Chemistry 432
Problem Set 10
Spring 2020
Solutions

1. Consider the molecule

$$H_2 - C = C = C - H_2$$

Use Hückel theory to determine the electronic energy of the π-electrons in the molecule, and predict whether the binding energy of the molecule would increase or decrease by the addition of an electron to form $C_3H_4^-$.

Answer:

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = (\alpha - E)[(\alpha - E)^2 - \beta^2] - \beta^2(\alpha - E)$$

$$= (\alpha - E)[(\alpha - E)^2 - 2\beta^2] = 0$$

Then

$$E = \alpha, \alpha \pm \sqrt{2}\beta$$

$\underline{\quad}$ $\alpha - \sqrt{2}\beta$
$\underline{\uparrow\downarrow}$ α
$\underline{\uparrow\downarrow}$ $\alpha + \sqrt{2}\beta$

$$E_\pi = 4\alpha + 2\sqrt{2}\beta$$

$C_3H_4^-$ is less strongly bound, because the extra electron fills an anti-bonding orbital.

2. Use Hückel theory to predict the electronic configuration of the benzene anion and the benzene cation. Estimate the π-energy in each case.

Answer:

Anion

$\underline{\quad}$ $\alpha - 2\beta$

$\underline{\uparrow\ }$ $\underline{\quad}$ $\alpha - \beta$

$\underline{\uparrow\downarrow}$ $\underline{\uparrow\downarrow}$ $\alpha + \beta$

$\underline{\uparrow\downarrow}$ $\alpha + 2\beta$

$$E_\pi = 2(\alpha + 2\beta) + 4(\alpha + \beta) + \alpha - \beta = 7\alpha + 7\beta$$

Cation

$\underline{\quad}$ $\alpha - 2\beta$

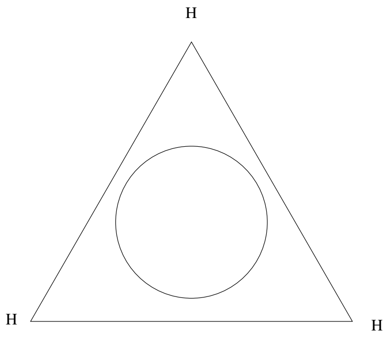
$\underline{\quad}$ $\underline{\quad}$ $\alpha - \beta$

$\underline{\uparrow\downarrow}$ $\underline{\uparrow}$ $\alpha + \beta$

$\underline{\uparrow\downarrow}$ $\alpha + 2\beta$

$$E_\pi = 2(\alpha + 2\beta) + 3(\alpha + \beta) = 5\alpha + 7\beta$$

3. Consider the $C_3H_3\cdot$ radical containing a total of three π electrons as pictured below. Set up the Hückel determinant for the radical, and expand the determinant to give a cubic equation for the energies of the system. Given the solutions to the cubic equation are $E = \alpha + 2\beta$, $\alpha - \beta$, and $\alpha - \beta$, calculate the π-electron energy for $C_3H_3\cdot$. Compare the π-electron energy for $C_3H_3\cdot$ with the π-electron energy for $C_3H_3^-$, and predict whether the radical or the anion is most strongly bound.



Answer:

$$\begin{vmatrix} \alpha - E & \beta & \beta \\ \beta & \alpha - E & \beta \\ \beta & \beta & \alpha - E \end{vmatrix} = 0$$

$$(\alpha - E)[(\alpha - E)^2 - \beta^2] - \beta[\beta(\alpha - E) - \beta^2] + \beta[\beta^2 - \beta(\alpha - E)] = 0$$

$\underline{\uparrow}$ $\underline{\quad}$ $\alpha - \beta$

$\underline{\uparrow\downarrow}$ $\alpha + 2\beta$

$$E^{\cdot}_\pi = 2\alpha + 4\beta + \alpha - \beta = 3\alpha + 3\beta$$

$\underline{\uparrow}$ $\underline{\uparrow}$ $\alpha - \beta$

$\underline{\uparrow\downarrow}$ $\alpha + 2\beta$

$$E^-_\pi = 2\alpha + 4\beta + 2\alpha - 2\beta = 4\alpha + 2\beta$$

The radical has fewer antibonding electrons and is more strongly bound.

4. The allyl radical has two equivalent resonance structures

$$\mathrm{CH_2{=}CH\text{-}CH_2\cdot} \leftrightarrow \mathrm{CH_2\text{-}CH{=}CH_2\cdot}$$

Construct the Hückel determinant for the allyl radical and expand the determinant to give the secular equation for the energies of the π orbitals. Given the solutions to the resulting cubic equation are $E = \alpha + \sqrt{2}\beta, \alpha$ and $\alpha - \sqrt{2}\beta$, calculate the total π-electron energy in terms of α and β.
Answer:

$$\begin{vmatrix} \alpha - E & \beta & 0 \\ \beta & \alpha - E & \beta \\ 0 & \beta & \alpha - E \end{vmatrix} = (\alpha - E)[(\alpha - E)^2 - \beta^2] - \beta^2(\alpha - E)$$

$$= (\alpha - E)[(\alpha - E)^2 - 2\beta^2] = 0$$

The energy ordering of the orbitals is $\alpha + \sqrt{2}\beta < \alpha < \alpha - \sqrt{2}\beta$. There are 3 π electrons so the total π-electron energy is

$$E_\pi = 2(\alpha + \sqrt{2}\beta) + \alpha = 3\alpha + 2\sqrt{2}\beta$$

5. Consider the KNa molecule, and let $3s$ be the $3s$-orbital centered about the soduium nucleus and $4s$ be the $4s$-orbital centered about the potassium nucleus.

   (a) Regarding KNa as being formed entirely from the $3s$-orbital centered about the Na atom and the $4s$-orbital centered about the K atom, give the molecular orbital wavefunction for KNa.
   Answer:

   $$\psi_{mo} = N[3s(1) + 4s(1)][3s(2) + 4s(2)]$$

   (b) In terms of $3s$ and $4s$, give the covalent valence bond wavefunction for KNa. Give the resonance structure implied by this wavefunction.
   Answer:

   $$\psi_{vb} = N'[3s(1)4s(2) + 3s(2)4s(1)] \qquad \text{K-Na}$$

   (c) Give two singly ionized resonance structures for KNa and give the associated terms in the molecular wavefunction.
   Answer:

   $$\psi_{ion1} = 3s(1)3s(2) \qquad \mathrm{Na^-K^+}$$

   $$\psi_{ion2} = 4s(1)4s(2) \qquad \mathrm{Na^+K^-}$$

6. Write the valence-bond wavefunction for the LiH molecule regarding it as being formed entirely from an H 1s-orbital and a Li $2s$-orbital. Give the wavefunction under the assumptions

(a) that the molecule is pure covalent;
Answer:

$$\psi_{covalent} = N[1s(1)2s(2) + 1s(2)2s(1)]$$

(b) that the molecule is pure ionic [include only the chemically important resonance structure with the negative charge on the hydrogen atom];
Answer:

$$\psi_{ionic} = N'1s(1)1s(2)$$

(c) that the molecule is 60 per cent covalent and 40 percent ionic.
Answer:

$$\psi = c_1\psi_{covalent} + c_2\psi_{ionic}$$
$$|c_1|^2 = .6 \qquad c_1 = .77$$
$$|c_2|^2 = .4 \qquad c_2 = .63$$
$$\psi = .77\psi_{covalent} + .63\psi_{ionic}$$

7. The electronic absorption spectrum of KH from its ground to first excited electronic state has vibrational fine structure with two adjacent lines at 22478 cm^{-1} and 22706 cm^{-1}. The fluorescence spectrum from the excited electronic state to the ground state also shows vibrational fine structure with two adjacent lines at 11321 cm^{-1} and 10341 cm^{-1}. Assume both the ground electronic state and the excited electronic state potential curves to be pure harmonic oscillators.

(a) Calculate the fundamental frequency of vibration of the electronic ground state.
Answer:

$$\Delta\left(\frac{1}{\lambda}\right) = 11321\text{cm}^{-1} - 10341\text{cm}^{-1} = 980\text{cm}^{-1}$$
$$\nu = (980\text{cm}^{-1})(2.998\times10^{10}\text{cm s}^{-1}) = 2.94\times10^{13}\text{s}^{-1}$$

(b) Calculate the fundamental frequency of vibration of the electronic excited state.
Answer:

$$\Delta\left(\frac{1}{\lambda}\right) = 22706\text{cm}^{-1} - 22478\text{cm}^{-1} = 228\text{cm}^{-1}$$
$$\nu = (228\text{cm}^{-1})(2.998\times10^{10}\text{cm s}^{-1}) = 6.835\times10^{12}\text{s}^{-1}$$

(c) Calculate the period of vibration of the ground state.
Answer:

$$\tau = \nu^{-1} = 3.404\times10^{-14}\text{s}$$

8. The electronic absorption spectrum of the N_2 molecule from the ground electronic state to an excited electronic state consists of a series of spectral lines adjacent members of which occur at frequencies 69283.06 cm^{-1}, 70977.26 cm^{-1}, 72671.46 cm^{-1}, ... The electronic fluorescence emission spectrum of N_2 between the same excited electronic state and the ground state consists of adjacent spectral lines at frequencies 69283.06

cm^{-1}, 66924.49 cm^{-1}, 64565.92 cm^{-1}, ... Calculate the vibrational force constant in the N_2 molecule in its ground electronic state. You should assume both the ground and excited electronic states to be represented by pure harmonic potential curves.

Answer:

$$\Delta\nu_{emission} = 69283.06\text{cm}^{-1} - 66924.49\text{cm}^{-1} = 2358.6\text{cm}^{-1}$$

$$(2358.6\text{cm}^{-1})(2.998 \times 10^{10}\text{cm s}^{-1}) = 7.08 \times 10^{13}\text{s}^{-1}$$

$$\omega = 2\pi\nu = 4.45 \times 10^{14}\text{s}^{-1}$$

$$k = \mu\omega^2 = \frac{14^2}{28}\frac{1}{6.022 \times 10^{26}}\text{kg}(4.45 \times 10^{14}\text{s}^{-1})^2 = 2300\text{N m}^{-1}$$

9. In the electronic fluorescence spectrum of CO, the transition from the ground vibrational state of the first excited electronic state of the CO molecule to the ground vibrational state of the ground electronic state occurs at 66593.9 cm^{-1}. The force constant of CO in its ground state electronic is 1.86 $\times 10^3$ N m^{-1}. Assuming a pure harmonic oscillator potential energy curve, calculate the location of second spectral line in the fluorescence spectrum; i.e. the first line adjacent to the line at 66593.9 cm^{-1}.

   Answer:

$$k = 4\pi^2\mu\nu^2$$

$$\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$= \frac{1}{2\pi}\sqrt{\frac{1.86 \times 10^3\text{N m}^{-1}}{\frac{(12)(16)}{12+16}\frac{\text{kg}}{6.022 \times 10^{26}}}} = 6.43 \times 10^{13}\text{ s}^{-1}$$

$$\nu_{osc} = \frac{6.43 \times 10^{13}\text{s}^{-1}}{2.998 \times 10^{10}\text{ cm s}^{-1}} = 2145.6\text{ cm}^{-1}$$

$$\nu_2 = 66593.9\text{ cm}^{-1} - 2145.6\text{ cm}^{-1} = 64448.3\text{ cm}^{-1}$$

10. The $n = 0$ to $n = 0$ (n represent the vibrational quantum numbers) spectroscopic, electronic transition between the ground and first excited electronic states in the CH molecule is measured to be 23189. cm^{-1}. The harmonic force constants for the ground electronic state and the first excited electronic states are respectively $k_{gs} = 444.4$ N m^{-1} and $k_{es} = 467.2$ N m^{-1}. Calculate the frequency of the absorption line between the $n = 0$ vibrational state of the ground electronic state and the $n = 5$ vibrational line of the excited electronic state. Also, calculate the frequency in the fluorescence spectrum from the $n = 0$ vibrational state of the excited electronic state to the $n = 2$ vibrational state of the ground electronic state. You should assume both the ground and excited electronic potential curves are accurately represented by harmonic oscillators.

    Answer:

$$k = 4\pi^2\mu\nu^2 \qquad \nu = \sqrt{\frac{k}{4\pi^2\mu}}$$

$$\mu = \left(\frac{(1.0)(12.0)}{13.0}\right)\frac{\text{kg}}{6.022 \times 10^{26}} = 1.533 \times 10^{-27}\ \text{kg}$$

$$\nu_{gs} = \left[\frac{444.4\ \text{N m}^{-1}}{4\pi^2(1.533 \times 10^{-27}\ \text{kg}}\right]^{1/2}\frac{\text{s}}{2.998 \times 10^{10}\ \text{cm}} = 2858.3\ \text{cm}^{-1}$$

$$\nu_{es} = \left[\frac{467.2\ \text{N m}^{-1}}{4\pi^2(1.533 \times 10^{-27}\ \text{kg}}\right]^{1/2}\frac{\text{s}}{2.998 \times 10^{10}\ \text{cm}} = 2930.7\ \text{cm}^{-1}$$

Absorption

$$23189.\ \text{cm}^{-1} + 5(2930.7)\ \text{cm}^{-1} = 37843.\ \text{cm}^{-1}$$

Fluorescence

$$23189.\ \text{cm}^{-1} - 2(2858.3)\ \text{cm}^{-1} = 17472.\ \text{cm}^{-1}$$

11. The electronic absorption spectrum of the SB molecule in the gas phase between the ground electronic state and first excited electronic state consists of a series of lines at frequencies 15876. s^{-1}, 16630 s^{-1}, 17384 s^{-1} .... The lines in the fluorescence spectrum between the same two electronic states has spectral lines at 15876 s^{-1}, 14696 s^{-1}, 13516 s^{-1},.... Let k_{gs} be the force constant for SB in the ground electronic state and k_{es} be the excitied-state force constant. Calculate the value of the ratio k_{es}/k_{gs}.
Answer:

$$\nu_{gs} = (15876. - 14696.)\ \text{s}^{-1} = 1180.\ \text{s}^{-1}$$

$$\nu_{es} = (16630. - 15876.)\ \text{s}^{-1} = 754.\ \text{s}^{-1}$$

$$k = 4\pi^2\mu\nu^2$$

so

$$\frac{k_{es}}{k_{gs}} = \left(\frac{754.}{1180.}\right)^2 = 0.41$$

12. The electronic absorption spectrum of the gas-phase O_2 molecule from its ground electronic state to its first excited electronic state consists of a series of the series of lines 35397.8 cm^{-1}, 36196.9 cm^{-1}, 36995.9 cm^{-1} .... The fluorescence emission spectrum connecting the same two electronic states consists of the series of lines 35397.8 cm^{-1}, 33817.6 cm^{-1}, 32237.4 cm^{-1} .... Assuming both the ground-state and excited-state potential curves are harmonic, calculate the ratio of the Hooke's law force constants of the ground to excited electronic states.
Answer:

$$\nu_{gs} = (35397.8\ \text{cm}^{-1} - 33817.6\ \text{cm}^{-1})(2.998 \times 10^{10}\ \text{cm s}^{-1}) = 4.7374 \times 10^{13}\ \text{s}^{-1}$$

$$\nu_{es} = (36196.9\ \text{cm}^{-1} - 35397.8\ \text{cm}^{-1})(2.998 \times 10^{10}\ \text{cm s}^{-1}) = 2.3597 \times 10^{13}\ \text{s}^{-1}$$

$$k = 4\pi^2\mu\nu^2$$

$$\frac{k_{gs}}{k_{es}} = \left(\frac{4.7374}{2.3957}\right)^2 = 3.910$$

13. The absorption spectrum of the gas-phase F_2 molecule consists of a series of lines with wave numbers 105520.14 cm^{-1}, 106608.33 cm^{-1}, 107696.52 $\text{cm}^{-1}, \ldots$, and the fluorescence spectrum of the same molecule between the same two electronic states consists of a series of lines with wave numbers 105520.14 cm^{-1}, 104603.50 cm^{-1}, 103686.86 $\text{cm}^{-1}, \ldots$. Assuming both states are well represented by harmonic forces, calculate the vibrational period in seconds of the ground state of F_2 in the gas phase.
Answer:

$$\nu = (105520.14\ \text{cm}^{-1} - 104603.50\ \text{cm}^{-1})(2.998 \times 10^{10}\ \text{cm s}^{-1}) = 2.748 \times 10^{13}\ \text{s}^{-1}$$

$$\tau = \frac{1}{\nu} = 3.639 \times 10^{-14}\ \text{s}$$

14. The electronic absorption spectrum of the gas-phase AgH molecule consists of a series of lines with wave numbers 41261. cm^{-1}, 42850. cm^{-1}, 44439. $\text{cm}^{-1}, \ldots$, and the fluorescence spectrum of the same molecule between the same two electronic states consists of a series of lines with wave numbers 41261. cm^{-1}, 39501. cm^{-1}, 37741. $\text{cm}^{-1}, \ldots$. Let τ_{gs} be the vibrational period of the ground state of AgH and let τ_{es} be the vibrational period of the excited state of AgH. Assuming both states are well represented by harmonic forces, calculate the ratio τ_{es}/τ_{gs}.
Answer:
Ground State

$$\nu_{gs} = \Delta\nu_{photons} = (41261.\ \text{cm}^{-1} - 39501.\ \text{cm}^{-1})(2.998 \times 10^{10}\ \text{cm s}^{-1}) = 5.276 \times 10^{13}\ \text{s}^{-1}$$

$$\tau_{gs} = \frac{1}{\nu_{gs}} = 1.895 \times 10^{-14}\ \text{s}$$

Excited State

$$\nu_{es} = \Delta\nu_{photons} = (42850.\ \text{cm}^{-1} - 41261.\ \text{cm}^{-1})(2.998 \times 10^{10}\ \text{cm s}^{-1}) = 4.764 \times 10^{13}\ \text{s}^{-1}$$

$$\tau_{es} = \frac{1}{\nu_{es}} = 2.099 \times 10^{-14}\ \text{s}$$

$$\frac{\tau_{es}}{\tau_{gs}} = \frac{2.099}{1.895} = 1.108$$

15. The electronic absorption spectrum of the gas-phase zirconium oxide (ZrO) molecule consists of a series of lines with wave numbers 15333. cm^{-1}, 16192. cm^{-1}, 17051. $\text{cm}^{-1}, \ldots$, and the fluorescence spectrum of the same molecule between the same two electronic states consists of a series of lines with wave numbers 15333. cm^{-1}, 14363. cm^{-1}, 13394. $\text{cm}^{-1}, \ldots$. Let τ_{gs} be the vibrational period of the ground state of ZrO and let τ_{es} be the vibrational period of the excited state of ZrO. Assuming both states are well represented by harmonic forces, calculate the ratio τ_{es}/τ_{gs}.

Answer:
Ground State

$$\nu_{gs} = \Delta\nu_{photons} = (15333.\ \text{cm}^{-1} - 14363.\ \text{cm}^{-1})(2.998 \times 10^{10}\ \text{cm s}^{-1}) = 2.908 \times 10^{13}\ \text{s}^{-1}$$

$$\tau_{gs} = \frac{1}{\nu_{gs}} = 3.439 \times 10^{-14}\ \text{s}$$

Excited State

$$\nu_{es} = \Delta\nu_{photons} = (16192.\ \text{cm}^{-1} - 15333.\ \text{cm}^{-1})(2.998 \times 10^{10}\ \text{cm s}^{-1}) = 2.575 \times 10^{13}\ \text{s}^{-1}$$

$$\tau_{es} = \frac{1}{\nu_{es}} = 3.883 \times 10^{-14}\ \text{s}$$

$$\frac{\tau_{es}}{\tau_{gs}} = \frac{3.883}{3.439} = 1.129$$