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5.80 Small-Molecule Spectroscopy and Dynamics
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Lecture # 3 Supplement

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1. Anharmonic Oscillator, Vibration-Rotation Interaction

The Hamiltonian is

$$\mathbf{H} = \underbrace{\frac{\mathbf{P}_R^2}{2\mu} + \frac{k}{2}\mathbf{x}^2}_{\text{harmonic oscillator}} + ax^3 + \underbrace{\frac{\mathbf{J}^2}{2\mu R^2}}_{\text{non-rigid rotor}} \quad (1.1)$$

First we must re-express $\frac{1}{R^2}$ in terms of a quantity whose matrix elements we know such as the displacement x .

$$x = R - R_e$$

$$R = R_e + x = R_e \left(1 + \frac{x}{R_e}\right) \quad (1.2)$$

$$\frac{1}{R^2} \approx \frac{1}{R_e^2} \left(1 - 2\left(\frac{x}{R_e}\right) + 3\left(\frac{x}{R_e}\right)^2\right) \quad \text{power series expansion} \quad (1.3)$$

where we truncate expansion after $(x/R_e)^2$.

The Hamiltonian operator becomes

$$\mathbf{H} = \frac{\mathbf{P}_R^2}{2\mu} + \frac{k}{2}\mathbf{x}^2 + ax^3 + \frac{\mathbf{J}^2}{2\mu R_e^2} \left[1 - \frac{2x}{R_e} + \frac{3x^2}{R_e^2}\right] \quad (1.4)$$

Let us choose a basis $\{|v\rangle |J\rangle\}$ where $|v\rangle$ is the harmonic oscillator basis and $|J\rangle$ is the rigid rotor basis. The rotational matrix elements we need are

$$\langle J|\mathbf{J}^2|J'\rangle = J(J+1)\delta_{JJ'} \quad (1.5)$$

$$\langle J|\text{constant}|J'\rangle = \delta_{JJ'} \text{ constant} \quad (1.6)$$

$$\langle J|\text{vibr.coord.}|J'\rangle = \delta_{JJ'} \text{ vibr.coord.} \quad (1.7)$$

$$\text{and } B_e \text{ (in energy units)} = \frac{\hbar^2}{2\mu R_e^2} J. \quad (1.8)$$

Thus the rotational expectation values of the Eq.(1) Hamiltonian become

$$\langle J|\mathbf{H}|J\rangle = \left(\frac{\mathbf{P}^2}{2\mu} + \frac{k}{2}\mathbf{x}^2\right) + a\mathbf{x}^3 + B_e J(J+1) \left[1 - \frac{2\mathbf{x}}{R_e} + \frac{6\mu B_e}{\hbar^2}\mathbf{x}^2\right] \quad (1.9)$$

where $\frac{1}{R_e^2}$ was replaced by $\frac{2\mu B_e}{\hbar^2}$.

Now we need some \mathbf{x} matrix elements. Let

$$\gamma = \frac{\sqrt{k\mu}}{\hbar} \quad h\nu = \hbar\omega = \frac{k}{\gamma} \quad (1.10)$$

$$x_{v,v+1} = \left(\frac{v+1}{2\gamma}\right)^{1/2} \quad (1.11)$$

$$x_{v,v+2}^2 = \frac{1}{2\gamma}[(v+1)(v+2)]^{1/2} \quad (1.12)$$

$$x_{v,v}^2 = \frac{v + \frac{1}{2}}{\gamma} \quad (1.13)$$

$$x_{v,v+3}^3 = \left[\frac{(v+1)(v+2)(v+3)}{8\gamma^3}\right]^{1/2} \quad (1.14)$$

$$x_{v,v+1}^3 = 3\left[\frac{v+1}{2\gamma}\right]^{3/2} \quad (1.15)$$

Remember that the harmonic oscillator part of our Hamiltonian is diagonal in the harmonic oscillator basis we have chosen.

$$\langle vJ|\mathbf{H}|v'J'\rangle = h\nu\left(v + \frac{1}{2}\right)\delta_{JJ'}\delta_{vv'} + ax_{vv'}^3\delta_{jj'} + B_e J(J+1)\left[\delta_{vv'}\delta_{JJ'} - \frac{2}{R_e}x_{vv'}\delta_{JJ'} + \frac{6\mu B_e}{\hbar^2}x_{vv'}^2\delta_{JJ'}\right] \quad (1.16)$$

Note that the Hamiltonian matrix is completely diagonal in J .

The remaining problem is how to arrange the \mathbf{H} matrix now that we have two indices J and v . The Hamiltonian matrix is a super-matrix consisting of a v, v' matrix of J, J' matrices. However, since there are no matrix elements off-diagonal in J , it is convenient to alter our perspective and think of a set of single v, v' matrices, one for each value of J . Thus the Hamiltonian matrix is given by

$$\langle v|\mathbf{H}|v\rangle = h\nu\left(v + \frac{1}{2}\right) + B_e J(J+1) + B_e^2 \frac{6\mu}{\gamma\hbar^2}\left(v + \frac{1}{2}\right)J(J+1) \quad (1.17)$$

$$\langle v|\mathbf{H}|v+1\rangle = 3a\left[\frac{v+1}{2\gamma}\right]^{3/2} - \frac{2B_e}{R_e}\left(\frac{v+1}{2\gamma}\right)^{1/2}J(J+1) \quad (1.18)$$

$$\langle v|\mathbf{H}|v-1\rangle = 3a\left[\frac{v}{2\gamma}\right]^{3/2} - \frac{2B_e}{R_e}\left(\frac{v}{2\gamma}\right)^{1/2}J(J+1) \quad (18a)$$

$$\langle v|\mathbf{H}|v+2\rangle = \frac{3B_e^2\mu}{\gamma\hbar^2}J(J+1)[(v+1)(v+2)]^{1/2} \quad (1.19)$$

$$\langle v|\mathbf{H}|v-2\rangle = \frac{3B_e^2\mu}{\gamma\hbar^2}J(J+1)[(v-1)v]^{1/2} \quad (19a)$$

$$\langle v|\mathbf{H}|v+3\rangle = a\left[\frac{(v+1)(v+2)(v+3)}{8\gamma^3}\right]^{1/2} \quad (1.20)$$

$$\langle v|\mathbf{H}|v-3\rangle = a\left[\frac{v(v-1)(v-2)}{8\gamma^3}\right]^{1/2} \quad (20a)$$

We are now in a position to use perturbation theory to determine the contributions of the various terms in the Hamiltonian to the eigenvalues. Note that when faced with an infinite Hamiltonian matrix it will always be necessary to use the Van Vleck transformation in order to truncate the matrix. We act as if part of the matrix isn't there, yet we know that the Van Vleck transformed energies will be a very good approximation to the eigenvalues of the infinite matrix. In this example, the matrix will be treated entirely by first and second order perturbation theory and no diagonalization will be carried out. For our choice of basis, the zero-order Hamiltonian is diagonal by definition.

$$\mathbf{H}^{(0)} = \left[h\nu \left(v + \frac{1}{2} \right) + B_e J(J+1) \right] \delta_{JJ'} \delta_{vv'} = E_{vJ}^{(0)} \quad (1.21)$$

The perturbation terms are what is left over

$$\mathbf{H}^{(1)} = \left(a\mathbf{x}^3 - \frac{2B_e}{R_e} J(J+1)\mathbf{x} + \frac{6\mu B_e^2}{\hbar^2} J(J+1)\mathbf{x}^2 \right) \delta_{JJ'} \quad (1.22)$$

The first order corrections to the energy are given by

$$\langle v, J | \mathbf{H}^{(1)} | v, J \rangle = B_e^2 \frac{6\mu}{\gamma \hbar^2} \left(v + \frac{1}{2} \right) J(J+1) \quad (1.23)$$

but $\frac{\mu}{\gamma \hbar^2} = \frac{1}{h\nu}$.

Thus

$$E^{(1)} = 6 \frac{B_e^2}{h\nu} \left(v + \frac{1}{2} \right) J(J+1) \quad (1.24)$$

This is a harmonic vibrational correction to the rotational constant. Compare with the leading term in Dunham's expression for $Y_{11} \sim -\alpha_e$.

Note that this term causes $B(v)$ to increase as v increases. This is puzzling because everyone knows that $B(v)$ decreases for real diatomics.

The second order corrections are

$$E^{(2)} = \sum_{v' \neq v} \frac{\langle v, J | \mathbf{H}^{(1)} | v', J \rangle \langle v', J | \mathbf{H}^{(1)} | v, J \rangle}{E_{(v,J)}^{(0)} - E_{(v',J)}^{(0)}} \quad (1.25)$$

Note that for each of the three allowed off-diagonal matrix elements of equations 18-20, there will be two nonzero terms in the summation over v' .

From the $\langle v | \mathbf{H} | v \pm 3 \rangle$ matrix elements we get

$$E_{\pm 3}^{(2)} = \frac{a^2}{3h\nu} \left[\frac{v(v-1)(v-2) - (v+1)(v+2)(v+3)}{8\gamma^3} \right] \quad (1.26)$$

$$E_{\pm 3}^{(2)} = -\frac{a^2}{8\gamma^3 h\nu} [(3v^2 + 3v + 2)] \quad (1.27)$$

The $3h\nu$ in the denominator of (26) comes from $E_{v,J}^{(0)} - E_{v\pm 3,J}^{(0)}$. From the $\langle v | \mathbf{H} | v \pm 2 \rangle$ matrix elements we get

$$E_{\pm 2}^{(2)} = \frac{9B_e^4 \mu^2 J^2 (J+1)^2}{\gamma^2 \hbar^4} \frac{1}{2h\nu} [(v-1)v - (v+1)(v+2)]$$

$$E_{\pm 2}^{(2)} = -\frac{9B_e^4 \mu^2 J^2 (J+1)^2}{\gamma^2 \hbar^4 \cdot h\nu} [2v+1] = -\frac{18B_e^4 J^2 (J+1)^2 (v + \frac{1}{2})}{(h\nu)^3} \quad (1.28)$$

This is a harmonic vibrational correction term to a centrifugal distortion constant. This will not agree with Dunham's result because we only kept terms in the expansion of B in powers of $\frac{x}{R_e}$ through the second power. This second order correction to the energy is actually a $2 \times 2 = 4^{\text{th}}$ power correction in $\frac{x}{R_e}$. Terms in the B expansion through $\left(\frac{x}{R_e}\right)^4$ also contribute.

From the $\langle v|\mathbf{H}|v \pm 1\rangle$ matrix elements we obtain

$$\begin{aligned} E_{\pm 1}^{(2)} &= \frac{9a^2(v^3 - (v+1)^3)}{(2\gamma)^3 h\nu} + \frac{4B_e^2 J^2(J+1)^2[v - (v+1)]}{2\gamma R_e^2 h\nu} - \frac{12aB_e J(J+1)[v^2 - (v+1)^2]}{R_e(2\gamma)^2 h\nu} \\ E_{\pm 1}^{(2)} &= -\frac{9}{8} \left(\frac{a^2}{h\nu\gamma^3}\right) (3v^2 + 3v + 1) - \frac{2B_e^2 J^2(J+1)^2}{\gamma R_e^2 h\nu} + 6 \left(\frac{a}{h\nu\gamma^2}\right) \frac{B_e J(J+1)(v + \frac{1}{2})}{R_e} \end{aligned} \quad (1.29)$$

The first term of (29) should be added to a similar term which occurs in equation (27). The sum will be the first term in equation (30) below. The second term may be simplified using

$$\frac{\mu}{\gamma\hbar^2} = \frac{1}{h\nu} \quad \text{and} \quad \frac{1}{R_e^2} = \frac{B_e 2\mu}{\hbar^2}$$

giving $-\frac{4B_e^3 J^2(J+1)^2}{(h\nu)^2}$ which should be compared with Dunham's Y_{02} .

This term is the harmonic oscillator contribution to the centrifugal distortion constant.

In summary

$$E^{(2)} = -\left(\frac{a^2}{h\nu\gamma^3}\right) \left(\frac{15}{4}\right) \left[\left(v + \frac{1}{2}\right)^2 + \frac{7}{60}\right] + \left(\frac{a}{h\nu\gamma^2}\right) \frac{6B_e J(J+1)(v + \frac{1}{2})}{R_e} - \frac{4B_e^3 J^2(J+1)^2}{(h\nu)^2} - \frac{18B_e^4 J^2(J+1)^2(v + \frac{1}{2})}{(h\nu)^3} \quad (1.30)$$

The first term is an anharmonic contribution to $\omega_e x_e (v + \frac{1}{2})^2$ and to the zero point energy. In fact, this is why $\omega_e x_e$ is called the anharmonicity constant.

The second term is an anharmonic correction to the rotational energy. Note that this correction is of the same sign as the harmonic correction we obtained in first-order in equation (24). $B = B_e - \alpha_e (v + \frac{1}{2})$. However the sign of a is negative for realistic potential curves.

If $|a|$ is large enough, the negative anharmonic contribution to α_e will be larger than the positive harmonic contribution and $B(v)$ will decrease as v increases.

The third term is the harmonic contribution to centrifugal distortion. $E_J = BJ(J+1) - DJ^2(J+1)^2$.

The fourth term is a harmonic vibrational correction to the centrifugal distortion constant $D = D_e - \beta_e (v + \frac{1}{2})$.

2. Energy Levels of a Vibrating Rotor: Dunham's Expression for $E(v, J)$ Derived from $E(r)$

Following is an excerpt from Microwave Spectroscopy by C. Townes and A. Schawlow, pages 9–11, which describes the results of Dunham's inversion of the potential energy, $V(r)$, expressed as a power series in the dimensionless displacement coordinate ξ , into a power series in the rotational and vibrational quantum numbers, $J(J+1)$ and $(v + 1/2)$. The Rydberg-Klein-Rees procedure is exactly the reverse of this, converting $E(v, J)$ into $V(r)$.

Dunham's Solution for Energy Levels

Dunham¹ has calculated the energy levels of a vibrating rotor, by a Wentzel-Kramers-Brillouin method, for any potential which can be expanded as a series of powers of $(r - r_e)$ in the neighborhood of the potential minimum. This treatment shows that the energy levels can be written in the form

$$E_{vJ} = \sum_{\ell,j} Y_{\ell j} \left(v + \frac{1}{2} \right)^\ell J^j (J+1)^j \quad (2.1)$$

where ℓ and j are summation indices, v and J are, respectively, vibrational and rotational quantum numbers, and $Y_{\ell j}$ are coefficients which depend on molecular constants. The effective potential function of the vibrating rotor may be written in the form

$$U = a_0 \xi^2 (i + a_1 \xi + a_2 \xi^2 + \dots) + B_e J(J+1) (1 - 2\xi + 3\xi^2 - 4\xi^3 + \dots) \quad (2.2)$$

where $\xi = (r - r_e)/r_e$, $B_e = h/8\pi^2 \mu r_e^2$. The term involving $B_e J(J+1)$ allows for the influence of the rotation on the effective potential.

Examination of the Harmonic Oscillator part of the potential energy, U , will give a value for a_0 .

$$\begin{aligned} U &= 1/2k(r - r_e)^2 = 2\pi^2 \mu \omega_e^2 (r - r_e)^2 = 2\pi^2 \mu \omega_e^2 \xi^2 r_e^2 \\ \text{if } B_e &\equiv \frac{h}{8\pi^2 \mu r_e^2} \quad \text{then } U = \frac{h\omega_e^2}{4B_e} \xi^2 \\ \therefore a_0 &= h \frac{\omega_e^2}{4B_e} \end{aligned}$$

Dunham¹ shows that the first 15 $Y_{\ell j}$'s are

$$\left. \begin{aligned} Y_{00} &= B_e/8(3a_2 - 7a_1^2/4) \\ Y_{10} &= \omega_e [1 + (B_e^2/4\omega_e^2)(25a_4 - 95a_1a_3/2 - 67a_2^2/4 \\ &\quad + 459a_1^2a_2/8 - 1155a_1^4/64)] \\ Y_{20} &= (B_e/2)[3(a_2 - 5a_1^2/4) + (B_e^2/2\omega_e^2)(245a_6 - 1365a_1a_5/2 \\ &\quad - 885a_2a_4/2 - 1085a_3^2/4 + 8535a_1^2a_4/8 + 1707a_2^3/8 \\ &\quad + 7335a_1a_2a_3/4 - 23,865a_1^3a_3/16 - 62,013a_1^2a_2^2/32 \\ &\quad + 239,985a_1^4a_2/128 - 209,055a_1^6/512)] \\ Y_{30} &= (B_e^2/2\omega_e)(10a_4 - 35a_1a_3 - 17a_2^2/2 + 225a_1^2a_2/4 \\ &\quad - 705a_1^4/32) \\ Y_{40} &= (5B_e^3/\omega_e^2)(7a_6/2 - 63a_1a_5/4 - 33a_2a_4/4 - 63a_3^2/8 \\ &\quad + 543a_1^2a_4/16 + 75a_2^3/16 + 483a_1a_2a_3/8 - 1953a_1^3a_3/32 \\ &\quad - 4989a_1^2a_2^2/64 + 23,265a_1^4a_2/256 - 23,151a_1^6/1024) \end{aligned} \right\} \quad (2.3)$$

$$\left. \begin{aligned}
Y_{01} &= B_e \{1 + (B_e^2/2\omega_e^2)[15 + 14a_1 - 9a_2 + 15a_3 - 23a_1a_2 \\
&\quad + 21(a_1^2 + a_1^3)/2]\} \\
Y_{11} &= (B_e^2/\omega_e) \{6(1 + a_1) + (B_e^2/\omega_e^2)[175 + 285a_1 - 335a_2/2 \\
&\quad + 190a_3 - 225a_4/2 + 175a_5 + 2295a_1^2/8 - 459a_1a_2 \\
&\quad + 1425a_1a_3/4 - 795a_1a_4/2 + 1005a_2^2/8 - 715a_2a_3/2 \\
&\quad + 1155a_1^3/4 - 9639a_1^2a_2/16 + 5145a_1^2a_3/8 \\
&\quad + 4677a_1a_2^2/8 - 14,259a_1^3a_2/16 \\
&\quad + 31,185(a_1^4 + a_1^5)/128]\} \\
Y_{21} &= (6B_e^3/\omega_e^2)[5 + 10a_1 - 3a_2 + 5a_3 - 13a_1a_2 \\
&\quad + 15(a_1^2 + a_1^3)/2] \\
Y_{31} &= (20B_e^4/\omega_e^3)[7 + 21a_1 - 17a_2/2 + 14a_3 - 9a_4/2 + 7a_5 \\
&\quad + 225a_1^2/8 - 45a_1a_2 + 105a_1a_3/4 - 51a_1a_4/2 + 51a_2^2/8 \\
&\quad - 45a_2a_3/2 + 141a_1^3/4 - 945a_1^2a_2/16 + 435a_1^2a_3/8 \\
&\quad + 411a_1a_2^2/8 - 1509a_1^3a_2/16 + 3807(a_1^4 + a_1^5)/128]
\end{aligned} \right\} \quad (2.4)$$

$$\left. \begin{aligned}
Y_{02} &= -(4B_e^3/\omega_e^2) \{1 + (B_e^2/2\omega_e^2)[163 + 199a_1 - 119a_2 + 90a_3 \\
&\quad - 45a_4 - 207a_1a_2 + 205a_1a_3/2 - 333a_1^2a_2/2 + 693a_1^2/4 \\
&\quad + 46a_2^2 + 126(a_1^3 + a_1^4/2)]\} \\
Y_{12} &= -(12B_e^4/\omega_e^3) \left(\frac{19}{2} + 9a_1 + 9a_1^2/2 - 4a_2 \right) \\
Y_{22} &= -(24B_e^5/\omega_e^4)[65 + 125a_1 - 61a_2 + 30a_3 - 15a_4 \\
&\quad + 495a_1^2/4 - 117a_1a_2 + 26a_2^2 + 95a_1a_3/2 - 207a_1^2a_2/2 \\
&\quad + 90(a_1^3 + a_1^4/2)]
\end{aligned} \right\} \quad (2.5)$$

$$\left. \begin{aligned}
Y_{03} &= 16B_e^5(3 + a_1)/\omega_e^4 \\
Y_{13} &= (12B_e^6/\omega_e^5)(233 + 279a_1 + 189a_1^2 + 63a_1^3 - 88a_1a_2 - 120a_2 + 80a_3/3) \\
Y_{04} &= (64B_e^7/\omega_e^6)(13 + 9a_1 - a_2 + 9a_1^2/4)
\end{aligned} \right\} \quad (2.6)$$

It should be noted that B_e is generally much smaller than ω_e . For most molecules the ratio B_e^2/ω_e^2 is of the order of 10^{-6} , although for light molecules such as H_2 it approaches more nearly to 10^{-5} . In such cases more terms are required in the expressions for the various coefficients.

If B_e/ω_e is small, the Y 's can be related to the ordinary band spectrum constants as follows:

$$\begin{array}{lll}
Y_{10} \approx \omega_e & Y_{20} \approx -\omega_e x_e & Y_{30} \approx \omega_e y_e \\
Y_{01} \approx B_e & Y_{11} \approx -\alpha_e & Y_{21} \approx \gamma_e \\
Y_{02} \approx -D_e & Y_{12} \approx -\beta_e & Y_{40} \approx \omega_e z_e \\
Y_{03} \approx H_e & &
\end{array} \quad (2.7)$$

where these symbols refer to the coefficients in the Bohr theory expansion for the molecular energy levels:

$$F_{v,J} = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 + \omega_e y_e \left(v + \frac{1}{2} \right)^3 + \omega_e z_e \left(v + \frac{1}{2} \right)^4 + B_v J(J+1) - D_e J^2(J+1)^2 + H_e J^3(J+1)^3 + \dots \quad (2.8)$$

where $B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right) + \gamma_e \left(v + \frac{1}{2} \right)^2 \dots$ (*cf.*², p. 92, pp. 107-108).

Sandeman³ has extended Dunham's treatment to include other terms of the same order of magnitude which involve higher powers of the vibrational quantum number.

For the special case of the Morse potential function, Dunham shows that all the $Y_{\ell 0}$'s except Y_{10} and Y_{20} vanish and all but the first terms in the expressions for Y_{10} and Y_{20} are zero. Because of the simplicity of the expressions obtained with the Morse function, and because it does give a quite good fit to the actual potential in the region of $r = r_e$, the Morse function has been widely used.

Several important relationships between constants have been derived for Morse potential functions. These are often useful for estimating otherwise unknown parameters.

The Kratzer relation $D_e = \frac{4B_e^3}{\omega_e^2}$.

The Pekeris relation

$$\alpha_e = \frac{6}{\omega_e} \left[(\omega_3 x_e B_e^3)^{1/2} - B_e^2 \right]$$

The constant Y_{00} is exactly zero for Harmonic and Morse oscillators, but an approximate value for general oscillators is

$$Y_{00} = \frac{B_e - \omega_e x_e}{4} + \frac{\alpha_e \omega_e}{12B_e} + \left(\frac{\alpha_e \omega_e}{12B_e} \right)^2 \frac{1}{B_e}.$$

3. References

1. J. L. Dunham, *Phys. Rev.* **41**, 721 (1932). Also see *ibid* page 713.
2. G. Herzberg, Spectra of Diatomic Molecules, D. Van Nostrand, New York (1950).
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