pattern appearing as a set of concentric rings. The pump-induced change of the radial intensity distribution is related, through Fourier transformation, to the pair-distribution function, and provides a "fingerprint" of the characteristic interatomic distances (see the figure). The scattering data are one-dimensional, but a molecule's structure is three-dimensional. Consequently, a structure "determination" from liquid scattering data requires much help from theory. First, the solvent contribution to the scattering pattern must be accurately calculated and subtracted from the data. This procedure is far from trivial. Next, the diffraction patterns from three-dimensional models of putative intermediates must be calculated and compared with the solvent-corrected curves. Finding a match between the experimental and theoretical curves should not be confused with a structure determination in the crystallographic sense; nevertheless, a match that exhibits significantly higher fidelity than other proposed structures makes a compelling case for that structural assignment.

Ihee and co-workers chose their system wisely. When comparing the scattering patterns from bridged and anti iodoethane radicals with their solvent-subtracted scattering curves, the bridged form gave a much better match, thereby providing the most direct and compelling case for the structural assignment of this important radical intermediate. This achievement was aided by the fact that iodine atoms scatter x-rays more than 10 times as strongly as methanol, thereby enhancing the signal arising from iodo radical intermediates. Because diiodoethane ($C_2H_4I_2$) has only four heavy atoms (hydrogen scatters very weakly), scattering from it and its photo-generated intermediates is relatively easy to assign and interpret. Moreover, the iodo radical intermediate is sufficiently long-lived to be easily captured with 100-ps time-resolved snapshots. Finally, the radical is produced with relatively high quantum efficiency, so a sizable population could be generated and characterized. Although it should be possible to study molecules that lack heavy-atom substituents, such systems would require that the signal-to-noise ratio of the scattering data be improved. For example, to recover a signal that is 10 times weaker, the data integration time would have to be increased by at least that factor squared, or 100 times longer. One could envision studying more complex molecules as well; however, diffraction rings from disordered solutions are not sharply defined, so the amount of structural information that can be extracted from the radial intensity distribution is limited. Therefore, there is a molecular size beyond which it would prove increasingly difficult to cor-

rectly match the scattering pattern to a specific three-dimensional molecular structure.

When seeking a match to a "fingerprint," the correct structure must be included in the lineup. As more candidates are included, the chance for a false-positive becomes greater. As a result, one must exercise sound chemical intuition when selecting candidate structures for comparison, as was done in the study by Ihee and co-workers.

Although it has a few limitations, the technique of picosecond time-resolved liquid diffraction can provide an unprecedented glimpse into the structures of reactive intermediates involved in solution-phase chemistry. Once efforts to generate high-flux x-ray pulses on the few-picosecond (13) and the femtosecond (14–16) time scales are realized, the time resolution of liquid diffraction studies could be extended to the so-called chemical time scale, where a wealth of new insights into chemical reaction pathways awaits discovery.

References and Notes
1. J. Davidsson et al., Phys. Rev. Lett. **94**, 245503 (2005).
2. H. Ihee et al., Science **309**, 1223 (2005); published online 14 July 2005 (10.1126/science.1114782).
3. V. Srajer et al., Science **274**, 1726 (1996).
4. M. Brunori, D. Bourgeois, B. Vallone, J. Struct. Biol. **147**, 223 (2004).
5. H. Ihee et al., Proc. Natl. Acad. Sci. U.S.A. **102**, 7145 (2005).
6. F. Schotte et al., Science **300**, 1944 (2003).
7. F. Schotte, J. Soman, J. S. Olson, M. Wulff, P. A. Anfinrud, J. Struct. Biol. **147**, 235 (2004).
8. H. Ihee et al., Science **291**, 458 (2001).
9. A. Rousse et al., Nature **410**, 65 (2001).
10. B. J. Siwick, J. R. Dwyer, R. E. Jordan, R. J. Miller, Science **302**, 1382 (2003).
11. S. Chen, M. T. Seidel, A. H. Zewail, Proc. Natl. Acad. Sci. U.S.A. **102**, 8854 (2005).
12. M. Wulff et al., Faraday Discuss. **122**, 13 (2003).
13. K.-J. Kim, D. M. Mills, "Workshop Generation and Use of Short X-ray Pulses at APS" (Advanced Photon Source, Argonne National Laboratory, 2005); www.aps.anl.gov/News/Conferences/2005/Generation_and_Use_of_Short_Xray_Pulses.
14. T. Åberg et al., in Conceptual Design Report of a 500 GeV e+e- Linear Collider with Integrated X-ray Laser Facility, G. Materlik, Ed. (DESY, Hamburg, 1997).
15. M. Cornacchia et al., "Linac Coherent Light Source (LCLS) Design Study Report," Tech. Rep. No. SLAC-R-512 (Stanford Linear Accelerator Center, Stanford University, CA, 1998).
16. A. Cho, Science **296**, 1008 (2002).
17. Supported by the Intramural Research Program of the NIH, NIDDK.

EVOLUTION

Is Invariance Across Animal Species Just an Illusion?

Gerdien de Jong

There is obvious variation in the way different animals live their lives—in their life span, in their age and size at maturity, and in their size as full-grown adults, to name a few attributes. But are there fundamental similarities in the life history strategies that different animals use? Charnov (1) argued that there are: He proposed fundamental similarities—"life history invariants"—to be a major explanatory ingredient of life history evolution. Life history invariants generalize a life history model over species boundaries and over a wide range of animal sizes, leading to an understanding of universal life history strategies. On page 1236 of this issue, Nee et al. (2) call into question the principal method to detect life history invariants. The authors have determined that the approach is misleading, throwing the very existence of the concept into doubt.

Life history invariants are dimensionless ratios of two life history traits—for instance,

age at maturity and average length of life. Such a ratio is used to answer questions such as "At what relative age do animals first reproduce?" Whether we talk about rabbits or whales, we hope the ratio will enable us to forget about differences in life span, size, environment, and taxonomy. Thus, life history invariants point to common properties of organisms not immediately clear from direct observation. As such, they are potentially very useful for understanding and modeling life history evolution: The models are meant to be general, doing away with the need to model each species separately. The existence of life history invariants is a major argument for one general theory of life history evolution, rather than a theory as a set of recipes for how to make species-specific models.

Life history invariants are canonically identified from a log-log plot of two life history traits involved in a dimensionless ratio. In such a plot, the slope is expected to equal 1. Consider two life history traits, a and b, and ask whether their dimensionless ratio a/b is a life history invariant. If their ratio is constant (c), a log-log plot with $\ln(b)$ on the x axis and $\ln(a)$ on the y axis

The author is in the Evolutionary Population Biology Group, Utrecht University, Padualaan 8, NL-3584 CH Utrecht, Netherlands. E-mail: g.dejong@bio.uu.nl

would show points on a line defined by $\ln(a) = \ln(c) + \ln(b)$, with a slope of 1 and intercept $\ln(c)$ (see the top figure). The line is the regression line and the intercept can be used to estimate the life history invariant, c. A log-log plot of two traits involved in a life history invariant leads to a slope of 1 with all variation in the dependent variable on the y axis explained by the variable on the x axis (that is, $R^2 = 1$ for an ideal invariant where R^2 of the regression is the proportion of the variation in the dependent variable a explained by the variation in the independent variable b). An empirically determined slope of 1 at high explained variance R^2 has therefore been taken to indicate a life history invariant. This is common experimental logic, but treacherous, as it disregards the potential existence of other ways to arrive at the predicted slope of 1 and very high R^2. If a life history invariant is the only way to arrive at a slope of 1 and very high R^2, then one can conclude from an empirical slope of 1 and very high R^2 that a life history invariant exists.

Many such log-log plots of traits that indicate potential life history invariants exist. Allsop and West (3) presented data on relative body size at sex change for animals ranging from a 2-mm shrimp to a 1.5-m fish. The log-log plot of body size at sex change versus maximum body size showed a slope of 1.05, and all the points were near the regression line, with $R^2 = 0.98$. The life invariant "relative body size at sex change" was perfectly present.

Buston et al. (4) then threw a spanner in the works. Commenting on Allsop and West's data, Buston et al. pointed out that random distributions of both total body size and size at sex change lead to identical properties in a log-log plot as a life history
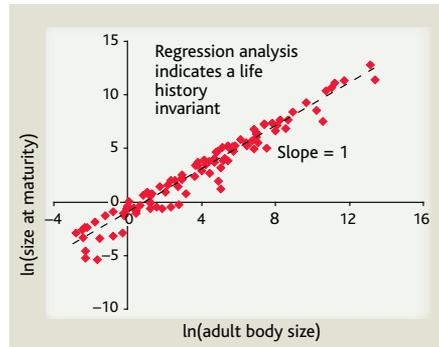
What log-log plots reveal about life histories. The log-log plot shows a life history invariant. Size at maturity seems a constant fraction of adult size for all animals over a body size range from 6×10^{-2} to 6×10^5. The slope equals 1.01 and R^2 equals 0.95. The life history invariant estimated would equal 0.34. The plot has been generated from values that were randomly produced according to Nee et al. (2), indicating the misleading nature of regression analysis.

invariant: a slope of 1 and an R^2 of >0.95. More null models followed (5, 6), using different random distributions of traits. But Nee et al. (2) describe the general rationale of how slopes of 1 at high R^2 arise in log-log plots, independent of the distributions of the traits. The culprit is a variable on the y axis that is a fraction of the x-variable: The plot is of $y = cx$, with $c < 1$. In a log-log plot of cx versus x, a slope of 1 follows automatically. A wide range on the x axis—from rabbit to whale—guarantees a high R^2. The evidence for life history invariants vanishes as the method of finding them evaporates.

Suppose full-grown body size is plotted on the x axis, and size at maturity of the same individual on the y axis [see the bottom figure; (4)]. Size at maturity might be any fraction of full-grown body size, with

fractions $c = 0.1, 0.2, …, 0.9$ in nine different groups of animals. Each animal group has its own relative size at maturity. Relative size at maturity is invariant within each group but varies among groups. All possible combinations of full-grown body size and size at maturity can be found over the nine groups. When data from multiple animal groups are plotted directly, the variance among them is quite apparent. The same data can be depicted in a log-log plot for the total range of body sizes, still distinguishing each animal group. Each group now has its own line $\ln(y) = \ln(c) + \ln(x)$, all with a slope of 1 but each with different intercepts $\ln(c)$, again revealing variation between animal groups. However, if the same data are again depicted on a log-log plot, but without differentiation as to which animal group the data points belong, a single regression line can be drawn over all groups together that now seems to indicate a life history invariant ratio of body size at maturity to full-grown body size over all groups. The regression analysis is therefore misleading.

If life history invariants are important in evolution, we expect them to surface in models that use their component variables. That would validate the idea of invariants, especially if a model restricts them to certain values. Kozlowski (7) modeled growth in animals and optimal body size. In his model and simulation, many life history variables that partake in life history invariants can be evaluated. The slopes in log-log plots of model values are 1 for the proposed life history invariants. Yet very much variation in the simulated traits and their ratios exists, and direct observation of the values will not give the impression of life history invariants. Kozlowski (7) concluded that "Charnov's life history invariants can be
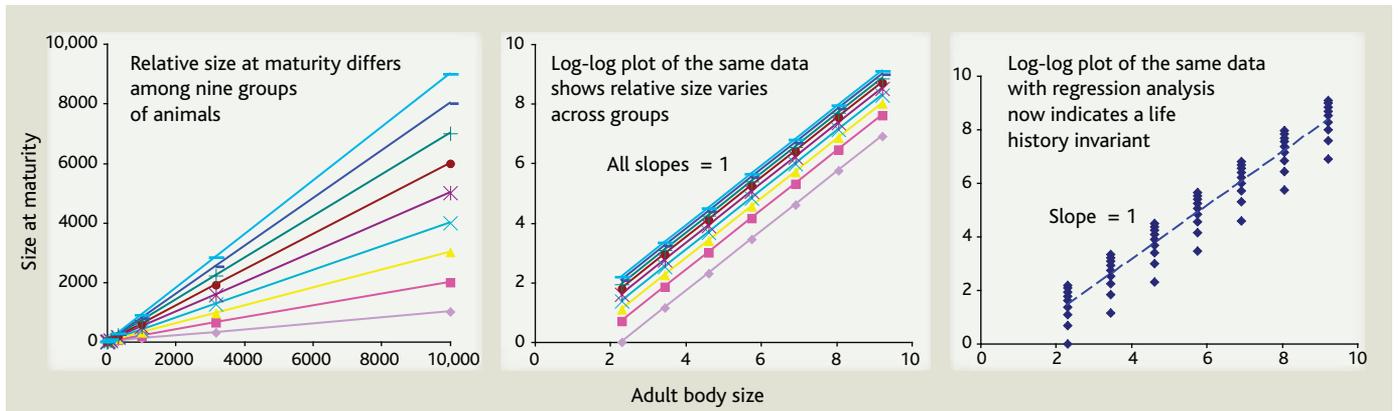
A mirage of invariance. Consider nine groups of animals that differ in whether they mature at large or small size. In group 1, size at maturity equals one-tenth of adult body size; in group 2, size at maturity equals two-tenths of adult body size, and so on. [Adapted from (4)] **(Left)** Size at maturity is plotted as a function of body size for the nine groups and for seven body sizes: 10, $10\sqrt{10}$, 100, $100\sqrt{10}$, 1000, $1000\sqrt{10}$, and 10,000. The lines give $y = cx$ for nine values of c ($c = 0.1, 0.2, …, 0.9$). **(Middle)** The same data are plotted on a log-log plot. The lines are now $\ln(y) = \ln(c) + \ln(x)$, and all lines show a slope of 1 but possess different intercepts. Within each group, the relative size at maturity is invariant, but not across groups. **(Right)** A log-log plot of the same data but without assignment to different animal groups reveals a regression line with a slope of 1, an intercept of −0.88, a high R^2 of 0.92, and a life history invariant of 0.42. The estimated "life history invariant" is actually a complicated way of averaging all nine values for c. Any conclusion that a life history invariant exists is spurious.

called invariants only in the sense that the regression lines between their components have slopes close to +1 or –1."

Life history evolution is not the only field where invariants or universal constants are proposed. The Universal Temperature Dependence of metabolism proposal asserts that the metabolism of all organisms can be described by a single equation (*8*). Scaling laws (as, for instance, basic metabolic rate scale as mass to the power $^3/_4$) are called universal over all life (*9*, *10*). This hankering for universal explanations has been criticized not only on technical grounds (*11*) but also for ignoring biology and the variation between organisms (*12*). Interesting biology might not be in life history invariants but in biological variation.

Consider again the issue of relative body size at sex change. Allsop and West (*3*) collected data on this question and interpreted their log-log plot as showing a life history invariant indicating that a fundamental similarity exists among all animals in the fitness components leading to sex change. However, looking at specific cases of sex change does not strengthen that impression. In both the clown fish and the bluebanded goby, an individual's sex is determined by its rank in the social hierarchy. Among

clown fish, the largest fish of the group is female, the second largest fish is male, and lower ranking group members are queuing for their turn to reproduce (*13*). Among bluebanded gobies, the fish at the top of the hierarchy is male and below him are several breeding females; the group has no non-breeding adults (*14*). In both fish species, the second ranking member in the hierarchy changes sex and starts growing in size when the top brass exits (*13*, *14*). The interesting biology is to identify what determines differences such as those between these two fish species.

This brings us back to species-specific life histories and back to looking at biological mechanisms. If a fundamental similarity does exist among all animals in the fitness components leading to sex change, it has to be shown that relative body size at sex change for both the clown fish and the bluebanded goby can be directly described by similar fitness relations. The model of optimal relative body size at sex change (*15*) must be shown to work by direct estimation of its parameters for both fish species, not by log-log plot.

We should be wary of treating an average across species as an explanatory general life history invariant. That's not to say

that we might not keep searching for invariants that indicate fundamental similarities in the biology of all living organisms. We just need to know for certain how to identify them.

References
1. E. L. Charnov, *Life History Invariants: Some Explorations of Symmetry in Evolutionary Ecology* (Oxford Univ. Press, Oxford, 1993).
2. S. Nee, N. Colegrave, S. A. West, A. Grafen, *Science* **309**, 1236 (2005).
3. D. J. Allsop, S. A. West, *Nature* **425**, 783 (2003).
4. P. M. Buston, P. L. Munday, R. R. Warner, *Nature* **428**, 10.1038/nature02512 (2004).
5. A. Gardner, D. J. Allsop, E. L. Charnov, S. A. West, *Am. Nat.* **165**, 551 (2005).
6. R. Cipriani, R. Collin, *J. Evol. Biol.*, 10.1111/j.1420-09101.2005.00949.x (2005).
7. J. Kozlowski, *Proc. R. Soc. London Ser. B* **263**, 559 (1996).
8. J. F. Gillooly, J. H. Brown, G. B. West, V. M. Savage, E. L. Charnov, *Science* **293**, 2248 (2001).
9. G. B. West, W. H. Woodruff, J. H. Brown, *Proc. Natl. Acad. Sci. U.S.A.* **99**, 2473 (2002).
10. G. B. West, J. H. Brown, *Phys. Today* **57**, 36 (September 2004).
11. J. Kozlowski, M. Konarzewski, *Funct. Ecol.* **18**, 283 (2004).
12. A. Clarke, *Funct. Ecol.* **18**, 252 (2004).
13. P. Buston, *Nature* **424**, 145 (2003).
14. E. W. Rodgers, S. Drane, M. S. Grober, *Biol. Bull.* **208**, 120 (2005).
15. E. L. Charnov, U. Skuladottir, *Evol. Ecol. Res.* **2**, 1067 (2000).

CHEMISTRY

Geometric Phase in Chemical Reactions

David C. Clary

Quantum mechanical effects such as tunneling through a classically impenetrable potential energy barrier have long been known to occur in chemical reactions (*1*). More subtle quantum effects can also arise for reactions in which two different electronic states touch (that is, coincide in energy) to produce a conical intersection (see the figure). An example is the geometric or Berry phase, which refers to a change in sign of an electronic wave function when nuclei of atoms involved in the reaction complete an odd number of loops around the conical intersection (*2–4*). The effect of the geometric phase on the energy levels of bound-state molecules is well understood (*5*). However, the conditions under which the geometric phase effect can be detected for

chemical reactions are less certain. Studies of this effect have largely been directed at the simplest chemical reaction, $H + H_2 \rightarrow H_2 + H$, which serves as the benchmark for
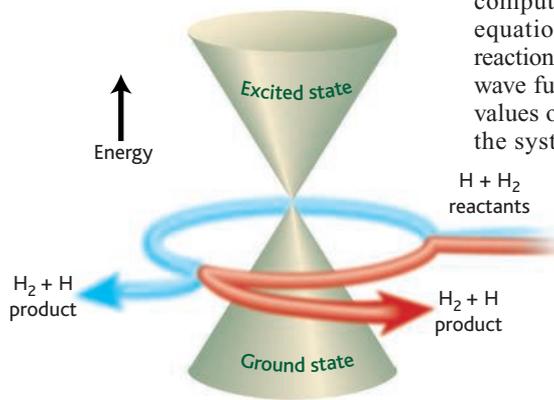
Chemical topology. Conical intersection shown in plot of energy versus two reaction coordinate dimensions with direct (red) and looping (blue) reaction paths. The cones correspond to the upper excited-state and lower ground-state potential energy surfaces.

definitive experimental and theoretical studies of reaction dynamics. On page 1227 of this issue, Juanes-Marcos *et al.* (*6*) provide a novel topological argument to show when the geometric phase is likely to be observable in this hydrogen exchange reaction and also clarify the findings of previous calculations.

To understand chemical reactions, theorists solve the Schrödinger equation for the electrons to calculate potential energy surfaces on which the nuclei move. These surfaces are then used in quantum dynamical computations that solve the Schrödinger equation for the nuclei taking part in the reaction at different energies (*7*). The nuclear wave functions are calculated for different values of the total angular momentum J of the system of three hydrogen atoms, and these partial wave functions are summed to produce quantities that can be observed in molecular beam experiments such as the angular distributions of the $H_2 + H$ products. These quantum dynamical calculations can be done with time-independent or time-dependent theory. One set of time-independent quantum dynamical calculations on an accurate potential energy surface suggested that the geometric phase effect might be

The author is in the Department of Physical and Theoretical Chemistry, University of Oxford, South Parks Road, Oxford OX1 3QZ, UK. E-mail: david.clary@chem.ox.ac.uk