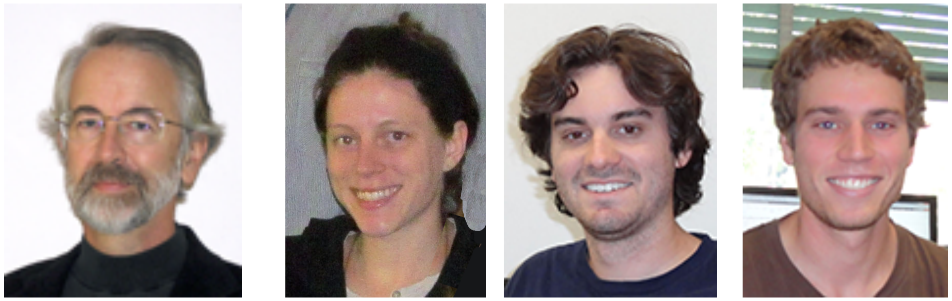
1) Gas adsorption studies, and
2) Motions of ions and molecules in crystals and on nanostructured surfaces

Brent Fultz, Sally Tracy, Max Murialdo, Nick Stadie



$\langle \mathrm{AP} | \hat{h} | \mathrm{MS} \rangle$

Dept. of Applied Physics and
Materials Science
California Institute of Technology

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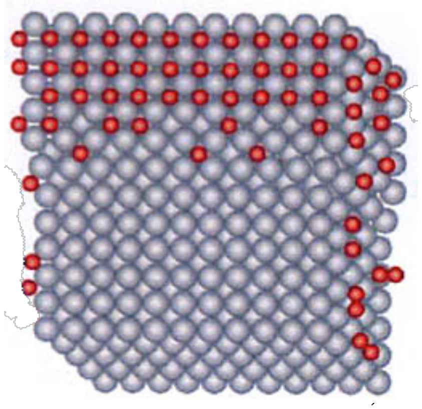
1) Gas Physisorption
   nanostructured surfaces, gases at high pressure
   technical comments about measurements

2) Jump Mechanisms — use pressure to determine V_A
   transient structure for the jump
   polarons, ions, and molecules

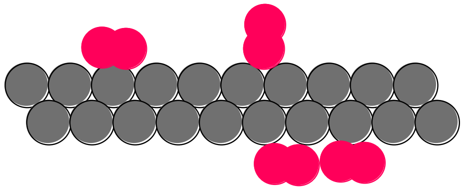
Sorption Methods for Hydrogen Storage

ABsorption (chemisorption)



Something new in bcc VTiNiCr

ADsorption (physisorption)



Graphene from graphite oxide
Nanostructured surfaces

Adsorption Isotherms *f*(*T*,*P*)

For a fixed temperature, the probability that a surface site is occupied is

$$f_{\mathrm{ad}} = \frac{e^{(\mu-\varepsilon)/k_BT}}{1+e^{(\mu-\varepsilon)/k_BT}}, \tag{16.26}$$

two possibilities –

empty site (with Gibbs factor $e^0 = 1$)
site with an adsorbed molecule (with Gibbs factor $e^{(\mu-\varepsilon)/k_BT}$)

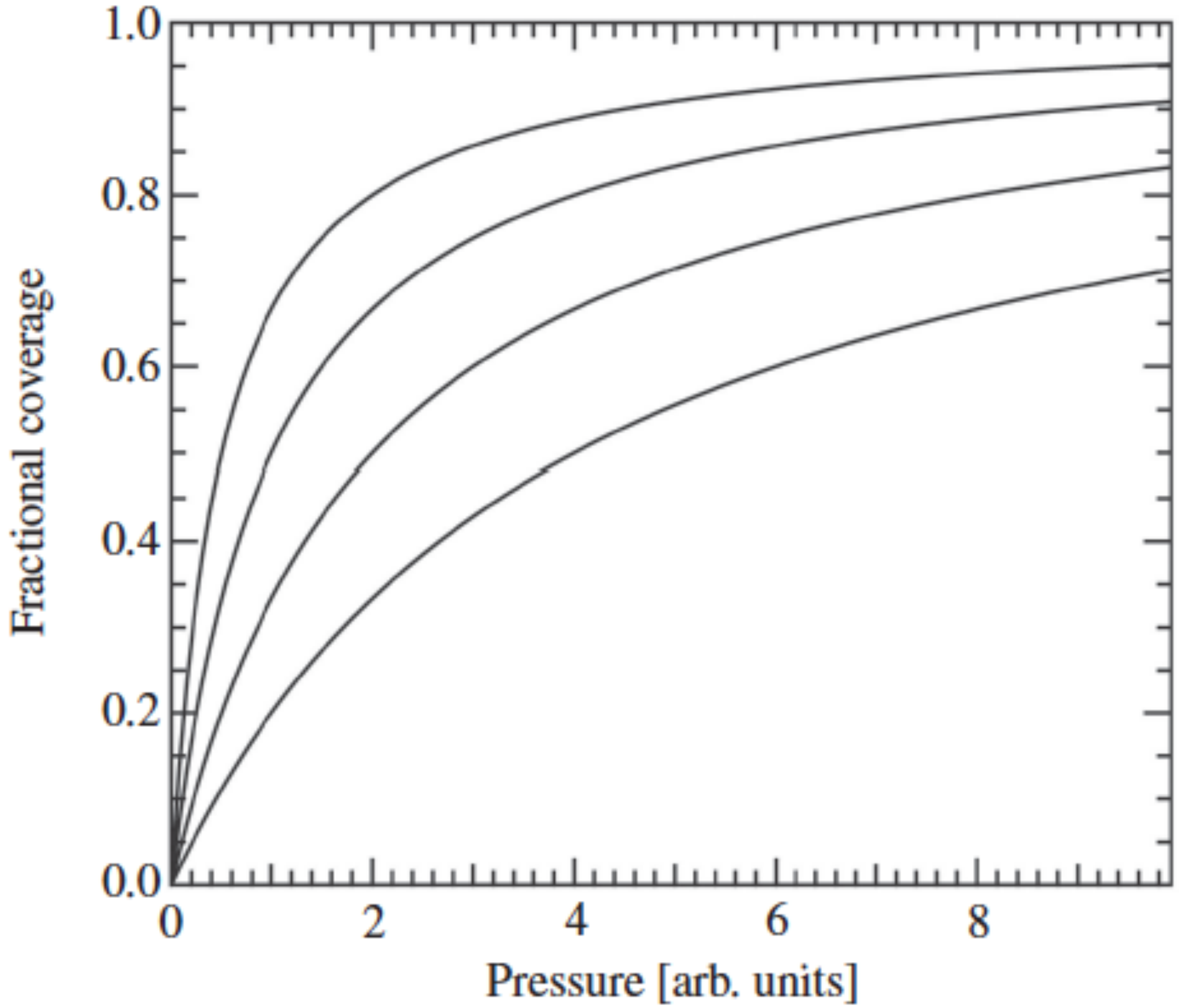
Equilibrium: chemical potential of adsorbed molecule equals that of a molecule in the gas. Get chemical potential of ideal gas:

$$e^{\mu/k_BT} = \frac{N V_Q}{V}$$

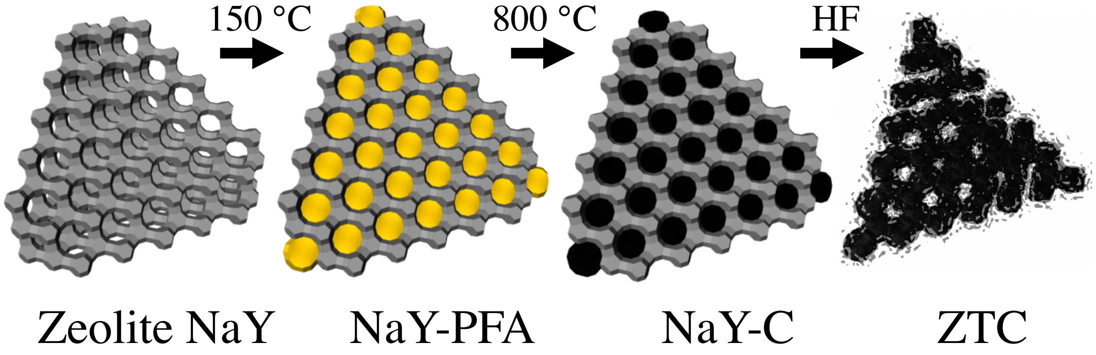
$$pV = Nk_BT$$

$$f_{\mathrm{ad}} = \frac{p}{\frac{k_BT}{V_Q}e^{\varepsilon/k_BT} + p} \qquad p_0(T) \equiv \frac{k_BT}{V_Q}e^{\varepsilon/k_BT} \qquad \boxed{f_{\mathrm{ad}} = \frac{p}{p_0(T)+p}}$$

Langmuir isotherms for four values of p_0 $\quad f_{\text{ad}} = \dfrac{p}{p_0(T) + p}$



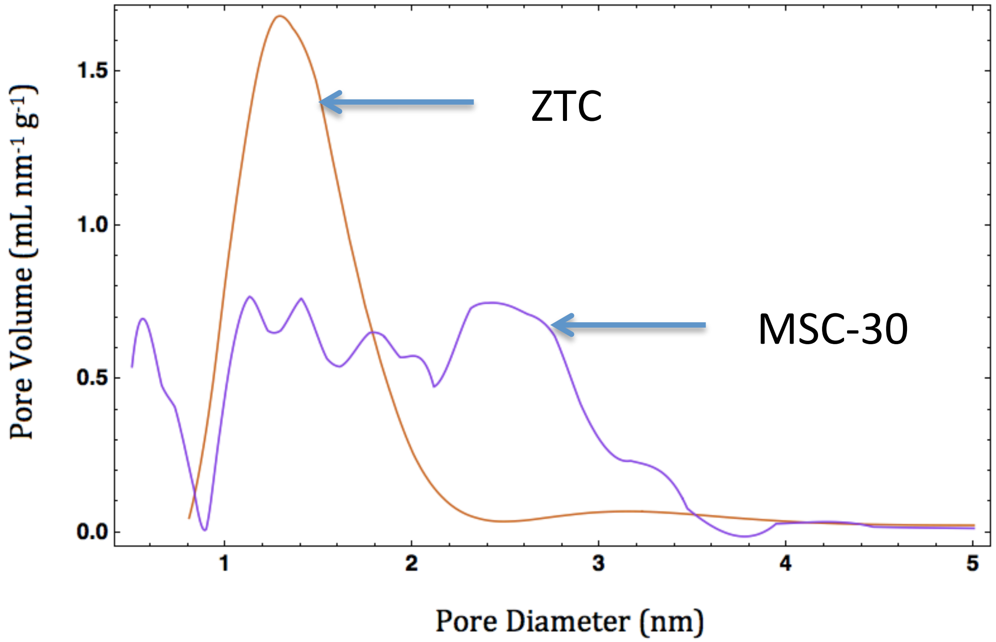
Tuning Physisorption Thermodynamics with Nanostructured Surfaces



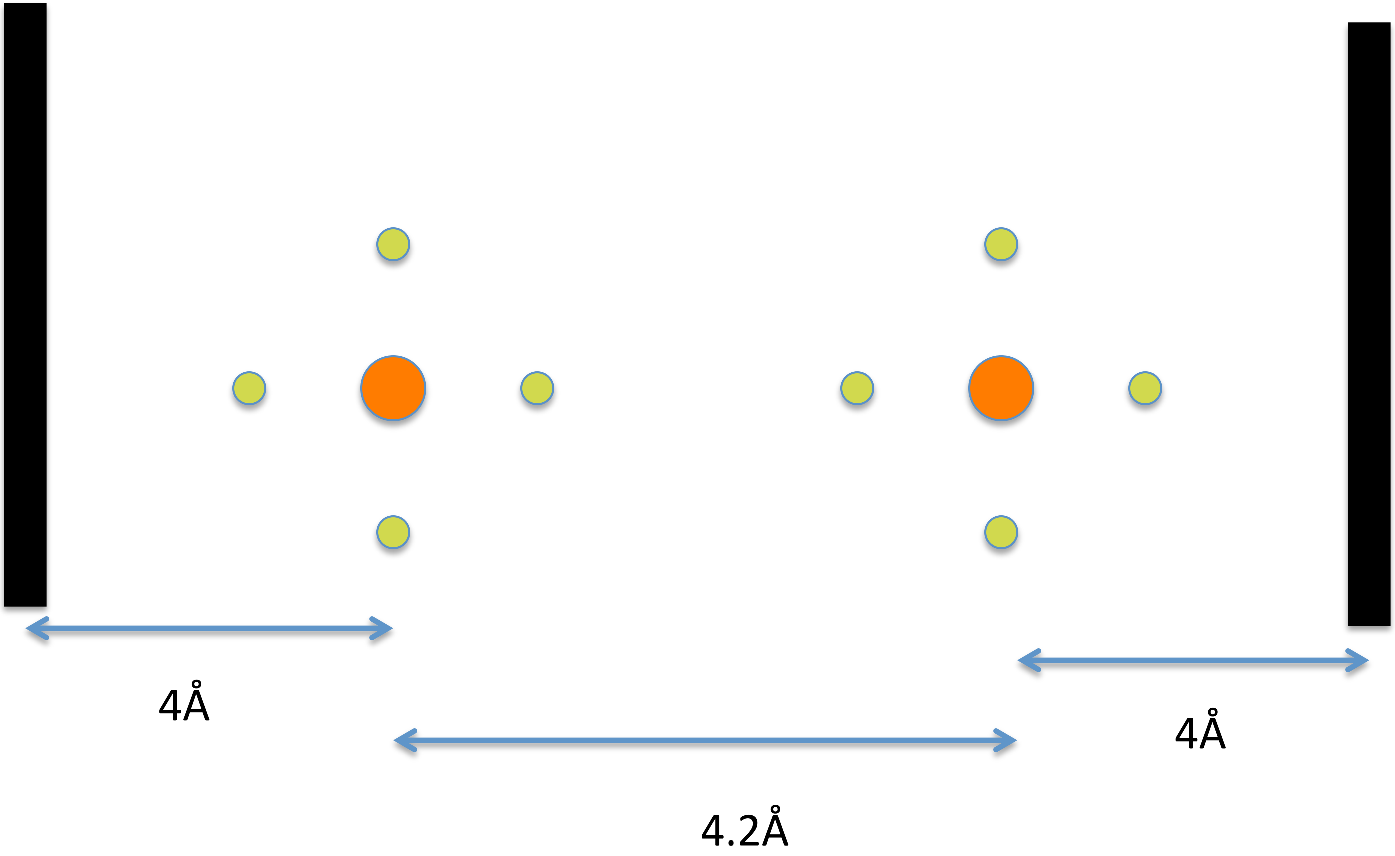
A porous material surface enhanced non-ideal gas interactions between methane molecules at high pressures.

Adsorbent Properties

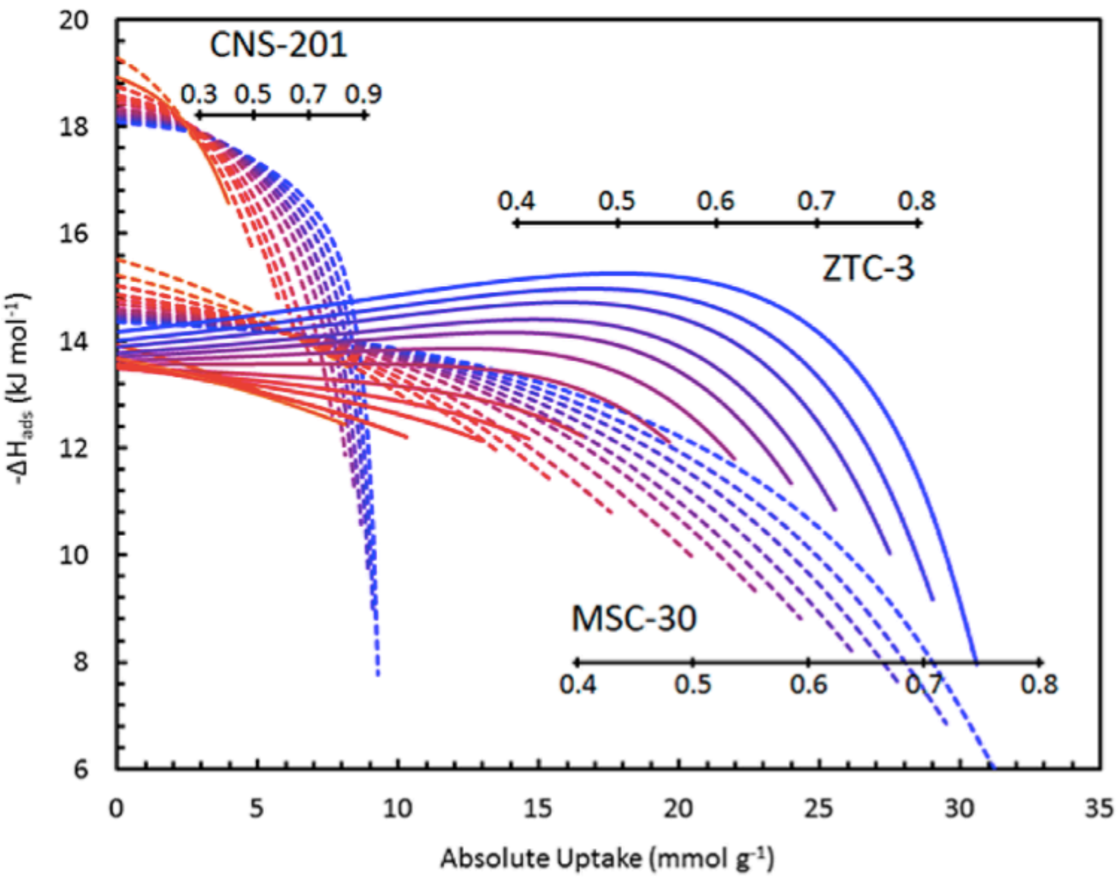
	MSC-30	ZTC-3
Description:	commercial superactivated carbon	zeolite-templated carbon
BET Surface Area ($m^2\ g^{-1}$)	3244 ± 28	3591 ± 60
Mean Pore Width (nm)	2.2 (broad)	1.2 (sharp)



Methane Intermolecular Interactions on Nanostructured Surface

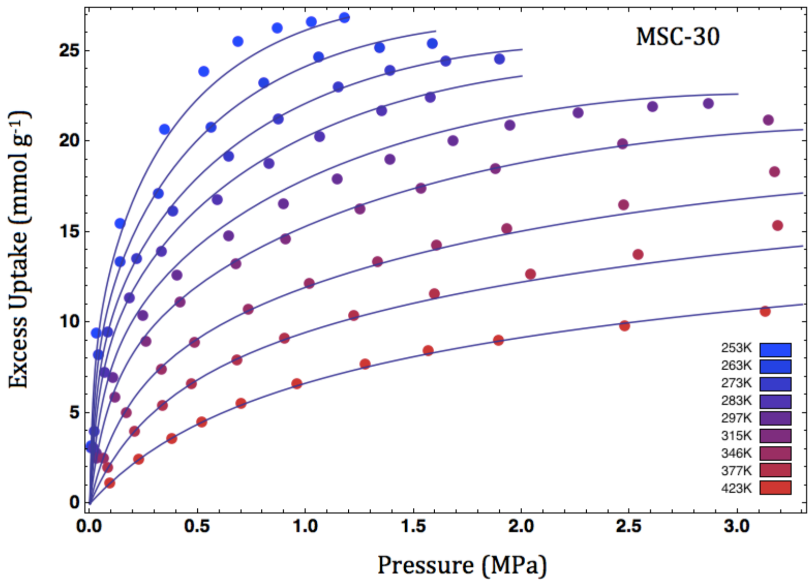


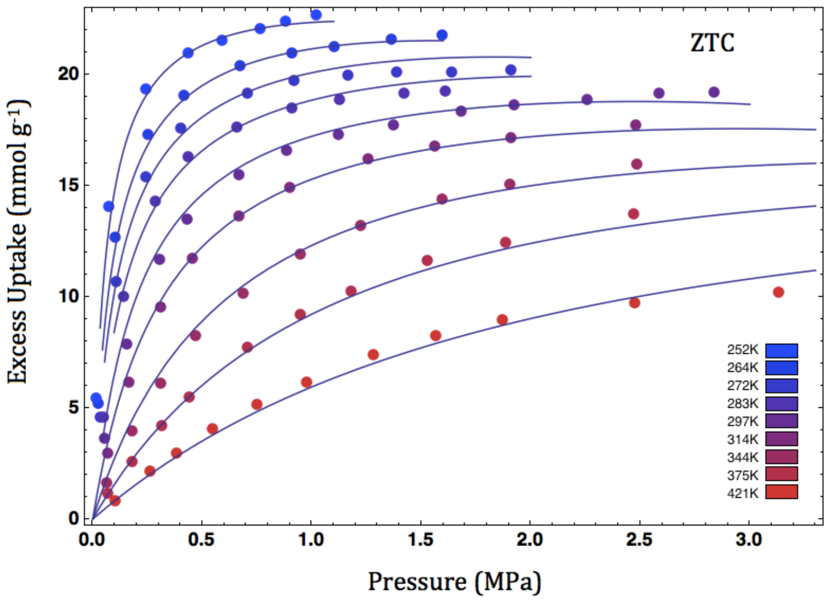
Methane Shows Anomalous Isosteric Heat for ZTC



Together Methane and Ethane account for ~98% of natural gas.

Ethane Data Fitted with Superposition of Langmuir Isotherms

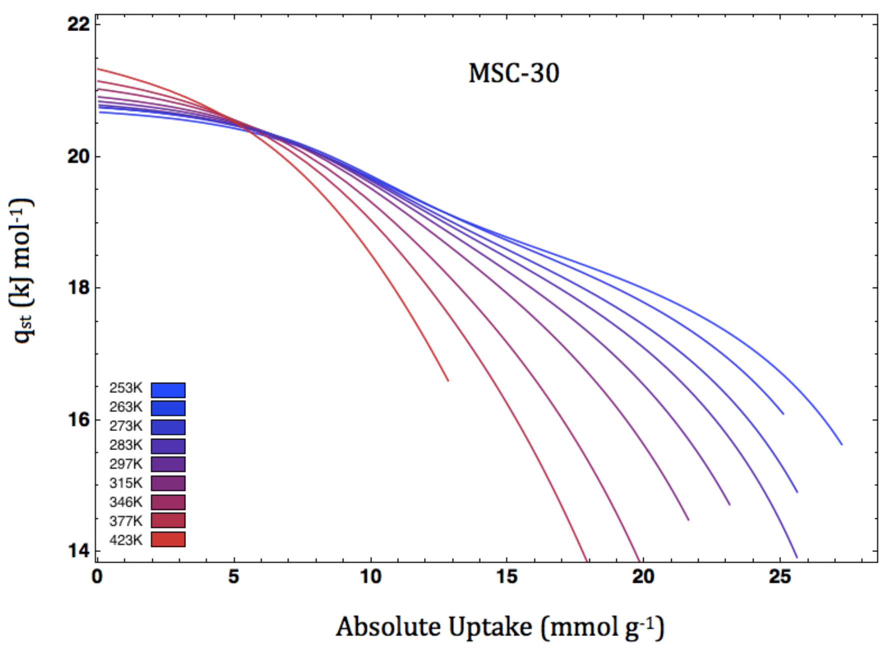


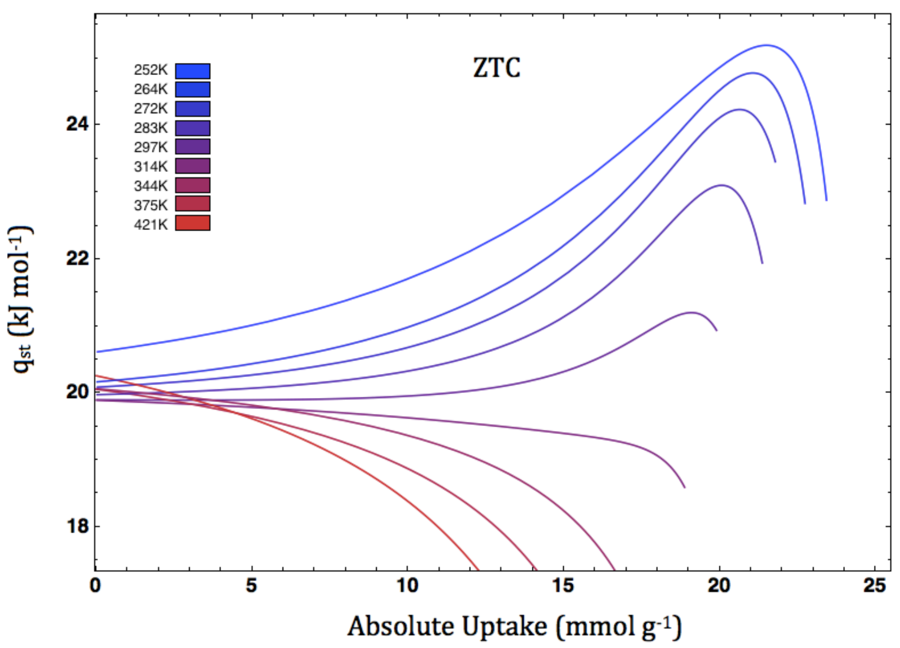


Fit data with:

$$n_e(P,T) = (n_{max} - V_{max}\rho(P,T))\left[\sum_i \alpha_i \frac{K_i P}{1 + K_i P}\right]$$

Isosteric Heat of Ethane Adsorption

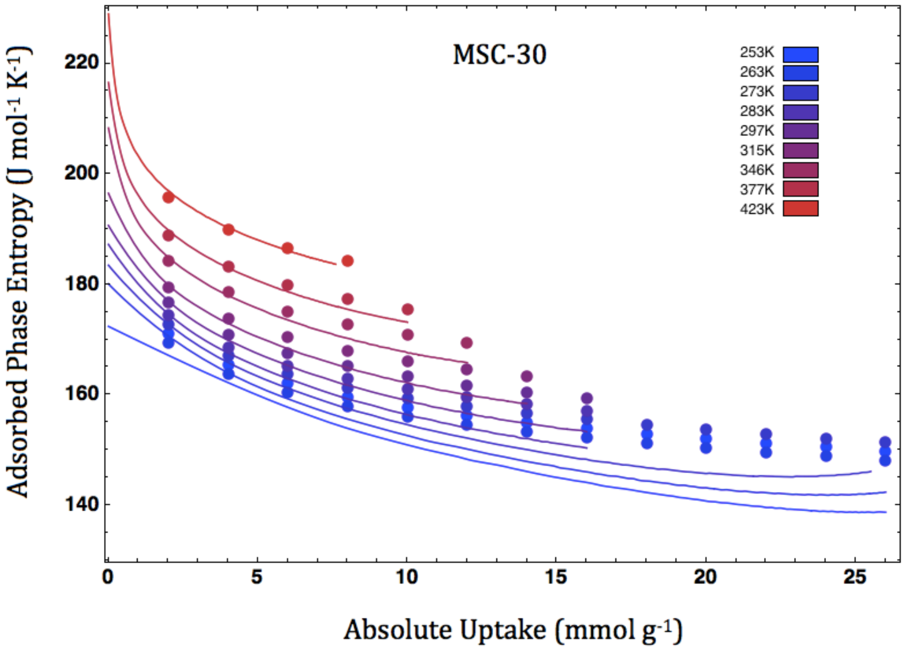


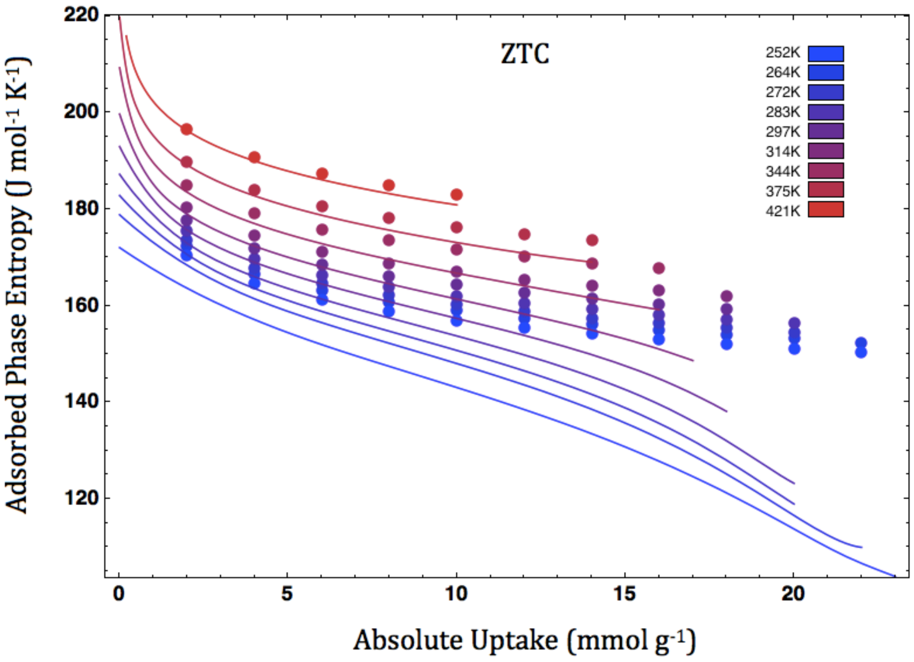


Calculated with the Clapeyron Equation:

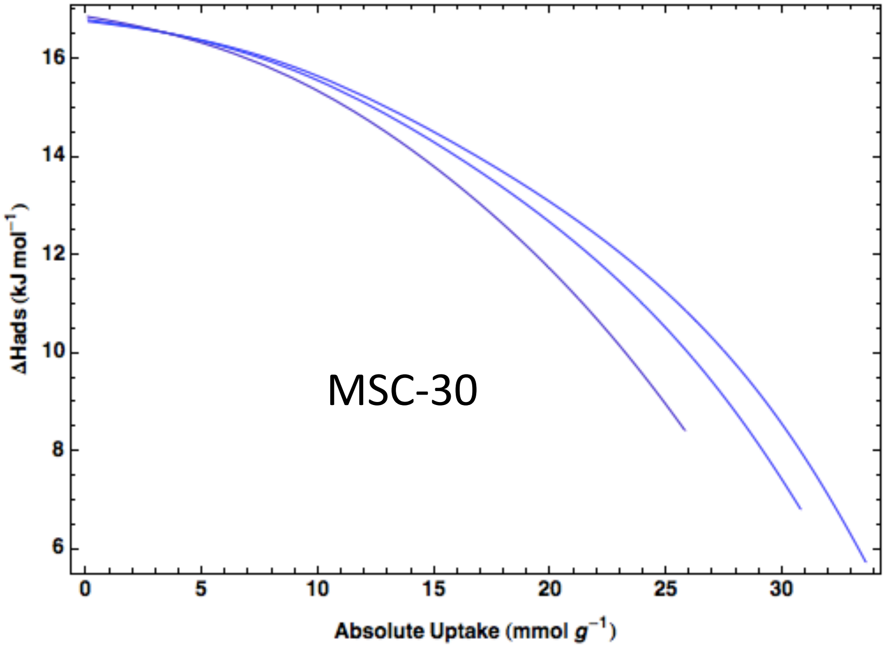
$$q_{st} = -\Delta H_{ads}(n_a) = -T\left(\frac{\partial P}{\partial T}\right)_{n_a}(\Delta v_{ads})$$

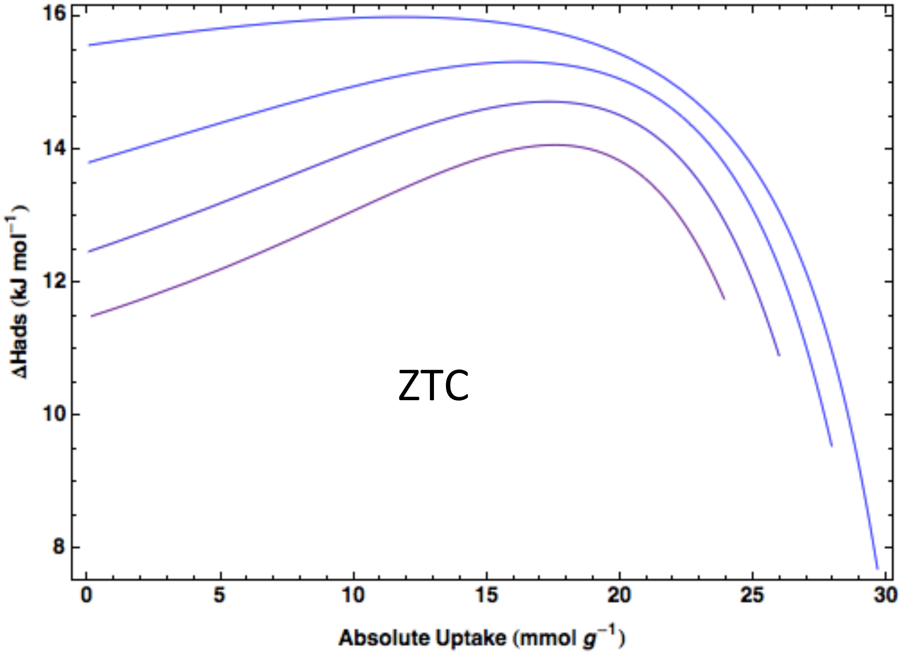
Entropy of the Adsorbed Phase (Ethane)





Ongoing Work: Krypton Adsorption





Similarities Between Methane and Krypton

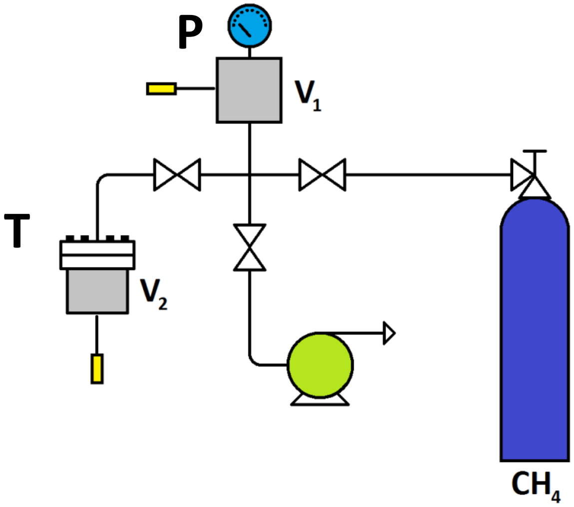
	Methane	Krypton
Boiling Point	112 K	120 K
Critical Temperature	190 K	209 K
Sigma	3.8 Å	3.9 Å
Epsilon	148K / K_b	154K / K_b

Volumetric Adsorption Measurements

Sieverts method:

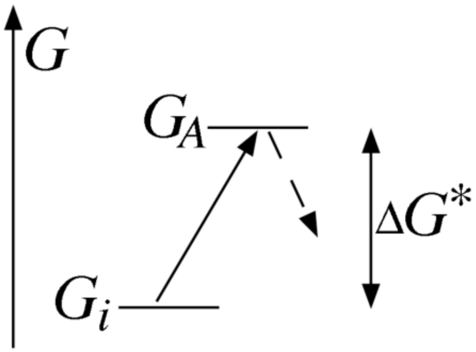
$$\rho(P_i, T)\, V_i = \rho\left(P_f, T\right)\, V_f + n_{ads}$$

(whole apparatus at uniform temperature)



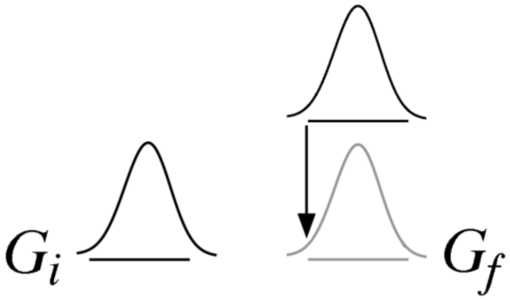
For Samples of ~1000 m^2 signal to noise ≈ 100:1
For Sample of ~100 m^2 signal to noise ≈ 10:1
100 m^2 is minimum for adsorption measurements

Activation Volumes of Kinetic Mechanisms



Classical: Ion or atom

Li+ senses only initial state and transition state



Quantum: Polaron

Electron (hole) samples both initial and final states.

Measure $I(E,P,T) \rightarrow \Gamma(P,T) \rightarrow V_A$ Get Activation Volume

Activation volume gives a picture of atoms in transition state

Activation Volume in Li_xFePO_4

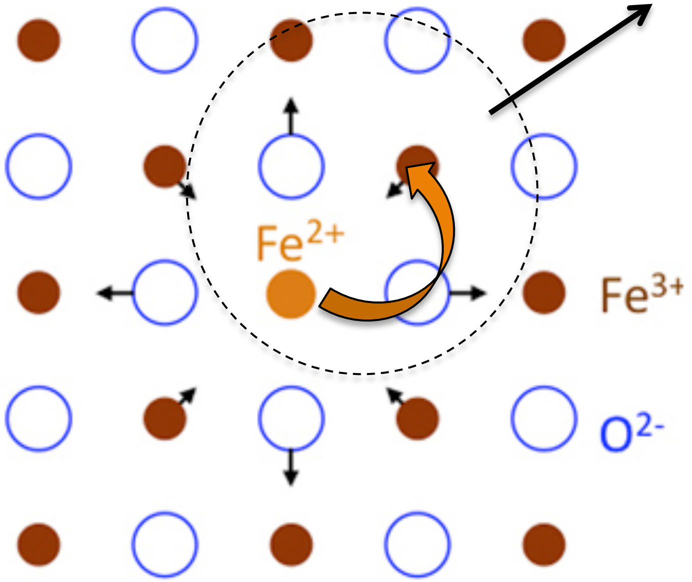
Originates from the local atomic distortions that bring the electron levels of the initial and final states into coincidence, facilitating electron transfer

$$\Gamma = \Gamma_0 \exp(-2\alpha R)\exp\left(-\frac{E_a + PV_a}{kT}\right)$$

V_a is determined by measuring the effect of applied pressure on the polaron hopping frequency

Electrical conductivity of oxides showed: $V_a = -0.2$ Å^3
We found: $V_a = +6$ Å^3

Is V>0 or V<0 ?



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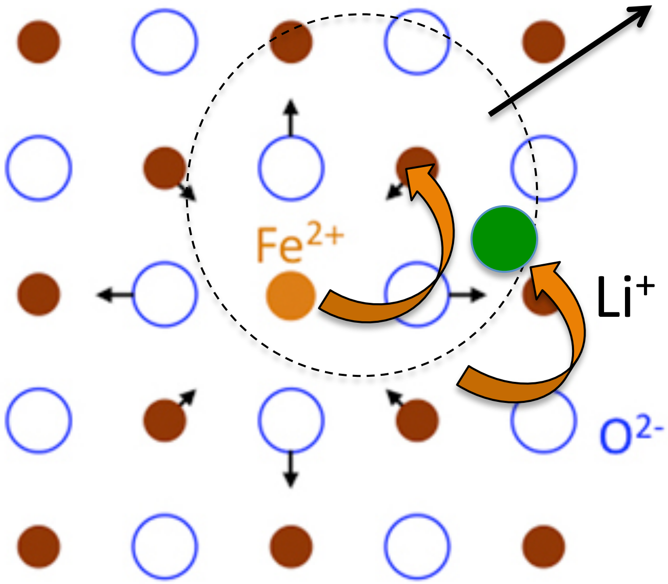
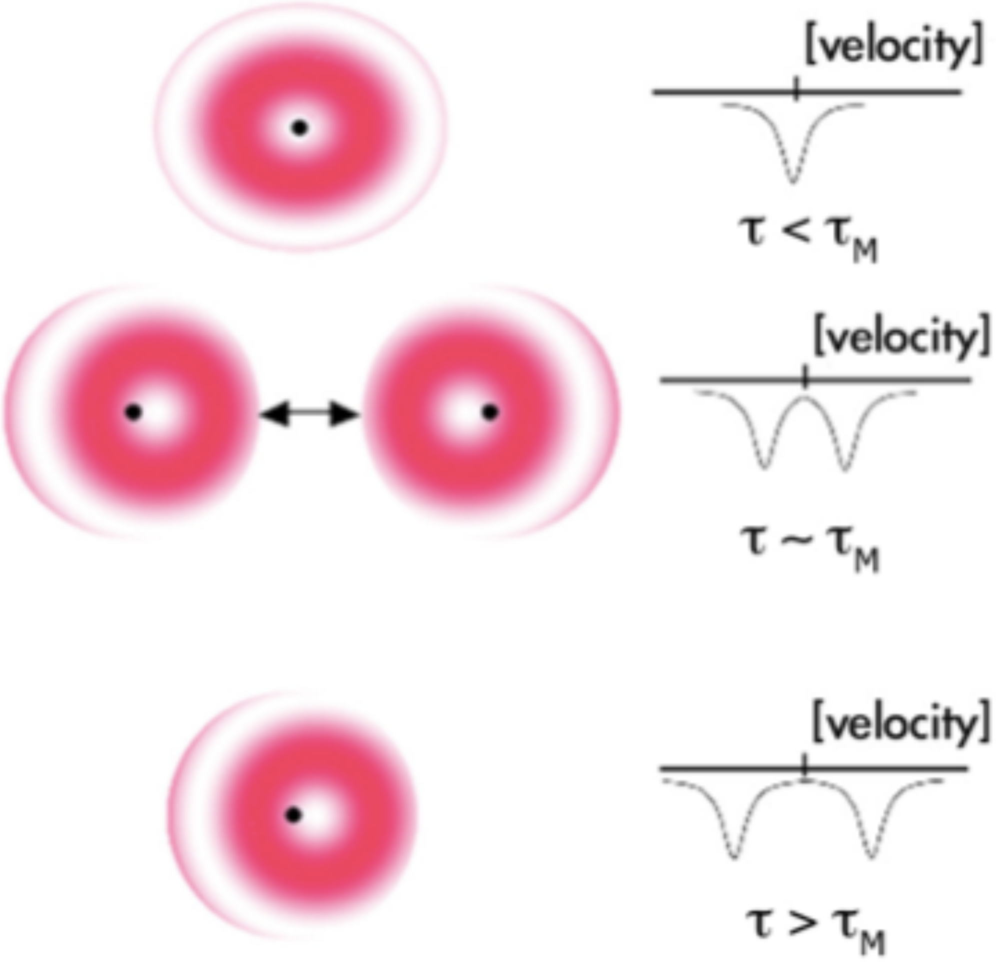


Dynamical Effects in Mössbauer Spectra

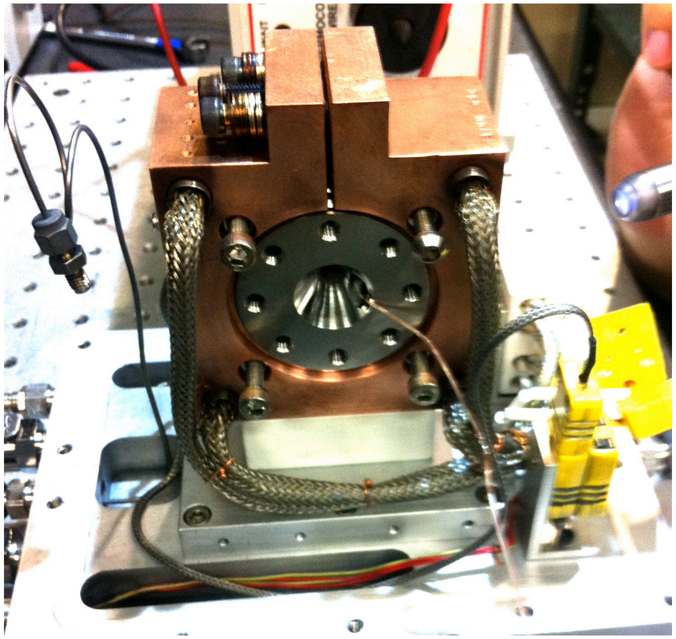
$$\tau_M = \frac{\hbar}{E_{HF}}$$

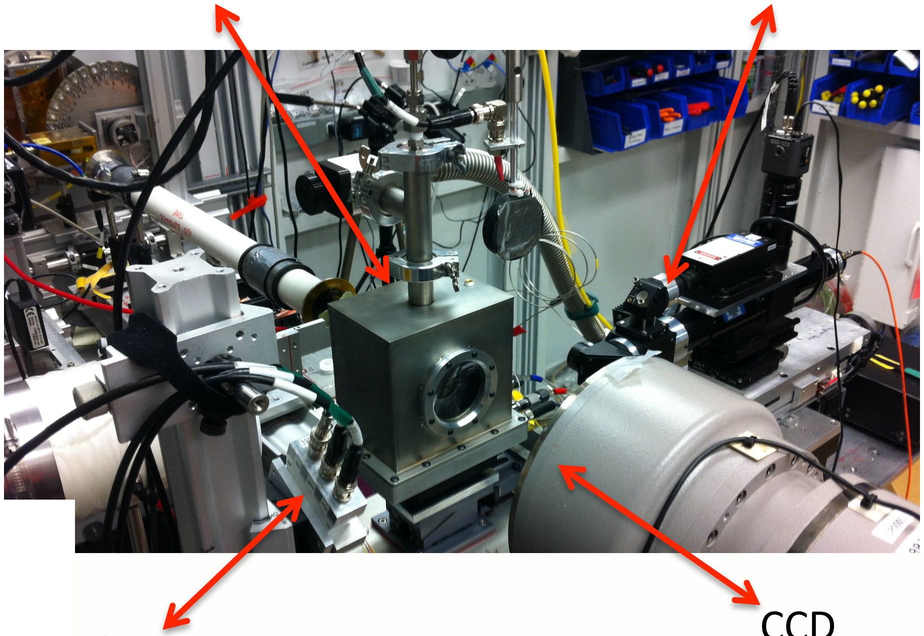
- Observe ^{57}Fe spectral relaxations from Fe^{2+}–Fe^{3+}
- Account for the time correlations of a fluctuating Hamiltonian with Blume-Tjon model.

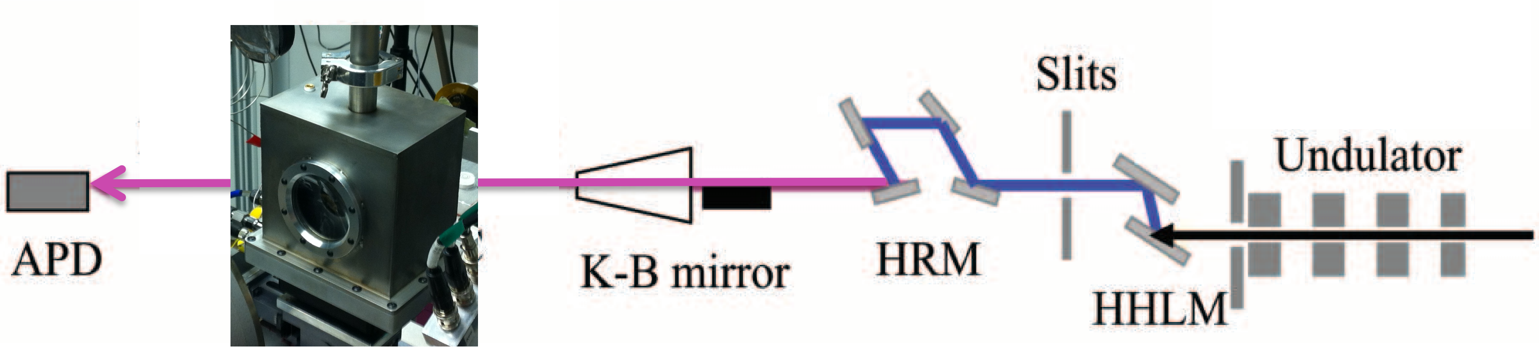


Nuclear Forward Scattering at APS 16ID-D (HPCAT)

DAC in Copper Block Furnace







Heating HPCAT Block
For Symmetric DAC

Uniform heating up to 500C

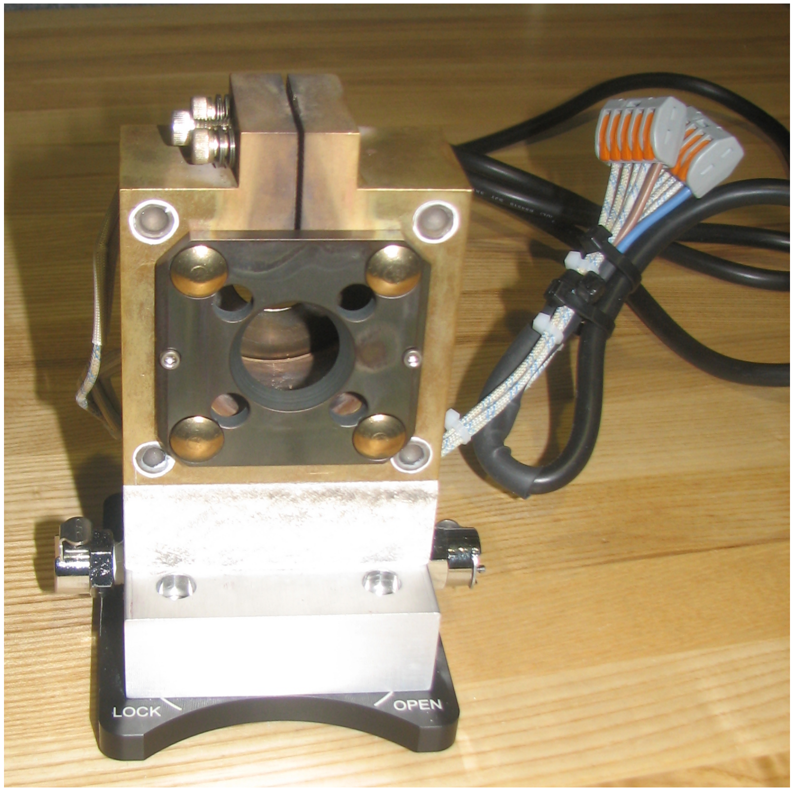
Good temperature stability

Integrated membrane pressure control

Remote Temperature & Pressure Control

Front plate has access holes for the symmetric cell bolts

back side plate constrains a membrane for remote pressure control

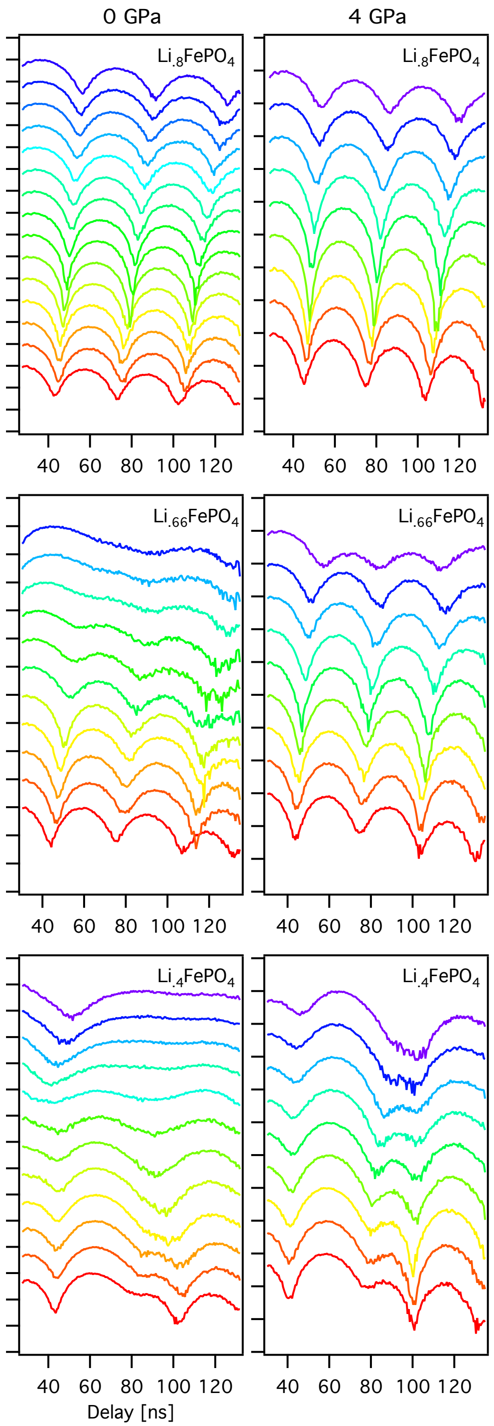


Li_xFePO_4
Nuclear Forward Scattering

Spectra at 0 GPa show large distortions, consistent with the polaron dynamics reported by conventional Mössbauer

At elevated pressure these large spectral distortions do not occur until higher temperature

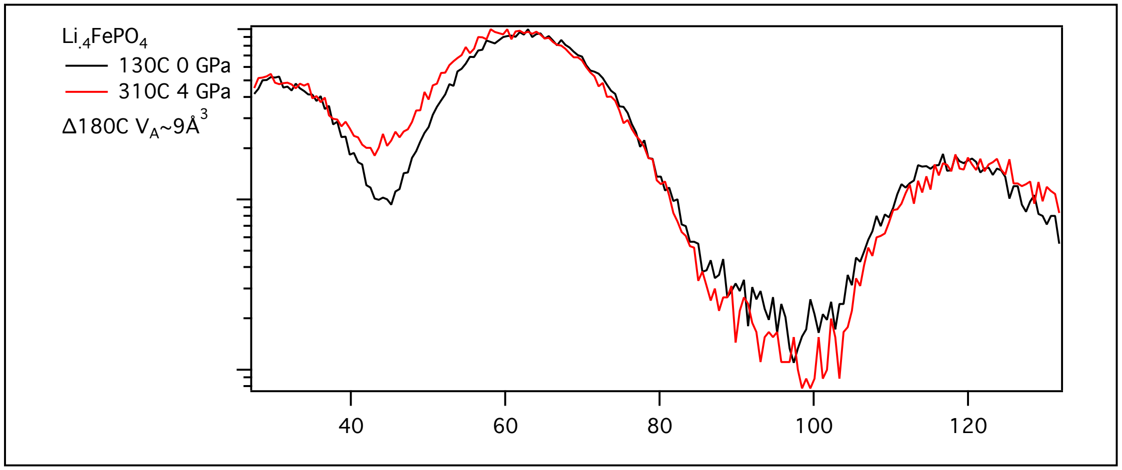
Spectral Distortions appear to be more pronounced at low Lithium concentration

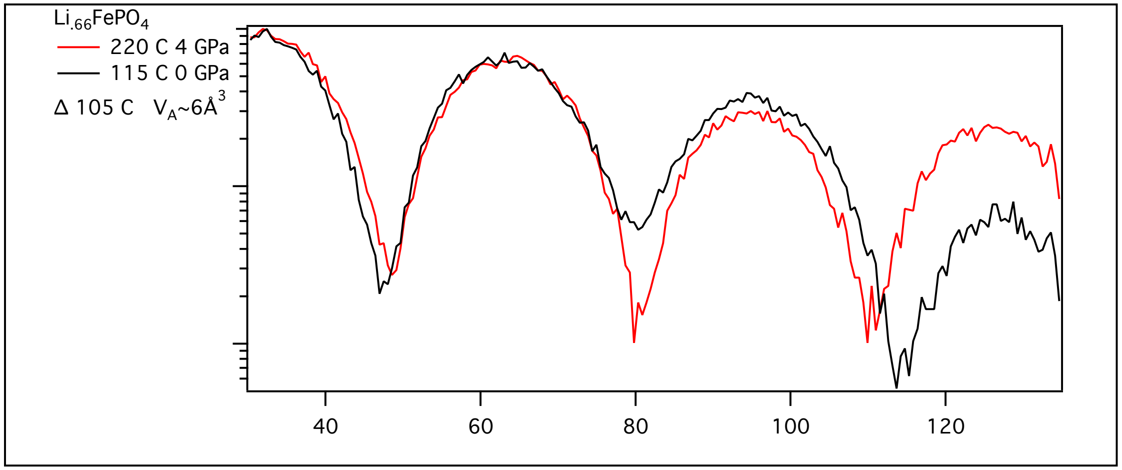


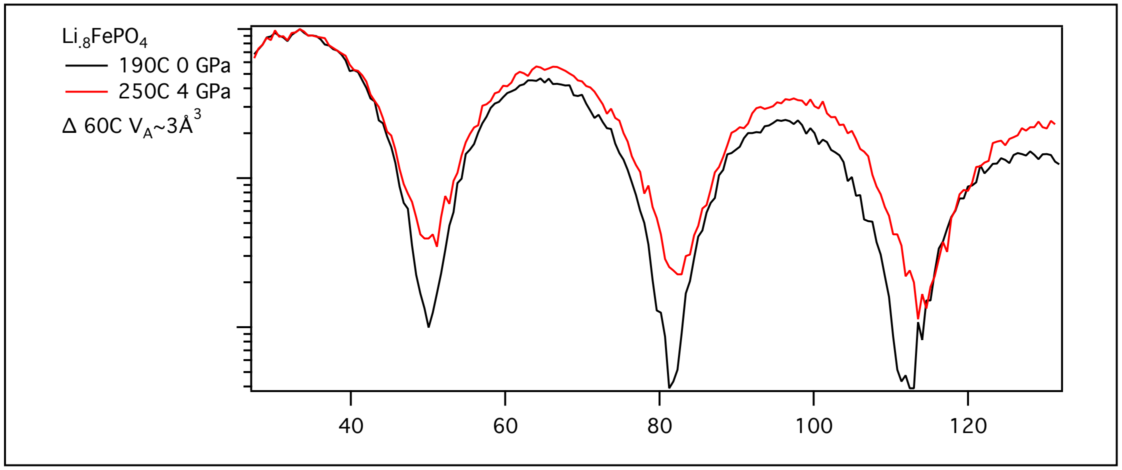
Estimates of Concentration Dependence of Activation Volume

$Li_{.4}FePO_4$ $V_A \sim 9\text{Å}^3$
$Li_{.66}FePO_4$ $V_A \sim 6\text{Å}^3$
$Li_{.8}FePO_4$ $V_A \sim 3\text{Å}^3$

Activation volume has a roughly linear increase as lithium concentration is reduced







Compressibility and Activation Volume

Destabilization of an electron polaron centered at a Fe^{2+} ion because the compressibility of ferrous-oxygen bonds is greater than for ferric-oxygen bonds

The Fe^{3+}-oxygen bonds are shorter and stiffer than the Fe^{2+}-oxygen bonds
→we expect a larger the effect of pressure on the ferrous Fe-O bonds

Overall reduction of activation volume should be greater at low Li concentrations

Opposite trend seen in experimental results → not dominant effect

Perhaps the dominant effect is how pressure alters the activation volume for Li^{+} ions in materials with higher Li concentration?

Quasielastic Scattering (Neutrons and Hydrogen)

Incoherent scattering, analysis of diffusion is good (diffraction is not).

^{1}H has neutron scattering cross section σ~80 barns

(10 barns is big for other isotopes)

For inelastic scattering, σ/m of ^{1}H is unbeatable

Neutron scattering from pressure cells can be less than from ^{1}H

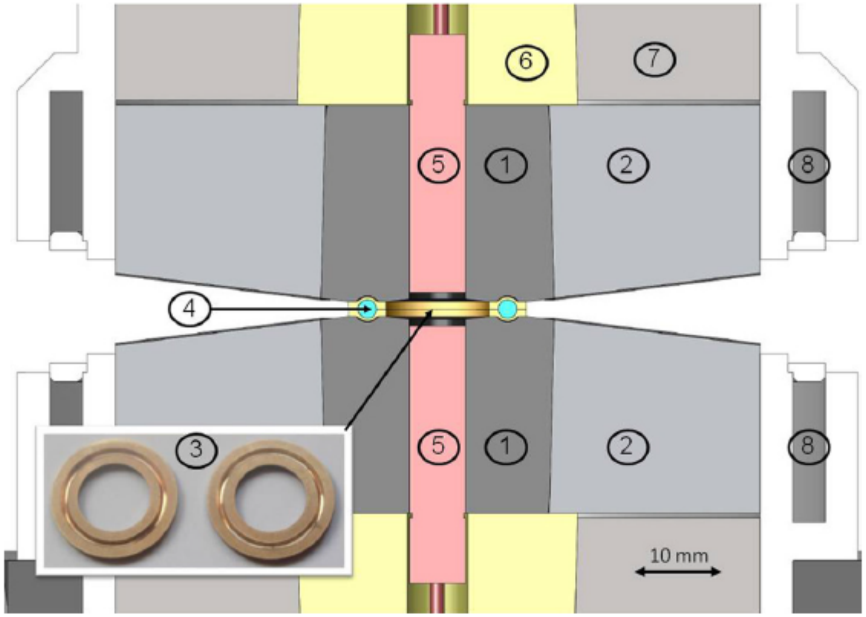


FIG. 1. Gasket-anvil assembly for high pressure QENS measurements. (1) and (2) anvil made of sintered cBN die supported by steel binding ring; (3) split CuBe gasket; (4) high pressure sample chamber; (5) cartridge heater; (6) and (7) anvil backing seat made of zirconia die and steel supporting ring; (8) cooling rings. Conical anvil faces (thick lines) are covered with gadolinium film.

Bove, et al, "Translational and Rotational Diffusion in Water in the Gigapascal Range," PRL 111, 185901 (2013).

Quasielastic Scattering (General)

Van Hove function $G(\boldsymbol{r},t)$

$$G(\vec{r},t) \equiv \frac{1}{\tau}\int_{t'=0}^{+\tau}\int_{\vec{r}=-\infty}^{+\infty} f^*(\vec{r}',t')\, f(\vec{r}+\vec{r}',t+t')\, \mathrm{d}^3\vec{r}'\,\mathrm{d}t'$$

$$S(\vec{Q},\omega) = \frac{1}{2\pi\hbar}\iint_{-\infty}^{+\infty} G(\vec{r},t)\, \mathrm{e}^{-\mathrm{i}(\vec{Q}\cdot\vec{r}-\omega t)}\, \mathrm{d}^3\vec{r}\,\mathrm{d}t$$

$$S(\vec{Q},\omega) = \frac{1}{2\pi\hbar} F_{\vec{r}} F_t G(\vec{r},t)\,,$$

Calculate the Van Hove function for diffusion (different atoms are uncorrelated)

$$c(x,t) = \frac{c'}{\sqrt{4\pi D t}}\,\mathrm{e}^{-\frac{x^2}{4Dt}} \qquad G_{\mathrm{diff}}(x,t) = \int_{-\infty}^{+\infty} c(x',0)\, c(x'+x,t)\, \mathrm{d}x'$$

$$S(Q,\omega) = \frac{c'}{2\pi\hbar}\, \frac{DQ^2}{(DQ^2)^2+\omega^2} \qquad \Delta E = \hbar\, D\, Q^2$$

Quasielastic Scattering and Pressure

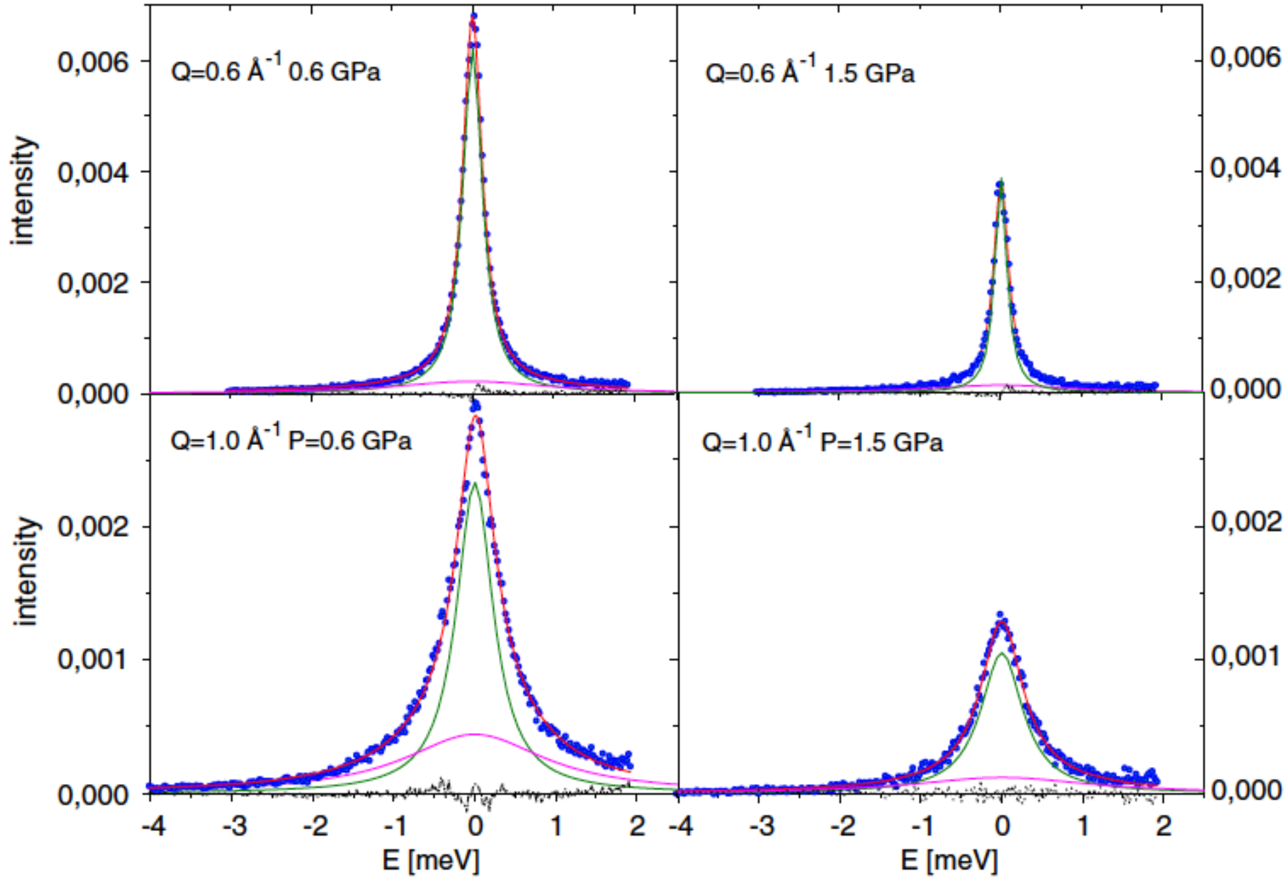


FIG. 3 (color online). Example of fit result (red line) compared to the measured intensity (blue dots) from water at 400 K at $P = 0.6$ and 1.5 GPa for Q-selected values.

Quasielastic Scattering and Pressure

Klotz, et al., "Quasi-elastic neutron scattering in the multi-GPa range and its application to liquid water", APL 103, 193504 (2013).

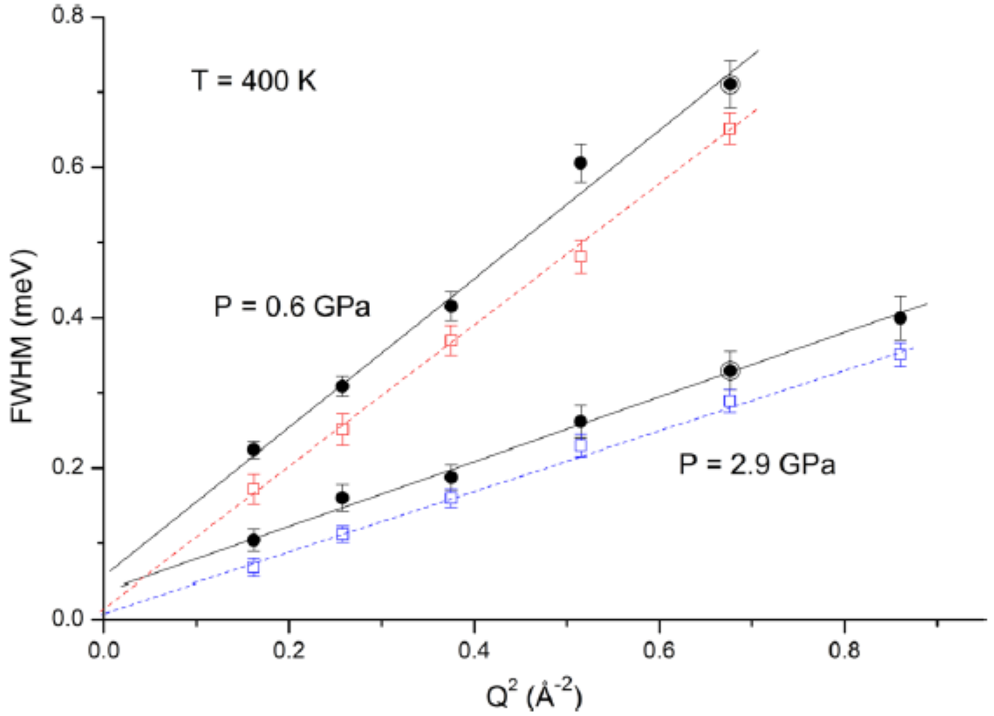


FIG. 3. Full width at half maximum (FWHM) of the fitted QENS signal plotted as a function of Q^2, at 0.6 GPa and 2.9 GPa. The marked dots (⊙) at 0.86 Å^{-2} are those shown in Figure 2. Full symbols correspond to analysis

Activation volume:

My estimate is +2 Å^3 for translational diffusion of water molecule in liquid.

(*T*-Dependence?)

Activation Volume for ^{1}H Diffusion

- Activation volume is of interest for both physisorption and chemisorption.
- Plans at the SNS to do inelastic scattering under pressure.
- If the activation volumes are several Å^3, pressure of only 1 GPa are required for measuring V_A.
- Coordination with the SNS needs thought.