Transition State Spectroscopy of the F + NH₃ Reaction

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Abstract:

Transition state spectroscopy experiments based on negative ion photodetachment directly probe the vibrational structure and metastable resonances that are characteristic of the neutral reactive potential energy surface (PES). Here, we study the five-atom reaction F + NH₃ → HF + NH₂ using slow photoelectron velocity-map imaging spectroscopy of cryogenically cooled FNH₃⁻ anions. Reduced-dimensional quantum dynamical simulations performed on a global potential energy surface show excellent agreement with the experimental results, allowing for the assignment of spectral structure and demonstrating that key dynamics of this bimolecular reaction are well described by this theoretical framework. Our combined experimental-theoretical study reveals features associated with a manifold of vibrational Feshbach resonances in the product well of the F + NH₃ PES. At higher energies, the spectra reveal structure attributed to resonances localized across the transition state and into the reactant complex well, which may impact the bimolecular reaction dynamics.
Introduction:

Fundamental to the modern conception of chemistry is the transition state (TS), the transient species located near a saddle point in the reaction potential energy surface (PES) where chemical bond formation and cleavage occur. As the TS controls not only the reaction rate, but also the dynamics of the chemical transformation, it is essential to probe this key region of the PES in order to gain insight into the fundamental interactions that govern chemical reactivity. Such motivation led to the development of crossed molecular beam experiments of increasing complexity to determine properties of the TS, including the barrier height and geometry. While these experiments have greatly improved our understanding of chemical reactions, they provide only an indirect probe of the TS region of the PES. Complementary experiments utilizing anion photoelectron spectroscopy, however, have yielded vibrationally-resolved structure characteristic of the TS region of the PES for both unimolecular and bimolecular reactions.

In these experiments, a stable anion whose geometry is similar to the TS 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 wave-packet created by photodetachment, resulting in a photoelectron spectrum that reveals vibrational structure of complexes near the transition state region. By improving the resolution of the photoelectron spectrometer, one can observe sharp structure associated with resonances that are quasi-bound along the reaction coordinate. Resonances spanning the transition state region have been identified for the atom-diatom reactions \( \text{I} + \text{HI} \) and \( \text{F} + \text{H}_2 \), while entrance and exit channel resonances have been characterized for the \( \text{F} + \text{CH}_4 \) and \( \text{F} + \text{CH}_3\text{OH} \) reactions, respectively. Dynamical resonances – quasibound states along the reaction pathway lying high in energy than the reactant asymptote – have been shown to strongly influence reactivity and dynamics.

Here, we present a joint photoelectron imaging and quantum dynamics study of the \( \text{F} + \text{NH}_3 \rightarrow \text{HF} + \text{NH}_2 \) hydrogen-abstraction reaction, based on high-resolution photodetachment of the \( \text{FNH}_3^- \) anion. The \( \text{F} + \text{NH}_3 \) reaction is highly exoergic (10422 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 dimensionality. Previous experimental work on the title reaction has studied the vibrational distribution of the HF product via infrared chemiluminescence. More recent crossed beam experiments by Yang and co-workers have shown that the HF products (or DF in the \( \text{F} + \text{ND}_3 \) 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 and the calculated differential cross sections agreed reasonably well with the values determined by Yang.

The neutral PES features a reactant complex (RC), a submerged barrier serving as the TS, and a product complex (PC) well, as shown in Fig. 1. The hydrogen-bonded \(\text{FNH}_3^-\) anion geometry is similar to the TS. Together, this system presents as an ideal case for TS 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\(^{-1}\)\(^{32-33}\). The experiment is complemented by reduced-dimensional quantum dynamical calculations on the neutral PES.

This combination of experiment and theory show that photodetachment from \(\text{FNH}_3^-\) directly accesses both sides of the TS barrier, revealing a large number of resonances, several of which may be relevant to the neutral reaction (dynamical resonances). In the product channel, we observe sharp structure corresponding to a manifold of vibrational Feshbach resonances supported by the post-TS well. In addition, complex and irregular features associated with the transition state and reactant well are observed, with some able to be assigned to resonances by comparison to theory. The results presented here thus represent the most complete mapping to date of the transition state region for a polyatomic reaction.

**Results:**

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, which are in good agreement with previous theoretical studies on the \(\text{F} + \text{NH}_3\) reaction\(^{30,34-35}\). The PES here resembles that of the \(\text{F} + \text{CH}_3\text{OH}\) system\(^{33}\) in that the TS, RC, and PC all lie below the energy of the free reactants. The RC is bound by 4326 cm\(^{-1}\) with respect to the reactants and lies only 285 cm\(^{-1}\) below the TS barrier. The PC is a hydrogen-bonded complex between HF and the \(\text{NH}_2\) radical bound by 2521 cm\(^{-1}\) with respect to the product asymptote.

Experimental cryo-SEVI spectra of \(\text{FNH}_3^-\) are shown in Fig. 2 and show the photoelectron intensity as a function of electron binding energy (eBE). The overview spectrum in blue shows a smoothly rising background from 26050 to 29050 cm\(^{-1}\), after which there is a series of steps out to 32000 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 26050 cm\(^{-1}\), there is an extended progression of peaks a-m that progressively become more tightly spaced as eBE increases. Spacings between peaks a-b and k-l, for example, are 293 and 187 cm\(^{-1}\), respectively. At higher eBE, a series of broad features n-p spaced by ~700 cm\(^{-1}\) is seen, followed by a third progression, peaks q-t, spaced by ~300 cm\(^{-1}\). A full listing
of peak positions and spacings can be found in the SI (Table S1). The locations of the reactant asymptote (black arrow) and the TS (gray arrow) are also indicated in the figure, at 33022 and 28981 cm$^{-1}$, respectively.

Intensities in the experimental and theoretical spectra are largely governed by Franck-Condon considerations. All peaks below the TS 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 TS (1.515 Å) and much larger than that of the PC (0.939 Å). Hence, photodetachment to PC-like states should be accompanied by vibrational excitation in the HF stretching mode, resulting in larger FC factors to vibrationally-excited HF products. However, the HF frequency is much larger than the observed peak spacings in the PC region, indicating that there is also considerable excitation of the low-frequency vibrations of the NH$_2$-HF complex. These could arise from the low-frequency NH$_2$-HF stretch, analogous to previous cryo-SEVI work on the F + CH$_3$OH reaction that found a series of quasibound vibrational progressions of the CH$_3$O-HF product complex with translational motion along the dissociation coordinate.$^{23}$ In addition, the pyramidal structure of NH$_3$ in FNH$_3^-$ 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-NH$_2$ complex. The anion geometry also has good geometric overlap with the neutral TS, leading to structure in the spectrum at higher eBE as discussed in more detail below.

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 shifted 104 cm$^{-1}$ higher in eBE (details given in SI). 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 PC equilibrium geometry, these wavefunctions show two nodes along $r_{HF}$, indicating that these peaks correspond to HF ($v_{HF} = 2$) complexed to NH$_2$, while only one such node is seen at large NH$_2$-HF distances. This feature suggests that these quasibound resonances dissociate to HF ($v_{HF} = 1$) + NH$_2$ products. Moreover, there is nodal structure along the NH$_2$-HF coordinate, indicating excitation of the NH$_2$-HF translational mode that leads to dissociation to products. Finally, as discussed in the SI, 2D cuts along angular coordinates reveal additional nodal structures, indicating that these transitions involve excitations of at least one other soft mode of the PC.
complex. The observed spacing of ~300 cm\(^{-1}\) is assigned to excitations in the HF-NH\(_2\) translational mode \((v_8 = 251 \text{ cm}^{-1})\) and the pseudo-rotation of HF coupled with the NH\(_2\) out-of-plane wagging \((v_6 = 829 \text{ cm}^{-1})\).

The wavefunctions corresponding to the peaks \(k-o\) are dominated by three nodes in the H-F coordinate, implying the involvement of \(v_{HF} = 3\). Notably, these features reside only slightly above the TS barrier and are considerably broader than the features that precede them. The large difference in geometry between the anion and the RC 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 the peaks \(k-m\) reflect excitations of the out-of-plane wagging mode of NH\(_2\) \((v_7 = 318 \text{ cm}^{-1})\), while the large spacing among peaks \(m-o\) 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 even more complex nodal structure, but all involving a higher HF vibrational excitation. In particular, the wavefunction corresponding to feature \(p\) displays four nodes along \(r_{HF}\), indicating resonances with \(v_{HF} = 4\).

These results can be understood with reference to the vibrational adiabatic potentials (VAPs) in Fig. 1, leading to the NH\(_2\) + 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\((v_{HF} = 1-4) + \text{NH}_2\) 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, owing to the high frequency of HF which can only weakly couple to the dissociation coordinate, causing 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 + NH\(_3\) reaction\(^{26-28}\).

As the energy increases further, the representative wavefunctions for features \(q-t\) spread to both the PC and RC channels, as shown in Fig. 3. While this delocalization obscures some of the structure, the wavefunctions are dominated by four nodes in HF and thus are tentatively assigned as arising from HF \((v_{HF} = 4)\), owing in part to the VAP here becoming less well defined due to its proximity to the TS. Unlike the wavefunctions for the preceding features, these include a large component that is delocalized in the RC channel, as displayed in Fig. 3. Such wavefunctions are thus qualitatively different from the product channel Feshbach resonances at lower energies discussed above and represent a key observation of this work. 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 SI, these features are tentatively attributed to excitations in the pseudo-rotational mode of NH$_3$ in the F-NH$_3$ 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$_2$O reaction.$^{36}$ Among these, peak $r$ is of particular interest, as it lies only 4 cm$^{-1}$ above the calculated energy of the free reactants.

The dynamics here differ considerably from those seen in the cryo-SEVI study of the F + CH$_3$OH reaction despite remarkably similar neutral reactive surfaces.$^{23}$ In particular, the simple low frequency progressions observed in that system within each vibrationally adiabatic manifold, which were assigned to the excitation in the CH$_3$O-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 FNH$_3^-$.$^\text{FNH}_3^-$ For example, in addition to excitation in the dissociation coordinate, there is ample excitation in the out-of-plane modes in the PC complex, resulting from the NH$_3$ pyramidal-to-planar transition discussed above. In this respect, this system bears some similarities with the F + H$_2$O system,$^{37-38}$ for which high-level calculations have determined the involvement of the HO-HF bending mode in the dynamics of this system. Further, the observation of structure localized in the entrance channel here is reminiscent of F + CH$_4$, for which resonances in this region have been previously characterized.$^{39}$ Finally, our observation of resonances spanning both sides of the TS is notable, as such observations were previously restricted to much simpler triatomic systems, such as the F + H$_2$ 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 significant advance from previous work, highlighting the rich dynamics accessible through TS spectroscopy.

Conclusions:

We have investigated the photodetachment of FNH$_3^-$ using slow photoelectron velocity-map imaging spectroscopy and reduced-dimensional quantum 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 PC complex with increasing HF vibrational excitation, coupled with excitation of soft modes such as the HF-NH$_2$ translational mode, the pseudo-rotation of HF, and/or the torsional modes of NH$_2$. While higher-eBE features also exhibit significant HF vibrational excitation, some exhibit significant population in the RC well with possible excitation in the pseudo rotation mode of the NH$_3$ moiety. These TS resonances straddling both sides of the
saddle point can impact the bimolecular $\text{F} + \text{NH}_3 \rightarrow \text{HF} + \text{NH}_2$ reaction dynamics. Together, this work highlights the ability of cryo-SEVI transition-state-spectroscopy experiments to probe complex dynamical features near the TS and represents a rare glimpse into quantum resonances supported by the PES shaped by the submerged saddle point of a bimolecular reaction.
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References:


Experimental Methods:

The cryo-SEVI method has been described in detail previously. In this work, FNH₃⁻ anions are generated by expanding trace NF₃ and ammonia vapor in helium gas through a pulsed Even-Lavie solenoid valve fitted with a circular filament ionizer. Dissociative electron attachment to NF₃ produces F⁻ atomic ions, which then cluster with ammonia. The ions pass through a skimmer, radiofrequency (RF) hexapole ion guide, and RF quadrupole mass filter as they are directed into a linear RF 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 result in effective vibrational, rotational, and electronic cooling of the ions, leading to internal temperatures near 10 K. After ~40 ms, the ions are extracted from the trap into an orthogonal Wiley-McLaren time-of-flight mass spectrometer and focused into the interaction region of a three-plate velocity-map imaging (VMI) electrostatic lens assembly. In the VMI spectrometer, ions are 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 are projected onto a 2D detector comprising two chevron-stacked microchannel plates coupled to a phosphor screen, which is photographed by a CCD camera after each laser shot. Each image is analyzed for individual electron events for which the centroids are calculated and binned in a grid sufficiently fine to ensure that resolution is not limited by pixel size. The resulting images are used to reconstruct the original electron velocity distribution using the inverse-Abel method of Hansen and Law, returning the electron kinetic energy (eKE) distribution. The radial positions of features in the reconstructed image are related to electron kinetic energy (eKE) by acquiring VMI images for detachment from atomic Cl⁻ at several photon energies. The VMI spectrometer has an approximately constant resolving power, ∆eKE/eKE, yielding the best eKE resolution for slow electrons. As such, a SEVI spectrum is acquired by first taking an overview spectrum at a relatively high photon energy before tuning the detachment laser to energies slightly above features of interest. This procedure results in a series of high-resolution spectra over narrow energy windows that are concatenated and scaled to match intensities in the overview spectrum, which is less sensitive to variation of the photodetachment cross section with photon energy. Spectra are plotted as a function of electron binding energy (eBE), given by eBE = hν - eKE.
Theoretical Methods:

The photodetachment dynamics are characterized using diatom-triatom (AB+CDE) Jacobi coordinates, corresponding to the product well complex HF + NH2, as shown in the upper panel of Fig. S1. The nine-dimensional Hamiltonian with a given total angular momentum $J_{\text{tot}}$ can be written as ($\hbar = 1$ hereafter):

$$
\hat{H} = -\frac{1}{2\mu_R} \frac{\partial^2}{\partial R^2} - \frac{1}{2\mu_{r_1}} \frac{\partial^2}{\partial r_{1}^2} - \frac{1}{2\mu_{r_2}} \frac{\partial^2}{\partial r_{2}^2} - \frac{1}{2\mu_{r_3}} \frac{\partial^2}{\partial r_{3}^2} + \frac{(J_{\text{tot}} - J)^2}{2\mu_R R^2} + \frac{\hat{J}_1^2}{2\mu_1 r_1^2} + \frac{\hat{J}_2^2}{2\mu_2 r_2^2} + \frac{\hat{J}_3^2}{2\mu_3 r_3^2} + \hat{V}(R, r_1, r_2, r_3, \theta_1, \theta_2, \theta_3, \varphi_1, \varphi_2),
$$

where $R$, $r_1$, $r_2$, and $r_3$ are the distance between centers of mass of AB and CDE, the interatomic distance of AB, the distance from C to the center of mass of DE, and the interatomic distance of DE, respectively, with $\mu_R$, $\mu_1$, $\mu_2$, and $\mu_3$ as the corresponding reduced masses. $\hat{J}_1$ is the rotational angular momentum operator of AB, $\hat{I}_2$ is the orbital angular momentum operator along $r_2$, and $\hat{J}_3$ is the rotational angular momentum operator of DE. $\hat{J}_{23} = \hat{J}_3 + \hat{I}_2$, and $\hat{J} = \hat{J}_1 + \hat{J}_{23}$. As the two non-reactive NH bonds are nearly spectators along the reaction path, their lengths are fixed at 1.93 $a_0$, leading to $r_2$ and $r_3$ fixed at 1.97 and 1.93 $a_0$, respectively. Hence, the two terms $-\frac{1}{2\mu_{r_2}} \frac{\partial^2}{\partial r_{2}^2}$ and $-\frac{1}{2\mu_{r_3}} \frac{\partial^2}{\partial r_{3}^2}$ vanish, resulting in a reduced seven-dimensional model.

Within the Condon approximation, the initial wave packet on the neutral PES is taken as the ground rovibrational state of the anion obtained by diagonalizing the seven-dimensional Hamiltonian on the anion PES. It is then propagated using the Chebyshev propagator, 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 wave packet. The details of the quantum dynamics calculations, along with a discussion of the internal coordinates and the vibrational modes of the neutral complex, are given in the Supplementary Information (SI).

As discussed in a previous publication, the neutral PES is constructed by fitting $\sim$41000 ab initio energy points calculated at the unrestricted coupled cluster level with singles, doubles, and perturbative triples with Dunning’s augmented correlation-consistent polarized valence triple zeta basis set and core electrons frozen (FC-UCCSD(T)-F12a/aug-cc-pVTZ) using the fundamental-invariant neural network (FI-NN) method. An anion PES is newly constructed for this work by fitting a total of $\sim$11000 energy points at the same level of theory used to construct the neutral PES.
**Figure 1:** Energy diagram for photodetachment of FNH$_3^-$ onto the TS region of the neutral F + NH$_3$ reaction. The upper solid curve is the neutral reaction minimum energy path that connects the reactants and products to their ground vibrational states. Sketched above the PC well are vibrational adiabatic potentials for the excited HF stretching mode ($v_{HF} = 1-4$). The lower solid curve depicts the anion PES. Geometries are shown for the reactant complex (RC), product complex (PC), transition state (TS), and anionic stationary points using grey (H), dark blue (N), and light blue (F). Energies for stationary points on the PES are shown in cm$^{-1}$, relative to the reactant asymptote, and are zero-point energy corrected.
Figure 2: Experimental (top) and theoretical (bottom) photodetachment spectra of FNH$_3^-$ showing transitions to the F + NH$_3$ reactive PES. Experimental cryo-SEVI spectra of FNH$_3^-$ detachment are plotted with an overview spectrum (blue) atop high-resolution traces (black). Raw simulated spectra (red) are plotted as well as a theoretical spectrum convoluted with a 50 cm$^{-1}$ full-width-at-half-maximum (purple) for comparison with experiment, see text for details. Theoretical spectra are shifted 104 cm$^{-1}$ higher in eBE to match with experiment. Calculated energies of the onset of each $v_{HF}$ vibrational adiabatic potential are plotted as vertical bars. The calculated reactant asymptote (black arrow) and location of the TS barrier (grey arrow) are marked.
Figure 3: Plots of the anion wavefunction and resonance wavefunctions on the neutral F + NH₃ reactive PES. The labels of resonances can be found in Fig. 2. The wavefunctions are superimposed on the neutral PES and the TS is marked with a red star.