Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for:

Structural and Reorientational Dynamics of Tetrahydroborate (BH_4^-) and Tetrahydrofuran (THF) in $Mg(BH_4)_2 \cdot 3THF$ Adduct: Neutron-Scattering Characterization

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N.B., for all the following figures, standard uncertainties are commensurate with the observed scatter in the data, if not explicitly designated by vertical error bars.

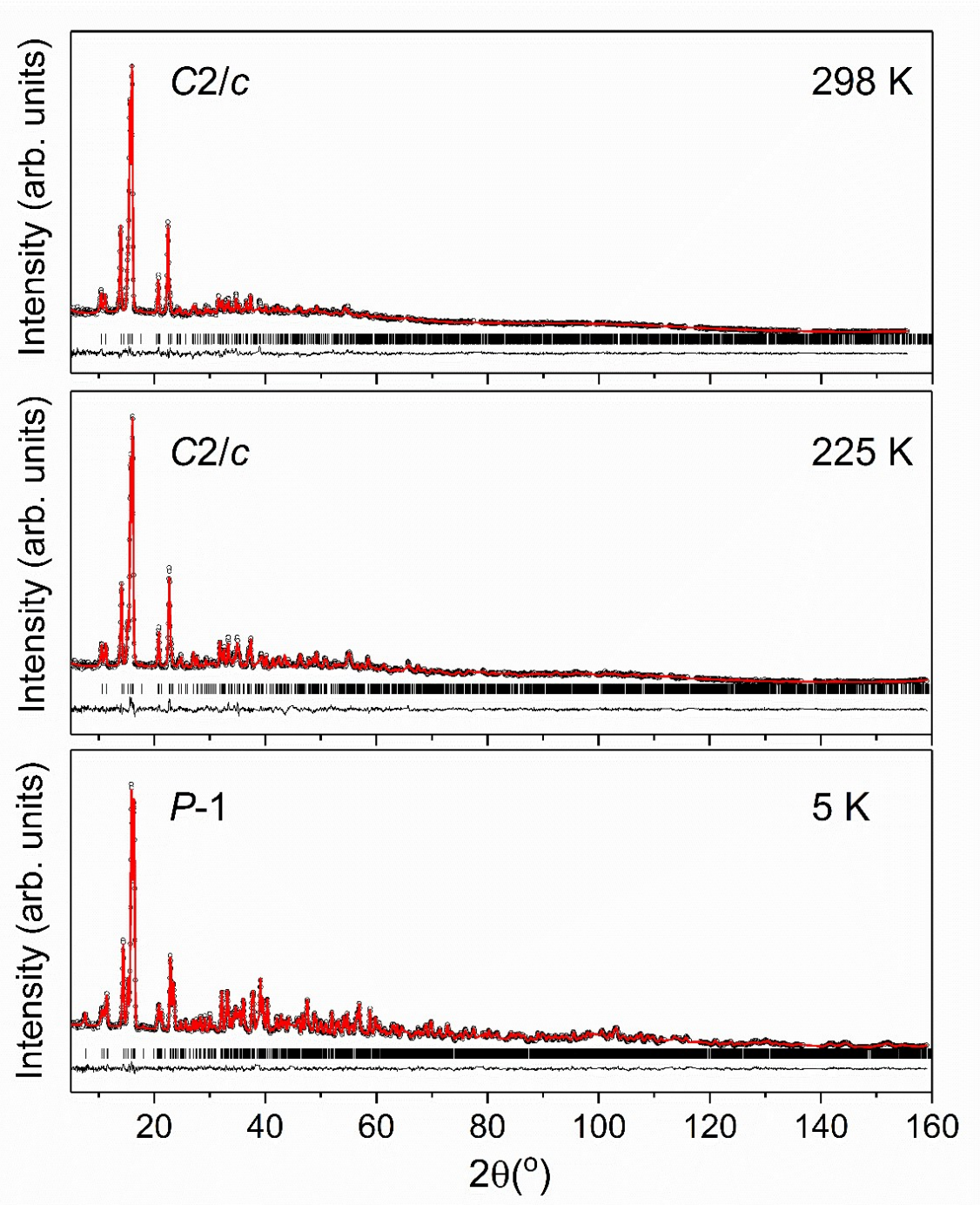

Figure S1. Temperature-dependent NPD patterns [λ = 1.5397 Å] and model refinements for $Mg(BH_4)_2 \cdot 3TDF$ at 5 K (*P*-1), 225 K (*C*2/*c*), and 298 K (*C*2/*c*): experimental data (black circles), fitted patterns (red lines), and differences (black lines beneath the patterns). Vertical bars indicate the calculated positions of Bragg peaks. Extra peaks from Al container are excluded.

Table S1. The refined $Mg(BH_4)_2 \cdot 3TDF$ structural parameters derived from the NPD data.

***T* (K)**	**5**	**225**	**298**
Symmetry	*P*-1	*C*2/*c*	*C*2/*c*
***a* (Å)**	8.3616(4)Å	11.960(1)	12.115(2)
***b* (Å)**	8.6328(4)	12.490(1)	12.623(2)
***c* (Å)**	12.2557(5)	19.949(2)	20.199(4)
α (°)	102.5965(33)	90	90
β (°)	103.984(4)	144.456(3)	144.992(4)
γ (°)	92.2394(32)	90	90
***V* (Å^3)**	833.84(6)	1732.5(2)	1772.2(2)
Z	8	4	4
R_{wp}	0.0172	0.0191	0.0157
R_p	0.0144	0.0166	0.0136
χ^2	1.43	1.22	1.21

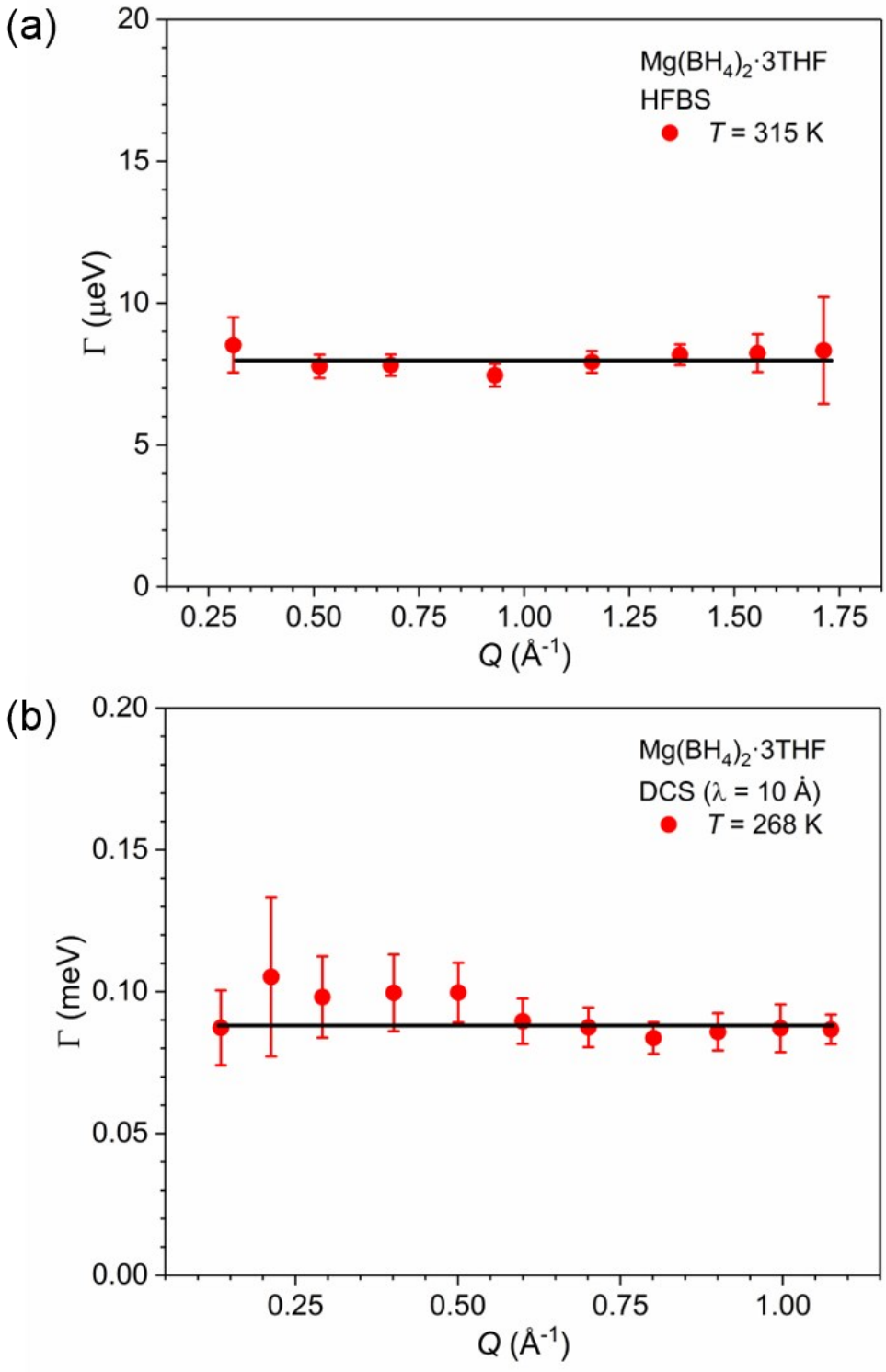

Figure S2. *Q*-dependence of the Lorentzian (quasielastic) fwhm linewidths for $Mg(BH_4)_2 \cdot 3THF$ obtained on (a) the HFBS spectrometer at 315 K, and (b) the DCS spectrometer at 268 K.

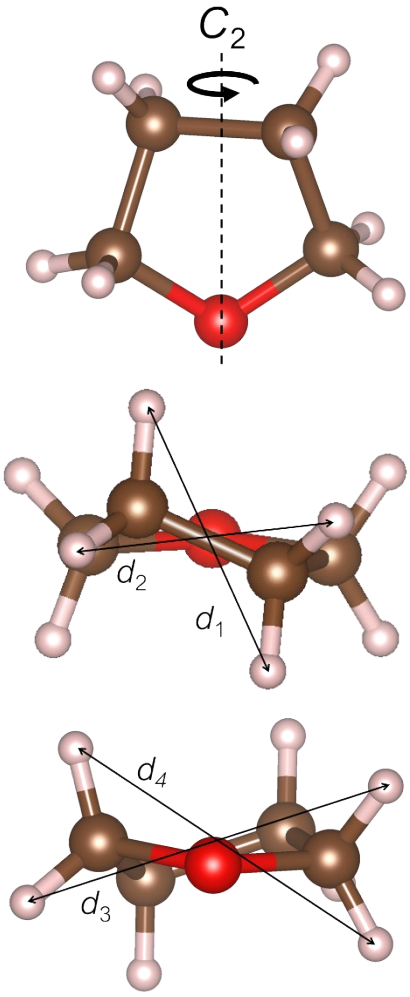

Figure S3. Three views of THF groups. Red, brown and pink spheres denote the respective O, C and H atoms. Distances used in this study to represent the "ideal" anion polyhedral size and shape are estimated from the room-temperature neutron powder diffraction results for $Mg(BH_4)\cdot 3TDF$.

Table S2. Binding energies for THF in (kJ/mol) [E – total energy, E_{zpc} – binding energy, H – enthalpy; G – free Gibss energy]

Reaction	E	E_{zpc}	H	G
$Mg(BH_4)_2$+THF → $Mg(BH_4)_2$·THF	-91.9	-85.7	-85.0	-37.8
$Mg(BH_4)_2$·THF+THF→$Mg(BH_4)_2$·2THF	-66.4	-60.7	-59.9	-11.1
$Mg(BH_4)_2$·2THF+THF→$Mg(BH_4)_2$·3THF	-29.0	-23.0	-22.4	30.0

Table S3. Absolute energies for the molecular structures (in hartree) [E – total energy, E_{zpc} – binding energy, H – enthalpy; G – free Gibss energy]

Structure	E	E_{zpc}	H	G
$Mg(BH_4)_2$	-254.6226	-254.54428	-254.53674	-254.57294
THF	-232.45938	-232.34218	-232.33631	-232.37094
$Mg(BH_4)_2$·THF	-487.11710	-486.91914	-486.90544	-486.95830
$Mg(BH_4)_2$·2THF	-719.60180	-719.28445	-719.26458	-719.33347
$Mg(BH_4)_2$·3THF	-952.07226	-951.63541	-951.60944	-951.69296

Table S4. Optimized structures in angstroms (Å)

DFT (B3LYP/6-31+G)

$Mg(BH_4)_2$			
Mg	0.27155728	0.00110728	-0.00169945
B	0.35334054	2.10157160	-0.01075611
B	0.18690129	-2.09898265	0.00703603
H	0.70888078	-1.66581838	-1.04006706
H	0.14003901	-3.29012383	0.01258057
H	0.85807208	-1.66303174	0.96411819
H	-0.95090907	-1.59462912	0.09094832
H	0.39983746	3.29275831	-0.01568733
H	-0.31701871	1.66519965	-0.96769047
H	-0.16739333	1.66708403	1.03650077
H	1.49194314	1.59900711	-0.09487669
THF			
O	0.01523478	-1.16914638	-0.41043542
C	1.14466242	-0.45125379	0.08462154
H	1.32481825	-0.72314192	1.13836297
H	2.01287221	-0.75273836	-0.50730549
C	-1.13002443	-0.46407659	0.06634880
H	-1.98515459	-0.77528297	-0.53942375
H	-1.32399506	-0.73806967	1.11708761
C	0.77759474	1.04271712	-0.04460302
H	1.17074435	1.45898011	-0.97762970
H	1.18845673	1.63364650	0.78084353
C	-0.77779314	1.03394602	-0.05710065
H	-1.20851141	1.62013191	0.76157907
H	-1.16057046	1.44584944	-0.99635537
$Mg(BH_4)_2 \cdot THF$			
Mg	-0.14285001	1.75585963	-0.03458671
O	0.00856405	-0.30358883	-0.01864692
B	-2.23334503	2.28261937	0.12827051
B	1.84837632	2.57998165	-0.20783754
H	1.05207765	3.51666348	-0.19860699
H	2.98562663	2.94180865	-0.29762941
H	1.67941298	1.92580939	0.84152826
H	1.54925980	1.83425431	-1.16114602
H	-3.41133814	2.47579689	0.21373813
H	-1.96942817	1.64418724	-0.91113806
H	-1.82950543	1.60329775	1.09254405
H	-1.58234651	3.32532593	0.10370471

C	1.25266841	-1.05214492	-0.21756652
C	-1.11272027	-1.22304940	0.19331815
C	-0.56996811	-2.59714779	-0.19015226
H	-1.39412095	-1.16635554	1.25006340
H	-1.94639191	-0.87459581	-0.41847353
C	0.91644452	-2.48481155	0.18765625
H	1.52399100	-0.97115736	-1.27536093
H	2.02556483	-0.57595533	0.38789960
H	1.05074330	-2.62145238	1.26726581
H	1.54817356	-3.21388548	-0.32860642
H	-1.08866090	-3.40272130	0.33821194
H	-0.68161164	-2.76872125	-1.26734540
$Mg(BH_4)_2 \cdot 2THF$			
Mg	1.03381577	-0.20407512	-0.40488750
O	0.01333143	1.55708858	0.16605102
O	-0.40920979	-1.70166410	-0.02442706
C	-0.38846034	-2.58772739	1.13705373
C	-0.96837767	-3.90657552	0.63579560
C	-1.99565920	-3.43524767	-0.40556244
C	-1.28642838	-2.24936727	-1.05990864
B	1.13163557	-0.08583528	-2.62211695
B	2.57023759	-0.49458468	1.17682641
H	2.53268781	-1.45688008	0.40241670
H	3.41161590	-0.65017825	2.01960079
H	2.79158726	0.52250361	0.51036544
H	1.45064048	-0.37604760	1.68882497
H	1.55024882	-1.17116694	-2.20447120
H	-0.03667290	0.04114991	-2.23651941
H	1.19134307	-0.03267808	-3.82044691
H	1.80108884	0.81054901	-2.09834197
H	-1.41241269	-4.49527190	1.44460100
H	-0.18647473	-4.51124235	0.16132964
H	0.64162300	-2.64721862	1.48868716
H	-1.01164576	-2.13417998	1.91752426
H	-0.65789547	-2.54669454	-1.90410865
H	-1.95961199	-1.45254849	-1.38411160
H	-2.25597739	-4.20725825	-1.13619543
H	-2.91943748	-3.11041999	0.08870347
C	0.25475339	2.27960013	1.41288081
C	-0.69870789	2.41389825	-0.78275157
C	-1.09201757	3.65958887	0.01155553
H	-0.01494723	2.63682775	-1.60669979
H	-1.54844694	1.84829033	-1.17172888
C	0.02001737	3.74706423	1.06868042
H	-0.46049013	1.91189637	2.15873549

H	1.26773614	2.04473213	1.73994768
H	0.92744421	4.18806960	0.63948656
H	-0.26398798	4.33579617	1.94653285
H	-1.15284281	4.54672392	-0.62630956
H	-2.06748342	3.52048008	0.49351939
$Mg(BH_4)_2 \cdot 3THF$			
C	1.65712819	2.86039468	-0.77980693
O	0.49750713	2.13579059	-0.25889606
C	-0.28082575	3.00376730	0.61355087
C	0.55476148	4.27152452	0.79117133
C	1.34813276	4.33212321	-0.52393206
Mg	0.62322062	0.00798601	-0.00688577
O	-1.53213778	-0.03564749	0.00650197
O	0.57263130	-2.13953908	0.28986438
C	1.44858693	-2.87215328	1.18524164
C	2.27965719	-3.75120505	0.25132264
C	1.30093416	-4.08016599	-0.90686906
C	0.12960094	-3.09452546	-0.70732217
B	1.48736685	-0.29085081	-2.28246716
B	1.53274933	0.43664622	2.23015345
H	2.21656717	0.20973057	1.21554202
H	1.88291286	-0.32863223	3.10208015
H	1.65240383	1.60771240	2.52558060
H	0.33292574	0.20742671	1.98672269
H	1.75692674	-1.39416629	-2.70984177
H	0.28169601	-0.27779995	-1.97349343
H	1.67610838	0.60686012	-3.07500142
H	2.18223469	-0.07995574	-1.27332294
H	1.23376322	4.15459703	1.64280269
H	-0.06886298	5.15491148	0.96317281
H	-1.23377053	3.21057215	0.10948725
H	-0.46287541	2.47059838	1.54812649
H	1.76291586	2.58398643	-1.82902830
H	2.53977932	2.52678847	-0.22295787
H	0.73130551	4.74448616	-1.33231470
H	2.25886067	4.93464863	-0.44864553
H	2.65424280	-4.64623926	0.75855016
H	3.13891613	-3.18663919	-0.12306292
H	2.00815645	-2.14168800	1.76727090
H	0.82099326	-3.47038013	1.86196793
H	-0.12498005	-2.53129784	-1.60395537
H	-0.76422227	-3.60026925	-0.31543768
H	1.77586083	-3.92728458	-1.87920623
H	0.94669602	-5.11540933	-0.85993313
C	-2.32687409	-0.64548567	1.06544734

C	-2.39165805	0.40535779	-1.08339702
C	-3.73568020	-0.27417299	-0.82999807
H	-2.47060119	1.49803421	-1.03487621
H	-1.90821076	0.12616082	-2.02130934
C	-3.78151771	-0.34154927	0.70544717
H	-2.11524511	-1.72033619	1.06628158
H	-1.99912706	-0.22068609	2.01672229
H	-4.08809603	0.62542005	1.12225247
H	-4.46689643	-1.10580210	1.08489505
H	-4.56970948	0.28667574	-1.26321830
H	-3.74371323	-1.28273206	-1.26066895

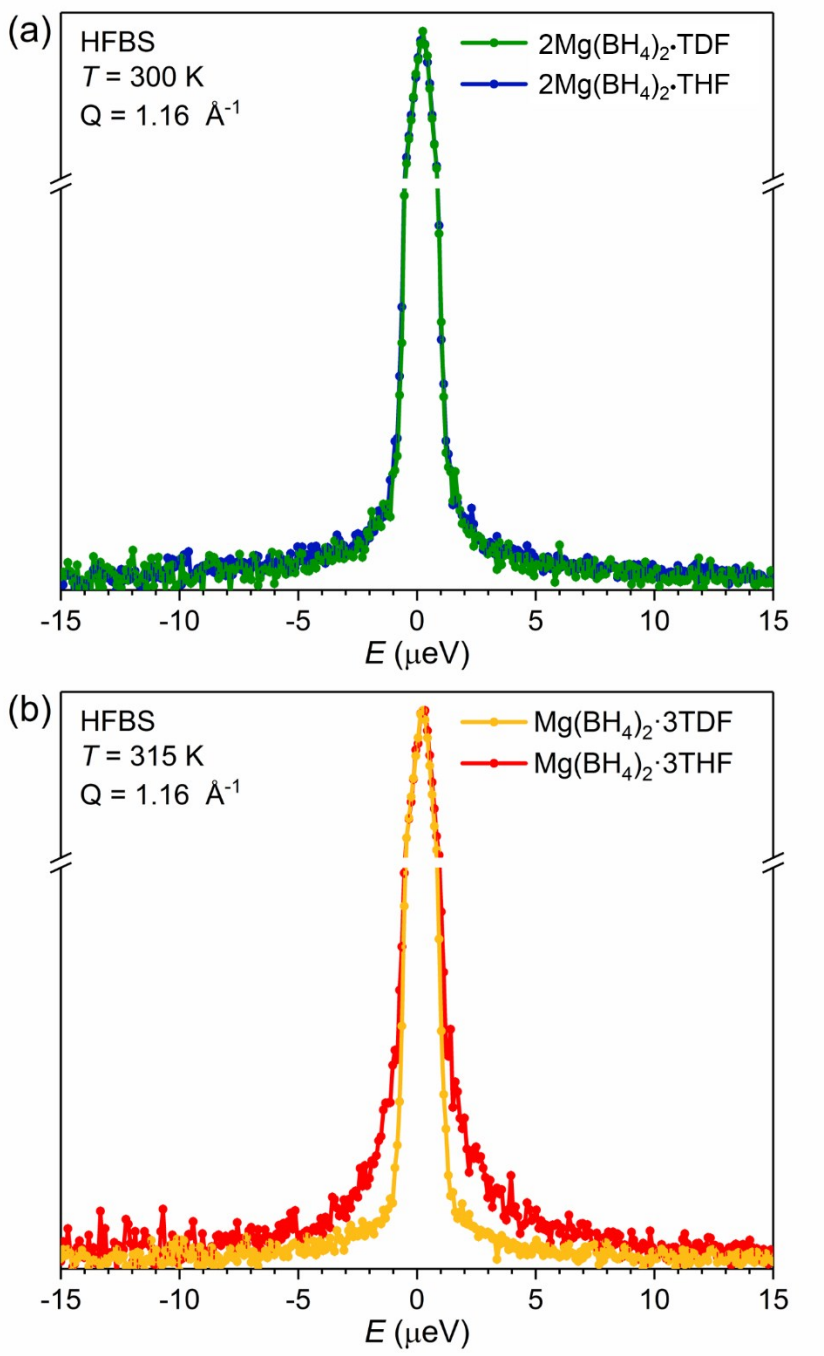

Figure S4. Comparison of QENS spectra for (a) $2Mg(BH_4)_2 \cdot TDF$ and $2Mg(BH_4)_2 \cdot THF$ at 300K, and (b) $Mg(BH_4)_2 \cdot 3TDF$ and $Mg(BH_4)_2 \cdot 3THF$ measured at 315 K on HFBS at Q = 1.16 Å^{-1}, 0.8 μeV resolution. No additional broadening is observed between the QENS spectra of $2Mg(BH_4)_2 \cdot TDF$ and $2Mg(BH_4)_2 \cdot THF$, leading to the conclusion that the THF dynamics in this case is much slower than the detection limit of the instrument. In contrast, considerable differences in the QENS spectra of $Mg(BH_4)_2 \cdot 3TDF$ and $Mg(BH_4)_2 \cdot 3THF$ showing that the THF rings are orientationally mobile.

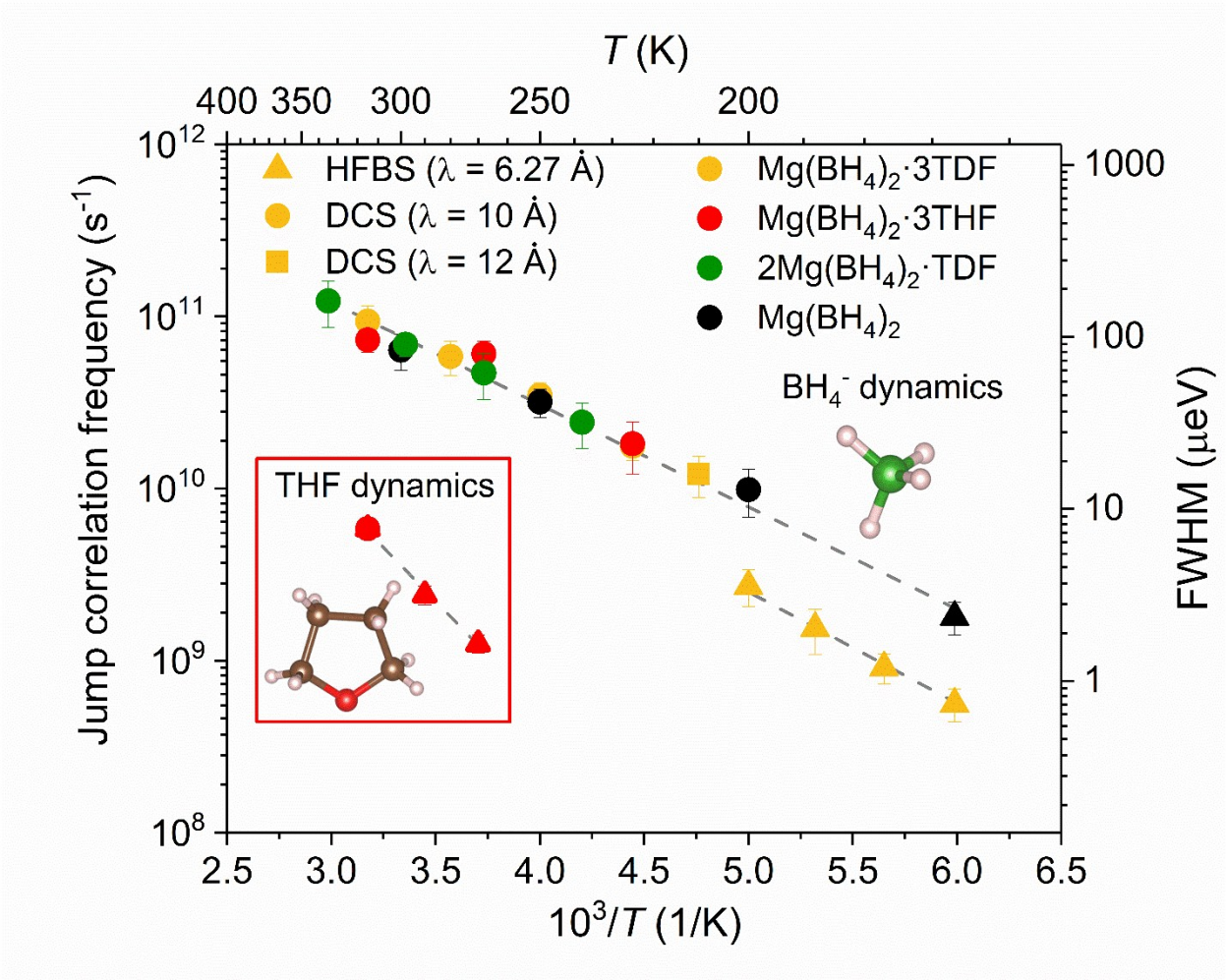

Figure S5. Jump correlation frequencies τ_{i1}^{-1} vs. inverse temperature for $Mg(BH_4)_2 \cdot 3TDF$, $Mg(BH_4)_2 \cdot 3THF$, $2Mg(BH_4)_2 \cdot TDF$ and pristine $Mg(BH_4)_2$. Different symbols denote the different instruments used. Different colors denote the different samples. Dashed lines represent linear fits to the QENS data.

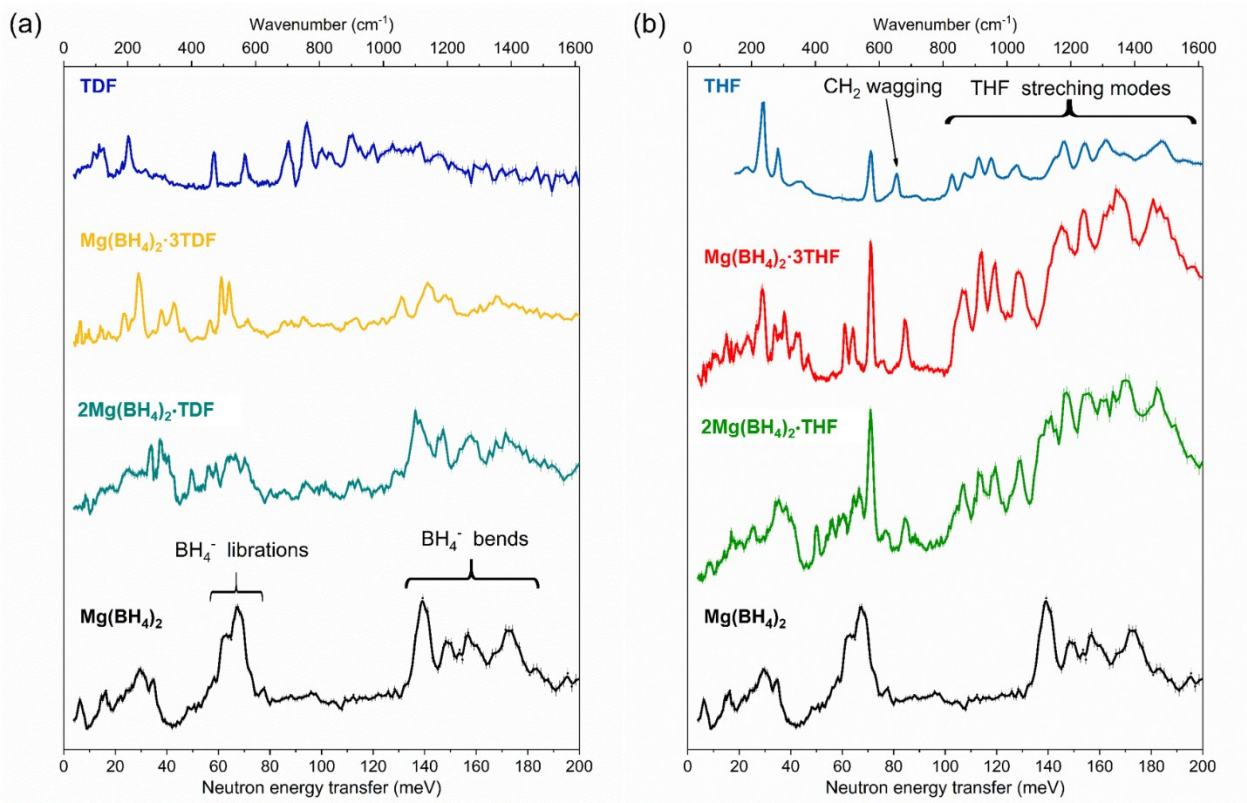

Figure S6. Comparison of the NVS spectra for (a) $Mg(BH_4)_2$, $2Mg(BH_4)_2{\cdot}TDF$, $Mg(BH_4)_2{\cdot}3TDF$ and TDF, and (b) $Mg(BH_4)_2$, $2Mg(BH_4)_2{\cdot}THF$, $Mg(BH_4)_2{\cdot}3THF$ and THF measured at 4K. The Cu(220) and pyrolytic graphite (002) monochromators were used above and below 40 meV, respectively. Vertical error bars denote ±1 σ. A slight decrease in the frequency of the BH_4^- librational and bending modes is observed with the increase in THF content. This can be explained by the changes in the intramolecular interactions. The red shift of the BH_4^- modes reflects the elongation in the Mg-B bond length caused by a changed Mg^{2+}-THF coordination, as confirmed by the DFT calculations.

Elastic Incoherent Structure Factor (EISF) calculation for the THF molecule

For the reorientational dynamics of the THF molecule and BH_4^- anions situated within a solid lattice of $Mg(BH_4)_2 \cdot 3THF$, the EISF for each due to the H-atom reorientions can be written as:

$$EISF(THF) = \frac{E_{THF}}{E_{THF} + q_{THF}} \tag{S1}$$

$$EISF(BH_4^-) = \frac{E_{BH_4^-}}{E_{BH_4^-} + q_{BH_4^-}} \tag{S2}$$

where E_{THF} and q_{THF} are the respective elastic and quasielastic scattering intensity contributions due only to the THF reorientational dynamics, while $E_{BH_4^-}$ and $q_{BH_4^-}$ are the respective elastic and quasielastic scattering intensity contributions due only to the BH_4^- reorientational dynamics. Similarly, the EISF [EISF(total)] of the $Mg(BH_4)_2 \cdot 3THF$ adduct can be calculated as the total elastic scattering intensity coming from both THF molecules and BH_4^- anions, divided by the sum of their total elastic and quasielastic scattering intensity contributions:

$$EISF(total) = \frac{E_{THF} + E_{BH_4^-}}{E_{THF} + E_{BH_4^-} + q_{THF} + q_{BH_4^-}} \tag{S3}$$

On the other hand, the EISF(total) can also be calculated as a weighted sum of the partial EISFs of the THF^- molecule and BH_4^- anions by including the appropriate weighting factors based on the number of H atoms associated with each chemical group. Considering that there are a total of 32 H atoms with 24 present in the three THF rings and 8 present in the two BH_4^- anions, the total EISF is given as:

$$EISF(total) = \frac{24}{32} \cdot EISF(THF) + \frac{8}{32} \cdot EISF\left(BH_4^-\right) \tag{S4}$$

Finally, substituting Eq. (S1), (S2) and (S3) in the Eq. (S4), the following equation is obtained:

$$\frac{E_{THF} + E_{BH_4^-}}{E_{THF} + E_{BH_4^-} + q_{THF} + q_{BH_4^-}} = \frac{24}{32} \cdot \frac{E_{THF}}{E_{THF} + q_{THF}} + \frac{8}{32} \cdot \frac{E_{BH_4^-}}{E_{BH_4^-} + q_{BH_4^-}} \tag{S5}$$

In the HFBS data measured, the elastic scattering intensity contribution is actually the sum of the elastic peak intensities due to both THF and BH_4^- reorientations:

$$E_T = E_{THF} + E_{BH_4^-} \tag{S6}$$

whereas the fitted quasielastic scattering intensity contribution is due only to the slower THF reorientations (q_{THF}). Both values, (E_T and q_{THF}) can be obtained directly from the fits of the QENS data measured on the HFBS instrument. The much faster BH_4^- reorientations yield quasielastic scattering ($q_{BH_4^-}$) that is an order of magnitude too broad to be observed by HFBS and resides as broad background scattering buried under the flat baseline and cannot be directly determined from the HFBS measurements.

In order to extract the EISF solely due to the THF molecules, it is necessary to determine the amount of THF elastic scattering intensity (E_{THF}), as the quasielastic contribution (q_{THF}) is already known directly from the fits of the QENS measurements. This can be done with the aid of Eq. (S5) and (S6), and the fact that the EISF behavior for the BH_4^- anions is known, and can be calculated as:

$$EISF\left(BH_4^-\right) = \frac{1}{2}\left(1 + j_0(Qd)\right) = \frac{E_{BH_4^-}}{E_{BH_4^-} + q_{BH_4^-}} \tag{S7}$$

where $j_0(x)$ is a zeroth-order Bessel function equal to $\sin(x)/(x)$, and $d \approx 2.0$ Å is the jump distance between two BH_4^- hydrogen atom positions.

Considering Eq. (S5), (S6) and (S7), as well as the known variables (E_T, q_{THF}, and $EISF\left(BH_4^-\right)$), it is possible to calculate the THF elastic scattering intensity (E_{THF}) as:

$$E_{THF} = \frac{3 \cdot E_T - EISF\left(BH_4^-\right) \cdot q_{THF}}{3 + EISF\left(BH_4^-\right)} \tag{S8}$$

The EISF solely due to the THF molecules can then be calculated by inserting Eq. (S8) into the Eq. (S1):

$$EISF(THF) = \frac{3 \cdot E_T - EISF\left(BH_4^-\right) \cdot q_{THF}}{3 \cdot \left(E_T + q_{THF}\right)} \tag{S9}$$

How to view phonon animations using the V_Sim software*

The animation files named as **file_name_anime.ascii**, contain the information needed to view the animated (gamma-point) phonon normal modes from the DFT-optimized structures, respectively, and can be opened following the steps below:

- Get the V_Sim software (It is free, and there is no need to install).
- Go to the following webpage and download the Win32 binaries:
  http://inac.cea.fr/L_Sim/V_Sim/download.html
- Unzip the zip file to wherever you want to put the software.
- Click "~V_Sim\bin\V_sim.exe" to start the V_Sim program, then open the **file_name_anime.asci** file to view the phonon animations.
- To build bonds in the structure, check the box on the left side of the "Pairs" button, and click the "Pairs" button.
- Highlight a pair and click the "Auto set" button to allow bonding.
- Adjust the "Link parameters," if desired.
- Adjust the element color, radius, etc. on the "Elements" tab, if desired.
- Go to the "Phonons" tab, highlight a phonon mode, and click the "Play" button to view a phonon animation. N.B. The mode energies are indicated in wavenumbers cm^{-1} (1 meV ≈ 8.066 cm^{-1}).

* N.B., the use of this software does not imply its recommendation or endorsement by NIST