

Due at the beginning of class Monday, October 16
NO LATE PAPERS ACCEPTED!

Complete these problems on separate paper and staple it to these sheets when you are finished. Please put your name or initials on each sheet as well. Clearly mark your answers. YOU MUST SHOW YOUR WORK TO RECEIVE CREDIT.

Instructions

- This is **NOT** an open-book, open-note take exam. You MAY NOT consult any human or nonhuman resource besides Dr. Lamp as you complete the exam. This exam MUST be completed INDIVIDUALLY and in your own words. Group work or plagiarism will result in a zero for the exam.
- You will be allowed to ask Dr. Lamp a maximum of two (2) questions regarding the exam. Additional questions may be asked at a 3-point penalty per question. If you are working on the exam in the evening, you may try to reach Dr. Lamp on his cell phone at 660-341-0067 before 10:00 PM.
- Before opening the exam, prepare for it like you would for a traditional, in-class exam. Review concepts and examples from the text, as well as those discussed in class. This preparation will help to maximize your effort on the exam and allow you to complete it more efficiently.

Time Restriction

You may spend no more than two (2) hours working on this exam. This must be in one continuous block of time. You are on your honor to adhere to this restriction and record the time spent in the chart below.

Date	Time Began	Time Finished	Total Time
Total Time Spent on the Exam			

Pledge

I pledge on my honor that I have completed the exam in accordance with the above instructions and that I have not provided or received unethical assistance. I realize that failure to comply with these instructions will result in a score of zero on the exam.

Signature

Date

Complete these problems on separate paper and staple it to this sheet when you are finished. Please initial each sheet as well. Clearly mark your answers. YOU MUST SHOW YOUR WORK TO RECEIVE CREDIT.

Warm-up (2 points each)

1. A cascade of electrons between a series of _____ **dynodes** _____ in an electron multiplier results in the high sensitivity of the device.
2. A fourier transform must be applied to deconvolute the mass spectrum from data obtained from an _____ **ion cyclotron resonance** _____ mass analyzer..

Answer in a sentence or two, or with a calculation. Complete seven of the following. Clearly indicate which problem is not to be graded. (14 points each)

3. Mass spectra from electron impact (EI) sources are typically much more complicated than those from chemical ionization (CI), explain why this is the case. Why do typical MS instruments designed for organic mass spectrometry often have both EI and CI capabilities?
EI sources are hard ionization sources, with ions formed after collision with high energy electrons, producing excited state ions that are typically susceptible to extensive fragmentation. As a result, the molecular ion peak (M^+) is typically very small or nonexistent in a mass spectrum collected using an EI source.

CI sources are soft ionization sources, with ions produced by collisions with lower energy reagent gas ions, that tend to produce spectra with much less fragmentation. As a result of reactions with the ionizing gas in the source, the molecular ion peak, which is typically strong, occurs at $(M+1)^+$ or $(M-1)^+$.

The combination of EI and CI capabilities is fairly trivial in terms of hardware and provide the opportunity to get both molecular ion and fragmentation information.

4. The overall resolving power of a mass spectrometer is the result of limitations from all components of the MS. Describe how each of the following serves to limit resolution in a MS experiment.

a. The ionization source (such as an EI source)

Most mass analyzers separation ions on the basis of their kinetic energy, velocity, or momentum. Each of these parameters depends on the extraction of a packet of ions from the ionization source that has a very narrow spread in the parameter being filtered. Depending on the design of the source and extraction ion optics, ions of a single m/z may exit the source with a spread in kinetic energy (or velocity or momentum). The larger the spread, the less effective the mass separation will be.

b. The mass analyzer (such as a quadropole)

In their filtering mechanism, most mass analyzers utilize controlled electric or magnetic fields to manipulate ions. Therefore, the ability to precisely control these fields plays a major role in differentiating ions of similar mass to charge.

c. The detector (such as an electron multiplier)

Since the role of the detector is to basically count ions, it has very little impact on the resolution of the MS experiment. I suppose in a TOF experiment, the response time of the detector would be very important, so that ions with slightly different flight times could be resolved.

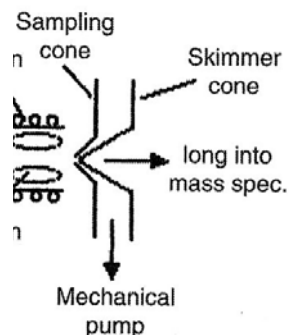
- Electrospray ionization (ESI) and MALDI are two relatively new approaches to ionizing large molecules. Compare how ions are formed in each process and discuss the similarities and differences in the spectra observed from the two sources.

The two main big molecule ionization sources we discussed were MALDI and Electrospray ionization.

MALDI: The analyte is dispersed in a MALDI matrix (a molecule that readily sublimates when it absorbs energetic photons) and deposited onto a target. The target is irradiated with a laser pulse, resulting in absorption and sublimation of the matrix (including the analyte) and ionization. The result is the formation of intact molecular ions, most are singly charged. Benefits: Soft ionization source. Good for molar mass determination. Challenges: Pulsed source, need mass analyzer that can handle pulsed introduction. Need appropriate matrix.

Electrospray: The sample solution flows through a needle which is subject to a large electric field. As solution leaves the needle, it obtains a charge. Electrostatic repulsion causes the charged stream to break into smaller charged droplets, which continue to “explode” until solvent is essentially evaporated and ionized analyte remains. This is a more energetic ionization source, capable of producing multiply charged ions and fragments. Benefits: Continuous source. No additional sample handling steps. Challenges: May lead to complex spectra. Need to remove some sample to produce lower pressure for mass analyzer.

- Both inductively coupled plasma (ICP) and atmospheric pressure chemical ionization (APCI) sources use similar approaches to interface the source to a mass analyzer. Sketch the interface used and describe how the interface allows the two different pressure regimes to work together.



I'd expect a diagram like the portion of Figure 9.14 from your text, shown above. The key to the interface is its ability to step the pressure down from atmospheric to the vacuum necessary for the MS to function. This is accomplished by inserting cooled “cones” between the ionization source and the MS. The sampler cone is a small cooled orifice whose purpose is to allow only a small fraction of the gas expelled from the plasma to pass. Since the sample is on the central axis of the source, it is transmitted somewhat preferentially to the argon plasma gas. As the gas passes through the sampler, it moves into a region of lower pressure, where the gas expands. The central region passes through another orifice, the skimmer cone, and into the mass analyzer.

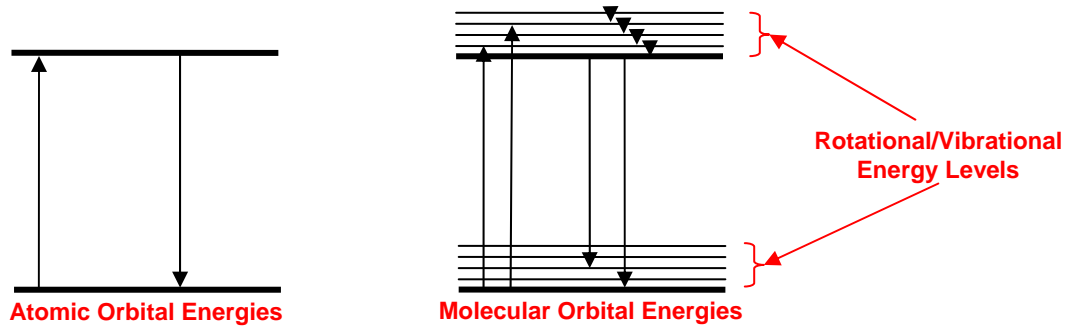
- Describe the phenomena that give rise to Raman scattering.

As a photon interacts with a molecule, electronic couple can excite the molecule of a short-lived *virtual state*. These virtual states differ in energy from the ground states by the size in energy of the incident photon. If a molecule is excited from the lowest ground vibrational state to a virtual state and falls back to a vibrationally excited ground state, the energy of the

scattered photon will be diminished (Stokes Scattering). If a vibrationally excited state molecule is excited to a virtual state and relaxes to a non-vibrationally excited ground state, an increase in the energy of the scattered photon results (Anti-Stokes). Since the transitions for Stokes scattering are more probable than Anti-Stokes, Stokes lines are more intense.

8. Generally, absorption bands in atomic spectra are much narrower than those in spectra of molecules. Clearly explain why this is so, using orbital energy diagrams to illustrate your points.

I'd expect a diagram like this:



Your discussion should focus on the fact that while molecules, like atoms, have discrete electronic energy levels, they also possess rotational and vibration energy levels. These rotational and vibration states sit on top of each electronic energy level, providing a much larger number of possible transitions for the molecule to undergo. Any diagrams that you draw should indicate these additional transitions.

9. Currently, two of the most popular mass analyzers are the quadrupole mass filter and the time of flight mass analyzer. These two devices have very different principles of operation. Clearly describe how each device serves to separate ions and the key benefits and limitations of each device.

Quad: As they move through the mass filter, ions are subject to both AC and DC potentials. Depending on their size, ions may be influenced differently by the RF and DC components. For example, heavy ions are least influenced by the RF component, while light ions are most influenced by the RF. The balance between DC and RF determines whether an ion will have a stable path. Spectra can be scanned by systematically adjusting either the RF or DC voltages. Benefits: Small, able to handle higher pressures, able to scan spectra rapidly. Challenges: relatively low resolving power.

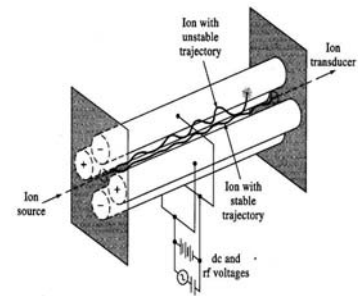


Figure 11-4 A quadrupole mass spectrometer.

TOF: The TOF mass analyzer relies on the fact that ions that have different mass but the same kinetic energy will be moving at different velocities ($KE = mv^2/2$). Therefore, ions are formed in a pulse and the time that takes the ions to move through the field free region of the flight tube is measured. Once calibrated, these times can be used to determine the mass to charge of individual ions. Benefits: potential for high resolution and very fast analysis. Challenges: depending on the length of the drift tube, vacuum requirements might be demanding. Need to coordinate ionization and detection timing.

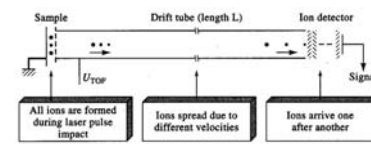


Figure 11-8 Principle of a time-of-flight mass spectrometer. A bunch of

- The mating of mass spectrometry and separations techniques has been and continues to be an area of great interest. Why is this so? Select one separation technique and clearly describe how mass spectrometry has been incorporated as a detection scheme for the separation. Draw a diagram of the instrument and describe in detail how the separation and mass analysis components are interfaced and how ions are formed.

Mating separations and MS allows the analyst to work with more complex samples while obtaining both quantitative and identification information on components of the sample. The key challenge in interfacing separations and MS is the very different conditions at which each instrument operates. For example, in traditional HPLC, eluent exits the column at mL/min flow rates, resulting in a large amount of material exiting the LC in a short time. If all of this material were introduced into the MS, it would be impossible to maintain the high vacuum conditions required to provide a large mean free path for the ions produced in the MS. Therefore, a significant effort has been made optimizing the interface. Since it can tolerate larger pressures, quadrupole mass analyzers have been the most popular for interfacing with separation techniques.

GC: For capillary column GC, the low mass flow of gas allows the end of the capillary to be inserted directly into the ionization source of the MS. For packed column GC, a jet separator is typically used to preferentially allow analyte to pass into the source, discarding much of the carrier gas.

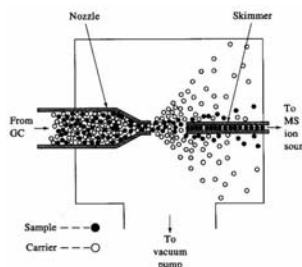


Figure 27-14 Schematic of a jet separator. (Courtesy of DuPont Inst Wilmington, DE.)

LC: The advent of split sample introduction as well as capillary columns, combined with the higher working pressure of quadrupole or ion trap MS has been instrumental in combining LC and MS.

CE: The most common interface for CE is electrospray. Since the volume of material leaving the separation capillary is smaller (nL) than that for LC (mL), the challenge of decreasing pressure between the separation and mass spectrometer is somewhat diminished. Similar approaches are used for LC and CE (sampler and skimmer, etc...)

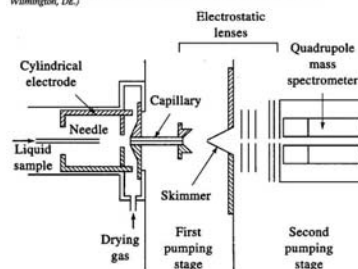


Figure 20-8 Apparatus for electrospray ionization. (From J. B. Fenn et al., Science, 1989, 246, 65.)

Possibly Useful Information

$E = \frac{hc}{\lambda} = hv$	$c = 3.00 \times 10^8 \text{ ms}^{-1}$
$\lambda = \frac{RT}{\sqrt{2\pi d^2 N_A P}} \approx \frac{5 \text{ cm}}{\text{mtorr}}$	$F_M = Bzev = \frac{mv^2}{r} = F_c$
$\frac{m}{z} = \frac{B^2 r^2 e}{2V} = F_c$	$U_{dc} + V_{ac} \cos \omega t$

PERIODIC CHART OF THE ELEMENTS

IA	IIA	IIIB	IVB	VB	VIB	VIIIB	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	INERT GASES		
1 H 1.00797														1 H 1.00797	2 He 4.0026		
3 Li 6.939	4 Be 9.0122										5 B 10.811	6 C 12.0112	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.183	
11 Na 22.9898	12 Mg 24.312										13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.064	17 Cl 35.453	18 Ar 39.948	
19 K 39.102	20 Ca 40.08	21 Sc 44.956	22 Ti 47.90	23 V 50.942	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.847	27 Co 58.9332	28 Ni 58.71	29 Cu 63.54	30 Zn 65.37	31 Ga 69.72	32 Ge 72.59	33 As 74.9216	34 Se 78.96	35 Br 79.909	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.905	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc (99)	44 Ru 101.07	45 Rh 102.905	46 Pd 106.4	47 Ag 107.870	48 Cd 112.40	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.30
55 Cs 132.905	56 Ba 137.34	*57 La 138.91	72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.09	79 Au 196.967	80 Hg 200.59	81 Tl 204.37	82 Pb 207.19	83 Bi 208.980	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	†89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (266)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 ? (271)	111 ? (272)	112 ? (277)						

Numbers in parenthesis are mass numbers of most stable or most common isotope.

Atomic weights corrected to conform to the 1963 values of the Commission on Atomic Weights.

The group designations used here are the former Chemical Abstract Service numbers.

* Lanthanide Series

58 Ce 140.12	59 Pr 140.907	60 Nd 144.24	61 Pm (147)	62 Sm 150.35	63 Eu 151.96	64 Gd 157.25	65 Tb 158.924	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.97
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† Actinide Series

90 Th 232.038	91 Pa (231)	92 U 238.03	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (256)	103 Lr (257)
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