The Abdus Salam International Centre for Theoretical Physics

IAEA International Atomic Energy Agency
*Atoms for Peace*

# Molecular Spectroscopy 2

Christian Hill

Joint ICTP-IAEA School on Atomic and Molecular Spectroscopy in Plasmas

6 – 10 May 2019

Trieste, Italy

# Vibrational spectroscopy

# Vibrational spectroscopy

THE ASTROPHYSICAL JOURNAL

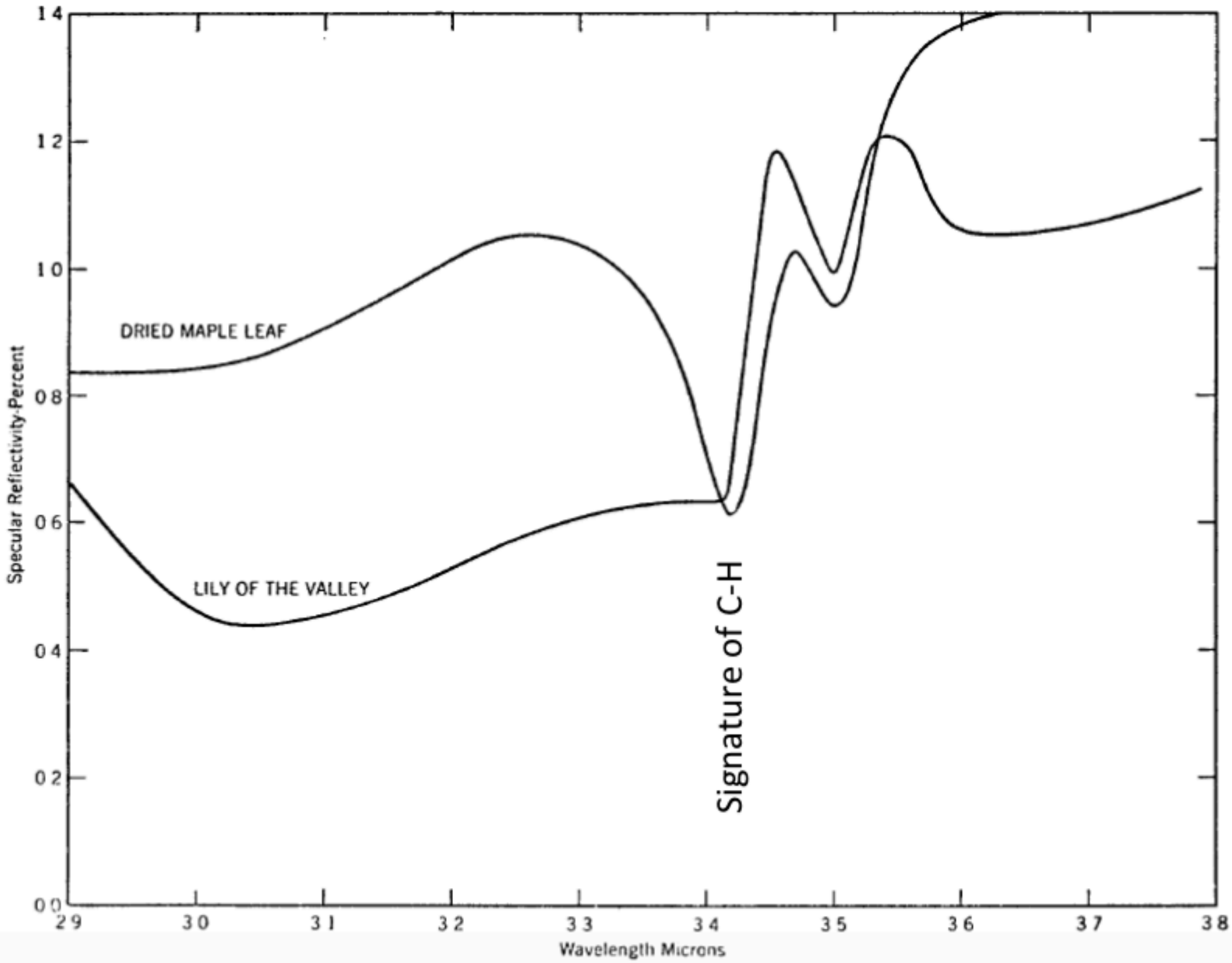
AN INTERNATIONAL REVIEW OF SPECTROSCOPY AND ASTRONOMICAL PHYSICS

VOLUME 126 SEPTEMBER 1957 NUMBER 2

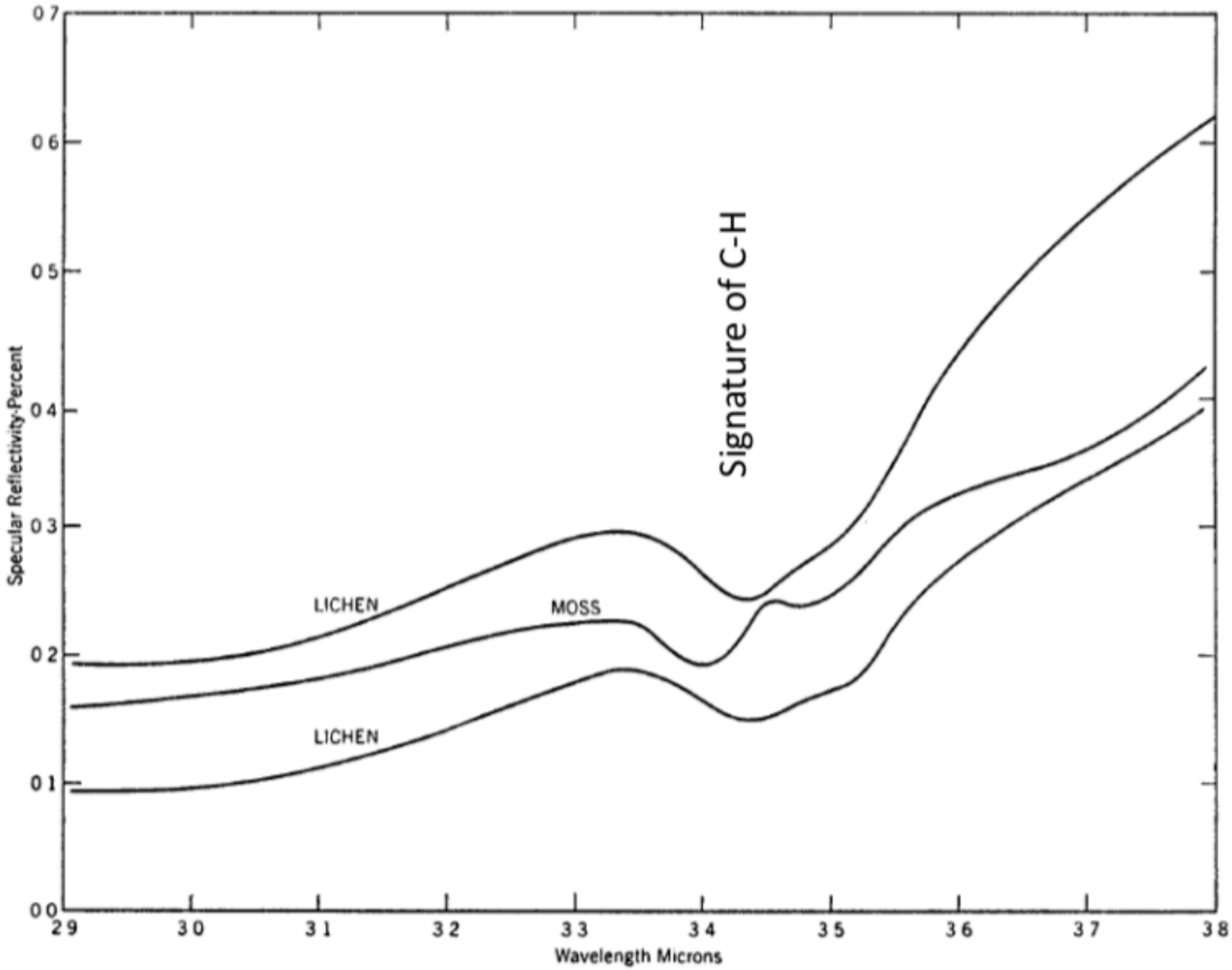
## SPECTROSCOPIC EVIDENCE FOR VEGETATION ON MARS

WILLIAM M. SINTON
Smithsonian Astrophysical Observatory
*Received May 6, 1957*

# Vibrational spectroscopy



# Vibrational spectroscopy



# Vibrational spectroscopy

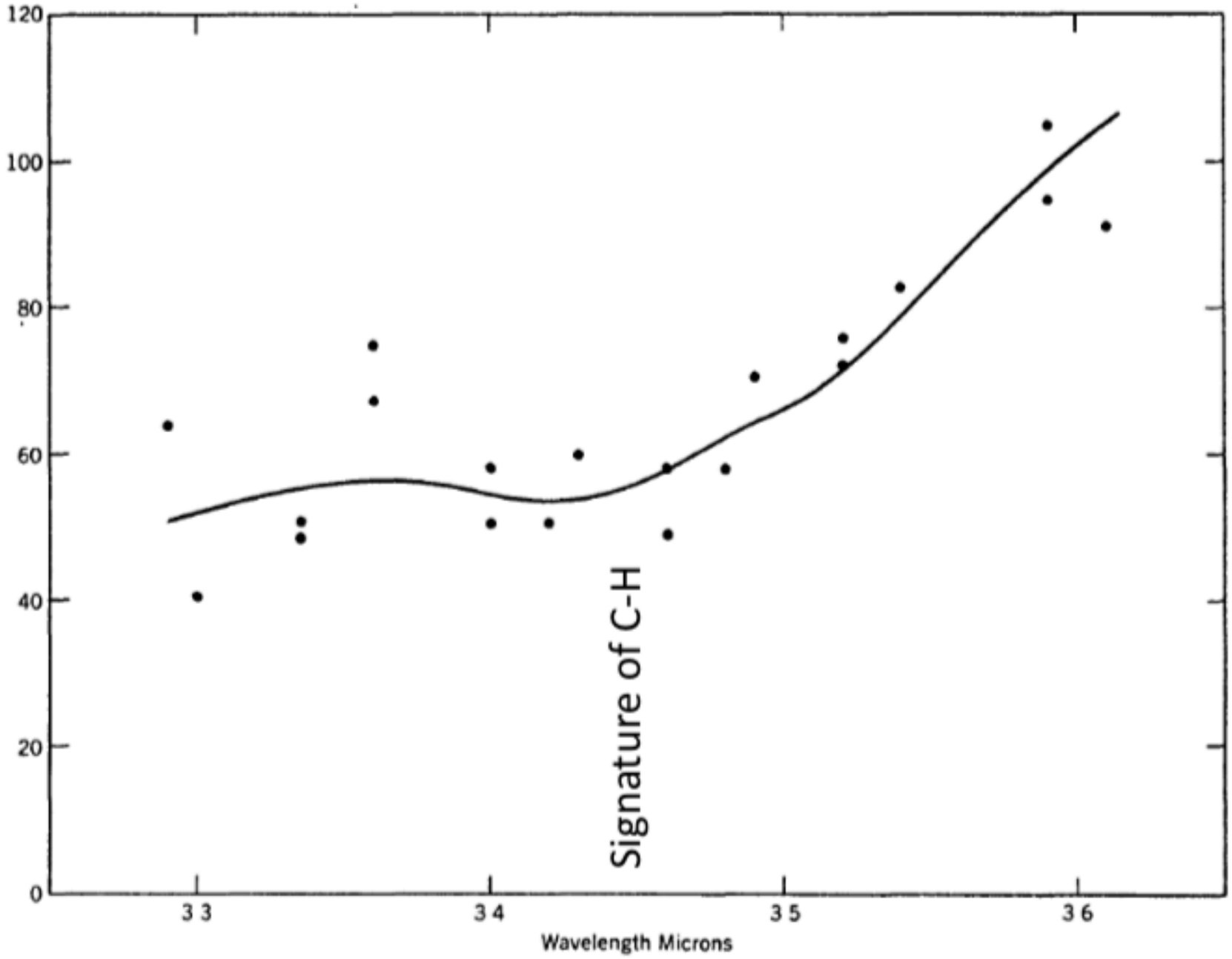
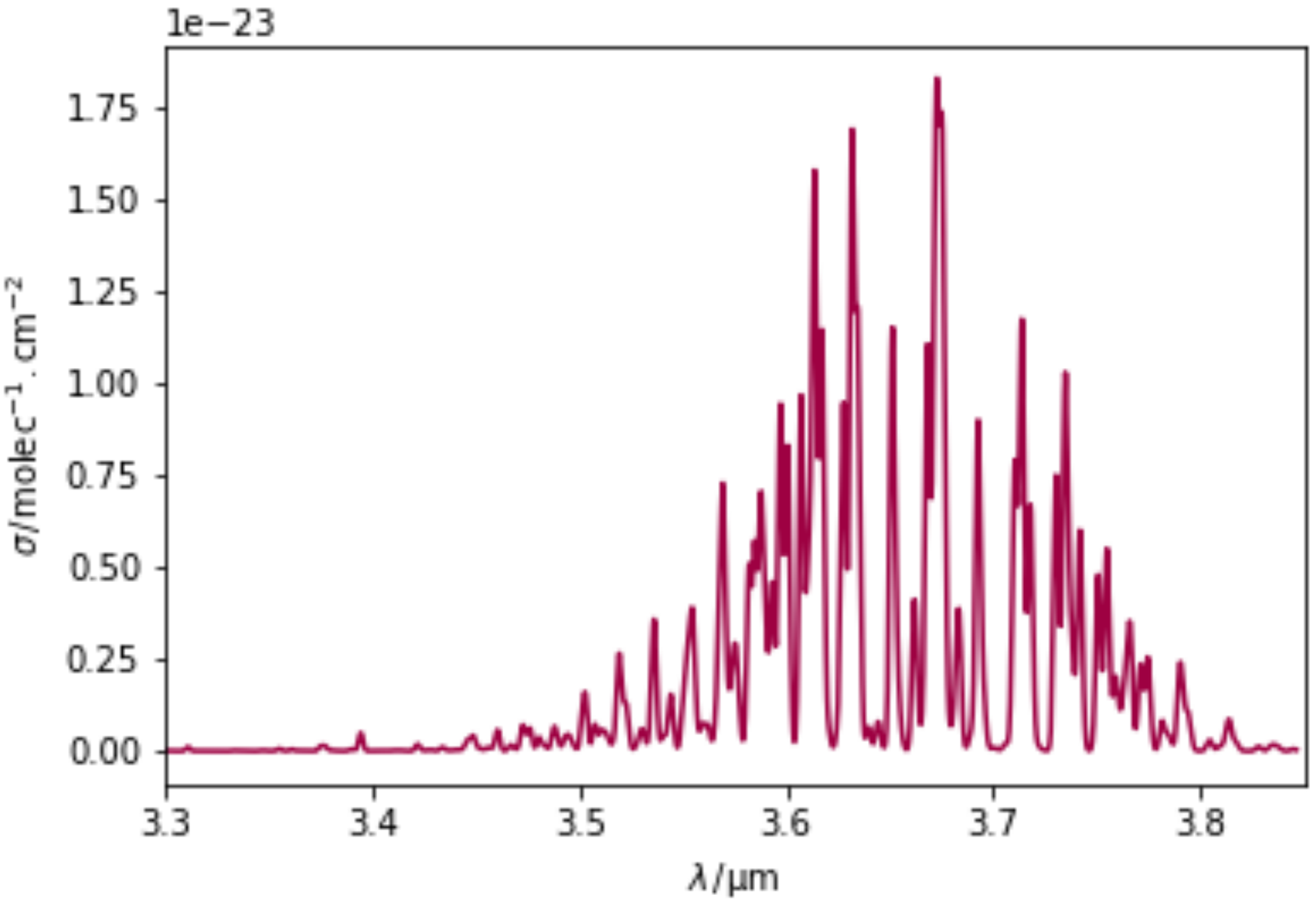



FIG. 3.—Observations of the spectrum of Mars obtained on four nights and after division by the solar spectrum (*solid curve* of Fig. 2).

# Vibrational spectroscopy

Telluric HDO!



# Vibrational motion

- First consider the the vibration of a non-rotating molecule:

$$\frac{1}{R^2}\frac{\mathrm{d}}{\mathrm{d}R}\left(R^2\frac{\mathrm{d}S}{\mathrm{d}R}\right)+\frac{2\mu}{\hbar^2}\left(E-V_n(R)-\frac{J(J+1)\hbar^2}{2\mu R^2}\right)S=0$$

becomes:

$$\frac{1}{R^2}\frac{\mathrm{d}}{\mathrm{d}R}\left(R^2\frac{\mathrm{d}S}{\mathrm{d}R}\right)+\frac{2\mu}{\hbar^2}(E-V_n(R))\,S=0$$

# Vibrational motion

- First consider the the vibration of a non-rotating molecule:

$$\frac{1}{R^2}\frac{\mathrm{d}}{\mathrm{d}R}\left(R^2\frac{\mathrm{d}S}{\mathrm{d}R}\right)+\frac{2\mu}{\hbar^2}\left(E-V_n(R)-\frac{J(J+1)\hbar^2}{2\mu R^2}\right)S=0$$

  becomes:

$$\frac{1}{R^2}\frac{\mathrm{d}}{\mathrm{d}R}\left(R^2\frac{\mathrm{d}S}{\mathrm{d}R}\right)+\frac{2\mu}{\hbar^2}(E-V_n(R))\,S=0$$

- $V_n(R)$ is in general a complex function that depends on the electronic wavefunction, but for small displacements from $R_e$:

$$V_n(R)=V_n(R_e)+\left.\frac{\mathrm{d}V_n}{\mathrm{d}R}\right|_{R_e}(R-R_e)+\frac{1}{2}\left.\frac{\mathrm{d}^2V_n}{\mathrm{d}R^2}\right|_{R_e}(R-R_e)^2+\cdots$$

# Vibrational motion

$$V_n(R) = V_n(R_e) + \left.\frac{\mathrm{d}V_n}{\mathrm{d}R}\right|_{R_e} (R - R_e) + \frac{1}{2}\left.\frac{\mathrm{d}^2V_n}{\mathrm{d}R^2}\right|_{R_e} (R - R_e)^2 + \cdots$$

- We can choose the first term to be zero

# Vibrational motion

$$V_n(R) = V_n(R_e) + \left.\frac{\mathrm{d}V_n}{\mathrm{d}R}\right|_{R_e} (R - R_e) + \frac{1}{2}\left.\frac{\mathrm{d}^2 V_n}{\mathrm{d}R^2}\right|_{R_e} (R - R_e)^2 + \cdots$$

- We can choose the first term to be zero
- The second term *is* zero

# Vibrational motion

$$V_n(R) = V_n(R_e) + \left.\frac{\mathrm{d}V_n}{\mathrm{d}R}\right|_{R_e} (R - R_e) + \frac{1}{2}\left.\frac{\mathrm{d}^2 V_n}{\mathrm{d}R^2}\right|_{R_e} (R - R_e)^2 + \cdots$$

- We can choose the first term to be zero
- The second term *is* zero
- We can define the “bond force constant”:

$$k = \left.\frac{\mathrm{d}^2 V_n}{\mathrm{d}R^2}\right|_{R_e}$$

# Vibrational motion

$$V_n(R) = V_n(R_e) + \left.\frac{dV_n}{dR}\right|_{R_e} (R - R_e) + \frac{1}{2}\left.\frac{d^2V_n}{dR^2}\right|_{R_e} (R - R_e)^2 + \cdots$$

- We can choose the first term to be zero
- The second term *is* zero
- We can define the “bond force constant”:

$$k = \left.\frac{d^2V_n}{dR^2}\right|_{R_e}$$

- So:

$$V_n(R) \approx \frac{1}{2}k(R - Re)^2$$

(the parabolic potential used earlier)

# Vibrational motion

- Within this approximation:

$$\frac{1}{R^2}\frac{\mathrm{d}}{\mathrm{d}R}\left(R^2\frac{\mathrm{d}S}{\mathrm{d}R}\right)+\frac{2\mu}{\hbar^2}\left(E-\frac{1}{2}k(R-R_e)^2\right)S=0$$

# Vibrational motion

- Within this approximation:

$$\frac{1}{R^2}\frac{\mathrm{d}}{\mathrm{d}R}\left(R^2\frac{\mathrm{d}S}{\mathrm{d}R}\right)+\frac{2\mu}{\hbar^2}\left(E-\frac{1}{2}k(R-R_e)^2\right)S=0$$

- Make the substitution:

$$S(R)=\frac{\psi(x)}{x+R_e},\quad \text{where } x=R-R_e$$

is the displacement of the nuclei from equilibrium to get:

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\psi}{\mathrm{d}x}+\frac{1}{2}kx^2=E\psi$$

# Vibrational motion

- Within this approximation:

$$\frac{1}{R^2}\frac{\mathrm{d}}{\mathrm{d}R}\left(R^2\frac{\mathrm{d}S}{\mathrm{d}R}\right)+\frac{2\mu}{\hbar^2}\left(E-\frac{1}{2}k(R-R_e)^2\right)S=0$$

- Make the substitution:

$$S(R)=\frac{\psi(x)}{x+R_e},\quad \text{where } x=R-R_e$$

  is the displacement of the nuclei from equilibrium to get:

$$-\frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2\psi}{\mathrm{d}x}+\frac{1}{2}kx^2=E\psi$$

- Harmonic motion with frequency $\omega=\sqrt{k/\mu}$

# Vibrational motion

- Further transformation to “natural units”: $q = \left(\mu k/\hbar^2\right)^{1/4} x$

$$-\frac{1}{2}\frac{\mathrm{d}^2\psi}{\mathrm{d}q} + \frac{1}{2}q^2 = \frac{E}{\hbar\omega}\psi$$

# Vibrational motion

- Further transformation to “natural units”: $q = \left(\mu k/\hbar^2\right)^{1/4} x$

$$-\frac{1}{2}\frac{\mathrm{d}^2\psi}{\mathrm{d}q} + \frac{1}{2}q^2 = \frac{E}{\hbar\omega}\psi$$

- The energy levels are quantized in terms of a quantum number, $v = 0, 1, 2, \ldots$

$$E_v = \hbar\omega(v + \frac{1}{2})$$

# Vibrational motion

- Further transformation to "natural units": $q = \left(\mu k/\hbar^2\right)^{1/4} x$

$$-\frac{1}{2}\frac{\mathrm{d}^2\psi}{\mathrm{d}q} + \frac{1}{2}q^2 = \frac{E}{\hbar\omega}\psi$$

- The energy levels are quantized in terms of a quantum number, $v = 0, 1, 2, \ldots$

$$E_v = \hbar\omega(v + \frac{1}{2})$$

- The wavefunctions have the form:

$$\psi(q) = N_v H_v(q) \exp\left(-q^2/2\right),$$

where $N_v$ is a normalization constant and $H_v(q)$ is a *Hermite polynomial.*

# The Hermite polynomials

- Starting with:

$$-\frac{1}{2}\frac{\mathrm{d}^2\psi}{\mathrm{d}q} + \frac{1}{2}q^2 = \frac{E}{\hbar\omega}\psi$$

define $C = 2E/\hbar\omega$ and rearrange:

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}q^2} + (C - q^2)\psi = 0$$

# The Hermite polynomials

- Starting with:

$$-\frac{1}{2}\frac{\mathrm{d}^2\psi}{\mathrm{d}q}+\frac{1}{2}q^2=\frac{E}{\hbar\omega}\psi$$

define $C=2E/\hbar\omega$ and rearrange:

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}q^2}+(C-q^2)\psi=0$$

- For $C=1$ (*i.e.* $E_0=\frac{1}{2}\hbar\omega$) the solution is $\psi_0(q)=N_0e^{-q^2/2}$

# The Hermite polynomials

- Starting with:

$$-\frac{1}{2}\frac{\mathrm{d}^2\psi}{\mathrm{d}q}+\frac{1}{2}q^2=\frac{E}{\hbar\omega}\psi$$

define $C=2E/\hbar\omega$ and rearrange:

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}q^2}+(C-q^2)\psi=0$$

- For $C=1$ (*i.e.* $E_0=\frac{1}{2}\hbar\omega$) the solution is $\psi_0(q)=N_0e^{-q^2/2}$
- This is the *ground state* (and $E$ is *non-zero*)

# The Hermite polynomials

- Starting with:

$$-\frac{1}{2}\frac{\mathrm{d}^2\psi}{\mathrm{d}q}+\frac{1}{2}q^2=\frac{E}{\hbar\omega}\psi$$

define $C=2E/\hbar\omega$ and rearrange:

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}q^2}+(C-q^2)\psi=0$$

- For $C=1$ (*i.e.* $E_0=\frac{1}{2}\hbar\omega$) the solution is $\psi_0(q)=N_0e^{-q^2/2}$
- This is the *ground state* (and $E$ is *non-zero*)
- The more general ansatz is $\psi_v(q)=H_v(q)e^{-q^2/2}$ where $H_v(q)$ is some finite polynomial which must satisfy

$$\frac{\mathrm{d}^2H_v}{\mathrm{d}q^2}-2q\frac{\mathrm{d}H_v}{\mathrm{d}q}+(C-1)H=0.$$

# The Hermite polynomials

$$\frac{\mathrm{d}^2 H_v}{\mathrm{d}q^2} - 2q\frac{\mathrm{d}H_v}{\mathrm{d}q} + (C-1)H = 0.$$

- This equation is well known and its solutions are the Hermite polynomials, defined by

$$H_v(q) = (-1)^v e^{q^2} \frac{\mathrm{d}^v}{\mathrm{d}q^v}\left(e^{-q^2}\right),$$

where $v = 0, 1, 2, \ldots$

# The Hermite polynomials

$$\frac{\mathrm{d}^2 H_v}{\mathrm{d}q^2} - 2q\frac{\mathrm{d}H_v}{\mathrm{d}q} + (C-1)H = 0.$$

- This equation is well known and its solutions are the Hermite polynomials, defined by

$$H_v(q) = (-1)^v e^{q^2} \frac{\mathrm{d}^v}{\mathrm{d}q^v}\left(e^{-q^2}\right),$$

  where $v = 0, 1, 2, \ldots$

- $H_v(q)$ are orthogonal with respect to the weight function $e^{-q^2}$

$$\int_{-\infty}^{\infty} H_m(q) H_n(q) e^{-q^2}\,\mathrm{d}q = \sqrt{\pi} 2^q q! \delta_{nm},$$

# The Hermite polynomials

$$\frac{\mathrm{d}^2 H_v}{\mathrm{d}q^2} - 2q\frac{\mathrm{d}H_v}{\mathrm{d}q} + (C-1)H = 0.$$

- This equation is well known and its solutions are the Hermite polynomials, defined by

$$H_v(q) = (-1)^v e^{q^2} \frac{\mathrm{d}^v}{\mathrm{d}q^v}\left(e^{-q^2}\right),$$

  where $v = 0, 1, 2, \ldots$

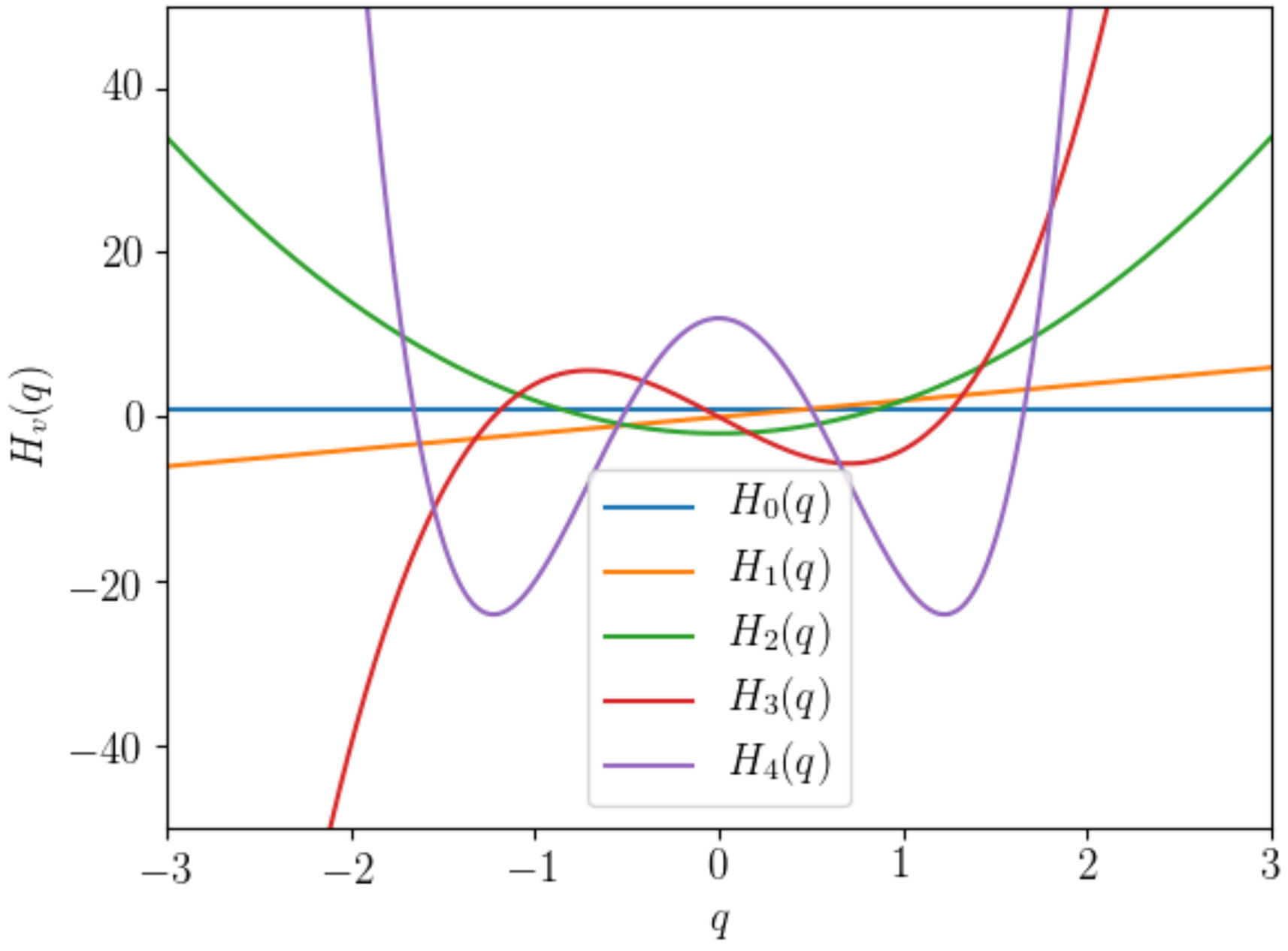
- $H_v(q)$ are orthogonal with respect to the weight function $e^{-q^2}$

$$\int_{-\infty}^{\infty} H_m(q) H_n(q) e^{-q^2}\,\mathrm{d}q = \sqrt{\pi} 2^q q! \delta_{nm},$$

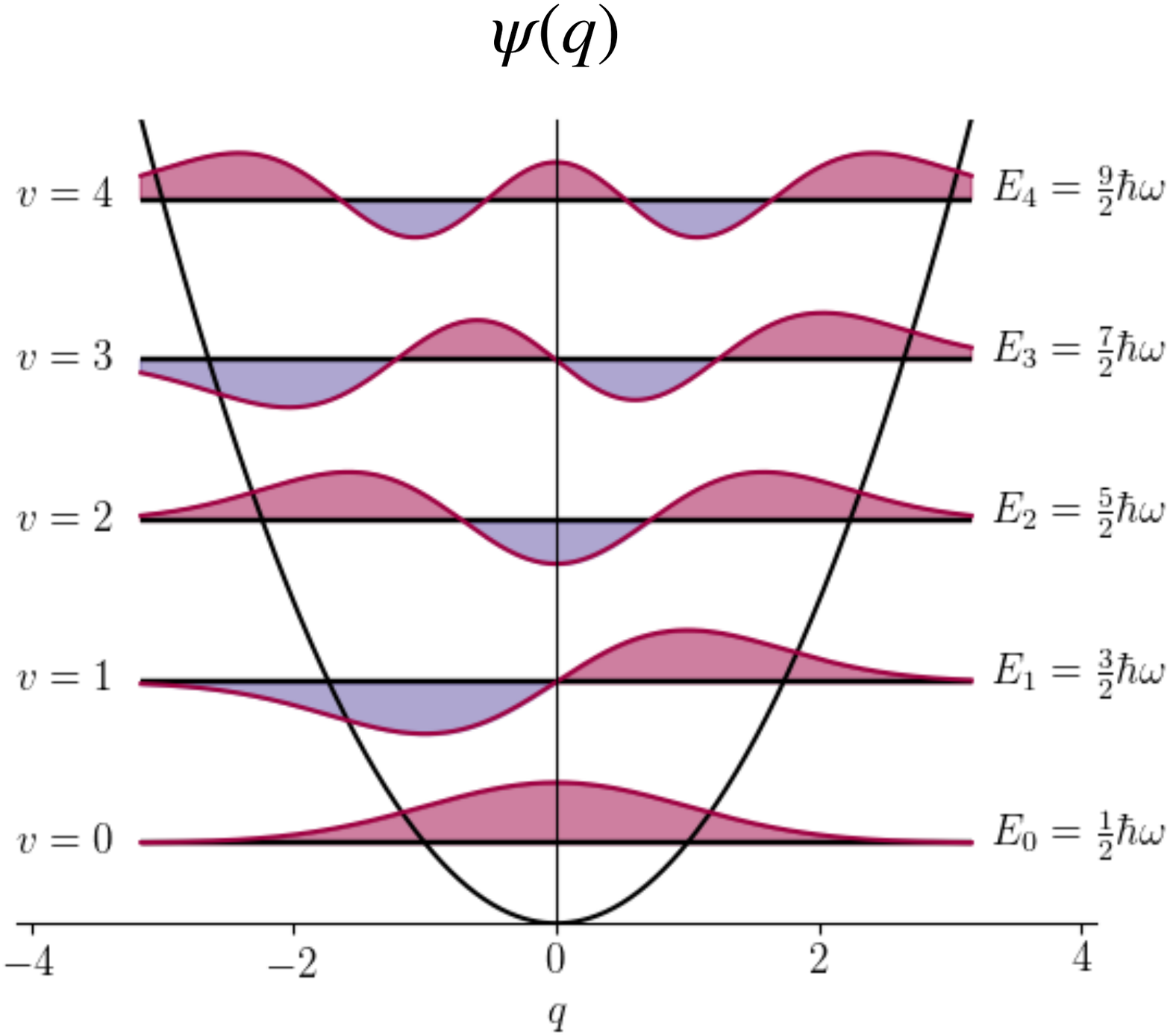
- And obey the recursion relation:

$$H_{n+1}(q) = 2qH_n(q) - 2nH_{n-1}(q).$$

# The Hermite polynomials

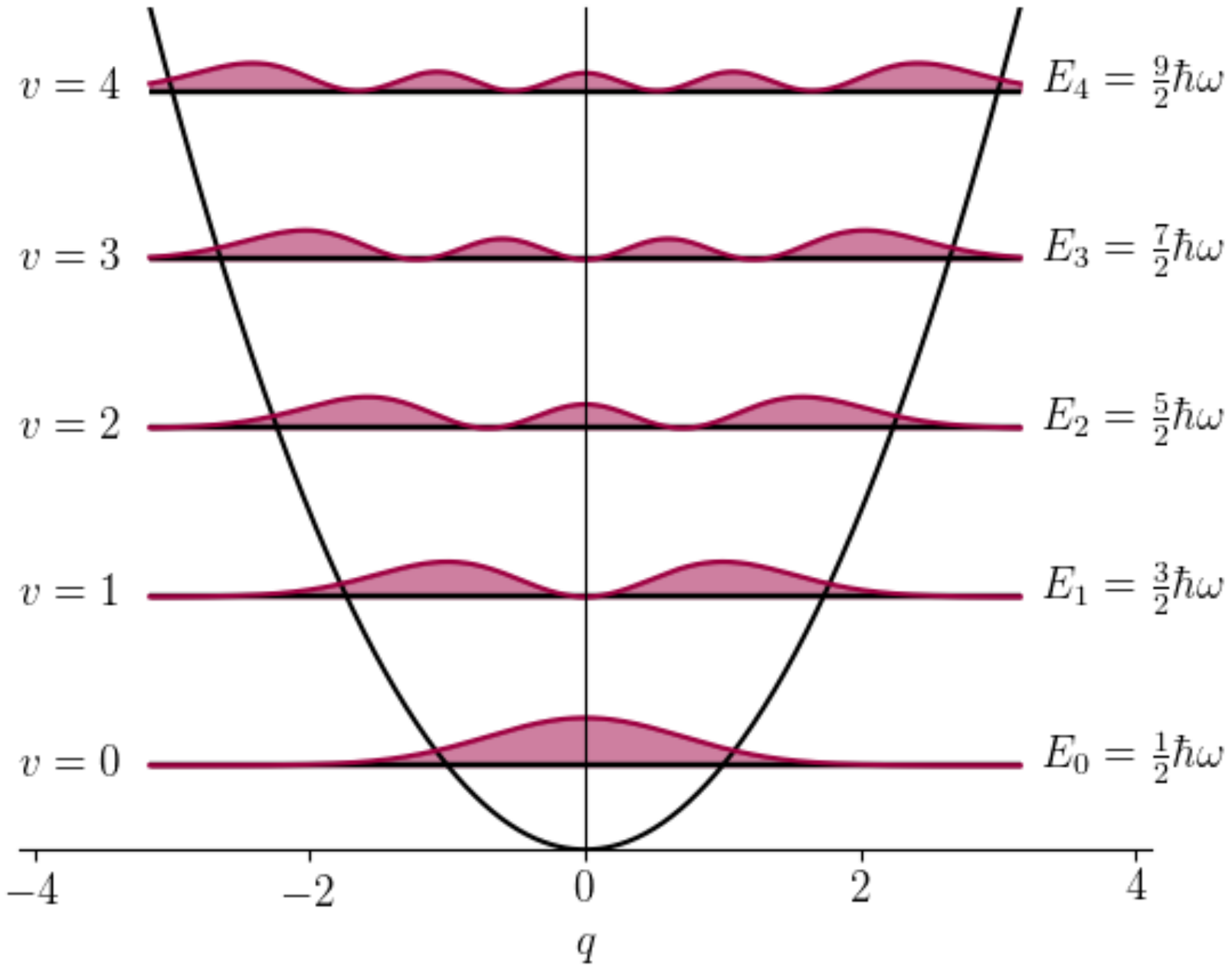


# Harmonic oscillator wavefunctions

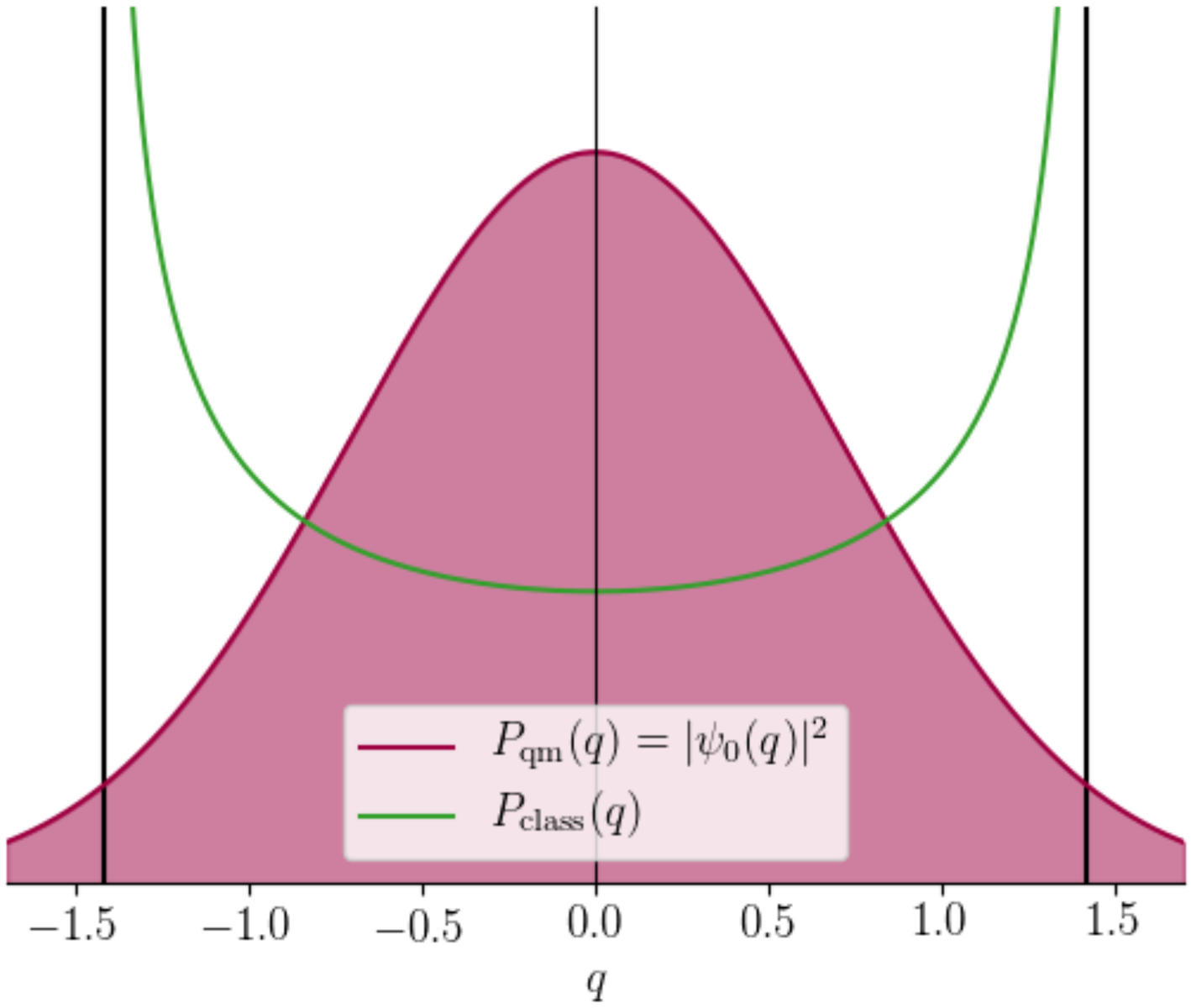


# Harmonic oscillator probabilities

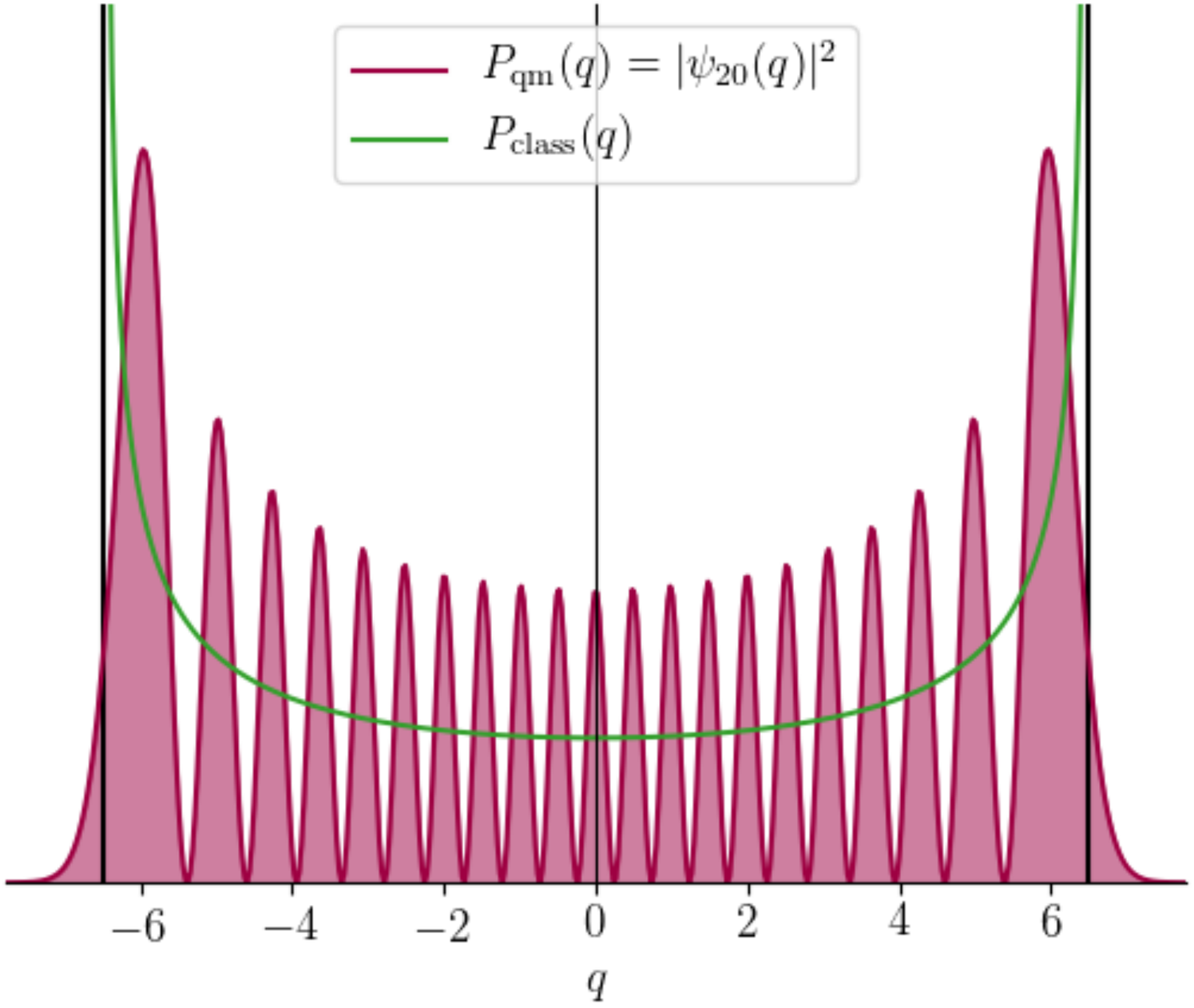
$$|\psi(q)|^2$$



# Harmonic oscillator probabilities



# Harmonic oscillator probabilities



# Harmonic vibrational transitions

- The transition probability from one vibrational state, $v''$ to another $v'$ is the square of the transition dipole moment:

$$M_{v'v''} = \int_{-\infty}^{\infty} \psi_{v'}^{*} \hat{\mu}(q) \psi_{v''} \, \mathrm{d}q.$$

# Harmonic vibrational transitions

- The transition probability from one vibrational state, $v''$ to another $v'$ is the square of the transition dipole moment:

$$M_{v'v''} = \int_{-\infty}^{\infty} \psi_{v'}^{*} \hat{\mu}(q) \psi_{v''} \, \mathrm{d}q.$$

- The dipole moment operator is a complex function of $q$ but may be expanded in a Taylor series:

$$\hat{\mu} = \mu_0 + \left.\frac{\mathrm{d}\mu}{\mathrm{d}q}\right|_0 q + \cdots$$

# Harmonic vibrational transitions

- The transition probability from one vibrational state, $v''$ to another $v'$ is the square of the transition dipole moment:

$$M_{v'v''} = \int_{-\infty}^{\infty} \psi_{v'}^{*} \hat{\mu}(q) \psi_{v''} \, \mathrm{d}q.$$

- The dipole moment operator is a complex function of $q$ but may be expanded in a Taylor series:

$$\hat{\mu} = \mu_0 + \left.\frac{\mathrm{d}\mu}{\mathrm{d}q}\right|_0 q + \cdots$$

- Therefore,

$$M_{v'v''} = \mu_0 \int_{-\infty}^{\infty} \psi_{v'}^{*} \psi_{v''} \, \mathrm{d}q + \left.\frac{\mathrm{d}\mu}{\mathrm{d}q}\right|_0 \int_{-\infty}^{\infty} \psi_{v'}^{*} \cdot q \cdot \psi_{v''} \, \mathrm{d}q$$

# Harmonic vibrational transitions

- The transition probability from one vibrational state, $v''$ to another $v'$ is the square of the transition dipole moment:

$$M_{v'v''} = \int_{-\infty}^{\infty} \psi_{v'}^{*} \hat{\mu}(q) \psi_{v''} \, \mathrm{d}q.$$

- The dipole moment operator is a complex function of $q$ but may be expanded in a Taylor series:

$$\hat{\mu} = \mu_0 + \left.\frac{\mathrm{d}\mu}{\mathrm{d}q}\right|_0 q + \cdots$$

- Therefore,

$$M_{v'v''} = \mu_0 \int_{-\infty}^{\infty} \psi_{v'}^{*} \psi_{v''} \, \mathrm{d}q + \left.\frac{\mathrm{d}\mu}{\mathrm{d}q}\right|_0 \int_{-\infty}^{\infty} \psi_{v'}^{*} \cdot q \cdot \psi_{v''} \, \mathrm{d}q$$

$$M_{v'v''} = \left.\frac{\mathrm{d}\mu}{\mathrm{d}q}\right|_0 N_{v''} N_{v'} \int_{-\infty}^{\infty} e^{-q^2} H_{v''}(q) q H_{v'} \, \mathrm{d}q.$$

# Harmonic vibrational transitions

$$M_{v'v''} = \left.\frac{\mathrm{d}\mu}{\mathrm{d}q}\right|_0 N_{v''} N_{v'} \int_{-\infty}^{\infty} e^{-q^2} H_{v''}(q) q H_{v'} \, \mathrm{d}q.$$

# Harmonic vibrational transitions

$$M_{v'v''} = \left.\frac{\mathrm{d}\mu}{\mathrm{d}q}\right|_0 N_{v''} N_{v'} \int_{-\infty}^{\infty} e^{-q^2} H_{v''}(q) q H_{v'}\, \mathrm{d}q.$$

- From the recursion relation $H_{n+1}(q) = 2qH_n(q) - 2nH_{n-1}(q).$

$$M_{v'v''} = \left.\frac{\mathrm{d}\mu}{\mathrm{d}q}\right|_0 N_{v''} N_{v'} \int_{-\infty}^{\infty} e^{-q^2} \left[\frac{1}{2} H_{v''+1}(q) + v'' H_{v''-1}(q)\right] H_{v''}(q)\, \mathrm{d}q,$$

# Harmonic vibrational transitions

$$M_{v'v''} = \left.\frac{d\mu}{dq}\right|_0 N_{v''} N_{v'} \int_{-\infty}^{\infty} e^{-q^2} H_{v''}(q) q H_{v'}\, dq.$$

- From the recursion relation $H_{n+1}(q) = 2qH_n(q) - 2nH_{n-1}(q).$

$$M_{v'v''} = \left.\frac{d\mu}{dq}\right|_0 N_{v''} N_{v'} \int_{-\infty}^{\infty} e^{-q^2} \left[\frac{1}{2} H_{v''+1}(q) + v'' H_{v''-1}(q)\right] H_{v''}(q)\, dq,$$

- The “selection rules” are:

$$\left.\frac{d\mu}{dq}\right|_0 \neq 0 \quad \text{and } \Delta v = v' - v'' = \pm 1.$$

# Harmonic vibrational transitions

$$M_{v'v''} = \left.\frac{d\mu}{dq}\right|_0 N_{v''} N_{v'} \int_{-\infty}^{\infty} e^{-q^2} H_{v''}(q) q H_{v'}\, dq.$$

- From the recursion relation $H_{n+1}(q) = 2qH_n(q) - 2nH_{n-1}(q).$

$$M_{v'v''} = \left.\frac{d\mu}{dq}\right|_0 N_{v''} N_{v'} \int_{-\infty}^{\infty} e^{-q^2} \left[\frac{1}{2} H_{v''+1}(q) + v'' H_{v''-1}(q)\right] H_{v''}(q)\, dq,$$

- The "selection rules" are:

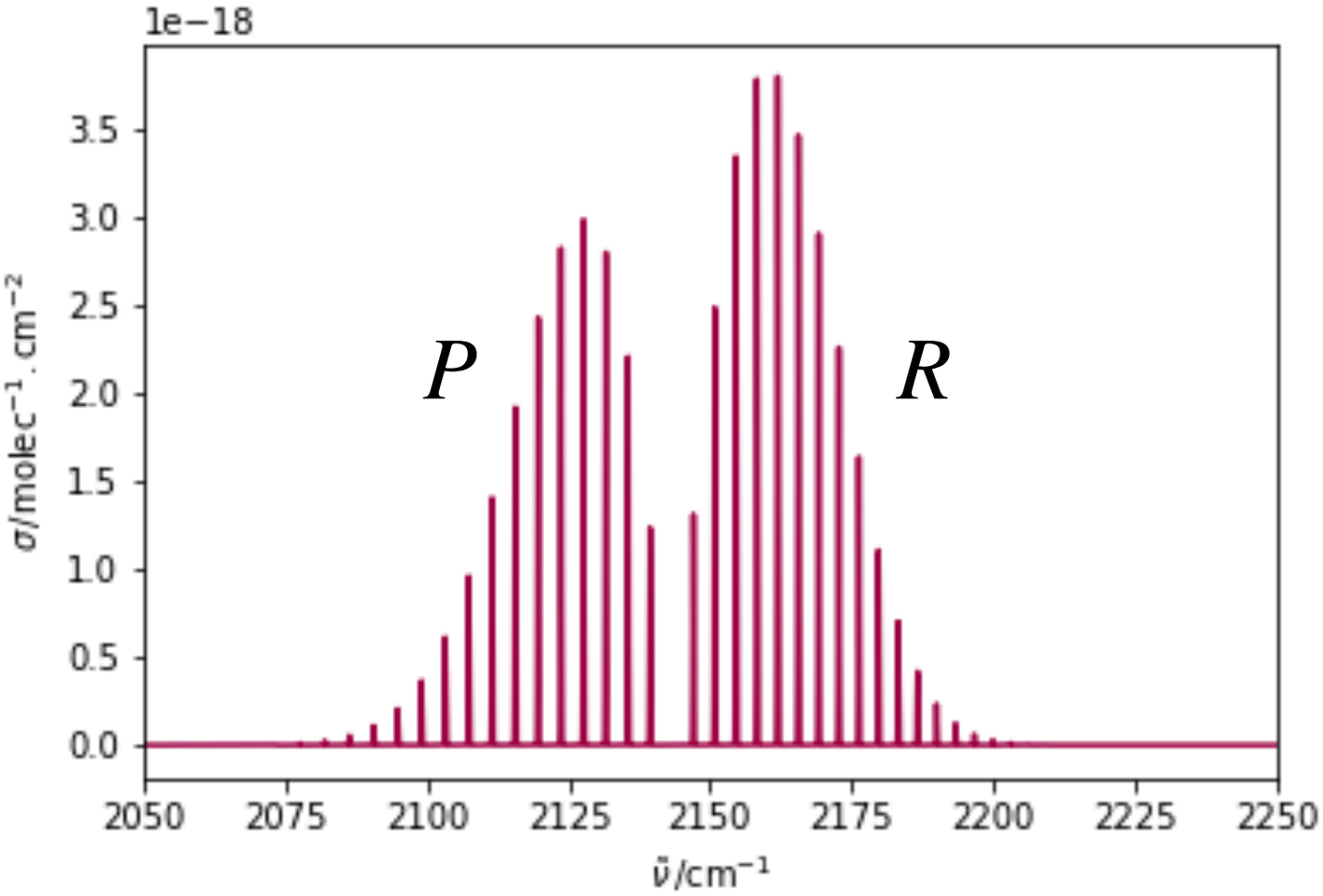
$$\left.\frac{d\mu}{dq}\right|_0 \neq 0 \quad \text{and} \quad \Delta v = v' - v'' = \pm 1.$$

"gross" selection rule

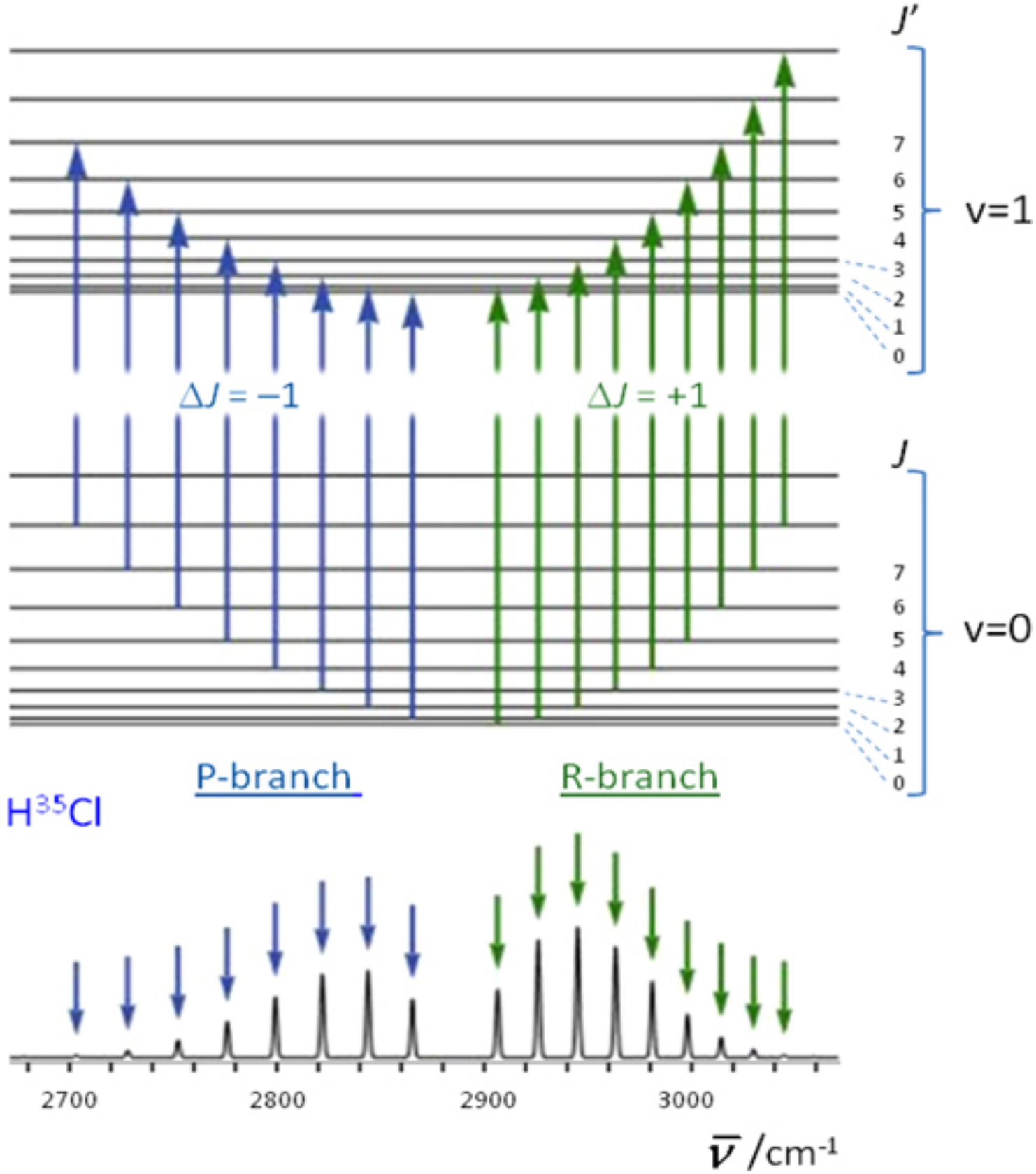
- *Homonuclear diatomic molecules (e.g. $H_2$) do not have an electric-dipole allowed vibrational spectrum*

# Rovibrational transitions

- Further selection rule on $J$: $\Delta J = \pm 1$
- P ($\Delta J = -1$) and R ($\Delta J = +1$) branches:
- e.g. CO fundamental band: $v = 1 \leftarrow 0$



# Rovibrational transitions



# Anharmonic vibrations

- The harmonic potential deviates from the real interatomic potential at higher energies …
- … and does not allow for dissociation

# Anharmonic vibrations

- The harmonic potential deviates from the real interatomic potential at higher energies …
- … and does not allow for dissociation
- A better approximation is provided by the *Morse potential*:

$$V(x) = D_e \left[1 - e^{-ax}\right]^2$$

# Anharmonic vibrations

- The harmonic potential deviates from the real interatomic potential at higher energies …
- … and does not allow for dissociation
- A better approximation is provided by the *Morse potential*:

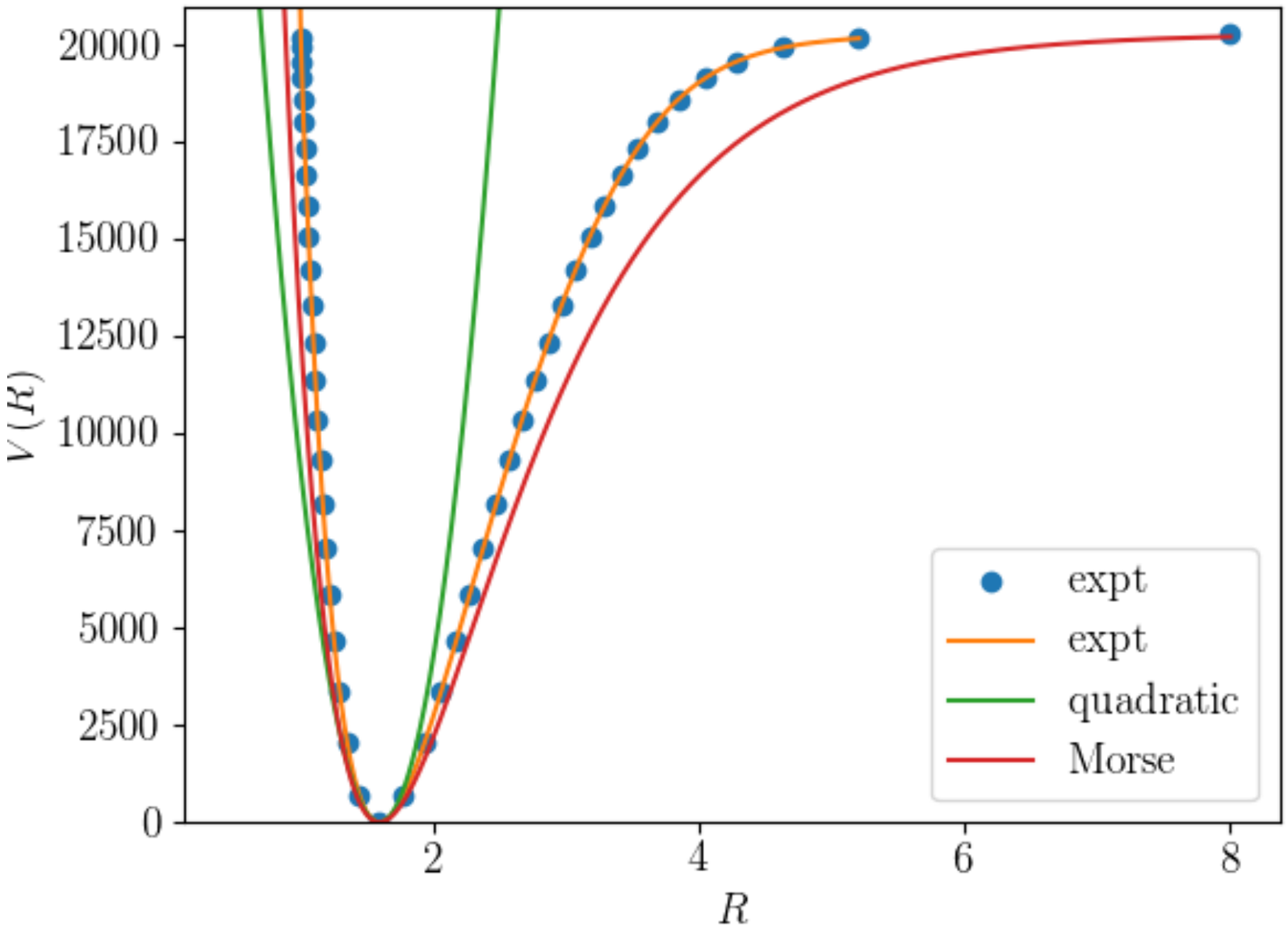
$$V(x) = D_e \left[1 - e^{-ax}\right]^2$$

- Morse term values in terms of constants $\omega_e$ and $\omega_e x_e$ (which can be related to $D_e$, $a$):

$$F(v) = \omega_e (v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2$$

# The Morse potential

- $^{7}Li^{1}H$:



# Vibration-rotation interaction

- Real molecules vibrate and rotate at the same time
- When a molecule vibrates its moment of inertia, $I = \mu R^2$, changes

# Vibration-rotation interaction

- The vibrational frequency is typically 10 – 100× faster than the rotational frequency

# Vibration-rotation interaction

- The vibrational frequency is typically 10 – 100× faster than the rotational frequency
- To a first approximation we may consider the rotational energy as a time-average over a vibrational period:

$$\langle E_{\mathrm{rot}}(J;v)\rangle = \frac{\hbar^2 J(J+1)}{2\mu}\left\langle \frac{1}{R^2} \right\rangle$$

$$\left\langle \frac{1}{R^2} \right\rangle = \int_{-\infty}^{\infty} \psi_v^* \frac{1}{R^2} \psi_v \mathrm{d}R$$

# Vibration-rotation interaction

- The vibrational frequency is typically 10 – 100× faster than the rotational frequency
- To a first approximation we may consider the rotational energy as a time-average over a vibrational period:

$$\langle E_{\mathrm{rot}}(J;v)\rangle = \frac{\hbar^2 J(J+1)}{2\mu}\left\langle \frac{1}{R^2} \right\rangle$$

$$\left\langle \frac{1}{R^2} \right\rangle = \int_{-\infty}^{\infty} \psi_v^* \frac{1}{R^2} \psi_v \mathrm{d}R$$

- Hence:

$$B_v = \frac{h}{8\pi^2 c\mu}\left\langle \frac{1}{R^2} \right\rangle$$

# Vibration-rotation interaction

- The vibrational frequency is typically 10 – 100× faster than the rotational frequency
- To a first approximation we may consider the rotational energy as a time-average over a vibrational period:

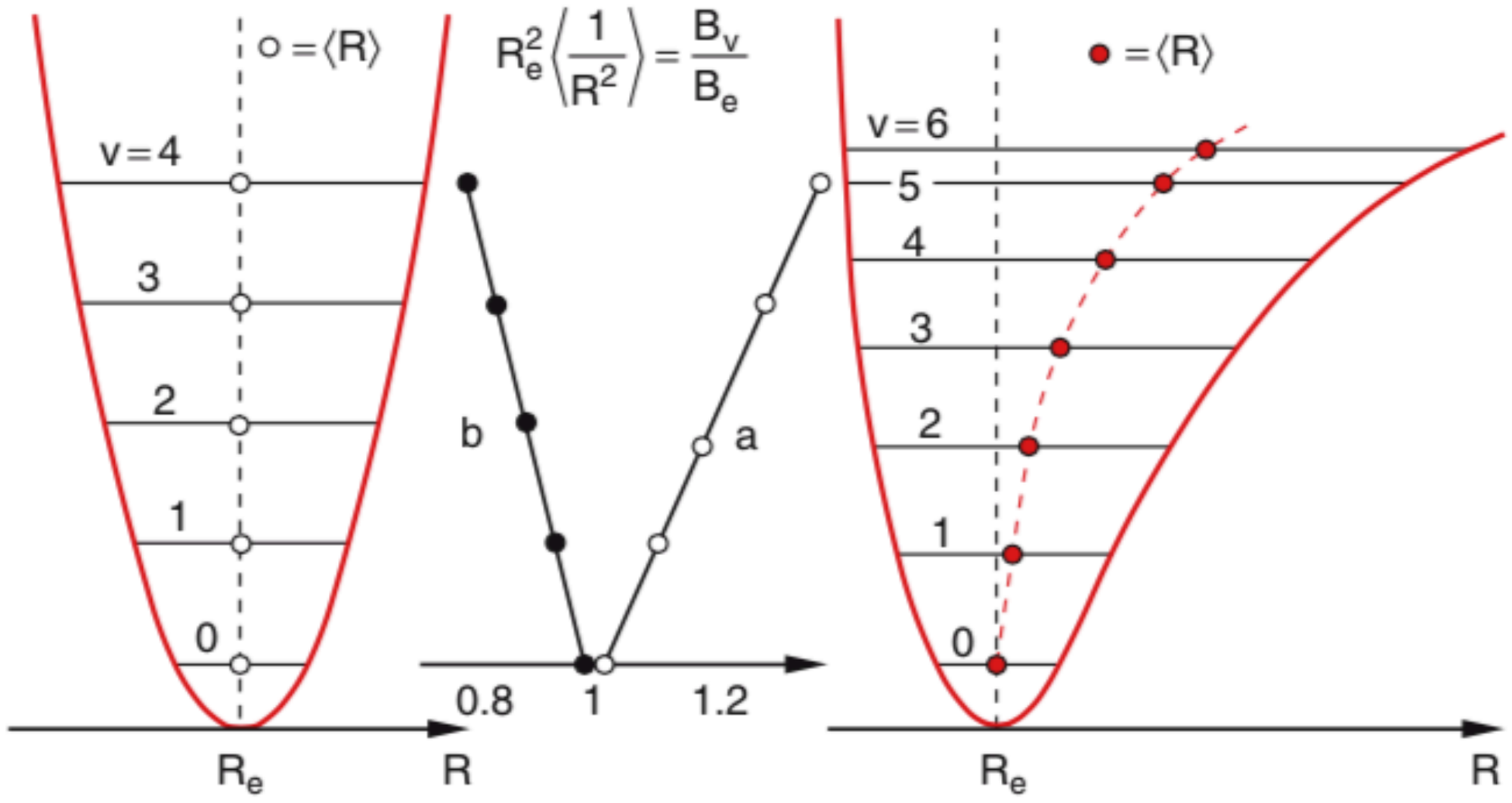
$$\langle E_{\mathrm{rot}}(J;v)\rangle = \frac{\hbar^2 J(J+1)}{2\mu}\left\langle \frac{1}{R^2} \right\rangle$$

$$\left\langle \frac{1}{R^2} \right\rangle = \int_{-\infty}^{\infty} \psi_v^* \frac{1}{R^2} \psi_v \mathrm{d}R$$

- Hence:

$$B_v = \frac{h}{8\pi^2 c\mu}\left\langle \frac{1}{R^2} \right\rangle = B_e - \alpha_e(v+\frac{1}{2}) + \gamma_e(v+\frac{1}{2})^2 + \cdots$$

# Vibration-rotation interaction




$$B_v = \frac{h}{8\pi^2 c\mu}\left\langle\frac{1}{R^2}\right\rangle = B_e - \alpha_e(v+\frac{1}{2}) + \gamma_e(v+\frac{1}{2})^2 + \cdots$$

$\alpha_e > 0$

# Vibration-rotation interaction

- Term values:

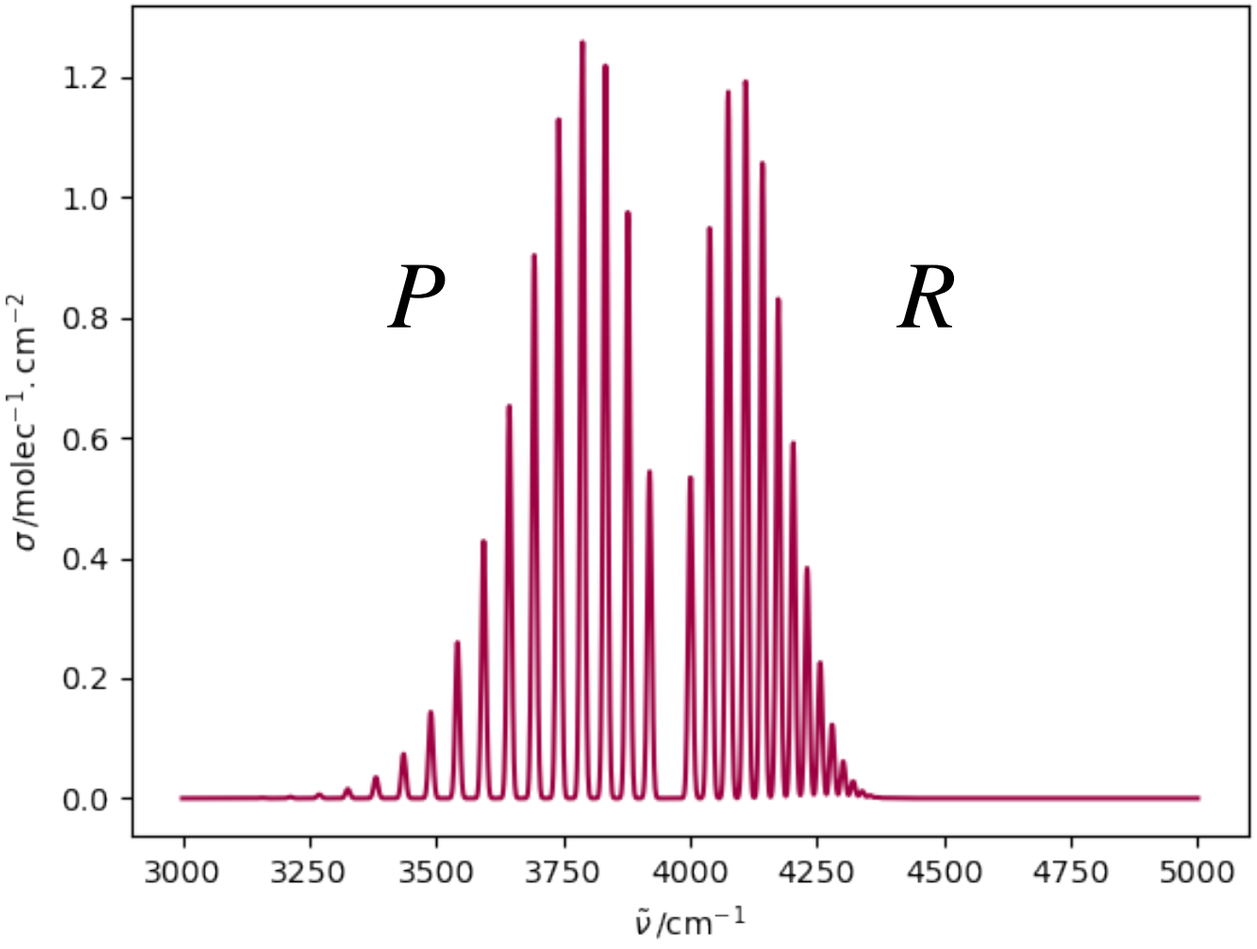
$$F(J,v) = T_e + \omega_e(v+\frac{1}{2}) - \omega_e x_e(v+\frac{1}{2})^2 + \omega_e y_e(v+\frac{1}{2})^3 + \cdots$$
$$+ B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 + \cdots$$

# Vibration-rotation interaction

- Term values: $$F(J,v) = T_e + \omega_e(v+\frac{1}{2}) - \omega_e x_e(v+\frac{1}{2})^2 + \omega_e y_e(v+\frac{1}{2})^3 + \cdots$$
$$+ B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 + \cdots$$

- Even ignoring centrifugal distortion:

$$\nu(v=1, J' \leftarrow v=0, J) = \omega_e - 2\omega_e x_e + B_1 J'(J'+1) - B_0 J(J+1),$$




$$B_1 < B_0$$

# Vibration-rotation interaction

$$\nu(v = 1, J' \leftarrow v = 0, J) = \boxed{\omega_e - 2\omega_e x_e \\ \tilde{\nu}_0} + B_1 J'(J' + 1) - B_0 J(J + 1),$$

- Rewritten for the two branches (P: $\Delta J = -1$, R: $\Delta J = +1$)

$$\nu_P(J) = \tilde{\nu}_0 - (B_1 + B_0)J + (B_1 - B_0)J^2$$
$$\nu_R(J) = \tilde{\nu}_0 + (B_1 + B_0)J' + (B_1 - B_0)J'^2$$

# Vibration-rotation interaction

$$\nu(v = 1, J' \leftarrow v = 0, J) = \underbrace{\omega_e - 2\omega_e x_e}_{\tilde{\nu}_0} + B_1 J'(J'+1) - B_0 J(J+1),$$

- Rewritten for the two branches (P: $\Delta J = -1$, R: $\Delta J = +1$)

$$\nu_P(J) = \tilde{\nu}_0 - (B_1 + B_0)J + (B_1 - B_0)J^2$$
$$\nu_R(J) = \tilde{\nu}_0 + (B_1 + B_0)J' + (B_1 - B_0)J'^2$$

$$\Rightarrow \quad \tilde{\nu}_{P,R} = \tilde{\nu}_0 + (B_1 + B_0)m + (B_1 - B_0)m^2 \qquad m = \begin{cases} -J'' & \text{if } \Delta J = -1 \\ +J' & \text{if } \Delta J = +1 \end{cases}$$

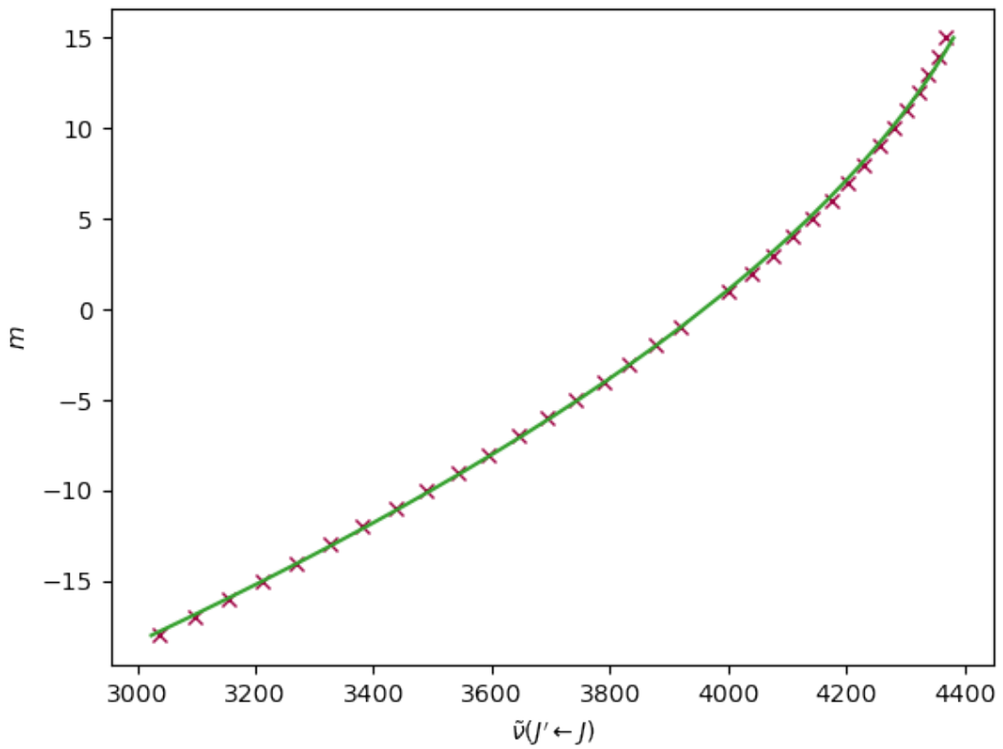
# Vibration-rotation interaction

$$\nu(v=1, J' \leftarrow v=0, J) = \boxed{\begin{matrix}\omega_e - 2\omega_e x_e \\ \tilde{\nu}_0\end{matrix}} + B_1 J'(J'+1) - B_0 J(J+1),$$

- Rewritten for the two branches (P: $\Delta J = -1$, R: $\Delta J = +1$)

$$\nu_P(J) = \tilde{\nu}_0 - (B_1 + B_0)J + (B_1 - B_0)J^2$$
$$\nu_R(J) = \tilde{\nu}_0 + (B_1 + B_0)J' + (B_1 - B_0)J'^2$$

$$\Rightarrow \quad \tilde{\nu}_{P,R} = \tilde{\nu}_0 + (B_1 + B_0)m + (B_1 - B_0)m^2 \qquad m = \begin{cases} -J'' & \text{if } \Delta J = -1 \\ +J' & \text{if } \Delta J = +1 \end{cases}$$




Linear least-squares fit to the "Fortrat parabola":

$B_0 = 19.84424$ cm$^{-1}$
$B_1 = 19.12415$ cm$^{-1}$
$B_e = 20.20428$ cm$^{-1}$
$\alpha_e = \ \ 0.72009$ cm$^{-1}$

# Hot bands and overtones

- Anharmonicity relaxes the selection rule $\Delta v = \pm 1$, allowing overtone bands with $\Delta v = \pm 2, \pm 3, \ldots$

# Hot bands and overtones

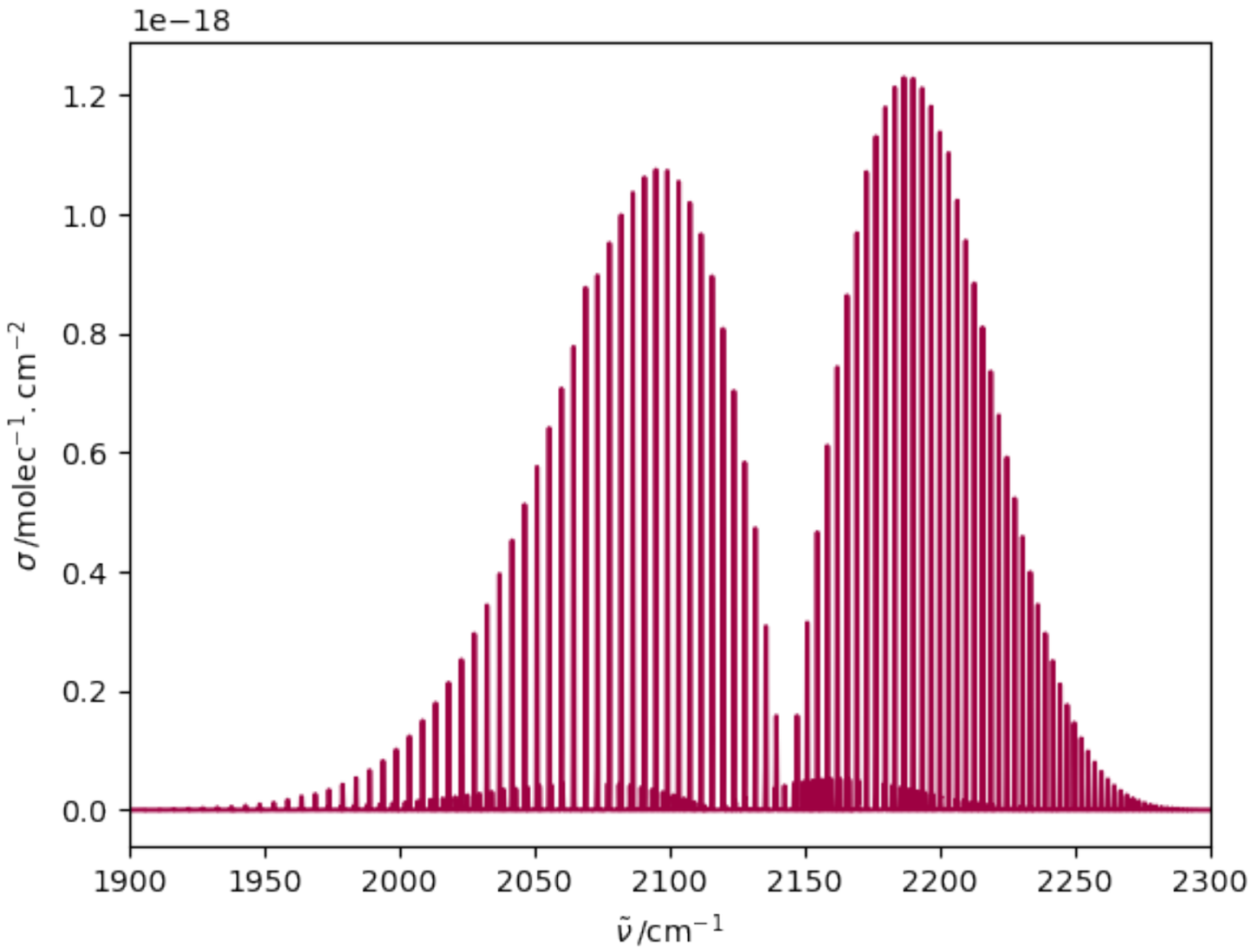
- Anharmonicity relaxes the selection rule $\Delta v = \pm 1$, allowing overtone bands with $\Delta v = \pm 2, \pm 3, \ldots$
- At low temperature, for most diatomic molecules, only the $v = 0$ level is appreciably occupied ( $\hbar\omega \gg k_B T \Rightarrow e^{-Ev/k_B T} \ll 1$ ).

# Hot bands and overtones

- Anharmonicity relaxes the selection rule $\Delta v = \pm 1$, allowing overtone bands with $\Delta v = \pm 2, \pm 3, \ldots$
- At low temperature, for most diatomic molecules, only the $v = 0$ level is appreciably occupied ( $\hbar\omega \gg k_B T \Rightarrow e^{-Ev/k_B T} \ll 1$ ).
- As T increases, transitions originating on $v = 1$ and higher appear.

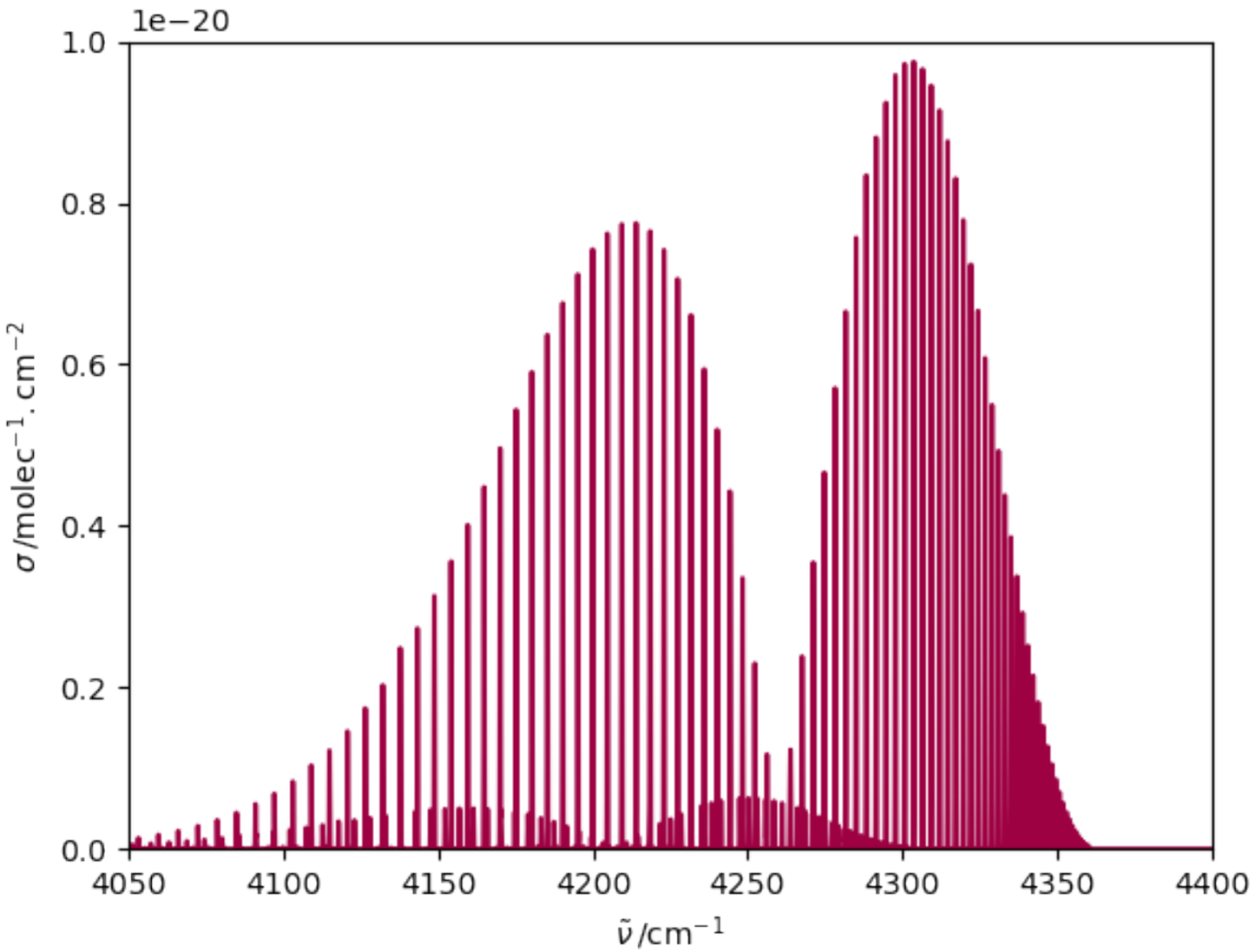
# Rovibrational spectrum of CO (800 K)

- CO fundamental band ($v = 1 \leftarrow 0$), and hot band ($v = 2 \leftarrow 0$)



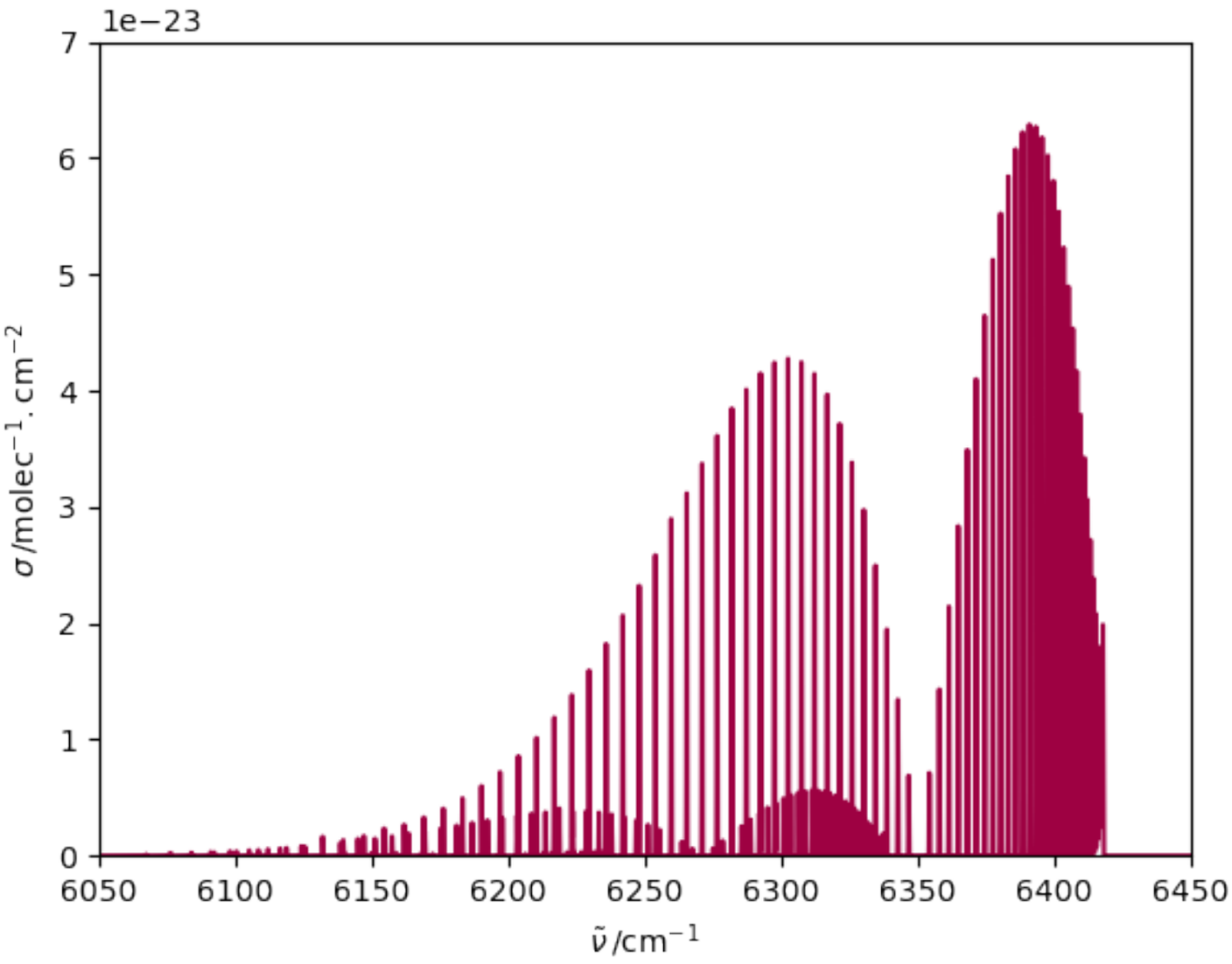
# Rovibrational spectrum of CO (800 K)

- CO first overtone band ($v = 2 \leftarrow 0$), and hot band ($v = 3 \leftarrow 1$)



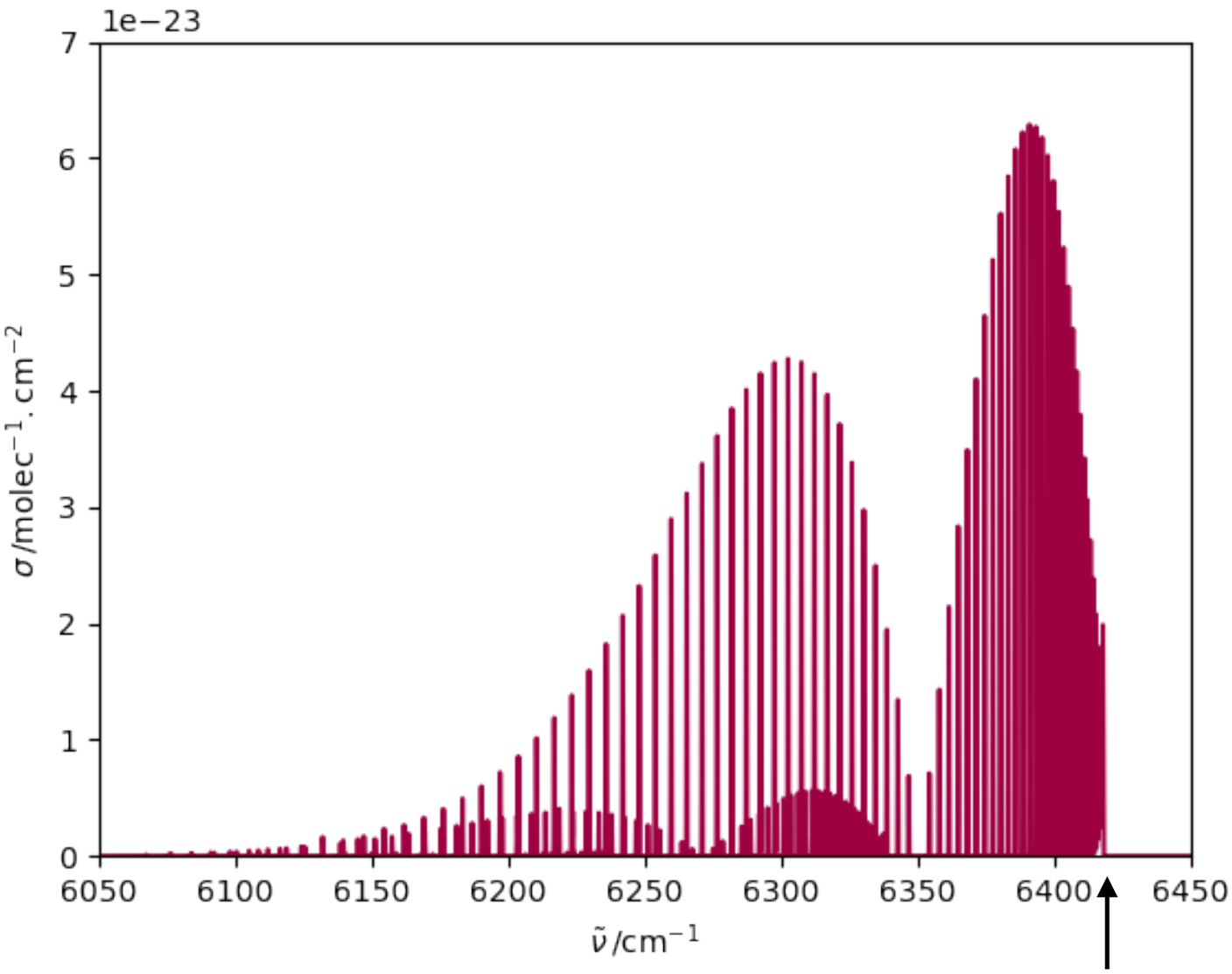
# Rovibrational spectrum of CO (800 K)

- CO second overtone band ($v = 3 \leftarrow 0$), and hot band ($v = 4 \leftarrow 1$)



# Rovibrational spectrum of CO (800 K)

- CO second overtone band ($v = 3 \leftarrow 0$), and hot band ($v = 4 \leftarrow 1$)




*band head*

# Rotational spectroscopy of polyatomics

- The moment of inertia of any three-dimensional object can be described with a component about each of its three *principal axes*. Define:

$$I_a \leq I_b \leq I_c$$

# Rotational spectroscopy of polyatomics

- The moment of inertia of any three-dimensional object can be described with a component about each of its three *principal axes*. Define:

$$I_a \leq I_b \leq I_c$$

- For a linear molecule (e.g. HCl, $CO_2$) has: $I_a = 0, I \equiv I_b = I_c$

# Rotational spectroscopy of polyatomics

- The moment of inertia of any three-dimensional object can be described with a component about each of its three *principal axes*. Define:

$$I_a \leq I_b \leq I_c$$

- For a linear molecule (e.g. HCl, $CO_2$) has: $I_a = 0, I \equiv I_b = I_c$
- An *spherical top* (e.g. $CH_4$, $SF_6$) has: $I_a = I_b = I_c$

# Rotational spectroscopy of polyatomics

- The moment of inertia of any three-dimensional object can be described with a component about each of its three *principal axes*. Define:

$$I_a \leq I_b \leq I_c$$

- For a linear molecule (e.g. HCl, $CO_2$) has: $I_a = 0, I \equiv I_b = I_c$
- An *spherical top* (e.g. $CH_4$, $SF_6$) has: $I_a = I_b = I_c$
- An asymmetric top (e.g. $H_2O$) has: $I_a \neq I_b \neq I_c$

# Rotational spectroscopy of polyatomics

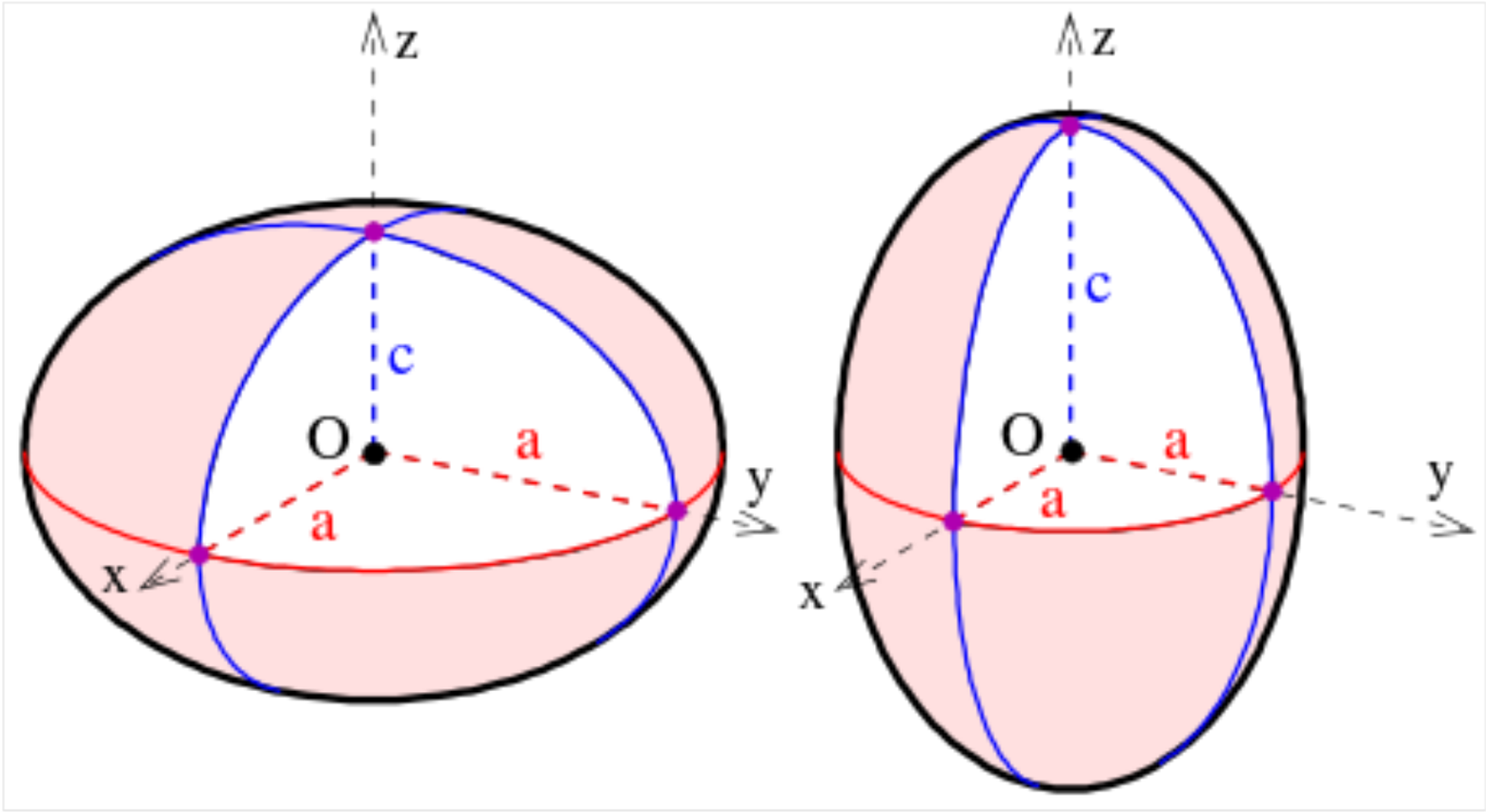
- The moment of inertia of any three-dimensional object can be described with a component about each of its three *principal axes*. Define:

$$I_a \leq I_b \leq I_c$$

- For a linear molecule (e.g. HCl, $CO_2$) has: $I_a = 0, I \equiv I_b = I_c$
- An *spherical top* (e.g. $CH_4$, $SF_6$) has: $I_a = I_b = I_c$
- An asymmetric top (e.g. $H_2O$) has: $I_a \neq I_b \neq I_c$
- We will briefly consider the remaining case: the *symmetric top*.

# Symmetric top molecules

- There are two cases:
  - *Prolate* (rugby ball-shaped): $I_a < I_b = I_c$
  - *Oblate* (flying saucer-shaped): $I_a = I_b < I_c$



# Symmetric top molecules

- The general rotational kinetic energy operator:

$$\hat{H}_{\text{rot}} = \frac{\hat{J}_a^2}{2I_a} + \frac{\hat{J}_b^2}{2I_b} + \frac{\hat{J}_c^2}{2I_c}$$

# Symmetric top molecules

- The general rotational kinetic energy operator:

$$\hat{H}_{\text{rot}} = \frac{\hat{J}_a^2}{2I_a} + \frac{\hat{J}_b^2}{2I_b} + \frac{\hat{J}_c^2}{2I_c}$$

- Rewrite in terms of the total rotational angular momentum operator, $\hat{J}^2 = \hat{J}_a^2 + \hat{J}_b^2 + \hat{J}_c^2$ :

$$\hat{H}_{\text{rot}} = \frac{\hat{J}^2}{2I_b} + \hat{J}_a^2 \left( \frac{1}{2I_a} - \frac{1}{2I_b} \right),$$

# Symmetric top molecules

- The general rotational kinetic energy operator:

$$\hat{H}_{\text{rot}} = \frac{\hat{J}_a^2}{2I_a} + \frac{\hat{J}_b^2}{2I_b} + \frac{\hat{J}_c^2}{2I_c}$$

- Rewrite in terms of the total rotational angular momentum operator, $\hat{J}^2 = \hat{J}_a^2 + \hat{J}_b^2 + \hat{J}_c^2$ :

$$\hat{H}_{\text{rot}} = \frac{\hat{J}^2}{2I_b} + \hat{J}_a^2 \left( \frac{1}{2I_a} - \frac{1}{2I_b} \right),$$

- This Hamiltonian is diagonal in the basis $|J, K\rangle$ :
  - $J = 0, 1, 2, \ldots$: total angular momentum quantum number
  - $K = -J, -J+1, \ldots, J$: projection of J along the symmetry axis

# Symmetric top molecules

- Rotational term values for a prolate symmetric top:

$$F(J,K) = BJ(J+1) + K^2(A-B).$$

where: $A = \hbar/(8\pi^2 c I_a)$ and $B = \hbar/(8\pi^2 c I_b)$.

(For an oblate symmetric top, replace $I_a$ with $I_c$, $A$ with $C$).

# Symmetric top molecules

- Rotational term values for a prolate symmetric top:

$$F(J,K) = BJ(J+1) + K^2(A-B).$$

where: $A = \hbar/(8\pi^2 c I_a)$ and $B = \hbar/(8\pi^2 c I_b)$.

(For an oblate symmetric top, replace $I_a$ with $I_c$, $A$ with $C$).

- But… the selection rules are $\Delta J = \pm 1$ and $\Delta K = 0$ (no change of dipole moment as the molecule rotates about its symmetry axis), so:

$$\tilde{\nu}(J,K) = F(J+1,K) - F(J,K) = 2B(J+1)$$

# Symmetric top molecules

- Rotational term values for a prolate symmetric top:

$$F(J,K) = BJ(J+1) + K^2(A-B).$$

where: $A = \hbar/(8\pi^2 c I_a)$ and $B = \hbar/(8\pi^2 c I_b)$.

(For an oblate symmetric top, replace $I_a$ with $I_c$, $A$ with $C$).

- But… the selection rules are $\Delta J = \pm 1$ and $\Delta K = 0$ (no change of dipole moment as the molecule rotates about its symmetry axis), so:

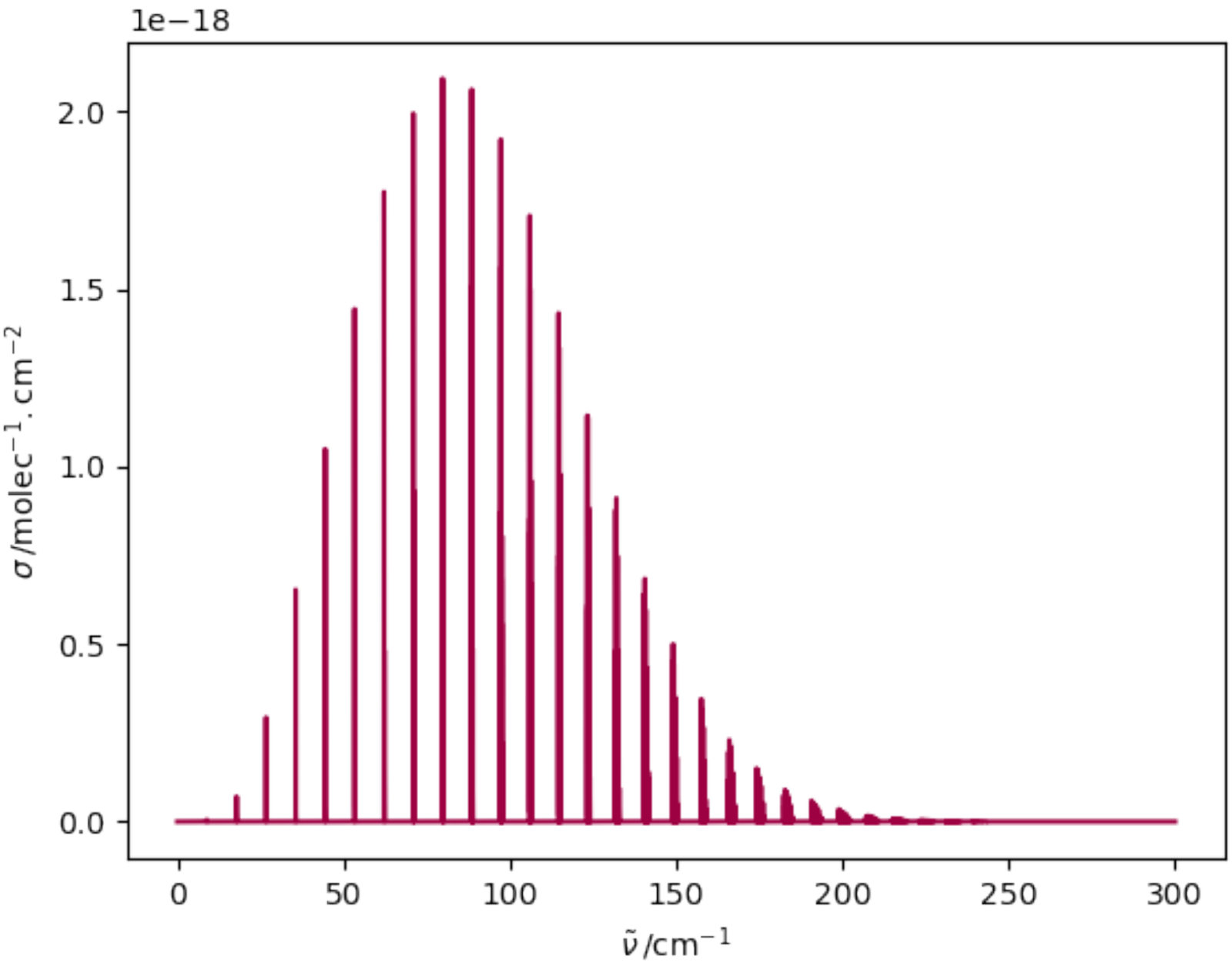
$$\tilde{\nu}(J,K) = F(J+1,K) - F(J,K) = 2B(J+1)$$

- Unless we consider *centrifugal distortion*:

$$\tilde{\nu}(J,K) = 2(B - D_{JK}K^2)(J+1) - 4D_J(J+1)^3,$$

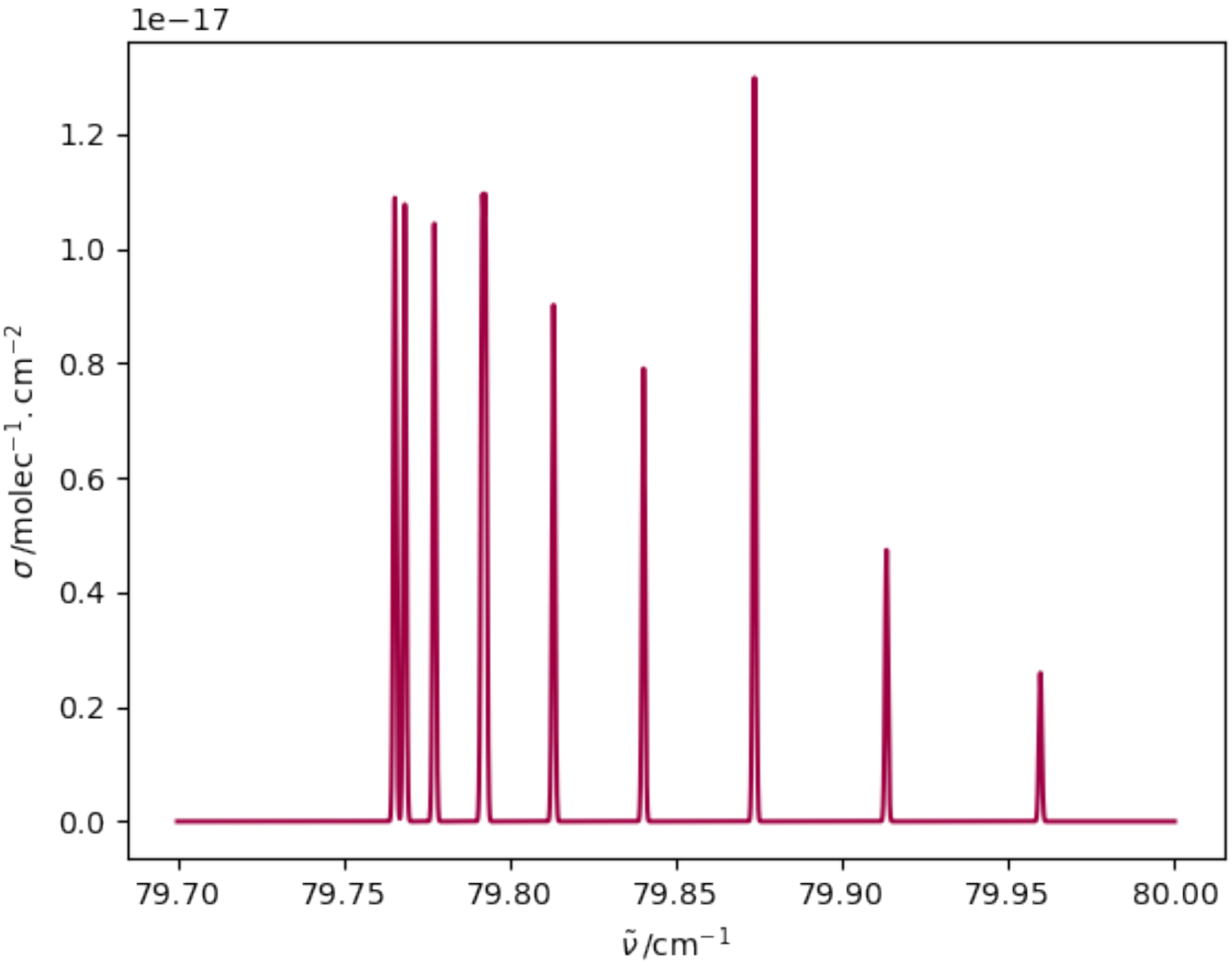
# Rotational spectrum of phosphine

- Phosphine ($PH_3$) is an oblate symmetric top



# Rotational spectrum of phosphine

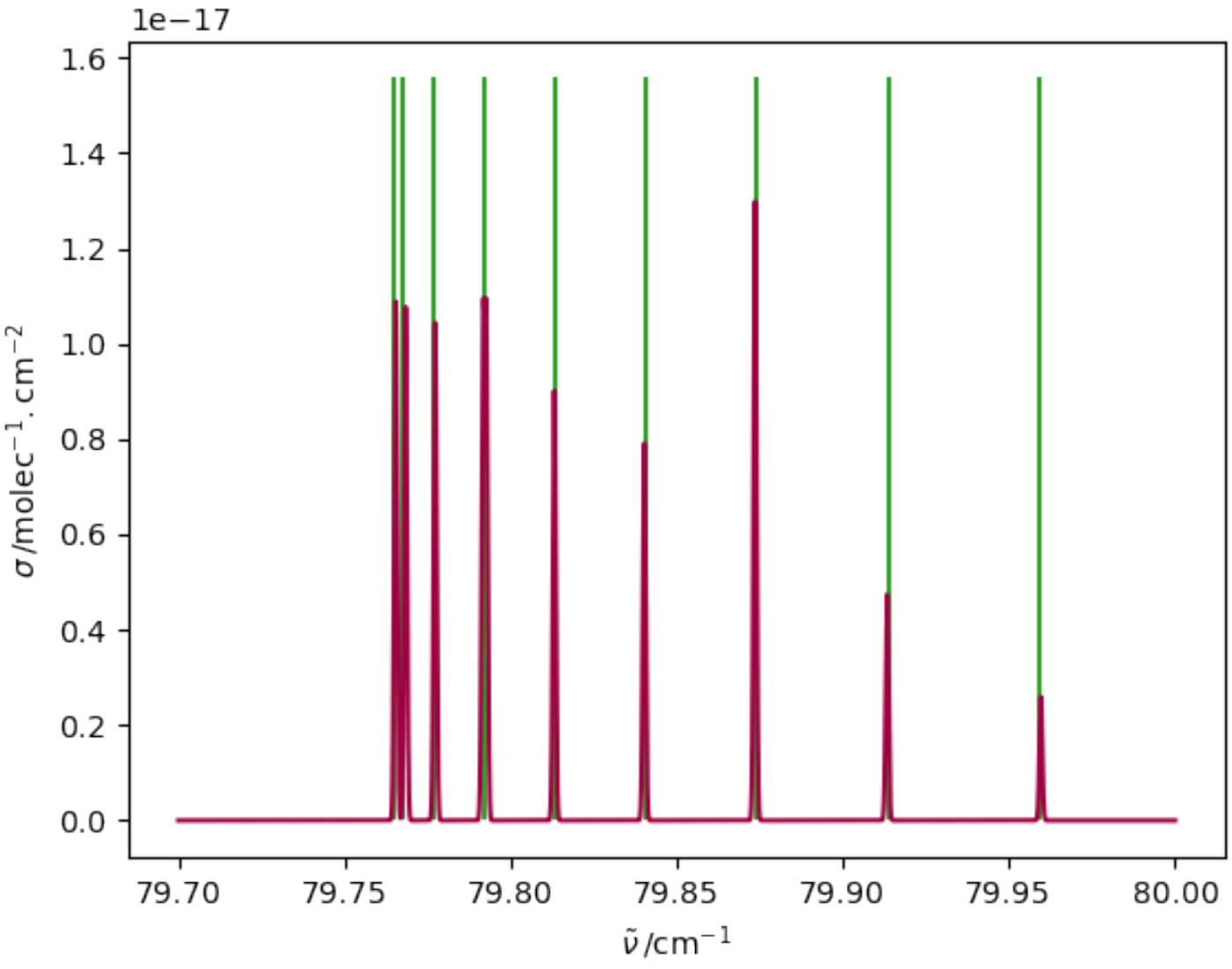
- The pure rotational transition $J = 9 \leftarrow 8$ in $PH_3$:



# Rotational spectrum of phosphine

- Fit the spectroscopic parameters $B$, $D_{JK}$, $D_J$

$$\tilde{\nu}(J,K) = 2(B - D_{JK}K^2)(J+1) - 4D_J(J+1)^3,$$




In this case, we get:

$B = 4.45236169$ cm$^{-1}$

$D_{JK} = -0.00016877$ cm$^{-1}$

$D_J = 0.00012956$ cm$^{-1}$

# Vibrational spectroscopy: polyatomics

- A molecule with more than two atoms will have several vibrational motions available to it

# Vibrational spectroscopy: polyatomics

- A molecule with more than two atoms will have several vibrational motions available to it
- For small vibrational amplitudes, all possible motions can be composed as a linear combination of *normal vibrational modes* for which the nuclei all move through their equilibrium positions at the same time.

# Vibrational spectroscopy: polyatomics

- A molecule with more than two atoms will have several vibrational motions available to it
- For small vibrational amplitudes, all possible motions can be composed as a linear combination of *normal vibrational modes* for which the nuclei all move through their equilibrium positions at the same time.
  - Non-linear molecules: $3N - 6$ normal modes
  - Linear molecules: $3N - 5$ normal modes

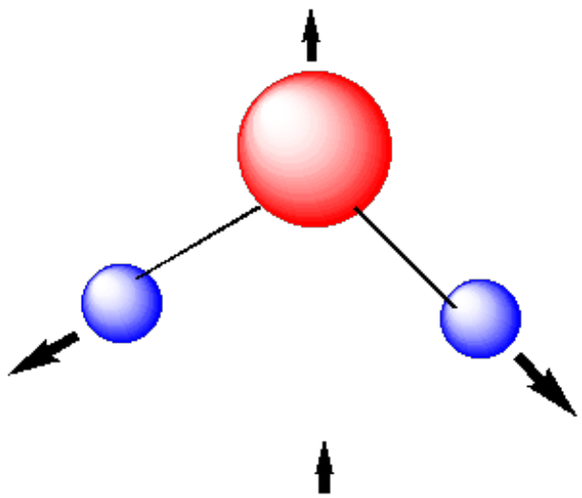
# Vibrational spectroscopy: polyatomics

- A molecule with more than two atoms will have several vibrational motions available to it
- For small vibrational amplitudes, all possible motions can be composed as a linear combination of *normal vibrational modes* for which the nuclei all move through their equilibrium positions at the same time.
  - Non-linear molecules: $N_{\text{vib}} = 3N - 6$ normal modes
  - Linear molecules: $N_{\text{vib}} = 3N - 5$ normal modes
  - A normal mode may be degenerate ($d_k$)

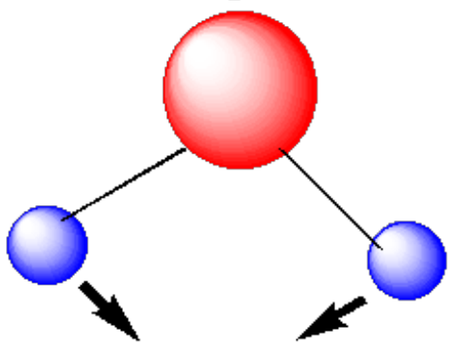
$$E_{\text{vib}} = \sum_{k=1}^{N_{\text{vib}}} \hbar\omega_k \left( v_k + \frac{d_k}{2} \right)$$

# Vibrational spectroscopy: polyatomics

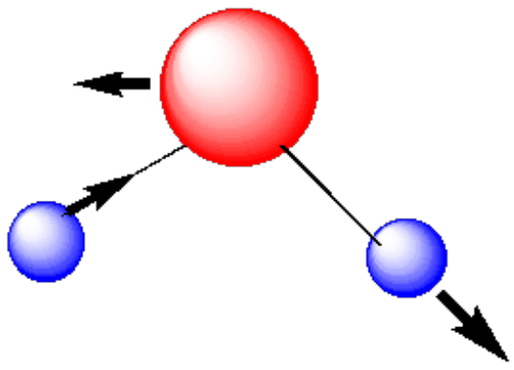
- Example: $H_2O$ normal modes



Symmetric Stretch
3657 $cm^{-1}$



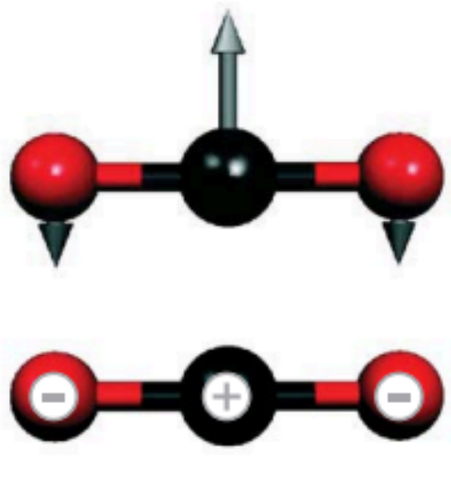
Bend 1595 $cm^{-1}$



Asymmetric Stretch
3756 $cm^{-1}$

# Vibrational spectroscopy: polyatomics

- Example: $CO_2$ normal modes – parallel and perpendicular

$\Pi_u$  $\nu_{2a}$ 667 $cm^{-1}$ $\perp$

$\nu_{2b}$

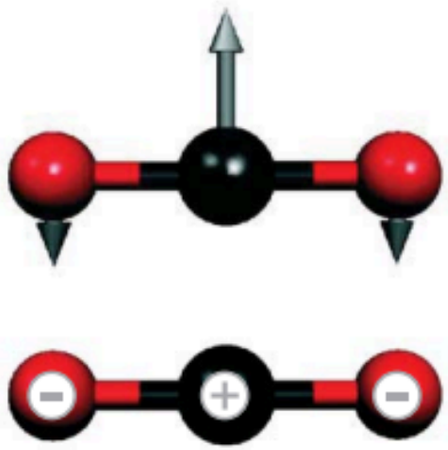
$\Sigma_g^+$  $\nu_1$ 1336 $cm^{-1}$ $\parallel$

$\Sigma_u^+$  $\nu_3$ 2349 $cm^{-1}$ $\parallel$

# Vibrational spectroscopy: polyatomics

- Example: $CO_2$ normal modes – parallel and perpendicular

$\Pi_u$



$\nu_{2a}$

667 $cm^{-1}$

$\nu_{2b}$

$\perp$

$\Sigma_g^+$

$\nu_1$ 1336 $cm^{-1}$

$\parallel$

$\Sigma_u^+$

$\nu_3$ 2349 $cm^{-1}$

$\parallel$

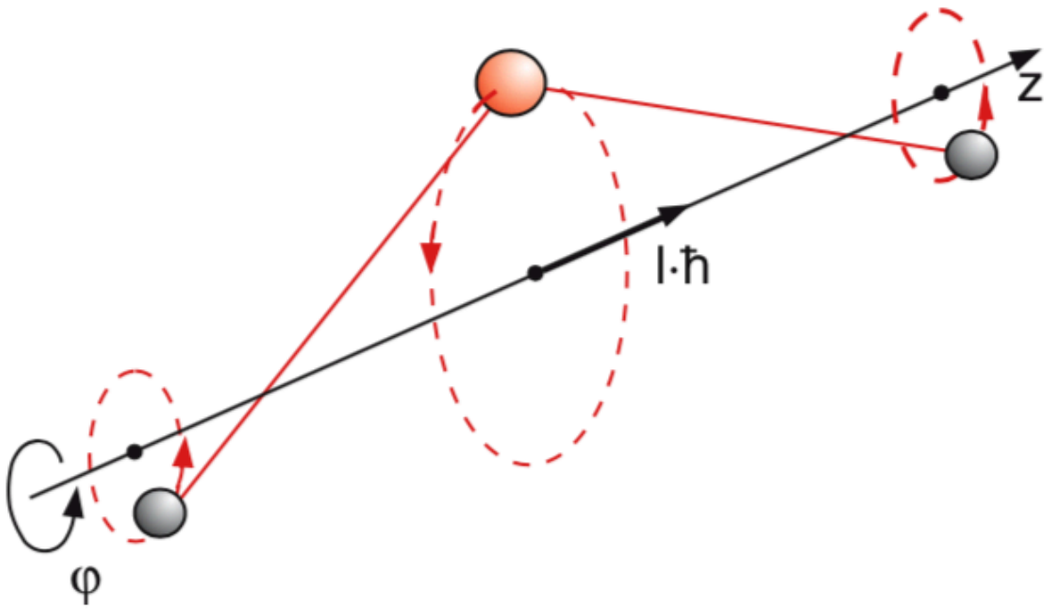
Only modes with a change in dipole moment on vibration are allowed ("IR-active") (electric dipole gross selection rule)

# Vibrations of linear polyatomics

- Selection rules
  - Parallel vibrations: $\Delta J = \pm 1$

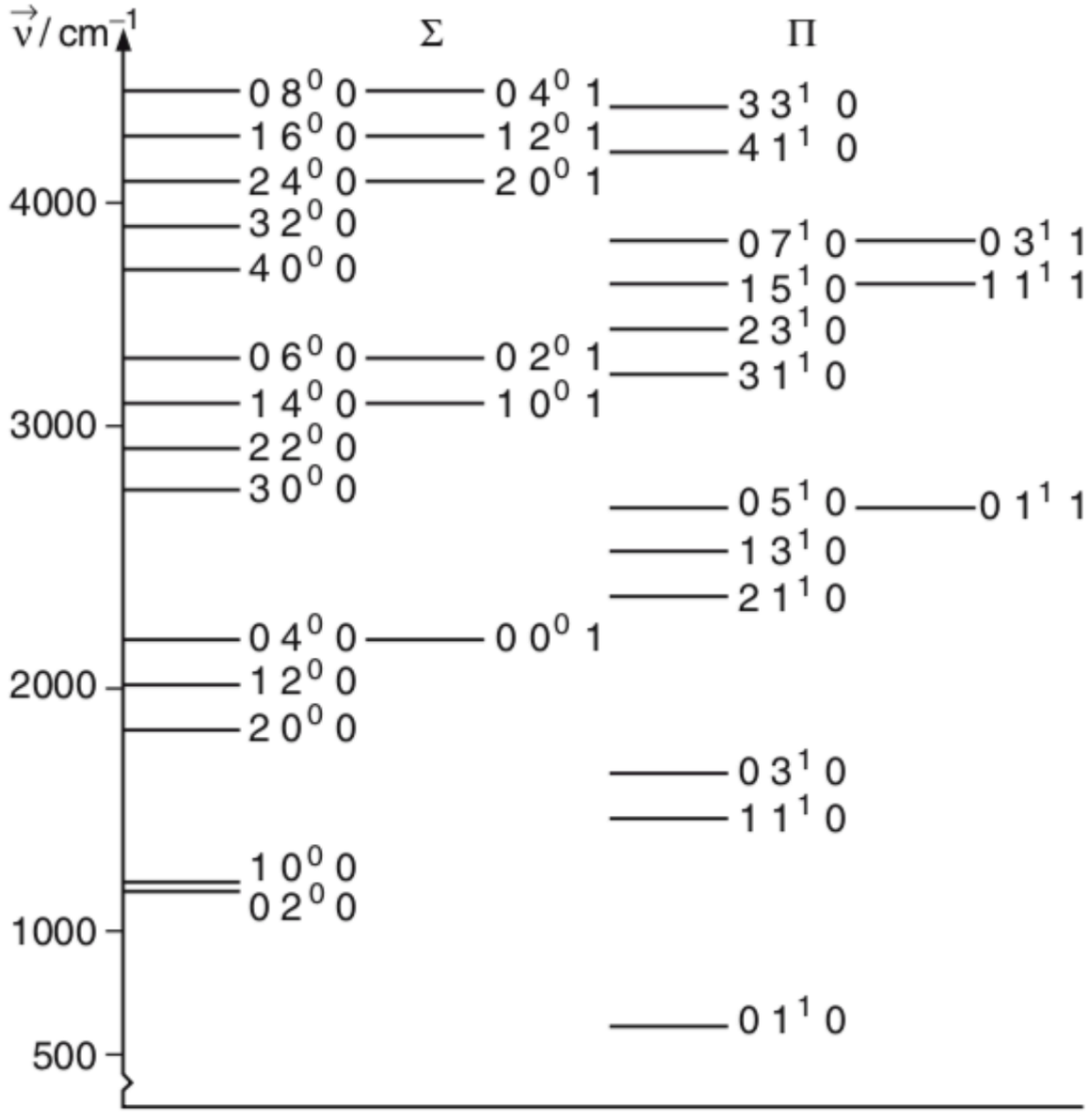
# Vibrations of linear polyatomics

- Selection rules
  - Parallel vibrations: $\Delta J = \pm 1$
  - Perpendicular vibrations: $\Delta J = 0, \pm 1$
    - Vibrational angular momentum:



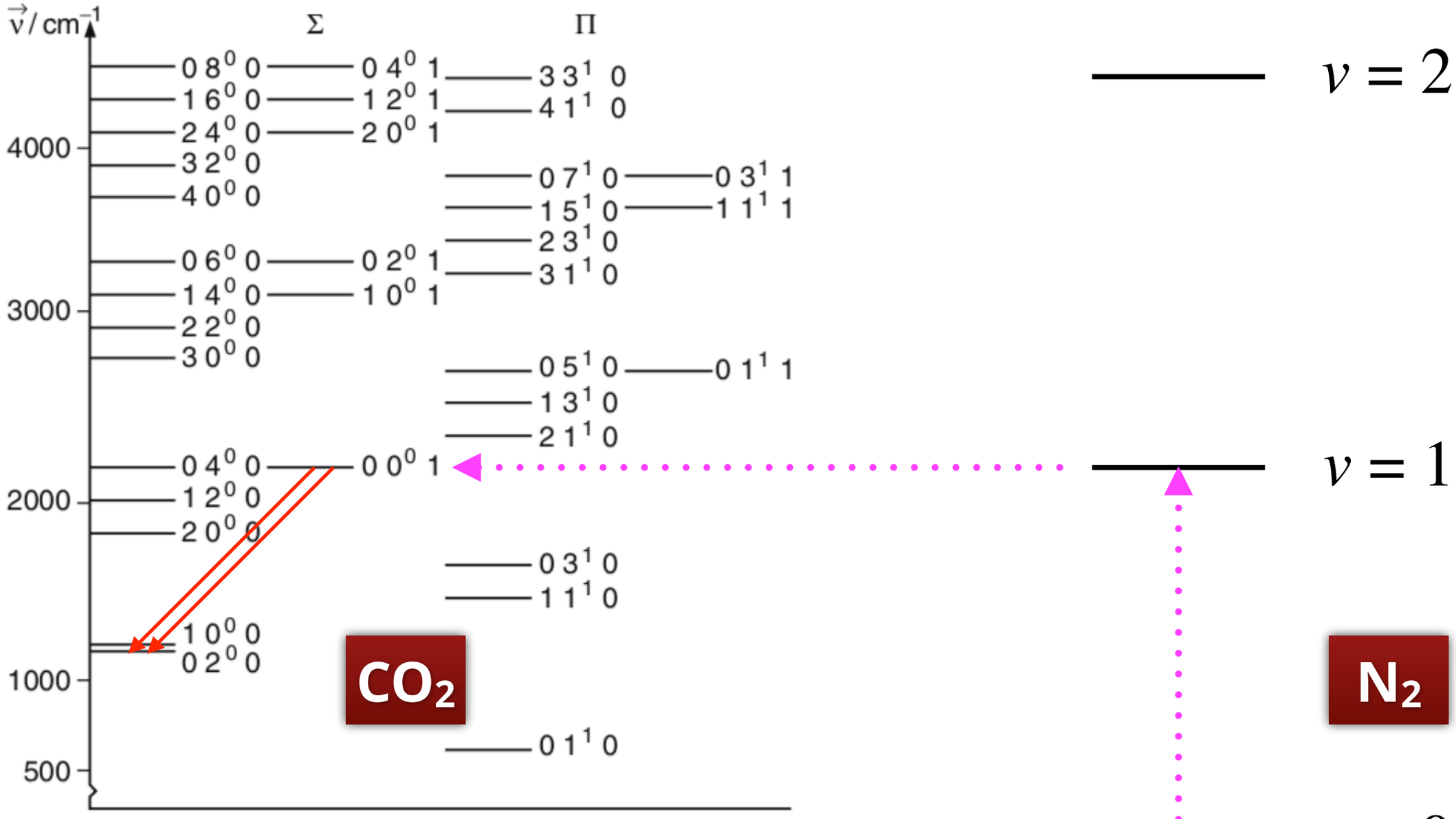
# Vibrational spectroscopy: polyatomics

- Example: $CO_2$ vibrational energy levels
  - The notation used: $(v_1 v_2^l v_3)$, $l = -v_2, -v_2+2, \cdots, v_2-2, v_2$



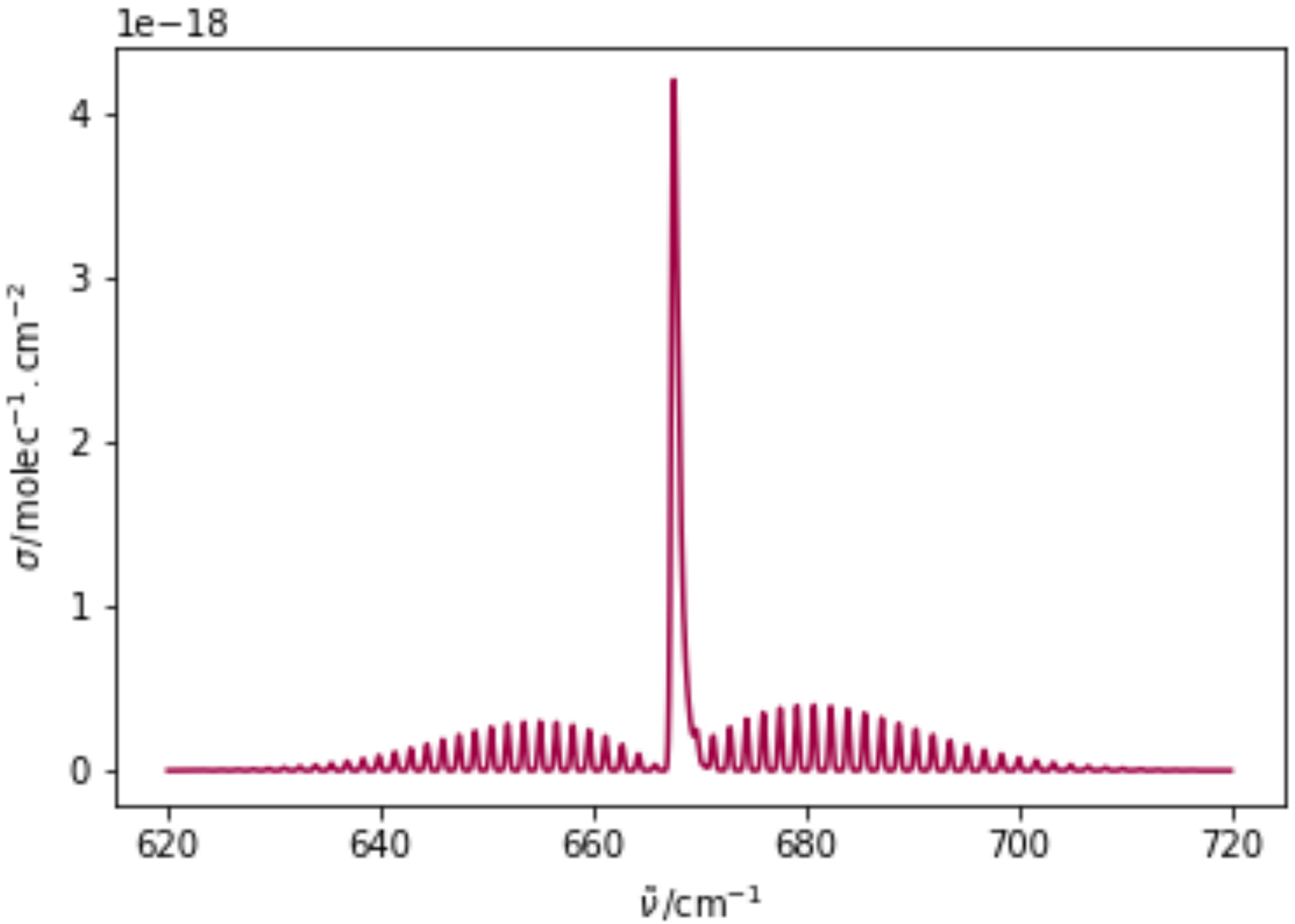
# Vibrational spectroscopy: polyatomics

- Example: $CO_2$ vibrational energy levels
  - The notation used: $(v_1 v_2^l v_3)$, $l = -v_2, -v_2+2, \cdots, v_2-2, v_2$



# Vibrations of linear polyatomics

- The $(01^{1}0) - (00^{0}0)$ band (P, Q and R branches)



# Vibrations of linear polyatomics

- The $(00^0 1) - (00^0 0)$ band (P, Q and R branches)