Vibrational spectroscopy

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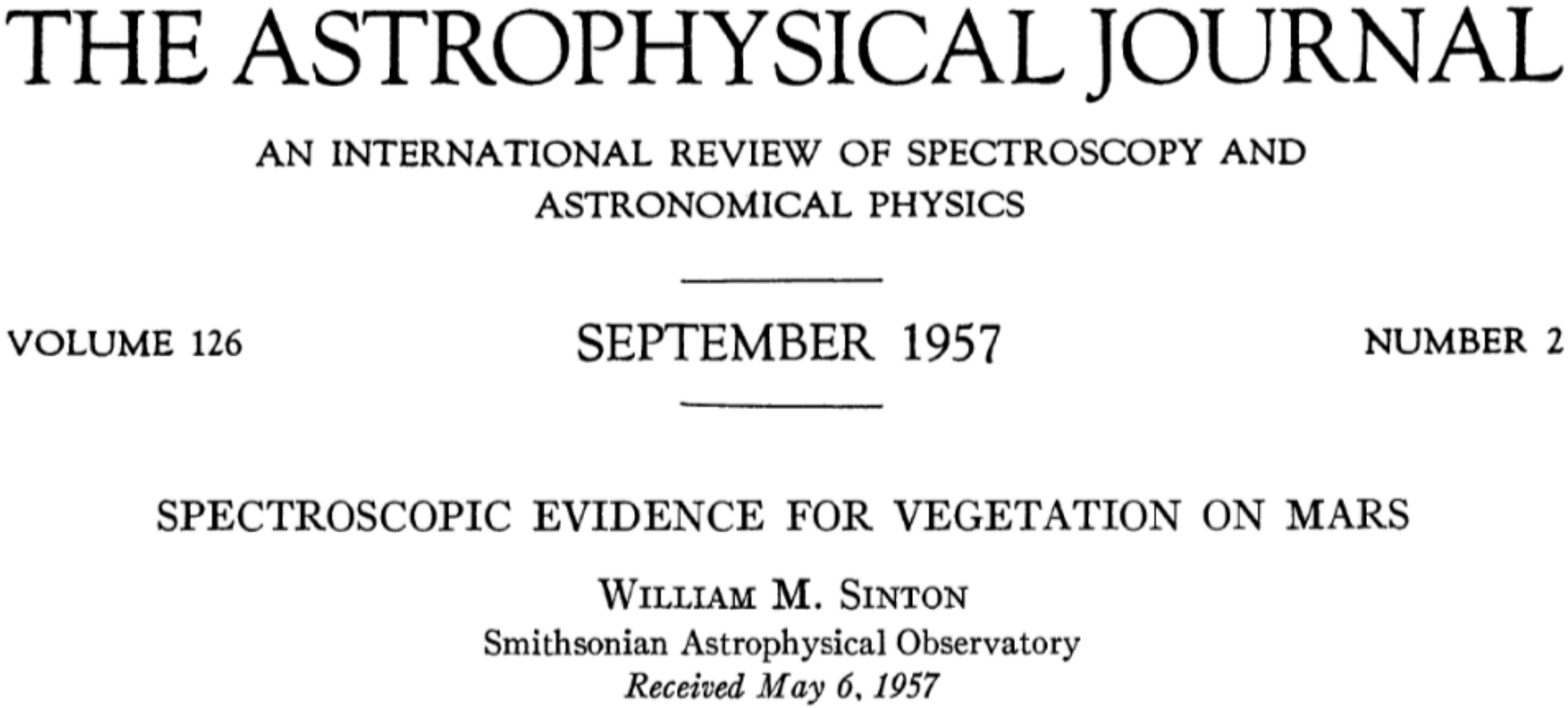

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SPECTROSCOPIC EVIDENCE FOR VEGETATION ON MARS

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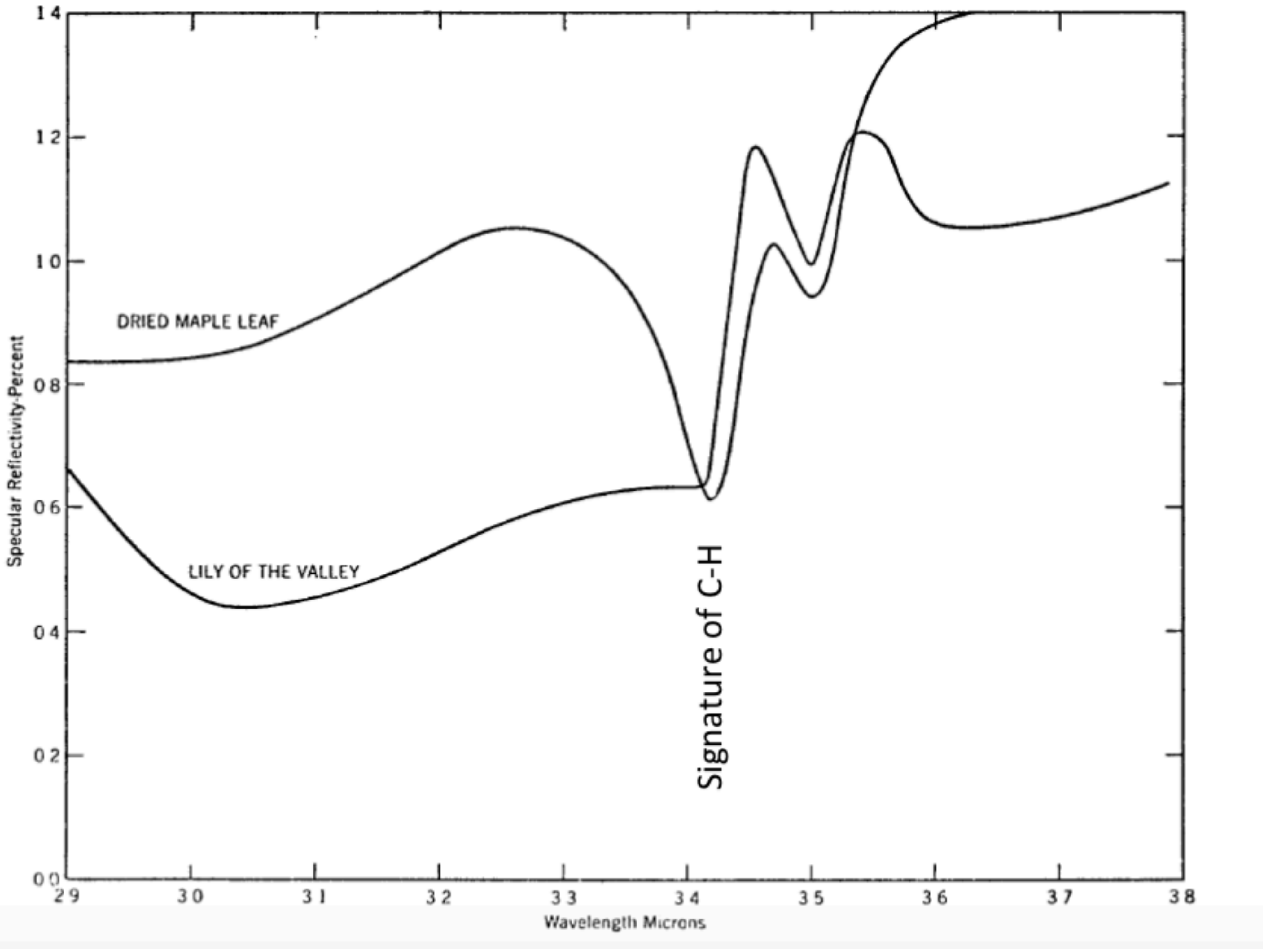

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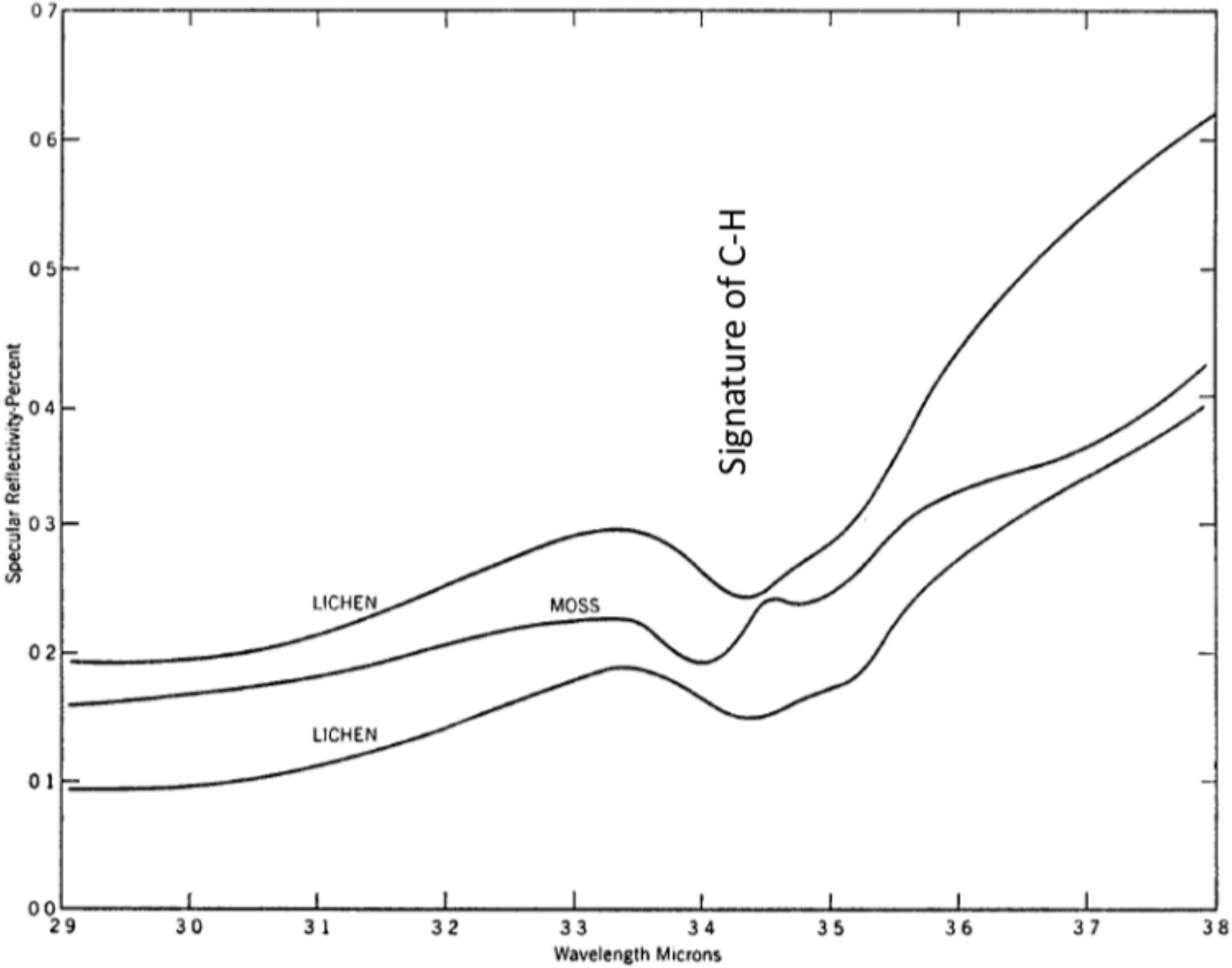


Signature of C-H

Vibrational spectroscopy

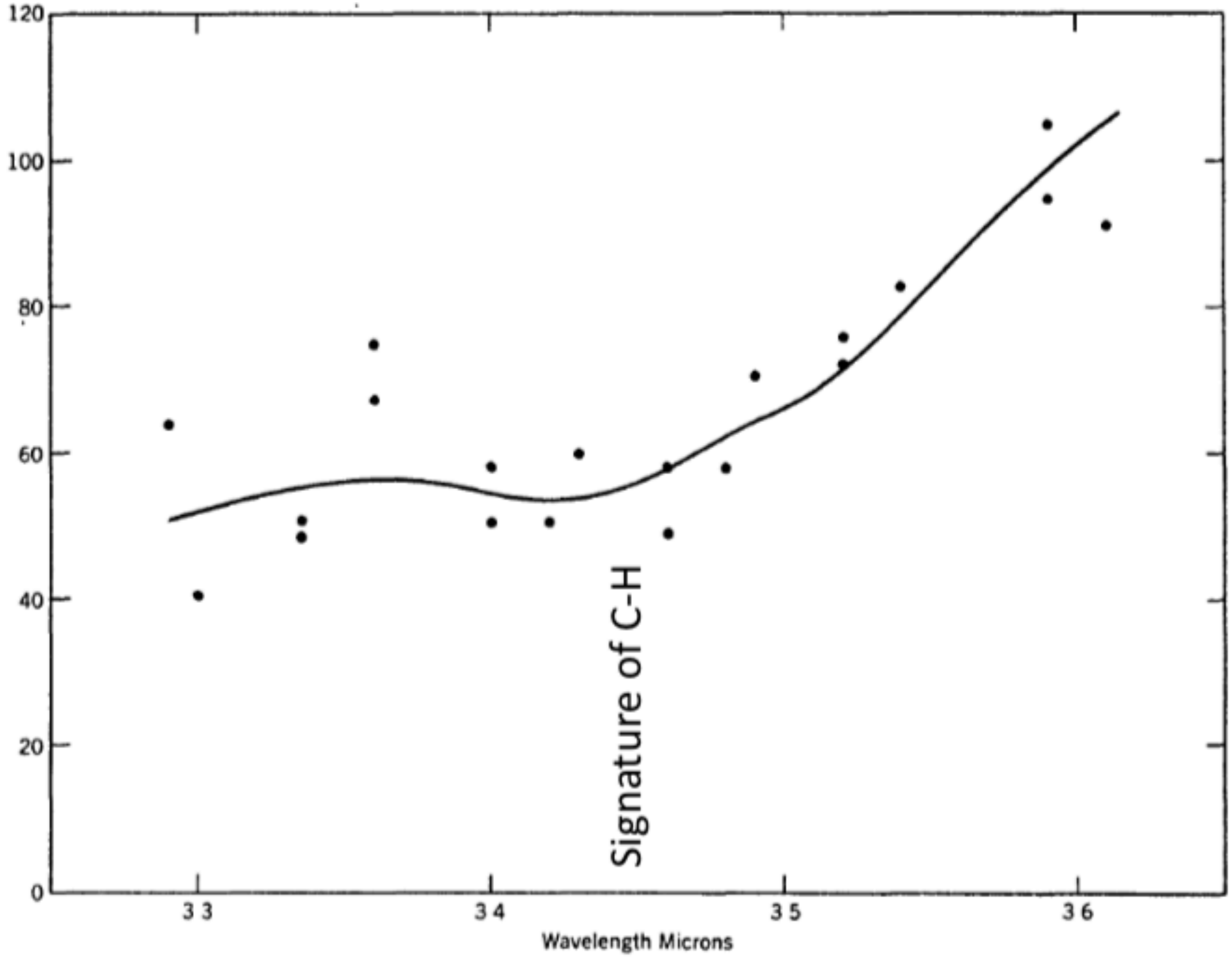
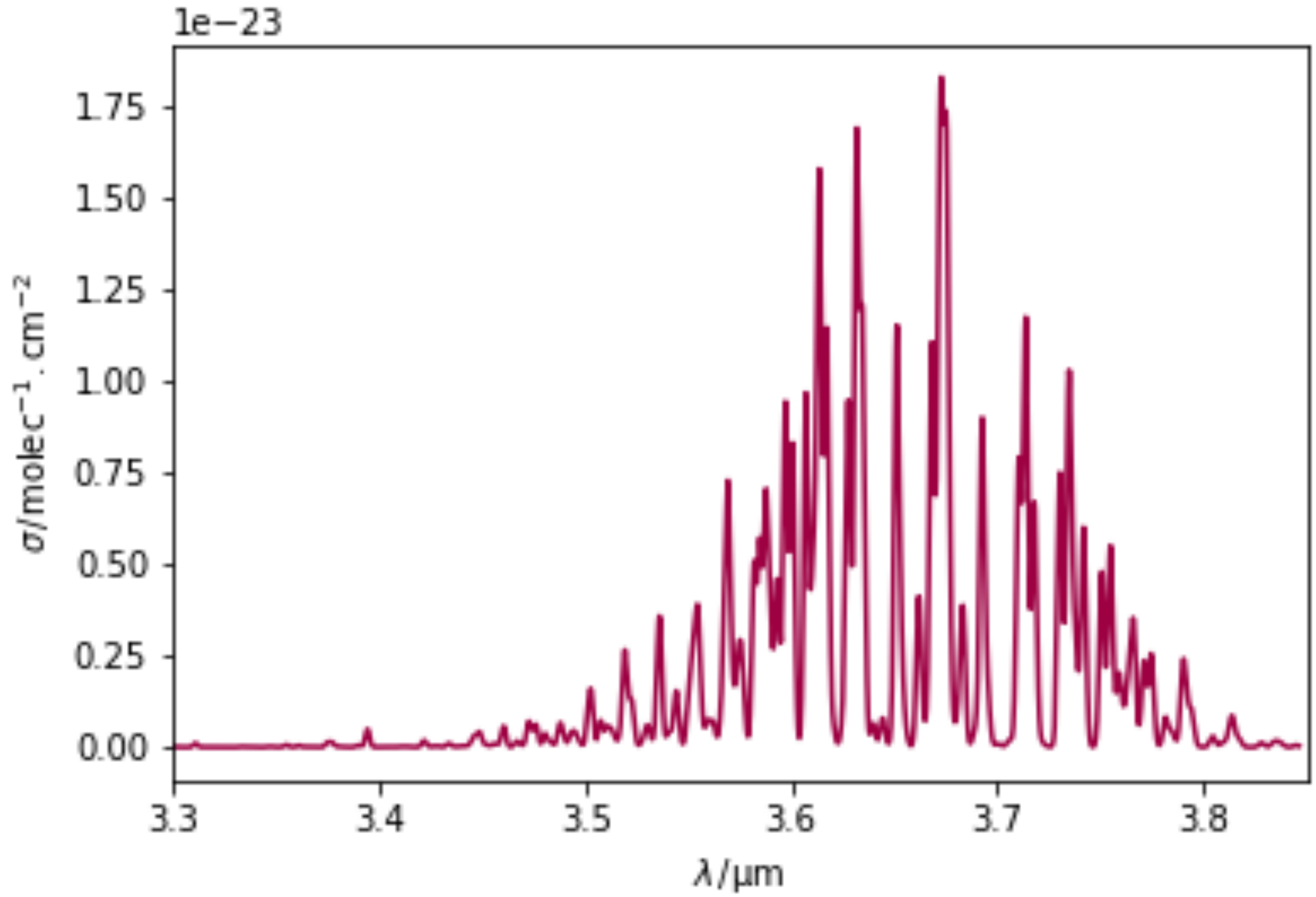


FIG. 3.—Observations of the spectrum of Mars obtained on four nights and after division by the solar spectrum (*solid curve* of Fig. 2).

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:

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

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

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

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

(the parabolic potential used earlier)

Vibrational motion

- Within this approximation:

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

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- 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:

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

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

Vibrational motion

- Further transformation to “natural units”:

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q=\alpha x \Rightarrow x &= q/x \\
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&\Rightarrow -\frac{1}{2}\frac{\mathrm{d}^2\psi}{\mathrm{d}q^2}+\frac{1}{2}q^2\frac{k\mu}{\hbar^2\alpha^4}\psi=E\frac{\mu}{\hbar^2\alpha^2}\psi
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- Choose

$$\frac{k\mu}{\hbar^2\alpha^4}=1\Rightarrow\alpha=\left(\frac{k\mu}{\hbar^2}\right)^{1/4}\quad\Rightarrow -\frac{1}{2}\frac{\mathrm{d}^2\psi}{\mathrm{d}q^2}+\frac{1}{2}q^2\psi=E\frac{\mu}{\hbar^2}\frac{\hbar}{\sqrt{k\mu}}\psi=\frac{E}{\hbar}\sqrt{\frac{\mu}{k}}\psi=\frac{E}{\hbar\omega}\psi$$

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

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

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- 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:

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

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

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- 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

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

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

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

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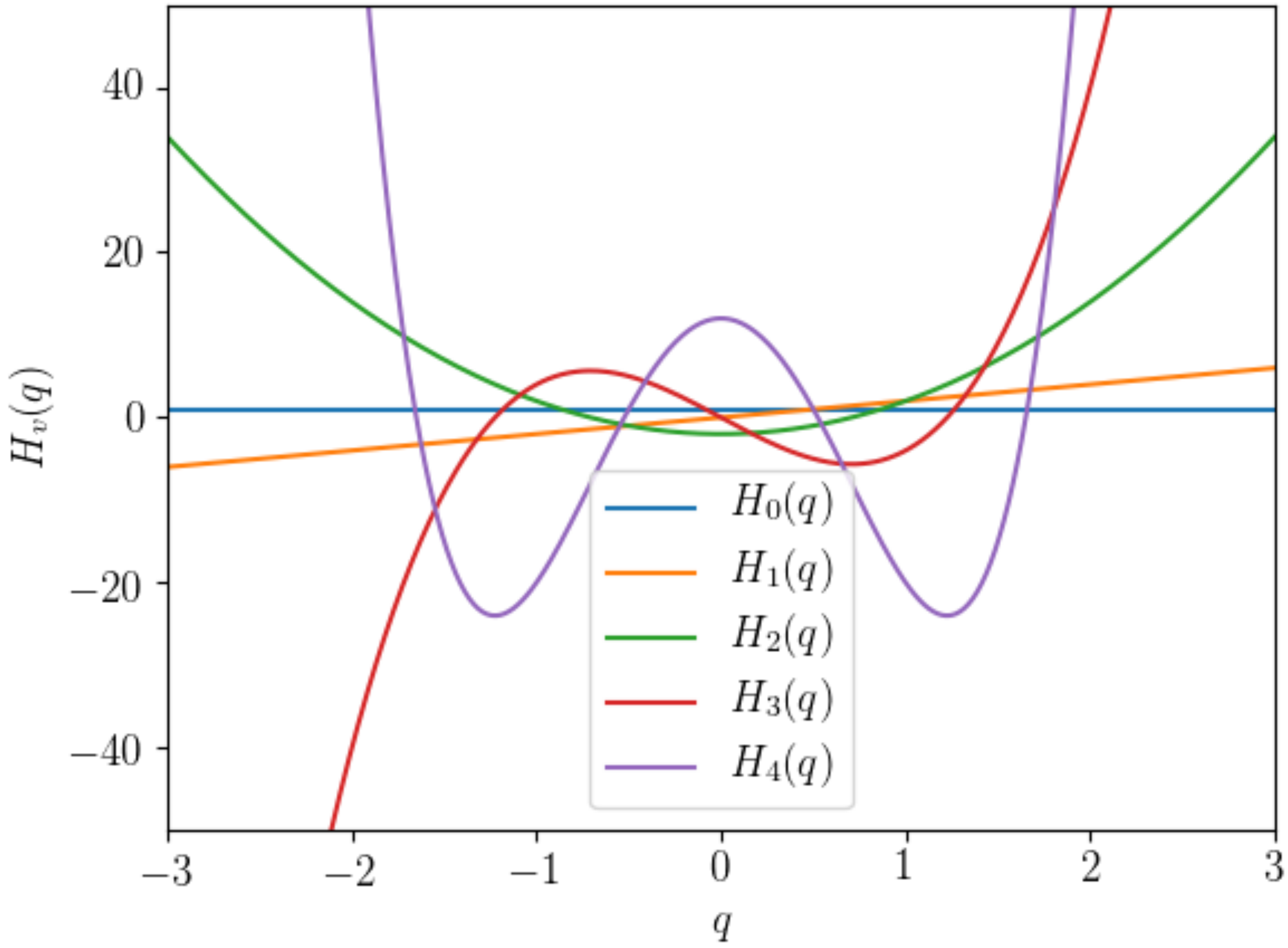
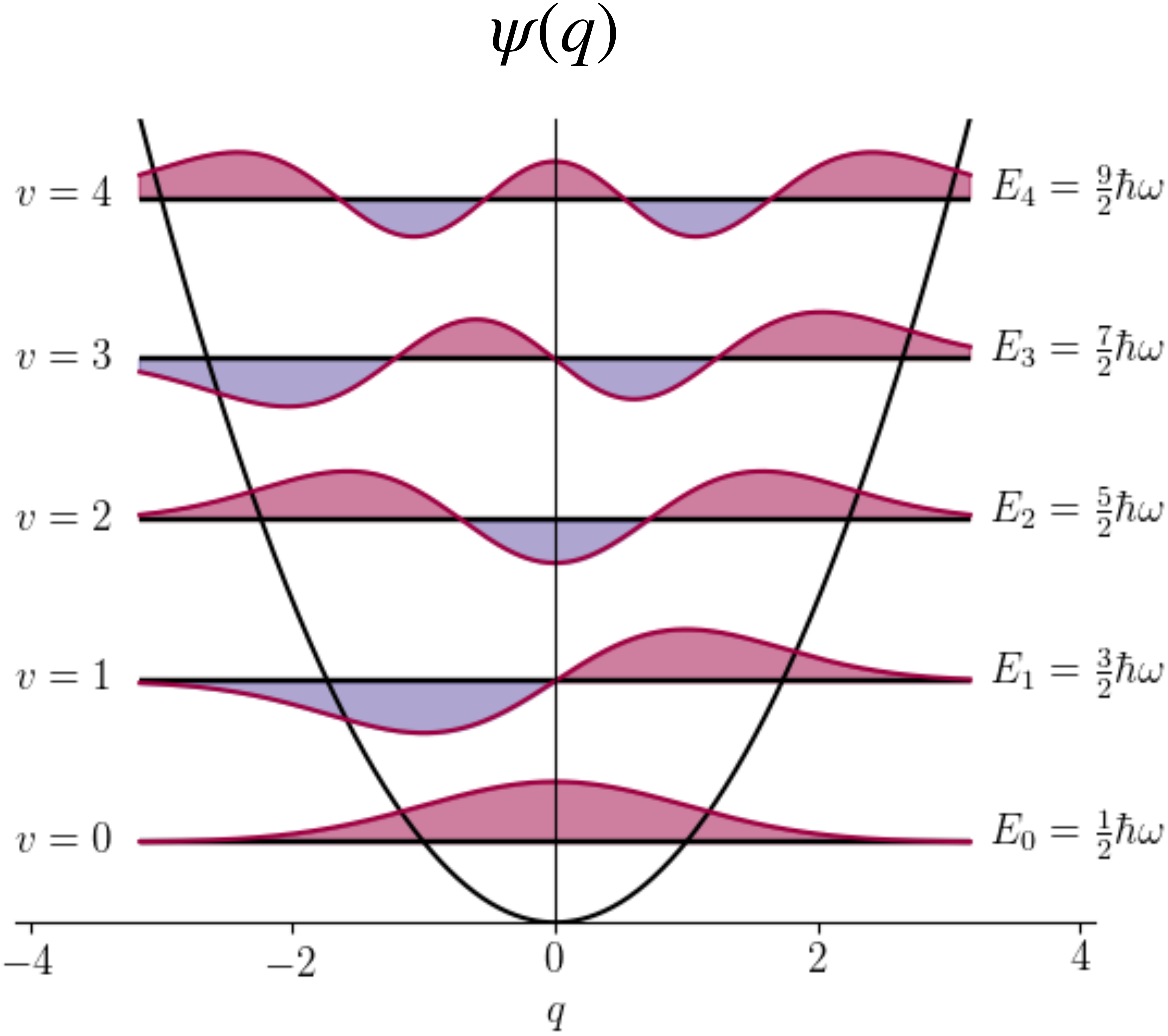
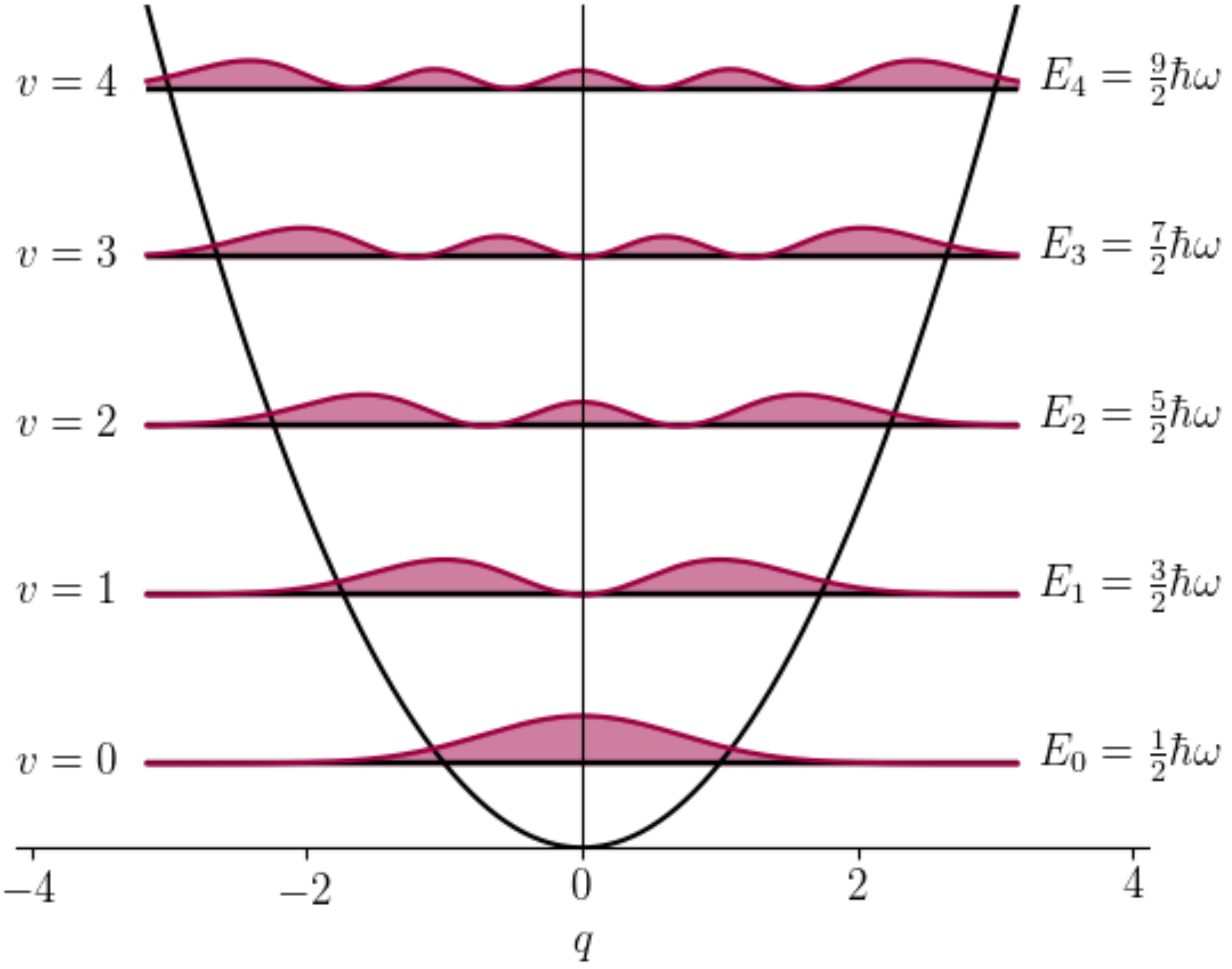


Harmonic oscillator wavefunctions



Harmonic oscillator probabilities

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



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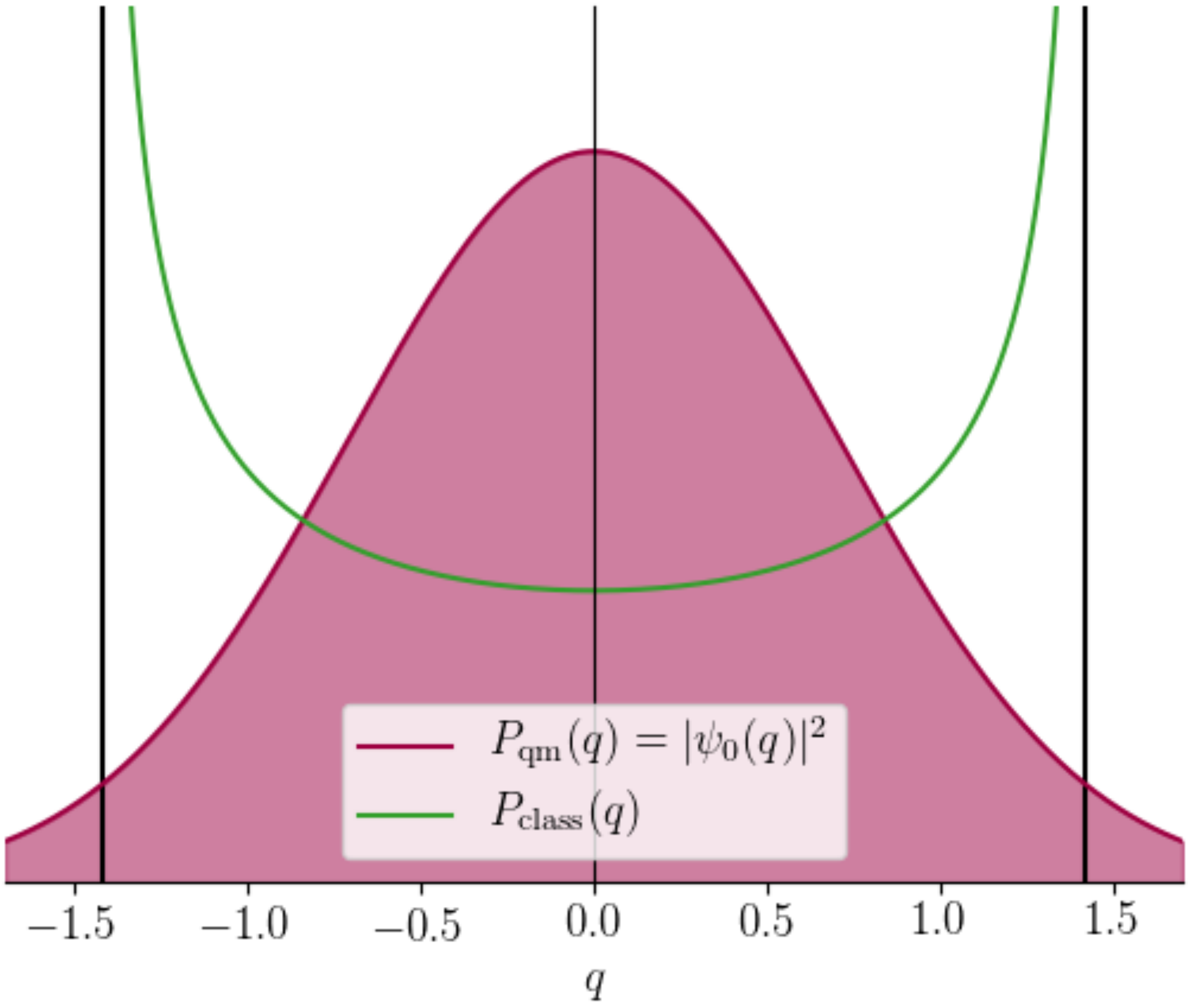

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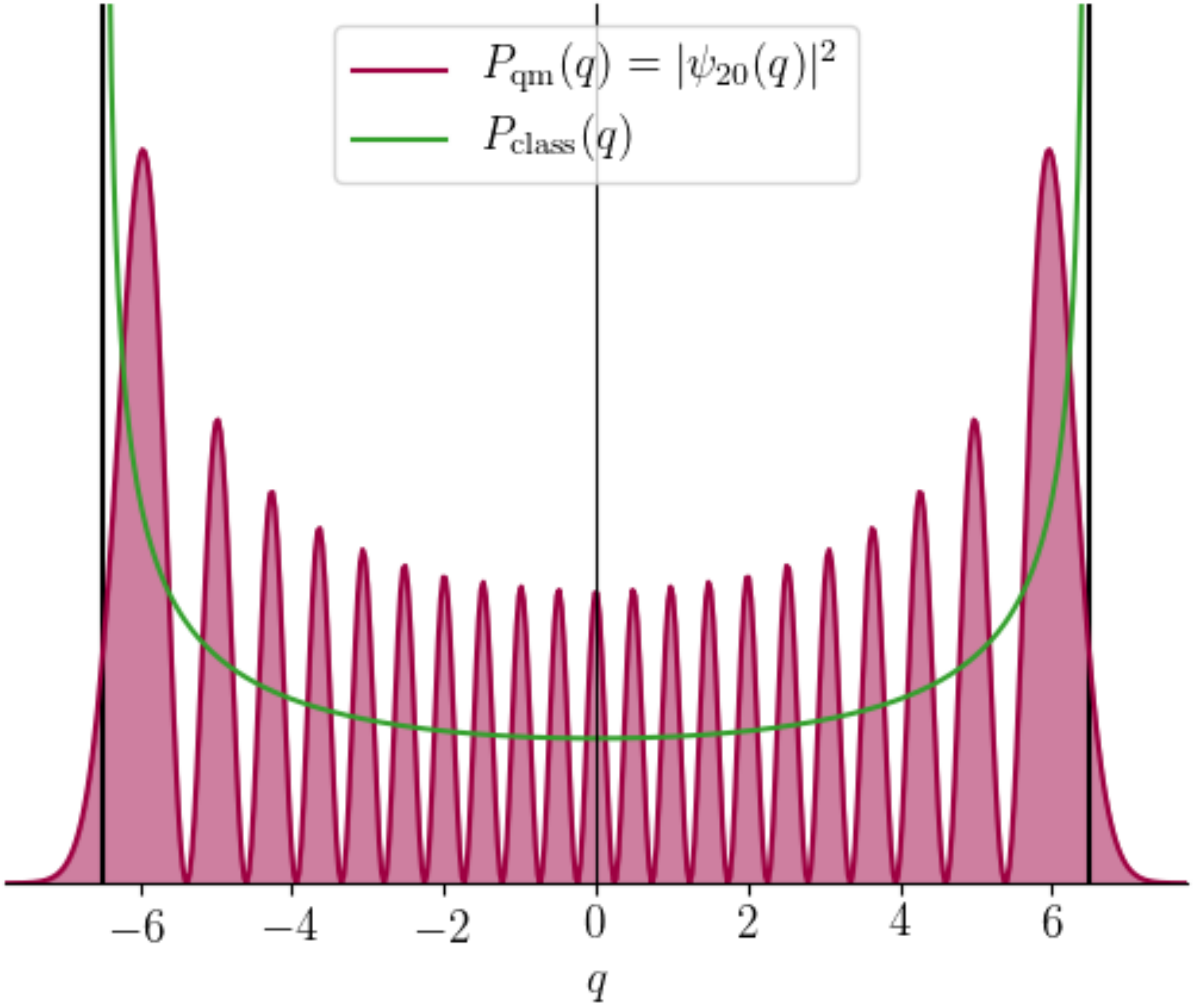

Harmonic vibrational transitions

- The transition probability from one vibrational state, *v*” to another *v*’ is the square of the transition dipole moment:

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

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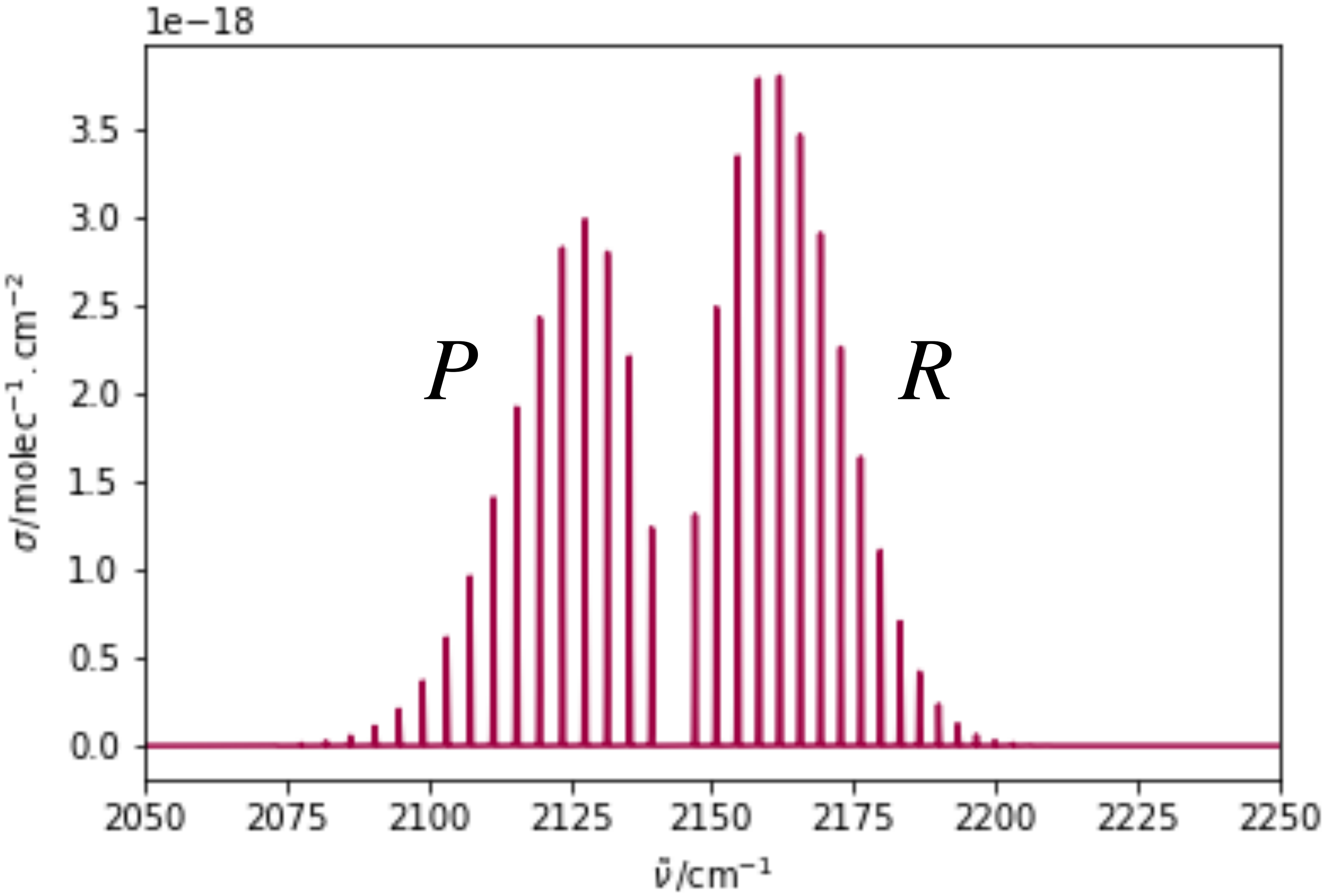
“gross” selection rule

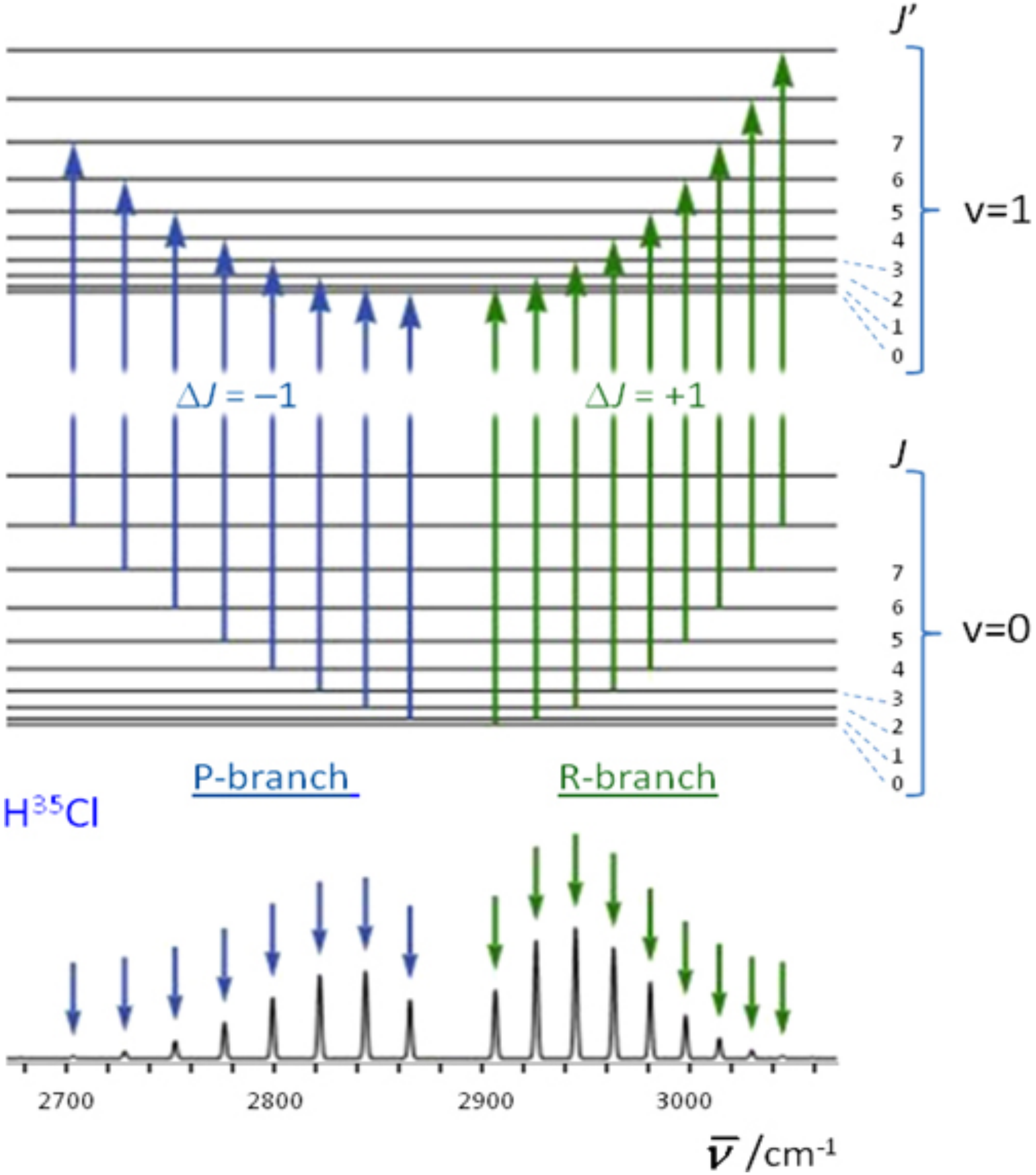
- *Homonuclear diatomic molecules (e.g. H_2) do not have an electric-dipole allowed vibrational spectrum*

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



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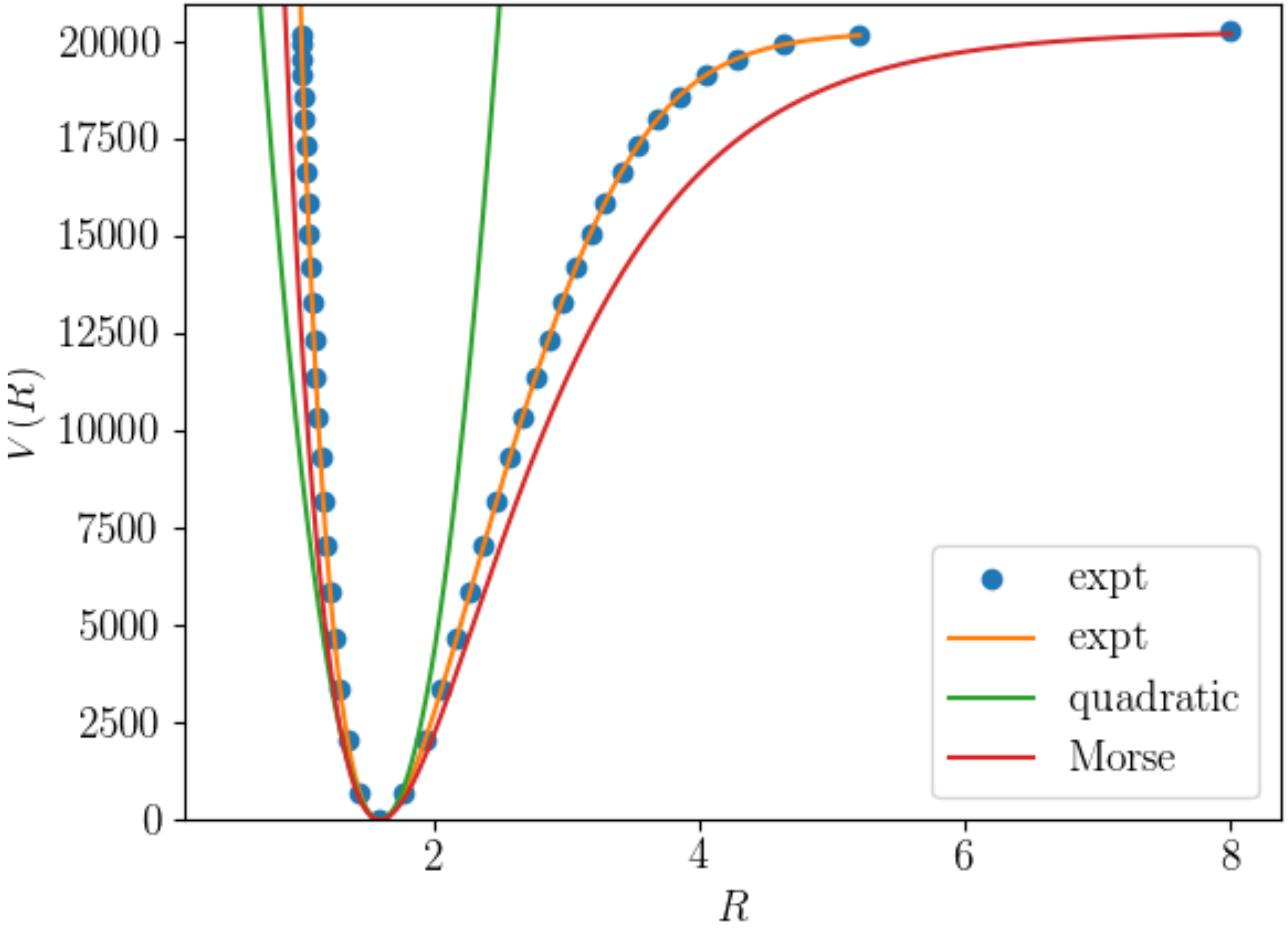
- Morse term values in terms of constants ω_e and $\omega_\mathrm{e}x_\mathrm{e}$ (which can be related to D_e, a):

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

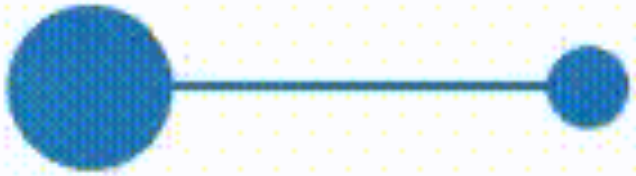
The Morse potential

- ^{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



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

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- Hence:

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

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- To a first approximation we may consider the rotational energy as a time-average over a vibrational period:

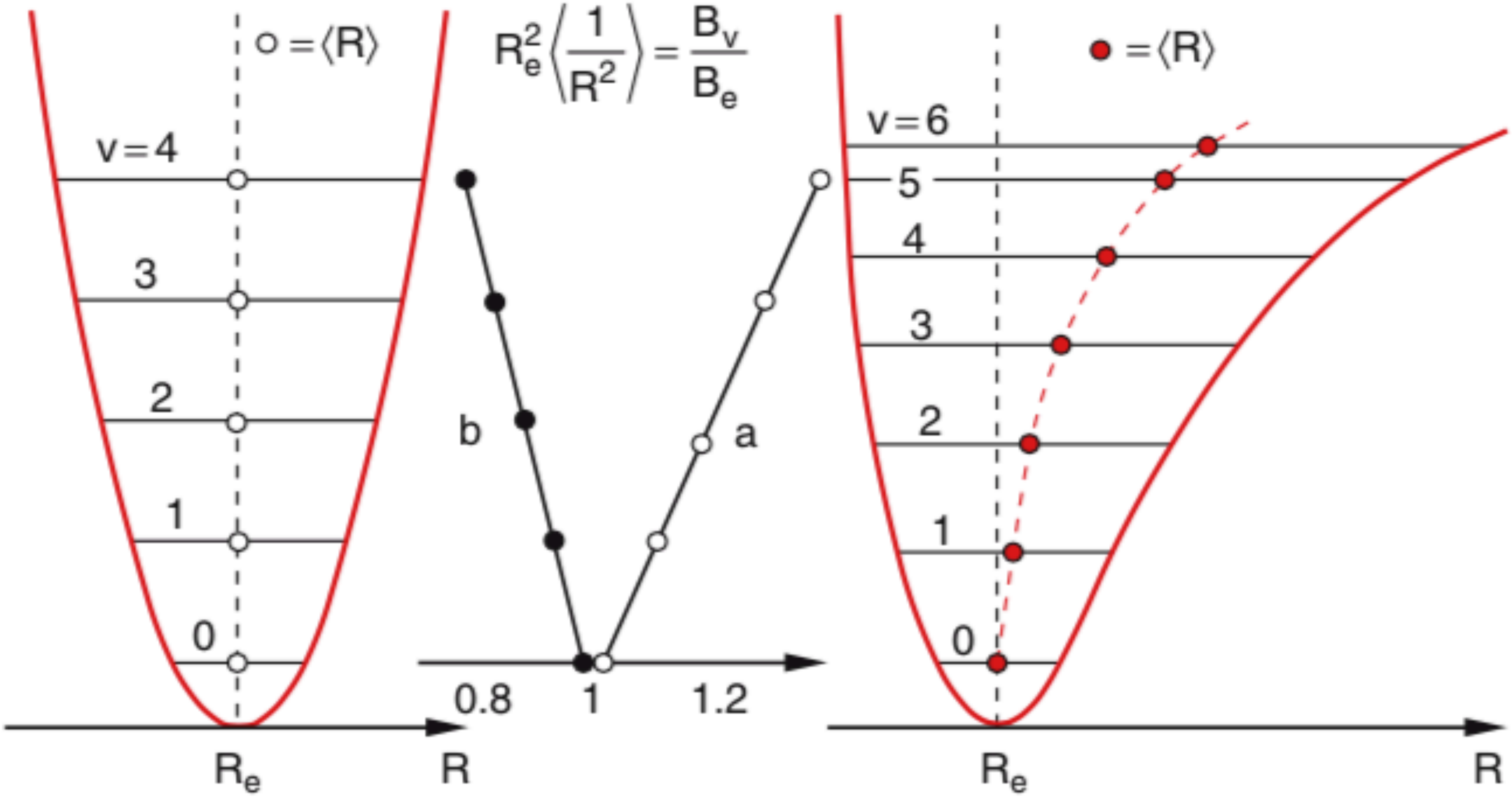
$$\langle E_{\mathrm{rot}}(J;v)\rangle = \frac{\hbar^2 J(J+1)}{2\mu}\left\langle \frac{1}{R^2}\right\rangle$$

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

- Hence:

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

Vibration-rotation interaction



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$$\boxed{\alpha_e > 0}$$

Vibration-rotation interaction

- Term values:

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

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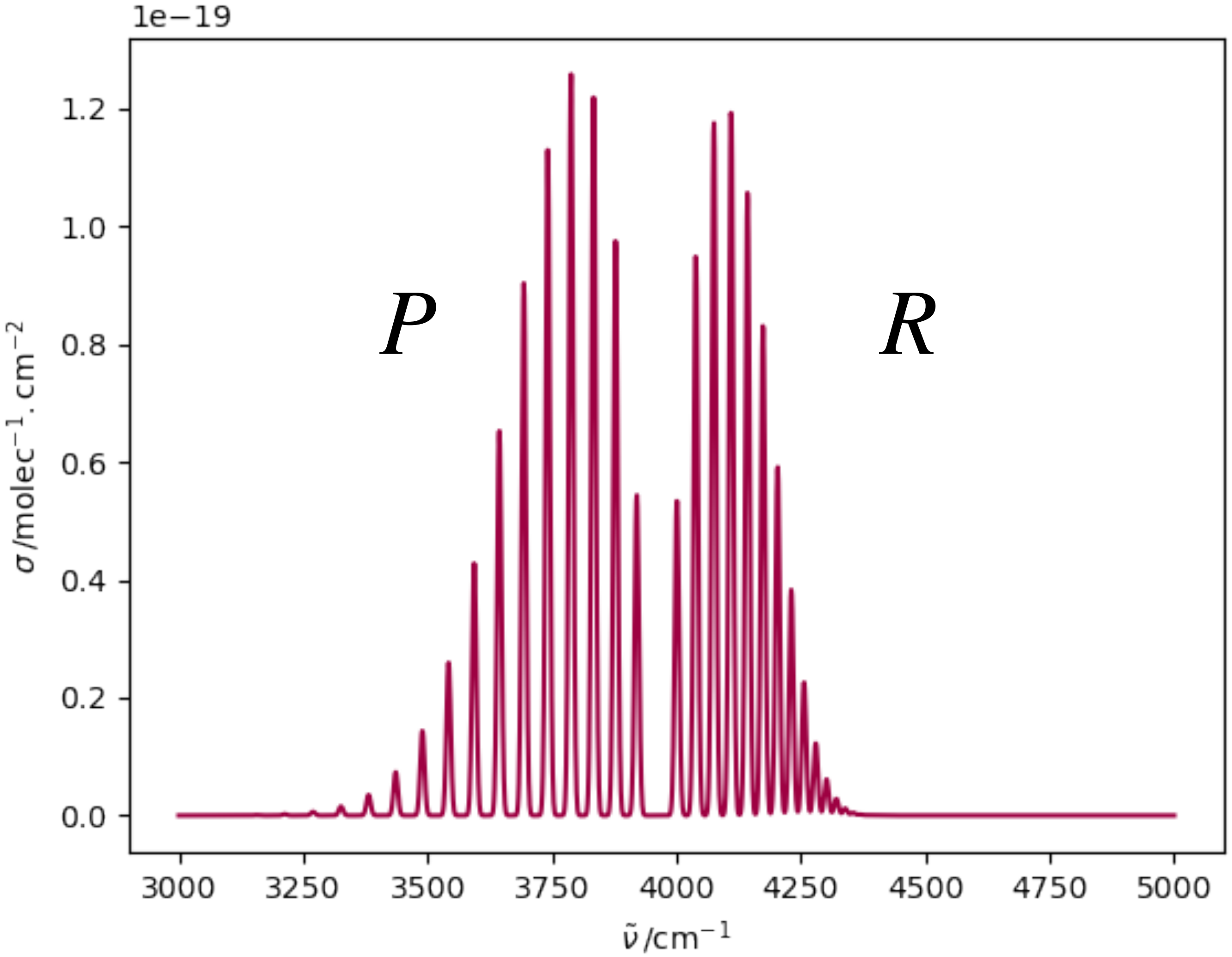
- Even ignoring centrifugal distortion:

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



$$\boxed{B_1 < B_0}$$

Vibration-rotation interaction

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

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

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

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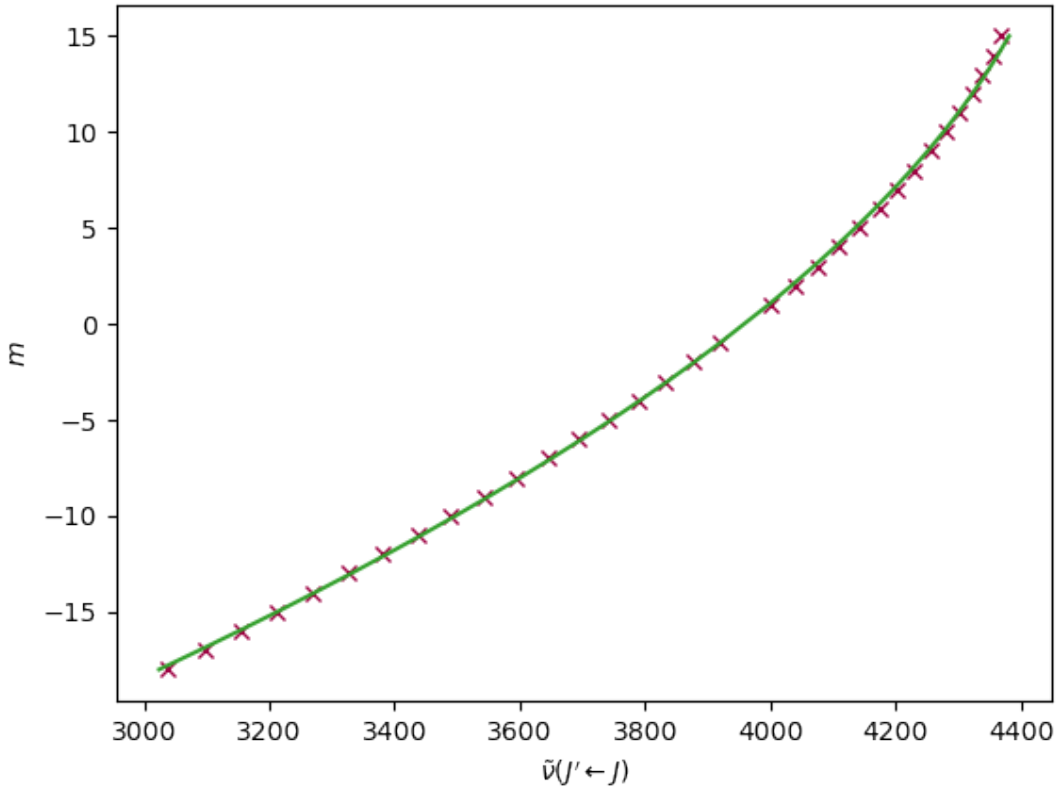

Linear least-squares fit to the "Fortrat parabola":

B_0 = 19.84424 cm^{-1}
B_1 = 19.12415 cm^{-1}
B_e = 20.20428 cm^{-1}
α_e = 0.72009 cm^{-1}

Hot bands and overtones

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

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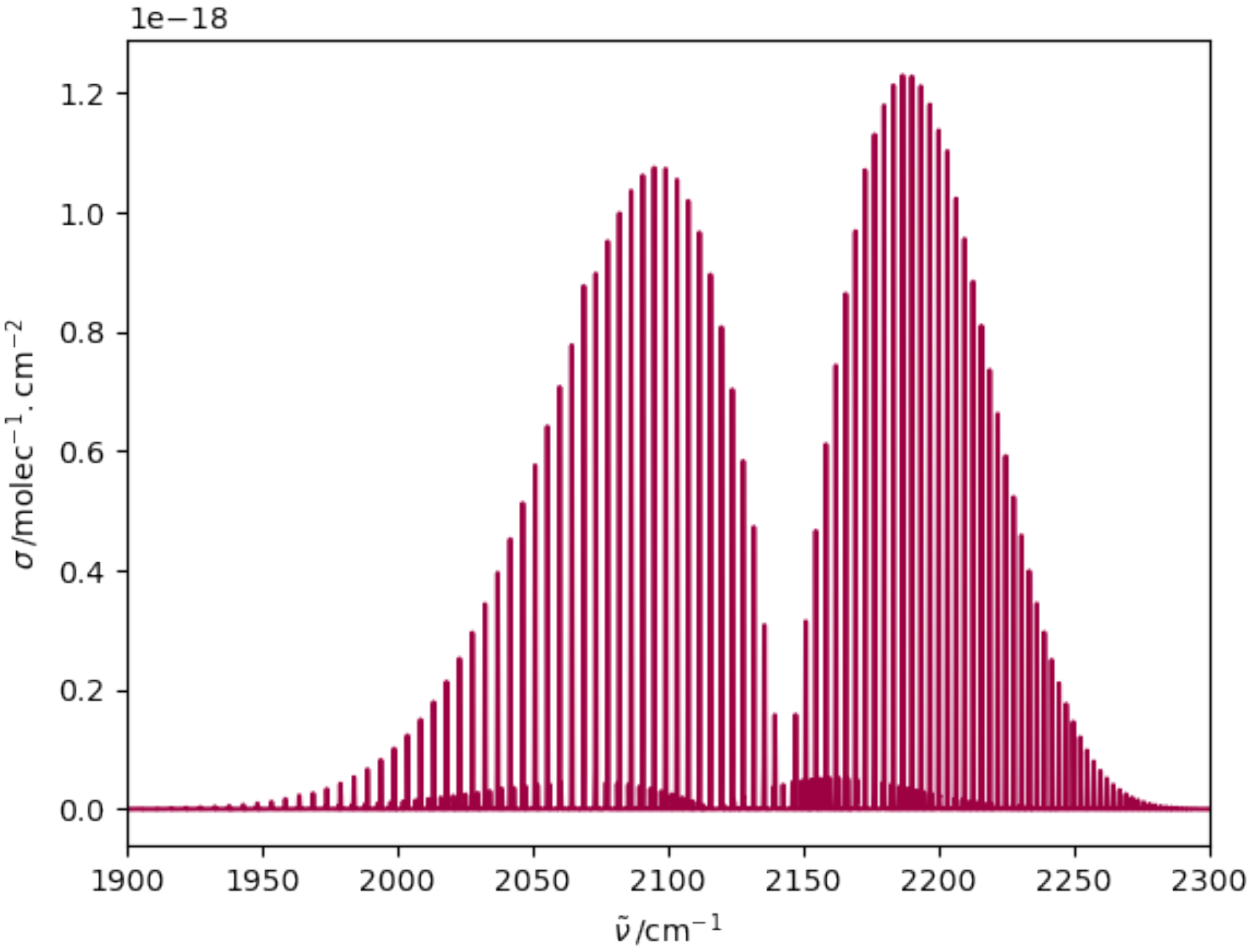
- As T increases, transitions originating on $v = 1$ and higher appear.

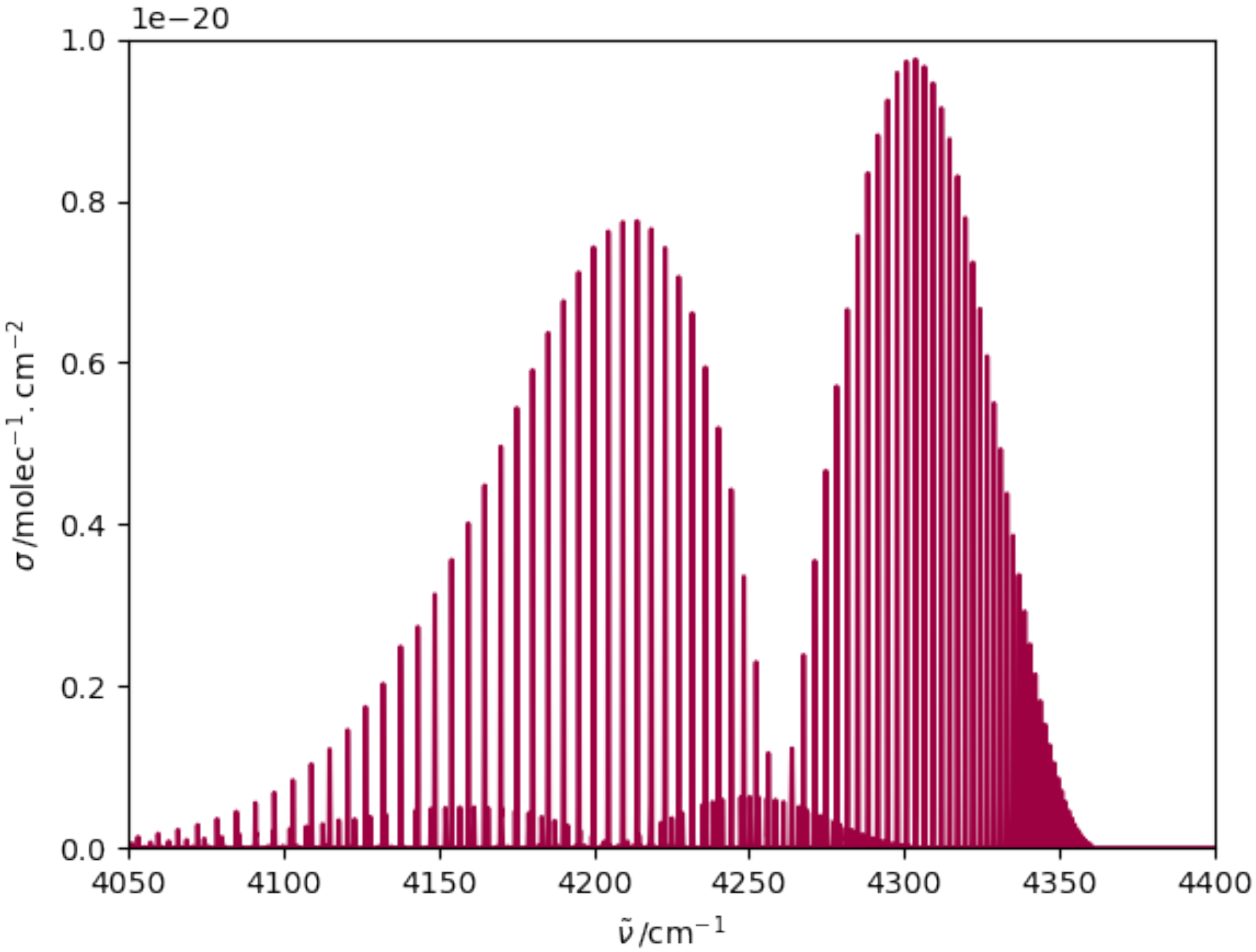
Rovibrational spectrum of CO (800 K)

- 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)

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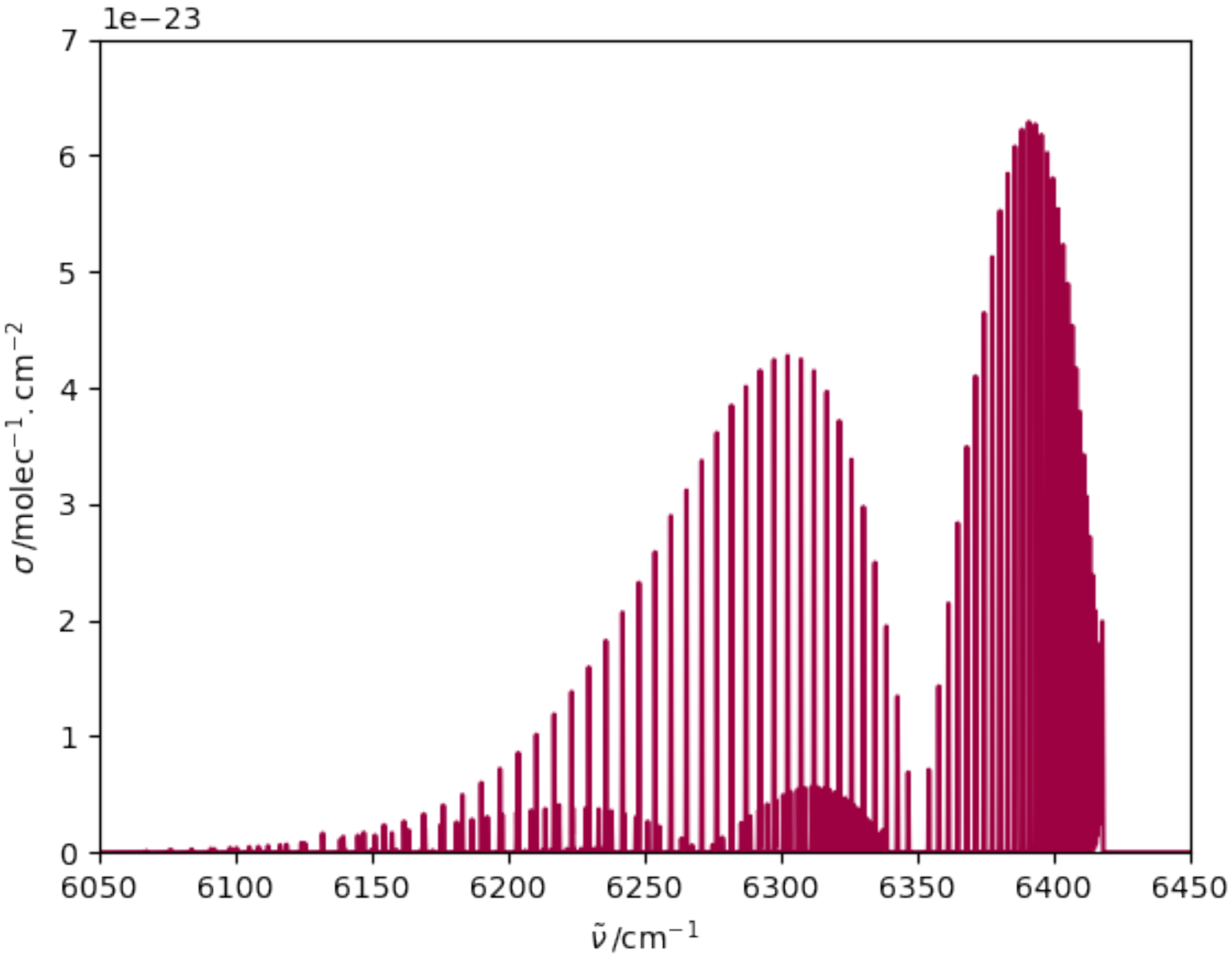

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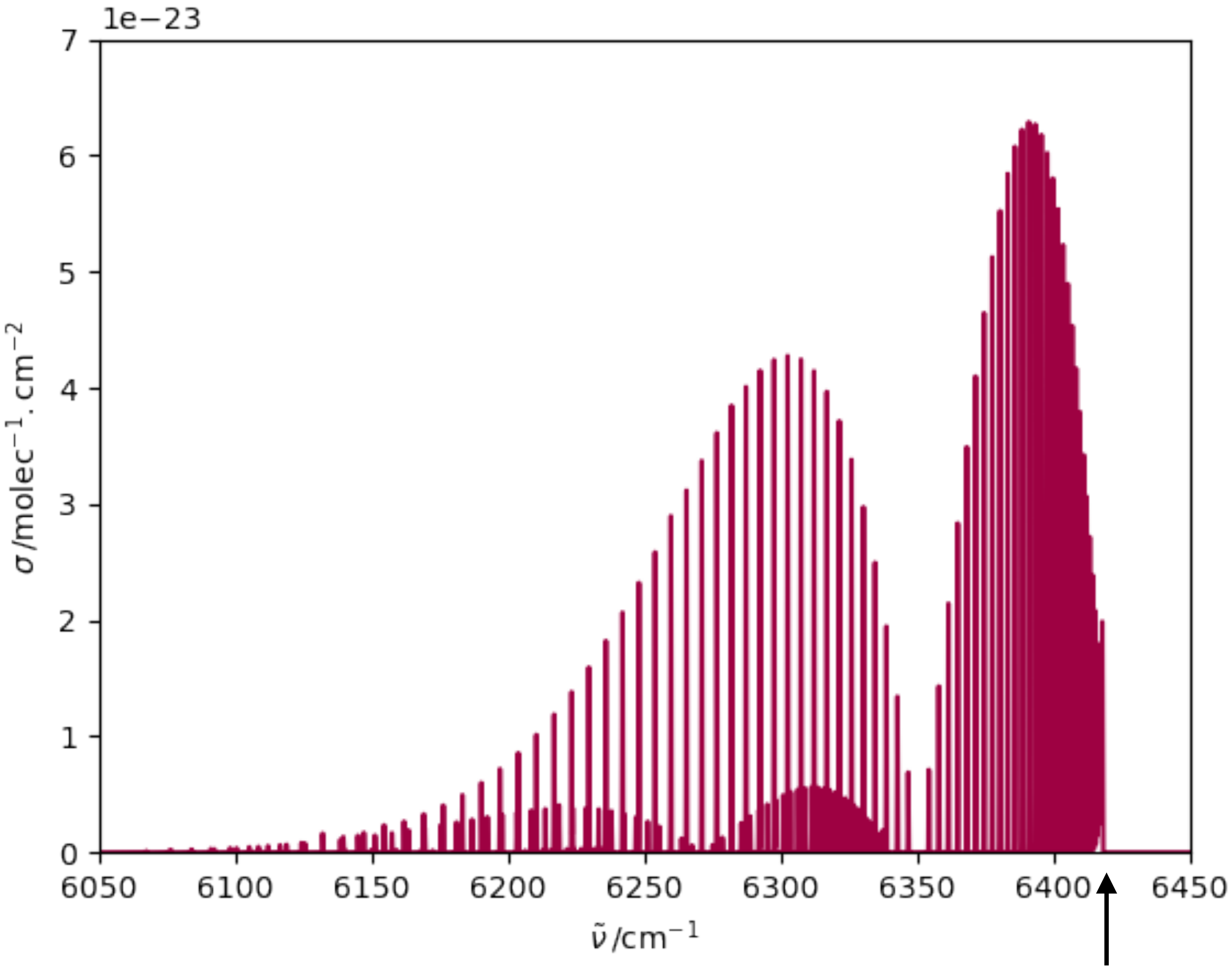

band head

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:

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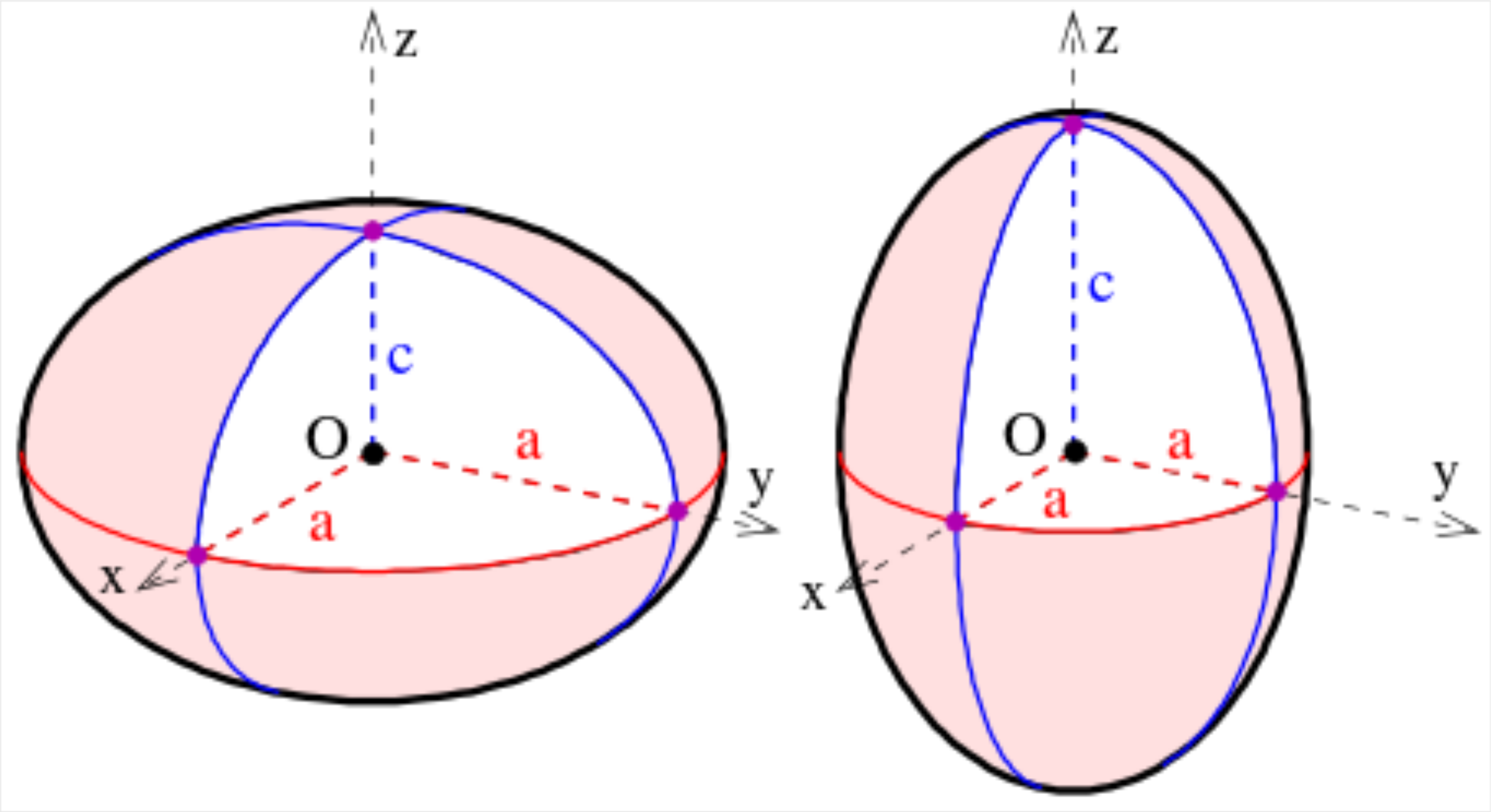
- An asymmetric top (e.g. H_2O) has: $I_a \ne I_b \ne I_c$
- We will briefly consider the remaining case: the *symmetric top*.

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:

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

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

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- This Hamiltonian is diagonal in the basis $|J, K\rangle$:
  - $J = 0, 1, 2, \ldots$: total angular momentum quantum number
  - $K = \text{-}J, \text{-}J{+}1, \ldots, J$: 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).

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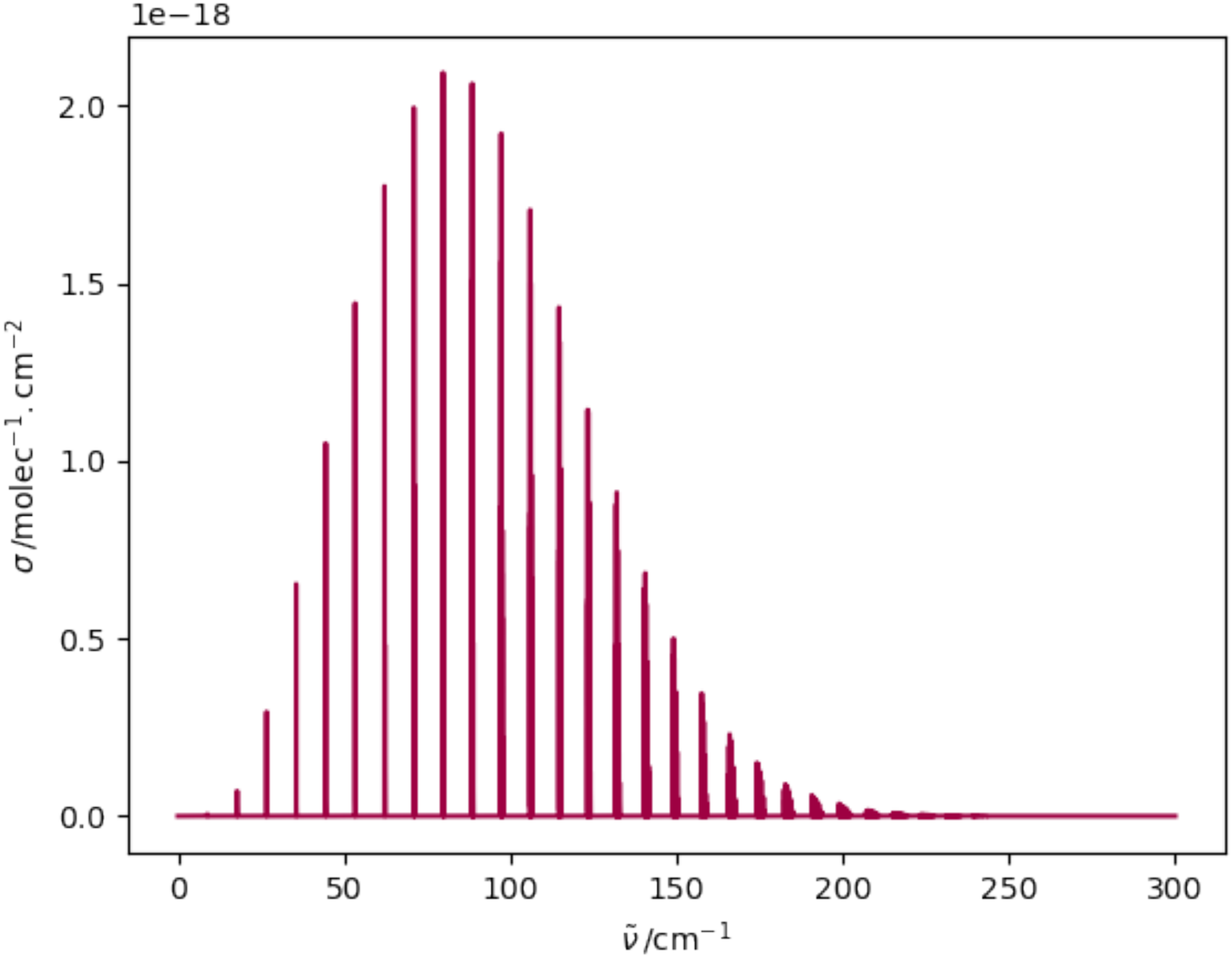
- Unless we consider *centrifugal distortion*:

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

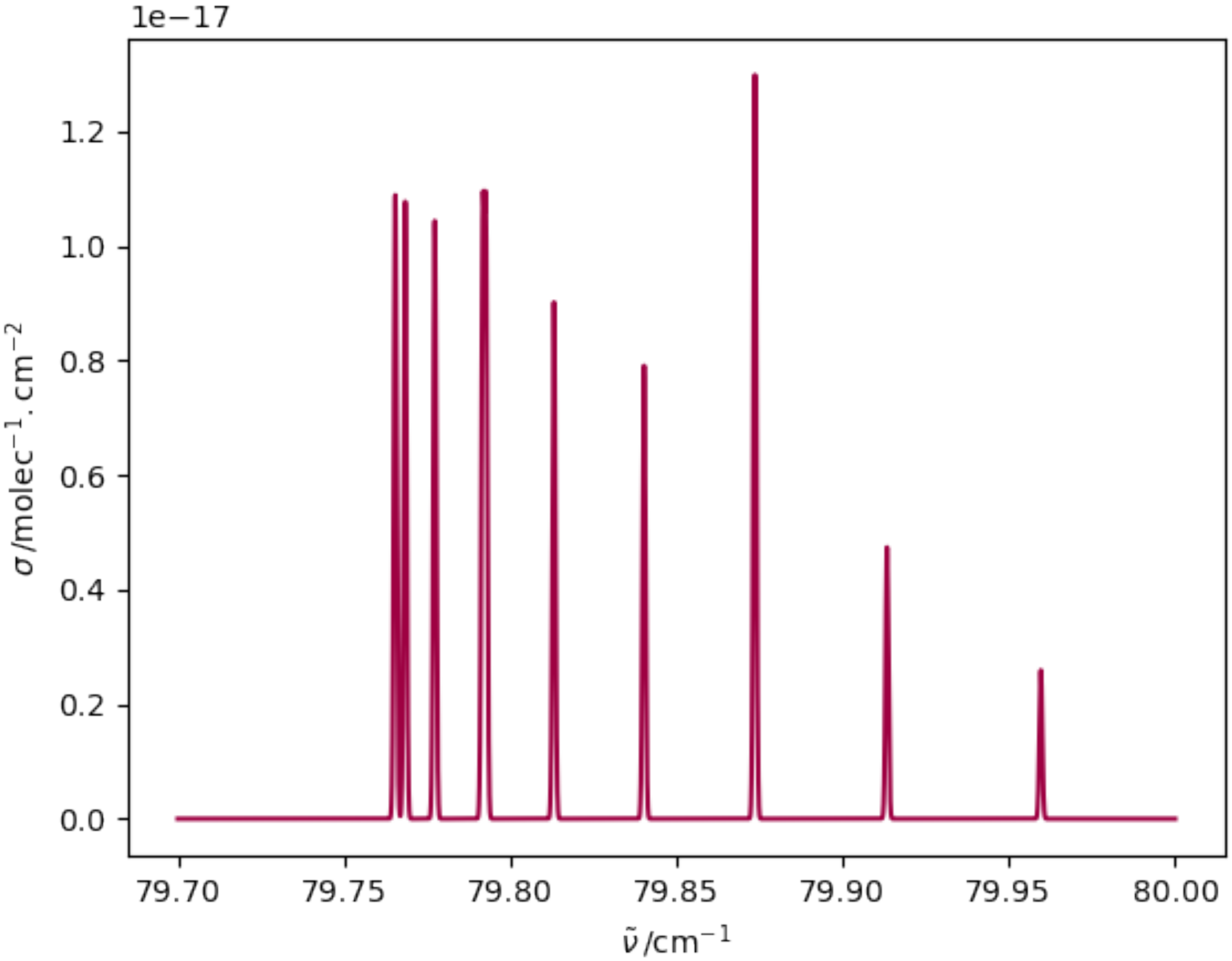
Rotational spectrum of phosphine

- Phosphine (PH_3) is an oblate symmetric top



Rotational spectrum of phosphine

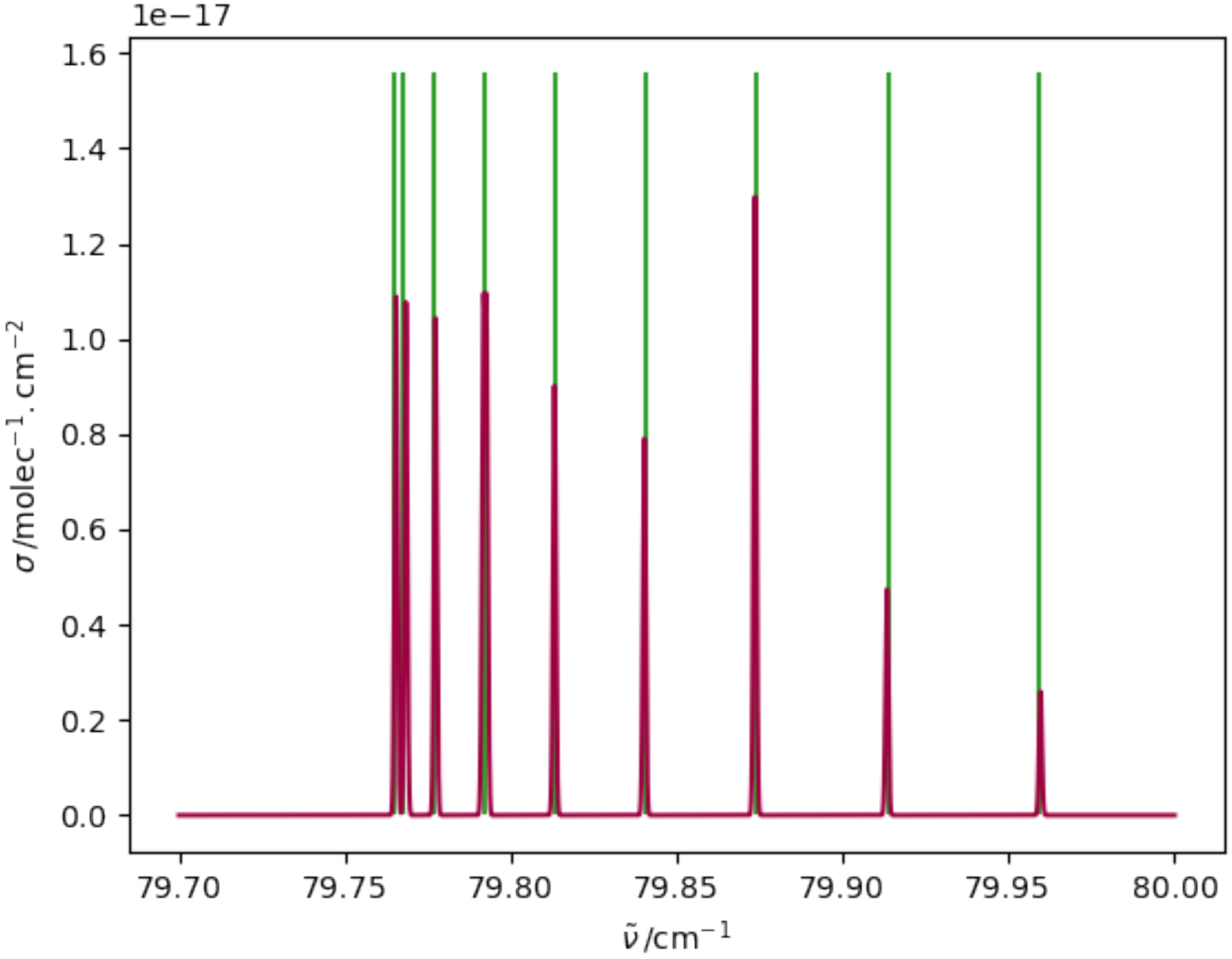
- The pure rotational transition $J = 9 \leftarrow 8$ in PH_3:



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:

$B = 4.45236169\ \mathrm{cm^{-1}}$
$D_{JK} = -0.00016877\ \mathrm{cm^{-1}}$
$D_J = 0.00012956\ \mathrm{cm^{-1}}$

Vibrational spectroscopy: polyatomics

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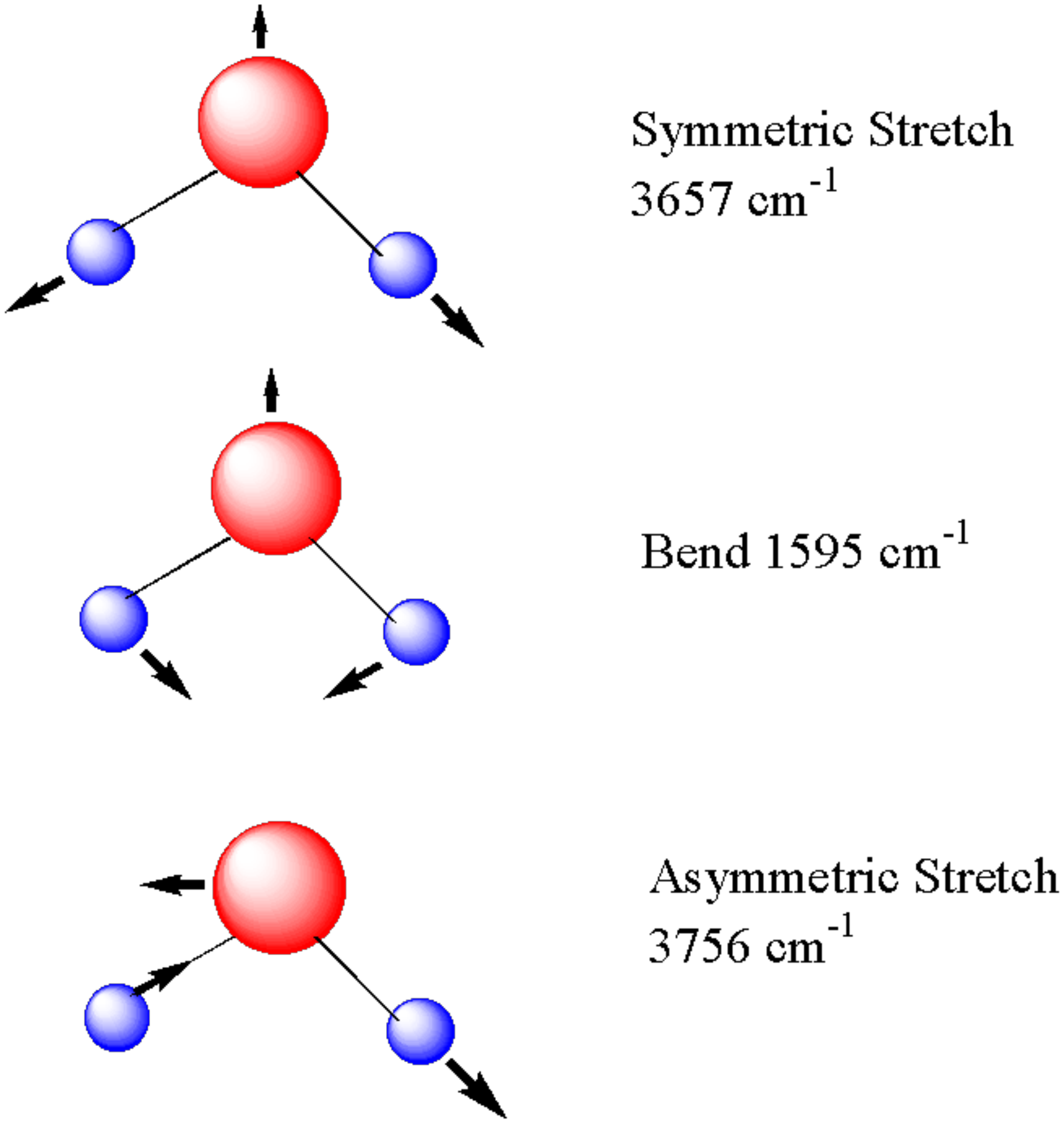
  - Non-linear molecules: $N_{\text{vib}} = 3N - 6$ normal modes
  - Linear molecules: $N_{\text{vib}} = 3N - 5$ normal modes
  - A normal mode may be degenerate (d_k)

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

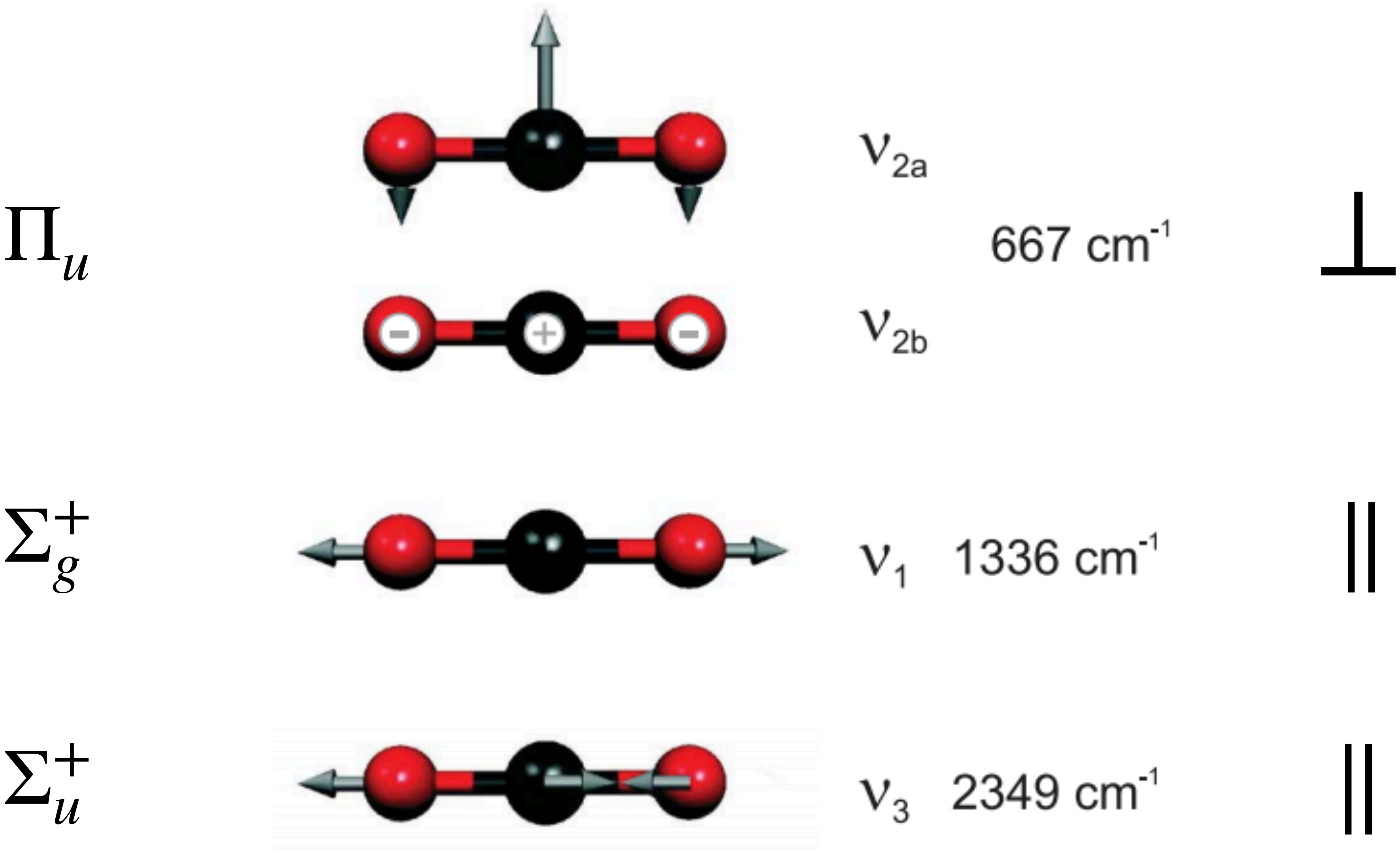
Vibrational spectroscopy: polyatomics

- Example: H_2O normal modes



Vibrational spectroscopy: polyatomics

- Example: CO_2 normal modes – parallel and perpendicular



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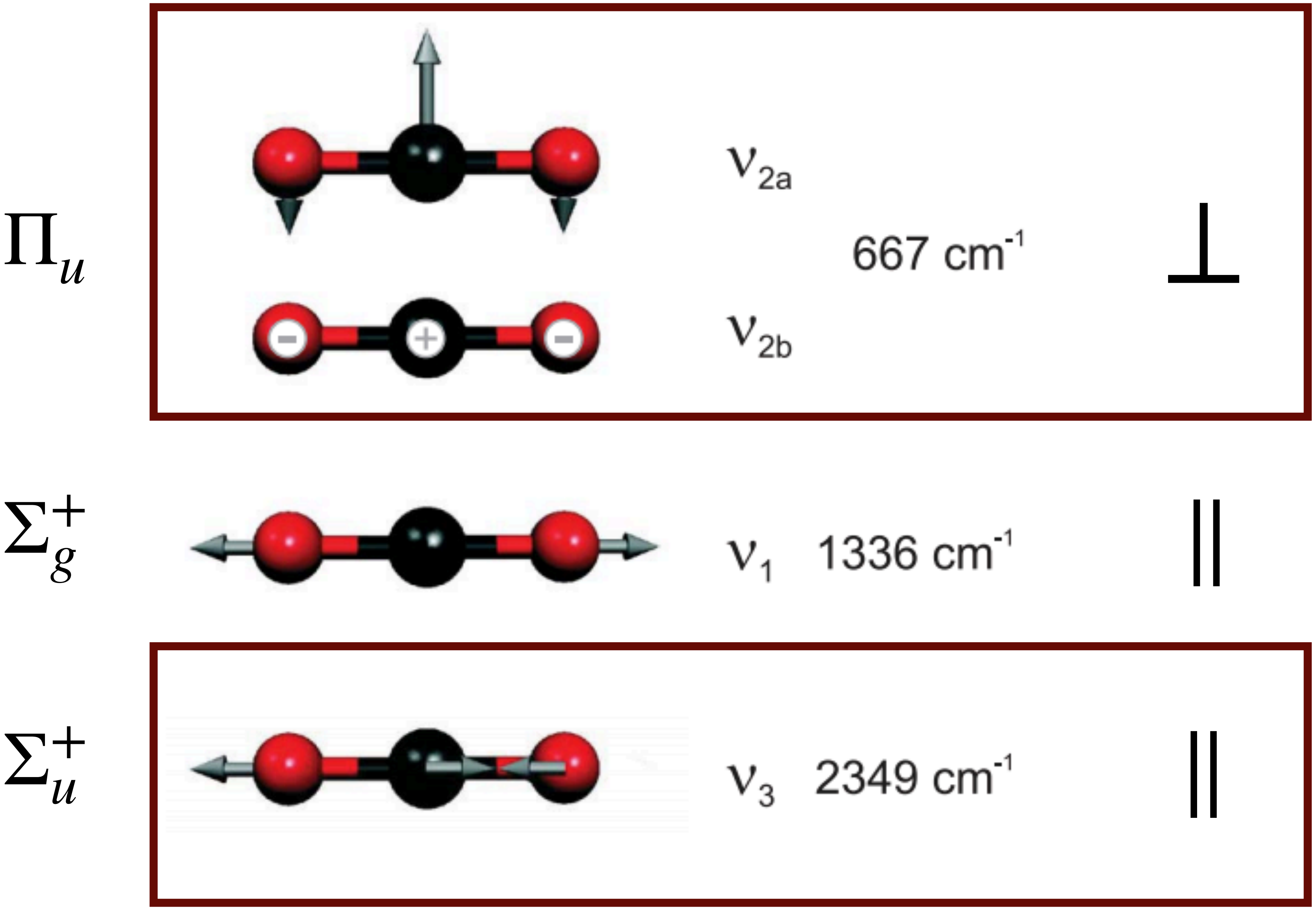

Only modes with a change in dipole moment on vibration are allowed (“IR-active”) (electric dipole gross selection rule)

Vibrations of linear polyatomics

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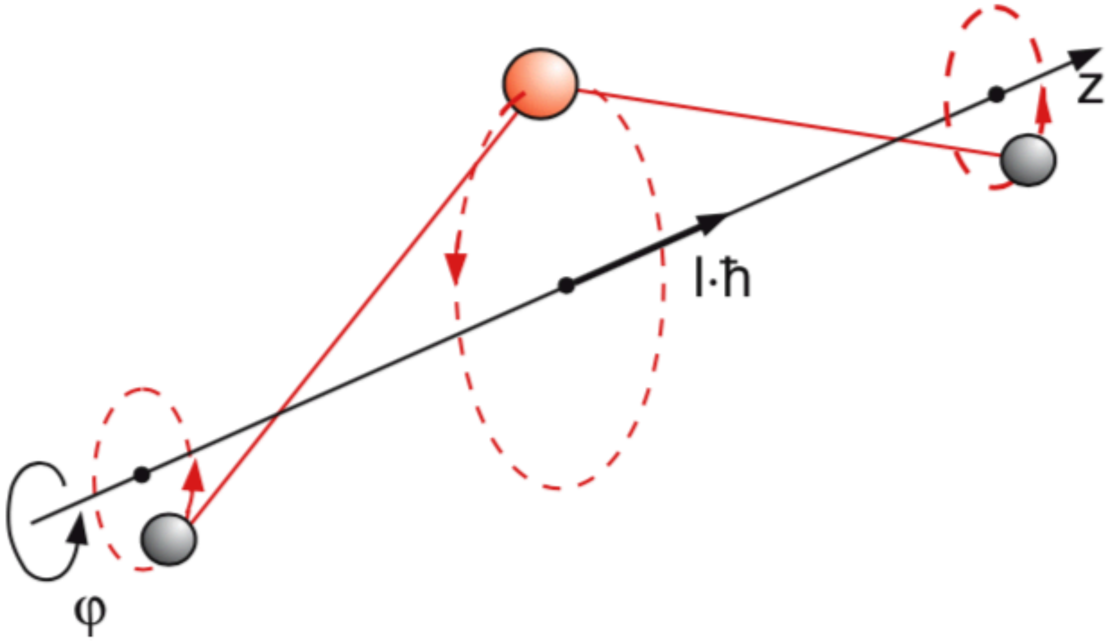
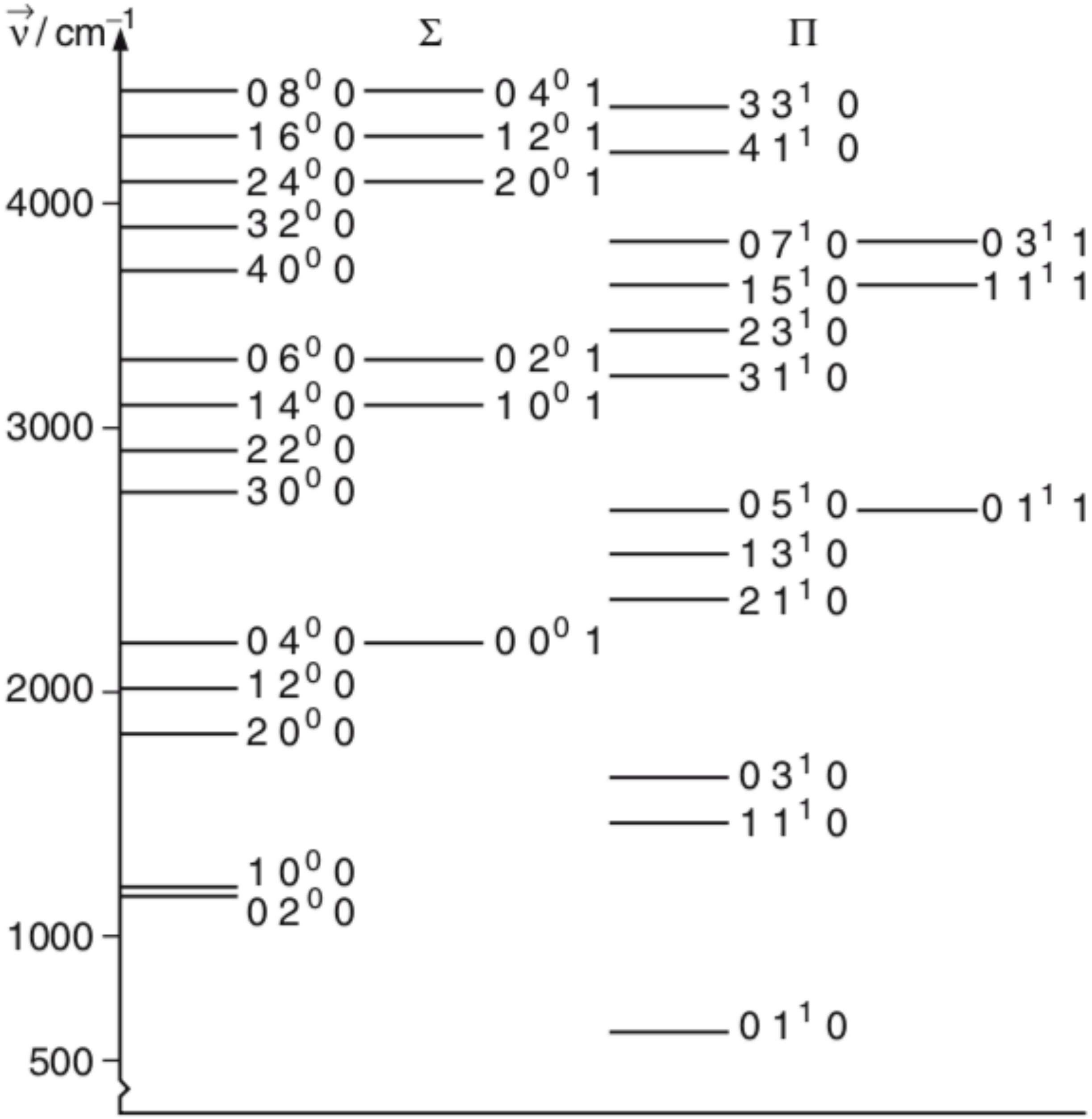
  - Parallel vibrations: $\Delta J = \pm 1$
  - Perpendicular vibrations: $\Delta J = 0, \pm 1$
    - Vibrational angular momentum:



Vibrational spectroscopy: polyatomics

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



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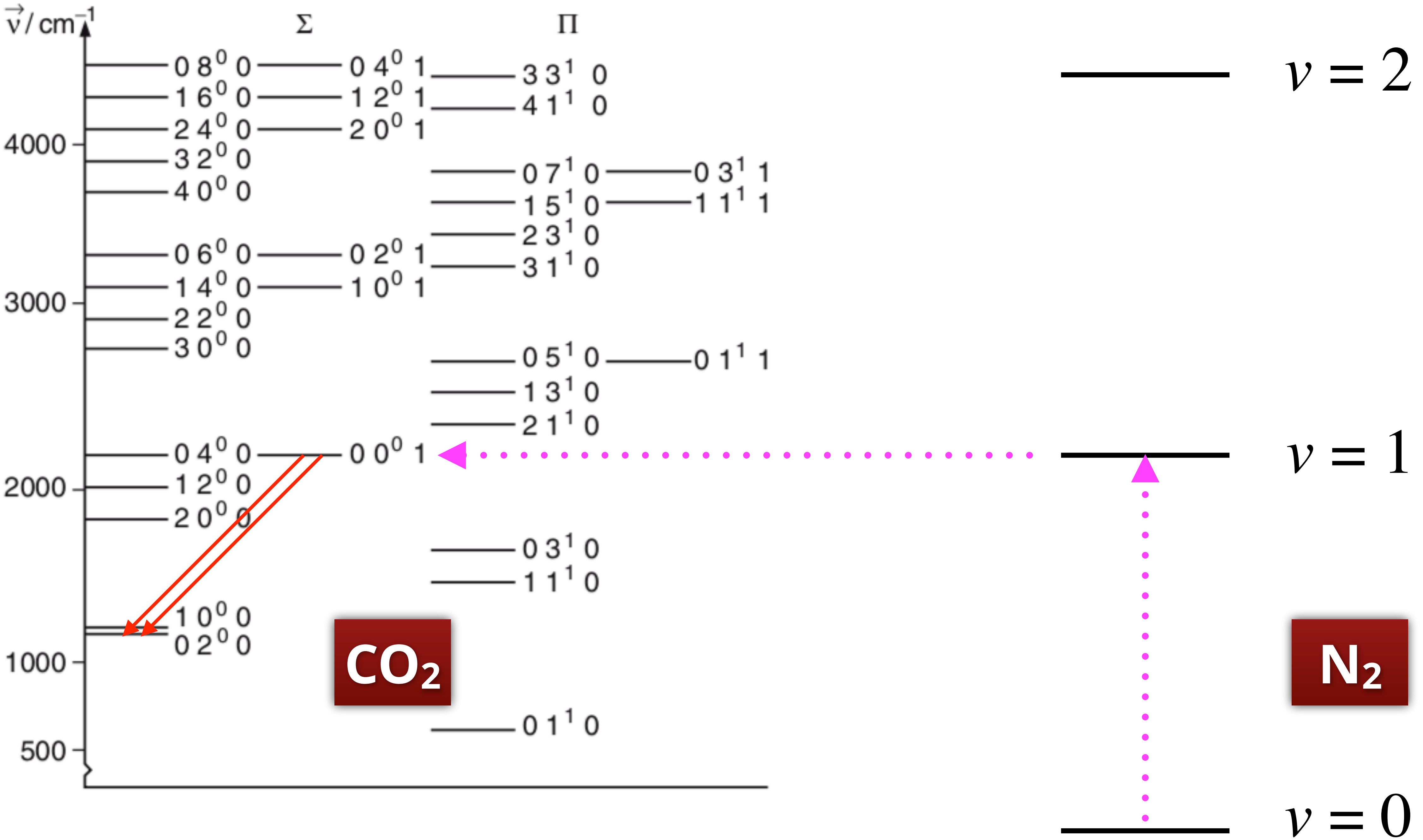
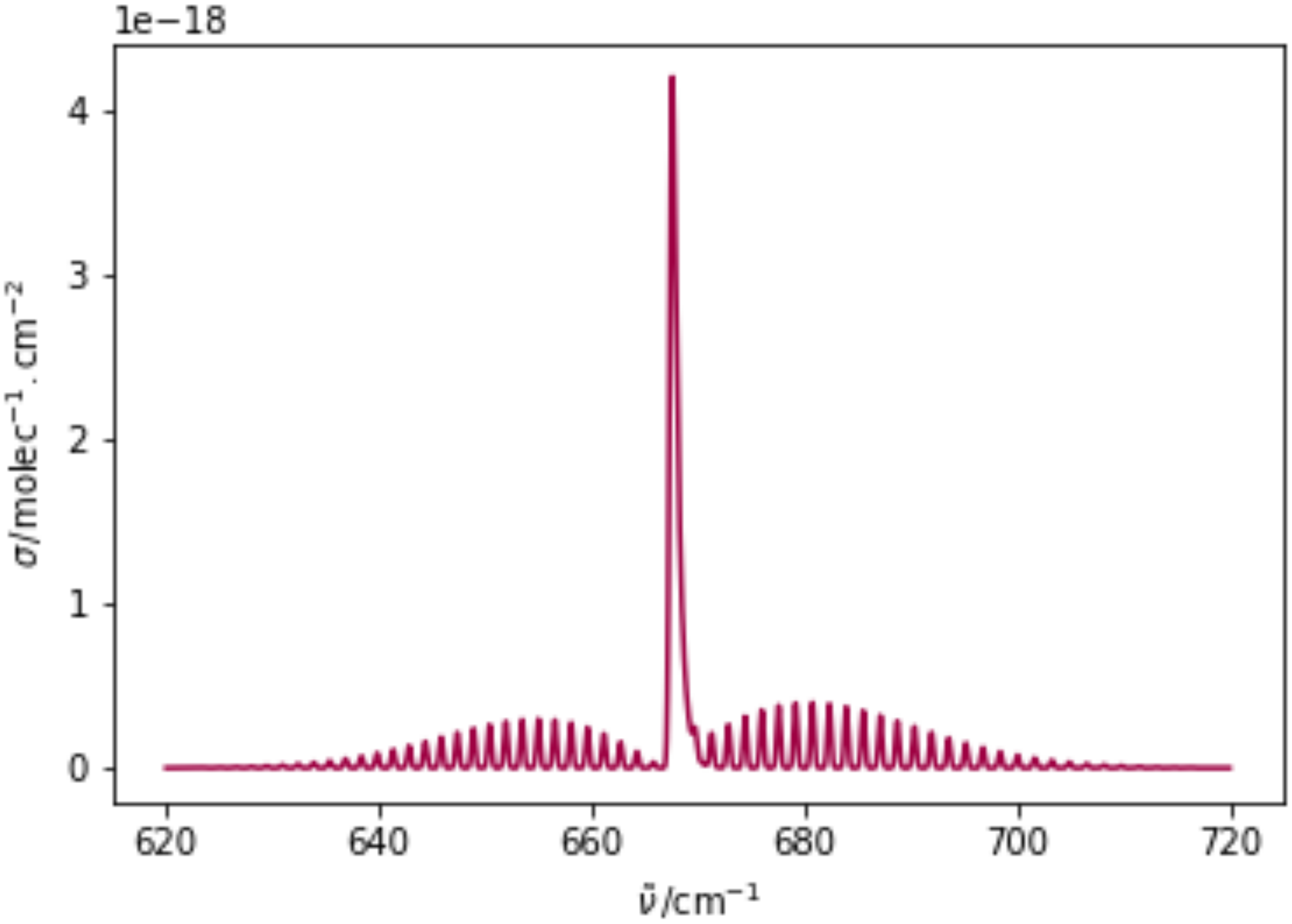


Vibrations of linear polyatomics

- The $(01^10) - (00^00)$ band (P, Q and R branches)



Vibrations of linear polyatomics

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