

Lecture I-3: The Molecular Ion

(McLafferty Chapter 3)

CU- Boulder

CHEM 5181

Mass Spectrometry & Chromatography

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Fall 2007

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Issues for Start of Class

- HW#5 due today
- HW#4 graded
 - Better grades for wrong molecule, right arguments
 - Always explain **WHY** you are concluding something
- Schedule adjustments
 - See updated handout, hopefully no more changes
 - 2nd Midterm on 13-Nov (interpretation)
- Progress on projects?
 - Everything due Nov. 15
 - Summary due today

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Clicker Question

- With an error level of +/-15% or 1% absolute, whichever is greater
- If $[A+2]/[A]$ for the molecular ion is 2.3%
 - A. The molecule cannot contain Cl and Br, but can contain S or Si
 - B. The molecule cannot contain Cl, Br, and S, but can contain Si
 - C. The molecule can contain 21 carbons
 - D. The molecule can contain 55 carbons
 - E. I don't remember that stuff any more...

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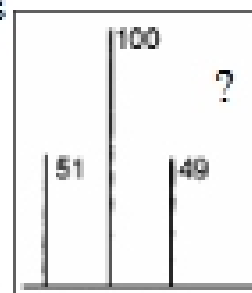
Standard Interpretation Procedure

2. Using isotopic abundances (where possible) deduce the **elemental composition** of each peak in the spectrum; calculate **rings plus double bonds** (last day).
3. Test **molecular ion** identity; must be the highest mass peak in spectrum, odd-electron ion, and give logical neutral losses. Check with CI or other soft ionization (**TODAY**).
4. Mark **'important' ions**: odd-electron and those of highest abundance, highest mass, and/or highest in a group of peaks (**TODAY**).

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The Molecular Ion

- **Most valuable** info of the mass spectrum
 - Molecular mass
 - Elemental composition
 - Fragments **must** be consistent with it
- **Not always** stable with EI
 - Careful about overinterpreting peak of highest m/z !
 - Use **soft**-ionization such as CI in parallel
- MS Definition:
 - m/z of the molecular ion is the peak that contains the most abundant isotope of all the elements involved (by convention)
 - Won't always be most abundant peak



Requirements for the Molecular Ion

- Necessary **but not sufficient** conditions
 - It must be the ion of highest mass (isotope caveat)
 - It must be an **odd-electron** ion (for EI)
 - It must be capable of yielding the most important ions in the high-mass region by loss of **logical** neutral species
- If candidate fails either test, cannot be MI
- If candidate passes all tests, may or may not be MI