Identifying Functional Groups with Raman Spectroscopy

Purpose Characteristic Raman peaks associated with specific organic functional groups will be analyzed. This information will be used to determine the composition of an unknown sample containing various functional groups similar to those studied in this lab.

References Lin-Vien, D.; Colthup, N.; Fateley, W.; Grasselli, J. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, 1st ed.; Academic Press: San Diego, 1991.

Apparatus Snowy Range Instruments IM-52 Raman spectrometer
Computer with Peak acquisition software, Microsoft Excel software
2mL glass vials
Pipettes

Chemicals

n-Hexane	1-pentyne	Methyl $tert$-butyl ether
n-Heptane	3-hexyne	Acetic acid
2,2,4-trimethylpentane	Benzene	Ethyl acetate
Cyclohexane	Toluene	Triethylamine
Trichloromethane	Ethanol	Dimethylacetamide
1-hexene	Acetone	Acetonitrile
Unknown sample		

Your instructor may provide you with different chemicals than are listed above; as long as each functional group is represented, the lab – including the characteristic peaks in the Treatment section table – will be relatively unchanged. However, subtle changes in the functional group (such as whether the alkyne you are provided with is a primary or secondary alkyne) may change the values of your Raman analysis.

Theory A prominent application for Raman spectroscopy is determining the chemical composition of unknown substances. The laser used in a Raman spectrometer causes specific parts of the target molecule to vibrate; thus, specific chemical bonds and structures display characteristic Raman peaks. Many factors determine the wavenumber shift and intensity at which each functional group's peak or peaks will be found. Some functional groups are more Raman active than others, and will produce more intense peaks. For example, the C=O bond characteristic of aldehydes is not strongly Raman-active. Alternatively, the aromatic ring breathing mode in toluene is strongly Raman-active. By assigning all of the functional groups in a Raman spectrum, the identity of a substance can be accurately determined.

Procedure Prepare neat 2mL samples of each of the chemicals above and take Raman spectra of each one. Average ten acquisitions, adjusting the integration time as necessary for each chemical. Upload each spectrum data file into a separate Microsoft Excel spreadsheet and plot the spectra.

Treatment Each substance you collected was chosen as representative of a certain functional group. Below is a table containing frequencies for some characteristic Raman peaks of those functional groups. Fill in the table with the values you observed for each chemical that most closely match the reference values, as well as the intensity at that peak and the integration time. Not all peaks in the spectrum will be represented by this chart, and you may see analogous peaks between different chemicals. For instance, the alkane peaks will be found in almost all other samples, because the C-C bond forms the backbone of most organic compounds. In addition, because of the difference in intensity between different functional groups, the chosen peak may not be the most prominent peak in your spectrum.

All reference peak values come from *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*, as listed in the References above. For the Observed Values

and Unknown columns, fill in the wavenumber shift (in cm^{-1}), Intensity (arbitrary units) and integration time (s).

Functional group	**Chemical**	**Formula**	**Reference Values (cm^{-1})**	**Observed Values**	**Unknown**
Alkane	n-Hexane	C_6H_{14}	CH_2 in-phase twist: 1305-1295		
	n-Heptane	C_7H_{16}	C-C skeletal stretch (n-alkane): 1100-1040 900-800 (2 peaks)		
Branched alkane	2,2,4-Trimethylpentane	C_8H_{18}	C-C skeletal stretch (branched alkane): 1175-1165 1170-1140 1060-1040 950-900		
Cycloalkane	Cyclohexane	C_6H_{12}	Cyclohexane ring breathing: 802		
Haloalkane	Trichloromethane	$CHCl_3$	C-Cl stretch: 760-740 675-655 635-630 615-605		
Alkene	1-hexene	C_6H_{12}	Monoalkyl C=C stretch: 1650-1638		
Alkyne	3-hexyne	C_6H_{10}	Disubstituted C≡C stretch: 2237-2230		
Aromatic	Benzene	C_6H_6	Unsubtituted aromatic ring breathing: 992		
	Toluene	C_7H_8	Monosubstituted aromatic ring breathing: 1010-990		
Alcohol	Ethanol	C_2H_5OH	In-phase CCO stretch: 900-800		
Aldehyde	Acetaldehyde	C_2H4O	Alkyl aldehyde C=O stretch: 1740-1725		
Ketone	Acetone	$(CH_3)_2CO$	Alkyl ketone C=O stretch: 1720-1712		
Ether	Methyl $tert$-butyl ether	$(CH_3)_3COCH_3$	Symmetrical COC stretch: 890-820		
Carboxylic acid	Acetic acid	CH_3COOH	Dimer C=O stretch: 1687-1625		

Ester	Ethyl acetate	$CH_3COOCH_2CH_3$	O-C=O in-plane deformation (acetate ester): 644-634		
Amine	Triethylamine	$(C_2H_5)_3N$	Trisubstituted amine C-N stretch: 1250-1000 833-740		
Amide	Dimethylacetamide	$CH_3CON(CH_3)_2$	Tertiary amide C-N stretch: 750-700		
Nitrile	Acetonitrile	CH_3CN	C≡N stretch: 2250-2230		

Analysis Your instructor will provide you with an unknown sample containing a chemical different from any that you analyzed earlier. Compare the spectra to the reference and observed frequencies in the table to determine what functional groups they contain, and determine the identity of the unknown samples.

Questions 1. Which functional groups had the strongest Raman peaks? Which had the weakest? Remember that Raman intensity is directly proportional to the integration time.

2. Suggest a reason that some functional groups presented more strongly in the Raman spectrum than did others.

3. What functional groups were present in the unknown sample? What peaks did you observe that are characteristic of those functional groups?

4. What is the unknown sample? Write the common name (if you know it), the systematic name, and draw a structural formula.

5. Comment on the possibility for errors in your determination of the unknown sample's identity.