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inorganic & structural chemistry

Bestimmung molekularer Strukturen in der Gasphase mittels GED

MHC7 – Freiberg 20.09.2014

Sebastian Blomeyer

Wie funktioniert GED?

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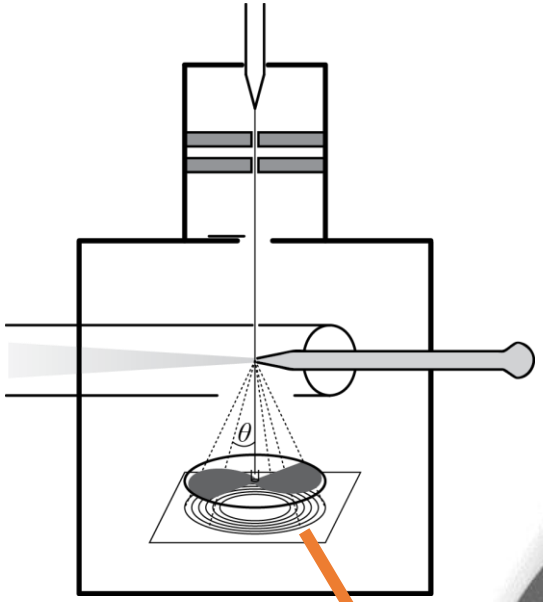

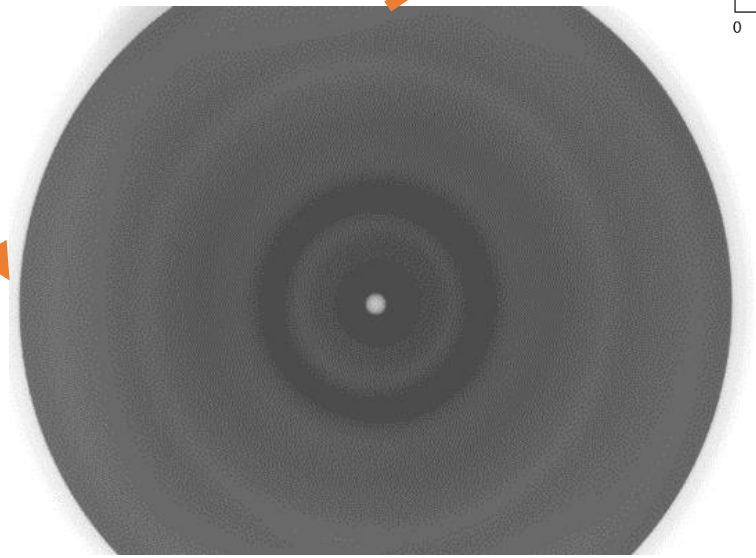

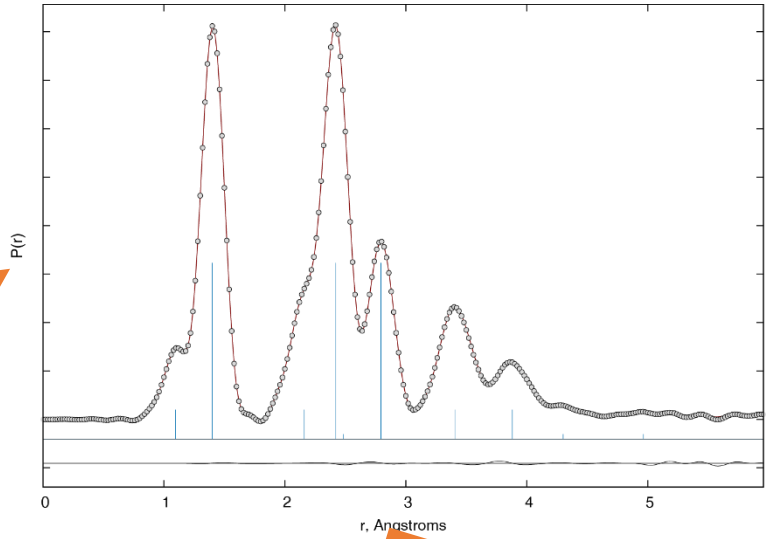

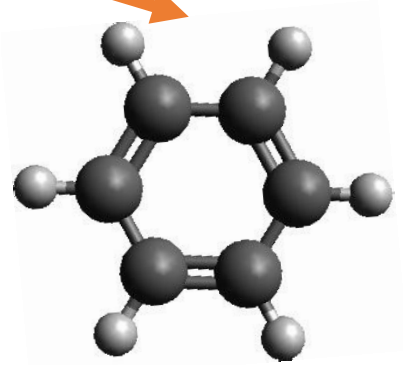

Wie funktioniert GED?

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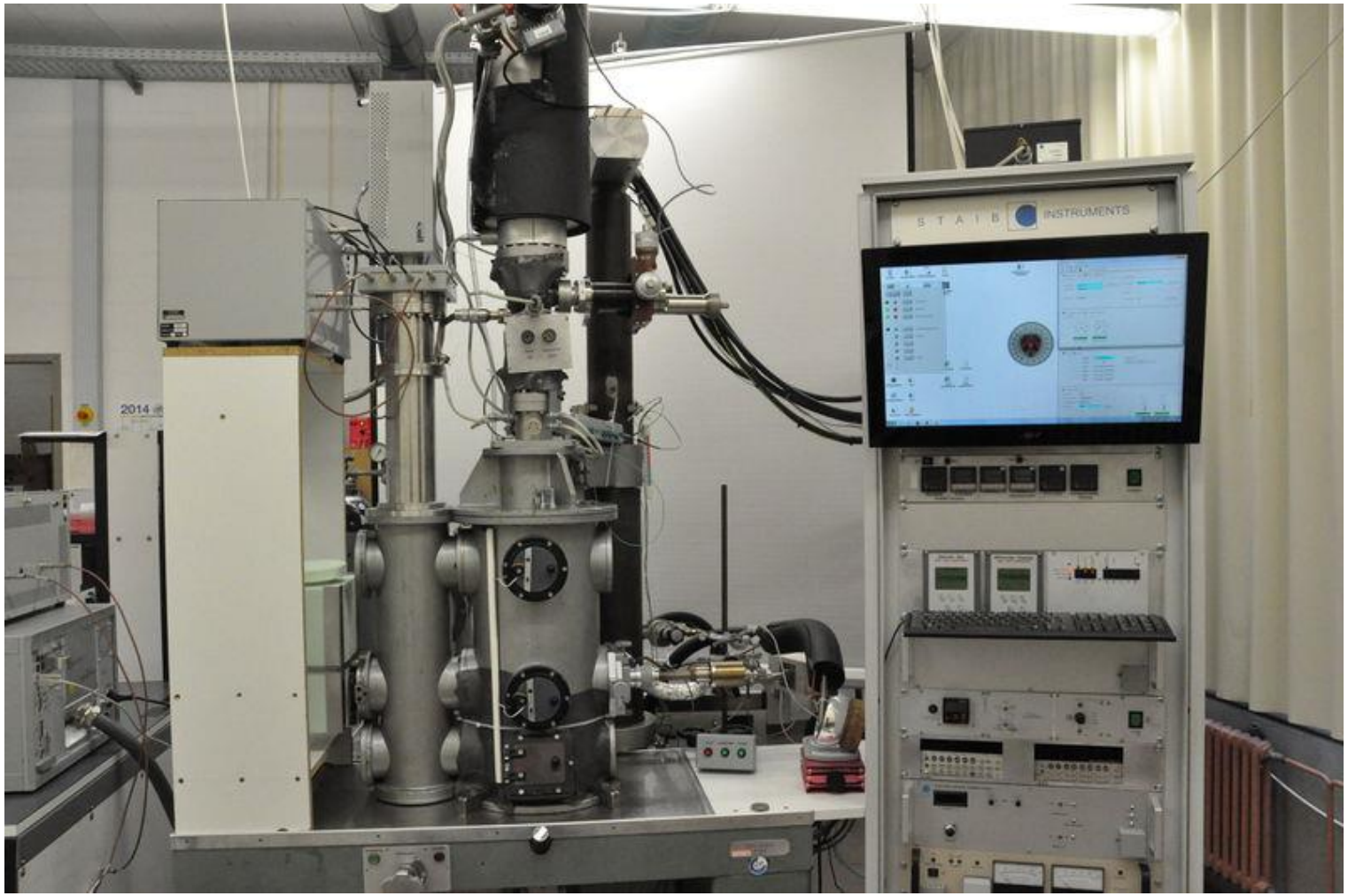

GED-Weltkarte

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Ferrocene – Struktur

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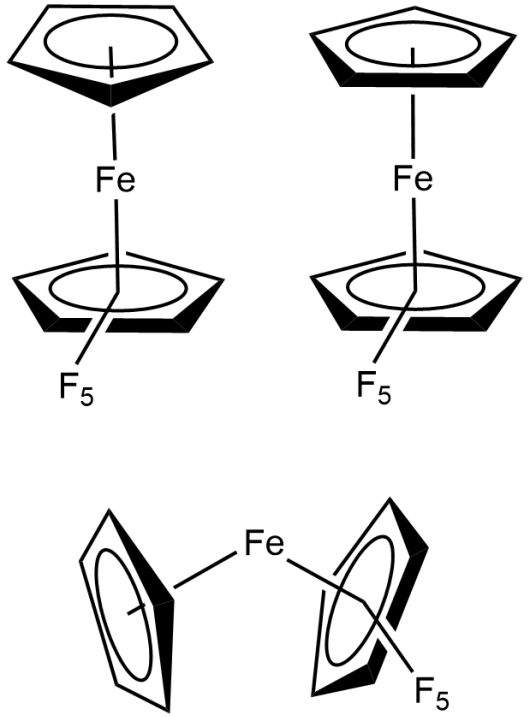

Verbindung	QC	GED	XRD
$Fe(C_5H_5)_2$	ekliptisch[1]	ekliptisch[2]	ekliptisch[3]
$Fe(C_5Me_5)_2$	gestaffelt[4]	gestaffelt[4]	gestaffelt[5]
$Fe(C_5Cl_5)_2$	gestaffelt[6]	gestaffelt[6]	–
$Fe(C_5F_5)(C_5H_5)$	???	???	ekliptisch[7]

[1] S. Coriani, A. Haaland, T. Helgaker, P. Jørgensen, *ChemPhysChem* **2006**, *7*, 245.
[2] R. K. Bohn, A. Haaland, *J. Organomet. Chem.* **1966**, *5*, 470.
[3] P. Seiler, J. D. Dunitz, *Acta Crystallogr.* **1982**, *38*, 1741.
[4] A. Almenningen, A. Haaland, S. Samdal, J. Brunvoll, J. L. Robbins, J. C. Smart, *J. Organomet. Chem.* **1979**, *173*, 293.
[5] D. P. Freyberg, J. L. Robbins, K. N. Raymond, J. C. Smart, *Acta Chem. Scand.* **1969**, *23*, 3224.
[6] L. Phillips, M. K. Cooper, A. Haaland, S. Samdal, N. I. Giricheva, G. V. Girichev, *Dalton Trans.* **2010**, *39*, 4631.
[7] K. Sünkel, S. Weigand, S. Blomeyer, C. G. Reuter, Yu. Vishnevskiy, N. W. Mitzel, *in preparation*.

$Fe(C_5H_5)(C_5F_5)$ – QC

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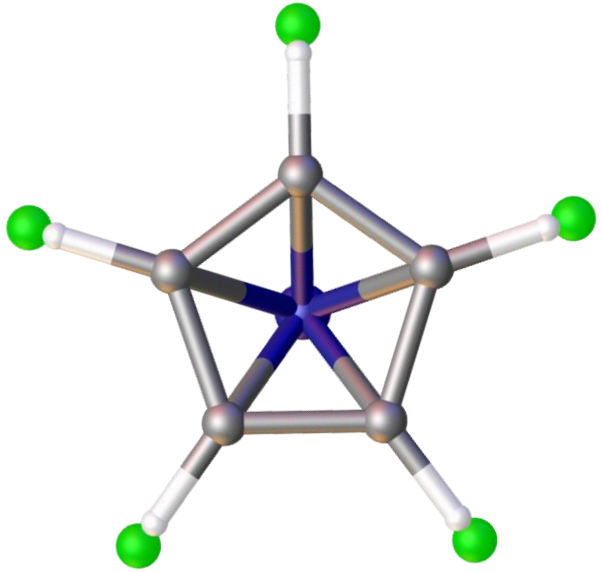
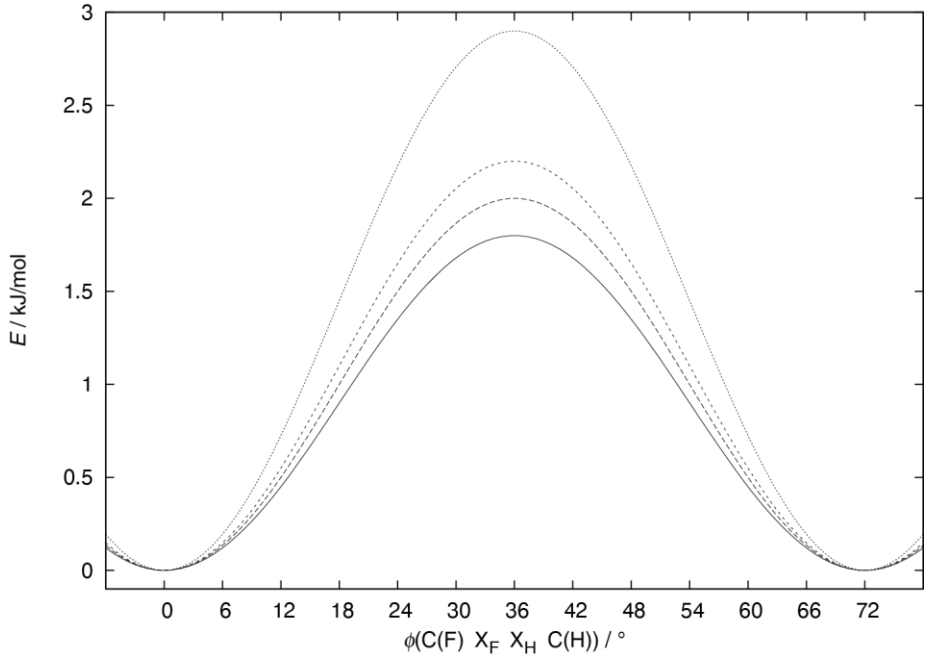
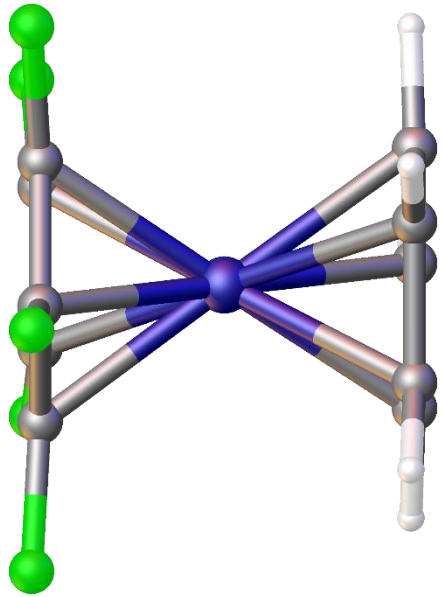
Quantenchemische Rechnungen (DFT[1] & Hybrid-DFT[2]):







[1] PBE0, PBE0+D3, B3LYP, TPSSh, B3P86, B3PW91 – cc-pVTZ, TZV2P+f
[2] B2PLYP – cc-pVTZ

$Fe(C_5H_5)(C_5F_5)$ – GED

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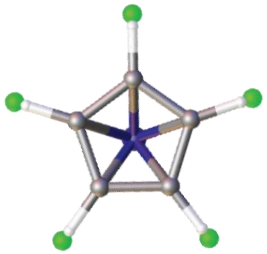
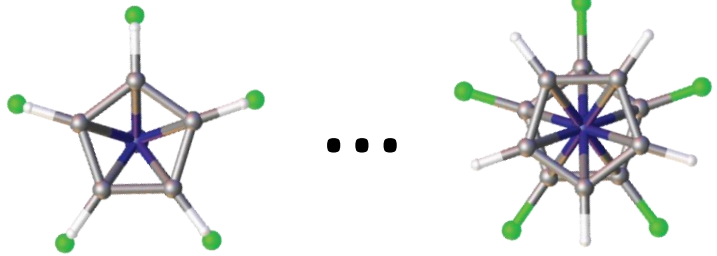
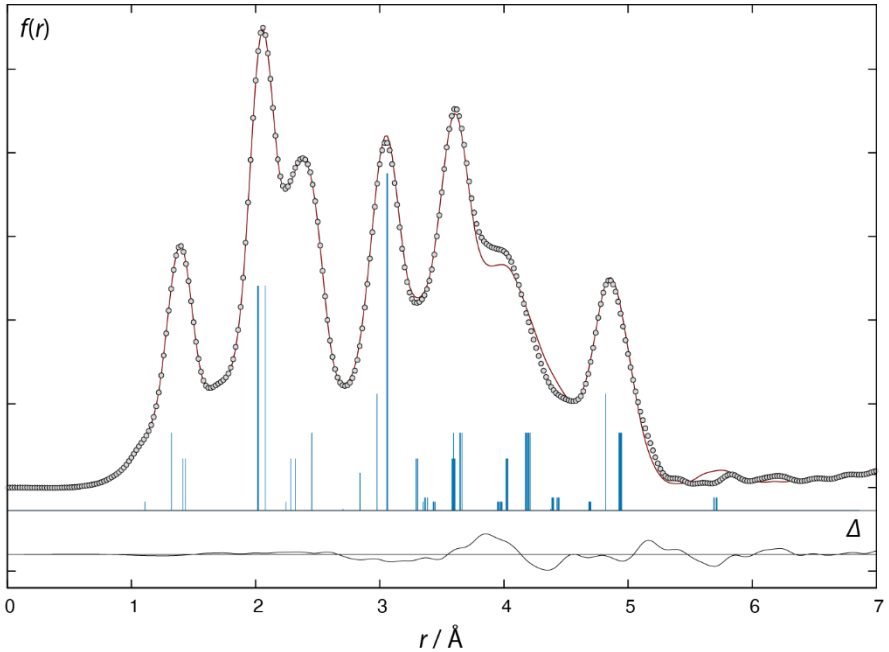


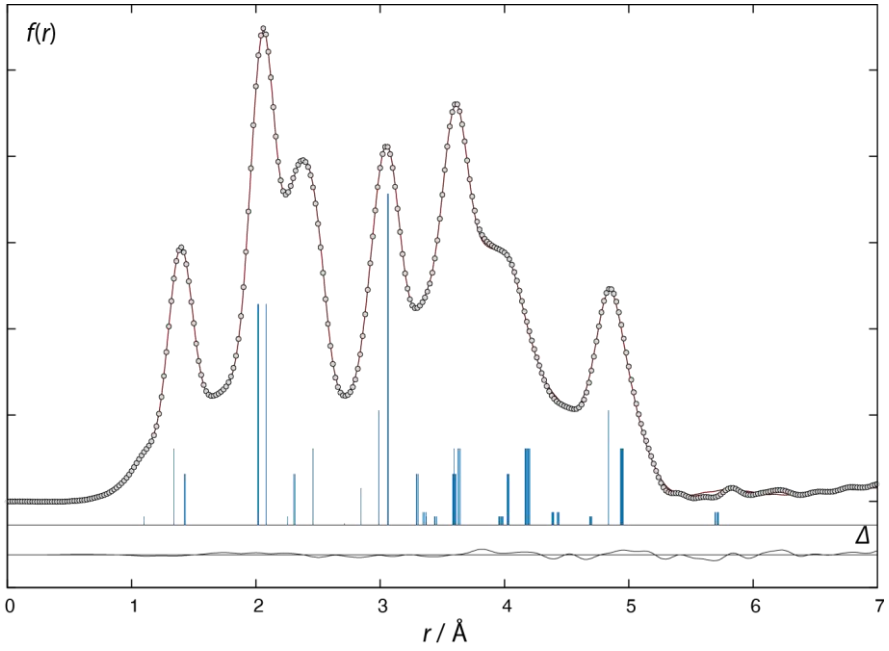
statisch



dynamisch



R_f = 5.8 %



R_f = 4.4 %

$Fe(C_5H_5)(C_5F_5)$ – GED

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Abstand/Winkel [Å/°]	GED	DFT	XRD
d(Fe–C_H)	2.071(1)	2.054	2.048(3) – 2.054(3)
d(Fe–C_F)	2.009(1)	2.012	1.997(3) – 2.005(3)
d(C–H)	1.085(7)	1.079	0.96(3) – 1.13(2)
d(C–F)	1.333(1)	1.323	1.331(4) – 1.341(4)
d(C_H–C_H)	1.425(1)	1.420	1.417(3) – 1.427(3)
d(C_F–C_F)	1.419(1)	1.420	1.410(3) – 1.416(3)
Φ(C_5-F)	−3.7(1)	−3.0	−3.5(3)
Φ(C_5-H)	+1.6(2)	+1.6	+2.1(4)

Fehler: 1σ

$Fe(C_5H_5)(C_5F_5)$ – GED

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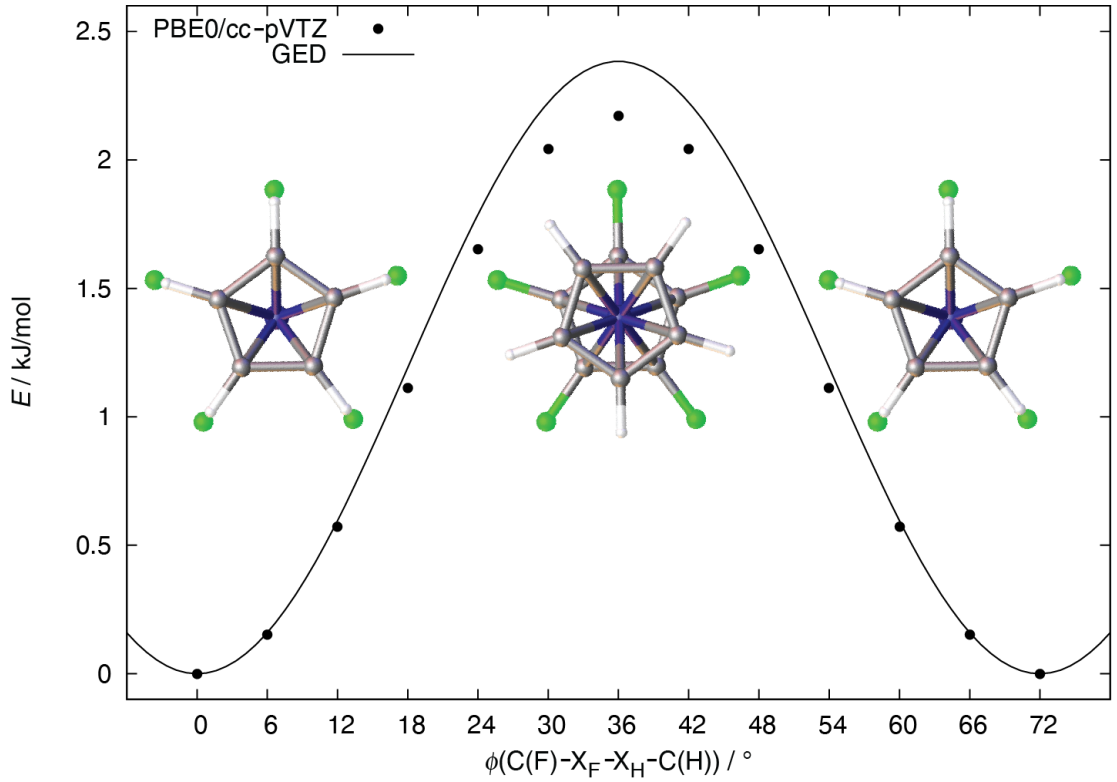

$$V(\Phi) = V_0(1 - \cos(5\Phi))/2$$

V_0 = 2.4(3) kJ mol^{-1}

Verbindung	$V_0=E_{stag}-E_{ecl}$ / kJ mol^{-1}
$Fe(C_5H_5)_2$	3.8(3)
$Fe(C_5Me_5)_2$	−4.0(3)
$Fe(C_5Cl_5)_2$	−0.8(2)

Ferrocene – Struktur

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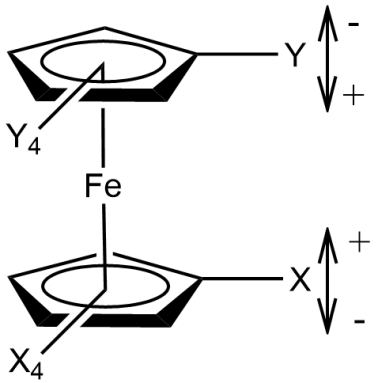

Verbindung	$a(C_5–X)$	$a(C_5–Y)$	Geometrie	Methode
$Fe(C_5H_5)_2$	+3.7(9)	+3.7(9)	ekliptisch	GED[1]
$Fe(C_5Cl_5)_2$	−3.7(3)	−3.7(3)	gestaffelt	GED[2]
$Fe(C_5H_5)(C_5Cl_5)$	+2.5	−3.6	ekliptisch	DFT
$Fe(C_5H_5)(C_5F_5)$	+1.6(6)	−3.7(3)	ekliptisch	GED[3]
$Fe(C_5F_5)_2$	−3.6	−3.6	ekliptisch	DFT

[1] R. K. Bohn, A. Haaland, *J. Organomet. Chem.* **1966**, *5*, 470.
[2] L. Phillips, M. K. Cooper, A. Haaland, S. Samdal, N. I. Giricheva, G. V. Girichev, *Dalton Trans.* **2010**, *39*, 4631.
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Résumé

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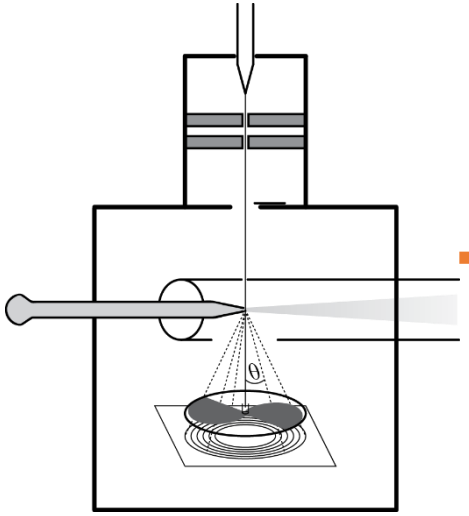

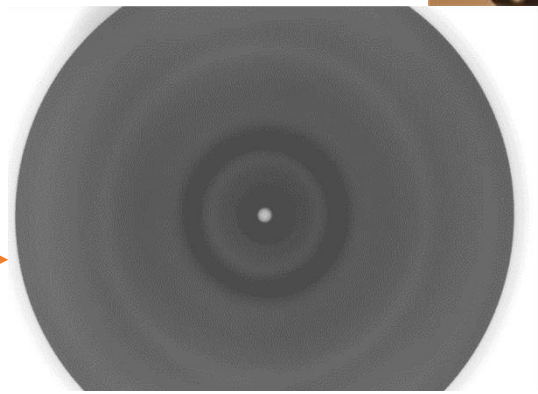

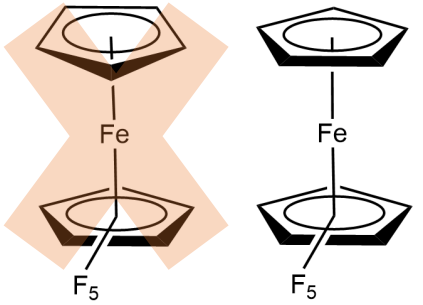

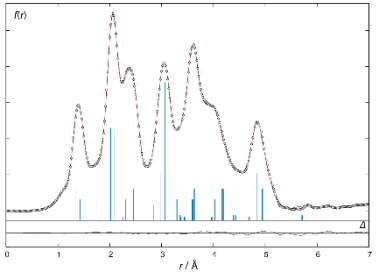

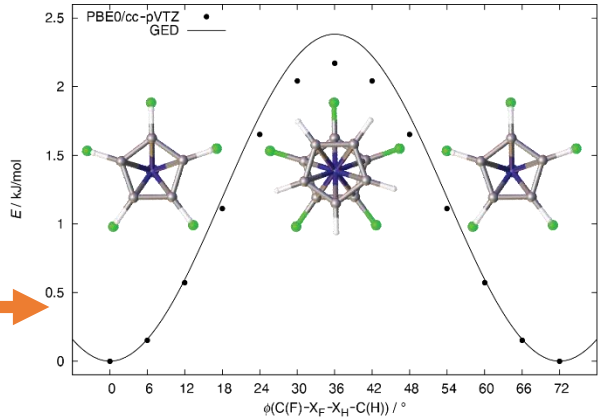

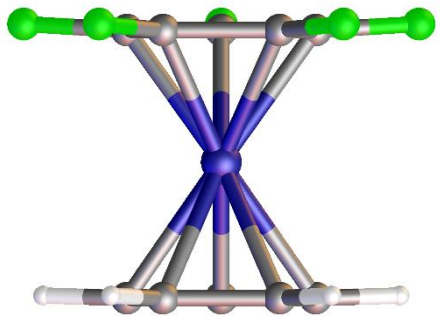

GED - Voraussetzungen

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