Universität Bielefeld

Mitzel Group inorganic & structural chemistry

How "experimental" are structures refined from gas electron diffraction data?

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GED: Refinement of Structure

$$I_{tot} = I_{mol} + I_{at} + I_{bgl}$$

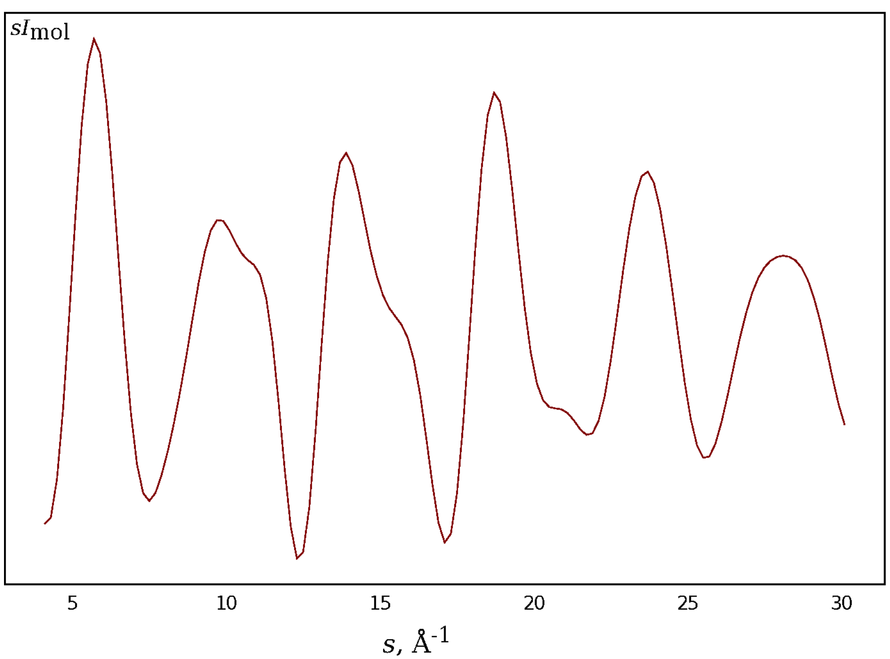
$$sM(s) = \frac{sI_{mol}}{I_{at}} = \sum_{i>j}^{N} g_{i,j}\, e^{-\frac{(sl_{i,j})^2}{2}} \frac{\sin(sr_{i,j} - a_{i,j}s^3)}{sr_{i,j}}$$

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

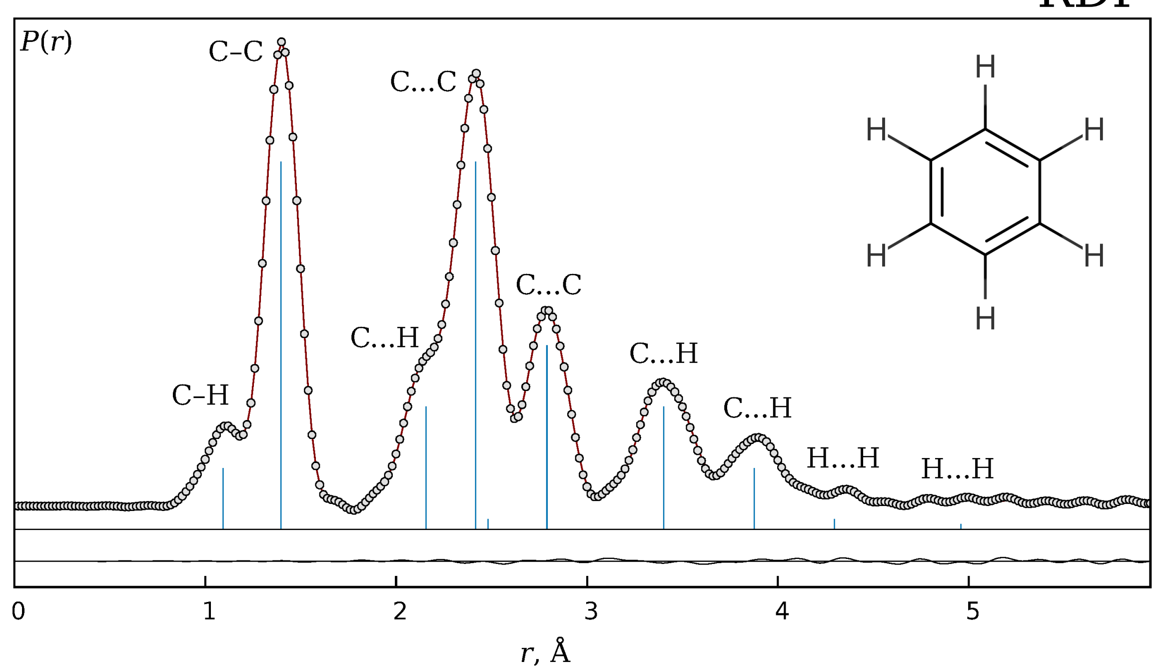
θ – scattering angle,
λ – electron wavelength,
g – scattering factors,
r – interatomic distances,
l – amplitudes,
a – asymmetry constants.

Inverse problem:

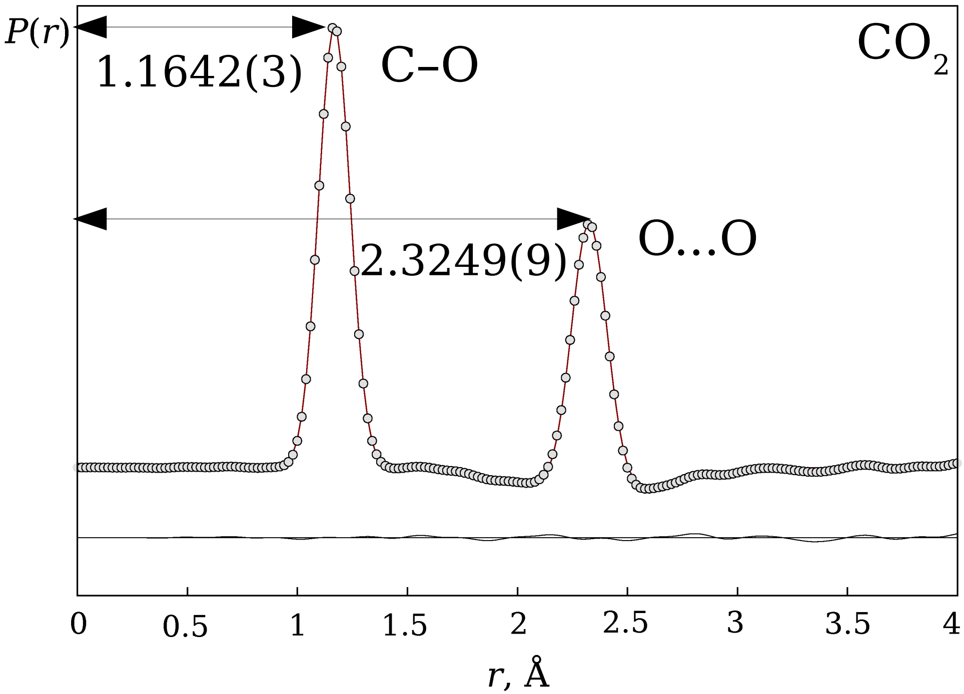
$$Q = \sum_{i}^{N} \left(sM(s|r,l,a)_{model} - sM(s)_{\exp}\right)^2 \to min$$



RDF



Experimental Average Structure



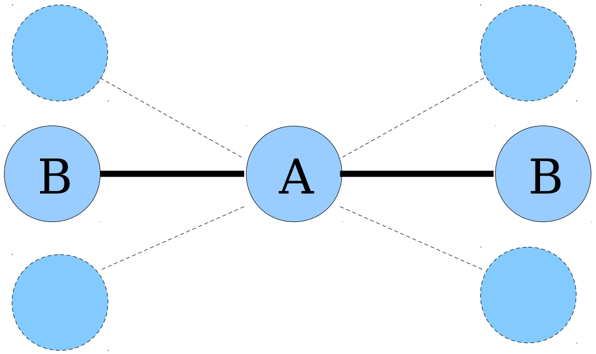
$\delta = 2r_a(\text{C–O}) - r_a(\text{O...O})$

0.0036(5) @ 298 K
0.0059(11) @ 463 K
0.0071(8) @ 627 K
0.0078(10) @ 731 K
0.0093(7) @ 937 K

$r_g = \langle r \rangle$
$r_a = \langle 1/r \rangle^{-1}$

Shrinkage effect:

$r_a(\text{B...B}) < 2r_a(\text{A–B})$



Example:
$\angle_a(\text{Br–Hg–Br}) \sim 170°$

R. J. Mawhorter, M. Fink, B. T. Archer, *J. Chem Phys.* 79, 1983, 170
R. Z. Deyanov, K. P. Petrov, V. V. Ugarov, B. M. Shchedrin, N. G. Rambidi, *J. Struct. Chem.* 26, 1985, 698.

Semi-experimental structure

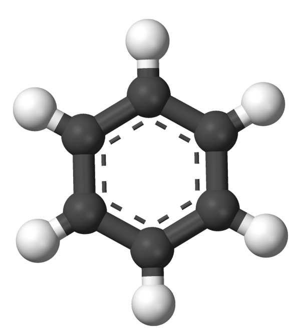
$$sM(s)=\frac{sI_{mol}}{I_{at}}=\sum_{i>j}^{N} g_{i,j}\, e^{-\frac{(sl_{i,j})^2}{2}} \frac{\sin\left(s\left(r_{i,j}-k_{i,j}\right)-a_{i,j}s^3\right)}{s\left(r_{i,j}-k_{i,j}\right)}$$

In most cases refined structures are in fact semi-experimental because of using supplementary theoretical data:

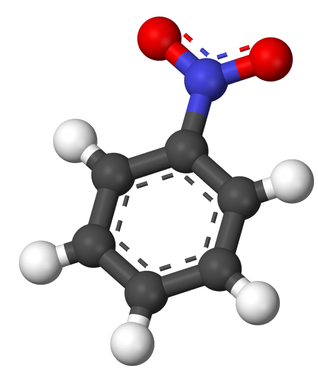
- Corrections to geometrically consistent structure (r_{h0}, r_{h1}, r_{e}).
- Assumed vibrational amplitudes and/or their differences.
- Assumed geometrical parameters and/or their differences.

and/or

- Regularization parameters.



vs.



Regularization

Tikhonov's regularization in GED: Bartel's “predicate observations”, SARACEN

Regularization of internal coordinates:

$$Q = \sum [sM(s)^e - sM(s)^{mod}]^2 + \alpha \sum_i w_i (p_i^0 - p_i^{mod})^2 \rightarrow min$$

Regularization of Cartesian coordinates:

$$Q = \sum [sM(s)^e - sM(s)^{mod}]^2 + \alpha \sum_i^{3N} w_i (x_i^0 - x_i^{mod})^2 \rightarrow min$$

$\alpha = 0 \longrightarrow$ Fully experimental structure (100 % experimental info. in refined prms.)

$\alpha = \infty \longrightarrow$ Fully theoretical structure (0 % exp. info. in refined prms.)

$\alpha = (0, \infty) \longrightarrow$ Semi-experimental structure (**???** %). Used in practice!

L. S. Bartell, D. J. Romenesko, T. C. Wong, in *Molecular Structure by Diffraction Methods,* The Chemical Society, London, 1975, Vol. 3, pp 72 – 79.
A. J. Blake, P. T. Brain, H. McNab, J. Miller, C. A. Morrison, S. Parsons, D. W. H. Rankin, H. E. Robertson, B. A. Smart, *J. Phys. Chem.*, 1996, 100, 12280.
A. N. Tychonoff, *Dokl. Akad. Nauk SSSR*, 1943, 39, 195.

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W2 Scheme

$$Q = \underbrace{\sum \left[sM(s)^{e} - sM(s)^{mod} \right]^2}_{Q_{GED}} + \alpha \underbrace{\sum w \left(x^{0} - x^{mod} \right)^2}_{Q_{REG}} \rightarrow min$$

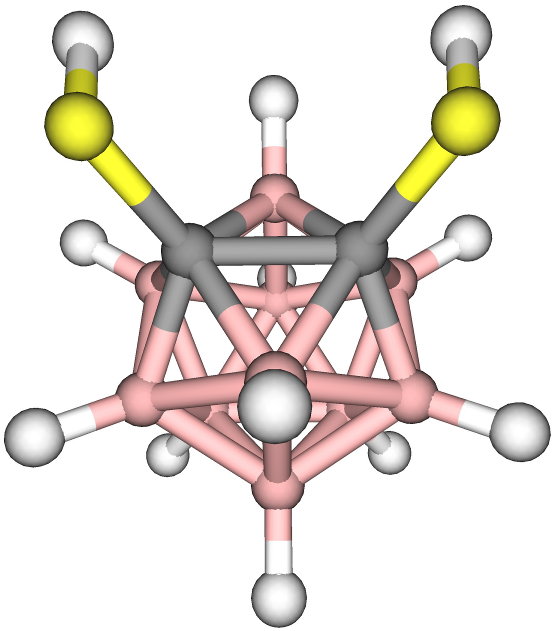
First empirical idea: use second derivatives $\frac{\partial^2 Q_{GED}}{\partial p^2}$ $\frac{\partial^2 Q_{REG}}{\partial p^2}$

$$W_{GED} = \frac{\frac{\partial^2 Q_{GED}}{\partial p^2}}{\frac{\partial^2 Q_{GED}}{\partial p^2} + \frac{\partial^2 Q_{REG}}{\partial p^2}}$$

See coming paper for theoretical basis, generalization.

T. Baše, P. D. Lane, Yu. V. Vishnevskiy, D. Tikhonov, C. G. Reuter, N. W. Mitzel, D. A. Wann, D. Hnyk, *Inorg. Chem.*, in preparation.

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



	MP2/cc-pVTZ	GED		
	r_e	r_e	r_g	w_{GED}
*r*B–H	1.181	1.186(5)	1.209(5)	0.001
*r*S–H	1.339	1.341(5)	1.361(5)	0.007
*r*C–B	1.704	1.702(4)	1.722(4)	0.168
*r*C–C	1.756	1.755(7)	1.765(7)	0.079
*r*B–B	1.782	1.777(5)	1.793(5)	0.176
*r*C–S	1.769	1.755(4)	1.770(4)	0.357
∠C–B–C	61.5	61.6(2)		?
∠C–B–B	58.3	58.4(2)		?
∠B–C–B	63.4	63.3(2)		?
∠B–B–B	60.0	60.0(2)		?
∠S–C–C	118.0	118.0(1)		?
∠C–B–H	116.7	116.7(3)		?
|∠CCSH(syn)|	95.2	95.2(2)		?

Angles: coincidence?

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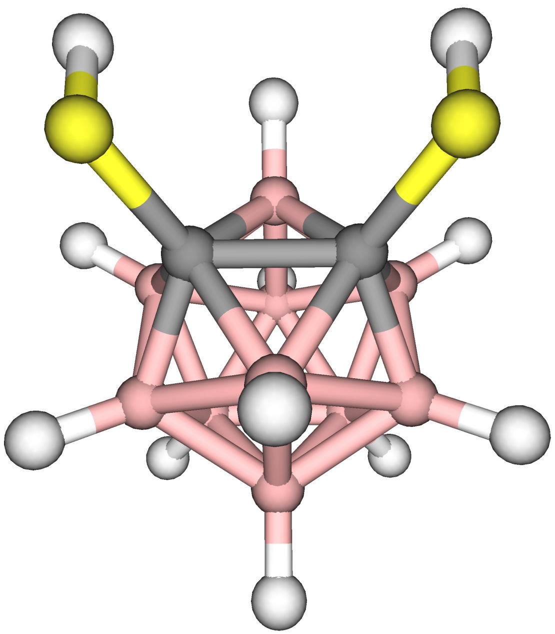
closo-1,2-$(SH)_2$-1,2-$C_2B_{10}H_{10}$



	MP2/cc-pVTZ	GED		
	r_e	r_e	r_g	w_{GED}
*r*B–H	1.181	1.186(5)	1.209(5)	0.001
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*r*C–S	1.769	1.755(4)	1.770(4)	0.357
∠C–B–C	61.5	61.6(2)		0.051
∠C–B–B	58.3	58.4(2)		0.055
∠B–C–B	63.4	63.3(2)		0.053
∠B–B–B	60.0	60.0(2)		0.036
∠S–C–C	118.0	118.0(1)		0.128
∠C–B–H	116.7	116.7(3)		0.015
|∠CCSH(syn)|	95.2	95.2(2)		0.0007

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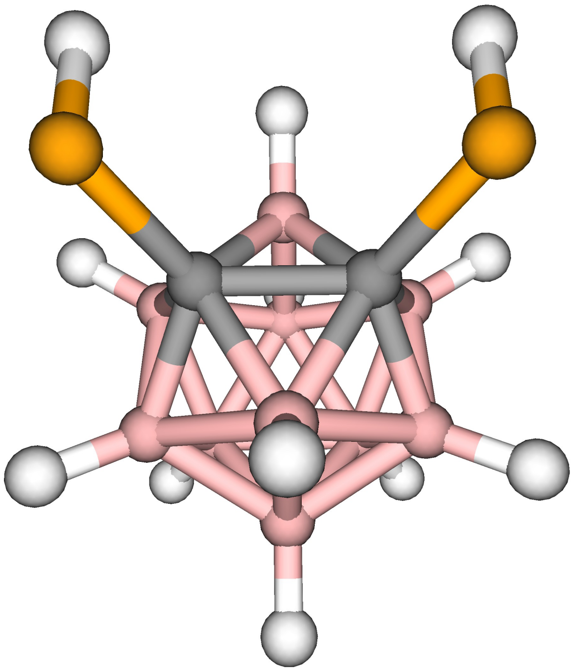
closo-1,2-$(SeH)_2$-1,2-$C_2B_{10}H_{10}$



	MP2/cc-pVTZ	GED			
		α = 0.7		α = 43	
	r_e	r_e	w	r_e	w
*r*B–H	1.181	1.197(20)	**0.145**	1.188(4)	**0.002**
*r*Se–H	1.454	1.508(17)	**0.388**	1.457(4)	**0.024**
*r*C–C	1.731	1.750(28)	**0.933**	1.726(5)	**0.172**
*r*B–B	1.782	1.777(19)	**0.943**	1.775(3)	**0.236**
*r*C–Se	1.904	1.902(10)	**0.987**	1.904(3)	**0.521**
∠C–B–B	58.3	58.2(7)	**0.908**	58.4(1)	**0.123**
∠B–B–B	60.0	60.0(7)	**0.764**	60.0(1)	**0.055**
∠Se–C–C	119.2	119.2(4)	**0.971**	119.3(1)	**0.319**
∠Se–C–B	118.9	119.1(9)	**0.908**	118.9(2)	**0.172**
∠B–B–H	123.1	123.0(12)	**0.506**	123.1(2)	**0.016**
|∠CCSeH|	92.1	93.9(7)	**0.243**	92.7(1)	**0.002**
R_f, %	10.8	4.0		5.1	

Want more “experiment” in refined parameters? No problem, but be ready to pay for this!

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W12 Scheme: more theory

General form of functional: $\Phi = \sum_i \Phi_i \to min$

Associated distributions (Gaussian approximation): $p_i = \frac{1}{\sqrt{2\pi}\sigma_i} \exp\left(\frac{-(\xi - \mu_i)^2}{2\sigma_i^2}\right)$

Kullback-Leibler divergence: $J(f_1, f_2) = \int f_1 \ln\left(\frac{f_2}{f_1}\right) dx + \int f_2 \ln\left(\frac{f_1}{f_2}\right) dx$

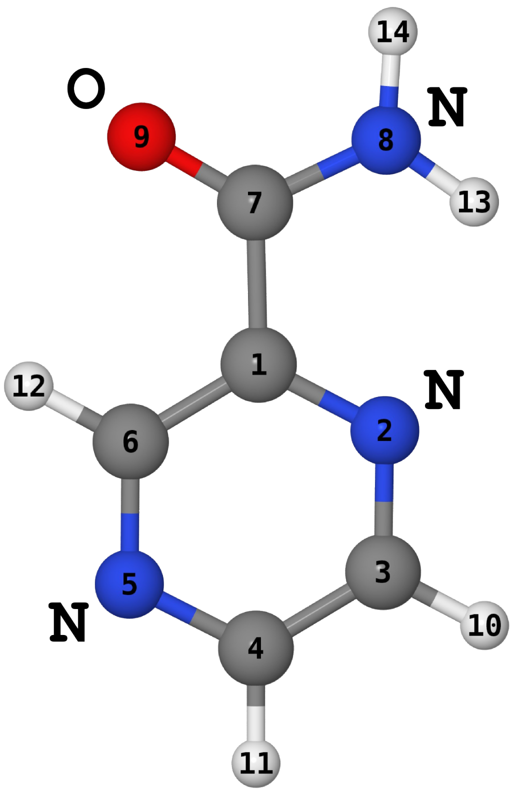
Derivatives: $a_i^{(k)} = \frac{\partial^k \Phi_i}{\partial \xi^k}$ $\qquad a^{(k)} = \sum_i a_i^{(k)}$

$$J(p_i, p) = \frac{1}{2}\left[\left(\frac{a_i^{(1)}}{a_i^{(2)}} - \frac{a^{(1)}}{a^{(2)}}\right)^2 (a_i^{(2)} + a^{(2)}) + \frac{a^{(2)}}{a_i^{(2)}} + \frac{a_i^{(2)}}{a^{(2)}} - 2\right]$$

$$w_i = \frac{\frac{1}{J(p_i, p)}}{\sum_j \frac{1}{J(p_j, p)}} = \frac{1}{1 + J(p_i, p) \sum_{j \neq i} \frac{1}{J(p_j, p)}}$$

S. Kullback, R. A. Leibler, *Ann. Math. Stat.*, 22, 1951, 79.
D. Tikhonov, Yu. V. Vishnevskiy, A. N. Rykov, O. E. Grikina, L. S. Khaikin, *J. Mol. Struct.*, 2016, in press.

W12 vs. W2: Pyrazinamide

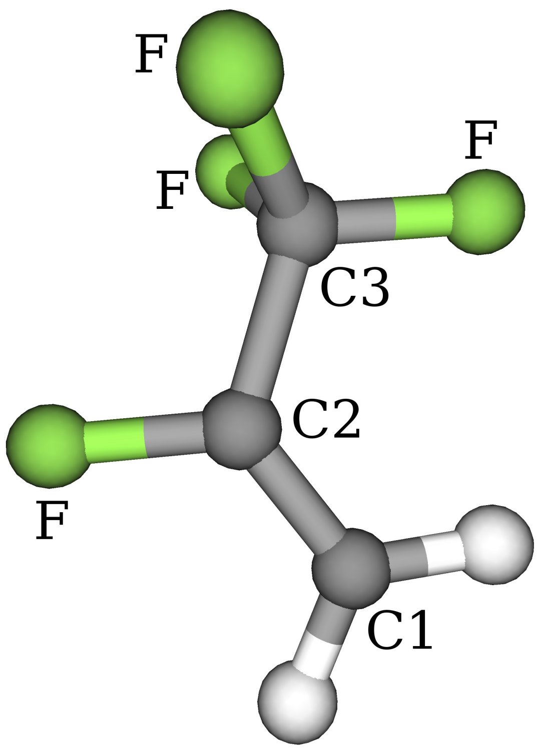


	MP2(full)/ cc-pwCVTZ	GED		
	r_e	r_e	$w12$	$w2$
rC1–N2	1.336	1.341(2)	**1.00**	**0.96**
rC1–C6	1.391	1.404(2)	**1.00**	**0.96**
rC3–H10	1.081	1.082(4)	**0.02**	**0.21**
∠N2–C3–C4	122.0	122.1(2)	**0.90**	**0.68**
∠N8–C7–O9	125.2	124.9(2)	**1.00**	**0.88**
$\angle(\text{X–C3–H10})_{av}$	119.1	119.0(3)	**0.26**	**0.39**
∠H13–N8–H14	121.8	121.8(3)	**0.00**	**0.03**

D. Tikhonov, Yu. V. Vishnevskiy, A. N. Rykov, O. E. Grikina, L. S. Khaikin, *J. Mol. Struct.*, 2016, in press.

GED Data + Rotational Constants

$$Q = \underbrace{\sum \left[sM(s)^{\exp} - sM(s)^{mod} \right]^2}_{Q_{GED}} + \alpha \underbrace{\sum w \left(B^{\exp} - B^{mod} \right)^2}_{Q_{ROT}} \rightarrow min$$



Parameter	Calcd.	MW	GED	GED+MW	W_{GED}
rC1–C2	1.323	1.319(2)	1.324(1)	1.317(1)	**0.15**
rC2–C3	1.503	1.503(2)	1.494(1)	1.497(1)	**0.15**
rC2–F	1.335	1.333(1)	1.333(1)	1.334(1)	**0.23**
$r(\text{C3–F})_{av}$	1.333	1.333(1)	1.334(1)	1.335(1)	**0.23**
$r(\text{C1–H})_{av}$	1.078	1.070(29)	1.098(4)	1.085(3)	**0.36**
∠C1–C2–C3	125.9	126.1(1)	124.7(1)	125.8(1)	**0.22**
φC1–C2–C3–F	120.3	120.5(1)	121.5(1)	120.5(1)	**0.02**
R_f, %			4.45	4.72	

Calcd. = full-CCSD(T)/cc-pwCVTZ

GED+MW: $|B^{\exp} - B^{mod}|$ were approx. 1% of dB.

M. D. Marshall, H. O. Leung, B. Q. Scheetz, J. E. Thaler, J. S. Muenter, *J. Mol. Spectr.*, 266, 2011, 37-42.

Conclusions

Nobody believes theoretical calculations,
except the one who did them.

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

Thank you for your attention!