4-12-2022

Using Potential Energy Surfaces of Diatomic Molecules to Determine the Bond Dissociation Energy via Computational Chemistry

Skye Curry

Nathaniel Holbrook

Recommended Citation

Curry, Skye and Holbrook, Nathaniel, "Using Potential Energy Surfaces of Diatomic Molecules to Determine the Bond Dissociation Energy via Computational Chemistry" (2022). *Research and Creativity Symposium*. 139.
https://scholar.umw.edu/rcd/139

UNIVERSITY OF MARY WASHINGTON

Variation of Bond Length to Determine Dissociation Energy of Diatomic Molecules
Carbon Monoxide (CO), Sulfur Monoxide (SO), and Hydrochloric Acid (HCl)

Skye Curry & Nathaniel Holbrook
Department of Chemistry and Physics
University of Mary Washington, Fredericksburg, VA, 22401, USA

INTRODUCTION

ChemCompute is software that utilizes computational chemistry, used in computer modeling, to examine structures and properties of compounds in different environments through ab initio and empirical basis sets. A helpful tool which is used in the determination analysis for bond dissociation energy of the diatomic molecules, specifically carbon monoxide (CO), sulfur monoxide (SO), and hydrochloric acid (HCl). 6-31G* is an ab initio basis set used for analysis of bond dissociation energy (Do") which is a linear combination of six primitive gaussians with three and one primitive being separated to analyze the inner and outermost valence shell of the atoms.

The harmonic oscillator is a general representation of a potential energy curve; however, the Morse potential corrects for anharmonicity and for bond dissociation. Anharmonicity considers changes in energy between vibrational levels not being equal: restoring and displacement forces are not the same. Bond dissociation occurs when the internuclear distance between two atoms is larger than the attractive forces holding the atoms together: resulting in two individual atoms.

A potential energy curve maps the change in internuclear distance between atoms and their corresponding energy. The bond dissociation energy can be determined from this potential energy curve as the well depth (D_e") minus the zero-point energy (ZPE). The well depth is the change in energy from bond dissociation to the bottom of the curve, or to the equilibrium/average bond length (r_e). Zero-point energy is the vibrational frequency (v_e) divided in half.

The bond dissociation of diatomic molecules CO, SO, and HCl are examined to evaluate the relationship between single to triple bonds and their effect in bond dissociation.

EXPERIMENTAL METHOD

- Diatomic molecule (CO, SO, or HCl) is drawn or added to ChemCompute
- Molecule is symmetrized: z-coordinates and bond length are recorded for the molecule
- 6-31G* basis set, single point energy calculation, and "B3LYP" DFT functional were set as the parameters
- Submit job: record job number and electronic energy in kJ/mol for the molecule at its respective bond length
- The steps above were repeated, with the z-coordinates altered to adjust for the bond length between atoms
- Repeated until an error occurred or no bond was seen at a longer bond length

- Using the electronic energy and bond lengths, a potential energy plot was constructed
- A relative potential energy curve was created using the error or no bond electronic energy

- Equilibrium bond length and well depth were recorded
- Vibrational frequency and zero-point energy were calculated
- Dissociation energy was calculated using well depth and zero point energy for each molecule

POTENTIAL & RELATIVE POTENTIAL ENERGY CURVES

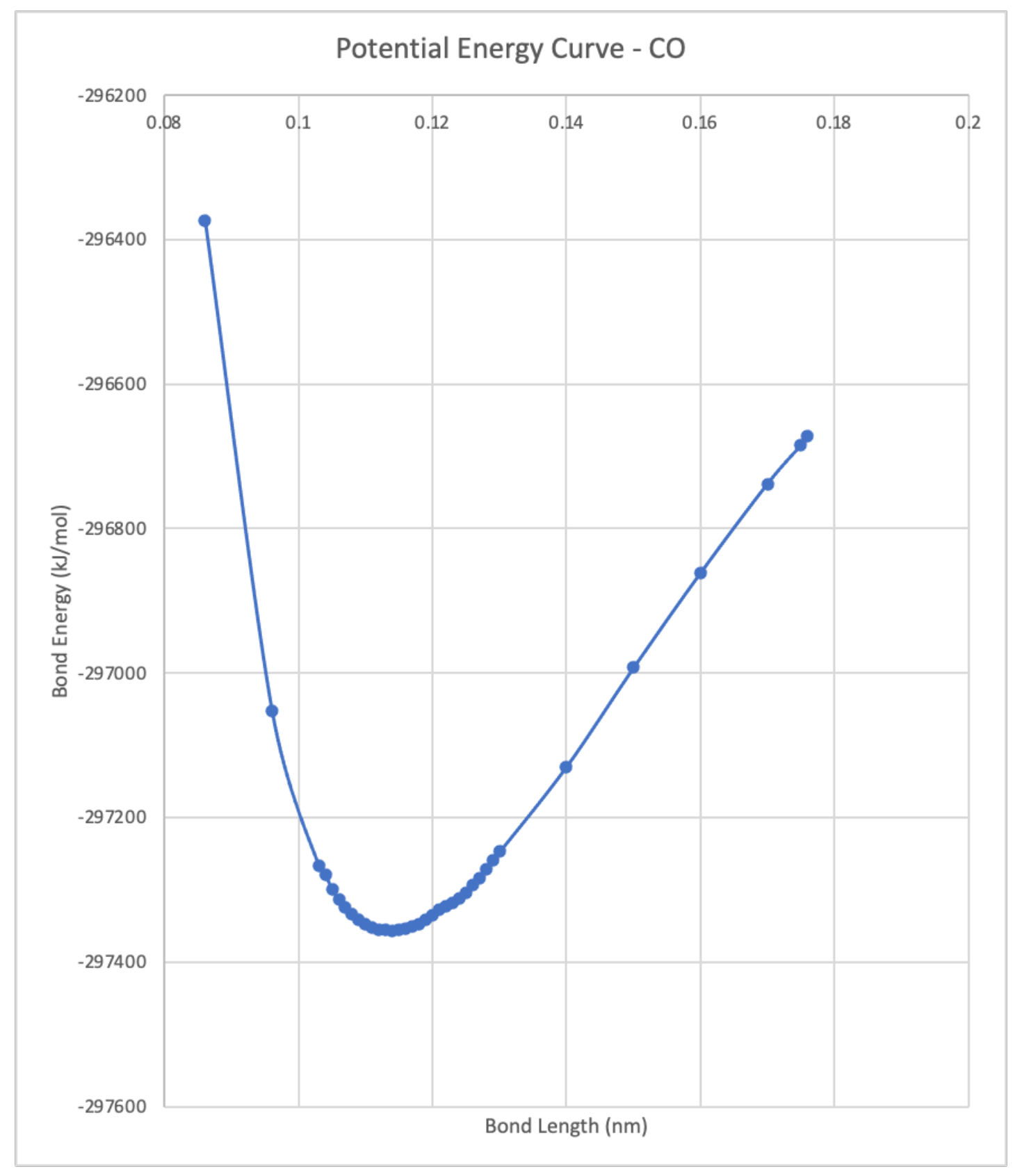

Figure 1A. Potential energy curve of CO as a function of bond length

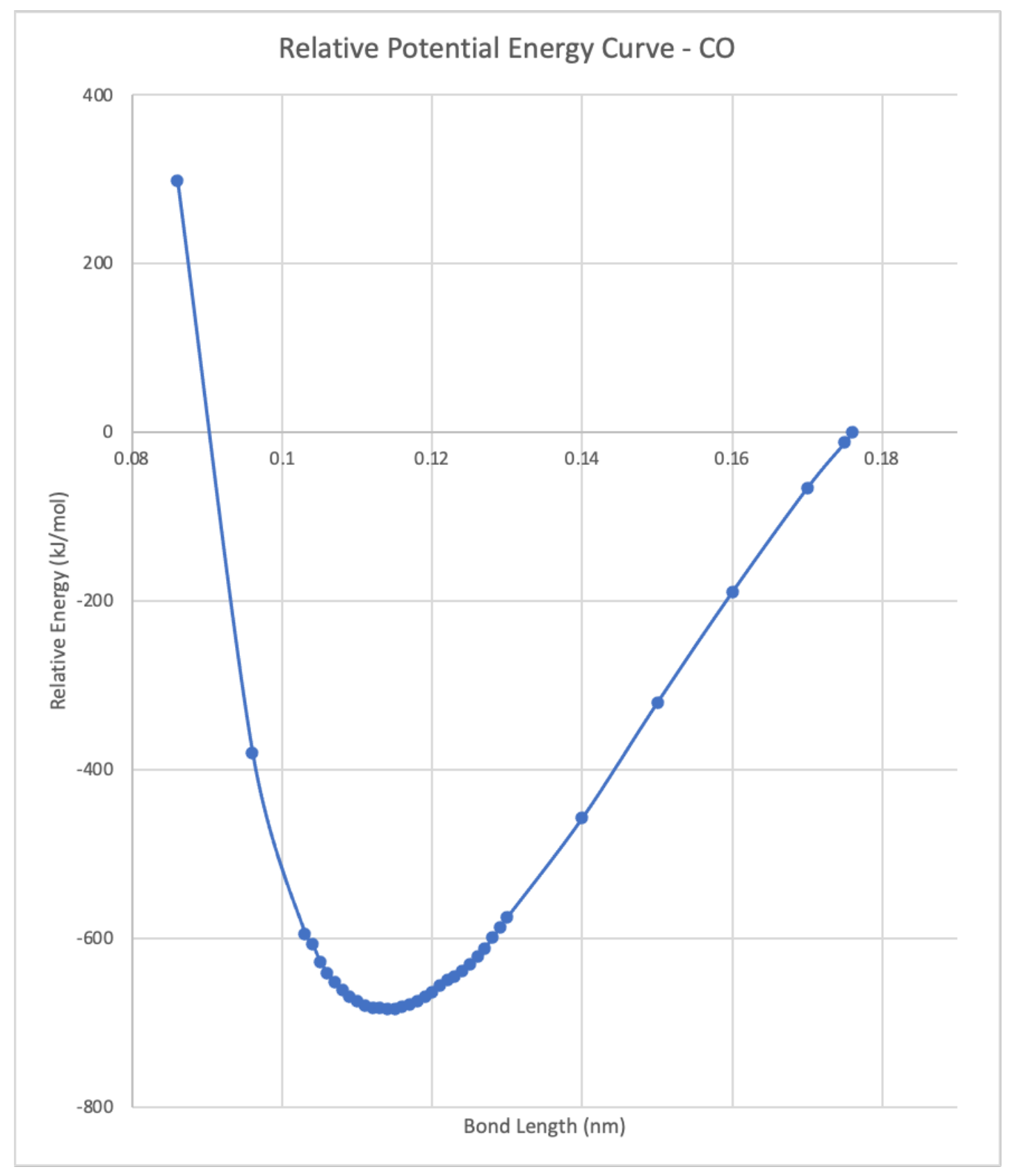

Figure 1B. Relative potential energy curve of CO adjusted using energy where the bond dissociates

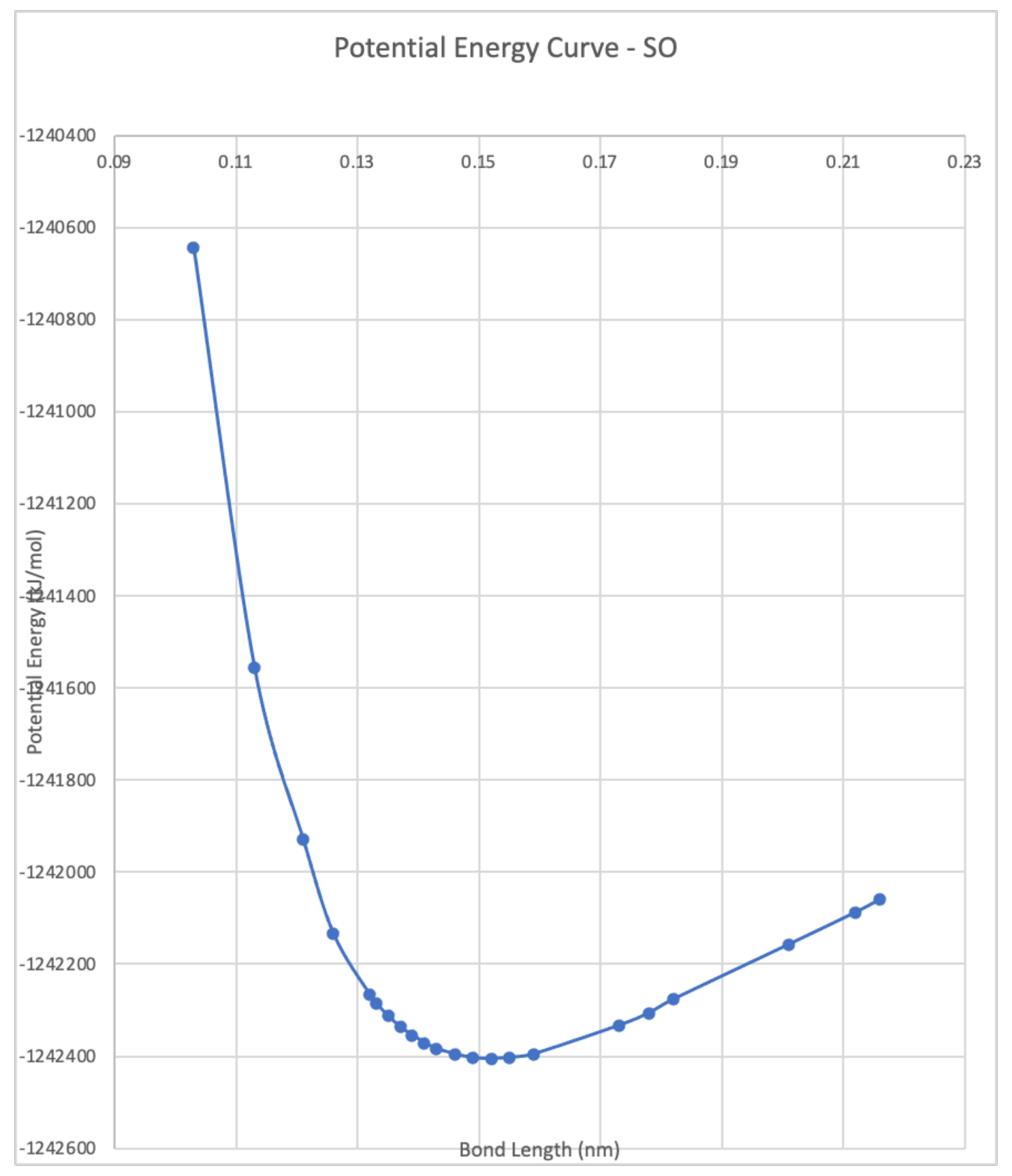

Figure 2A. Potential energy curve of SO as a function of bond length

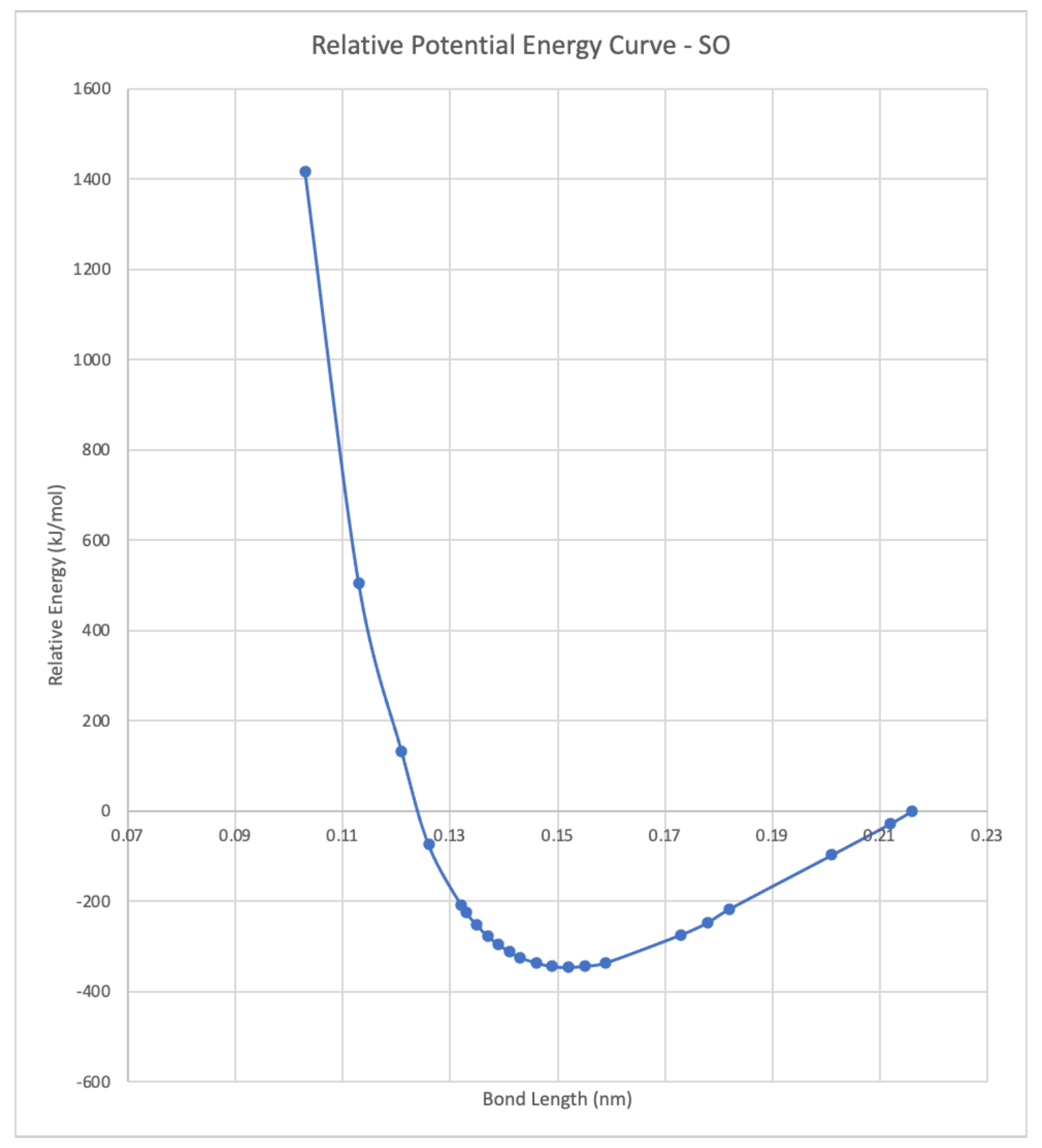

Figure 2B. Relative potential energy curve of SO adjusted using energy where the bond dissociates

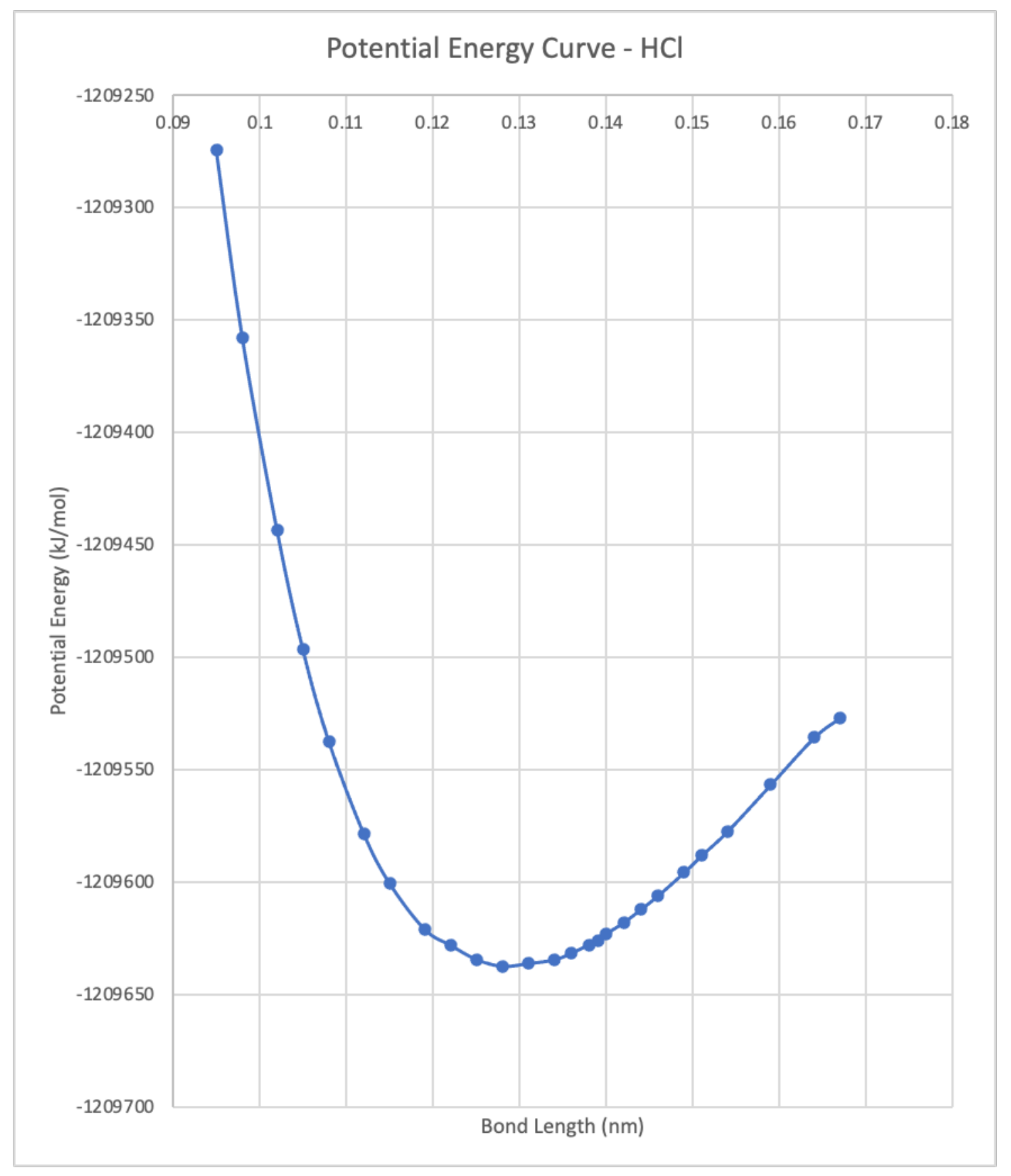

Figure 3A. Potential energy curve of HCl as a function of bond length

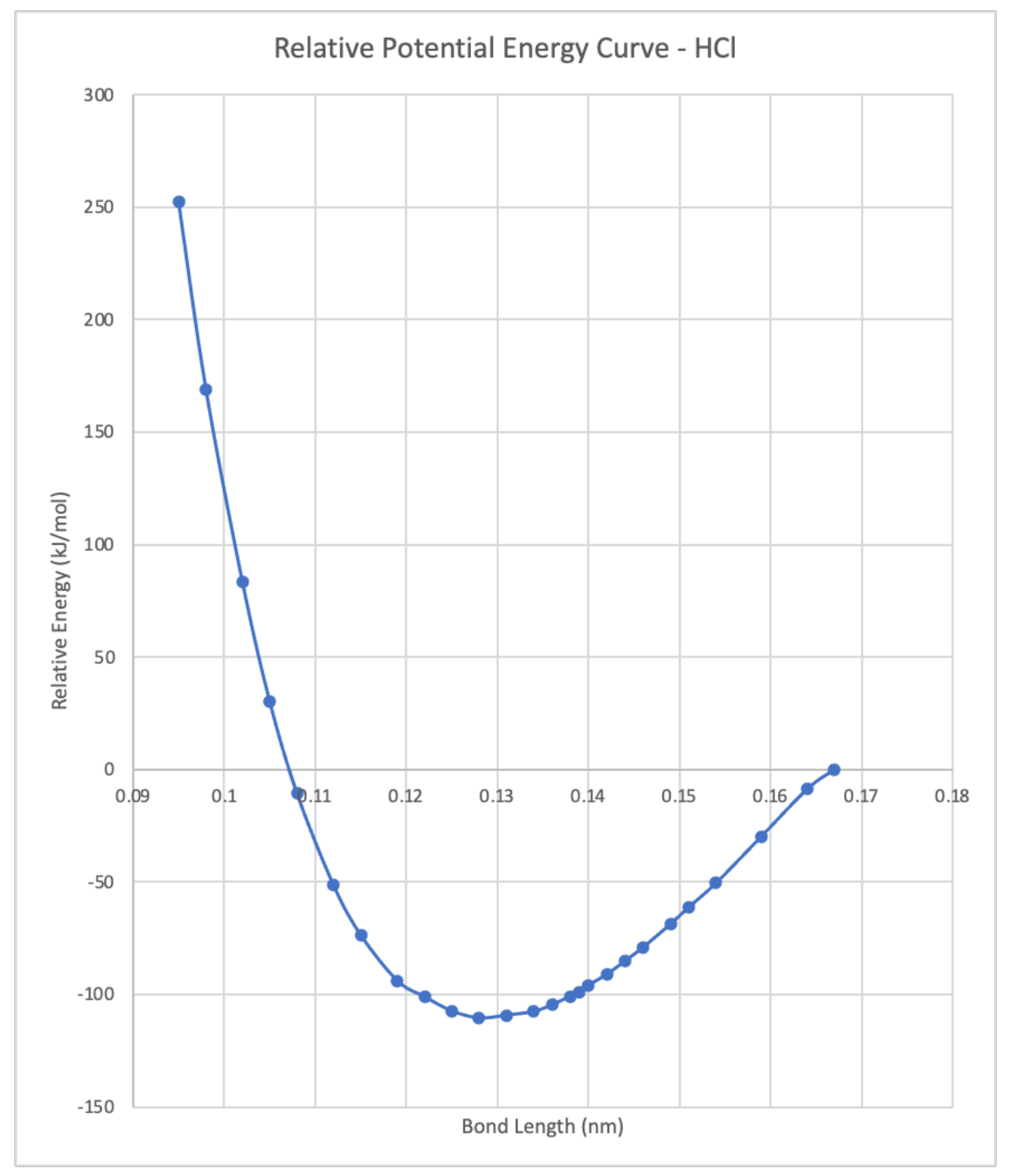

Figure 3B. Relative potential energy curve of HCL adjusted using energy where the bond dissociates

DISSOCIATION ENERGY CALCULATIONS

Table 1. Well depth, Vibrational Frequency, ZPE, and Dissociation Energies

	CO	SO	HCl
re (nm)	0.113	0.135	0.128
De" (kJ/mol)	682.539	252.974	43.431
k (N/m)	1902	893	516
ve (cm-1)	2169.3	1685.4	3.15E+03
ZPE (cm-1)	1084.7	842.7	1573.8
Do" (kJ/mol)	669.6	242.9	24.6
Do" % Error	37.5%	53.4%	94.5%

CONCLUSION

- Experimental bond dissociation energies of CO, SO, and HCl were found to be 669.6 kJ/mol with 37.5% error, 242.9 kJ/mol with 53.4% error, and 24.6 kJ/mol with 94.5% error, respectively

- As the number of bonds decreased (triple for CO to single for HCl), the error in bond dissociation energy increased

- Error in bond dissociation energy due to number of bonds could be due to:
  - Bond strength
  - Energy needed to break the bond
  - Electronegativity/Interactions between atoms
  - DFT Functional: stabilization energy

- Changing DFT and perhaps other computational methods could allow for more accurate bond dissociation energies

REFERENCES

(1) Anharmonic Oscillator https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Quantum_Mechanics/06._One_Dimensional_Harmonic_Oscillator/Anharmonic_Oscillator (accessed 2022 -04 -18).
(2) Calculation of vibrational frequencies http://openmopac.net/manual/vibrational_frequencies.html (accessed 2022 -04 -18).
(3) ChemCompute — Free Computational Chemistry for Undergraduates https://chemcompute.org/gamess/submit (accessed 2022 -04 -18).
(4) Engel, T. *Quantum Chemistry and Spectroscopy,* 4th edition; Pearson Education: New York, 2019; Chapter 8.
(5) Force Constants for Bond Stretching https://hbcp.chemnetbase.com/faces/documents/09_06/09_06_0004.xhtml (accessed 2022 -04 -18).
(6) T. L. Cottrell, The Strengths of Chemical Bonds, 2d ed., Butterworth, London, 1958; B. deB. Darwent, National Standard Reference Data Series, NationalBureau of Standards, no. 31, Washington, 1970; S. W. Benson, J. Chem. Educ. 42:502 (1965); and J. A. Kerr, Chem. Rev. 66:465 (1966).

ACKNOWLEDGEMENTS

We would like to express our gratitude to:
- University of Mary Washington (UMW) Department of Chemistry
- UMW Research and Creativity Day
- Professor Leanna Giancarlo