Spectroscopic methods in organic chemistry (KEMB01)
UV-, IR- och NMR-spectroscopy och MS (mass spectrometri)

The course literature

- *Organic Chemistry,* 2e, Clayden, Warren and Greeves
- Seminar power point presentations
- Exercise problems
- Data tables
- Internet resources on spectroscopic data

Exam credits on spectroscopy are 25 out of 80 in total.

Spectroscopic methods in organic chemistry (KEMB01)
UV-, IR- och NMR-spectroscopy och MS (mass spectrometri)

The course: 4 seminars + 6 exercise sessions

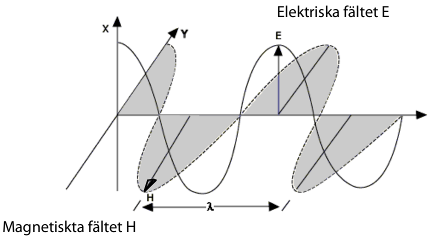
S1	Overview of spectroscopy + mass spectrometri + IR spectroscopy
S2	NMR-spectroscopy – chemical shifts
E1	MS, IR and NMR chemical shifts
E2	continued from E1
S3	NMR-spectroscopy – spin-spin coupling
E3	spin-spin couplings
S4	NMR-spectroscopy – 2D (two dimensional NMR) experiments
E4	2D NMR
E5	Combined problems
E6	Solving old exam problems

The exercise sessions will include additional theoretical issues not treated in the seminars and are essential for a full understanding of possible exam problems.

UV-, IR- och NMR-spektroskopi

All of the spectroscopic methods are based on the interaction between electromagnetic radiation and the atoms of the molecule. Electromagnetic radiation, from ultraviolet range down to the range of radio frequency, propagates with the speed of light as an alternating electric field together with it's magnetic field orthogonally arranged. One quanta of energy from electromagnetic radiation is the energy of the photon associated with the radiation and it's size is given by Planck's relationship.

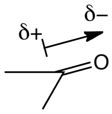
$E_{photon} = hv$ h Planck's constant, v frequency

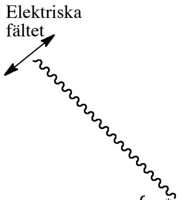


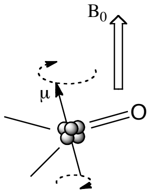
UV-, IR- och NMR-spectroscopy

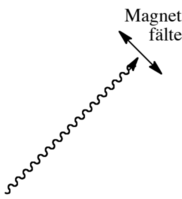
IR-absorption
4000-400 cm^{-1}

$$E_{photon} = h \cdot v = h \cdot c/\lambda = \hbar\sqrt{\frac{k}{m_{red}}}$$







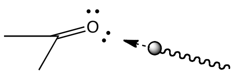


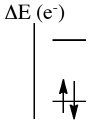
$$E_{photon} = h \cdot v = h \cdot \frac{\gamma B_0}{2\pi}$$

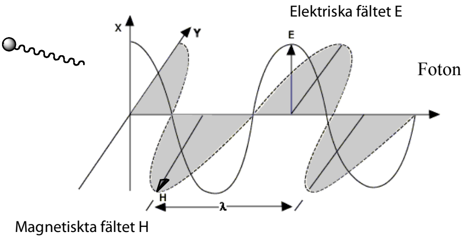
NMR-spektroskopi
1000-20 MHz

UV-absorption
190-400 nm

$$E_{photon} = h \cdot v = h \cdot c / \lambda = \Delta E\left\{\pi^* - \pi\right\}$$





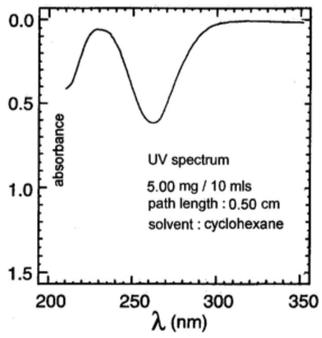


Foton - elektromagnetisk vågrörelse

UV-absorption is predominantly used for quantitative purposes

UV-absorption in a molecule happens if the energy of the irradiation matches the difference between ground state energy and the energy for the excited state of an electron in the molecule. The probability of such a transition will determine the amount of energy absorbed. The UV-absorbance of a compound refers to λ_{max} [nm], where the absorbance is at maximum and is quantified in the extinction coefficient ε (the molar absorptivity), [1000 $cm^2\,mol^{-1}$], which is the proportionality constant in

$$Absorbans\quad A = \log_{10}\frac{I_0}{I} = \varepsilon\cdot c\cdot l$$



with c concentration [mol L^{-1}]
and l cuvette length [cm]

Example: Structure problem 7

UV-spectra of a molecule of molar mass= 156

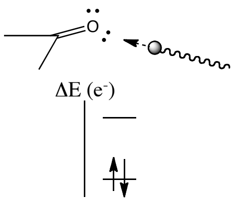
$$\varepsilon_{max} = \frac{1}{c\cdot l}\log_{10}\frac{I_0}{I}$$

$$\varepsilon_{max} = \frac{156}{5.00\cdot 10^{-3}}\cdot\frac{10}{1000}\cdot\frac{1}{0.5}\cdot 0.7 = 437$$

UV-absorbance in π-orbital systems
- the most obvious application of UV absorbance in organic chemistry

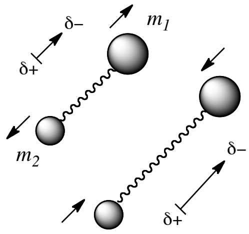
Transitions of π–electrons from ground state into excited state, π -> π* transitions, electrons in bonding π-orbitals going to antibonding π*-orbitals are readily accomplished by the act of UV-light. In molecules having conjugated π-bonds the general rule is that the higher the number of conjugated bonds the lower the energy gap will be for such a transition. This will be obvious from a molecular orbital diagram and in the recorded UV-spectrum where the λ_{max} and ε_{max} both increases with the number of conjugated bonds.

Transitions of nonbonding electrons, such as electrons in the lone par of oxygen, into antibonding π*-orbitals, n -> π* transitions, is exemplified in carbonyl compounds, where the non bonded free electron pars of oxygen give rise to absorbance of UV light. Absorption from n -> σ* transitions usually occur in the far UV range, < 200 nm, and are usually obscured by absorption of the solvent used.



IR-absorption *4000-400* cm^{-1}

$$E_{photon} = h \cdot \nu = h \cdot c/\lambda = \hbar\sqrt{\frac{k}{m_{red}}}$$

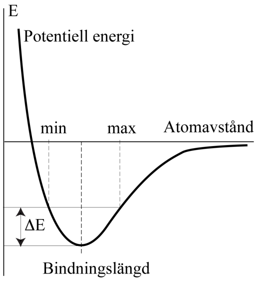


A molecule will absorb IR radiation if any vibrational mode in the molecule, eg. stretching of a bond, give rise to a change of the dipole moment of the molecule.

The energy E_{photon} will be absorbed by a bond in the molecule if the "force constant" k of the bond and the reduced mass of the atoms in the bond m_{red} satisfies the relationship in

$$E_{photon} = \hbar\sqrt{\frac{k}{m_{red}}}$$

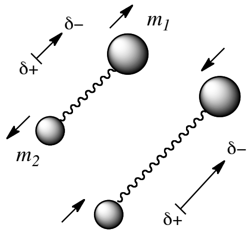
Although a "force constant" may be calculated with minor approximations for any bond in the ground state, it suffice here to treat k conceptually.



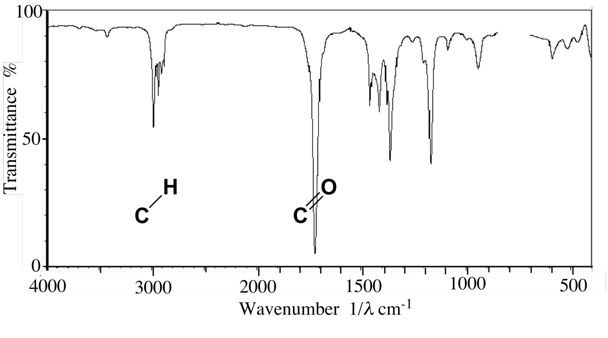
IR-spectrum

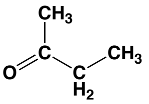
The harmonics of bond stretching

$$\frac{1}{\lambda} = const \cdot \sqrt{\frac{k}{m_{red}}}$$



Stretching of bonds is of major importance in the IR spectra. Due to the simple relationship between the wave number λ^{-1}, bond strength k and atom masses m_1 and m_2 these IR absorption bands are land marks in the spectrum for several functional groups.



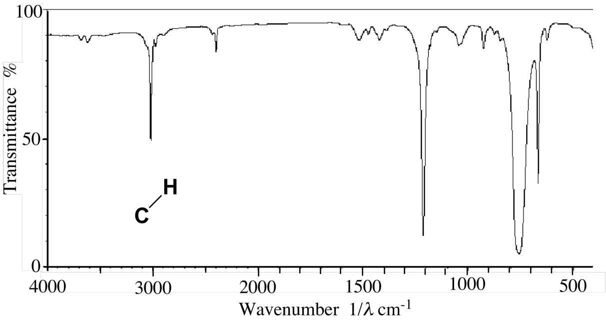


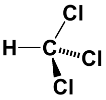
IR-spectrum

The harmonics of bond stretching

$$\frac{1}{\lambda} = const \cdot \sqrt{\frac{k}{m_{red}}} \qquad \frac{1}{m_{red}} = \frac{1}{m_1} + \frac{1}{m_2}$$

IR spectrum of $CHCl_3$
C-H stretching at 3019 cm^{-1}





IR-spectrum and isotope effect

The harmonics of bond stretching

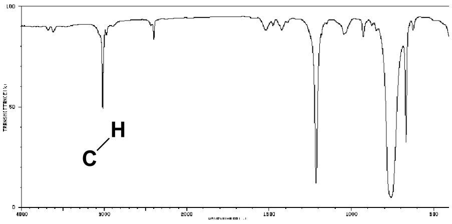
$$\frac{1}{\lambda} = const \cdot \sqrt{\frac{k}{m_{red}}} \qquad \frac{1}{m_{red}} = \frac{1}{m_1} + \frac{1}{m_2} \qquad m_{red} = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

$$m_{red}\left({}^{1}\text{H-}{}^{12}\text{C}\right) = 12/13$$

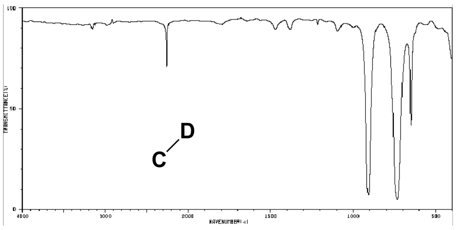
$$m_{red}\left({}^{2}\text{H-}{}^{12}\text{C}\right) = 24/14$$

$$\frac{m_{\text{red DC}}}{m_{\text{red HC}}} \approx 2 \qquad \frac{\lambda_{\text{HC}}^{-1}}{\lambda_{\text{DC}}^{-1}} \approx 1.4$$

IR spectrum of $CHCl_3$
C-H stretching at 3019 cm^{-1}



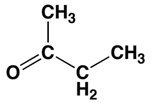
IR spectrum of $CDCl_3$
C-D stretching at 2254 cm^{-1}

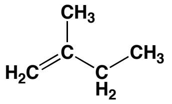


IR-absorption *4000-400* cm^{-1}

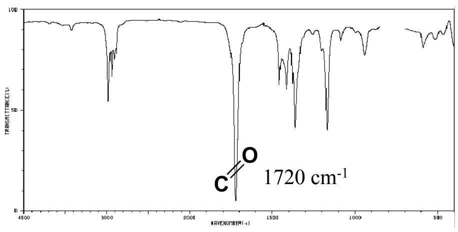
The degree of absorption increases with size of the dipolar moment affected by the vibration.

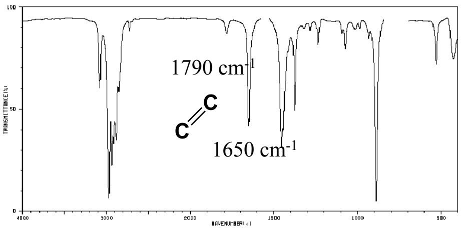
etylmetylketon





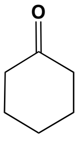
2-metyl-1-buten



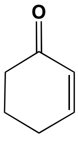


IR-absorption *4000-400* cm^{-1}

cyclohexanone

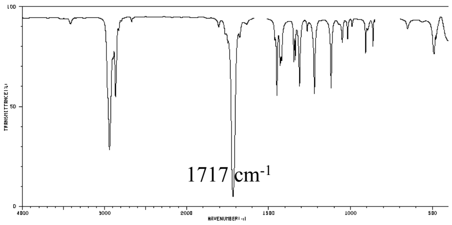


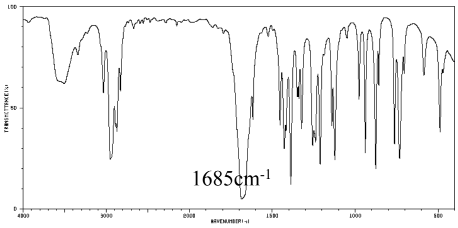
cyclohexenone



C=O stretch 6-membered ring
1720 cm^{-1}

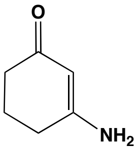
C=O α,β-unsaturated
1685-1665 cm^{-1}



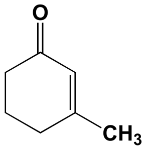


IR-absorption *4000-400* cm^{-1}

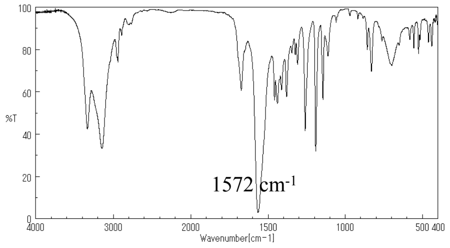
3-amino-2-cyclohexene-1-one

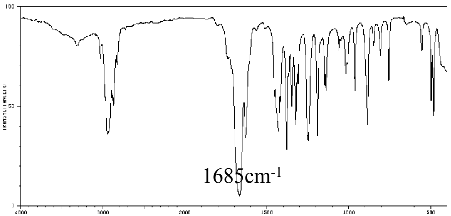


3-methyl-cyclohexenone



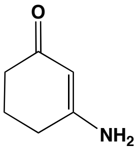
C=O α,β-unsaturated
1685-1665 cm^{-1}

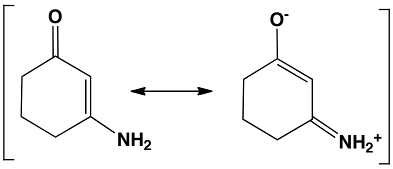


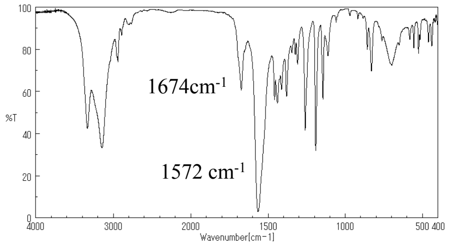


IR-absorption *4000-400* cm^{-1}

3-amino-2-cyclohexene-1-one

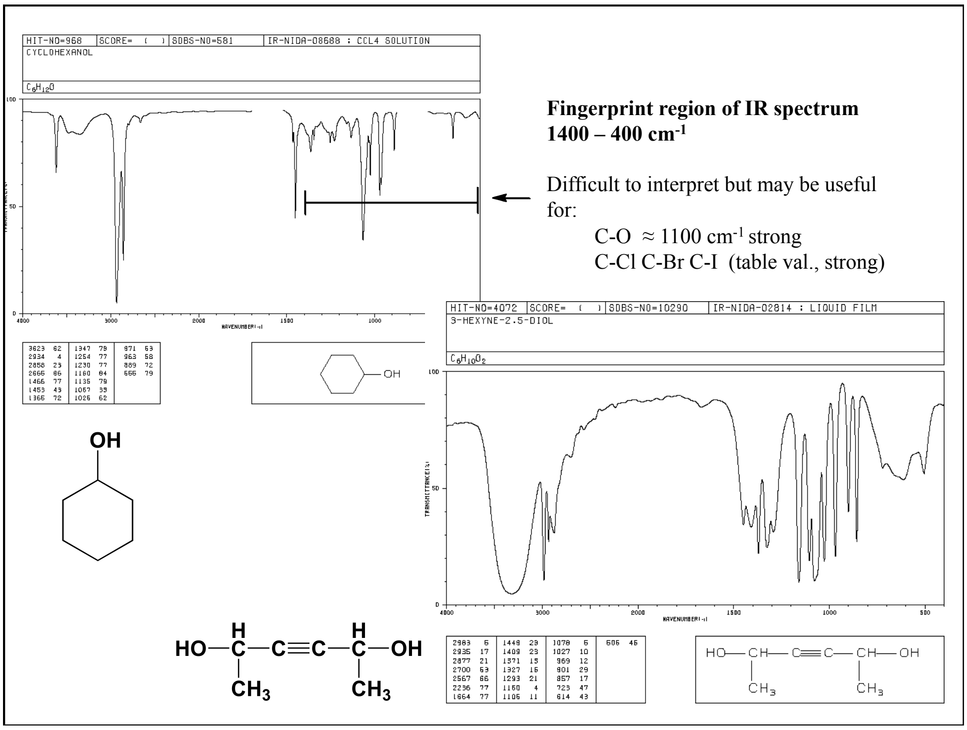






C=O bond is prolonged (weakened) due to conjugation with non bonding electron pair at nitrogen.

Decreasing value of C=O stretching in IR absorption is observed.



HIT-NO=968 | SCORE= ( ) | SDBS-NO=581 | IR-NIDA-08688 : CCL4 SOLUTION

CYCLOHEXANOL

$C_6H_{12}O$

3623	62	1347	79	971	63
2934	4	1254	77	963	58
2858	23	1230	77	889	72
2666	86	1160	84	666	79
1466	77	1135	79		
1453	43	1067	39		
1366	72	1026	62		

Fingerprint region of IR spectrum 1400 – 400 cm^{-1}

Difficult to interpret but may be useful for:

C-O ≈ 1100 cm^{-1} strong
C-Cl C-Br C-I (table val., strong)

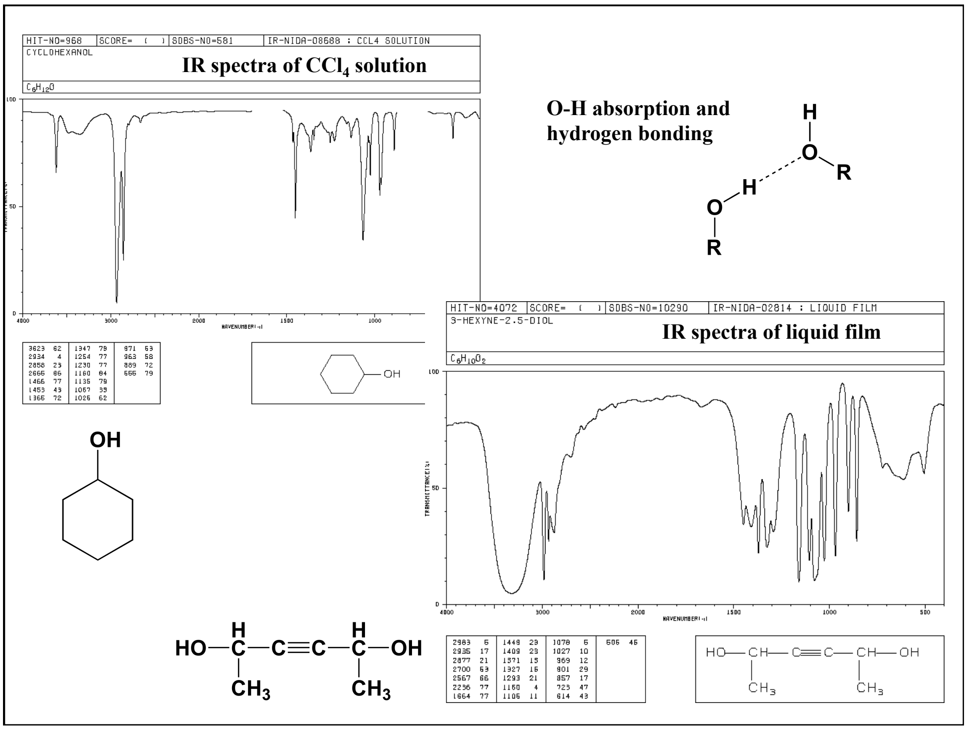
HIT-NO=4072 | SCORE= ( ) | SDBS-NO=10290 | IR-NIDA-02814 : LIQUID FILM

3-HEXYNE-2.5-DIOL

$C_6H_{10}O_2$

2983	6	1449	29	1078	6	606	46
2935	17	1409	23	1027	10		
2877	21	1371	15	969	12		
2700	63	1327	16	901	29		
2567	66	1293	21	857	17		
2236	77	1160	4	723	47		
1664	77	1106	11	614	43		

$$\mathrm{HO{-}\overset{H}{\underset{CH_3}{C}}{-}C{\equiv}C{-}\overset{H}{\underset{CH_3}{C}}{-}OH}$$



HIT-NO=968 | SCORE= ( ) | SDBS-NO=581 | IR-NIDA-08688 : CCL4 SOLUTION

CYCLOHEXANOL

IR spectra of CCl_4 solution

$C_6H_{12}O$

3623	62	1347	79	971	63
2934	4	1254	77	963	58
2858	23	1230	77	889	72
2666	86	1160	84	666	79
1466	77	1135	79		
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O-H absorption and hydrogen bonding

HIT-NO=4072 | SCORE= ( ) | SDBS-NO=10290 | IR-NIDA-02814 : LIQUID FILM

3-HEXYNE-2.5-DIOL

IR spectra of liquid film

$C_6H_{10}O_2$

2983	6	1449	29	1078	6	606	46
2935	17	1409	23	1027	10		
2877	21	1371	15	969	12		
2700	63	1327	16	901	29		
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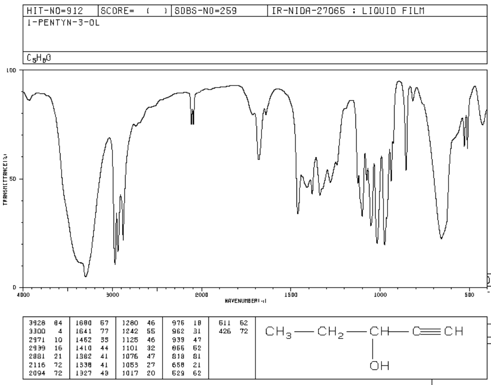
$$\mathrm{HO{-}\overset{H}{\underset{CH_3}{C}}{-}C{\equiv}C{-}\overset{H}{\underset{CH_3}{C}}{-}OH}$$



HIT-NO=912 | SCORE= ( ) | SDBS-NO=259 | IR-NIDA-27065 : LIQUID FILM

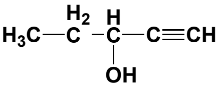
1-PENTYN-3-OL

C_5H_8O

3928	84	1680	67	1280	46	976	18	611	62
3300	4	1641	77	1242	55	962	31	426	72
2971	10	1462	35	1125	46	939	47		
2939	16	1410	44	1101	32	866	62		
2881	21	1382	41	1076	47	818	81		
2116	72	1338	41	1053	27	658	21		
2094	72	1327	49	1017	20	629	62		

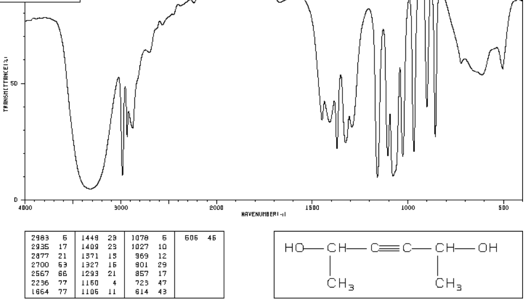
$CH_3-CH_2-\underset{OH}{CH}-C\equiv CH$

Alkyne triple bond stretching in non symmetrical cases vs. symmetrical


$H_3C-\overset{H_2}{C}-\underset{OH}{\overset{H}{C}}-C\equiv CH$

072 | SCORE= ( ) | SDBS-NO=10290 | IR-NIDA-02814 : LIQUID FILM

-2.5-DIOL



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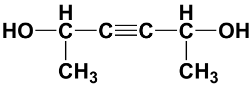
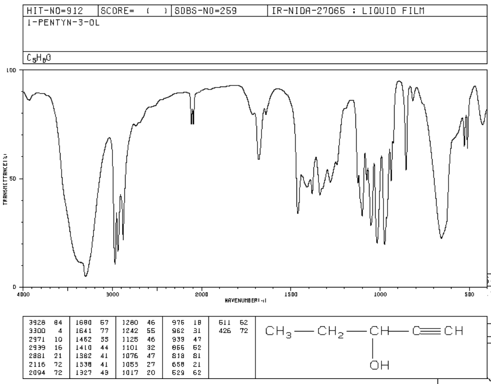
2567	66	1293	21	857	17		
2236	77	1160	4	723	47		
1664	77	1106	11	614	43		

$HO-\underset{CH_3}{CH}-C\equiv C-\underset{CH_3}{CH}-OH$


$HO-\underset{CH_3}{\overset{H}{C}}-C\equiv C-\underset{CH_3}{\overset{H}{C}}-OH$



HIT-NO=912 | SCORE= ( ) | SDBS-NO=259 | IR-NIDA-27065 : LIQUID FILM

1-PENTYN-3-OL

C_5H_8O

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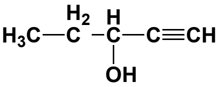
2094	72	1327	49	1017	20	629	62		

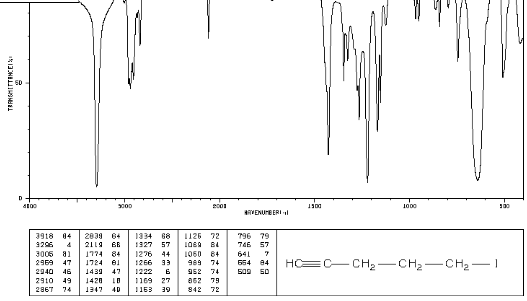
$CH_3-CH_2-\underset{OH}{CH}-C\equiv CH$

Terminal alkyne C-H stretching


$H_3C-\overset{H_2}{C}-\underset{OH}{\overset{H}{C}}-C\equiv CH$

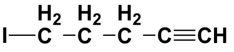
42 | SCORE= ( ) | SDBS-NO=38172 | IR-NIDA-64300 : LIQUID FILM

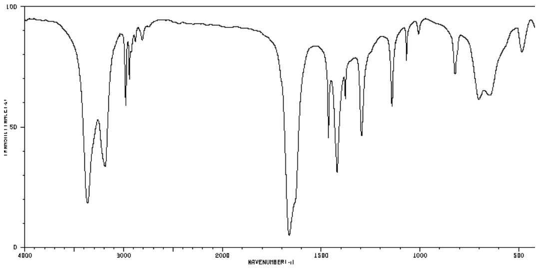
-PENTYNE



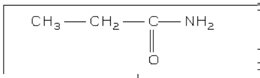
3918	84	2839	64	1334	68	1126	72	796	79
3296	4	2119	66	1327	57	1069	84	746	57
3005	81	1774	84	1276	44	1060	84	641	7
2969	47	1724	81	1266	33	969	74	664	84
2940	46	1439	47	1222	6	952	74	509	50
2910	49	1428	18	1169	27	862	79		
2867	74	1347	48	1163	39	842	72		

$HC\equiv C-CH_2-CH_2-CH_2-I$


$I-\overset{H_2}{C}-\overset{H_2}{C}-\overset{H_2}{C}-C\equiv CH$



3366	17	2811	84	1068	74
3189	32	1662	4	1008	84
2978	57	1464	45	822	88
2957	81	1420	29	702	68
2942	66	1378	58	691	60
2924	79	1298	44	647	80
2880	81	1143	67	483	79

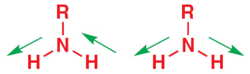


$$CH_3 — CH_2 — \underset{\underset{O}{\|}}{C} — NH_2$$

N-H stretching in NH_2

antisymmetric NH_2 stretch

symmetric NH_2 stretch

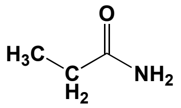


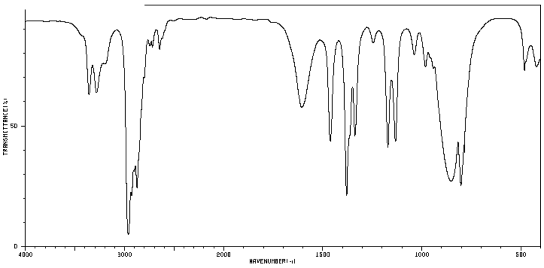
about 3400 cm^{-1}

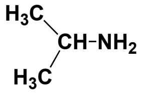
about 3300 cm^{-1}

gives double absorption bands.

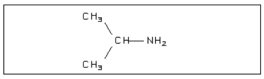
= ( ) SDBS-NO=2446 IR-NIDA-03867 : LIQUID FILM

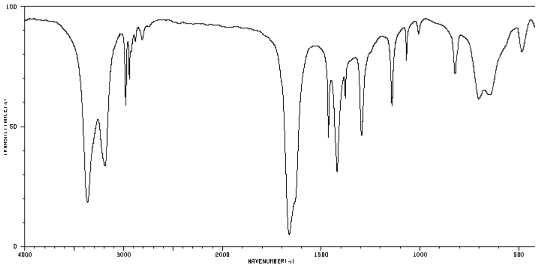




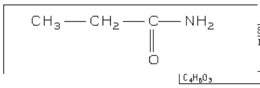


3368	60	2647	79	1172	39	482	70
3282	62	2620	84	1133	42		
2962	4	1608	55	1038	77		
2929	20	1461	42	981	72		
2874	23	1380	20	853	26		
2743	79	1338	44	803	24		
2718	79	1246	81	786	37		





3366	17	2811	84	1068	74
3189	32	1662	4	1008	84
2978	57	1464	45	822	88
2957	81	1420	29	702	68
2942	66	1378	58	691	60
2924	79	1298	44	647	80
2880	81	1143	67	483	79



$$CH_3 — CH_2 — \underset{\underset{O}{\|}}{C} — NH_2$$

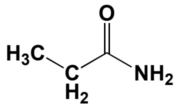
Symmetric or antsymmetric stretching of C=O bond in anhydrides of carboxylic acids

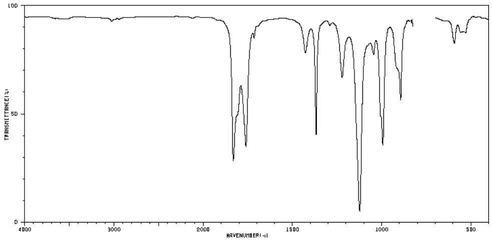
gives double absorption bands.

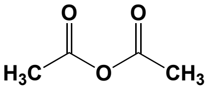
SCORE= ( ) SDBS-NO=1034 IR-NIDA-08651 : CCL4 SOLUTION

IDE

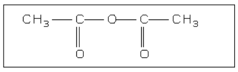
$C_4H_6O_3$





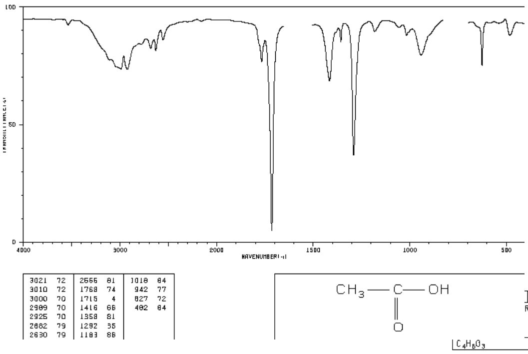


1832	26	1046	74	640	84
1761	33	1005	46		
1715	81	994	34		
1428	74	894	63		
1368	38	603	84		
1222	64	593	79		
1124	4	647	84		



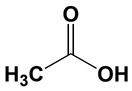
$$CH_3 — \underset{\underset{O}{\|}}{C} — O — \underset{\underset{O}{\|}}{C} — CH_3$$

Carboxylic acid compared to the corresponding anhydride



3021	72	2666	81	1018	84
3010	72	1768	74	942	77
3000	70	1715	4	827	72
2989	70	1416	66	482	84
2925	70	1358	81		
2862	79	1292	35		
2630	79	1183	86		

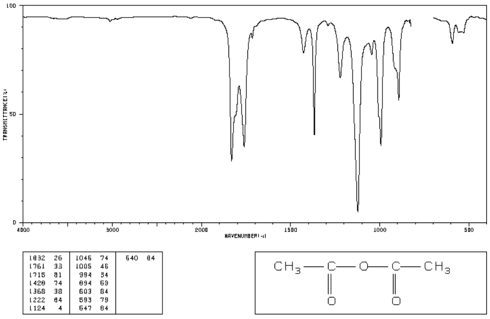
$CH_3-\underset{\displaystyle \overset{\|}{O}}{C}-OH$



SCORE= ( ) | SDBS-NO=1034 | IR-NIDA-08651 : CCL4 SOLUTION

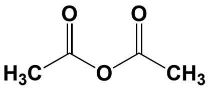
RIDE

$C_4H_6O_3$



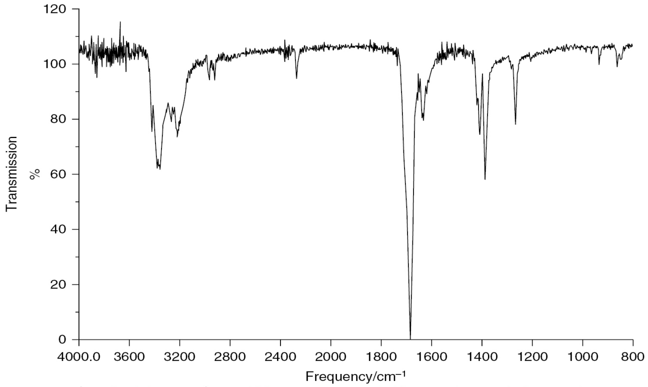
1832	26	1045	74	640	84
1761	33	1005	46		
1715	81	994	34		
1428	74	894	63		
1368	38	603	84		
1222	64	593	79		
1124	4	647	84		

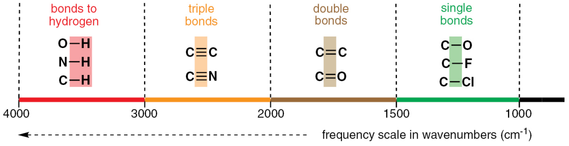
$CH_3-\underset{\displaystyle \overset{\|}{O}}{C}-O-\underset{\displaystyle \overset{\|}{O}}{C}-CH_3$



Clayden & Warren page 65

What are the key features of this IR spectra?

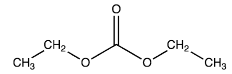


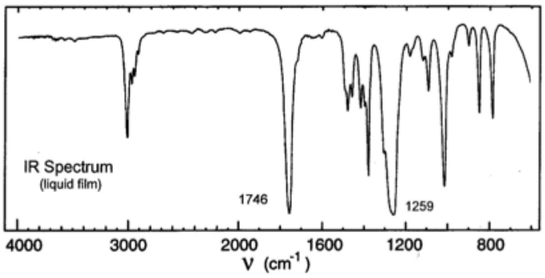


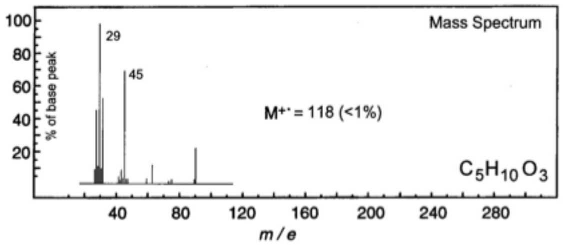
Mass spectrometry in organic chemistry

Synthetic product

Interpretation of spectra

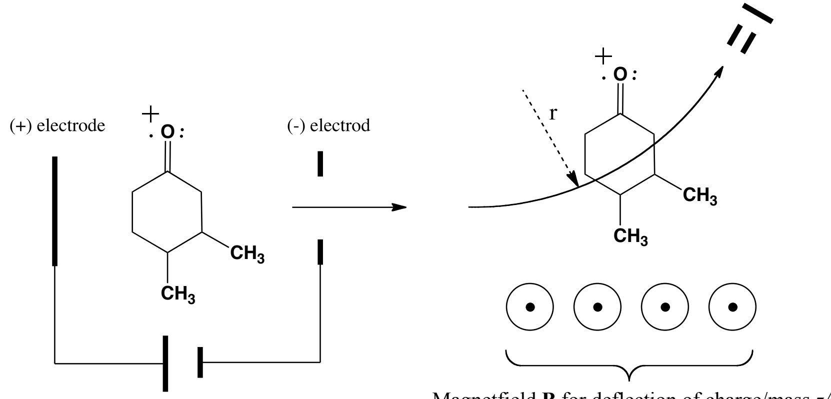






Key features of the mass spectrometer

- Ionization of the compounds
- Separation of charged compound ions to get their mass



Acceleration voltage

Magnetfield **B** for deflection of charge/mass *z/m*
(or an electric field or the combination of both)

Key features of the mass spectrometer

- Ionization of the compounds
- Separation of charged compound ions to get their mass

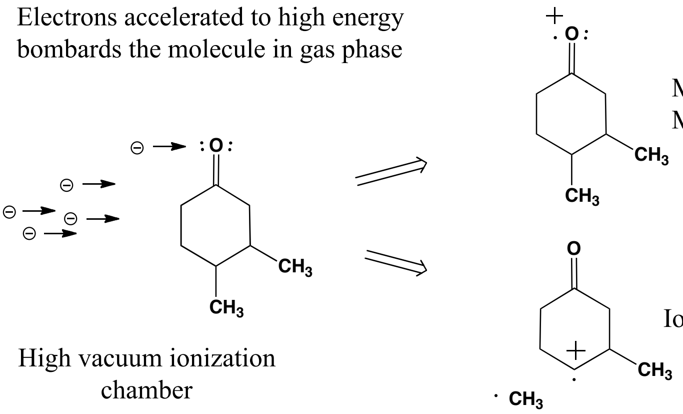
The ionization technique is more important for the chemist than the separation. Two methods are dominating in organic chemistry:

- EI – electron impact
- CI – chemical ionization

Ionization techniques in mass spectrometry

EI – electron impact ionization

Electrons accelerated to high energy bombards the molecule in gas phase



Molecular ion
M^+ 126

Ion fragment (111)

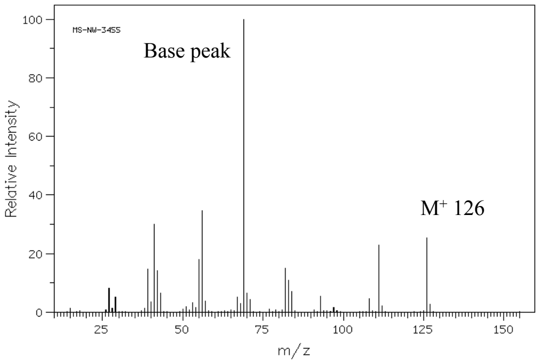
High vacuum ionization
chamber

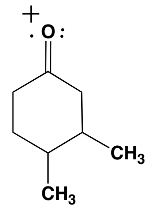
Neutral fragment (15)

Ionization techniques in mass spectrometry

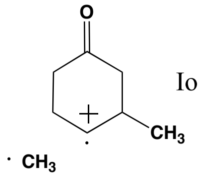
EI – electron impact ionization

EI-MS





Molecular ion
M^+ 126



Ion fragment (111)

Neutral fragment (15)

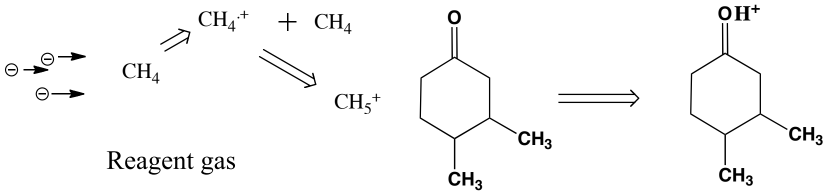
Ionization techniques in mass spectrometry

CI – chemical ionization (give less fragmentation)

High energy electrons produce radical cat ions from an reagent gas, eg. CH_4, propane or NH_3.

Most commonly the molecular ion produced is $[M+1]^+$ also denoted MH^+.

Molekyljon
MH^+ 127



Reagent gas

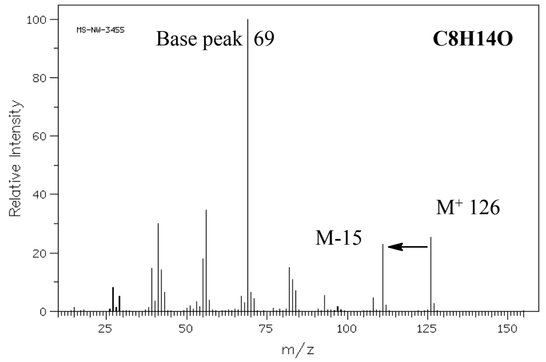
EI-MS

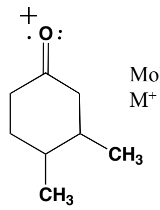
Key features in EI-MS spectra

- **Molecular ion M^+**
- **Base peak (characteristic for compound)**
- **Fragment ions**
- **(calculated possible molecular formula)**

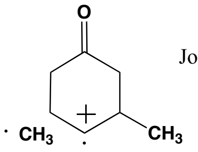
Common neutral fragments

eg.	M-15	CH_3
	M-16	NH_2
	M-17	OH





Molekyljon
M^+ 126

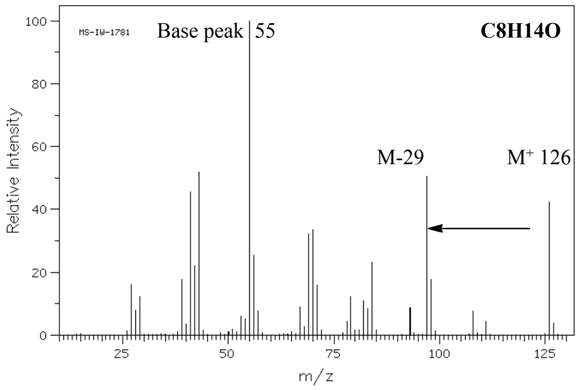


Jonfragment (111)

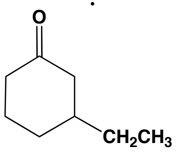
Neutralt fragment (15)

EI-MS

		Previous slide
Molecular ion M^+	**M^+ 126**	M^+ 126
Base peak (characteristic for compound)	**55**	69
Fragment ions	**M-29**	M-15
(calculated possible molecular formula)	**C8H14O**	C8H14O



?

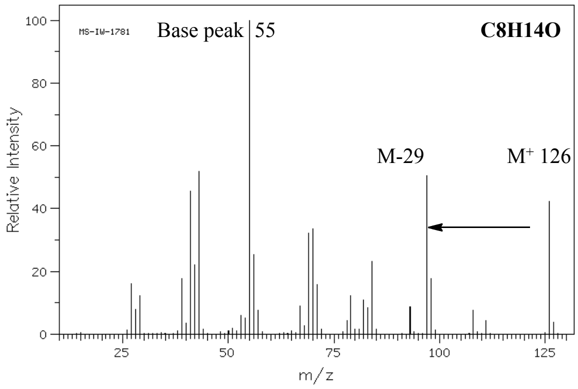


DBE – double bond equivalents

The number of double bonds and rings in organic molecules may be calculated if the number of carbons and hydrogens are known. (If nitrogen or halogens are present there numbers are needed.)

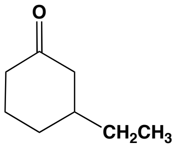
$$DBE = \frac{(2 \cdot C + 2) - H - X + N}{2}$$

C = antal kol, H = antal väten
X = halogner, N = antal kväve



C8H14O

$$DBE = \frac{(2 \cdot 8 + 2) - 14}{2} = 2$$

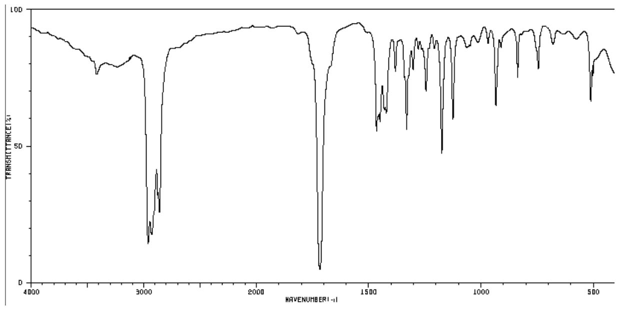


Combining IR- and MS-data with DBE

EI-MS M^+126, M-29 **IR (cm^{-1}) 2800-2950, 1717**

M-29	CH_3CH_2 (neutral fragment)	2800-2950	C-H
M 126	may be C8H14O	1717	C=O keton

$$DBE = \frac{(2 \cdot 8 + 2) - 14}{2} = 2$$



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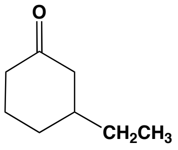
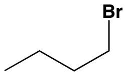
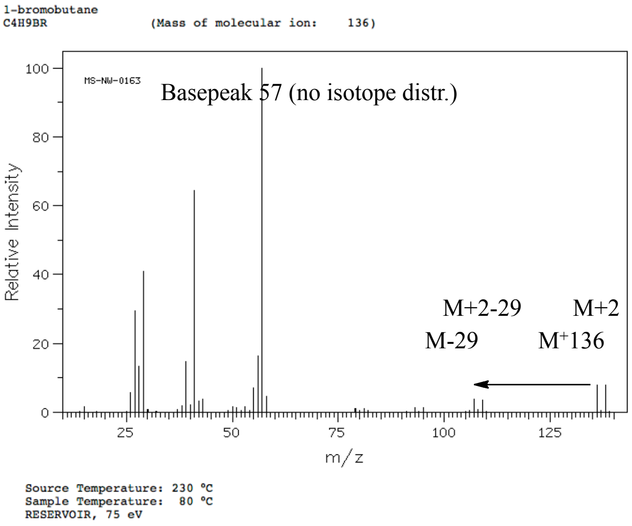


Isotope mass in MS





1-bromobutane
C4H9BR (Mass of molecular ion: 136)

Source Temperature: 230 °C
Sample Temperature: 80 °C
RESERVOIR, 75 eV

Basepeak 57 (no isotope distr.)

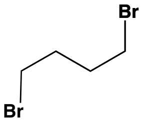
M+2-29 M+2

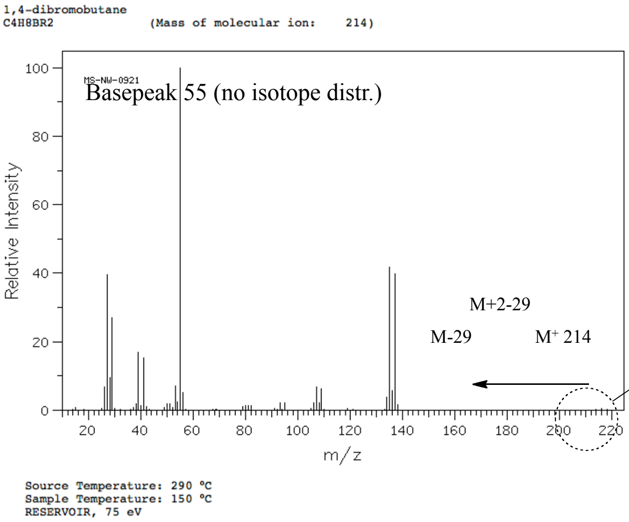
M-29 M^+136

Br isotope distribution

^{79}Br 50.69%
^{81}Br 49.31%

Isotope mass in MS





1,4-dibromobutane
C4H8BR2 (Mass of molecular ion: 214)

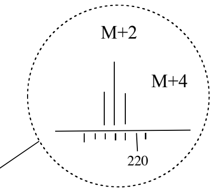
Source Temperature: 290 °C
Sample Temperature: 150 °C
RESERVOIR, 75 eV

Basepeak 55 (no isotope distr.)

M+2-29

M-29 M^+ 214

^{79}Br 50.69%
^{81}Br 49.31%



1* (^{79}Br + ^{79}Br)
2* (^{79}Br + ^{81}Br)
1* (^{81}Br + ^{81}Br)

Isotope mass in MS

^{35}Cl 75.77%
^{37}Cl 24.23%

Typical M^+ pattern of Cl_5-containing compound

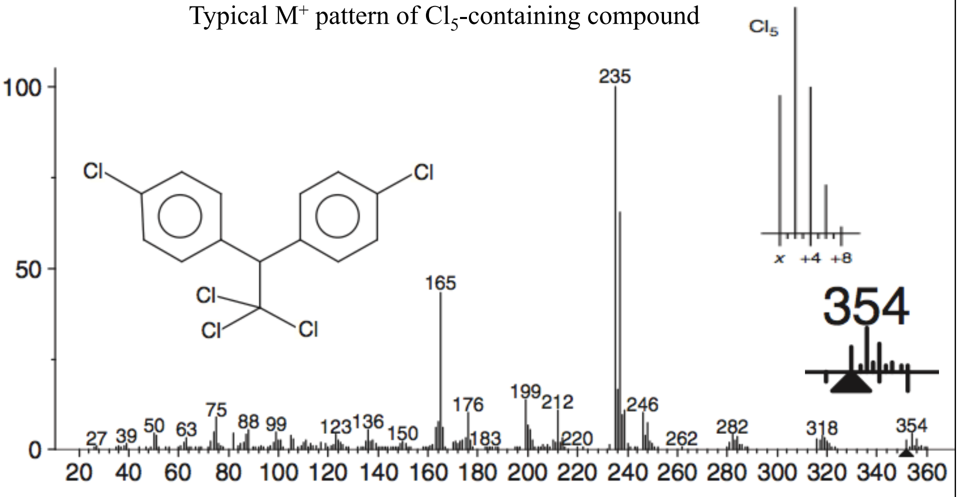
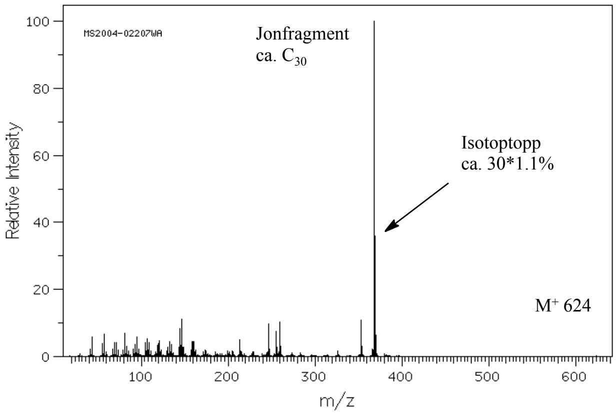


Figure 28.2 EI mass spectrum of DDT.

Isotope mass in MS

cholesteryl palmitate
$C_{43}H_{76}O_2$ (Mass of molecular ion: 624)



Jonfragment
ca. C_{30}

Isotoptopp
ca. 30*1.1%

M^+ 624

Carbon natural isotope distr.

^{12}C 98.9%
^{13}C 1.1%

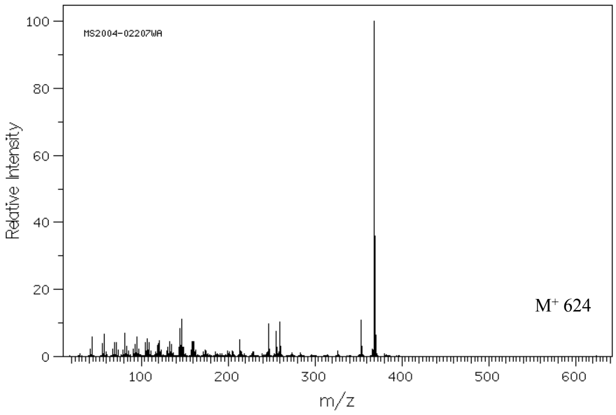
Source Temperature: 250 °C
Sample Temperature: 120 °C
Direct, 70 eV

High resolution MS for exact mass

Exact mass in High Resolution MS of cholesteryl palmitate
624.58453 12C -> $C_{43}H_{76}O_2$

```
cholesteryl palmitate
C43H76O2          (Mass of molecular ion:    624)
```

Unambiguously determination of molecular formula from MS data.



Other possibilities for
M = 624 D

eg.
$C_{42}H_{72}O_3$
12C: 624.548146

$C_{40}H_{70}N_2O_3$
12C/14N: 624.522994

etc.

```
Source Temperature: 250 °C
Sample Temperature: 120 °C
Direct, 70 eV
```

Other MS techniques

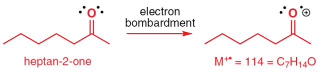
Non-fragmenting ionization techniques for large molecules

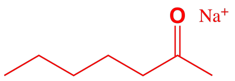
- **Fast-atom Bombardment — FAB-MS**
- **Matrix-assisted Laser Desorption Ionization — MALDI-MS**

useful in HPLC/MS

- **Electro-spray Ionization — ESI-MS**

EI-MS vs. ESI-MS textbook p. 47-48





$[M+Na]^+$