Def2 Basis Sets and 1-Iodopentane

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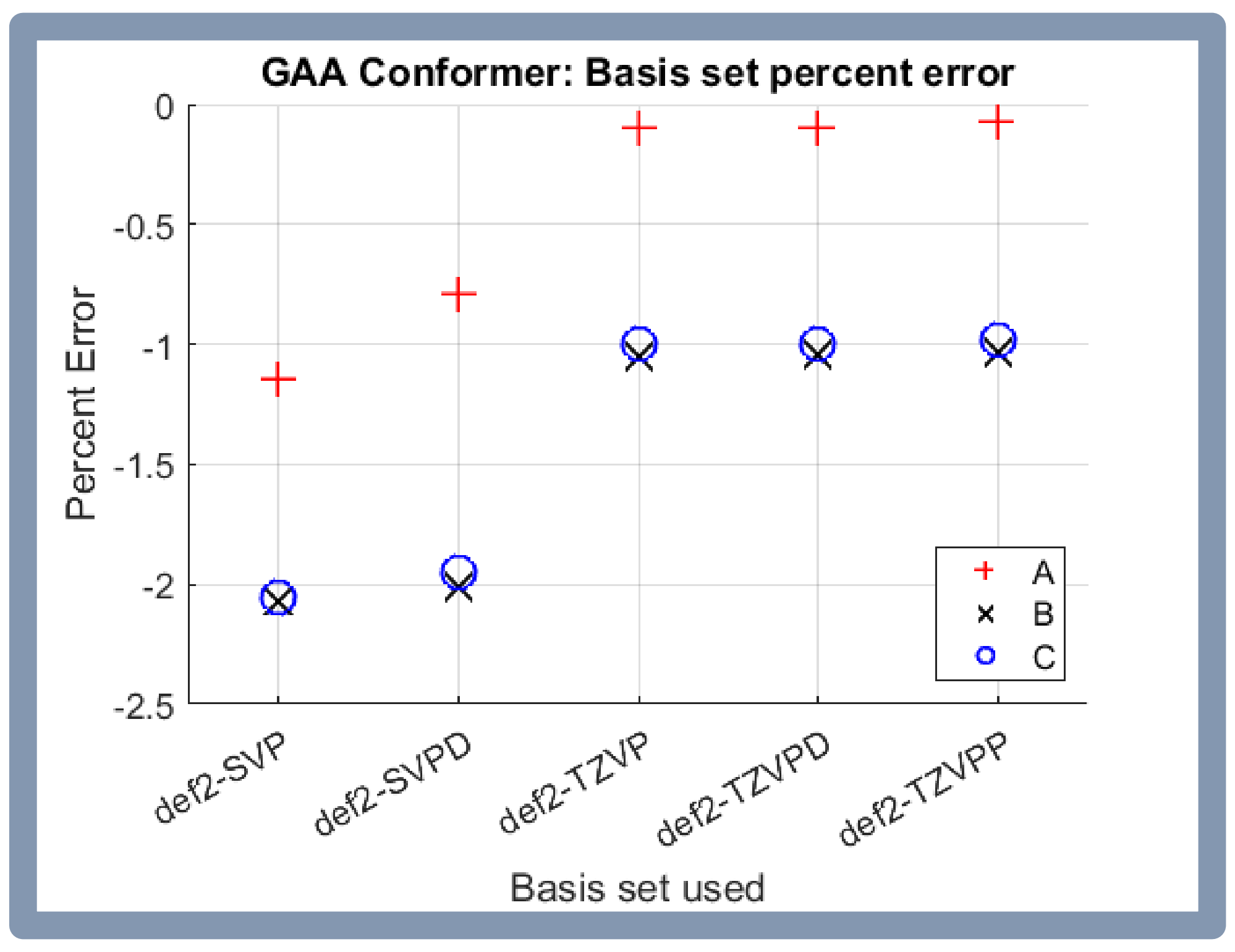
INTRODUCTION 1-iodopentane is one in a series of iodine-containing molecules the Novick Lab has studied. Iodine is a good substitute for xenon, being close in structure and significantly cheaper in cost. The quantity of electrons iodine possesses, however, poses a unique issue when simulating the molecule to determine its structure. Gaussian 16 Rev. C.01 simulations were conducted to obtain rotational constants and were compared to data obtained from our Balle-Flygare Fourier-transform microwave (FTMW) spectrometer.

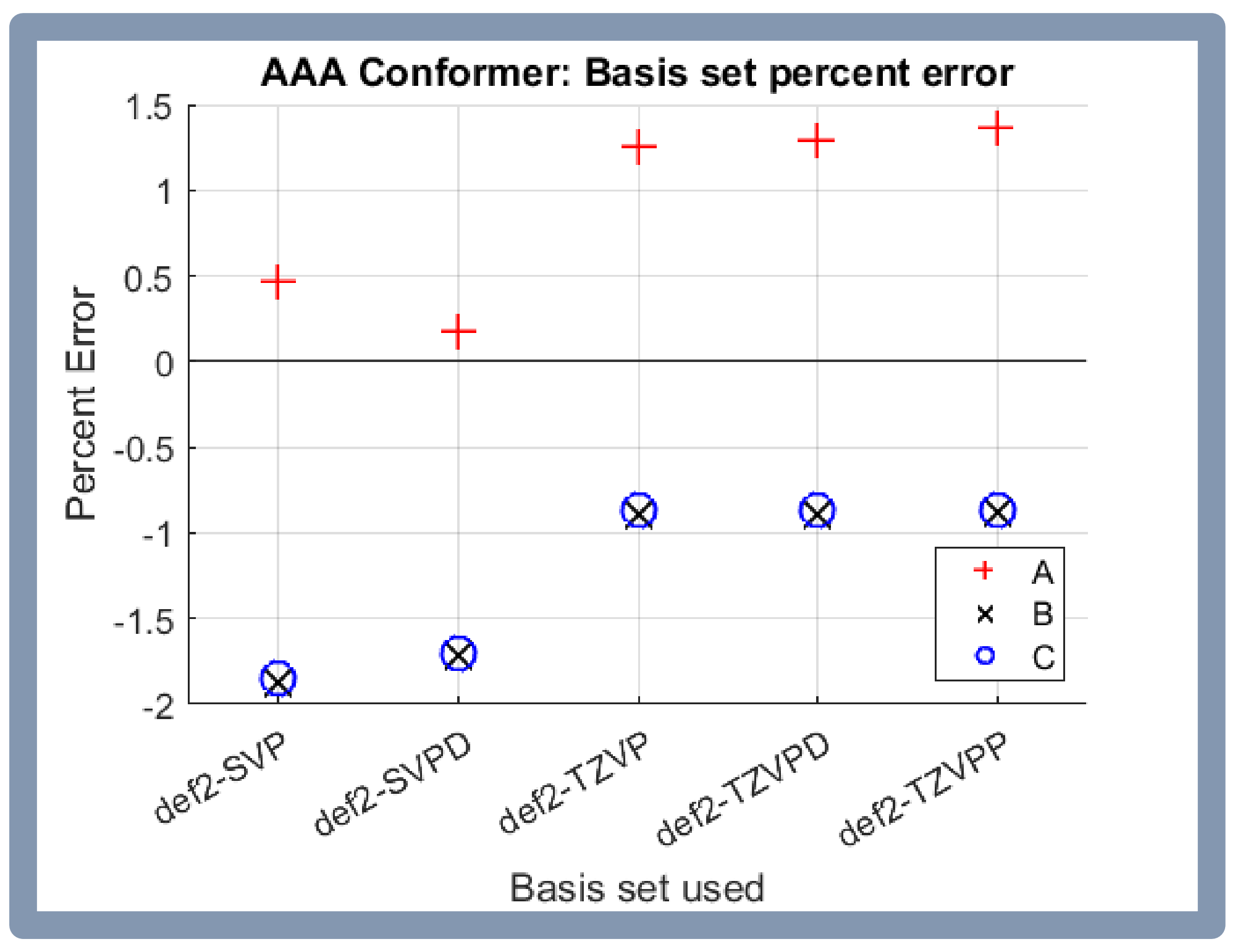
While carbons and hydrogens are easier to simulate in their entirety, iodine usually requires approximations. This is done by treating the "inner core" of electrons with an electric core potential (ECP). The electrons in the valence are then treated as individuals. The more electrons included in the valence, the more computationally intensive the simulation is. The method used was DFT. The level of theory used was B3LYP, with D3(BJ) dispersion correction. The def2 basis sets at various sizes were used. The basis sets are shown in chart 1.

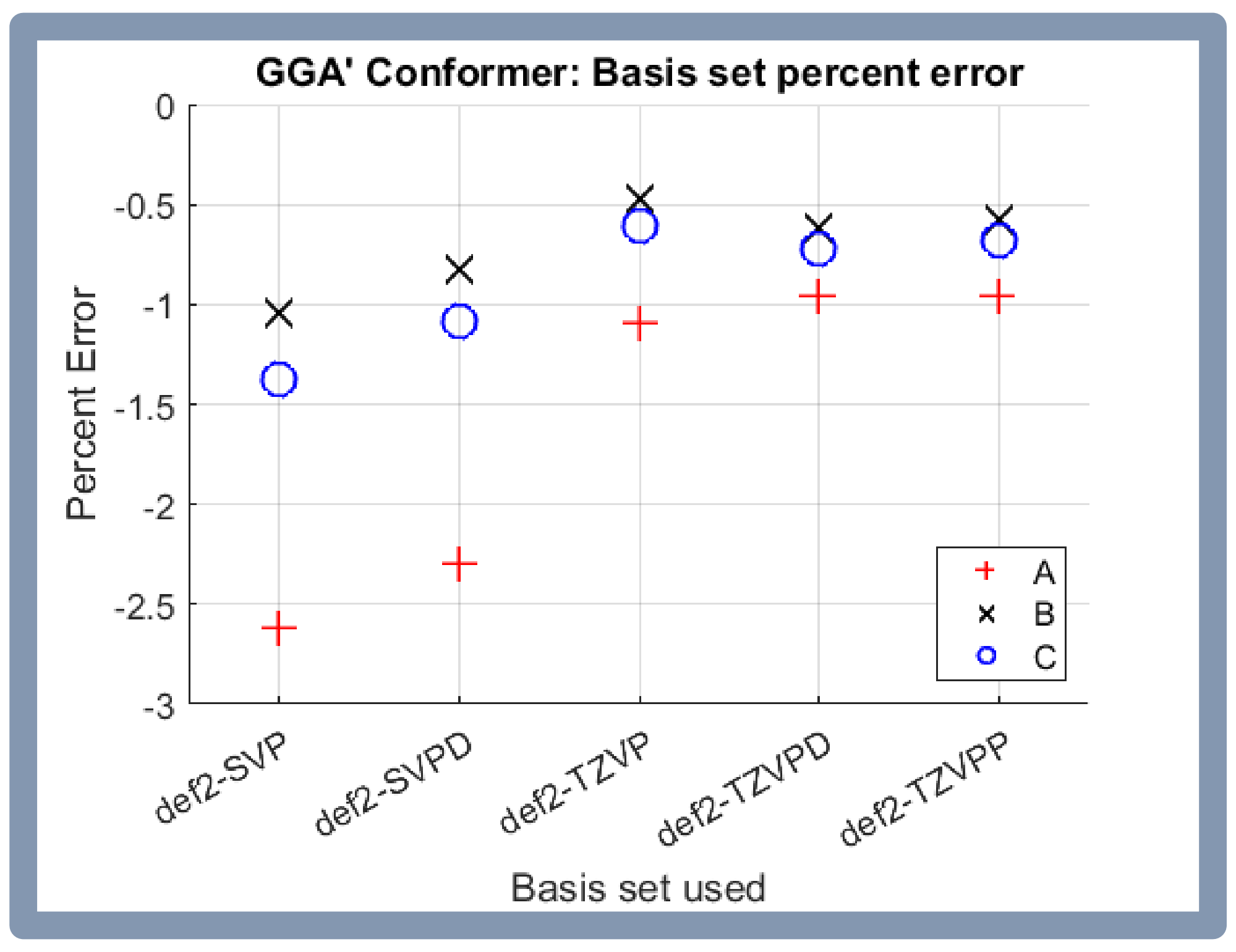
EXPERIMENTAL Rotational spectra for 1-iodopentane were obtained prior to the start of this experiment.

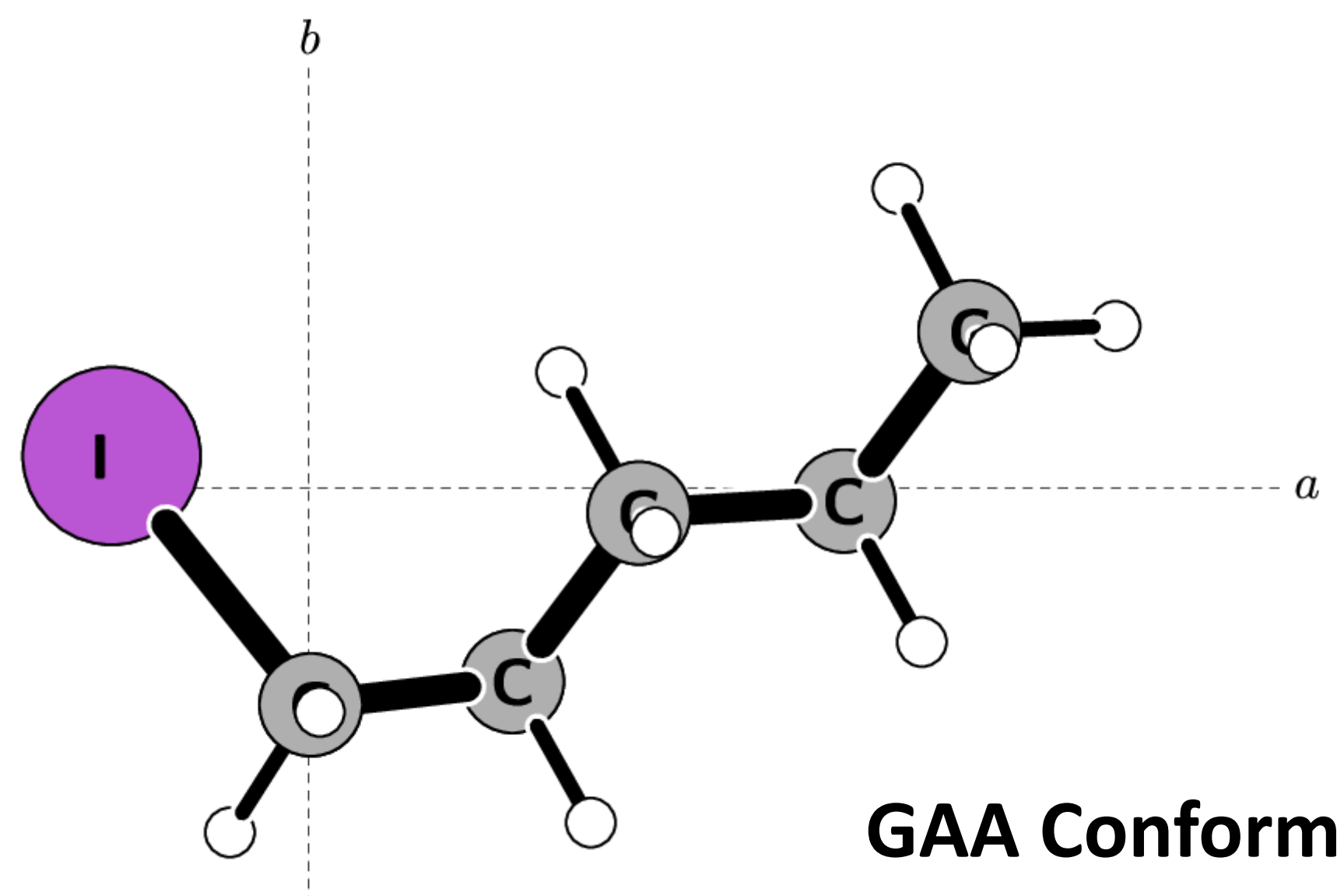
Figure 1: Calculated and fitted rotational constants A, B, & C, and relative energies for the def2-TZVPP basis set.

(in MHz)		GAA	AAA	GGA'
Fit	A	4898.107(44)	13805.353(85)	3796.221(75)
	B	618.942(15)	442.202(03)	772.085(99)
	C	568.660(89)	434.363(75)	690.400(61)
def2-SVP	A	4841.9	13869.9	3696.8
	B	606.1	433.9	764.0
	C	557.0	426.4	680.9
def2-SVPD	A	4859.2	13829.0	3708.9
	B	606.5	434.6	765.7
	C	557.6	427.0	682.9
def2-TZVP	A	4893.1	13977.8	3754.8
	B	612.5	438.3	768.5
	C	563.0	430.6	686.2
def2-TZVPD	A	4893.2	13983.3	3759.9
	B	612.5	438.3	767.3
	C	563.0	430.6	685.4
def2-TZVPP	A	4894.7	13993.2	3759.7
	B	612.5	438.3	767.6
	C	563.1	430.6	685.7
Relative Energy (E_h)		0.00001	0.00035	0.00000

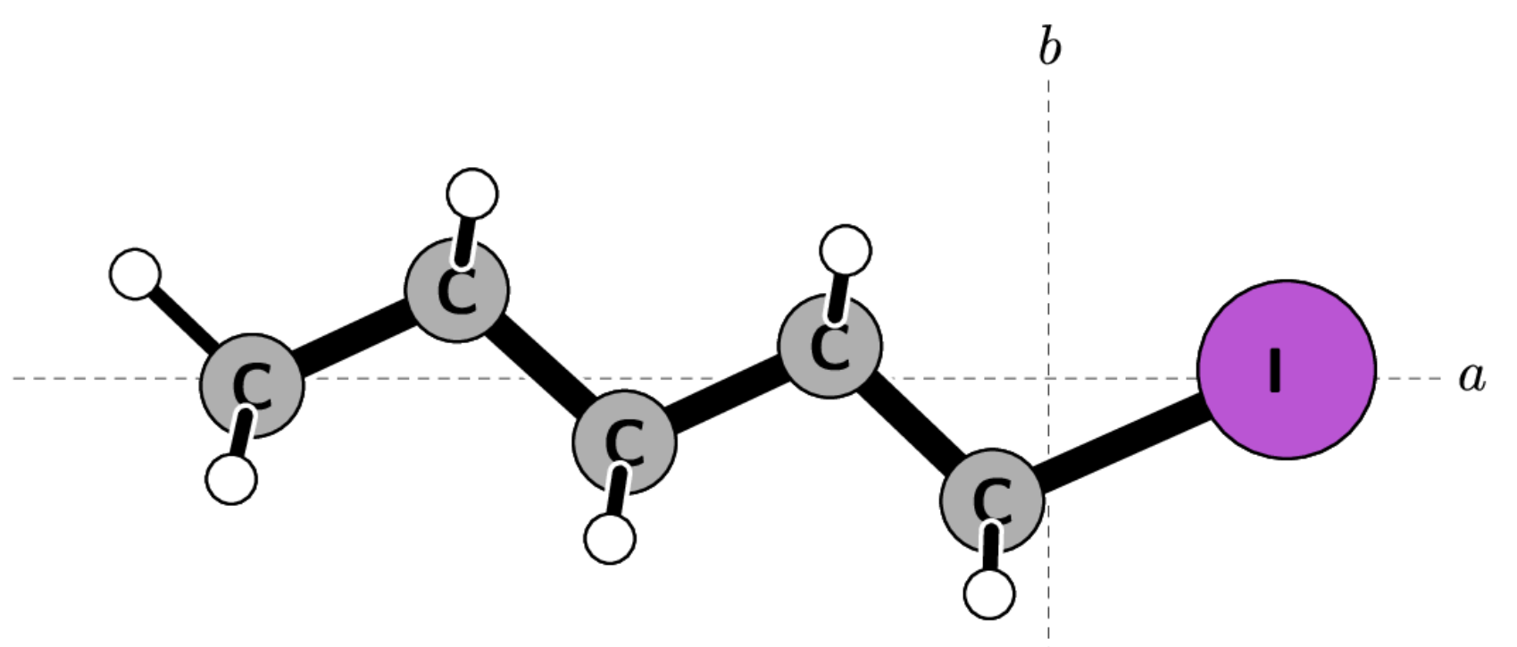




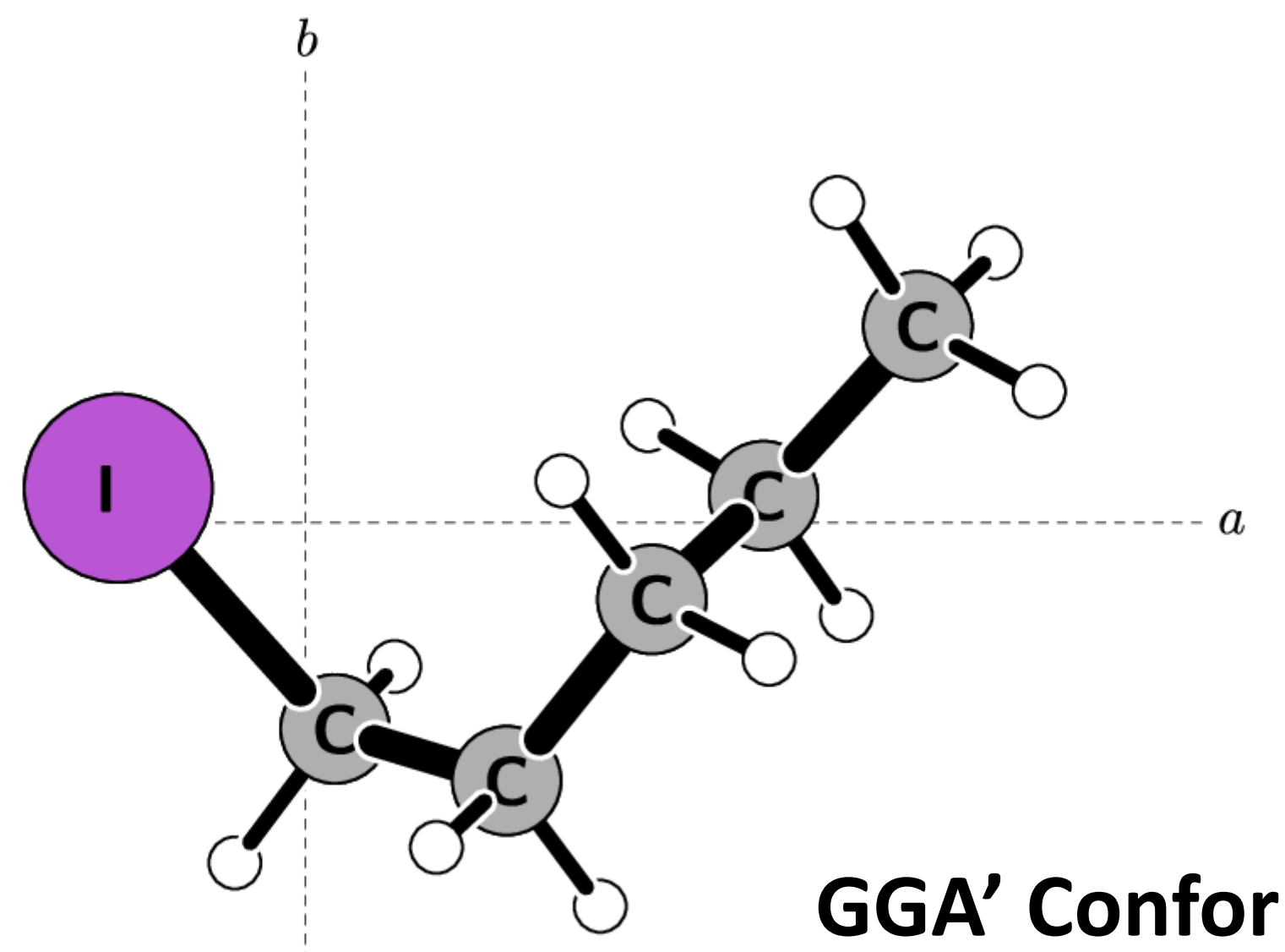




GAA Conformer
def2-TZVPP



AAA Conformer
def2-TZVPP

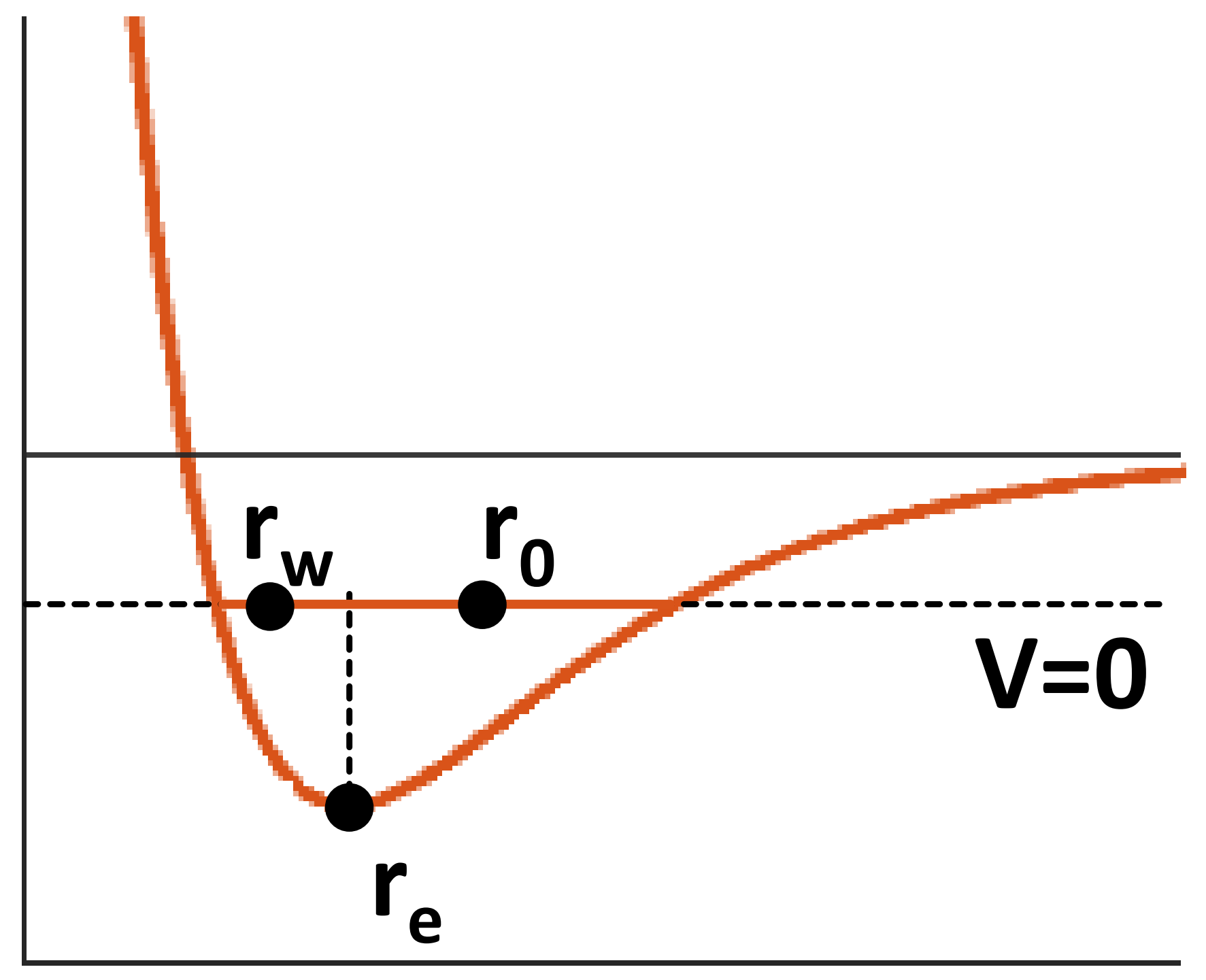


GGA' Conformer
def2-TZVPP

DISCUSSION Iodine was chosen to study because of its similarity to xenon, and testing iodine-containing molecules is significantly cheaper than anything involving xenon. By comparing the results of various forms of the def2 basis set to empirical data, the accuracy of the basis sets is tested, and results could be applied to xenon calculations. The results above suggest that as the basis set gains new polarization functions and more valence splitting, the predicted rotational constants for the GAA and GGA' conformers are closer to the fitted constants, meaning the prediction is more accurate. Most constants were within 1% (typically <10 MHz) of the fitted values. The relative energies of the three conformers all agree.

However, the A constant for the AAA conformer was greater than the fitted value. This means that the basis sets used were unable to correctly predict the rotational constants for that conformer. Predicted constants slightly lower than the fitted constants suggest that the prediction could be predicting constants properly. However, since the A constant is greater than the fit, something must be failing in the basis sets' prediction of this conformer, as this is physically impossible.

FUTURE WORK To check if the predictions are functioning properly, and not calculating the right number but the wrong way, nuclear quadrupole coupling constants must be compared between the simulations and the fit. In addition, there are unassigned peaks in the rotational spectra of 1-iodopentane that could be the result of argon or water complexes, or unidentified conformers and/or isotopologues.



DISCUSSION, CONT'D On the left is shown a potential well for a diatomic molecule. The x-axis is bond length, the y-axis is the inter-atomic forces. The calculations performed optimize the molecule to r_e, the equilibrium radius. In reality, the molecules we study are at the lowest vibrational state, v=0. A possible value for the radius at that state could be r_0, and a physically impossible radius would be r_w.

A higher rotational constant, like A in conformer AAA, means that the moment of inertia in that direction is decreased. That then means that r has decreased, suggesting movement towards r_w, which cannot be true.

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