Examination

Advanced Inorganic Chemistry

M.Sc. Chemical Engineering / Material Science and Engineering

February 05th, 2024

(Part: Prof. Dr. Thomas Jüstel)

Name, Given name: ______________________________

Enrolment number: ______________________________

Birthday: ______________________________

Duration: 180 minutes (for both parts)

Achievable score: 50 Points (for this part)

Please use these sheets only (you might also use the reverse)! Please employ IUPAC units solely. Assign axes of graphs and parts of sketches properly!

Success!

Task 1) **(10 Points)**

Astrochemistry and Spectroscopy

CO is the second most molecule in the interstellar medium (ISM) due to its extraordinarily high thermodynamic stability.

a) Sketch the two possible conjugated acids, i.e. protonation products, of the base CO! (2 Points)

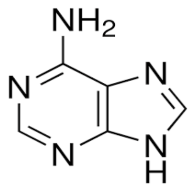
b) The bond energy of CO is 11.16 eV. Please calculate the absorption edge in nanometer and speculate whether CO can be detected due to this transition by ground-based telescopes! (2 Points)

c) CO is a rigid rotator whereby the energy levels are E(J) = BJ(J + 1) with J = 0, 1, 2, 3, … and B = h/2πI. Calculate the frequency of the first two rotational transitions (J = 2 → J = 1 and J = 1 → J = 0) for the momentum of inertia I = $9.2 \cdot 10^{-46}$ kg/m^2! Are these transitions detectable by ground-based radio telescopes? Explain your answer! (2 Points)

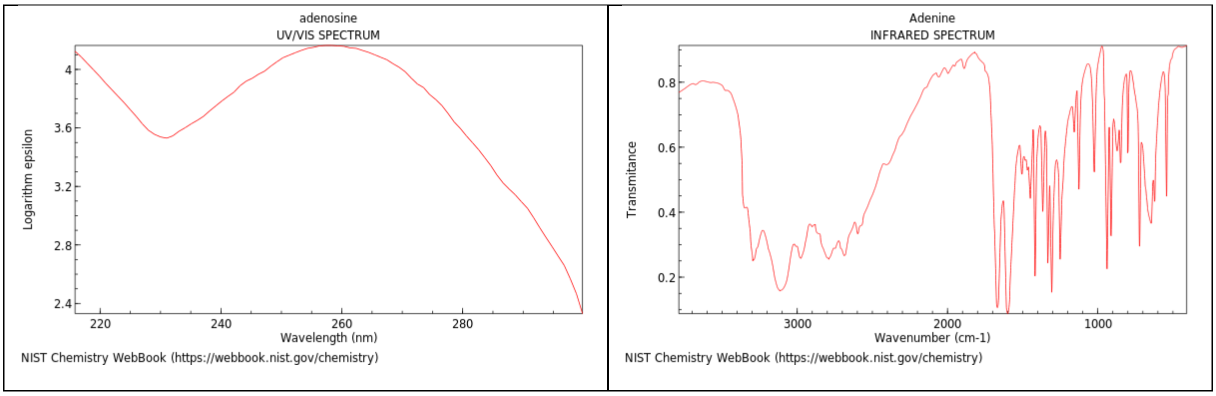
d) Propose reaction products for the following photochemical reactions occurring in space! (2 Points)

$CO + NH_3 \rightarrow$

$CO + H_2 \rightarrow$



e) HCN pentamerise in space to the nucleobase adenine (see image).



Speculate about the origin of the strongest optical transitions causing the absorption band in the UV at 260 nm and in the IR at 1600 cm^{-1}? Are these bands of adenine in space detectable from the ground (0 m), from stratosphere (20 km) or from space telescopes (> 500 km) solely? (2 Points)

Task 2) **(10 Points)**

Point Groups

a) Determine the corresponding point group labels (Schoenflies symbols) next to the image and symmetry operations of each molecule mentioned below. The point group flowchart is provided in the appendix. (0.5 Points for each cell)

Molecule	**Image**	**symmetry operations**	**Point group**
NH_3			
CH_2O			
Fluoroacetylene			
1,5-Dibrom-naphtalene			

b) Give an example for an inorganic or organic molecule with the following point groups! (1 Point each)

- C_{4v}
- D_{2d}
- D_{4h}
- C_3

Task 3) (10 Points)

MO Theory

a) Construct the MO diagram of CO by using the 2s and 2p AOs upon using the UPS determined AO energies (C 2s: -19.4 eV, C 2p: -10.7 eV, O 2s: -32.4 eV, O 2p: -15.8 eV) Please also assign the optical transition resulting in the weakening of the CO molecule with a very strong bond energy of about 1072 kJ/mol! (2 Points)

b) The water molecule is bent and belong to the point group C_{2v}. Determine the symmetry representation labels (see appendix) for the 2s-, $2p_z$-, $2p_x$-, $2p_y$-orbitals of the central O-Atom! (4 Points)

c) In the framework of MO theory 3-atomic molecules can be treated by defining a central atom and outer group atoms. On this basis construct the MO-diagram for H_3^+! Why is H_3^+ more stable than H_3, even though the bond order is the same? (4 Points)

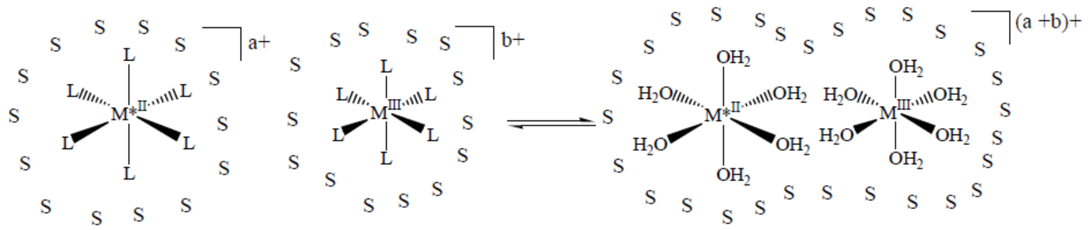
Task 4) **(10 Points)**

Marcus-Theory and inner- or outer-sphere reactions

a) The Marcus theory links reaction kinetics of electron transfer (ELT) or atom transfer (AT) reactions with the thermodynamic equilibrium constant, while in the Marcus regime the following equation for the transfer rate holds: $k_{12} = (k_{11}k_{22}K_{12})^{1/2}$. Explain the meaning of the different constants and also explain the term self-exchange reaction! (2 Points)

b) Give an example for an inner-sphere reaction and assign the precursor and the successor complex according to the Robin and Day (type I, II, III) classification! (2 Points)

c) The first step in outer-sphere reactions is the formation of a precursor complex as shown below:



precursor complex

Discuss the effect of the solvent S on the formation of the precursor complex and on the rate of the subsequent electron transfer reaction! (2 Points)

d) The following table give reaction rates of self-exchange reactions:

Self-exchange reaction	electron configuration	k_{11} [$M^{-1}s^{-1}$]
$[Cr(H_2O)_6]^{2+/3+}$	$t_{2g}^3e_g^1/t_{2g}^3e_g^0$	$1.0{\cdot}10^{-5}$
$[V(H_2O)_6]^{2+/3+}$	$t_{2g}^3e_g^0/t_{2g}^2e_g^0$	$1.0{\cdot}10^{-2}$
$[Fe(H_2O)_6]^{2+/3+}$	$t_{2g}^4e_g^2/t_{2g}^3e_g^2$	$4.0{\cdot}10^{0}$
$[Ru(H_2O)_6]^{2+/3+}$	$t_{2g}^6e_g^0/t_{2g}^5e_g^0$	$4.0{\cdot}10^{3}$

Explain the reaction rate differences by the aid of the electron configuration and the Jahn-Teller effect! (4 Points)

Task 5) **(10 Points)**

Spectroscopy and Catalysis: “The Copper Case”

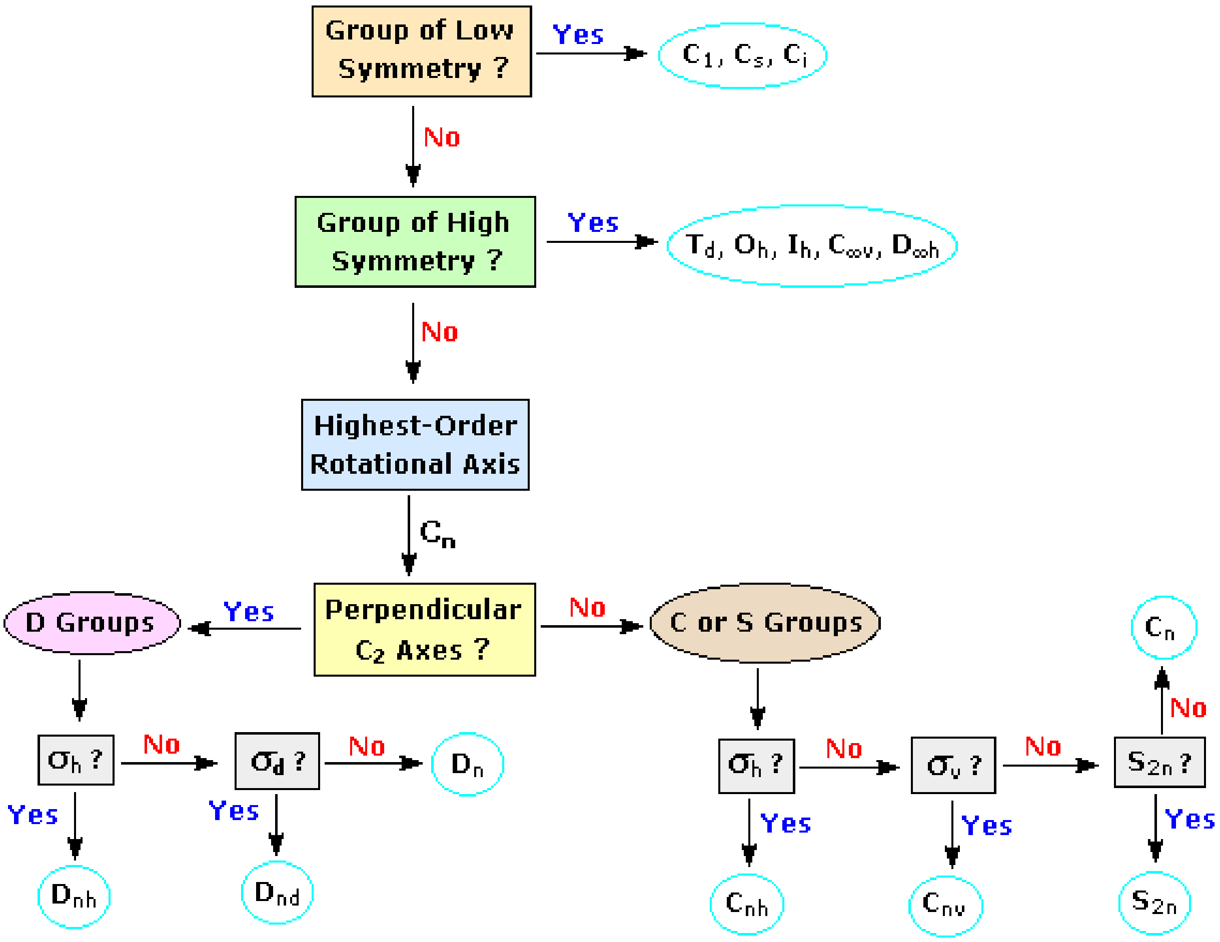
a) Cu^{2+} complexes show mostly either tetrahedral, octahedral or square-planar coordination. Determine the Russell-Saunders ground state term of Cu^{2+} and sketch the splitting of this term in these three crystal fields. Also assign by the aid of the tables in the appendix the terms to crystal-field labels! (4 Points)

b) Explain the color of the Cu^{2+} pigments Egyptian and Han blue on the basis of the optical transitions expected for Cu^{2+} in square-planar symmetry! (2 Points)

c) The redox-couple Cu^{2+}/Cu^{+} is widely applied in electron transfer reactions, e.g. in the respiratory chain and in the electron transport chain of PSII. Sketch a self-exchange reactions for this redox couple with arbitrary ligands L. Please also speculate about the advantage of square-planar Cu^{2+} complexes for the catalysis of redox reactions! (4 Points)

Appendix

Decision tree for the determination of point groups



Number of irreducible representations

$$\text{\# of irreducible representations of a given type} = \frac{1}{\text{order}} \sum_R \left(\text{\# of operations in the class} \times \text{character of reducible representation} \times \text{character of irreducible representation} \right)$$

Character table C_{2v}

Point Group Label

Symmetry Operations – The *Order* is the total number of operations

In C_{2v} the order is 4: 1 E, 1 C_2, 1 σ_v and 1 σ'_v

C_{2v}	E	C_2	σ_v (xz)	σ'_v (yz)
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Character

Representation of B_2

Symmetry Representation Labels

Nomenclature of symmetry representation labels

Crystal-field term	degeneracy
A	1
B	1
E	2
T	3

by symmetry:	Principal rotation axis (C_n)	Center of inversion (i)	plane ‖ to princip. axis (σ_v)	plane ⊥ to princip. axis (σ_h)
symmetric	A	g	1	′
antisymmetric	B	u	2	″

Splitting of the wavefunctions (orbitals) in selected crystal field geometries

<table>
<tr><th>ψ_i G</th><th>R_3</th><th>O_h</th><th>T_d</th><th>D_{4h}</th><th>C_{4v}</th><th>C_{2v}</th><th>D_{3v}</th></tr>
<tr><td>s</td><td>s_g</td><td>A_{1g}</td><td>A_1</td><td>A_{1g}</td><td>A_1</td><td>A_1</td><td>A_{1g}</td></tr>
<tr><td>p_x</td><td rowspan="3">p_u</td><td rowspan="3">T_{1u}</td><td rowspan="3">T_1</td><td rowspan="2">E_u</td><td rowspan="2">E</td><td>B_1</td><td rowspan="2">E_u</td></tr>
<tr><td>p_y</td><td>B_2</td></tr>
<tr><td>p_z</td><td>A_{2u}</td><td>A_1</td><td>A_1</td><td>A_{2u}</td></tr>
<tr><td>d_{z2}</td><td rowspan="5">d_g</td><td rowspan="2">E_g</td><td rowspan="2">E</td><td>A_{1g}</td><td>A_1</td><td>A_1</td><td rowspan="2">E_g</td></tr>
<tr><td>d_{x2-y2}</td><td>B_{1g}</td><td>B_1</td><td>A_1</td></tr>
<tr><td>d_{xy}</td><td rowspan="3">T_{2g}</td><td rowspan="3">T_2</td><td>B_{2g}</td><td>B_2</td><td>A_2</td><td>A_{1g}</td></tr>
<tr><td>d_{xz}</td><td rowspan="2">E_g</td><td rowspan="2">E</td><td>B_1</td><td rowspan="2">E_g</td></tr>
<tr><td>d_{yz}</td><td>B_2</td></tr>
</table>

Periodic Table of the Elements (PTOE)

hydrogen 1 **H** 1.0079																		helium 2 **He** 4.0026
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.0122												boron 5 **B** 10.811	carbon 6 **C** 12.011	nitrogen 7 **N** 14.007	oxygen 8 **O** 15.999	fluorine 9 **F** 18.998	neon 10 **Ne** 20.180
sodium 11 **Na** 22.990	magnesium 12 **Mg** 24.305												aluminium 13 **Al** 26.982	silicon 14 **Si** 28.086	phosphorus 15 **P** 30.974	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.948
potassium 19 **K** 39.098	calcium 20 **Ca** 40.078		scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.39	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.61	arsenic 33 **As** 74.922	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.80
rubidium 37 **Rb** 85.468	strontium 38 **Sr** 87.62		yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.94	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41	indium 49 **In** 114.82	tin 50 **Sn** 118.71	antimony 51 **Sb** 121.76	tellurium 52 **Te** 127.60	iodine 53 **I** 126.90	xenon 54 **Xe** 131.29
caesium 55 **Cs** 132.91	barium 56 **Ba** 137.33	57-70 *	lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.38	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.98	polonium 84 **Po** [209]	astatine 85 **At** [210]	radon 86 **Rn** [222]
francium 87 **Fr** [223]	radium 88 **Ra** [226]	89-102 * *	lawrencium 103 **Lr** [262]	rutherfordium 104 **Rf** [261]	dubnium 105 **Db** [262]	seaborgium 106 **Sg** [266]	bohrium 107 **Bh** [264]	hassium 108 **Hs** [269]	meitnerium 109 **Mt** [268]	ununnilium 110 **Uun** [271]	unununium 111 **Uuu** [272]	ununbium 112 **Uub** [277]		ununquadium 114 **Uuq** [289]				

*Lanthanide series	lanthanum 57 **La** 138.91	cerium 58 **Ce** 140.12	praseodymium 59 **Pr** 140.91	neodymium 60 **Nd** 144.24	promethium 61 **Pm** [145]	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.96	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.93	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.93	erbium 68 **Er** 167.26	thulium 69 **Tm** 168.93	ytterbium 70 **Yb** 173.04
* *Actinide series	actinium 89 **Ac** [227]	thorium 90 **Th** 232.04	protactinium 91 **Pa** 231.04	uranium 92 **U** 238.03	neptunium 93 **Np** [237]	plutonium 94 **Pu** [244]	americium 95 **Am** [243]	curium 96 **Cm** [247]	berkelium 97 **Bk** [247]	californium 98 **Cf** [251]	einsteinium 99 **Es** [252]	fermium 100 **Fm** [257]	mendelevium 101 **Md** [258]	nobelium 102 **No** [259]