Crystal violet quantum calculations for general chemistry students: Easing the load by combining interactive webpages with WebMO and Gaussian

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Background

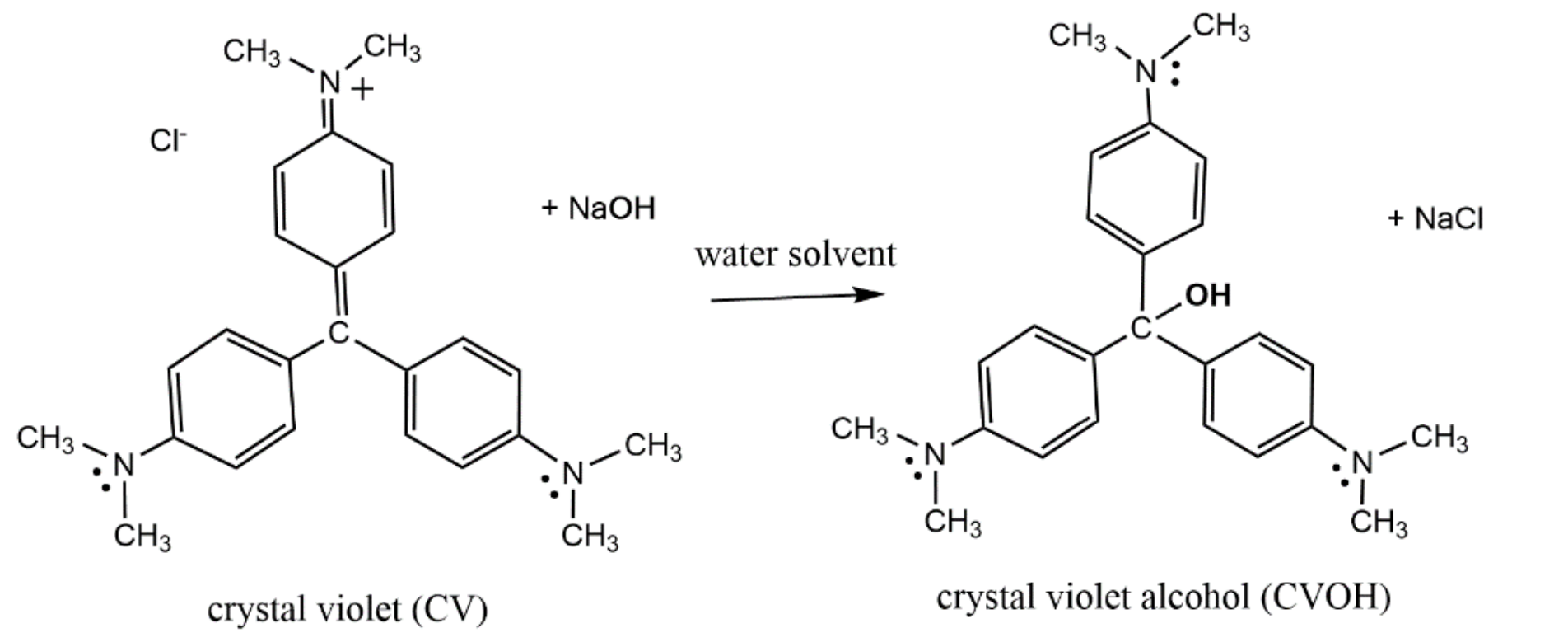
Computational chemistry has made its way into the undergraduate chemistry curriculum to some extent in recent years. In general chemistry these activities tend to focus on re-computing the geometries of small molecules and comparing the results to VSEPR predictions (1,2).

Moving into larger chemical systems faces certain barriers. With some students, the complexity of larger organic molecules leads to sensory overload. But also, obtaining realistic results may require density functional theory (DFT) calculations that cannot be completed within a 3-h lab period. Even with the WebMO GUI (3), a full build-optimize-analyze cycle for a larger molecule is still a challenge, even for organic chemistry students.

Our workaround uses a **secondary website** for viewing the molecule. After downloading from the site, a single-point calculation requires only about 2 min.

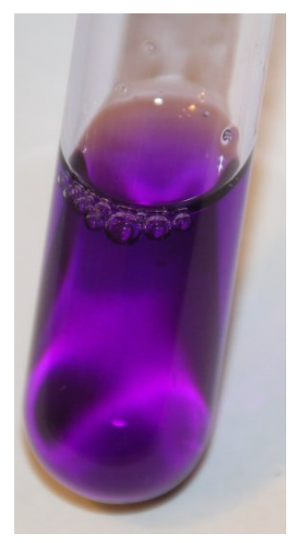
This approach – combining a JSmol website with WebMO – would be useful for any molecular modeling exercise requiring an energy or MO calculation on a somewhat complex molecule.

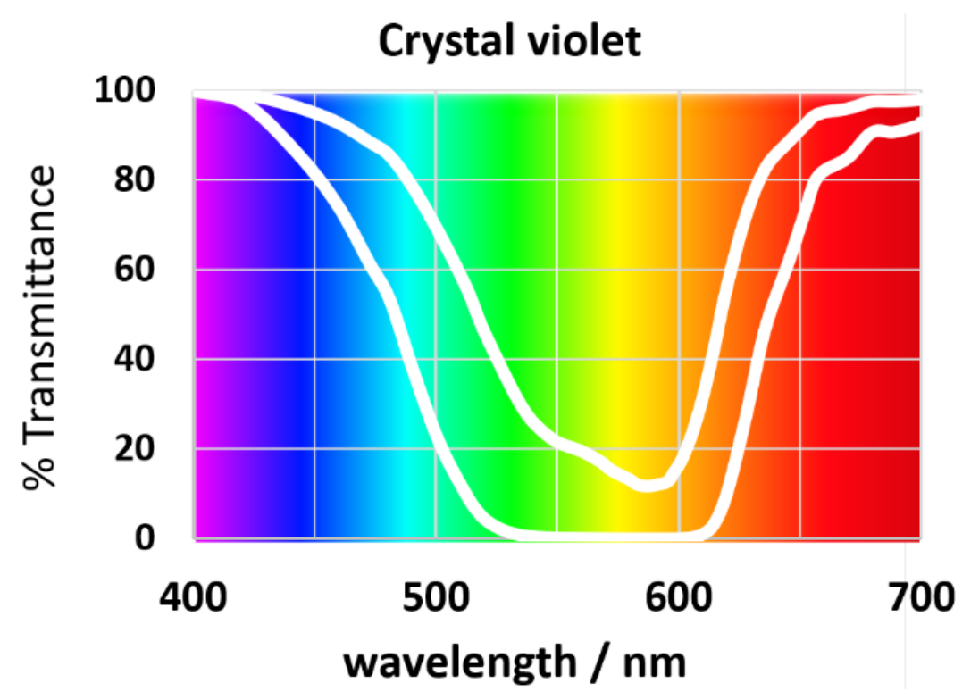
This lab exercise is focused on five structures: crystal violet cation, crystal violet alcohol, OH^--4-water cluster, crystal violet alcohol-4-water cluster, and the reaction transition state. These occur in the crystal violet bleaching reaction, which is the subject of a popular general chemistry kinetics experiment (4,5).



crystal violet (CV)

crystal violet alcohol (CVOH)





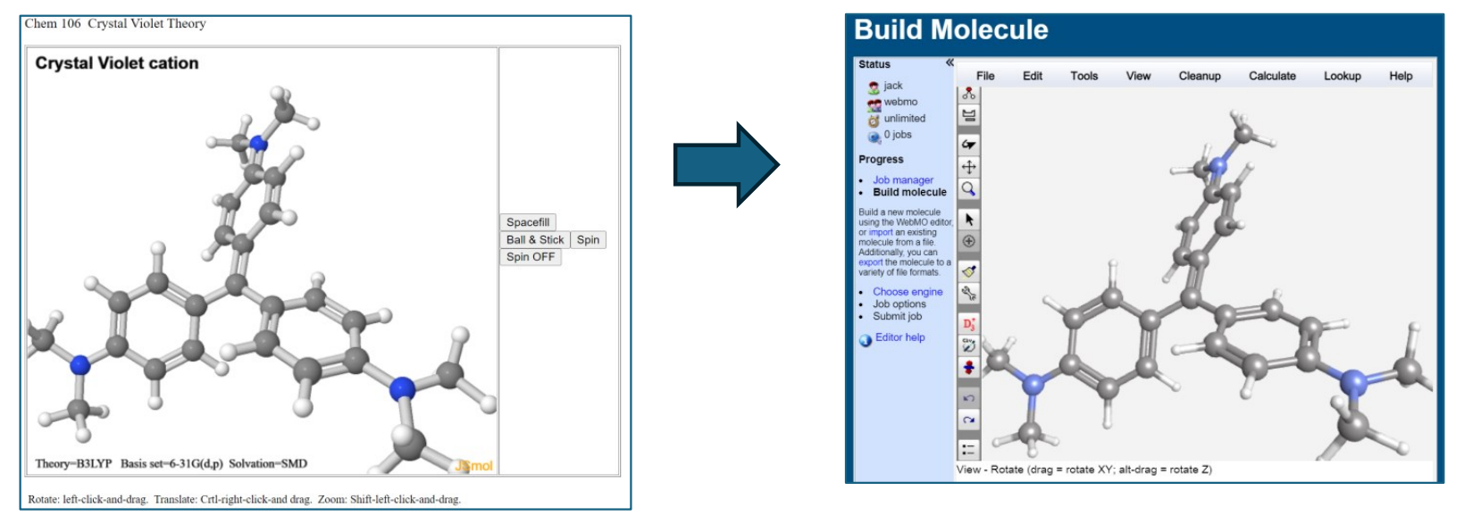
Learning goals

- Quantify reaction energies and reaction barriers using computational results.
- Relate color, or lack thereof, to electron transitions between molecular orbitals, especially HOMO and LUMO.
- Become familiar with WebMO and the Gaussian (or ORCA) programs.

Lab procedure

For each calculation, students visit a website with an interactive model of the molecule. This provides visual clues and a structure file to be imported into WebMO.

Students then carry out a single point energy calculation on each at the B3LYP/6-31G(d,p)/SMD level of theory.



Theory=B3LYP Basis set=6-31G(d,p) Solvation=SMD

Rotate: left-click-and-drag. Translate: Crtl-right-click-and drag. Zoom: Shift-left-click-and-drag.

Build a new molecule using the WebMO editor, or import an existing molecule from a file. Additionally, you can export the molecule to a variety of file formats.

View - Rotate (drag = rotate XY; alt-drag = rotate Z)

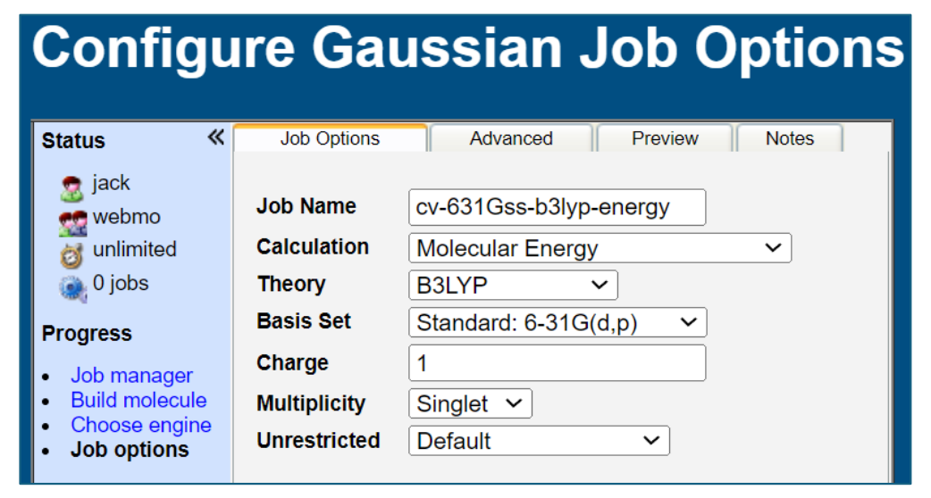
View the JSmol webpages by following this QR code:
See also https://doi.org/10.6084/m9.figshare.26940481.v1

WebMO setup and time requirement

- Default job options are defined for theory, basis set, multiplicity, and solvent by editing WebMO's gaussian.html (or orca.html) file.

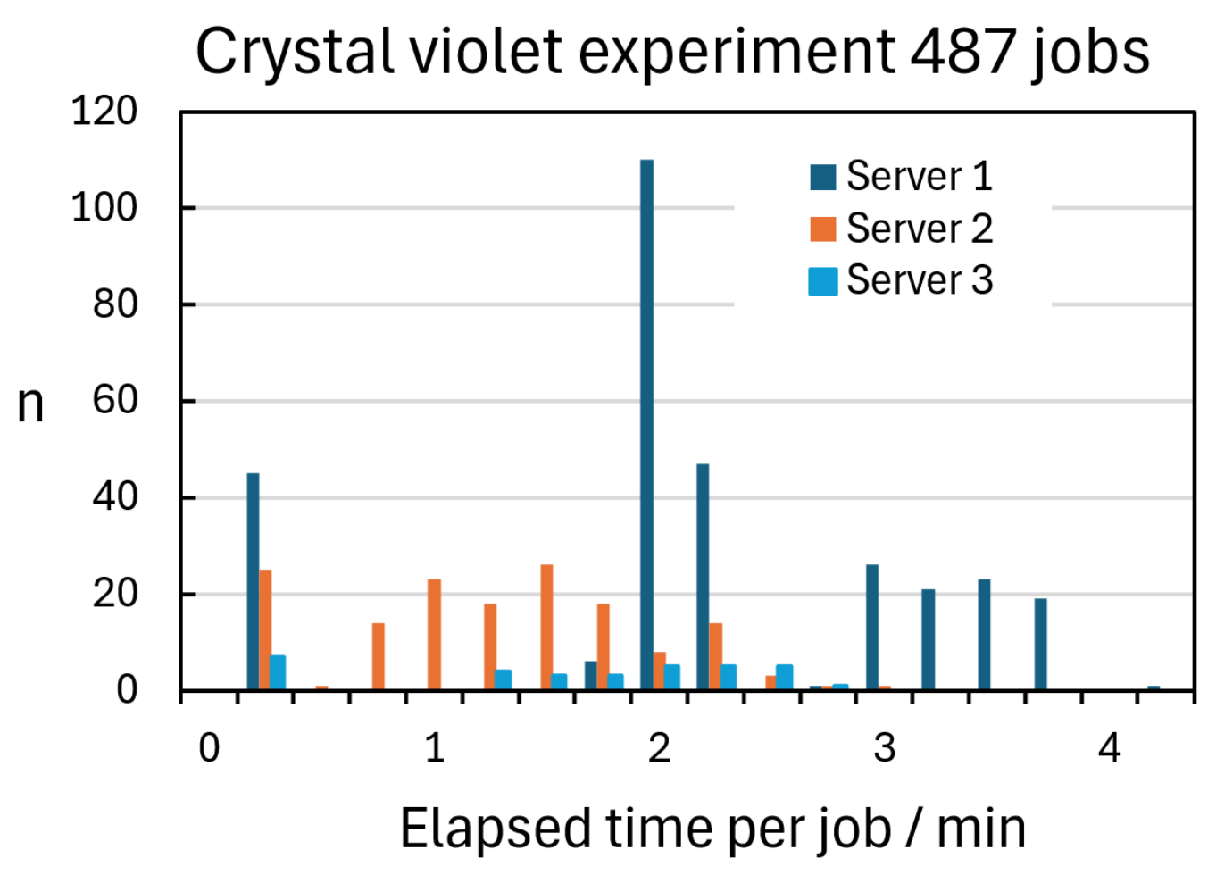
```
<OPTION VALUE="B3LYP" SELECTED>B3LYP
<OPTION VALUE="6-31G(d,p)" SELECTED=>Standard: 6-31G(d,p)
<OPTION VALUE="1" SELECTED>Singlet
<OPTION VALUE="SCRF=(SMD,Solvent=Water)" SELECTED=>Water
```

- Charge value is taken from the imported .mol file.



Job Name: cv-631Gss-b3lyp-energy
Calculation: Molecular Energy
Theory: B3LYP
Basis Set: Standard: 6-31G(d,p)
Charge: 1
Multiplicity: Singlet
Unrestricted: Default

- The default number of cores (8) is set in the Interface Manager.
- Three 24-core servers were used for calculations.



Seven 20-person labs with students working in pairs, submitting ~7 jobs per pair.

Server details:

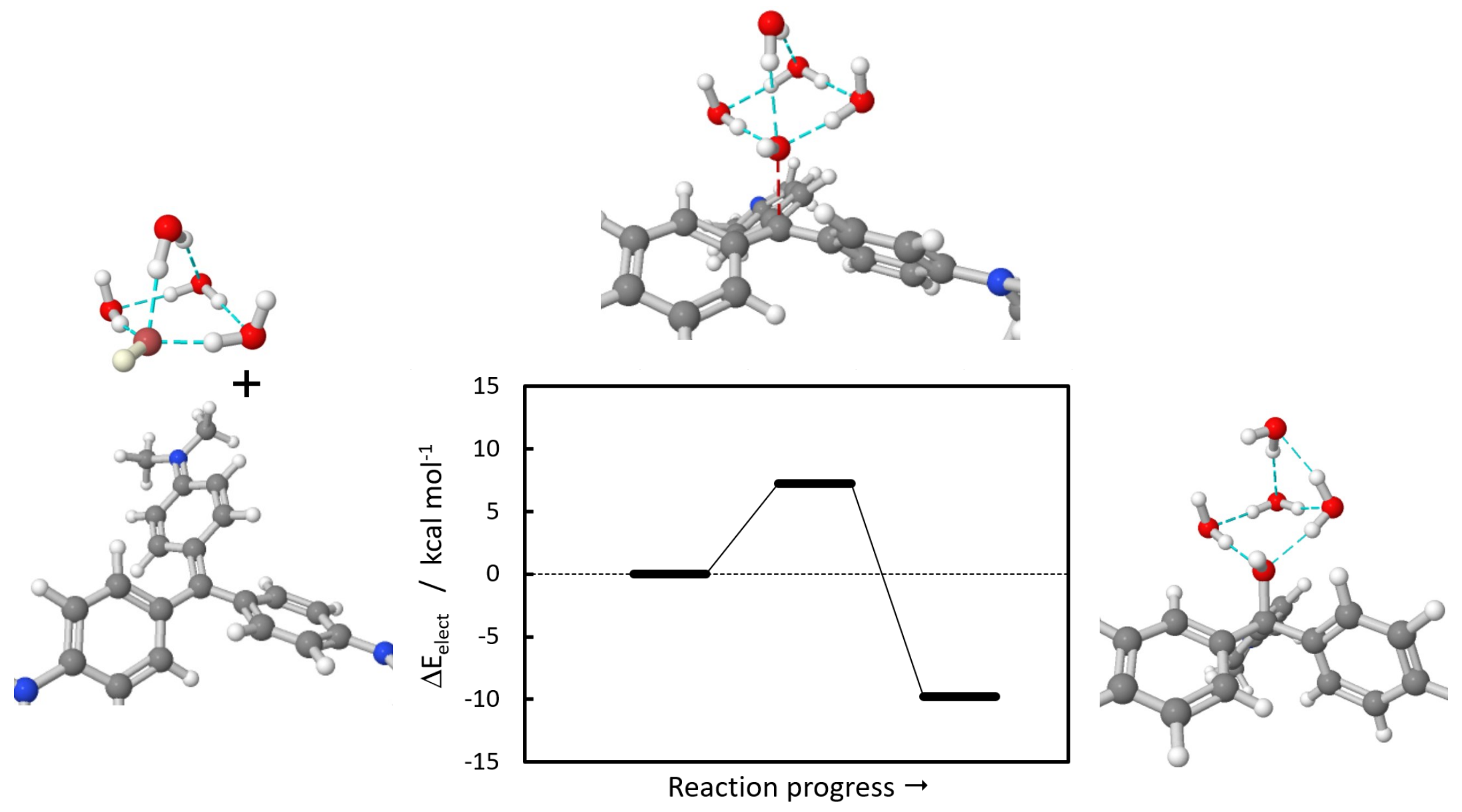
Molecule webpages

- JSmol interactive webpages require access to a server running Apache and JSmol. In our experience this must be a **separate machine** from the WebMO server.
- We installed a VirtualBox VM on the WebMO server, with the two OSs sharing one LAN connection.
  Here's how:
- Alternatively, one could use a separate server or a cloud instance.

Informal student feedback

As a guide for future improvements, an optional comment sheet was made available to students. About half the attendees returned the form, with the responses to a "how difficult" question falling between "OK" and "too hard." Also, students suggested that there should be more discussion of the lab's rationale and significance by the instructor .

$CV^+ + OH^-$ energy changes

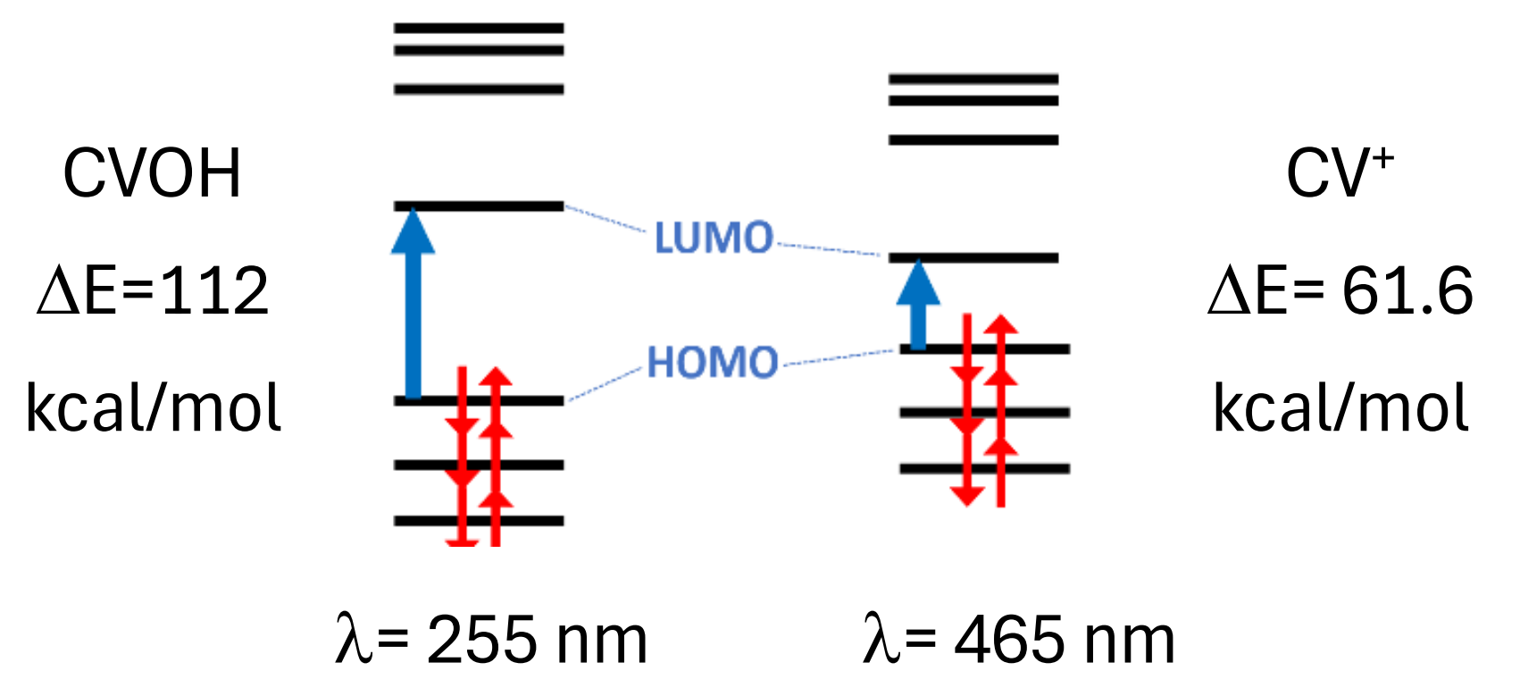


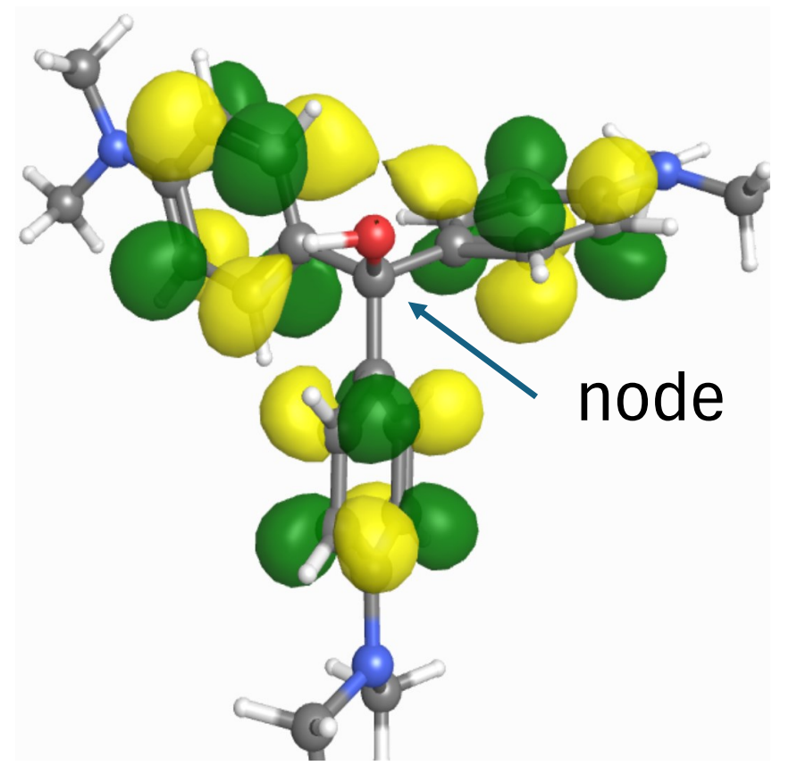
The calculated ΔE_{rxn} and ΔE_{act} (-9.9 and 7.5 kcal/mol) are about as close to the experimental ΔH_{rxn} and ΔH_{act} (-6.0 and 14 kcal/mol) (6-8) as one might hope at this level of theory. A water cluster is required to give $\Delta E_{act} > 0$.

Why is crystal violet alcohol colorless?

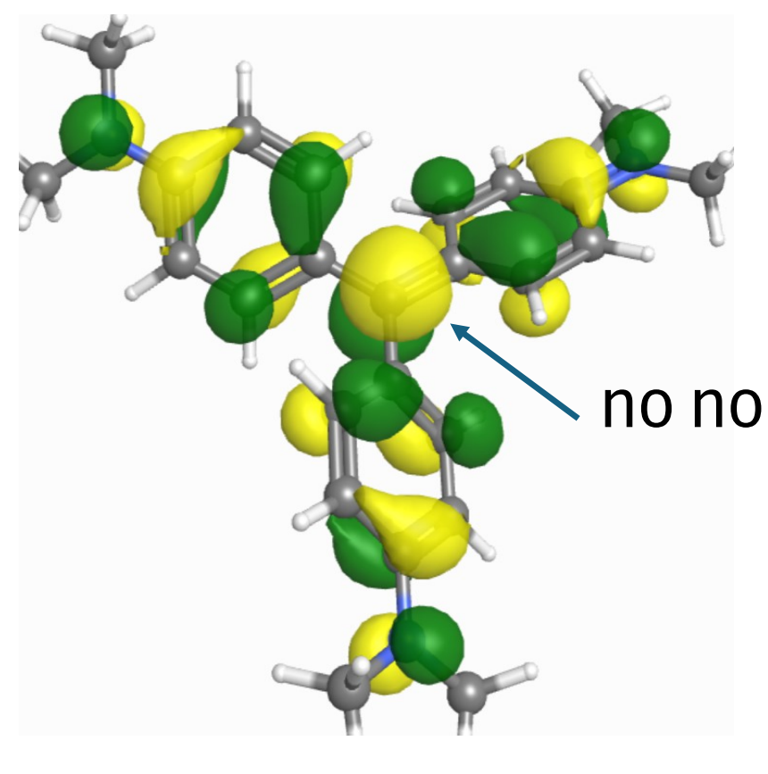
- Adding the OH group destabilizes CVOH's LUMO and increases the LUMO-HOMO gap.

In the last part, students are first asked to review atomic spectroscopy from 1st semester general chemistry and the related equation $\Delta E = h\nu = hc/\lambda$. After carrying out molecular orbital calculations, ΔE, ν, and λ are calculated from the HOMO and LUMO energies.





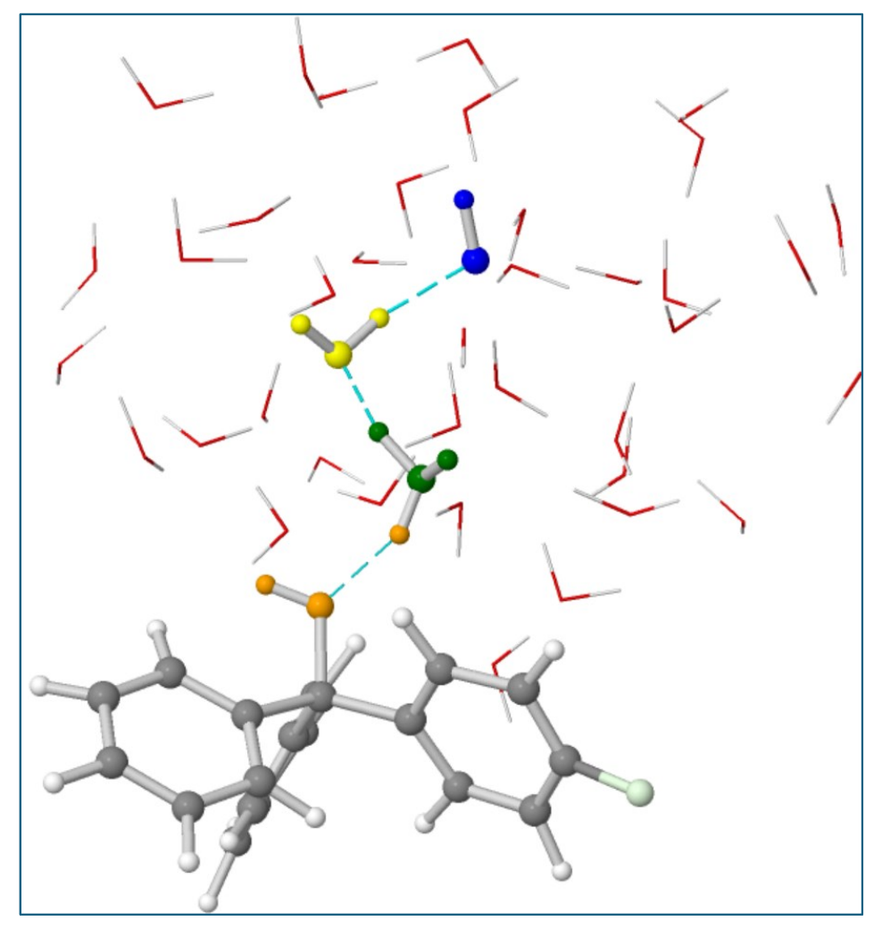
CVOH LUMO: Localized within the aromatic rings



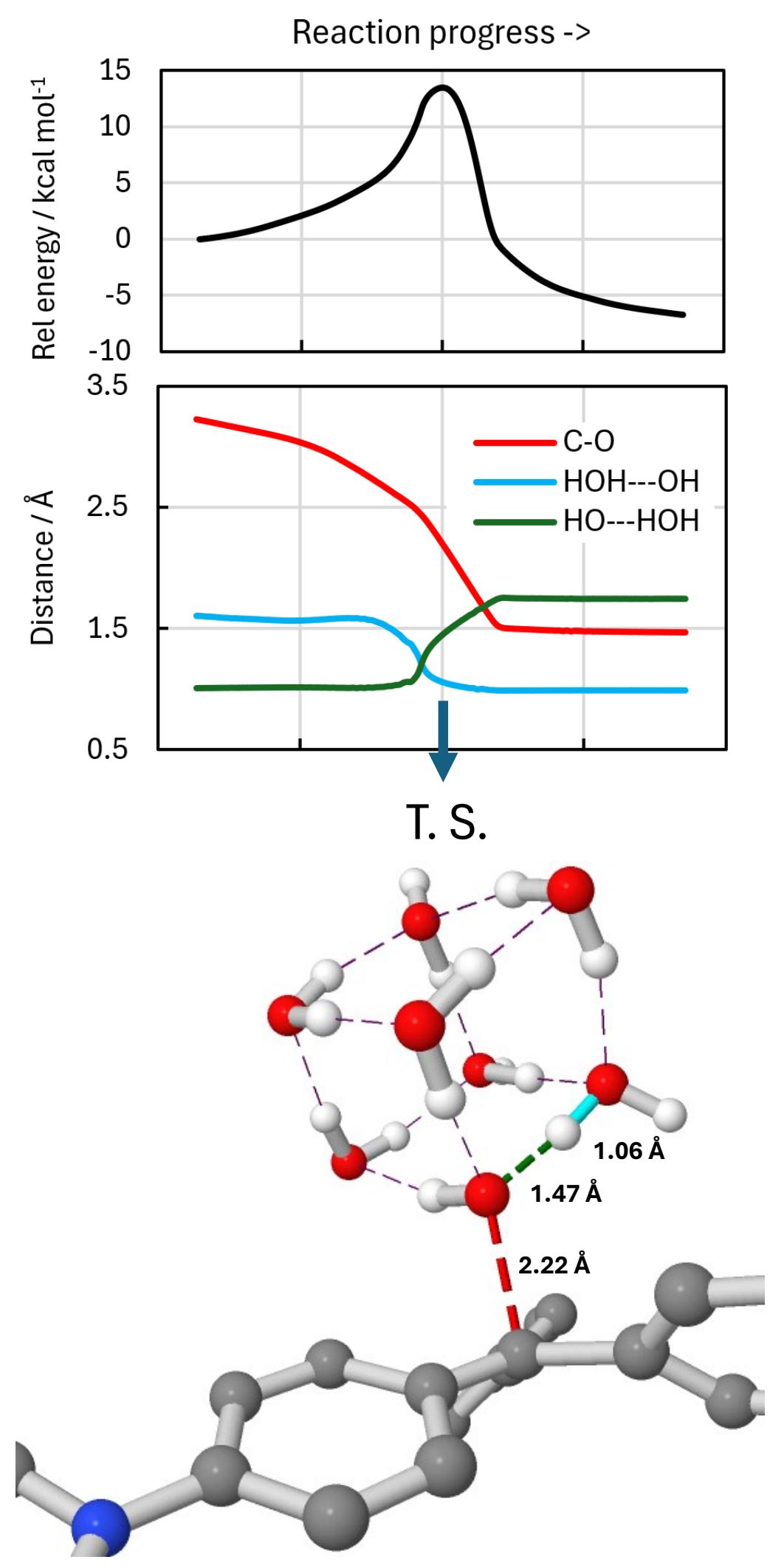
CV^+ LUMO: Spread out across 22 atoms

Research Direct or indirect OH^- addition?

Direct addition of OH^- to CV^+ as described in the left panels may occur to some extent. However, our ongoing MD studies of triaryl cation-OH^--water clusters using xTB theory (9) indicate that H_2O itself can be the initial nucleophile. OH^- then removes a proton either directly or through a H-bond network. In this trajectory (*l*) the C-O bond forms first, followed by 3 proton transfers during about 50 femtoseconds. Thus, OH^- adds by a concerted general base mechanism with asynchronous proton transfer.



F-trityl cation + 42 waters + OH-. GFN2-xTB; temperature = 298.15 K; time step = 1 fs; save interval = 10 fs; NVT ensemble; no shake constraint; hmass = 4; wall potential = logfermi; sphere = 48 Bohr.



B3LYP/6-31G(d,p)/SMD

Similarly, DFT study of CV^+ reacting with a 7-water-OH^- cluster shows an asynchronous mechanism, but with this theory, proton removal occurs prior to the TS. At the left is the intrinsic reaction coordinate (IRC) path calculated from the transition state. ΔE_{rxn} and ΔE_{act} are -3.8 and 17.5 kcal/mol, respectively.

Taharchaouche et al. also studied the CV^+ - OH^- reaction, but without the inclusion of explicit waters (10).

Acknowledgements

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References

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