1) Aerosol mass spectrometer is a relatively new development in atmospheric chemistry that analyzes the chemical composition of individual particles by decomposing them with laser pulses and measuring the m/e ratio of the fragments. Three common aerosol species in the Midwest are ammonium nitrate, ammonium bisulfate, and ammonium sulfate. Based on the below spectra (ignore pink and green lines) write the ion species for:

   a. Identify the ambient air components (Black)? \(28 = N2^+, \ 32 = O2^+, \ 18 = H2O^+, \ 14 = N2^{++}, \ 16 = O2^{++}\)

   b. What is the expected value for M+ for each aerosol? \(NH4NO3^+ = 80, \ NH4HSO4^+ = 115, \ (NH4)2SO4^+ = 132\)

   c. Ammonium nitrate (Blue) \(31 = NO3^{++}, \ 47 = NH4NO3^{++} \text{ maybe } NO2^+ \text{ at } 46\)

   d. Ammonium sulfate (Red) \(48 = SO4^{++}, \ 64 = SO2^+ \text{ and/or } NH4(NH2)SO4^{++} \ 80 = SO3^+ \ 81 = HSO3^- \ 98 = H2SO4^+\)

   e. If you could collect aerosols on a filter, name another technique to determine ammonium nitrate and sulfate concentrations and why that technique might be ideal. \textit{All are electrolytes and soluble, so ion chromatography (HPLC) with a conductivity detector.}
2) Ozone is an important oxidant and secondary pollutant in the atmosphere and regulated by the EPA to be 60 ppbv or less in healthy air. Concentrations are often monitored by using absorption of UV radiation at 254 nm generated by Hg discharge and passing air containing O3 through a detection cell and applying the Beer-Lambert Law.

![Absorption Cross Section](image)

- What is the number of O3 molecules per cm$^3$ at the EPA limit of 60 ppbv at STP? $Pv=NRT P=101kPa, T=273K$ or $T=293K$ (NIST) $\rightarrow N = 2.5 \times 10^{19}$ molecules air/cm$^3$ x 60 O3/1 x $10^6$ molecules air = $1.5 \times 10^{12}$ molecule O3/cm$^3$
- What is Hg? Symbol for mercury
- Briefly explain how electric discharge of Hg would generate 254 nm light? Electron impact from discharge excites an Hg electron into a higher energy orbital, an electronic transition; a spontaneous transition from the higher E orbital to a lower orbital emits a photon of light whose energy is $= 250$nm via $E=\hbar \nu = h \nu$.
- Write the equation and define the terms for the Beer's-Lambert law. $I/Io = EXP(-\sigma \lambda)$. $I$ = intensity of light, $Io$ = initial intensity of light, $l$ = path length, $\sigma$ = molecular absorption cross section, $c$ = concentration
- Assuming 254 nm is the only light absorbed by O3 and the detection cell is 10 cm in length, what would be the change in intensity of 254 nm if air had an O3 content at the EPA limit of 60 ppbv? Absorption cross section from figure; $I/Io = EXP(-1.5 \times 10^{12} x 100 x 1 \times 10^{17}) = .99985$

3) Nitric oxide is an important primary pollutant emitted by automobiles and power plants. It reacts with O3 in the atmosphere into a chemiluminescence reaction that forms excited NO2 that reverts to the ground state. Air quality agency measure NO using instruments that generate excess ozone in a chamber and measure chemiluminescence.
- Write out the balanced reaction between NO and O3. $NO + O3 \rightarrow NO2 + O2 + h\nu$
- What is the oxidation state N in the products and reactants? What is being reduced? N$= +2$ to $+4$, O3 is reduced
- Define chemiluminescence. Reaction that generates light by electronic transition excited during the reaction.
d. NO2 has a bound excited state below the dissociation energy of the ground state, the minimum of this excited state relative to the ground is separated by 199.4 kJ/mol. If one fixes one degree of freedom, the potential energy surfaces can be drawn as a diatomic representation. Draw an approximate PES for NO2. A diatomic well inside a well, below the asymptote, minimums separated by 199.4kJ/mol.

e. What is the frequency of a photon emitted going from the excited minimum to the ground state minimum? \(E = h \nu \) 
\[ E = 199.4 \times 10^3 \text{ J/mol} \times \frac{6.02 \times 10^{23} \text{ molecules}}{1 \text{ mole}} = 3.3 \times 10^{19} \text{ J/molecule}. \]
\[ \nu = 3.3 \times 10^8 \frac{19^\text{j/molecule}}{6.626 \times 10^{-34} \text{ J/s}} = 5 \times 10^{14} \text{ Hz} \]

f. What is the wavelength of this light and the type (UV, VIS, IR, MW etc).
\[ \lambda = \frac{c}{\nu} = \frac{6.626 \times 10^{-34} \text{ J/s}}{3 \times 10^8 \text{ m/s}} = \frac{3.3 \times 10^{-7}}{19^\text{j/molecule}} = 600 \times 10^{-9} \text{ m} = 600 \text{ nm} = \text{ visible} \]

g. What device would be a logical choice to measure chemiluminescence and give a brief explanation why. Photomultiplier tube since it is efficient at converting and amplifying visible photons into electrical current.

h. Explain why the absorption structure of NO2, which dissociates at energies with wavelengths less than 420 nm, looks the way it does; use part d for simplicity. Below 400 nm transition from vibrational levels between excited state and ground state are below dissociation, the bound-bound transitions give vibronic structure, above this repulsive curve leads to dissociation and a smooth curve.
4) CO2 is an important greenhouse gas that is a linear tri-atomic. Its absorption spectra is shown below.

How many fundamental vibrational modes does CO2 have? Vibrations = 3n-5 (linear) = 3(3) – 5 = 4

What property dictates whether CO2 is optically active? A permanent or temporary dipole is usually required for absorption. CO2 has no permanent dipole, but has induced dipoles by vibrations.

How many CO2 modes would you expect to be optically active and why? 3, Asymmetric stretch, doubly degenerate bend induce a temporary dipole and absorb, symmetric stretch = no dipole, absent absorption.

What is the wavelength of the 2400 cm\(^{-1}\) absorption in the spectra and type of light? \(\lambda = \frac{1}{\nu} = \frac{1}{2400 \times 1m/100cm} = 4.16 \times 10^{-6} \text{ m} = 4.1 \mu\text{m} = \text{IR}\)

Why is CO2 relevant for global warming based on the above questions? Out going IR radiation from the earth is absorbed by CO2 and vibrations excitation is converted into heat by energy transfer by vib → rotation, trans.
No Biochemistry crib available
February 11, 2012
Written by Professor Regnier
Ph# 43878

No Organic crib available
February 11, 2012
Written by Professor Wei
Ph# 45257

No Physical crib available
February 11, 2012
Written by Professor Zwier
Ph# 45278
Inorganic Cumulative Exam  
Feb. 11, 2012  
Key

(1). Partial charges, substituent on sulfur vs. nitrogen  
See also, William Jolly Advances in Chem. vol. 110 1972  
Ch. 6, pp 92-102.

(2). Mo Te Ru Rh all in oxidation state 6+  
\(d^0 \quad d^1 \quad d^2 \quad d^3\)  
J-T no yes yes no

W Re Os Ir Pt  
\(d^0 \quad d^1 \quad d^2 \quad d^3 \quad d^4\)  
J-T no yes yes no yes

in On field  \(\longrightarrow\) \(eg\)  
\(\longrightarrow\) \(t_{2g}\)  
Distortion occurs when degenerate orbitals have unequal occupancy.

(3). (a). Reductive elimination proceeds via dihydrogen complex.  
The KIE is a combination of adduct formation and dissociation

\[L_2Pt(H)_2 \rightarrow L_2Pt\overset{H}{\leftarrow}H \rightarrow [L_2Pt]+H_2\]
(3) \( \text{Cr(CO)}_6 \) 18 electron species

\( \text{V(CO)}_6 \) 17 electron species

an organometallic radical

(4) \[
\frac{-d([\text{Fe}^{2+}])}{dt} = k_{\text{on}} [\text{Fe}^{2+}]_e ([\text{NO}]_o) - k_{\text{off}} [\text{Fe(NO)}^{2+}]_e
\]

\[
k_{\text{on}} [\text{Fe}^{2+}]_e ([\text{NO}]_o) = k_{\text{off}} [\text{Fe(NO)}^{2+}]_e
\]

\[
[\text{Fe}^{2+}]_o + ([\text{Fe}^{2+}]_o) = [\text{Fe}^{2+}]_e + [\text{Fe(NO)}^{2+}]_e
\]

\[
= ([\text{Fe}^{2+}]_e + [\text{Fe(NO)}^{2+}]_e)
\]

\[
-\frac{d([\text{Fe}^{2+}])}{dt} = (k_{\text{on}} [\text{NO}] + k_{\text{off}}) \left[ [\text{Fe}^{2+}] - [\text{Fe}^{2+}]_e \right]
\]

Integrating affords, \( [\text{Fe}^{2+}]_e = [\text{Fe}^{2+}]_o + ([\text{Fe}^{2+}]_o - [\text{Fe}^{2+}]_e) \exp \left[-(k_{\text{on}} [\text{NO}] + k_{\text{off}}) t \right] \)

\[
k_{\text{obs.}} = k_{\text{on}} [\text{NO}] + k_{\text{off}}
\]

A plot of \( k_{\text{obs.}} \) vs \([\text{NO}]\) yield \( k_{\text{on}} = \text{slope} \)

\( k_{\text{off}} = \text{intercept} \)

\[
K_d = \frac{k_{\text{off}}}{k_{\text{on}}} = \frac{3240}{1.42 \times 10^6} \text{ mol L}^{-1}
\]