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MEMORANDUM FOR PR (In-House Publication)

FROM: PROI (TI) (STINFO)

30 Jun 2000

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-TP-2000-144
M. Fajardo, S. Tam, "High Resolution Infrared Absorption Spectroscopy in Doped Parahydrogen Solids: CO/pH₂ - a Molecular Thermometer"

3rd International Conference on Cryocrystals and Quantum Crystals (Statement A)
(Szklarska Poreba, Poland, 28 Jul - 04 Aug 00) (Submission Deadline: 28 Jul 00)

1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.

Comments: _____

Signature _____ Date _____

2. This request has been reviewed by the Public Affairs Office for: a.) appropriateness for public release and/or b) possible higher headquarters review.

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Comments: _____

Signature _____ Date _____

4. This request has been reviewed by PR for: a.) technical accuracy, b.) appropriateness for audience, c.) appropriateness of distribution statement, d.) technical sensitivity and economic sensitivity, e.) military/national critical technology, and f.) data rights and patentability

Comments: _____

APPROVED/APPROVED AS AMENDED/DISAPPROVED

LESLIE S. PERKINS, Ph.D (Date)
Staff Scientist
Propulsion Directorate

High Resolution Infrared Absorption Spectroscopy in Doped Parahydrogen Solids: CO/pH₂ -- a Molecular Thermometer

20021121 013

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- * HEDM Cryosolid Propellants
- * Trapping of Metal Atoms in Cryogenic Solid Hydrogen
- * Rapid Vapor Deposition of Transparent Parahydrogen (pH₂) Solids
- * High Resolution IR Absorption Spectroscopy in Doped pH₂ Solids
- * CO/pH₂ "Thermometer" Depositions
- * Summary

DISTRIBUTION STATEMENT A
Approved for Public Release
Distribution Unlimited

HEDM Cryosolid Propellants Payoffs

Increased Specific Impulse

$$I_{sp} \propto \sqrt{\Delta H_{sp}}$$

$$\text{LOX/LH}_2 : I_{sp} = 390 \text{ s}$$

$$5\% \text{ B/sH}_2 + \text{LOX} : I_{sp} = 500 \text{ s (+30%)*}$$

* calculated for $P_{\text{chamber}} = 1000 \text{ PSIA}$, $P_{\text{exhaust}} = 14.7 \text{ PSIA}$

Greater Propellant Density

liquid H_2 @ 20 K : $\rho = 0.070 \text{ g/cm}^3$

solid H_2 @ 2 K : $\rho = 0.087 \text{ g/cm}^3$ (+25%)

50/50 liquid He/solid H_2 : $\rho = 0.105 \text{ g/cm}^3$ (+50%)

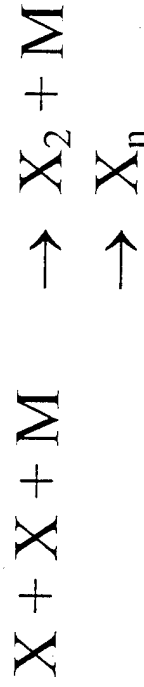
Dopant recombination/reaction in solid pH_2

* ideally:



isolated atoms

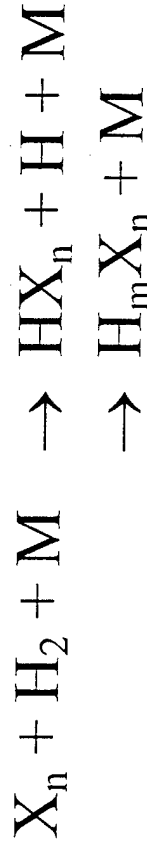
* in practice:



recombination

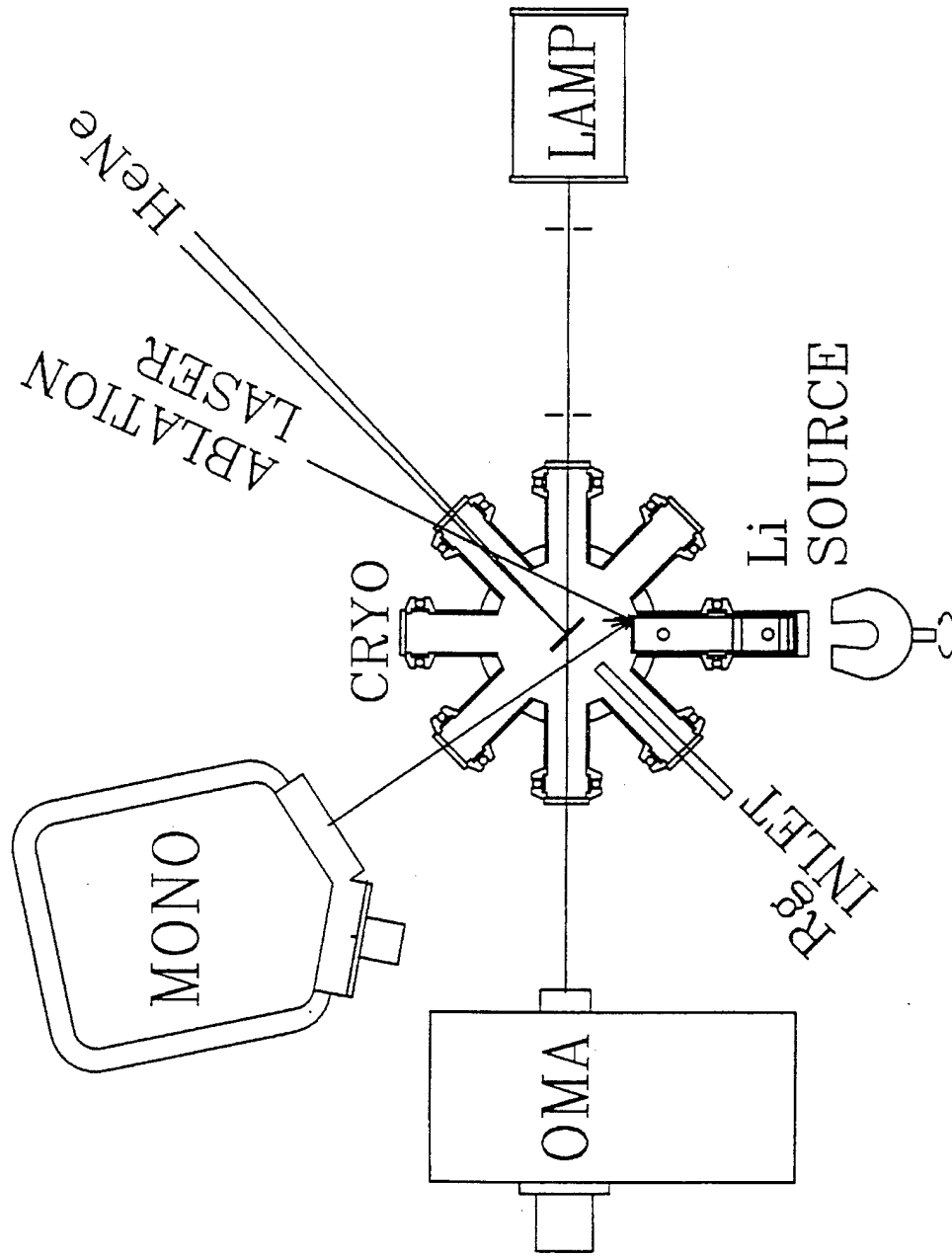


reaction

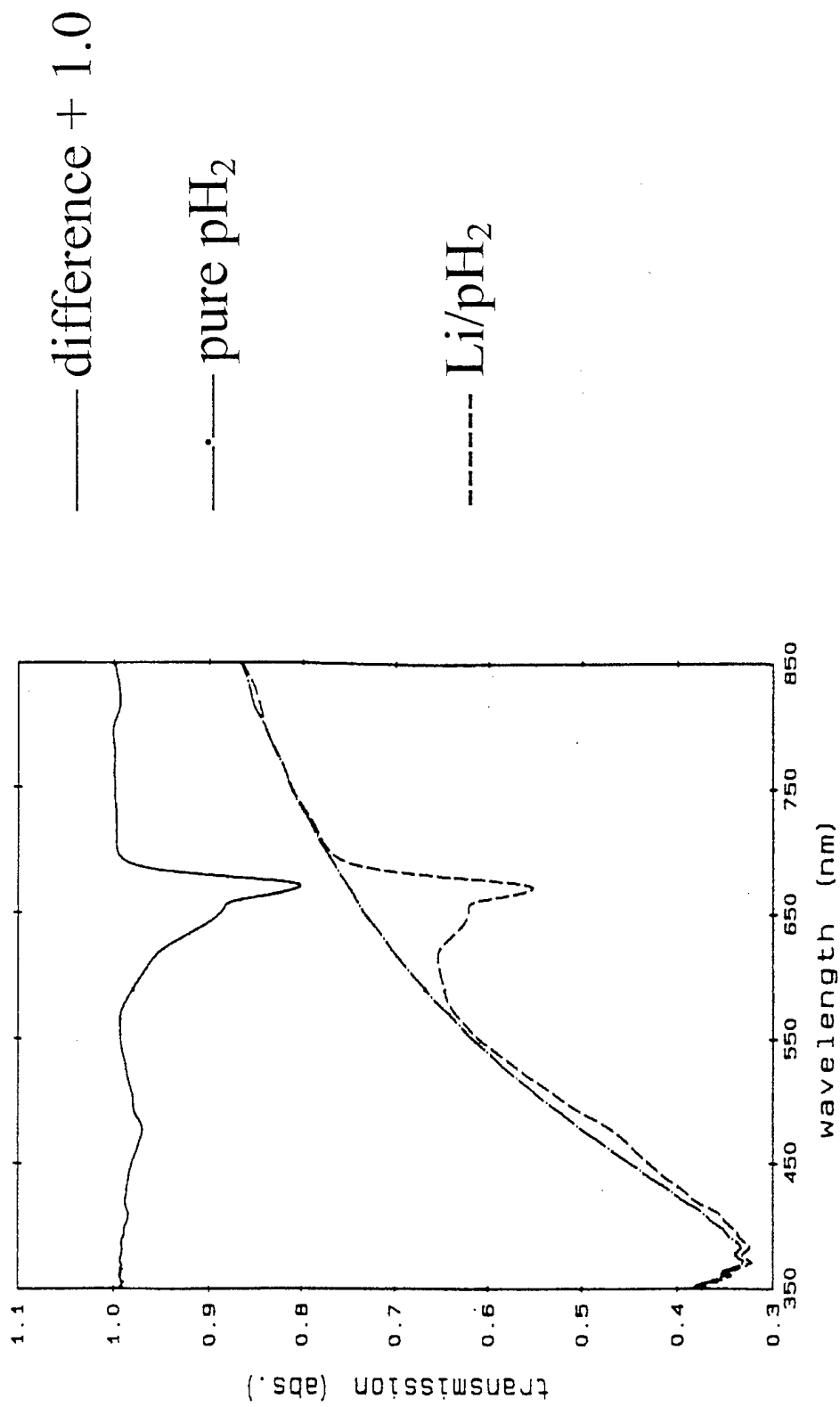


both

Experimental Diagram (c1993)



Transmission Spectrum of Li/nH_2 , $d \approx 10 \mu$



M.L. Fajardo, J. Chem. Phys. 98, 110 (1993).

Optical Scattering in Solid Hydrogen

Crystal Growing and Quality (p. 81)

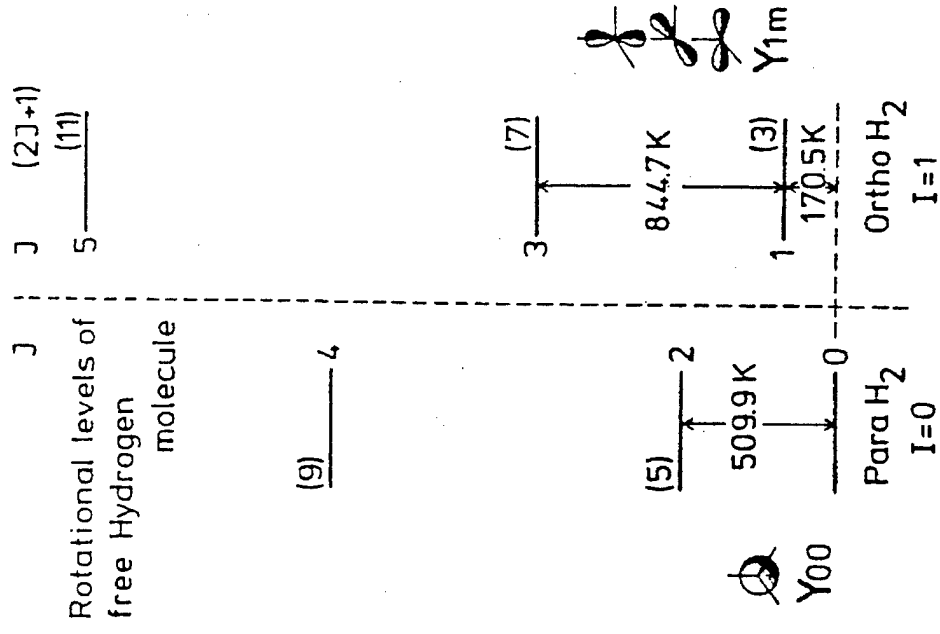
“There is a considerable art to growing hydrogen crystals of high quality. Good crystals are always grown slowly from the melt; a rapid freeze from the gas produces snow.”

Crystallite Light Scattering (p. 83)

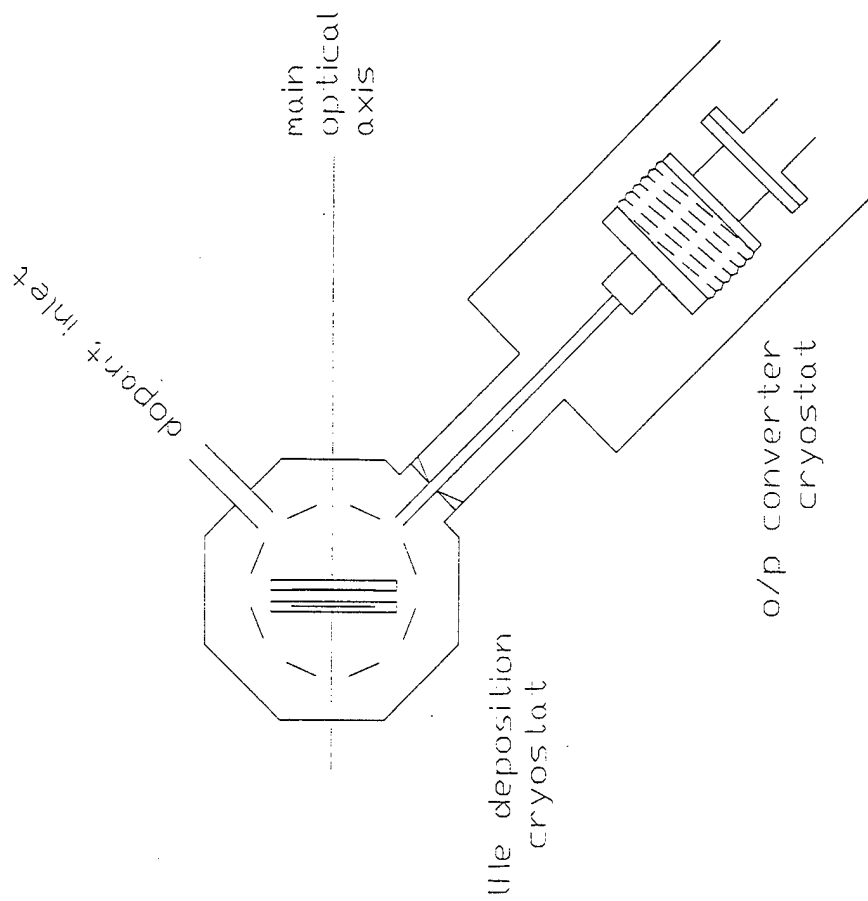
“The reason that a good hydrogen crystal is so hard to see is its low refractive index...an estimated 1.16!

Yet a 1 mm-thick layer of hydrogen crystallites can be a completely opaque brown-black.”

ortho- and para-hydrogen



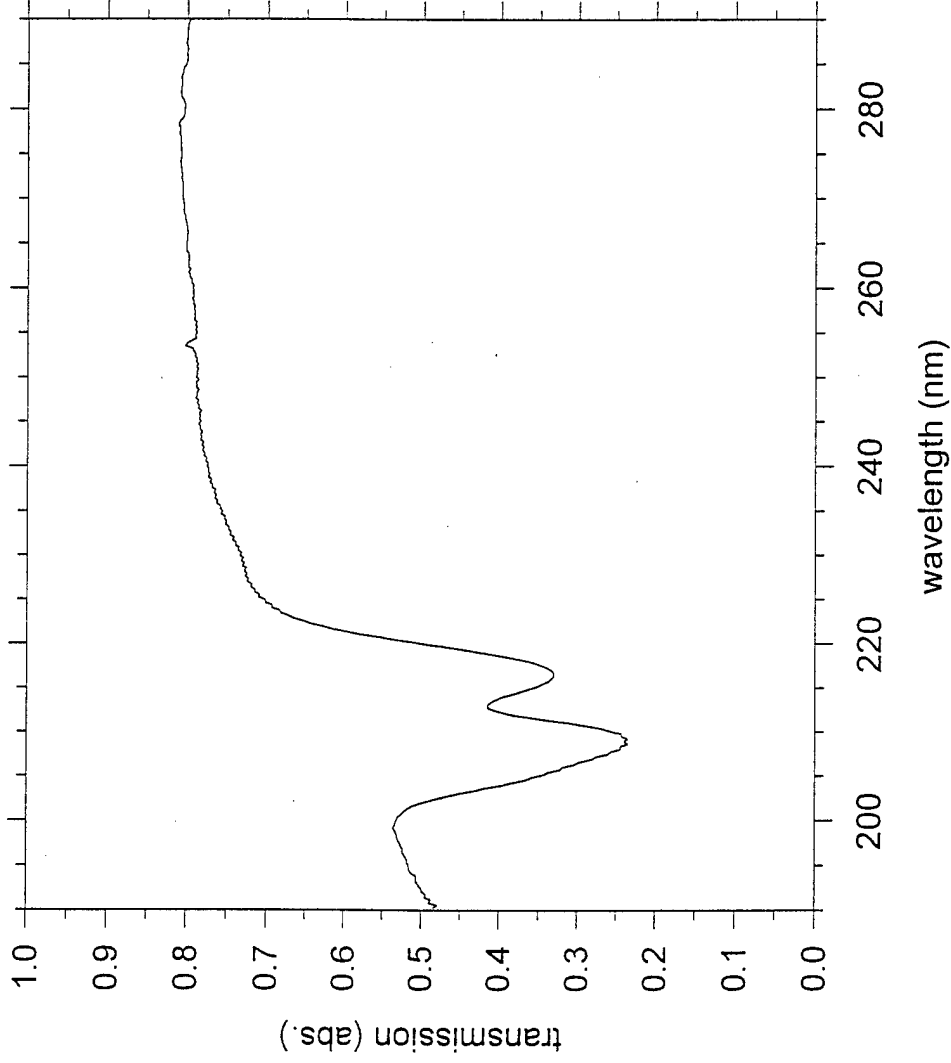
Experimental Diagram (c1997)



M.E. Fajardo and S. Tam, *J. Chem. Phys.* **108**, 4237 (1998).

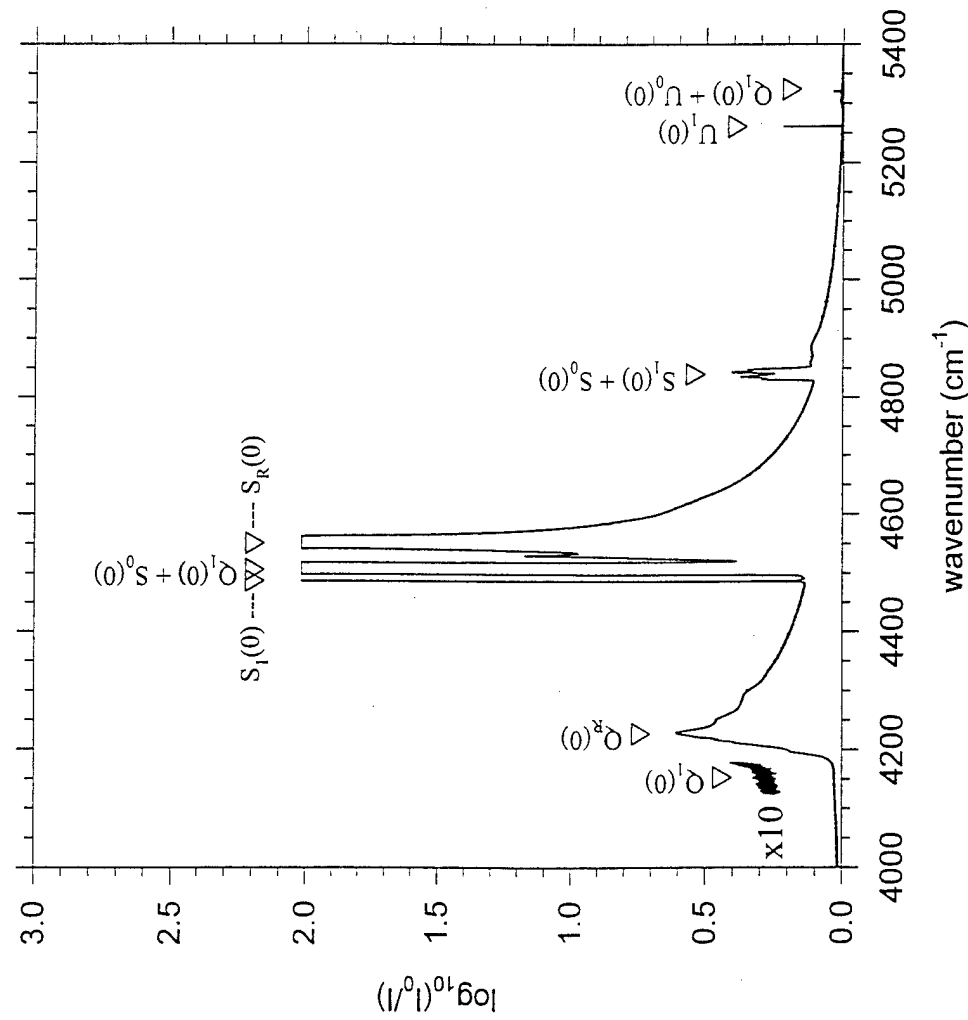
S. Tam and M.E. Fajardo, *Rev. Sci. Instrum.* **70**, 1926 (1999).

Transmission Spectrum of B/pH₂ d_≈1mm



M.E. Fajardo and S. Tam, *J. Chem. Phys.* **108**, 4237 (1998).
S. Tam, M. Macler, M.E. DeRose, and M.E. Fajardo, *J. Chem. Phys.*, submitted (2000).

IR Absorption of 6 mm Thick pH_2 Solid



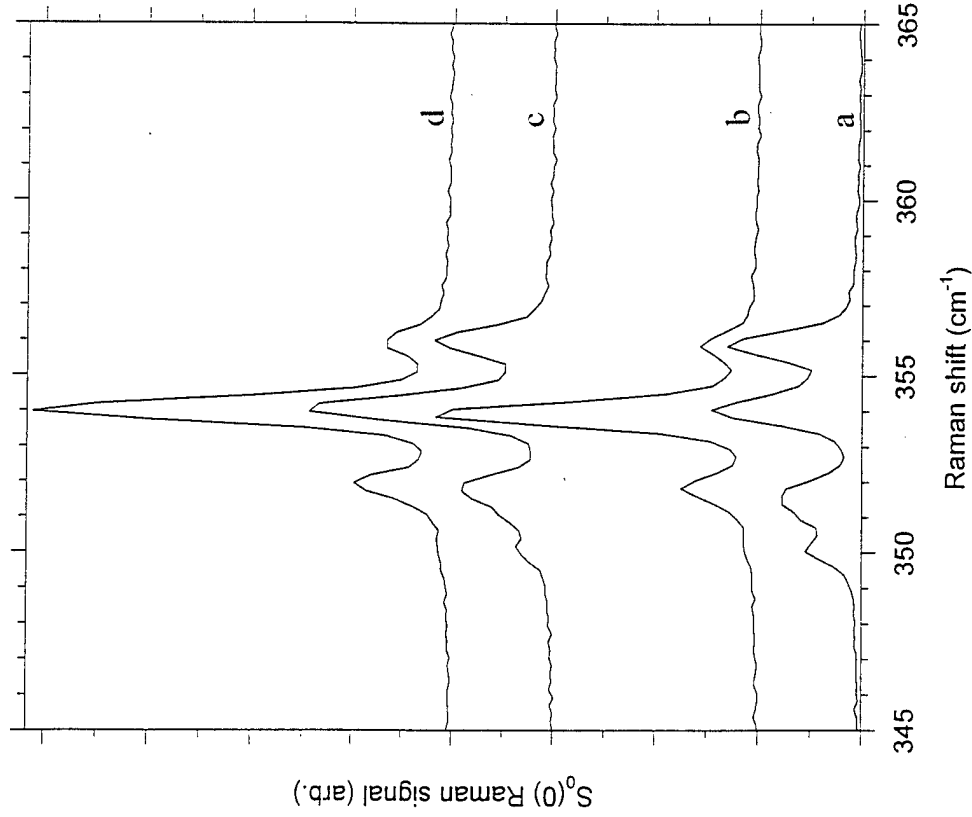
Non-observation of the $Q_1(0)$ transition demonstrates the absence of oH_2 impurities, and that the microscopic structure is not amorphous or porous.

Observation of $S_1(0)$ transition demonstrates the absence of inversion symmetry for some H_2 molecular environments.

[van Kranendonk and Gush, Phys. Lett. **1**, 22 (1962)]

M.E. Fajardo and S. Tam, J. Chem. Phys. **108**, 4237 (1998).

Raman Spectra of pH₂ Solids



Mixed hcp/fcc as-deposited structure, anneals to hcp.

[G.W. Collins, et al., Phys. Rev. B **53**, 102 (1996)]

(d) sample in (c) warmed to 4.5 K.
(c) 4.5 mm sample as deposited at 3.3 K ($\Phi = 290$ mmol/hr).

(b) sample in (a) warmed to 4.5 K.
(a) 6 mm sample as deposited at 3.1 K ($\Phi = 200$ mmol/hr).

High Res. IR Spectroscopy in Solid pH_2

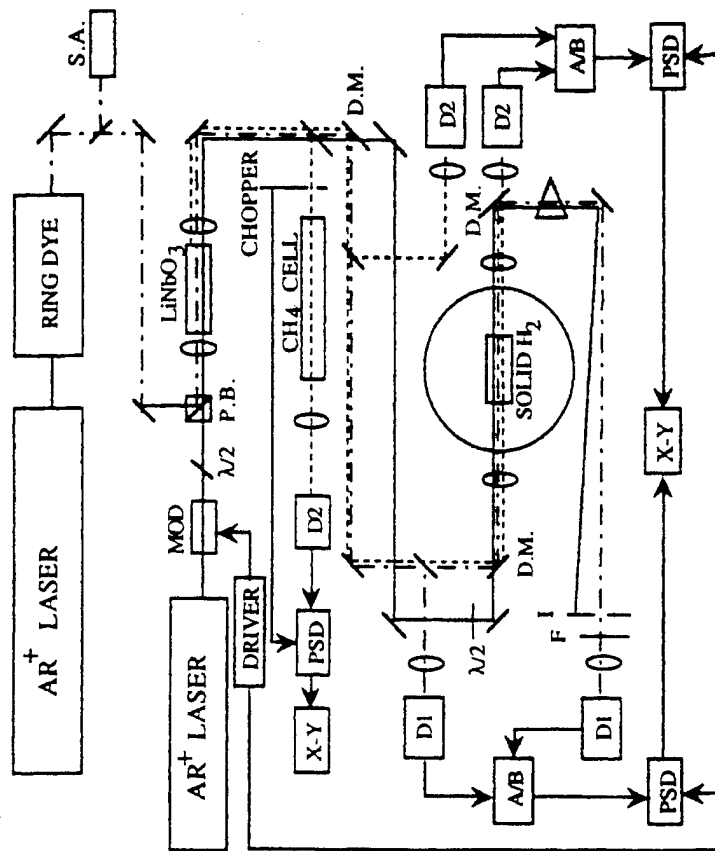
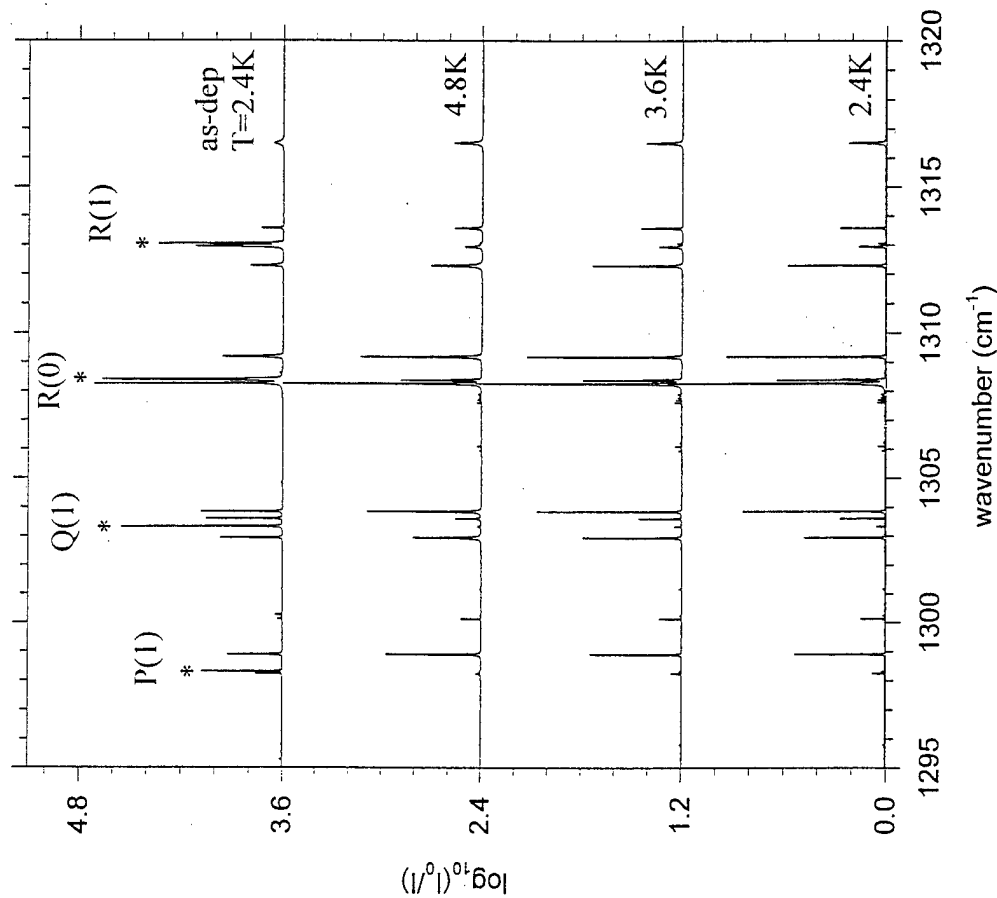
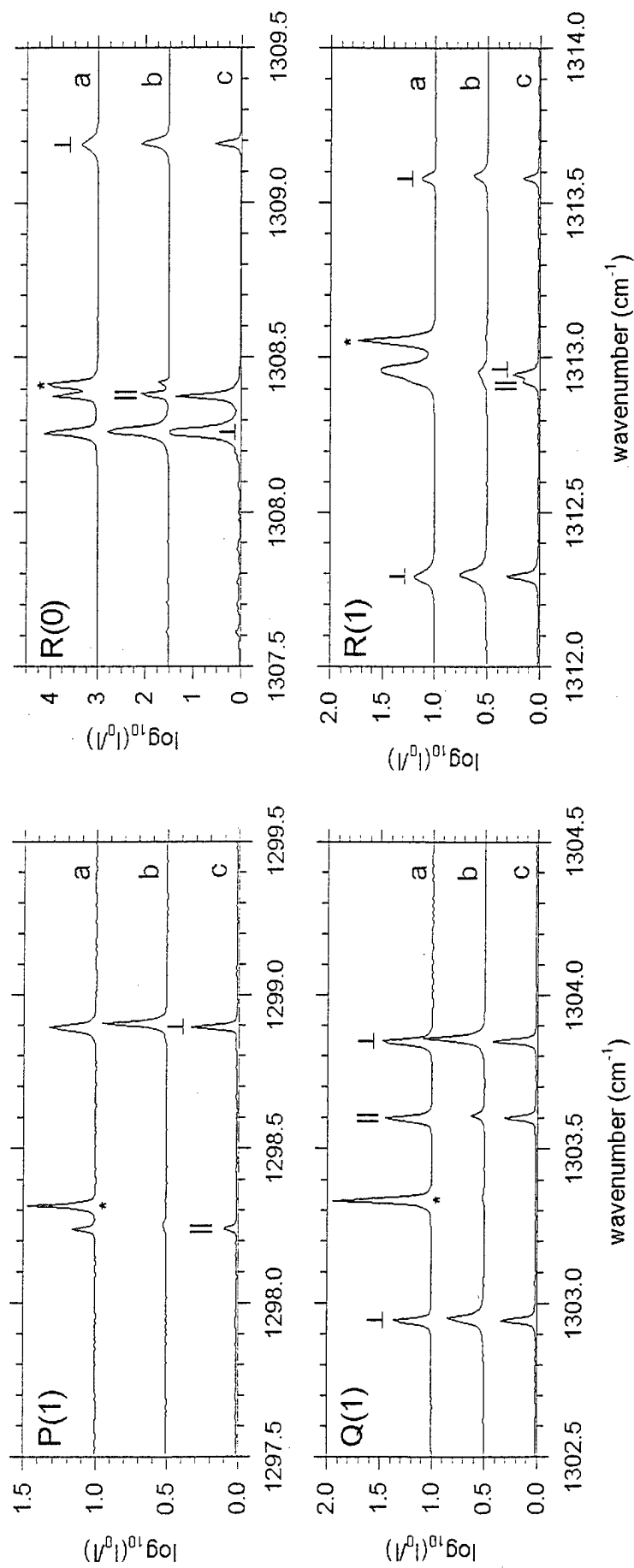


FIG. 1. Apparatus for the simultaneous spectroscopy of the infrared and Raman transitions. The nonlinearity of $LiNbO_3$ is used for the former and that of solid H_2 is used for the latter. D.M., dichroic mirror; S. A., spectrum analyzer; P. B., polarizer beamsplitter.

ν_4 CH₄/pH₂ IR Absorptions (res = 0.01 cm⁻¹)

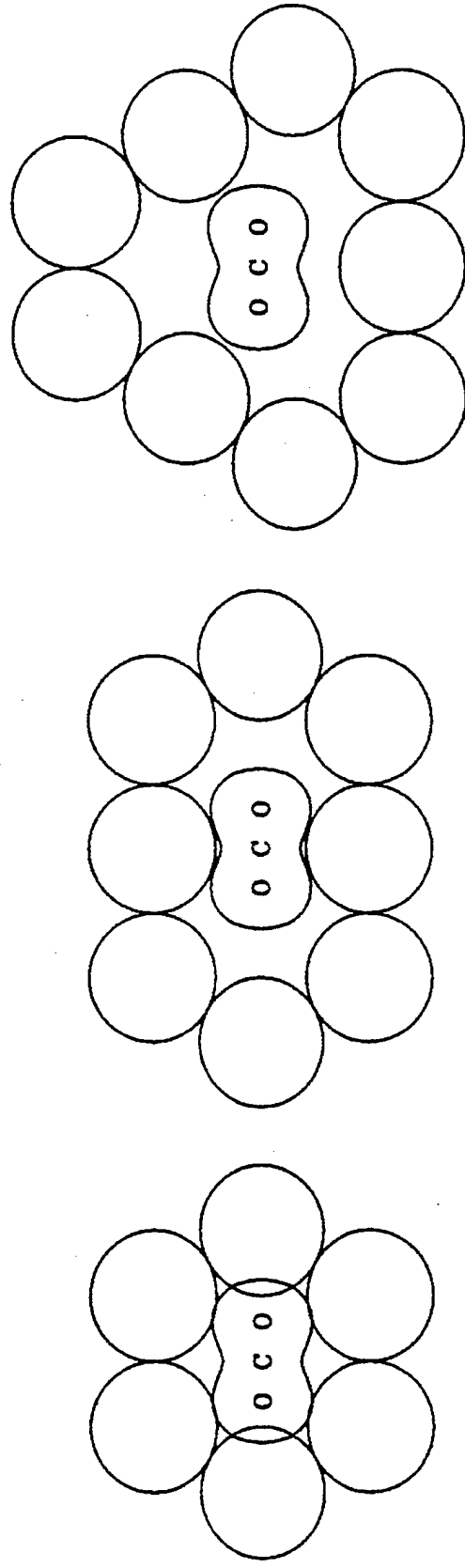


ν_4 CH₄/pH₂ IR Absorptions



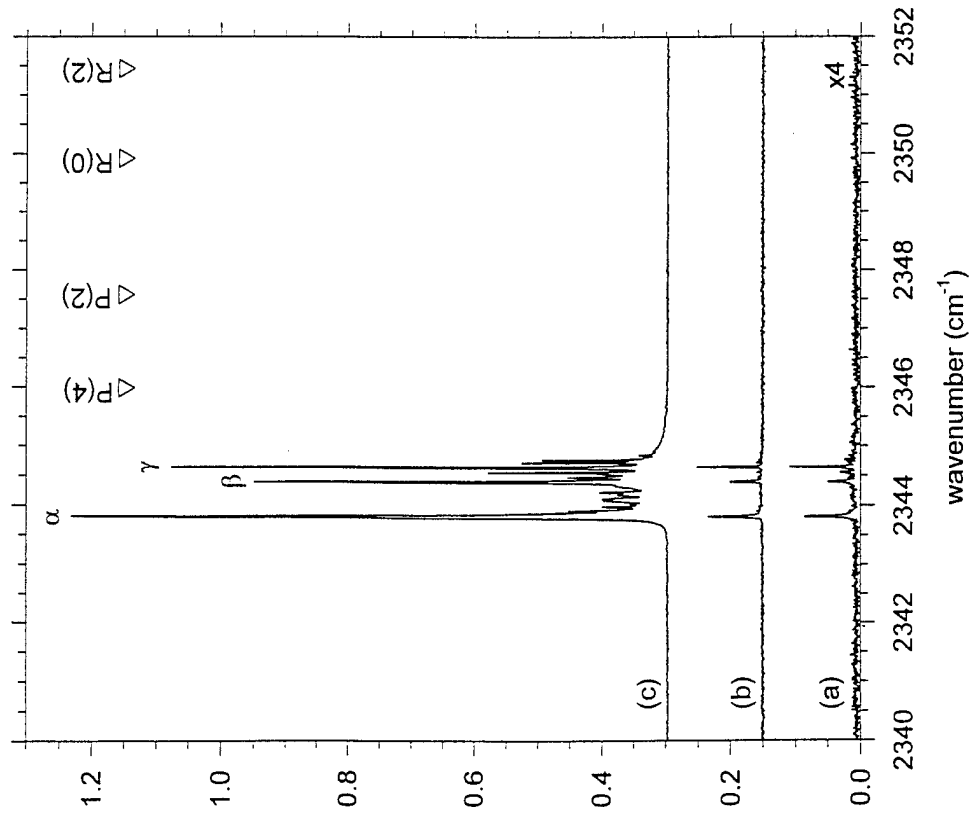
- (a) Rapid Vapor Deposited sample: as-deposited at 2.4 K
- (b) Rapid Vapor Deposited sample: annealed to 4.8 K
- (c) Enclosed Cell Condensed sample: cooled to 4.8 K

CO₂/pH₂ Trapping Sites



S. Tam and M.E. Fajardo, Fiz. Nizk. Temp. [Low Temp. Phys.] accepted (2000).

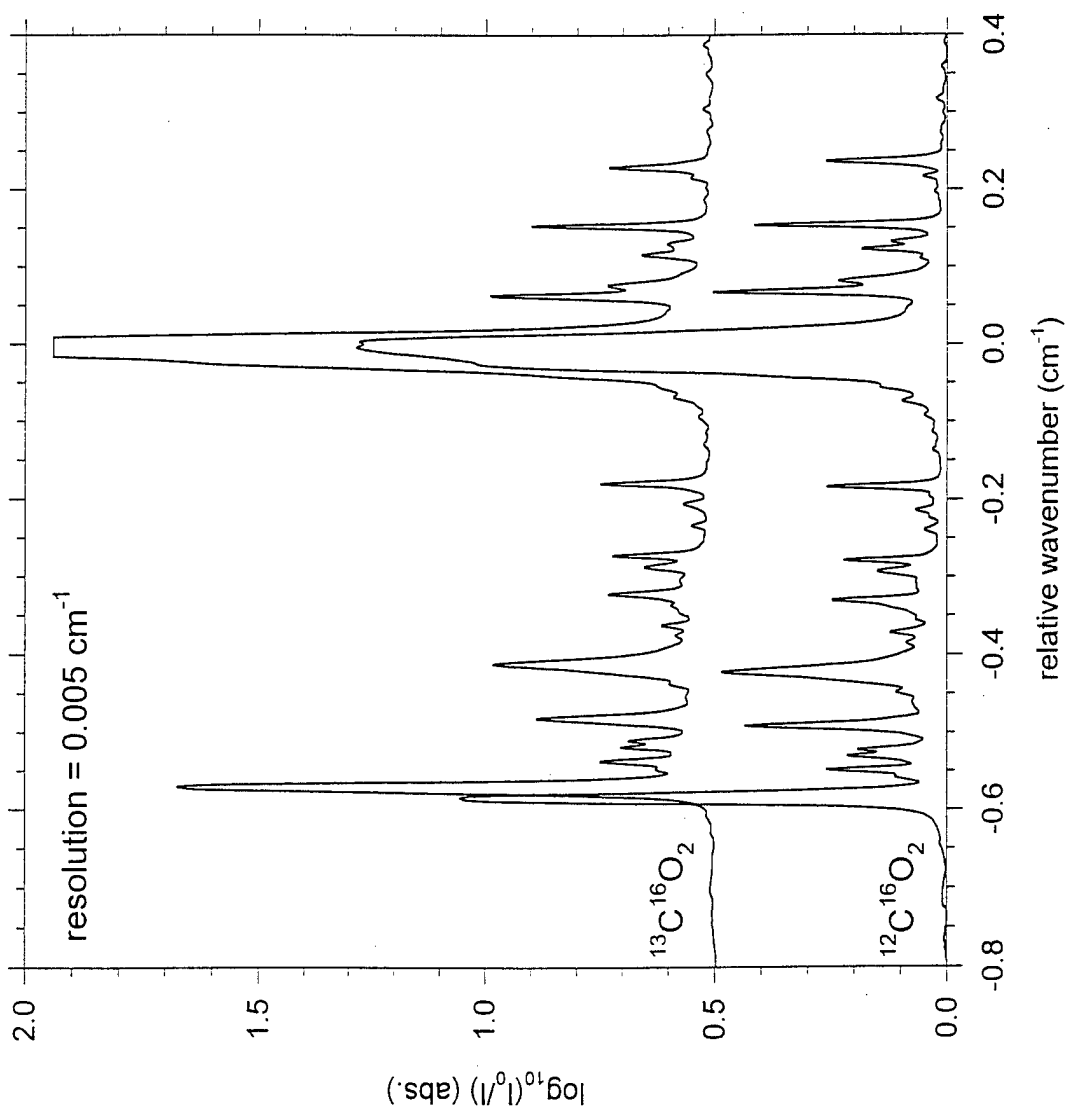
CO_2/pH_2 IR Absorptions (res = 0.008 cm^{-1})



as-deposited at $T = 2.4 \text{ K}$

- (c) 1.2 ppm CO_2/pH_2
- (b) 0.04 ppm CO_2/pH_2
- (a) 0.01 ppm CO_2/pH_2

$^{13}\text{C}^{16}\text{O}_2/\text{pH}_2$ vs. $^{12}\text{C}^{16}\text{O}_2/\text{pH}_2$

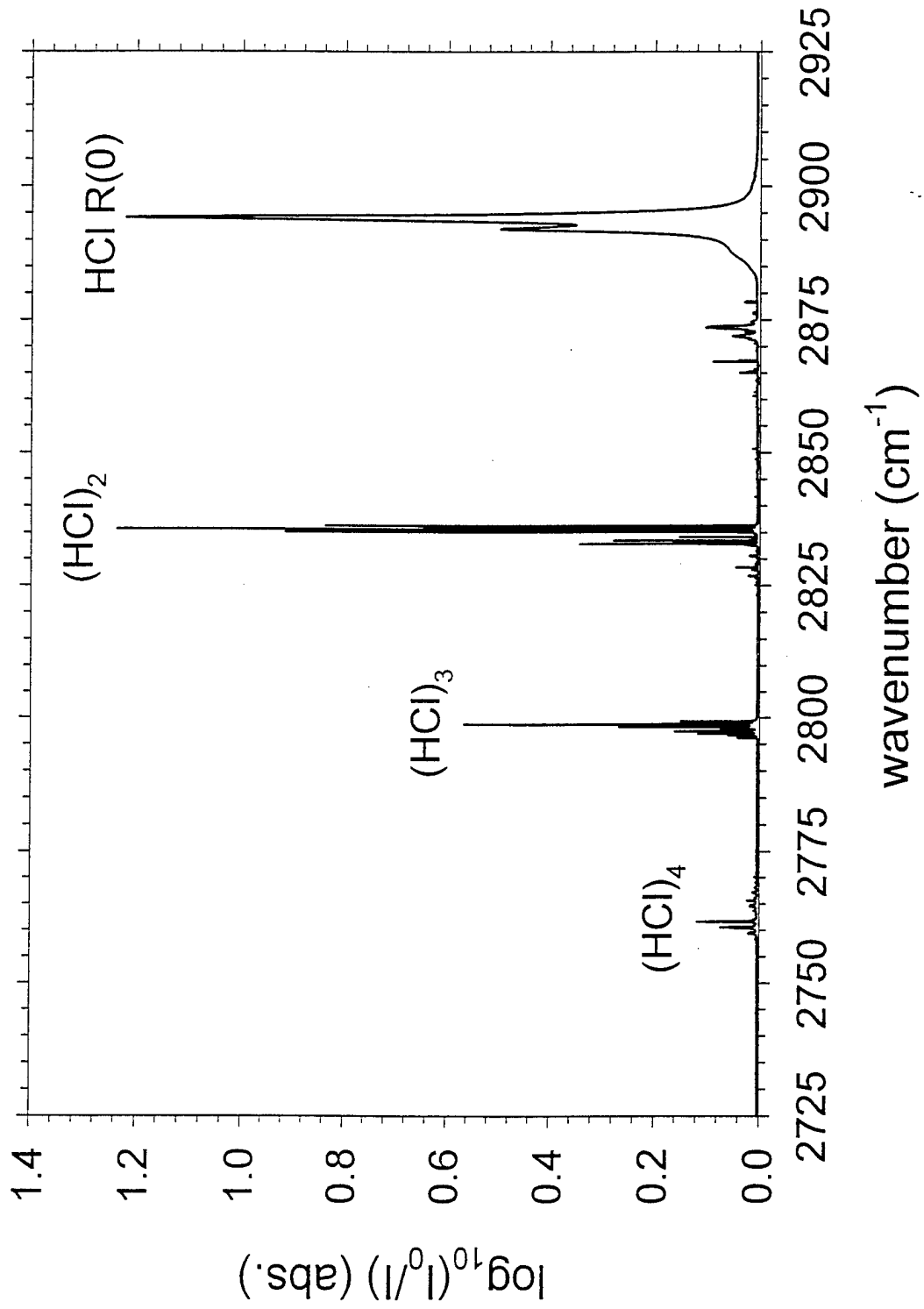


annealed, $T = 2.4\text{ K}$

$d = 1.0\text{ mm}$

2 ppm $^{13}\text{C}^{16}\text{O}_2$ and
2 ppm $^{12}\text{C}^{16}\text{O}_2$

88 PPM HCl/pH₂



Gas Phase (HCl)₂

High resolution, jet-cooled infrared spectroscopy of (HCl)₂: Analysis of ν_1 and ν_2 HCl stretching fundamentals, interconversion tunneling, and mode-specific predissociation lifetimes

Michael D. Schuder,^{a)} Christopher M. Lovejoy,^{b)} Robert Lascola,^{c)} and David J. Nesbitt^{d)}
Joint Institute for Laboratory Astrophysics, National Institute of Standards and Technology and University of Colorado, and the Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309

(Received 5 April 1993; accepted 7 June 1993)

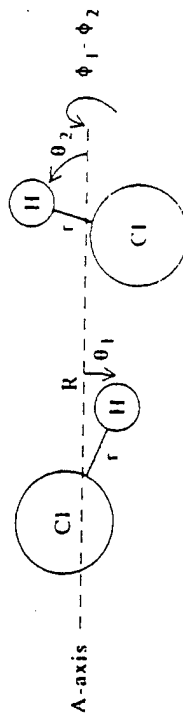
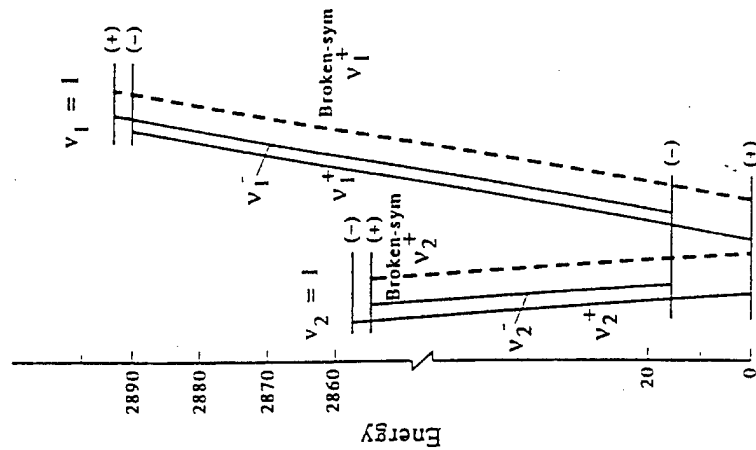
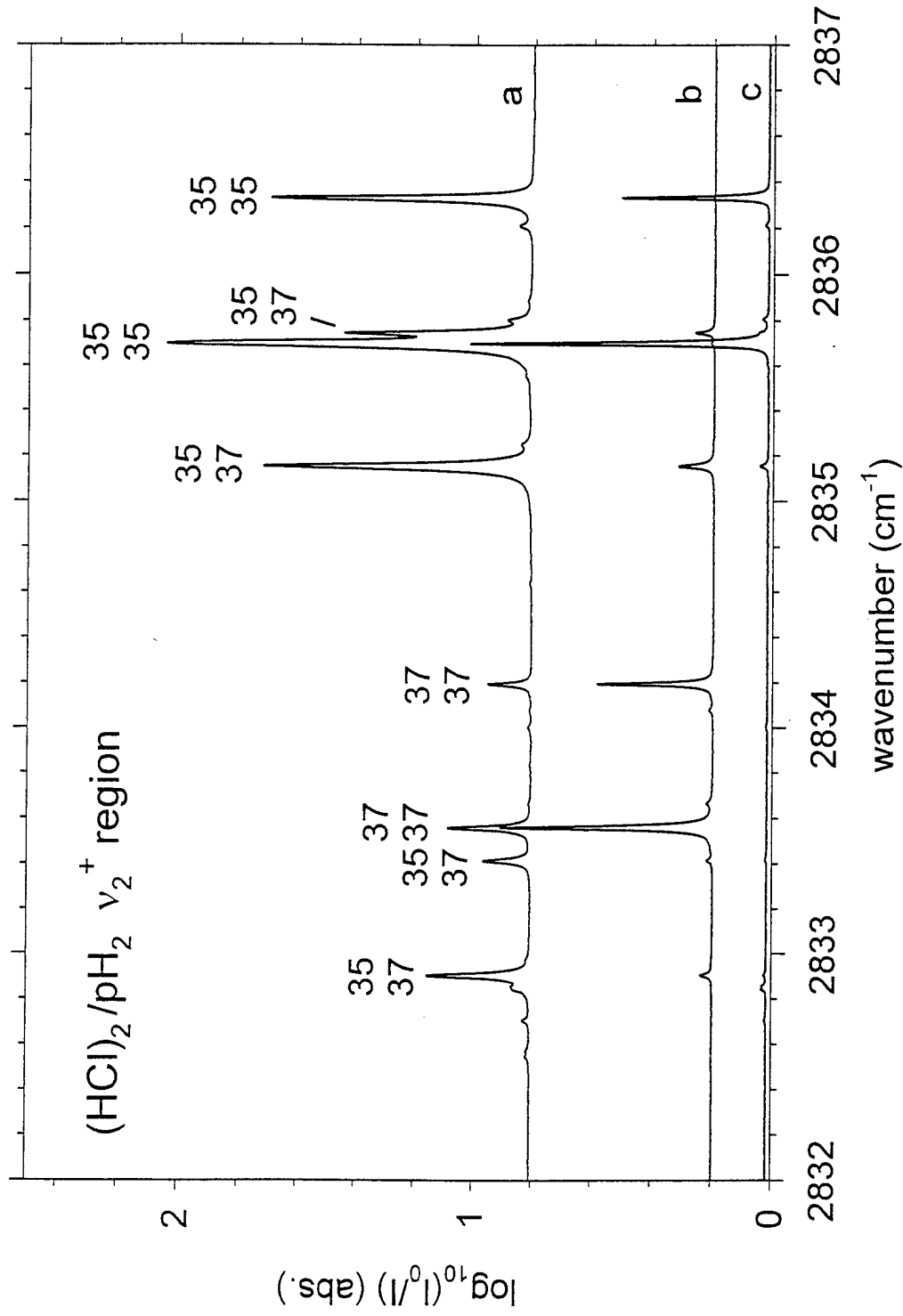


FIG. 1. Vibrationally averaged structure and internal coordinates for HCl dimer. The intermolecular axis R connects the HCl centers of mass. The internal angles, θ_1 and θ_2 , are measured from the intermolecular axis to the HCl bonds r . The torsion angle, $\phi = \phi_1 - \phi_2$, is shown at 180° (planar). The minimum energy configuration shown is for $\theta_1 = 16^\circ$, $\theta_2 = 87^\circ$ with $\phi_1 - \phi_2 = 180^\circ$. The HCl subunit on the left is referred to as the bonded HCl with an associated vibration labeled ν_2 . The proton on the other HCl is not involved with the hydrogen bond, and this subunit is referred to as the free HCl, with a vibration labeled ν_1 .

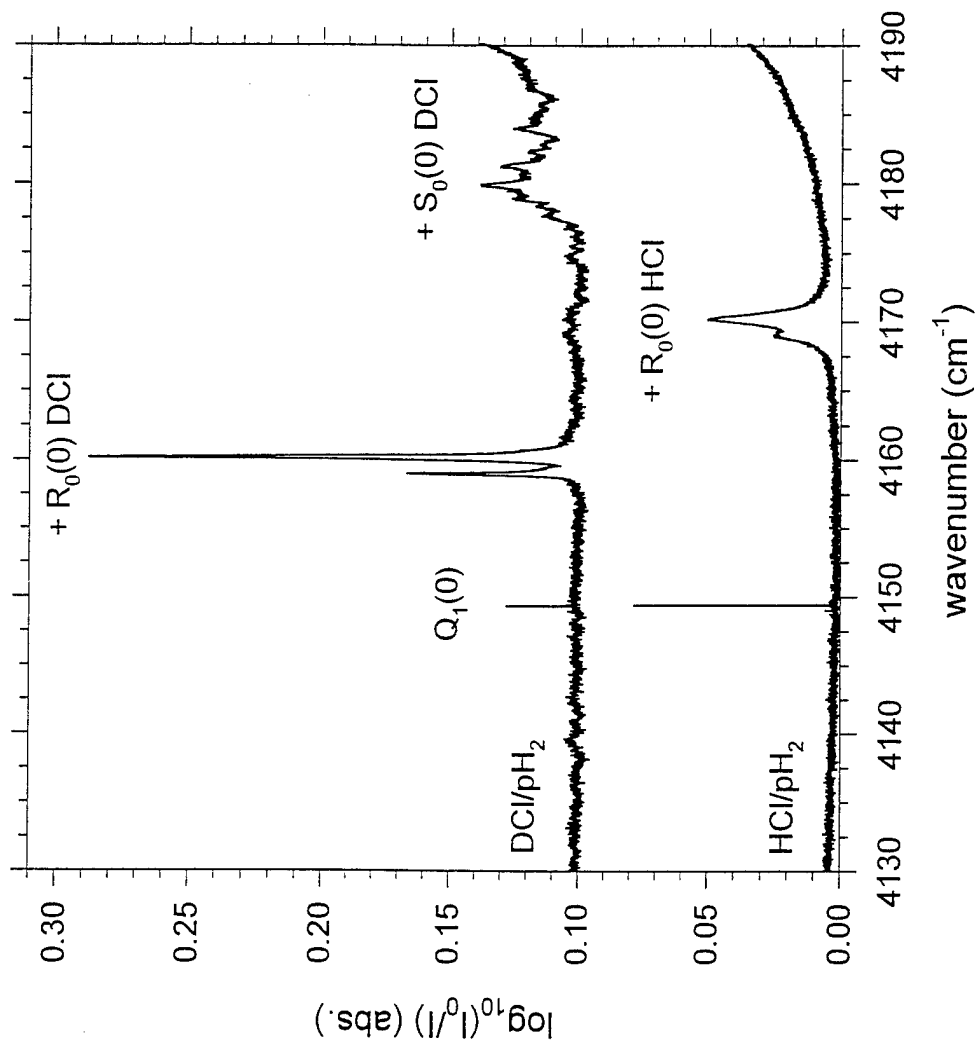


$(\text{HCl})_2/\text{pH}_2$ isotopomers



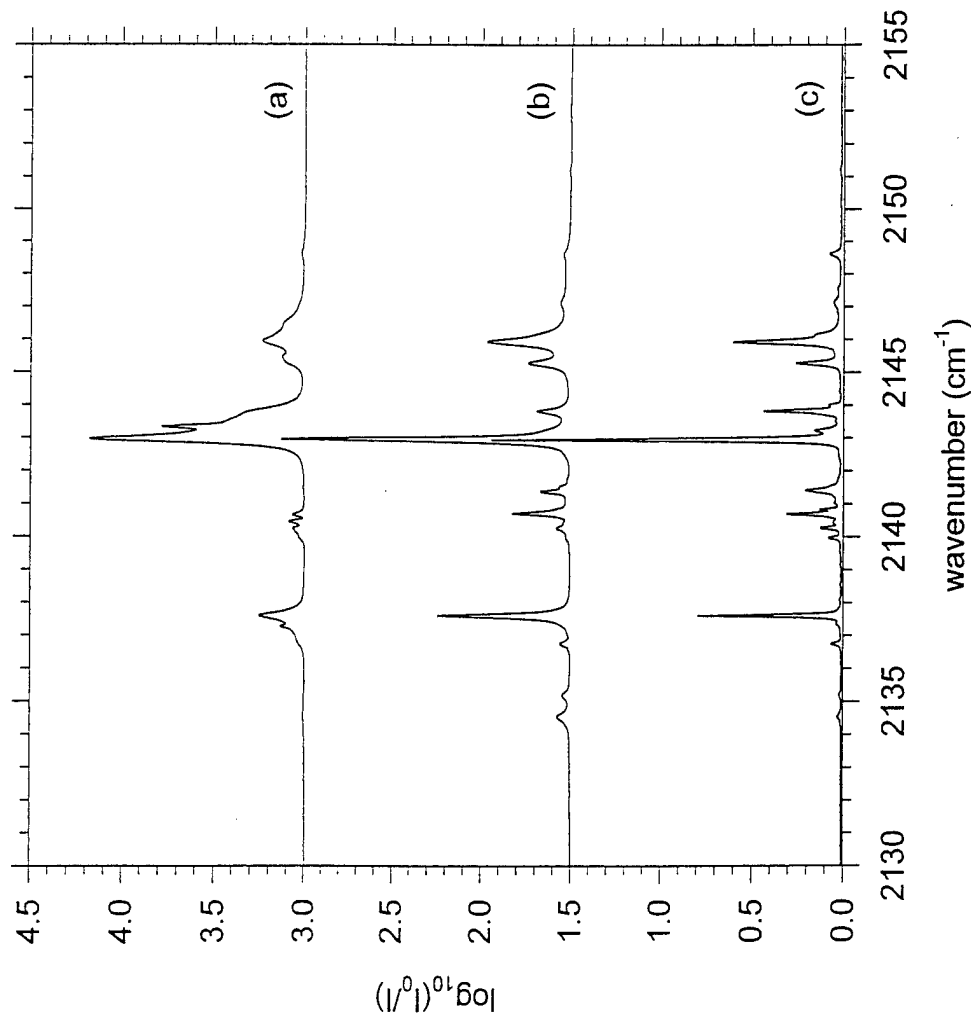
analysis in collaboration with D.T. Anderson, U. Wyoming.

Co-operative IR absorptions



analysis in collaboration with R.J. Hinde, U. Tennessee, Knoxville.

80 PPM CO/pH₂ (res = 0.1 cm⁻¹)



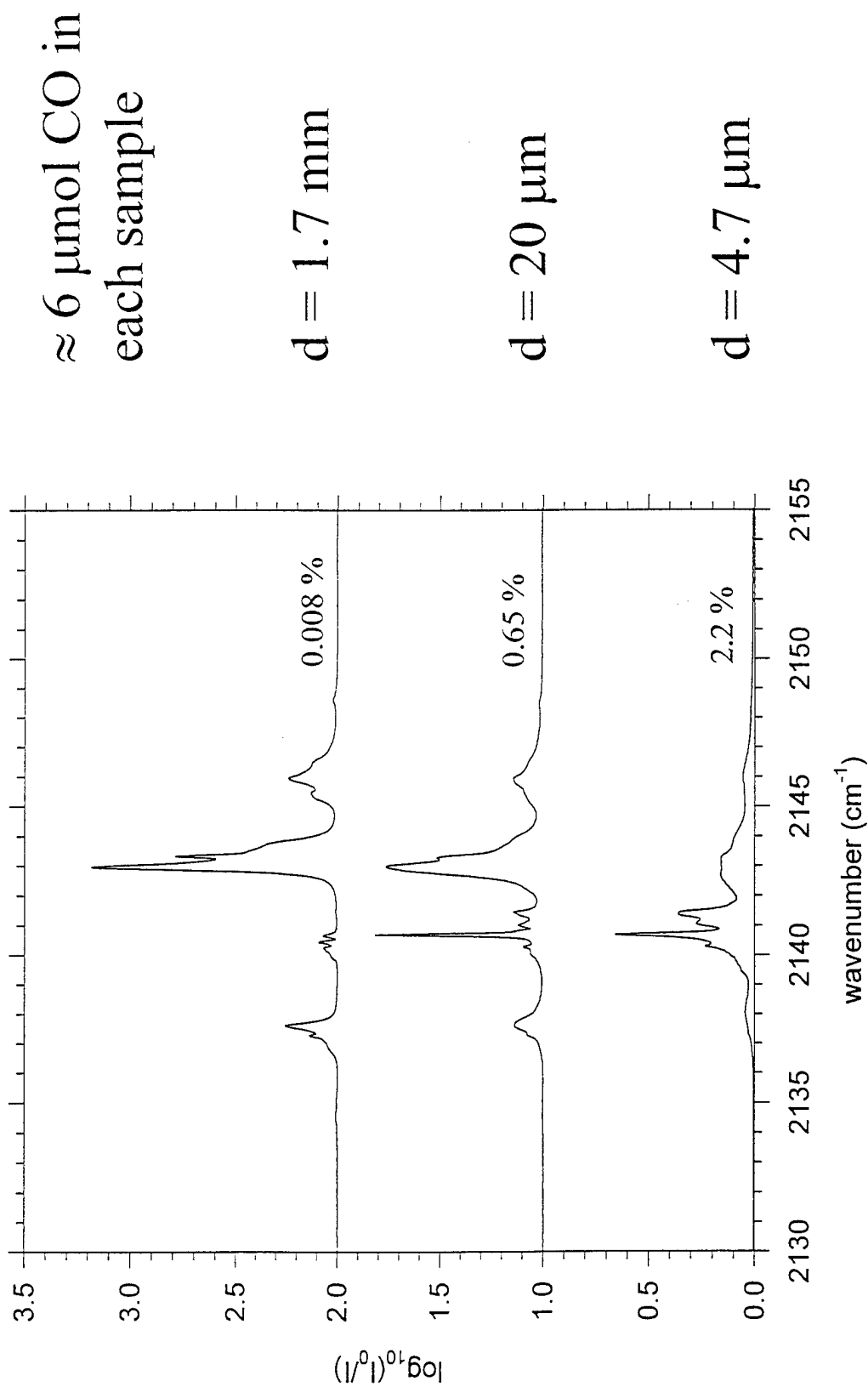
(a) as deposited at $T = 2.4 \text{ K}$

(b) warmed to $T = 4.8 \text{ K}$

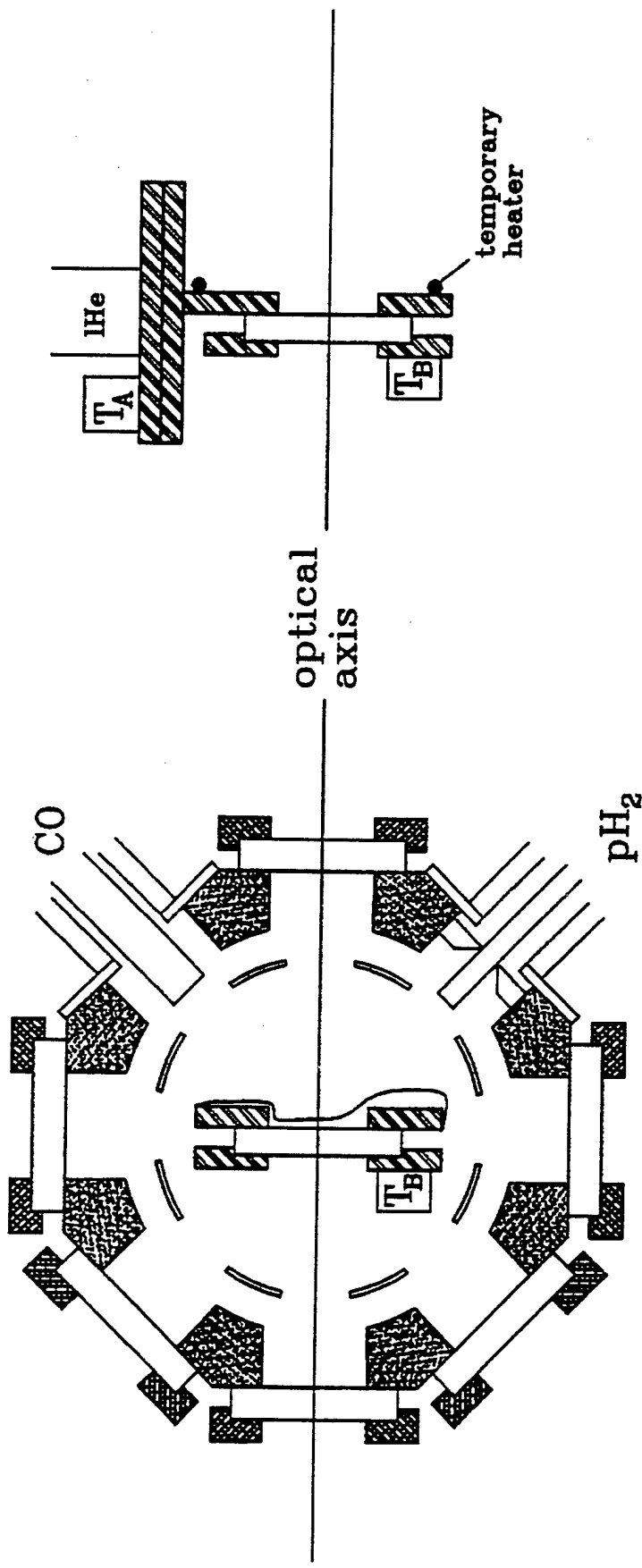
(c) re-cooled to $T = 2.4 \text{ K}$

analysis in collaboration with T. Momose, Kyoto U.

$(\text{CO})_n/\text{pH}_2$ IR Absorptions



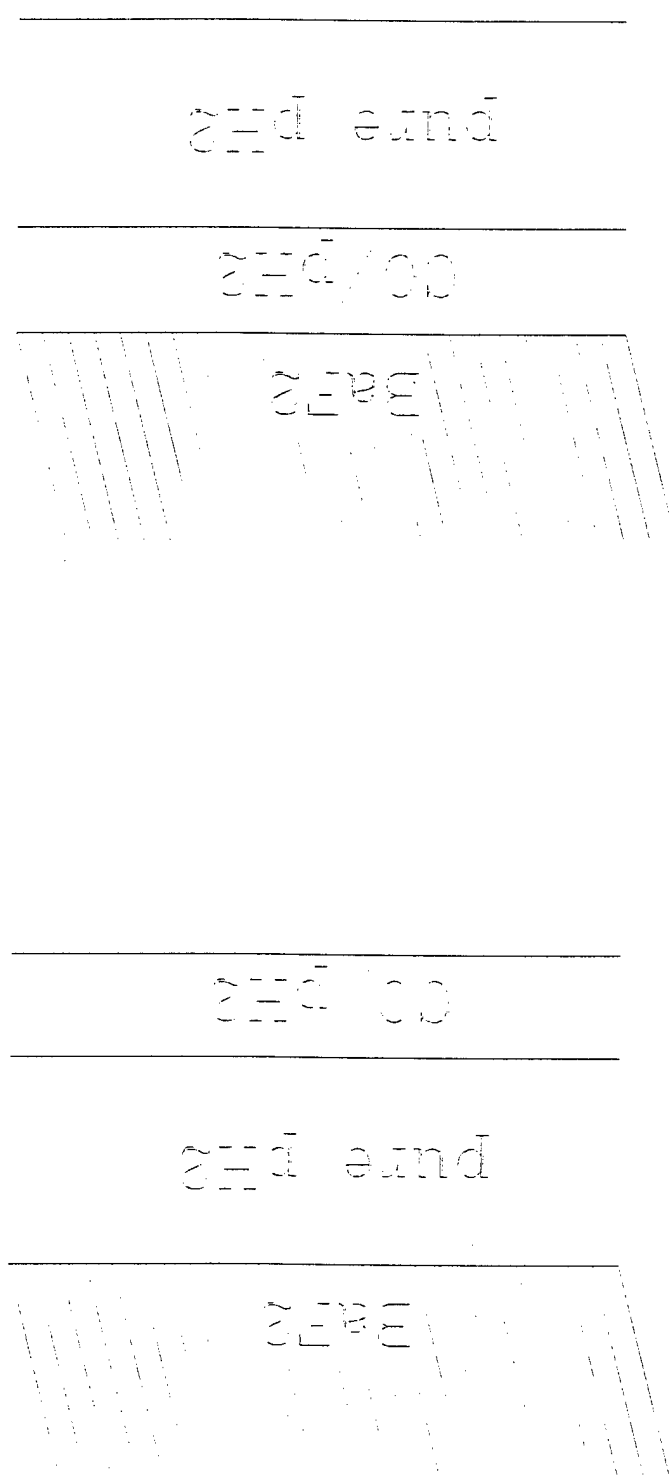
Experimental Diagram



Top View

Side View

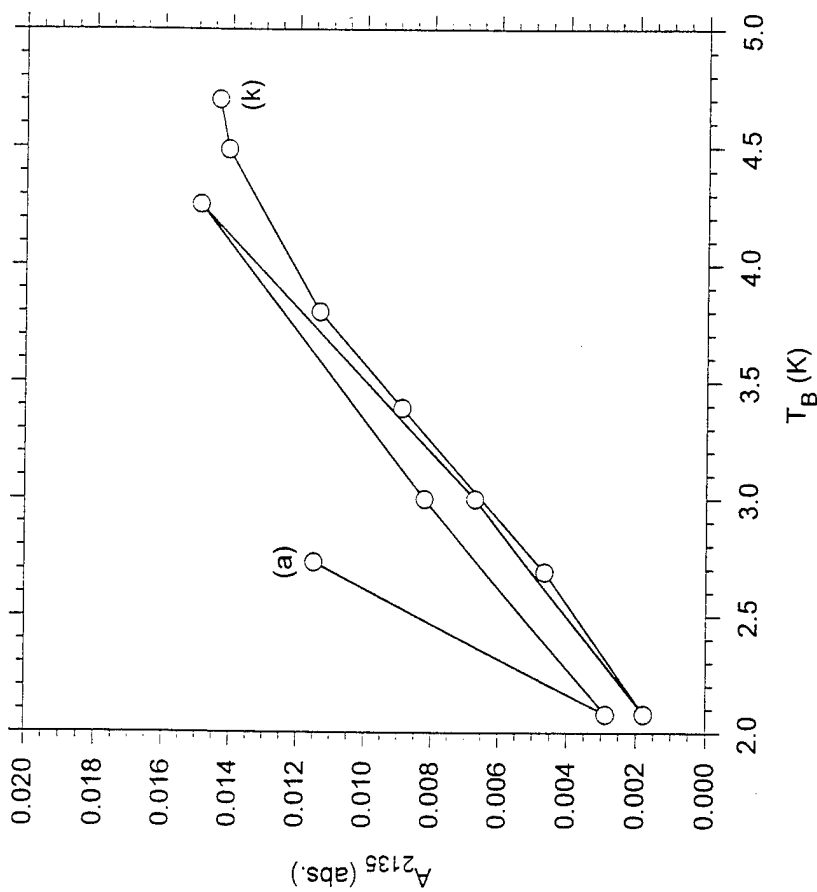
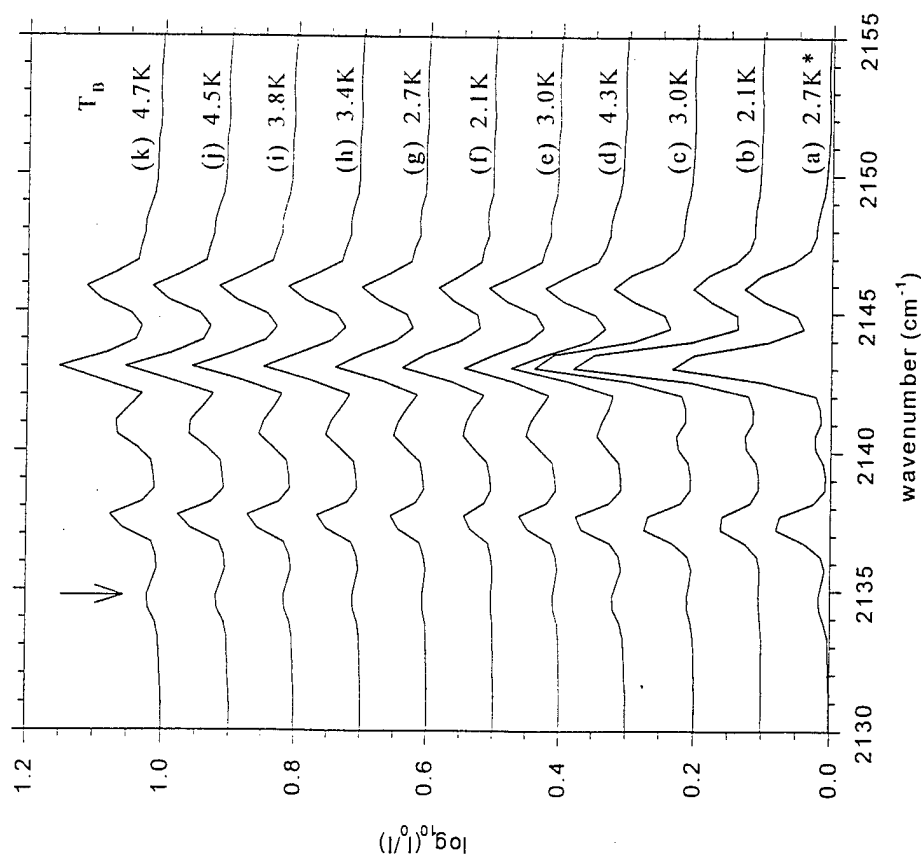
Experimental Protocol



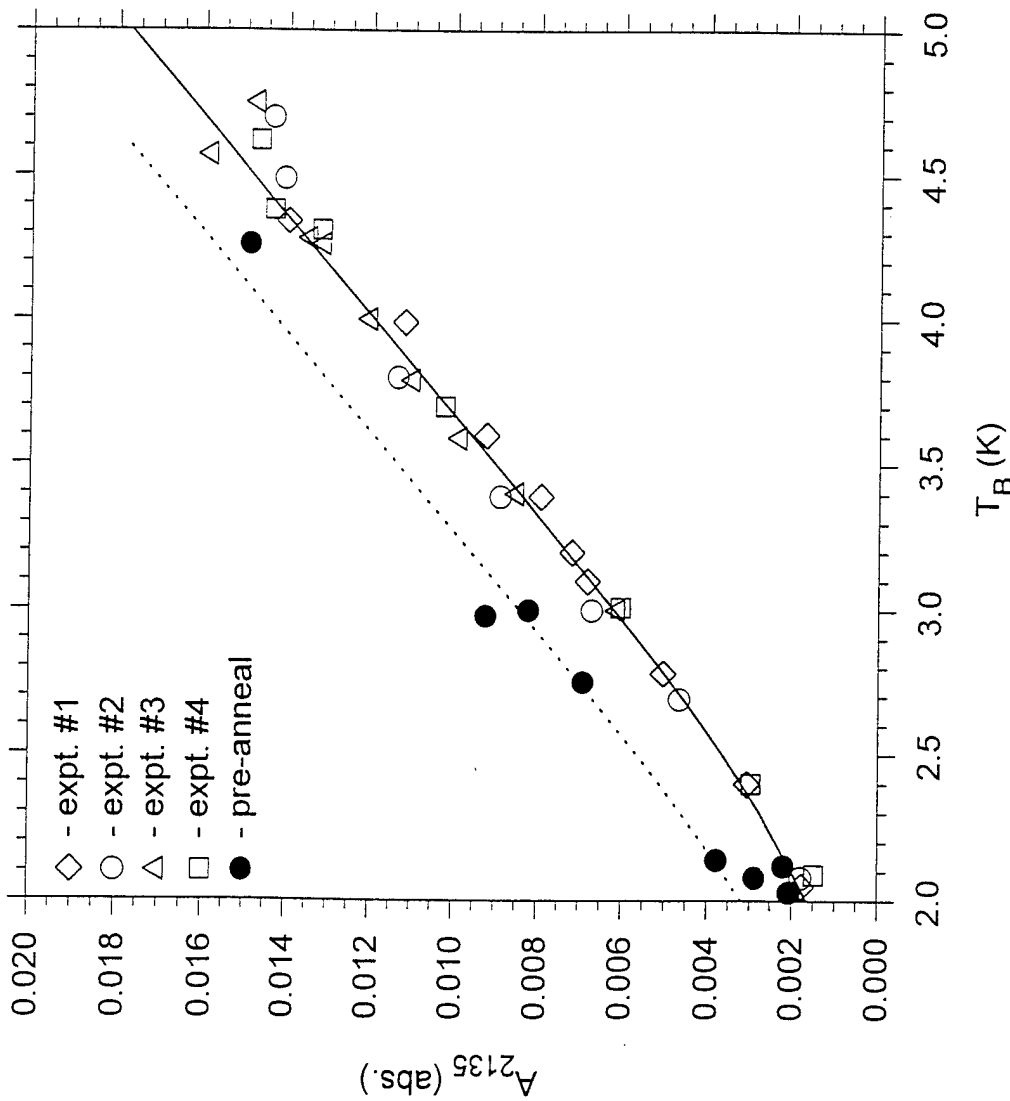
Thermometer experiments: control experiment

CO₂ P110

CO₂/pH₂ Thermometer Peak



Calibration of CO/pH₂ Thermometer



simplified Boltzmann:

$$A_{2135} = N \exp(-E/T_{CO})$$

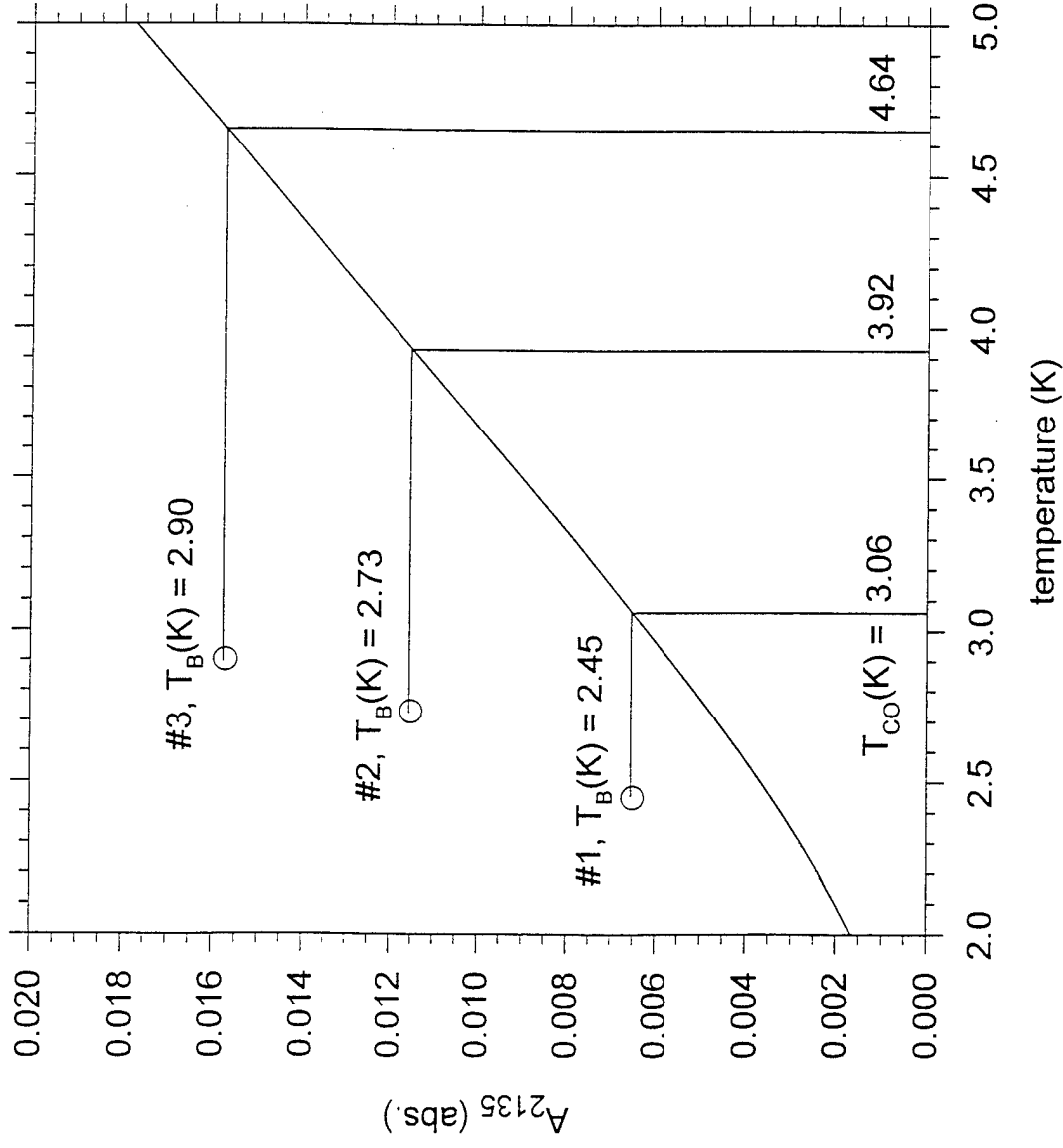
$$N = 0.0860$$

$$E = 7.896 \text{ K}$$

include $Q_{rot} \Rightarrow E \approx 11 \text{ K}$

$6 B_{CO/pH_2} \approx 12 \text{ K}$

Deposition Temperatures

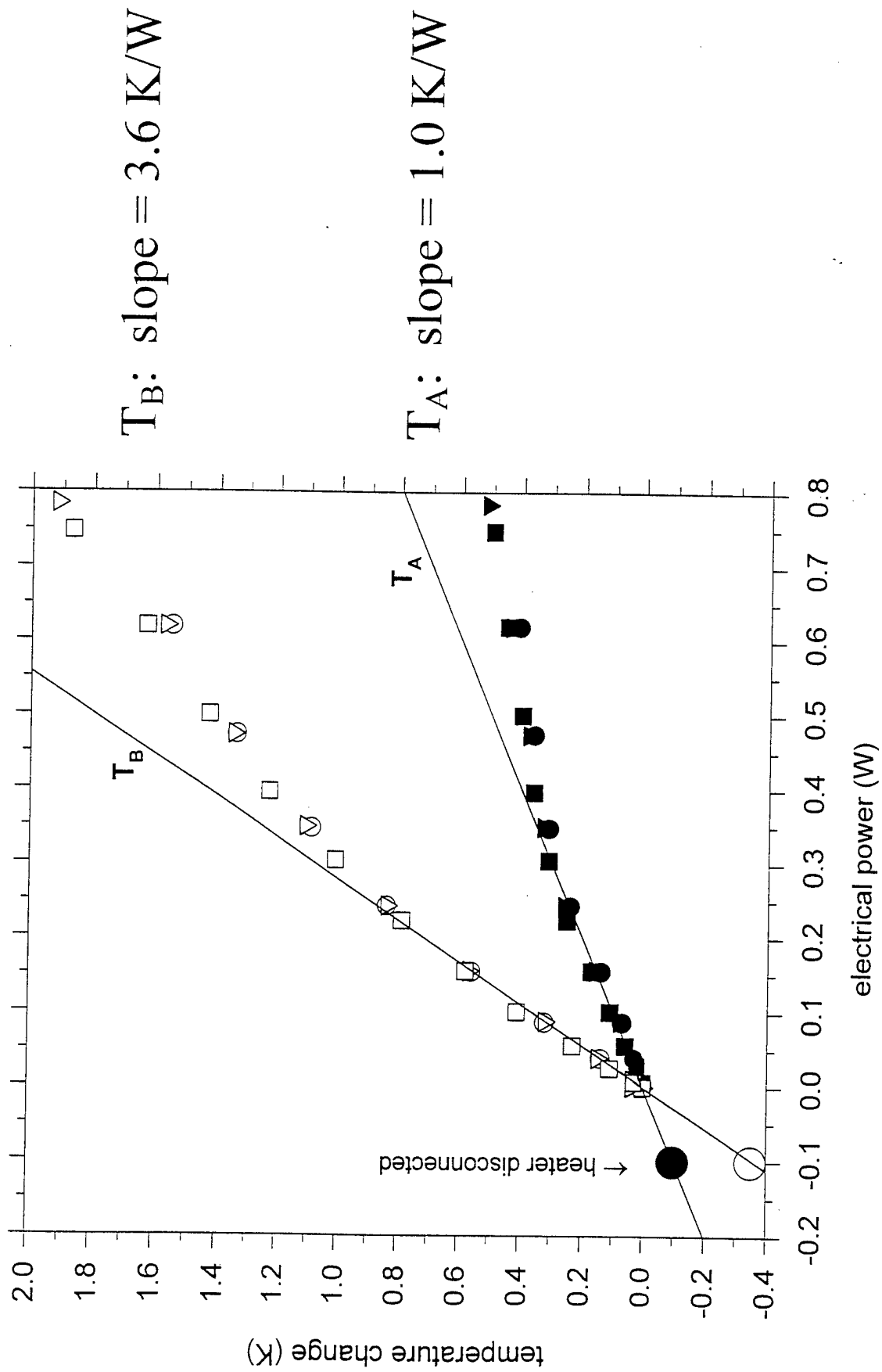


#3:
 $\Phi_{H_2} = 240$ mmol/hr
 $\dot{R} = 55$ $\mu\text{m}/\text{min}$

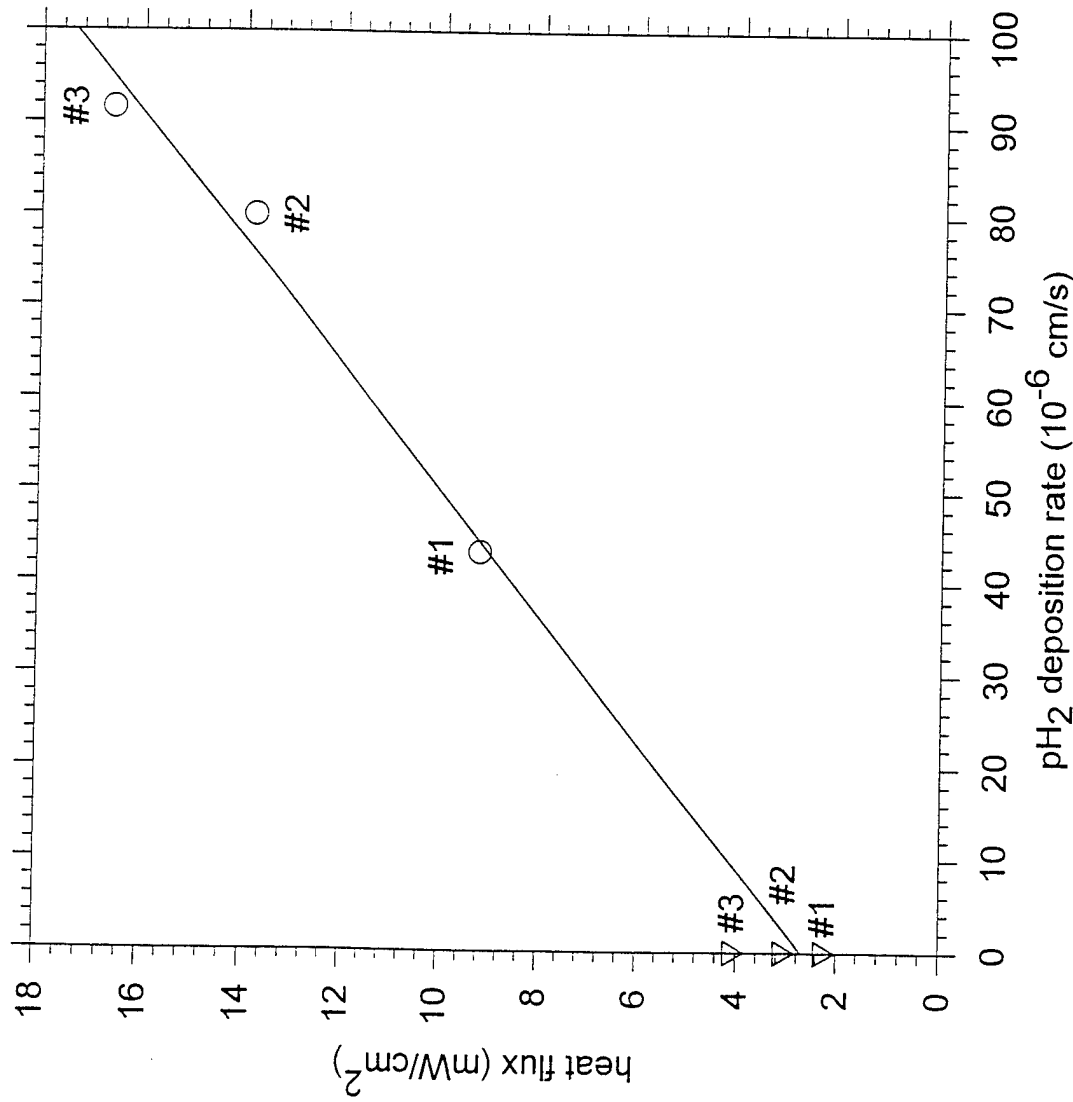
#2:
 $\Phi_{H_2} = 200$ mmol/hr
 $\dot{R} = 48$ $\mu\text{m}/\text{min}$

#1:
 $\Phi_{H_2} = 110$ mmol/hr
 $\dot{R} = 26$ $\mu\text{m}/\text{min}$

Cryostat Thermal Response



Deposition Heat Loads



heat fluxes calculated from
 $\Delta T = T_B - T_B(\text{prior dep.})$

slope of fit line \Rightarrow

$$E_{\text{dep}} = 3.3 \text{ kJ/mol}$$

compare with:

$$E_{\text{vap}} = 1.1 \text{ kJ/mol}$$

\leftarrow note post-deposition radiative(?) heat loads

pH₂ Thermal Conductivity Calculations

expt.#	$\Delta x(\text{cm})$	$\Delta T_{\text{max}}(\text{K})$	$\Delta T_{\text{min}}(\text{K})$	$(\dot{Q}/A)_{\text{max}}$	$(\dot{Q}/A)_{\text{min}}$	K_{min}	K_{max}
1	0.108	0.61	0.21	9.2	6.9	1.2	4.7
2	0.203	1.19	0.79	13.8	10.7	1.8	3.5
3	0.232	1.74	1.34	16.6	12.5	1.7	2.9

Units: \dot{Q}/A (mW/cm^2), κ ($\text{mW}/\text{cm}\cdot\text{K}$).

Summary: $\kappa = 3(\pm 2)$ $\text{mW}/\text{cm}\cdot\text{K}$, averaged over $2 < T < 5$ K range.

Comparison with Literature

Previous studies on pH_2 solids grown from the gas phase in an enclosed cell near 10 K

$$\Rightarrow \bar{\kappa} \approx 4000 \text{ mW/cm-K}$$

$$\& L_{ph} \sim 0.1 \text{ cm.}$$

$$\kappa = C v L_{ph} / 3$$

[V.G. Manzhelii, B.Ya. Gorodilov, and A.I. Krivchikov, Low Temp. Phys. 22, 131 (1996)]

Suggests $L_{ph} \sim 1 \mu\text{m}$ in our rapid vapor deposited solids.

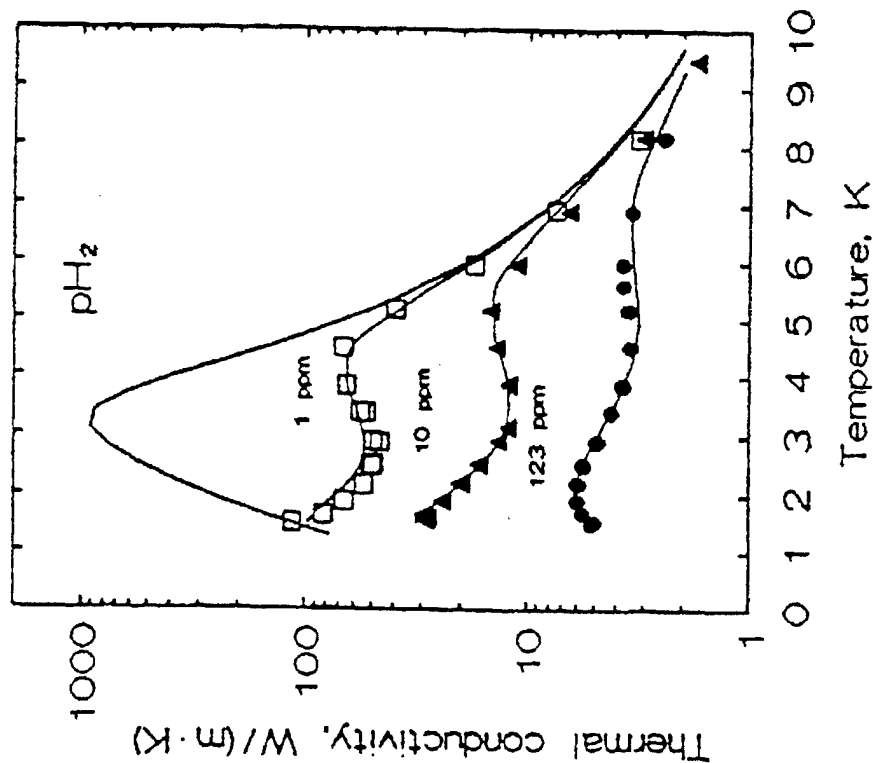


FIG. 1. Thermal conductivity of crystals of pure pH_2 and pH_2 with Ne impurity (the concentration in ppm are indicated); the solid lines are calculated results.

Summary

- * Demonstrated production of millimeters-thick transparent pH_2 solids by rapid vapor deposition.
- * Demonstrated that vapor deposited pH_2 solids are densest close-packed solids, NOT amorphous.
- * Demonstrated suitability of vapor deposited pH_2 solids as hosts for high resolution IR absorption spectroscopy of chemically interesting dopants.
- * Generalized phenomenon of dopant induced IR activity.
- * Exploited CO/pH_2 spectroscopy to probe sample temperature during deposition, and to estimate thermal conductivity.

Collaborators

- * Mr. Simon Tam and Ms. Michelle E. DeRose, AFRL/PRSP responsible for our experimental data.
- * Prof. Takamasa Momose, Kyoto U. spectroscopy of CH₄, C₆₀, and CO doped pH₂ solids.
- * Prof. Robert J. Hinde, U. Tennessee at Knoxville dopant-induced IR absorptions.
- * Prof. David T. Anderson, U. Wyoming spectroscopy of (HCl)₂ in solid pH₂.