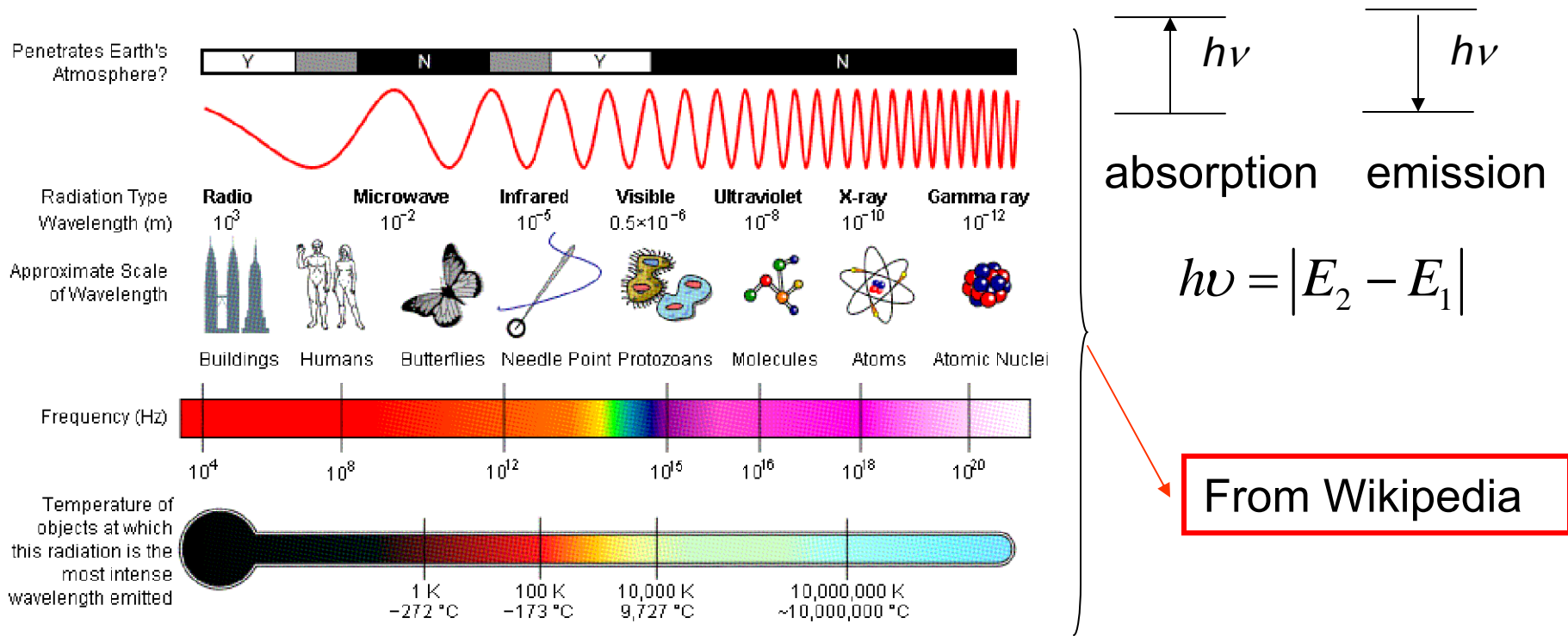


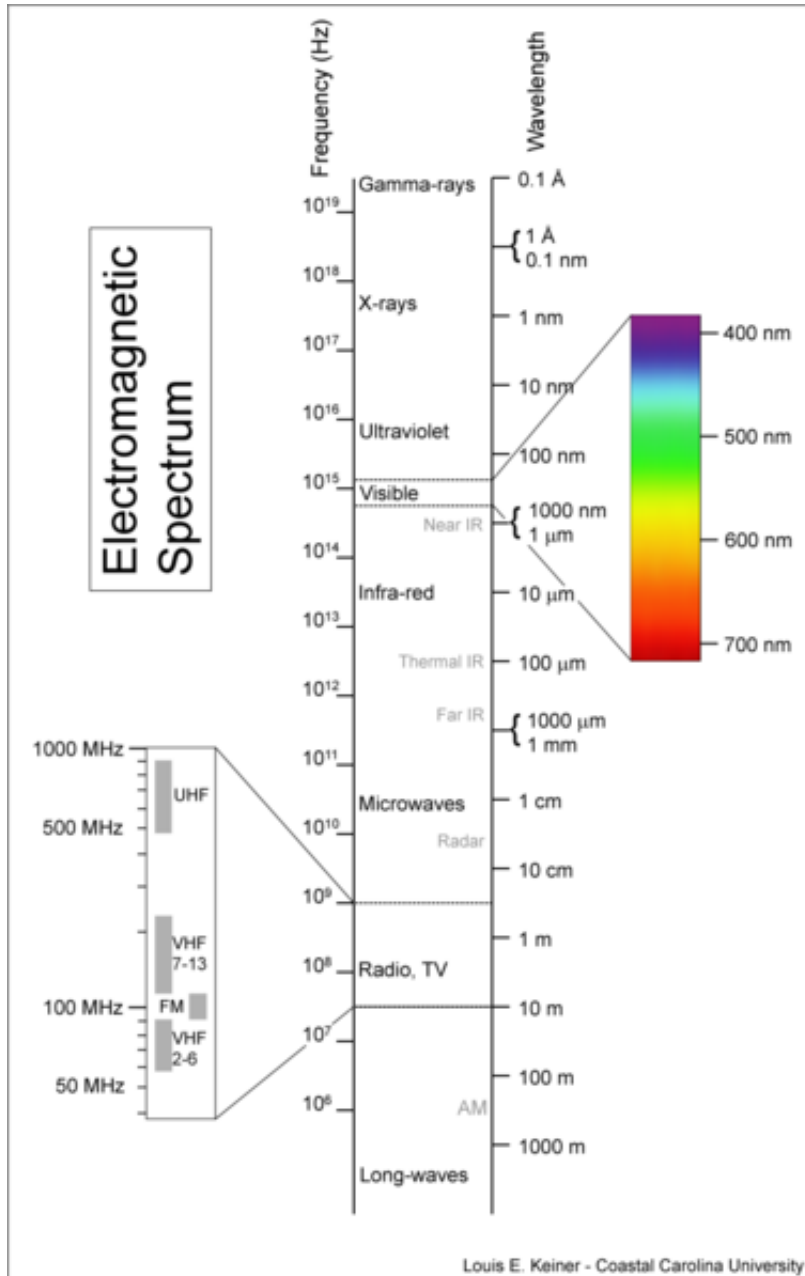
# Chapter 8 – Vibrational & Rotational Spectroscopy - Diatomics

Rotational spectra → Geometries  
 Vibrational spectra → Curvature of potential energy surface



AM radio	530 – 1700 kHz	$\lambda \sim 600 - 200 \text{ m}$	resonant
FM radio	88 - 108 MHz	$\lambda \sim 3.3 - 2.7 \text{ m}$	dipole antenna
Cell phone	2.4 GHz	$\lambda \sim 0.125 \text{ m}$	$\lambda/2$

Why are x-rays dangerous?      How are  $\gamma$  rays formed?



CLASS	FREQUENCY	WAVELENGTH	ENERGY
Y	300 EHz	1 pm	1.24 MeV
HX	30 EHz	10 pm	124 keV
SX	3 EHz	100 pm	12.4 keV
EUV	300 PHz	1 nm	1.24 keV
NUV	30 PHz	10 nm	124 eV
	3 PHz	100 nm	12.4 eV
NIR	300 THz	1 μm	1.24 eV
MIR	30 THz	10 μm	124 meV
FIR	3 THz	100 μm	12.4 meV
EHF	300 GHz	1 mm	1.24 meV
SHF	30 GHz	1 cm	124 μeV
UHF	3 GHz	1 dm	12.4 μeV
VHF	300 MHz	1 m	1.24 μeV
HF	30 MHz	10 m	124 neV
MF	3 MHz	100 m	12.4 neV
LF	300 kHz	1 km	1.24 neV
VLF	30 kHz	10 km	124 peV
VF/ULF	3 kHz	100 km	12.4 peV
SLF	300 Hz	1 Mm	1.24 peV
ELF	30 Hz	10 Mm	124 feV
	3 Hz	100 Mm	12.4 feV

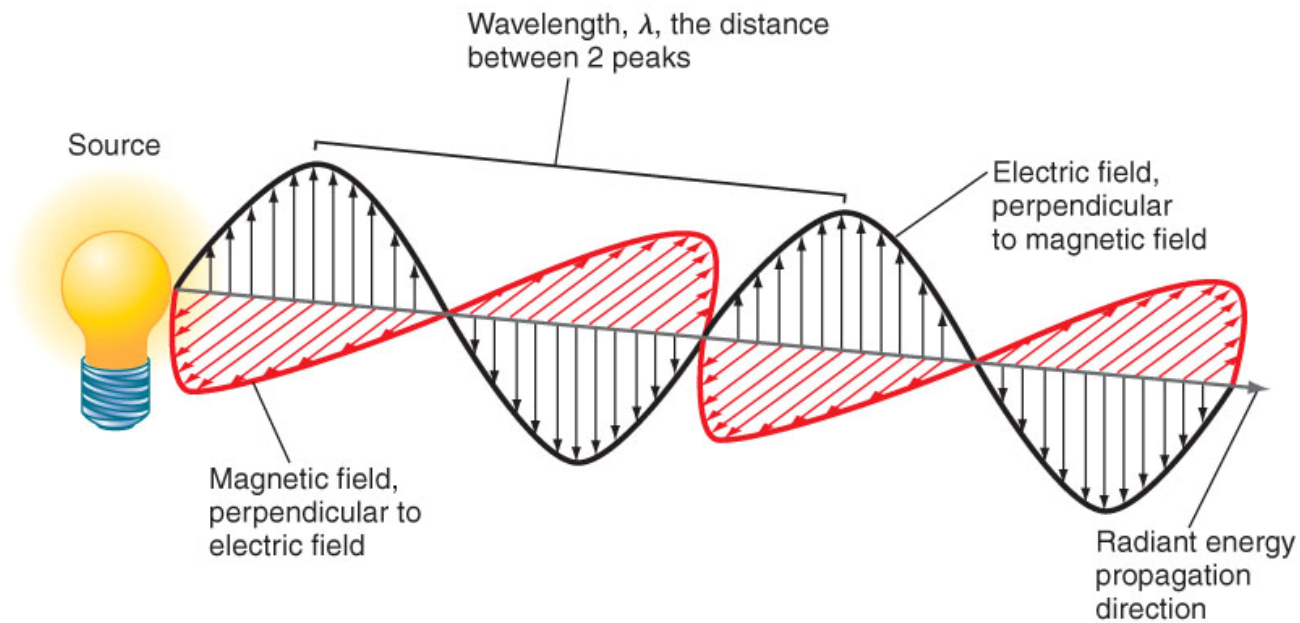
[http://en.wikipedia.org/wiki/Electromagnetic\\_spectrum](http://en.wikipedia.org/wiki/Electromagnetic_spectrum)

wave number units  $\tilde{\nu} = \frac{1}{\lambda}$ , in  $\text{cm}^{-1}$

$8066 \text{ cm}^{-1} \equiv 1 \text{ eV}$

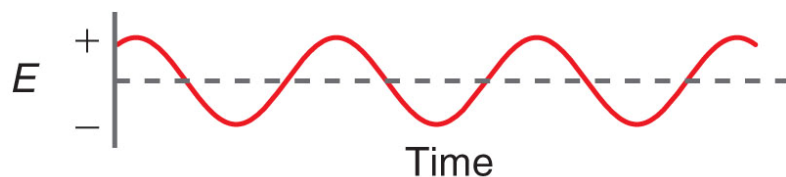
$$\Delta E = h\nu = h c \tilde{\nu}$$

(be careful about cm and m)  
has to be in cm/s in this case

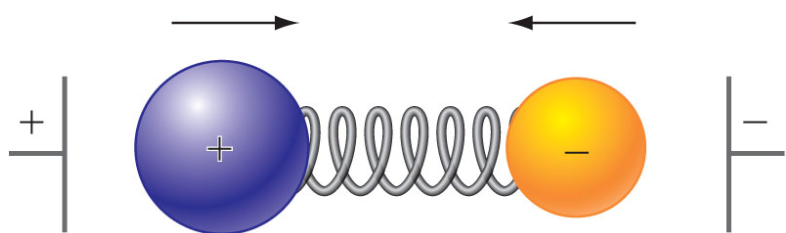
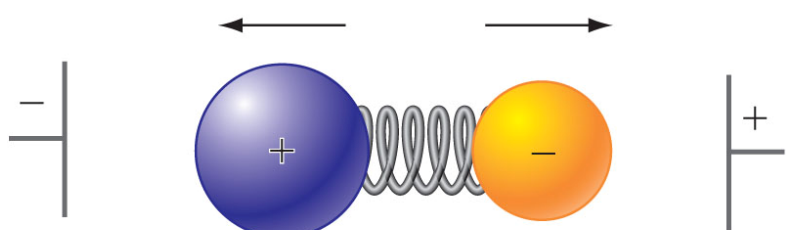


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electric and magnetic fields  $\perp$  to one another and  
to the propagation direction

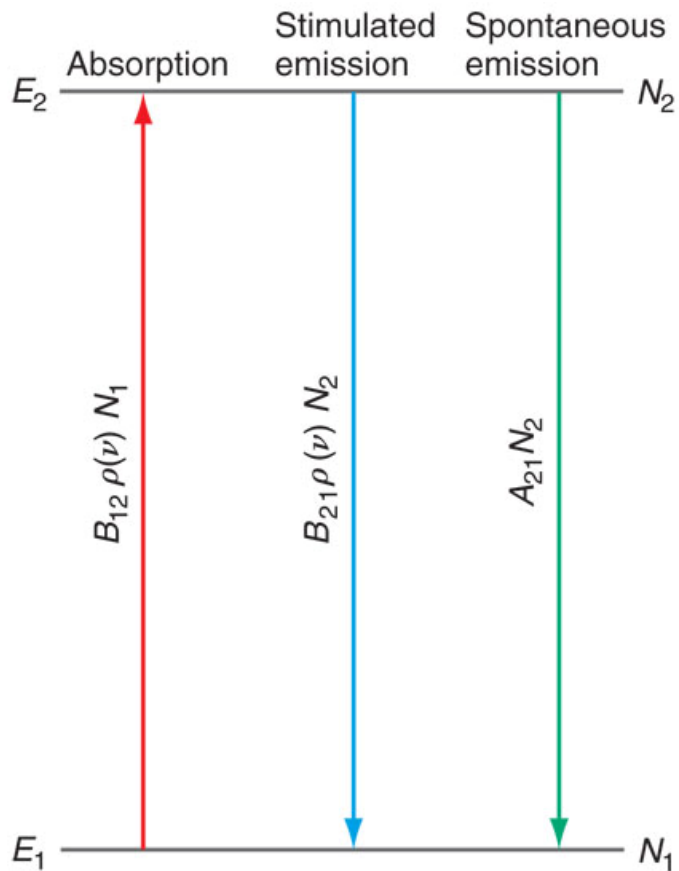


If the frequency of the oscillating field = that of the oscillator, the oscillator is driven into resonance, *i.e.*, vibrates. Note – a dipole is essential for coupling with the field.



For a diatomic molecule treated quantum mechanically, the key is the dynamic (changing) dipole, *i.e.*,  $d\mu/dR$ .

For rotational spectroscopy, the key is the static dipole.



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- |   |                       |                      |
|---|-----------------------|----------------------|
| 1 | Absorption:           | $B_{12}\rho(\nu)N_1$ |
| 2 | Stimulated emission:  | $B_{21}\rho(\nu)N_2$ |
| 3 | Spontaneous emission: | $A_{21}N_2$          |

$\rho(\nu)$  = radiation density

$$B_{12}\rho(\nu)N_1 = B_{21}\rho(\nu)N_2 + A_{21}N_2$$

$N_1, N_2$  = # of molecules in each level – given by Boltzman expression

Einstein showed that

$$B_{12} = B_{21}$$
$$\frac{A_{21}}{B_{21}} = \frac{16\pi h\nu^3}{c^3}$$

using the  
expression  
for black-body  
radiation

spontaneous emission: random, emitted photons incoherent  
(phases and direction random)

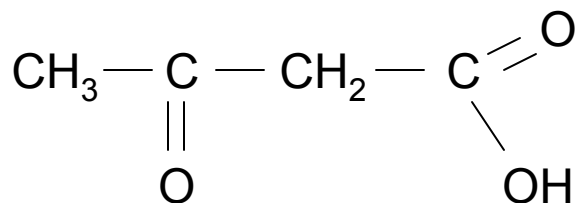
stimulated emission: emitted photons have same phase and  
direction as incident photon (coherent)

lasers are based on stimulated emission

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A closer look at vibrational spectroscopy

Useful due to characteristic frequencies (group frequencies)



CH, C=O, C-O, O-H all have very different frequencies

In general  $\frac{N_1}{N_0} \ll 1$  for vibrational energy levels

So we can assume that only  $n = 0$  level is populated before photon absorption

Selection rule  $\Delta n = \pm 1$

Usually only  $n = 0 \rightarrow n = 1$  important

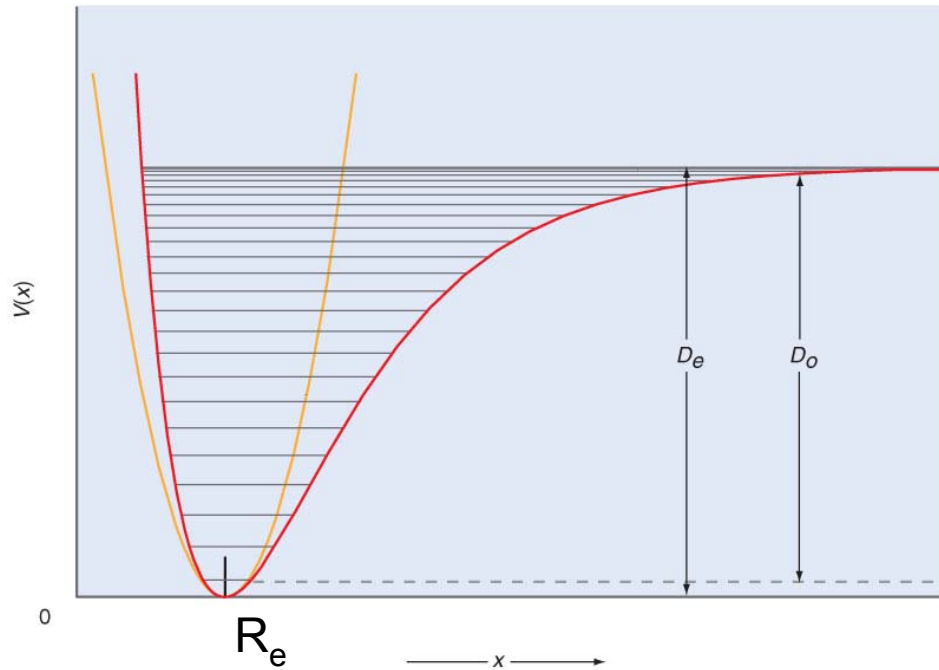
Actually, if the potential is anharmonic, may see weak overtone bands ( $\Delta n = 2, 3$ )

Morse potential: 
$$V(R) = D_e \left[ 1 - e^{-\alpha(R-R_e)} \right]^2$$

A good model for true potential energy curves

$$E_n = hv \left( n + \frac{1}{2} \right) - \frac{(hv)^2}{4D_e} \left( n + \frac{1}{2} \right)^2$$

vibrational anharmonicity



What does vibrational anharmonicity due to the Bond length?

$R_0$  vs.  $R_e$



## transition dipole moment

$$\mu_x^{mn} = \langle m | \mu_x | n \rangle = \int \psi_m^*(x) \mu_x(x) \psi_n(x) dx$$

$$\mu_x = \underbrace{\mu_{ox}} + x(t) \left( \frac{d\mu}{dx} \right)_{x=0} + \dots$$

↑  
permanent  
dipole in x  
direction

$$\langle 0 | \mu_x | 1 \rangle$$

only second term in expansion  
of  $\mu_x$  contributes  
→  $\Delta n = 1$  selection rule

## Vibrational Selection Rule

0  $\rightarrow$  n

$$\langle \psi_0 | \mu_x | \psi_n \rangle = \underbrace{\mu_0 \langle \psi_0 | \psi_n \rangle}_{0} + \left. \frac{d\mu}{dx} \right|_{x=0} \cdot \langle \psi_0 | x | \psi_n \rangle$$

Need  $\left. \frac{d\mu}{dx} \right|_{x=0} \neq 0$  and  $\langle \psi_0 | x | \psi_n \rangle \neq 0$

$$\langle \psi_0 | x | \psi_n \rangle = A_0 A_n \int_{-\infty}^{\infty} H_0 x H_n e^{-\alpha x^2} dx$$

Nonzero only if  $n = 1$

Absorption: only  $\Delta n = 1$  ( $0 \rightarrow 1$ ) allowed

Emission: only  $\Delta n = -1$  ( $1 \rightarrow 0$ ), ( $2 \rightarrow 1$ ), ( $3 \rightarrow 2$ ), etc.  
allowed

If the potential is harmonic.

$\text{N}_2$ ,  $\text{H}_2$ ,  $\text{O}_2$ : 99.9% of atmosphere

do not absorb IR radiation emitted by earth

so most IR radiation escapes into space

$\text{CO}_2$ ,  $\text{CH}_4$  absorb, emit IR radiation

greenhouse gases

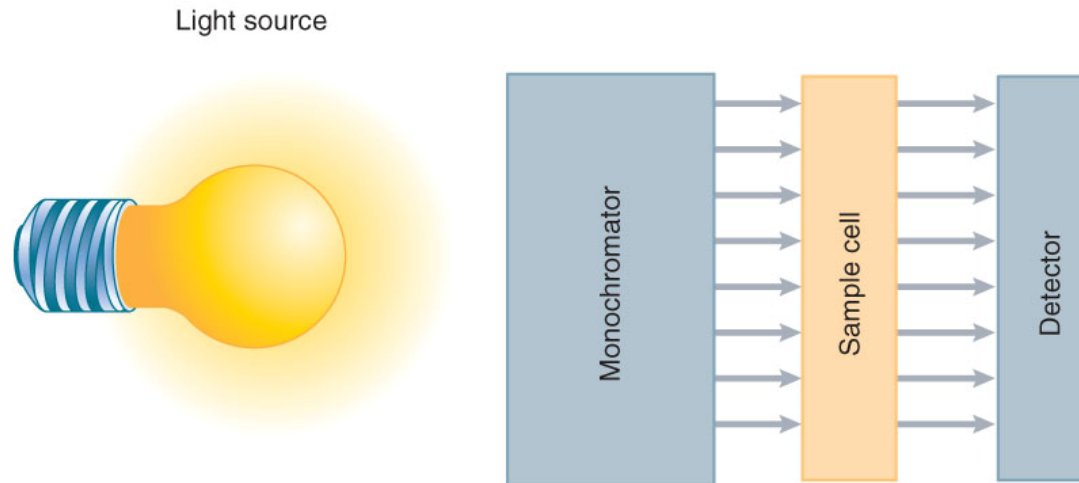
Beer's law:  $I(\lambda) = I_o(\lambda)e^{-\varepsilon(\lambda)mL}$

m = concentration

L = path length

$\varepsilon$  = molar absorption coefficient

often have mirrors to reflect light → increase path length



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monochromator – generates light of know wavelength,  
generally tunable.