

K. Tsumoto, Mie Univ., Tsu). The snag is, of course, that these systems contain components taken from contemporary cells, and are far from being self-sufficient.

Replication can also happen in liposomes. RNA from the phage Q β (a virus infecting bacteria) can be incorporated in liposomes (T. Yomo) and be replicated by a replicase enzyme provided by the experimenter. A common by-product of RNA replication is the advent of smaller, faster-replicating mutant RNA molecules, which take over the population. This apparently failed to happen in these experiments, but the reason is debatable. Maybe self-association of template and copy strands reduced competition to such an extent that coexistence is guaranteed (G. von Kiedrowski, Univ. Bochum). Or perhaps the efficient mutants simply failed to arise owing to the small number of replication cycles (E. Szathmáry).

Experimental work is increasingly being complemented by computational investigations. For example, it is possible to account for the growth and fission of compartments in simulations of molecular-assembly dynamics (T. Ikegami, Univ. Tokyo). On the genetic side, the origin of heredity was demonstrated in a simulated system of cross-catalytic autocatalytic networks (K. Kaneko, Univ. Tokyo). Kaneko argued that 'minority control' is a possible origin of heredity in a

bag of genes that constitutes a primordial genome, in that genes with a lower copy number have a more decisive influence on the protocell's simulated behaviour. It is difficult to assess the importance of this finding, as there is no example of the particular network modelled. But the idea may prove helpful in attempts to produce more realistic constructions.

According to the 'composome' model, in which micelles or vesicles are formed from amphiphilic compounds — those having one end that is hydrophilic and the other hydrophobic — there is the prospect of constructing a 'lipid world'. Here, a hereditary component arises from alternative autocatalytic sets of lipids (D. Segré, Harvard Med. School).

Clearly, there is a divide between the top-down and bottom-up approaches, and between theoretical and experimental investigations. In the future, for example, one would like to see more realistic models of the primordial genome and, conversely, an experimental approach to the lipid world. An aim in the coming years will be to bridge those gaps — hence the great value of meetings such as this. ■

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reactions and its limitations are known, the situation for reactions at surfaces is much less clear.

In their experiments, White and colleagues¹ prepared nitric oxide molecules in highly excited vibrational states, so that the atoms were subjected to large motion, close to the limit at which the molecules will break up. The excited molecules were scattered from a specially prepared metal surface from which electrons could escape easily. A detector above the surface picked up any electron emission. The experiment's main observation was that when the vibrational energy of the incident nitric oxide molecule exceeded the binding energy of electrons in the surface, electrons were directly emitted from the surface. This finding points to a coupling between nuclear motion and electronic excitation, and therefore indicates that the Born–Oppenheimer approximation is invalid in this case.

The research by White *et al.* extends work in which electronic excitation was produced at metal surfaces by bombardment with various gas-phase species (mostly atoms such as oxygen, hydrogen and nitrogen, high-kinetic-energy rare gases and some molecules)^{2,3}. In one of these experiments³, electrons in the metal tunnelled through a potential-energy barrier to a semiconductor substrate as a result of the bombardment. The charge flow induced in the semiconductor as a result of the tunnelling electrons was termed a 'chemicurrent', to reflect the chemical cause of the electronic excitation.

Although these previous results also point to a breakdown of the Born–Oppenheimer approximation, the situation is somewhat harder to interpret because the electronic excitation is most probably mediated by 'phonons' — vibrational excitations in the substrate itself. White and colleagues' experiment bypasses this poorly defined intermediate step.

Experiments of the type presented by White *et al.* (and the closely related chemicurrent work³) serve as a warning over the widespread use of potential-energy surface models, and should act as an impetus for modifying the conceptual framework used in surface chemistry. There have been attempts to include electronic excitation in theoretical models, but the task is a daunting one and has been limited by a lack of clear experimental findings. The new experiments provide well-characterized results to guide further theoretical development. ■

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Surface chemistry

Approximate challenges

Greg Sitz

There is growing evidence that the usual approach to modelling chemical events at surfaces is incomplete — an important concern in studies of the many catalytic processes that involve surface reactions.

To describe all the transformations through which a molecule must go during a chemical reaction is a daunting task. The intermediate transition states of a reaction are hard to examine directly, and theory is needed to obtain a full understanding of all the relevant interactions. In 1927, Born and Oppenheimer formulated an 'approximation', which greatly simplified such calculations. Their theory has been crucial to advances in theoretical and chemical physics. It is therefore of great interest when the Born–Oppenheimer approximation breaks down, which may be the case particularly for reactions that take place at surfaces. On page 503 of this issue¹, Jason White and colleagues provide the clearest example to date of such a case.

The break-up of a chemical bond involves a large bond vibration — in other words, a large relative motion of the two atoms that make up the bond. Rather than taking into account all the interactions

involved, the Born–Oppenheimer approximation treats the motion of atomic nuclei separately from electronic excitation. This is justified by the fact that nuclei are much heavier than electrons and move more slowly. Therefore — it is assumed — when nuclei move, as they do during the formation or breaking of a bond, electrons will simply readjust quickly.

Many theoretical methods use this approximation, and solve the Schrödinger equation (the fundamental equation that describes all such interactions) in terms of electrons moving in slowly changing, stationary frameworks of nuclear arrangements. The result can be visualized as a 'potential-energy surface', which plots the solutions of the Schrödinger equation as a function of a molecule's changing structure during a reaction — a popular method for describing chemical reactions. However, although the Born–Oppenheimer approximation has been widely tested for gas-phase