FINAL EXAM (SPECTROSCOPY)

(1½ hours + ½ hour)

(5)

(1) CONSIDER A QUANTUM PARTICLE OF MASS M CONFINED IN A ONE-DIMENSIONAL INFINITE POTENTIAL WELL OF LENGTH L. AN EXTERNAL ELECTROMAGNTIC WAVE EXCITES THE PARTICLE FROM AN INITIAL STATE DENOTED BY THE QUANTUM NUMBER n_i TO A FINAL STATE WITH THE QUANTUM NUMBER n_f. DETERMINE THE SELECTION RULE FOR $n_i \rightarrow n_f$ TRANSITIONS. DO YOU THINK THAT $n_i = 1 \rightarrow n_f = 2$ IS AN ALLOWED TRANSITION? JUSTIFY YOUR ANSWER.

(4)

(2) THE INTERNUCLEAR POTENTIAL ENERGY OF A HYDROGEN MOLECULE IS GIVEN AS $U(R) = D_e \left[1 - e^{-a(R-R_o)}\right]^2$ WHERE D_e IS THE DEPTH OF THE WELL, R_o IS THE EQUILIBRIUM INTERNUCLEAR SEPARATION, AND a IS AN EMPIRICAL CONSTANT. GIVEN THAT $R_o = 0.749\,\text{Å}$, $D_e = 456\ \text{kJ/mol}$, AND $a = 1.963 \times 10^8\ \text{cm}^{-1}$, CALCULATE THE FUNDAMENTAL VIBRATIONAL FREQUENCY OF H_2 AND COMPARE IT TO THE EXPERIMENTAL VALUE OF $4.40 \times 10^3\ \text{cm}^{-1}$. YOU CAN USE THE HARMONIC OSCILLATOR APPROXIMATION FOR THIS PROBLEM. HOW WOULD THE FUNDAMENTAL VIBRATIONAL FREQUENCY CHANGE IF WE EMPLOY AN ANHARMONIC OSCILLATOR MODEL FOR THIS PROBLEM.

(1)

(3) DISCUSS THE BORN-OPPENHEIMER APPROXIMATION. WHY DO WE NEED IT?

(4) USING THE EXPLICIT FORMULAS FOR THE SPHERICAL HARMONICS, SHOW THAT THE ROTATIONAL TRANSITION $J=0 \rightarrow J=1$ IS ALLOWED, BUT $J=0 \rightarrow J=2$ IS FORBIDDEN IN MICROWAVE SPECTROSCOPY. (USE THE RIGID-ROTATOR APPROXIMATION). (4)

(5) (a) WE KNOW THAT THE ELECTRIC AND MAGNETIC FIELDS OF AN ELECTROMAGNETIC WAVE VARY IN SPACE AND TIME. HOWEVER, WHEN WE DISCUSSED THE LIGHT-MATTER INTERACTION, WE IGNORED THE SPATIAL VARIATION OF THESE FIELDS. HOW DO YOU JUSTIFY THIS ASSUMPTION? UNDER WHAT CONDITIONS YOU WOULD NEED SPATIAL VARIATIONS OF THESE FIELDS. (2)

(b) FOR LIGHT-MATTER INTERACTION, WE CONSIDERED ONLY THE ELECTRIC FIELD OF THE ELECTROMAGNETIC WAVE. WE IGNORED THE INTERACTION OF MAGNETIC FIELD WITH MATTER. JUSTIFY THIS ASSUMPTION. (2)

(6) USING JABLONSKI DIAGRAMS, DISCUSS THE FLUORESENCE AND PHOSPHORESCENCE PROCESSES. (1)

(7) (a) DISCUSS ABOUT 90° AND 180° PULSES IN NMR EXPERIMENTS. (2)

(b) WHAT ARE T_1 AND T_2 RELAXATIONS IN NMR EXPERIMENTS? (1)

(8) DISCUSS THE FRANCK-CONDON PRINCIPLE. (1)

(9) DISCUSS THE THEORY OF RAMAN SPECTROSCOPY. (2)