

pattern of uplift rates inferred from marine isotope stage 5.5 marine terrace elevations (33). If uplift rate does play a role, it may be in modulating channel steepness as a function of sinuosity (fig. S3).

References and Notes

- J. D. Milliman, J. P. M. Syvitski, *J. Geol.* **100**, 525 (1992).
- F. J. Pazzaglia, M. T. Brandon, *Am. J. Sci.* **301**, 385 (2001).
- Y. S. Hayakawa, T. Oguchi, *Geomorphology* **111**, 27 (2009).
- S. J. Dadson *et al.*, *Nature* **426**, 648 (2003).
- T. Suzuki, *Trans. Jpn. Geomorphol. Union* **3-1**, 1 (1982).
- T. Suzuki, *Trans. Jpn. Geomorphol. Union* **4-1**, 33 (1983).
- M. Hirano, *Trans. Jpn. Geomorphol. Union* **1-2**, 117 (1981).
- R. Yagi, H. Ikeda, *Bull. Environ. Res. Center Univ. Tsukuba* **22**, 1 (1997).
- A. Nakano, H. Ikeda, *Bull. Environ. Res. Center Univ. Tsukuba* **24**, 1 (1999).
- J. R. Barbour *et al.*, *Geophys. Res. Lett.* **36**, L04401 (2009).
- C. P. Stark, *Geophys. Res. Lett.* **33**, L04402 (2006).
- J. M. Turowski, D. Lague, N. Hovius, *J. Geophys. Res.* **114** (F3), F03016 (2009).
- J. B. H. Shyu, K. Sieh, J.-P. Avouac, W.-S. Chen, Y.-G. Chen, *J. Geophys. Res.* **111** (B8), B08403 (2006).
- J. M. Turowski, D. Lague, N. Hovius, *J. Geophys. Res.* **112**, (F4), F04006 (2007).
- W. M. Davis, *Science* **21**, 225 (1893).
- A. Winslow, *Science* **22**, 31 (1893).
- R. H. Mahard, *J. Geomorphol.* **5**, 32 (1942).
- H. Blank, *Geol. Soc. Am. Bull.* **81**, 3135 (1970).
- G. H. Dury, *Am. J. Sci.* **252**, 193 (1954).
- D. R. Harden, *Geol. Soc. Am. Bull.* **102**, 233 (1990).
- G. S. Hancock, R. S. Anderson, *Geol. Soc. Am. Bull.* **114**, 1131 (2002).
- S. Ikeda, G. Parker, K. Sawai, *J. Fluid Mech.* **112**, 363 (1981).
- G. Seminara, *J. Fluid Mech.* **554**, 271 (2006).
- J. G. A. Bitter, *Wear* **6**, 169 (1963).
- L. S. Sklar, W. E. Dietrich, *Geology* **29**, 1087 (2001).
- K. Hartshorn, N. Hovius, W. B. Dade, R. L. Slingerland, *Science* **297**, 2036 (2002).
- F. Guzzetti, S. Peruccacci, M. Rossi, C. P. Stark, *Meteorol. Atmos. Phys.* **98**, 239 (2007).
- See supporting material on Science Online.
- J. Galewsky *et al.*, *J. Geophys. Res.* **111** (F3), F03014 (2006).
- S. D. Willett *et al.*, Eds., *GSA Spec. Pap.* **398**, Penrose Conf. Ser. (2006).
- J. C. L. Chan, *Annu. Rev. Fluid Mech.* **37**, 99 (2005).
- Y. Maeda *et al.*, *Quat. Int.* **115–116**, 15 (2004).
- Y. Ota, M. Yamaguchi, *Quat. Int.* **120**, 105 (2004).
- This study was supported by NASA, NSF (Earth Sciences Division, Geomorphology and Land-use Dynamics Program), and the Taiwan National Science Council. We thank W. E. Dietrich, G. Parker, and E. E. Wohl for enlightening discussions and C.-H. Jen, C. Huang, T.-C. Yi, and M. Tajikara for help in the field.

Supporting Online Material

www.sciencemag.org/cgi/content/full/327/5972/1497/DC1

Methods

Figs. S1 to S3

Table S1

9 November 2009; accepted 5 February 2010

10.1126/science.1184406

Transition-State Spectroscopy of Partial Wave Resonances in the F + HD Reaction

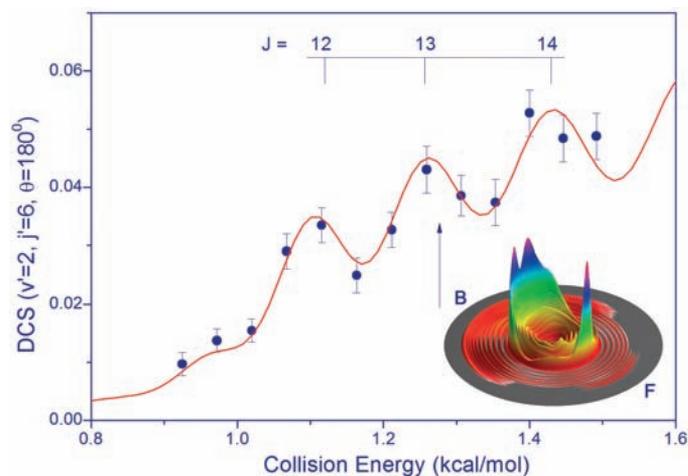
Wenrui Dong,* Chunlei Xiao,* Tao Wang, Dongxu Dai, Xueming Yang,† Dong H. Zhang†

Partial wave resonances, quasi-bound resonance states with well-defined rotation in the transition state region of a chemical reaction, play a governing role in reaction dynamics but have eluded direct experimental characterization. Here, we report the observation of individual partial wave resolved resonances in the $F + HD \rightarrow HF + D$ reaction by measuring the collision energy-dependent, angle- and state-resolved differential cross section with extremely high resolution, providing a spectroscopic probe to the transition state of $F + HD \rightarrow HF + D$. The agreement of the data with the high-level theoretical calculations confirms the sensitivity of this probe to the subtle quantum mechanical factors guiding this benchmark reaction.

Direct characterization of transition states, the fleeting structures at the boundary between the reactants and products in molecular transformations, is one of the grand challenges in physical chemistry (1–3). Substantial progress toward this goal has been made in the past two decades by using negative-ion photodetachment spectroscopy, which probes a reaction transition state by directly photodetaching an electron from an appropriate negative-ion precursor that has a similar geometric structure to the transition state (4). However, it is much more difficult to measure the transition-state structures in crossed molecular-beam experiments, even with full quantum mechanical state resolution of the initial and final states, because in most chemical reactions experimental observables come from the contributions of collisions with many partial waves, or in classical terms, of collisions with a range of impact parameters or total angular momentum. A partial wave is a quantum-scattering

state with a well-defined total angular momentum quantum number (J), which specifies the overall rotation of the reaction system and is conserved in the reaction process. A full reaction

Fig. 1. Experimental and theoretical DCS of the $HF(v' = 2, j' = 6)$ product of the $F(^2P_{3/2}) + HD(j = 0)$ reaction in the backward scattering direction. The solid circles are experimental data; the red curve, the result of full quantum dynamics calculations convoluted with the experimental resolution and shifted 0.03 kcal/mol lower in energy. The error bars in the experimental data are the estimated measurement errors ($\pm 1\sigma$) for the $HF(v' = 2, j' = 6)$ product peak intensity (fig. S1) in the collision energy scan. The three peaks are assigned to the partial wave Feshbach resonances of $J = 12, 13,$ and 14 in the $F + HD \rightarrow HF + D$ reaction, as explained in the text. The three-dimensional DCS shown was measured at 1.285 kcal/mol, with F and B indicating the forward- and backward-scattering, respectively, directions for HF with respect to the F-atom beam direction.



State Key Laboratory of Molecular Reaction Dynamics, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, People's Republic of China.

*These authors contributed equally to this work.

†To whom correspondence should be addressed. E-mail: xmyang@dicp.ac.cn (X.Y.); zhangdh@dicp.ac.cn (D.H.Z.)

F + H₂ reaction system has been a textbook case in the study of resonances (5–8). In this work, we report the experimental observation of partial wave resolved resonances in the F + HD → HF + D reaction, providing an extremely accurate probe of its reactive resonance potential energy surface (PES).

We performed a fully quantum state-resolved, crossed-beam reactive scattering experiment on the F(²P_{3/2}) + HD(*j* = 0) → HF(*v*', *j*') + D reaction by using the D-atom Rydberg tagging technique (9). A unique double-stage discharge F-atom beam was used in this experiment so that a high-intensity F-atom beam with high-speed ratio (*v*'/δ*v*') could be obtained (10). Both beam sources (F and HD) were cooled cryogenically to maximize resolution.

Time-of-flight (TOF) spectra of the D atom products from the F + HD reaction in the backward scattering direction were measured at various collision energies from 0.9 to 1.5 kcal/mol and are shown in fig. S1. Full product (HF) rotational state resolution was achieved, and differential cross sections (DCS) for HF(*v*' = 2) products in individual rotational states were obtained. A clear oscillatory structure is evident (Fig. 1) in the collision energy dependence of the DCS for the HF(*v*' = 2, *j*' = 6) product in the backward scattering direction. Theoretically, we carried out full quantum scattering calculations on a recently reported PES (11). The theoretical DCS in the backward direction for the HF(*v*' = 2, *j*' = 6) product were computed at various collision energies. For better comparison, the experimental resolution factor was included in the theoretical simulation. The original theoretical results are shifted

lower in energy by 0.03 kcal/mol in Fig. 1 to compare with the experimental results. With this small shift, the agreement between the theory and the experiment is remarkable.

In order to trace the dynamical origin of the oscillatory structures, we calculated the DCS in the backward direction for the HF(*v*' = 2, *j*' = 6) product with different *J*_{max}. It turns out that the three main peaks exhibited in Fig. 1 emerge subsequently by taking *J*_{max} = 12, 13, and 14 (fig. S2). In other words, the assigned *J* = 12 peak in Fig. 1 emerges only after including the *J* = 12 partial wave in the calculations. The same is true for the peaks labeled *J* = 13 and 14. This clearly confirms that the detected oscillations are contributed by the *J* = 12, 13, and 14 partial wave Feshbach resonances in the F + HD → HF + D reaction. It is interesting to point out that the final heights of the specific peaks of these oscillations can be obtained only by including larger *J* contributions in the calculations, implying that quantum interference among the partial wave resonances is quite significant in the observed DCS. In addition to the HF(*v*' = 2, *j*' = 6) product, partial wave resonances are also observed in the DCS of other well-resolved rotationally excited HF(*v*' = 2) products in the backward direction.

The partial wave resolved resonances can only be observed in both angle- and state-resolved DCS measurement with extremely high translational energy resolution in a scattering experiment. It is necessary to point out that the reaction resonance that we are dealing with here is the same resonance studied in (7) and (11). DCS in different scattering directions was also measured in this

work at the collision energy of 1.285 kcal/mol (Fig. 1). The three-dimensional DCS plot shows a narrow forward-scattering peak with a broader backward-scattering distribution, indicating a strong resonance effect in the reaction. The present experiment provides a spectroscopic probe of the resonance potential far beyond the generally accepted “chemical accuracy” of about 1 kcal/mol. The observation of the partial wave resolved resonances provides opportunities to study their effect on chemical reactivity at the truly state-to-state-to-state level.

References and Notes

- G. C. Schatz, *Science* **288**, 1599 (2000).
- F. Fernández-Alonso, R. N. Zare, *Annu. Rev. Phys. Chem.* **53**, 67 (2002).
- J. C. Polanyi, A. H. Zewail, *Acc. Chem. Res.* **28**, 119 (1995).
- D. M. Neumark, *Science* **272**, 1446 (1996).
- D. E. Manolopoulos *et al.*, *Science* **262**, 1852 (1993).
- R. T. Skodje *et al.*, *Phys. Rev. Lett.* **85**, 1206 (2000).
- R. T. Skodje *et al.*, *J. Chem. Phys.* **112**, 4536 (2000).
- M. Qiu *et al.*, *Science* **311**, 1440 (2006).
- The experimental technique used in this work is described in detail in the supporting materials available on *Science Online*.
- Z. Ren *et al.*, *Rev. Sci. Instrum.* **77**, 016102 (2006).
- Z. Ren *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **105**, 12662 (2008).
- We acknowledge the support of this work by the Chinese Academy of Sciences, the National Natural Science Foundation of China, and the Ministry of Science and Technology of China.

Supporting Online Material

www.sciencemag.org/cgi/content/full/327/5972/1501/DC1

Materials and Methods

Figs. S1 and S2

References

8 December 2009; accepted 28 January 2010

10.1126/science.1185694

Mechanosensitive Self-Replication Driven by Self-Organization

Jacqui M. A. Carnall,¹ Christopher A. Waudby,^{1,2} Ana M. Belenguer,¹ Marc C. A. Stuart,^{3,4} Jérôme J.-P. Peyralans,⁴ Sijbren Otto^{4*}

Self-replicating molecules are likely to have played an important role in the origin of life, and a small number of fully synthetic self-replicators have already been described. Yet it remains an open question which factors most effectively bias the replication toward the far-from-equilibrium distributions characterizing even simple organisms. We report here two self-replicating peptide-derived macrocycles that emerge from a small dynamic combinatorial library and compete for a common feedstock. Replication is driven by nanostructure formation, resulting from the assembly of the peptides into fibers held together by β sheets. Which of the two replicators becomes dominant is influenced by whether the sample is shaken or stirred. These results establish that mechanical forces can act as a selection pressure in the competition between replicators and can determine the outcome of a covalent synthesis.

The ability to replicate is an essential component of evolvable life, yet how replication emerged during the origin of life remains an unanswered question (1–3). The experimental approach to this subject has focused largely on kinetically controlled autocatalysis, whereby a molecule is able to catalyze its own formation from a set of precursors. This outcome has been achieved using both biological molecules—

such as DNA (4, 5), RNA (6) and α-helical peptides (7, 8)—and nonbiological molecules (9–12). Also, cross-catalytic systems have been reported wherein two or more sets of compounds induce one another's synthesis (13, 14). These relatively simple systems are still far from the complexity exhibited by contemporary organisms, which can undergo Darwinian evolution and exhibit a complex internal organization.

We previously proposed that it should be possible to use dynamic combinatorial libraries to develop molecules capable of promoting their own formation, while forming extended assemblies at the same time (15). Dynamic combinatorial libraries are created by mixing building blocks that can react with each other through the formation of reversible covalent bonds, leading to a mixture of products that are all in rapid equilibrium. We reasoned that if two or more molecules of a particular product could stabilize one another through noncovalent binding, the equilibrium would shift toward formation of this product at the expense of the other library members. A number of examples have very recently appeared that exploit this principle. Giuseppone described a dynamic equivalent of the Rebek replicator (16) as well as an autopoietic system

¹University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge CB2 1EW, UK. ²Department of Structural and Molecular Biology, University College London, London WC1E 6BT, UK. ³Groningen Biomolecular Sciences and Biotechnology Institute, University of Groningen, Nijenborgh 4, 9747 AG Groningen, Netherlands. ⁴Centre for Systems Chemistry, Stratingh Institute, University of Groningen, Nijenborgh 4, 9747 AG Groningen, Netherlands.

*To whom correspondence should be addressed. E-mail: s.otto@rug.nl.

Transition-State Spectroscopy of Partial Wave Resonances in the F + HD Reaction

Wenrui Dong, Chunlei Xiao, Tao Wang, Dongxu Dai, Xueming Yang and Dong H. Zhang

Science **327** (5972), 1501-1502.

DOI: 10.1126/science.1185694

Partial View

Skilled billiard players can easily predict how spinning of one ball will affect the trajectory of the second ball it strikes in a collision. In principle, quantum mechanics can be used to predict the analogous impact of the angular momentum of reagents on the outcome of a chemical reaction. In practice, however, observation of most chemical reactions—even in the confines of a molecular beam apparatus—encompasses a vast number of collisions over multiple angular momentum distributions. **Dong *et al.*** (p. 1501; see the Perspective by **Althorpe**) have honed their spectroscopic resolution sufficiently to distinguish the impact of subtle angular momentum variations on the reactivity of fluorine with hydrogen atoms. Their data agree with theory and reveal oscillating peaks in reaction probability, termed partial wave resonances.

ARTICLE TOOLS

<http://science.sciencemag.org/content/327/5972/1501>

SUPPLEMENTARY MATERIALS

<http://science.sciencemag.org/content/suppl/2010/03/16/327.5972.1501.DC1>

RELATED CONTENT

<http://science.sciencemag.org/content/sci/327/5972/1460.full>

REFERENCES

This article cites 10 articles, 4 of which you can access for free
<http://science.sciencemag.org/content/327/5972/1501#BIBL>

PERMISSIONS

<http://www.sciencemag.org/help/reprints-and-permissions>

Use of this article is subject to the [Terms of Service](#)