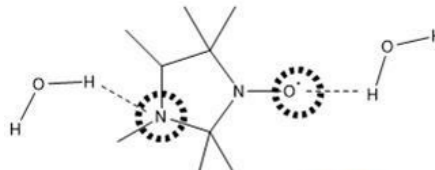


Microsolvation of multifunctional nitroxide spin labels in inert gas matrices

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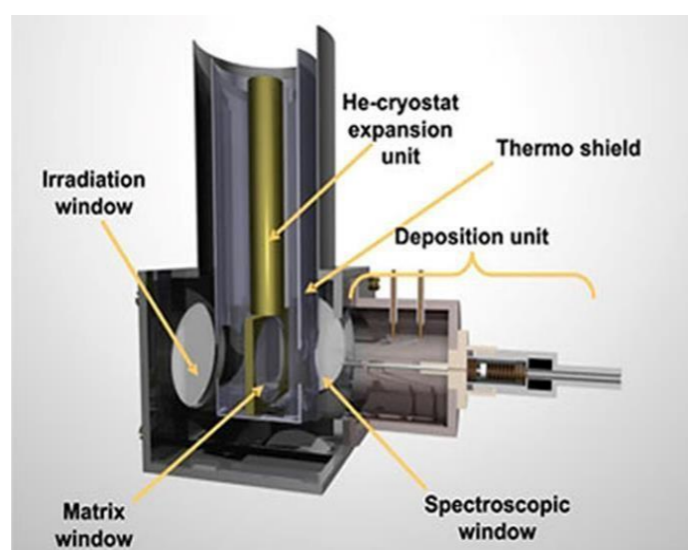


- Nitroxide radicals are EPR active spin labels used as highly sensitive probes for local pH
- Investigation of 1:1 hydrogen bonded complexes of nitroxide radicals (HMI and TEMPO) with solvent molecules such as water and methanol.
- Technique used -Matrix Isolation FTIR spectroscopy

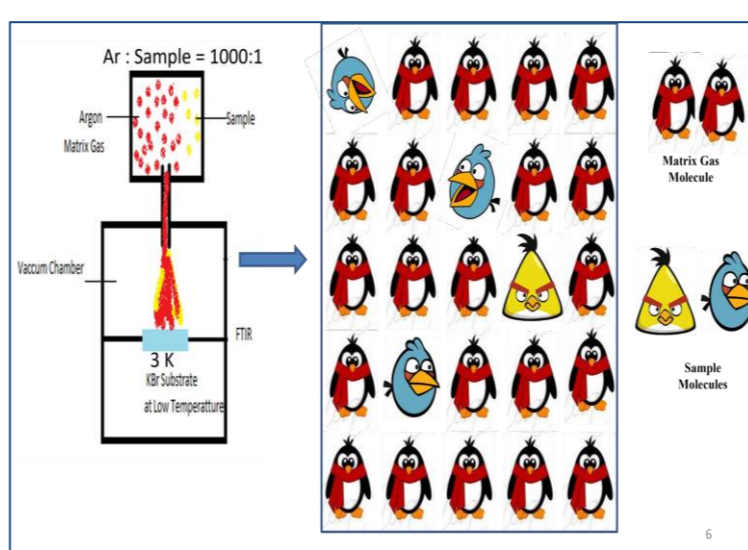
Challenges :

- Extremely hygroscopic.
- Competing hydrogen bonding sites in HMI
- Rich conformational landscape

Introduction and Methodology

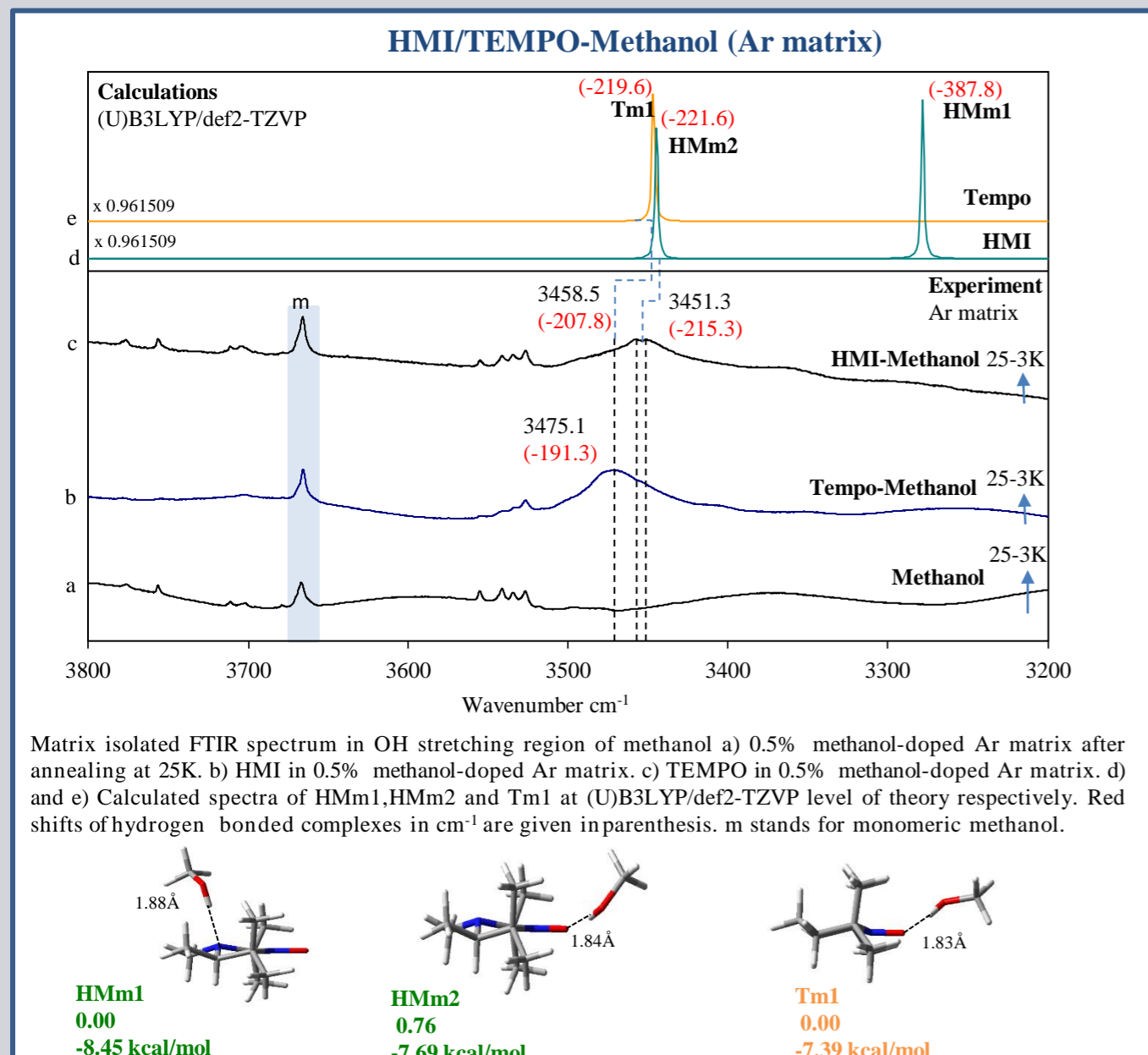
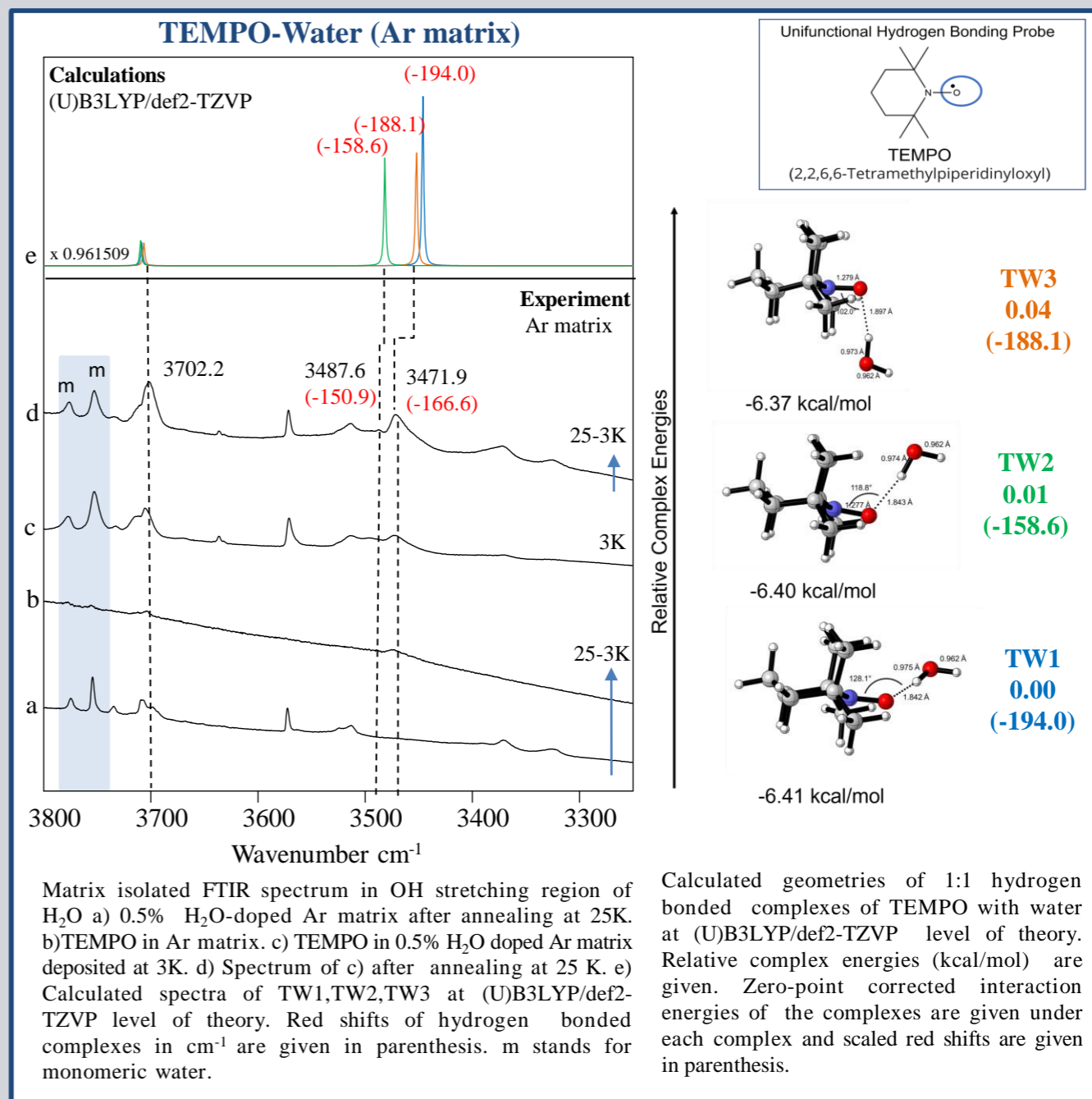
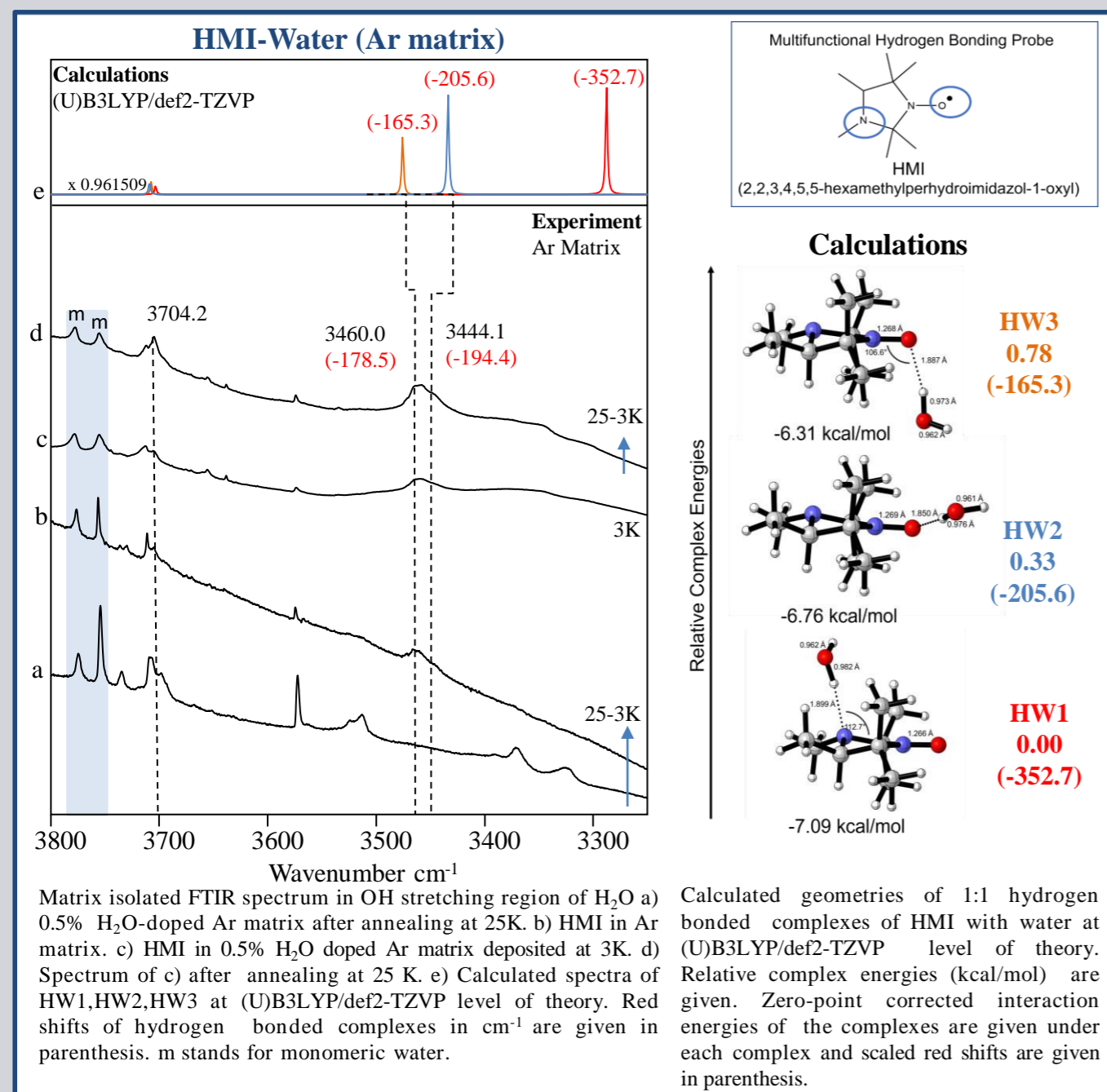


Matrix Isolation Set Up



This thin solid film at 3K can then be probed by FTIR, EPR, UV-Vis Spectroscopy

Annealing (25K) the matrix allows diffusion of molecules encouraging intermolecular interactions.



Conclusions

Phenoxy radical-water	HMI radical-water	TEMPO radical-water
PW1 -167.5	HW2 -194.4 (-205.6)	TW3 -166.6 (-188.1)
	HW3 -178.5 (-165.3)	TW2 -150.9 (-158.6)

*Experimental Shifts in Ar Matrix are shown. Computed shifts are given in parenthesis

- 1:1 hydrogen bonded complexes of HMI and TEMPO radical were successfully isolated in Ar matrices and characterized using FTIR spectroscopy.
- Comparable red shift of HMI and TEMPO complexes confirm the observation of 1:1 hydrogen bonded complexes of HMI with water at NO site !! The shift was also comparable to Phenoxy-water complex.¹
- In HMI NO site is preferentially solvated as compared to ring nitrogen.

References

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