Chemistry 21b

Problem set # 5

Out: 15 February 2008
Due: 22 February 2008

The problems are worth: 1=30 (10 each); 2=40 (20 each for a,b); 3=20 (10 for each problem); 4=10 (5 each for a,b).

1. The three infrared spectra on the next page are from compounds whose elemental composition is given at the upper left hand corner of each plot (C_3H_3Br, $C_4H_4O_3$, $C_3H_5O_2Cl$). From the spectra and the summary tables of characteristic vibrational frequencies in the notes, deduce the structure of each compound, explaining your reasoning throughout. (Hint: For the $C_4H_4O_3$ case it is helpful to know about the so-called α substitution effect. When heteroatoms are put on the alpha carbon next to a carbonyl group, those which remove electrons from the carbon of the carbonyl group shift the absorption to higher frequency, and vice versa.)

2. For the molecules CO, O_2, and CF, spectra associated with the following states have been observed, and produced the equilibrium bond lengths in each state:

CO	$X^1\Sigma^+$	$r_e = 1.1283$ Å	$C^1\Sigma^+$	$r_e = 1.1219$ Å
O_2	$X^3\Sigma_g^-$	$r_e = 1.2075$ Å	$B^3\Sigma_u^-$	$r_e = 1.6042$ Å
CF	$X^2\Pi$	$r_e = 1.2718$ Å	$A^2\Sigma^+$	$r_e = 1.1535$ Å

(a) Sketch the potential energy curves and Franck-Condon progressions of the vibrational bands for transitions from the X ground state for these three molecules given the equilibrium bond lengths provided.

(b) Now consider the rotational substructure of an individual vibrational band. For each of the three molecules, are the bands red-shaded or blue-shaded, and at what J value does the $R-$ or $P-$branch band head occur?

3. Do problems 11.5 and 11.6, Atkins & Friedman, p. 406.

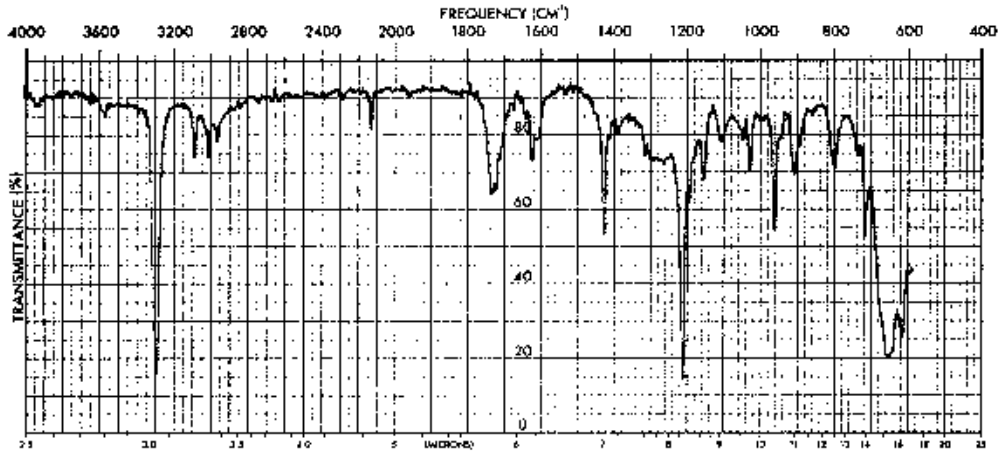
4. A problem to get you thinking about semiconductors. Use the Boltzmann distribution to answer the following:

a) Calculate the ratio of he electrons at the bottom of the conduction band to those at the top of the valence band for pure silicon (Si) at 300 K. The Si band gap is 1.1 eV, and the degeneracies can be treated as the same for both bands.

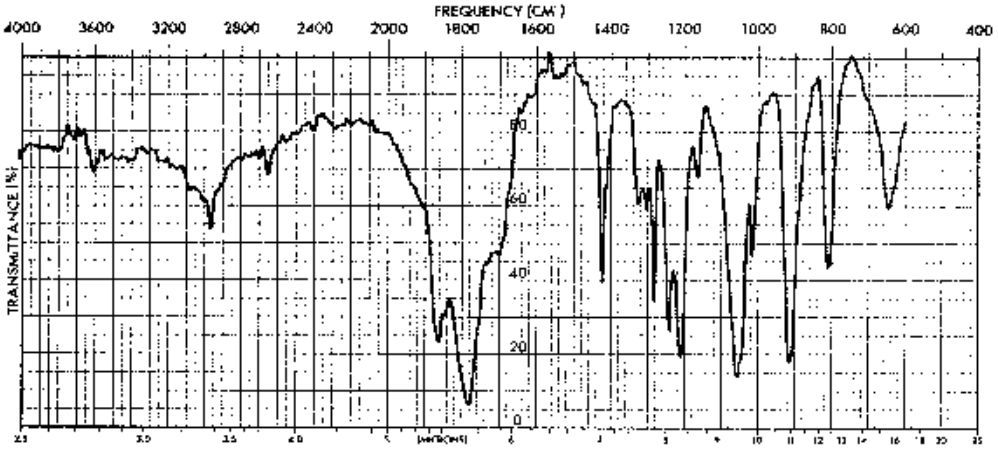
b) Calculate the ratio of electrons at the bottom of the conduction band to those at the top of the band for P-doped Si at 300 K. The top of the dopant band lies 0.04 eV below the bottom of the Si conduction band. What do these answers suggest about integrated circuits?

Responsible TA for Problem Set #5: Evans Boney (boney@caltech.edu)

C_3H_3Br



$C_4H_4O_3$



$C_3H_5O_2Cl$