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INFRARED SPECTROSCOPY OF HYDROGEN CYANIDE IN SOLID PARAHYDROGEN (BRIEFING CHARTS)

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CONFERENCE PAPER

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14. ABSTRACT

Solid parahydrogen features:

- Weak intermolecular interactions
- Slow relaxation timescales
- Quantum crystal: self-annealing via tunneling
- Homogeneous environment
- Large intermolecular distance, 3.78 Å

Parahydrogen as a matrix:

- Very small matrix shifts, predictable (-0.5 %)
- Nearly free rotation for small molecules
- High impurity mobility
- Narrow spectral linewidths (<100 MHz possible)
- Dopants induce infrared activity in matrix

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& Dr. Mario E. Fajardo
AFRL/MNME

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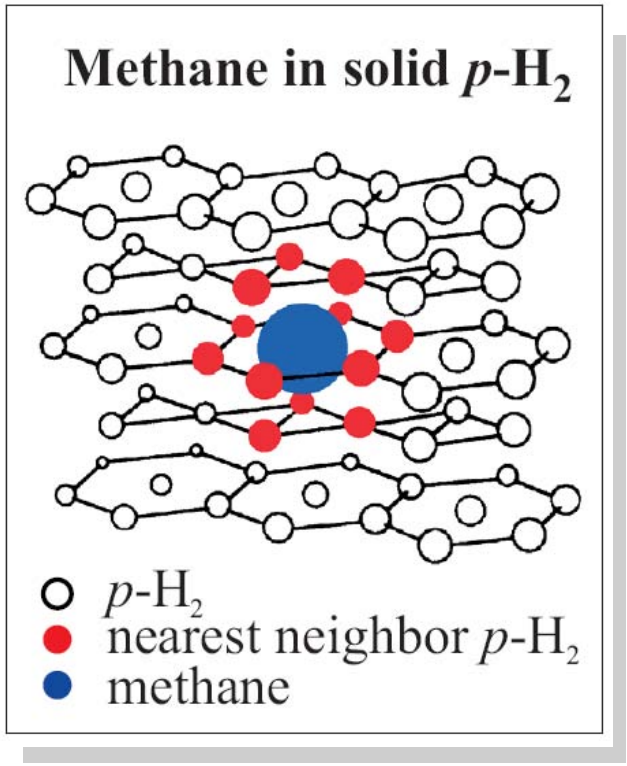
Solid parahydrogen

Solid parahydrogen features:

- Weak intermolecular interactions
- Slow relaxation timescales
- Quantum crystal: self-annealing via tunneling
- Homogeneous environment
- Large intermolecular distance, 3.78 Å



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- Nearly free rotation for small molecules
- High impurity mobility
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- Dopants induce infrared activity in matrix

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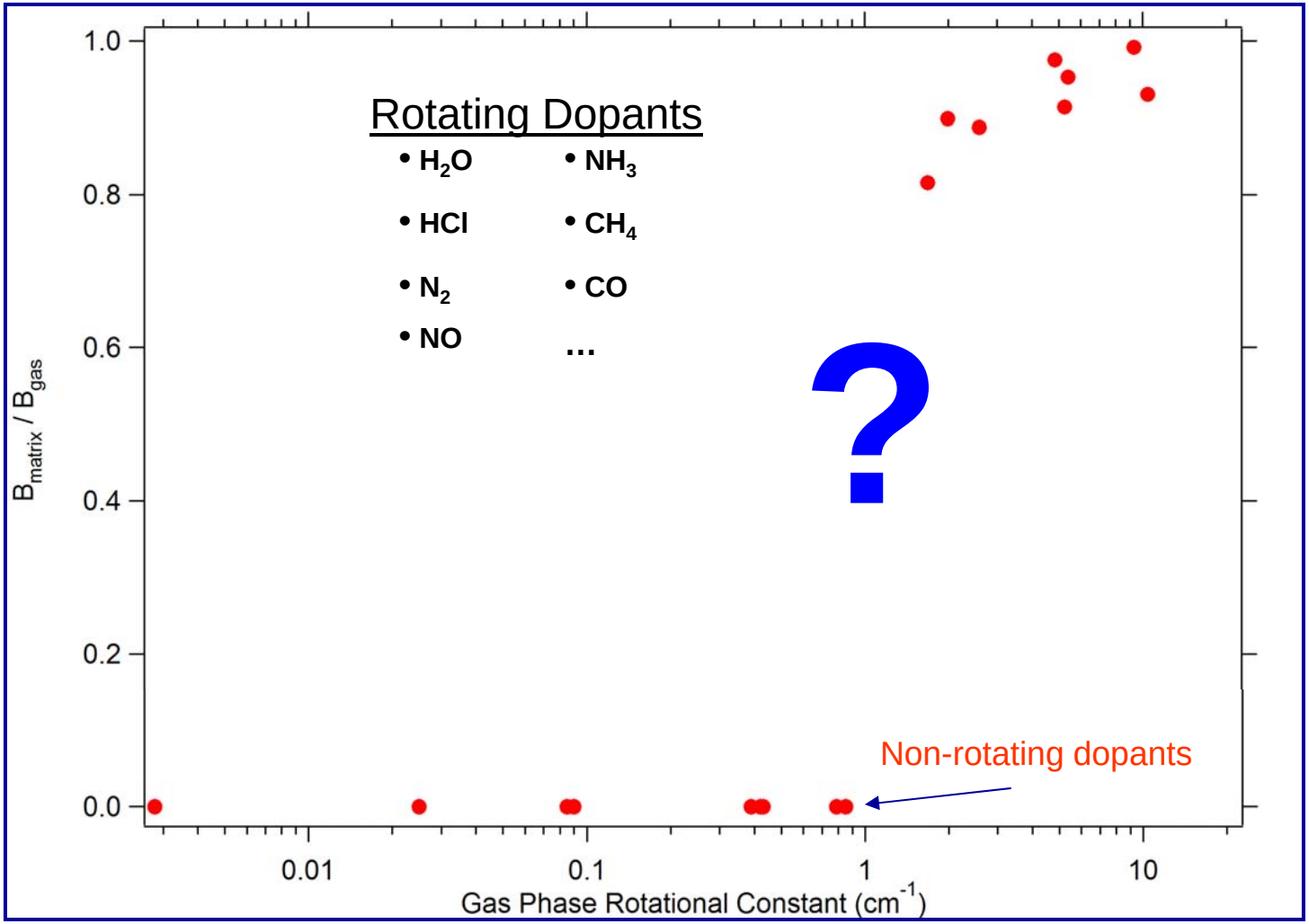
Rotation of Molecules in Solid Parahydrogen



Data from the groups of M. E. Fajardo, Y.-P. Lee, and T. Momose (1995-2006).

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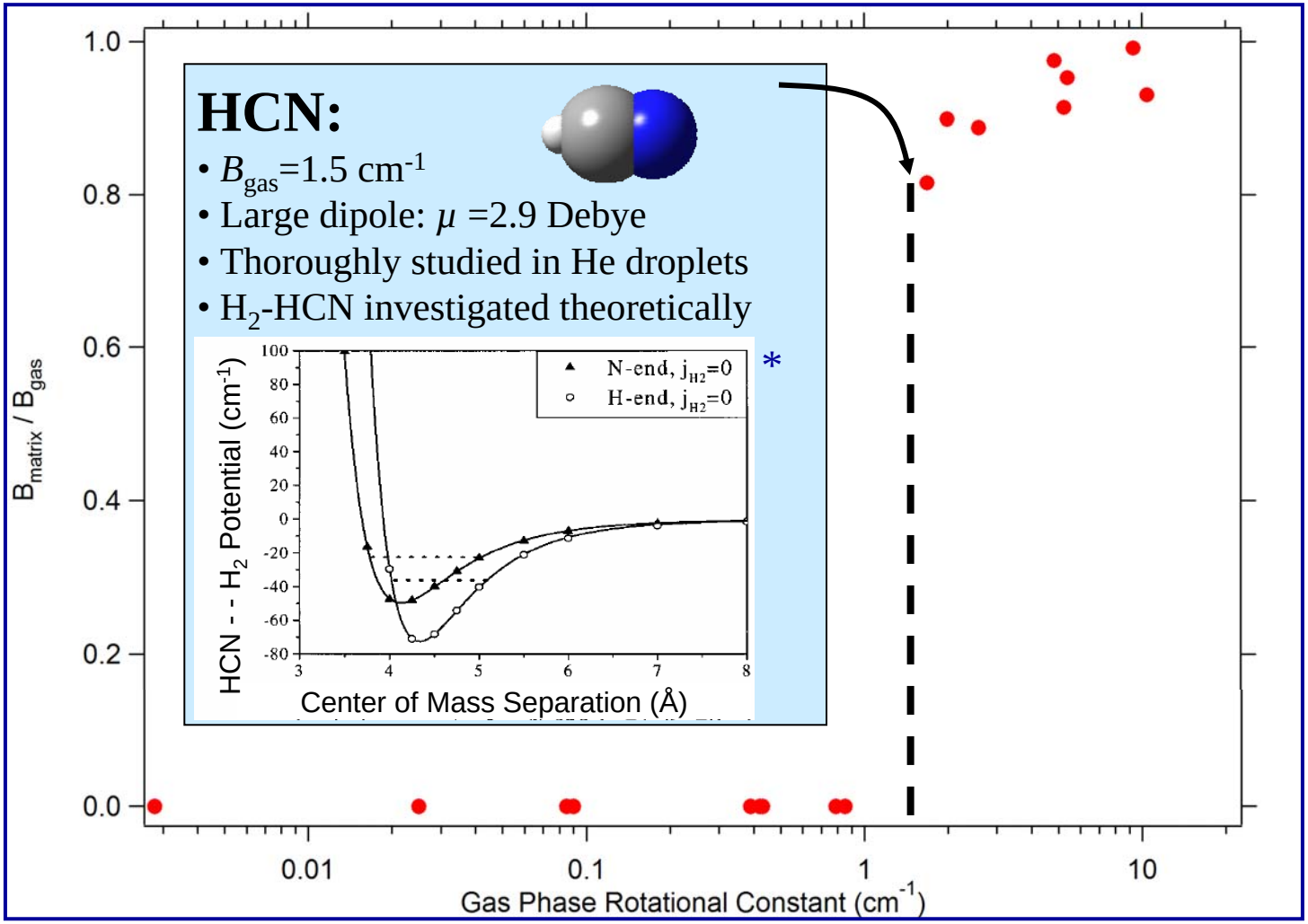
Why study HCN?



** D. T. Moore, M. Ishiguro, and R. E. Miller, JCP 115, 5144 (2001)*

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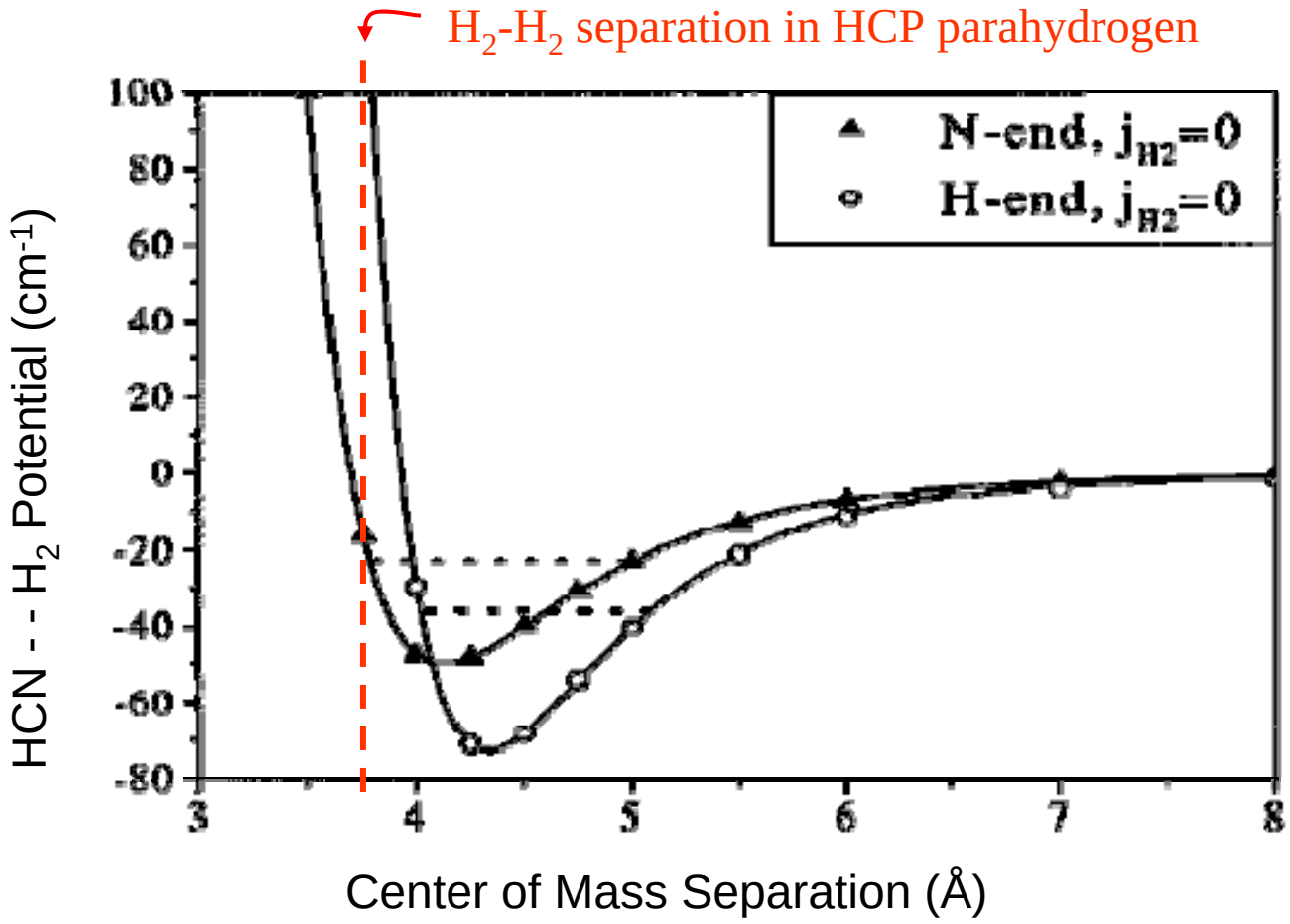
H_2-HCN Potential



If solid parahydrogen behaved classically, the HCN will not rotate…

CCSD(T)/aug-cc-pVTZ calculations D. T. Moore, M. Ishiguro, and R. E. Miller, JCP 115, 5144 (2001)

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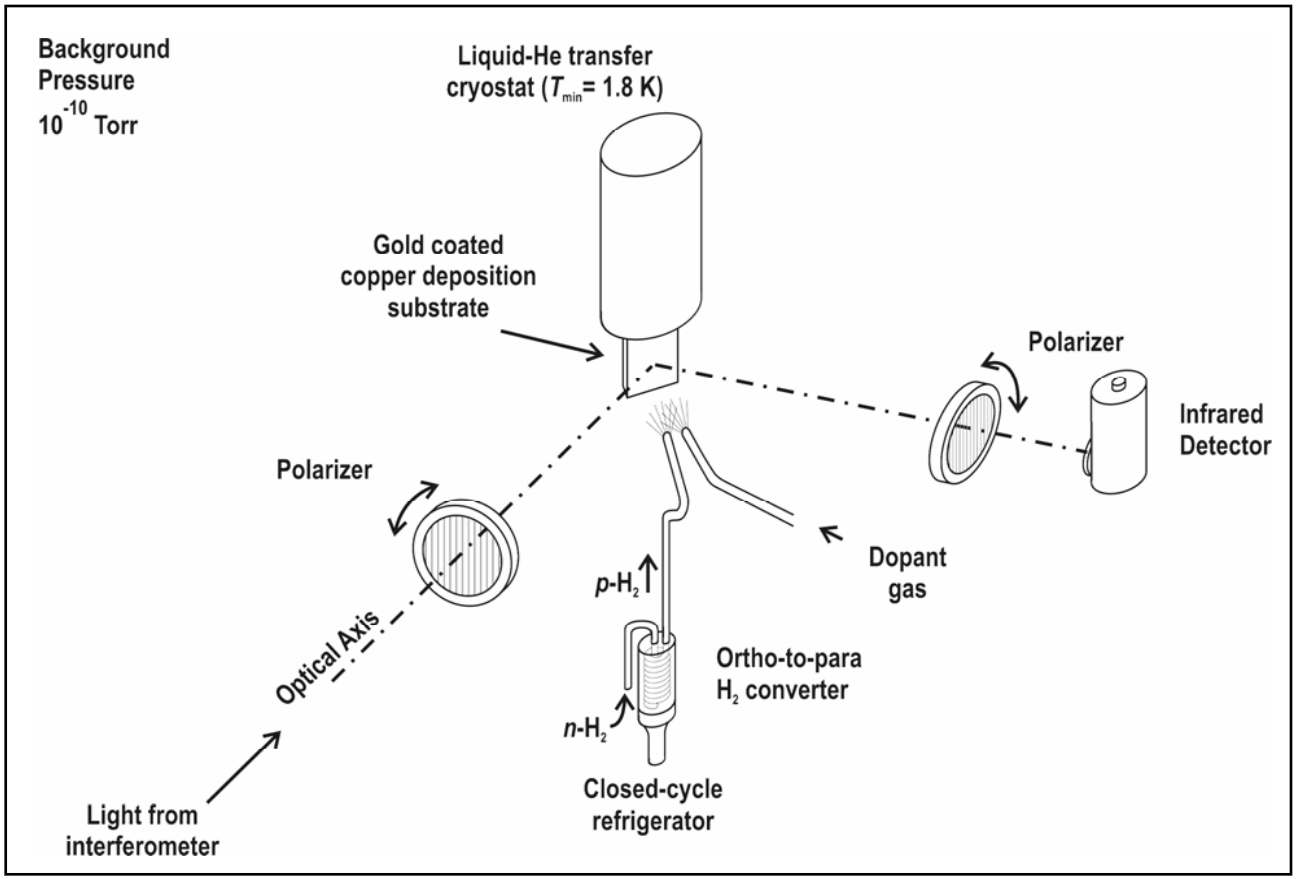
Rapid vapor deposition of *p*-H_2



- Reflection based set-up (FTIR)
- [*o*-H_2] < 100 ppm
- *p*-H_2 deposition rate ~150 mmol/hr → ~1 mm/hr thickness
- Deposition at 2.3 K. Sample annealed at 4.3 K for 30 min.

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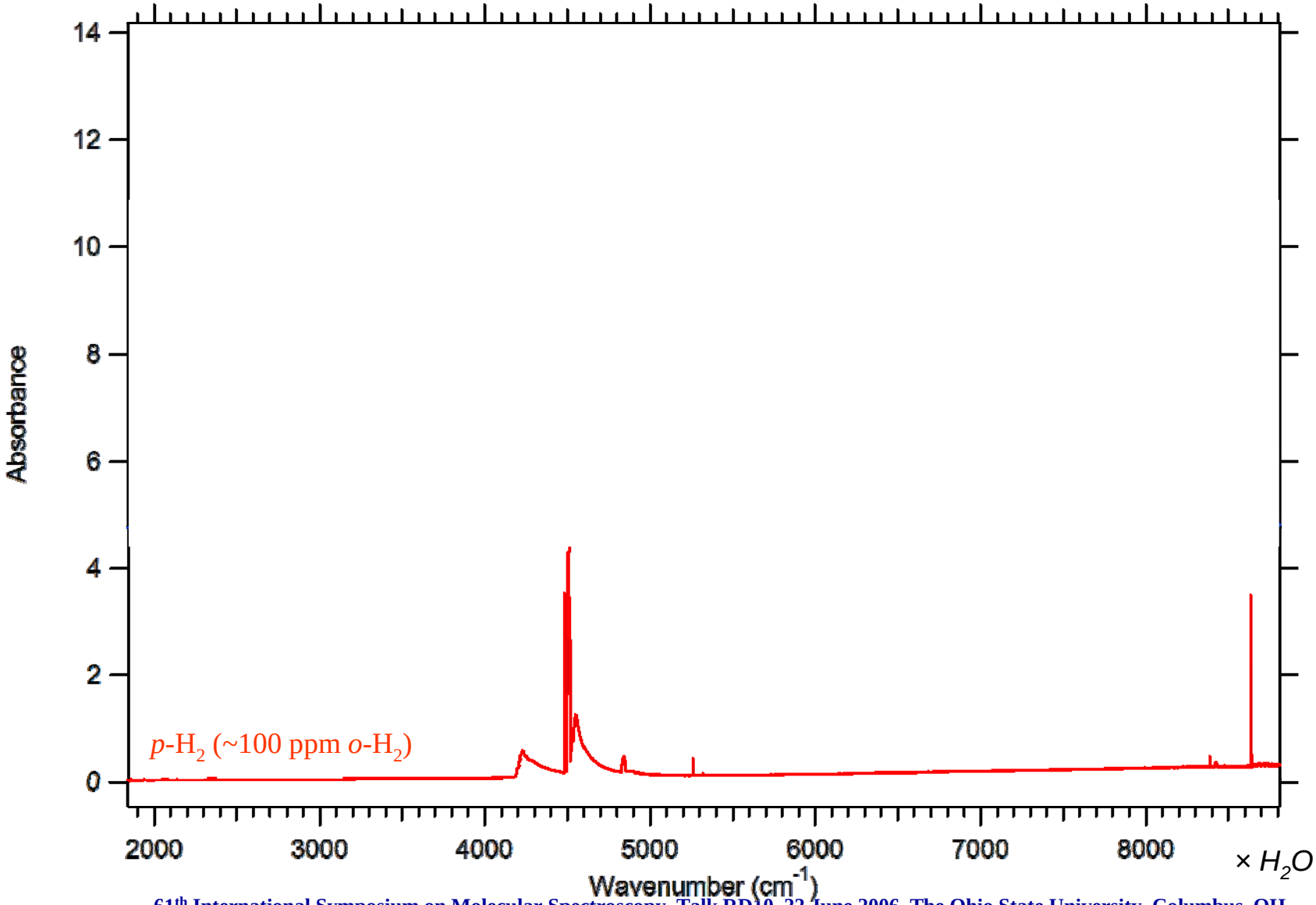
Spectrum of annealed solid *p*-H_2 with and without HCN



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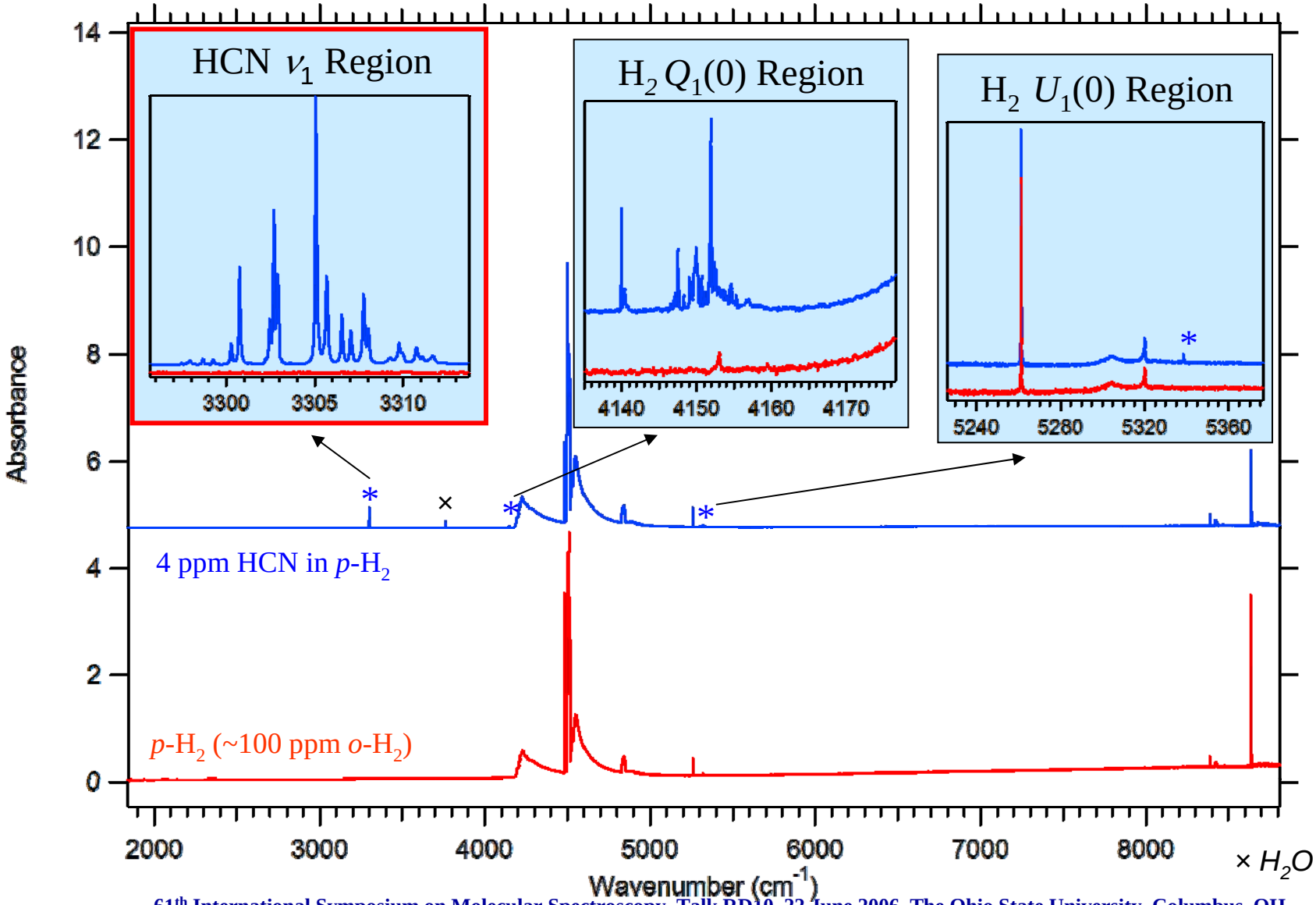

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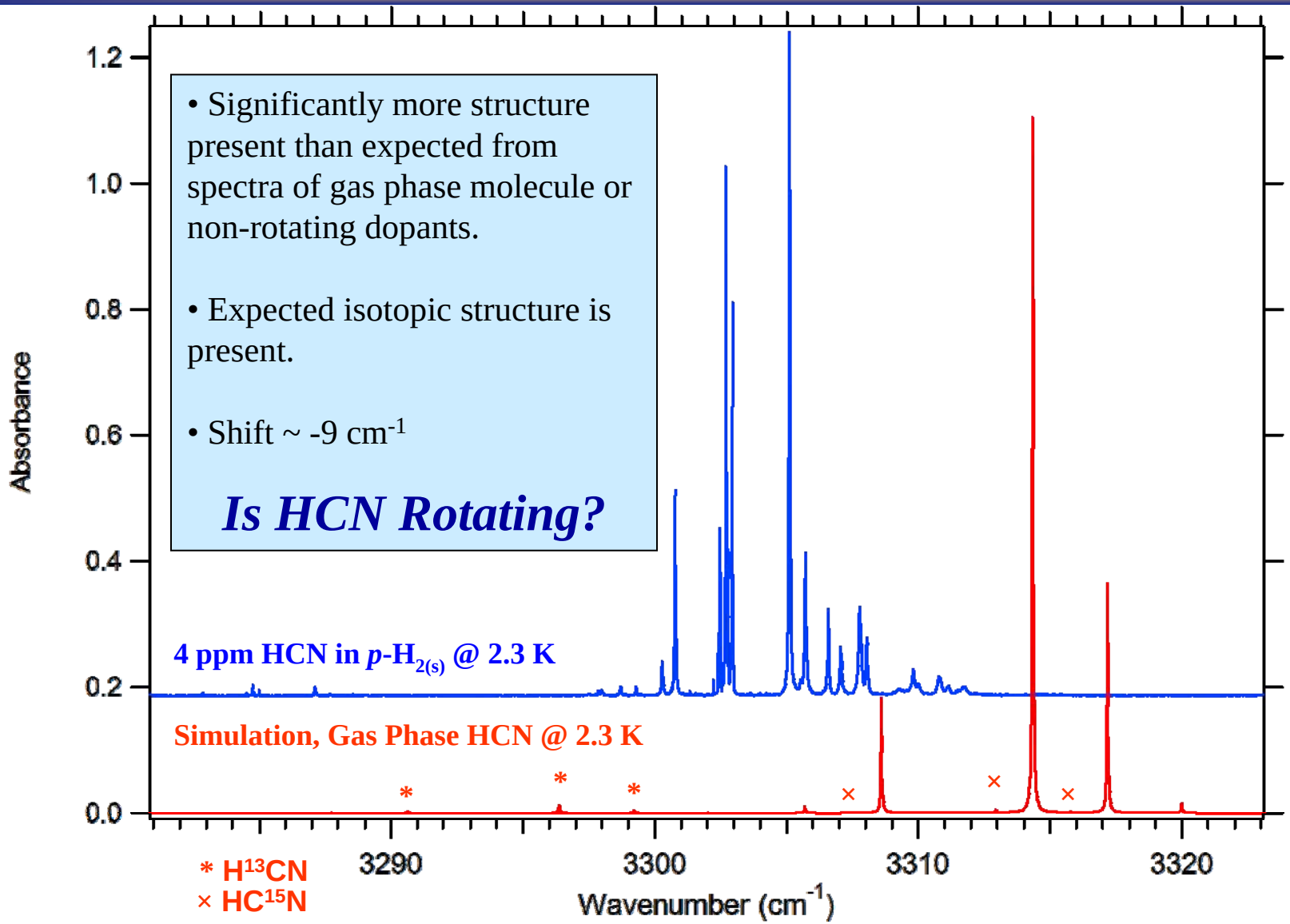
HCN ν_1 region



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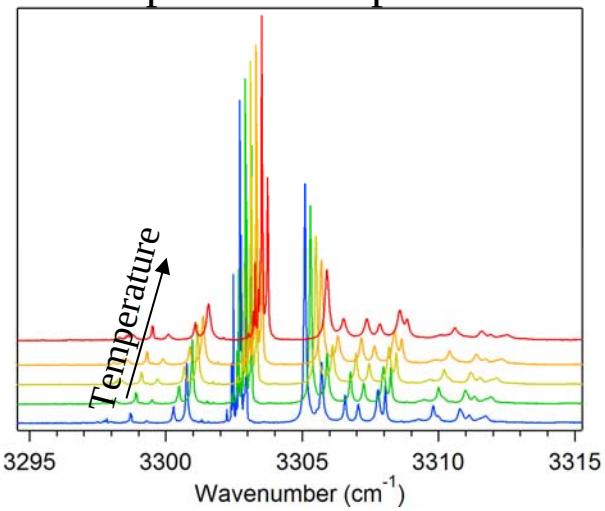
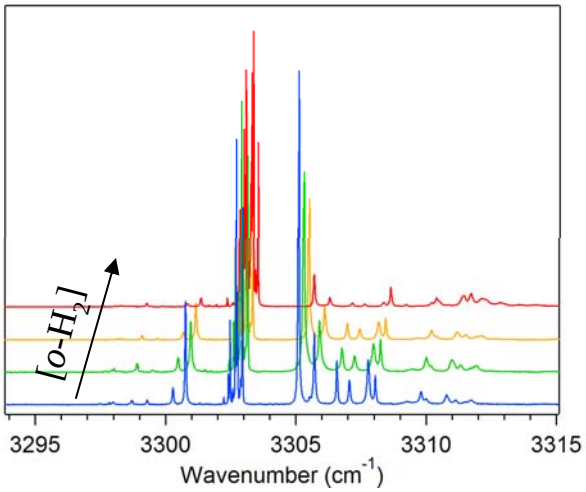
Assignment tools

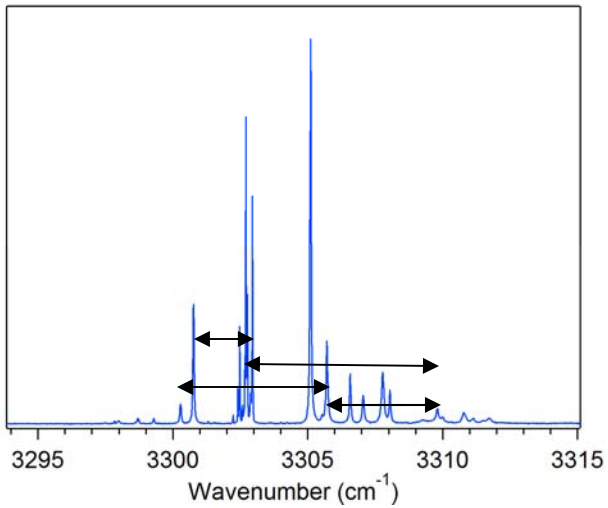
Temperature Dependence



Orthohydrogen Dependence



Combination Differences



Spectrum was interpreted by its:

- **Temperature dependence**
- **Orthohydrogen concentration dependence**
- **Transition frequency combination differences**
- **Polarization dependence!**

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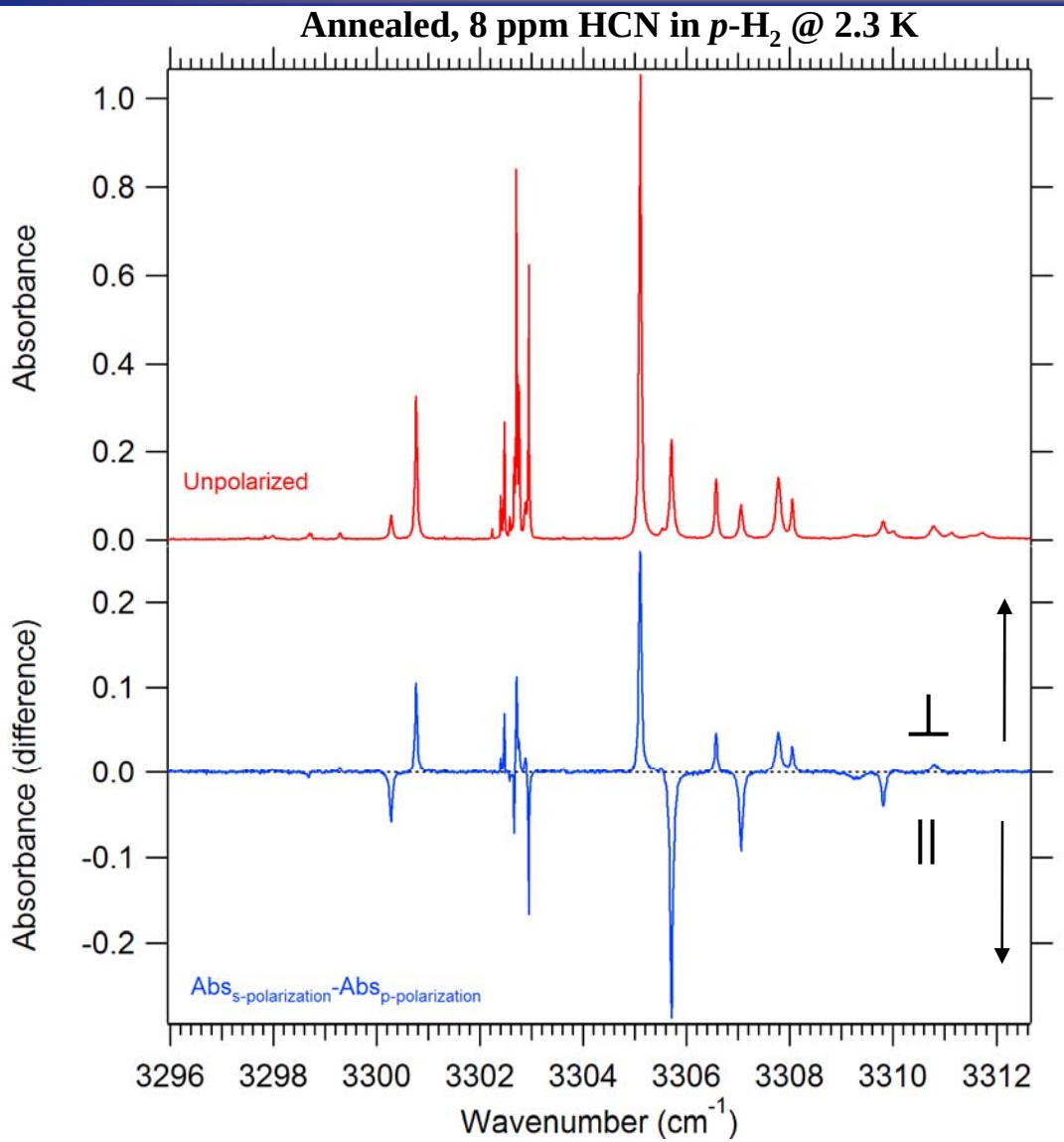
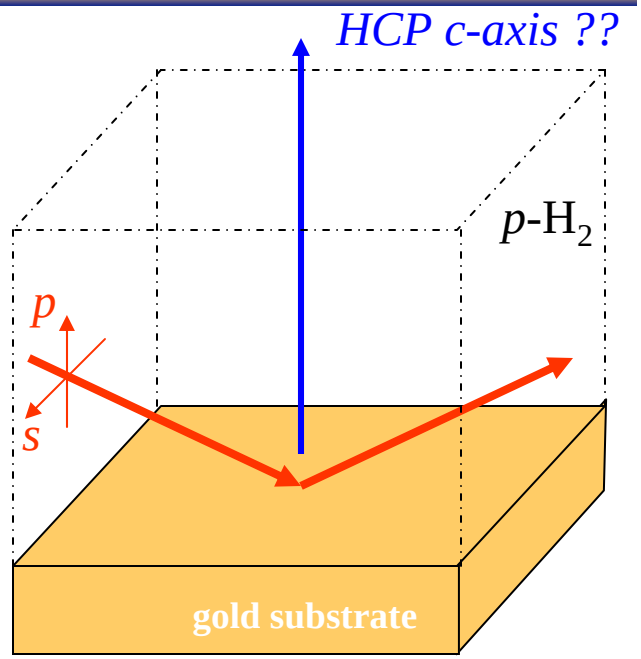
Polarization spectroscopy





Polarization analysis provides:

- **An assignment of the perpendicular and parallel components to the crystal field perturbed rotational structure (*i.e.* Δm)**
- **$Abs_{s\text{-}pol} - Abs_{p\text{-}pol} = \frac{1}{2}\mu^2_{\perp} - \frac{1}{2}\mu^2_{\parallel}$**
- **A measures of the fraction of HCP lattice with c-axis normal to substrate:**

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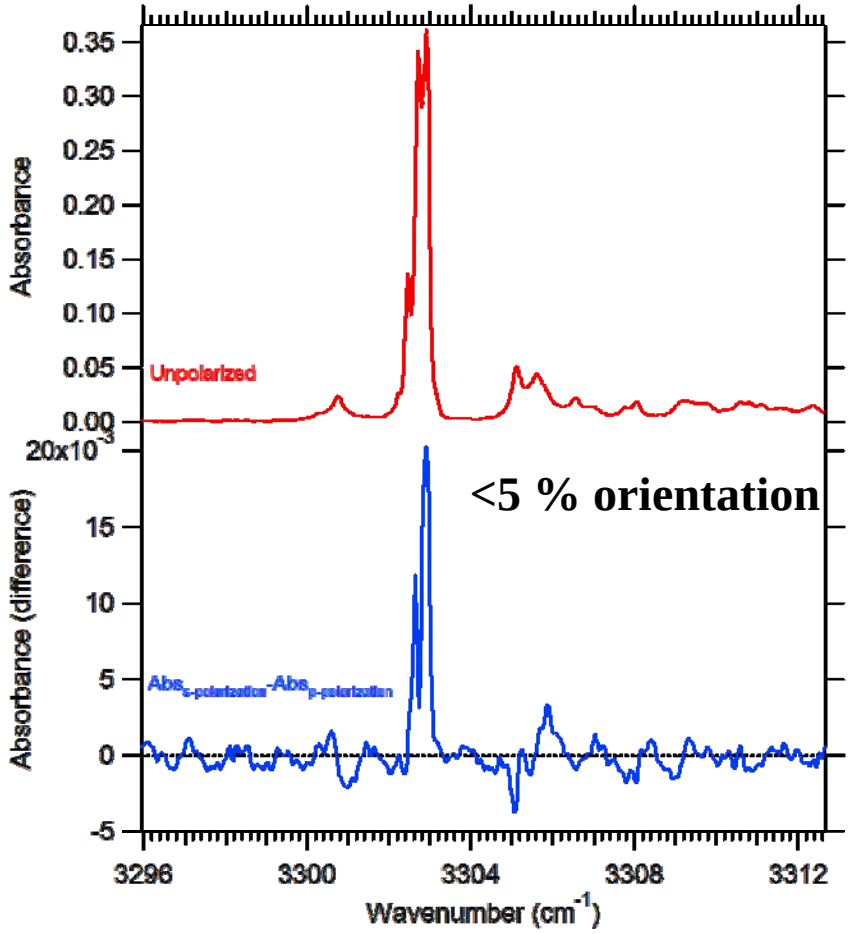
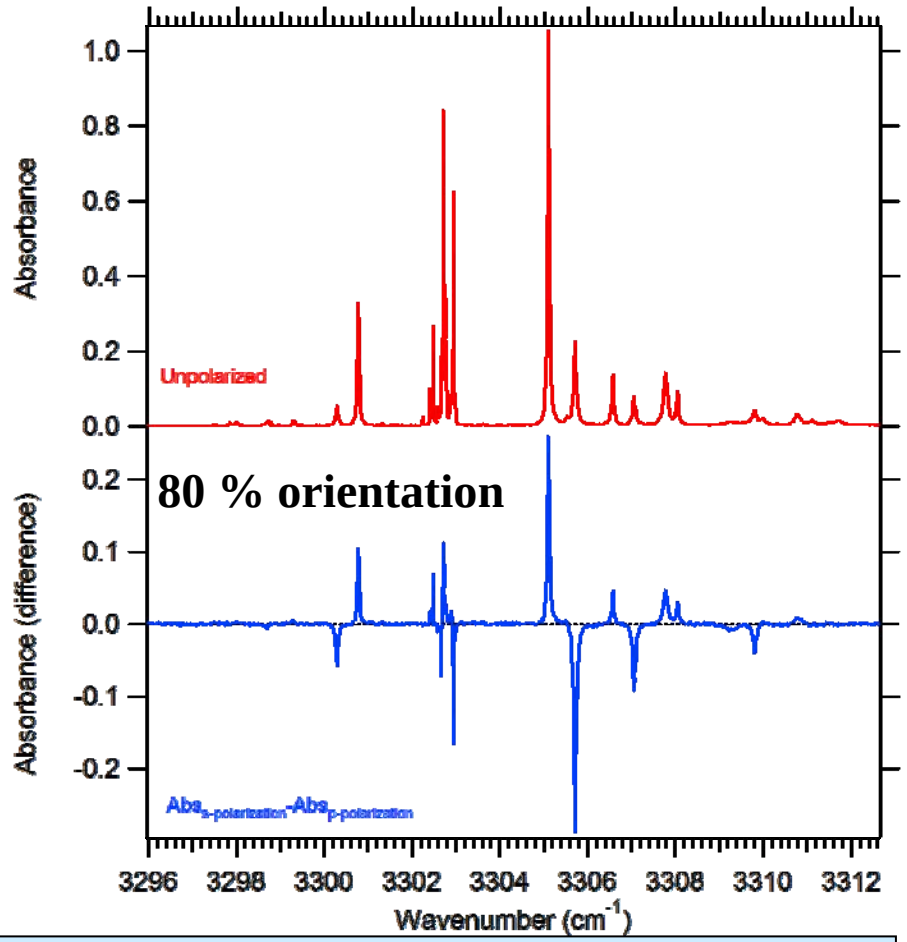
An aside… new insights into annealing mechanism in *p*-H_2

As-deposited, 8 ppm HCN in *p*-H_2 @ 2.3 K



Annealed, 8 ppm HCN in *p*-H_2 @ 2.3 K



- **Before annealing, less than 5% of the HCP features are oriented normal to the substrate.**
- ***After annealing*, ~80% of the HCP features are oriented normal to substrate!!**

  → Upon deposition, HCP lattices randomly oriented, but upon annealing gain a macroscopic orientation to the laboratory frame.

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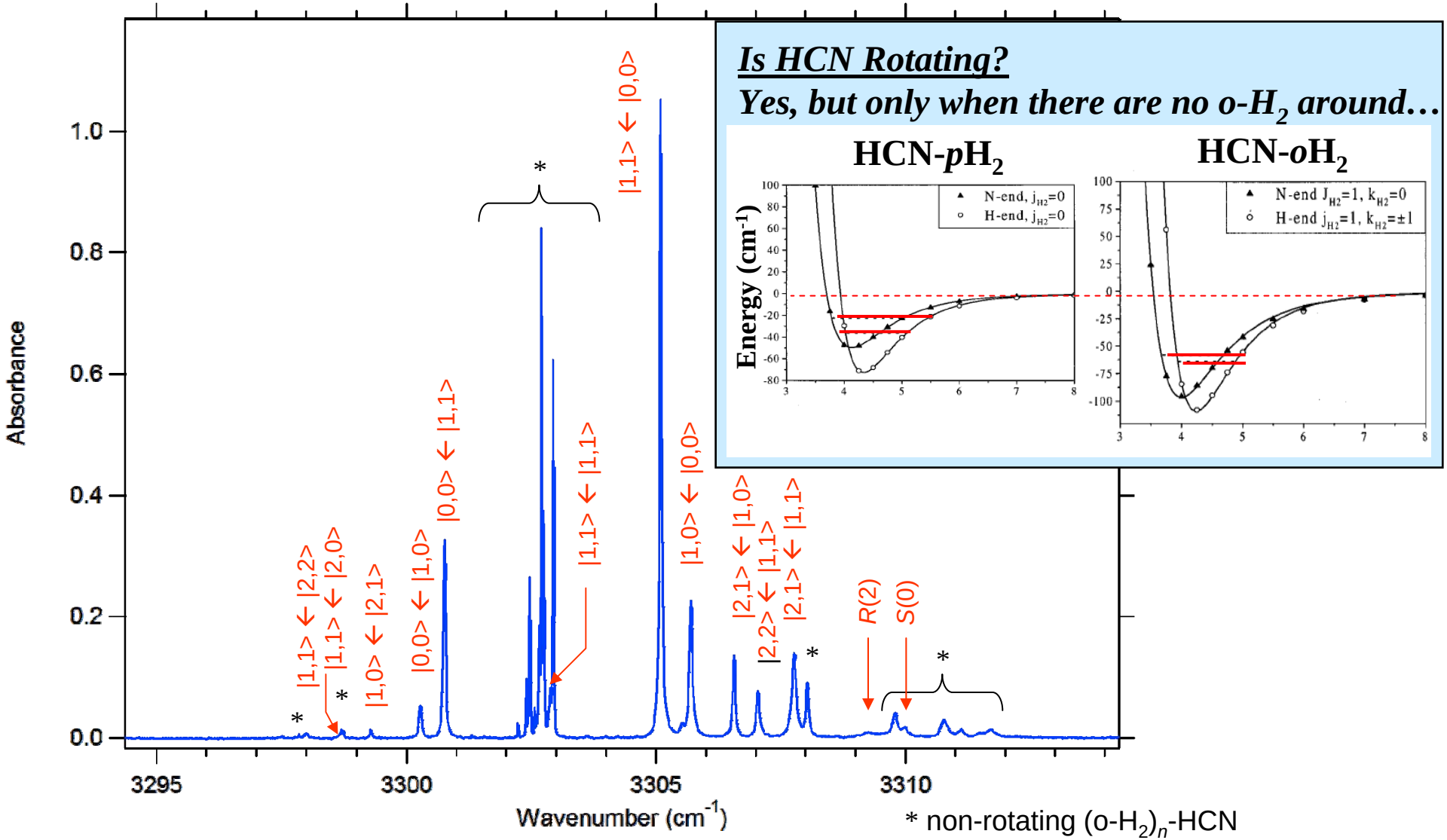
Interpretation of the fine structure



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Interpretation of the fine structure in the HCN ν_1 fundamental region

- All peaks assigned!
- Each transition fit to a Lorentzian profile. Standard deviation of the fit for the last digits is shown in parentheses.
- Polarization dependence was not as clear for the higher order clusters.

Species	|J',M'> ← |J",M">	Polarization	ν_0
HCN	|1,1> ← |2,2>	_|_	3297.989(5)
HCN	|1,1> ← |2,1>	||	3298.678(3)
HCN	|1,0> ← |2,1>	_|_	3299.285(10)
HCN	|0,0> ← |1,0>	||	3300.282(1)
HCN	|0,0> ← |1,1>	_|_	3300.764(1)
HCN	|1,1> ← |1,1>	_|_	3302.880(1)
HCN	|1,1> ← |0,0>	_|_	3305.105(1)
HCN	satellite	_|_	3305.530(2)
HCN	|1,0> ← |0,0>	||	3305.709(1)
HCN	|2,1> ← |1,0>	_|_	3306.572(1)
HCN	|2,1> ← |1,1>	||	3307.055(1)
HCN	|2,2> ← |1,1>	_|_	3307.778(1)
HCN	R(2)?	||	3309.328(16)
HCN	|2,2> ← |0,0>	_|_	3310.001(5)
HCN-oH2 (ip)	in-plane cluster	_|_	3302.708(1)
HCN-oH2 (op)	out-of-plane cluster	||	3302.946(1)
oH2-HCN (ip)	in-plane custer	_|_	3308.046(1)
oH2-HCN (op)	out-of-plane cluster	||	3309.803(1)
(oH2)n-HCN			3302.238(1)
(oH2)n-HCN			3302.405(1)
(oH2)n-HCN			3302.474(1)
(oH2)n-HCN			3302.579(1)
(oH2)n-HCN			3302.663(1)
(oH2)n-HCN			3302.760(1)
(oH2)n-HCN			3310.775(7)
(oH2)n-HCN			3310.859(25)
(oH2)n-HCN			3311.128(5)
(oH2)n-HCN			3311.479(12)
(oH2)n-HCN			3311.717(9)
(HCN)n			3297.771(11)
(HCN)n			3297.844(4)
(HCN)n			3298.697(4)
(HCN)n			3298.739(4)

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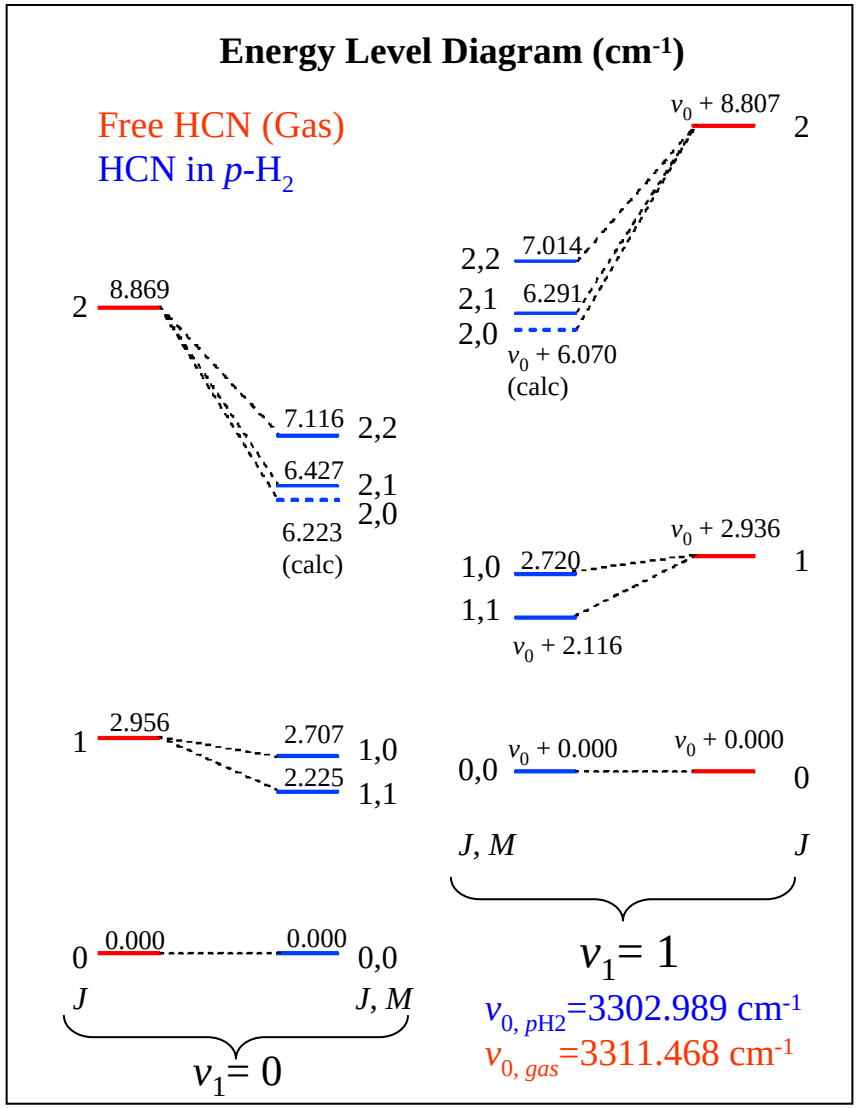
Interpretation of the fine structure



Crystal field theory (linear molecule in HCP lattice) *

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

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

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

"Fitting" Results: (10 levels, 9 parameters)

	p-H_2	Gas	
B	1.475(5)	1.478	Identical!
ΔB	-0.005(5)	-0.010	
D	0.0675(5)	2.910×10^{-6}	× 20,000!
ΔD	0.0032(5)	0.025×10^{-6}	
ν_0	3302.989(5)	3311.4770	
ε_2	-1.274(5)	-	very large!
$\Delta\varepsilon_2$	-0.193(5)	-	
ε_3	6.850(5)	-	
$\Delta\varepsilon_3$	0.767(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.

** Perturbation terms determined by T. Momose, unpublished.*

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Summary

- **AFRL matrix isolation spectroscopy lab back in business (after 5 years!)**
- **Polarization spectroscopy is helpful with reflection configuration**
  1) New insights into annealing process
  2) Powerful assignment tool
- **Despite size, and strong interaction, HCN does rotate in HCP *p*-H_2**
  1) Large crystal field perturbation (perturbation theory may not be appropriate)
  2) Large effective centrifugal distortion constant, (*D*), but *B* unchanged!
  3) Crystal field calculation does not converge properly when *D* is large
  4) Incorporating *D* after the crystal field calculation works well
  5) A single *o*-H_2 inhibits rotation of HCN
- **Other interesting features left out of the talk…**
  1) Rotational excitation lifetime is sensitive to HCN concentration
  2) Strong induced IR activity in H_2 fundamental region
  3) HCN cluster formation

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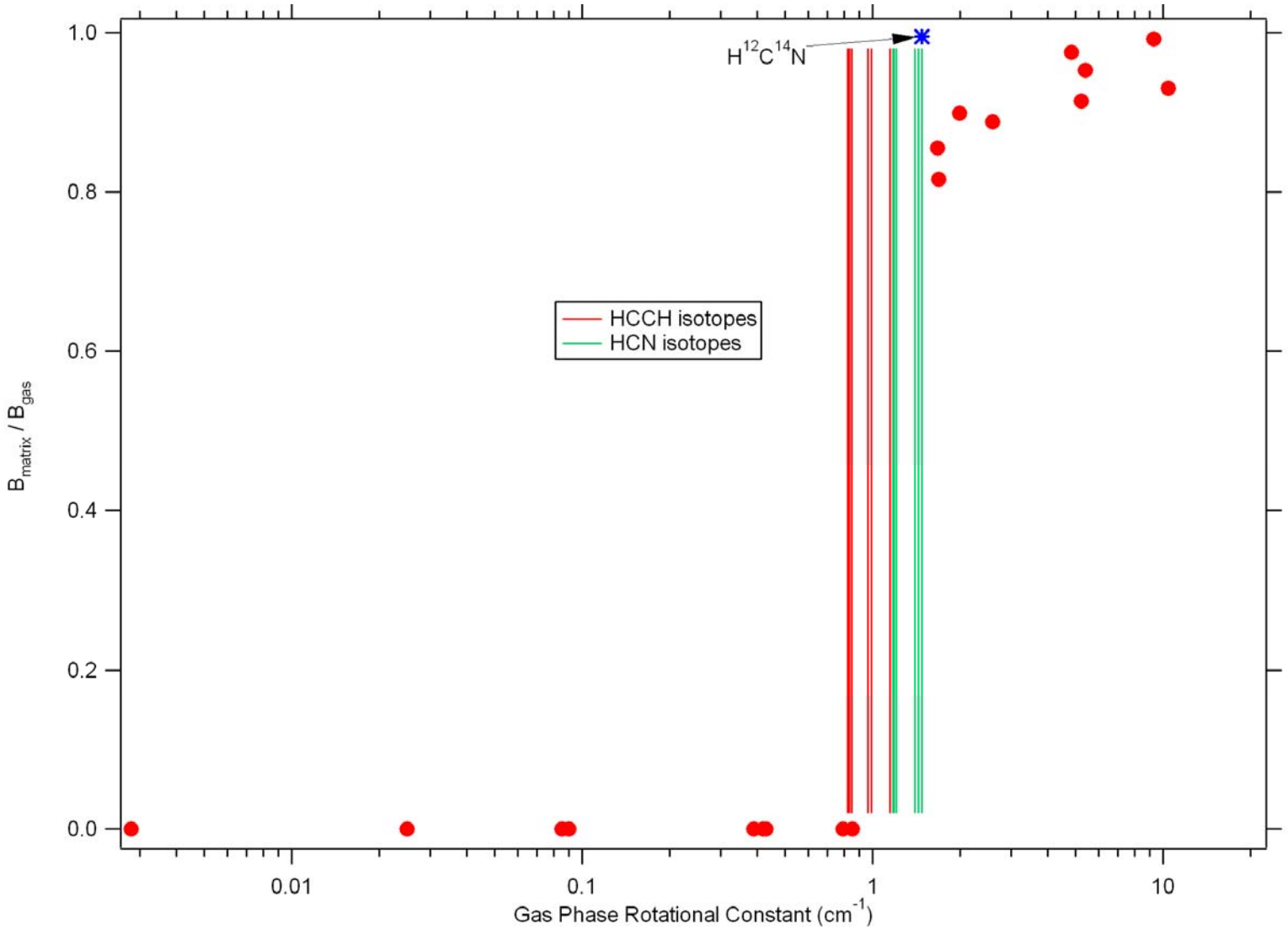
Molecular rotation in solid *p*-H_2… What should be next



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