Problem sets 09/04/2008

1) True or False

A) Electrons are particles, and always behave like particles ?	☐ T ☑ F
B) Photons are waves, and always behave like waves ?	☐ T ☑ F
C) The electric and magnetic field vectors of a photon are in phase ?	☐ T ☑ F
D) The Balmer Series describes transitions in molecular hydrogen, and the common energetic ground state is characterized by n=2?	☑ T ☐ F
E) The probability for an electron to reside within the nucleus is non-zero for all s-orbitals, but essentially zero for other orbitals ?	☑ T ☐ F
G) It is possible to calculate exact line positions for vibrational transitions from solving the Schroedinger Equation of an harmonic oscillator?	☐ T ☑ F
H) It is possible to calculate exact line positions for rotational transitions from solving the Schroedinger Equation of a rigid rotor?	☐ T ☑ F
I) The transition dipole moment is expressed in units of debye ?	☑ T ☐ F
J) The width of an absorption line at zero temperature and low pressure is determined only by the lifetime of the excited state ?	☑ T ☐ F
K) The Einstein coefficient of absorption is directly related to the width of an absorption line at zero temperature and low pressure ?	☑ T ☐ F
L) The de Broglie principle applies only to the world of quantum mechanics ?	☐ T ☑ F
M) The speed of light in air is different from that in vacuum ?	☑ T ☐ F
N) Wavenumber and frequency are two units that can be interconverted without need for additional information, i.e. are directly related ?	☑ T ☐ F
O) Wavenumber and wavelength are two units that can be interconverted without need for additional information, i.e. are directly related ?	☐ T ☑ F
P) The strength of an absorption line is fully determined if the Einstein coefficient of absorption, and the line position are known?	☐ T ☑ F

1a) Explain your reasoning in answering questions A, B, E, G, H, J, K, L, N, O, and P.

2) Make the necessary conversions in order to fill in the table

Wavelength (A)	420	10^6	2441	36523
Wavenumber (cm^{-1})	$2,38 \times 10^5$	100	40961	2738
Energy (J)	$4,73 \times 10^{-18}$	$1,99 \times 10^{-24}$	$8,18 \times 10^{-19}$	$5,44 \times 10^{-20}$
Energy (kJ / mole)	2847,8	1,196	490	32,76
Frequency (Hz)	$7,14 \times 10^{15}$	$2,98 \times 10^{12}$	$1,22 \times 10^{15}$	8.21×10^{13}

3a) What is the momentum and the de Broglie wavelength associated with a human weighing 70kg and running at 20 km/hr ? $\lambda = \frac{h}{p} = 1,7\ 10^{-36}$ m

3b) What is the momentum and the de Broglie wavelength of an electron accelerated through a voltage of 100 V ? $\lambda = 1,2\ 10^{-10}$ m $\approx$ 1 Å

4)At what pressure will the Doppler broadening (FWHM) equal the pressure broadening (FWHM) for a room temperature (20C) sample of CO gas for a pure rotational transition at 115 GHz, a vibrational-rotational transition at 2140 cm^{-1}, and an electronic transition at 1537 Å ? Use a "typical" pressure-broadening coefficient of 10 MHz/Torr in all three cases.

$P_{Rot} = 0.03$ Torr
$P_{Vib} = 14,9$ Torr
$P_{el} = 451$ Torr

5) The absorption cross section of Mercury atoms is 3.3 10^{-14} cm^2 (measured at 253.65nm with a spectral resolution of 0.015nm). Your instrument is capable of detecting an optical density of 10^{-4}, and measures over a pathlength of 1 m. What Hg concentration is detectable ?

$c = 3 \times 10^{7}\ \frac{molec}{cm^3}$

6a) Calculate kT at room temperature (20C) in J, kJ/mole, eV, and cm^{-1}.

4×10^{-21} J
2,4 kJ/mol
0.025 eV (1/40 eV)
203,6 cm^{-1}

6b) Calculate the frequency of a photon for which the energy is equivalent to kT, 0.05 x kT, and 100 x kT. $6,1\ 10^{12}$ Hz ; $3,05 \times 10^{11}$ Hz ; $6,1\ 10^{14}$ Hz

6c) What is the wavelength of the respective photons (choose appropriate units for the respective wavelength region) ? What are the respective wavenumbers ?

49 µm ; 983 µm ; 491 nm 204 cm^{-1} 10,2 cm^{-1} $2,04\ 10^{4}$ cm^{-1}

6d) Calculate the ratio of molecules in a typical excited rotational, vibrational and electronic energy level to that in the lowest energy level for transitions characterized by the three energies from 2b at 20C and at 6000K (sun surface temperature).

	293K	6000K
	0.95	0.998
	0.37	0.952
	4×10^{-44}	$2 \times 10^{-}$

6e) What do the above results tell you about the temperature sensitivity of absorption spectra in the different spectral ranges? Name and define the spectral ranges in your answer.

FIR sensitive
IR somewhat sensitive
UV insensitive

7) The refractive index of dry air at 15C and 1023mbar pressure is given by the Cauchy formula: $10^7 (n-1) = 2726.43 + 12.288 \times 10^8 / \lambda^2 + 0.3555 \times 10^{16}/\lambda^4$
Where λ is in Å (CRC Handbook of Chemistry and Physics, CRC Press).

7a) Calculate the refractive index of air at 2000 Å, 5000 Å and 10000 Å.

$n = 1.000326 ; 1.000278 ; 1.000274$

7b) What is the wavelength shift in 1 bar of air compared to vacuum? What are the corresponding shifts in units of wavenumber (cm^{-1})? $\lambda_{air} = \frac{\lambda_{vac}}{n}$

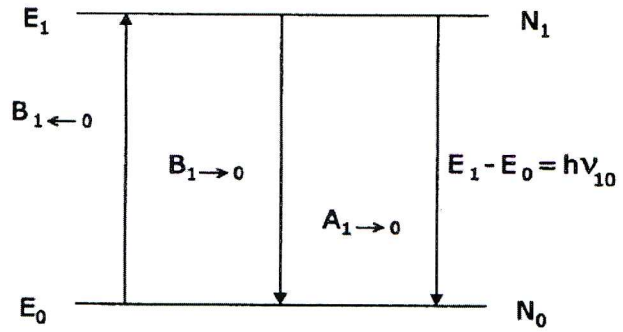
$2000 Å \Rightarrow 0.65 Å$ or $16.3\ cm^{-1}$

7c) What is the speed of light in air and in vacuum? $c_{air} = \frac{c_{vac}}{n}$

7d) What is the wavelength shift in quartz glass (refractive index is 1.5) compared to air?

$\Delta\lambda = \lambda_{air} - \lambda_{vac} = \lambda_{air}(1-n)$

8) Consider the following two level system at room temperature (20C), and in the photosphere of the sun (6000K).



	293 K	6000 K
6000 Å	10^{-36}	0.018
1000 cm^{-1}	0.008	0.79
100 GHz	0.984	0.999
1 GHz	0.9998	0.9999

What are the relative populations N_1/N_0 corresponding to transitions that would occur at 6000 Å, 1000 cm^{-1}, 100 GHz, and 1 GHz ?

9) The lifetime of the $3\ ^2P_{1/2}$ -> $3\ ^2S_{1/2}$ transition of the Na atom at 5896 Å is measured to be 16.4 ns.

9a) What are the Einstein A and B coefficients for this transition ? $A = \frac{1}{\tau_{sp}}$ $B = A\frac{c^3}{8\pi\nu^3}$

9b) What is the transition dipole moment in debye ? Note: 1 D = 3.336×10^{-30} C m $\quad 6.3\ D$

9c) What is the peak absorption cross section for the transition in $Å^2$, assuming that the linewidth is determined by lifetime broadening ? $\sigma_{peak} = 1.4 \times 10^{-10}\ cm^2 = 1.4 \times 10^6\ Å^2$

10) What are the Doppler linewidth (in cm^{-1}) for the pure rotational transition of CO at 115 GHz, the infrared transition of CO_2 at 667 cm^{-1}, and the ultraviolet transition of the Hg atom at 2573 Å, all at room temperature (20C) ?

$\Delta\tilde{\nu}_{CO} = 9 \cdot 10^{-6}\ cm^{-1}$

$\Delta\tilde{\nu}_{CO_2} = 1.2 \times 10^{-3}\ cm^{-1}$

$\Delta\tilde{\nu}_{Hg} = 0.03\ cm^{-1}$