CHAPTER 19

19-1. In a continuous wave NMR experiment, the intensity of the absorption signal is monitored as the frequency of the source or the field strength of the magnet is scanned. In a Fourier Transform NMR experiment, the analyte is subjected to periodic pulses of radio-frequency radiation. After each pulse, the decay of the emitted signal is monitored as a function of time. This free induction decay signal is then converted to a frequency domain signal by a Fourier Transformation.

19-2. One of the advantages of Fourier Transform NMR is much greater sensitivity, which results in marked improvements in signal-to-noise ratios. This makes possible recording proton spectra on microgram quantities of sample and carbon-13 spectra on samples that contain the isotope in natural abundance concentrations. Another advantage is a significant reduction in time required to record spectra. The frequency reproducibility is also greater as is the resolution. The main disadvantage of Fourier Transform NMR instruments is their cost.

19-3. First, if the line width is constant, resolution improves with field strength. Second, sensitivity improves with field strength according to Equation 19-8. Third, as the $\Delta \nu/J$ ratio increases, spectral interpretation becomes easier.

19-4. By varying the magnetic field strength. Spin-spin splitting is independent of the magnetic field strength, whereas chemical shifts increase with increases in field strength.

19-5. (a) Magnetic anisotropy is a property of a molecule having magnetic properties that vary with molecular orientation.
(b) The screening constant $\sigma$ is a measure of the degree to which circulation of electrons around the nucleus reduce (or sometimes increase) the magnetic field felt by the nucleus. It is defined by the equation

$$\sigma = \frac{B_{\text{appl}} - B_0}{B_0}$$

where $B_{\text{appl}}$ is the external field and $B_0$ is the field felt by the nucleus.

(c) The chemical shift parameter measures the shift in parts per million of the peak for a given nucleus from that of a reference (usually TMS). It is defined by Equations 19-18 and 19-19

$$\delta = \left( \frac{\nu_r - \nu_s}{\nu_r} \right) \times 10^6$$

where $\nu_r$ and $\nu_s$ are the resonance frequencies of the reference and sample, respectively.

(d) Continuous wave NMR measurements are performed by measuring the amplitude of the NMR signal as the radio frequency of the source is varied or the field strength of the magnet is scanned.

(e) The Larmor frequency $\nu_0$ is the frequency of precession of a nucleus in an external field. It is given by

$$\nu_0 = \gamma B_0 / 2\pi$$

where $\gamma$ is the magnetogyric ratio for the nucleus and $B_0$ is the magnetic field at the nucleus.

(f) The coupling constant is the spacing in frequency units between the peaks produced by spin-spin splitting.
(g) First-order NMR spectra are those in which the chemical shift between interacting
groups $\Delta \nu$ is large with respect to their coupling constant ($\Delta \nu / J > 10$).

19-6. The number of magnetic energy states is given by $2I + 1$, where $I$ is the spin quantum
number. Thus, the number of energy states is $2(5/2) + 1 = 6$, and the magnetic quantum
number of each is $+5/2, +3/2, +1/2, -1/2, -3/2, and -5/2$.

19-7. $\nu_0 = \gamma B_0 / 2\pi$

(a) For $^1\text{H}$, $\gamma = 2.68 \times 10^8 \text{T}^{-1}\text{s}^{-1}$ (Table 19-1) and
$$\nu_0 = \frac{2.68 \times 10^8 \text{T}^{-1}\text{s}^{-1} \times 7.05 \text{T}}{2\pi} = 3.007 \times 10^8 \text{ Hz} = 300.7 \text{ MHz or } 301 \text{ MHz}$$

(b) For $^{13}\text{C}$, $\gamma = 6.73 \times 10^7 \text{T}^{-1}\text{s}^{-1}$ and $\nu_0 = 75.5 \text{ MHz}$

(c) For $^{19}\text{F}$, $\gamma = 2.52 \times 10^8 \text{T}^{-1}\text{s}^{-1}$ and $\nu_0 = 283 \text{ MHz}$

(d) For $^{31}\text{P}$, $\gamma = 1.08 \times 10^8 \text{T}^{-1}\text{s}^{-1}$ and $\nu_0 = 121 \text{ MHz}$

19-8. $\nu_0 = \gamma B_0 / 2\pi$

(a) At 1.41 T, $\nu_0 = \frac{2.68 \times 10^8 \text{T}^{-1}\text{s}^{-1} \times 1.41 \text{T}}{2\pi} = 60.1 \times 10^6 \text{ Hz or } 60 \text{ MHz}$

(b) At 4.69 T, $\nu_0 = \frac{2.68 \times 10^8 \text{T}^{-1}\text{s}^{-1} \times 4.69 \text{T}}{2\pi} = 200 \times 10^6 \text{ Hz or } 200 \text{ MHz}$

(c) At 7.05 T, $\nu_0 = 301 \text{ MHz}$ (see answer to Problem 19-7)

(d) At 11.7 T, $\nu_0 = 499 \text{ MHz}$

(e) At 18.8 T, $\nu_0 = 802 \text{ MHz}$

(f) At 21.2 T, $\nu_0 = 904 \text{ MHz}$

19-9. The frequency difference is directly proportional to the magnetic field strength (see
(a) At 4.69 T, $\Delta \nu = 90 \text{ Hz} \times 4.69/1.41 = 299 \text{ Hz}$

(b) At 7.05 T, $\Delta \nu = 90 \text{ Hz} \times 7.05/1.41 = 450 \text{ Hz}$

(c) At 18.8 T, $\Delta \nu = 90 \text{ Hz} \times 18.8/1.41 = 1200 \text{ Hz}$

Since $\delta$ is independent of field strength $B_0$, a 90 Hz shift at 60 MHz is a $\delta$ value of

$$\delta = \left( \frac{90 \text{ Hz}}{60 \times 10^6 \text{ Hz}} \right) \times 10^6 = 1.5$$

This will be the same at the other magnetic field values.

19-10. Because of the natural abundance of $^{13}\text{C}$, it is highly improbable that two $^{13}\text{C}$ atoms will be adjacent to one another in ordinary organic compounds. Hence, $^{13}\text{C}$ spin-spin splitting is not observed.

19-11. Here, we employ Equation 19-7 and write

$$\frac{N_j}{N_0} = \exp \left( -\gamma h B_0 \frac{T}{2\pi kT} \right) = \exp \left( -\frac{6.73 \times 10^7 \text{ T}^{-1} \text{s}^{-1} \times 6.626 \times 10^{-34} \text{ Js} \times 7.05 \text{ T}}{2\pi \times 1.38 \times 10^{-23} \text{ J K}^{-1} \times 298 \text{ K}} \right)$$

$$= \exp(-1.217 \times 10^{-5}) = 0.9999878$$

19-12. Longitudinal, or spin-lattice, relaxation arises from the complex magnetic fields that are generated by the rotational and vibrational motions of the host of other nuclei making up a sample. At least some of these generated magnetic fields must correspond in frequency and phase with that of the analyte nucleus and can thus convert it from the higher to the lower spin state. Transverse, or spin-spin, relaxation, in contrast is brought about by interaction between neighboring nuclei having identical precession rates but different magnetic quantum states. Here, the nucleus in the lower spin state is excited while the excited nucleus relaxes. Not net change in the spin state population occurs, but the average lifetime of a particular excited nucleus is shortened.
19-13. The radio-frequency excitation pulse in FT NMR causes the sample magnetization vector to tip away from the direction of the external magnetic field. When the pulse terminates, the same magnetic moment rotates around the external field axis at the Larmor frequency. This motion constitutes a radio-frequency signal that decays to zero as the excited nuclei relax. This decreasing signal is the free induction decay (FID) signal.

19-14. A rotating frame of reference consists of a set of mutually perpendicular coordinates (usually labeled $x'$, $y'$ and $z'$) in which the $x'$ and $y'$ coordinates rotate at a constant rate around the $z'$ coordinate.

19-15. Writing Equation 19-4 for the two nuclei gives

$$\Delta E(^{13}\text{C}) = \frac{\gamma_C h B_0}{2\pi} = 6.73 \times 10^7 \frac{hB_0}{2\pi}$$

$$\Delta E(^1\text{H}) = \frac{\gamma_H h B_0}{2\pi} = 2.68 \times 10^8 \frac{hB_0}{2\pi}$$

Dividing the first equation by the second gives

$$\frac{\Delta E(^{13}\text{C})}{\Delta E(^1\text{H})} = 0.251$$

19-16. (a) $\gamma_F = 2.5181 \times 10^8 \text{ T}^{-1}\text{s}^{-1}$

$$\nu_0 = \frac{\gamma_F B_0}{2\pi} = 2.5181 \times 10^8 \text{ T}^{-1}\text{s}^{-1} \times 7.05 \text{ T}/(2\pi) = 283 \text{ MHz}$$

(b) $\gamma_p = 1.0841 \times 10^8 \text{ T}^{-1}\text{s}^{-1}$

$$\nu_0 = 1.0841 \times 10^8 \text{ T}^{-1}\text{s}^{-1} \times 7.05 \text{ T}/(2\pi) = 122 \text{ MHz}$$

19-17. 

$$\frac{N_j}{N_0} = \exp(-\Delta E / kT)$$

For the proton in a 500 MHz instrument

$$\nu_0 = \frac{\gamma_H B_0}{2\pi} \quad \text{and} \quad B_0 = \frac{2\pi\nu_0}{\gamma_H}$$

5
For $^{13}\text{C}$

$$\Delta E = \frac{\gamma_C h B_0}{2\pi} = \frac{\gamma_C h}{2\pi} \frac{2\pi v_0}{\gamma_H} = \frac{\gamma_C}{\gamma_H} h v_0$$

and

$$\frac{N_I}{N_0} = \exp\left(-\frac{\gamma_C}{\gamma_H} \frac{h v_0}{kT}\right) = \exp\left(-\frac{6.73 \times 10^7 \times 6.626 \times 10^{-34} \text{ J s} \ 500 \times 10^6 \text{ Hz}}{2.68 \times 10^8 \times 1.38 \times 10^{-23} \text{ J K}^{-1} \times 300 \text{ K}}\right)$$

$$= \exp(-2.0096 \times 10^{-5}) = 0.99998$$

19-18. For $^1\text{H}$, $v_0 = \gamma_H B_0 / 2\pi = 2.68 \times 10^8 \text{ T}^{-1}\text{s}^{-1} \times 4.69 / 2\pi = 200 \text{ MHz}$

For $^{31}\text{P}$, $v_0 = \gamma_P B_0 / 2\pi = 1.08 \times 10^8 \text{ T}^{-1}\text{s}^{-1} \times 4.69 / 2\pi = 80 \text{ MHz}$

The lower frequency at which $^{31}\text{P}$ resonates means that the energy gap for this nucleus is smaller than that of the proton. Therefore, the net magnetization vector for $^{31}\text{P}$ will be smaller and the signal per atom for $^{31}\text{P}$ will be lower even though isotopic abundances are approximately the same. This means that the $^1\text{H}$ signal will be much more intense than that due to $^{31}\text{P}$.

Weak spin-spin coupling means the $^1\text{H}$ signal will be split into a doublet while the $^{31}\text{P}$ signal will be given as the coefficients of the expansion of $(1 + x)^9$. 
19-19. According to entries 21 and 23 in Figure 19-17, the chemical shifts in methanol should be \(~3.6\) ppm and \(~6.0\) ppm for the methyl and hydroxyl protons, respectively. In reality both of these are considerably different than their empirical values, but the order is correct and will thus be used.

19-20.
19-21. The data in Figure 19-29 are used for assigning chemical shifts.
19-22. We assume in the figures below that $^1$H only couples to the $^{13}$C to which it is bonded.

19-23. A field frequency lock system is used in NMR instruments in order to overcome the effect of magnetic field fluctuations. In this device, a reference nucleus is continuously irradiated, and its output signal is continuously monitored at its resonance maximum. Changes in the intensity of this signal control a feedback circuit, the output of which is fed into coils to correct for drift in the magnetic field. The drift correction is applicable
to signals for all types of nuclei because the ratio of field strength to resonance frequency is constant and independent of the type of nuclei.

19-24. Shim coils are pairs of wire loops through which carefully controlled currents are passed. These produce small magnetic fields that compensate for inhomogeneities in the primary magnetic field.

19-25. Liquid samples in NMR are spun along their longitudinal axis to overcome the effects of small field inhomogeneities. In this way, nuclei experience an averaged environment that produces less band broadening.

19-26. $\text{CH}_3\text{CH}_2\text{COOH}$

From Table 19-2 and Figure 19-17, we deduce that the carboxylic acid proton should produce a single peak at $\delta = 11$ to 12. The methylene proton should produce four peaks (area ratio = 1:3:3:1) centered about $\delta = 2.2$, and the methyl proton three peaks (area ratio 1:2:1) at about $\delta = 1.1$.

19-27. (a) Acetone-$(\text{CH}_3)_2\text{C}=\text{O}$ Because all the protons are identical there should be a single peak at about $\delta = 1.6$.

(b) Acetaldehyde-$\text{CH}_3\text{CHO}$ The single proton should produce four peaks (area ratio 1:3:3:1) at $\delta = 9.7$ to 9.8; the methyl protons should yield a doublet at $\delta = 2.2$.

(c) Methyl ethyl ketone-
The protons on carbon atom \( a \) will yield a singlet at \( \delta = 2.1 \). The protons on atom \( b \) should yield a quartet (1:3:3:1) at about \( \delta = 2.4 \), while the proton on atom \( c \) will give triplet peaks (1:2:1) at \( \delta = 1.1 \).

19-28. (a) Ethyl nitrite-\( \text{CH}_3\text{CH}_2\text{NO}_2 \) The methylene protons should yield a quartet (area ratio 1:3:3:1) centered about \( \delta = 4.4 \); the methyl protons should give a triplet (ratio 1:2:1) centered about \( \delta = 1.6 \).

(b) Acetic acid-\( \text{CH}_3\text{COOH} \) The carboxylic acid proton should produce a single peak at \( \delta = 11 \) to 12, while the three methyl protons should also give a singlet at \( \delta = 2.2 \).

(c) methyl-\( i \)-propyl ketone

\[
\begin{array}{c}
\text{CH}_3 \\
\text{O} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{C} \\
\text{CH}_3
\end{array}
\]

The methyl group adjacent to the carbonyl will give a singlet at \( \delta = 2.1 \). The other six methyl protons will yield a doublet (1:1), while the single proton should yield seven peaks centered at \( \delta = 2.6 \).

19-29. (a) Cyclohexane-\( \text{C}_6\text{H}_{12} \) All the protons are equivalent. Thus, the compound will yield a singlet at \( \delta = 1.2 \) to 1.4.

(b) Diethyl ether-\( \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 \) The two methylene protons should give rise to a quartet at about \( \delta = 3.4 \). The methyl protons should produce a triplet at \( \delta = 1.2 \).

(c) 1,2-dimethoxyethane-\( \text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3 \) The protons on the two methyl groups should yield a singlet at \( \delta = 3.2 \). The protons on the other two carbon atoms will also yield a single peak at \( \delta = 3.4 \). The ratio of peak areas should be 6:4.

19-30. (a) Toluene-\( \text{C}_6\text{H}_5\text{CH}_3 \) The five aromatic ring protons will produce a single peak at \( \delta = 6.5 \) to 8. The three methyl protons will produce a triplet at \( \delta = 2.2 \).
(b) Ethyl benzene-C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}CH\textsubscript{3} The five aromatic ring protons will produce a single peak at \(\delta = 6.5\) to 8. The two methylene protons will yield a quartet centered at \(\delta = 2.6\). The methyl proton will give a triplet at \(\delta = 1.1\).

(c) \textit{i}-butane-(CH\textsubscript{3})\textsubscript{3}CH The nine methyl protons should appear as a doublet at \(\delta = 0.9\). The single proton will appear as ten peaks centered at about \(\delta = 1.5\).

19-31. The triplet patterns at \(\delta = 1.6\) to 1.7 suggest a methyl group with a brominated methylene group in the \(\alpha\) position. The quartet at \(\delta = 3.4\) would then arise from the protons on the methylene group. The compound is ethyl bromide-CH\textsubscript{3}CH\textsubscript{2}Br.

19-32. The empirical formula and the peak at \(\delta = 11\) suggests a carboxylic acid. The triplet at \(\delta = 1.1\) would appear to be a methyl group adjacent to a methylene group. The upfield triplet at \(\delta = 4.2\) is compatible with a \(-\text{CHBr}—\) group. Thus the compound is \(\text{CH}_3\text{CH}_2\text{CHCOOH}\).

19-33. The strong singlet suggests a methyl group adjacent to a carbonyl group. The absence of a peak at \(\delta > 9.7\) eliminates the possibility of an aldehyde group and suggests the compound is a ketone. The four peaks at \(\delta = 2.5\) would appear to be from a methylene group adjacent to a methyl group as well as a carbonyl group (ketone). Thus, the compound appears to be methyl ethyl ketone.

19-34. The strong singlet at \(\delta = 2.1\) and the empirical formula suggests a methyl group adjacent to a \(-\text{COOR}—\) group. The triplet and quartet structure is compatible with an ethylene group. Thus, the compound appears to be ethyl acetate.
CHAPTER 20

20-1. With gaseous ionization sources, the sample is first volatilized (by heating if necessary) and then transmitted to the ionization area for ionization. In a desorption source, a probe is used and ionization takes place directly from the condensed phase. The advantage of desorption ionization is that it can be applied to high molecular weight and thermally unstable samples. The advantage of gaseous ionization sources are their simplicity and speed (no need to use probe and wait for probed area to be pumped out).

20-2. The most fragmentation and thus the most complex spectra are encountered with electron impact ionization. Field ionization produces the simplest spectra. Chemical and electron impact ionization result in higher sensitivities than does field ionization.

20-3. Both field ionization and field desorption ionization are performed at anodes containing numerous sharp tips so that very high electrical fields are realized. In field ionization, the sample is volatilized before ionization, whereas field desorption takes place an an anode that has been coated with the sample. The latter requires the use of a sample probe.

20-4. (a) The total kinetic energy acquired by an electron moving between the filament and the target will be \( eV \), where \( e \) is the charge on the electron and \( V \) is the potential difference. Because \( SS \) is approximately half way between the filament and the target, the total difference in potential must be 140 V, if the electron is to have 70 eV of energy at \( SS \).

(b) An ion formed at point \( P \) will almost certainly collide with a solid part of the exit slit as a result of the repeller-accelerating plate voltage.

20-5. (a) For \( \text{CH}_4^+ \), \( m/z = 16 \) and
Similarly for \( m/z = 250 \)

\[
250 = kB^2
\]

Dividing the second equation by the first yields

\[
\frac{250}{16} = \frac{B^2}{(0.126 \text{ T})^2}
\]

\[
B = 0.498 \text{ T}
\]

Thus, to scan the range of \( m/z \) from 16 to 250, the field strength would be scanned from 0.126 to 0.498 T.

(b) Here, Equation 20-9 takes the form

\[
16 = \frac{B^2r^2e}{2V} = \frac{k'}{V} = \frac{k'}{3.00 \times 10^3}
\]

At \( m/z = 250 \)

\[
250 = k'/V
\]

Dividing the first equation by the second gives

\[
\frac{16}{250} = \frac{k'/3.00 \times 10^3}{k'/V} = \frac{V}{3.00 \times 10^3}
\]

or

\[
V = 16 \times 3.00 \times 10^3/250 = 192 \text{ V}
\]

Thus, scan from 3000 to 192 V.

20-6. Here,

\[
m = 7500 \text{ g mol}^{-1} \times \frac{1 \text{ mol}}{6.02 \times 10^{23} \text{ ions}} \times \frac{1 \text{ kg}}{10^3 \text{ g}} \times \frac{1.246 \times 10^{-23} \text{ kg}}{\text{ion}}
\]
Substituting into Equation 20-9 gives, after rearranging,

\[ V = \frac{(0.240 \text{Vs/m}^2)^2 (0.127 \text{m})^2 \times 1.60 \times 10^{-19} \text{C/ion}}{2 \times 1.246 \times 10^{-23} \text{kg/ion}} = 5.96 \left(\frac{\text{Vs}^2 \text{C}}{\text{m}^2 \text{kg}}\right) = 5.97 \text{V} \]

20-7. After acceleration the velocity \( v \) can be calculated with the aid of Equation 20-4. Thus,

\[ z e V = \frac{1}{2} m v^2 \]

where \( m \) for cyclohexane (\( M = 84 \)) is given by

\[ m = 84.0 \text{g C}_6 \text{H}_{12} \text{mol}^{-1} \times \frac{1 \text{mol}}{6.02 \times 10^{23} \text{ions}} \times \frac{1 \text{kg}}{10^3 \text{g}} = 1.395 \times 10^{-25} \text{kg/ion} \]

\[ v = \sqrt{\frac{2 z e V}{m}} = \sqrt{\frac{2 \times 1.60 \times 10^{-19} \text{C/ion} \times 5.00 \left(\frac{\text{Vs}^2 \text{C}}{\text{m}^2 \text{kg}}\right)}{1.395 \times 10^{-25} \text{kg/ion}}} = 3.39 \times 10^1 \text{m/s} \]

\[ \text{time} = \frac{15.0 \text{cm} \times 10^{-2} \text{m/cm}}{3.39 \times 10^3 \text{m/s}} = 4.43 \times 10^{-5} \text{s} = 44.3 \mu\text{s} \]

20-8. The presence of a negative dc voltage in the \( yz \) plane causes positive ions to move toward the rods where they are annihilated. In the presence of an added ac voltage, this movement is inhibited during the positive half of the cycle with the lighter ions being more affected than the heavier ions. Thus the \( yz \) plane acts as a low-pass filter removing heavier ions (see Figure 11-????).

20-9. The resolution of a single focusing mass spectrometer is limited by the initial kinetic energy spread of the sample molecules. This spread is minimized in a double focusing instrument by accelerating the sample through an electrostatic analyzer, which limits the range of kinetic energies of ions being introduced into the magnetic sector analyzer. Significantly narrower peaks are the result.
20-10. A quadrupole ion trap is similar to a linear quadrupole filter except it as a spherical 3-dimensional configuration. By a combination of fields, ions are temporarily stored within the trap. They are then released sequentially by increasing the radio frequency voltage applied to the ring electrode. The ejected ions then strike a detector. A plot of detector signal vs. the radio frequency voltage, related to the \( m/z \) value, is the mass spectrum. In an FT ICR instrument, ions are trapped in a cell by an electric trapping voltage and a magnetic field. Each ion assumes a circular motion in a plane perpendicular to the direction of the field. The cyclotron frequency depends on the inverse of the \( m/z \) value. In modern instruments a radio frequency pulse that increases linearly in frequency is employed. A time domain image current is generated after termination of the pulse. Fourier transformation of the time decay signal yields the mass spectrum.

20-11. Resolution = \( m/\Delta m \)

(a) \( m = (28.0187 + 28.0061)/2 = 28.012 \)
\[ \frac{m}{\Delta m} = \frac{28.012}{28.0187 - 28.0061} = 2.22 \times 10^3 \]

(b) \( m/\Delta m = 28.013/(28.0313 - 27.9949) = 770 \)

(c) \( m/\Delta m = 85.0647/(85.0653 - 85.0641) = 7.09 \times 10^4 \)

(d) \( m/\Delta m = 286.158/(286.1930 - 286.1240) = 4.15 \times 10^3 \)
20-12.

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Spreadsheet Documentation
- Cell B5=A5/$B$3
- Cell D5=A5/$D$3
- Cell F5=A5/$F$3
- Cell H5=A5/$H$3

20-13. (a) In Table 20-3, we find that for every 100 $^{79}$Br atoms there are 98 $^{81}$Br atoms.

Because the compound in question has two atoms of bromine

$$(M + 2)^+ / M^+ = 2 \times 98/100 = 1.96$$

and

$$(M + 4)^+ / M^+ = (98/100)^2 = 0.96$$

(b) Table 20-3 reveals that for every 100 $^{35}$Cl atoms there are 32.5 $^{37}$Cl atoms. Thus,

$$(M + 2)^+ / M^+ = (1 \times 98/100) + (1 \times 32.5/100) = 1.30$$

$$(M + 4)^+ / M^+ = (1 \times 98/100) \times (1 \times 32.5/100) = 0.32$$

(c) $$(M + 2)^+ / M^+ = 2 \times 32.5/100 = 0.65$$

$$(M + 4)^+ / M^+ = (0.325/100)^2 = 0.106$$

20-14. (a) Because all conditions except accelerating voltage are constant, Equation 20-9 can be abbreviated to $(m/z)_s = K/V_s$ and $(m/z)_u = K/V_u$. 

5
where the subscripts $s$ and $u$ designate standard and unknown respectively. Dividing one of these equations by the other gives the desired relationship.

\[
\frac{(m/z)_s}{(m/z)_u} = \frac{K/V_s}{K/V_u} = \frac{V_u}{V_s}
\]

(b) \[\frac{69.00}{(m/z)_u} = 0.965035\]

\[(m/z)_u = 71.50\]

(c) The approximately half-integral $m/z$ value suggests that the ion being studied in part (b) was doubly charged. This conclusion is in agreement with the fact that the molecular mass of the unknown is 143. The second conclusion is that the unknown must contain an odd number of nitrogen atoms.

20-15. The difference in mass between $^{12}$C and $^{13}$C is 1.00335. Therefore, making the assumption that $(P + 1)^+$ is due only to $^{13}$C means

\[
\text{mass } (P + 1)^+ = \text{mass } P^+ + 1.00335
\]

In Problem 20-14, we derived the following relationship

\[
\frac{(m/z)_s}{(m/z)_u} = \frac{V_u}{V_s}
\]

Taking into account the fact that only singly charged ions were specified, and rewriting this equation with $V_1$ representing the standard and $V_2$ the unknown, we find

\[
\frac{m(P^+)}{m(P + 1)^+} = \frac{m(P^+)}{m(P^+)+1.00335} = \frac{V_2}{V_1}
\]

(b) Substituting the voltage ratio into the last equation allows $m(P^+)$ to be calculated

\[
\frac{m(P^+)}{m(P^+)+1.00335} = \frac{V_2}{V_1} = 0.987753
\]
20-16. In tandem in space instruments, two independent mass analyzers are used in two different regions in space. This is a rather straight-forward way to do tandem ms and some conventional mass spectrometers can be converted to tandem instruments. The advantages are that it is relatively easy to take all the different types of spectra (product ion, precursor ion, neutral loss, multidimensional. The disadvantages are that the efficiency can be very low and thus the sensitivity can be low. Tandem in time instruments form the ions in a certain spatial region and then at a later time expel the unwanted ions and leave the selected ions to be dissociated and mass analyzed in the same spatial region. The efficiency can be fairly high and the process can be repeated many times. It is, however, only straight forward to take product ion spectra. Both approaches require quite expensive instrumentation.

20-17. \( m/z = 131 \) due to \( ^{35}\text{Cl}_3\text{CCH}_2^+ \) \( m/z = 133 \) due to \( ^{37}\text{Cl}^{35}\text{Cl}_2\text{CCH}_2^+ \)  
\( m/z = 135 \) due to \( ^{37}\text{Cl}_2^{35}\text{ClCCH}_2^+ \) \( m/z = 117 \) due to \( ^{35}\text{Cl}_3\text{C}^+ \)  
\( m/z = 119 \) due to \( ^{37}\text{Cl}^{35}\text{Cl}_2\text{C}^+ \) \( m/z = 121 \) due to \( ^{37}\text{Cl}_2^{35}\text{ClC}^+ \)  
20-18. \( m/z = 84 \) due to \( ^{35}\text{Cl}_2\text{C}^+ \) \( m/z = 85 \) due to \( ^{35}\text{Cl}_2^{13}\text{CH}_2^+ \)  
\( m/z = 86 \) due to \( ^{37}\text{Cl}^{35}\text{Cl}^{12}\text{CH}_2^+ \) \( m/z = 87 \) due to \( ^{37}\text{Cl}^{35}\text{Cl}^{13}\text{CH}_2^+ \)  
\( m/z = 88 \) due to \( ^{37}\text{Cl}_2^{12}\text{CH}_2^+ \)