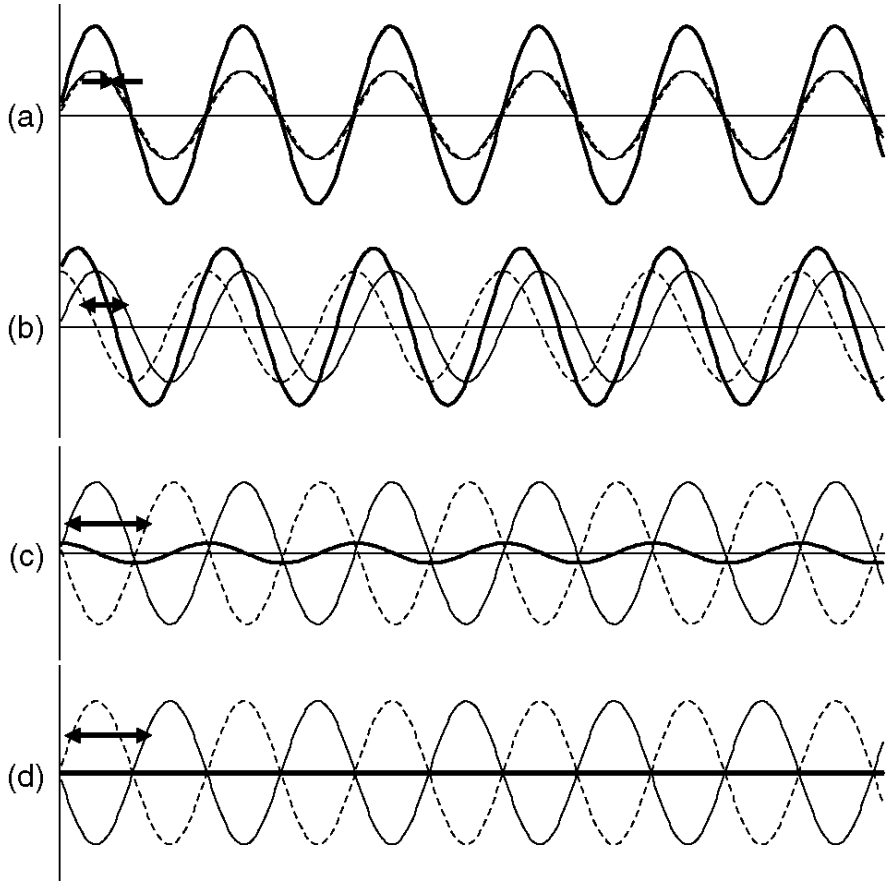
Strukturaufklärung in der molekularen anorganischen Chemie

8. Diffraktion

Interferenz

konstruktiv



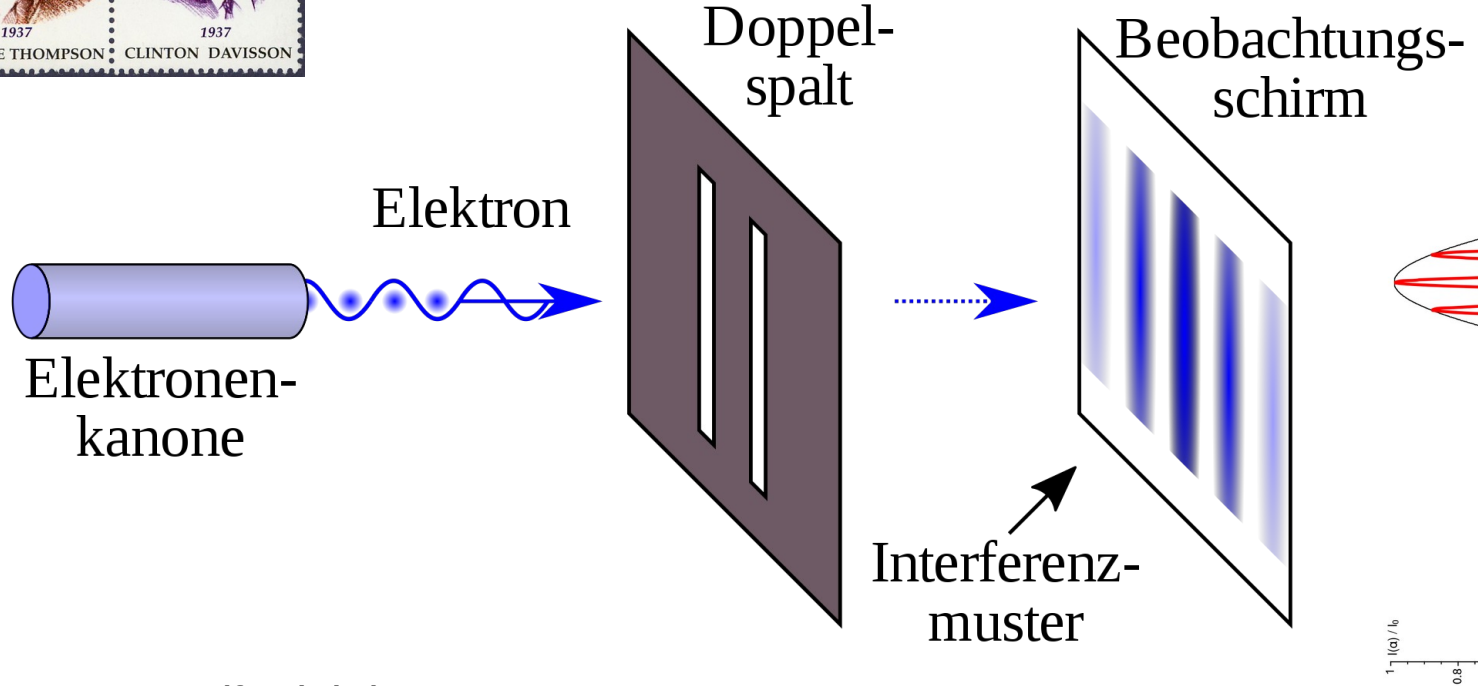
destruktiv

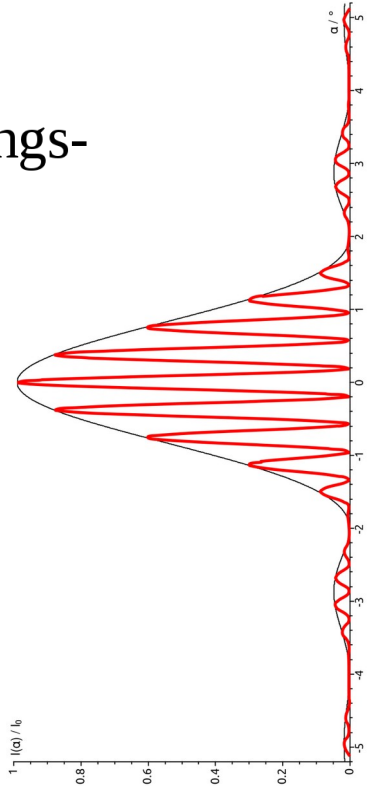
Anwendungen:

Interferometer,
Antischall,
etc….

Diffraktion ≠ Interferenz !

Doppelspaltexperiment



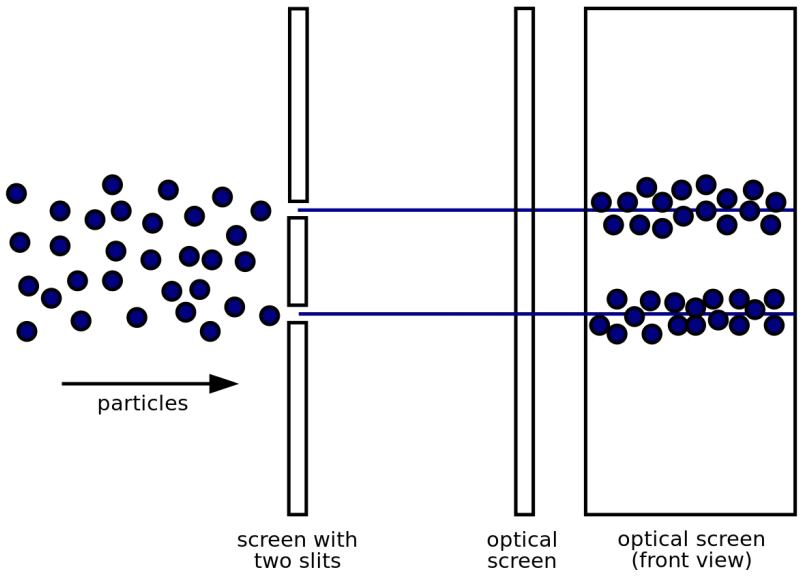


Thomas Young, 1801 (f. Licht)
Davisson, Germer, Thompson 1927 (f. Elektronen)

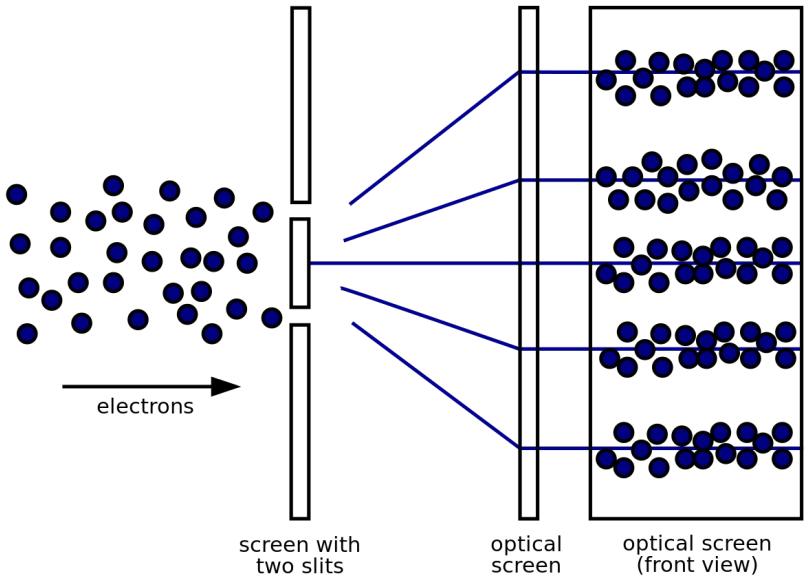
(s. Movie f. klassische Wellen)

Doppelspaltexperiment

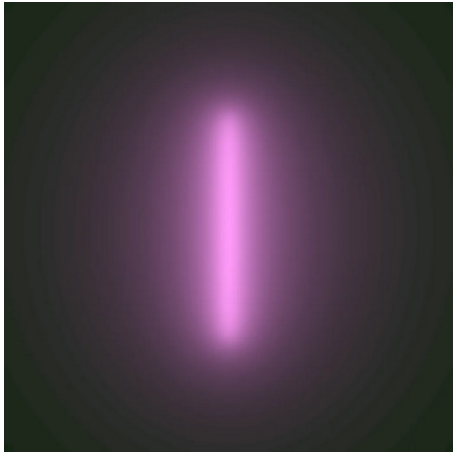
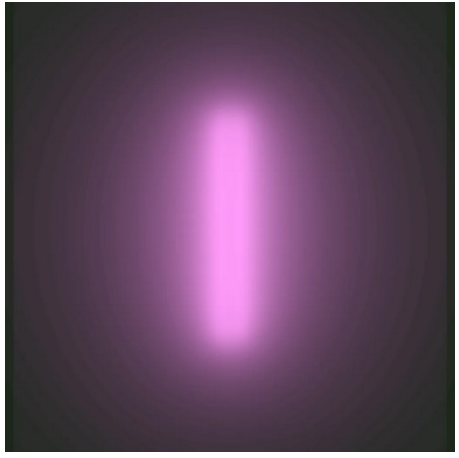
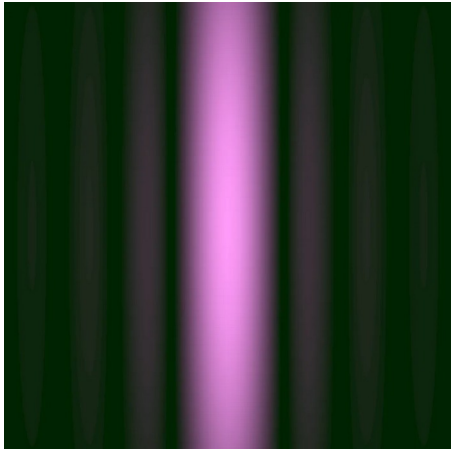
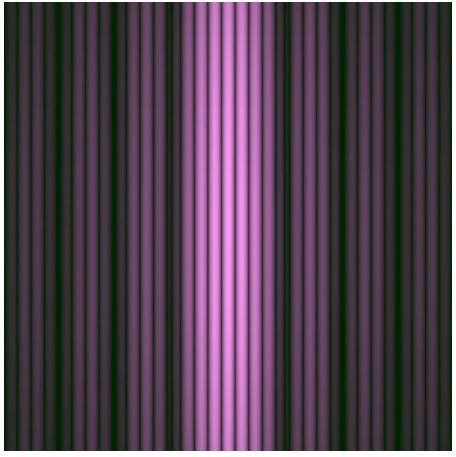
Teilchen-Modell



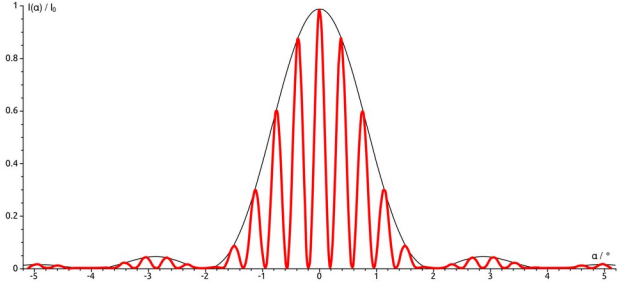
Wellen-Modell



Spaltexperiment-Simulationen

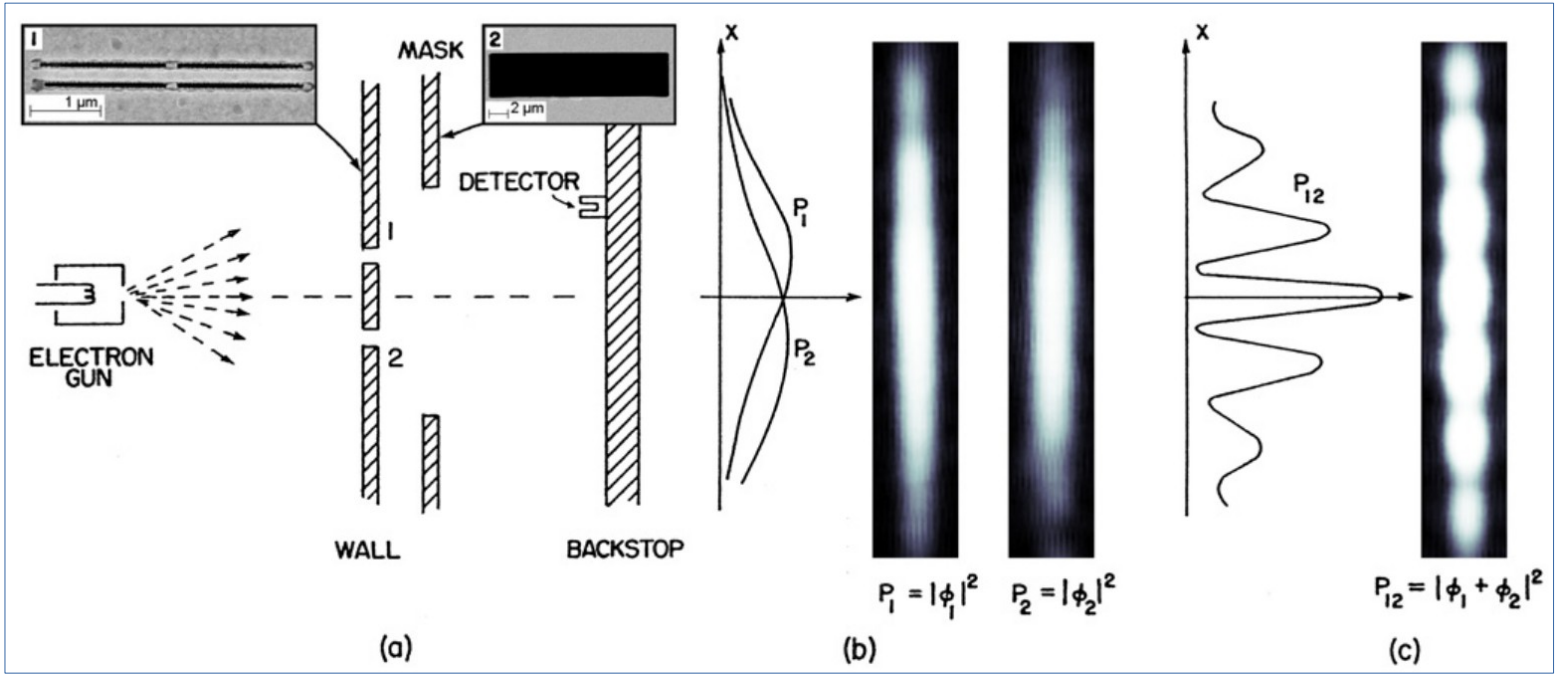
Teilchen-Modell		Wellen-Modell	
Einzelspalt	Doppelspalt	Einzelspalt	Doppelspalt
			

Experiment:



J. Mellor, 2022

Kontrollierte Experimente

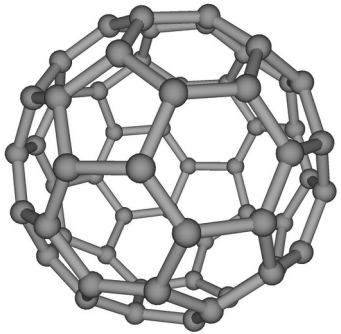


- Welle-Teilchen-Dualismus
- Interferenz einzelner Teilchen

(siehe Animationen!)

R. Bach, D. Pope, S.-H. Liou, H. Batelaan, New J. Phys. 2013, 15, 033018.

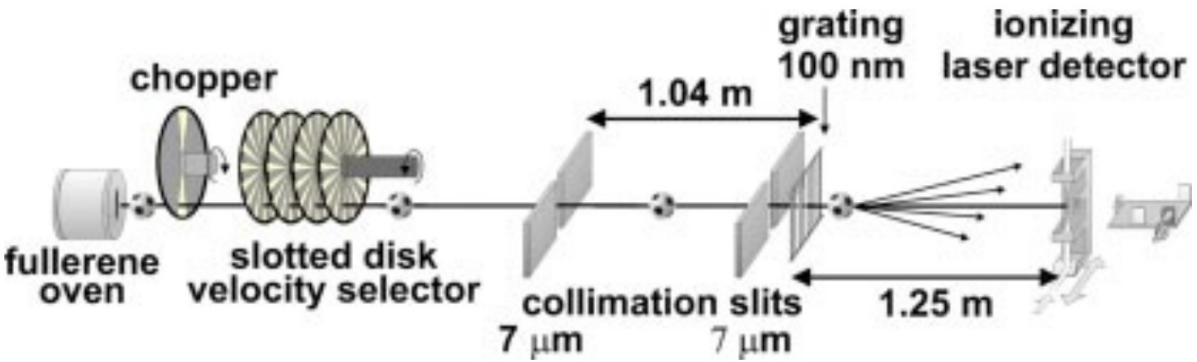
Doppelspaltexperiment mit C_{60}

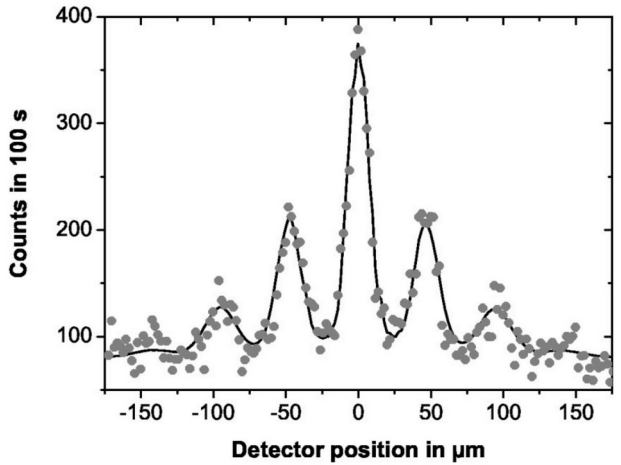


De-Broglie-Welle $\lambda = \frac{h}{mv}$

$m = 1.2 \times 10^{-24}$ kg $\quad v = 200$ m/s

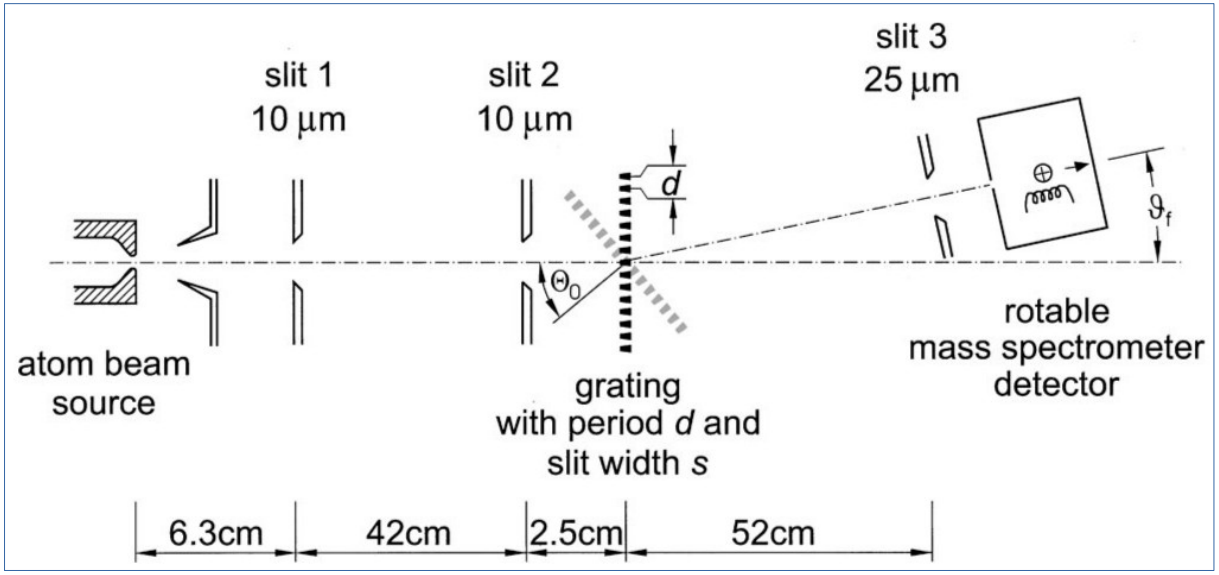
$\lambda = 2.8$ pm



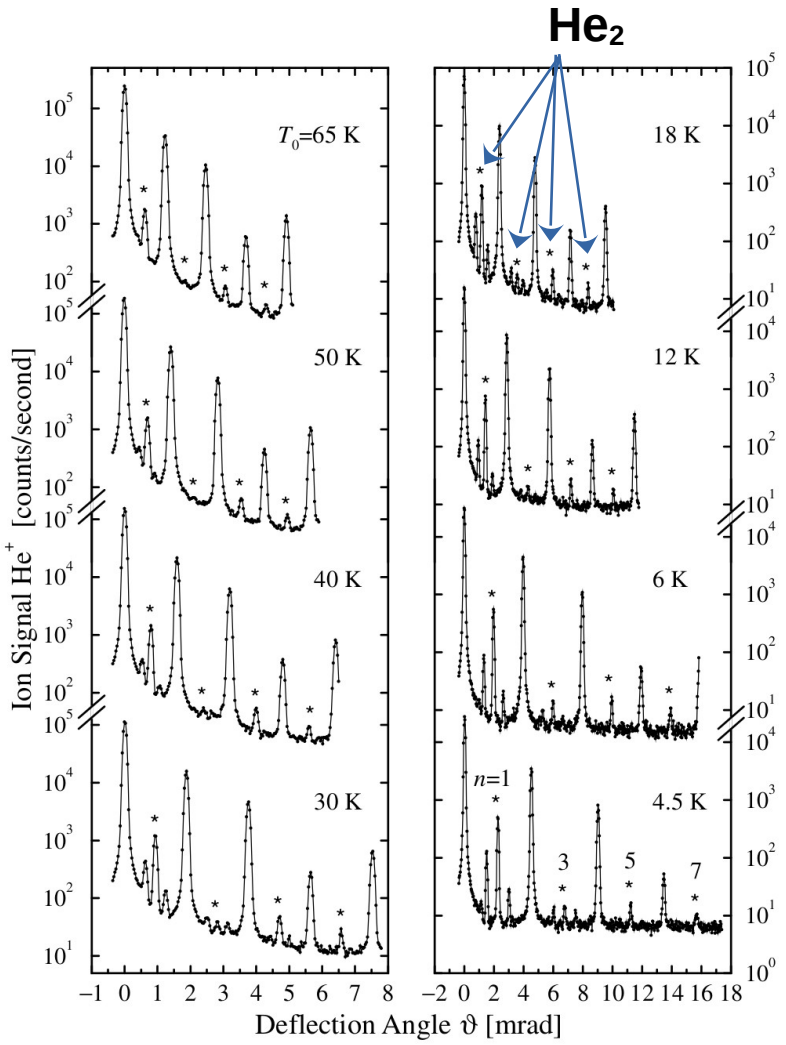


O. Nairz, M. Arndt, A. Zeilinger, *Am. J. Phys.* 2003, 71, 319.

Beugung von He an Gitter

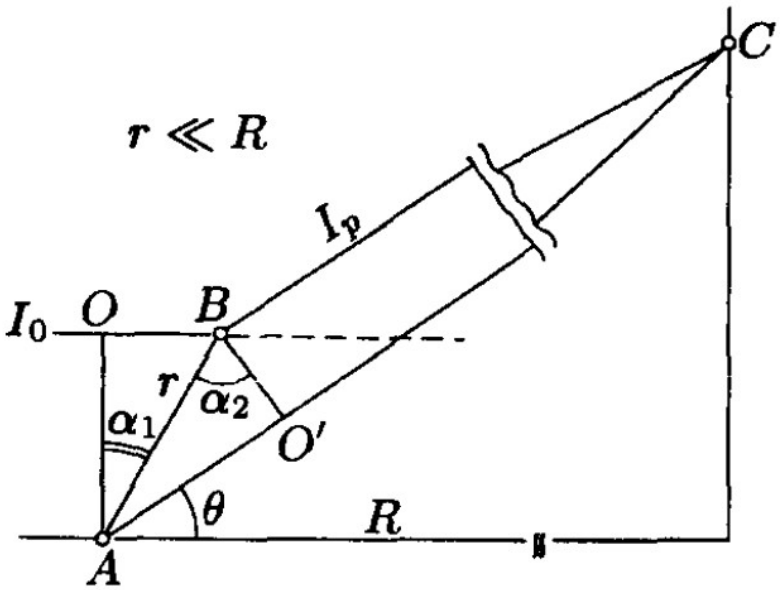


r_0(He...He) = 52 ± 4 Å (aus diesem Experiment)
r_e(He...He) = 3.087 Å (ae-CCSDTQ/cc-pV6Z)



R. E. Grisenti, W. Schöllkopf, J. P. Toennies, J. R. Manson, T. A. Savas, H. I. Smith, Phys. Rev. A 2000, 61, 033608.
R. E. Grisenti, W. Schöllkopf, J. P. Toennies, G. C. Hegerfeldt, T. Köhler, M. Stoll, Phys. Rev. Lett. 2000, 85, 2284.

Interferenz, klassisch



$$\Delta = AO' - BO = r(\sin\alpha_2 - \sin\alpha_1)$$

$\Delta = n\lambda \quad (n \in \mathbb{Z})$ → konstruktiv

$\Delta = \frac{2n+1}{2}\lambda$ → destruktiv

$$\lambda = \frac{r}{n}(\sin\alpha_2 - \sin\alpha_1)$$

$$\left[\frac{(\sin\alpha_2 - \sin\alpha_1)}{n} < 1\right] \Rightarrow \boxed{\lambda \leq r}$$

Diffraktionsmethoden

γ-ray	Hard X-ray	Soft X-ray	Vacuum UV	Near UV	Visible blue red	Near IR	Mid IR	Far IR	Sub-mmw	mm-wave	Micro-wave	Radio-wave	
← < 0.1Å	5Å	100Å 10 nm	2000Å 200 nm	400 nm	0.7 µm 700 nm	2.5 µm 2500 nm	25 µm		1 mm		10 cm	→	λ
> 10^9	2×10^7	10^6	5×10^4	2.5×10^4	1.4×10^4	4000	400		10		0.1		$\tilde{\nu}$ / cm^{-1}
1.2×10^7	2.4×10^5	1200	600	300	170	48	4.8		0.12		1.2×10^{-3}		E / kJ mol^{-1}
120 000	2400	120	6	3	1.7	0.5	0.05		0.001		0.00001		E / eV
3×10^{19}	6×10^{17}	3×10^{16}	1.5×10^{15}	7.5×10^{14}	4×10^{14}	1.2×10^{14}	1.2×10^{13}		3×10^{11}		3×10^9		ν / Hz

λ: ~**0.05** Å (GED); ~**0.003** Å (UED); **0.5** – **2.5** Å (XRD); **0.5** – **5.0** Å (ND)

Charakteristische Zeit: $\Delta E \times \Delta t \geq \hbar \rightarrow \Delta t \geq \hbar/\Delta E = 1/(2\pi\nu) \rightarrow \Delta t \geq 10^{-20}$ Sek.
Aber wenn λ << Mol. Größe (z.B. in GED), dann $\Delta t \geq 10^{-18}$ Sek.

Diffraktionsmethoden

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

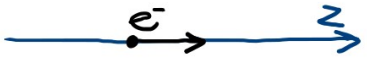
Charakteristische Zeit:

- Langsame Methode
- Mittelschnelle Methode
- Schnelle Methode

Aggregatzustand der Probe:

- Gas
- Flüssigkeit
- Feststoff

El.-Streuung, quantenmechanisch

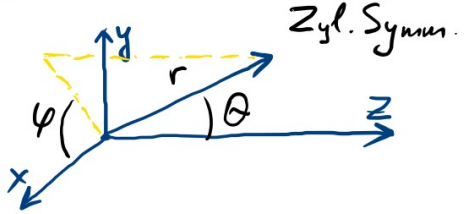


$\hat{H}\Psi = E\Psi$ $\quad -\frac{\hbar^2}{2m}\Delta\Psi = \frac{mv^2}{2}\Psi$

$\Psi(z) = e^{-ikz}$ ← Ebene Welle

$k = \frac{2\pi}{\lambda}$ ← Wellenvektor

Atom: 

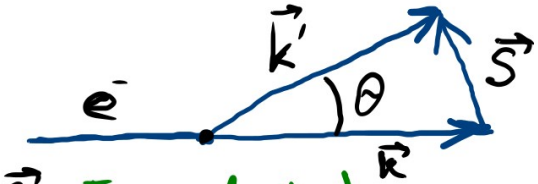


$-\frac{\hbar^2}{2m}\Delta\Psi + V(r)\Psi = E\Psi$

$\Psi = \frac{f(\theta)}{r}\cdot e^{-ikr}$ ← Kugelwelle

$f^B(\theta) \rightarrow f^B(s) = \frac{2}{a_0 \cdot s^2}\left[Z - F(s)\right]$

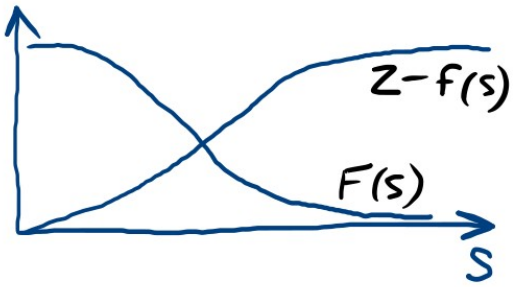
$I = I_0 |\Psi|^2 = I_0 \cdot \frac{|f(s)|^2}{R^2}$ ← Elastische Streuung

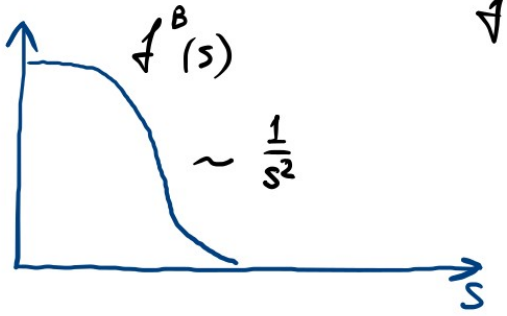


$|s| = \frac{4\pi}{\lambda}\cdot\sin\left(\frac{\theta}{2}\right)$

Streuung, quantenmechanisch

$$F(s) = \int 4\pi\rho(r) r^2 \frac{\sin(sr)}{sr} dr$$ ← Formfaktor

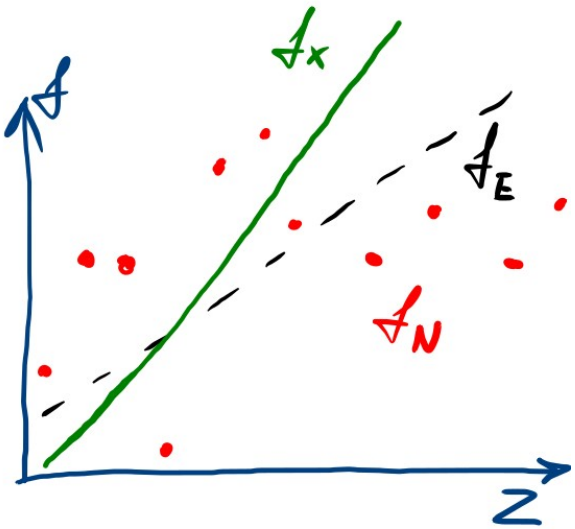




$$f^B(s) = \frac{2}{a_0 \cdot s^2}\left[Z - F(s)\right]$$

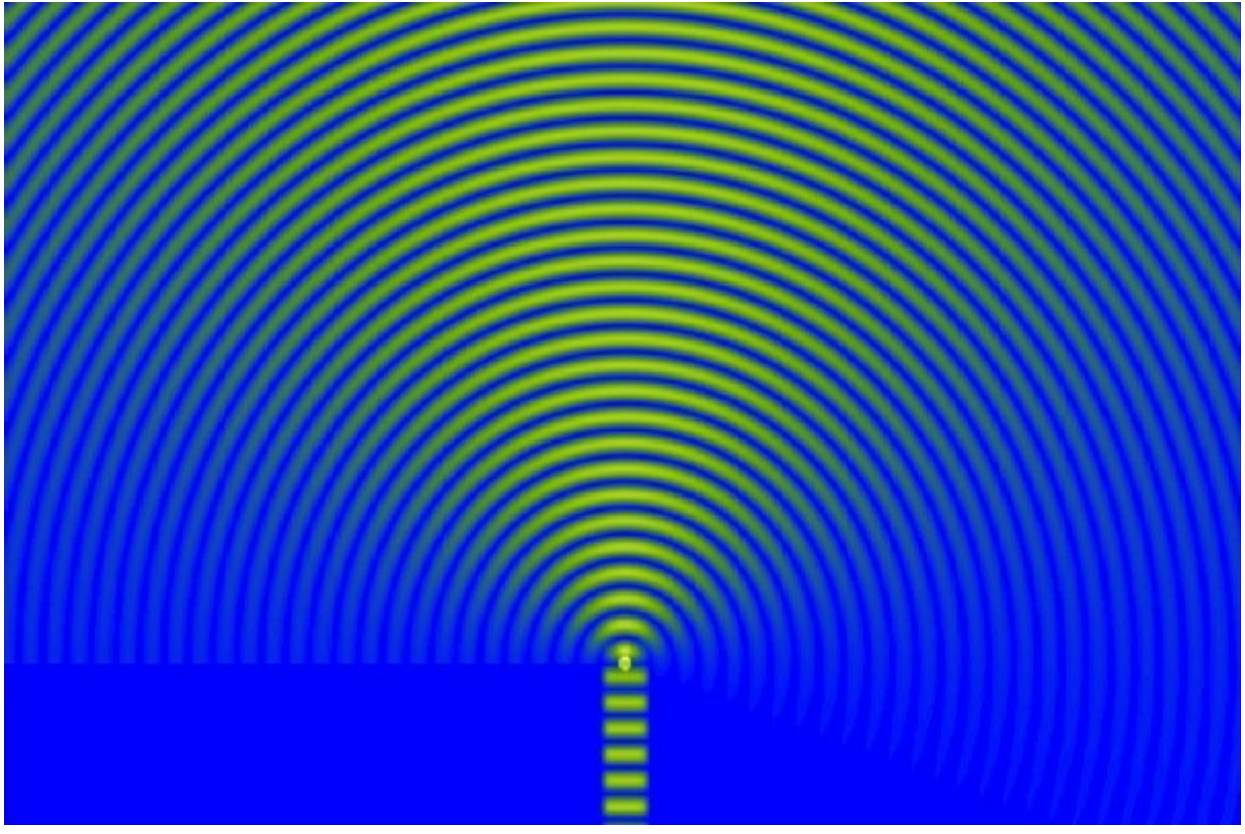
Für Röntgenstrahlung: $f_x(s) = \frac{e^2}{mc} \cdot F(s)$

Für Neutronenstrahlung: $f_N(s)$ aus Experiment



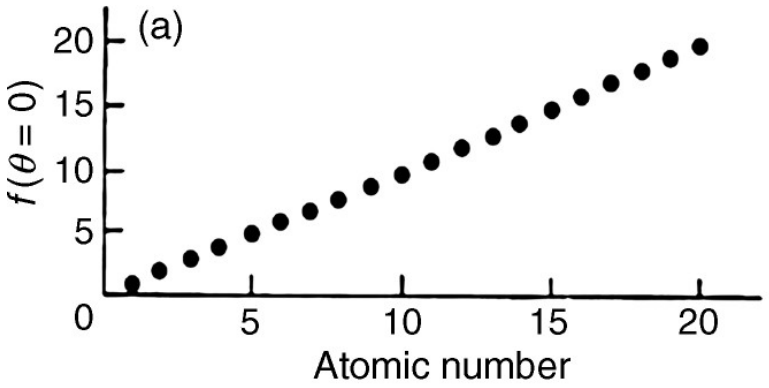
ND ist gut für H Atome!

Elektronenwelle trifft auf ein Atom

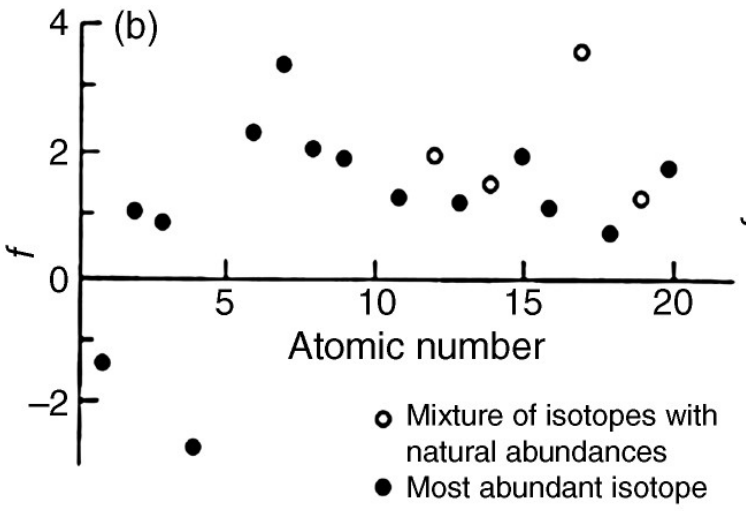


Streuamplituden: GED, XRD, ND

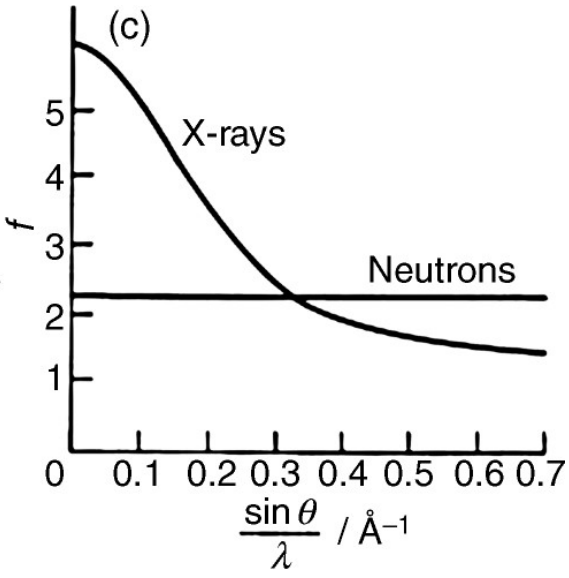
GED, XRD



ND



Winkelabhängigkeit



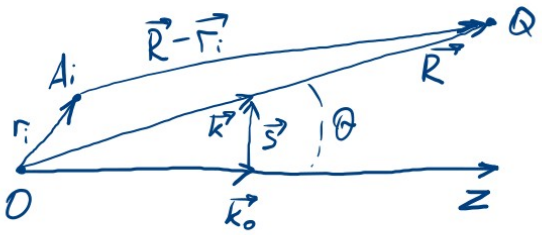
Vergleich XRD – GED – ND

	XRD	GED	ND
Wellenlänge	0.5 – 2.5 Å	~ 0.05 Å	0.5 – 4.0 Å
E_{kin}	10.000 eV	40.000 – 90.000 eV	0.025 eV
Wechselwirkung mit	Elektronen	elektrischen Potentialen	Kernen
$f_X : f_{El} : f_N$	1	10^3	10^{-1}
$I_X : I_{El} : I_N$	1	10^6	10^{-2}

El.-Diffraktion an Molekülen

Atom A_i in Molekül:

$$\Psi_i \simeq f_i(s) \frac{e^{ikR}}{R} \cdot e^{i\vec{r}_i \vec{s}}$$



$$\Psi_{ges} = \sum_i \Psi_i$$

$$I = I_0 |\Psi|^2 \simeq \frac{I_0}{R^2} \sum_i \sum_j f_i(s) \cdot f_j(s) \cdot e^{i\vec{s}\cdot\vec{r}_{ij}}$$

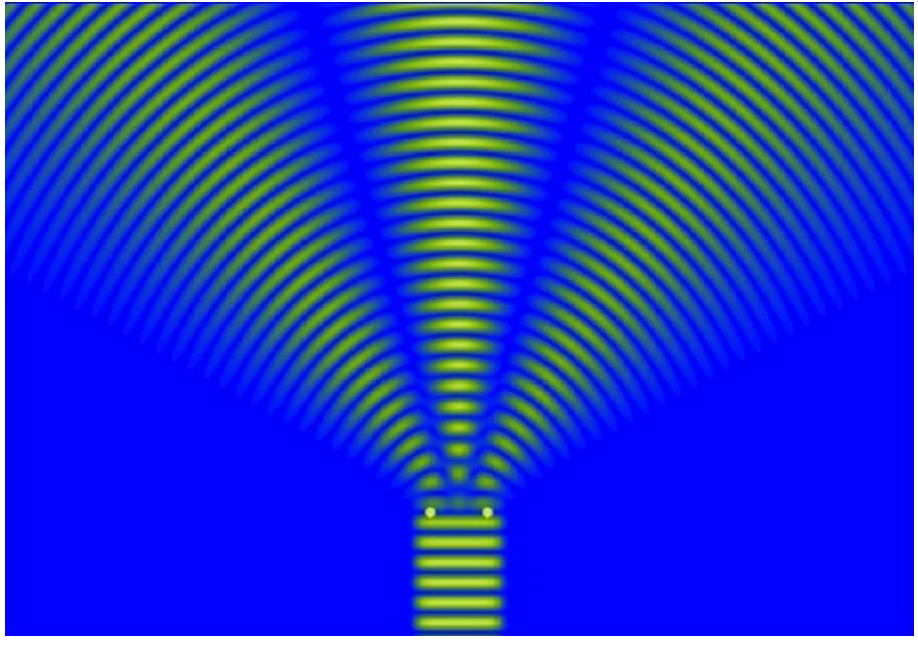
Mittelung: a) Orientierungen $\rightarrow$ $I = \frac{I_0}{R^2} \sum_i \sum_j f_i(s) \cdot f_j(s) \cdot \frac{\sin(s r_{ij})}{s \cdot r_{ij}}$

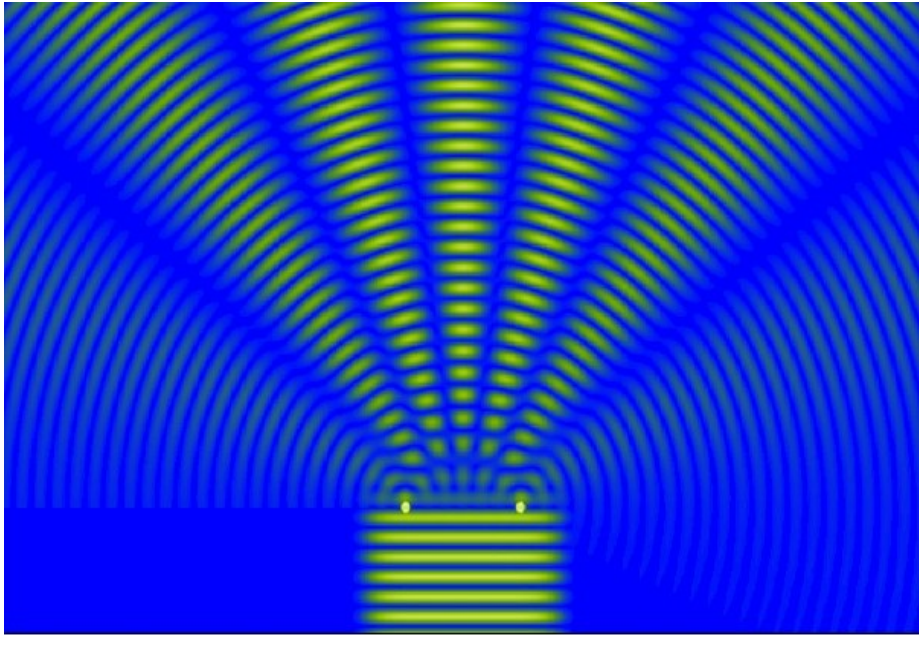
b) Schwingungen $\rightarrow P(r) \sim e^{-\frac{(r-r_e)^2}{2\ell^2}}$

$$\rightarrow I = \frac{I_0}{R^2} \cdot \sum_i \sum_j f_i \cdot f_j \cdot \int_0^\infty P_{ij}(r_{ij}) \frac{\sin(s r_{ij})}{s \cdot r_{ij}} \, dr_{ij} = \frac{I_0}{R^2} \cdot \sum_i \sum_j f_i \cdot f_j \cdot e^{-\frac{\ell^2 s^2}{2}} \cdot \frac{\sin(s r_a)}{s \cdot r_a}$$

Elektronenwelle trifft auf zwei Atome

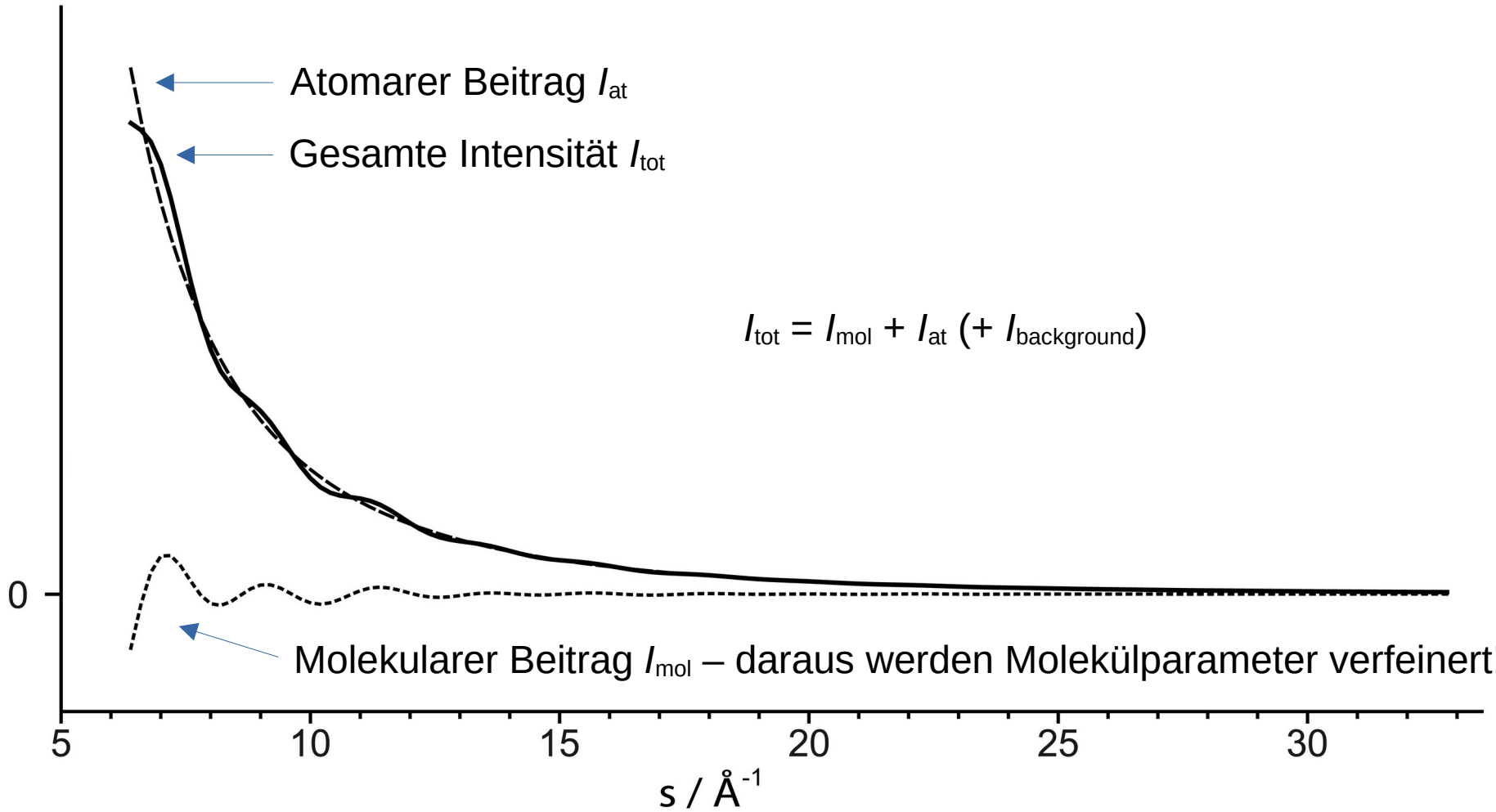
Abstand r $2r$



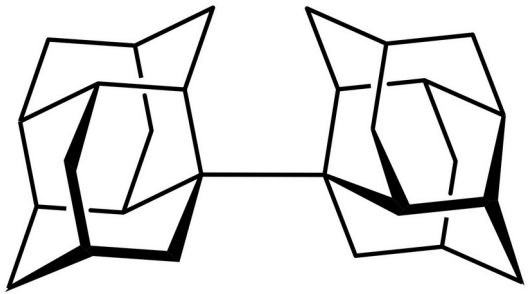


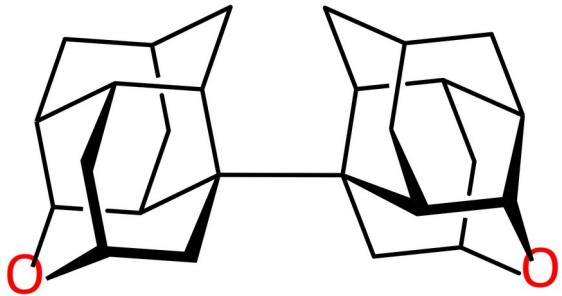
(Ohne Mittlerung über Orientierungen und Schwingungen)

GED: Intensität



Molekül(e) des Tages



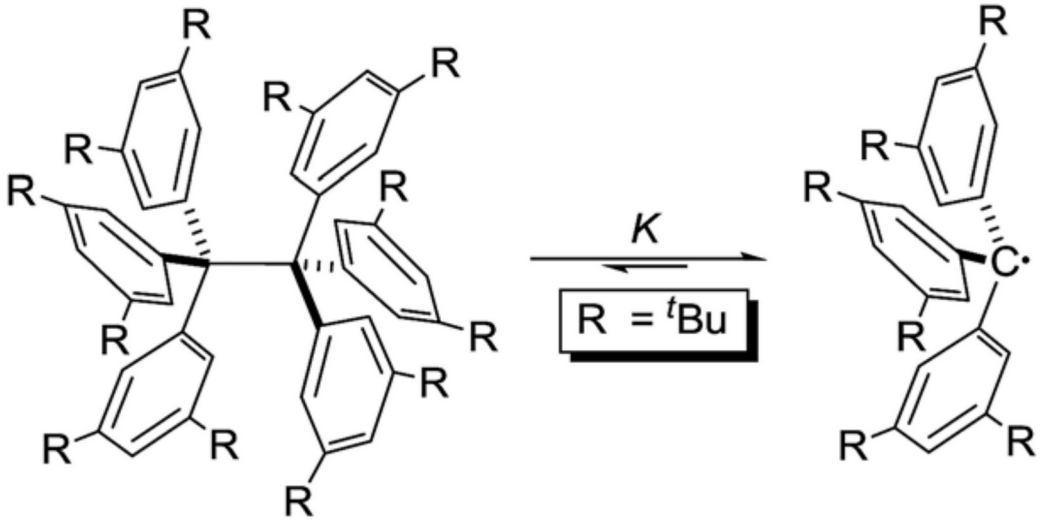


Intramolecular London Dispersion Interaction Effects on Gas-Phase and Solid-State Structures of Diamondoid Dimers

Andrey A. Fokin,[*,∞,‡] Tatyana S. Zhuk,[∞] Sebastian Blomeyer,[§] Cristóbal Pérez,[∥] Lesya V. Chernish,[∞] Alexander E. Pashenko,[∞] Jens Antony,[⊥] Yury V. Vishnevskiy,[§] Raphael J. F. Berger,[#] Stefan Grimme,[⊥] Christian Logemann,[▽] Melanie Schnell,[*,∥] Norbert W. Mitzel,[*,§] and Peter R. Schreiner[*,‡]

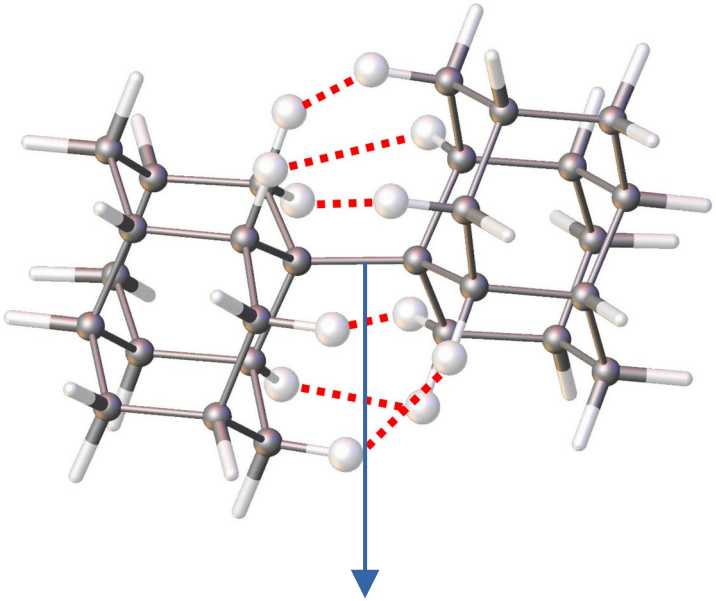
A. A. Fokin et al., *J. Am. Chem. Soc.* 2017, 139, 16696.

Sterische Hinderung

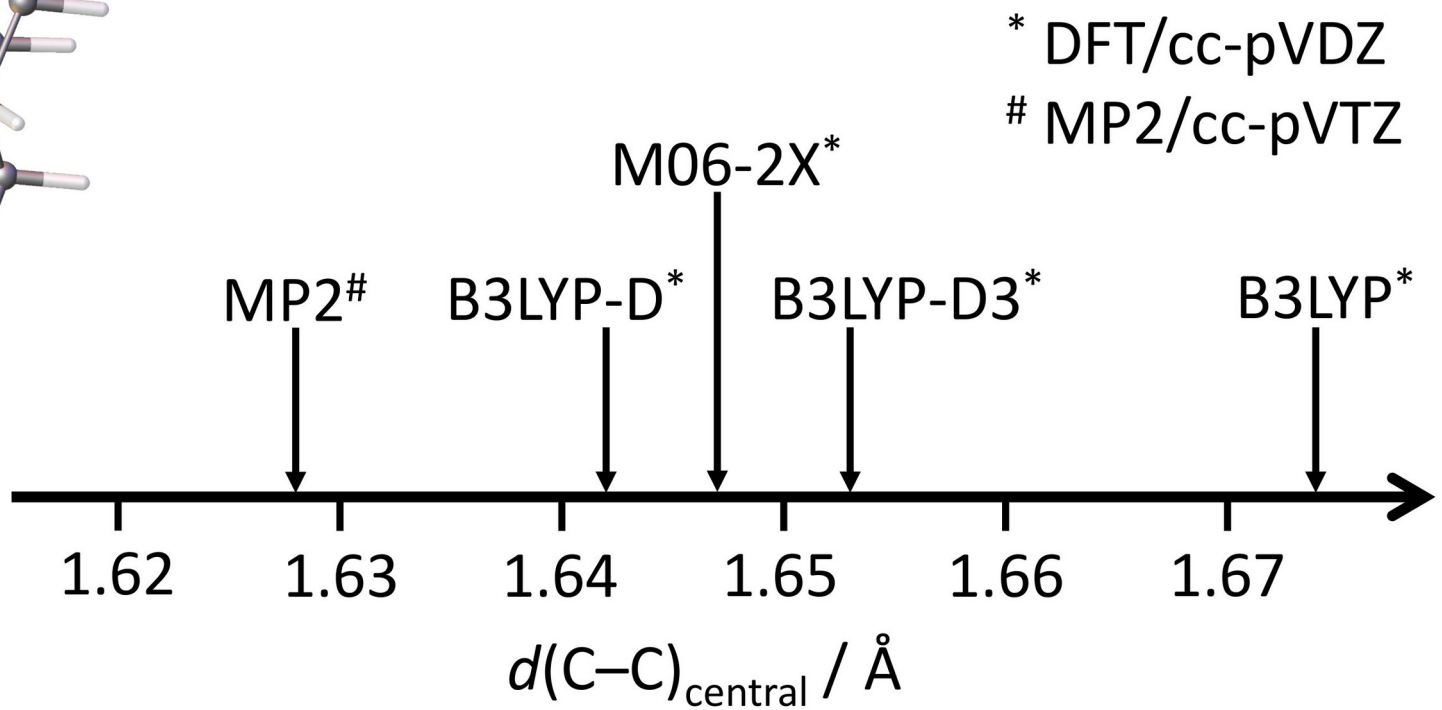


S. Rösel, C. Balestrieri, P. R. Schreiner, *Chem. Sci.*, 2016, 8(1), 405.

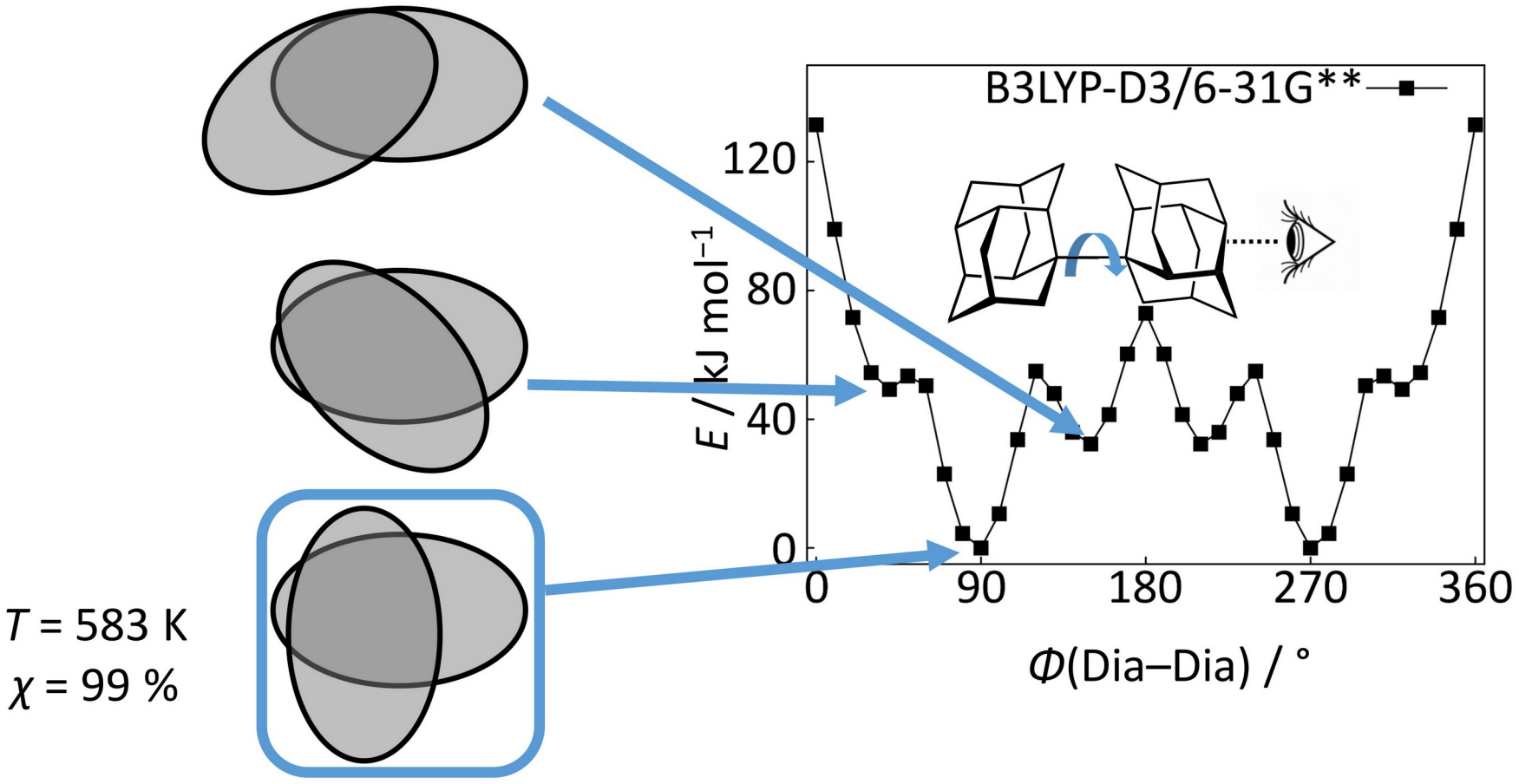
Rechnungen, *r*(C—C)



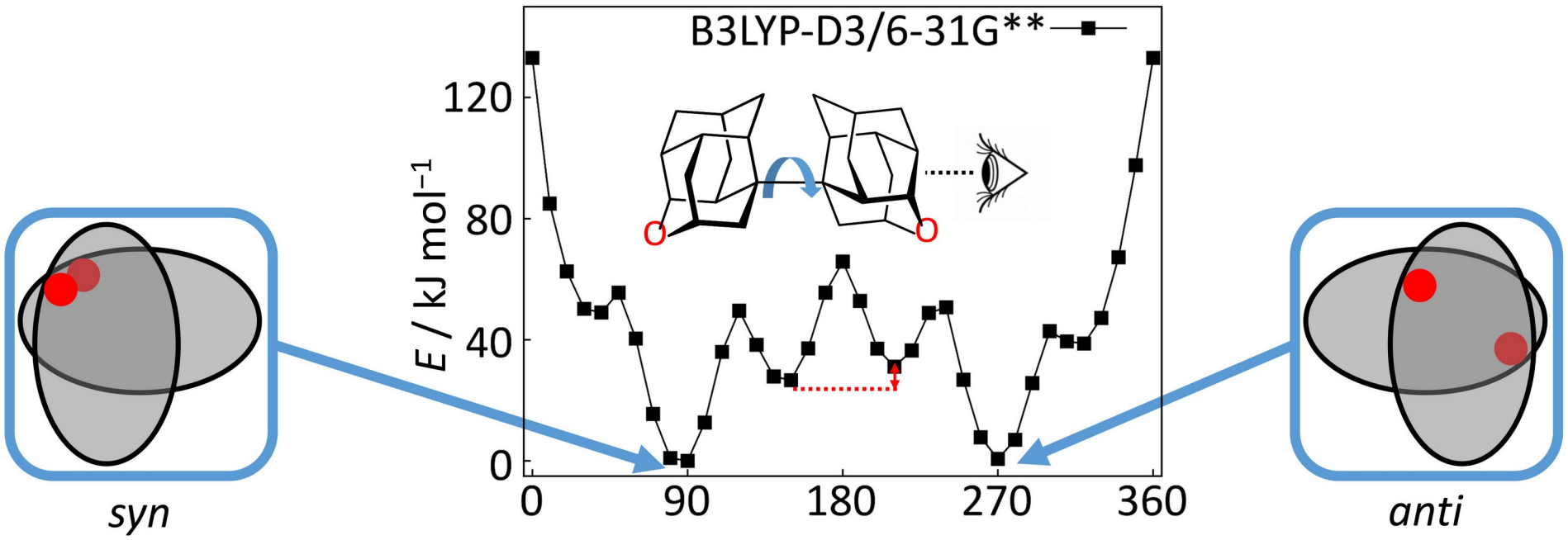
$d(\mathrm{C—C})_{\mathrm{central}}$



Rechnungen, Konformere



Rechnungen, O-Diamondoid-Dimer



$\Delta E_{syn-anti}$ = 1.2 kJ mol^{-1}

→ zwei-Konfomer-Modell

Zusätzliche Parameter:

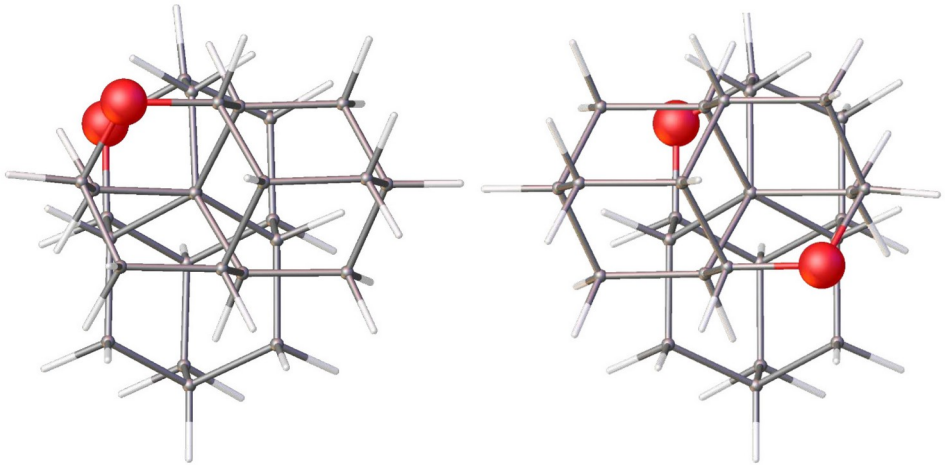
- d(C–O)
- Φ_2(Dia–Dia)
- $\chi_{syn:anti}$

GED/MW Strukturanalyse

syn

$\mu_A = \mu_B = 0$ D

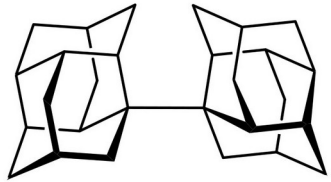
$\mu_C = 2.5$ D*



anti

$\mu_A = \mu_B = 0$ D

$\mu_C = 0.4$ D*



$\mu_A = \mu_B = 0$ D

$\mu_C = 0.05$ D*

*PBEh-3c

Rotationskonstanten:

$A = 396.3518(1)$ MHz

$B = 158.91216(8)$ MHz

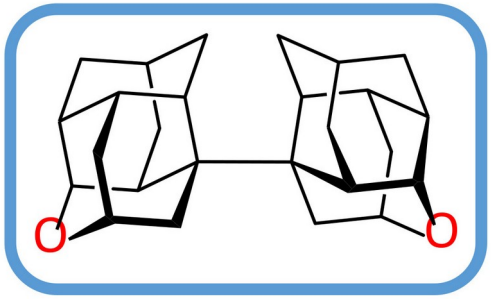
$C = 158.83150(8)$ MHz

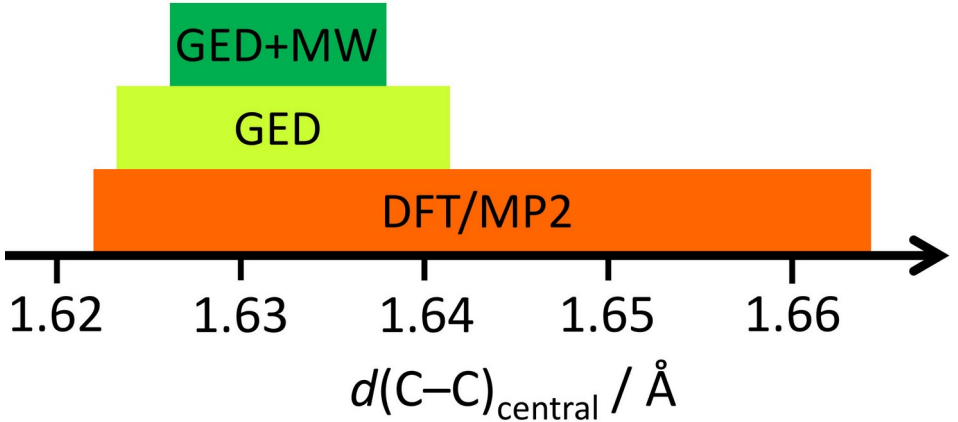
MW → B_0 → B_e ↘

GED → r_a → r_e ↗

GED+MW Verfeinerung

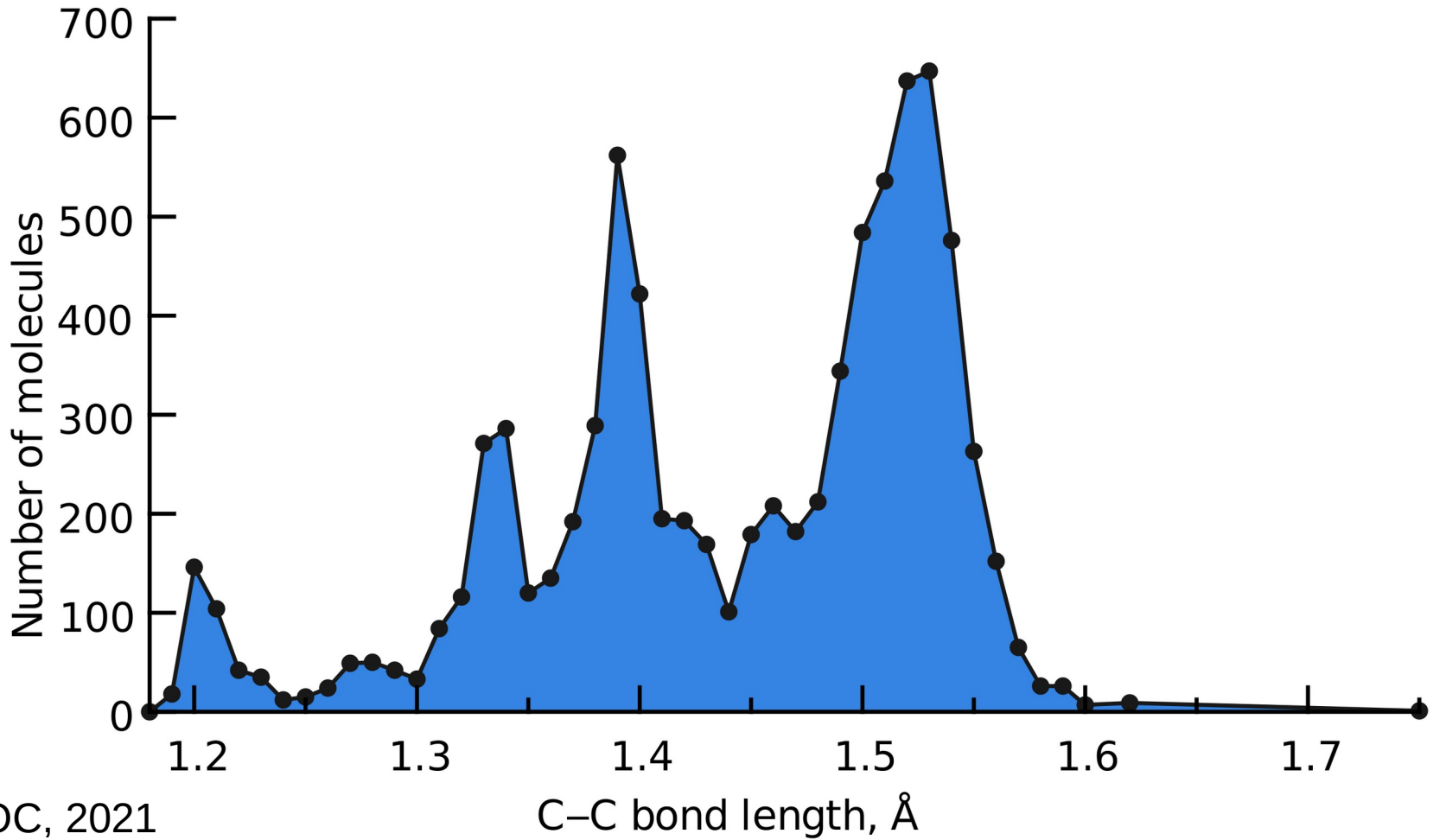
Ergebnisse: r_e(C–C)



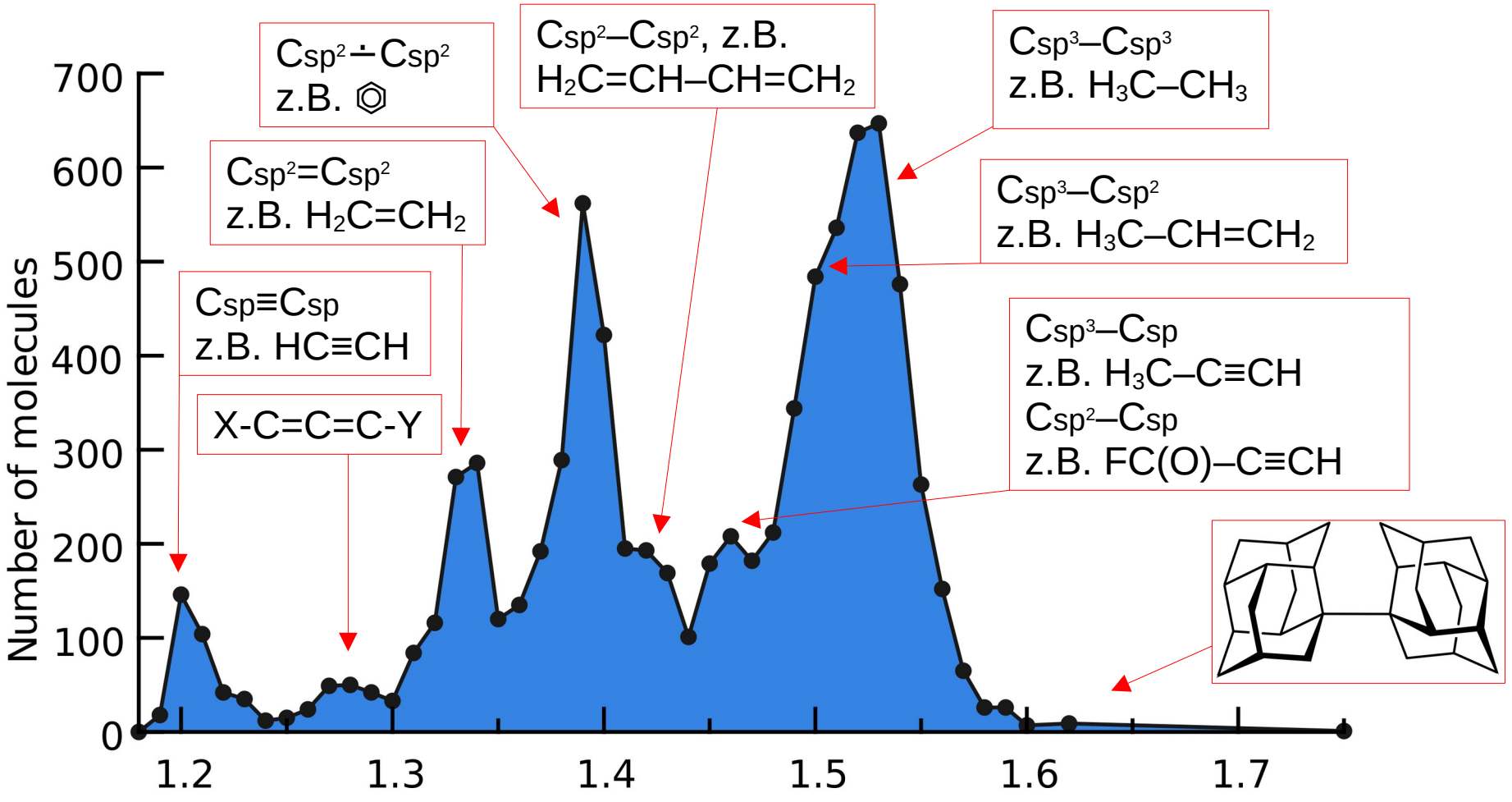


Methode	O-Dimer	Dimer
XRD	1.643(1)	1.647(4)
GED	1.632(9)	**1.630(5)**
GED+MW	**1.632(5)**	-
B3LYP/cc-pVTZ	1.662	1.674
TPSS/cc-pVTZ	1.658	1.668
HF/cc-pVTZ	1.652	1.664
B97-D3/cc-pVTZ	1.651	1.662
B3PW91/cc-pVTZ	1.646	1.657
TPSS-D3/cc-pVTZ	1.642	1.652
B3LYP-D3/cc-pVTZ	1.642	1.653
ωB97XD/cc-pVTZ	1.638	1.648
PBE0/cc-pVTZ	1.637	1.648
M06-2X/cc-pVTZ	1.636	1.647
PBEh-3c	**1.632**	1.642
SCS(1.2;2/3)-MP2/def2-QZVP	1.629	1.640
PBE0-D3/cc-pVTZ	1.628	1.638
B3PW91-D3/cc-pVTZ	1.627	1.636
PW6B95-D3/def2-QZVP	1.626	1.636
ae-MP2/cc-pwCVTZ	1.622	**1.633**

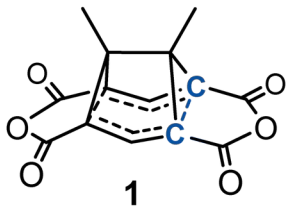
r(C–C): Experimentelle Daten



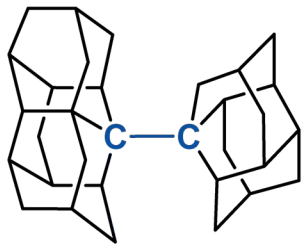
r(C–C): Experimentelle Daten



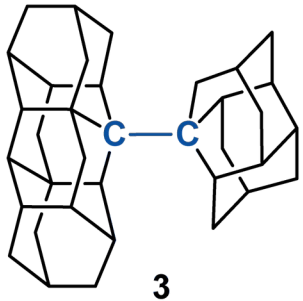
r(C–C): noch länger?



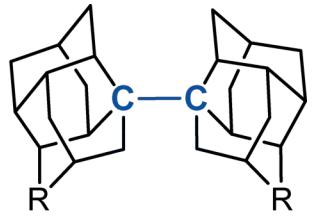
1



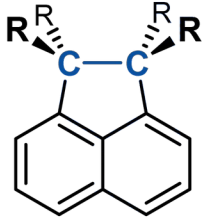
2



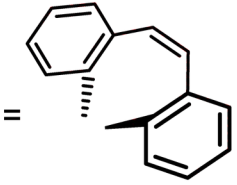
3



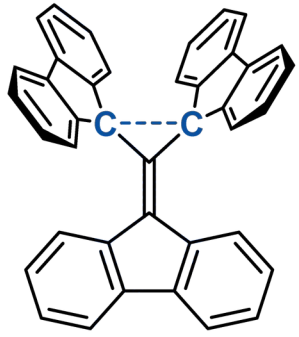
R = CH_2 (**4a**)
R = O (**4b**)



R = H (**5a**)
R = 4-*t*-Bu-C_6H_4 (**5b**)
R = C_6H_5 (**5c**)



R,R = (**5d**)



6

	d(C–C) (s) [Å]	*d*(C–C) (g) [Å]
1	1.670(1)	1.737(44)
2	1.704(4)	n.a.
3	1.71	n.a.
4a	1.647(4)	1.630(5)
4b	1.642(2)	1.632(5)
5a	1.5640(4)	1.560(4)
5b	1.708(4)	n.a.
5c	1.701(3)	n.a.
5d	1.746(3)	n.a.
6	2.0415(5)	n.a.

6: T. Kubo et al., *J. Am. Chem. Soc.* 2021, 143, 14360–14366

Die längste C–C Bindung in der Gasphase

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CHEMISTRY A European Journal Full Paper

Carboranes

Icosahedral Carbaboranes with Peripheral Hydrogen–Chalcogenide Groups: Structures from Gas Electron Diffraction and Chemical Shielding in Solution

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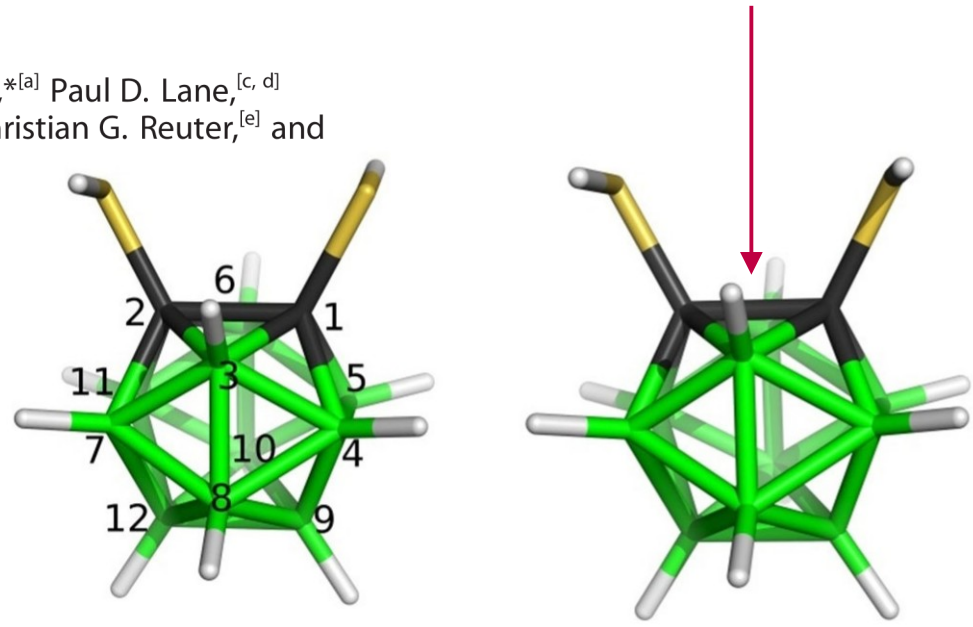
r_e = 1.750(28) Å



1,2-$(EH)_2$-*closo*-1,2-$C_2B_{10}H_{10}$

E = S, Se

Quellen/Literatur

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