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Hydrolysis of uranium hexafluoride: mechanism, spectroscopy, and thermochemical kinetics

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Project Overview

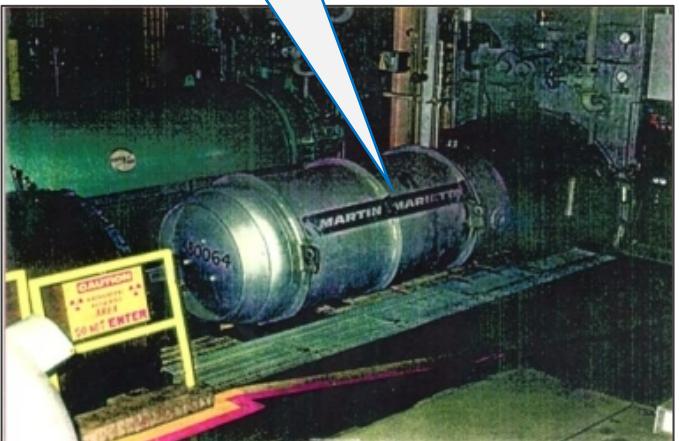
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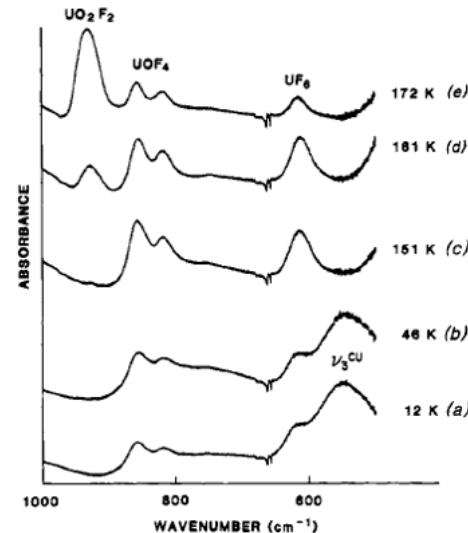
RH~100%



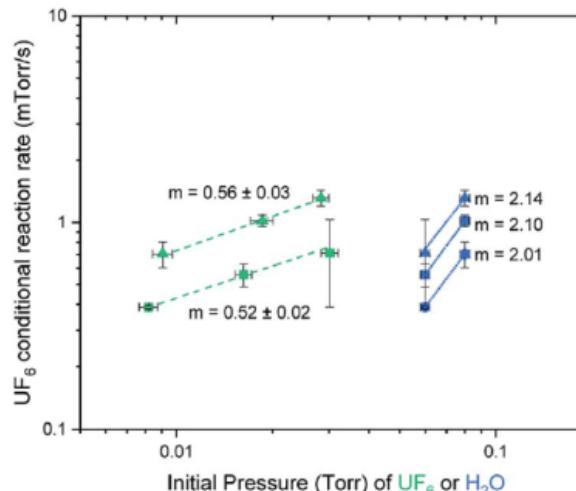
UO₂F₂
microscopy
images [2]



UF₆ cylinder operations [1]



IR spectra [3]



Reaction rates [8]

- Develop more unified theory of UF₆ hydrolysis consistent with experimental observations
- Enable development of detailed chemistry and physics models (gaseous and particulates)
 - Reaction mechanism, kinetics, and thermodynamics
- Facilitate design of experiments, development of measurement techniques and instrumentation
 - Vibrational spectra, species concentrations



We aim to answer

What?
Where?
& When?



Uranium hexafluoride hydrolysis: $\text{UF}_6(\text{g}) + 2\text{H}_2\text{O}(\text{g}) \rightarrow \text{UO}_2\text{F}_2(\text{s}) + 4\text{HF}(\text{g})$

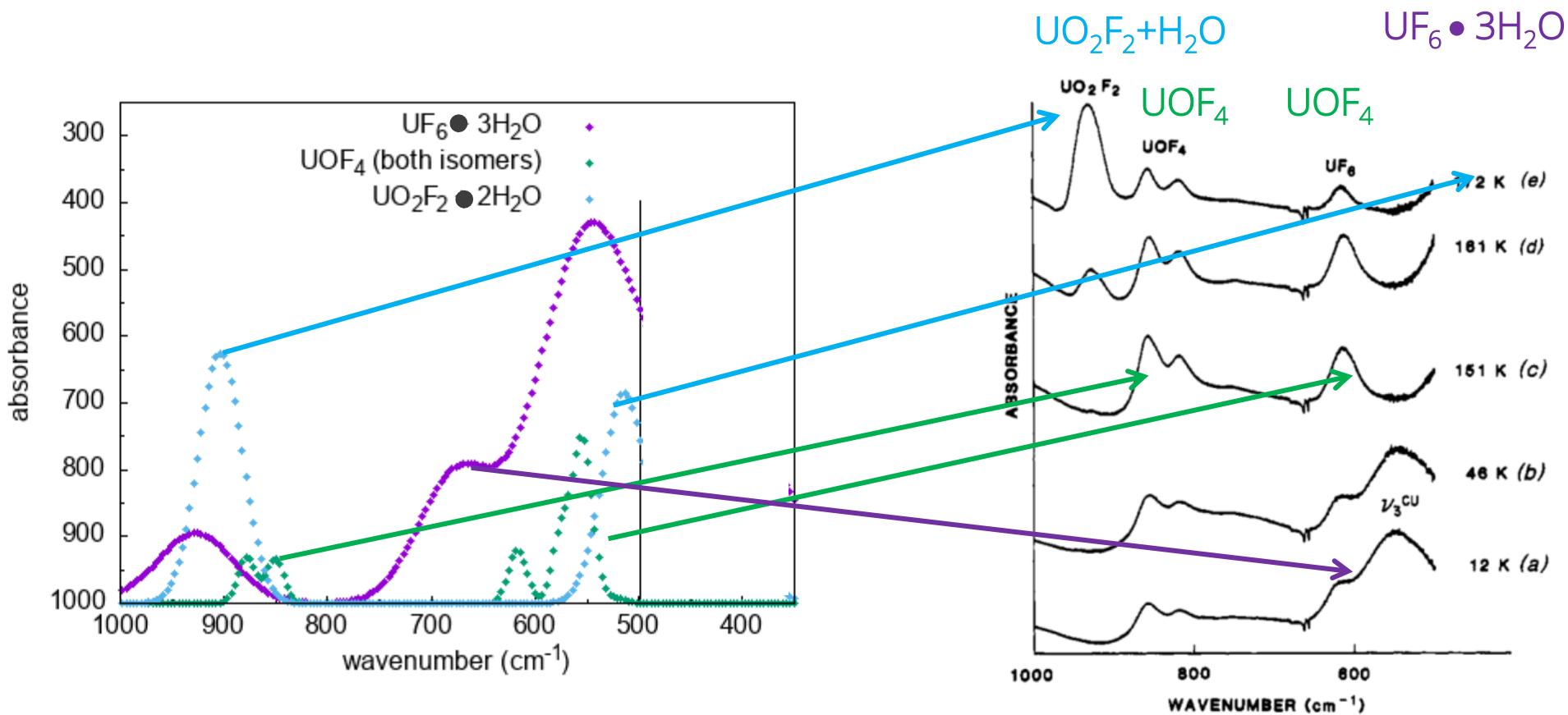
Goals:

- **What** are we looking for?
 - Investigate the gas-phase **reaction mechanism** and identify expected intermediates
- **Where** do we look for it?
 - Predict characteristic features of intermediates detectable by **infrared spectroscopy**
- **When** will species appear?
 - Develop a **chemical kinetics** model which describes existing kinetics measurements



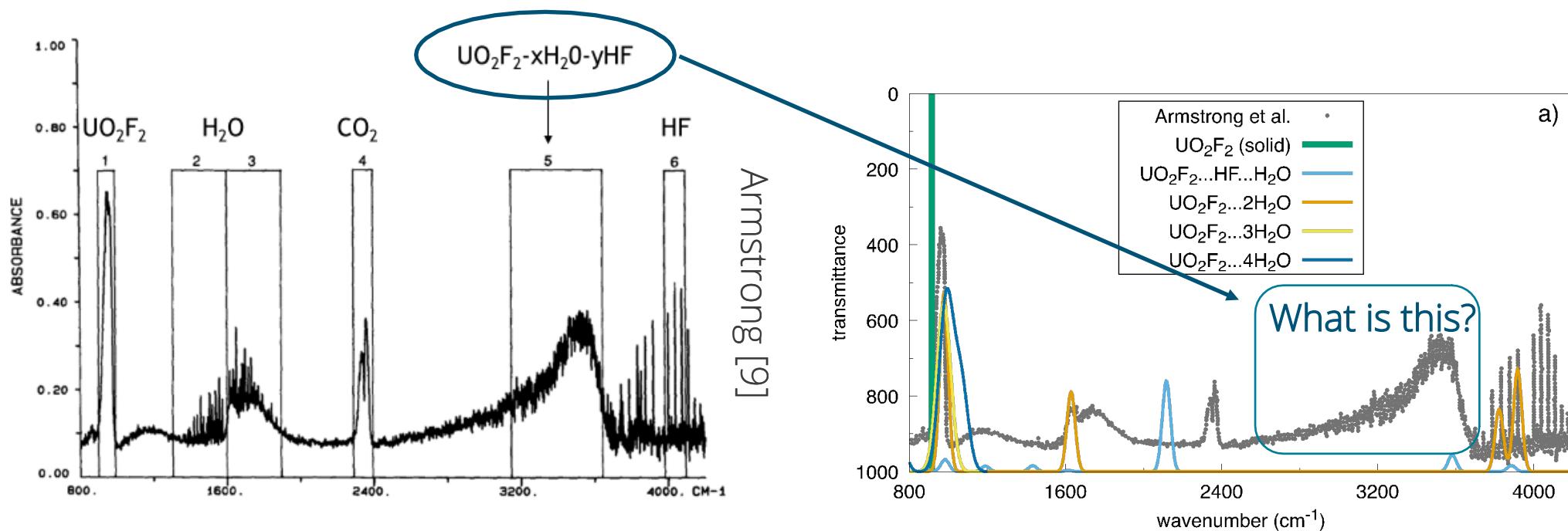
Part I: What are we looking for?

Gas phase mechanism: What are we looking for?



Reassignment of co-deposited species
based on simple harmonic simulations

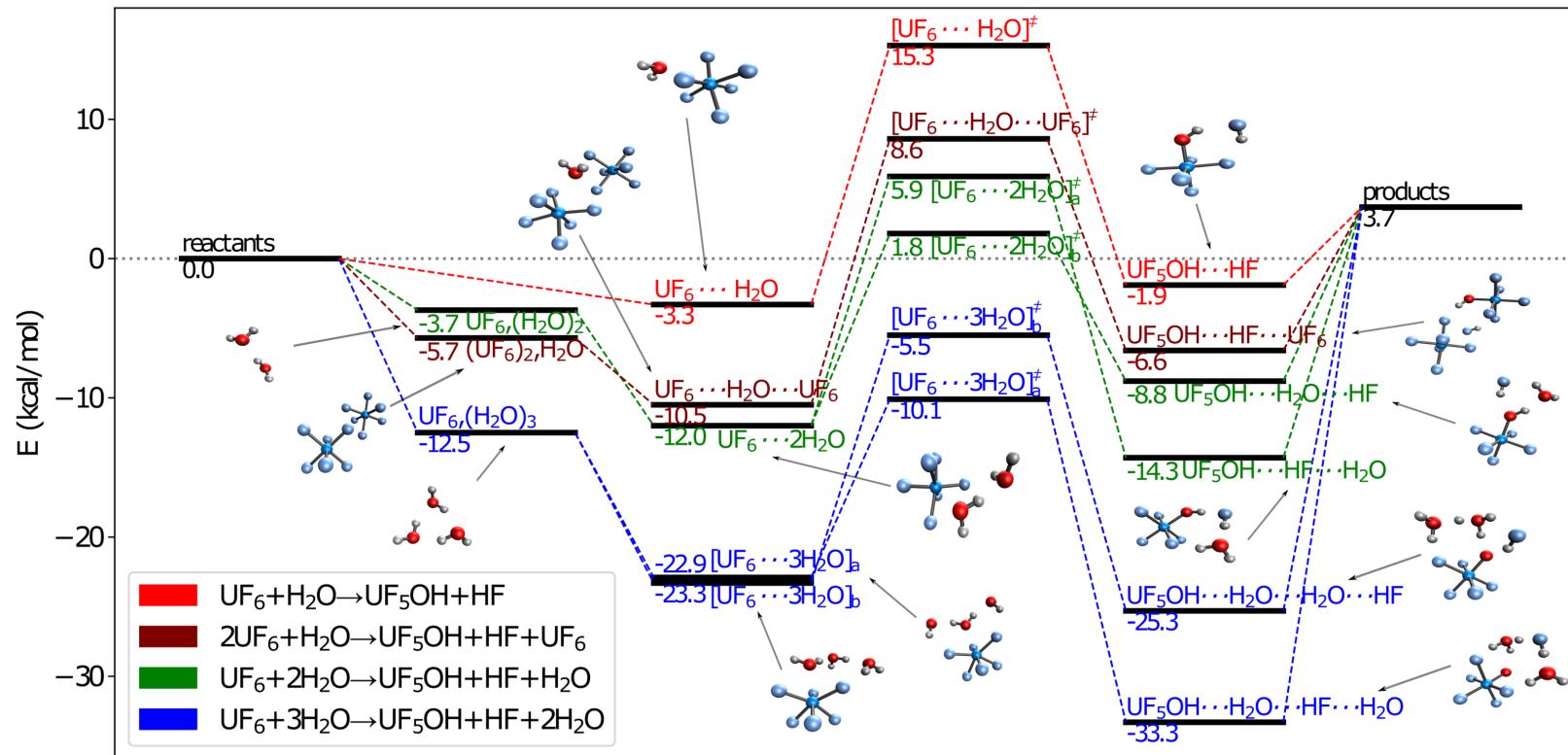
Gas phase mechanism: What are we looking for?



Interval	Range (cm^{-1})	Assignment by Armstrong et al.	Revisions to assignments
1	900-985	asymmetric stretching of molecular UO_2F_2	solid UO_2F_2
2	1300-1600	P-branch of the v_2 mode of H_2O	plus $\text{UF}_6\cdots\text{H}_2\text{O}$
3	1600-1900	R-branch of the v_2 mode of H_2O	none
4	2290-2390	the v_3 mode of CO_2	none
5	3150-3640	unassigned; potentially UO_2F_2 complexes	???
6	3800-4200	P- and R-branches of the HF vibration	none

Lutz et al. [10]

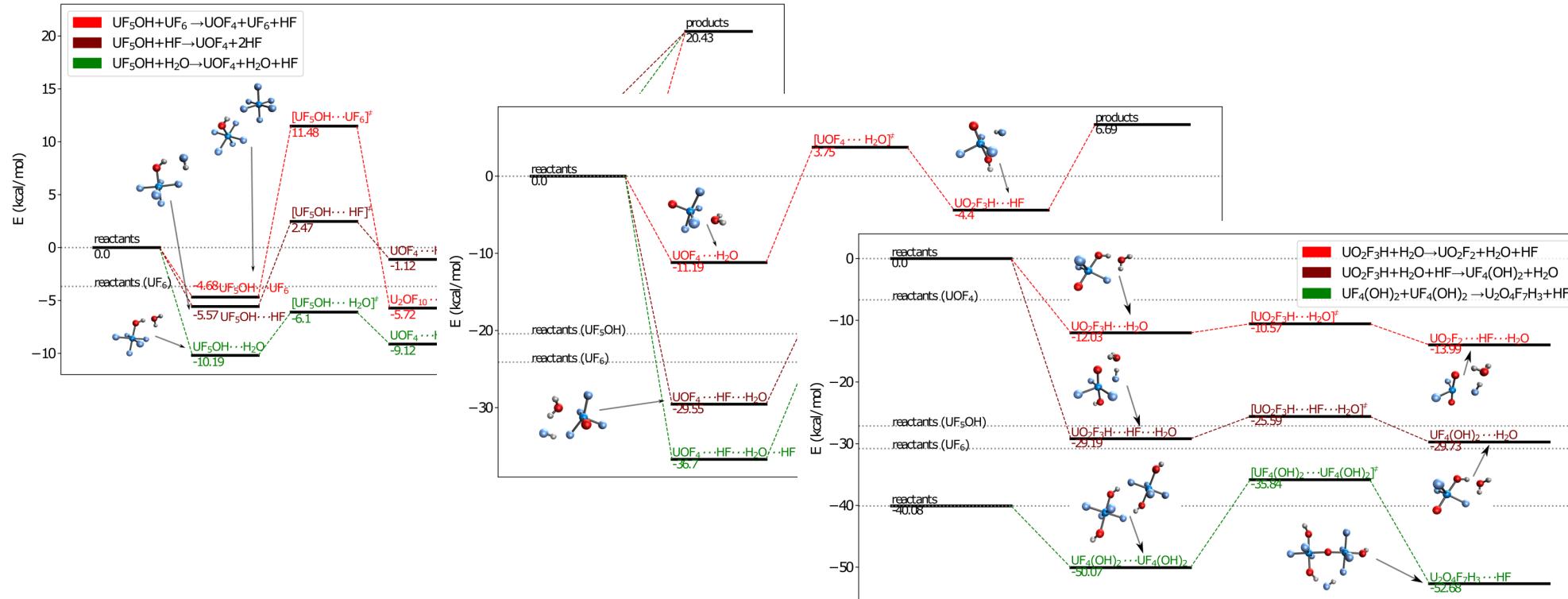
Gas phase mechanism: What are we looking for?



Considering several possible initiation steps

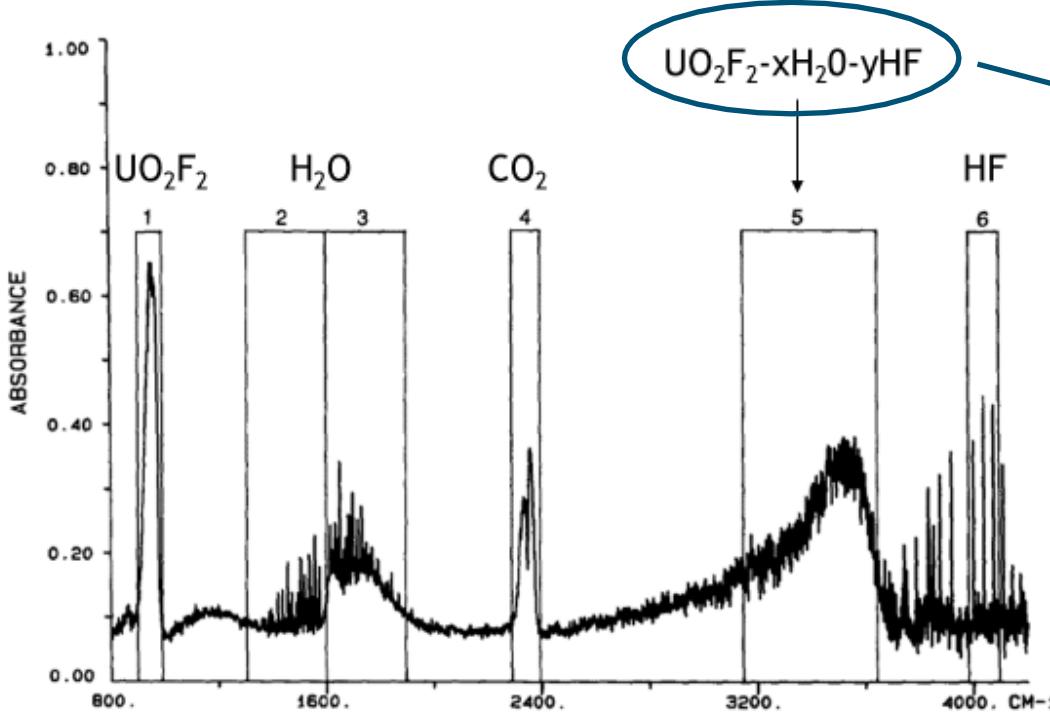
$$n\text{UF}_6 + m\text{H}_2\text{O} \rightarrow \text{UF}_5\text{OH} + \text{HF} + (n-1)\text{UF}_6 + (m-1)\text{H}_2\text{O}$$

Gas phase mechanism: What are we looking for?

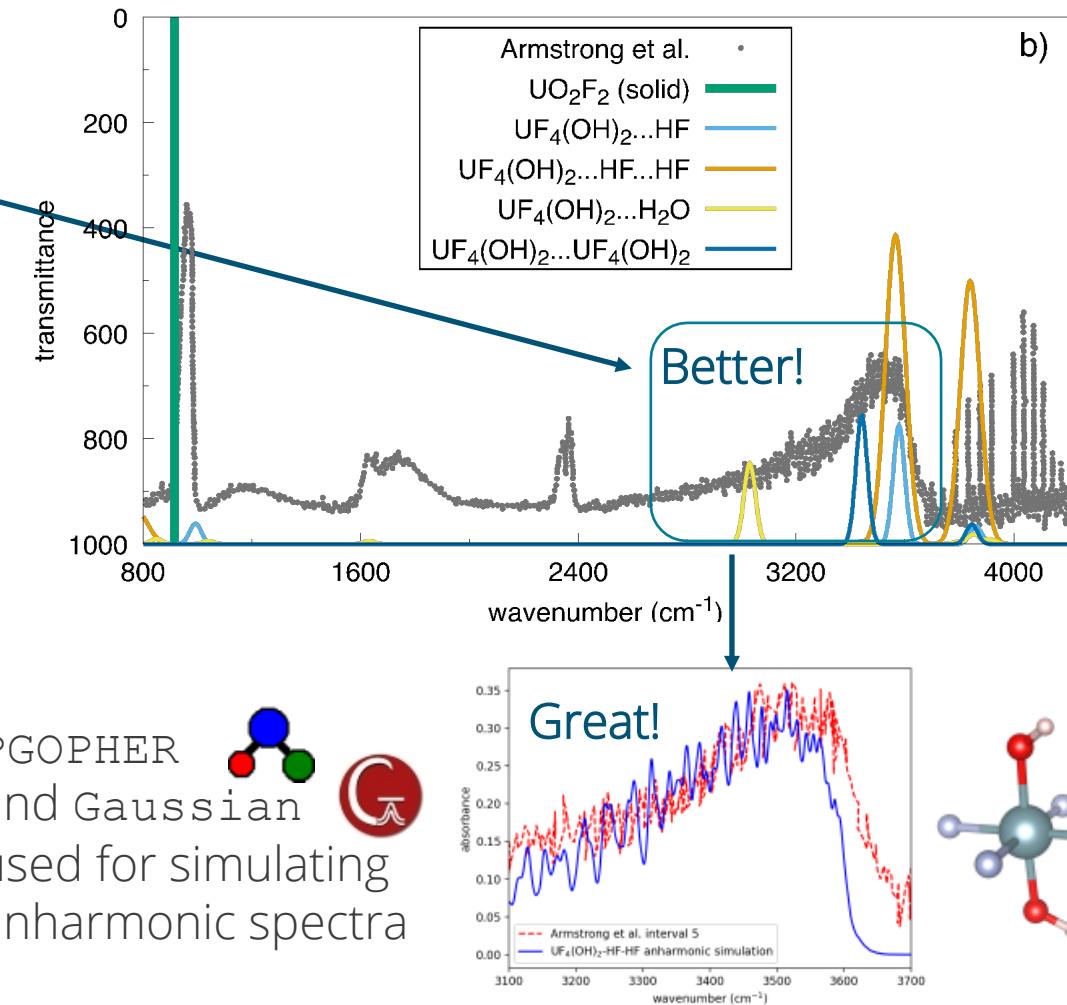


Reaction proceeds through several subsequent intermediates
 $\text{UF}_6 \rightarrow \text{UF}_5\text{OH} \rightarrow \text{UOF}_4 \rightarrow \text{UF}_4(\text{OH})_2$

Gas phase mechanism: What are we looking for?



Armstrong [9]



In contrast with the hypothesis of Armstrong et al.,
the unassigned peak may be attributable to UF₄(OH)₂

The background of the slide features a large, semi-transparent white triangle centered on a dark blue diamond. This diamond contains the main text. Behind the white triangle, there are several other triangles of different sizes and colors (light blue, orange, green, red, dark blue) that overlap each other, creating a layered effect. A thin, multi-colored line (light blue, orange, green, red, dark blue) runs diagonally across the slide, intersecting the text area.

Part II: Where do we look for it?

Spectroscopic properties: Where do we look for it?

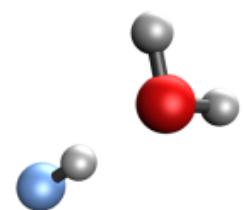
Quality anharmonic infrared spectra can be predicted from:

- 1) Harmonic vibrational frequencies
- 2) Dipole derivatives for harmonic vibrational states
- 3) Rotational constants for anharmonic vibrational states

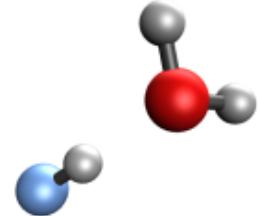
Far-IR (i.e. van der Waals) spectroscopy is difficult to describe:

- Slow convergence with respect to method and basis set
- Special techniques negate **basis set superposition error (BSSE)**
- High accuracy required to distinguish isomers and isotopes

Start with a simple yet relevant system for benchmarking: H_2O ... HF



Spectroscopic properties: Where do we look for it?



Harmonic frequency survey:

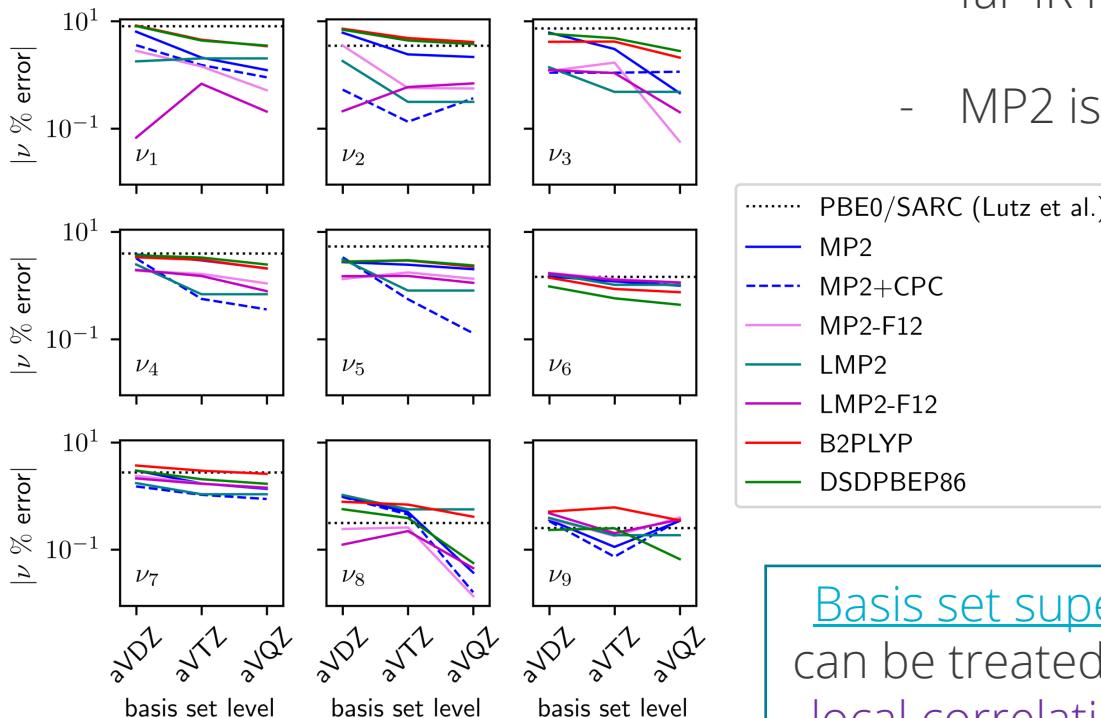
Reference values are
CCSD(T) / aug-cc-pVDZ

Method	4902]			
	mean	unsigned	% error	
	far-IR	mid-IR	far-IR	NPE
MP2	1.11	1.39	0.73	2.82
PAPT	1.12	0.60	1.98	4.61
MP3	1.37	0.67	1.99	4.87
MP4(SDQ)	1.95	1.47	0.85	3.53
SCS-MP2	1.87	1.49	0.21	3.87
LMP2	6.54	5.58	0.56	7.49
LRPA	8.80	7.08	3.41	16.5
SCS-LMP2	9.61	8.46	0.53	13.3
DSDPBEP86	1.84	1.35	0.73	3.73
B2PLYP	2.16	1.21	0.91	4.65
B2PLYP+D3(BJ)	2.26	1.41	0.92	5.29
mPW2PLYP	2.39	1.62	0.97	5.03
mPW2PLYPD2	3.35	2.93	1.06	8.10
DSDPBEP86+D2	3.78	2.75	0.82	7.19
PBEQIDH	3.43	3.88	1.94	3.88
PBE0DH	3.99	4.27	1.74	5.30
PBE0	5.27	4.54	1.63	9.38
PBE0+D3(BJ)	5.53	4.72	1.64	9.37
PBE	8.27	5.15	4.62	18.1
PBE+D3(BJ)	8.67	5.42	4.64	19.0
MP2-F12	1.50	0.78	0.57	2.90
LMP2-F12	1.66	0.68	0.65	3.11
DSDPBEP86-F12	1.84	1.35	0.73	7.64
LCCSD(T)-F12	2.25	1.45	0.48	4.66
B2PLYP-F12	2.40	1.26	0.98	6.97

Basis set convergence:

Reference values are
CCSD(T) / aug-cc-pV5Z

[Sexton et al., *J. Phys. Chem. A* 2018, 122,



Take aways:

- Harmonic frequencies are not straightforward with the far-IR region a special challenge
- MP2 is closest to CCSD(T)
- The local (LMP2) methods are uniquely suited for treating weakly-bound clusters

Basis set superposition error (BSSE)

can be treated w/ explicitly-correlated local correlation methods instead of conventional counterpoise corrections!

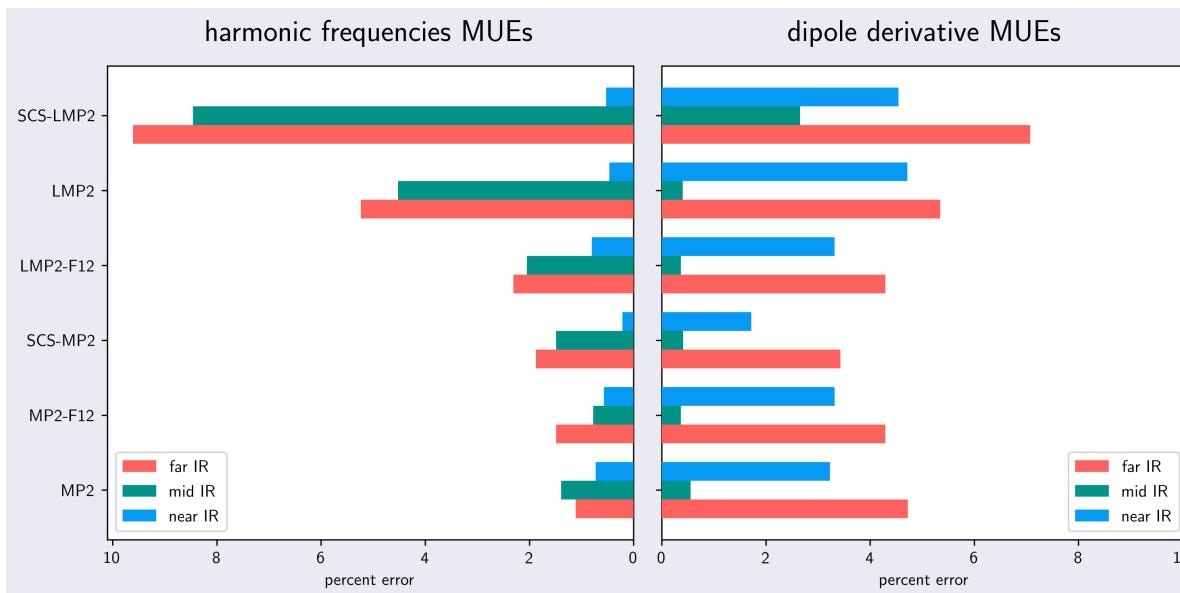
Spectroscopic properties: Where do we look for it?



Dipole derivative survey:

Reference values are

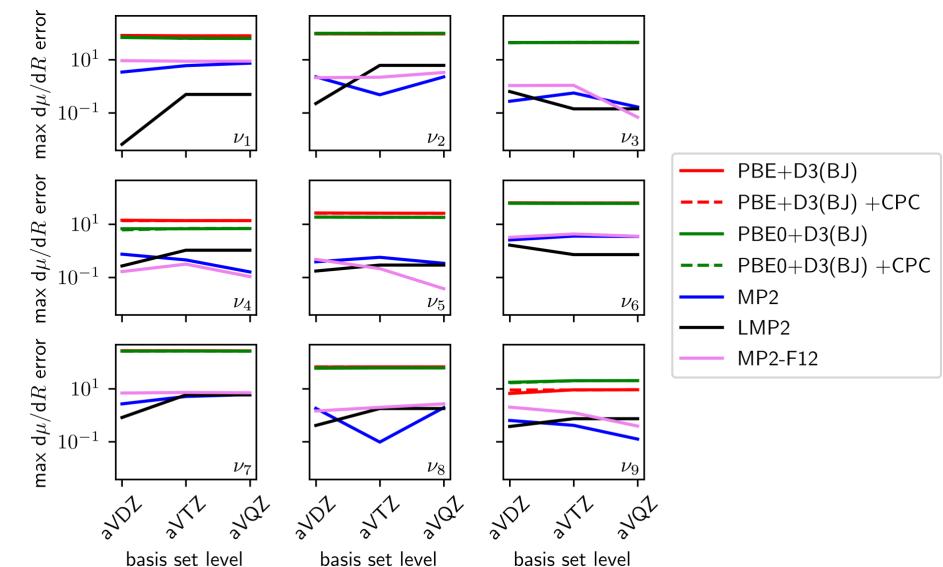
CCSD(T)-F12/aug-cc-pVDZ



Basis set convergence:

Reference values are

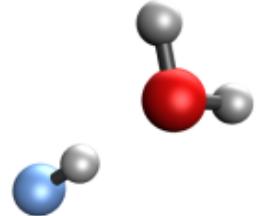
CCSD(T)-F12/aug-cc-pVQZ



Take aways:

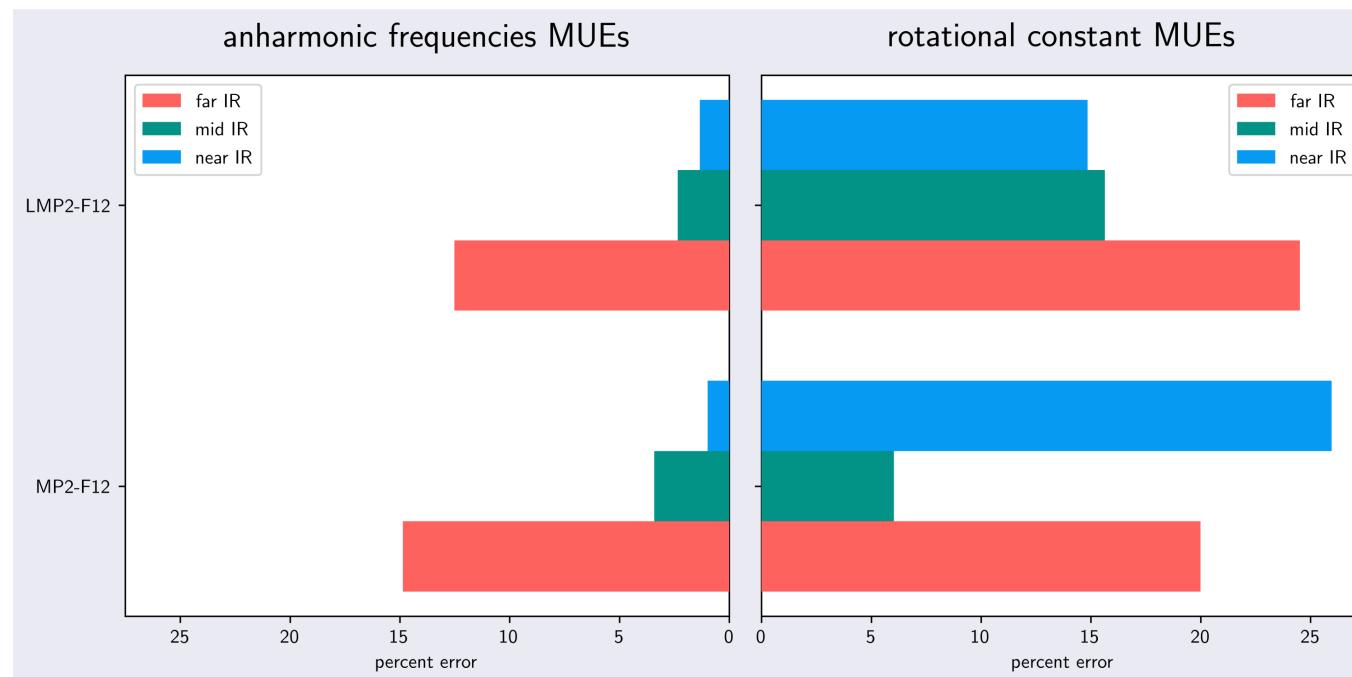
- MP2-F12 and LMP2-F12 provide *dipole derivatives* to within 10 % of CCSD(T)-F12

Spectroscopic properties: Where do we look for it?



Anharmonic frequencies and properties

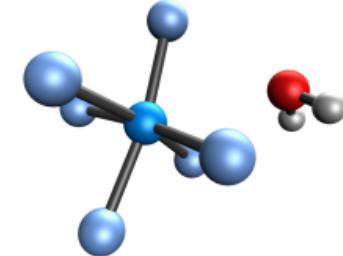
Reference values: CCSD(T)-F12/aug-cc-pVDZ



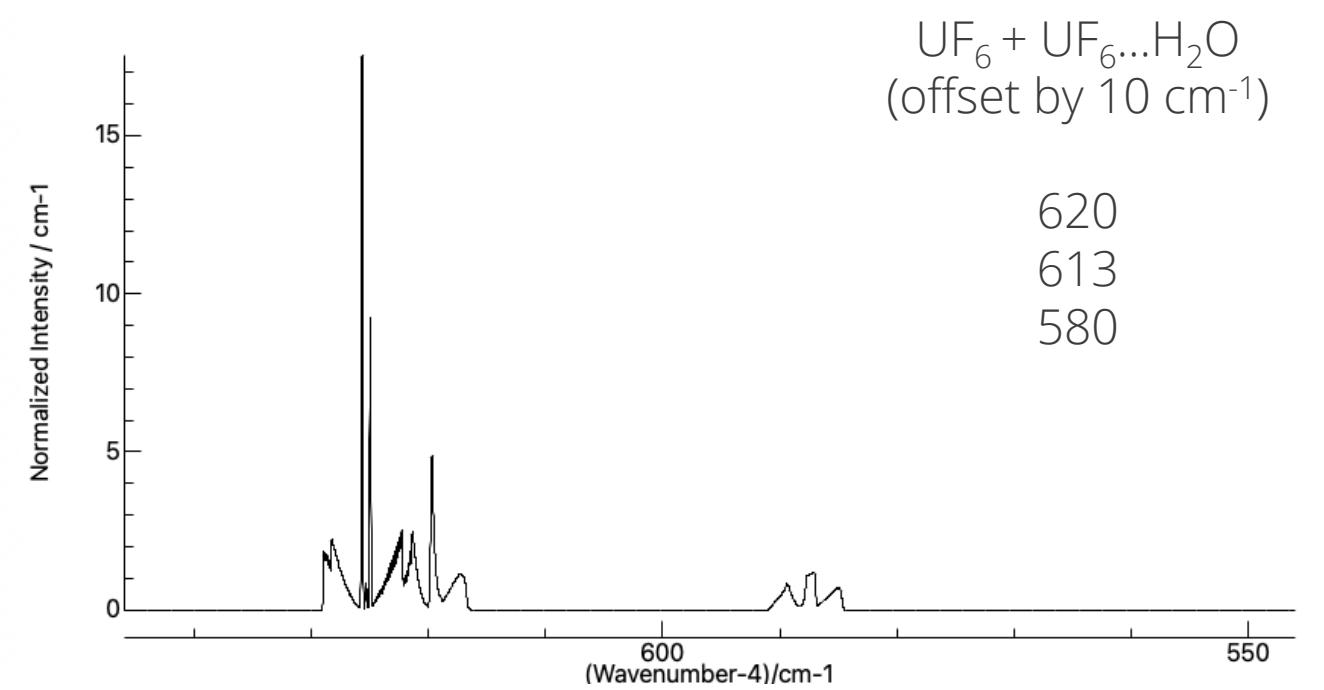
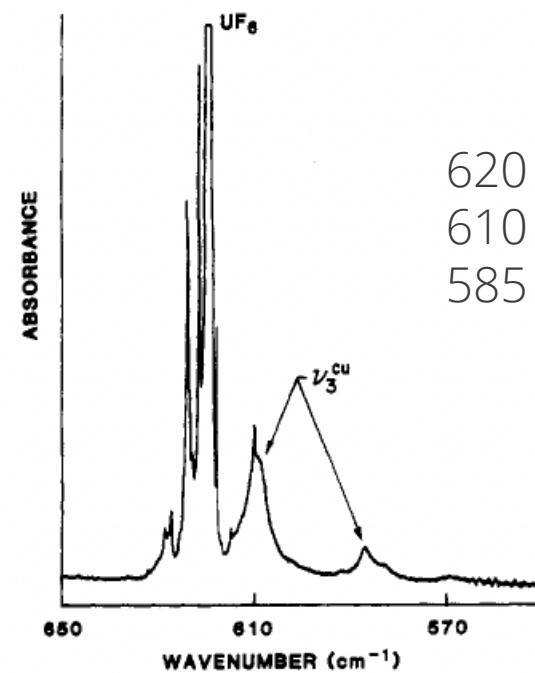
Take aways:

- Even MP2-F12 and LMP2-F12 struggle to describe anharmonic frequencies and properties
- Transfer learning is a promising alternative (S. Käser et al., *J. Chem. Theory Comput.* 2021, 17, 6, 3687)

Spectroscopic properties: Where do we look for it?

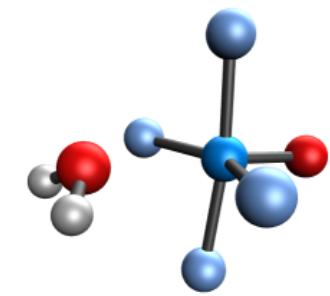


We can generate simulated spectra which closely resemble measurements

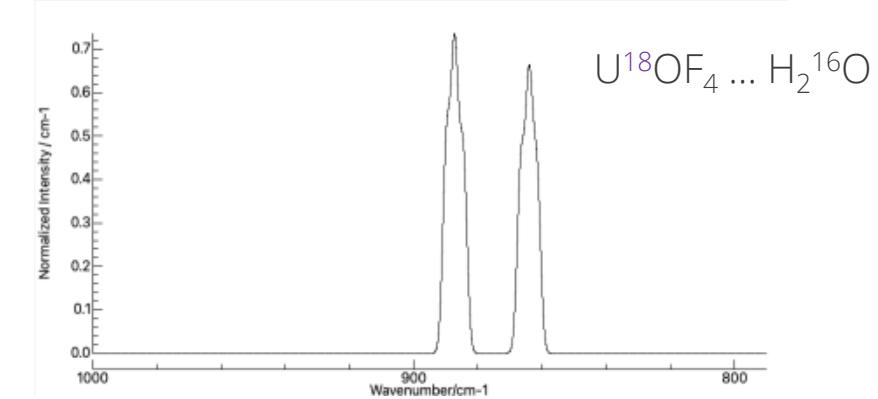
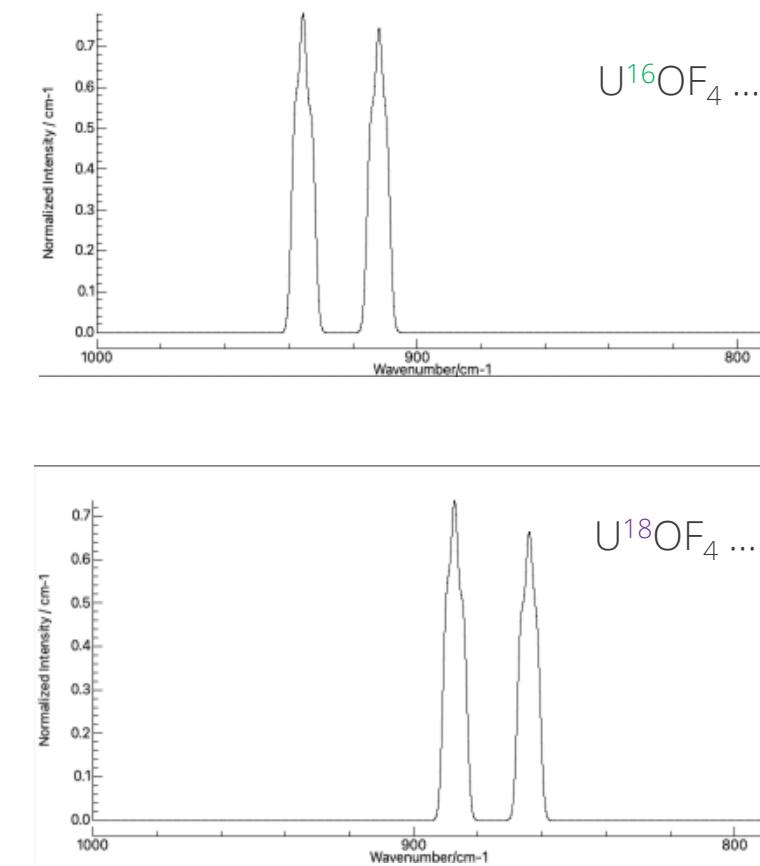
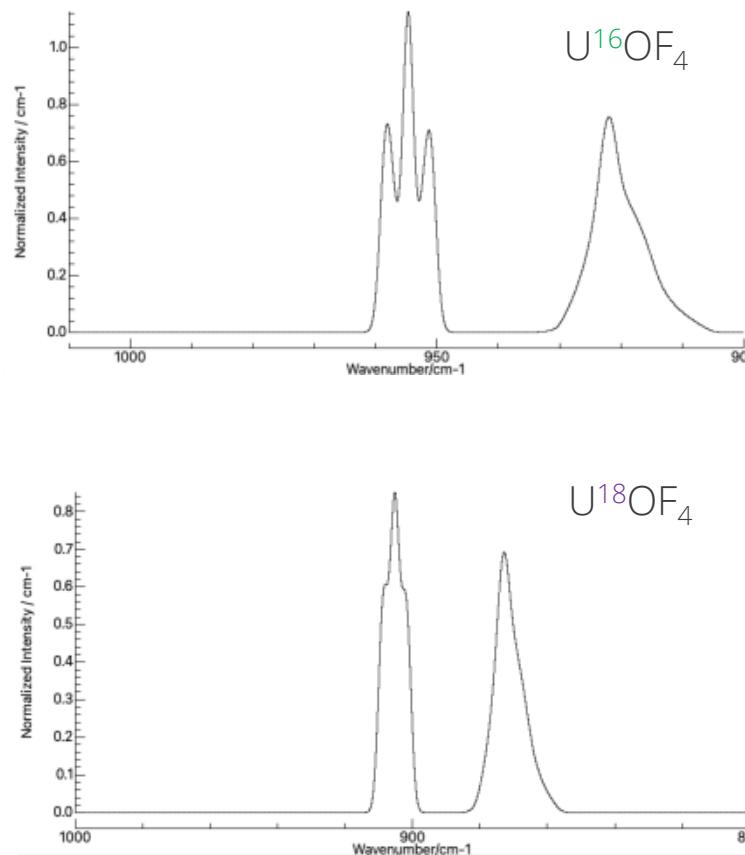
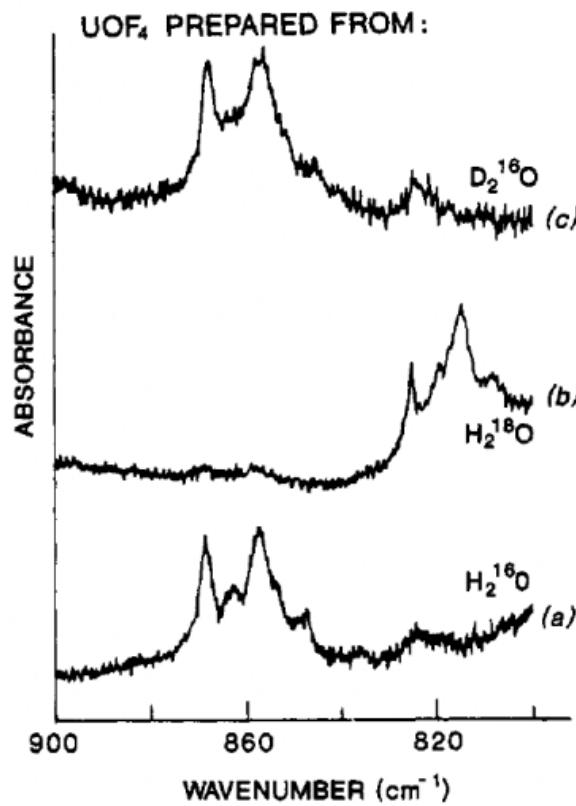


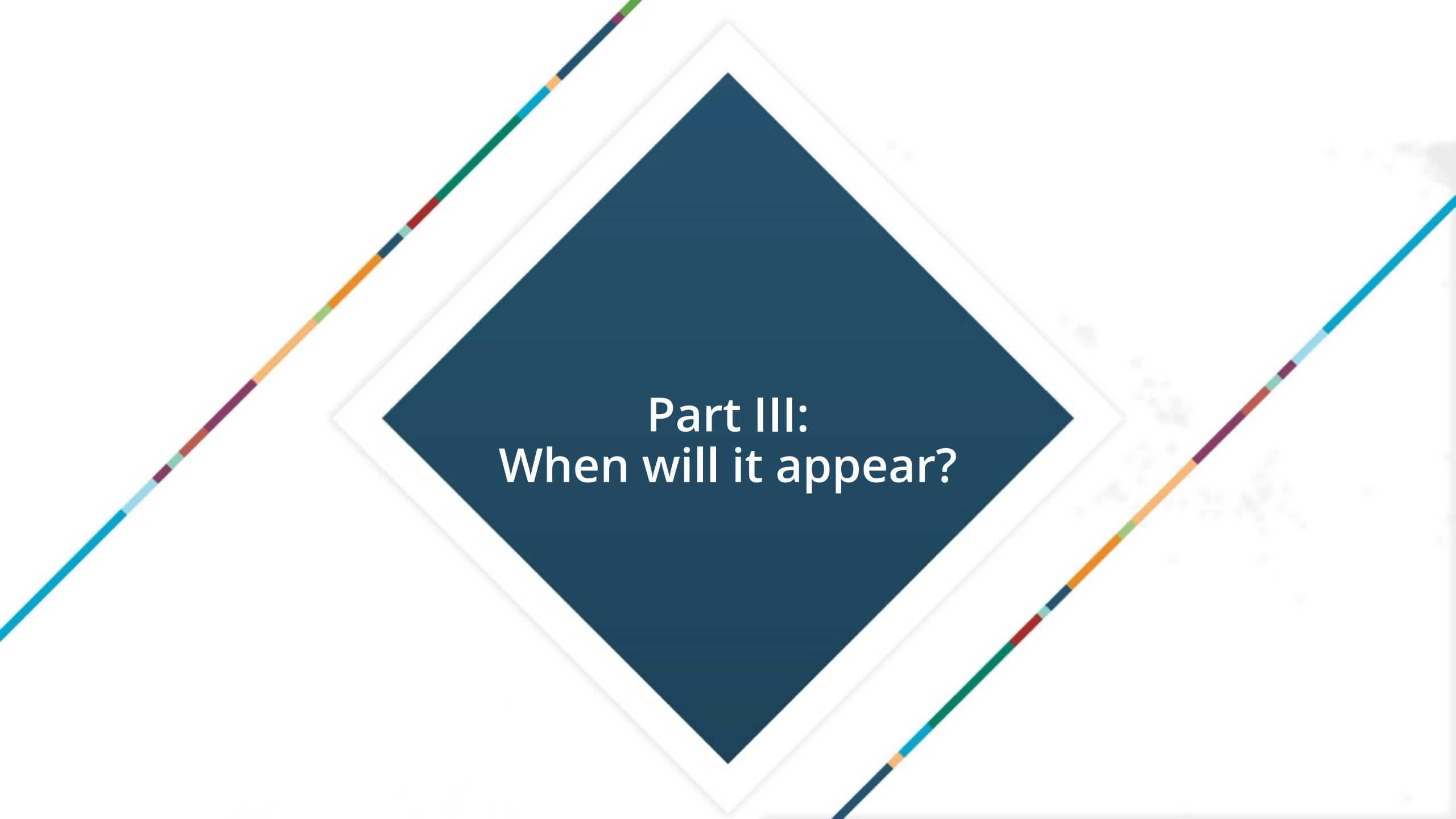
R.D. Hunt, L. Andrews, and L. M.
Toth
J. Phys. Chem. (1991) 95 1184

Spectroscopic properties: Where do we look for it?



We can predict relative absorbances of isomers and isotopes

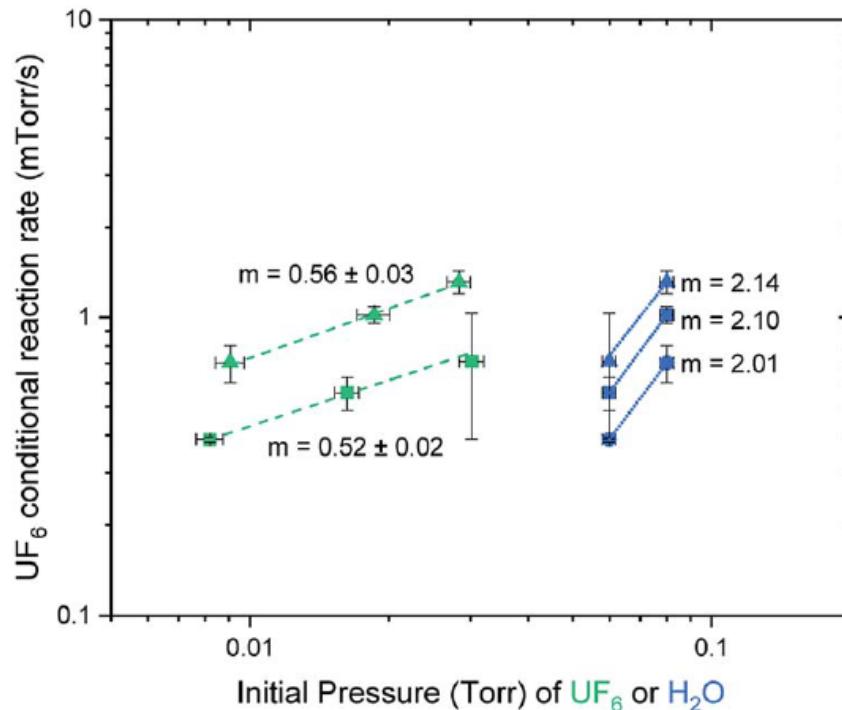




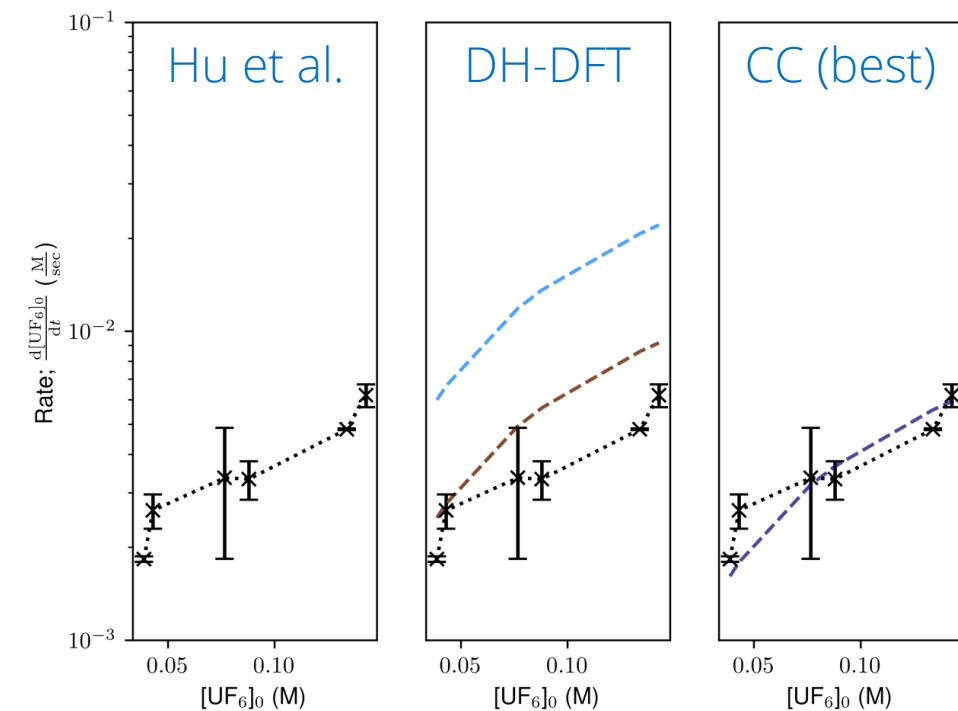
Part III: When will it appear?

Gas Phase Initiation Kinetics: When will it appear?

Reaction rates from Richards et al. (2020)



Fully *ab initio* simulation of initiation rates



The barrier height for a 1:1 ratio of $\text{UF}_6:\text{H}_2\text{O}$
is consistent with published initiation rate data



Summary

- Developing more unified theory of UF_6 hydrolysis consistent with observations
- Employing Density Functional Theory and higher order quantum methods to determine reaction pathways, thermodynamics, and kinetics.
- Enabling development of detailed chemistry and physics models (gaseous aggregation and particulate physics)
- Facilitating design of experiments, development of measurement techniques and instrumentation
- Developed $\text{UF}_6 + n\text{H}_2\text{O}$ pathways and reconciled our simulations with IR spectroscopy reported in the literature.
- Proposed a previously unappreciated intermediate species and hypothesized a feasible route to the observed product.
- Preliminary kinetic modeling shows good agreement with Richards et al (2020).
- Good progress toward automation of complex quantum chemistry workflows.



References

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10. **Lutz, J. J., Byrd, J. N., Lotrich, V. F., Jensen, D. S., Zádor, J. and J. A. Hubbard** (2022). "Theoretical investigation of the hydrolysis of uranium hexafluoride: Initiation mechanism and vibrational spectroscopy", *Phys. Chem. Chem. Phys. in press*.

Thank you for your attention

