



Cooperative Effects in the Mechanism of Friedel-Crafts Reactions

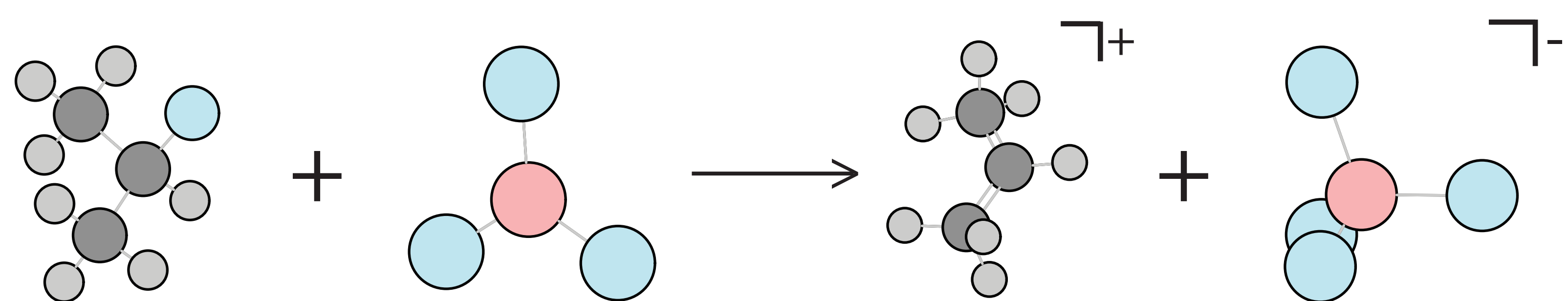
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Background: RF-BF₃ Complex Intermediates

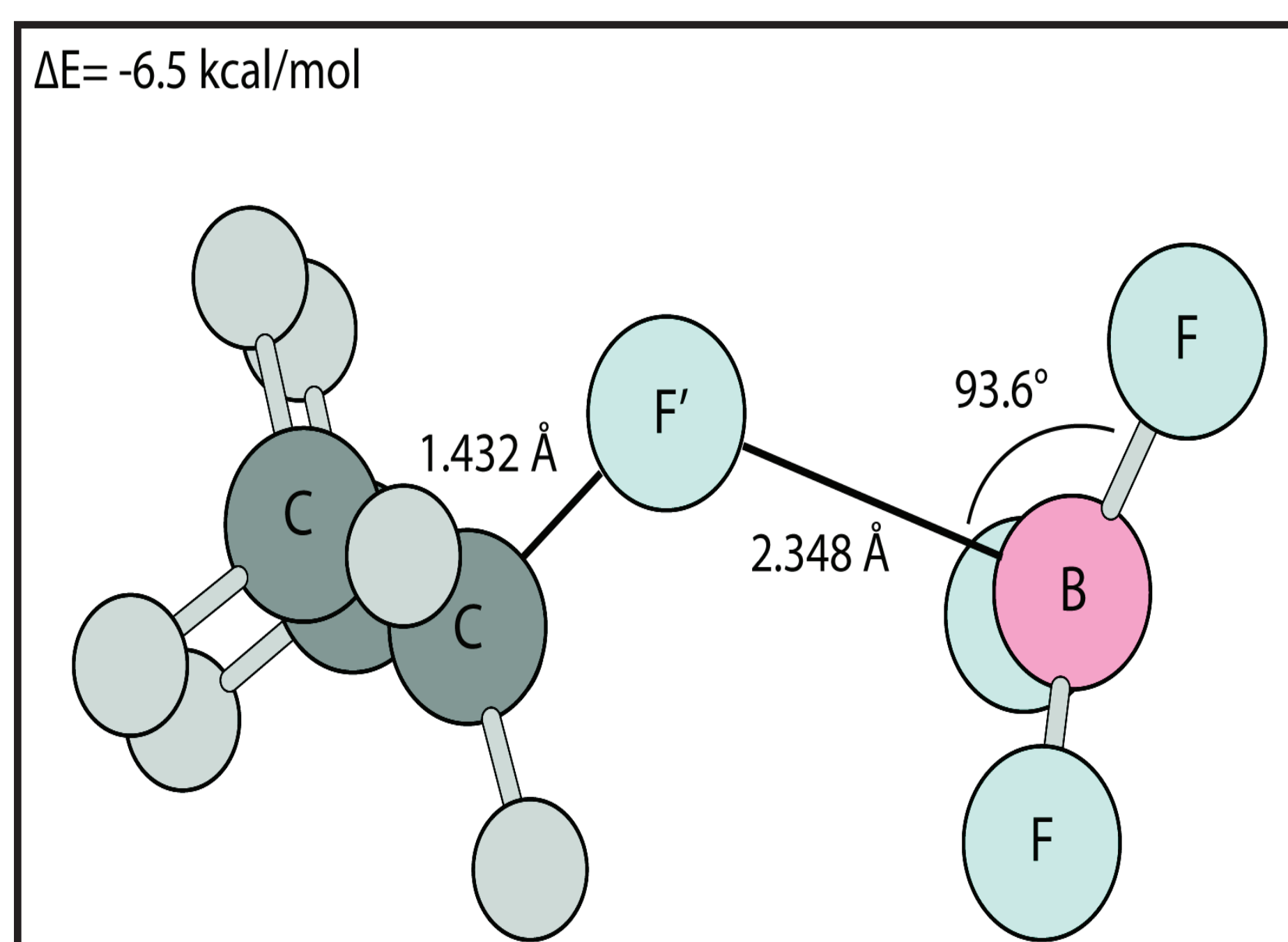
1. Alkyl-Fluoride/BF₃ Solutions: Olah *et al.* (1957),^{1,2} Nakane *et al.* (1966)³



- * Secondary, tertiary and larger primary alkyl fluorides form ions in RF/BF₃ solution
- * Methyl- and ethyl- fluorides form weak donor-acceptor complexes
- * Presumed ions to be R⁺ and BF₄⁻
- * Characterization via conductivity measurements only

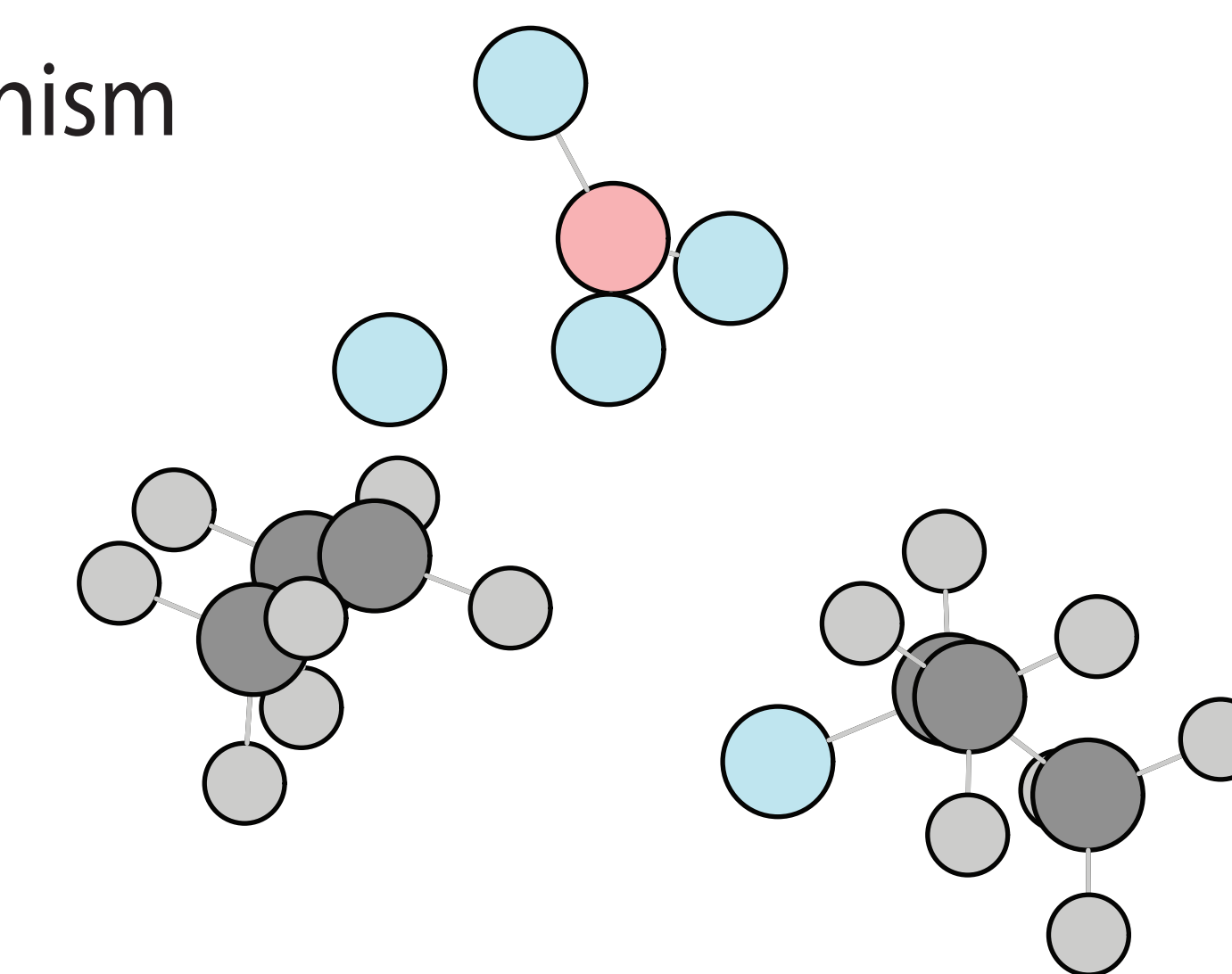
2. Alkyl-Fluoride-BF₃ Complexes: Knauf *et al.* (2011)⁴

- * Gas-phase RF-BF₃ complexes are weak with long B-F distances (2.3-2.4 Å)
- * Essentially no ionic character in the C-F' bonds
- * Structures with short B-F' distances lie 6-9 kcal/mol higher in energy, both in the gas-phase and in bulk dielectric media

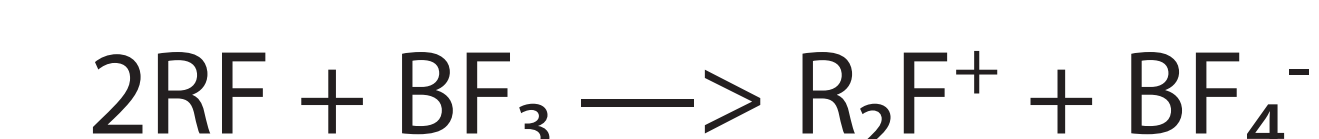
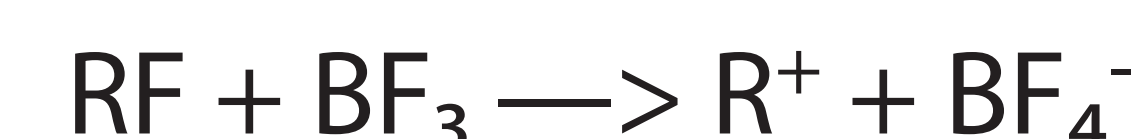


Hypothesis: Cooperative Effects

- * Additional RF molecules may play a specific role in reaction mechanism
- * Ions formed in solution may not be simply R⁺ and BF₄⁻
- * Ions stabilized by additional RF molecules



Energetics: Effect of 2nd Alkyl Fluoride



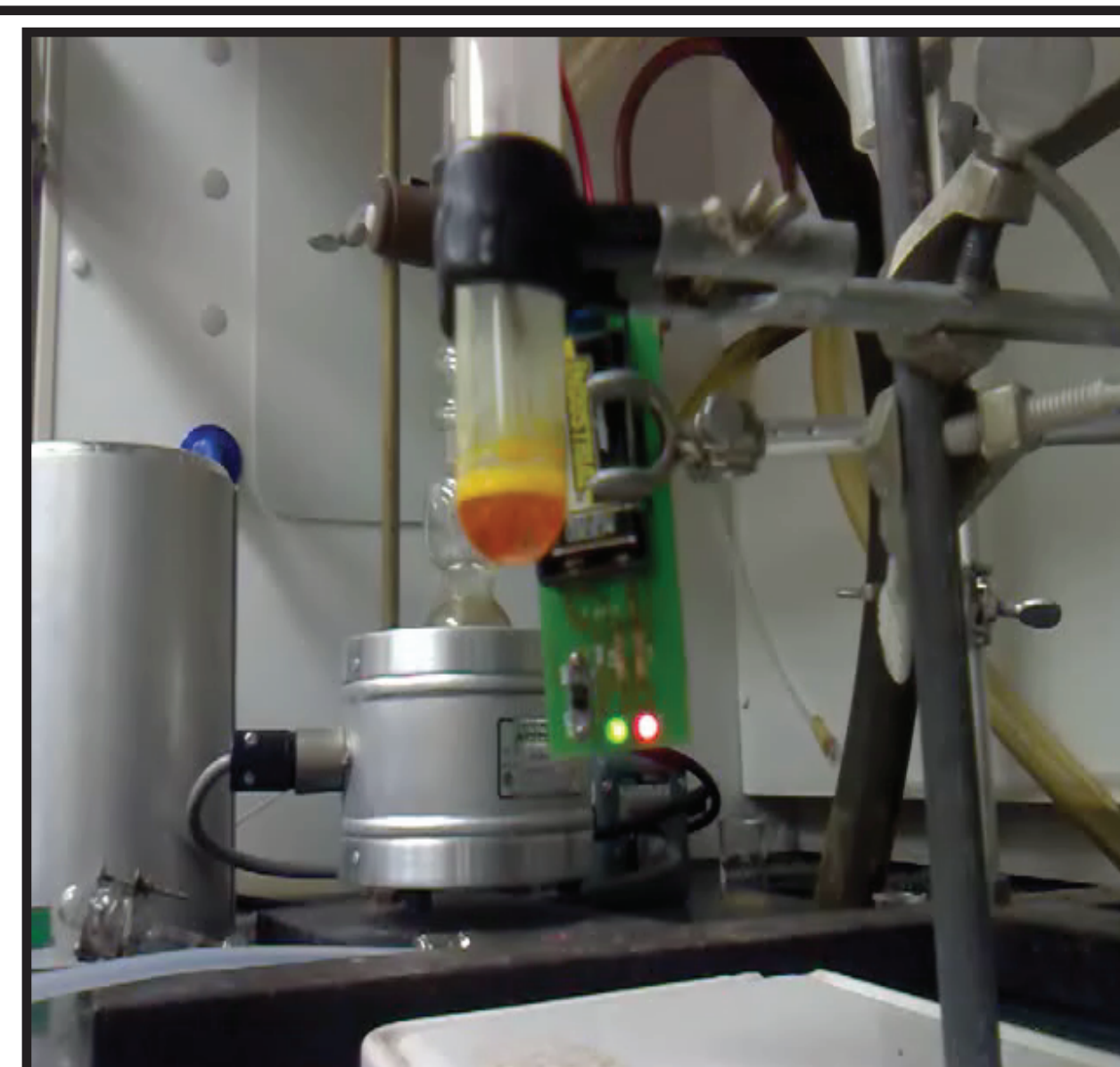
RF	ΔE^+	ΔE^+
Methyl-Fluoride	181.4 kcal/mol	129.5 kcal/mol
Isopropyl-Fluoride	124.3 kcal/mol	105.8 kcal/mol
Cyclohexyl-Fluoride	117.0 kcal/mol	100.2 kcal/mol
Tertbutyl-Fluoride	109.8 kcal/mol	97.6 kcal/mol

[†] X3LYP/aug-cc-pVTZ (Gas Phase)

- * Involvement of a second alkyl fluoride significantly lowers the overall reaction energy
- * R₂F⁺ ions are proposed not to exist in solution⁵/not observed in thin film IR experiments

Bulk Experiments: Reactivity

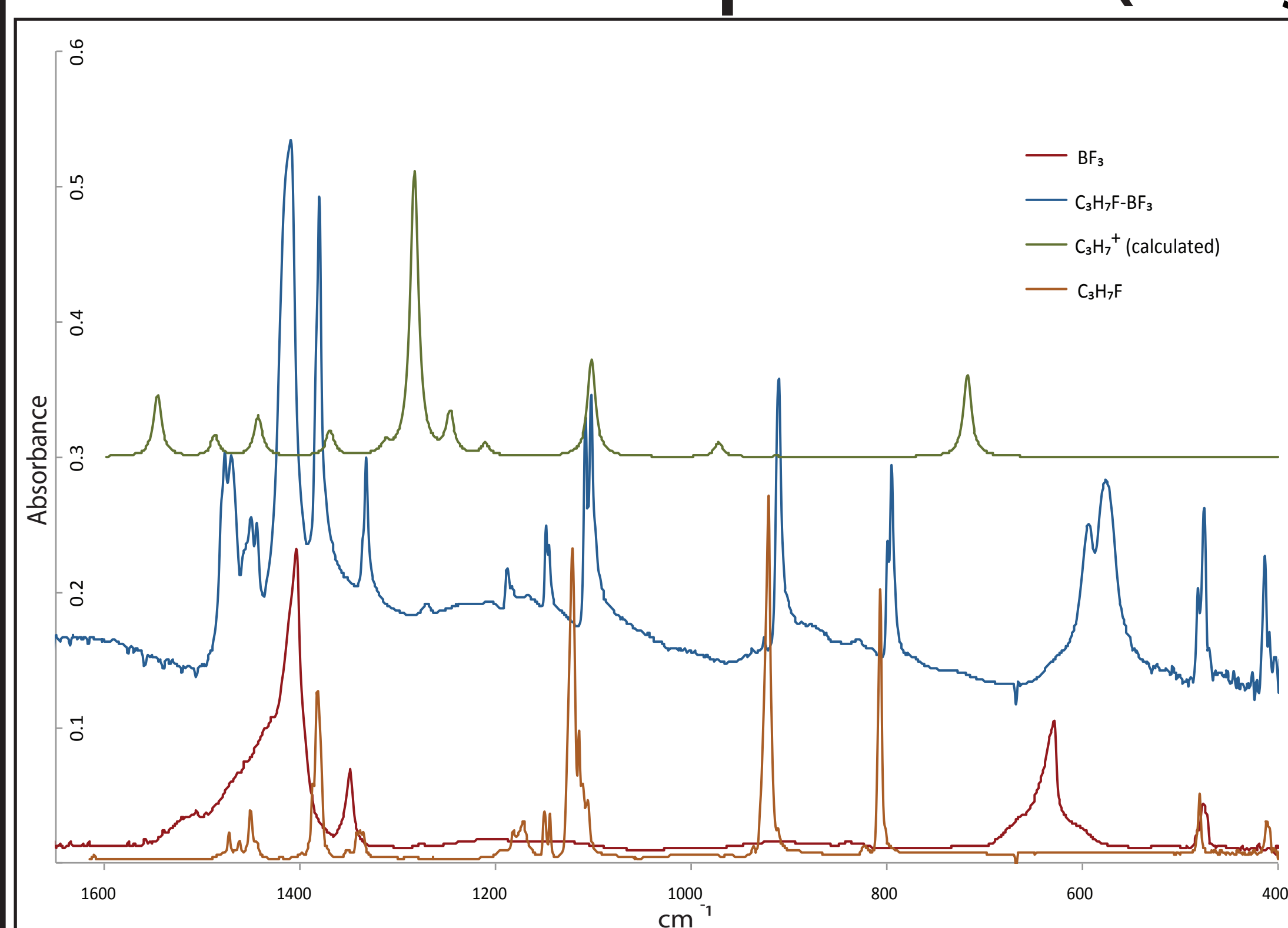
- * Bulk reaction of C₆H₁₁F with BF₃ confirms formation of ions in solution
- * Reaction intermediates are unstable in solution, and presumably react via self-condensation reactions to form polymerized products



Conclusion/Future Work:

- * Ions are formed in bulk solution, however, there is no evidence for a simple carbocation or BF₄⁻ ions in a matrix or thin film environment
- * Calculated binding energies suggest additional alkyl-fluoride units play a role in reducing energy
- * Planned low-temperature liquid-phase IR spectroscopy - identify and characterize ionic intermediates

Thin Film IR Spectra: (CH₃)₂CHF/BF₃



- * No indication of C₃H₇⁺ or BF₄⁻ ions
- * Shift of BF₃ out-of-plane bending frequency, from ~630 cm⁻¹ to ~570 cm⁻¹
- * Shift consistent with neon matrix data,⁴ indicates formation of a weak donor-acceptor complex

Acknowledgements:

- * ACS Petroleum Research Fund
- * National Science Foundation
- * UWEC Office of Research and Sponsored Programs
- * Chris Cramer (U of MN)
- * Robin Knauf and Heather Helminiak
- * Thomas Paine (UWEC LTS)

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