

Chem 106

TA _____ Name _____ Partner _____

Worksheet: Crystal Violet and Quantum Theory

****Where short answers are required, please use complete sentences.****

This experiment requires 5 Molecular Energy calculations using WebMO and ORCA. List the job numbers your answers are based on:

	Job Number
Crystal violet cation CV	_____
Crystal violet alcohol CVOH	_____
OH...4-water cluster	_____
CVOH..4-water product	_____
CVOH..4-water transition state	_____

A. Partial charges and geometry of CV



Preferences
tool

Answer the following questions using the results from the **Molecular Energy** calculation for **CV**. Check that the atoms are labeled with the **index number**. (If not, click the Preferences tool on the left toolbar, and under Labels, select Index.)



1. (a) Scroll down to the Partial Charges table. **Fill in** the following table using the Partial Charges table or the graphical display (click the magnifying glass icon in that table). To switch back to atom indexes, click the Reset Viewer button at the bottom of the display.

CV	
Atom	Charge Round off to the nearest 0.001
N 2	
N 24	
N 43	
C 7	
C 19	
C 38	
Central C 15	
Total charge	1.000
Total MINUS C15	

(b) What **percent** of the total charge is on the **central carbon** (#15)? _____

What **percent** of the total charge is on **all** the other atoms together? _____

In the table on the left, look at the charges on the N's and the attached C's. It appears that the 3 rings are

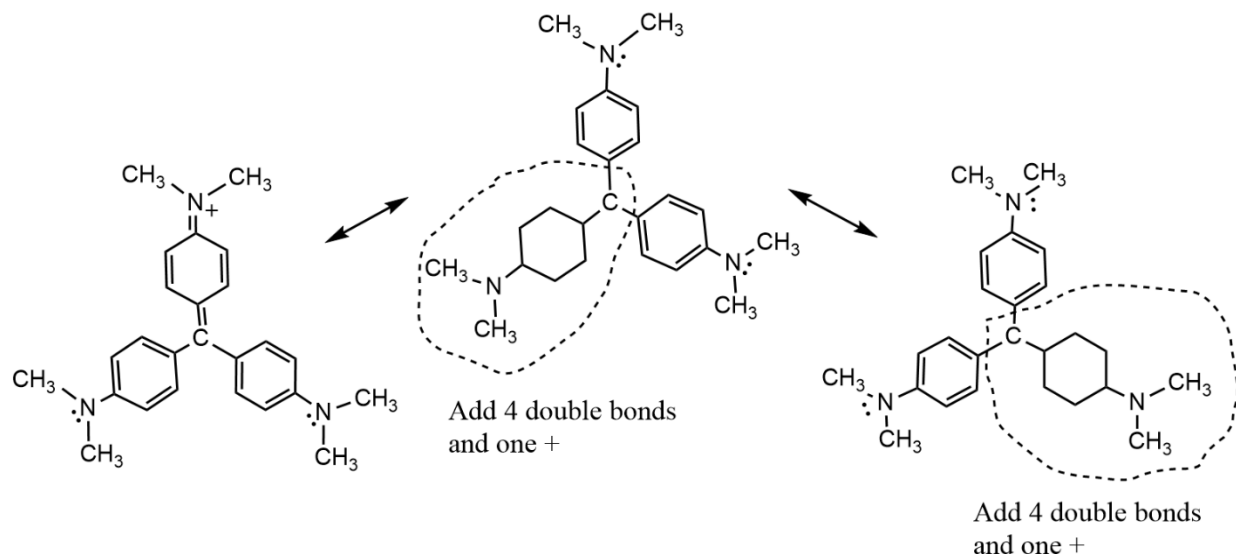
(circle one):

quite different

essentially identical

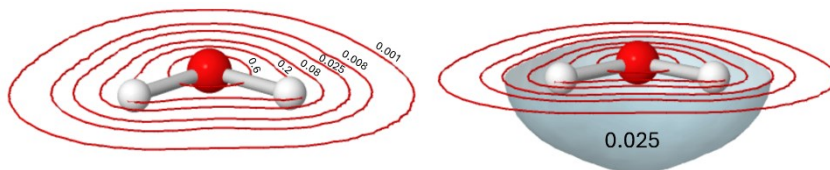
(c). Calculations show that **CV is resonance stabilized** with the (+) charge spread out equally among the three aromatic rings - analogous to the way negative charge is shared in the formate ion. See page 2 in the handout.

Shown below are several formulas for CV^+ , that is, three resonance forms. Two of the formulas are incomplete. Complete these by adding **four double bonds** and **one "+" symbol** within each circled region. Hint: make these look like the resonance form on the left.



2. Go back to the [informational webpage](#) and follow the links to several **CV cation surfaces**:

- the **total electron density** surface shows the volume around the nuclei where the electron density is equal to or greater than 0.025 electrons per unit volume. Recall that electron density is highest close to the nuclei, and gradually decreases going out from the nuclei. Thus, an electron density surface can be drawn at any value between about 0.001 and 0.60 electrons per unit volume. Cross-sections of a water molecule are shown as an example. The 0.025 surface is consistent with our notion of the **shape** of a molecule.



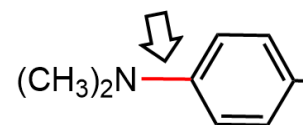
- The **electrostatic potential** surface combines the total electron density surface with a color scale that reports a **local excess of electrons** (orange or red) or **lack of electrons** (blue) at points around the surface. **Orange** or **red** spots occur where electrons protrude, such as **lone pairs** or **π bonds**. **Green** areas occur where there is zero formal charge and no relative excess or lack of electrons. **Blue** areas are where electrons have shifted away, revealing more positive nuclear charge.
- The **electrophilic reactivity** surface combines the total electron density surface with a color scale showing the preferred location for **addition of electrons** (**green** and **blue**), for example that might originate from OH^- ion. This coincides with the center of the LUMO.

Examine these surfaces, then provide brief answers:

Is the overall appearance of the **electron density** surface consistent with the **resonance description** of CV? What do you see, and what is the significance of this?

What is the color of the **electrostatic potential** surface **directly above the N atoms**? What causes this color to appear on the surface there?

3. Open your CV calculation in WebMO. Use the **Adjust tool** to measure all three of the **N to ring C** bonds. What do you find? How do you interpret this finding?



B. The OH⁻ reactant and the CV-OH⁻ transition state

1. Reaction energy and activation energy

Open the completed molecular energy jobs of CV, OH⁻-4water complex, the CVOH⁻-4water complex, and the CVOH⁻-4water transition state. For each one, record the energy (labelled “Final Single Point Energy” under Calculated Quantities, Overview) in the table below. Then calculate the energy change for the overall reaction ($\Delta E_{\text{reaction}}$) and the energy of activation ($\Delta E_{\text{activation}}$).

For the right-hand column, convert hartrees to kcal/mol using the conversion factor

$$1 \text{ hartree} = 627.5095 \text{ kcal/mol}.$$

(Optionally, this question can be carried out using **Excel, Numbers, or Google Sheets**.. In WebMO, highlight the four jobs using the checkboxes and choose Download, Spreadsheet.)

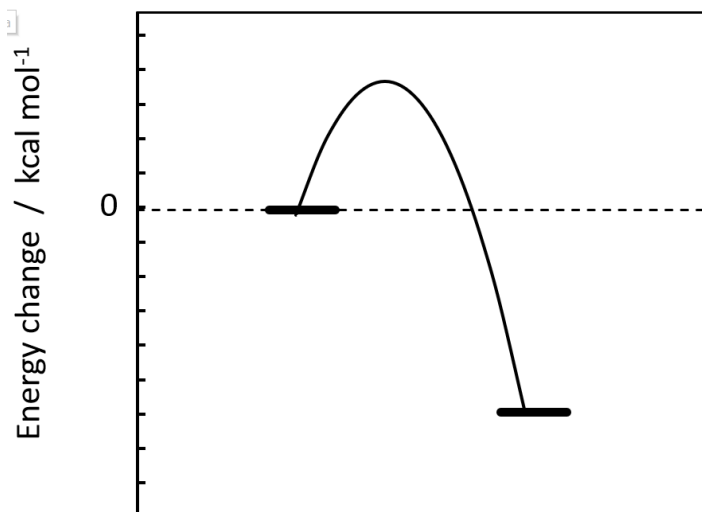
		Final Single Point Energy (hartrees) (round off to the 6 th decimal place)
Reactants	OH-4-water	
	CV	
Product	CVOH-4-water	
Transition state	CVOH-4-water TS	

	Energy change ΔE	
	hartrees	kcal/mol
$\Delta E_{\text{reaction}}$		
$\Delta E_{\text{activation}}$		

$$\Delta E_{\text{reaction}} = E_{\text{product}} - (E_{\text{CV}} + E_{\text{OH4wat}})$$

$$\Delta E_{\text{activation}} = E_{\text{transitionstate}} - (E_{\text{CV}} + E_{\text{OH4wat}})$$

- Label the graph at the right with “**reactants**,” “**TS**” and “**product**”. Hint: refer to Figure 2 in the handout.
- Label several **tick marks** on the y-axis that are **consistent with** the ΔE values in the table.
- Draw a vertical up arrow and label it $\Delta E_{\text{activation}}$.
- Draw a vertical down arrow and label it $\Delta E_{\text{reaction}}$.



Is the crystal violet + OH⁻ reaction

endothermic _____ or

exothermic _____? (Check one)

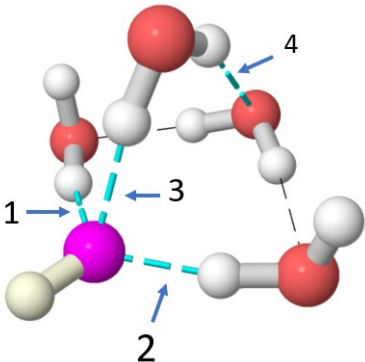
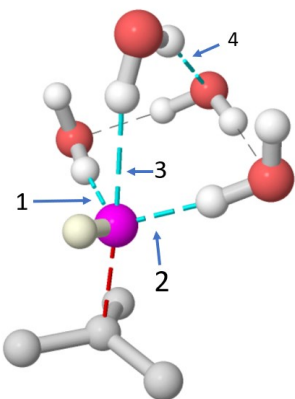
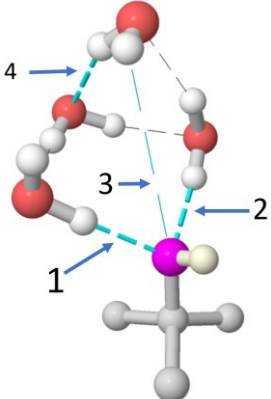
Reaction progress ->

2. C-O and hydrogen bond changes during the crystal violet – OH⁻ reaction

(a) In addition to forming a new C-O bond, several hydrogen bonds undergo significant changes during the CV + OH⁻ reaction. In WebMO, open the molecular energy jobs for the OH-4-water reactant, the CVOH-4-water transition state, and the CVOH-4-water product. In each one, use the **Adjust tool** to click the C-O and H-O pairs indicated in the table on the next page. The distance is displayed in the **lower left-hand corner**. Enter distances in the table.



To help identify hydrogen bonds, you may wish to visit the various interactive webpages and click the **Show H-bonds** and **Number H-bonds** buttons. Also, a second table below shows the corresponding atom numbers.

H-bond #	C-O or O.....H distance (Å)		
	OH...4-water	CV-OH-TS-4-water	CVOH-4-water
1			
2			
3			
4			
C-O			
			
(The ring-groups have been removed from these structures to clarify the graphics.)			

H-bond #	Indexes of the H-bonded atoms (as they appear in WebMO)		
	OH...4-water	CV-OH-TS-4-water	CVOH-4-water
1	4, 13	62, 71	46, 72
2	4, 6	62, 64	46, 64
3	4, 11	62, 69	46, 68 (not an H-bond, but record the distance)
4	1, 10	59, 68	69, 61

(b) Describe how these H-bond distances **change** during the OH⁻ addition reaction.

#1.

#2.

#3.

#4.

C--O

(c) **Why** – in terms of the **bond changes described above** - does the energy go **up to the transition state**, then **down to the product**?

C. The violet color of CV

In WebMO open your CV Molecular Energy calculation job by clicking the job name in the Job Manager. Scroll down to the Molecular Orbitals table near the bottom of the View Job page. Record the energies of the HOMO and LUMO in the table below. Repeat for the CVOH Molecular Energy calculation.

Here is a section of the MO table for CV with some explanatory annotations. Note that the MOs are listed in order of most stable (lowest energy) at the top, to least stable (highest energy) at the bottom.

Orbital MO #	Symmetry	Occupancy electrons/MO	Energy hartrees
97	1a	2	-0.254533
98	1a	2	-0.229201
99	1a	2	-0.191209
100	1a	2	-0.191149 ← HOMO
101	1a	0	-0.093109 ← LUMO
102	1a	0	-0.012298
103	1a	0	-0.001700
104	1a	0	-0.001626

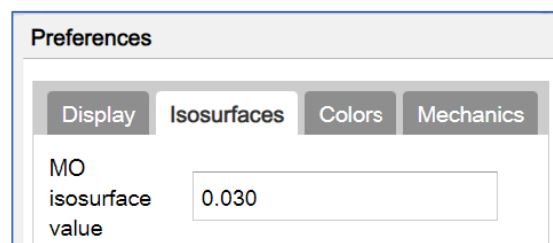
1. In the table on the next page, fill in the boxes based on the entries in WebMO's Molecular Orbitals table. Calculate the predicted λ_{max} for each species. Assume that the main peak in the UV-VIS spectrum is due to absorption of a photon whose energy equals the LUMO-HOMO gap.

This is a rather crude approximation and so your calculated λ_{max} values will be lower, i.e. at higher energy, than the experimental values. The reason for this discrepancy is that when an electron jumps up to the LUMO, the LUMO (and other MOs) instantly readjust to lessen the excitation energy, which requires a lower energy (longer wavelength) photon. Nevertheless, you should still be able to clearly distinguish between the spectral properties of CV and CVOH.

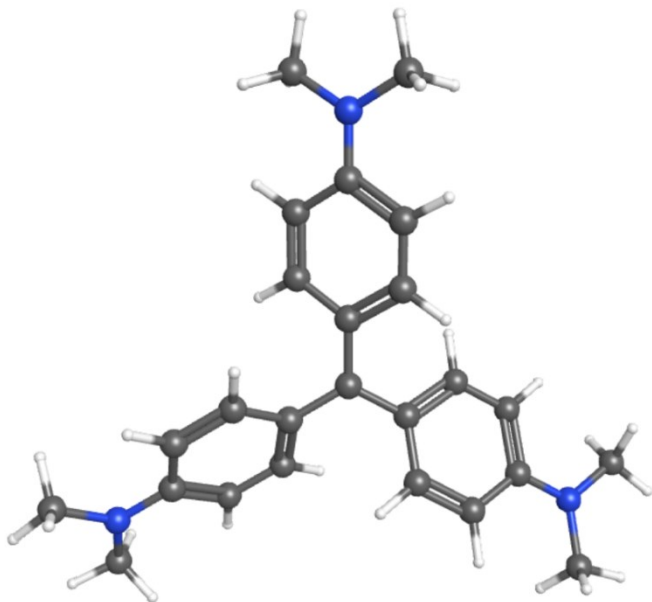
	CV	CVOH
HOMO energy (hartrees)		
LUMO energy (hartrees)		
$\Delta E_{\text{LUMO-HOMO}}$ (hartrees)		
$\Delta E_{\text{LUMO-HOMO}}$ (kcal/mol)*		
Calculated λ (nm) (the λ_{max}) [#]		
*1 hartree = 627.5095 kcal/mol		
[#] Use $\Delta E = h\nu = hc/\lambda$ h = Planck's constant = 6.626×10^{-34} Joule-sec c = speed of light = 3.000×10^{10} cm/sec		Avogadro's number = 6.022×10^{23} mol ⁻¹ 1 kcal = 4.184×10^3 Joule

Show your work here. Include units and the correct number of **significant figures**. Hint: Compare your CV answer to Fig. 5 in the handout.

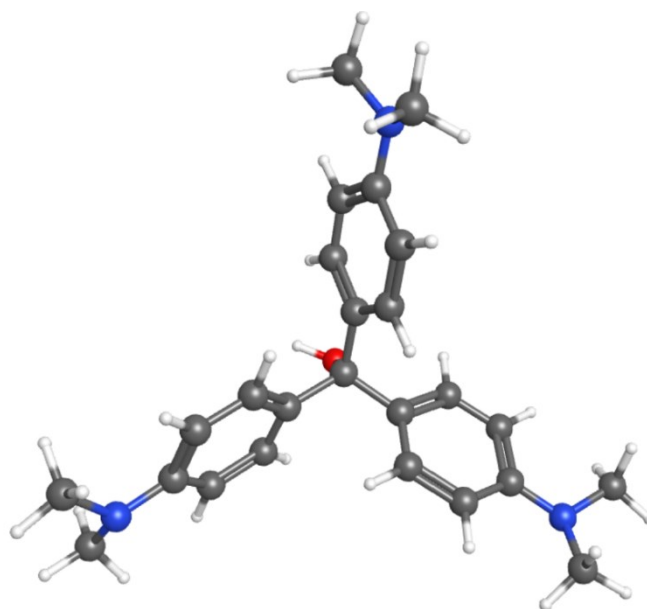
2. Compared to the LUMO in CVOH, the **LUMO of CV is spread over more atoms**, which is the main reason for the lower energy of CV's LUMO. Make rough drawings of the two LUMOs on the structures below. Hint: To get the best view of these MOs, set the "MO Isosurface value" to 0.030 by clicking Preferences button on the left-hand toolbar.



CV⁺



CVOH



3. Review Section 3.2 in your text on the **electromagnetic spectrum** (or visit the Wikipedia article on the same topic). Circle the spectral range where the calculated λ_{max} wavelengths occur.

CVOH	x-ray	ultraviolet	visible	infrared	microwave	radio
CV	x-ray	ultraviolet	visible	infrared	microwave	radio

4. When an **electron-rich ion**, such as **OH⁻**, reacts with a cation like CV, it pours its excess valence electrons into the cation's LUMO because the LUMO provides the lowest energy orbital to hold the electrons. The CV atom where the **largest lobe of the LUMO** is located is therefore the one most likely to bond to OH⁻.

Which CV atom is this - judging from your drawing in (2) or looking at the LUMO graphic in WebMO?
