台灣大學開放式課程

有機化學乙

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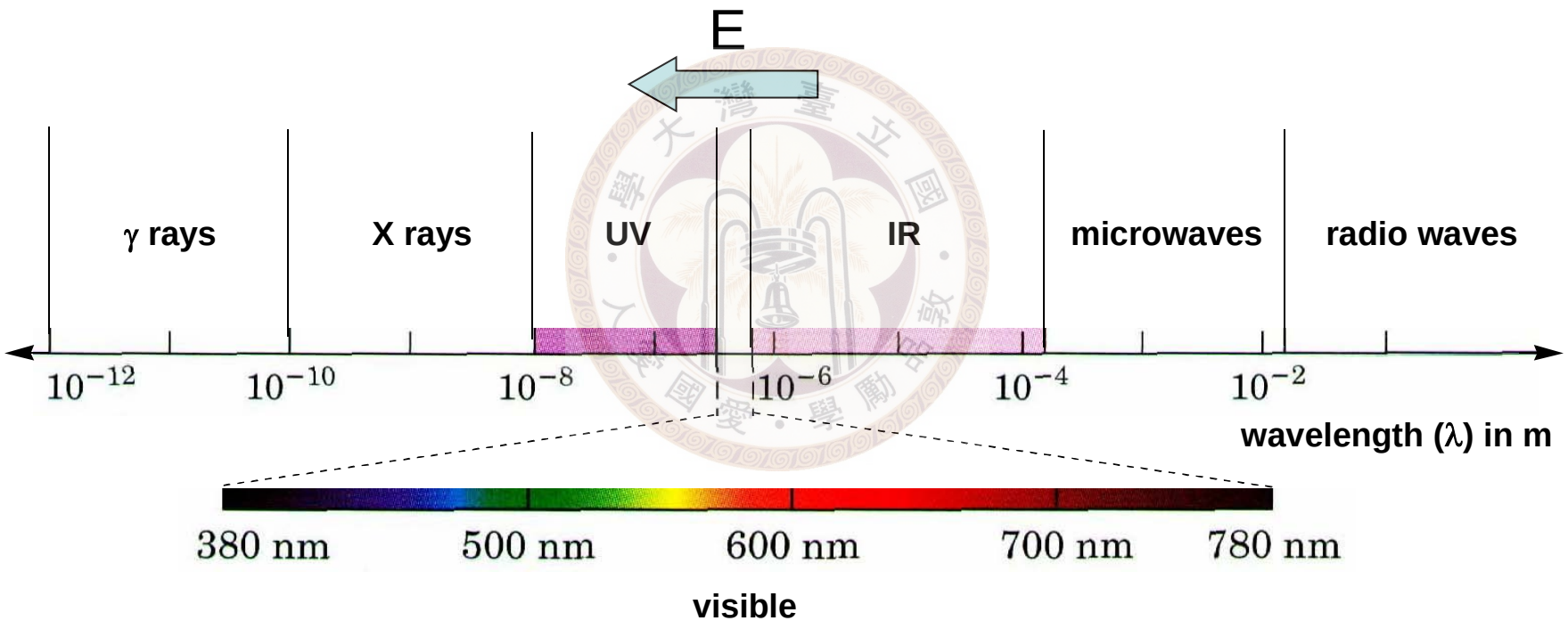
Infrared Spectroscopy
紅外線光譜 (IR)

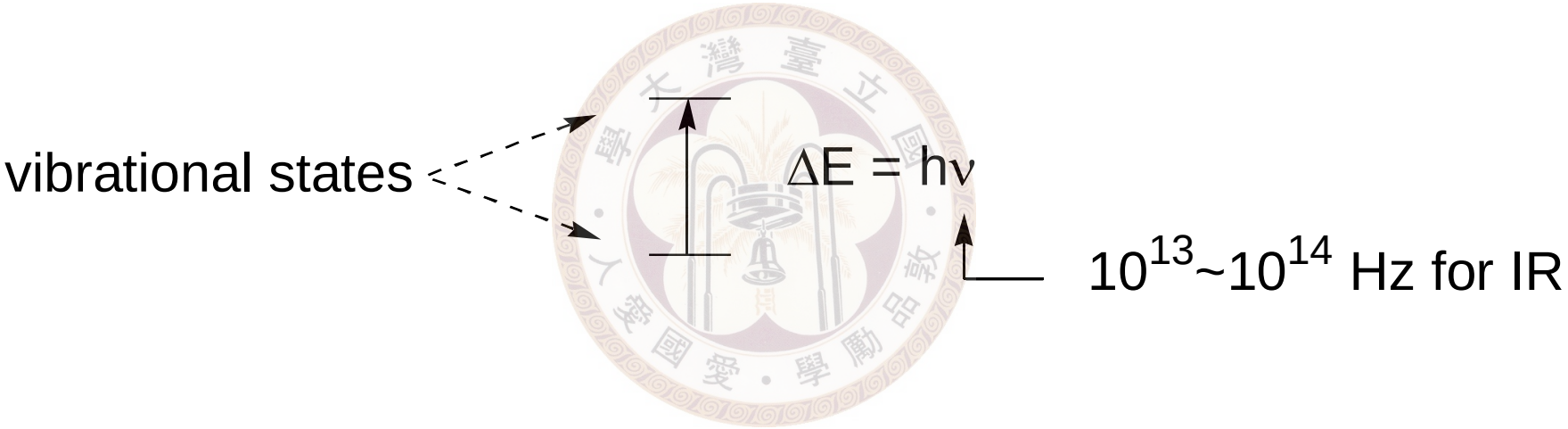
不斷舞動的分子

◎ Light is electromagnetic radiation

It has a wave nature: $E = h\nu$



For IR:
the energy corresponds to the change of molecular vibrational states



◎ Units of IR

Wavenumber $1/\lambda$ in cm^{-1}

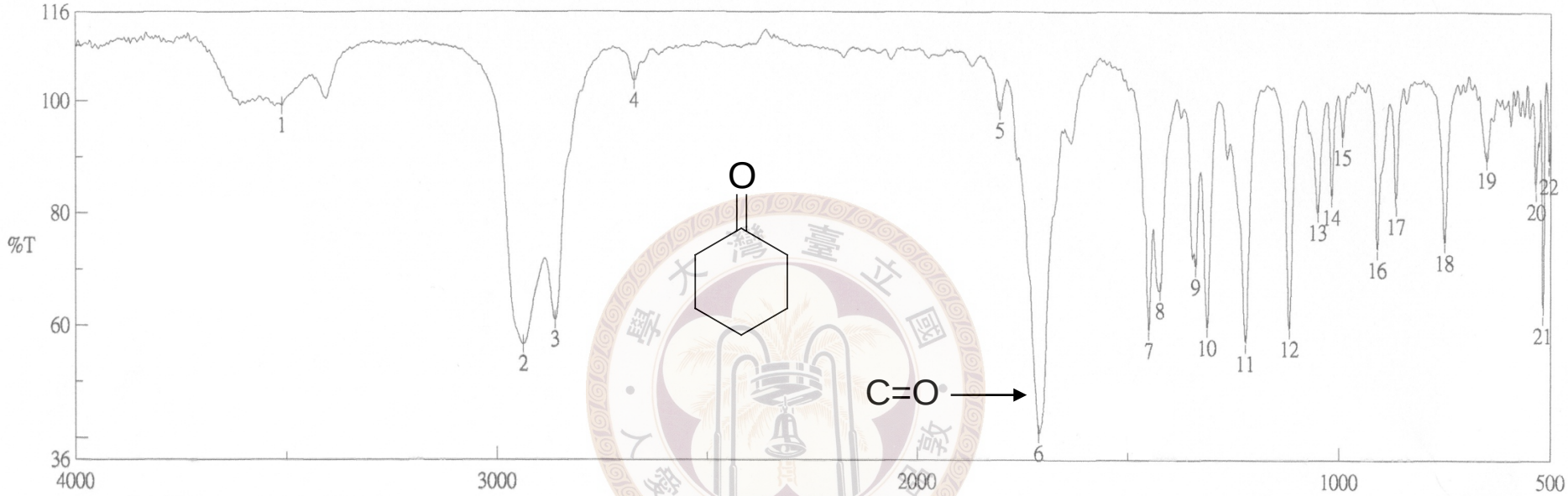
$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

$\bar{\nu}\uparrow \Rightarrow \nu\uparrow \Rightarrow E\uparrow$

Useful range: 4000 – 600 cm^{-1}

(50 – 8 kJ/mol)

✓ A typical IR spectrum



Resolution 4 cm-1

1: 3510.77, 99.1063	2: 2938.98, 56.672	3: 2862.81, 60.9826	4: 2671.89, 103.681
5: 1805.05, 98.2342	6: 1713.44, 40.7181	7: 1449.24, 59.0585	8: 1423.21, 66.1525
9: 1339.32, 70.4228	10: 1311.36, 59.5336	11: 1221.68, 56.792	12: 1118.51, 59.4434
13: 1051.01, 80.0872	14: 1018.23, 82.7983	15: 991.232, 93.4955	16: 908.308, 73.4451
17: 863.953, 81.2047	18: 750.174, 74.6205	19: 651.822, 89.4739	20: 534.185, 83.8492
21: 517.793, 61.8276	22: 503.33, 88.5239		

◎ Instrumentation

光源 → Sample cell → detector

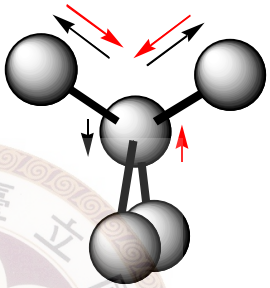
A thin film of neat liquid sample between two NaCl or KBr discs

or a solution

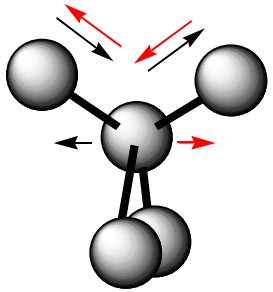
or a solid sample mixed with KBr and pressed into a thin disc

◎ Molecular vibrations

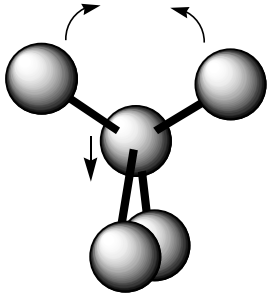
- stretching
- bending



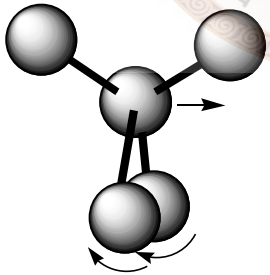
symmetric stretching



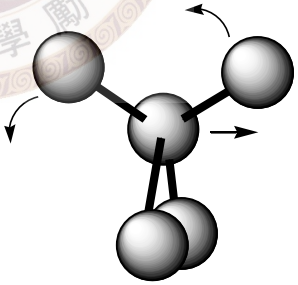
antisymmetric stretching



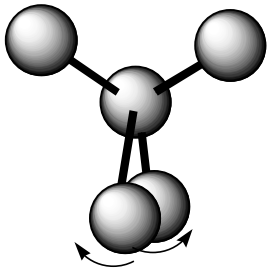
in-plane bending (scissoring)



out-of-plane bending (wagging)



in-plane bending (rocking)



out-of-plane bending (twisting)

- ✓ Stretching: change of bond length
  - ⇨ change of bond energy
  - ⇨ more difficult
  - ⇨ appears at higher wavenumber

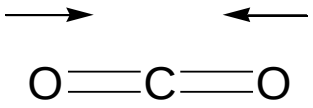
- ✓ Bending: change of bond angle
  - ⇨ change of angle strain
  - ⇨ easier
  - ⇨ appears at lower wavenumber

◎ Selection rule for IR

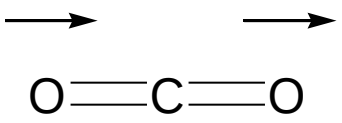
Vibrations with dipole moment change

⇨ IR active

例



IR inative
(no dipole moment change)



IR active

C=O stretching: usually strong absorption

Larger dipole moment change

C=C stretching: usually weak absorption

small dipole moment change
unless highly unsymmetrical in substitution

◎ A model

Hooke's law $\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$

k: force constant

μ: reduced mass

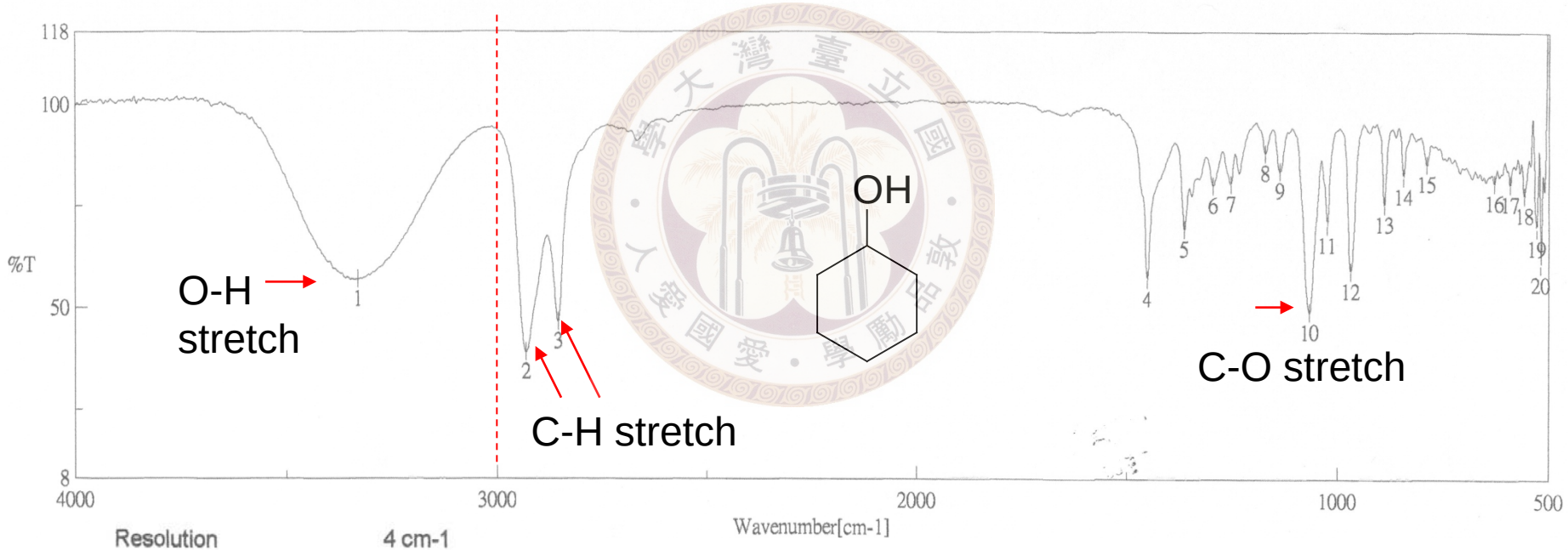
k ∝ bond strength

k ↑ $\bar{\nu}$ ↑

μ ↑ $\bar{\nu}$ ↓

O-H stretching 3200 ~ 3650 cm^{-1} (broad)
N-H stretching 3100 ~ 3550 cm^{-1} (broad)
C-H stretching 2700 ~ 3300 cm^{-1} (broad)

O-H is a stronger bond → higher wavenumber
(free OH at ~3650 as a small sharp peak)



Resolution 4 cm-1

1: 3328.53, 56.9243	2: 2931.27, 39.1572	3: 2854.13, 46.7435	4: 1451.17, 57.0843
5: 1363.43, 69.4239	6: 1296.89, 80.0929	7: 1255.43, 80.3827	8: 1173.47, 88.1104
9: 1138.76, 83.7738	10: 1067.41, 48.9262	11: 1024.98, 70.2792	12: 968.09, 59.0425
13: 889.023, 75.4979	14: 843.704, 82.3626	15: 788.743, 85.3335	16: 630.609, 80.8697
17: 593.004, 80.6061	18: 558.291, 77.8374	19: 529.364, 69.6958	20: 518.758, 60.7209

stronger bond →

C=O stretch 1630 – 1820

C-O stretch 1000 – 1300

C=C stretch 1600 – 1680

C≡C stretch 2100 – 2260 ← weak absorption but very unique (usually flat between 2600 – 1600 cm^{-1})

C-H
2700 – 3300

C=C
1600 – 1680

↑

Stronger bond but small wavenumber?

⇒ The effect of mass

◎ Problems

Peaks overlap

Overtones
Combination bands } Usually weak but complicate the spectrum
Difference bands

Only useful for functional group identification

However, 1000 – 400 cm^{-1}: fingerprint region

◎ Alkanes, Alkenes and Alkynes

C-H stretch

sp^3	< 3000 cm^{-1}	strong but not useful
sp^2	> 3000 cm^{-1}	
sp	~ 3300 cm^{-1}	very characteristic
C≡C stretch	2200 cm^{-1}	very characteristic
C=C stretch	~ 1650 cm^{-1}	usually weak
C-H bending	< 1500 cm^{-1}	complicate