \right)$$

where $v$ is the vibrational frequency and $v_0$ is the zero-point frequency. The ZPE correction is important for understanding the reaction dynamics and the role of quantum effects in chemical reactions.

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energy goes above the barrier (Fig. 1b). In some cases, however, quasi-bound quantum states can exist in a peculiar adiabatic potential well along the reaction coordinate, as shown in Fig. 1c. These transiently trapped quantum states are called reactive or dynamical resonance states, and normally live from a few tens to hundreds of femtoseconds (Fig. 1d). The presence of such features can significantly enhance the reaction probability through resonance-mediated tunneling, as seen clearly in the calculated reaction probability in Fig. 1d. However, directly detecting the structure and dynamics of these reaction resonances is a great experimental challenge.

Two primary experimental methods have been developed and applied to probe reactive resonances in bimolecular reactions: anion photoelectron spectroscopy (PES) and high-resolution crossed molecular beam scattering. Using anion photoelectron spectroscopy, photodetachment of a bound anion similar in geometry to the desired neutral transition state can yield a spectrum showing a structure very sensitive to the shape of the neutral potential energy surface. Given sufficient energy resolution, the geometry, energetics, and vibrational frequencies of the transition state can be illuminated, as well as the positions and spectral widths of resonances bound or quasi-bound along the reaction coordinate. Using high-resolution crossed molecular beam scattering, one can obtain product quantum state-resolved scattering patterns, which can be used to trace the dynamics of reactive resonances. By focusing specifically on the backward scattered products, one can determine the energy and lifetime of reaction resonances.

In recent years, significant progress has been made in both the experimental and theoretical study of reactive resonances, and there have been several comprehensive reviews published on this topic. In this review, we will provide a brief summary of the basics and experimental methods in this area of research (Section II), discussion of recent measurements of reactive resonances in several benchmark systems (Section III), and implications for future work (Section IV).

II. Development of new experimental methods

Resonances in bimolecular chemical reactions are difficult to probe experimentally due to their short (typically a few femtoseconds) lifetimes and their low number densities. Furthermore, because it is not possible to precisely initiate a bimolecular reaction on a femtosecond time scale, conventional ultrafast spectroscopy methods cannot easily be applied to investigate reactive resonances. Over the last few decades, two experimental methods, anion photoelectron spectroscopy and high-resolution crossed molecular beam scattering, have elevated the understanding of reactive resonances, in conjunction with accurate quantum dynamics theory.

II.1 Anion photoelectron spectroscopy

Anion photoelectron spectroscopy is a powerful tool to study the vibrational and electronic structure of transient neutral species through photodetachment of a stable negative anion. Experimentally, a packet of mass-selected anions, \( A^- \), is irradiated with light. A photoelectron may be detached if the photon energy exceeds the binding energy of the electron:

\[
A^- + \nu \rightarrow A + e^- \tag{1}
\]
The photon energy $h\nu$ is conserved between the binding energy of the final neutral state ($eBE$) and the kinetic energy of the outgoing photoelectron after detachment ($eKE$) according to

$$eBE = h\nu - eKE$$  \hspace{1cm} (2)$$

The $eKE$ distribution is measured, and can show discrete features corresponding to detachment to specific neutral electronic and vibrational quantum states. The resulting photoelectron spectra are typically plotted in $eBE$, as this quantity is independent of the choice of photon energy.

Anion PES is one of the few ways to spectroscopically access neutral transition states on unimolecular and bimolecular reactive surfaces. Photodetachment of a bound anion similar in geometry to a relevant part of the neutral reactive surface can provide a direct spectroscopic probe of the Franck–Condon (FC) structure in modes perpendicular to the reaction coordinate, as well as sharper features corresponding to discrete reactive resonances lying along the reaction coordinate (Fig. 2). Analysis of transition state spectra can therefore reveal detailed information about the geometry, vibrational frequencies, energetics, and resonances of the transition state and reactant and product complexes. By extension, characterization of short-lived quantized states in the transition state region provides a wealth of information about how the reactive surface governs chemistry.

In recent years, anion PES has made significant progress in transition state spectroscopy because of the development of a high-resolution variant of this technique, slow photoelectron velocity-map imaging of cryogenically cooled anions (cryo-SEVI). The cryo-SEVI technique has been discussed extensively elsewhere. Anions are photodetached with a tunable laser at various fixed wavelengths, and the kinetic energy distribution of the resulting photoelectrons is measured using a velocity-map imaging (VMI) lens. Energy resolution is optimized by carrying out photodetachment very close to threshold, and by using low VMI extraction voltages to magnify the photoelectron image and selectively detect the slowest electrons. By tuning the detachment laser above each spectral feature of interest, the entire spectrum can be acquired in high-resolution energy windows. Under these conditions, SEVI can achieve instrumental energy resolution down to a wavenumber. With cryo-SEVI, the anions are collisionally cooled with cold, inert buffer gas in a radiofrequency ion trap before photodetachment, allowing thermalization to their ground vibrational and electronic states. This method has demonstrated complete suppression of hot bands and dramatically narrowed rotational envelopes for detachment of molecular anions. Ion temperatures as low as 10 K and spectral peak widths as narrow as 2–3 cm$^{-1}$ have been reported for molecular systems. Photodetachment of cold ions is particularly advantageous for resolving resonances in a transition state spectroscopy experiment, as one avoids the averaging over angular momentum partial waves found in crossed beam scattering experiments.

The new capabilities of cryo-SEVI have allowed for exquisite spectral characterization of many systems that were previously not feasible. Its applications for transition state spectroscopy have been recently demonstrated through the study of reactive resonances in the benchmark F + H$_2$ reaction, the five-atom F + CH$_4$ reaction, and the seven-atom F + CH$_3$OH reaction, all of which will be discussed further below. In these systems, resonance features are newly resolved, serving as excellent points of comparison for state-of-the-art theoretical treatment of bimolecular reactive surfaces, as well as with high-resolution crossed molecular beam scattering results.

II.2 State-resolved crossed beam reactive scattering with backward scattering spectroscopy

High-resolution crossed molecular beam scattering experiments have also been a key method in the study of elementary chemical reaction dynamics. In a crossed molecular beam scattering experiment, two beams are crossed in a high vacuum chamber at a specific collision energy, and the resulting reaction products are scattered in different directions. Various detection methods have been applied to detect reaction products and to measure their scattering patterns. These scattering patterns can report on the reaction dynamics, and in certain cases can provide evidence of reactive resonances at certain collision energies via features like forward scattered peaks. However, important properties of reactive resonances, such as the resonance energy and lifetime, cannot be directly determined. We rely solely on theoretical dynamics calculations to obtain this crucial information.
A significant complication in using crossed beam scattering to probe reactive resonances is the partial wave averaging effect. In a typical reactive scattering event, the product scattering pattern is the result of many partial waves with different total angular momentum \( J \). The signatures of reactive resonances in the scattering pattern can be easily smeared out by averaging over many different partial waves, and thus important properties such as the resonance state energy and lifetime are not possible to measure experimentally at a specific collision energy. Partial wave averaging makes it very difficult to observe many resonances in a total cross section measurement as a function of collision energy, which would be the most intuitive way to see them. However, one can look at the back-scattered signal as a function of collision energy, where averaging effects are mitigated for reasons discussed further below.

In recent years, various high-resolution crossed molecular beam techniques have been developed and applied for the improved study of elementary chemical reactions. Crossed beam methods are designed to measure scattering reaction product flux intensities from the crossing region at different scattering angles, which let us to determine the differential cross sections (DCS). Yang and co-workers have developed the quantum state specific backward scattering spectroscopy method, where reactive scattering differential cross sections are measured in the backward direction with quantum state resolution as a function of collision energy. The efficacy of this method is based on the principle that in a hard sphere scattering process, backward scattered products are formed through collisions with impact parameters near \( b \approx 0 \). This principle is also applicable to molecular reactive scattering processes, in which backward scattered products are primarily formed from scattering with low \( J \) partial waves. Since the signatures of reactive resonances are most clear in the low \( J \) partial wave scattering, directly measuring the backward scattering differential cross section as a function of collision energy can provide the most sensitive probe of reactive resonances. This method can be used to measure both the position and lifetime of the resonance state. In the last decade or so, this approach has been successfully applied to study reactive resonances in benchmark systems such as \( \text{F} + \text{H}_2 \) and \( \text{Cl} + \text{H}_2 \), in combination with the high-resolution H-atom Rydberg tagging technique.

The high-resolution H-atom Rydberg tagging time-of-flight (HRTOF) technique was developed by Welge and co-workers and has been widely applied by the Davis and Yang groups for the study of elementary chemical reactions. The central scheme of this technique is the two-step efficient excitation of an H or D atomic product from its ground state to a long-lived high-n Rydberg state without ionization. These “tagged” neutral H or D atoms fly free of space charge and stray field effects, and are field-ionized at the end of the TOF before detection with microchannel plates.

In comparing the methods outlined in Sections II.1 and II.2, note that, depending on the anion geometry, anion photoelectron spectroscopy can be sensitive to quantized resonance structure in the entire transition state region on either side of the barrier, while crossed beam scattering experiments can only detect those resonance states that have significant influence on the reaction dynamics of bimolecular reaction processes. It is of great interest to relate the two experimental methods and identify the features observed in anion PES that manifest in scattering experiments.

III. Resonances in chemical reactions

The contributions of molecular beam scattering and anion PES experiments to the search for reactive resonances and transition state structure are well demonstrated through the history of the benchmark \( \text{F} + \text{H}_2 \) reaction. In the 1970s, reactive resonances were theoretically predicted in the \( \text{F} + \text{H}_2 \) reaction on two-dimensional potential energy surfaces for collinear reactions. Theoretical results showed a sharp Lorentzian-like peak in the total integral cross section as a function of collision energy, a clear signature of a reactive resonance, but the physical origin of this resonance was not clarified. In 1985, Lee and coworkers performed a milestone crossed beam experiment on the \( \text{F} + \text{H}_2 \) reaction with vibrational state resolution of the HF products. The \( \text{HF}(v' = 1, 2) \) products were mainly backward scattered, while a clear forward-scattering peak for the \( \text{HF}(v' = 3) \) product was observed (Fig. 3) and initially attributed to a reactive resonance. Forward scattering for the \( \text{DF}(v' = 4) \) product of the \( \text{F} + \text{D}_2 \) reaction as well as the \( \text{HF}(v' = 3) \) product of the \( \text{F} + \text{HD} \) reaction was also reported. However, both quasi-classical trajectory (QCT) calculations and quantum mechanical scattering studies on the Stark-Werner potential energy surface (SW-PES) show forward scattering peaks of \( \text{HF}(v' = 3) \), with the peak of the quantum calculations larger than that of the classical calculations. This implies that the \( \text{HF}(v' = 3) \) forward scattering peak may be of classical origin.

In 1993, Neumark and coworkers carried out transition state spectroscopy experiments via photodetachment of \( \text{FH}^- \) anions, and observed a progression of bending levels of the \( \text{FH}_2 \) transition state complex, but saw no signs of sharp reactive resonances from trapped states along the reaction coordinate. In 2000, Liu and coworkers reported a crossed molecular beam scattering study of the \( \text{F} + \text{HD} \) reaction measuring the excitation function, or integral cross section as a function of collision energy, with quantum dynamics calculations carried out on the SW-PES. A clear step structure in the excitation function of the \( \text{F} + \text{D} \) product channel was observed around 0.5 kcal mol\(^{-1}\) (Fig. 4a). This step-like feature was reproduced by quantum dynamics calculations, but not by QCT calculations, suggesting that this structure is purely a quantum phenomenon. Further analysis shows that this feature is due to a single reactive resonance. In contrast, the excitation function of the \( \text{DF} + \text{H} \) channel shows no resonant features (Fig. 4b). Features were also observed in the \( \text{F} + \text{H}_2 \) and \( \text{F} + \text{D}_2 \) reaction excitation functions, and theoretical results based on the SW-PES predicted the existence of a resonance in the \( \text{F} + \text{H}_2 \) reaction.
More recently, resonances in the F + H₂ and F + HD reactions have been further investigated using the high-resolution crossed beam scattering method and more accurate dynamics theory to understand the accurate quantum dynamics of resonances in these isotopologs. Scattering resonances involving vibrationally excited reactants, such as F + HD(v = 1) and Cl + H₂, have also been studied. Resonances in the F + H₂(D₂) reactions have also been investigated using the cryo-SEVI method. In addition, resonances in much more complex polyatomic reaction systems, such as the F + CH₄ reaction and the F + CH₃OH reaction, can now be experimentally investigated with the same technique. These studies have pushed our understanding of reaction resonances to a much higher level. In the following sections, we will provide a comprehensive review of these new developments.

III.1 Probing reactive resonances in the F + H₂ reaction using cryo-SEVI spectroscopy

The recently improved capabilities of cryo-SEVI transition state spectroscopy are perhaps best-illustrated for the F + H₂-H + HF reaction. This system represents a fairly ideal case for anion PES transition state spectroscopy, as the corresponding FH₂⁻ anion is bound and has similar bond lengths to the neutral transition state, providing good Franck-Condon overlap. However, FH₂⁻ is linear while the F + H₂ transition state is bent. As a result, the photoelectron spectrum is dominated by an FC progression in the H-H hindered rotor (or F-H-H bending states) of the FH₂ transition state complex. An early anion photoelectron spectrum of F + H₂ resolved this bending progression.

Improved photodetachment simulations later indicated that sharp features corresponding to bound and quasi-bound resonances in the F + H₂ reactant and product van der Waals (vdW) wells should be visible in a photoelectron spectrum with 1 meV resolution. Traditional anion PES methods lacked the energy resolution to observe these features. The poor threshold photodetachment cross section of the FH₂⁻ anion also made a study using zero electron kinetic energy spectroscopy intractable. The first SEVI study of FH₂⁻, before cryogenic anion cooling was incorporated into the instrument, showed a hint of a predicted product resonance.

Recently, Neumark and coworkers returned to the F + H₂ reaction and its fully deuterated isotopolog with the cryo-SEVI technique, allowing for unambiguous resolution of resonances in the product and reactant wells and near the transition state. The reaction of F with para-H₂ (p-H₂) was investigated in particular, as spectral congestion is reduced and the resonances are predicted to be more pronounced than in the normal-H₂ (n-H₂) case. para-FH₂⁻ and n-FD₂⁻ ions were synthesized by introducing F⁻ into the cryogenic ion trap and allowing clustering with p-H₂ or n-D₂ buffer gas, respectively. This method produced substantially higher ion yields than a molecular beam ion source, and proved essential for achieving the required high signal-to-noise ratio needed to discern small resonance features on top of intense broader features. The resolution and sensitivity of the measurements were also much enhanced via improvements in image acquisition and processing, to better reproduce weak resonance features on top of a broad signal.
Cryo-SEVI spectra for $p$-$FH_2^-$ and $n$-$FD_2^-$ are shown in Fig. 6a and b, with overview traces in green, and high-resolution traces in purple. Theoretical spectra calculated by Alexander and Manolopoulos are also shown (red and blue traces), making use of newly developed high-quality potential energy surfaces.\textsuperscript{75} For both $FH_2^-$ and $FD_2^-$, excellent agreement between the experimental and calculated spectra has been achieved. The calculated scattering wavefunctions at the energy of each peak can also be extracted to aid in the state assignments of observed features. The neutral wavefunctions corresponding to labeled spectral peaks are shown in Fig. 7 in red and blue, with the initial anion wavefunctions shown in green.

The broad features A, B, and C in the $FH_2^-$ spectrum and peaks D and E in the $FD_2^-$ spectrum have been detected previously and assigned to the H–H (D–D) hindered rotor direct scattering states. Several additional features are newly observed. For $FH_2^-$, peak a, lying just slightly above peak A, is clearly resolved, as is peak α, which manifests experimentally as a shoulder on the low-eBE side of peak A. Both a and α are well-reproduced in the calculated spectrum as sharp resonances. For $FD_2^-$, two weak features, peaks b and c, are observed at low eBE and also manifest clearly in the simulation.

The nature of these resonance features is unambiguously revealed by their localization and nodal structure in the wavefunction plots in Fig. 7. Peak A had previously been assigned to a delocalized direct scattering state, but it is now clear that it is in fact a quasibound resonance localized at the $F + H_2$ transition state, with three quanta of excitation in the $H-F$ stretching mode. Peaks a, b, and c are quasibound resonances supported by the $H\cdot H-F (D\cdot D-F)$ product vdW well in the exit channel, with different quanta in the $H-F (D-F)$ and $H-HF (D-DF)$ stretching modes, while peak α is a resonance supported by the $F\cdot H_2$ vdW reactant well in the entrance channel. This resonance was predicted and analyzed for the first time by the time-independent Q-matrix method.\textsuperscript{76} Peak a was predicted by Russell and Manolopoulos in 1996,\textsuperscript{74} but peaks b and c in the $FD_2^-$ spectrum were not previously predicted or observed. The fact that there are two resonances supported in the $D\cdot D-F$ product well, yet only one resonance in the $H\cdot H-F$ well is simply a consequence of the reduced mass difference of the two isotopologs.

The experimental positions, widths, and intensities of these newly resolved reactive resonances are exquisite probes of the $F + H_2$ transition state region, and make an exceptional point of comparison with theory. The experimental results can be used to quantitatively benchmark the quality of calculated $FH_2^-$ anion vibrational wavefunctions and neutral reactive surfaces.

III.2 Probing resonances in the $F + H_2$ reaction using state-resolved crossed beam scattering

In-depth studies of the $F + H_2$ reaction using high-resolution crossed beam backward scattering spectroscopy in combination
with state-of-the-art quantum dynamics calculations have also helped to reveal the true physical nature of reaction resonances in this benchmark system. In this section, we will describe the new advances in this system, starting from the $F + H_2 (v=0, j=0)$ reaction.

Experiments on the $F + H_2 (v=0, j=0)$ reaction were carried out by Yang and co-workers using crossed beam reactive scattering in combination with H-atom Rydberg tagging detection.\textsuperscript{62} A beam of cryogenic para-$H_2$ in only the $j=0$ state was obtained by cooling the beam source with liquid nitrogen. TOF spectra of the hydrogen atom reaction products were measured in a range of scattering angles at the collision energy of 0.52 kcal mol\textsuperscript{-1}. From conservation of energy and momentum in the scattering process, HF product rovibrational state-resolved differential cross sections were determined. Fig. 8a shows the experimental three dimensional product DCS contour plot. A pronounced forward scattering peak for the HF($v'=2$) product, which was not observed previously by Lee and coworkers,\textsuperscript{51} in the collision energy range of 0.7 to 3.4 kcal mol\textsuperscript{-1} was clearly detected. Full quantum scattering calculations based on an accurately constructed potential energy surface, XXZ-PES,\textsuperscript{63} were carried out (Fig. 8b). The excellent agreement between experiment and theory provides a solid basis for understanding the dynamics of resonances for this reaction.

Fig. 9 shows the calculated total reaction probabilities for the $F + H_2 (v=0, j=0)$ reaction as a function of collision energy for the $J=0$ partial wave. It is clear that there are two reaction resonance states in the low energy region, lying at collision energies of 0.26 and 0.46 kcal mol\textsuperscript{-1} on the XXZ-PES. Dynamical analysis indicates that the pronounced forward scattering of the HF($v'=2$) product is enhanced by the constructive interference of these two resonance states. At a collision energy of 0.52 kcal mol\textsuperscript{-1}, the contribution of the first resonance (see Fig. 9) to the cross section is in the partial wave range $J=5-11$, while the contribution of the second one is in the range $J=0-4$ on the XXZ-PES.\textsuperscript{62} Note that the two resonances cross at different partial waves on different potential energy surfaces.\textsuperscript{77} The $J=0$ wave function of the ground state resonance shows the
existence of three nodes along the H–F coordinate in the HF–H′ complex with no nodes along the reaction coordinate (Fig. 10a). This state is therefore the ground resonance state supported by the $v_1 = 0$, $v_2 = 0$, $v_3 = 3$, where $v_1$ is the quantum number for the H–HF stretching mode, $v_2$ for the bending mode, and $v_3$ for the HF stretching mode. The second resonance state ($J = 0$) at 0.46 kcal mol$^{-1}$ exhibits three nodes along the H–F coordinate in the HF–H′ complex with one node along the reaction coordinate (Fig. 10b). This resonance state can be assigned to the $(103)$ resonance state with one quantum of vibrational excitation along the reaction coordinate in the $v = 3$ adiabatic potential of the exit channel. 62

Fig. 11 shows the resonance-mediated reaction mechanism in a one-dimensional vibrationally adiabatic picture. 62 The HF($v′ = 3$)–H′ vibrational adiabatic potential (VAP) well has a deep well in the post barrier region as well as a shallow vdW well. The one-dimensional wave function for the ground resonance state shows that this state is mainly trapped in the inner deep well of the HF($v′ = 3$)–H′ VAP with almost no vdW character, while the excited resonance wave function is mainly a vdW resonance. The collision energy 0.52 kcal mol$^{-1}$ is well below the reaction barrier, indicating that the reaction takes place through a post-barrier, resonance-enhanced tunneling mechanism. In addition, the main product is HF($v′ = 2$), rather than HF($v′ = 3$). The resonance states are trapped in the HF($v′ = 3$)–H′ VAP and decay to the HF($v′ = 1, 2$) product channels via strong couplings between HF($v′ = 3$)–H′ and HF($v′ = 1, 2$)–H′ adiabatic curves.

The HF($v = 3$) channel was investigated in a similar high-resolution crossed beam experiment to understand the nature of the forward scattering at higher collision energies. 78 The excitation function of the HF($v = 3$) channel from 0.4 to 1.2 kcal mol$^{-1}$ shows that the threshold of the HF($v′ = 3$) channel is around 0.52 kcal mol$^{-1}$, indicating that this channel has no significant exit barrier for reaction, in good agreement with the quantum dynamics calculations. If the reaction energy is below the threshold for the HF($v′ = 3$) channel, the resonance-trapped complex decays into the lower HF($v′ = 2, 1, 0$) channels.

Because the centrifugal potential makes the effective potential well increasingly shallow as total $J$ increases, the HF($v′ = 3$)–H′ product well cannot support the excited resonance state at higher $J$. Theoretical analysis shows that the ground resonance state can form the HF($v′ = 3$) product via tunneling through the centrifugal barrier via a shape resonance mechanism. 78 This shape resonance mechanism can only happen in a narrow collision energy range, from 0.60 to 0.85 kcal mol$^{-1}$. For total $J > 10$, no resonance state can be supported on the effective potential, and thus a slowdown type mechanism dominates the formation of HF($v′ = 3$) over the exit centrifugal barrier, similar to the time-delay mechanism in the H + HD reaction. 79–81 This suggests that the HF($v′ = 3$) forward scattering at higher collision energies is...
related to the adiabatic potential involved in the resonance, but not induced by a specific resonance state. Shape resonances have also been observed in the reaction of $^1S(^1D_2) + H_2$ using the crossed beam method. Previous theoretical studies using time independent Q-matrix calculations show that the resonance contributes to the differential cross sections of the HF($v'=3$) product until about $j = 20$. Resonance contributions to the differential cross section at the collision energy of 1.3 kcal mol$^{-1}$ were also analyzed by the Regge Pole Theory. While this work appears to draw different conclusions than the results shown in ref. 78, the slowdown mechanism at high $j$ described above and the resonance mechanism are hard to distinguish in these analyses.

In the F + H$_2$ reaction, there are also long lived vdW resonance states that have been predicted and analyzed on the FXZ PES. Similar structures are also seen in the F + HD reaction. However, these resonances have yet to be observed in a crossed beam experiment, most likely because they are usually too sharp to be detected with backward scattering spectroscopy, which has limited energy resolution relative to the narrow width of vdW resonances. In addition, these sharp resonances are also mixed with the direct reaction channel, making them very difficult to detect in experiment.

### III.3 Isotope effects and partial wave resonances in the F + HD → FH + D reaction

The energies and lifetimes of reactive resonance states, and thus the reaction dynamics, can be affected by isotope substitution effects. For instance, it is well known that the F + HD → HF + D reaction behaves quite differently from the F + H$_2$ → HF + H reaction. Illuminating the dynamical differences between isotopolog systems would aid in understanding resonance isotope effects and thus also the nature of reactive resonances. The F + HD → HF + D reaction has thus been reinvestigated using the high-resolution D-atom Rydberg tagging TOF method. The quantum state-resolved differential cross sections have been measured for this reaction in the collision energy range of 0.3 to 1.2 kcal mol$^{-1}$ and are shown in Fig. 12. The most striking observation is the dramatic variation of the DCS around the collision energy of 0.5 kcal mol$^{-1}$.

Quantum state-resolved differential cross sections of the F + HD → HF + D reaction have also been measured in the backward scattering direction for the collision energy range of 0.2–1.2 kcal mol$^{-1}$. Fig. 13 shows the backward scattering DCS of the HF($v'=2, j'=0$–3) product of the F + HD → FH + D reaction as a function of collision energy; a clear peak in the experimental spectrum is observed at 0.39 kcal mol$^{-1}$ and is attributed to a reactive resonance, which is the lowest resonance in the F + HD → HF + D reaction. Quantum dynamics calculations on the XXZ-PES and a more recent FXZ-PES for this reaction have also been performed and compared with the experimental results. Though the theoretical results based on the XXZ-PES agree well with the experimental differential cross sections of the F + H$_2$ reaction at 0.52 kcal mol$^{-1}$, the calculated peak in Fig. 11 for the F + HD reaction appears at higher collision energy relative to the observed peak position in the backward scattering DCS spectrum, suggesting that this potential surface is not sufficiently accurate to describe this resonance. In contrast, the calculated resonance peak position based on the FXZ-PES is in much better agreement with the experimental result. For total angular momentum $J = 0$, the calculated energy for this resonance state is 0.40 kcal mol$^{-1}$, very close to the observed peak position of 0.39 kcal mol$^{-1}$. In addition to the peak position, the width of the resonance peak is also in very good agreement with the experimental result. The excellent agreement between the experiment and the most accurate dynamics theory also suggests that quantum state-resolved backward DCS spectroscopy can indeed provide detailed spectroscopic information on the resonance state. From the 0.15 kcal mol$^{-1}$ width of the resonance peak, the resonance state lifetime is determined to be about 100 fs for the
$J = 0$ partial wave, in good agreement with the theoretically calculated value. This again suggests that backward scattering spectroscopy can provide accurate information on the lifetime of resonance states.

Excellent agreement between experimental results and quantum dynamics calculations on the FXZ-PES has also been achieved in a very small collision energy range with dramatic DCS variations.\(^\text{64,65}\) Theoretical analysis reveals that the HF($\nu^0 = 3$)--D adiabatic well is deeper by about 0.3 kcal mol\(^{-1}\) on the FXZ-PES than on the XXZ-PES (Fig. 14). This results in the ground resonance state energy being 0.16 kcal mol\(^{-1}\) lower when calculated with FXZ-PES for the F + HD reaction. The reason that XXZ-PES agrees well with the F + H\(_2\) reaction but not the F + HD reaction is that for F + H\(_2\), the results at 0.52 kcal mol\(^{-1}\) are dominated by the excited resonance state, which is similar on the XXZ-PES and FXZ-PES. There are also other potential energy surfaces available for the system, such as the LWAL-PES, which reproduces the FH\(_3^-\) anion photoelectron spectrum better than the FXZ-PES, and the CSZ-PES, which further refines the FXZ-PES.\(^\text{66,67}\) Recently, a comprehensive comparison among FXZ, CSZ, SW and LWAL PESs for the F + HD reaction dynamics has been given; the theoretical results are also compared with the available crossed molecular beam data.\(^\text{88}\)

For a longer lived resonance state as in the F + HD $\rightarrow$ HF + D reaction, rotational structure could be well resolved. Yang and co-workers carried out a high-resolution crossed beam experiment, using quantum state specific backward scattering spectroscopy, to detect the fine rotational structure of reactive resonances.\(^\text{89}\) In order to achieve higher TOF resolution as well as a narrow collision energy distribution, both beam sources (F and HD) were cooled to liquid nitrogen temperature. Fig. 15 shows the backward experimental (solid circles) and theoretical (red curve) DCS of the HF($\nu^0 = 2, J^0 = 6$) product of the F + HD($j = 0$) reaction. Clear oscillatory structures are observed and are attributed to partial wave Feshbach resonance structures with $J = 12, 13$ and 14. These fine oscillation structures observed are essentially the rotational states of transient resonances, observed here for the first time.

### III.4 Resonances in reactions with vibrationally and rotationally excited reagents

#### III.4.1 Resonances in the F + HD($\nu = 1$) reaction

In the previous sections, we have described recent advances in the study of reactive resonances in the reactions of the F atom with ground state H\(_2\) and HD molecules. It is well known that vibrational excitation of reactants has a profound effect on the chemical reaction dynamics and reactivity.\(^\text{90}\) For example, enhanced reactivity and bond-selectivity have been observed in the H + H\(_2\)O (HOD, D\(_2\)O) reactions when reactants are vibrationally excited.\(^\text{91–94}\) Recently, Liu and coworkers have also studied how vibrational excitation affects polyatomic reactions, specifically F/Cl + CH\(_4\) and their isotopologs.\(^\text{95–97}\) It is worth investigating how reactant vibrational excitation affects reactive resonances.

Recently, Yang and coworkers have studied the F + HD($\nu = 1$) reaction using the D-atom Rydberg tagging crossed beam technique with backward scattering spectroscopy.\(^\text{87}\) Vibrationally excited HD($\nu = 1, J = 0$) molecules were prepared efficiently using stimulated Raman pumping, with the help of high-power narrow band nanosecond pulsed lasers. TOF spectra of

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**Fig. 14** (a) The one-dimensional adiabatic resonance potentials of (a) HF($\nu^0 = 3$)--H for the F + H\(_2\) reaction and (b) HF($\nu^0 = 3$)--D for the F + HD reaction traced out from the XXZ-PES and the FXZ-PES. Reproduced from ref. 64 with permission from the National Academy of Sciences, copyright 2008.

**Fig. 15** Experimental (solid circles) and theoretical (red curve) DCS of the HF($\nu^0 = 2, J^0 = 6$) product of the F + HD($j = 0$) reaction in the backward scattering direction. The theoretical result was convoluted with the experimental resolution and shifted 0.03 kcal mol\(^{-1}\) lower in energy. The 3D DCS shown as the inset was measured at 1.285 kcal mol\(^{-1}\). Reproduced from ref. 89 with permission from the AAAS, copyright 2010.
the D atom products from the F + HD\((v = 1, j = 0)\) reaction were measured by subtracting the TOF spectra with the Stokes laser on \((F + HD(v = 0 \text{ and } 1, j = 0))\) and off \((F + HD(v = 0, j = 0))\). Fig. 16 shows the experimental and theoretical 3D product contour plots for F + HD\((v = 1, j = 0)\) → HF + D at collision energies of 0.23 (A and C) and 0.63 kcal mol\(^{-1}\) (B and D). The HF product was mainly produced in the \(v’ = 3\) state for both collision energies, in contrast to the main HF\((v_0 = 2)\) products of the F + HD\((v = 0)\) reaction. The backward scattering product dominates at the collision energy of 0.23 kcal mol\(^{-1}\), while forward scattering peaks appear at 0.63 kcal mol\(^{-1}\). The backward scattering DCS spectrum of HF\((v’ = 2, 3)\) shows two broad peaks at 0.21 and 0.62 kcal mol\(^{-1}\) (Fig. 17).

The dynamics calculations based on the improved FXZ-PES reproduce very well the experimentally measured DCSs (Fig. 16) and the backward scattering spectrum (Fig. 17). The calculated excitation function for the total angular momentum \(J = 0\), obtained by time-dependent quantum wavepacket calculations, exhibits two distinct peaks at 0.20 and 0.66 kcal mol\(^{-1}\), corresponding to two reactive resonance states. Analysis of the scattering wave functions for \(J = 0\) reveals the two resonance states, \((204, v_1 = 2, v_2 = 0, v_3 = 4)\) and \((304)\), at the collision energies of 0.20 and 0.66 kcal mol\(^{-1}\) respectively, where \(v_1\) is the quantum number for the D–HF stretching mode, \(v_2\) for the bending mode, and \(v_3\) for the HF stretching mode. These two resonance states are the second and third excited resonance states trapped in the HF\((v’ = 4)\)–D VAP well as shown in Fig. 18. Further theoretical calculations indicate that the resonance mediated reaction can only be accessed \(\text{via}\) the HD\((v = 1)\) reaction pathway, while the HD\((v = 0)\) reaction path cannot access these resonances, even at high collision energies. This implies that the reagent vibrational excitation not only provides the energy required for the reaction but also leads to a different reaction pathway on a distinct VAP inaccessible to the ground state reaction.

III.4.2 Short-lived dynamical resonances in the Cl + HD\((v = 1)\) reaction. The Cl + H\(_2\) reaction is also an important benchmark system in the study of chemical reaction dynamics,\(^{98}\) and has been recognized as a prototypical direct abstraction reaction with a collinear reaction barrier.\(^{99-102}\) No clear signature of reaction resonances has been previously observed for this reaction, although bound states in the van der Waals well of the entrance valley were characterized by SEVI of ClH\(_2\) and ClD\(_2\).\(^{103}\) In a recent study, however, Yang and coworkers detected reactive resonances in the Cl reaction with vibrationally excited HD.\(^{68}\) The experiment for the Cl + HD\((v = 1)\) → DCl + H reaction is similar to that of F + HD\((v = 1)\) described above, with the HD\((v = 1)\) molecular beam prepared by stimulated
Raman pumping and the Cl atom beam generated in a discharge source. Experimental measurements of the DCS at collision energies of 2.4 and 4.3 kcal mol\(^{-1}\) have been performed. Fig. 19(A and B) shows 3D product contour plots for the Cl + HD\((v = 1)\) → DCl + H reaction. At both collision energies, the DCl products are predominantly backward scattered. However, at 4.3 kcal mol\(^{-1}\), the experimental DCS shows a small forward scattering signal, suggesting that a longer lived resonance state might play a role in this reaction. The collision-energy dependence of DCS in the backward scattering direction was also measured (Fig. 20). This DCS exhibits two clear peaks at 2.4 kcal mol\(^{-1}\) (peak a) and 4.3 kcal mol\(^{-1}\) (peak b), suggesting that there are two resonance states in this reaction. Theoretical calculations on a new PES reproduce the angular distribution shown in Fig. 19(C and D). Excellent agreement between theory and experiment is achieved in the backward scattering excitation function only by shifting the collision energy of the theoretical DCS lower by 0.15 kcal mol\(^{-1}\). This small discrepancy indicates that the PES is sufficiently accurate for the dynamics. The calculated quantum dynamics reaction probability for the \(J = 0\) partial wave as a function of collision energy also shows two peaks, confirming that there may be two resonance states in this collision energy region.

Scattering wave function analyses are performed to understand the nature of these resonance states. From the nodal structures of the wavefunctions (Fig. 21), two resonance states can be assigned to \((v_1 = 1, v_2 = 0, v_3 = 2)\) and \((122)\), at the collision energies of 2.4 and 4.3 kcal mol\(^{-1}\) respectively, where \(v_1\) is the quantum number for the H–DCl stretching mode, \(v_2\) for the bending mode, and \(v_3\) for the DCl stretching mode. These two resonance states are transiently trapped in the H–DCl\((v' = 2)\) VAP well as shown in Fig. 21. From the estimation of the widths of the resonance peaks, the lifetimes for these two resonance states are determined to be 28 and 14 fs, which are considerably shorter-lived than those in the F + HD\((v = 1)\) reaction. This is the reason that only small forward scattering signals are observed in the Cl + HD\((v = 1)\) → DCl + H reaction. Fig. 21 shows a single barrier located at the product side on the ground VAP. However, on the vibrationally excited H–DCl VAP, the interaction between H and DCl in the transition state region softens the DCl bond, manifesting in a lower vibrational frequency.
III.4.3 | Effects of rotationally excited reactants on resonances.

The effect of a single quantum of rotational excitation of H\(_2\) has been investigated in the F + H\(_2\) reaction at low collision energies.\(^{104}\) To study the effects from the rotational excitation of H\(_2\), two different H\(_2\) samples were used in the experiment: normal H\(_2\) (n-H\(_2\)) and p-H\(_2\).\(^{105,106}\) The H\(_2\) molecules in the molecular beam are produced via supersonic expansion from a cryogenically cooled beam source, resulting in population of only the lowest rotational states: \(j = 0\) (100%) for p-H\(_2\), and \(j = 0\) (25%) and \(j = 1\) (75%) for n-H\(_2\). The purity of p-H\(_2\) was measured by Raman spectroscopy of the prepared sample.\(^{104}\) Using a simple calculation from the TOF signals of the H atom product measured from the F + n-H\(_2\) and F + p-H\(_2\) reactions, the TOF signals from the F + H\(_2\) (\(j = 0\)) and F + H\(_2\) (\(j = 1\)) reactions can be determined.

In the F + H\(_2\) (\(v = 0, j = 0\)) reaction at a collision energy of 0.19 kcal mol\(^{-1}\), the reaction products are mainly backward scattered, while a large HF (\(v = 2\) forward scattering peak was observed in the F + H\(_2\) (\(j = 1\)) reaction at the same collision energy (Fig. 22). The scattering picture of the H\(_2\) (\(j = 0\)) and H\(_2\) (\(j = 1\)) reactions at 0.56 kcal mol\(^{-1}\) seems to be completely reversed from that at 0.19 kcal mol\(^{-1}\), in which the reaction products are mainly backward scattered for the F + H\(_2\) (\(j = 1\)) reaction, while a large HF (\(v = 2\) forward scattering peak was observed in the F + H\(_2\) (\(j = 0\)) reaction. Forward scattering of the HF (\(v = 2\)) product for the H\(_2\) (\(j = 1\)) reaction has also been measured as a function of collision energy. A peak around 0.17 kcal mol\(^{-1}\) was observed in the excitation function, and is similar to that of F + H\(_2\) (\(j = 0\)),\(^{104}\) except that its peak is shifted to lower energy by about 0.35 kcal mol\(^{-1}\), which is roughly equal to the rotational energy of the H\(_2\) (\(j = 1\)) level. Theoretical calculations suggest that the F + H\(_2\) (\(j = 1\)) reaction at 0.56 kcal mol\(^{-1}\) proceeds predominantly via the continuum tunneling reaction mechanism, without contribution from the two reaction resonances in the system, very different from the F + H\(_2\) (\(j = 0\)) reaction.\(^{62}\) These experimental and theoretical results show clearly that the rotational excitation of H\(_2\) only shifts the resonance energy to lower collision energy because of the addition of the rotational energy, while the resonance picture does not change in a significant way.

III.5 | Resonances in polyatomic reactions using cryo-SEVI

The cryo-SEVI study of F + H\(_2\) demonstrated that high-resolution transition state spectroscopy experiments can serve as benchmarks for state-of-the-art theoretical treatment of bimolecular reactive surfaces. The cryo-SEVI technique has also been applied to systems with considerably more degrees of freedom. Here we review studies of the 5-atom F + CH\(_4\) \(\rightarrow\) HF + CH\(_3\) reaction and the 7-atom F + CH\(_3\)OH \(\rightarrow\) HF + CH\(_2\)O reaction. These reactions are on the forefront of what is possible to treat theoretically, due to the difficulty of performing accurate dynamical calculations on multi-dimensional polyatomic potential energy surfaces with many degrees of freedom.

The F + CH\(_4\) \(\rightarrow\) HF + CH\(_3\) reaction and its isotopologs have become benchmark polyatomic reactions, especially with regard to the roles that vibrational degrees of freedom and mode-selective vibrational excitation play in reaction dynamics.\(^{107,108}\) F + CH\(_4\) is a textbook early barrier reaction, with a low-lying transition state that inherits much of its character from the entrance channel vdW complex. This reactant complex therefore has an emphasized role in the reaction dynamics, and the transition state spectroscopy of this region of the reactive surface is of great interest.

A schematic showing the relevant F + CH\(_4\) surfaces is given in Fig. 23. There are three low-lying electronic states in the entrance channel region. Working within the C\(_{3v}\) point group, the ground A\(_1\) state is reactive (plotted with a solid curve in Fig. 23), while two non-reactive E states lie nearby (dotted curves). The reactive surface has a C\(_{3v}\)-symmetric local minimum entrance channel complex where the F atom is in a linear H–C⋅⋅⋅F arrangement. At the transition state, the C\(_{3v}\) symmetry is broken, and the F atom lies close to a single H atom, in preparation for abstraction. The CH\(_4\)F\(^{-}\) anion has a C\(_{3v}\)-symmetric structure.
with a linear C–H···F arrangement. Photodetachment from this anion structure yields good Franck–Condon overlap with both the entrance channel and transition state complexes on the neutral reactive surface.

Low-resolution overview cryo-SEVI spectra\(^{71}\) are shown for detachment of both CH\(_4\)F\(^-\) and CD\(_4\)F\(^-\) in Fig. 24. Photodetachment simulations calculated by Manthe and coworkers are also shown, based on full-dimensional (12D) quantum dynamics on six spin–orbit and vibronically coupled potential energy surfaces. For each isotopolog, the experimental and theoretical spectra both show two main peaks. The low-eBE peaks centered around 30 000 cm\(^{-1}\) are ascribed to transitions to the ground A\(_1\) reactive surfaces. The higher-lying peaks centered around 31 250 cm\(^{-1}\) result from transitions to the E excited states, and are spectrally broader due to the repulsive nature of these surfaces.

High-resolution cryo-SEVI spectra of the A\(_1\) bands of CH\(_4\)F\(^-\) and CD\(_4\)F\(^-\) are shown in Fig. 25. In this narrow eBE region between 29 500 and 30 000 cm\(^{-1}\), the spectra become highly structured. For both species, small peaks are experimentally resolved, spaced by 15–25 cm\(^{-1}\). Similar progressions appear in the simulations. As these resonances lie below the free reactant energy asymptote, they must reside in the entrance complex vDW well. To better understand the dynamic processes that give rise to these resonances, we turn to the results of the quantum dynamics simulations and analyze the evolution of the anion wavefunction after projection onto the neutral reactive surface. Chaotic dynamics and a high density of states prevent assignment of resonances with specific quantum numbers. However, the wavefunction motion following photodetachment is dominated by F···CH\(_4\) stretching and relative rotation of the fluorine and methane moieties with respect to one another, suggesting that the observed resonances stem from recurrences of these periodic motions in the entrance well. These resonances are activated owing to the difference in geometries between the anion and the entrance channel minimum-energy complex. The dense manifold of quasi-bound entrance channel states accessed here is likely to affect steering of the F + CH\(_4\) reaction at low temperature.

With the improvement in experimental and theoretical methods, the reaction dynamics of the more complex F + CH\(_3\)OH reaction have become a subject of recent study.\(^{109}\) This hydrogen abstraction reaction can proceed barrierlessly with the fluorine atom attacking either the hydroxyl or the methyl site, leading respectively to methoxy (CH\(_3\)O) or hydroxymethyl (CH\(_2\)OH) radical products.\(^{110}\) While H-atom abstraction at the methyl group is more exothermic and statistically three times as likely as abstraction at the hydroxyl group, the hydroxyl-abstraction pathway is favored due to stabilization of its entrance complex and transition state via hydrogen bonding.
The \( \text{F} + \text{CH}_3\text{OH} \rightarrow \text{HF} + \text{CH}_3\text{O} \) reaction represents a favorable case for transition state spectroscopy, with a hydrogen-bonded \( \text{CH}_3\text{OHF}^− \) anion similar in geometry to the transition state for abstraction of the hydroxyl H atom, as shown in Fig. 26. \(^{72}\) Interestingly, while photodetachment of the \( \text{CH}_4\text{F}^− \) anion, discussed above, predominantly accessed the entrance channel side of the transition state, photodetachment of \( \text{CH}_3\text{OHF}^− \) preferentially accesses the structure in the exit channel.

Cryo-SEVI spectra of \( \text{CH}_3\text{OHF}^− \) and \( \text{CH}_3\text{ODF}^− \) are shown in Fig. 27. \(^{72}\) The experimental results are accompanied by a high-level simulation of the \( \text{CH}_3\text{OHF}^− \) photodetachment spectrum calculated by Guo and coworkers by running quantum dynamics trajectories on a 6-dimensional subsurface of a new 15-dimensional PES constructed for the \( \text{F} + \text{CH}_3\text{OH} \) reaction. The experimental spectra are dominated by broad steps (labeled a–e), with an a–b spacing of \( \sim 3600 \text{ cm}^{-1} \) for \( \text{CH}_3\text{OHF}^− \) detachment and \( \sim 2700 \text{ cm}^{-1} \) for \( \text{CH}_3\text{ODF}^− \). Previous photodetachment experiments \(^{111,112}\) also observed this stepped structure and assigned it to an H–F stretching progression of the \( \text{CH}_3\text{O}–\text{HF} \) product complex (PC). The location of the structure with respect to the product and reactant asymptotes confirms that indeed the observed structure can only lie in the PC well. The states in feature a lie below the product asymptote and are therefore bound with respect to free products, while features b–e are metastable and will eventually dissociate via vibrational predissociation as vibrational energy flows to translational motion along the reaction coordinate. As all resonances seen here lie below the reactant asymptote, they are inaccessible to \( \text{F} + \text{CH}_3\text{O} \) scattering experiments and therefore uniquely accessible with an anion photodetachment scheme.

With cryo-SEVI, an additional fine structure is newly resolved, superimposed on the broad steps and spaced by \( \sim 200 \text{ cm}^{-1} \). This fine structure is well-reproduced by the simulation, including the subtlety that the spacing of resonances within each step increases with increasing eBE (e.g. peaks a1–a2 are more finely spaced than peaks b1–b2, which are more finely spaced than peaks c1–c2). The nature of this fine structure can be explained with reference to the VAPs sketched in Fig. 26, which correlate to free HF(\( \nu \)) + CH\(_3\)O products. The spectral steps a–e each represent detachment to an HF(\( \nu = 0–4 \)) VAP, while the fine peaks within each step are resonances supported in the VAP wells with excitation in the CH\(_3\)O–HF vdW stretching mode. VAP wells are known to deepen with increasing vibrational excitation, through dynamical vibrational bonding. \(^{113}\) In this case, the VAP wells are stabilized as the HF stretching excitation is increased and the
H atom becomes more delocalized between the heavier F and CH₃O fragments. This gives rise to the observed increase in CH₃O–HF level spacing with increasing eBE.

These vibrational assignments can be confirmed with reference to vibrational wavefunctions extracted from the photodetachment simulations. Wavefunctions corresponding to several relevant spectral peaks are plotted in Fig. 28. Based on the localization of these states, it is again clear that they are bound or quasi-bound resonances supported in the product well; the quasi-bound states are vibrational Feshbach resonances that can dissociate to products. Considering the nodal structure of the plotted wavefunctions, each subsequent spectral hump (e.g. the a₁–b₁–c₁ progression) shows an increasing integer number of nodes along the HF stretching coordinate (vertical axis). These broad humps do therefore correspond to increasing excitation of the product complex HF stretching vibration.

Within each hump (e.g. the a₁–a₂–a₃ progression), the narrow spectral features show increasing nodes along the CH₃O–HF coordinate (horizontal axis), confirming the assignment of the fine vibrational structure to excitation of the stretching mode between the two product complex fragments. The increased intensity of the higher-eBE peaks is also explained by these vibrational wavefunctions: for instance, d₁ has considerably better FC overlap with the CH₃OHF⁻/C₀ anion wavefunction than a₁ does.

Taken together, the F + CH₄ and F + CH₃OH studies illustrate the utility and clarity of cryo-SEVI spectroscopy for probing detailed dynamical resonances in the transition state regions of increasingly intricate bimolecular reactions. These studies permit benchmarking of state-of-the-art quantum dynamics calculations, which have only recently become capable of treating multi-dimensional systems of this size and complexity.
IV. Concluding remarks

As illustrated by this overview of recent advances in the study of reactive resonances in a few benchmark reactions, the combination of improved experimental methods and highly accurate quantum dynamics calculations has yielded a detailed understanding of the nature of these resonances and how they affect reaction dynamics. Using high-resolution anion photoelectron spectroscopy, resonance states lying to either side or directly on top of the reaction barrier can be detected, yielding a clearer picture of the entire transition state region. However, not all quantized states in the transition state region have a significant effect on the reaction dynamics. High-resolution crossed beam backward scattering spectroscopy has proved to be a very powerful tool to understand which resonances affect reactivity, by directly measuring the collision energies that access reaction resonance states, the lifetime of these resonances, and the resulting product states formed. The examples provided in this review have demonstrated that slow photoelectron velocity-map imaging of cryo-cooled anions and crossed beam backward scattering spectroscopy provide complementary insights and allow one to understand reactive resonances at an unprecedented level.

This review article has focused mainly on recent progress made in the study of reactive resonances in two benchmark systems: F + H₂(D), and Cl + HD. In addition to these systems, resonance phenomena in other reactions have been investigated. In the S(1D₂) + HD → SH + D reaction, three resonances at very low collision energy have been observed by Costes and coworkers; however, quantum dynamics theory has not been able to identify and assign these resonances.

Now that the existence of resonances has been confirmed for a number of benchmark reactions, it is of considerable interest to determine how widespread resonances are and to develop new experimental and theoretical methods to characterize them. For example, using backward scattering spectroscopy, it may be possible to observe resonances for polyatomic reactions in scattering experiments. The new field of cold molecule chemistry enables the study of chemical reactions at extremely low temperatures. Such experiments are likely to be very sensitive to the presence of reactive resonances, since quantum mechanical tunneling and related effects will play an outsize role in the measured cross sections and rate constants.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We acknowledge financial support from the National Natural Science Foundation of China (NSFC Center for Chemical Dynamics, grant no. 21688102), and the Air Force Office of Scientific Research (AFOSR) under grant no. FA9550-12-1-0160.

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