NAME:_____
(please print)

Chemistry 237 — Tellinghuisen
Second Exam — 4/29/10

Honor Code Pledge: I have neither given nor received aid on this exam. _____
(Signature)

A. (25 points) For this question, refer to the accompanying potential diagram (below) for a hypothetical diatomic molecule.

1. Using this diagram, give numerical estimates of T_e, R_e, ω_e, D_e, and D_0 for the X and B electronic states.
2. What is the photodissociation limit (in cm^{-1}) for $B \leftarrow X$ absorption from (a) $\upsilon'' = 0$, and (b) $\upsilon'' = 1$?
3. On the basis of the Franck-Condon principle, do you expect to see significant $B \leftarrow X$ absorption in the region of the photodissociation limit, for absorption at room T? Explain briefly.
4. Estimate the fraction of molecules in level $\upsilon'' = 1$ in thermal equilibrium at (a) 300 K, and (b) 3000 K.

B. (25) For the ground state (X) of $^{131}Xe^{19}F$, $\omega_e = 225.40\ cm^{-1}$, $\omega_e x_e = 10.874\ cm^{-1}$, $B_e = 0.1933\ cm^{-1}$, and $\alpha_e = 0.00699\ cm^{-1}$.

1. Calculate the internuclear distance R_e. [Hint: To avoid messy constants, just use the mass numbers. Also, take advantage of the following information: For I_2 (X) ($M_I = 126.9$), $B_e = 0.03736\ cm^{-1}$ and $R_e = 2.666$ Å.]
2. If B_e for $^{131}Xe^{19}F$ is uncertain by $0.0003\ cm^{-1}$, what is the percent uncertainty in R_e?
3. Estimate the dissociation energy D_e in the Morse approximation.
4. Calculate the centrifugal distortion constant D_e.
5. For $\upsilon = 2$, $D_\upsilon = 9.62\times10^{-7}\ cm^{-1}$. Estimate the centrifugal distortion energy for $\upsilon = 2$, $J = 60$.
6. Calculate the wavenumber of the R(25) line in the first overtone band of the rotation-vibration spectrum. (Neglect centrifugal distortion here.)

C. (25) **Absorption, Beer's Law, and Uncertainty.**

1. At 22°C the vapor pressure of $I_2(g)$ is 0.238 torr. A 20.3-cm gas cell containing I_2 vapor at 22°C shows an absorbance of 0.134 at 490 nm. Calculate the transmittance T and ε for $I_2(g)$ at 490 nm.
2. If I and I_0 are both uncertain by 1.3%, what is the percent uncertainty in their ratio, $T = I/I_0$?
3. Obtain an expression for the uncertainty in ε (s_ε) in terms of that in T, assuming negligible uncertainty in the concentration and path length. [Note: $10^x = \exp(\ln 10\, x)$]
4. Apply your results from 3 to the measurements in 1 to obtain the percent uncertainty in the estimated ε, assuming the 1.3% uncertainties in I and I_0 apply.

Fundamental Constants:

$N_0 = 6.022137\times10^{23}$/mol
$c = 2.99792458\times10^{10}$ cm/s
$h = 6.626076\times10^{-27}$ erg s
$e = 1.6021773\times10^{-19}$ C

$R = 1.98722$ cal K^{-1} mol^{-1}
$= 82.058\ cm^3\ atm\ K^{-1}\ mol^{-1}$
$= 8.31451$ J K^{-1} mol^{-1}
1 atm $= 1.0133\times10^6$ dyne/cm^2

D. (10) **Laser-Induced Fluorescence.** In the demonstration of LIF, we directed laser beams from a green laser pointer through cells containing (1) $I_2(g)$ at low pressure, and (2) $I_2(g)$ together with ~500 Torr Ar.

1. We observed an unexpected behavior when we used the green laser pointer with the low-*P* cell. Describe this behavior and tell how we explained it.
2. What did we see when the beam was directed through the cell containing Ar, and how did we explain it?

E. (25) **Diatomic Spectra.** Consider the $B \leftarrow X$ absorption spectrum of I_2 shown below. (This spectrum was recorded on the Shimadzu UV-visible spectrophotometer.) Several υ'–υ'' bands are marked.

1. Identify υ' and υ'' for each of the marked bands, a–d.
2. What is the *degradation* of the bands, violet or red? Hence, is the internuclear distance in the *B* state larger or smaller than that in the *X* state?
3. Give the wavelengths (to the nearest 0.1 nm) and wavenumbers (within 1 cm^{-1}) for the heads of each of the three identified bands. (Treat the wavelength scale as true, vacuum for the latter purpose.)
4. In this wavelength region, the air-vacuum wavelength difference (absolute) is about 1.57 Å. If you included this correction, what would be the wavenumber of the 15-0 band?
5. Again treating the wavelength scale as true vacuum, estimate $\Delta G_0''$ and $\Delta G_{20}'$.
6. Briefly discuss how the intensity patterns in the $\upsilon'' = 0$ and 1 progressions manifest the Franck-Condon reflection principle. On this basis, where do you expect to see the nearest $\upsilon'' = 2$ bands?