Chemistry 410A   **Exam 6**   **Spring 2016**
Solutions

1. **40 points.**

   (a) Name the process (for example, "collisional relaxation") that occurs in each of the experiments described below:

      i. Benzene is excited to its $^3B_{1u}$ excited state, which emits light over a period of several seconds to return to the singlet ground state. $\boxed{\text{phosphorescence}}$

      ii. When the N—H stretches of alanine, $NH_2CH(CH_3)COOH$, are highly excited by infrared radiation, within a few vibrational periods the C—H bonds in the CH_3 group have started to stretch. $\boxed{\text{vibrational relaxation}}$

      iii. This one has **2** processes. A sample of acetylene is excited by laser radiation at $187\,\text{nm}$. After approximately $10^{-10}\,\text{s}$, radiation is observed from an allowed emission transition in hydrogen atom. (The duration of a typical molecular vibration is about $10^{-12}\,\text{s}$). $\boxed{\text{predissociation, followed by fluorescence}}$

   (b) Estimate the following energies.

      i. The $v = 3 \to 5$ transition energy for a molecule with a vibrational constant of $1000\,\text{cm}^{-1}$.
      Solution: $E_{\text{vib}} = \omega_e(v + \frac{1}{2})$:

      $$\Delta E = \left[\left(5 + \tfrac{1}{2}\right) - \left(3 + \tfrac{1}{2}\right)\right] = 2\omega_e = \boxed{2000\,\text{cm}^{-1}.}$$

      ii. The $J = 3 \to 5$ transition energy for a molecule with a rotational constant of $1.0\,\text{cm}^{-1}$.
      Solution: $E_{\text{rot}} = B_e J(J + 1)$:

      $$\Delta E = B_e\left[5(5 + 1) - 3(3 + 1)\right] = B_e(30 - 12) = 18B_e = \boxed{18\,\text{cm}^{-1}.}$$

   (c) The ground state vibrational constant of $^{65}Cu^{35}Cl$ is $415.3\,\text{cm}^{-1}$. Estimate the force constant in SI units (two significant digits is fine). **Solution:**

   $$\omega_e\,(\,\text{cm}^{-1}) = 130.28\sqrt{\frac{k\,(\,\text{N m}^{-1})}{\mu\,(\,\text{amu})}}$$

   $$k\,(\,\text{N m}^{-1}) = \mu\,(\,\text{amu})\left(\frac{\omega_e\,(\,\text{cm}^{-1})}{130.28}\right)^2 = (22.75)\left(\frac{415.3}{130.28}\right)^2 = \boxed{231\,\text{N m}^{-1}.}$$

   (d) The interaction energy between two rotating water molecules averages to $-1.0\,\text{kJ mol}^{-1}$. If the distance between them is cut in half, what is the new interaction energy? **Solution:** Because $\langle u_{2-2}(R)\rangle$ is proportional to R^{-6}, if R *decreases* by a factor of 2, then the magnitude of the potential energy *increases* by $2^6 = 64$, so the energy is now $\boxed{-64\,\text{kJ mol}^{-1}.}$

2. A molecule with the molecular formula N_xH_y has the following complete set of predicted vibrational constants, with the symmetry representations given:

$$
\begin{array}{lll}
1347\,\text{cm}^{-1} & a_u & \text{out-of-plane bend} \\
1360\,\text{cm}^{-1} & b_u & \text{antisymmetric N-H bend} \\
1601\,\text{cm}^{-1} & a_g & \text{symmetric N-H bend} \\
1651\,\text{cm}^{-1} & a_g & \text{N-N stretch} \\
3220\,\text{cm}^{-1} & a_g & \text{symmetric N-H stretch} \\
3252\,\text{cm}^{-1} & b_u & \text{antisymmetric N-H stretch}
\end{array}
$$

(a) How many atoms are in the molecule? **Solution:** The molecule must be non-linear (since the representations are labeled by a's and b's). $3N_{\text{atom}} - 6 = 6$ so $N_{\text{atom}} = 12/3 = \boxed{4.}$

(b) What is the molecular formula (in other words, what are the values of x and y)? **Solution:** The only possibilities for the molecular formula with four atoms are NH_3, N_2H_2, and N_3H. From the g and u labels on the representations, we know that inversion must be an element of the point group. Inversion will exchange the locations of pairs of equivalent atoms, and only an atom at the origin will be left unaffected. Therefore, all the atoms but one (if there is one ta the origin) must occur in equivalent pairs. Only $\boxed{N_2H_2}$ makes this possible.

(c) What is the point group of the molecule? **Solution:** The a and b labels also tell us that there is rotational symmetry. Since the atoms of N_2H_2 occur in pairs, the rotation axis must be a $\hat{C}_2$ rotation. The only possible point groups for N_2H_2 with $\hat{C}_2$ proper rotation are C_{2v} and C_{2h}, and of these only $\boxed{C_{2h}}$ has $\hat{I}$.

(d) Draw a Lewis structure of the molecule. **Solution:**
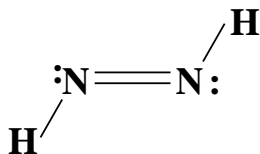
(e) For **four** of the vibrational modes in the list above, either label the type of motion *clearly* or sketch a picture showing the displacement arrows for the mode.

3. The Morse oscillator has energy levels $E_v = \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2$ where $\omega_e x_e = \omega_e^2/(4D_e)$. Find the value of v, in terms of ω_e and D_e, at which the $v \to v+1$ transition energy becomes zero. Then find the value of E_v for this vibrational state in terms of ω_e and D_e. **Solution:**

$$\Delta E = \left[\omega_e \left(v + \frac{3}{2}\right) - \omega_e x_e \left(v + \frac{3}{2}\right)^2\right] - \left[\omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2\right]$$

$$= \omega_e \left[\left(v + \frac{3}{2}\right) - \left(v + \frac{1}{2}\right)\right] - \omega_e x_e \left[\left(v^2 + 3v + \frac{9}{4}\right) - \left(v^2 + v + \frac{1}{4}\right)\right]$$

$$= \omega_e - 2\omega_e x_e (v + 1) = 0$$

$$v = \frac{\omega_e}{2\omega_e x_e} - 1 = \frac{4D_e \omega_e}{2\omega_e^2} - 1 = \boxed{\frac{2D_e}{\omega_e} - 1}$$

$$E = \omega_e \left(v + \frac{1}{2}\right) - \omega_e x_e \left(v + \frac{1}{2}\right)^2$$

$$= \omega_e \left[\left(\frac{2D_e}{\omega_e} - 1\right) + \frac{1}{2}\right] - \frac{\omega_e^2}{4D_e} \left[\frac{2D_e}{\omega_e} - \frac{1}{2}\right]^2$$

$$= 2D_e - \frac{1}{2}\omega_e - \frac{\omega_e^2}{4D_e} \left[\left(\frac{2D_e}{\omega_e}\right)^2 - \frac{2D_e}{\omega_e} + \frac{1}{4}\right]$$

$$= 2D_e - \frac{1}{2}\omega_e - \frac{\omega_e^2}{4D_e} \left[\frac{4D_e^2}{\omega_e^2} - \frac{2D_e}{\omega_e} + \frac{1}{4}\right]$$

$$= 2D_e - \frac{1}{2}\omega_e - D_e + \frac{\omega_e}{2} - \frac{\omega_e^2}{16D_e}$$

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$$= \boxed{D_e - \frac{\omega_e^2}{16D_e}}.$$

This energy is very close to the dissociation limit, so at the point the energy levels converge, the molecule falls apart.

4. The distribution of charges given below is the same as we used to derive the formula for $u_{2-2}(R)$, except that one of the charges on molecule B has been doubled. Find an expression for the potential energy $u(R)$ between A and B in terms of μ_A, q_B, and R.
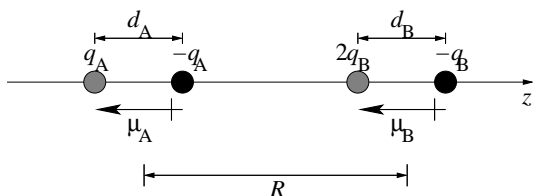
Solution:

$$u(R) = -\frac{\mu_A(2q_B)}{4\pi\epsilon_0\left(R - \frac{d_B}{2}\right)^2} + \frac{\mu_A q_B}{4\pi\epsilon_0\left(R + \frac{d_B}{2}\right)^2}$$

$$= \frac{\mu_A q_B}{4\pi\epsilon_0 R^2}\left[-2\left(1 - \frac{d_B}{2R}\right)^{-2} + \left(1 + \frac{d_B}{2R}\right)^{-2}\right]$$

$$\approx \frac{\mu_A q_B}{4\pi\epsilon_0 R^2}\left[-2\left(1 + 2\frac{d_B}{2R}\right) + \left(1 - 2\frac{d_B}{2R}\right)\right]$$

$$= \frac{\mu_A q_B}{4\pi\epsilon_0 R^2}\left[-2 - \frac{2d_B}{R} + 1 - \frac{d_B}{R}\right]$$

$$= \frac{\mu_A q_B}{4\pi\epsilon_0 R^2}\left[-1 - 3\frac{d_B}{R}\right]$$

$$= -\frac{\mu_A q_B}{4\pi\epsilon_0 R^2} - \frac{\mu_A(3q_B d_B)}{4\pi\epsilon_0 R^3}.$$

This is the same as the monopole-dipole energy for the interaction between μ_A and $-q_B$ (the net charge on B) plus the dipole-dipole energy for the interaction between μ_A and a dipole of strength $\mu_B = \frac{3}{2}q_B d_B$.