

Probing a Quantum Solid with Deuterated Acetylene

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Parahydrogen: A Unique Quantum Solid

What is a quantum solid?

A quantum solid consists of a highly ordered array of particles that undergo intrinsic large amplitude zero-point lattice vibrations, even at absolute zero – as prescribed by Heisenberg's uncertainty principle – where emphasis on low particle mass and weak nearest neighbor interactions is important. Supersolid He (well-known for superfluidity at $T_\lambda = 2.17$ K) and solid H_2 , whose additional vibrational and rotational degrees of freedom add to the complexity of the simplest, yet most fundamental molecular crystal, are the only two quantum crystalline species known to exist in nature.

Solid Molecular Hydrogen

Statistical Weighting of Quantum States

❖ Pauli Symmetrization postulate – with respect to nuclear exchange:

$$\Psi_{total} = \psi_{vibronic} \times \psi_{rot}(J) \times \psi_{ns}(I) = \begin{cases} \text{symmetric} : \text{boson} \\ \text{asymmetric} : \text{fermion} \end{cases}$$

- Bosons and fermions take on integer and half-integer spins, respectively.
- Focus on nuclear spin component, $\psi_{ns} = \psi_{I,m_I}$

$$\hat{I}^2 \cdot \psi_{I,m_I} = I(I+1)\hbar^2 \cdot \psi_{I,m_I}; |\hat{I}| = \{I(I+1)\}^{1/2}\hbar$$

$$\hat{I}_z \cdot \psi_{I,m_I} = m_I \hbar \cdot \psi_{I,m_I}; m_I = I, I-1, \dots, -I; \text{multiplicity} = 2I+1$$

❖ Nuclear spin analysis of $H_2 = H(1)-H(2)$

$$\Psi_{H_2} = \text{asymmetric}; {}^1H(I = 1/2) = \text{fermion}$$

$$I = 1 : \text{multiplicity} = 3$$

$$\psi_{1,m_1} = \text{symmetric} = \begin{cases} \alpha(1)\alpha(2); \text{spin up}, & +1 \\ \{\alpha(1)\beta(2) + \beta(1)\alpha(2)\}/\sqrt{2}, & 0 \\ \beta(1)\beta(2); \text{spin down}, & -1 \end{cases}$$

$$\Psi_{H_2} = \text{even} \times (\text{odd } J) \times \text{even} = \text{odd} \Rightarrow \text{ortho-}H_2(oH_2)$$

$$I = 0 : \text{multiplicity} = 1$$

$$\psi_{0,m_0} = \text{asymmetric} = \{\alpha(1)\beta(2) - \beta(1)\alpha(2)\}/\sqrt{2}, \quad 0$$

$$\Psi_{H_2} = \text{even} \times (\text{even } J) \times \text{odd} = \text{odd} \Rightarrow \text{para-}H_2(pH_2)$$

❖ “Normal” H_2 : statistical 3:1 *ortho/para*- H_2 admixture

- Natural 3:1 ratio of *odd:even* J rotational states
- Slow *ortho*→*para*- H_2 nuclear spin conversion via thermal relaxation

Physical and Quantum Properties of Solid Parahydrogen

❖ Hexagonal close packed crystal structure ($T_{\text{fusion}} = 14.01$ K)

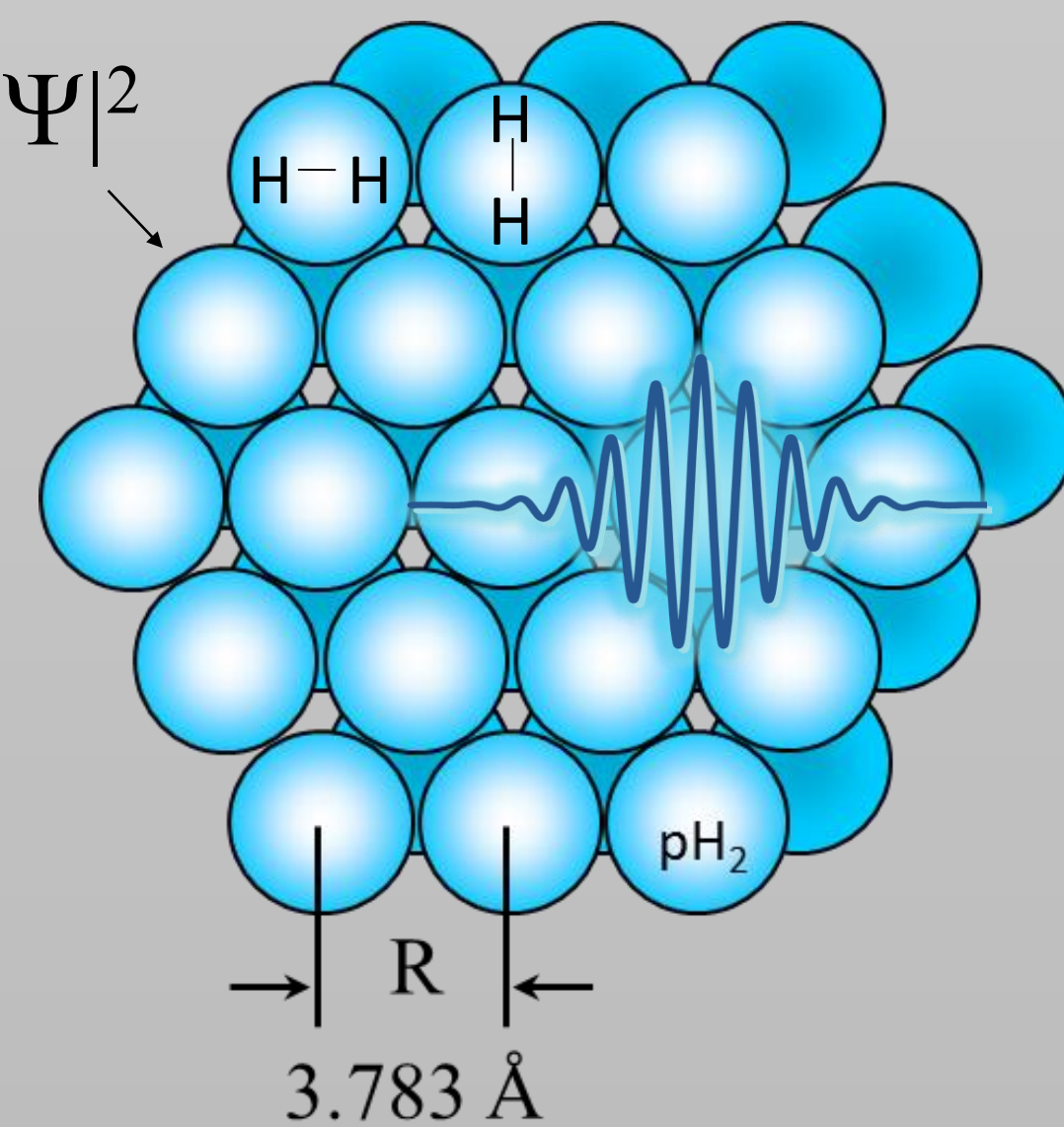
- Weakly bound by $pH_2 - pH_2$ dispersion interactions
- Homonuclear H_2 does not exhibit IR activity in gaseous phase...

❖ Preservation of coherent quantum states

- pH_2 ($v = J = I = 0$) is spherically symmetric and spatially isotropic
- oH_2 ($J = I = 1$) impurities rotate freely¹ & undergo rotational diffusion²

❖ Delocalization of pH_2 wavefunction < 4.5 K

- Weak $pH_2 - pH_2$ potential and light mass
- RMS $|\Psi|^2$ width $\sim 0.18 \cdot R = 0.68$ Å
- de Broglie wavelength $\lambda = 11$ Å (> R) at 4 K
- ⇒ Translational quantum solid!



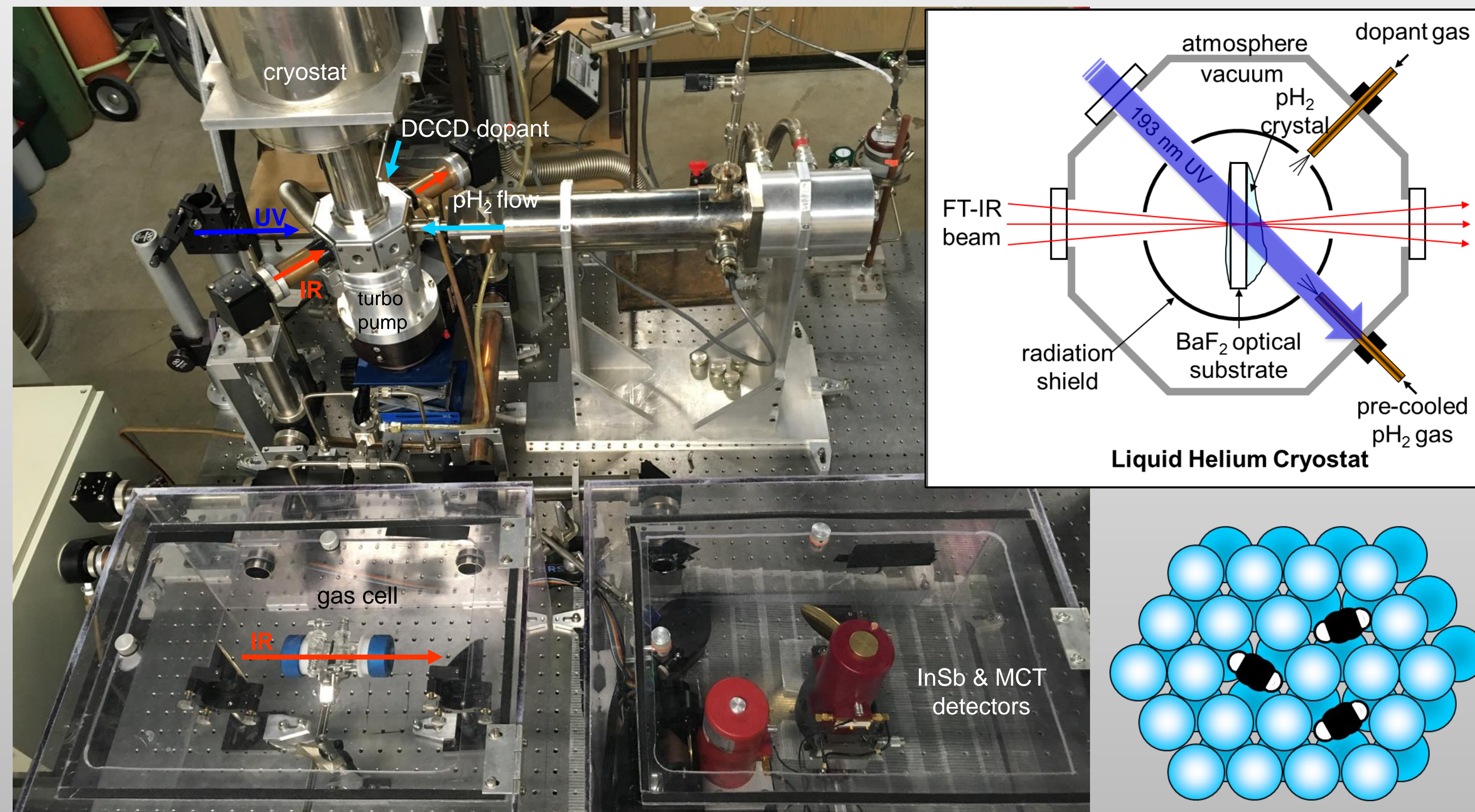
❖ Ideal host matrix³

- “Soft” and nearly nonperturbing environment
- Probe pH_2 -dopant interactions and solvation

❖ Quasiparticle interactions

- Excitons, rotons, phonons and vibrons

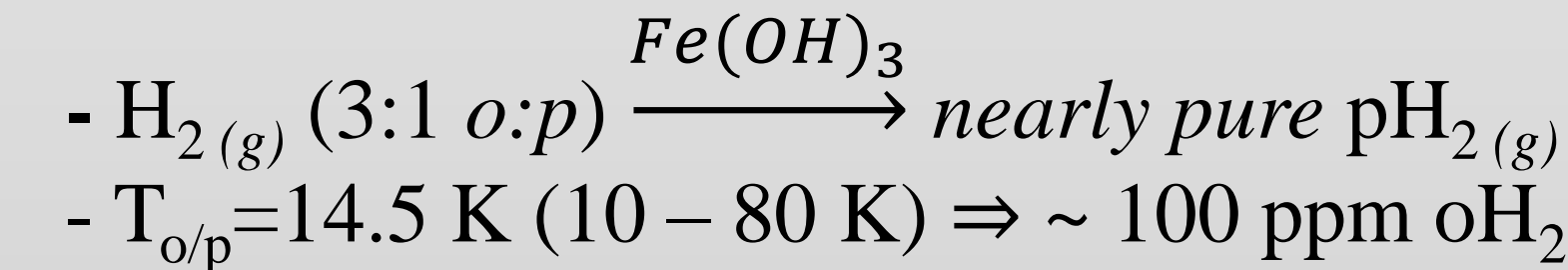
Fourier Transform Infrared Absorption Spectroscopy of Deuterated Acetylene



Matrix Isolation Experiments

- ❖ Sample-in-a-vacuum liquid helium-bath cryostat
 - 1.7 – 5.0 K (pre-cool w/ liq. N_2 to 77 K)
 - Helium recovery system under construction

❖ Variable temperature catalytic converter



❖ Rapid vapor co-deposition of doped pH_2 host < 2.5 K

- Contains 24 ± 1 ppm DCCD
- Crystal thickness: 1.61 ± 0.08 mm
- Thermal annealing at 4.3 K

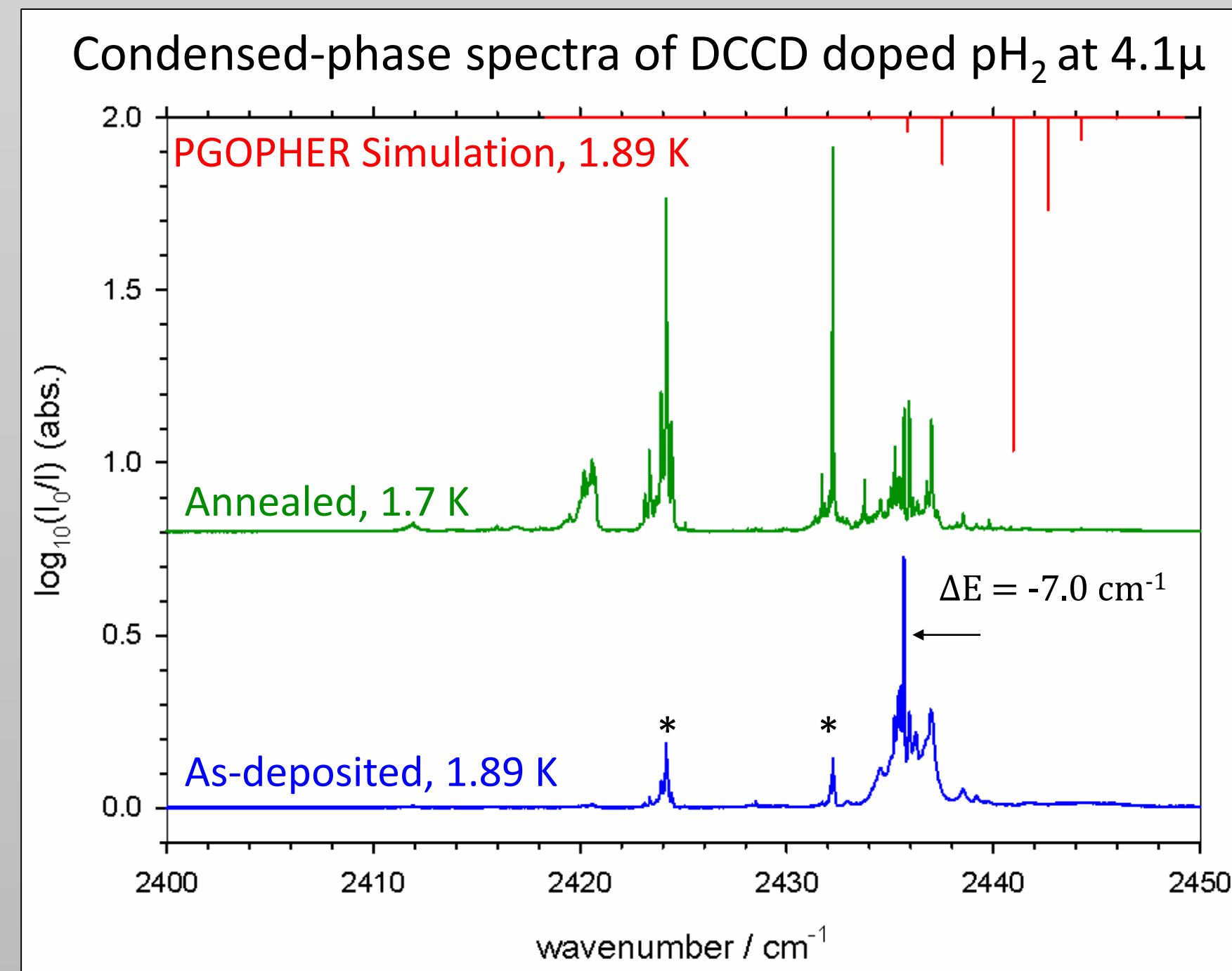
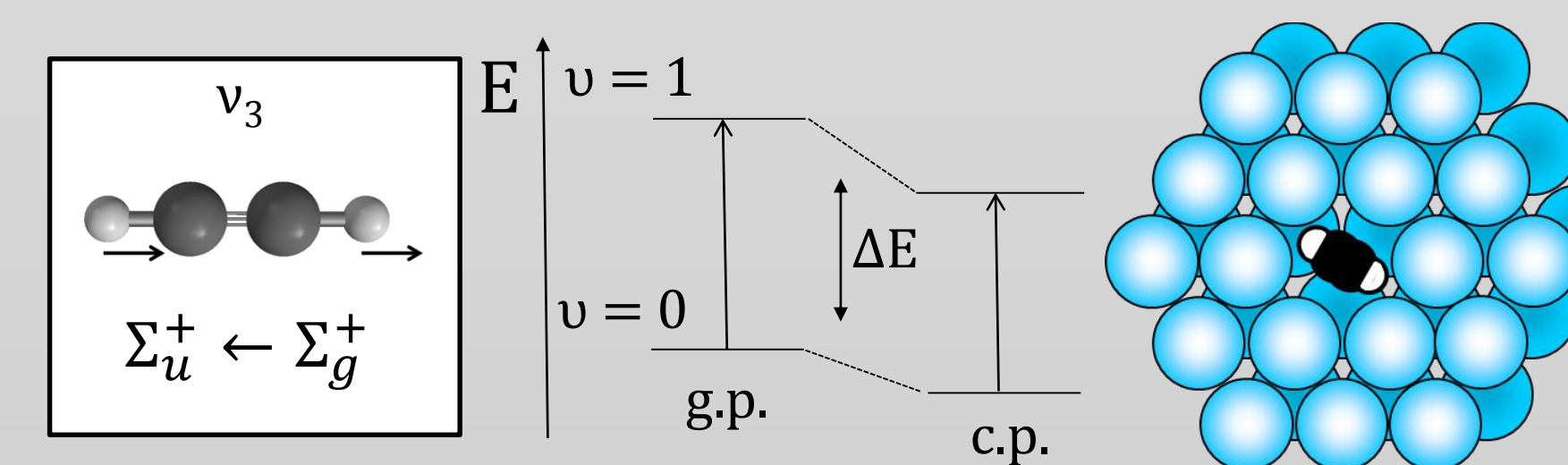
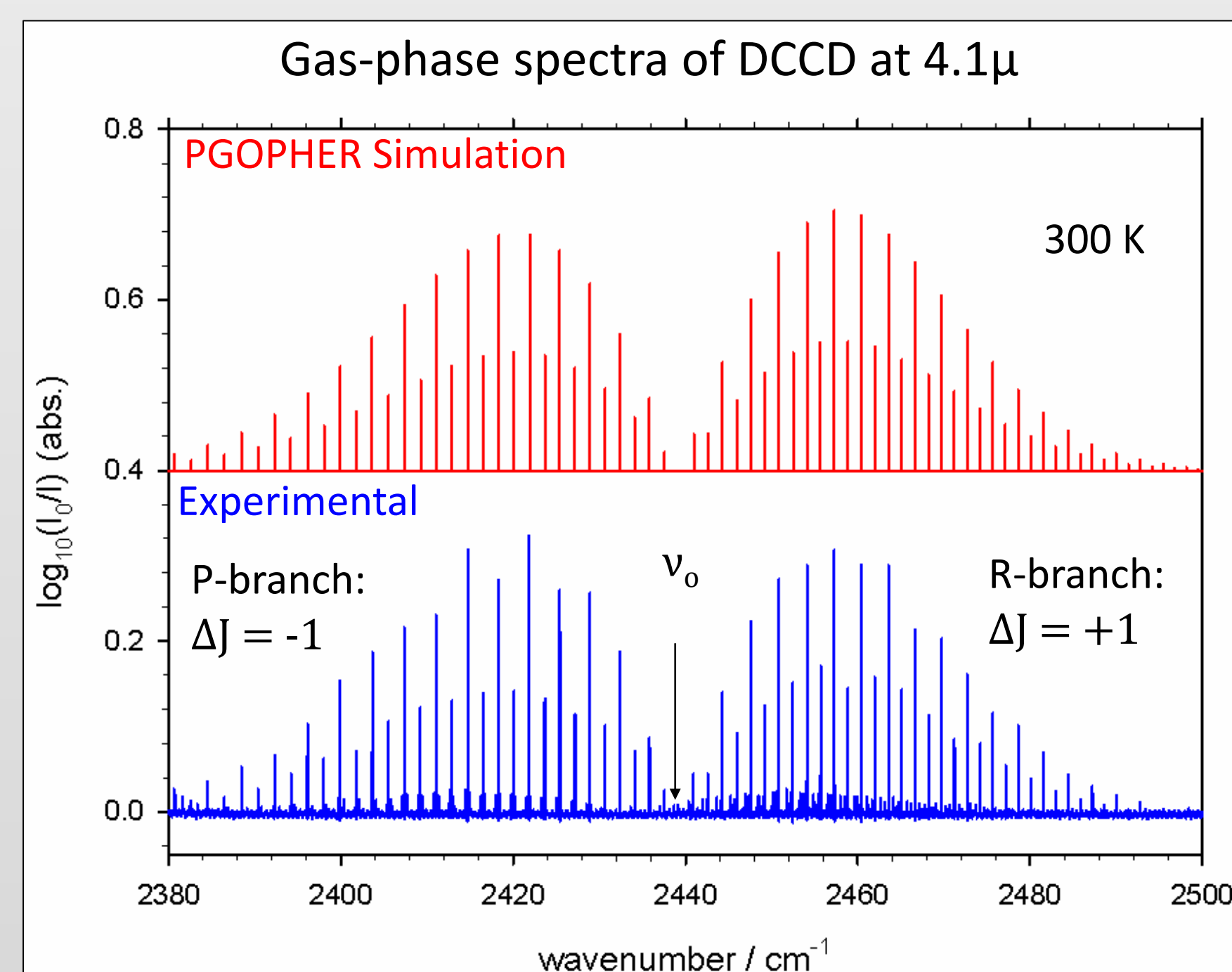
Gas-phase Control Experiments

- ❖ Single-pass gas cell, $l = 10$ cm
- Low pressure, RT sample: $p_{DCCD} \sim 0.1$ Torr

FTIR Diagnostics (MIR)

- ❖ Bruker IFS120 Spectrometer (0.01 cm^{-1} resolution)

Molecular Rovibrational Dynamics in Parahydrogen: “Does DCCD Rotate?”



Gas-phase Analysis

❖ Assignment of DCCD R & P-branch rovibrational transitions of the v_3 asymmetric stretch region at 4.1μ

❖ Fit data with rigid rotor Hamiltonian eigenenergies

$$\hat{H}\Psi = E\Psi$$

$$E(J' \leftarrow J'') = \nu_0 + B'J'(J' + 1) - D'(J'(J' + 1))^2 - \{B''J''(J'' + 1) - D''(J''(J'' + 1))^2\}$$

State:	Ground	Excited
$v_1 v_2 v_3 v_4^l v_5^l$	0000 ⁰ 0	0010 ⁰ 0
Vibrational Origin: ν_0	-	2439.24191(7)
Rotational Constants: B'', B'	0.847868(2)	0.843368(2)
Centrifugal Distortion Constants: D'', D'	$7.984(8) \times 10^{-7}$	$7.932(8) \times 10^{-7}$
$\Sigma S / \text{ppm}$		9.379

❖ Nuclear spin analysis of $^{12}C_2D_2 \rightleftharpoons D_2(I(^{12}C) = 0)$

$$\Psi_{D_2} = \text{symmetric}; D = {}^2H(I = 1) = \text{boson}$$

$$I = 2, 0 : \text{multiplicity} = 5 + 1 = 6$$

$$\Rightarrow \text{ortho-DCCD: even } I, J$$

$$I = 1 : \text{multiplicity} = 3$$

$$\Rightarrow \text{para-DCCD: odd } I, J$$

Expect 6:3 weighting of symmetric:asymmetric states!

Condensed-phase Analysis

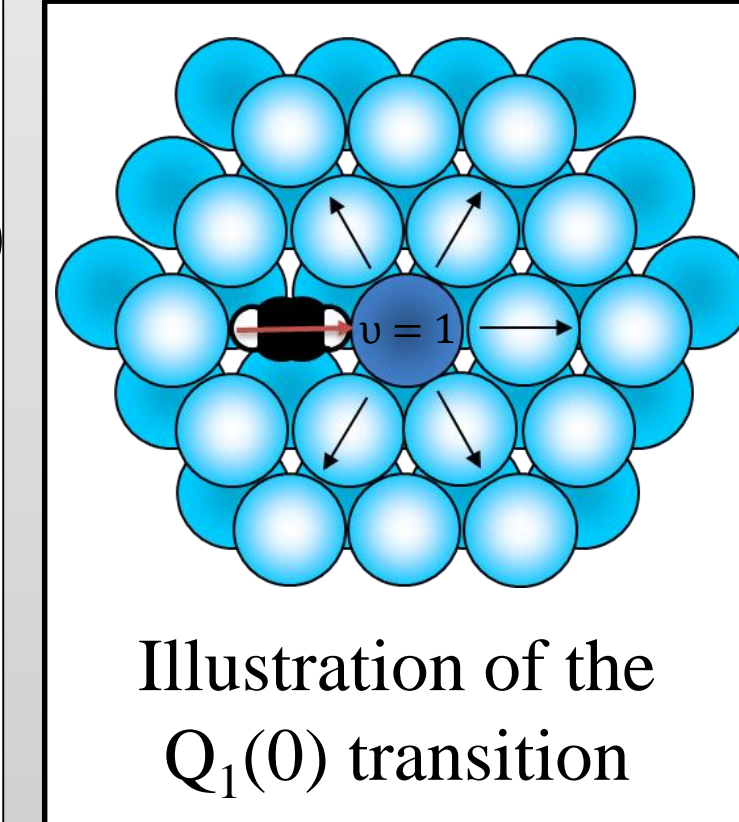
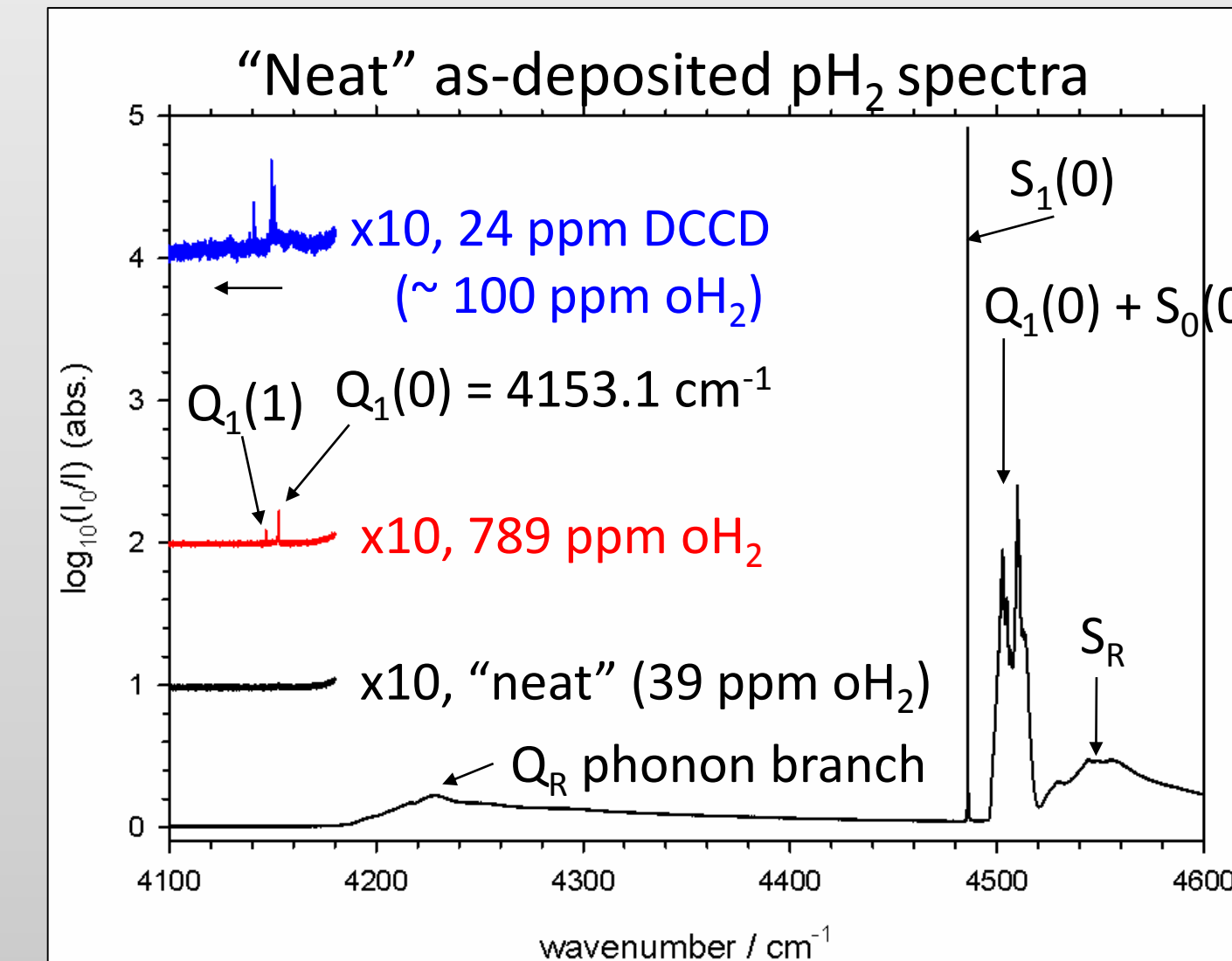
❖ Simulate spectra with PGOPHER: RT → < 4 K

- ❖ Observe collapse of v_3 rovibrational band & red shift
 - Spectra lack rotational structure; NS weighting absent
 - Sharp peaks indicative of long lifetime
 - Inhomogeneous broadening of states

❖ Irreversible conglomeration upon thermal annealing (*)

- Dimer, trimers and larger clusters likely formed

Induced FTIR Spectrum of Parahydrogen



❖ Impurity induced pure vibrational $Q_1(0)$ transition of pH_2 shifted, or perturbed by DCCD dopant

- Sharp lineshape may indicate localized vibron⁴ about 12 nm pH_2 molecules near DCCD trapping site (top of poster)

Conclusions

❖ The DCCD probe does not exhibit rigid rotor behavior within solid pH_2 trapping sites and cluster species are formed post thermal annealing of the sample.

❖ Spectral changes in the DCCD dopant and induced pH_2 spectra unveil valuable information on dopant-host interactions and perturbations, and the physics of solvation in a quantum solid at the microscopic scale.

References

- 1) L. Pauling, “The Rotational Motion of Molecules in Crystals,” *Physical Review* **36**, 430 (1930).
- 2) A.E. Meyerovich, “Quantum diffusion and pairing of *ortho*- H_2 impurities in *para*- H_2 ,” *Physical Review B* **42**, 6068 (1990).
- 3) R.J. Hinde, D.T. Anderson, S. Tam, M.E. Fajardo, “Probing quantum solvation with infrared spectroscopy: infrared activity induced in solid parahydrogen by N_2 and Ar dopants,” *Chemical Physics Letters* **356**, 355 (2002).
- 4) R.J. Hinde, “Infrared-active vibron bands associated with substitutional impurities in solid parahydrogen,” *The Journal of Chemical Physics* **119**, 6 (2003).