

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 $\mu = M_1M_2/(M_1 + M_2)$ 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:

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

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

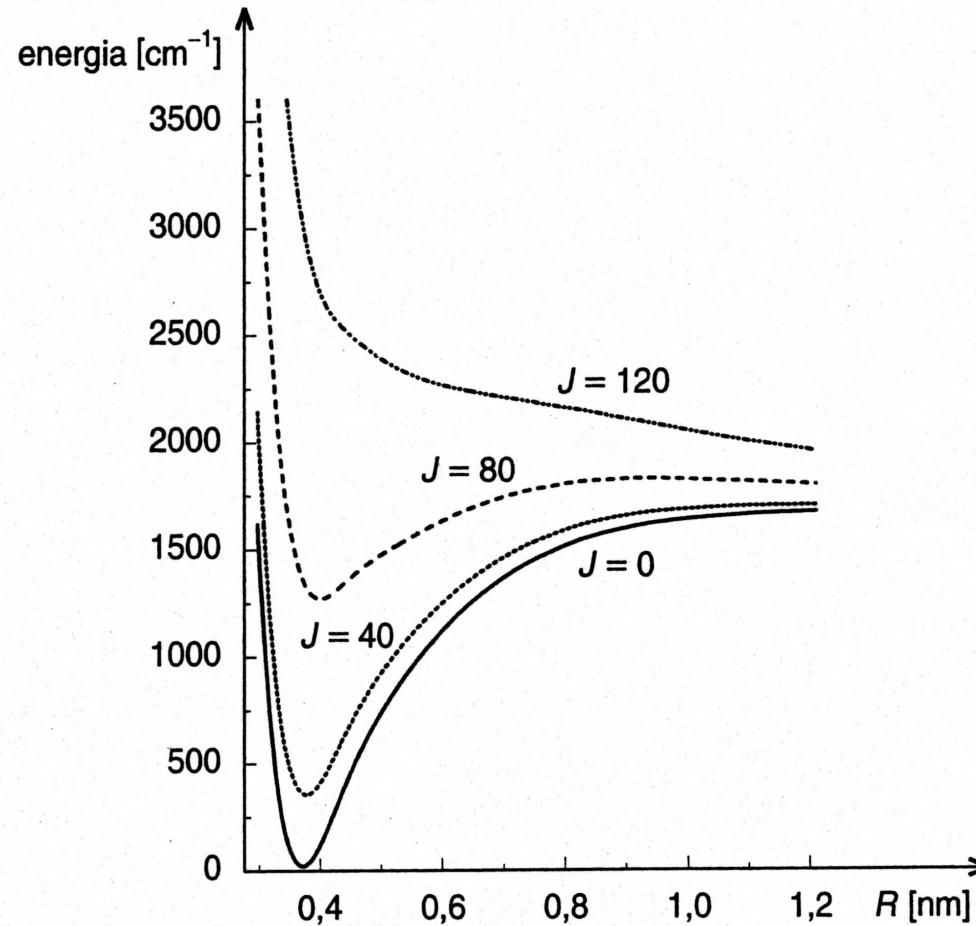
$$\left[-\frac{1}{2\mu} \frac{d^2}{dR^2} + V_J^{\text{eff}}(R) \right] \chi(R) = E_{vJ} \chi(R)$$

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

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

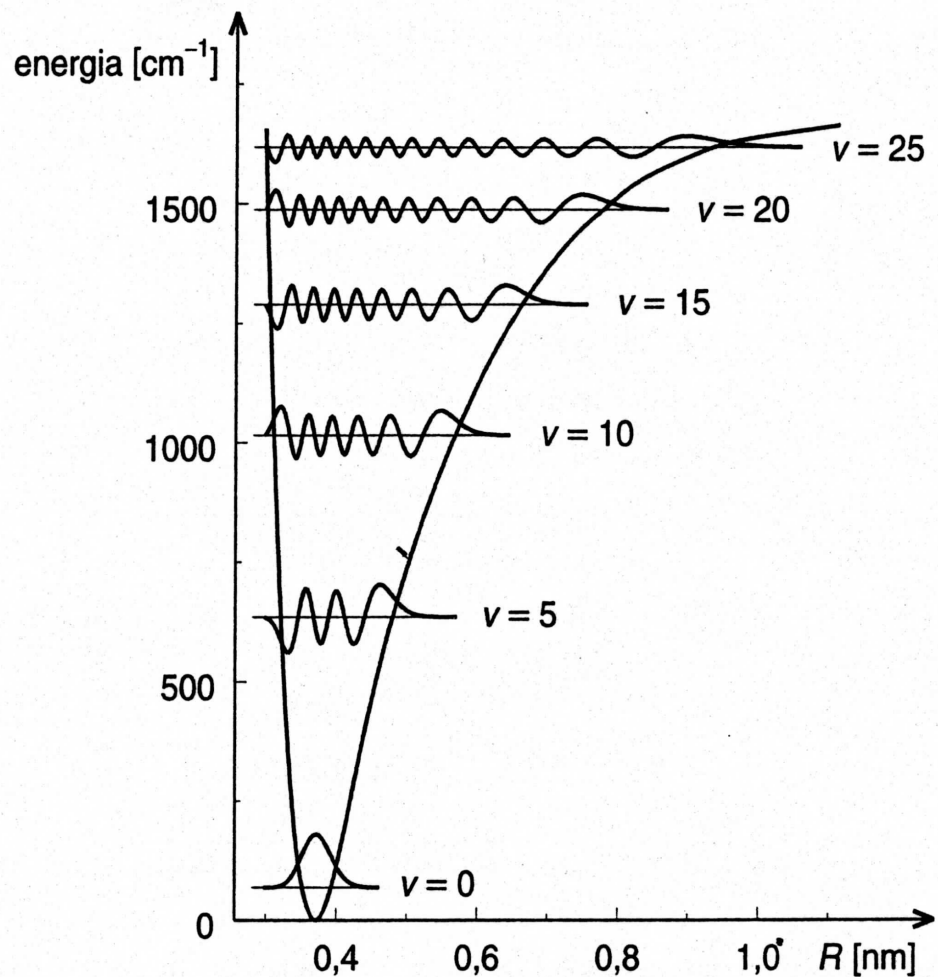
containing the repulsive term due to the centrifugal force, proportional to $J(J+1)$, and therefore growing quickly with the increase of the **rotational quantum number J** .

Dependence of the effective potential $V_J^{\text{eff}}(R)$ on J .



Rys. 4.2. Efektywny potencjał $V_{\text{ef}}(R)$ 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 $B^1\Pi$ cząsteczki KLi

Rotations and vibrations of diatomic molecule, continued

For small J and for small values of the **vibrational quantum number ν** (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

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

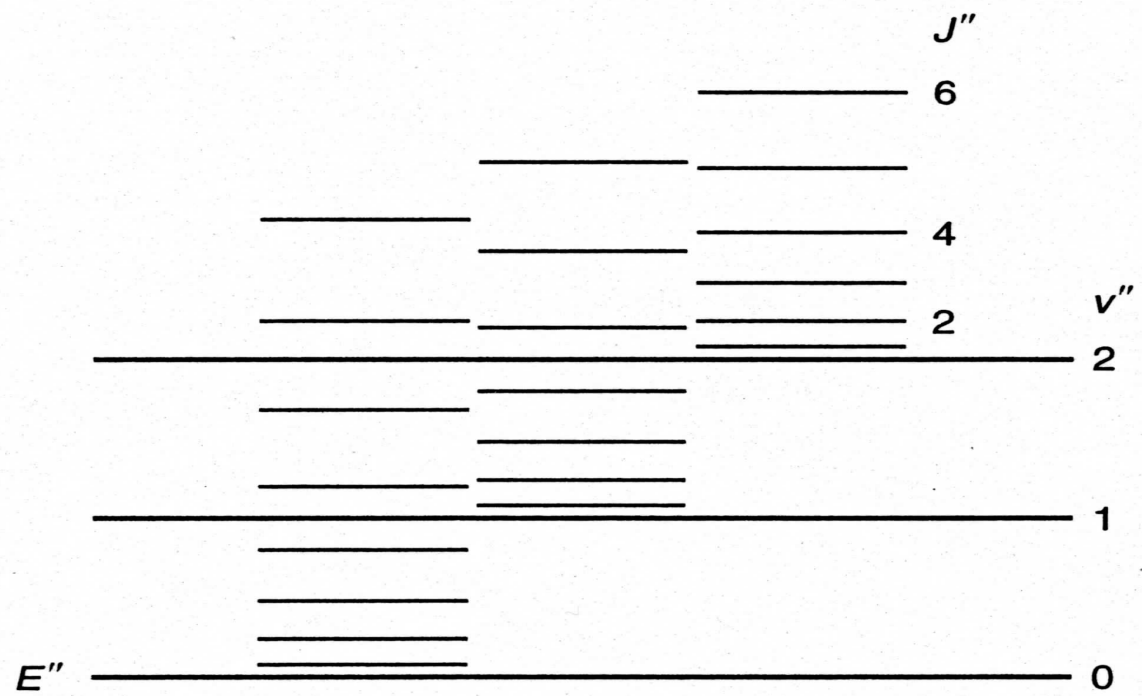
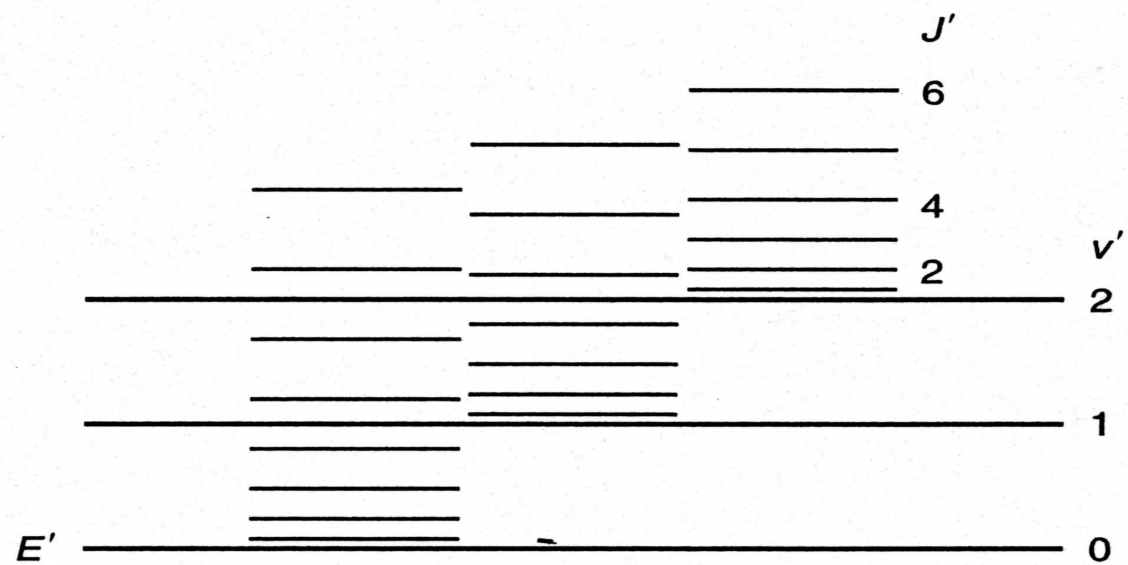
The equation for the vibration function $\chi(R)$ becomes then the equation for the harmonic oscillator and has the following eigenvalues (in arbitrary units):

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

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

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

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**

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

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:

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

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

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