

Name: \_\_\_\_\_

Chemistry 5.04 (F 04)  
Exam 3

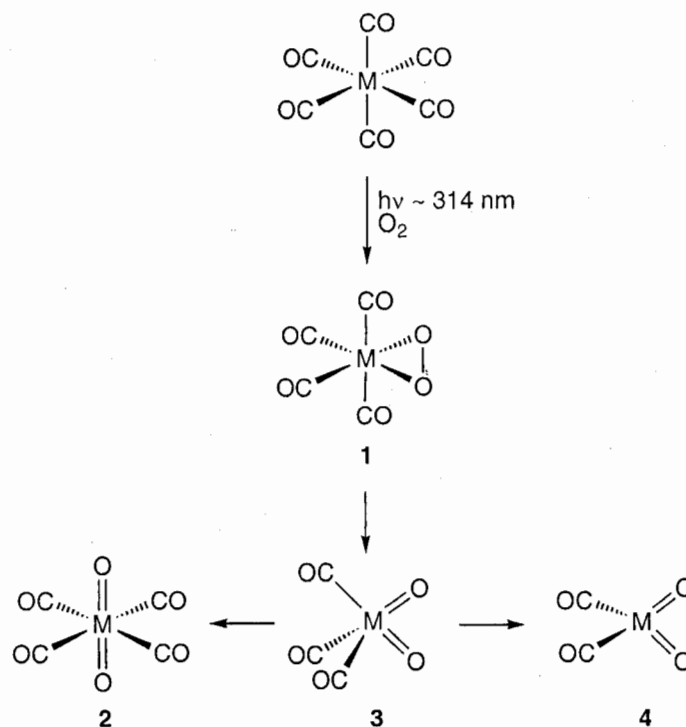
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Friday, 10 December

1. (10 pts) Titanium(I) has a ground-state electron configuration of  $[\text{Ar}]3d^24s^1$ . Normally, excited states are produced by the promotion of a single electron to  $[\text{Ar}]3d^14s^2$ . What is the lowest energy term for the  $[\text{Ar}]3d^24s^1$  ground state and the lowest energy term for the  $[\text{Ar}]3d^14s^2$  excited state? Remember that the lowest energy term will be of the highest S; for states of the same multiplicity, states with highest L will be lowest in energy.

2. (15 pts) For trigonal bipyramidal *trans*-CrCl<sub>3</sub>(NMe<sub>3</sub>)<sub>2</sub> (axial amines) complexes, three ligand field bands are observed in the absorption spectrum: 10,100, 17,600 and 30,200 cm<sup>-1</sup>. Assign the transitions.

3. When  $M(\text{CO})_6$  ( $M = \text{Cr}, \text{Mo}, \text{or W}$ ) complexes are irradiated in the presence of oxygen, dioxo compounds **2** and **4** are obtained. The reaction scheme is as follows,

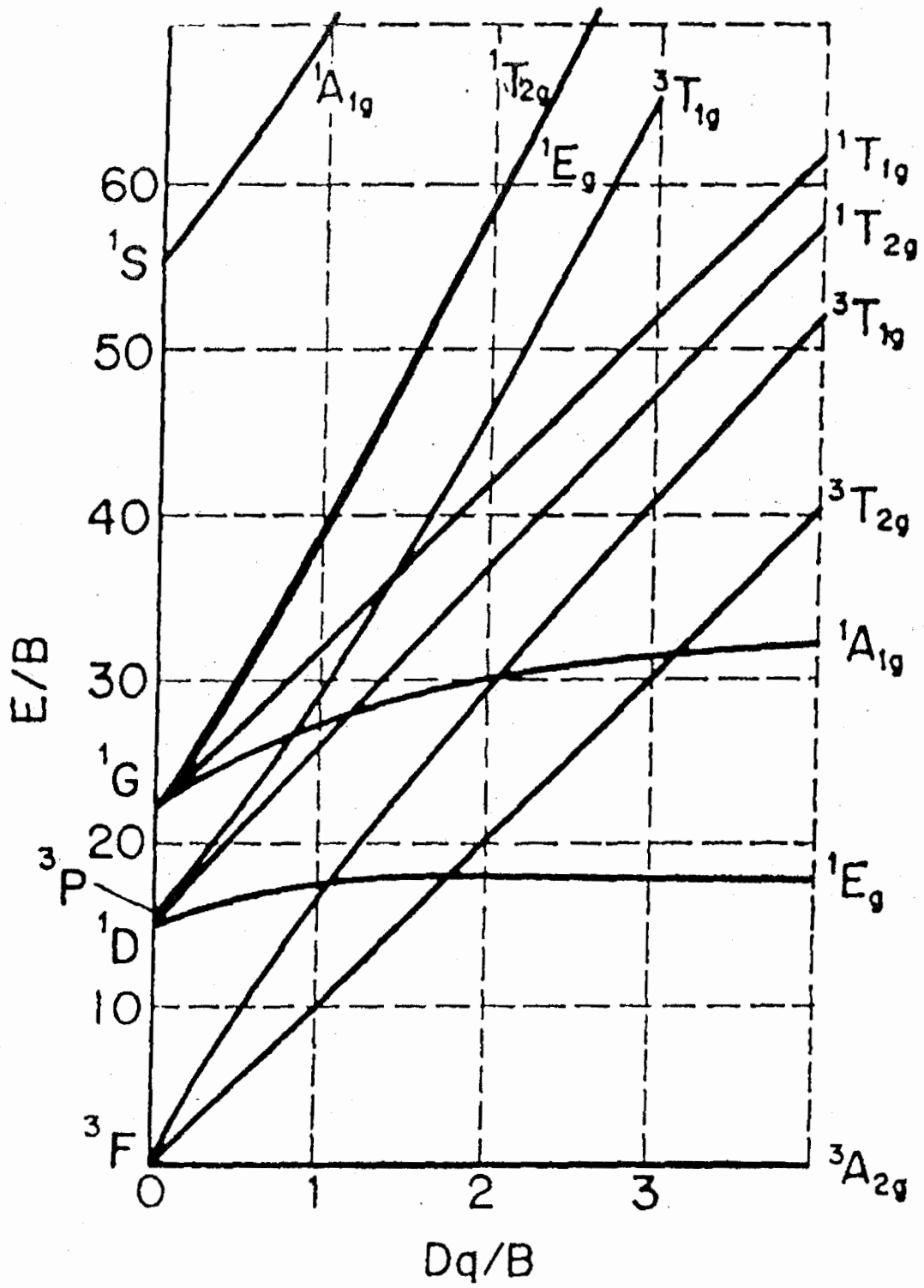


The final products **2** and **4**, and oxygenated intermediates **1** and **3** were identified by monitoring the number of CO stretches by Raman and infrared spectroscopy.

- (20 pts) Determine the symmetries for the normal modes of the C—O *stretching* vibrations for **1-4**.
- (16 pts) Of these, identify the modes that are Raman and infrared allowed.
- (9 pts) Show the symmetry coordinated for the CO stretching vibrations in **2**.

4. In 1926, jack bean urease became the first enzyme to be isolated in crystalline form. However, it was not until 49 years later that it was discovered that this urease is a metalloenzyme, containing two Ni(II) ions per 100,000 molecular weight. Measurement of the electronic spectrum of the enzyme played an important role in this discovery. The spectrum has  $\lambda_{\text{max}}$  values of 23,500, 13,800, and 9,400  $\text{cm}^{-1}$ , which have been assigned to ligand field transitions of an octahedral Ni(II) chromophore.

- (a) (25 pts) Using a Tanabe-Sugano diagram below, evaluate  $\Delta_o$  ( $10Dq$ ) and the B term ( $B = 1040 \text{ cm}^{-1}$  for free Ni(II)).
- (b) (5 pts) For  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Ni}(\text{en})_3]^{2+}$ ,  $\Delta_o = 8340$  and  $11,500 \text{ cm}^{-1}$ , respectively. On the basis of the  $\Delta_o$ s, suggest a composition for the coordination environment of the urease site.



The d<sup>8</sup> Tanabe-Sugano diagram