

$$\begin{aligned}\mu_{v,v'} &= \left(\frac{d\mu}{dx} \right)_{x=0} N_v N_{v'} \int_{-\infty}^{+\infty} H_{v'}(\sqrt{\alpha} x) \exp(-\alpha x^2) \hat{x} H_v(\sqrt{\alpha} x) dx \\ &= \left(\frac{d\mu}{dx} \right)_{x=0} N_v N_{v'} \int_{-\infty}^{+\infty} H_{v'}(\sqrt{\alpha} x) \exp(-\alpha x^2) \left[v H_{v-1}(\sqrt{\alpha} x) + \frac{1}{2} H_{v+1}(\sqrt{\alpha} x) \right] dx\end{aligned}$$

The orthogonality of the Hermite polynomials and properties of even/odd functions then require that

$$v' = v - 1 \quad \text{OR} \quad v' = v + 1.$$

Thus, the selection rule for a harmonic oscillator transition is $\Delta v = \pm 1$.

The physical meaning of the vibrational selection rule is this: The vibration must **change** the molecular dipole moment to have a non-zero (electric) transition dipole moment. Molecules **CAN** have a zero net dipole moment, yet **STILL UNDERGO** transitions when stimulated by infrared light. Some examples will help here.

Homonuclear diatomic molecules such as molecular hydrogen, nitrogen, and oxygen have no net dipole moment. As the molecule stretches and compresses itself in its one vibrational mode, the symmetry is unchanged, and at no time does a dipole moment exist. Thus, infrared transitions are truly '*forbidden*', since symmetry requires that the molecular dipole moment can never vary from zero.

On the other hand, heteronuclear diatomics such as HCl and CO have a permanent dipole moment, which changes in magnitude as the molecule vibrates. Hence, HCl and CO have electric dipole-allowed transitions (for which the transition matrix elements $\mu_{v,v'}$ are non-zero) and therefore show infrared absorptions corresponding to vibrational excitation.

Linear symmetric molecules such as carbon dioxide, represented as O=C=O, have zero net dipole moments. The symmetric stretching mode doesn't change the dipole moment away from zero, so is infrared-inactive, or $\mu_{0,1} = 0$. On the other hand, the anti-symmetric stretch and both bending modes create transient dipole moments, and so are infrared active.

To summarize selection rules: These are rigorous only for the harmonic oscillator **model**. In some special cases, higher-order electric multipole moments (such as the quadrupole tensor) can permit a transition to occur. Also, distortion of the potential energy curve away from the parabolic Harmonic Oscillator can make other transitions allowed, but with lower intensity. We can see this in the case for carbon monoxide that the $v=0$ to $v=2$, or 3 transitions, "*forbidden*" in the harmonic oscillator model, are much less intense (or much less probable) but are easily observed with the sensitivity of a modern Fourier-transform research spectrometer. Lastly, there is usually no such thing as a "*forbidden*" transition for a real molecule. The *forbidden* and *allowed* terminology for transitions means *near-zero* and large probability for the transition to occur, respectively. In the case of a *forbidden* transition, except for diatomic molecules it is quite rare that the molecular dipole is always non-zero. It is just that the probability is so low that we

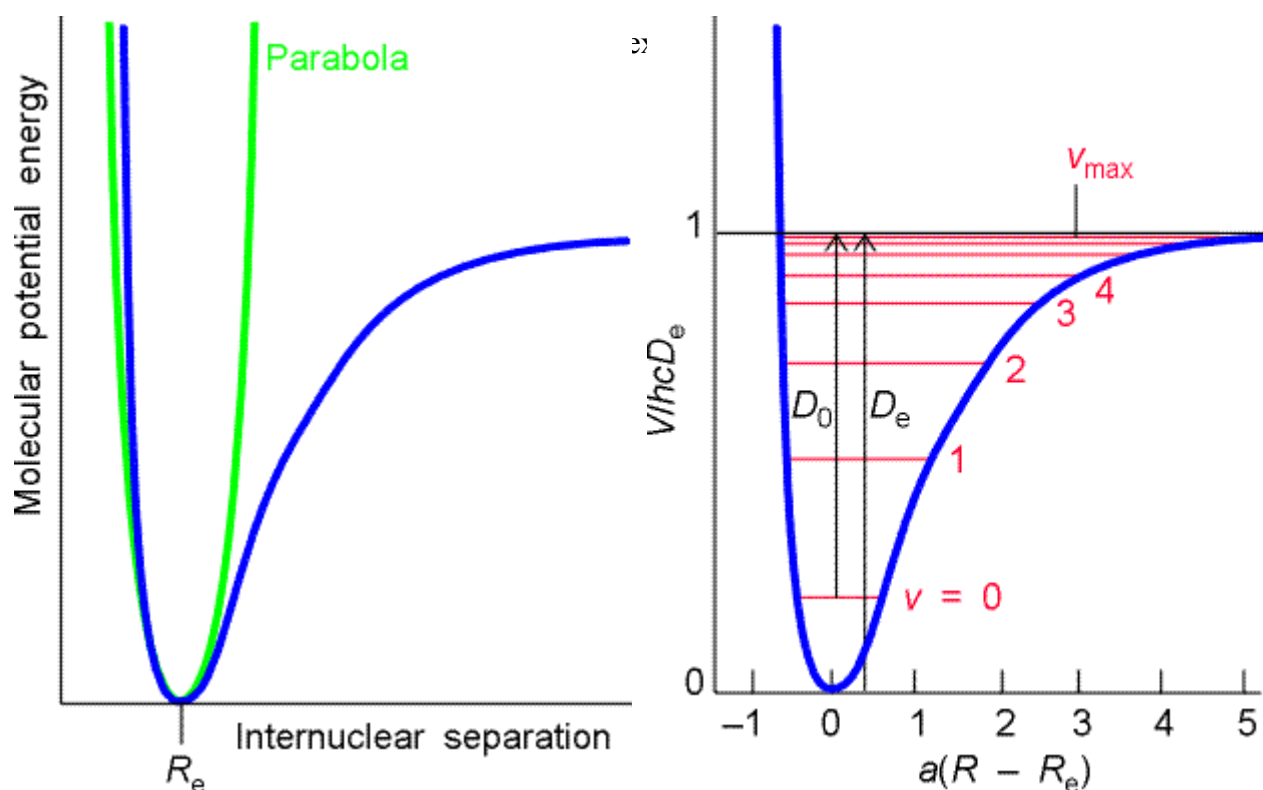
would have to wait for much longer than the age of the universe before we could observe the transition occurring.

Beyond the Harmonic Oscillator Model: Anharmonicity

The potential energy for vibrating molecules is usually represented very well by the harmonic oscillator for the $\nu = 0$ to $\nu = 1$ transition. However, for large values of the vibrational quantum number ν , the potential energy no longer resembles the green parabola. Repulsive forces make the potential steeper than parabolic when the bond length is compressed, and less steep when the bond length is expanded, as shown in the blue model below.

This blue curve in the figure below is an empirical functional form called the *Morse potential*. The *Morse potential* is actually an excellent representation for the molecular potential energy all the way up to the dissociation limit. An important feature is that the vibrational energy levels become increasingly dense with larger quantum number ν . At some large value of ν , the molecule no longer vibrates, but dissociates.

The functional form for the *Morse potential* is



where the parameter a is $a = [\mu\omega^2/(2hcD_e)]^{1/2}$. The parameter D_e represents the energy required for molecular dissociation measured from the minimum in the potential energy well. While fine as a classical quantity, D_e is not correct quantum mechanically, because the lowest energy

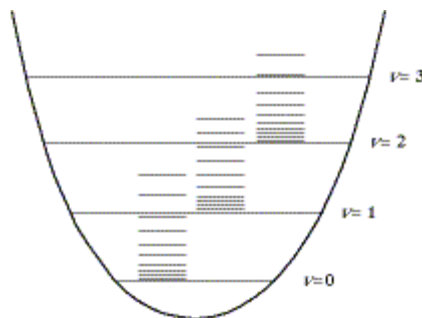
quantum state for $v=0$ does **not have zero energy**. The correct dissociation energy is shown as D_0 .

When the Schrödinger equation is solved for the Morse potential using perturbation theory, the energy eigenvalues are

$$E_{\text{morse}}(v) = h\nu \left[\left(v + \frac{1}{2} \right) - \left(v + \frac{1}{2} \right)^2 \chi_e \right], \text{ with } \chi_e = \frac{\nu}{4hcD_e}.$$

Molecular Vibrations Are Accompanied by Rotations

The diagram below shows the simplest model for a vibrating and rotating diatomic molecule: the potential energy curve is parabolic, as one expects for the **harmonic oscillator** model, and the rotational energy levels as found from solutions to the **rigid rotor** model are present for each vibrational level.



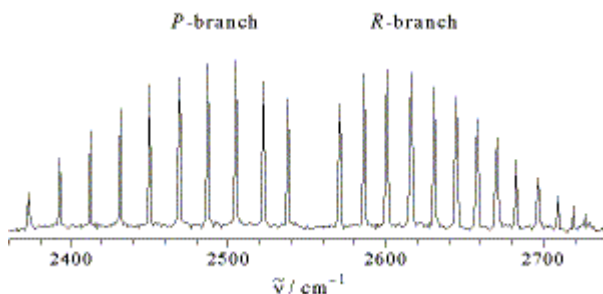
Combining the selection rules for **rigid rotor** and **harmonic oscillator** gives us the following:

$$\Delta v = \pm 1; \Delta J = 0, \pm 1.$$

Spectroscopic notation gives us the three branches of the “*ro-vibrational*” spectrum:

- P branch: $\Delta J = -1$;
- Q branch: $\Delta J = 0$; and
- R branch: $\Delta J = +1$.

A sample ro-vibrational spectrum is shown below for gas-phase HBr. As is true for other heteronuclear diatomic molecules, the Q branch ($\Delta J = 0$) is absent from this spectrum.



Rotation-Vibration Coupling

As a molecule is excited to higher lying vibrational quantum states, one can see that the atoms will spend an increasing amount of time at a greater distance from the equilibrium bond length. This has the effect of increasing the average bond length with increasing vibrational quantum number v . However, one of the central parameters in using the rigid rotor approximation to describe molecular rotations is the moment of inertia, I . Since $I = \mu R^2$ for a diatomic molecule, a slight increase in the bond length R becomes squared in the moment of inertia. Since the rotational constant B is given by $B = h / (8 \pi^2 I)$, the rotational constant must decrease slightly with increasing vibrational quantum numbers v . For rotational constants in wavenumber units, this is represented by the following empirical formula:

$$\tilde{B}_v = \tilde{B}_e - \tilde{\alpha}_e (v + \frac{1}{2})$$

where the vibration-rotation coupling constant (in units of cm^{-1}) is given by

$$\tilde{\alpha}_e$$

Thus, this formula predicts that the observed rotational constant B_v will decrease linearly as the molecule is excited to higher lying vibrational quantum states. The normal rotational constant for vibrational ground state molecules ($v = 0$) is then given as $B = B_e - \alpha_e$.

Full Term Equation for Ro-Vibrational State Energies of Molecules

Since any vibrationally excited molecule must also have some quantum numbers for simultaneous rotational excitation, we see that there will be five terms in the energy for a ground electronic state, vibrating, rotating molecule:

1. Vibrational energy
2. Anharmonic vibrational energy correction
3. Rotational energy
4. Rotation-vibration coupling term, and
5. Centrifugal distortion correction to the rotational energy.

Thus, the complete term equation (in cm^{-1} units) is given by

$$E_{v,J}(\text{cm}^{-1}) = \tilde{\nu}_e (v + \frac{1}{2}) - \tilde{\chi}_e \tilde{\nu}_e (v + \frac{1}{2})^2 + \tilde{B}_v J(J+1) - D_v J^2(J+1)^2$$

Vibrations of polyatomic molecules

For a molecule with N atoms, each atom has three motional degrees of freedom- one each for the translation about the x, y, and z Cartesian axes of the molecule-based coordinate system. Thus, the molecule possesses a total of $3N$ degrees of freedom. Chemical bonds, which for the moment can be thought of as spring connectors between atoms, serve to constrain the motion of the atoms to well defined vibrational modes.

Linear molecules have three unique translations, but only two unique rotations. (The rotation about the bond axis does not count, since it changes neither positions of the atoms, nor does it