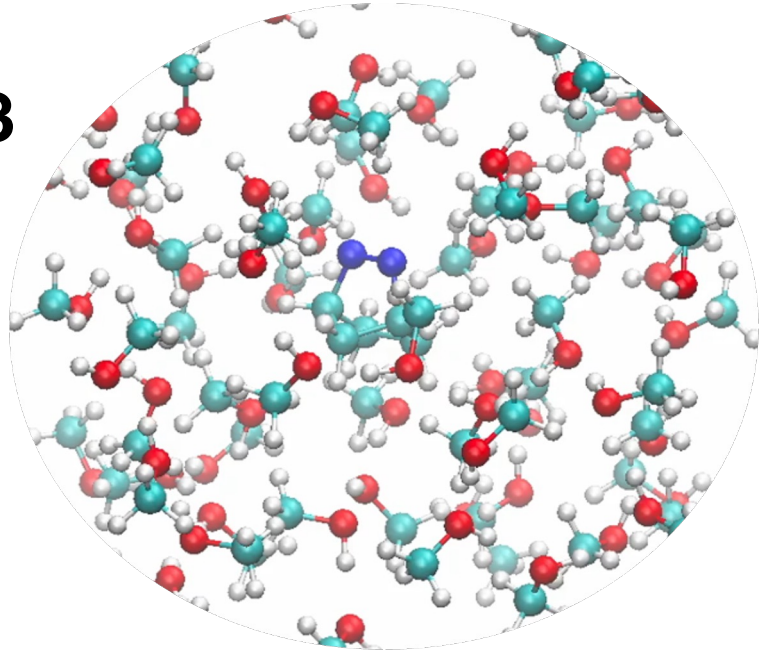
Northeastern University

Excited State QMMM using NWChem

Cyber Training Workshop 2023

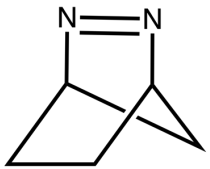


July 1, 2023

Leticia Gomes
Lopez Group

@nodecrashers
@leticia_a_gomes

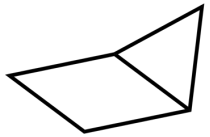
Photochemical reactions are a valuable tool in synthesis



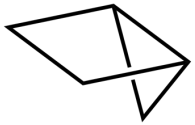
1

λ = 333-364 nm, n-C_5H_{12}

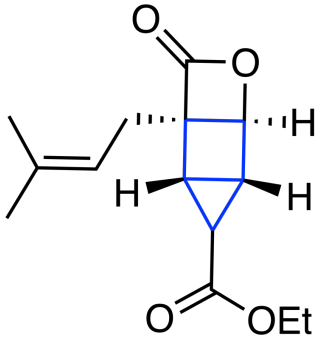
Φ = 1.00



exo-2
75

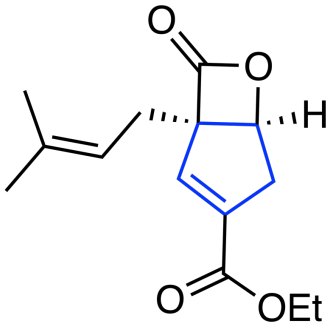


endo-2
25



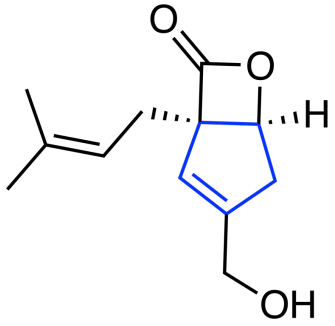
1.5 equiv DBU
PhH, 18 h, 75°C

69% yield



2.9 equiv DIBAL-H
THF/PhH, 1.5h,
-40 to 0 °C

34% yield



(±)-vibralactone

Adam, W.; Denninger, U.; Finzel, R.; Kita, F.; Platsch, H.; Walter, H.; Zang G. *J. Am. Chem. Soc*. **1992**,*114,* 5027-5035
Nistanaki, S. K.; Boralsky, L. A.; Pan, R. D.; Nelson H. M. *Angew. Chem. Int. Ed.* **2019**, *58*, 1724 –1726

Set up QMMM

```
ATOM      2  C2  DBH     1       1.227   0.783   0.349
ATOM      3  C3  DBH     1      -0.155   1.113  -0.303
ATOM      4  C4  DBH     1      -0.156  -1.113  -0.303
ATOM      5  C5  DBH     1      -0.297   0.000  -1.361
ATOM      6  N1  DBH     1      -1.166   0.635   0.752
ATOM      7  N2  DBH     1      -1.167  -0.635   0.752
ATOM      8  H1  DBH     1      -1.267   0.000  -1.866
ATOM      9  H2  DBH     1       0.508   0.000  -2.099
ATOM     10  H3  DBH     1      -0.335  -2.149  -0.574
ATOM     11  H4  DBH     1      -0.335   2.149  -0.573
```

PDB for DBH formatted for use on NWChem

Preparation

.top – connectivity information
.seq – list of atoms
.rst – atom position

5.3 $Å^3$ box
AMBER force field (GAFF)
Methanol as solvent

Apra, E.; et al. *J Chem Phys* **2020**, *152* (18), 184102.
Wang, J.; et al. *J Comput Chem* **2004**, *25* (9), 1157-1174.

Set up QMMM

Optimization

PBE0/6-311G** on QM

Optimize the QM region and solvent MM region iteratively

Equilibrating MM

200 ps with 0.002 timestep
DBH fixed at the center
Berendsen's thermostat

Wong, M.; et al. *The Journal of Physical Chemistry* **1988**, *92* (17), 4875-4880
Krishnan, R.; et al. *The Journal of Chemical Physics* **2008**, *72* (1), 650-654.
Adamo, C.; et al. *The Journal of Chemical Physics* **1999**, *110* (13), 6158-6170.
Berendsen, H. J. C.; et al. *The Journal of Chemical Physics* **1984**, *81* (8), 3684-3690.

Set up QMMM

Equilibrating QM/MM

0.05 ps with 0.0005 timestep

Dynamics
DBH centered in the box
PBE0/6-311G** on QM

5 Excited States
S_1 was the target

500 timesteps

DFT: 2 houts
TD-DFT: 31.5 hours

Apra, E.; et al. *J Chem Phys* **2020**, *152* (18), 184102.
Wong, M.; et al. *The Journal of Physical Chemistry* **1988**, *92* (17), 4875-4880
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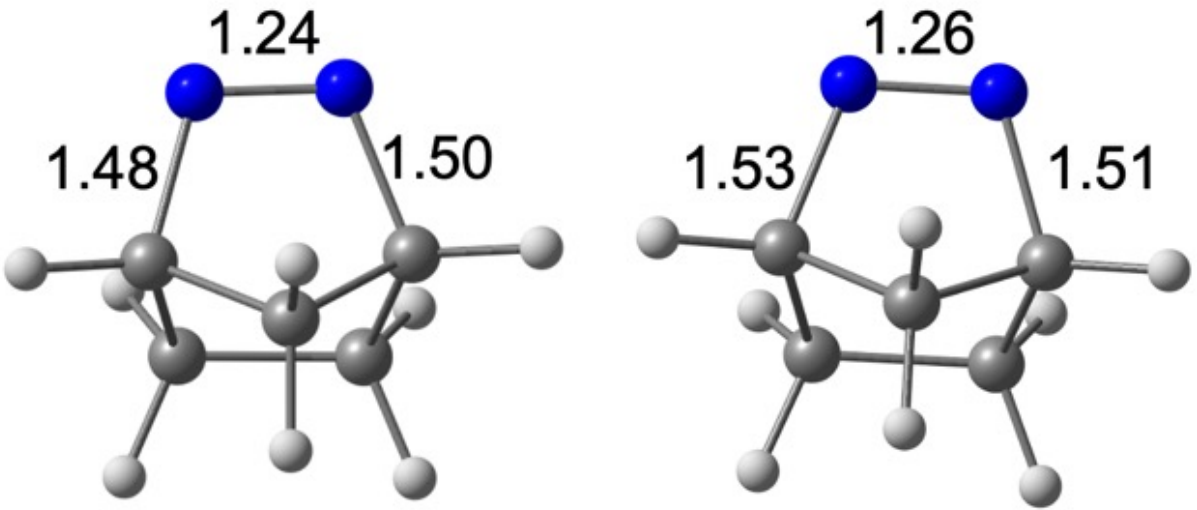
S_0 and S_1 optimized geometries



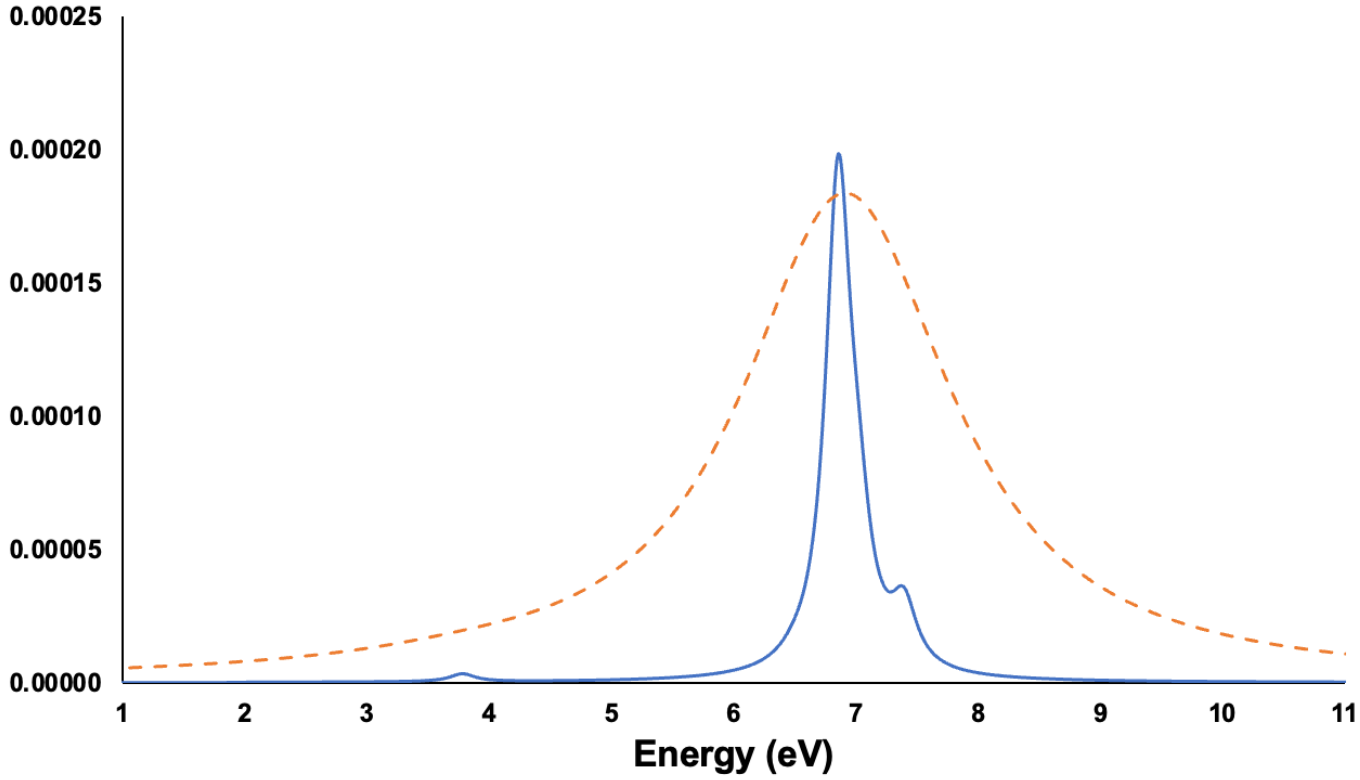
Bond length in Å

Vertical Excitation Energies (eV)

State	Energy (eV)	Wavelength (nm)	Oscillator strength
S_1	3.51	353	0.0004
S_2	6.14	202	0.0002
S_3	6.91	179	0.0057
S_4	6.98	178	0.0290
S_5	7.10	175	0.0067

Experimental λ^{max} = 338 nm (3.67 eV)

Spectrum

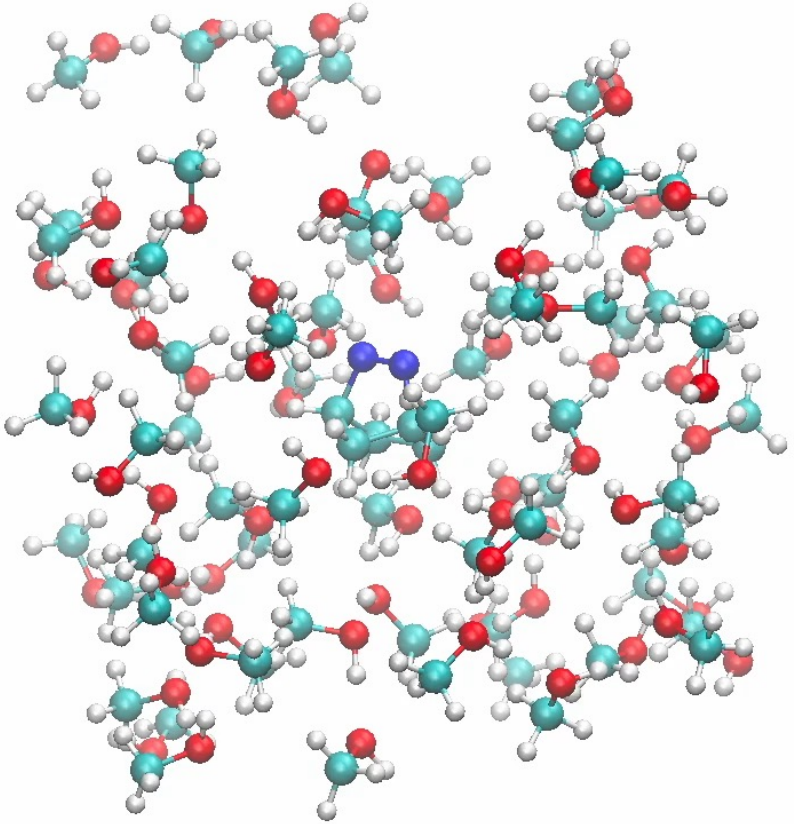


Broadening

0.25

2.00

QMMM



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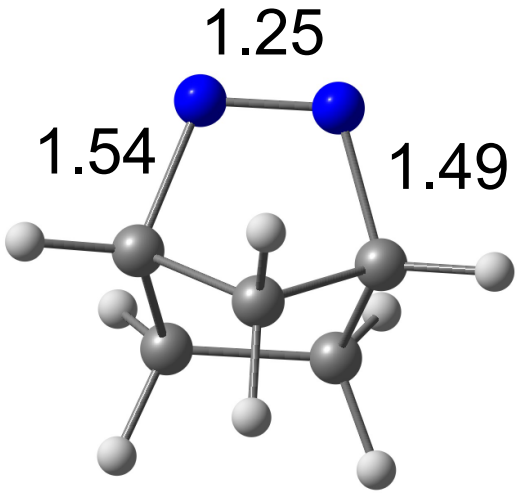
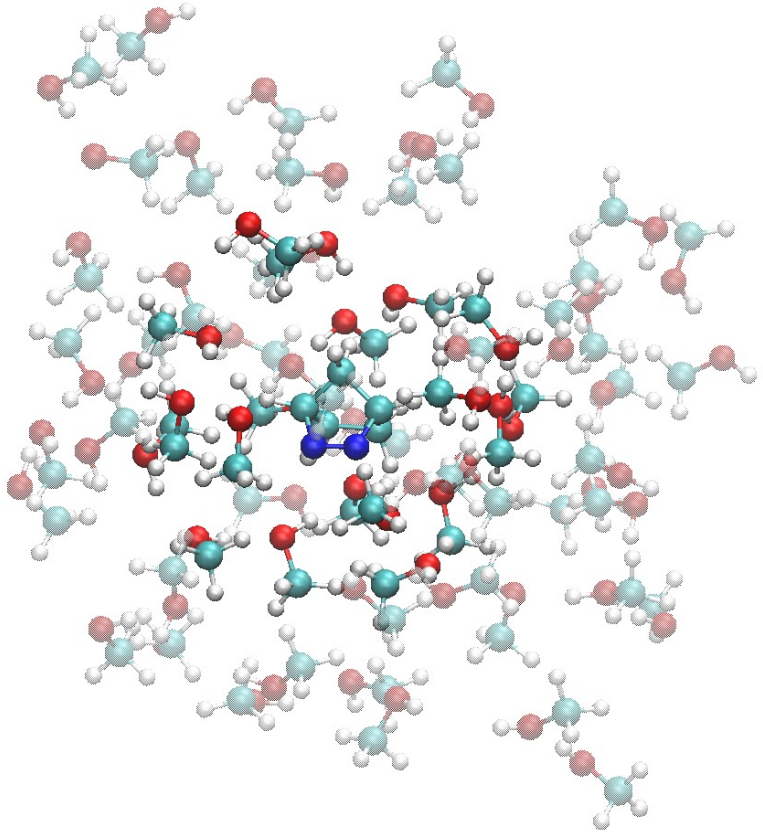


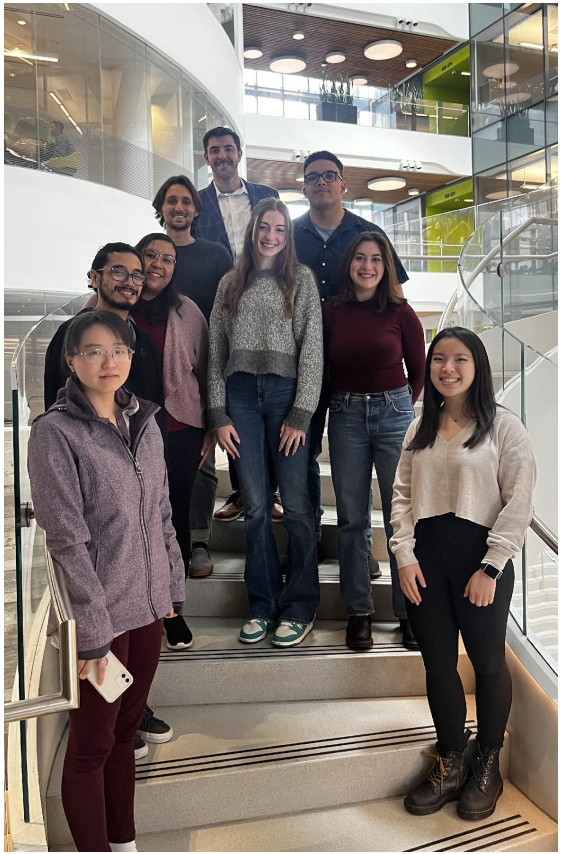
Future Steps

- Perform QMMM for 1ps and sample initial condition
- Create droplet including DBH and few molecules of methanol to be treated with QM, and treat other solvent molecules with MM
- Perform QMMM with another solvents and derivatives



Acknowledgements

Prof. Steven A. Lopez



Computational Chemistry Cyber Training

University at Buffalo

- Prof. Alexey Akimov
- Cyber Training Instructors
- Fellow classmates

Northeastern University Boston, Massachusetts

NSF

Northeastern University

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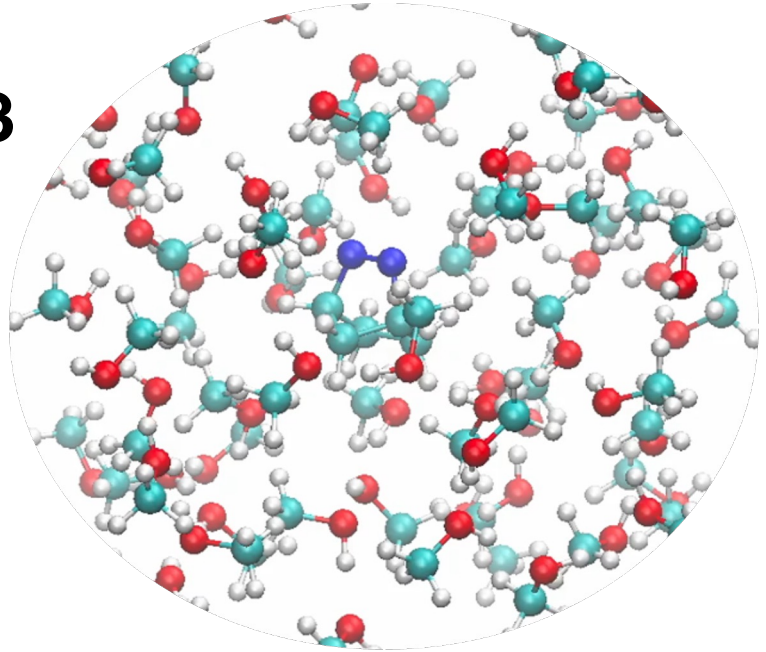

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