Vibrational Spectroscopy

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Remote Sensing Gone Wrong

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SPECTROSCOPIC EVIDENCE FOR VEGETATION ON MARS

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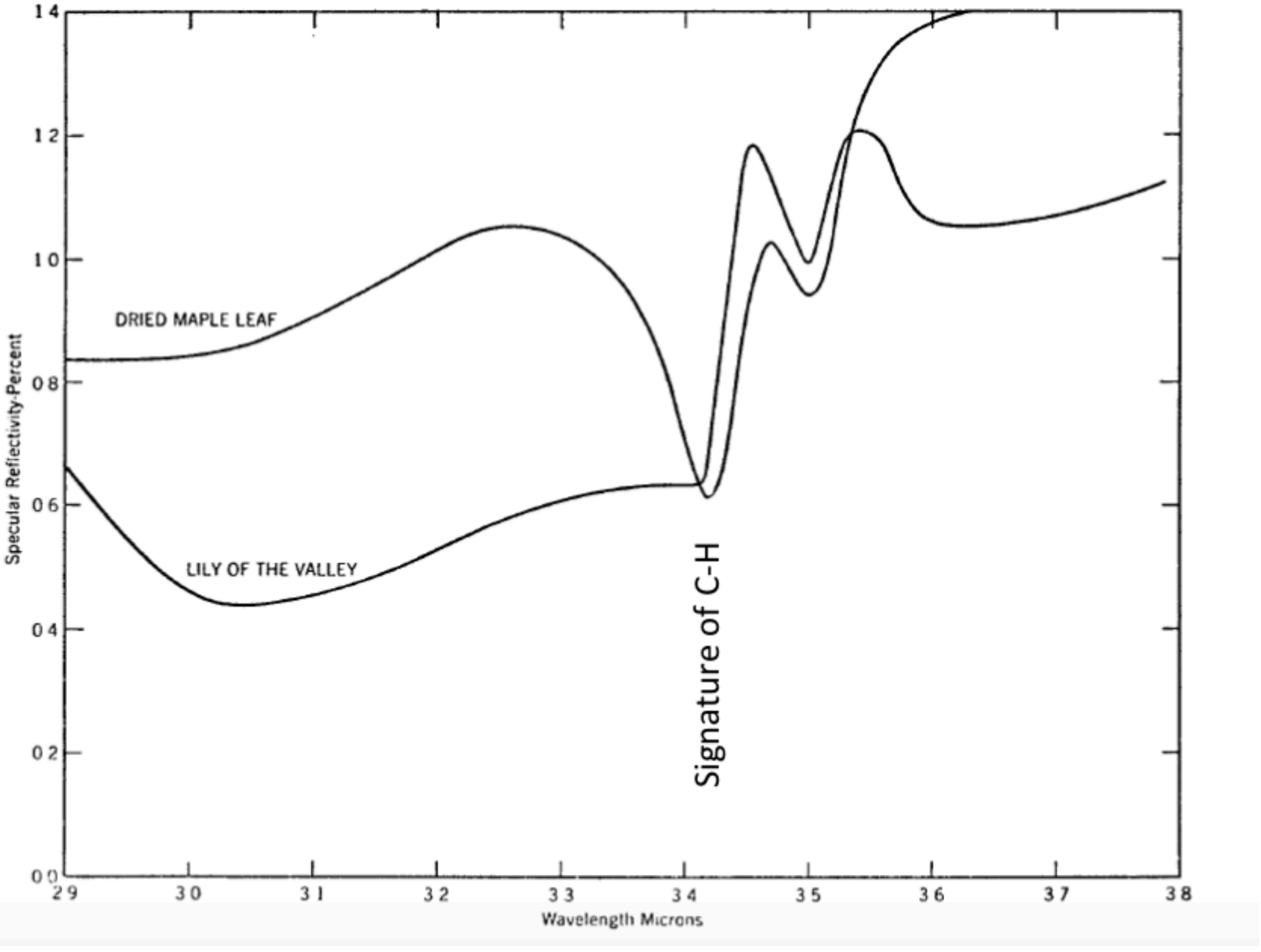

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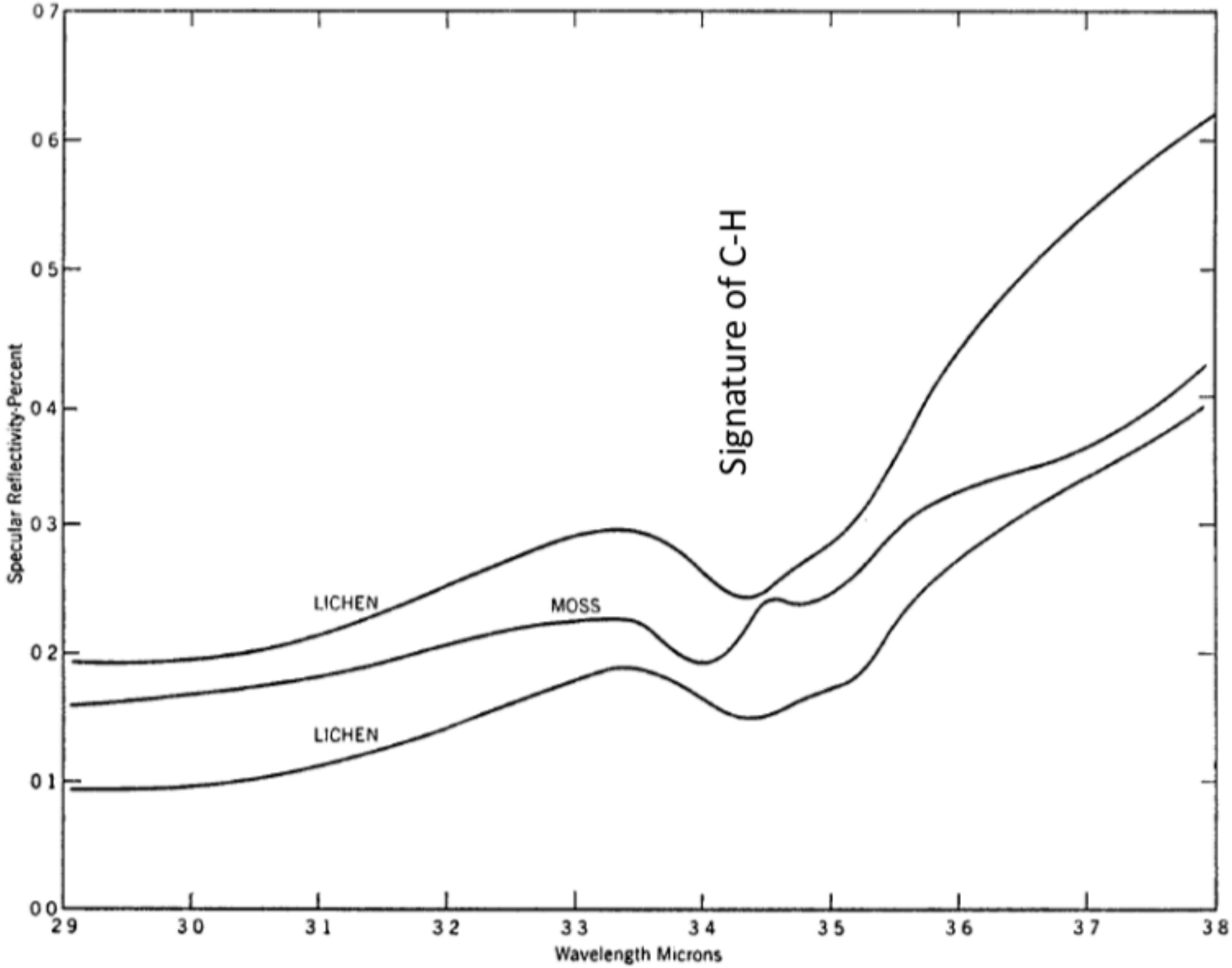

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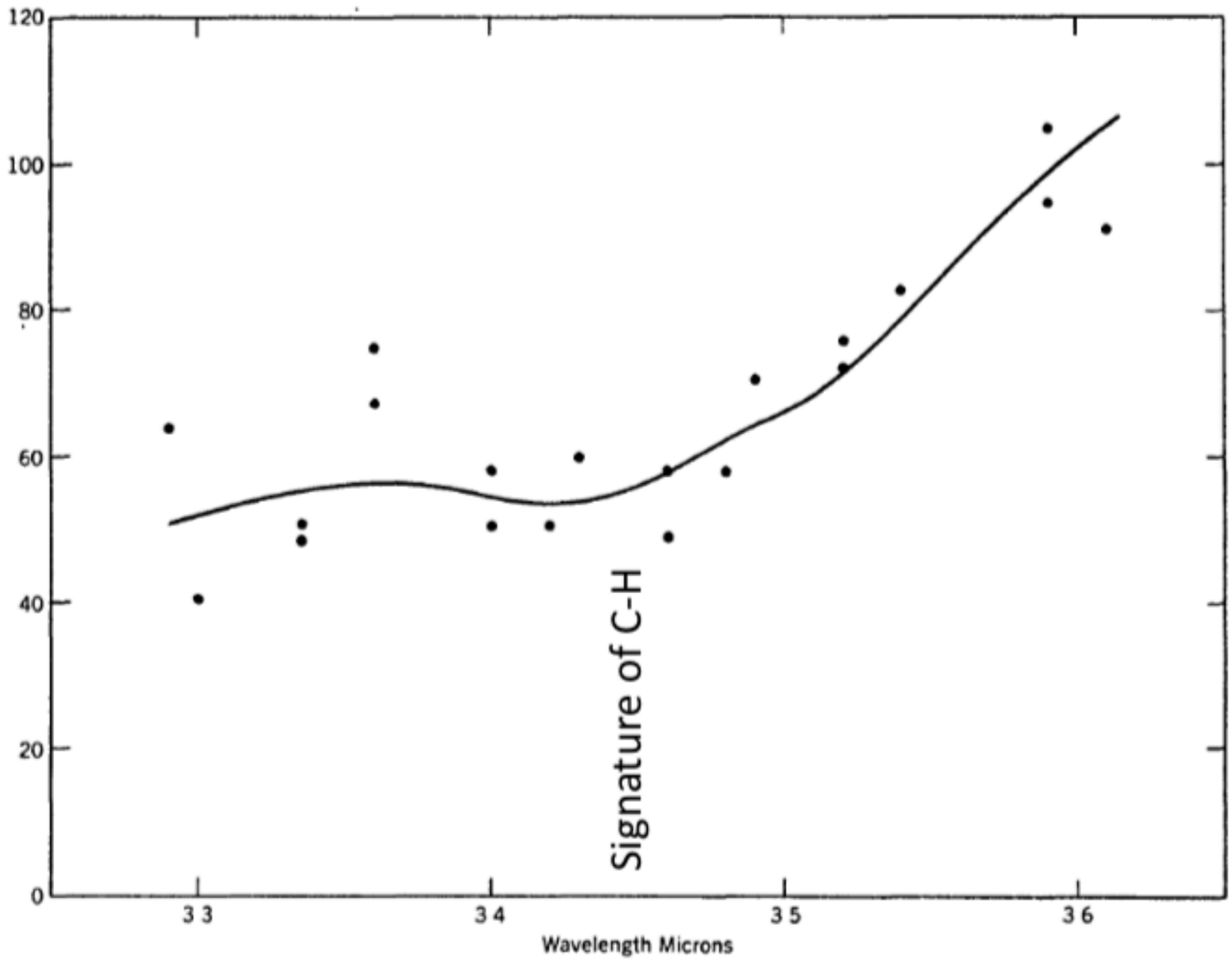
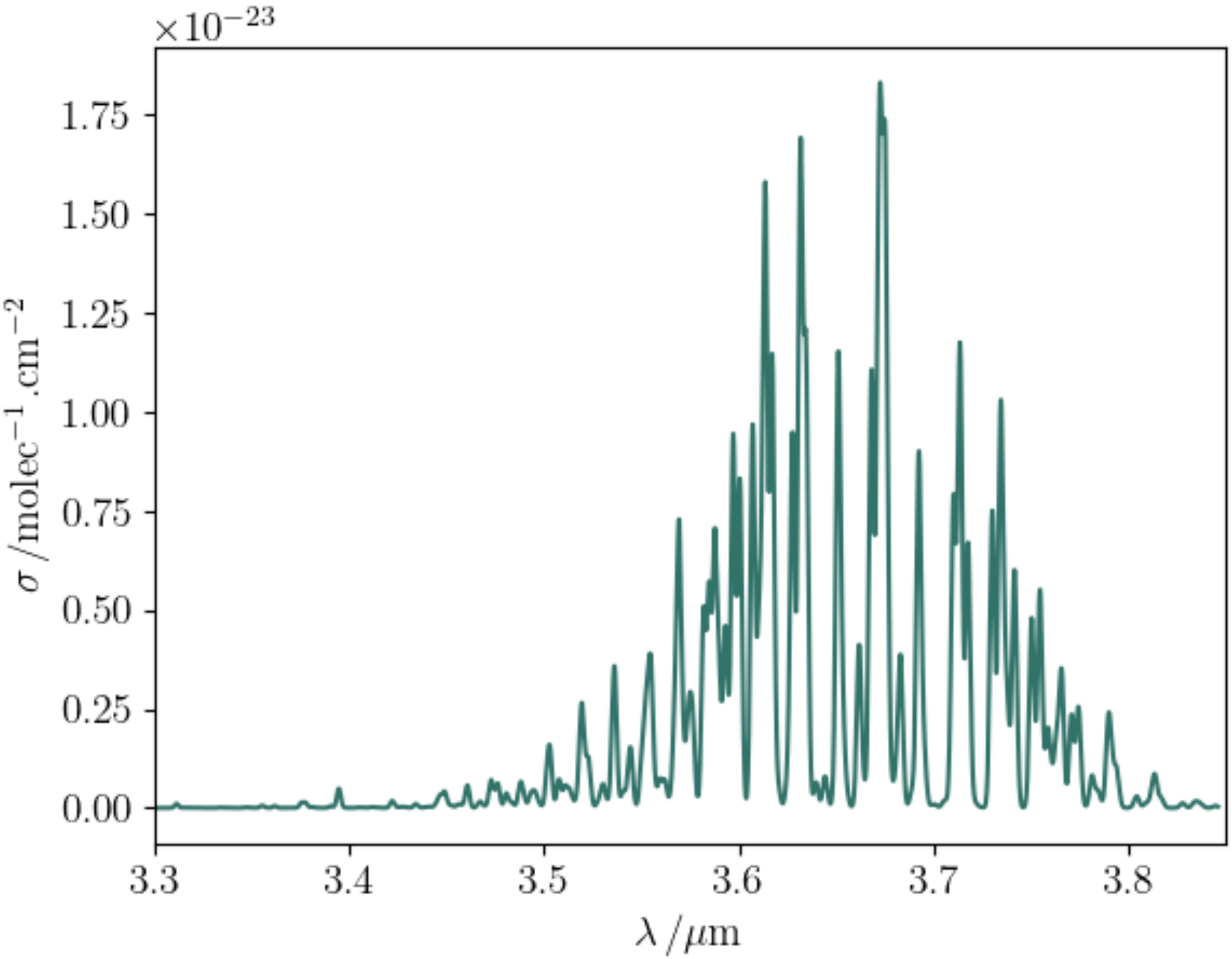


FIG. 3.—Observations of the spectrum of Mars obtained on four nights and after division by the solar spectrum (*solid curve* of Fig. 2).

Remote Sensing Gone Wrong



The Vibrational Hamiltonian

$$\nabla_R^2 S + \frac{2\mu}{\hbar^2}\left[E_{n,m} - V_n(R) - \frac{\hbar^2}{2\mu R^2}J(J+1)\right] S = 0$$

For the non-rotating molecule ($J = 0$):

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

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

$$V_n(R) = V_n(R_\mathrm{e}) + \frac{\mathrm{d}V_n}{\mathrm{d}R}(R - R_\mathrm{e}) + \frac{1}{2}\frac{\mathrm{d}^2 V_n}{\mathrm{d}R^2}(R - R_\mathrm{e})^2 + \ldots$$

The Vibrational Hamiltonian

$$V_n(R) = V_n(R_\mathrm{e}) + \frac{\mathrm{d}V_n}{\mathrm{d}R}(R - R_\mathrm{e}) + \frac{1}{2}\frac{\mathrm{d}^2 V_n}{\mathrm{d}R^2}(R - R_\mathrm{e})^2 + \ldots$$

We can choose the first term to be zero.

The second term *is* zero.

Defining the *bond force constant*,

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

we get $V_n(R) \approx \frac{1}{2}k(R - R_\mathrm{e})^2$

(the parabolic potential used earlier).

The Vibrational Hamiltonian

The resulting Schrödinger equation,

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

can be solved exactly. Substitute $S(R)=\psi(x)/(x+R_\mathrm{e})$, where $x=R-R_\mathrm{e}$ is the displacement of the nuclei from equilibrium to get:

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

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

The Vibrational Hamiltonian

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

There is a characteristic length that we can scale x by: $\alpha = \hbar^p \mu^q k^r$ where the dimensions, $[\hbar] = [ML^2T^{-1}]$, $[\mu] = [M]$ and $[k] = [MT^{-2}]$. Since $[\alpha] = [L]$ we must have

$$\begin{aligned} L &: 1 = 2p \\ M &: 0 = p + q + r \\ T &: 0 = -p - 2r \end{aligned}$$

and hence $p = \frac{1}{2}, q = -\frac{1}{4}$ and $r = -\frac{1}{4}$:

$$\alpha = \left(\frac{\hbar^2}{\mu k}\right)^{1/4}$$

The Vibrational Hamiltonian

With the new coordinate, $q = x/\alpha = (\mu k/\hbar^2)^{1/4} x$ the Schrödinger equation is:

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

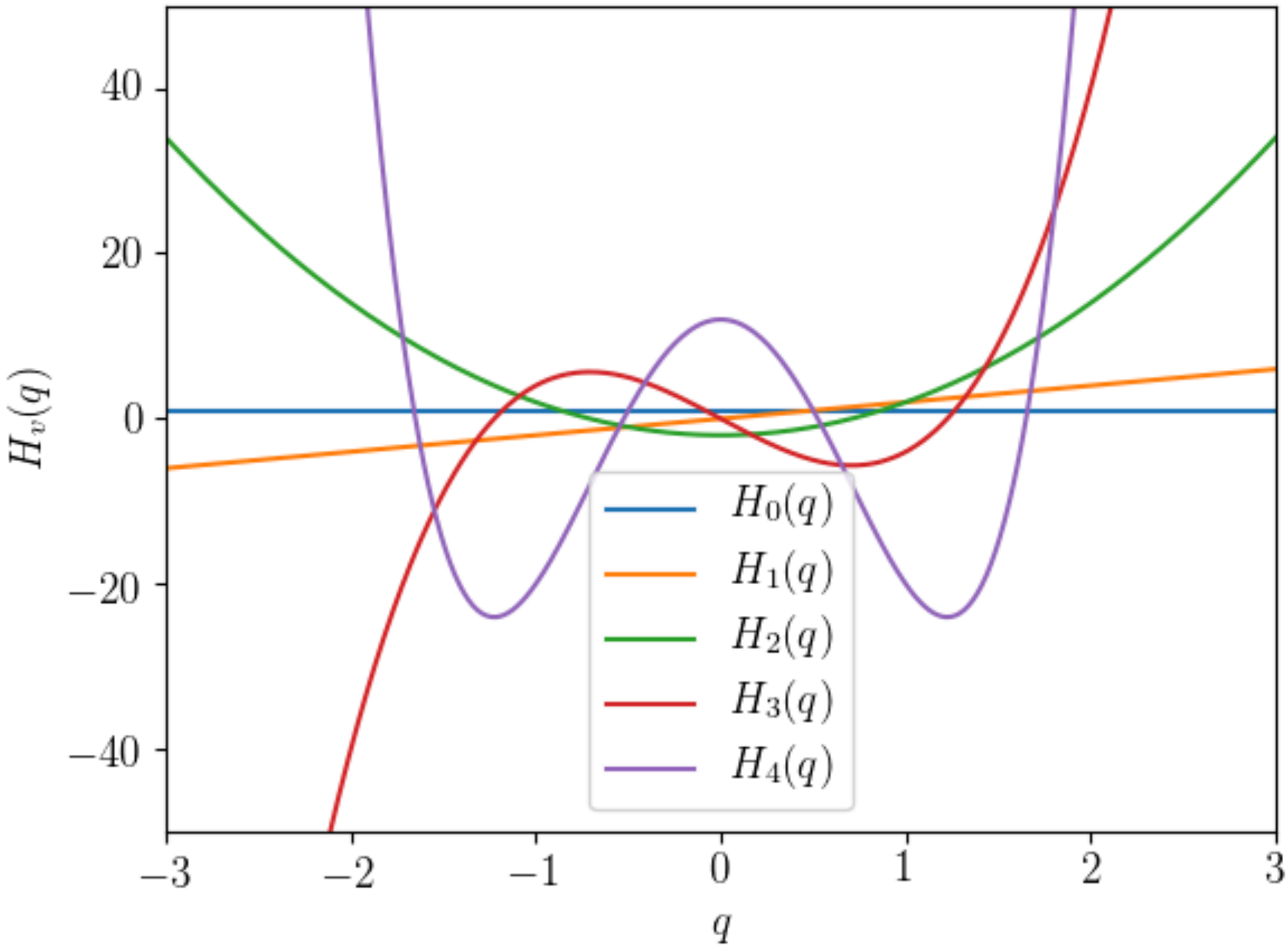
where $\omega = \sqrt{\ } k/\mu$ and its solutions are:

$$\psi(q) = N_\upsilon H_\upsilon(q) \exp(-q^2/2),$$

where $H_\upsilon(q)$ are *Hermite polynomials* and N_υ is a normalization constant. The energy,

$$E_\upsilon = \hbar\omega(\upsilon + \tfrac{1}{2}) \quad \text{for } \upsilon = 0, 1, 2, \ldots .$$

Hermite Polynomials



Hermite Polynomials

- Definition:

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

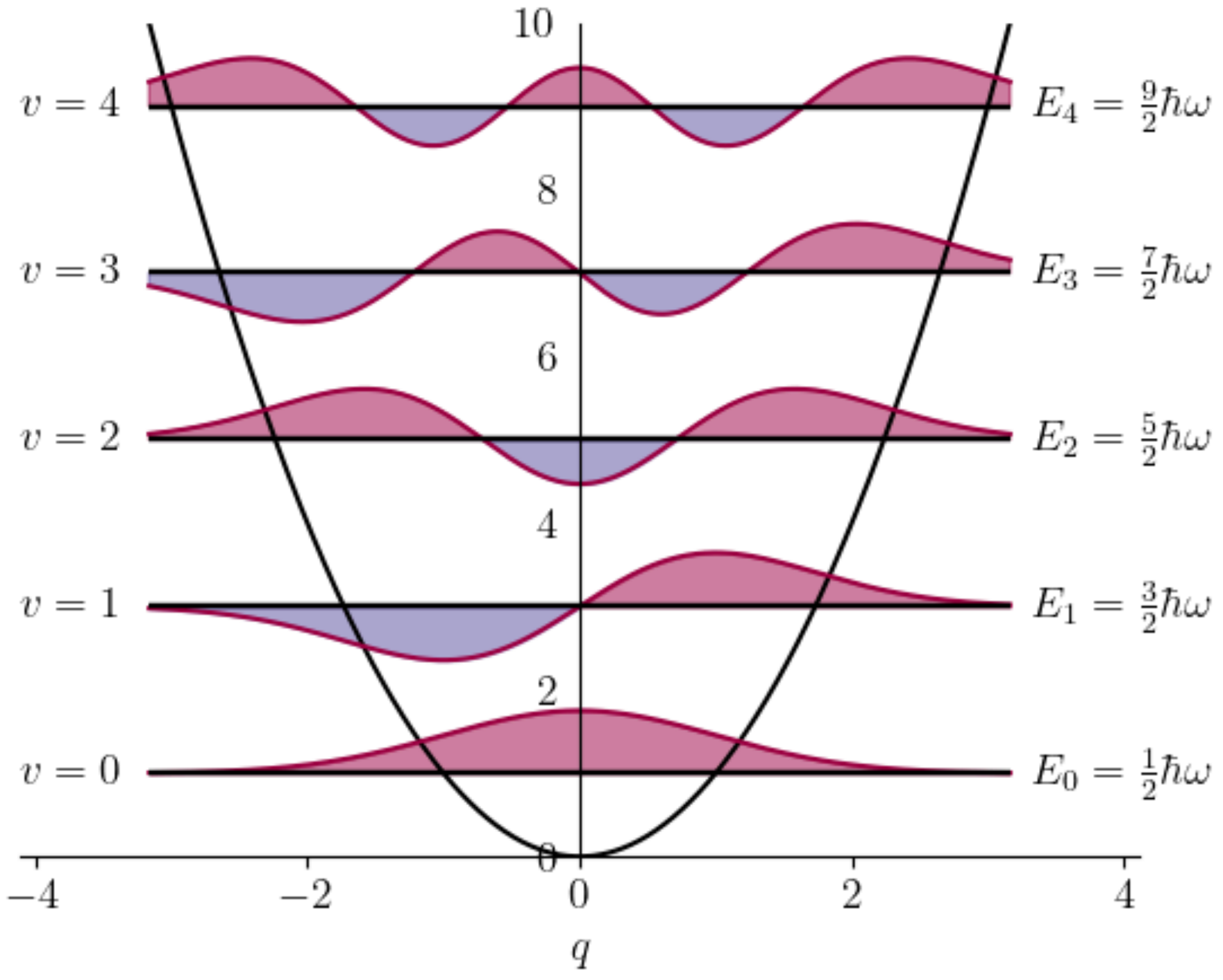
- Orthogonality with respect to weight function e^{-q^2}:

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

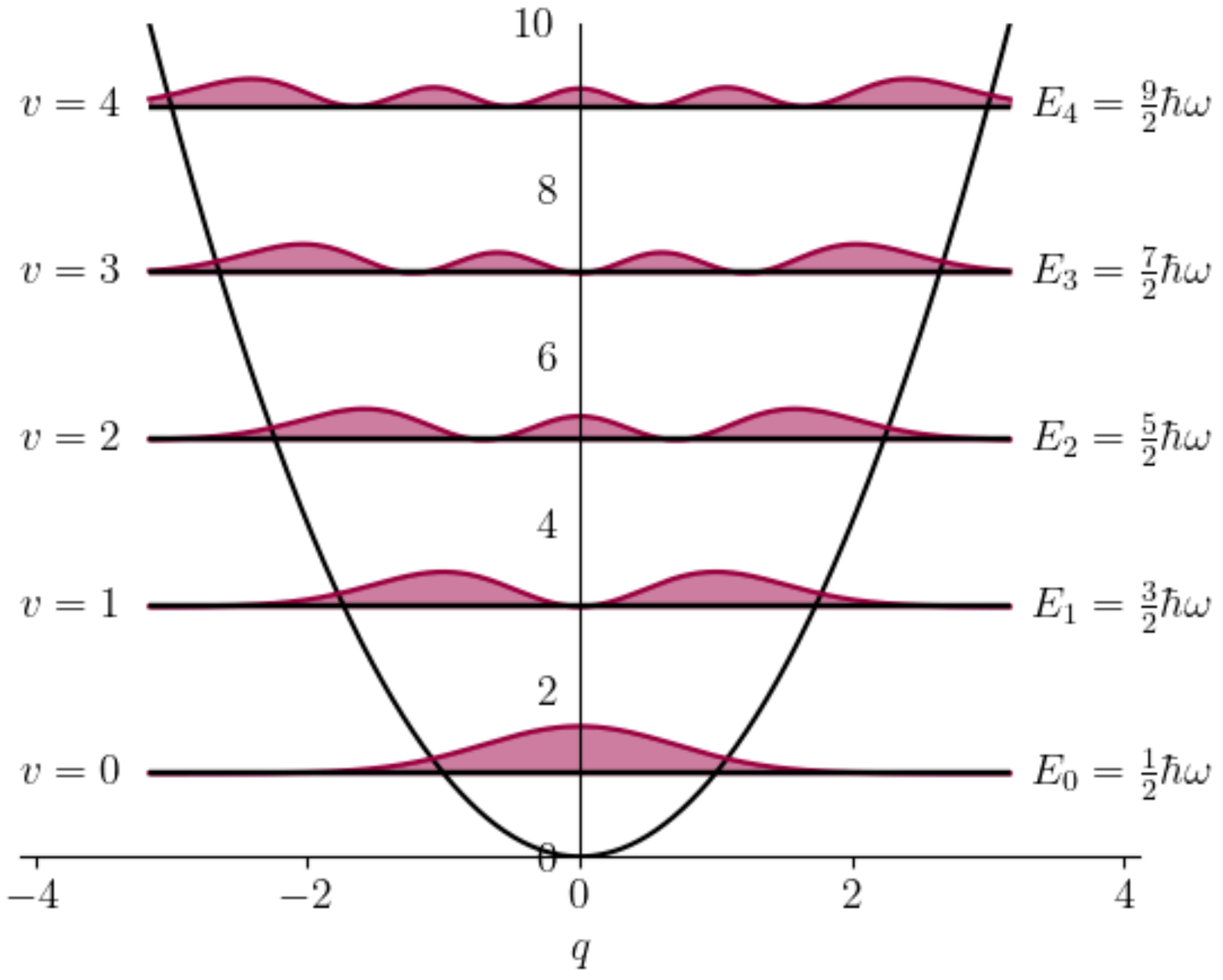
- Recursion:

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

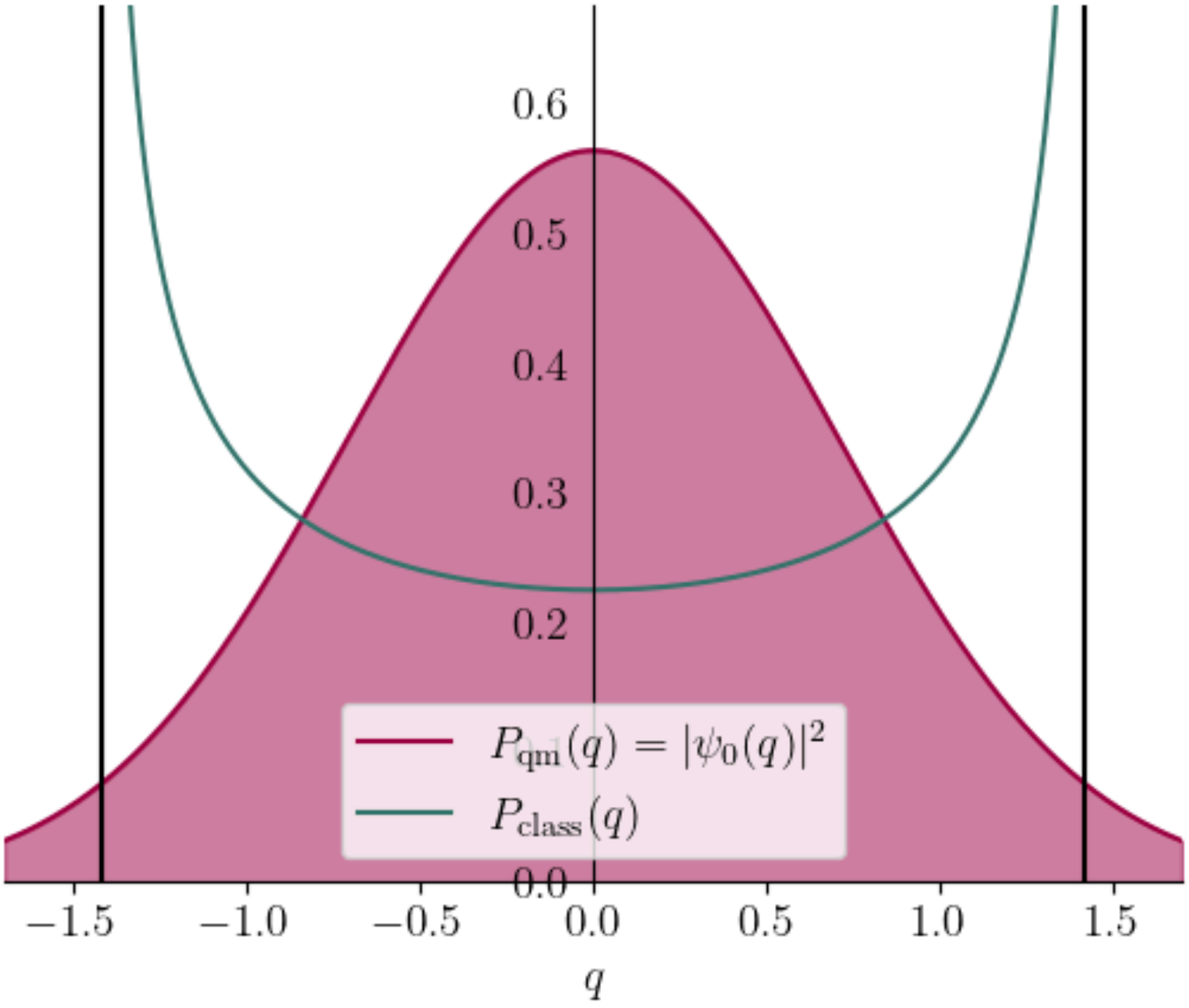
Harmonic Oscillator Wavefunctions



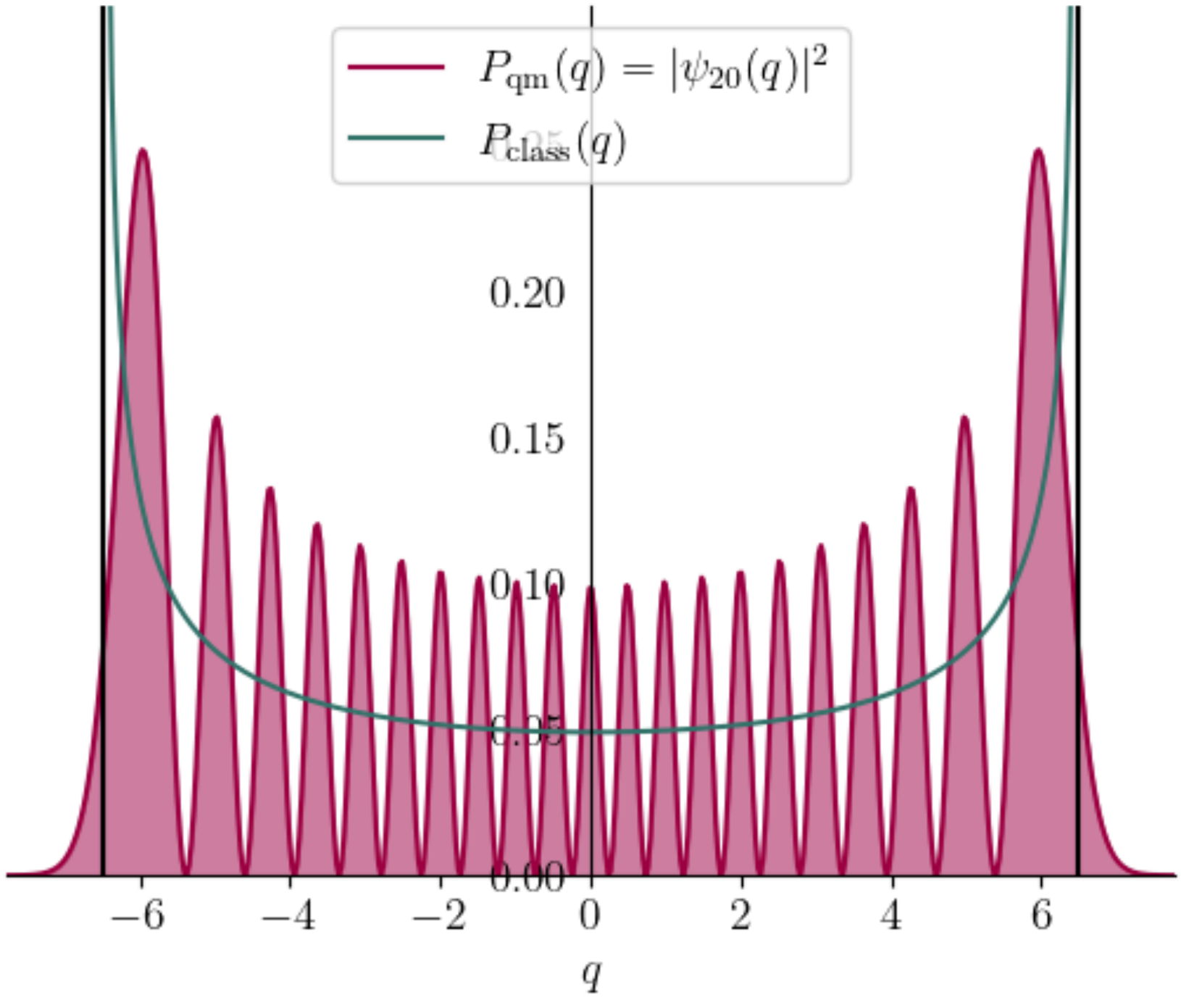
Harmonic Oscillator Probabilities



Harmonic Oscillator Probabilities



Harmonic Oscillator Probabilities



- 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,

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

Vibrational Transitions

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

The first term here is zero by orthogonality of the Hermite polynomials, leaving

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

Using the recursion relation

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

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

Vibrational Transitions: Selection Rules

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

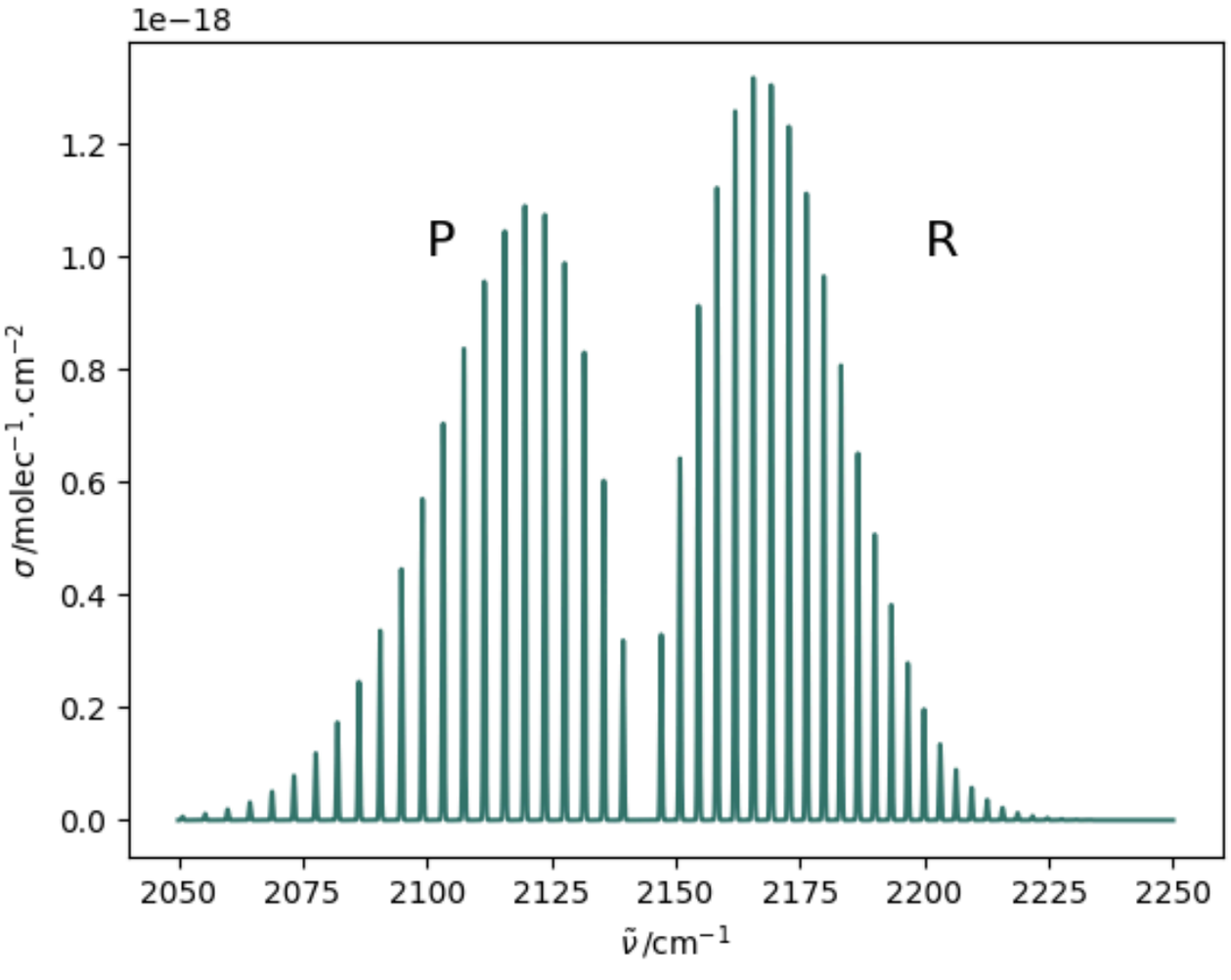
- *Gross selection rule*:

$$\frac{\mathrm{d}\mu}{\mathrm{d}q}\Big|_0 \neq 0$$

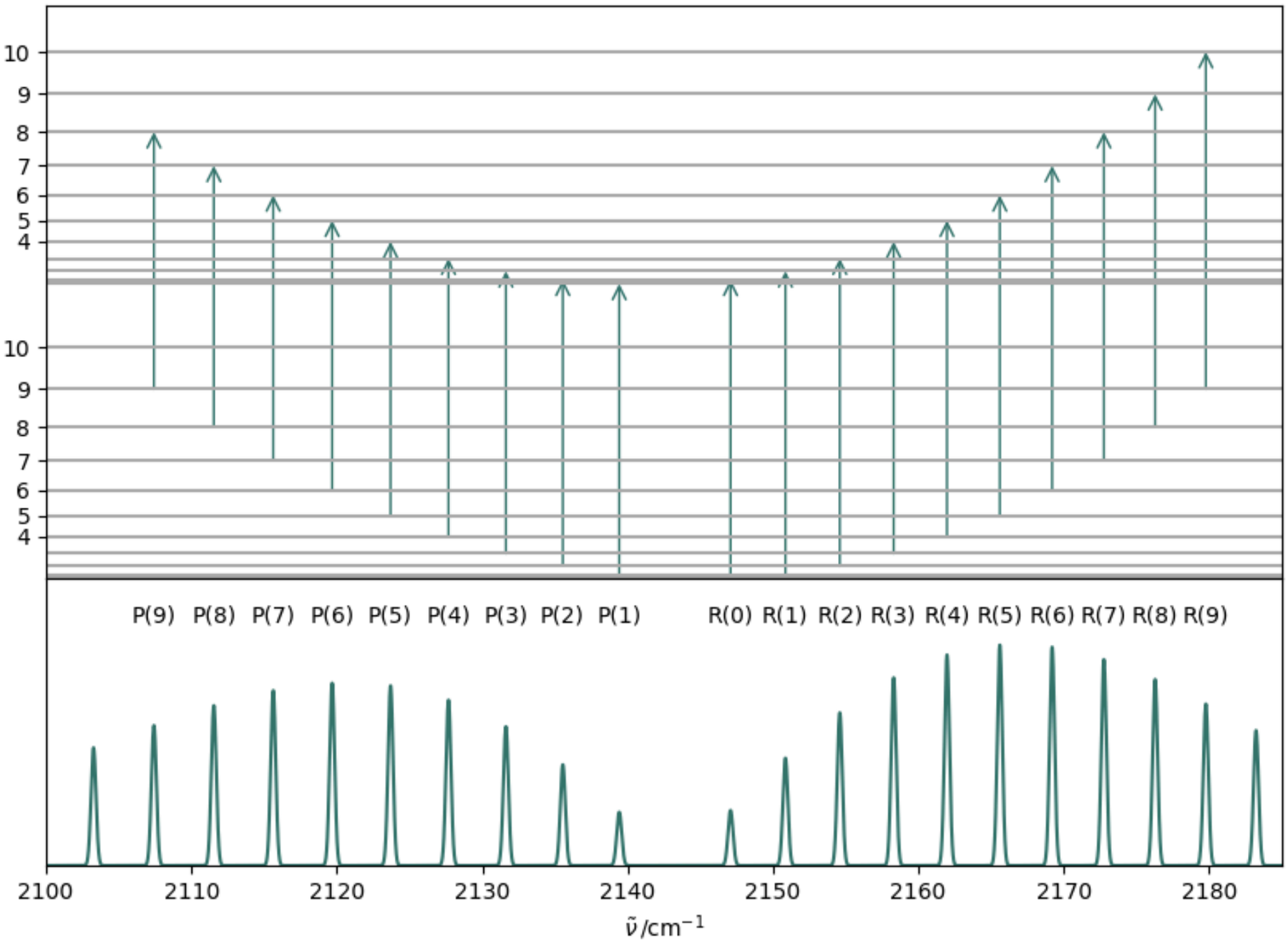
- $\Delta v = v' - v'' = \pm 1$
- NB homonuclear diatomics (e.g. H_2) do not have an (electric-dipole allowed) vibrational spectrum.

Rovibrational Transitions

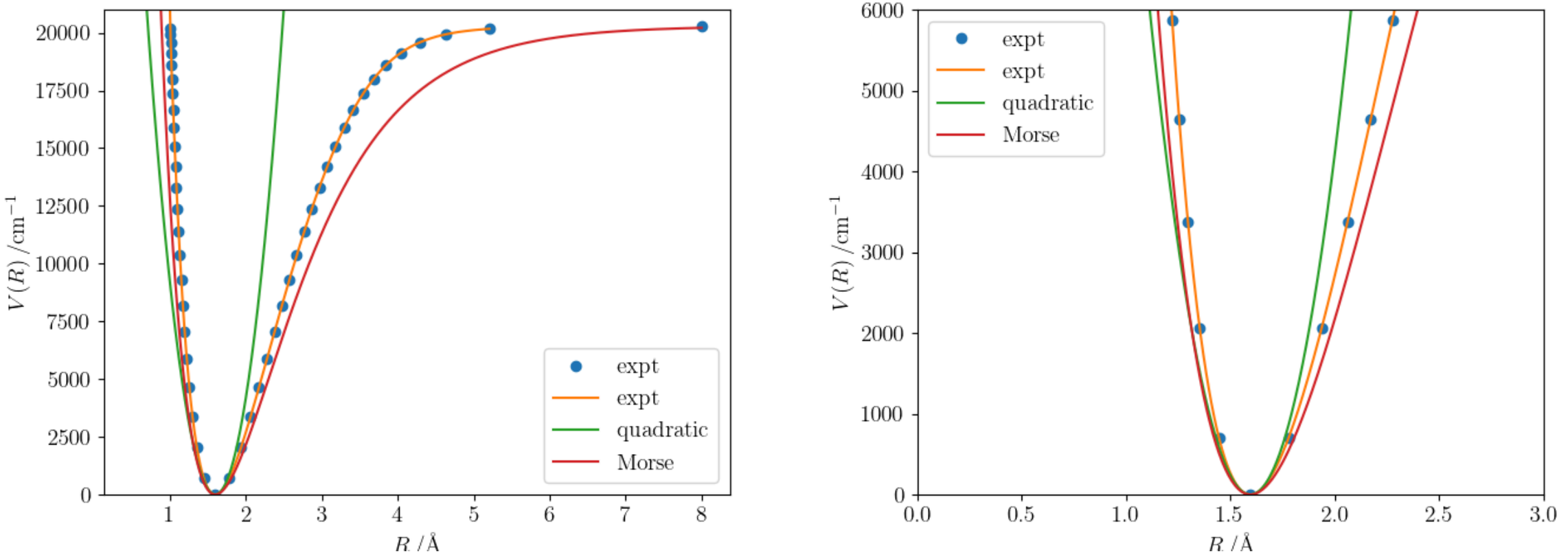
- Further selection rule on J: $\Delta J = \pm 1$
- P ($\Delta J = -1$) and R ($\Delta J = +1$) branches
- e.g. CO “fundamental” band: $v = 1 \leftarrow 0$



Rovibrational Transitions



Anharmonicity



- Real molecules dissociate
- Transitions with $\Delta v = \pm 2, \pm 3, \ldots$ are (weakly) allowed
- $v = 0 \rightarrow 2, v = 0 \rightarrow 3$ *overtones*

Vibration-Rotation Interaction

When a molecule vibrates its moment of inertia, $I = \mu R^2$ changes

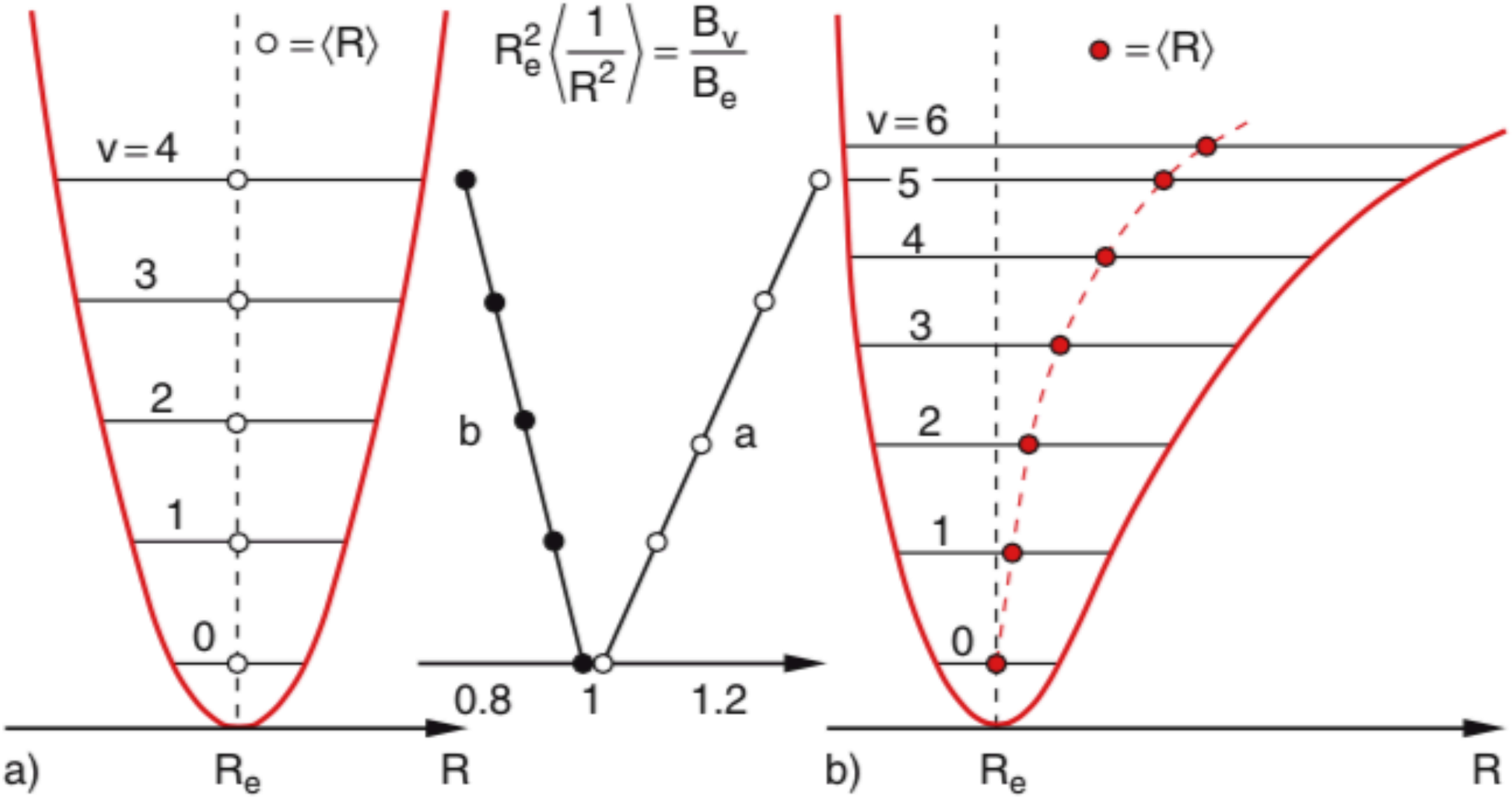
- The vibrational frequency is typically 10 – 100× faster than the rotational frequency
- Calculate the rotational energy using a time-average over a vibrational period:

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

where

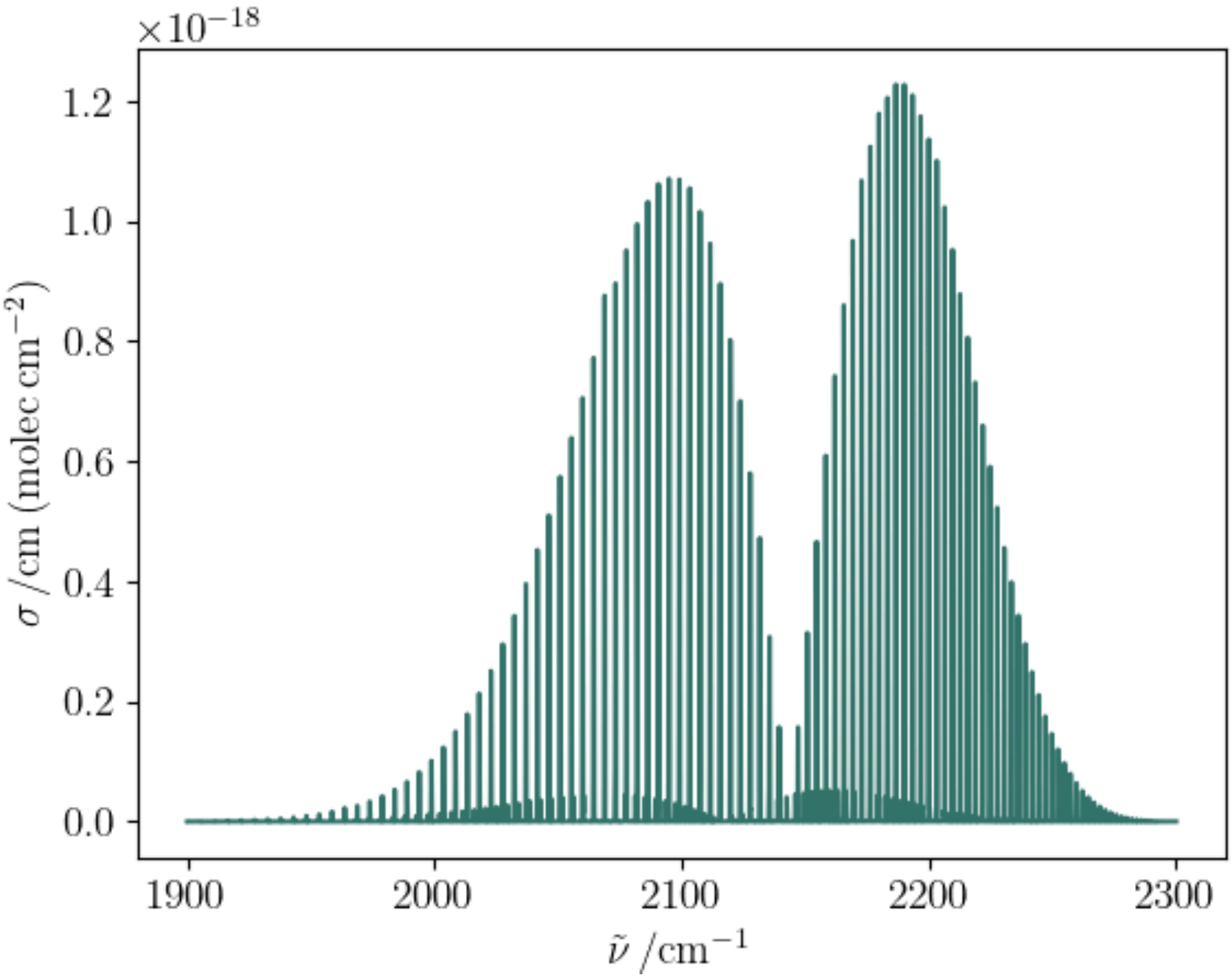
$$\left\langle \frac{1}{R^2} \right\rangle = \int_{-\infty}^{\infty} \psi_\upsilon^* \frac{1}{R^2} \psi_\upsilon \, \mathrm{d}R$$

Vibration-Rotation Interaction



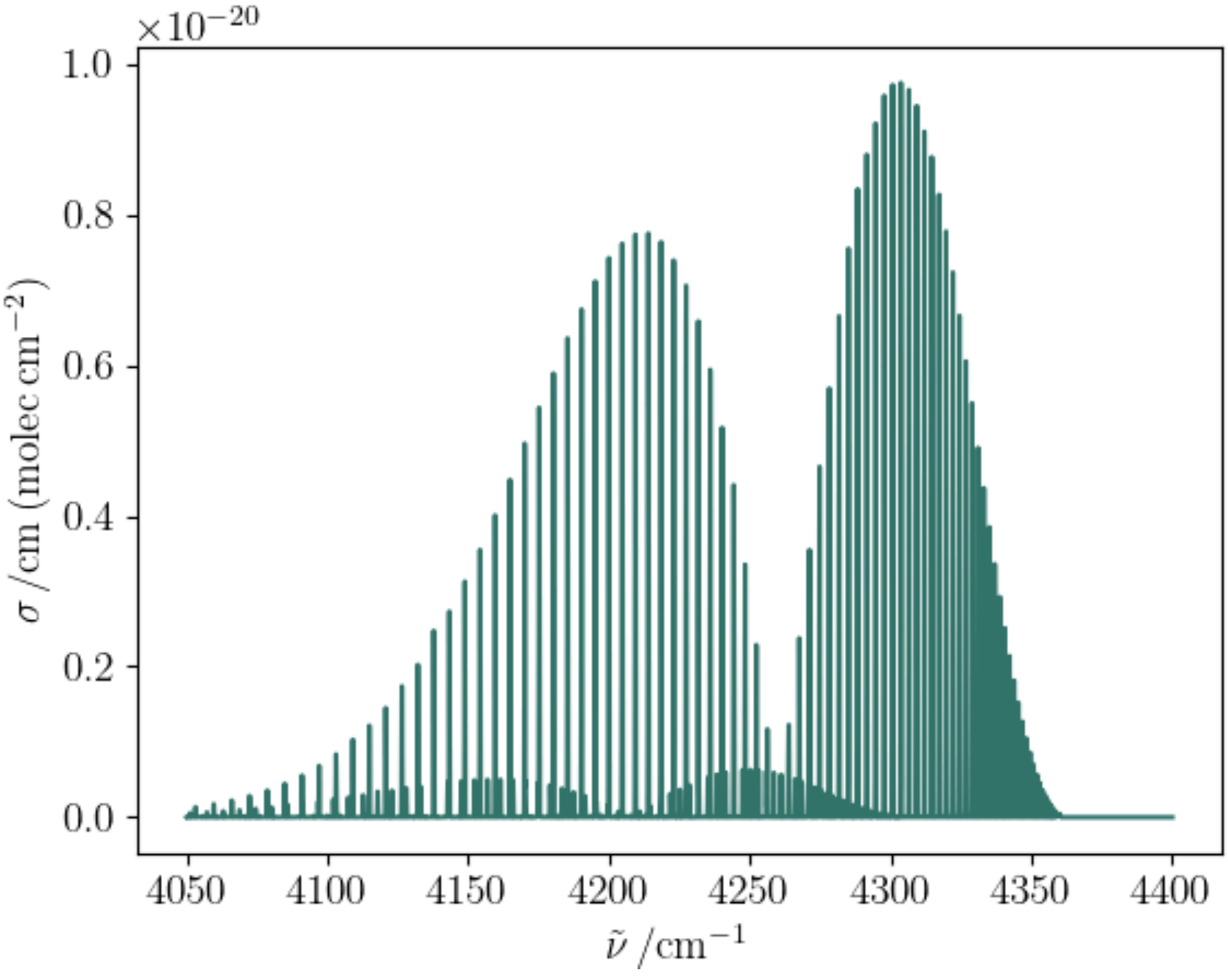
$$B_\upsilon = \frac{h}{8\pi^2 c\mu}\left\langle\frac{1}{R^2}\right\rangle = B_e - \alpha_e\left(\upsilon+\frac{1}{2}\right) + \gamma_e\left(\upsilon+\frac{1}{2}\right)^2 + \cdots$$

Vibration-Rotation Interaction



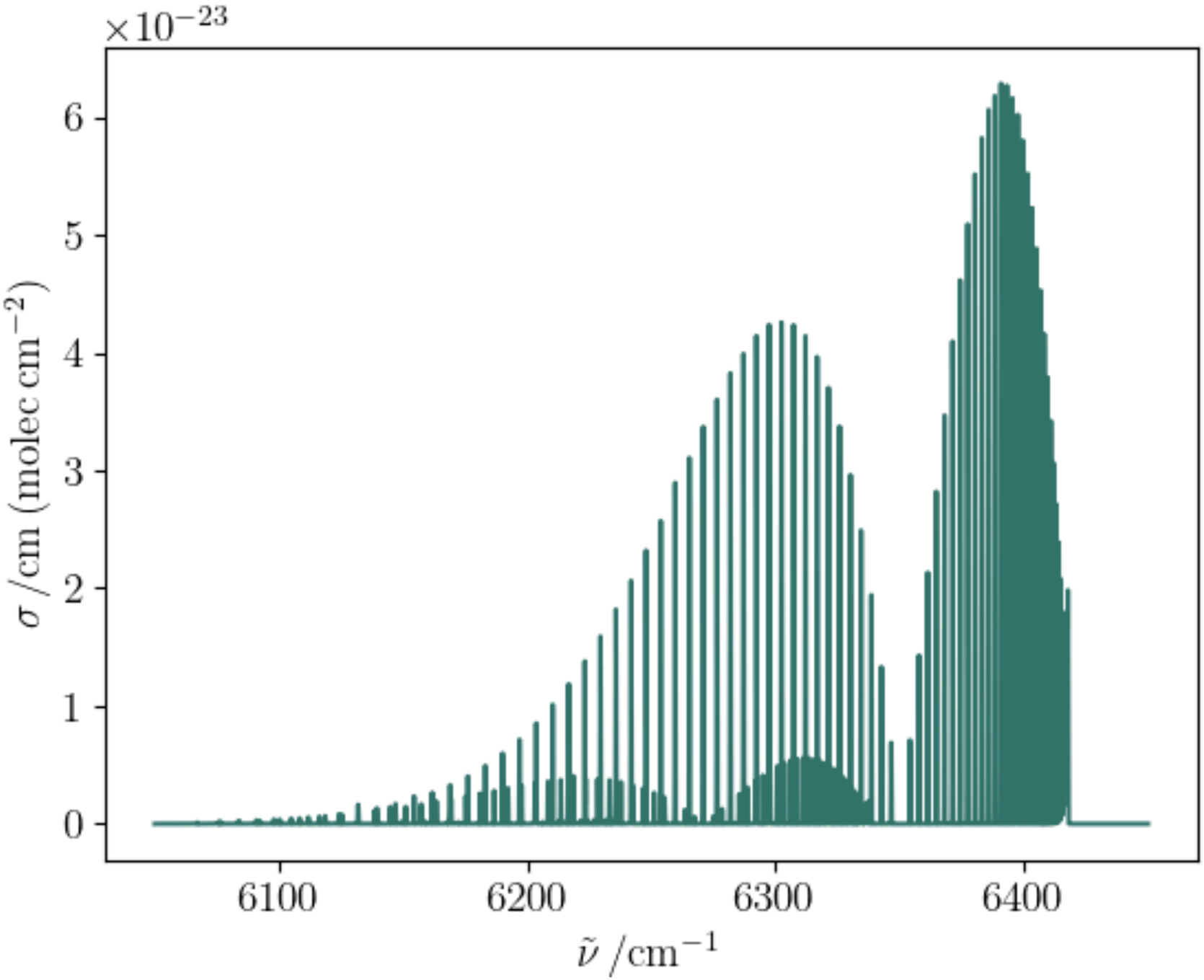
The 0-1 band of CO

Vibration-Rotation Interaction



The 0-2 band of CO

Vibration-Rotation Interaction



The 0-3 band of CO