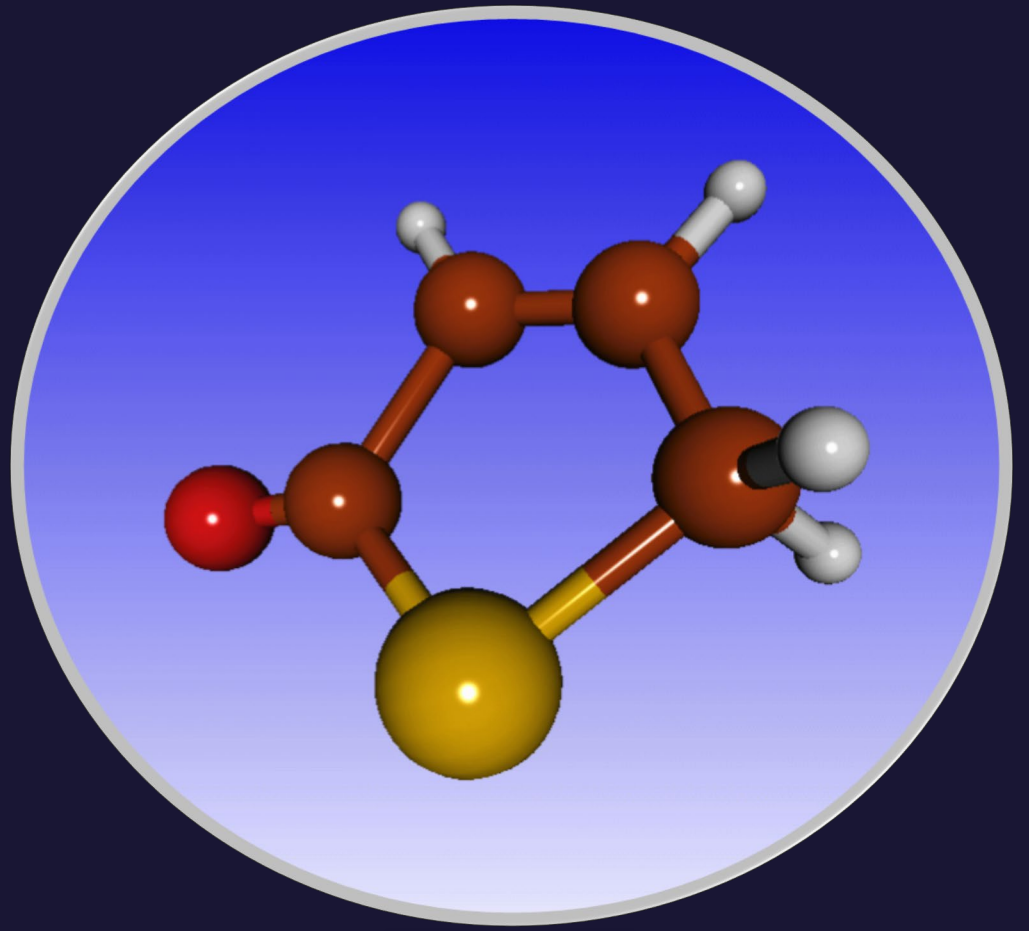
Theoretical Computational Ultrafast Dynamics For Thiophenone



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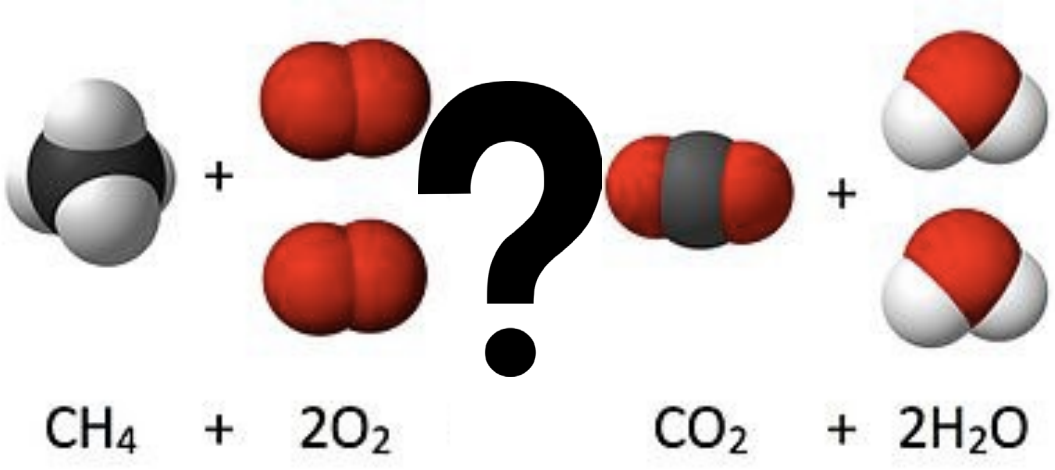
Chemistry's Missing Link

What happens during photoionization?

- Are there local minimums to trap it?
- What state does it fall into?
- Can you predict what state it ends in?
- The hope is to create a better picture of the overall process using thiophenone' s potential energy throughout fragmentation



How Do You Find The Potential?

nuc KE | el KE | el-nuc attraction | el-el repulsion | nuc-nuc repulsion

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{U}_{e-n} + \hat{U}_{e-e} + \hat{U}_{n-n}$$

$$-\sum_i \frac{\nabla_i^2}{2} - \sum_{i,I} \frac{Z_I}{|\mathbf{R}_I - \hat{r}_i|} \quad \sum_{i \neq j} \frac{1}{|\hat{r}_i - \hat{r}_j|} \quad \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_i - \mathbf{R}_j|}$$

a parameter

$$\hat{H}\Psi(r_i; \mathbf{R}_I) = E(\mathbf{R_I})\Psi(r_i; \mathbf{R}_I)$$

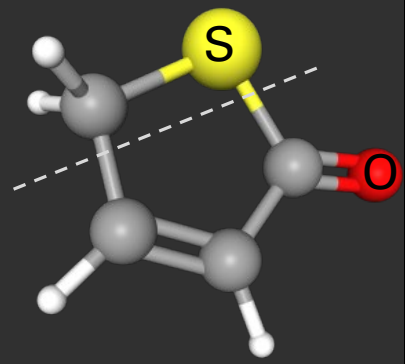
electronic wavefunction | electronic energy

Computational Methods

- Utilize Cori supercomputer to run calculations
- Create z-matrix to model molecular geometry
- Slowly pull apart molecule
- Perform Hartree-Fock and geometry optimization
- Finish with MCSCF to the fifth excited state

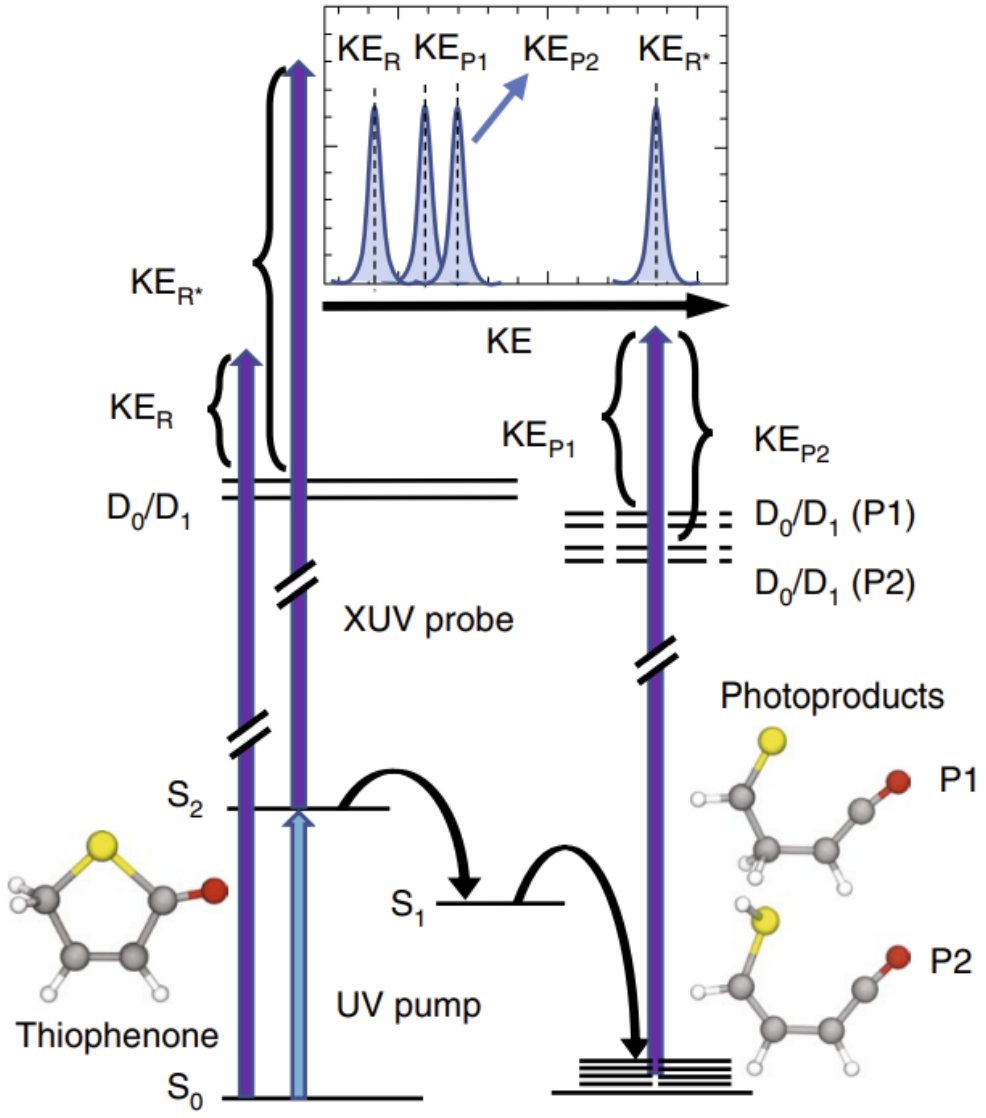
```
CS2   = 2.0           ANG
CC3   = {{CC3}}       ANG
CCS3  =  107.585      DEGREES
CS4   = {{CS4}}       ANG
CSC4  =   90.349      DEGREES
DIH4  =    0.000      DEGREES
CC5   =  2.0          ANG
CSC5  =  102.593      DEGREES
DIH5  =  0.0          DEGREES
OC6   =  1.130226     ANG
OCS6  =  118.930      DEGREES
DIH6  =  180.000      DEGREES
HC7   =  1.078924     ANG
HCC7  =  131.078      DEGREES
DIH7  =  180.000      DEGREES
HC8   =  1.085171     ANG
HCC8  =  115.785      DEGREES
DIH8  =  180.000      DEGREES
HC9   =  1.088436     ANG
HCS9  =  104.830      DEGREES
DIH9  = -121.668      DEGREES
HC10  =  1.088436     ANG
HCS10=   104.830      DEGREES
DIH10=   121.668      DEGREES

geom={
s1
c2     s1 cs2
c3     c2 cc3          s1 ccs3
c4     s1 cs4          c2 csc4          c3 dih4
c5     c4 cc5          s1 csc5          c2 dih5
o6     c4 oc6          s1 ocs6          c2 dih6
h7     c5 hc7          c3 hcc7          c2 dih7
h8     c3 hc8          c2 hcc8          s1 dih8
h9     c2 hc9          s1 hcs9          c4 dih9
h10    c2 hc10         s1 hcs10         c4 dih10
}
```



Experimental Results

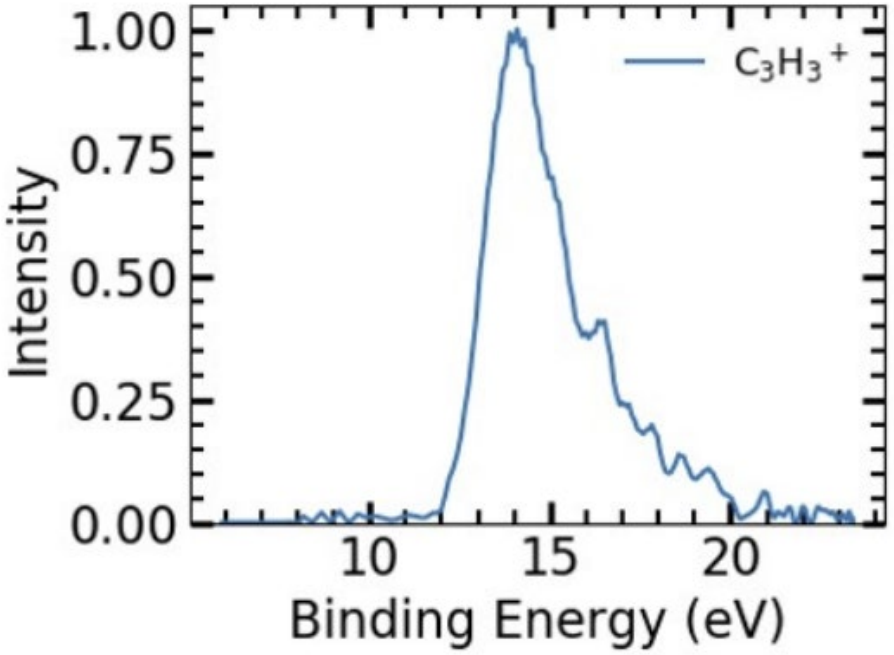
- I will be comparing my results to Dr. Shashank Pathak's, a former grad student.
- Thiophenone was excited and fragmented with laser pulses
- They caught the jettisoned electron and the charged fragment



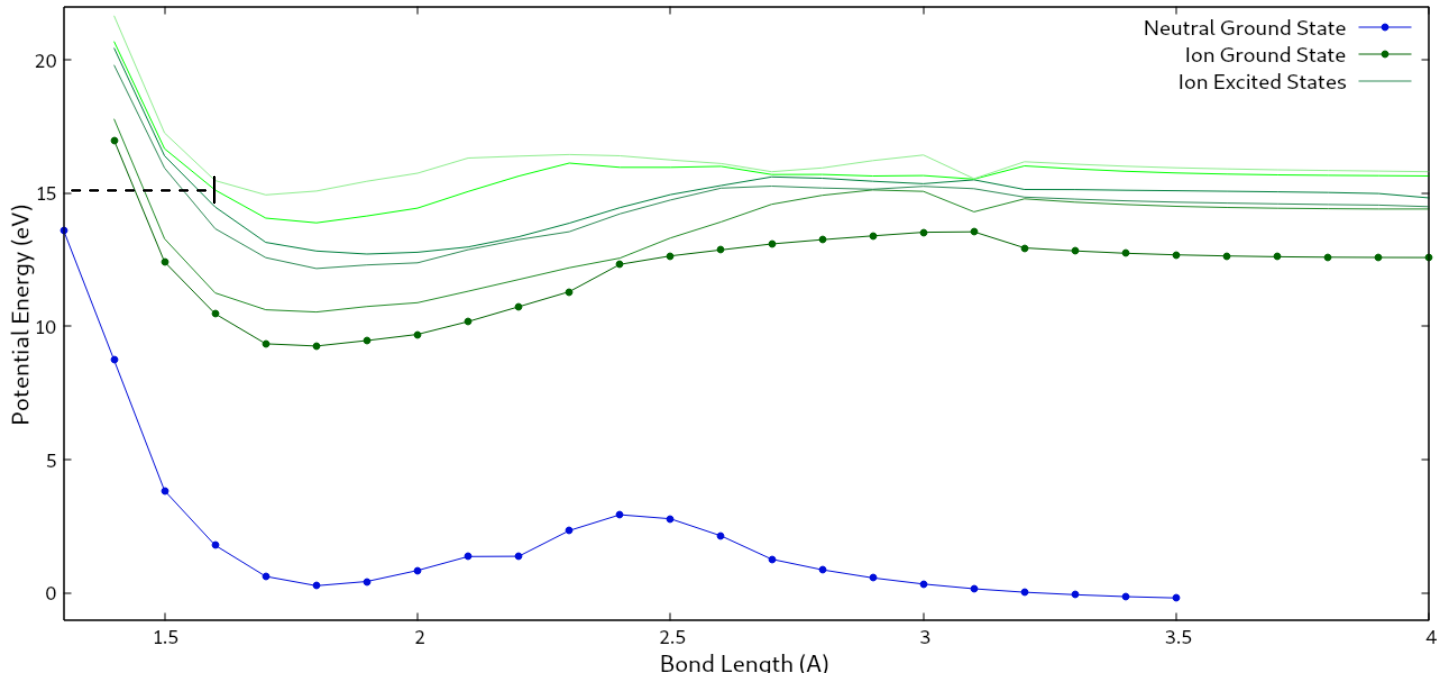
Pathak, S. (2021). Schematic of the UV excitation, ring opening and photoionization of thiophenone [Graph]. Isomerization and Fragmentation of Polyatomic Molecules Induced by Ultraviolet and Extreme UV Light.

$C_3H_4^+$ Potential Energy (eV) Vs. Bond Length (Å)

- Experimental data shows fragmenting at 14 eV
- Theoretical fifth excited state data has a shallow well at 15 eV
- The similar energies seem to correspond to each other

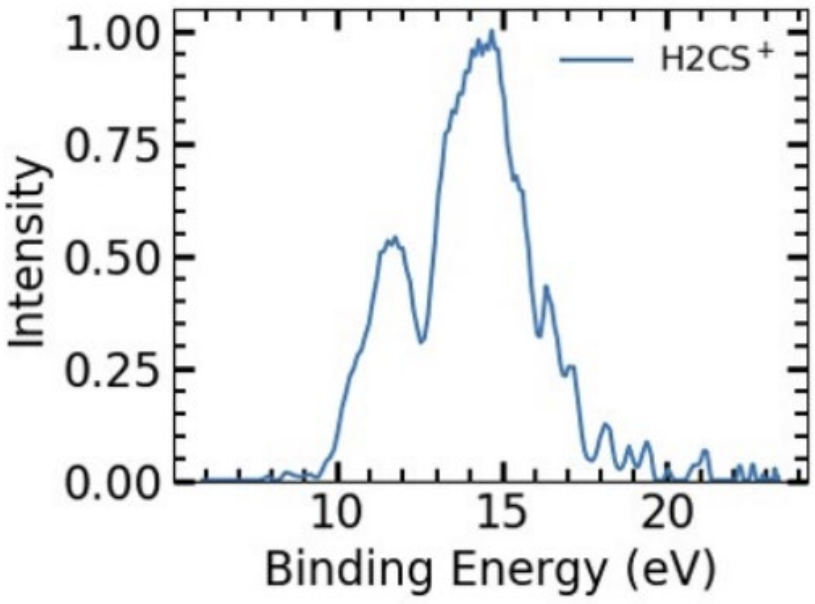


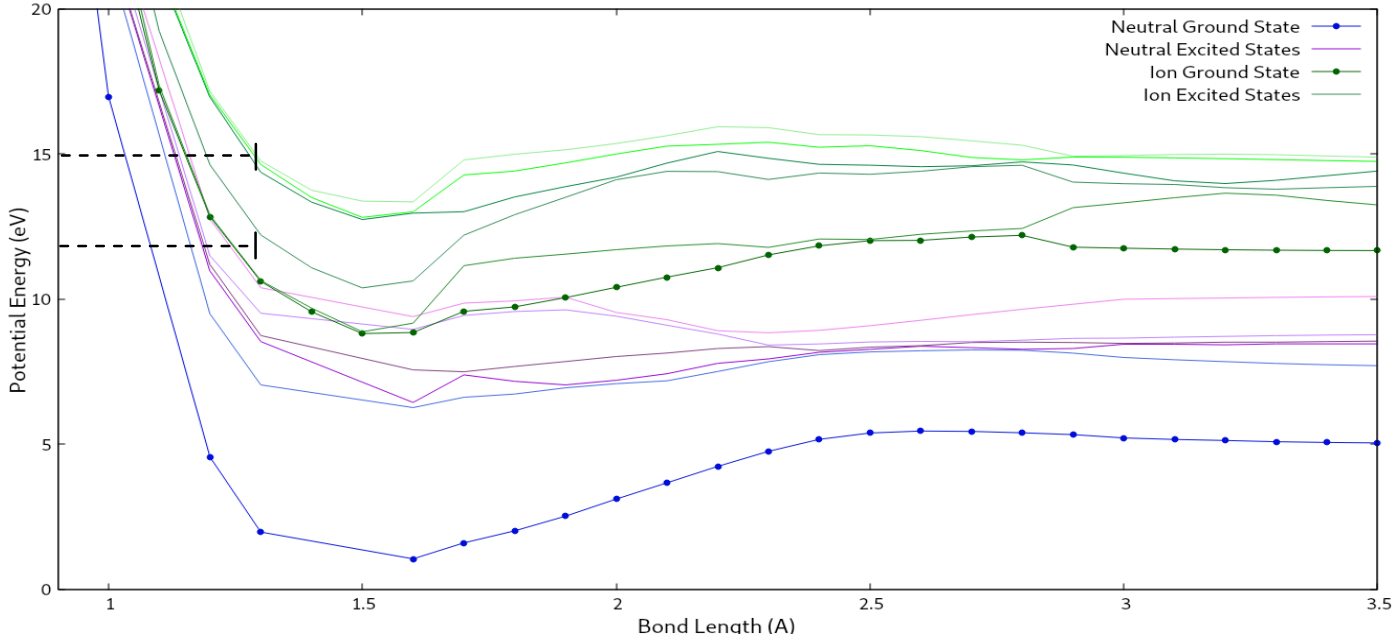
Pathak, S. (2021). *C3H3 Intensity Vs. Bonding Energy* [Graph]. Isomerization and Fragmentation of Polyatomic Molecules Induced by Ultraviolet and Extreme UV Light.



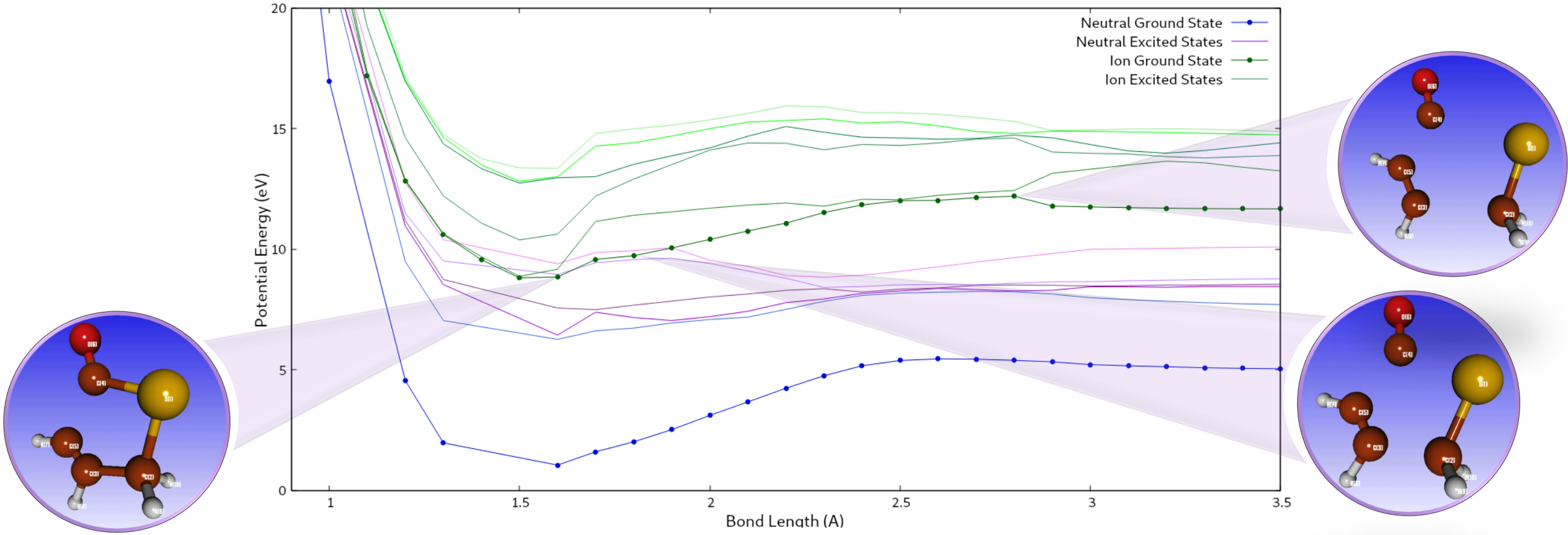
H_2CS^+ Potential Energy (eV) Vs. Bond Length (Å)

- Experimental data shows fragmenting at 12 and 15 eV
- Theoretical data shows shallow wells at:
  - Second excited state (11 eV)
  - Fifth and sixth excited states (14 – 15 eV)





Pathak, S. (2021). *H2CS Intensity Vs. Bonding Energy* [Graph]. Isomerization and Fragmentation of Polyatomic Molecules Induced by Ultraviolet and Extreme UV Light.

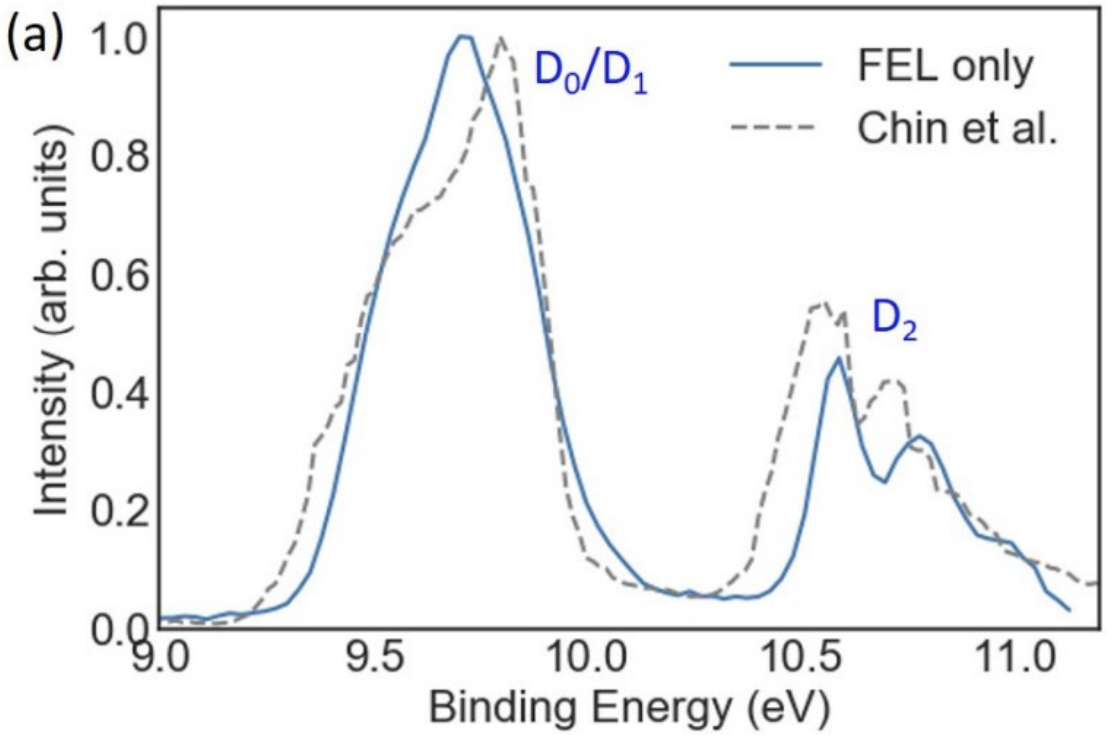


H_2CS^+ Potential Energy (eV) Vs. Bond Length (Å)

- The first image is at the equilibrium point, the best optimized geometry
- The second image is near the critical point, the point at which fragmentation occurs
- The third image confirms fragmentation

Creating a Thiotheory

- The black line is the accepted photoelectric spectrum, without fragments
- The blue line is the result of the experimental data
- Future calculations may lead to the possibility of predicting photoionization outcomes






Acknowledgements

KANSAS STATE UNIVERSITY

College of Arts & Sciences

Department of Physics

NSF Grant No. 175778

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