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Gas-Phase Electron Diffraction: A Story of One Molecule

UNEX Project

Yury V. Vishnevskiy

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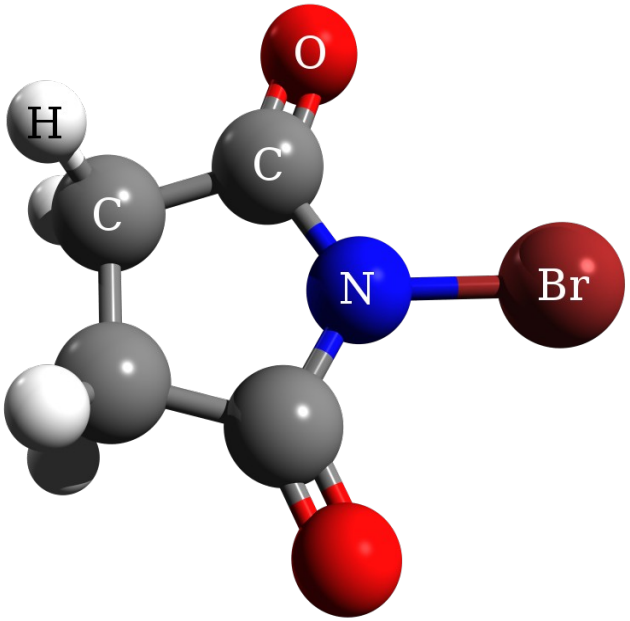
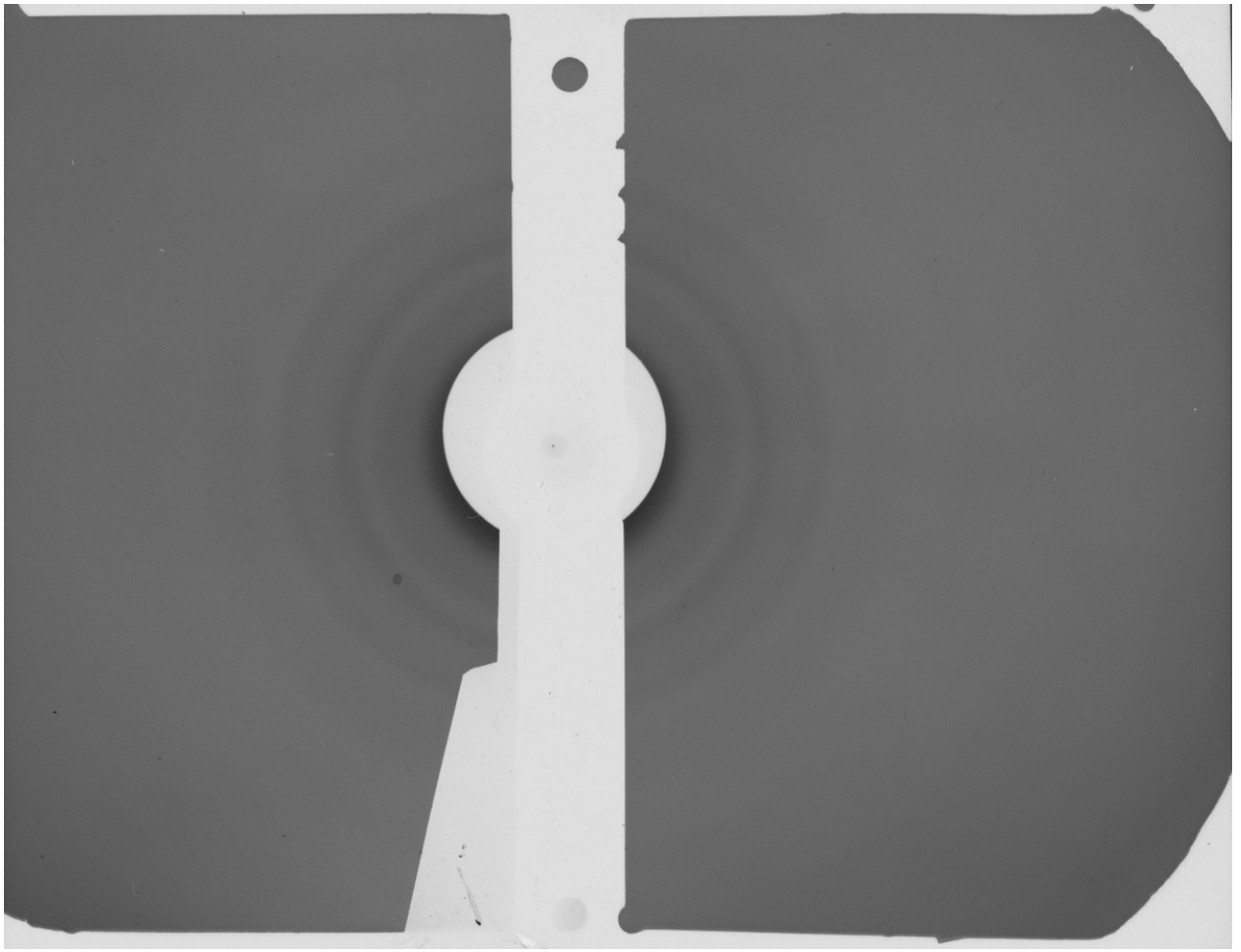
N-Bromosuccinimide (NBS)





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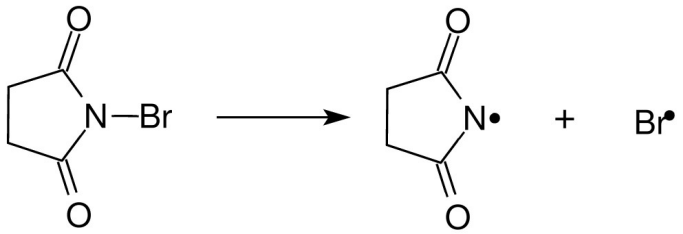
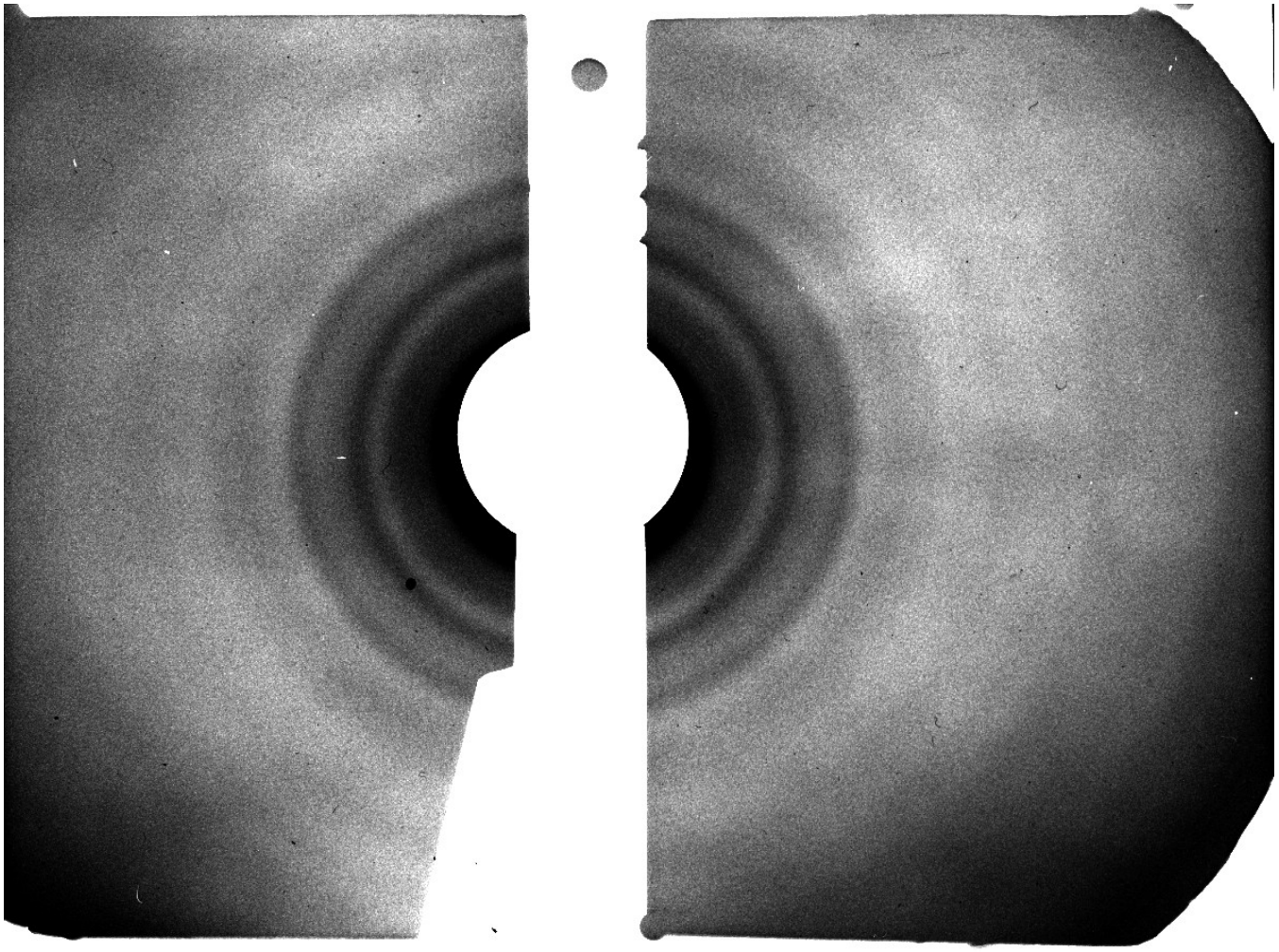
GED Data Reduction: a Complicated Case

Main Problem: Weak diffraction pattern

Problems:

- High noise-to-signal ratio
- Asymmetry of diff. pattern
- Non-uniform background



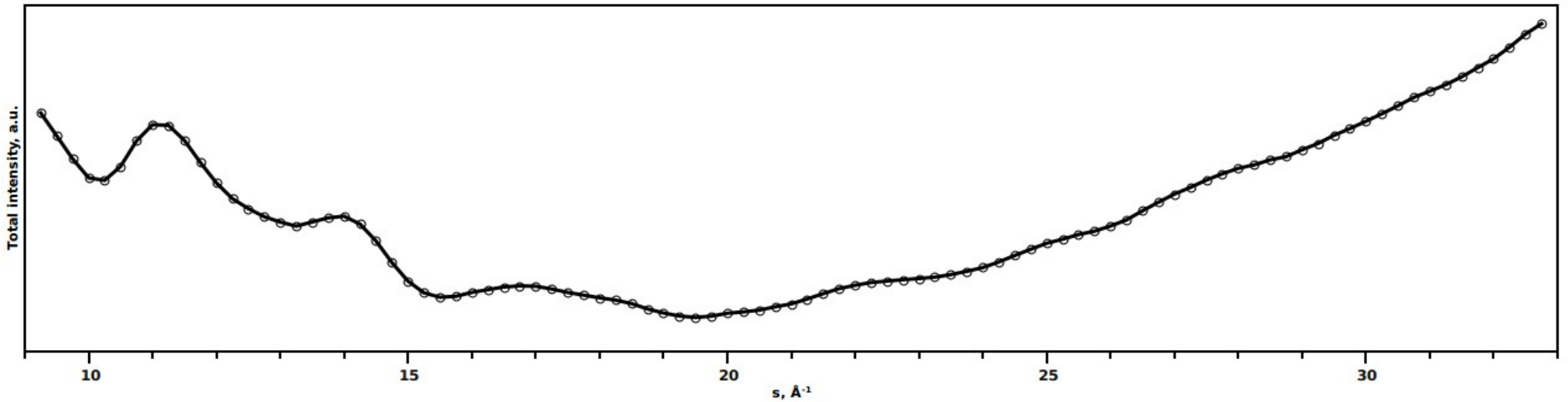


New Method

Main ideas:

- Using model of diffraction pattern: $I_{xy} = f\left(X_c, Y_c, X_s, Y_s, J, F_{xy}\right)$
- Applying the least squares method: $Q = \sum_{ij} W_{ij}\left(I_{ij}^{\exp} - I_{ij}^{theor}\right)^2 \rightarrow min$

The model: $$I_{xy} = \frac{r_s^3 K\left(r_s\right)}{r_c^3} J\left(r_c\right) + F_{xy}$$



Vishnevskiy, Yu. V. Journal of Molecular Structure 2007, 833, 30–41.

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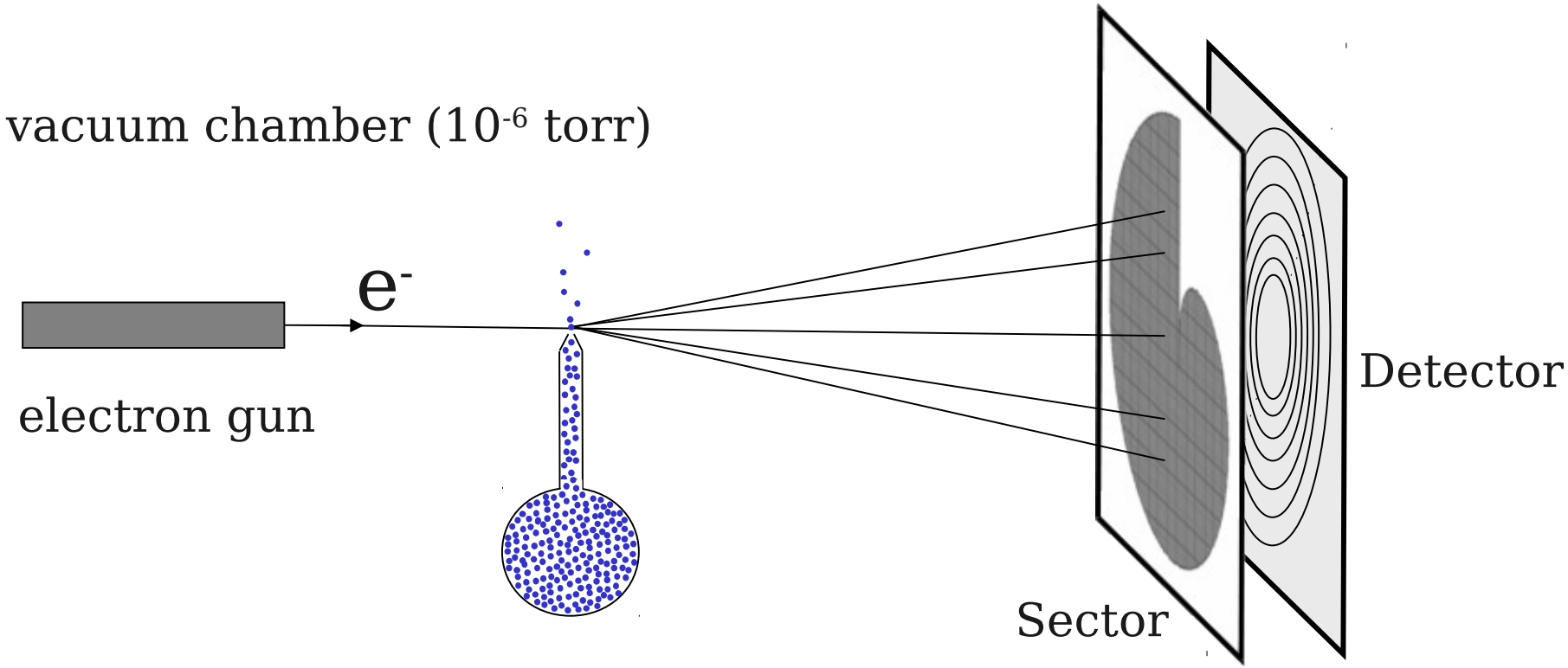
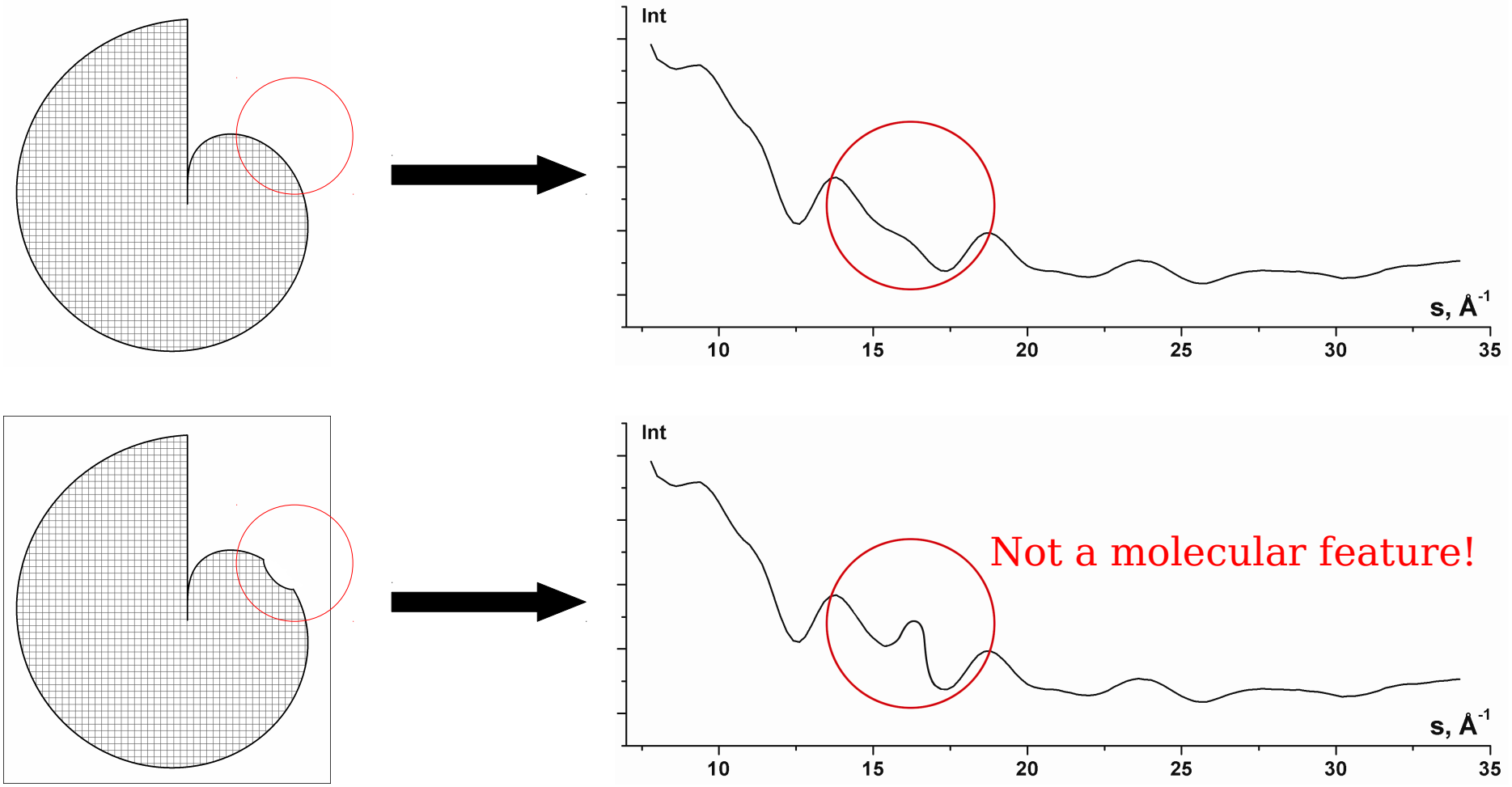
Calibration:
Sector Function and Gas Standard

Sector in GED Experiment



The Role of Sector Shape



It is important to know the sector function!

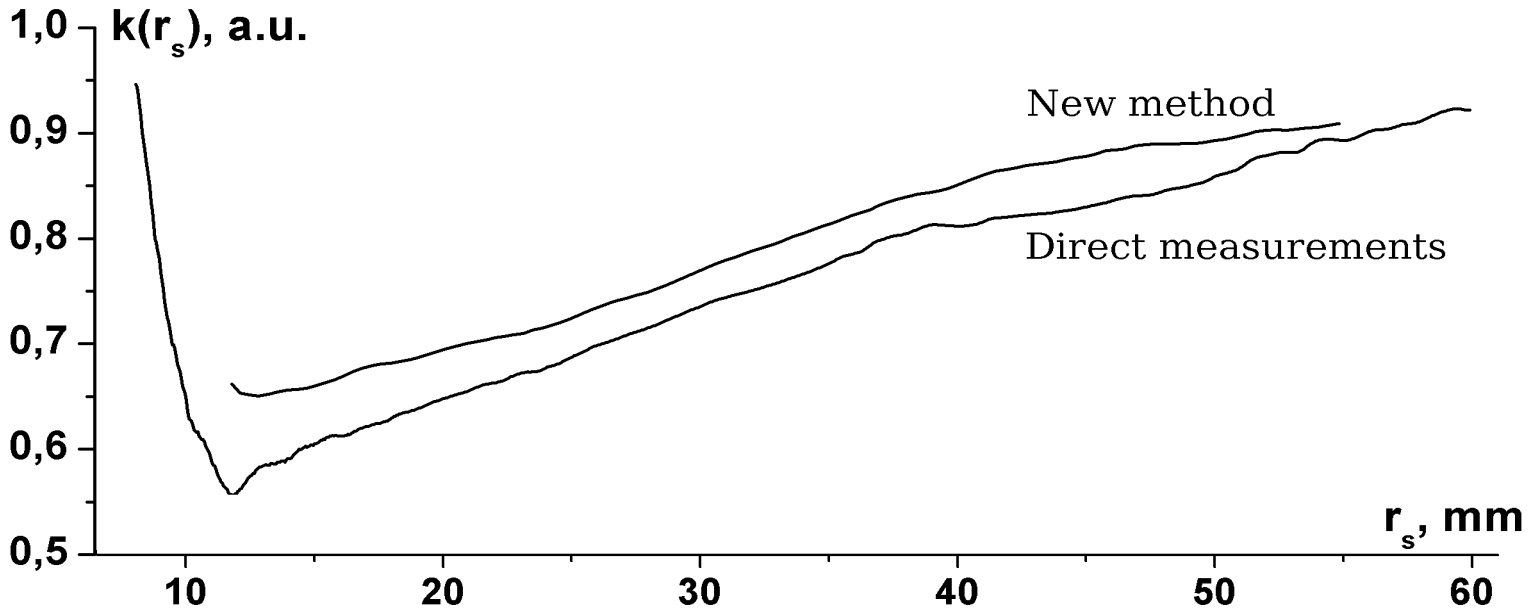
New Method

Main ideas:

- Using of diffraction patterns of gas standards (CCl_4, C_6H_6).
- Applying the least squares method for the estimation of sector function.
- Utilizing of results of direct measurements for regularization.

Model: $$I(s) = t \times K(r) \times I_{at} \times (M(s) + 1 + \beta(s))$$

Functional: $$Q = \sum_i \sum_j W_{i,j} (I^{\exp}_{i,j} - I^{theor}_{i,j})^2 + \alpha \sum_i (k^{\exp}_i - k_i)^2 \to min$$

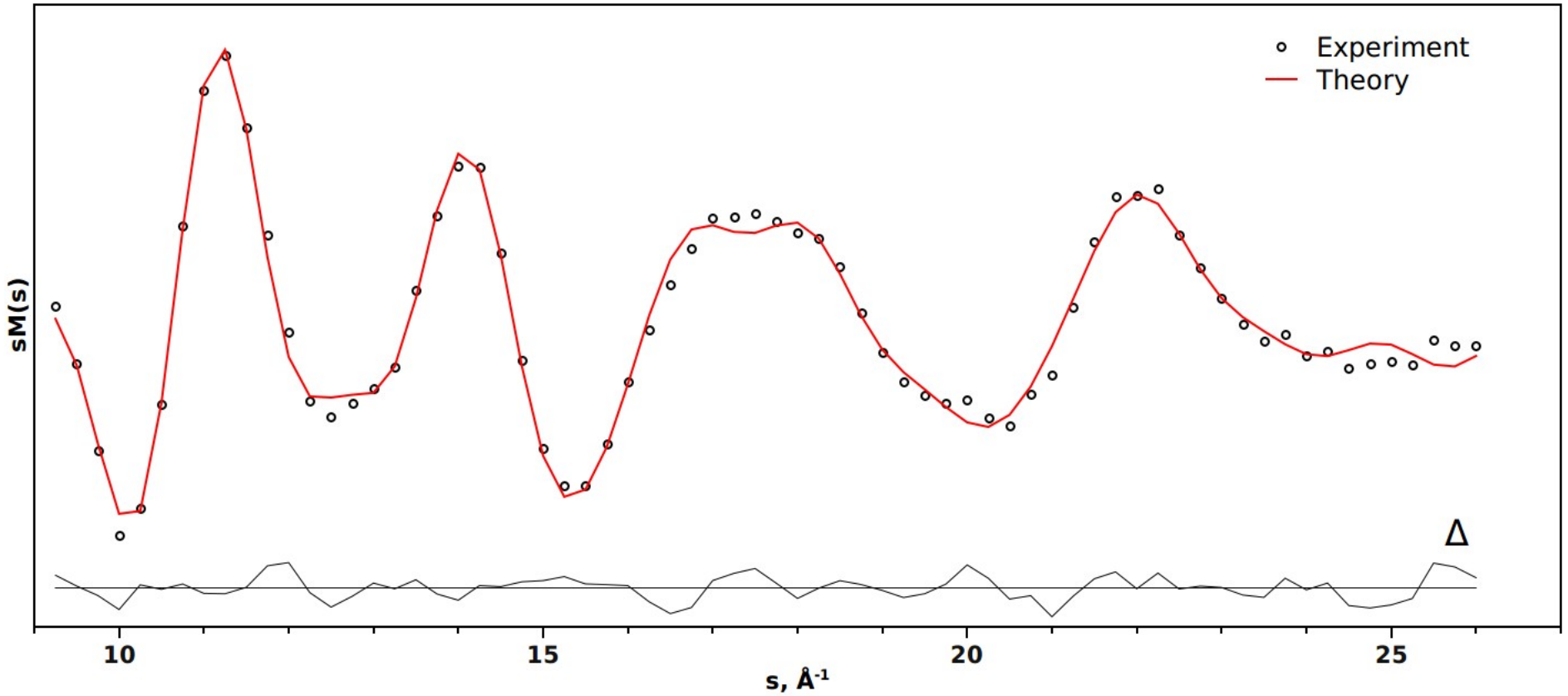


Vishnevskiy, Yu. V. Journal of Molecular Structure 2007, 871, 24–32.

Refinement of Molecular Parameters

Least Squares Method

$$Q = \sum_i W_i \left(sM(s)_i^{\exp} - sM(s)_i^{theor} \right)^2 \rightarrow min$$



Serious disadvantage: the results are unstable in the presence of outliers!

Least Modules Method

$$Q = \sum_i W_i \left| sM(s)_i^{\exp} - sM(s)_i^{theor} \right| \rightarrow min$$

(+) Less sensitive to outliers,
(-) but hard to implement!

Tukey's Bisquare Weights

$$Q=\sum_i W_i\left(sM\left(s\right)_i^{\exp}-sM\left(s\right)_i^{theor}\right)^2\rightarrow min$$

A little magic with weights of experimental data:

$$\Delta_i=\left|sM\left(s\right)_i^{\exp}-sM\left(s\right)_i^{theor}\right| \qquad \delta_i=\frac{\Delta_i}{1.4826\mathrm{m}}$$

m – median of Δ sampling

$$\begin{cases} W_i=\left(1-\left(\frac{\delta_i}{4.685}\right)^2\right)^2, & \delta_i<4.685 \\ W_i=0, & \delta_i\geq 4.685 \end{cases}$$

N. Vogt, Yu. Vishnevskiy, A. Ivanov, J. Vogt, L. Vilkov, Russ. J. Phys. Chem. A, 2008, 82, 2286-2292.
F. Mosteller, J. W. Tukey, Data Analysis and Regression, Addison-Wesley, Reading, MA, 1977

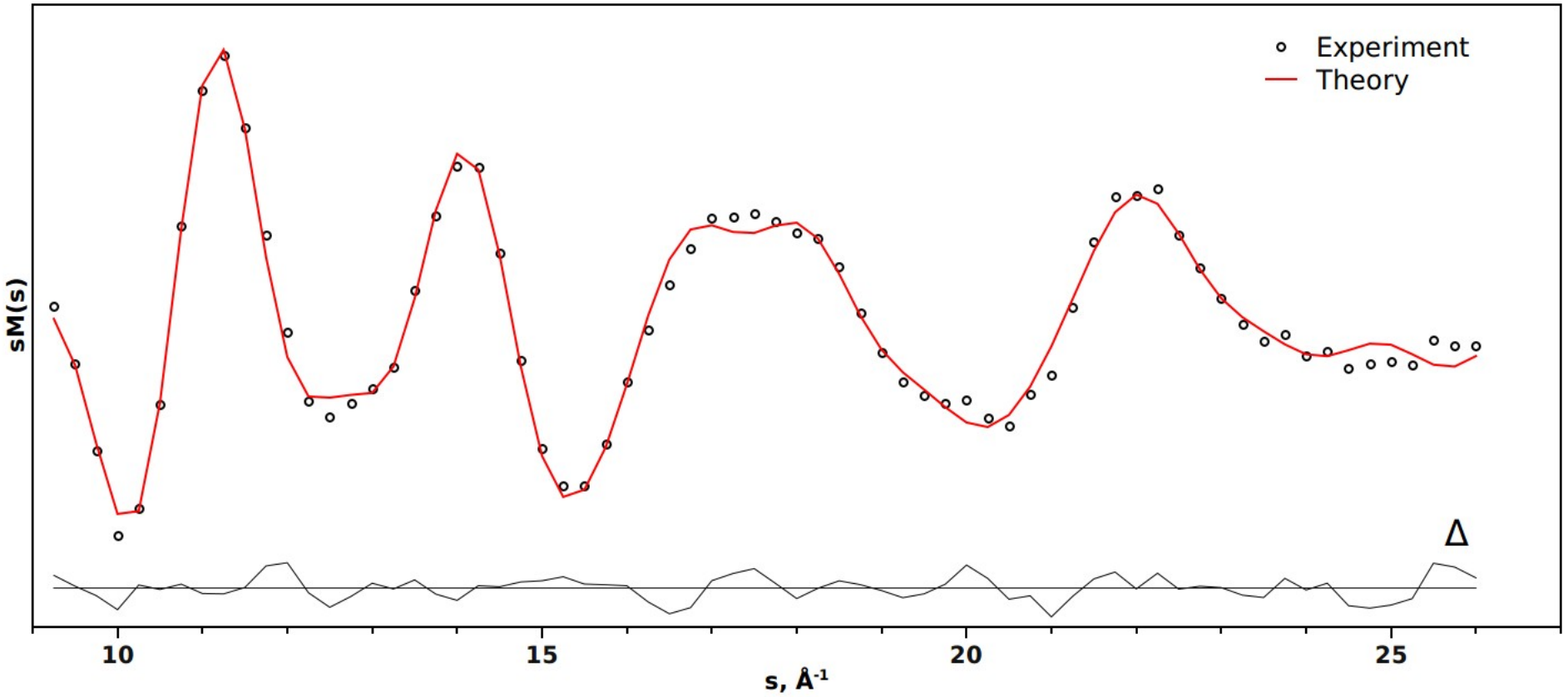
Experiment vs. Model

Structural R-factor

$$R_{str} = \sqrt{\frac{\sum_i \left(sM(s)_i^{\exp} - sM(s)_i^{theor} \right)^2}{\sum_i \left(sM(s)_i^{\exp} \right)^2}} \times 100\,\%$$

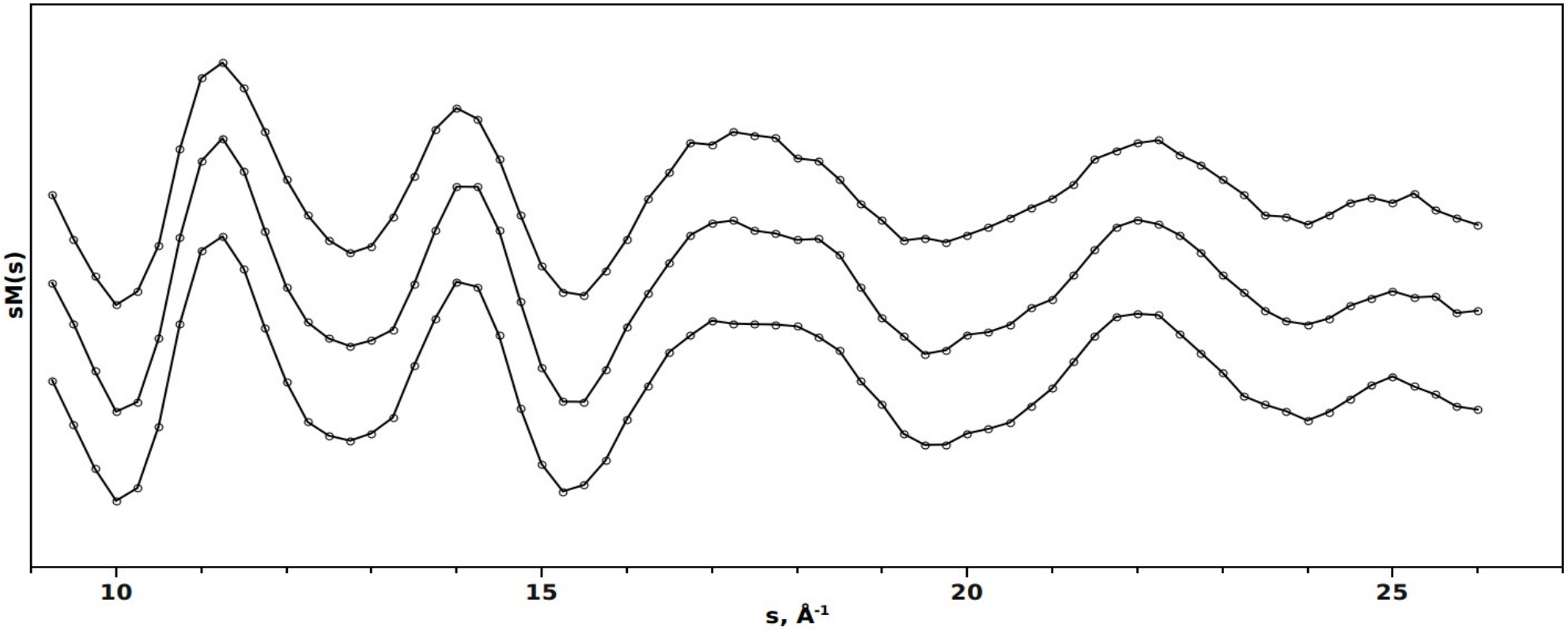
$R_{str} = 7.3\%$

How much is this?



Experimental R-factor

$$R_{\mathrm{exp}} = \sqrt{\frac{\sum_i \sum_j \left(sM(s)^{\mathrm{exp}}_{i,j} - sM(s)^{av}_{i} \right)^2}{\sum_i \sum_j \left(sM(s)^{\mathrm{exp}}_{i,j} \right)^2}} \times 100\,\%$$



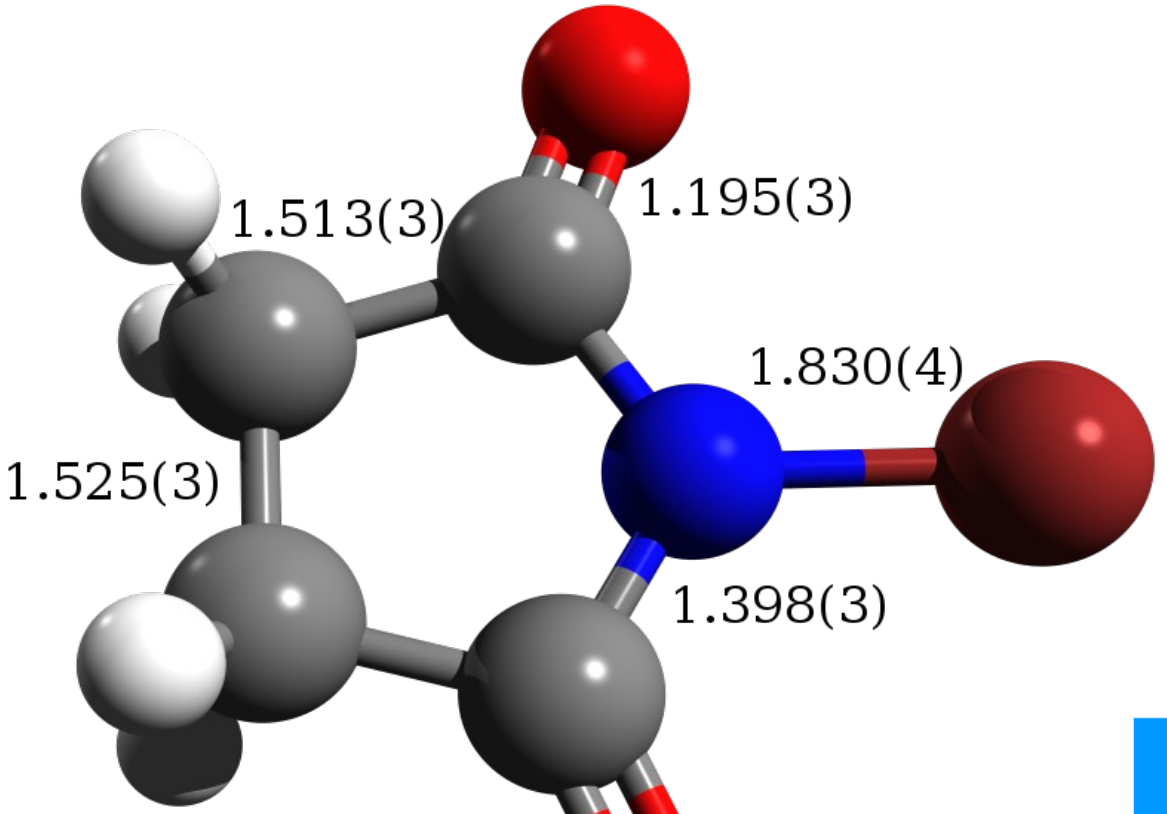
Structural *R*-factor vs. Experimental *R*-factor

1) $R_{str} >> R_{exp}$: Model is worse than experimental data.
2) $R_{str} << R_{exp}$: Model describes experimental noise.
3) $R_{str} \approx R_{exp}$: Optimal agreement between model and data.

Data\R-factor	R_{str}, %	R_{exp}, %
L (361.8 mm)	5.9	7.1
S (196.0 mm)	10.7	7.8
Total	7.3	7.5

Optimal agreement

Equilibrium Experimental Structure of NBS



(C-N-C) = 116.2(6)
(C-C-C) = 106.3(2)
(C-C-N) = 105.7(4)
(N-C=O) = 126.5(6)

Units: angstroms, degrees.

Comparison:

r_a(N-Br)	
$N(CF_3)_2Br$	1.869(4)
$N(CF_3)Br_2$	1.880(3)

Ю. В. Вишневский, ..., IV Национальная кристаллохимическая конференция, 2006, 322.
Minkwitz R., Lamek D., Oberhammer H., Mack H.-G. Zeitschrift für anorganische und allgemeine Chemie, 1994, V. 620, p. 353-356.

What about reliability of results?

To be continued...