

Allotropes and Polymorphs

The term “allotrope” refers to different structural forms of the same pure element, regardless of the state (gas, liquid, solid). If you have a given molecular structure for a pure element, it is possible for that to pack in different ways into different solid crystalline forms, and these are called “polymorphs”, not allotropes. Some elements have many known allotropes, with greatly varying properties, while others have strikingly few known allotropes.

P_4 and AsP_3 Electronic Structure and Photoelectron Spectra

White phosphorus is the name given to the substance that is composed entirely of tetrahedral P_4 molecules. WP would be the acronym for white phosphorus, but WP is also the name given to this substance by the military, who refer to it alternately as “willy pete” (white phosphorus has military applications that include its use in tracer fire).

The tetrahedral P_4 molecule can be regarded as a cluster of P atoms that has “spherical aromatic” electronic character, explaining in part why this is the only molecular allotrope of the element phosphorus that is encountered under normal conditions. Despite the small bond angles in P_4 , this molecule has exceptional stability. Using Lewis structures, we would draw a lone pair of electrons at each vertex of the P_4 tetrahedron, but the molecule has scarce basicity, and this is because the “lone pair” orbitals are mostly 3s in character, and there is not much sp mixing taking place in the MOs.

The two highest energy occupied MO energy levels of P_4 are respectively doubly and triply degenerate, have contributions mainly from 3p atomic orbitals, and correspond to bonding along the edges of the P_4 tetrahedron. This is why, when P_4 is protonated, the site of protonation to give HP_4^+ is an edge, such that HP_4^+ has C_{2v} symmetry, rather than C_{3v} symmetry.

Lying two below the HOMO (HOMO–2) in the MO energy level scheme for P_4 is a singly degenerate MO that belongs to the totally symmetric representation, and arises from the overlap of four p orbitals that point directly to the center of the P_4 tetrahedron. When an electron is ejected from this orbital under the ionizing conditions of photoelectron spectroscopy, one sees a corresponding band at 11.89 eV that exhibits well-resolved vibrational fine structure. This vibrational fine structure has a spacing that corresponds to the highest energy totally symmetric stretching mode of the P_4 molecule as observed in its Raman spectrum. Vibrational fine structure can help with assigning the peaks observed in molecular photoelectron spectra, which are acquired using gas-phase samples. While P_4 is a solid at room temperature, it has appreciable vapor pressure, and the irradiation/ionization takes place in a vacuum.

Photoelectron spectra of molecules are usually acquired using radiation from a helium discharge lamp that has a strong line at 58.4 nm; this radiation leads to ionization of valence molecular orbitals. The spectra so obtained are likened to “experimental MO diagrams” of the molecules involved. This type of spectroscopy is called ultraviolet photoelectron spectroscopy, or UPS. Helium(II) has a strong line at 30.4 nm. Different elements have varying ionization cross-sections upon going from He I to He II radiation, so the acquisition of spectra for the same molecule using the two types of radiation can give information about the elemental composition of each molecular orbital. In the case of P_4 and AsP_3 , this type of investigation showed that the two have nearly identical electronic structure, and that charge is distributed evenly in both molecules (formal oxidation state zero for *both* As and P in AsP_3).

Synthesis of White Phosphorus

The alchemist Hennig Brand synthesized white phosphorus by concentrating down large quantities of human urine into a paste, which then was subjected to reductive distillation. Urine has a high concentration of phosphate, the source of the phosphorus. In modern times, white phosphorus is synthesized industrially in an electric arc furnace at very high temperature (ca. 1500 °C). This energy intensive process requires a source of cheap electricity, explaining why the Thermphos plant in the Netherlands is situated adjacent to a nuclear power plant. This same plant is located close to the North Sea, such that raw materials (apatite, coke, sand) can easily be brought to the site on barges. The phosphate rock (mineral apatite) supply for Thermphos previously was from Florida, but the Florida deposits of apatite have now been mined out, so Thermphos now obtains its phosphate rock from elsewhere in the world. Large deposits exist in Morocco, China, and Russia. Apatite deposits are essentially the remains of dried-up sea beds where the bones and teeth of ancient marine organisms have become concentrated. The form of apatite known as “hydroxylapatite” corresponds to the formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. Other forms of apatite have the two hydroxide ions replaced by halide ions but are otherwise the same as concerns their chemical composition.

By far the majority of the apatite mined from deposits around the globe is used for fertilizer in agriculture. In many of Earth’s ecosystems, phosphorus, by far the least abundant of the biogenic elements (C, H, N, S, O, P) is life-limiting. The low abundance of phosphorus can be traced to the genesis of ^{31}P nuclei in extremely hot stars by a very improbable sequence of nuclear reactions.

Phosphorus Allotropes

There are many known phosphorus allotropes that differ from white phosphorus in that they are not composed of discrete molecules. Here, there is a nice analogy with carbon. C_{60} is a molecular form of carbon, while graphite is a solid containing infinite 2D sheets of carbon atoms, and diamond has a 3D extended lattice. Red phosphorus has a tubular structure of phosphorus cages; the 1D tubes can be cross-linked together in various ways. The variations in the cages and in the cross-links give rise to such allotropes as violet phosphorus. Black phosphorus is an allotrope having 2D sheets, but unlike in the case of graphite the sheets are not flat but puckered. Having the same structure as black phosphorus is metallic gray arsenic. All allotropes of phosphorus have been obtained starting from white phosphorus.