

applied Spectroscopy

Physical and Chemical Kinetics

Final Examination

03-04-2014

Please use the provided paper sheets to write down the solutions of the problems. Write your name and student ID number on a first page and enumerate all subsequent pages. Do not forget to hand in your paperwork after the examination.

Problem 1

- Without taking into consideration parity and spin determine the possible molecular terms for a molecule obtained by combining two different atoms in the states S and D .
- Determine the possible terms for the molecule HCl which can be obtained by combining H in the state 2S and Cl atom in the state $^2P^o$. The superscript o depicts an odd state.
- Find possible molecular terms which can be derived from the electron configuration $(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2$ and $(1s\sigma)^2(2s\sigma)^2(2p\pi)^2$.

Problem 2

- Prove that the dipole moment of the neutral system is independent upon the choice of the origin of the frame of reference.
- 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 zero.
- When one of the nuclei with mass m_1 is replaced by its isotope with mass m_2 how much will change the total dipole moment?

Problem 3

A ground electron term of OH molecule is approximated by the potential $U(R) = \epsilon \left(\left(\frac{a}{R} \right)^{12} - \left(\frac{b}{R} \right)^6 \right)$, where $\epsilon = 1 \times 10^3 \text{ cm}^{-1}$, $a = 1 \text{ nm}$ and $b = 1.5 \text{ nm}$. Molecular weight of OH is 17 g/mol.

- Find the distance R_e where the potential has a minimum and calculate the magnitude of the potential energy at R_e .
- Find the frequency ω_0 of small vibrations around the equilibrium distance R_e .
- Find the bond energy and dissociation energy for the ground electron state of OH molecule.

Problem 4

The ground state of MgO molecule has the rotational constant $B_e = 0.5743 \text{ cm}^{-1}$ and the vibrational frequency $\omega_e = 785.0 \text{ cm}^{-1}$. The electron excited state $B^1\Sigma^+$ has the rotational constant $B_e = 0.5822 \text{ cm}^{-1}$ and the vibrational frequency $\omega_e = 824.0 \text{ cm}^{-1}$. Difference between minima of the potential curves $B^1\Sigma^+$ and $X^1\Sigma$ is $19\,984.0 \text{ cm}^{-1}$. The absorption vibration band $X^1\Sigma^+(v'' = 0) \rightarrow B^1\Sigma^+(v' = 0)$ is considered. Using the approximation of harmonic oscillator and rigid rotator find for this vibrational band:

- The minimal wavenumber in the R-branch.
- The minimal wavenumber in the Q-branch.
- The minimal wavenumber in the P-branch.

1 Introduction

Electron mass	$m_e = 9.10939 \times 10^{-28} \text{ g}$
Proton mass	$m_p = 1.67262 \times 10^{-24} \text{ g}$
Atomic unit of mass	$m_a = \frac{1}{12} m(^{12}\text{C}) = 1.66054 \times 10^{-24} \text{ g}$
Planck constant	$h = 6.62619 \times 10^{-27} \text{ erg cm}$ $\hbar = 1.05457 \times 10^{-27} \text{ erg cm}$
Light velocity	$c = 2.99792 \times 10^{10} \text{ cm/s}$
Electron charge	$e = 1.60219 \times 10^{-19} \text{ C}$
Avogadro number	$N_A = 6.02214 \times 10^{23} \text{ mol}^{-1}$
Molar volume	$V_m = 22.4141 \text{ /mol}$
Universal gas constant	$R = 8.314 \times 10^7 \text{ erg/mol K}$
Boltzmann constant	$k = R/N_A = 1.3807 \times 10^{-16} \text{ erg/K}$

2 Adiabatic Approximation and the Concept of Molecular Potentials

$$\hat{H}\Psi = E\Psi, \quad (2.1)$$

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

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

$$\left(-\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 - \frac{\hbar^2}{2} \sum_{k=1}^K \frac{1}{M_k} \nabla_k^2 + V(\mathbf{r}, \mathbf{R}) \right) \Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}) \quad (2.4)$$

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

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

$$\hat{H}_0 \phi(\mathbf{r}, \mathbf{R}) = E^{(0)}(\mathbf{R}) \phi(\mathbf{r}, \mathbf{R}) \quad (a)$$

$$\hat{H}' \chi_n(\mathbf{R}) + \sum_m \hat{c}_{nm} \chi_m(\mathbf{R}) = (E - E_n^{(0)}(\mathbf{R})) \chi_n(\mathbf{R}) \quad (b) \quad (2.7)$$

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

$$\hat{H}_0 \phi_n^{el}(\mathbf{r}, \mathbf{R}) = E_n^{(0)} \phi_n^{el}(\mathbf{r}, \mathbf{R}) \quad (a)$$

$$\left(\hat{T}_{nuc} + E_n^{(0)} \right) \chi_{n,i}(\mathbf{R}) = E_{n,i} \chi_{n,i}(\mathbf{R}) \quad (b) \quad (2.9)$$

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

$$[\hat{H}' + U'_n(\mathbf{R})]\chi_n = E\chi_n \quad (2.11)$$

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

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

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

$$\hat{l}_z = -i\hbar \frac{\partial}{\partial \phi} \quad (2.15)$$

$$\Lambda = |M_L|, \quad \Lambda = 0, 1, \dots, L \quad (2.16)$$

$$\Sigma = M_S = S, S-1, \dots, -S$$

$$\Omega = \Lambda + \Sigma. \quad (2.17)$$

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

$${}^{2S+1}\Lambda_{\Omega} \quad (2.19)$$

$$L_B \Sigma^+ \text{ terms and } L_B \Sigma^- \text{ terms} \quad (2.20)$$

$$\Sigma^+ \quad \text{if } (-1)^{L_A+L_B} P_A P_B = +1 \quad (2.21)$$

$$\Sigma^- \quad \text{if } (-1)^{L_A+L_B} P_A P_B = -1$$

$$N_g = N_u \quad \text{if } \Lambda \text{ is odd} \quad (2.22)$$

$$N_g = N_u + 1 \quad \text{if } \Lambda \text{ is even and } S \text{ is even } (S = 0, 2, 4, \dots)$$

$$N_u = N_g + 1 \quad \text{if } \Lambda \text{ is even and } S \text{ is odd } (S = 1, 3, \dots)$$

$$N_g^+ = N_u^- + 1 = L + 1 \quad \text{if } S \text{ is even } (S = 0, 2, 4, \dots)$$

$$N_u^+ = N_g^- + 1 = L + 1 \quad \text{if } S \text{ is odd } (S = 1, 3, \dots) \quad (2.23)$$

where $L_1 = L_2 = L$

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) + \dots + c_m(H_{1m} - ES_{1m}) = 0$$

$$c_2(H_{21} - ES_{21}) + c_2(H_{22} - ES_{22}) + \dots + c_m(H_{2m} - ES_{2m}) = 0$$

\vdots

$$c_m(H_{m1} - ES_{m1}) + c_m(H_{22} - ES_{m2}) + \dots + c_m(H_{mm} - ES_{mm}) = 0 \quad (2.24)$$

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

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

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

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

$$\phi = \phi_1(1)\phi_1(2) = \frac{1}{2 + 2S} \times \quad (2.29)$$

$$[\phi_A(1)\phi_A(2) + \phi_B(1)\phi_B(2) + \phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)]$$

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

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

$$\hat{H} = \left(-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{e^2}{4\pi\epsilon_0 r_{A_1}} \right) + \left(-\frac{\hbar^2}{2m} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_{A_2}} \right) \quad (2.32)$$

$$+ \frac{e^2}{4\pi\epsilon_0} \left[-\frac{1}{r_{A_2}} - \frac{1}{r_{B_1}} + \frac{1}{r_{12}} + \frac{1}{R} \right] = H_A + H_B - H_{AB} = 2H_A - H_{AB}$$

$$\phi_+ = \frac{1}{\sqrt{2(1+S^2)}} [\phi_A(1)\phi_B(2) + \phi_A(2)\phi_B(1)] \quad (2.33)$$

$$\phi_- = \frac{1}{\sqrt{2(1+S^2)}} [\phi_A(1)\phi_B(2) - \phi_A(2)\phi_B(1)]$$

3 Rotation, Vibration, and Potential Curves of Diatomic Molecules

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

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

$$\chi(R, \theta, \phi) = S(R)Y(\theta, \phi) \quad (3.3)$$

$$\frac{1}{R^2} \frac{d}{dR} \left(R^2 \frac{dS}{dR} \right) + \frac{2\mu}{\hbar^2} \left[E - E_n^0(R) - \frac{C\hbar^2}{2\mu R^2} \right] S = 0 \quad (a) \quad (3.4)$$

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial Y}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2 Y}{\partial\phi^2} + CY = 0 \quad (b)$$

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

$$F(J) = B_e J(J+1) \quad (3.6)$$

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

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

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

$$D_e = \frac{\hbar^3}{4\pi k c \mu^2 R_e^6} \quad (3.10)$$

$$H_e = \frac{3\hbar^5}{4\pi k^2 c \mu^3 R_e^{10}}$$

$$F(J, \Lambda) = B_e [J(J+1) - \Lambda^2] - D_e J^2(J+1)^2 + H_e J^3(J+1)^3 \quad (3.11)$$

$$\frac{d^2 U}{dR^2} + \frac{2\mu}{\hbar^2} [E - E_n^0(R)] U = 0 \quad (3.12)$$

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

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

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

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

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

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

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

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

$$T_v = \omega_e \left(v + \frac{1}{2} \right) - \omega_e x_e \left(v + \frac{1}{2} \right)^2 \quad (3.21)$$

$$\omega_e = \omega_0/2\pi c \quad \text{and} \quad \omega_e x_e = \hbar^2 \omega_0^2 / 8\pi c E_b = \hbar c \omega_e^2 / 4E_b$$

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

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

$$B_v = \frac{\hbar}{4\pi\mu c} \int \psi_{vib} \frac{1}{R^2} \psi_{vib} dR. \quad (3.24)$$

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

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

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

$$D_e = \frac{4B_e^3}{\omega_e^2} \quad (3.28)$$

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

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

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

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

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

$$\frac{d^2\Psi}{dR^2} + k^2\Psi = 0 \quad (3.34)$$

$$\Psi(R) = \frac{C}{\sqrt{p(R)}} \exp \left[\pm \frac{i}{\hbar} \int p(R) dR \right] \quad (3.35)$$

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

$$\frac{1}{2\pi\hbar} \oint p(R) dR = v + \frac{1}{2} \quad (3.37)$$

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

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

$$q = \sum_i q_i \quad \text{is the total charge,}$$

$$\mathbf{p} = \sum_i q_i \mathbf{r}_i \quad \text{is the total dipole moment,}$$

$$Q_{\alpha\beta} = \frac{1}{2} \sum_i q_i [3x_{i\alpha} x_{i\beta} - r_i^2 \delta_{\alpha\beta}] \quad \text{is the quadrupole momentum tensor}$$

$$E_{pot}(R) = \frac{\langle q \rangle}{4\pi\epsilon_0 R} + \frac{\langle \mathbf{p} \rangle \mathbf{R}}{4\pi\epsilon_0 R^3} + \frac{\langle Q_{\alpha\beta} \rangle X_\alpha X_\beta}{4\pi\epsilon_0 R^5} + \dots \tag{3.40}$$

$$E_0 = \hbar\omega_0 - \frac{\hbar\lambda^2}{8m^2\omega_0^3} = \hbar\omega_0 - \frac{\hbar e^4}{8m^2\omega_0^3(4\pi\epsilon_0)^2 R^6} \tag{3.41}$$

$$E_{pot}(R) = \frac{a}{R^{12}} - \frac{b}{R^6} \tag{3.42}$$

$$E_{pot}(R) = E_b \left(\left(\frac{R_e}{R} \right)^{12} - 2 \left(\frac{R_e}{R} \right)^6 \right) \tag{3.43}$$

4 Spectra of Diatomic Molecules

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

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

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

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

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

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

$$\left(\frac{dW_{mk}}{dt}\right)_{abs} = \frac{2\pi}{\hbar^2} |\langle m | \mathbf{E}_0 \cdot \mathbf{D} | k \rangle|^2 \quad (4.7)$$

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

$$\mathbf{D}_{mk} = \int \chi_m^* \mathbf{D}(\mathbf{R}) \chi_k d\tau_{nuc} \quad (4.9)$$

$$\text{where } \mathbf{D}(\mathbf{R}) = \int (\psi_m^* \mathbf{d}_{el} + \mathbf{d}_{nuc}) \psi_k d\tau_{el}$$

$$\mathbf{D}_{mk} = \int \chi_m^* \mathbf{D}_{mk}^{el} \chi_k d\tau_{nuc} \quad (4.10)$$

$$\text{where } \mathbf{D}_{mk}^{el}(\mathbf{R}) = \int \phi_m^* \mathbf{d}_{el} \phi_k d\tau_{el}$$

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

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

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

$$\begin{aligned} &\mathbf{D}_{mk}(J'', M'', J', M') \\ &= D(R_e) C_{J'' M''} C_{J' M'} \int_{\theta} \int_{\varphi} P_{J''}^{M''} P_{J'}^{M'} \hat{\mathbf{R}}_0 e^{i(M'' - M')\varphi} \sin \theta d\theta d\varphi \end{aligned} \quad (4.14)$$

$$\left[\frac{dW_{J, M \rightarrow J+1, M}}{dt} \right]_{lin} = \frac{2\pi E_0^2}{\hbar^2} D^2(R_e) \frac{(J+1)^2 - M^2}{(2J+1)(2J+3)} \quad (4.15)$$

$$\left(\frac{dW_{J \rightarrow J+1}}{dt} \right)_{lin} = \frac{2\pi E_0^2}{3\hbar} D^2(R_e) \frac{J+1}{2J+1} \quad (4.16)$$

$$\left[\frac{dW_{J, M, J+1, M \pm 1}}{dt} \right]_{circ} = \frac{\pi E_0^2}{\hbar^2} D^2(R_e) \frac{(J \pm M + 1)(J \pm M + 2)}{(2J+1)(2J+3)} \quad (4.17)$$

$$\left(\frac{dW_{mk}}{dt} \right)_t = \frac{2\pi}{\hbar^2} E_{0z}^2 D^2(R_e) \frac{J+1}{2J+1}, \quad (4.18)$$

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

$$\tilde{\nu}_P = \tilde{\nu}_0 - (B'_v + B''_v)J + (B'_v - B''_v)J^2, \quad (4.20)$$

$$\mathbf{D}_{mk} = \int \psi_{vib}(v'') D_{mk}^{el} \psi_{vib}(v') dR \iint \mathbf{R}_0 Y_{J''}^{M''} Y_{J'}^{M'} \sin \theta d\theta d\varphi \quad (4.21)$$

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

$$\frac{d}{dt} (W_{km}^{el}) \propto |D_{mk}^{el}|^2 q_{v'',v'} S_{J''J'}. \quad (4.23)$$

$$\frac{dW_{mk}^{abs}}{dt} \propto |D_{mk}^{el}|^2 q_{v'',v'} S_{J''J'} |\hat{\mathbf{r}}_0 \cdot \mathbf{E}_0|^2, \quad (4.24)$$

$$\langle R^n \rangle_{v'',v'} = \frac{\int \psi_{v''} R^n \psi_{v'} dR}{\int \psi_{v''} \psi_{v'} dR} \quad (4.25)$$

$$S_{v''v'} = |D_{mk}^{el}(R_{v''v'})|^2 q_{v''v'} \quad (4.26)$$

$$\begin{aligned} \tilde{\nu} &= [T_{el}' - T_{el}''] + [G(v') - G(v'')] + [F(J') - F(J'')] \\ &= \tilde{\nu}_0 + [B_v' J'(J'+1) - D_v' J'^2 (J'+1)^2] \\ &\quad - [B_v'' J''(J''+1) - D_v'' J''^2 (J''+1)^2] \end{aligned} \quad (4.27)$$

$$\begin{aligned} \Delta J &= 0, \pm 1; \quad 0 \leftrightarrow 0 \\ \Sigma^+ &\leftrightarrow \Sigma^-; \quad u \leftrightarrow g \end{aligned} \quad (4.28)$$

$$\tilde{\nu}_R(J) = \tilde{\nu}_0 + (B_v' - B_v'')J(J+1) + 2B_v'(J+1), \quad (4.29)$$

$$\tilde{\nu}_P(J) = \tilde{\nu}_0 + (B_v' - B_v'')J(J+1) - 2B_v'J, \quad (4.30)$$

$$\tilde{\nu}_Q(J) = \tilde{\nu}_0 + (B_v' - B_v'')J(J+1), \quad (4.31)$$

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

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

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

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

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

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

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

$$W_{if} \sim \frac{\gamma_{if} I_1 I_2}{[\omega_{if} - \omega_1 - \omega_2 - \mathbf{v} \cdot (\mathbf{k}_1 + \mathbf{k}_2)]^2 + (\gamma_{if}/2)^2} \times \left| \sum_k \frac{(\mathbf{R}_{ik} \cdot \hat{\mathbf{e}}_1)(\mathbf{R}_{kf} \cdot \hat{\mathbf{e}}_2)}{\omega_{ik} - \omega_1 - \mathbf{k}_1 \mathbf{v}} + \frac{(\mathbf{R}_{ik} \cdot \hat{\mathbf{e}}_2)(\mathbf{R}_{kf} \cdot \hat{\mathbf{e}}_1)}{\omega_{ik} - \omega_2 - \mathbf{k}_2 \mathbf{v}} \right|^2 \quad (4.39)$$

$$\Delta J = 0, \pm 2. \quad (4.40)$$

$$\Delta\nu_s = -2B(2J + 3) \quad (4.41)$$

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

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

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

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

