1. (20%) What additional components must be added to the above apparatus to perform a TPEPICO experiment? Include in your answer an explanation of how the internal energy of the ions measured by a simple single photon ionization experiment vary from those measured in a TPEPICO experiment. Hint: The additional component is not the Mckenna Burner, which you can assume would also be swapped out for a gas source.

2. (10%) Collision activated dissociation (CAD) is the most common method for increasing internal energy in a parent ion to induce fragmentation and it is experimentally simpler than TPEPICO. What is the primary difficulty in using CAD for precise thermochemical measurements?

3. (10%) Name two different light sources that can be used for TPEPICO experiments. Hint: they must produce vacuum ultraviolet (VUV) photon energies from ~8 – 15 eV.
Sb(CH₃)₃ and Bi(CH₃)₃ are single photon ionized to form their parent ions and the fragments Sb(CH₃)₂⁺ and Bi(CH₃)₂⁺, respectively in a TPEPICO experiment. Photon energies vary as shown on the x-axis. Intensity of the two ions from each molecule (y-axis) vs. photon energy (hv, x-axis) are measured experimentally (Hornung, *J. Phys. Chem. A* 113 (2009) 8091).

4. (10%) The ionization potential of both Sb(CH₃)₃ and Bi(CH₃)₃ were determined by data not shown to both be ~8.05 eV. Draw what that data might look like if measured with a TPEPICO apparatus and explain its interpretation.

5. (10%) Which species binds methyl more strongly? Justify your answer with a simple calculation based upon the above data. Ignore the E₀ values.

6. (10%) The fully analyzed experimental data yielded onset energies E₀ for methyl radical loss of 10.068 and 9.445 eV for Sb(CH₃)₃ and Bi(CH₃)₃ respectively. These E₀ values appear at very different ratios of parent to fragment ions for the two compounds. Why? Explain what data analysis might have been used to get E₀ values.

7. (10%) Bi(CH₃)₃ is ionized in a different mass spectrometer by a new ionization technique: it yields no Bi(CH₃)₃⁺ but only Bi(CH₃)₂⁺ & Bi(CH₃)⁺. What specifically can you say about internal energy imparted to the parent ion by the new ionization method. Explain your answer.
TPEPICO was used to record breakdown diagrams of propene taken under the indicated conditions. Circles and triangles are experimental points, and lines are best-fit simulations using identical parameters. This data was discussed by Tom Baer during his UIC Chemistry seminar on 1/28/10.


8. (20%) The heat of formation of the allyl ion (CH2CHCH2+) was determined to be $\Delta H^\circ_{f,0K} = 967.2$ kJ/mol from the above TPEPICO data and additional literature data obtained by other methods. Draw a thermochemical diagram and equation showing how this determination was made and what literature data values were required to complete it. Note: do not worry about the differences in the data at various temperatures or using different time of flight instruments (ReTOF vs. LinTOF).