SPECTROSCOPY

Spin-off for solid-state studies

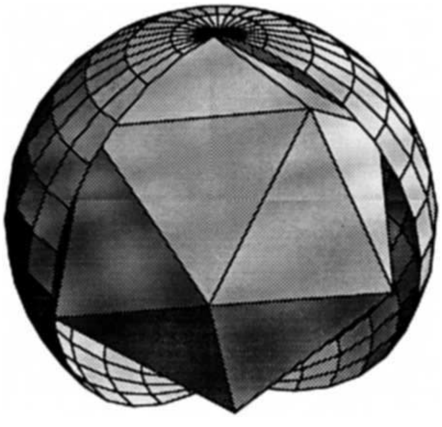
Jacek Klinowski

EXPERIMENTS reported by Wu *et al.* on page 550 of this issue[1] have resulted in the best-resolved ^{27}Al nuclear magnetic resonance (NMR) spectra yet measured in the solid state, bringing together recent developments in synthetic inorganic chemistry, catalysis, physics, group theory and crystallography and opening up exciting perspectives for the future. The authors have studied the industrially important aluminophosphate zeolite VPI-5, a molecular sieve containing channels which comprise 18-membered rings of tetrahedrally coordinated aluminium and phosphorus atoms, using the NMR technique of double rotation recently developed by Pines (one of the present authors) and colleagues. The results demonstrate the ability of this technique to yield unique structural information on this mineralogically important element.

Wilson *et al.*[2] discovered in 1982 that under certain conditions aluminium phosphate can form open crystalline structures containing systems of channels and cavities of molecular dimensions, similar to those of aluminosilicate zeolites. The $AlPO_4$ molecular sieves are built from alternating AlO_4 and PO_4 tetrahedra. Some of them have the framework topologies of known zeolites, but many have novel structures. $AlPO_4$ sieves are synthesized from gels containing aluminium, phosphorus and at least one organic structure-directing template. Incorporation of a silicon source into an aluminophosphate gel results in the formation of silicoaluminophosphates (SAPO), and the incorporation of a metal M (such as Mg, Mn, Fe, Co or Zn) into $AlPO_4$ and SAPO gives the MAPO and MAPSO sieves respectively[3]. Some of these have high Brønsted acidities and thus a considerable potential to act as catalysts as well as media for ion exchange and molecular separation.

Until recently the largest channels in any molecular sieve were based on 12-membered rings of tetrahedral atoms and were invariably less than 10 Å wide. In 1984 Smith and Dytrych[4] described a hypothetical series of molecular sieves, one of which had channels 12 Å in diameter. The article aroused little interest, however, until Davis *et al.*[5] described the preparation of a crystalline aluminophosphate, VPI-5, with the precise structure predicted by Smith and Dytrych. The new development caused much excitement, especially as related SAPO and MAPO materials could also be prepared. They have possible applications in the pharmaceutical industry for the purification of large molecules and in petroleum refining, where they could be used to crack very large hydrocarbons which are at present discarded as bottom-of-the-barrel residue. VPI-5 can be hydrated reversibly, and this is the process that Wu *et al.*[1] have now examined.

NMR spectra cannot normally be measured in solids in the same way that they are obtained routinely in liquids. This is because of the presence in solids of net anisotropic interactions, which in liquids are averaged by the rapid thermal molecular motions. Although molecular motions in certain solids are sufficiently unconstrained for NMR spectra to be obtained without resorting to special techniques, in general conventional NMR of the solid state yields not sharp spectral lines but a broad hump which conceals most of the interesting information. Individual lines corresponding to nuclei of the same species in different magnetic environments, for example, cannot be resolved.



Euclid's last problem — inscribing an icosahedron in a sphere: a starting point for ^{27}Al NMR.

Andrew *et al.*[6] and Lowe[7] came up with a partial solution to this problem. They showed that when powdered samples of many solids are spun rapidly about an axis inclined at an angle of 54° 44′ 8″ (the so-called 'magic angle') to the direction of the magnetic field, the resolution of the spectrum improves dramatically: the broad line is reduced to a narrow peak. Magic-angle spinning (MAS) imposes an average axial symmetry on an otherwise asymmetric environment. The magic angle (at which the second-order Legendre polynomial $3\cos^2\theta - 1$ equals zero) is the angle between the body diagonal of a cube and each of its faces. The most common magnetic interactions, such as the chemical-shift anisotropy and dipole–dipole coupling, can all be represented in terms of second-rank spherical harmonics, so to average these interactions we do not need to move the sample over a complete sphere (as occurs naturally in liquids), but only to impose cubic symmetry by spinning around the magic angle.

MAS works very well with spin-half nuclei such as ^{13}C, ^{15}N, ^{29}Si and ^{31}P, but is less successful with the so-called quadrupolar nuclei, such as ^{11}B, ^{17}O, ^{23}Na and ^{27}Al, which have an asymmetric distribution of nuclear charge. Although MAS does reduce the linewidth of NMR spectra for the latter nuclei, this is often insufficient for the spectra to be fully interpreted. In particular, ^{27}Al MAS NMR in solids has in the past been something of a disappointment in comparison with, for example, ^{29}Si, which gives well resolved MAS spectra. This shortcoming is unfortunate because aluminium is the second most abundant element in the Earth's crust, and over half of all known minerals are silicates and aluminosilicates. To obtain high-resolution spectra of this nucleus is therefore a highly worthwhile goal; so the success of Wu *et al.*[1] will come as welcome news to many chemists, mineralogists, metallurgists and materials scientists.

Quadrupolar nuclei interact not only with the magnetic field in which the sample is immersed but also with the electric-field gradient; the combination of both effects results in an anisotropy that can no longer be removed by magic-angle spinning alone. Group theory indicates that the quadrupolar interaction transforms as a fourth-rank spherical harmonic, and is averaged by motion corresponding to icosahedral symmetry. The icosahedron is a better approximation to a sphere than is a cube (see figure), and the task of inscribing an icosahedron inside a sphere is the famous 'Euclid's last problem' (A. Mackay, personal communication). Icosahedral symmetry cannot be achieved by rotating the sample about a single axis[8]. Pines and his group, together with Samoson and Lippmaa, realized that there were two different ways of implementing the symmetry of an icosahedron. One, which they call dynamic angle spinning (DAS), is to rotate the sample sequentially about two different axes, inclined to the magnetic field at angles of 37.38° and 79.19°: the sample is rotated about the first axis, reoriented, rotated about the second axis and so on. DAS NMR probeheads are already commercially available. The other possibility is double rotation, in which the sample is spun simultaneously about two axes, the first inclined to the magnetic field at the magic angle and the second at the angle given by the zero of the fourth-order Legendre polynomial. This polynomial is $35\cos^4\theta - 30\cos^2\theta + 3$, one of the solutions being 30.6°.

To achieve double rotation in practice is an awesome engineering task. The spinning rotors are driven by a flow of gas, which must be delivered to one rotor embedded in another. And if the inner rotor (which contains the sample) is to spin freely, its net angular momentum must lie exactly along the axis of the outer rotor. The first DOR experiments in 1988 showed that the widths of the peaks are greatly reduced in comparison with MAS, being little greater than those measured in liquids. The greater spectral resolution is accompanied by an improvement in sensitivity (that is, the NMR-active nuclei can be more dilute). It is interesting to note (A. Mackay, personal communication) that the principle of DOR is similar to that of the Gandolfi camera[9,10], used by crystallographers to obtain X-ray powder patterns of very small single crystals, which also rotates about two independent axes. There is also an intriguing link between DAS/DOR and the icosahedral quasicrystals predicted by Mackay[11] and subsequently prepared[12,13].

DAS and DOR have considerable potential for the study of minerals, heterogeneous catalysts, zeolites, glasses, polymers and superconductors. For example, the ^{17}O DOR NMR spectrum of diopside[14] clearly reveals the three crystallographically inequivalent oxygen sites in this mineral. Wu *et al.*, using Pine's apparatus, now provide the important extension of DOR to ^{27}Al. Whereas the conventional ^{27}Al MAS NMR spectra of VPI-5 feature a broad single signal corresponding to tetrahedrally coordinated aluminium, the DOR spectra contain a wealth of structural information. We learn that, although the structure of VPI-5 calls for only two crystallographically distinct sites for Al (or P), hydration of the material creates further structural inequivalence. The various inequivalent aluminium atoms in the structure (as many as eight can be monitored simultaneously in these astonishingly well-resolved spectra) evidently differ in their affinity for water. Furthermore, unlike the ^{17}O and ^{23}Na DOR spectra, there are no spinning sidebands, because of the relatively small anisotropy involved. And last but not least, the results provide interesting information on the chemical environment of water inside the molecular sieve. □

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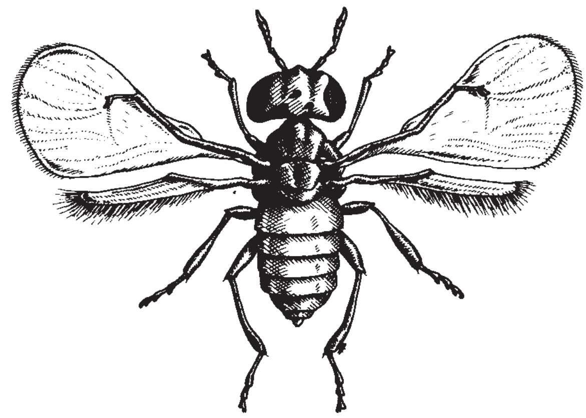
EVOLUTION

Antibiotics cure asexuality

Laurence D. Hurst, H. C. J. Godfray and Paul H. Harvey

EGGS contribute cytoplasm to embryos and sperm do not. Extra-nuclear genetic material in males is therefore at an evolutionary dead end. As a consequence, genes in the cytoplasm that cause an egg or embryo to become female will be favoured by selection; for example mitochondrial DNA that finds itself in a male will not be passed on to the next generation, and any mutant in that DNA which causes a mammalian egg to be fertilized by an X-bearing sperm will be favoured, until countered by modifiers on nuclear genes which favour a 50:50 sex ratio. Cytoplasmic elements bias sex ratios through several mechanisms[1–4]. Now, Stouthamer, Luck and Hamilton[5] reveal another — extraordinary — one. A genetic factor in the cytoplasm of some female wasps converts presumptive male eggs into female ones; what is more, the genetic factor may be a microorganism because, after treatment with antibiotics, male-to-female sex change can be 'cured' and the females produce males.



David Nash

Parasitoid wasp of the genus *Trichogramma* — the wasp parasitizes the eggs of the ant-tended lycaenid butterfly, *Jalmenus evagoras*.

Viable populations from which males are absent must reproduce asexually. Such asexual reproduction is reasonably common in the Hymenoptera, the group that contains the social ants, bees and wasps, as well as non-social wasps, parasitoid wasps and saw flies. Parasitoids of the genus *Trichogramma* are minute wasps (about 1 mm in length) that parasitize the eggs of other insects, particularly moths (see figure). A large number of *Trichogramma* species are known, some of which reproduce wholly sexually or asexually whereas others are composed of mixtures of sexual and asexual strains. Stouthamer and colleagues[5] discovered that if females of asexual species or strains are allowed to feed on honey containing certain antibiotics, or are kept at elevated temperatures (over 30 °C), they begin to produce males and females just as sexual strains do. If very small doses of antibiotic are prescribed, or if the temperature is lowered, then the strains revert to asexual reproduction. But, if antibiotic treatment is continued over several generations then the population becomes permanently sexual and does not revert after cessation of treatment.

One likely explanation for these results, as previously suggested by Legner[6], is that the expression of asexuality is controlled by a cytoplasmically inherited microorganism. This microorganism is destroyed by antibiotics and either destroyed or inhibited by high temperatures. Evidence for the cytoplasmic inheritance of asexuality and sex change also comes from breeding experiments in which sexual females, caught in the wild, are crossed with males derived from asexual strains through heat treatment. The strains remain sexual even when, after many generations of backcrossing, most of the nuclear genome is derived from asexual strains. Stronger evidence for the influence of a microorganism would require the identification of an organism present in asexual individuals that is absent from sexual females. The spectrum of antibiotics that can cause a switch in reproductive behaviour suggests that the organism is a prokaryote. Stouthamer and his colleagues at the University of Rochester say that their preliminary, unpublished studies have revealed a candidate bacterium which may be the causal agent.

Is asexual reproduction induced by microorganisms a curiosity of wasps of the genus *Trichogramma*, or is it more widespread? There are numerous reports of asexual populations of various hymenopterans in both laboratory and field being rendered sexual by exposure to high temperatures. Subsequent exposure to milder temperatures typically allows reversion to asexuality[5]. According to Stouthamer (personal communication), when asexuality is curable by high temperature, it is also curable by antibiotics; and, importantly, when organisms maintain asexuality at high temperature, antibiotic treatment is equally ineffective. This is circumstantial evidence but it does point to the phenomenon being widespread within the group.

Asexuality induced by microbes has been suspected amongst other groups. *Lecanium cerasifex*, a soft-scale homop-