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MEMORANDUM FOR IN-HOUSE PUBLICATIONS

FROM: PROI (TI) (STINFO) 30 Apr 98

SUBJECT: Authorization for Release of Technical Information, Control Number: AFRL-PR-ED-**TP-1998-091**
Simon Tam and Mario Fajardo "CO/pH_2 – a Molecular Thermometer"
HEDM Conference Presentation **(Statement A)**

HIGH ENERGY DENSITY MATTER CONTRACTORS CONFERENCE, Monterey, CA 20-22 May 1998.

CO/pH_2 -- a Molecular Thermometer

Simon Tam and Mario E. Fajardo
US Air Force Research Laboratory, Propulsion Directorate
(AFRL/PRSP Bldg. 8451, Edwards AFB, CA 93524-7680)

We utilize reversible temperature dependent changes in the infrared absorption spectrum of CO molecules in solid parahydrogen (pH_2) to probe the temperature profiles of the matrices during deposition. The intensity of a well-resolved absorption feature near 2135 cm^{-1} shows a monotonic increase with temperature over the 2 to 5 K range. The initial state of this transition is estimated to be 7.9(±0.5) K above the ground state of CO/pH_2. During the deposition of 100 PPM CO/pH_2 samples, we detect temperature gradients of ~ 10 K/cm in samples subjected to estimated heat loads of ~ 10 mW/cm^2. The resulting estimated thermal conductivities of ~ 1 mW/cm-K (0.1 W/m-K) are four orders of magnitude lower than the conductivity of single crystal solid pH_2, and more than an order of magnitude lower than previously measured for pH_2 solids doped with 100 PPM concentrations of heavy impurities [V.G. Manzhelli, et al., Low Temp. Phys. v22, p131 (1996)].

High Energy Density Matter (HEDM) Cryosolid Propellants

Objectives

* Trap 5% molar concentration of energetic additives in solid hydrogen.
* Demonstrate size-scaleable sample production method.

Payoffs

Increased Specific Impulse

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

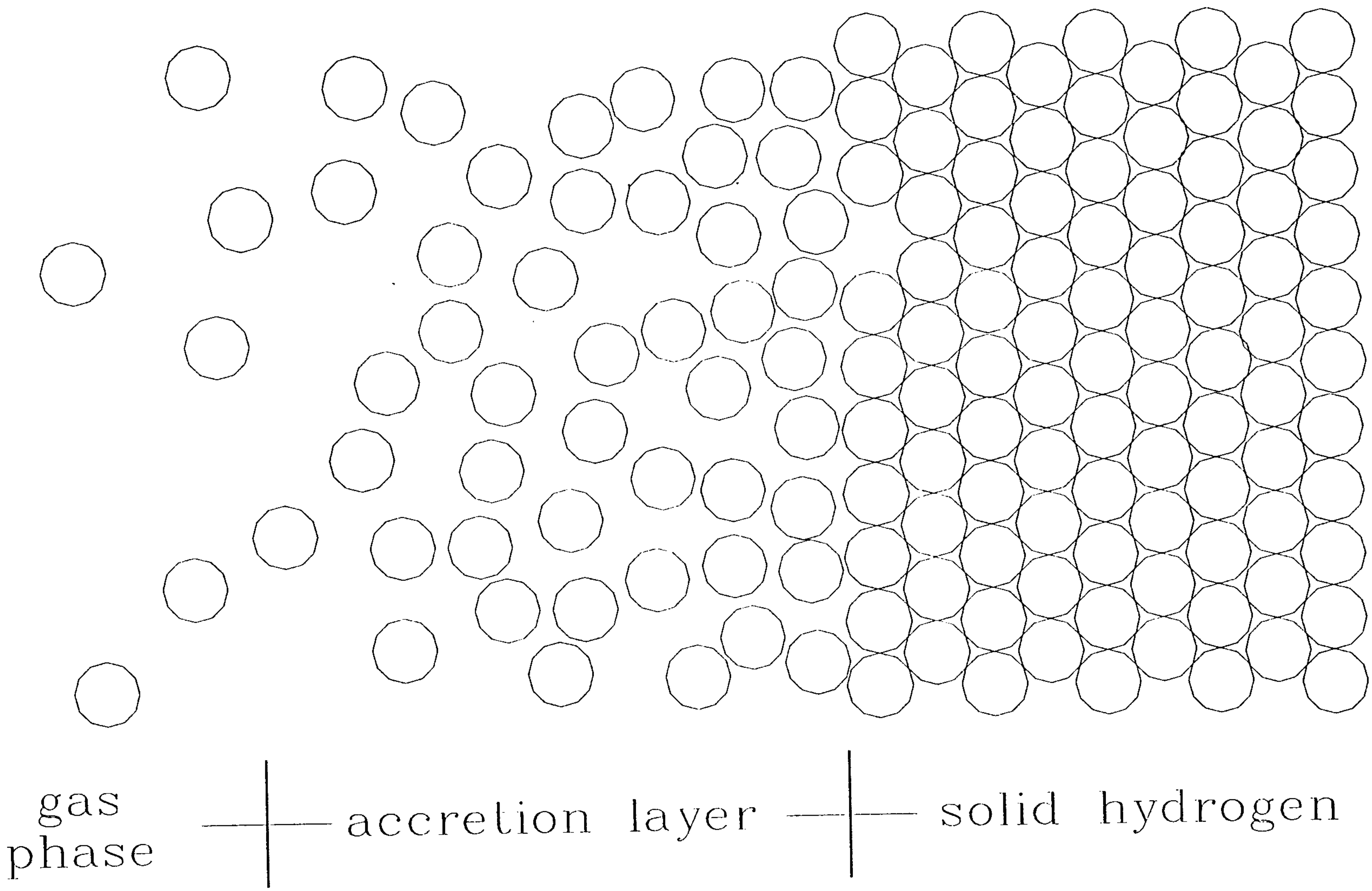
$$\text{LOX/LH2} : I_{sp} = 390 \text{ s}$$
$$5\%\ B/H_2 + \text{LOX} : I_{sp} = 500 \text{ s } (+30\%)^*$$

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

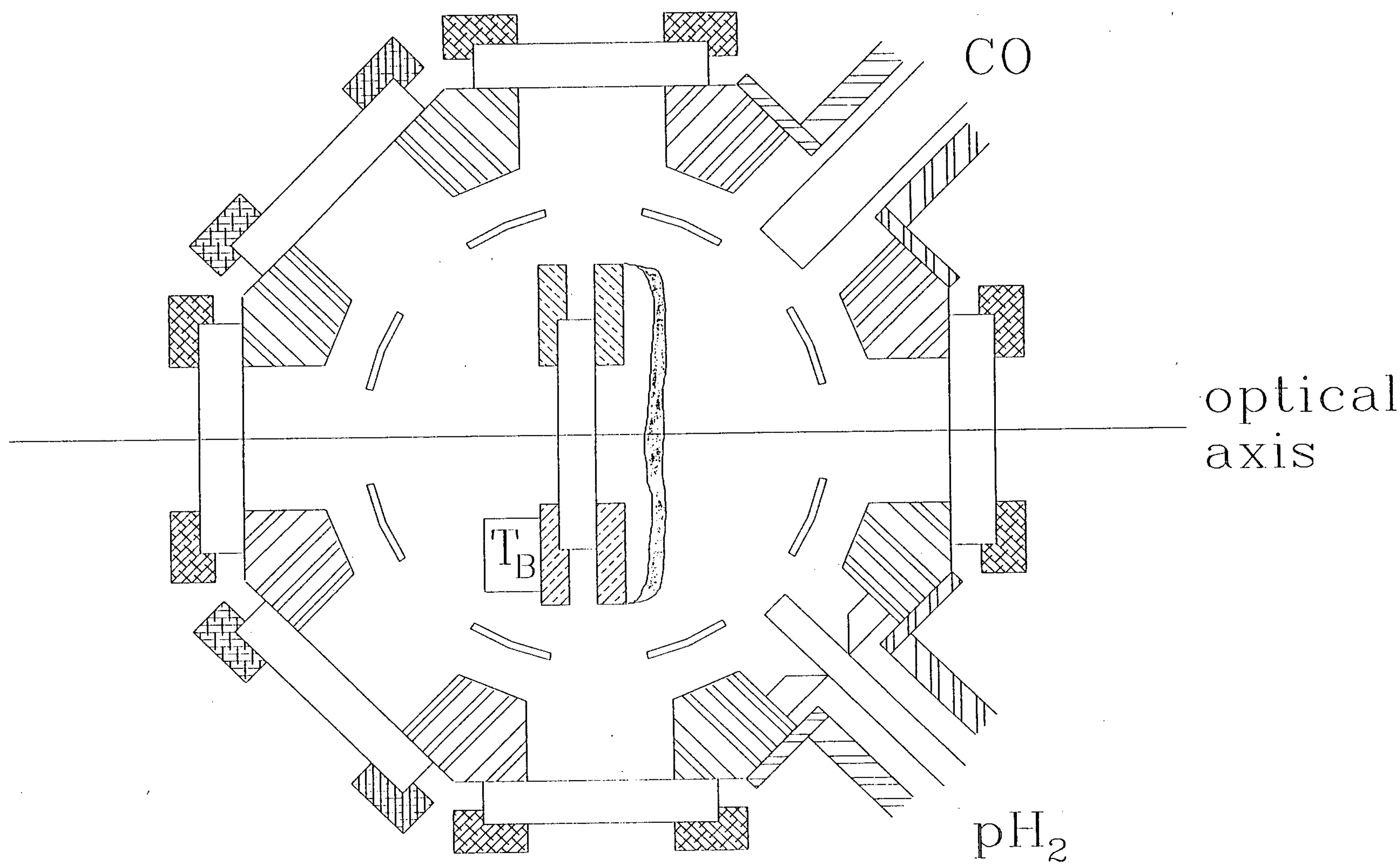
Greater Propellant Density

liquid H_2 : $\rho = 0.070$ g/cm^3
solid H_2 : $\rho = 0.087$ g/cm^3 (+25%)
50/50 liquid He/solid H_2 : $\rho = 0.105$ g/cm^3 (+50%)

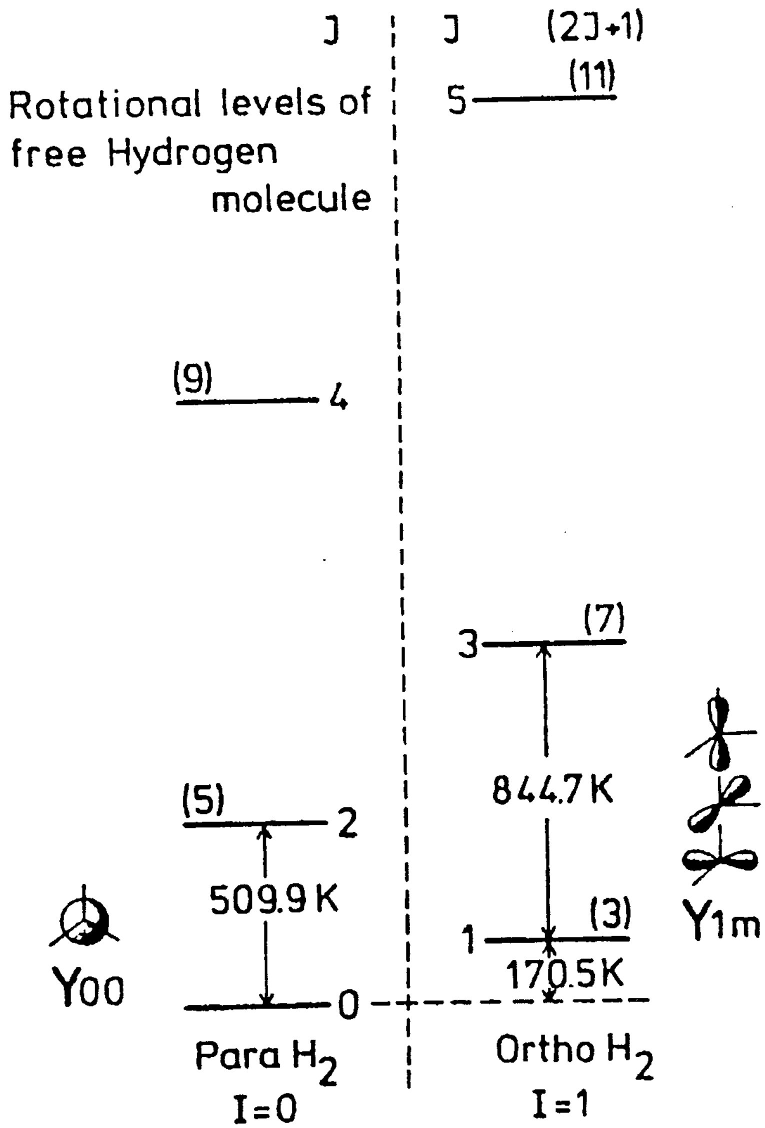
Deposition Cartoon



Experimental Diagram – Sample Deposition

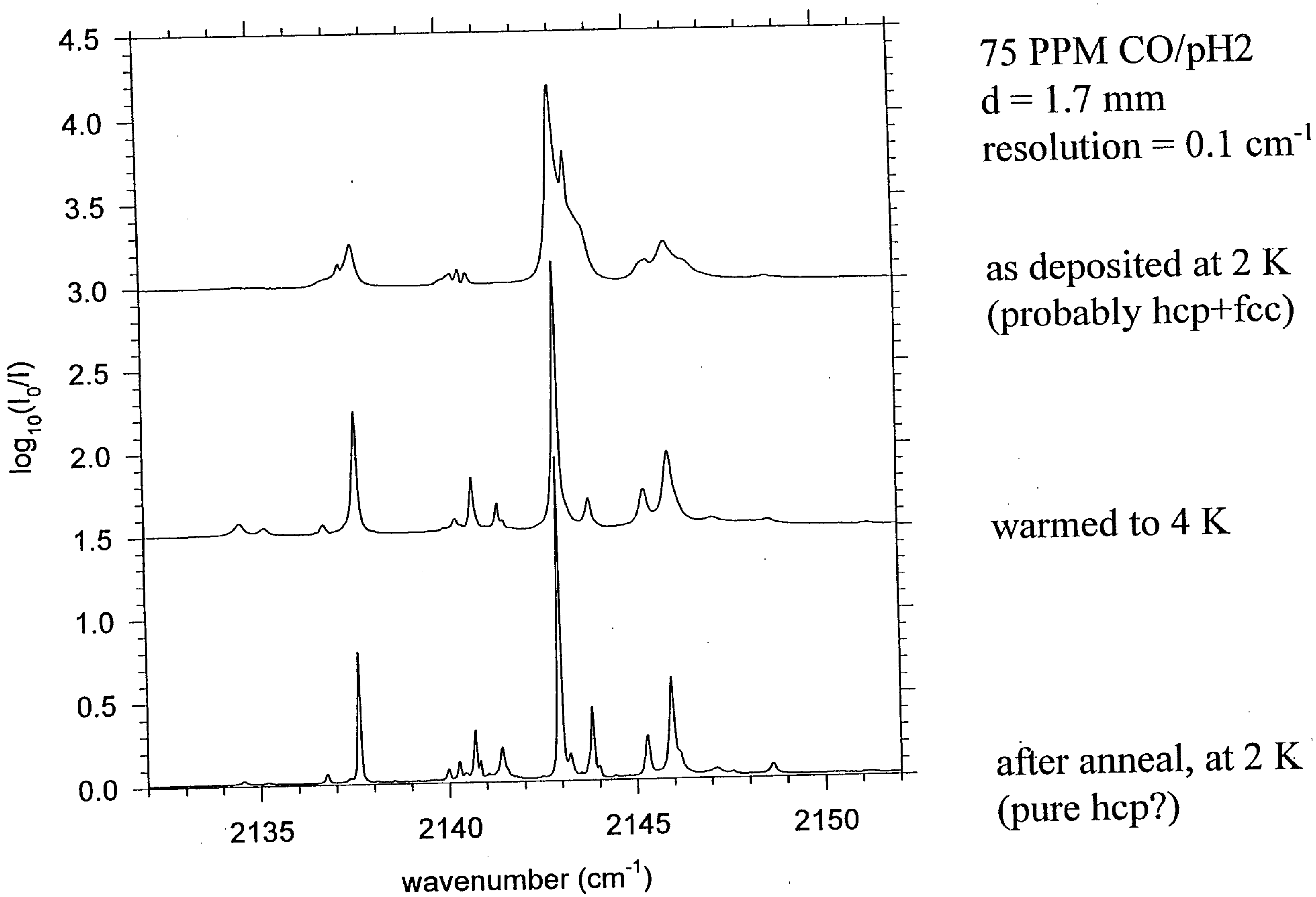


Ortho and Para Hydrogen

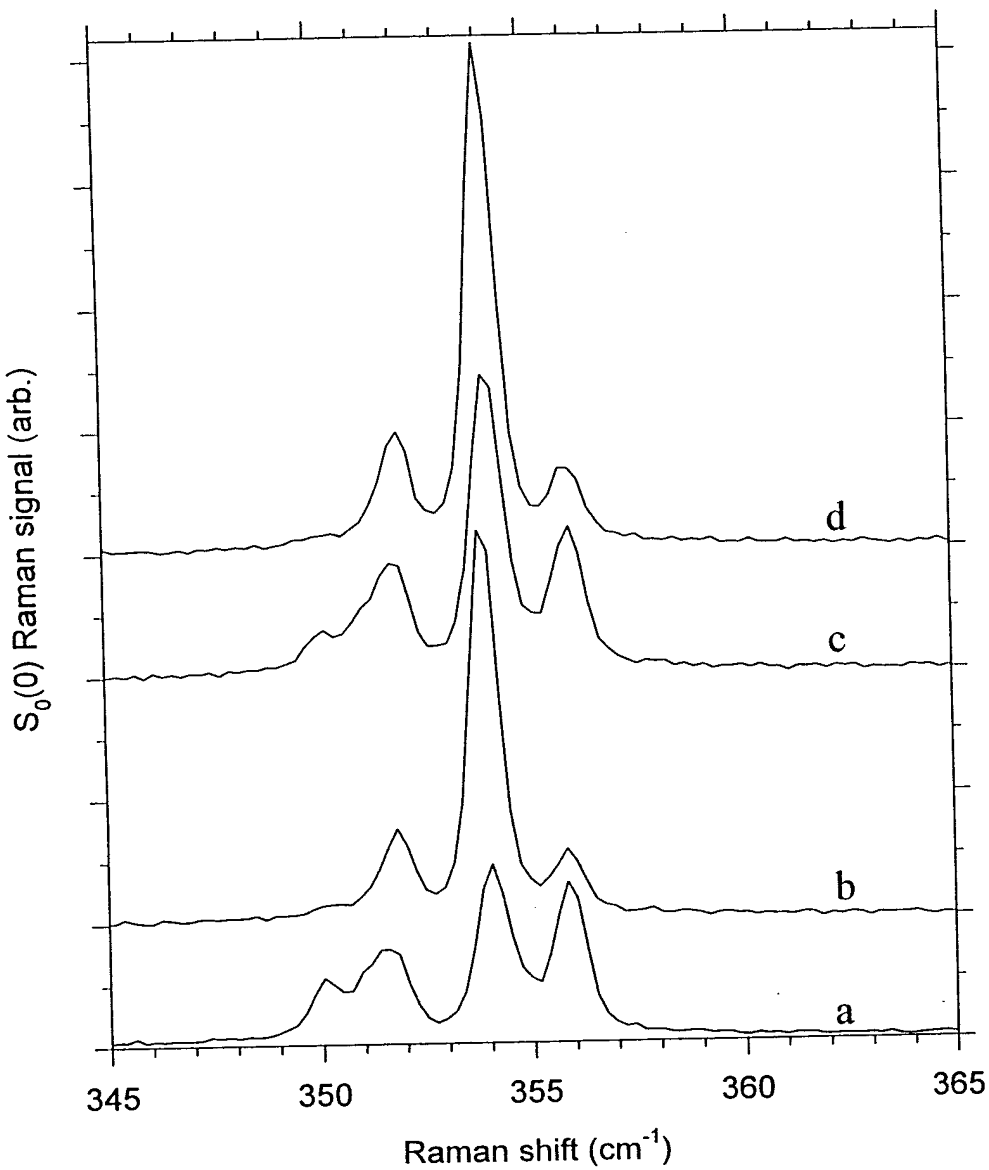


I.F. Silvera,
Rev. Mod. Phys. **52**, 393 (1980).

IR Absorptions of CO/pH_2



Raman Spectra of 4.5 and 6 mm Thick Parahydrogen Solids



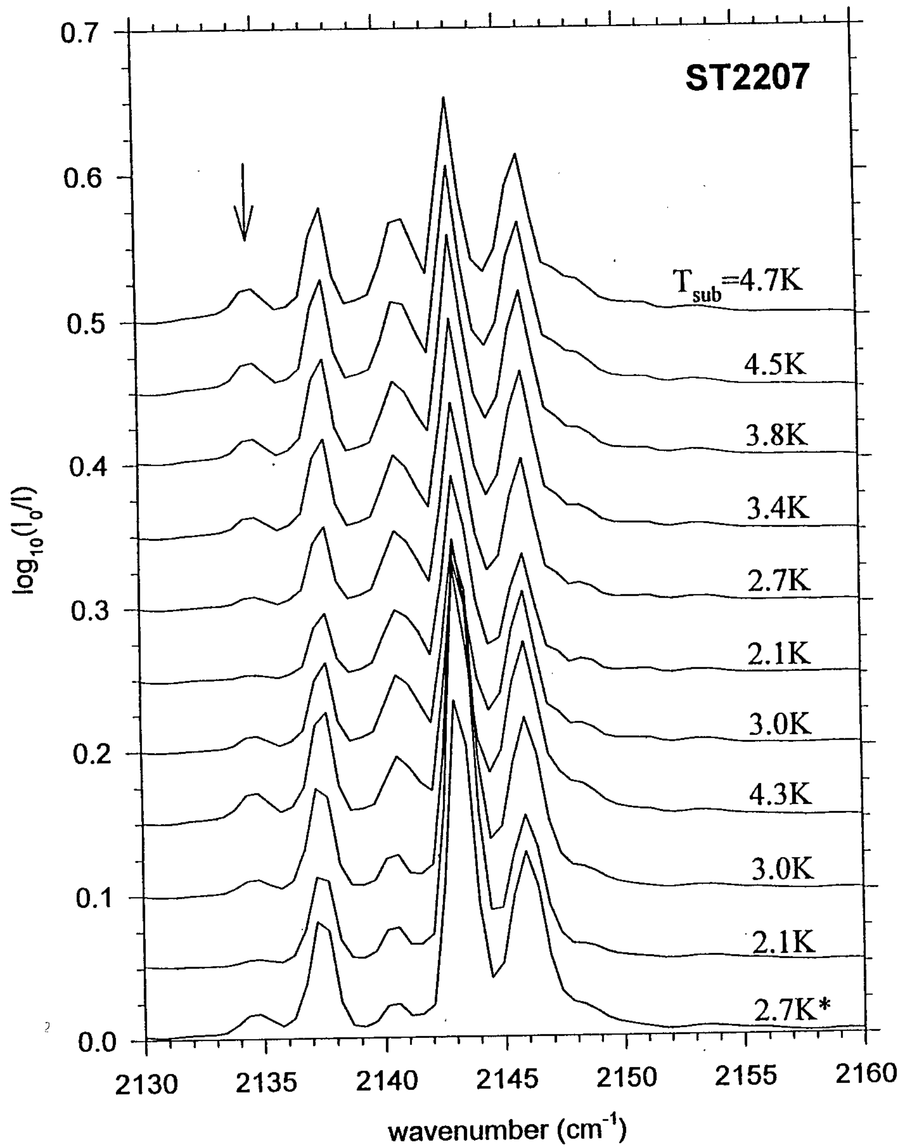
Mixed hcp/fcc as-deposited structure, anneals to hcp; compare with:

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).

Reversible Temperature Dependence of CO/pH_2 Spectrum

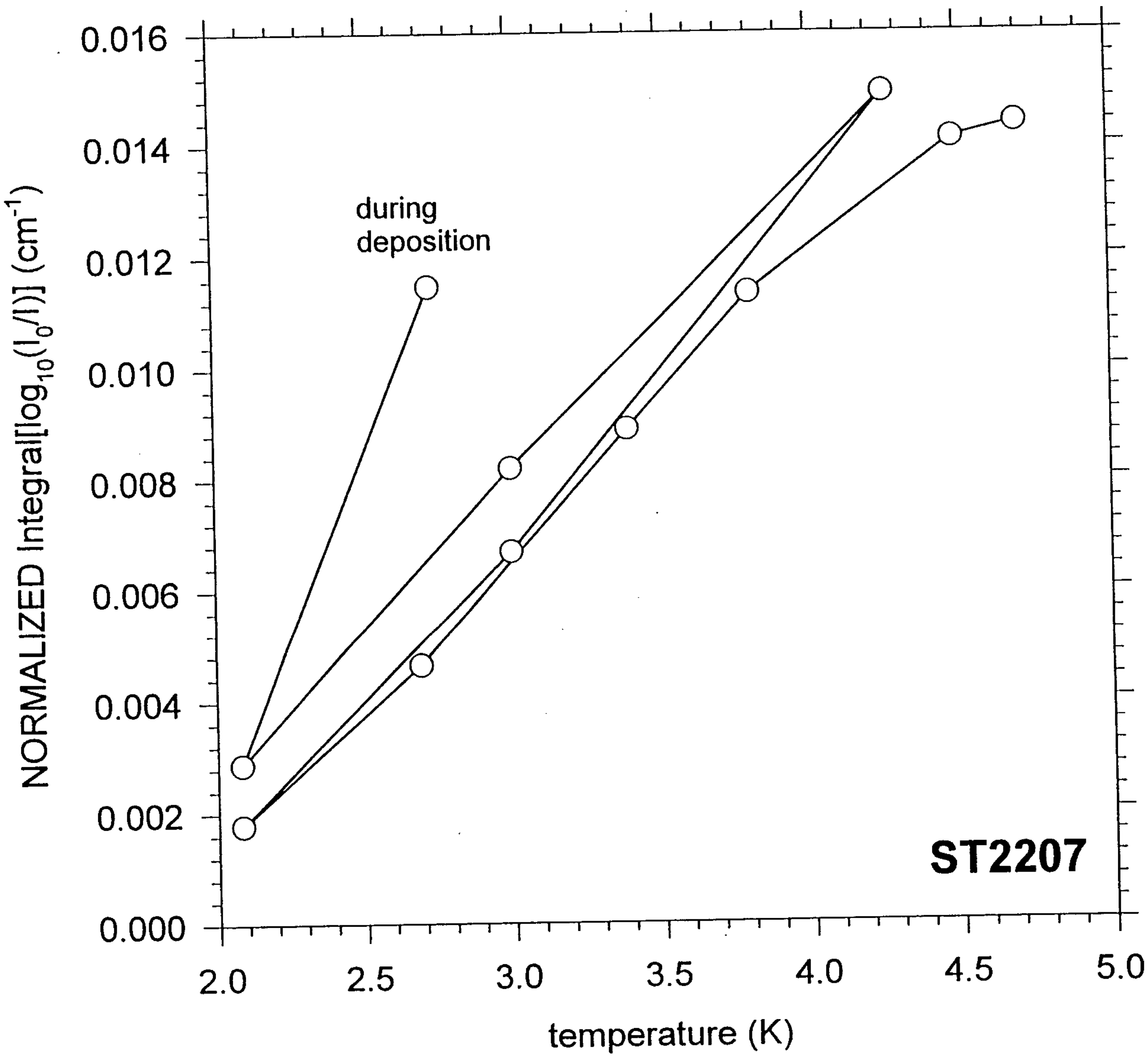


time sequence from bottom to top

lower trace shows spectrum obtained during deposition, other spectra obtained after deposition at various substrate temperatures

arrow indicates "2135 cm^{-1} band"

Intensity of 2135 cm^{-1} band vs. Temperature

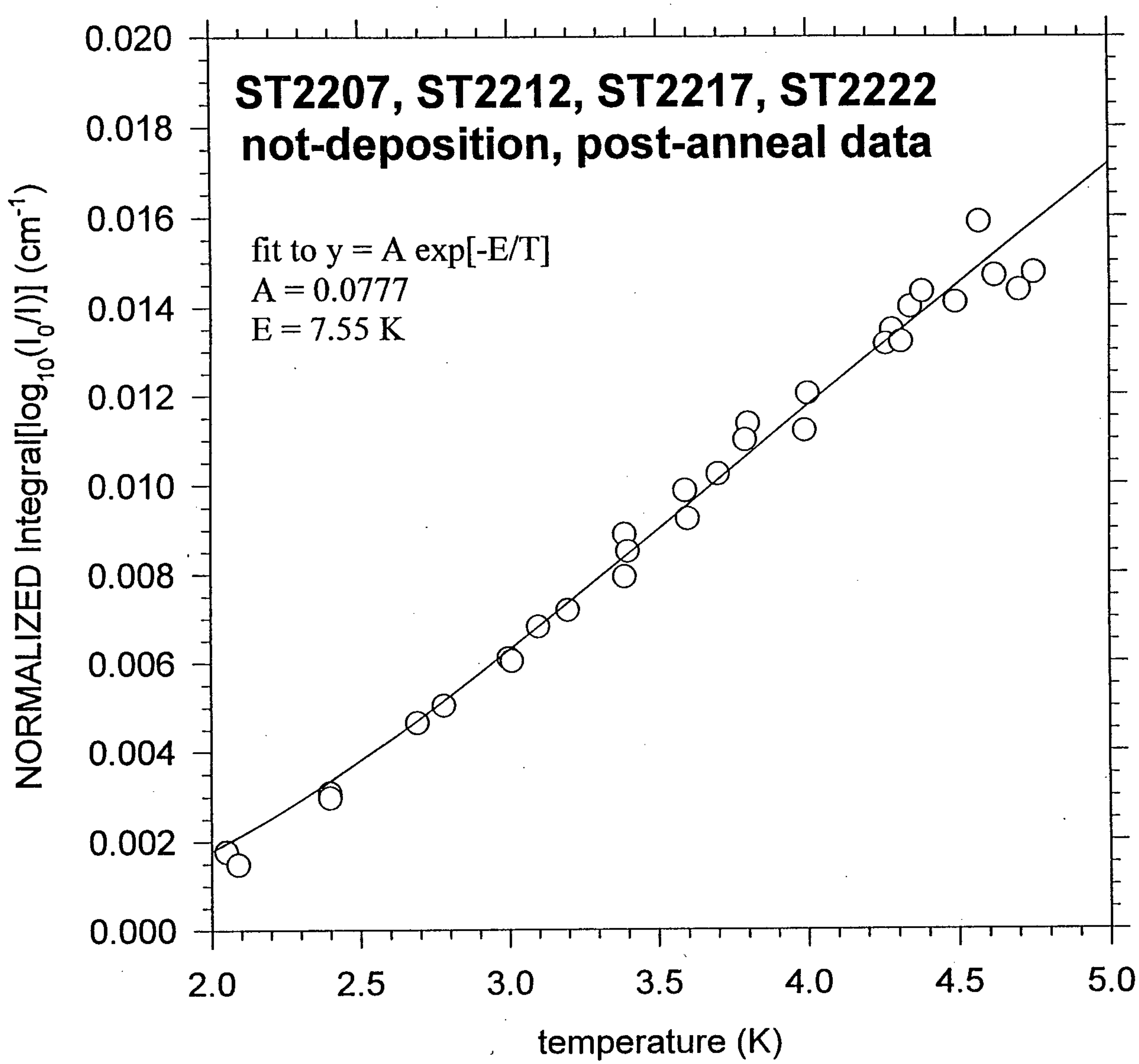


0.9 mm CO/pH_2 layer deposited on top of 1.9 mm pure pH_2 layer.

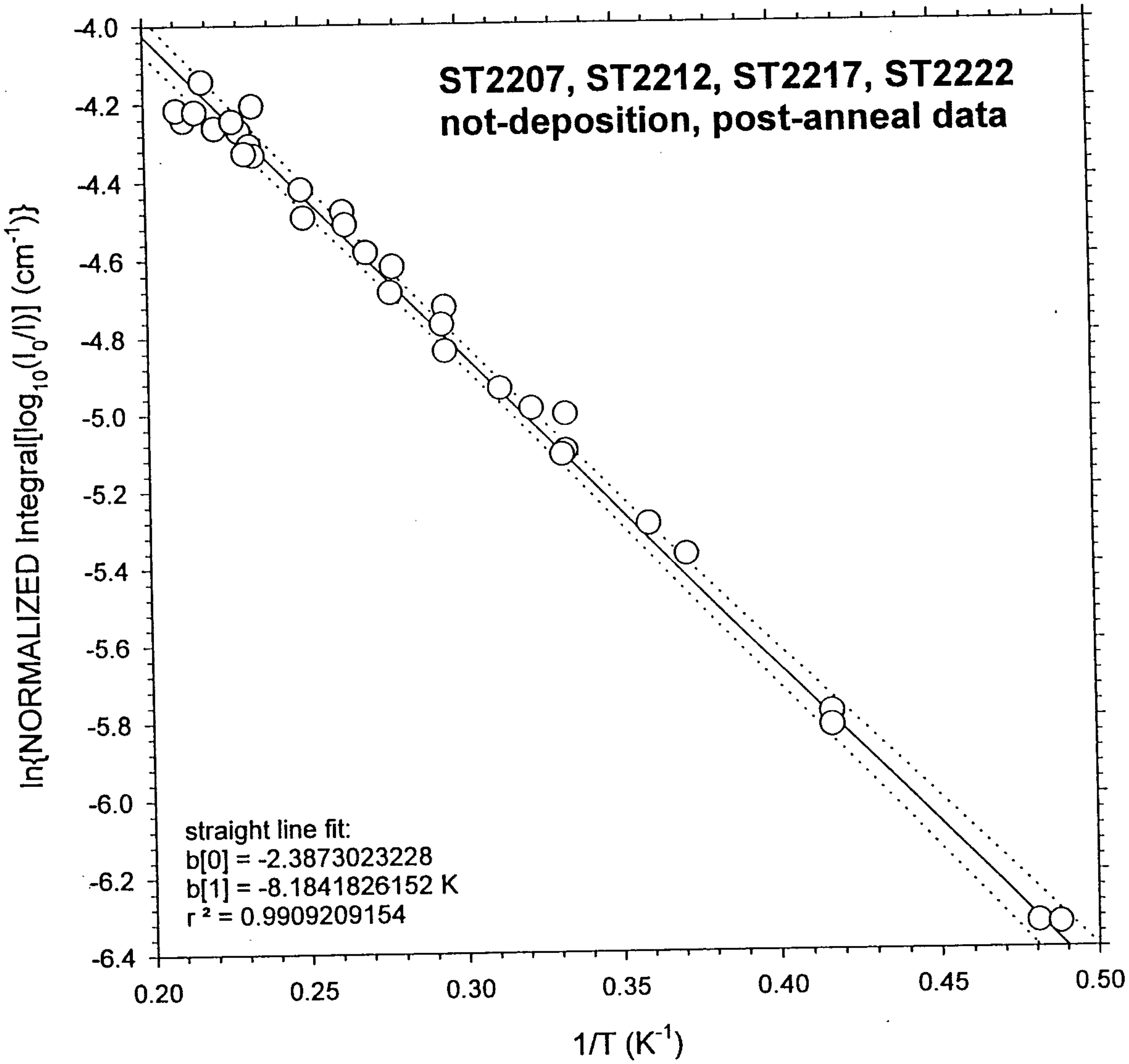
Integrated intensity of 2135 cm^{-1} band normalized to integral over entire CO band for as-deposited sample.

Irreversible shift upon annealing attributed to fcc $\rightarrow$ hcp conversion (introduces T measurement error $\approx +0.2$ K).

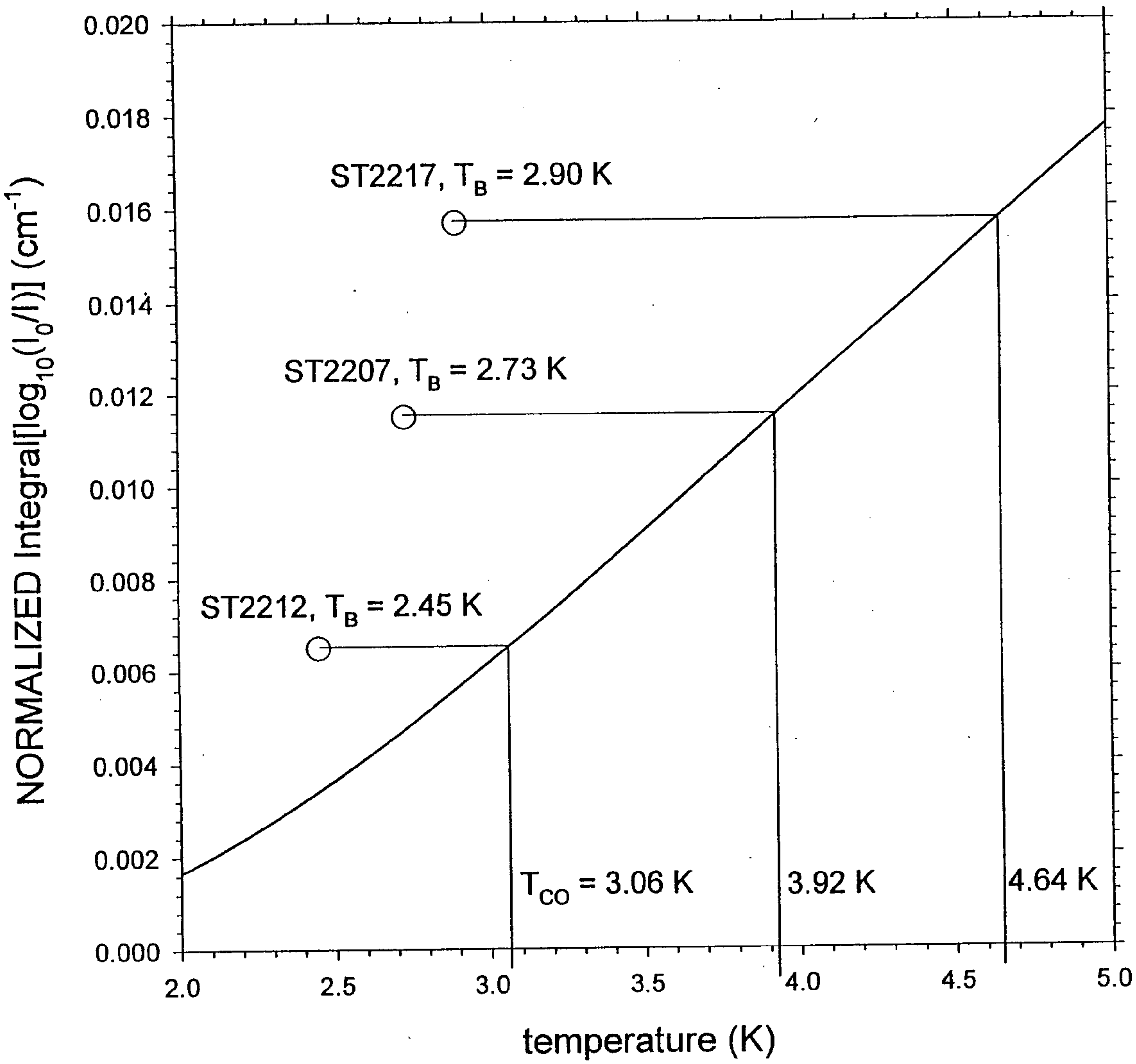
CO/pH_2 Calibration vs. Si Diodes



“Van’t Hoff Plot”



Substrate and Bulk Hydrogen Temperatures During Deposition



"thermometer curve:"

$y = A \exp[-E/T]$

$A = 0.08602$

$E = 7.896$ K

Prior to depositions

$T_B = 1.89(\pm 0.02)$ K

After depositions

$T_B = 2.08(\pm 0.05)$ K

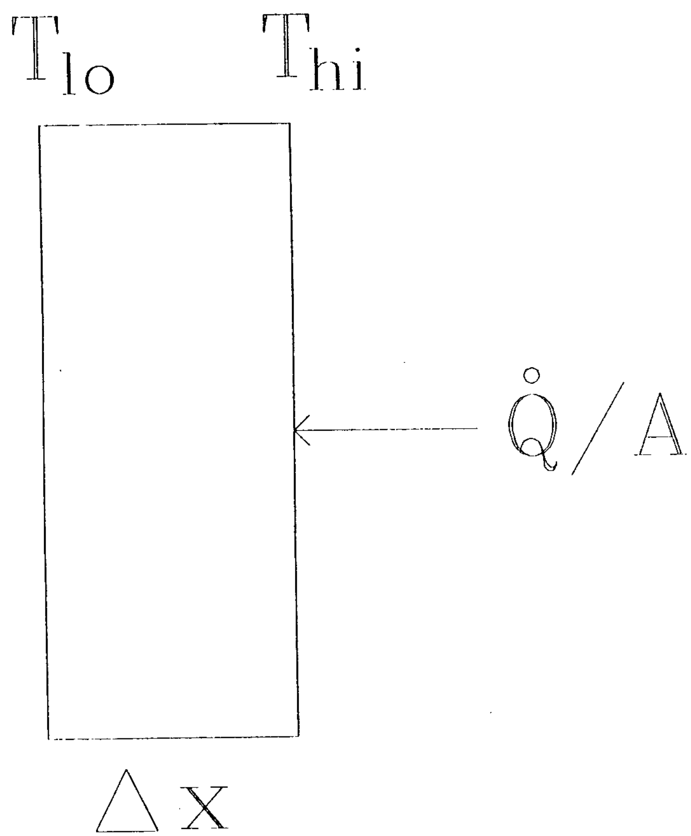
pH_2 inlet & deposition rates:

ST2212: 110 mmol/hr
26 μm/min

ST2207: 200 mmol/hr
48 μm/min

ST2217: 240 mmol/hr
55 μm/min

1-D Heat Transfer



$\dot{Q}/A = - \kappa \, \Delta T/\Delta x$

$\Delta T = T_{hi} - T_{lo}$

κ is the thermal conductivity

units:

$\dot{Q}/A$ (mW/cm^2)

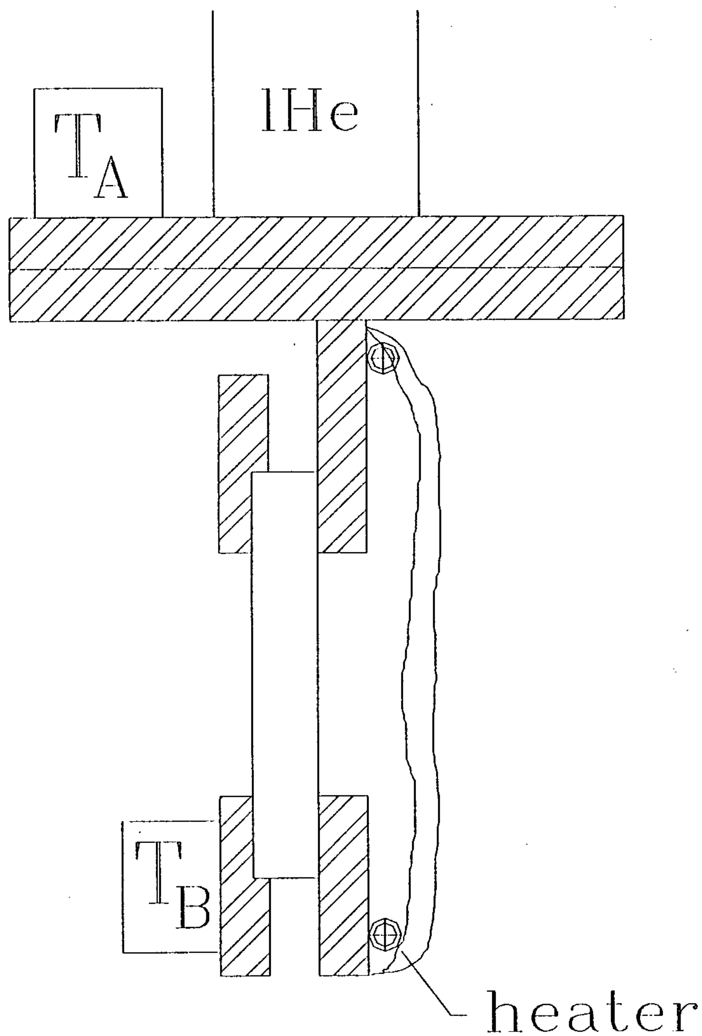
ΔT (K)

Δx (cm)

κ (mW/cm-K)

note: 1 mW/cm-K = 0.1 W/m-K

Experimental Diagram – Heat Flux Calibration

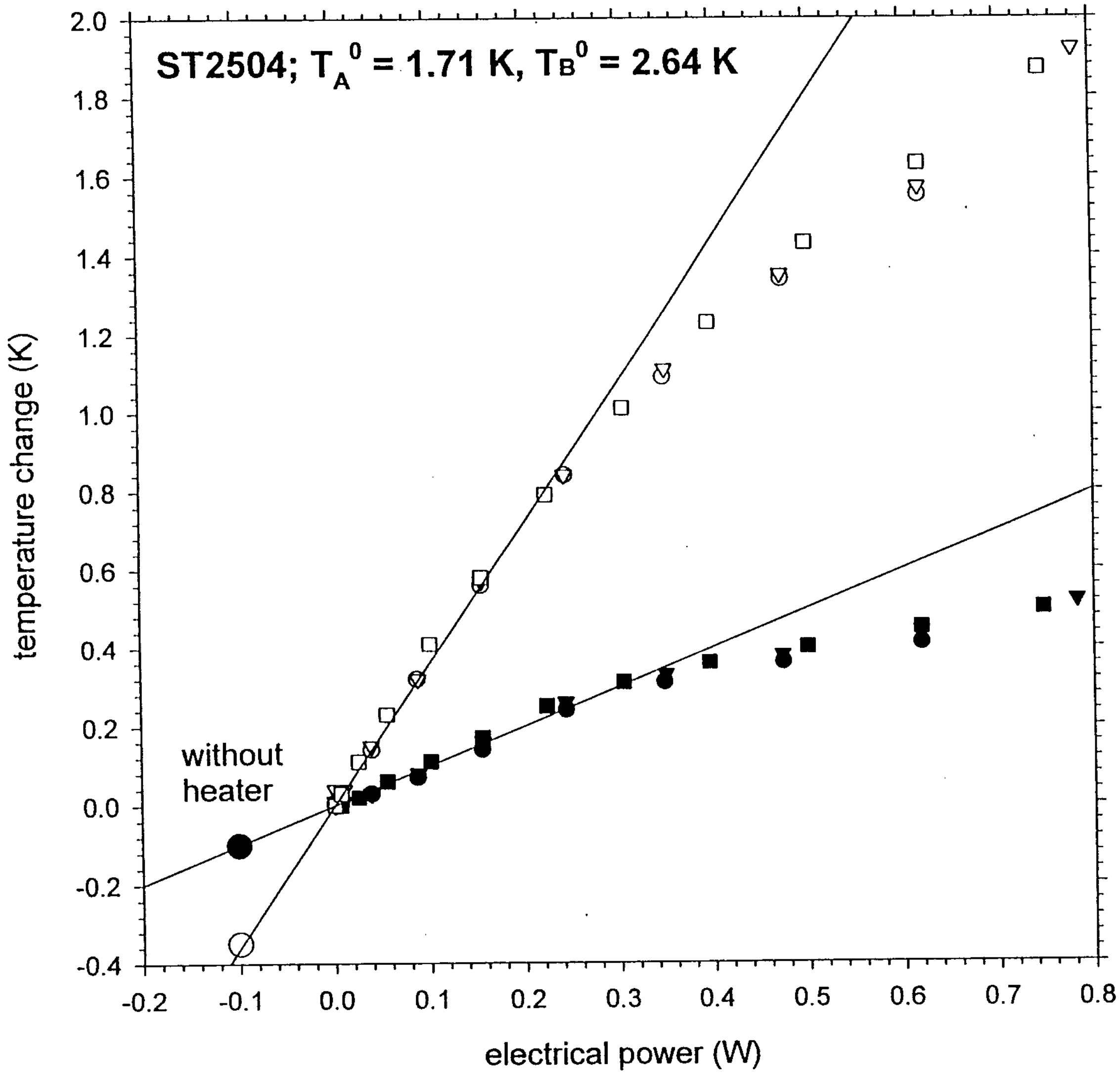


Mimic deposition heat load on substrate holder by using an electrical heater (loop of nichrome wire glued to substrate holder).

Monitor response of Si diode temperature sensors at positions A and B.

Match observed temperature rises during electrical heating and during depositions to estimate heat fluxes during depositions.

Thermal Response of lHe Cryostat

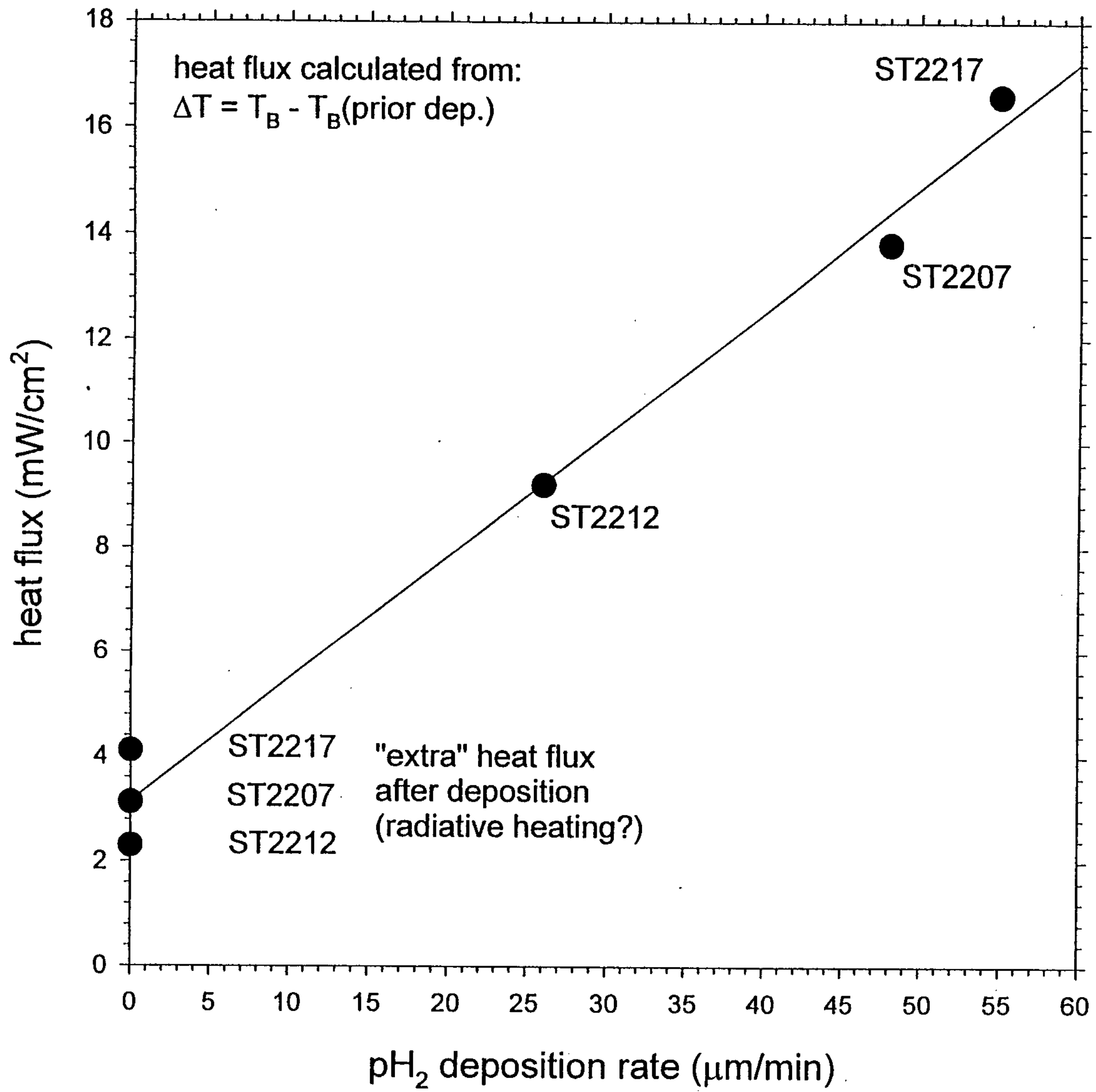


T_A closed symbols
T_B open symbols

Slopes:
T_A: 1.0 K/W
T_B: 3.6 K/W

Minimum temperatures without electrical heater fit same trend assuming 100 mW heat load through phosphor-bronze leads.

Calculated Heat Flux vs. pH_2 Deposition Rate



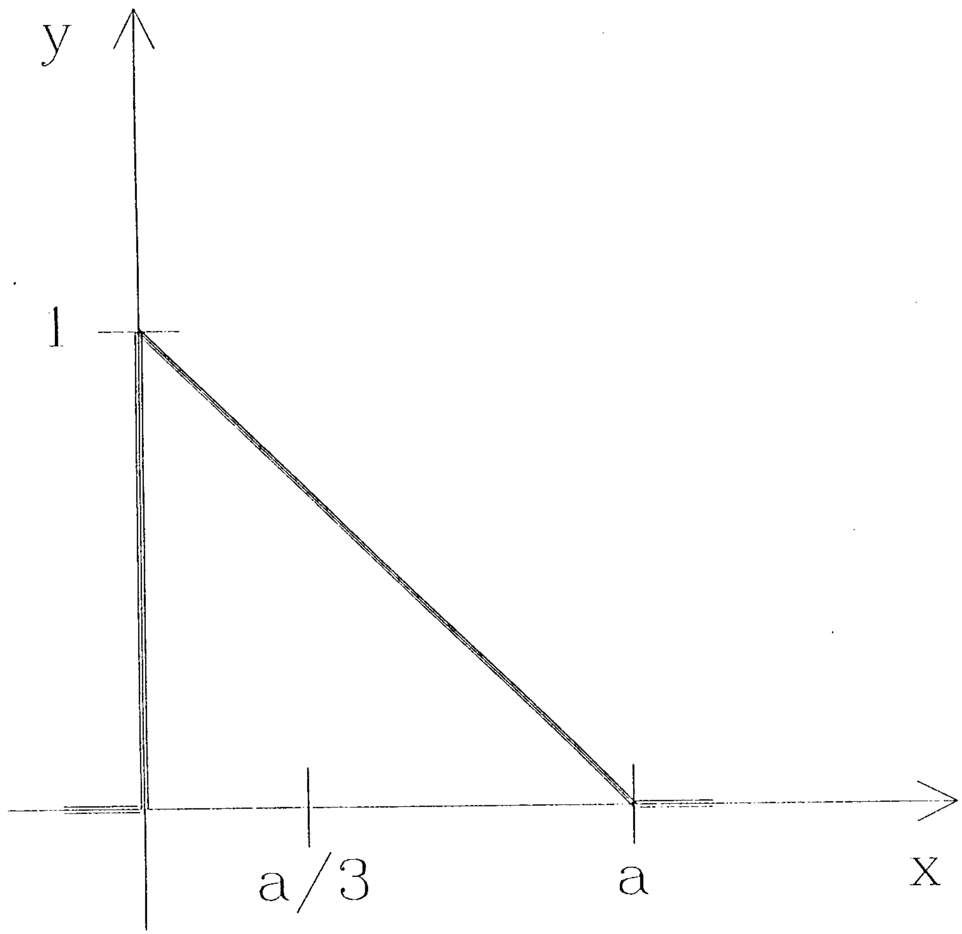
Total deposition heat fluxes:
ST2212 9.2 mW/cm^2
ST2207 13.8 mW/cm^2
ST2217 16.6 mW/cm^2

Total – extra:
ST2212 6.9 mW/cm^2
ST2207 10.7 mW/cm^2
ST2217 12.5 mW/cm^2

Slope of fit line ⇒
$E_{dep}(pH_2)$ = 3.25 kJ/mol
(390 K)

Compare with:
$E_{sub}(pH_2)$ = 0.9 kJ/mol
(110 K)

Time-Weighted Average Position of CO Thermometer



$$y = 1 - x/a$$

$$\bar{x} = \int xydx \,/\, \int ydx$$

$$= \int_0^a (x - x^2/a)dx \,/\, \int_0^a (1 - x/a)dx$$

$$= (x^2/2 - x^3/3a)\Big|_0^a \,/\, (x - x^2/2a)\Big|_0^a$$

$$= (a^2/2 - a^2/3) \,/\, (a - a/2)$$

$$= a^2/6 \,/\, a/2$$

$$= a/3$$

Thermal Conductivity of Rapid Vapor Deposited pH_2

Expt.	$[T_{CO} - T_B]$ (K)	Δx (cm)	$\dot{Q}/A$ (mW/cm^2)	κ (mW/cm-K)	κ (W/m-K)
ST2212	0.61	0.12	9.2	1.8	0.18
ST2207	1.19	0.22	13.8	2.6	0.26
ST2217	1.74	0.25	16.6	2.4	0.24

Expt.	$[T_{CO} - T_B]$ (K)	Δx (cm)	$\dot{Q}/A$ (mW/cm^2)	κ (mW/cm-K)	κ (W/m-K)
ST2212	0.61	0.12	6.9	1.4	0.14
ST2207	1.19	0.22	10.7	2.0	0.20
ST2217	1.74	0.25	12.5	1.8	0.18

Summary

Absorption spectrum of ~100 PPM CO/pH_2 shows reversible temperature dependent changes which can be used to measure the temperature of the bulk pH_2 during sample deposition.

During a typical rapid deposition ($R \approx 50$ μm/min), the substrate temperature rises about 1 K, and the pH_2 bulk temperature rises about another 1 K in ~0.1 cm thick samples.

Heat flux during a typical rapid deposition is ~ 10 mW/cm^2. This value is about 3x larger than the lower limit estimated from the heat of sublimation of solid pH_2.

Calculated thermal conductivities are ~ 1 mW/cm-K, about an order of magnitude smaller than previously measured for doped samples grown in an enclosed cell near 10 K.

Our lower thermal conductivities remain unexplained; speculations include:

- polycrystalline nature of our samples,
- random-stacked close-packed microscopic structure,
- systematic errors in our measurements.

Future efforts will include a more careful analysis of possible errors due to radiative heating and other effects.