

The Tetrahedral P4 Molecule

James R. Arnold

Citation: *The Journal of Chemical Physics* **14**, 351 (1946); doi: 10.1063/1.1724148

View online: <http://dx.doi.org/10.1063/1.1724148>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/14/5?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Monolayer solids of tetrahedral molecules](#)

J. Chem. Phys. **87**, 5518 (1987); 10.1063/1.453636

[Tunneling states of a tetrahedral molecule in a tetrahedral field](#)

J. Chem. Phys. **73**, 4483 (1980); 10.1063/1.440685

[Force Constants of Tetrahedral Molecules](#)

J. Chem. Phys. **28**, 514 (1958); 10.1063/1.1744177

[Normal Frequencies of Tetrahedral M\(XY\)₄ Molecules](#)

J. Chem. Phys. **26**, 1355 (1957); 10.1063/1.1743539

[LeastSquares Calculation of OVFF Force Constants for XY₄ Tetrahedral Molecules](#)

J. Chem. Phys. **23**, 1727 (1955); 10.1063/1.1742428



Rice and I have never disagreed on the physical occurrence of a considerable amount of fluctuation entropy in a real solid for which any intuitively "natural" choice of cell size is made. I agree with him completely as to the "naturalness" of choosing a definition of cell size which will be most appropriate to the purpose one has in view. I now agree with him also in accepting as significant the closeness of the agreement between the fluctuation entropy found, for his cell size, in solid argon and the theoretical value $3R$ which he has established.

The Tetrahedral P_4 Molecule

JAMES R. ARNOLD

Institute for Nuclear Studies, University of Chicago, Chicago, Illinois
April 15, 1946

THE methods developed by Pauling¹ in his treatment of the tetrahedral bond orbitals of carbon (and applied by him and others to a number of individual cases) have been extended and systematized by Kimball² into the theory of directed valence. This scheme serves to predict the bond configurations for covalent molecules with remarkable success.

One of the few remaining anomalies is the tetrahedral P_4 molecule (with its analog As_4). The bond angles for a trivalent P atom might be expected to be somewhat over 90° , as typical p bonds, and, in fact, all other compounds which have been investigated show angles in the neighborhood of 100° . Pauling³ has suggested that the P_4 molecule is merely a strained structure, but the great amount of distortion involved seems to render this explanation improbable. The purpose of this note is to point out a set of orbitals with more suitable bond angles.

The symmetry group of the three bonds extending from one P atom is C_{3v} , and from group theoretical considerations we can reduce the possible orbitals to p^3 , sp^2 , pd^2 , sd^2 . The bond angles for p^3 are obviously 90° , while for sp^2 and sd^2 they are 120° . The combination $p_x d_{xz} d_{yz}$, as for example in the set:

$$\begin{aligned}\psi_1 &= 1/\sqrt{3}\psi_{p_z} + \sqrt{2}/\sqrt{3}\psi_{d_{xz}} \\ \psi_2 &= 1/\sqrt{3}\psi_{p_z} - 1/(6)^{1/2}\psi_{d_{xz}} + 1/\sqrt{2}\psi_{d_{yz}} \\ \psi_3 &= 1/\sqrt{3}\psi_{p_z} - 1/(6)^{1/2}\psi_{d_{xz}} - 1/\sqrt{2}\psi_{d_{yz}}\end{aligned}$$

yields bond angles of $66^\circ 26'$. This is the smallest possible angle for orbitals involving s , p , and d states only. The bond-forming strength (in Pauling's terminology) is 2.29, compared to 1.73 for pure p orbitals.

Some distortion is still required to compress these angles to 60° , but the strain is not now excessive. The advantage gained in replacing a triple bond by three single bonds may be used to account for the promotional energy required to produce a pd^2 structure from the p^3 ground state, and the stability of P_4 relative to P_2 .

The above explanation sheds no light on the 60° bond angles found in carbon compounds, but it does account for the absence of a tetrahedral nitrogen molecule.

¹ L. Pauling, *Proc. Nat. Acad. Sci.* **14**, 359 (1928).

² G. Kimball, *J. Chem. Phys.* **8**, 188 (1940).

³ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, New York, 1944), second edition, p. 80.

Ultra-High Frequency Denaturation of Proteins

GEORGE A. BOYD

University of Rochester, Rochester, New York
April 18, 1946

ELECTROMAGNETIC waves in the ultra-high frequency range offers a new method for the study of protein-type molecules in the following suggested manner. From dielectric studies it is known that protein molecules are not rotated by frequencies above 10^7 cycles per second (below 30 meters). However, atomic and electronic polarization of the proteins do occur at the higher frequencies.

During each half-cycle, polarization on the molecule builds up to a peak and decays to zero. This produces a pulsating strain of twice the frequency of the electromagnetic wave. The pulsating strain will place the molecule in forced vibrations except at a resonant frequency, f_r , where the molecular energy absorption will rise sharply. The frequency f_r will depend upon whether the entire molecule vibrates as a two-body oscillator with each half of the mass of the molecule acting as one body or whether a prosthetic group and the remaining portion act as the two bodies. Because of the low strength of the hydrogen cross bonds and the small number required to be broken for denaturation, it is probably that at polarization resonance sufficient energy will be absorbed to denature the protein for the first type of vibration. Denaturation will result for the second type of vibration if the prosthetic group is broken off.

Now let us assume that each protein molecule of our laboratory experience is characterized by a unique energy state. For example, let us suppose that egg albumin has the energy E_1 , and lactoglobulin, the energy E_2 and that each energy state will resonate with one particular frequency. Thus, there will be a frequency f_{r1} which will denature egg albumin and another frequency f_{r2} which will denature lactoglobulin. It then follows that each of the proteins, enzymes, viruses, genes, and other protein-like molecules can be denatured by frequencies which are related to their energy states. This would lead to a systematic identification of the molecules by their resonant frequencies.

In this connection it seems that we should not conceive of a large number of lactoglobulin molecules, for example, as having identical energy states. It is perhaps more probable that these molecules have a distribution of energy states, say a normal distribution with the mean state having the energy E_2 . Thus, the question arises as to the sharpness of the effect of the resonant frequency, i.e., how broad is the band of energy states about the mean which will be denatured by f_{r2} .

We do not know how to determine this band width at present but the concept is of value in setting up biological experiments. Let us assume two proteins, for example, egg albumin and lactoglobulin with mean energy states E_1 and E_2 , respectively, with distributions of states such that the denaturable band of states do not overlap. If we irradiate the two proteins in a common solution with a frequency f_{r1} , which will resonate with the band of states about E_1 , but does not resonate with the band about E_2 , we can visualize the denaturation of egg albumin without the denaturation of the lactoglobulin. There follows the

implications that a virus could be denatured without denaturing the proteins of the host, or that the energy state of one protein, enzyme, or gene could be changed without changing the states of neighboring molecules having different energies.

The Recognition of Phase Transitions in Adsorbed Films on Solids

D. H. BANGHAM

British Coal Utilization Research Association Laboratories,
Grosvenor Gardens, London

April 19, 1946

IN a recent note Jura, Loeser, Basford, and Harkins¹ have given evidence of a first-order phase transition taking place in a film adsorbed at a solid/vapor interface (*n*-heptane on silver). This is not, however, the first case of its kind to come to light, earlier instances having been reported from the University of Egypt where a study was made of the *swelling* effects which accompany adsorption on charcoal; water (23.5°C)² and methanol (0°C)³ are cases in point.

The purpose of this note is to draw attention to the advantages which accrue in studies of the molecular structure of films on solids when the adsorbent is used in the form of a block which responds elastically by dimensional changes to the pressure *F* in the adsorbed films. The form of relation between *F* and the quantity adsorbed per g (*s*) can then be determined in two ways, *viz*: By direct measurements of the dimensional changes which accompany adsorption (Method I); and by use of Gibb's equation in its integrated form $F = (RT/M\Sigma) \int_0^p s d \log_e p$

(Method II); here *p* is the pressure of vapor, *M* its molecular weight, Σ the area per g of adsorbent. In Method I it is necessary first to establish that the adsorbent block does in fact respond elastically to changes of *F*. This done, however, the method gives far more reliable information than Method II as to phase relationships.

The statement of Brunauer⁴ that in the experiments referred to my colleagues and I "unfortunately did not measure the adsorption isotherms of the vapours they used in the expansion experiments" is contrary to fact. We did, however, consider that Method I gave more reliable results than II because: (1) Unless a region of obedience to Henry's law can be established experimentally, the integration of the isotherms in the region of low pressures is not merely difficult but hazardous, especially if transitions occur. (2) We were unable to satisfy ourselves that Gibb's equation was obeyed over regions of phase transition, even when "time" effects and hysteresis were absent.^{2,3}

By Method I it was established that: (1) films adsorbed from vapors on the charcoal blocks used were mobile, and obeyed similar equations of state to films at liquid/gas interfaces;⁵ (2) definite phase transitions occurred;^{2,3} (3) metastable films were of frequent occurrence, transition to a stable state manifesting itself by a *contraction* signifying increase of interfacial energy at constant adsorption;^{2,3} (4) while some adsorbed phases could be

classed as "gaseous" and some "liquid," in other cases the behavior was intermediate;^{2,3,*} (5) that a two-dimensional condensed phase does not necessarily confer complete wettability nor render capillary condensation in cavities inevitable;⁶ (6) that film thickening occurs with some adsorbates at quite small relative pressures.^{3,7}

These conclusions—perplexing though they appeared when first published—have been generally confirmed by later work, notably by Jura, Harkins, and collaborators in the course of their elaborate investigation. The general similarity of phase relationships at solid/gas and liquid/gas interfaces has been stressed by Gregg,⁸ who also emphasizes some of the difficulties attaching to Method II.

* In the papers quoted these were referred to as "equilibrium" or "annealed" films to avoid implications as to their classification. Their properties were, however, fully described (see D. H. Bangham, Proc. Roy. Soc. A **147**, 175 (1934)).

¹ Jura, Loeser, Basford, and Harkins, J. Chem. Phys., **13**, 535 (1945).
² Bangham, Fakhoury, and Mohamed, Proc. Roy. Soc. A **138**, 162 (1932).

³ Bangham, Fakhoury, and Mohamed, Proc. Roy. Soc. A **147**, 152 (1934).

⁴ S. Brunauer, *Physical Adsorption* (Princeton University Press, New Jersey, 1943), p. 433.

⁵ Bangham and Fakhoury, J. Chem. Soc. **1324** (1931).

⁶ Bangham and Razouk, Trans. Faraday Soc. **33**, 1463 (1937).

⁷ Bangham, Proc. Roy. Soc. A **147**, 175 (1934).

⁸ S. J. Gregg, J. Chem. Soc. **696** (1942).

Aggregational States in Adsorbed Films on Incompletely Wettable Solid Surfaces

D. H. BANGHAM

British Coal Utilization Research Association Laboratories,
Grosvenor Gardens, London

April 19, 1946

IF a solid surface fails to provide nuclei of condensation for a saturated vapor (i.e., supersaturation can occur), the adsorbed film must necessarily be in a state of aggregation different from the bulk liquid. If the bulk liquid is brought into contact with the solid there will be a finite contact angle.

It is not generally recognized that such saturated films adsorbed at incompletely wettable surfaces are usually of more than unimolecular thickness. Charcoal and methanol^{1,2} charcoal and water,^{1,3} graphite and water,⁴ mica and benzene⁵ are cases in point. De Boer has recorded other instances of essentially the same phenomena but in which the bulk adsorbate was solid (iodine on calcium fluoride;⁶ caesium on calcium fluoride⁷). Earlier instances in which the adsorbent was liquid (water on mercury⁸) have been reported by Frumkin and co-workers.

It is remarkable that, where full data are available, the films at saturation frequently appear to be limited to about three molecules in thickness.^{2,3} Even where the isotherms are sigmoid and rise steeply near saturation (this being the common type for non-porous solids) they converge to an asymptote *beyond* saturation pressure and the saturation adsorption appears limited to about four molecular layers. The data of Palmer⁹ for various organic vapors adsorbed on vitreous silica (the surface area of which was measured independently) provide numerous examples.

For explanation of such steeply rising isotherms (convex to pressure axis) we must clearly think in terms of a *patterned assembly* of adsorbed molecules, the interaction be-