

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.

Bonus: (6 points) What experimental challenges are each of the following designed to address?

- Calibration with an internal standard. **Run-to-run variability**
- Calibration using standard additions. **Matrix effects**

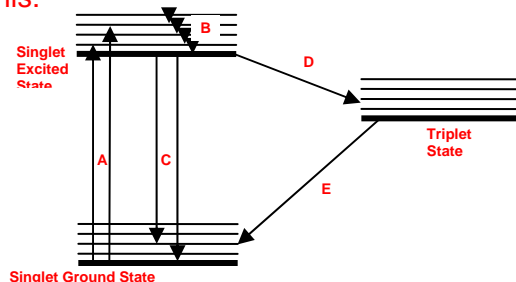
Warm-up (2 points each).

- The **dispersion** _____ is a quantitative measure of how a grating spreads incident wavelengths along the focal plane of the monochromator.
- In **Raman Spectroscopy** _____ molecules are promoted to metastable virtual states before relaxing to lower energy levels.
- A series of cascades between either continuous or discrete **dynodes** _____ in an electron multiplier results in improved sensitivity over a Faraday cup detector.
- The **charge coupled device (CCD)** _____ uses a series of electrodes to “hold” charge in a potential well so that it can accumulate and increase the sensitivity of the detector.

Complete five of the following. Be clear and concise. Clearly indicate which problems are not to be graded. (10 points each)

- Sketch an energy-level diagram for a generic molecule and identify transitions in the molecule that either result from the interaction of the molecule with electromagnetic radiation, or result in the emission of electromagnetic radiation. Also identify the region of the spectrum (UV, Visible, IR, etc.) that typically corresponds to each transition.

I'd expect a diagram like this:



Label	Transition	Region of Spectrum
A	Absorbance of EMR	UV, Vis, IR
B	Vibrational relaxation, possibly results in emission of EMR	IR
C	Fluorescence of EMR	UV, Vis
D	Intersystem crossing (spin inversion)	Nonradiative
E	Phosphorescence of EMR	UV, Vis

6. Compare and contrast the operation of a PMT versus a PDA as a detector in a spectroscopic measurement, as well as any benefits or challenges associated with each device. Why do neither of these devices find much utility in the infrared? Feel free to use well-labeled sketches to clarify your discussion.

A PMT utilizes the photoelectric effect to eject an electron at a photoemissive cathode when a photon strikes the surface. This ejected electron is accelerated toward a dynode where it collides with the dynode surface, causing the ejection of many secondary electrons. This process repeats down a series of dynodes until the large number of electrons produced in this cascade are collected and converted into a current. The key benefit of the PMT is the large gain due to the fact that a single photon can produce many ($>10^6$) electrons. In order to collect a spectrum, the monochromator must physically scan its output across the PMT.

A PDA is a semiconductor device that consists of several individual detectors (pixels) arranged in a two (or three) dimensional array. When light of appropriate energy strikes a pixel, an electron-hole pair is created in the semiconductor. With the appropriate bias voltage, this electron-hole pair produces a current. The magnitude of the current is directly related to the number of photons striking the pixel. While the PDA does not afford the high gain of a PMT (it is a "unity gain" device), it offers the benefit of being able to collect spectra rapidly by dispersing light across the pixels in the array.

For either of these two devices to function, the incident photon must have sufficient energy to dramatically perturb an electron. For common device construction materials, infrared photons typically do not have sufficient energy to induce photoemission or photoconduction.

7. Deuterium (D_2), is a fairly simple molecule with only one bond. Given this simplicity, how can a deuterium lamp serve as a continuum source in the UV?

In a deuterium lamp, D_2 is excited by the application of a fairly high voltage. One pathway for relaxation of these excited state deuterium molecules is through bond breaking, accompanied by the ejection of an electron as shown below.



The total energy of the system must be conserved, but the two deuterium atoms can have a variety of energies (their energies are non-quantized). Therefore, the energy (frequency, wavelength) of the photon produced can vary in a non-quantized fashion as well.

8. Often, the resolution of a mass spectrometric measurement is not limited by the mass analyzer, but is limited by another component of the instrument instead. Identify this component and describe how its function limits resolving power for most mass analyzers.

Most mass analyzers separate 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.

9. A major challenge in mass spectrometry of large molecules is the production of gas-phase ions. Describe an ionization approach for large molecules such as proteins and polymers. Include a brief discussion of the advantages and disadvantages of the approach.

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, some of which may be multiply 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.

10. In simplest terms, most types of mass analyzers operate by adjusting experimental conditions to allow ions of only a small range on m/z to have a “stable” path from the inlet to the outlet of the mass analyzer. Briefly describe how *either* a quadrupole mass filter *or* a dual sector mass analyzer accomplishes this. Include in your description how a mass spectrum is “scanned” in 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.

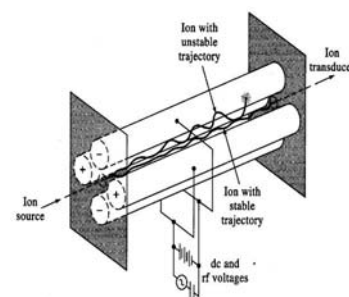


Figure 11-4 A quadrupole mass spectrometer.

Dual Sector: The flight of an ion through the magnetic sector is a balance of centripetal force of the ion with the magnetic force of the magnetic sector or the electrical force of the electrical sector. Ions with too large or too small of a centripetal force will not be able to make the bend through the magnetic sector. Only ions whose centripetal force matches the opposing force will have a stable path.

Spectra can be scanned by systematically adjusting either the magnetic field or the accelerating voltage.

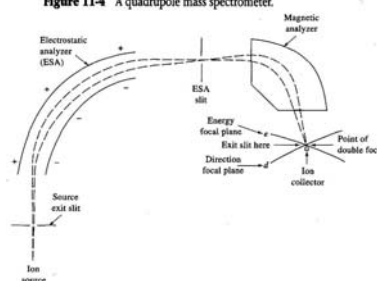


Figure 20-13 Nier-Johnson design of a double-focusing mass spectrometer.

11. Consider the analysis of a relatively small organic molecule like epinephrine ($C_9H_{13}NO_3$, molar mass 183.20 g/mol). Assuming you use the same mass analyzer and detector, how would mass spectra of epinephrine from electron impact, chemical ionization and ICP sources differ? What aspects of the sources lead to these differences?

You need to consider the energetics of the ionization source and the impact of these energetics on the species that form.

Electron Impact: This is an energetic or hard ionization source. As a result, parent ions that are formed possess significant internal energy. This leads to significant fragmentation for most organic compounds. Therefore we would expect to see several fragment peaks and only a small (if any) molecular ion peak.

Chemical Ionization: By using a gas such as methane in the ionization source, parent ions that are formed have much less internal energy. As a result, mass spectra from CI exhibit strong molecular ion peaks and minimal fragmentation.

ICP: The high temperature in an ICP would serve to completely decompose the small molecule, leading to essentially no signal from the sample. Remember, ICP is predominantly useful for elemental (and typically metals) analysis.

Possibly Useful Information

$\lambda = \frac{RT}{\sqrt{2\pi}d^2N_A P} \approx \frac{5\text{ cm}}{\text{mtorr}}$	$\frac{m}{z} = \frac{B^2 r^2 e}{2V} = F_c$
$F_M = Bzev = \frac{mv^2}{r} = F_c$	$\frac{N}{N_0} = \frac{g}{g_0} e^{-E/kT}$
$A = \log(P_0/P) = \epsilon bc$	$T = P/P_0$
$E = \frac{hc}{\lambda} = hv$	$c = 3.00 \times 10^8 \text{ ms}^{-1}$
$k = 1.38 \times 10^{-23} \text{ JK}^{-1}$	$\eta_1 \sin \theta_1 = \eta_2 \sin \theta_2$
$\text{Planck's Constant} = 6.63 \times 10^{-34} \text{ Js}$	$n\lambda = d(\sin i + \sin r)$
$\Delta\lambda = wD^{-1}$	$R = \frac{\lambda}{\Delta\lambda} = nN$
$D = \frac{dy}{d\lambda} = F \frac{dr}{d\lambda}$	$\frac{dr}{d\lambda} = \frac{n}{d \cos r}$
$D^{-1} = \frac{d\lambda}{dy} = \frac{d}{nF}$	<p style="text-align: center;">Nothing useful in this cell...sorry!</p>