In order to be able to utilize mass spectrometry in an intelligent manner, one has to have a basic understanding of the properties of gas-phase ions and radical ions. In order to demonstrate this, please answer the following questions:

1. Which site in each of the molecules shown below is the most basic site? Justify your choices. **8 pts**

![Chemical structures](image1)

C=O  
Resonance  
2 pts each answer

2. Which one(s) of the following cations are resonance stabilized? Draw all reasonable resonance structures for the ones you chose. **16 pts**

![Chemical structures](image2)

Yes (1 pt)  
No (1 pt)  
yes (1 pt)  
no (1 pt)  
no (1 pt)  

4 pts  
8 pts
3. Which C-H or N-H bond in each of the following cations has the lowest homolytic dissociation energy? Justify for each case. 8 pts
Arrows 1 pt each correct one

Resonance resonance resonance distonic ions are more stable
1 pt for each correct answer α-C; COOH: resonance

4. Arrange the following molecules in the order from most to least acidic. 10 pts

2nd 3rd 1st 4th 5th
2 pts each

5. Arrange the following molecules in the order from most to least basic: 10 pts

H2 1st 2nd / 3rd 4th 2nd / 3rd

5th 1st 2nd / 3rd 4th 2nd / 3rd

6. Which one(s) of the following cations are likely to rearrange? Show the rearrangement product(s). 18 pts

3 pts each case no no
7. Show the mechanism of a favorable unimolecular fragmentation pathway for each of the following cations. \textbf{15 pts}

\begin{align*}
\text{[Diagram showing cations and their fragmentation mechanisms]} \\
3 \text{ pts each correct answer} \\
\text{Loss of CO: 1 pt} \quad \text{\(\alpha\)-cleavage: 1 pt}
\end{align*}

8. Which cation shown above undergoes McLafferty rearrangement? \textbf{4 pts}

\textbf{The aldehyde}

9. Which cation shown in question 8 undergoes an \(\alpha\)-cleavage? \textbf{4 pts}

\textbf{The amine}

10. Which one(s) of the mechanisms shown for question 8 involve a rearrangement reaction and which one(s) involve a direct bond cleavage? Which type of reactions are usually faster? \textbf{7 pts}

Aldehyde: rearrangement; all others: direct bond cleavage: 5 pts
Direct bond cleavages are faster: 2 pts
Biochemistry Cumulative Exam

Title: Posttranslational Modifications

April 25\textsuperscript{th}, 2015

1. (20 points) (i) What is sumoylation? Provide the steps that lead to sumoylation.

SUMO (Small ubiquitin-related modifier) is an ubiquitin-like protein that is covalently attached to a variety of target proteins.

(ii) Which amino acids are modified during sumoylation?

Lysine

2. (10 points) Provide any two examples by which proteins are activated by limited proteolysis.

Trypsin is generated by the proteolysis of trypsinogen. Similarly, chymotrypsin is generated by the proteolysis of chymotrypsinogen.

3. (10 points) Draw the chemical structure of any N-linked glycosylated peptide.
4. (40 points) (i) Which enzyme catalyzes sulfation in cells? Provide the complete enzymatic reaction of sulfation.

Tyrosyl protein sulfotransferases catalyze sulfation.

(ii) Where does it occur in cells? Which amino acids are sulfated in cells?

It occurs in Golgi apparatus. Tyrosine is the only amino acid that is known to be sulfated.

(iii) What is the most common consequence of sulfation?

Sulfation plays a role in strengthening protein-protein interactions.

(iv) Is it a reversible or irreversible process?
Irreversible

5. **(20 points)** What is the most common post-translational modification that can lead to epigenetic silencing? Provide the enzymatic reaction and a brief molecular mechanism by which it leads to epigenetic silencing.

Methylation at K or R on histones can lead to epigenetic silencing.

Methylated histones bind chromatin binding domain containing proteins leading to transcription repression or epigenetic silencing.
No Inorganic crib available
April 25, 2015
Written by Professor Abu-Omar
Ph# 45302

No Organic crib available
April 25, 2015
Written by Professor Ghosh
Ph# 45323
7 pts. each

April 2015 Course Answers

(a) \[-\frac{\hbar^2}{2m a^2} \frac{\partial^2 \Phi}{\partial \phi^2} - \frac{\hbar^2}{2m} \frac{\partial^2 Z}{\partial z^2} = E \Phi \]

(b) Assume \( \Phi(\phi, z) = \Phi(\phi) Z(z) \)

(c) \[-\frac{\hbar^2}{2ma^2} Z(z) \frac{\partial^2 \Phi}{\partial \phi^2} - \frac{\hbar^2}{2me} \frac{\partial^2 Z(z)}{\partial z^2} = E \Phi Z \]

Dividing through by \( \Phi Z \):

\[-\frac{\hbar^2}{2ma^2} \frac{1}{\Phi(\phi)} \frac{\partial^2 \Phi}{\partial \phi^2} - \frac{\hbar^2}{2me} \frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} = E \]

Collecting all the \( \phi \) dependence on one side of the eqn and the \( z \)-dependence on the other:

\[-\frac{\hbar^2}{2ma^2} \frac{1}{\Phi(\phi)} \frac{\partial^2 \Phi}{\partial \phi^2} = E + \frac{\hbar^2}{2me} \frac{1}{Z(z)} \frac{\partial^2 Z(z)}{\partial z^2} \]

The only way for this eqn to hold for all \( \phi, z \) is for each side of eqn to separately be constant.

(1) \[-\frac{\hbar^2}{2ma^2} \frac{\partial^2 \Phi}{\partial \phi^2} = E_\phi \Phi(\phi) \quad \text{2 ordinary differential eqns.} \]

(2) \[-\frac{\hbar^2}{2me} \frac{\partial^2 Z}{\partial z^2} = \frac{(E - E_\phi) Z(z)}{E_z} \]

E_z
d) Circumference = $2\pi a = 9.420 \text{ pm} = 3780 \text{ pm}$

\[ \cos 60^\circ = \frac{1}{2} \quad \Rightarrow \quad 1 \text{ repeat sub-unit} = 420 \text{ pm} \]

\[ \Rightarrow \quad \alpha = 600 \text{ pm} \]

\[ \text{radius of nanotube.} \]

e) \[-\frac{e^2}{2me^2} \frac{d^2\Phi}{d\phi^2} = E_\phi \Phi \]

\[ \Rightarrow \frac{d^2\Phi}{d\phi^2} = -\frac{E_\phi}{\left(\frac{e^2}{2me^2}\right)} \Phi(\phi) = -m^2 \Phi(\phi) \] (eqn)

\[ \Rightarrow \text{by inspection,} \quad \Phi(\phi) = A_m e^{im\phi} \]

\[ \Rightarrow \quad \frac{d\Phi}{d\phi} = im A_m e^{im\phi} \]

\[ \Rightarrow \frac{d^2\Phi}{d\phi^2} = -m^2 \Phi \]

f) \[ \Phi(\phi) = \Phi(\phi + 2\pi) \quad \text{(Wave function must be single-valued).} \]

\[ A_m e^{im\phi} = A_m e^{im\phi} \cdot e^{i2\pi} \Rightarrow e^{i2\pi m} = 1 \]

\[ \Rightarrow \quad m = \text{integer} = 0, \pm 1, \pm 2, \ldots \]

g) \[ \int_{0}^{2\pi} \Phi^* \Phi = 1 \quad \Rightarrow \quad A_m^2 \int_{0}^{2\pi} e^{-im\phi} e^{+im\phi} d\phi = 1 \]

\[ \Rightarrow \quad A_m = \sqrt{\frac{1}{2\pi}} \]
(h) Looking at eqn (1) we see that

\[ E_g = \frac{h^2}{2me^2} \cdot M^2 = B \cdot m^2 \]

\[ \frac{E_g}{\hbar c} \text{ (cm}^{-1} \text{)} = \left( \frac{h}{8\pi^2 m_e c \cdot a^2} \right) \cdot m^2 \]

\[ B \text{ (cm}^{-1} \text{)} = \frac{h}{8\pi^2 m_e c \cdot a^2} = \frac{6.6 \times 10^{-34} \text{ J sec}}{8\pi^2 (9.1 \times 10^{-31} \text{ kg})(3 \times 10^8 \text{ cm/sec})} \cdot (6 \times 10^{-10} \text{ m})^2 \]

\[ B = 850 \text{ cm}^{-1} \]

(i) \[ -\frac{h^2}{2m_e} \frac{d^2Z(z)}{dz^2} = E \cdot Z(z) \]

This is the 1D particle-in-a-box time-independent Schrödinger eqn.

\[ \Rightarrow \text{ free motion of e}^- \text{ along length of tube, } \]

infinite barrier at end of tube.

Since one end of the tube is set at \( z = 0 \)

\[ Z(z) = \sqrt{\frac{L}{\pi}} \sin \left( \frac{n\pi z}{L} \right) \]

\[ \Rightarrow E_n = \frac{n^2 \hbar^2}{8mL^2} \]

where \( n = 1, 2, 3, \ldots \)

(j) \[ L = 8.240 = 2.0 \text{ nm} \]

\[ \frac{E_n}{\hbar c} = \frac{h}{8m_e c \cdot L^2} \cdot n^2 = (750 \text{ cm}^{-1}) n^2 \]
Combining the two:

\[ E_{\text{tot}} = E_z + E_\phi \]

\[ E_{\text{tot}} = 750 \cdot n^2 + 850 \cdot m^2 \quad \text{where} \quad n=1,2,3,... \\
\quad m=0, \pm 1, \pm 2, ... \]

\[ \psi(z, \phi) = Z(z) \cdot \Phi(\phi) \]

\[ \psi(z, \phi) = \left\{ \sqrt{\frac{2}{L}} \sin \frac{n\pi z}{L} \right\} \left\{ \frac{1}{\sqrt{2\pi}} e^{i\mu\phi} \right\} 
\quad n=1,2,3,... \\
\quad m=0, \pm 1, \pm 2, ... \]

(l) Energy-level diagram:

<table>
<thead>
<tr>
<th>( n )</th>
<th>( m )</th>
<th>( E_{n,m} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>750</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>3000</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>6750</td>
</tr>
<tr>
<td>1</td>
<td>±1</td>
<td>1600</td>
</tr>
<tr>
<td>2</td>
<td>±1</td>
<td>3850</td>
</tr>
<tr>
<td>3</td>
<td>±1</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>±2</td>
<td>4150</td>
</tr>
</tbody>
</table>

(m) \# of \( e^- \)s = 1 per C
\[ 9 \times 6 \times 8 = (432 \pi e^-) \]