# On the Molecular Structures of $P_4$ and $AsP_3$

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DIE XIII. NOV. A°. M.D.C.XIX.

# Overview

1. $P_4$
2. $P_3As$

# $P_4$ experimental I

- GED (Maxwell, Hendricks, Mosley, **1935**, Washington DC, US)
  $r_a$ = 2.21 Å @ 200°C , optical method, incremental refinement

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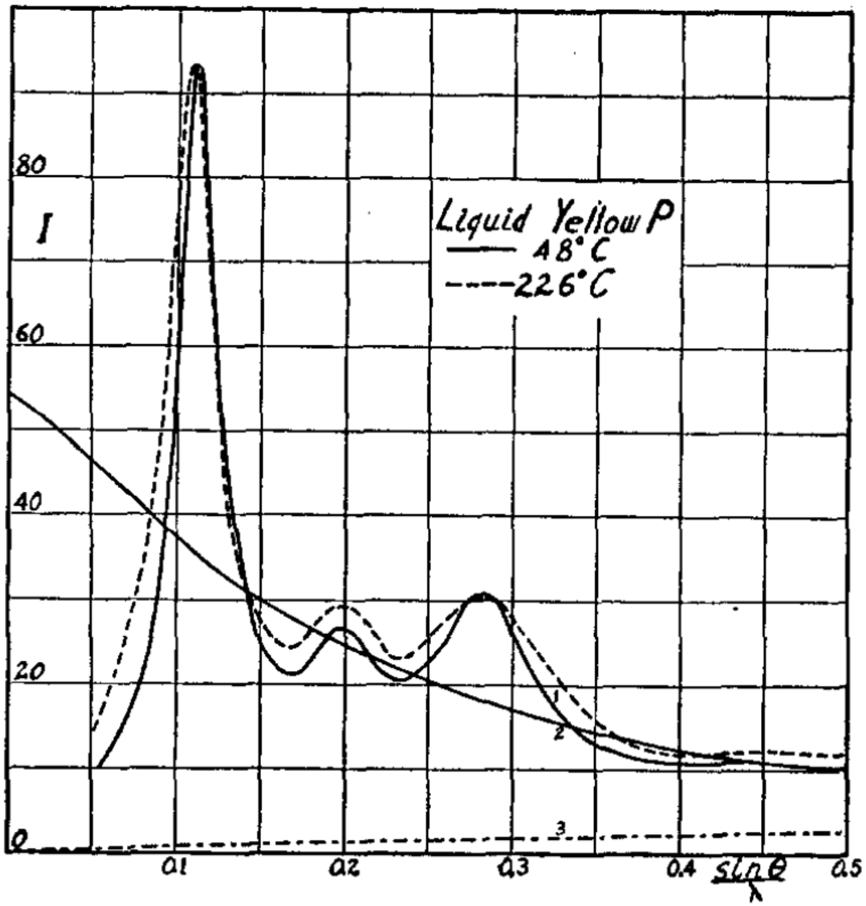
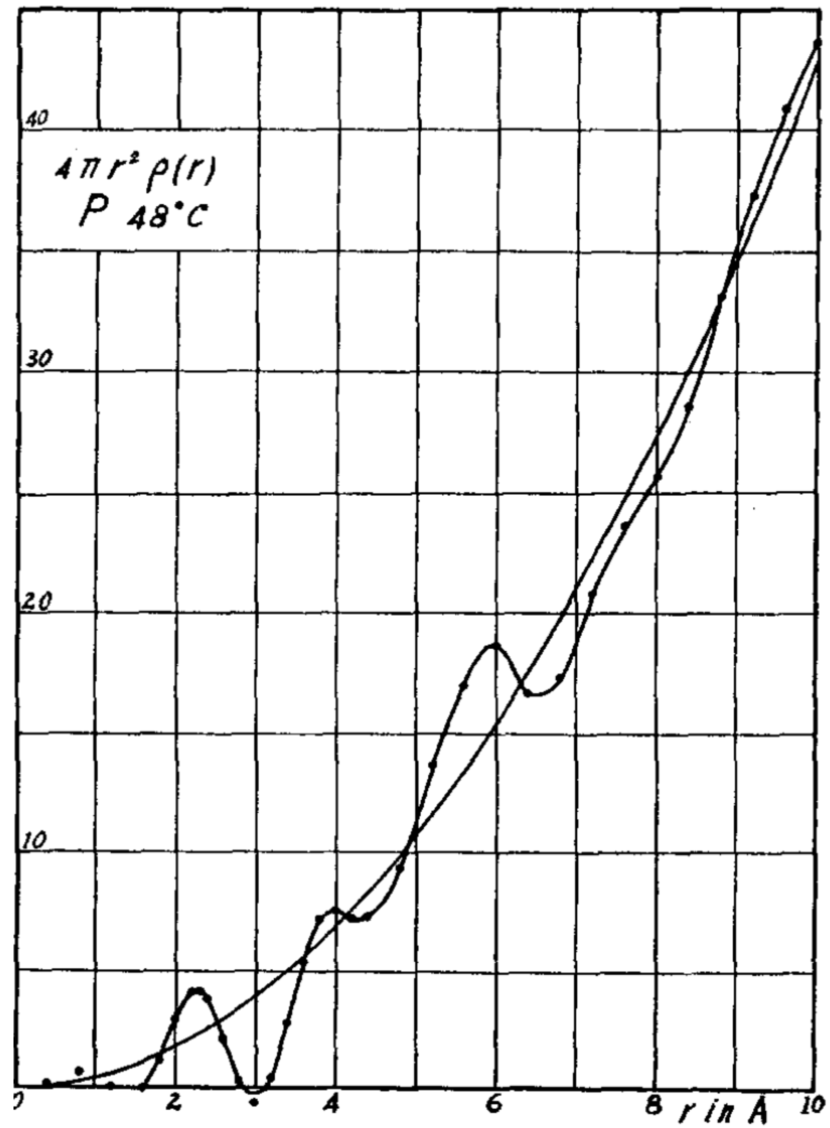
  $r$ = 2.25 Å @ 48°C and 226°C

# XRD (liquid $P_4$)




J. Chem. Phys. 6 (1938) 659

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- XRD β-$P_4$ (Simon, Borrmann, Craubner, 1987, Stuttgart, DE)
  $r$ = 2.2095(5) @ -115°C

# XRD (β-$P_4$)

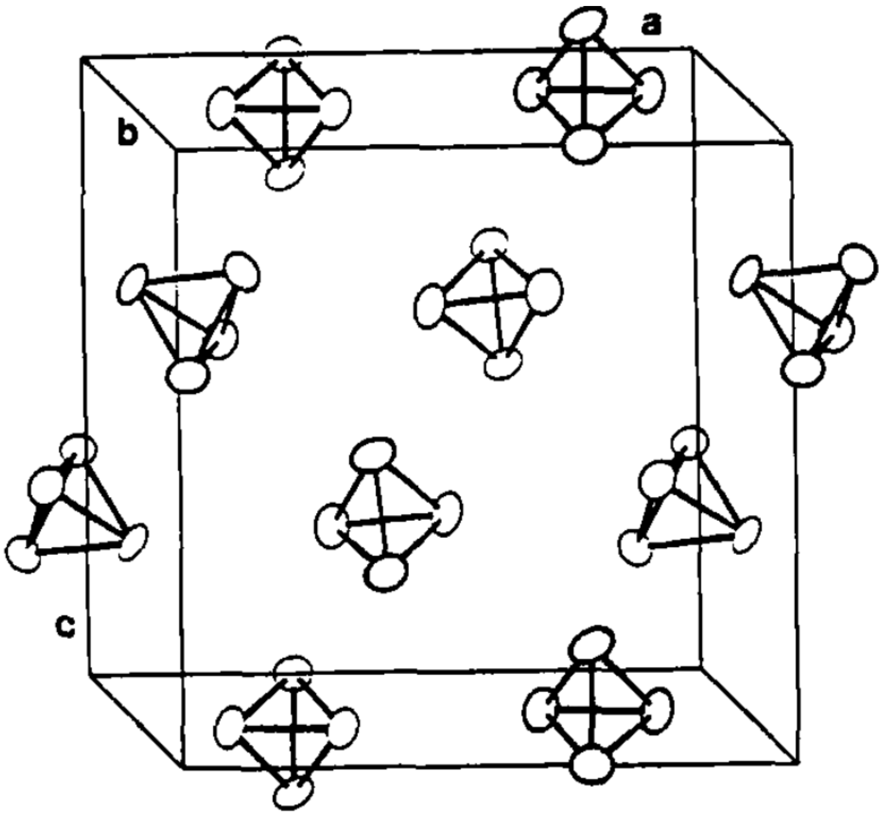


**FIGURE 1**

Projection of the structure of ß-P on (010). The thermal ellipsoids are drawn at 50% probability.

J. Mol. Struct. 30 (1987) 507

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# $P_4$ experimental II

- Vib.-rot resolved RAMAN (Brassington, Edwards, Long, **1981**, Bradford, UK)

  $r_0$ = 2.2228(5) Å @ 176.9°C

  - **(100) -> 22%, (010) -> 80%, (001) -> 93%**
  - **$J_{max.}$ = 58 @ 176.9°C**
  - **symmetric top is not Boltzmann-populated**

# $P_4$ theoretcial

- $r_e$ = 2.194 Å (Häser, Treutler, **1995**, Karlsruhe, DE)

Marco Häser

*1996 01:00 at cottage close to Bernina after 20 h climb (courtesy Dage Sundholm)*

- lead development of TM with Ahlrichs
- Predicted fibrous red-P modification which was found exp. 2004
- † 1997

# $P_4$ theoretcial I

- $r_e$ = 2.194 Å (Häser, Treutler, **1995**, Karlsruhe, DE)
  approx. CCSD(T)/(*11s10p6d5f1g*)
  - $r_0$ from RAMAN study 2.2228(5) Å „is likely to be in error and should be reinvestigated“
  - -0.001 Å relativistic correction [scalar]
  - -0.007 Å core correlation effect

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- $r_e$ = 2.186 Å (Persson, Taylor, Lee, **1997**, San Diego, US)

  JCP 107 (1997) 5051
  - CCSD(T)/(*17s12p7d5f1g)/[6s5p4d3f2g1h] ->* 2.188 Å
  - estimated 2.186 Å as BO-limit
    - almost basis set saturation
    - no rel. effect
    - very close to full correlation [?] $T_1$ = 0.018
    - core correlation included (estimate)
    - $r_0 - r_e$ = 0.005 Å

# $P_4$ theoretcial II

- CCSD(T)/(*17s12p7d5f1g*)/[*6s5p4d3f2g1h*]: $r_e$= **2.188 Å**
  - Almost basis set saturation
  - no rel. Effect (Häser: -0.001 Å)
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  - core correlation (Häser): -0.007 Å
  - estimated $r_e$ = 2.186 Å
  - $r_0 - r_e$ = 0.005 Å (based on anharmonic force field)
- F12-CCSD(T)/(*20s15p7d5f3g1h*)/*[10s9p7d5f3g1h]*:$r_e$=**2.1860 Å**

  JACS 132 (2010) 8459
  - basis set limit (F12 and aug-cc-pwCVQZ)
  - core correlation ( -0.0072 Å)
  - Shrink: $r_{h1}$ - $r_e$ = 0.003 Å
  - relativity (no or -0.001 Å)?
  - full correlation?

# $P_4$ experimental II

- high-res. IR (Budon, Mkadmi, Bürger, Pierre, **1999**, Dijon/ Wuppertal, FR/DE) $r_0$ = 2.1958 Å
- GED (Berger, Mitzel, Hayes, **2010**, Bielefeld, DE)

  $r_g$ = 2.1994(3) Å @ 100°C

  We remember Brassington, Edwards, Long:

  - (100) -> 22%, (010) -> 80%, (001) -> 93%
  - $J_{max.}$ = 58
  - symmetric top is not Boltzmann-populated
  - SHRINK would give $r_{a3,1}$ = 2.196 Å (but 2.1860 Å is the best theor. value) => we stick to $r_g$!

# $P_4$ experimental III

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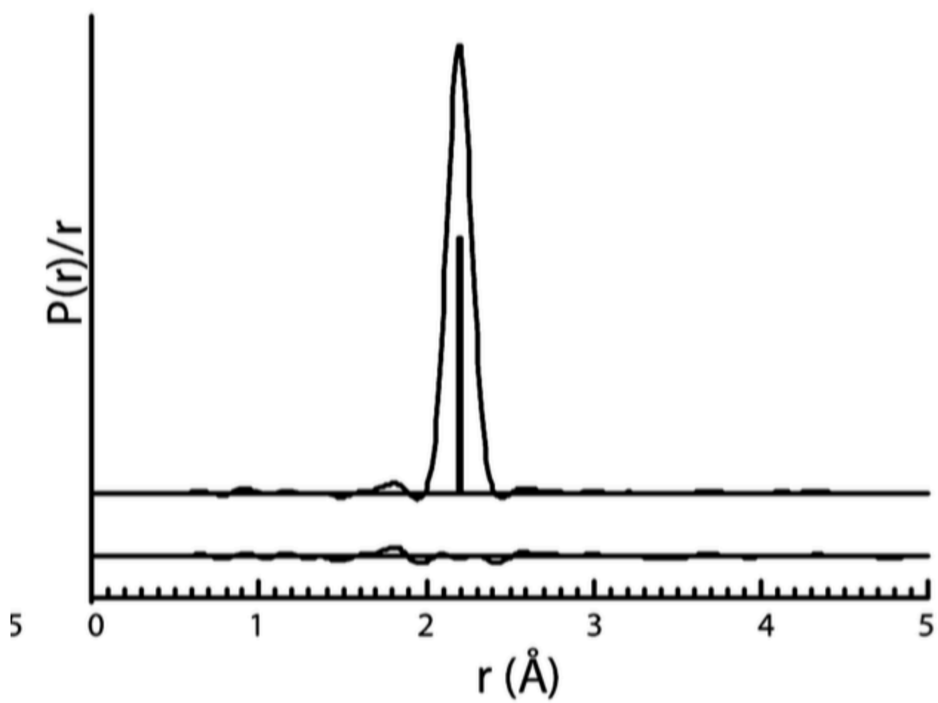

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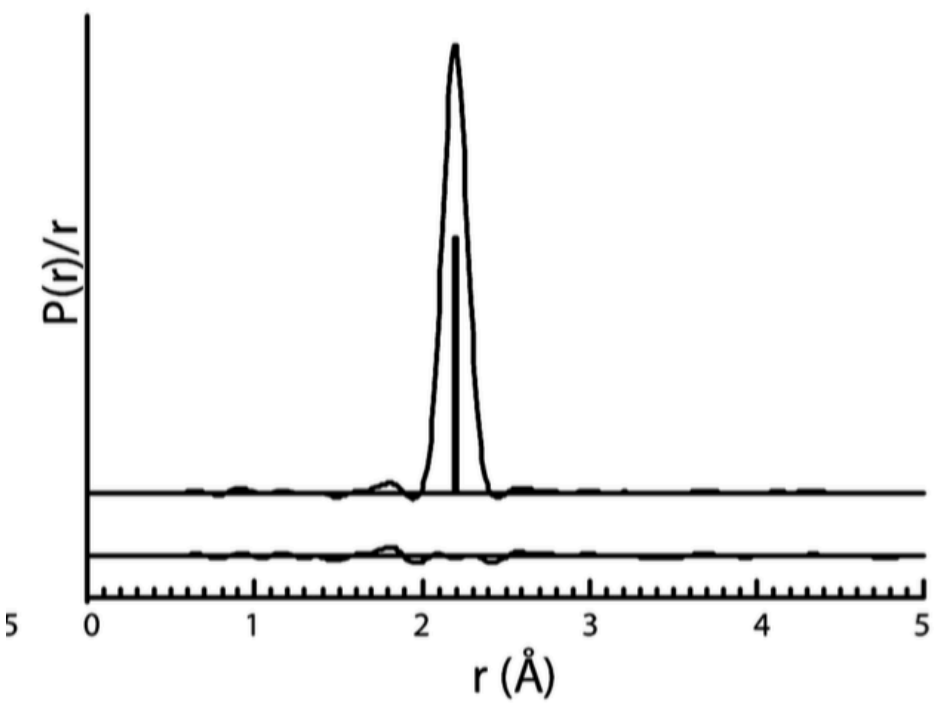


the height in the equilateral P trianlge:

2.1994(3) * $(3)^{-1/2}$ / 2 Å =

**1.9047 Å**

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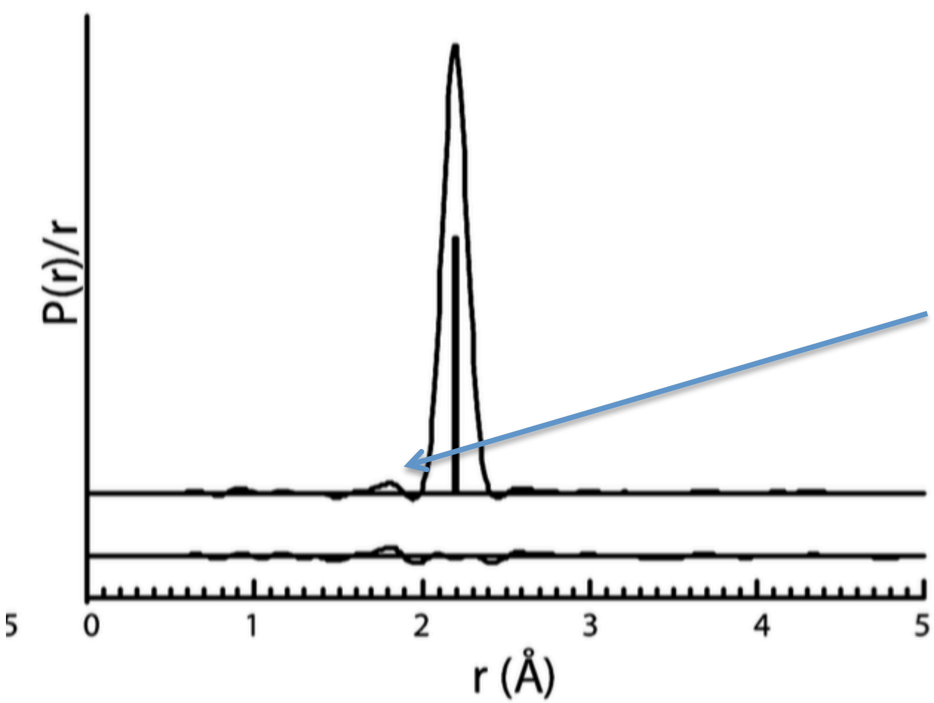


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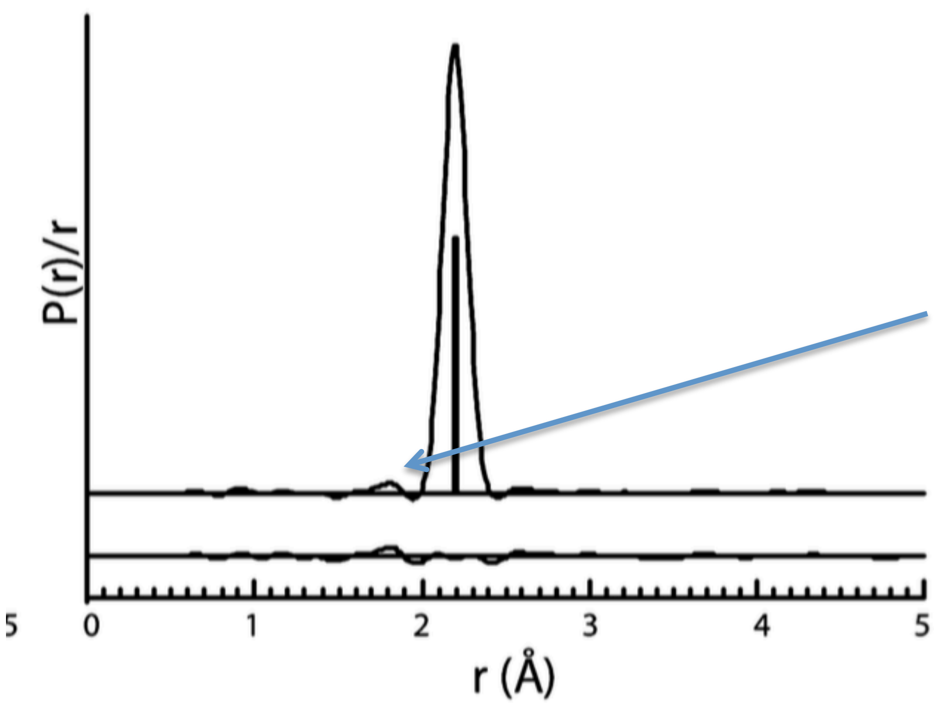


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⇒ **three-atom scattering**

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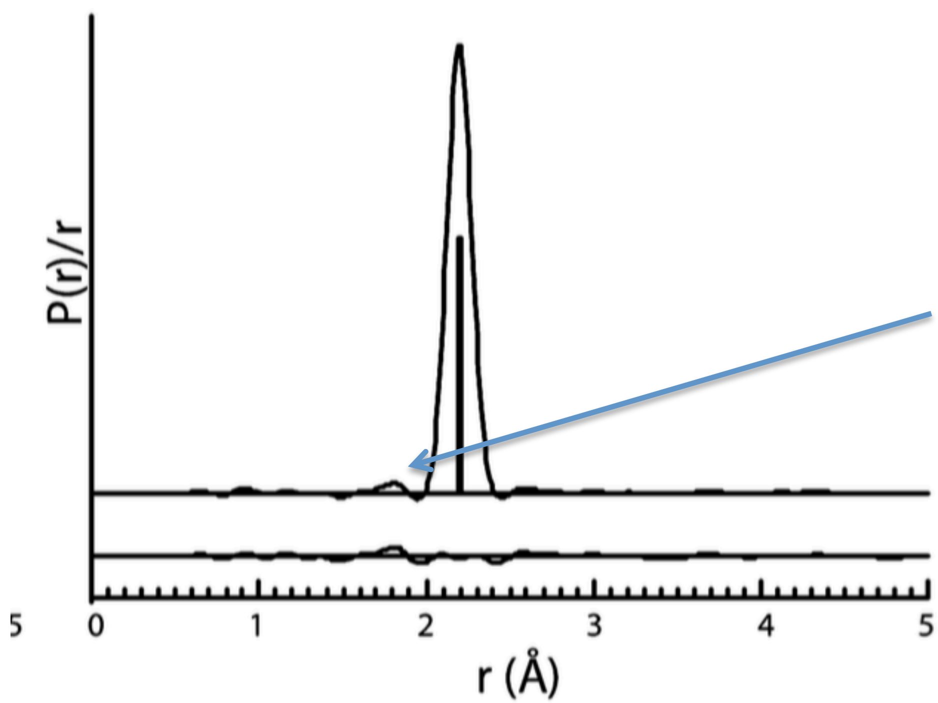


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⇒ **three-atom scattering**

Confirmed by Edico!

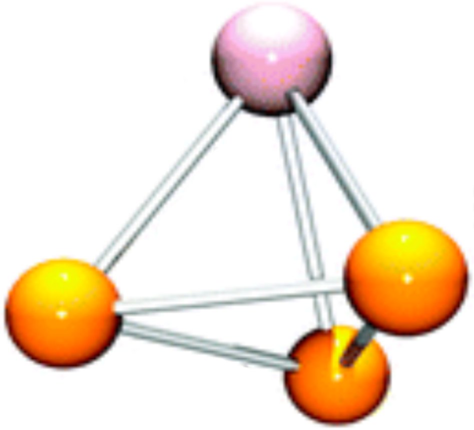
# $P_4$ summary

- $\boldsymbol{r_0}$ **= 2.1958** Å
- $\boldsymbol{r_e}$ **= 2.1860** Å
  - relativity could effect by -0.001 Å
  - higher correlation than CCSD(T) was never tested,
    $T_1$ = 0.018 (probably ok, Q => maybe very small elongation?)
- $r_0 - r_e$ corrections are very problematic
  - Non-Boltzmann population of sph. top
  - $J_{max}$ = 58 (@ exp. temperatures)
  - best calc. Value of 0.005 Å is yet 100% off
- $r_g$ = 2.1994(3*)* Å
  - no three-atom scattering (probably no major influence)
  - Shrink corrections to $r_{h1}$ may be implausible:
    (100), (010) and (001) -> 22, 80 and 93 % occupation (the ensemble is not well represented by (000) at exp. temperatures
  - moreover the same as for $r_0 - r_e$ *applies for* $r_{h1}$ *and* $r_{a3,1}$ corrections
- QZVPP/ B3-LYP,TPSS, B97-D3, PBE0: 2.204, 2.016, 2.194, 2.184 Å
  DFT methods are of unpredictable reliability.

# $AsP_3$ experimental I

- GED (JACS 132 (**2010**) 8459)

  $r_g$ (P-P) = 2.1949(28), $r_g$ (As-P) = 2.3041(12) Å @ 115°C



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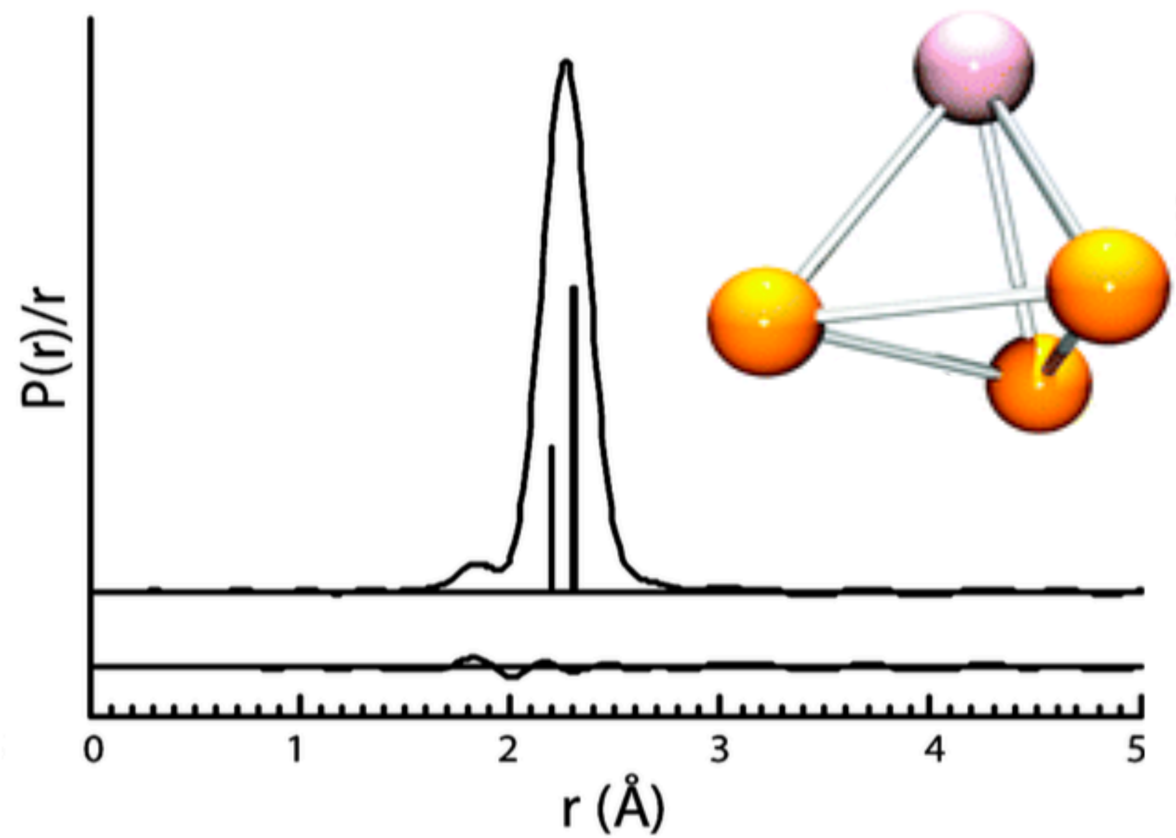

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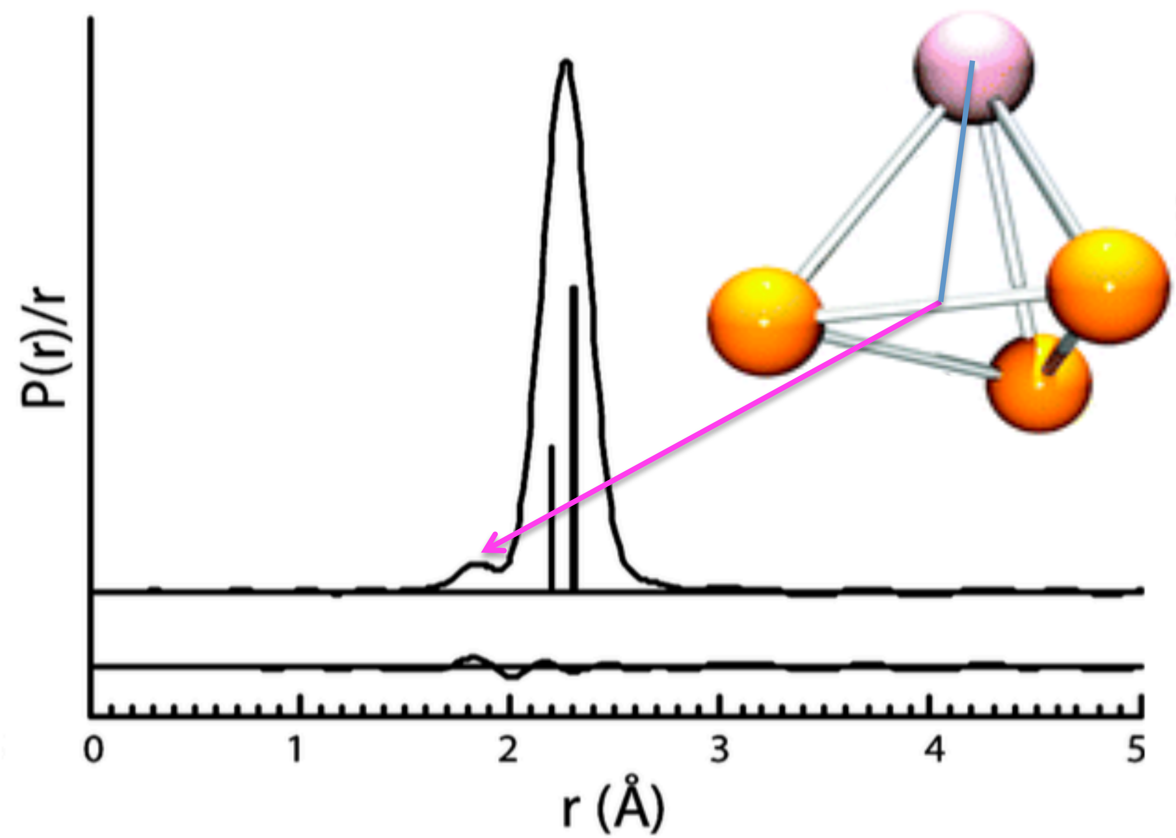

# $AsP_3$ theoretical

$P_4$: best method : F12-CCSD(T)(full)/aug-cc-pwCVQZ => **2.1860** Å
slightly smaller: F12-CCSD(T)(4ef)/cc-pwCVQZ => 2.1859 Å

$AsP_3$ => $r_e$ (P-P) = **2.190** Å, $r_e$ (P-As) = **2.307** Å

$T_1$ diagnostic = 0.018 =>
correlation could be close to exact

**but**: relativity could have larger influence (As-P would shrink) – no methods available as yet for F12-CCSD(T).

(DFT methods are of unpredictable reliability,
MP2(fc) is too inaccurate)

# $AsP_3$ experimental II

MW (J. Mol. Spect. 278 (**2012**) 68): $B_0$ = 2201.394 MHz

=> „scaled GED distances to fit $B_0$“:

$r_0$ (P-P) = 2.201 Å; $r_0$ (P-As) = 2.311 Å

a problem for comparability might be again highly populated rotational and vibrational states in GED exp.

compare: $r_g$ (P-P) = 2.195 Å; $r_g$ (P-As) = 2.304 Å

$r_e$ (P-P) = 2.190 Å, $r_e$ (P-As) = 2.307 Å

# $AsP_3$ summary

- F12-CCSD(T)/cc-pCVQZ: $r_e$ (P-P) = 2.190 Å, $r_e$ (P-As) = 2.307 Å close to BO-value; infuence of higher correlation could be, relativity should be tested!
- DFT cannot contribute to increase accuracy to +- 0.001 Å
- GED [$r_g$ (P-P, P-As) = 2.195, 2.304 Å] should be re-refined with three-atom scattering, and MW $B_0$ constant
- High resolution vibrational spectroscopy could be attempted to determine also $A_0$ and finally accurate $r_0$ for P-P and As-P
- $r_0 - r_e$ corrections need to be calculated

# Conclusion

There are still open questions regarding the gas phase structure Parameters of $P_4$ and $AsP_3$. Further investigations are required.

Thank you for your attention!