CHM 504 - Vibrational Spectroscopy of Diatomic Molecules

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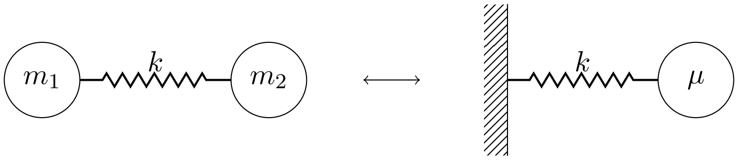
Having covered the eigenstates and light-induced transitions for the rotation of rigid quantum mechanical bodies, we now move on to consider the dynamcis of the relative motion of nuclei.

1 The diatomic harmonic oscillator

Consider two masses m_1 and m_2 connected by a spring. We can imagine that this system might be a reasonable model for the vibration of a diatomic molecule connected by a chemical bond, which like a mechanical spring has an equilibrium position and resists being compressed or extended.



We can reduce the movement of these two connected bodies to a one-body problem concerning the motion of an effective inertial mass relative to a fixed rigid wall using the reduced mass:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{1}$$

If our molecule is in a bound electronic state that is stable with respect to dissociation, the potential energy $V(R)$ for this motion will have a minimum value $-D_e$ at equilibrium bond length R_e. Expanding the potential in powers of $R - R_e$, we can write:

$$V(R) = V(R_e) + \left(\frac{dV}{dR}\right)_{R_e} (R - R_e) + \frac{1}{2}\left(\frac{d^2V}{dR^2}\right)_{R_e} (R - R_e)^2 + \dots \tag{2}$$

at $R = R_e$, the first derivative vanishes, and including up to quadratic terms:

$$V(R) \simeq -D_e + \frac{1}{2}k(R - R_e)^2 \tag{3}$$

with $k = \frac{d^2V}{dR^2}|_{R_e}$. This harmonic potential is a reasonable approximation for that of a chemical bond, as long as we only consider small displacements from equilibrium. This corresponds to the assumption that Hooke's Law holds, with a linear restoring force $F = -kx$.

2 Solutions to the HO Schrödinger equation

Let's briefly review the wavefunctions and energy eigenvalues for the harmonic oscillator. The Schrödinger equation is:

$$\hat{H}\psi_n(x) = \left[-\frac{\hbar^2}{2\mu}\frac{d^2}{x^2} + \frac{1}{2}kx^2\right]\psi_n(x) = E_n\psi_n(x) \tag{4}$$

$$\rightarrow \frac{d^2\psi_n(x)}{dx^2} = \frac{2\mu}{\hbar^2}\left(\frac{1}{2}kx^2 - E_n\right)\psi_n(x) \tag{5}$$

over the window $-\infty < x < \infty$.

The solutions to this differential equation take the form of a Hermite polynomial H_n multiplied by an Gaussian exponential decay:

$$\psi_n(x) = N_n\, H_n(\alpha^{1/2}x)\, e^{-\alpha x^2/2}, \qquad n = 0, 1, 2, \ldots \tag{6}$$

where

$$\alpha \equiv \sqrt{\frac{k\mu}{\hbar^2}} \tag{7}$$

and the normalization constant for each wavefunction is

$$N_n = \frac{1}{(2^n\, n!)^{1/2}}\left(\frac{\alpha}{\pi}\right)^{1/4} \tag{8}$$

The first few Hermite polynomials are:

$$H_0(y) = 1 \tag{9}$$

$$H_1(y) = 2y \tag{10}$$

$$H_2(y) = 4y^2 - 2 \tag{11}$$

$$H_3(y) = 8y^3 - 12y \tag{12}$$

$$H_4(y) = 16y^4 - 48y^2 + 12 \tag{13}$$

$$\cdots$$

The general form of the energy eigenvalues for the quantum HO are of course

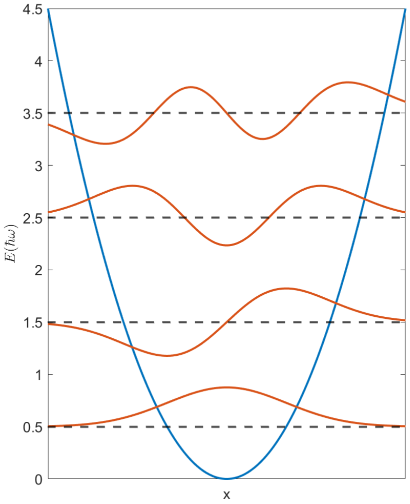
$$E_n = \hbar\left(\frac{k}{\mu}\right)^{1/2}\left(n + \frac{1}{2}\right) \quad = \quad \hbar\omega_0\left(n + \frac{1}{2}\right) \tag{14}$$

where

$$\omega_0 \equiv \sqrt{\frac{k}{\mu}} \tag{15}$$

Note that the $n = 0$ state has zero-point energy $E_0 = \frac{1}{2}\hbar\omega_0$, and the quantum number n is the same as the number of nodes in the n^{th} wavefunction.

The energy eigenvalues are evenly spaced with separation $\Delta E = \hbar\omega_0$ within the harmonic oscillator approximation. The uniform spacing of these discrete states is peculiar to the HO. In reality, this is a good approximation for the lowest few vibrational levels, but the higher levels will lie much closer together due to "anharmonicities" in the potential curve as you approach the bond dissociation energy.



3 The ladder operator formulation

Let's also write down here the formulation of the HO Schrödinger equation and its solutions using the much more elegant ladder operator formalism. Starting again with the HO Hamiltonian:

$$\hat{H} = -\frac{\hbar^2}{2\mu}\frac{d^2}{dx^2} + \frac{1}{2}\mu\omega_0^2 x^2 \tag{16}$$

we make the coordinate substitution $x = \sqrt{\frac{\hbar}{\mu\omega_0}}q$, and find

$$\begin{aligned}\hat{H} &= \frac{\hbar\omega_0}{2}\left[-\frac{d^2}{dq^2} + q^2\right] &(17)\\ &= \frac{\hbar\omega_0}{2}\left[\left(-\frac{d}{dq} + q\right)\left(\frac{d}{dq} + q\right) + \frac{d}{dq}q - q\frac{d}{dq}\right] &(18)\\ &= \frac{\hbar\omega_0}{2}\left[\left(-\frac{d}{dq} + q\right)\left(\frac{d}{dq} + q\right) + 1\right] &(19)\end{aligned}$$

where we've used the commutation relation $\frac{d}{dq}q - q\frac{d}{dq} = 1$; you can verify this by applying these operators to a dummy function $f(q)$.

At this point it is convenient to introduce our ladder operators:

$$\hat{a}^\dagger \equiv \frac{1}{\sqrt{2}}\left[-\frac{d}{dq}+q\right] = \frac{1}{\sqrt{2}}\left[q - ip_q\right] \qquad \text{raising/creation operator} \tag{20}$$

$$\hat{a} \equiv \frac{1}{\sqrt{2}}\left[\frac{d}{dq}+q\right] = \frac{1}{\sqrt{2}}\left[q + ip_q\right] \qquad \text{lowering/annihilation operator} \tag{21}$$

q and its conjugate momentum p_q can equivalently be expressed as linear combinations of ladder operators:

$$q = \frac{1}{\sqrt{2}}\left[\hat{a}^\dagger + \hat{a}\right] \quad \rightarrow \quad x = \sqrt{\frac{\hbar}{2\mu\omega_0}}\left[\hat{a}^\dagger + \hat{a}\right] \tag{22}$$

$$p_q = \frac{i}{\sqrt{2}}\left[\hat{a}^\dagger - \hat{a}\right] \quad \rightarrow \quad p_x = i\sqrt{\frac{\hbar\mu\omega_0}{2}}\left[\hat{a}^\dagger - \hat{a}\right] \tag{23}$$

The Hamiltonian can therefore be rewritten very simply as

$$\hat{H} = \hbar\omega_0\left[\hat{a}^\dagger\hat{a} + \frac{1}{2}\right] \tag{24}$$

Though we won't review it here, it's straightforward to show that

$$\hat{a}^\dagger|\psi_n\rangle = \sqrt{n+1}\,|\psi_{n+1}\rangle \tag{25}$$

$$\hat{a}|\psi_n\rangle = \sqrt{n}\,|\psi_{n-1}\rangle \tag{26}$$

which is of course the property that gives rise to the names "raising" and "lowering" operators, and allows us an elegant means to iteratively calculate harmonic oscillator wavefunctions.

In preparation for calculating the absorption spectrum of our harmonic oscillator when irradiated with light, it's also useful to write down the time-dependent forms of the ladder operators within the Heisenberg picture:

$$\hat{a}(t) \equiv e^{i\hat{H}t/\hbar}\;\hat{a}\;e^{-i\hat{H}t/\hbar} \tag{27}$$

$$= e^{i\omega_0(\hat{N}+\frac{1}{2})t}\;\hat{a}\;e^{-i\omega_0(\hat{N}+\frac{1}{2})t} \tag{28}$$

$$= e^{i\omega_0\hat{N}t}\;\hat{a}\;e^{-i\omega_0\hat{N}t} \tag{29}$$

where $\hat{N}|\psi_n\rangle = n|\psi_n\rangle$.

It is now instructive to take the first derivative of $\hat{a}(t)$:

$$\frac{d}{dt}\left[\hat{a}(t)\right] = \frac{d}{dt}\left[e^{i\omega_0\hat{N}t}\right]\hat{a}\;e^{-i\omega_0\hat{N}t} + e^{i\omega_0\hat{N}t}\;\hat{a}\;\frac{d}{dt}\left[e^{-i\omega_0\hat{N}t}\right] \tag{30}$$

$$= i\omega_0\hat{N}\cdot e^{i\omega_0\hat{N}t}\;\hat{a}\;e^{-i\omega_0\hat{N}t} + e^{i\omega_0\hat{N}t}\;\hat{a}\cdot(-i\omega_0\hat{N})\cdot e^{-i\omega_0\hat{N}t} \tag{31}$$

$$= i\omega_0\cdot e^{i\omega_0\hat{N}t}\left[\hat{N}\hat{a} - \hat{a}\hat{N}\right]e^{-i\omega_0\hat{N}t} \tag{32}$$

We can evaluate the commutator:

$$\left[\hat{N}\hat{a} - \hat{a}\hat{N}\right]|\psi_n\rangle = \hat{N}\hat{a}|\psi_n\rangle - \hat{a}\hat{N}|\psi_n\rangle \tag{33}$$

$$= \hat{N}\sqrt{n}|\psi_{n-1}\rangle - \hat{a}\,n|\psi_n\rangle \tag{34}$$

$$= (n-1)\sqrt{n}|\psi_{n-1}\rangle - n\sqrt{n}|\psi_{n-1}\rangle \tag{35}$$

$$= -\sqrt{n}|\psi_{n-1}\rangle = -\hat{a}|\psi\rangle \tag{36}$$

Therefore

$$\frac{d}{dt}\left[\hat{a}(t)\right] = -i\omega_0 \cdot e^{i\omega_0 \hat{N} t}\, \hat{a}\, e^{-i\omega_0 \hat{N} t} \tag{37}$$

$$= -i\omega_0\, \hat{a}(t) \tag{38}$$

And we find that

$$\hat{a}(t) = e^{-i\omega_0 t}\hat{a} \tag{39}$$

Following a similar process, we can also find

$$\hat{a}^\dagger(t) = e^{i\omega_0 t}\, \hat{a}^\dagger \tag{40}$$

4 Selection rules for infrared spectroscopy

Let's now evaluate the absorption lineshape for transitions between harmonic oscillator wavefunctions induced by monochromatic radiation at frequency ω. Recall that we want to evaluate

$$\sigma(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_n p_n \langle n|\mu_z(0)\cdot \mu_z(t)|n\rangle \tag{41}$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_n p_n \langle n|\mu_z \cdot e^{+i\hat{H}t/\hbar} \cdot \mu_z \cdot e^{-i\hat{H}t/\hbar}|n\rangle \tag{42}$$

Where again we have assumed a laser field polarized along the lab frame z axis. We will need an expression for μ_z that accounts for the vibrational dynamics of the system.

In the case of a vibrating diatomic molecule, the nuclear dipole moment lies along the bond axis, and its magnitude may change as the bond length oscillates during vibration. For the moment, let's neglect rotational motion and assume that our molecule is oriented along the z axis, so we can use μ interchangeably with μ_z. We take the nuclear dipole moment to be weakly dependent on the displacement of the vibrational coordinate by Taylor expanding it about its value at the equilibrium bond length R_e:

$$\mu(R) = \mu_0 + \left(\frac{d\mu}{dR}\right)_{R_e}(R-R_e) + \frac{1}{2}\left(\frac{d^2\mu}{dR^2}\right)_{R_e}(R-R_e)^2 + \cdots \tag{43}$$

where μ_0 is the dipole moment at bond length R_e. Let's define $x = R - R_e$. For small displacements from equilibrium

$$\Delta\mu \equiv \mu - \mu_0 \simeq \left(\frac{d\mu}{dx}\right)_{x=0} \cdot x \tag{44}$$

In order to evaluate $\sigma(\omega)$, we can either work within the Heisenberg picture as laid out in Eqn. 41, or evaluate the product of operators explicitly in Eqn. 42. When we evaluated this expression for the rigid rotor in a previous lecture, we took the latter strategy, so let's use the Heisenberg strategy for variety this time. In this case, we need to write down an expression for the time-dependent dipole moment operator. For simplicity, we will work with $\Delta\mu(t)$ rather than $\mu(t)$, which contains all the time-dependent information necessary to evaluate $\sigma(\omega)$.

$$\begin{aligned}
\Delta\mu(t) &= \left(\frac{d\mu}{dx}\right)_{x=0} \cdot x(t) && (45)\\
&= \left(\frac{d\mu}{dx}\right)_0 \cdot \sqrt{\frac{\hbar}{2\mu\omega_0}} \left[\hat{a}^\dagger(t) + \hat{a}(t)\right] && (46)\\
&= \left(\frac{d\mu}{dx}\right)_0 \cdot \sqrt{\frac{\hbar}{2\mu\omega_0}} \left[\hat{a}^\dagger \cdot e^{i\omega_0 t} + \hat{a} \cdot e^{-i\omega_0 t}\right] && (47)
\end{aligned}$$

Let's begin by just considering the inner product:

$$\langle n|\Delta\mu(0) \cdot \Delta\mu(t)|n\rangle \tag{48}$$

$$=\langle n| \left(\tfrac{d\mu}{dx}\right)_0 \cdot \sqrt{\tfrac{\hbar}{2\mu\omega_0}} \left[\hat{a}^\dagger + \hat{a}\right] \cdot \left(\tfrac{d\mu}{dx}\right)_0 \cdot \sqrt{\tfrac{\hbar}{2\mu\omega_0}} \left[\hat{a}^\dagger \cdot e^{i\omega_0 t} + \hat{a} \cdot e^{-i\omega_0 t}\right] |n\rangle \tag{49}$$

$$=\tfrac{\hbar}{2\mu\omega_0} \cdot \left(\tfrac{d\mu}{dx}\right)_0^2 \langle n| \left[\cancel{\hat{a}^\dagger\hat{a}^\dagger e^{i\omega_0 t}} + \hat{a}^\dagger\hat{a}e^{-i\omega_0 t} + \hat{a}\hat{a}^\dagger e^{i\omega_0 t} + \cancel{\hat{a}\hat{a}e^{-i\omega_0 t}}\right] |n\rangle \tag{50}$$

$$=\tfrac{\hbar}{2\mu\omega_0} \cdot \left(\tfrac{d\mu}{dx}\right)_0^2 \left[\langle n|\hat{a}^\dagger\hat{a}|n\rangle e^{-i\omega_0 t} + \langle n|\hat{a}\hat{a}^\dagger|n\rangle e^{i\omega_0 t}\right] \tag{51}$$

$$=\tfrac{\hbar}{2\mu\omega_0} \cdot \left(\tfrac{d\mu}{dx}\right)_0^2 \left[n e^{-i\omega_0 t} + (n+1)e^{i\omega_0 t}\right] \tag{52}$$

Because the $|n\rangle$ states are orthonormal within the same electronic state, the only terms which survive are the cross terms involving both $\hat{a}^\dagger$ and $\hat{a}$, which connect $|n\rangle$ to $|n \pm 1\rangle$, then return it to itself.

Let's now return to evaluating the entire expression for $\sigma(\omega)$ using our result from Eqn. 52:

$$\begin{aligned}
\sigma(\omega) &= \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_n p_n \langle n|\Delta\mu(0) \cdot \Delta\mu(t)|n\rangle && (53)\\
&= \frac{\hbar}{4\pi\mu\omega_0} \cdot \left(\frac{d\mu}{dx}\right)_0^2 \sum_n \frac{e^{-\beta\hbar\omega_0(n+\frac{1}{2})}}{Q_{vib}} \int_{-\infty}^{+\infty} dt\, e^{-i\omega t} \left[n e^{-i\omega_0 t} + (n+1)e^{i\omega_0 t}\right] && (54)\\
&= \frac{\hbar}{4\pi\mu\omega_0} \cdot \left(\frac{d\mu}{dx}\right)_0^2 \sum_n \frac{e^{-\beta\hbar\omega_0(n+\frac{1}{2})}}{Q_{vib}} \left[n \cdot \delta(\omega+\omega_0) + (n+1) \cdot \delta(\omega-\omega_0)\right] && (55)
\end{aligned}$$

At reasonably low temperatures $k_B T << \hbar\omega_0$, the population is nearly entirely in the ground vibrational state, and this expression reduces to:

$$\sigma(\omega) \propto \left(\frac{d\mu}{dx}\right)_0^2 \delta(\omega-\omega_0) \tag{56}$$

Note that this low-temperature limit is applicable to most vibrations at room temperature.

From our expression for $\sigma(\omega)$, we can glean the major selection rules of vibrational spectroscopy within the harmonic oscillator limit:

- $\left(\frac{d\mu}{dx}\right)_0^2 \neq 0$. Motion along the vibrational coordinate x must change the dipole moment of the molecule in order to observe an infrared spectrum. Homonuclear diatomics like H_2 or N_2 therefore feature neither a pure infrared spectrum nor a pure microwave spectrum.

- Within the harmonic oscillator approximation, transitions are only allowed between neighboring levels, with $\Delta n = \pm 1$. This is because to first order, the transition dipole operator looks like x, which can be expressed as a linear combination of ladder operators. The μ operator therefore only serves to connect states on adjacent rungs of the ladder. Two phenomena can relax this selection rule: (a) contributions higher order terms in the dipole expansion, and (b) anharmonicity of the vibrational potential well (*vide infra*). In most cases, the "fundamental" $\Delta n = \pm 1$ transitions always have vastly larger probabilites than "overtone" transitions with $\Delta n = \pm 2, \pm 3, \cdots$.

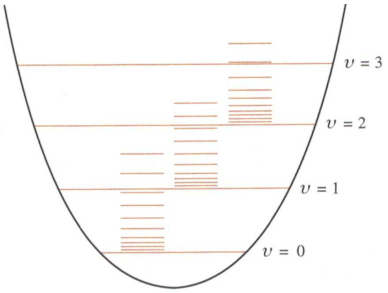
5 Rovibrational spectroscopy of diatomic molecules

In reality, there is no such thing as pure vibrational spectroscopy, as each vibrational level has an associated stack of rotational levels that must also be considered. When we discussed rotational spectroscopy earlier, we considered transitions between rotational energy levels associated with the same vibrational level (typically $v = 0$). In vibration-rotation (or rovibrational) spectroscopy, we consider transitions between the sets of rotational energy levels associated with two different vibrational levels. Thus, a vibrational "band" associated with $v' \leftrightarrow v''$, is actually associated with a series of "lines" corresponding to $v'J' \leftrightarrow v''J''$.

Assuming for the moment that the rotational and vibrational motion are independent, we can express the total rotational-vibrational energy by simply taking the sum of the rotational and vibrational energies, and labeling each state with both a vibrational quantum number, n, and a rotational quantum number J:

$$E_{n,J} = (n + \tfrac{1}{2})\hbar\omega + B_n J(J+1) \tag{57}$$

Where we label the rotational constant in vibrational state n as B_n to indicate that it's value may depend slightly on the vibrational state.



Because we're taking our vibrational and rotational motion to be independent, the selection rules we have already derived still hold:

$$\Delta n = \pm 1 \tag{58}$$
$$\Delta J = \pm 1 \tag{59}$$

The fact that $J = \pm 1$ during a transition leads to two "branches":

$$\textbf{R-branch:} \quad n \to n+1, \quad J \to J+1 \qquad \text{“richer”} \tag{60}$$

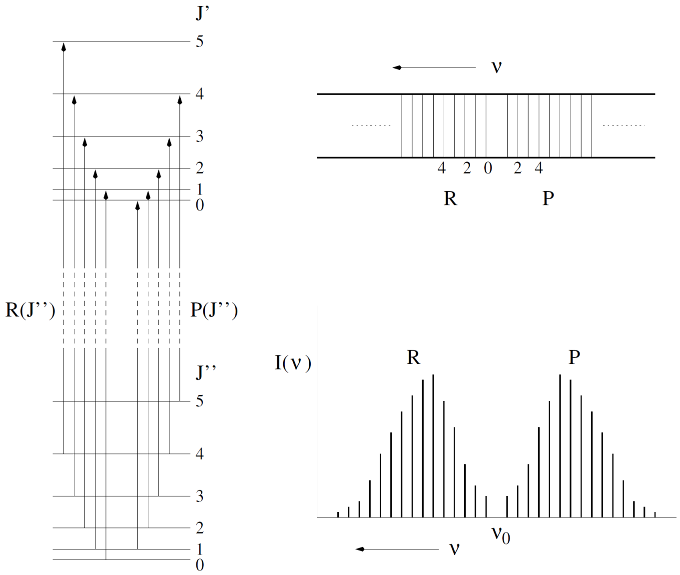
$$\textbf{P-branch:} \quad n \to n+1, \quad J \to J-1 \qquad \text{“poorer”} \tag{61}$$

Assuming $B_n \sim B$ for all n, we can evaluate the transition energies, where J always labels the angular momentum in the lower vibrational state:

$$\begin{aligned} \textbf{R-branch:} \quad \tilde{E}_{n+1,J+1} - \tilde{E}_{n,J} &= (n+1+\tfrac{1}{2})\tilde{\nu} + \tilde{B}(J+1)(J+2) \quad &(62) \\ &- (n+\tfrac{1}{2})\tilde{\nu} - \tilde{B}J(J+1) \quad &(63) \\ &= \tilde{\nu} + 2\tilde{B}(J+1), \quad J = 0,1,2,\ldots \quad &(64) \end{aligned}$$

$$\begin{aligned} \textbf{P-branch:} \quad \tilde{E}_{n+1,J-1} - \tilde{E}_{n,J} &= (n+1+\tfrac{1}{2})\tilde{\nu} + \tilde{B}(J-1)J \quad &(65) \\ &- (n+\tfrac{1}{2})\tilde{\nu} - \tilde{B}J(J+1) \quad &(66) \\ &= \tilde{\nu} - 2\tilde{B}J, \quad J = 1,2,3,\ldots \quad &(67) \end{aligned}$$

We therefore find a manifold of evenly spaced rotational transitions clustered around the "band origin" at wavenumber $\tilde{\nu}$ where the $\Delta J = 0$ vibrational transition would occur.



Note that the selection rule $\Delta J = \pm 1$ holds only for a molecule in a Σ electronic state. Transitions with $\Delta J = 0$ can appear and give rise to a "Q branch" when the electronic angular momentum of the diatomic molecule is non-zero. Q-branches also appear for certain bands in non-linear polyatomic molecules.

A closer look at actual spectra reveals that the P and R branches are not actually symmetric, resulting from the fact that the value of the rotational constant does depend on vibrational state, and $B_n \neq B_{n+1}$ in general. Measuring the exact positions of transitions in both the P and R branches would allow you to fit the state-dependent rotational constants.

6 Beyond the harmonic oscillator / rigid rotor approximation

For a diatomic molecule, there are two major ways in which the rigid rotor / harmonic oscillator approximation can break down: anharmonicity, and centrifugal distortion. Their inclusion leads to a more accurate expression for rovibrational energy given by:

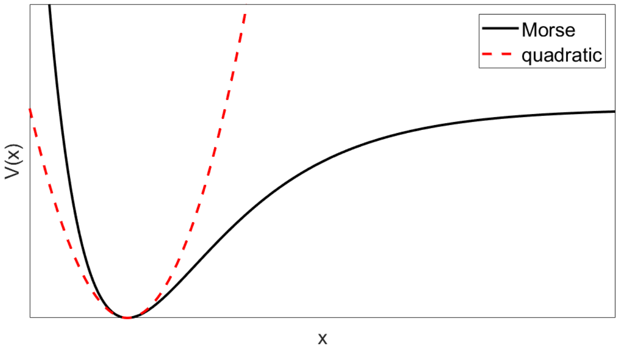
$$E_{vr} = \hbar\omega_e(n + \tfrac{1}{2}) - \hbar\omega_e x_e(n + \tfrac{1}{2})^2 + \cdots + B_v J(J+1) - D_v J^2(J+1)^2 + \cdots \tag{68}$$

6.1 Anharmonicity

The harmonic potential is clearly not a perfect approximation for the vibrational motion of a diatomic molecule. A more appropriate potential would approach zero as $R \to 0$ and the nuclei become non-interacting, have a minimum at $R = R_e$, and go to large values as $R \to 0$ and the nuclei overlap. A simple potential which achieves these criteria is the Morse potential, given by:

$$V(R) = D_e(1 - e^{-\beta(R-R_e)^2} \tag{69}$$

where the dissociation energy D_e, the equilibrium bond length R_e, and the curvature of the potential a near the minimum are the three adjustable parameters. The major qualitative problem with the Morse potential is that it does not in fact approach ∞ as $R \to 0$. However, we know that wavefunctions tail away to zero in classically forbidden regions, so as long as the potential is sufficiently large at small R, this should not pose a significant problem.



The Morse potential is useful because the Schrödinger equation for its energy eigenvalues can be solved analytically. The energies are

$$E_n = \hbar\omega_e(n + \frac{1}{2}) - \frac{\left[\hbar\omega_e(n + \frac{1}{2})\right]^2}{4D_e} \tag{70}$$

where

$$\omega_e = \beta\sqrt{\frac{2D_e}{\mu}} \tag{71}$$

is expressed in radians/second.

You also commonly see these energies expressed in wavenumbers as "term values" $G(n)$:

$$G(n) = \frac{E_n}{hc} = \tilde{\omega}(n + \tfrac{1}{2}) - \tilde{\omega}_e\tilde{x}_e(n + \tfrac{1}{2})^2 \tag{72}$$

$$\tilde{\omega}_e = \beta \left[\frac{D_e\hbar}{\pi c\mu}\right]^{\frac{1}{2}} \tag{73}$$

$$\tilde{\omega}_e\tilde{x}_e = \frac{\hbar\beta^2}{4\pi c\mu} \tag{74}$$

$$v = 0, 1, 2, \ldots \tag{75}$$

and where $\tilde{\omega}_e\tilde{x}_e$ is called the anharmonicity constant. Typically $\tilde{\omega}_e\tilde{x}_e << \tilde{\omega}_e$.

Of course, the Morse oscillator is also an approximation, and a more perfect model must make use of electronic structure calculations to map out the real curvature of the potential.

6.2 Centrifugal distortion

We already touched on this idea in our discussion of the rigid rotor. Rotational and vibrational motion couple, and as the molecule spins more quickly, with larger angular momentum at larger values of J, the bond lengthens. The effective moment of inertia increases, and the effective B constant decreases at high J. This *centrifugal distortion* is often expressed to second order as:

$$E_v(J) = B_vJ(J+1) - D_vJ^2(J+1)^2 + \cdots \tag{76}$$

where the rotational constant and centrifugal distortion constants are labeled with a v subscript to indicate that their values depend on the vibrational state of the system.

7 Raman spectroscopy

We've talked now about infrared absorption spectroscopy - how absorption or emission of light can drive transitions between pairs of (ro)vibrational states. Raman scattering is another extremely common form of vibrational spectroscopy which does not involve direct absorption or emission of radiation. Instead, it involves the elastic or inelastic scattering of incident radiation, accompanied by a change in the internal state of the molecule in the case of inelastic scattering.

Technically we need second-order perturbation theory to describe Raman scattering, because transitions between pairs of states are induced by the action of *two* light fields whose frequency difference equals the energy splitting between states. However, we can describe Raman scattering quite accurately if we replace the dipole operator with an induced dipole moment generated by the incident field: $\underline{\mu} \rightarrow \underline{\mu}_i$.

The incident field of light with electric field $\underline{E}_i$ polarizes the molecule according to its electric polarizability $\underline{\underline{\alpha}}$, which describes the ease with which the distribution of charges in a molecule is distorted by an external electric field:

$$\underline{\mu}_i = \underline{\underline{\alpha}}\,\underline{E}_i(t) \qquad \text{or} \tag{77}$$

$$\begin{bmatrix}\mu_{ix}\\ \mu_{iy}\\ \mu_{iz}\end{bmatrix} = \begin{bmatrix}\alpha_{xx} & \alpha_{xy} & \alpha_{xz}\\ \alpha_{yx} & \alpha_{yy} & \alpha_{yz}\\ \alpha_{zx} & \alpha_{zy} & \alpha_{zz}\end{bmatrix} \begin{bmatrix}E_{ix}\\ E_{iy}\\ E_{iz}\end{bmatrix} \tag{78}$$

where $\underline{\underline{\alpha}}$ is the polarizability tensor. This is a second rank tensor which tells you how well a light field polarized along axis i can induce a dipole moment in the s direction. Note that in an atom, where symmetry is spherical, the polarizability will be the same in all directions and can be expressed by a single scalar quantity. For molecules with lower-than-spherical symmetry, the polarizability is not the same in all directions, and, just as is true for moment(s) of inertia, describing the full polarizability requires the use of a tensor. Just as the principal axes diagonalize the moment of inertia tensor, so too can the polarizability tensor be diagonalized and a polarizability ellipsoid defined.

In any event, the perturbation to the Hamiltonian from the *scattered* field $E_s(t)$ interacting with this induced dipole is

$$\begin{aligned} V(t) &= \underline{E}_s(t) \cdot \underline{\mu}_i && (79) \\ &= \underline{E}_s(t) \cdot \underline{\underline{\alpha}}\, \underline{E}_i(t) && (80) \\ &= E_s(t) \cdot E_i(t) \cdot \hat{\epsilon}_s \cdot \underline{\underline{\alpha}} \cdot \hat{\epsilon}_i && (81) \end{aligned}$$

where ϵ_i and ϵ_s are unit vectors along the field directions of the incident and scattered fields.

This leads to an expression for the Raman lineshape as:

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \, \langle \hat{\epsilon}_s \cdot \underline{\underline{\alpha}}(0) \cdot \hat{\epsilon}_i \cdot \hat{\epsilon}_s \cdot \underline{\underline{\alpha}}(t) \cdot \hat{\epsilon}_i \rangle \tag{82}$$

Let's assume for the moment that we can set $\hat{\epsilon}_i = \hat{\epsilon}_s = \hat{z}$ with our experimental configuration, though the following process would work just as well for any pair of laboratory coordinates. Then:

$$\sigma(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_n p_n \langle n | \alpha_{zz}(0) \cdot \alpha_{zz}(t) | n \rangle \tag{83}$$

How to proceed from here? We can follow much the same procedure that we did for the absorption spectrum of the harmonic oscillator. We take the polarizability to be a weak function of vibrational displacement x:

$$\alpha_{zz} = \alpha_{zz,0} + \left(\frac{d\alpha_{zz}}{dx} \right)_0 \cdot x + \cdots \tag{84}$$

Just as we did for the harmonic oscillator, we can use the time-dependent ladder operator expansion of x to find, very qualitatively:

$$\sigma(\omega) \sim \left(\frac{d\alpha_{zz}}{dx} \right)_0^2 \cdot \delta(\omega \pm \omega_0) \tag{85}$$

The big takeaways from this exercise are:

- The zeroth order components of the polarizability like $\alpha_{zz,0}$ give rise to elastic Rayleigh scattering, where the incident and scattered fields have the same frequency, and the vibrational state of the molecule is unchanged.

- For proper Raman scattering, the vibrational quantum number of the molecule can be changed by $\Delta n = \pm 1$ just as we saw for infrared absorption. $\Delta n = +1$ corresponds to Stokes shifted Raman scattering, where the molecule absorbs energy and scatters a photon of a lower frequency, while $\Delta n = -1$ corresponds to anti-Stokes shifted Raman scattering, where the molecule gives up energy to the scattered field.

- Raman active vibrations must feature motion of the nuclei along a coordinate which changes the polarizability of the system, e.g. $\left(\frac{d\alpha}{dx}\right)_0 > 0$. In a polyatomic molecule, vibrational modes of different symmetries can enable Raman scattering along different polarization axes.