Olfactory Design: Smell and Spectroscopy

Our sense of smell is actually a complex system designed to detect thousands of chemicals. It helps warn us of danger, for example, rotting food — we can sense one component of rotten meat, ethyl mercaptan, at a concentration of 1/400,000,000th of a milligram per litre of air.[1] Smell also helps us distinguish types of foods and flowers. The sense of smell is actually responsible for most of the different 'tastes' of foods. In many animals, this sense is even more important than in humans — it helps bees find nectar, for example.

The nose contains millions of receptors, of 500-1,000 different types. They are in the yellow **olfactory epithelium,** that covers about 2.5 cm^2 on each side of the inner nose. The different types of receptors are proteins folded so a particularly shaped odour molecule can dock. Each receptor is coupled to a **g-protein.** When the odour molecule docks, the g-protein is released (see Figure 1). This sets off a second messenger to stimulate a neuron to send a signal. This is transmitted by olfactory nerve fibres which enter either of two specialized structures **(olfactory bulbs),** stem-like projections under the front part of the brain. They sort the signals, and transmit them to the brain for processing.[12]

Recently, Luca Turin, a biophysicist at University College, London, proposed a mechanism where an electron tunnels from a donor site to an acceptor site on the receptor molecule, causing it to release the g-protein. Tunnelling requires both the starting and finishing points to have the same energy, but Turin believes that the donor site has a higher energy than the receptor. The energy difference is precisely that needed to excite the odour molecule into a higher vibrational quantum state. Therefore when the odour molecule lands, it can absorb the right amount of the electron's energy, enabling tunnelling through its orbitals[3] (see Figure 1 again).

This means the smell receptors actually detect the energy of vibrational quantum transitions in the odour molecules, as first proposed by G. M. Dyson in 1937.[4] This energy decreases with increasing mass of the atoms, and increases with increasing bond strength. It also depends on the symmetry of the molecule. For a diatomic molecule,[5] the fundamental transition energy is:

$$E = \hbar(k / \mu)^{1/2}$$

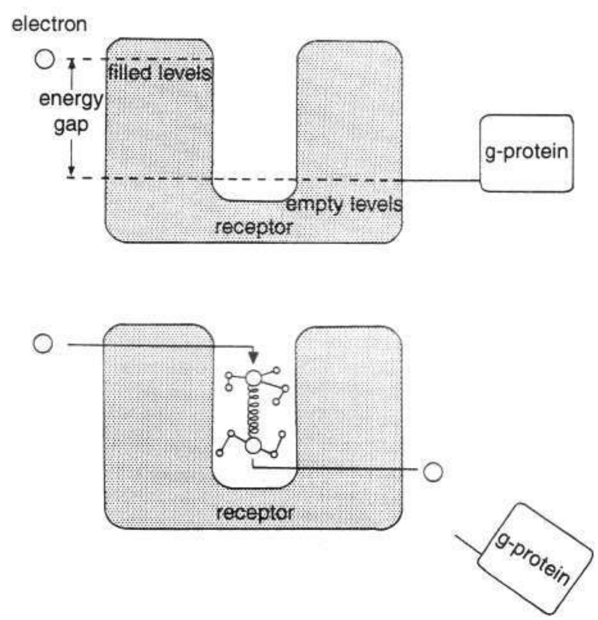

Figure 1. *Analogy of a nose bay —a docked odorant allows an electron to tunnel through the receptor to release a signal to the brain* (top: *before,* bottom: *after).*

where $\hbar$ is $h/2\pi$; h is Planck's constant; k is the force constant of the bond; and μ is the reduced mass, which is related to the masses of the two atoms by:

$$\mu = m_1 m_2 / (m_1 + m_2)$$

A transition can sometimes be caused by incident electromagnetic radiation of the right frequency (υ). This is related to the energy by:

$$E = h\upsilon$$

Vibrational energy and the corresponding radiation is normally measured in wavenumbers, the reciprocal of the wavelength, related to energy by:

$$\tilde{\upsilon} = E/hc$$

As this energy is in the infrared region, **infrared absorption spectroscopy** is a common tool for measuring vibrational energies and bond strengths (together with the complementary technique of **Raman spectroscopy).**

This means certain groups of atoms have similar energies, so have similar vibrational spectra. For example, chemicals with sulphur-hydrogen bonds tend to vibrate at about 2500 cm^{1} and this is often perceived as a 'rotten' smell — rotten eggs produce chemicals like hydrogen sulphide (H_2S), and ethyl mercaptan produced by rotting meat is C_2H_5SH.

Turin supports his theory by noting that decaborane ($B_{10}H_{14}$) smells very similar to S-H compounds, and it has nothing in common with them apart from similar vibrational energies. Although boron has a much lower atomic mass than sulphur, B-H bonds are much weaker than S-H bonds, and these effects happen to cancel out.

Further support was provided by the analogous compounds ferrocene and nickelocene. These have a divalent metal ion (iron and nickel respectively) sandwiched between two cyclopentadienyl anions ($C_5H_5^-$). The main vibrational difference between them is that the metal-ring bond in ferrocene vibrates at 478 cm^{1}, while in nickelocene it is 355 cm^{1}. Ferrocene smells rather spicy, while nickelocene smells like the aromatic hydrocarbon rings. Turin proposes that below a threshold of 400 cm^1, the vibrational signal is swamped by 'background noise', so is not detected by the nose.

As different isotopes have different masses but similar chemical properties, they affect the vibrational energy. It can be seen from the formula for reduced mass that the biggest difference results from replacing hydrogen (A_r = 1) with deuterium (A_r = 2) — the numerator is doubled. Indeed, deuterated acetophenone smells fruitier than ordinary acetophenone ($C_6H_5COCH_3$). It also smells slightly of bitter almonds, just like many compounds containing the cyanide or nitrile group (ON) — both C-D and ON bonds vibrate at about 2200 cm^1.

One challenge to Turin's theory is the different smells of some enantiomers (optical isomers), as they have identical vibrational spectra. For example, R-carvone smells like spearmint, and S-carvone like caraway. The answer is: the spectra are identical only in an **achiral** medium, as in solution or gas phase. But the smell receptors are **chiral** and orient the two enantiomers differently. This means that different vibrating groups lie in the tunnelling direction in each enantiomer. Turin thinks that the caraway S-carvone is oriented so a carbonyl (C=0) group lies in that direction, so is detected; in the minty R-carvone, it lies at right angles, so is ignored. Turin supported this by manufacturing a caraway scent by mixing the minty carvone with the carbonyl-containing butanone ($C_2H_5COCH_3$).

If Turin's theory were true, then infrared and Raman spectroscopy would be essential tools for the perfume industry! Turin is also using **inelastic tunnelling spectroscopy** — 'inelastic' refers to the energy loss before tunnelling, as with the proposed sensory mechanism.

The precise chemistry of olfaction is still little understood. But Turin believes he has found a sequence of amino acid residues that could function as the electron donor together with NADPH. He has also found five residues coordinated to a zinc atom that could be the acceptor site. One warning sign of zinc deficiency is loss of the sense of smell, and zinc is often involved in biological electron-transfer reactions.

Whether or not Turin's idea is correct, the olfactory system exhibits what the biochemist Michael Behe calls **irreducible complexity,**[6] and is therefore evidence of design. This means the system requires many parts for it to work, and would not function if any were missing. The chemical sensing machinery needs proteins with just the right shape to accommodate the odour molecules. And under Turin's model, the right energy levels as well. And even if the sensors were fully operational, the chemical information gathered by the nose would be useless without nerve connections to transmit it and the brain to process it.

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Aboriginal Paintings 'Whodunnit'

In the remote Kimberley region of northern Western Australia, a group of rock paintings are causing a scientific and political controversy of international proportions. The paintings are collectively known as the 'Bradshaws', after a 19th Century explorer in the region. They feature delicate human figures *'exquisitely painted in mulberry-tree juice'* on sandstone[1] (see Figure 1).

The big furore turns on just who painted the Bradshaws, which, by current dating estimates, are assigned 'dates' of at least 17,000 years, ranging up to 60,000 years.

The Ngarinyin tribe claims that the paintings had to be made by their ancestors, and are a direct link to their cultural past. This is tied to land rights issues, which is what makes this more than a scientific dispute.

The counter claim is that the paintings are 'too good . . . too distinctive . . .' and portray too sophisticated a culture to have been painted by the Ngarinyin's ancestors. Proponents of this view are led by rock art enthusiast Grahame Walsh, who thinks they were done by a previous, totally different group of people. Bradshaw himself said it was almost like *'viewing the painted walls of an Egyptian temple'.*

By looking at the evidence put forward by both sides, a picture of great interest emerges in relation to the Biblical account of human dispersion after Babel. Before looking at the controversy further, let's first run through a Biblically-based scenario.

The catastrophic, supernatural

Figure 1. *Aboriginal paintings on a 'wall' of sandstone in Carnarvon Gorge, Queensland.*