CHEMISTRY 133
Spring, 2017 Homework Set 2.3
Solutions (Just Text Problems)

Harris Text, Ch. 21: 5, 10, 13a-b, e, 24, 28

5. Measure the width at half-height of the tallest peak in the spectrum below and calculate the resolving power of the spectrometer from the expression $m/m_{1/2}$. Would you expect to be able to distinguish two peaks at 10,000 and 10,001 Da?
peak width at half height ~ 1.5 mm with 1 amu corresponding to 9.2 mm. So m ~ 0.16 amu.
Resolving power = 2846/0.16 = 17,500. So, it would be possible to distinguish two peaks at 10,000 and 10,000 Da.

10. Isotope patterns. Referring to Exercise 21-C, predict the relative amounts of $C_2H_2{}^{79}Br_2$, $C_2H_2{}^{79}Br^{81}Br$, and $C_2H_2{}^{81}Br_2$ in 1, 2, dibromoethylene. Compare your answer with Figure 22-7.
- Br abundances: ratio of ^{81}Br to ^{79}Br (see Table 22-1) of 49.31/50.69 = 0.973 = 97.3/100 (also in Table 22-2)
Ratios - $^{79}Br^{81}Br$/2 ^{79}Br's (or M+2/M): $2*97.3*100/(100)^2$ = **195/100 (= 1.95)**
2 ^{81}Br's/2 ^{79}Br's (or M+4/M): $(97.3)^2/(100)^2$ = **94.7/100 (= 0.947)**
Notes: 2 is included because of ratio of 1:2:1 for possible combinations to give 2 ^{79}Br's, 1 ^{79}Br, or 0 ^{79}Br, respectively. Also, you could have used equations listed in Table 22-2.

13. Peak intensitites of the molecular ion region are listed in parts (a)-(g) and shown in the figure. Identify which peak represents the molecular ion, suggest a composition for it, and calculate the expected isotopic peak intensities. Restrict your attention to elements in Table 21-1.
a) m/z (intensity): 112 (999), 113 (69), 114 (329), 115(21)
*Since the ratio of the M+2 to the M peak is 32.9/100, this suggests one Cl present (32.0 ratio expected if no other source of M+2 peak). Subtracting 35 from 112, leaves 77, which suggests a benzene ring (C_6H_5 has a weight of 77 Da). The ratio of M+1/M = 6.9/100 vs. 6.5 for 6 C atoms. This gives **chlorobenzene** as the compound.*
The expected intensities are (vs. 999 for the M peak)
*113 peak: [6(1.08) + 5(0.012)]*9.99 = **65.3***
*114 peak: 32.0*9.99 (for 1 ^{37}Cl) + $[15(1.08)^2/100]$*9.99 (for 2 ^{13}Cs, rest negelected) = **321***
115 peak: 6(32.0)(1.08)*9.99/100 = **21** [for 1 ^{37}Cl and 1 ^{13}C – rest of terms neglected]*
b) m/z (intensity): 146 (999), 147 (56), 148 (624), 149(33), 150 (99), 151 (5)
The M+2 to M ratio is 62.5/100 – close to that expected for having two Cls (64/100). If the two ^{35}Cls are removed from 146, the remaining mass is 76 which suggests the remaining benzene ring in **dichlorobenzene**.
The expected intensities are (vs. 999 for the M peak)
*147 peak: [6(1.08) + 4(0.012)]*9.99 = **65.3***
*148 peak: 2*32.0*9.99 (for either of the Cls as ^{37}Cl) + $[15(1.08)^2/100]$*9.99 (for 2 ^{13}Cs, rest negelected) = **641***
*149 peak: 6*2*(32.0)(1.08)*9.99/100 =**41** [for 1 ^{37}Cl and 1 ^{13}C – rest of terms neglected]*
*150 peak: $(32.0)^2$*9.99/100 =**102** [for two ^{37}Cls – rest of terms neglected]*
*151 peak: $(32.0)^2$*1.08*6*9.99/10000 = **7** [for two ^{37}Cls and 1 ^{13}C – rest of terms neglected]*

e) m/z (intensity): 172(531), 173(12), 174(999), 175(10), 176(497)

The M+2/M ratio is 188/100 and the M+4/M ratio is 93.6/100. The reasonably large M+4 and large M+2 peaks indicate the possibility of 2 Br atoms. Ratios of 2(97)/100 = 194/100 for M+2/M and $(97)^2$/100/100 = 94/100 are close to those observed. If we remove 79 x 2 from 172, we are left with 14, which is CH_2. This indicates CH_2Br_2. The M+1/M ratio is 2/100, close to the 1.1/100 expected.

24. What is collisionally activated dissociation? At what point in a mass spectrometer does it occur?

Collisionally activated dissociation is the fragmentation of a stable ion. It occurs before a mass analyzer but is most common between two mass analyzer to allow further analysis of compounds produced by electrospray ionization or to produce fragments with fewer overlaps in MS-MS analysis.

28. An electrospray/transmission quadrupole mass spectrum of the α chain of hemoglobin from acidic solution exhibies nine peaks corresponding to MH_n^{n+}. Find the charge, n, for peaks A-I. Calculate the molecular mass of the neutral protein, M, from peaks A, B, G, H, and I, and find the mean value.

Peak	m/z	Amplitude
A	1261.5	0.024
B	1164.6	0.209
G	834.3	0.959
H	797.1	0.546
I	757.2	0.189

If peak A is for MH_n^{n+} (and since M is constant, the peaks with the highest m/z ratios will have the smallest z values), then the next higher m/z peak (peak B) is for MH_{n+1}^{n+1+}.

For A, $(m/z)_A = [M + n(1.008)]/n$, or $(m/z)_A = M/n + 1.008$ or $M/n = (m/z)_A - 1.008$

For B, $(m/z)_B = [M + (n + 1)(1.008)]/(n + 1) = M/(n + 1) + 1.008$ or $(m/z)_B - 1.008 = M/(n + 1)$

$[(m/z)_A - 1.008]/[(m/z)_B - 1.008] = (M/n)/[M/(n + 1)] = (n + 1)/n$

Now, cross multiply and solve for n: $[(m/z)_A - 1.008]n = [(m/z)_B - 1.008](n + 1)$

$n\{[(m/z)_A - 1.008] - [(m/z)_B - 1.008]\} = [(m/z)_B - 1.008]$

$n = [(m/z)_B - 1.008]/\Delta(m/z)$

Once n is determined, $M = (m/z)_A n - n(1.008)$

Note: one can also use the method shown in class:

$M+n/M+n+1 \approx n+1/n$: A and B peaks: 1261.5/1164.5 = 1.083 = n+1/n or 1.083n = n + 1 or 0.083n = 1 or n = 1/0.083 = 12.01

The rest are shown in the table below:

Peak	*M+n/M+n+1 (= R)*	*n = 1/(R – 1)*	*M+n = (m/z)*n-12*	*Comments*
A	*1.083*	*12.01*	*15,126*	
B		*13 (based on A)*	*15,127*	
G	*1.0467*	*~~21.4~~ 18*	*14,999??*	*n?? not used*
H	*1.0527*	*18.98*	*15,126*	
I		*20*	*15,124*	