Universität Bielefeld

Mitzel Group
inorganic & structural chemistry

Low-Pressure Gas Electron Diffraction

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16th ESGED, Frauenchiemsee, June 21 – 26, 2015

New project

GED for low-volatile and thermally unstable compounds.

Normal GED: P_{sample} ~ 1 – 10 mbar
LP GED: $P_{sample} < 10^{-2}$ mbar

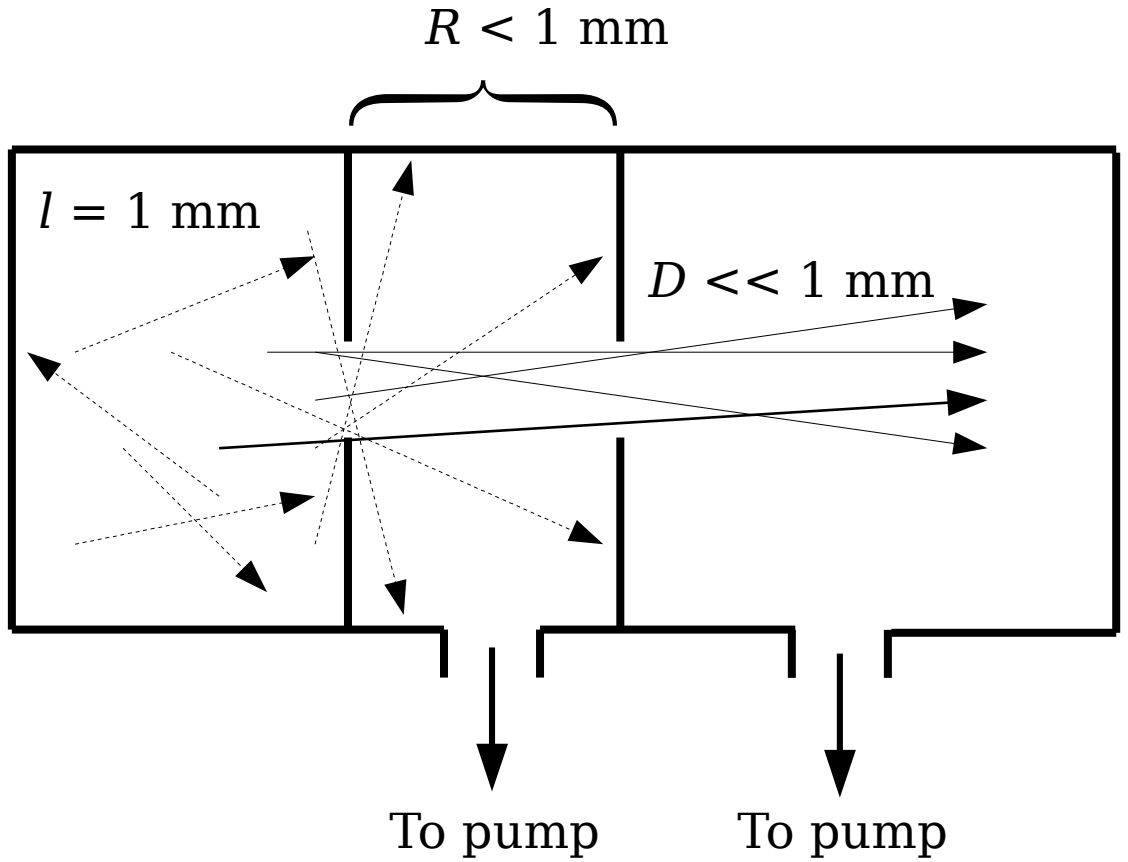
- High-temperature GED.
- Combined MS+GED experiments.
- Molecular beams.
- Highly reproducible experimental conditions.
- Experimental background.

P. A. Akishin, V. P. Spiridonov, *Kistallografiya*, 2, 1957, 475. (in Russian)
P. A. Akishin, N. G. Rambidi, E. Z. Zasorin, *Kistallografiya*, 4, 1959, 186. (in Russian)
N. G. Rambidi, E. Z. Zasorin, *Teplofiz. Vys. Temp.*, 2, 1964, 705. (in Russian)
I. Hargittai, M. Hargittai, V. P. Spiridonov, E. V. Erokhin, *J. Mol. Struct.*, 8, 1971, 31.
A. A. Ivanov, *Prib. Tekh. Eksp.*, 2, 1974, 237. (in Russian)
J. Tremmel, I. Hargittai, *Hung. Sci. Instrum.*, 50, 1980, 43.
I. Hargittai, S. Bohatka, J. Tremmel, I. Berecz, *Hung. Sci. Instrum.*, 50, 1980, 51.
A. A. Ivanov, E. Z. Zasorin, *Prib. Tekh. Eksp.*, 6, 1980, 170. (in Russian)
L. S. Bartell, R. K. Heenan, M. Nagashima, *J. Chem. Phys.*, 78, 1983, 236.
K. S. Krasnov, *Zh. Strukt. Khin.*, 24, 1983, 3. (in Russian)
J. Tremmel, I. Hargittai, *J. Phys. E Sci. Instrum.*, 18, 1985, 148.
G. V. Girichev, S. A. Shlykov, Yu. F. Revichev, *Prib. Tekh. Eksp.*, 4, 1986, 167. (in Russian)
G. V. Girichev, S. A. Shlykov, S. B. Lapshyna, *Z. Fiz. Khim.*, 64, 1990, 899. (in Russian)
A. Haaland, K. G. Martinsen, J. Tremmel, *Acta Chem. Scand.*, 46, 1992, 589.
S. L. Masters, G. V. Girichev, S. A. Shlykov, *Dalton Trans.*, 42, 2013, 3581.

Molecular beams

Mean free path $l = \frac{k_B T}{\sqrt{2}\pi d^2 p}$

T, K	p, mbar	d, Å	l, mm
300	10	10	~10^{-3}
300	10^{-2}	10	~1
600	10^{-2}	20	~0.5
600	10^{-3}	20	5

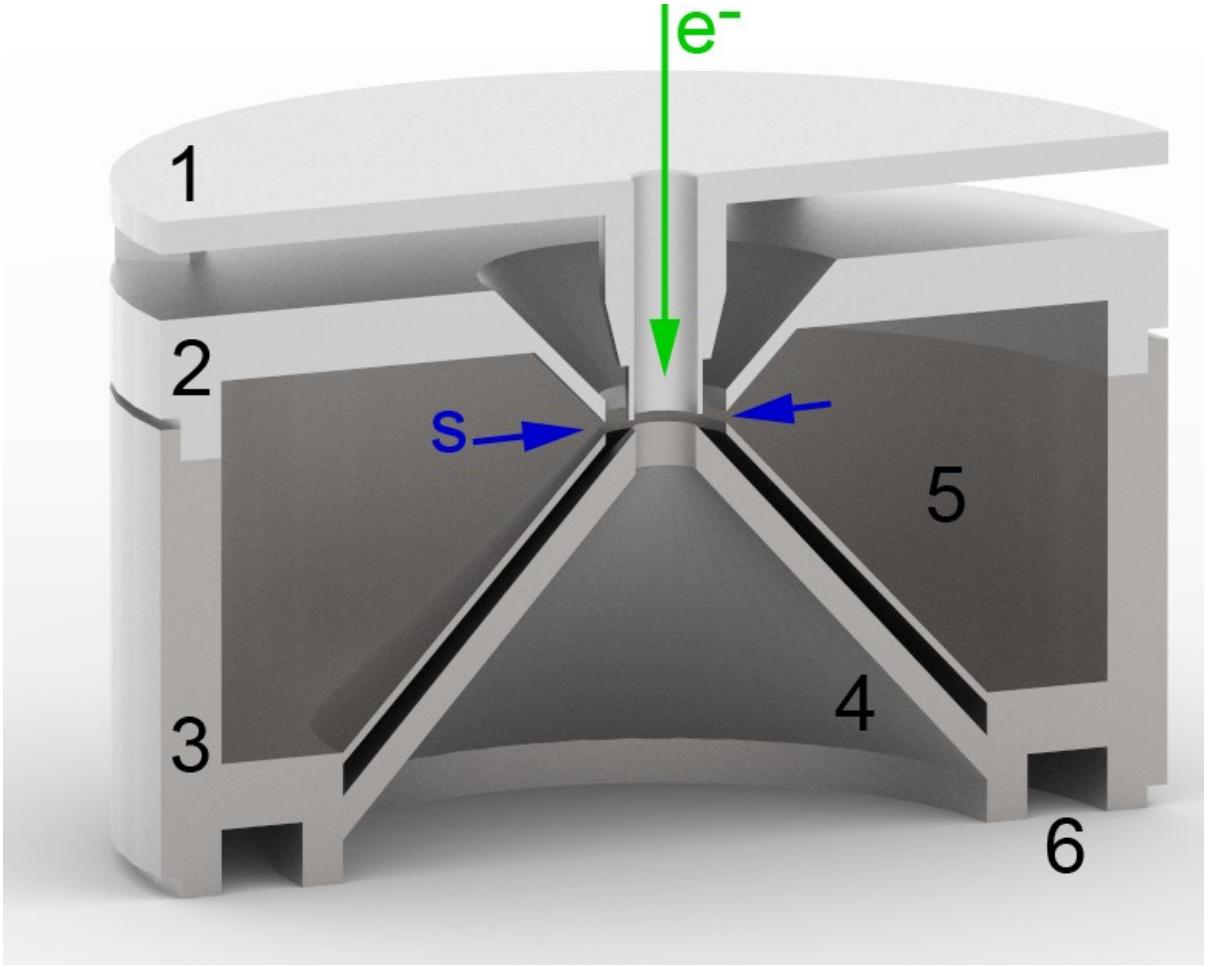


C. B. Lucas, *Atomic and Molecular Beams*, CRC Press, 2014.

Ring cell for GED

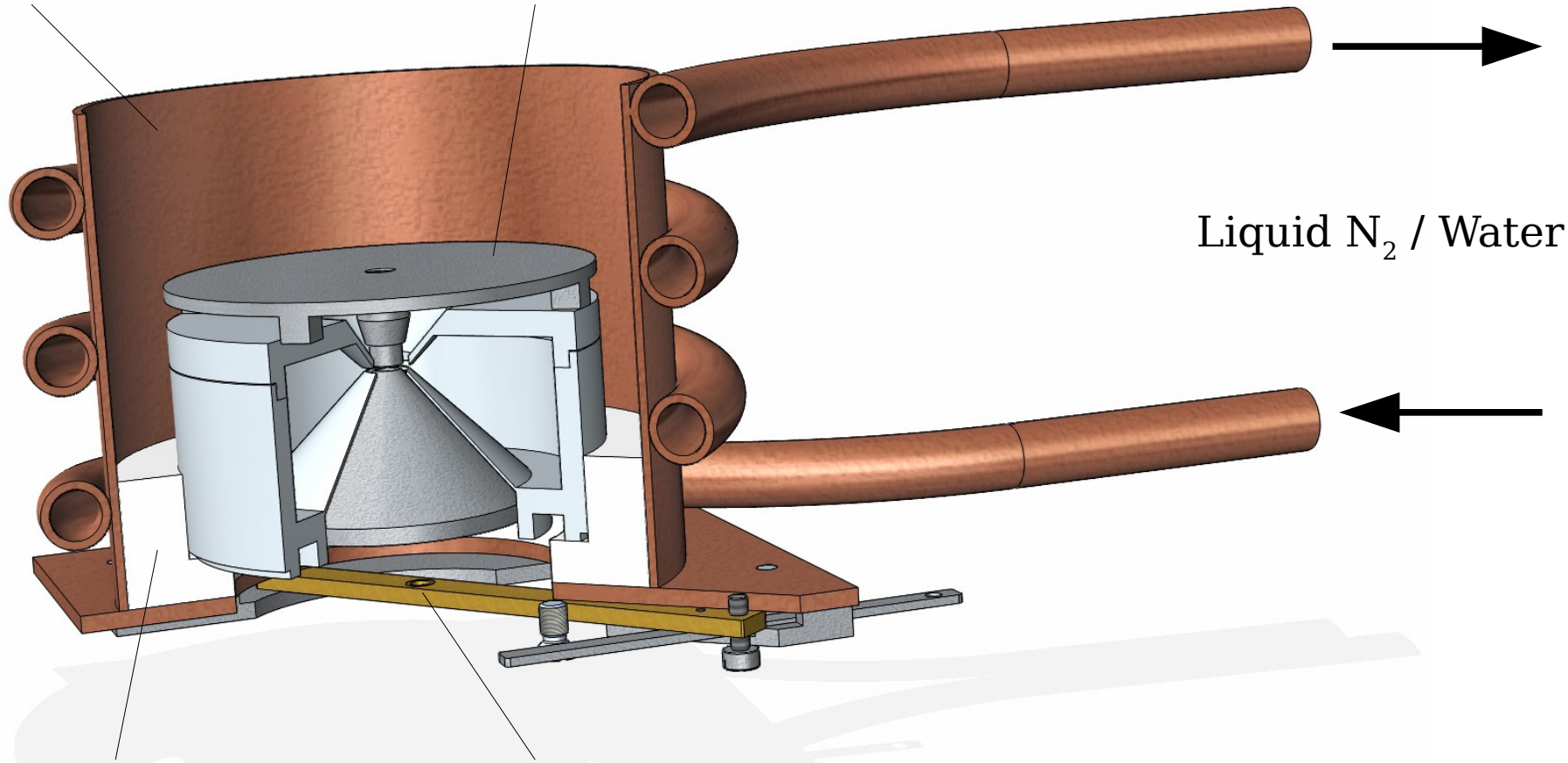
Proposed by A. A. Ivanov (MSU).

Target — “Molecular film”.

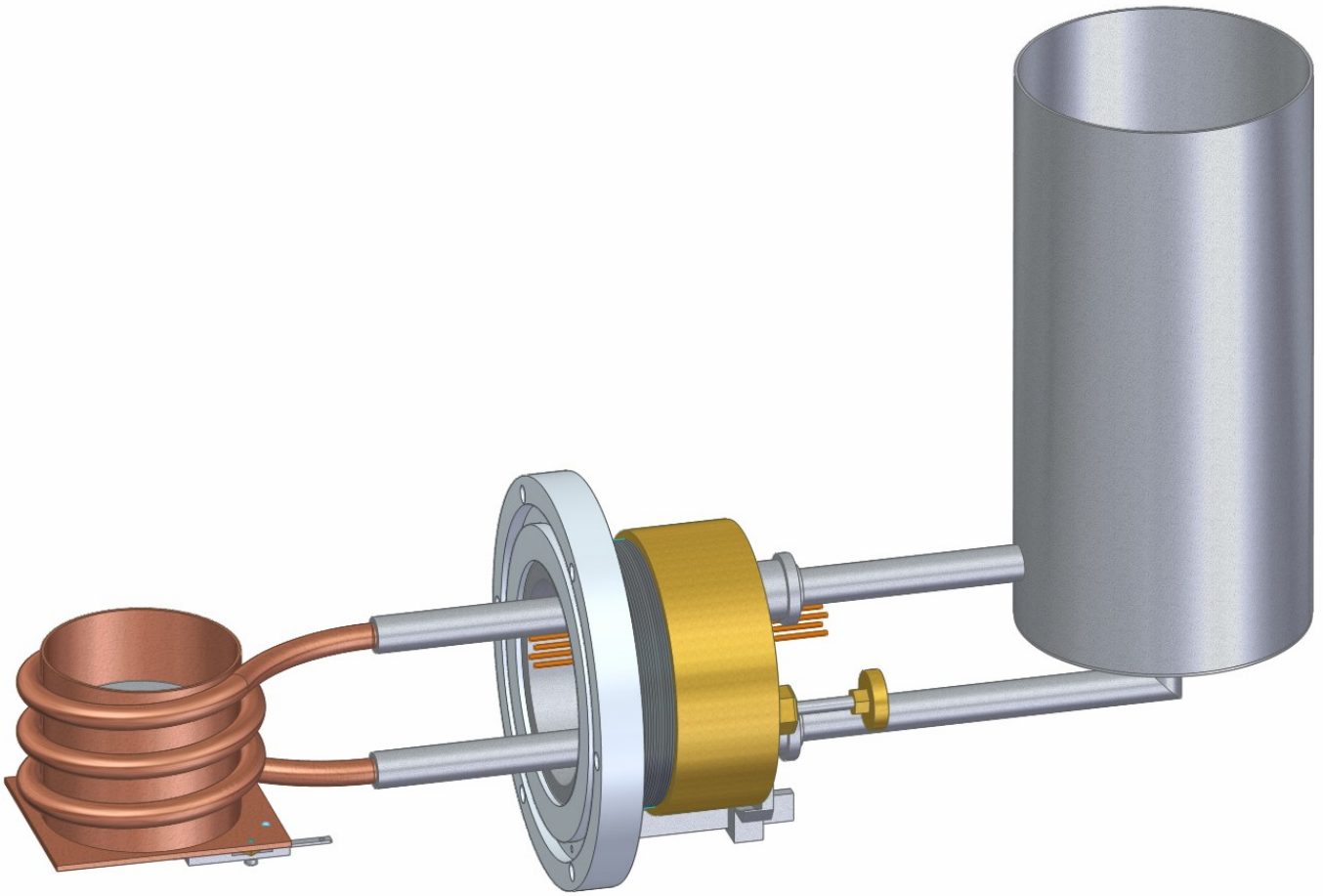


A. A. Ivanov, Russ. patent 2377688, 2009.

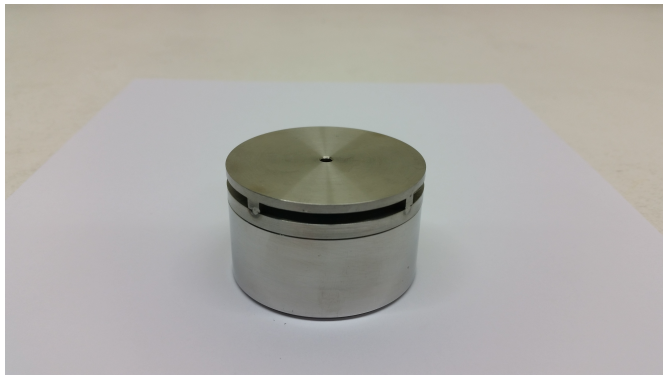
CAD Model

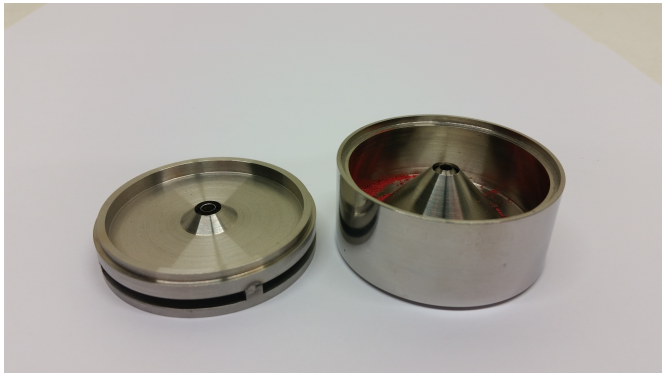

Cold trap
Effusion cell
Liquid N_2 / Water
Thermal isolator
Crystal standard

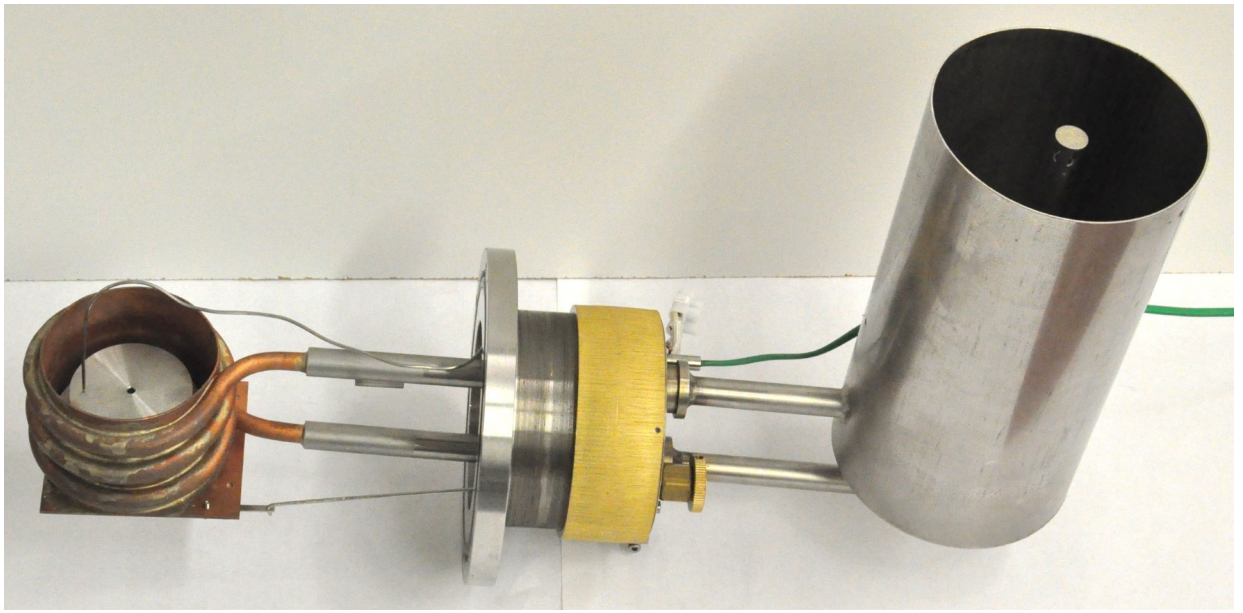
Inlet system



Real prototype







MS+GED @ Bielefeld

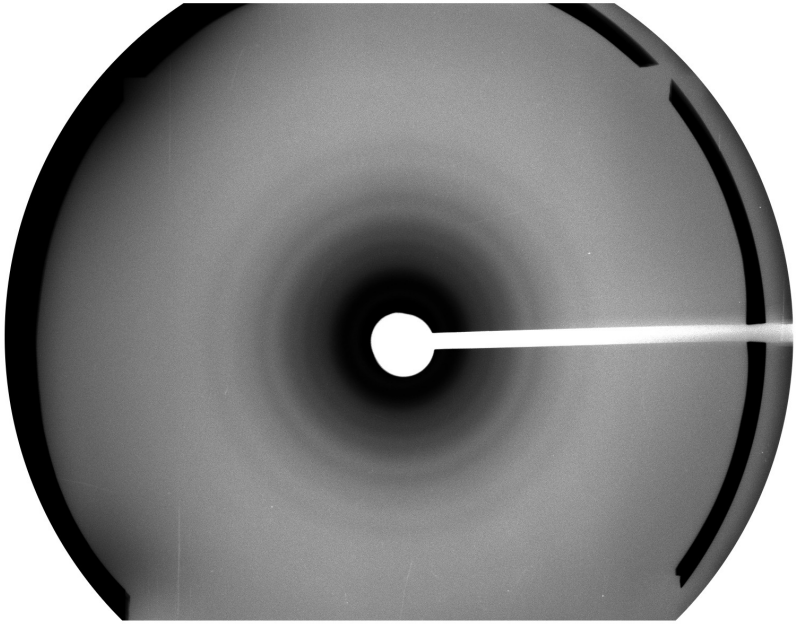
MS →

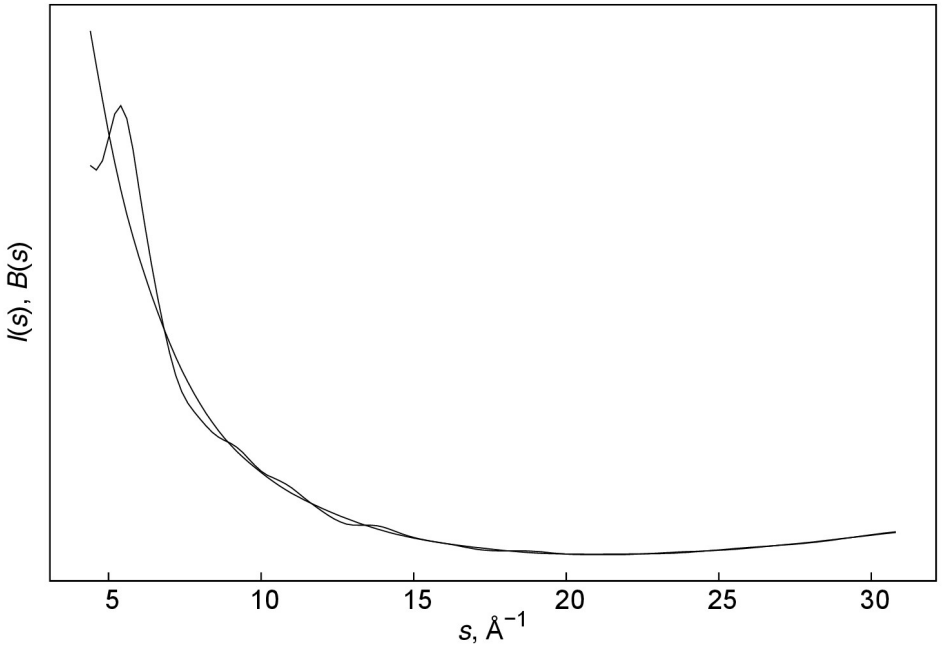
Hiden EPIC ion counting detector (up to 2500 amu)

Test measurements

First measurements: Benzoic acid

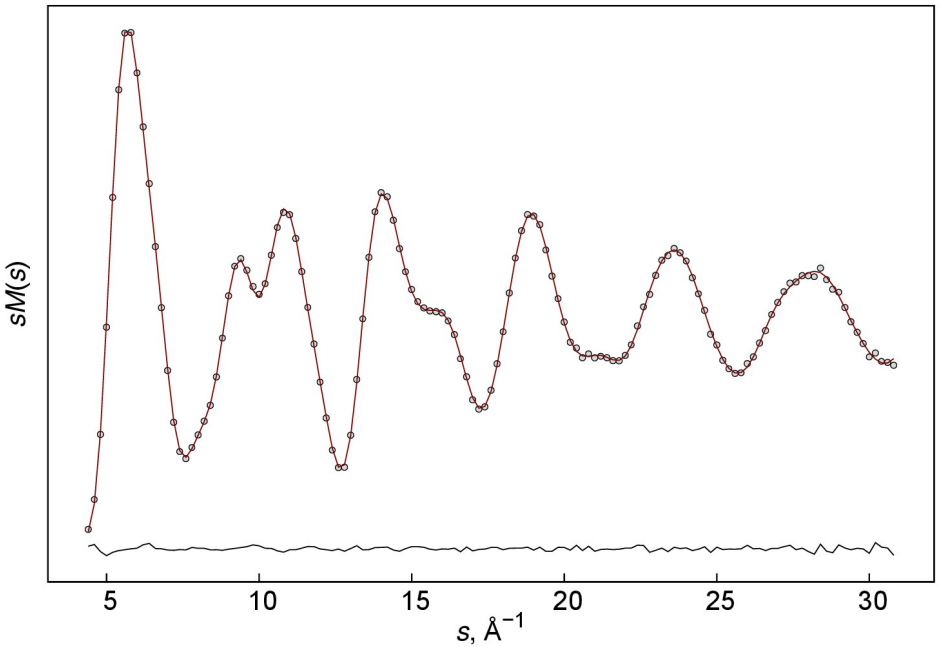
	Vishnevskiy et al., 2015	Aarset et al., 2006
Temperature, K	287	406
Sample pressure, mbar	2.7×10^{-4}	17
Background pressure, mbar	1×10^{-7}	?
Electron beam current, μA	10.9	?
Exposure time, s	60	?

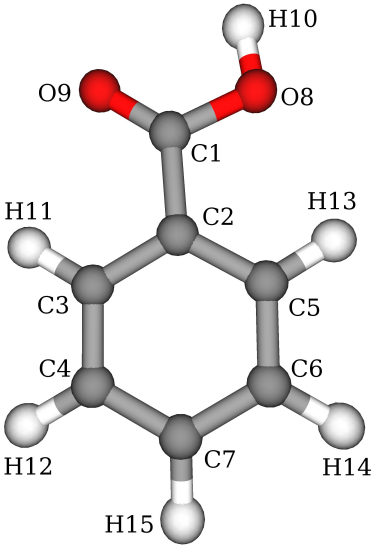


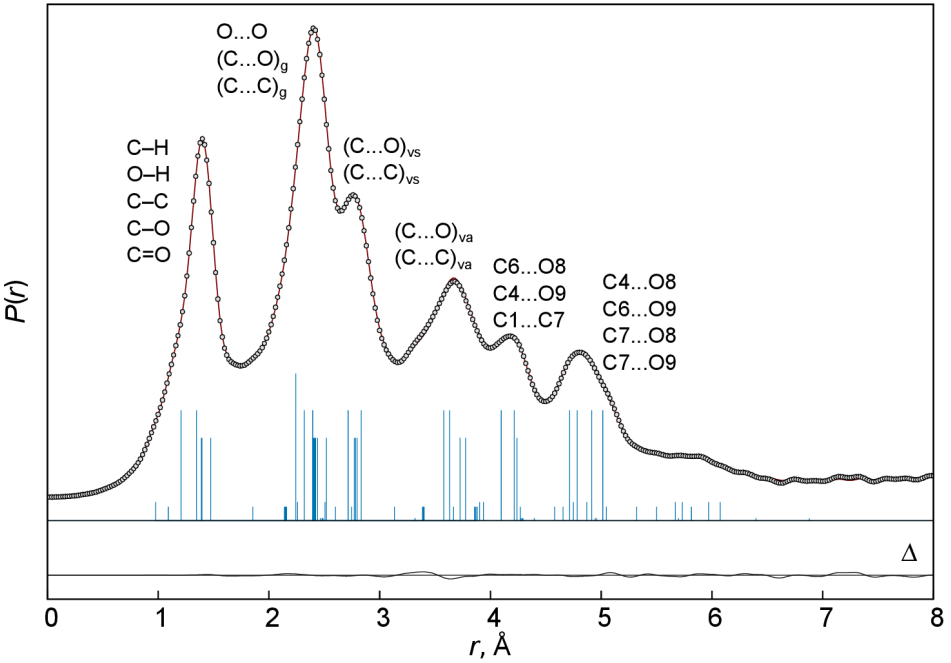


K. Aarset, E. M. Page, D. A. Rice, *J. Phys. Chem. A*, 110, 2006, 9014.
M. Colomina, P. Jimenez, C. Turrion, *J. Chem. Thermodyn.*, 14, 1982, 779.
C. G. de Kruif, J. G. Blok, *J. Chem. Thermodyn.*, 14, 1982, 201.

Benzoic acid







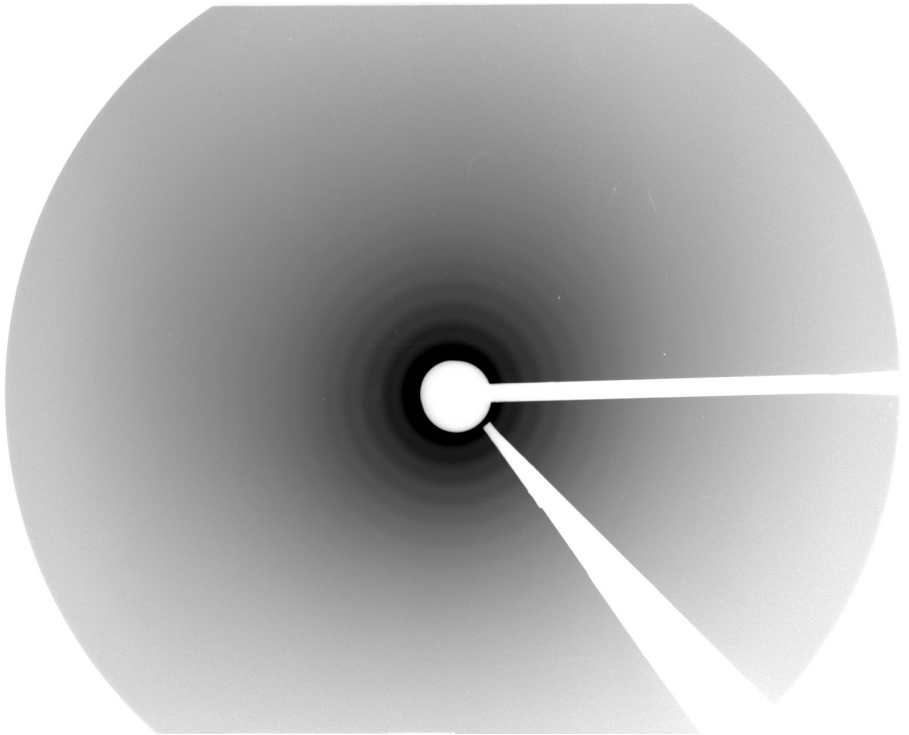
Parameter, [Å, °]	Vishnevskiy et al., 2015	Aarset et al., 2006
$r_a(C_{ar}–C_{ar})_{av}$	1.393(1)	1.397(6)
$r_a(C_{ar}–C)$	1.475(7)	1.475(21)
$r_a(C=O)$	1.207(4)	1.220(18)
$r_a(C–O)$	1.347(8)	1.359(24)
$l(C_{ar}–C_{ar})$	0.053(2)	0.054(18)
R_f, %	2.6	?

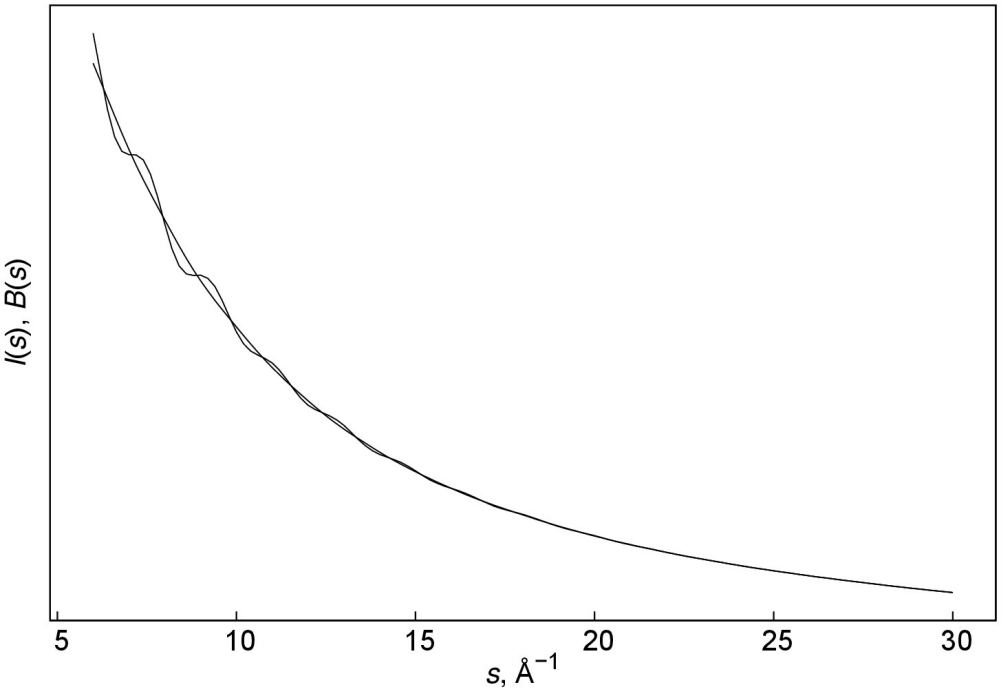
Errors: 3σ

K. Aarset, E. M. Page, D. A. Rice, *J. Phys. Chem. A*, 110, 2006, 9014.

Iodoform, CHI_3

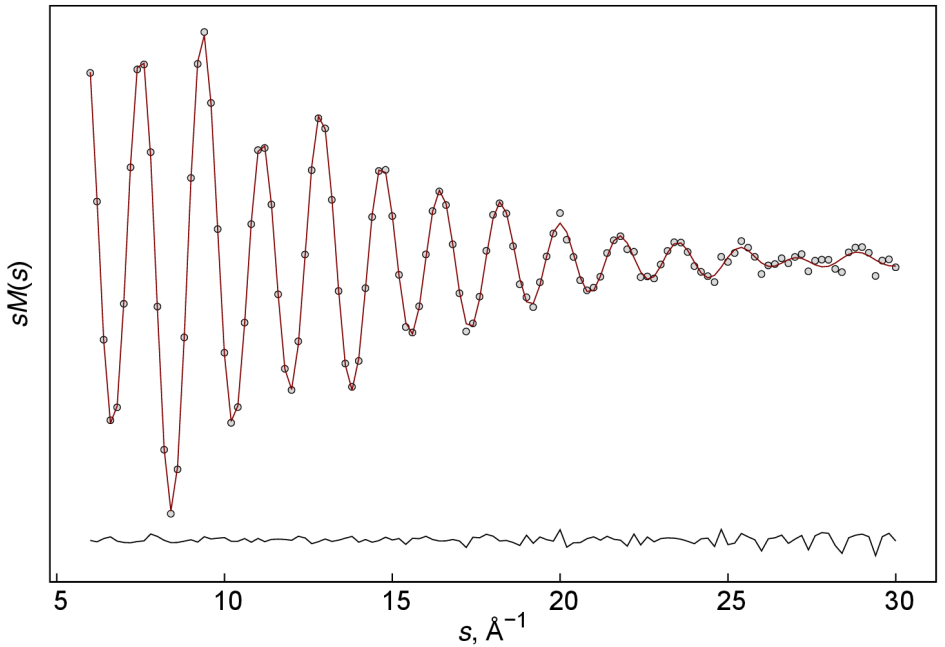
	Vishnevskiy et al., 2015	Takeuchi et al., 2003
Temperature, K	288	395
Electron beam current, μA	0.9	1.5
Exposure time, s	45 – 90	110 – 140

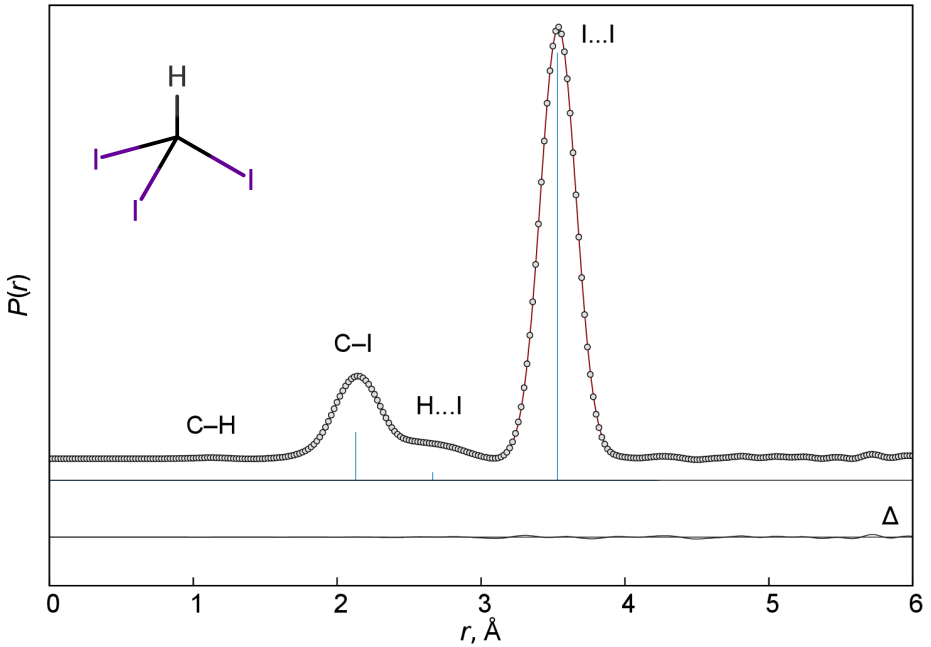




H. Takeuchi, T. Ozaki, T. Takeshima, T. Egawa, S. Konaka, *J. Mol. Struct.*, 657, 2003, 381.

Iodoform, CHI_3





Parameter, [Å, °]	Takeuchi et al., 2003 r_g	Vishnevskiy et al., 2015 r_g	Vishnevskiy et al., 2015 r_e	Calculated r_e
r(C–H)	1.111 assumed	1.128(107)	1.107(107)	1.081
r(C–I)	2.145(8)	2.130(6)	2.119(6)	2.125
r(I...I)	3.549(2)	3.536(1)	3.522(1)	3.531
l(C–I)	0.067(7)	0.067(1)		0.055
l(I...I)	0.108(2)	0.101(2)		0.084
R_f, %	?	5.1		

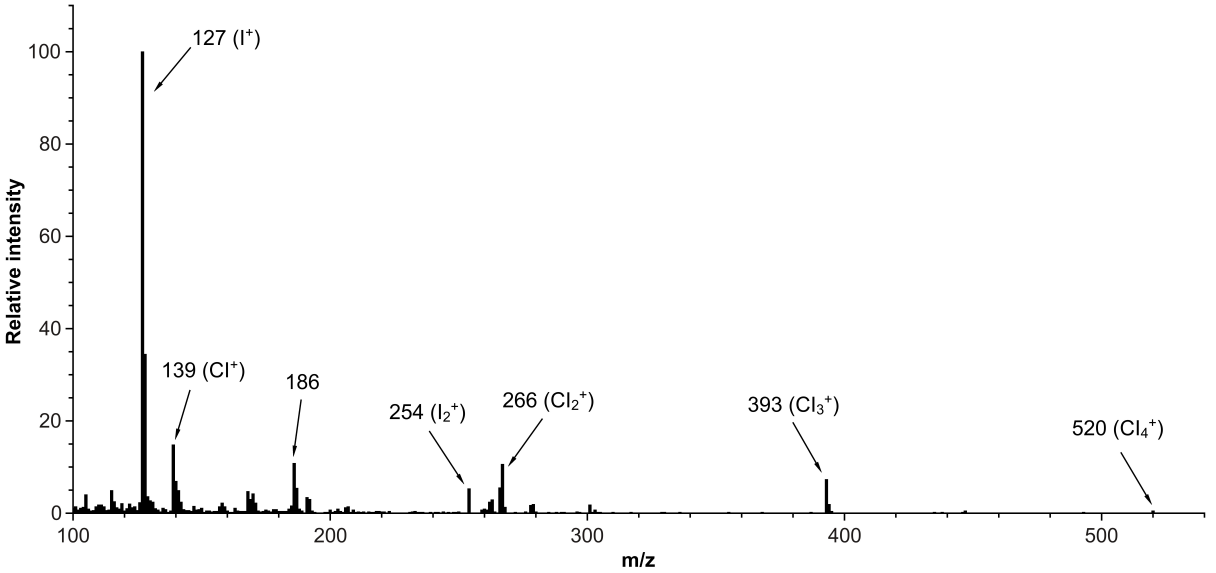
QC geometry: CCSD(T)/CBS-PP, Amplitudes: MP2/SDB-cc-pVTZ Errors: 3σ

H. Takeuchi, T. Ozaki, T. Takeshima, T. Egawa, S. Konaka, *J. Mol. Struct.*, 657, 2003, 381.

Carbon tetraiodide, CI_4

	Vishnevskiy et al., 2015	Hargittai et al., 2001
Temperature, K	290	396
Electron beam current, μA	4.8	?
Exposure time, s	20 – 60	?

Combined GED+MS @ 290 K



Hargittai: ~ 20% I_2 @ 396 K

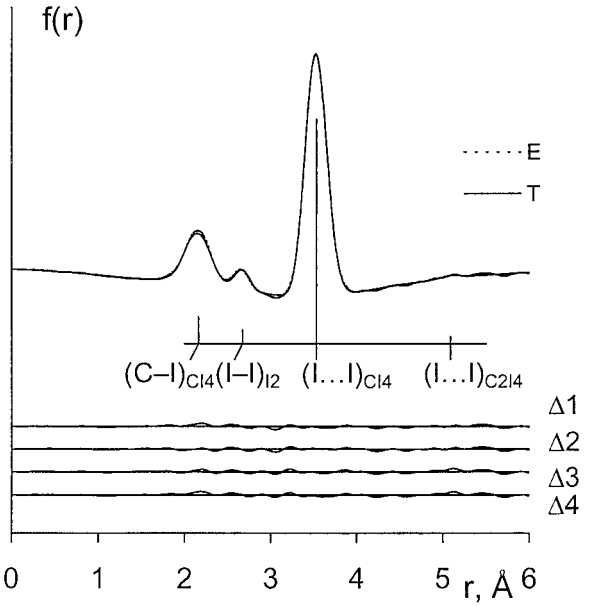
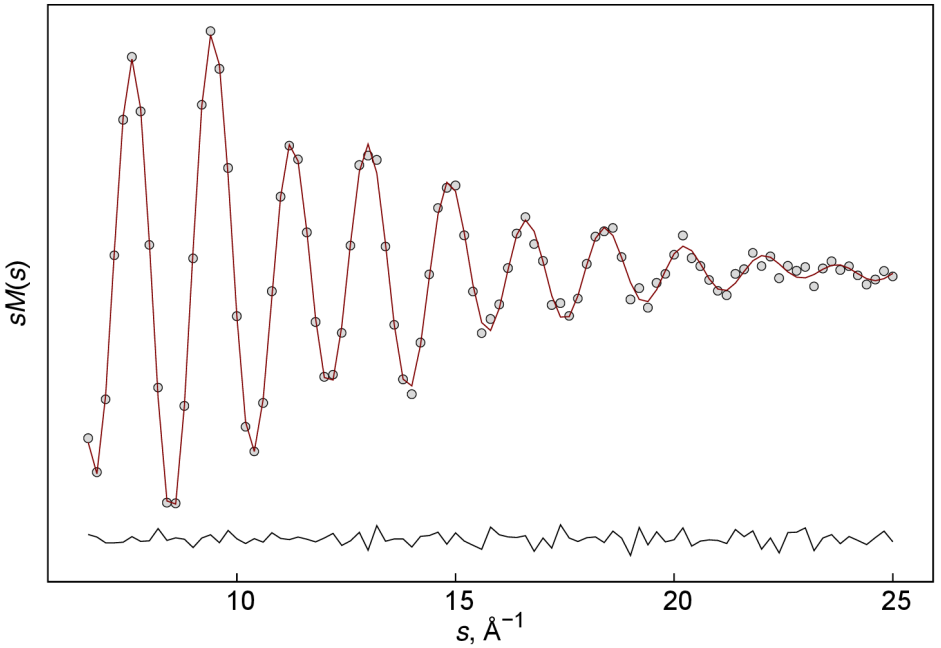
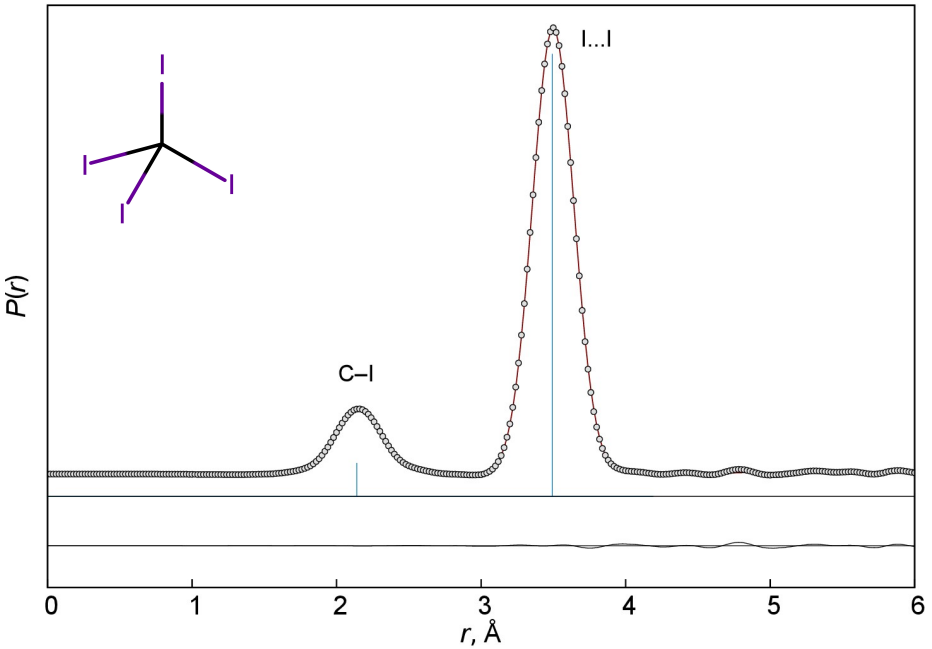


Fig. 2. Experimental (E) and calculated (T) radial distributions for Model 1 and their differences (Δ) for the three models of Table VII. The contribution of the distances of CI_4 and I_2, and the position of the longest I···I distance of C_2I_4 from Model 1 are indicated. Δ4 corresponds to a model with CI_4 and I_2 only.

M. Hargittai, G. Schultz, P. Schwerdtfeger, M. Seth, *Struct. Chem.*, 12, 2001, 377.

Carbon tetraiodide, CI_4





Parameter, [Å, °]	Hargittai et al., 2001 r_g	Vishnevskiy et al., 2015 r_g	Vishnevskiy et al., 2015 r_e	Calculated r_e
r(C–I)	2.157(6)	2.142(1)	2.132(1)	2.144
r(I...I)	3.530(7)	3.496(2)	3.482(2)	3.501
l(C–I)	0.063 assumed	0.046(22)		0.058
l(I...I)	0.106(23)	0.114(3)		0.083
R_f, %	5.4	7.1		

QC geometry: CCSD(T)/CBS-PP, Amplitudes: MP2/SDB-cc-pVTZ

Errors: 3σ, 2σ+se

M. Hargittai, G. Schultz, P. Schwerdtfeger, M. Seth, *Struct. Chem.*, 12, 2001, 377.

Conclusions / To Do

- Ring cell works!
- Successfully tested MS+GED.
- It is possible to avoid substance decomposition.
- Refined parameters are
  - a) precise and accurate,
  - b) consistent with published data.

- Implement heating of the effusion cell.
- Tune mass-detector and optimize its position.
- Measure new compounds.

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DFG

Thank you for your attention!