

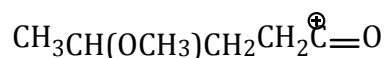
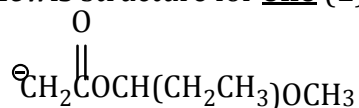
Dr. Richter

PRINT NAME _____.

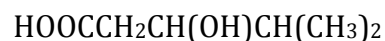
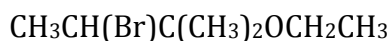
SIGN NAME _____.

You are required to answer all question sets. Please note that some of the question sets offer you a choice of questions - do only the number of questions asked for. Please write legibly and draw clearly. Points will be deducted for illegible and unclear answers. The point total for this exam is 100 and the value of each question set is shown in parenthesis beside that set. **READ ALL QUESTIONS CAREFULLY AND APPORTION YOUR TIME ACCORDINGLY.**

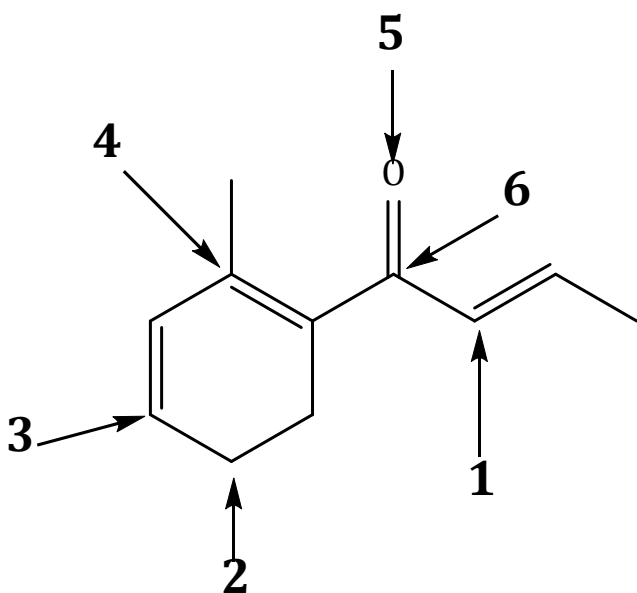
1. Draw a *Lewis* structure for **one** (1) of the following ions: (6)



2. Draw a *skeletal* structure for **one** (1) of the following molecules: (6)



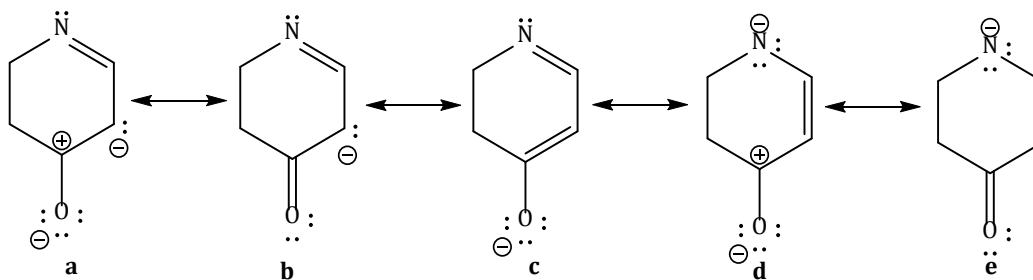
3. The structure below belongs to a family of compounds called the “damascenones.” These compounds are responsible for the fragrance of roses. Indicate the hybridization of each of the numbered atoms in the provided list on the right. Remember, use the resonance **hybrid** as your guide. If an atom is “in between,” label it as such. (12)



ANSWERS:

1. _____
 2. _____
 3. _____
 4. _____
 5. _____
 6. _____

4. Consider the five structures below (a-e).



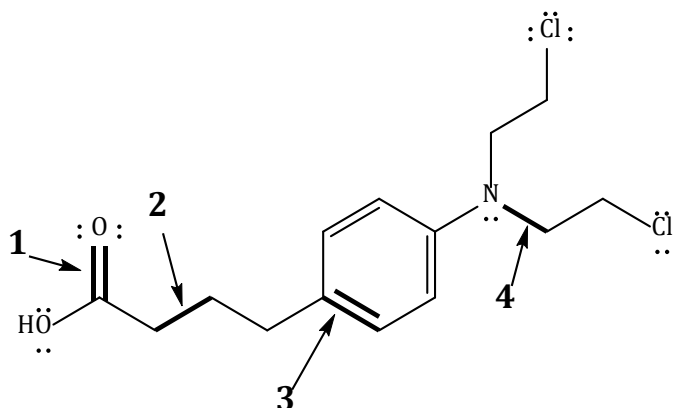
- A. Draw the resonance hybrid of the ion represented by structures a-e. (4)

- B. Rank resonance structures a-e according to contribution to the resonance hybrid. (5)

Answers: _____

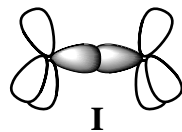
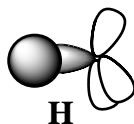
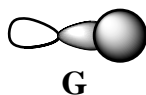
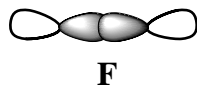
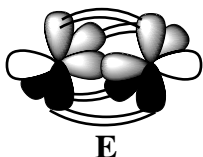
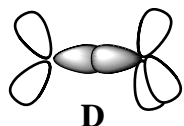
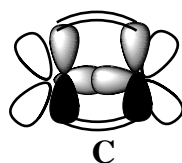
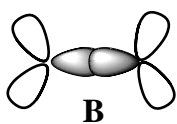
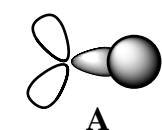
greatest contribution $\xrightarrow{\hspace{10em}}$ least contribution

5. Consider the molecule (chlorambucil, a chemotherapeutic agent) shown below. (16)



For each of the highlighted bonds **1-4**, match the bond with a 3-D orbital picture AND the description of the orbital overlap forming the σ and/or π bond(s). Write your answers in the table below. **Notes:** **1.** Do NOT consider the resonance hybrid for this exercise, **2.** You may need to use more than one description per bond, **3.** Not all choices will be used.

Orbital Picture Choices



Description Choices

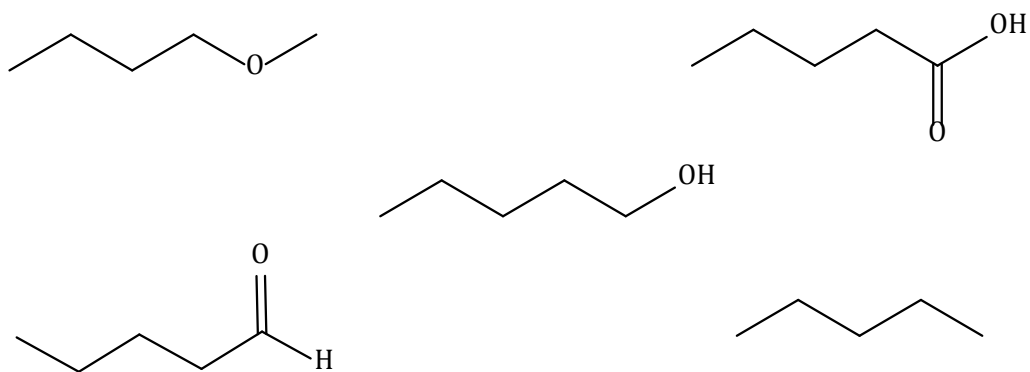
- | | |
|--|---|
| 1: σ Csp ³ -H _{1s} | 8: σ Nsp ³ -Csp ³ |
| 2: σ Csp ³ -Osp ² | 9: σ Csp ² -Csp ² |
| 3: σ Csp ² -Osp ² | 10: σ Csp ³ -Csp ³ |
| 4: σ Csp ² -Nsp ² | 11: σ Csp ² -Csp ³ |
| 5: σ Csp ² -Nsp ³ | 12: π Op-Cp |
| 6: σ Nsp-Nsp ² | 13: π Cp-Np |
| 7: σ Nsp ² -Nsp ² | 14: π Cp-Cp |

Answers:

Bond	Orbital Picture	Description(s)	Bond	Orbital Picture	Description(s)
1			3		
2			4		

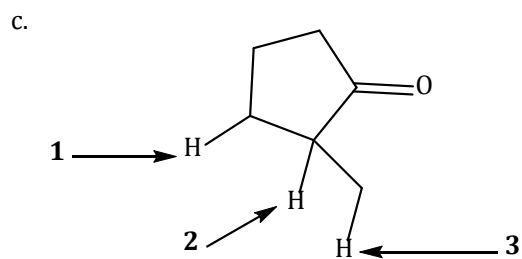
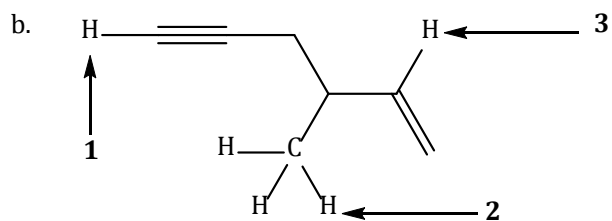
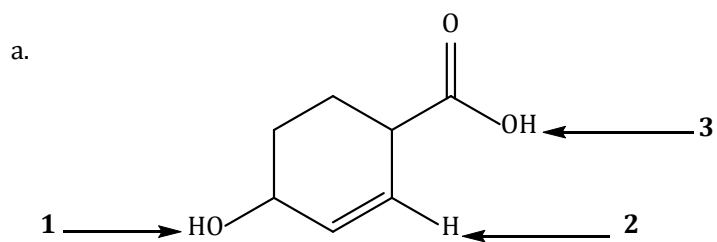
7. Of the 5 pure substances below, circle the one with the **highest** boiling point.

(5)



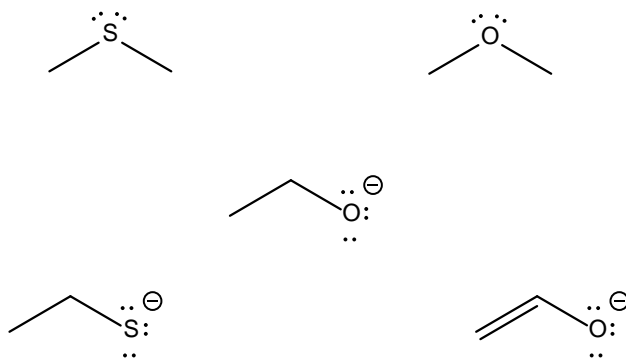
8. For **each** compound below (a-c), circle which proton (1, 2, or 3) has the lowest pKa.

(6)



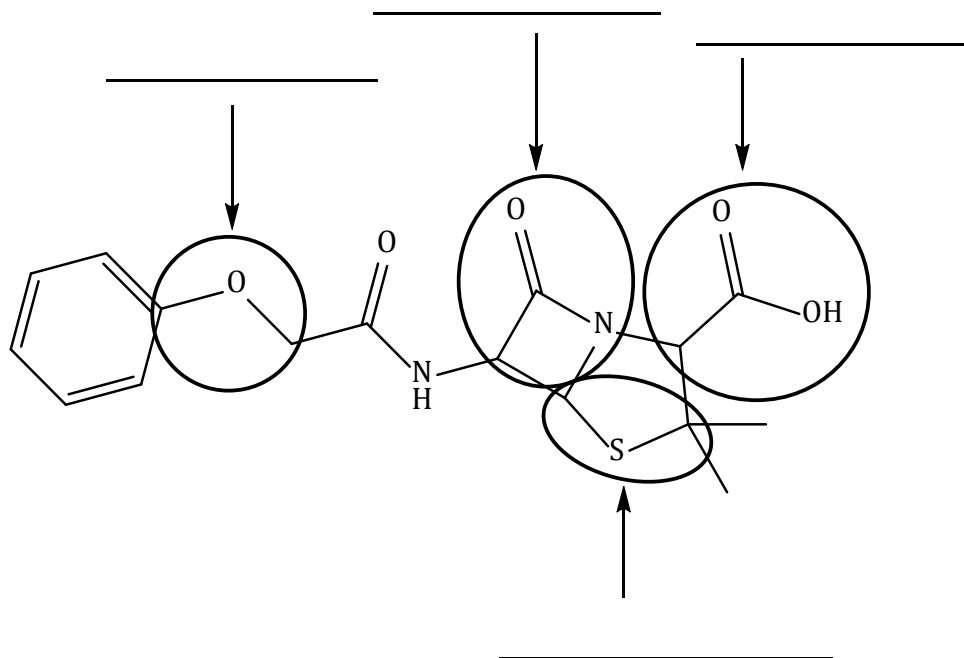
9. Of the 5 bases below, circle the *weakest (i.e. least reactive)*.

(5)

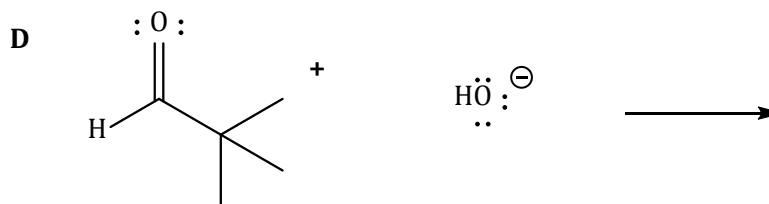
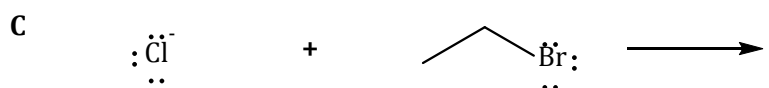
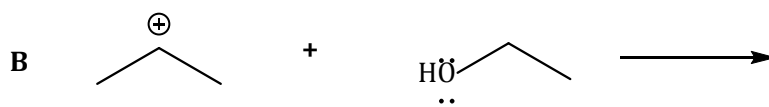
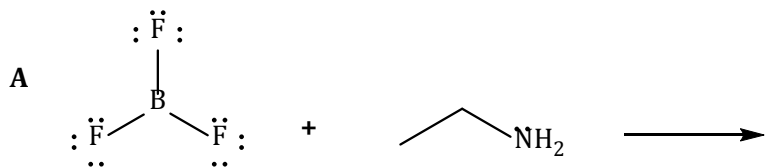


10. Identify the circled functional groups in the structure below. Reminder: use the term that Smith calls the "Type of Compound." For example, use "ether," not "alkoxy." Write your answer in the blanks provided.

(8)



11. For each of the following reactions (A-D) **a. label** the Lewis base (nucleophile) and the Lewis acid (electrophile) and **b. draw** reaction arrows to show the appropriate *electron movement* between the nucleophile and electrophile. **You do not need to show the products.** (8)



12. Indicate whether each statement **a-e** is **true (T)** or **false (F)**. (10)

_____ a. IR spectroscopy can be used to obtain functional group information about a compound.

_____ b. When matter absorbs infrared radiation, it causes vibrational excitations to take place within the matter.

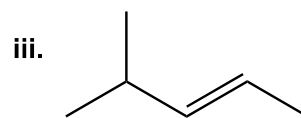
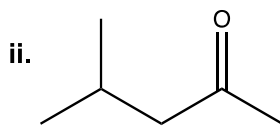
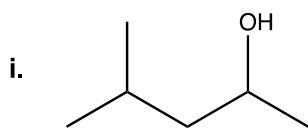
_____ c. IR spectral data is reported in parts per million or "ppm."

_____ d. In general, bonds between lighter atoms will absorb a higher frequency of IR radiation than will bonds between heavier atoms.

_____ e. Bonds between sp^3 atoms tend to vibrate at lower frequencies than do bonds between sp^2 - or sp -hybridized atoms.

13. Match each IR spectrum a-c below to one of the structures i-iii.

(9)



ANSWERS

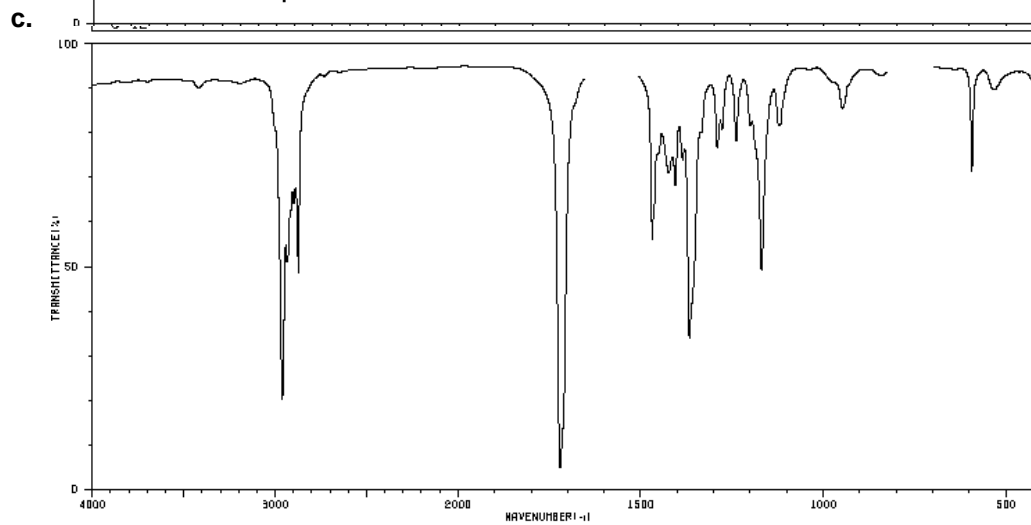
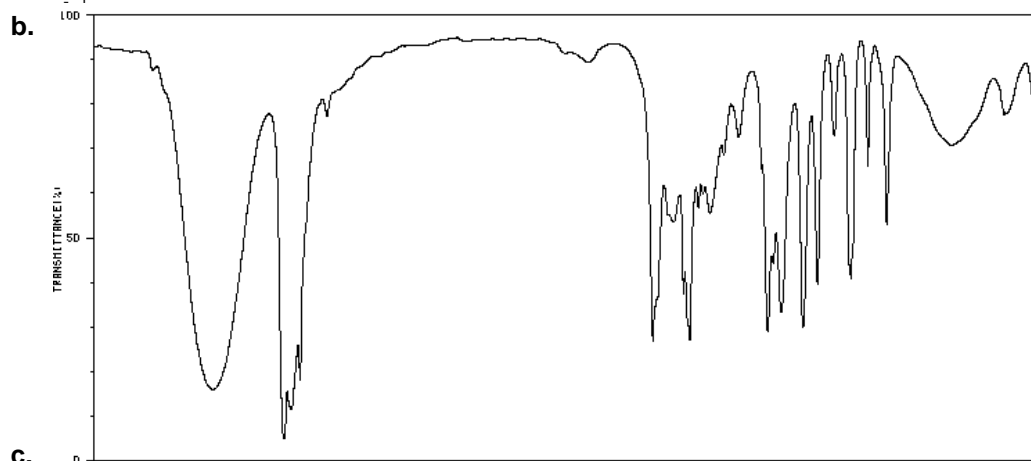
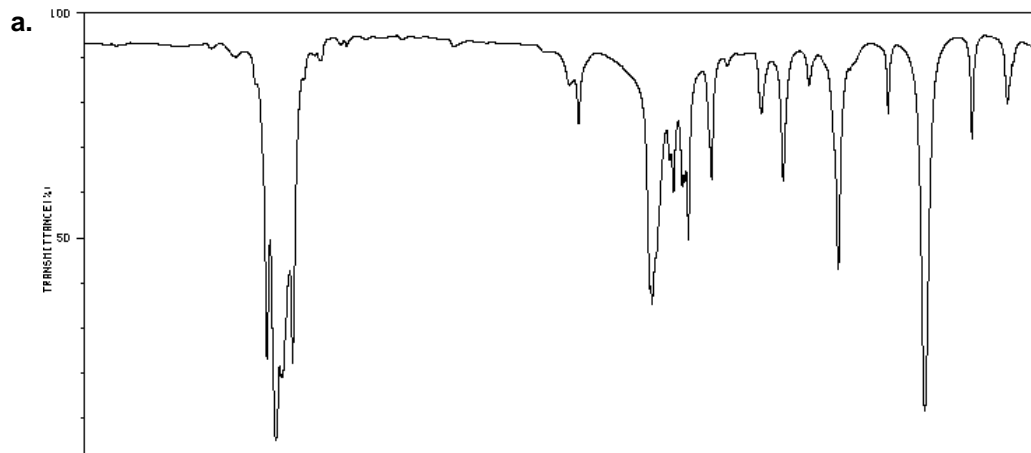


TABLE 7-2 An Alphabetical Listing of Some Functional Groups and Classes of Compounds with Their Absorption Frequencies in the Infrared

Group or Class	Frequency Ranges (cm ⁻¹) and Intensities ^a	Assignment and Remarks
Acid halides $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{X}$		
aliphatic	1810–1790 (s) 965–920 (m) 440–420 (s)	C=O stretch; fluorides 50 cm ⁻¹ higher C–C stretch Cl–C=O in-plane deformation
aromatic	1785–1765 (s) 890–850 (s)	C=O stretch; also a weaker band (1750–1735 cm ⁻¹) due to Fermi resonance C–C stretch (Ar–C) or C–Cl stretch
Alcohols		
primary $-\text{CH}_2\text{OH}$	3640–3630 (s) 1060–1030 (s)	OH stretch, dil CCl ₄ soln C–OH stretch; lowered by unsaturation
secondary $-\text{CHROH}$	3630–3620 (s) 1120–1080 (s)	OH stretch, dil CCl ₄ soln C–OH stretch; lower when R is a branched chain or cyclic
tertiary $-\text{CR}_2\text{OH}$	3620–3610 (s) 1160–1120 (s)	OH stretch, dil CCl ₄ soln C–OH stretch; lower when R is branched
general $-\text{OH}$	3350–3250 (s) 1440–1260 (m–s, br) 700–600 (m–s, br)	OH stretch; broad band in pure solids or liquids C–OH in-plane bend C–OH out-of-plane deformation
Aldehydes $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$	2830–2810 (m) } 2740–2720 (m) } 1725–1695 (vs) 1440–1320 (s) 695–635 (s) 565–520 (s)	Fermi doublet; CH stretch with overtone of CH bend (see page 164) C=O stretch; slightly higher in CCl ₄ soln H–C=O bend in aliphatic aldehydes C–C–CHO bend C–C=O bend
Alkenes		
monosubst $-\text{CH}=\text{CH}_2$	—	See Vinyl
disubst $-\text{CH}=\text{CH}-$	—	See Vinylene
trisubst $\begin{array}{c} \diagup \\ \text{C}=\text{CH}_2 \\ \diagdown \\ \text{C}=\text{CH}- \end{array}$	—	See Vinylidene
tetrasubst $\begin{array}{c} \diagup \quad \diagdown \\ \text{C}=\text{C} \\ \diagdown \quad \diagup \end{array}$	3050–3000 (w) 1690–1655 (w–m) 850–790 (m) 1690–1670 (w)	CH stretch C=C stretch CH out-of-plane bending C=C stretch, may be absent for symmetrical compounds
Alkyl	2980–2850 (m) 1470–1450 (m) 1400–1360 (m) 740–720 (w)	CH stretch, several bands CH ₂ deformation CH ₃ deformation CH ₂ rocking
Alkynes $\text{RC}\equiv\text{C}-\text{H}$	3300–3250 (m–s) 2250–2100 (w–m) 680–580 (s)	terminal $\equiv\text{C}-\text{H}$ stretch C \equiv C, frequency raised by conjugation –C \equiv CH bend

^as = strong; m = medium; w = weak; v = very; br = broad.

TABLE 7-2 (Continued)

Group or Class	Frequency Ranges (cm ⁻¹) and Intensities ^a	Assignment and Remarks	
Amides			
primary —CONH ₂	3540–3520 (m) 3400–3380 (m) 1680–1660 (vs) 1650–1610 (m)	NH ₂ stretch (dil solns); bands shift to 3360–3340 and 3200–3180 in solid C=O stretch (Amide I band) NH ₂ deformation; sometimes appears as a shoulder (Amide II band)	
secondary —CONHR	1420–1400 (m-s) 3440–3420 (m) 1680–1640 (vs) 1560–1530 (vs) 1310–1290 (m) 710–690 (m)	C—N stretch (Amide III band) NH stretch (dil soln); shifts to 3300–3280 in pure liquid or solid C=O stretch (Amide I band) NH bend (Amide II band) C—N stretch assignment uncertain	
tertiary —CONR ₂ general —CONR ₂	1670–1640 (vs) 630–570 (s) 615–535 (s) 520–430 (m-s)	C=O stretch N—C=O bend C=O out-of-plane bend C—C=O bend	
Amines			
primary —NH ₂	3460–3280 (m) 2830–2810 (m) 1650–1590 (s)	NH stretch; broad band, may have some structure CH stretch NH ₂ deformation	
secondary —NHR	3350–3300 (vw) 1190–1130 (m) 740–700 (m)	NH stretch C—N stretch NH deformation	
tertiary —NR ₂	450–400 (w, br) 510–480 (s)	C—N—C bend C—N—C bend	
Amine hydrohalides	RNH ₃ ⁺ X ⁻ R ⁺ NH ₂ R X ⁻	NH ₃ ⁺ stretch, several peaks NH deformation (one or two bands)	
Amino acids	$\begin{array}{c} \text{NH}_2 \\ \\ \text{—C—COOH} \\ \end{array}$ (or —C ⁺ NH ₃ COO ⁻)	H-bonded NH ₂ and OH stretch; v broad band in solid state COO ⁻ antisym stretch —NH ₃ ⁺ deformation COO ⁻ sym stretch COO ⁻ rocking	
Ammonium NH ₄ ⁺	3350–3050 (vs) 1430–1390 (s)	NH stretch; broad band NH ₂ deformation; sharp peak	
Anhydrides	$\begin{array}{c} \text{—CO} \\ \diagdown \\ \text{O} \\ \diagup \\ \text{—CO} \end{array}$	1850–1780 (variable) 1770–1710 (m-s) 1220–1180 (vs)	antisym C=O stretch sym C=O stretch C—O—C stretch (higher in cyclic anhydrides)
Aromatic compounds	3100–3000 (m) 2000–1660 (w) 1630–1430 (variable) 900–650 (s) 580–420 (m-s)	CH stretch, several peaks overtone and combination bands aromatic ring stretching (four bands) out-of-plane CH deformations (one or two bands depending on substitution) ring deformations (two bands)	
Azides	$\text{—}\overset{-}{\text{N}}=\overset{+}{\text{N}}\equiv\text{N}$	2160–2080 (s) N≡N stretch	

TABLE 7-2 (Continued)

Group or Class	Frequency Ranges (cm ⁻¹) and Intensities ^a	Assignment and Remarks
Bromo —C—Br	650–500 (m)	C—Br stretch
<i>t</i> -Butyl (CH ₃) ₃ C—	2980–2850 (m) 1400–1370 (m) and 1380–1360 (s)	CH stretch; several bands CH ₃ deformations
Carbodiimides —N=C=N—	2150–2100 (vs)	N=C=N antisym stretch
Carbonyl $\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array}$	1870–1650 (vs, br)	C=O stretch
Carboxylic acids $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ \diagdown \\ \text{OH} \end{array}$	3550–3500 (s) 3300–2400 (s, v br) 1800–1740 (s) 1710–1680 (vs) 960–910 (s) 700–590 (s) 550–465 (s)	OH stretch (monomer, dil soln) H-bonded OH stretch (solid & liq states) C=O stretch of monomer (dil soln) C=O stretch of dimer (solid & liq states) C—OH deformation O—C=O bend C—C=O bend
Chloro $\begin{array}{c} \\ -\text{C}-\text{Cl} \\ \end{array}$	850–550 (m)	C—Cl stretch
Cycloalkanes	580–430 (s)	ring deformation
Diazonium salts —N≡N ⁺	2300–2240 (s)	N≡N stretch
Esters $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C} \\ \diagdown \\ \text{OR}' \end{array}$	1765–1720 (vs) 1290–1180 (vs) 645–575 (s)	C=O stretch C—O—C antisym stretch O—C—O bend
Ethers —C—O—C—	1280–1220 (s) 1140–1110 (vs) 1275–1200 (vs) 1250–1170 (s) 1050–1000 (s)	C—O—C stretch in alkyl aryl ethers C—O—C stretch in dialkyl ethers C—O—C stretch in vinyl ethers C—O—C stretch in cyclic ethers R(alkyl)—C—O stretch in alkyl aryl ethers
Fluoroalkyl —CF ₃ , —CF ₂ —, etc.	1400–1000 (vs)	C—F stretch
Isocyanates —N=C=O	2280–2260 (vs)	N=C=O antisym stretch
Isothiocyanates —N=C=S	2140–2040 (vs, br)	C=N=S antisym stretch
Ketones $\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{O} \\ \diagup \\ \text{R}' \end{array}$	1725–1705 (vs) 1700–1650 (vs) 1705–1665 (s) and 1650–1580 (m)	C=O stretch in saturated aliphatic ketones C=O stretch in aromatic ketones C=O and C=C stretching in α,β-unsaturated ketones
Lactones $\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2-\text{C} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{CH}_2-\text{O} \end{array}$	1850–1830 (s) 1780–1770 (s) 1750–1730 (s)	C=O stretch in β-lactones C=O stretch in γ-lactones C=O stretch in δ-lactones
Methyl —CH ₃	2970–2850 (s) 2835–2815 (s) 2820–2780 (s) 1470–1440 (m) 1390–1370 (m-s)	CH stretch in C—CH ₃ compounds CH stretch in methyl ethers (O—CH ₃) CH stretch in N—CH ₃ compounds CH ₃ antisym deformation CH ₃ sym deformation

TABLE 7-2 (Continued)

Group or Class	Frequency Ranges (cm ⁻¹) and Intensities ^a	Assignment and Remarks	
Methylene —CH ₂ —	2940–2920 (m)	CH stretches in alkanes	
	and 2860–2850 (m)		
	3090–3070 (m)	CH stretches in alkenes	
	and 3020–2980 (m)		
	1470–1450 (m)	CH ₂ deformation	
Naphthalenes	645–615 (m-s)	in-plane ring bending	
	and 545–520 (s)		
		490–465 (variable)	out-of-plane ring bending
Nitriles —C≡N	2260–2240 (w)	C≡N stretch in aliphatic nitriles	
	2240–2220 (m)	C≡N stretch in aromatic nitriles	
	580–530 (m-s)	C—C—CN bend	
Nitro —NO ₂	1570–1550 (vs)	NO ₂ stretches in aliphatic nitro compounds	
	and 1380–1360 (vs)		
	1480–1460 (vs)	NO ₂ stretches in aromatic nitro compounds	
	and 1360–1320 (vs)		
	920–830 (m)	C—N stretch	
	650–600 (s)	NO ₂ bend in aliphatic compounds	
	580–520 (m)	NO ₂ bend in aromatic compounds	
530–470 (m-s)	NO ₂ rocking		
Oximes =NOH	3600–3590 (vs)	OH stretch (dil soln)	
	3260–3240 (vs)	OH stretch (solids)	
	1680–1620 (w)	C=N stretch; strong in Raman	
Phenols Ar—OH	720–600 (s, br)	O—H out-of-plane deformation	
	450–375 (w)	C—OH deformation	
Phenyl C ₆ H ₅ —	3100–3000 (w-m)	CH stretch four weak bands; overtones and combinations	
	2000–1700 (w)		
	1625–1430 (m-s)	aromatic C=C stretches (four bands)	
	1250–1025 (m-s)	CH in-plane bending (five bands)	
	770–730 (vs)	CH out-of-plane bending	
	710–690 (vs)	ring deformation	
	560–420 (m-s)	ring deformation	
	Phosphates (RO) ₃ P=O R = alkyl	1285–1255 (vs)	P=O stretch
1050–990 (vs)		P—O—C stretch	
R = aryl		1315–1290 (vs)	P=O stretch
1240–1190 (vs)		P—O—C stretch	
Phosphines —PH ₂ , —PH	2410–2280 (m)	P—H stretch	
	1100–1040 (w-m)	P—H deformation	
	700–650 (m-s)	P—C stretch	
Pyridyl —C ₅ H ₄ N	3080–3020 (m)	CH stretch	
	1620–1580 (vs)		
	and 1590–1560 (vs)	C=C and C=N stretches	
	840–720 (s)	CH out-of-plane deformation (one or two bands, depending on substitution)	
	635–605 (m-s)	in-plane ring bending	
Silanes —SiH ₃ —SiH ₂ —	2160–2110 (m)	Si—H stretch	
	950–800 (s)	Si—H deformation	

TABLE 7-2 (Continued)

Group or Class	Frequency Ranges (cm ⁻¹) and Intensities ^a	Assignment and Remarks
Silanes (fully substituted)	1280-1250 (m-s) 1110-1050 (vs) 840-800 (m)	Si-C stretch Si-O-C stretch (aliphatic) Si-O-C deformation
Sulfates R-O-SO ₂ -O-R R-O-SO ₃ ⁻ M ⁺ (M = Na ⁺ , K ⁺ , etc.)	1140-1350 (s) and 1230-1150 (s) 1260-1210 (vs) and 810-770 (s)	S=O stretches in covalent sulfates S=O stretches in alkyl sulfate salts C-O-S stretch
Sulfides C-S-	710-570 (m)	C-S stretch
Sulfones -SO ₂ -	1360-1290 (vs) 1170-1120 (vs) 610-545 (ms)	SO ₂ antisym stretch SO ₂ sym stretch SO ₂ scissor mode
Sulfonic acids -SO ₂ OH	1250-1150 (vs, br)	S=O stretch
Sulfoxides $\begin{array}{c} \diagup \\ \text{S}=\text{O} \\ \diagdown \end{array}$	1060-1030 (s, br) 610-545 (m-s)	S=O stretch SO ₂ scissoring
Thiocyanates -S-C≡N	2175-2160 (m) 650-600 (w) 405-400 (s)	C≡N stretch S-CN stretch S-C≡N bend
Thiols -S-H	2590-2560 (w) 700-550 (w)	S-H stretch; strong in Raman C-S stretch; strong in Raman
Triazines C ₃ N ₃ Y ₃ 1,3,5-trisubst	1600-1500 (vs) 1380-1350 (vs) 820-800 (s)	ring stretching ring stretching CH out-of-plane deformation
Vinyl -CH=CH ₂	3095-3080 (m) and 3030-2980 (w-m) 1850-1800 (w-m) 1645-1615 (m-s) 1000-950 (s) 950-900 (vs)	=CH ₂ stretching =CH stretching overtone of CH ₂ out-of-plane wagging C=C stretch CH out-of-plane deformation CH ₂ out-of-plane wagging
Vinylene -CH=CH-	3040-3010 (m) 1665-1635 (w-m) 1675-1665 (w-m) 980-955 (s) 730-665 (s)	=CH ₂ stretching C=C stretch (cis isomer) C=C stretch (trans isomer) <i>trans</i> CH out-of-plane deformation (trans isomer) CH out-of-plane deformation (trans isomer) <i>cis</i>
Vinylidene $\begin{array}{c} \diagup \\ \text{C}=\text{CH}_2 \\ \diagdown \end{array}$	3095-3075 (m) 1665-1620 (w-m) 895-885 (s)	=CH ₂ stretching C=C stretch CH ₂ out-of-plane wagging