

QUIZ 3

1. (30%) (0,12,6,12)

The vibrational wavenumber of the oxygen molecule in its ground electronic state ($X^3\Sigma_g^-$) is 1580 cm^{-1} , whereas that in its first excited state ($B^3\Sigma_u^-$), to which there is an allowed transition, is 700 cm^{-1} . The separation in energy between the minima in their respective potential energy curves of these two electronic states is 6.175 eV .

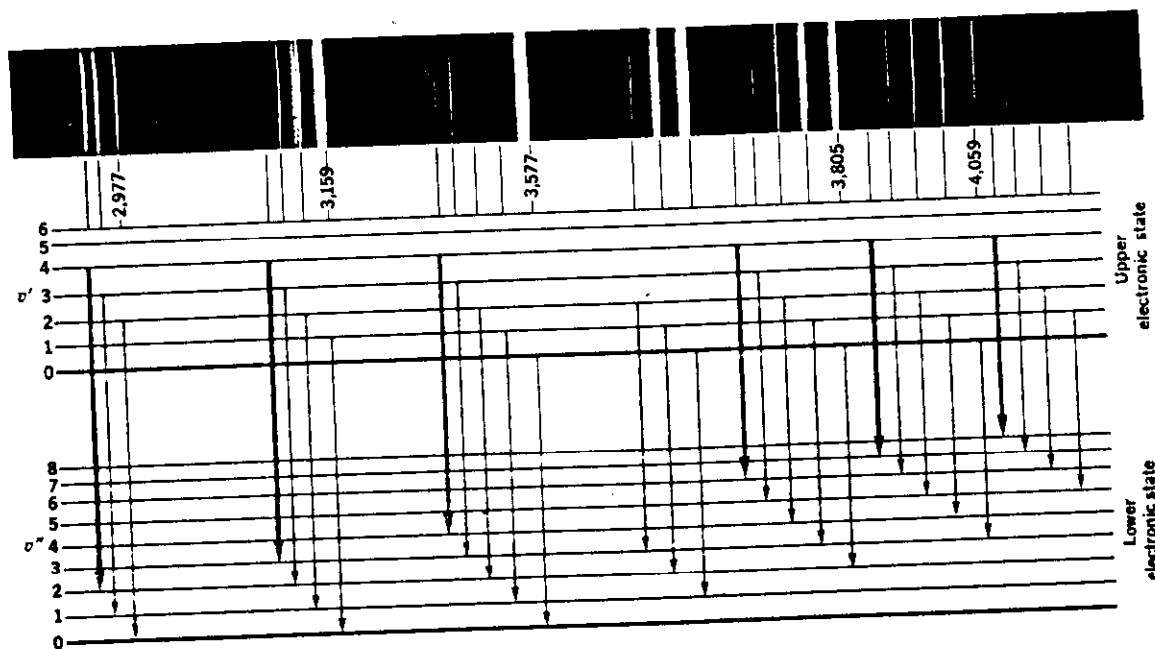
- a. Give the electronic configurations giving rise to these two terms.
- b. Calculate the wavenumber of the lowest energy transition in the band of transitions from the $v = 0$ vibrational state of the electronic ground state to this excited state. Illustrate the given and the required energy differences in a neat and clearly labeled diagram. (Ignore any rotational structure or anharmonicity)

A Birge-Sponer extrapolation yields 7760 cm^{-1} as the area under the curve for the B state of the oxygen molecule. The B state dissociates to ground-state atoms (at zero energy, 3P) and atoms at 15870 cm^{-1} (1D). Also, the lowest vibrational state of the B state is 49363 cm^{-1} above the lowest vibrational state of the ground electronic state.

- c. Write the electronic configurations for the two dissociative atomic states.
- d. Calculate the dissociation energy (eV) of the molecular ground state to the ground state atoms (3P). Illustrate your calculations in a diagram.

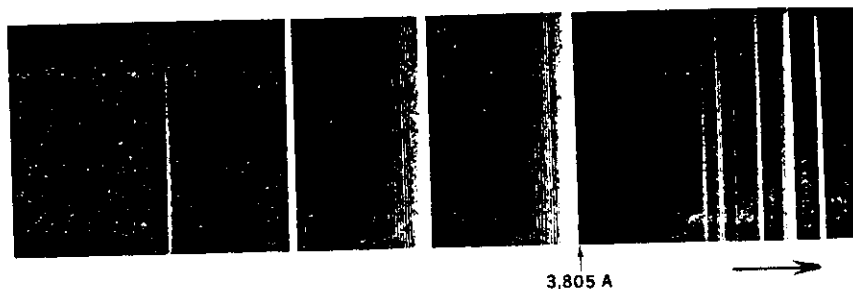
2. (33%) (12,7,9,5) The following diagram shows a portion of the electronic emission spectrum of N_2 , representing transitions between two electronic states.

- a. Setting the Franck-Condon factor of the most intense transition equal to unity, devise a method to estimate the Franck-Condon factors $\langle v'|v'' \rangle$ for the next six intense transitions.

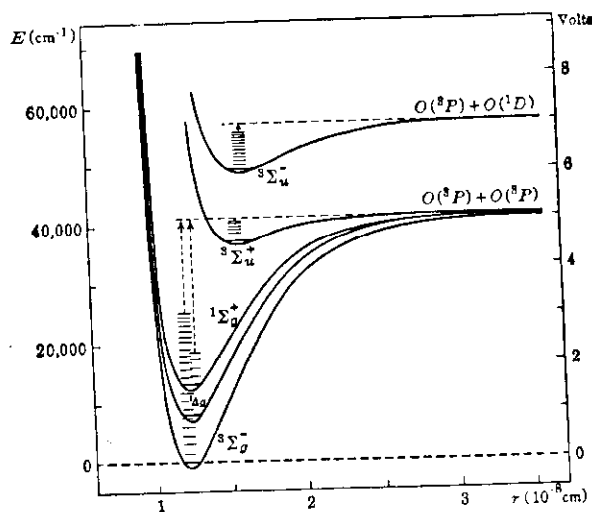


- b. Explain by sketching potential energy curves for the two states, those observed intensities.

Now consider the following high resolution component of an emission band in the spectrum.



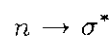
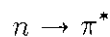
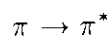
- c. Explain clearly the appearance of the thin lines. What information does this fine structure give us about the structure of the ground and excited electronic states? How does this result compare with the picture obtained in b.?
 - d. Sketch a Fortrat diagram representing the arrangement of the rotational lines.
3. (18%) Consider the following potential energy curves for the ground state and some excited electronic states of the O_2 molecule.



Write the electronic configuration (or explain it with the aid of a diagram) for each of the electronic states shown. Label each π orbital as either π_x or π_y and take the xz -plane as a reference molecular plane.

HINT: For O_2 The $2p \pi$ orbitals are higher in energy than the $2p \sigma$ orbital. Excitation involves only one electron and not necessarily from the highest energy MO.

4. (19%) (4,15) Consider the following transitions involving the p electrons in the carbonyl group of a formaldehyde molecule.



- a. Using the symmetry selection rules and ignoring vibronic coupling, indicate which transitions are allowed and which ones are forbidden.
- b. Now taking vibronic coupling into account, indicate in each case which vibrational mode(s) of the excited electronic state is accessible from the ground state, using y -polarized radiation.

Good Luck

USEFUL INFORMATION

Planck's constant $h = 6.626 \times 10^{-34}$ J s

Speed of light: $c = 2.998 \times 10^{10}$ cm s⁻¹

1 eV $\equiv 1.602 \times 10^{-19}$ J

Symmetry of the p electron molecular orbitals in formaldehyde

$\sigma(a_1)$ $\pi(b_1)$ $n(b_2)$ $\pi^*(b_1)$ $\sigma^*(a_1)$

Symmetry species for the fundamental vibrational modes of formaldehyde

| | |
|-----------------------|-------|
| ν_1, ν_2, ν_3 | a_1 |
| ν_4 | b_1 |
| ν_5, ν_6 | b_2 |

Symmetry species for the components of the electric dipole moment in the C_{2v} point group

| | |
|---------|-------|
| μ_x | B_1 |
| μ_y | B_2 |
| μ_z | A_1 |

$$\bar{\nu}_{P,R} = \bar{\nu}_{(v',v'')} + (B' + B'')p + (B' - B'')p^2$$

$$\bar{\nu}_Q = \bar{\nu}_{(v',v'')} + (B' - B'')q + (B' - B'')q^2$$