Feshbach resonances in the exit channel of the F + CH$_3$OH $\rightarrow$ HF + CH$_3$O reaction observed using transition-state spectroscopy

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The transition state governs how chemical bonds form and cleave during a chemical reaction and its direct characterization is a long-standing challenge in physical chemistry. Transition state spectroscopy experiments based on negative-ion photodetachment provide a direct probe of the vibrational structure and metastable resonances that are characteristic of the reactive surface. Dynamical resonances are extremely sensitive to the topography of the reactive surface and provide an exceptional point of comparison with theory. Here we study the seven-atom F + CH$_3$OH $\rightarrow$ HF + CH$_3$O reaction using slow photoelectron velocity-map imaging spectroscopy of cryo-cooled CH$_3$OHF anions. These measurements reveal spectral features associated with a manifold of vibrational Feshbach resonances and bound states supported by the post-transition state potential well. Quantum dynamical calculations yield excellent agreement with the experimental results, allow the assignment of spectral structure and demonstrate that the key dynamics of complex bimolecular reactions can be captured with a relatively simple theoretical framework.

Since the development of crossed molecular beam experiments in the 1960s$^{1-3}$, studies of reaction dynamics via reactive scattering experiments and accompanying theoretical advances have led to major insights into the fundamental interactions that govern chemical reactivity$^{4}$. A key concept in chemistry is that during the course of a reactive collision, chemical bond formation and cleavage occur in the transition-state (TS) region of the potential energy surface (PES)$^{4-6}$. Hence, there is much interest in characterizing the reaction TSs experimentally and theoretically$^{7}$.

Increasingly sophisticated scattering experiments that involve state-selective reactant preparation and state-resolved product detection provide new ways to observe properties of the TS—such as the reaction barrier height and geometry—that dictate the mode specificity and the most favourable reactant orientation to promote a reactive collision$^{8-10}$. However, such experiments do not probe the TS region of the PES directly. Complementary experiments based on negative-ion photodetachment yield a vibrationally resolved structure characteristic of the TS$^{11}$, and have been applied with considerable success to benchmark bimolecular$^{12}$ and unimolecular$^{13,14}$ reactions.

Here we report a joint high-resolution photoelectron imaging and theoretical quantum dynamics study of the F + CH$_3$OH $\rightarrow$ HF + CH$_3$O hydrogen-abstraction reaction, based on the photodetachment of the stable CH$_3$OHF$^-$ anion. The spectra are obtained via slow photoelectron velocity-map imaging of cryogenically cooled anions (cryo-SEVI)$^{15-17}$, which yields photoelectron spectra of complex species with a kinetic-energy resolution as high as 1 cm$^{-1}$ (refs 18,19). The resolution of the cryo-SEVI spectra of CH$_3$OHF$^-$ and CH$_3$ODF$^-$ is substantially improved over previous photodetachment experiments$^{20,21}$; it reveals low-frequency progressions assigned to the exit-channel-bound states and Feshbach resonances and provides new insights into the TS region of this polyatomic reaction. The experimental spectrum is assigned with the help of reduced-dimensional quantum dynamical calculations on a global PES determined by fitting a large number of high-level ab initio points in full dimensionality.

Dynamical Feshbach resonances of the type probed here are transient metastable states supported by the reactive PES. These resonances have sufficient vibrational energy to dissociate, but decay slowly because of the inefficient energy flow from the excited modes to the reaction coordinate. Quantum-scattering calculations indicate that the energies and widths of these resonances are exquisitely sensitive to the topography of the reactive PES$^{7,12,22}$. Dynamical resonances can strongly mediate reactivity and can manifest as peaks in the integral or differential cross-section as a function of collision energy$^{23-26}$. These effects have been sought out and, in some cases, clearly observed in molecular beam reactive scattering experiments$^{9,26-30}$.

Anion photoelectron TS spectroscopy offers an alternative and often more direct means to detect dynamical resonances$^{11,12}$. In such an experiment, a bound anion similar in geometry to the neutral TS is photodetached. The vibrational wavefunction of the anion is vertically projected onto the neutral PES, and the kinetic energy of the nascent photoelectron reports on the wave-packet evolution under the influence of the neutral Hamiltonian. The resulting photoelectron spectrum may show a broad structure if the photodetachment accesses a repulsive Franck–Condon region of the neutral PES. However, direct detachment to discrete bound or quasi-bound neutral states will manifest as sharp, well-defined features in the photoelectron spectrum$^{31}$. These features provide valuable information on the neutral PES in strongly interacting regions, such as reactive intermediate wells and TSs. Resonances identified

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These features were also seen in the lower-resolution photoelectron spectra of CH₃OHF systems, and the somewhat irregular structure in the entrance channel of the F + CH₄ reaction is attributed to the fact that the hydroxyl-anion is similar in geometry to the hydroxyl-anion of CH₃OH. The product asymptote for the F + CH₃OH reaction lies at 26,820 cm⁻¹ on the ZPE-corrected PIP-NN surface. These asymp-
totes are marked in Fig. 2a with filled circle and diamond symbols, respectively, and have also been shifted to higher eBE by 0.28 eV relative to the free reactants, but lies only slightly lower in energy than the TS. The PC is a hydrogen-bonded complex between HF and the methoxy radical bound by 0.25 eV relative to the free products. The stationary point geometries are consistent across different levels of theory and agree well with the available experimental results (Supplementary Figs 2 and 3). The corresponding harmonic frequencies of these stationary points are compared in Supplementary Table 3.

The product asymptote for the F + CH₃OH reaction lies at 26,820 cm⁻¹, while the reactant asymptote lies at 38,220 cm⁻¹ on the ZPE-corrected PIP-NN surface. These asymptotes are marked in Fig. 2a with filled circle and diamond symbols, respectively, and have also been shifted to higher eBE by 250 cm⁻¹ for comparison with the experiment. The energies of these asymptotes indicate that much of the observed structure can lie only in the PC well. The peaks in the a manifold fall below the product asymptote and are thus bound with respect to free HF + CH₃O products. Ray et al. accordingly found that the a manifold was associated with the production of non-dissociating neutral complexes, whereas the higher-lying peaks were correlated largely with prior studies assigned this stepped structure to an HF stretching progression of the CH₃O–HF product complex (PC). The considerably higher spectral resolution afforded by cryo-SEVI reveals an additional layer of vibrational structure not seen previously. We now resolve a much finer structure spaced by ~200 cm⁻¹ superimposed on the broad steps with typical peak widths of 75–125 cm⁻¹ (full-width at half-maximum (FWHM)). Peak positions and spacings are listed in Supplementary Tables 1 and 2. A key trend is that the spacing of resonances within each step increases with increasing HF stretching excitation. For example, the a₁–a₂, b₁–b₂, c₁–c₂ and d₁–d₂ gaps are measured experimentally as 192, 248, 255 and 315 cm⁻¹, respectively.

Accurate quantum dynamical studies on a reactive PES are necessary to interpret the experimental spectra. We model the F + CH₃OH reaction using a full 15-dimensional (15D) PES constructed with ~121,000 points calculated at the explicitly correlated unrestricted coupled cluster level with singles, doubles and perturbative triples with the augmented correlation-consistent polarized valence double zeta basis set and core electrons frozen (FC-UCP-CCSD(T)-F12a/AVDZ). The CCSD(T)-F12a/AVDZ method is expected to yield results of a quality comparable to that of the conventional CCSD(T)/AVQZ level. The PES is fit using the permutation invariant polynomial–neural network (PIP-NN) method.

Figure 1 shows a schematic of the F + CH₃OH → HF + CH₃O reaction path. The upper bold line is the zero-point energy (ZPE) corrected minimum energy path that connects the reactants and products in their ground vibrational states. The reported stationary point energies derived from the PIP-NN PES are in good agreement with prior work (Supplementary Fig. 1 gives a detailed comparison). The TS, RC and PC all lie below the energy of the free reactants. The RC is a covalent three-electron two-centre semi-hydrogen-bonded complex, similar to that between F and H₂O (ref. 50), which is bound by 0.28 eV relative to the free reactants, but lies only slightly lower in energy than the TS. The PC is a hydrogen-bonded complex between HF and the methoxy radical bound by 0.23 eV relative to the free products. The stationary point geometries are consistent across different levels of theory and agree well with the available experimental results (Supplementary Figs 2 and 3). The corresponding harmonic frequencies of these stationary points are compared in Supplementary Table 3.

To simulate the photoelectron spectrum, wave-packet-based quantum dynamics were investigated with a reduced 6D model by freezing the methyl moiety. The CH₃OHF detachment spectrum simulated with a ~200 fs wave-packet propagation is given in Fig. 2a and compares favourably with the experimental results. The electron-binding energy (eBE) of the bottom of the PC well is calculated to lie at 24,810 cm⁻¹, close to the experimental onset of the structure at 25,058(25) cm⁻¹ (peak a₁) and to previous measurements. The simulated spectrum has therefore been shifted to a higher eBE by 250 cm⁻¹, so that the onset of the structure at a low eBE matches that observed experimentally. Experimental and theoretical peak positions are compared for the CH₃OHF detachment in Supplementary Table 1; the theory reproduces the trend of increasing resonance peak spacings mentioned above.

The product asymptote for the F + CH₃OH → HF + CH₃O reaction lies at 26,820 cm⁻¹, while the reactant asymptote lies at 38,220 cm⁻¹ on the ZPE-corrected PIP-NN surface. These asymptotes are marked in Fig. 2a with filled circle and diamond symbols, respectively, and have also been shifted to higher eBE by 250 cm⁻¹ for comparison with the experiment. The energies of these asymptotes indicate that much of the observed structure can lie only in the PC well. The peaks in the a manifold fall below the product asymptote and are thus bound with respect to free HF + CH₃O products. Ray et al. accordingly found that the a manifold was associated with the production of non-dissociating neutral complexes, whereas the higher-lying peaks were correlated largely with...
A well-known phenomenon in heavy triatomic9,54 systems that VAPs can support increasingly stabilized dissociated fragments. The agreement of experiment and theory unambiguously identifies the newly resolved low-frequency progressions as derived from discrete bound states and Feshbach resonances on the product side of the TS.

Discussion

The presence of the low-frequency progressions and the trend of their increasing spacing within steps a–d can be explained intuitively with reference to the vibrational adiabatic potentials (VAPs) shown in Fig. 1. These VAPs correspond to the HF vibrational levels plotted along the reaction coordinate and correlate to vibrationally excited free HF(ν)+CH3O products. The HF vibrational adiabaticity is expected to be strong because of its high vibrational frequency, which couples weakly with the dissociation coordinate.

Each spectral step a–e represents a detachment to an HF(ν = 0–4) VAP. The finely spaced progressions within each step are resonances supported in the wells of the VAPs and reflect increasing quanta of excitation in the low-frequency CH3O–HF stretching mode. The VAP wells deepen as the HF excitation is increased, resulting in more widely spaced states within each well. The deepening of the PC VAPs can be explained by dynamical vibrational bonding. It is a well-known phenomenon in heavy–light–heavy51–53 and other triatomic9,54 systems that VAPs can support increasingly stabilized wells as the vibrationally excited light atom is more delocalized between the two outer fragments.

To better understand the vibrational character of the observed spectral features, the simulated wavefunctions of all the peaks were extracted. Relevant examples are shown in Fig. 3. From the localized character of these wavefunctions, it is clear that they are stable bound states or metastable resonances supported by the PC well. The ~100 cm⁻¹ FWHM peak widths of the observed spectral features allow us to place a lower bound of 50 fs on the lifetimes of the Feshbach resonance states that lie above the HF+CH3O dissociation limit, although the highest-resolution theoretical results suggest that these states are much longer lived. The final dissociation of these resonance states is expected to proceed via vibrational pre-dissociation facilitated by energy flow from the HF stretching coordinate to translational motion along the dissociation coordinate. The large frequency mismatch means that such an energy flow is expected to be slow and result in long lifetimes for these resonances. Similar long-lived Feshbach resonance states were observed in F+H2O (ref. 34) and this picture holds even in the presence of many degrees of freedom for the F+CH3OH system.

Vibrational assignments can be confirmed by examining the resonance wavefunction nodal structure. Peaks in the a1–b1–c1–d1–e1 progression show an increasing integer number of nodes along the HF stretching coordinate (vertical axis in Fig. 3). Therefore, the broad shelves in the spectrum indeed correspond to a progression of the HF stretching vibrational states of the PC. The isotope effect observed in the CH3ODF cryo-SEVI spectrum (Fig. 2c) further validates this assignment. The increasing number of nodes in the a1–a2–a3 progression along the CH3O–HF coordinate (horizontal axis in Fig. 3) confirms that the finely spaced progressions are resonances with increasing quanta of excitation in the stretching mode between the product fragments. The experimental and theoretical Franck–Condon factors increase along with HF stretching excitation, as the PC vibrational states with higher quanta of excitation in the HF stretch have more wavefunction density at a larger HF displacement. Compare, for instance, the vibrational wavefunctions for peaks a1 and d1: the latter has a substantially better Franck–Condon overlap with the anion wavefunction, which leads to an increased intensity in the photoelectron spectrum.

To illustrate the evolution of these resonances further, a simulated photoelectron spectrum is shown in Supplementary Fig. 4 for three different propagation times. The low-resolution spectrum obtained in the first 40 fs of propagation suggests that the short-time dynamics on the neutral PES are along the HF vibrational coordinate, as the spectrum clearly resolves peaks related to the HF vibrational frequency. By 200 fs, the fine-structure peaks emerge because of the recursion of the wave packet along the CH3O–HF dissociation coordinate. By 800 fs, the fine-structure peaks split further into sharper peaks related to H3C–O–HF bending excitation, although these are not resolved experimentally.
The vibrational assignments made here are also sensible in the context of the Franck–Condon principle. Comparison of the anion and PC geometries (Supplementary Figs 2 and 3) indicates that photodetachment to the PC well should be accompanied by vibrational excitation in the HF stretching and the CH$_3$O–HF stretching and bending modes. Indeed, the HF bond length in the anion (1.32 Å) is considerably longer than that of free HF (0.92 Å). The geometry of the methyl moiety is largely unchanged by detachment, so freezing its internal degrees of freedom during photodetachment to the PC well. On the other hand, the long-lived feature observed by Ray et al.21 tentatively assigned a spectral feature that lies below the reactant asymptote to an RC well. All sharp features that fall below the reactant asymptote (marked with a filled diamond in Fig. 2a) have wavefunctions localized on the product side of the TS (Fig. 3). Ray et al.21 tentatively assigned a spectral feature that lies below the reactant asymptote to an RC resonance, as it appeared to have a longer lifetime than neighbouring peaks. In the cryo-SEVI spectra this feature is resolved as peaks $d_4, d_5$ and $d_6$, which are well-reproduced by theory as resonances in the PC well. On the other hand, the long-lived feature observed by Ray et al.21 represents a sufficiently small fraction of the total dissociative signal that there may not be a reasonable expectation of resolving it in our present experiment. Furthermore, such a state may not be captured accurately by our simulations as the reduced-dimensional model, which is ideal for the HF + CH$_3$O product channel, might not be sufficient for the F + CH$_3$OH reactant channel.

The resonances we report here are non-reactive as they are not resolved experimentally, as the spectrum becomes congested at higher photon energies. The poor agreement between the experimental and theoretical results for the position and intensity of peak $e_1$ could also be caused by experimental congestion. The laser-noise background becomes a limiting factor at high photon energies. It is also possible that detachment to excited F + CH$_3$OH surfaces, analogous to those predicted in F + H$_2$O (ref. 55), contributes at higher eBE, and leads to the increased baseline of the experimental spectra compared with theory. Additionally, the Wigner threshold law$^{56}$ can distort relative peak intensities close to the threshold, which may further hamper our ability to resolve peaks $e_1$ and $x$ at the relatively low electron kinetic energies accessible here.

In conclusion, we investigated the photodetachment of CH$_3$OH$^{-}$ and its singly deuterated isotope using slow photoelectron velocity-map imaging spectroscopy and quantum dynamical calculations on a new $ab$ initio based PES. The cryo-SEVI spectrum is dominated by Feshbach resonances supported in the product well of the F + CH$_3$OH → HF + CH$_3$O reaction. These resonances are fully reproduced by theory, which allows their unambiguous assignment to the vibrational HF and CH$_3$O–HF stretching states of the PC. This work demonstrates the utility of cryo-SEVI TS spectroscopy experiments for probing detailed multidimensional dynamical features near the TS as well as theoretical advances in modelling the dynamics of increasingly complex bimolecular reactions. It also illustrates that, despite much increased complexity, the key dynamical features of this seven-atom reaction remain largely local and can still be captured by a relatively simple physical picture.

**Methods**
The cryo-SEVI method has been described in detail elsewhere$^{15-17}$. CH$_3$OH$^{-}$ and CH$_3$OD$^{-}$ anions are prepared by expanding trace NF$_3$ and either methanol or methanol-d$_4$ vapour in helium gas through an Even–Lavie pulsed valve$^{78}$ fitted with a circular filament ionizer. Dissociative electron attachment to NF$_3$ produces F$^{-}$ atomic ions, which then cluster with methanol-d$_4$. The anions are cooled by collisions with an 80:20 He:H$_2$ buffer gas mixture in a radiofrequency ion trap held at 5 K. After thermalization to their ground vibrational and electronic states, the ions are extracted from the trap and mass-selected by time-of-flight. The ions are photodetached at various photon energies with tunable light from the frequency-doubled output of a dye laser pumped by either the second or third harmonic of a neodymium:yttrium–aluminium–garnet laser. The electron kinetic energy distribution of the resulting photoelectrons is measured with a velocity-map imaging spectrometer$^{79}$ using relatively low extraction voltages. This magnifies the electron image on the detector and achieves a 1 cm$^{-1}$ instrumental energy resolution for slow electrons$^{14}$.
The quantum dynamical calculations are performed with a reduced-dimensional model, in which the methyl moiety is fixed at the geometry associated with the PC well. This is a reasonable approximation as the methyl group behaves largely as a spectator in the F + CH3OH → HF + CH2O channel. The remaining six coordinates are represented by the diatom–diatom Jacobi coordinates, in the same fashion as in our recent work on F(H2O) photodetachment. The photodetachment process is simulated with the motion approximation, in which the anion wavefunction is placed on the neutral PES in a vertical transition. The subsequent dynamics are followed by propagating the initial wave packet in the Chevboysev order domain and the photoelectron spectrum is computed by a discrete cosine transform of the Chevboysev autocorrelation function. Additional theoretical details, including descriptions of the benchmark calculations and the construction of the PESs, are given in the Supplementary Information.

Data availability. The experimental and theoretical data that support the findings of this study are available from the corresponding authors on reasonable request.

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References

8. Neumark, D. M. Slow electron velocity-map imaging of negative ions: molecular reaction dynamics of the benchmark calculations and the construction of the PESs, are given in the Supplementary Information.
9. Yang, T. Slow electron velocity-map imaging of negative ions: molecular reaction dynamics of the benchmark calculations and the construction of the PESs, are given in the Supplementary Information.

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Author contributions
The experimental research was conceived and supervised by D.M.N. The experiments were carried out by M.L.W., J.A.D. and M.C.B. Experimental data analysis and interpretation was performed by M.L.W. Theoretical calculations were conceived by J.L., J.M. and H.G. and performed by J.L., L.G. and J.M. The paper was written by M.L.W., with the theoretical sections contributed by J.L., J.M. and H.G. All of the authors contributed to discussions about the results and manuscript.

Additional information
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Competing financial interests
The authors declare no competing financial interests.