A COMPUTATIONAL STUDY OF SCN⁻

REPORT INSTRUCTIONS

Create a computational study page in the Week 5’s folder. All Spartan files and tables for this experiment must be attached to or in the ELN. No formal lab report sections are needed.

INTRODUCTION

Lewis structures are created by summing the valence electrons of all the atom’s of a chemical species and then arranging those electrons so each atom typically has an octet of electrons. For example, the Lewis structure of NO₂⁻ has a total of 18 valence electrons – 6 from both oxygen atoms, 5 from the nitrogen atom, and 1 extra because of the negative charge.

\[
\begin{array}{c}
\text{O} \quad \text{N} \quad \text{O} \\
\text{N} \quad \text{O} \\
\end{array}
\]

When the Valence Shell Electron Pair Repulsion (VSEPR) theory is applied, the shape of the chemical species can be determined. The lone pair of electrons on the nitrogen atom will result in a bent molecule.

\[
\begin{array}{c}
\text{O} \quad \text{N} \quad \text{O} \\
\text{O} \quad \text{N} \\
\end{array}
\]

The placement of the double bond between the nitrogen atom and the oxygen on the right is arbitrary.

\[
\begin{array}{c}
\text{O} \quad \text{N} \quad \text{O} \\
\text{O} \\
\end{array}
\]

When two or more Lewis structures differ only by the placement of double or triple bonds, they are referred to as resonance structures. An imbalance of the number of lone and bonding pairs around a particular atom can potentially create a charge localized on that atom. The charge on that atom is referred to as formal charge and is calculated by the following equation:

\[
\text{Formal Charge} = \# \text{ of valence e'}\text{s} - (\# \text{ of lone pair e'}\text{s} + \frac{1}{2} \# \text{ of bonding pair e'}\text{s})
\]

For the oxygen atom singly bound to the nitrogen atom above, the formal charge is calculated as follows:

\[
\text{Formal Charge} = 6 - (6 + \frac{1}{2} (2)) = -1
\]

So, a more accurate representation of NO₂⁻ places the negative charge on the oxygen atom singly bound to the nitrogen atom and shows both resonance structures.

\[
\begin{array}{c}
\text{O} \quad \text{N} \quad \text{O} \\
\text{O} \quad \text{N} \\
\end{array}
\]
Note: Major resonance structures minimize the magnitude of formal charge on any one atom and the number of atoms assigned a formal charge.

What do the two resonance structures of NO$_2^-$ indicate about bond order and bond length?

Bond order indicates the degree of multiple bonding: A bond order of 1 indicates a single bond; a bond order of 2 indicates a double bond; and, a bond order of 3 indicates a triple bond. Bond order and bond length are inversely related. When comparing the same two atoms, a single bond is the longest and a triple bond is the shortest. In the two resonance structures of NO$_2^-$, a double bond is found between the nitrogen atom and either one of the oxygen atoms. The result is an averaging of bond length and bond order. The two N-O bond lengths have been empirically determined to be equal and in between single and double NO bond lengths, making the hybrid structure below a reasonable way to depict the ion.

\[
\begin{array}{c}
\text{O} \quad \text{N} \quad \text{O} \\
\end{array}
\]

When a chemical species absorbs the right energy of infrared radiation (IR), its bonds stretch and contract like a spring. Bond order directly correlates with the energy (frequency) of IR radiation absorbed. As the bond order increases, the bond is shorter because it is stronger. More energy (a higher frequency of radiation) must be absorbed to cause the bond to stretch. The absorption of the IR can be modeled with Spartan.

The IR of NO$_2^-$ is shown below:

The thiocyanate ion, SCN$, is a reagent in this week’s wet lab. In this assignment the resonance structures of this ion will be investigated with Spartan.
PROCEDURES

Creating the Resonance Structures:
1. Determine the two major resonance structures for SCN⁻. Both structures should have two atoms with zero formal charge and one atom with a -1 formal charge. Use the Sketch Entry Editor to draw both on the ELN page for this assignment.

2. Into two separate Spartan files, build both structures with the Inorganic Model Kit. Click on the button and then choose S (sulfur). Click anywhere in the workspace area to add the sulfur. Click on the button, choose C (carbon), and then add bond to the sulfur in the Workspace area. Click on the button, choose N (nitrogen), and then add bond to the carbon in the Workspace area. Bonds can be set to double or triple by selecting the appropriate button ( or ) and then double clicking on the single bond between the two atoms. Set the appropriate bond lengths for each resonance structure using the data in the table above to set the bond lengths.

3. Choose Measure Distance from the Geometry menu. Click on the two atoms involved in the bond (or directly on the bond itself). Enter the appropriate bond length (from the table below) in the Distance field in the bottom right hand corner of the program window. Hit Enter. Do NOT optimize the structure.

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Bond Length (Å)</th>
<th>IR Stretch (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-C</td>
<td>1.813</td>
<td>727</td>
</tr>
<tr>
<td>S=C</td>
<td>1.594</td>
<td>1190</td>
</tr>
<tr>
<td>S≡C</td>
<td>1.523</td>
<td>1418</td>
</tr>
<tr>
<td>C-N</td>
<td>1.472</td>
<td>1095</td>
</tr>
<tr>
<td>C=N</td>
<td>1.256</td>
<td>1849</td>
</tr>
<tr>
<td>C≡N</td>
<td>1.137</td>
<td>2395</td>
</tr>
</tbody>
</table>

4. Perform an Energy calculation with the Hartree-Fock 3-21G method for each resonance structure. Remember to set the Total Charge to Anion. Before submitting the calculation, click on the boxes to the left of Infrared Spectra and Vibrational Modes in the Calculation window.

5. Once the calculations are complete, check the bond lengths, they should be unchanged. (If they have changed, repeat the calculation, making sure you choose Energy instead of Equilibrium Geometry.) Go to the Display menu and choose Spectra. Click on + and select IR calculated. Click on the peaks in the Spectra window. The ion will be animated to show the vibration of bond length or angle at each frequency. Record the S-C and C-N bond lengths used and the frequencies that result in stretching vibrations of the same bonds in a table in your ELN.
Creating the *Actual Structure*:

1. Build SCN⁻ with the *Inorganic Model Kit*. Build the model as above. *Because two significant resonance structures exist for SCN⁻, double or triple bonds will not be added here. We will let Spartan decide the real structure (which is an unequal average of the two resonance structures).* Optimize the structure; click **Build**, and then **Minimize**.

2. Perform an **Equilibrium Geometry** calculation with the **Hartree-Fock 3-21G method**. Before submitting the calculation, click on the boxes to the left of **Infrared Spectra** and **Vibrational Modes** in the **Calculation** window.

3. Add to the table started above for S-C and C-N bond lengths and IR stretching frequencies.

4. Measure the bond lengths by clicking on the gray bond until a yellow “mask” appears around the bond. The bond length will then be displayed in the bottom right corner of the program window.

5. Go to the **Display** menu and choose **Spectra**. Click on + and select **IR calculated**. Click on the peaks in the Spectra window. Record the frequencies that result in stretching vibrations of the sulfur-carbon bond and for the carbon-nitrogen bonds.

*Log onto Sapling and complete the questions.*