Exam - Chemistry 314: Structural Analysis

Name:

Signature:

Sciper Number:

Grading scale: 100 points

Problem 1: 10 points

Problem 2: 6 points

Problem 3: 14 points

Problem 4: 12 points

Problem 5: 8 points

Problem 6: 12 points

Problem 7: 8 points

Problem 8: 12 points

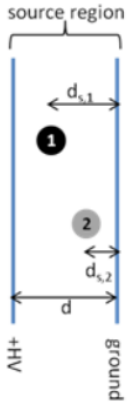
Problem 9: 13 points

Problem 10: 5 points

Problem 1 (10 points)

Indicate if the following statements are true or false:

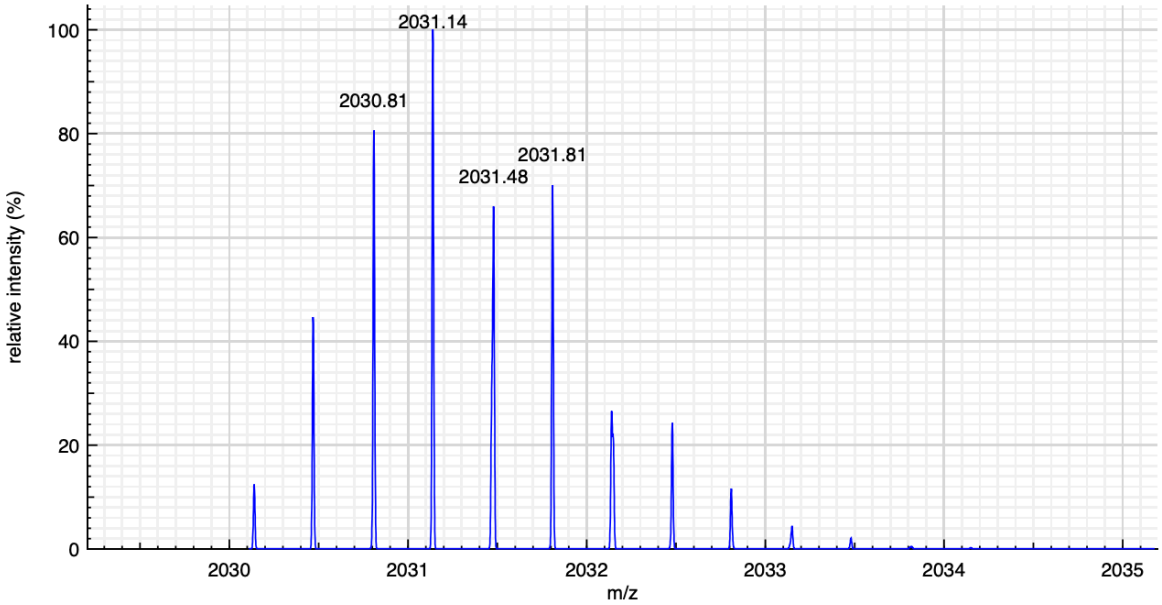
		True	False
a)	The monoisotopic mass of an element is always the most abundant.	❑	❑
b)	Consider the situation diagrammed below, in which two positive ions of the same mass and charge start at slightly different positions in the source region of a time-of-flight mass spectrometer. Ion 1 will leave the source region with higher velocity.	❑	❑



c)	A mass spectrometer can determine an ion's m/z but not its charge.	❑	❑
d)	$C_7H_6NO_2^-$ is an odd-electron ion.	❑	❑
e)	N_2^+ and $C_2H_4^+$ can be resolved by a mass spectrometer with a resolving power of 2500.	❑	❑
f)	The efficiency of electron impact ionization depends upon the wavelength of the electron.	❑	❑
g)	In a 3D quadrupole ion trap, increasing V_{RF} will eject high mass ions first.	❑	❑
h)	In an Orbitrap mass spectrometer, the mass is measured by detecting the frequency of the radial oscillations of the ions.	❑	❑
i)	In an ICR mass spectrometer, ions are ejected and their masses analyzed by applying an RF voltage to the entrance and exit electrodes.	❑	❑
j)	The mass resolution of a Fourier transform instrument depends upon the pressure of residual gas.	❑	❑

Problem 2 (6 points)

Shown below is part of a mass spectrum generated by electrospraying a solution of a peptide.



(6 points) Determine the monoisotopic mass of the neutral peptide to a precision of 0.1 Da.

Problem 3 (14 points)

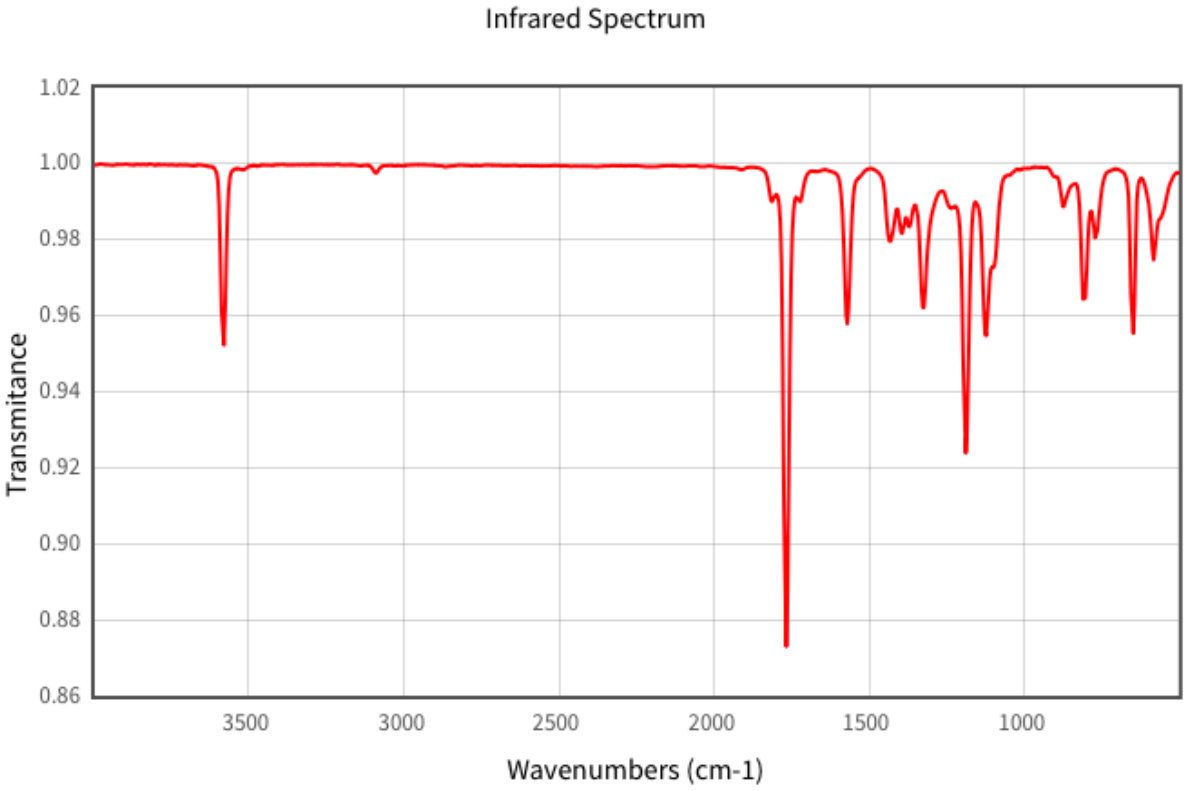
The electron impact mass spectrum of an unknown compound gives the following isotopic distribution (with relative abundances shown in red):

m/z	Intensity
190	69
191	5.4
192	45.1
193	3.5
194	7.5
195	0.55

(a) (6 points) Write down all possible molecular formulas that are consistent with this isotopic distribution.

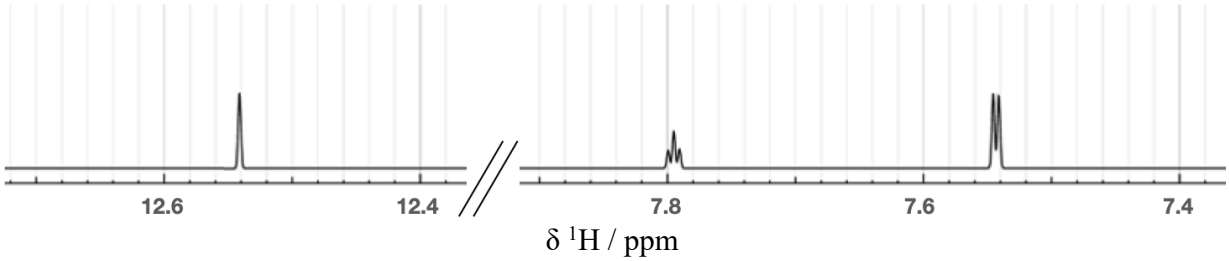
(b) (3 points) What resolution would be needed to distinguish between the possible formulas on the basis of their exact mass to 10% from the baseline?

(c) (5 points) Determine the degree of unsaturation (DoU or Rings + Double Bonds) for each possible molecular formula. Then, using the infrared spectrum below, propose the most reasonable molecular formula and make sure that it is consistent with the DoU. Explain your reasoning.

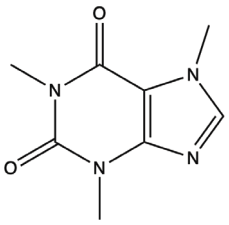


Problem 4 Chemical shifts and couplings (12 points)

(a) Given the following ^{1}H NMR spectrum for the molecule of Problem 3, what is the structure of the molecule? (2 points)



(b) How many peaks do we expect in the ^{13}C NMR spectrum of caffeine (shown) for: (2 points)

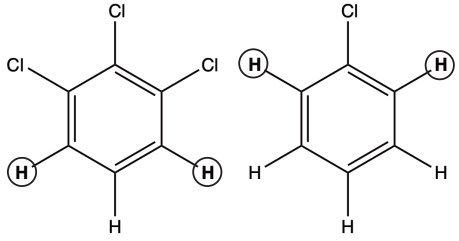


(i) a spectrum of the sample dissolved in chloroform solution, without ^{1}H decoupling?

(ii) the solution spectrum with ^{1}H decoupling?

(iii) in the magic-angle spinning spectrum of a powder sample of a solid form that contains two molecules in the asymmetric unit cell, with ^{1}H decoupling?

(c) For each of the two compounds below, determine whether the two circled protons are magnetically or chemically equivalent. Explain your answers. (2 points)



(d) The ^{11}B spectrum of BF_4^- is a quintet. The ^{19}F spectrum has four equally spaced lines with the same intensity. What is the nuclear spin of ^{11}B? (1 point)

(e) For each of the following compounds determine whether the protons are magnetically or chemically equivalent. (a) benzene, (b) the 2,5 protons in furan and (c) $F_2C{=}C{=}CH_2$ (2 points)

(f) True or false (3 points)

	True	**False**
(i) NMR spectroscopy uses ultraviolet radiation to flip nuclear spins	☐	☐
(ii) A deshielded proton will resonate at a higher ppm value	☐	☐
(iii) ^{13}C spectra are usually quantitative	☐	☐
(iv) 2850 Hz is equal to 454 rad/s	☐	☐
(v) Magic angle spinning averages out scalar couplings	☐	☐
(vi) The nuclear Overhauser effect causes transfer of polarization through bond	☐	☐

Problem 5 Chemical exchange (8 points)

(a) The –OH proton of pure propanol, CH_3CH_2OH, can undergo a fast exchange on the NMR timescale when a catalytic amount of hydrochloric acid is added to the medium. Draw the ^1H spectrum of the propanol molecule with and without acid. Use qualitative estimates for the expected chemical shifts. (2 points)

(b) A molecule undergoes unsymmetrical two-site exchange, A↔B. When the exchange is slow, the ^1H spectrum contains two lines with chemical shifts, δ_A = 3.0 ppm and δ_B = 5.0 ppm. In fast exchange a single line is observed at 3.01 ppm. What are the relative populations of the two forms? (2 points)

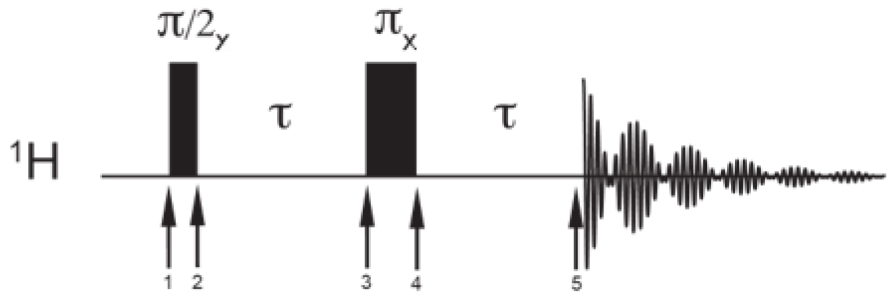
(c) The rate constant (in s^{-1}) for a symmetrical two-site exchange has the temperature dependence k = 10^{13}exp[-7500/T]. The rate constant in Hz for which the two peaks merge together is $k_{\mathrm{merge}} = \frac{\pi\delta\nu}{\sqrt{2}}$.

(i) Show how you would find the temperature at which the peaks merge together (T_{merge}). (2 points)

(ii) Assuming that T_{merge} is 350 K, draw schematically the spectra that would be recorded at the following temperatures: 305 K, 350 K and 400 K. (2 points)

Problem 6 The vector model (12 points)

(a) Consider two uncoupled spins I=1/2 with different chemical shifts undergoing the following pulse sequence:



(i) Use the vector model to show what happens to the magnetization of the two spins at each of the 5 indicated timepoints. Fill in a table describing the values of x, y and z magnetization after timepoints 2, 3 and 4. Use M_0 for magnetization and Ω for offset. (6 points)

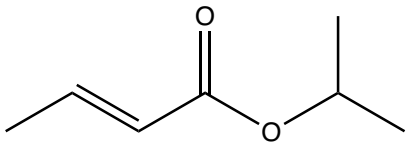
component	timepoint			
	1	2	3	4
x	0			
y	0			
z	M_0			

(ii) What is the end result if the 180° pulse is about the y axis? What is this pulse sequence called? What information can be extracted from a series of experiments where τ is incremented? (3 points)

(b) Draw the inversion recovery pulse sequence and explain how it can be used to measure longitudinal relaxation. Sketch a plot of the z-component of the magnetization as a function of the recovery delay τ. (3 points)

Problem 7 Two dimensional NMR (8 points)

(a) Consider the following molecule



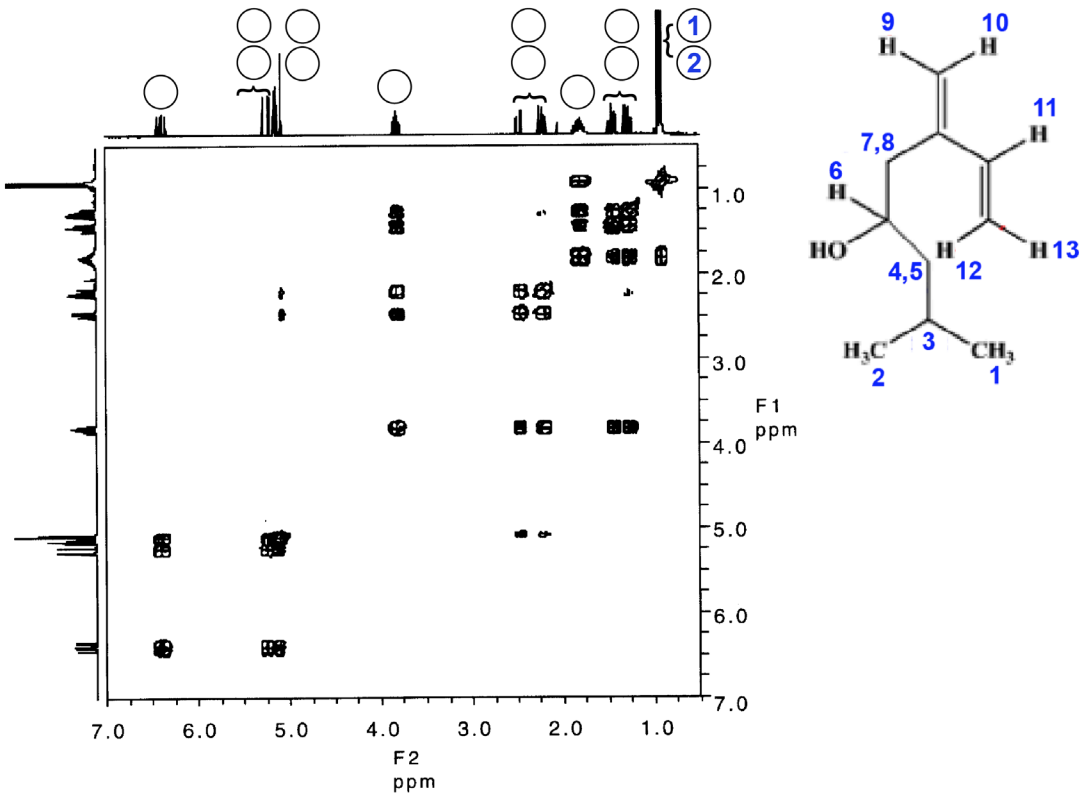
(i) Draw schematically the solution state ^{1}H spectrum of the molecule in $CDCl_3$ and label the peaks. Use qualitative estimates for the expected chemical shifts. Consider only $^{3}J_{HH}$ couplings. (2 points)

(ii) Draw schematically the ^{1}H-^{13}C HSQC. (2 points)

b) Consider the COSY spectrum of ipsenol (shown in the figure).

(i) Draw the COSY pulse sequence and identify the preparation and mixing elements. (1 point)

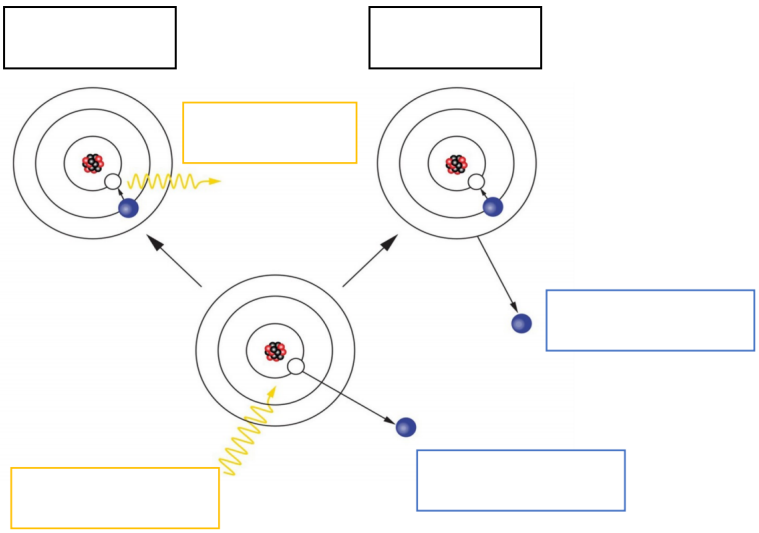
(ii) Assign the protons in the COSY spectrum of ipsenol, given the assignment shown for protons 1 and 2 (note that some, but not all, $^4J_{HH}$ couplings are observed.) (2 points)



(iii) What would be the consequence for the assignment if no cross peaks due to $^4J_{HH}$ couplings were present? (1 point)

Problem 8 – Fundamental X-ray matter interactions (total 12 points)

(a) (3 points) X-rays dominantly interact with core electrons. Name the following processes (black boxes), define the emitted electrons (blue boxes) and label primary and secondary channels (yellow boxes) by filling in the boxes. Define what are the primary and secondary (decay) processes in the yellow boxes?



(b) (4 points) The atomic scattering factor is given by $f(Q, hv) = f^0(Q)+f'(hv)+if''(hv)$

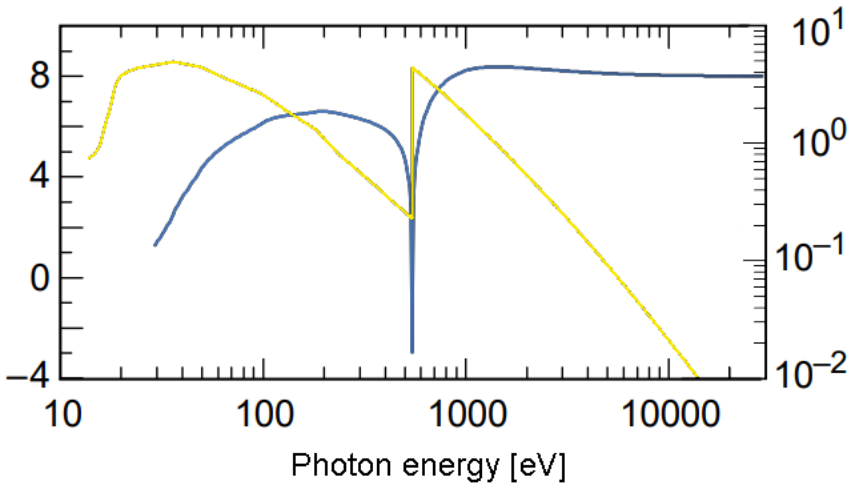
Which component is the atomic form factor?

What does the atomic form factor represent for Q -> 0?

What components describe f1 and what is the meaning of f1?

What components describe f2 and what is the meaning of f2?

(c) (2 points) The following figure shows the atomic scattering factors for an element from approx. 10 eV to 12 keV:



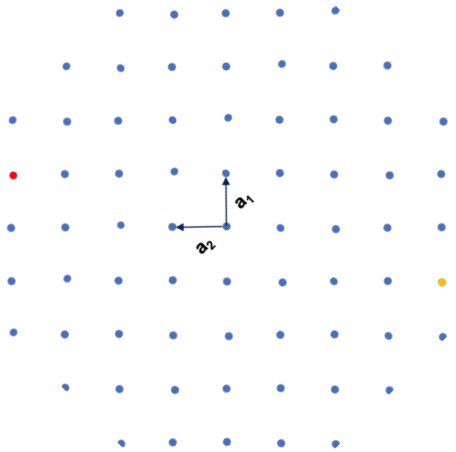
Which graph describes f1 and f2? Label in figure.

Which vertical axis describes f1 and f2? Label next to figure.

(d) (3 points) To which element does the graph belong? Explain your conclusion based on f1 and f2, respectively. Use table in appendix as reference.

Problem 9 X-ray diffraction (total 13 points)

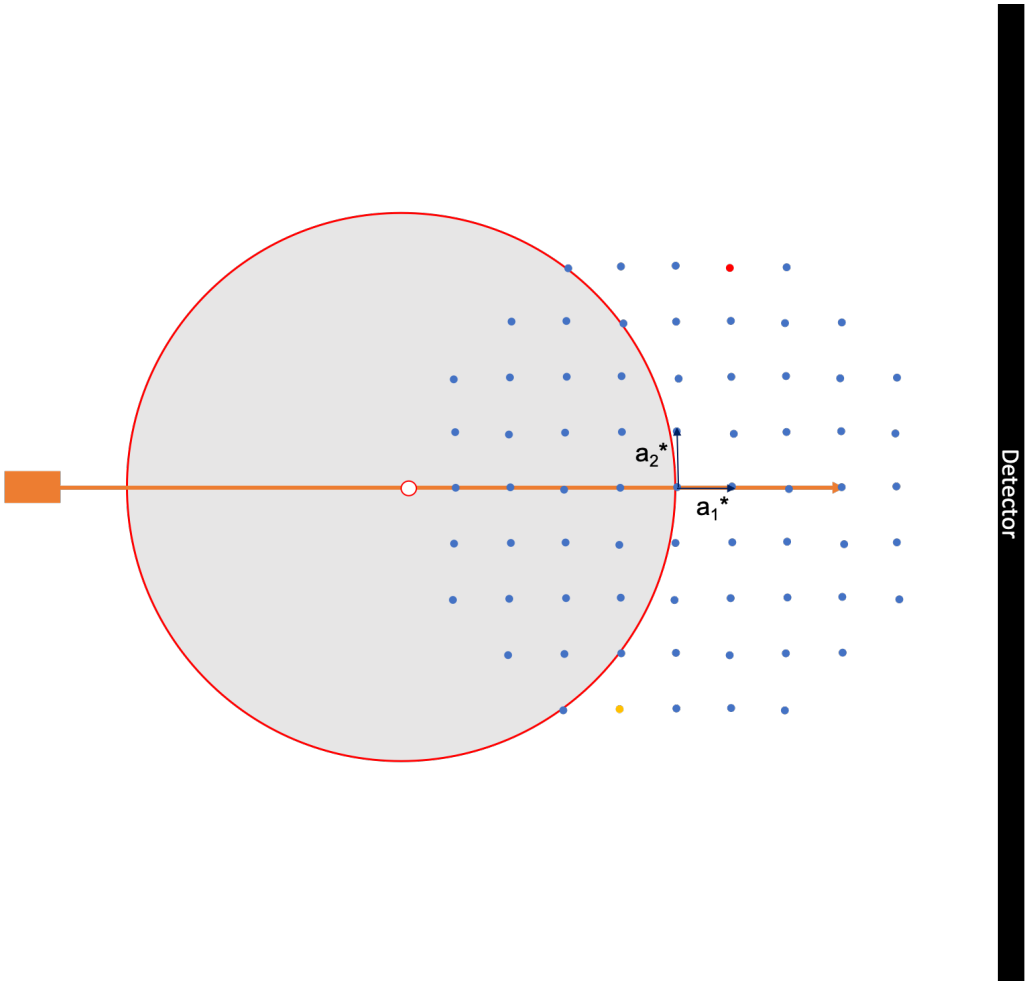
(a) (2 points) Lattice planes. In the following figure, sketch and label the (10), (01), (11), and (21) lattice planes.



(b) (4 points) The Bragg condition is given by $\lambda = 2d\sin\theta$. In the following figure, sketch the Bragg condition, label $\boldsymbol{k}$, d, and θ.

(c) (2 points) Explain the interference condition based on your sketch.

(d) (5 points) The next figure shows a x-ray diffraction experiment in an Ewald sphere construction. The inverse lattice vector $\mathbf{a_1}^*$ has a length of 1 nm^{-1}



Which points will yield a diffraction peak?

Which Bragg peaks will be observable on the detector?

What do you need to do to observe the (01) peak)?

Draw the scattering vector $\boldsymbol{Q}$ for the (-13) peak)?

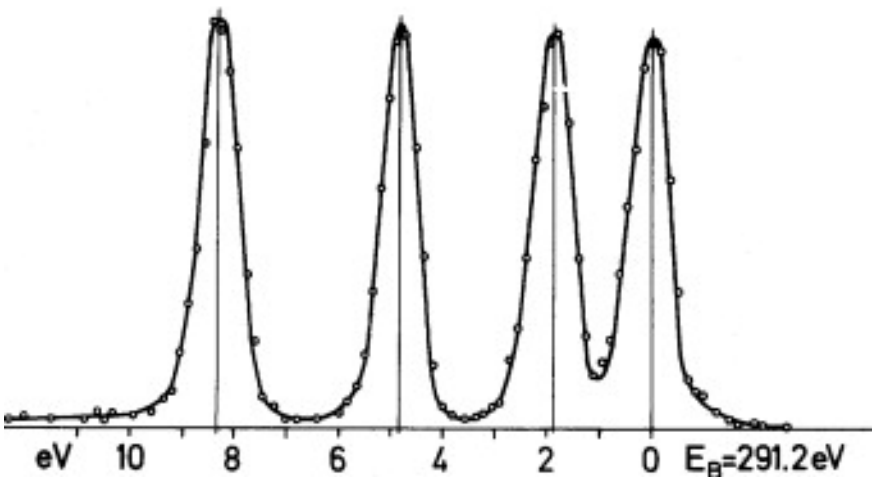
What is the photon energy in this experiment? Remember that 1.24 keV corresponds to a wavelength of 1 nm.

Problem 10 X-ray spectroscopy (total 5 points)

In X-ray photoelectron spectroscopy the chemical shift of the binding energy E_B is related to the oxidation state of the targeted atom. The following figure represents a core-level photoelectron spectrum of ethyl-trifluoroacetate (CF_3-CO-O-CH_2-CH_3).

(a) (1 point) Which core-level is investigated (compare appendix)

(b) (4 points) Label the figure with the respective subgroups



Appendix 1 – Electron binding energies, in electron volts, for the elements in their natural forms

Element	K 1s	L_1 2s	L_2 $2p_{1/2}$	L_3 $2p_{3/2}$	M_1 3s	M_2 $3p_{1/2}$	M_3 $3p_{3/2}$
1 H	13.6						
2 He	24.6*						
3 Li	54.7*						
4 Be	111.5*						
5 B	188*						
6 C	284.2*						
7 N	409.9*	37.3*					
8 O	543.1*	41.6*					
9 F	696.7*						
10 Ne	870.2*	48.5*	21.7*	21.6*			
11 Na	1070.8†	63.5†	30.65	30.81			
12 Mg	1303.0†	88.7	49.78	49.50			
13 Al	1559.6	117.8	72.95	72.55			
14 Si	1839	149.7*b	99.82	99.42			
15 P	2145.5	189*	136*	135*			
16 S	2472	230.9	163.6*	162.5*			
17 Cl	2822.4	270*	202*	200*			
18 Ar	3205.9*	326.3*	250.6†	248.4*	29.3*	15.9*	15.7*
19 K	3608.4*	378.6*	297.3*	294.6*	34.8*	18.3*	18.3*
20 Ca	4038.5*	438.4†	349.7†	346.2†	44.3 †	25.4†	25.4†
21 Sc	4492	498.0*	403.6*	398.7*	51.1*	28.3*	28.3*
22 Ti	4966	560.9†	460.2†	453.8†	58.7†	32.6†	32.6†

Table of constants and isotopic abundances

Planck's constant: $h = 6.626 \cdot 10^{-34}$ Joule sec or kg m^2 sec^{-1}

Speed of light: $3.00 \cdot 10^{8}$ m sec^{-1}

Mass of proton: $M_p = 1.007276$ Da

Mass of electron: $m_e = 0.0005486$ Da

Isotope	% abondance nat.	Atomic mass (Da)
^{1}H	99.985	1.007825
^{2}H	0.015	2.0140
^{12}C	98.89	12 (definition)
^{13}C	1.11	13.00335
^{14}N	99.64	14.00307
^{15}N	0.36	15.00011
^{16}O	99.76	15.99491
^{17}O	0.04	16.99913
^{18}O	0.2	17.99916
^{28}Si	92.2	27.976926
^{29}Si	4.7	28.976494
^{30}Si	3.1	29.973770
^{32}S	94.99	31.972071
^{33}S	0.75	32.971458
^{34}S	4.24	33.967867
^{35}Cl	75.77	34.96885
^{37}Cl	24.23	36.96590
^{79}Br	50.69	78.9183
^{81}Br	49.31	80.9163