

Gas-Phase Electron Diffraction (GED)

Heinz Oberhammer

Universität Tübingen, Germany

History:

Schrödinger 1925-26.: wave equation

Davisson and Germer 1927: electrons possess wave
property

Mark and Wierl (BASF) 1930: GED, CCl_4 , C_6H_6 etc.

Brockway, Pauling, Debye, Hedberg, Schomaker,

Bartell, Bauer, Karle in USA

Sutton in Great Britain

Hassel, Finbak in Norway

Morino, Kuchitsu in Japan

Spiridonov, Naumov, Vilkov in Russia

Content

Introduction

Scattering theory

Atoms

Rigid molecules

Vibrating molecules

Fourier transformation

Experiment

Examples

Combination of GED and quantum chemical calculations

Literature for gas electron diffraction:

Stereochemical Applications of Gas-Phase Electron Diffraction

Edited by I. Hargittai and M. Hargittai,
VCH Publishers 1988

Part A: The electron diffraction Technique.

Part B: Structural information for selected classes of compounds.

M. I. Davies: Electron Diffraction in Gases
Marcel Dekker, N. Y. 1971

S. H. Bauer: Diffraction of Electrons by Gases
Physical Chemistry, an Advanced Treatise,
Vol. IV, Academic Press 1970
Academic Press

Roald Hoffmann:

„There is no more basic enterprise in chemistry than the determination of a geometrical structure of a molecule.”

Jerome Karle:

“Structural research not only has inherent scientific interest, it also stimulates and provides the conceptual basis on which many related fields of science can progress.”

Why gas-phase structures ?

Some compounds exist only in the gas-phase

e.g. SF_2 , PCl_5 , Me_4PF or radicals

Some compounds do not form single crystals

Gas-phase structures are not affected by intermolecular interactions or packing effects.

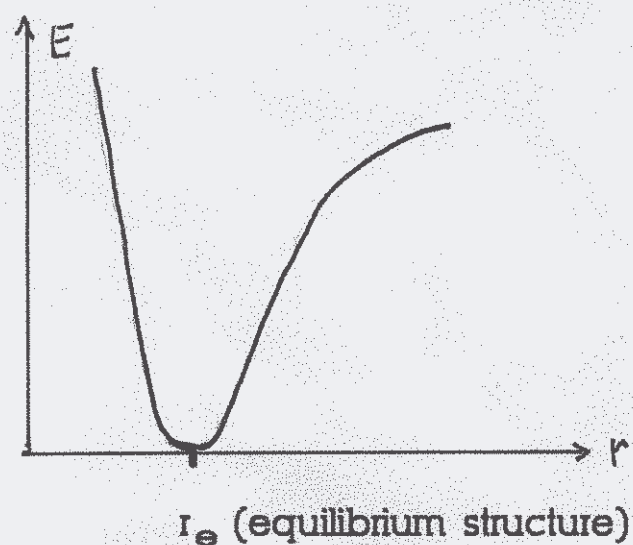
Vibrational effects for free molecules are in general small and can be taken into account.

Conformational studies are possible and meaningful only in the gas or liquid phase.

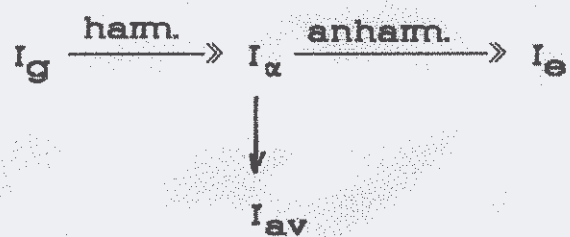
Gas-phase structures can be compared with results from theoretical methods and can be used for parameterizing empirical or semiempirical methods.

Methods

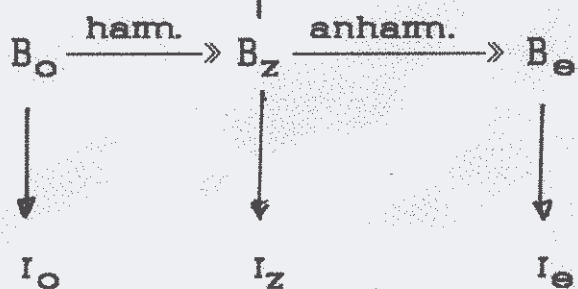
- 1) Theoretical Calculations
ab initio, semiempirical
Molecular mechanics



- 2) Electron diffraction



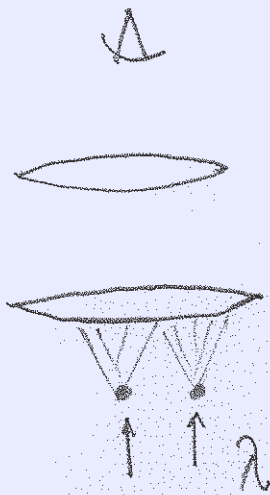
- 3) Rotational Spectroscopy
Microwave
High resolution infrared



Diffraction Methods

Molecules: interatomic distances $\approx 1 \text{ \AA} = 0.1 \text{ nm} = 100 \text{ pm}$

Microscope



$$\text{Resolution } d_{\min} = \lambda / 2A$$

A = numerical apperture (~ 1 for optical lenses)

Visible light $\lambda \sim 600 \text{ nm}$

X-rays $\lambda \sim 0.1 \text{ nm}$ but $A = 0$

Electrons $\lambda \sim 5 \text{ pm}$ (0.05 \AA)

$$\lambda = h/(2meU)^{1/2} = 12.3/U^{1/2} \quad U \text{ in Volt, } \lambda \text{ in \AA}$$

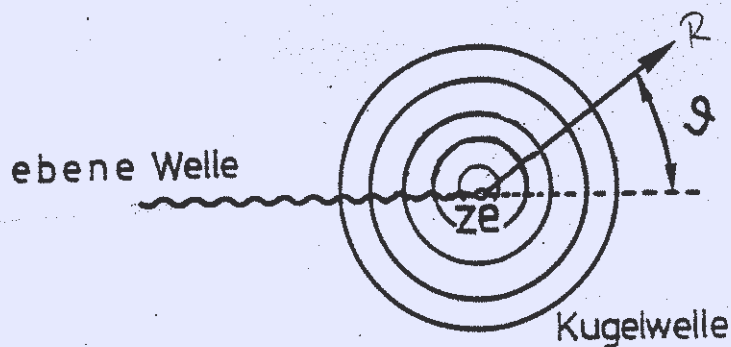
$$\text{for } U = 60 \text{ kV} \quad \lambda = 0.05 \text{ \AA}$$

Electron microscope: A very small (lens defects)

$$d_{\min} \sim 1 \text{ nm} (10 \text{ \AA})$$

Solution: Diffraction with high resolution +
Fourier transformation

Scattering at atom



plane wave $\psi = e^{ikz}$

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

spherical wave $\psi = f(s) \frac{e^{ikR}}{R}$ $s = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$

Schrödinger: $\hat{H}\psi = E\psi$ $\hat{H} = \hat{T} + \hat{V} = \frac{\hbar^2}{2m} \Delta + V(r)$

$$E = \frac{mv^2}{2} = \frac{p^2}{2m} = \frac{\hbar^2 \cdot k^2}{2m}$$

$$\Delta\psi + \left(\frac{2m}{\hbar^2} V(r) - k^2 \right) \psi = 0$$

$$V(r) = \frac{ze}{r} \quad (\text{nucleus})$$

$$E_{\text{pot}} > E_{\text{kin}} \quad \text{bound}$$

$$E_{\text{pot}} < E_{\text{kin}} \quad \text{diffraction}$$

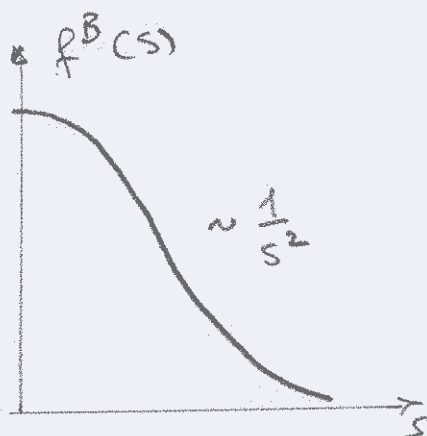
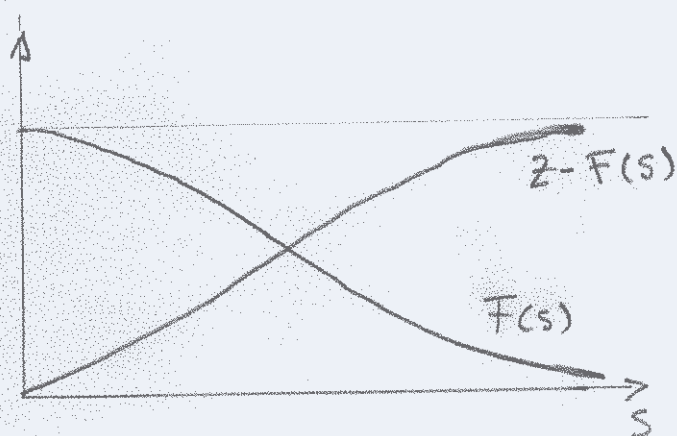
$$f(s) = \frac{2me^2}{\hbar^2} \cdot \frac{Z}{s^2}$$

Atom: $V(r) = V_{\text{nucel}} + V_{\text{cloud}}$
 \downarrow
 depends on $\rho_{\text{ee}}(r)$

1st Born approximation

$$f^B(s) = \frac{2me^2}{\hbar^2} \cdot \frac{Z - F(s)}{s^2}$$

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



Higher approximation: partial wave method

$$f(s) = |f(s)| e^{i\eta} \quad \eta(z,s) \text{ scattering phase}$$

problem with UF_6

Comparison

X-ray

electrons

neutrons

λ 50 – 250 pm

50 – 400 pm

E_{kin} 10.000 eV

50.000 eV

0.025 eV

Scattering on

electrons, $\rho_{\text{el}}(\mathbf{r})$

$V_{\text{nuc}} + \rho_{\text{el}}(\mathbf{r})$

nucleus + magn.

Scattering ampl.

$$f_X = \frac{e^2}{mc^2} \cdot \bar{F}(s)$$

$$f_{\text{ee}} = \frac{2me^2}{\hbar^2} \cdot \frac{Z - F(s)}{s^2}$$

f_N (experiment)

$$\bar{F}(s) = \int 4\pi r^2 \rho_{\text{ee}}(r) \frac{\sin sr}{sr} \cdot dr$$

$f_X : f_{\text{el}} : f_N$

1

:

10^3

:

10^{-1}

$I_X : I_{\text{el}} : I_N$

1

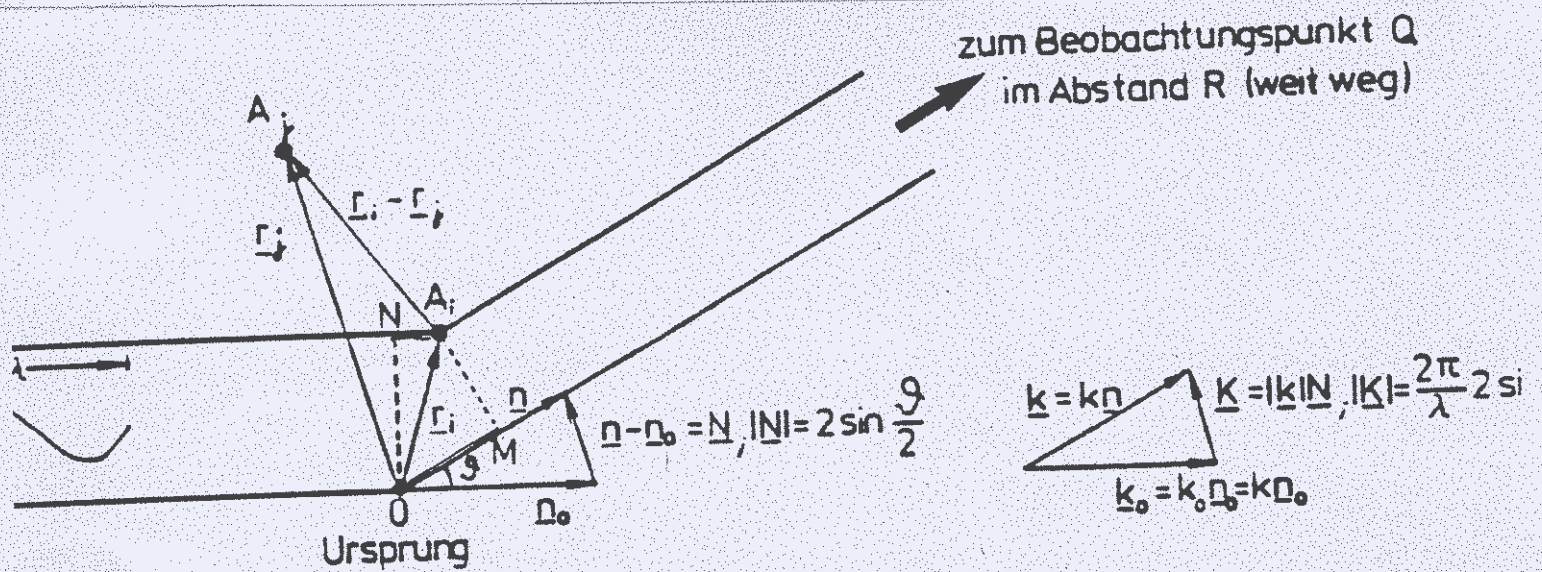
:

10^6

:

10^{-2}

Scattering at rigid molecule



spherical wave from origin: $\psi_0 = C \frac{e^{ikR}}{R}$

spherical wave from atom A_i : $\psi_i = f_i(s) \frac{e^{ik(R+d_i)}}{R}$

path difference $d_i = \underline{r}_i \cdot \underline{N}$

total wave: $\psi = \sum \psi_i = \frac{e^{ikR}}{R} \cdot \sum_i f_i(s) e^{ik \underline{r}_i \cdot \underline{N}}$

intensity $I_{tot}(s) = |\psi|^2 = \psi \psi^*$

$$\bar{I}_{tot}(s) = \frac{1}{R^2} \sum_i \sum_j f_i \cdot f_j e^{-ik \underline{N} \cdot \underline{r}_{ij}} ; \quad \underline{r}_{ij} = \underline{r}_i - \underline{r}_j$$

Single crystal

$$I_{\text{tot}} = \left(\underbrace{\sum_{\text{unit cell}} f_i e^{ik \cdot \underline{r}_i}}_{F_{hke} \text{ structure factor}} \right)^2 \cdot \text{lattice factor}$$

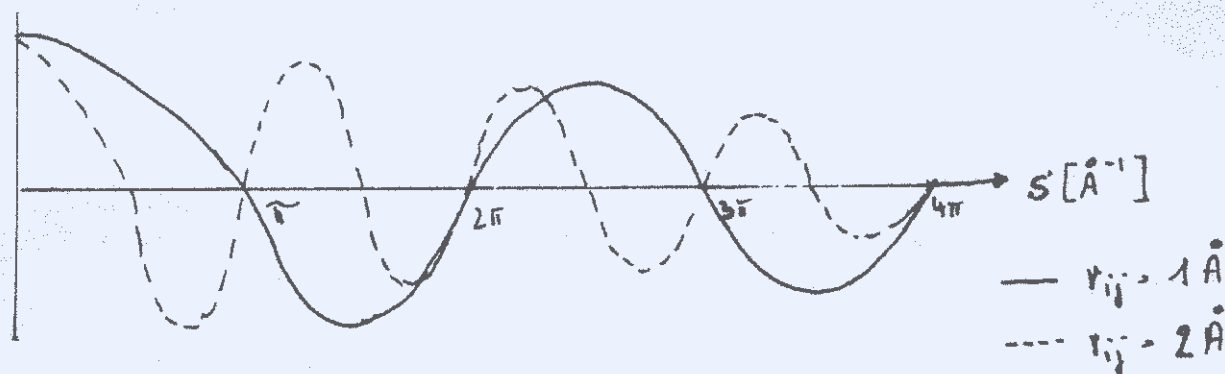
powder: \rightarrow Debye - Scherrer

$$\text{gas: } I_{\text{tot}}(s) \rightarrow \frac{1}{4\pi} \int I_{\text{tot}}(s) d\Omega$$

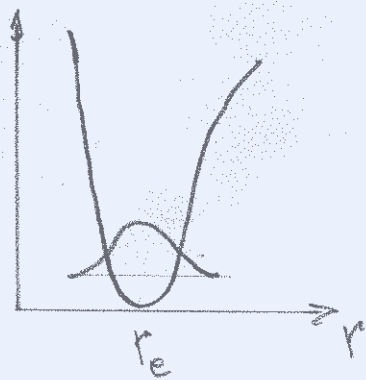
$$I_{\text{tot}}(s) = \frac{1}{R^2} \sum_i \sum_j' f_i f_j \frac{\sin s r_{ij}}{s r_{ij}}$$

$$\bar{I}_{\text{tot}}(s) = \frac{1}{R^2} \left[\underbrace{\sum_i f_i^2}_{I_a \text{ atomic}} + \underbrace{\sum_{i \neq j} \sum_j' f_i f_j \frac{\sin s r_{ij}}{s r_{ij}}}_{I_m \text{ molecular}} \right]$$

$$\frac{\sin s r_{ij}}{s r_{ij}}$$



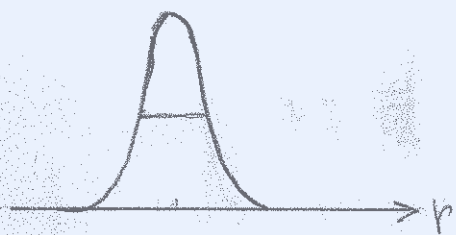
Vibrating molecule



$\phi(r)$ wave function for harmonic oscillator

$P(r) = |\phi(r)|^2$ distribution function

$$P(r) \sim e^{-\frac{(r-r_e)^2}{2L^2}} \quad \text{Gauss}$$



L : vibrational amplitude

examples:

- $C-H \sim 0.080 \text{ \AA}$
- $C-C \sim 0.050 \text{ \AA}$
- $C=O \sim 0.035 \text{ \AA}$
- $\begin{array}{c} H \\ \diagup \\ C \\ \diagdown \\ H \end{array} \sim 0.130 \text{ \AA}$
- $\begin{array}{c} F \\ \diagup \\ C \\ \diagdown \\ F \end{array} \sim 0.060 \text{ \AA}$

rigid molecule: $I_{mol} \sim \frac{\sum m_i r_{ij}^2}{\sum r_{ij}^2}$

vibrating molecule: $I_{mol} \sim \int P_{ij}(r) \cdot \frac{\sum m_i r^2}{\sum r^2} dr$

$$\int P_{ij}(r) \frac{\sin sr}{sr} dr = \frac{\sin sr_{ij}^a}{sr_{ij}^a} \cdot e^{-\frac{l_{ij}^2 s^2}{2}}$$

$$r_{ij}^a = r_{ij}^e + \frac{l_{ij}^2}{r_{ij}^e}$$

mean value for harmonic oscillator

$$I_{tot}(s) = I_a(s) + \sum_i \sum_j f_i f_j \underbrace{\frac{\sin sr_{ij}^a}{sr_{ij}^a} e^{-\frac{l_{ij}^2 s^2}{2}}}_{\int P_{ij}(r) \frac{\sin sr}{sr} dr}$$

Fourier transformation

$$g(x) = \int_{-\infty}^{+\infty} f(y) e^{ixy} dy$$

x, y reciprocal dimensions

NMR : $x = \nu (s^{-1})$, $y = t (s)$

FTIR : $x = \bar{\nu} (cm^{-1})$, $y = \text{distance (cm)}$

Diffraction: $x = s (\text{\AA}^{-1})$, $y = r (\text{\AA})$

Reciprocity of FT.

$$f(y) = \int g(x) e^{ixy} dx ; \quad e^{ixy} = \cos xy + i \sin xy$$

F.T. for GED

modified molecular intensity

$$S.M(s) = \frac{I_{mol}}{I_a} = S \frac{I_{tot} - I_a}{I_a}$$

$$S.M(s) = \sum_{i \neq j} \sum \frac{f_i f_j}{I_a} \int \frac{P_{ij}(r)}{r} \sin sr \, dr$$

2-atomic molecule A-B

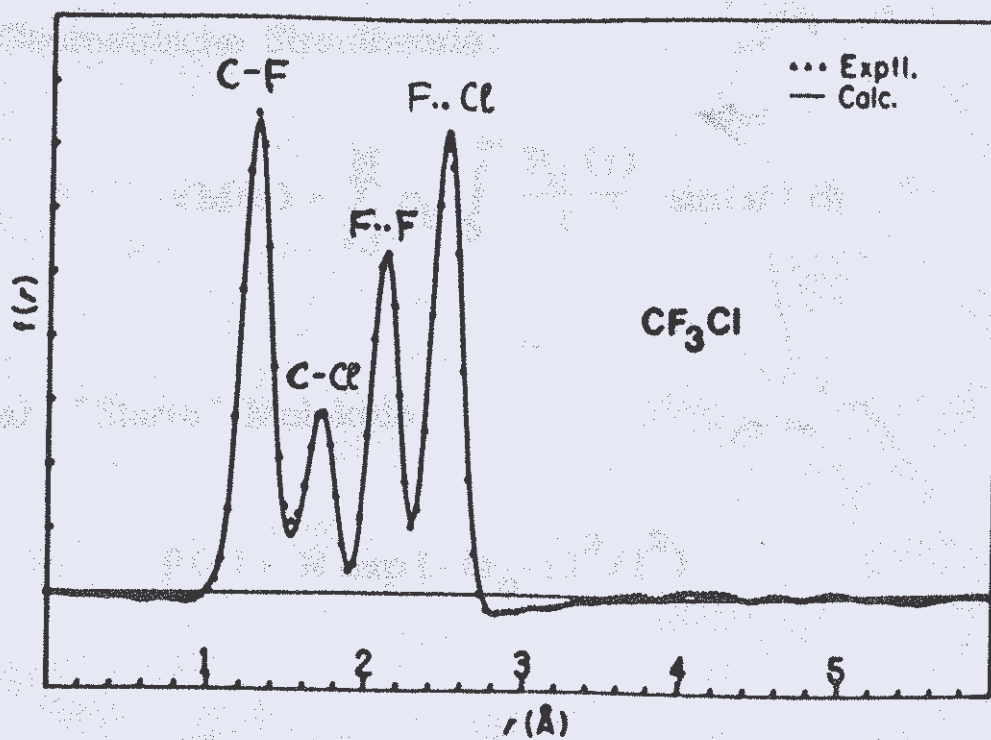
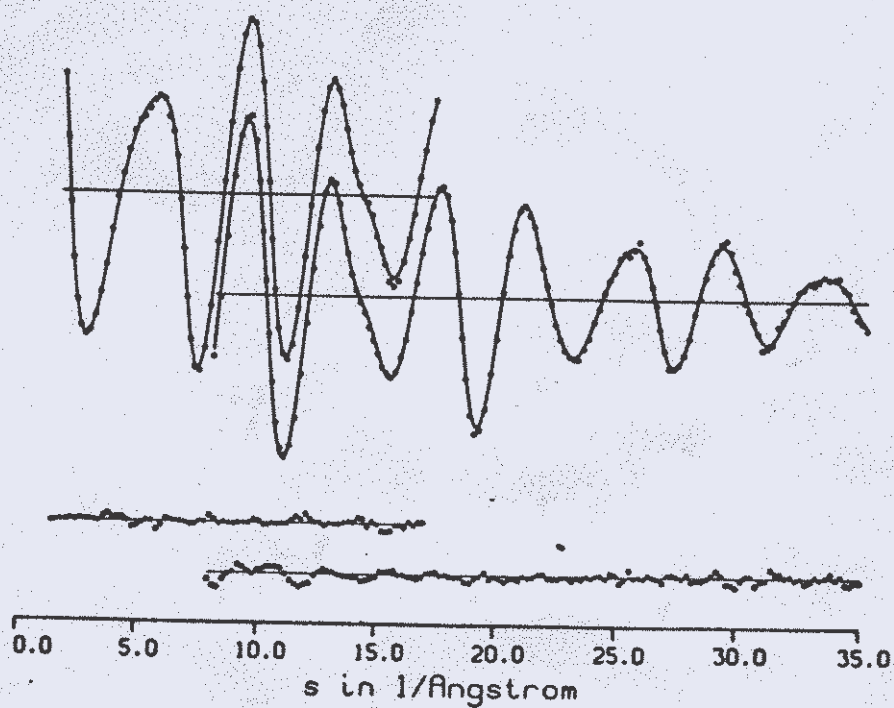
$$S.M(s) = \underbrace{\frac{f_A \cdot f_B}{f_A^2 + f_B^2}}_{C_{AB}(s)} \int \frac{P_{AB}(r)}{r} \sin sr \, dr$$

$$\frac{S.M(s)}{C_{AB}(s)} = \int \frac{P_{AB}(r)}{r} \sin sr \, dr$$

$$\frac{P_{AB}(r)}{r} = \int \frac{S.M(s)}{C_{AB}(s)} \cdot \sin sr \, ds$$

polyatomic molecule

$$f(r) = \int S.M(s) \cdot \sin sr \, ds \approx \sum_{i \neq j} \sum \frac{P_{ij}(r)}{r}$$



Anharmonic vibrations

harmonic: $r_a = r_e + l^2/r_e$ $r_a - r_e \sim 0.001 - 0.002 \text{ \AA}$

anharmonic: $r_a = r_g + l^2/r_g$ $r_a - r_g \sim 0.001 - 0.002 \text{ \AA}$

$$r_g = r_e + 3/2a_3 l^2 \quad r_g - r_e \sim 0.003 - 0.006 \text{ \AA}$$

a_3 cubic anharmonicity for diatomic molecules $1 - 2 \text{ \AA}^{-1}$

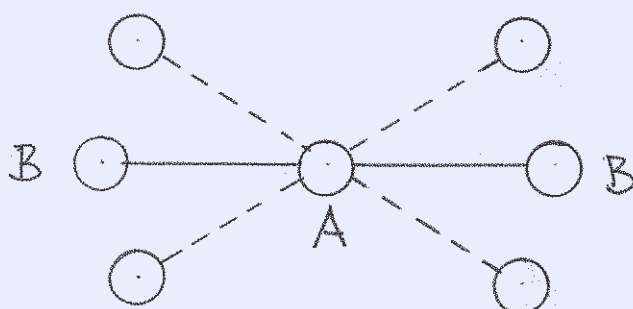
rule of thumb:

r_a bond distances are about $0.004 - 0.007 \text{ \AA}$ longer than r_e values.

r_a and r_g are mean interatomic distances

Shrinkage Effect

Effect of vibrations on nonbonded distances



$$r_a(B \cdots B) < 2r_a(A-B)$$

linear molecules appear to be slightly bent

(example: Br-Hg-Br at high temperature $\angle(\text{BrHgBr}) \sim 160^\circ$)

Planar molecules appear to be slightly nonplanar.

Contributions of molecular vibrations for nonbonded distances

from force field $\rightarrow r_\alpha$ structure

r_α distance between mean atomic positions

$$r_\alpha(B \cdots B) = 2r_\alpha(A-B)$$

crystal structures (neutron and X-ray diffraction) are r_α

structures (molecular vibrations + lattice vibrations)

Mixture of compounds or conformers

$$I_{\text{tot}}(s) = a I_{\text{tot}}^{(1)}(s) + (1-a) I_{\text{tot}}^{(2)}(s)$$

a = contribution of compound or conformer) (1)

Large amplitude vibration

e.g. rotation around single bond, ring puckering

$$I_{\text{mol}}(s) = \int I_{\text{mol}}(q,s) P(q) dq \approx \sum I_{\text{mol}}(q_i,s) P(q_i)$$

q large amplitude coordinate

structure with q_i ... pseudoconformer

$$P(q) = \exp(-V(q)/RT)$$

$V(q)$... potential function for large amplitude coordinate

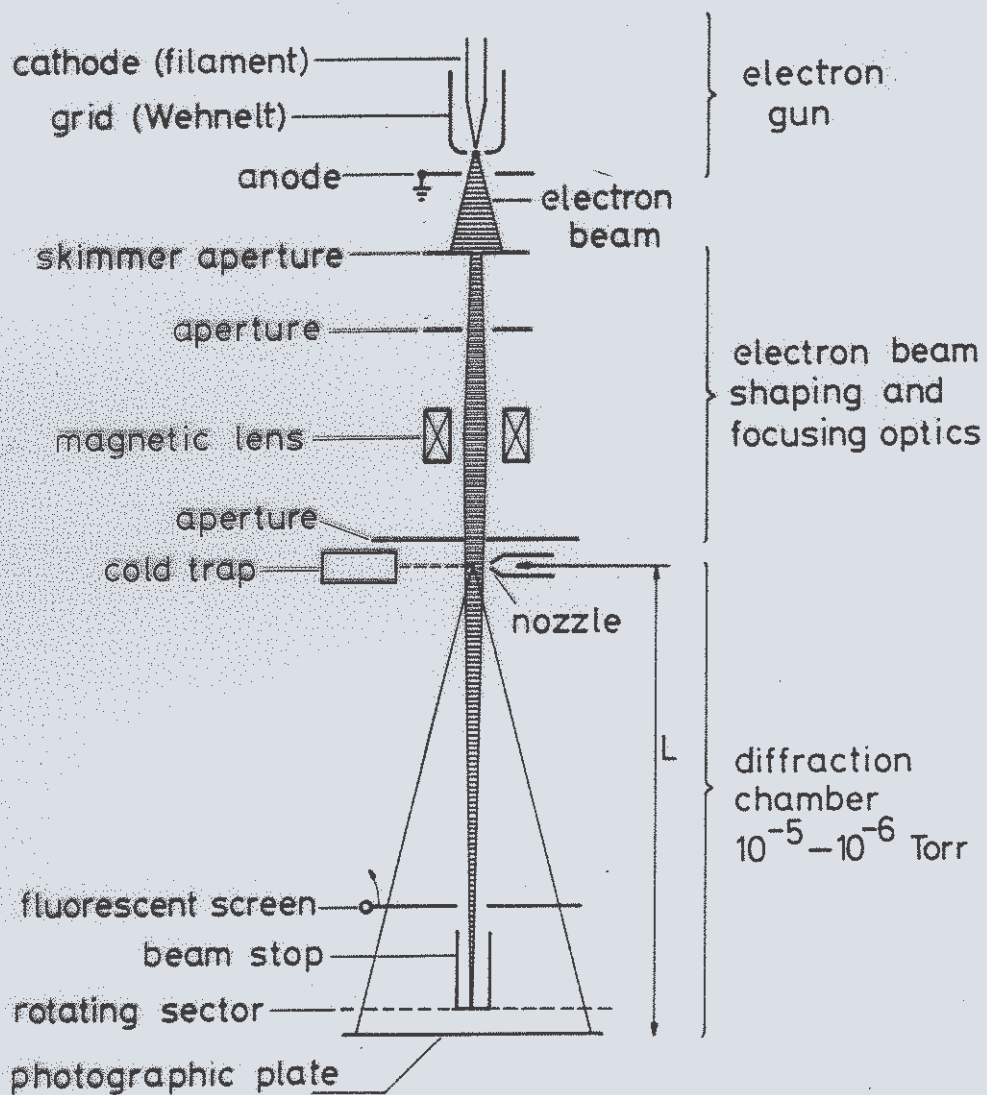
Ultrafast Electron diffraction

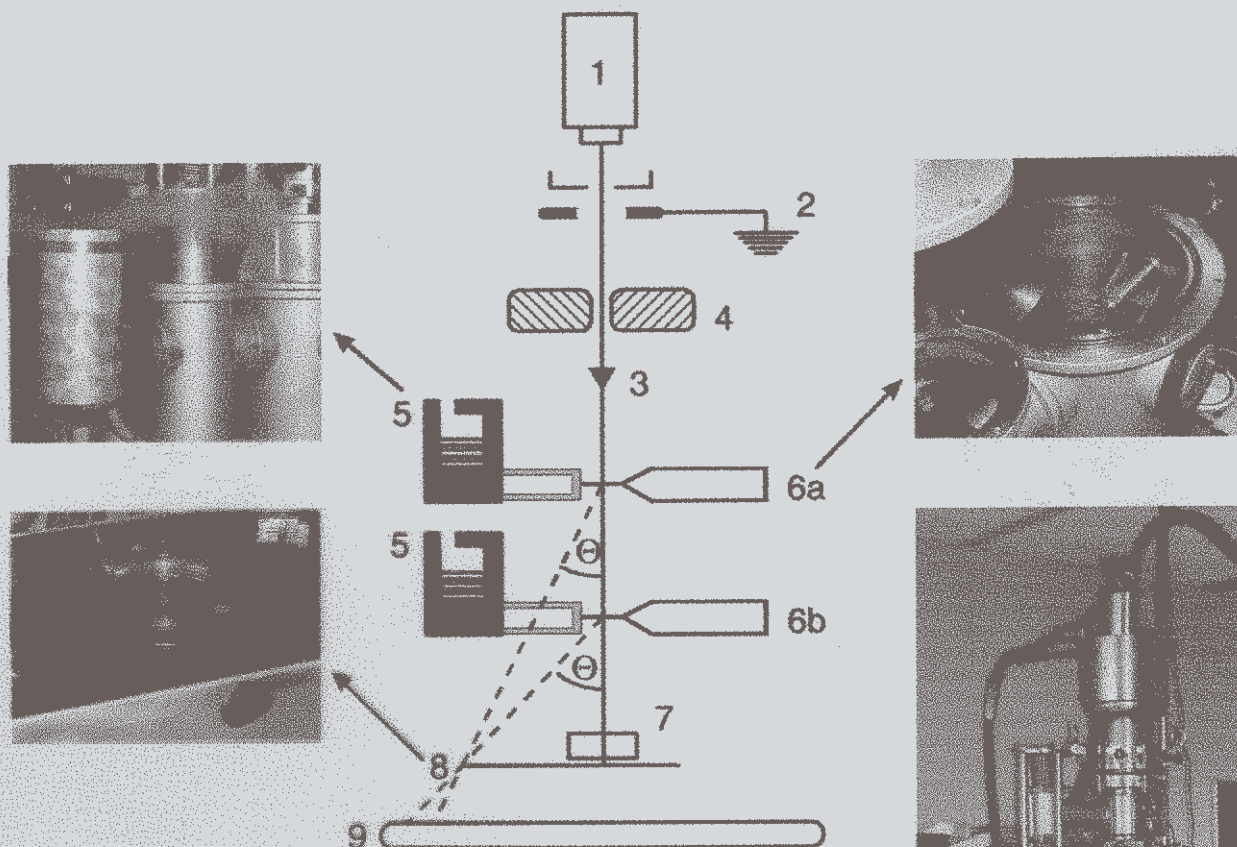
Interaction between electron and molecule $\sim 10^{-18}$ sec

Technical difficulties of fast recording of data

Goal: femtosecond time resolution

Electron Diffraction Apparatus



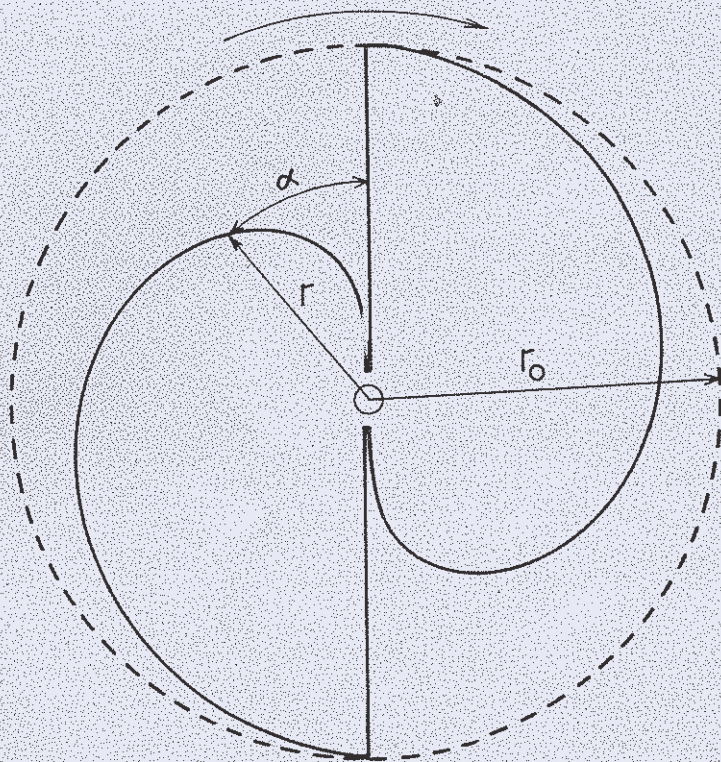


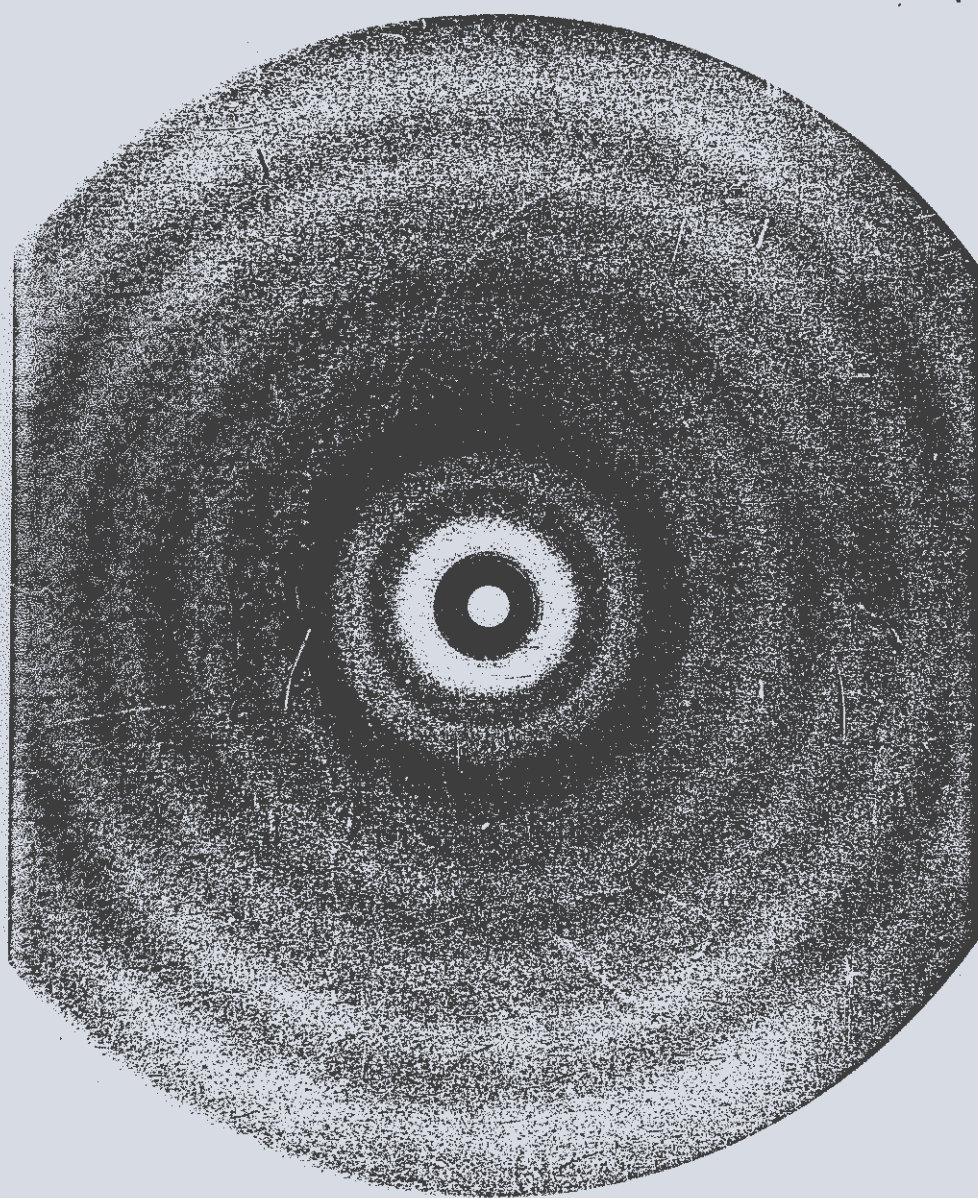
- 1 Kathode
- 2 Anode
- 3 Elektronenstrahl
- 4 Magnetlinsensystem
- 5 Kühlfalle
- 6a Gaseinlaßdüse (großer Kameraabstand)
- 6b Gaseinlaßdüse (kleiner Kameraabstand)
- 7 Beamstop
- 8 Rotierender Sektor
- 9 Photoplatte

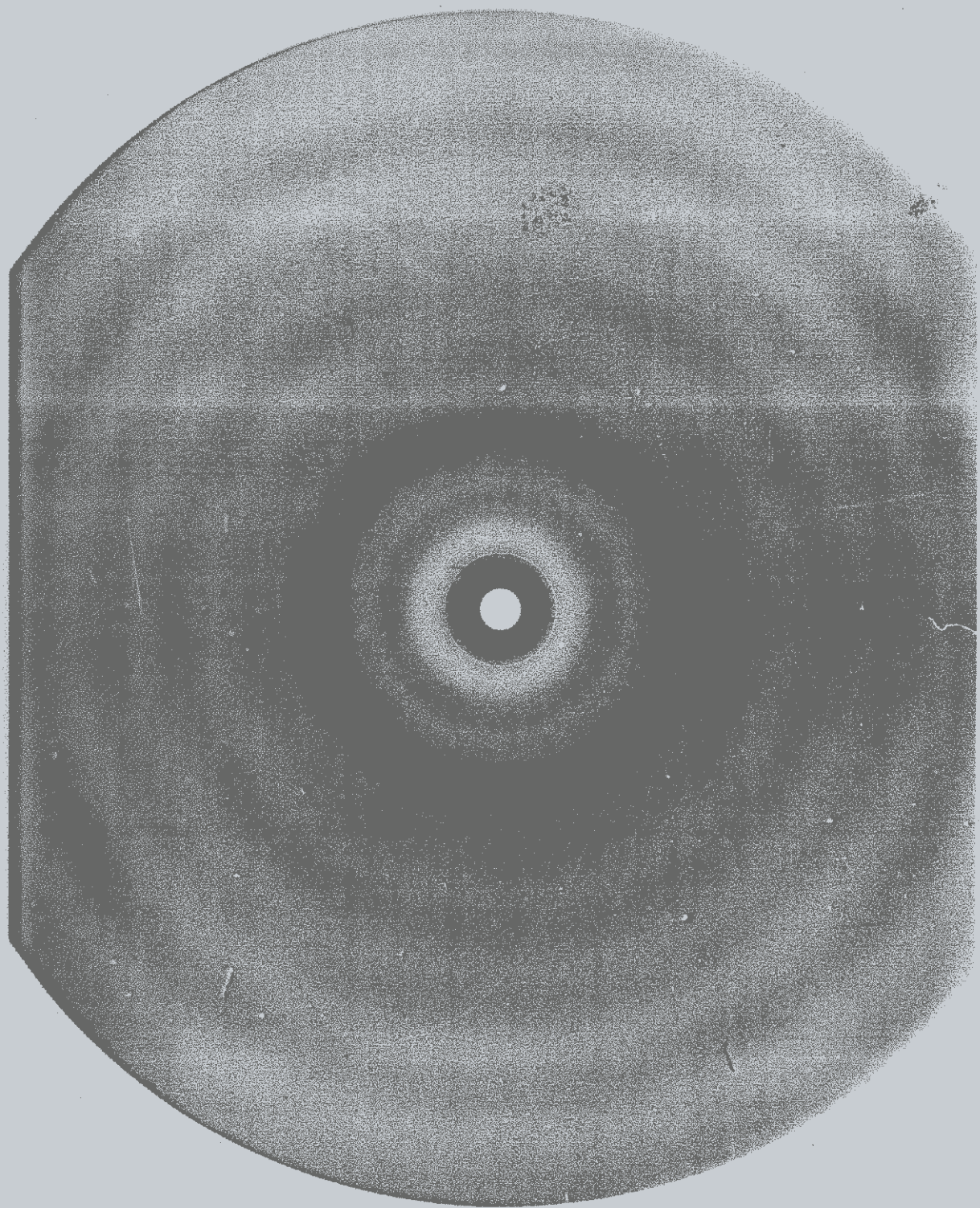
Registration of diffraction intensities with photographic plates
or Imaging plates (small dynamic range)

$$I_{\text{tot}}(s) \sim 1/s^4$$

Rotating sector compensates approximately this steep slope





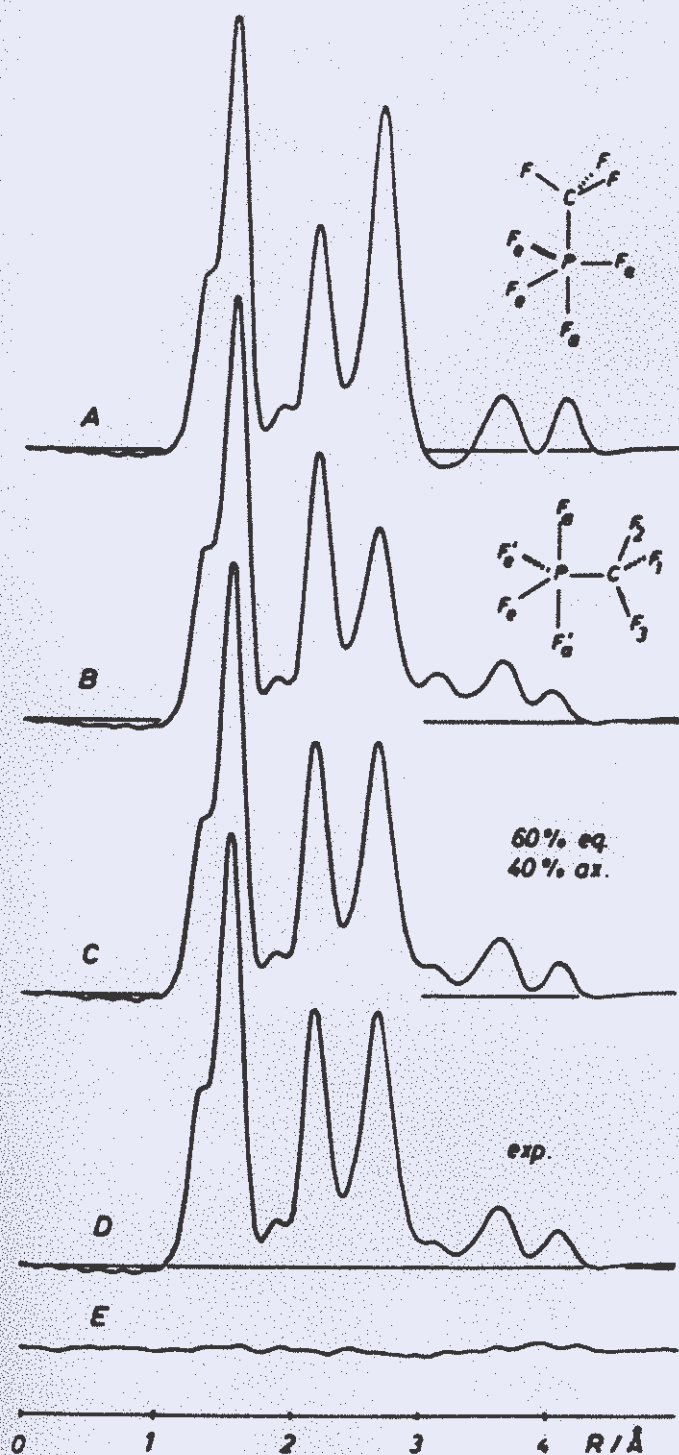


Phosphoranes

„More electronegative substituents occupy axial positions of the trigonal bipyramid.”

Confirmed for $\text{PF}_n(\text{CH}_3)_{5-n}$ and $\text{PF}_n\text{Cl}_{5-n}$ and many other phosphoranes.





ED 1981:

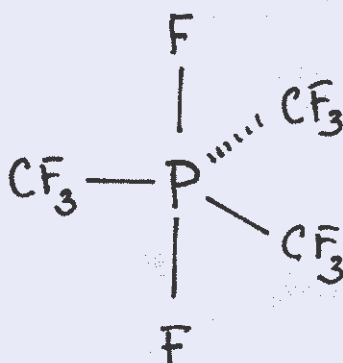
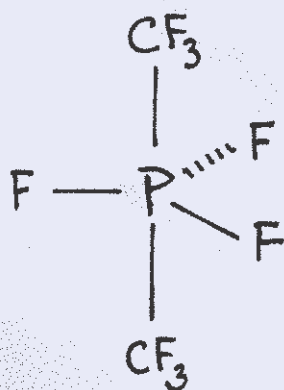
mixture of 60(10)% equatorial
and 40(10)% axial

Matrix IR spectra 1991
(H. Willner et al)

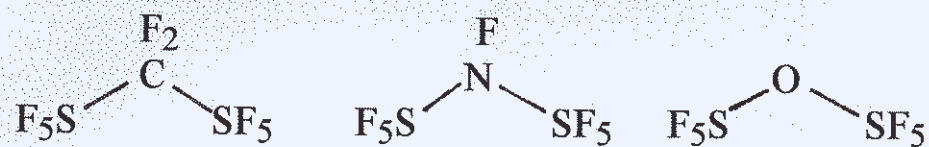
$\Delta H_{298} = 4.32(5) \text{ kJ/mol}$
(axial more stable)

$\Delta S_{298} = 15.4(10) \text{ J/mol K}$
(equatorial higher)

For $T = 20^\circ\text{C}$: 53(7)% equatorial

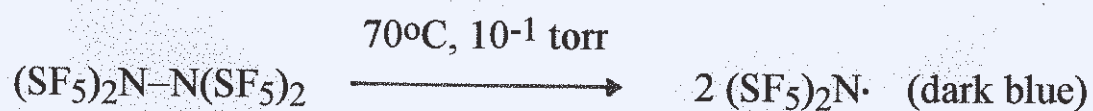
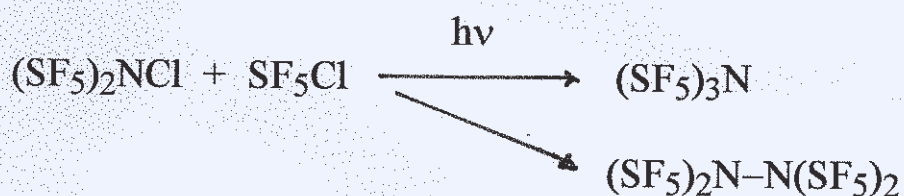


Steric Effects of SF₅ Groups

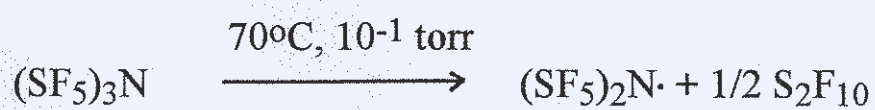
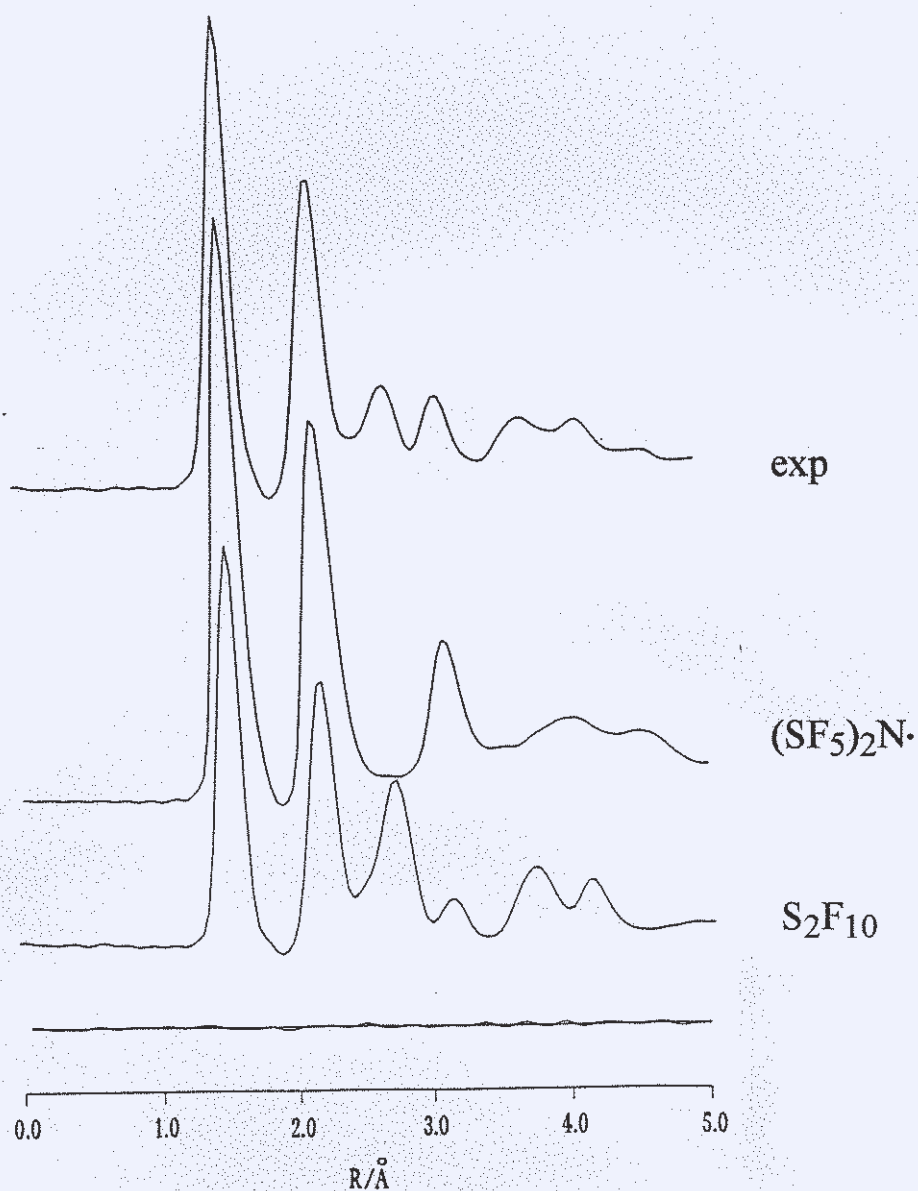


(X-S) _{SS}	181	174	170
(X-S) _{GED}	190.8 (7)	168.5 (5)	158.8 (11)
(S-X-S) _{GED}	124 (1)	138 (2)	143 (2)
S...S	337	314	300

J. S. Thrasher (University of Alabama):



GED for radical at -55°C



	N-S	S-N-S
$(\text{SF}_5)_2\text{NF}$	168.5 (5)	138 (2)
$(\text{SF}_5)_2\text{N}\cdot$	169.2 (4)	135 (1)
$(\text{SF}_5)_3\text{N}$	182.9 (6)	119.7 (2)

Combination of GED and QC

Problems in GED analyses	Support from QC
very similar bond distances	differences between distances of the same type
position of hydrogen atoms	respective parameter (e.g. HXH angle)
high correlations between geometric parameters and vibrational amplitudes	vibrational amplitudes and corrections from harmonic or anharmonic force fields
determinationn of r_{α} or r_e sructure	
several conformations	conformational space (type of possible conformers) and differences between geometric parameters of various conformers

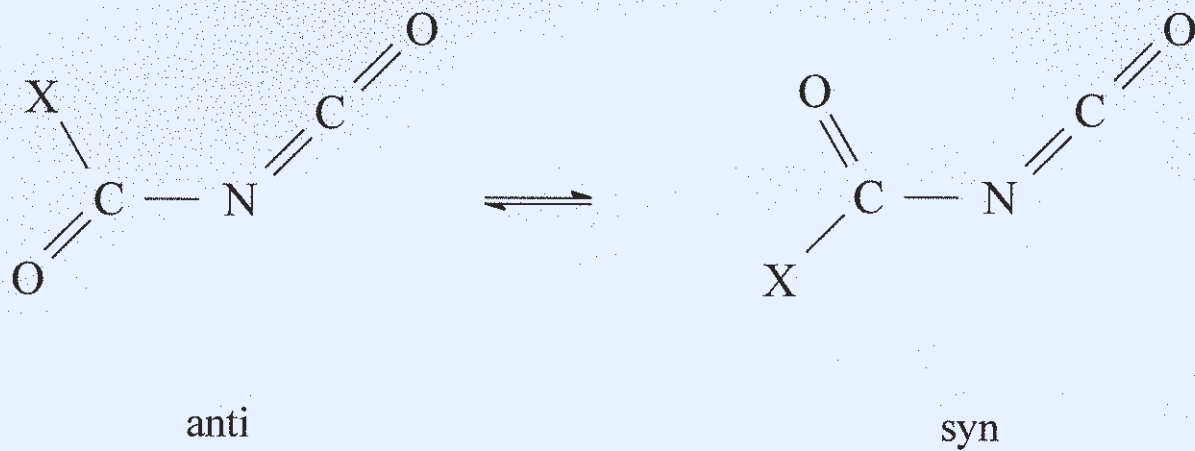
Advantage for QC:

test of computational methods whether they are suitable for a certain type of compounds

Comparison between experiment and theory

experiment	theory	exp. - theory	„expectation“
$\langle r \rangle$	r_e	+0.004 to +0.009 Å	± 0.03 Å
$\langle \alpha \rangle$	α_e	$\sim 0^\circ$	$\pm 3^\circ$
$\langle \varphi \rangle$	φ_e	up to $\pm 10^\circ$	$\pm 10^\circ$
ΔG^0	ΔG^0	0 kcal/mol	± 0.3 kcal/mol

Carbonylisocyanate



$$\Delta E = E(\text{syn}) - E(\text{anti})$$

(kcal/mol)

CH₃C(O)NCO

EB und IR:

nur syn

ab initio

- 2.4 bis -3.8

FC(O)NCO

EB 75 (10) % syn

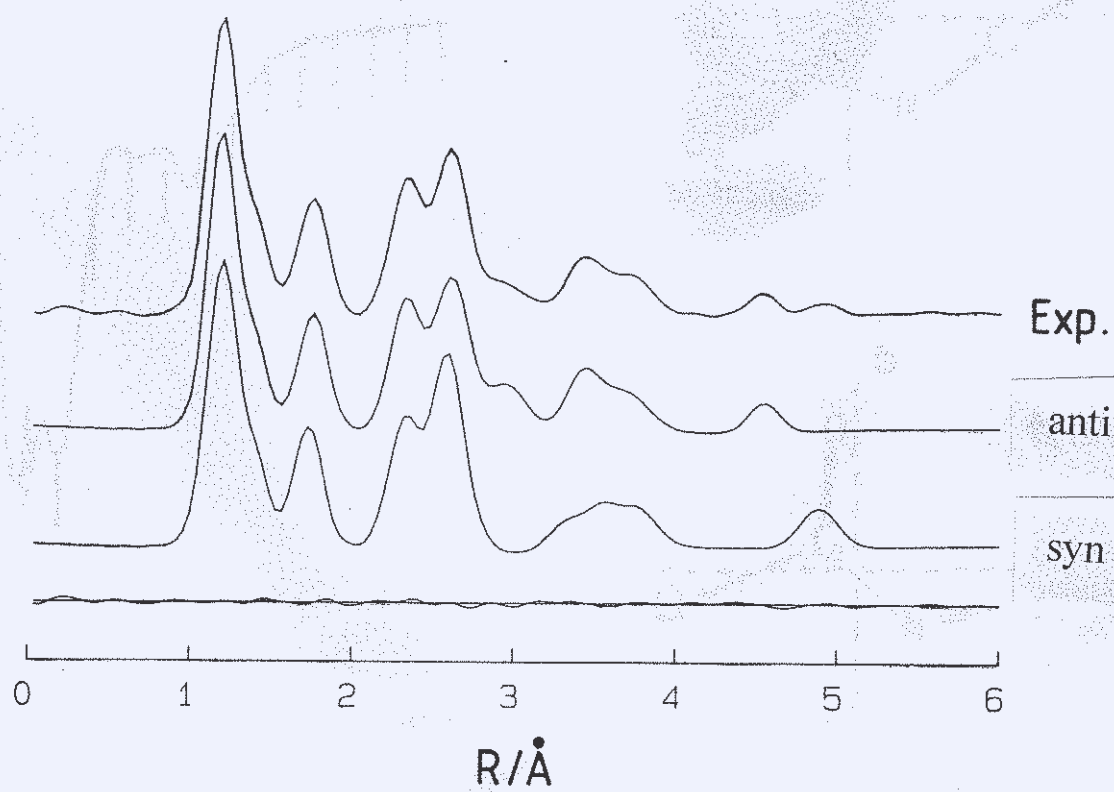
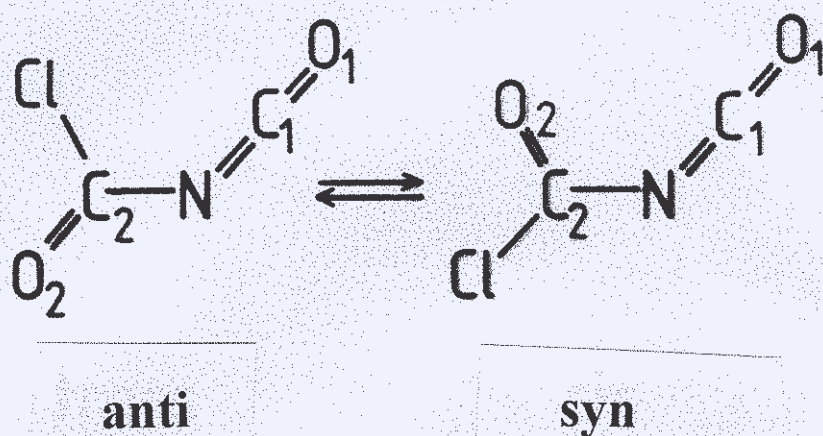
- 0.7 (3)

IR 65(8) % syn

- 0.4 (2)

ab initio

- 0.6 bis -1.7



Chlorocarbonyl isocyanate ClC(O)NCO

$$\Delta E = E(\text{syn}) - E(\text{anti})$$

(kcal/mol)

GED: 75 (8) % anti

+ 0.6 (3)

IR: 79 (5) % anti

ab initio (12 methods)

- 0.4 bis -1.6

("How reliable are ab initio methods")

Nguyen et al. (1991):

" best value "

+ 1.7

Jonas and Frenking (1991):

" best value "

+ 0.7

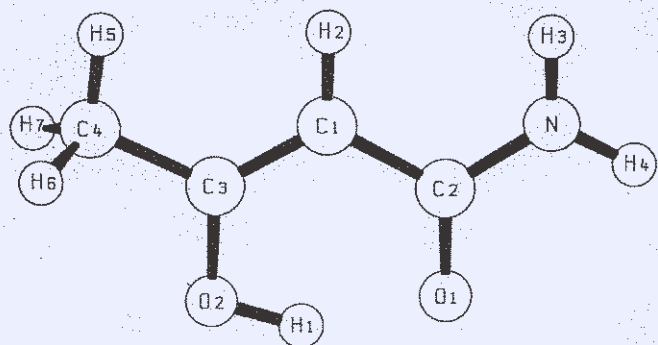
39 different ab initio calculations

+ 4.9 bis -7.4

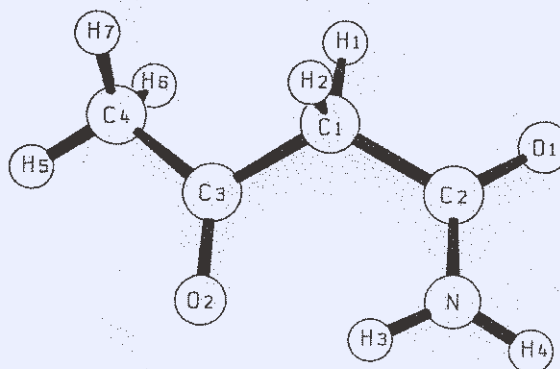
Only two methods reproduce the experimental value within its error limits.

Acetoacetamide, $X = \text{CH}_3$, $Y = \text{NH}_2$

ED (Belova, G. Girichev, Shlykov, Oberhammer, 2006)



63(7)% enol 1



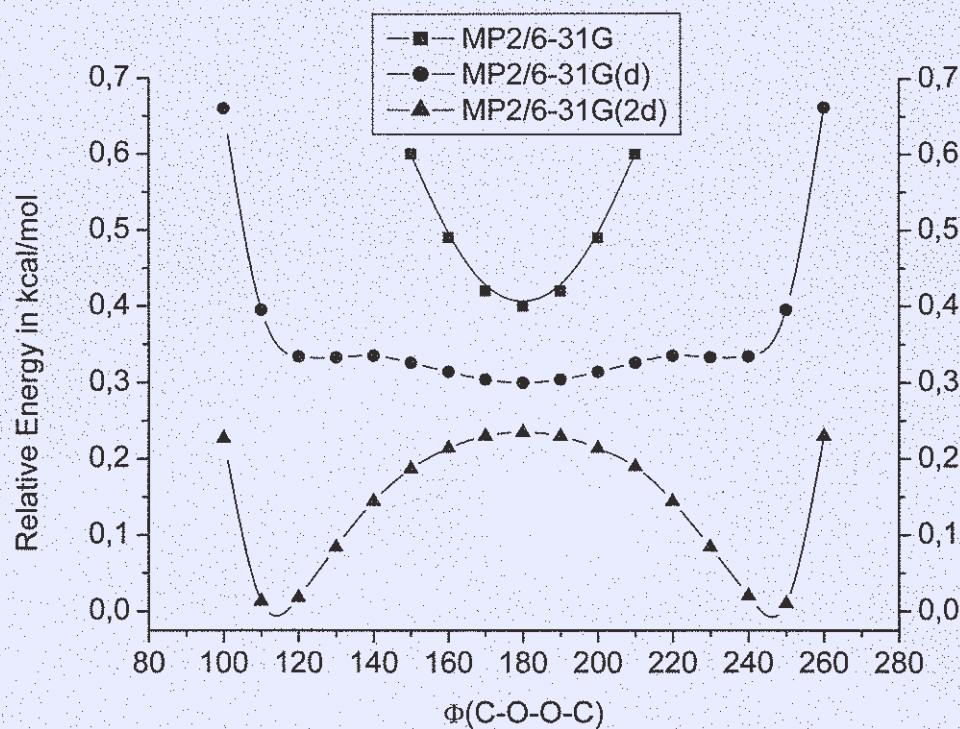
37(7)% keto (sc,ac)

ΔG^0_{347} (keto-enol) kcal/mol

ED	+ 0.37(15)
MP2/6-31G(d,p)	- 3.64
MP2/6-311++G(3df,pd)	- 0.44
B3LYP/6-31G(d,p)	+ 0.35
B3LYP/6-311++G(3df,pd)	+ 1.28

**Experimental (in bold letters) and theoretical values for the
COOC dihedral angle in dimethylperoxide, CH₃OOCH₃.**

Method	year	$\Phi(\text{COOC})$
IR/Raman	1971	skew (C₂ symmetry)
PES	1975	180.0
CNDO/2	1975	180.0
STO-2G	1976	101.7
MINDO/2	1977	96.5
PES	1979	170
MINDO/3	1980	110.7
GVB-CI	1982	180.0
HF/4-21G*	1984	115.5
MM2	1984	107.0
GED	1984	119 (4)
FAR-IR	1986	120.0 (1)
HF/3-21G	1988	180.0
HF/6-31G*	1988	180.0
MP2/6-31G*	1988	180.0
CISD/6-31G*	1988	180.0
MP4/6-31G*// MP2/6-31G*	1988	121.2
MP2/6-31G*	1995	180.0
MP2/6-31G*	1996	180.0
MP2/6-311G(2d,p)	1997	116.3



Extensive QC for $\text{CH}_3\text{O-OCH}_3$

A. Karpfen et.al. J. Phys. Chem. A, **2002**, 106, 438

Ab initio:

Six methods (MP2, MP3, MP4(SDQ), MP4(SDTQ), CCSD, CCSD(T)) with Dunning (cc-pVDZ to cc-pVQZ and aug-cc-pCDZ to aug-cc-pVTZ) and Pople basis sets (6-31G(2d) to 6-311+G(2d,2p))

Total of 53 calculations

Results: 8 calculations predict single minimum potential

28 calculations predict double minimum potential

17 calculations predict triple minimum potential

DFT: 3 methods with 6-31G(2d) and aug-cc-pVTZ basis sets

Total of six calculations

Results: B3LYP/6-31G(2d) predicts double minimum potential

All other calculations predict single minimum potential

M. J. S. Dewar (1985):

„Any valid use of ab initio procedures in chemistry has therefore to be on a purely **empirical** basis, limited to situations where specific tests have shown the procedure in question to give satisfactory results.”

**Nowbody believes theoretical calculations,
Except the one who did them.**

**Everybody believes experimental results,
except the one who obtained them.**