Workshop 30
Using IR, MS and NMR Data for Structure Elucidation

Fragrance chemists frequently use spectroscopic tools to try to determine what molecules are responsible for a particular natural scent—so that, say, the smell of lavender can be reproduced with synthetic organic molecules and incorporated into a shampoo or perfume. In this Workshop, we'll imagine that we are employees of International Flavors & Fragrances, trying to determine the structure of two different molecules we've isolated from a natural source.[1] The Workshop walks you through the process of using spectral information to guess the structure of each molecule.

a. First, we submit the two molecules to an external lab for high-resolution mass spectrometry analysis. The results that come back, interestingly, assign the same exact mass to the two molecules: 88.0524 atomic mass units (amu). When we plug this value into a composition calculator (like the one at http://library.med.utah.edu/masspec/elcomp.htm), it gives the following output, predicting possible formulae for a molecule containing an unknown number of C, H, N, O, S and P atoms:

```
Elemental Composition Calculator v1.0

Calculations for :    88.0524 +/-  0.003 amu
monoisotopic mass

atom     mass      min   max
  C     12.0000    0     10
  H      1.0078    0     20
  N     14.0030    0     10
  O     15.9949    0     10
  S     31.9720    0      2
  P     30.9737    0      2

possible molecular formulae:
  C  H  N  O  S  P      mass       diff

  0  4  6  0  0  0    88.0497     0.0026
  2  6  3  1  0  0    88.0510     0.0013
  4  8  0  2  0  0    88.0524     0.0000

Number of hits       :      3
```
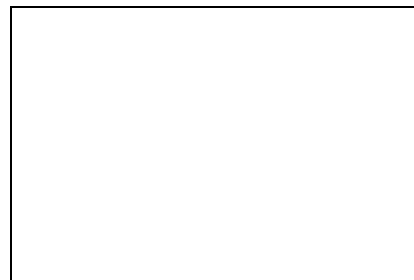
Given this output, what do you think the molecular formula for both unknown molecules is?

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[1] Time magazine and CNN produced an interesting profile of IFF's business at http://www.time.com/time/specials/2007/perfume.

The back two pages contain IR, electron-ionization MS, and ^{1}H and ^{13}C NMR spectra for each of the two molecules, which we'll call **A** and **B**.

b. The IR spectra of both molecules show a sharp, strong peak at $v \approx 1742$ cm^{-1}. What type of bond might this correspond to? (It might be helpful to reference your class notes, or the IR peak tables in Appendix 2 of Wade.) Does the frequency tell you anything more? What kind of functional group might be present in the two molecules that would give a peak at this frequency?
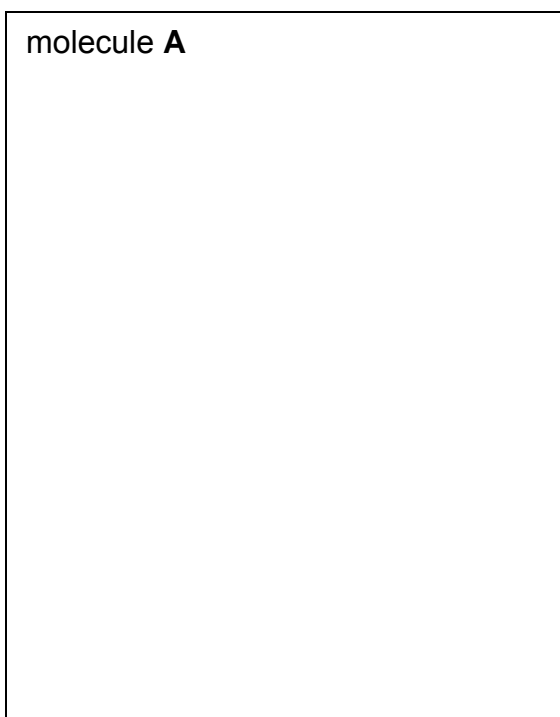
c. The ^{13}C NMR spectra of the two molecules are similar (but not identical)—each shows four peaks, presumably corresponding to four unique carbons in each molecule. In each spectrum, one of the four peaks is far downfield (left) of the other three. What type of carbon might this peak correspond to? (Is this consistent with your answer to part *b* above?
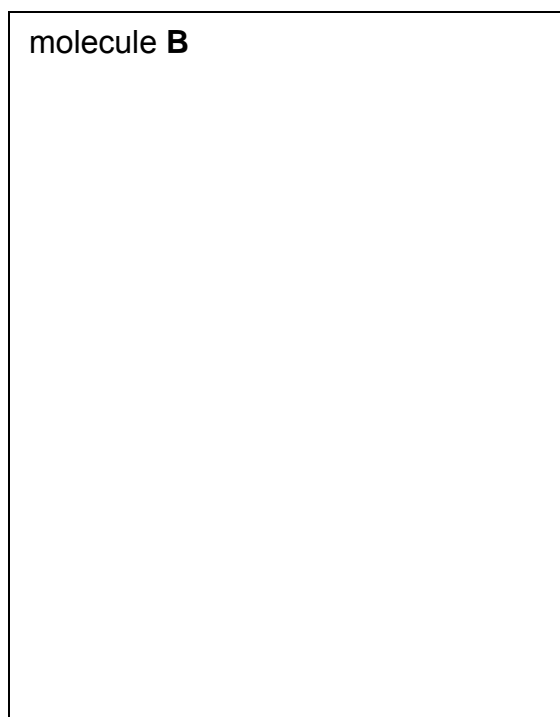
d. The ^{1}H NMR spectra of the two molecules are also similar (but again, not identical). Each has three resonances, two of which show splitting patterns. In each spectrum, label the resonances *a*, *b* and *c*. In each case, what is coupled to what? How many protons are represented by each resonance? What do these resonances mean in terms of the arrangement of protons in our two molecules?

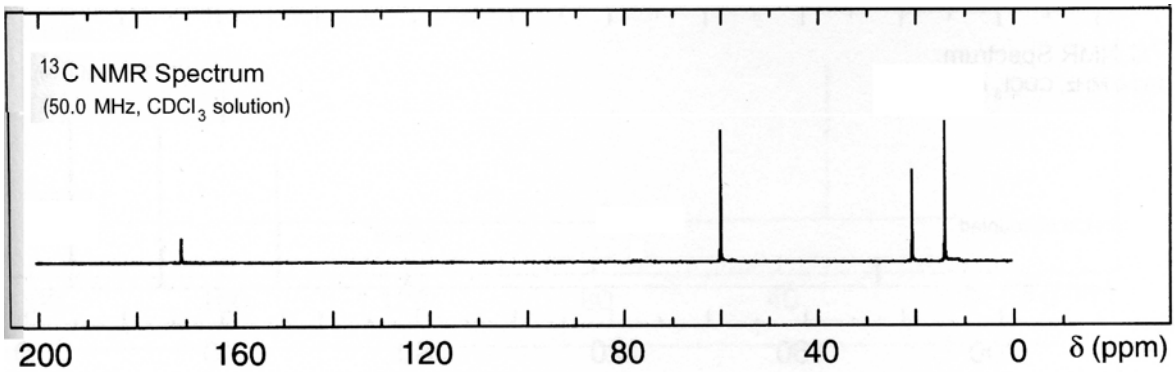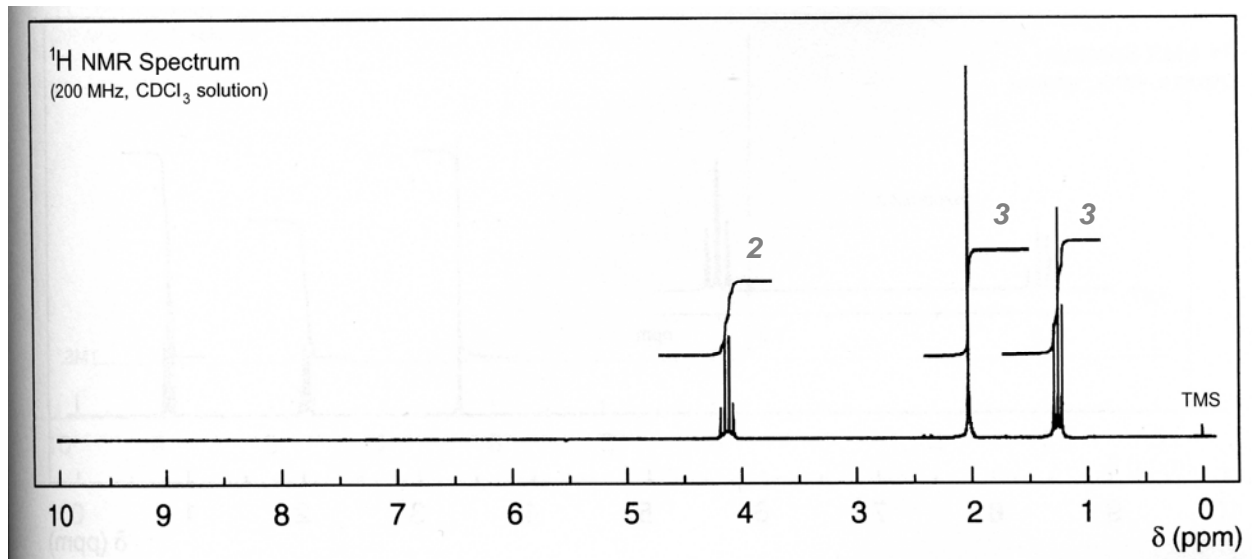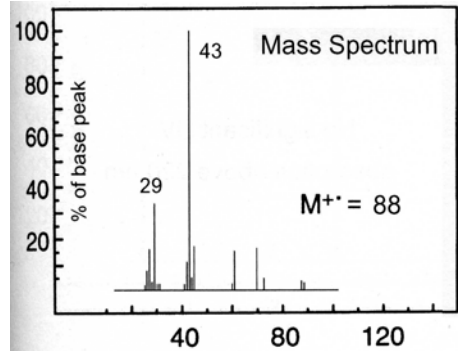| molecule **A**	molecule **B**

e. Given your answers to parts *a-d*, sketch some possible structures for molecules **A** and **B**. Can you assign a single structure to each, or can you narrow the choices down to a few?

f. The mass spectra of the two molecules are very different, in that each shows a unique fragment mass not present in the other molecule's spectrum. In each of the boxes below, draw your best guess for what the molecule's structure might be, and then circle the portion of the molecule that would give the indicated fragment mass.

molecule **A**: mass 43	molecule **B**: mass 57

molecule **A**:

IR Spectrum
(liquid film)

2984
1741
1243

ν (cm⁻¹)

Mass Spectrum

% of base peak

100
80
60
40
20

29
43

M⁺˙ = 88

40   80   120

¹H NMR Spectrum
(200 MHz, CDCl₃ solution)

2

3   3

TMS

δ (ppm)

¹³C NMR Spectrum
(50.0 MHz, CDCl₃ solution)

δ (ppm)

molecule **B**:

IR Spectrum
(CCl$_4$ solution)

1744

Mass Spectrum

29

57

M$^{+\cdot}$ = 88

% of base peak

40   80   120

^{1}H NMR Spectrum
(200 MHz, CDCl$_3$ solution)

expansion

2.0   1.0   ppm

3   2   3

TMS

10   9   8   7   6   5   4   3   2   1   0
δ (ppm)

^{13}C NMR Spectrum
(100.0 MHz, CDCl$_3$ solution)

200   160   120   80   40   0   δ (ppm)