Vibrational Spectroscopy Tutorial: Sulfur and Phosphorus

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Fall 2010 Organic Spectroscopy
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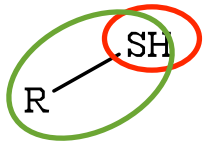
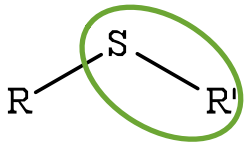
Part I: Sulfur Containing Compounds

Sulfur: overview of naming

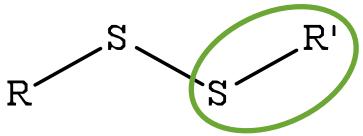
- Thiols



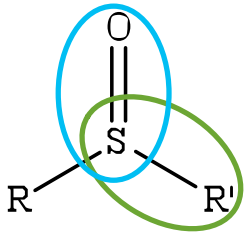
- Sulfides



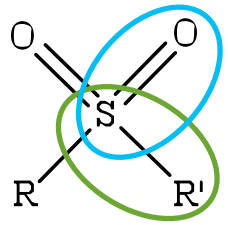
- Disulfides



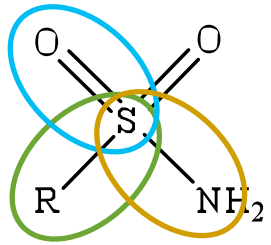
- Sulfoxides



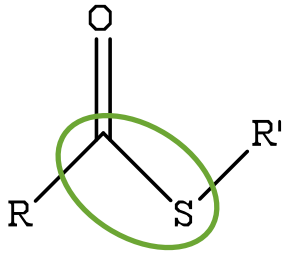
- Sulfones



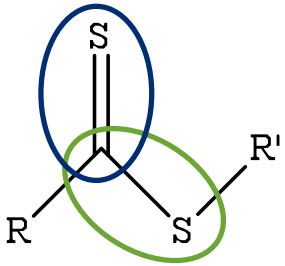
- Sulfonamides



- Thiocarboxylic acid esters

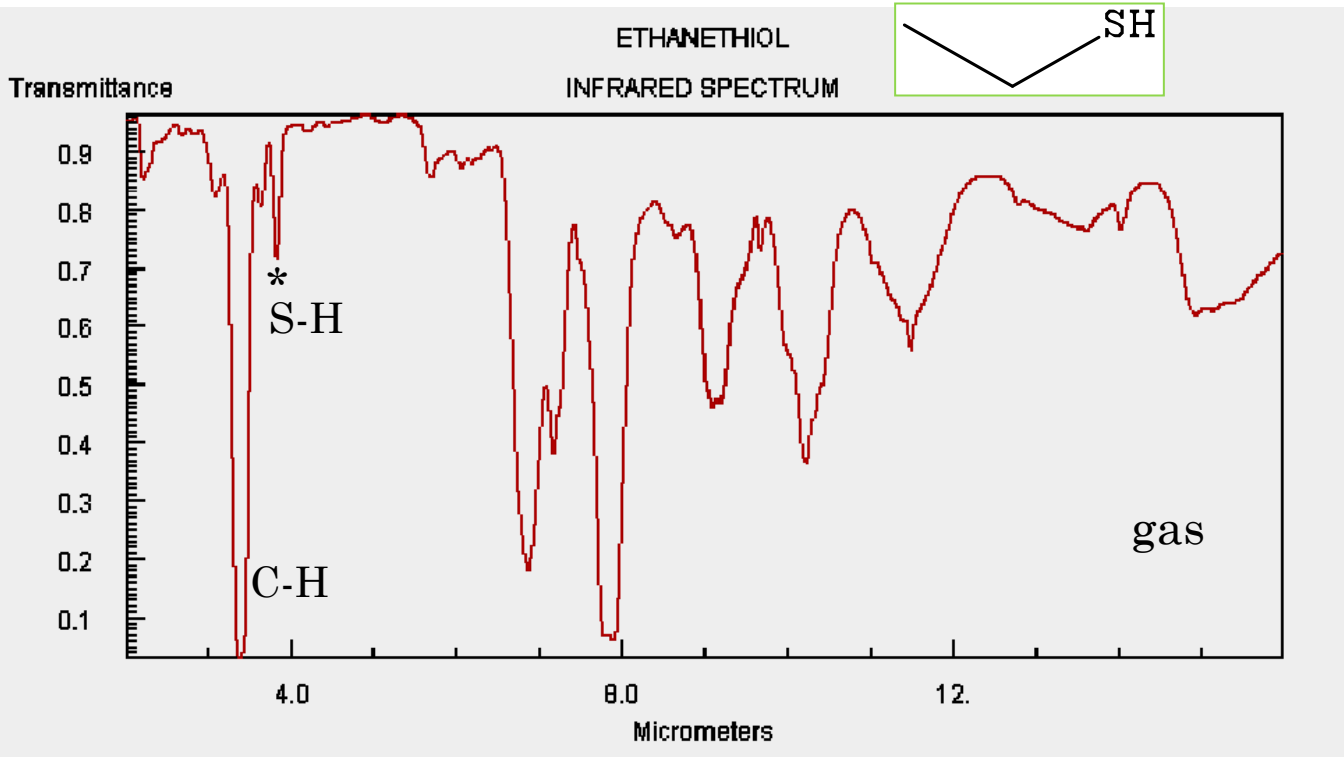


&



SULFUR: S-H STRETCH

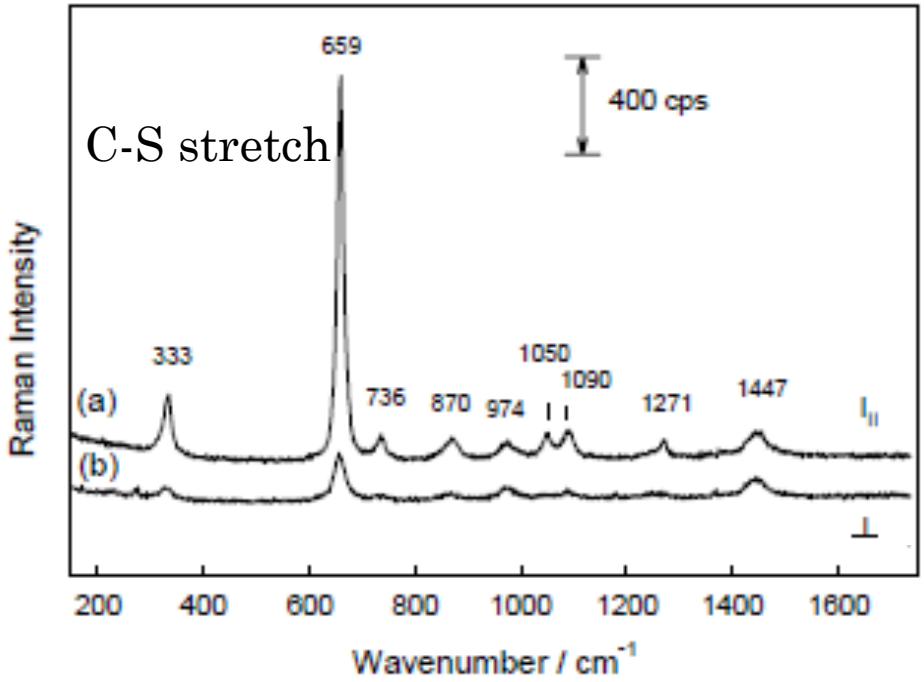
- 2600-2540 cm^{-1} weak (strong in Raman) [4.0-3.8 μm]

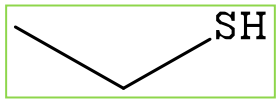


NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

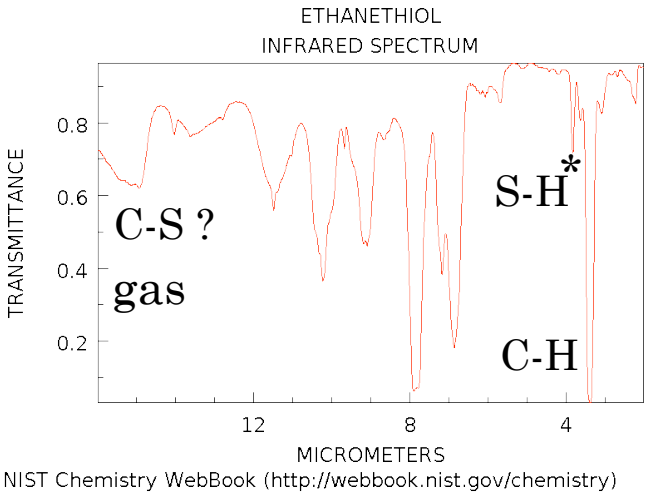
SULFUR: C-S STRETCH

- 710-570 cm^{-1} weak (strong in Raman) [17.5-14 μm]





Ethanethiol

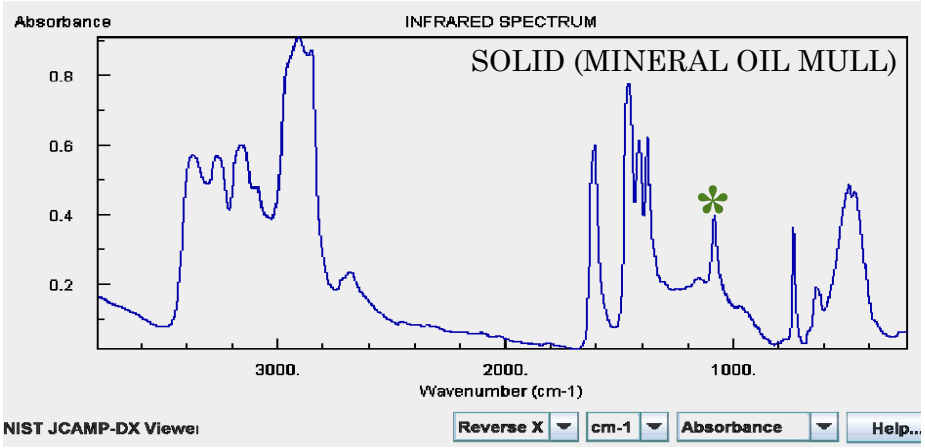


NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

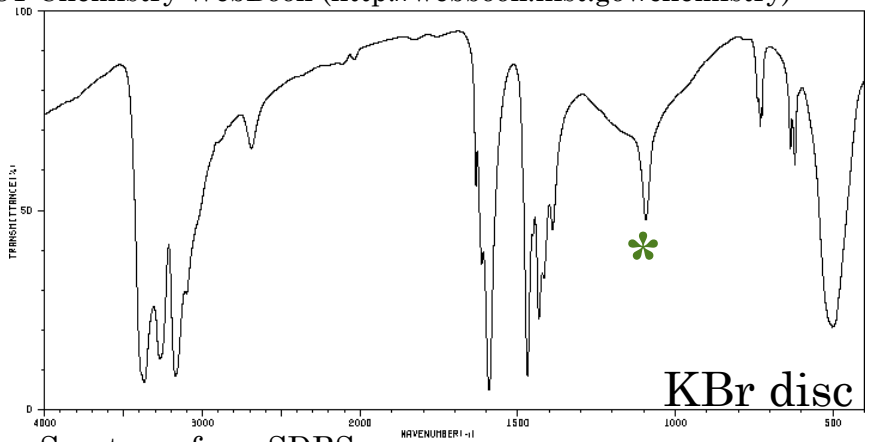
S. Bloxham, O. Eicher-Lorka, R. Jakubėnas, and G. Niaura. *CHEMIJA*, **2002**, *13*, 185.

Sulfur: C=S Stretch

- 1275-1030 cm^{-1} (strong in both IR and Raman)



NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)



Spectrum from SDBS

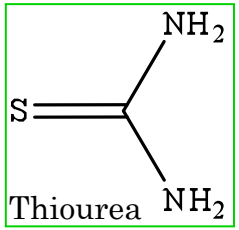
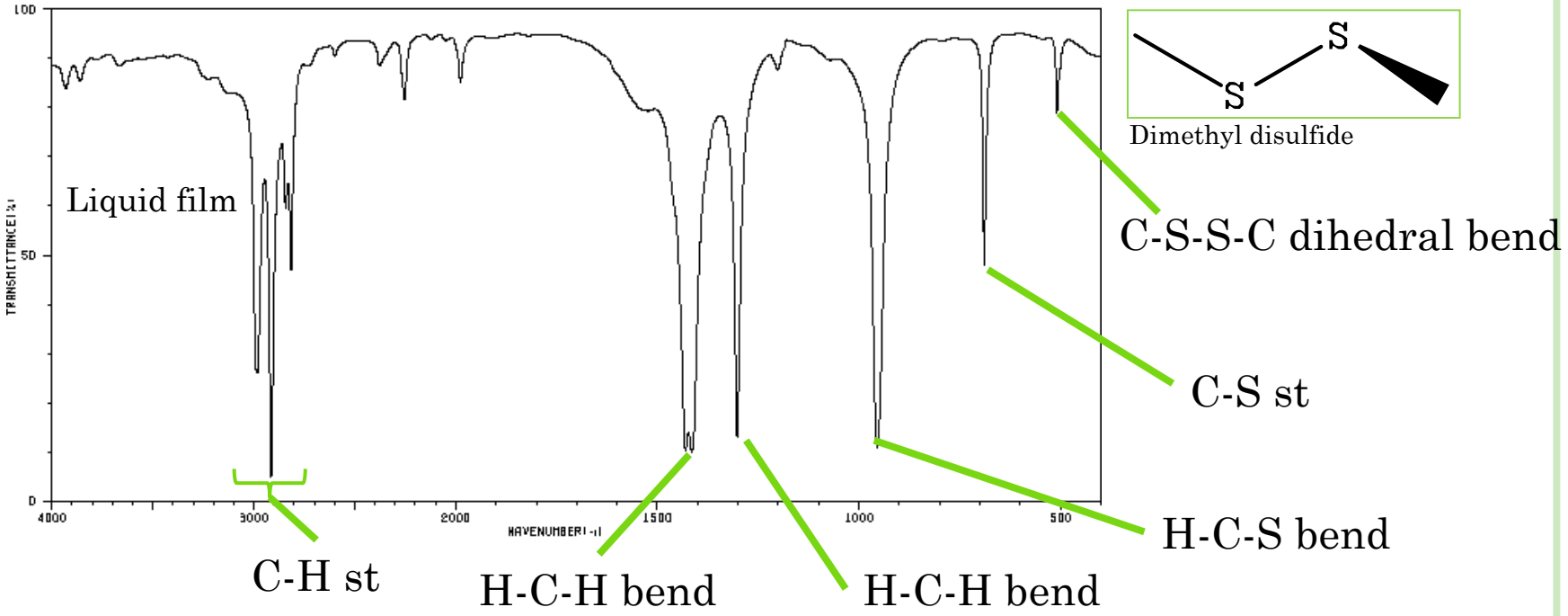


Figure 1. (a) Normal Raman spectrum of solid thiourea; (b) Normal Raman spectrum of thiourea in 0.1 M thiourea and 0.1 M $NaClO_4$; (c) SERS spectrum of thiourea adsorbed on an electrochemically activated iron electrode in 0.1 M thiourea and 0.1 M $NaClO_4$. Laser line: 632.8 nm; acquisition time: 10 s; accumulation: 4.

P. Cao, J. Yao, B. Ren, R. Gu, and Z. Tian. *J. Phys. Chem. B,* **2002**, *106*(39), 1050.

Sulfur: S-S Stretch

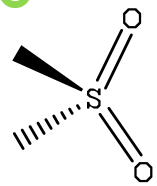
- 700-550 cm^{-1} weak, of no practical significance



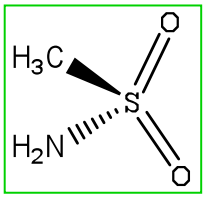
Spectrum from SDBS
Assignments made using gas phase calculation (B3LYP/6-31+G**) of dimethyl disulfide (C_2 symmetry) with *Gaussian03* and *GaussView4.1.2*.

Sulfur: S=O Stretch

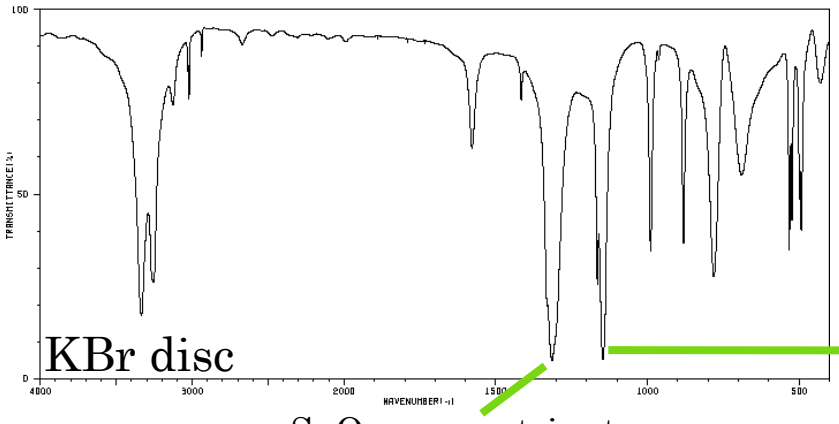
- 1225-980 cm^{-1} strong in IR
  - Sometimes multiple bands
- asymmetric stretch 1420-1300 cm^{-1} very strong
  - Often missing in Raman



- symmetric stretch 1200-1000 cm^{-1} very strong
  - Strong in Raman



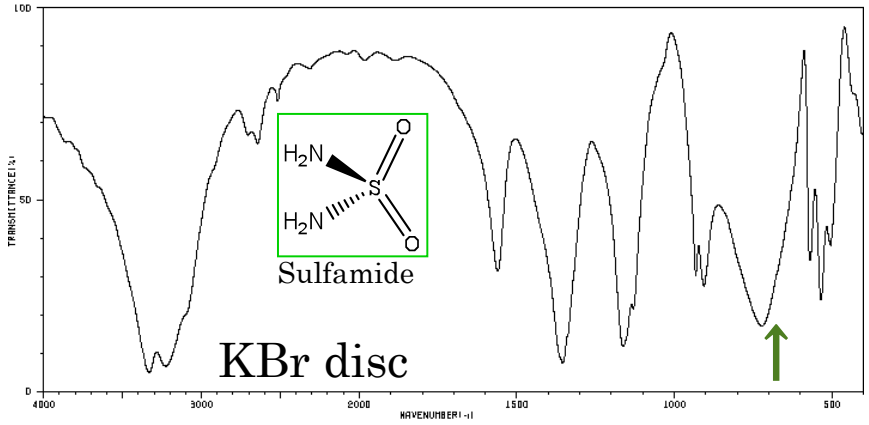
Methanesulfonamide



Spectrum from SDBS
Assignments corroborated using gas phase calculation (B3LYP/6-31+G**) of methanesulfonamide (C_1 symmetry) with *Gaussian03* and *GaussView4.1.2*.

Sulfur: S-N Stretch

- ~700 cm^{-1} visible in both IR and Raman



Spectrum from SDBS
Assignments corroborated using gas phase calculation (B3LYP/6-31+G**) of sulfamide (C_2 symmetry) with *Gaussian03* and *GaussView4.1.2*.

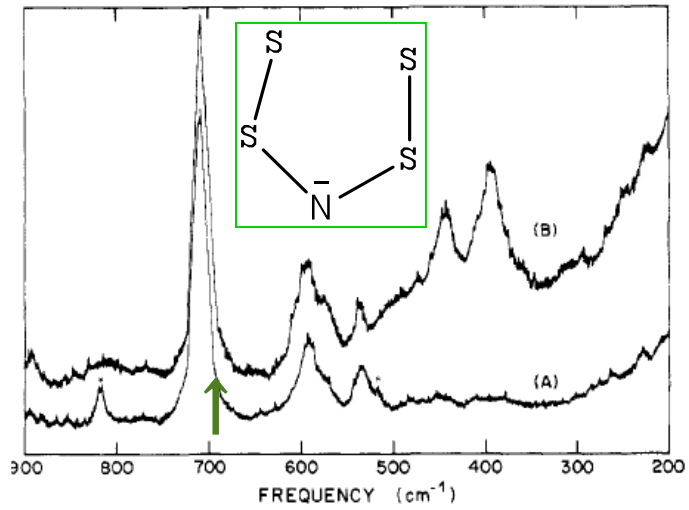


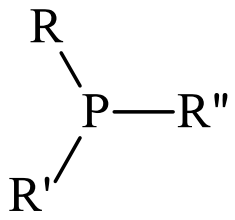
Figure 2. Raman spectra of a solution of sulfur in liquid ammonia (1.3×10^{-1} M) with (A) 600-nm and (B) 514.5-nm excitation. Bands due to the laser are marked with an asterisk.

T. Chivers and C. Lau. *Inorg. Chem.* **1982**, *21*, 453.

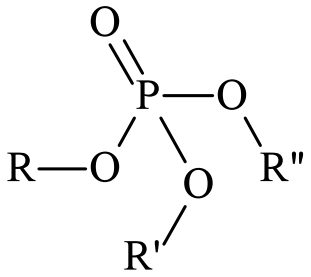
Part II: Phosphorus Containing Compounds

Phosphorus: Overview

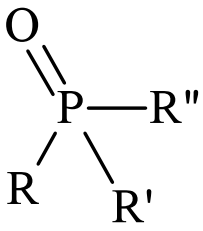
- Phosphines



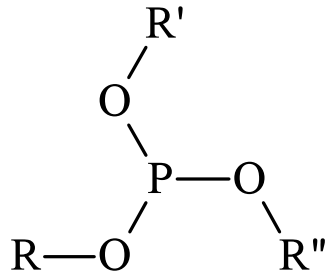
- Phosphate esters



- Phosphine oxides

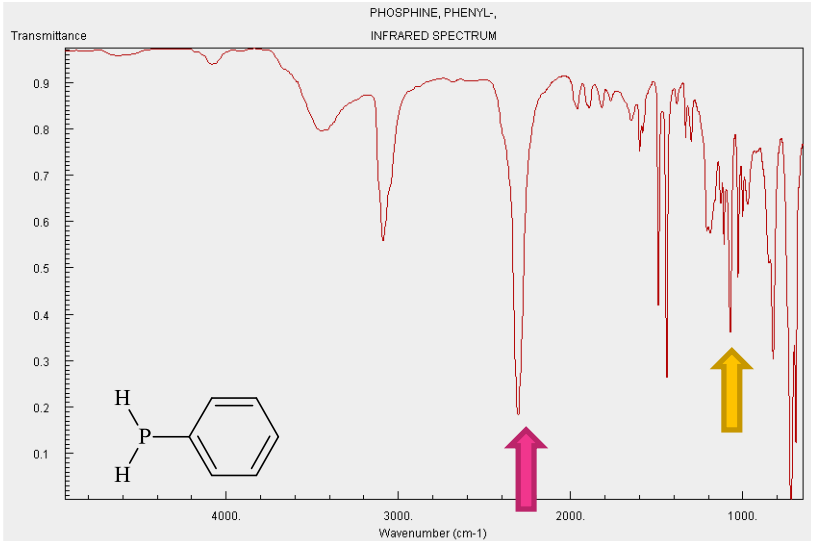


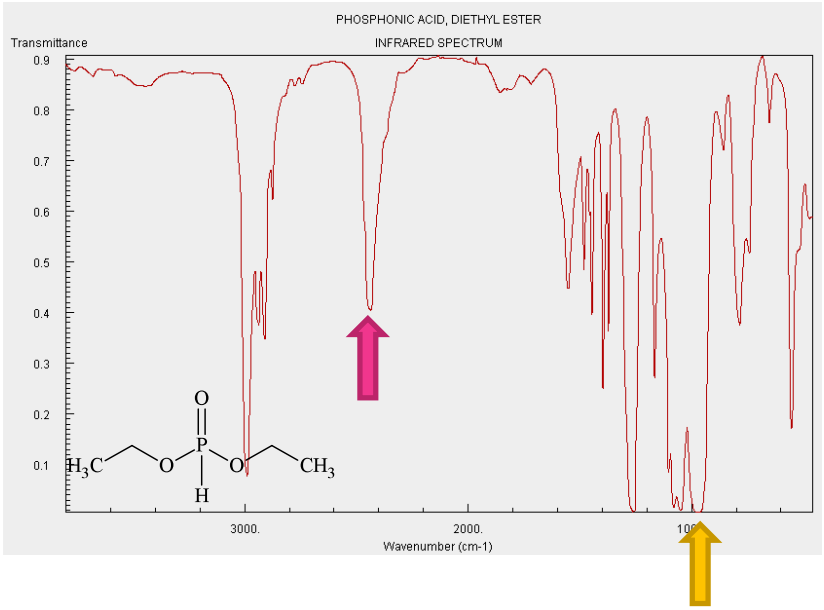
- Phosphite esters



Phosphorus: P-H Stretch/Bend

- P-H_2 stretch 2505-2222 cm^{-1} sharp, strong
  - Symmetric and asymmetric not resolved
- P-H stretch 2440-2275 cm^{-1} sharp, strong in both IR and Raman
  - Dependent upon substituents attached
- HPH bends
  - Scissors 1090-1075 cm^{-1}
  - Wag 840-810 cm^{-1}
  - Both medium-strong in IR and medium weak in Raman
- PH bend
  - Wag 990-885 cm^{-1}, strong in molecules with C-O-P, interacts with C-O-P stretch

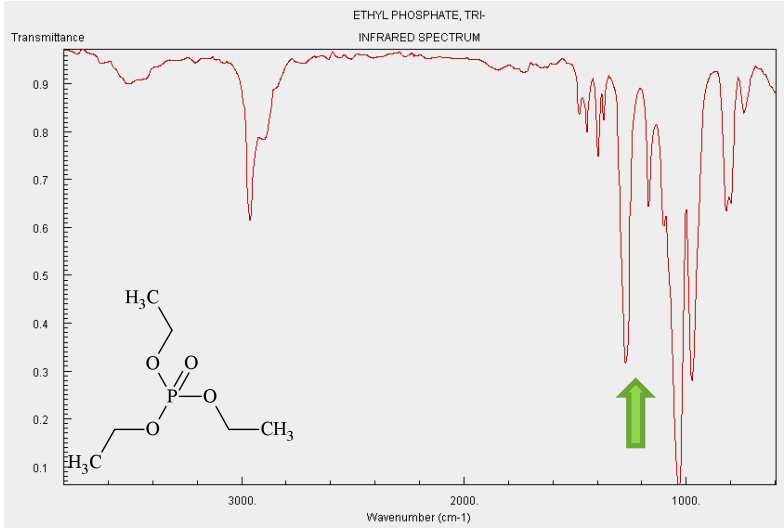


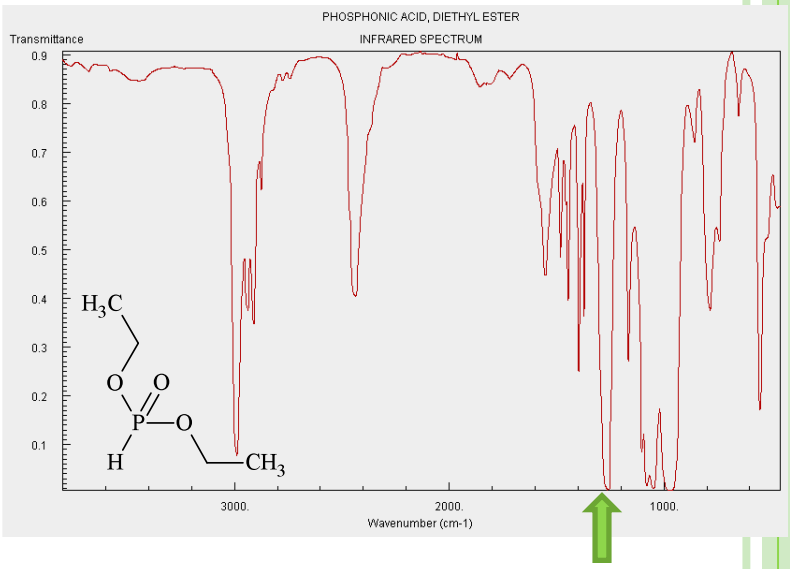


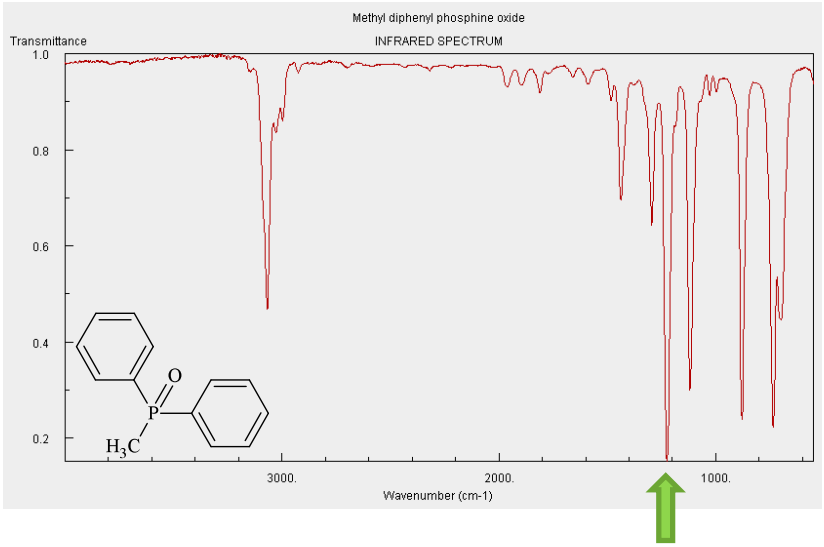
NIST Chemistry Web Book
http://webbook.nist.gov

Phosphorus: P=O Stretch

- P=O stretch
  1320-1140 cm^{-1} strong in IR, medium in Raman
  - Substituents such as F or –OH cause the range to increase to 1415-1085 cm^{-1}







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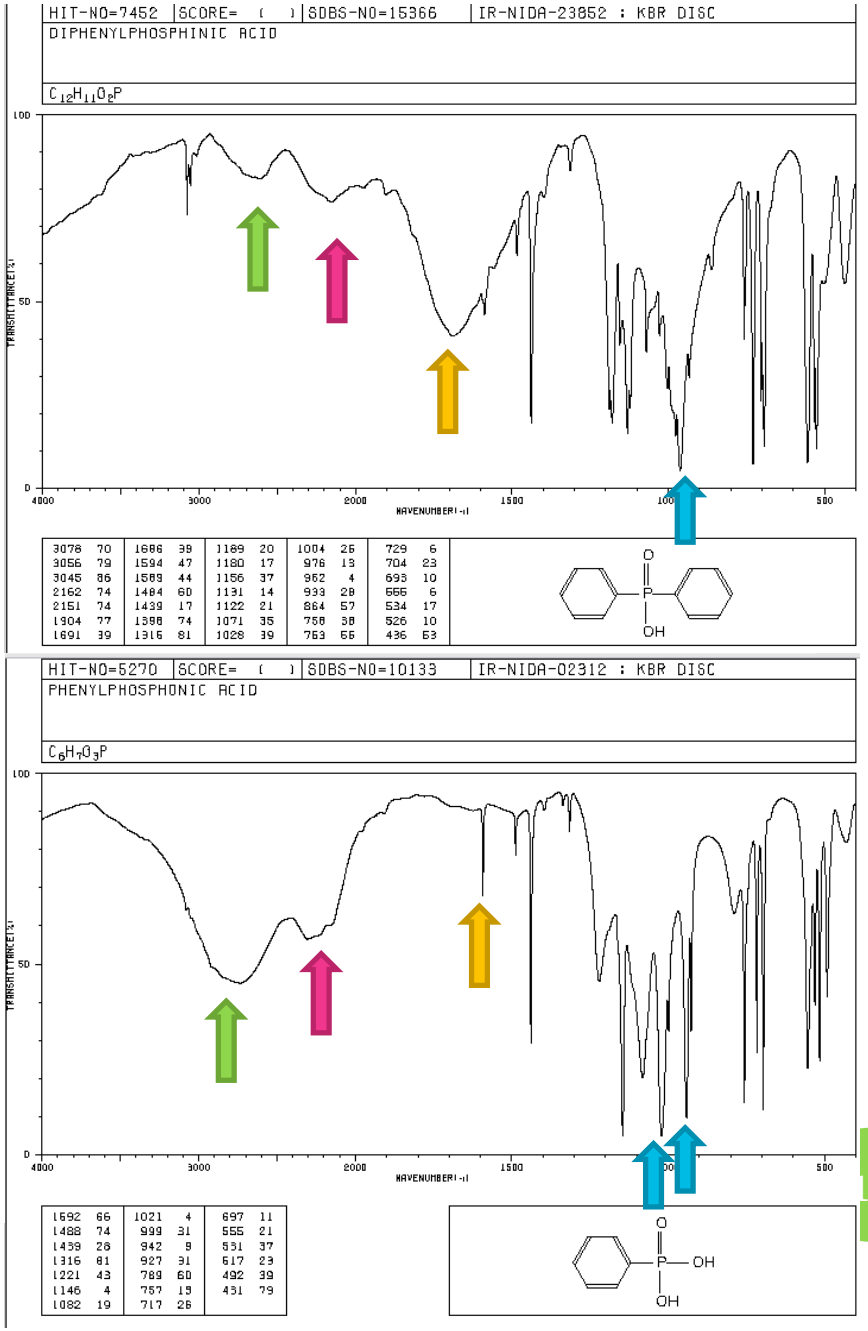
PHOSPHORUS: P-OH STRETCH

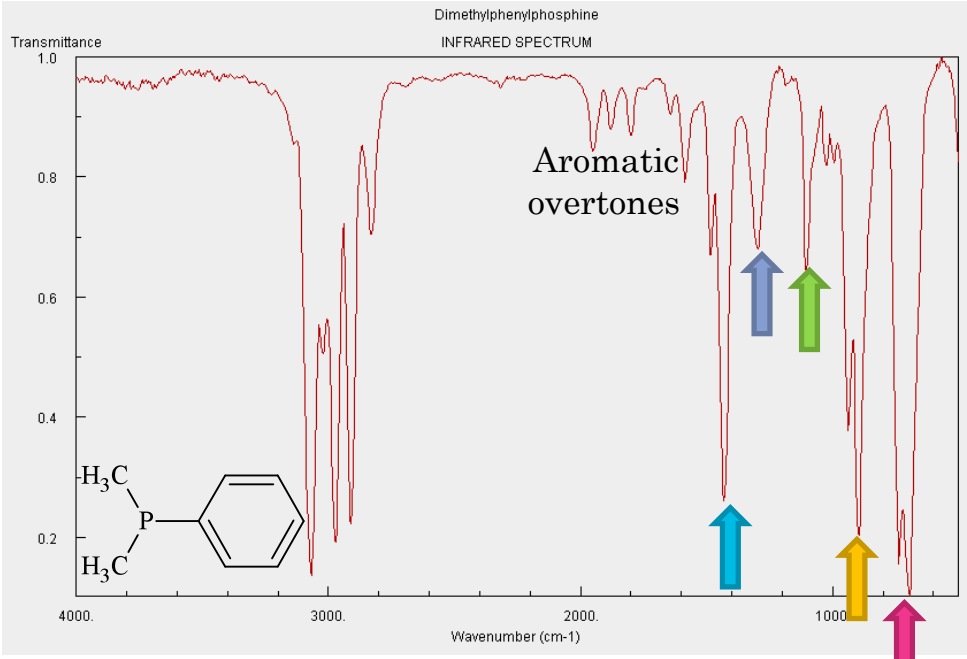
- O=P-OH broad IR bands involving OH stretch from 2725-1600 cm^{-1}
  - maxima at 2725-2525 cm^{-1} , 2350-2080 cm^{-1} , and 1740-1600 cm^{-1}
- 1 –OH group
  - Peak at 1740-1600 cm^{-1} is strongest
  - P-O stretch at 1040-909 cm^{-1}
- 2 –OH groups
  - Peak at 1740-1600 cm^{-1} is weakest, if present at all
  - P-O stretches at 1030-972 cm^{-1} and 950-917 cm^{-1}

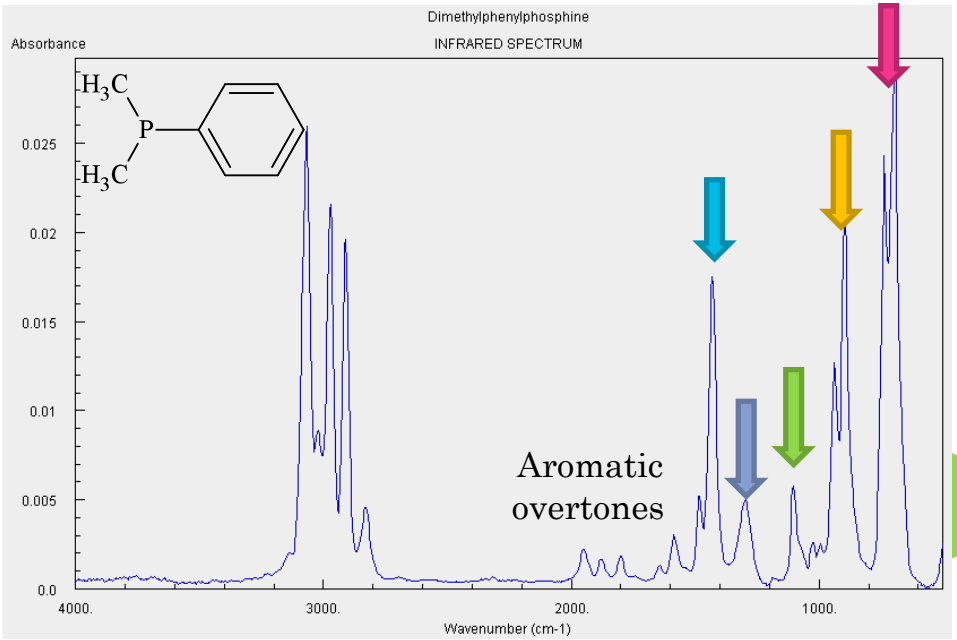


SDBS

PHOSPHORUS: P-C STRETCH

- $P\text{-}CH_3$
  - Asymmetrical deformation at 1450-1395 cm^{-1}
  - Symmetric deformation at 1346-1255 cm^{-1}
  - Rock at 977-842 cm^{-1}
- $P\text{-}CH_2\text{-}CH_3$ and $P\text{-}CH_2\text{-}R$ have deformation band at 1440-1400 cm^{-1}
- P-Ar stretch 1130-1090 cm^{-1} medium in IR, weak in Raman
- P-C stretch 754-634 medium-weak in IR, strong in Raman
  - Interacts with other bonds on phosphorus; not very characteristic





NIST Chemistry Web Book
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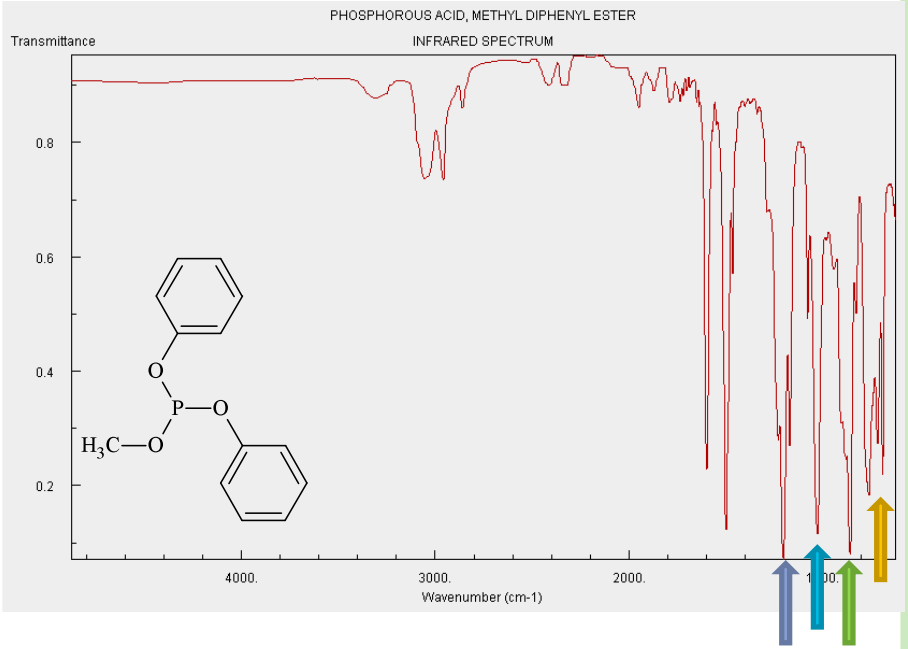
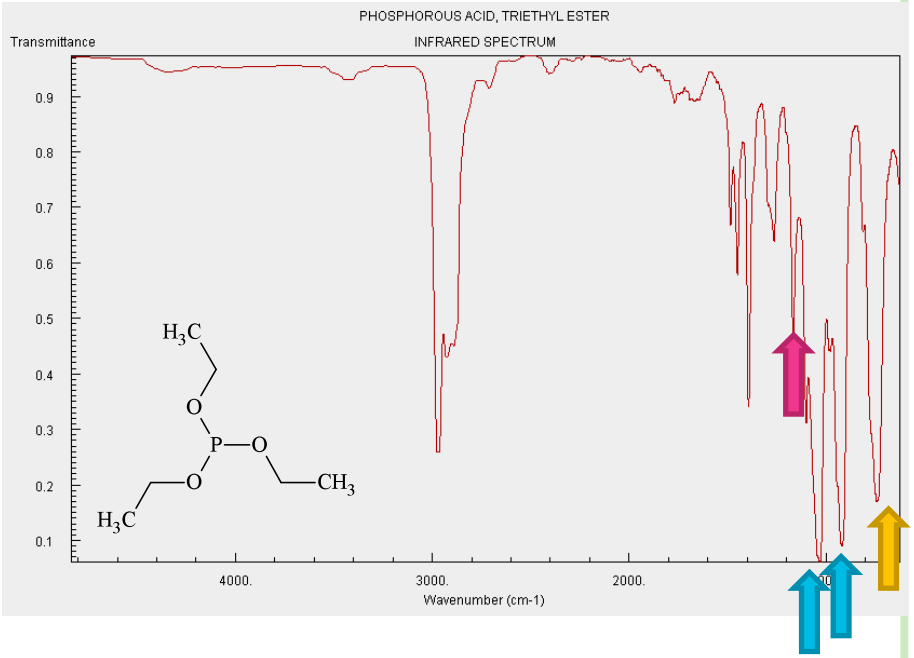
Phosphorus: P-O-C Stretch

- Out-of-phase P-O-C stretch 1088-920 cm^{-1} strong in IR, medium-weak in Raman (mostly C-O)
  - P-O-Et show second band
- In-phase P-O-C stretch 845-725 cm^{-1} (mostly P-O)
  - Larger R groups have little P-O absorption
- Rocking vibrations for P-O-Me and P-O-Et at 1190-1170 cm^{-1} and 1167-1155 cm^{-1} respectively
- P-O-Ar shows 2 bands: O-Ar 1242-1110 cm^{-1} and P-O 996-905 cm^{-1} (pentavalent) or 875-830 cm^{-1} (trivalent)





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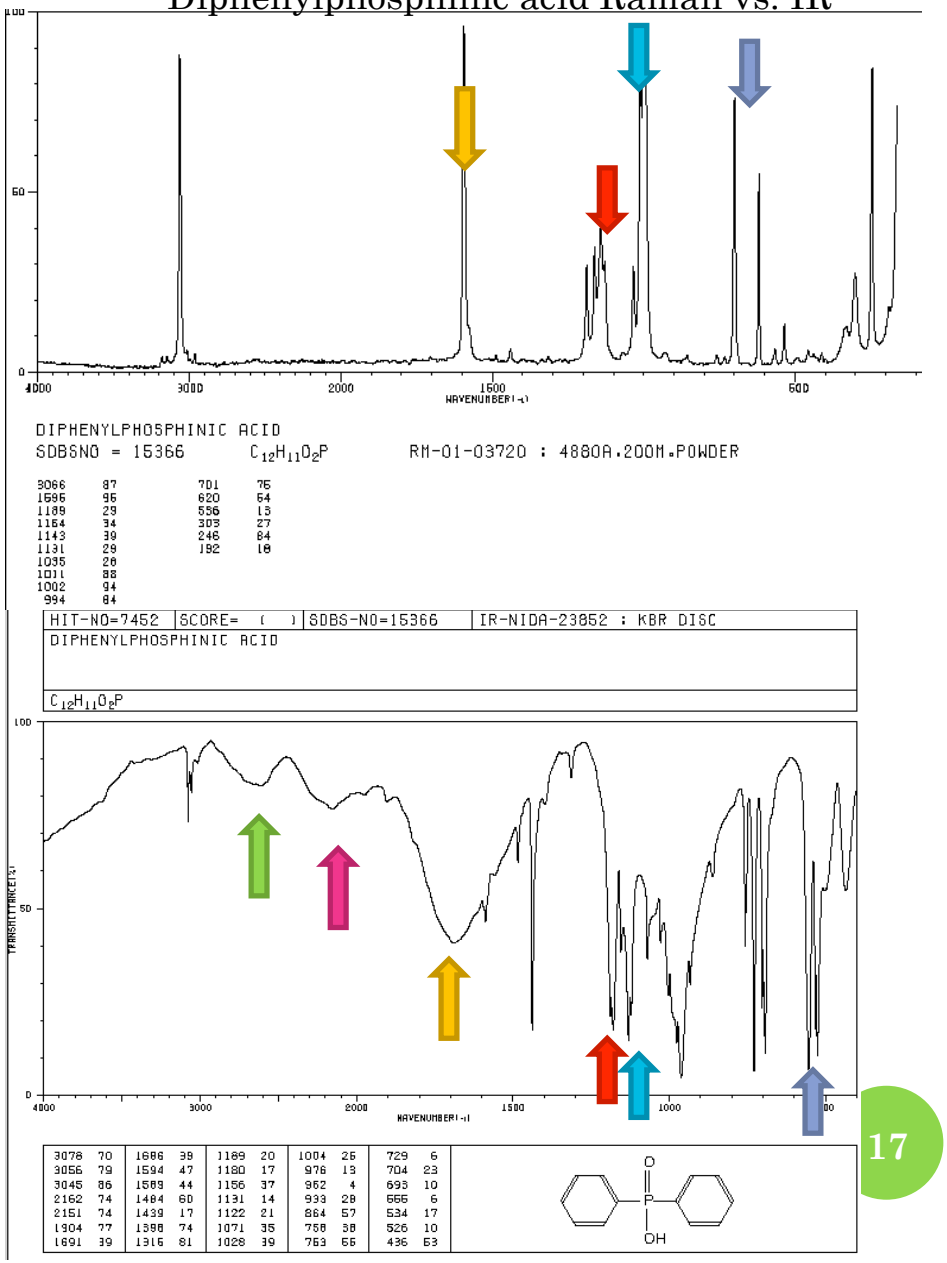
Phosphorus: IR vs. Raman

- P=O stretch 1320-1140 cm^{-1} strong. Medium in Raman
- O=P-OH broad IR bands involving OH stretch from 2725-1600 cm^{-1}
  - maxima at 2725-2525 cm^{-1} , 2350-2080 cm^{-1} , and 1740-1600 cm^{-1}
- P-Ar stretch 1130-1090 cm^{-1} medium in IR, weak in Raman
- P-C stretch 754-634 medium-weak in IR, strong in Raman
  - Interacts with other bonds on phosphorus; not very characteristic

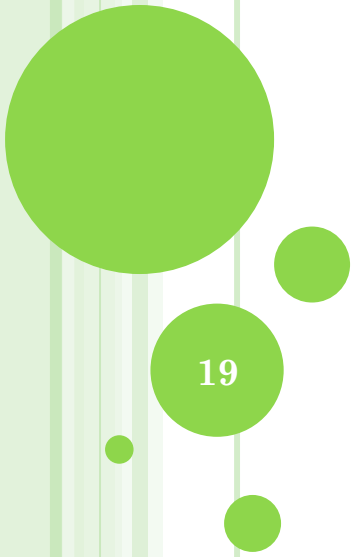
Diphenylphosphinic acid Raman vs. IR[1]



[1]SDBS

Conclusions: Points to Remember

- Strong IR stretch
  - C=S1275-1030 cm^{-1}
  - S=O 1225-980 cm^{-1}
  - S-N ~700 cm^{-1}
- C-S and S-H stretch stronger in Raman
- S-S stretch not visible in IR or Raman
- Strong P-H stretch 2440-2275 cm^{-1}
- P=O stretch 1320-1140 cm^{-1}
- Only see P-O stretch when R is small alkyl groups in P-O-R
- O=P-OH broad IR bands involving OH stretch from 2725-1600 cm^{-1}
- All P-O-C stretches and bends are below 1200 cm^{-1}
- P-C deformation bands and stretches



QUESTIONS?