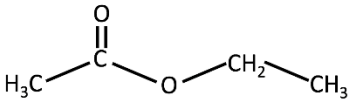
Spectroscopy and the Dirty Water Detective

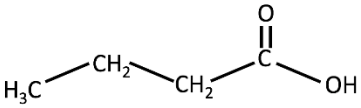
IMAGINE: After completing your degree, you start working for a Municipal Water Department as the Water Quality Manager. Although your job has many pressing concerns, a recent complaint about the taste of the water in the community has topped your to-do list since many residents have complained of feeling listless and unable to concentrate. You suspect there may be a serious contaminant in the water. Having taken Chem 1B-AL, you are well aware that scientists use spectroscopic techniques to identify chemical structures. The UC chemistry department has both Infrared (IR) and Nuclear Magnetic Resonance (NMR) spectroscopy instruments that they have made available for your investigation. After collecting water samples from different locations, you run a separation column that allows you to isolate 3 unknown contaminants, each at a different concentration. You then analyze them with IR and NMR spectroscopy. Your initial analysis of the spectra reveals that the empirical chemical formula of each contaminant is the same! This molecular formula is $C_4O_2H_8$.

Considering possible Lewis structures, you are able to arrive at the following three structural isomers. Two of these, butanoic acid and isopropyl formate, can be very dangerous if ingested in high doses (>10 mg/L), but ethyl acetate is relatively benign even at concentrations >50 mg/L. Your job is to match each structure below to the paired IR and NMR spectra on the following three pages. Consult the reference tables at the back of the packet to identify the IR and NMR peaks. For your final report, fill out the table and answer the following questions.

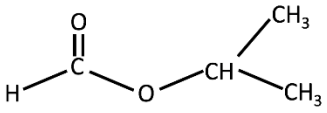
Hint: *In distinguishing the molecules, you will require one new bit of information that you haven't covered in class. We often use the "chemical shift" (the exact radio wave frequency required to flip the hydrogen nucleus) to identify an H atom in a particular chemical environment. The one in the table that you might find useful is that the hydrogen in an H-C=O environment has a relatively large chemical shift (listed a 9.2-9.9 ppm in table on page 4, but could actually be in the range 8-10 ppm)*



Ethyl acetate

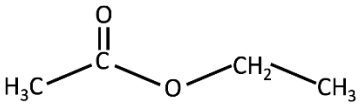


Butanoic Acid

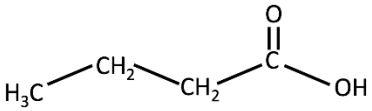


Isopropyl formate

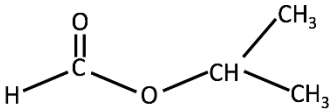
Contaminant Molecule	*Concentration in Municipal Drinking Water (mg/L)*	*Contaminant IR and NMR Spectra*	*Diagnostic stretches (IR) and chemical shifts (NMR)*
	2	1	IR: NMR:
	2	2	IR: NMR:
	100	3	IR: NMR:



Ethyl acetate

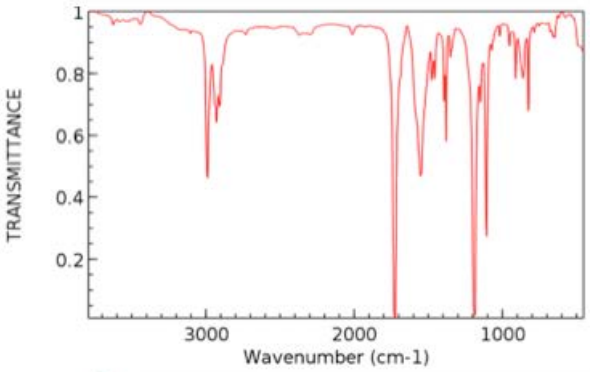


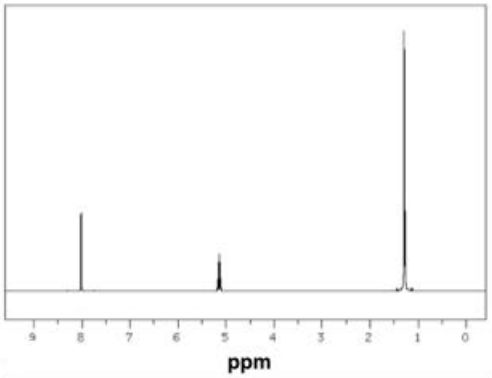
Butanoic Acid



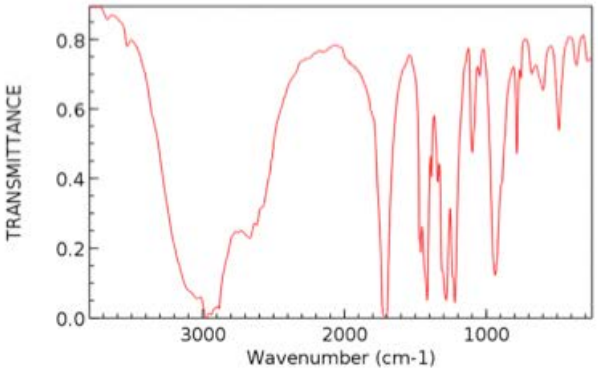
Isopropyl formate

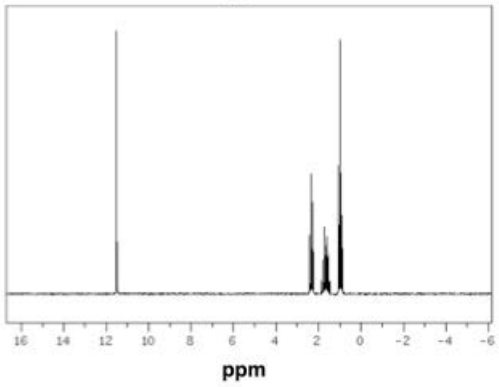
a. sample 1



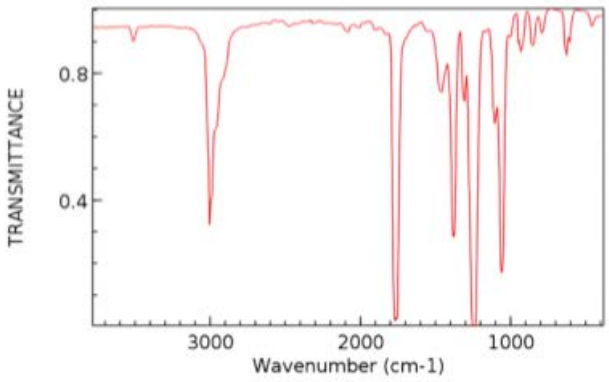


b. sample 2





c. sample 3



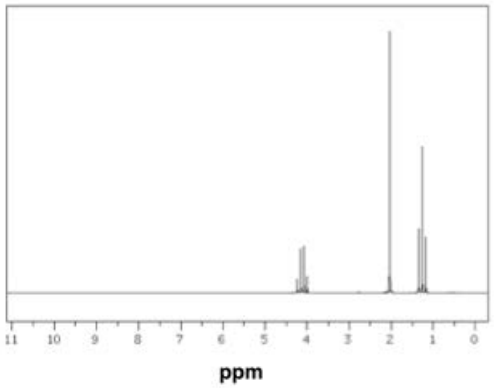


Figure 1: IR (left) and NMR (right) spectra

Problem 1) Synthesis questions:

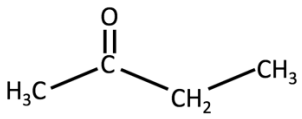
1) Based on your assignment of spectra to each molecule and your knowledge of which contaminants are particularly dangerous at high concentrations, do you think the municipal drinking water is safe to drink (lives are at stake here)?

2) Which features, either in the IR spectra or the NMR spectra, are the easiest to identify, which are the hardest? Another way to think about this is to determine which functional groups are easiest to identify in the spectra and which are the hardest.

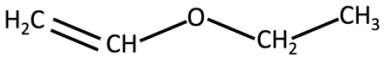
3) What functional group do all 3 molecular structures have in common? Where does that appear in the IR spectrum?

Problem 2) Once again the Municipal Water supply has been compromised! This time the likely culprit is an industrial plant working overtime to produce enough PVC for the citizens of the community to make their Burning Man art projects. You instruct the trusty undergrads that work for you to isolate the contaminant and take IR and NMR spectra. They have collected spectra and narrowed it down to three structures, but they need your help to determine which the contaminant is.

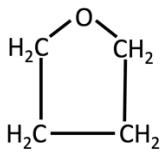
Look carefully at the following three isomers and the IR and NMR spectra of the contaminant below, by identifying stretches and chemical shifts, determine which one of the structures is the contaminant. After doing so please answer the questions on page 2.



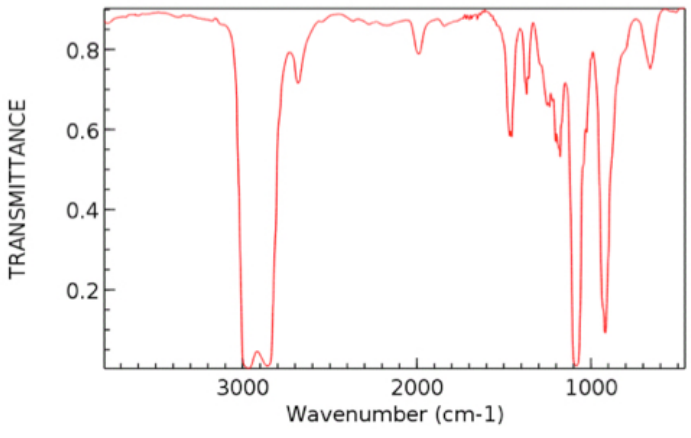
2-Butanone



Ethyl vinyl ether



Tetrahydrofuran



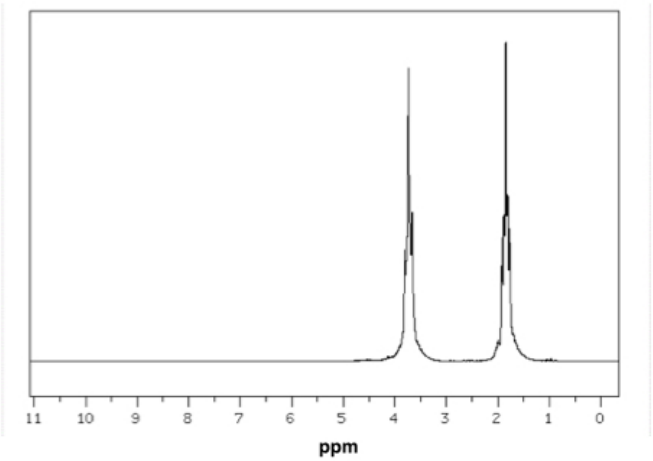


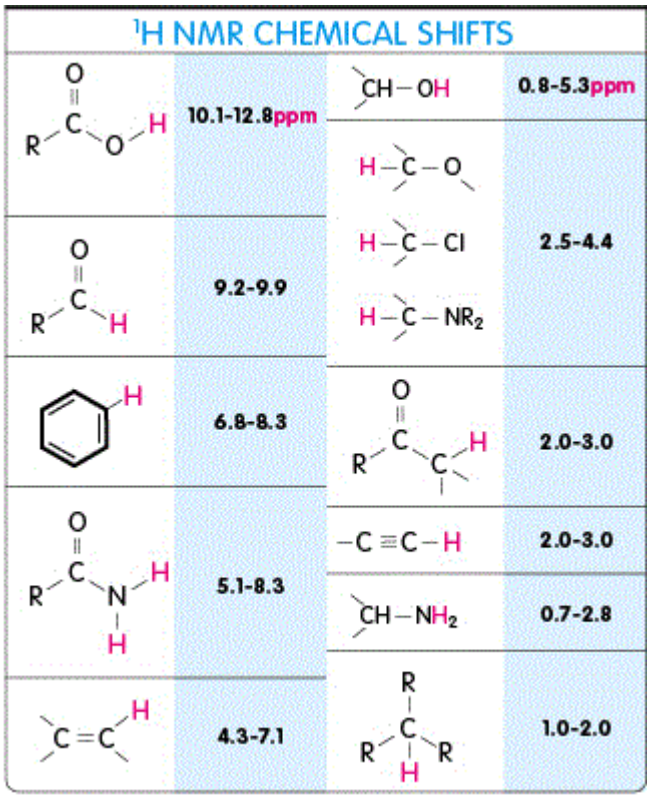
Figure 2: IR (left) and NMR (right) spectra

Problem 2) Synthesis Questions:

1) What is the mysterious contaminant in the municipal water supply?

2) What special property does the structure of the contaminant exhibit that might make it easier to identify using NMR?

3) Using either the IR or the NMR spectra (or both!), how did you rule out the other two structures?



Type of bond	Wavenumber (cm^{-1})	Intensity
C≡N	2260–2220	medium
C≡C	2260–2100	medium to weak
C=C	1680–1600	medium
C=N	1650–1550	medium
	~1600 and ~1500–1430	strong to weak
C=O	1780–1650	strong
C—O	1250–1050	strong
C—N	1230–1020	medium
O—H (alcohol)	3650–3200	strong, broad
O—H (carboxylic acid)	3300–2500	strong, very broad
N—H	3500–3300	medium, broad
C—H	3300–2700	medium