Feshbach resonances in the F + H₂O → HF + OH reaction

Xiaoren Zhang¹,²,⁵, Lulu Li¹,³,⁵, Jun Chen⁴, Shu Liu¹* & Dong H. Zhang¹*
Feshbach resonances of a chemical reaction are transiently trapped quantum states along the reaction coordinate in the transition-state region. They not only have a profound influence on both the rate and product distribution, but also provide sensitive probes to the potential energy surface (PES) of the reaction. Over the past decades, great efforts have been devoted to detecting resonances in chemical reactions and to studying their structures and dynamics. Thanks to the close interaction between theory and experiment, an accurate physical picture of dynamical resonances in the $F + H_2 (HD) \rightarrow HF + H (D)$ reaction has been well established. Detailed quantum dynamics studies on increasingly more accurate PESs uncovered that the interaction between $H(D)$ and HF in the post-barrier region softens the HF bond and creates a peculiar well on the HF ($v' = 3$)-$H(D)$ vibrationally adiabatic potential (VAP), which supports resonance states producing mainly $HF(v' = 2)$ product.

Similar to the $F + H_2$ system, the $F + H_2O \rightarrow HF + OH$ reaction is highly exothermic ($\Delta H^0 = -17.6$ kcal/mol) and has a low and "early" barrier on the ground electronic state. There is a relatively deep valley in the entrance channel and a hydrogen bond (HB) well ($\sim 6$ kcal/mol) in the exit channel. The reaction is of great importance in atmospheric and astrochemistry, and has attracted a large number of experimental and theoretical studies. The reaction dynamics was first investigated experimentally by Setser and colleagues, who found the HF product is vibrationally excited and rotationally cold. After that, Neshbitt and colleagues observed a highly nascent vibrational population inversion for the HF ($v = 1$) product. Theoretically, as the number of the electrons is relatively small, this system represents an attractive prototype for the electronic structure and reaction dynamics calculations. Guo and colleagues developed a full-dimensional global PES for the $F + H_2O$ system using a multireference configuration interaction (MRCI) method and applied a standard quasi-classical trajectory (QCT) study. In agreement with experiment, the product state distribution is dominated by HF vibrationally excited states. The subsequent QCT and quantum mechanical (QM) calculations found that the pre-reaction vdw well enhance reactivity at low energies due to stereodynamics and the vibrational excitation of $H_2O$ is much more efficient at promoting the reactivity than the translational energy. On the other hand, Guo and colleagues also found the coupled-cluster method with higher excitations than singles and doubles gives a better description than the MRCI method for the barrier height. They scaled the original MRCI PES with an external correlation scaling method and provided both kinetic and dynamical data for the reaction on the scaled-MRCI PES.

In 2014, Otto et al. carried out a joint experimental and theoretical study on the FH$_2$O$^-$ photodetachment dynamics. Both the measured and calculated photoelectron spectra of the anion were found to possess both broad and sharp features. The former were attributed to short-lived reactive Feshbach resonances and the latter to long-lived nonreactive Feshbach resonances, both supported by product well. At about the same time, Zhao and Guo reported a state-to-state quantum dynamics study on the reaction by using transition-state wave packet method for collision energy up to 2 kcal/mol on the scaled-MRCI PES. Strong oscillatory structures were observed for the $J = 0$ quantum reaction probabilities as a function of collision energy. However, they attributed these oscillations to tunneling resonances supported by the pre-reaction vdw well. Therefore, the following questions clearly emerge: Can the reactive Feshbach resonances observed in the photodetachment study be observed in the $F + H_2O$ reaction? And how do these resonances affect the reaction?

Here we report an accurate state-to-state quantum scattering study of the title reaction on an accurately constructed neural network (NN) PES by using the time-dependent wave packet (TDWP) method. The total reaction probabilities for collision energy below 0.2 eV exhibit many pronounced oscillatory structures especially. Analysis of scattering wave functions and VAPs reveal that these oscillating structures originate from the Feshbach resonance states trapped in the HF($v' = 2$)-OH VAP well, producing mainly the HF($v' = 1$) product. This suggests the Feshbach resonances observed in the photodetachment study can be accessed by the neutral reaction.

**Results**

**Total reaction probabilities and the product-state distributions.** The converged total reaction probabilities for the total angular momentum $J = 0$ in Fig. 1a exhibit many sharp and narrow oscillatory structures especially for collision energy below 0.2 eV. Overall, the reaction probabilities on the present PES resemble those obtained on the scaled-MRCI permutation invariant polynomial NN PES with spin-orbit (SO) corrections rather well, except the oscillatory structures and a shift of energy by $\sim 0.015$ eV apparently due to different barrier heights for these two PESs, but larger than those obtained on the original MRCI PES (Supplementary Fig. 3). Figure 1b shows the product HF vibrational state-resolved reaction probabilities as a function of collision energy. The HF($v = 1$) state has the largest population in the entire energy region considered here, indicating an inverted HF vibrational state distribution. Before the opening of the HF ($v = 2$) channel, the HF($v = 0$) and HF($v = 1$) probabilities have rich oscillating structures. The HF($v = 2$) channel opens at the collision energy of 0.191 eV and also has some small oscillating structures in probability. Meanwhile the HF($v = 0$) and HF($v = 1$) probabilities become rather smooth at high collision energies.

To compare with the experimental and previous QCT results, we calculated the rovibrational state-resolved integral cross-sections based on the reaction probabilities for total angular momentum $J = 0$ by using the J-shifting approximation, i.e., $P_{J=0}^{0} (E) = \int_{E=0}^{E} P_{J} (E - \Delta E) dE$, where $\Delta E = B^* (J + 1)$. The rotational constant is approximately calculated by $B^* = (2\mu r)^{-1} (r^*)^2$ with $r^*$ being the length of the scattering coordinate at the transition-state. Figure 2a shows the normalized vibrational populations...
and Fig. 2b–d show the normalized rotational populations for each \( v' = 1 \)–3, of product HF at the collision energy of 0.234 eV (5.4 kcal/mol). The present QM vibrational state distributions agree quite well with the experiment, while the previous QCT results overestimate the population for \( v' = 2 \). The calculated rotational state distributions, which changes from a broad one with a maximum at \( j = 6 \) for \( v' = 0 \) to a narrow one with a maximum at \( j = 0 \) for \( v' = 2 \), are also consistent with the experiment.

**Analysis of scattering wave functions and VAP.** To investigate the dynamical original of the oscillatory structures, we extract the scattering wave function at the collision energy of 0.126 eV for \( J = 0 \). Inspection of the two-dimensional contour of the wave function in the product region shown in Fig. 3a reveals there exist two nodes along the H–F coordinate (correlating to the HF product) inside the HB well, but only one node for the outgoing wave function with a sudden decrease in amplitude. This sudden change of nodal structure and amplitude in wave function is the characteristic feature of a Feshbach resonance, indicating the resonance is trapped in HF\((v' = 2)\) vibrational adiabatic well and produces mainly HF\((v' = 1)\) product. To further confirm the mechanism of the resonance, we calculated the VAP for HF\((v' = 0–3)\) in the product region. As shown in Fig. 3b, the calculated VAP for all these vibrational states of HF have HB wells, which may support resonance states for the system. The HF\((v' = 2)\)-OH VAP has an asymptotic value of 0.193 eV measured from the ground state of the reactants and has a well with a well depth of 0.26 eV at a separation distance between HF and OH equal to 5.0 \( a_0 \), i.e., the bottom of well is lower than the ground state of the reactants by 0.067 eV. The calculations show that the zero-point energy of the HF–OH in the well is also lower than the ground state of reactant. This means the F + H\(_2\)O reaction can access to the Feshbach resonances supported by HF\((v' = 2)\)-OH VAP well even with zero collision energy and the oscillating structures on the HF\((v' = 0)\) and HF\((v' = 1)\) probabilities in Fig. 1b originate from these Feshbach resonance states. In addition, the small oscillating structures on the HF\((v' = 2)\) probabilities at the collision energy above 0.191 eV apparently originate from the bending excited HF\((v' = 2)\)-OH VAP supported resonance states.

As can be seen from Fig. 3b, the minimum positions for the HF\((v' = 0)\)-OH VAP wells for \( v' = 0–2 \) all locate \( R \sim 5.0 \ a_0 \), whereas the well depth increases with \( v' \), from 0.19 eV for \( v' = 0 \), to 0.22 eV for \( v' = 1 \), and 0.26 eV for \( v' = 2 \). Therefore, these VAP wells are HB wells for the HF and OH products mainly through dipole–dipole interaction. With increase of the HF vibrational state, HF dipole moment increases, resulting in a deeper well depth. The Feshbach resonances for the F + H\(_2\)O reaction are trapped in HF\((v' = 2)\)-OH HB well.

It is well known that in the F + H\(_2\) reaction, the interaction between H and HF in the transition-state region softens the HF bond, manifesting a larger anharmonicity for HF vibration. This anharmonicity considerably lowers the energy level for the HF\((v' = 3)\) vibrationally excited state, resulting in a peculiar well on the HF–OH potential energy surface. As such, the resonance is trapped in HF\((v' = 2)\)-OH VAP well right after the barrier position. This well is substantially deeper and locates much closer to barrier than the \( H-HF(v' = 0–2) \) VAP wells, which originate from the vdw interaction between H and HF. Therefore, the resonance supporting HF\((v' = 2)\)-OH well in the F + H\(_2\)O reaction is very
different in nature from the $H\text{-HF}(\nu' = 3)$ VAP well, which support resonance states in the $F\text{+H}_2\text{O}(\nu = 0)$ reaction\(^6,34,35\).

Relation between FH$_2$O - photoelectron spectra and neutral reaction probabilities. The photodetachment of the FH$_2$O$^-$ anion is also investigated quantum mechanically in full-dimensions on the present accurate NN PES. The anion PES is a newly constructed one by this group based on 11,936 CCSD(T)-F12a/O and F: cc-pCVTZ-F12, H: cc-pVTZ-F12)\(^36\) ab initio energies with fundamental invariants NN (Fi-NN) method\(^37\), yielding a root-mean-square-error of 0.043 meV. Accurate NN PESs developed in this work are available from the corresponding authors upon request.

Methods

Potential energy surface. The PES used in the calculation is a full-dimensional global one constructed using NN method based on ~26,429 AE-UCCSD(T)-F12a/CVTZ-F12 ab initio energies. The correction terms considering the inaccuracy of the larger system as well as SO couplings were further implemented. With an overall fitting error of ~1.78 meV measured in terms of root-mean-square-error (Supplementary Table 1), the PES is expected to have a quantitative level of accuracy. The static barrier height for the PES is 1.922 kcal/mol (and raised to 2.262 kcal/mol with SO energy included), lower than the value of 3.838 kcal/mol for the MRCl PES\(^38\) and very close to the value of 1.919 suggested by Dawes and colleagues\(^39\).

Quantum dynamics calculations. Our state-to-state quantum calculation ($J = 0$) is carried out by using the product coordinates basis\(^30,38\) scheme-based TDWP method with the coordinate systems shown in Supplementary Fig. 1. Test calculations reveal that the potential-averaged five-dimensional method with the non-reactive OH frozen at the ground vibrational state is of quantitative accuracy for the total reaction probabilities when compared with the full six-dimensional results as shown in Supplementary Fig. 2. The details of the PES and dynamics calculation are provided in Supplementary Information.

Data availability

The data that support the findings of this study are available from the corresponding author upon request.

Code availability

The accurate NN PESs developed in this work are available from the corresponding authors upon request.

Received: 25 October 2019; Accepted: 18 December 2019;
Published online: 13 January 2020

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Acknowledgements
This work was supported by the National Natural Science Foundation of China (grant numbers 21773235, 21590804, and 21688102), the Chinese Academy of Sciences (XDB17010200), and DICP (Grant: DICP ZZZS201611).

Author contributions
D.H.Z. and S.L. conceived and supervised the research. X.Z. and J.C. developed the PES. S.L. performed the quantum dynamical calculation. L.L. simulated the photoelectron spectra. S.L. and D.H.Z. wrote the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41467-019-14097-y.

Correspondence and requests for materials should be addressed to S.L. or D.H.Z.

Peer review information Nature Communications thanks William Hase, and the other, anonymous, reviewer(s) for their contribution to the peer review of this work.

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