

Problem 1

- a. 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 .

Solution

The total orbital momentum $L = 2$, therefore $M = -2, -1, 0, +1, +2$. Thus, the possible molecular states are Σ , Π and Δ .

- b. 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.

Solution

The total spin number can take values $S = 0, 1$. The total orbital momentum $L = 1$, therefore $M = -1, 0, 1$. From the rules for parity we get Σ^+ state. Thus we have the following states for HCl molecule

$$^1\Sigma^+, ^3\Sigma^+, ^1\Pi, ^3\Pi$$

- c. Find possible molecular terms which can be derived from the electron configuration $(1s\sigma)^2(2s\sigma)^2(2p\sigma)^2$ and $(1s\sigma)^2(2s\sigma)^2(2p\pi)^2$.

Solution

Using Pauli principle we get the following molecular terms:

$$\begin{aligned} (1s\sigma)^2(2s\sigma)^2(2p\sigma)^2 & \quad ^1\Sigma \\ (1s\sigma)^2(2s\sigma)^2(2p\pi)^2 & \quad ^1\Sigma, \quad ^3\Sigma, \quad ^1\Delta \end{aligned}$$

Problem 2

- a. Prove that the dipole moment of the neutral system is independent upon the choice of the origin of the frame of reference.

Solution

Suppose that \mathbf{r}_i is a position of a charge q_i . In the new coordinate system the position will be $\mathbf{r}'_i = \mathbf{r}_i - \mathbf{R}_0$. Taking into account that $\sum_i q_i = 0$, we receive for the dipole momentum in the new system,

$$\mathbf{p}' = \sum_i q_i(\mathbf{r}_i - \mathbf{R}_0) = \sum_i q_i\mathbf{r}_i - \mathbf{R}_0 \sum_i q_i = \sum_i q_i\mathbf{r}_i = \mathbf{p}$$

- b. 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.

Solution

Because the total dipole moment is independent upon the position of origin of the frame of reference, we can write

$$-eZ_1x + (R - x)eZ_2 + D^{el} = D$$

where x is the distance from the origin of frame of reference to the nuclei with charge eZ_1 . Because $D^{el} = 0$, we have

$$x = \frac{ReZ_2 - D}{eZ_2 + eZ_1}$$

- c. 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?

Solution

By definition a dipole moment is independent upon mass. The equilibrium position and electron wavefunctions are also independent upon nuclei math. Therefore, isotopologues have the same dipole moment.

Problem 3

A ground electron term of OH molecule is approximated by the Lennard Jones 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 .

- a. Find the distance R_e where the potential has a minimum and calculate the magnitude of the potential energy at R_e .

Solution

At R_e the derivative of the potential is zero,

$$\frac{12}{R} \left(\frac{a}{R} \right)^{12} - \frac{6}{R} \left(\frac{b}{R} \right)^6 = 0 \Rightarrow R_e = \frac{a^2}{b} 2^{1/6}$$

and

$$U_{min} = \epsilon \left(\left(\frac{b}{a 2^{1/6}} \right)^{12} - \left(\frac{b^2}{a^2 2^{1/6}} \right)^6 \right) = \epsilon \left(\frac{b^{12}}{4a^{12}} - \frac{b^{12}}{2a^{12}} \right) = -\epsilon \frac{b^{12}}{4a^{12}}$$

After substituting numeric values we get

$$R_e = 0.75 \text{ nm}$$

and

$$U_{min} = -32\,436.6 \text{ cm}^{-1}$$

- b. Find the frequency ω_0 of small vibrations around the equilibrium distance R_e .

Solution Using a Taylor series expansion we get

$$\begin{aligned} U(R) - U(R_e) &\approx \frac{1}{2} \left. \frac{d^2U(R)}{dR^2} \right|_{R=R_e} = \epsilon \left(\frac{12 \cdot 13a^{12}}{R_e^{14}} - \frac{6 \cdot 7b^6}{R_e^8} \right) \frac{(R - R_e)^2}{2} \\ &= \epsilon \left(\frac{39b^{14}}{2^{1/3}a^{16}} - \frac{21b^{14}}{2^{1/3}a^{16}} \right) \frac{(R - R_e)^2}{2} = \epsilon \left(\frac{18b^{14}}{2^{1/3}a^{16}} \right) \frac{(R - R_e)^2}{2} \end{aligned}$$

For the frequency we get

$$\begin{aligned} \omega_0 &= \sqrt{\frac{k}{\mu}} = \sqrt{\frac{18b^{14}\epsilon}{2^{1/3}a^{16}\mu}} \\ &= (1.5)^7 \sqrt{\frac{18}{2^{1/3}}} \sqrt{\frac{1 \times 10^5 \text{ m}^{-1} \times 6.6262 \times 10^{-34} \text{ J s} \times 2.99792 \times 10^8 \text{ cm/s}}{1 \times 10^{-18} \text{ m}^2 \times 0.94 \times 1.66 \times 10^{-27} \text{ kg}}} \\ &= 17 \times 3.78 \times 4.597 \times 10^{12} \text{ s}^{-1} = 2.95 \times 10^{14} \text{ s}^{-1} = 1568 \text{ cm}^{-1} \end{aligned}$$

- c. Find the bond energy and dissociation energy for the ground electron state of OH molecule.

Solution The bond energy is

$$E(\infty) - E(R_e) = 32\,436.6 \text{ cm}^{-1}$$

and the dissociation energy is

$$D_e = E(\infty) - (E(R_e) + \frac{\hbar\omega_0}{2}) = 32\,436.6 \text{ cm}^{-1} - 0.5 \times 1568 \text{ cm}^{-1} = 31\,652.6 \text{ cm}^{-1}$$

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:

- a. The minimal wavenumber in the R-branch.

Solution

The R branch increases monotonically, therefore the line $R(0)$ has the lowest wavenumber,

$$\tilde{\nu}_R(0) = \tilde{\nu}_0 = 2B'_v = 20003.5 + 2 \cdot 0.5822 = 20\,004.664 \text{ cm}^{-1}$$

- b. The minimal wavenumber in the Q-branch.

Solution

The Q branch increases monotonically, therefore the line $Q(1)$ ($Q(0)$ is forbidden) has the lowest wavenumber,

$$\tilde{\nu}_Q(1) = \tilde{\nu}_0 + 2(B'_v - B''_v) = 20003.5 + 2(0.5822 - 0.5743) = 20\,003.5158 \text{ cm}^{-1}$$

c. The minimal wavenumber in the P-branch.

Solution

The band origin is

$$\tilde{\nu}_0 = T_e + 0.5(\omega'_e - \omega''_e) = 19984 + 0.5(824 - 785) = 20\,003.5 \text{ cm}^{-1}$$

The position of P branch,

$$\tilde{\nu}_P = \tilde{\nu}_0 + (B'_v - B''_v)J(J+1) - 2B'_v J$$

Because $B'_v > B''_v$ the wavenumber of the P branch reaches minimum when $\frac{d\tilde{\nu}_P}{dJ} = 0$,

$$(B'_v - B''_v)(2J+1) - 2B'_v = 0 \Rightarrow J_{min} = \frac{B'_v + B''_v}{2(B'_v - B''_v)} = \frac{0.5822 + 0.5743}{2(0.5822 - 0.5743)} = 73$$

and position

$$\tilde{\nu}_P = 20003.5 + 0.0079 \cdot 73 \cdot 74 - 2 \cdot 0.5822 \cdot 73 = 19\,961.1746 \text{ cm}^{-1}$$