

Chemistry 21b – Spectroscopy

Lecture # 7 – Vibration-Rotation Spectra of Diatomic Molecules

What happens to the rotation and vibration spectra of diatomic molecules if more realistic potentials are used to describe the interatomic interaction? So far we have just assumed that $R = R_e$, and that no change in the bond length is possible. Clearly, for a realistic interatomic potential, such as those outlined in Figure 4.1, considerable changes in bond length with occur as one moves up in energy from the ground vibrational state. As a one-dimensional equation, the radial nuclear motion described by Eq. (4.15) can be solved numerically quite simply, and there are in fact computer routines which invert experimental data to yield diatomic potentials $V(R) = E^{el}(R)$ with spectroscopic precision. Considerable physical insight, however, can be gained by using simple, analytical potentials for $V(R)$, and analyzing the resulting energy level expressions. One of the simplest and most useful potentials was developed by Morse in the early part of this century, which we'll proceed to examine now.

7.a. The Morse Potential

Clearly, an appropriate potential must go to small values as $R \rightarrow \infty$, have a minimum at $R = R_e$, and go to very large values as $R \rightarrow 0$. A simple potential which does this, the Morse potential, is given by

$$V(R) = D_e(1 - e^{-a(R-R_e)})^2, \quad (7.1)$$

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

If the Morse potential is placed into the radial nuclear motion equation, Eq. (7.15) on page 25 of the notes, we find:

$$\frac{d^2 S(R)}{dR^2} + \left\{ -\frac{J(J+1)}{R^2} + \frac{2\mu}{\hbar^2} [E - D_e - D_e e^{-2a(R-R_e)} + 2D_e e^{-a(R-R_e)}] \right\} S(R) = 0, \quad (7.2)$$

where the substitution $F(R) = \frac{1}{R}S(R)$ has been made.

Like all such problems in quantum mechanics, the challenge is in finding the right substitution of variables that allows Eq. (7.2) to be recast in a form that has well-known solutions. We'll only briefly outline the procedure here. The first set of substitutions involve the equations

$$y = e^{-a(R-R_e)} \quad \text{and} \quad A = J(J+1) \frac{\hbar^2}{2\mu R_e^2}. \quad (7.3)$$

If these are substituted into Eq. (11.2), we find

$$\frac{d^2 S}{dy^2} + \frac{1}{y} \frac{dS}{dy} + \frac{2\mu}{a^2 \hbar^2} \left(\frac{E - D_e}{y^2} + \frac{2D_e}{y} - D_e - \frac{AR_e^2}{y^2 R^2} \right) = 0 \quad (7.4)$$

For $A \neq 0$, the last (R_e^2/R^2) term must be expanded in order to generate an equation containing only y . The first three terms of the Taylor expansion are given by

$$\frac{R_e}{R^2} = \frac{1}{[1 - (\ln y/aR_e)]^2} = 1 + \frac{2}{aR_e}(y-1) + \left(-\frac{1}{aR_e} + \frac{3}{a^2 R_e^2} \right) (y-1)^2 + \dots \quad (7.5)$$

Retaining these first three terms and regrouping yields

$$\frac{d^2 S}{dy^2} + \frac{1}{y} \frac{dS}{dy} + \frac{2\mu}{a^2 \hbar^2} \left(\frac{E - D_e - c_1}{y^2} + \frac{2D_e - c_1}{y} - D_e - c_2 \right) S = 0, \quad (7.6)$$

in which

$$\begin{aligned} c_0 &= A \left(1 - \frac{3}{aR_e} + \frac{3}{a^2 R_e^2} \right) \\ c_1 &= A \left(\frac{4}{aR_e} - \frac{6}{a^2 R_e^2} \right) \\ c_2 &= A \left(-\frac{1}{aR_e} + \frac{3}{a^2 R_e^2} \right) \end{aligned} \quad (7.7)$$

Eq. (11.6) can be further simplified by the substitutions

$$S(y) = e^{-z/2} z^{b/2} F(z) \quad z = 2dy$$

$$d^2 = \frac{2\mu}{a^2 \hbar^2} (D_e + c_2) \quad b^2 = -\frac{8\mu}{a^2 \hbar^2} (E - D_e - c_0) \quad (7.8)$$

so that it becomes

$$\frac{d^2 F}{dz^2} + \left(\frac{b+1}{y} - 1 \right) \frac{dF}{dz} + \frac{v}{z} F = 0, \quad (7.9)$$

where

$$v = \frac{\mu}{a^2 \hbar^2 d} (2D_e - c_1) - \frac{1}{2}(b+1) \quad (7.10)$$

is the vibrational quantum number. Eq. (7.9) should look familiar from your discussion of the hydrogen atom in Ch21a because it is the Laguerre equation. From this analysis, we know that to have smooth wavefunctions which decay to zero at appropriate boundaries the quantum number $v = 0, 1, 2, 3, \dots$. Mathematically speaking, this condition which holds is $s \rightarrow 0$ as $R \rightarrow -\infty$, which is not strictly the boundary condition we are interested in. However, the Morse potential is large enough at small R that this is not a serious problem.

Now that we have the values of v , it is possible to invert Eqs. (7.8) and (7.10) to discover the allowed energy levels, which are:

$$E_{Jv} = \omega_e(v + \frac{1}{2}) - \omega_e x_e (v + \frac{1}{2})^2 + J(J+1)B_e - D_J J^2(J+1)^2 - \alpha_e (v + \frac{1}{2})J(J+1) \quad (7.11)$$

where

$$\begin{aligned} \omega_e &= \frac{a}{2\pi} \sqrt{\frac{2D_e}{\mu}} & x_e &= \frac{h\omega_e}{4D_e} & B_e &= \frac{h}{8\pi^2\mu R_e^2} \\ D_J &= \frac{4B_e^3}{\omega_e^2} & \alpha_e &= 6\sqrt{\frac{x_e B_e^3}{\omega_e} - \frac{6B_e^2}{\omega_e}} \end{aligned} \quad (7.12)$$

if ω_e, α_e, B_e are expressed in cycles/sec, or Hz.

The great utility of the Morse potential lies in the physical significance associated with each of the terms, and the way it explicitly links measureable experimental parameters with important physical properties of the molecule such as its equilibrium bond length and dissociation energy. The first two terms are clearly that of a vibrating harmonic oscillator and the first anharmonic correction, the third and fourth terms are the rotational and centrifugal distortion constants from Lecture 6, and the last term allows for the change in average moment-of-inertia due to vibration and the consequent change in rotational energy.

From the expression for the distortion constant, we see that even if only the rotational constants are known, it is possible to predict the vibrational frequency and to place constraints on the dissociation energy D_e , and this is one of the facets which makes the Morse potential so popular. The α_e term, in principal, could be either positive or negative, but in realistic situations the first term dominates and the vibrational constants in higher vibrational states are *lower* than that of the ground state. Finally, the simple dependence of the results on μ enables investigators to predict the location of the spectral features of various isotopomers once a single variant has been measured. Specifically, the isotopic dependence of the constants from a Morse analysis are:

$$\omega_e \propto \frac{1}{\mu^{1/2}} \quad B_e \propto \frac{1}{\mu} \quad \alpha_e \propto \frac{1}{\mu^{3/2}} \quad D_J \propto \frac{1}{\mu^2} \quad (7.13)$$

7.b. Energy levels and selection rules

If even larger expansions of the potential near R_e are used, the vibrational energy levels of a diatomic molecule can be expressed as

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e (v + 1/2)^2 + \omega_e y_e (v + 1/2)^3 + \dots \quad (7.14)$$

Again, the first term in (7.14) is the harmonic oscillator term, and the higher order terms result from anharmonicity. The constants $\omega_e x_e, \omega_e y_e, \dots$ are the anharmonic constants, and cause the higher v levels to be closer together than the lower v levels (see Figure 7.1). For

example, for $^1\text{H}^{35}\text{Cl}$, $\omega_e x_e = 52.8186\text{cm}^{-1}$, $\omega_e y_e = 0.2244\text{cm}^{-1}$ and $\omega_e z_e = -0.0122\text{cm}^{-1}$. A useful summary of these constants has been given by Huber and Herzberg, 1977 “Constants of Diatomic Molecules”.

The strength of a transition between two vibrational states v' and v'' is again proportional to the square of the transition moment R_v :

$$R_v = \langle v' | \mu | v'' \rangle \quad (7.15)$$

where μ is the dipole moment defined in Lecture #5. The dipole moment can be expanded in a Taylor series around the equilibrium distance R_e :

$$\mu = \mu_e + \left(\frac{d\mu}{dR} \right)_{R_e} (R - R_e) + \frac{1}{2} \left(\frac{d^2\mu}{dR^2} \right)_{R_e} (R - R_e)^2 + \dots \quad (7.16)$$

so that R_v becomes:

$$R_v = \mu_e \langle v' | v'' \rangle + \left(\frac{d\mu}{dR} \right)_{R_e} \langle v' | R - R_e | v'' \rangle + \dots \quad (7.17)$$

Since the vibrational functions $\Psi^{v'}$ and $\Psi^{v''}$ are eigenfunctions of the same Hamiltonian, they are orthogonal for $v' \neq v''$:

$$\langle v' | v'' \rangle = \delta_{v'v''} \quad (7.18)$$

so that the leading term of Equation (7.17) is, without approximation,

$$R_v = \left(\frac{d\mu}{dR} \right)_{R_e} \langle v' | R - R_e | v'' \rangle . \quad (7.19)$$

Thus, the strength of a vibrational band in the infrared depends on the magnitude of the *derivative* of the dipole moment with internuclear distance. Figure 7.1 shows how the dipole moment μ varies with R in a typical heteronuclear diatomic molecule. Obviously, $\mu \rightarrow 0$ when $R \rightarrow 0$, since the nuclei coalesce. For neutral diatomics, $\mu \rightarrow 0$ when $R \rightarrow \infty$ because the molecule dissociates into neutral atoms. Therefore, between $R = 0$ and ∞ , there must be a maximum value of μ . In Figure 7.1, this maximum occurs at $R < R_e$, giving a negative slope $d\mu/dR$ at R_e . If the maximum were at $R > R_e$, there would be a positive slope at R_e .

A molecule with a relatively small dipole moment may still have a large dipole derivative, and, conversely, a molecule with a very large dipole moment may have a small dipole derivative if the dipole moment is near its maximum value at $R = R_e$, so that $d\mu/dR = 0$ at R_e . For example, CO, which has a permanent moment of only 0.11D, possesses a large dipole derivative, and thus one of the strongest known infrared absorptions. A homonuclear molecule, however, for which $\mu = 0$ at all internuclear separations, has a dipole derivative that is zero everywhere, and thus no electric dipole vibrational absorption at all. Thus, homonuclear molecules such as H_2 , O_2 and N_2 have neither vibrationally nor rotationally electric dipole allowed transitions.

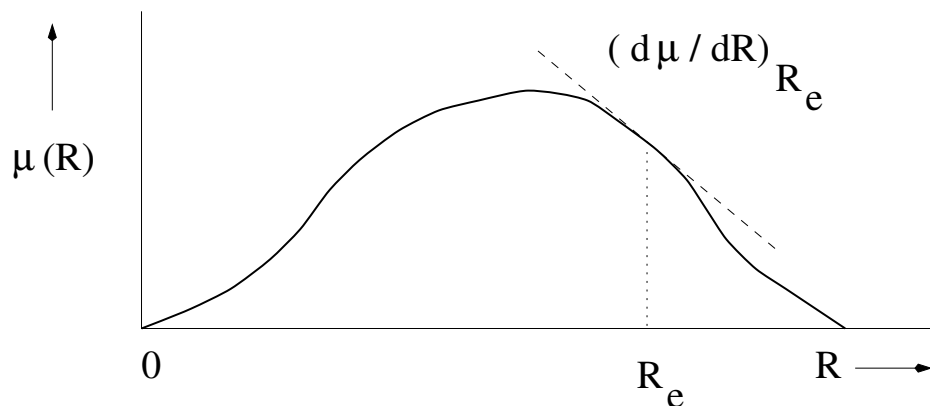


Figure 7.1 Variation of dipole moment with internuclear distance in a heteronuclear diatomic molecule.

In the pure harmonic oscillator approximation, only $\Delta v = v' - v'' = \pm 1$ transitions can occur. For real, anharmonic molecules, there is no selection rule on the change in vibrational quantum number v , although the $\Delta v = \pm 1$ transitions always have vastly larger probabilities than $\Delta v > 1$ transitions. Transitions with $\Delta v = \pm 1$ are called “fundamental bands”, whereas those with $\Delta v = \pm 2, \pm 3, \dots$ are called “overtone bands”.

7.c. Vibration-rotation spectroscopy

Associated with each vibrational level is a stack of rotational energy levels. In the rotational spectroscopy discussed in § VIII, we considered transitions between rotational energy levels associated with the same vibrational level (usually $v=0$). In vibration-rotation spectroscopy, we consider transitions between the sets of rotational energy levels associated with two different vibrational levels. Thus, a vibrational “band”, that is a transition $v' \leftrightarrow v''$, is composed of a number of “lines” $v'J' \leftrightarrow v''J''$. The energy levels are given by the sum of the rotational term values $F_v(J)$ and the vibrational term values $G(v)$

$$E^{vr} = G(v) + F_v(J) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \dots + B_v J(J+1) - D_v J^2(J+1)^2 \quad (7.20)$$

Figure 11.2 illustrates the rotational levels associated with two vibrational levels v' and v'' . The selection rules on rotational quantum number, parity etc.. derived previously still apply. Thus, in addition to the vibrational selection rules, we have

$$\Delta J = \pm 1. \quad (7.21)$$

The selection rule $\Delta J = \pm 1$ holds strictly only for a molecule in a Σ state. Transitions with $\Delta J = 0$ can occur when the electronic angular momentum of the molecule is non-zero.

The “band origin” is the mythical place where the $J' = J'' = 0$ transition would occur, if it were not forbidden. The vibrational band is then composed of a number of ‘branches’, which in the simplest case are:

$$\begin{array}{ll} \text{R-branch:} & \Delta J = J' - J'' = +1 \\ \text{Q-branch:} & \Delta J = 0 \\ \text{P-branch:} & \Delta J = J' - J'' = -1 \end{array} \quad (7.22)$$

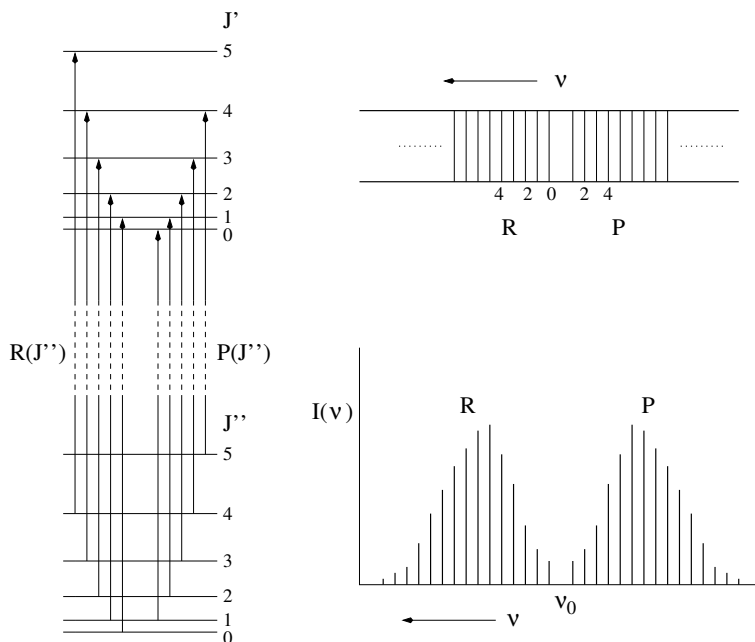


Figure 7.2 Schematic vibration-rotation spectrum of a $^1\Sigma$ heteronuclear diatomic molecule.

Note that the Q branch transitions do not occur for Σ states. The frequencies of each of the lines are (neglecting distortion for now)

$$\begin{aligned}
 \tilde{\nu}_P(J) &= \tilde{\nu}_0 + B'J'(J' + 1) - B''J''(J'' + 1) \\
 &= \tilde{\nu}_0 + B'(J - 1)J - B''J(J + 1) \\
 &= \tilde{\nu}_0 - (B' + B'')J + (B' - B'')J^2.
 \end{aligned} \tag{7.23}$$

Similarly:

$$\tilde{\nu}_R(J) = \tilde{\nu}_0 + (B' + B'')(J + 1) + (B' - B'')(J + 1)^2. \tag{7.24}$$

The appearance of such a vibration-rotation band is indicated in Figure 7.2. The band appears fairly symmetrical about the band center ν_0 , and there is approximately equal spacing between adjacent R-branch lines, and between adjacent P-branch lines, but there is twice as large a space between the first R and P branch lines, R(0) and P(1). This spacing between R(0) and P(1) is called the zero gap, and it is in this region where the band origin ν_0 falls. Also, the Q branch, if present, would occur in this gap.

The approximate symmetry of the band is due to the fact that $B' \approx B''$, that is, the vibration-rotation interaction constant α is small. Then:

$$\begin{aligned}
 \tilde{\nu}_P &= \tilde{\nu}_0 - 2BJ \\
 \tilde{\nu}_R &= \tilde{\nu}_0 + 2B(J + 1)
 \end{aligned} \tag{7.25}$$

so that the zero gap $\tilde{\nu}(R(0) - P(1)) = 4B$.

A closer look at actual spectra (see Harris & Bertolucci) reveals that the bands are not quite symmetrical, but show a convergence in the R branch and a divergence in the P branch, resulting from the fact that B' and B'' are not quite equal. The observed energy levels can then be used to determine these two quantities separately.