to place the four dots on a plane. The molecules have been synthesized with several different clusters and centers in an effort to understand the role of the linkers in electron hopping and design molecules with appropriate switching behavior. Marya Lieberman and her team are investigating another kind of potential QCA molecules, in which each dot consists of a single ruthenium atom (see panel C in the figure).

The QCA approach to molecular electronics is very promising, but creating functional QCA molecules is just the first step. In a device, the molecules need to be attached to a surface in a predetermined geometry, inputs and clocking signals need to be applied, and the state of the output cells must be read. Each of these steps presents substantial challenges. In addition, the whole approach to circuit architecture must be rethought if circuits are going to be based on QCA cells rather than transistors. Work along these lines is under way (*8*, *9*).

References and Notes

1. C. S. Lent, P. D. Tougaw, W. Porod, G. H. Bernstein, *Nanotechnology* **4**, 49 (1993).
2. C. S. Lent and P. D. Tougaw, *Proc. IEEE* **85**, 541 (1997).
3. A. O. Orlov, I. Amlani, G. H. Bernstein, C. S. Lent, G. L. Snider, *Science* **277**, 928 (1997).
4. I. Amlani *et al.*, *Science* **284**, 289 (1999).
5. A. O. Orlov, I. Amlani, C. S. Lent, G. H. Bernstein, G. L. Snider, *Appl. Phys. Lett.* **74**, 2875 (1999).
6. Another large-scale implementation in magnetic systems was recently demonstrated by R. P. Cowburn and M. E. Welland [*Science* **287**, 1466 (2000)].
7. X. Lei, E. E. Wolf, T. P. Fehlner, *Eur. J. Inorg. Chem.* **1998** (no. 12), 1835 (1998).
8. M. Niemier and P. M. Kogge, in *Proceedings of the Ninth Great Lakes Symposium on VLSI*, Ann Arbor, Michigan (IEEE Computer Society, Los Alamitos, CA, 1999), pp. 118–121.
9. A. I. Csurgay and W. Porod, in *Proceedings of the European Conference on Circuit Theory and Design ECCTD '99*, C. Beccari, M. Biey, P. P. Civalleri, M. Gilli, Eds. (Levrotto and Bella, Torino, Italy, 1999), pp. 815–818.

PERSPECTIVES: REACTION DYNAMICS

Detecting Resonances

George C. Schatz

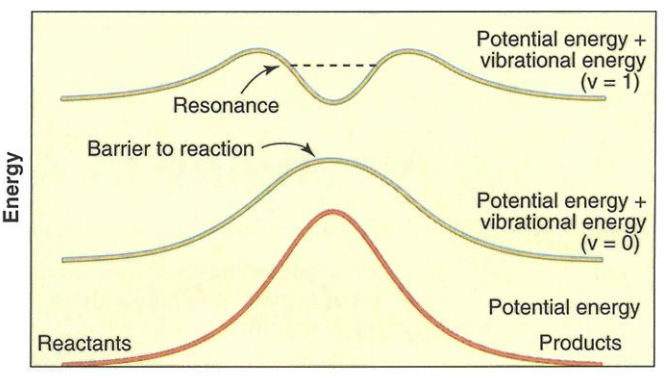
An important advance in the field of chemical reaction dynamics was recently achieved with the observation of isolated resonances in gas phase bimolecular chemical reactions that have no intermediate bound states (*1*, *2*). A "resonance" is a transient, metastable state produced during the reaction. Transient intermediates are well known in many kinds of chemical reactions (and also in nuclear and particle physics). What makes the newly observed resonances special is that they occur near the top of a reaction barrier (the "transition state"), where one would not normally expect to find metastable states.

Such nonintuitive resonances first showed up in theoretical simulations of simple gas phase reactions in the early 1970s (*3*, *4*). Numerous attempts have been made to detect them experimentally, including ground-breaking molecular beam studies by Neumark and co-workers (*5*). But the several reported "sightings" of resonances were later shown to be either ambiguous or erroneous (*6*–*8*). The new observations show resonant behavior for several different properties of the reaction dynamics and are consistent with high-quality theoretical simulations: It appears that the long search is over.

The two reactions studied, $H + D_2 \rightarrow HD + D$ (*1*) and $F + HD \rightarrow HF + D$ (*2*), are deuterated variants of two fundamental chemical reactions, namely the $H + H_2$ and $F + H_2$ reactions. $F + H_2$ is an important reaction in chemical lasers. $H + H_2$ is often considered to be the simplest atom-transfer reaction, and interest in this reaction goes back to the discovery of quantum mechanics. London (*9*) and Eyring and Polanyi (*10*) used this reaction to determine the first potential energy surface for a chemical reaction. Such surfaces are now widely used in chemistry and biology to describe the forces on nuclei during chemical reactions.

On the $H + H_2$ surface, a 9.6 kcal/mol barrier separates reactants from products (see the figure below). The top of this potential energy barrier corresponds to the linear symmetrical species H-H-H. It is this intermediate that is used to determine reaction rate coefficients with transition state ("activated complex") theory. The term "activated complex" might imply a metastable intermediate, but the latter term is inappropriate for $H + H_2$, because the barrier is usually surmounted within a few femtoseconds—not enough time for a resonance to establish itself. Nevertheless, theoretical studies (*3*, *4*) showed that there can be resonances in which the H-H-H intermediate oscillates across the barrier a few times before falling apart. The figure shows that these states can arise because vibrational frequencies associated with motion perpendicular to the reaction path are lower at the barrier top than in the reactants or products. A similar picture applies to the $F + H_2$ reaction, but in contrast to $H + H_2$, it is highly exothermic, with a barrier of only 1.5 kcal/mol.

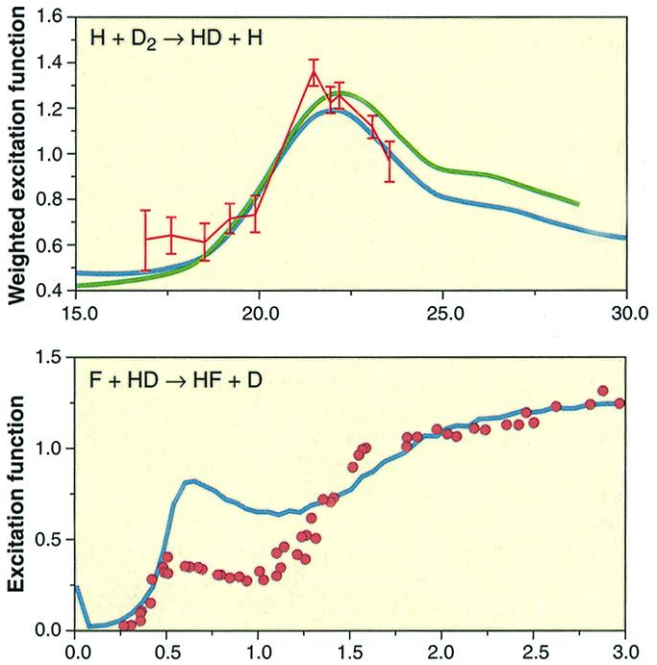
In nuclear and particle physics, resonances are often seen in scattering experiments, where they show up as peaks in cross sections determined as a function of the collision energy. (A cross section is the effective area of a nucleus for a scattering or absorption process.) Analogous measurement of cross sections for chemical reactions can be done in either crossed molecular beam or laser photolysis experiments. But observing resonances in these experiments is extremely difficult, because the measurements are averaged over a range of orientations, translational energies, and directions of approach of the colliding species. Thus, although resonances are often seen in theoretical simulations (where no averaging is done), they often disappear when



Schematic reaction path from reactants to products for $H + H_2$. Lowest curve: potential energy function, showing the barrier that must be surmounted for reaction to occur. Middle curve: sum of the potential energy and the zero point energy (v = 0) associated with vibrational motion perpendicular to the reaction path. Top curve: potential plus vibrational energy associated with the first excited vibrational state (v = 1). Because the vibrational frequencies are lower near the barrier top than in the reactants or products, the vibrational energy is lowest at the barrier, and the potential plus vibrational energy shows a well for the first excited state. This well can support one or more metastable (resonance) states. It is these states that have now been observed in chemical reactions for the first time (*1*, *2*).

The author is in the Department of Chemistry, Northwestern University, Evanston, IL 60208–3113, USA. E-mail: schatz@chem.nwu.edu

measurable properties are determined either by experiment or simulation. As a result, past studies of H + H_2, F + H_2, and similar reactions have been unable to attribute observed features to resonances with certainty.



Now you see it. Excitation function (cross section versus translational energy) for H + D_2 [top panel, based on data from (*1*)] and F + HD [bottom panel, based on data from (*2*)]. Each plot presents the measured results (data points in red) and the results of theoretical simulations (blue and/or green curves). The peak seen in each panel is a characteristic signature of resonance behavior. In the case of H + D_2, the measured results involve an average over scattering angles that depends on experimental parameters. This results in two slightly different theoretical estimates (blue and green curves), depending on the estimated uncertainty.

One way to circumvent the averaging problem is to perform a direct spectroscopic measurement of the transition state for the chemical reaction. Such measurements were pioneered by Neumark and coworkers in 1990 (*11*), who used photodetachment spectroscopy on the anion precursor to the neutral transition state. With this technique, resonances were seen in the transition state of the I + HI reaction. But the corresponding measurements for F + H_2 were dominated by other dynamical features (*12*), and no definitive assignment of resonances could be made.

The new reports of resonances in H + D_2 and F + HD are based on measurements under circumstances where resonance behavior is not canceled out by collisional averaging. The studies of F + HD reported by Skodje *et al.* (*2*) involve crossed molecular beam measurements at low collision energies, with simultaneous measurements of the angular and translational energy distributions of the products. The H + D_2 laser photolysis work by Kendrick *et al.* (*1*) involves simultaneous measurements of product translational and rotational energies. In both studies, a peak in the energy dependence of the cross sections is observed, which is characteristic of resonance behavior (see figure on the left). The resonance in H + D_2 has a very short lifetime (~10 femtoseconds), whereas that in F + HD is longer lived (~100 femtoseconds). The very short lifetime in H + D_2 barely allows the HD_2 intermediate to oscillate twice. The longer lifetime of the FHD intermediate corresponds to tens of vibrational periods. The key factor stabilizing this resonance is the low mass of H relative to F and D.

The new measurements provide unique information about transition state properties that will be important to understanding properties of potential energy surfaces. In addition, the observations should pave the way for more routine observations of reactive resonances in the future.

References and Notes

1. B. K. Kendrick, L. Jayasinghe, S. Moser, M. Auzinsh, N. Shafer-Ray, *Phys. Rev. Lett.* **84**, 4325 (2000).
2. R. T. Skodje *et al.*, *J. Chem. Phys.* **112**, 4536 (2000).
3. G. C. Schatz and A. Kuppermann, *J. Chem. Phys.* **59**, 964 (1973).
4. R. D. Levine and S.-F. Wu, *Chem. Phys. Lett.* **11**, 557 (1971).
5. D. M. Neumark *et al.*, *J. Chem. Phys.* **82**, 3067 (1985).
6. F. J. Aoiz, V. Herrero, V. Saez Rabanos, *J. Chem. Phys.* **97**, 7423 (1992).
7. F. J. Aoiz, V. Herrero, M. Noqueira, V. Saez Rabanos, *Chem. Phys. Lett.* **204**, 259 (1993).
8. E. Wrede and L. Schnieder, *J. Chem. Phys.* **107**, 786 (1997).
9. F. London, *Z. Elektrochem.* **35**, 532 (1929).
10. H. Eyring and M. Polanyi, *Z. Phys. Chem.* **B12**, 279 (1931).
11. I. M. Waller, T. Kitsopoulos, D. M. Neumark, *J. Phys. Chem.* **94**, 2240 (1990).
12. D. E. Manolopoulos *et al.*, *Science* **262**, 1852 (1993).
13. I acknowledge support from NSF grant CHE-9873892.

PERSPECTIVES: PLANT BIOLOGY

Flower Arranging in *Arabidopsis*

Paul F. Devlin and Steve A. Kay

One of the key factors contributing to the success of flowering plants is their ability to regulate the timing of flowering so that they can take maximum advantage of the most environmentally favorable conditions. Unraveling the signal transduction pathways that regulate flowering is one of the most exciting areas of plant biology research. Now, Samach *et al.* (*1*) on page 1613 of this issue and Blázquez and Weigel (*2*) in a recent issue of *Nature* reveal the integrated network of molecular signals that induce flowering in the weed *Arabidopsis thaliana* under different environmental conditions.

Many plants show a strong seasonality in their flowering, which ensures that their seeds are produced when conditions are optimal for germination and growth. Plants are able to accurately measure day length by integrating signals from photoreceptors and an endogenous circadian clock. In long-day species such as winter wheat (*Triticum aestivum*), flowering is induced when the duration of light exceeds a certain critical length. In contrast, short-day plants such as soybean (*Glycine max*) measure the dark period and flower when the night exceeds a certain critical length (*3*). Many plants also flower in response to cold temperatures (vernalization), mimicking the transition from winter to spring when conditions for seed germination are more favorable (*4*). Flowering can also be triggered by environmental stresses such as shading by neighboring vegetation. In this case, plant species can best succeed by channeling all of their available energy into reproduction (*5*).

Arabidopsis is a facultative long-day plant, that is, it flowers vigorously during long days (it also flowers in response to cold). These flowering responses are regulated by the photoperiodic and autonomous signaling pathways (see the figure). However, in the absence of promoting signals, *Arabidopsis* eventually flowers through a day length–independent pathway that follows an age-dependent developmental program (*6*). The study of *Arabidopsis* flowering mutants reveals much about the signal-

The authors are in the Department of Cell Biology and National Science Foundation for Biological Timing, Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, CA 92037, USA. E-mail: pdevlin@scripps.edu, stevek@scripps.edu