Chapter 6. Vibrational Spectroscopy

6.1 Diatomic molecules

On the basis of harmonic oscillator approximation, the vibrational energy levels $E_v$ are given

$$E_v = \hbar \nu \left( \nu + \frac{1}{2} \right)$$  \hspace{1cm} \text{Eq. (6.1)}

where the vibrational quantum number $\nu = 0, 1, 2, \ldots$

The classical vibrational frequency $\nu$ is related to the reduced mass $\mu \left[ = m_1 m_2 / (m_1 + m_2) \right]$ and the force constant $k$ by

$$\nu = (1/2 \pi) \left[ k / \mu \right]^{1/2}$$  \hspace{1cm} \text{Eq. (6.2)}

Vibrational term values in unit of wavenumber are given

$$\frac{E_v}{\hbar c} = G(\nu) = \omega \left( \nu + \frac{1}{2} \right)$$  \hspace{1cm} \text{Eq. (6.3)}

where $\omega$ is the vibrational wavenumber.
6.1.1 Infrared spectra

The transition moment is given

\[ R_v = \int \psi'_v \ast \mu \psi''_v \, dx \] \hspace{1cm} \text{Eq. (6.4)}

where \( x = (r-r_e) \), the displacement of the internuclear distance from equilibrium.

For homogeneous diatomics, \( \mu = 0 \), thus, \( R_v = 0 \). For heterogeneous diatomics, \( \mu \neq 0 \) and \( \mu \) varies with \( x \) as follows:

\[ \mu = \mu_e + \left( \frac{d\mu}{dx} \right)_e x + \frac{1}{2!} \left( \frac{d^2\mu}{dx^2} \right)_e x^2 + \ldots \] \hspace{1cm} \text{Eq. (6.5)}

where "e" refers to the equilibrium configuration.
The transition moment becomes

\[ R_v = \mu_e \int \psi'_v \psi''_v dx + \left( \frac{d\mu}{dx} \right)_e \int \psi'_v x \psi''_v dx + \ldots \quad \text{Eq. (6.6)} \]

Because the wavefunctions of the lower and upper states are of the same hamiltonian, they are orthogonal for \( v' \neq v'' \), namely

\[ \int \psi'_v \psi''_v dx = 0 \quad \text{Eq. (6.7)} \]

Eq. (6.6) becomes

\[ R_v = \left( \frac{d\mu}{dx} \right) \int \psi'_v x \psi''_v dx + \ldots \quad \text{Eq. (6.8)} \]

The first term in Eq. (6.6) is non-zero only if

\[ \Delta v = \pm 1 \quad \text{Eq. (6.9)} \]

which is the vibrational selection rule.
The intensities of transition bands in a vibrational spectrum usually decrease rapidly as \( \nu'' \) increases because the population \( N_{\nu} \) of the \( \nu \)th vibrational level is related to \( N_0 \) by Boltzmann factor

\[
\frac{N_{\nu}}{N_0} = \exp(-\frac{E_{\nu}}{kT}) \quad \text{Eq. (6.10)}
\]

All bands with \( \nu'' \neq 0 \) are called “hot bands” whose population \( N_{\nu} \) increases with temperature.

Note:

1. transition intensity \( \propto |R_{\nu}|^2 \), i.e. \( \propto (d\mu/dx)_e^2 \)
2. \( \mu \) varies with internuclear distance \( r_e \) in diatomics.
Variation of dipole moment ($\mu$) with internuclear distance ($r$)

Note: Using Eq. (6.5)

$\mu \rightarrow 0$ as $r = 0$

or $r \rightarrow \infty$

$r < r_e$, $(d \mu / dr)$ is negative at $r_e$;

$r > r_e$, $(d \mu / dr)$ is positive at $r_e$;

$r = r_e$, $(d \mu / dr) = 0.$
6.1.2 Raman spectra

The vibrational Raman effect is similar to the rotational Raman effect. With Eq. (5.46), the dipole moment $\mu$ of a molecule induced by intense monochromatic radiation is given by

\[
\mu = \alpha_{0,v} A \sin 2 \pi c \tilde{\nu} t - \frac{1}{2} \alpha_{1,v} A \cos 2 \pi c (\tilde{\nu} + \omega) t + \frac{1}{2} \alpha_{1,v} A \cos 2 \pi c (\tilde{\nu} - \omega) t
\]

Eq. (6.11)

where $\alpha_{0,v}$ is the average polarizability during vibration, $\alpha_{1,v}$ is the amplitude of the change of polarization due to vibration, $A$ is the amplitude of the oscillating electric field of the incident radiation, and $\omega$ is the vibrational wavenumber.

All three terms in Eq. (6.11) represent scattering of the radiation. The first term corresponds to Rayleigh scattering, where the wavenumber $\tilde{\nu}$ remains unchanged. The second and third correspond to the anti-Stokes and Stokes Raman scattering with wavenumbers of $(\tilde{\nu} + \omega)$ and $(\tilde{\nu} - \omega)$, respectively.
Similar to the case for dipole moment, the change of polarizability with vibrational displacement $x$ can be expressed as a Taylor series:

$$\alpha = \alpha_e + \left( \frac{d\alpha}{dx} \right)_e x + \frac{1}{2!} \left( \frac{d^2\alpha}{dx^2} \right)_e x^2 + .... \quad \text{Eq. (6.12)}$$

Then, the vibrational Raman transition moment $R_v$ is given by

$$R_v = \left( \frac{d\alpha}{dx} \right)_e A \int \psi'_v * x \psi''_v dx + .... \quad \text{Eq. (6.13)}$$

The first term in Eq. (6.13) is non-zero only if

$$\Delta v = \pm 1 \quad \text{Eq. (6.14)}$$

Which constitutes the vibrational Raman selection rule.
Variation of mean polarizability with internuclear distance ($r$)

$\frac{d\alpha}{dr}$ varies very little with $r$. Thus, vibrational Raman intensities are less sensitive than infrared intensities to the environment of the molecule, e.g. in solution.
Stokes and anti-Stokes vibrational Raman scattering
6.1.3 Anharmonicity

Electrical anharmonicity
As seen in Eqs. (6.5) and (6.12), $\mu$ and $\alpha$ can be expressed in terms of Taylor series. If $\mu$ and $\alpha$ vary linearly with $x$, it is said to be harmonic and the selection rule is $\Delta v = \pm 1$ as applied in infrared and Raman spectroscopy. If the higher terms are concerned, it is referred to as anharmonicity.

When electrical properties of a molecule is concerned, it is called electrical anharmonicity, which has little effect on the spectral band intensity resulting from $\Delta v = \pm 2, \pm 3, \ldots$ transitions, which are known as vibrational overtones.

Mechanical anharmonicity
The vibrational motion of a diatomic molecule can be treated by a mechanical ball-and-spring model. Hooke’s law [restoring force = $-dV(x)/dx = -kx$] holds only when $x$ is small $\langle r \approx r_e \rangle$. 

$\mu(t)$ and $\alpha(t)$ are the coefficients for the Taylor series of the electrical properties of the molecule.
Potential energy curve for a diatomic molecule

when \( r \to \infty \) (the diatomic molecule dissociates),
\( k = 0, \ V = D_e \) (dissociation energy)
The vibrational motion of a diatomic molecule can be treated by a mechanical ball-and-spring model. Hooke’s law [restoring force = \(-dV(x)/dx = -kx\)] holds only when \(x\) is small \((r \approx r_e)\).

The mechanical anharmonicity modifies the \(\Delta \nu = \pm 1\) IR and Raman selection rule to \(\Delta \nu = \pm 1, \pm 2, \pm 3,..\) but the overtone transitions with \(\Delta \nu = \pm 2, \pm 3,..\).

The harmonic oscillator term values of Eq. (6.3) can be modified to

\[
G(\nu) = \omega_e (\nu + \frac{1}{2}) - \omega_x e (\nu + \frac{1}{2})^2 + \omega_y e (\nu + \frac{1}{2})^3 + \ldots \quad \text{Eq. (6.16)}
\]

where \(\omega_e\) is the vibration wavenumber which a classical oscillator with \(x = \infty\). \(\omega_x e, \omega_y e, \ldots\) are anharmonic constants and are always positive for diatomics.

E.g. for \(^1\text{H}^3\text{Cl}\), \(\omega_e = 2990.946\ \text{cm}^{-1}\), \(\omega_x e = 52.8186\ \text{cm}^{-1}\), \(\omega_y e = 0.2244\ \text{cm}^{-1}\), \(\omega_z e = -0.0122\ \text{cm}^{-1}\).
Since $\omega$ cannot be directly determined, one defines $\Delta G_{v+1/2}$ for $(v+1) - (v)$ transitions as follows,

$$\Delta G_{v+1/2} = G(v+1) - G(v) = \omega_e - \omega_e x_e (2v + 2) + \omega_e y_e (3v^2 + 6v + 13/4) + \ldots$$

Eq. (6.18)

In order to determine $\omega_e$ and $\omega_e x_e$, at least two transition wavenumbers, e.g. $G(1) - G(0) = \omega_0$ and $G(2) - G(1) = \omega_1$ must be obtained.

Then, the dissociation energy can be approximated to be

$$D_e \approx (\omega_e)^2/[4 \omega_e x_e]$$

Eq. (6.19)

Experimentalists can only determine the dissociation energy relative to the zero-point level, i.e. $D_0$

Note that $D_e$ is isotope-independent whereas $D_0$ isotope-dependent.
Wave functions and probability density functions for an anharmonic oscillator

$\phi_v$ -- dashed line

$(\phi_v^* \phi)^2$ -- solid lines
The zero-point energy corresponds to the term value $G(0)$

$$G(0) = \frac{1}{2} \omega_e - \frac{1}{4} \omega_e x_e + (1/8) \omega_e y_e + \ldots \quad \text{Eq. (6.21)}$$

Since $\omega_e$ for $^2\text{H}_2$ is less than for $^1\text{H}_2$, so that

$$D_0(^2\text{H}_2) > D_0(^1\text{H}_2) \quad \text{Eq. (6.22)}$$

In 1929, Morse suggested

$$V(x) = D_e[1 - \exp(-ax)]^2 \quad \text{Eq. (6.23)}$$

as a potential function relating to the behavior of an anharmonic oscillator.

In the Morse function, $x = r - r_e,$

$$V(x) \rightarrow D_e \text{ as } x \rightarrow \infty$$
6.1.4 Vibration-rotation spectroscopy

6.1.4.1 Infrared spectra

In vibration-rotation spectroscopy one observes transitions between stacks of rotational levels associated with two different vibrational states. The vibration-rotation total term values $S$ are the sum of the rotational term value (Eq. 5.23) and the vibrational term value (Eq. 6.16)

$$S = G(v) + F_v(J)$$

$$= \omega_e(v + \frac{1}{2}) - \omega_e \chi_e (v + \frac{1}{2})^2 + \cdots + B_v J(J + 1) - D_v J^2 (J + 1)^2$$

Eq. (6.24)

Recall: allowed vibrational transition: $\Delta v = \pm 1$

allowed rotational transition: $\Delta J = \pm 1$

The location corresponding to $\Delta J$ is called the band center.

Note: NO is exceptional. The rotational selection rule for NO is $\Delta J = 0, \pm 1$. [why?]
Rotational transitions accompanying a vibrational transition in (a) an infrared spectrum and (b) a Raman spectrum of a diatomic molecule.
The $\nu = 1-0$ infrared spectrum of $^{1}\text{H}^{35}\text{Cl}$ and $^{1}\text{H}^{37}\text{Cl}$. 

The spacing between the adjacent $R$-branch lines is about equal to that between the adjacent $P$-branch lines. This is due to the fact that $B_1 \approx B_0$, i.e. the vibration-rotation interaction constant ($\alpha$ in Eq. 5.25) is small.

The spacing between $R(0)$ and $P(1)$ is called the zero gap, where the band center.
Assume that $B_1 = B_0 = B$ and neglect centrifugal distortion, the wavenumbers of the $R$-branch transitions are given by

$$\tilde{\nu}[R(J)] = \tilde{\nu}_0 + B(J + 1)(J + 2) - BJ(J + 1)$$

Eq. (6.27)

$$= \tilde{\nu}_0 + 2BJ + 2B$$

where $\tilde{\nu}_0$ is the wavenumbers of the pure vibrational transition.

Similarly, the wavenumbers of the $P$-branch transitions are given by

$$\tilde{\nu}[P(J)] = \tilde{\nu}_0 + B(J - 1)J - BJ(J + 1)$$

Eq. (6.28)

$$= \tilde{\nu}_0 - 2BJ$$

Eqs. (6.27) and (6.28) give the zero gap value of $4B$ and the spacing between the $R$-branch and $P$-branch adjacent lines of $2B$. 

wbt
6.1.4.2 Raman spectra

The rotational selection rule for vibration-rotation Raman transitions in diatomic molecules is $\Delta J = 0, \pm 2$, giving a $Q(\Delta J = 0)$, an $S(\Delta J = +2)$, and an $O(\Delta J = -2)$ branch.

Assume that $B_1 = B_0 = B$ and neglect centrifugal distortion, the wavenumbers of the $S$-, $O$-, and $Q$-branch transitions are given by

\[
\tilde{\nu} \; [S(J)] = \tilde{\nu}_0 + B(J + 2)(J + 3) - BJ(J + 1) \quad \text{Eq. (6.36)}
\]

\[
= \tilde{\nu}_0 + 4BJ + 6B
\]

\[
\tilde{\nu} \; [O(J)] = \tilde{\nu}_0 + B(J - 2)(J - 1) - BJ(J + 1) \quad \text{Eq. (6.37)}
\]

\[
= \tilde{\nu}_0 - 4BJ + 2B
\]

\[
\tilde{\nu} \; [Q(J)] = \tilde{\nu}_0 \quad \text{Eq. (6.38)}
\]
The 1-0 Stokes Raman spectrum of CO showing $O$, $Q$, and $S$-branch rotational structure.