

1. 40 points.

- (a) When $^{12}\text{C}^{32}\text{S}$ is excited from its $X^1\Sigma^+$ ground state to the $A^1\Sigma^+$ excited state, the bond length increases from 1.535 Å to 1.944 Å. The ground state rotational constant is 0.8200 cm^{-1} . Find the excited state value of B . **Solution:**

$$B(A) = \frac{\hbar^2}{2\mu R(A)^2} = \frac{\hbar^2}{2\mu R(X)^2} \left(\frac{R(X)}{R(A)}\right)^2 = B(X) \left(\frac{R(X)}{R(A)}\right)^2 = (0.8200\text{ cm}^{-1}) \left(\frac{1.535}{1.944}\right)^2 = \boxed{0.5113\text{ Å}}$$

- (b) Identify the strongest bonding interaction you would expect for each pair of atoms and/or molecules listed below.

i. Ar and Ar: no charges or dipoles so dispersion

ii. HF and Kr: polar HF induces dipole in Kr so dipole-induced dipole

iii. Na^+ and N_2 : ion induces dipole in Na^+ so monopole-induced dipole

iv. NH_3 and Cl^- : Cl^- is charged, NH_3 is polar so monopole-dipole

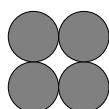
v. HI and NH_3 : both polar so dipole-dipole

- (c) Estimate the dispersion energy in kJ/mol between two naphthalene molecules ($\alpha = 17.5\text{ Å}^3$, $\Delta E \approx 8\text{ eV}$) at a separation of 6.5 Å. **Solution:**

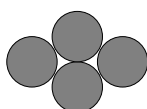
$$-(17.5\text{ Å}^3)^2(8\text{ eV})(96.4\text{ kJ mol}^{-1}/\text{eV})/[8(6.5\text{ Å})^6] = \boxed{-0.39\text{ kJ/mol}}$$

- (d) Four geometries for the Ar_4 cluster are sketched below. Number them from 1 to 4 in order of decreasing stability, so that 1 is the **most stable** and 4 is the **least stable**.

square planar



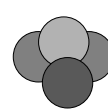
rhomboidal



linear



tetrahedral



Solution: The most stable should have the most pair interactions (atoms in direct contact). The square has 4 interactions, the rhomboidal has 5, linear has 3, tetrahedral has 6. The order is tet (1), rhom (2), square (3), linear (4).

2. The spacing between the $R(0)$ and $R(1)$ lines of the $v = 0 \rightarrow 1$ transition of $^{12}\text{C}^{16}\text{O}$ and the $v' - 1 \rightarrow v'$ transition of $^{14}\text{N}^{16}\text{O}^+$ are almost exactly equal. Find the upper state v' of the $^{14}\text{N}^{16}\text{O}^+$ transition.

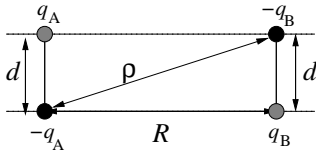
Solution: The vibration-rotation coupling term $-\alpha_e J(J+1)(v+1/2)$ effectively reduces the value of the rotational constant as v increases, so the spacing between the lines gets smaller. We use the equation for the transition energies in the R -

branch to get the spacing Δ between $R(0)$ and $R(1)$ as a function of v' :

$$\begin{aligned}\Delta E[R(0)] &= \omega_e - 2v'\omega_e x_e + 2(1)B_e - (1)(2v' + 1)\alpha_e \\ \Delta E[R(1)] &= \omega_e - 2v'\omega_e x_e + 2(2)B_e - (2)(2v' + 2)\alpha_e \\ \Delta(\text{NO}^+) &= \Delta E[R(1)] - \Delta E[R(0)] \\ &= [4 - 2]B_e - [(4v' + 4) - (2v' + 1)]\alpha_e = 2B_e - (2v' + 3)\alpha_e = \Delta(\text{CO}) \\ \Delta(\text{CO}) &= 2(1.9313 \text{ cm}^{-1}) - (5)(0.0175 \text{ cm}^{-1}) = 3.7751 \text{ cm}^{-1} \\ v' &= \frac{1}{2} \left[\frac{2B_e - \Delta(\text{CO})}{\alpha_e} - 3 \right] = \frac{1}{2} \left[\frac{2(1.9982) - 3.7751}{0.0190} - 3 \right] = 4.3\end{aligned}$$

Rounding to the nearest integer gives $v' = 4$. For the $v = 3 \rightarrow 4$ transition in $^{14}\text{N}^{16}\text{O}^+$, $\Delta = 3.79 \text{ cm}^{-1}$, compared to 3.78 cm^{-1} for $^{12}\text{C}^{16}\text{O}$.

3. Derive a formula in terms of μ_A , μ_B , and R for two polar molecules with their dipoles aligned **in parallel**. **Solution:**



We combine the Coulomb potential energies for the four interactions between the two molecules, where the distance ρ between charges of the same sign is $\sqrt{R^2 + d^2}$:

$$\begin{aligned}u(R) &= \frac{1}{4\pi\epsilon_0} \left[\frac{-q_A q_B}{R} + \frac{-q_A q_B}{R} + \frac{q_A q_B}{(R^2 + d^2)^{1/2}} + \frac{q_A q_B}{(R^2 + d^2)^{1/2}} \right] \\ &= \frac{1}{4\pi\epsilon_0} \left[\frac{-2q_A q_B}{R} + \frac{2q_A q_B}{(R^2 + d^2)^{1/2}} \right] = \frac{-2q_A q_B}{(4\pi\epsilon_0)R} \left[1 - \left(1 + \frac{d^2}{R^2} \right)^{-1/2} \right] \\ &\approx \frac{-2q_A q_B}{(4\pi\epsilon_0)R} \left[1 - \left(1 - \frac{d^2}{2R^2} \right) \right] = \frac{-2q_A q_B}{(4\pi\epsilon_0)R} \left(\frac{d^2}{2R^2} \right) = \frac{-\mu_A \mu_B}{(4\pi\epsilon_0)R^3}\end{aligned}$$

4. Find the potential energy due to dispersion between two electrons trapped in one-dimensional boxes of length a and separated by a distance R , under the same approximations we used to obtain our (more general) expression for the dispersion energy. **Solution:** The idea is to find an expression for u_{disp} before we plugged in the polarizabilities, and then use the expressions we know for the particle in a box to evaluate anything we need. One equation to start from would be Eq. 9.30, which depends on the wavefunctions and energies of the system:

$$\begin{aligned}u_{\text{disp}}(R) &\approx \frac{e^4}{(4\pi\epsilon_0)^2 R^6} \frac{[\int \psi_{A1} z_A \psi_{A2} dz_A]^2 [\int \psi_{B1} z_B \psi_{B2} dz_B]^2}{(E_{A1} + E_{B1}) - (E_{A2} + E_{B2})} \\ &= \frac{e^4}{(4\pi\epsilon_0)^2 R^6} \frac{[(\frac{2}{a}) \int_0^a \sin(\frac{\pi z_A}{a}) \sin(\frac{2\pi z_A}{a}) z_A dz_A]^2 [(\frac{2}{a}) \int_0^a \sin(\frac{\pi z_B}{a}) \sin(\frac{2\pi z_B}{a}) z_B dz_B]^2}{(2 - 8)\pi^2 \hbar^2 / (2ma^2)}.\end{aligned}$$

That's an adequate solution. The integrals turn out to each be equal to $8a^2/(9\pi^2)$, so the final value is

$$u_{\text{disp}}(R) \approx -\frac{[32a/(9\pi^2)]^4 e^4}{6\pi^2 (4\pi\epsilon_0)^2 \hbar^2 R^6 / (2ma^2)} = -\frac{2(32/9)^4 a^6 m e^4}{6\pi^{10} (4\pi\epsilon_0)^2 \hbar^2 R^6} = -\frac{2(32/9)^4 a^6}{6\pi^{10} R^6} E_h$$