Chem 106

TA_____   Name_____KEY_____

Worksheet: Crystal Violet and Quantum Theory

Where short answers are required, please use complete sentences.

This experiment requires 4 Molecular Energy, and 2 Molecular Orbital calculations. List the job numbers your answers are based on:

	Molecular Energy	Molecular Orbitals
Crystal violet cation CV	_____	_____
Crystal violet alcohol CVOH		_____
OH-..4-water cluster	_____	
CV-OH..4-water product	_____	
CVOH..4-water transition state	_____	

A. Partial charges in the CV⁺ ion
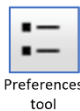
In WebMO, open your completed **Molecular Energy** calculation for **CV**. Check that the atoms are labeled with the **index number**. (If not, click the Preferences tool on the left toolbar, and under Labels, select Index.)

Preferences tool

1. (a) Scroll down to the Partial Charges table. **Fill in** the following table using the tabulated values or click the blue magnifying glass icon within the column heading of the table: To switch back to atom indexes, click the Reset Viewer button at the bottom of the display.

CV	
Atom	Charge (±0.001)
N 2	-0.500
N 24	-0.500
N 43	-0.500
C 7	0.358
C 19	0.358
C 38	0.358
Central C 15	0.036
Total charge	**1.000**
Total minus C15	0.964

(b) What **percent** of the total charge is on the **central carbon** (C 15)? _____3.6%_____

What **percent** of the total charge is on **all** the other atoms together? _____96.4%_____

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   slightly different   identical

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

The following formulas show several resonance forms of CV. Within each circled region change **four** single bonds into double bonds and add **one** "+" symbol. There are several ways of doing this, but **only one i**s consistent with the charges in the table in (a).

Add four C=C's
and one +

Add four C=C's
and one +
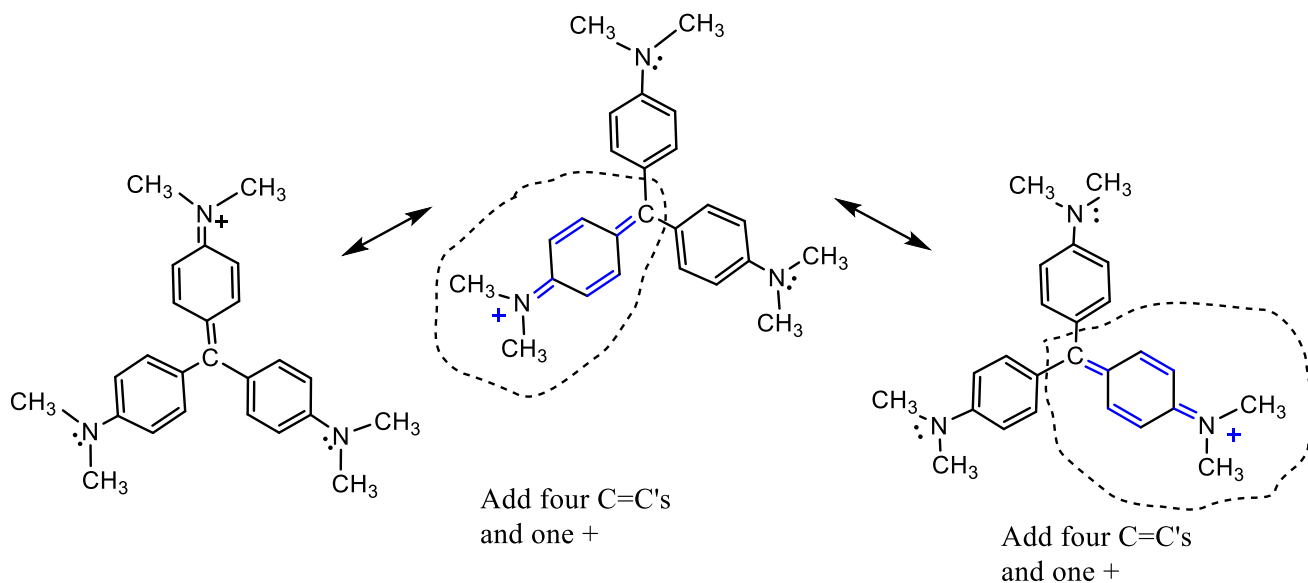
(d) Go back to the informational webpage and follow the link to **CV cation surfaces.** This page shows several surfaces:

- the **total electron density** distribution of the ion. 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 nucleus, and gradually decreases going out from the nucleus. Thus, an electron density surface can be drawn at any arbitrary value. The value used here is consistent with our notion of the **shape** of the molecule.
- The **electrostatic potential** surface combines the total electron density surface with a color scale that reports a **local excess of electrons** (red) or **lack of electrons** (blue) at points around the surface. **Red** spots occur where electrons protrude, such as lone pairs or π bonds. **Green** areas occur where there is zero formal charge and no excess or relative lack of electrons.
- The **electrophilic reactivity** surface combines the total electron density surface with a color scale showing the preferred location for **addition of electrons** (**blue**), which, for example, might originate from OH^- ion⁻. This happens to coincide with the center of the lowest unoccupied molecular orbital (LUMO).

Examine these surfaces, then provide brief answers:

(1) 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?

The electron density surface is **symmetric** around the whole structure. This is consistent with the resonance structures in part c that place an **equal charge (~ +0.3)** on each branch of the CV ion.

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

The electrostatic potential surface appears red above the N atoms (equally so for all 3 N's). As shown in part c above two out of three resonance formulas carry **a lone pair of electrons on each N.** So, you might say each of these N's carry 2/3 of a lone pair.

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, on the View Job page, record the energy in the table below. Look for "RB3LYP Energy" under Calculated Quantities, Overview.

For the ΔE rows, convert Hartrees to kcal/mol using the factor 627.5095 kcal/mol per Hartree.

		RB3LYP (Hartrees)* (to the 6th decimal place)	
Reactants	OH-4-water	-381.7193742	
	CV	-1134.879306	
Product	CVOH-4-water	-1516.614264	
Transition state	CVOH-4-water TS	-1516.587178	
			kcal/mol (record out to the 3rd decimal place)
	ΔE$_{reaction}$	-0.015585	-9.780
	ΔE$_{activation}$	0.011501	7.217

*"**R**" stands for **R**estricted, meaning all the electrons occur in pairs in the molecule. "B3LYP" is the type of density functional theory we are using to calculate molecular energy.

- Label the graph at the right with "reactants," "TS" and "product".
- 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 "ΔE$_{activation}$".
- Draw a vertical **down** arrow and label it "ΔE$_{reaction}$".
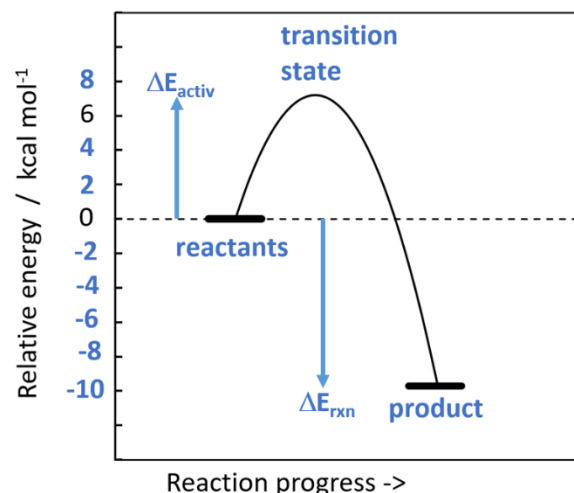
Is the crystal violet + OH- reaction

endothermic _____ or **exothermic**____✓____?
(Check one)

2. Carbon-oxygen and hydrogen bond changes

(a) In addition to formation of a new C-O bond, several H-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 below. The next page has a table with corresponding atom numbers. The distance is displayed in the **lower left-hand corner**. Enter distances in the table.

H-bond	C-O or O…..H distance (Å)		
	OH-..4-water	**CV-OH-TS-4-water**	**CVOH-4-water**
1	1.537	1.630	1.834
2	1.537	1.655	1.904
3	1.678	2.159	3.841
4	2.058	1.963	1.882
C-O		2.138	1.472

(The ring-groups removed to clarify the graphics.)

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

(b) Describe how these bonds **change** going from **reactants to T.S.** and from **T.S.to products**.

#1. H-bond #1 initially short and strong, remains in place but lengthens significantly.

#2. H-bond #2 initially short and strong, remains in place but lengthens significantly

#3. In the "top" water molecule one H-bond (#3) breaks off completely..

#4. and the other one (#4) shortens.

C—O   This bond is partially formed at the TS and fully formed in the reactant.

(c) Qualitatively, what is the overall energy impact of these changes during reaction? In other words, why does the energy **go up** to the transition state, then **down** to the product?

The energy goes up at the transition state because three H-bonds are broken or lengthened, while only one is strengthened. It is difficult to put exact values on the separate H-bond changes because they are strongly interrelated. Nevertheless, we can make a rough estimate by noting that the traditional value assigned to breaking an H-bond is about 3 kcal/mol. Thus, seriously weakening or breaking 2 or 3 H-bonds costs about 6 or 9 kcal/mol, which is about equal to the calculated activation energy ΔE_{act}.

The system becomes more stable as product forms due to the C-O bond formation. The full bond dissociation energy of a C-O bond (92 kcal/mole). Clearly ΔE does not come close to -92 kcal/mol – because the CV part of the molecule is also changing.

C. The violet color of CV

  In WebMO open your CV and CVOH Molecular Orbital calculation jobs by clicking the job name in the Job Manager. Scroll down to the Molecular Orbitals table near the bottom of the View Job page. For each, record the energies of the HOMO and LUMO in the table (next page).
Here is a section of the CV MO table 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.

1. Fill in the boxes based on your two Molecular Orbital calculations. 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 energy gap (ΔE) between LUMO and HOMO.

	CV	CVOH
HOMO energy (Hartrees)	-0.19421	-0.18474
LUMO energy (Hartrees)	-0.09613	-0.00560
$\Delta E_{LUMO-HOMO}$ (Hartrees)	0.09808	0.17914
$\Delta E_{LUMO-HOMO}$ (kcal/mol)*	61.55	112.4
Calculated λ_{max} (nm)	464.8	254.5
*1 Hartree = 627.5095 kcal/mol		
Use $\Delta E = h\nu = hc/\lambda$ h = Planck's constant = 6.626 x 10^{-34} Joule-sec c = speed of light = 3.000 x 10^{10} cm/sec Avogadro's number = 6.022 x 10^{23} mol^{-1} 1 kcal = 4.184 x 10^3 Joule		

(The calculated λ_{max} value for CV is far off from the experimental value of 590 nm. To get closer to the experimental value, a higher level of theory is required. For large molecules like CV, that will require much more computational time.)

Show your work here. Include units and the correct number of significant figures.

CV$^+$

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{\left(6.626x10^{-34}\ Js\right)\left(3.00x10^{10}\ cm\cdot s^{-1}\right)}{\left(61.55\,kcal\cdot mol^{-1}\right)\left(\frac{4.184x10^3\ J}{kcal}\right)\left(\frac{1\,mol}{6.022x10^{23}}\right)}$$

$$\lambda = 4.648x10^{-5}\ cm$$

$$\lambda = 4.648x10^{-5}\ cm \times \frac{10^7\ nm}{cm} = 464.8\,nm$$

CVOH

$$\Delta E = h\nu = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{\left(6.626x10^{-34}\ Js\right)\left(3.00x10^{10}\ cm\cdot s^{-1}\right)}{\left(112.4\,kcal\cdot mol^{-1}\right)\left(\frac{4.184x10^3\ J}{kcal}\right)\left(\frac{1\,mol}{6.022x10^{23}}\right)}$$

$$\lambda = 2.545x10^{-5}\ cm$$

$$\lambda = 2.545x10^{-5}\ cm \times \frac{10^7\ nm}{cm} = 254.5\,nm$$

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.

Preferences

Display	Isosurfaces	Colors	Mechanics

MO isosurface value: 0.030

CV⁺
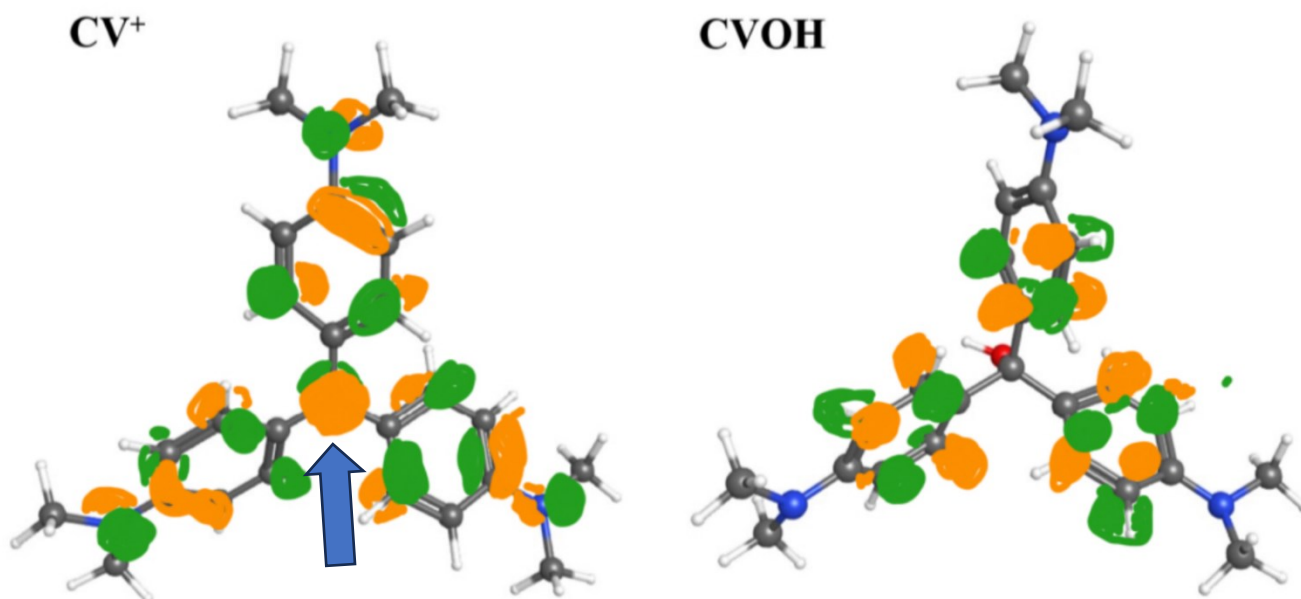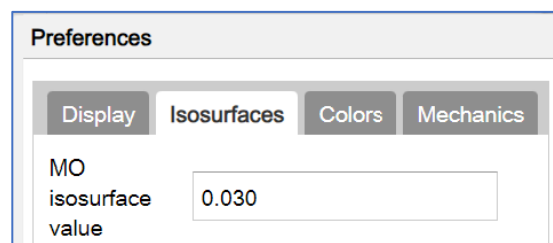
CVOH

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   ultraviolet   visible   infrared

CV   ultraviolet   visible   infrared

4. In the reactions of CV with electron-rich reactants such as OH⁻ ion, the CV atom with the **largest lobe of the LUMO** is most likely to receive the OH⁻ electrons to form a bond. Judging from your drawing in (2) or looking at the LUMO graphic in WebMO, which atom is this? _____#C 15 (arrow above)_____