Applied Spectroscopy
Reexamination
01-05-2014

Problem 1

a. Without taking into consideration parity and spin determine the possible molecular terms for a molecule obtained by combining two different atoms in the states P and D.

b. Determine the possible terms for the molecule Cl_2 which can be obtained by combining two Cl atoms in the state ^2P.

c. Find possible molecular terms which can be derived from the electron configuration $(1s\sigma)^2(2s\sigma)^2(2p\pi)^3$.

Problem 2

a. CO_2 molecule has a linear structure with C atom in the center. The distance between C and O is 1 nm. Find the dipole moment of CO_2 molecule.

b. A diatomic molecule with the distance R between nuclei of charges Z_1e and Z_2e has a total dipole moment D. Find the position of origin of the frame of reference where the mean electron dipole moment is $D/2$.

c. When in a diatomic molecule nuclei with masses m_1 and m_2 are replaced by their isotopes with masses m_1' and m_2', respectively, how much will change the vibrational frequency?

Problem 3

A ground electron term of CaO molecule is approximated by the potential $U(R) = E_b\left(1 - e^{-a(R-b)}\right)^2$, where $E_b = 3.5 \times 10^4\,\mathrm{cm}^{-1}$, $a = 10\,\mathrm{nm}^{-1}$ and $b = 1.5\,\mathrm{nm}$. The atomic weights of Ca and O are 40 g/mol and 16 g/mol,respectively.

a. Find the distance R_e where the potential has a minimum and calculate the magnitude of the potential energy at R_e.

b. Find the frequency ω_0 of small vibrations around the equilibrium distance R_e.

c. Find the bond energy and dissociation energy for the ground electron state of CaO molecule.

Problem 4

The ground state of BeO molecule has the rotational constant $B_e = 1.651\,\mathrm{cm}^{-1}$ and the vibrational frequency $\omega_e = 1487.0\,\mathrm{cm}^{-1}$. The electron excited state $A^1\Pi$ has the rotational constant $B_e = 1.366\,\mathrm{cm}^{-1}$ and the vibrational frequency $\omega_e = 1144\,\mathrm{cm}^{-1}$. Difference between minima of the potential curves $A^1\Pi$ and $X^1\Sigma$ is $9405.5\,\mathrm{cm}^{-1}$. The absorption vibration band $X^1\Sigma(v'' = 0) \rightarrow B^1\Pi(v' = 0)$ is considered. Using the approximation of harmonic oscillator and rigid rotator find for this vibrational band:

a. The maximal wavenumber in the P-branch.

b. The maximal wavenumber in the Q-branch.

c. The maximal wavenumber in the R-branch.

1 Introduction

Electron mass	$m_e = 9.109\,39 \times 10^{-28}\,\mathrm{g}$
Proton mass	$m_p = 1.672\,62 \times 10^{-24}\,\mathrm{g}$
Atomic unit of mass	$m_a = \frac{1}{12}m(^{12}\mathrm{C}) = 1.660\,54 \times 10^{-24}\,\mathrm{g}$
Planck constant	$h = 6.626\,19 \times 10^{-27}\,\mathrm{erg\,cm}$
	$\hbar = 1.054\,57 \times 10^{-27}\,\mathrm{erg\,cm}$
Light velocity	$c = 2.997\,92 \times 10^{10}\,\mathrm{cm/s}$
Electron charge	$e = 1.602\,19 \times 10^{-19}\,\mathrm{C}$
Avogadro number	$N_A = 6.022\,14 \times 10^{23}\,\mathrm{mol}^{-1}$
Molar volume	$V_m = 22.414\,\mathrm{l/mol}$
Universal gas constant	$R = 8.314 \times 10^{7}\,\mathrm{erg/mol\,K}$
Boltzmann constant	$k = R/N_A = 1.3807 \times 10^{-16}\,\mathrm{erg/K}$

2 Adiabatic Approximation and the Concept of Molecular Potentials

$$\hat{H}\Psi = E\Psi, \tag{2.1}$$

$$\hat{H} = \hat{T} + \hat{V} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\nabla_i^2 - \frac{\hbar^2}{2}\sum_{k=1}^{K}\frac{1}{M_k}\nabla_k^2 + V(\mathbf{r},\mathbf{R}) \tag{2.2}$$

$$\begin{aligned} V(\mathbf{r},\mathbf{R}) &= V_{nuc,nuc} + V_{nuc,el} + V_{el,el} \\ &= \frac{e^2}{4\pi\epsilon_0}\left[\sum_{k>k'}\sum_{k'=1}\frac{Z_k Z_{k'}}{R_{k,k'}} - \sum_{k=1}\sum_{i=1}\frac{Z_k}{r_{i,k}} + \sum_{i>i'}\sum_{i'=1}\frac{1}{r'_{i,i'}}\right] \end{aligned} \tag{2.3}$$

$$\left(-\frac{\hbar^2}{2m}\sum_{i=1}^{N}\boldsymbol{\nabla}_i^2 - \frac{\hbar^2}{2}\sum_{k=1}^{K}\frac{1}{M_k}\boldsymbol{\nabla}_k^2 + V(\mathbf{r},\mathbf{R})\right)\Psi(\mathbf{r},\mathbf{R}) = E\Psi(\mathbf{r},\mathbf{R}) \tag{2.4}$$

$$\hat{H}_0\phi^{el}(\mathbf{r},\mathbf{R}) = E^{(0)}(\mathbf{R})\phi^{el}(\mathbf{r},\mathbf{R}) \tag{2.5}$$

$$\hat{c}_{nm} = \int \phi_n^*\hat{H}'\phi_m \mathrm{d}r - \frac{\hbar^2}{2}\left[\int \phi_n^*\sum_k\frac{1}{M_k}\frac{\partial}{\partial R_k}\phi_m\,\mathrm{d}r\right]\frac{\partial}{\partial R_k} \tag{2.6}$$

$$\begin{aligned} \hat{H}_0\phi(\mathbf{r},\mathbf{R}) &= E^{(0)}(\mathbf{R})\phi(\mathbf{r},\mathbf{R}) && (a) \\ \hat{H}'\chi_n(\mathbf{R}) + \sum_m \hat{c}_{nm}\chi_m(\mathbf{R}) &= \left(E - E_n^{(0)}(\mathbf{R})\right)\chi_n(\mathbf{R}) && (b) \end{aligned} \tag{2.7}$$

$$\left[\hat{H}' + E_n^{(0)}(\mathbf{R})\right]\chi_n(\mathbf{R}) = E\chi_n(\mathbf{R}). \tag{2.8}$$

$$\begin{aligned} \hat{H}_0\phi_n^{el}(\mathbf{r},\mathbf{R}) &= E_n^{(0)}\phi_n^{el}(\mathbf{r},\mathbf{R}) && \text{(a)} \\ \left(\hat{T}_{nuc} + E_n^{(0)}\right)\chi_{n,i}(\mathbf{R}) &= E_{n,i}\chi_{n,i}(\mathbf{R}) && \text{(b)} \end{aligned} \tag{2.9}$$

$$\hat{c}_{nn} = \int \phi_n^{el*}\hat{H}'\phi_n^{el}\,\mathrm{d}r = \sum_N\frac{\hbar^2}{2M_N}\int\left(\frac{\partial\phi_n^{el}}{\partial\mathbf{R}_N}\right)^2\mathrm{d}r \tag{2.10}$$

$$\left[\hat{H}' + U_n'(\mathbf{R})\right]\chi_n = E\chi_n \tag{2.11}$$

$$U_n'(\mathbf{R}) = E_n^{(0)}(\mathbf{R}) + \sum_N \frac{\hbar^2}{2M_N}\int\left(\frac{\partial\phi_n^{el}}{\partial\mathbf{R}_N}\right)^2 \mathrm{d}\mathbf{r} \tag{2.12}$$

$$E_m = E_m^{(0)} + H'_{mm} + \sum_{n\neq m}\frac{H'_{mn}H'_{nm}}{E_m^{(0)} - E_n^{(0)}} \tag{2.13}$$

$$E_b = E_n^{el}(\infty) - E_n^{el}(R_e) \tag{2.14}$$

$$\hat{l}_z = -i\hbar\frac{\partial}{\partial\phi} \tag{2.15}$$

$$\begin{aligned}\Lambda = |M_L|, \quad \Lambda = 0, 1, \ldots, L\\ \Sigma = M_S = S, S-1, \ldots, -S\end{aligned} \tag{2.16}$$

$$\Omega = \Lambda + \Sigma. \tag{2.17}$$

$$T_{el}^{\Lambda,\Sigma} = T_0 + A\Lambda\Sigma. \tag{2.18}$$

$$^{2S+1}\Lambda_\Omega \tag{2.19}$$

$$L_B\,\Sigma^+ \text{ terms and } L_B\,\Sigma^- \text{ terms} \tag{2.20}$$

$$\begin{aligned}\Sigma^+ \quad \text{if} \quad (-1)^{L_A+L_B}P_AP_B = +1\\ \Sigma^- \quad \text{if} \quad (-1)^{L_A+L_B}P_AP_B = -1\end{aligned} \tag{2.21}$$

$$\begin{aligned}N_g &= N_u \quad \text{if} \quad \Lambda \text{ is odd}\\ N_g &= N_u + 1 \quad \text{if} \quad \Lambda \text{ is even and } S \text{ is even } (S = 0, 2, 4, \ldots)\\ N_u &= N_g + 1 \quad \text{if} \quad \Lambda \text{ is even and } S \text{ is odd } (S = 1, 3, \ldots)\end{aligned} \tag{2.22}$$

$$\begin{aligned}N_g^+ &= N_u^- + 1 = L + 1 \quad \text{if} \quad S \text{ is even } (S = 0, 2, 4, \ldots)\\ N_u^+ &= N_g^- + 1 = L + 1 \quad \text{if} \quad S \text{ is odd } (S = 1, 3, \ldots)\\ &\text{where } L_1 = L_2 = L\end{aligned} \tag{2.23}$$

$$\begin{aligned}&c_1(H_{11} - ES_{11}) &&+c_2(H_{12} - ES_{12}) + \cdots + c_m(H_{1m} - ES_{1m}) &&= 0\\ &c_2(H_{21} - ES_{21}) &&+c_2(H_{22} - ES_{22}) + \cdots + c_m(H_{2m} - ES_{2m}) &&= 0\\ &\vdots\\ &c_m(H_{m1} - ES_{m1}) &&+c_m(H_{22} - ES_{m2}) + \cdots + c_m(H_{mm} - ES_{mm}) &&= 0\end{aligned} \tag{2.24}$$

$$E_1(R) = \frac{H_{AA} + H_{AB}}{1 + S_{AB}}, \quad E_2(R) = \frac{H_{AA} - H_{AB}}{1 - S_{AB}} \tag{2.25}$$

$$\phi_+ = \frac{\phi_A + \phi_B}{\sqrt{2 + 2S_{AB}}}, \quad \phi_- = \frac{\phi_A - \phi_B}{\sqrt{2 - 2S_{AB}}} \tag{2.26}$$

$$\Phi(1,2,\ldots,N) = \begin{vmatrix} \phi_1(1)\chi_1(1) & \phi_1(2)\chi_1(2) & \ldots & \phi_1(N)\chi_1(N) \\ \phi_2(1)\chi_2(1) & \phi_2(2)\chi_2(2) & \ldots & \phi_2(N)\chi_2(N) \\ \vdots & & & \vdots \\ \phi_N(1)\chi_N(1) & \phi_N(2)\chi_N(2) & \ldots & \phi_N(N)\chi_N(N) \end{vmatrix} \tag{2.27}$$

$$\phi(1,2) = \frac{1}{\sqrt{2}} \begin{vmatrix} \phi_1(1)\alpha(1) & \phi_1(2)\alpha(2) \\ \phi_1(1)\beta(1) & \phi_1(2)\beta(2) \end{vmatrix} = \phi_1(1)\phi_1(2)\frac{\alpha(1)\beta(2)-\alpha(2)\beta(1))}{\sqrt{2}} \tag{2.28}$$

$$\begin{aligned} \phi =& \phi_1(1)\phi_1(2) = \frac{1}{2+2S}\times \\ & [\phi_A(1)\phi_A(2)+\phi_B(1)\phi_B(2)+\phi_A(1)\phi_B(2)+\phi_A(2)\phi_B(1)] \end{aligned} \tag{2.29}$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \tfrac{e^2}{4\pi\epsilon_0}\left(\tfrac{1}{r_{12}} - \tfrac{1}{R}\right) \tag{2.30}$$

$$\langle E\rangle = \langle\phi|\hat{H}|\phi\rangle = \langle\phi|\hat{H}_1|\phi\rangle + \langle\phi|\hat{H}_2|\phi\rangle + \frac{e^2}{4\pi\epsilon_0}\left\langle\phi\left|\frac{1}{r_{12}} - \frac{1}{R}\right|\phi\right\rangle \tag{2.31}$$

$$\begin{aligned} \hat{H} =& \left(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{e^2}{4\pi\epsilon_0 r_{A_1}}\right) + \left(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_{A_2}}\right) \\ &+ \frac{e^2}{4\pi\epsilon_0}\left[-\frac{1}{r_{A_2}} - \frac{1}{r_{B_1}} + \frac{1}{r_{12}} + \frac{1}{R}\right] = H_A + H_B - H_{AB} = 2H_A - H_{AB} \end{aligned} \tag{2.32}$$

$$\begin{aligned} \phi_+ =& \frac{1}{\sqrt{2(1+S^2)}}[\phi_A(1)\phi_B(2)+\phi_A(2)\phi_B(1)] \\ \phi_- =& \frac{1}{\sqrt{2(1+S^2)}}[\phi_A(1)\phi_B(2)-\phi_A(2)\phi_B(1)] \end{aligned} \tag{2.33}$$

3 Rotation, Vibration, and Potential Curves of Diatomic Molecules

$$\left[-\frac{\hbar^2}{2M_1}\nabla_1^2 - \frac{\hbar^2}{2M_2}\nabla_2^2 + E_n^0(R)\right]\chi_{nm}(\mathbf{R}_1,\mathbf{R}_2) = E_n\chi_{nm}(\mathbf{R}_1,\mathbf{R}_2) \tag{3.1}$$

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2 + E_n^0(R)\right]\chi_{nm}(\mathbf{R}) = E_n\chi_{nm}(\mathbf{R}), \tag{3.2}$$

$$\chi(R,\theta,\phi) = S(R)Y(\theta,\phi) \tag{3.3}$$

$$\begin{aligned} \frac{1}{R^2}\frac{\mathrm{d}}{\mathrm{d}R}\left(R^2\frac{\mathrm{d}S}{\mathrm{d}R}\right) + \frac{2\mu}{\hbar^2}\left[E - E_n^0(R) - \frac{C\hbar^2}{2\mu R^2}\right]S = 0 \quad (a) \\ \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} + CY = 0 \quad (b) \end{aligned} \tag{3.4}$$

$$E_{rot}(J) = \frac{J(J+1)\hbar^2}{2\mu R_e^2} \tag{3.5}$$

$$F(J) = B_e J(J+1) \tag{3.6}$$

$$B_e = \frac{\hbar}{4\pi c\mu R_e^2} \tag{3.7}$$

$$\tilde{\nu}_{rot} = F(J+1) - F(J) = 2B_e(J+1) \tag{3.8}$$

$$F_{rot} = B_e J(J+1) - D_e J^2(J+1)^2 + H_e J_e^3(J+1)^3 + \dots \tag{3.9}$$

$$\begin{aligned} D_e &= \frac{\hbar^3}{4\pi k c\mu^2 R_e^6} \\ H_e &= \frac{3\hbar^5}{4\pi k^2 c\mu^3 R_e^{10}} \end{aligned} \tag{3.10}$$

$$F(J,\Lambda) = B_e\left[J(J+1) - \Lambda^2\right] - D_e J^2(J+1)^2 + H_e J^3(J+1)^3 \tag{3.11}$$

$$\frac{\mathrm{d}^2 U}{\mathrm{d}R^2} + \frac{2\mu}{\hbar^2}\left[E - E_n^0(R)\right]U = 0 \tag{3.12}$$

$$E_{pot}(R) = \frac{1}{2}k_r(R-R_e)^2 = \frac{1}{2}k_r r^2 \tag{3.13}$$

$$\frac{\mathrm{d}^2 H}{\mathrm{d}\xi^2} - 2\xi\frac{\mathrm{d}H}{\mathrm{d}\xi} + \left(\frac{\alpha}{\beta} - 1\right)H = 0 \tag{3.14}$$

$$E_v = \hbar\omega_0\left(v + \frac{1}{2}\right) \quad \text{with} \quad \omega_0 = \sqrt{\frac{k_r}{\mu}} \tag{3.15}$$

$$G_v = \omega_e\left(v + \frac{1}{2}\right) \tag{3.16}$$

$$H_v(\xi) = (-1)^n e^{\xi^2}\frac{\mathrm{d}^v}{\mathrm{d}\xi^v}\left(e^{-\xi^2}\right) \tag{3.17}$$

$$\psi_{vib} = \sqrt{\frac{1}{\sqrt{\pi}v!2^v}}H_n(\xi)\exp(-\xi^2/2) \tag{3.18}$$

$$E_p(R) = E_b\left[1 - e^{-a(R-R_e)}\right]^2 \tag{3.19}$$

$$E_v = \hbar\omega_0\left(v + \frac{1}{2}\right) - \frac{\hbar^2\omega_0^2}{4E_b}\left(v + \frac{1}{2}\right)^2 \text{ where } \omega_0 = a\sqrt{2E_b/\mu} \tag{3.20}$$

$$\begin{aligned} T_v &= \omega_e\left(v + \frac{1}{2}\right) - \omega_e x_e\left(v + \frac{1}{2}\right)^2 \\ \omega_e &= \omega_0/2\pi c \quad \text{and} \quad \omega_e x_e = \hbar^2\omega_0^2/8\pi c E_b = hc\omega_e^2/4E_b \end{aligned} \tag{3.21}$$

$$\begin{aligned} G(v) = \omega_e&\left(v + \frac{1}{2}\right) + \omega_e x_e\left(v + \frac{1}{2}\right)^2 \\ &+ \omega_e y_e\left(v + \frac{1}{2}\right)^3 + \omega_e z_e\left(v + \frac{1}{2}\right)^4 + \dots \end{aligned} \tag{3.22}$$

$$E_{p,eff}(R,J) = E_p(R) + \frac{J(J+1)\hbar^2}{2\mu R^2} \tag{3.23}$$

$$B_v = \frac{\hbar}{4\pi\mu c}\int \psi_{vib}\frac{1}{R^2}\psi_{vib}\,\mathrm{d}R\,. \tag{3.24}$$

$$\begin{aligned} T(v,J) &= G(v) + F(v,J) \\ &= \omega\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2 + B_v J(J+1) - D_v J^2(J+1)^2 \end{aligned} \tag{3.25}$$

$$\begin{aligned} B_v &= B_e - \alpha_e\left(v+\frac{1}{2}\right) \quad \text{with } B_e = \frac{\hbar}{4\pi c\mu R_e^2} \quad \text{and} \quad \alpha_e = \frac{3\hbar^2\omega_e}{4\mu R_e^2 E_b}\left(\frac{1}{aR_e} - \frac{1}{a^2R_e^2}\right) \\ D_v &= D_e + \beta_e\left(v+\frac{1}{2}\right) \quad \text{with } \beta_e = D_e\left(\frac{8\omega_e x_e}{\omega_e} - \frac{5\alpha_e}{\omega_e} - \frac{\alpha_e^2\omega_e}{24B_e^3}\right) \end{aligned} \tag{3.26}$$

$$\omega_e = \frac{a}{2\pi c}\sqrt{\frac{2E_b}{\mu}};\quad \omega_e x_e = \frac{hc\omega_e^2}{4E_d} = \frac{ha^2}{8\pi^2\mu c} \tag{3.27}$$

$$D_e = \frac{4B_e^3}{\omega_e^2} \tag{3.28}$$

$$B_v = B_e - \alpha_e\left(v+\frac{1}{2}\right) + \gamma_e\left(v+\frac{1}{2}\right)^2 + \ldots \tag{3.29}$$

$$D_v = D_e + \beta_e\left(v+\frac{1}{2}\right) + \delta_e\left(v+\frac{1}{2}\right)^2 + \ldots \tag{3.30}$$

$$\begin{aligned} T(v,J) = {}&\omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2 + \omega_e y_e\left(v+\frac{1}{2}\right)^3 + \omega_e z_e\left(v+\frac{1}{2}\right)^4 + \ldots \\ &+ B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 \ldots \end{aligned} \tag{3.31}$$

$$T(v,J) = \sum_i\sum_k Y_{ik}\left(v+\frac{1}{2}\right)^i [J(J+1)]^k \quad \text{Dunham expansion} \tag{3.32}$$

$$\begin{matrix} Y_{10}\approx\omega_e; & Y_{01}\approx B_e; & Y_{11}\approx -\alpha_e \\ Y_{20}\approx -\omega_e x_e; & Y_{02}\approx D_e; & Y_{12}\approx \beta_e \\ Y_{30}\approx \omega_e y_e; & Y_{03}\approx H_e; & Y_{21}\approx \gamma_e \end{matrix} \tag{3.33}$$

$$\frac{\mathrm{d}^2\Psi}{\mathrm{d}R^2} + k^2\Psi = 0 \tag{3.34}$$

$$\Psi(R) = \frac{C}{\sqrt{p(R)}}\exp\left[\pm\frac{i}{\hbar}\int p(R)\,\mathrm{d}R\right] \tag{3.35}$$

$$\Psi(R) = \frac{C}{\sqrt{|p(R)|}}\exp\left[\pm\frac{1}{\hbar}\int |p(R)|\,\mathrm{d}R\right] \tag{3.36}$$

$$\frac{1}{2\pi\hbar}\oint p(R)\,\mathrm{d}R = v + \frac{1}{2} \tag{3.37}$$

$$\oint \sqrt{2\mu(E - V_{eff}(R))}\,\mathrm{d}R = \left(v+\frac{1}{2}\right)h \tag{3.38}$$

$$
\begin{aligned}
V_{pot}(\mathbf{R},\mathbf{r}) &= \frac{1}{4\pi\epsilon_0}\sum_i \frac{q_i}{|\mathbf{R}-\mathbf{r}_i|} \\
&= \frac{1}{4\pi\epsilon_0 R}\sum_i q_i\left[1+\frac{r_i}{R}\cos\theta_i+\frac{1}{2}\frac{r_i^2}{R^2}(3\cos^2\theta_i-1)+\dots\right] \\
&= \frac{q}{4\pi\epsilon_0 R}+\frac{\mathbf{pR}}{4\pi\epsilon_0 R^3}+\frac{\sum_{\alpha,\beta}Q_{\alpha\beta}X_\alpha X_\beta}{4\pi\epsilon_0 R^5}+\dots
\end{aligned}
\tag{3.39}
$$

$$
\begin{aligned}
q &= \sum_i q_i && \text{is the total charge,} \\
\mathbf{p} &= \sum_i q_i \mathbf{r_i} && \text{is the total dipole moment,} \\
Q_{\alpha\beta} &= \frac{1}{2}\sum_i q_i\left[3x_{i\alpha}x_{i\beta}-r_i^2\delta_{\alpha\beta}\right] && \text{is the quadrupole momentum tensor}
\end{aligned}
\tag{3.40}
$$

$$
E_{pot}(R) = \frac{\langle q\rangle}{4\pi\epsilon_0 R}+\frac{\langle \mathbf{p}\rangle\,\mathbf{R}}{4\pi\epsilon_0 R^3}+\frac{\langle Q_{\alpha\beta}\rangle\,X_\alpha X_\beta}{4\pi\epsilon_0 R^5}+\dots \tag{3.41}
$$

$$
E_0 = \hbar\omega_0-\frac{\hbar\lambda^2}{8m^2\omega_0^3} = \hbar\omega_0-\frac{\hbar e^4}{8m^2\omega_0^3(4\pi\epsilon_0)^2R^6} \tag{3.42}
$$

$$
E_{pot}(R) = \frac{a}{R^{12}}-\frac{b}{R^6} \tag{3.43}
$$

$$
E_{pot}(R) = E_b\left(\left(\frac{R_e}{R}\right)^{12}-2\left(\frac{R_e}{R}\right)^{6}\right) \tag{3.44}
$$

4 Spectra of Diatomic Molecules

$$
\begin{aligned}
B_{mk} &= \frac{g_k}{g_m}B_{km} \\
A_{km} &= \frac{8\pi h\nu^3}{c^3}B_{km}
\end{aligned}
\tag{4.1}
$$

$$
\int \alpha(\nu)\,\mathrm{d}\nu = \left(N_m-\frac{g_k}{g_i}N_k\right)B_{mk}\frac{h\nu}{c} \tag{4.2}
$$

$$
\overline{P} = \frac{1}{3}\frac{d_0^2\omega^4}{4\pi\epsilon_0 c^3} \tag{4.3}
$$

$$
\mathbf{D}_{mk} = e\int \psi_m^*\mathbf{r}\psi_k\,\mathrm{d}\tau \tag{4.4}
$$

$$
\langle P_{mk}\rangle = \frac{1}{3}\frac{\omega_{mk}^4}{\pi\epsilon_0 c^3}|\mathbf{D}_{mk}|^2, \tag{4.5}
$$

$$
A_{mk} = \frac{2}{3}\frac{e^2\omega_{mk}^3}{\epsilon_0 c^3 h}\left|\int \psi_m^*\mathbf{r}\psi_k\,\mathrm{d}\tau\right|^2. \tag{4.6}
$$

$$\left(\frac{\mathrm{d}W_{mk}}{\mathrm{d}t}\right)_{abs} = \frac{2\pi}{\hbar^2}|\langle m|\mathbf{E}_0\cdot\mathbf{D}|k\rangle|^2 \tag{4.7}$$

$$\begin{aligned}\mathbf{D}_{mk} &= \int \phi_m^*\chi_m^*(\mathbf{d}_{el}+\mathbf{d}_{nuc})\phi_k\chi_k\,\mathrm{d}\tau_{el}\,\mathrm{d}\tau_{nuc}\\ &= \int \chi_m^*\left[\int \phi_m^*\mathbf{d}_{el}\phi_k\,\mathrm{d}\tau_{el}\right]\chi_k\,\mathrm{d}\tau_{nuc}\\ &+ \int \chi_m^*\mathbf{d}_{nuc}\left[\int \phi_m^*\phi_k\,\mathrm{d}\tau_{el}\right]\chi_k\,\mathrm{d}\tau_{nuc}\end{aligned} \tag{4.8}$$

$$\begin{aligned}\mathbf{D}_{mk} &= \int \chi_m^*\mathbf{D}(\mathbf{R})\chi_k\,\mathrm{d}\tau_{nuc}\\ \text{where } \mathbf{D}(\mathbf{R}) &= \int (\psi_m^*\mathbf{d_{el}}+\mathbf{d_{nuc}})\psi_k\,\mathrm{d}\tau_{el}\end{aligned} \tag{4.9}$$

$$\begin{aligned}\mathbf{D}_{mk} &= \int \chi_m^*\mathbf{D}_{mk}^{el}\chi_k\,\mathrm{d}\tau_{nuc}\\ \text{where } \mathbf{D}_{mk}^{el}(\mathbf{R}) &= \int \phi_m^*\mathbf{d}_{el}\phi_k\,\mathrm{d}\tau_{el}\end{aligned} \tag{4.10}$$

$$\left(\frac{\mathrm{d}W_{mk}}{\mathrm{d}t}\right)_{abs} = \frac{2\pi e^2}{\hbar^2}\left|\int \chi_m^* d(R)\mathbf{E}_0\cdot\hat{\mathbf{R}}_0\chi_k\,\mathrm{d}\tau_{nuc}\right| \tag{4.11}$$

$$\mathbf{D}_{mk} = \int \psi_m^{vib}d(R)\psi_k^{vib}\,\mathrm{d}R\int_{\theta,\varphi}\psi_m^{rot}\hat{\mathbf{R}}_0\psi_k^{rot}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi \tag{4.12}$$

$$\begin{aligned}D_{mk}^{vib} &= d(R_e)\int(\psi_m^{vib})^*\psi_k^{vib}\,\mathrm{d}R\\ &+ \left.\frac{\mathrm{d}D}{\mathrm{d}R}\right|_{R_e}\int(\psi_m^{vib})^*(R-R_e)\psi_k^{vib}\,\mathrm{d}R+\dots\end{aligned} \tag{4.13}$$

$$\begin{aligned}&\mathbf{D}_{mk}(J'',M'',J',M')\\ &= D(R_e)C_{J''M''}C_{J'M'}\int_\theta\int_\varphi P_{J''}^{M''}P_{J'}^{M'}\hat{\mathbf{R}}_0e^{i(M''-M')\varphi}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi\end{aligned} \tag{4.14}$$

$$\left[\frac{\mathrm{d}W_{J,M\to J+1,M}}{\mathrm{d}t}\right]_{lin} = \frac{2\pi E_0^2}{\hbar^2}D^2(R_e)\frac{(J+1)^2-M^2}{(2J+1)(2J+3)} \tag{4.15}$$

$$\left(\frac{\mathrm{d}W_{J\to J+1}}{\mathrm{d}t}\right)_{lin} = \frac{2\pi E_0^2}{3\hbar}D^2(R_e)\frac{J+1}{2J+1} \tag{4.16}$$

$$\left[\frac{\mathrm{d}W_{J,M,J+1,M\pm1}}{\mathrm{d}t}\right]_{circ} = \frac{\pi E_0^2}{\hbar^2}D^2(R_e)\frac{(J\pm M+1)(J\pm M+2)}{(2J+1)(2J+3)} \tag{4.17}$$

$$\left(\frac{\mathrm{d}W_{mk}}{\mathrm{d}t}\right)_t = \frac{2\pi}{\hbar^2}\overline{E_{0z}^2}D^2(R_e)\frac{J+1}{2J+1}, \tag{4.18}$$

$$\tilde{\nu}_R = \tilde{\nu}_0 + 2B_v' + (3B_v' - B_v'')J + (B_v' - B_v'')J^2, \tag{4.19}$$

$$\tilde{\nu}_P = \tilde{\nu}_0 - (B_v' + B_v'')J + (B_v' - B_v'')J^2, \tag{4.20}$$

$$\mathbf{D}_{mk} = \int \psi_{vib}(v'')D_{mk}^{el}\psi_{vib}(v')\,\mathrm{d}R\iint \mathbf{R}_0Y_{J''}^{M''}Y_{J'}^{M'}\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\varphi \tag{4.21}$$

$$q_{v'',v'} = \left| \int \psi_{vib}(v'')\psi_{vib}(v')\,\mathrm{d}\mathbf{R} \right|^2 \tag{4.22}$$

$$\frac{\mathrm{d}}{\mathrm{d}t}(W^{el}_{km}) \propto \left|\mathbf{D}^{el}_{mk}\right|^2 q_{v''v'} S_{J''J'}. \tag{4.23}$$

$$\frac{\mathrm{d}W^{abs}_{mk}}{\mathrm{d}t} \propto \left|D^{el}_{mk}\right|^2 q_{v''v'} S_{J''J'} |\hat{\mathbf{r}}_0 \cdot \mathbf{E}_0|^2, \tag{4.24}$$

$$\langle R^n \rangle_{v''v'} = \frac{\int \psi_{v''} R^n \psi_{v'}\,\mathrm{d}R}{\int \psi_{v''}\psi_{v'}\,\mathrm{d}R} \tag{4.25}$$

$$S_{v''v'} = \left|D^{el}_{mk}(R_{v''v'})\right|^2 q_{v''v'} \tag{4.26}$$

$$\begin{aligned} \tilde{\nu} &= \left[T'_{el} - T''_{el}\right] + \left[G(v') - G(v'')\right] + \left[F(J') - F(J'')\right] \\ &= \tilde{\nu}_0 + \left[B'_v J'(J'+1) - D'_v J'^2 (J'+1)^2\right] \\ &- \left[B''_v J''(J''+1) - D''_v J''^2 (J''+1)^2\right] \end{aligned} \tag{4.27}$$

$$\begin{aligned} &\Delta J = 0, \pm 1; \quad 0 \not\leftrightarrow 0 \\ &\Sigma^+ \not\leftrightarrow \Sigma^-; \quad u \leftrightarrow g \end{aligned} \tag{4.28}$$

$$\tilde{\nu}_R(J) = \tilde{\nu}_0 + (B'_v - B''_v)J(J+1) + 2B'_v(J+1), \tag{4.29}$$

$$\tilde{\nu}_P(J) = \tilde{\nu}_0 + (B'_v - B''_v)J(J+1) - 2B'_v J, \tag{4.30}$$

$$\tilde{\nu}_Q(J) = \tilde{\nu}_0 + (B'_v - B''_v)J(J+1), \tag{4.31}$$

$$\begin{aligned}
\Delta\Lambda = 0 \quad & S_R(J'') = \frac{(J''+1+\Lambda'')(J''+1-\Lambda'')}{J''+1} \\
& S_P(J'') = \frac{(J''+\Lambda'')(J''-\Lambda'')}{J''} \\
& S_Q(J'') = \frac{(2J''+1)\Lambda''^2}{J''(J''+1)} \\
\Delta\Lambda = 1 \quad & S_R(J'') = \frac{(J''+2+\Lambda'')(J''+1+\Lambda'')}{4(J''+1)} \\
& S_P(J'') = \frac{(J''-1-\Lambda'')(J''-\Lambda'')}{4J''} \\
& S_Q(J'') = \frac{(J''+1+\Lambda'')(J''-\Lambda')(2J''+1)}{4J''(J''+1)} \\
\Delta\Lambda = -1 \quad & S_R(J'') = \frac{(J''+2-\Lambda'')(J''+1-\Lambda'')}{4(J''+1)} \\
& S_P(J'') = \frac{(J''-1+\Lambda'')(J''+\Lambda'')}{4J''} \\
& S_Q(J'') = \frac{(J''+1-\Lambda'')(J''+\Lambda'')(2J''+1)}{4J''(J''+1)}
\end{aligned} \tag{4.32}$$

$$I(\omega) = \frac{I_0 \frac{\gamma}{2\pi}}{(\omega-\omega_0)^2 + \left(\frac{\gamma}{2}\right)^2} \tag{4.33}$$

$$\delta\omega_n = \gamma \quad ; \quad \delta\nu_n = \frac{\gamma}{2\pi} \tag{4.34}$$

$$\delta\nu_D = \frac{2\nu_0}{c}\sqrt{\frac{2RT\ln 2}{M}} = 7.16\times 10^{-7}\nu_0\sqrt{\frac{T}{M}} \tag{4.35}$$

$$I(\omega) = I(\omega_0)exp\left[-\left(\frac{\omega-\omega_0}{0.6\delta\omega_D}\right)^2\right] \tag{4.36}$$

$$S_{ik} = N_B\sigma_{ik}\sqrt{\frac{8kT}{\pi\mu}} \tag{4.37}$$

$$I(\omega) = I_0\frac{[(\gamma+\gamma_{inel})/2+N\overline{v}\sigma_b]^2}{(\omega-\omega-N\overline{v}\sigma_s)^2+[(\gamma+\gamma_{inel})/2+N\overline{v}\sigma_b]^2} \tag{4.38}$$

$$\begin{aligned} W_{if} \sim & \frac{\gamma_{if}I_1I_2}{[\omega_{if}-\omega_1-\omega_2-\mathbf{v}\cdot(\mathbf{k}_1+\mathbf{k}_2)]^2+(\gamma_{if}/2)^2} \\ \times & \left|\sum_k \frac{(\mathbf{R}_{ik}\cdot\hat{\mathbf{e}}_1)(\mathbf{R}_{kf}\cdot\hat{\mathbf{e}}_2)}{\omega_{ik}-\omega_1-\mathbf{k}_1\mathbf{v}}+\frac{(\mathbf{R}_{ik}\cdot\hat{\mathbf{e}}_2)(\mathbf{R}_{kf}\cdot\hat{\mathbf{e}}_1)}{\omega_{ik}-\omega_2-\mathbf{k}_2\mathbf{v}}\right|^2 \end{aligned} \tag{4.39}$$

$$\Delta J = 0, \pm 2. \tag{4.40}$$

$$\Delta\nu_s = -2B(2J+3) \tag{4.41}$$

$$\Delta\nu_{as} = +2B(2J-1) \tag{4.42}$$

$$\tilde{\nu}_S^{St} = \tilde{\nu}_0 - \omega_e - 6B_1 - (5B_1-B_0)J - (B_1-B_0)J^2, \tag{4.43}$$

$$\tilde{\nu}_Q^{St} = \tilde{\nu}_0 - \omega_e - (B_1-B_0)J - (B_1-B_0)J^2, \tag{4.44}$$

$$\tilde{\nu}_O^{St} = \tilde{\nu}_0 - \omega_e - 2B_1 + (3B_1+B_0)J - (B_1-B_0)J^2, \tag{4.45}$$