ChemE 2200 – Applied Quantum Chemistry Lecture 5

Today:

The Interaction of Electromagnetic Radiation with Matter:
Vibrational Transitions and Infrared Spectroscopy

Defining Question:

What molecular property is required for a diatomic molecule to absorb/emit infrared radiation?

Reading for Today's Lecture:

McQuarrie & Simon, 5.1 – 5.7.

Reading for Quantum Lecture 6:

McQuarrie & Simon, 13.3, 13.13.

RUSH ALPHA CHI SIGMA

Cornell's Professional Co-Ed Chemistry Fraternity!

We are open to anyone interested in chemistry!

Info Session:

7pm January 29th at Baker 135

Interest Form:

axs_cornell

Rush Schedule:

All Events: 7pm at 425 Wyckoff Avenue

*must attend at least 2 events!

Monday 02/03: GAME NIGHT!

Tuesday 02/04: HOT CHOCOLATE CONTEST!

Wednesday 02/05: ART NIGHT!

Thursday 02/06: BINGO NIGHT!

Recap: Rotational Transitions and Microwave Spectroscopy

1. Describe the molecule with quantum mechanics.

$\Psi = Y_{J,mJ}(\theta,\varphi)$ The Spherical Harmonics $J = 0, 1, 2, \ldots$ $m_J = 0, \pm 1, \pm 2, \ldots, \pm J$

2. Calculate the molecular energy levels $E_1, E_2, \ldots$

$$\tilde{\nu}_J = \frac{E_J}{hc} = \frac{\hbar}{4\pi c I} J(J+1) = BJ(J+1)$$

$$B \equiv \text{rotational constant} = \frac{\hbar}{4\pi c I}$$

$$I \equiv \text{moment of inertia} = \frac{m_1 m_2}{m_1 + m_2} R^2$$

3. Determine the selection rules for photon-induced transitions.

Conservation of energy: $E_{\text{photon}} = E_{\text{final}} - E_{\text{initial}}$

Conservation of angular momentum: $J_{\text{photon}} = J_{\text{final}} - J_{\text{initial}}$

$\Delta J = \pm 1$ and $\Delta m_J = 0, \pm 1$

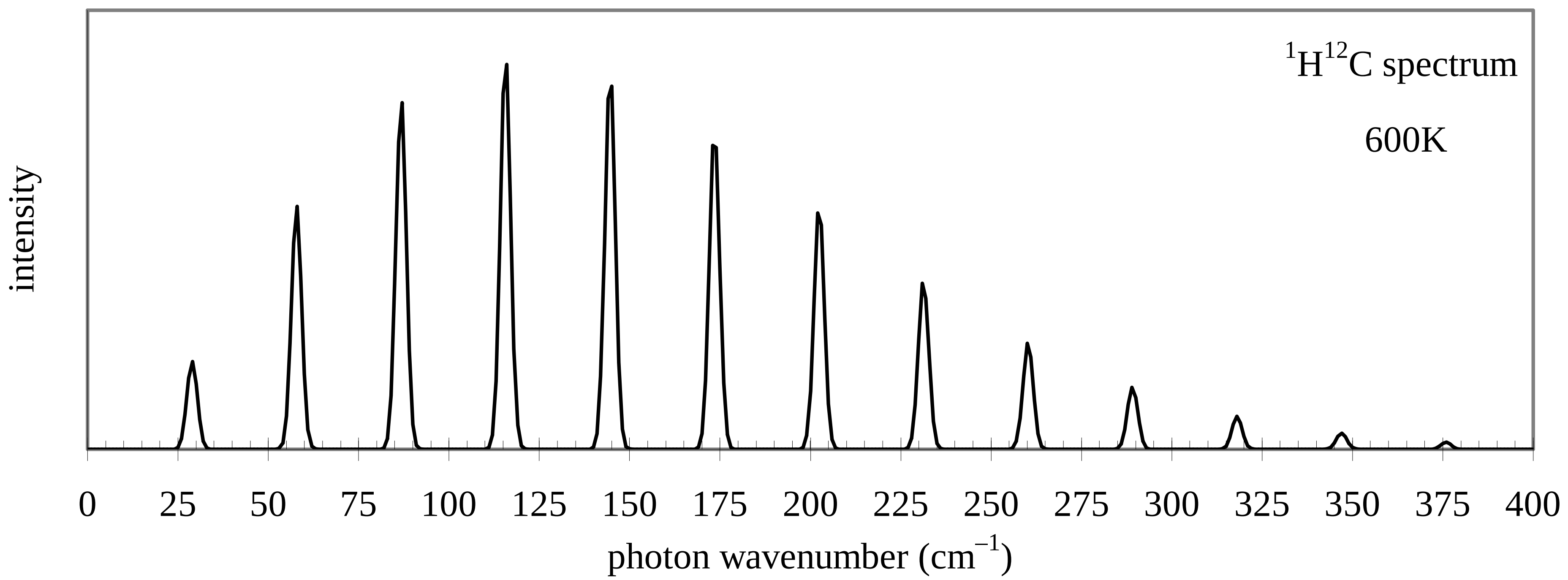
$$\tilde{\nu}_{\text{photon}} = \tilde{\nu}_{J+1} - \tilde{\nu}_J = 2B(J+1)$$

4. Determine the spectral intensities (peak heights in the photon spectrum).

peak intensity ∝ (number of states at initial energy) × (Boltzmann population at initial energy)

$$\text{peak intensity} \propto (2J+1) \times \exp\left[\frac{-BJ(J+1)hc}{kT}\right]$$

Recap: Rotational Transitions and Microwave Spectroscopy



Because B is typically 0.1 to 10 cm^{-1}, rotational transitions are in the *microwave* portion of the electromagnetic spectrum.

Spacing between peaks is $2B$.

In the spectrum above, $2B = 28.91\ cm^{-1} \quad \Rightarrow \quad R = 1.06$ Å

Envelope of peak intensity indicates sample temperature.

Molecular Spectroscopy

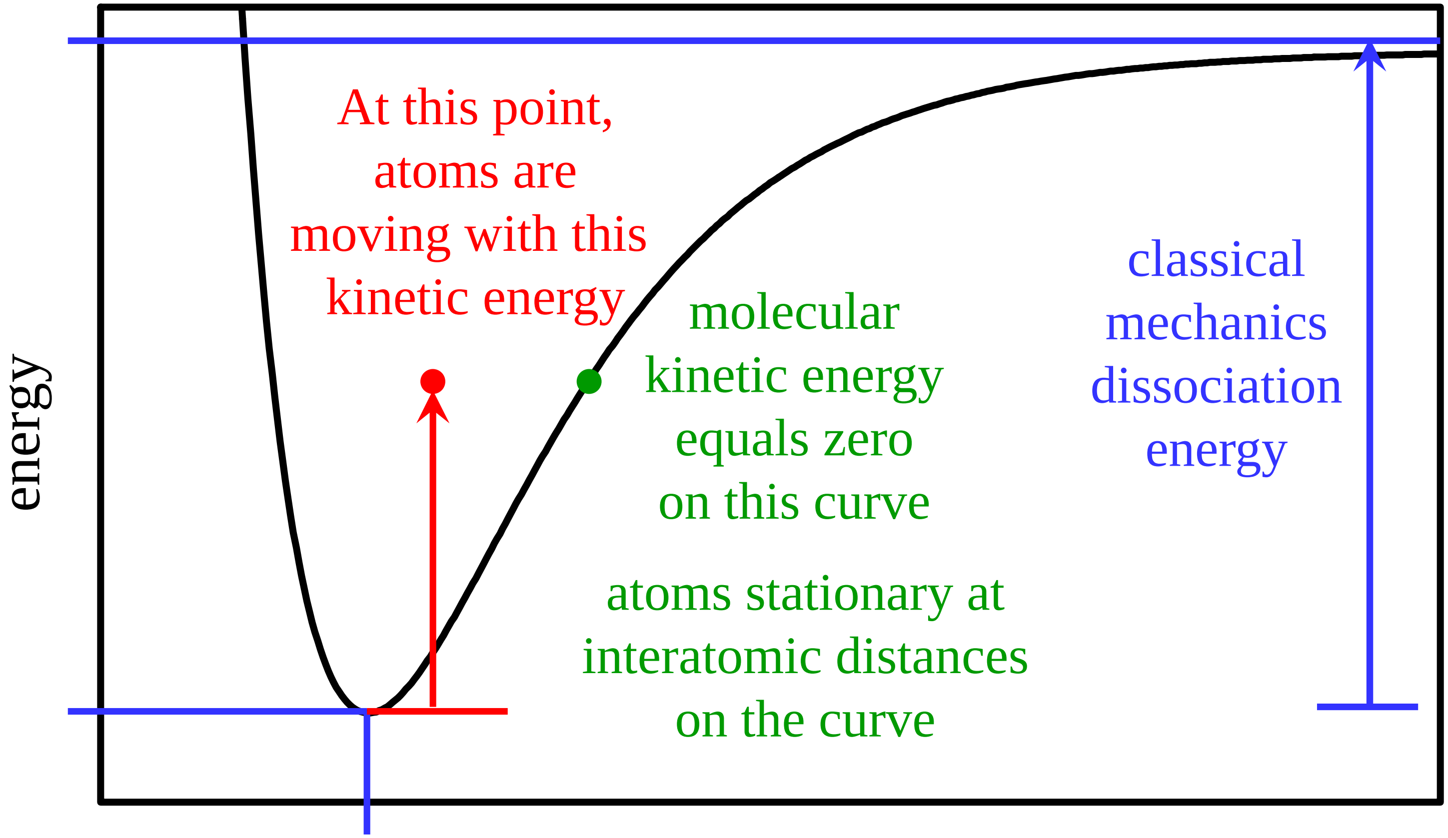
rotational transitions ✓

vibrational transitions today

electronic transitions

Molecular Vibrations

Molecular orbital theory: molecular potential energy depends on bond length



At this point, atoms are moving with this kinetic energy

molecular kinetic energy equals zero on this curve

atoms stationary at interatomic distances on the curve

classical mechanics dissociation energy

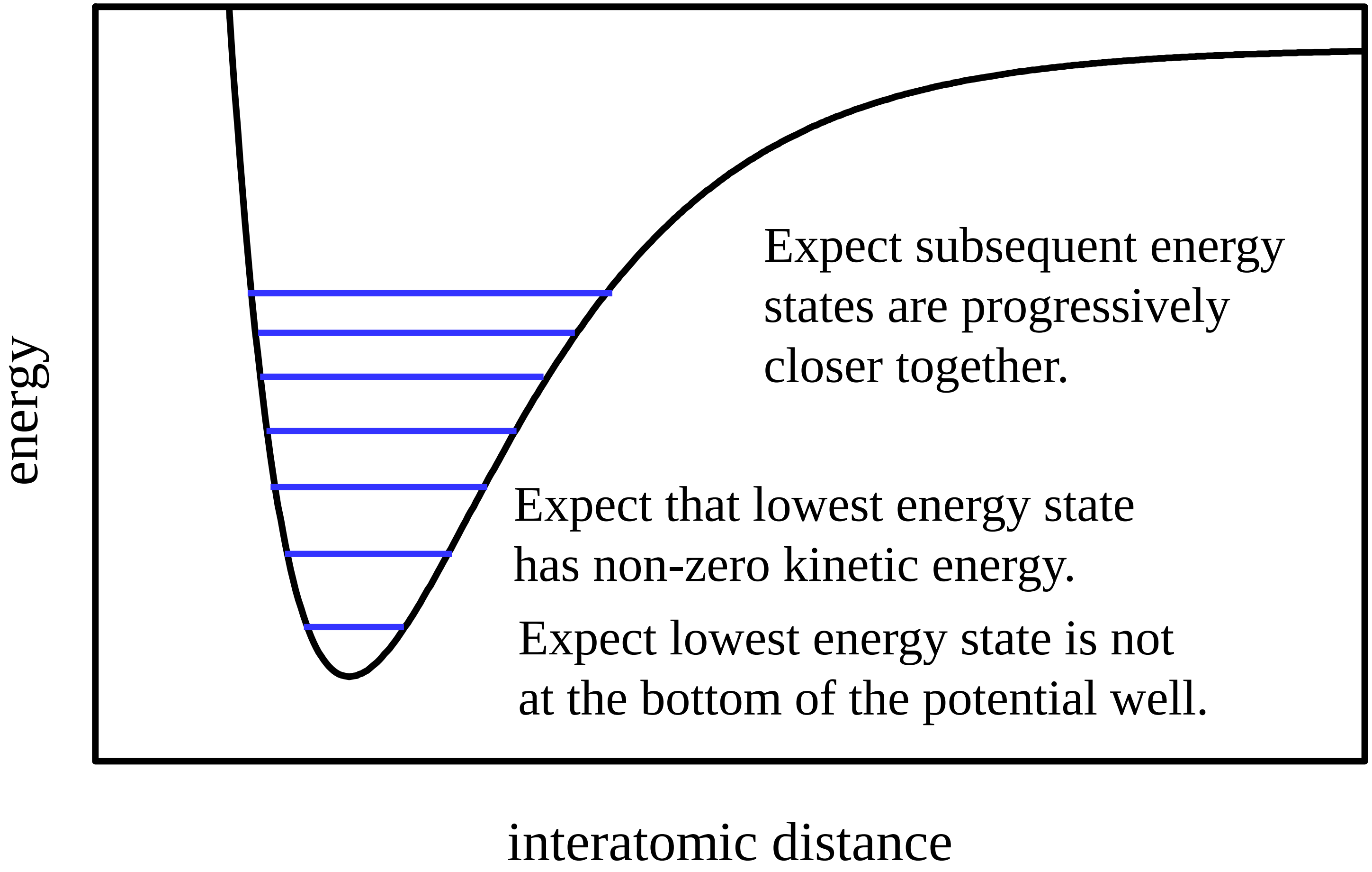
energy

classical mechanics equilibrium interatomic distance

interatomic distance

Molecular Vibrations

Potential energy curve is analogous to the square-well potential for particle in a box.



Expect subsequent energy states are progressively closer together.

Expect that lowest energy state has non-zero kinetic energy.

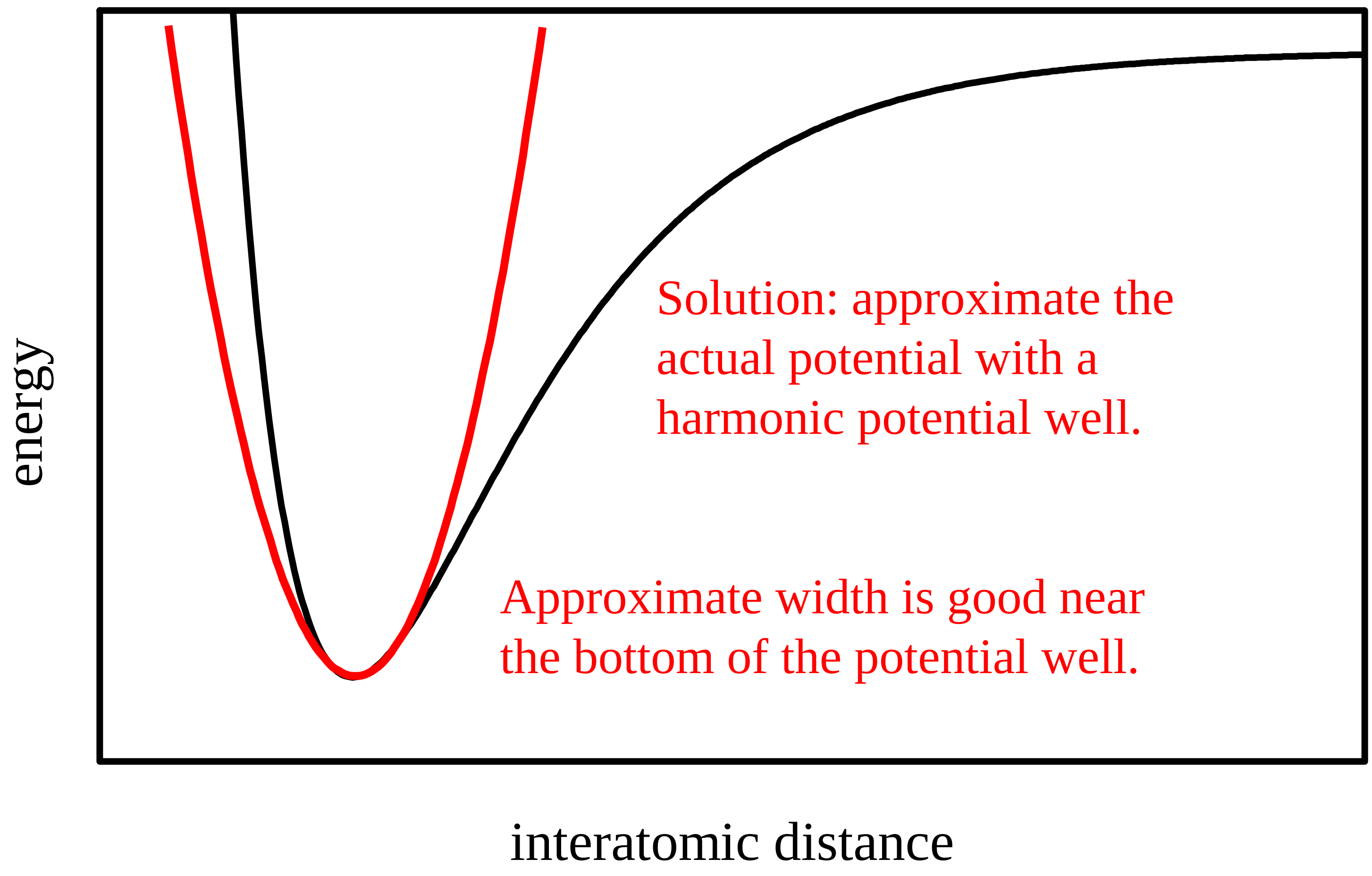
Expect lowest energy state is not at the bottom of the potential well.

Next: 1. Describe the molecular vibrations with quantum mechanics.

Solve Schrödinger’s equation for the interatomic potential.

Molecular Vibrations

Schrödinger’s equation is difficult to solve for the actual potential.



Solution: approximate the actual potential with a harmonic potential well.

Approximate width is good near the bottom of the potential well.

Wavefunctions for the actual potential are unnecessarily complicated.

And unnecessarily obtuse.

1. Describe the molecule with quantum mechanics

Schrödinger's equation for the harmonic potential:

$$\frac{-\hbar^2}{2\mu}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi \qquad \text{such that } x = R - R_0$$

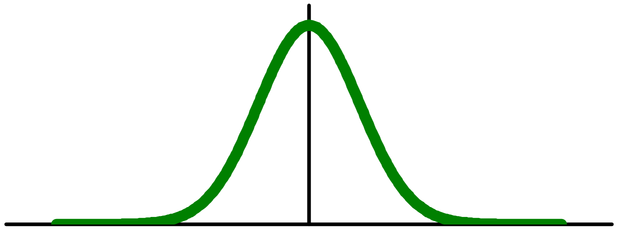
$$\mu \equiv \text{reduced mass} = \frac{m_1 m_2}{m_1 + m_2} \qquad k \equiv \text{spring constant}$$

Convert to a dimensionless equation:

$$\text{substitute } x = \left(\frac{\hbar^2}{\mu k}\right)^{1/4} y \quad \Rightarrow \quad -\frac{d^2\psi}{dy^2} + y^2\psi = \frac{2}{\hbar}\left(\frac{\mu}{k}\right)^{1/2} E\psi$$

The solutions are $\psi_{\mathrm{v}} = N_{\mathrm{v}} H_{\mathrm{v}}(y) e^{-y^2/2}$ N_v are normalization constants

$e^{-y^2/2}$ is a Gaussian (normal) distribution

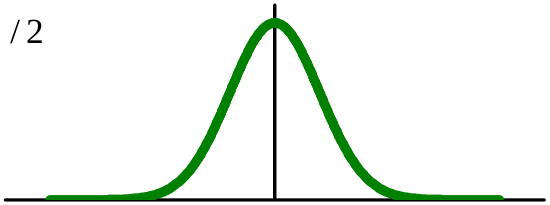


$H_{\mathrm{v}}(y)$ are the Hermite polynomials

Wavefunctions for Vibrational States

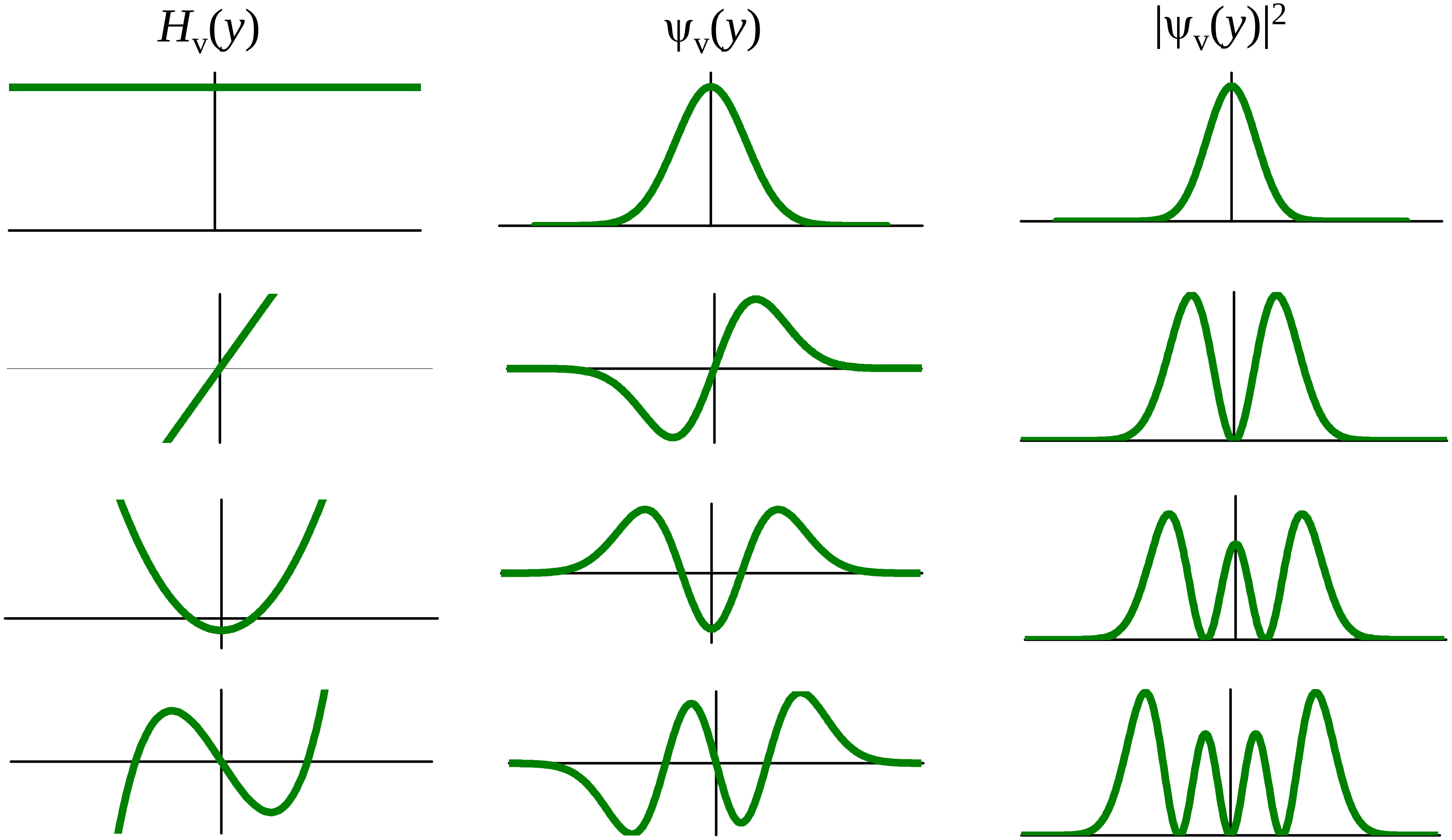
$$\psi_v = N_v H_v(y) e^{-y^2/2}$$

$e^{-y^2/2}$ is a Gaussian (normal) distribution:



Some Hermite polynomials and vibrational wavefunctions:

v	$H_v(y)$
0	1
1	$2y$
2	$4y^2 - 2$
3	$8y^3 - 12y$
v+1	$H_{v+1} = 2yH_v - 2vH_{v-1}$



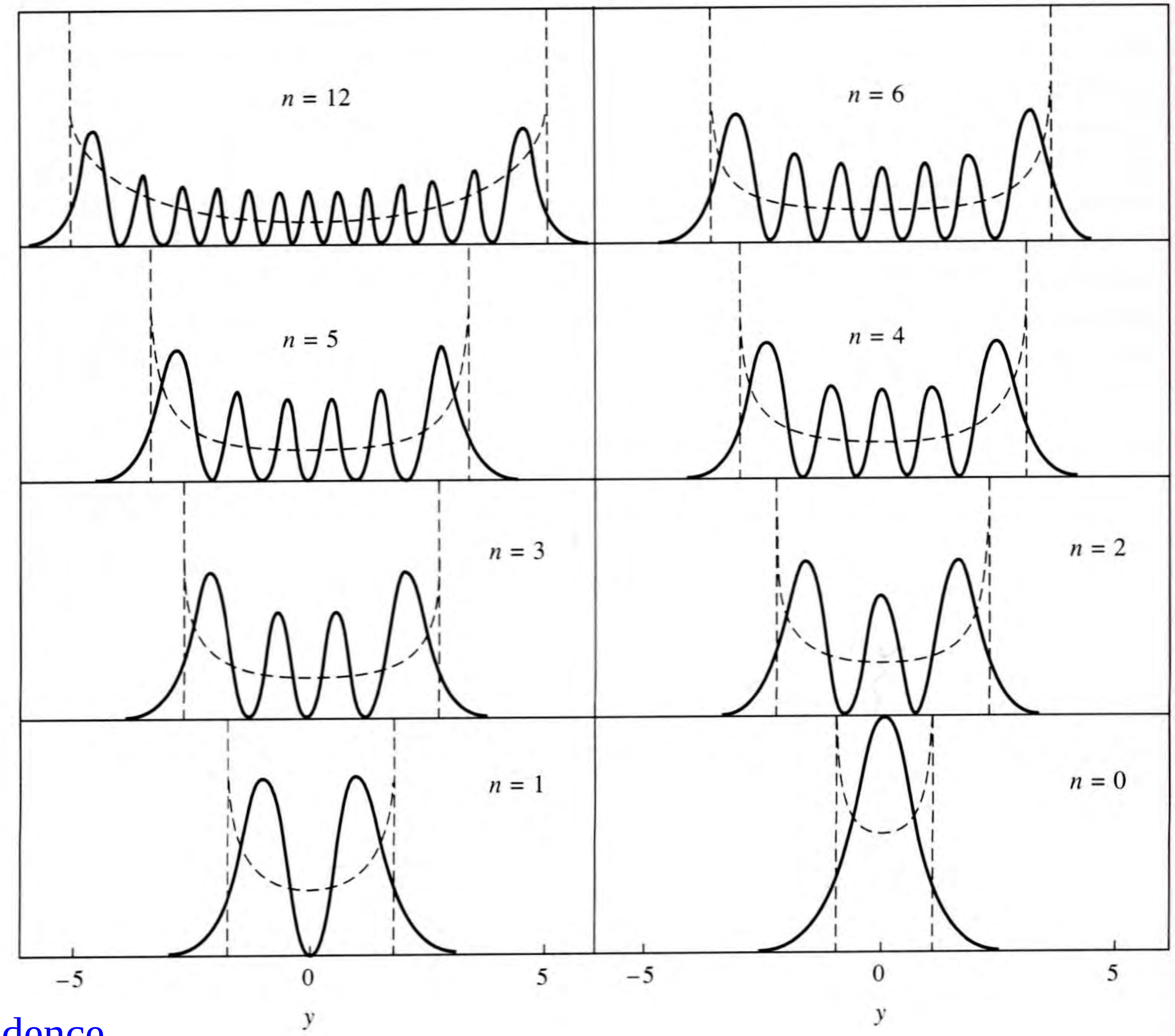
Wavefunctions for Vibrational States

Comparison of Quantum and Classical Probability Densities

Quantum probability densities have nodes.

Number of nodes equals the quantum number v.

Largest difference at v = 0. Classical and quantum converge at large v.



Quantum probability density extends beyond the classical limit

Tunnelling!

The Correspondence Principle!

Reference: J. H. Noggle, Physical Chemistry, 1996, Fig 11.11, p. 654.

2. Calculate the Molecular Energy Levels

Substitute the vibrational wavefunction into Schrödinger's equation for the harmonic potential:

$$-\frac{d^2\psi}{dy^2} + y^2\psi = \frac{2}{\hbar}\left(\frac{\mu}{k}\right)^{1/2} E\psi \qquad \text{such that } y = \left(\frac{\mu k}{\hbar^2}\right)^{1/4}(R - R_0)$$

$$\psi_\text{v} = N_\text{v} H_\text{v}(y) e^{-y^2/2} \qquad \text{with normalization factor } N_\text{v} = \left[\frac{(\mu k)^{1/4}}{\sqrt{\pi\hbar}\, 2^\text{v}\, \text{v}!}\right]^{1/2}$$

Energy levels: $E_\text{v} = (\text{v} + ½)\hbar\left(\frac{k}{\mu}\right)^{1/2}$ $\quad \text{v} = 0, 1, 2, 3, \ldots$ $\quad k \equiv$ spring constant

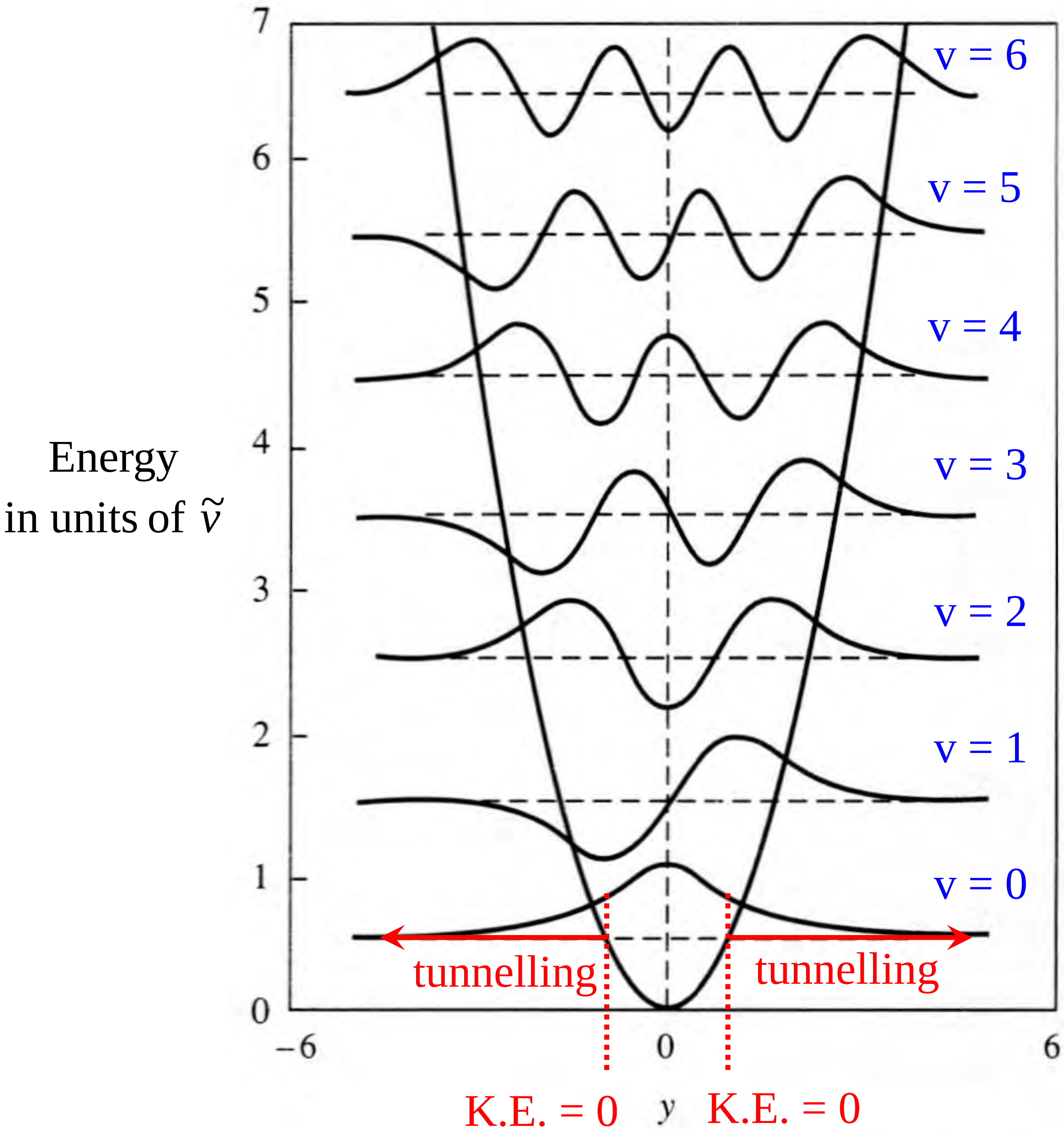
$\mu \equiv$ reduced mass $= \dfrac{m_1 m_2}{m_1 + m_2}$

Convert E_v (in Joules) to $\tilde{v}_\text{v}$ (in cm^{-1})

$$\tilde{v}_\text{v} = \frac{v}{c} = \frac{E_\text{v}}{hc} = \frac{1}{hc}(\text{v} + ½)\hbar\left(\frac{k}{\mu}\right)^{1/2} = (\text{v} + ½)\frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} = (\text{v} + ½)\tilde{v}$$

$\tilde{v} \equiv$ vibrational constant $= \dfrac{1}{2\pi c}\left(\dfrac{k}{\mu}\right)^{1/2}$ $\qquad$ Analogous to *B*, the rotational constant.

Vibrational Energy Levels $\tilde{\nu}_v = (v + ½)\tilde{\nu}$



$E_0 = ½\tilde{\nu}$

Like particle in a box,
wavelength decreases
as energy level increases.

More kinetic energy
at higher energy level!

$\lambda_{\text{center}} < \lambda_{\text{edge}}$

K.E. = E_v – P.E.

kinetic energy is
greater in the center!

Vibrational Constants

$$\tilde{\nu} \equiv \text{vibrational constant} = \frac{1}{2\pi c}\left(\frac{k}{\mu}\right)^{1/2} \qquad k \equiv \text{spring constant} \qquad \mu \equiv \text{reduced mass} = \frac{m_1 m_2}{m_1 + m_2}$$

diatomic	bond order	bond length	spring constant k (N/m)	reduced mass, μ	vibrational constant $\tilde{\nu}$ (cm^{-1})
$^{1}H_2$	1	0.741 Å	575	0.5	4401
$^{2}H_2$	1	0.741 Å	577	1.0	3118
$^{1}H^{19}F$	1	0.917 Å	966	0.950	4138
$^{1}H^{35}Cl$	1	1.275 Å	516	0.972	2886
$^{1}H^{79}Br$	1	1.414 Å	408	0.988	2630
$^{1}H^{127}I$	1	1.609 Å	314	0.992	2230
$^{12}C^{16}O$	3	1.128 Å	1903	6.857	2170
$^{14}N^{16}O$	2½	1.151 Å	1550	7.467	1876

infrared
portion
of EM
spectrum

3. Determine the Selection Rules for Photon-Induced Transitions.

Angular momentum is conserved. ⟹ $\mathrm{v}_{\mathrm{final}} - \mathrm{v}_{\mathrm{initial}} = \pm 1$

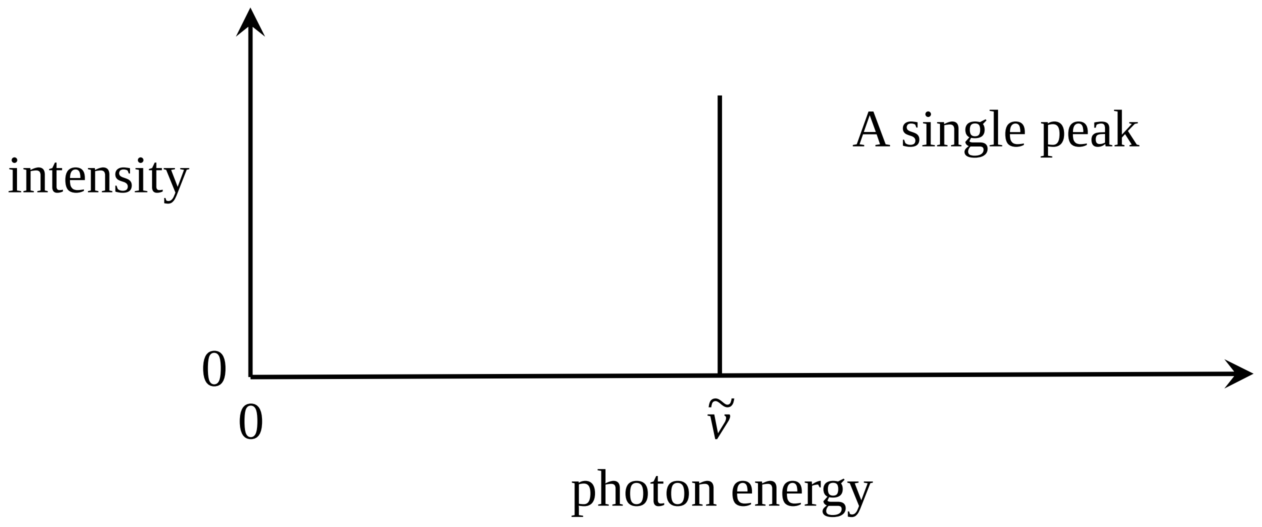
$$\boxed{\Delta \mathrm{v} = \pm 1}$$

Energy is conserved. ⟹ $E_{\mathrm{v}+1} - E_{\mathrm{v}} = E_{\mathrm{photon}}$

$$\tilde{\nu}_{\mathrm{photon}} = \tilde{\nu}_{\mathrm{v}+1} - \tilde{\nu}_{\mathrm{v}} = (\mathrm{v} + \tfrac{1}{2} + 1)\tilde{\nu} - (\mathrm{v} + \tfrac{1}{2})\tilde{\nu} = \tilde{\nu}$$

$$\boxed{\tilde{\nu}_{\mathrm{photon}} = \tilde{\nu}} \quad \text{for } \textbf{\textit{all}} \text{ v}$$

Photon spectrum of a harmonic oscillator:



Selection Rules for Vibrational Transitions

The oscillating EM field of the photon interacts
with the oscillating EM field of the molecule.

For diatomic molecules, there must be an electric dipole moment.

Vibration causes oscillating electric and magnetic fields.

Infrared-active diatomics: HF, HCl, HBr, HI, CO, NO

Infrared-inactive diatomics: H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2

For polyatomic molecules, the transition must change the molecule’s oscillating EM field.

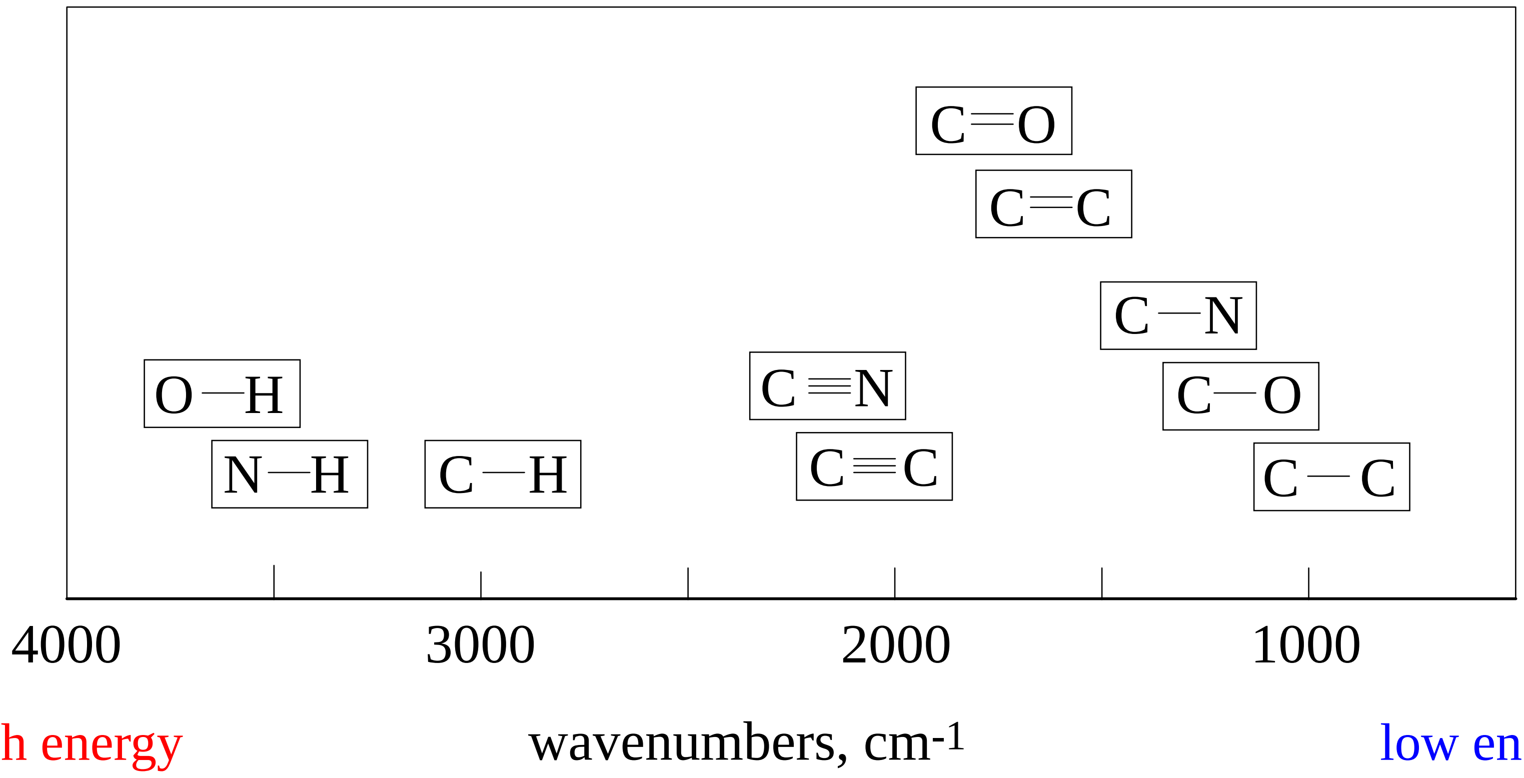
Infrared-active polyatomics with electric dipole moments: CO_2, H_2O

Infrared-active polyatomics without electric dipole moments: CH_4, O_3

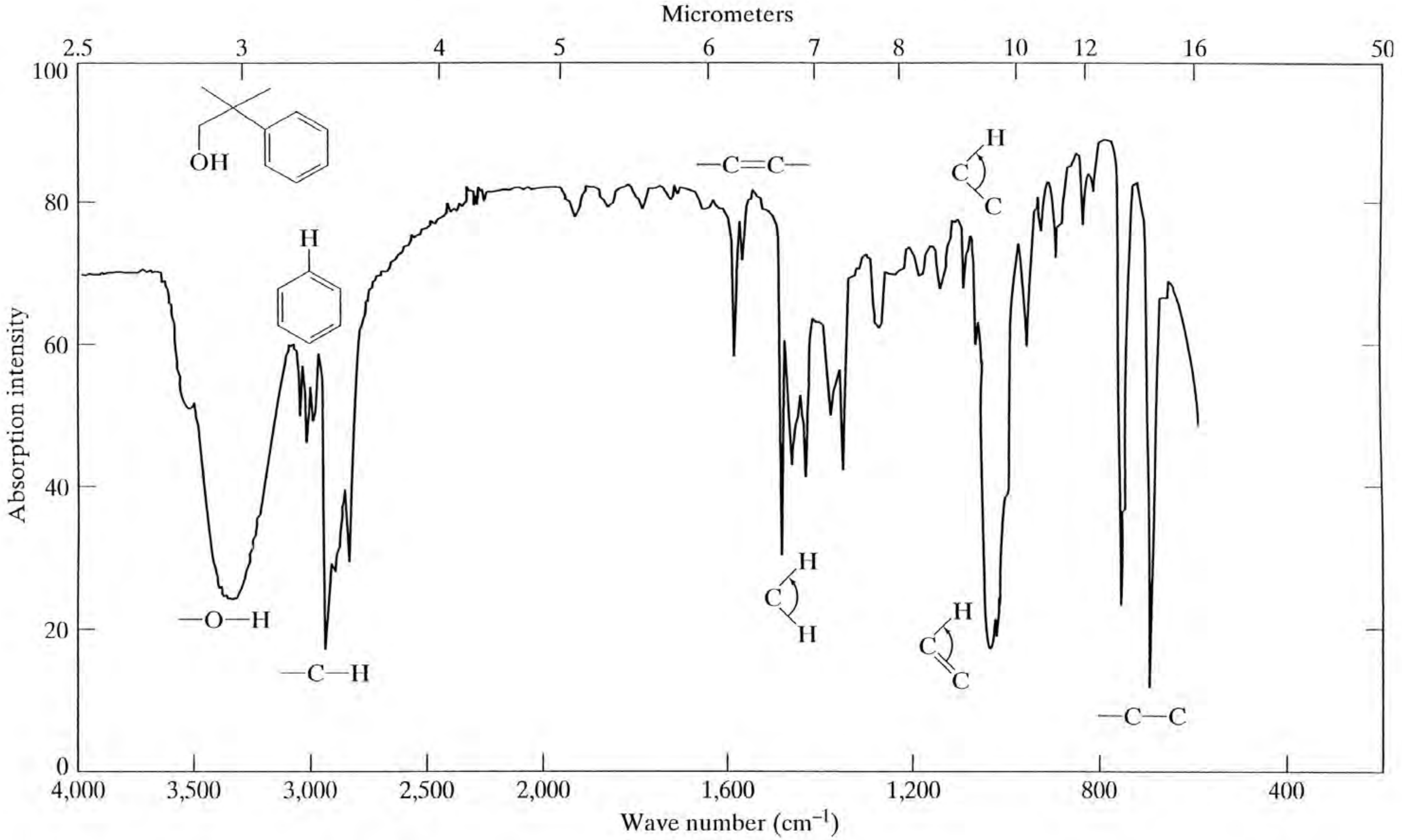
Asymmetric stretching and bending (not possible in diatomics)
almost always creates an oscillating EM field.

Infrared Spectroscopy for Chemical Identification

Typical Vibrational Constants for Functional Groups in Organic Compounds

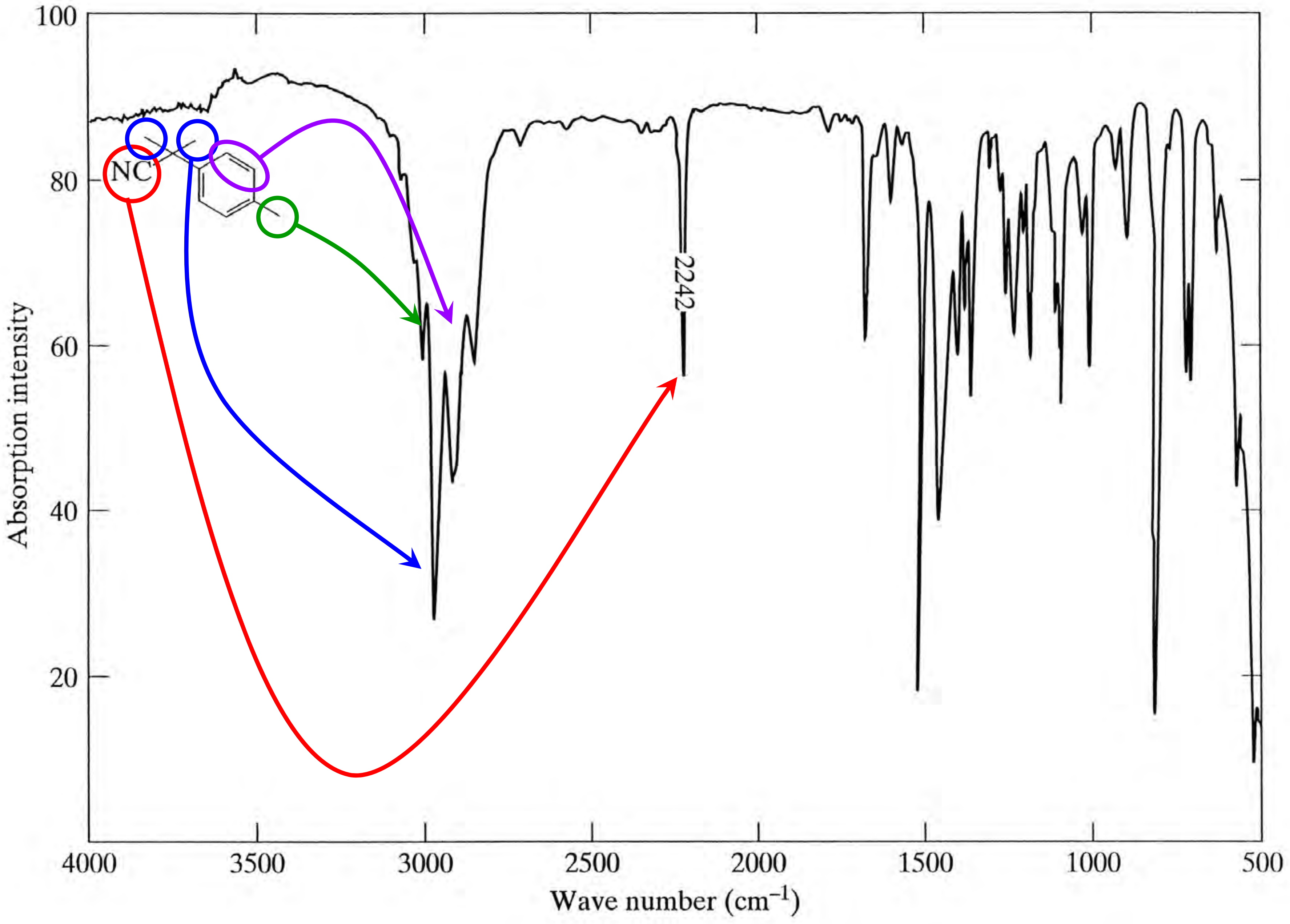


Infrared Spectroscopy for Chemical Identification



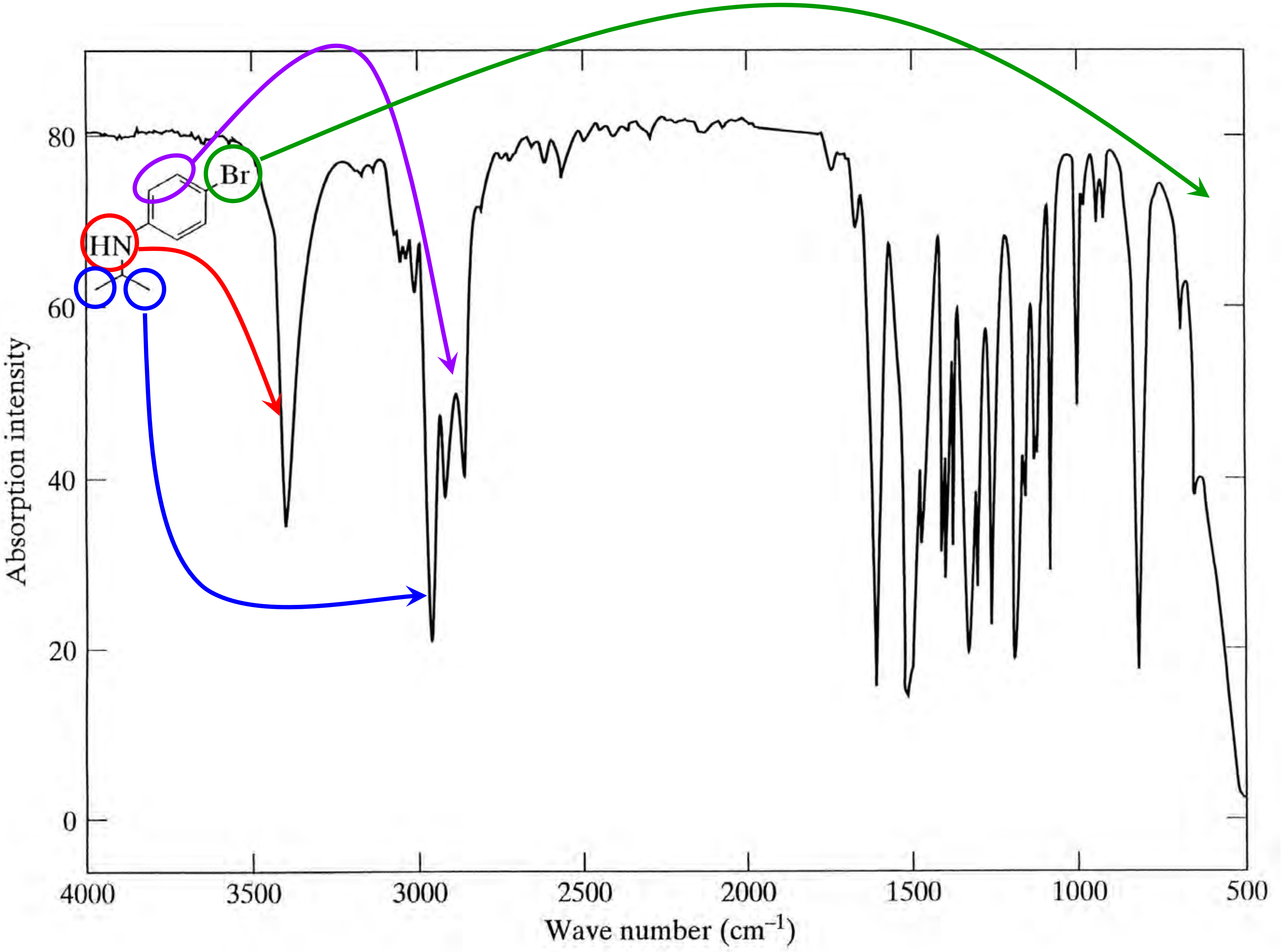
Infrared spectrum of 2-methyl-2-phenylpropanol from L. M. Raff, *Principles of Physical Chemistry*, 2001, p. 869.

Infrared Spectroscopy for Chemical Identification



Infrared spectrum 2-methyl-2-(4-methylphenyl) propanonitrile from L. M. Raff, *Principles of Physical Chemistry*, 2001, p. 895.

Infrared Spectroscopy for Chemical Identification



Infrared spectrum 4-bromo-*N*-isopropylaniline from L. M. Raff, *Principles of Physical Chemistry*, 2001, p. 895.

Infrared Photons Emitted by Ambient Objects

The Electromagnetic Spectrum

frequency, ν (cycles/sec)	band name	phenomenon	photon energy = hν		wavelength	wavenumber	source
			eV	kJ/mol	$\lambda = c/\nu$	$\tilde{\nu} = 1/\lambda$	temperature*
10^{23}	cosmic rays	supernovae	4×10^{8}		3 fm		10^{12} K
10^{22}	gamma rays	nuclear decay	4×10^{7}		30 fm		10^{11} K
10^{21}			4×10^{6}		0.3 pm		10^{10} K
10^{20}	x rays	ejection of core electrons	4×10^{5}		3 pm		10^{9} K
10^{19}			4×10^{4}		30 pm		10^{8} K
10^{18}			4×10^{3}		0.3 nm		10^{7} K
10^{17}	ultraviolet	excitation of valence electrons	400	40,000	3 nm		10^{6} K
10^{16}			40	4000	30 nm		10^{5} K
10^{15}	visible light		4	400	0.3 μm		10^{4} K
10^{14}	infrared	molecular vibrational levels	0.4	40	3 μm	3000 cm^{-1}	10^{3} K
10^{13}			0.04	4	30 μm	300 cm^{-1}	100 K
10^{12}				0.4	0.3 mm	30 cm^{-1}	10 K
10^{11}	microwaves	molecular rotational levels		0.04	3 mm	3 cm^{-1}	1 K
10^{10}					3 cm		0.1 K
10^{9}					30 cm		10 mK
10^{8}	radio waves	TV, FM radio, computer chips, shortwave radio, AM radio			3 m		1 mK
10^{7}					30 m		
10^{6}					300 m		
10^{5}					3 km		
10^{4}	power	ac electricity			30 km		
10^{3}					300 km		
100					3×10^{3} km		
10					3×10^{4} km		
1					3×10^{5} km		

298K

$1 \text{ eV} = 1.60 \times 10^{-19} \text{ J} = 8066 \text{ cm}^{-1}$

*temperature of a body that will emit photons chiefly at this energy. The maximum of the Planck distribution, $T = h\nu/(5k)$