



Skilizium-2018

Yury Vishnevskiy, Georg Stammler

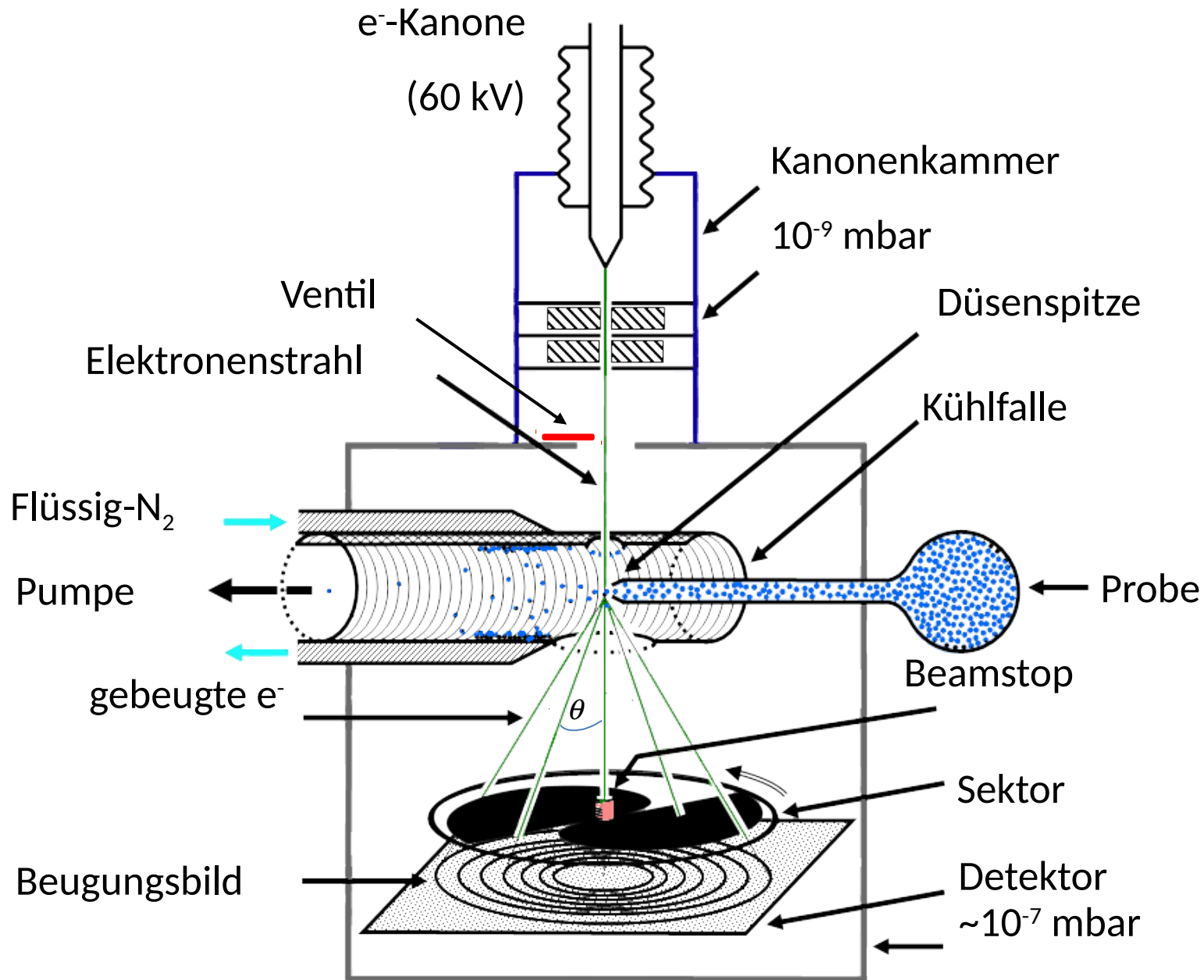


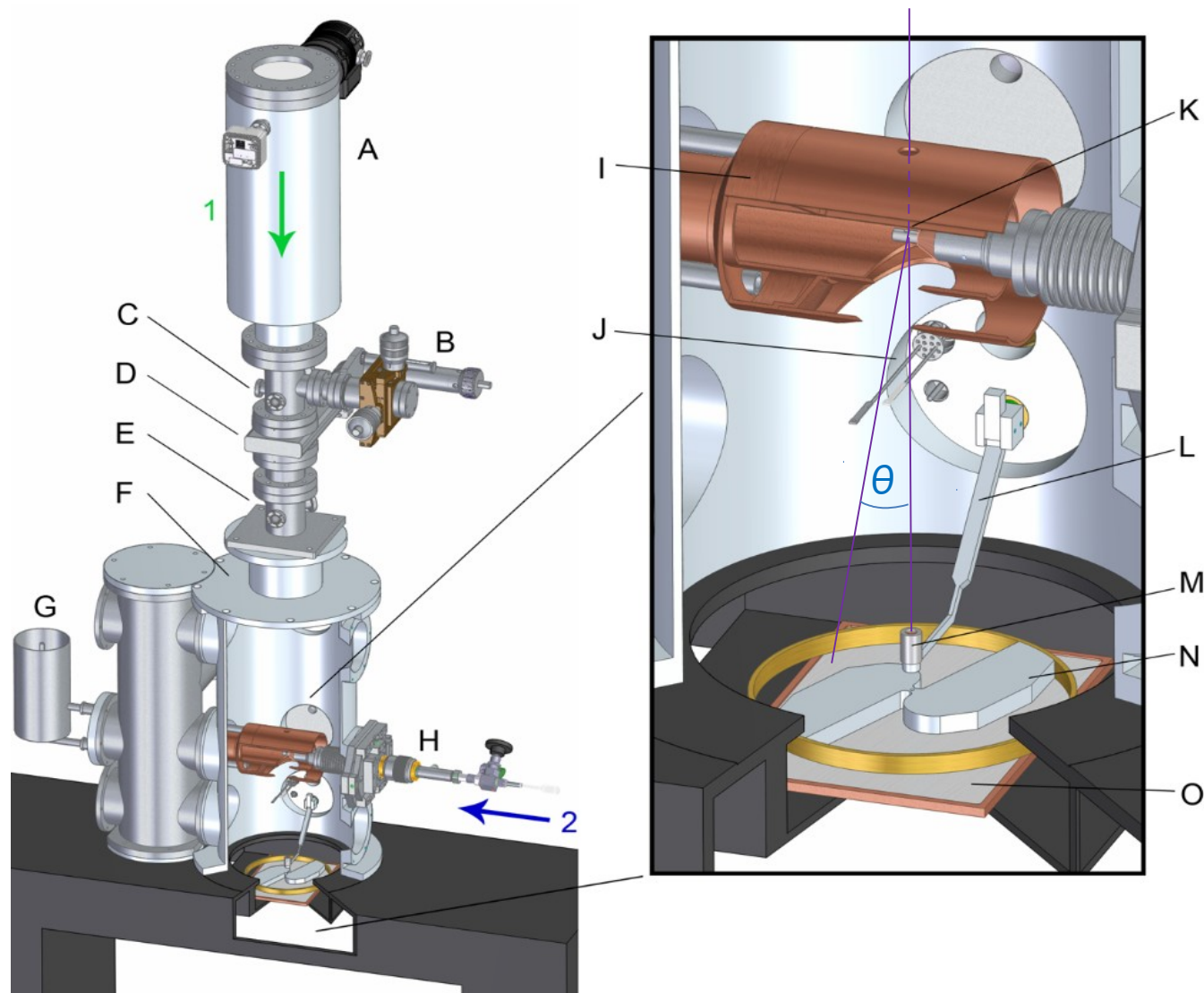
**Cover Picture**

*N. W. Mitzel et al.*

Tetranitromethane: A Nightmare of Molecular Flexibility  
in the Gaseous and Solid States

# Gas-Elektronen-Beugung (GED)

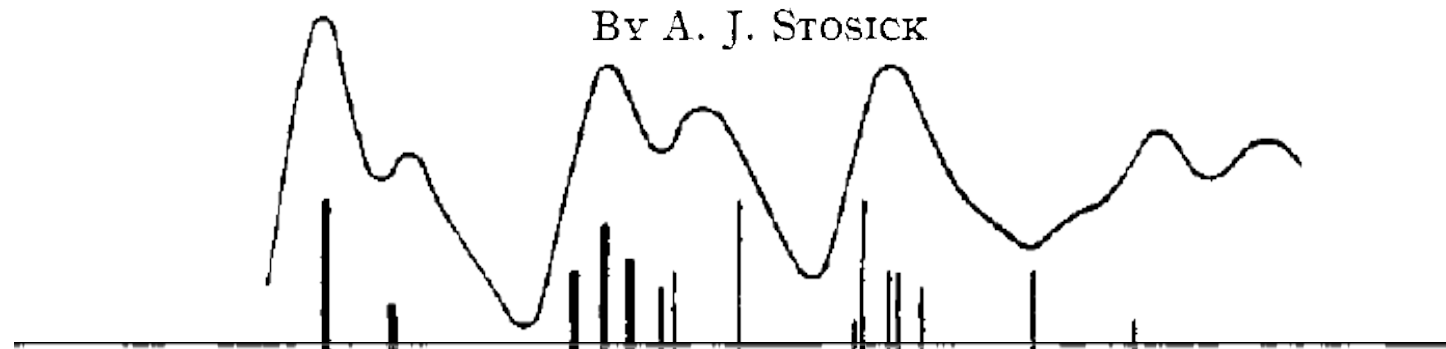




[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 688]

## The Determination of the Molecular Structure of Tetranitromethane by the Electron Diffraction Method

BY A. J. STOSICK



Model	Type	Equilib. position	Amplitude
I	Static	0°	0°
II	Static	90°	0°
III	Static	30°	0°
IV	Oscillating; no temperature factor	0°	30°
V	Oscillating; no temperature factor	0°	40°
VI	$\varphi$ Independent distances only	...	...
VII	Oscillating; temperature factor	30°	20°
VIII	Oscillating; temperature factor	0°	30°
IX	Oscillating; temperature factor	25°	20°

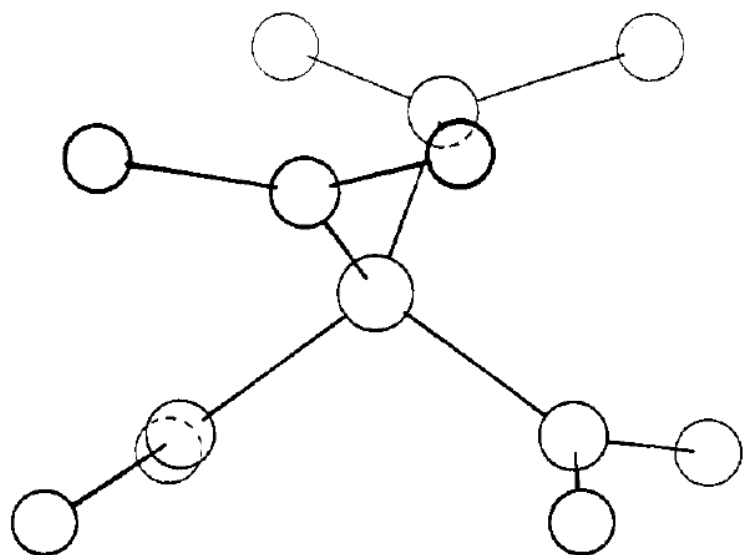


Fig. 1.

In all models  $C-N = 1.46 \text{ \AA.}$ ,  $N-O = 1.21 \text{ \AA.}$ ,  $\angle O-N-O = 127^\circ$ , and  $\angle N-C-N = 109^\circ 28'$ .

## The Infrared Spectra of Tetranitromethane\*†

P. H. LINDENMEYER‡ AND P. M. HARRIS

*Department of Chemistry, The Ohio State University, Columbus, Ohio*

(Received June 19, 1952)

Cooling curve investigations show that the transition between the two crystalline forms of tetranitromethane occurs at  $-99.8^{\circ}\text{C}$  and its character suggests an order-disorder transformation. The infrared spectra of tetranitromethane were obtained at  $25^{\circ}\text{C}$  (vapor),  $18^{\circ}\text{C}$  (liquid),  $-40^{\circ}\text{C}$  (solid I),  $-88^{\circ}\text{C}$  (solid I),  $-104^{\circ}\text{C}$  (solid II) and  $-126^{\circ}\text{C}$  (solid II). The spectra of the vapor are best interpreted by a molecule with  $S_4-\bar{4}$  symmetry whereas reported Raman spectra indicate  $D_{2d}-\bar{4}2m$  symmetry in the liquid. Satisfactory agreement between these and the x-ray diffraction data require molecules of both symmetries. A complete lack of selection rules was observed in the spectra throughout the solid range.

### SUMMARY

1. Crystalline tetranitromethane undergoes transition from a cubic lattice to one of lower symmetry at  $-98.8^{\circ}\text{C}$ .

2. The infrared absorption spectra of gaseous tetranitromethane may be most reasonably explained by assuming a molecular symmetry of  $S_4-\bar{4}$ .

3. The reported Raman polarizabilities<sup>3,4</sup> require the presence of molecules with  $D_{2d}-\bar{4}2m$  symmetry in the liquid.

4. The assignment of frequencies to torsional motion of the  $\text{NO}_2$  groups about the C-N bonds requires that groups do not rotate in the solid state.

5. Although the site symmetry of solid I is at least  $T_d$ , its infrared spectra show a complete lack of selection rules. This is consistent with the spectra to be expected from a disordered crystal.<sup>2</sup>

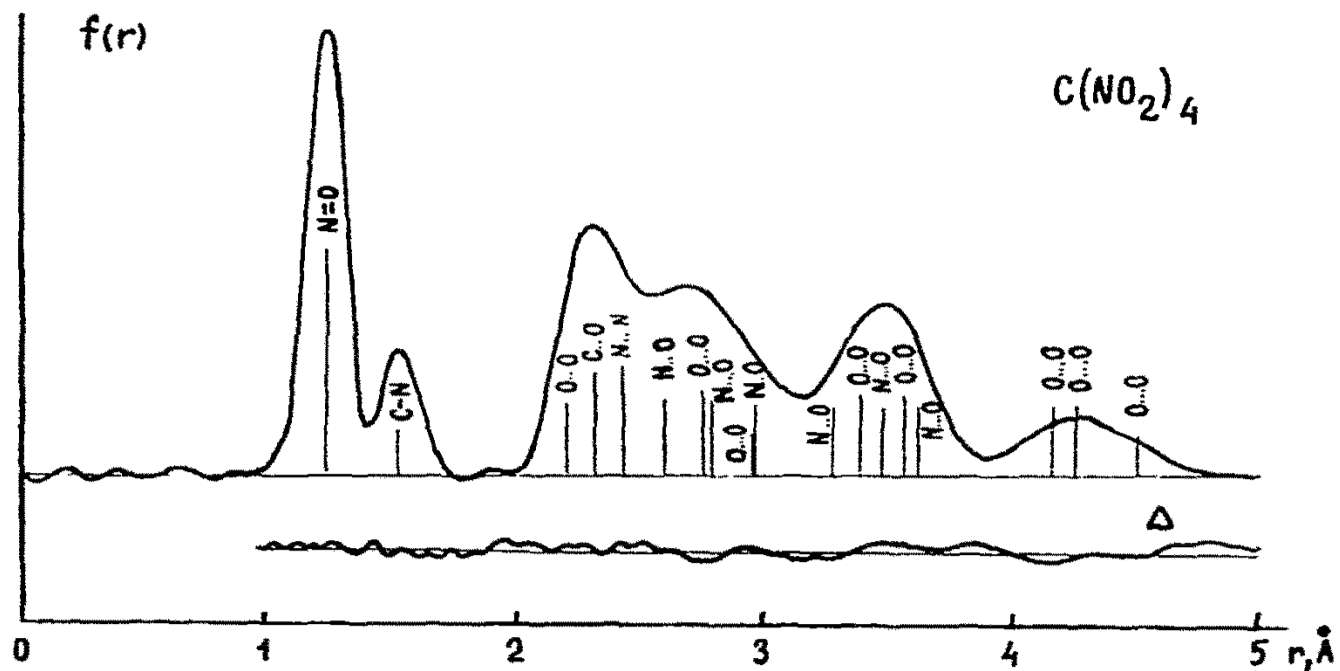
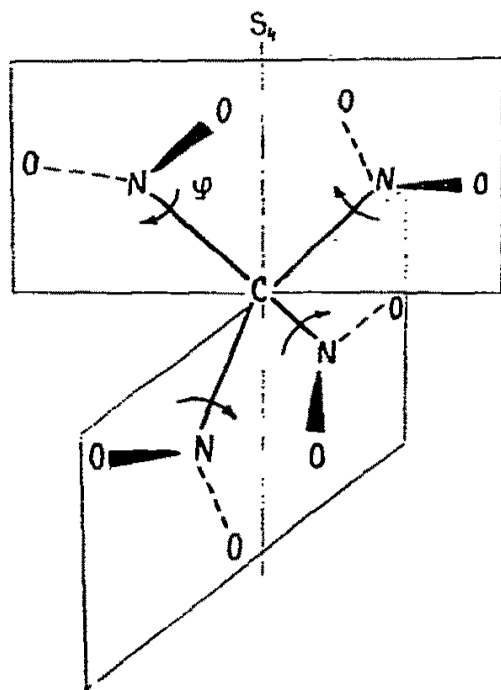
Short communication

ELECTRON DIFFRACTION STUDY OF TETRANITROMETHANE

N. I. SADOVA, N. I. POPIK and L. V. VILKOV

Department of Chemistry, Moscow State University, Moscow 117234 (U.S.S.R.)

(Received 6 March 1975)

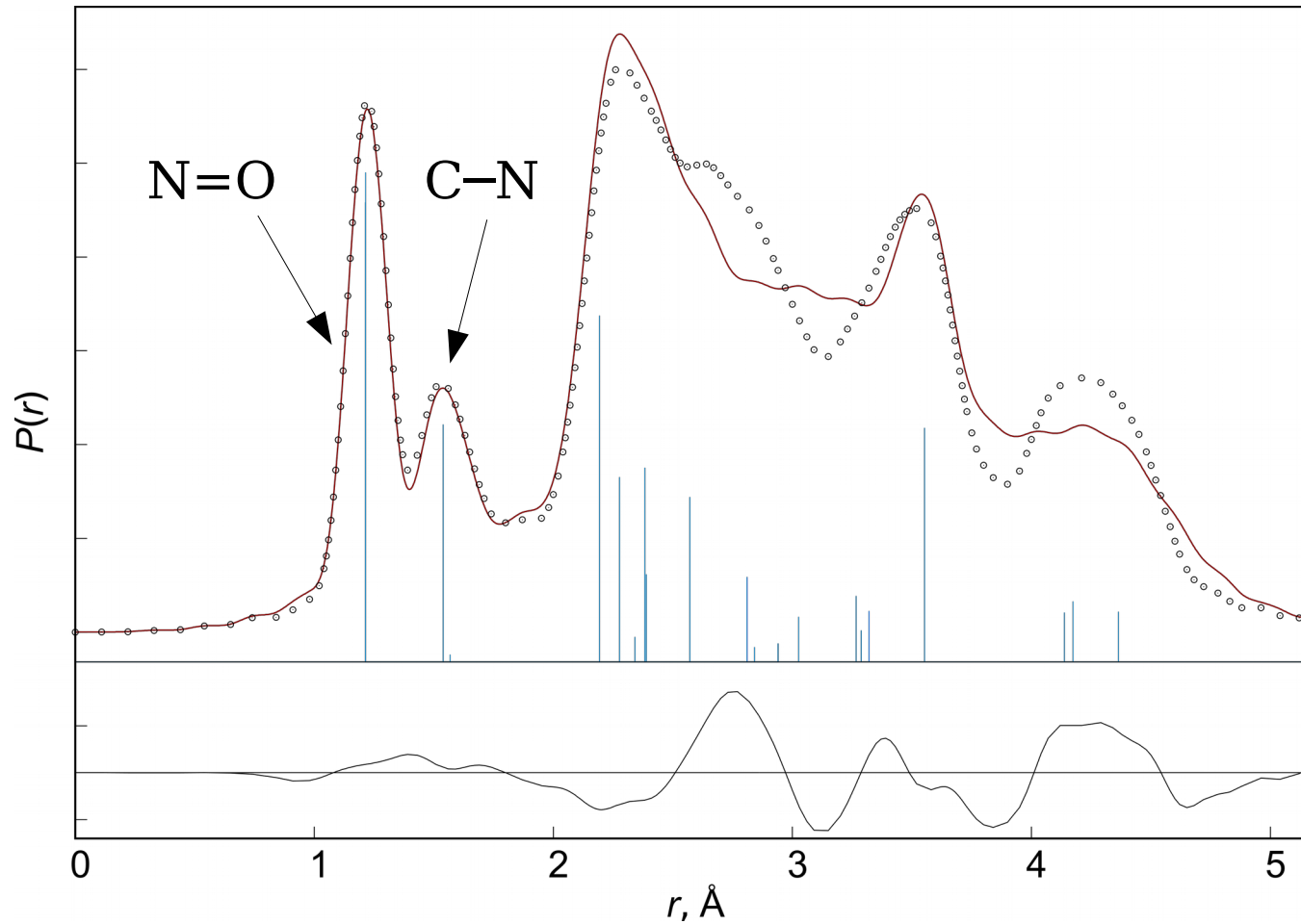
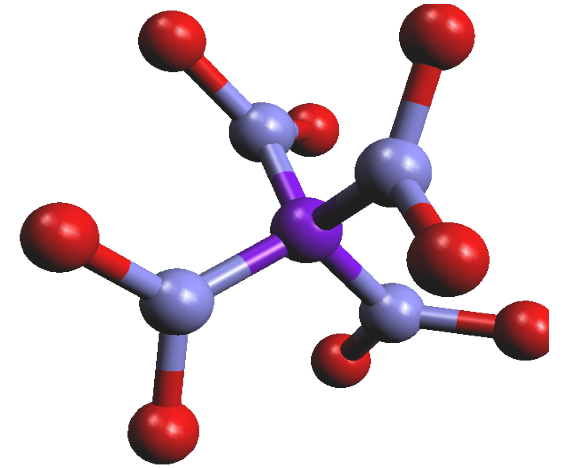


$S_4$ -Symmetrie, Standardmodell; **R-faktor ???**

# GED von $\text{C}(\text{NO}_2)_4$ - 2017 Bielefeld

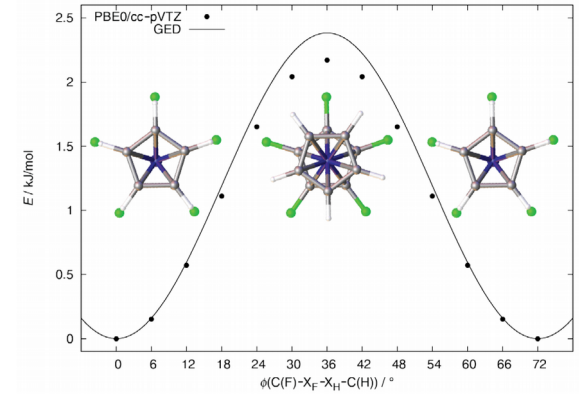
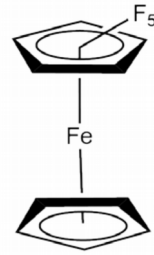
Alle Rechnungen:  $S_4$ -Symmetrie

Standard GED Modell  $\rightarrow$   $R$ -Faktor **15-20** %

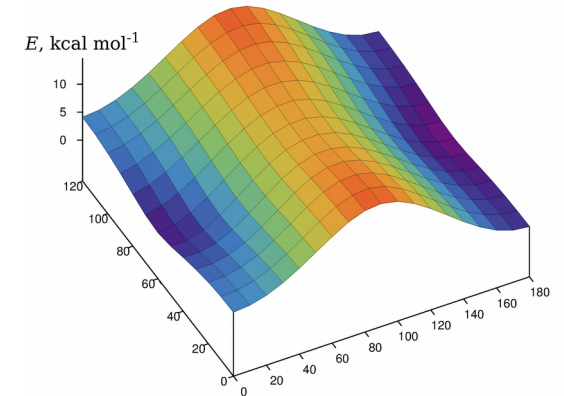


# Dynamische Modelle in GED

**1D: viel**, z.B. Pentafluorferrocen



**2D:  $\approx 10$** , z.B. 1,3-dichloropropanone  
(ClCH<sub>2</sub>)<sub>2</sub>C=O



**3D: nur ein Beispiel:** 1,3,5-trinitrobenzol

**C(NO<sub>2</sub>)<sub>4</sub>:**

Niedrigste Frequenzen bei: 57 (E), 64 (A) 84 (B) cm<sup>-1</sup>

die nächst höhere: 174 cm<sup>-1</sup>

die ersten 3 adiabatisch separierbar

→ **4-dimensionales Modell nötig**, um Torsions-Moden zu beschreiben



# Dynamisches Modell für $C(NO_2)_4$

Standardmethode:

$\approx 10000$  Pseudokonformere wären nötig

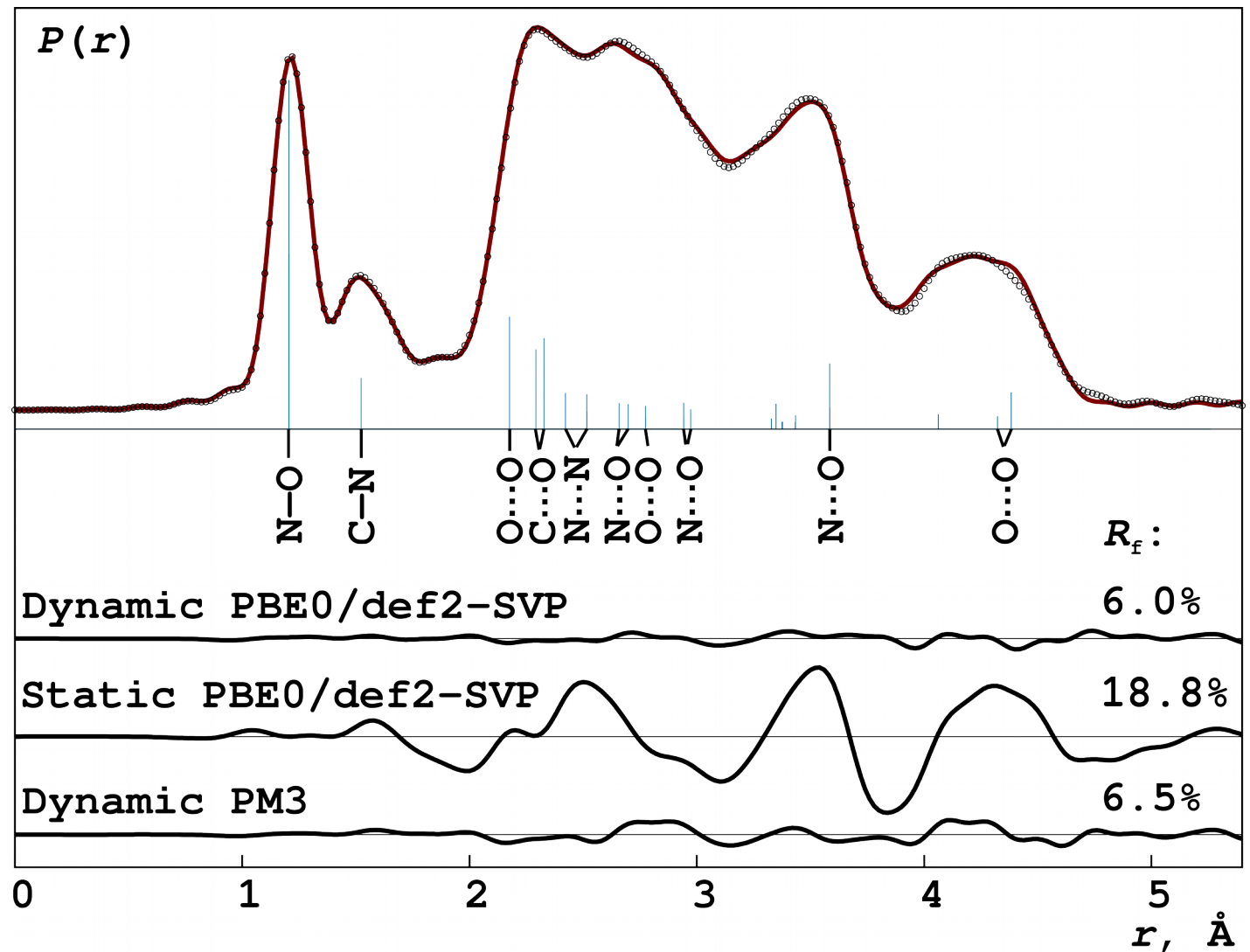
Neu:

Monte-Carlo-Technik:

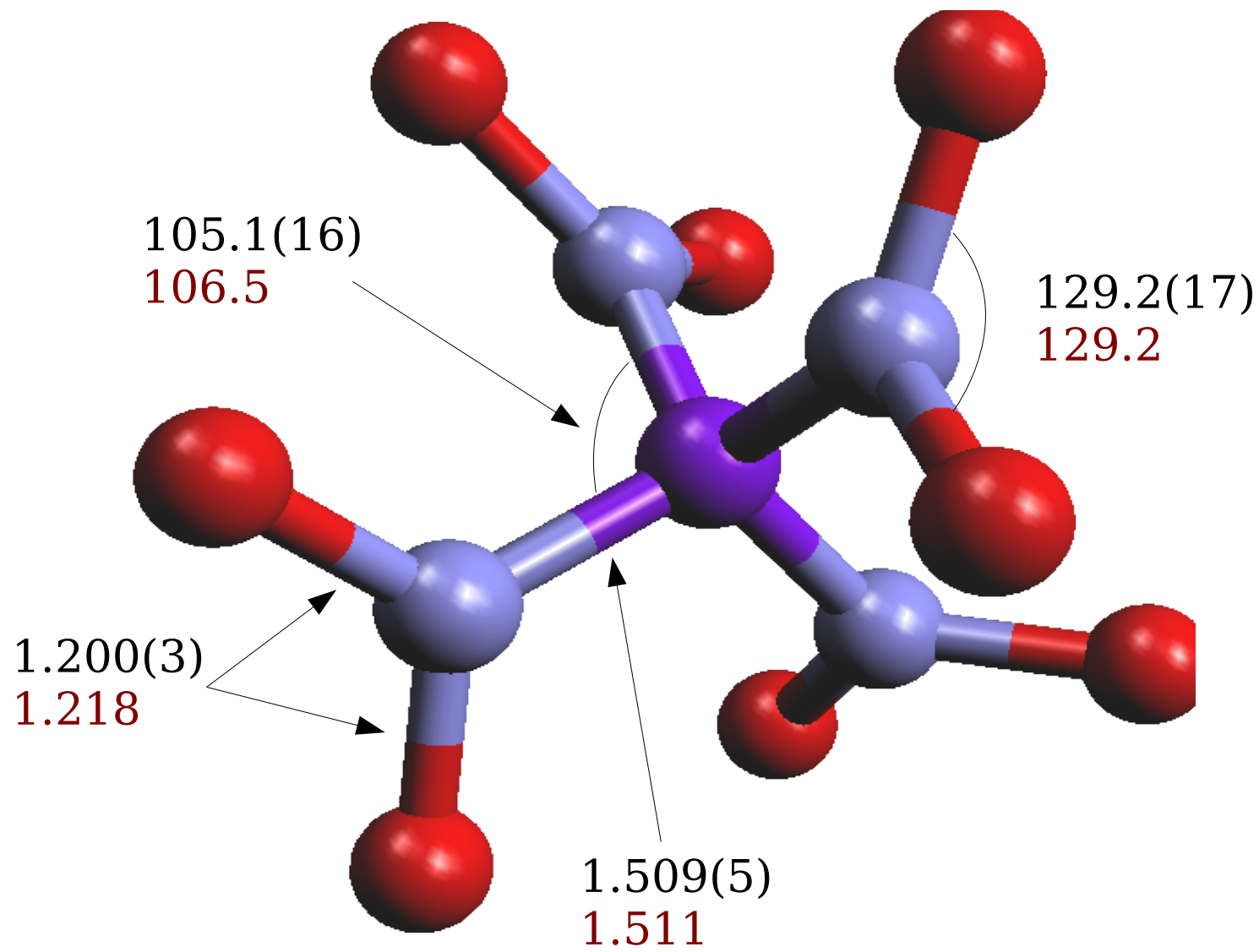
208 Pskonf. @ PM3

82 Pskonf. @

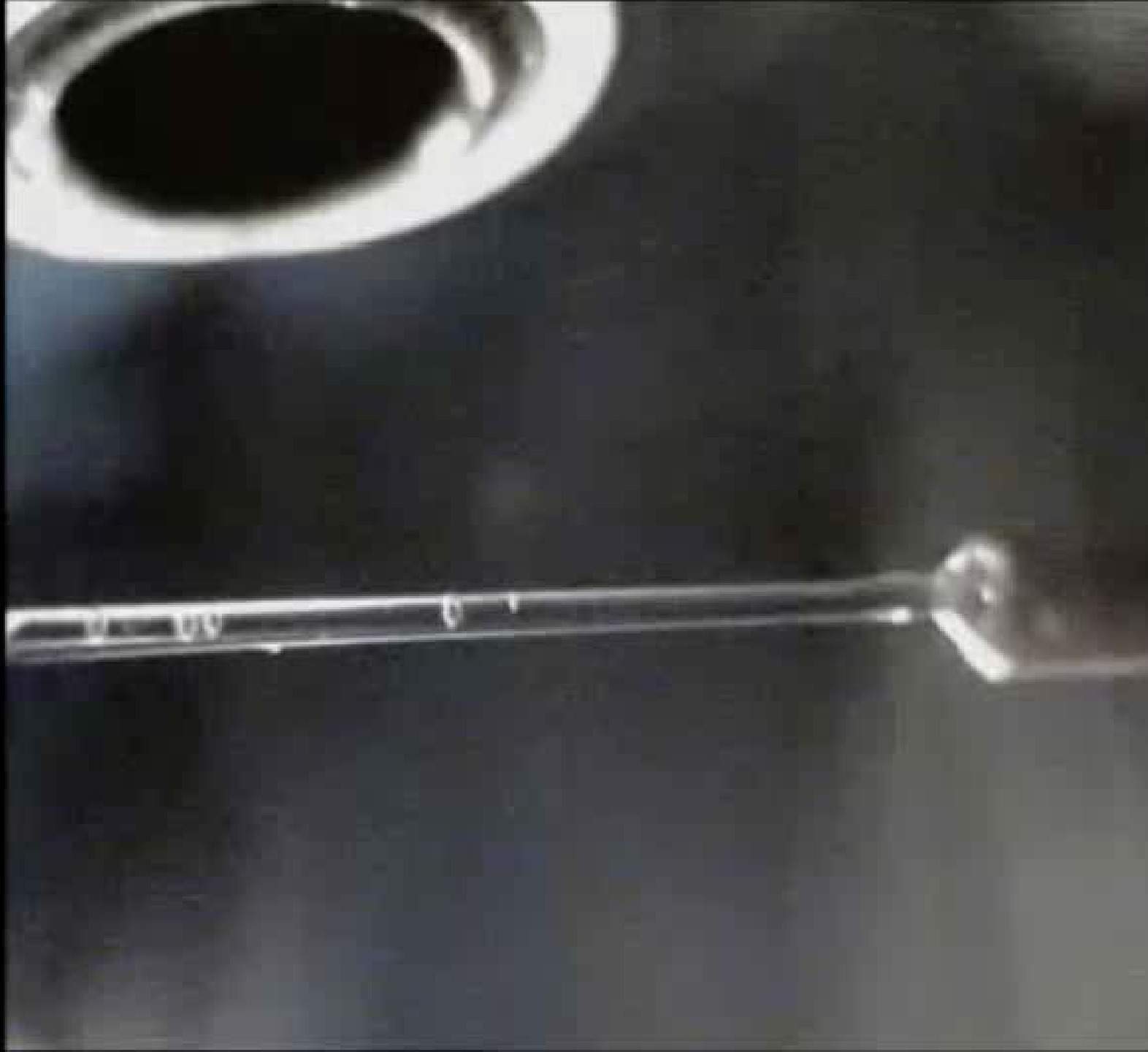
PBE0/def2-SVP



Nur mit der neuen Verfeinerungsmethode können GED  
Daten erfolgreich interpretiert werden.

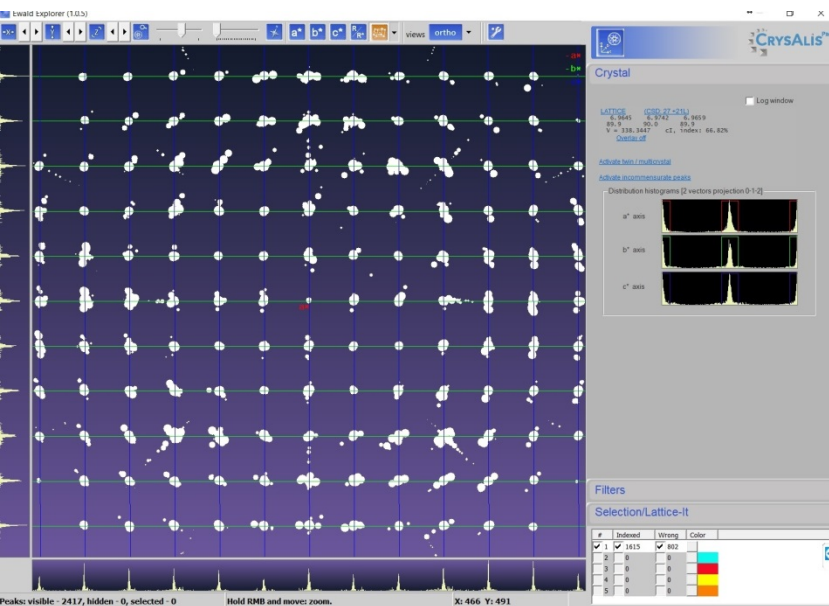


GED  
MP2(full)/cc-pwCVTZ

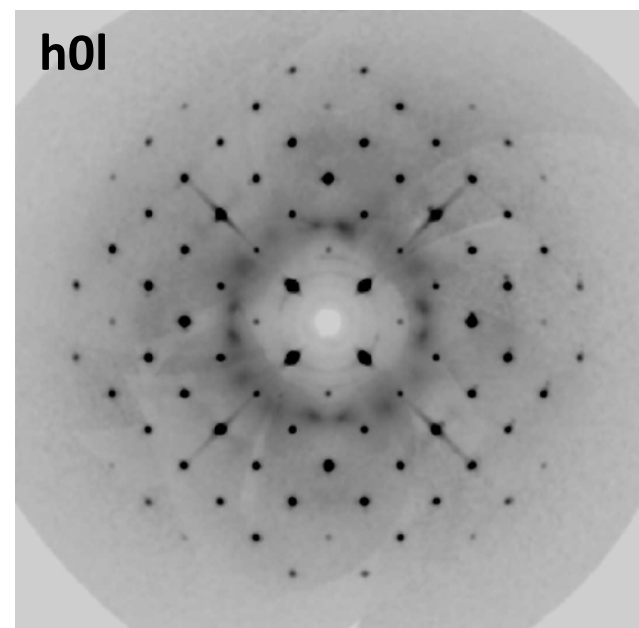
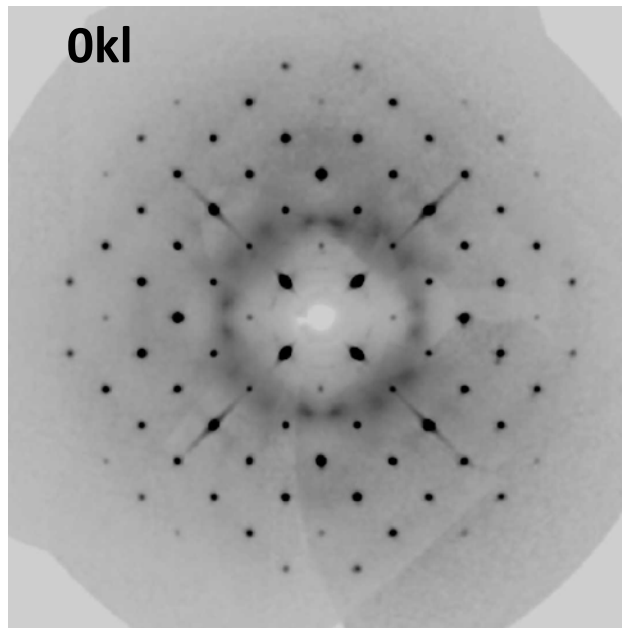
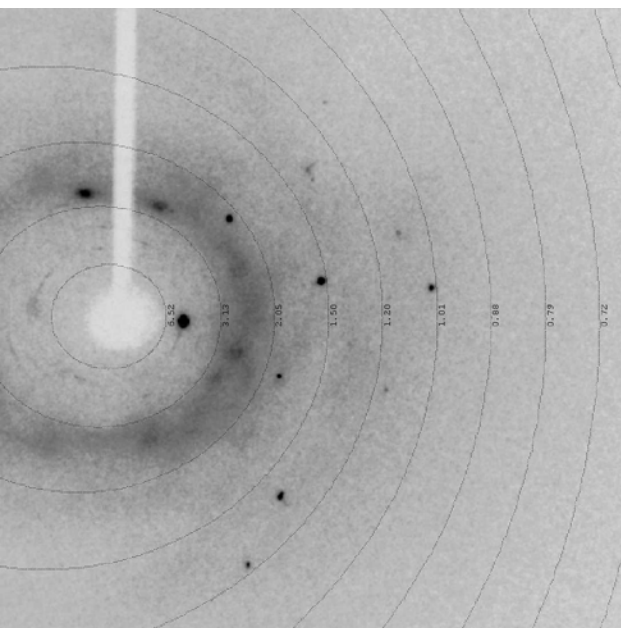


x 1.5

200 K



System	cubic
Space group	I-43m
a	6.9871(3) Å
V	341.11(4) Å <sup>3</sup>
$\rho_{\text{calc}}$	1.91 Mg/m <sup>3</sup>



200 K

Raumgruppe  $I\bar{4}3m$

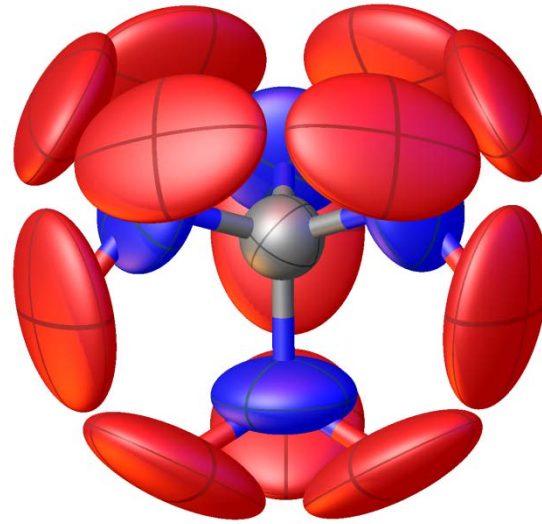
C auf  $\bar{4}$

O auf  $m$  (s.o.f.  $\frac{2}{3}$ )

**N auf 3**

**$R_1 = 14.6\%$**

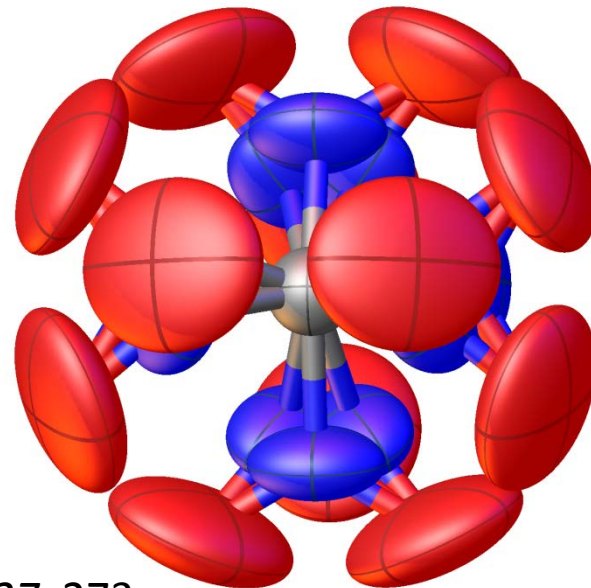
$\rho_{\text{res}} = 0.3 \text{ e \AA}^{-3}$



**N neben 3 (s.o.f.  $\frac{1}{3}$ )**

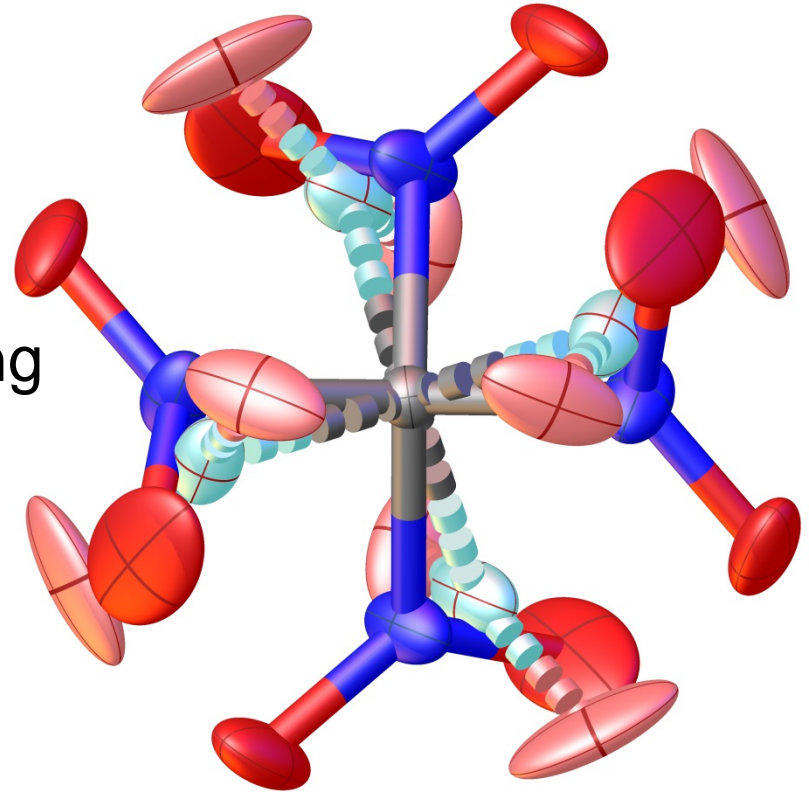
**$R_1 = 13.0 \%$**

$\rho_{\text{res}} = 0.3 \text{ e \AA}^{-3}$



200 K

$\bar{4}3m$ -Symmetrie ignoriert  
 $\bar{4}$ -Symmetrie angenommen  
=> Pseudo-merohedrischer Zwilling  
Raumgruppe  $I\bar{4}$   
 $a = 6.9893(3) \text{ \AA}$   
 $c = 6.9866(7) \text{ \AA}$   
 $R_1 = 4.0\%$   
 $\rho_{\text{res}} = 0.07 \text{ e \AA}^{-3}$

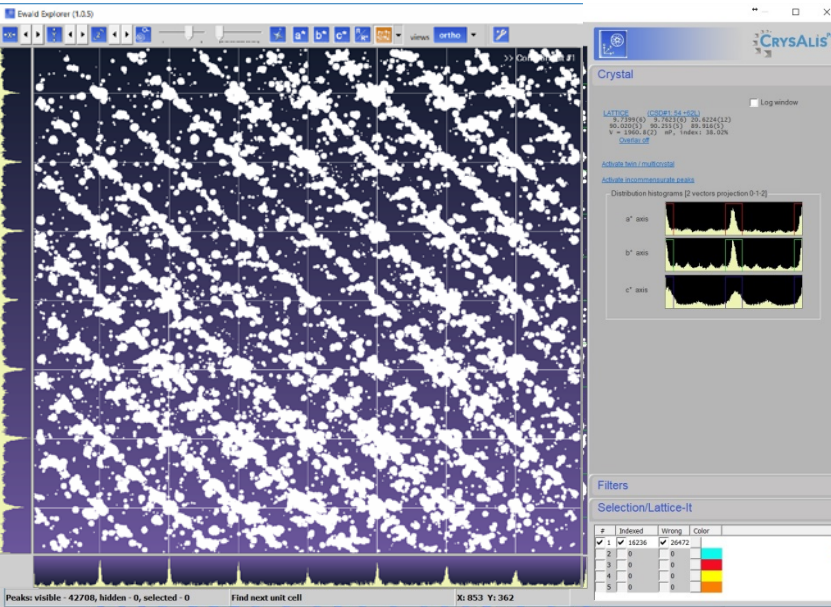


Schwingungsellipsoide mit 10% Aufenthaltswahrscheinlichkeit  
Zu 45% besetzter Teil gestrichelt gezeichnet

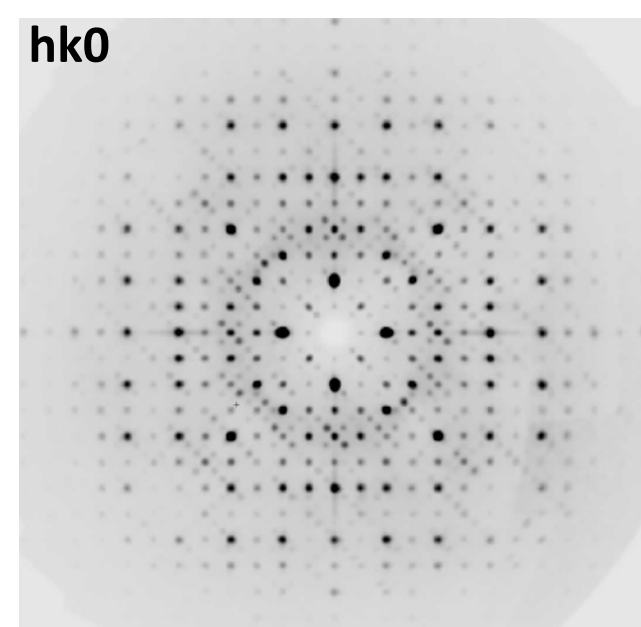
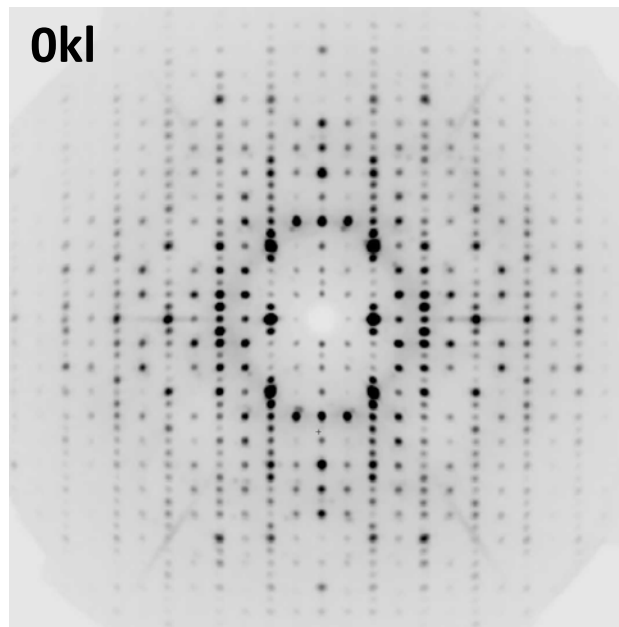
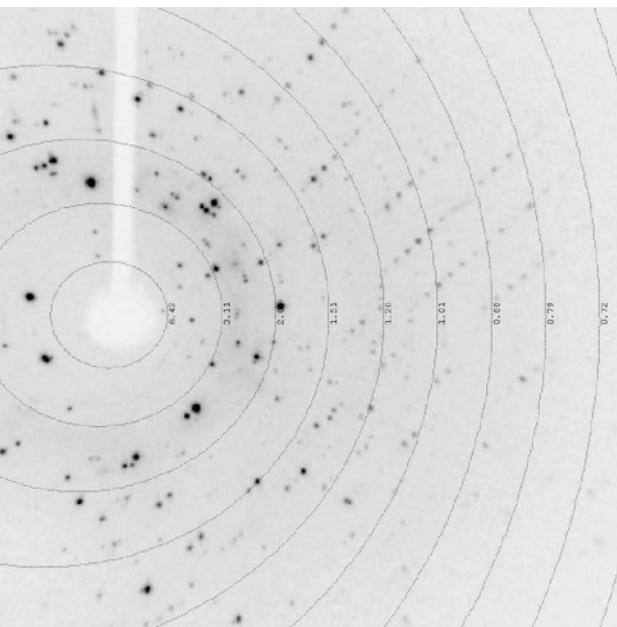
P. H. Lindenmeyer, P. M. Harris, *J. Chem. Phys.* **1953**, 21, 408.

# Oligo-kristallin

100 K



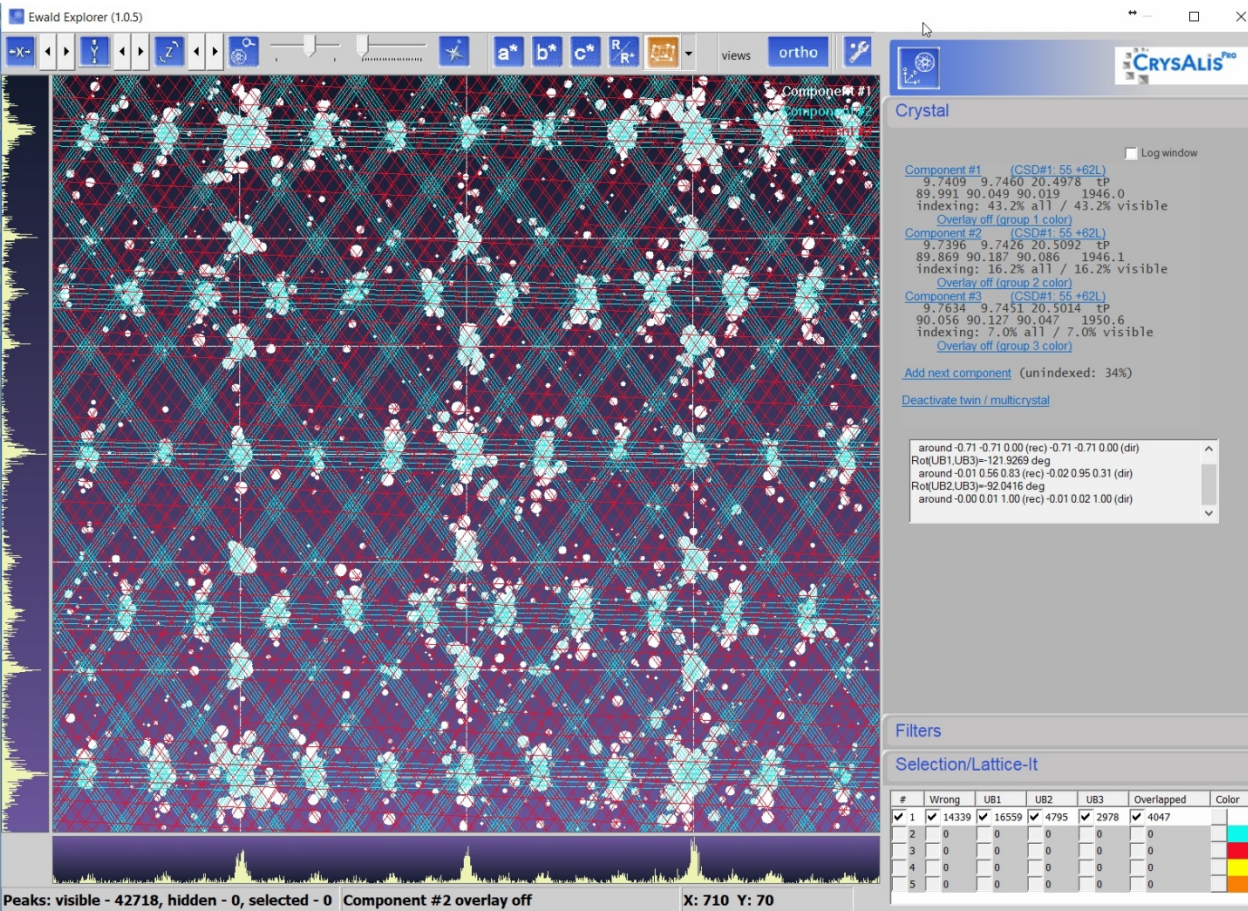
System	Tetragonal
Space group	P 4 <sub>2</sub>
a	9.7550(4) Å
c	20.5493(11) Å
V	1940.01(6)
ρ <sub>calc</sub>	2.01 Mg/m <sup>3</sup>



100 K

P4<sub>2</sub> keine Strukturlösung!!

3 Domänen indiziert (ca. 2/3 aller Reflexe)  
und integriert



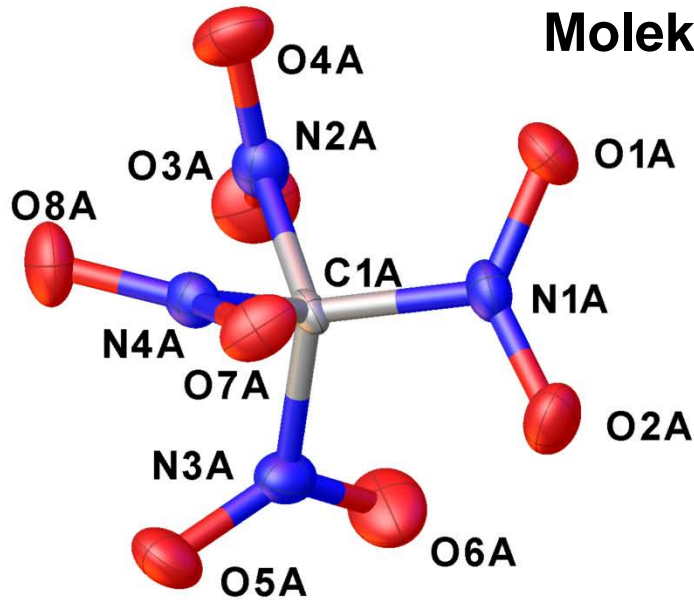


Strukturlösung in **P1** möglich:

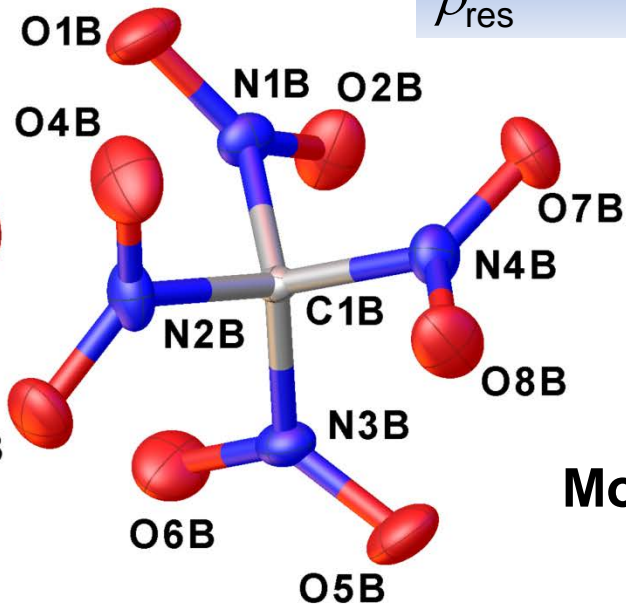
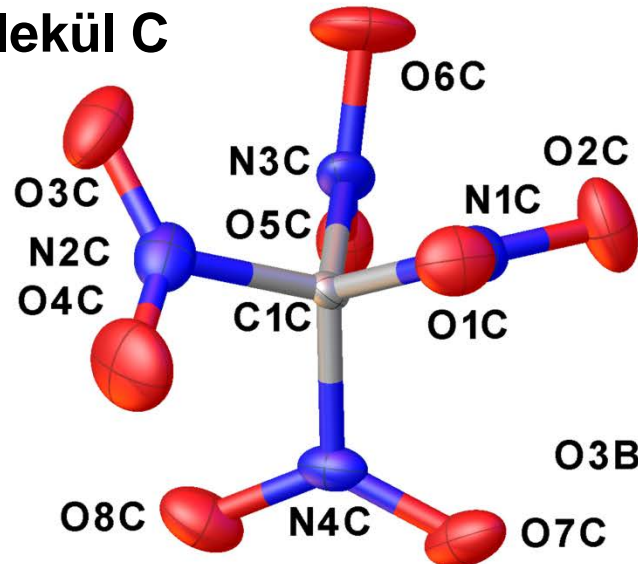
- SHELXD
- keine Verfeinerung der Atomparameter
- Fourier-Synthese statt Differenzfourier
- ca. 20 Iterationen um fast alle Atome zu finden
- R-Wert ca. 60%
  
- Vorsichtiges Verfeinern der Atomparameter
- Fehlende Atome iterativ lokalisieren
- 12 Moleküle
- R-Wert > 30%
  
- Symmetrie der 12 Moleküle entspricht **Pca2<sub>1</sub>**
- In **Pca2<sub>1</sub>** mit drei Domänen integrieren
- Als Pseudo-mercedrischen Zwilling verfeinern (Rotation 90° um c, Verhältnis 57:43)

100 K

Molekül A



Molekül C

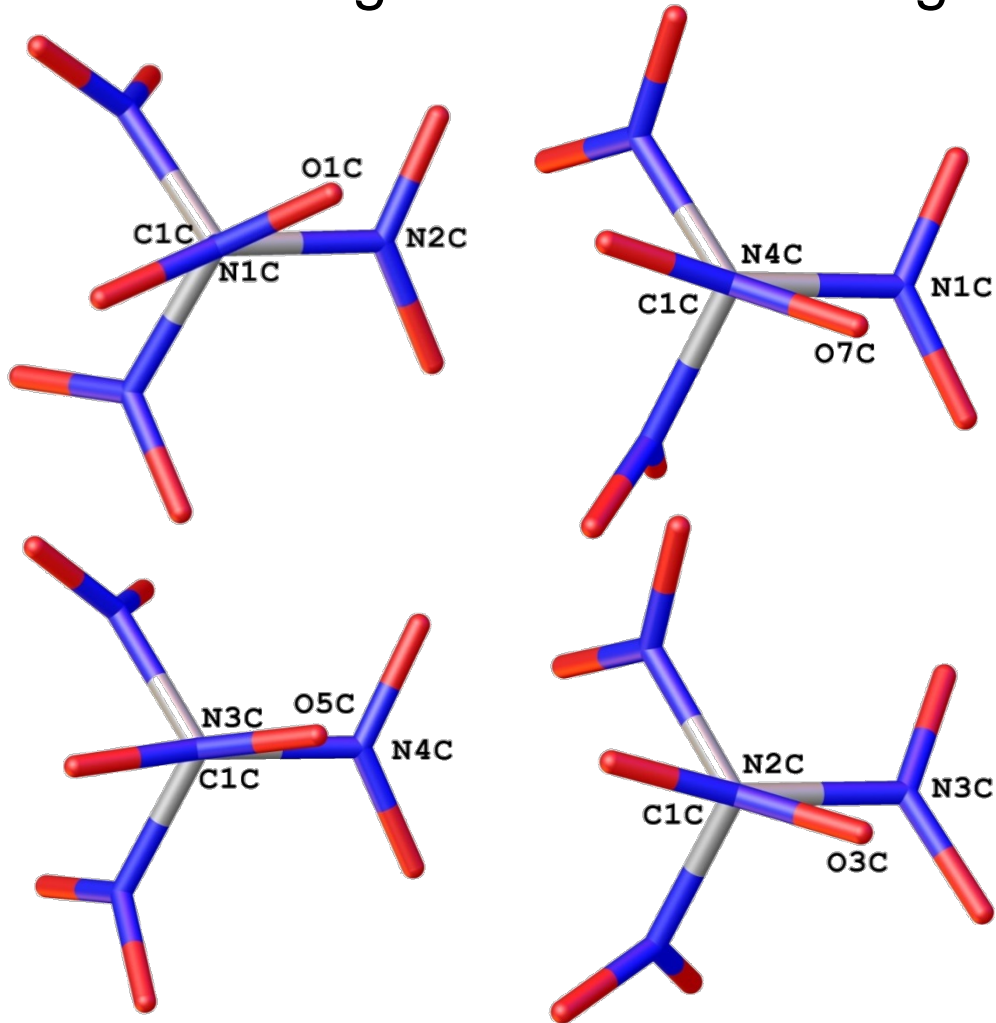


Molekül B

System	Orthorhombic
Space group	$Pca2_1$
a	9.7331(2) Å
b	9.7317(2) Å
c	20.4635(5) Å
V	1938.28(7)
$\rho_{\text{calc}}$	2.02 Mg/m <sup>3</sup>
$R_1$	3.7%
$\rho_{\text{res}}$	0.07 e

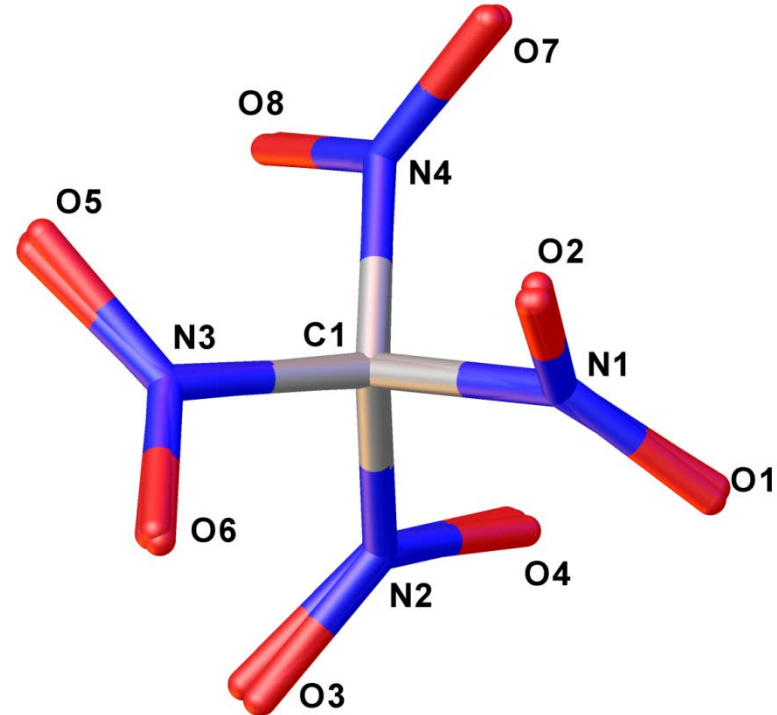
100 K

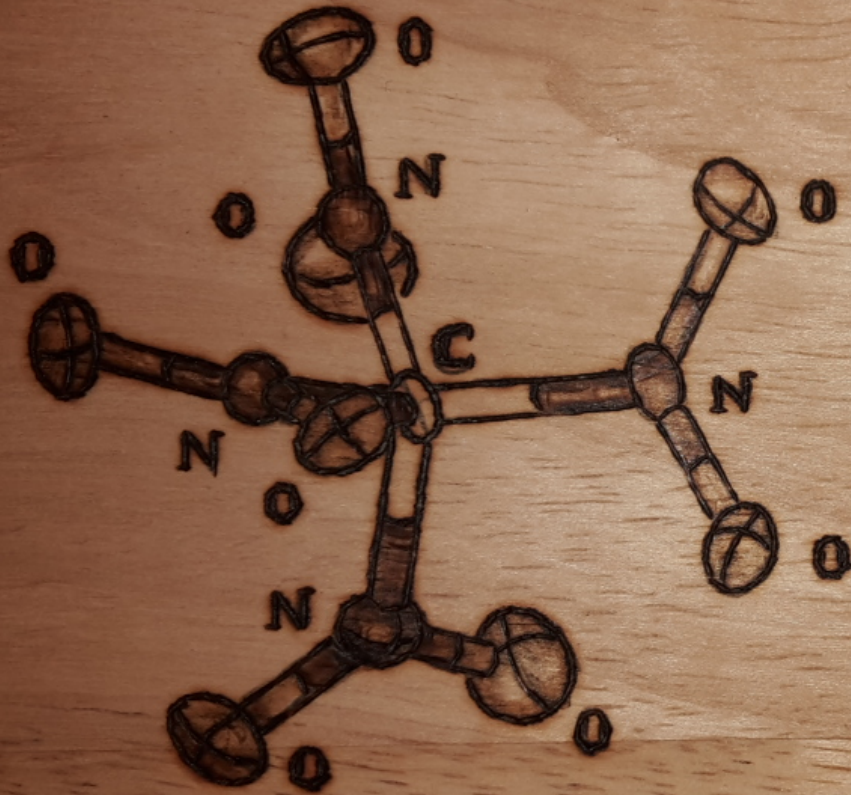
Eines der unabhängigen Moleküle  
Blick entlang der 4 N–C Bindungen



Keine  $\bar{4}$  Symmetrie:  $\tau(N-C-N-O)$ :  $5.9(4)^\circ - 23.9(4)^\circ$

Überlagerung der  
3 unabhängigen Moleküle





Tetranitromethan



Danke für die Aufmerksamkeit!