Chem 106

TA_____   Name_____   Partner_____

Worksheet: Malachite Green 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 that your answers are based on:

	Job Number
Malachite green cation MG	_____
Malachite green alcohol MGOH	_____
OH-..4-water cluster	_____
MGOH..4-water product	_____
MGOH..4-water transition state	_____

A. Partial charges of MG

Answer the following questions using the results from the **Molecular Energy** calculation for **MG**. 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 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.

MG	
Atom	Charge **Round off to the nearest 0.001**
N 2	
N 24	
C 7	
C 19	
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 those two rings are ….
(**circle one**):

quite different   essentially identical

(c). Calculations show that **MG is resonance stabilized** with the (+) charge spread out 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 formulas for two resonance forms of MG⁺. One of the formulas is incomplete. Complete the formula by adding **four bond lines** and add **one** "+" symbol within the circled region. Hint: make it look like the resonance form on the left.

Add four C=C's
and one +
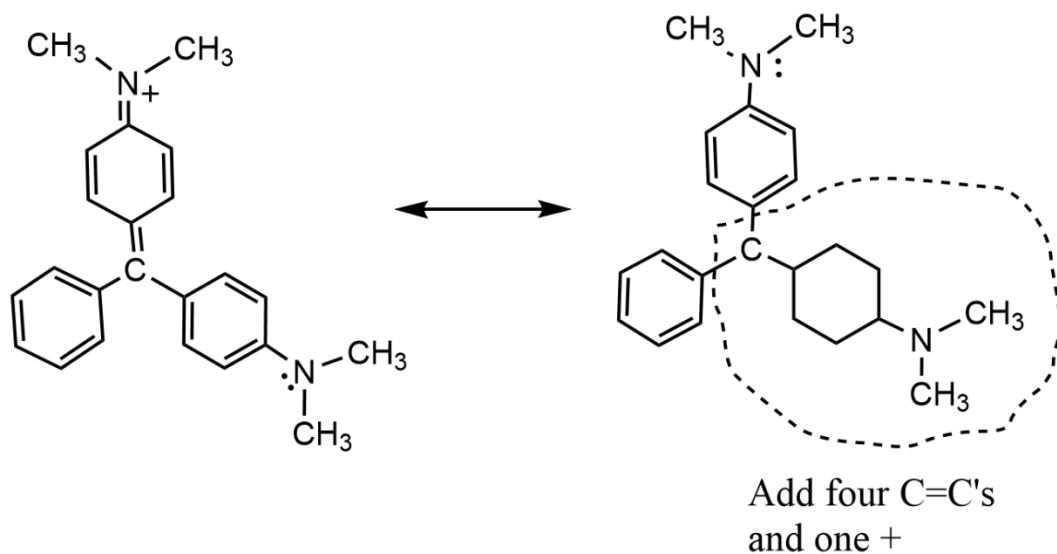
(d) Go back to the informational webpage and follow the links to several **surfaces** of the **malachite green cation**:

- 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.
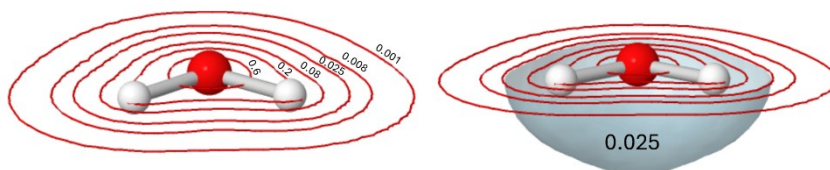
- The **electrostatic potential** surface combines the total electron density surface with a color scale that reports a **local excess of electrons** (orange or red) or **lack of electrons** (blue) at points around the surface. **Orange** or **red** spots occur where electrons protrude, such as **lone pairs** or **π bonds**. **Green** areas occur where there is no excess or lack of electrons. **Blue** areas are where electrons have shifted away, revealing more of the underlying 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:

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

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

B. The OH⁻ reactant and the MG⁺-OH⁻ transition state

1. Reaction energy and activation energy

Open the completed molecular energy jobs of MG, OH-4water complex, the MGOH-4water complex, and the MGOH-4water transition state. For each one, record the **energy** in the table below (labelled "Final Single Point Energy" under Calculated Quantities, Overview). Calculate the energy change for the overall reaction ($\Delta E_{reaction}$) and the energy of activation ($\Delta E_{activation}$).

For the right-hand column, convert Hartrees to kcal/mol using the conversion factor 627.5095 kcal/mol per Hartree.

(Optionally, this question can be carried out using **Excel, Numbers, or Google Sheets**. You can get all these numbers directly out of WebMO by first, highlighting the four jobs using the checkboxes, and second, choosing **Download, Spreadsheet**. In Excel, the energy values appear in **Column M**.)

		Final Single Point Energy (Hartrees) (round off to the 6th decimal place)	
Reactants	OH-4-water		kcal/mol (round off to the 3rd decimal place)
	MG		
Product	MGOH-4-water		
Transition state	MGOH-4-water TS		
Energy change	$\Delta E_{reaction}$		
	$\Delta E_{activation}$		

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

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

- Label the graph below 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 $\Delta E_{activation}$.

- Draw a vertical down arrow and label it $\Delta E_{reaction}$.

- Is the malachite green + OH- reaction **endothermic** _____ or **exothermic**_____? (Check one)
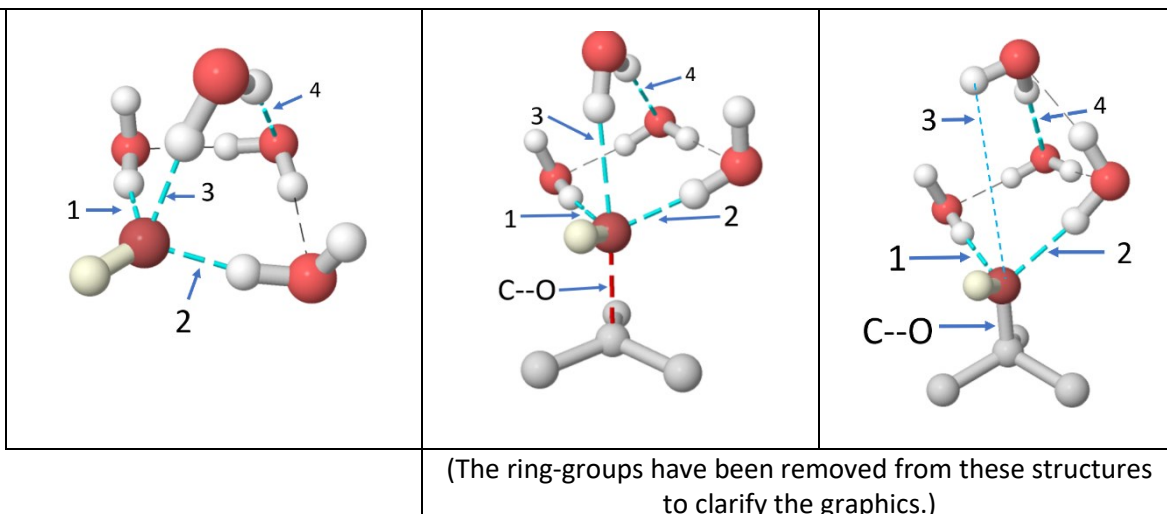

Reaction progress →
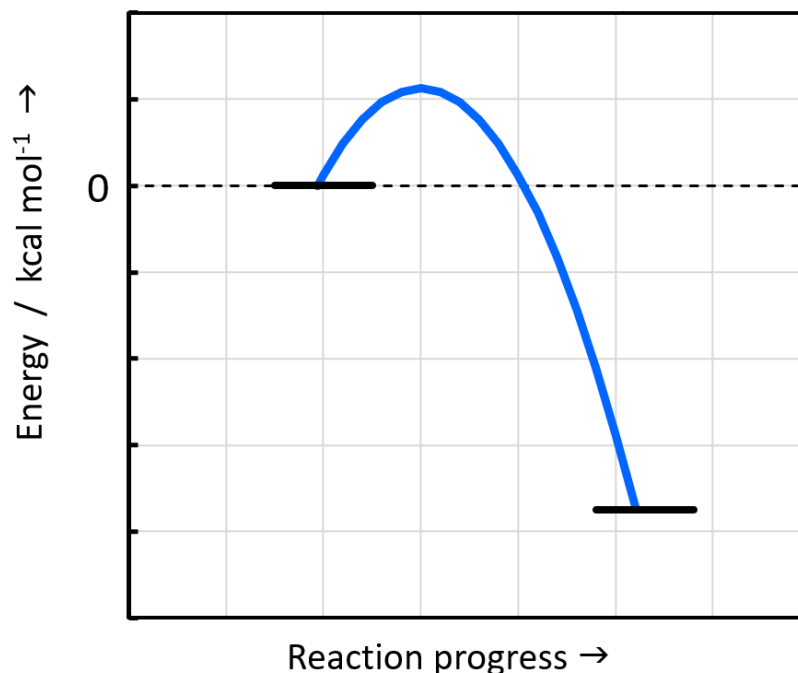
2. C-O and hydrogen bond changes during the malachite green – OH- reaction

(a) In addition to formation of a new C-O bond, several H-bonds undergo significant changes during the MG + OH⁻ reaction. In WebMO, open the molecular energy jobs for the OH-4-water reactant, the MGOH-4-water transition state, and the MGOH-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. In WebMO, 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	**MG-OH-TS-4-water**	**MGOH-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	MG-OH-TS-4-water	MGOH-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 and C-O distances **change** during the OH⁻ addition reaction.

#1.

#2.

#3.

#4.

C--O

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

C. The green color of MG

In WebMO open your MG 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 MGOH Molecular Energy calculation.

Here is a section of the MO table for MG 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	Symmetry	Occupancy	Energy	
MO #		electrons/MO	Hartrees	occupied
97	1a	2	-0.254533	
98	1a	2	-0.229201	
99	1a	2	-0.191209	
100	1a	2	-0.191148 ←HOMO	
101	1a	0	-0.093107 ← LUMO	
102	1a	0	-0.012298	
103	1a	0	-0.001700	
104	1a	0	-0.001626	unoccupied

1. Fill in the boxes based on the entries in the Molecular Orbitals tables. 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.
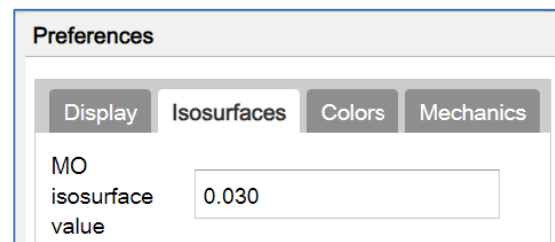
	MG	MGOH
HOMO energy (Hartrees)		
LUMO energy (Hartrees)		
$\Delta E_{LUMO-HOMO}$ (Hartrees)		
$\Delta E_{LUMO-HOMO}$ (kcal/mol)*		
Calculated λ (nm) (the λ_{max})#		
*1 Hartree = 627.5095 kcal/mol		
# Use $\Delta E = h\nu = hc/\lambda$ h = Planck's constant = 6.626 x 10^{-34} Joule-sec c = speed of light = 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		

Show your work here and on the next page. Include units and the correct number of **significant figures**.

Hint: Compare your answers to the spectrum in Fig. 5 in the handout.

2. Compared to the LUMO in MGOH, the **LUMO of MG is spread over more atoms,** which is the main reason for its lower energy of MG'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

MG⁺   **MGOH**

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.

MGOH	xray	ultraviolet	visible	infrared	microwave	radio
MG	xray	ultraviolet	visible	infrared	microwave	radio

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

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