Project ID: ST135

HyMARC: Technical Activities at NIST

Craig Brown, Terrence Udovic (NIST)

Mirjana Dimitrievska, Thomas Gennett (NREL)

National Renewable Energy Laboratory & National Institute of Standards and Technology

2019 DOE Annual Merit Review

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Overview

Timeline and Budget

- **Timeline:**

  Phase 1: 10/1/2015 to 9/30/2018

  Phase 2: 10/1/2018 to 9/30/2022

- **Budget:**

  2 post-docs are provided for this effort through HyMARC/NREL

- **Barriers Addressed:**

General:

A. Cost; B. Weight and Volume; C. Efficiency;
E. Refueling Time;

Reversible Solid-State Material:

M. Hydrogen Capacity and Reversibility;
N. Understanding of Hydrogen Physi- and Chemisorption;
O. Test Protocols and Evaluation Facilities;

- **HyMARC Collaborators**
  - LBNL – Jeff Long, Martin Head-Gordon
  - PNNL – Tom Autrey, Mark Bowden
  - SNL – Vitalie Stavila ,
  - LLNL – Brandon Wood
  - HyMARC seedling - Eric Majzoub (Univ. Missouri-St. Louis)

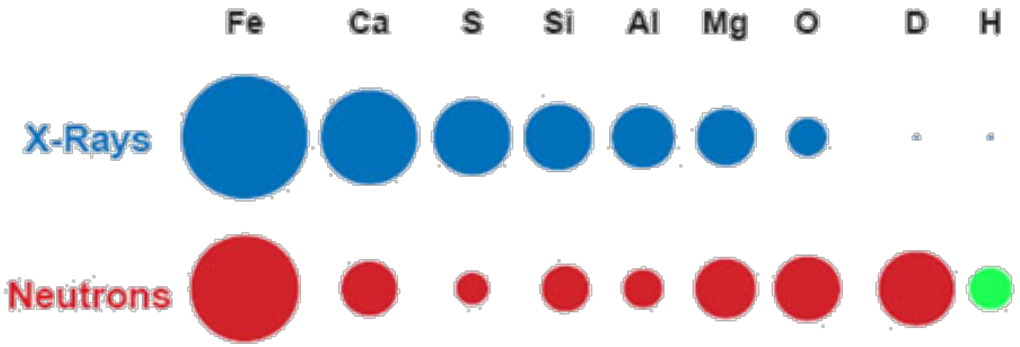
Relevance: Project Objectives

An synergistic collaboration and research effort among HyMARC participants to:

- *develop* and *enhance* hydrogen-storage core capabilities, i.e. characterization techniques
- *validate* claims, concepts, and theories of hydrogen-storage materials
- *double* hydrogen storage energy density (increase from 25g/L to 50 g/L)

Relevance: Impact of Neutron Analyses

- Neutrons provide unique specificity towards determination of hydrogen properties
  - Enables identification of isotopically-labelled hydrogen location within complex structures
  - Enables identification of hydrogen dynamics within complex structures



http://www.ne.ncsu.edu/nrp/npdf.html

Approach: Neutron Scattering

Utilize neutrons to characterize and validate hydrogen storage media

NIST provides neutron-scattering-based characterization of materials of interest within HyMARC and other DOE-funded projects

- Solvent addition as a solution for enhancing hydrogen storage properties of magnesium borohydride ($Mg(BH_4)_2$) — **HyMARC** (PNNL/ LBNL/NREL)
- Quantum rotational tunneling of BH_4^- anions in lithium benzimidazolate-borohydride $Li_2(bIm)BH_4$ — **NIST**
- H_2 adsorption in a Cu(I) MOF — **U.C. Berkeley/ NIST**

Accomplishments and Progress:
Enhancing hydrogen storage properties of $Mg(BH_4)_2$

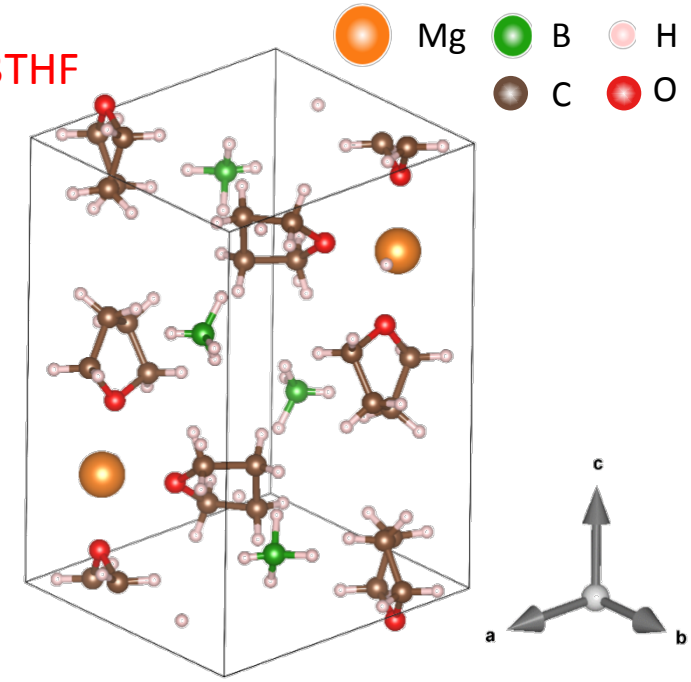
decomposition

$$Mg(BH_4)_2 \xrightarrow[200\ ^oC]{5\ weeks} 1/3\ Mg(B_3H_8)_2 + 2/3\ MgH_2 + 2/3\ H_2$$

L – solvent: tetrahydrofuran (THF)

$$Mg(BH_4)_2 \bullet \mathbf{L} \xrightarrow[200\ ^oC]{24\ h} 1/5\ MgB_{10}H_{10} \bullet \mathbf{L} + 4/5\ MgH_2 + 11/5\ H_2$$

$Mg(BH_4)_2 \cdot 3THF$



"…The modified coordination may play a role in the dehydrogenation mechanism…"[1]

Objective: Look into the fundamental properties of $Mg(BH_4)_2 \cdot L$ and try to explain how the solvent coordination might have the beneficial effect of enhancing dehydrogenation kinetics.

[1] M. Chong et al. *Inorganics* **2017**, *5*, 89.

Accomplishments and Progress:
Enhancing hydrogen storage properties of $Mg(BH_4)_2$

Samples: $Mg(BH_4)_2 \cdot L$ were prepared by adding an excess of solvent to $Mg(BH_4)_2$ at room temperature.

$Mg(BH_4)_2$

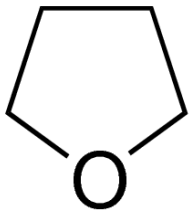
$Mg(BH_4)_2 \cdot 1/2THF \longrightarrow Mg(BH_4)_2 \cdot 1/2TDF$

Selective deuteration

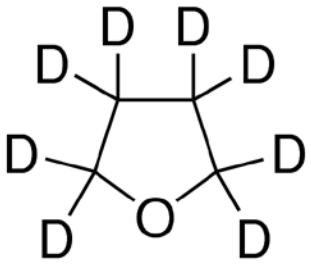
$Mg(BH_4)_2 \cdot 3THF \longrightarrow Mg(BH_4)_2 \cdot 3TDF$

D - Deuterium

Reference samples:



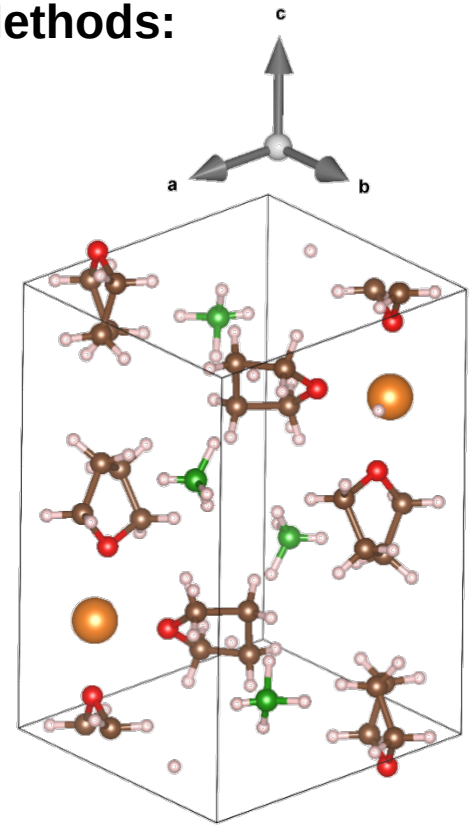
Tetrahydrofuran (THF)



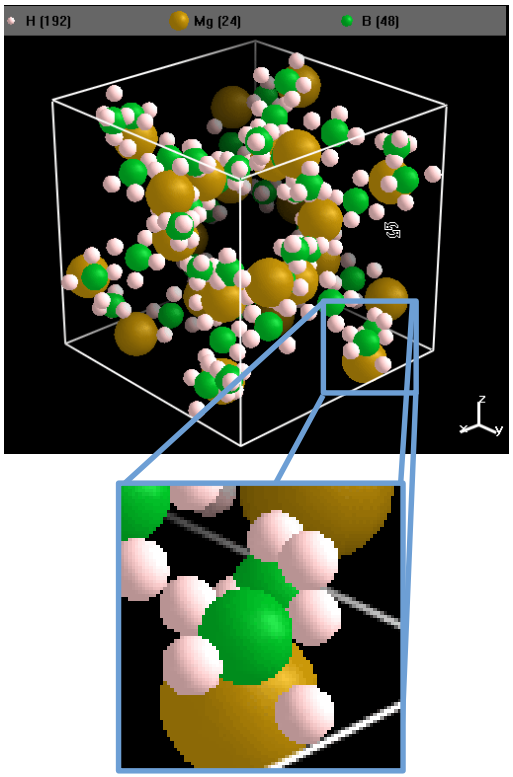
Tetrahydrofuran-d_8 (TDF)

Accomplishments and Progress:
Enhancing hydrogen storage properties of $Mg(BH_4)_2$

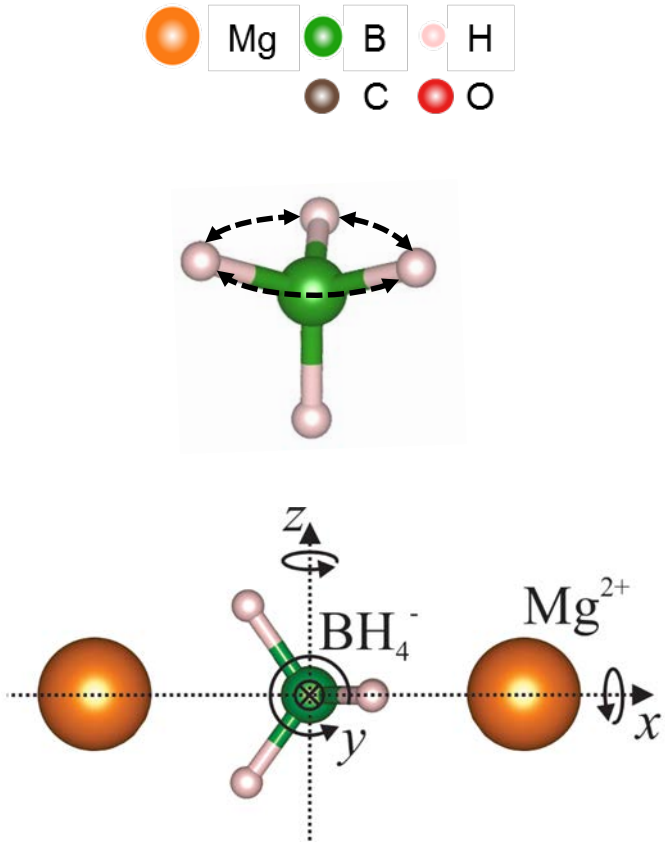
Methods:



Neutron powder diffraction (NPD): structure and phases



Neutron vibrational spectroscopy (NVS): vibrational modes

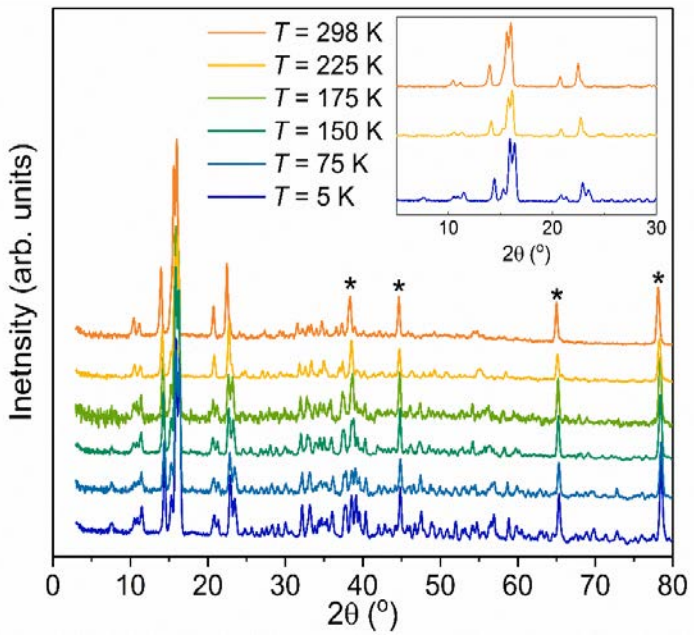


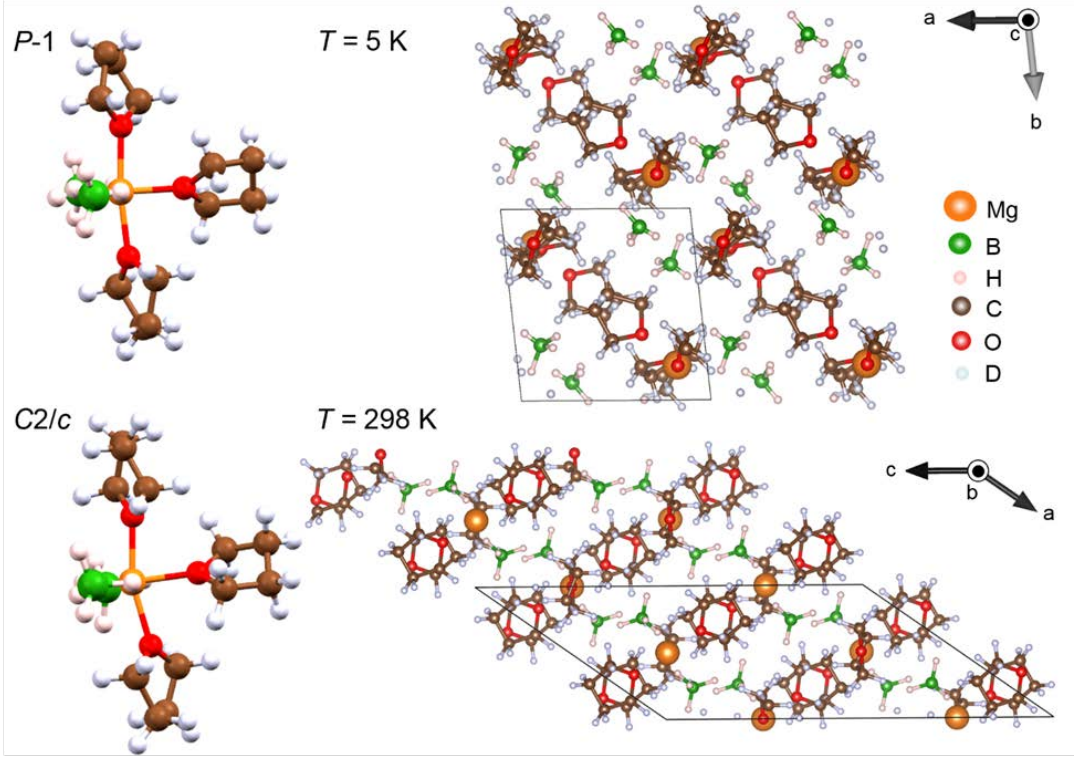
Quasielastic neutron scattering (QENS): reorientational dynamics

NREL NATIONAL RENEWABLE ENERGY LABORATORY · Sandia National Laboratories · Lawrence Livermore National Laboratory · Berkeley Lab · Pacific Northwest National Laboratory · NIST · SLAC National Accelerator Laboratory

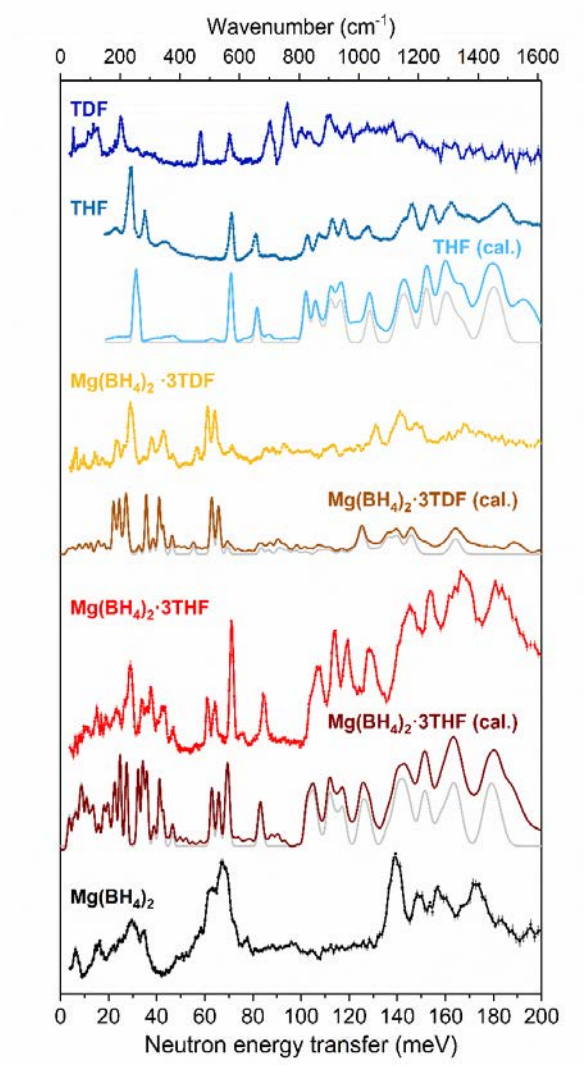
Accomplishments and Progress:
Enhancing hydrogen storage properties of $Mg(BH_4)_2$

Neutron powder diffraction measurements of $Mg(BH_4)_2 \cdot 3TDF$ upon heating from 5 K to 298 K indicate a phase transition in the temperature range between 175 and 225 K, from triclinic (*P*-1) to monoclinic (*C*2/*c*) structure.

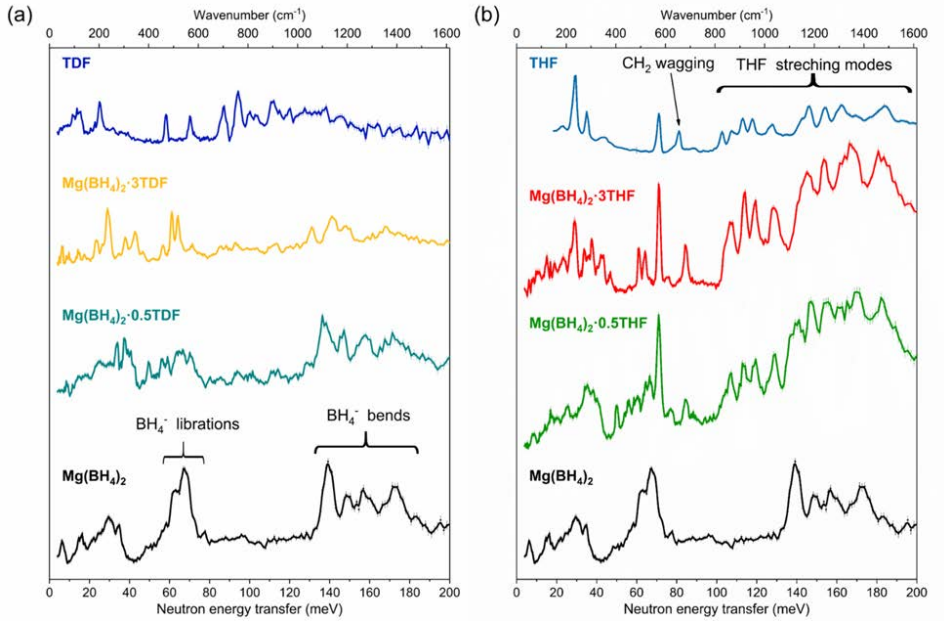




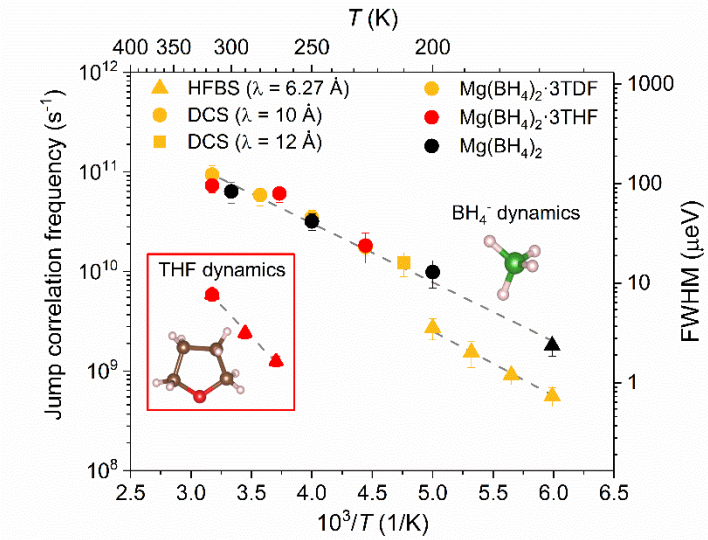
Accomplishments and Progress:
Enhancing hydrogen storage properties of $Mg(BH_4)_2$

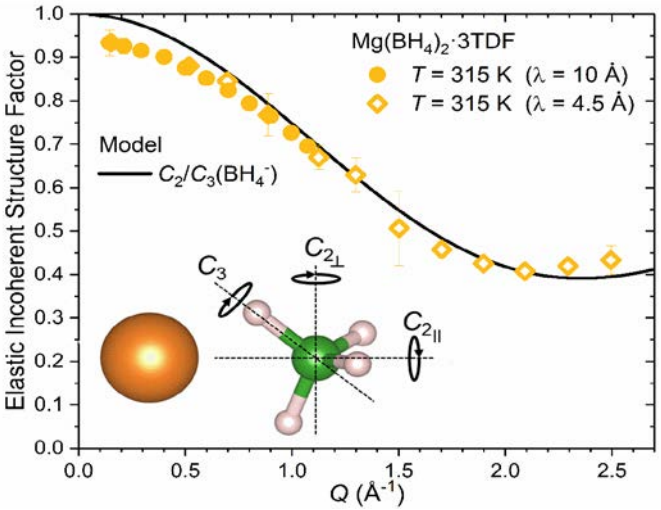


- Vibrational properties are strongly influenced by the THF environment.
- In particular, there is a shift towards lower energies of the BH_4^- librational and bending modes with THF present as a result of changes in the bond lengths and force constants. Splitting in spectral features is also observed and explained by the lowering of the overall symmetry of $Mg(BH_4)_2 \cdot 3THF$.

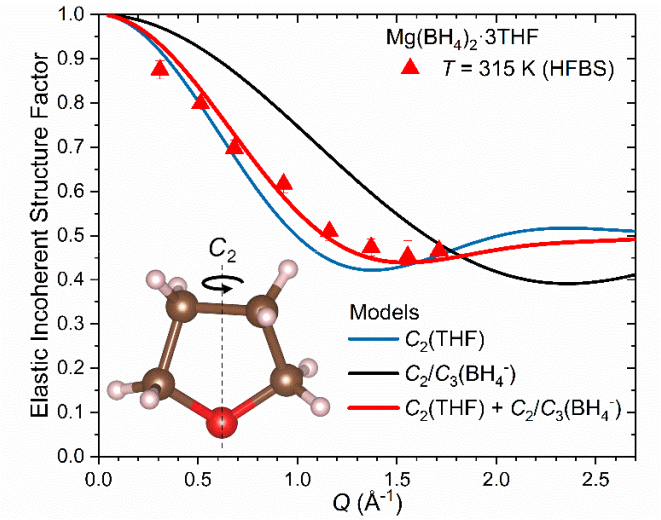


Accomplishments and Progress:
Enhancing hydrogen storage properties of $Mg(BH_4)_2$

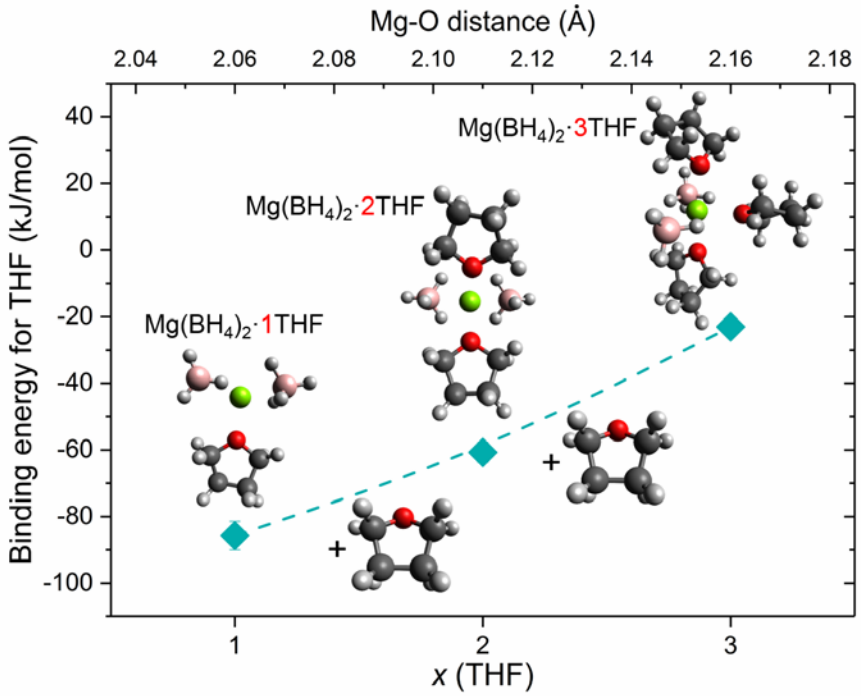




- Orientational mobilities of the BH_4^- anions obtained from QENS are not particularly sensitive to the presence of THF or TDF and compare well with the mobilities of BH_4^- anions in unsolvated $Mg(BH_4)_2$
- the THF molecules in $Mg(BH_4)_2 \cdot 3THF$ are also found to be orientationally mobile, undergoing 180° reorientational jumps around their C_2 molecular symmetry axis.



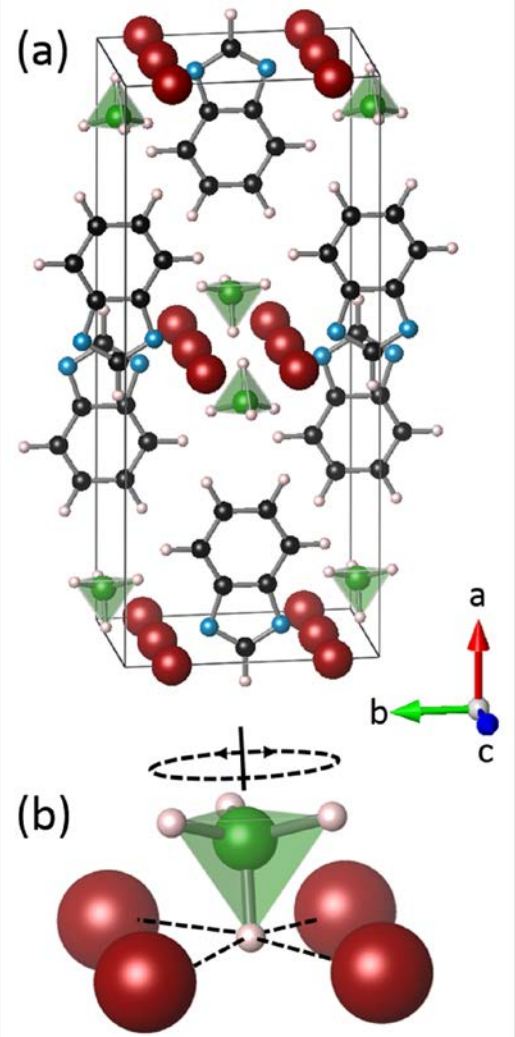
Accomplishments and Progress: Enhancing hydrogen storage properties of $Mg(BH_4)_2$



- Computational results for the solid state using the crystal structures suggest the static binding energy of each THF molecule averages to -27 kJ/mol THF. On the other hand, DFT calculations for the hypothetical $Mg(BH_4)_2$·1THF complex suggests the binding energy is greater for the first THF, then the subsequent ·2THF and ·3THF adducts.

- From this combined experimental and computational study of THF adducts of $Mg(BH_4)_2$, we find little direct interaction between the THF and the BH_4^- anion. We propose that using fractions of THF to $Mg(BH_4)_2$ is beneficial in (i) preventing weakly bound THF from coming free from the Mg^{2+} cation and (ii) disrupts the stability of crystalline phase leading to a lower melting point and enhanced kinetics.

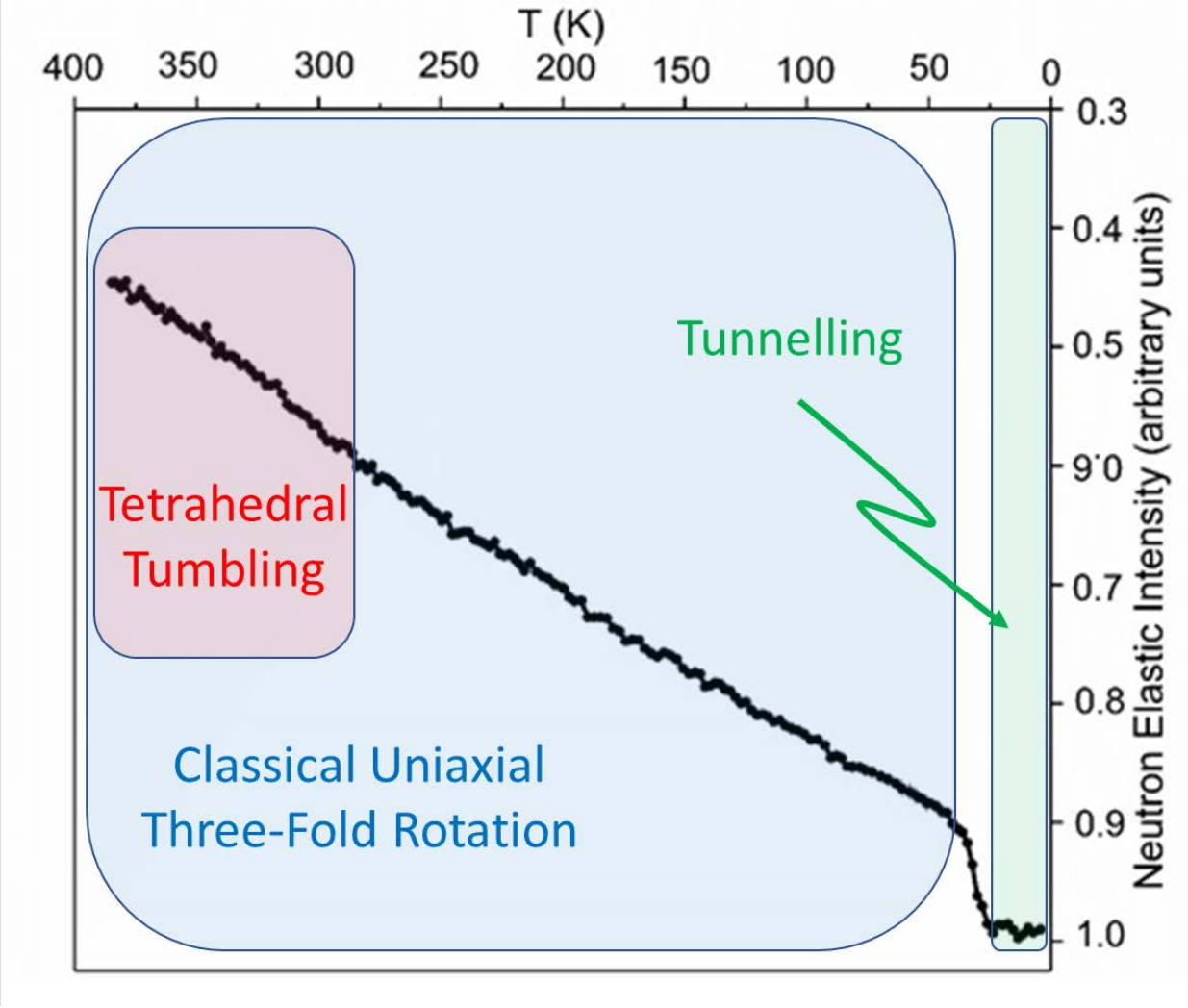
Accomplishments and Progress: Quantum BH_4^- Rotational Tunneling in $Li_2(bIm)BH_4$



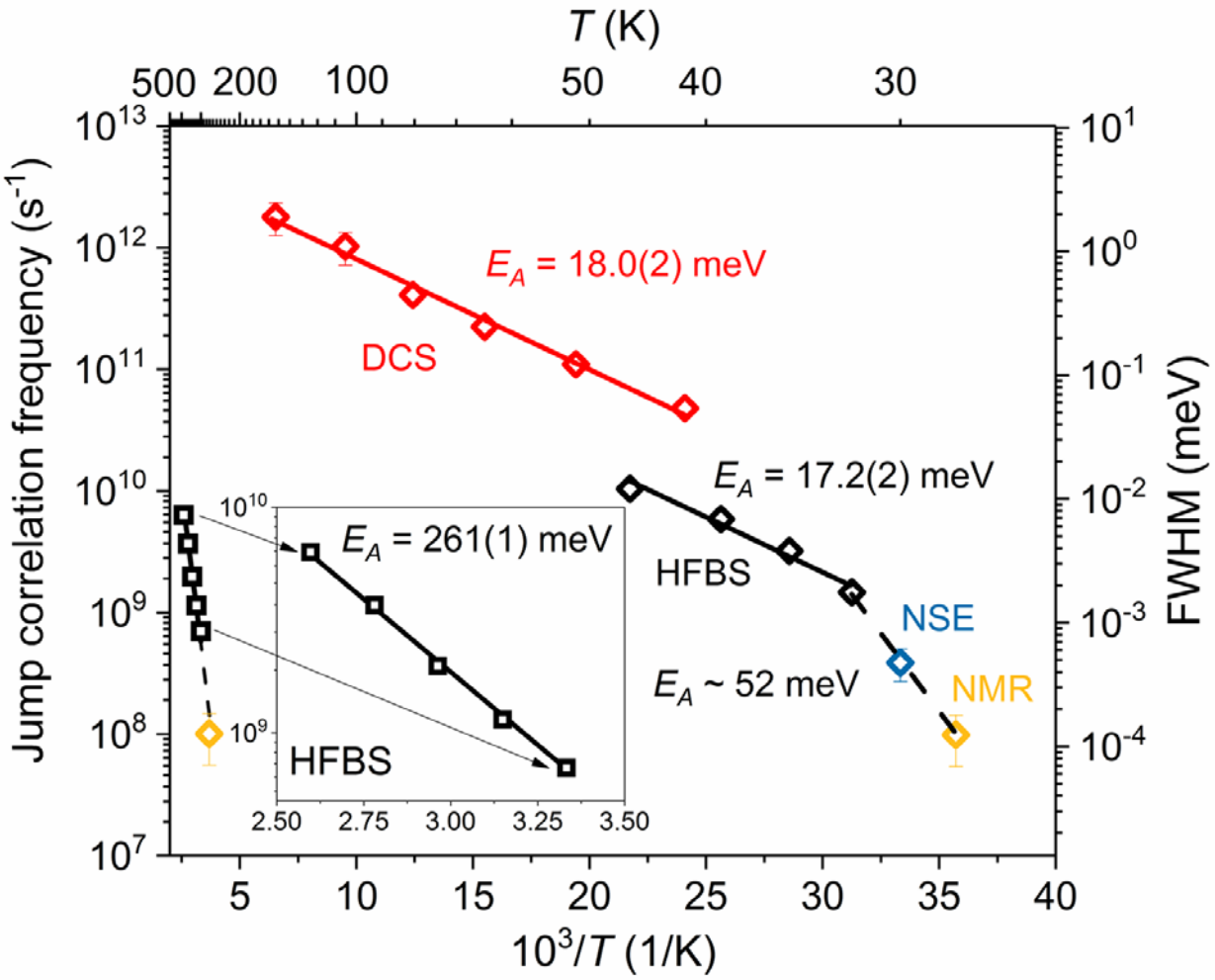
- Reorientational BH_4^- motion is known to contribute strongly to the balance of energies determining the thermodynamic stability of borohydrides.
- Therefore, information on the reorientational dynamics is important for understanding the fundamental properties of these compounds.
- The hydrogen dynamics in lithium benzimidazolate-borohydride, $Li_2(bIm)(BH_4)$ (bIm = $C_7H_5N_2$) was studied using various neutron scattering techniques and DFT calculations, in order to get better insights into the possible application of this material in hydrogen storage.

Accomplishments and Progress: Quantum BH_4^- Rotational Tunneling in $Li_2(bIm)BH_4$

Neutron-elastic-scattering fixed-window scan on the High-Flux Backscattering Spectrometer (HFBS) upon heating at 1 K min^{-1} from 4 K to 385 K at 1.2 $Å^{-1}$ neutron momentum transfer.

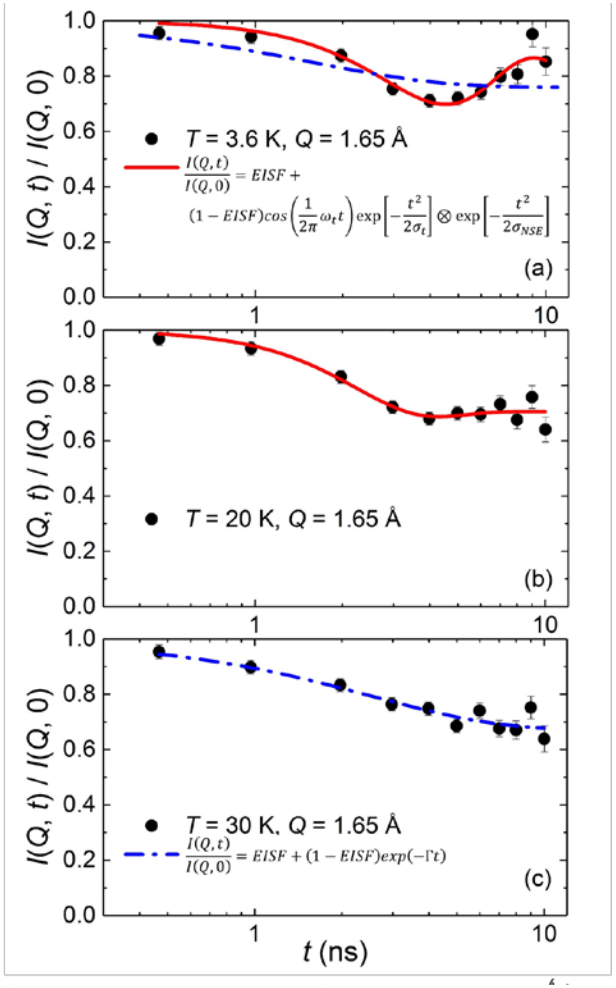


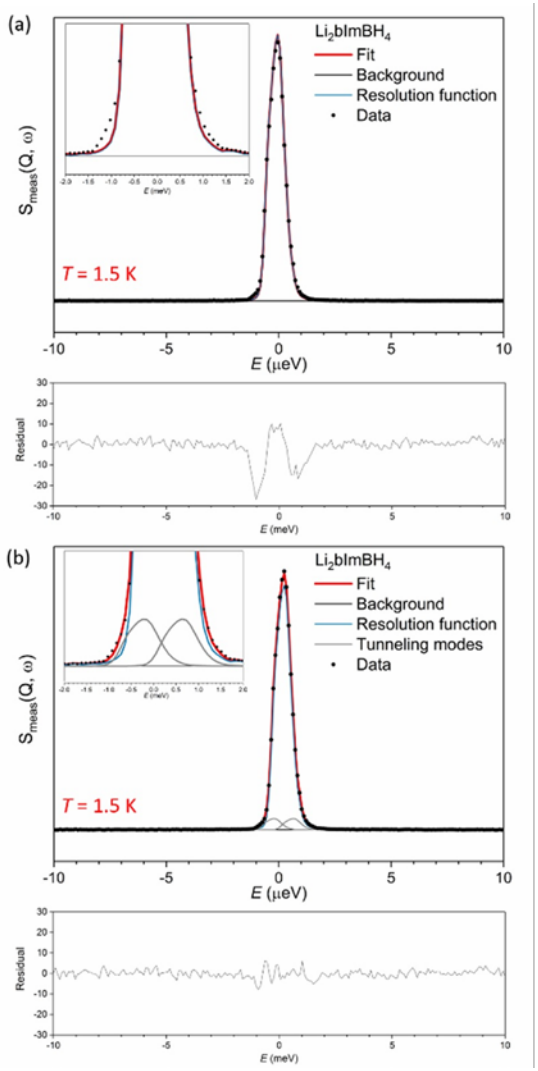
Accomplishments and Progress:
Quantum BH_4^- Rotational Tunneling in $Li_2(bIm)BH_4$



Arrhenius-type plots of the derived jump correlation frequencies τ_1^{-1} versus $1/T$ from the various QENS and NMR results for the much more rapid three-fold reorientations of the three H atoms associated with the $-BH_3$ fragment, as well as for the much slower exchange of these H atoms with the remaining, Li_4-anchored H atom.

Accomplishments and Progress: Quantum BH_4^- Rotational Tunneling in $Li_2(bIm)BH_4$

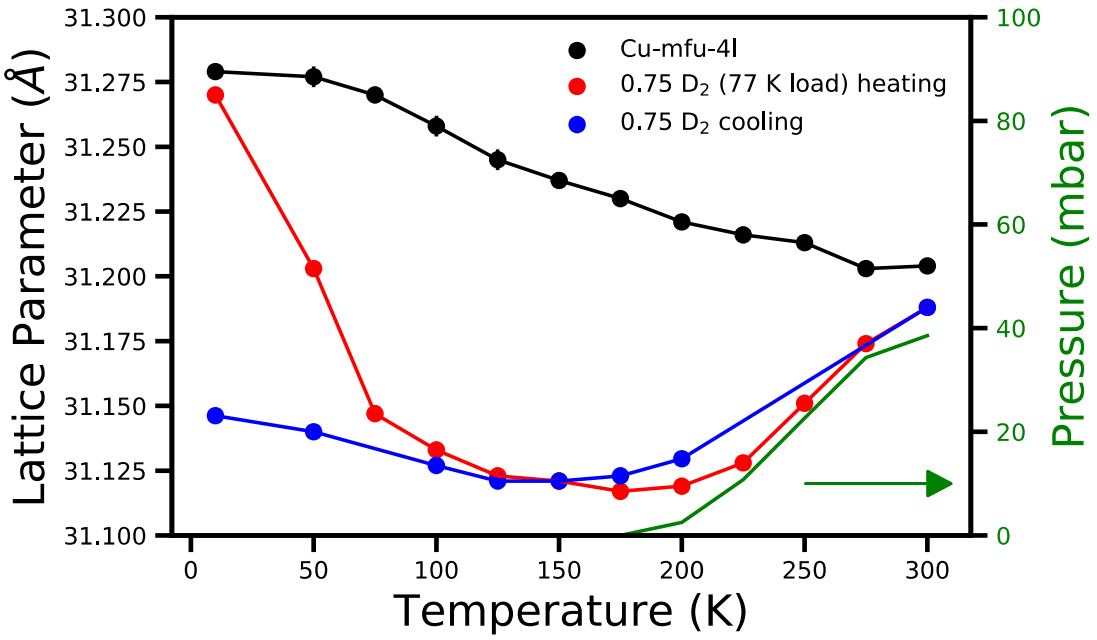




It is a rare observation of rotational tunneling of the BH_4^- anion via neutron scattering, and possibly the second neutron-spin-echo (NSE) observation of tunnelling phenomena after an early work on dimethylacetylene.

Both NMR and neutron scattering results for $Li_2(bIm)(BH_4)$ are described in terms of a gradual transition from the regime of low-temperature quantum dynamics (rotational tunneling of BH_4^- anions) to the regime of classical three-fold uniaxial jump reorientations at higher temperatures.

Accomplishments and Progress: H_2 adsorption in a Cu(I) MOF



Gas adsorption isotherms and Infra-red spectra indicate a strong temperature dependence of H_2 adsorption characteristics in a Cu(I) MOF.

We performed variable-temperature diffraction to monitor how the H_2 is interacting with the framework.

- The bare framework shows a moderate negative thermal expansion (NTE).
- 0.75 D_2:Cu dosed at 77 K and then cooled to base (prior to heating) shows a strong NTE.
- Recooling to base shows a large hysteresis away form the physisorbed system at low temperature. Rietveld refinement is consistent with two types of H_2, one being much closer to the Cu(I) site.

Summary

- Orientational mobilities of the BH_4^- anions in $Mg(BH_4)_2 \cdot x$THF adducts are found not to be particularly sensitive to the presence of THF and compare well with the mobilities of BH_4^- anions in unsolvated $Mg(BH_4)_2$. The THF molecules in $Mg(BH_4)_2 \cdot 3$THF are also found to be orientationally mobile, undergoing 180° reorientational jumps around their C_2 molecular symmetry axis.

- Both NMR and neutron scattering results for $Li_2(bIm)(BH_4)$ are described in terms of a gradual transition from the regime of low-temperature quantum dynamics (rotational tunneling of BH_4^- anions) to the regime of classical three-fold uniaxial jump reorientations at higher temperatures. This uncommon behavior is due to the unique BH_4^- coordination in this compound.

- Gas adsorption isotherms and infra-red spectra of H_2 in a Cu(I) MOF indicate a strong temperature dependence of the H_2 adsorption behavior. Rietveld refinement analysis of complementary diffraction data is consistent with two types of H_2, one being much closer to the Cu(I) site.

Collaboration and Coordination

- NREL/NIST collaboration
  - Characterizing ultra-microporous materials using neutron diffraction and neutron spectroscopy
- NREL/NIST collaboration with LBNL and PNNL
  - Characterizing hydrogen adsorption in metal organic framework materials using neutron diffraction and neutron spectroscopy
  - Characterizing various hydrogen storage materials at the Advanced Photon Source
  - Various neutron scattering characterization of $Mg(BH_4)_2 \cdot x$THF

Responses to Previous Year Reviewers' Comments

Project was not reviewed last year.

Proposed Future Work

- Perform QENS measurements on recently synthesized $Mg(^{11}BH_4)_2 \cdot x$THF and $Mg(^{11}BH_4)_2 \cdot x$TDF materials to gain insights into the reorientation dynamics and mobilities of BH_4^- anions and provide more information on the interaction between THF and $Mg(BH_4)_2$.
- Continue neutron diffraction/NVS characterizations of new MOF materials

Any proposed future work will depend on the available funding.

Publications

1. M. Dimitrievska, V. Stavila, A. V. Soloninin, R. V. Skoryunov, O. A. Babanova, H. Wu, W. Zhou, W. S. Tang, A. Faraone, J. D. Tarver, B. A. Trump, A. V. Skripov, and T. J. Udovic, The Nature of Decahydro-*Closo*-Decaborate Anion Reorientations in an Ordered Alkali-Metal Salt: $Rb_2B_{10}H_{10}$, , **J. Phys. Chem. C**, 122, 15198-15207 (2018).

2. M. Dimitrievska, J.-N. Chotard, R. Janot, A. Faraone, W. S. Tang, A. V. Skripov, and T. J. Udovic, Tracking the Progression of Anion Reorientational Behavior between α-phase and β-phase Alkali-Metal Silanides by Quasielastic Neutron Scattering, **J. Phys. Chem. C**, 122, 23985-23997 (2018).

3. M. Dimitrievska, P. Shea, K. E. Kweon, M. Bercx, J. B. Varley, W. S. Tang, A. V. Skripov, V. Stavila, T. J. Udovic, B. C. Wood, Carbon Incorporation and Anion Dynamics as Synergistic Drivers for Ultrafast Diffusion in Superionic $LiCB_{11}H_{12}$ and $NaCB_{11}H_{12}$, **Adv. Energy Mater.**, 1703422 (2018).

4. W. S. Tang, M. Dimitrievska, V. Stavila, W. Zhou, H. Wu, A. A. Talin, T. J. Udovic, Order–Disorder Transitions and Superionic Conductivity in the Sodium nido-Undeca(carba)borates, **Chem. Mater.**, 29, 10496–10509 (2017).

5. Asgari, M., Semino, R., Schouwink, P., Kochetygov, I., Trukhina, O., Tarver, J.D., Bulut, S., Yang, S., Brown, C.M., Ceriotti, M., Queen, W.L., An In-Situ Neutron Diffraction and DFT Study of Hydrogen Adsorption in a Sodalite-Type Metal–Organic Framework, Cu-BTTri, **Eur. J. Inorganic Chem.** 2019, 1147-1154 (2019).

6. Kapelewski, M.T., Runčevski, T., Tarver, J.D., Jiang, H.Z.H., Hurst, K.E., Parilla, P.A., Ayala, A., Gennett, T., FitzGerald, S.A., Brown, C.M., Long, J.R., Record High Hydrogen Storage Capacity in the Metal–Organic Framework Ni_2(m-dobdc) at Near-Ambient Temperatures, **Chem. Mater.** 30, 8179-8189 (2018).

7. Strobel, T.A., Ramirez-Cuesta, A.J., Daemen, L.L., Bhadram, V.S., Jenkins, T.A., Brown, C.M., and Cheng, Y., Quantum Dynamics of H_2 Trapped within Organic Clathrate Cages, **Phys. Rev. Lett.** 120, 120402 (2018).

Presentations

1. M. Dimitrievska: "Neutron Scattering Studies of Hydrogenous Materials for Next-Generation Energy Storage", ACS National Meeting & Exposition, New Orleans, LA, Mar. 2018.
2. M. Dimitrievska: "Role of Solvent Adducts in Hydrogen Dynamics of Metal Borohydrides: Neutron-Scattering Characterization", ACS National Meeting & Exposition, New Orleans, LA, Mar. 2018.
3. M. Dimitrievska: "Carbon Incorporation and Anion Dynamics as Synergistic Drivers for Ultrafast Diffusion in Superionic $LiCB_{11}H_{12}$ and $NaCB_{11}H_{12}$", MRS Spring meeting, Phoenix, AR, Apr. 2018.
4. M. Dimitrievska: "HySCORE: Technical Activities at NIST", DOE-EERE-FCTO Annual Merit Review, Washington DC, Jun. 2018.
5. M. Dimitrievska: "Complex Borohydrides as Superionic Electrolytes", Review of the NIST Center for Neutron Research at the National Institute of Standards and Technology (NIST), Gaithersburg, MD, Jul. 2018.
6. M. Dimitrievska: "Neutron Backscattering Studies of Hydrogenous Materials for Next-Generation Energy Storage", National Science Foundation Site Visit Review of the Center for High Resolution Neutron Scattering (CHRNS), Gaithersburg, MD, Apr. 2018.
7. M. Dimitrievska: "Role of Solvent Adducts in Hydrogen Dynamics of Metal Borohydrides—Neutron-Scattering Characterization", American Conference on Neutron Scattering, Collage Park, MD, Jun. 2018.
8. C.M. Brown: "Shedding Light on Molecular Separations in Metal-Organic Frameworks through Neutron Scattering", International MOF Conference 2018, Auckland, New Zealand, Dec. 2018.
9. C.M. Brown: "Shedding Light on Industrial Separations in Metal-Organic Frameworks through Neutron Scattering", ACS Regional Meeting, Atlanta, GA, Nov. 2018.
10. C.M. Brown: "Neutron Scattering Studies of Small Molecules Adsorbed in Metal-Organic Frameworks", Materials Science & Technology Conference, Columbus, OH, Oct. 2018.
11. C.M. Brown: "Neutron Measurements of Hydrogen Storage Materials", ACS National Meeting, New Orleans, LA, Mar. 2018.
12. A. Faraone: "Tunnelling H Motion in Lithium Benzimidazolate-Borohydride $Li_2(bIm)(BH_4)$: Neutron Spin Echo, Quasielastic Neutron Scattering and Nuclear Magnetic Resonance Results", 'Neutron Spin-Echo Spectroscopy 2018 – 40 Years of User Operation of NSE' Workshop, Grenoble, France, Oct. 2018.
13. A. V. Skripov: "Low-Temperature Rotational tunneling of BH_4^- Groups in Lithium Benzimidazolate-Borohydride $Li_2(bIm)(BH_4)$: Nuclear Magnetic Resonance and Neutron Scattering Studies", 16th International Symposium on Metal-Hydrogen Systems (MH2018), Guangzhou, China, Nov. 2018.