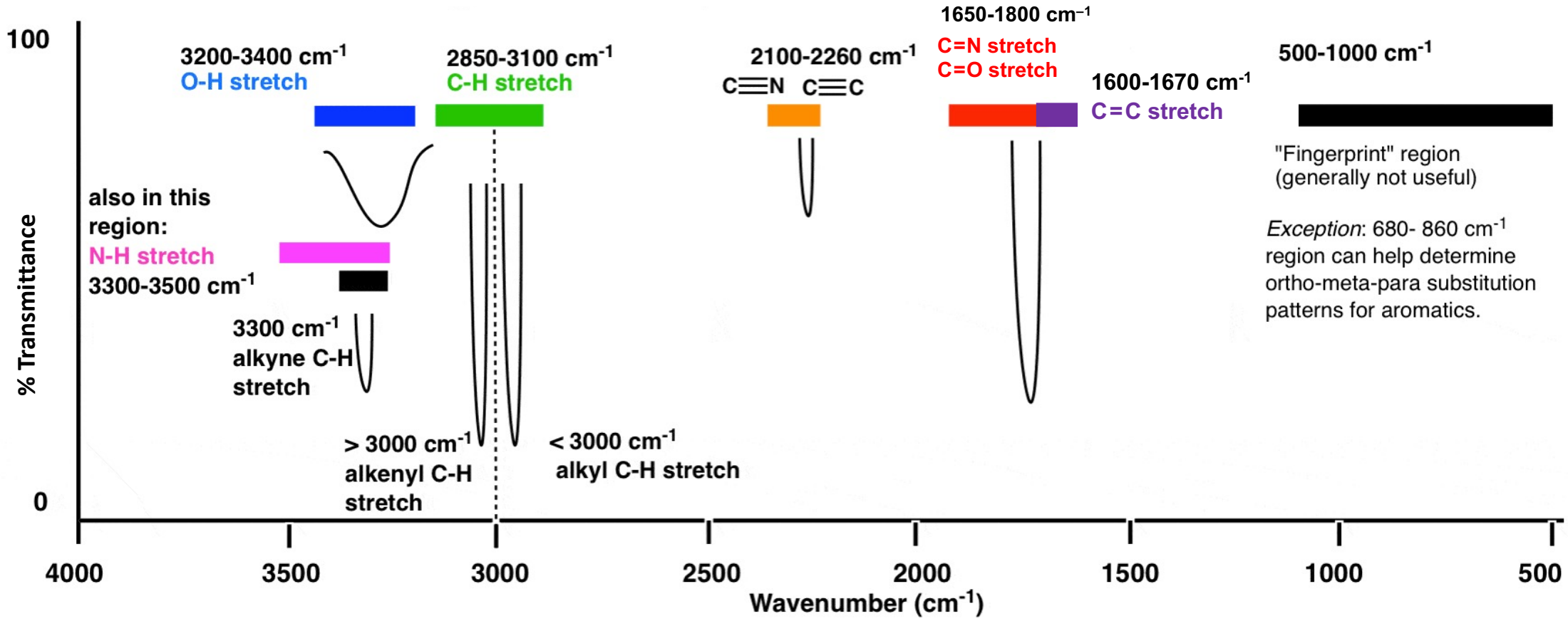
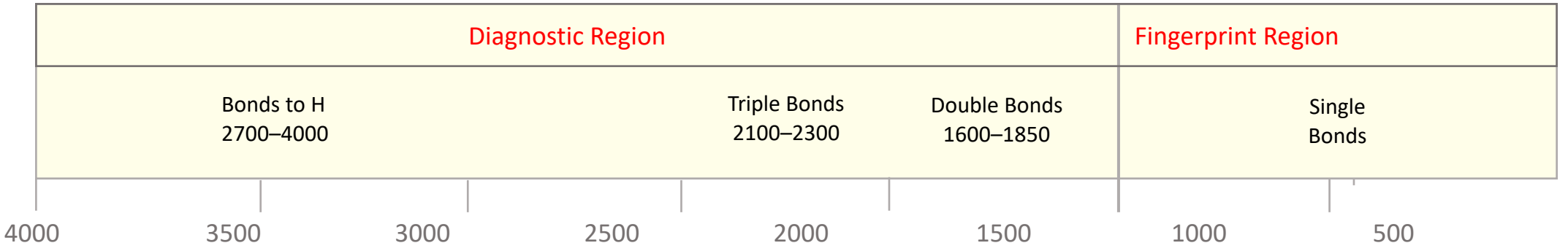
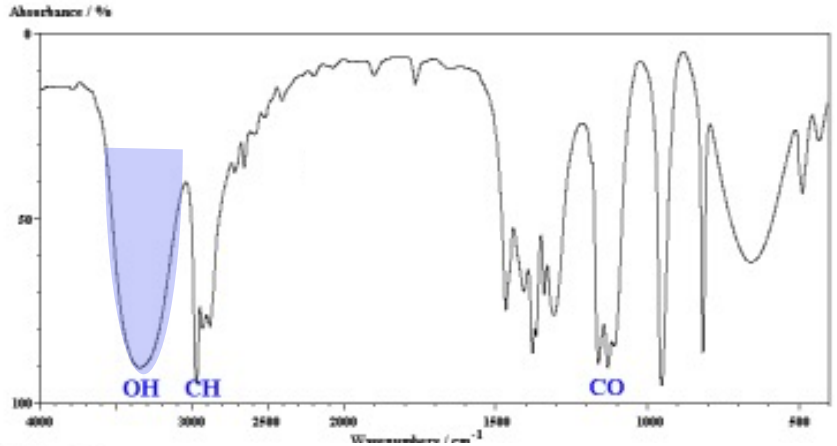
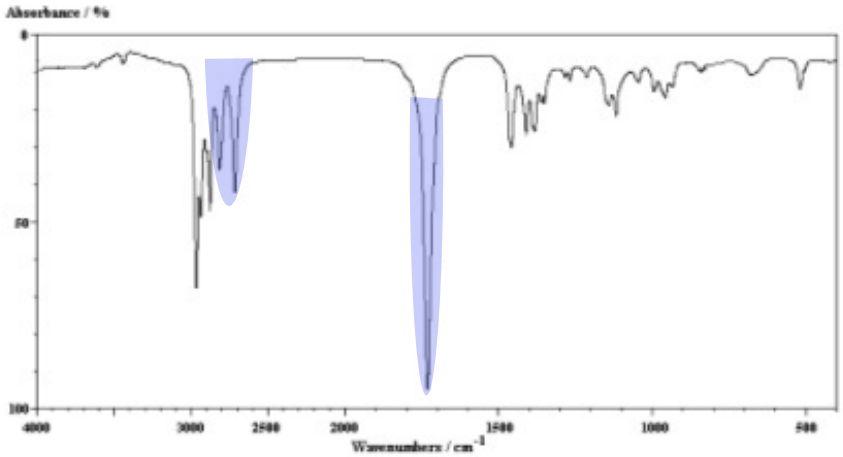
IR Spectroscopy


100
% Transmittance
0
3200-3400 cm-1
O-H stretch
2850-3100 cm-1
C-H stretch
2100-2260 cm-1
C≡N C≡C
1650-1800 cm-1
C=N stretch
C=O stretch
1600-1670 cm-1
C=C stretch
500-1000 cm-1
"Fingerprint" region
(generally not useful)
Exception: 680- 860 cm-1
region can help determine
ortho-meta-para substitution
patterns for aromatics.
also in this
region:
N-H stretch
3300-3500 cm-1
3300 cm-1
alkyne C-H
stretch
> 3000 cm-1
alkenyl C-H
stretch
< 3000 cm-1
alkyl C-H stretch
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm-1)

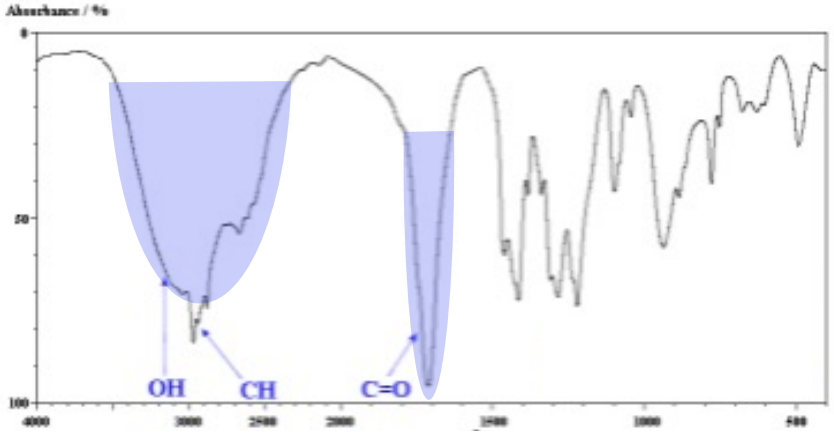

Diagnostic Region
Fingerprint Region
Bonds to H
2700–4000
Triple Bonds
2100–2300
Double Bonds
1600–1850
Single
Bonds
4000
3500
3000
2500
2000
1500
1000
500



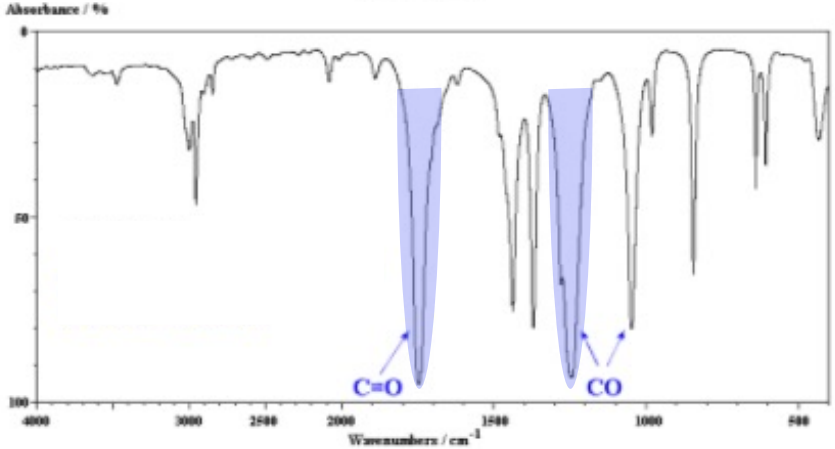
ALCOHOL
"bubble" from
3200-3600 cm^{-1}



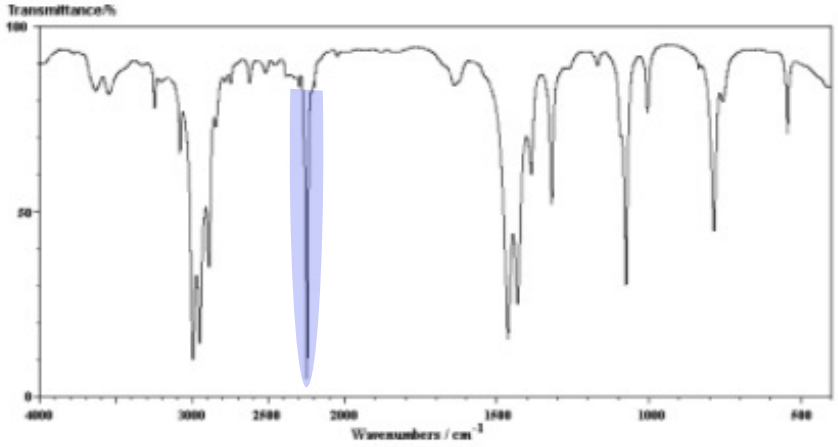
ALDEHYDE
C=O peak at
~1710 cm^{-1}
doublet at
~2700, 2800 cm^{-1}



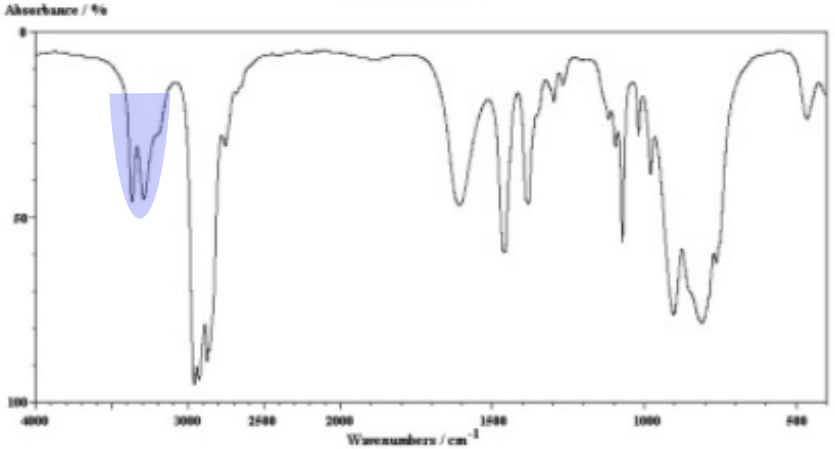
CARBOXYLIC ACID
"beard" from
2500-3600 cm^{-1}
C=O peak at
~1750 cm^{-1}



ESTER
C=O peak at
~1750 cm^{-1}
C–O peak at
~1100-1200 cm^{-1}



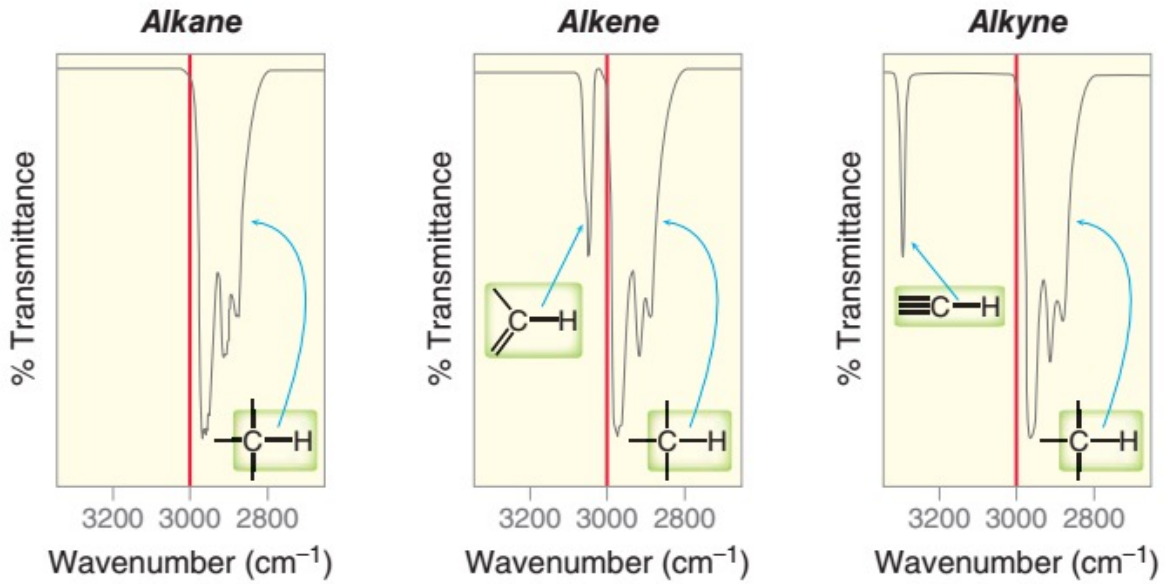
NITRILE
sharp peak at
~2200-2400 cm^{-1}

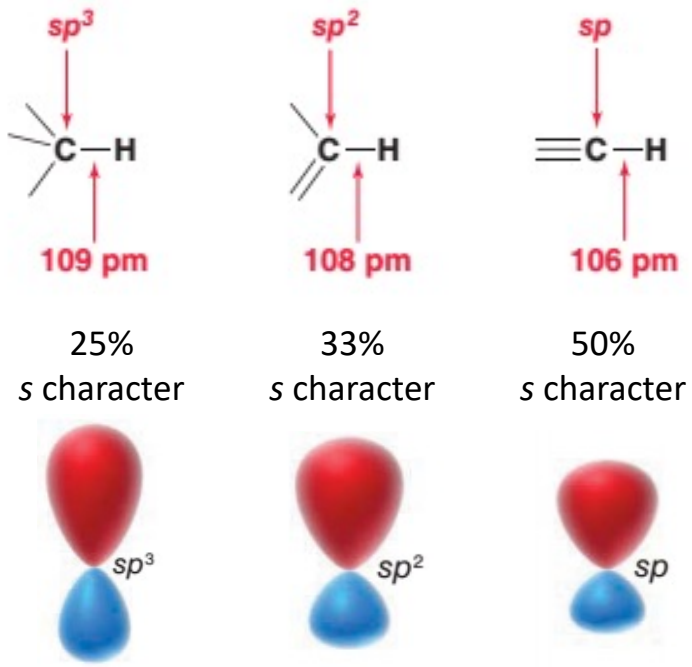


AMINE (1°)
N–H doublet at
~3400 cm^{-1}
Note: a singlet
Is a 2° amine

Table 14.2 Important Signals in IR Spectroscopy

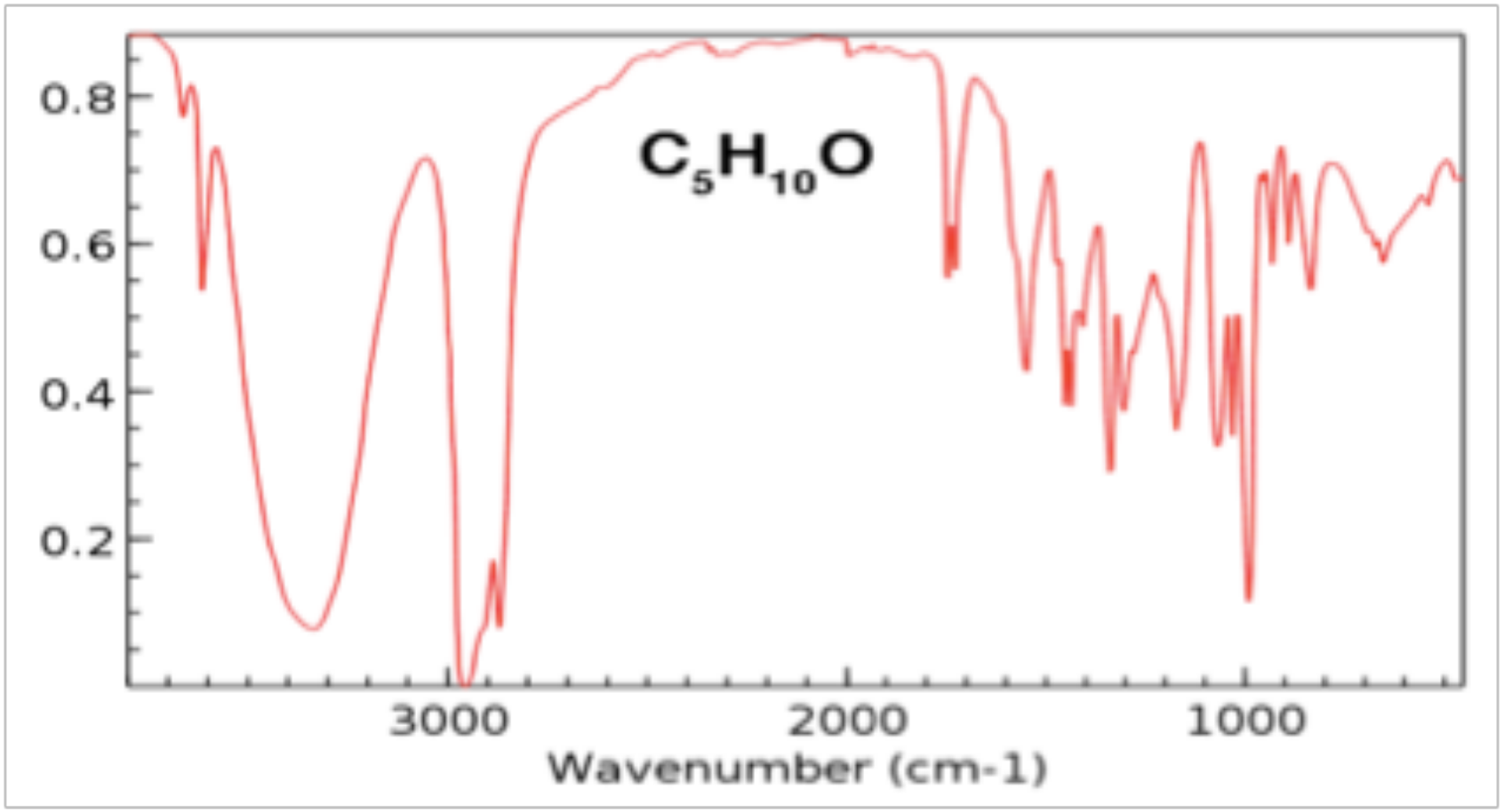
Single Bonds (X— H)		Double Bonds	
O—H	3200–3600	Cl, C=O	1750–1850
O, O—H	2200–3600	RO, C=O, R	1700–1750
N—H	3350–3500	HO, C=O, R	1700–1750
C—H	~3300	R, C=O, R	1680–1750
C—H	3000–3100	H_2N, C=O, R	1650–1700
C—H	2850–3000	C=C	1600–1700
O, C—H	2750–2850		
Triple Bonds			
C≡C	2100–2200		1450–1600 1650–2000
C≡N	2200–2300		

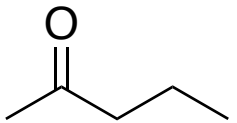


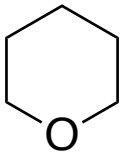


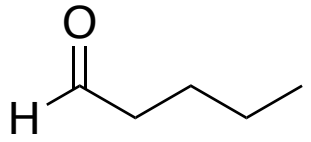
1

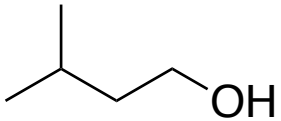
Which of the following molecules best corresponds to the IR spectrum below?

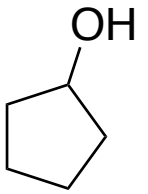


(a) 

(b) 

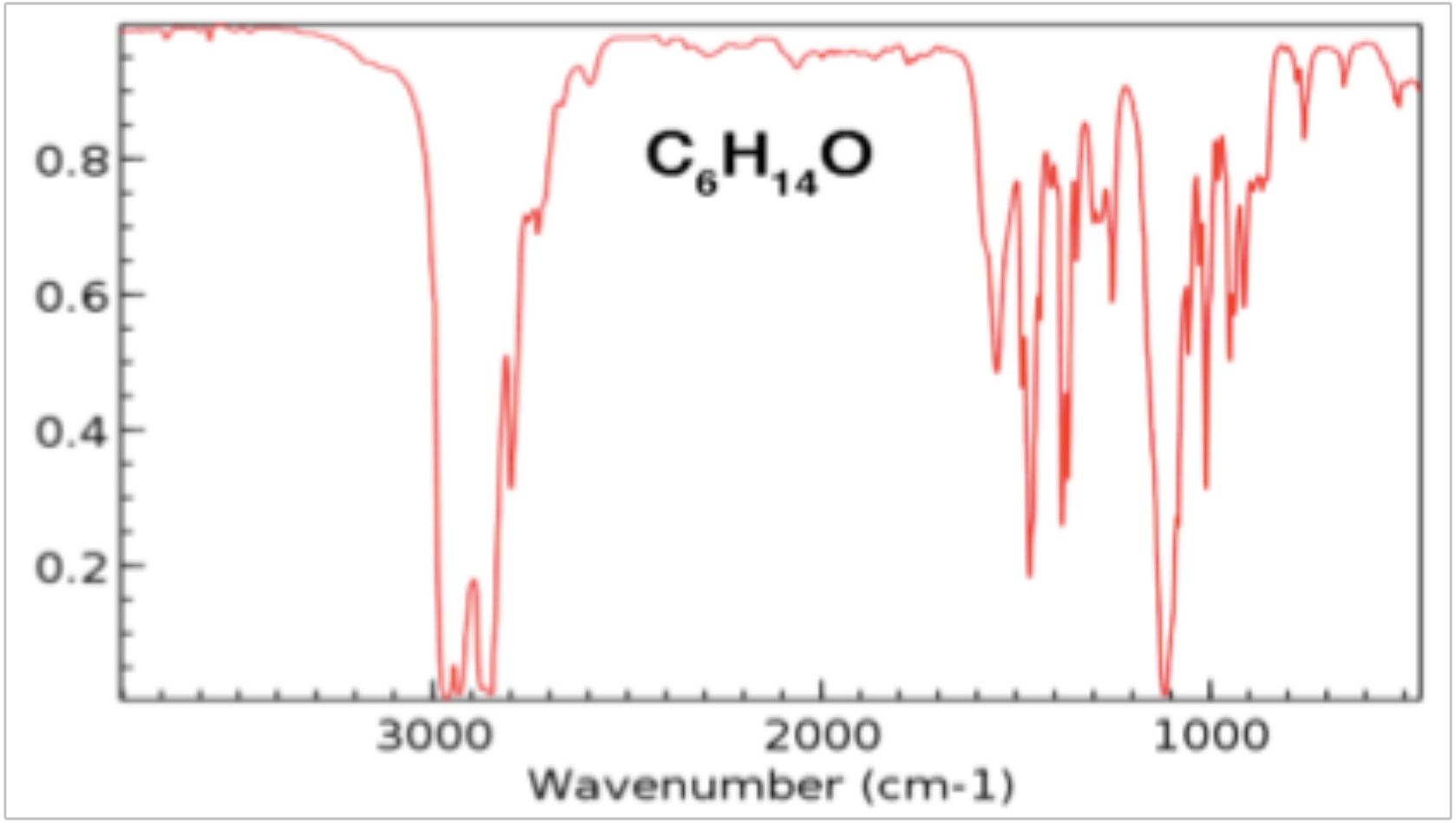
(c) 

(d) 

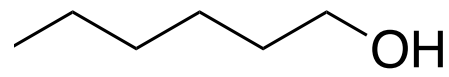
(e) 

2

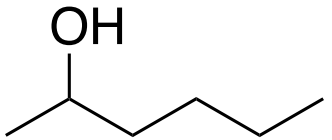
Which of the following molecules best corresponds to the IR spectrum below?



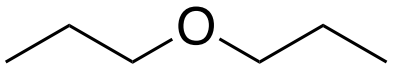
(a)



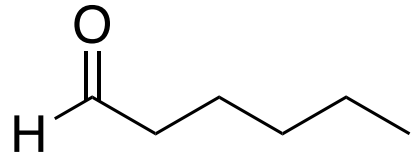
(b)



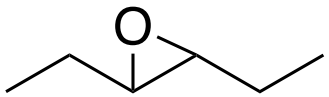
(c)



(d)

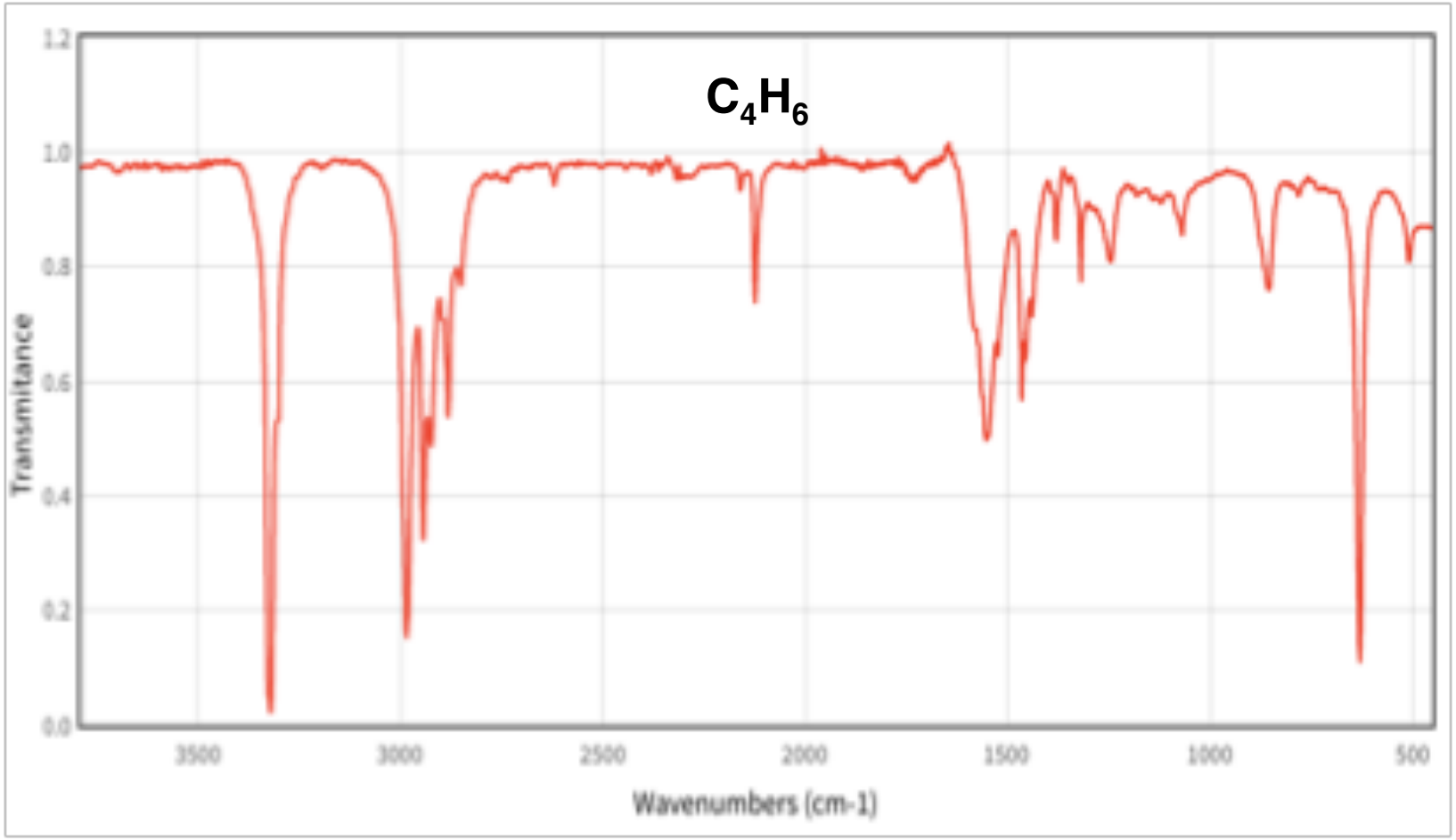


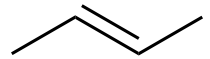
(e)

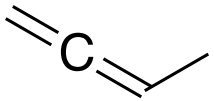


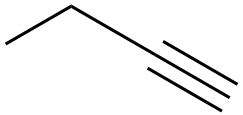
3

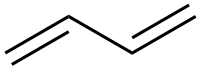
Which of the following molecules best corresponds to the IR spectrum below?

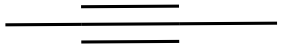


(a) 

(b) 

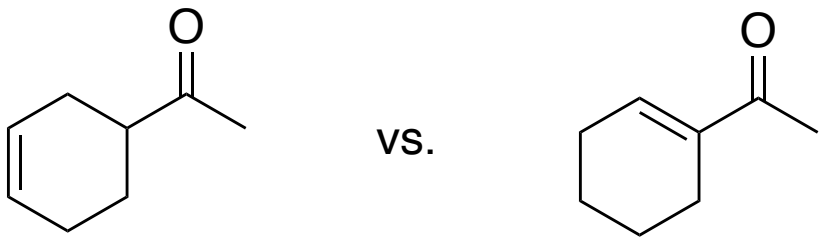
(c) 

(d) 

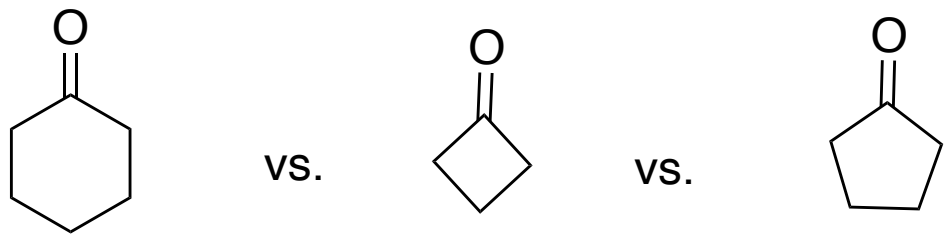
(e) 

1. Which compound would have the highest wavenumber for the carbonyl stretch in the IR spectrum?
   Hint: Which compound has more C=O double-bond character?

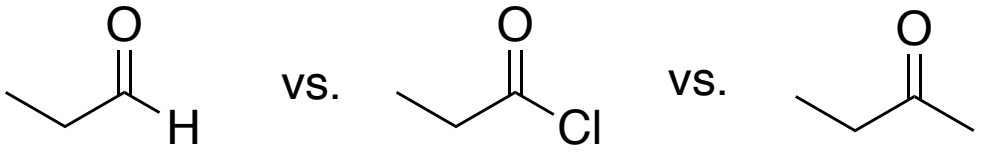
a)



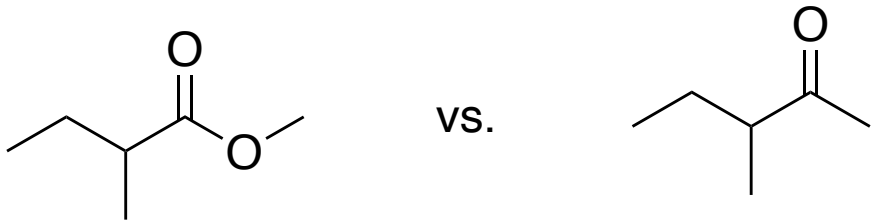
b)



c)

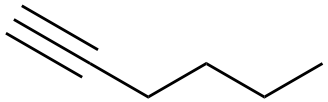


d)

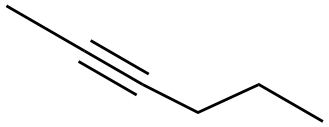


2. How would you differentiate between the following compounds using IR spectra?

(a)



(b)

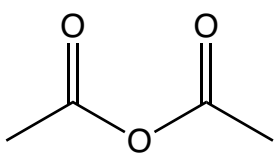


(c)

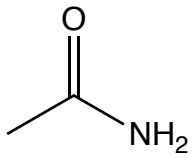


CHALLENGE: Rank the following compounds from lowest to highest wavenumber for the carbonyl stretch.

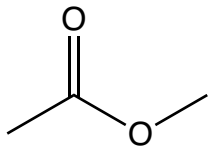
Hint: compare resonance and inductive effect.



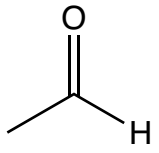
I.



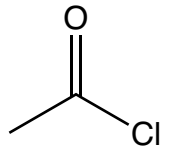
II.



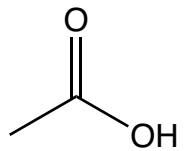
III.



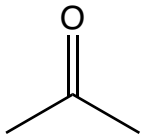
IV.



V.



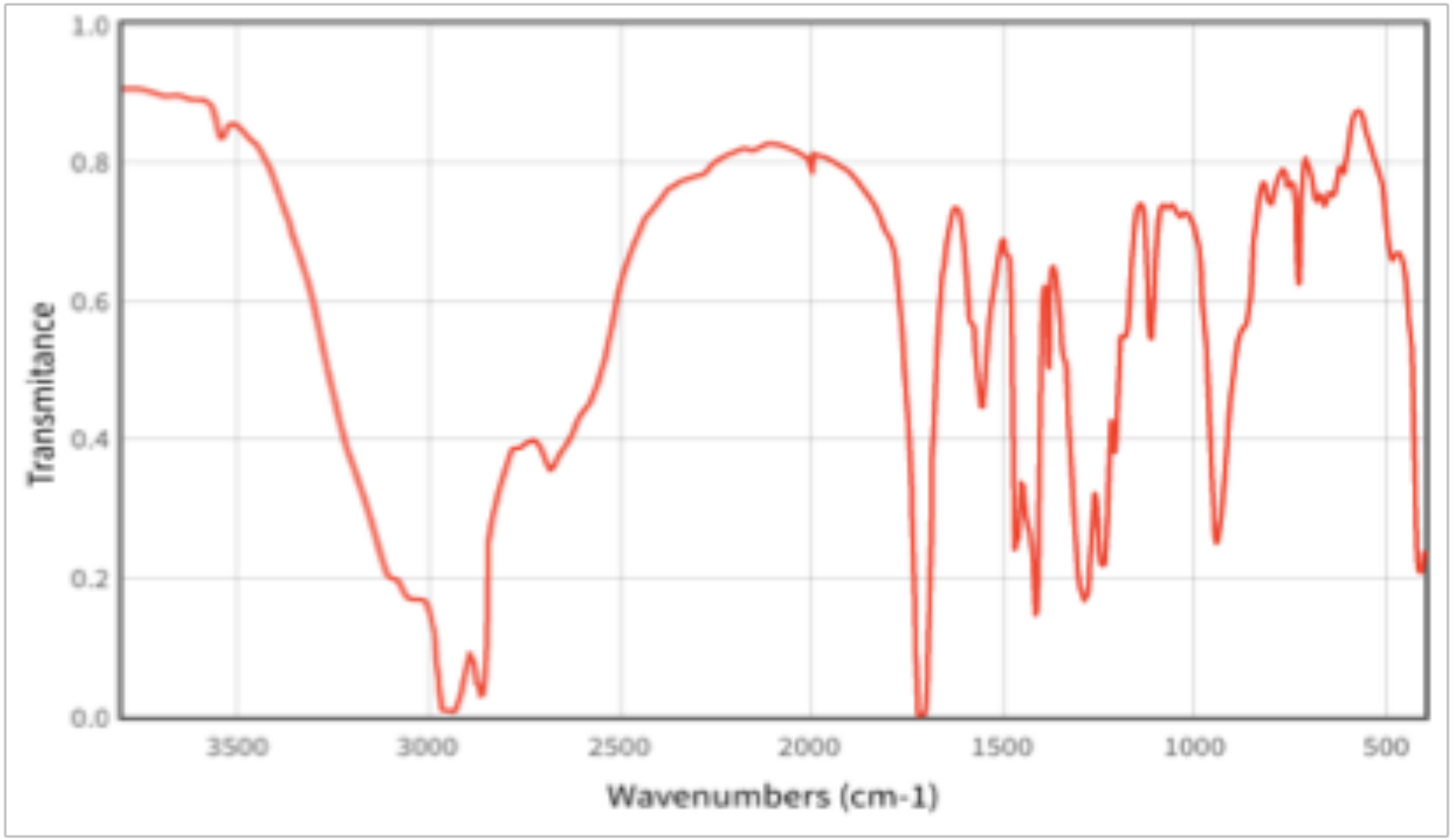
VI.



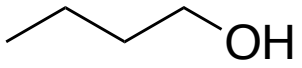
VII.

6

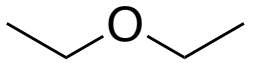
Which of the following molecules best corresponds to the IR spectrum below?



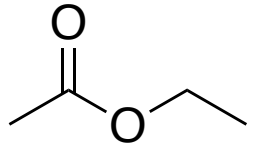
(a)



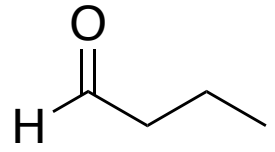
(b)



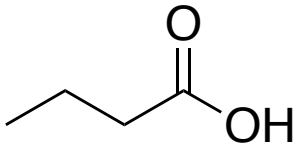
(c)



(d)

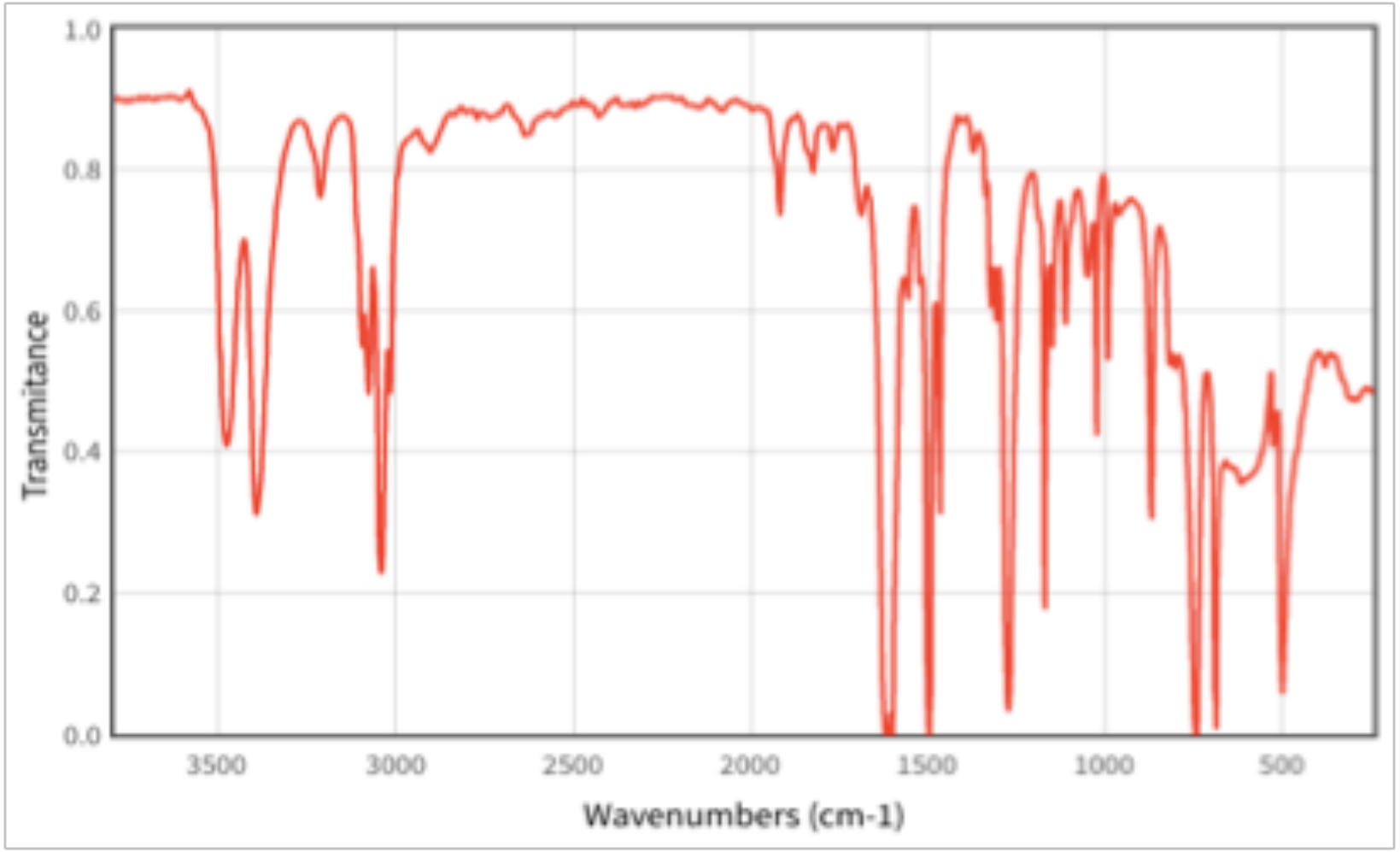


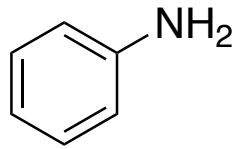
(e)

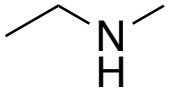


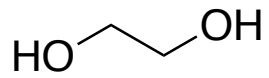
7

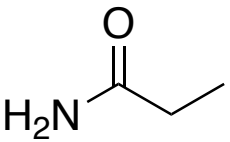
Which of the following molecules best corresponds to the IR spectrum below?

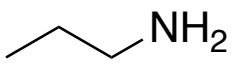


(a) 

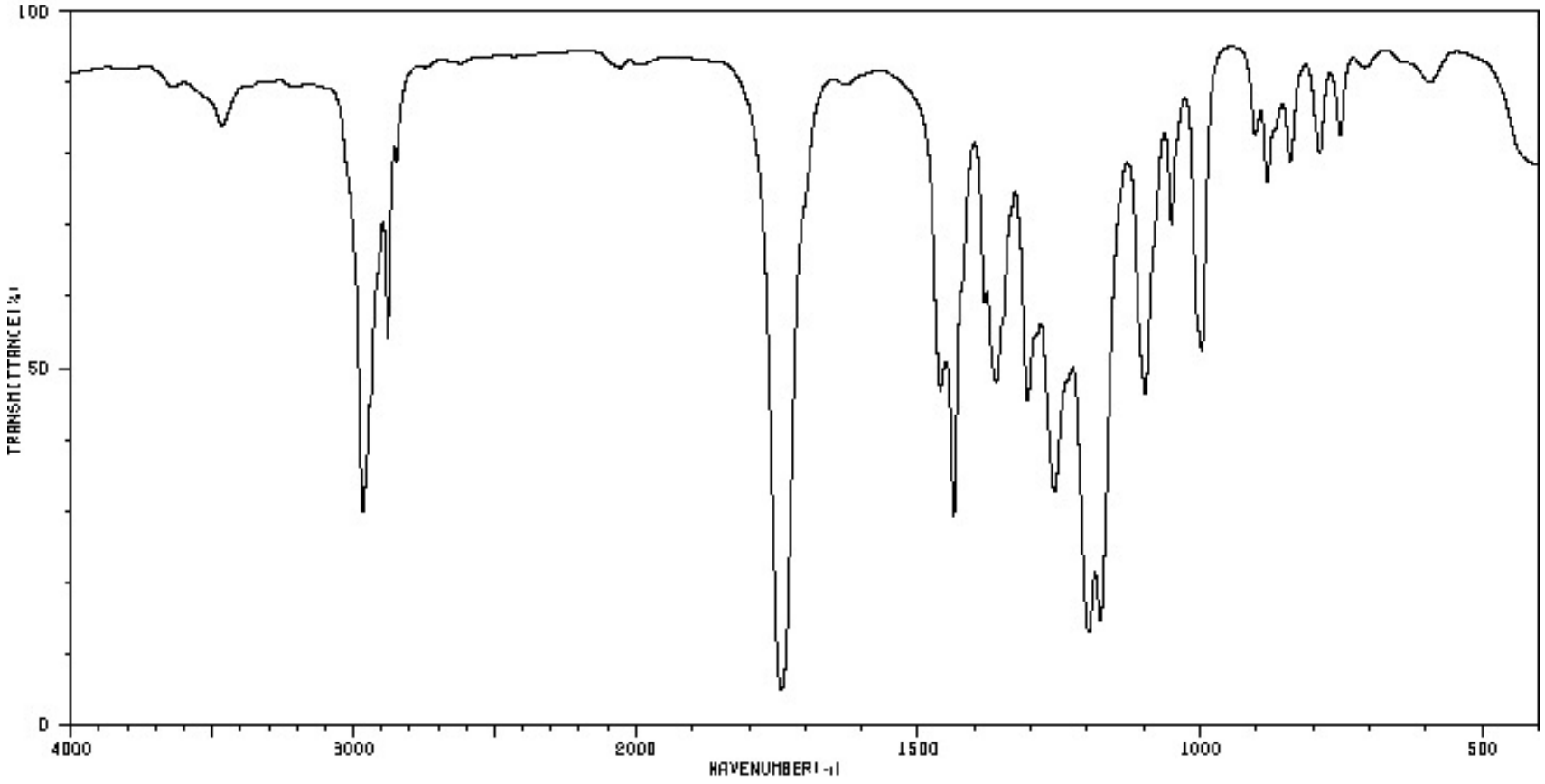
(b) 

(c) 

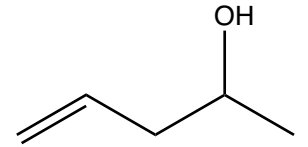
(d) 

(e) 

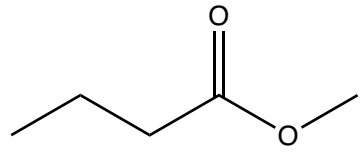
Which of the following molecules best corresponds to the IR spectrum below?



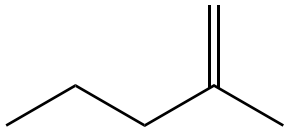
(a)



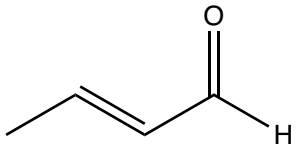
(b)



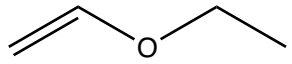
(c)



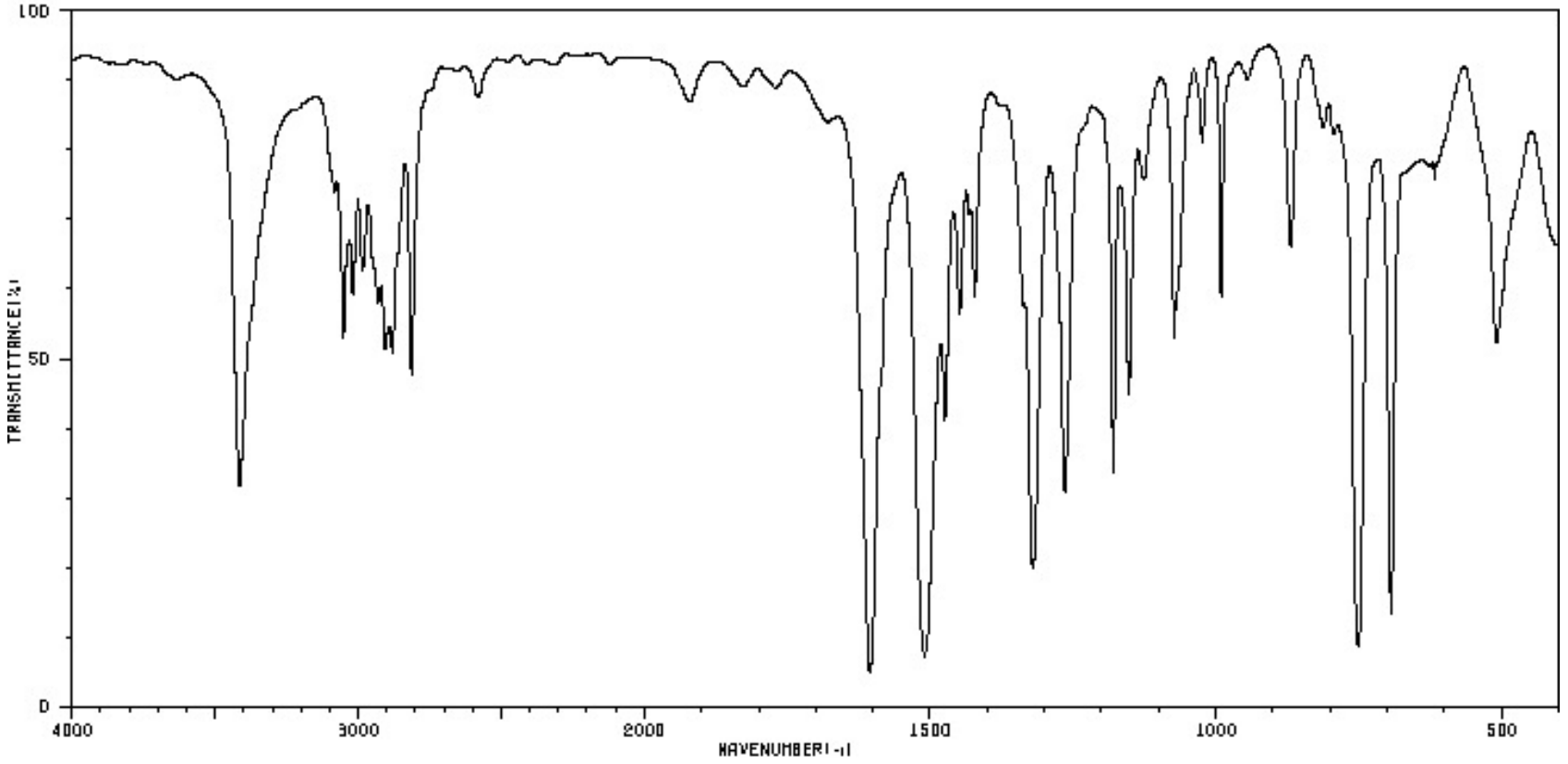
(d)



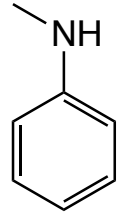
(e)



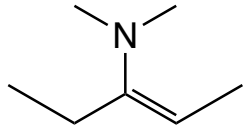
Which of the following molecules best corresponds to the IR spectrum below?



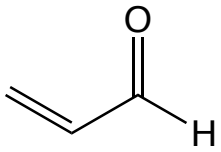
(a)



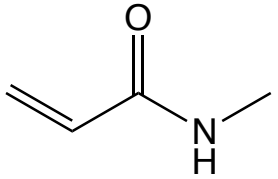
(b)



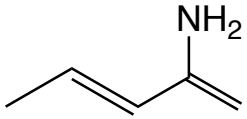
(c)



(d)

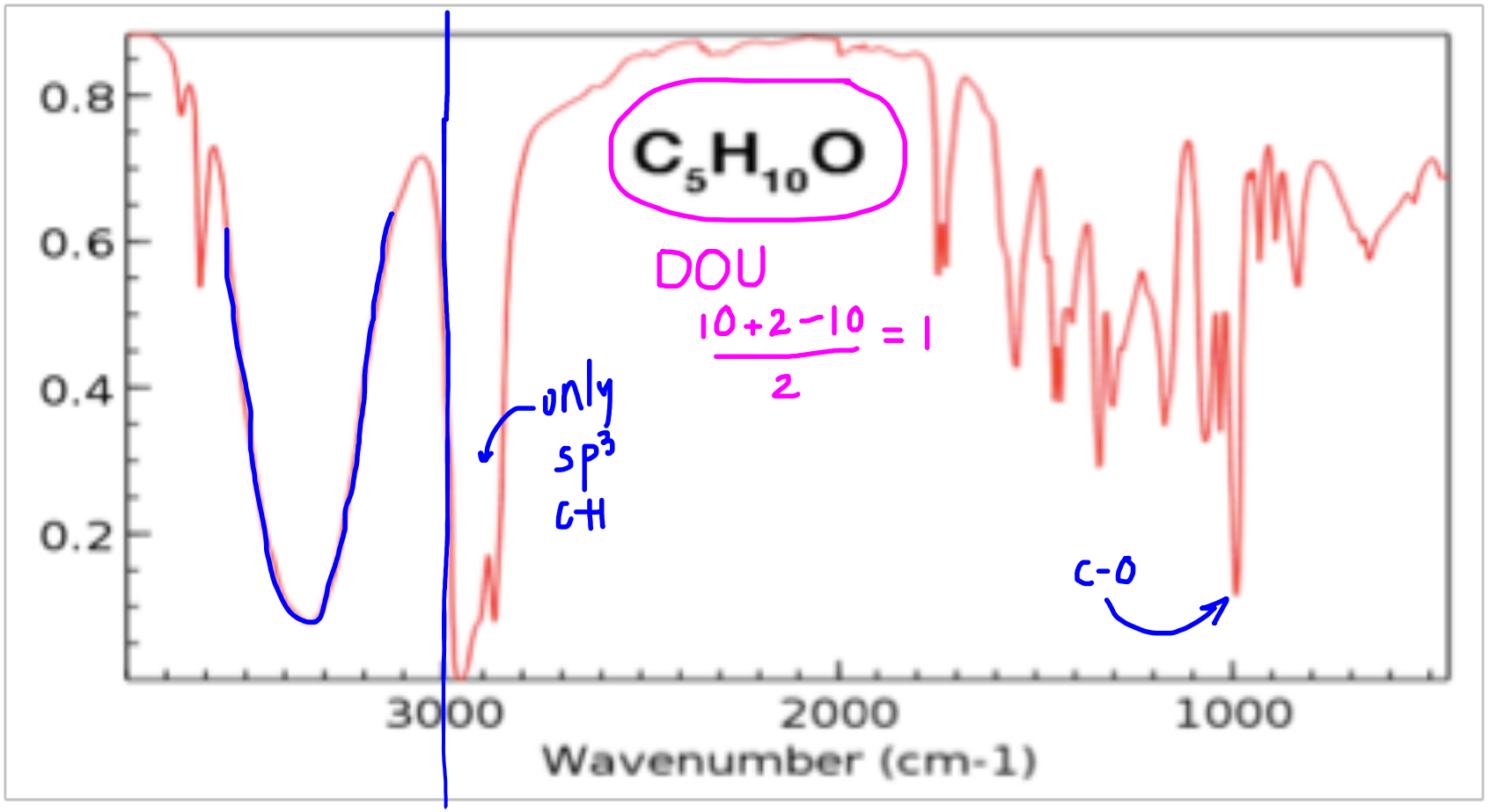


(e)

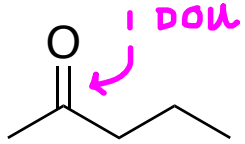


ANSWER: 1

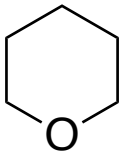
Which of the following molecules best corresponds to the IR spectrum below?



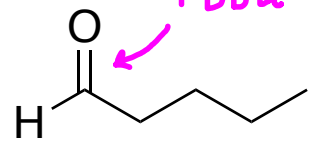
(a) ~~(a)~~ 1 DOU



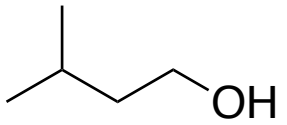
(b) ~~(b)~~ (ring) 1 DOU



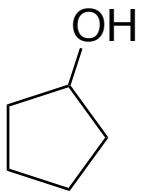
(c) ~~(c)~~ 1 DOU



(d) ~~(d)~~

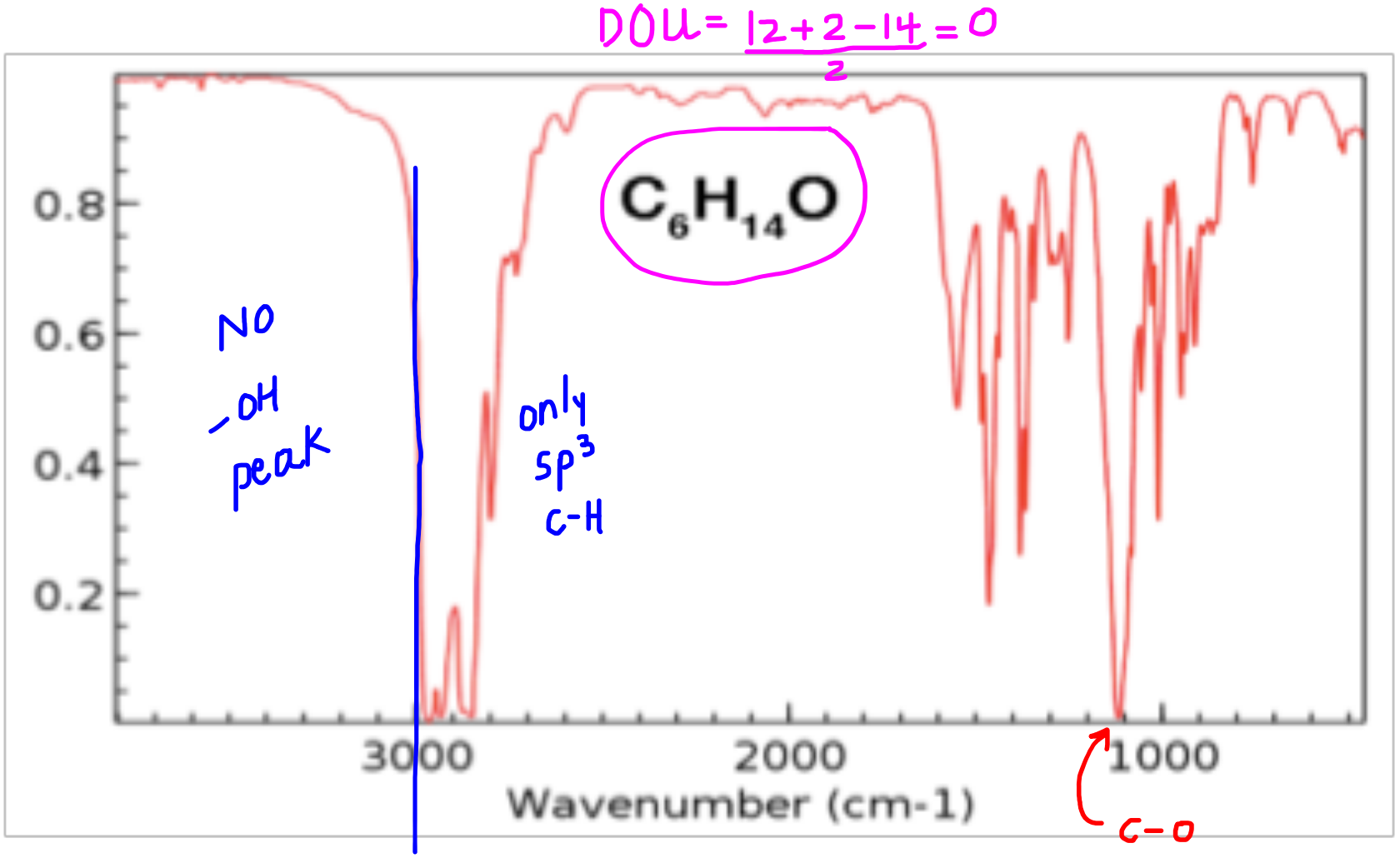


(e) 1 DOU

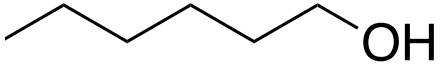


ANSWER: 2

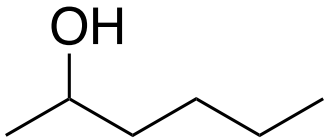
Which of the following molecules best corresponds to the IR spectrum below?



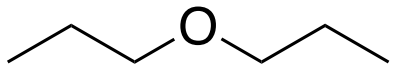
(a)



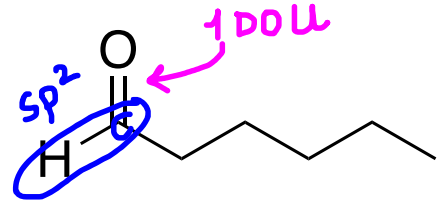
(b)



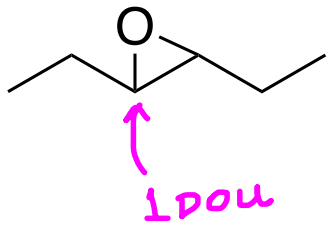
(c)



(d)



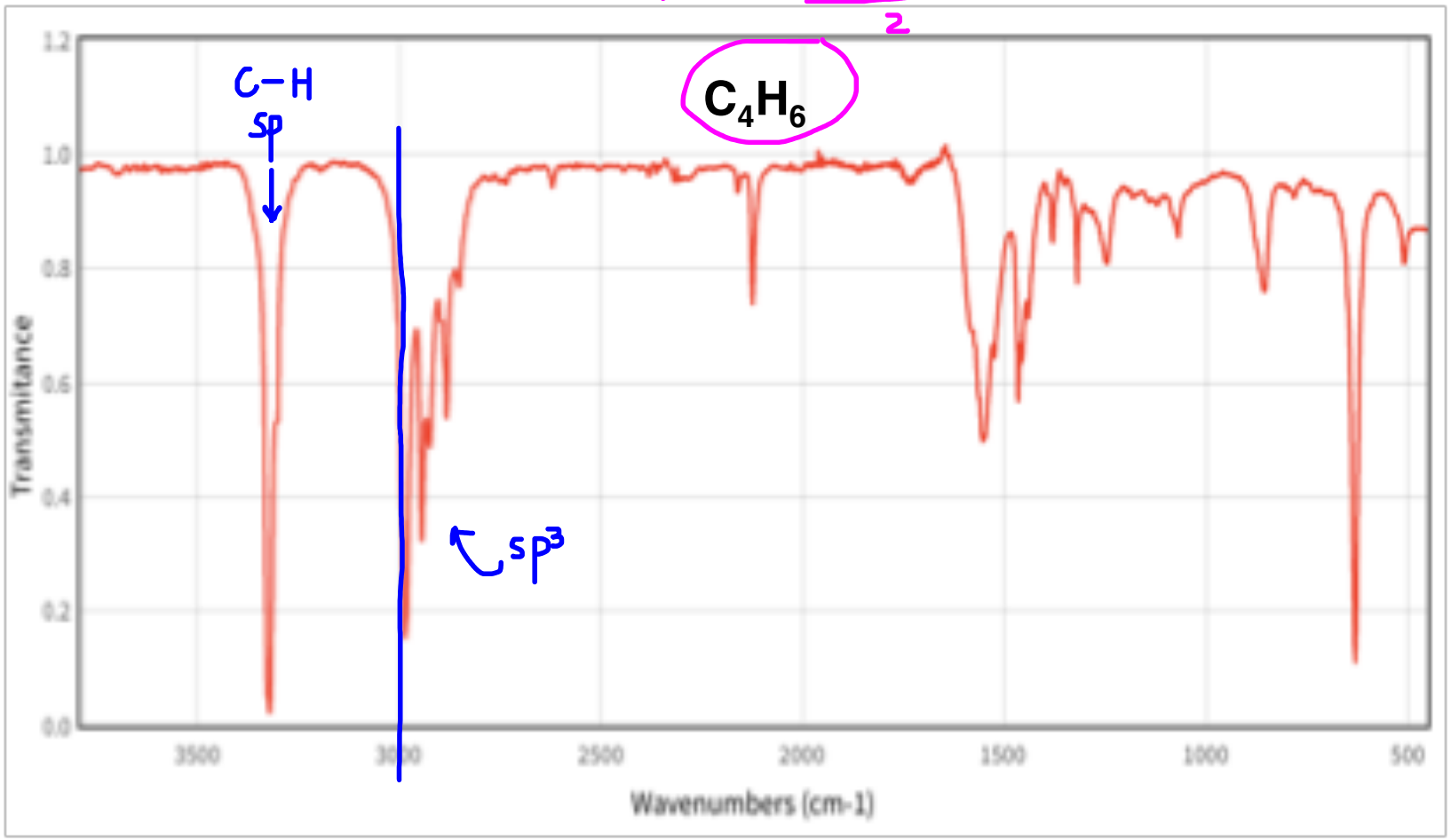
(e)



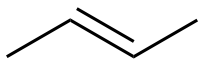
ANSWER: 3

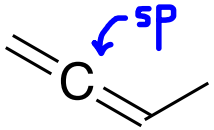
Which of the following molecules best corresponds to the IR spectrum below?

DOU = $\frac{8+2-6}{2} = 2$

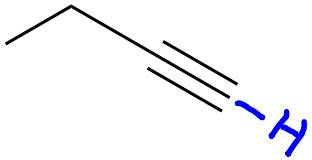


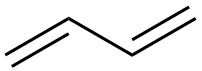
only C–H bonds

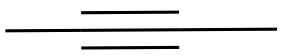
(a) 

(b) 

C–H no sp

(c) 

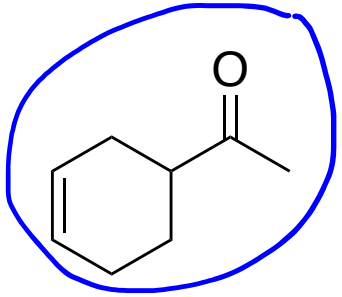
(d) 
no sp or sp³

(e) 
sp C but NO sp C–H

ANSWER: 4

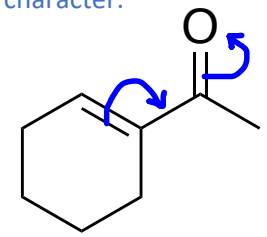
1. Which compound would have the highest wavenumber for the carbonyl stretch in the IR spectrum?
   Hint: Which compound has more C=O double-bond character?

a)



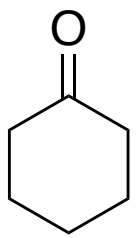
approx. **1715 cm^{-1}**

vs.



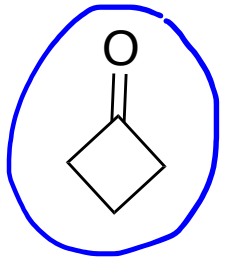
approx. **1700 cm^{-1}**
Stable resonance structure weakens C=O character.

b)

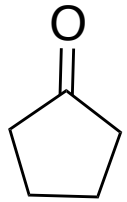


Ring strain reinforces C=O bond.

vs.



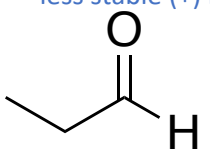
vs.



approx. **1750 cm^{-1}**
– O acts as EWG, strengthening (+) charge on C, which reinforces C=O

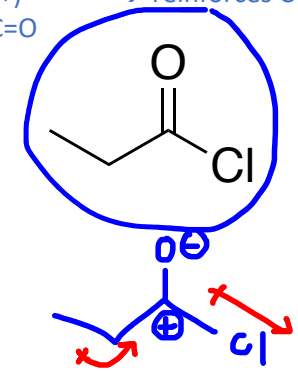
approx. **1715 cm^{-1}**
– 2 R groups stabilize (+) charge by acting as weak EDGs.
– EDGs weaken C=O character.

c)



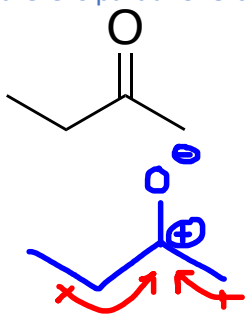
approx. **1725 cm^{-1}**
– only 1 R groups stabilizes (+)
– H does *not* help stabilize (+)
– less stable (+) reinforces C=O

vs.



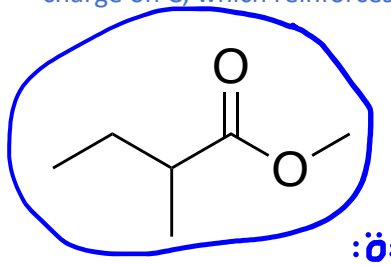
approx. **1800 cm^{-1}**
– halogen acts as EWG
– strengthens (+) charge
→ reinforces C=O

vs.

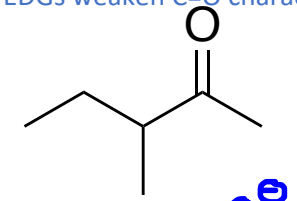


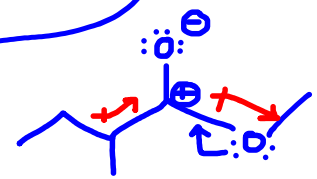
approx. **1715 cm^{-1}**
– 2 R groups stabilize (+)
– partially weakens C=O, so there is partial C–O character

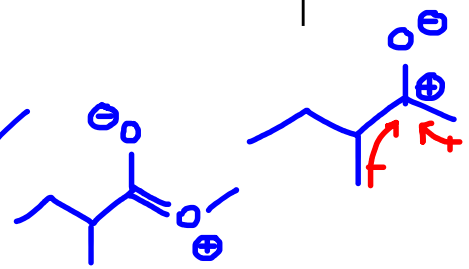
d)



vs.

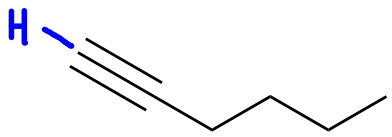






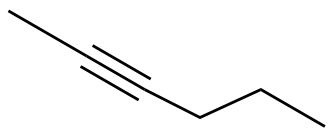
2. How would you differentiate between the following compounds using IR spectra?

(a)



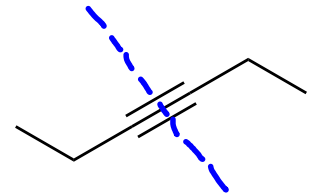
sp C-H peak around 3300 cm^{-1}

(b)



NO sp C-H peak around 3300 cm^{-1}

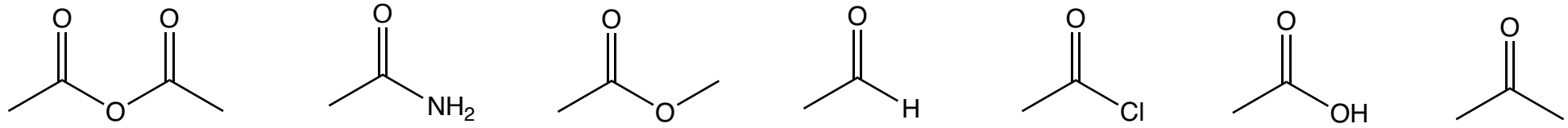
(c)



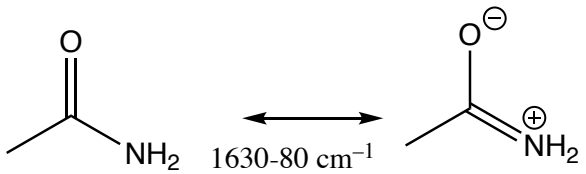
NO peaks at all, symmetrical structures do not appear on IR.

ANSWER: 5

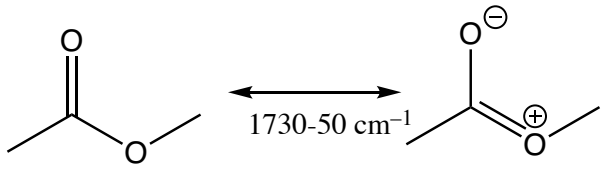
CHALLENGE: Rank the following compounds from lowest to highest wavenumber for the carbonyl stretch. (*Hint*: compare resonance and inductive effect.)



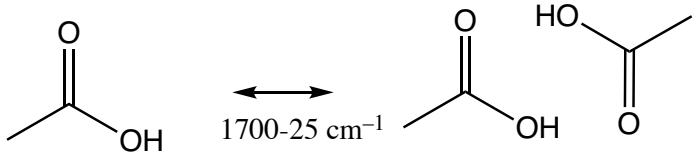
I. II. III. IV. V. VI. VII.



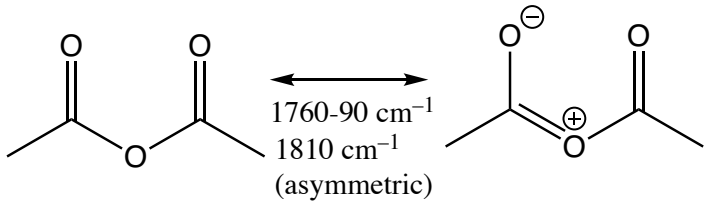
N favors resonance because it holds (+) well due to its low EN relative to O.
As N donates its lone pair, O withdraws electrons, thus weakening the C=O bond.



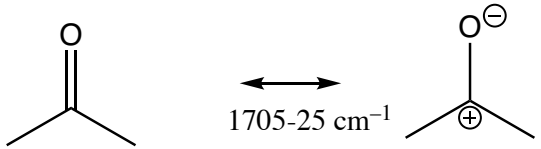
The O acts as a strong electron-withdrawing group, which strengthens the (+) charge of the C. As the (+) charge on C increases, the C=O is reinforced.



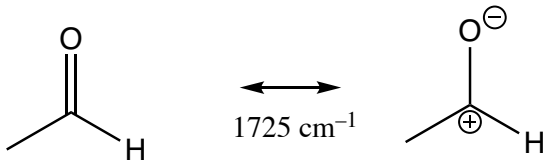
H-bonding interactions weakens C=O bond by withdrawing electron-density into each individual O to pair w. nearby H's.



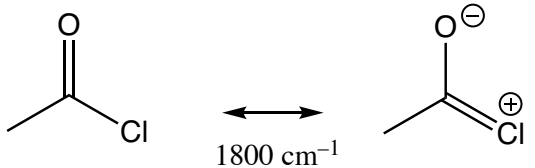
The central O withdraws electron density from both neighboring C's and thus, both carbonyl C=O bonds are strengthened.



The 2 alkyl groups act as weak electron-donating groups, that stabilize the (+) charge. The stability weakens the C=O character, because we have a relatively stable resonance structure.



There is only 1 alkyl group while the H does not provide electron-density. This strengthens the (+) which encourages C=O formation (i.e. the resonance structure is not very stable).



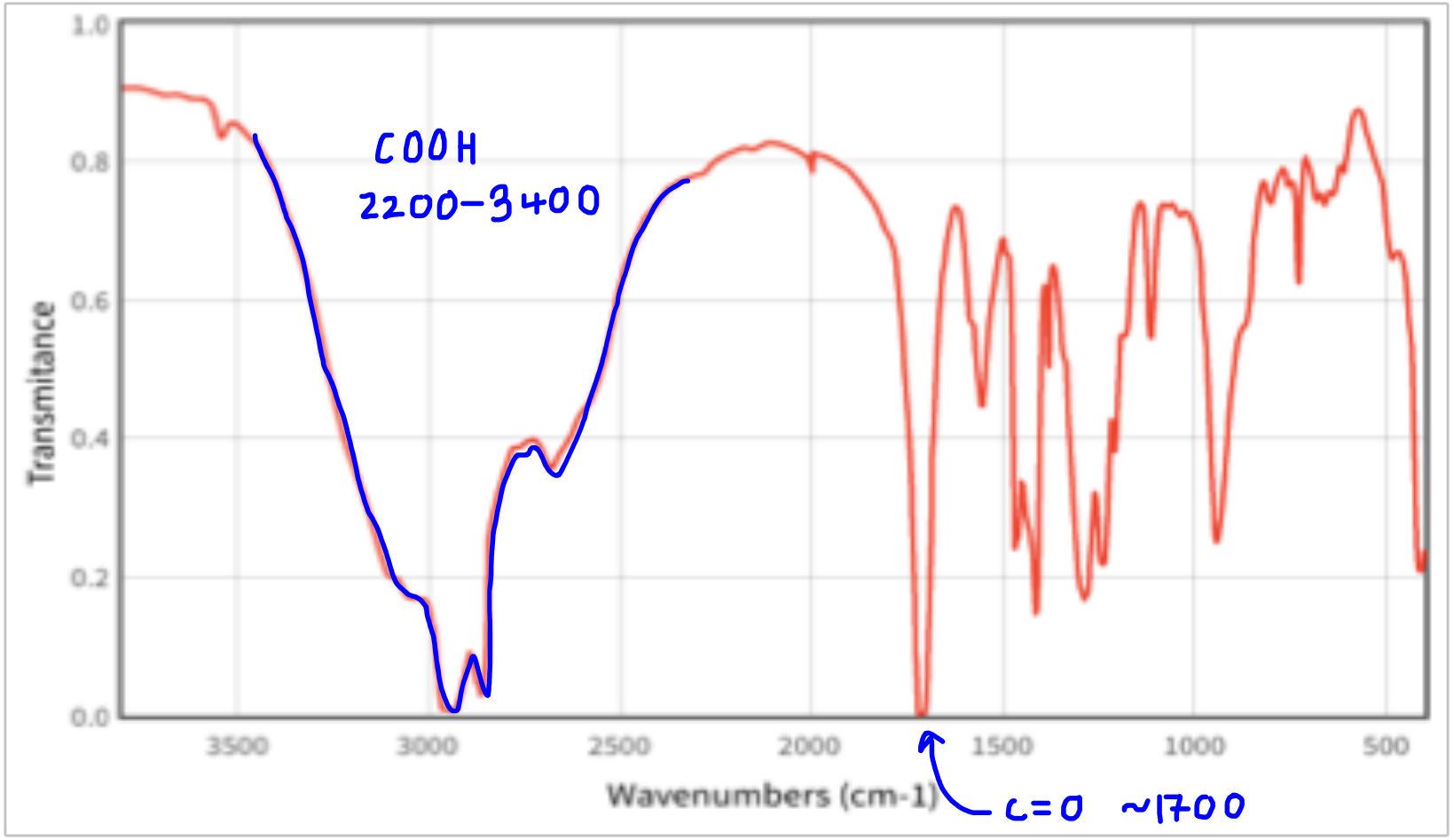
Acyl chlorides are a challenge to explain:

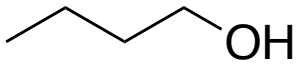
(1) The Cl does <u>not</u> like to participate in resonance. As a **halogen**, Cl acts as a strong *electron-withdrawing* group. By withdrawing e-density from C, it strengthens the C and reinforces the C=O.

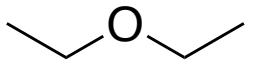
(2) As a halogen with a decent atomic radius, Cl prefers to act as a "leaving group" rather than participate in resonance. Its high reactivity also contributes to its high wavenumber.

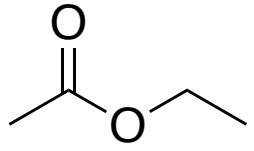
ANSWER: 6

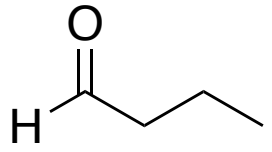
Which of the following molecules best corresponds to the IR spectrum below?

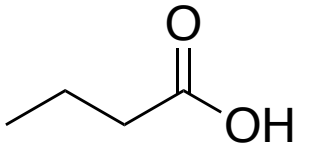


(a) 

(b) 

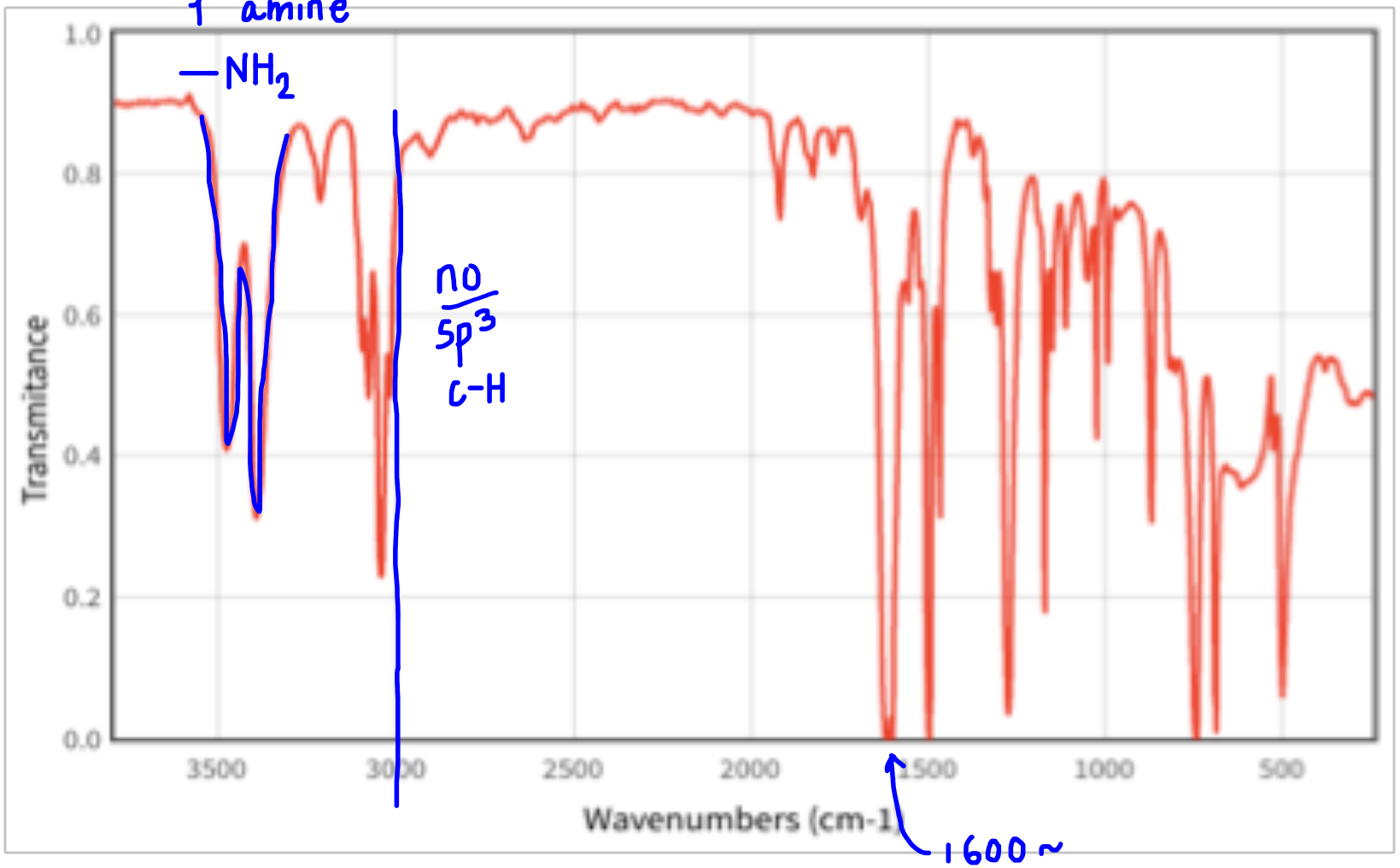
(c) 

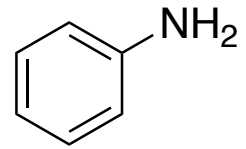
(d) 

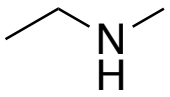
(e) 

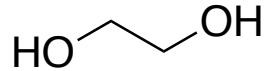
ANSWER: 7

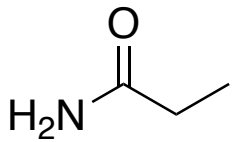
Which of the following molecules best corresponds to the IR spectrum below?

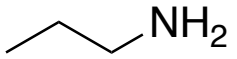


(a) 

(b) 

(c) 

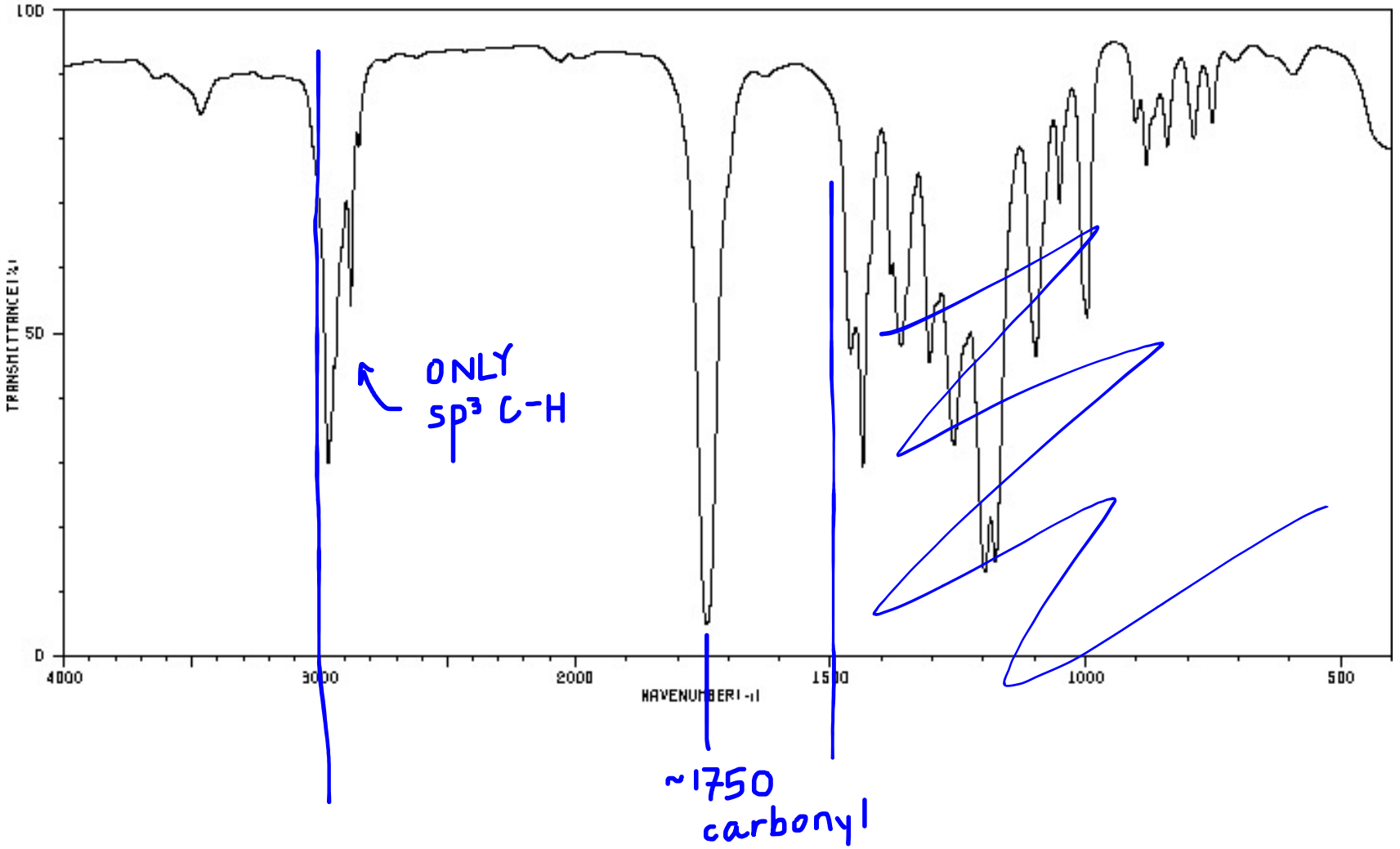
(d) 

(e) 

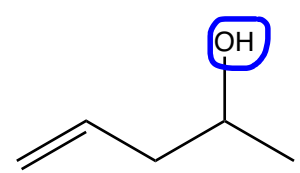
all have sp^3 C-H

ANSWER: 8

Which of the following molecules best corresponds to the IR spectrum below?

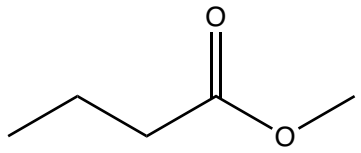


(a) ~~

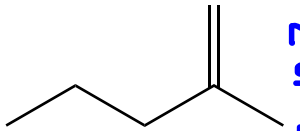


NO alcohol peak

(b)

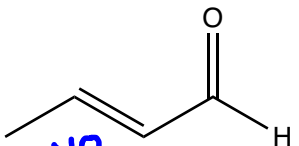


(c) ~~



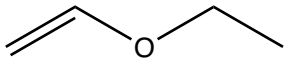
NO sp² C-H
NO carbonyl

(d) ~~



NO sp² C-H

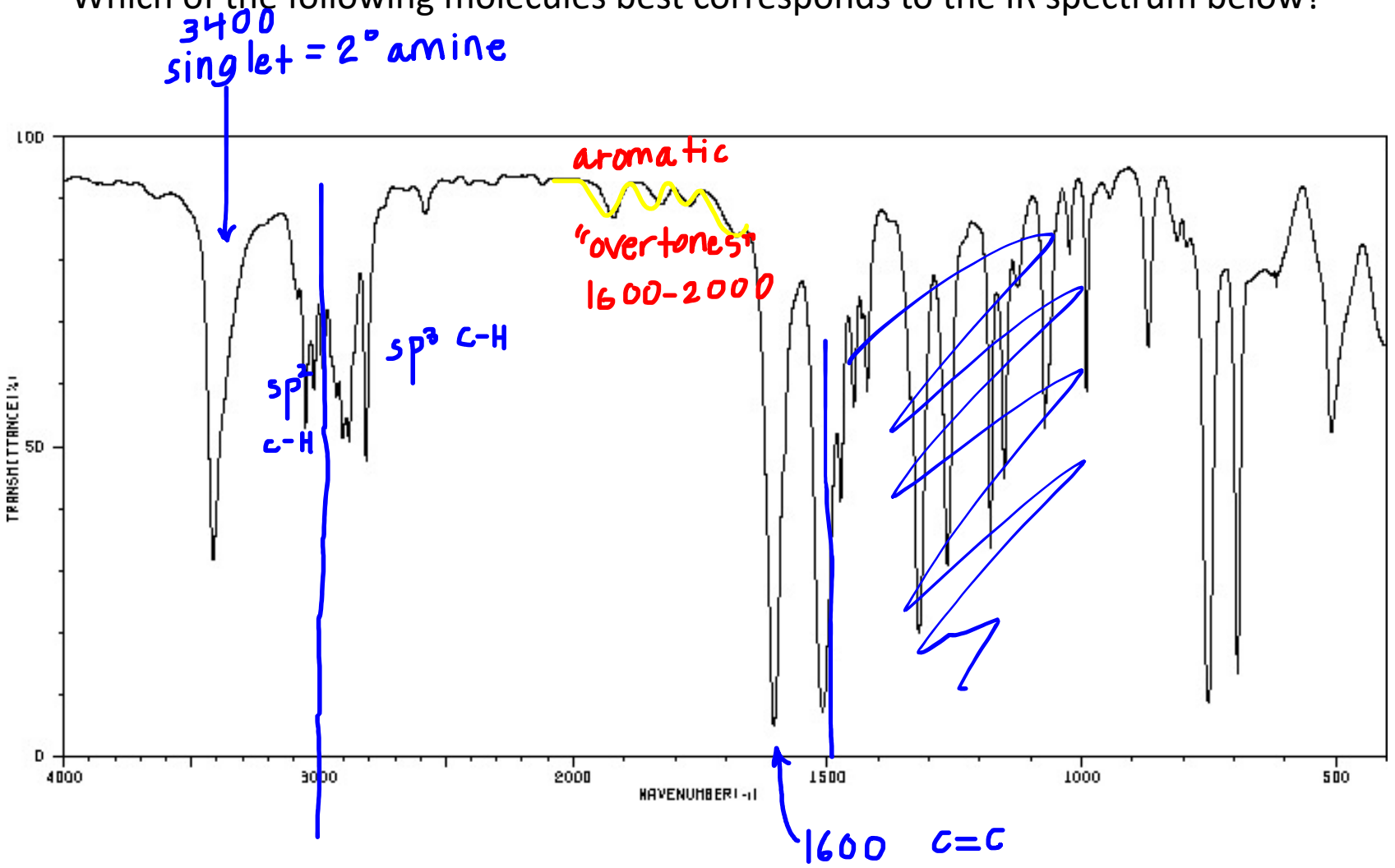
(e) ~~



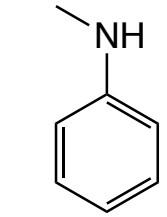
NO sp² C-H

ANSWER: 9

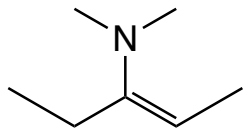
Which of the following molecules best corresponds to the IR spectrum below?



(a)

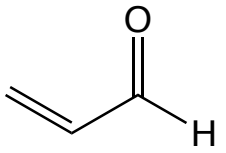


(b)



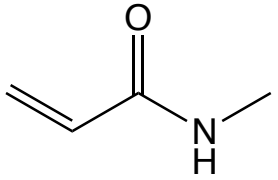
NOT 2°

(c)



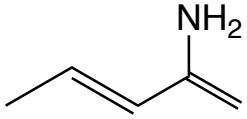
NO sp^3 C-H
1700 C=O MISSING

(d)



NO 1650-80 C=O peak

(e)



NOT 2°