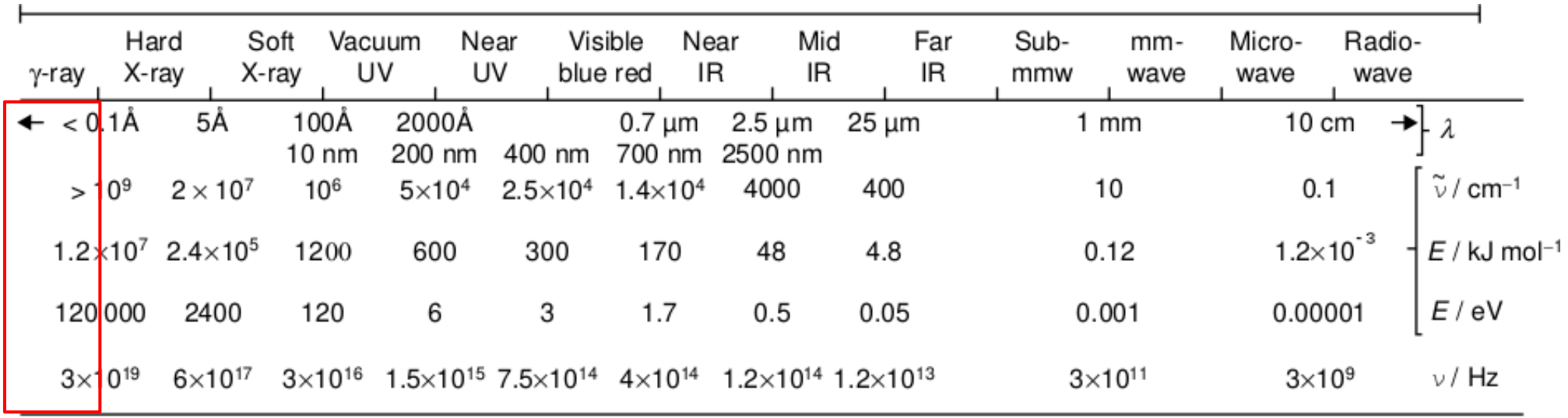
Strukturaufklärung in der molekularen anorganischen Chemie

9. Gasphasen-Elektronenbeugung

Gasphasen-Elektronenbeugung



Gasphasen-Elektronenbeugung ≡ Gasphasen-Elektronendiffraktion (GED)

Ultrafast Gasphasen-Elektronendiffraktion (UED)

λ: ~**0.05** Å (GED); ~**0.003** Å (UED)

Charakteristische Zeit: ~10^{-18} Sek.

GED

Wechselwirkung mit Strahlung:

- (Optische/Radio) Spektroskopie
- Streuung/Diffraktion
- Resonanzmethode
- Elektrische Methode
- Ionisation

Probe Beeinflussung:

- Destruktiv
- Nicht destruktiv

Anwendung:

- Identifizierung/Sauberkeit
- Elementaranalyse
- Chemische Gruppen
- Chemische Konnektivität
- Konformations-Eigenschaften
- Symmetrie
- Geometrie (Längen, Winkel)
- Schwingungen
- Elektronische Struktur (/Dichte)
- (Elektrische) Dipolmomente

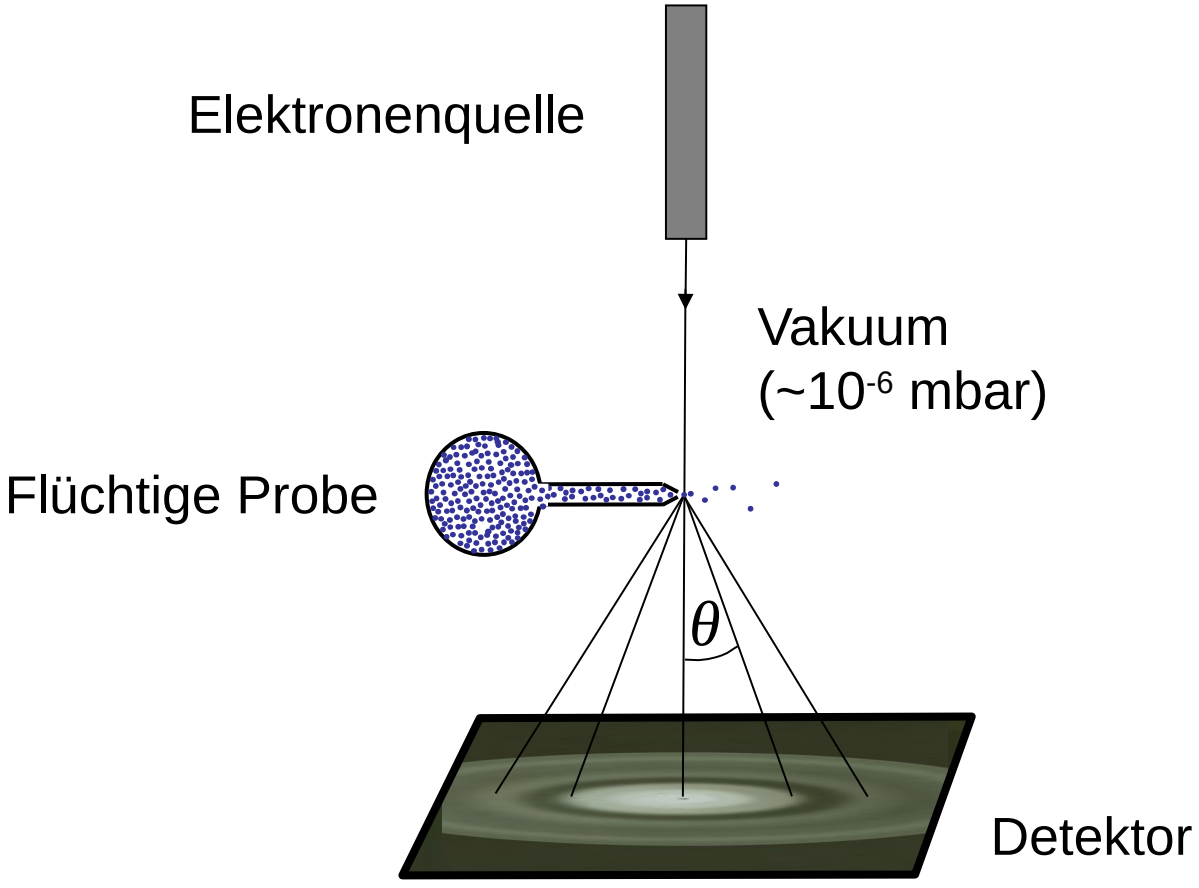
Charakteristische Zeit:

- Langsame Methode
- Mittelschnelle Methode
- Schnelle Methode

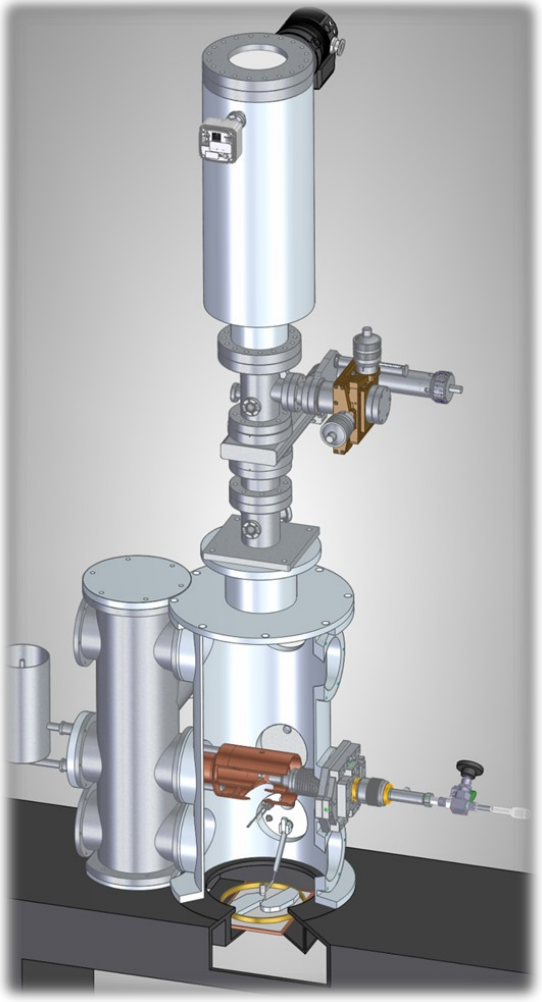
Aggregatzustand der Probe:

- Gas
- Flüssigkeit
- Feststoff

GED: prinzipielles Schema

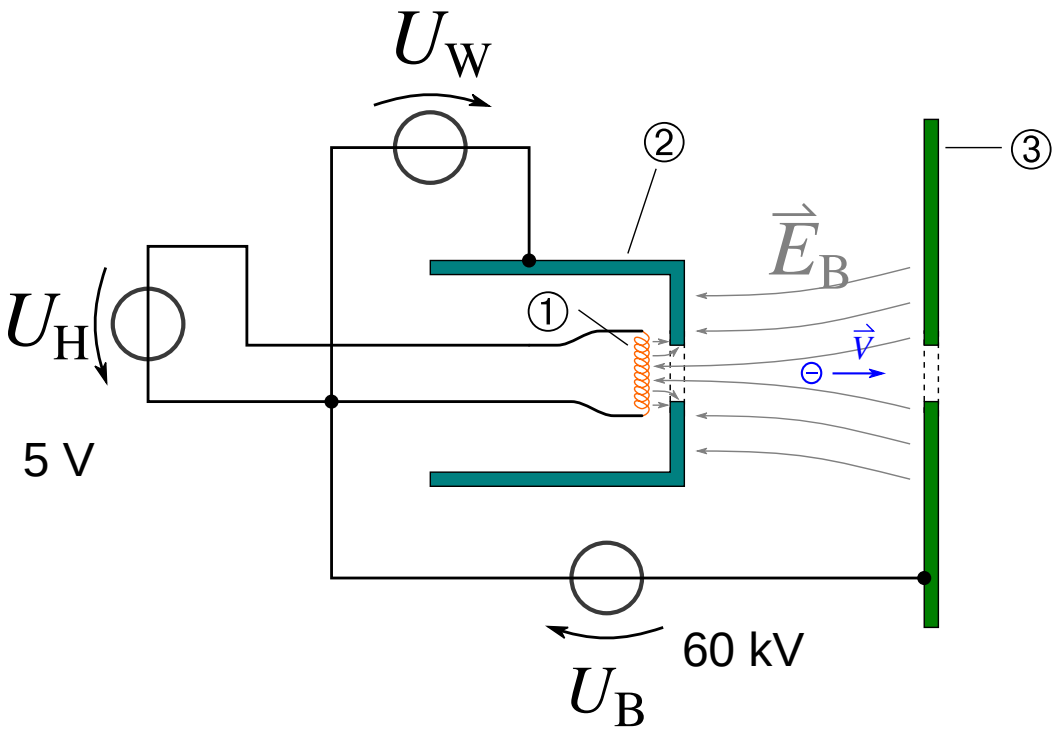


GED in Bielefeld



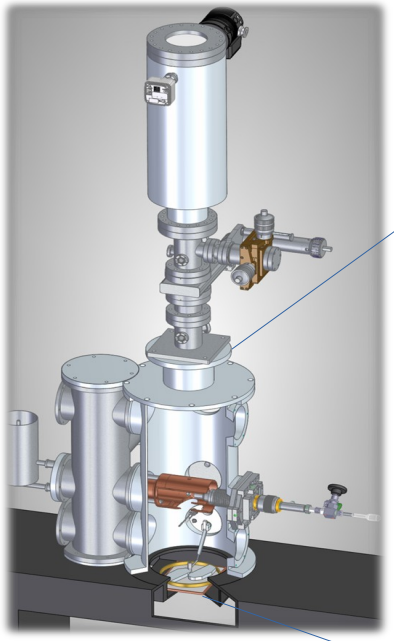
Y. V. Vishnevskiy et al., *Rev. Sci. Instrum.* 2020, 91, 073103.

Elektronenquelle



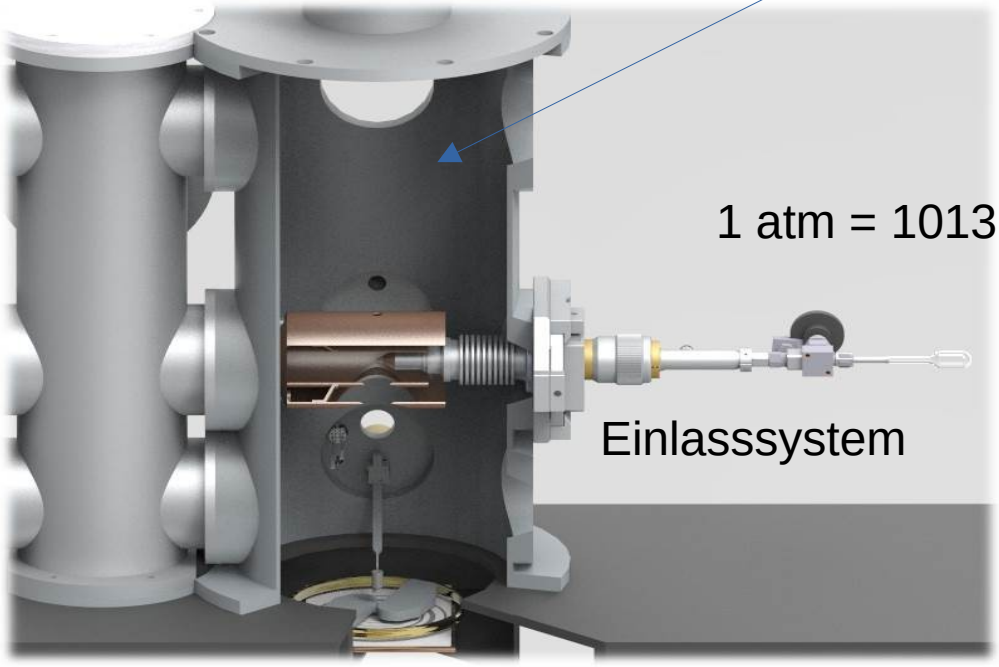
① Glühkathode
② Wehneltzylinder
③ Anodenblende

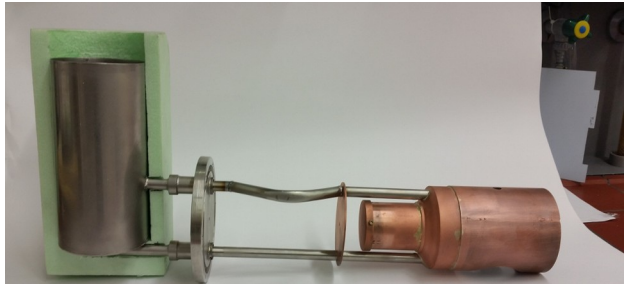
Diffraktionskammer



Hochvakuum 10^{-7} mbar

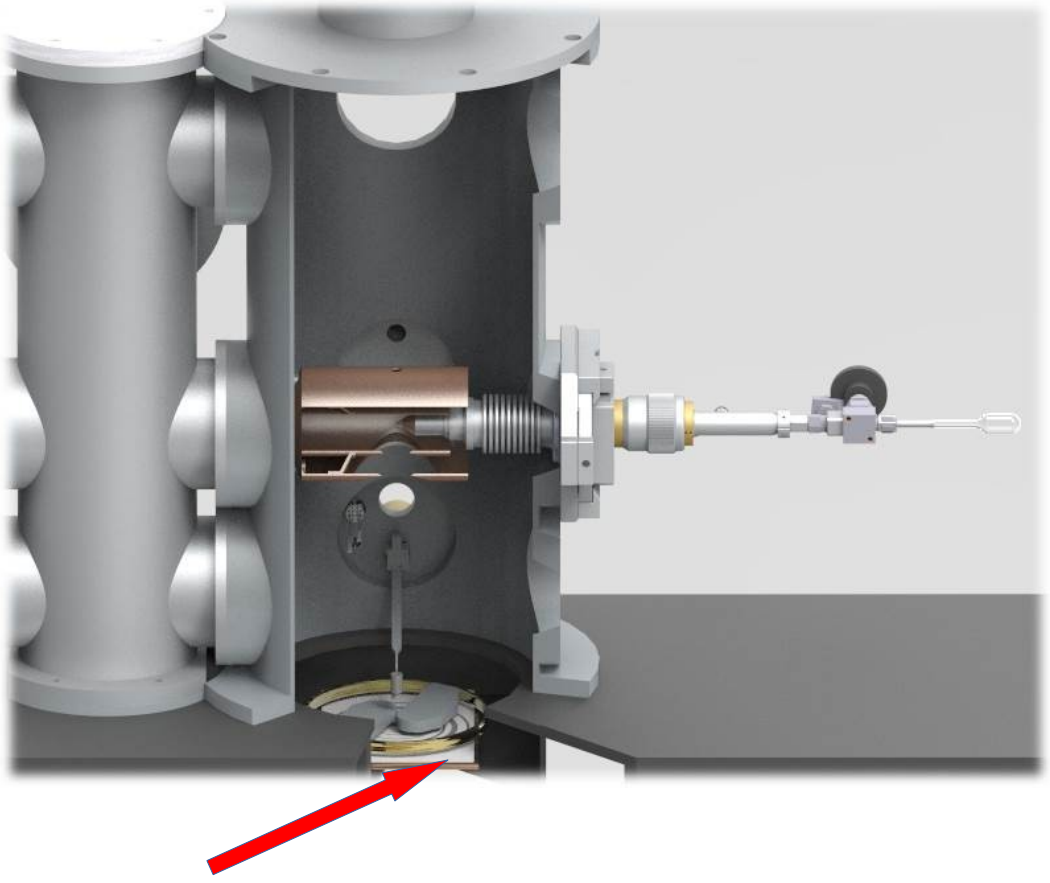
1 atm = 1013.25 mbar





Kühlfalle für flüssigen N_2 (77.355 K = −195.795 °C)

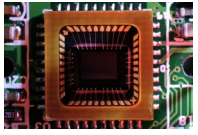
Detektorsystem



Detektor

Detektorsystem

CCD – Charge-coupled device
IP – Imaging plate
CMOS – Complementary metal-oxide-semiconductor

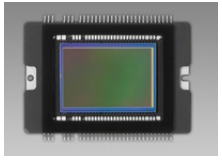


	Photo	CCD	IP	CMOS
Auflösung	+	+/-	+/-	-
Dynamic range	--	+/-	+	++
Empfindlichkeit	+/-	+	+	++
Größe	++	--	+	+
Ablesung	--	+	+/-	+
Wiederverwendung	--	++	+	++
Preis	++	+/-	+/-	--

Imaging Plate Detektor

Imaging plates: Flexible Polyester-Basis überzogen mit hochdispersem Bariumfluorohalogenid dopiert mit Eu^{2+} [$BaF(Br,I):Eu^{2+}$]

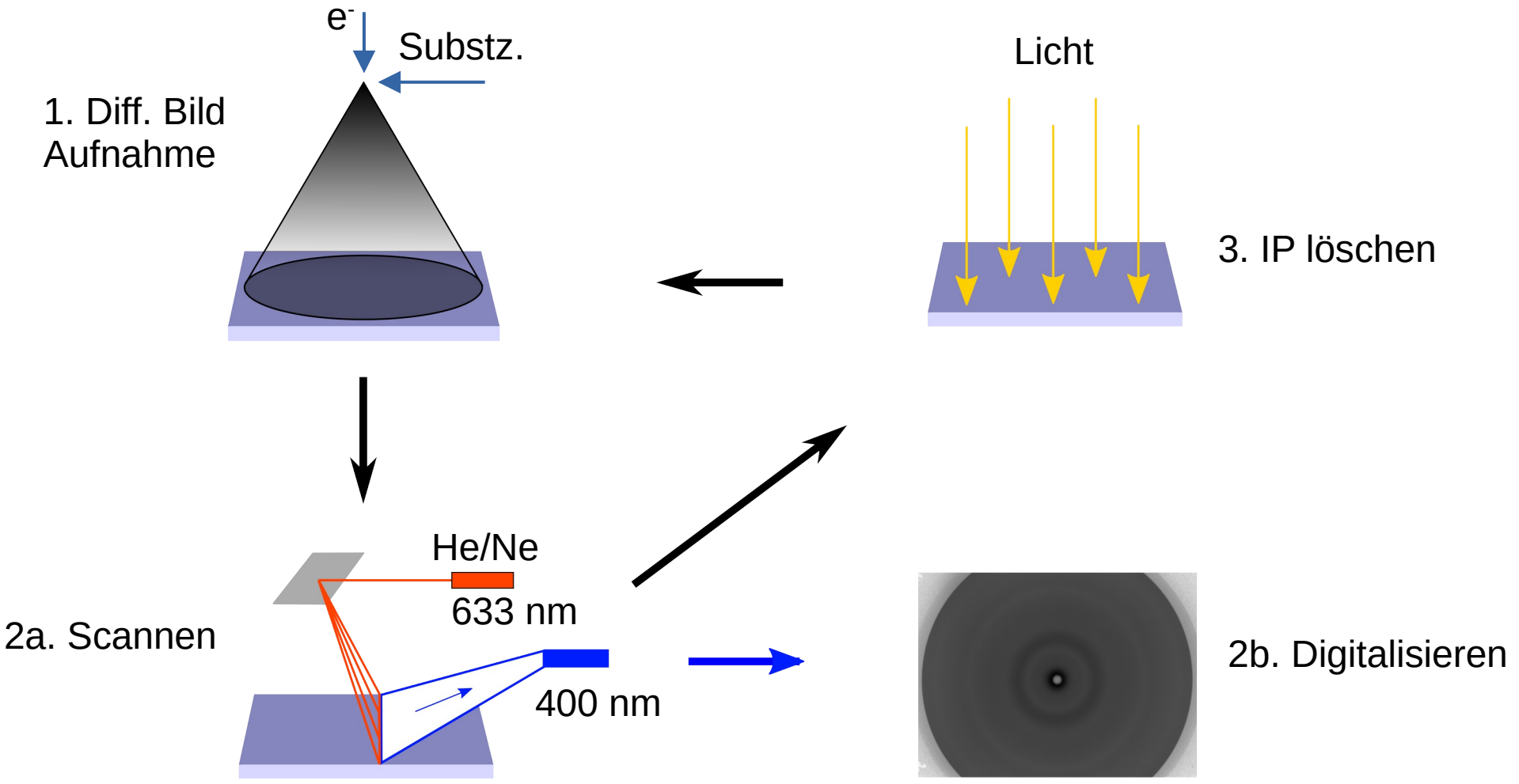
Die Elektronenenergie wird in Form von angeregten Elektronen („trapped electrons“) als angeregte Farbzentren („F-Zentren“) und Eu^{2+}-Ionen-Löchern gespeichert ($Eu^{2+} \rightarrow Eu^{3+}$).

F-Zentren: Absorption ~ 600 nm

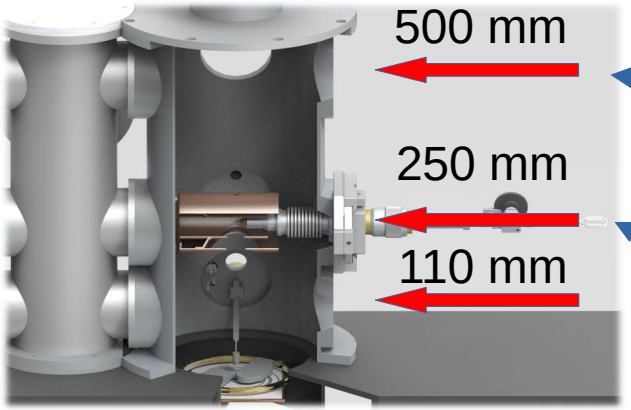
Scannen: (He-Ne-Laser 633 nm)
„trapped electrons“ werden freigesetzt und vereinigen sich mit den Eu^{2+}-Löchern ($Eu^{3+} \rightarrow Eu^{2+}$).

Photonen von ~400 nm werden emittiert, d. h. photo-stimulierte Lumineszenz.

Messungen auf IPs

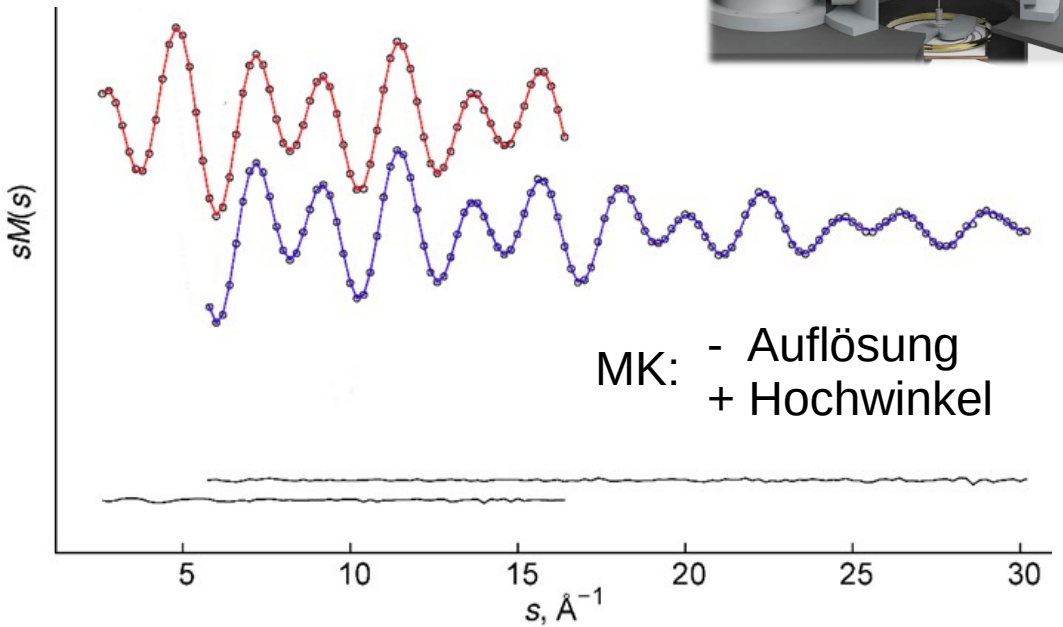


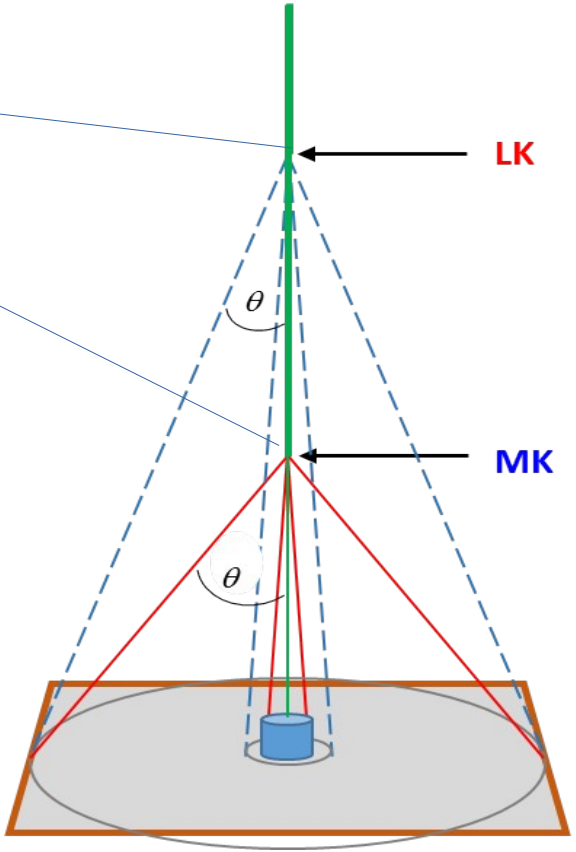
Kameraabstände



LK: + Auflösung
- Winkelbereich

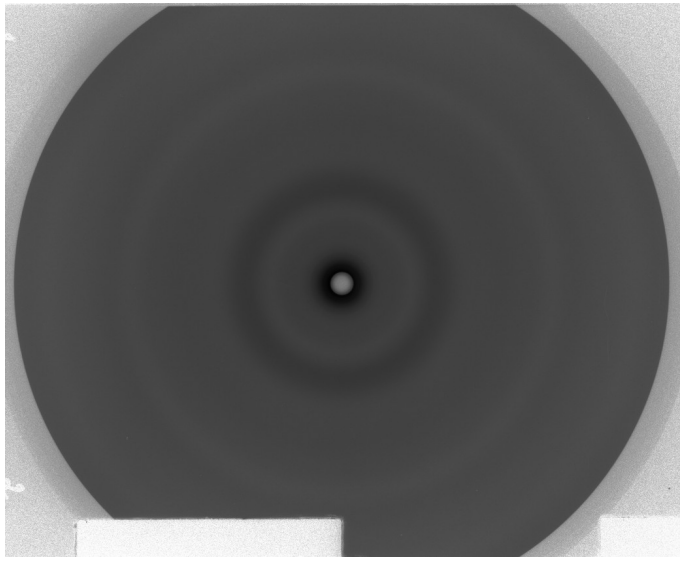
MK: - Auflösung
+ Hochwinkel





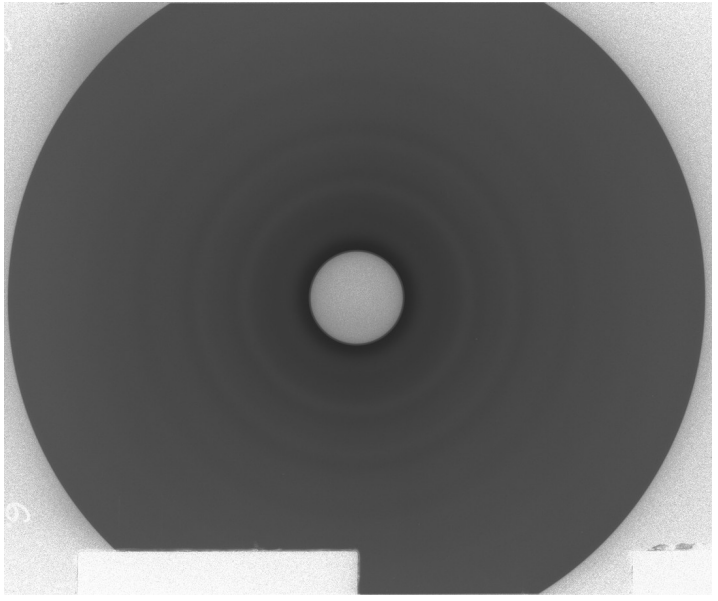
$\theta^{MK}_{max} \gg \theta^{LK}_{max}$

Beugungsmuster: C_6H_6



LK (*L* = 500 mm)

MK (*L* = 250 mm)



Vom Beugungsbild zu I_m

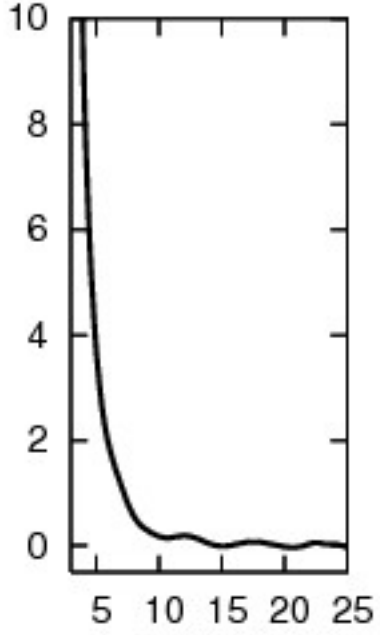
$$I = I_a + I_m + I_{background}$$

atomarer molekularer Beitrag

Daten-reduktion

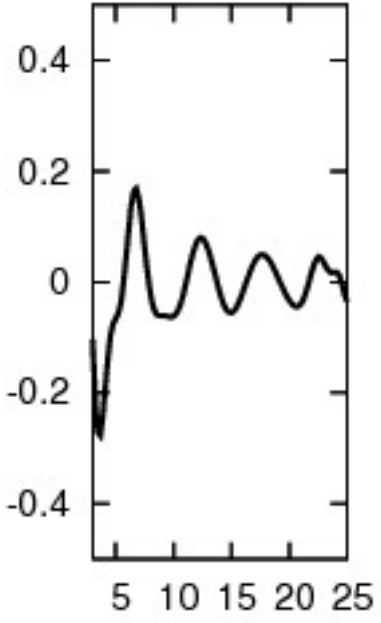
$\theta \leftrightarrow s$

Gesamte Intensität I



$-I_a$, $-I_b$

Molekular-Intensität I_m



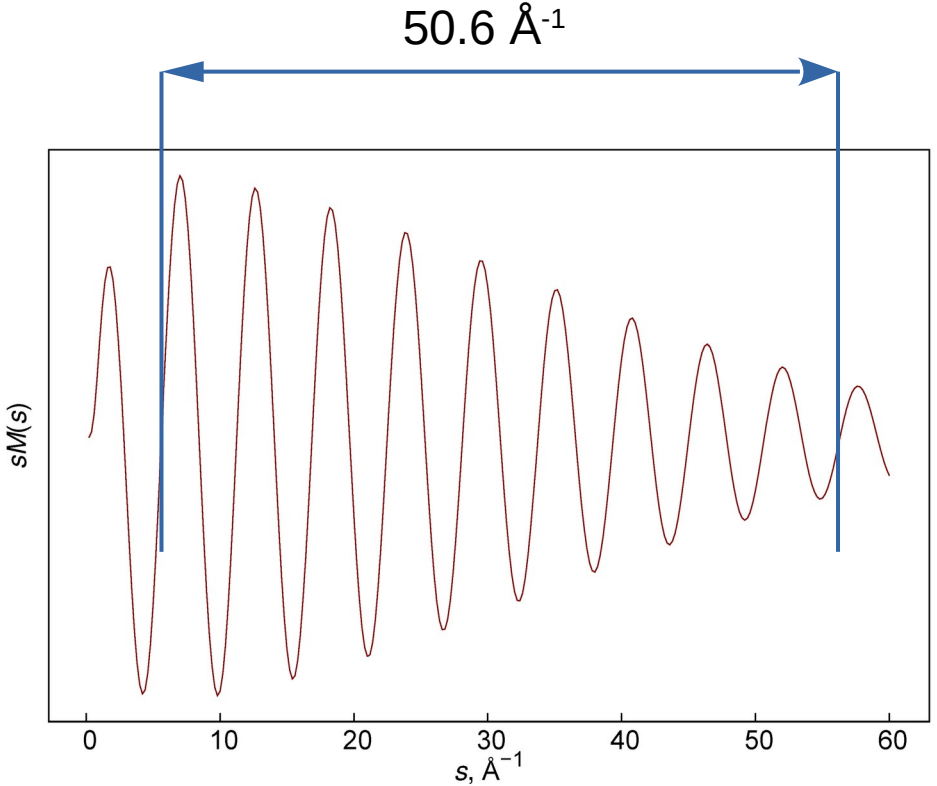
Modell: $$I_m = \sum_{i>j} f_i f_j e^{\frac{-l_{ij}^2 s^2}{2}} \frac{\sin(sr_{ij})}{sr_{ij}}$$

$$sM(s) = s\frac{I_m}{I_a}$$

Zweiatomiges Molekül

Z. B.: N_2

Daten (simuliert):



Modell:

$$I_m = g_{NN}\, e^{\frac{-l_{NN}^2 s^2}{2}} \frac{\sin\left(sr_{NN}\right)}{sr_{NN}}$$

Eine Periode = 50.6/9 = 5.62 Å^{-1}

↓

Frequenz = 2π/5.62 = 1.12 Å

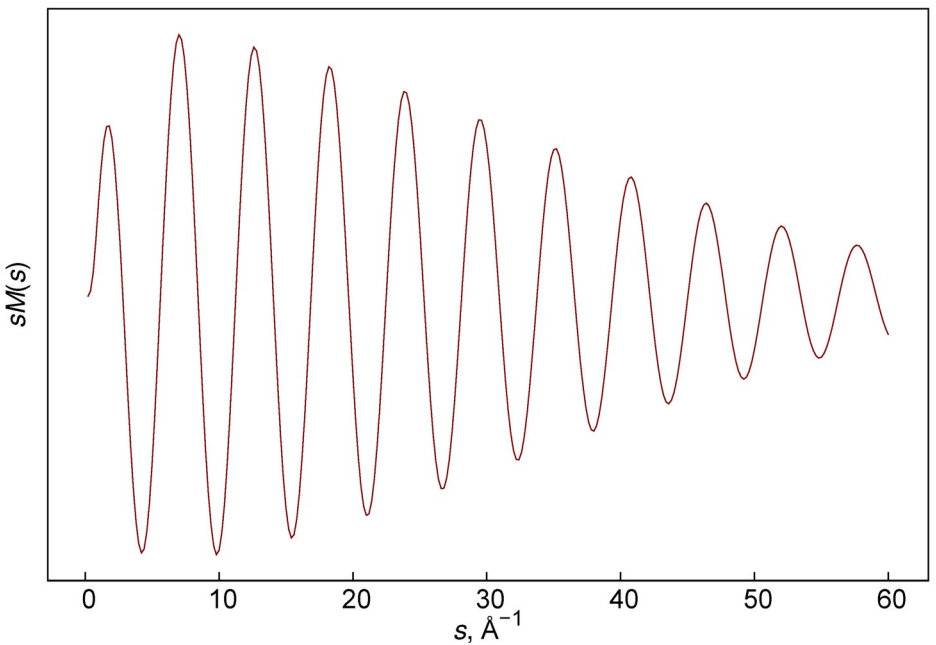
↓

r(N-N) = 1.12 Å

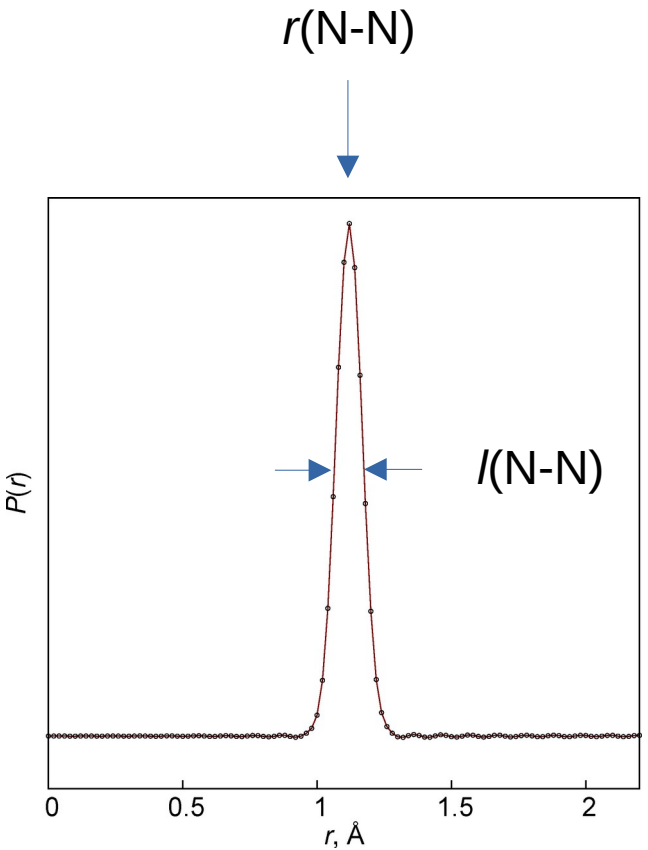
Fourier-Transformation: RDF

$$I_m = g_{\mathrm{NN}}\, \mathrm{e}^{-\left(\frac{l^2 s^2}{2}\right)} \frac{\sin(sr)}{sr}$$

$$P(r) = \int_0^{\infty} I_m \sin(sr)\, ds$$

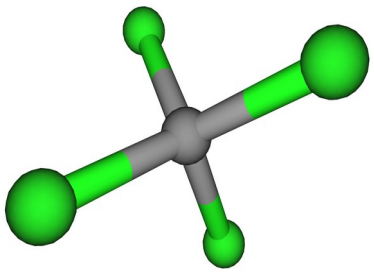


sin-FT



Radial distribution function (RDF)

Zwei unterschiedliche Terme: CCl_4

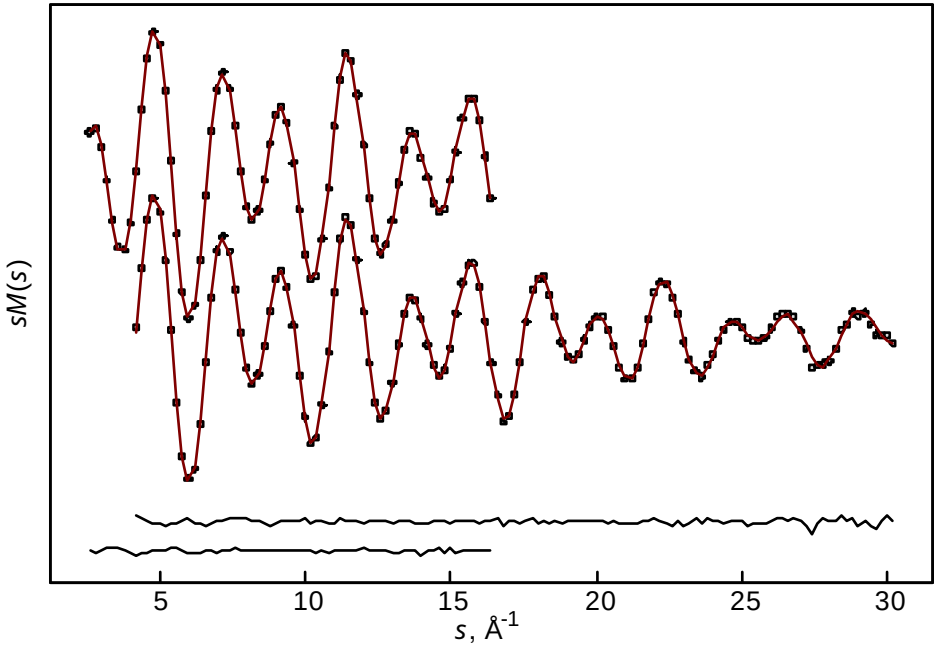


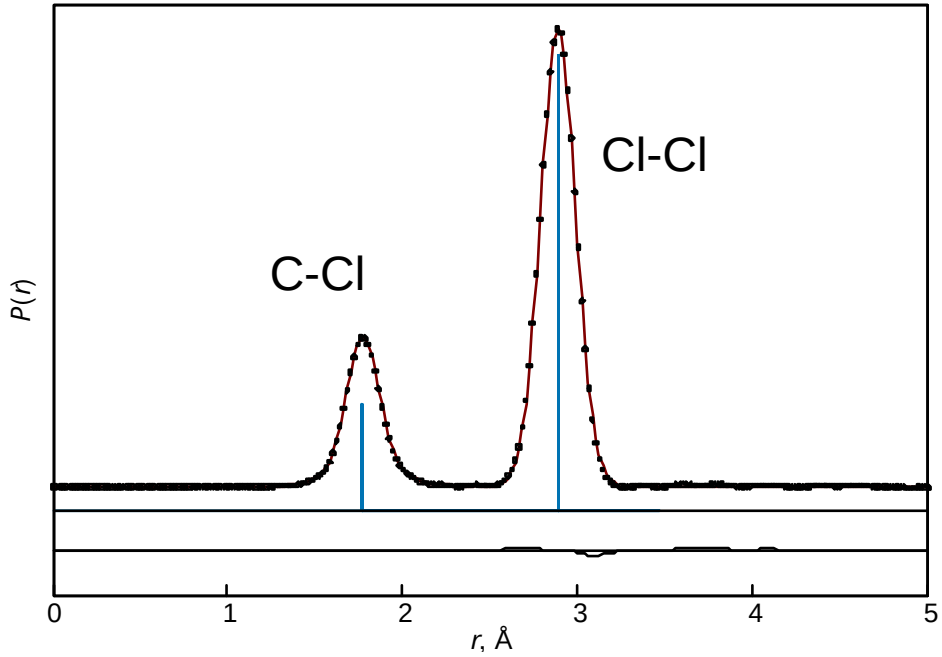
r(C–Cl) = 1.7663(3) Å

r(Cl...Cl) = 2.8827(6) Å

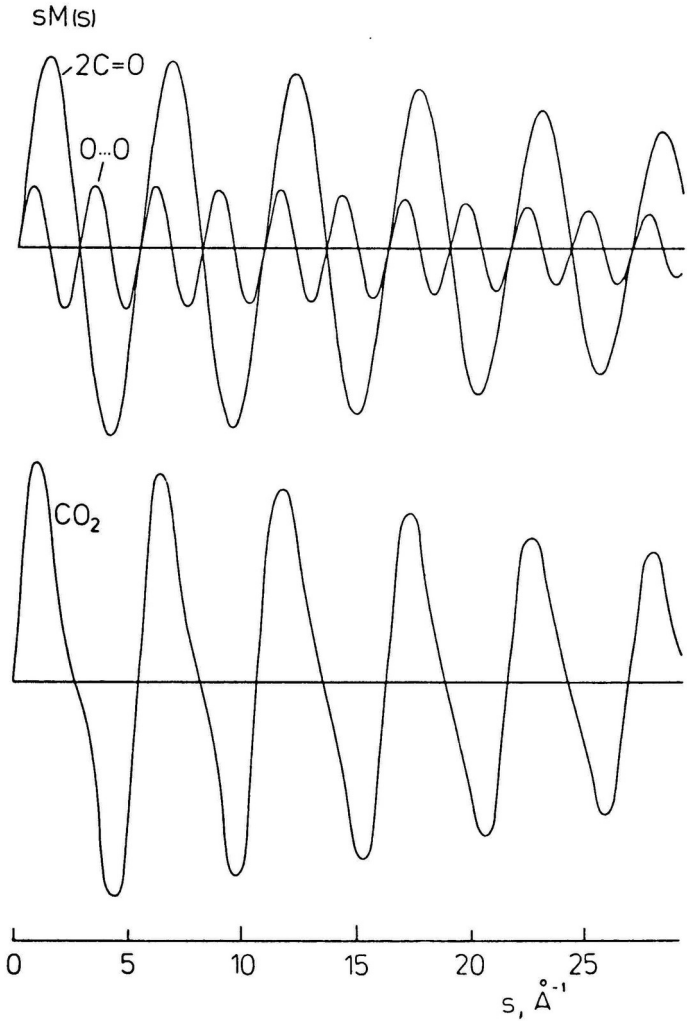
l(C–Cl) = 0.0483(12) Å

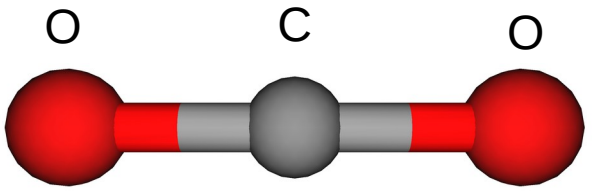
l(Cl...Cl) = 0.0715(7) Å





Zwei Terme: CO_2



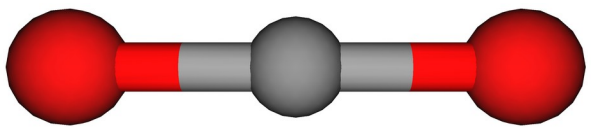


$$I_{\mathrm{m}}(s) = 2 g_{CO} \mathrm{e}^{\frac{-l_{CO}^2 s^2}{2}} \sin\frac{(s r_{CO})}{r_{CO}} + g_{OO} \mathrm{e}^{\frac{-l_{OO}^2 s^2}{2}} \sin\frac{(s r_{OO})}{r_{OO}}$$

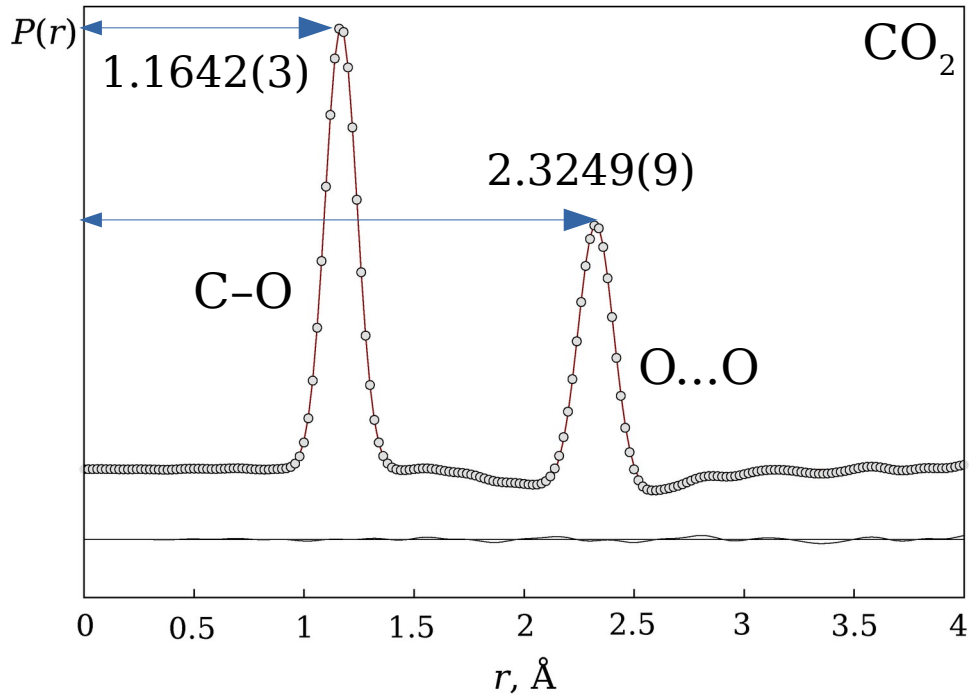
Gemittelte Struktur: CO_2

$\delta = 2r_a(C–O) – r_a(O...O)$

0.0036(5) @ 298 K
0.0059(11) @ 463 K
0.0071(8) @ 627 K
0.0078(10) @ 731 K
0.0093(7) @ 937 K

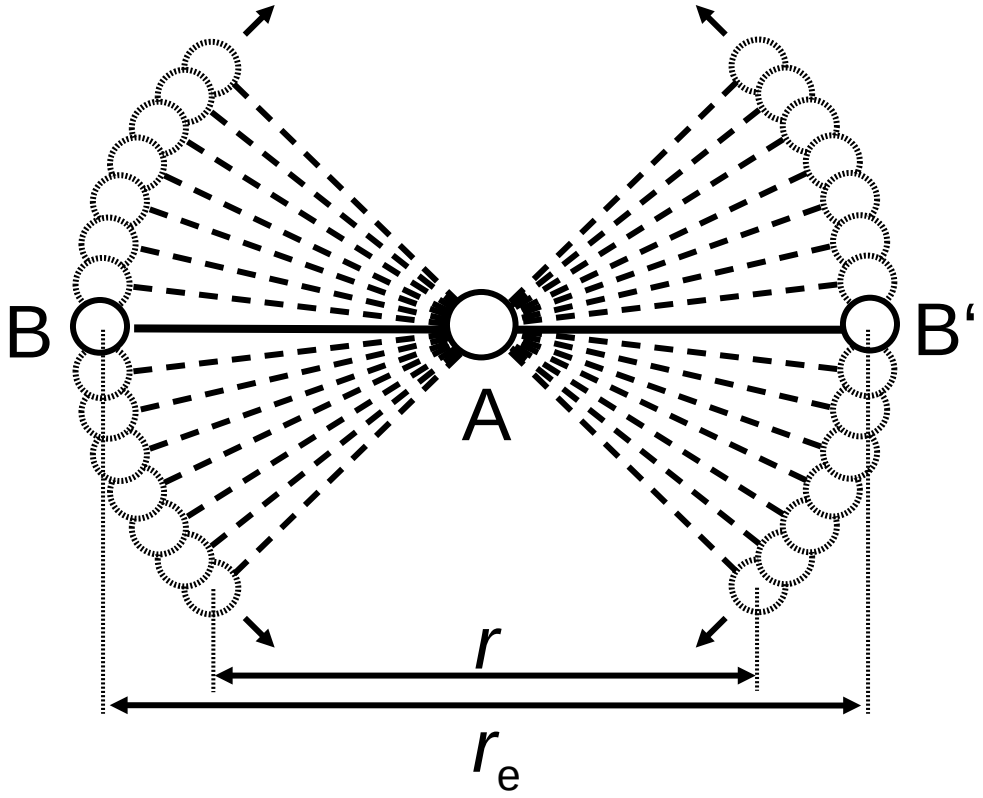


Linear ???



R. J. Mawhorter, M. Fink, B. T. Archer, *J. Chem Phys.* 79 (1983) 170.

Shrinkage Effekt



Beispiel: $HgBr_2$

$<_a$(Br–Hg–Br) ~ 170°

Korrekturen zu geometrisch konsistenten Strukturen: (r_z, r_α, r_{h0}, r_{h1}, r_e):

- Störungstheorie
  Kraftfelder + XYZ
- Molekulardynamik
  Trajektorie

Shrinkage Effekt:

$r_a(B...B) < 2r_a(A–B)$

Atomabstandsparameter

r_a thermisch gemittelter Abstand
direkt aus GED zugänglich

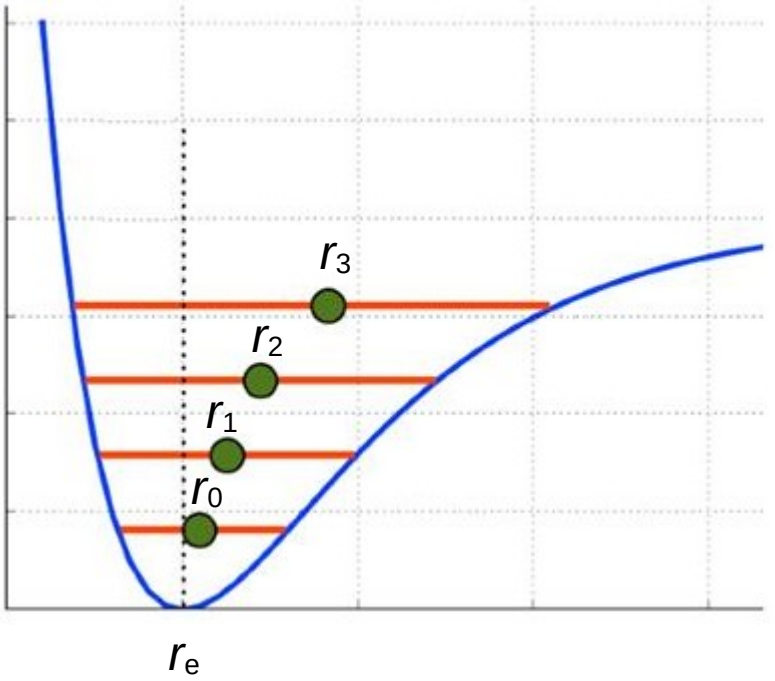
r_e Abstand der Atome im Gleichgewicht
(Potentialminimum)

r_g thermisch gemittelter Abstand

r_α Abstand zwischen mittleren Kernpositionen
im thermischen Gleichgewicht bei Temperatur T

r_α^0, r_z Abstand zwischen mittleren Kernpositionen
im Schwingungsgrundzustand

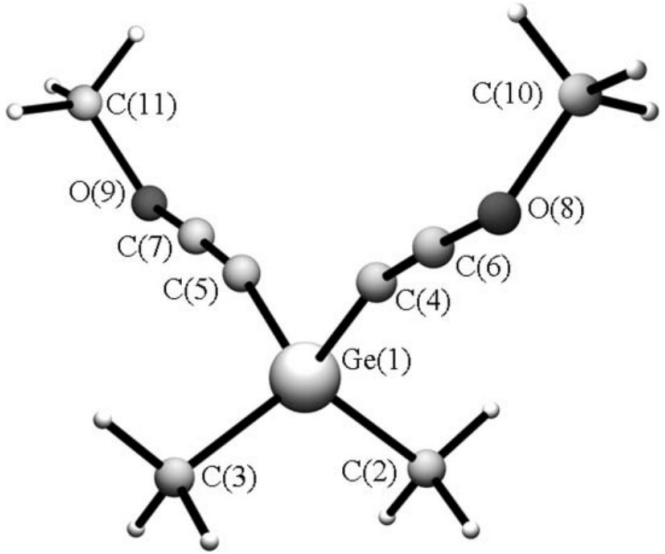
$$r_g = \langle r \rangle_T \qquad r_a = \left(\left\langle \frac{1}{r} \right\rangle_T \right)^{-1}$$



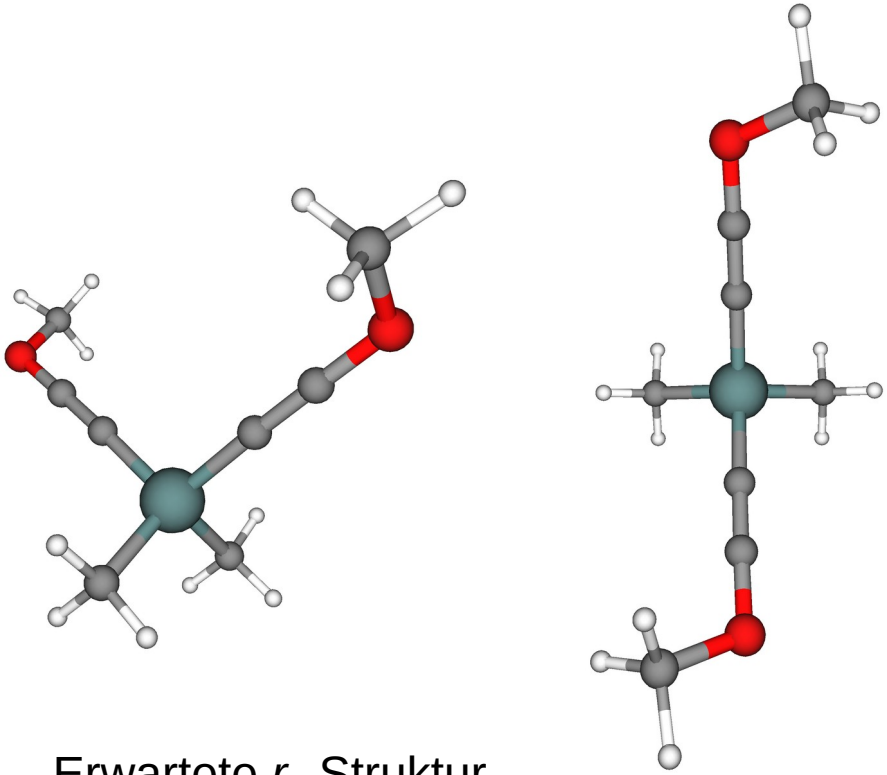
Normalerweise für Bindungen: $r_e < r_\alpha^0 < r_\alpha \approx r_a < r_g$

Thermisch gemittelte Struktur

Dimethyl-bis(methoxyethynyl) germanium



Verfeinert aus GED Daten @ 382 K



Erwartete r_e-Struktur

K. B. Borisenko et all., *Dalton Trans.* 2004, 3878.

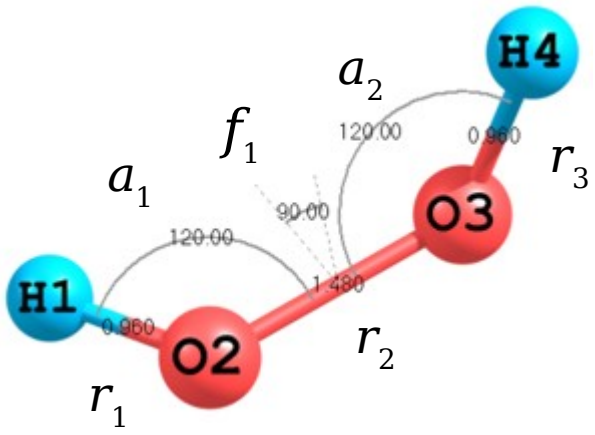
Geometrie Verfeinerung: Z-Matrix

Anzahl Parameter:

(x,y,z): 3*N*

(r, <, φ): 3*N*-6

r_{ij}: *N*(*N*-1)/2



1 **H**
2 **O** 1 *r1*
3 **O** 2 *r2* 1 *a1*
4 **H** 3 *r3* 2 *a2* 1 *f1*
Parameter:
r1 = 1.0
r2 = 1.5
r3 = 1.0
a1 = 120.0
a2 = 120.0
f1 = 100.0

$(r, <, \varphi) \rightarrow (x,y,z) \rightarrow r_{e,ij} \rightarrow r_{a,ij} \rightarrow sM(s)$

Vorteile: direkte Kontrolle für Parameter (z.B. *Δp* fixieren).

Nachteile: keine Kontrolle für abhängige Parameter oder sub-optimale Z-Matrizen.

Parameter Verfeinerung

Methode der kleinsten Quadrate:

$$Q = \sum [sM(s)_{exper} - sM(s)_{modell}]^2 \rightarrow min$$

Mit Regularisierung:

$$Q = \sum [sM(s)_{exper} - sM(s)_{modell}]^2 + \alpha \times \sum [p_0 - p_{modell}]^2 \rightarrow min$$

Mit zusätzlichen Daten:

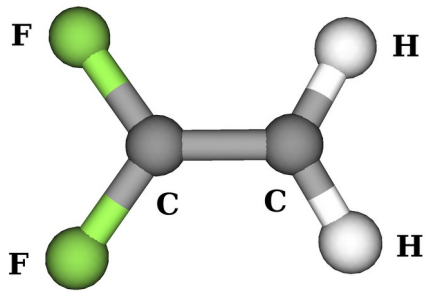
$$\begin{aligned} Q = & \sum [sM(s)_{exper} - sM(s)_{modell}]^2 \\ & + \alpha \times \sum [B_{exper} - B_{modell}]^2 \\ & + \beta \times \sum [\nu_{exper} - \nu_{modell}]^2 \\ & + \gamma \times \sum [D_{exper} - D_{modell}]^2 \rightarrow min \end{aligned}$$

- Rotationskonstanten
- Schwingungsfrequenzen
- Dipol-Dipol Kopplungskonstanten

α, β, γ – Gewichte.

GED + MW

$F_2C{=}CH_2$



Probleme:
MW: ^{19}F (keine Isotopensubstitution),
ein C ist nah zum Schwerpunkt.

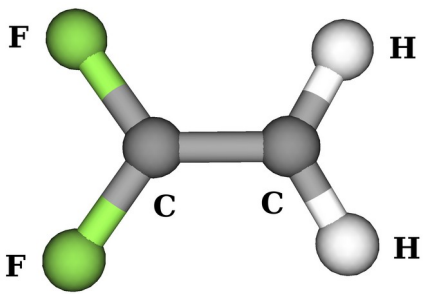
GED: r(C=C) ≈ r(C–F) → Große Korrelation in Verfeinerung.

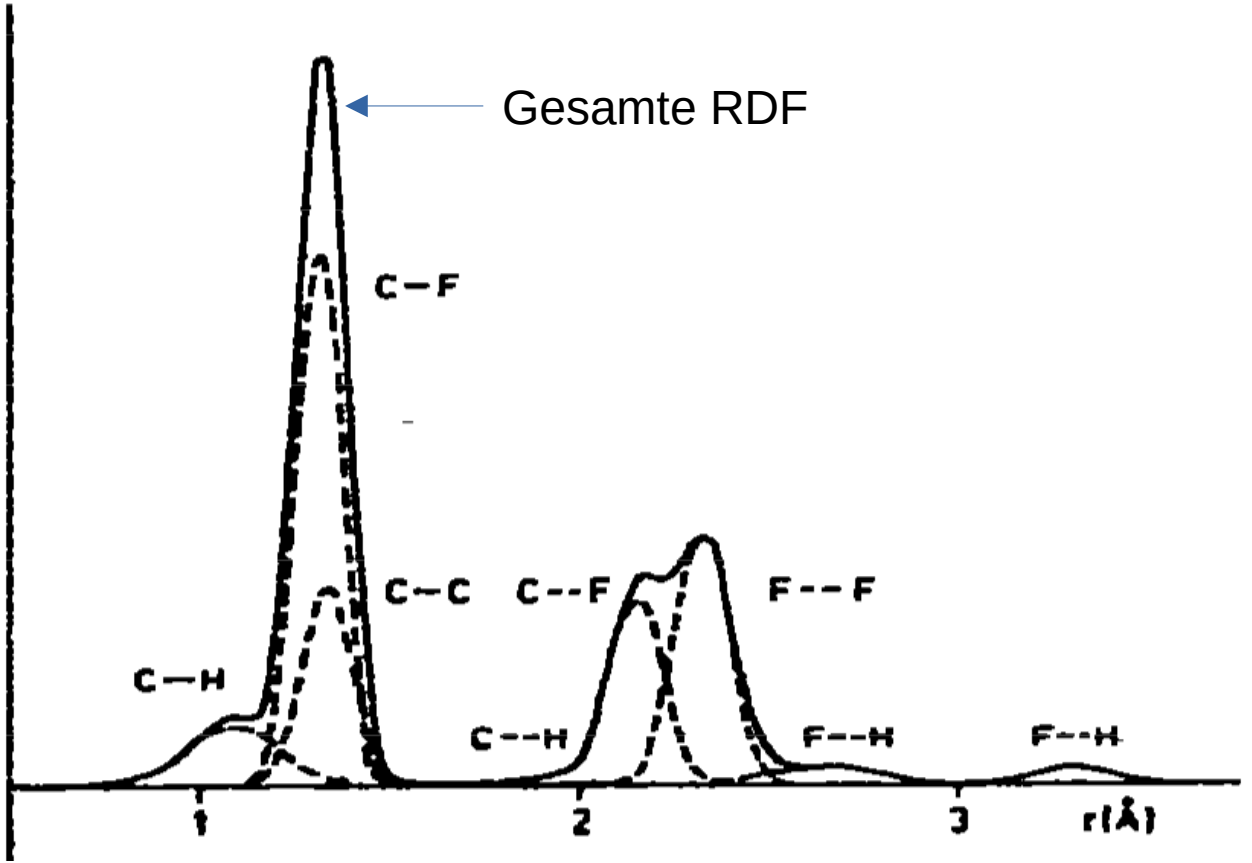
Besser wenn GED + MW:

r_g(C=C) = 1.340(6) Å
r_g(C–F) = 1.315(3) Å

F. C. Mijlhoff, G. H. Renes, K. Kohata, K. Oyanagi, K. Kuchitsu, *J. Mol. Struct.* 39 (1977) 241.

RDF Auflösung



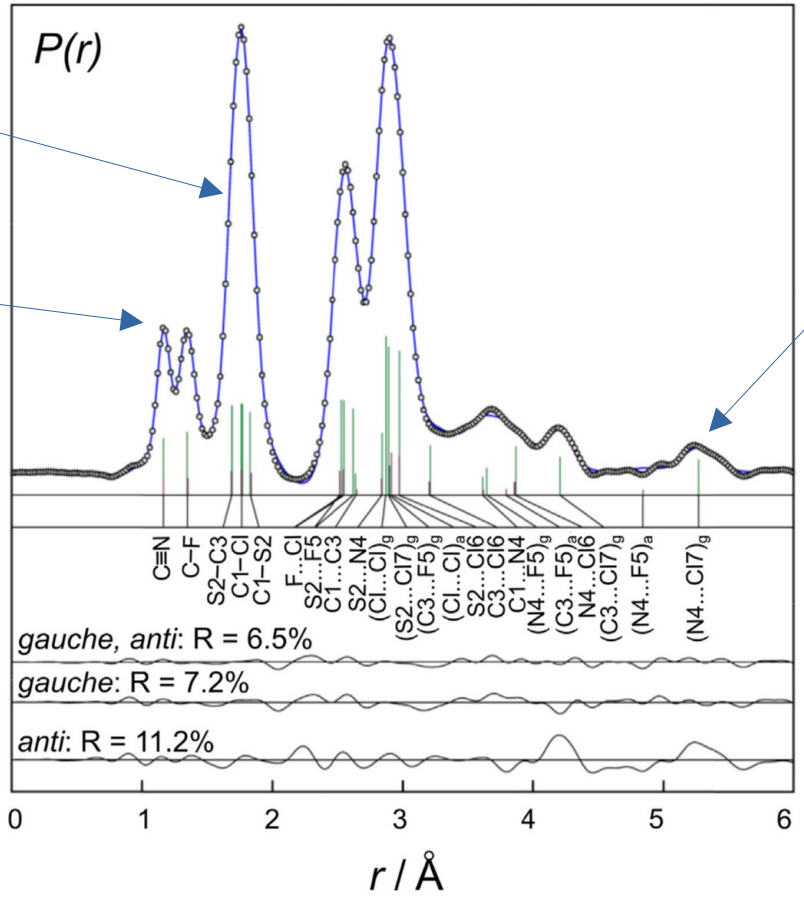


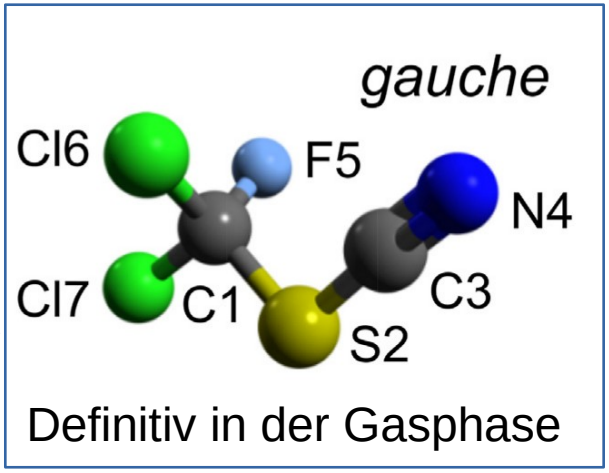
F. C. Mijlhoff, G. H. Renes, K. Kohata, K. Oyanagi, K. Kuchitsu, *J. Mol. Struct.* 39 (1977) 241.

RDF Auflösung

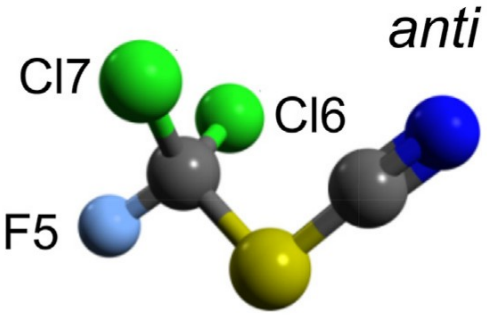
r(C-S), *r*(C-Cl) sind korreliert.

r(C≡N) und *r*(C-F) sind unabhängig verfeinerbar.



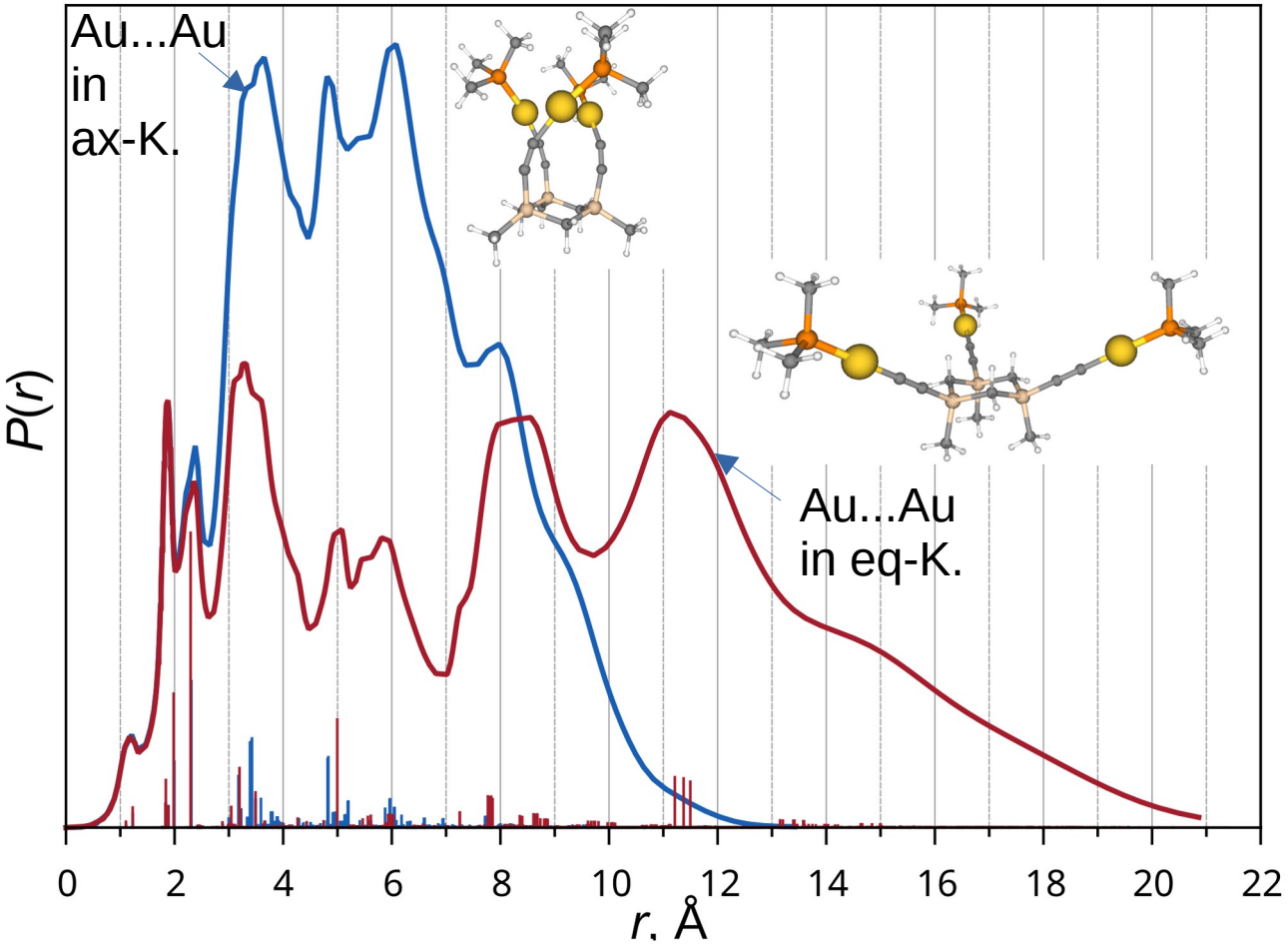


Definitiv in der Gasphase

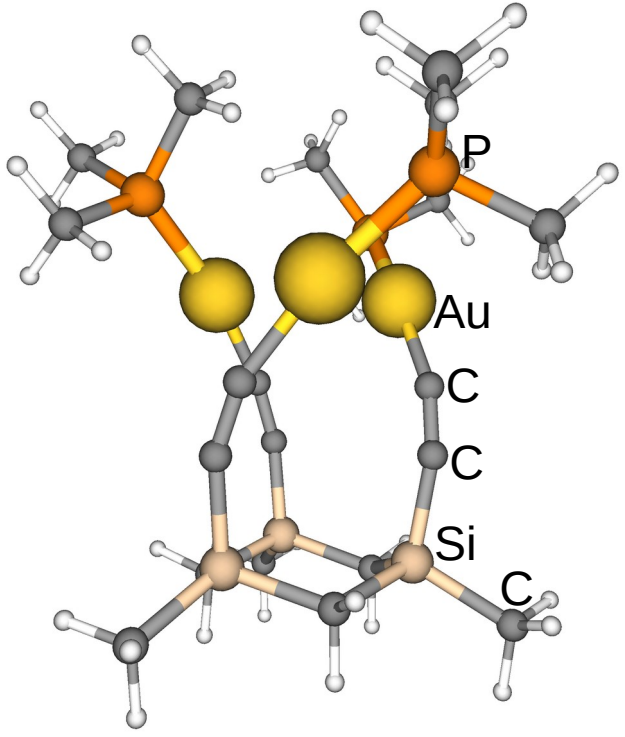


Y. B. Martínez et al., *J. Mol. Struct.* 2017, 1132, 175.

RDF Modellierung



Wegen Streuung an Au...Au muss Konformationsproblem leicht lösbar sein!



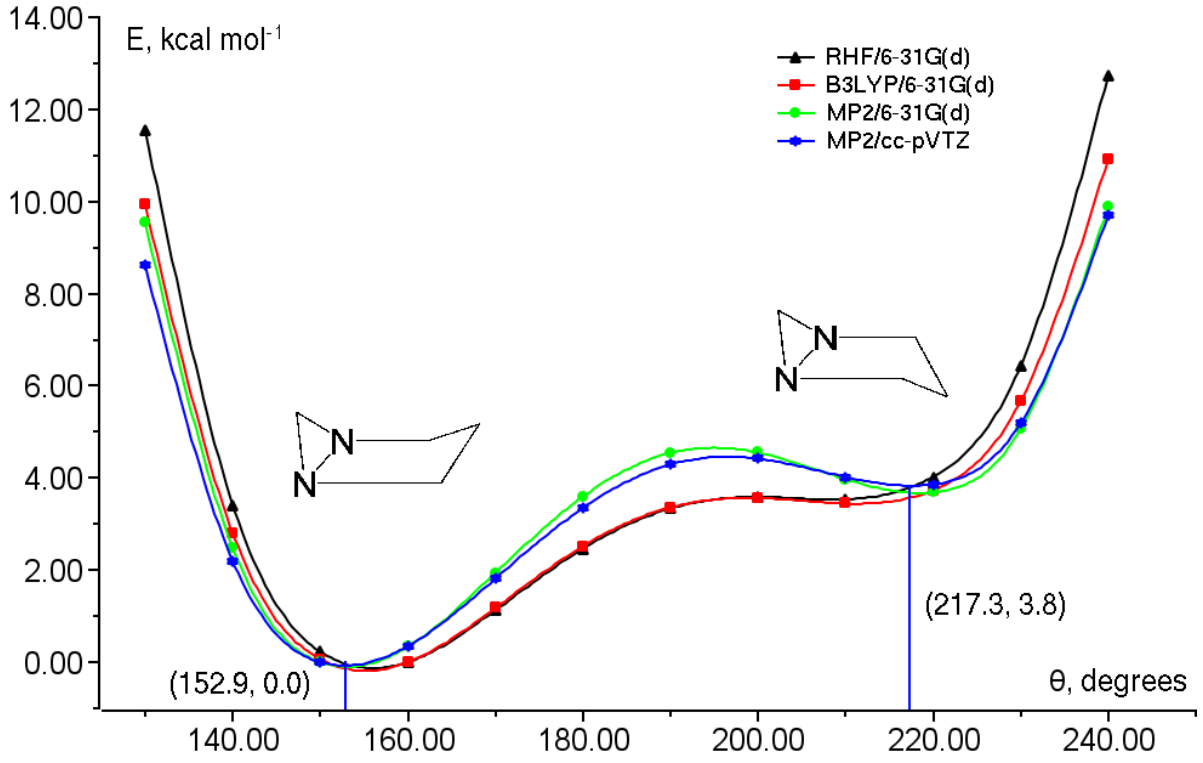
P. Heinrichs et al., *Eur. J. Inorg. Chem.* 2024, 27, e202400151.

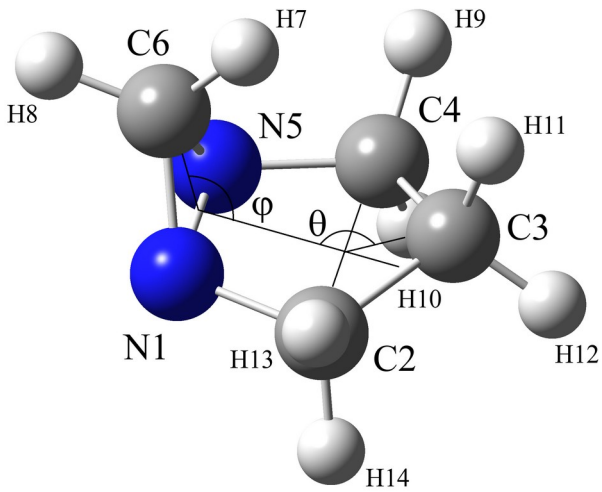
Konformerverhältnisse

$$sM(s)_{total} = x_1 \times sM(s)_{mol\,1} + x_2 \times sM(s)_{mol\,2}$$
$$x_1 + x_2 = 1$$

1,5-diazabicyclo[3.1.0]hexan (DABH)

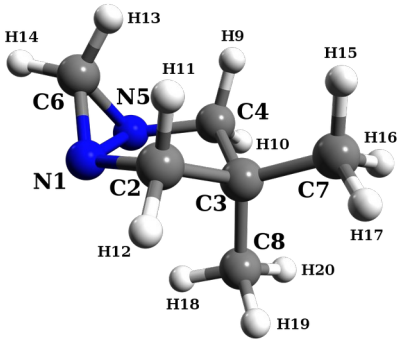
J. Phys. Chem. A, 112 (2008) 5243

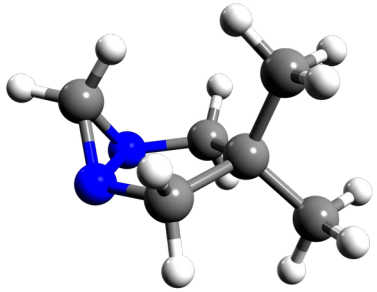


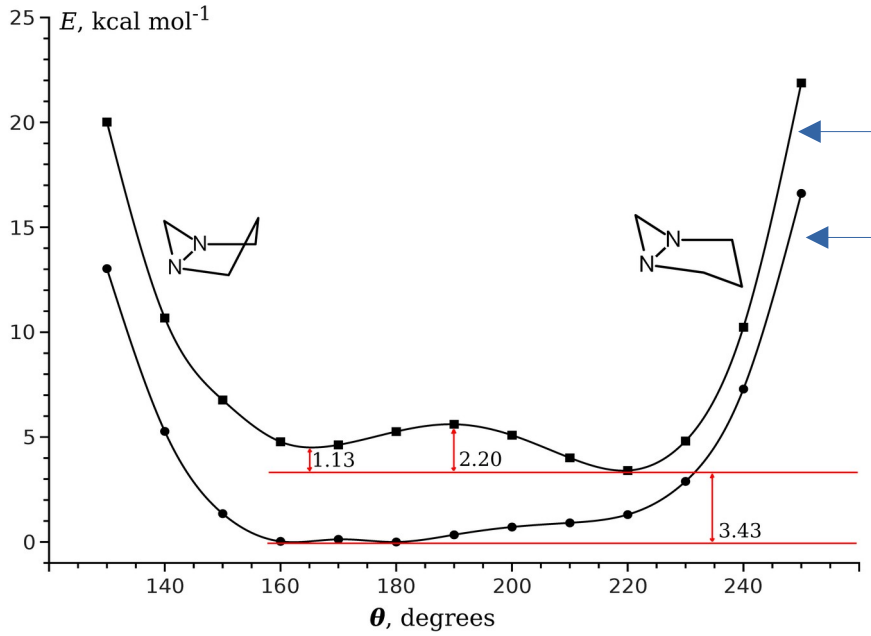


Nur Wanne @ 293 K

Konformerverhältnis: 3,3-Me_2-DABH





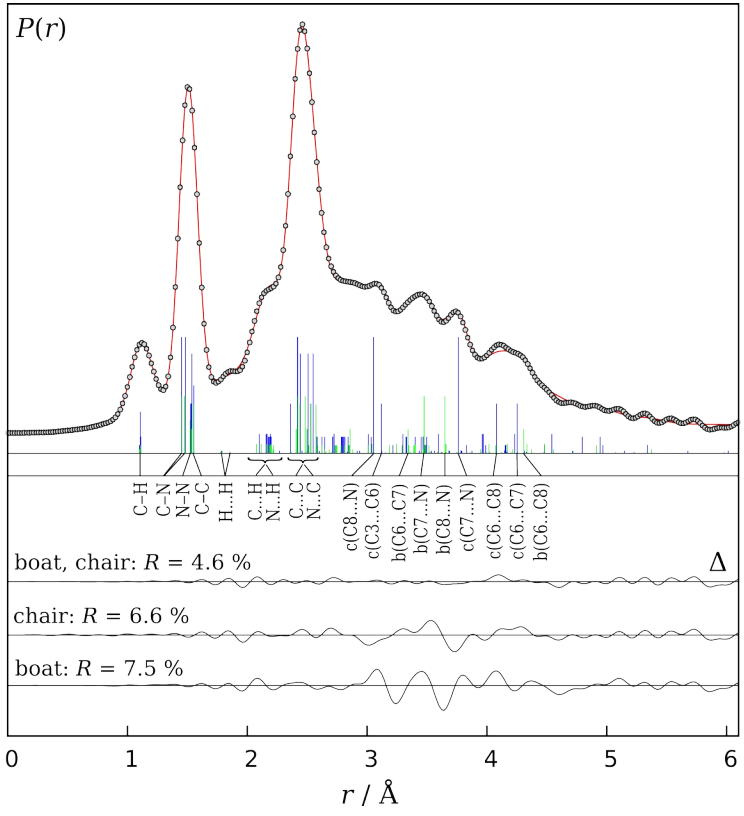


32(8) % Wanne,
68(8) % Sessel
@ 293 K

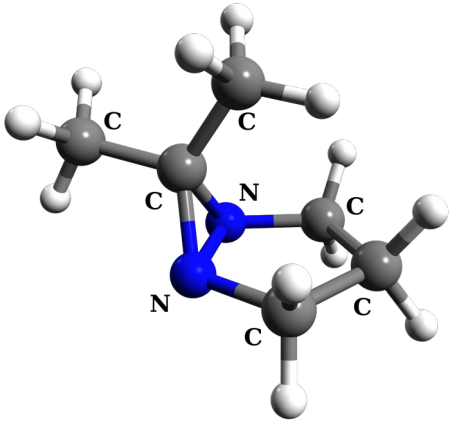
3,3-Me_2-DABH

6,6-Me_2-DABH

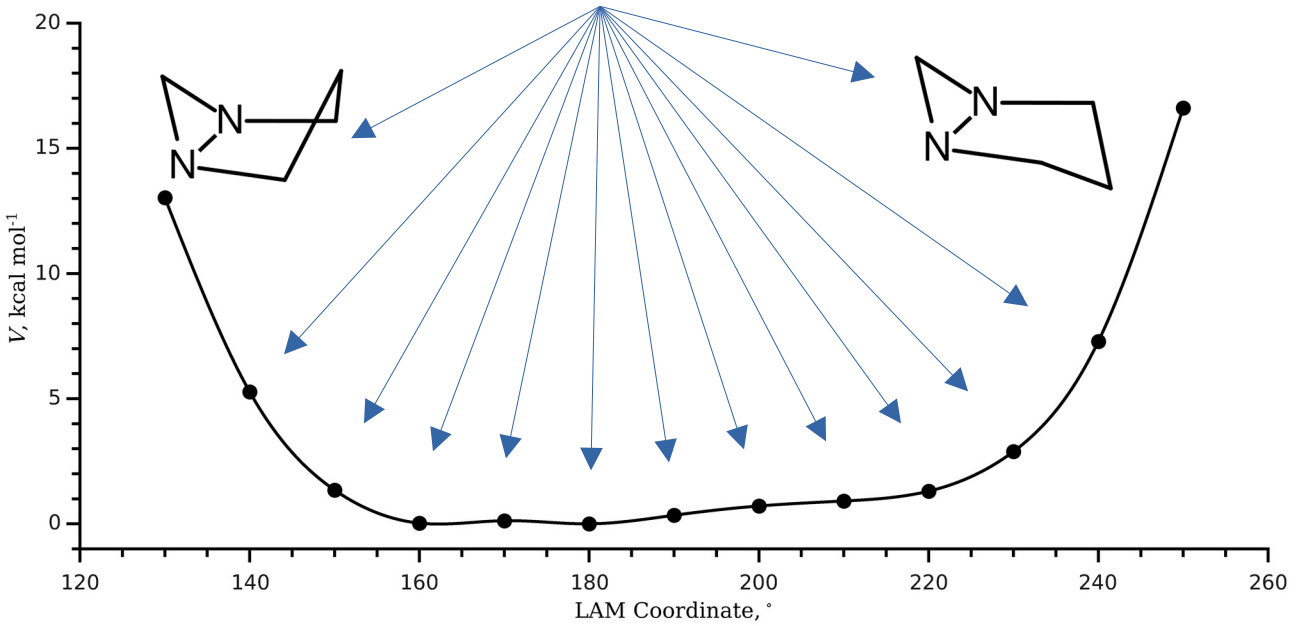
J. Phys. Chem. A, 119 (2015) 10871



Dynamisches Modell: 6,6-Me$_2$-DABH



Pseudokonformere:



$$sM(s)_{tot} = \int P(\phi)\, sM(\phi, r, l)\, d\phi$$

Boltzmann Verteilung:

$$P(\phi) \sim e^{\frac{-V(\phi)}{kT}}$$

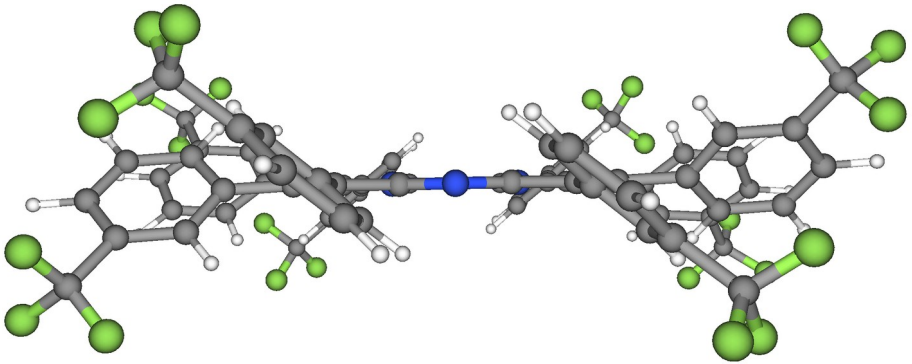
J. Phys. Chem. A, 119 (2015) 10871

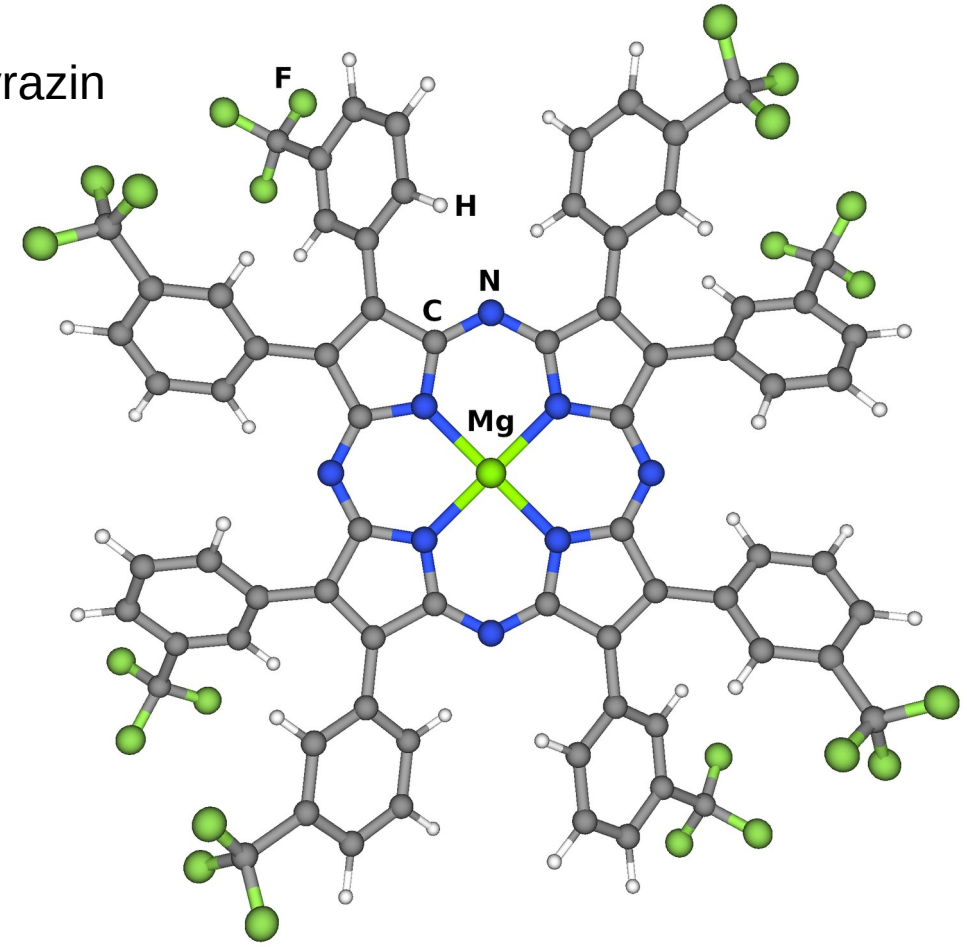
Größte Moleküle in GED

Magnesium octa(m-trifluoromethylphenyl)porphyrazin

Symmetrie: D_4 (50 geom. Freiheitsgrade)

$r_{max} \approx 20$ Å





Y. A. Zhabanov, A. V. Zakharov, N. I. Giricheva, S. A. Shlykov, O. I. Koifman, G. V. Girichev, *J. Mol. Struct.* 1092 (2015) 104.

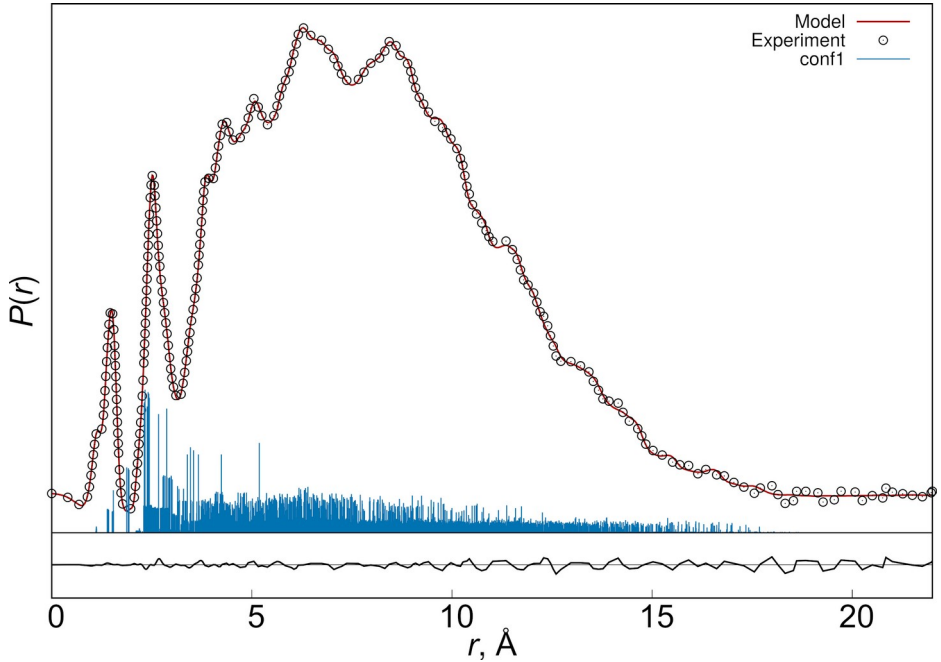
Größte Moleküle in GED

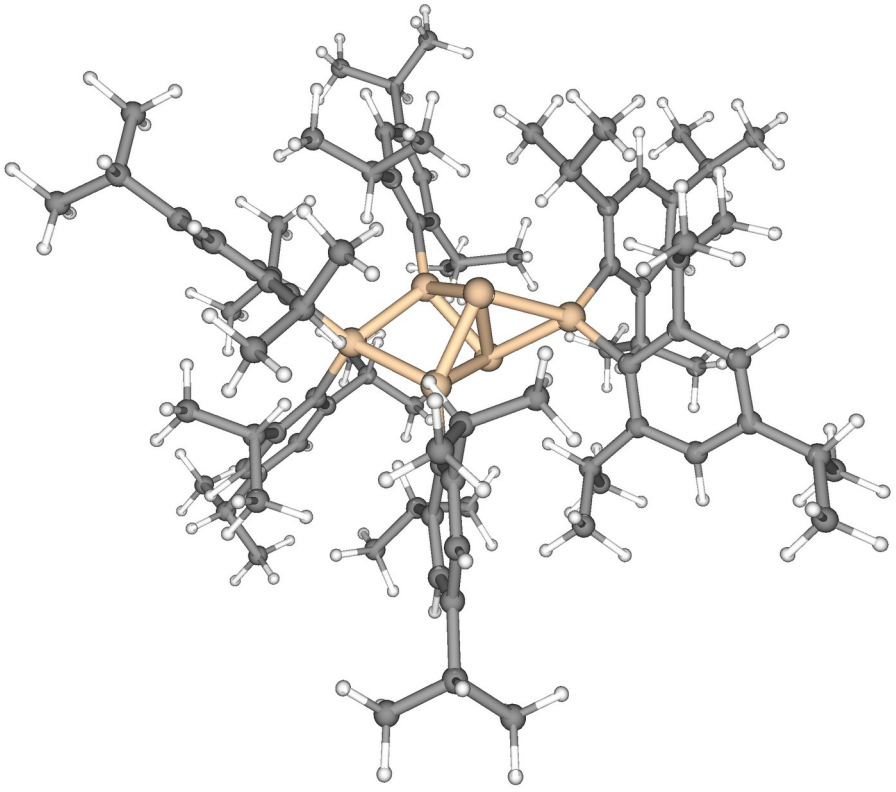
Si_6Tip_6, Tip = 2,4,6-$iPr_3C_6H_2$

GED @ Uni-Bielefeld

Symmetrie: C_1 (696 geom. Freiheitsgrade)

$r_{max} \approx 20$ Å (27261 Terme)

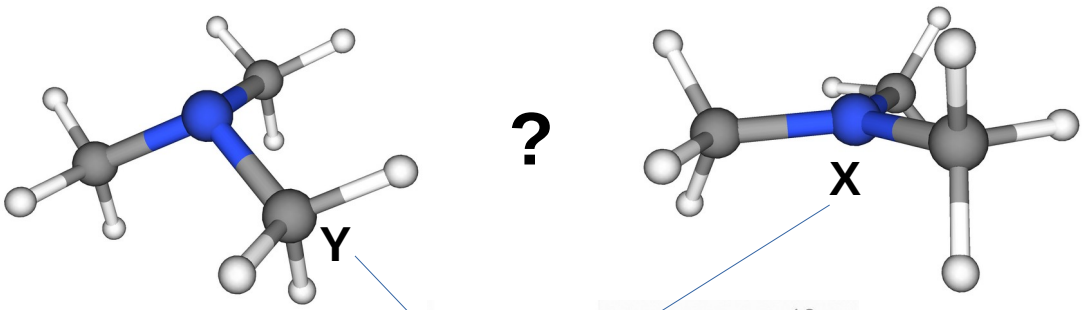




Y. V. Vishnevskiy, Y. Heider, D. Scheschkewitz, *J. Chem. Phys.* 2024, 161, 054307.

Molekül(e) des Tages: $Pn(TH_3)_3$

flach oder pyramidal?

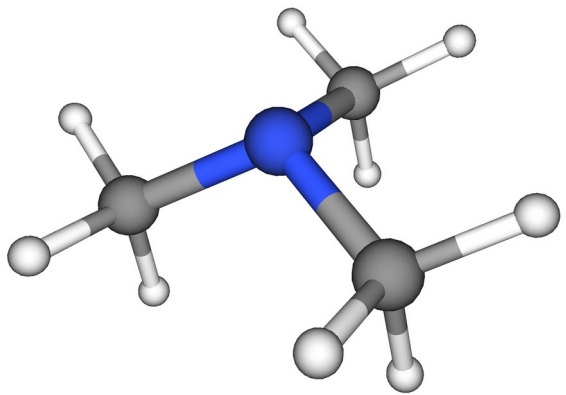


	1*												13	14	15	16	17	18
1	1 H	2																2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg	3	4	5	6	7	8	9	10	11	12	13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Mc	116 Lv	117 Ts	118 Og

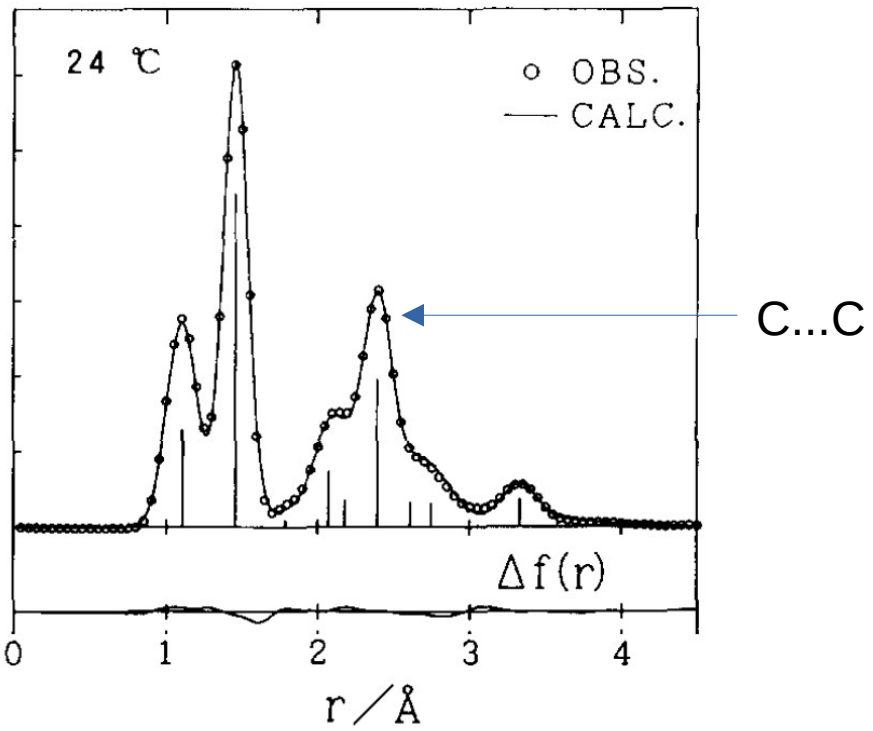
Trimethylamin $N(CH_3)_3$

Wollrab et al. (1969) MW: **pyramidal**

Fujiwara et al, (1995) GED: **pyramidal**



Erklärung: VSEPR-Modell



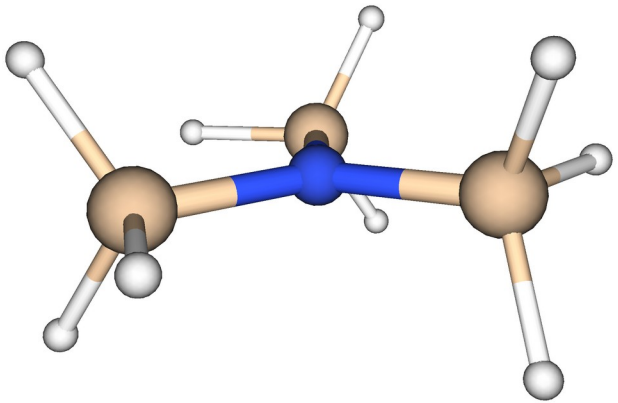
H. Fujiwara, T. Egawa, S. Konaka, *J. Mol. Struct.* 1995, 344, 217.

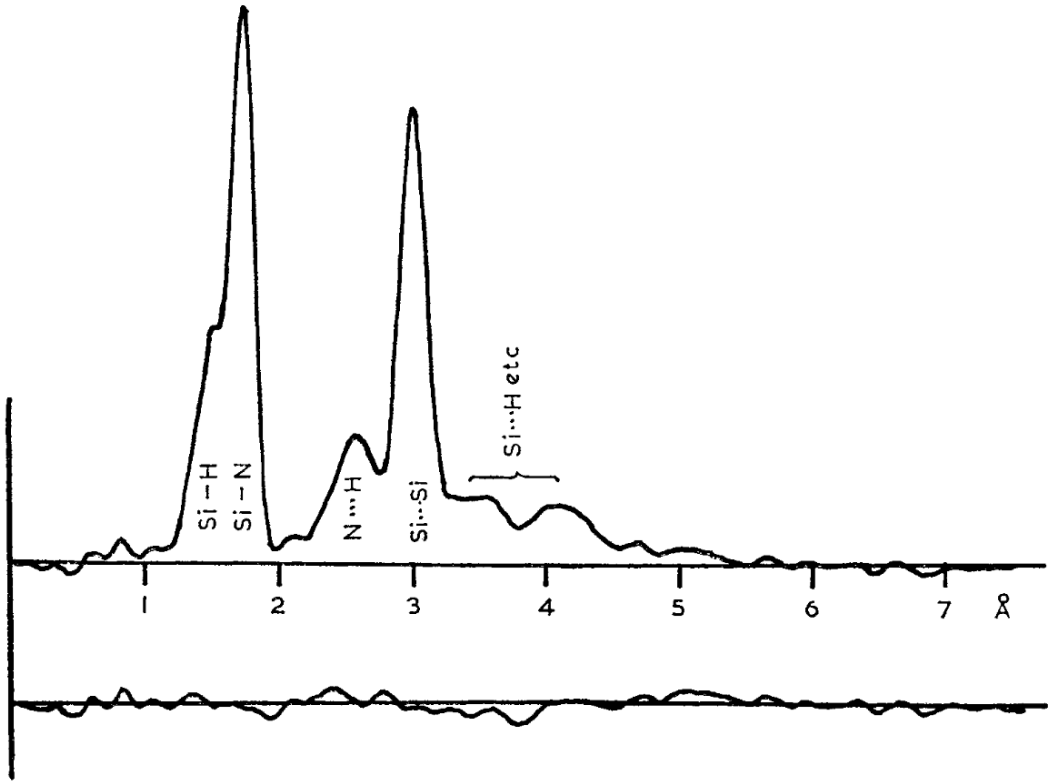
Trisilylamin $N(SiH_3)_3$

Hedberg (1955) GED: **flach**!

Ebsworth et al. (1958) IR+Raman: **flach**

Beagley et al. (1970) GED: **flach**





B. Beagley, A. R. Conrad, *Trans. Faraday Soc.* 1970, 66, 2740–2744.

Trisilylphosphin $P(SiH_3)_3$

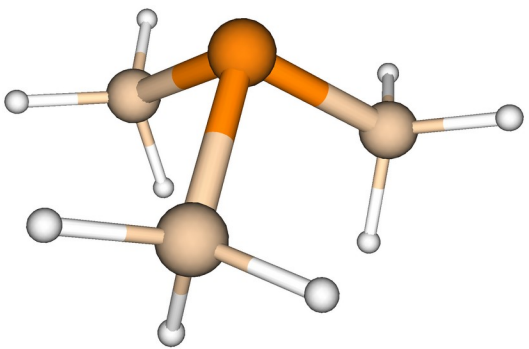
Vibrational Spectra of Trisilylphosphine: Evidence for Planar PSi_3 Structure

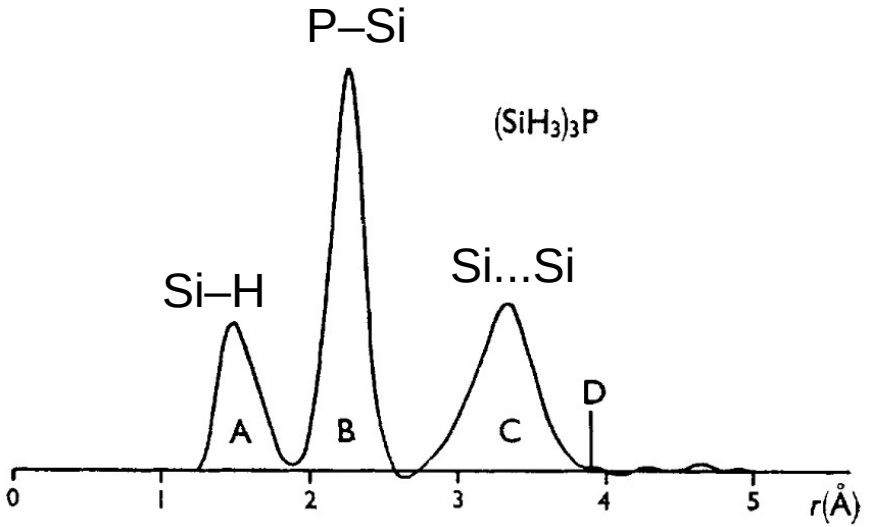
By G. Davidson, E. A. V. Ebsworth, G. M. Sheldrick, and L. A. Woodward

[*Inorganic Chemistry Laboratory, Oxford University (G.D. and L.A.W.), and University Chemical Laboratory, Cambridge (E.A.V.E. and G.M.S.)*]

Davidson et al. (1965) IR+Raman: **flach** (!?)

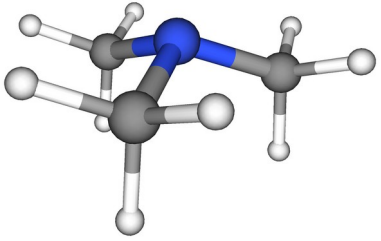
Beagley et al. (1967, 1977) GED: **pyramidal**,
α(Si-P-Si) = 96.8(5)°





B. Beagley, A. G. Robiette, G. M. Sheldric, *Chem. Commun. (London)* 1967, 601.

Natural bond orbital (NBO), Ladungen

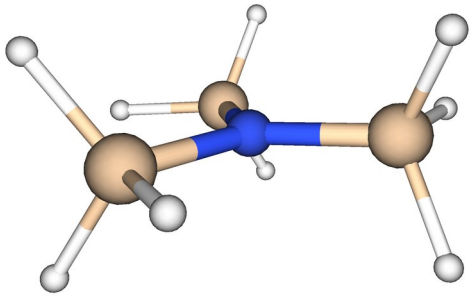


$N(CH_3)_3$:

q(N) = -0.5

q(C) = -0.4

q(H) = 0.2

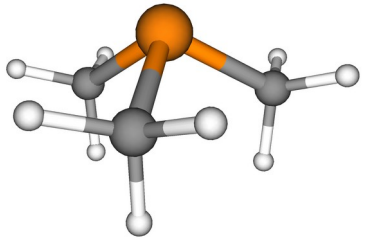


$N(SiH_3)_3$:

q(N) = -1.7

q(Si) = 1.1

q(H) = -0.2

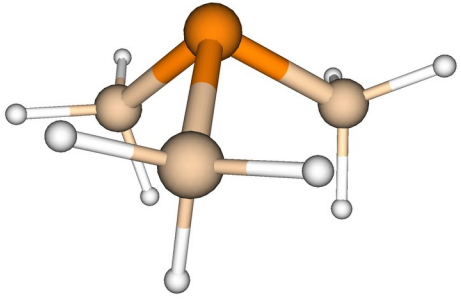


$P(CH_3)_3$:

q(P) = 0.7

q(C) = -0.9

q(H) = 0.2



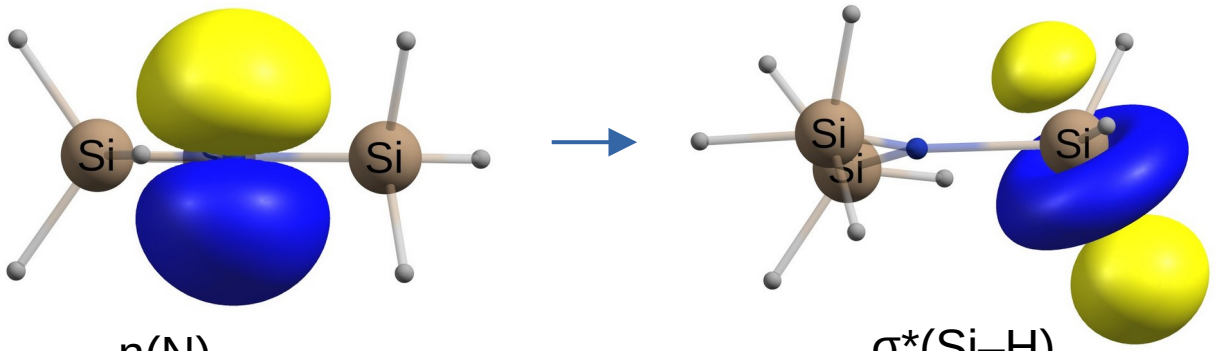
$P(SiH_3)_3$:

q(P) = -0.5

q(Si) = 0.6

q(H) = -0.1

$N(SiH_3)_3$: NBO Wechselwirkungen



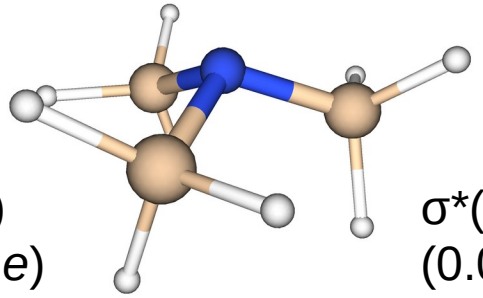
n(N)
(1.85 *e*)

σ*(Si–H)
(0.04 *e*)

6 x n(N) → σ*(Si-H) $E^{(2)}$ = -6.0 kcal/mol
3 x n(N) → σ*(Si-H) < 0.5 kcal/mol

NLMO *d*E zur sterischen Energie [kcal/mol]:
n(N) -1.4
σ(N–Si) 59.5 (je Orb.)
σ(Si–H) 4.8 (je Orb., gemittelt)
Gesamt: **219.9** kcal/mol

Gerechnet für *α*(Si–N–Si)=110.0°
*Δ*E = +6.5 kcal/mol



n(N)
(1.86 *e*)

σ*(Si–H)
(0.04 *e*)

3 x n(N) → σ*(Si-H) -6.3 kcal/mol
3 x n(N) → σ*(Si-H) -3.5 kcal/mol
3 x n(N) → σ*(Si-H) < 0.5 kcal/mol

NLMO *d*E zur sterischen Energie:
n(N) -13.3
σ(N–Si) 62.0 (je Orb.)
σ(Si–H) 6.0 (je Orb., gemittelt)
Gesamt: **226.7** kcal/mol

α(X–Y–X): **GED** und [Theorie]

	X = CH_3	SiH_3	GeH_3	SnH_3	PbH_3
Y = N	**110.6(2)** [111.4]	**119.7(3)** [120.0]	**120.0** [119.5]	[120.0]	[115.4]
P	**98.8(3)** [99.4]	**96.8(5)** [95.2]	**95.7(5)** [96.2]	[95.6]	[95.7]
As	**96.1(5)** [97.0]	**94.1(2)** [92.5]	[93.7]	[92.9]	[93.3]
Sb	**94.1(5)** [94.5]	**89.0(3)** [89.4]	[90.6]	[89.4]	[90.3]
Bi	**97.1(10)** [93.0]	[87.1]	[88.8]	[87.4]	[88.6]

Quellen/Literatur

- D. W. H. Rankin, N. W. Mitzel, C. A. Morrison, Structural Methods in Molecular Inorganic Chemistry, John Wiley & Sons, Chichester, 2013.
- G. A. Sim, L. E. Sutton, Eds., Molecular Structure by Diffraction Methods: Volumes 1 – 6, The Royal Society Of Chemistry, 1973 – 1977.
- J. C. Lindon, Ed., *Encyclopedia of Spectroscopy and Spectrometry*, Academic Press, Amsterdam, Boston, 2010.