# NNL TSL Evaluations for Yttrium Hydride and Hexagonal Ice

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# NNL TSL Evaluations

| Material | MAT |
|---|---|
| $H(YH_2)$ | 5 |
| $Y(YH_2)$ | 55 |
| H(ice-Ih) | 10 |
| O(ice-Ih) | 50 |

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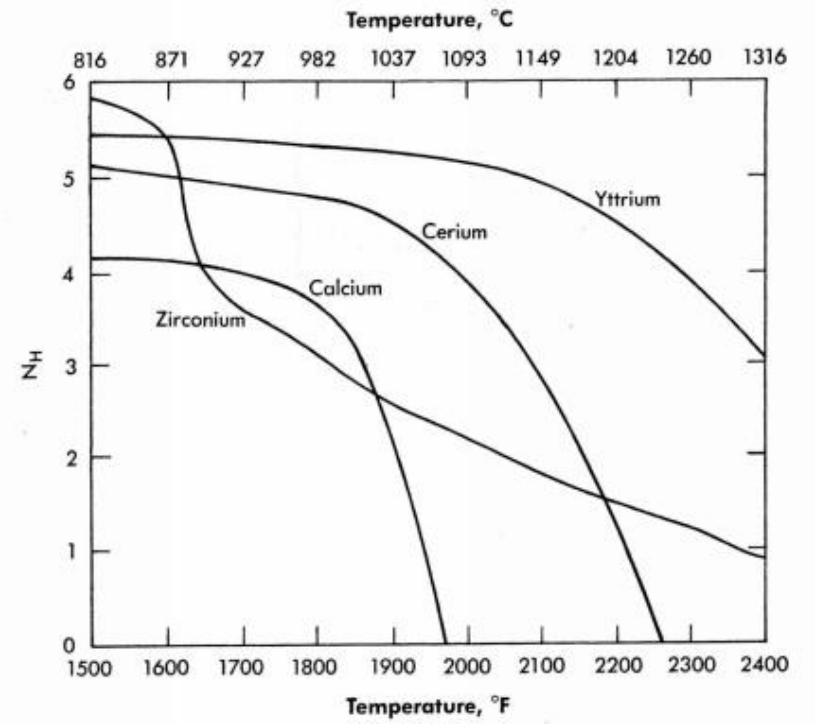
# $YH_2$ Background

- Yttrium hydride ($YH_2$) is an advanced high temperature moderator
- Superior hydrogen density ($N_H$) at elevated temperatures
- Keinert (1971) proposed $H(YH_2)$ TSL based on simple analytic frequency distributions
  - Debye-type for acoustic mode
  - Gaussian-type for optical mode
- Higher-fidelity TSLs for $H(YH_2)$ and $Y(YH_2)$ developed using first-principles calculations
  - Density Functional Theory (DFT) to calculate interatomic Hellman-Feynman forces for crystal structure
  - Lattice Dynamics (LD) to determine dispersion relations and phonon density of states (DOS)




Hydrogen in metallic Zr, Ce, Y and Ca in equilibrium with 1 atm $H_2$ at various temperatures.
(Source: *Metal Hydrides*, Academic Press, p. 442, 1968)

$N_H$ is number of hydrogen atoms/cc x $10^{-22}$

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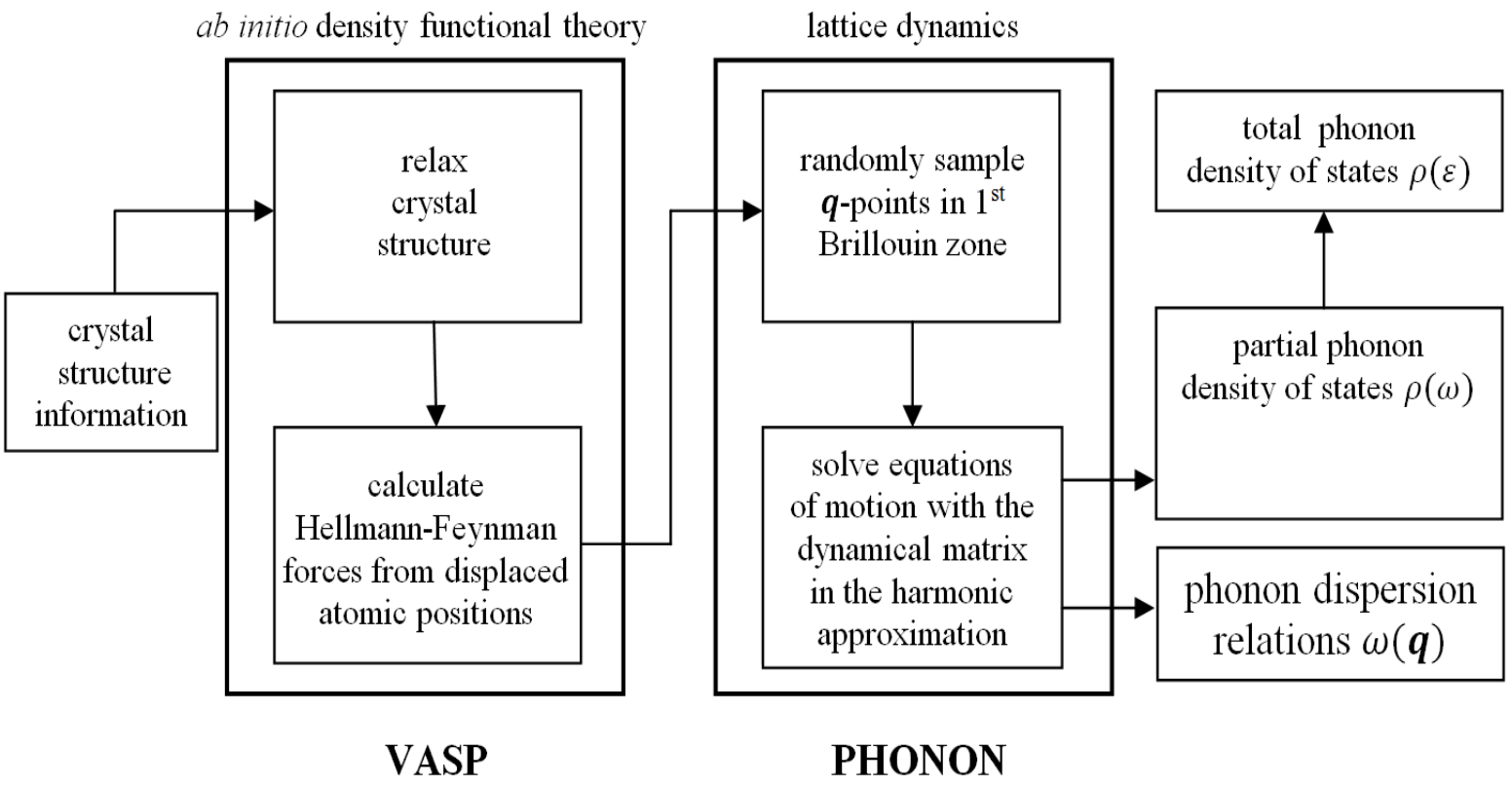
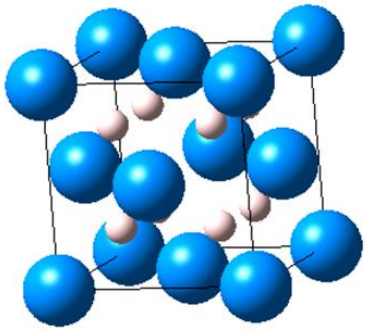
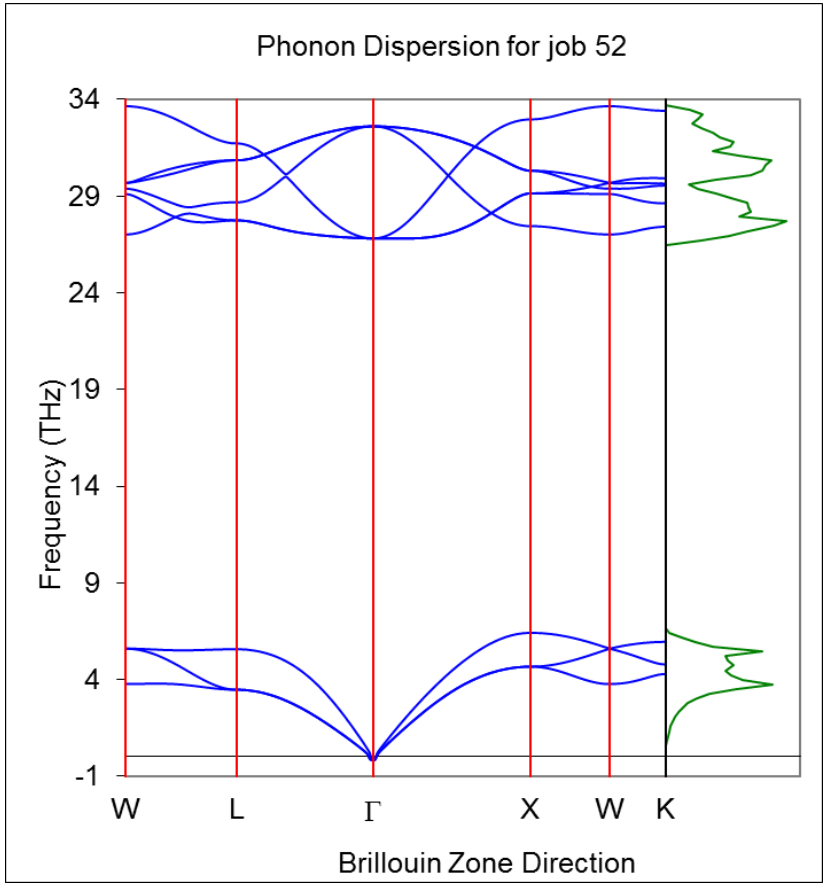
# *Ab Initio* Calculation of Phonon Spectra



# $YH_2$ Structure and Lattice Dynamics



- $YH_2$ has a $CaF_2$ type FCC structure
  - 12 atoms
  - 4 Y atoms (blue) at vertices and faces of unit cell
  - 8 H atoms (grey) in tetrahedral holes between Y atoms
- Dispersion relations (at right)
  - Well separated acoustical and optical modes
  - Lower branches are acoustical modes mainly due to heavy Y atom vibrations
  - Higher branches are optical modes mainly due to light H atom vibrations

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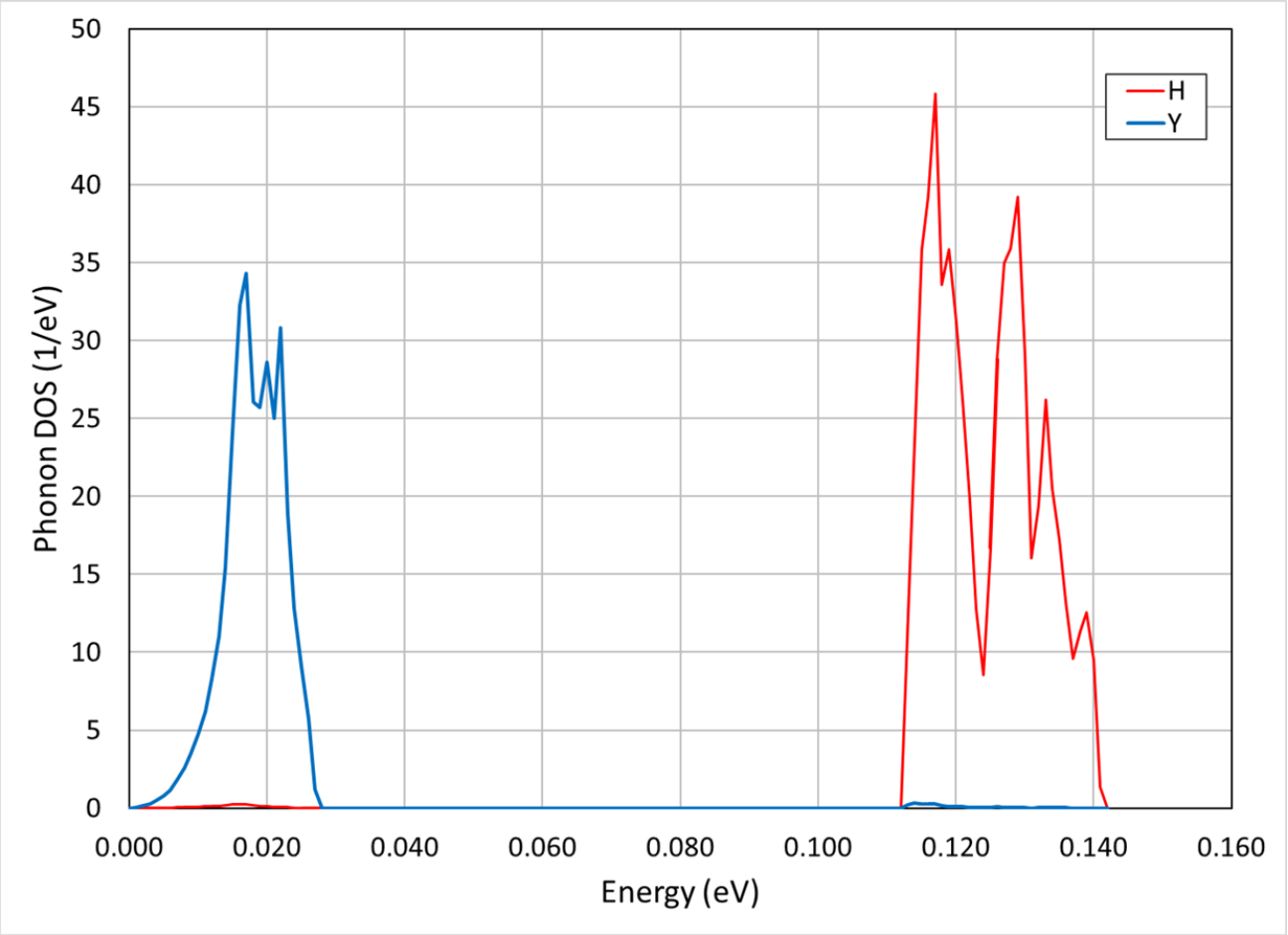
# $YH_2$ Phonon Density of States

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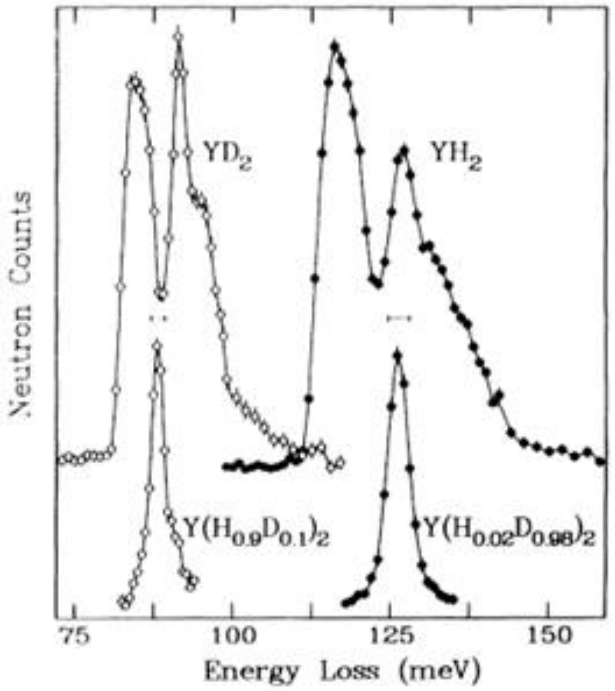
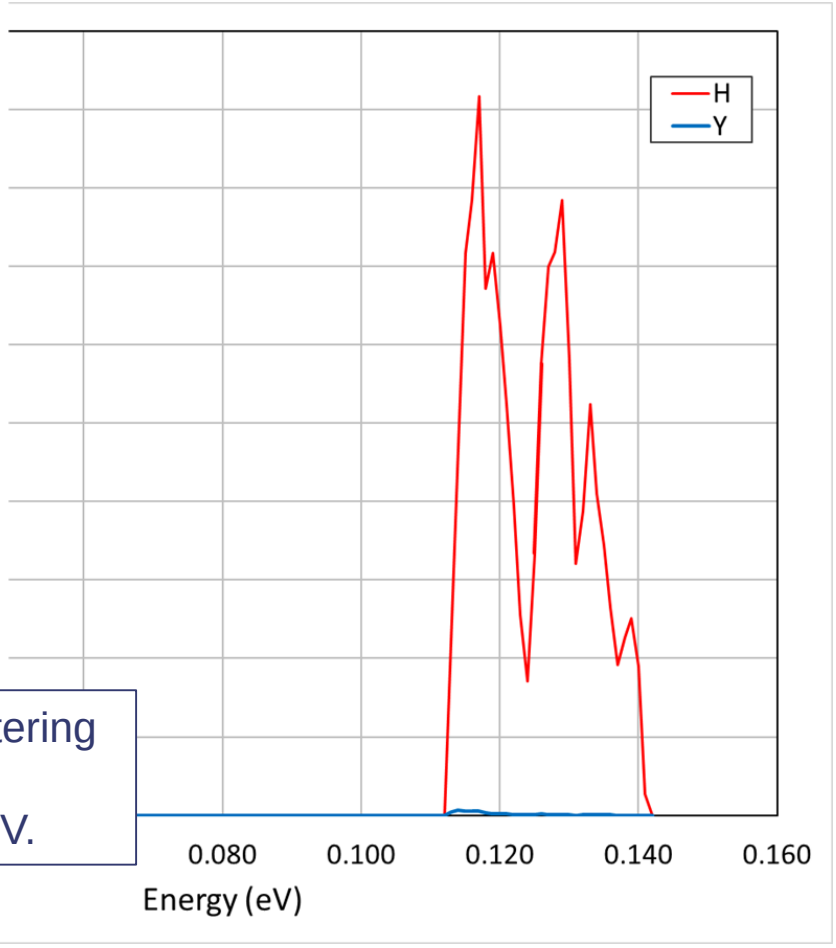
# $YH_2$ Phonon Density of States




High resolution inelastic neutron scattering spectra from Udovic shows similar structure for $YH_2$ centered on 0.127 eV.

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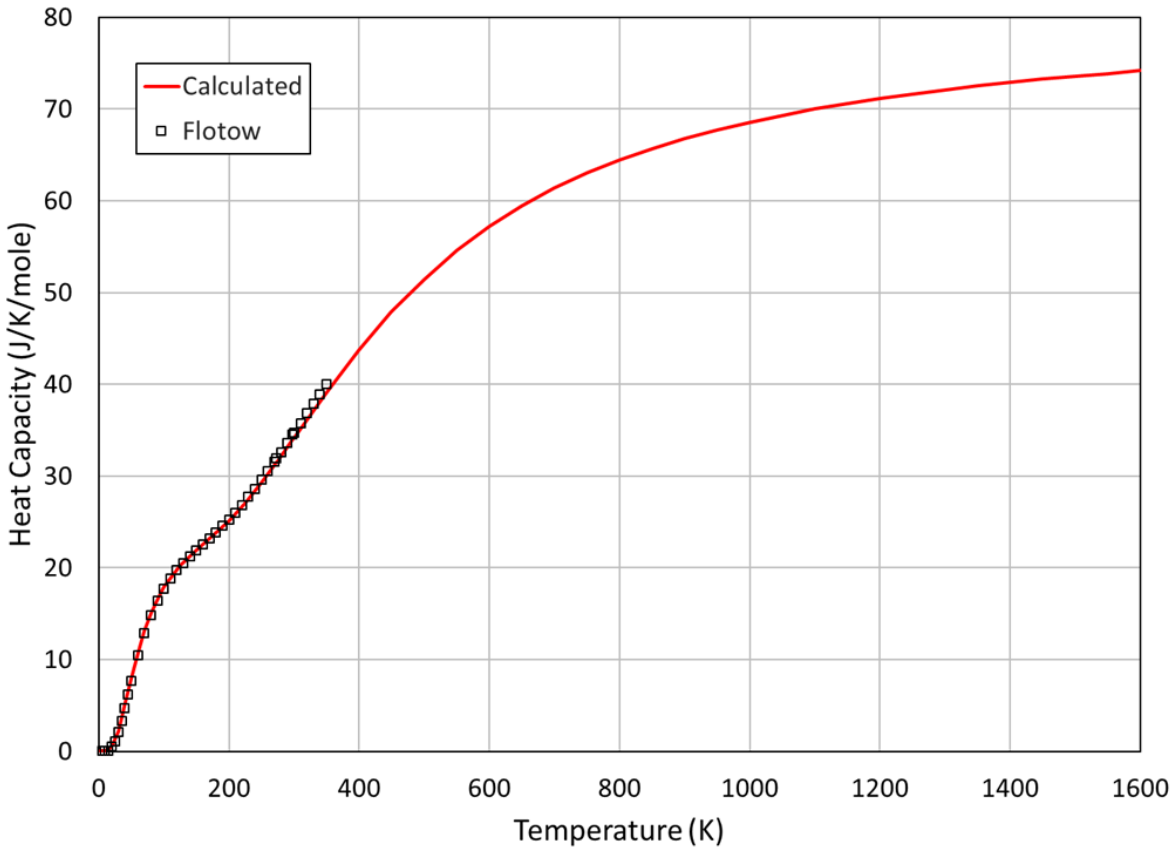
# Heat Capacity Based on $YH_2$ Phonon DOS Agrees with Measurement

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# LEAPR Models $YH_2$ and Ice I*h*

- H($YH_2$), Y($YH_2$), H(Ice-I*h*), and O(Ice-I*h*) TSLs generated using NJOY/LEAPR
- Phonon DOS from PHONON calculations
- Incoherent approximation
- Atomic mass ratios and free atom scattering cross sections from ENDF/B-VII.1 evaluations
  - Consistent with ENDF/B-VIII.0(beta3)
- $\alpha$ and $\beta$ grids optimized to treat scattering up to 5 eV

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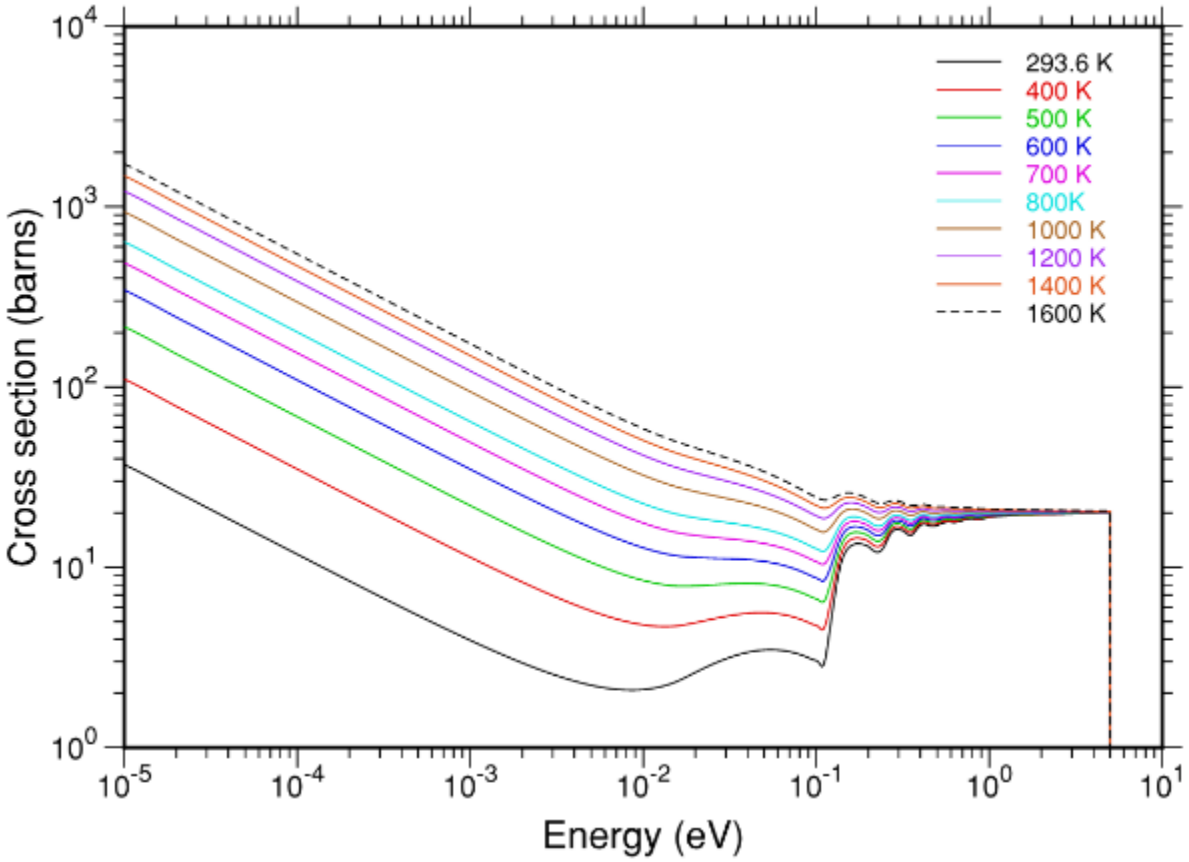
# $H(YH_2)$ Inelastic Scattering Cross Section

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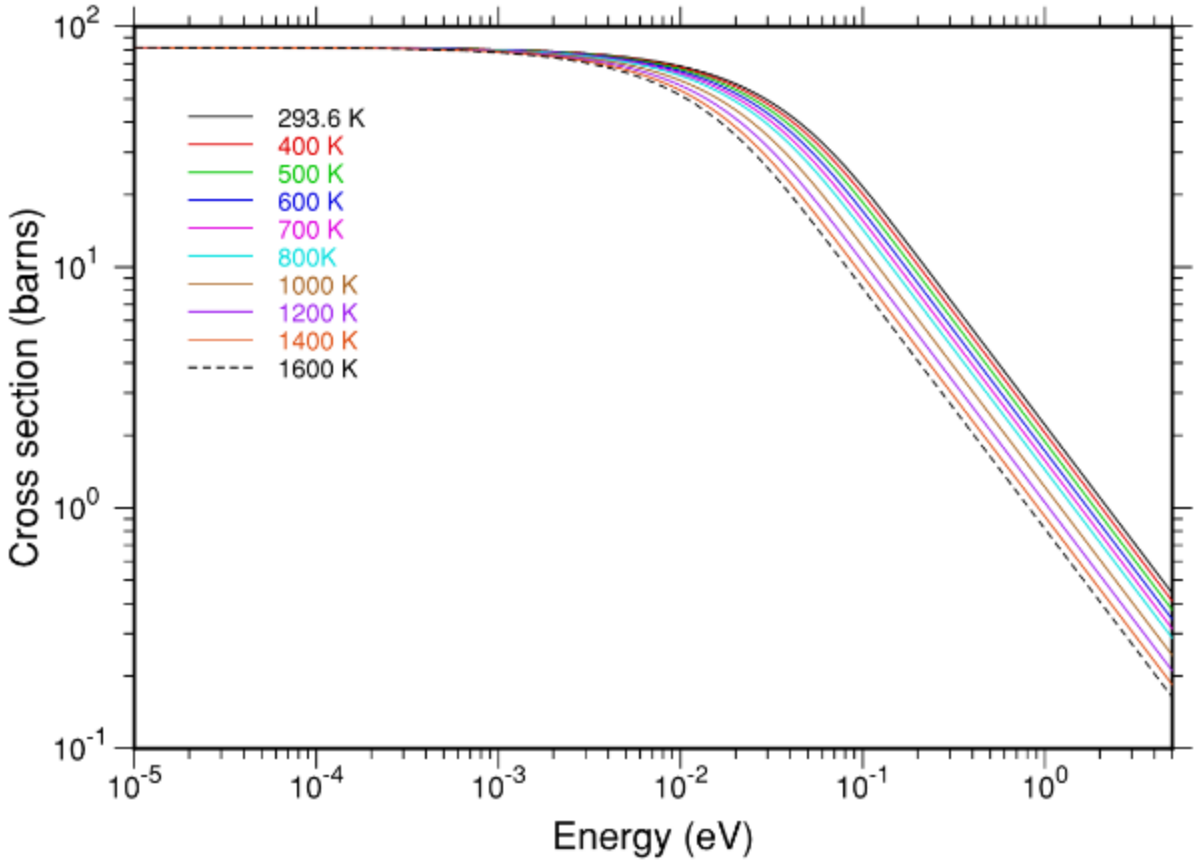
# $H(YH_2)$ Elastic Scattering Cross Section

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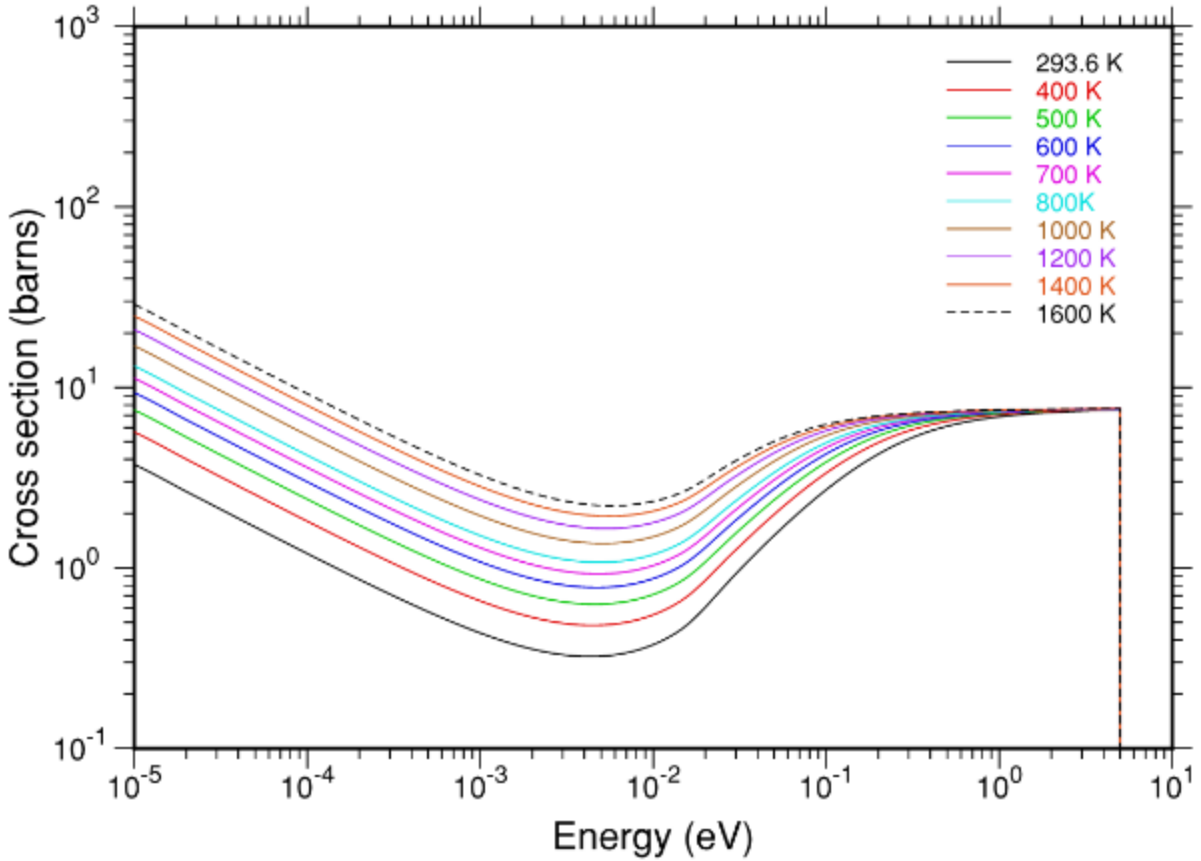
# $Y(YH_2)$ Inelastic Scattering Cross Section

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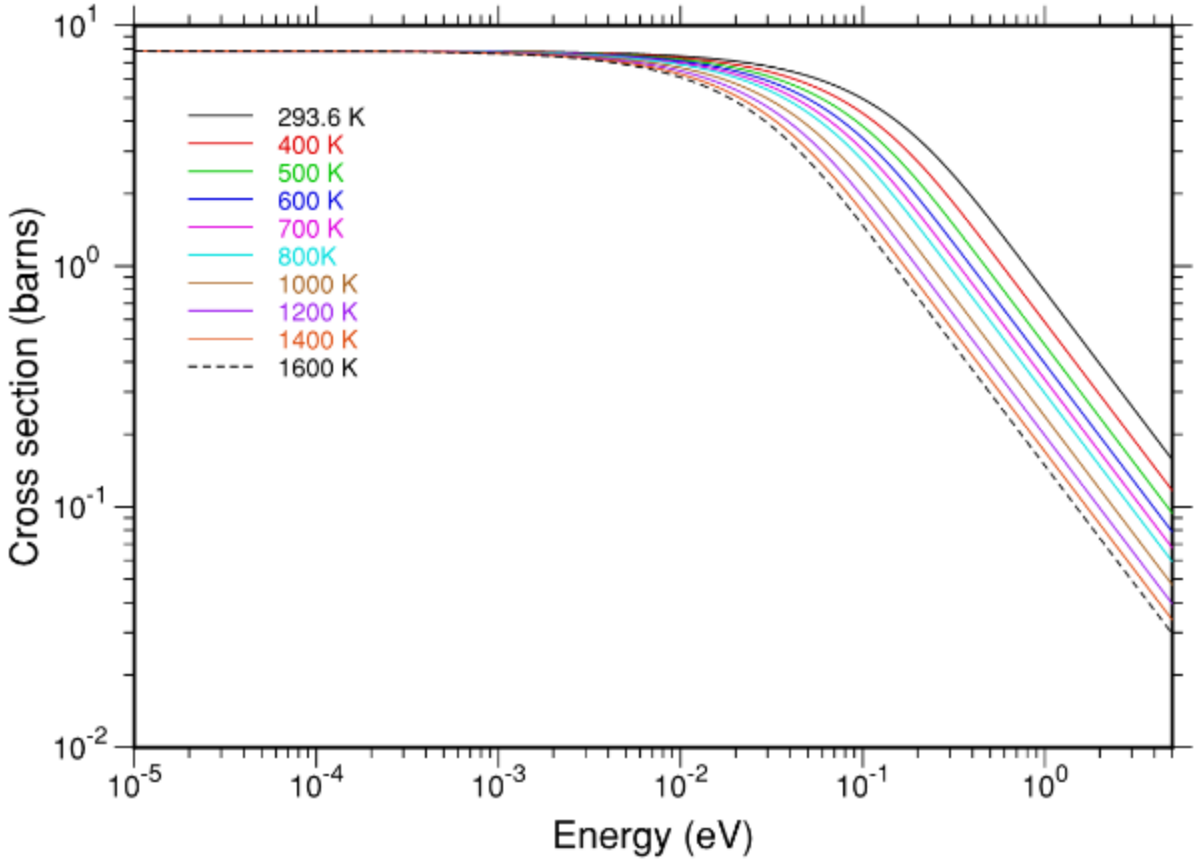
# $Y(YH_2)$ Elastic Scattering Cross Section

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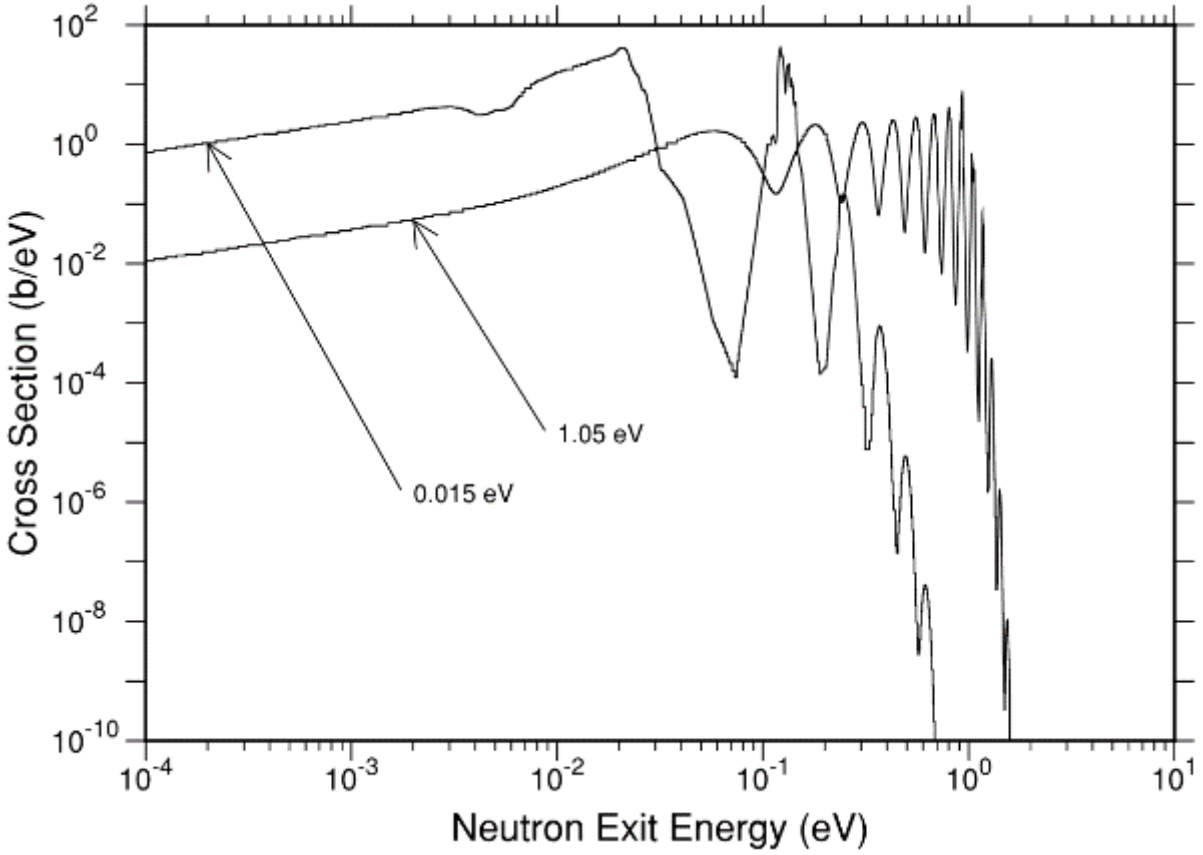
# $H(YH_2)$ Differential Inelastic Scattering Cross Section

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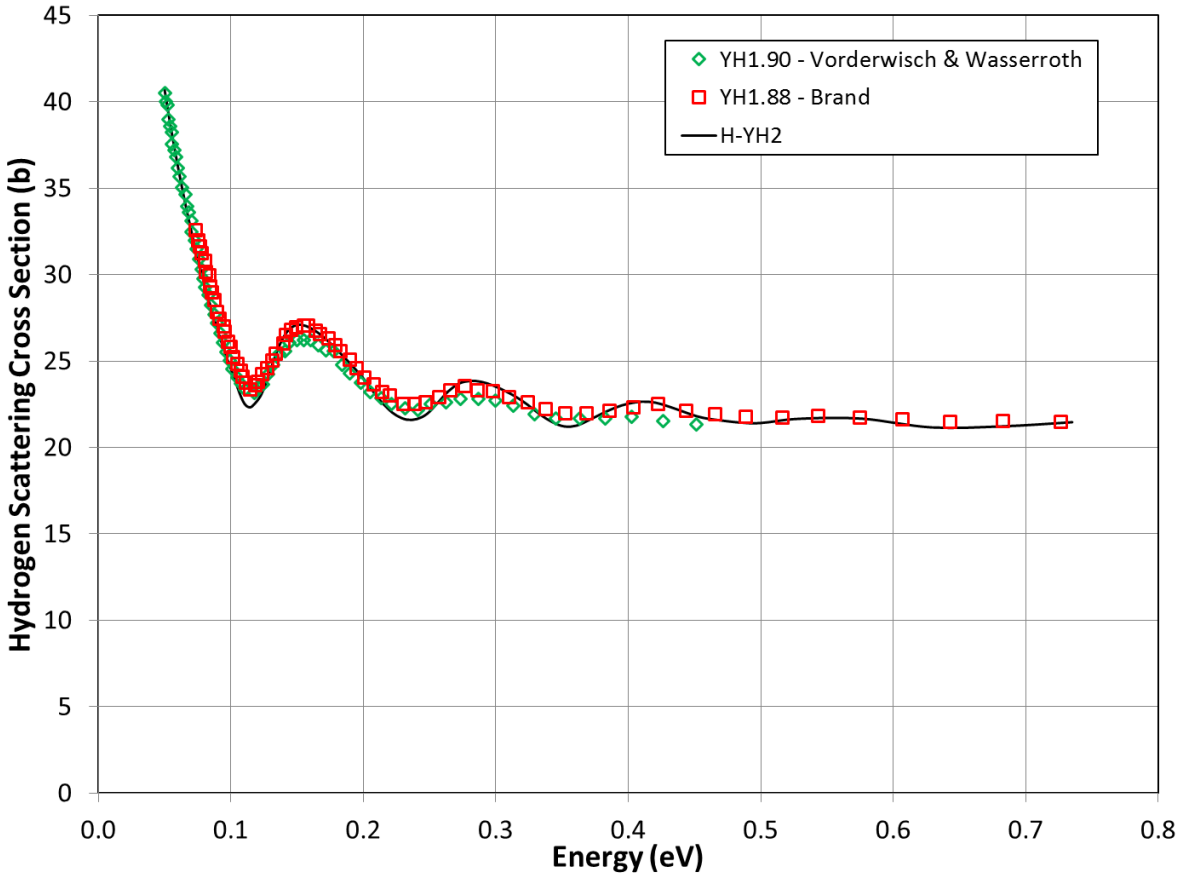
# $H(YH_2)$ Total Scattering Cross Section Agrees with Measurements

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# $YH_2$ Summary

- H($YH_2$) and Y($YH_2$) TSLs developed using first-principles DFT and LD calculations
- $\alpha$ and $\beta$ grids optimized to treat scattering up to 5 eV
  - $\beta$ grid can resolve 1-phonon and multiphonon scattering effects
- Validation
  - Measured lattice parameter
  - High-resolution inelastic neutron scattering spectra
  - Measured heat capacity
  - Measured H scattering cross section for $YH_{1.90}$ and $YH_{1.88}$

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# Hexagonal Ice I*h* (*why ice?*)

1. Criticality safety analyses routinely examine the reactivity effect of a liquid water environment during the transport and storage of nuclear fuel material.

2. 10 CFR 71 and IAEA SSR-6 transportation regulations require accident analysis at temperatures down to -20 F and -40 F, respectively. Consequently, there is a requirement for a thermal neutron scattering law (TSL) for ice which characterizes the impact of the chemically bound crystalline structure on neutron scattering, moderation, and reflection.

3. The thermal scattering kernel for liquid water has been extensively studied and is available in an ENDF library. However, no published ENDF File 7 TSL for water ice exists.

4. Crystalline ice is a significantly better reflector and less effective moderator than liquid water. Modifying the material density of liquid water to account for ice formation will not capture these effects in benchmark calculations.

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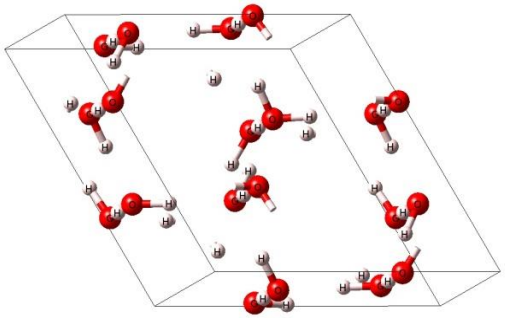
# Structure of Hexagonal Ice I*h*

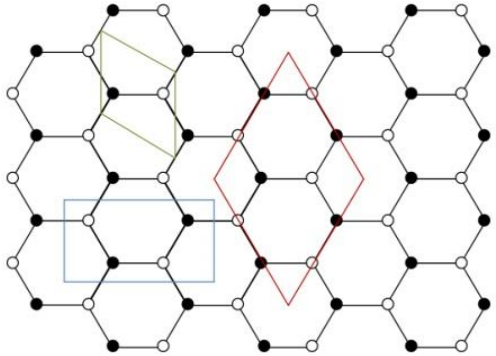
- $H_2O$ molecules are internally bound by strong covalent bonds. Weak intermolecular hydrogen bonds allow for many rotational configurations of the $H_2O$ molecules in ice on a fixed oxygen lattice.

- Ice I*h* is the most common form of $H_2O$ ice. This structure can be viewed as two superimposed hexagonal lattices, where each lattice site contains an oxygen. The molecular alignments are locally ordered but globally disordered.

- Ice I*h* has 4 molecules per primitive unit cell (green trapezoid). Larger unit cells can be defined to better capture the varying $H_2O$ alignments. The red diamond is a 2-D view of the 12-molecule 3-D unit cell used in this work (top right image).



3-D view of the ice I*h* structure.



2-D view of the ice I*h* oxygen lattice.

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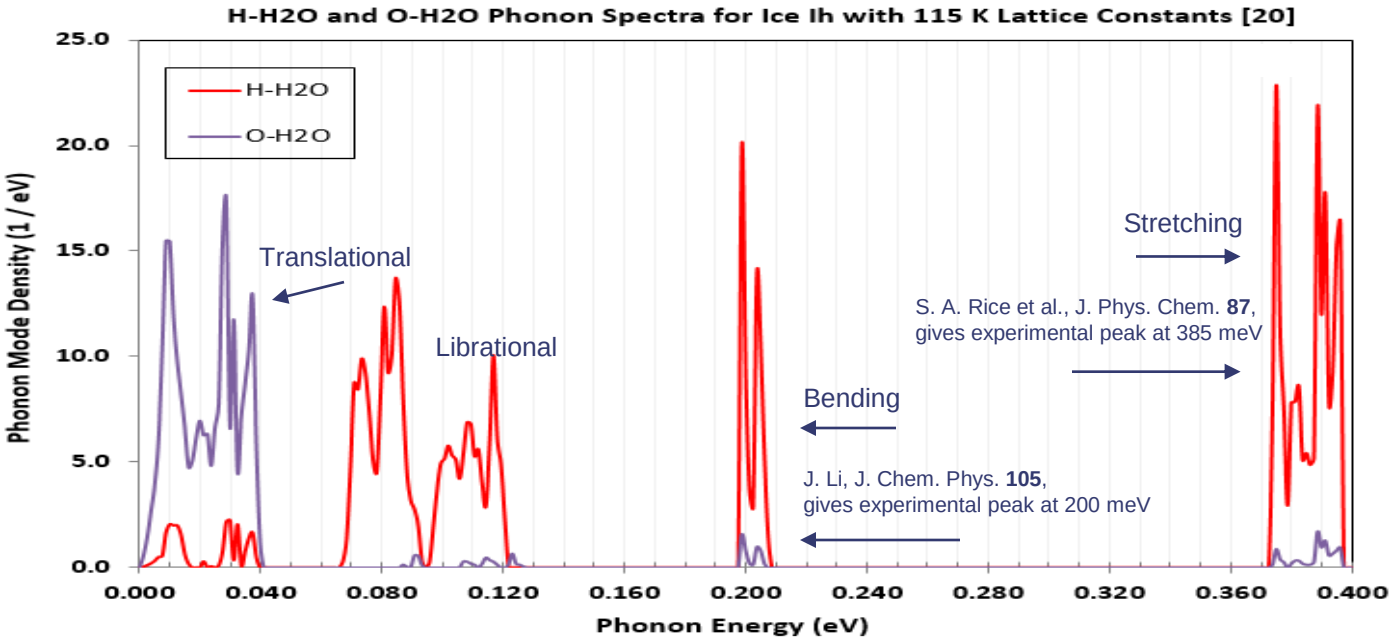
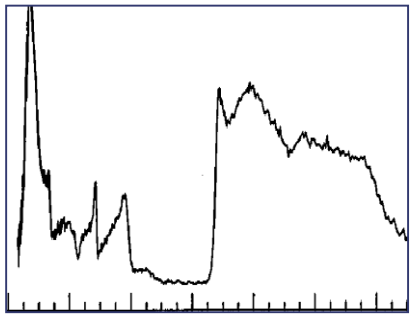
# Phonon Energy Spectra for Ice I*h*



Experimental inelastic neutron scattering spectrum for polycrystalline ice I*h* (same energy scale as above).

J. Li, "Inelastic Neutron Scattering Studies of Hydrogen Bonding in Ices," *Journal of Chemical Physics* **105**, 6733-6755 (1996).

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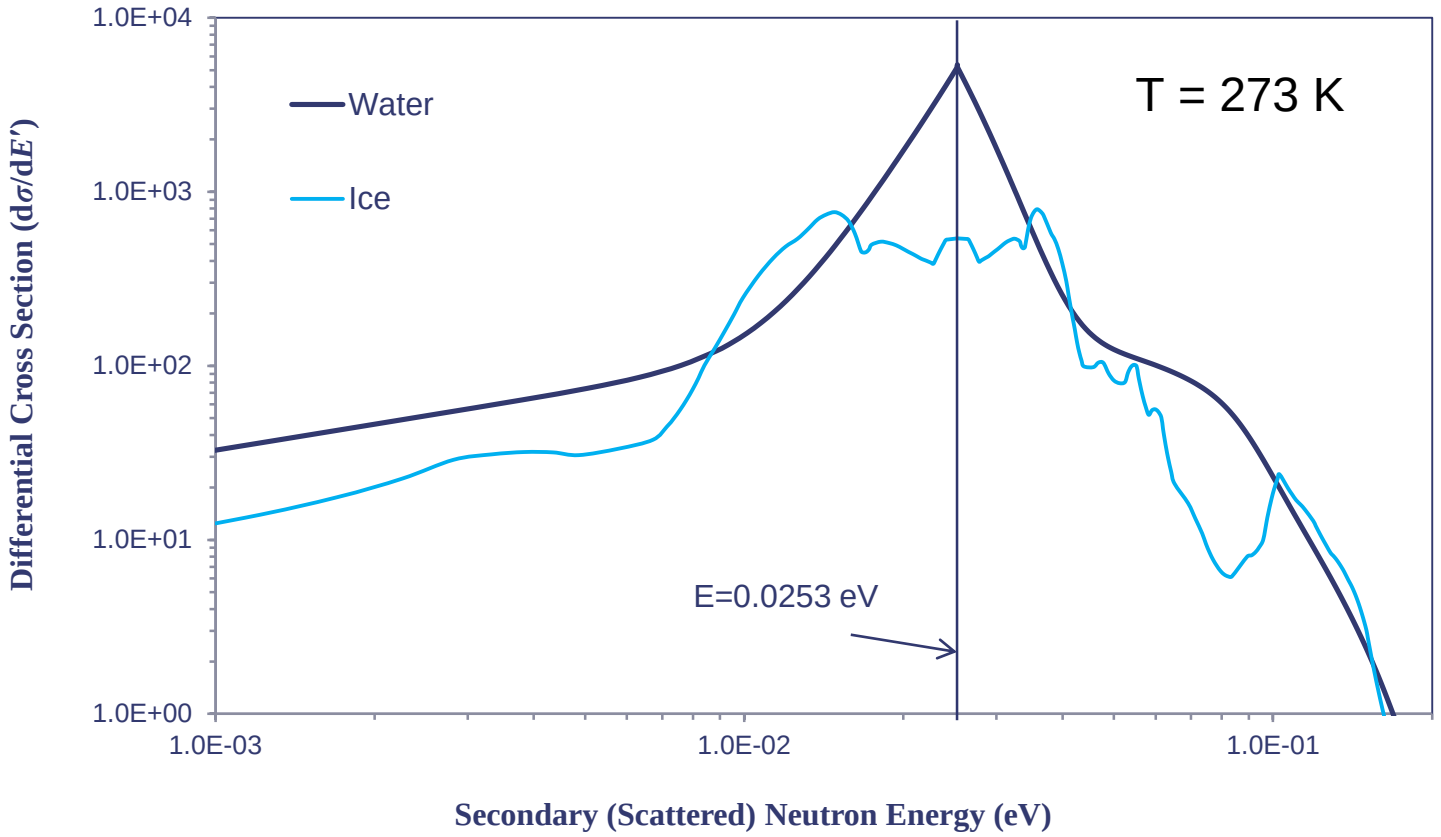
# Inelastic Scattering Energy Spectra for H in Liquid Water vs. Ice

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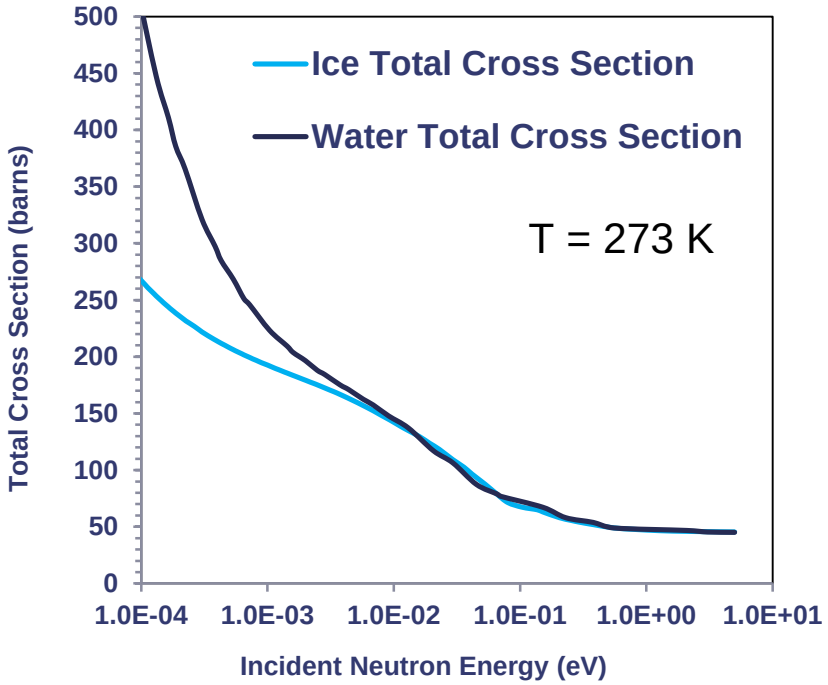
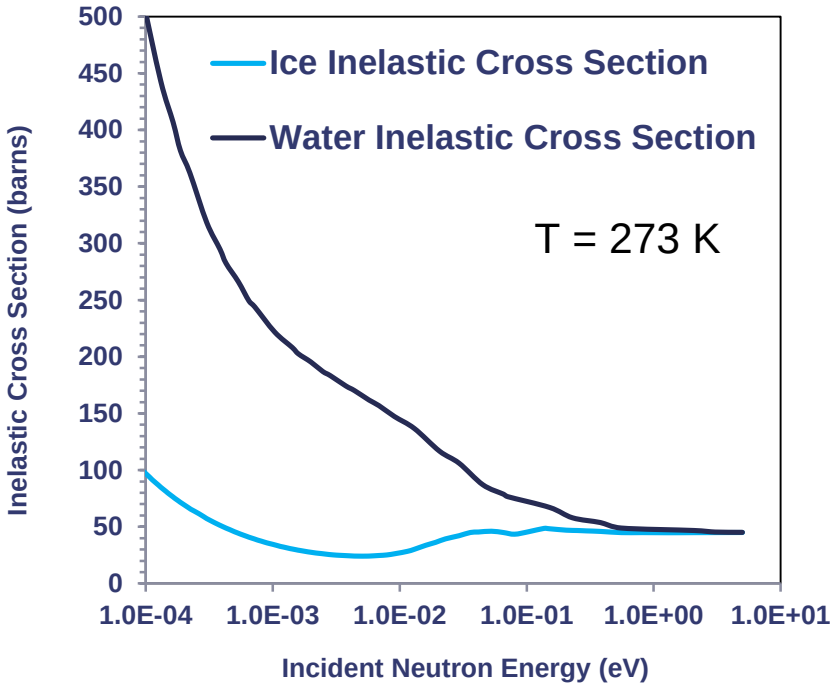
# Total and Inelastic Scattering for Liquid Water vs. Ice

**Total = Inelastic + Elastic + Absorption**




**Inelastic Only**
**(There is no elastic scattering in liquid water)**

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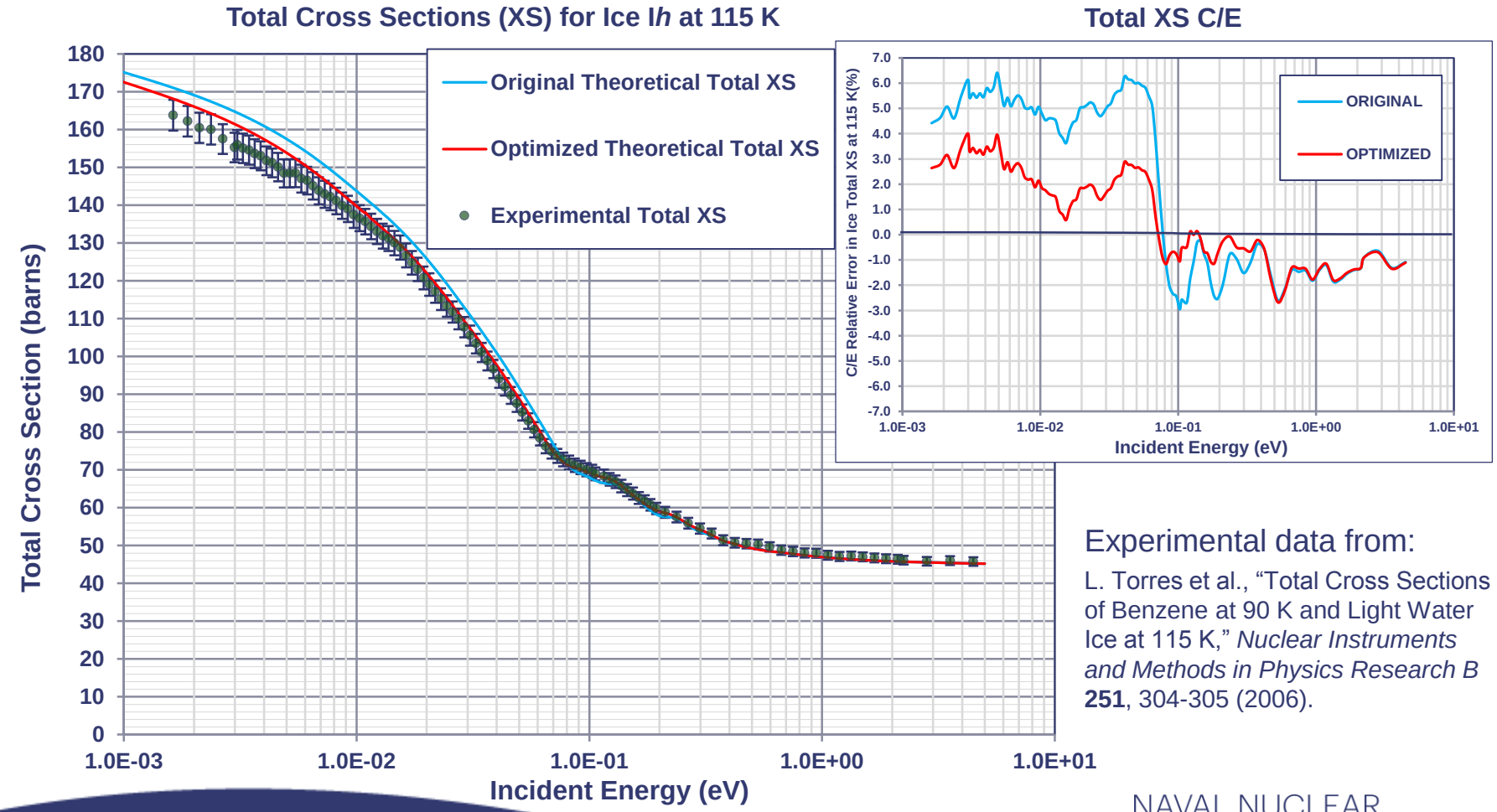
# Theoretical vs. Experimental Total Cross Sections for Ice I*h*




Experimental data from:

L. Torres et al., "Total Cross Sections of Benzene at 90 K and Light Water Ice at 115 K," *Nuclear Instruments and Methods in Physics Research B* **251**, 304-305 (2006).

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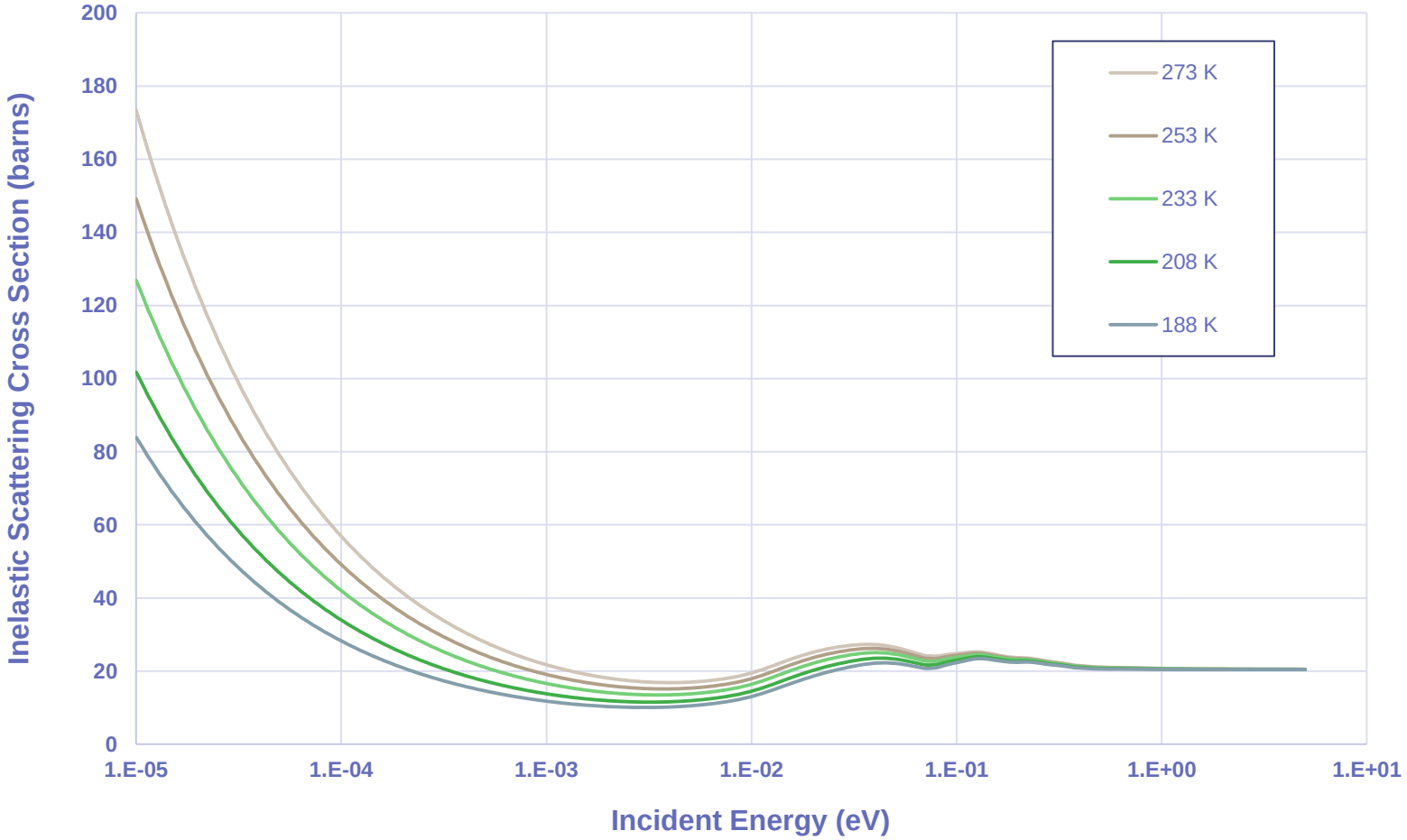
# Inelastic Scattering Cross Sections for H in Ice I*h*

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# A Diffusion Benchmark for TSL Validation

• E. G. Silver measured the diffusion parameters of Ice I*h* in the 1960s using a pulsed-neutron die-away experiment to determine the thermal flux decay time eigenvalues for various-sized cylinders of ice over a range of temperatures.

• After sufficient waiting time following the initial pulse, the neutron population is in thermal equilibrium and settles into the fundamental spatial mode with a single decay time eigenvalue. The experiment was modeled in MC21 and eigenvalue results were compared to measured data.

• In the one-speed diffusion model, the flux decay of the fundamental spatial mode can be expressed as

$\varphi(\mathbf{r},t) = \varphi_0(\mathbf{r}) \exp[-(v\Sigma_a + vDB^2 - CB^4)t]$, where the time eigenvalue $\alpha = v\Sigma_a + vDB^2 - CB^4$

$\Sigma_a$ is the macroscopic absorption cross section
$D = 1/\Sigma_{transport}$ is the diffusion parameter,
v = the effective average neutron velocity,
$B^2$ = geometric buckling, and
C = the diffusion cooling parameter

E. G. Silver, "A Pulsed-Neutron Investigation of the Effect of Temperature on the Decay of a Thermal-Neutron Population in $H_2O$ Ice," *Nuclear Science and Engineering* **34**, 275-284 (1968).

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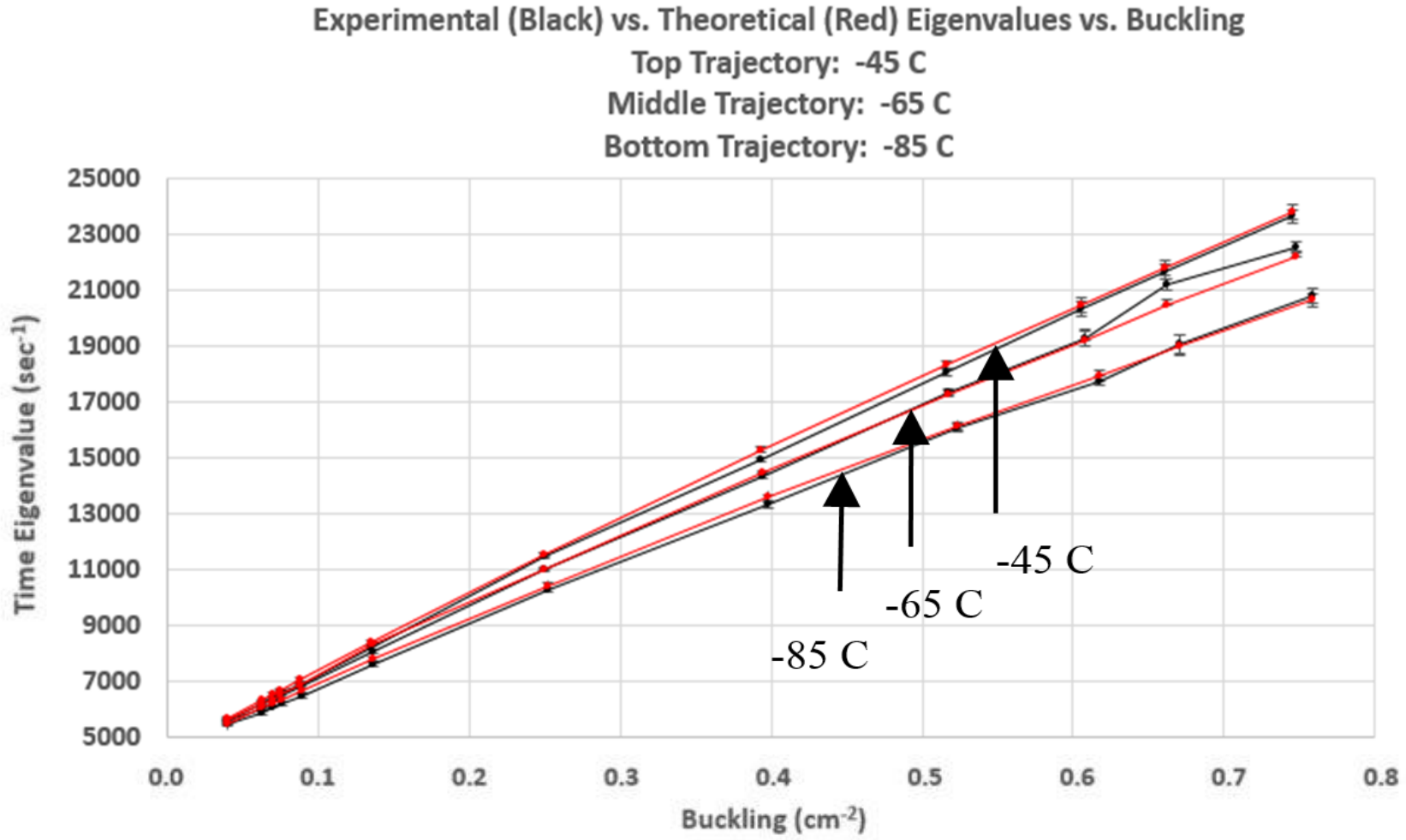
# Benchmark Testing Results

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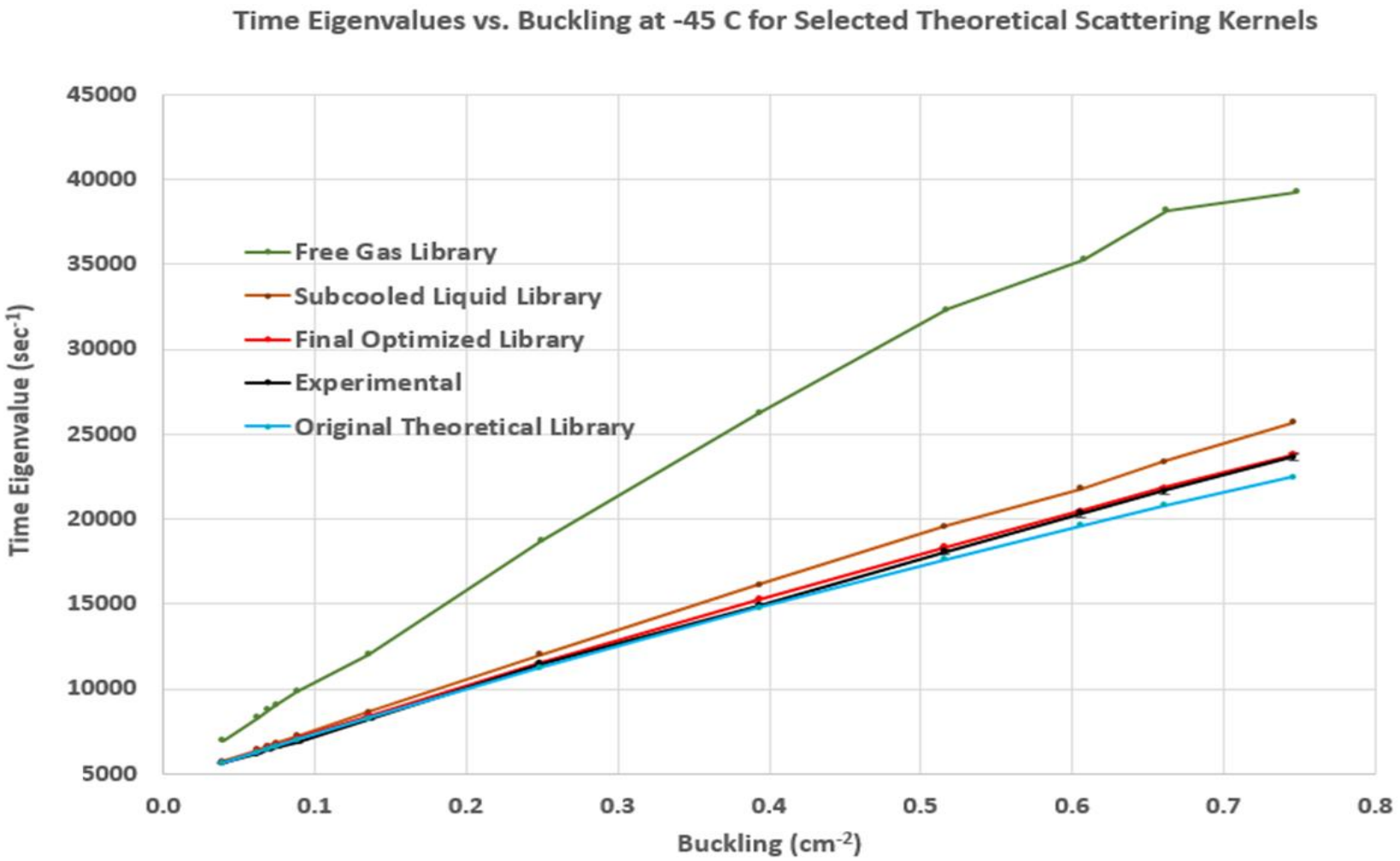
# Benchmark Testing Results

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# Benchmark C/E Fit

| SILVER EXPERIMENTAL | | | | | | | | | FINAL LIBRARY (-45 C) | | | | FINAL LIBRARY (-65 C) | | | | FINAL LIBRARY (-85 C) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| -45 C | | | -65 C | | | -85 C | | | MC21 α | σ | C/E | σ | MC21 α | σ | C/E | σ | MC21 α | σ | C/E | σ |
| $B^2$ | α | σ | $B^2$ | α | σ | $B^2$ | α | σ | | | | | | | | | | | | |
| 0.0394 | 5630 | 52 | 0.0395 | 5579 | 59 | 0.0396 | 5443 | 35 | 5659 | 6 | 1.0051 | 0.009 | 5589 | 3 | 1.0018 | 0.009 | 5504 | 3 | 1.0112 | 0.007 |
| 0.0621 | 6207 | 38 | 0.0621 | 6031 | 35 | 0.0624 | 5890 | 61 | 6325 | 5 | 1.0191 | 0.006 | 6190 | 4 | 1.0264 | 0.006 | 6057 | 1 | 1.0284 | 0.011 |
| 0.0689 | 6413 | 66 | 0.0690 | 6266 | 22 | 0.0693 | 6096 | 53 | 6523 | 2 | 1.0172 | 0.010 | 6370 | 2 | 1.0166 | 0.010 | 6217 | 4 | 1.0199 | 0.009 |
| 0.0748 | 6584 | 70 | 0.0749 | 6455 | 38 | 0.0752 | 6226 | 66 | 6697 | 2 | 1.0171 | 0.011 | 6530 | 2 | 1.0117 | 0.011 | 6365 | 2 | 1.0223 | 0.011 |
| 0.0880 | 6888 | 49 | 0.0881 | 6825 | 76 | 0.0885 | 6493 | 72 | 7074 | 3 | 1.0270 | 0.007 | 6876 | 3 | 1.0075 | 0.007 | 6682 | 2 | 1.0290 | 0.011 |
| 0.1352 | 8214 | 70 | 0.1354 | 8052 | 73 | 0.1362 | 7593 | 72 | 8415 | 3 | 1.0244 | 0.009 | 8356 | 5 | 1.0377 | 0.009 | 7804 | 3 | 1.0278 | 0.010 |
| | | | | | | | | | Low $B^2$ Avg. C/E | | 1.0183 | | Low $B^2$ Avg. C/E | | 1.0169 | | Low $B^2$ Avg. C/E | | 1.0231 | |
| 0.2490 | 11493 | 87 | 0.2494 | 10997 | 76 | 0.2514 | 10272 | 82 | 11546 | 12 | 1.0046 | 0.008 | 10985 | 10 | 0.9989 | 0.008 | 10427 | 8 | 1.0150 | 0.008 |
| 0.3933 | 14915 | 73 | 0.3941 | 14341 | 65 | 0.3981 | 13310 | 100 | 15302 | 56 | 1.0259 | 0.006 | 14458 | 43 | 1.0082 | 0.006 | 13598 | 33 | 1.0216 | 0.008 |
| 0.5161 | 18083 | 127 | 0.5174 | 17307 | 132 | 0.5233 | 16055 | 129 | 18350 | 59 | 1.0148 | 0.008 | 17259 | 45 | 0.9972 | 0.008 | 16158 | 47 | 1.0064 | 0.009 |
| 0.6058 | 20349 | 245 | 0.6078 | 19292 | 295 | 0.6172 | 17772 | 189 | 20482 | 52 | 1.0065 | 0.012 | 19232 | 39 | 0.9969 | 0.012 | 17952 | 30 | 1.0102 | 0.011 |
| 0.6606 | 21669 | 258 | 0.6624 | 21226 | 195 | 0.6710 | 19073 | 344 | 21818 | 104 | 1.0069 | 0.013 | 20449 | 77 | 0.9634 | 0.013 | 19033 | 57 | 0.9979 | 0.018 |
| 0.7460 | 23662 | 229 | 0.7482 | 22555 | 198 | 0.7586 | 20808 | 236 | 23795 | 105 | 1.0056 | 0.011 | 22199 | 77 | 0.9842 | 0.011 | 20663 | 57 | 0.9930 | 0.012 |
| | | | | | | | | | High $B^2$ Avg. C/E | | 1.0107 | | High $B^2$ Avg. C/E | | 0.9915 | | High $B^2$ Avg. C/E | | 1.0074 | |

For the six highest buckling geometries ($B^2$ is in units of $cm^{-2}$), which are the most sensitive to the supplied thermal scattering kernel, the average C/E across all three temperatures is 1.003.

For the six lowest buckling geometries, the average C/E across all three temperatures is 1.019. These cases are relatively insensitive to the supplied thermal scattering kernel, indicating there may be a slight positive bias in the absorption cross sections. These results are consistent with the ~2.5% ENDF quoted uncertainty for H absorption cross sections in the thermal energy range.

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# Hexagonal Ice I*h* Summary

- While the total cross sections for liquid water and solid ice are similar (except at extremely low incident energies), the details of the scattering kernels differ significantly and result in significant differences in the diffusion of neutrons through the material.

- Unlike liquid water, a large fraction of neutron scattering that takes place in ice is elastic. Consequently, Ice I*h has* enhanced reflective properties over liquid water that could have important criticality safety implications.

- Combining the first-principles VASP/PHONON methodology with experimentally measured scattering data and a diffusion benchmark has yielded the development and successful testing of a thermal neutron scattering kernel for Ice I*h.*

- A full ENDF File 7 thermal neutron scattering library has been submitted to the National Nuclear Data Center for the ice I*h* structure for a range of temperatures of interest.

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