IVANOVO STATE UNIVERSITY OF CHEMISTRY AND TECHNOLOGY

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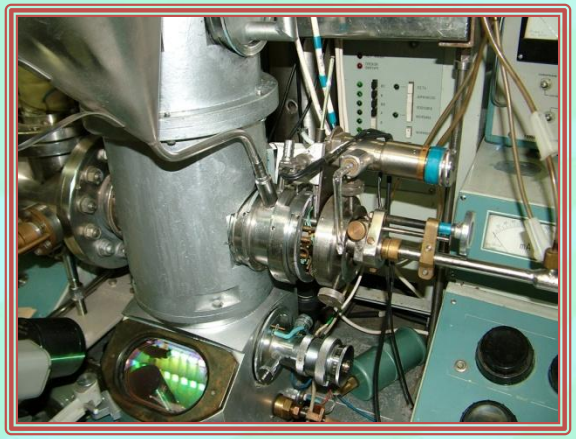
Combined gas-phase electron diffraction and mass spectrometry

Oleg A. Pimenov and Yuriy A. Zhabanov



Ivanovo GED group
(*Ivanovo state university of chemistry and technology + Ivanovo state university*)

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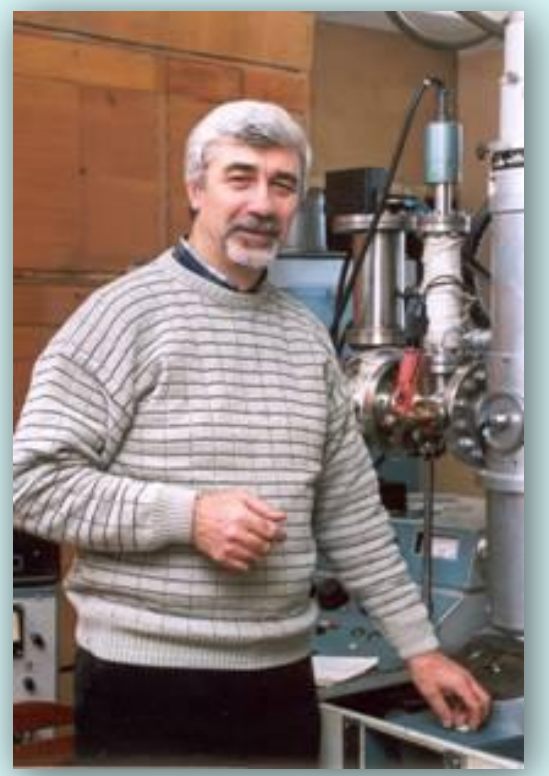
Foundation of Ivanovo GED group



Prof. George V. Girichev, the head of Ivanovo GED group

Prof. Sergey A. Shlykov

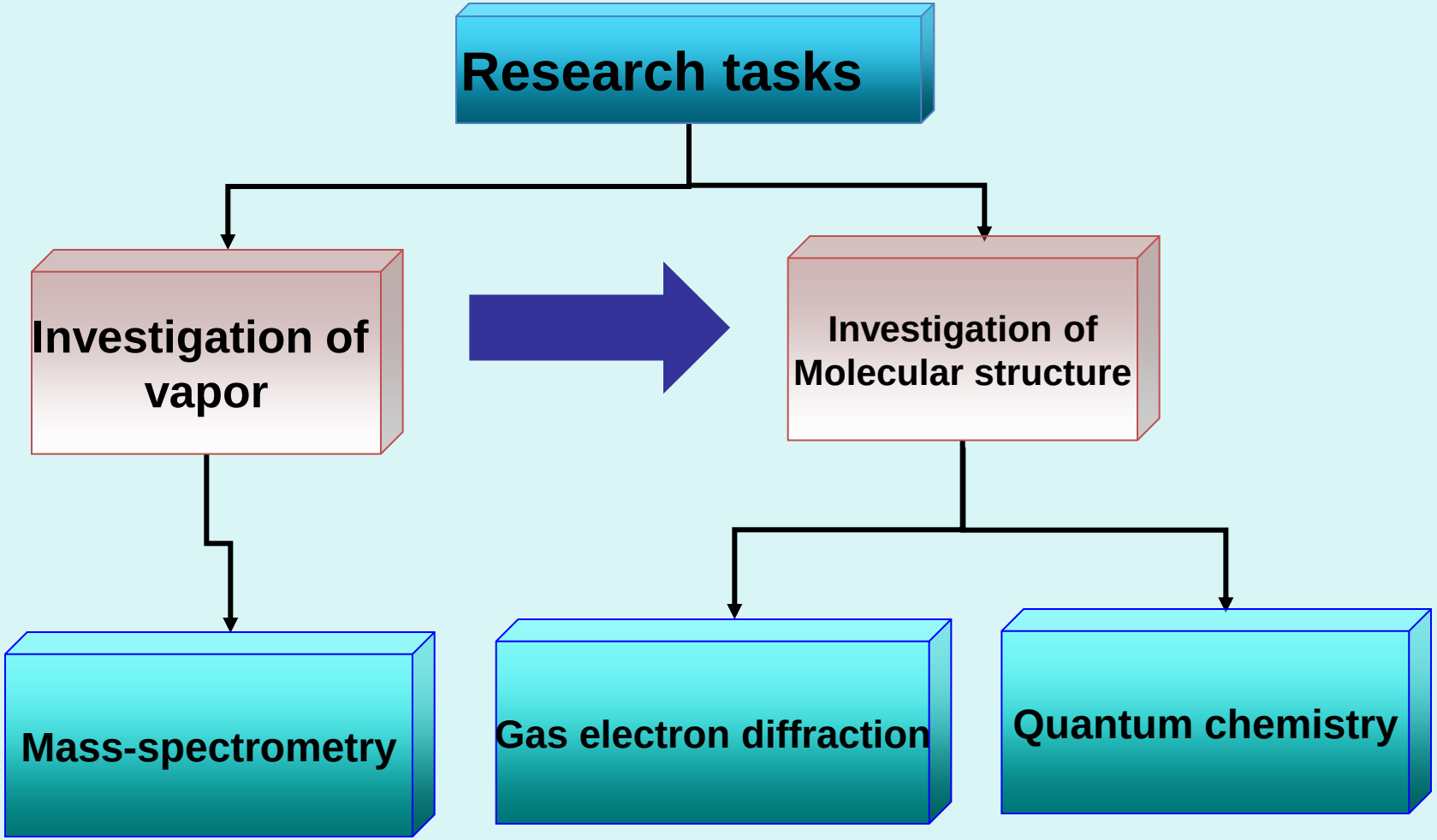
"electron diffractometer + mass spectrometer" (GED/MS)

1. *Girichev G. V., Utkin A. N., Revichev Yu. F., Prib. Tekh. Eksp. (Russian) 1984, N2, 187-190;*
2. *Girichev G. V., Shlykov S. A., Revichev Yu. F., Ibid. (Russian) 1986, N4, 167-169*

Complex approach







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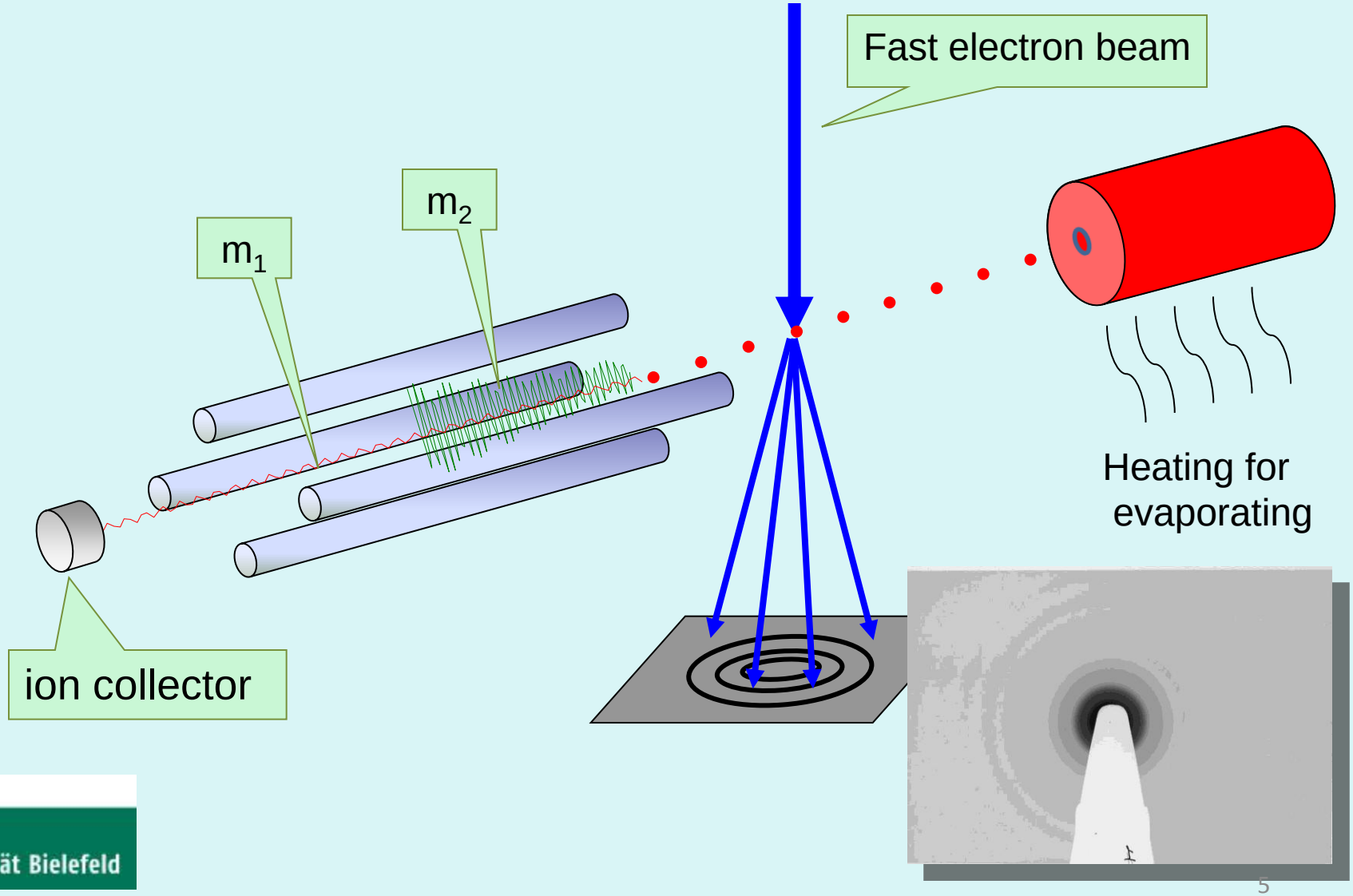
Synchronous gas electron diffraction and mass spectrometric experiment







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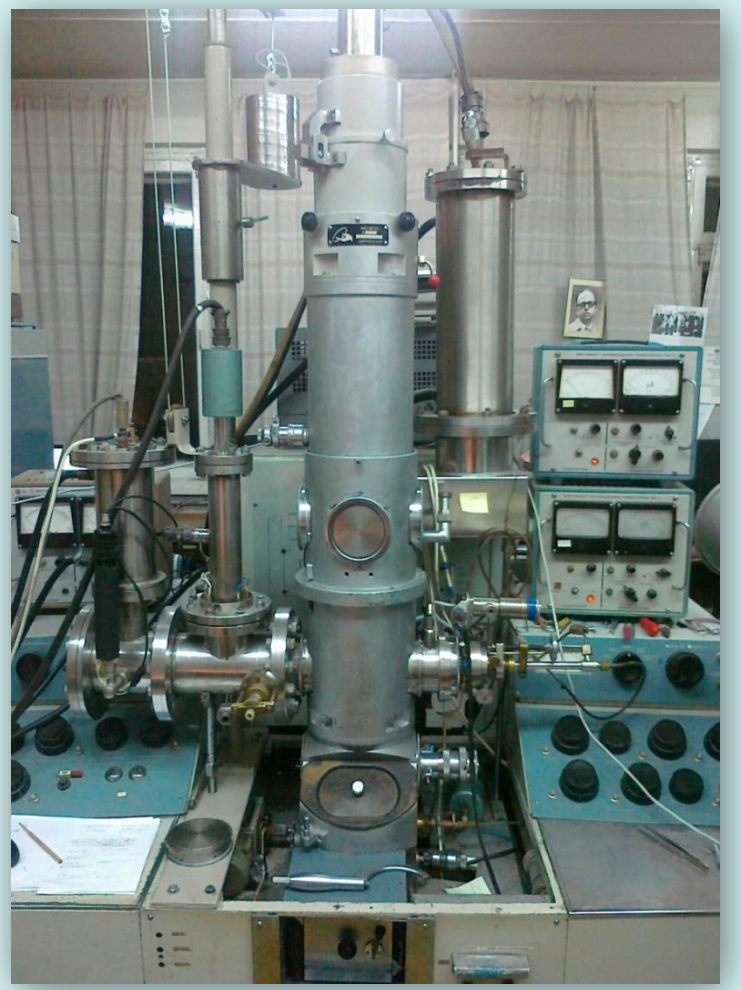
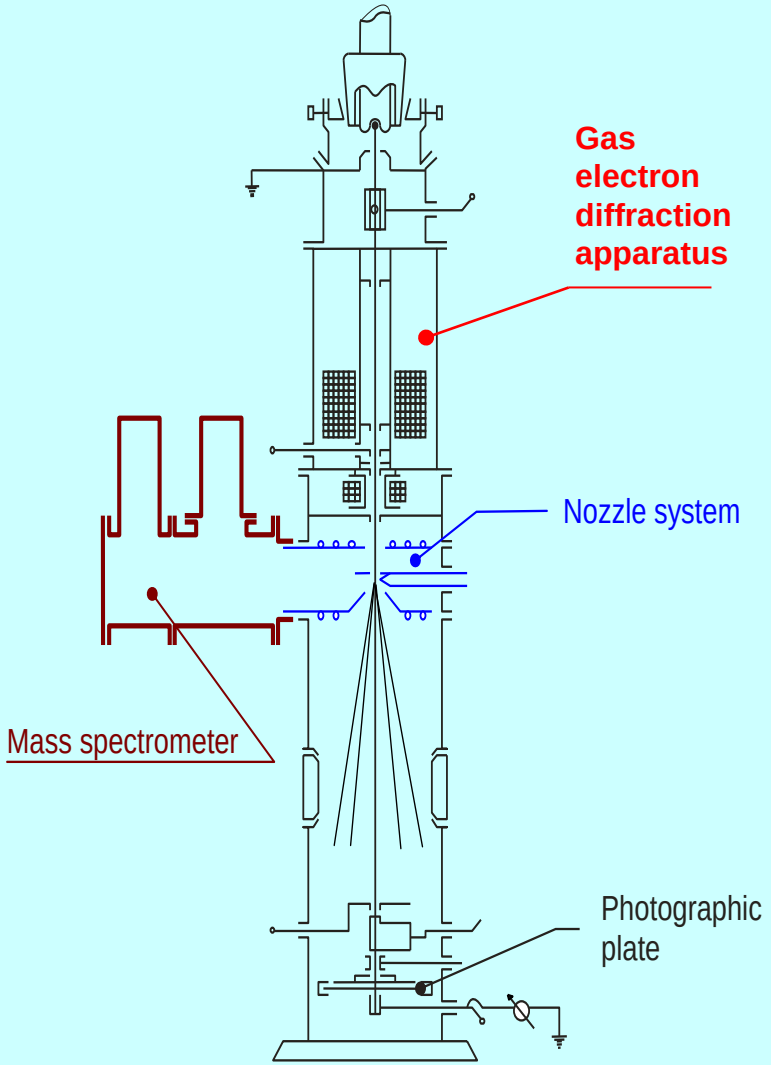
Ivanovo GED equipment









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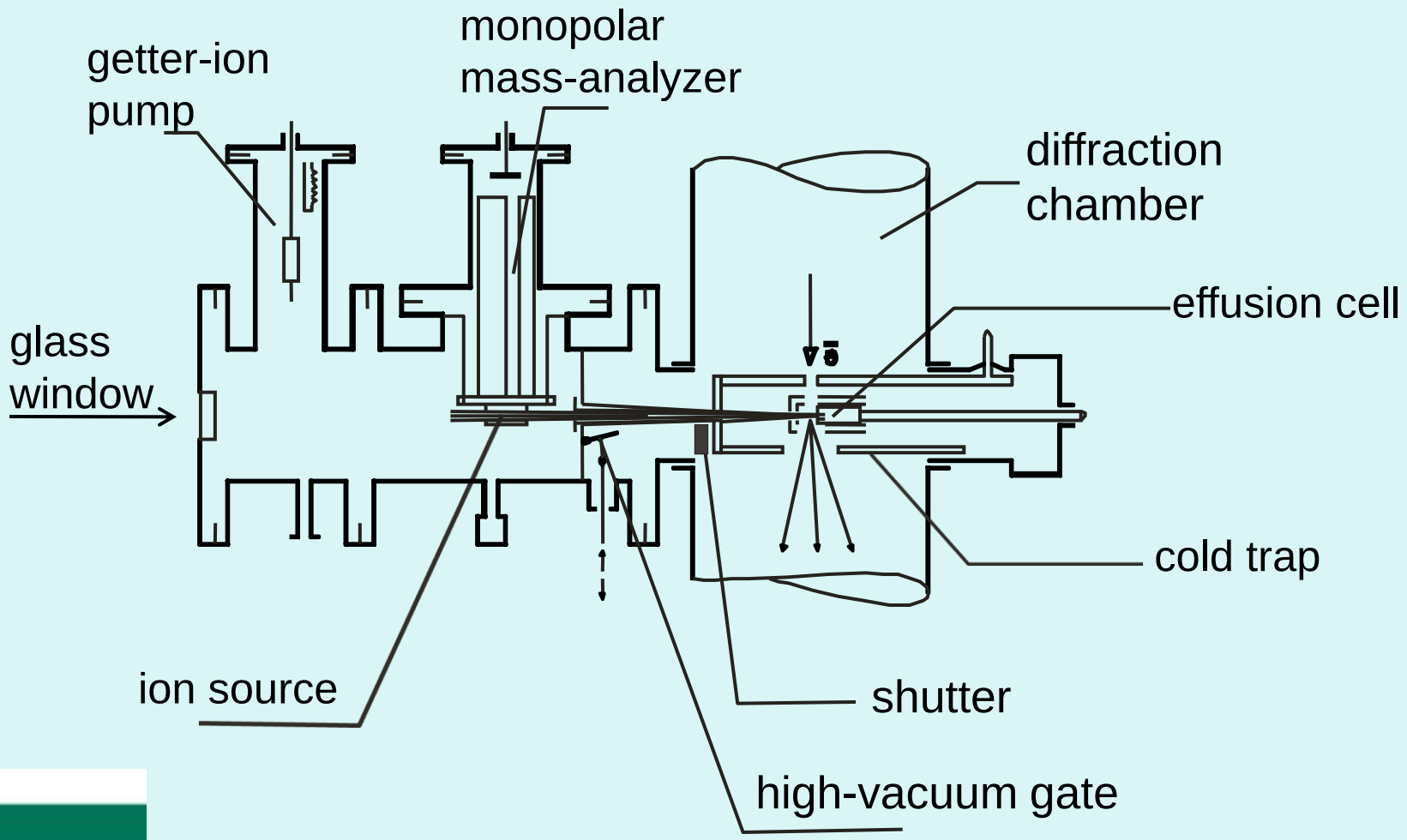
Ivanovo GED instrument/mass-spectrometer assembly







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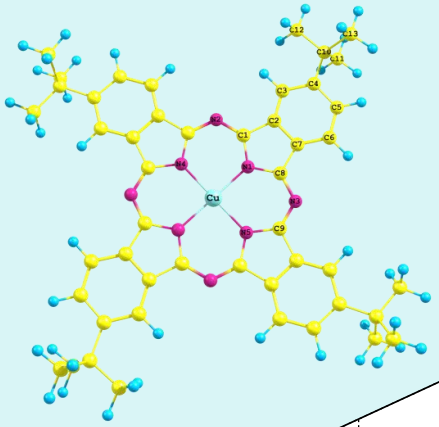
Mass-spectrometry is “eyes” of conventional electron diffraction

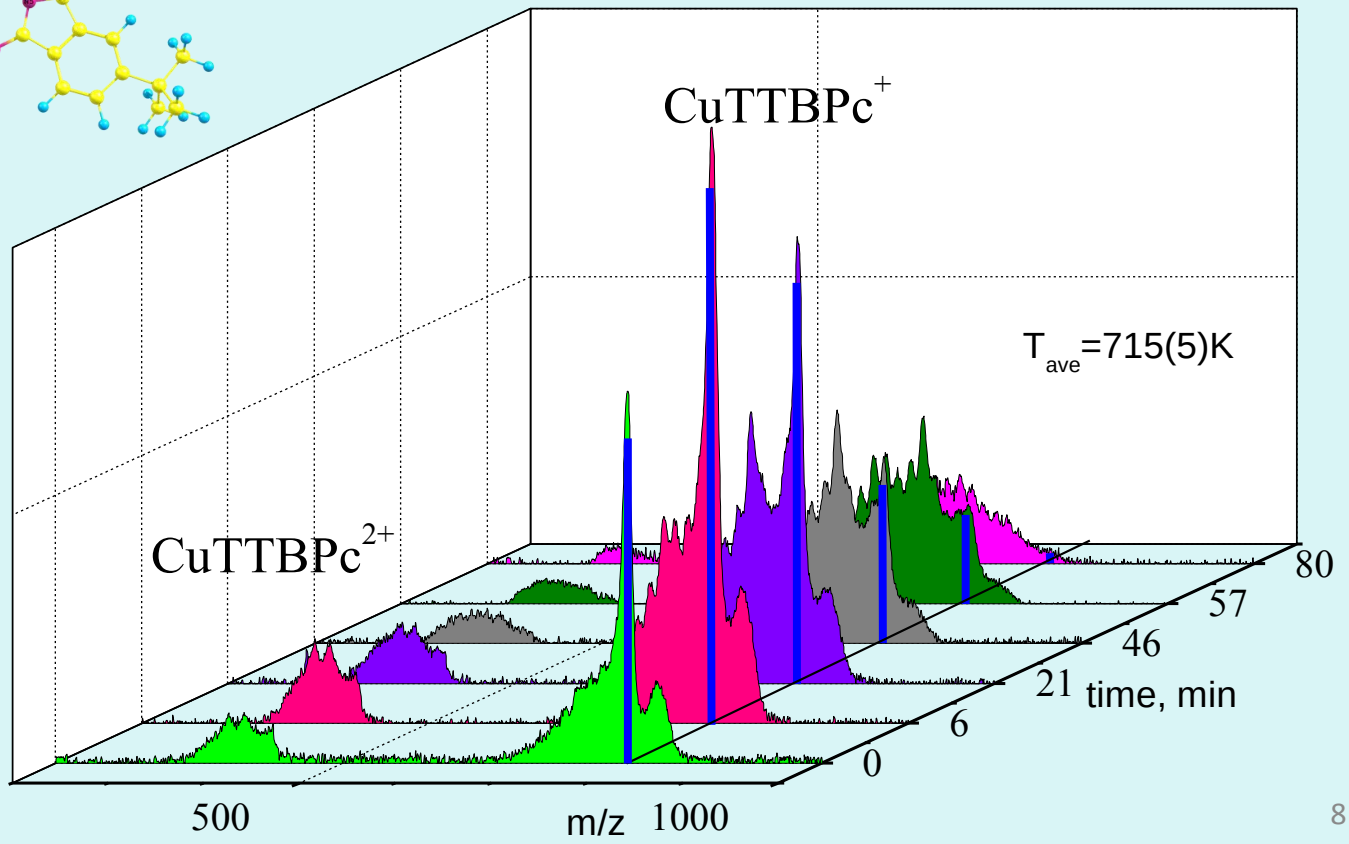




Copper (II) 2,9,16,23-tetra-*tert*-butyl-phthalocyanine (CuTTBPc)



Time dependence of CuTTBPc vapor composition



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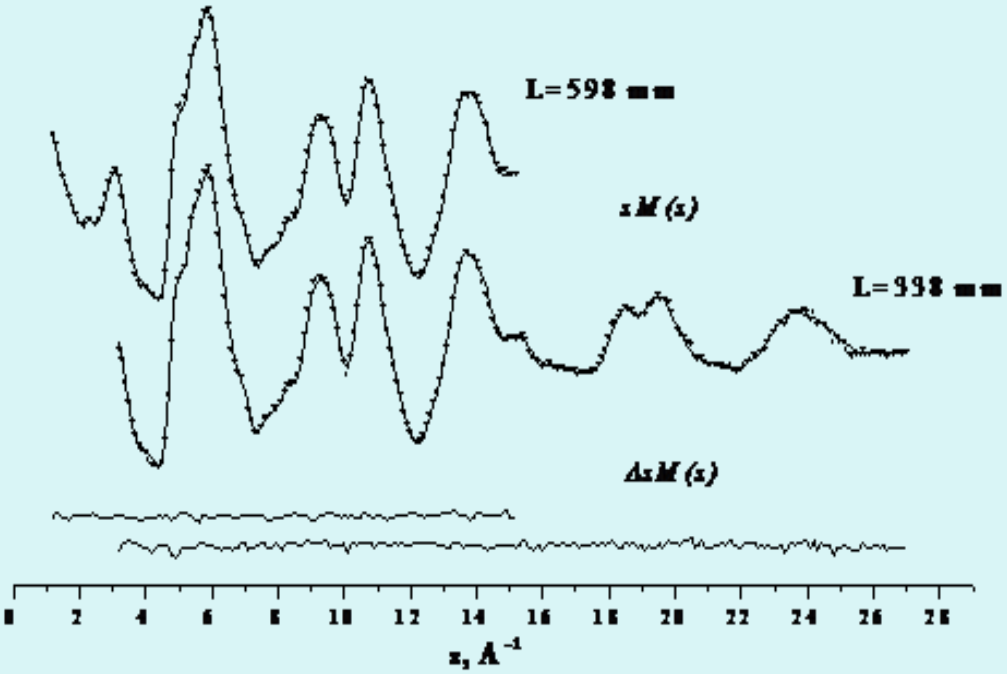
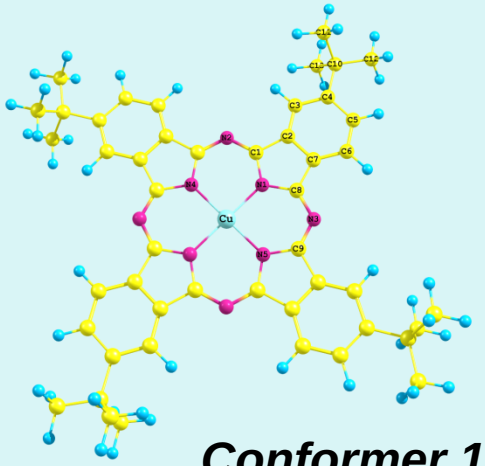
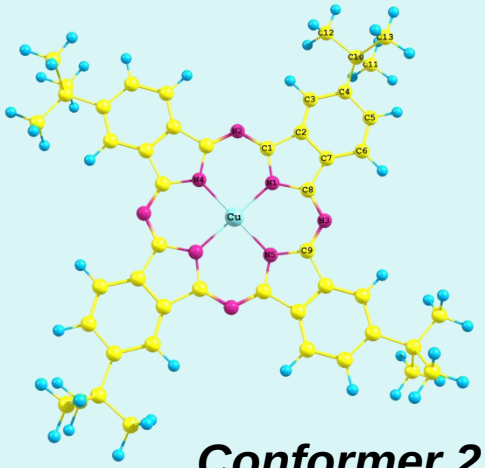
Molecular intensity functions sM(s) of CuTTBPc (dots – experimental; solid line – theoretical)



$R_{f2} / R_{f1} = 4.76 / 4.36 = 1.092 > 1.072$*



Conformer 1
(C_{4h} symmetry)



Conformer 2
(C_{4h} symmetry)

*Hamilton WC (1965) Acta Cryst 18:502

Even if all is not well, we smile…

Literature overview

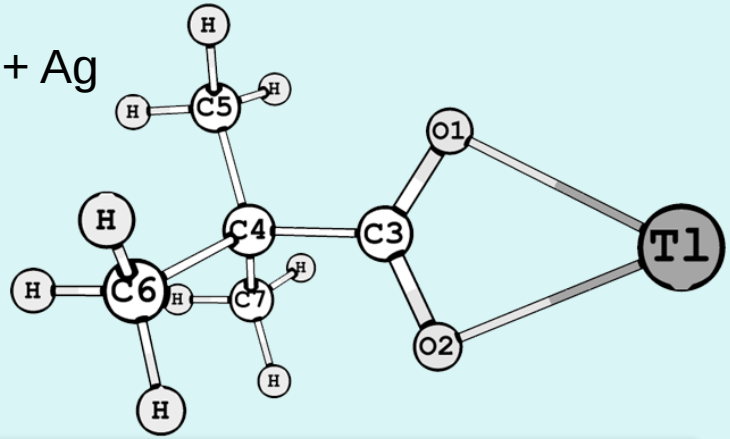




N.N. Kamkin, L.G. Kuz'mina, D.B. Kayumova, N.G. Yaryshev, I.A. Dementiev, and A.S. Alikhanyan. Synthesis and Thermodynamic and Structural Characteristics
of Thallium(I) Pivalate.Russian Journal of Inorganic Chemistry, 2012, Vol. 57, No. 9, pp. 1267–1271.

Thallium pivalate was synthesized and studied by mass spectrometry. It was shown that the set of characteristics makes thallium pivalate suitable as a precursor for the CVD preparation of oxide films and oxide materials.

Ag(piv) + Tl = Tl(piv) + Ag



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GED/MS experiment





Experimental conditions

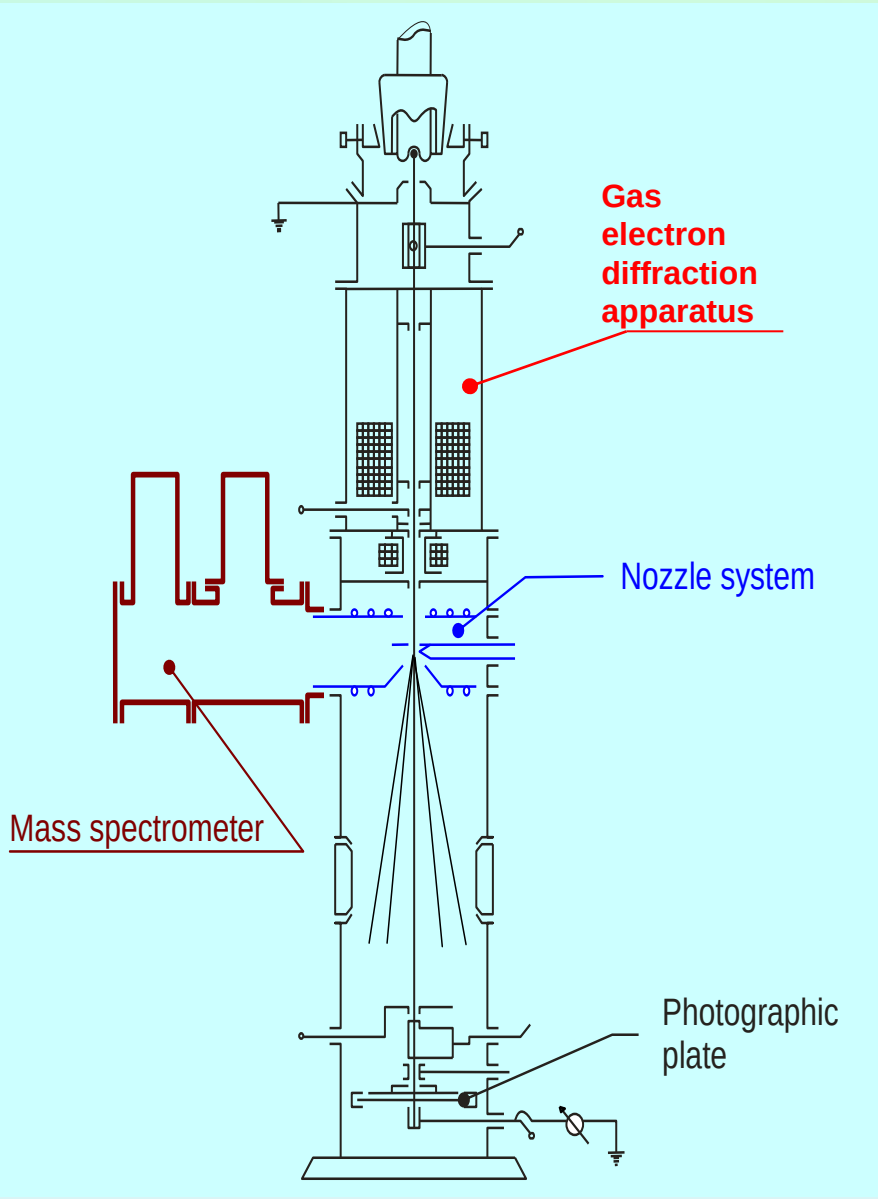
Effusion cell: graphite

Temperature: 425(5) K

Wavelength of electrons: 0.0417 Å

The synthesis of thallium(I) pivalate was carried out *in situ*

Ag(piv) + Tl = Tl(piv) + Ag



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Computational details





- Program : Gaussian 03
- Methods: DFT(B3LYP)
- Basis sets:

  - cc-pVTZ for **O**, **C** and **H**

  - ECP (60 electrons) + aug-cc-pVTZ-PP for **Tl**

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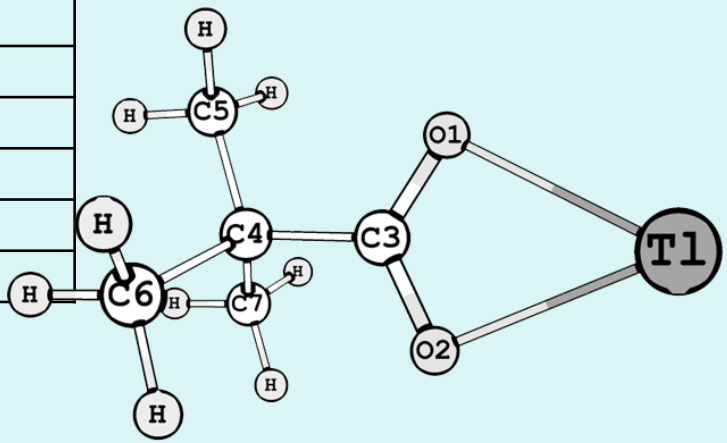
Structural parameters

Parameters[a]				
	r_e B3LYP/ cc-pVTZ	r_{h1}, $\angle_{h1}$ GED	l GED	l QC
r(Tl-O1)	**2.468**	**2.412(7)**[в]	0.143(4)	0.109
r(Tl-O2)	**2.457**	**2.423(7)**	0.146(4)	0.112
r(O1-C3)	1.266	1.263(4)	0.042(3)	0.043
r(O2-C3)	1.269	1.267(4)	0.042(3)	0.043
r(C3-C4)	1.539	1.533(4)	0.053(3)	0.055
r(C4-C5)	1.532	1.526(4)	0.053(3)	0.053
r(C4-C6)	1.540	1.534(4)	0.053(3)	0.055
r(C-H)[b]	1.091	1.096(5)	0.076(3)	0.077
r(O1…O2)	2.217	2.185(10)	0.086(4)	0.052
∠O2-M-O1	53.5	53.7(2)		
∠O2-C3-O1	122.0	119.5(6)		
∠O1-C3-C4	119.9	120.6(6)		
∠C3-C4-C5	111.1	110.7(4)		
∠C3-C4-C6	108.0	107.6(4)		
τ(O1-C3-C4-C5)	0.0	8.0(80)		

[a] Distances r, amplitudes l and shrinkage δ in Å, angle in deg.

[b] Uncertainties given in parentheses were taken as: $[(2.5s_{LS})^2 + s^2_{scale}]^{1/2}$ (σ_{scale} = 0.002r, σ_{LS} is a standard deviation in least-squares refinement) for bond distances; $3\sigma_{LS}$ for bond angles.



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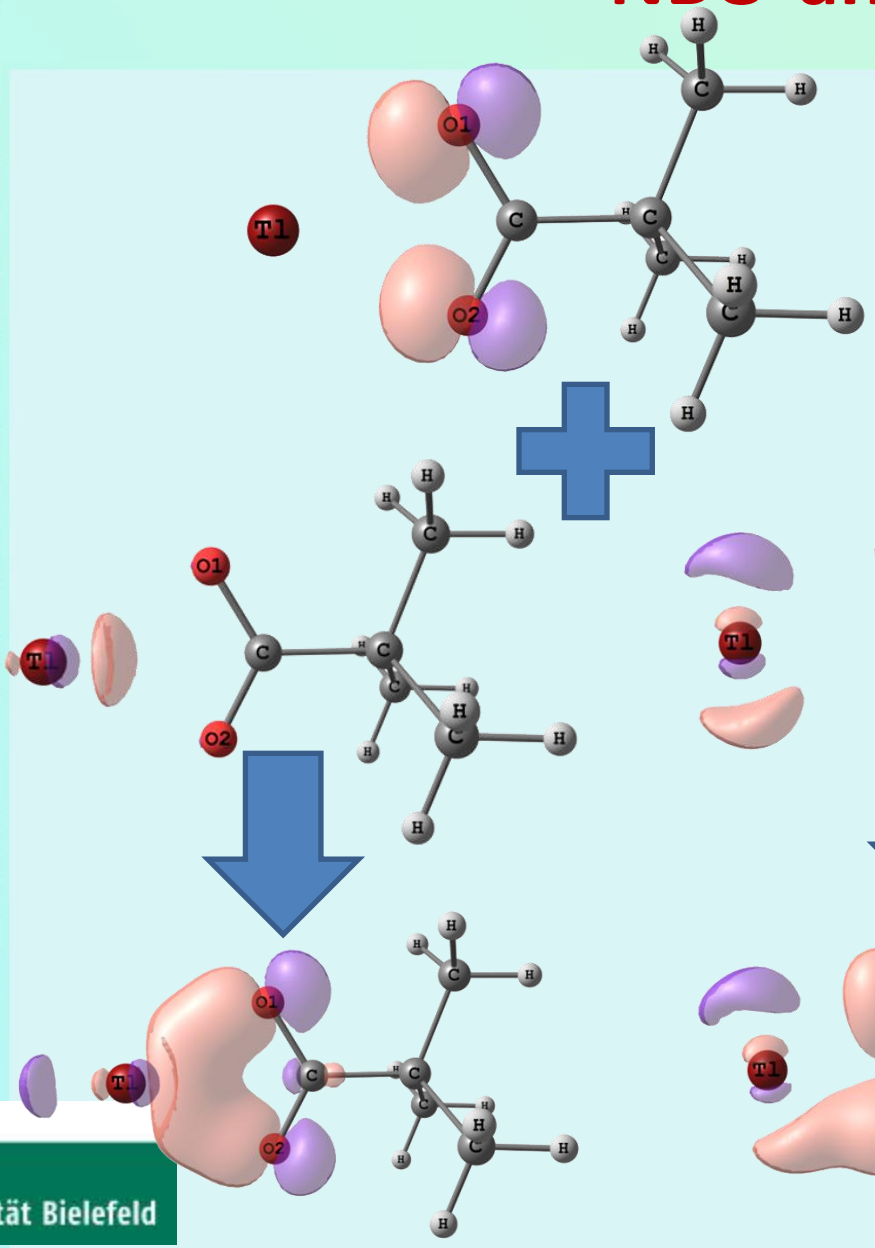
NBO-analysis



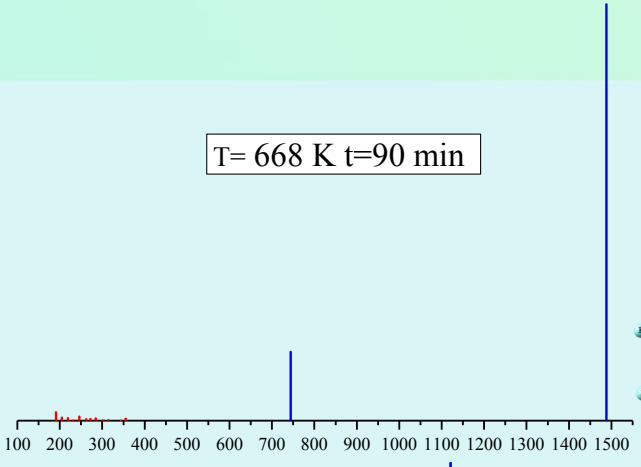
M←O direct donation	$E^{(2)}$	$\sum E^{(2)}$(M←N)
B3LYP/ECP(Tl), cc-pVTZ(N,C,H)		
$hsp^{1.76}$(O1)→ $6p_y$(Tl)	10.89	
$hsp^{1.76}$(O1)→ $6p_x$(Tl)	6.48	*17.37*
$hsp^{1.75}$(O2)→ $6p_y$(Tl)	11.64	
$hsp^{1.75}$(O2)→ $6p_x$(Tl)	6.57	*18.21*

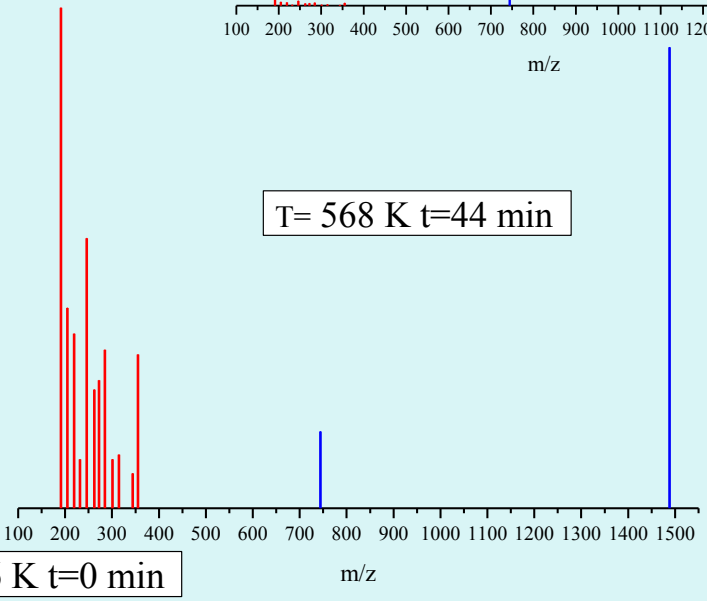
Second order perturbation energies $E^{(2)}$ (kcal/mol) of orbital interactions in the thallium(I) pivalate

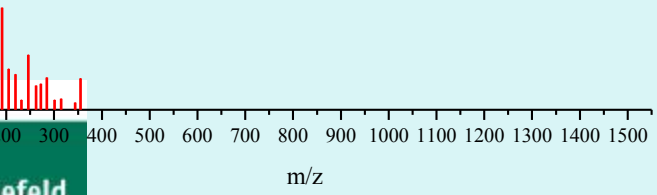
Magnesium Octa(m-trifluoromethylphenyl)porphyrazine

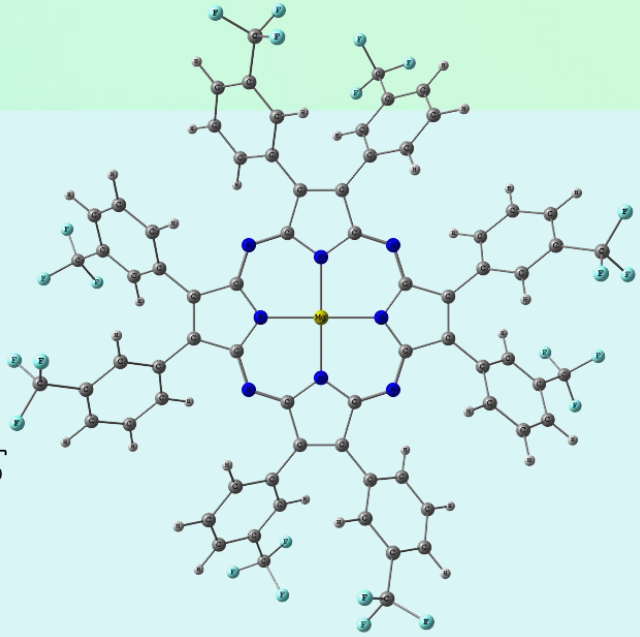


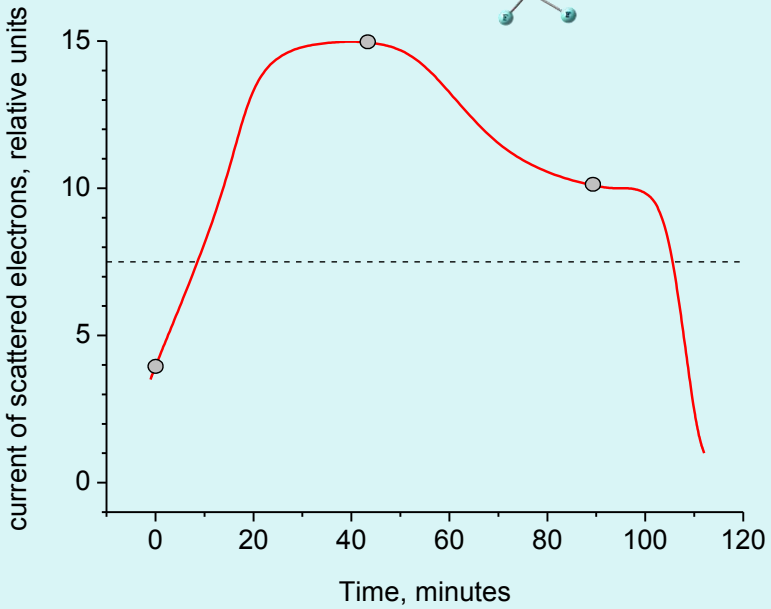












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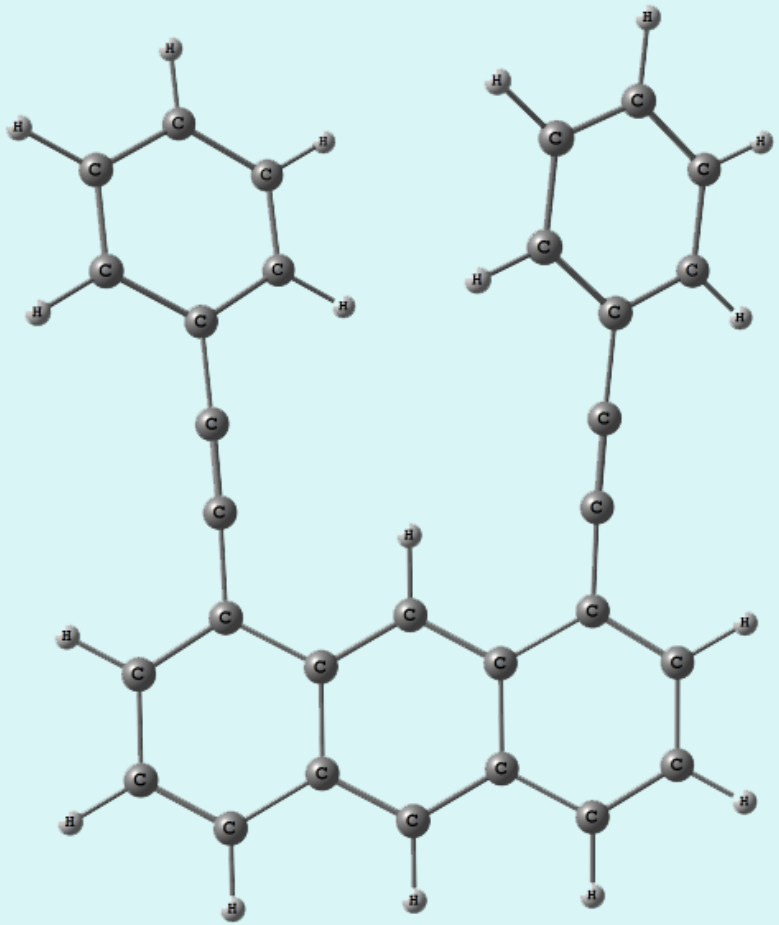
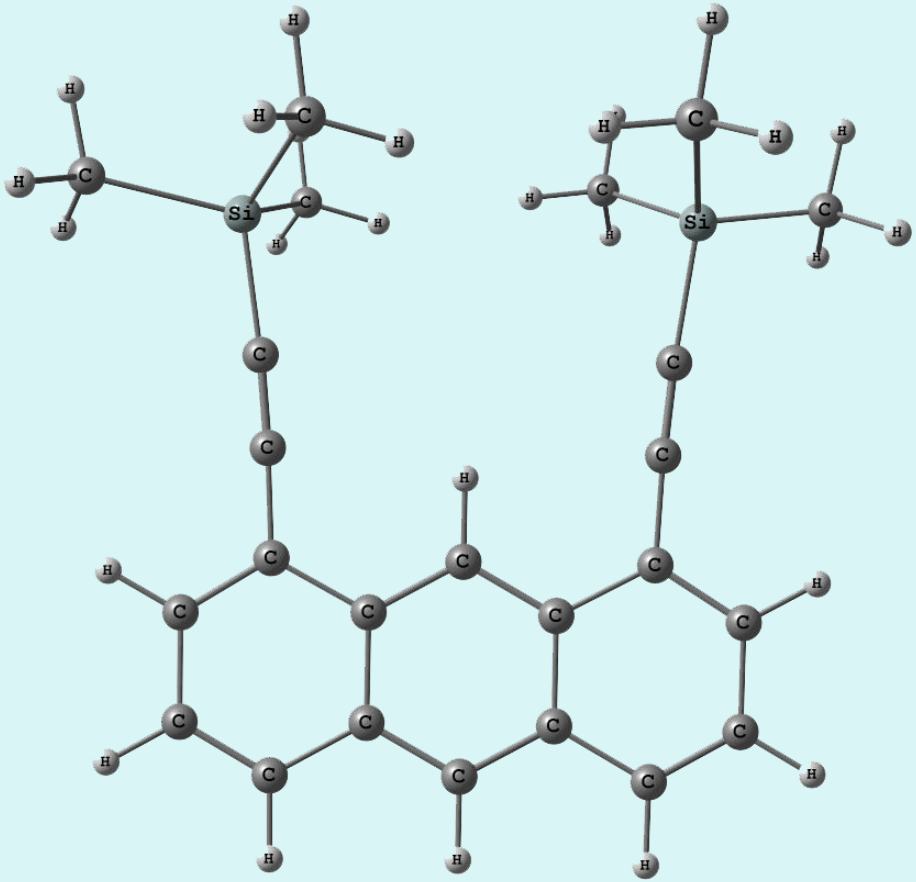
Objects of DAAD project









1,8-bis(phenylethinyl)anthracene

1,8-bis(trimethylsilylethinyl)anthracene

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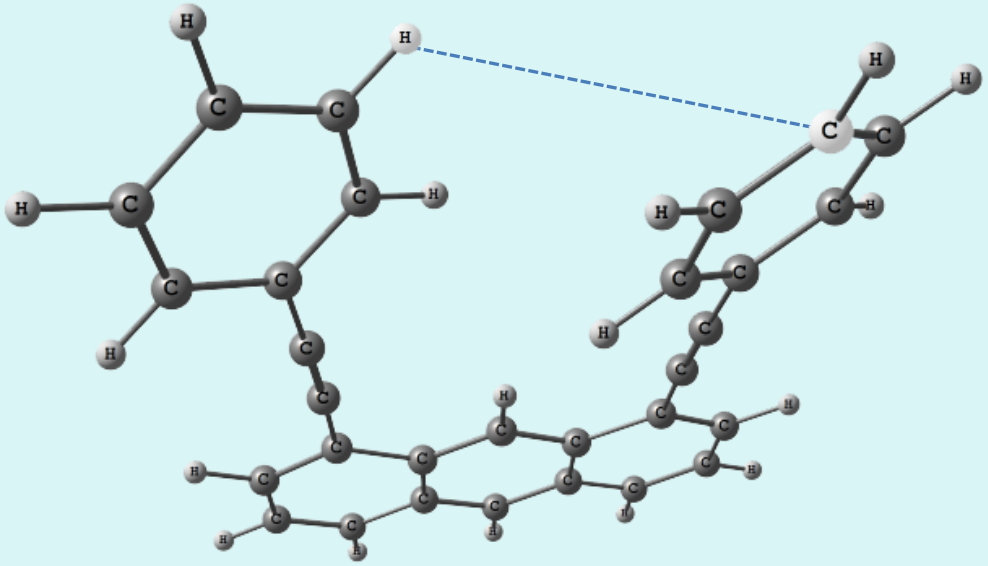
Problem of vibration corrections



r_e=4.602 Å

SHRINK
$\Delta r = r_{h1} - r_a$ =17.38 Å

MD simulation
cp2k
BLYP/DZVP

MDVibCor
$\Delta r = r_e - r_a$ = -0.975 Å

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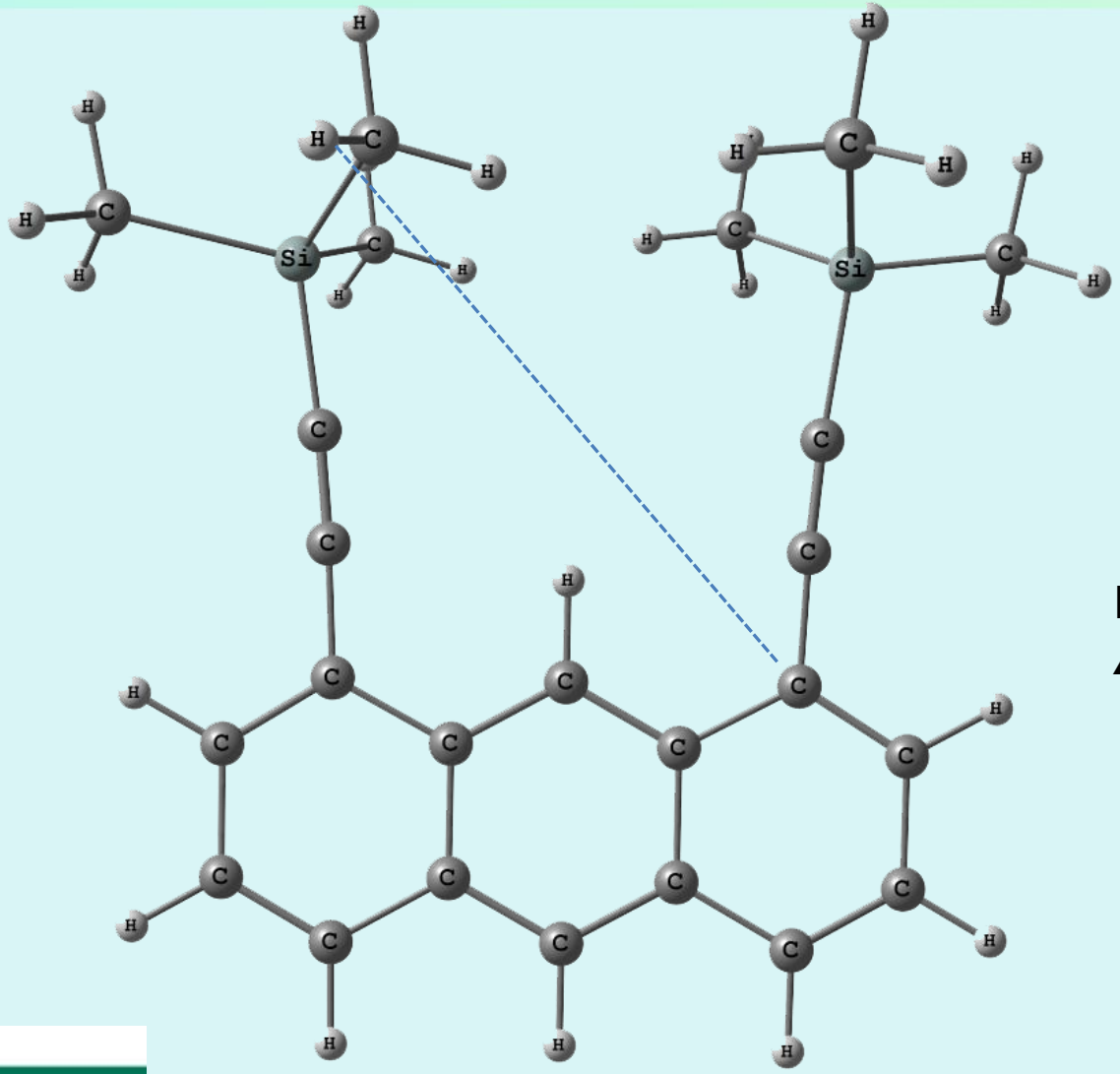

r_e=7.095 Å

SHRINK

$\Delta r = r_{h1} - r_a$ =9.616 Å

MDVibCor

$\Delta r = r_e - r_a$ = -0.258 Å

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Current state of research





Quantum chemistry calculations and structural analysis

Dr. Natalya Tverdova and stud. Arseniy Olyotov

MD simulation and calculation of vibration corrections

Dr. Yuriy Zhabanov

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Thank you for attention !