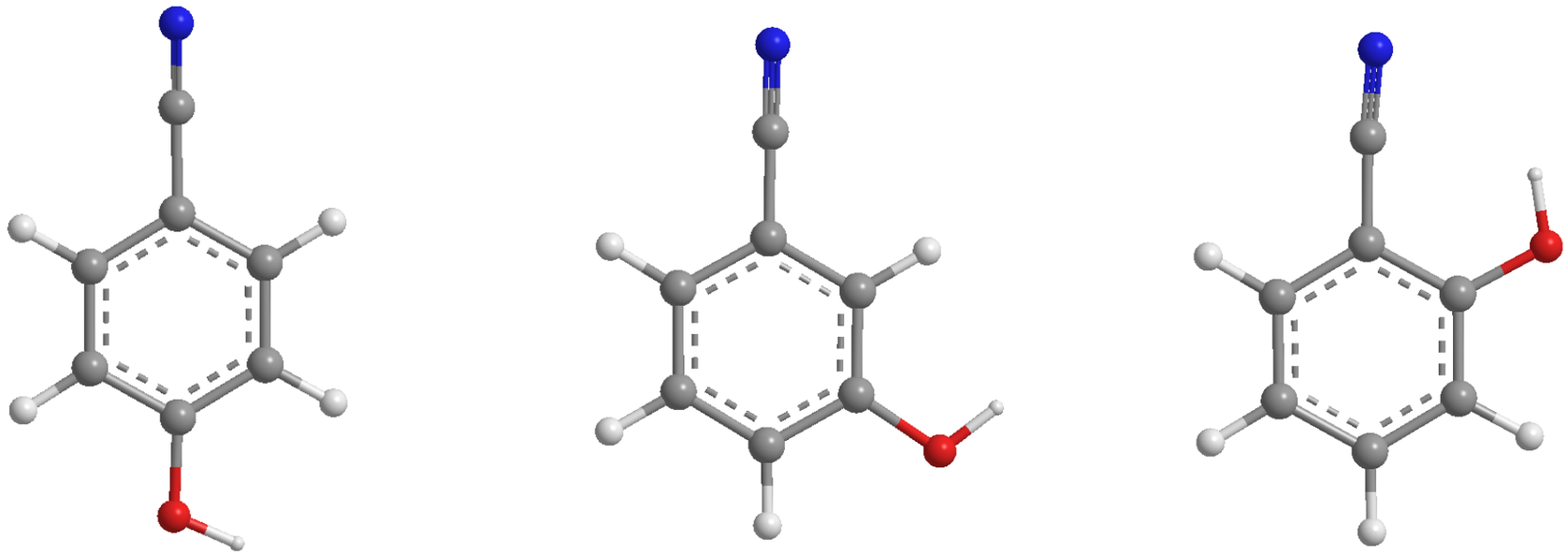
Rotational Spectra of p-, m-, and o-Cyanophenol and Internal Rotation of p-Cyanophenol



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CELEBRATE CENTENNIAL
KENT STATE UNIVERSITY
1910·2010

Outline

- Background
- Instrument
- Results:
  - o-Cyanophenol
  - m-Cyanophenol
  - p-Cyanophenol
- Internal Rotation of p-Cyanophenol
- Summary

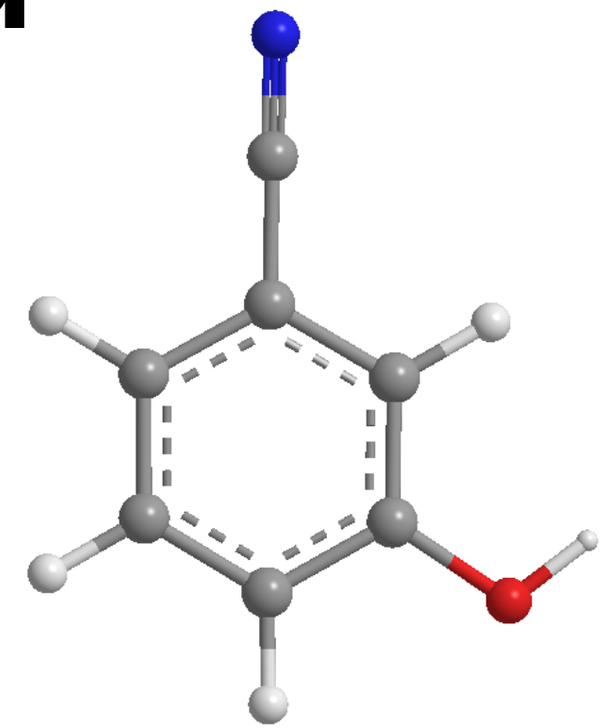
Motivation

- Assign all conformers of cyanophenols
- Explore internal motions of p-cyanophenol
- Lay groundwork for complexation studies
- Augment the existing electronic spectroscopy data

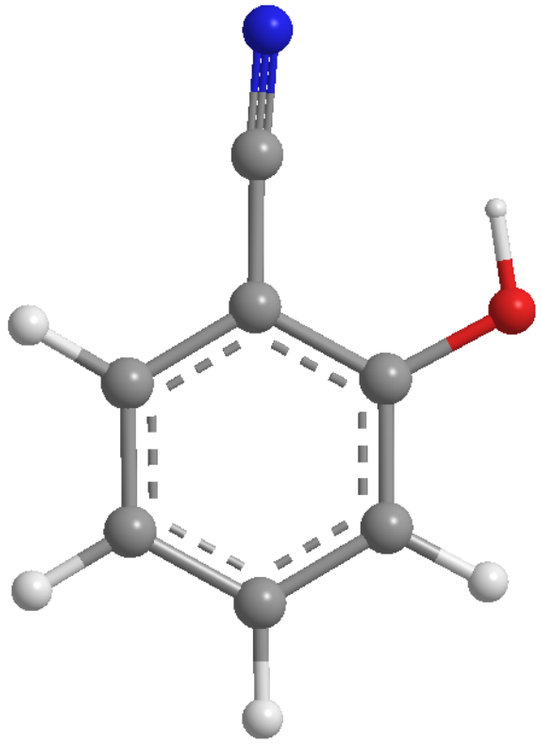
Background

LIF, IR-fluorescence dip, and ab initio study:
2 predicted conformers, both observed

N. Seurre, et al., Chem. Phys., 295, 2003, 21-33



m-Cyanophenol

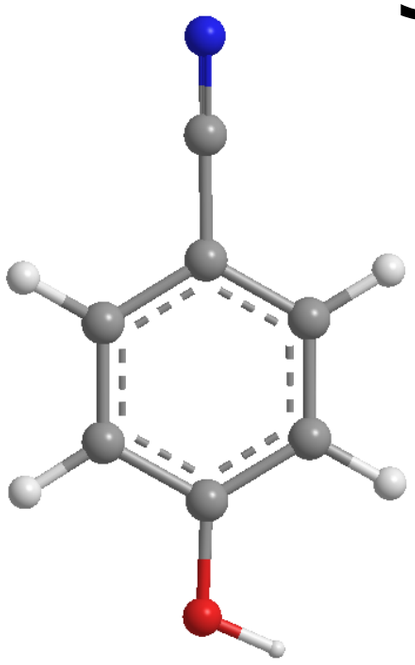


o-Cyanophenol

LIF and ab initio study:
2 predicted conformers, only cis observed

P. Imhof, et al., J. Chem. Phys. A, 105, 2001, 8922-8925

Symmetric Rings with V_2 Barriers



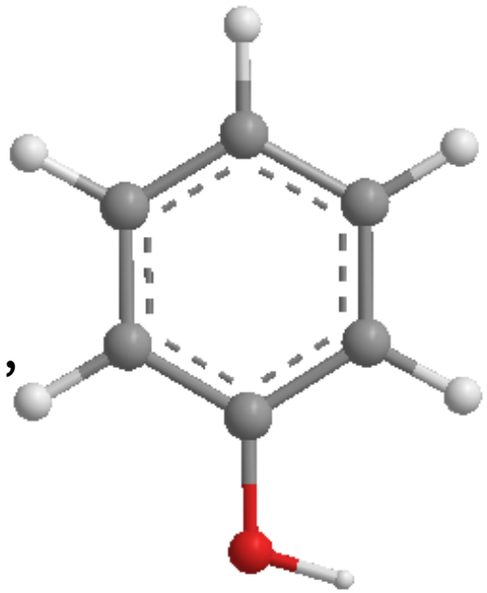
p-Cyanophenol

Rotationally resolved LIF and ab initio: determined rotational constants and V_2.

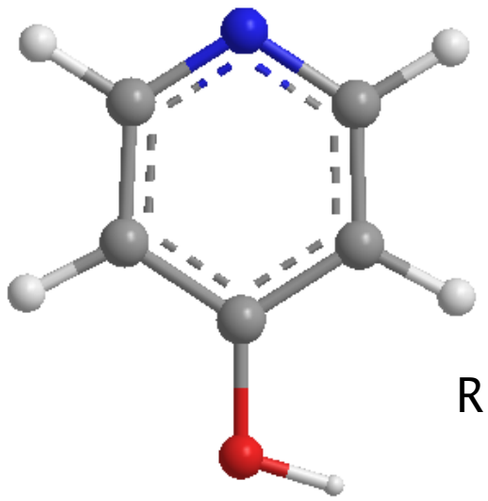
J. Küpper, et al., Phys. Chem. Chem. Phys., 4, 2002, 4634-4639

Microwave, IR, and high-res UV: V_2 is lower than p-CP.

E. Mathier, et al., J. Mol. Spectrosc., 37, 1971, 63-76,
G. Berden, et al., J. Chem. Phys., 104, 1996, 972-983



Phenol

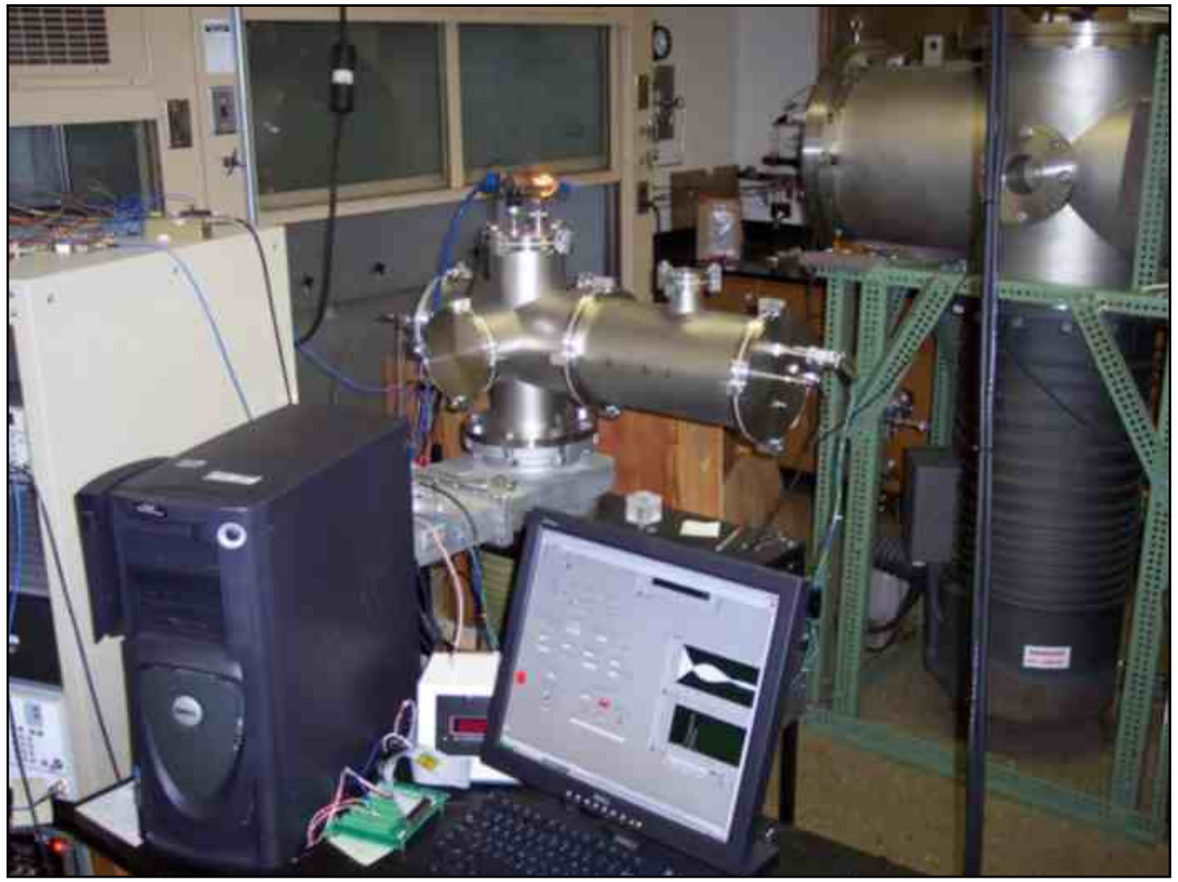


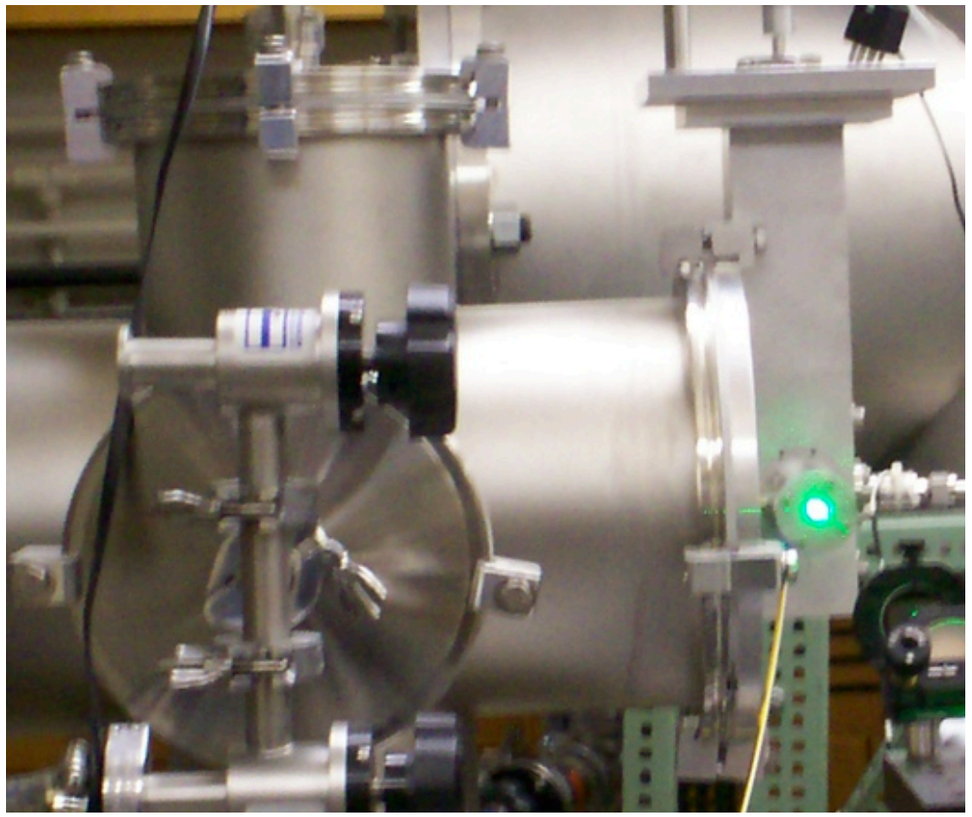
4-Hydroxypyridine

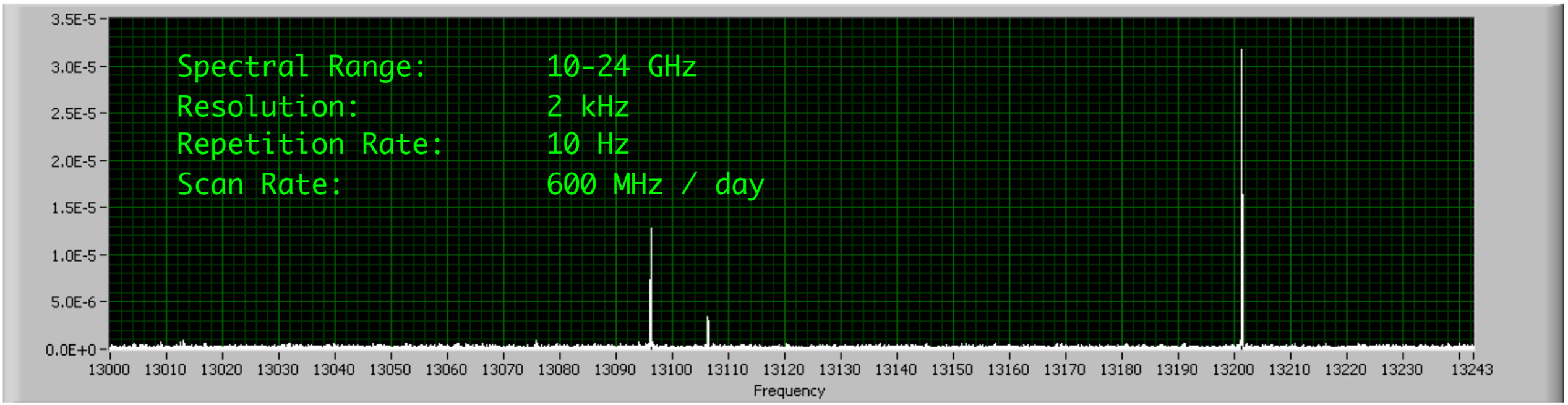
mm-wave and ab initio: V_2 is higher than phenol and p-CP; electron withdrawing effect on V_2

R. Sanchez, et al., Chem. Phys. Lett., 425, 2006, 6-9

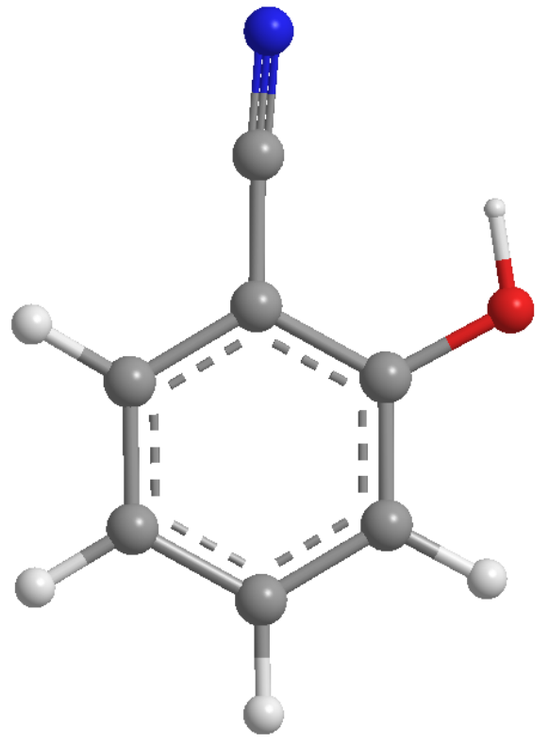
Kent State FTMW Spectrometer



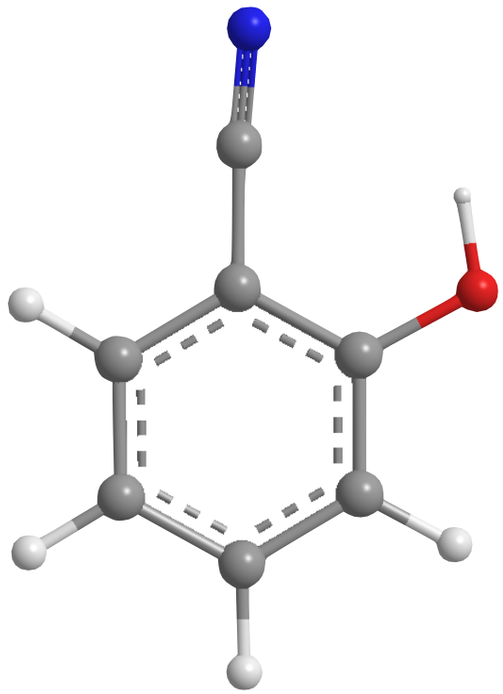




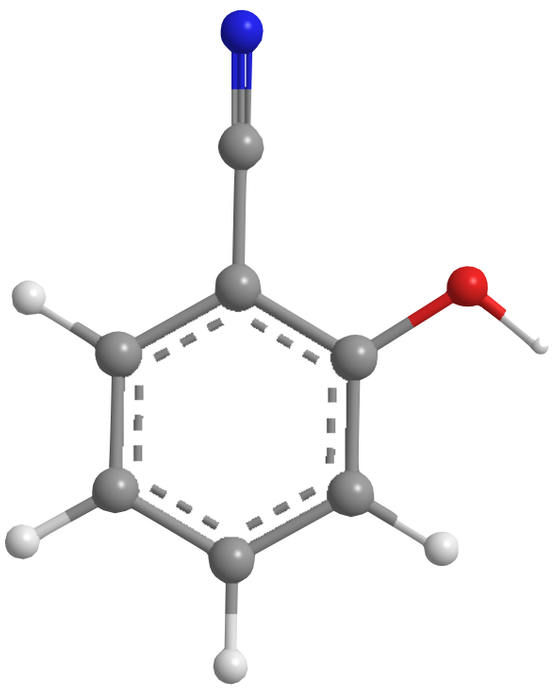
o-Cyanophenol



o-Cyanophenol: Ab Initio Results



ΔE = 0.00 kJ mol^{-1}



ΔE = 10.64 kJ mol^{-1}

Parameter	cis o-CP	trans o-CP
A/MHz	3024	2982
B/MHz	1500	1501
C/MHz	1002	998
μ_a/D	-4.0	-6.3
μ_b/D	0.5	1.5
μ_c/D	0.0	0.0
ΔE/kJ mol^{-1}	0.00	10.64

MP2/6-311++G**

O-H -- N = 2.7 Å

∠C-C-N = 176°

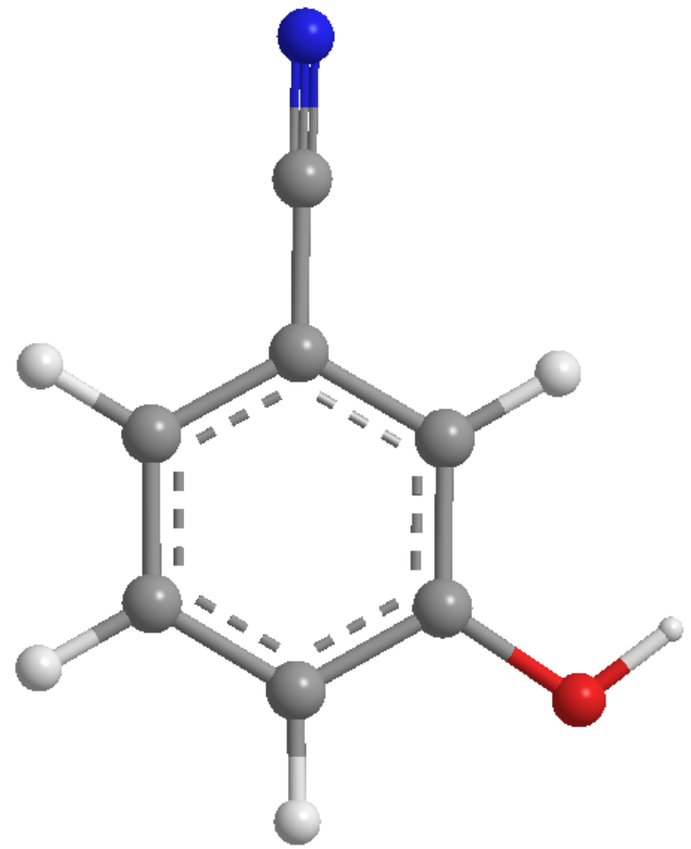
o-CP: Spectra and Fitting

$$\mathscr{H} = \mathscr{H}_R^{(A)} + \mathscr{H}_Q$$

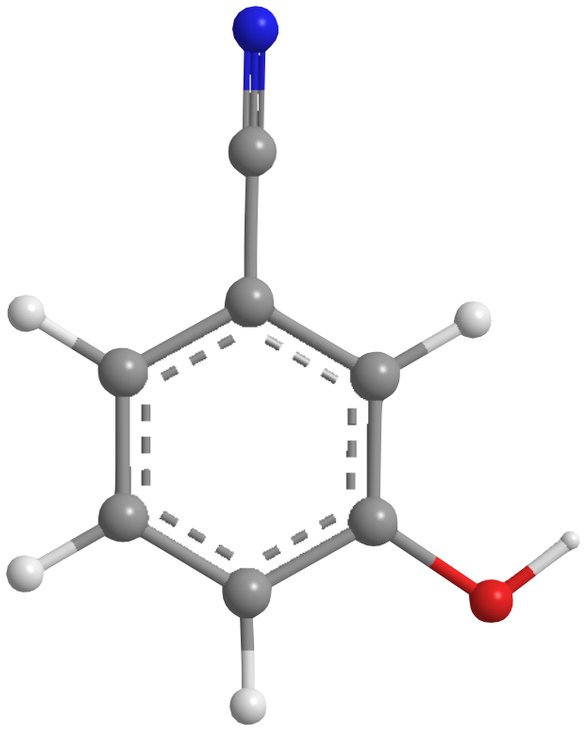
- 25 observed a- and b-type transitions; 68 hyperfine transitions.
- Simultaneous fit to rotational, centrifugal distortion, and nuclear quadrupole coupling constants.

Parameter	cis o-CP
A/MHz	3053.758(2)
B/MHz	1511.2760(3)
C/MHz	1010.7989(2)
Δ_J/kHz	0.038(2)
Δ_{JK}/kHz	0.624(6)
Δ_K/kHz	-0.1(5)
δ_J/kHz	0.0108(9)
δ_K/kHz	0.28(4)
X_{aa}/MHz	-4.213(4)
X_{bb}/MHz	2.53(2)
X_{cc}/MHz	1.68(1)
$\Delta\nu_{rms}$/kHz	1.9
N	25

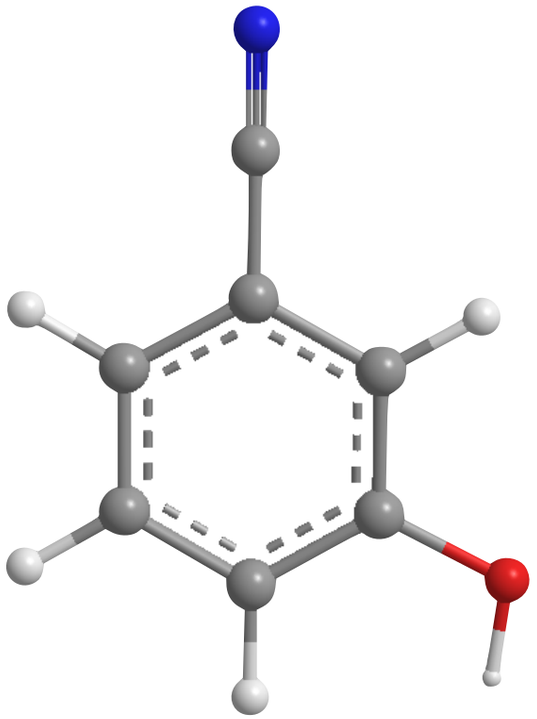
m-Cyanophenol



m-Cyanophenol: Ab Initio Results



ΔE = 0.00 kJ mol^{-1}



ΔE = 0.73 kJ mol^{-1}

Parameter	cis m-CP	trans m-CP
A/MHz	3391	3378
B/MHz	1196	1199
C/MHz	884	885
μ_a/D	-3.6	-5.6
μ_b/D	-0.6	-2.7
μ_c/D	0.0	0.0
ΔE/kJ mol^{-1}	0.00	0.73

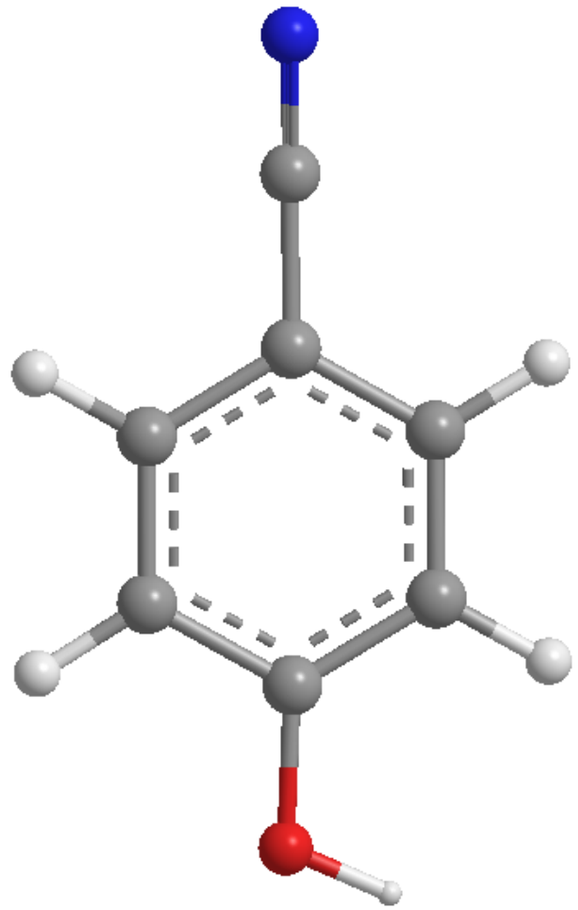
MP2/6-311++G**

m-CP: Spectra and Fitting

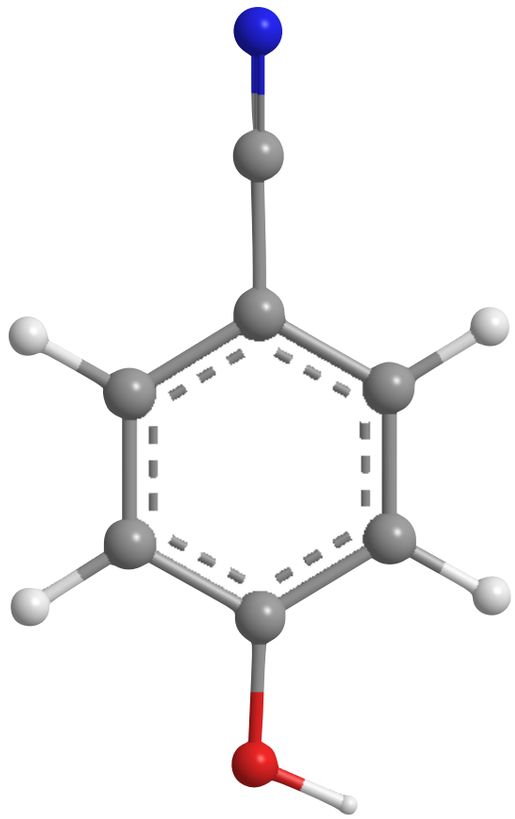
- 14 and 16 a- and b-types observed for cis and trans m-CP
- Total of 36 and 45 hyperfine transitions for cis and trans m-CP
- Simultaneous fit to constants

Parameter	cis m-CP	trans m-CP
A/MHz	3408.9200(2)	3403.1196(3)
B/MHz	1205.8269(2)	1208.4903(2)
C/MHz	890.6672(1)	891.7241(2)
Δ_J/kHz	0.041(2)	0.040(2)
Δ_{JK}/kHz	0.027(8)	0.02(1)
Δ_K/kHz	1.18(3)	1.13(3)
δ_J/kHz	0.0136(7)	0.0142(8)
δ_K/kHz	0.16(2)	0.22(3)
X_{aa}/MHz	-3.681(3)	-3.700(4)
X_{bb}/MHz	1.72(2)	1.72(2)
X_{cc}/MHz	1.96(2)	1.98(2)
$\Delta\nu_{rms}$/kHz	0.8	1.2
N	14	16

p-Cyanophenol



p-Cyanphenol: Ab Initio Results



MP2/6-311++G**

Parameter	p-CP
A/MHz	5598
B/MHz	981
C/MHz	835
μ_a/D	-5.0
μ_b/D	-1.5
μ_c/D	0.0

$V_2 = 1205\ cm^{-1*}$

*J. Küpper, et al., Phys. Chem. Chem. Phys., 4, 2002, 4634-4639

p-CP: Spectra and Fitting

- Observed 25 a- and b-type transitions; total of 82 hyperfine transitions.
- b-types are split due to internal rotation
- Simultaneous fit to spectroscopic constants and torsional constants

Parameter	p-CP
A/MHz	5612.94(3)
B/MHz	990.4280(7)
C/MHz	841.9367(6)
Δ_J/kHz	0.020(1)
Δ_{JK}/kHz	0.23(1)
Δ_K/kHz	-0.01(3)
δ_J/kHz	0.005(1)
δ_K/kHz	0.4(3)
X_{aa}/MHz	-4.17(3)
X_{bb}/MHz	2.36(3)
X_{cc}/MHz	1.81(2)
$\Delta\nu_{rms}$/kHz	2.8
N	25

Internal Rotation

- Fit transitions to ground state splitting

$$\mathscr{H} = \mathscr{H}_R^{(A)} + \mathscr{H}_Q + \Delta E$$

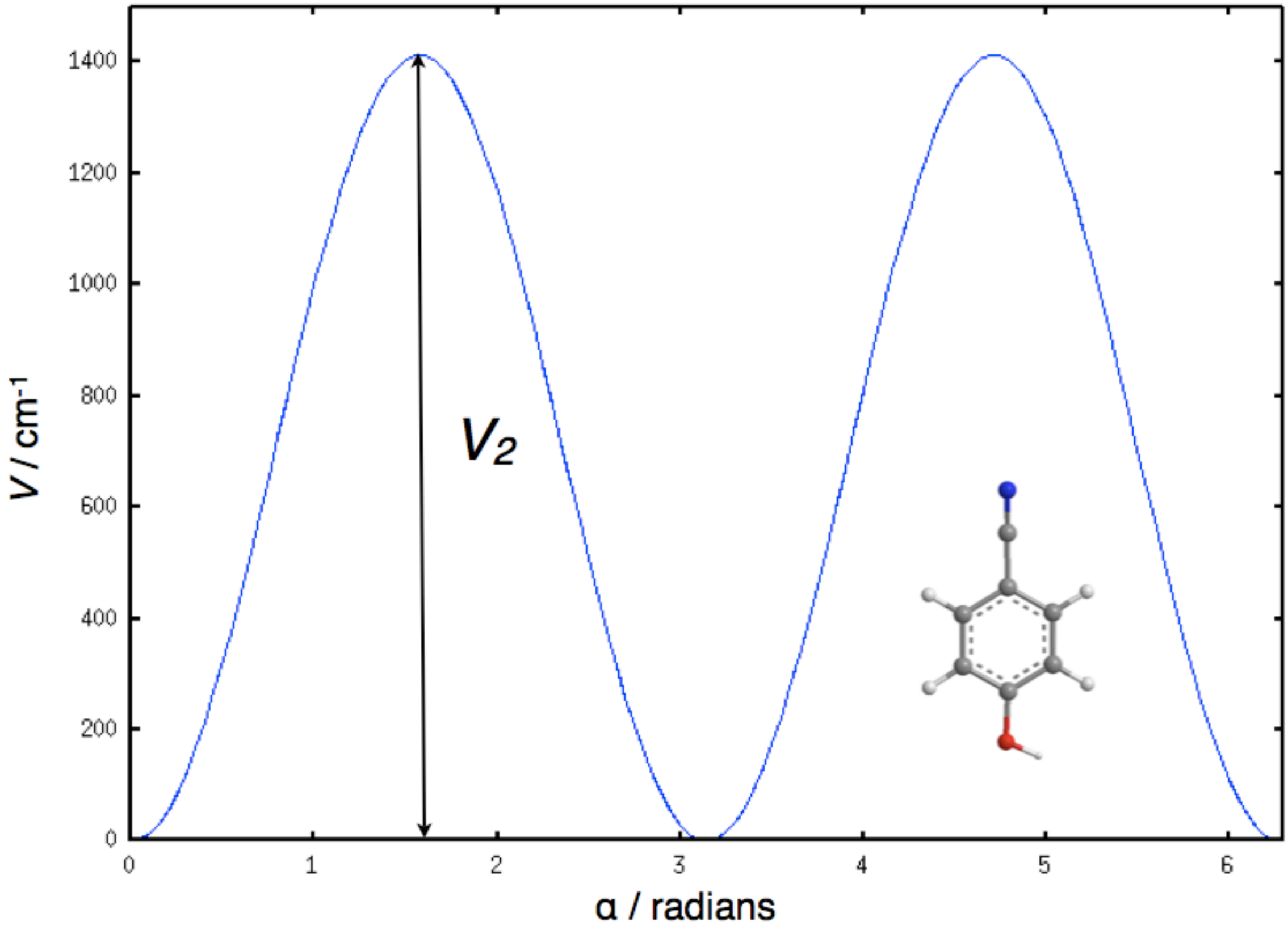
- Fit transitions to IAS Hamiltonian using IAMCALC and SPFIT to model barrier to internal rotation.

$$V(\alpha) = \frac{V_N}{2}(1 - \cos N\alpha)$$

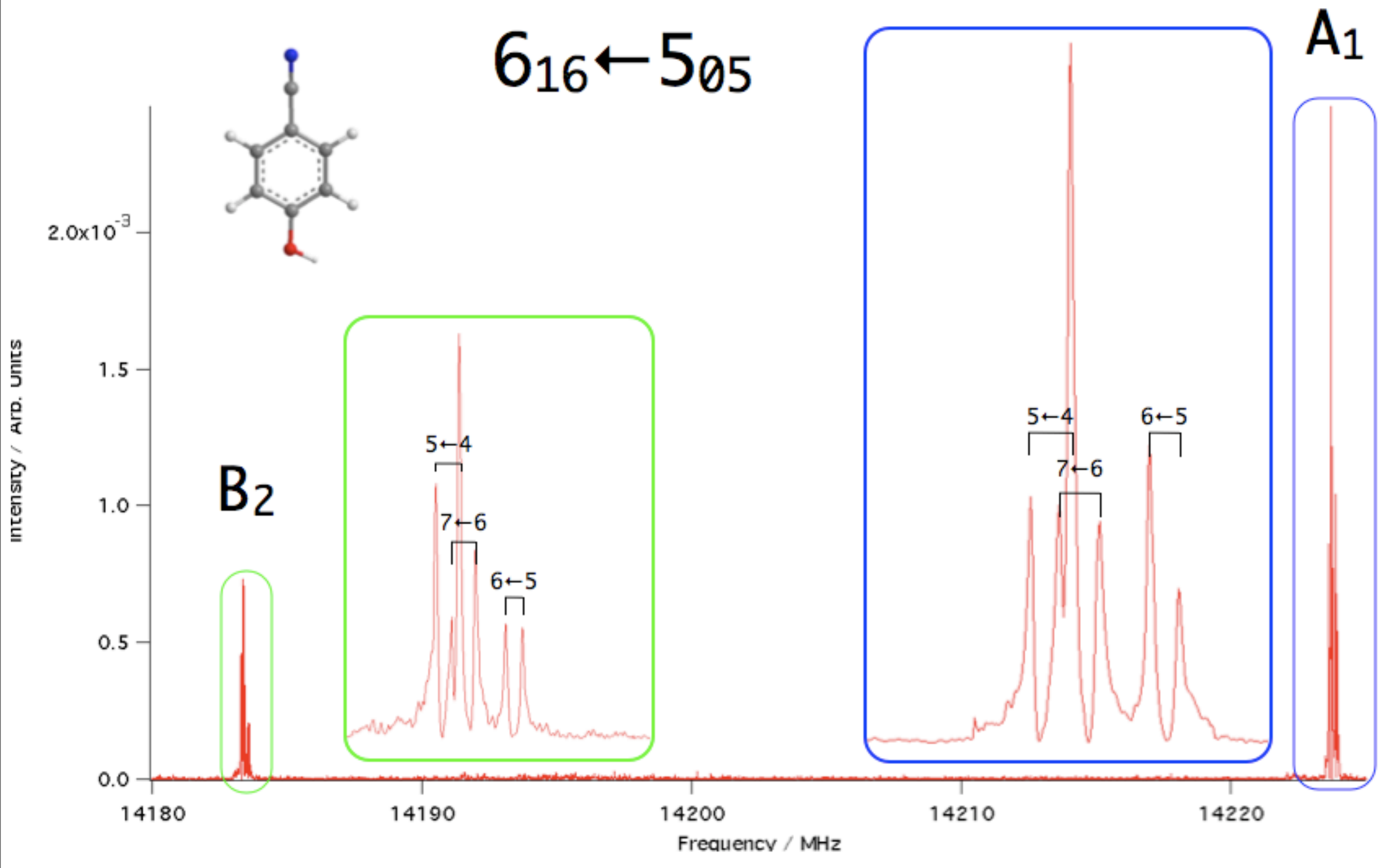
- IAS: Fourier expansion of parameters
- Used F for phenol; determined V_2

Internal Rotation

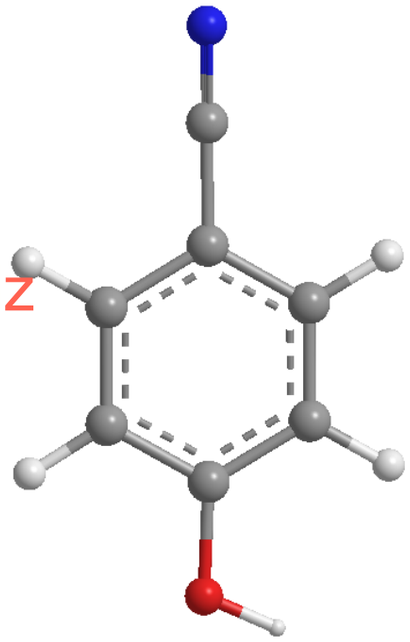
$$V(\alpha) = \frac{1}{2}V_2(1 - \cos 2\alpha)$$



Internal Rotation Splitting



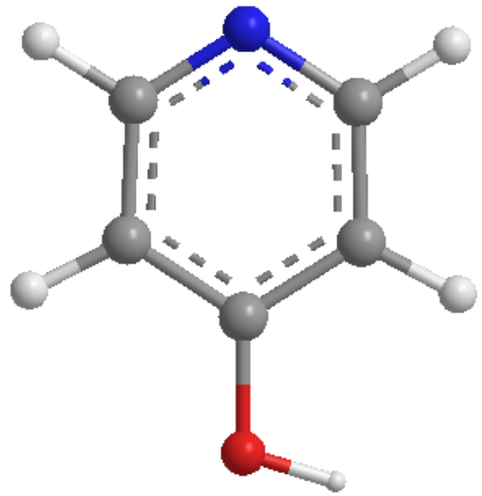
Substituent Effects on Internal Rotation



ΔE = 20.1608(6) MHz
V_2 = 1413(2) cm^{-1}

- p-CP V_2 agrees with LIF study*
- N-substitution: 25% increase in V_2
- CN group: 17% increase in V_2
- Agrees with electronegativity argument of effect on V_2 in phenolic systems

*J. Küpper, et al., Phys. Chem. Chem. Phys., 4, 2002, 4634-4639

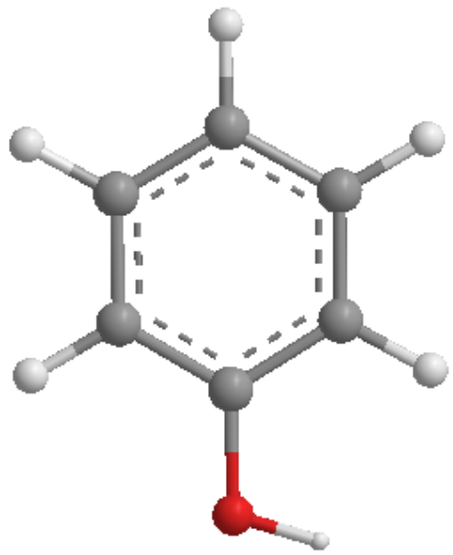


ΔE = 7.97(4) MHz
V_2 = 1513(10) cm^{-1}

R. Sanchez, et al., Chem. Phys. Lett., 425, 2006, 6-9

ΔE = 56(4) MHz
V_2 = 1215(10) cm^{-1}

G. Berden, et al., J. Chem. Phys., 104, 1996, 972-983



Summary

- Microwave spectra were measured and fit for the family of cyanophenol molecules
- Cis conformer observed for o-CP; cis and trans conformers observed for m-CP.
- p-CP undergoes internal rotation of hydroxyl group; ground state splitting and barrier to internal rotation were determined and compared to other phenolic systems

Acknowledgments

- National Science Foundation
- Ohio Supercomputer Center
- Kent State University GSS
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- Tubergen Group
  - Mike Tubergen
  - Nathan Barefoot (REU)