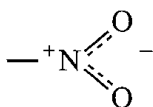


## المحاضرة التاسعة

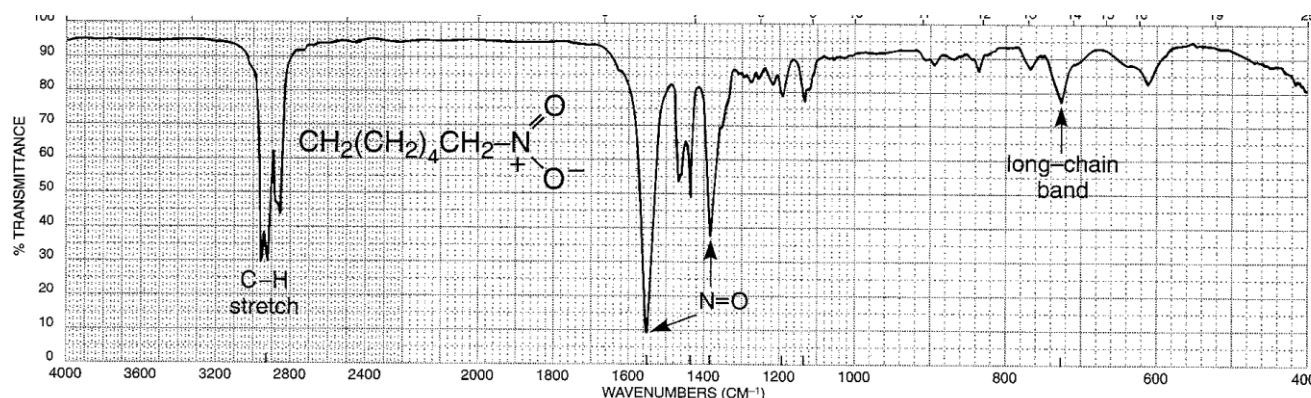
مركبات النيترو، النترات، النترينات، اليزوسيانات والامينات  
يمكن تلخيصها بالاتي

## NITRO COMPOUNDS



**Aliphatic nitro compounds:** asymmetric stretch (strong),  $1600\text{--}1530\text{ cm}^{-1}$ ;  
symmetric stretch (medium),  $1390\text{--}1300\text{ cm}^{-1}$ .

**Aromatic nitro compounds (conjugated):** asymmetric stretch (strong),  
 $1550\text{--}1490\text{ cm}^{-1}$ ; symmetric stretch (strong),  $1355\text{--}1315\text{ cm}^{-1}$ .

NITRILES  $\text{R}-\text{C}\equiv\text{N}$ 

$-\text{C}\equiv\text{N}$  Stretch is a medium-intensity, sharp absorption near  $2250\text{ cm}^{-1}$ . Conjugation with double bonds or aromatic rings moves the absorption to a lower frequency.

**Examples:** butyronitrile (Fig. 2.62) and benzonitrile (Fig. 2.63).

ISOCYANATES  $\text{R}-\text{N}=\text{C}=\text{O}$ 

$-\text{N}=\text{C}=\text{O}$  Stretch in an isocyanate gives a broad, intense absorption near  $2270\text{ cm}^{-1}$ .

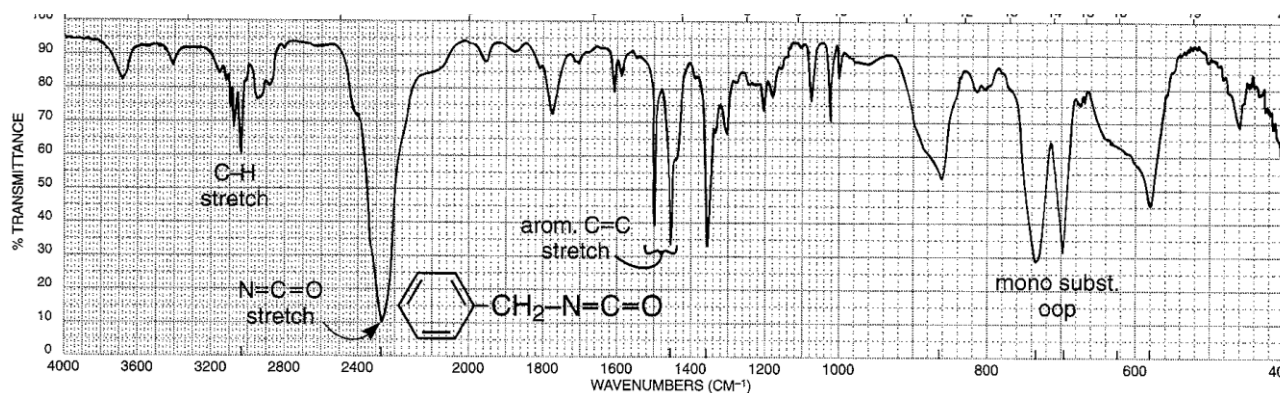
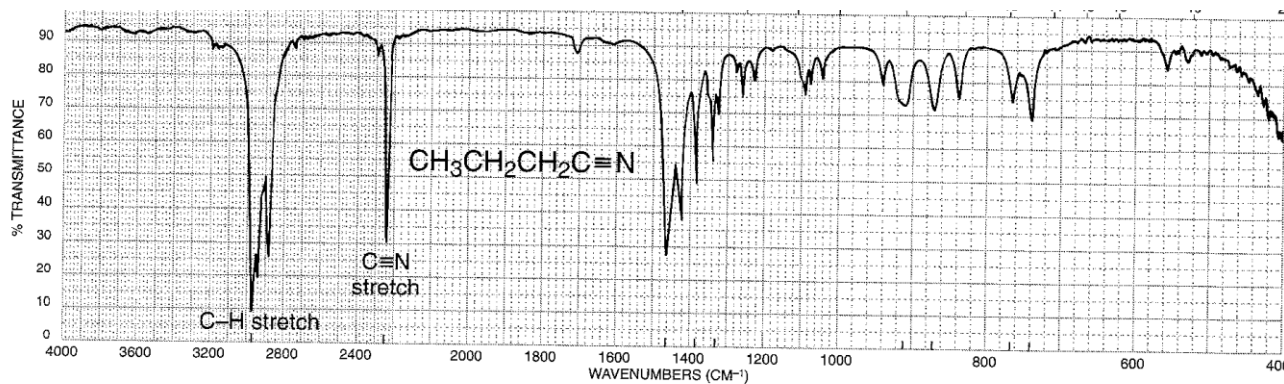
**Example:** benzyl isocyanate (Fig. 2.64).

ISOTHIOCYANATES  $\text{R}-\text{N}=\text{C}=\text{S}$ 

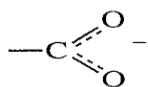
$-\text{N}=\text{C}=\text{S}$  Stretch in an isothiocyanate gives one or two broad, intense absorptions centering near  $2125\text{ cm}^{-1}$ .

IMINES  $\text{R}_2\text{C}=\text{N}-\text{R}$ 

$-\text{C}=\text{N}-$  Stretch in an imine, oxime, and so on gives a variable-intensity absorption in the range  $1690\text{--}1640\text{ cm}^{-1}$ .



### CARBOXYLATE SALTS $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^- \text{Na}^+$



Asymmetric stretch (strong) occurs near  $1600 \text{ cm}^{-1}$ ; symmetric stretch (strong) occurs near  $1400 \text{ cm}^{-1}$ .

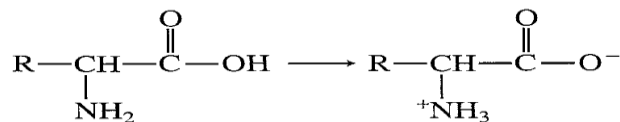
Frequency of C=O absorption is lowered from the value found for the parent carboxylic acid because of resonance (more single-bond character).

### AMINE SALTS $\text{NH}_4^+ \text{RNH}_3^+ \text{R}_2\text{NH}_2^+ \text{R}_3\text{NH}^+$

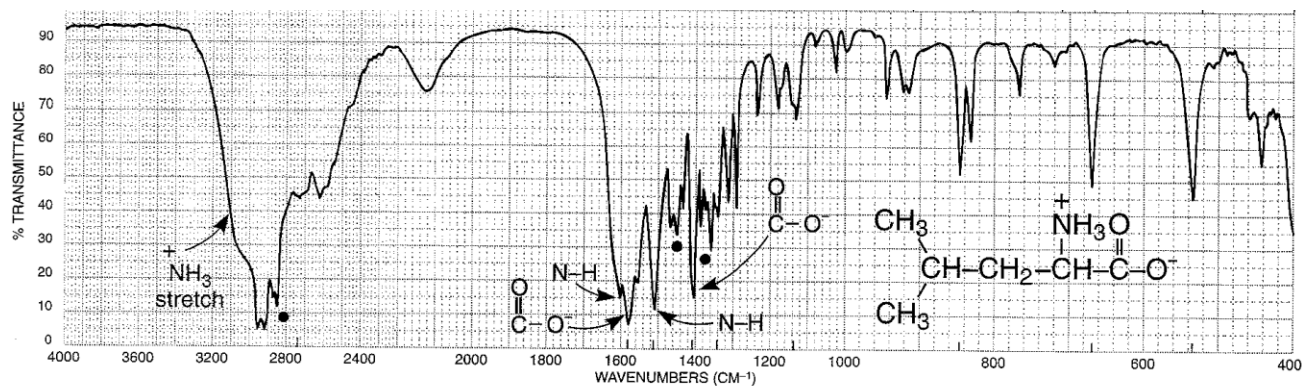
N-H Stretch (broad) occurs at  $3300\text{--}2600 \text{ cm}^{-1}$ . The ammonium ion absorbs to the left in this range, while the tertiary amine salt absorbs to the right. Primary and secondary amine salts absorb in the middle of the range,  $3100\text{--}2700 \text{ cm}^{-1}$ . A broad band often appears near  $2100 \text{ cm}^{-1}$ .

N-H Bend (strong) occurs at  $1610\text{--}1500 \text{ cm}^{-1}$ . Primary (two bands) is asymmetric at  $1610 \text{ cm}^{-1}$ , symmetric at  $1500 \text{ cm}^{-1}$ . Secondary absorbs in the range  $1610\text{--}1550 \text{ cm}^{-1}$ . Tertiary absorbs only weakly.

### AMINO ACIDS



These compounds exist as zwitterions (internal salts) and exhibit spectra that are combinations of carboxylate and primary amine salts. Amino acids show  $\text{NH}_3^+$  stretch (very broad), N-H bend (asymmetric/symmetric), and  $\text{COO}^-$  stretch (asymmetric/symmetric).



### MERCAPTANS R-S-H

S-H Stretch, one weak band, occurs near  $2550\text{ cm}^{-1}$  and virtually confirms the presence of this group, since few other absorptions appear here.

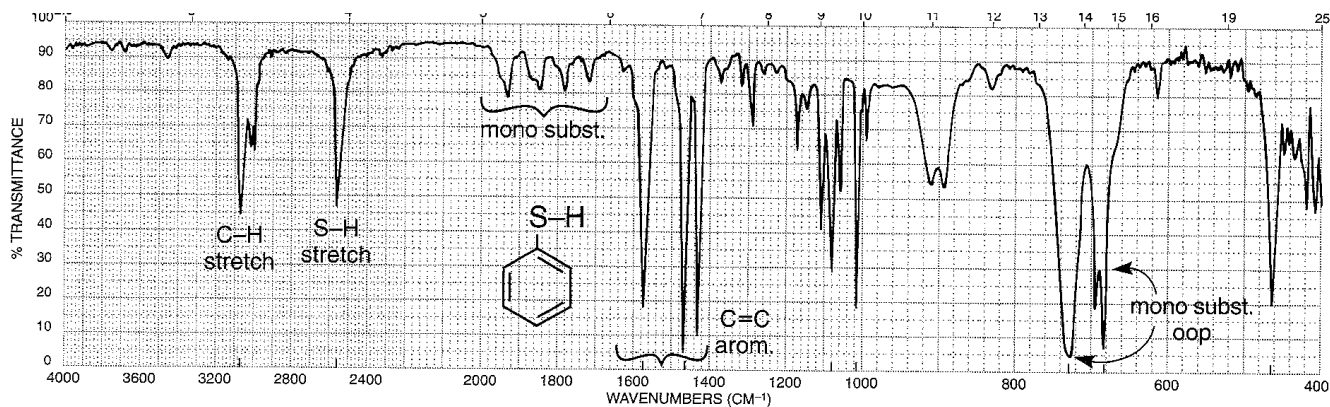
Example: benzenethiol (Fig. 2.68).

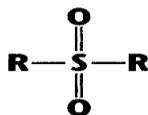
### SULFIDES R-S-R

Little useful information is obtained from the infrared spectrum.

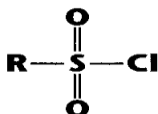
### SULFOXIDES R-S(=O)-R

S=O Stretch, one strong band, occurs near  $1050\text{ cm}^{-1}$ .



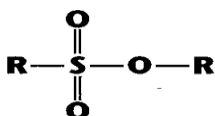
**SULFONES**

S=O Asymmetric stretch (strong) occurs at  $1300\text{ cm}^{-1}$ , symmetric stretch (strong) at  $1150\text{ cm}^{-1}$ .

**SULFONYL CHLORIDES**

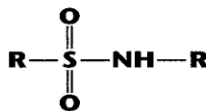
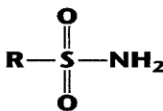
S=O Asymmetric stretch (strong) occurs at  $1375\text{ cm}^{-1}$ , symmetric stretch (strong) at  $1185\text{ cm}^{-1}$ .

**Example:** benzenesulfonyl chloride (Fig. 2.69).

**SULFONATES**

S=O Asymmetric stretch (strong) occurs at  $1350\text{ cm}^{-1}$ , symmetric stretch (strong) at  $1175\text{ cm}^{-1}$ .

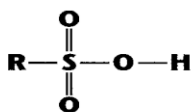
S-O Stretch, several strong bands, occurs in the range  $1000\text{--}750\text{ cm}^{-1}$ .

**SULFONAMIDES  
(Solid State)**

S=O Asymmetric stretch (strong) occurs at  $1325\text{ cm}^{-1}$ , symmetric stretch (strong) at  $1140\text{ cm}^{-1}$ .

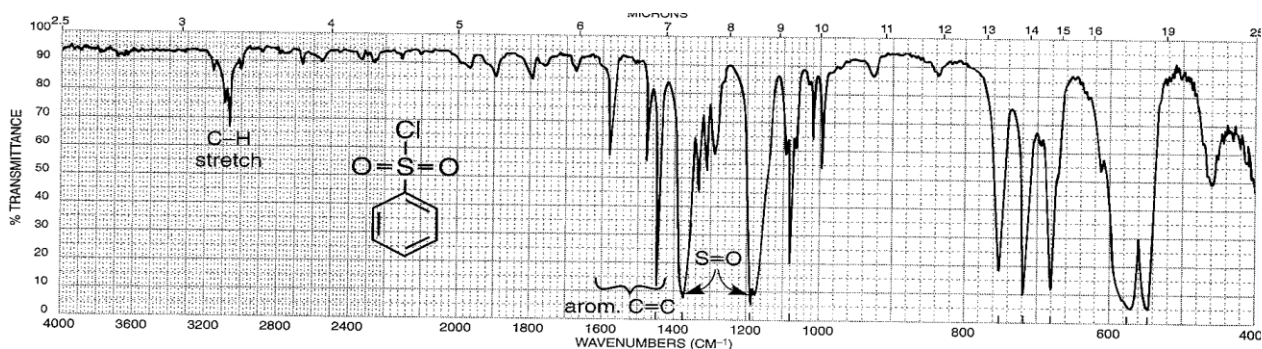
N-H Primary stretch occurs at  $3350$  and  $3250\text{ cm}^{-1}$ ; secondary stretch occurs at  $3250\text{ cm}^{-1}$ ; bend occurs at  $1550\text{ cm}^{-1}$ .

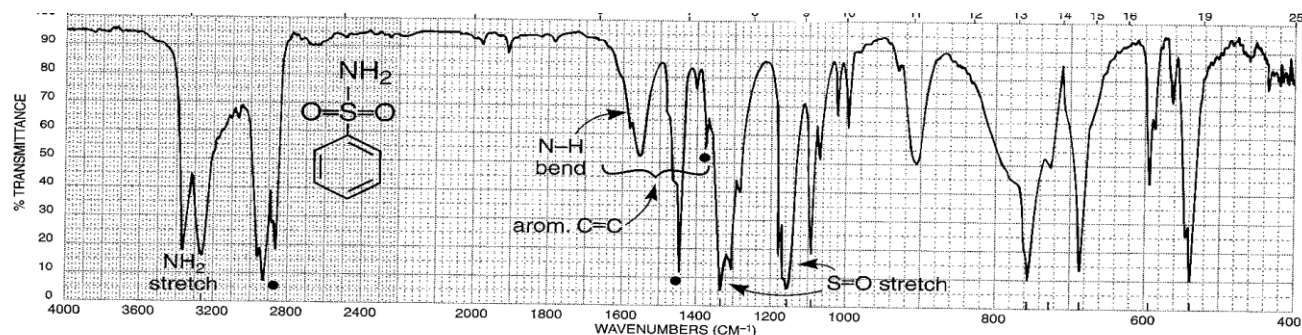
**Example:** benzenesulfonamide (Fig. 2.71).

**SULFONIC ACIDS  
(Anhydrous)**

S=O Asymmetric stretch (strong) occurs at  $1350\text{ cm}^{-1}$ , symmetric stretch (strong) at  $1150\text{ cm}^{-1}$ .

S-O Stretch (strong) occurs at  $650\text{ cm}^{-1}$ .





### PHOSPHINES $RPH_2$ $R_2PH$

- P—H Stretch, one strong, sharp band, at  $2320\text{--}2270\text{ cm}^{-1}$ .  
 PH<sub>2</sub> Bend, medium bands, at  $1090\text{--}1075\text{ cm}^{-1}$  and  $840\text{--}810\text{ cm}^{-1}$ .  
 P—H Bend, medium band, at  $990\text{--}885\text{ cm}^{-1}$ .  
 P—CH<sub>3</sub> Bend, medium bands, at  $1450\text{--}1395\text{ cm}^{-1}$  and  $1346\text{--}1255\text{ cm}^{-1}$ .  
 P—CH<sub>2</sub>— Bend, medium band, at  $1440\text{--}1400\text{ cm}^{-1}$ .

### PHOSPHINE OXIDES $R_3P=O$ $Ar_3P=O$

- P=O Stretch, one very strong band, at  $1210\text{--}1140\text{ cm}^{-1}$ .

### PHOSPHATE ESTERS $(RO)_3P=O$

- P=O Stretch, one very strong band, at  $1300\text{--}1240\text{ cm}^{-1}$ .  
 R—O Stretch, one or two strong bands, at  $1088\text{--}920\text{ cm}^{-1}$ .  
 P—O Stretch, medium band, at  $845\text{--}725\text{ cm}^{-1}$ .

### FLUORIDES $R-F$

- C—F Stretch (strong) at  $1400\text{--}1000\text{ cm}^{-1}$ . Monofluoroalkanes absorb at the lower-frequency end of this range, while polyfluoroalkanes give multiple strong bands in the range  $1350\text{--}1100\text{ cm}^{-1}$ . Aryl fluorides absorb between  $1250$  and  $1100\text{ cm}^{-1}$ .

### CHLORIDES $R-Cl$

- C—Cl Stretch (strong) in aliphatic chlorides occurs in the range  $785\text{--}540\text{ cm}^{-1}$ . Primary chlorides absorb at the upper end of this range, while tertiary chlorides absorb near the lower end. Two or more bands may be observed, due to the different conformations which are possible.

Multiple substitution on a single-carbon atom results in an intense absorption at the upper-frequency end of this range: CH<sub>2</sub>Cl<sub>2</sub> ( $739\text{ cm}^{-1}$ ), HCCl<sub>3</sub> ( $759\text{ cm}^{-1}$ ), and CCl<sub>4</sub> ( $785\text{ cm}^{-1}$ ). Aryl chlorides absorb between  $1100$  and  $1035\text{ cm}^{-1}$ .

- CH<sub>2</sub>—Cl Bend (wagging) at  $1300\text{--}1230\text{ cm}^{-1}$ .

### BROMIDES R-Br

C-Br Stretch (strong) in aliphatic bromides occurs at  $650-510\text{ cm}^{-1}$ , out of the range of routine spectroscopy using NaCl plates or cells. The trends indicated for aliphatic chlorides hold for bromides. Aryl bromides absorb between  $1075$  and  $1030\text{ cm}^{-1}$ .

CH<sub>2</sub>-Br Bend (wagging) at  $1250-1190\text{ cm}^{-1}$ .

### IODIDES R-I

C-I Stretch (strong) in aliphatic iodides occurs at  $600-485\text{ cm}^{-1}$ , out of the range of routine spectroscopy using NaCl plates or cells. The trends indicated for aliphatic chlorides hold for iodides.

CH<sub>2</sub>-I Bend (wagging) at  $1200-1150\text{ cm}^{-1}$ .

