Jet-FTIR-spectroscopy of pyrrole clusters

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Tammannstr. 6, 37077 Göttingen, Germany

61st Ohio State University International Symposium
on Molecular Spectroscopy
June 19–23, 2006

TB10 - Infrared / Raman

Outline

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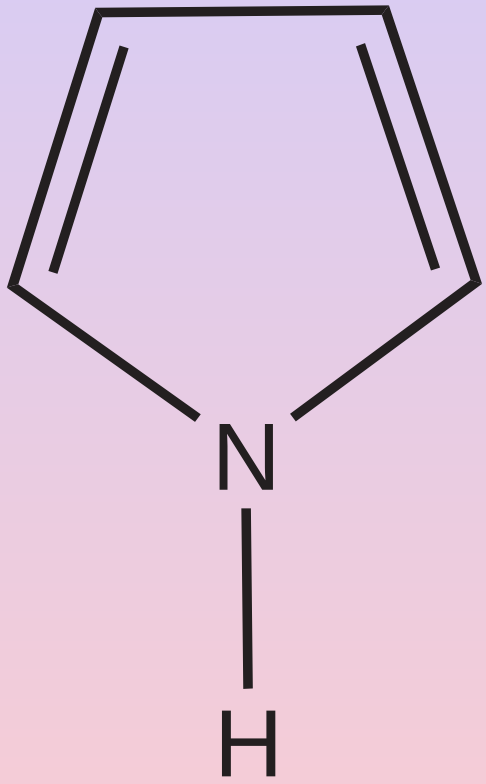
Motivation



Pyrrole

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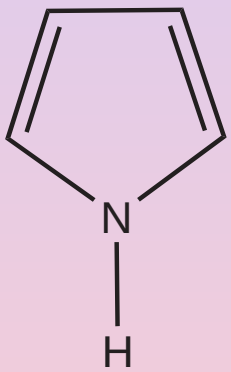
Motivation



Properties of pyrrole:

- heterocyclic aromatic ring
- electron rich aromatic (lone pair of N delocalized in aromatic ring)
- N–H functionality $\Rightarrow$ H-bond donor
- π-electrons $\Rightarrow$ H-bond acceptor (unconventional)
- $\hookrightarrow$ self clustering (N–H$\cdots\pi$)

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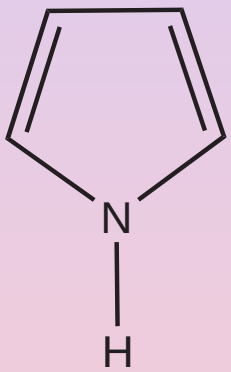

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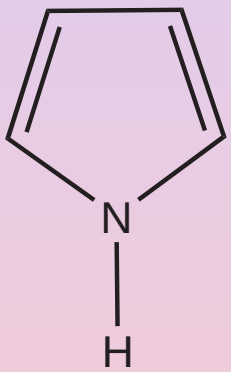

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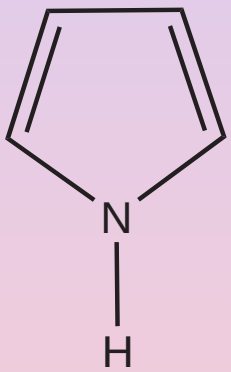

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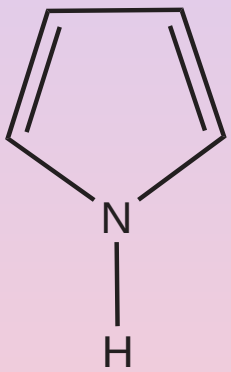

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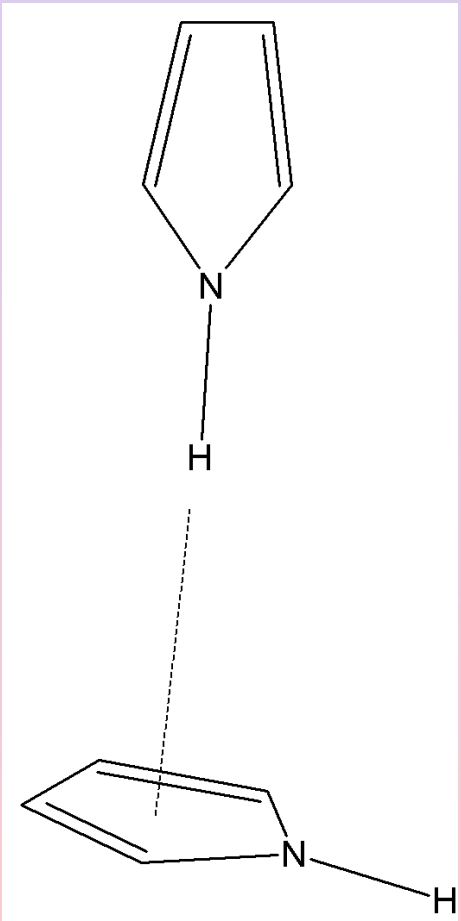
Motivation

Schematic structure of the pyrrole dimer:



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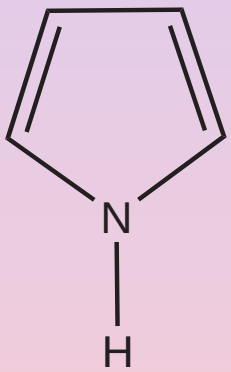

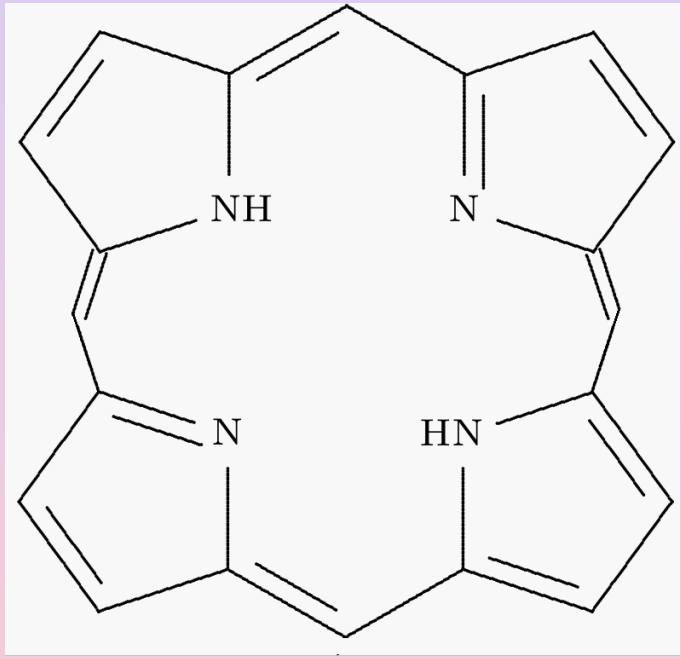

Porphyrin

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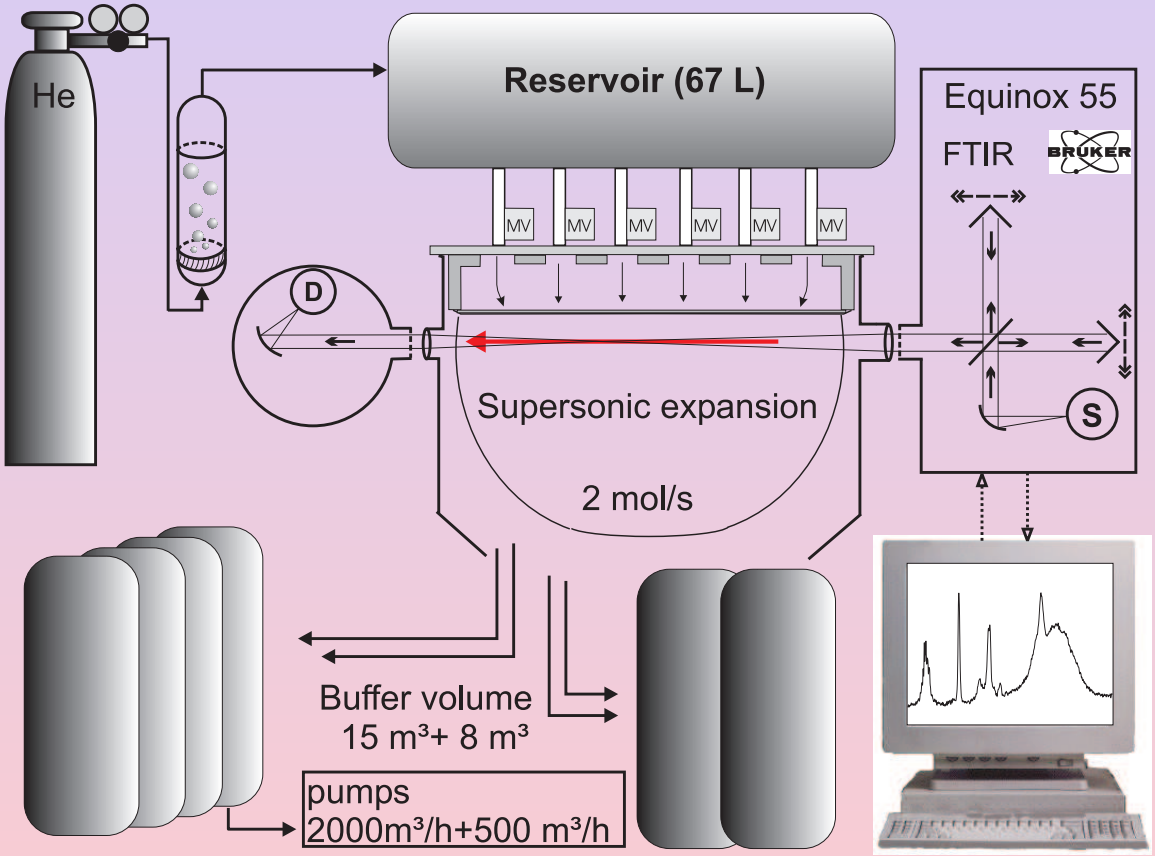
Experimental setup



Filet-Jet

(*fi*ne but *le*ng*t*hy)

Slit nozzle

$600 \times 0.2\ \mathrm{mm}^2$

C. A. Rice, N. Borho and M. A. Suhm, *Z. Phys. Chem.*, 219, **2005**, 379–388.

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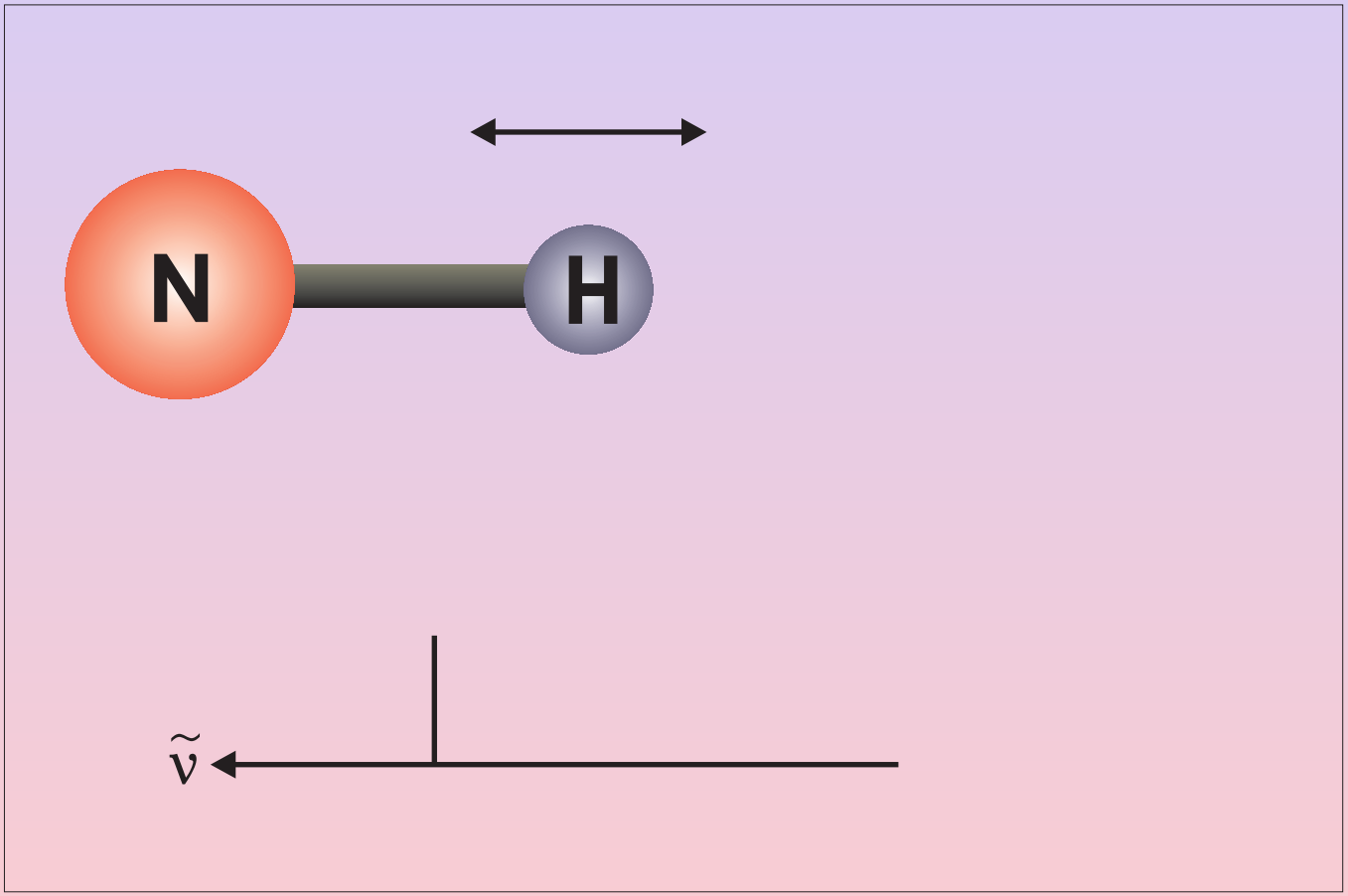
Vibrational spectroscopy of clusters



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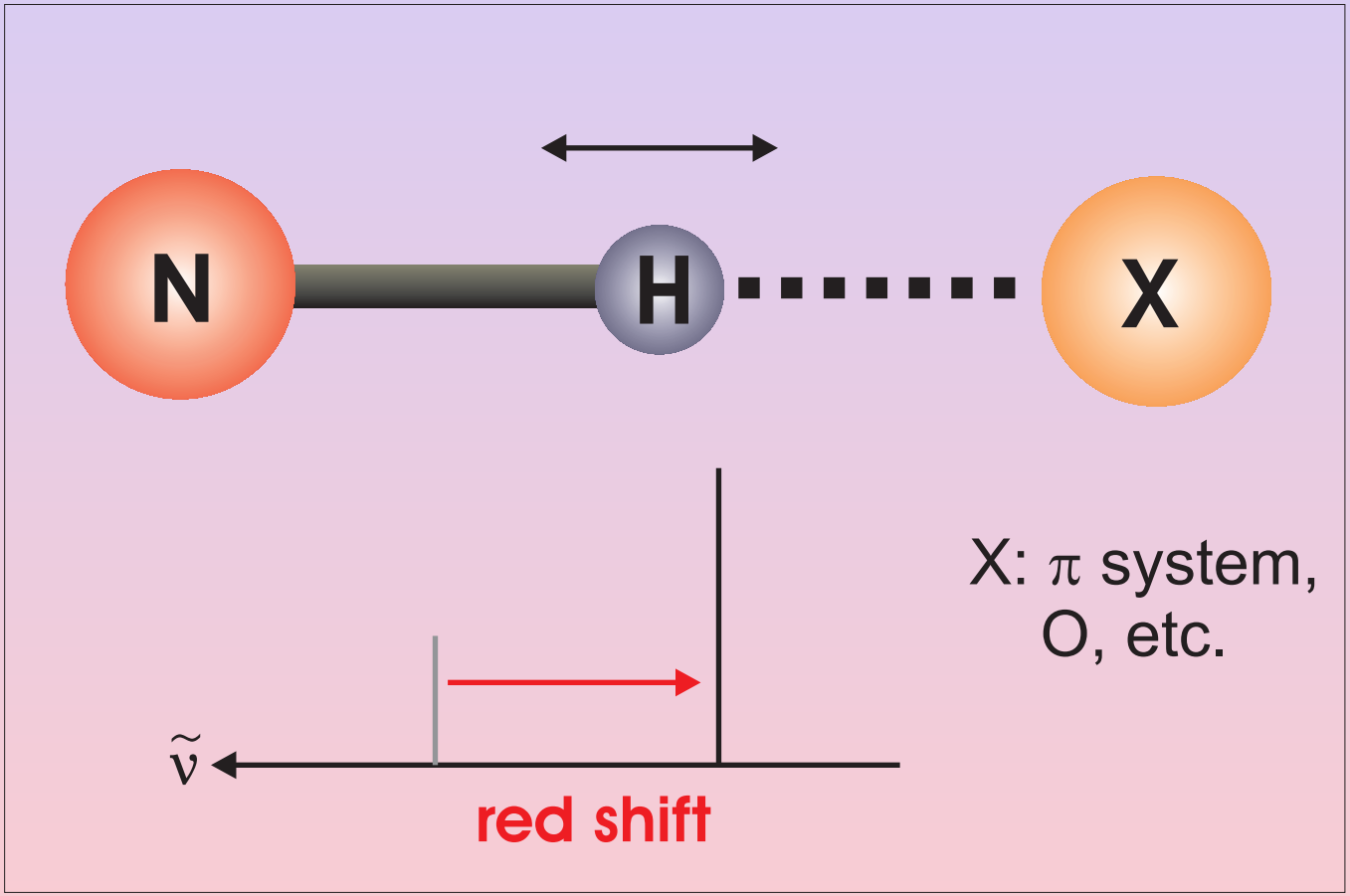
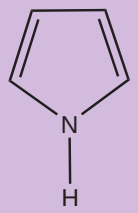
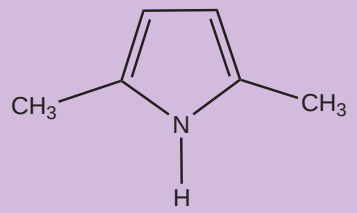


Overview of the measured systems

H-bond donors

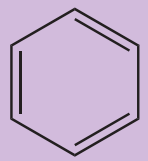


Pyrrole

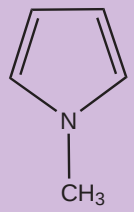


2,5-Dimethylpyrrole

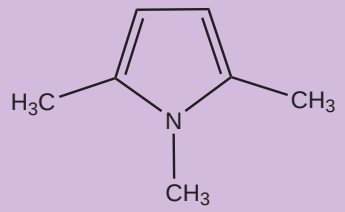
Pure H-bond acceptors



Benzene



N-Methylpyrrole



1,2,5-Trimethylpyrrole

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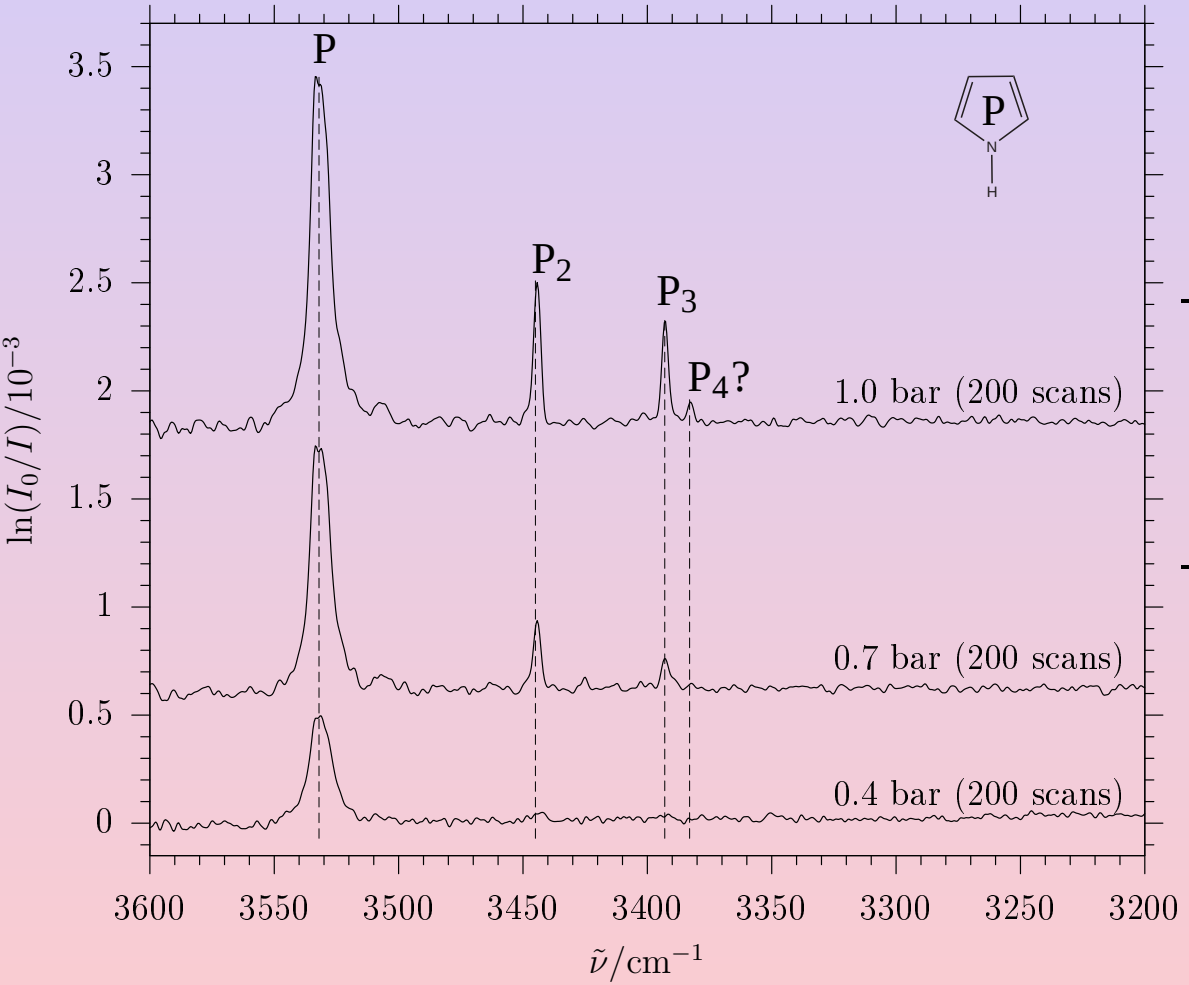
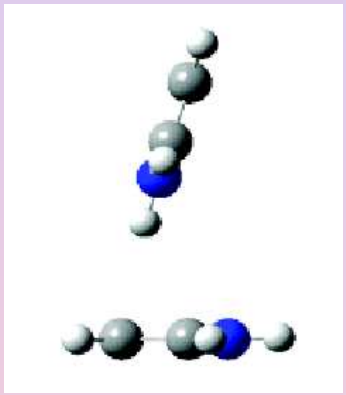
Pyrrole

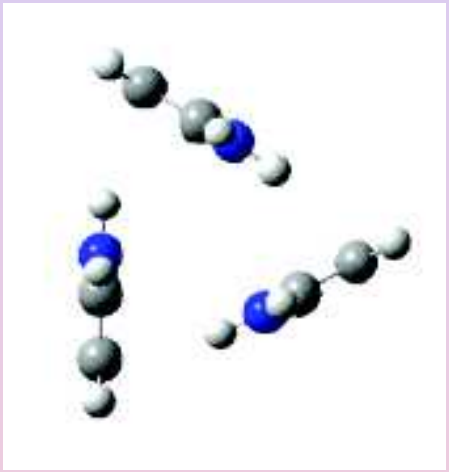


	$\tilde{\nu}_{\mathrm{N-H}}$ / cm^{-1}	$-\Delta\tilde{\nu}_{\mathrm{N-H}}$ / cm^{-1}
P	3533	–
P_2	3445	88
P_3	3393	140
P_4	3383	150

Pyrrole - structures of the clusters



P_2
Dimer



P_3
Trimer

P_4
Tetramer

B3LYP / 6-311++G**

A. Gómez-Zavaglia and R. Fausto, *J. Phys. Chem. A*, 108, **2004**, 6953–6967.

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Comparison - experiment and DFT calculations

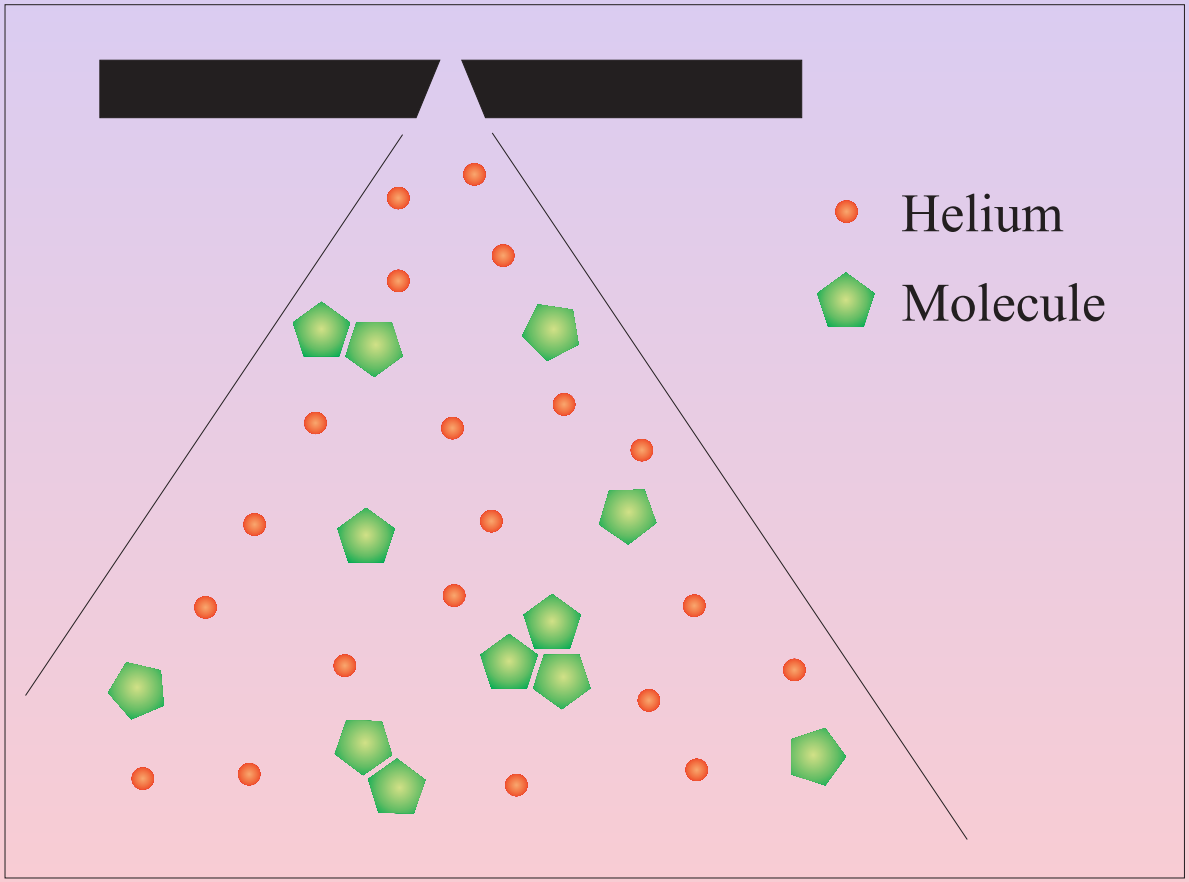
	this work in Helium		Gómez-Zavaglia *et al.* Calculation[a]	
	$\tilde{\nu}_{\mathrm{N-H}}$ / cm^{-1}	$-\Delta\tilde{\nu}_{\mathrm{N-H}}$ / cm^{-1}	$\tilde{\nu}_{\mathrm{N-H}}$[b] / cm^{-1}	$-\Delta\tilde{\nu}_{\mathrm{N-H}}$ / cm^{-1}
P	3533	–	3593	–
P_2	3445	88	3523	70
P_3	3393	140	3495	98
P_4	3383	150	3475	118

[a] B3LYP / 6-311++G**

[b] Scaling factor of 0.978

A. Gómez-Zavaglia and R. Fausto, *J. Phys. Chem. A*, 108, **2004**, 6953–6967.

Expansion in Helium vs. Argon



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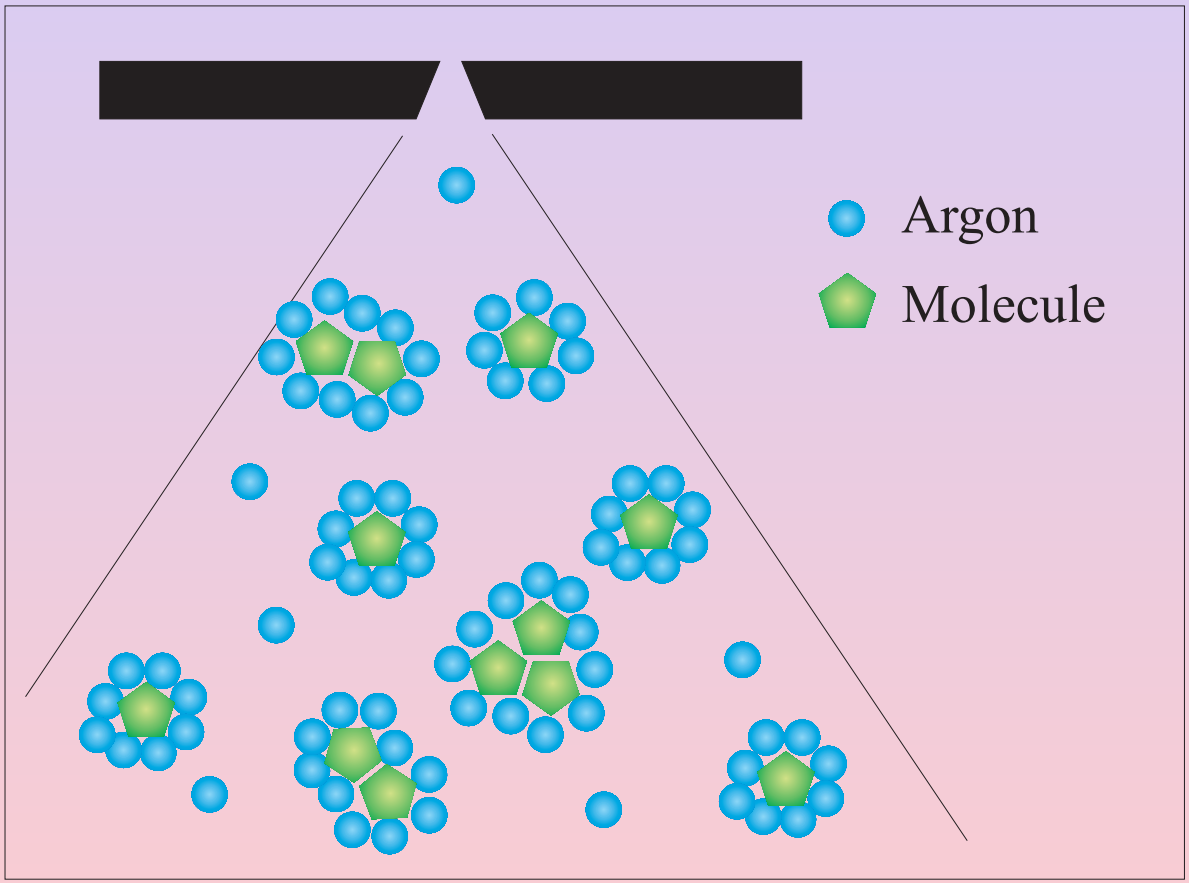
Expansion in Helium vs. Argon



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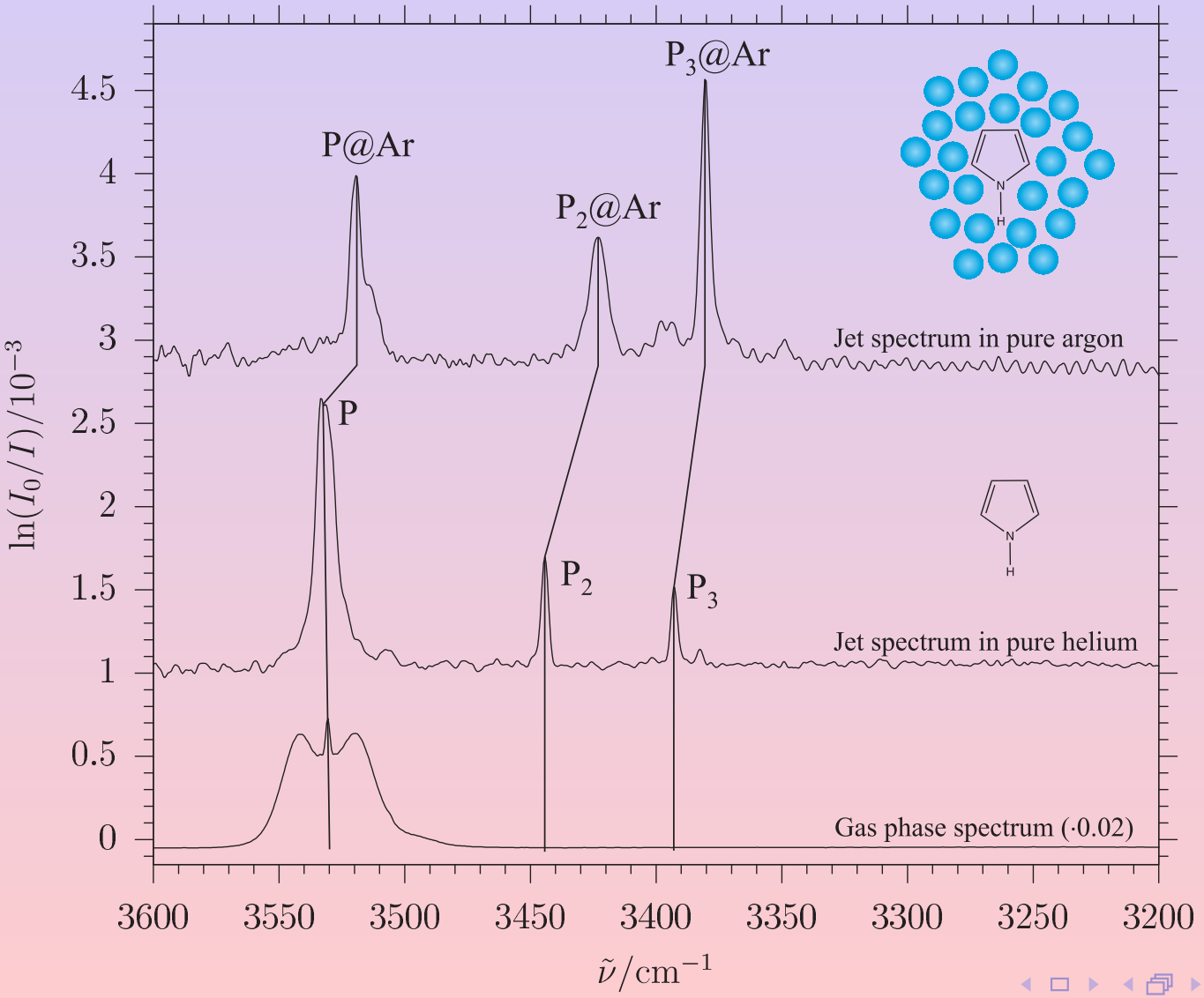
Pyrrole in Helium and Argon

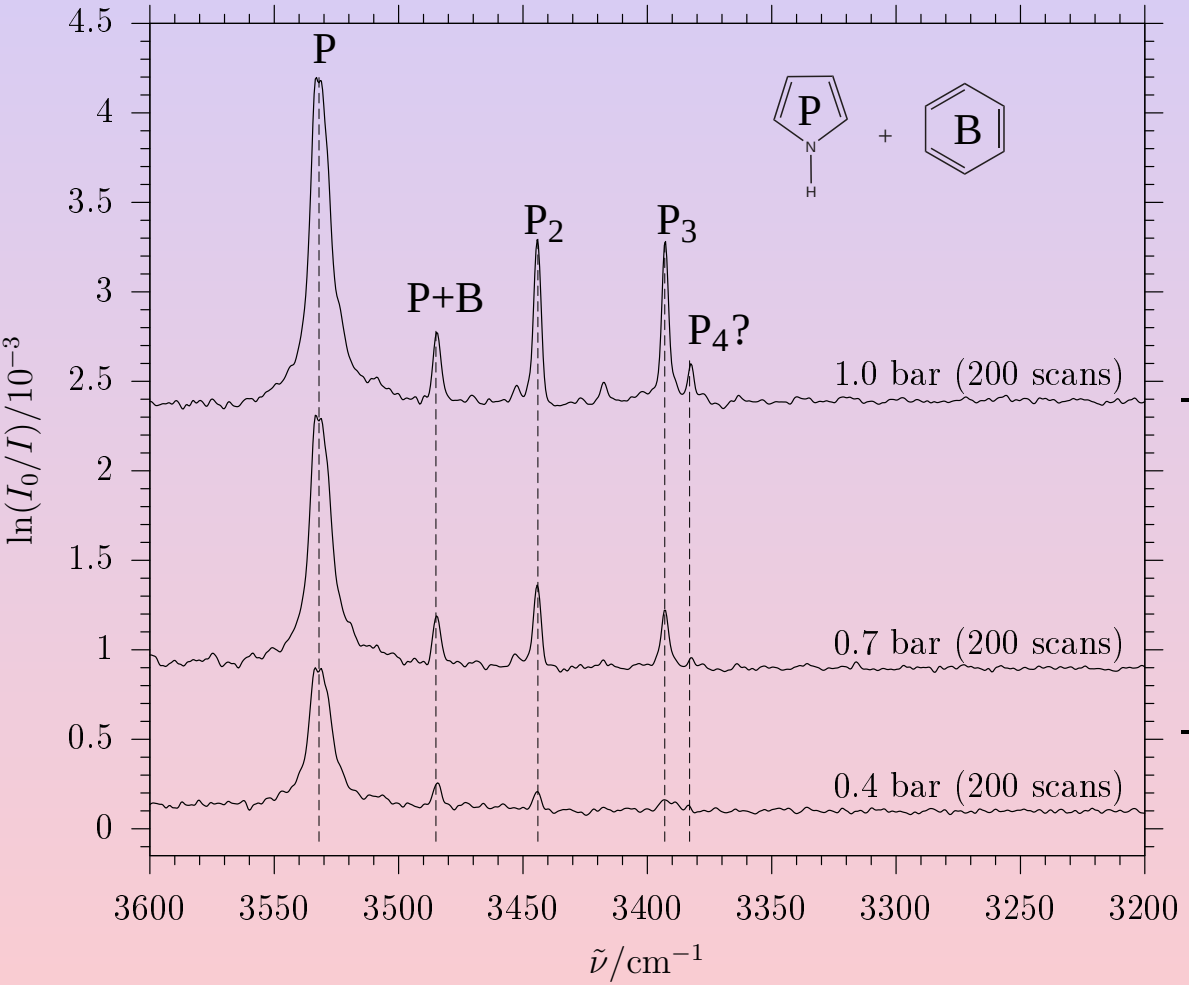


Comparision - Argon nanomatrix and Argon matrix

	this work in Argon		Gómez-Zavaglia *et al.* Argon matrix	
	$\tilde{\nu}_{\mathrm{N-H}}$ / cm^{-1}	$-\Delta\tilde{\nu}_{\mathrm{N-H}}$ / cm^{-1}	$\tilde{\nu}_{\mathrm{N-H}}$ / cm^{-1}	$-\Delta\tilde{\nu}_{\mathrm{N-H}}$ / cm^{-1}
P@Ar	3520	–	3523	–
P_2@Ar	3423	97	3418	105
P_3@Ar	3381	139	3396	127
P_4@Ar	–	–	3378	145

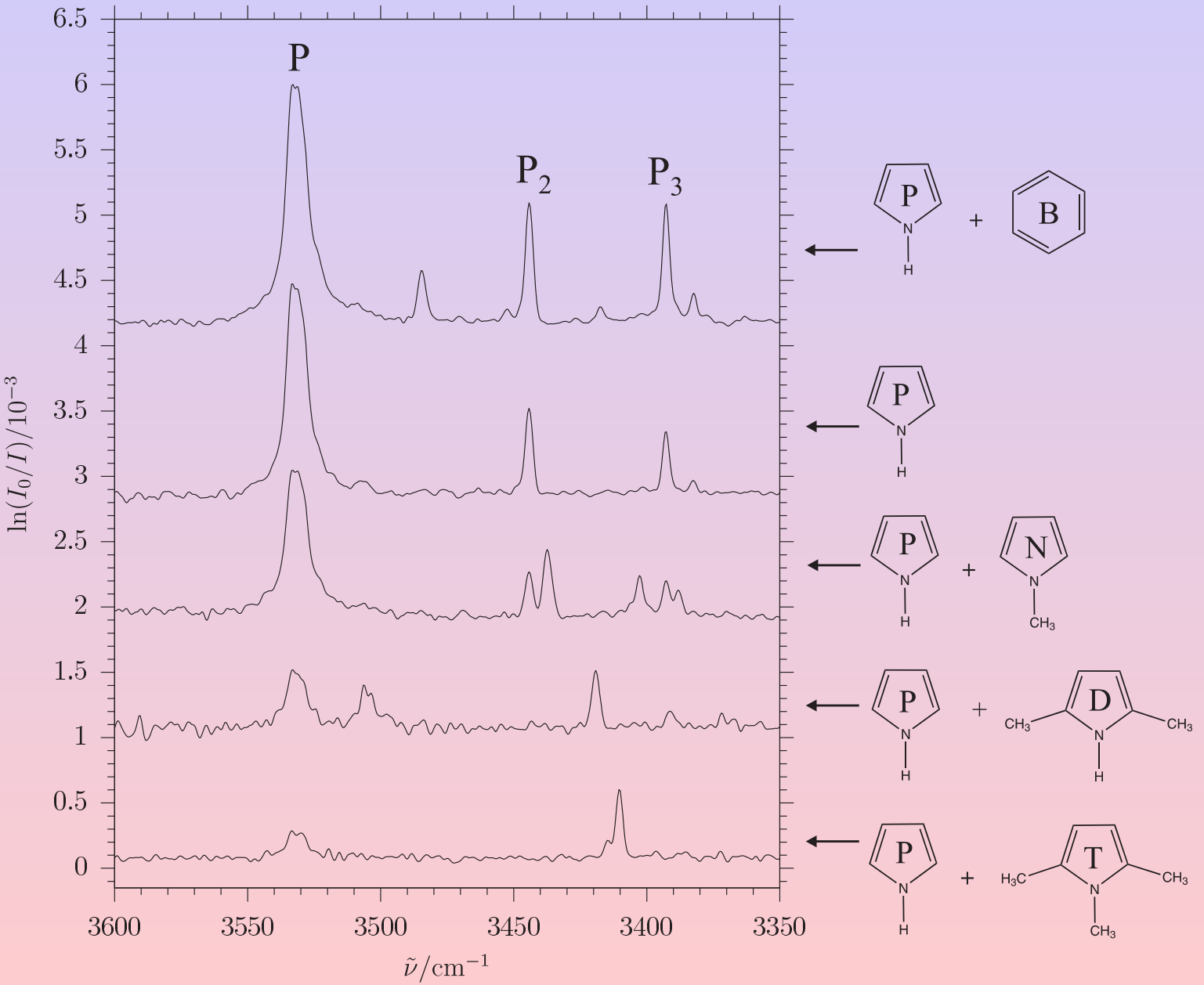
A. Gómez-Zavaglia and R. Fausto, *J. Phys. Chem. A*, 108, **2004**, 6953–6967.

Pyrrole / Benzene



	$\tilde{\nu}_{\mathrm{N-H}}$ / cm^{-1}	$-\Delta\tilde{\nu}_{\mathrm{N-H}}$ / cm^{-1}
P	3533	–
P+B	3485	48
P_2	3445	88
P_3	3393	140
P_4	3383	150

Pyrrole as donor - overview



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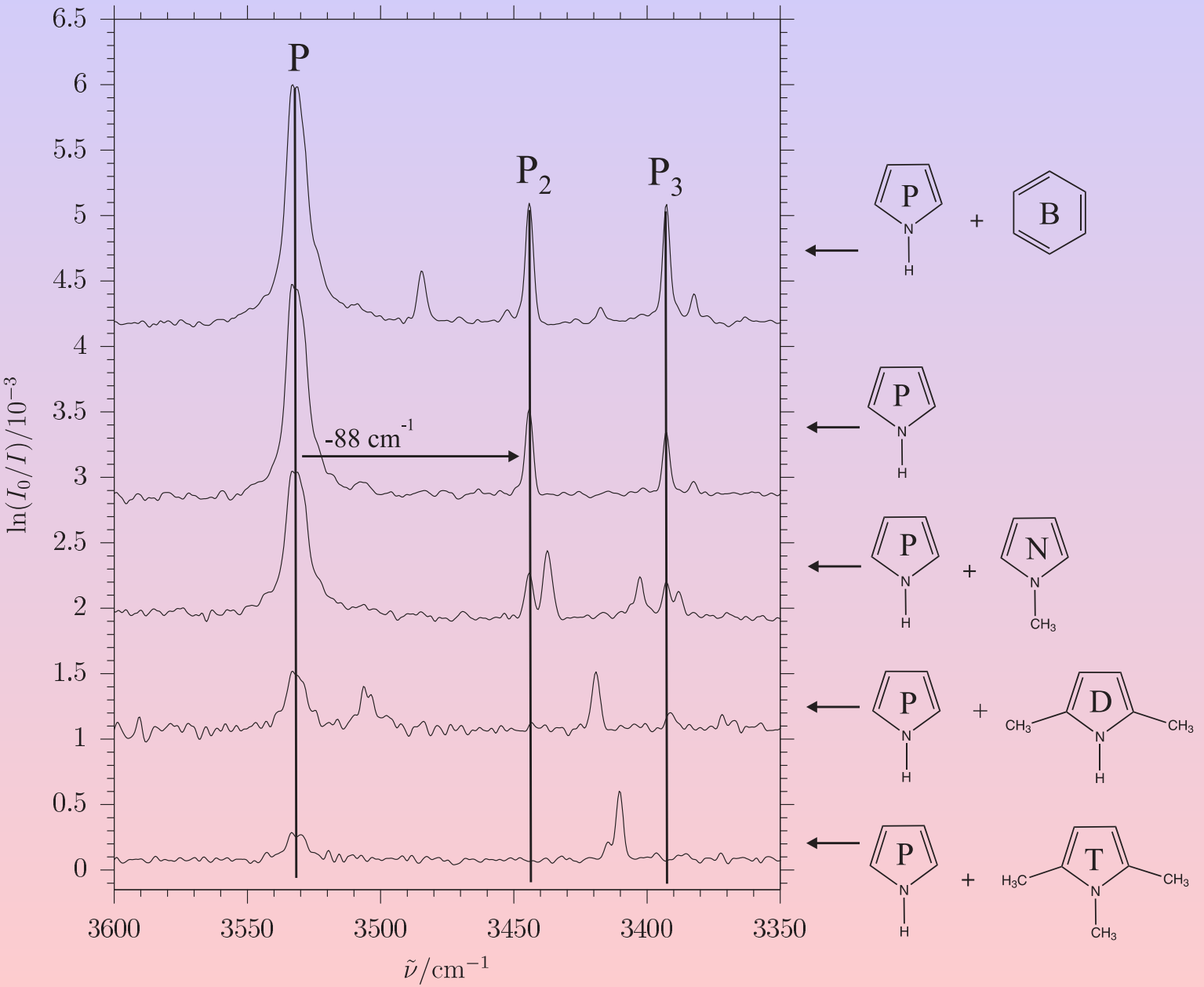

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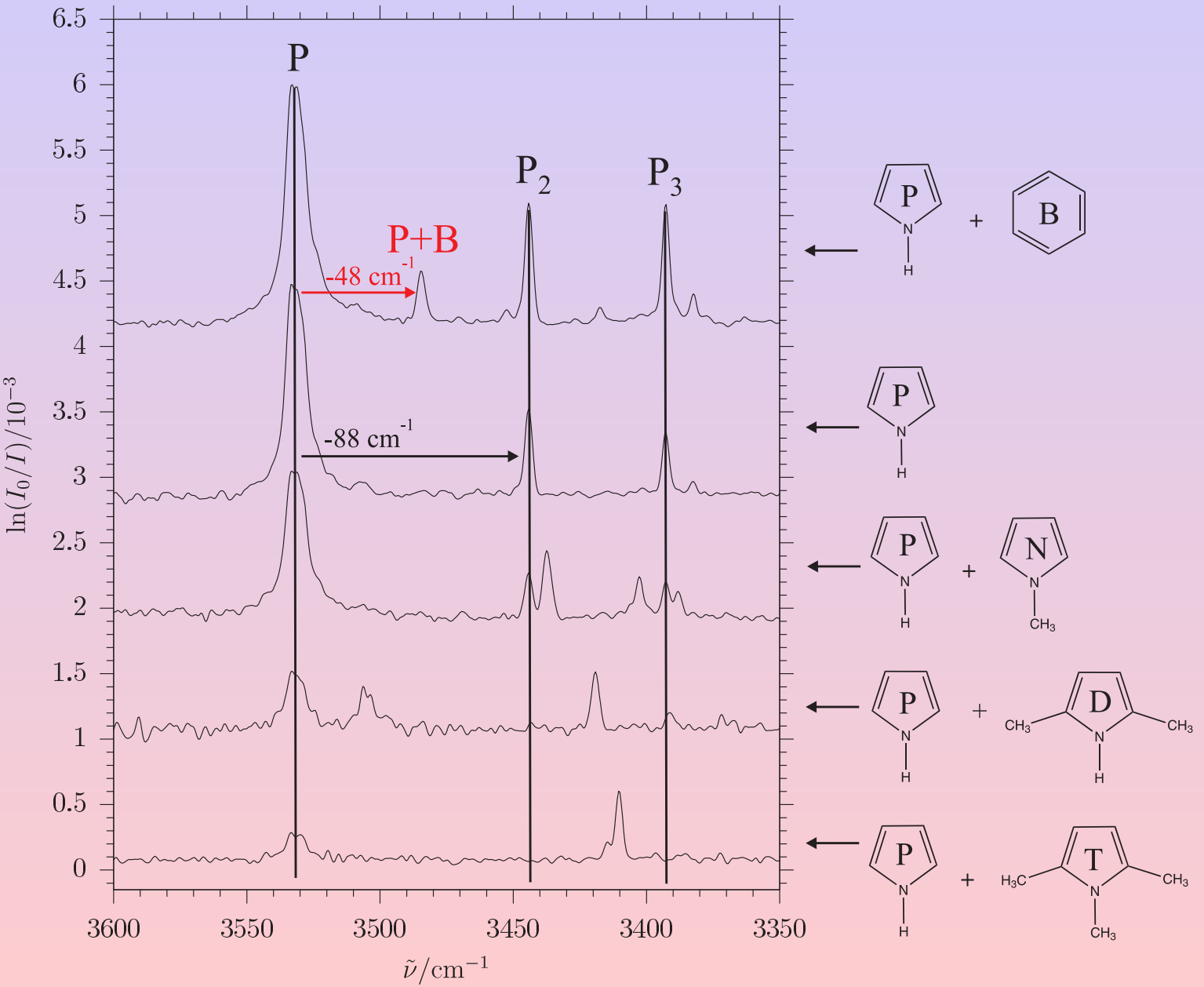

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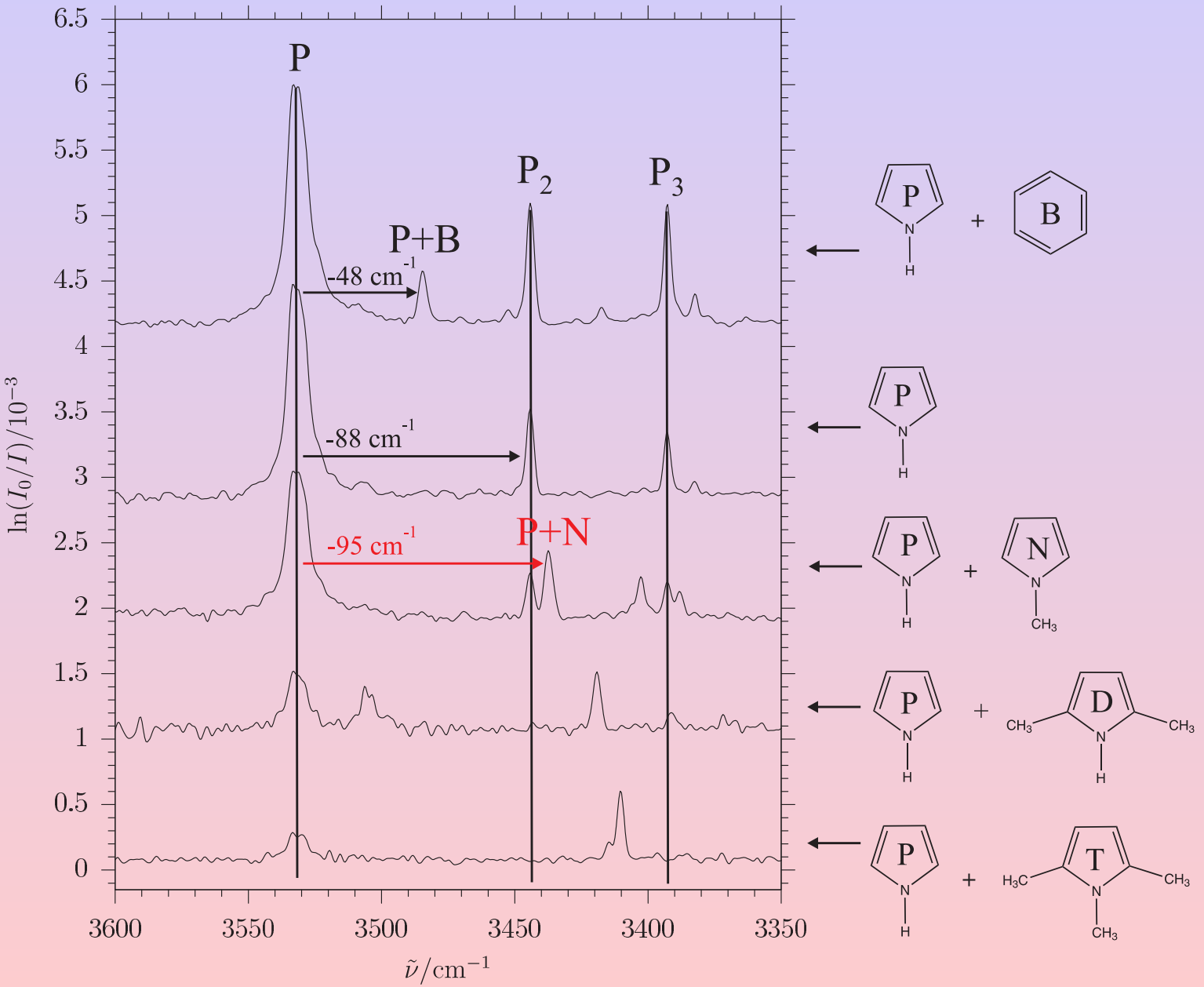

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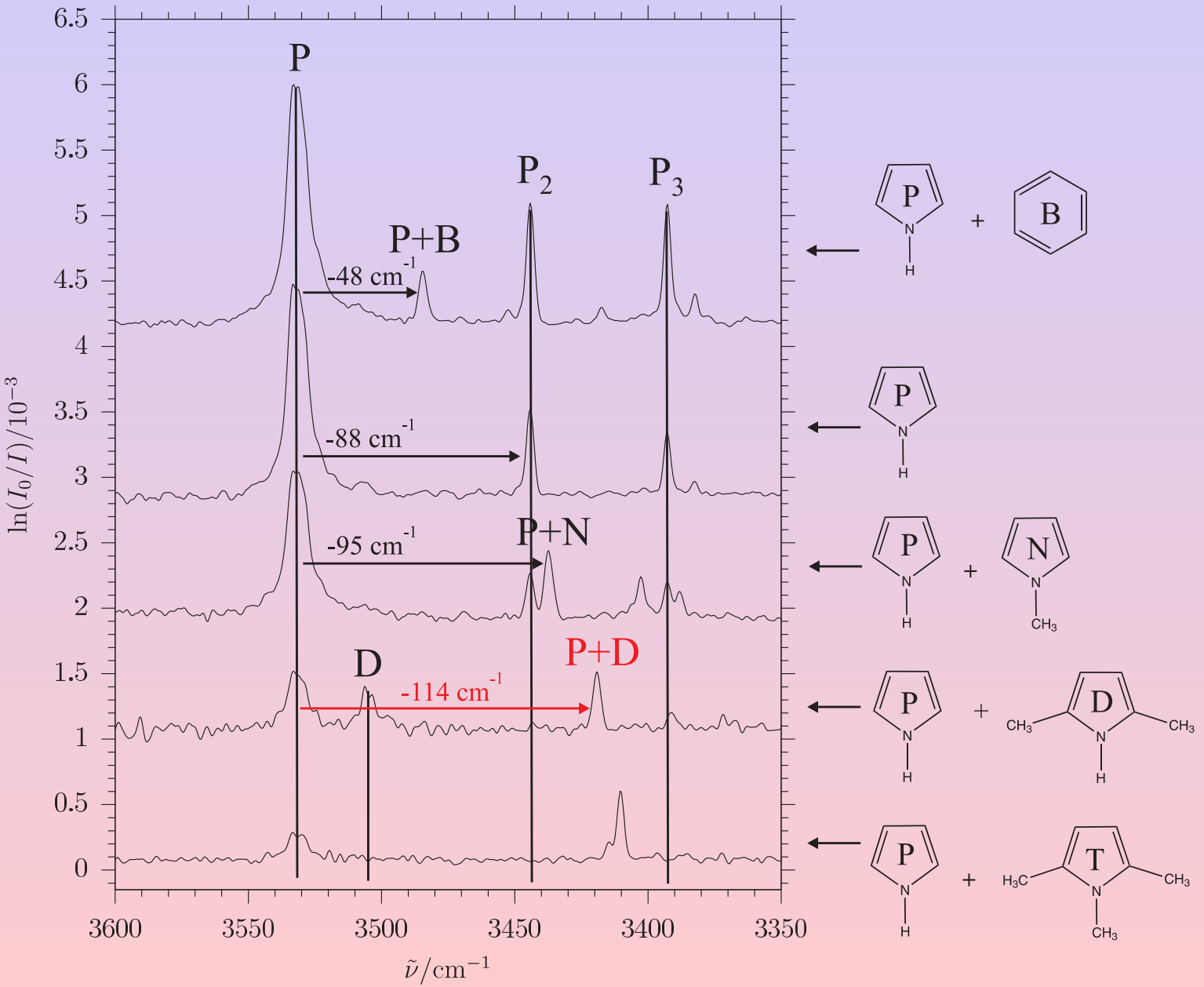

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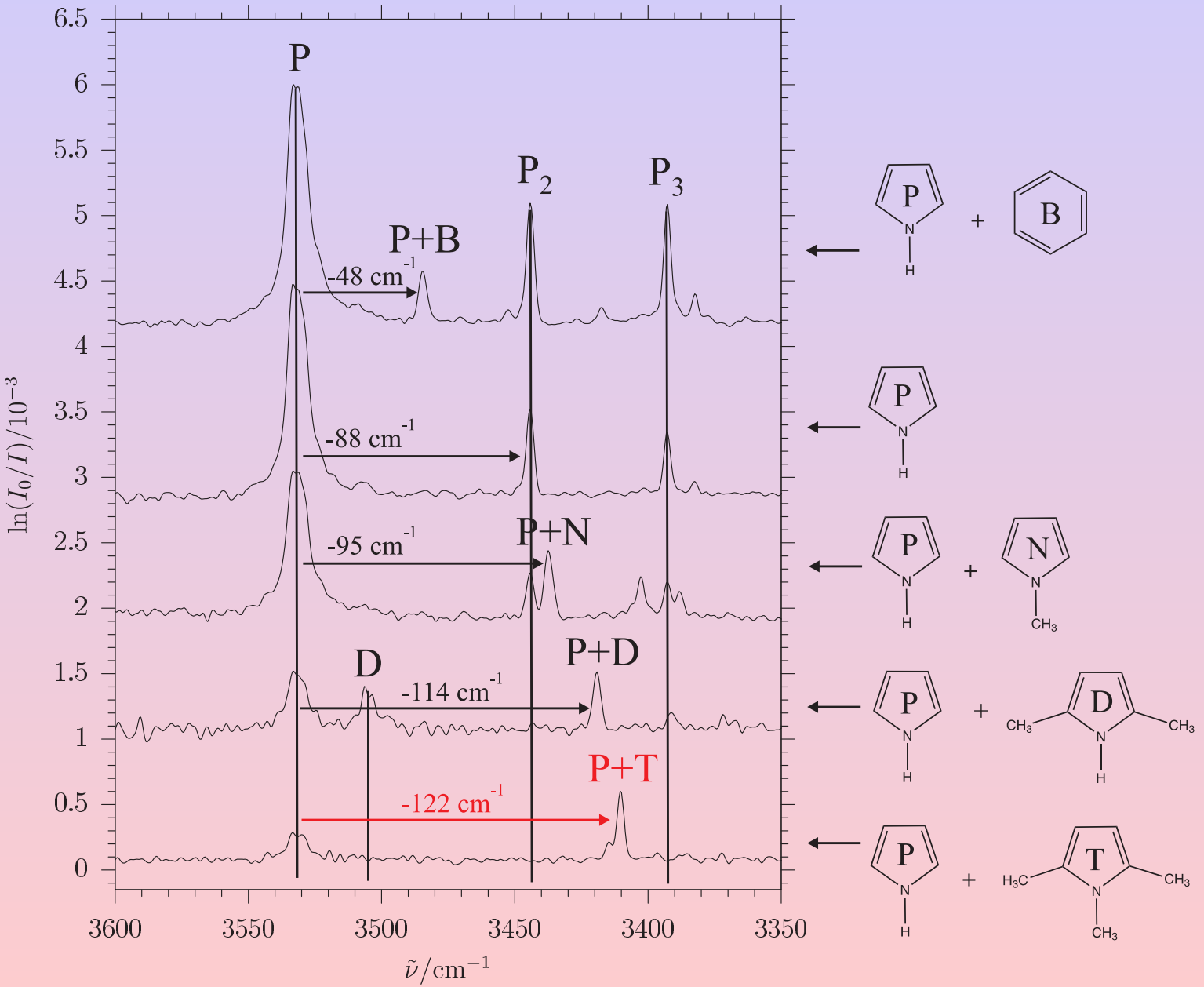
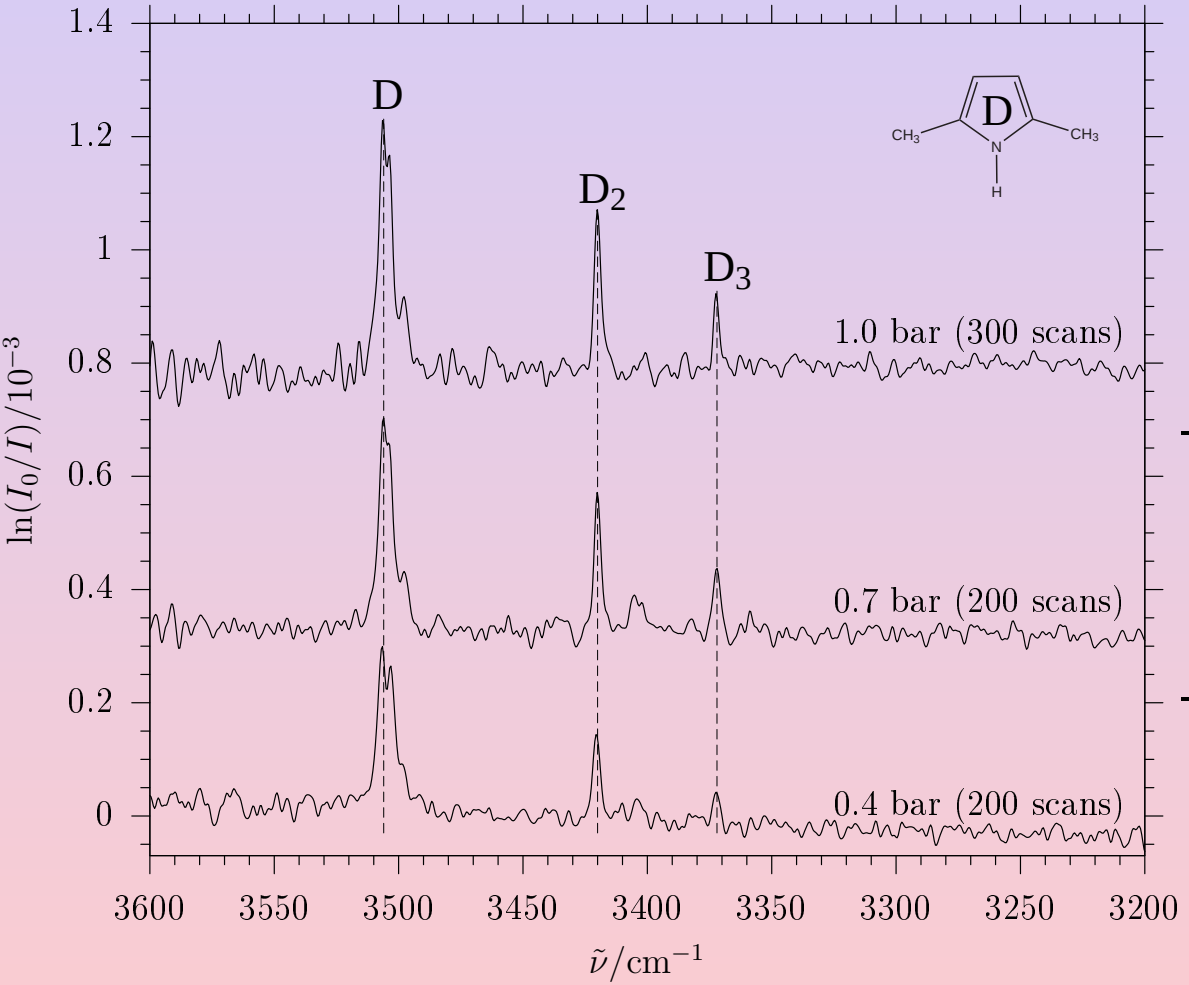
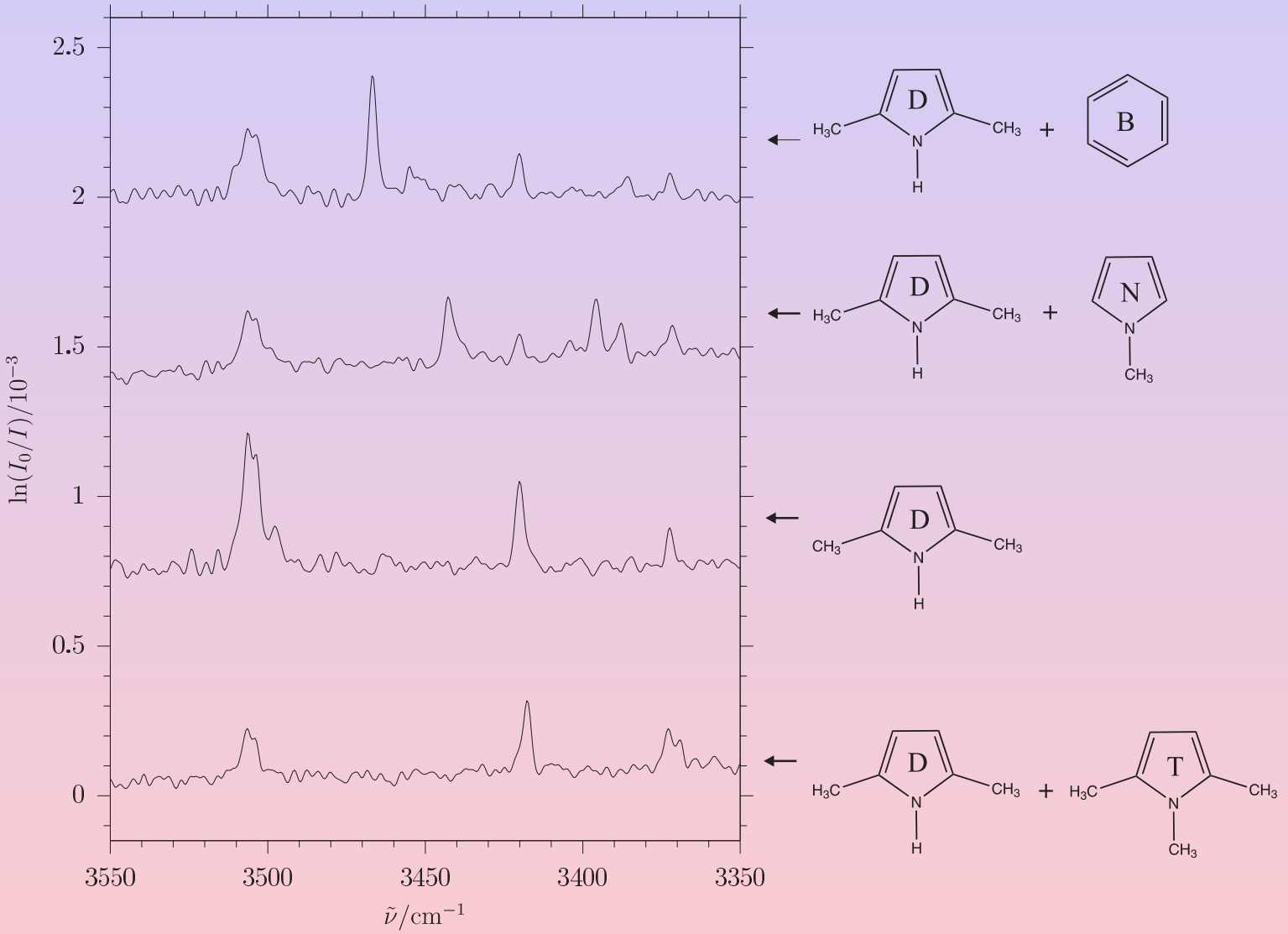


2,5-Dimethylpyrrole

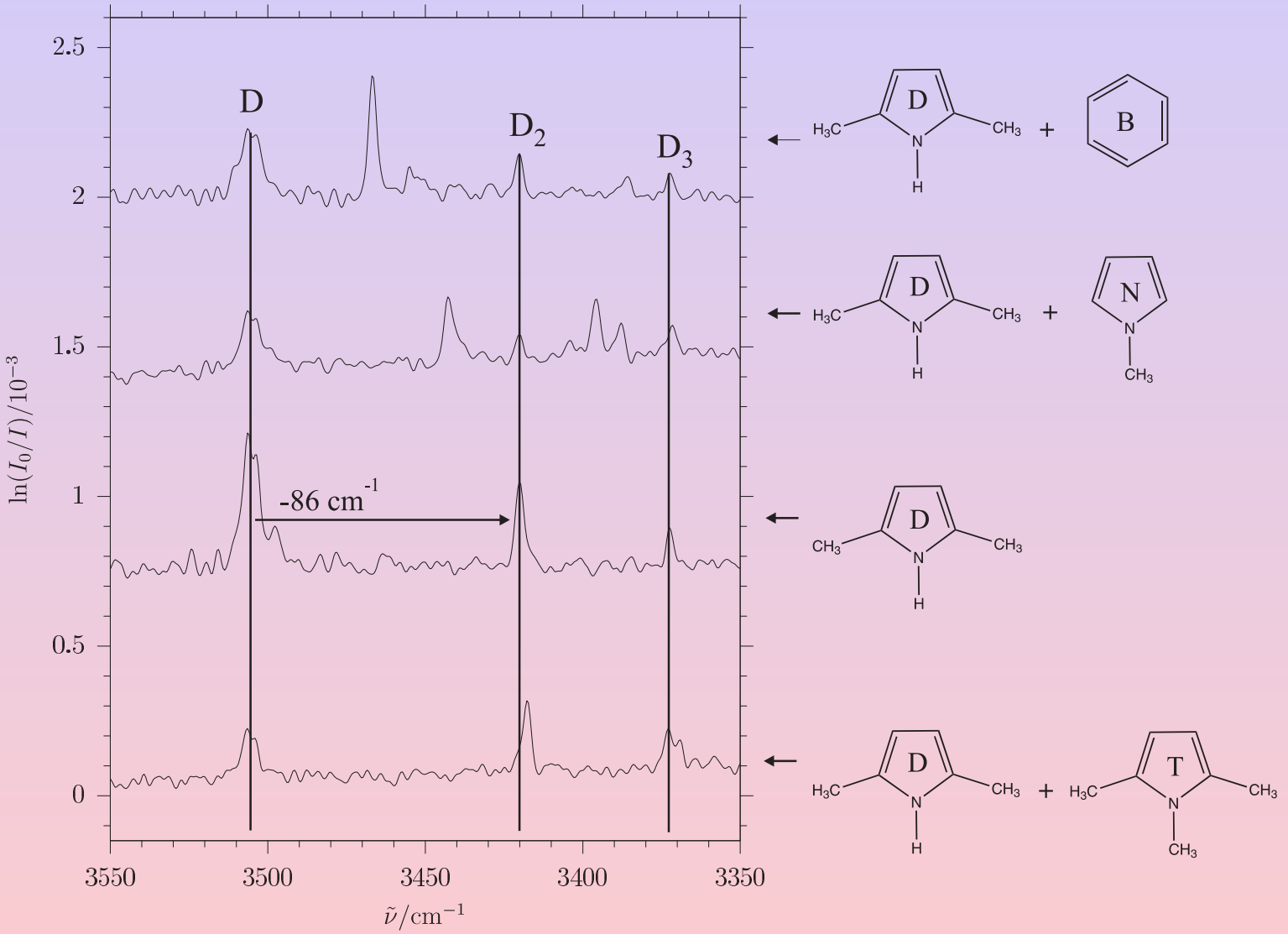


	$\tilde{\nu}_{\mathrm{N-H}}$ / cm^{-1}	$-\Delta\tilde{\nu}_{\mathrm{N-H}}$ / cm^{-1}
D	3506	–
–	3498	8
D_2	3420	86
D_3	3373	133

2,5-Dimethylpyrrole as donor - overview



2,5-Dimethylpyrrole as donor - overview



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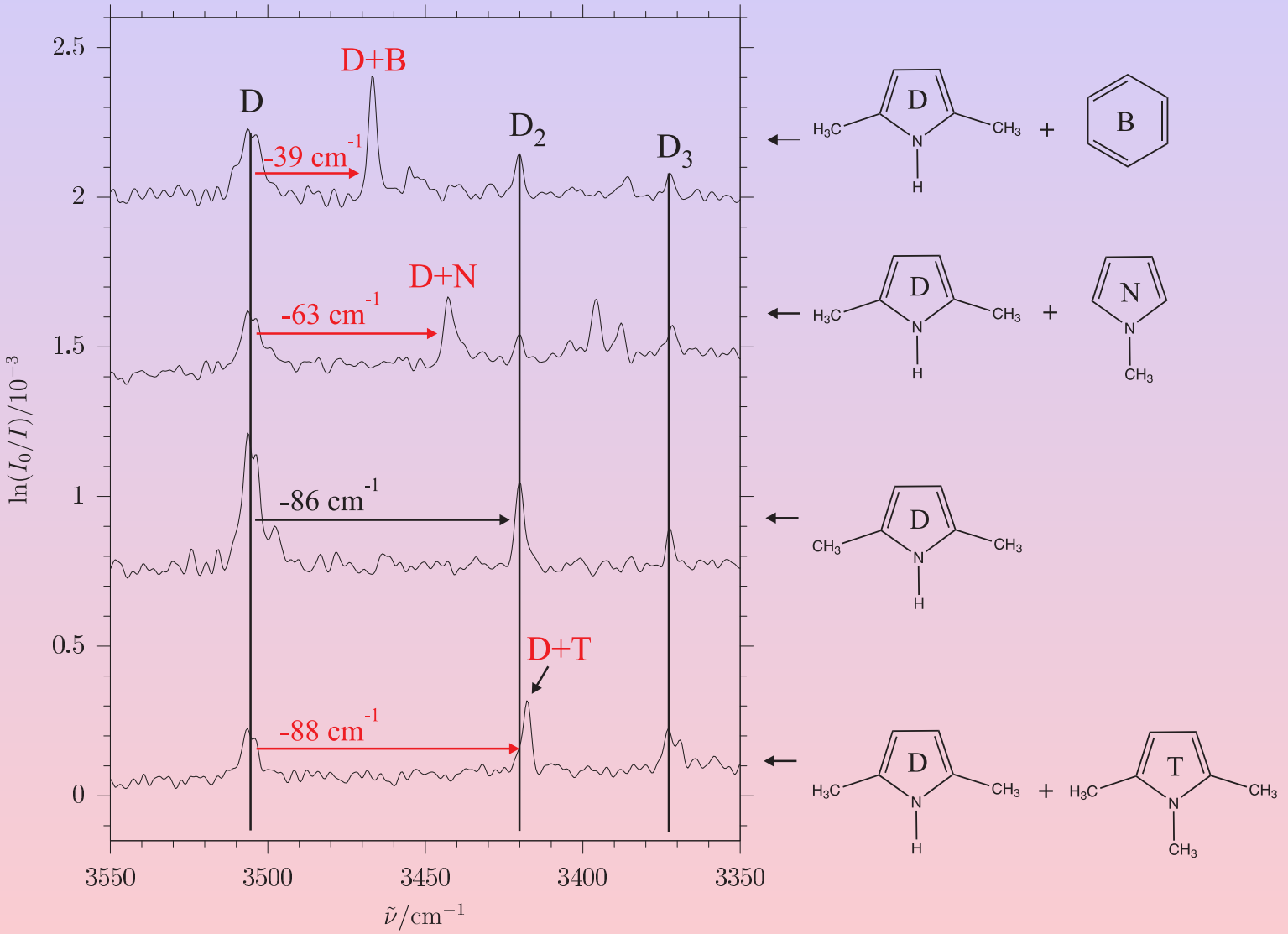
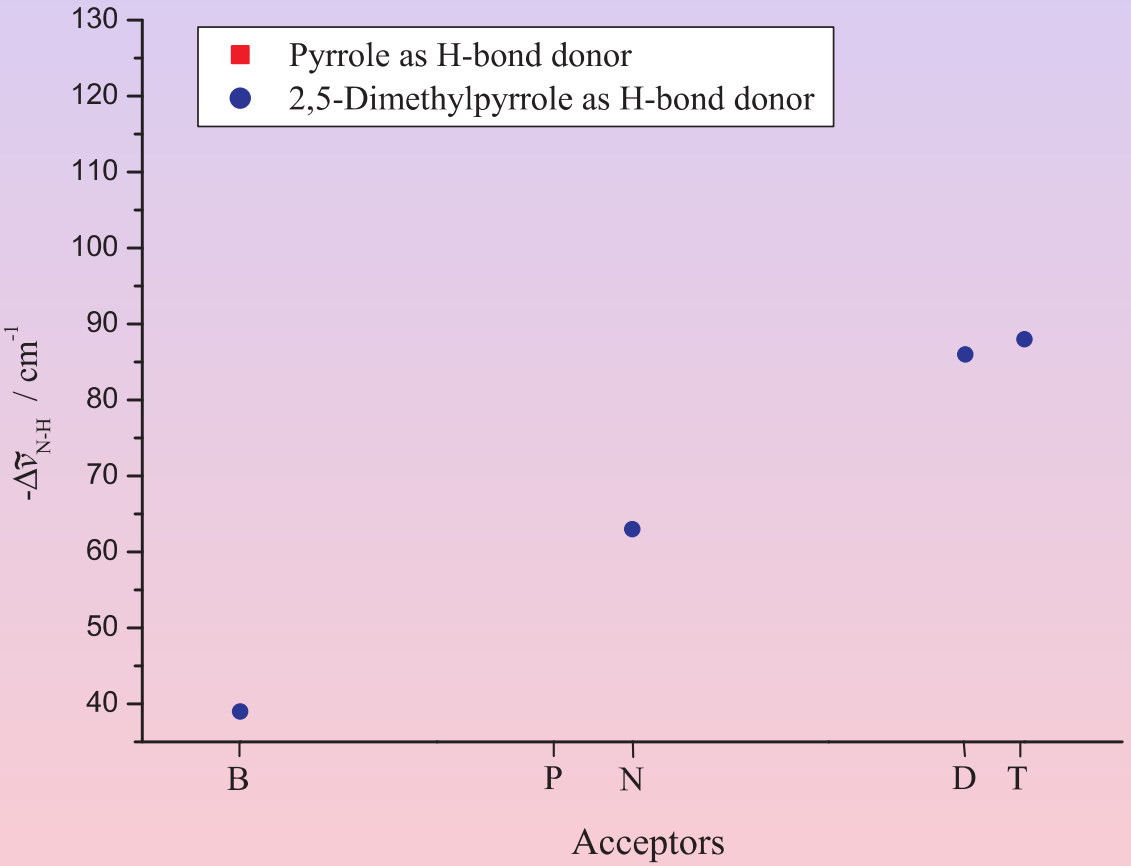
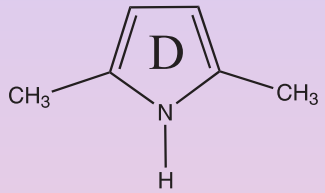
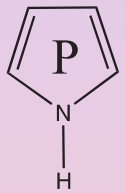
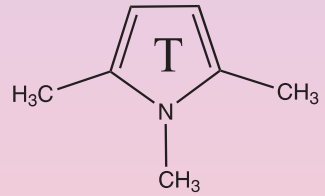


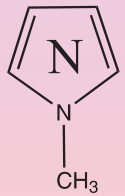
Red-shift of the donor bands











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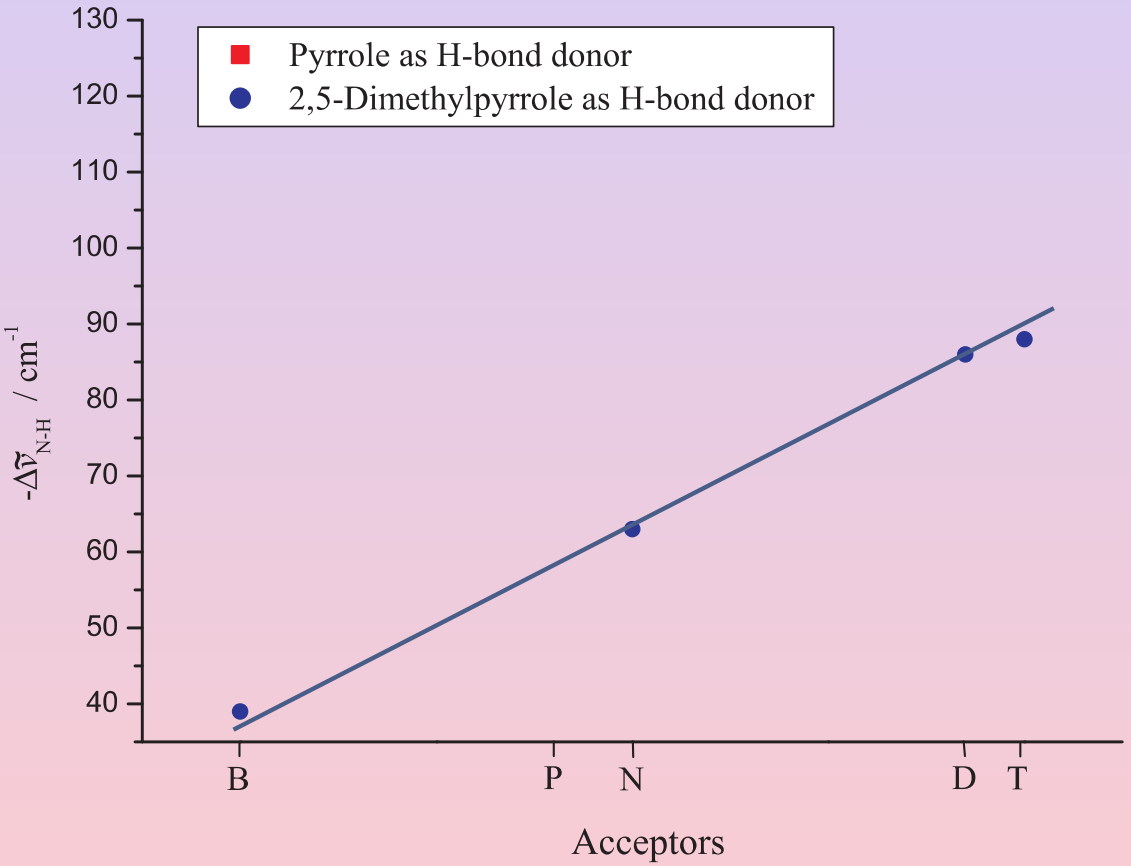

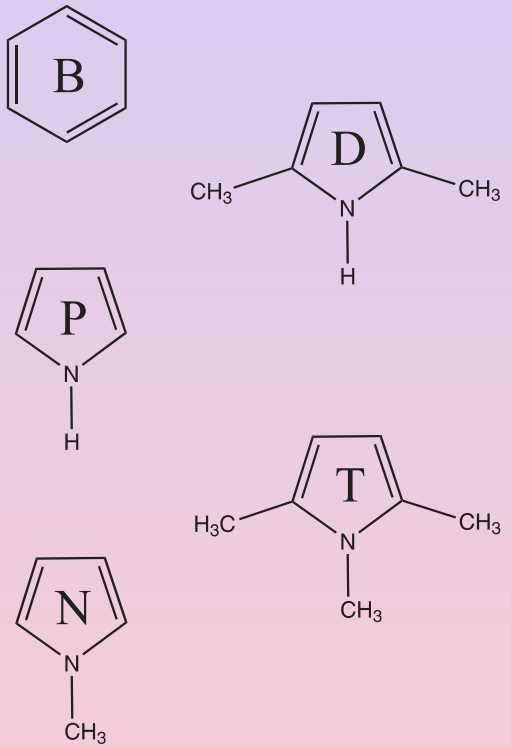

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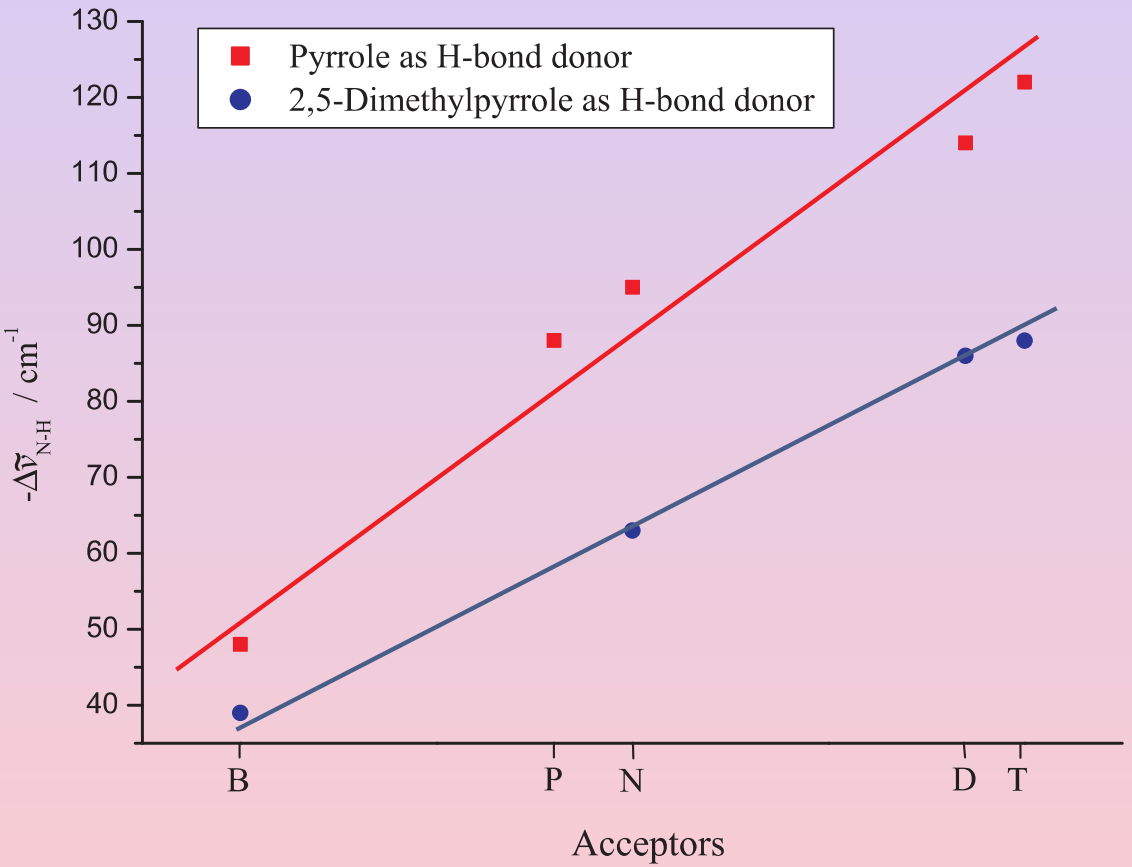

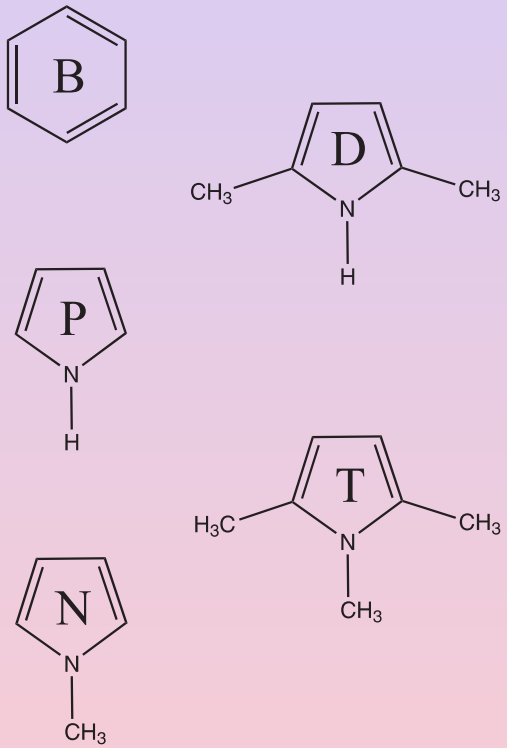

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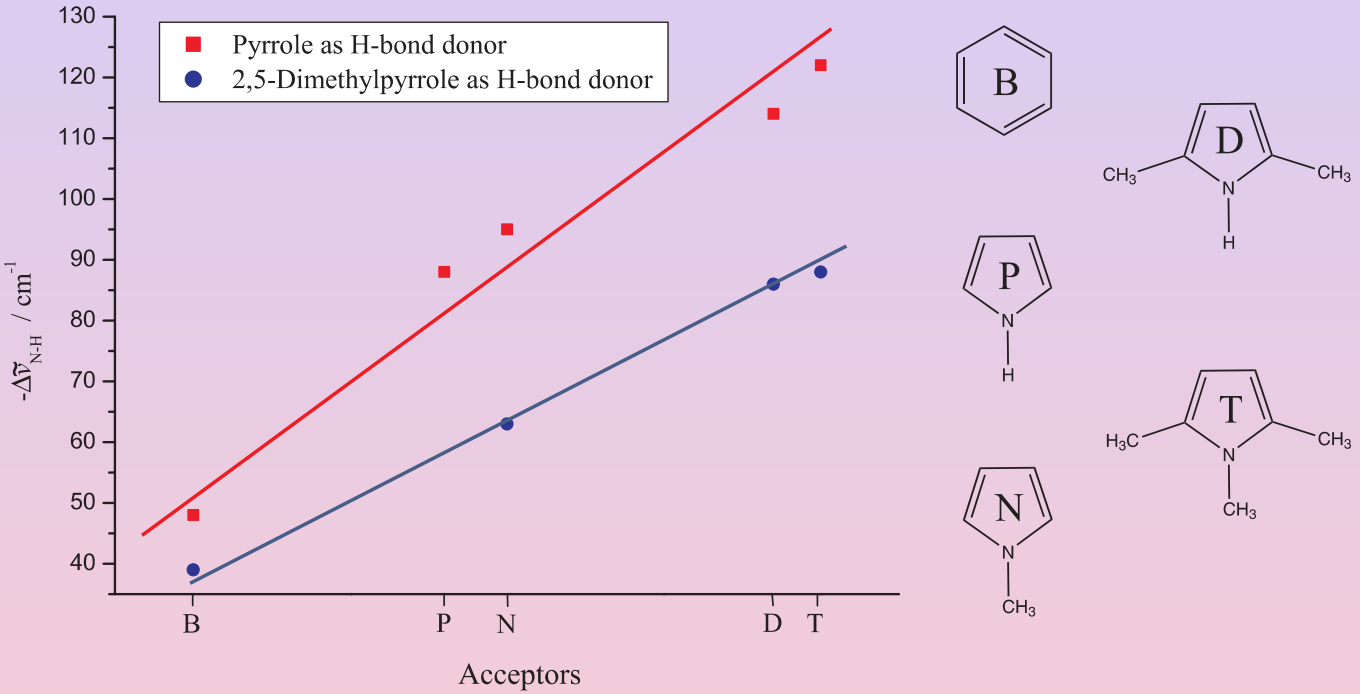

$\Rightarrow$ universal order

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Electron densities of the aromatic H-bond acceptors

Benzene

Pyrrole

N-Methylpyrrole

2,5-Dimethylpyrrole

1,2,5-Trimethylpyrrole

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Outline

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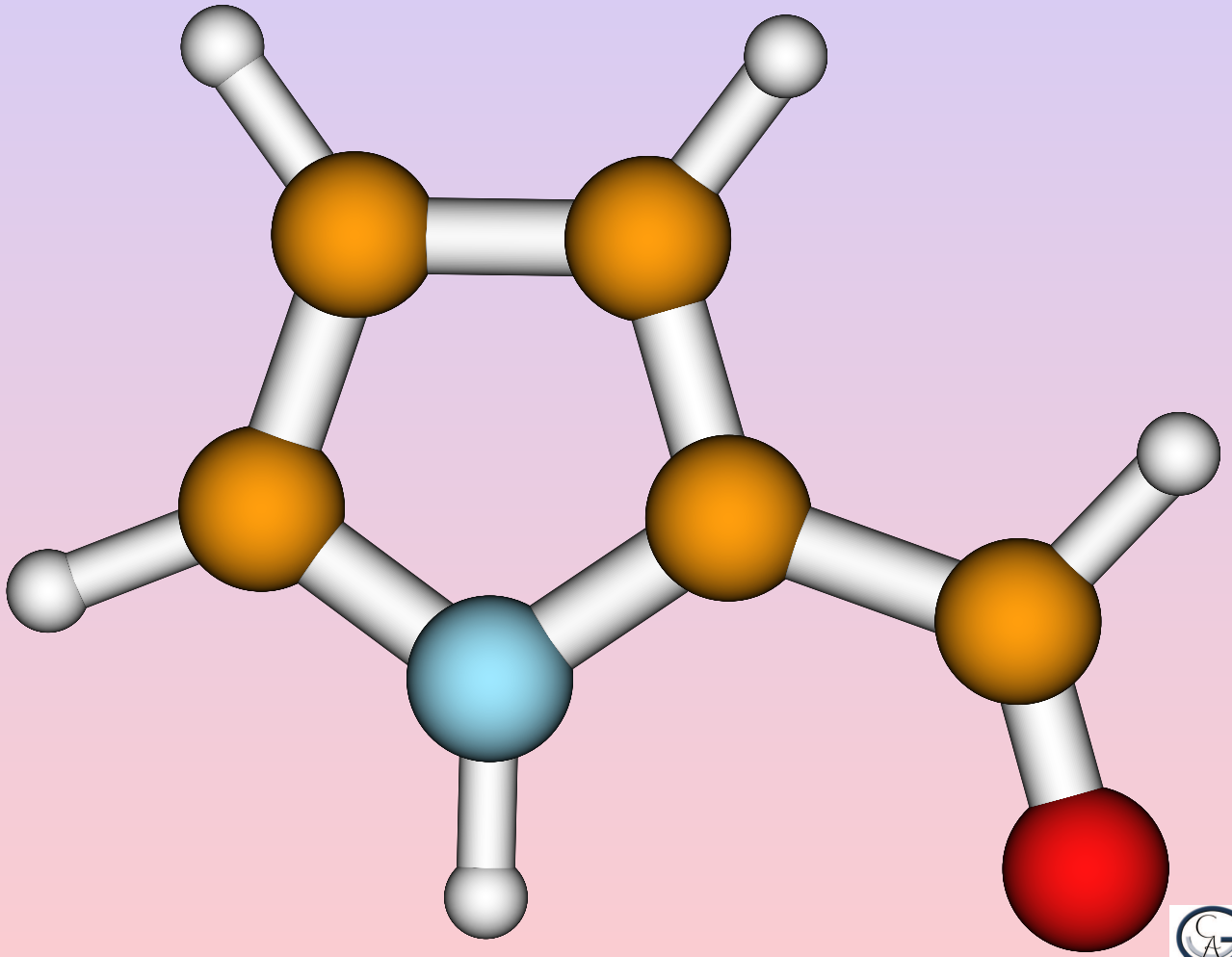
Structure



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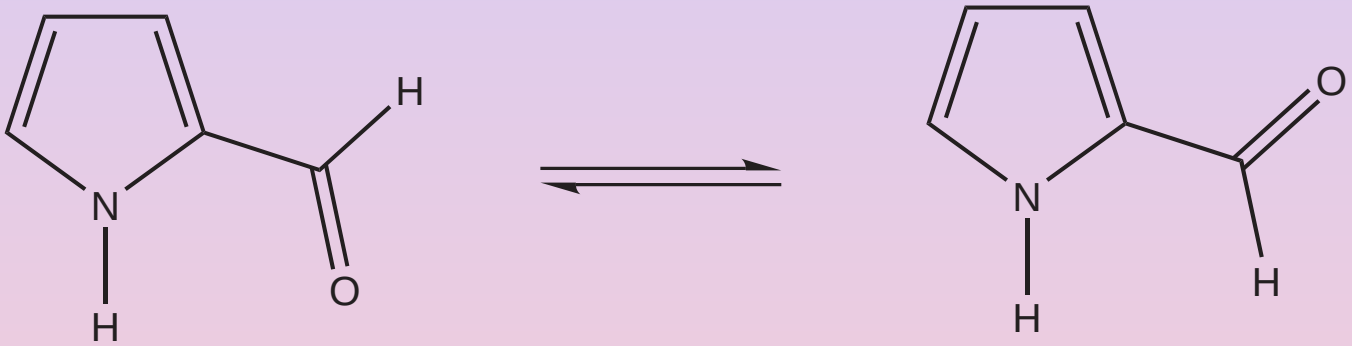
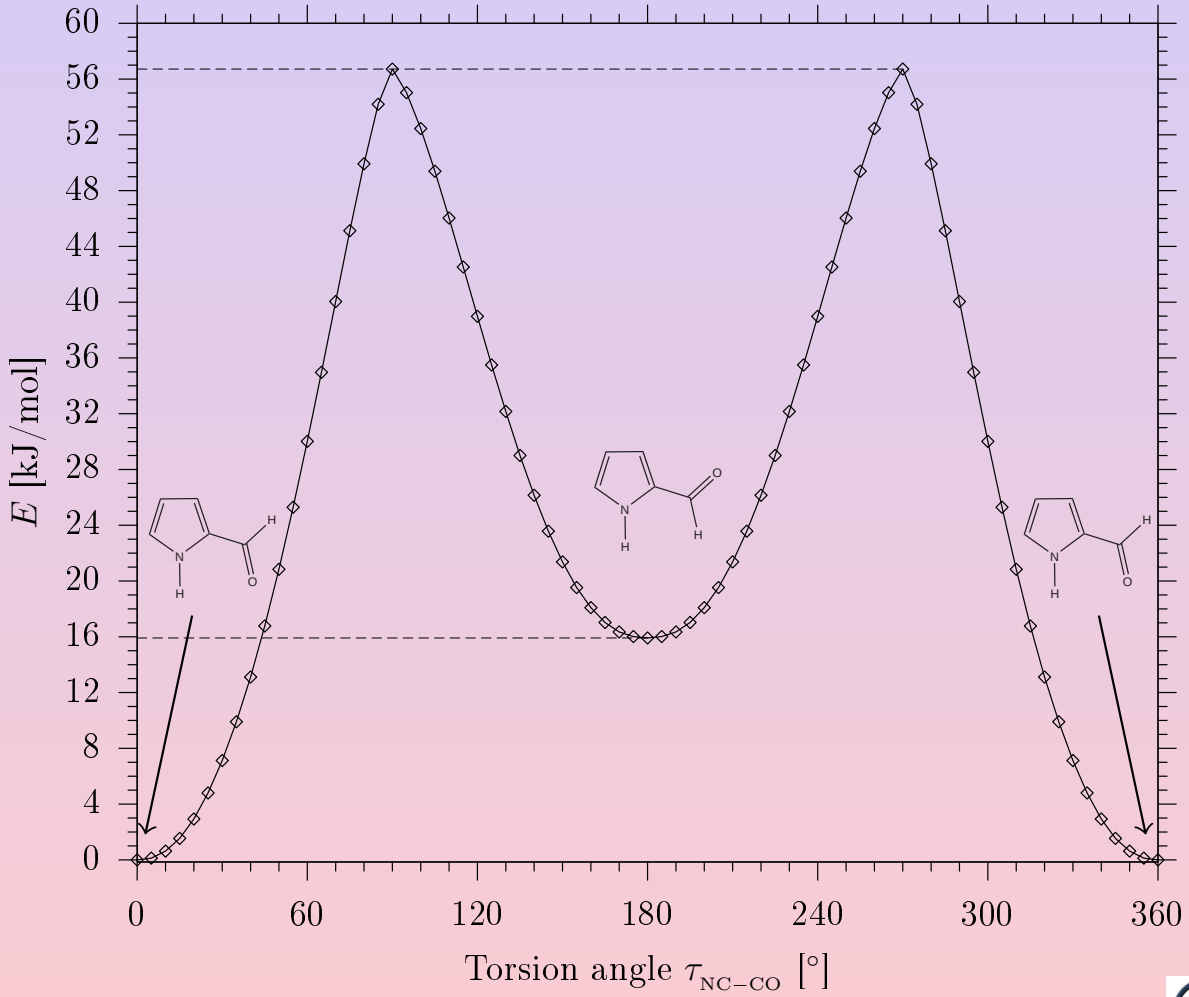
Structure



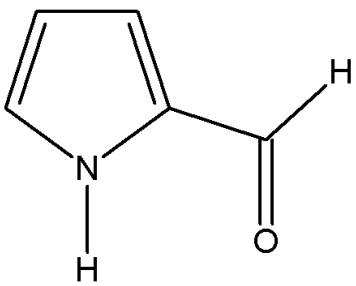
cis trans

Structure

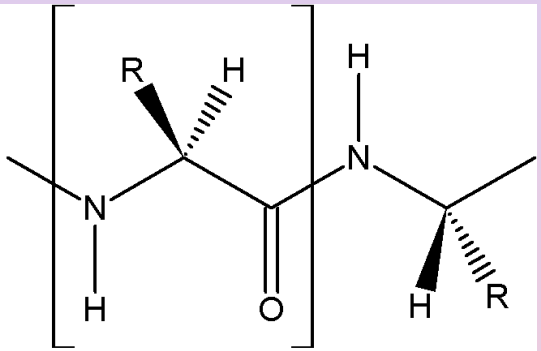


MP2 / 6-311++G**

Comparision with a peptide



Pyrrole-2-carboxaldehyde



Part of a peptide

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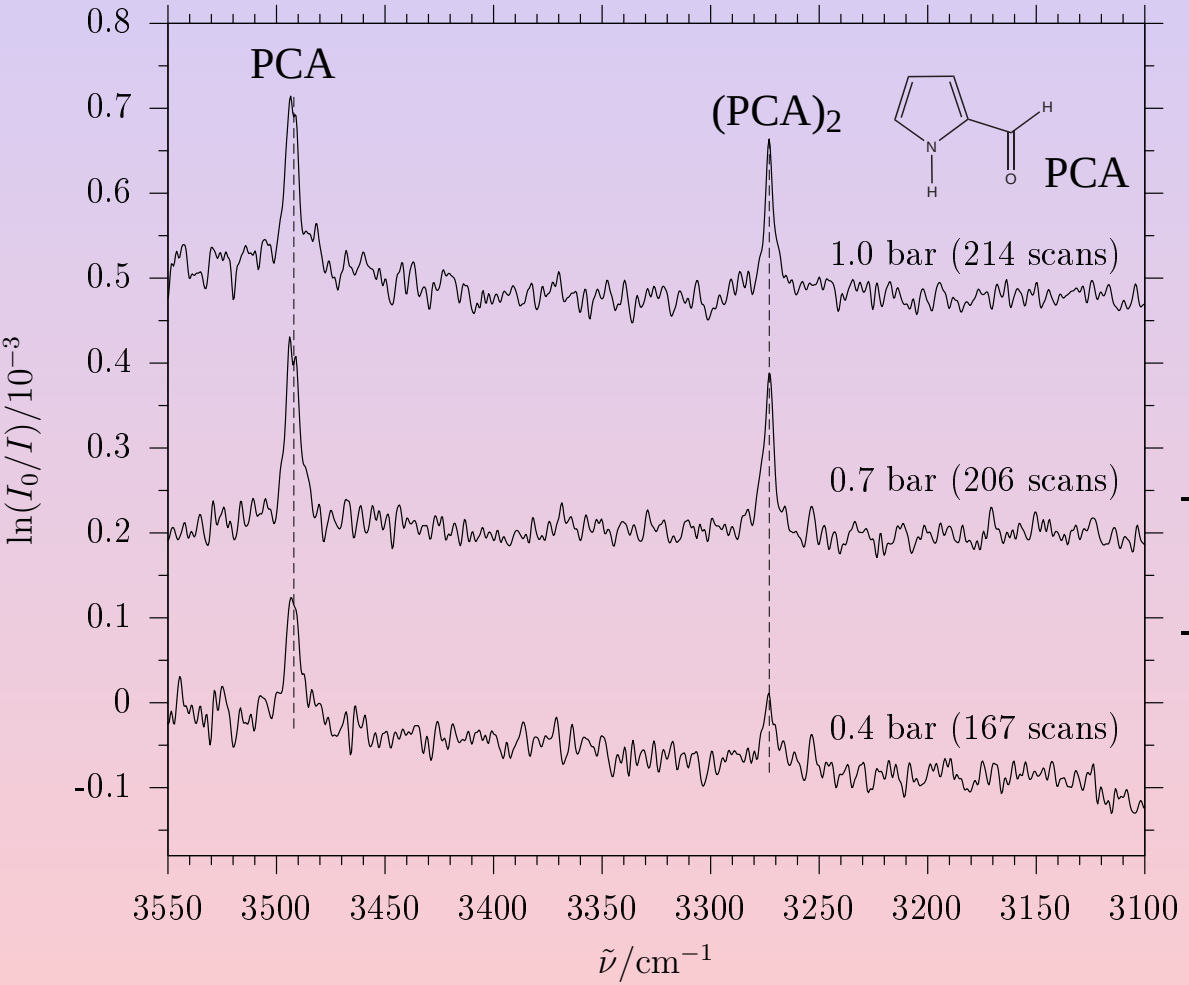
Filet-Jet spectrum of the N–H stretching vibration



	$\tilde{\nu}_{\mathrm{N-H}}$ / cm^{-1}	$-\Delta\tilde{\nu}_{\mathrm{N-H}}$ / cm^{-1}
PCA	3493	–
$(\mathrm{PCA})_2$	3273	220

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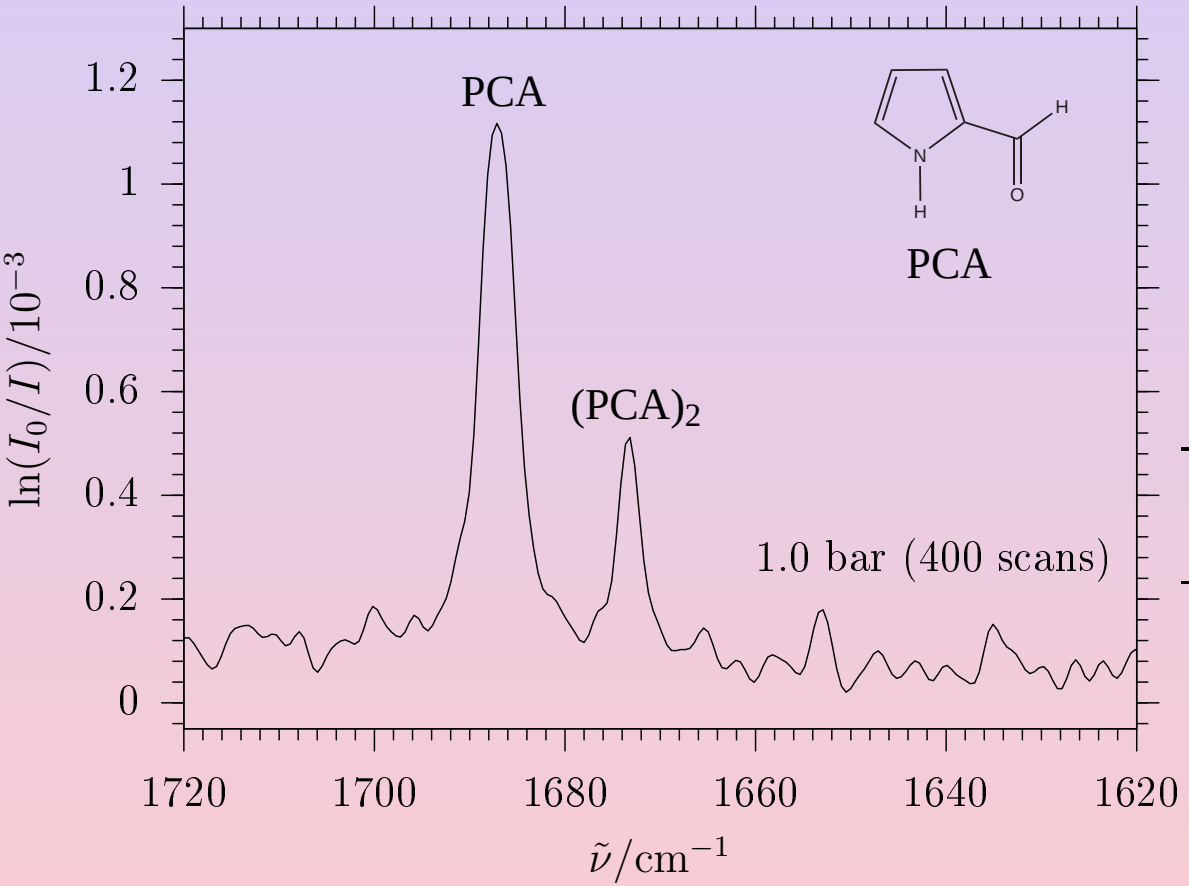
Filet-Jet spectrum of the C=O stretching vibration



	$\tilde{\nu}_{\mathrm{N-H}}$ / cm^{-1}	$-\Delta\tilde{\nu}_{\mathrm{N-H}}$ / cm^{-1}
PCA	1687	–
$(\mathrm{PCA})_2$	1673	14

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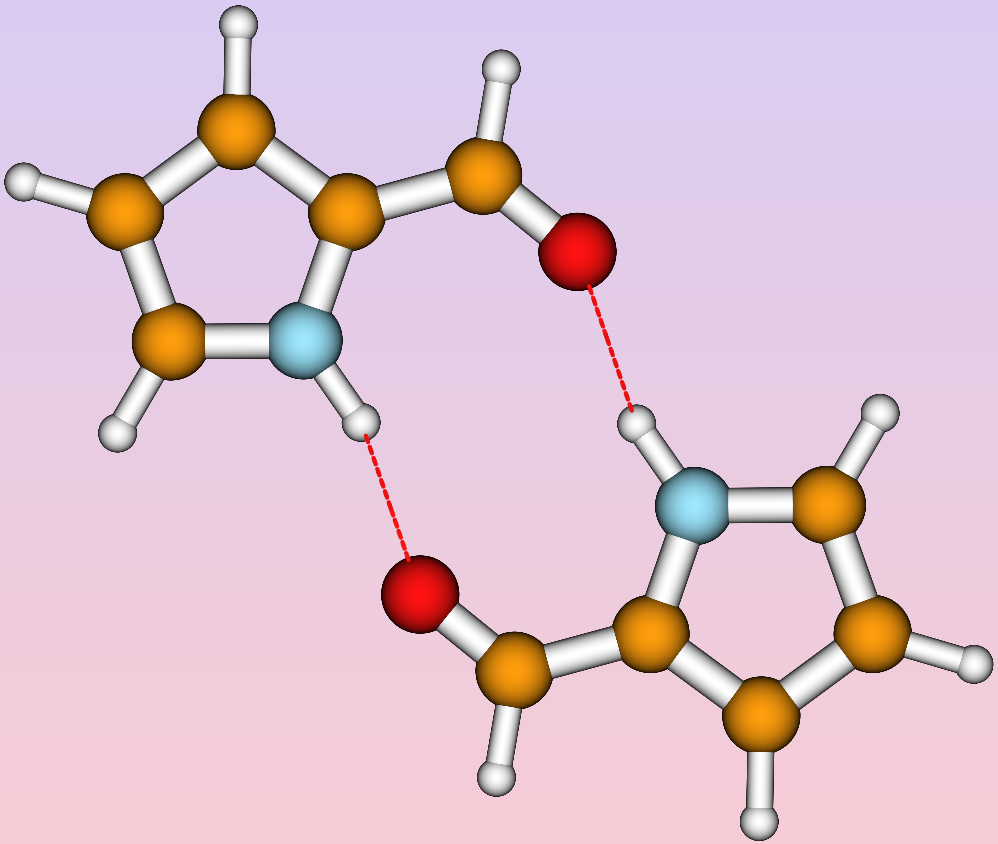
Structure of the dimer (top view)



B3LYP / 6-311++G**

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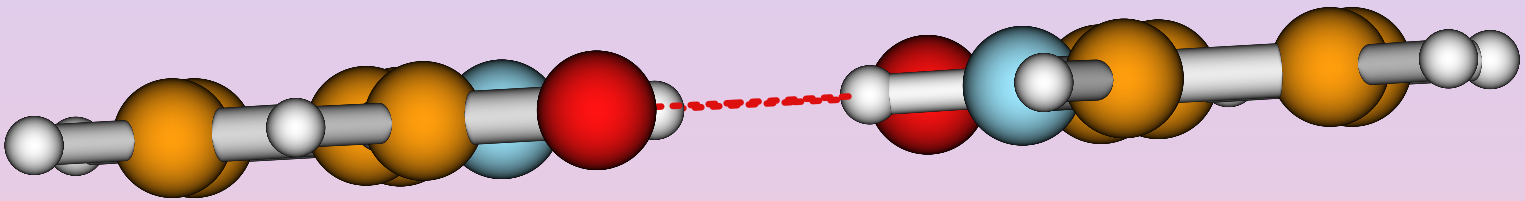
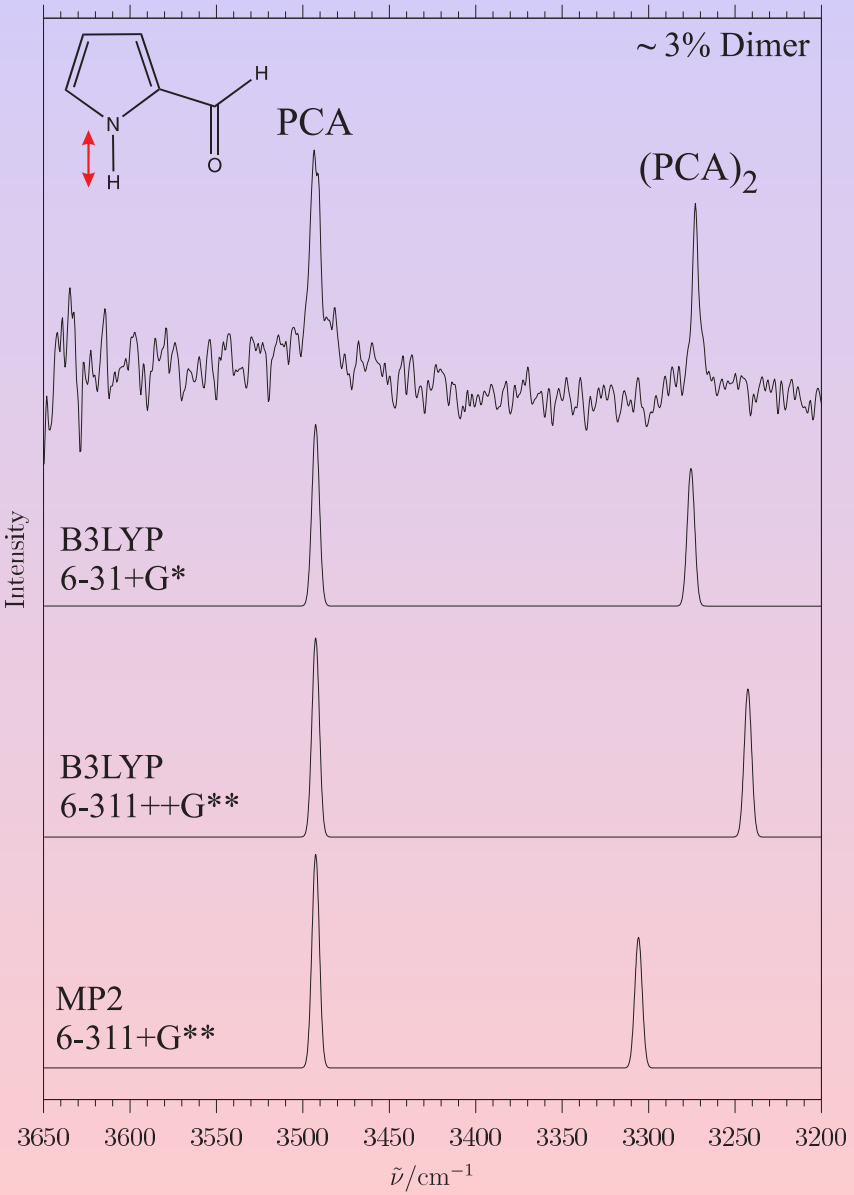
Structure of the dimer (side view)



B3LYP / 6-311++G**

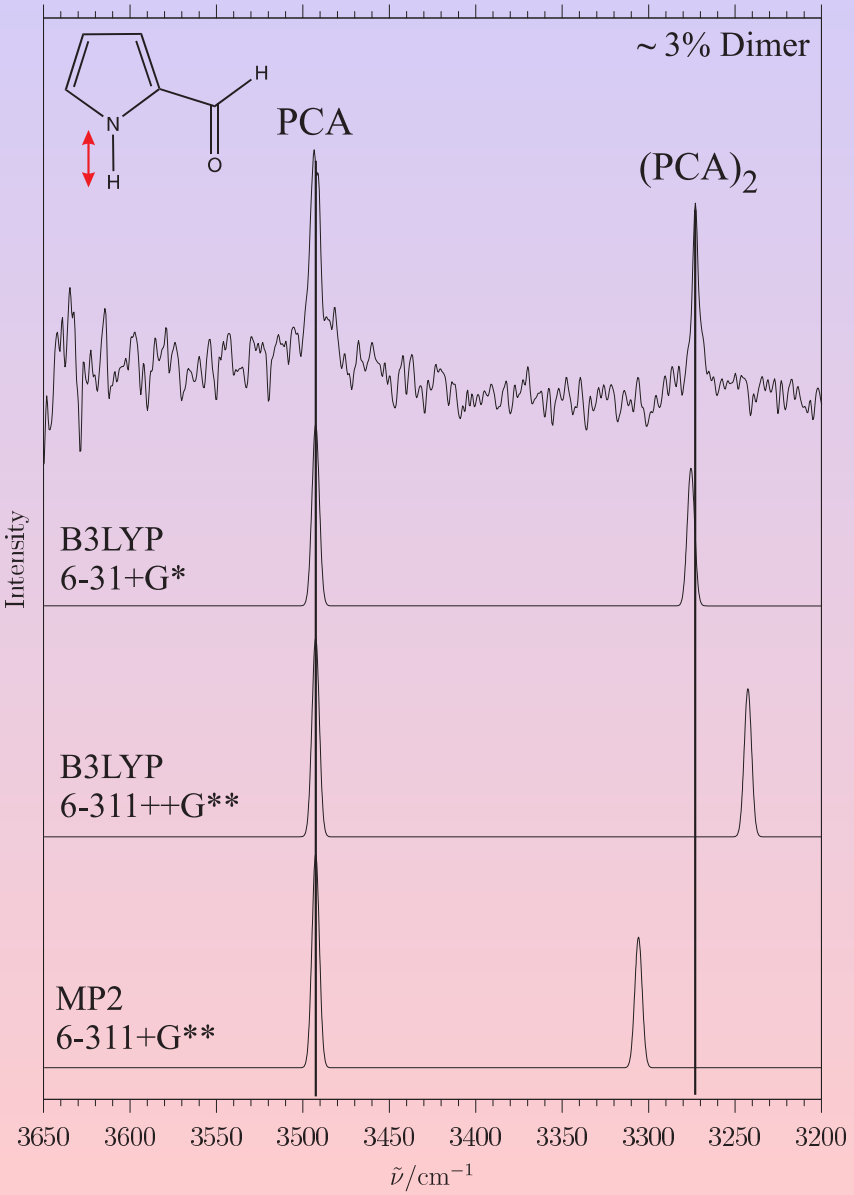
Frequency calculations

N–H stretching vibration



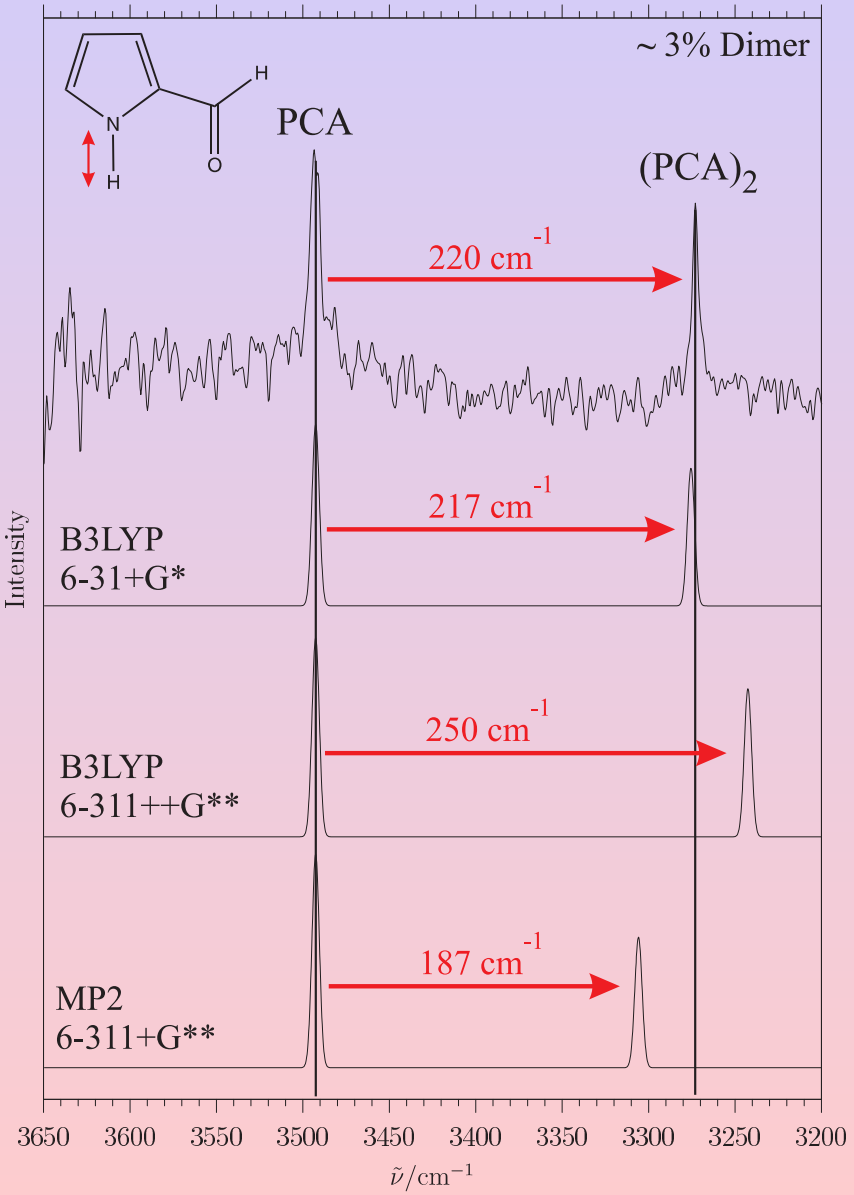
Frequency calculations

N–H stretching vibration



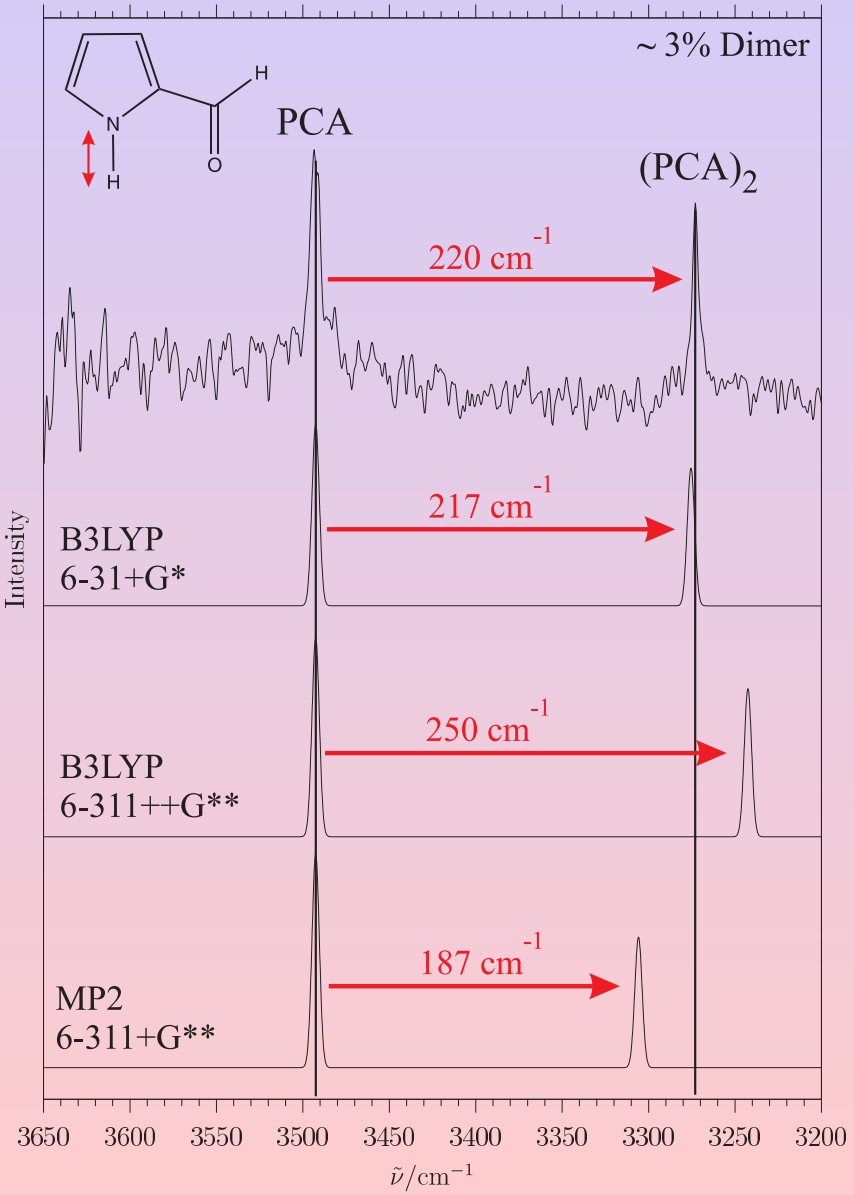
Frequency calculations

N–H stretching vibration

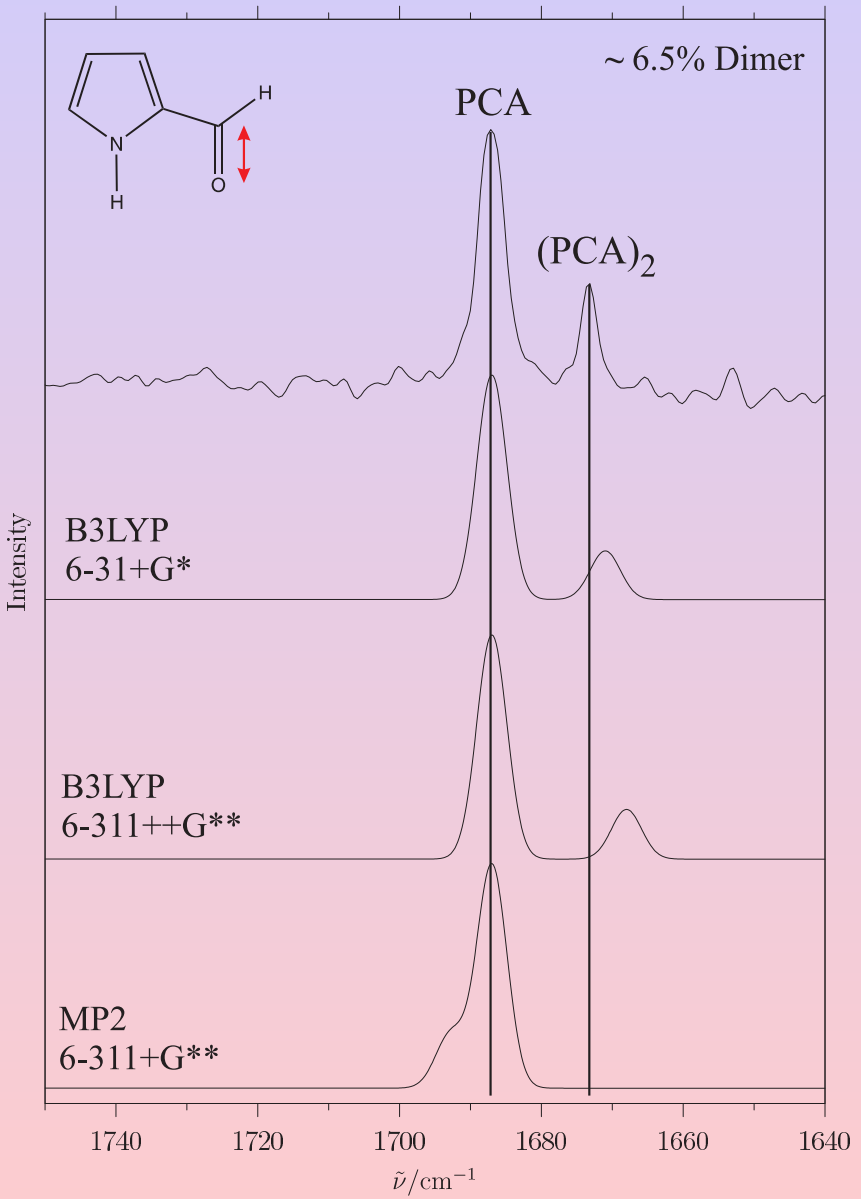


Frequency calculations

N–H stretching vibration

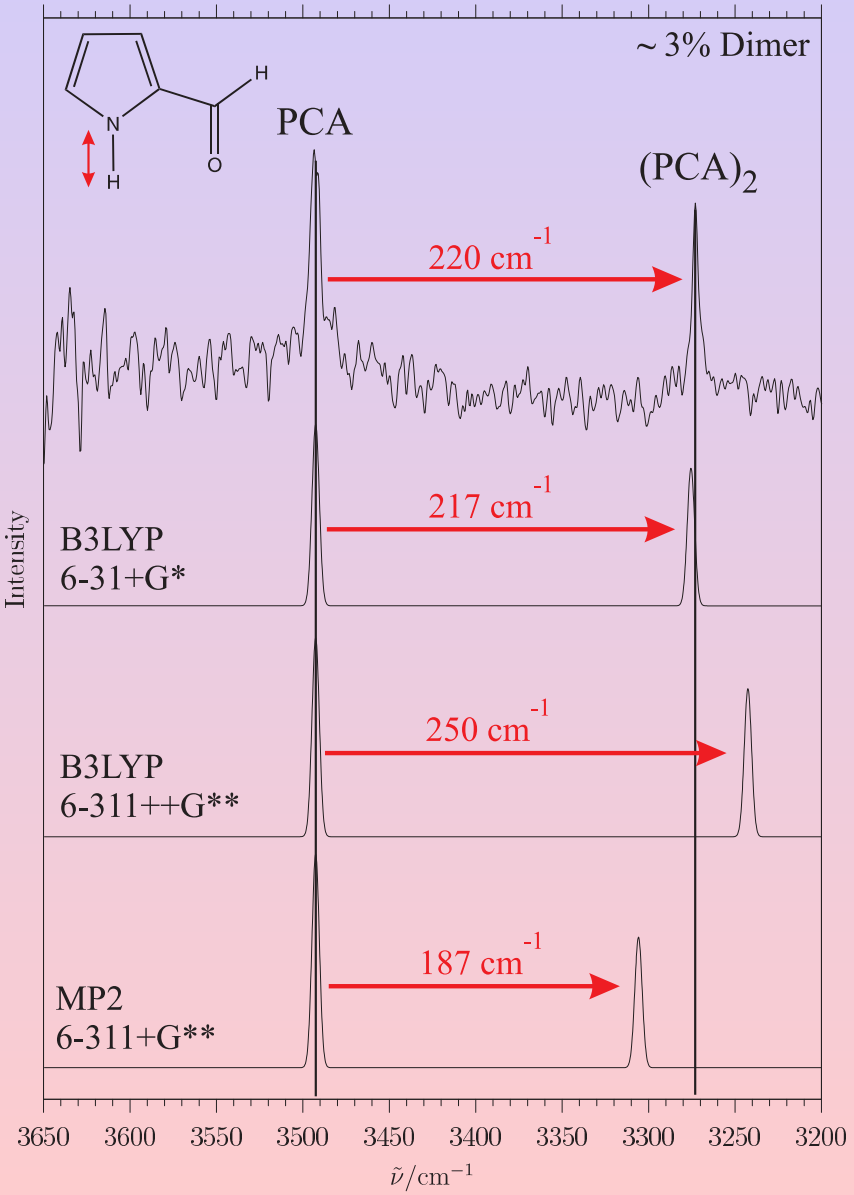


C=O stretching vibration

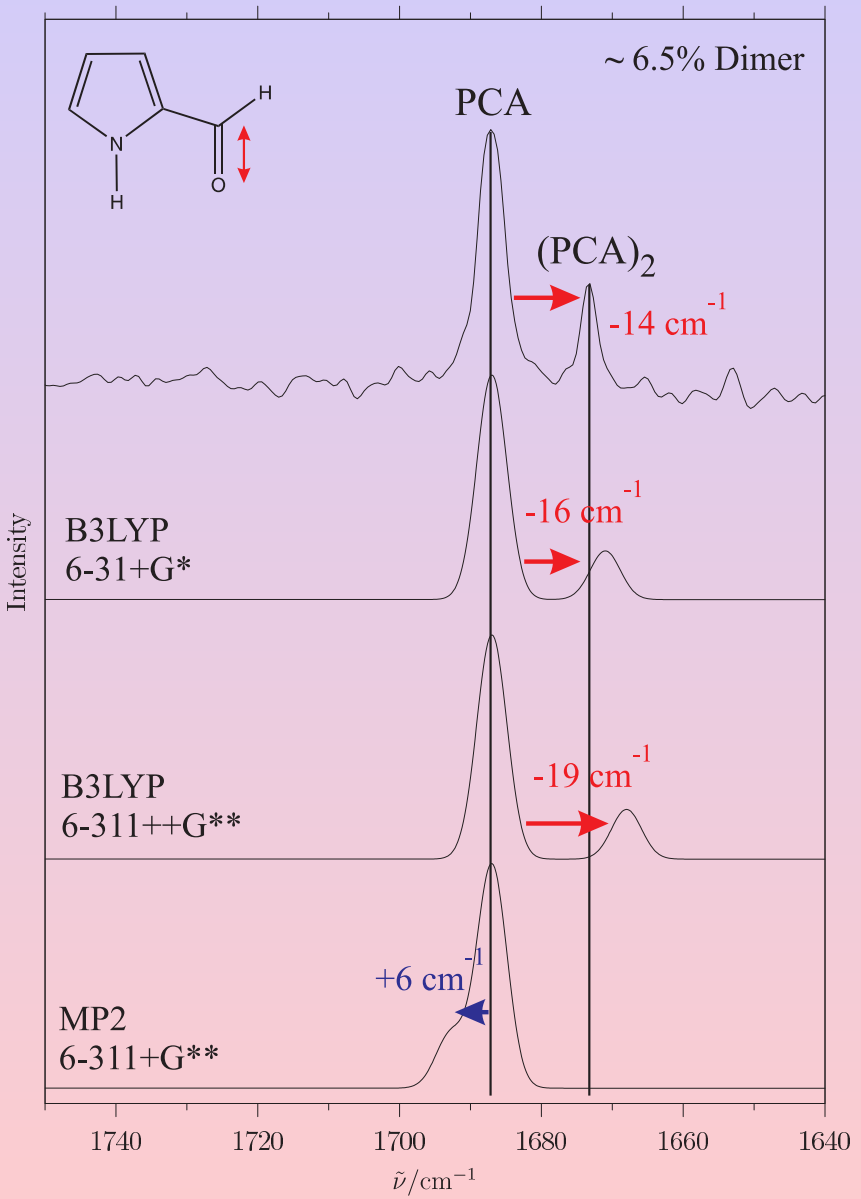


Frequency calculations

N–H stretching vibration

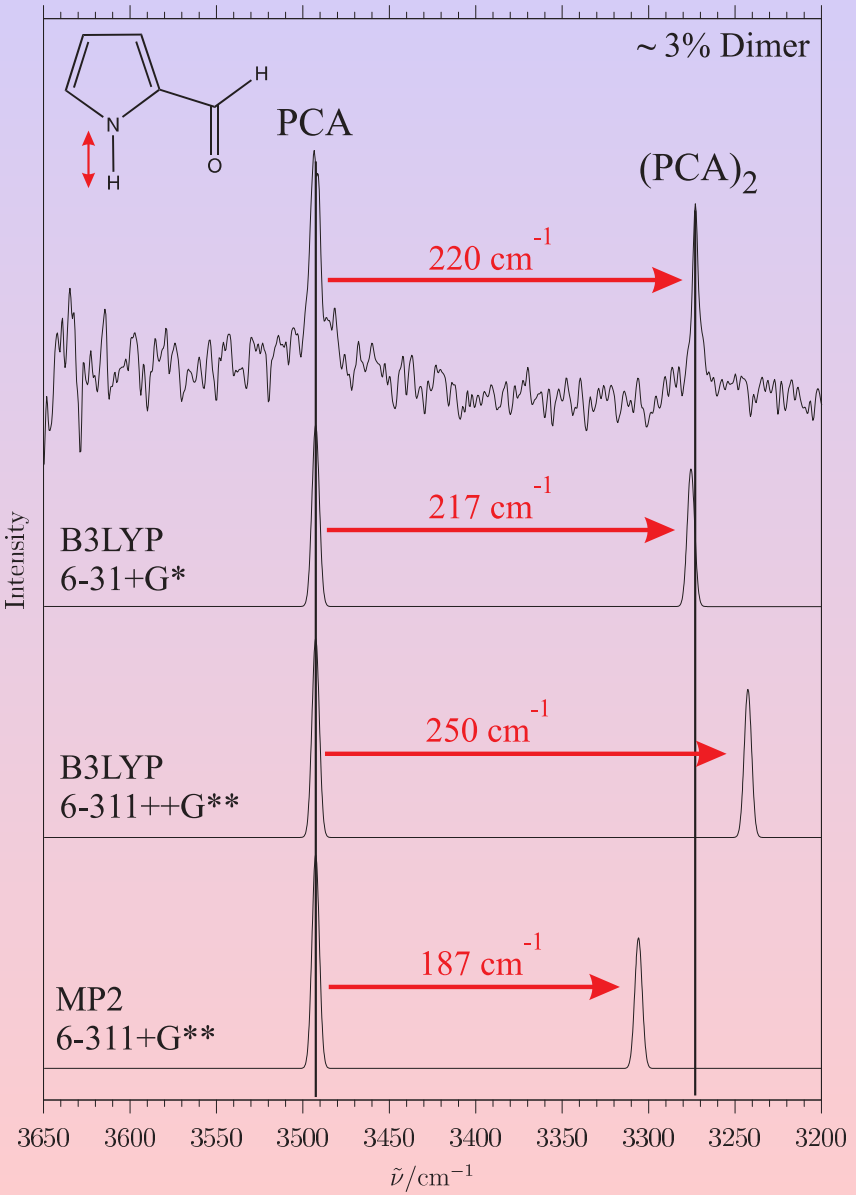


C=O stretching vibration

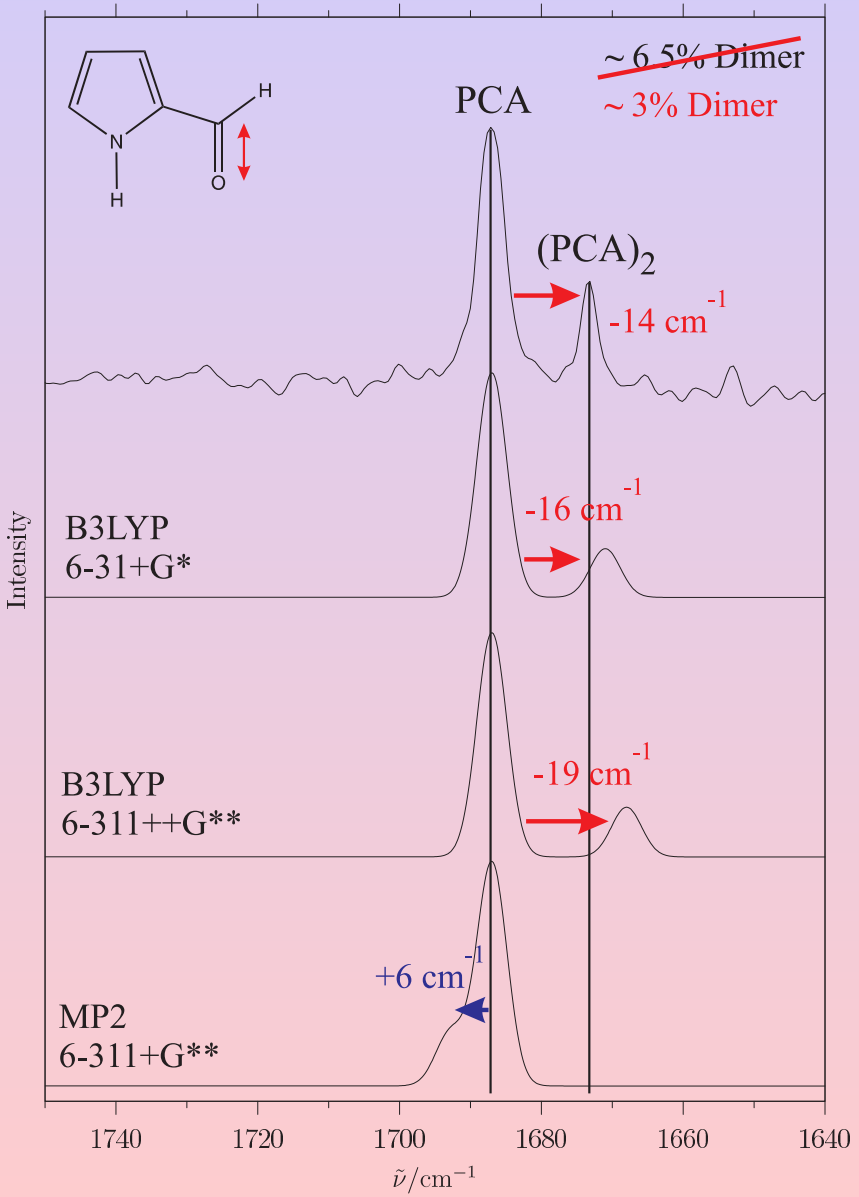


Frequency calculations

N–H stretching vibration

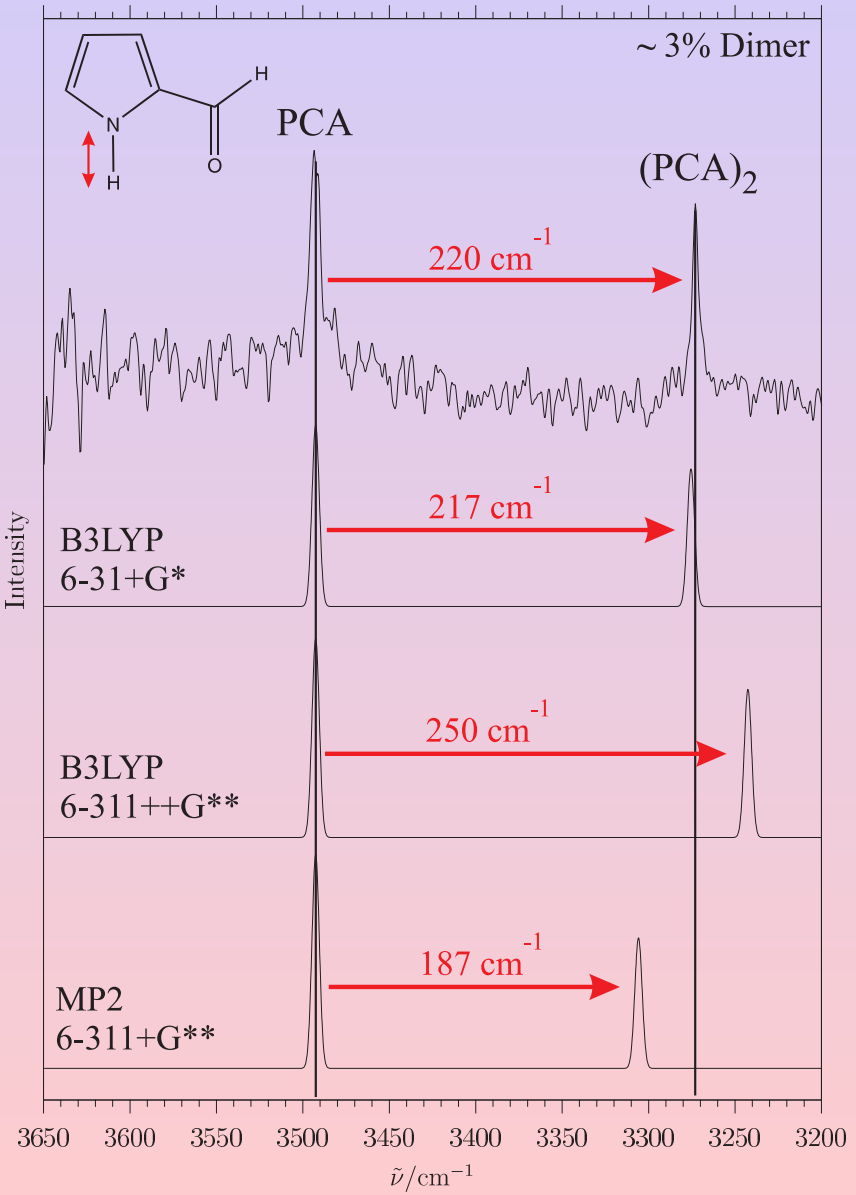


C=O stretching vibration

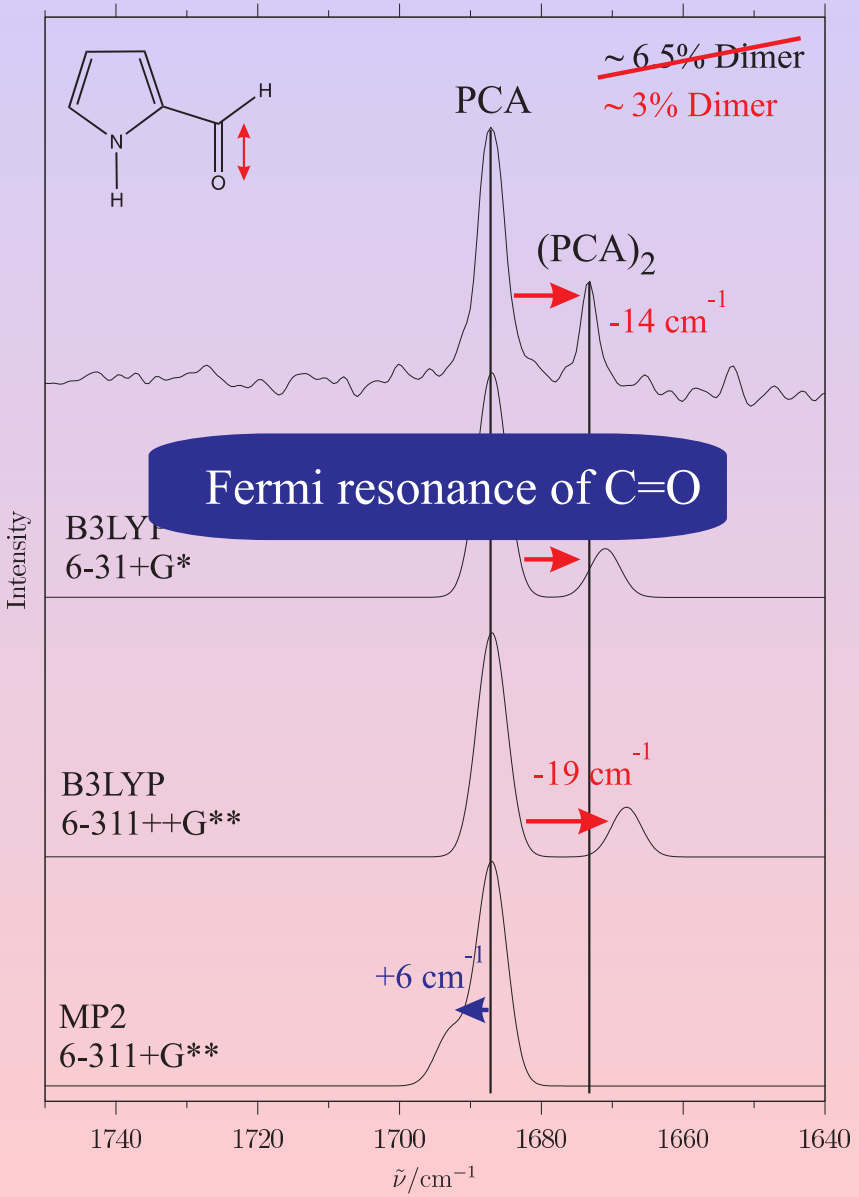


Frequency calculations

N–H stretching vibration



C=O stretching vibration



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Thank you for your attention!