## ChemE 2200 - Physical Chemistry II for Engineers – Spring 2025 Solution to Homework Assignment 3

- 1. The key feature is the extent of the envelope of peak heights, compared on the energy scale, as given by the equation  $(2J + 1)\exp(-E_J/kT)$ . Although differences in the rotational constant affect the envelope, these differences are minor. The two spectra with the most similar peak envelopes are A and D.
- 2. One needs to determine the positions and intensities of peaks in the NO vibration-rotation *emission* spectrum. It is useful to draw an energy level diagram showing the allowed transitions, as shown below.



NO vibration-rotation emission transitions

The center of the spectrum, the Q branch, is at  $1876.0 \text{ cm}^{-1}$ .

The peaks corresponding to  $\Delta J = \pm 1$  transitions are spaced around  $\tilde{v}_Q$  at intervals of 2B = 3.4 cm<sup>-1</sup>.

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$$\frac{N_n}{N_0} = \frac{(2J+1)\exp\left[-\frac{BJ(J+1)hc}{kT}\right]}{(2\times0+1)\exp[0]}$$
  
=  $(2J+1)\exp\left[-\frac{(1.705 \text{ cm}^{-1})J(J+1)(6.63\times10^{-34} \text{ J} \cdot \text{sec})(3\times10^{10} \text{ cm}/\text{sec})}{(1.38\times10^{-23} \text{ J} \text{ K}^{-1})(2 \text{ K})}\right] = (2J+1)\exp[-1.2J(J+1)]$ 

Make a table of the relative populations.

J=0 state. Use the Boltzmann distribution at 2 K.

J	$N_{\rm J}/N_0$
0	1.0
1	0.26
2	0.003
3	0.000003
4	$2 \times 10^{-10}$

Finally, combine these intensities with the peak positions and sketch a spectrum.



The peaks are evenly spaced at 3.4 cm<sup>-1</sup> with the center peak (the Q branch) at 1876.0 cm<sup>-1</sup>. The relative intensity is determined by the population of the initial state. For example, the peaks corresponding to the  $1\rightarrow 2$  and the  $1\rightarrow 0$  peaks are the same intensity.

- 3.(A) The dissociation energy of AZ in its electronic ground state can be estimated from the emission spectrum. The high energy peak at 4.0 eV represents transitions from v' = 0 to v = 0. The low energy peak at 1.2 eV represents transitions from v' = 0 to the vibrational level at the top of the ground state potential. Thus the ground state well has a depth of about 4.0 1.2 = 2.8 eV.
- (B) The dissociation energy of AZ in its first electronic excited state can be estimated from the absorption spectrum. The lowest energy peak at 4.0 eV represents transitions from v = 0 to v' = 0. The highest energy peak at 6.4 eV represents transitions from v = 0 to the vibrational level at the top of the excited state potential. Thus the first electronic excited state well has a depth of about 6.4 4.0 = 2.4 eV.

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- (C) The first two peaks in the emission spectrum correspond to transitions from v' = 0 to v = 0 and transitions from v' = 0 to v = 1. So the energy separation between these two peaks is the difference between v = 0 and v = 1, which is the vibrational constant for harmonic potentials (a good approximation for the actual anharmonic potentials). If we ignore any anharmonicity correction, the difference is just the vibrational constant,  $\tilde{v}$ . The first peak is at 4.0 eV and the second peak is at 3.7 eV, so the vibrational constant is about 0.3 eV = 2400 cm<sup>-1</sup>.
- (D) The first two peaks in the absorption spectrum correspond to transitions from v = 0 to v' = 0 and transitions from v = 0 to v' = 1. So the energy separation between these two peaks is the difference between v' = 0 and v' = 1, which is approximately the vibrational constant *v*. If we ignore the anharmonicity correction, the difference is just the excited state vibrational constant,  $\tilde{v}$  '. The first peak is at 4.0 eV and the second peak is at 4.2 eV, so the vibrational constant is about 0.2 eV = 1600 cm<sup>-1</sup>.
- (E) The strongest absorption is from v = 0 to v' = 0 and the strongest emission is from v' = 0 to v = 0. Thus the two lowest vibrational states in each well are at approximately the same internuclear distance,  $R'_{eq} \approx R_{eq}$ .
- (F) We need to estimate the difference between the potential wells at large internuclear separation. The distance from the bottom of the first electronic excited state well to the dissociation limit is 2.4 eV. The distance from the top of the ground state well to the bottom of the first electronic excited state well is 1.2 eV (the lowest energy peak in the emission spectrum). Thus the distance between the potential wells at large internuclear separation is 1.2 + 2.4 = 3.6 eV.
- 4.(A) The process begins with the absorption of a photon from the ground state. The most likely internuclear distance of the ground state is the center of the well. The internuclear distance is constant during the absorption (Franck-Condon principle) and the most likely transition is to v' = 3, the vibrational level whose classical turning radius equals the equilibrium bond length.

Molecular collisions cause the vibrational level to decay to v' = 0 without emission of photons. From the v' = 0 level the molecule emits a photon and falls to the ground electronic level and the most likely vibrational level is v = 2. Finally, collisions relax the molecule to the v = 0 vibrational level.



<sup>(</sup>B) Fluorescence.

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(C) The most probable transition has the most intense peak. There are three peaks at lower energy and 4 peaks at higher energy. Above 15.5 eV there is a continuum of peaks.



(D) The emission transitions all originate in the v' = 0 level of the electronic excited state. The strongest transition is from v' = 0 to v = 2, which is 10 eV. The lowest energy peak is at 3 eV.



(E) Absorption of an infrared photon promotes a molecule to the v = 1 vibrational level of the ground electronic state. The probability density for the v = 1 state has two maxima. Absorption of a UV photon when the molecule is at the shorter bond distance promotes the molecule above the dissociation limit of the electronic excited state, as shown below by the longer arrow.

Excitation from the longer-bond maximum results in fluorescence, as in part (A).



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