

3.5: Separation of Vibration and Rotation

It is common, in developing the working equations of diatomic-molecule rotational/vibrational spectroscopy, to treat the coupling between the two degrees of freedom using perturbation theory as developed later in this chapter. In particular, one can expand the centrifugal coupling $\hbar^2 \frac{J(J+1)}{2\mu R^2}$ around the equilibrium geometry R_e (which depends, of course, on J):

$$\hbar^2 \frac{J(J+1)}{2\mu R^2} = \hbar^2 \frac{J(J+1)}{2\mu [R_e^2 (1 + \Delta R)^2]}$$

$$\hbar^2 \frac{J(J+1)}{2\mu R_e^2} [1 - 2\Delta R + \dots],$$

and treat the terms containing powers of the bond length displacement ΔR^k as perturbations. The zeroth-order equations read:

$$\frac{-\hbar^2}{2\mu} \left[\frac{1}{R^2} \frac{\partial}{\partial R} \left(R^2 \frac{\partial}{\partial R} \right) \right] F_{j,J,v}^0(R) + E_j(R) F_{j,J,v}^0(R) + \hbar^2 \frac{J(J+1)}{2\mu R_e^2} F_{j,J,v}^0 F_{j,J,v}^0,$$

and have solutions whose energies separate

$$E_{j,J,v}^0 = \hbar^2 \frac{J(J+1)}{2\mu R_e^2} + E_{j,v}$$

and whose wavefunctions are independent of J (because the coupling is not R -dependent in zeroth order)

$$F_{j,J,v}^0(R) = F_{j,v}(R).$$

Perturbation theory is then used to express the corrections to these zeroth order solutions as indicated in Appendix D.

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