

low collision energies and negligible at higher energies. Experiment finds the opposite. This disagreement stands in contrast to results reported recently for the sibling reaction $F/F^* + D_2 \rightarrow DF + D$, where theory and experiment both find a small but significant effect at low collision energies and a negligible effect at higher energies (9).

The probability for a nonadiabatic, spin-orbit “hop” depends on both the energy difference between the two spin-orbit potentials (illustrated in the figure for $Cl/Cl^* + H_2$) and the magnitude of the spin-orbit coupling energy. If the two become comparable or if the latter exceeds the former, the “hop” probability increases. The report by Garand *et al.* pro-

vides new information on the likelihood of this nonadiabatic “hop” and validates the reliability of theoretical simulations.

Significant non-Born-Oppenheimer spin-orbit effects have also been reported for the reaction of S/S^* with H_2 (10, 11). As the collaborative work by Garand *et al.* shows, such non-Born-Oppenheimer effects continue to be assessed most effectively by joint theoretical-experimental research. The excellent agreement between theory and their experiment suggests that the reaction of Cl^* with H_2 is currently reproduced better by theory than experiment. New molecular beam experiments should resolve the disagreement.

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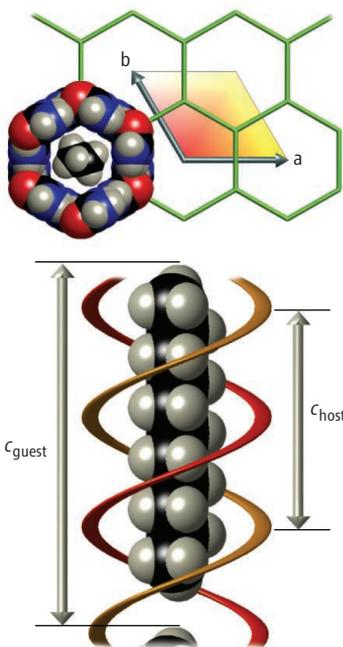
CHEMISTRY

A Phase Transition Hidden in Higher Dimensions

Philip Coppens

Our knowledge of the molecular solid state has greatly increased in recent years, driven by improvements in x-ray structure determination. Solids containing several different molecular components are especially interesting to chemists and materials scientists. Such supramolecular crystalline solids exhibit an almost infinite variety, which can be exploited by synthesis of novel materials with desirable properties (1–3). In addition, these solids can also form inert molecular frameworks with cavities in which chemical reactions can be studied (4).

When two different types of molecules, A and B, cocrystallize and the A-A and B-B interactions are strong, two parallel structures may occur in a single crystal, each with its own periodicity (i.e., distance over which the structure repeats) (5). However, because the two structures are intertwined, they are not fully independent, each being modulated by the interactions between the A and B mole-



Superspace structure. (Top) The structure of urea-nonadecane viewed along the column direction (*c* axis). The hexagons represent the host (urea structure). **(Bottom)** View perpendicular to the columns. The hydrogen-bonded urea molecules are represented by the helices. The orientation of the guest molecules is that of the low-temperature structure; a small distortion of the hexagons that occurs on cooling through the transition at 149 K is not shown. Red, oxygen atoms; black, carbon; gray, hydrogen. Toudic *et al.* discovered a phase transition that essentially affects the interaction between the two structures coexisting in the solid rather than the individual structures. [Adapted from (6)]

cules (that is, the periodicity of one is imposed on the other). On page 69, Toudic *et al.* report an unprecedented new type of phase transition in which the periodicity of the interaction changes but each of the component structures retains its original repeat (6).

In the *n*-alkane-urea solid studied by Toudic *et al.*, the linear alkane molecules are embedded in a columnar matrix of hydrogen-bonded urea molecules that form a honeycomb-like network with a channel diameter of about 5.5 Å (see the figure, top panel) (7). Because the length depends on the number of carbon atoms in the alkane, the repeat along the channel direction (the *c* direction in this case) in general differs from that of the urea matrix and is described by a “misfit” parameter, which is the ratio of the two repeats, c_{host} and c_{guest} (see the figure, bottom

panel). When the misfit parameter does not correspond to the ratio of two simple integers, the structure is said to be incommensurate. In this case, the crystal as a whole is no longer periodic.

The periodicity can be recovered, however, by a mathematical construction using a virtual superspace of $3 + i$ dimensions, where i (≤ 3) is the number of directions in which the two components have different periodicities (5, 8). Thus, for a column structure as exists in the *n*-nonadecane/urea crystals studied by Toudic *et al.* with a periodicity different in the columnar direction for the urea (host) and nonadecane (guest) columns, the proper superspace has four dimensions. As a result, accounting for all the features in the diffraction pattern of such a composite intergrowth structure requires four indices, with the usual Miller indices h, k, l replaced by the set h, k, l, m . Miller indices are the conventional way to denote the planes and directions in a crystal lattice, and thus the reflections caused by these planes; when new peaks appear that cannot be explained by the usual set, additional indices are needed.

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When the c axis is the column axis, as is the case for nonadecane/urea, the average structure of the urea (the A component), without the imposed modulation, is described by the $hk0$ reflections, and the average structure of the alkane (the B component) by the $hk0m$ reflections, whereas the remaining $hkml$ reflections are due exclusively to the mutual interaction between the two lattices. This implies that lattice A imposes a distortion on lattice B with the A periodicity, and vice versa.

At temperatures above 149 K, all nonadecane columns in the crystal distort in an identical way. However, below this temperature, the extra $hkml$ reflections that appear in the diffraction pattern show that the relative modulation of the host and guest lattices alternates from channel to channel in the a -axis direction (see the figure, top panel), even though the periodicity of the average structures of the host and the guest in this direction does not change, as indicated by the absence of additional $hk0$ and $hk0m$ reflections. This does not rule out small structural changes in the mean structures, but if they occur they

must have the same periodicity perpendicular to the column direction as at temperatures above the transition; otherwise, extra reflections would occur. This is most unusual, and below a second transition at 129 K those extra reflections indeed appear, indicating that the changed repeat of the distortion now also occurs in the mean structures. Such a transition, which only affects the mutual interaction, can only be described properly in super-space, even though the physical reality is obviously three-dimensional.

The n -alkanes are not the only species that can be encapsulated in the urea framework (9–12), and many other multicomponent composite structures are known, including minerals, extended inorganic structures, and other organic and organometallic solids (5, 8, 13, 14). Can the hidden phase transition be reproduced in other incommensurate materials? How do the electronic, spectroscopic, magnetic, ferroelastic, and transport properties of this type of material change when such a “hidden” intermediate phase is formed? Obviously, a great deal of work is needed to answer such questions, but the recent tremen-

dous advances in our understanding of the organic solid state and its applications warrant further work that may reveal important new properties.

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GENETICS

Functionally Degenerate— Y Not So?

William R. Rice and Urban Friberg

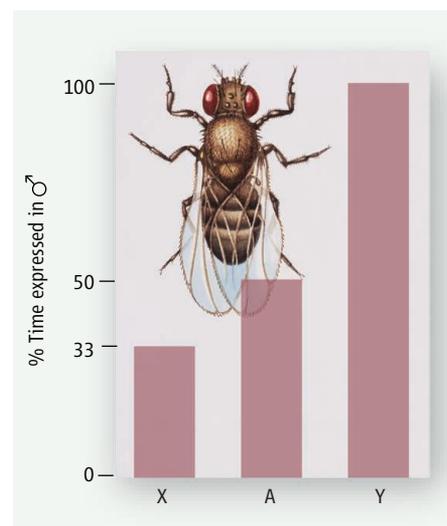
Genetic and theoretical studies of Y chromosomes have led to the conclusion that they evolve to become functionally degenerate. For example, in the fruit fly *Drosophila melanogaster*, a century of genetic research on its Y chromosome indicates that it codes for few traits besides a small number of male fertility factors (1). On page 91 of this issue (2), Lemos *et al.* change this perception of functional paucity by showing that the Y chromosome of *D. melanogaster* regulates the activity of hundreds of genes harbored on other chromosomes.

The theoretical rationale for the evolution of a degenerate Y chromosome is based on its lack of recombination, the process by which corresponding DNA segments are exchanged between homologous chromosomes, thus producing new genetic combinations. When

a primitive Y chromosome stops recombining, the efficiency of natural selection drops substantially because selection cannot act independently on different Y-linked mutations. This slows the accumulation of beneficial mutations and speeds that of mildly deleterious ones. As a consequence, the fitness of a Y-linked gene wanes relative to its X-linked homolog, and it can ultimately become silenced by persistent accumulation of deleterious mutations—a result made possible because of redundancy to its X-linked homolog. Gene silencing can also be selectively favored when a Y-linked null mutation (one that results in the absence of a gene product) increases fitness because it does not interfere with the expression of its fitter X-linked homolog.

Lemos *et al.* now challenge this evolutionary view of a continually decaying Y chromosome. The authors collected Y chromosomes from *D. melanogaster* spanning different latitudes and subspecies across Africa and North America so as to maximize functional polymorphism, and then substituted each one for

The Y chromosome of the common fruit fly has few functional genes but regulates the expression of hundreds of autosomal and X-linked genes.



Gene expression in males. A mutation in *D. melanogaster* that influences gene expression in males experiences selection in the male fly most often when it is Y-linked (Y), least often when X-linked (X), and at an intermediate level when located on the autosomes (A).

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