

Fig. 4. Exchange interaction. (**A** and **B**) Power spectral density measured in transmission for two qubits in resonance at $d \sim 3\lambda/4$ at the indicated Rabi drive rates $\Omega_{\rm R}$. Solid lines are as in Fig. 3.

from the center peak corresponding to the Rabi frequency induced by the drive.

When both qubits are tuned to 6.4 GHz corresponding to $d \sim \lambda$, we observe a Mollow triplet–like spectrum with a narrow resonance superimposed at its center frequency (Fig. 3). The narrow resonance becomes more discernible as the drive power is decreased (Fig. 3B). Here and below, the Rayleigh scattered contribution was removed from the data for clarity. These two distinct features, the Mollow triplet and narrow resonance, are due to the formation of super- and subradiant states, respectively.

The effective two-level system $\{|gg\rangle, |B\rangle\}$ is strongly dressed by the drive field, resulting in a Mollow triplet. The width ~52 MHz of the main peak, obtained by fitting to numerical calculations (black lines in Fig. 3), is consistent with the value of $\Gamma_{\rm B}$ extracted above. Ideally, the dark state $|D\rangle$ is neither excited by the drive nor does it decay into $|gg\rangle$ due to selection rules. In practice, however, it is weakly populated due to qubit dephasing, nonradiative decay from the state $|ee\rangle$, and unequal single-qubit relaxation rates (23). As a result, the dark state $|D\rangle$ appears as a narrow resonance superimposed on the bright-state Mollow triplet. Its linewidth, when compared to numerical results, is approximately $\Gamma_D/2\pi \sim 0.4 \pm$ 0.2 MHz. We obtain adequate quantitative agreement between the measured spectra and theory (see lines in Fig. 3) and find the ratio between super- and subradiant lifetimes to be as high as $\Gamma_B/\Gamma_D\!\geq\!100.$

When both qubits are tuned to 4.8 GHz, corresponding to $d = 3\lambda/4$, the resonance fluorescence spectra at high powers ($\Omega_R/2\pi \ge 15$ MHz, where Ω_R is the Rabi drive rate) also display the

expected Mollow triplet features (Fig. 4A). At drive powers much lower than the relaxation rate $\Omega_{\rm R}/2\pi \le 5$ MHz, the fluorescence spectrum displays a double-peak structure split by ~15 MHz (see Fig. 4B). This observation is a clear signature of the effective exchange interaction *J* between the two qubits mediated by virtual photons. The observed splitting is slightly larger than the expected value $2J/2\pi = \gamma_1/2\pi \approx 13$ MHz, which is consistent with theory predicting the splitting to be larger than 2*J* in transmission and smaller in reflection (*23*).

Our results present compelling evidence of strong interaction effects between two superconducting qubits separated by as much as a full wavelength $\lambda \sim 18.6$ mm in an open 1D environment. The observation of these effects presents opportunities to explore decoherence-free subspaces and entanglement over long distances in open environments and could lead to exciting applications in quantum communication technology.

References and Notes

- R. G. DeVoe, R. G. Brewer, *Phys. Rev. Lett.* 76, 2049–2052 (1996).
- J. Eschner, C. Raab, F. Schmidt-Kaler, R. Blatt, Nature 413, 495–498 (2001).
- 3. H. J. Kimble, Nature 453, 1023-1030 (2008).
- D. E. Chang, A. S. Sorensen, E. A. Demler, M. D. Lukin, *Nat. Phys.* 3, 807–812 (2007).
- J. Hwang *et al.*, *Nature* **460**, 76–80 (2009).
 P. M. Leung, B. C. Sanders, *Phys. Rev. Lett.* **109**, 253603 (2012).
- H. Zheng, D. J. Gauthier, H. U. Baranger, *Phys. Rev. A* 85, 043832 (2012).
- 8. D. E. Chang, A. S. Sørensen, P. R. Hemmer, M. D. Lukin, Phys. Rev. Lett. 97, 053002 (2006).
- 9. D. E. Chang, A. S. Sørensen, P. R. Hemmer, M. D. Lukin, *Phys. Rev. B* 76, 035420 (2007).
- 10. A. V. Akimov et al., Nature 450, 402-406 (2007).
- D. Martín-Cano, L. Martín-Moreno, F. J. García-Vidal, E. Moreno, *Nano Lett.* **10**, 3129–3134 (2010).
- 12. A. Gonzalez-Tudela et al., Phys. Rev. Lett. 106, 020501 (2011).

- 13. K. P. Nayak et al., Opt. Express 15, 5431-5438 (2007).
- 14. E. Vetsch et al., Phys. Rev. Lett. 104, 203603 (2010).
- D. E. Chang, L. Jiang, A. V. Gorshkov, H. J. Kimble, *New J. Phys.* 14, 063003 (2012).
- 16. A. Goban et al., Phys. Rev. Lett. 109, 033603 (2012).
- 17. J.-T. Shen, S. Fan, *Phys. Rev. Lett.* **95**, 213001 (2005).
- 18. O. Astafiev et al., Science 327, 840-843 (2010).
- A. A. Abdumalikov Jr. et al., Phys. Rev. Lett. 104, 193601 (2010).
- A. A. Abdumalikov Jr., O. V. Astafiev, Y. A. Pashkin, Y. Nakamura, J. S. Tsai, *Phys. Rev. Lett.* **107**, 043604 (2011).
- 21. I.-C. Hoi et al., Phys. Rev. Lett. 111, 053601 (2013).
- 22. I.-C. Hoi et al., Phys. Rev. Lett. 107, 073601 (2011).
- 23. K. Lalumière et al., Phys. Rev. A 88, 043806 (2013).
- 24. J. Koch et al., Phys. Rev. A 76, 042319 (2007).
- 25. Materials and methods are available as supplementary materials on *Science* Online.
- 26. I.-C. Hoi et al., Phys. Rev. Lett. 108, 263601 (2012).
- 27. Whereas correlated decay mediated by the exchange of real photons is absent when one of the qubits is at an antinode of the field, the exchange of virtual photons is still possible, as it is caused by virtual photons at all frequencies except the qubit transition frequency.
- 28. J. Majer et al., Nature 449, 443-447 (2007).
- 29. S. Filipp et al., Phys. Rev. A 83, 063827 (2011).
- 30. B. R. Mollow, Phys. Rev. 188, 1969-1975 (1969).

Acknowledgments: We acknowledge financial support by Canadian Institute for Advanced Research, Natural Sciences and Engineering Research Council of Canada, Alberta Innovates Technology Futures, and ETH Zurich, and we thank Calcul Québec and Compute Canada for computational resources. Furthermore, we thank L. Steffen for sample fabrication, C. Lang and Y. Salathé for realizing the firmware for measuring power spectral densities using field-programmable gate array-based electronics, M. Boissonneault for help with numerical simulations, and V. Sandoghdar for initial discussions motivating this work.

Supplementary Materials

www.sciencemag.org/content/342/6165/1494/suppl/DC1 Materials and Methods References

6 August 2013; accepted 16 October 2013 Published online 14 November 2013; 10.1126/science.1244324

Relaxation Mechanism of the Hydrated Electron

Madeline H. Elkins,¹ Holly L. Williams,¹ Alexander T. Shreve,² Daniel M. Neumark^{1,3}*

The relaxation dynamics of the photoexcited hydrated electron have been subject to conflicting interpretations. Here, we report time-resolved photoelectron spectra of hydrated electrons in a liquid microjet with the aim of clarifying ambiguities from previous experiments. A sequence of three ultrashort laser pulses (~100 femtosecond duration) successively created hydrated electrons by charge-transfer-to-solvent excitation of dissolved anions, electronically excited these electrons via the $s \rightarrow p$ transition, and then ejected them into vacuum. Two distinct transient signals were observed. One was assigned to the initially excited *p*-state with a lifetime of ~75 femtoseconds, and the other, with a lifetime of ~400 femtoseconds, was attributed to *s*-state electrons just after internal conversion in a nonequilibrated solvent environment. These assignments support the nonadiabatic relaxation model.

The hydrated electron e_{aq} is a species of fundamental interest in the chemistry of water. It has been implicated in phenomena ranging from aerosol nucleation to radiation

damage in DNA (1). As the simplest quantum solute, with only a single electronic degree of freedom, it has been the focus of many experimental and theoretical studies over the years (2-4). Nonetheless, many of its key attributes remain controversial. For example, the standard picture (5) of an electron residing in a cavity of radius ~2.4 Å has been repeatedly questioned (6). Another unresolved issue concerns the relaxation mechanism of e_{aq}^{-} subsequent to electronic excitation. This mechanism, which represents a subtle interplay between solute-solvent interactions and electronically non-adiabatic dynamics, is of critical importance in hydrated electron chemistry and radiation biology, given that excited states of e_{aq}^{-} are considerably more reactive than its ground state (7). The relaxation dynamics of e_{aq}^{-} upon excitation have been studied in bulk water by using transient absorp-

tion dynamics of e_{aq}^{-} upon excitation have been studied in bulk water by using transient absorption (TA) (8–10) and resonance Raman spectroscopy (11). Complementary studies have also been carried out in size-selected water cluster anions by using time-resolved photoelectron spectroscopy (TRPES) (12). In this work, we connect these very disparate experimental techniques using TRPES of hydrated electrons in liquid water microjets in order to resolve key questions regarding the relaxation mechanism of e_{aq}^{-} .

The hydrated electron has a characteristic electronic spectrum peaking at 720 nm that is attributed to excitation from its ground s-state to a manifold of excited *p*-states within the solvent cavity (13). The proposed relaxation mechanism after $s \rightarrow p$ excitation is shown in Fig. 1. It comprises solvent relaxation in the *p*-state, $p \rightarrow s$ internal conversion (IC), and solvent relaxation in the s-state. These three processes are characterized by time constants τ_p , τ_{IC} , and τ_s . In TA experiments by Barbara and coworkers (8), the $s \rightarrow p$ transition was excited with a femtosecond pump pulse, and the resulting dynamics were followed by the absorption of a broadband femtosecond probe pulse. Three time scales of 50 to 80 fs, 200 to 400 fs, and ~1.1 ps were identified and have been largely reproduced by other laboratories (9, 10). However, the assignment of these lifetimes to particular physical phenomena has been a matter of some debate. Two basic models (Fig. 1) are proposed: the "adiabatic" model and the "nonadiabatic" model (2). The adiabatic model assigns the rapid time scale (50 to 80 fs) to τ_p , the intermediate time scale to τ_{IC} , and the slow time scale to τ_s . Alternatively, the nonadiabatic model assigns the fastest observable time scale to τ_{IC} and the slower two to τ_s . From TA alone, one cannot easily distinguish between the two models, and differing theoretical treatments have favored both models (14, 15).

TRPES of anionic water clusters $(H_2O)_n^-$, provides a different perspective on hydrated electron relaxation dynamics (*16–19*). In these experiments, the excess electron is electronically excited with a femtosecond pump pulse and then photodetached with a femtosecond probe

*Corresponding author. E-mail: dneumark@berkeley.edu

pulse. The resulting time-dependent photoelectron spectra show a transient feature clearly associated with the cluster excited state and directly yield τ_{IC} at each cluster size. These experiments show that τ_{IC} decreases from 190 to 60 fs with increasing cluster size up to 200 water molecules. Extrapolating this trend to the bulk $(n \rightarrow \infty)$ limit implies $\tau_{IC} \sim 60$ fs for e_{aq} . This trend suggests that the fastest time constant seen in the TA experiments corresponds to τ_{IC} , which is consistent with the nonadiabatic relaxation model (Fig. 1).

The validity of this conclusion depends on whether water cluster anions are in fact gas-phase analogs of e_{aq}^{-} , which is a subject of considerable discussion (2, 20, 21). Recent experiments on liquid water microjets (22) have tested this correspondence directly by using photoelectron spectroscopy to measure the vertical detachment energy (VDE) of ground state hydrated electrons in liquid jets (23-26). The value obtained, 3.3 to 3.5 eV, agrees well with the extrapolated VDE obtained from photoelectron spectra of water cluster anions (18, 27, 28) and raises the question of whether the cluster dynamics will also extrapolate to an observable bulk quantity. We report TRPES experiments on liquid water jets that directly yield the *p*-state lifetime of e_{aq}^{-} , resolving which of the two models in Fig. 1 is more appropriate. Our results provide the missing link between the time-resolved water cluster anion experiments and the TA work on bulk hydrated electrons.

The principle of the experiment, in which three femtosecond laser pulses interact with a liquid water jet, is outlined in Fig. 2 and in Eq. 1:

$$A^{-}_{(aq)} \xrightarrow{hv_1,\Delta t_{12}} A_{(aq)} + e^{-}_{(aq)}(s)$$

$$e^{-}_{(aq)}(s) \xrightarrow{hv_2,\Delta t_{23}} e^{-}_{(aq)}(p) \xrightarrow{hv_3} e^{-}_{(vac)} (1)$$

The first pulse, hv_1 , is centered at 239 nm and generates hydrated electrons via charge transfer to solvent (CTTS) excitation of a precursor anion; results are reported here for a 100 mM solution of Γ , but identical results were obtained by using Fe(CN)₆^{4–}. The time (Δt_{12}) between hv_1 and the pump pulse hv_2 (800 nm, 1.55 eV, and 85 fs) is held at 200 ps so as to ensure a population of equilibrated, ground-state hydrated electrons (29). The pump pulse lies within the $s \rightarrow p$ absorption band and excites an electron to the *p*-state manifold. The probe pulse hv_3 (266 nm, 4.65 eV, and 125 fs) then detaches the electron to vacuum. The resulting photoelectron kinetic energy (eKE) distribution is measured as a function of Δt_{23} . Because TRPES measures the energy of populated states relative to vacuum, electrons ejected from the *p*-state will have higher eKE than those ejected from the *s*-state, which enables us to distinguish between them. The experimental set-up comprises a liquid jet source described elsewhere (25, 30), a 1-kHz femtosecond laser system, and a magnetic bottle electron spectrometer (26, 31).

Shown in Fig. 3 are TRPE spectra using two background subtraction schemes. The eKE scale is corrected for the liquid jet streaming potential as described previously (30, 32). The photoelectron spectrum is shown in Fig. 3A, with the individual one-color contributions from hv_1 and hv_3 subtracted from the three-pulse spectra. Each ultraviolet beam causes a delay-invariant twophoton signal from detachment of the precursor anion, which we treat as background. A shortlived transient feature above 2.0 eV and a broad, intense feature centered at 1.2 eV are shown in Fig. 3A. The latter corresponds to a VDE $(=hv_3 -$ 1.2 eV) of 3.45 eV and is readily assigned to detachment from the s-state of e_{aq}^{-} on the basis of previous work (23-26). Recent experiments (33, 34) suggest that the escape depth in liquid water for photoelectrons in this eKE range (1 to 3 eV) is at least 5 nm, which is approximately a factor of 20 larger than the cavity radius of e_{aq} . These results imply that the detached electrons seen here are not predominantly sampled from the jet surface.

The result of subtracting the $(hv_1 + hv_3)$ twopulse spectrum from the three-pulse spectrum is shown in Fig. 3B at each delay time. These difference spectra show how the photoelectron signal changes with the addition of the pump pulse, hv_2 . Here, positive signal is induced by hv_2 , whereas negative-going signal represents depletion by hv_2 . The depleted signal overlaps the groundstate feature in Fig. 3A. The positive signal in Fig. 3B exhibits a shoulder from 2.3 to 2.6 eV at the earliest delays that disappears within 100 fs. By 230 fs (Fig. 3B, green trace), the signal has evolved into a smaller transient feature peaking

 $p^{\dagger} \xrightarrow{\tau_p} p \xrightarrow{\tau_{IC}} s^{\dagger} \xrightarrow{\tau_s} s$ Vacuum Vacuum $\tau_p = 50 \text{ fs}$ $\tau_p = fast$ |p> |p> τ_{IC} = 400 fs τ_{IC} = 50 fs hv hv s> s> = 1 ps = 400 fs, 1 ps Adiabatic model Nonadiabatic model

Fig. 1. Proposed relaxation mechanism of the electronically excited hydrated electron. Initial *p*-state solvent relaxation is followed by IC and then *s*-state solvent relaxation. Adiabatic (left) and nonadiabatic (right) models differ primarily in τ_{IC} .

¹Department of Chemistry, University of California, Berkeley, CA 94720, USA. ²Intel Corporation, Hillsboro, OR 97124, USA. ³Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.

around 1.7 eV that continues to decay and shift toward lower eKE on a significantly longer time scale. The early-time behavior of the shoulder at high eKE can be more readily discerned by subtracting the curve at 230 fs from those at earlier times. The result, shown in Fig. 3C, is a peak centered around 2.5 eV.

To gain further insight into these dynamics, integrated signal is shown in Fig. 4 as a function of delay over three energy intervals indicated in Fig. 3A. Data are shown as points, and the solid lines are fitting functions. These regions are well fit by a simple, sequential three-step mechanism $(I \xrightarrow{\tau_1} II \xrightarrow{\tau_2} III)$, with time constants $\tau_1 = 75 \pm 20$ fs and $\tau_2 = 410 \pm 40$ fs. In Fig. 4, the blue curve is associated with I in the mechanism, red with II, and green with III. The fitting functions for each step in the mechanism are a convolution of the measured pump-probe cross-correlation (115 fs), with the kinetic rate equation for each step (supplementary text).

The blue curve in Fig. 4 corresponds to eKEs separated from the ground-state feature by $\sim hv_2$ and is assigned to the initially excited *p*-state. The green curve indicates that the ground state is





initially depleted by the pump pulse but that its population recovers as the *p*-state relaxes. The existence of an intermediate state II is inferred from the observation that ground-state recovery is noticeably slower than decay of the blue curve. With reference to Fig. 1, state II can be assigned either to *p*-state signal subsequent to solvent relaxation in the excited state, or to *s*-state signal just after IC, in which the electron is surrounded by a vibrationally excited, nonequilibrium distribution of solvent molecules. This assignment determines whether the decay of the blue signal in Fig. 4 corresponds to relaxation within the *p*-state or to IC to the *s*-state.

The latter assignment is supported by several factors. First, as shown in Fig. 3A, the energy interval corresponding to feature II falls on the high-eKE edge of the ground-state spectrum but clearly lies within the eKE range of the ground state, just where one would expect to see a contribution from vibrationally hot *s*-state signal. A close examination of Fig. 3B suggests that for $\Delta t_{12} \ge 230$ fs, the pump-induced signal shifts toward lower eKE as it loses intensity, as one might expect for signal associated with solvent relaxation on the ground state.

Moreover, assigning the red signal to the relaxed *p*-state signal would indicate an energy shift of around -0.8 eV within the p-state subsequent to photoexcitation, as seen from the difference between the blue and red energy windows and the data in Fig. 3B. Quantum-classical molecular dynamics simulations of hydrated electron pump-probe signal using various electron-water pseudopotentials do not support such a large energy shift (6, 14); instead, they find the p-state energy remains nearly constant, whereas the s-state energy exhibits large fluctuations. It thus appears more reasonable to attribute the decay of the blue signal I to IC, and the decay (recovery) of the red (green) signal to solvent relaxation on the s-state subsequent to IC. This assignment then yields $\tau_1 = \tau_{IC} = 75 \pm 20$ fs, whereas $\tau_2 =$ $\tau_s = 410 \pm 40$ fs represents the time constant for solvent relaxation subsequent to IC.

Our value of 75 ± 20 fs for τ_{IC} supports the nonadiabatic relaxation mechanism shown in Fig. 1, apparently resolving the ambiguity from the TA experiments (which yielded similar time constants). Moreover, this value is remarkably consistent with the extrapolated τ_{IC} of 60 fs obtained from size-selected water cluster anions, suggesting that both the relaxation dynamics and the VDEs for water cluster anions can be extrapolated to bulk values. The data as interpreted here also yield a measurement of the VDE for the *p*-state of the hydrated electron, 2.2 ± 0.2 eV, taking the center of the eKE distribution in Fig. 3C to be 2.5 eV.

We next considered whether our results show any evidence for *p*-state relaxation. Our more recent work on water cluster anions showed the *p*-state photoelectron signal shifting to lower eKE on the same time scale as IC, implying that these two processes occur in parallel (18). Similar dynamics are suggested here by Fig. 3C, which shows the early-time signal shifting toward lower eKE as it disappears. However, this p-state signal overlaps the hot s-state signal, which is shifting in the same direction, so the trend in Fig. 3C should be viewed with caution. We do not see evidence for the slowest time constant (1.1 ps) seen in the TA experiments, possibly because relatively few data points were taken at long time delays.

The experiments presented here open up the possibility of tracking solvated electron dynamics in methanol and other solvents, in which similar mechanistic issues have been raised from TA experiments (35). Furthermore, with differing excitation schemes (36) it should be possible to probe the relaxation dynamics of prehydrated and conduction-band electrons in liquid water jets. These electrons are more highly excited and delocalized than are the *p*-state electrons probed here, and their energetics and dynamics have been investigated but are not as well-characterized (37–39). Hence, TRPES in liquid jets offers considerable potential for unraveling electron dynamics in water and other solvents.



Fig. 3. Time-resolved photoelectron spectra. The plots show three-pulse spectra from which (**A**) the contribution from each one color spectrum has been subtracted and (**B**) the (hv1 + hv3) two-color spectrum has been subtracted. (**C**) Spectra from (B) at early times, showing curve at 167 fs subtracted.

Fig. 4. Integrated intensity as a function of delay over three eKE intervals. Colors are the same as in Fig. 3A.



References and Notes

- 1. B. C. Garrett et al., Chem. Rev. 105, 355–390 (2005).
- 2. L. Turi, P. J. Rossky, Chem. Rev. 112, 5641-5674 (2012).
- 3. B. Abel, Annu. Rev. Phys. Chem. 64, 533-552 (2013).
- R. M. Young, D. M. Neumark, Chem. Rev. 112, 5553–5577 (2012).
- 5. P. J. Rossky, J. Schnitker, J. Phys. Chem. 92, 4277-4285 (1988).
- 6. R. E. Larsen, W. J. Glover, B. J. Schwartz, Science 329,
- 65–69 (2010). 7. E. Alizadeh, L. Sanche, *Chem. Rev.* **112**, 5578–5602 (2012).
- K. Yokoyama, C. Silva, D. H. Son, P. K. Walhout, P. F. Barbara, J. Phys. Chem. A 102, 6957–6966 (1998).
- M. Assel, R. Laenen, A. Laubereau, *Chem. Phys. Lett.* **317**, 13–22 (2000)
- 10. M. S. Pshenichnikov, A. Baltuska, D. A. Wiersma, *Chem. Phys. Lett.* **389**, 171–175 (2004).
- M. J. Tauber, R. A. Mathies, J. Phys. Chem. A 105, 10952–10960 (2001).

- 12. D. M. Neumark, Mol. Phys. 106, 2183-2197 (2008).
- E. J. Hart, J. W. Boag, J. Am. Chem. Soc. 84, 4090–4095 (1962).
- B. J. Schwartz, P. J. Rossky, J. Chem. Phys. **101**, 6902 (1994).
 A. A. Zharikov, S. F. Fischer, J. Chem. Phys. **124**, 054506
- (2006). 16. J. M. Weber *et al., Chem. Phys. Lett.* **339**, 337–342 (2001).
- 17. A. E. Bragg, J. R. R. Verlet, A. Kammrath, O. Cheshnovsky,
- D. M. Neumark, *Science* **306**, 669–671 (2004).
- G. B. Griffin, R. M. Young, O. T. Ehrler, D. M. Neumark, J. Chem. Phys. 131, 194302 (2009).
- D. H. Paik, I.-R. Lee, D.-S. Yang, J. S. Baskin, A. H. Zewail, Science 306, 672–675 (2004).
- O. Marsalek, F. Uhlig, T. Frigato, B. Schmidt, P. Jungwirth, *Phys. Rev. Lett.* **105**, 043002 (2010).
- L. D. Jacobson, J. M. Herbert, J. Am. Chem. Soc. 133, 19889–19899 (2011).
- 22. B. Winter, M. Faubel, Chem. Rev. 106, 1176-1211 (2006).

- 23. K. R. Siefermann *et al.*, *Nat. Chem.* **2**, 274–279 (2010). 24. Y. Tang *et al.*, *Chem. Phys. Lett.* **494**, 111–116 (2010).
- 25. A. T. Shreve, T. A. Yen, D. M. Neumark, *Chem. Phys. Lett.*
- **493**, 216–219 (2010).
- 26. A. Lübcke, F. Buchner, N. Heine, I. V. Hertel, T. Schultz, *Phys. Chem. Chem. Phys.* **12**, 14629–14634 (2010).
- 27. J. V. Coe et al., J. Chem. Phys. 92, 3980 (1990).
- L. Ma, K. Majer, F. Chirot, B. von Issendorff, J. Chem. Phys. 131, 144303 (2009).
- J. A. Kloepfer, V. H. Vilchiz, V. A. Lenchenkov, A. C. Germaine, S. E. Bradforth, J. Chem. Phys. 113, 6288 (2000).
 A. J. Shrave, A. H. Fillier, D. M. Neural J. Chem. Cont. 5
- A. T. Shreve, M. H. Elkins, D. M. Neumark, Chem. Sci. 4, 1633 (2013).
- 31. P. Kruit, F. H. Read, J. Phys. E 16, 313-324 (1983).
- T. Horio, H. Shen, S. Adachi, T. Suzuki, *Chem. Phys. Lett.* 535, 12–16 (2012).
- F. Buchner, T. Schultz, A. Lübcke, *Phys. Chem. Chem. Phys.* 14, 5837–5842 (2012).
- 34. S. Thürmer *et al.*, *Phys. Rev. Lett.* **111**, 173005 (2013).
- A. Thaller, R. Laenen, A. Laubereau, J. Chem. Phys. 124, 024515 (2006).
- P. Kambhampati, D. H. Son, T. W. Kee, P. F. Barbara, J. Phys. Chem. A 106, 2374–2378 (2002).
- A. Migus, Y. Gauduel, J. L. Martin, A. Antonetti, *Phys. Rev. Lett.* 58, 1559–1562 (1987).
- X. Shi, F. H. Long, H. Lu, K. B. Eisenthal, J. Phys. Chem. 100, 11903–11906 (1996).
- C.-R. Wang, T. Luo, Q.-B. Lu, *Phys. Chem. Chem. Phys.* 10, 4463–4470 (2008).

Acknowledgments: This research is supported by the National Science Foundation (NSF) under grant CHE-1011819. The data presented in this paper are available upon request sent to dneumark@berkeley.edu.

Supplementary Materials

www.sciencemag.org/content/342/6165/1496/suppl/DC1 Materials and Methods Supplementary Text Fig. S1 Reference (*40*) 23 September 2013; accepted 20 November 2013 10.1126/science.1246291

Dynamical Resonances Accessible Only by Reagent Vibrational Excitation in the F + HD \rightarrow HF + D Reaction

Tao Wang,¹* Jun Chen,¹* Tiangang Yang,¹ Chunlei Xiao,¹† Zhigang Sun,¹† Long Huang,¹ Dongxu Dai,¹ Xueming Yang,^{1,2}† Dong H. Zhang^{1,2}†

Experimental limitations in vibrational excitation efficiency have previously hindered investigation of how vibrational energy might mediate the role of dynamical resonances in bimolecular reactions. Here, we report on a high-resolution crossed-molecular-beam experiment on the vibrationally excited $HD(v = 1) + F \rightarrow HF + D$ reaction, in which two broad peaks for backward-scattered HF(v' = 2 and 3) products clearly emerge at collision energies of 0.21 kilocalories per mole (kcal/mol) and 0.62 kcal/mol from differential cross sections measured over a range of energies. We attribute these features to excited Feshbach resonances trapped in the peculiar HF(v' = 4)–D vibrationally adiabatic potential in the postbarrier region. Quantum dynamics calculations on a highly accurate potential energy surface show that these resonance states correlate to the HD(v' = 1) state in the entrance channel and therefore can only be accessed by the vibrationally excited HD reagent.

Molecular vibrations have profound effects on chemical reactivity. Early studies on atom-diatom reactions led to the establishment of the Polanyi rules, which state that vibrational energy is more efficient than translational energy in promoting a late-barrier reaction, whereas the reverse is true for an early barrier reaction (1). Crim, Zare, and co-workers later observed great enhancements of reactivity in the late-barrier H + H₂O/HOD/D₂O reactions by reagent vibrational excitation (2–5), based on theoretical predictions made by Schatz and co-workers (6). More recently, experimental and theoretical studies have explored the generality and validity of the rules for polyatomic systems involving CH₄ and its isotopically substituted analogs (7–15). Most notably, Liu and co-workers carried out extensive experimental investigations on the dynamics of the $F/Cl + CHD_3$ reactions with preliminary CH stretching excitation, and their unexpected observations presented strong challenges to theory (10–15).

Reactive resonances, transiently trapped quantum states along the reaction coordinate in the transition-state region of a chemical reaction, have also occupied a central place in reaction dynamics research over the past few decades (16-19), particularly in the context of F + H₂/HD reactions (20-29). Recent experimental studies, in combination with quantum dynamics calculations on a

¹State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China. ²Center for Advanced Chemical Physics, University of Science and Technology of China, 96 Jinzhai Road, Hefei 230026, P. R. China.

^{*}These authors contributed equally to this work. †Corresponding author. E-mail: chunleixiao@dicp.ac.cn (C.X.), zsun@dicp.ac.cn (Z.S.), xmyang@dicp.ac.cn (X.Y.), and zhangdh@dicp.ac.cn (D.H.Z.)