# Exam November 2022 vibrations and x-rays

**Question 1: x-ray spectroscopy** [2.5]

a) Explain how an x-ray absorption spectrum is calculated for the oxygen K edge of $TiO_2$.

Start from the crystal structure
Calculate electronic structure
Calculate the projected oxygen p-DOS.[0.5]

b) Explain how an x-ray absorption spectrum is calculated for the titanium $L_{2,3}$ edge of $TiO_2$.

Perform multiplet calculations; choose a crystal field [0.5]

c) What is Hunds rule ground state of a $Co^{2+}$ ion that has a $3d^7$ configuration.

S=3/2, L = 3, J = 9/2: 4F9/2 [1]

d) How does an x-ray tube produce x-rays?

A high voltage difference accelerates electrons.
The electrons excite core electrons
The core electrons decay n an x-ray emission process.[0.5]

**Question 2: x-ray spectroscopy** [3.5]
Consider a carbon atom with a $2p^2$ configuration, which is split into states indicated with the following three term symbols: $^1S$, $^3P$ and $^1D$.
a) Give all term symbols after including 2p spin-orbit coupling.

1S0, 3P0, 3P1, 3P2, 1D2 [0.5]


b) What is the state with the lowest energy?

Hunds rules, max S, Max L, min J: 3P0 [0.5]


A 1s electron is excited to a 2p state, yielding a final state with a $1s^1 2p^3$ configuration. The $2p^3$ configuration has the term symbols $^2P$ $^4S$ and $^2D$. (Note that for atoms one always has to use multiplet theory)
c) Determine the term symbols after coupling to the 1s core hole (without spin-orbit coupling).

2P*2S = 1P + 3P   3+9 =12
4S* 2S= 3S + 5S   3 + 5 =8
2D*2S = 1D + 3D   5+15=20, total 40 [1]

d) What is the total degeneracy of a $1s^1 2p^3$ configuration? Explain.

2p3 has 6*5*4/1*2*3=20 states,
1s1 2p3 has 2*20 = 40 states [0.5]

e) How many peaks has the 1s XAS spectrum in the transition $2p^2 \rightarrow 1s^1 2p^3$ if one includes the 2p spin-orbit coupling? Explain.
Final state
1P1, 3P0 3P1 3P2
3S1 5S2
1D2 3D1 3D2 3D3

Ground state 3P0
Final state must have J=1: 4 peaks 1P1, 3P1, 3D1, 3S1 [1]
Transition from J=0 cannot be to J'=0

**Question 3: vibrational spectroscopy** [4.0]

a) Give (and explain) an example of a molecule that is (1) a spherical rotor and (2) a symmetric rotor.

Spherical rotor: CH4 (methane), SiF6{2-}, CF4, CCl4, etc. [0.5]
Symmetric rotor: NH3, CH3F, benzene, etc.[0.5]

b) Give (and explain) four reasons for the observed spectral broadening in an IR spectrum of a molecule in solution.
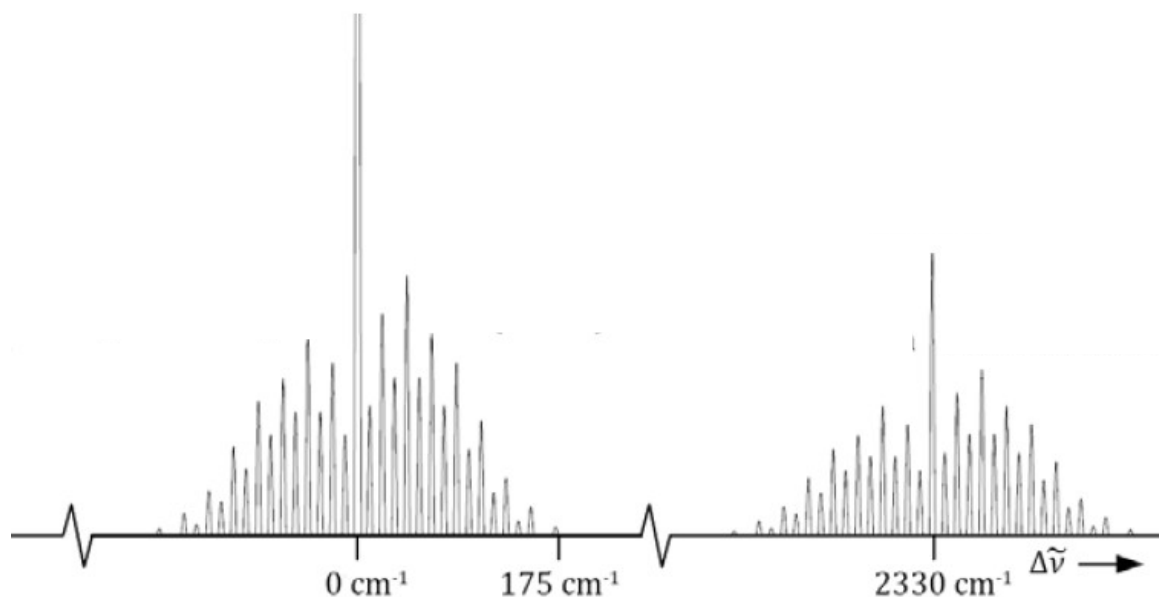
Experimental – Doppler – Lifetime - Multiple peaks [0.5]]

c) Give all selection rules for a rotational Raman spectrum of a linear molecule.

Molecule must be anisotropically polarizable [0.5]
DELTA J + -2, 0, +2 [0.5]

d) Explain the two spectra given in the figure below, including the names of the peaks/regions, the mechanisms for the transitions, the distance between the lines and the reason for the trends in intensity. If possible give additional details.



Left: Rotational Raman [0.3]
Right vibration-rotation Raman [0.3]
Excitation with visible/UV, decay to rotational & vibrational excitations
Distance between lines: 4B [0.3]
Rayleigh, Stokes and anti-stokes rotational peaks due to trend in occupation of rotational modes [0.3]
Up-down variation due to coupling with nuclear spin [0.3]