Pseudo-Rotation in XY_3 Compounds (X=I, Br, Cl; Y=F, Cl)

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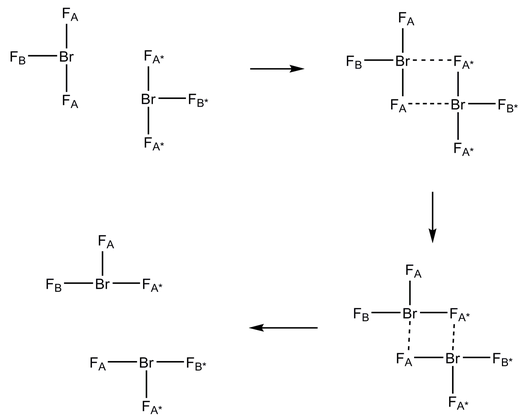
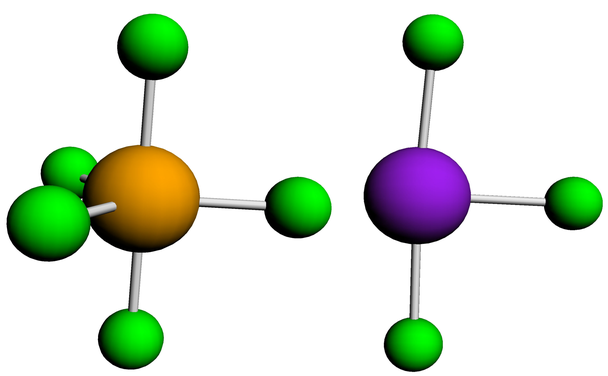
Introduction:

- PF_5 undergoes pseudo-rotation between two positions quickly
- BrF_3 is isolobal with PF_5
- Previous theoretical studies conclude that BrF_3 undergoes the same intramolecular pseudo-rotation slowly
- Experiment shows that BrF_3 pseudo-rotation occurs relatively quickly
- A resolution: exchange in BrF_3 is bimolecular (unlike that of PF_5):



- We use calculations with correlation to determine whether we can account for the apparent discrepancy between theory and experiment



Experimental:

- Uncorrelated calculations treat optimizations like two-body problems, considering a single electron and the average of all the other electrons
- In reality, one electron's instantaneous motion influences that of the others; correlated calculations correct for this interconnection

Results:

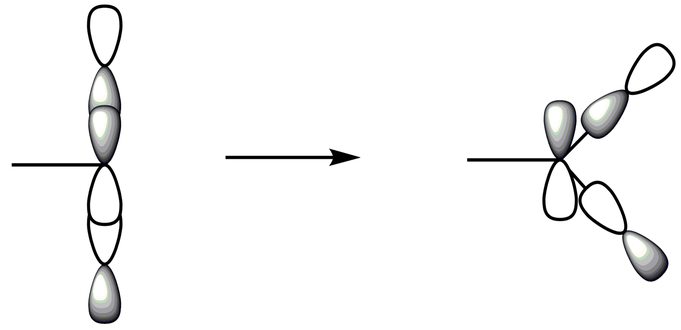
- In its ground state, BrF_3 is a T-shaped molecule. As it undergoes pseudo-rotation, it reaches a Y-shaped transition state then continues on to another T-shaped molecule with its F atoms in new positions:

- Correlated calculations of activation energy for the intramolecular pseudo-rotation of ClF_3, BrF_3, and IF_3 were found to be much lower than uncorrelated values:

Molecule	ΔE of activation (kcal/mole)	
	Uncorrelated	Correlated
ClF_3	38.34	8.99
BrF_3	31.88	6.92
IF_3	30.43	12.04

Discussion:

- The Y-shaped transition state causes a destabilization of the b_1 orbital interactions. This lengthens the Br-F bonds, which increases the correlation energy.



- We conclude that correlated calculations show the activation energy of intramolecular pseudo-rotation in BrF_3 and other XF_3 compounds to be much lower than uncorrelated predictions. This suggests that pseudo-rotation of BrF_3 can occur intramolecularly at rates observed experimentally.

References:

- Minyaev, R.M. Pseudorotation in ClF_3. *Chem. Phys. Lett.* **1992**, *196*, 203-207.

- Muetterties, E.L.; Phillips, W.D. Structure of ClF_3 and Exchange Studies on Some Halogen Fluorides by Nuclear Magnetic Resonance. *J. Am. Chem. Soc.* **1957**, *79*, 322-326.