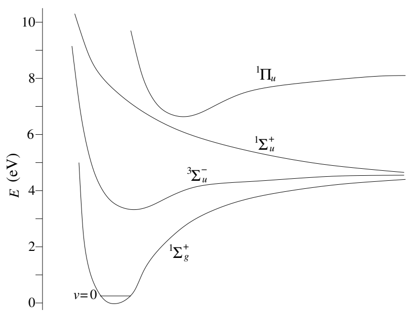
Chemistry 410A **Exam 6** **Fall 2011**

Solutions

1. **40 points.**

(a) Given the set of potential energy curves drawn below, what is the likeliest process to be induced by radiation at a photon energy of 8.0 eV, starting from the $v = 0$ state shown? Identify any of the electronic states involved.



Solution: $\boxed{\text{photodissociation from } ^1\Sigma_u^+.}$ Transition to the $^3\Sigma_u^-$ is forbidden, so not likely. The transition to the $^1\Pi_u$ is allowed, but because the transition must occur vertically from $v = 0$, 8.0 eV is not enough energy to reach that state. The transition to the dissociating $^1\Sigma_u^+$ state is both allowed and within the energy range of the photon.

(b) The vibrational constant of $^{14}N_2$ in the $^3\Delta_u$ excited state is 1539 cm^{-1}. Find the force constant in SI units to three significant digits. **Solution:**

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

$$k = \left(\frac{\omega_e\,(\mathrm{cm}^{-1})}{130.28}\right)^2 \mu\,(\mathrm{amu}) = \left(\frac{1539}{130.28}\right)^2 (7.000) = \boxed{977\,\mathrm{N\,m^{-1}}.}$$

(c) Using the table of vibrational and rotational constants attached to the exam, calculate the total energy in rotation and vibration of the $v = 0, J = 10$ state of $^{12}C^{16}O$, including any corrections for which the data is available. **Solution:**

$$\begin{aligned} E_{\mathrm{vib}} &= \omega_e\left(v + \tfrac{1}{2}\right) - \omega_e x_e\left(v + \tfrac{1}{2}\right)^2 \\ &= (2169.82\,\mathrm{cm}^{-1})(0.5) - (13.29\,\mathrm{cm}^{-1})(0.5)^2 = 1081.59\,\mathrm{cm}^{-1} \\ E_{\mathrm{rot}} &= [B_e - \alpha_e(v + \tfrac{1}{2})]J(J+1) - D_v[J(J+1)]^2 \\ &= [(1.9313\,\mathrm{cm}^{-1}) - (0.0175\,\mathrm{cm}^{-1})(0.5)](10)(11) - (6 \cdot 10^{-6}\,\mathrm{cm}^{-1})[(10)(11)]^2 = 211.41\,\mathrm{cm}^{-1} \end{aligned}$$

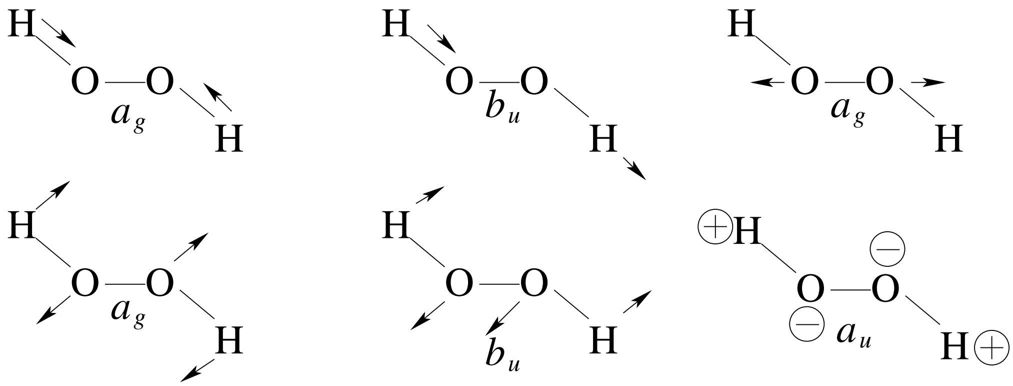
$$E_{\mathrm{vib}} + E_{\mathrm{rot}} = (1081.59 + 211.41)\,\mathrm{cm}^{-1} = \boxed{1293.00\,\mathrm{cm}^{-1}.}$$

2. Hydrogen peroxide, HOOH, has the structure shown below.

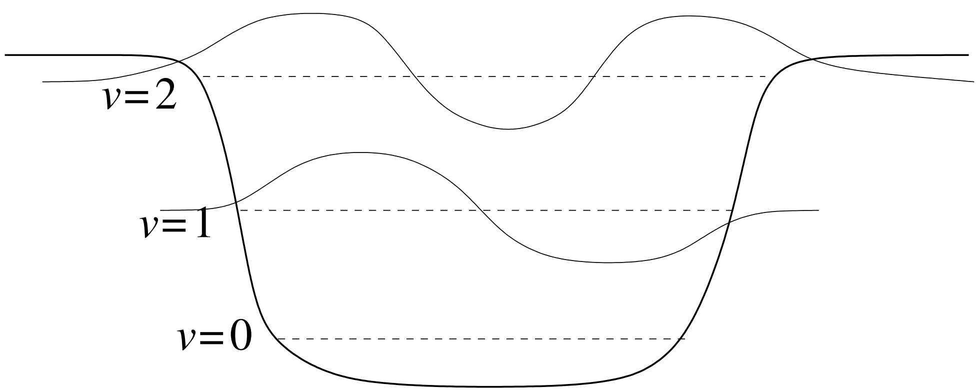
(a) How many vibrational modes does HOOH have? **Solution:** $3N_{\mathrm{atom}} - 6 = \boxed{6.}$

(b) Draw displacement arrows for each mode on the structures below.

(c) Label the representation for each mode.



3. The $v = 0$ state of a vibrational mode is shown on the potential energy curve below. Sketch as accurately as you can the energy levels and wavefunctions of the $v = 1$ and $v = 2$ states.



4. We found a formula for the potential energy of interaction for two fixed dipoles that were co-aligned. Use the same approach to find the potential energy as a function of R and in terms of the dipole moments μ_A and μ_B for the case when the two dipole moments are parallel. **Solution:** The distance q_A to $-q_B$ and $-q_A$ to q_B is R. Set R' equal to the distance q_A to q_B and $-q_A$ to $-q_B$. Then $R' = \sqrt{R^2 + d^2}$. The rest opf the analysis follows the same strategy as for obtaining the dipole-dipole interaction potential:

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