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CRYSTAL FIELD INTERACTIONS OF “LARGE” ROTORS EMBEDDED IN SOLID PARAHYDROGEN (BRIEFING CHARTS AND ABSTRACT)

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BRIEFING CHARTS AND ABSTRACT

The briefing charts were presented at the 63rd Ohio State University International Symposium on Molecular Spectroscopy held 16-20 June 2008, in Columbus, Ohio. The abstract shown in block 14 of attached Report Documentation Page is published in the conference proceedings found online in the Ohio State University's Knowledge Bank, <http://hdl.handle.net/1811/33333>.

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Crystal Field Interactions of “Large” Rotors Embedded in Solid Parahydrogen

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Rotation in the Solid Matrices

- Rare gas matrices and traditional molecular matrices:
 - Small hydrides: HX , H_2O , NH_2 , NH_3 , CH_3 , CH_4
 - *Perhaps* ClF , CN (ESR and IR spectra conflict)
 - fcc lattice structure
- Solid Parahydrogen:
 - Very low angular anisotropy, and weak intermolecular interactions
 - Small hydrides: HX , H_2O , NH_3 , CH_3 , CH_4
 - “*Large*” molecules: N_2 , O_2 , CO , HCN , ... *more?*
 - fcc (as deposited) and hcp (annealed) lattice structure

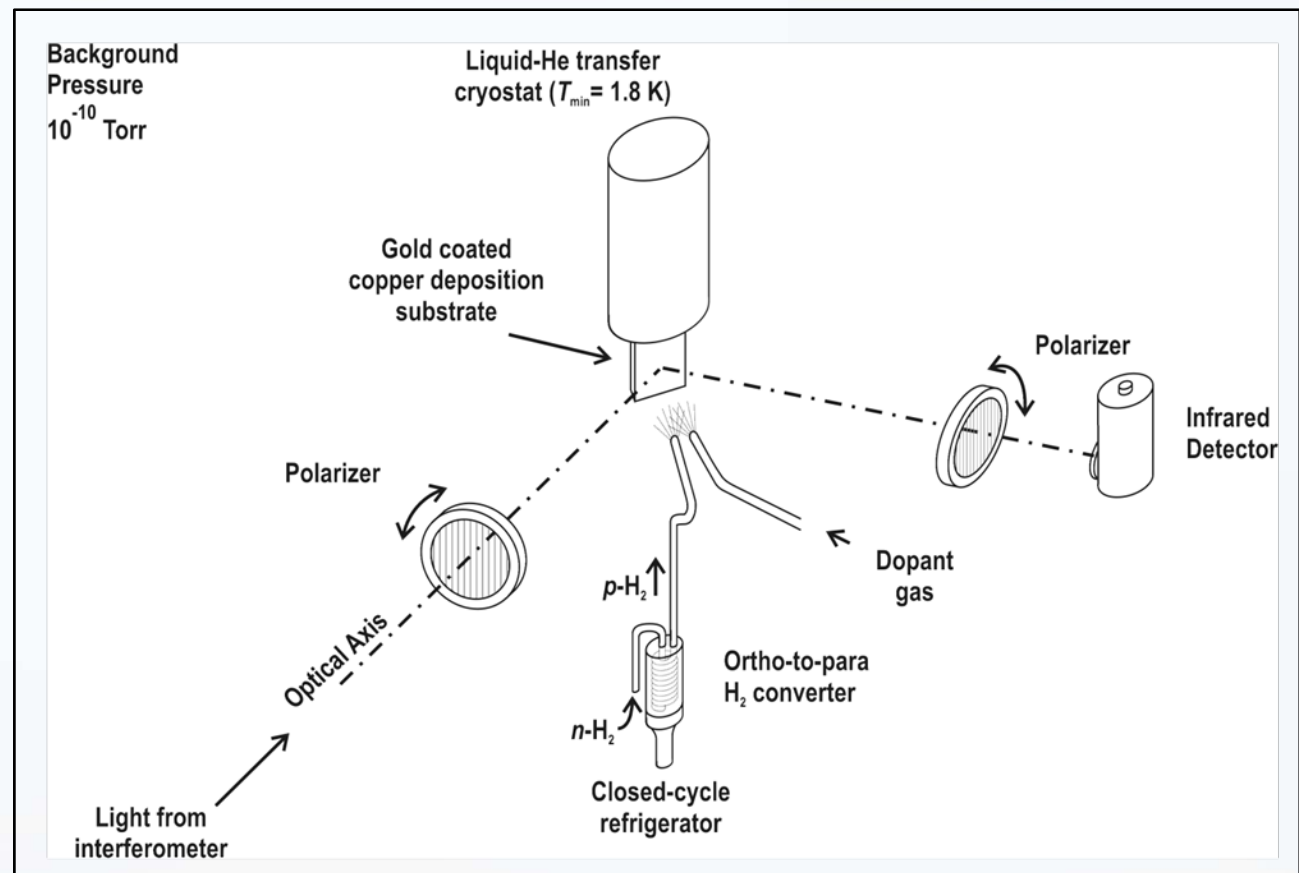
Narrow spectral lines widths and the ability to examine the rotation of larger molecules allows us to examine the impurity-matrix interactions with remarkable clarity





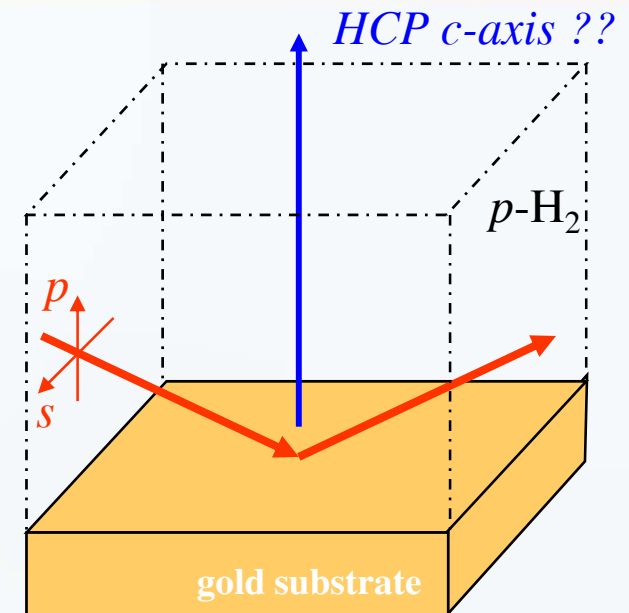
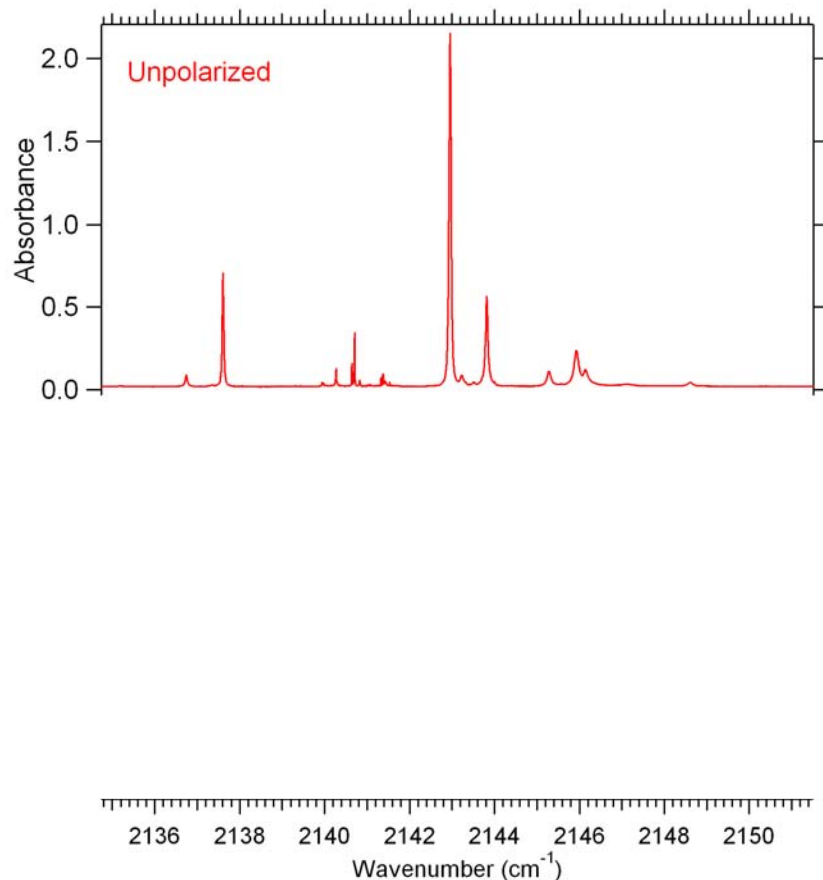
Rapid vapor deposition of p-H₂

- Reflection based set-up (FTIR).
- [*o*-H₂] < 100 ppm.
- *p*-H₂ deposition rate ~150 mmol/hr → ~1 mm/hr thickness.
- Deposition at 2.3 K. Sample annealed at 4.3 K for 30 min.





Polarization Spectroscopy



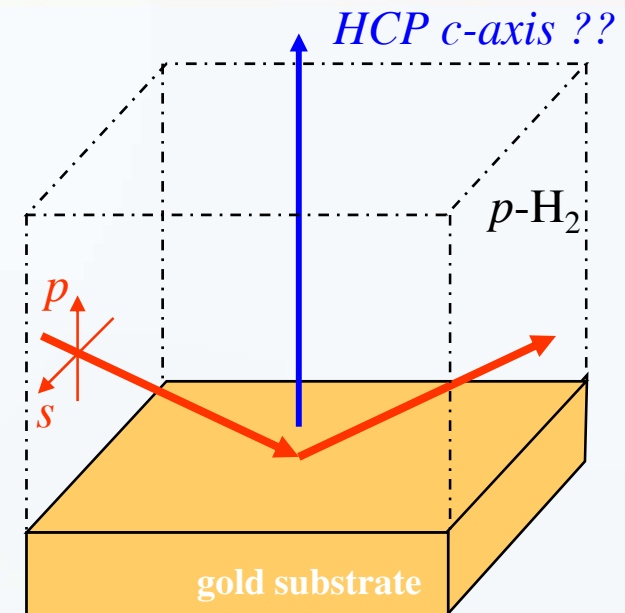
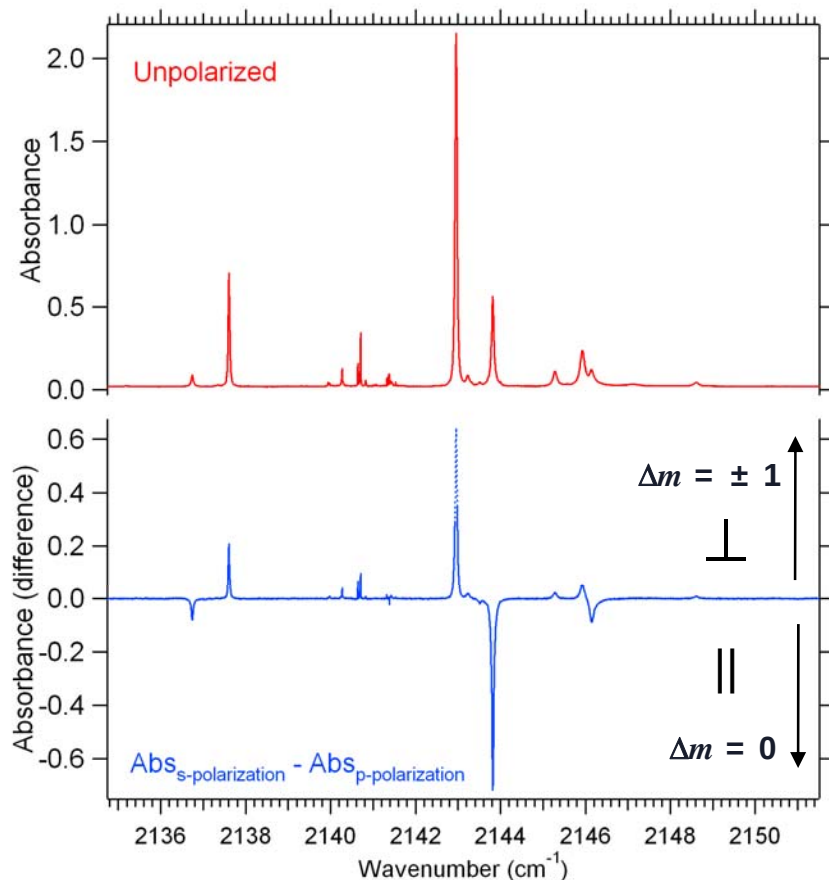
Polarization analysis provides:

- An assignment of the perpendicular and parallel components to the crystal field perturbed rotational structure (*i.e.* Δm)
- $Abs_{s\text{-pol}} - Abs_{p\text{-pol}} = \frac{1}{2} \mu_{\perp}^2 - \frac{1}{2} \mu_{\parallel}^2$



Polarization Spectroscopy

8ppm CO in *p*-H₂



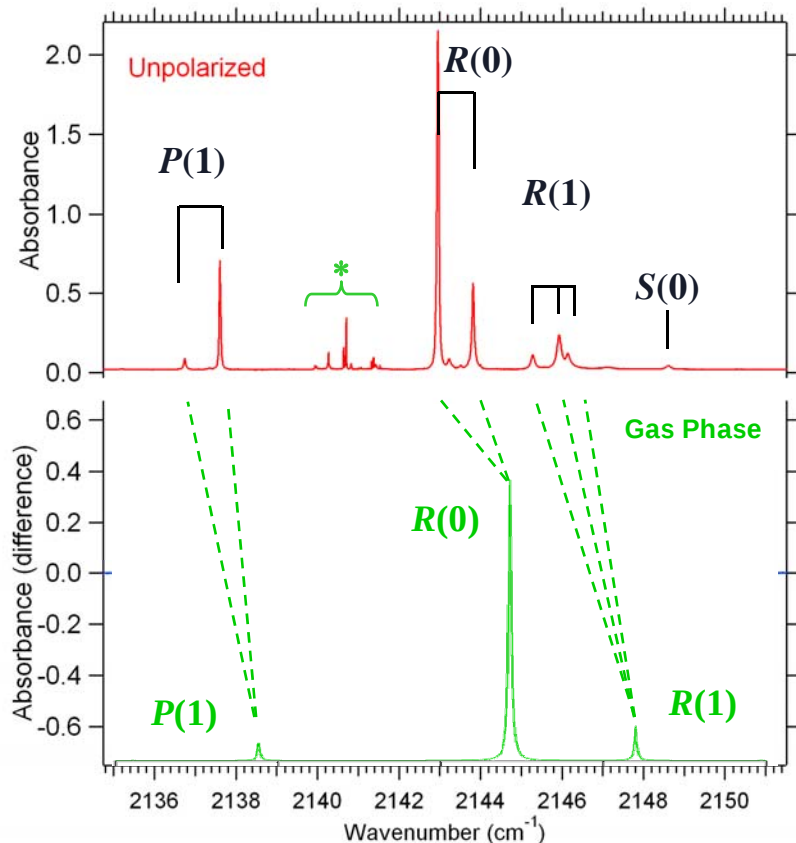
Polarization analysis provides:

- An assignment of the perpendicular and parallel components to the crystal field perturbed rotational structure (*i.e.* Δm)
- $Abs_{s-pol} - Abs_{p-pol} = \frac{1}{2} \mu_{\perp}^2 - \frac{1}{2} \mu_{\parallel}^2$



Rotation in parahydrogen

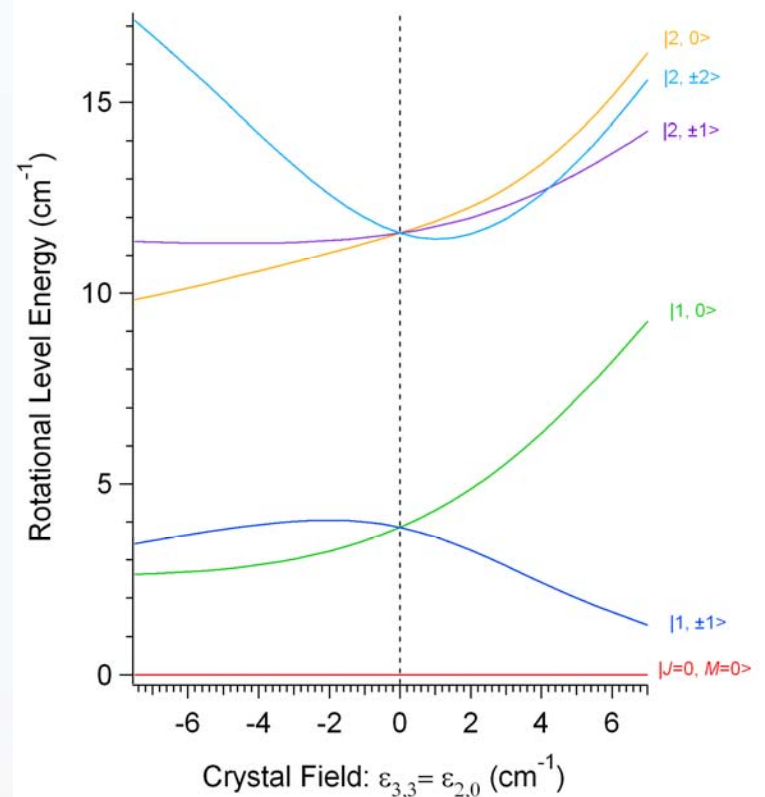
8 ppm CO in $p\text{-H}_2$



* $o\text{-H}_2$ clustering

Simulation:

Linear molecule in $h.c.p$ crystal field



Simulation uses theory of: Devonshire, Proc. Roy. Soc. London A **153**, 601 (1936);

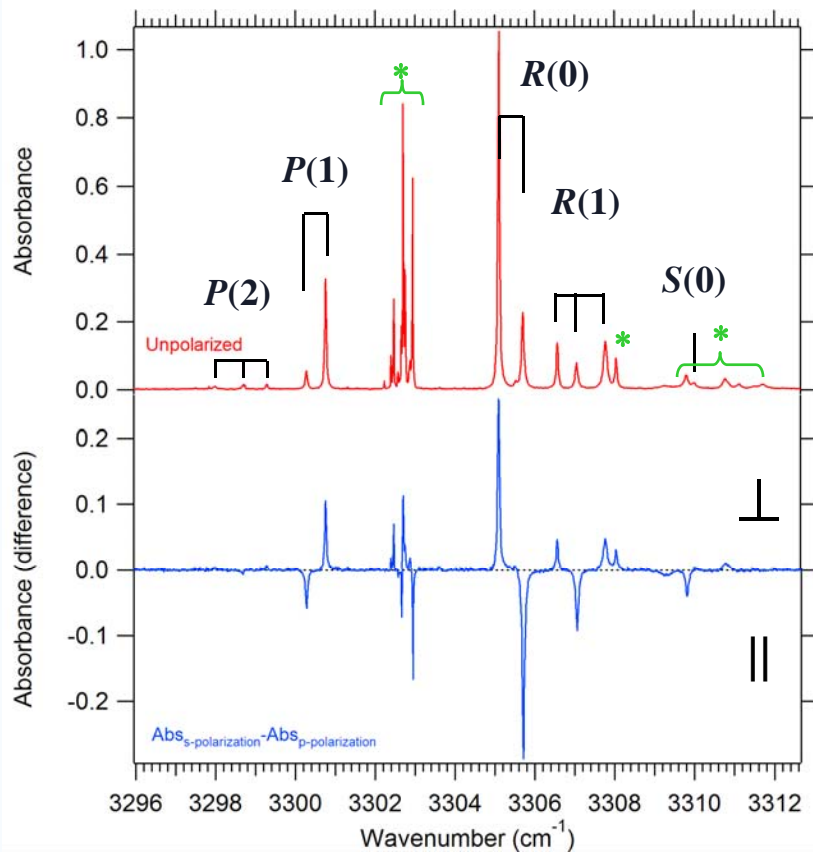
Bowers and Flygare, J. Chem. Phys., **44**, 1389 (1966).

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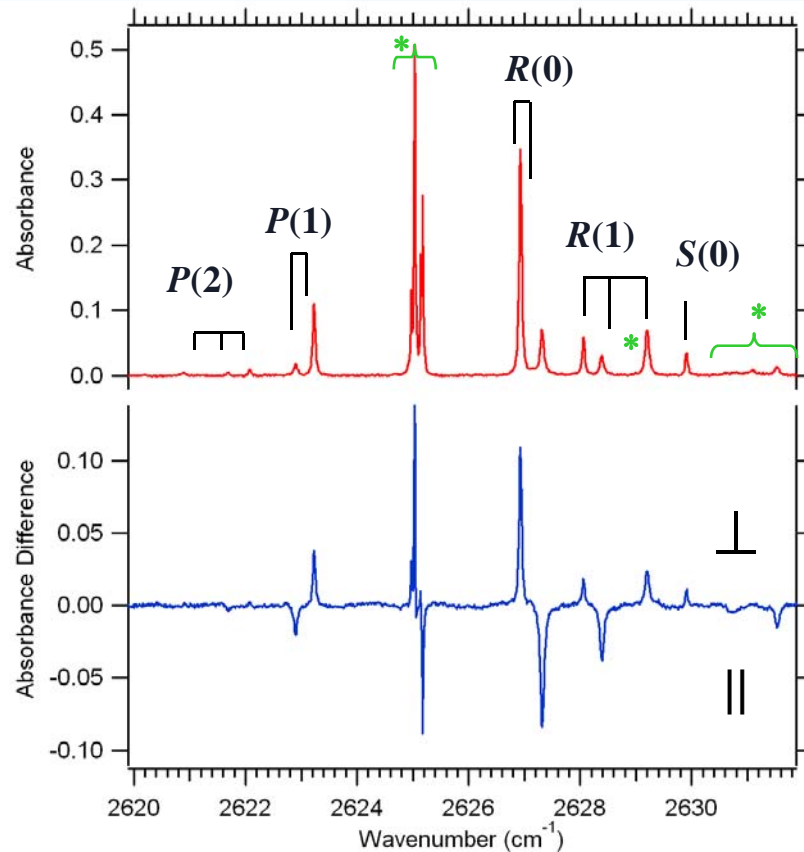


HCN in parahydrogen

8 ppm HCN in $p\text{-H}_2$



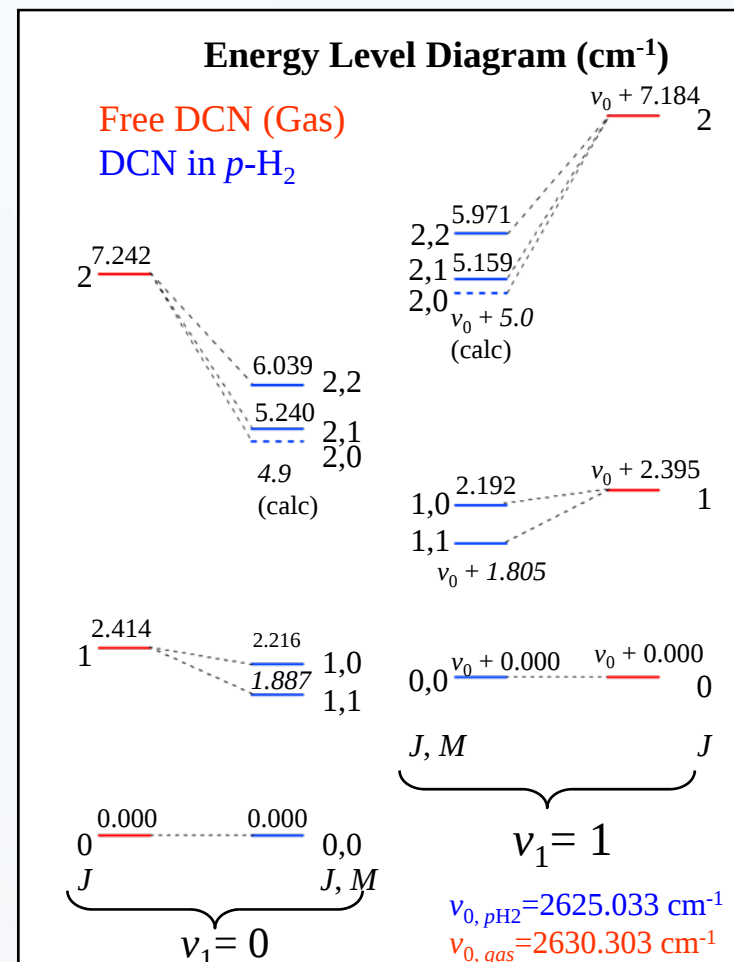
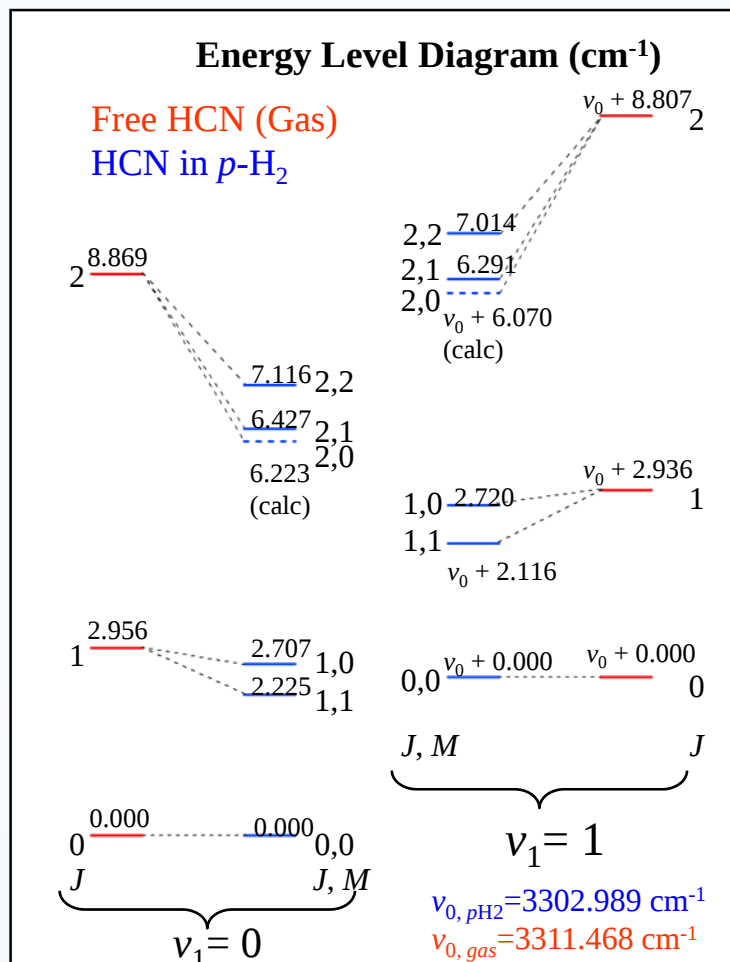
2 ppm DCN in $p\text{-H}_2$



* $o\text{-H}_2$ clustering

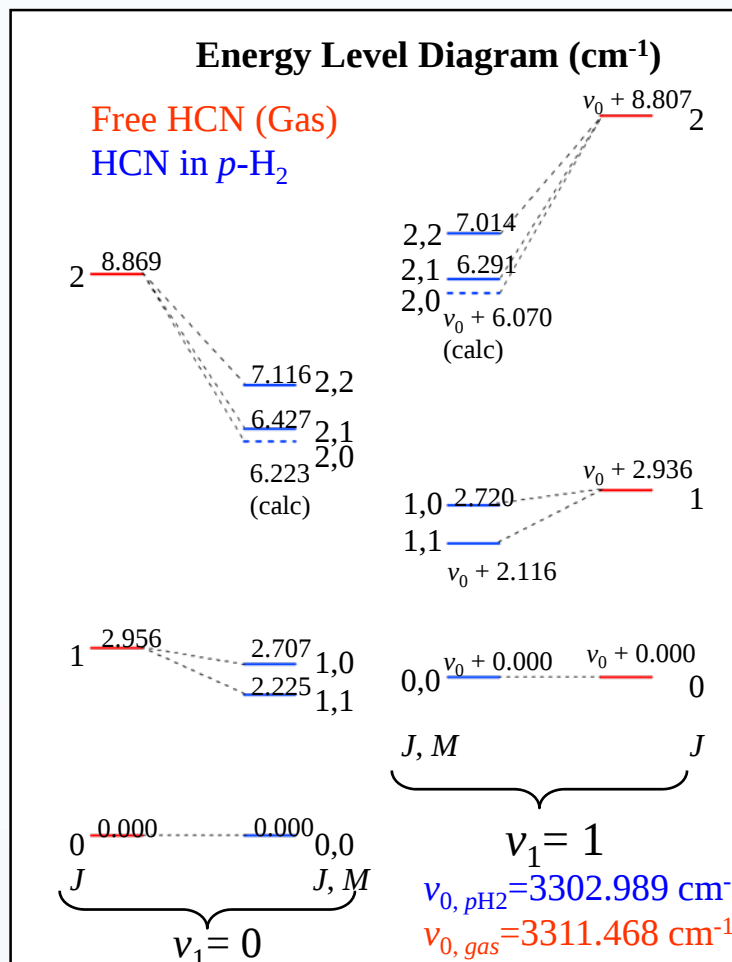


HCN / DCN Energy Level Diagrams





Interpretation of the Rotational Fine Structure- HCN + DCN



Crystal field theory (linear molecule in HCP lattice) *

$$H = H_{r,v} + V_{\text{cry}}$$

$$V_{\text{cry}} = \epsilon_2 C_{2,0}(\Omega_{\text{HCN}}) + \epsilon_3 [C_{3,-3}(\Omega_{\text{HCN}}) - C_{3,3}(\Omega_{\text{HCN}})]$$

$$\text{where } C_{l,m}(\Omega) = \left(\frac{4\pi}{2l+1} \right)^{1/2} Y_{l,m}(\Omega)$$

“Fitting” Results in cm⁻¹: (10 levels, 9 parameters)

	HCN		DCN	
	<i>p</i> -H ₂	Gas	<i>p</i> -H ₂	Gas
<i>B</i>	1.475(5)	1.478	1.2791(5)	1.207
ΔB	-0.005(5)	-0.010	-0.032(5)	-0.010
<i>D</i>	0.0675(5)	2.910 × 10 ⁻⁶	0.0654(5)	1.927 × 10 ⁻⁶
ΔD	0.0032(5)	0.025 × 10 ⁻⁶	-0.0028(5)	0.017 × 10 ⁻⁶
<i>v</i> ₀	3302.989(5)	3311.4770	2625.093(10)	2630.3033
ϵ_2	-1.274(5)	-	-2.142(5)	-
$\Delta \epsilon_2$	-0.193(5)	-	-0.047(5)	-
ϵ_3	6.850(5)	-	7.500(5)	-
$\Delta \epsilon_3$	0.767(5)	-	0.028(5)	-

NOTE: Above perturbation does not converge for large *D*!
Treatment was modified to incorporate centrifugal distortion after crystal field calculation to avoid this problem.

very large! × 20,000! Identical!

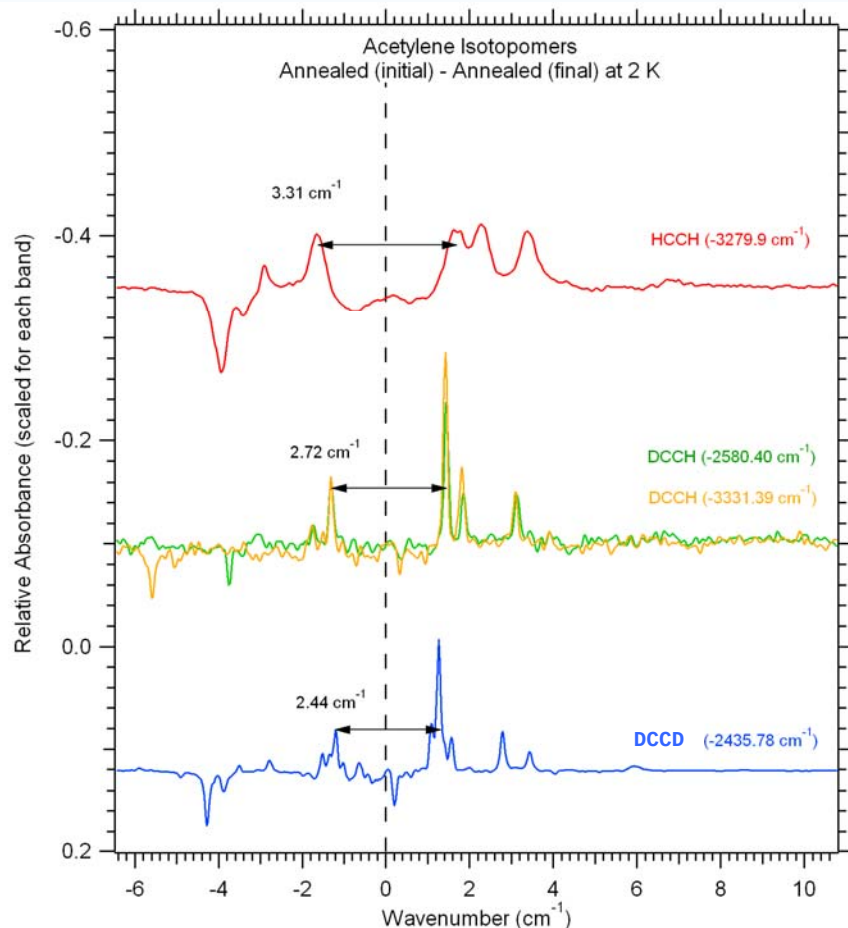


6 ppm NO in p -H₂





Preliminary C₂H₂ in parahydrogen



$E_{R(0)} - E_{P(1)} \quad (4B)$				
	<u>Gas</u>		<u>pH₂</u>	
	Wavenumber	Relative	Wavenumber	Relative
HCCH	4.71 cm ⁻¹	1.00	3.35 cm ⁻¹	1
DCCH	3.97 cm ⁻¹	0.84	2.74 cm ⁻¹	0.82
DCCD	3.39 cm ⁻¹	0.72	2.47 cm ⁻¹	0.74

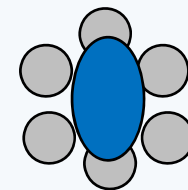
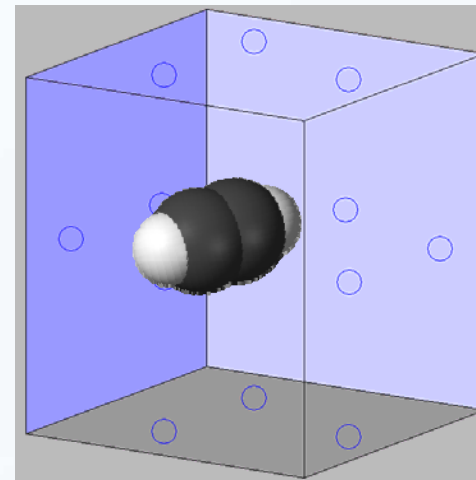
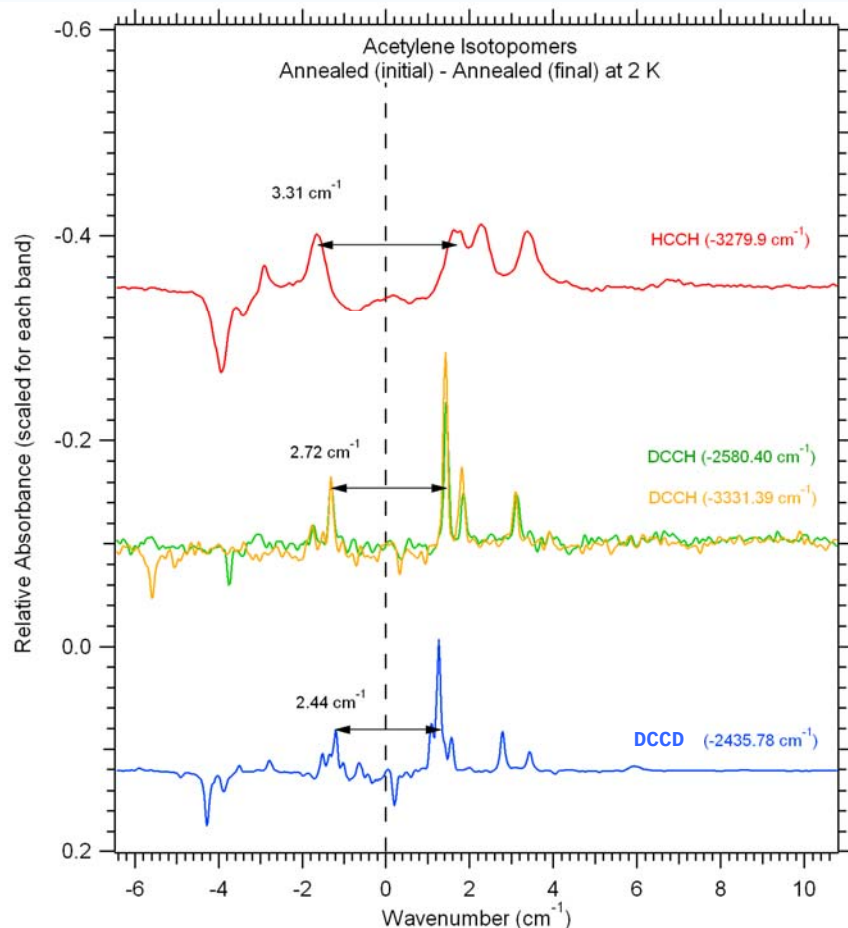
- Acetylene IR spectrum 'ages'... timescale of 30 minutes. Aging appears to be acetylene-acetylene clustering.
- "Rotational spectrum" disappears fairly quickly (but not with annealing!)

Y.P. Lee and collaborators *Chem. Phys. Lett.* **435** 247-251 (2007) – no rotation at 'high' [o-H₂]





Preliminary C_2H_2 in parahydrogen

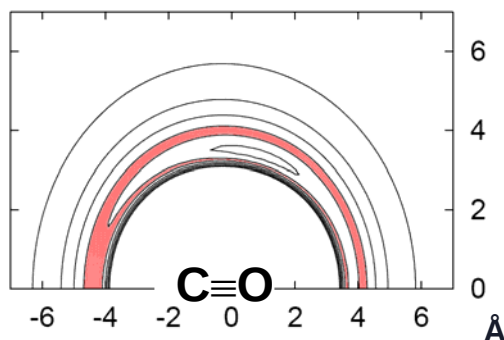


- HCCH Van der Waal diameter $\sim 6.4\text{ \AA}$
- $p\text{-H}_2$ intermolecular spacing – $3.8\text{ \AA}$
- Substantial overlap of wavefunctions



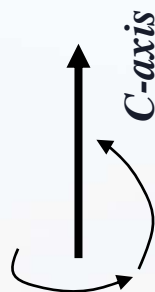
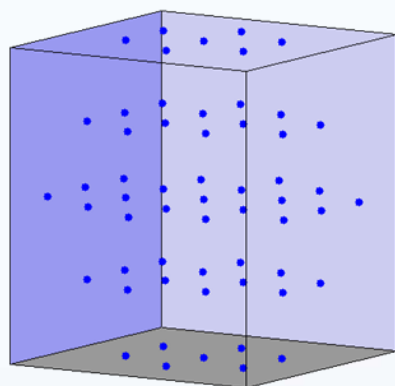
Prediction of Crystal Field Parameters: Truncation

Pair Potential



+

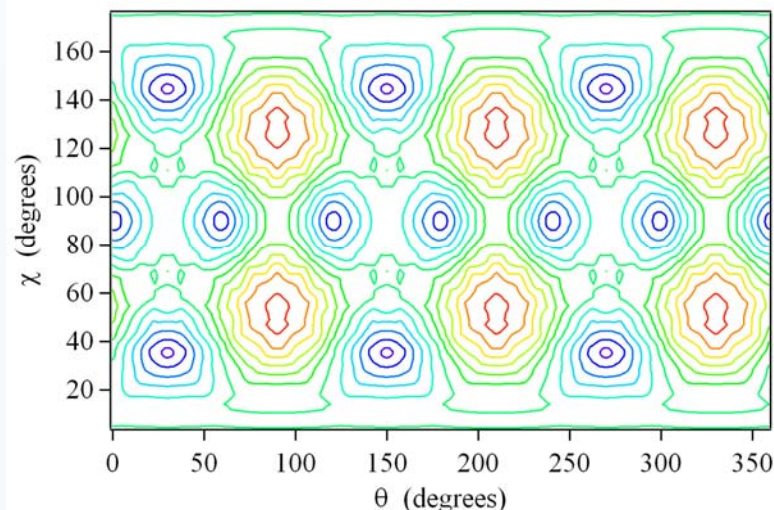
H_2 - *h.c.p.* lattice



θ (in-plane)

χ (out-of-plane)

Rotational PES dopant
in *h.c.p.* H_2 lattice (Rigid)



Crystal field theory (linear molecule in HCP lattice) *

$$H = H_{r,v} + V_{\text{cry}}$$

$$V_{\text{cry}} = \sum_{l,m} \epsilon_{l,\pm m} \left(\frac{4\pi}{2l+1} \right)^{1/2} Y_{l,\pm m}(\Omega)$$

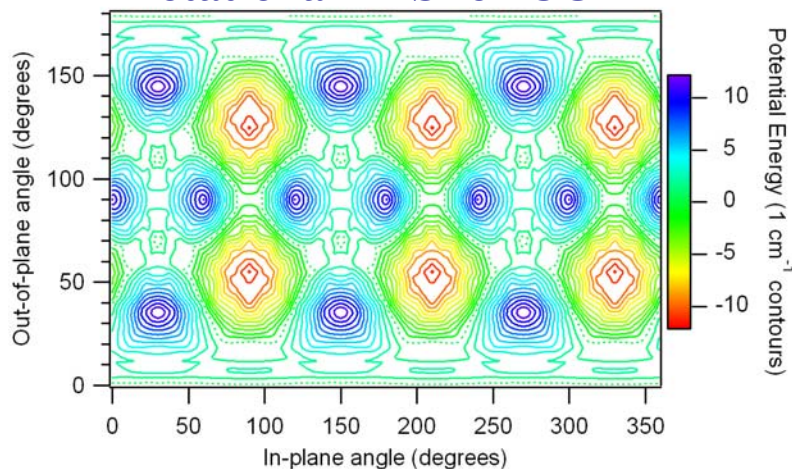
* SAPT/MC⁺BS, P. Jankowski and K. Szalwicz, *J. Chem. Phys.* **108**, 3554 (1998).



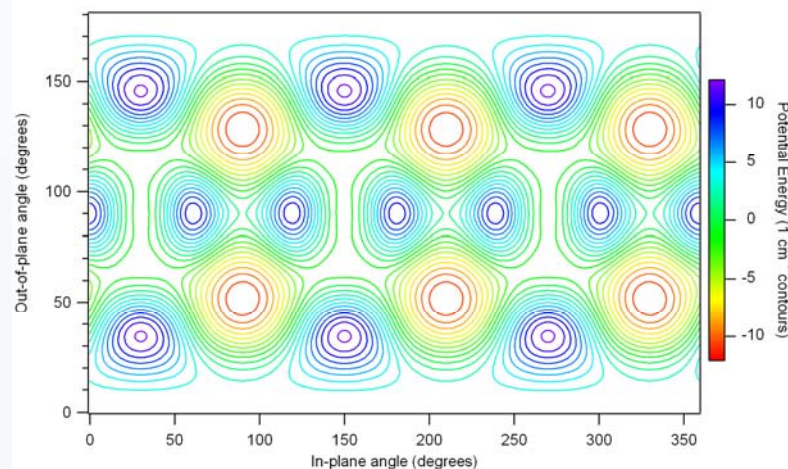


Prediction of Crystal Field Parameters: Truncation - CO

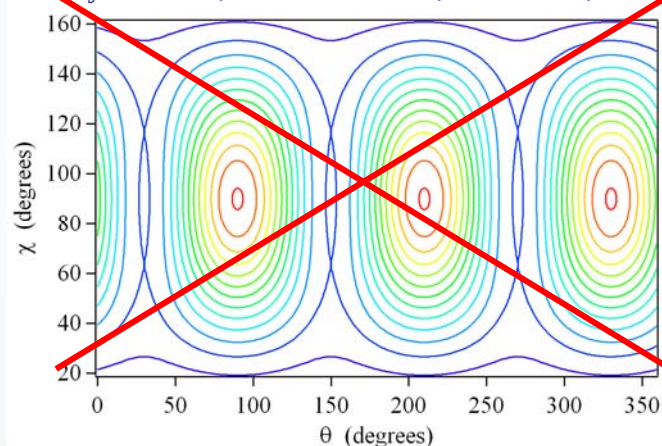
Rotational PES for CO



CFT –up to $C_{12,12}(\Omega)$



$$V_{\text{cry}} = \varepsilon_2 C_{2,0}(\Omega) + \varepsilon_3 [C_{3,-3}(\Omega) - C_{3,3}(\Omega)]$$



(2.52)*

ε (cm ⁻¹)	Term	ε (cm ⁻¹)	Term
4.86	$C_{3,3}(\Omega)$	0.65	$C_{9,3}(\Omega)$
6.74	$C_{5,3}(\Omega)$	0.55	$C_{12,6}(\Omega)$
6.54	$C_{4,0}(\Omega)$	0.46	$C_{8,0}(\Omega)$
3.68	$C_{6,6}(\Omega)$	0.43	$C_{12,12}(\Omega)$
-5.80	$C_{6,0}(\Omega)$	-0.02	$C_{12,0}(\Omega)$
2.61	$C_{7,3}(\Omega)$	-0.47	$C_{11,3}(\Omega)$
1.10	$C_{8,6}(\Omega)$	-0.22	$C_{2,0}(\Omega)$

* Experimentally fitted values.

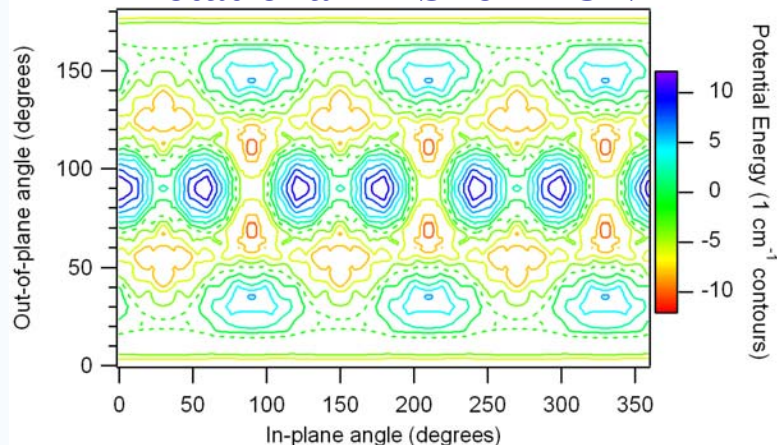
(1.03)*



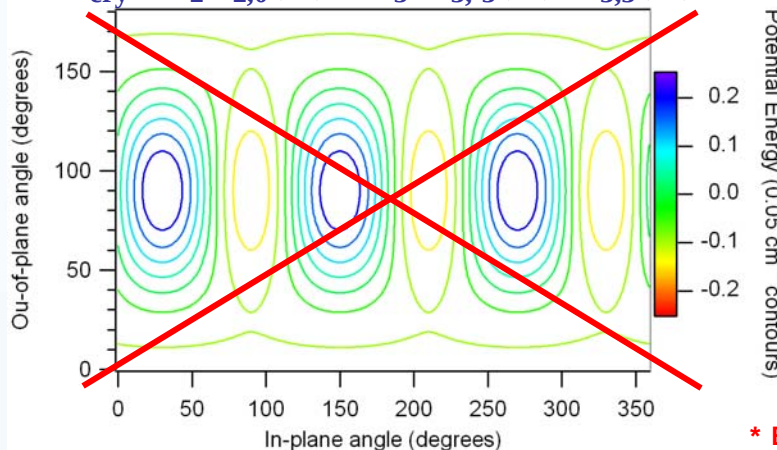


Prediction of Crystal Field Parameters: Truncation - HCN

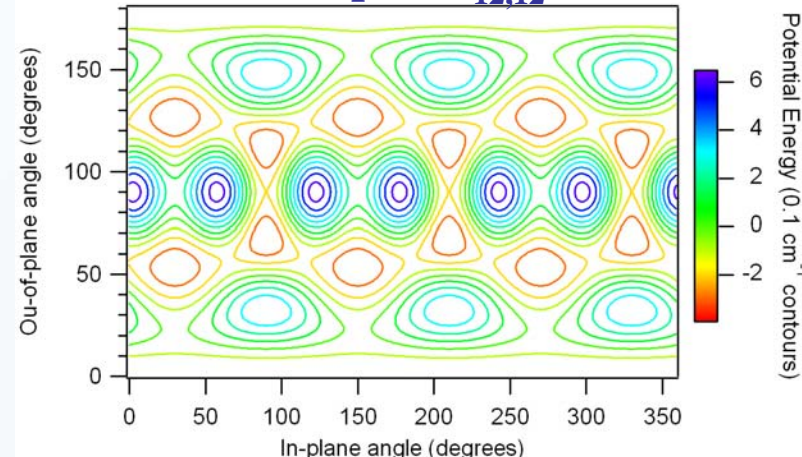
Rotational PES for HCN



$$V_{\text{cry}} = \varepsilon_2 C_{2,0}(\Omega) + \varepsilon_3 [C_{3,-3}(\Omega) - C_{3,3}(\Omega)]$$



CFT -up to $C_{12,12}(\Omega)$



ε (cm ⁻¹)	Term	ε (cm ⁻¹)	Term
-3.04	$C_{6,6}(\Omega)$	0.63	$C_{8,6}(\Omega)$
-2.28	$C_{5,3}(\Omega)$	0.09	$C_{8,0}(\Omega)$
3.35	$C_{4,0}(\Omega)$	-0.01	$C_{9,3}(\Omega)$
-4.82	$C_{6,0}(\Omega)$		
0.70	$C_{3,3}(\Omega)$	(6.85/7.50)*	
-1.24	$C_{7,3}(\Omega)$		
-0.47	$C_{2,0}(\Omega)$	(-1.27/-2.14)*	

* Experimental fitted values for HCN/DCN.

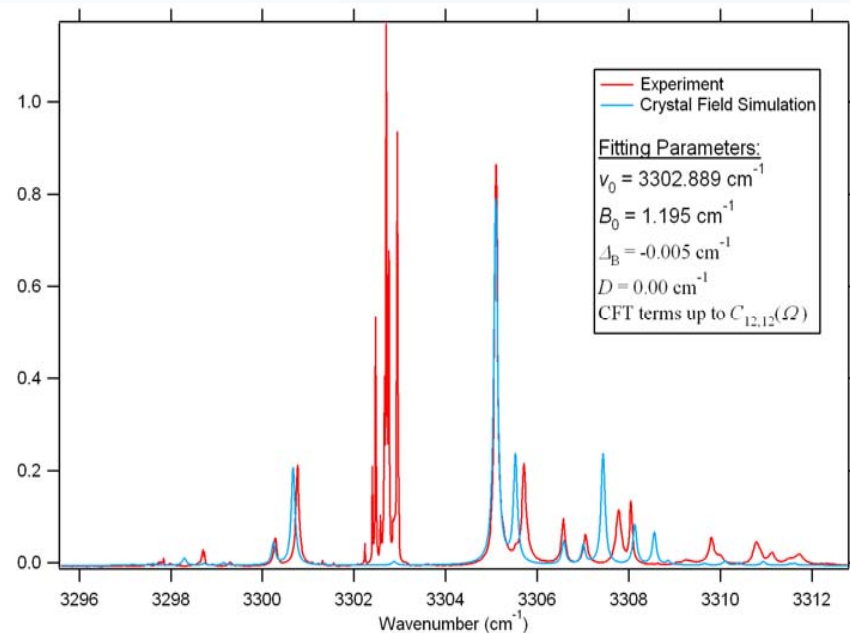
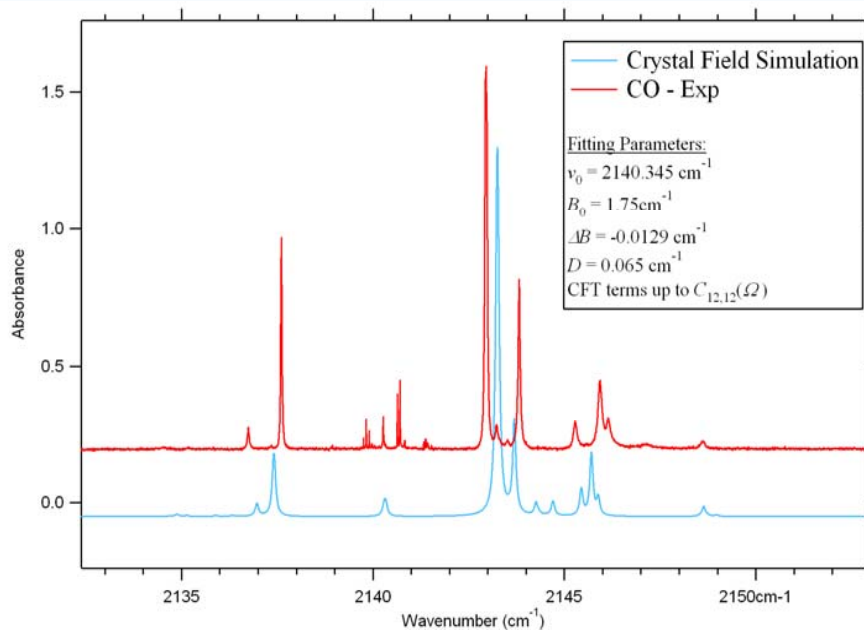
* HCN-H₂ Pair Potential - D. Moore, unpublished,

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Estimation of Crystal Field Parameters: Simulated Spectrum for CO + HCN



- Qualitative agreement with experiment
- Overestimates splitting in $J=1$ manifold – rigid lattice structure
- Underestimates $\epsilon_{2,0}$ parameter
- Compression of rotational fine structure (B_{eff}/D_{eff}) not accounted for by crystal field



Summary

Conclusions

- Parahydrogen is remarkably accommodating to rotating molecules... even HCCH!
- “reduction” in rotational constant can be thought as a large centrifugal distortion constant... B may not be affected at all
- Simulations using pair potentials and rigid lattice agree qualitatively with experiment

Acknowledgements:

- Takamasa Momose (Crystal field theory for CO)
- David Anderson (NO data)
- David Moore (H_2 -HCN potential calculations)





QUESTIONS?

