

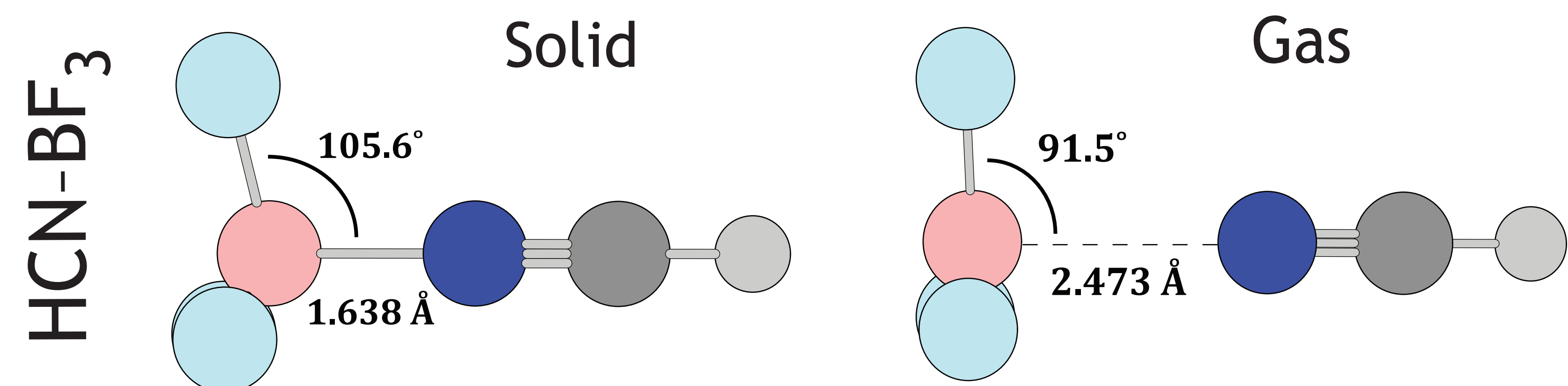
Structural and Energetic Properties of HCN-BCl₃ and HCN-BBr₃ via Computations

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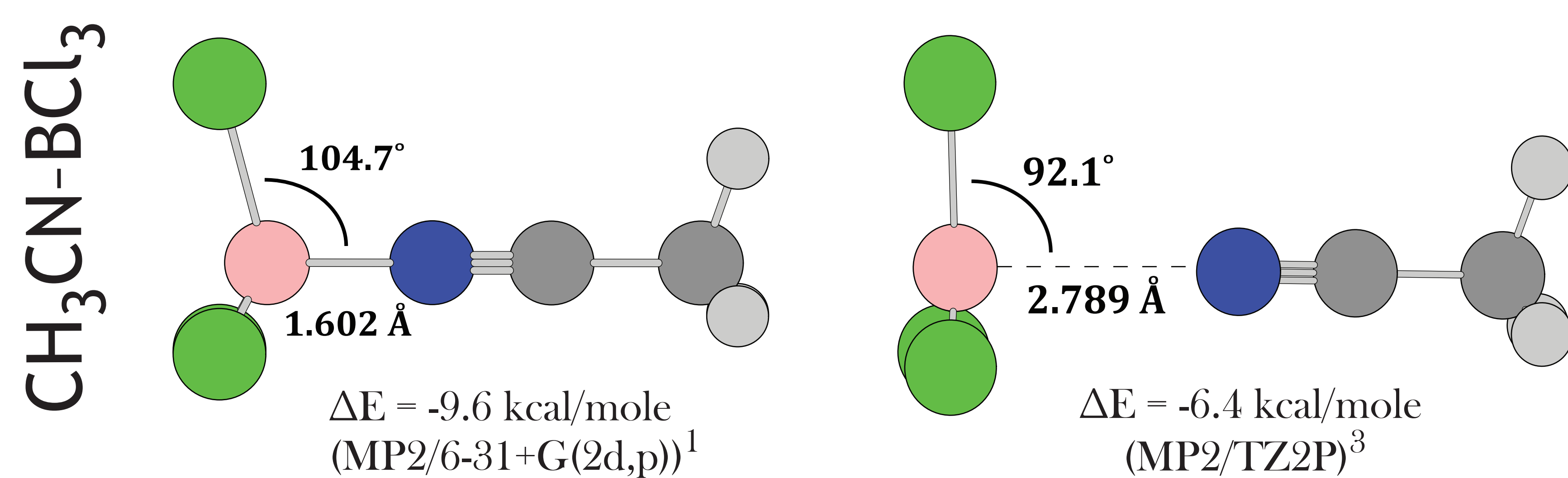


Context

1) Major Gas-Solid Structure Differences for HCN-BF₃.⁴



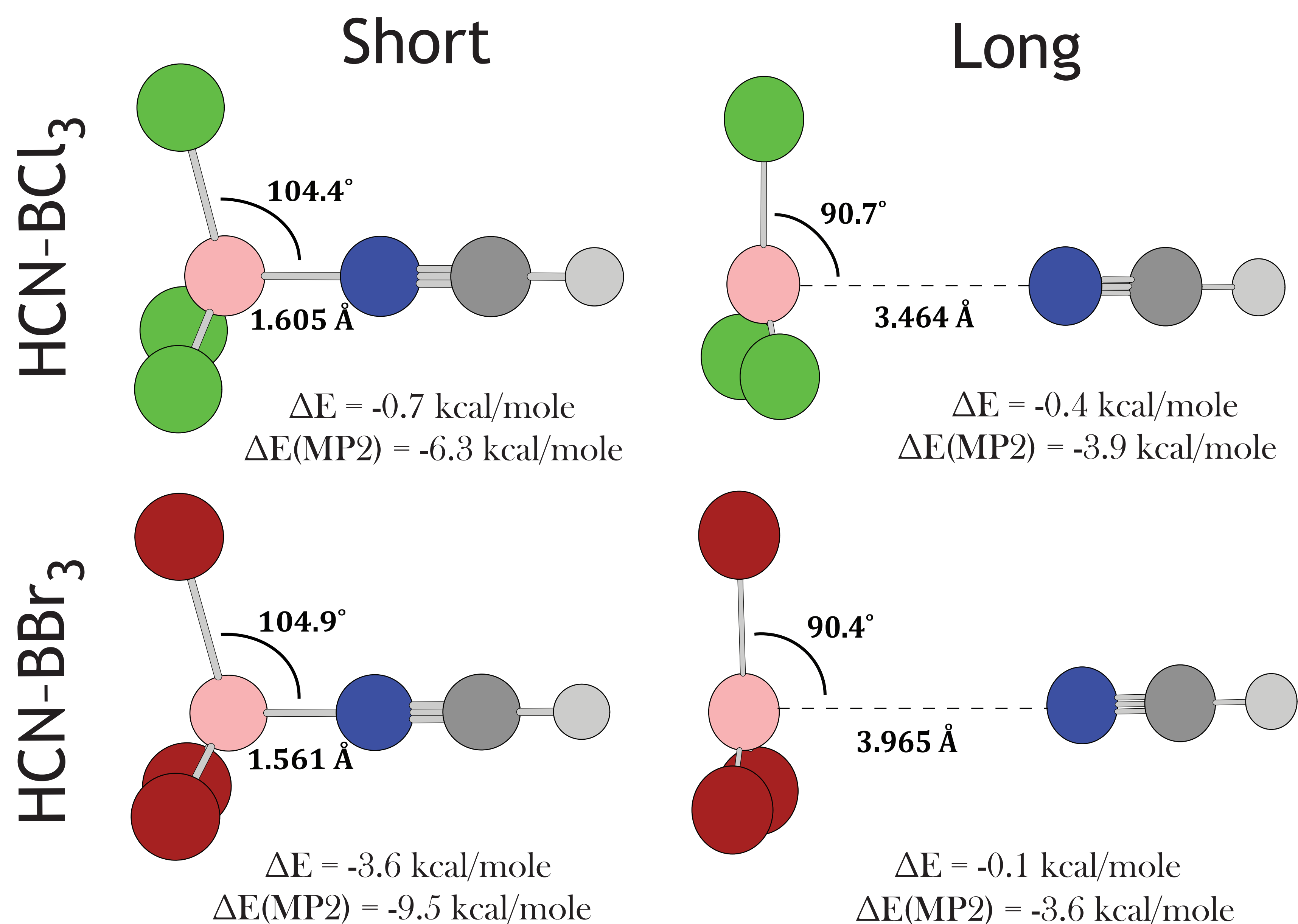
2) Two very different computational structures for CH₃CN-BCl₃.



Do the structures of HCN-BCl₃ and HCN-BBr₃ mimic either of these systems?

Structures

Two distinct equilibrium structures (B3PW91/aug-cc-pVTZ) were identified for both HCN-BCl₃ and HCN-BBr₃.

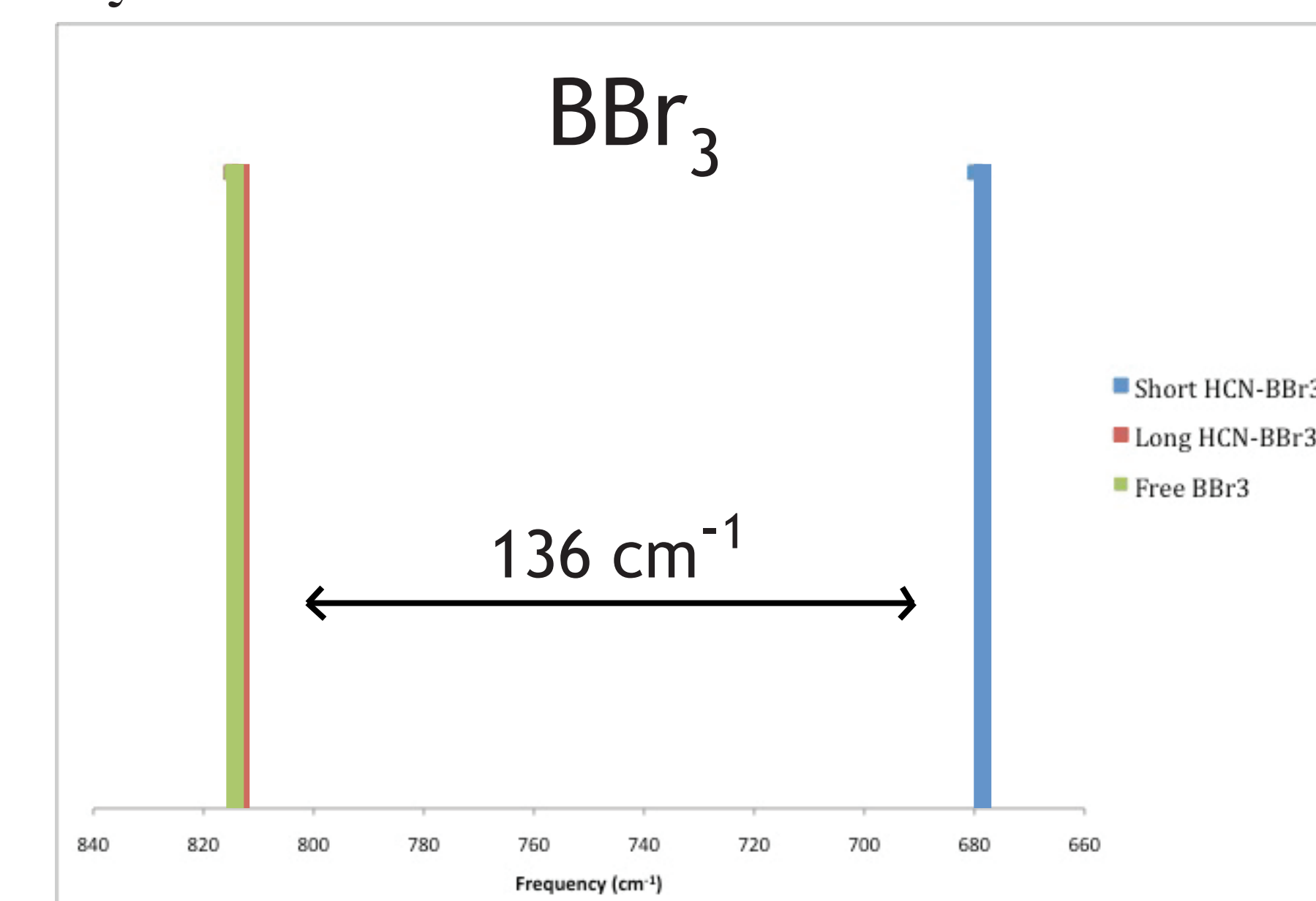
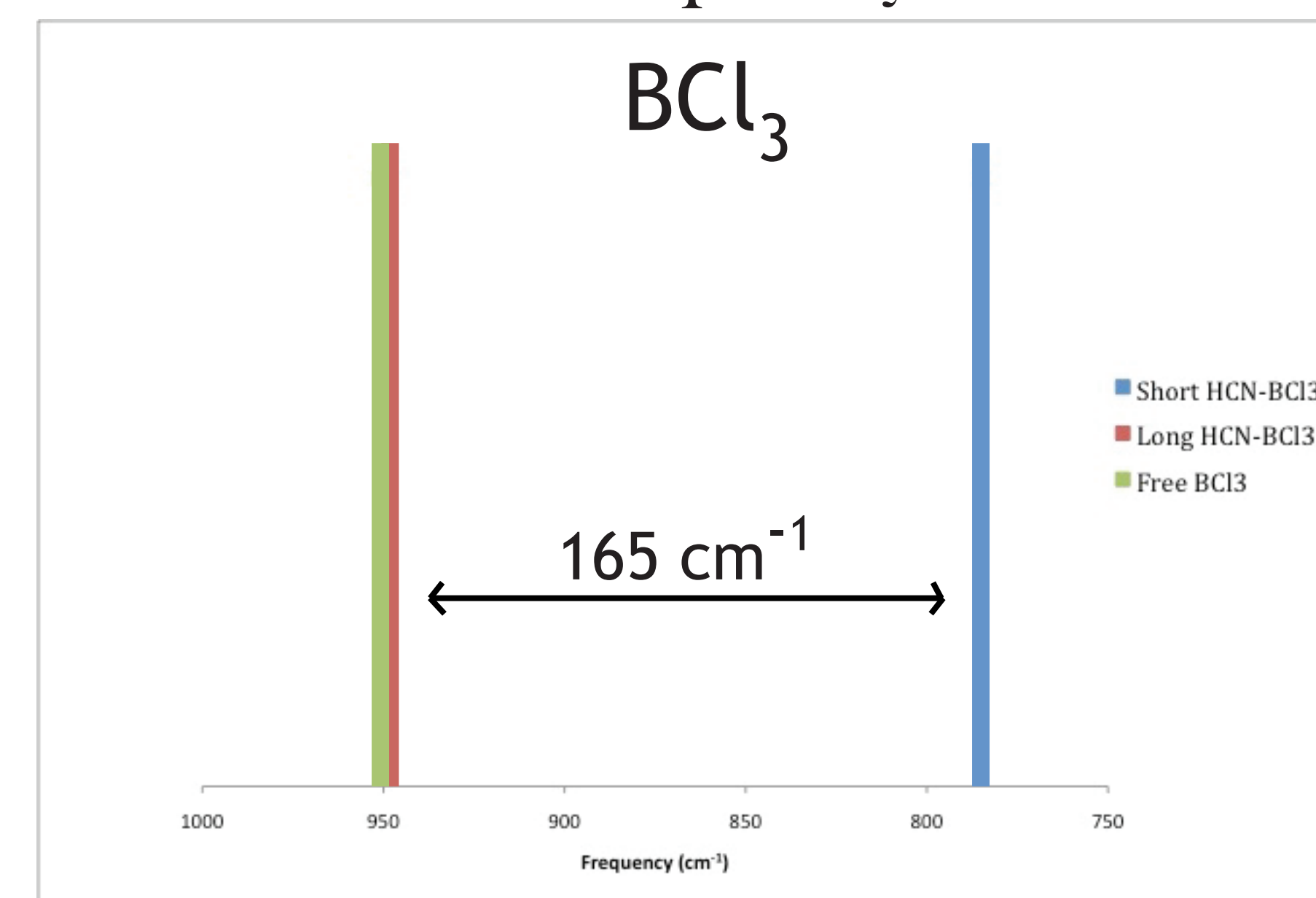


Vibrational Frequencies

We sought the DFT method which best reproduced the experimental frequencies for BCl₃ and BBr₃.

Method	BCl ₃ (cm ⁻¹)					BBr ₃ (cm ⁻¹)				
	v ₁	v ₂	v ₃	v ₄	RMS	v ₁	v ₂	v ₃	v ₄	RMS
B3LYP	252	451	466	930	15.6	150	276	382	794	7.9
B3PW91	252	451	472	951	8.0	150	281	382	815	6.8
B972	253	448	468	943	7.5	151	280	383	814	6.9
B98	251	448	468	943	10.9	150	279	381	807	4.6
HSEh1PBE	253	452	476	960	7.6	151	283	382	823	9.9
M06-2X	252	446	481	967	11.7	153	288	389	834	17.2
mPW1PW91	253	453	476	961	7.5	151	284	384	825	11.2
X3LYP	253	452	468	934	13.9	151	277	382	797	6.8
MP2	256	460	482	977	13.0	156	291	395	850	25.7
Experimental ²	243	462	471	958	-	151	279	372	806	-

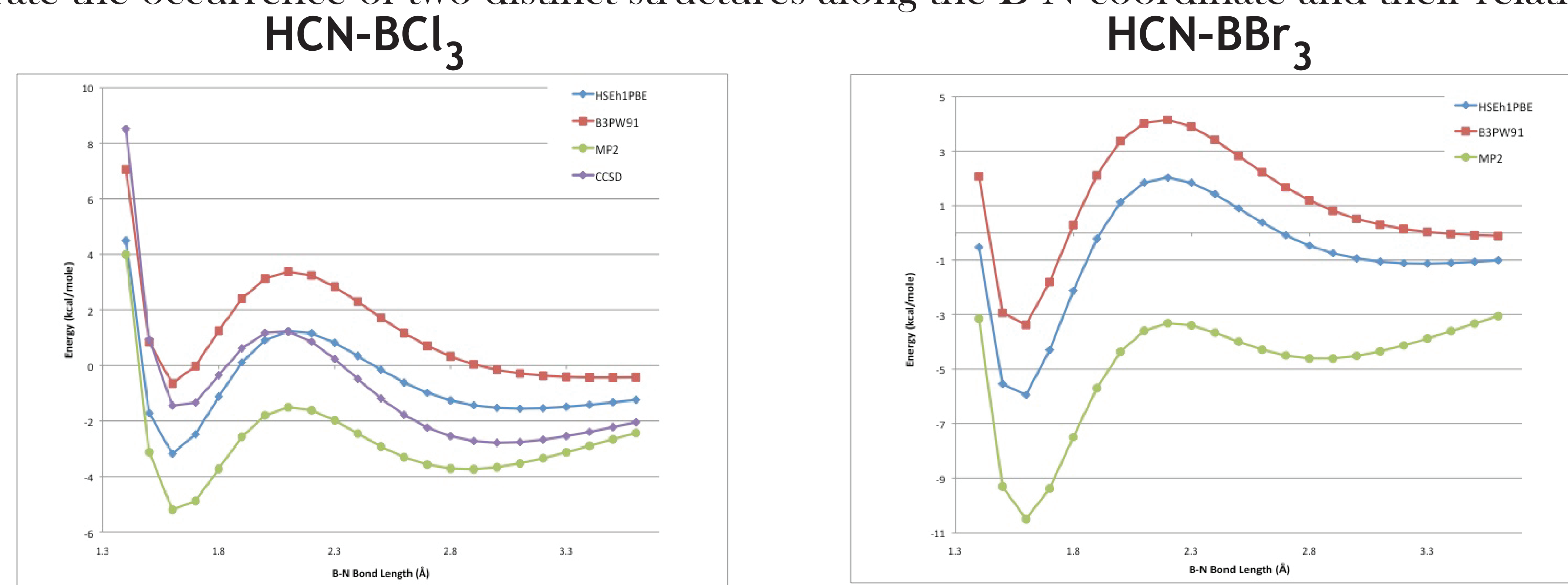
Frequency shifts of the BX₃ Asymmetric Stretch



The frequencies shift only slightly for the “long” structures but over 100 cm⁻¹ for the “short” structures.

Boron-Nitrogen Potentials

These illustrate the occurrence of two distinct structures along the B-N coordinate and their relative energies.



For both complexes, the MP2 energies are significantly lower. The short (1.6 Å) structures are approximately 1.5 and 6.0 kcal/mol lower in energy for HCN-BCl₃ and HCN-BBr₃, respectively. However, according to CCSD, the long-bond (3.0 Å) minimum is global for HCN-BCl₃ (1.3 kcal/mol lower in energy).

References

1. Cho, H.G.; Cheong, B.S.; *Journal of Molecular Structure-Theochem* **2000**, *496*, 185-198.
2. Herzberg, G.; *Molecular Spectra and Molecular Structure*; Krieger Publishing Co: Florida, 1945; pp 178.
3. Jonas, V.; Frenking, G.; Reetz, M.T.; *Journal of the American Chemical Society* **1994**, *116* (19), 8741-8753.
4. Leopold, K.R.; Canagaratna, M.; Phillips, J.A.; *Accounts of Chemical Research* **1997**, *30* (2), 57-64.

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