Rotations and vibrations of diatomic molecules

When we know the potential energy curve $V(R)$ we can compute the energy levels of a molecule. To this end we look for the eigenvalues of the Hamiltonian for the nuclear motion:

$$\hat{H}(\vec{R}_1, \vec{R}_2) = -\frac{1}{2M_1} \Delta_{\vec{R}_1} - \frac{1}{2M_2} \Delta_{\vec{R}_2} + V(R)$$

where $\Delta_{\vec{R}_1}$ and $\Delta_{\vec{R}_2}$ are the Laplace operators, $M_1$ and $M_2$ are nuclear masses in atomic units and $R = |\vec{R}_1 - \vec{R}_2|$ is the internuclear distance.

After separating out the center-of-mass motion we obtain the Hamiltonian for the internal energy of a molecule:

$$\hat{H}(\vec{R}) = -\frac{1}{2\mu} \Delta_{\vec{R}} + V(R)$$

where $\mu = M_1 M_2 / (M_1 + M_2)$ is the reduced mass and $\vec{R} = \vec{R}_2 - \vec{R}_1$. 
Rotations and vibrations of diatomic molecule, continued

To separate the rotation, the eigenfunction $\Psi(\vec{R})$ of the operator $\hat{H}(\vec{R})$ is represented in the form:

$$\Psi(\vec{R}) = \frac{\chi(R)}{R} Y^M_J(\theta, \phi)$$

The spherical function $Y^M_J(\theta, \phi)$ describes the rotation of a molecule with the angular momentum $J(J+1)$ and the function $\chi(R)$ describes its vibration:

$$\left[ -\frac{1}{2\mu} \frac{d^2}{dR^2} + V^\text{eff}_J(R) \right] \chi(R) = E_{vJ} \chi(R)$$

where $V^\text{eff}_J(R)$ is the effective potential

$$V^\text{eff}_J(R) = V(R) + \frac{J(J+1)}{2\mu R^2}$$

containing the repulsive term due to the centrifugal force, proportional to $J(J+1)$, and therefore growing quickly with the increase of the rotational quantum number $J$. 
Dependence of the effective potential $V_{j}^{\text{eff}}(R)$ on $J$. 

**Rys. 4.2.** Efektywny potencjał $V_{e}(R)$ dla stanu B$^1\Pi$ cząsteczki KLi przy różnych wartościach rotacyjnej liczby kwantowej $J$.
Accurate vibration wave functions $\chi_{vJ}(R)$ for $J = 0$. 

**Rys. 4.5.** Obliczone numerycznie energie i funkcje falowe wybranych poziomów oscylacyjnych w stanie $B^{1}I$ cząsteczki KLi
For small $J$ and for small values of the vibrational quantum number $v$ (i.e., for the lowest vibrational excitations) one can assume that

$$V(R) = V(R_e) + \frac{1}{2} f(R - R_e)^2 \quad \text{oraz} \quad \frac{J(J + 1)}{2\mu R^2} = \frac{J(J + 1)}{2\mu R_e^2}$$

where $R_e$ is the equilibrium internuclear distance, i.e., the distance at which $V(R)$ acquires minimum, and $f$ is the force constant

$$f = \left( \frac{d^2 V(R)}{dR^2} \right)_{R=R_e}$$

The equation for the vibration function $\chi(R)$ becomes then the equation for the harmonic oscillator and has the following eigenvalues (in arbitrary units):

$$E_{vJ} = V(R_e) + \hbar \nu \left( \nu + \frac{1}{2} \right) + \frac{J(J + 1)\hbar^2}{2\mu R_e^2}$$

where

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$
Rovibrational levels pattern for two lowest electronic states
Rotations and vibrations of diatomic molecule, continued

Real molecules are not harmonic oscillators. A better approximation to their levels is the formula

$$E_{vJ} = V(R_e) + h\nu \left( \nu + \frac{1}{2} \right) - h\nu_e x_e \left( \nu + \frac{1}{2} \right)^2 + \frac{J(J+1)\hbar^2}{2\mu R_e^2}$$

where $x_e$ is the anharmonicity constant proportional to the third derivative of the potential $V(R)$ at $R = R_e$.

Often one finds it useful to use the so-called Dunham expansion

$$E_{vJ} = \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} Y_{kl} \left( \nu + \frac{1}{2} \right)^k [J(J+1)]^l$$

The Dunham coefficients $Y_{kl}$ can be computed from the knowledge of the potential $V(R)$. There exist formulas to express $Y_{kl}$ in terms of derivatives of $V(R)$ at $R = R_e$. In particular one can easily find that:

$$Y_{00} = V(R_e) \quad Y_{10} = h\nu \quad Y_{20} = -h\nu_e x_e \quad Y_{01} = \frac{\hbar^2}{2\mu R_e^2}$$

The coefficient $Y_{11}$ describes the rotation-vibration coupling. Using a small number of Dunham coefficients we can correctly represent many levels $E_{vJ}$. 
Popular analytic representations of $V(R)$

Sometimes one uses the so called Morse potential to represent $V(R)$:

$$V(R) = D_e \left[ 1 - e^{-a(R-R_e)} \right]^2 - D_e$$

where $a$ is a parameter ($D_e$ is the well depth of the potential). For the Morse potential we know the analytic solution of the Schrödinger equation for $\chi(R)$.

In computer simulations one often uses the so-called Lennard-Jones potential (12-6 potential) because it can be very quickly computed:

$$V(R) = D_e \left[ (\frac{R_e}{R})^{12} - 2 \left( \frac{R_e}{R} \right)^6 \right]$$

In very accurate calculations one uses a more realistic and much more accurate potential resulting from the SAPT theory:

$$V(R) = e^{-\alpha R} \left( \frac{a}{R} + b + cR + dR^2 \right) - \sum_n f_n(\eta R) \frac{C_n}{R^n},$$

where $C_n$ are asymptotic (van der Waals) constants and $f_n(x)$ is a damping function

$$f_n(x) = 1 - e^{-x} \sum_{k=0}^n \frac{x^k}{k!}$$