

A Computational Study of Ligand Effects on First-Row Transition Metals

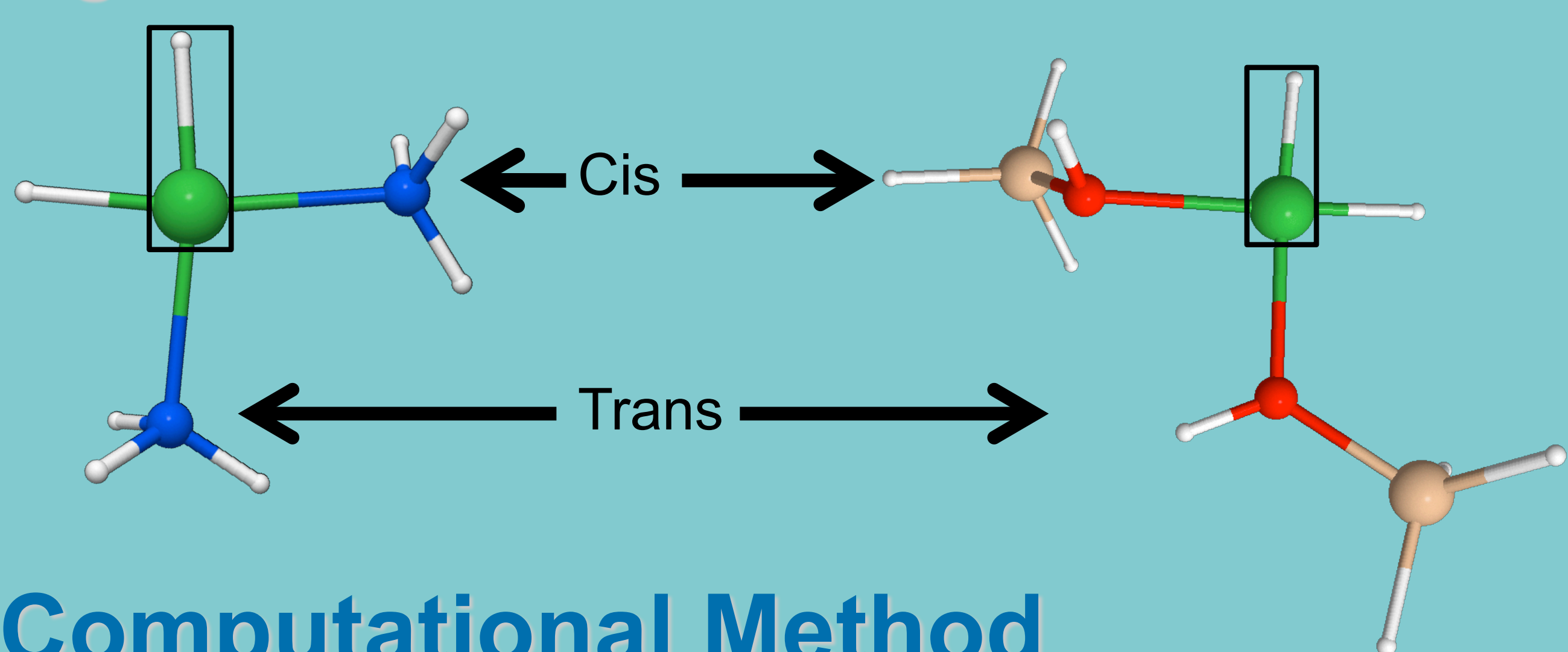


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Introduction

- ❖ This research investigates characteristics of metal-hydrogen bonds in coordination complexes.
- ❖ Ligand effects on metal-hydrogen bonding are studied.
- ❖ Ligands are: Carbon Monoxide, Acetonitrile, 1,3-bis(2,4,6-trimethylphenyl)imidazole (Carbene), Silanol and Ammonia.
- ❖ Metal-Hydrogen bond lengths and stability are influenced by the presence of trans-ligands.
- ❖ The influences of cis-ligands are not well understood.

Figure 1



Computational Method

- ❖ The metal complexes were designed using WebMO.
- ❖ Complexes were calculated using Density Functional Theory (DFT) specifically B3LYP, with the LANL2DZ ECP basis set. All calculations used Gaussian.
- ❖ DFT calculations are based on a relationship between total energy and the electron density. Calculated energies include exchange and correlation energy terms.
- ❖ Geometries are calculated by energy minimization, and vibrational frequencies are calculated from energy gradients near the equilibrium geometry.
- ❖ Bond strengths were calculated without geometry relaxation: $L_mMH_n \rightarrow H + L_mMH_{n-1}$ (unrelaxed)

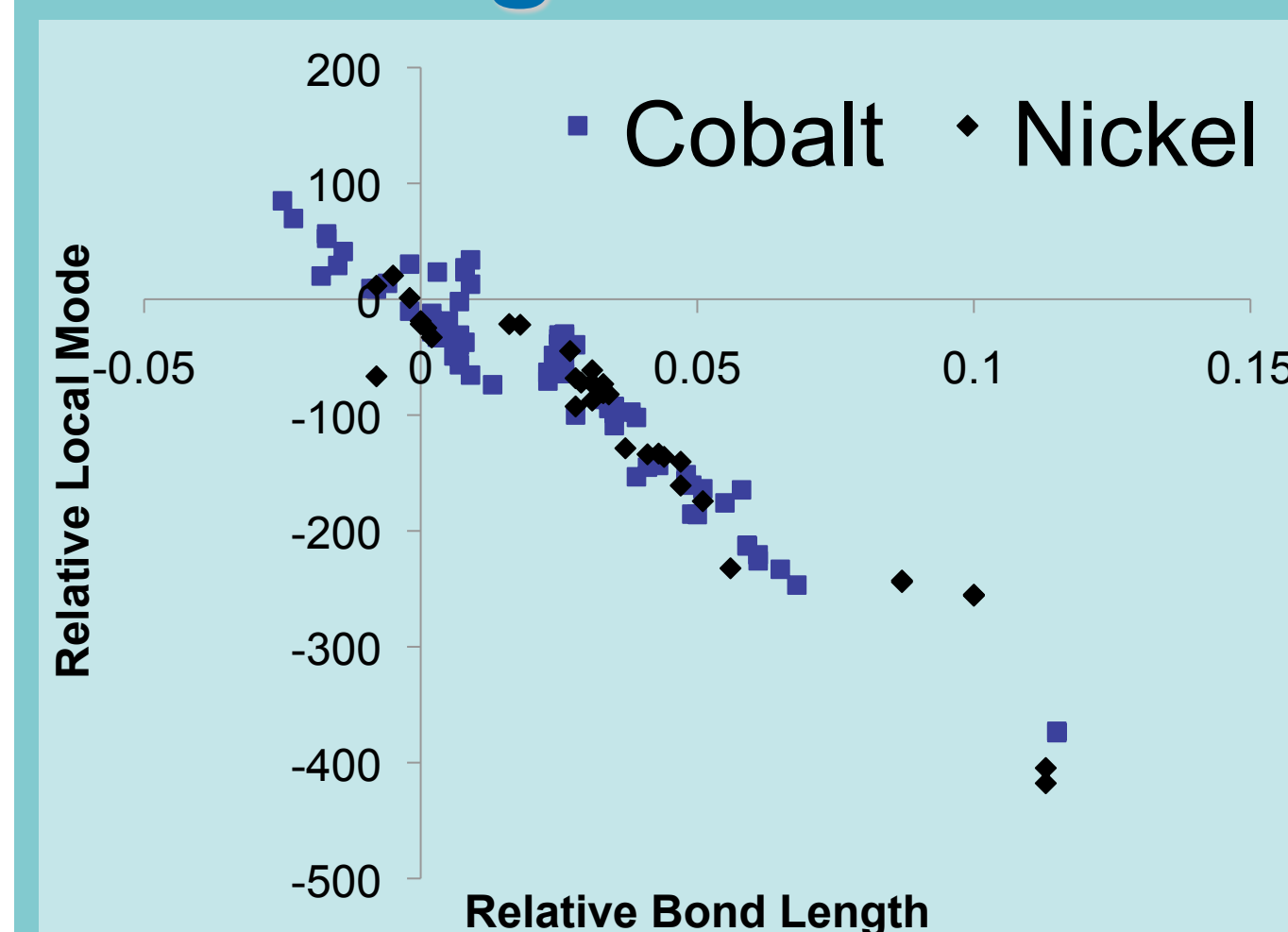
Results & Discussion

Experimental Values

Complex	Stretch type	Medium	Frequency (cm ⁻¹)	
			Experimental	Computed (Unscaled)
NiH ₂	Sym stretch	vacuo	2200	2010
NiH ₂	Asym stretch	vacuo		2000
NiH ₂	Sym stretch	Ar	2007	
NiH ₂	Asym stretch	Ar	1969	

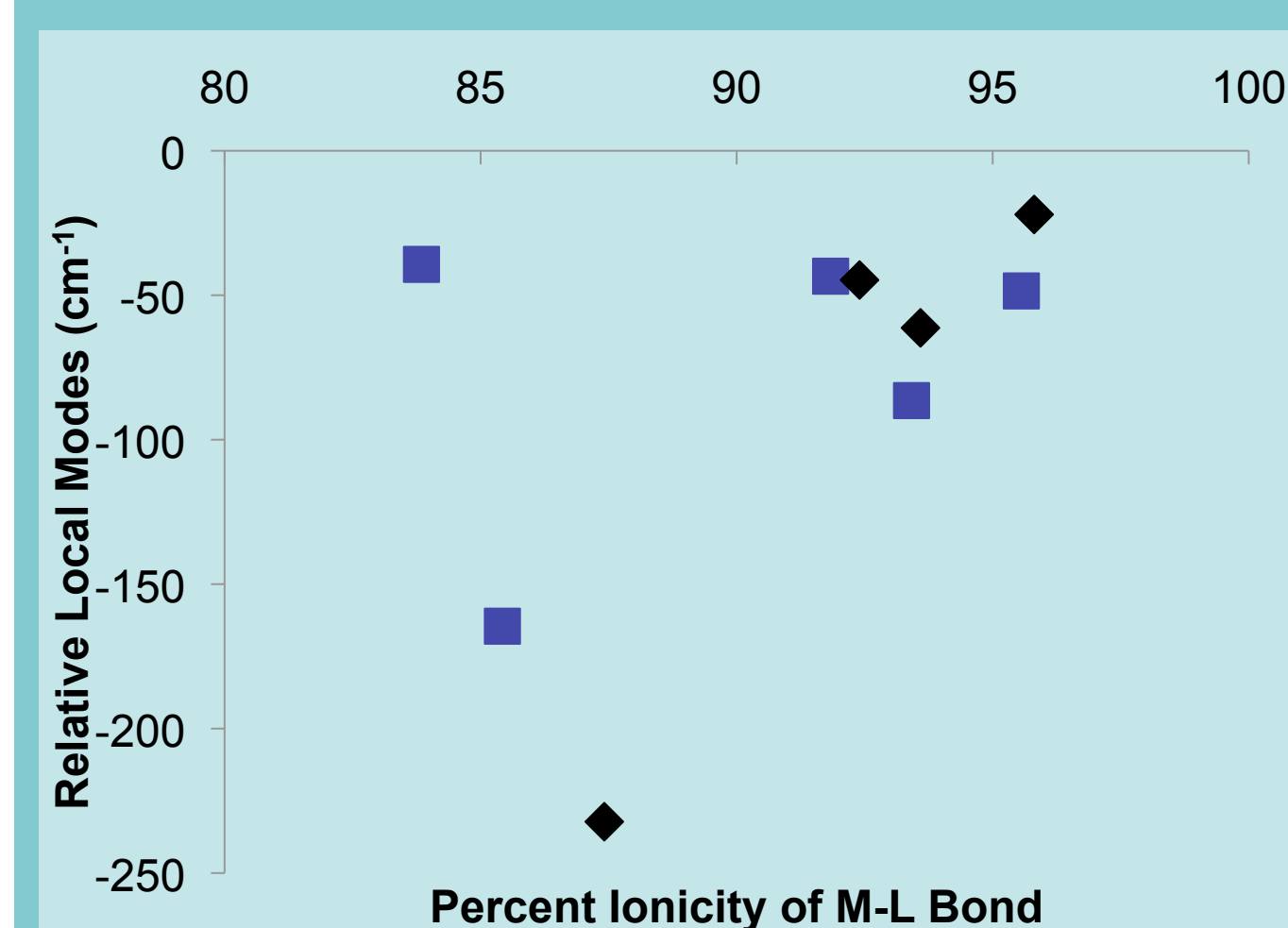
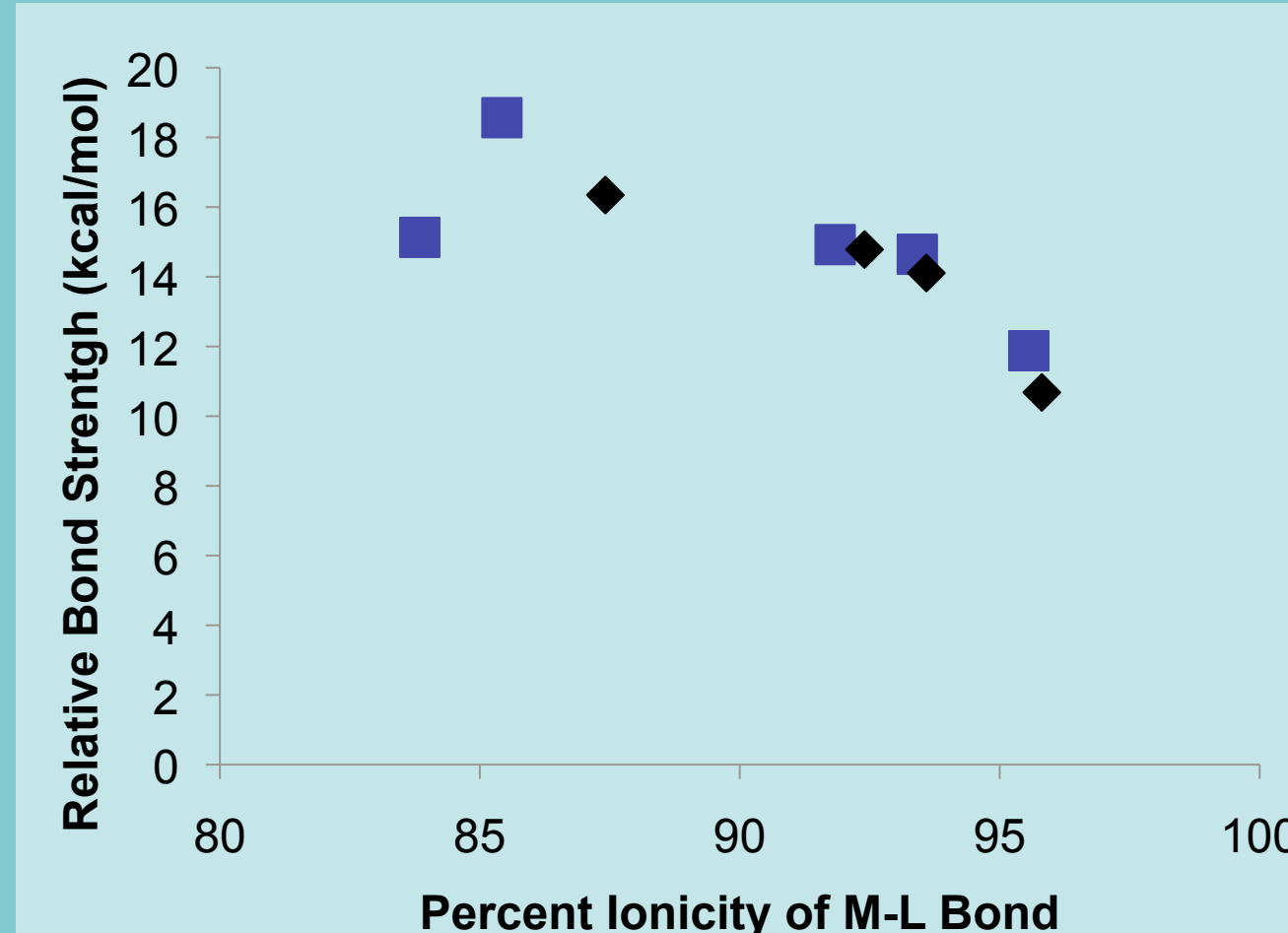
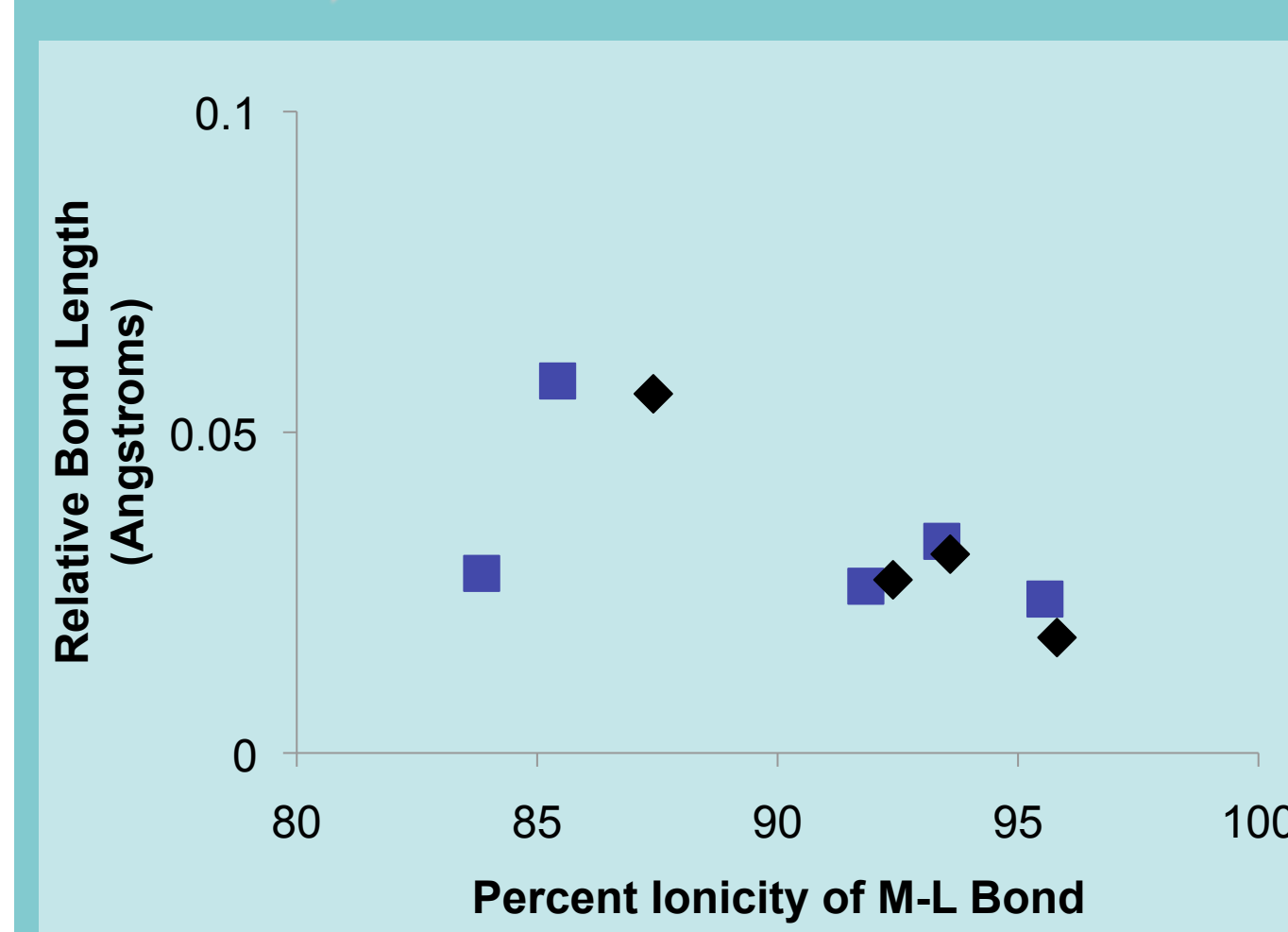
- ❖ Computed NiH₂ vibrational frequency is approximately 8% lower than experimental (References 1-2).

Ligand Influences on M–H Bonds



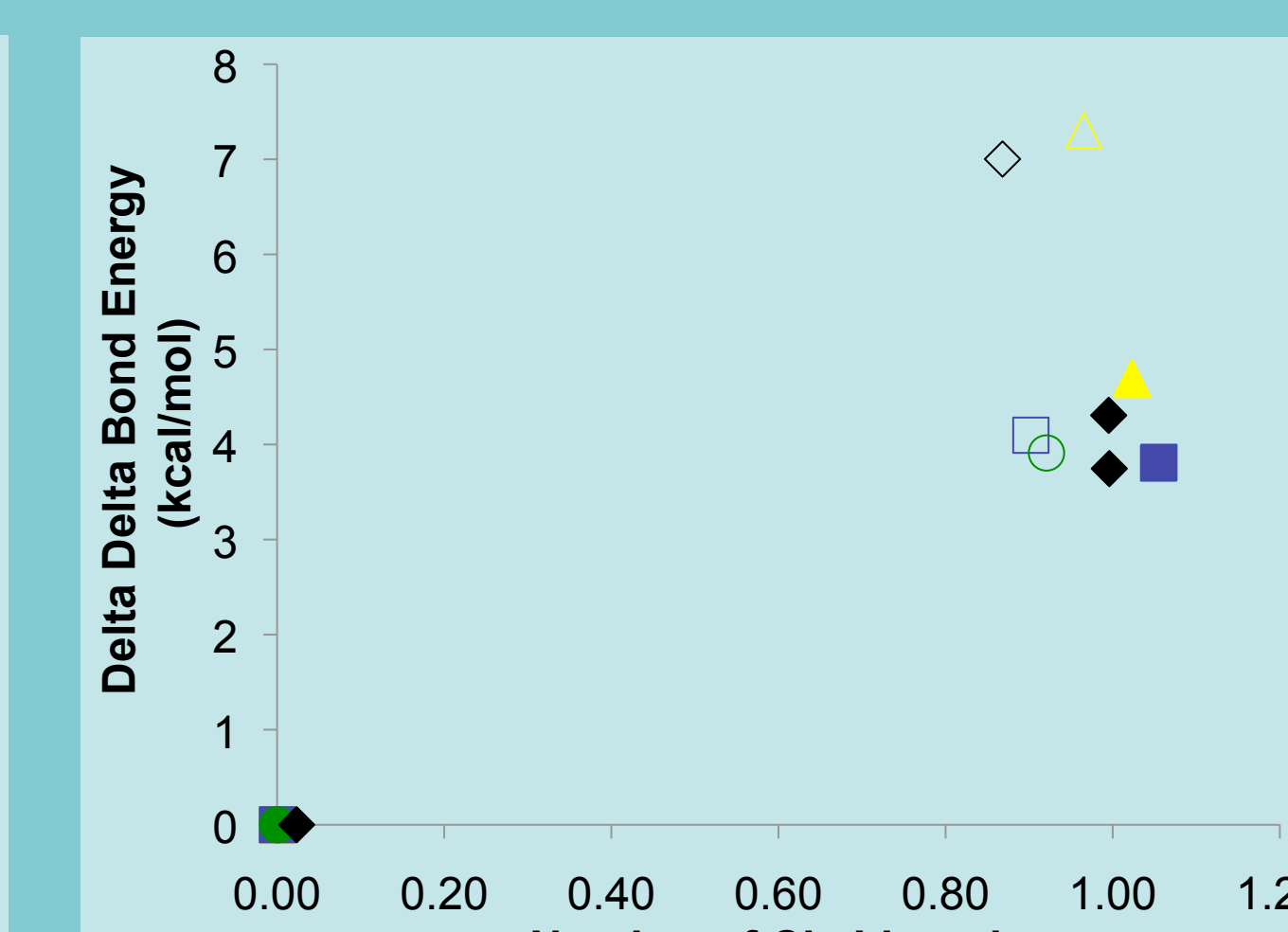
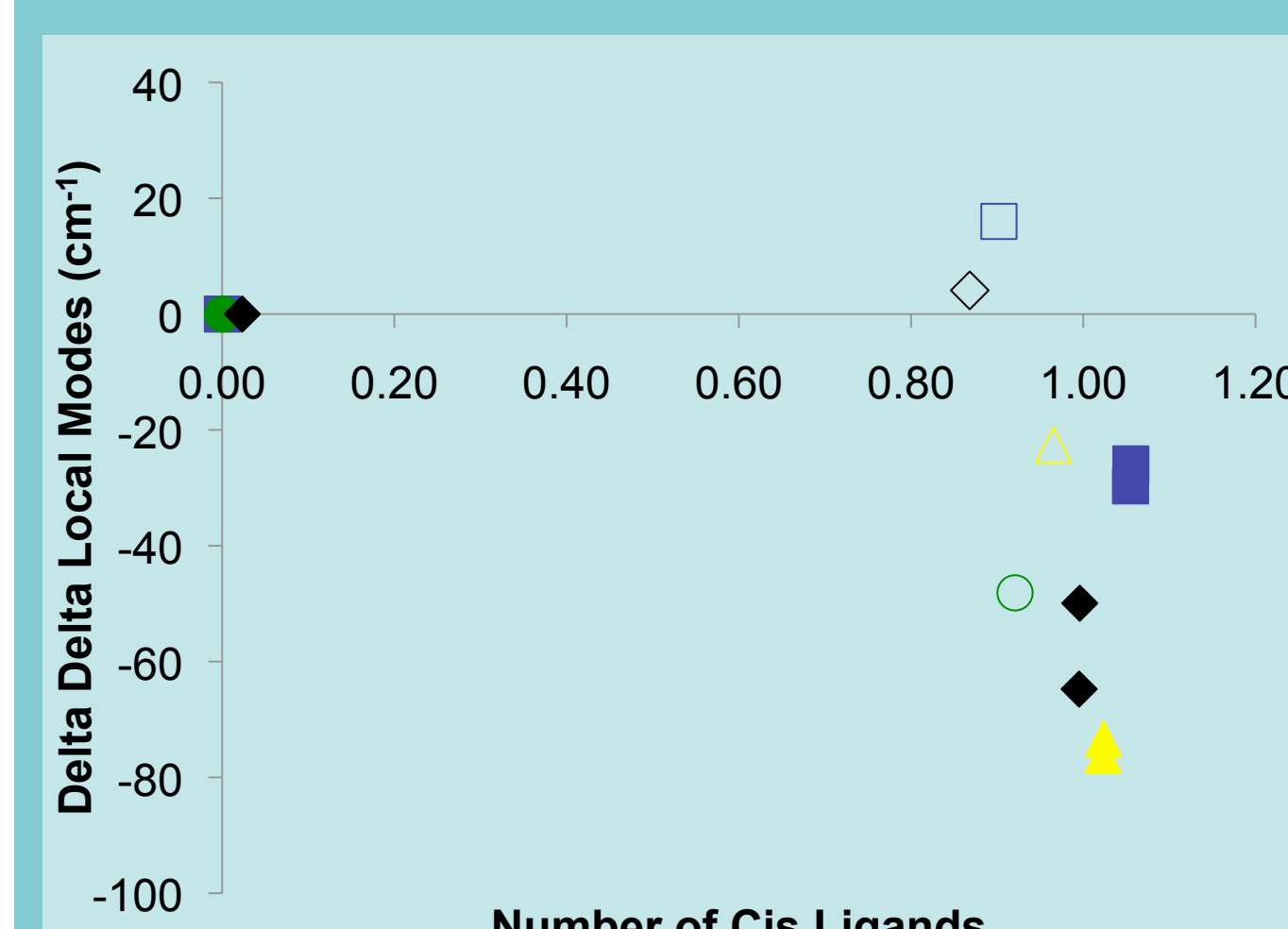
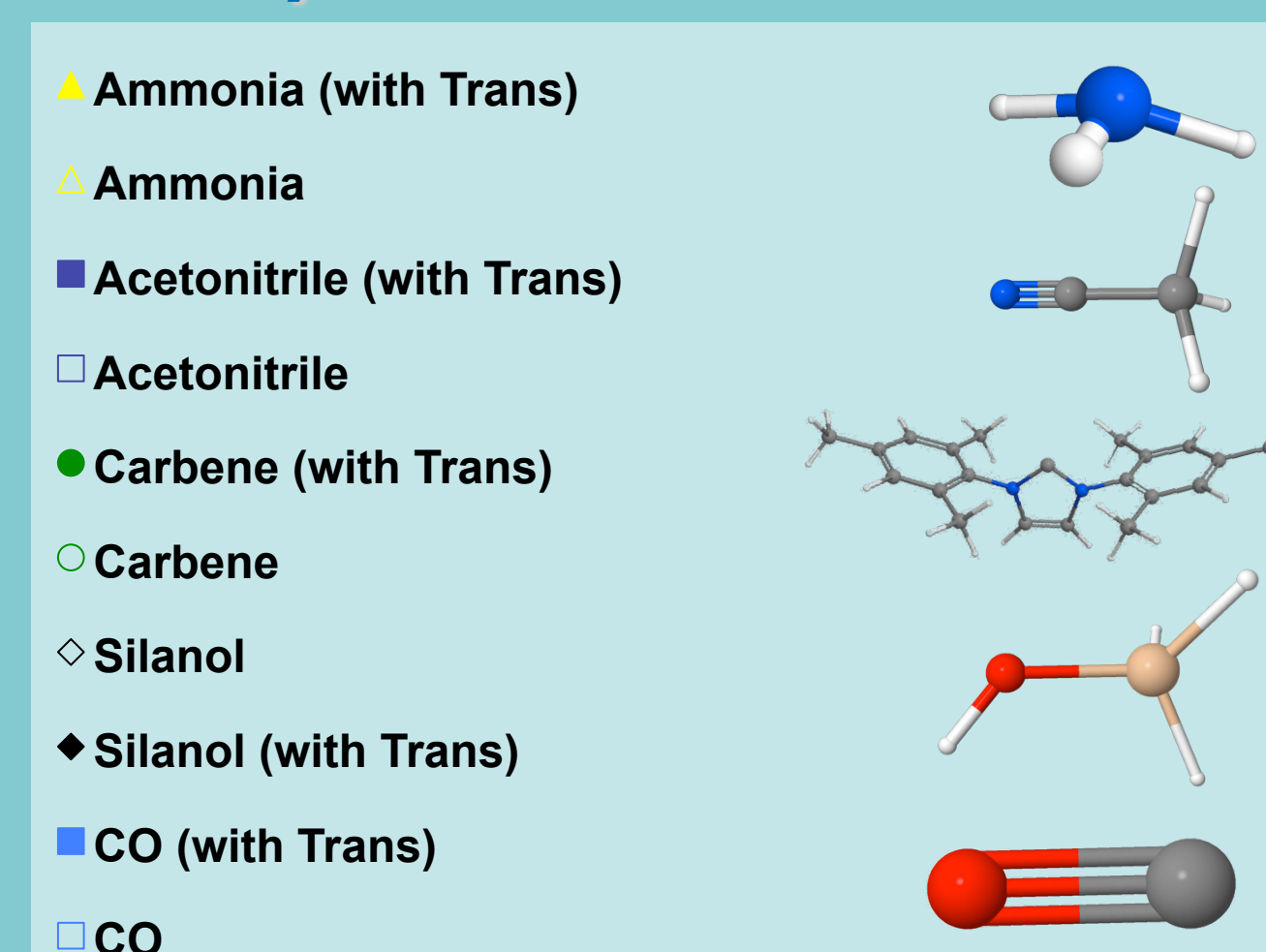
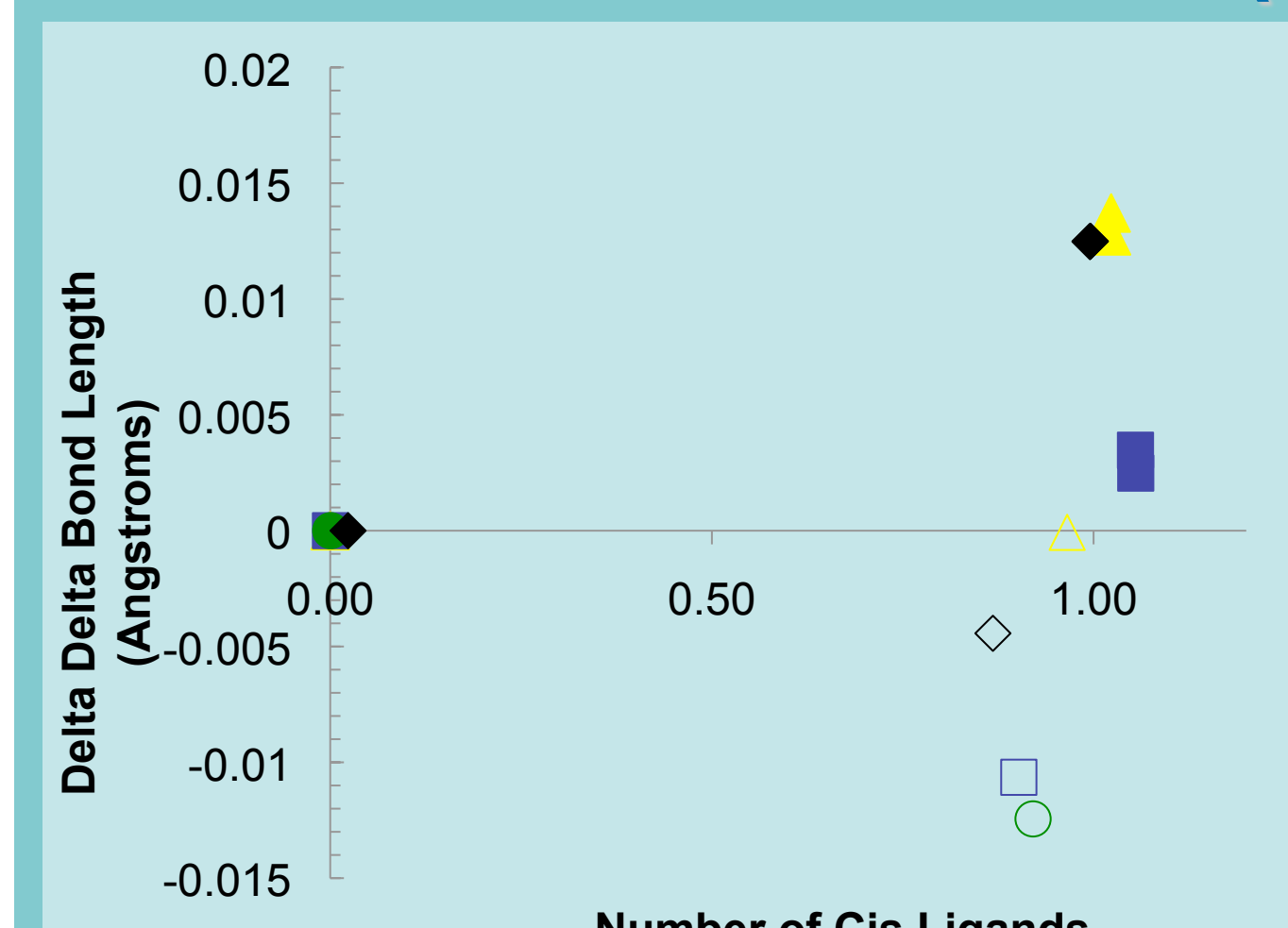
- ❖ Local Mode: Isolated M–H bond stretching frequency.
- ❖ This graph shows that when the bond lengthens it will vibrate slower.

Trans-Influences



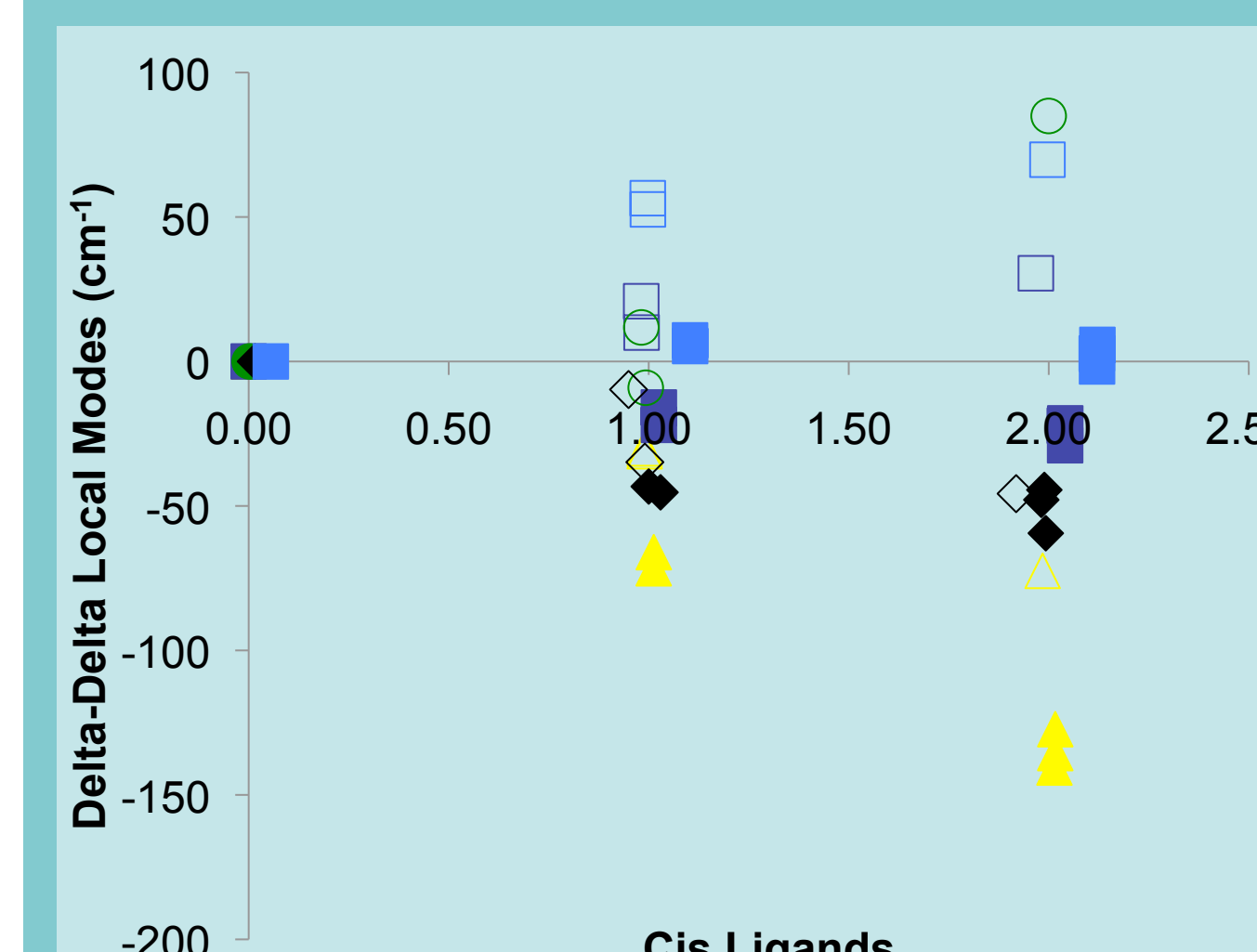
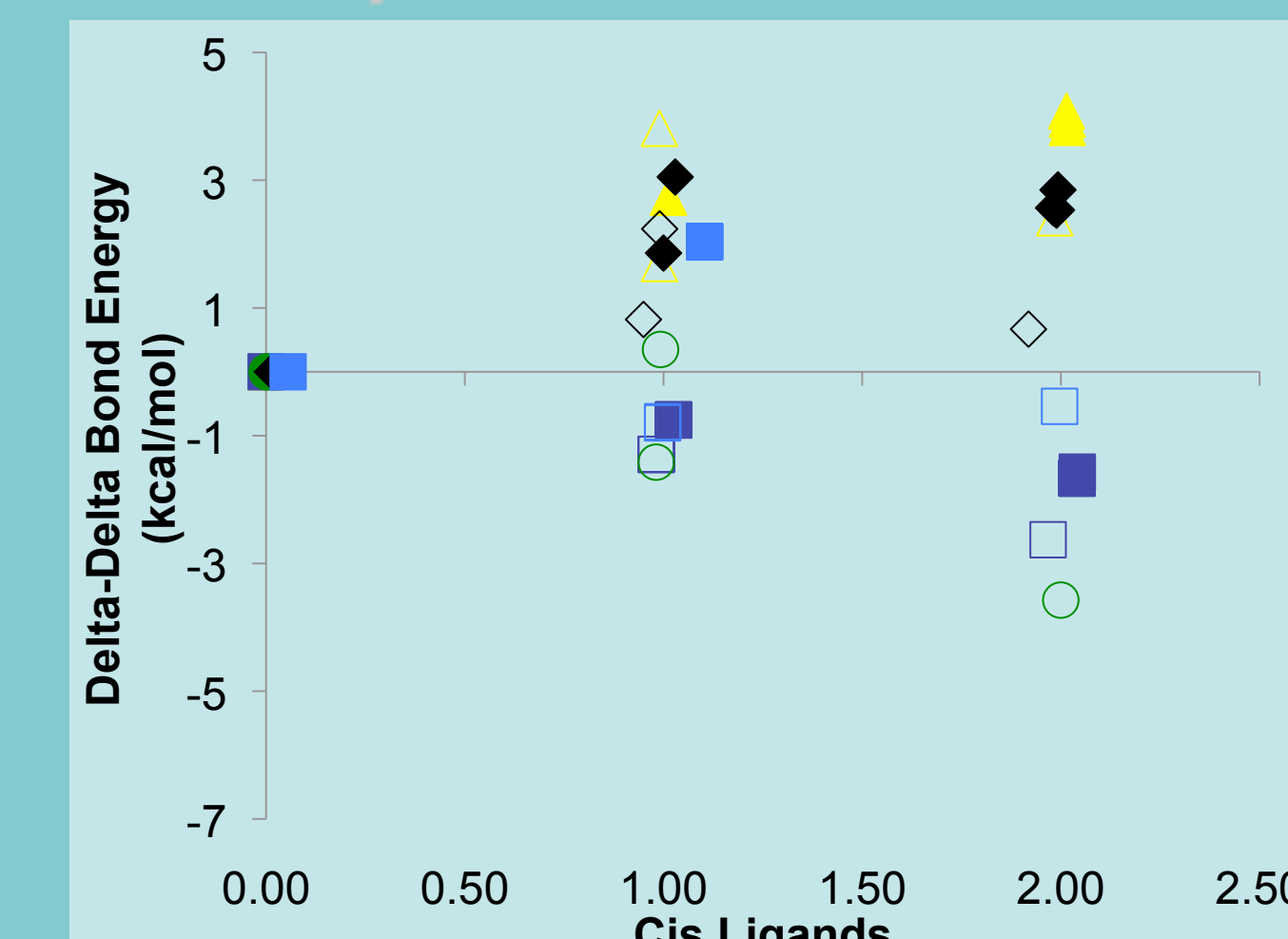
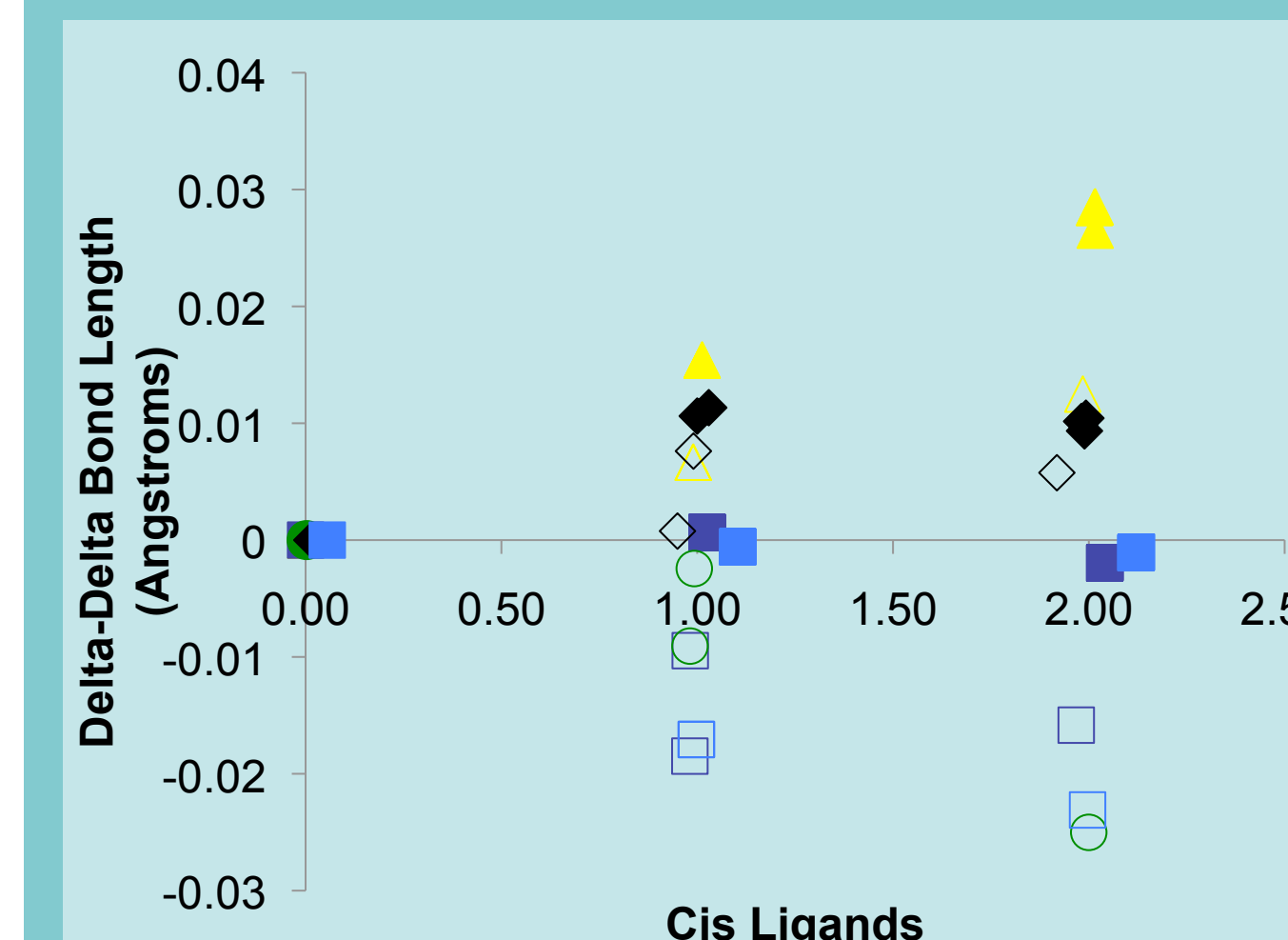
- ❖ M–H bonds are strengthened and lengthened by trans-coordinated ligands.
- ❖ M–L Bond ionicity increases with ligand electronegativity.
- ❖ Less electronegative ligands have an increased trans-influence.

Cis-Influences (Nickel)



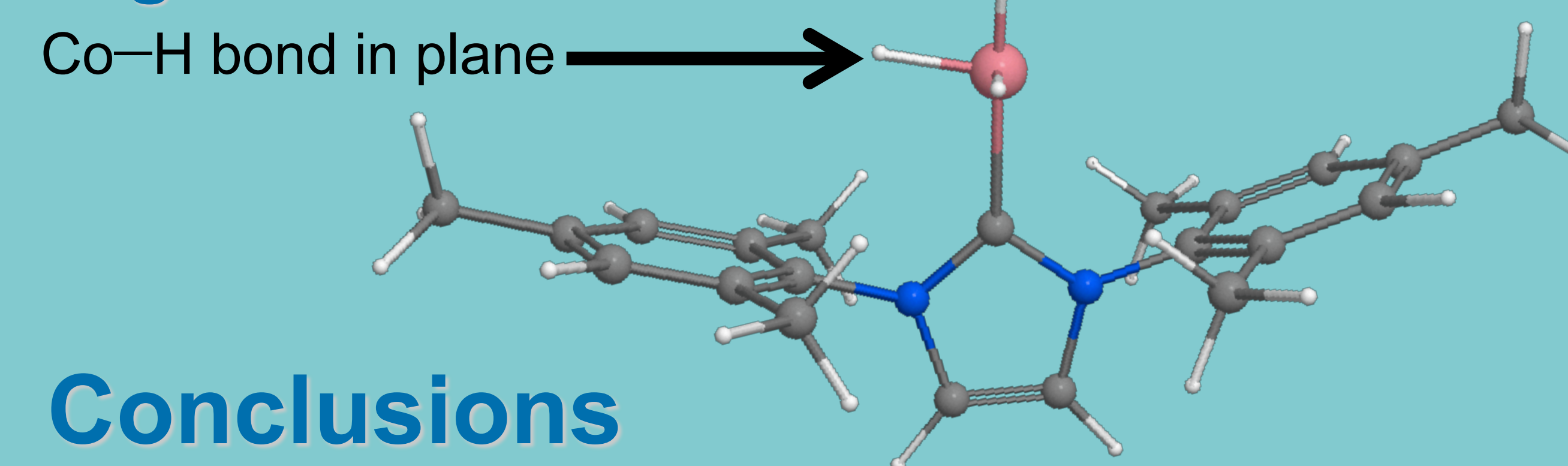
- ❖ How do cis-coordinated ligands affect nickel-hydrogen bonds?
- ❖ When a trans-coordinated ligand is present, the cis-influence is in the same direction as the trans-influence but smaller.
- ❖ If a trans-coordinated ligand is not present, the cis-influence shortens the Ni–H bond.

Cis-Influences (Cobalt)



- ❖ Cis-influences on Co–H bonds are smaller than for Ni–H bonds.
- ❖ For pi-backbonding ligands, cis-influences can weaken and shorten Co–H bonds.
- ❖ For applicable ligands, cis-influences on in-plane Co–H bonds differ.

Figure 2



Conclusions

Trans Effects

- ✧ Calculations confirm known trans-influences.
- ✧ M–H bonds are lengthened and strengthened.
- ✧ This lowers M–H stretching frequencies.

Cis Effects

- ✧ Cis-influences are smaller than trans-influences.
- ✧ In some cases, Co–H bonds are weakened.
- ✧ In some cases, M–H bonds are shortened.
- ✧ This can increase the M–H stretching frequencies.

Future Study

We hope to advance our understanding of first row transition metal-hydrides by including more ligands and more metals. These ligands, including Molecular Hydrogen, Methylamine, Dimethylamine and Trimethylamine, should clarify cis-influences for cobalt. In order to further understand M–H bonding, Copper, Scandium and Titanium complexes will be studied.

Acknowledgements

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References

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2. Li, S.; Van Zee, R.J.; Weltner, W., Jr.; Cory, M.G.; Zerner, M.C., *J. Chem. Phys.*, **1997**, *106*, 2055.