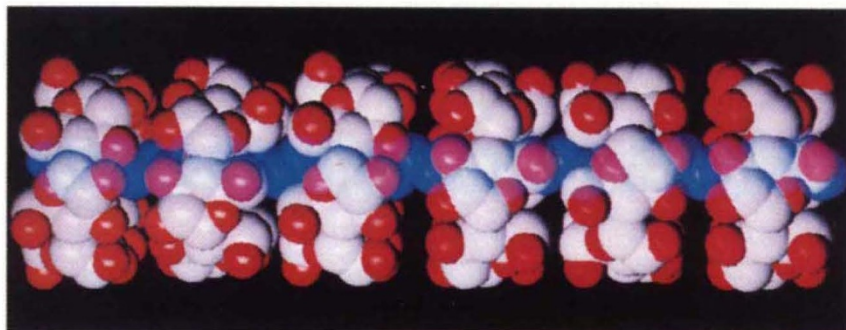


Picking up the chemical thread



THREADING the molecular needle — passing a linear molecule through a cyclic one — is an old trick: 'hooplane', an alicyclic ketol on a hydrocarbon axle, was fashioned in 1967 by researchers at Syntex Research in Palo Alto, and the term 'rotaxane' for these rotor-and-axle assemblies dates back to Gottfried Schill's similar construction in 1980. But whereas these were the products of conventional ring-closure syntheses, the principles of supramolecular host-guest chemistry are now making the molecular gymnastics of rotaxane synthesis far easier. The extent to which this is true should be apparent from the supramolecular complex described by A. Harada *et al.* on page 325 and pictured above, which contains twenty or more cyclodextrin rotors on a strand of polyethylene glycol.

A wide variety of threaded supermolecules has been developed in recent years, many by Fraser Stoddart's group and Jean-Pierre Sauvage and colleagues. Stoddart has used linear and cyclic paraquat-hydroquinone complexes to create the 'molecular shuttle', a rotaxane in which the rotor can switch between two docking points on the thread, and a range of catenanes, in which the ends of the thread are joined. A single bead threaded on a long loop with several docking points constitutes a 'molecular train' that can circle around the line until cooled to a standstill. Stoddart has made the whimsical suggestion that several beads on a strand might constitute a 'molecular abacus'.

The complex synthesized by Harada *et al.* shows that this is easier than might be supposed. The components are simply mixed in aqueous solution, and the resulting complex is capped at each end with 2,4-dinitrofluorobenzene. Diffraction and spectroscopic studies of the crystalline form confirm that it is a 'molecular necklace'. The polymer thread is about 266 Å long, and the cyclodextrins occupy only about 160 Å or so of this length — Harada *et al.* suspect that each sticks closely to its neighbours via hydrogen bonding when in the solid state, but that the molecular beads are mobile when the complex is in solution. **P.B.**

to vibrate around their surface sites. Energy and momentum conservation laws, together with the symmetries of the ground and excited states, yield distinct selection rules for what transitions are possible. The loss spectra and their dependence on scattering angles and adatom coverage can be used to obtain details on the nature of the adsorbed particles.

A simple measure of the importance of quantum effects for adsorbates can be obtained by comparing two competing effects. On the one hand, the more strongly the adsorbate prefers a particular site on the surface, the greater the potential-energy barrier separating that site from its neighbouring equivalents. On the other hand, the more tightly confined an adsorbate is, the greater is its quantum-mechanical zero-point motion about its equilibrium position. In the case of conduction electrons in a crystal, the zero-point energy overwhelms the binding energy, and the electrons are free to move throughout the material.

Cole *et al.* pointed out several years ago³ that in the case of physisorbed (weakly bound) helium on graphite, the zero-point energy is greater than the potential barriers and the resulting film can assume quantum effects. Although hydrogen is much more strongly bound on metals (chemisorbed), its mass is also four times smaller, so that its zero-point energy is raised proportionately. So quantum behaviour is not totally unexpected in this case. In fact, hints of unusual (that is, nonclassical) properties have accrued over the years.

Electron-diffraction experiments⁴ have revealed substantial disorder for low-coverage hydrogen phases, indicative of large adatom mobility. Surface diffusion monitored by field-emission studies⁵, shows anomalous behaviour suggestive of large tunnelling effects. Electron-energy-loss spectra and ion-scattering experiments were also difficult to reconcile with a picture of a classical particle vibrating around its equilibrium position on the surface.

Intrigued by these results, my col-

leagues and I performed quantitative calculations for the proton band structure on various nickel surfaces, discussing its consequences for diverse physical phenomena^{6,7}. These calculations, which allow for the screening of the proton charge by the metallic electrons, show substantial delocalization of the adatoms (Fig. 1, preceding page). In particular, we pointed out that the proper analysis of electron energy-loss spectra should be made in terms of the excitation of protons between different extended bands, not in terms of the vibrations of atoms tied to individual sites on the surface.

Astaldi *et al.* performed their experiments on the (110) face of copper. For this surface, expected to be qualitatively similar to Ni(110), the proton potential is such that hydrogen moves mainly along essentially one-dimensional troughs in the [110] direction. The spectra (Fig. 2) were taken for electrons scattering specularly in this direction, with the primary energy of 2.5 eV. The loss peaks at 79 and 118 meV correspond to dipole-allowed excitations of the surface hydrogens. The important observation is the peculiar coverage- and isotope-dependence of the spectra, which provide spectroscopic evidence for the gradual transition from quantum delocalized behaviour at low coverages to localized, ordered adatom structures at high coverages. With increasing hydrogen coverage, the mobile 'liquid' of adsorbed protons forms a highly correlated system with very strong short-range repulsive interactions. Astaldi *et al.* show that their experiments are consistent with the quantum picture by analysing it in terms of a one-dimensional model hamiltonian. The peak structure as well as the decrease of the linewidth with coverage can be explained.

The quantum motion of hydrogen on surfaces can have interesting consequences for various processes. There is already evidence for nonthermal mobility of hydrogen at low temperatures, both in bulk crystals and on surfaces. The proton motion has a component of quantum-mechanical tunnelling through potential barriers instead of mere classical hopping. This in turn may influence such surface reactions (as in catalysis) where hydrogen diffusion is an important reaction step: the adatoms can be hot in the sense that their mobility is much larger than one might expect with simple thermal motion.

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