A. (40 points) For this question, refer to the accompanying potential diagram for a hypothetical diatomic molecule.

1. Consider the 11 indicated absorption transitions. Classify these according to the region of the spectrum in which they lie: UV, visible, IR, or far-IR.

2. Suppose the diagram is for the H₂ molecule. Classify the 11 illustrated transitions as forbidden, allowed, or allowed but very weak, in absorption at room T and P = 1 atm. In the case of forbidden or very weak transitions, very briefly explain your designation. (For present purposes assume that electronic and rotational selection rules are satisfied in transitions 1-7, where rotational and electronic designations are not given explicitly.)

3. Now suppose the diagram is for HF and repeat the classification scheme of Problem 2.

4. Describe how you could distinguish between electronic transitions of the type A ← X and B ← X from the qualitative appearance of the spectrum. (ignore absolute wavelength differences here.)

5. Suppose you could observe the B → X system in emission, with a thermal distribution of J' levels but with v' = 0 the only v' level significantly populated.

   (a) Use the Franck-Condon principle to predict qualitatively the intensity distribution for the various bands in the spectrum.

   (b) What is the degradation of the bands, red or violet?

B. (25) For the ground state (X) of ¹²C¹⁶O, \( \omega_e = 2169.8 \text{ cm}^{-1} \), \( \omega_{ex} = 13.3 \text{ cm}^{-1} \), \( B_e = 1.9310 \text{ cm}^{-1} \), and \( \alpha_e = 0.0180 \text{ cm}^{-1} \).

1. Calculate \( G_0 \) and \( B_0 \) for \( v = 3 \) and \( v = 4 \) (in units \( \text{cm}^{-1} \)).

2. Calculate the wavenumber of the R(6) transition between the two levels \( v = 3 \) and \( v = 4 \).

3. Calculate the equilibrium internuclear distance \( R_e \) and the force constant \( k_e \), for CO in its X state.

4. If the uncertainties in \( B_e \) and \( \omega_e \) are 0.0008 \( \text{cm}^{-1} \) and 0.4 \( \text{cm}^{-1} \), respectively, what are the uncertainties in \( R_e \) and \( k_e \)?

C. (10) What two essential properties are required to produce lasing from stimulated emission? How are these properties achieved in the He-Ne laser?

D. (15) Consider the H₂⁺ molecular ion.

1. Construct the lowest energy \( \phi_g \) and \( \phi_u \) molecular orbitals from 1s atomic orbitals centered on nuclei A and B. Describe the symmetry and bonding/antibonding properties of these orbitals.

2. Assuming the 1s orbitals are normalized, determine the normalization constants for the MOs in terms of the overlap integrals.

3. What is the ground configuration of H₂⁺? What is the first excited configuration?

4. What is the ground configuration of H₂?
E. (20) Attached below are spectra for two emission band systems observed for the XeCl molecule, with vibrational assignments indicated. This is a "positive" replication, so brighter corresponds to more intense, and darker to less. [Note: You may ignore the difference between air and vacuum wavelength below.]

1. Using these spectra and rulers to be provided, estimate (a) $\omega_e$, and (b) $T_e$ for all three electronic states.

2. What is the degradation (violet, red, or none) of the bands (in which rotational structure is not resolved)? From this, can you determine whether $R_e$ in the $B$ and $D$ states is smaller or larger than in the $X$ state? If so, give the result.

3. From the $D \rightarrow X$ spectrum estimate (to the nearest 100 cm$^{-1}$) $D_e$ for the $X$ state.

Fundamental Constants

- $k = 1.380658 \times 10^{-16}$ erg/K
- $N_0 = 6.022137 \times 10^{23}$/mol
- $R = 1.98722$ cal K$^{-1}$ mol$^{-1}$
  - $= 82.058$ cm$^3$ atm K$^{-1}$ mol$^{-1}$
  - $= 8.31451$ J K$^{-1}$ mol$^{-1}$
- $c = 2.99792458 \times 10^{10}$ cm/s
- $h = 6.626076 \times 10^{-27}$ erg s
- $e = 1.6021773 \times 10^{-19}$ C
- 1 atm = $1.0133 \times 10^6$ dyne/cm$^2$
- 1 cal = 4.184 J