Chapter 13. Exercises

1. From the spectroscopic constants in the table, calculate the force constant k and the internuclear distance R_e for each of the hydrogen halides. The answers are given in the text.

2. The following spectroscopic constants have been assigned for the $^{14}N^{16}O$ molecule: $\tilde{\nu} = 1904\ \mathrm{cm}^{-1}$, $x_e\tilde{\nu} = 13.97\ \mathrm{cm}^{-1}$, $B = 1.705\ \mathrm{cm}^{-1}$

(i) Calculate the wavenumber of the $J = 0$ to $J = 1$ transition.

(ii) Calculate the equilibrium internuclear distance in pm.

(iii) Calculate the force constant in N/m.

(iv) Taking account of the anharmonic correction, calculate the wavenumber of the $v = 0$ to $v = 1$ transition.

3. Allowed electronic transitions in a homonuclear diatomic molecule obey the following selection rules: $\Delta S = 0$ and g $\leftrightarrow$ u; $\Sigma \leftrightarrow \Sigma$, $\Sigma \leftrightarrow \Pi$ and $\Pi \leftrightarrow \Pi$ are all allowed. Predict the lowest excited state of N_2 which can be attained by absorption of radiation from the ground state (not necessarily the lowest excited state).

Chapter 13. Solutions

2. (i)

$$hcE_J = BJ(J+1)$$

$$hc(E_1 - E_0) = 2B = 3.410\,\mathrm{cm}^{-1}$$

(ii)

$$R = 410.6 \Big/ \sqrt{\frac{14 \times 16}{14+16}\,B} = 115\,\mathrm{pm}$$

R=115 pm

(iii)

$$k = 58.9 \times 10^{-6}\,\tilde{\nu}^2\,\frac{14 \times 16}{14+16} = 1590\,\mathrm{N/m}$$

(iv)

$$hcE_v = (v + \tfrac{1}{2})\tilde{\nu} - (v + \tfrac{1}{2})^2 x_e \tilde{\nu}$$

$$hc(E_1 - E_0) = \left(\frac{3}{2} - \frac{1}{2}\right)\tilde{\nu} - \left[\left(\frac{3}{2}\right)^2 - \left(\frac{1}{2}\right)^2\right] x_e \tilde{\nu} = 1876\ \mathrm{cm}^{-1}$$

3. The ground state of N_2 has the MO configuration $\ldots 3\sigma_g^2\, 1\pi_u^4\ {}^1\Sigma_g$. The lowest-energy excitation would be $1\pi_u \rightarrow 1\pi_g$ (which could be classified as a $\pi \rightarrow \pi^*$ transition). This can give an excited state with term symbol ${}^1\Sigma_u$ with an allowed transition from the ground state.