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Observation of resonances in the transition state region of the F + NH_3 reaction using anion photoelectron spectroscopy

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The transition state of a chemical reaction is a dividing surface on the reaction potential energy surface (PES) between reactants and products and is thus of fundamental interest in understanding chemical reactivity. The transient nature of the transition state presents challenges to its experimental characterization. Transition-state spectroscopy experiments based on negative-ion photodetachment can provide a direct probe of this region of the PES, revealing the detailed vibrational structure associated with the transition state. Here we study the $F + NH_3 \rightarrow HF + NH_2$ reaction using slow photoelectron velocity-map imaging spectroscopy of cryogenically cooled FNH₃⁻ anions. Reduced-dimensionality quantum dynamical simulations performed on a global PES show excellent agreement with the experimental results, enabling the assignment of spectral structure. Our combined experimental-theoretical study reveals a manifold of vibrational Feshbach resonances in the product well of the F + NH₃ PES. At higher energies, the spectra identify features attributed to resonances localized across the transition state and into the reactant complex that may impact the bimolecular reaction dynamics.

Fundamental to the modern conception of chemistry is the transition state, the transient species located near a saddle point on the reaction potential energy surface (PES) where chemical bond formation and cleavage occur^{1,2}. As the transition state controls not only the reaction rate³, but also the dynamics of the chemical transformation⁴, it is essential to probe this key region of the PES to gain insight into the fundamental interactions that govern chemical reactivity. Such a motivation led to the development of crossed molecular-beam experiments of increasing complexity to determine the properties of the transition state, including barrier height and geometry^{5–7}. Although these experiments have greatly improved our understanding of chemical reactions,

they provide only an indirect probe of the transition-state region of the PES. Complementary experiments utilizing anion photoelectron spectroscopy have yielded vibrationally resolved structure characteristic of the transition-state region of the PES for both unimolecular⁸⁻¹⁰ and bimolecular reactions¹¹⁻¹³.

In these experiments, a stable anion whose geometry is similar to the transition state undergoes photodetachment, projecting the vibrational wavefunction of the anion vertically onto the neutral PES. The ejected photoelectrons carry with them information on the evolution of the wavepacket created by photodetachment^{14–16}, resulting in a photoelectron spectrum that reveals the vibrational structure of

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Reaction coordinate

Fig. 1 | **Energy diagram for photodetachment of FNH3**⁻ **onto the transitionstate region of the neutral F** + **NH3 reaction.** The upper thick curve is the neutral reaction minimum energy path that connects the reactants and products to their ground vibrational states. Sketched above the product complex well are vibrational adiabatic potentials for the excited HF stretching mode ($v_{HF} = 1-4$). The lower thick curve depicts the anion PES. Structures are shown for the reactant complex (RC), product complex (PC), transition state (TS) and anion using grey (H), dark blue (N) and light blue (F). The similarity in the geometry of the anion and transition state provides good Franck–Condon overlap with this region of the surface, allowing for the probing of this critical region via photodetachment. Energies for stationary points on the PES are shown in units of cm⁻¹ relative to the reactant asymptote and are zero-point energy corrected.

complexes near the transition-state region¹⁷. By improving the resolution of the photoelectron spectrometer^{18,19}, one can observe the sharp structure associated with resonances that are quasibound along the reaction coordinate. Resonances spanning the transition-state region have been identified for the atom-diatom reactions I + HI and $F + H_2$ (refs.^{20,21}), and entrance²² and exit²³ channel resonances have been characterized for the $F + CH_4$ and $F + CH_3OH$ reactions, respectively. So far, no resonances spanning the transition-state region have been observed in a polyatomic reaction, leaving their impact on the dynamics of these systems unexplored. Of particular import are dynamical resonances-quasibound states along the reaction pathway that lie higher in energy than the reactant asymptote-as these have been shown to strongly influence reactivity and dynamics²⁴. Such states are accessible to reactive scattering experiments, as highlighted by the observation of such reactive resonances in the bimolecular reactions of F + H₂, Cl + H₂ and Cl with vibrationally excited CH₄ (refs. $^{24-26}$).

In this Article we present a joint photoelectron imaging and quantum dynamics study of the $F + NH_3 \rightarrow HF + NH_2$ hydrogen-abstraction reaction based on high-resolution photodetachment of the FNH_3^- anion. The primary goal of this work is to probe the dynamics near the transition state of this polyatomic neutral reaction. The $F + NH_3$ reaction is highly exoergic (10,422 cm⁻¹), and an accurate global PES (Fig. 1) has recently been determined by fitting a large number of high-level ab initio points in full dimensionality²⁷. Previous experimental work on the title reaction has characterized the vibrational distribution of the HF product via infrared chemiluminescence²⁸⁻³⁰. More recent crossed-beam experiments by Yang and others³¹ have shown that the HF

products (or DF in the $F + ND_3$ reaction) are largely forward-scattered with respect to the incoming F atom. Quasi-classical trajectory studies on the dynamics and kinetics of this reaction have been reported on an analytical PES^{32,33}, and the calculated differential cross-sections agreed reasonably well with the experimental results.

The neutral PES features a reactant complex, a submerged barrier serving as the transition state, and a product complex well, as shown in Fig. 1. The hydrogen-bonded FNH_3^- anion geometry is similar to the transition state. Together, this system presents as an ideal case for transition-state spectroscopy and is probed using slow photoelectron velocity-map imaging of cryogenically cooled anions (cryo-SEVI), which yields photoelectron spectra of complex species with kinetic-energy resolution as high as 1 cm^{-1} (refs. ^{34,35}). The experiment is complemented by reduced-dimensional quantum dynamical calculations on the neutral PES.

This combination of experiment and theory shows that photodetachment from FNH₃⁻ directly accesses both sides of the transition-state barrier and the transition state itself. In the product channel, we observe sharp structure corresponding to a manifold of vibrational Feshbach resonances supported by the post transition-state well. Here, the involvement of the out-of-plane wagging modes of NH₂ highlights that this moiety plays an active role in the title reaction instead of acting as a spectator, as has been observed for the OH and CH₃O groups in other polyatomic systems^{23,36}. In addition, complex and irregular features associated with the transition state and reactant well are observed, several of which are assigned to resonances by comparison to theory. The resonance structure extends to energies above the reactant asymptote and thus includes so-called reactive or dynamical resonances that can influence the dynamics of the F + NH₃ reaction. The results presented here thus represent the most complete mapping so far of the transition-state region for a polyatomic reaction.

Results and discussion

Topography of the neutral potential energy surface

In Fig. 1, the minimum energy path (MEP) connecting the reactants and products in their ground vibrational states is presented along with stationary-point energies and geometries, which are in good agreement with previous theoretical studies on the F + NH₃ reaction^{32,37,38}. The PES here resembles that of the F + CH₃OH system²³ in that the transition state, reactant complex, and product complex all lie below the energy of the free reactants. The reactant complex is bound by 4,326 cm⁻¹ with respect to the reactants and lies only 285 cm⁻¹ below the transition-state barrier. The product complex is a hydrogen-bonded complex between HF and the NH₂ radical, bound by 2,521 cm⁻¹ with respect to the product asymptote.

Overview of photodetachment spectra

Experimental cryo-SEVI spectra of FNH₃⁻ are shown in Fig. 2 and show the photoelectron intensity as a function of electron binding energy (eBE). The experimental overview spectrum in blue shows a smoothly rising background from 26,050 to 29,050 cm⁻¹, after which there is a series of steps out to $32,000 \text{ cm}^{-1}$ (k-p). Above this, one observes a series of partially resolved peaks (q-t). Considerably more structure is observed in the higher-resolution composite spectra (black). Starting at 26,050 cm⁻¹, there is an extended progression of peaks a-m that become more tightly spaced with increasing eBE. Spacings between peaks a and b and k and l, for example, are 293 and 187 cm⁻¹, respectively. At higher eBE, a series of broad features n-p spaced by ${\sim}700\,cm^{\text{-1}}$ is seen, followed by a third progression, peaks q-t, spaced by ~300 cm⁻¹. A full listing of peak positions and spacings is provided in Supplementary Table 1. The locations of the reactant asymptote (black arrow) and the transition state (grey arrow) are also indicated at 33,022 and 28,981 cm⁻¹, respectively.

The intensities in the experimental and theoretical spectra are largely governed by Franck–Condon considerations. All peaks below



Fig. 2|**Photodetachment spectra of FNH**₃⁻. Experimental and theoretical photodetachment spectra of FNH₃⁻, showing transitions to the F + NH₃ reactive PES. The experimental cryo-SEVI spectra of FNH₃⁻ detachment are plotted as an overview spectrum (blue) above high-resolution traces (black). Peaks are labelled a-t. A full listing of peak positions and spacings is provided in Supplementary Table 1. Raw simulated spectra (red) are plotted as well as a theoretical spectrum convoluted with a 50-cm⁻¹ FWHM Gaussian function (purple) for comparison with the experiment. The theoretical spectra are shifted 104 cm⁻¹ higher in eBE to match the experiment, allowing for assignments of the experimental data to various resonances along the neutral reaction surface. The calculated energies of the onset of each $v_{\rm HF}$ vibrational adiabatic potential are plotted as vertical bars, highlighting the quanta of the mode involved in the observed resonances. The calculated reactant asymptote (black arrow) and location of the transition-state barrier (grey arrow) are marked.

the transition-state asymptote correspond to transitions in the product well on the neutral PES. The theoretically predicted anion geometry has a notably large HF bond length (1.592 Å), akin to that of the transition state (1.515 Å) and much larger than that of the product complex (0.939 Å). Hence, photodetachment to product complex-like states should be accompanied by vibrational excitation in the HF stretching mode, resulting in larger Franck-Condon factors to vibrationally excited HF products. However, the HF frequency is much larger than the observed peak spacings in the product complex region, indicating that there is also considerable excitation of the low-frequency vibrations of the NH₂·HF complex. These could arise from the low-frequency NH_2 ·HF stretch, analogous to previous cryo-SEVI work on the F + CH₃OH reaction that found a series of quasibound vibrational progressions of the CH₃O-HF product complex with translational motion along the dissociation coordinate²³. In addition, the pyramidal structure of NH₃ in FNH₃⁻ is flattened due to the loss of an H to F, which could lead to excitation of the out-of-plane mode of the FH-NH₂ complex. The anion geometry also has good geometric overlap with the neutral transition state, leading to structure in the spectrum at higher eBE, as discussed in more detail later.

Assignments and analysis

Accurate quantum dynamical studies are required to more quantitively interpret the experimental spectra; these are performed on the neutral PES schematically presented in Fig. 1. The simulated photoelectron spectra are displayed in Fig. 2. To better compare with the experimental data, the raw theoretical spectrum (red trace) is also convoluted with a 50-cm⁻¹ full-width at half-maximum (FWHM) Gaussian function (purple trace), and both are shifted 104 cm⁻¹ higher in eBE (details given in the 'Assignments' section of the Supplementary Information). The overall agreement with the main peaks of the experimental spectrum is excellent. To assign the experimental features, two-dimensional (2D) cuts of several representative wavefunctions, superimposed on the neutral

PES, are displayed in Fig. 3. The anion wavefunction is also shown in the same figure, along with the geometry of the submerged barrier.

For the states corresponding to peaks a-j, the representative wavefunctions are exclusively distributed in the product channel. In the region of highest amplitude near the product complex equilibrium geometry, these wavefunctions show two nodes along the HF bond length, $r_{\rm HF}$, indicating that these peaks correspond to HF ($v_{\rm HF}$ = 2) complexed to NH₂. Only one such node is seen at large NH₂-HF distances, suggesting that these quasibound resonances dissociate to HF $(v_{\rm HF} = 1) + \rm NH_2$ products. Moreover, there is nodal structure along the NH₂-HF coordinate, indicating that excitation of the NH₂-HF translational mode leads to dissociation to products. Finally, as discussed in the 'Assignments' section of the Supplementary Information, 2D cuts along angular coordinates reveal additional nodal structure, indicating that these transitions involve excitations of at least one other soft mode of the product complex. The observed spacing of ~300 cm⁻¹ is assigned to excitations in the HF-NH₂ translational mode ($v_8 = 251 \text{ cm}^{-1}$) and pseudo-rotation of HF coupled with NH₂ out-of-plane wagging $(v_6 = 829 \text{ cm}^{-1}).$

The wavefunctions corresponding to peaks k-o are dominated by three nodes in the H–F coordinate, implying the involvement of $v_{\rm HF}$ = 3. Notably, these features reside only slightly above the transition-state barrier and are considerably broader in the experimental spectrum (~200-800 cm⁻¹FWHM) than the features that precede them. The large difference in geometry between the anion and the reactant complex suggests that these features correspond to vertical transitions that project the anionic wavefunction onto a nuclear configuration that rapidly rearranges. This is mirrored in the simulated spectra, where the widths of features k-m progressively increase in both the high-resolution and convolved spectra. The smaller intervals (289 cm⁻¹) between peaks k-m reflect excitations of the out-of-plane wagging mode of NH₂ $(v_7 = 318 \text{ cm}^{-1})$, whereas the larger spacing for peaks m-o (655-cm⁻¹) average spacing) arises from excitation of the pseudo-rotational mode of HF coupled with out-of-plane wagging of $NH_2(v_6)$. In addition, the NH_2 -HF mode (v_8) might also be involved. The wavefunctions for features at higher energies (p-t) display an even more complex nodal structure, all involving higher HF vibrational excitation. In particular, the wavefunction corresponding to feature p displays four nodes along $r_{\rm HF}$, indicating resonances with $v_{\rm HF} = 4$.

These results can be understood with reference to the vibrational adiabatic potentials (VAPs) in Fig. 1 leading to the NH₂ + HF asymptote. The VAPs for HF ($v_{HF} = 1-4$) are generated from generalized normal-mode vibrational frequencies along the MEP and correlate to the HF ($v_{HF} = 1-4$) + NH₂ asymptotic energies. Each VAP can support a number of bound or metastable states corresponding to low-frequency vibrations of the complex; the latter are mostly Feshbach resonances. Each of the vibrationally excited HF levels has sufficient energy to dissociate, but the strong vibrational adiabaticity—because of the high frequency of HF, which can only weakly couple to the dissociation coordinate—causes them to decay slowly. We thus attribute peaks a–j and k–o to transitions to Feshbach resonances supported by the VAPs for $v_{HF} = 2$ and 3, respectively. These Feshbach resonances are also consistent with experimental evidence of vibrational excitation in the HF product for the F + NH₃ reaction²⁸⁻³⁰.

As the energy increases further, the representative wavefunctions for features q-t spread to both the product complex and reactant complex regions, as shown in Fig. 3, although the experiment-theory agreement is not as good as at lower energies. Such discrepancies may be due to the reduced-dimensional model, remaining errors in the PES, and the neglect of spin-orbit coupling. The resonance wavefunctions are clearly dominated by four nodes in HF, despite this delocalization. They are tentatively assigned as arising from HF ($v_{HF} = 4$), due in part to the VAP here becoming less well defined due to its proximity to the transition state. Unlike the wavefunctions for the preceding features, these include a large component that is delocalized in the reactant complex,



Fig. 3 | **2D plots of F** + **NH**₃ **wavefunctions accessed via photodetachment.** Plots of the anion wavefunction and resonance wavefunctions on the neutral F + NH₃ reactive PES. The labels for the resonances correspond to those in Fig. 2. The wavefunctions are superimposed on the neutral PES, and the transition state is marked with a red star. Nodes in these wavefunctions near the reactant

or product highlight the quanta of v_{HF} involved in the resonance. Notably, the localization of these wavefunctions transitions from the product complex well through the transition state and into the reactant complex well (see, for example, $o \rightarrow p \rightarrow q$) highlights the observations of resonances in each of these regions.

as displayed in Fig. 3. Such wavefunctions are thus qualitatively different from the product-channel Feshbach resonances at lower energies discussed above and represent the first spectroscopic observation of such resonances in a polyatomic system, a key observation of this work. Such evidence complements direct observations of reactive resonances in other polyatomic bimolecular reactions²⁵. The spacing of these features and their widths are considerably tighter than those involving HF (v_{HF} = 3), with an average spacing of 275 cm⁻¹ (compared to 775 cm⁻¹ in v_{HF} = 3). As discussed in the 'Assignments' section of the Supplementary Information, these features are tentatively attributed to excitations in the pseudo-rotational mode of NH₃ in the F–NH₃ complex.

We emphasize that some of these resonances (r, s, t) lie above the reactant asymptote and are thus reactive resonances that can potentially impact the bimolecular reaction dynamics, as shown in recent work on the $F + H_2O$ reaction²⁶. Among these, peak r is of particular interest, as it lies only 4 cm⁻¹ above the calculated energy of the free reactants. A lifetime of 100 fs for these resonances can be estimated from the average FWHM of features r-t (~200 cm⁻¹), although the possible overlap of nearby resonances sets this as a lower limit. Previous full-dimensional quantum dynamics calculations on the same neutral PES showed that the reaction probabilities (and integral cross-sections) of F + NH₃ from the ground state of NH₃ oscillate strongly at low collision energies, in sharp contrast to quasi-classical trajectories³⁹, providing tentative evidence for the existence of reactive resonances near the reaction threshold. However, direct evidence for their involvement in the bimolecular reaction dynamics will have to await further quantum scattering calculations.

Unique features of the dynamics

The dynamics here differ considerably from those seen in the cryo-SEVI study of the $F + CH_3OH$ reaction via photodetachment of CH_3OHF^- ,

despite remarkably similar neutral reactive surfaces²³. In particular, the simple low-frequency progressions observed in that system within each vibrationally adiabatic manifold, which were assigned to excitation in the CH₃O–HF translation dissociation coordinate, are replaced by less regular spectral patterns. These differences arise in part because there is a larger geometry change upon photodetachment for FNH₃⁻. For example, in addition to excitation in the dissociation coordinate, there is ample excitation in the out-of-plane modes in the product complex, resulting from the NH₃ pyramidal-to-planar transition discussed above. In this respect, this system bears some similarities with the F + H₂O system^{36,40}, for which high-level calculations have determined the involvement of the HO–HF bending mode in the dynamics of this system. Furthermore, the observation of structure localized in the entrance channel here is reminiscent of F + CH₄, for which resonances in this region have been previously characterized⁴¹.

Here, unlike in these previous studies, the activity of the out-of-plane bending mode in the resonances localized in the product complex represents the observation of the product moiety (NH₂) impacting the dynamics of the system, rather than acting as a spectator to the hydrogen abstraction. Moreover, our observation of resonances spanning both sides of the transition state is notable, as such observations were previously restricted to much simpler triatomic systems, such as the F + H₂ and I + HI reactions^{20,21}. Thus, the report and assignment of such resonances in tandem with characterization of the entrance and exit channels mark a substantial advance from previous work, highlighting the rich dynamics accessible through transition-state spectroscopy.

Conclusions

We have investigated the photodetachment of FNH_3^- using slow photoelectron velocity-map imaging spectroscopy and reduced-dimensional

guantum dynamical simulations on a global ab initio PES. The cryo-SEVI spectra display a wealth of structure originating from various metastable quantum states. These resonances are reproduced by theory, which allows for their unambiguous assignment in most cases. In particular, the lower-eBE features arise from Feshbach resonances in the product complex with increasing HF vibrational excitation, coupled with excitation of soft modes such as the HF-NH₂ translational mode, pseudo-rotation of the HF, and/or the torsional modes of NH₂. Although higher-eBE features also show substantial HF vibrational excitation, some exhibit significant population in the reactant complex well, with possible excitation in the pseudo-rotation mode of the NH₃ moiety. These transition-state resonances straddling both sides of the saddle point can impact the bimolecular $F + NH_3 \rightarrow HF + NH_2$ reaction dynamics. Together, this work highlights the ability of cryo-SEVI transition-state-spectroscopy experiments to probe complex dynamical features near the transition state and represents a rare glimpse into quantum resonances supported by the PES shaped by the submerged saddle point of a bimolecular reaction.

Online content

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Methods

The cryo-SEVI method has been described in detail previously^{19,42-44}. In this work, FNH_3^- anions were generated by expanding trace NF_3 and ammonia vapour in helium gas through a pulsed Even–Lavie solenoid valve fitted with a circular filament ionizer⁴⁵. Dissociative electron attachment to NF_3 produced F^- atomic ions, which then clustered with ammonia. The ions passed through a skimmer, a radiofrequency hexapole ion guide and radiofrequency quadrupole mass filter as they were directed into a linear radiofrequency octupole ion trap held at 5 K and filled with a buffer gas mixture of 20:80 H₂:He. Collisions with the cold buffer gas resulted in effective vibrational, rotational and electronic cooling of the ions, leading to internal temperatures near 10 K (refs. ^{10,19,46}).

After -40 ms, the ions were extracted from the trap into an orthogonal Wiley–McLaren time-of-flight mass spectrometer⁴⁷ and focused into the interaction region of a three-plate velocity-map imaging (VMI) electrostatic lens assembly^{34,48}. In the VMI spectrometer, ions were photodetached by the frequency-doubled output of a dye laser pumped by the second harmonic of a Nd:YAG laser operating at 20 Hz.

The resulting photoelectrons were projected onto a 2D detector composed of two chevron-stacked microchannel plates coupled to a phosphor screen, which was photographed by a charge-coupled device (CCD) camera after each laser shot⁴⁹. Each image was analysed for individual electron events, for which the centroids were calculated and binned in a grid sufficiently fine to ensure that the resolution was not limited by pixel size⁵⁰. The resulting images were used to reconstruct the original electron velocity distribution using the inverse-Abel method of Hansen and Law⁵¹, returning the electron kinetic energy (eKE) distribution. The radial positions of features in the reconstructed image were related to the electron kinetic energy (eKE) by acquiring VMI images for detachment from atomic Cl⁻ at several photon energies⁵².

The VMI spectrometer has an approximately constant resolving power, $\Delta e KE/e KE$ (ref. ⁴⁸), yielding the best eKE resolution for slow electrons. As such, a SEVI spectrum was acquired by first taking an overview spectrum at a relatively high photon energy before tuning the detachment laser to energies slightly above the features of interest. This procedure resulted in a series of high-resolution spectra over narrow energy windows. These were concatenated and scaled to match the intensities in the overview spectrum, which is less sensitive to variation of the photodetachment cross-section with photon energy. The spectra were plotted as a function of eBE, given by eBE = hv - eKE.

Theoretical methods

The photodetachment dynamics were characterized using diatomtriatom (AB + CDE) Jacobi coordinates, corresponding to the product well complex HF + NH₂, as shown in Supplementary Fig. 1. The 9D Hamiltonian with a given total angular momentum J_{tot} can be written as ($\hbar = 1$ hereafter)

$$\begin{split} \hat{H} &= -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_{r_1}} \frac{\partial^2}{\partial r_1^2} - \frac{1}{2\mu_{r_2}} \frac{\partial^2}{\partial r_2^2} - \frac{1}{2\mu_{r_3}} \frac{\partial^2}{\partial r_3^2} + \frac{(f_{\text{tot}} - f)^2}{2\mu_R R^2} + \frac{f_1^2}{2\mu_L r_1^2} + \frac{f_2^2}{2\mu_2 r_2^2} + \frac{f_3^2}{2\mu_3 r_3^2} \\ &+ \hat{V} \big(R, r_1, r_2, r_3, \theta_1, \theta_2, \theta_3, \varphi_1, \varphi_2 \big), \end{split}$$
(1)

where R, r_1, r_2 and r_3 are the distance between the centres of mass of AB and CDE, the interatomic distance of AB, the distance from C to the centre of mass of DE, and the interatomic distance of DE, respectively, with μ_R , μ_1 , μ_2 and μ_3 as the corresponding reduced masses. \hat{j}_1 is the rotational angular momentum operator of AB, \hat{l}_2 is the orbital angular momentum operator along r_2 , and \hat{j}_3 is the rotational angular momentum operator of DE. $\hat{j}_{23} = \hat{j}_3 + \hat{l}_2$ and $\hat{j} = \hat{j}_1 + \hat{j}_{23}$. The lengths of the two non-reactive NH bonds are fixed at 1.93 a_0 , leading to r_2 and r_3 being fixed at 1.97 a_0 and 1.93 a_0 , respectively. Hence, the two terms $-\frac{1}{2\mu_2}\frac{\partial^2}{\partial r_2^2}$

and $-\frac{1}{2\mu_{r_3}}\frac{\partial^2}{\partial r_3^2}$ vanish, resulting in a reduced 7D model. This approximatously^{19,42-44}.

tion is based on the fact that the two NH bond lengths are nearly unchanged along the minimum energy path. Therefore, the two NH bonds are expected to be spectators and should have negligible effect on the dynamics.

Within the Condon approximation, the initial wavepacket on the neutral PES is taken as the ground rovibrational state of the anion obtained by diagonalizing the 7D Hamiltonian on the anion PES. It is then propagated using the Chebyshev propagator⁵³, and the energy spectrum is extracted from a cosine Fourier transform of the Chebyshev autocorrelation function. The bound and resonance wavefunctions are obtained analogously from the Chebyshev wavepacket. The details of the quantum dynamics calculations, as well as a discussion of the internal coordinates and the vibrational modes of the neutral complex, are given in the 'Computational Methods' section of the Supplementary Information.

As discussed in a previous publication²⁷, the neutral PES is constructed by fitting -41,000 ab initio energy points calculated at the unrestricted coupled cluster level with singles, doubles and perturbative triples⁵⁴ with Dunning's augmented correlation-consistent polarized valence triple zeta basis set⁵⁵ and core electrons frozen (FC-UCCSD(T)-F12/aug-cc-pVTZ) using the fundamental-invariant neural network (FI-NN) method⁵⁶. However, we note that the spin–orbit correction is not included, which could lead to an uncertainty on the order of 100 cm⁻¹ in the peak positions, particularly those near the reaction threshold. This is because spin–orbit coupling in F typically decreases with the approach of another molecule. An anion PES is newly constructed for this work by fitting a total of -11,000 energy points at the same level of theory used to construct the neutral PES.

Data availability

Data are provided with this paper and can be downloaded at https://doi. org/10.5281/zenodo.7332846. Source data are provided with this paper.

Code availability

The associated code, such as the subroutine to generate anion and neutral PESs and the quantum scattering code, is available on GitHub at https://github.com/apmtcc/AB-CDE and described in the README file.

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Author contributions

M.C.B., M.D. and J.A.L. performed analysis of the data collected by M.L.W. and J.B.K., with support from D.M.N. All calculations were performed and analysed by H.S. with assistance from H.G. The paper was written by M.C.B. and H.S. with assistance from H.G. and D.M.N.

Competing interests

The authors declare no competing interests.

Additional information

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