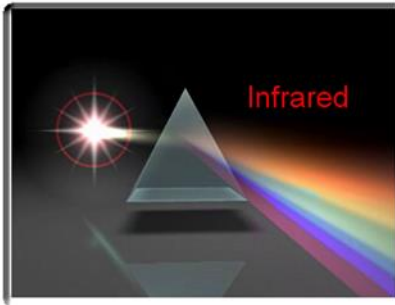
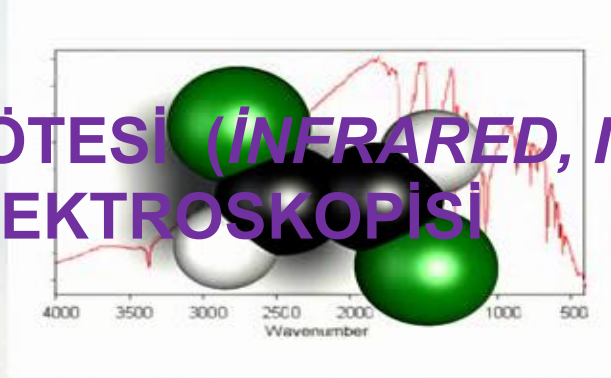
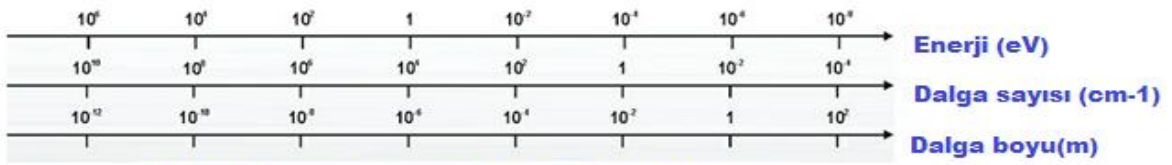
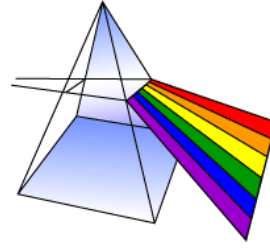


KIRMIZI ÖTESİ (INFRARED, IR) SPEKTROSKOPİSİ

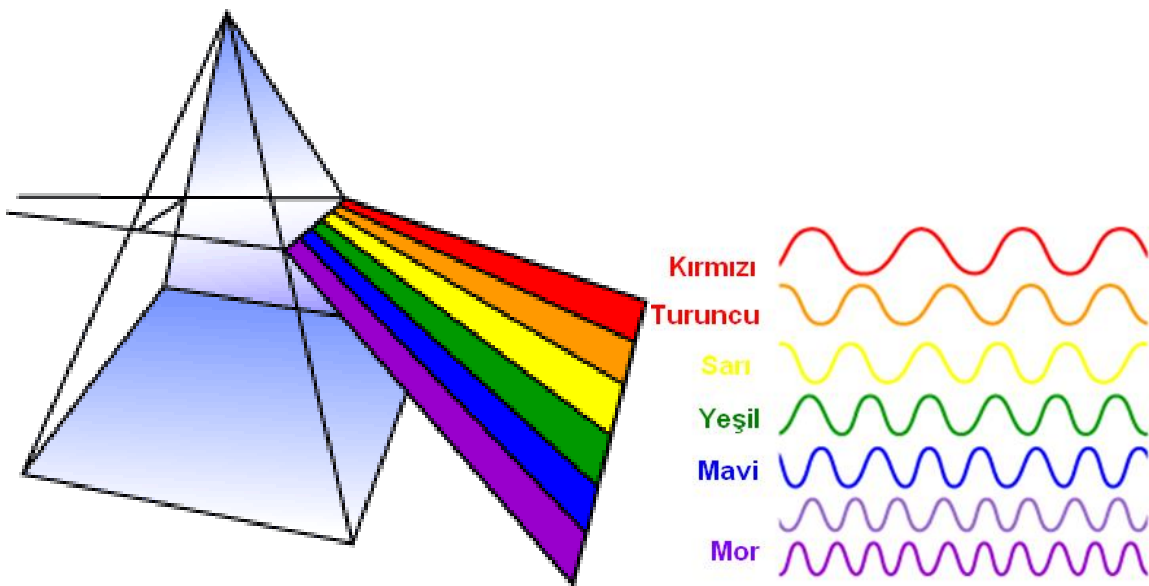
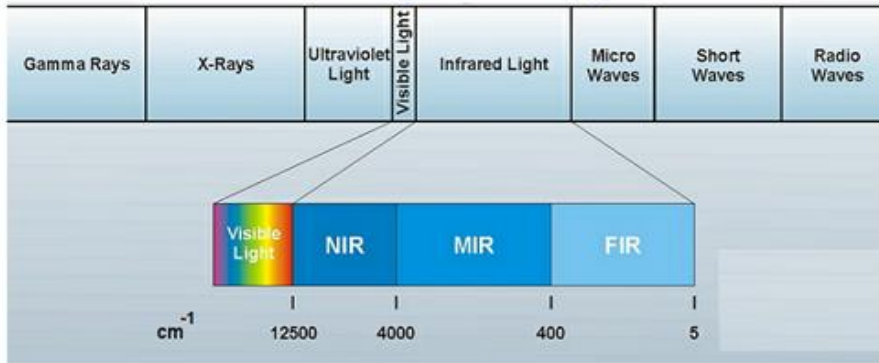


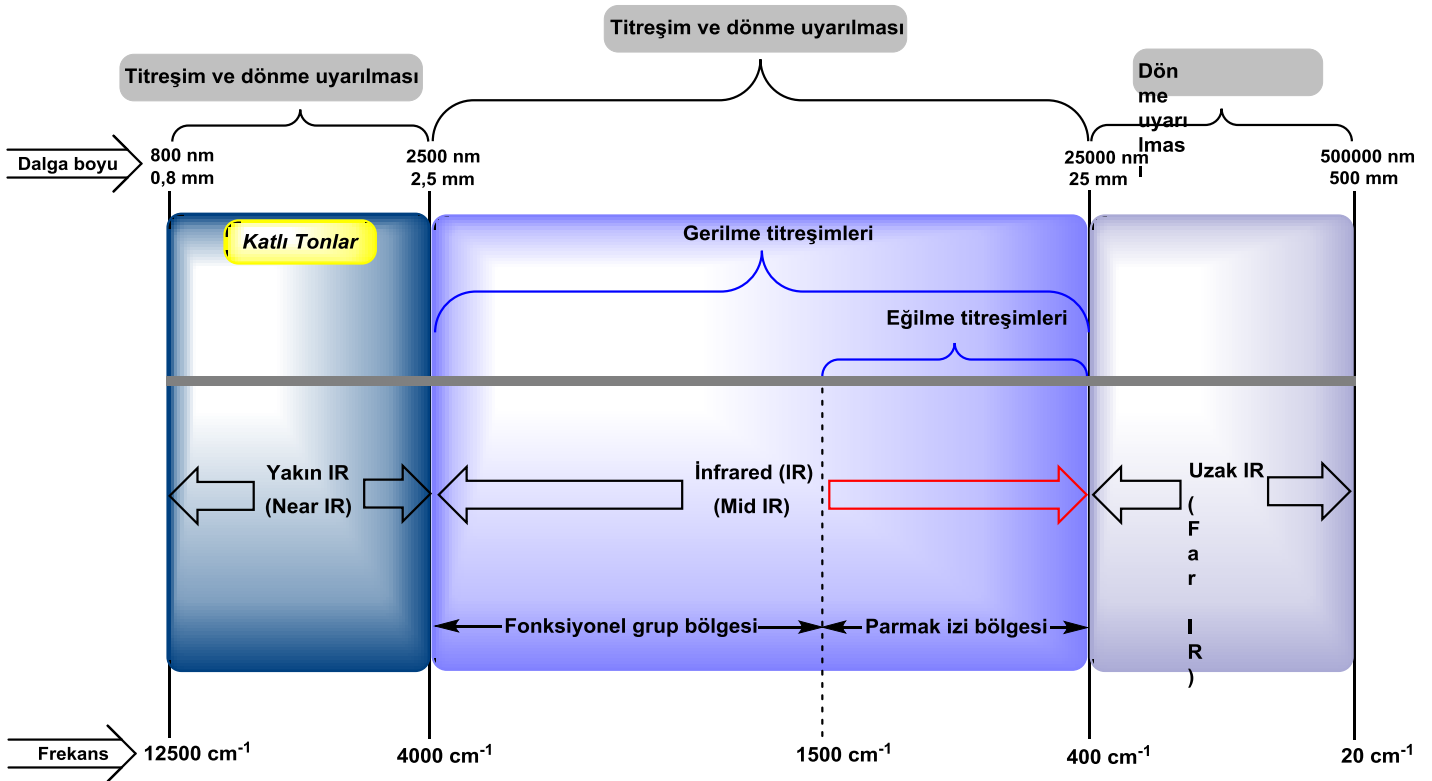
- Elektromagnetik ışımanın madde ile etkileşimini konu alan bilim dalına spektroskopi denir.
- Elektromagnetik ışımanın organik moleküller tarafından absorpsiyonu (soğurulması), moleküldeki atomların türüne, düzenlenmesine, moleküllerin şekline, büyüklüğüne bağlı olduğundan organik kimyada spektroskopik yöntemler,
- ❖ Organik maddelerin kalitatif ve kantitatif analizi,
- ❖ Yapıların aydınlatılması
- ❖ Saflık kontrolü gibi çok geniş bir alanda uygulanmaktadır.

Elektromanyetik Spektrum

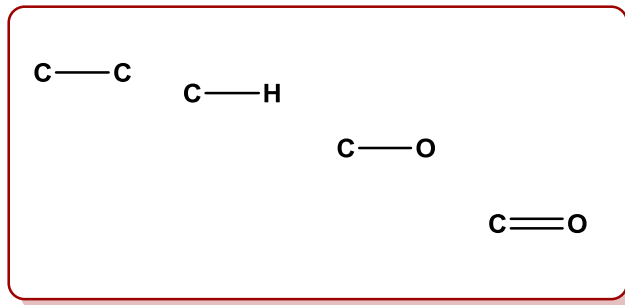


Elektromagnetik Spektrum





1. Kırmızı Ötesi (IR) Işıma ile Madde Etkileşimi

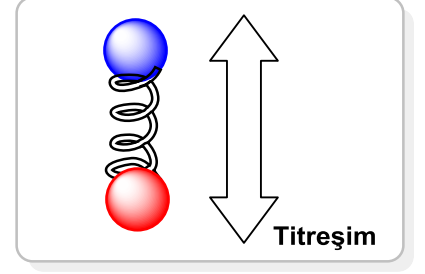
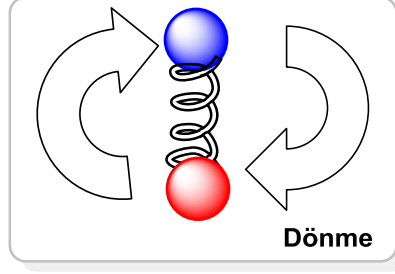
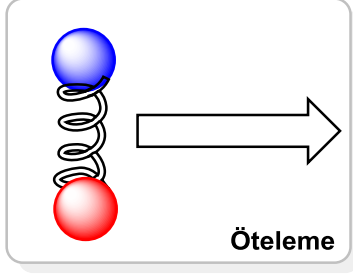


Kırmızı Ötesi Işınları

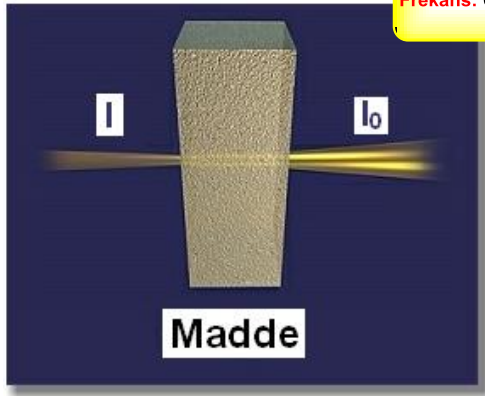
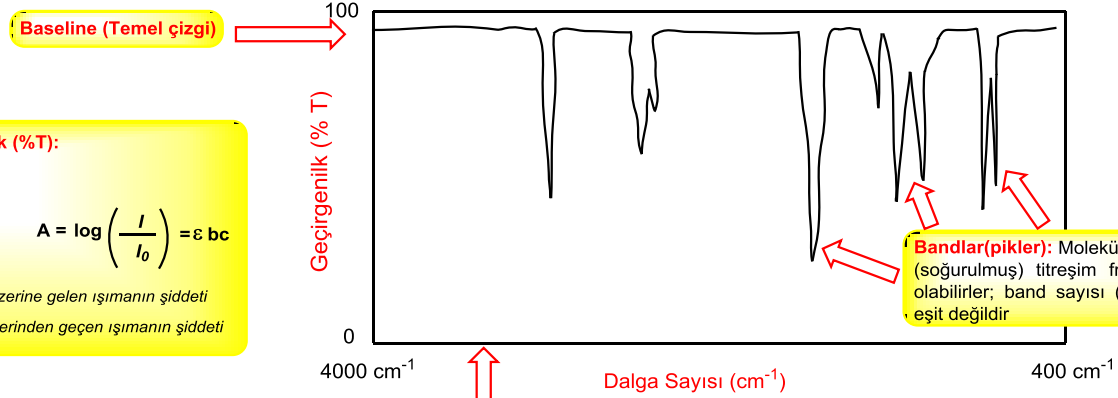
- Titreşim
- Dönme enerji düzeylerini uyarabilir

Kırmızı Ötesi (IR) bölgede absorbsiyon yapan organik moleküller

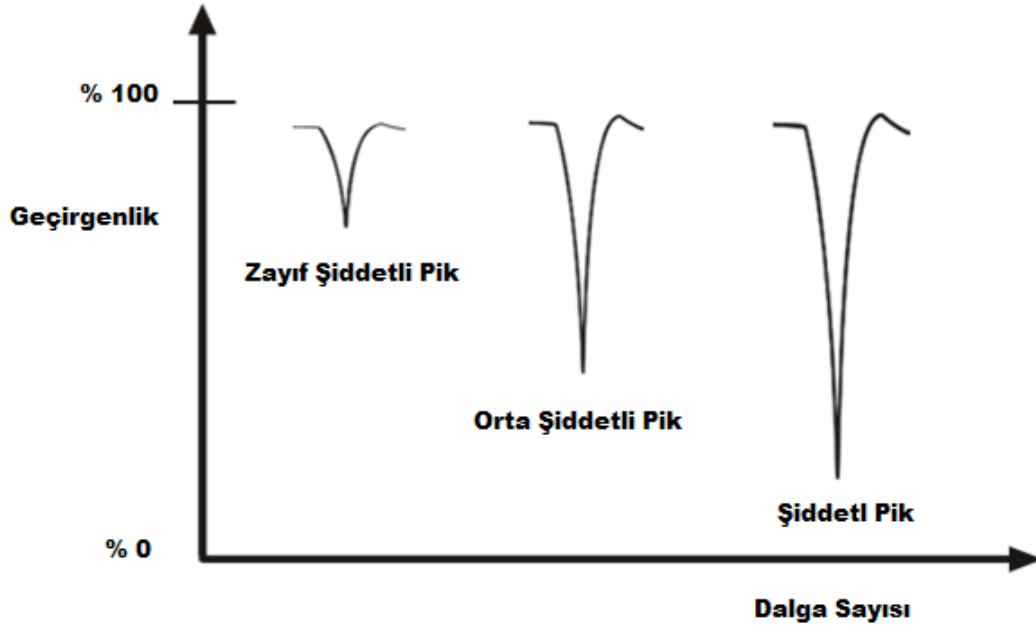
- 1) Titreşim hareketleri
- 2) Dönme (rotasyon) hareketleri
- 3) Ötelenme hareketleri olmak üzere üç tür hareket yaparlar.



2. Genel Kırmızı Ötesi (IR) Spektrumu



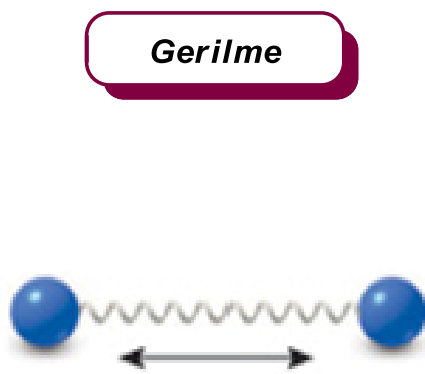
←
Işın yolu



Pikin Şiddeti : Bağıın dipol momenti (μ) ile ilgilidir. Bir sistemde dipol moment değışikliğı ne kadar fazla ise, yani sistem ne kadar polarsa IR piki o kadar şiddetlidir (C=O, C=N gibi).

3. Molekülde Gözlenebilecek Titreşimler

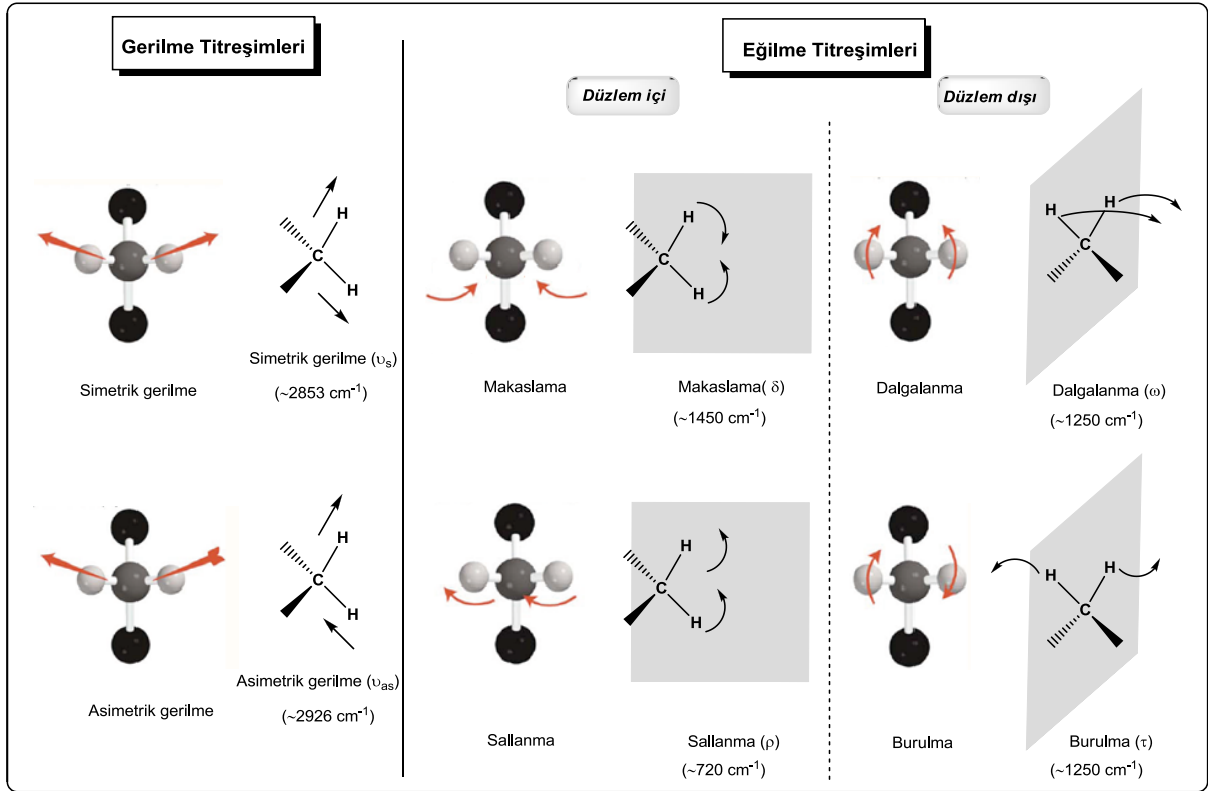
- Gerilme Titreşimi
- Eğilme Titreşimi



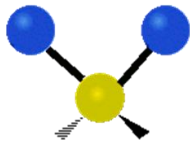
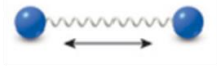
Bir bağ gerilebilir



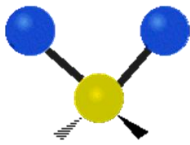
İki bağ eğilebilir



➤ Gerilme Titreşimi

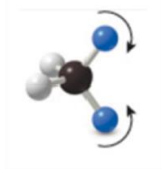


Simetrik Gerilme

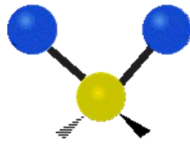


Asimetrik Gerilme

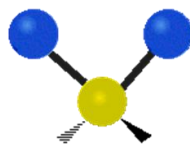
➤ Eğilme Titreşimi



Düzlem içi

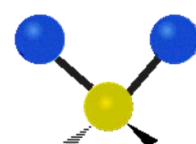


Makaslama

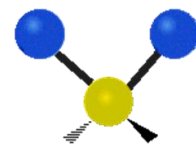


Sallanma

Düzlem dışı



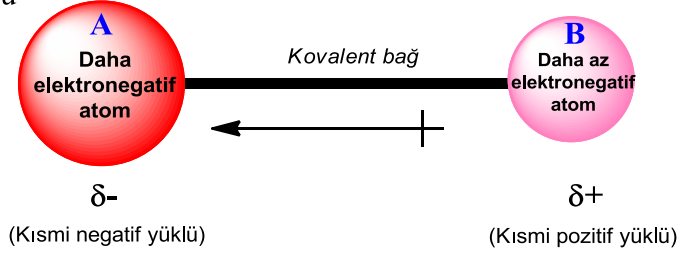
Dalgalanma



Burulma

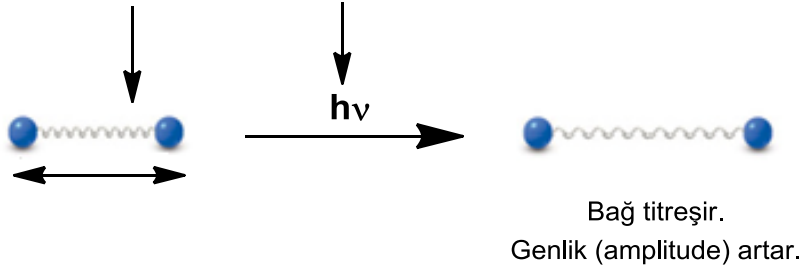
4. Hangi Moleküller IR Spektroskopisi ile incelenebilir

A–B molekülü

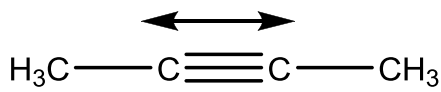


Bir kovalent bağın gerilme ve eğilme frekanslarını ölçmek için, kovalent bağ bir **dipol momente** sahip olmalıdır (μ)

IR ışığın frekansı (ν) = bağ titreşim frekansına (ν) eşit olduğunda, IR ışıması absorblanır



❗ Farklı bağ tipleri, farklı frekansta titreşir. Bu sebeple IR ışımının farklı frekanslarını absorblarlar.

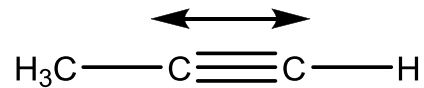


2-Bütün

Simetrik

Dipol momente sahip değil

IR inaktif

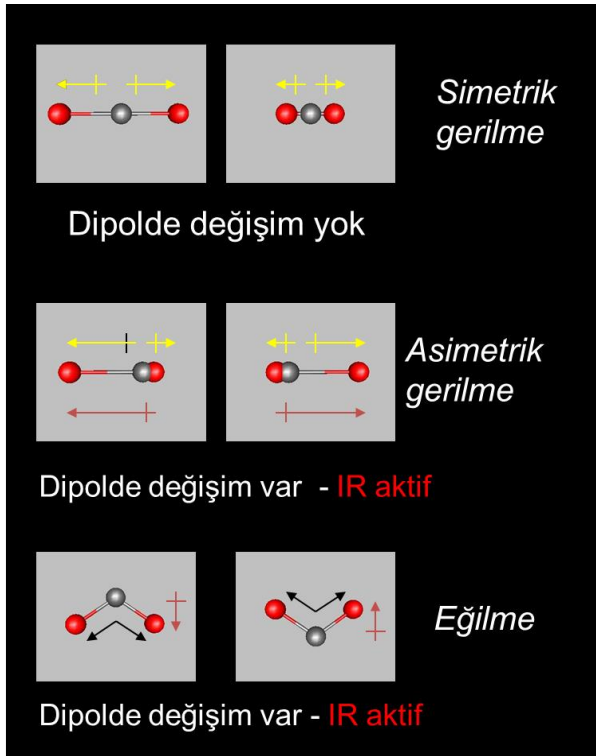


Propin

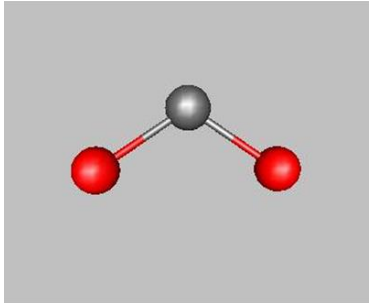
Asimetrik

Dipol momente sahip

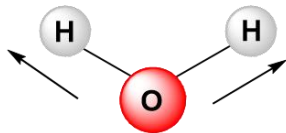
IR aktif



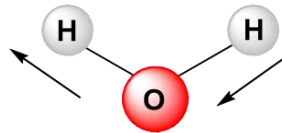
5. Molekölün Titreşim Sayısının (Pik Sayısının) Bulunması



3N-6

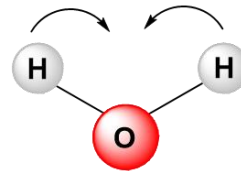


Simetrik gerilme
3625 cm⁻¹



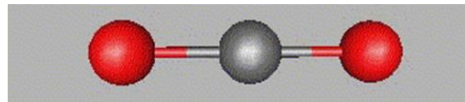
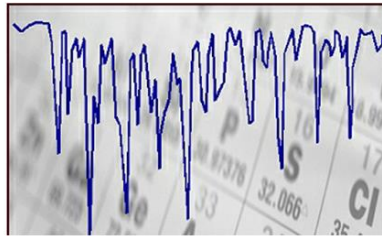
Asimetrik gerilme
3756 cm⁻¹

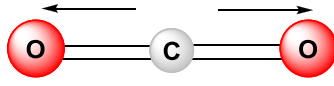
3N-5



Eęilme
1595 cm⁻¹

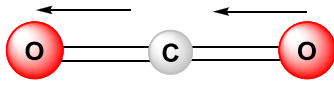
$$\text{Pik sayısı} = 3N-6 = 3 \cdot 3-6 = 3$$



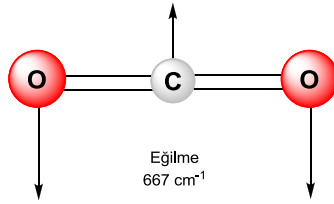


*Simetrik gerilme
1337 cm^{-1}

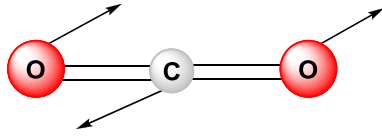
* Raman spektrumunda gözlenir.



Asimetrik gerilme
2349 cm^{-1}
(IR absorpsiyonu gözlenir)



Eğilme
667 cm^{-1}



Eğilme
667 cm^{-1}

Pik sayısı = $3N-5 = 3 \cdot 3-5 = 4$

CO₂ molekülünün temel titreşim hareketleri

6. Titreşim Modeli ve Bir Kimyasal Bağıın Frekansının Hesaplanması



$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m_{ind.}}}$$

ν = Titreşim Frekansı

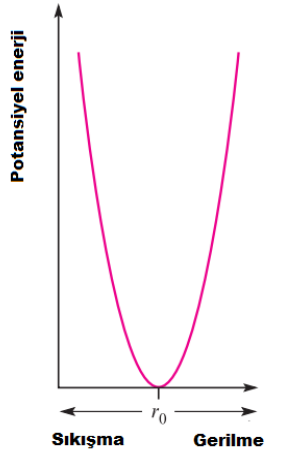
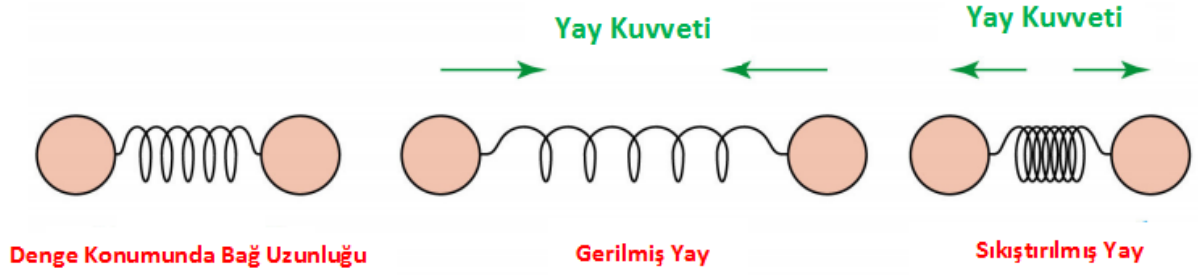
k = N/m olarak bağıın kuvveti

$m_{ind.}$ = İndirgenmiş kütle

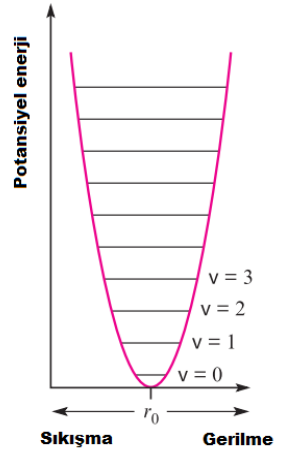
$$m_{ind.} = \frac{m_A \times m_B}{m_A + m_B}$$

m_A, m_B : Atomların kütlesi (Moleküler ağırlıkları değil)

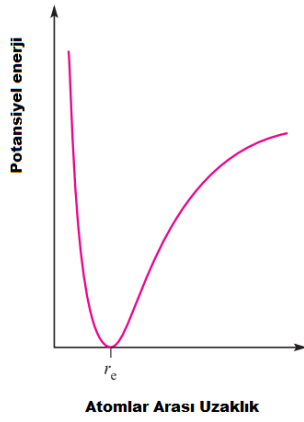
İndirgenmiş kütle hesabında birim olarak kg ($1 \text{ akb} : 1,66 \cdot 10^{-27} \text{ kg}$) kullanılır



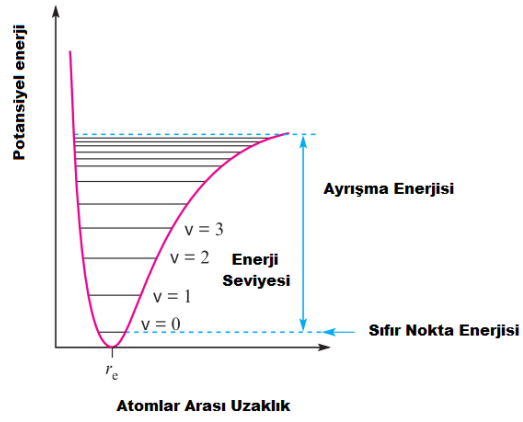
a)



b)

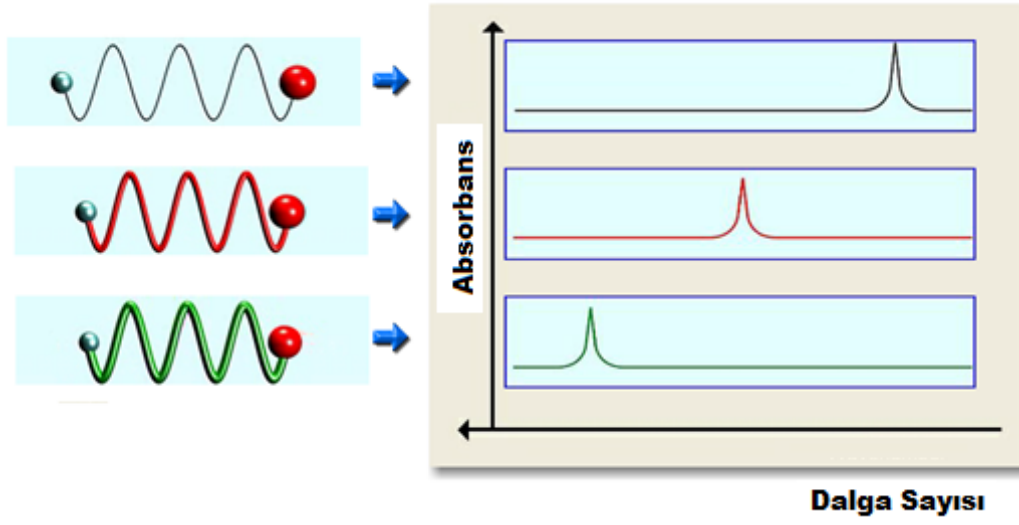


c)



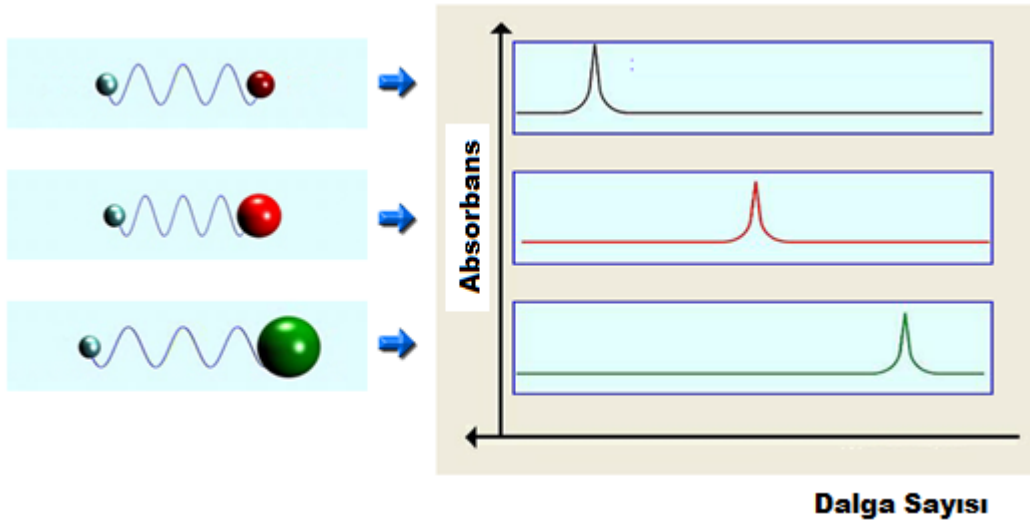
d)

Bağın kuvvet sabiti (k)



Kuvvet sabitini etkileyen faktörler

- ❖ Atomların kütlesi
- ❖ Bağın uzunluğu ve gücü
- ❖ Atomların elektronegatifliği



- ❖ Bir bağın kuvvet sabiti ve bağın iki yanındaki atomlar bilinirse, bağın frekansı hesaplanabilir.

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{m_{ind.}}}$$

v = Titreşim Frekans

k = N/m olarak bağın kuvveti

$m_{ind.}$ = İndirgenmiş kütle

$$m_{ind.} = \frac{m_A \times m_B}{m_A + m_B}$$

m_A, m_B : Atomların kütlesi (Moleküler ağırlıkları değil)

İndirgenmiş kütle hesabında birim olarak kg (1 akb : $1,66 \cdot 10^{-27}$ kg) kullanılır

$$v = \frac{c}{\lambda} \quad \lambda = \frac{1}{\bar{v}} \quad v = c \bar{v}$$

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{k}{m_{ind.}}}$$

c = Işık hızı, $3 \cdot 10^{10}$ cm/s

\bar{v} = Dalga sayısı, cm^{-1}

Titreşim frekansı (enerjisi), hem bağın gücüne (yay kuvvet sabiti) hemde bağ yapan atomların kütlelerine bağlıdır

Örnek: Karbonil grubunun, C=O, gerilme titreşimi sebebiyle meydana gelen temel absorpsiyon pikinin yaklaşık, **dalga sayısını** hesaplayınız.

Karbon için

6,02.10 ²³ tane Karbon (C) atomu	12.10 ⁻³ kg/mol ise
1 tane Karbon (C) atomu	x kg/mol

x = 2.10⁻²⁶ kg/mol

Oksijen için

6,02.10 ²³ tane Oksijen (O) atomu	16.10 ⁻³ kg/mol ise
1 tane Oksijen (O) atomu	x kg/mol

x = 2,7.10⁻²⁶ kg/mol

İndirgenmiş kütle


$$m_{ind.} = \frac{m_O \times m_C}{m_O + m_C} = \frac{2.10^{-26} \text{ kg/mol} \times 2,7.10^{-26} \text{ kg/mol}}{(2 + 2,7).10^{-26} \text{ kg/mol}} = 1,1.10^{-26} \text{ kg/mol}$$

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{m_{ind.}}} = \frac{1}{2,3,14.3.10^{10} \text{ cm/s}} \sqrt{\frac{1.10^3 \text{ N/m}}{1,1.10^{-26} \text{ kg/mol}}} = 1600 \text{ cm}^{-1}$$

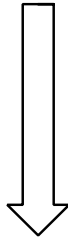
c = Işık hızı, 3.10¹⁰ cm/s

k = 1.10³ N/m (Çift bağ için)

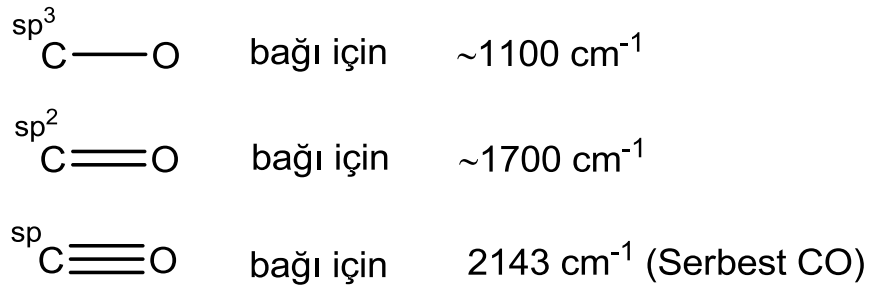
Karbonil grubunun gerilme pikinin deneysel olarak 1600-1800 cm⁻¹ (6,3-5,6 μm) bölgesinde olduğu bulunmuştur.



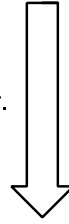
Hibritleşmede **s karakteri** aşağıya doğru artmaktadır. s Karakteri artıkça bağ elektronları çekirdek tarafından daha sıkı tutulduğundan üçlü bağ daha kuvvetli olacaktır.



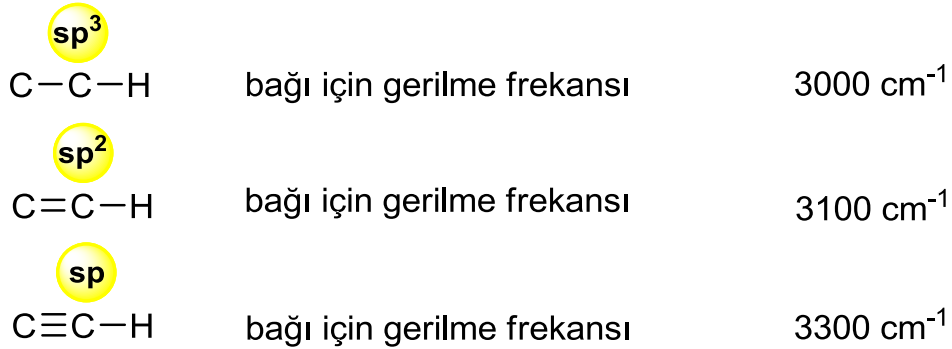
sp^3 C—C	bağı için	1300 - 800 cm^{-1}
sp^2 C=C	bağı için	1700 - 1500 cm^{-1}
sp C≡C	bağı için	2300 - 2100 cm^{-1}



Kütle artışıyla frekansın azaltığı görülmektedir.
Kütle artışıyla dalga sayısının azaltığı görülmektedir.
Kütle artışıyla titreşim hareketi zorlaşır.



C—H	bağı için	3000 cm^{-1}
C—C	bağı için	1200 cm^{-1}
C—O	bağı için	1100 cm^{-1}
C—Cl	bağı için	800 cm^{-1}
C—Br	bağı için	550 cm^{-1}
C—I	bağı için	500 cm^{-1}

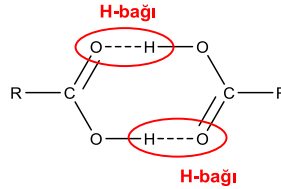
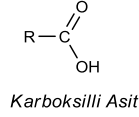
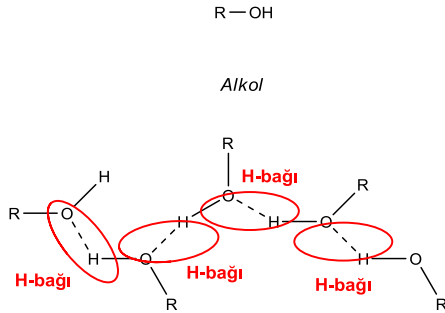


7. IR Spektrumuna Etki Eden Etkenler

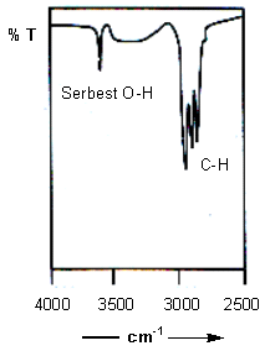
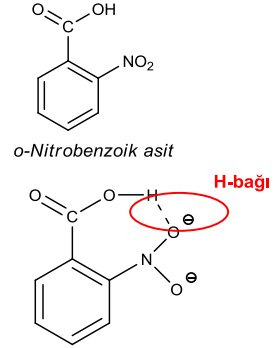
- ❖ Dış Etkenler
- ❖ İç Etkenler (Molekül Yapısına Bağlı Olan Yapısal Etkenler)
- ❖ Hidrojen Bağı
- ❖ Elektronik Etkiler (İndüktif ve Mezomerik Etki)
- ❖ Konjugasyon
- ❖ Halka Büyüklüğü
- ❖ Alan Etkieri

1) Hidrojen Bağı

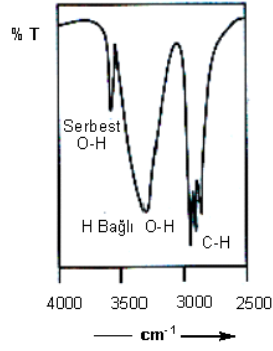
Moleküller arası H-bağı



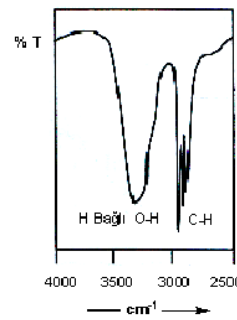
Molekül içi H-bağı



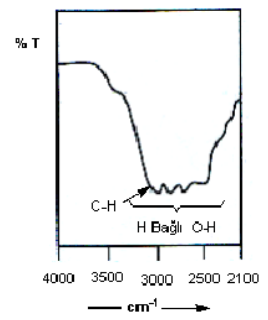
1



2



3



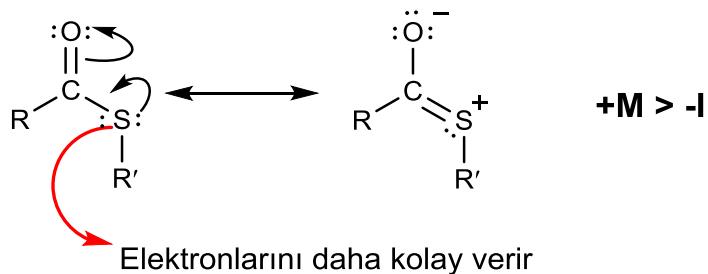
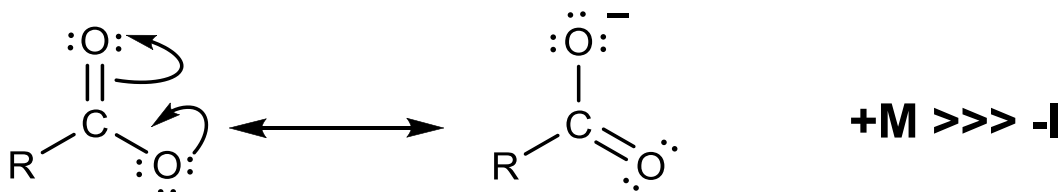
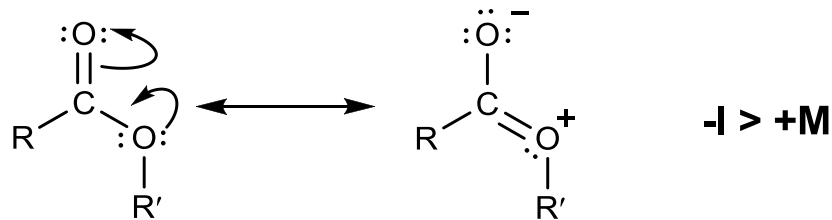
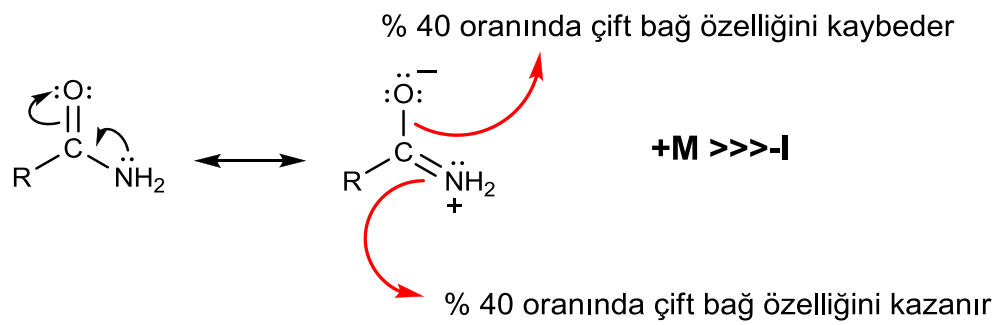
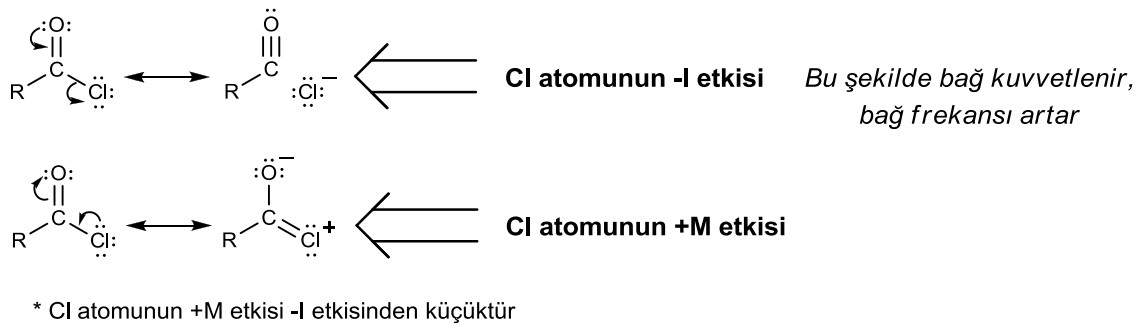
4

2) Elektronik Etkiler (İndüktif ve Mezomerik Etki)

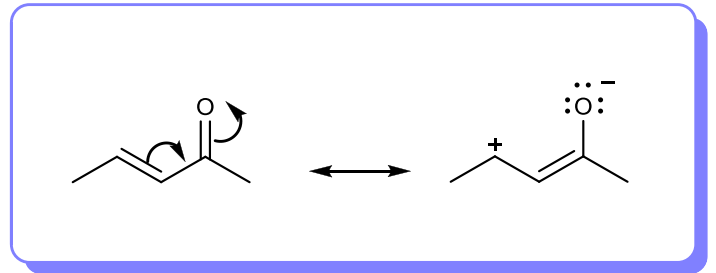
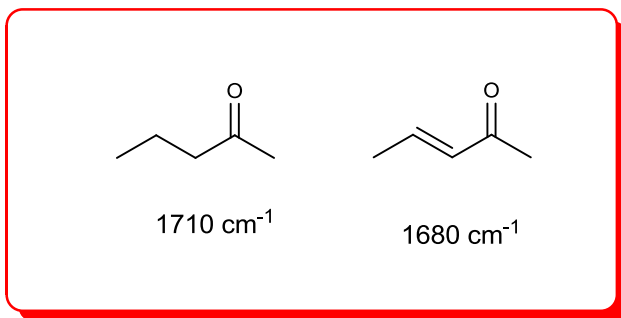
İndüktif etki: Bağlı grup ya da atomların σ -bağları aracılığı ile elektron itmesi veya çekmesi indüktif etkiyi (+I, -I) oluşturur.

Mezomerik etki: Bağlı grup ya da atomların n elektronları ya da π -bağlarının elektron vermesi veya alması mezomerik etkiyi (+M, -M) oluşturur. Bağ kuvvetini azaltan etkiler bu bağa ait absorpsiyon frekanslarının küçülmesine sebep olurken, tersi bir etki absorpsiyonun daha büyük frekanslarda gözlenmesi sonucunu doğurur.

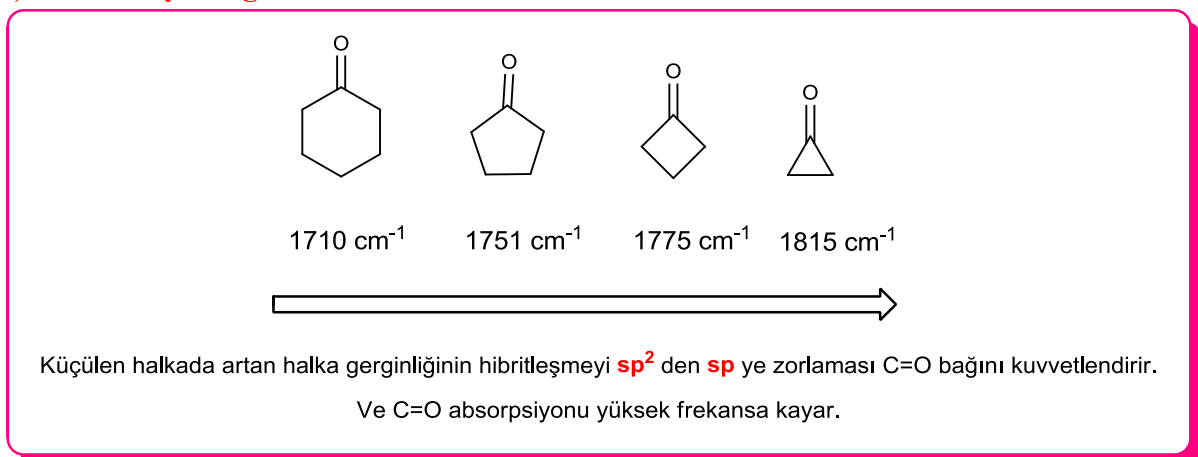
Fonksiyonel Grup	Aldehit	Keton	Karboksilli asit	Ester	Açıl klorür	Amit	Anhidrit
	$R-C(=O)H$	$R-C(=O)R'$	$R-C(=O)OH$	$R-C(=O)OR'$	$R-C(=O)Cl$	$R-C(=O)NH_2$	$R-C(=O)O-C(=O)R'$
Karbonil bileşiklerinin IR absorpsiyonları (cm^{-1})	1720	1710	1700 dimer 1760 monomer	1740	1800	1660-1600	1820-1760 (iki band)



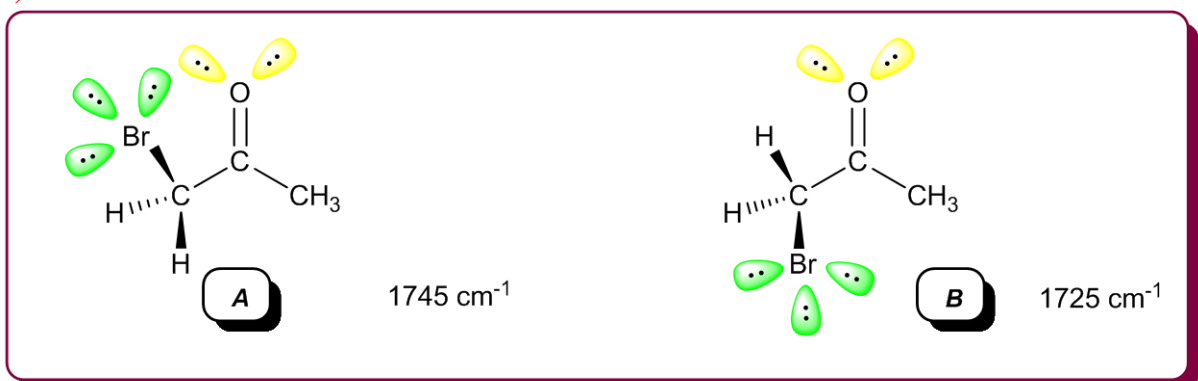
3) Konjugasyon



4) Halka Büyüklüğü

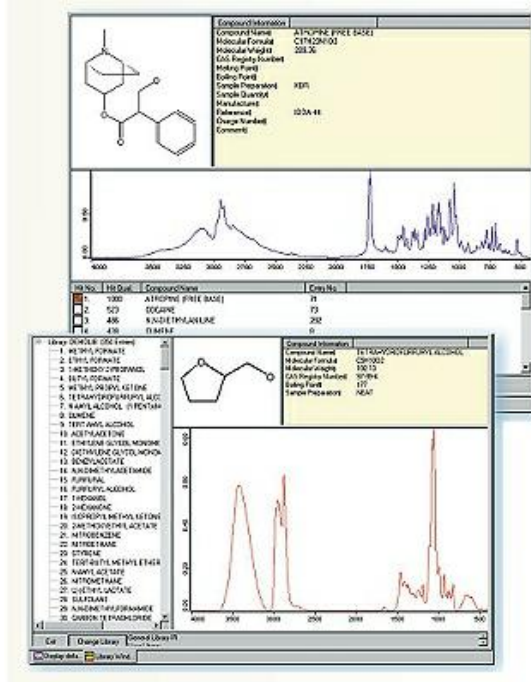


5) Alan Etkileri



8. Kırmızı Ötesi (IR) Spektroskopisinin Uygulamaları

- Yapı tayini
- Kalitatif Analiz
- Sağlık kontrolünde ve Endüstride Kullanılması



9. Kırmızı Ötesi (IR) Soğurma Bölgeleri

Yüksek Dalga Sayısı (cm^{-1})

Yüksek Frekans (ν)

Kısa Dalga Boyu (λ)

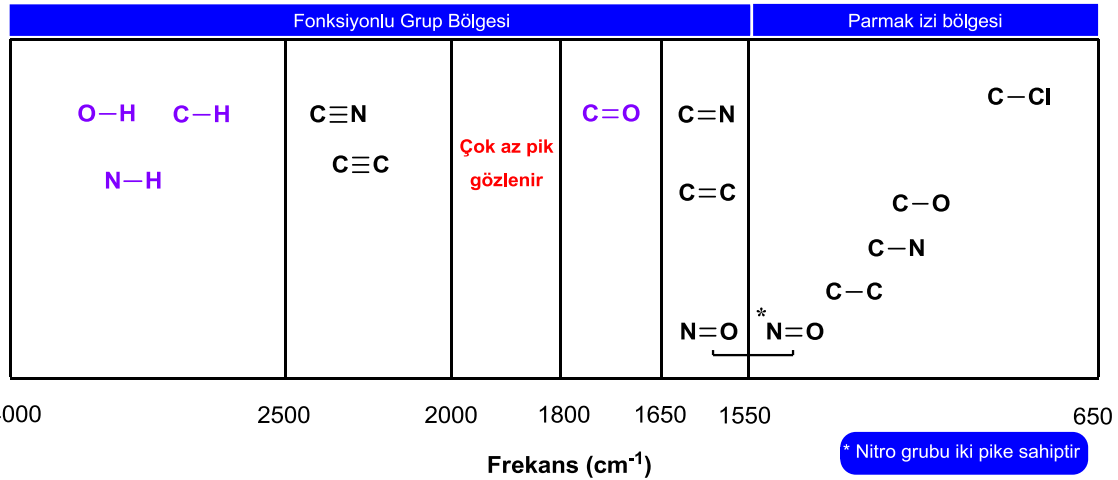
Yüksek Enerji (E)

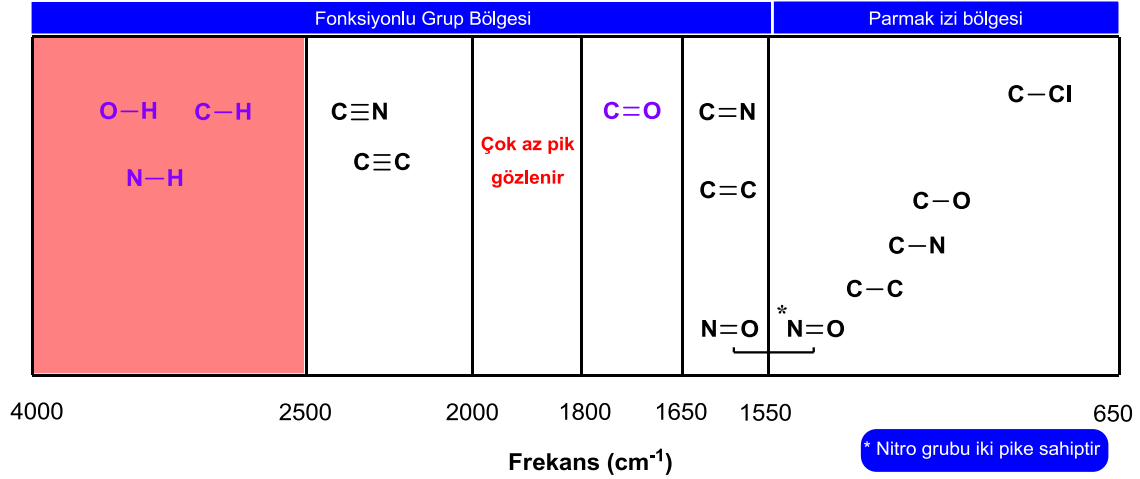
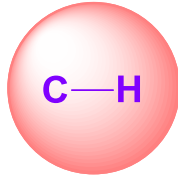
Düşük Dalga Sayısı (cm^{-1})

Düşük Frekans (ν)

Uzun Dalga Boyu (λ)

Düşük Enerji (E)





C-H Gerilme Bölgesi

Temel Değer = 3000 cm⁻¹

C-H sp gerilme ~3300 cm⁻¹

doymamış

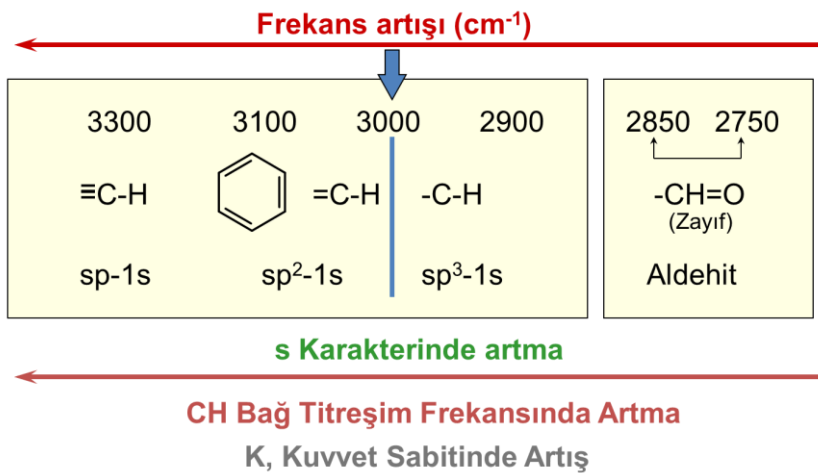
C-H sp² gerilme >3000 cm⁻¹

C-H sp³ gerilme <3000 cm⁻¹

doymuş

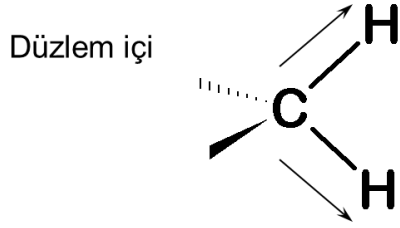
C-H aldehit, iki pik (ikisi de zayıf) ~2850 ve 2750 cm⁻¹

Güçlü Bağlar Büyük Kuvvet Sabitine Sahiptir ve Yüksek Frekansta IR Işınını Soğururlar (Absorplarlar)



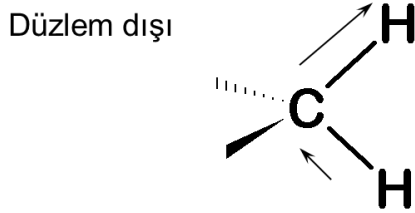
METİLEN GRUBU GERİLME TİTREŞİMİ

İki C-H Bağı Merkezi Bir Karbonu Paylaşırlar
(Hidrojenler Aynı C Bağlıdır)



Simetrik Gerilme

~2853 cm⁻¹

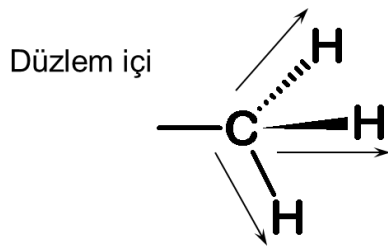


Asimetrik Gerilme

~2926 cm⁻¹

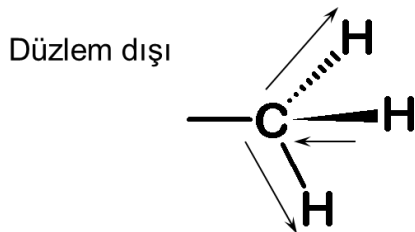
METİL GRUBU GERİLME TİTREŞİMLERİ

Üç C-H bağı Merkezi bir karbonu paylaşır



Simetrik Gerilme

~2872 cm⁻¹

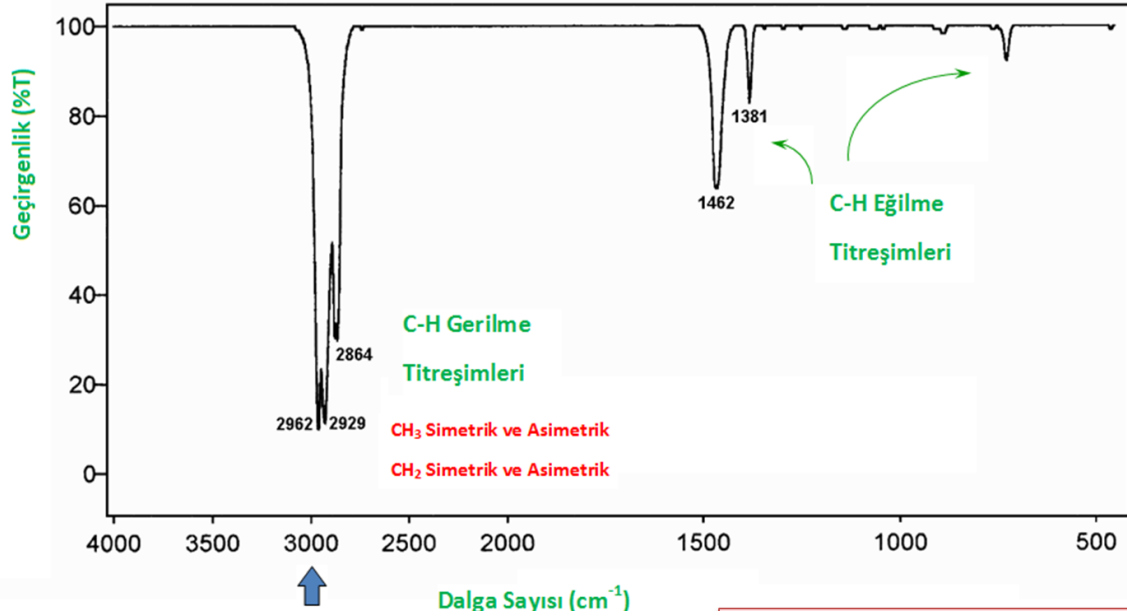
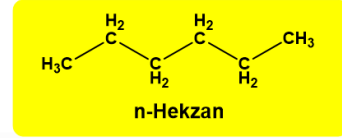


Asimetrik Gerilme

~2962 cm⁻¹

ALKANLAR

n-Hekzan

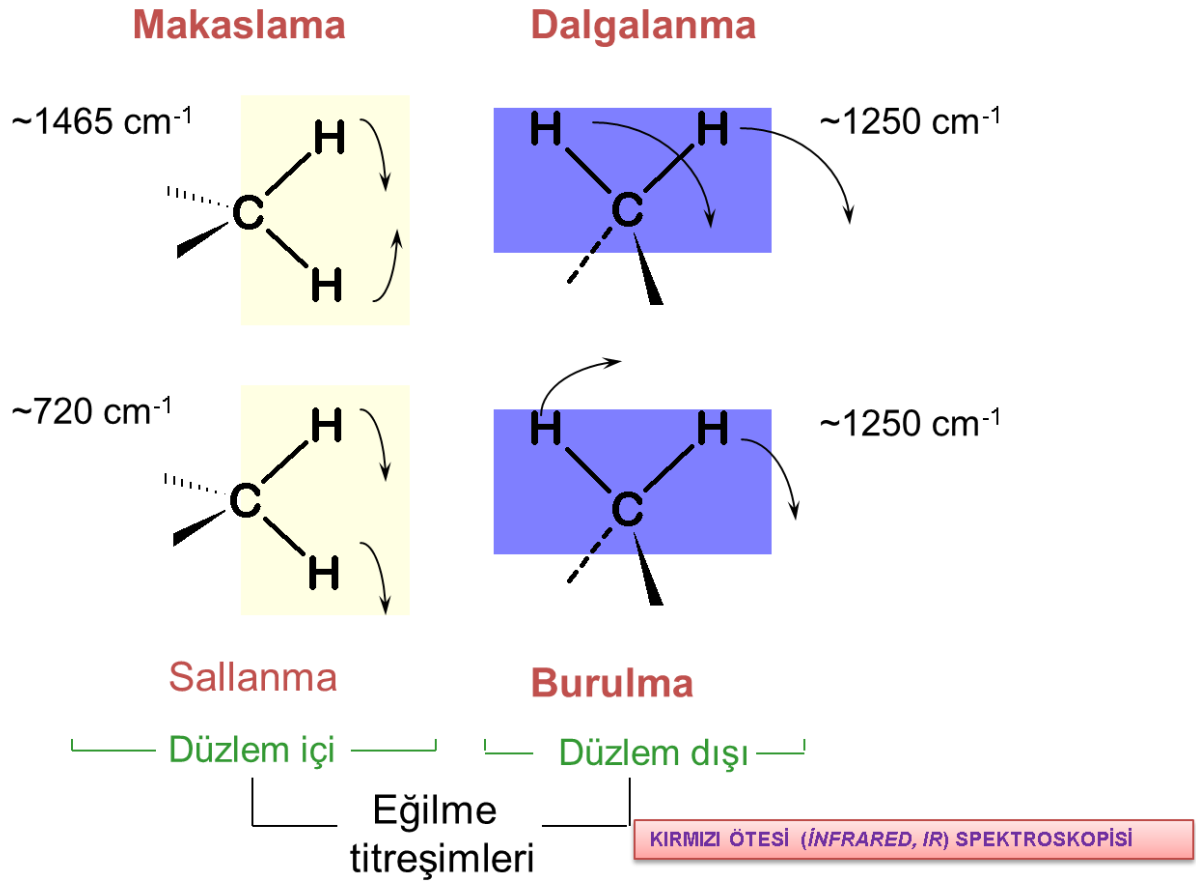


C-H EĞİLME BÖLGESİ

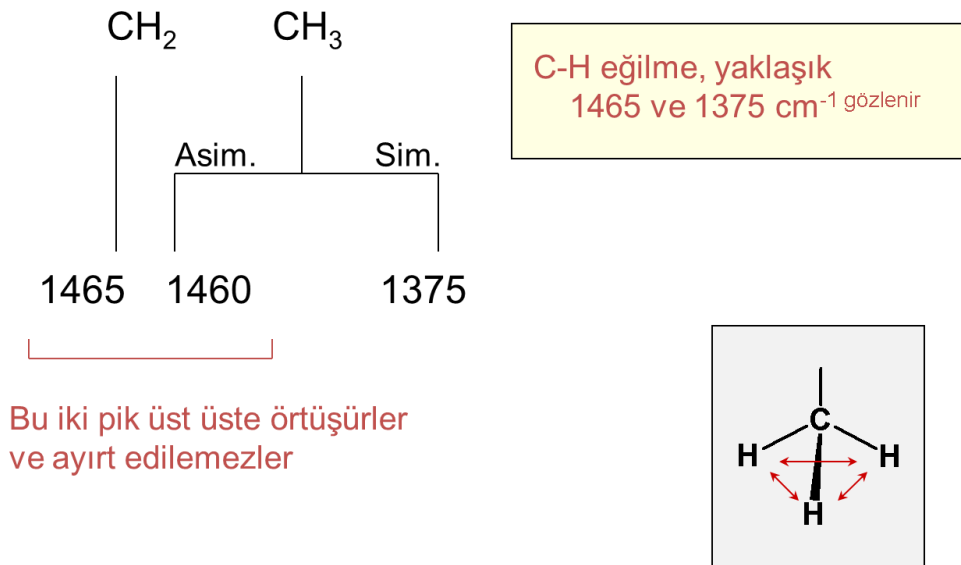
- CH₂ eğilme ~ 1465 cm⁻¹

- CH₃ eğilme (asim.) CH₂ ile aynı yerde ~ 1460 cm⁻¹ görülür
- CH₃ eğilme (sim.) ~ 1375 cm⁻¹

METİLEN GRUBU EĞİLME TİTREŞİMLERİ

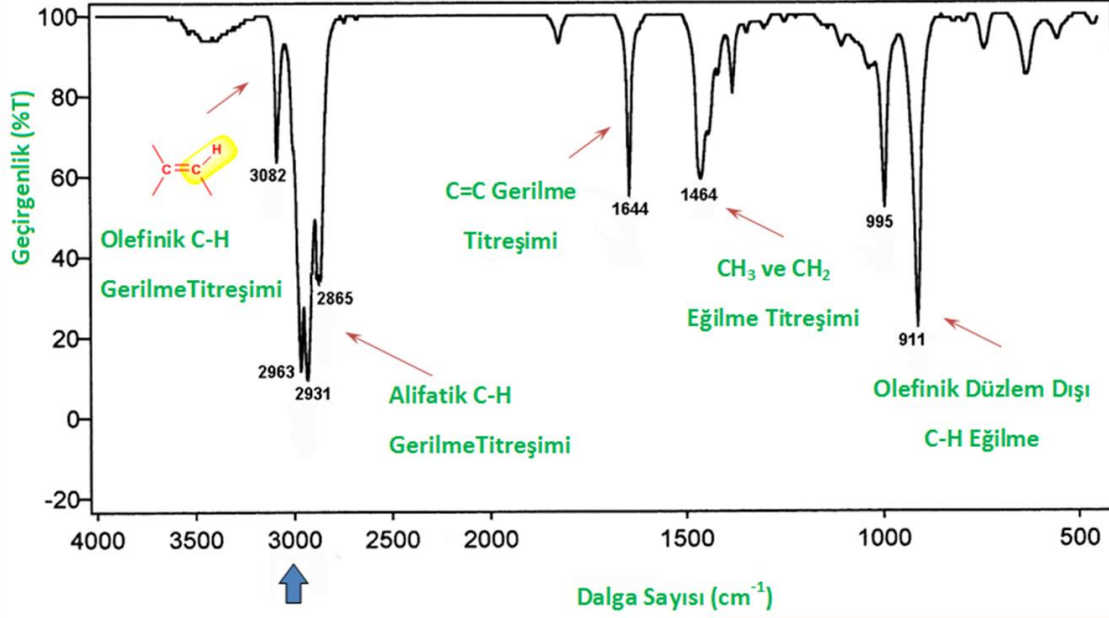


METİLEN ve METİL EĞİLME TİTREŞİMLERİ



ALKENLER

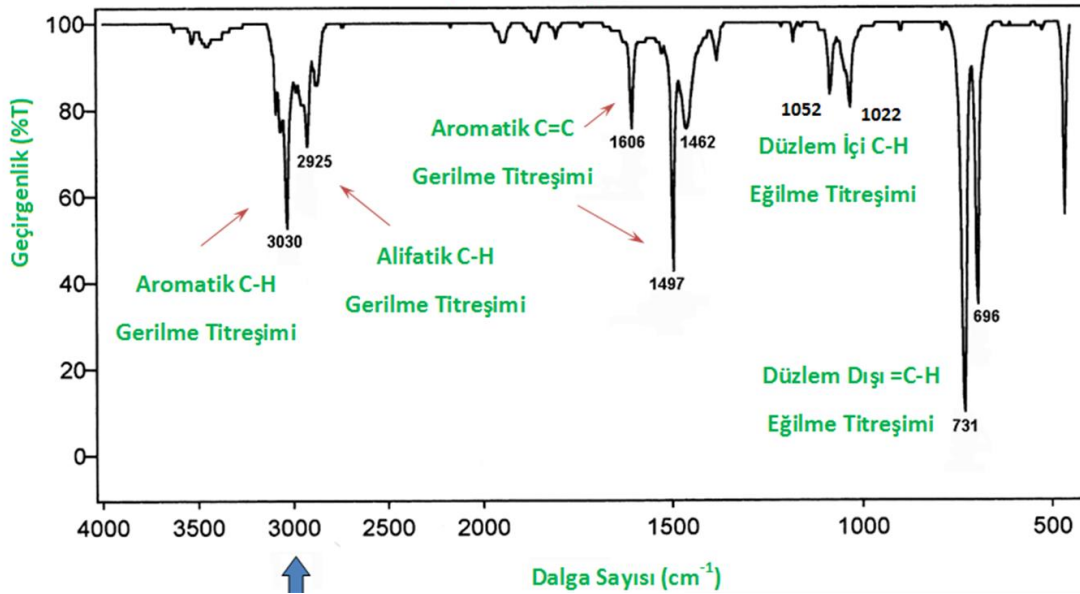
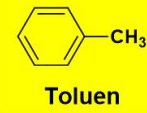
1-Hekzen



AROMATİK YAPILAR

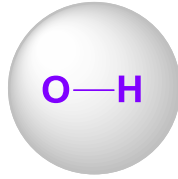
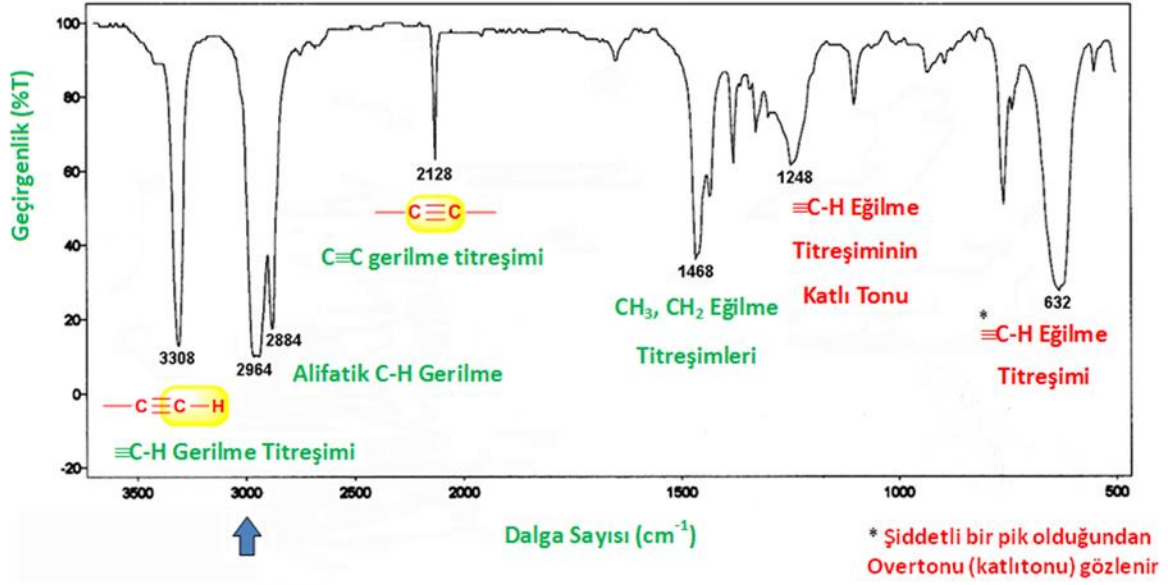
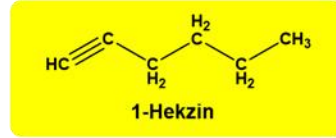
Katlı ton veya Kombinasyon bandları;

2000-1667 cm^{-1}



ALKİNLER

1-Hekzin



Fonksiyonlu Grup Bölgesi					Parmak izi bölgesi
O-H C-H N-H	C≡N	Çok az pik gözlenir	C=O	C=N	C-Cl
	C≡C			C=C	
				N=O	C-O
				* N=O	C-N
					C-C

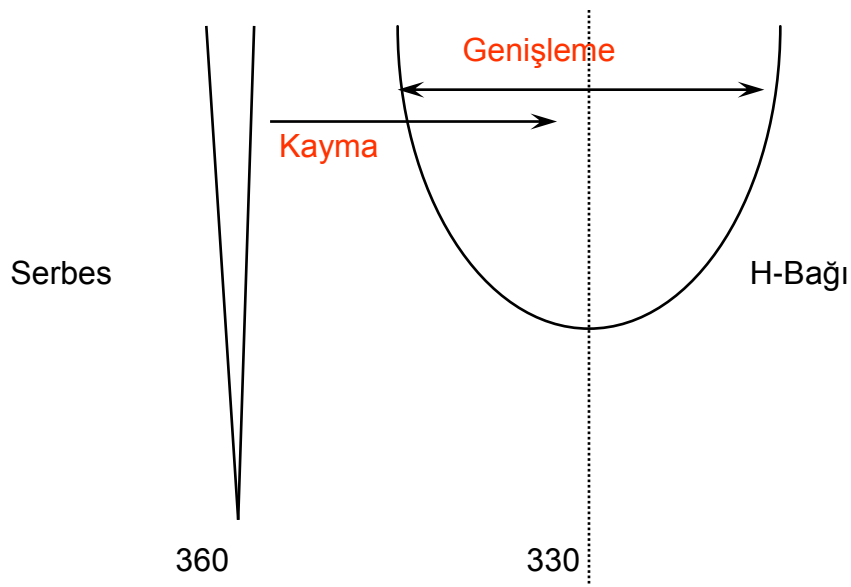
4000 2500 2000 1800 1650 1550 650

Frekans (cm⁻¹)

* Nitro grubu iki pike sahiptir

O-H Gerilme Bölgesi

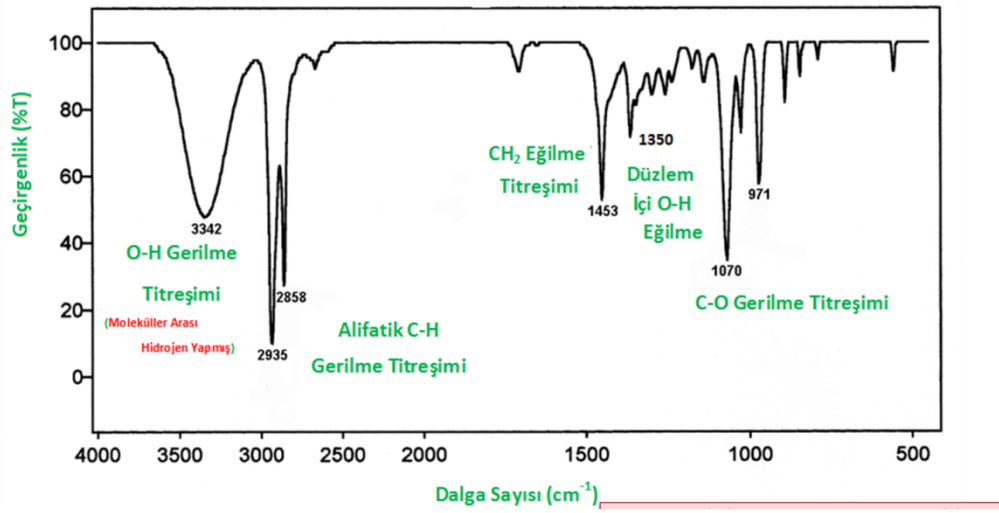
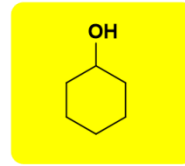
- O-H 3600 cm⁻¹ (alkol, serbest)
- O-H 3300 cm⁻¹ (alkoller & k.asitler, H-bağı yapmış)

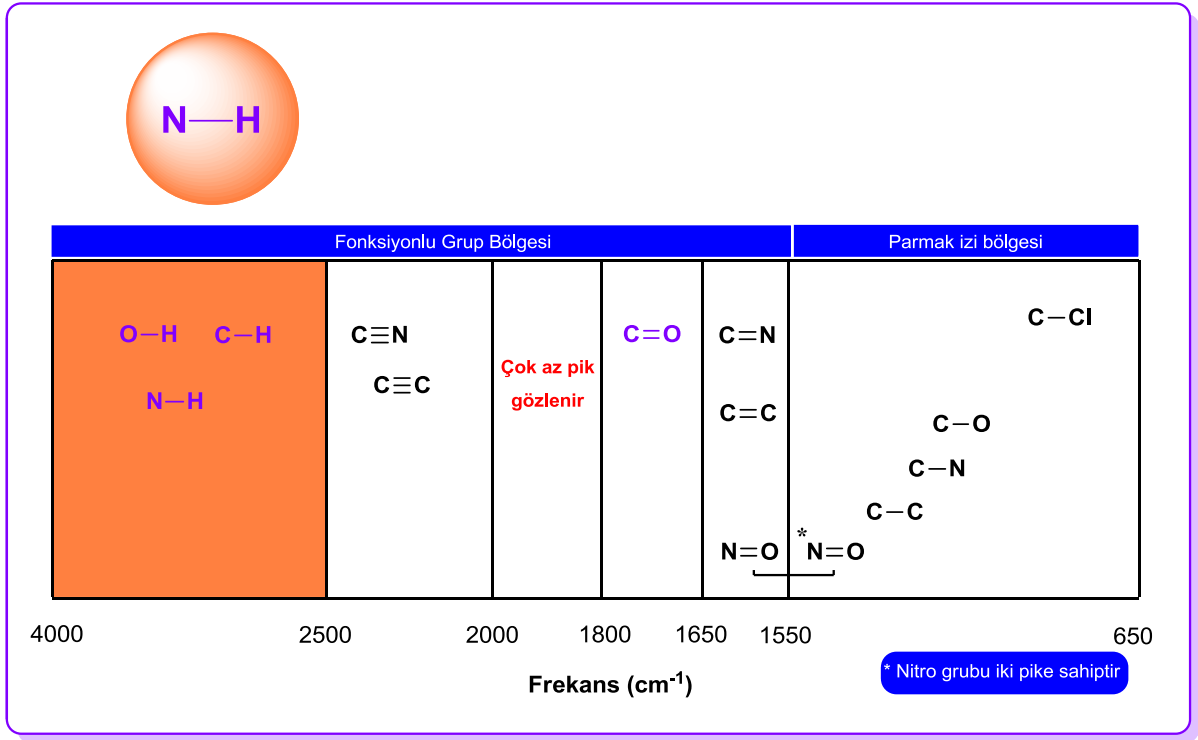


- Bu titreşimlerden ileri gelen absorpsiyonlar hidrojen bağına karşı hassastırlar.

ALKOLLER

Sikloheksanol

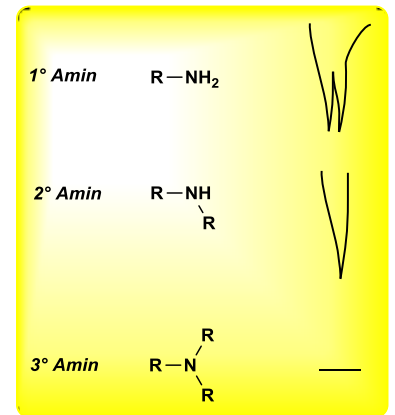
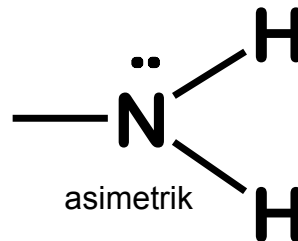
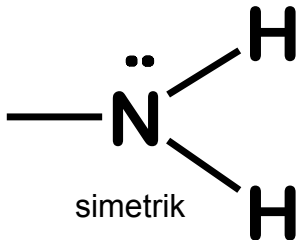




N-H gerilme bölgesi

N-H 3300 - 3400 cm^{-1}

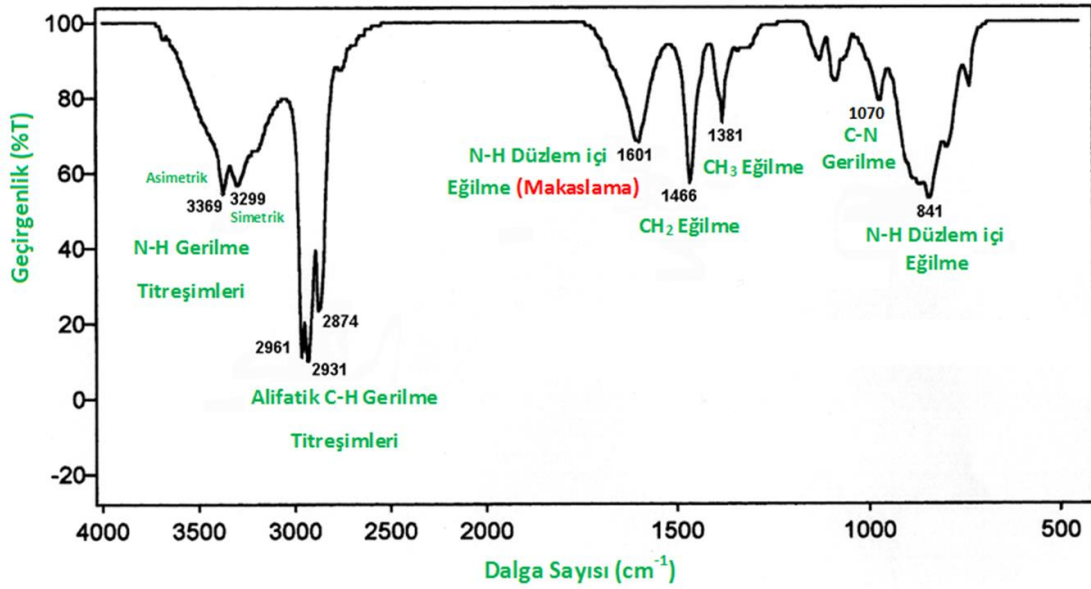
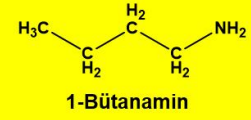
- Primer aminler iki pik verir.



- Sekonder aminler tek pik verir.
- Tersiyer aminler pik vermez.

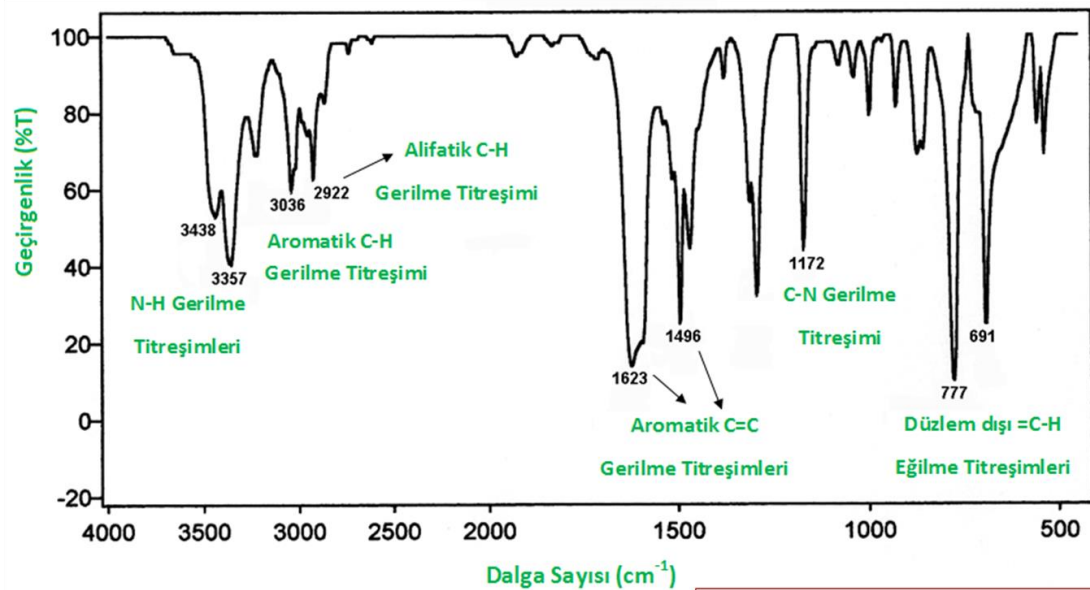
AMİNLER (Primer Aminler)

1-Bütanamin



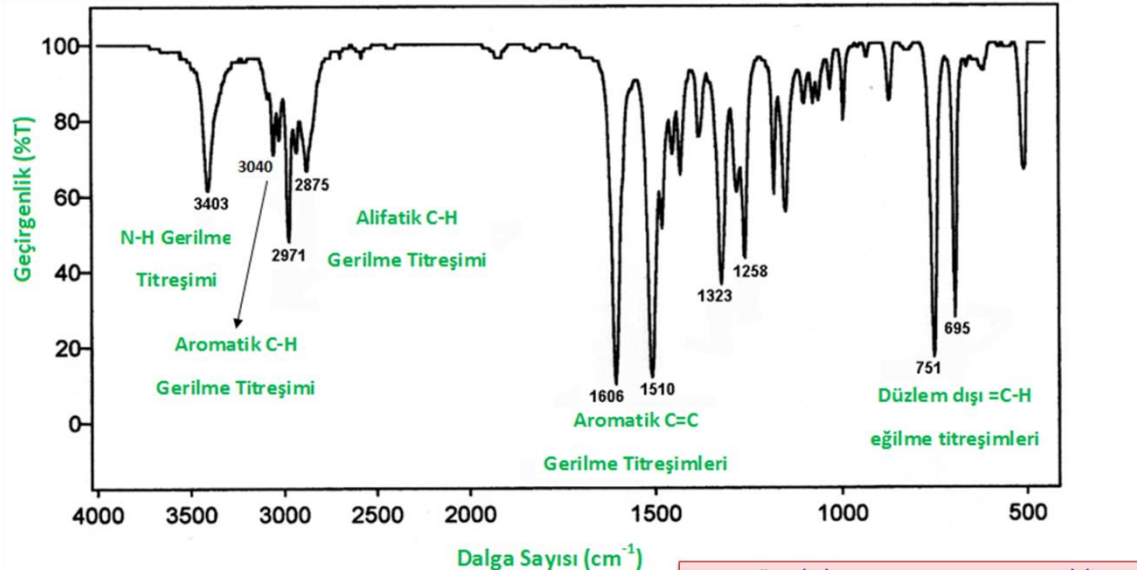
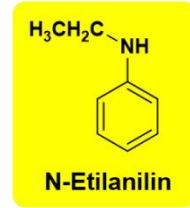
PRİMER AROMATİK AMİN (Primer Aminler)

3-Metilanilin



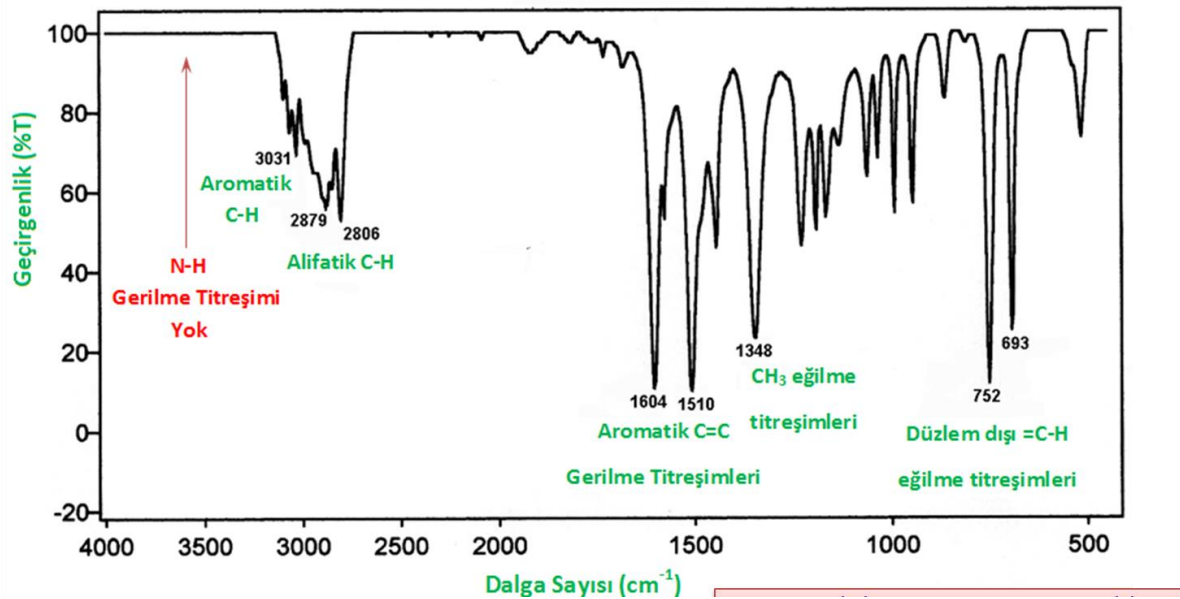
AMİNLER (Sekonder Aminler)

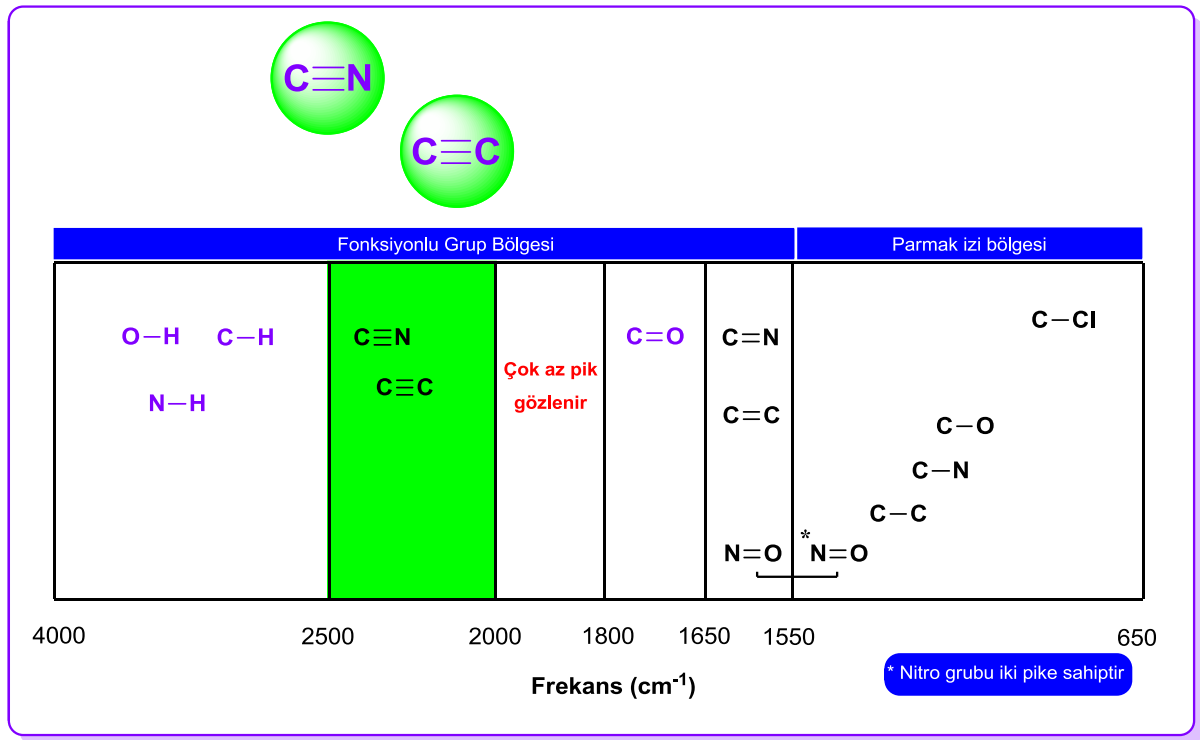
N-Etilanilin



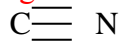
AMİNLER (Tersiyer Aminler)

N,N-Dimetilanilin

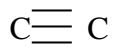




Üçlü Bağ Gerilme bölgesi



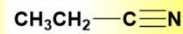
2250 cm⁻¹



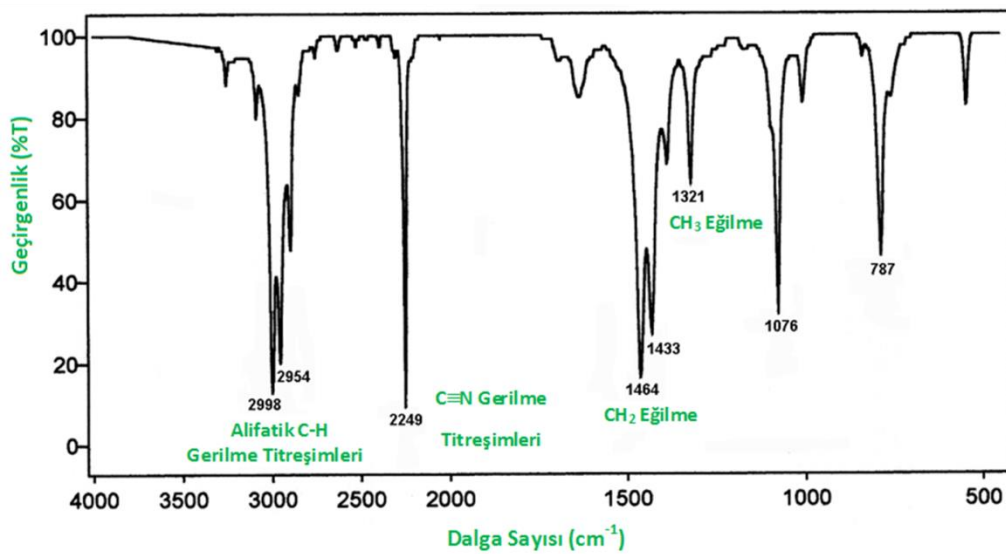
2150 cm⁻¹

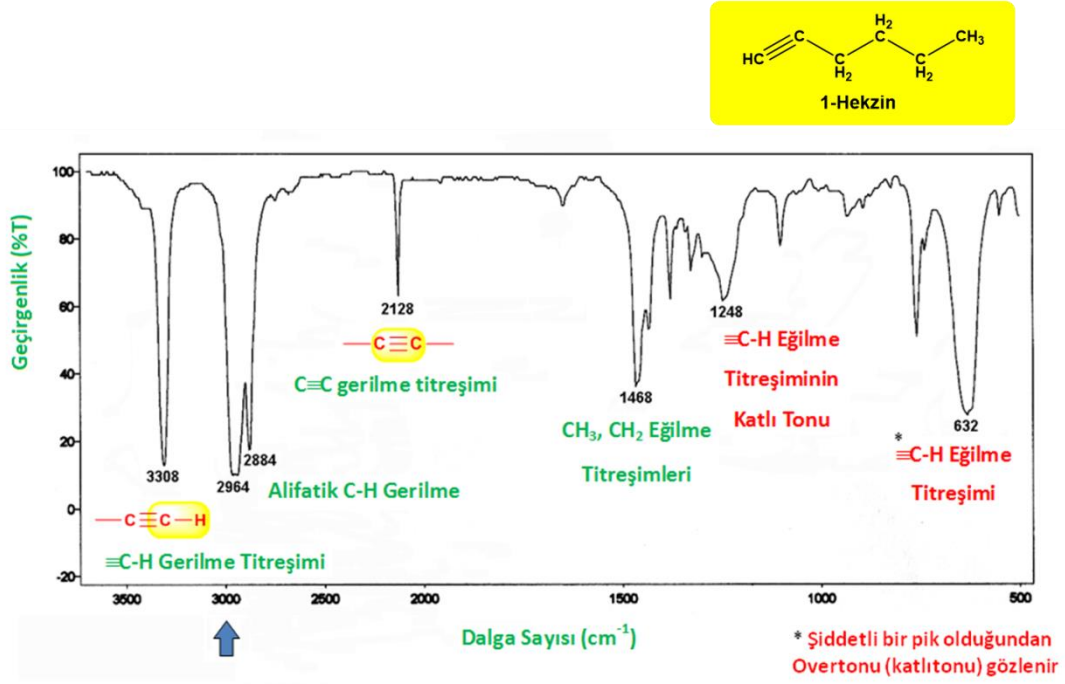
Siyano grubu büyük bir dipol momente sahip olduğundan keskin bir pik verir. Karbon-Karbon Üçlü Bağı Keskin bir Pik verir, fakat molekül simetrik ise bu pik zayıftır.

NİTRİLLER



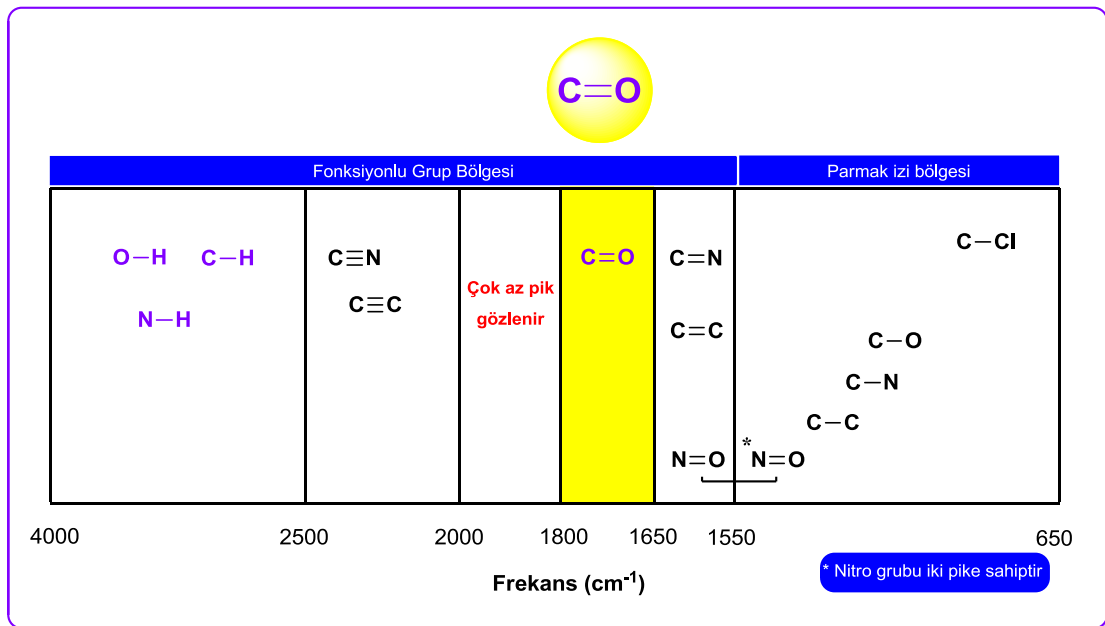
Propannitril





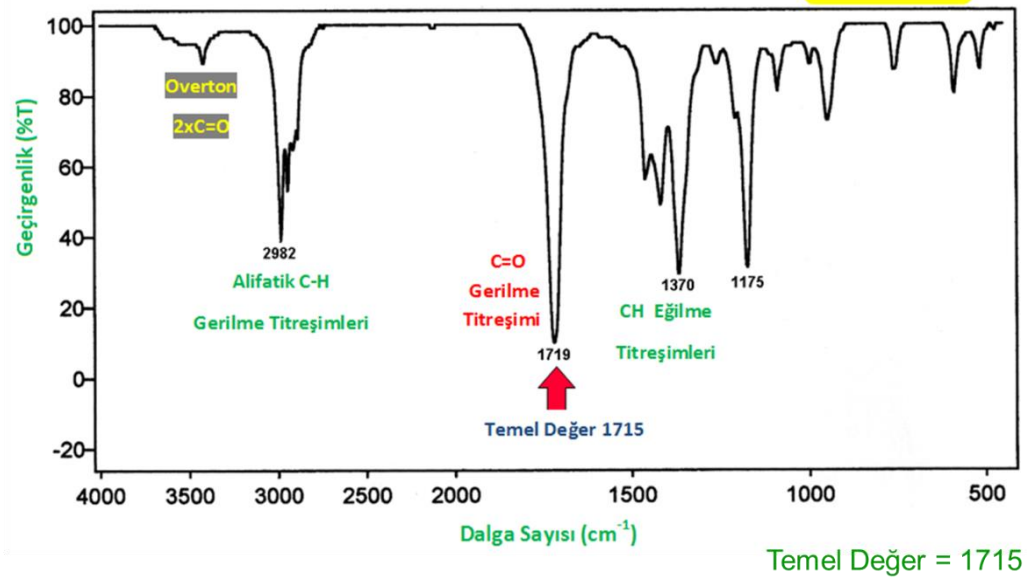
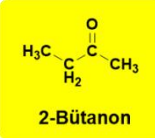
KARBONİL GERİLME BÖLGESİ

- Bu bölge gerilmeleri 1650 – 1800 cm⁻¹ Spektrumun ortasının sağında bulunur
- Temel değer 1715 cm⁻¹ (keton)
- Pikler çok güçlüdür.!!! C=O büyük bir dipol momente sahip olduğundan.
- C=O IR spektrumundaki en güçlü ve keskin piktir.



KETONLAR

2-Bütanon



C=O ÇEVRESİNE GÖRE ÇOK HASSASTIR

Açıl klorür

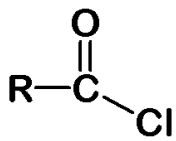
Ester

Aldehit

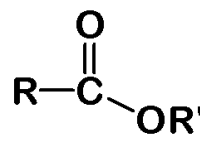
Keton

Karboksilli
asit

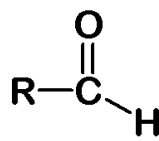
Amit



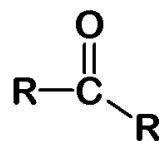
1800



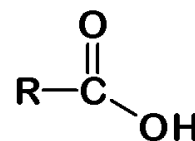
1735



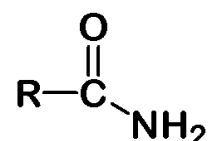
1725



1715

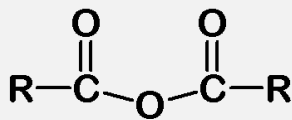


1710



1690

Anhidrit



1810 and 1760
(iki pik)

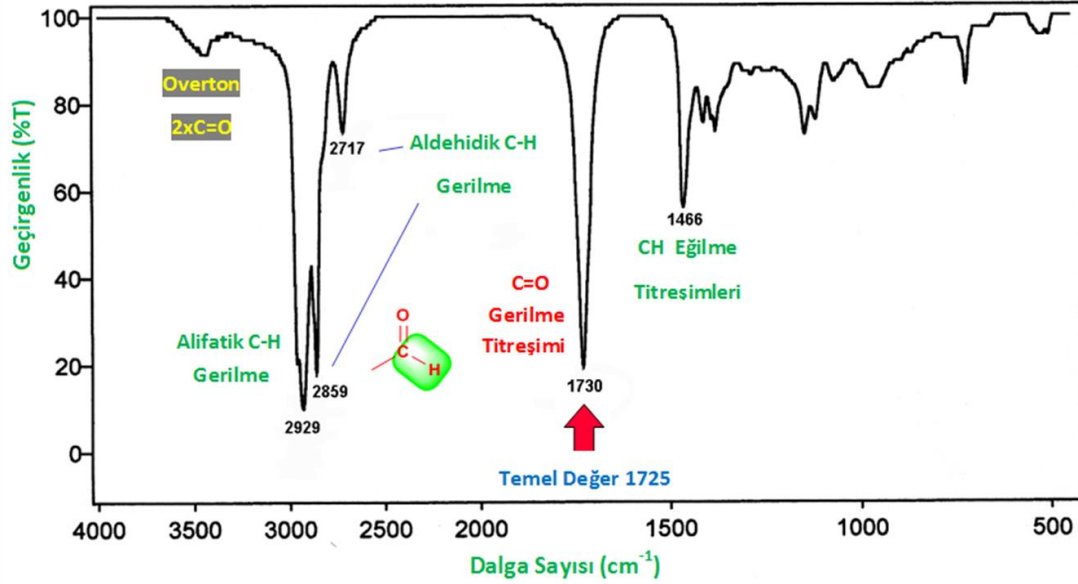
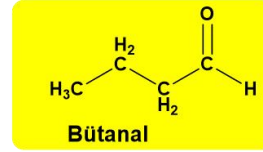


Temel
Değer

KIRMIZI ÖTESİ (İNFRARED, IR) SPEKTROSKOPİSİ

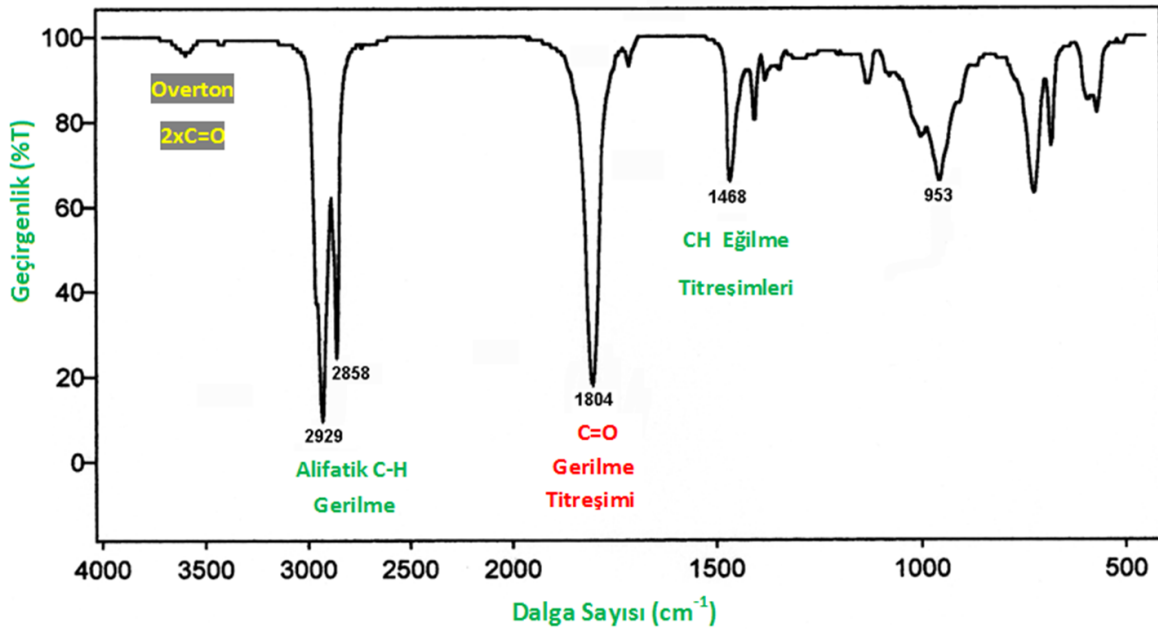
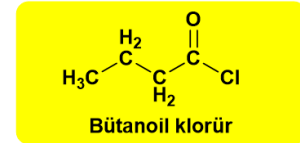
ALDEHİTLER

Bütanal



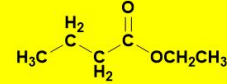
AÇIL KLORÜRLER

Bütanoil klorür

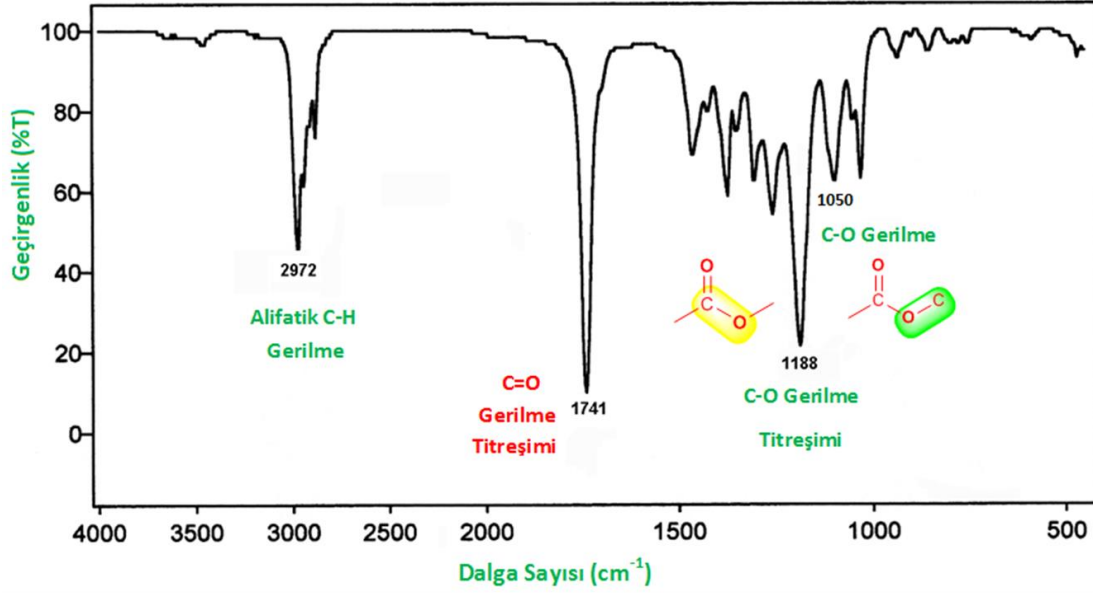


ESTERLER

Etilbütanoat

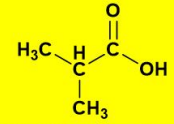


Etilbütanoat

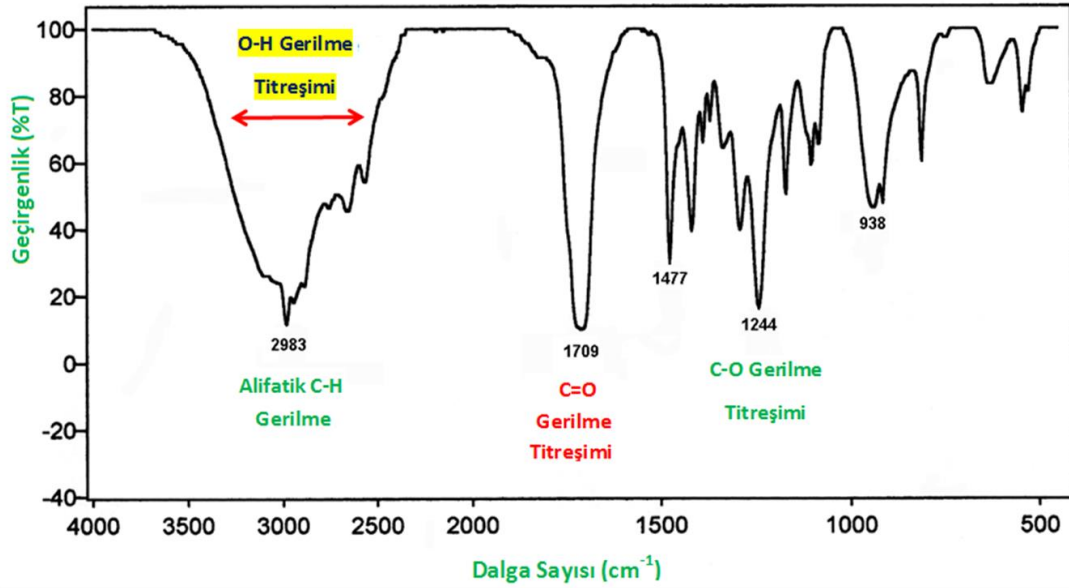


KARBOKSİLLİ ASİTLER

2-Metilpropanoik asit

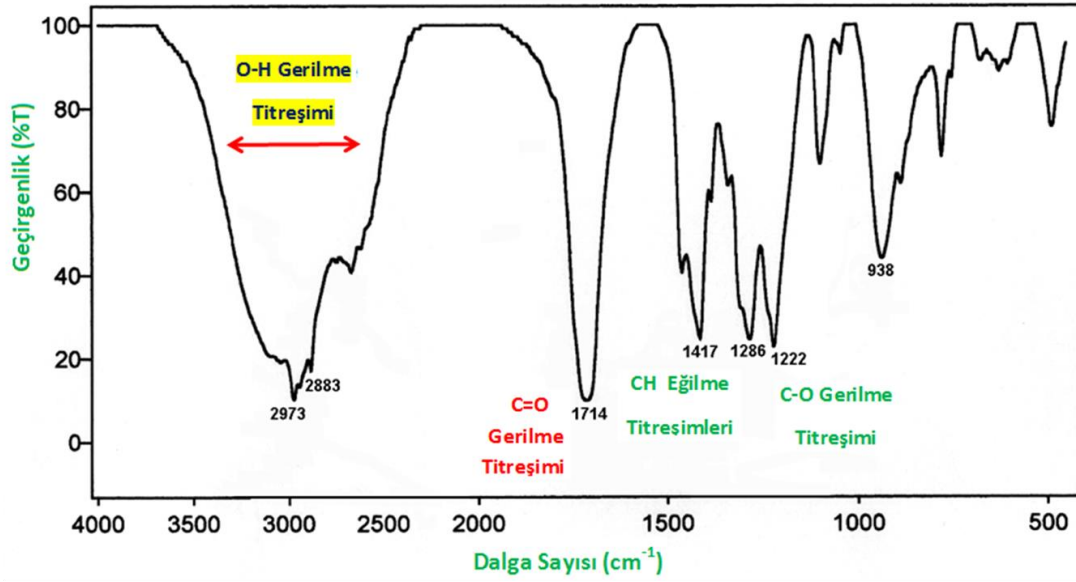
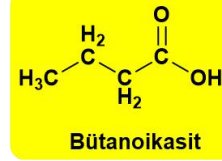


2-Metilpropanoik asit



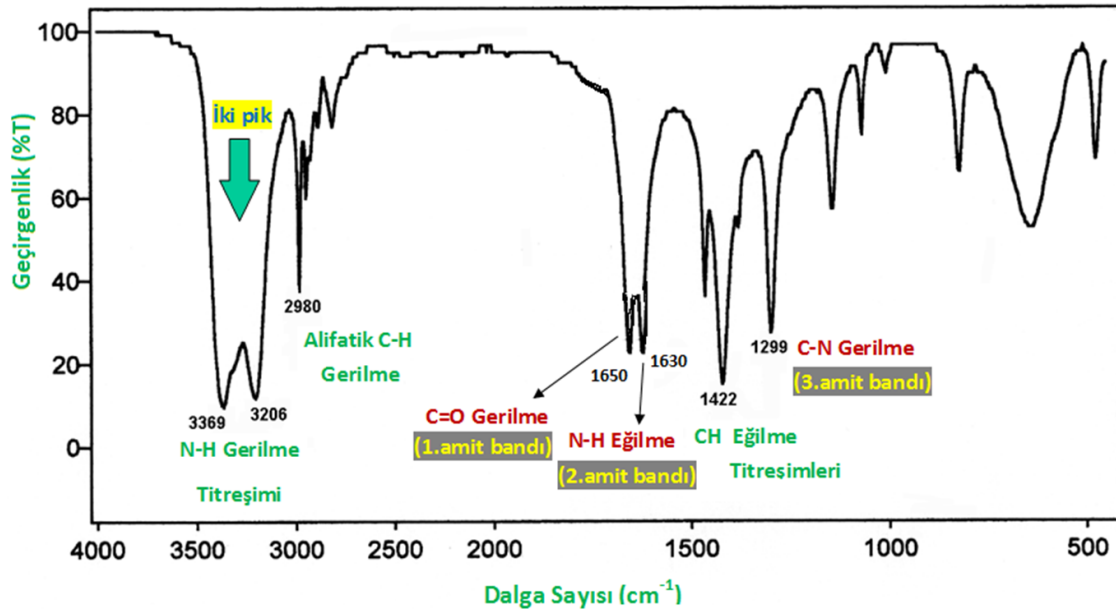
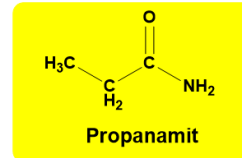
KARBOKSİLLİ ASİTLER-2

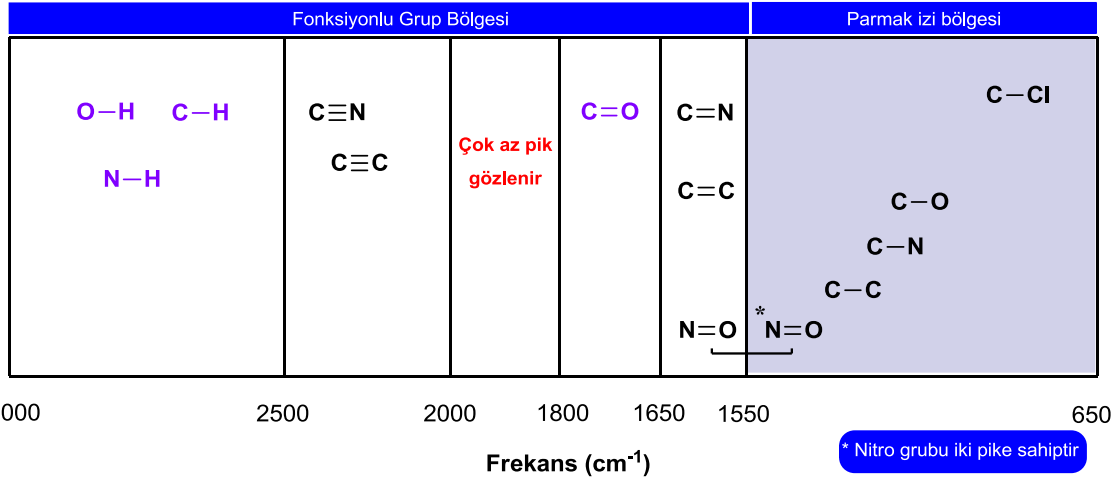
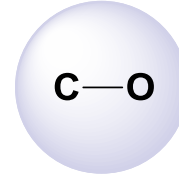
Bütanoikasit



AMİTLER

Propanamit





C-O gerilme bölgesi

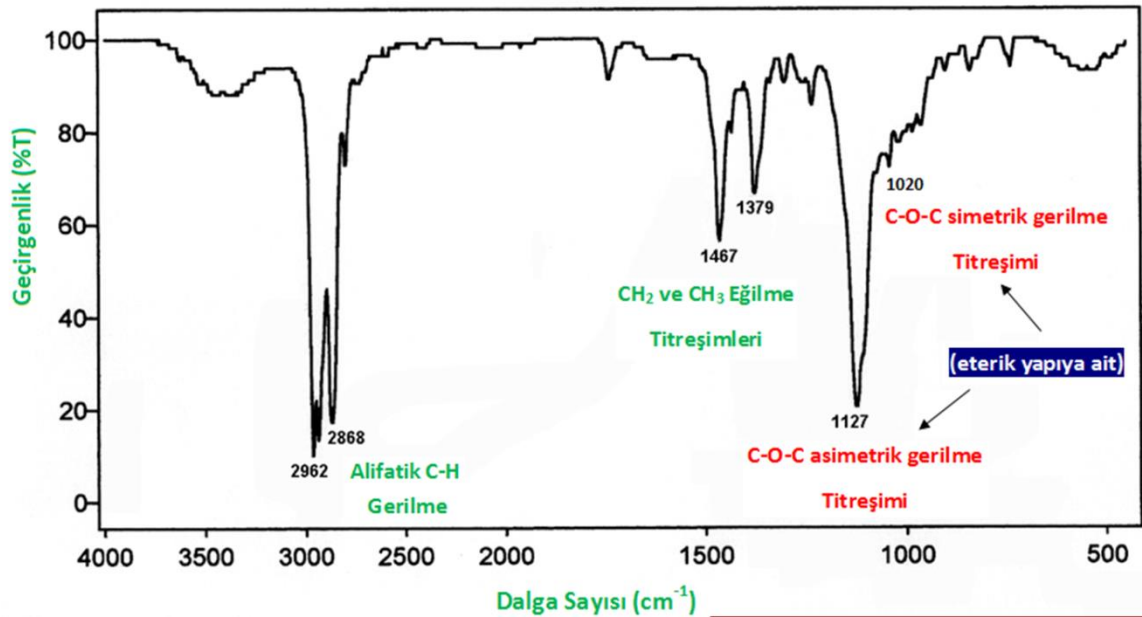
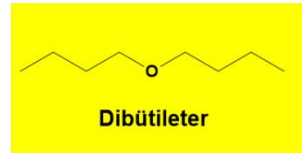
C-O piki 1000-1300 cm⁻¹ aralığında görülür

Bu aralıkta tek veya daha fazla güçlü pikler görülür

Eterler, alkoller, esterler ve karboksilik asitler C-O piki ne sahiptirler.

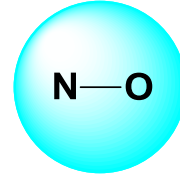
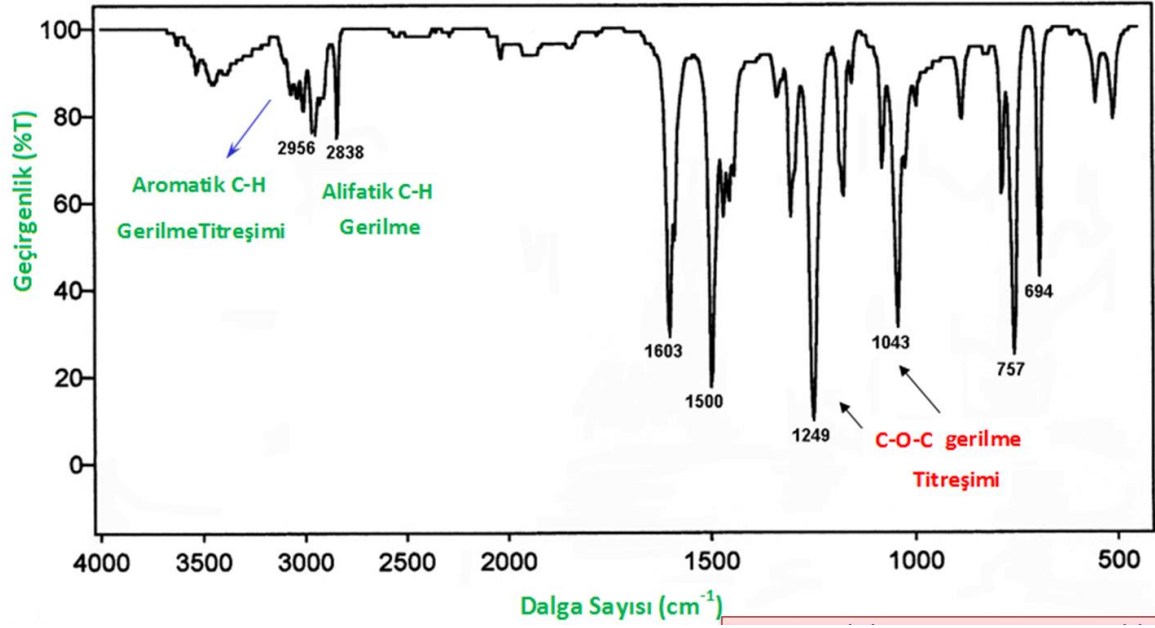
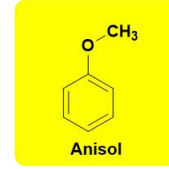
ETERLER

Dibütileter



ETERLER-2

Anisol (Metoksibenzen)



Fonksiyonlu Grup Bölgesi					Parmak izi bölgesi
O—H	C—H	C≡N	C≡C	C=O	C—Cl
N—H				C=N	
				C=C	
				N=O	
				* N=O	
					C—O
					C—N
					C—C

4000 2500 2000 1800 1650 1550 650

Frekans (cm⁻¹)

* Nitro grubu iki pike sahiptir

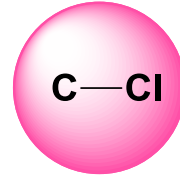
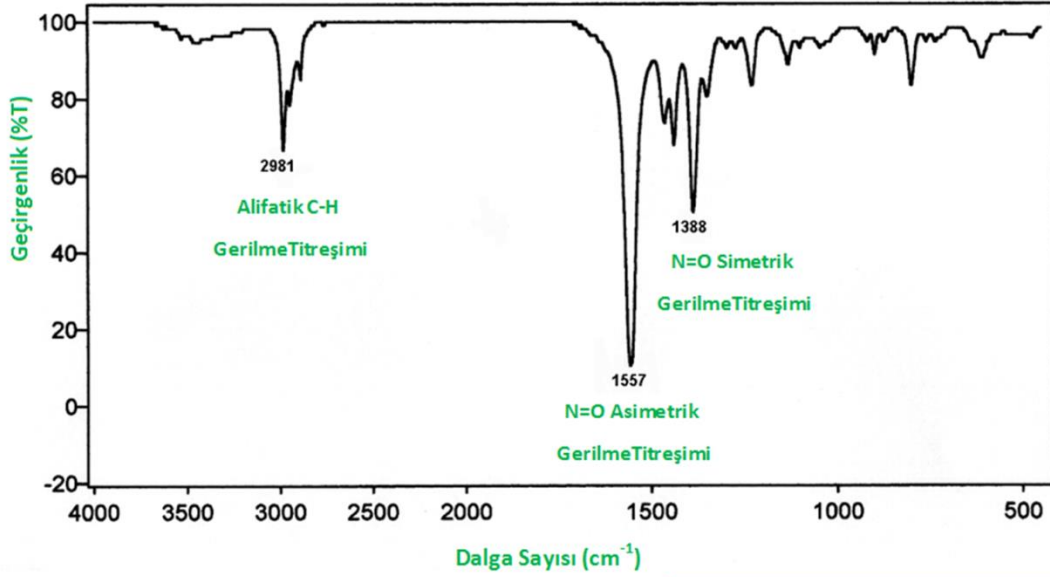
N=O gerilme bölgesi

N=O gerilmesi 1550 ve 1350 cm^{-1} asimetrik ve simetrik gerilmeler

1550 cm^{-1} asimetrik pik daha güçlüdür

NİTROALKANLAR

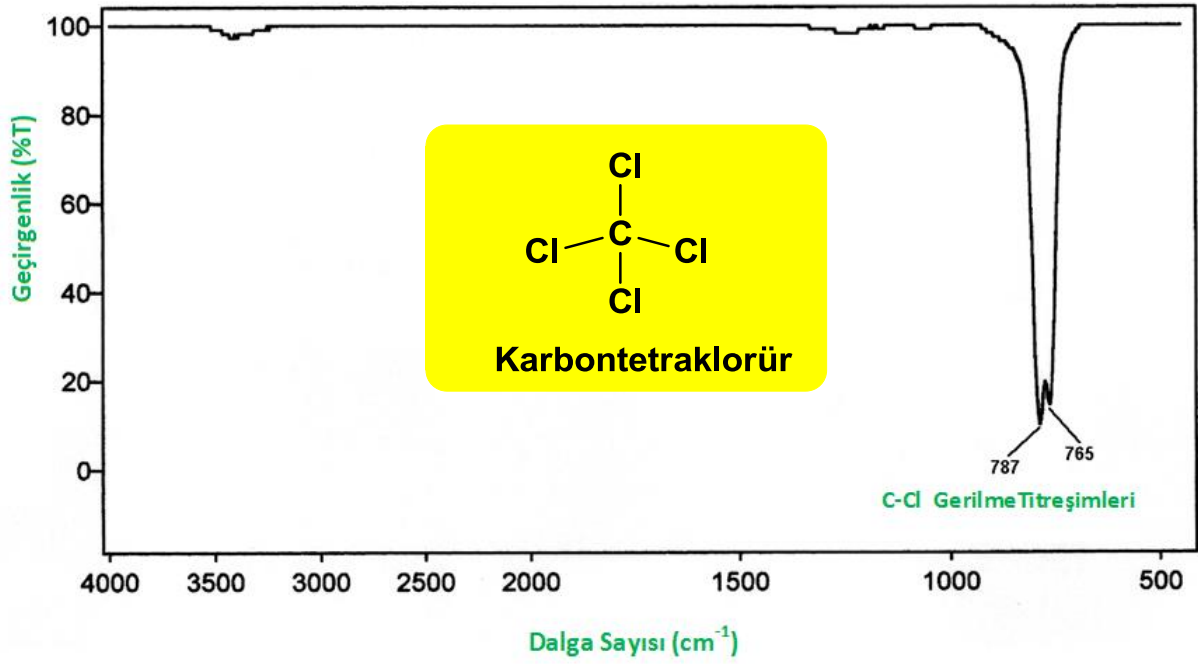
2-Nitropropane



Fonksiyonlu Grup Bölgesi					Parmak izi bölgesi
O—H C—H N—H	C≡N C≡C	Çok az pik gözlenir	C=O	C=N C=C N=O	C—Cl C—O C—N C—C * N=O
4000	2500	2000	1800	1650	1550
Frekans (cm^{-1})					650

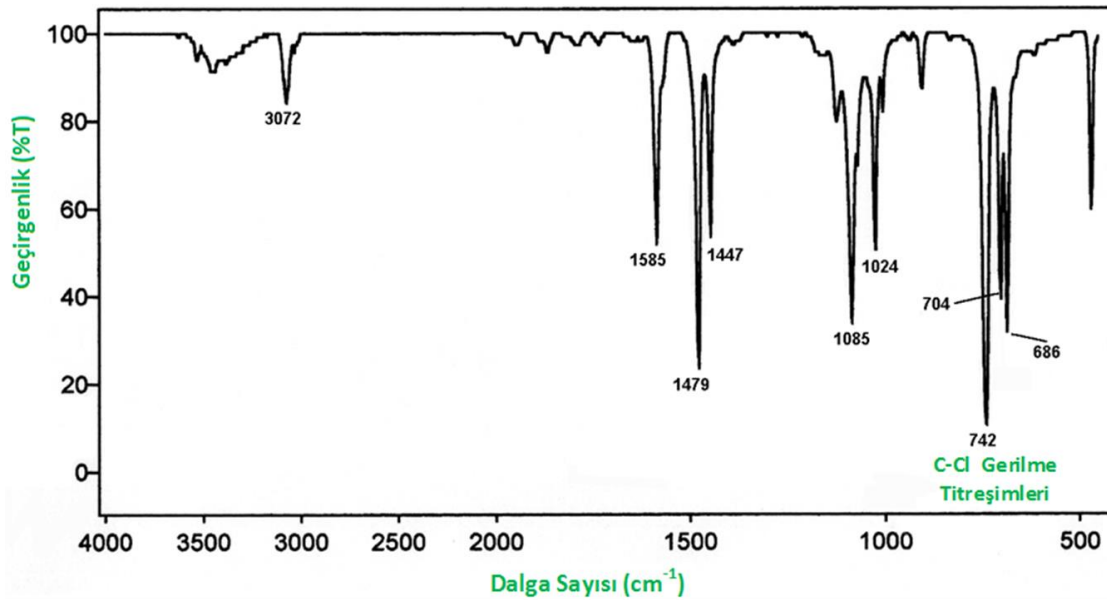
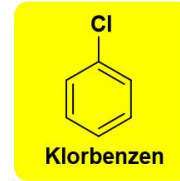
* Nitro grubu iki pike sahiptir

HALOJENÜR BİLEŞİKLERİ



ARİLHALOJENÜRLER

Klorbenzen



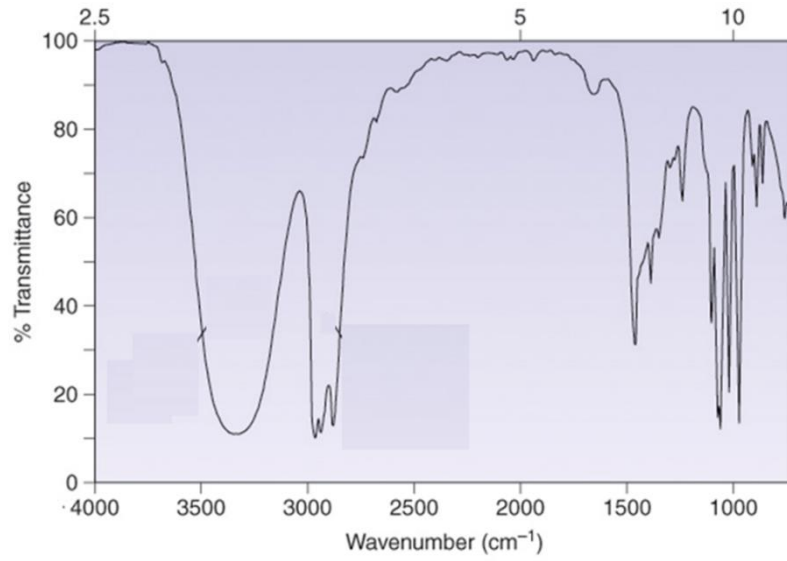
Kırmızı Ötesi (IR) Spektrumundan Yapı Analizi

DBE (Double Bond Equivalent); Çift bağ eşdeğeri veya Doymamışlık Derecesi

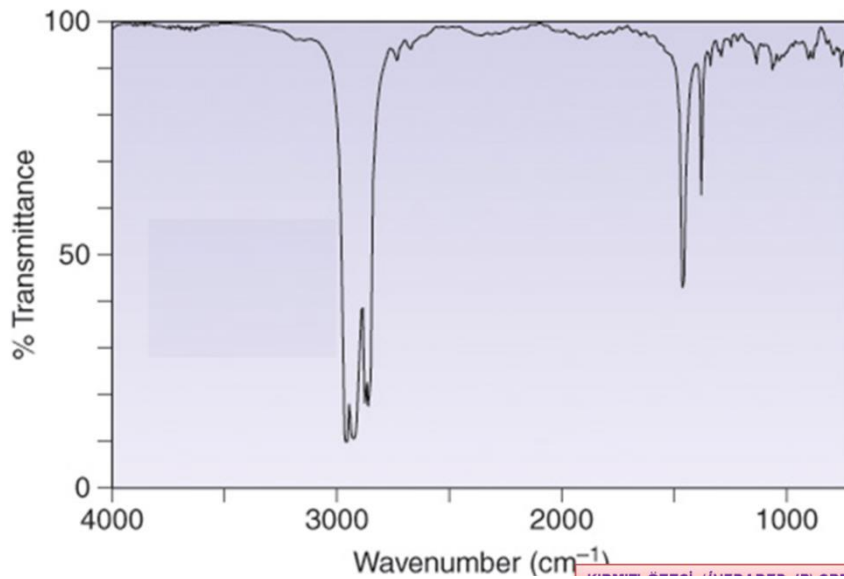
$$DBE = 1 + \frac{2N_C - N_H - N_X + N_N}{2}$$

N : Atom Sayısı

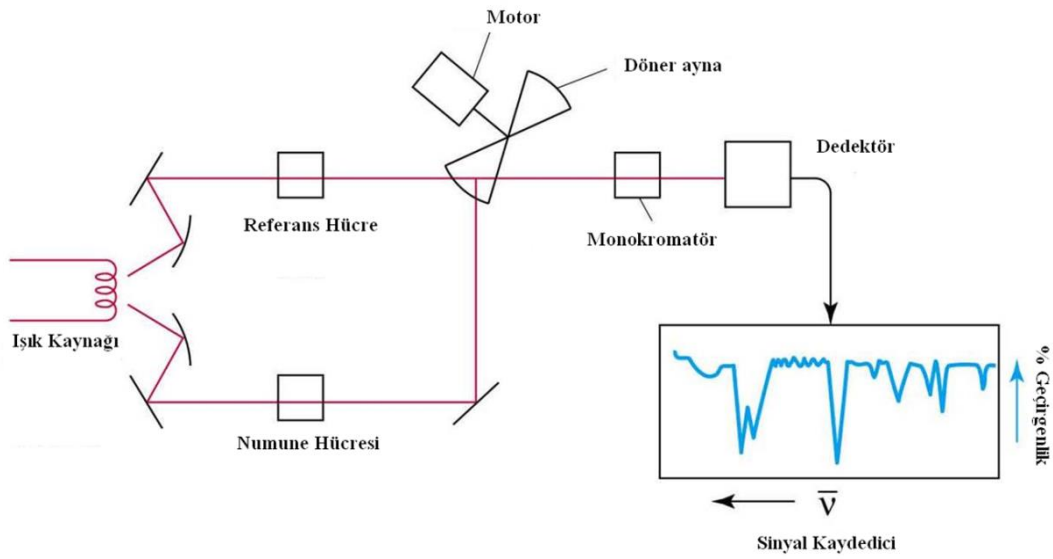
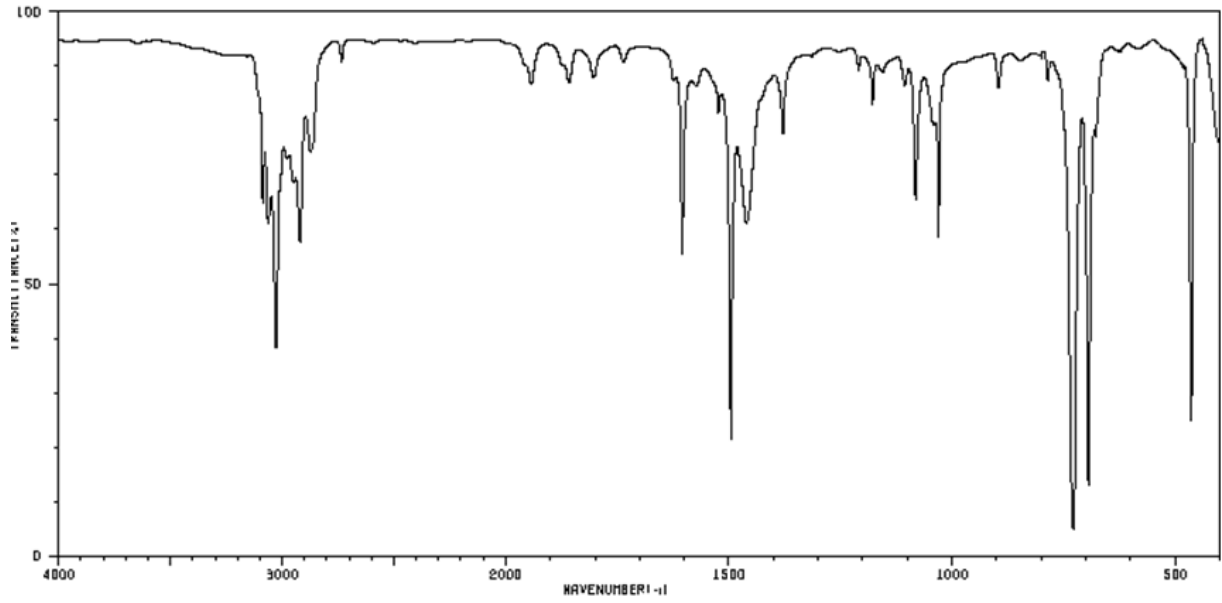
1) C_3H_8O



2) C_6H_{14}



3) C₇H₈O



Kırmızı Ötesi (IR) ışın kaynakları, elektrikle 1500 ile 2000 K'e kadar ısıtılabilen inert katılardır.

Nernst çubuğu

Civa arki

Globar çubuğu

Tungsten telli lamba

Numune Hazırlama

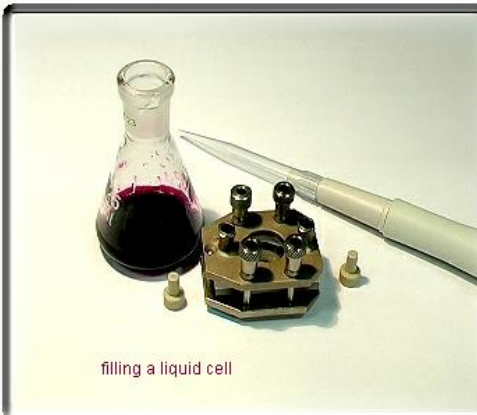
SIVI



GAZ



ÇÖZELTİ



KATI



IR ve UV arasındaki farklar

IR	UV-Vis
IR dalga sayısı olarak ifade edilir	UV dalgaboyu olarak ifade edilir
IR molekülde titreşim ve dönme hareketi yaptırır	UV elektronik uyarma yapar
IR de pikler daha keskindir	UV pikler geniştir
IR de maddeyi tanıma hakkında daha fazla bilgi elde edebiliriz	
IR de pik max. ları aşağı doğrudur	UV de pik max. ları yukarı doğrudur
Bir molekülün IR de absorpsiyon yapması için dipol momentinin olması gerekir. Molekülün polarlığından çok bağların polar olması gerekir. Molekül apolar olabilir.	