“Best Things dwell out of Sight
The Pearl — the Just — Our Thought.”
(Emily Dickinson)

Inversion and Super-resolution of Ultrafast Scattering

Adi Natan

16 March 2023

Ultrafast Imaging and Tracking Instrumentation, Methods and Applications Conference (ULITIMA)

U.S. DEPARTMENT OF ENERGY
Office of Science

Stanford PULSE Institute

SLAC NATIONAL ACCELERATOR LABORATORY

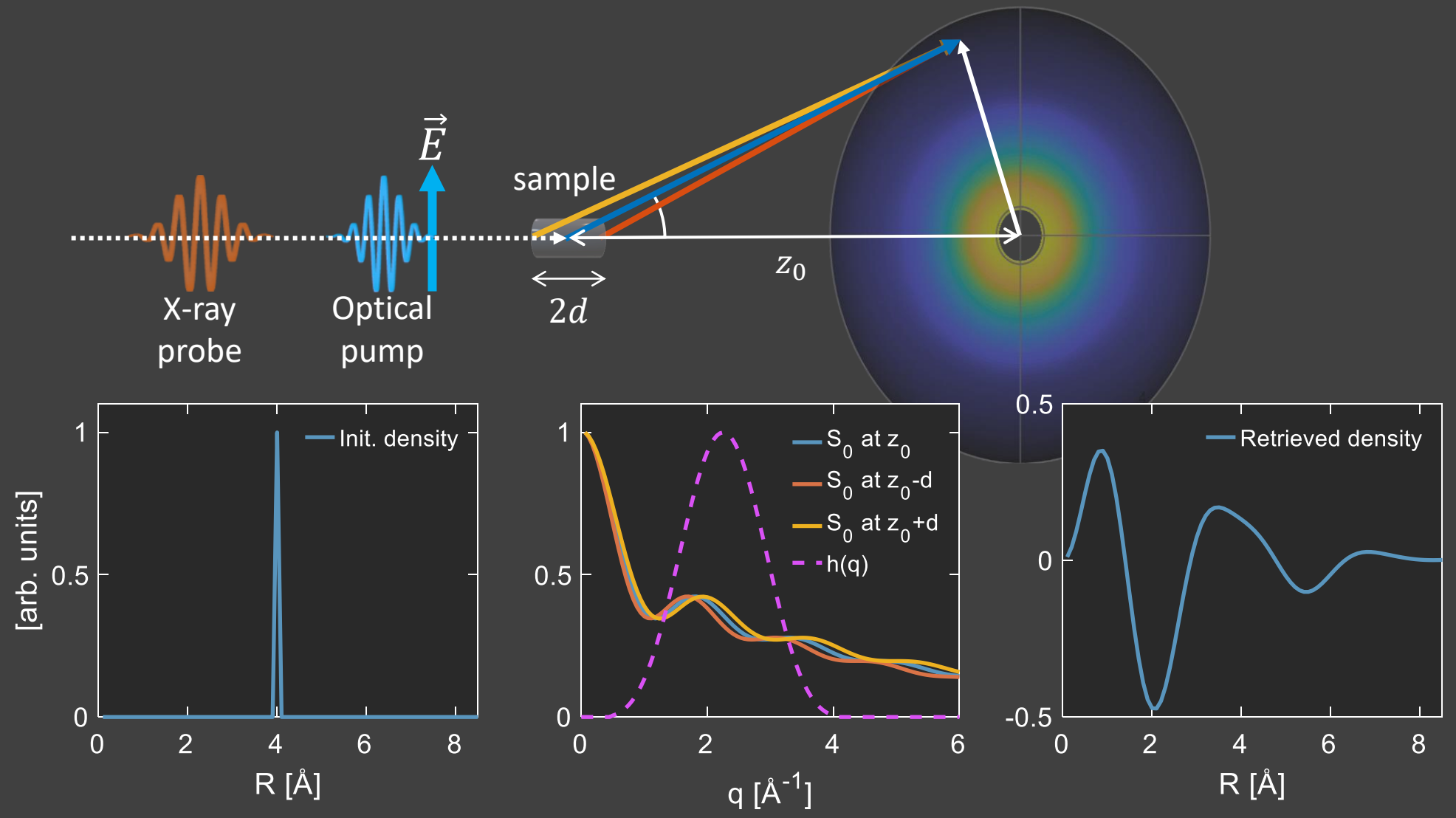
There’s no place like Real Space…

SLAC

- Intuitive view of structural dynamics.
- Without bias toward Franck-Condon active modes
- Model free approach.
- Pair Distribution Function analysis is a mature technique for static (mostly) periodic structures.

But there’s one challenge… the q-range

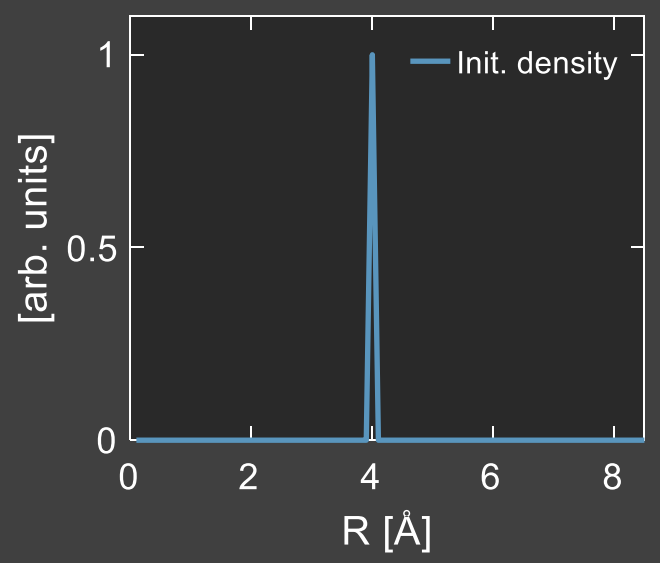
Distortions in Real-space inversion due to limited q-range

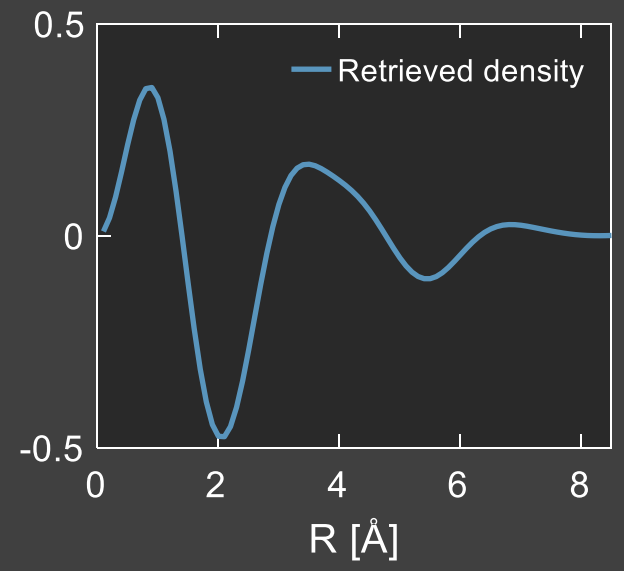


Natan, Physical Review A 107 (2), 023105 (2023)

Natural Scattering Kernels (NSK)

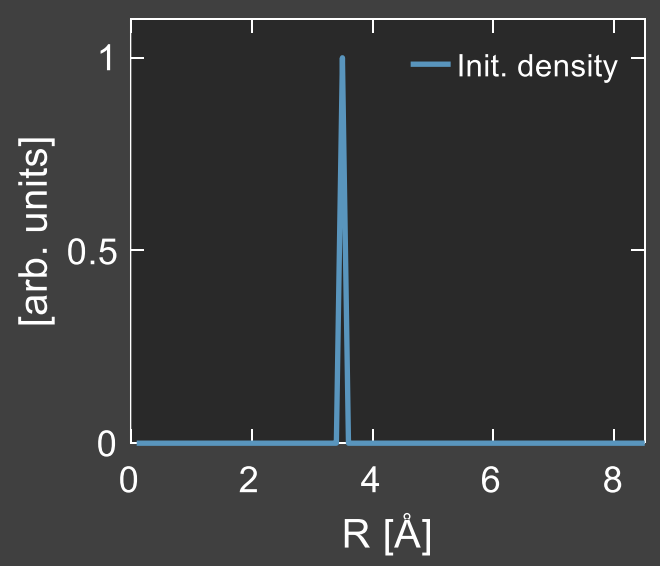
$NSK(4)$ is the function that describes the distortion that a $\delta(R-4)$ charge density undergoes in terms of the measurement and analysis.

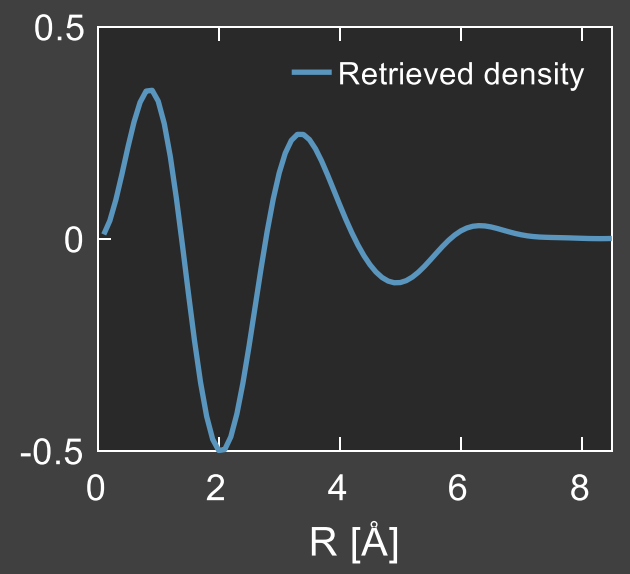




Natural Scattering Kernels (NSK)

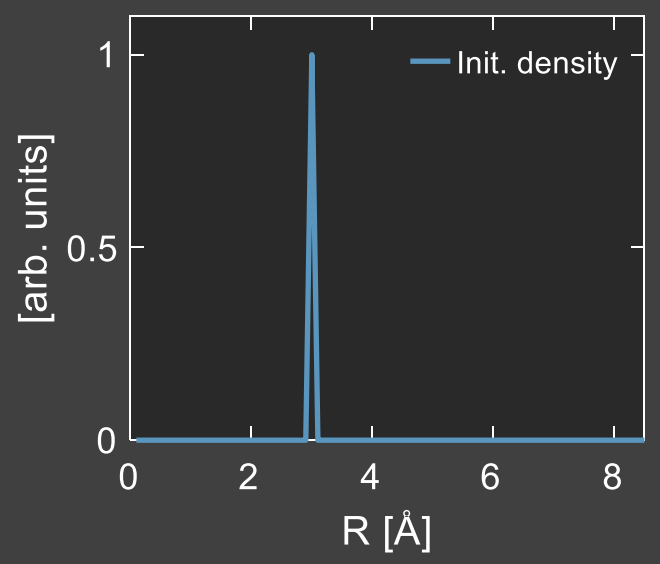
$NSK(3.5)$ is the function that describes the distortion that a $\delta(R-3.5)$ charge density undergoes in terms of the measurement and analysis.

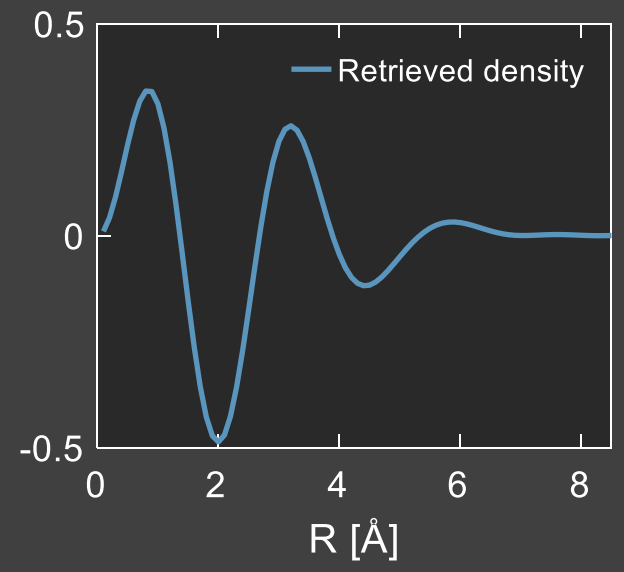




Natural Scattering Kernels (NSK)

$NSK(3)$ is the function that describes the distortion that a $\delta(R-3)$ charge density undergoes in terms of the measurement and analysis.

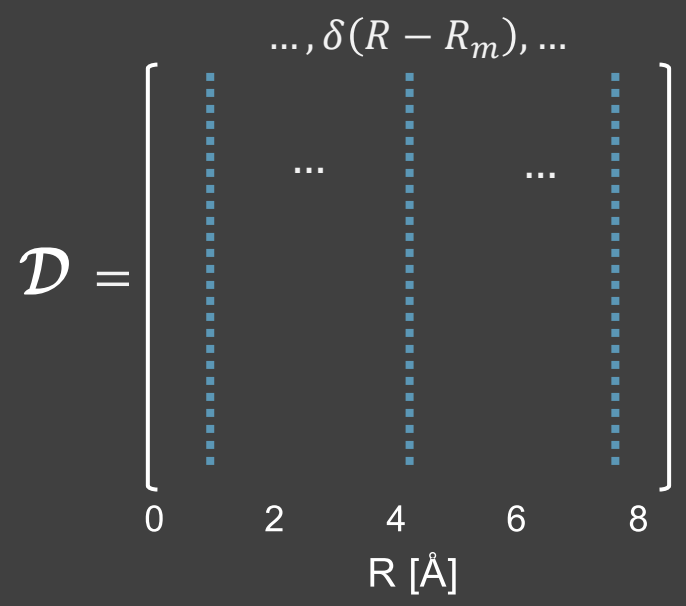


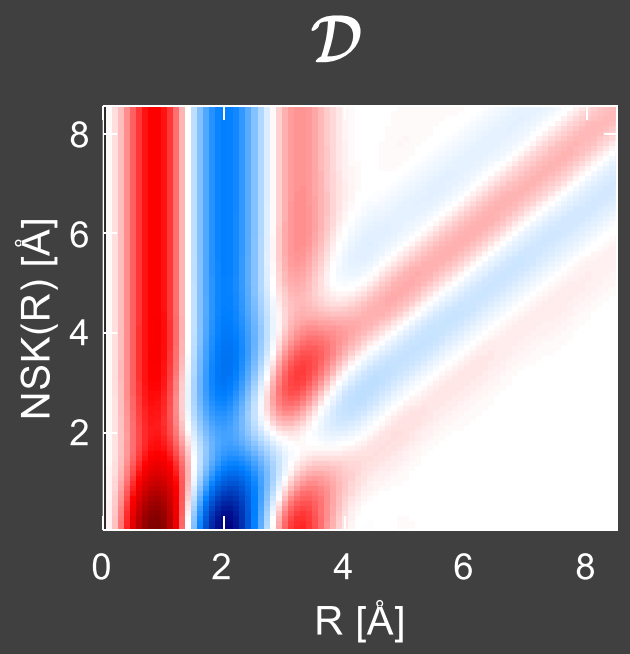


Natural Scattering Kernels (NSK)

$NSK(R_m)$ is the function that describes the distortion that a $\delta(R - R_m)$ charge density undergoes in terms of the measurement and analysis.

We can form a dictionary $\mathcal{D}$ to explain distorted real-space inversions:



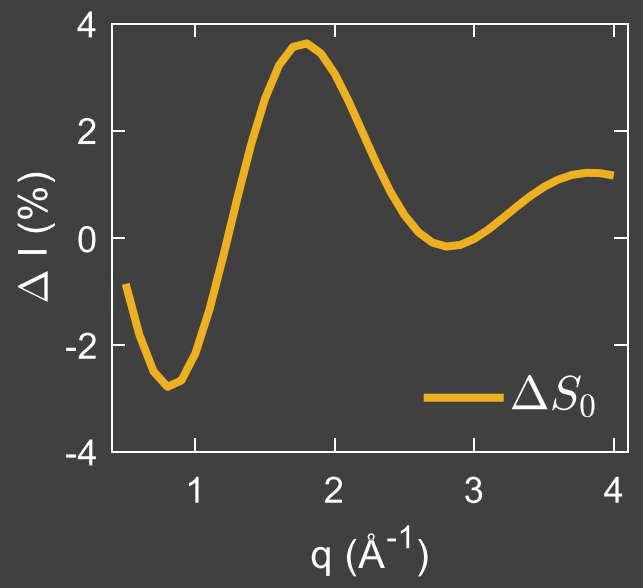


Natural Scattering Kernels (NSK)

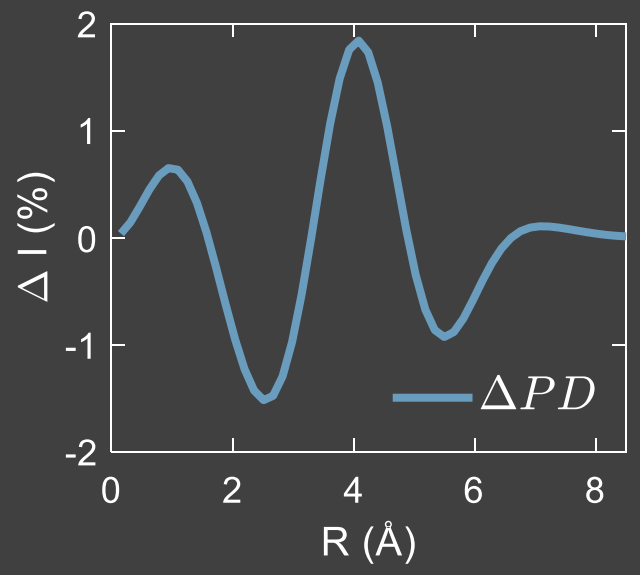
We represent the "distorted" real-space inversion in a linear model: $\Delta PD = \mathcal{D}\mathrm{w}$

"Measurement" → Inversion

ΔS_0

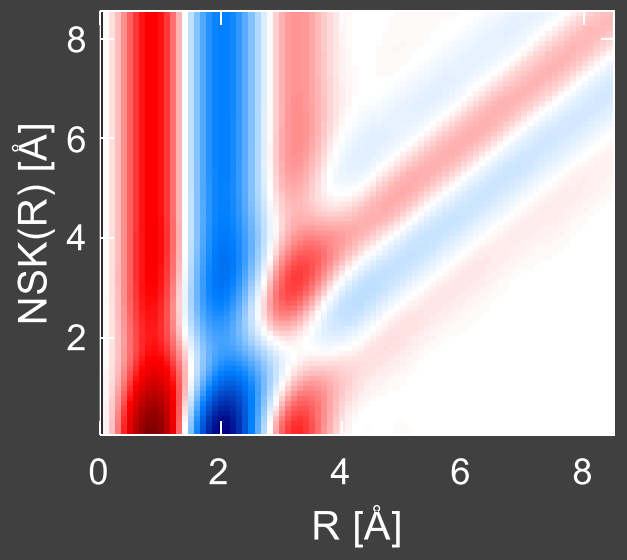


ΔPD



=

$\mathcal{D}$



$*$ w

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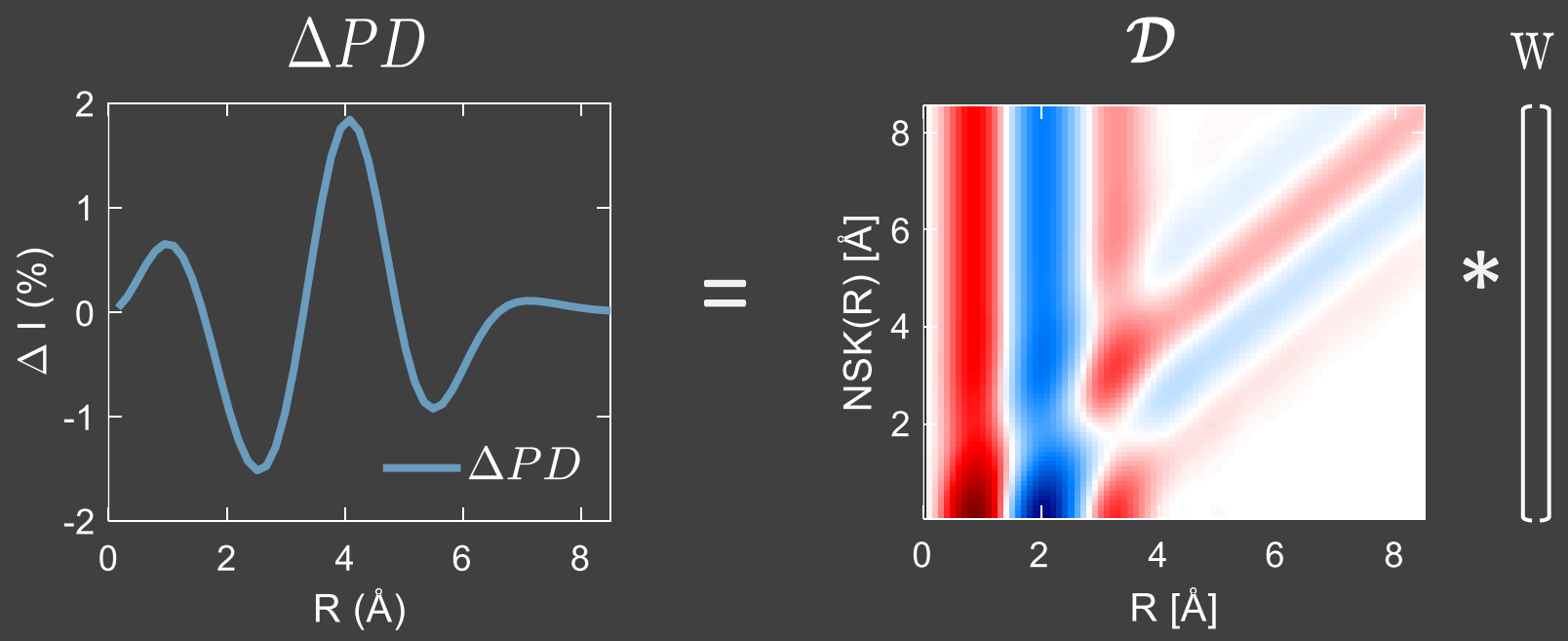
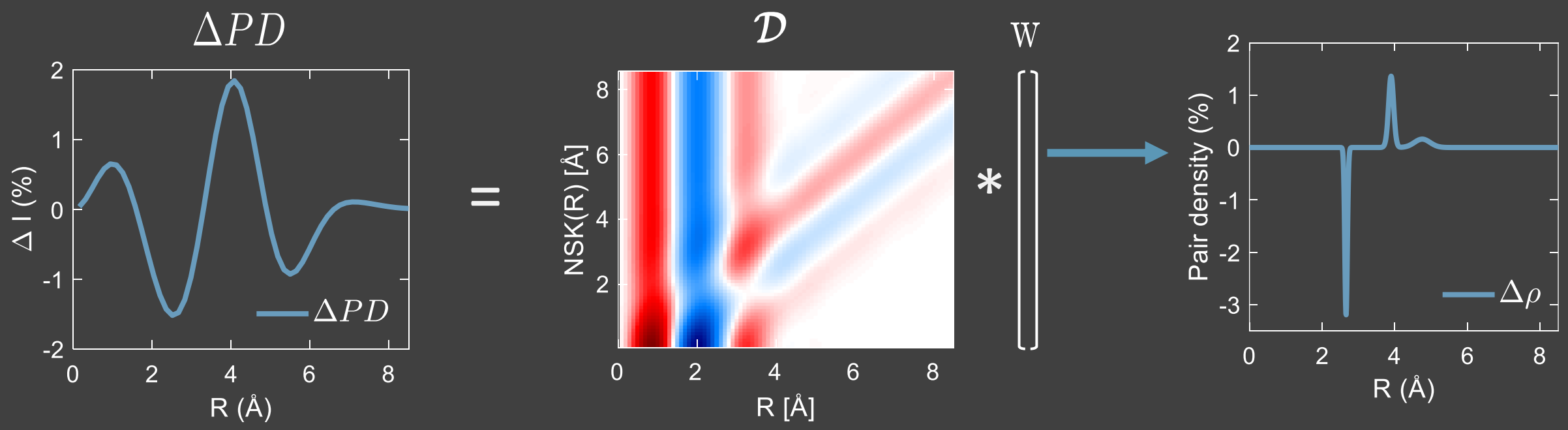


Natural Scattering Kernels (NSK)

We represent the "distorted" real-space inversion in a linear model: $\Delta PD = \mathcal{D}\mathrm{w}$

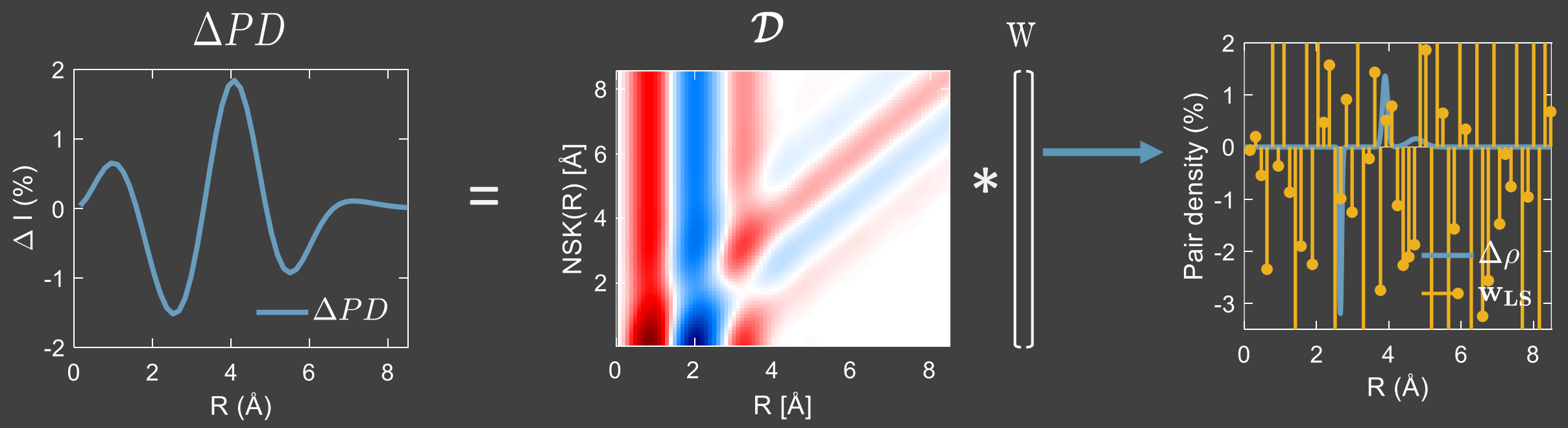
And want to estimate the weights vector to recover: $\Delta\rho(R) = \sum \mathrm{w}_m \delta(R - R_m)$



Natural Scattering Kernels (NSK)

Least squares (the naïve solution): minimize $\|\Delta PD - D\boldsymbol{w}\|^2$

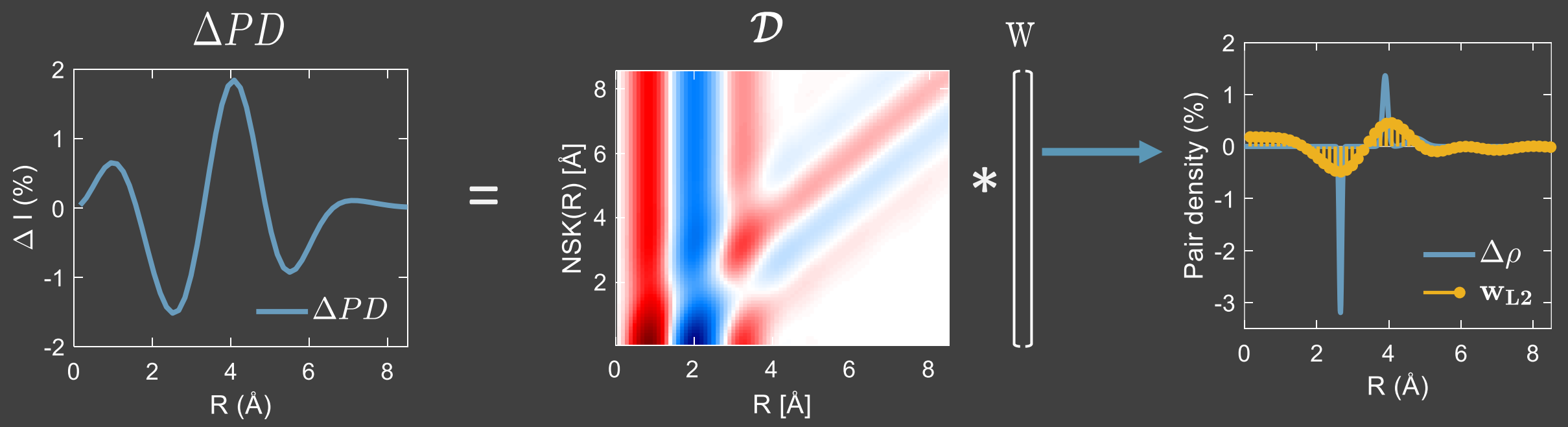
This has the analytic (and linear) solution: $\boldsymbol{w}_{LS} = D^{-1}\Delta PD$



Deconvolution - (smoothness prior):

L2 regularized Least squares: minimize $\|\Delta PD - D\boldsymbol{w}\|^2 + \epsilon\|\boldsymbol{w}\|_2$ $\qquad \|\boldsymbol{w}\|_2 = \sum w_m^2$

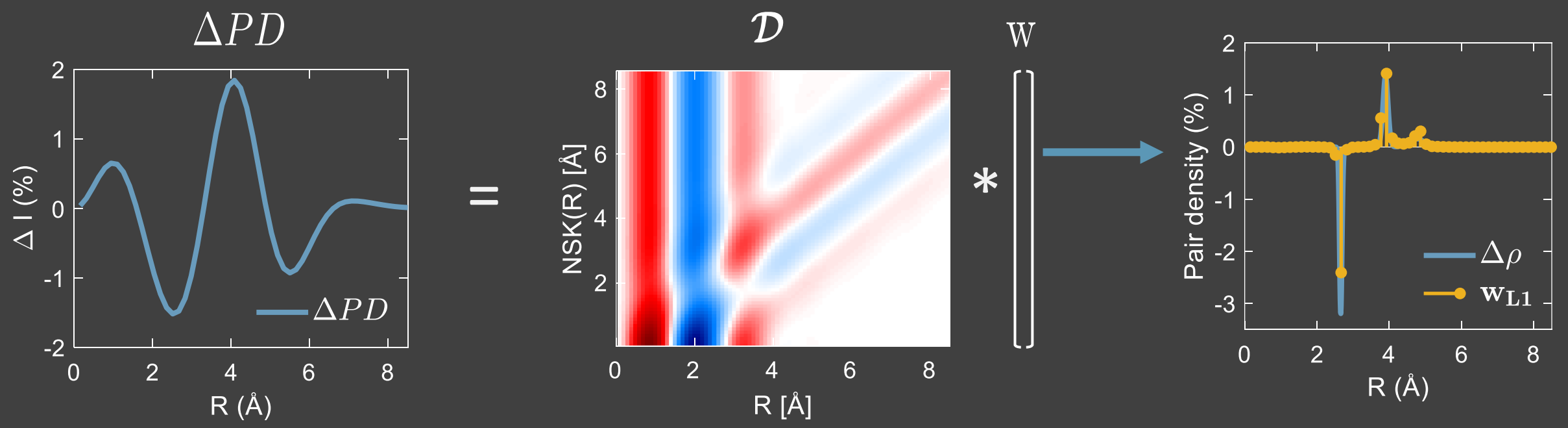
This has the analytic (and linear) solution: $\boldsymbol{w}_{L2} = (D^T D + \epsilon I)^{-1} D^T \Delta PD$



Deconvolution - (sparsity prior):

L1 regularized Least squares: minimize $\|\Delta PD - D\boldsymbol{w}\|^2 + \epsilon\|\boldsymbol{w}\|_1$ $\|\boldsymbol{w}\|_1 = \sum |w_m|$

can be solved using convex optimization (LASSO, BPDN) + minimal separation condition

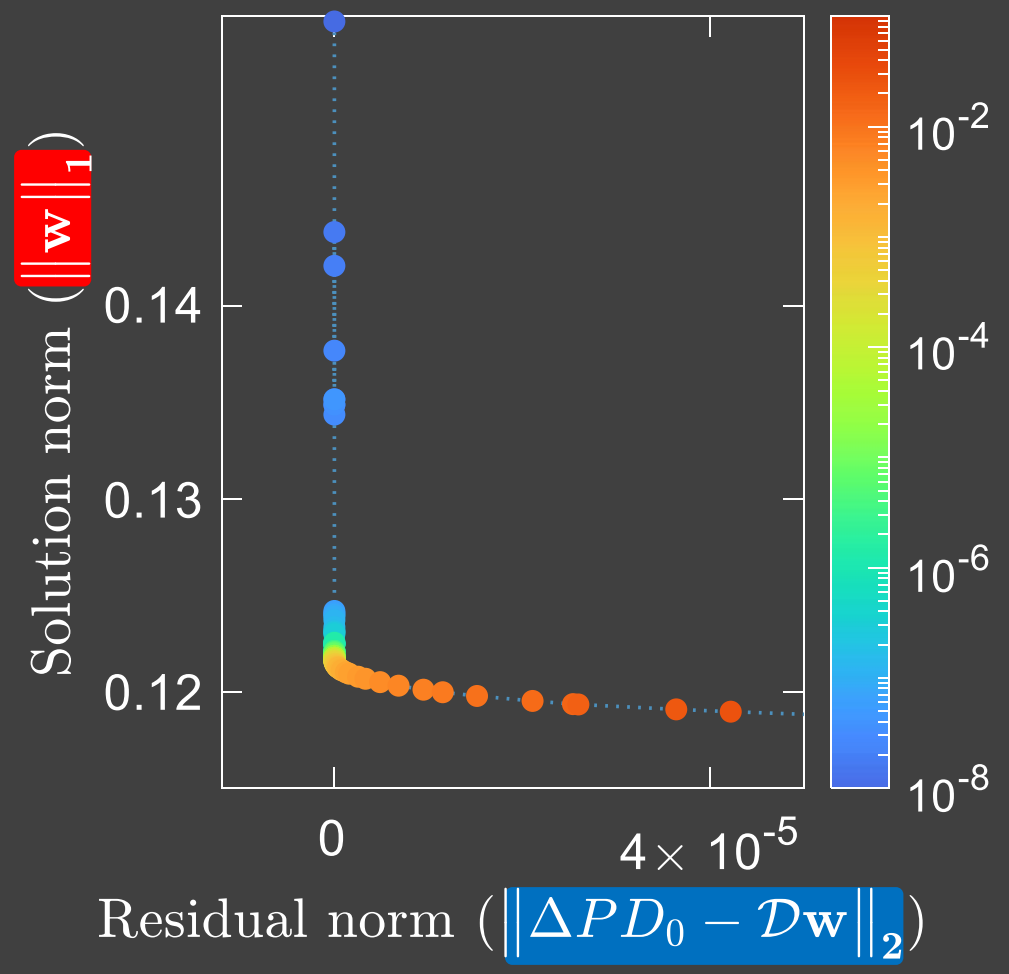


Natan, Physical Review A 107 (2), 023105 (2023)

How to find the regularization parameter ϵ ?

L1 regularized Least squares: minimize $\|\Delta PD - D\boldsymbol{w}\|^2 + \epsilon\|\boldsymbol{w}\|_1$

$$\|\boldsymbol{w}\|_1 = \sum |w_m|$$



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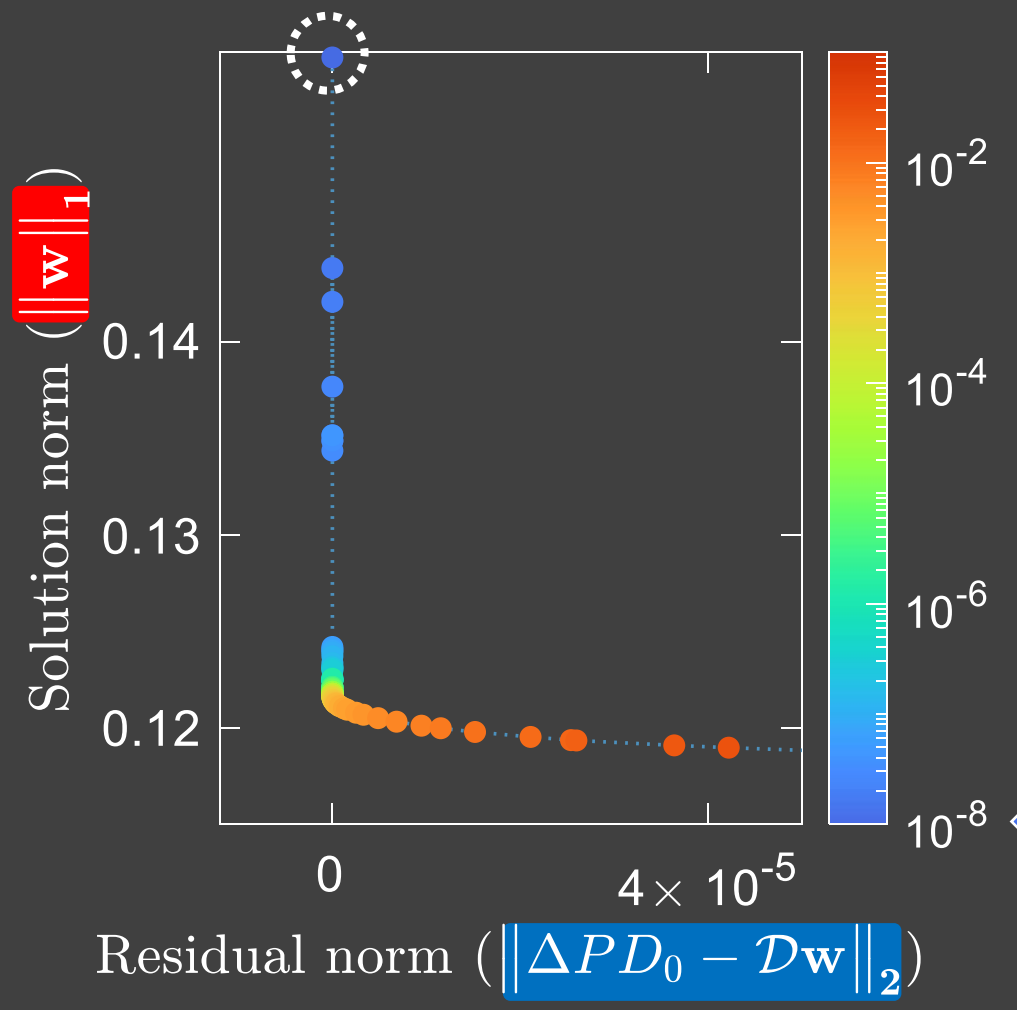
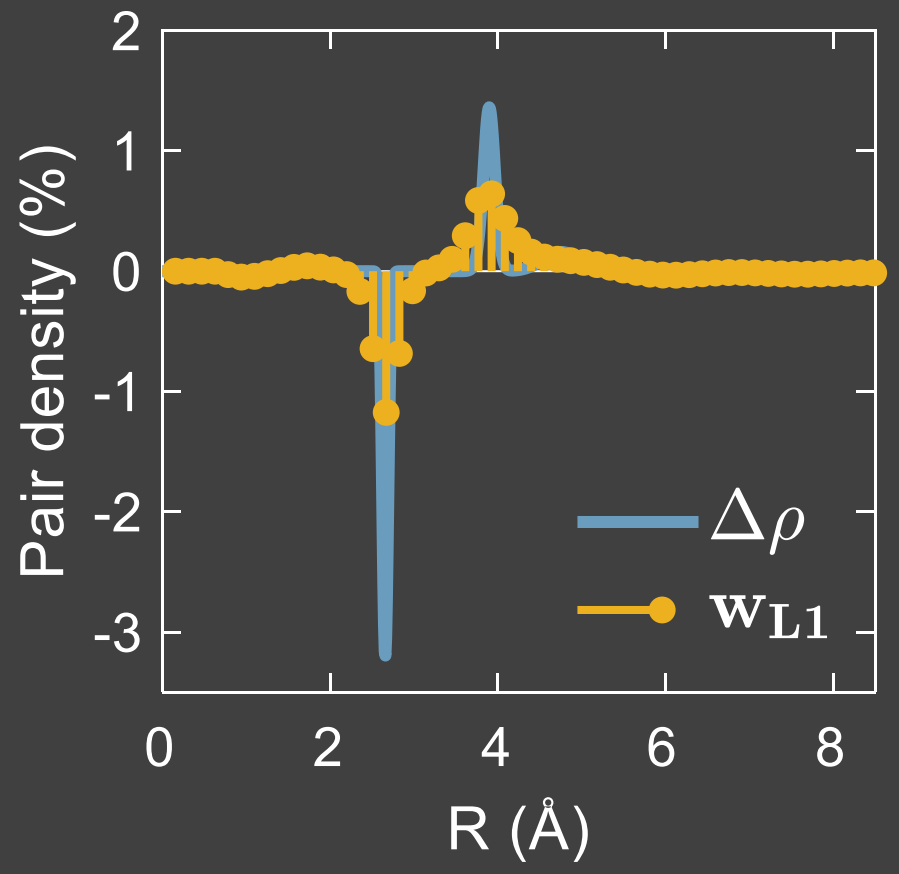


$\epsilon = 10^{-8}$



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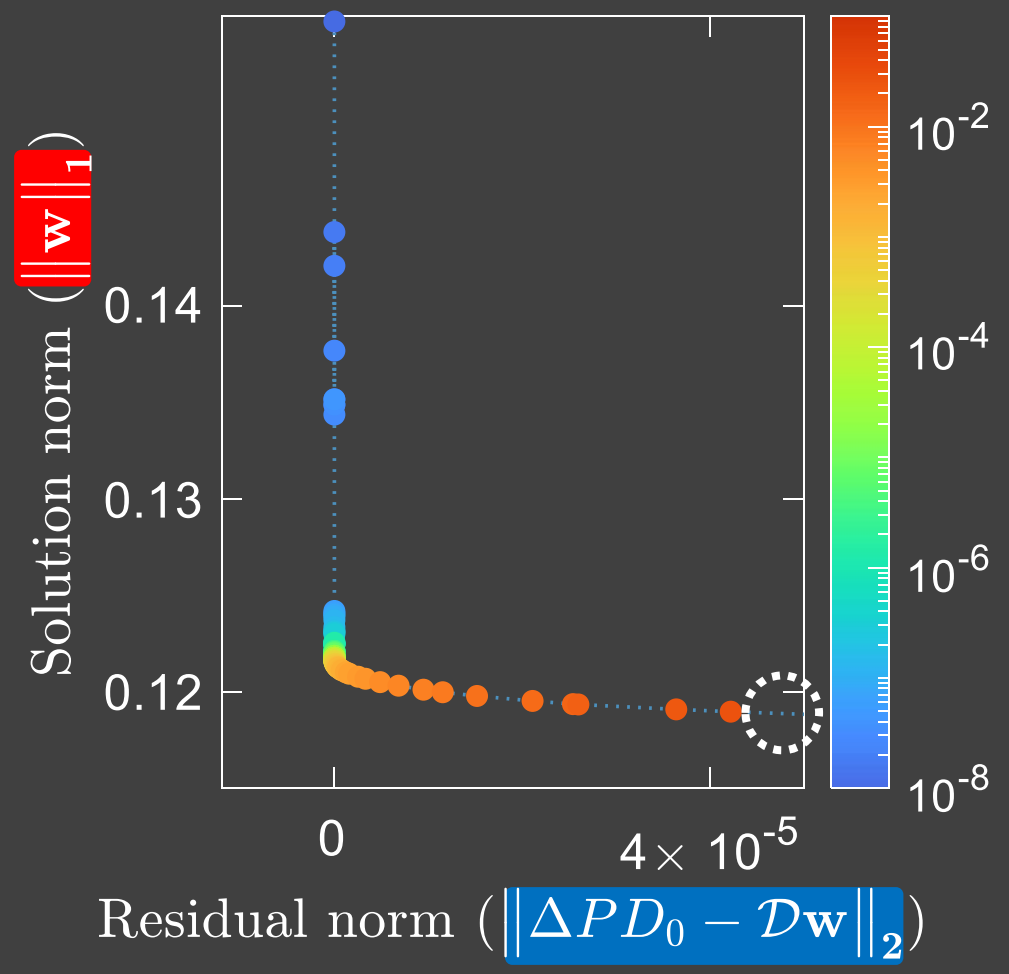

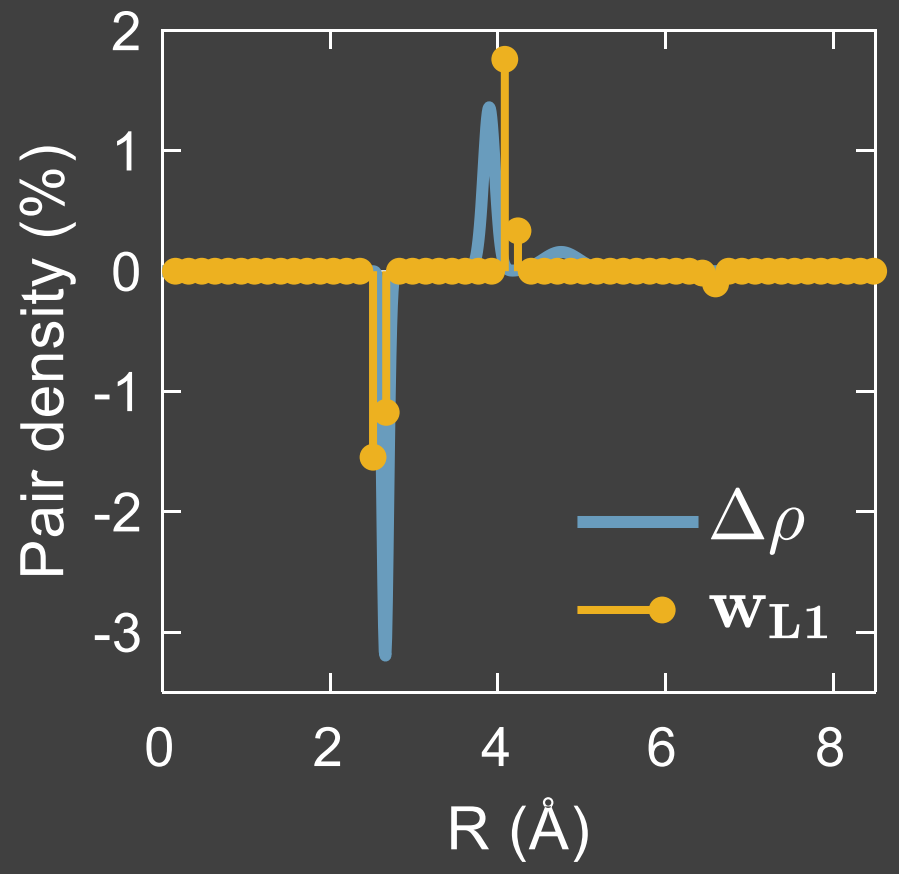

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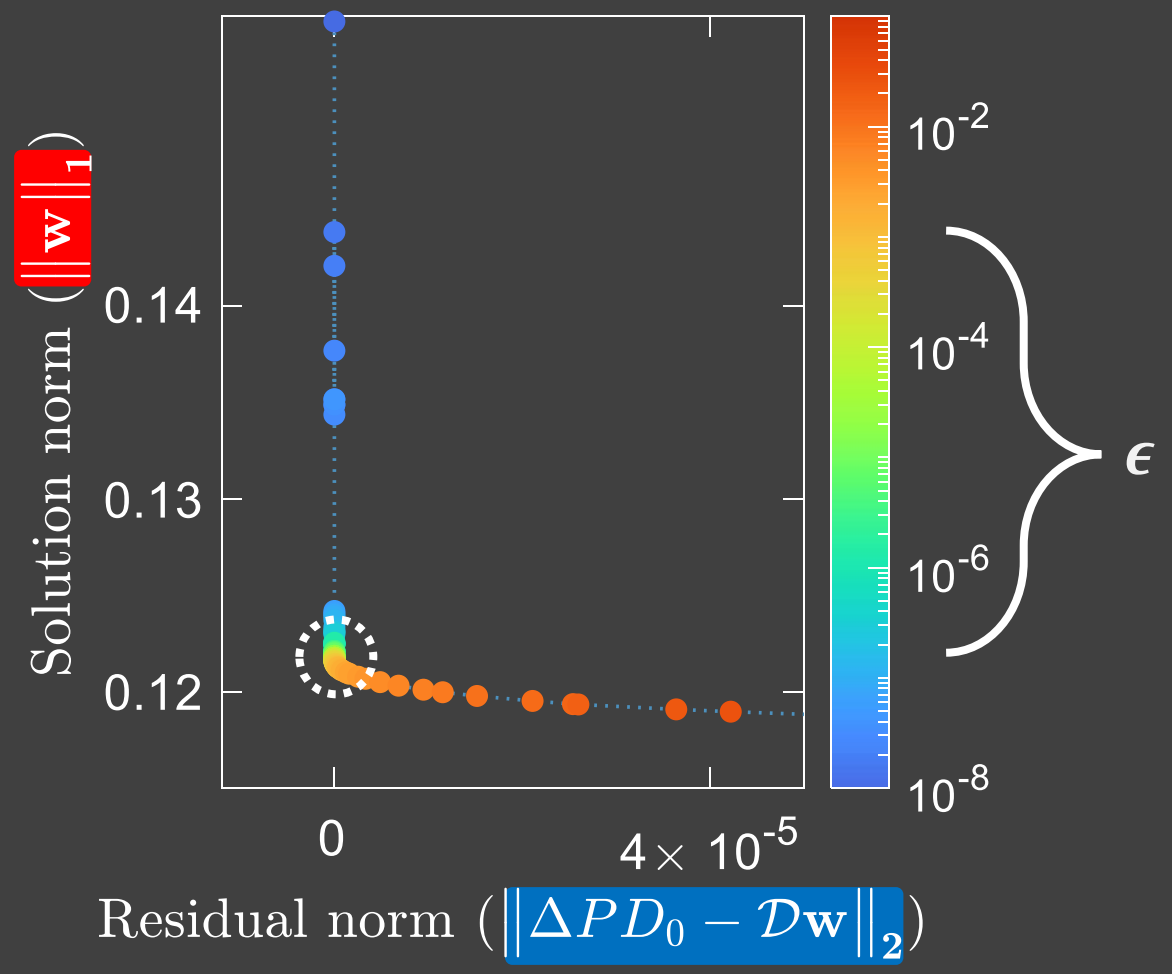

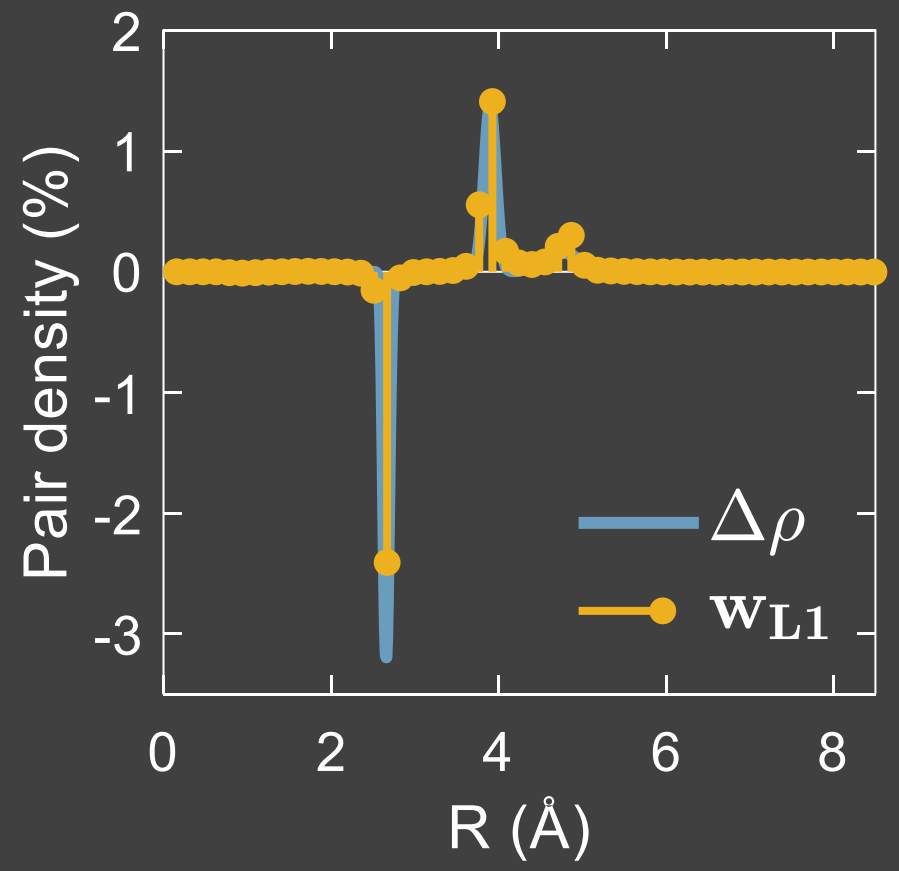

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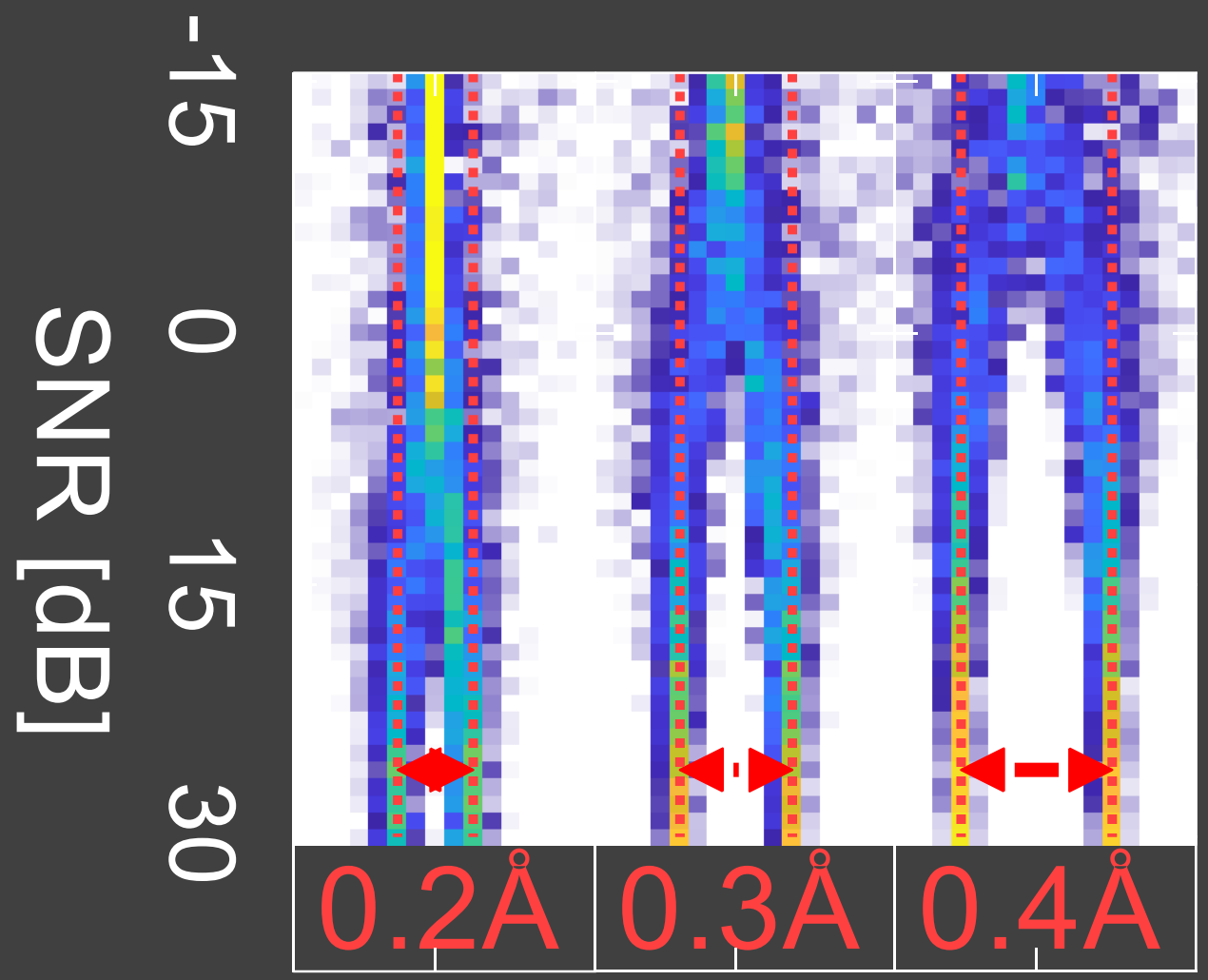
what is the de-facto resolution given noise?



$$ERR \propto \sigma \left(\frac{M}{N}\right)^2$$

$\Delta R = \pi / \mathrm{M}\Delta\mathrm{q}$

$q_{max} = \mathrm{N}\Delta q$

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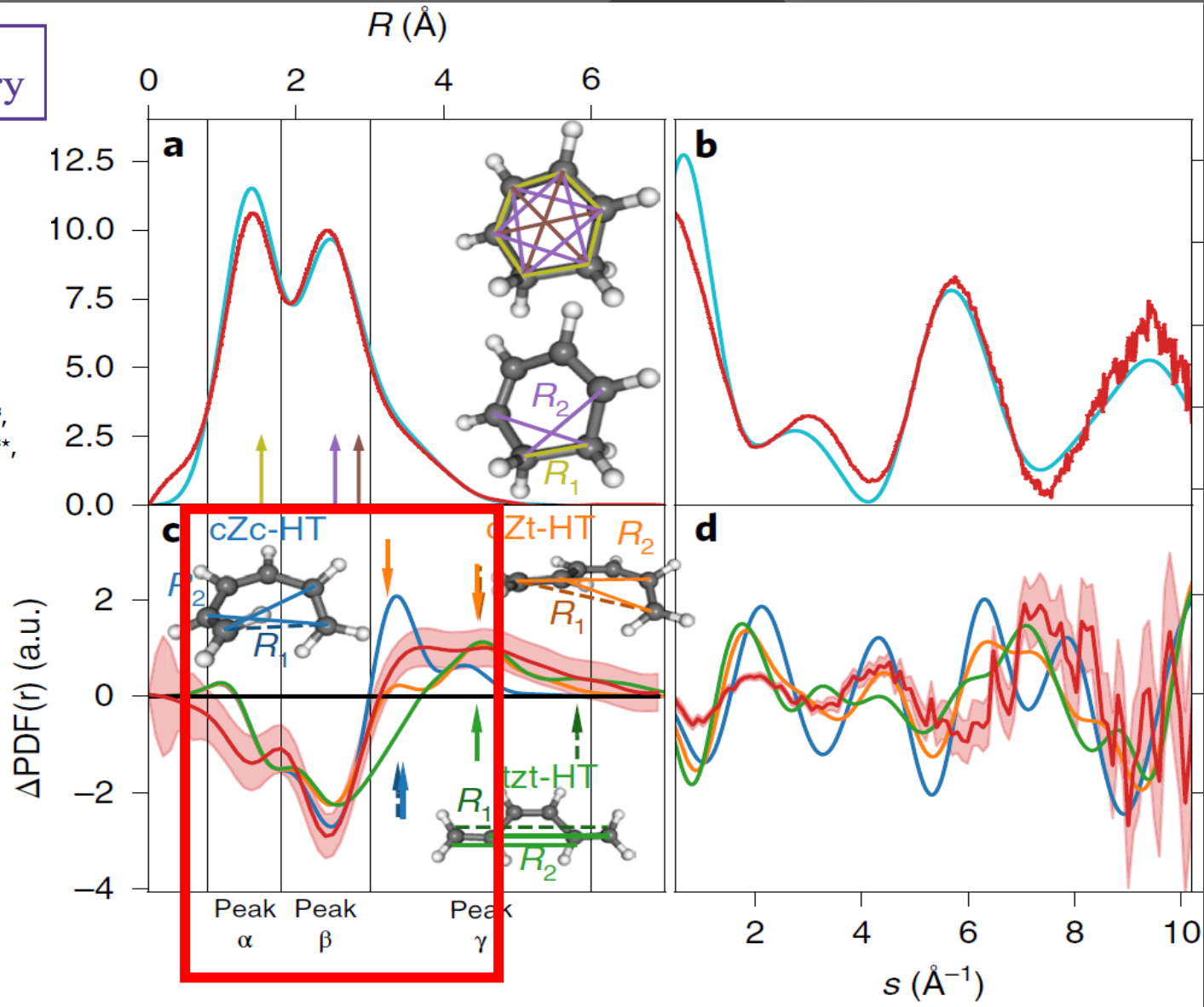
Experimental Example: Ring-opening dynamics in CHD

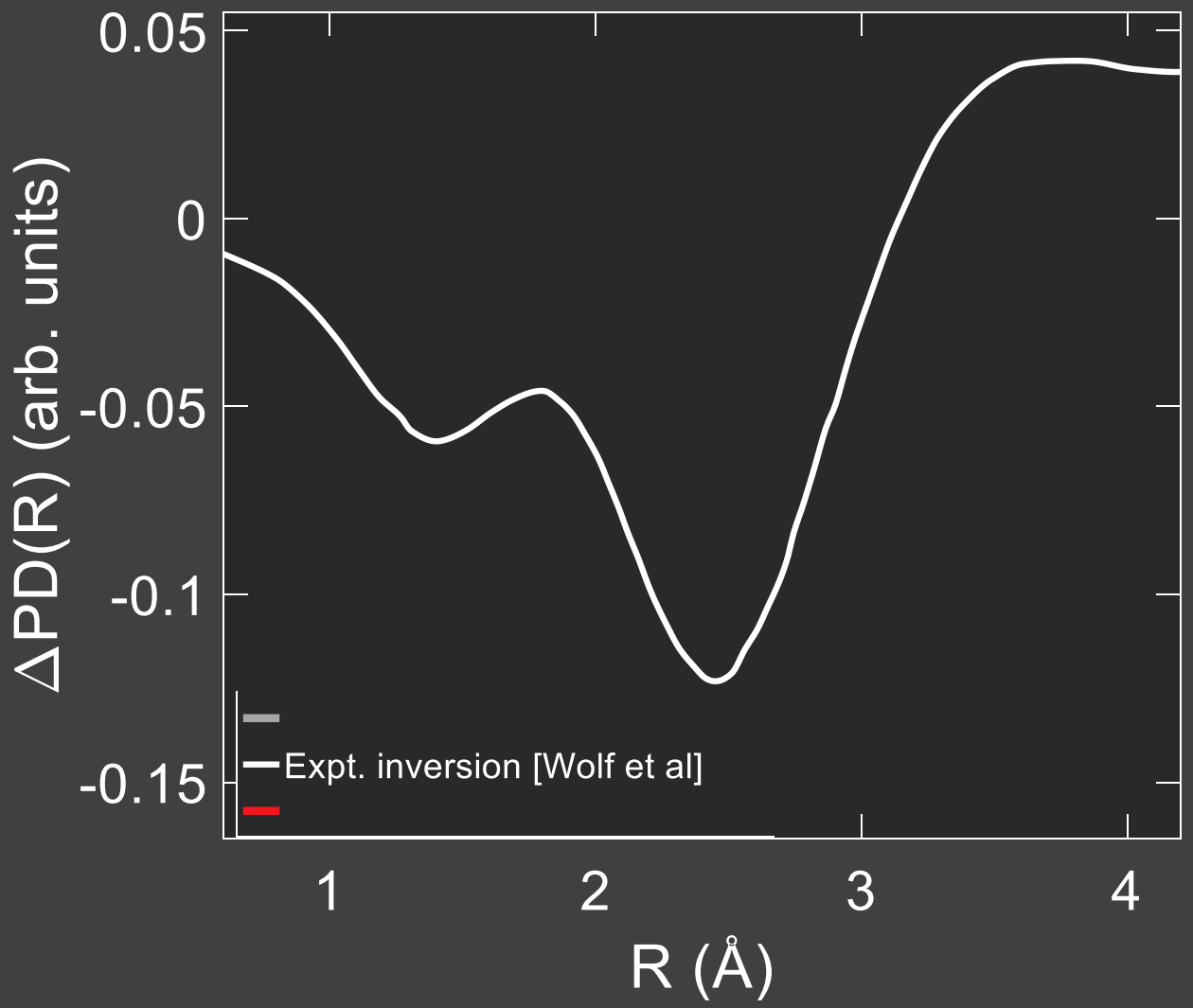
ARTICLES
https://doi.org/10.1038/s41557-019-0252-7
nature chemistry

The photochemical ring-opening of 1,3-cyclohexadiene imaged by ultrafast electron diffraction

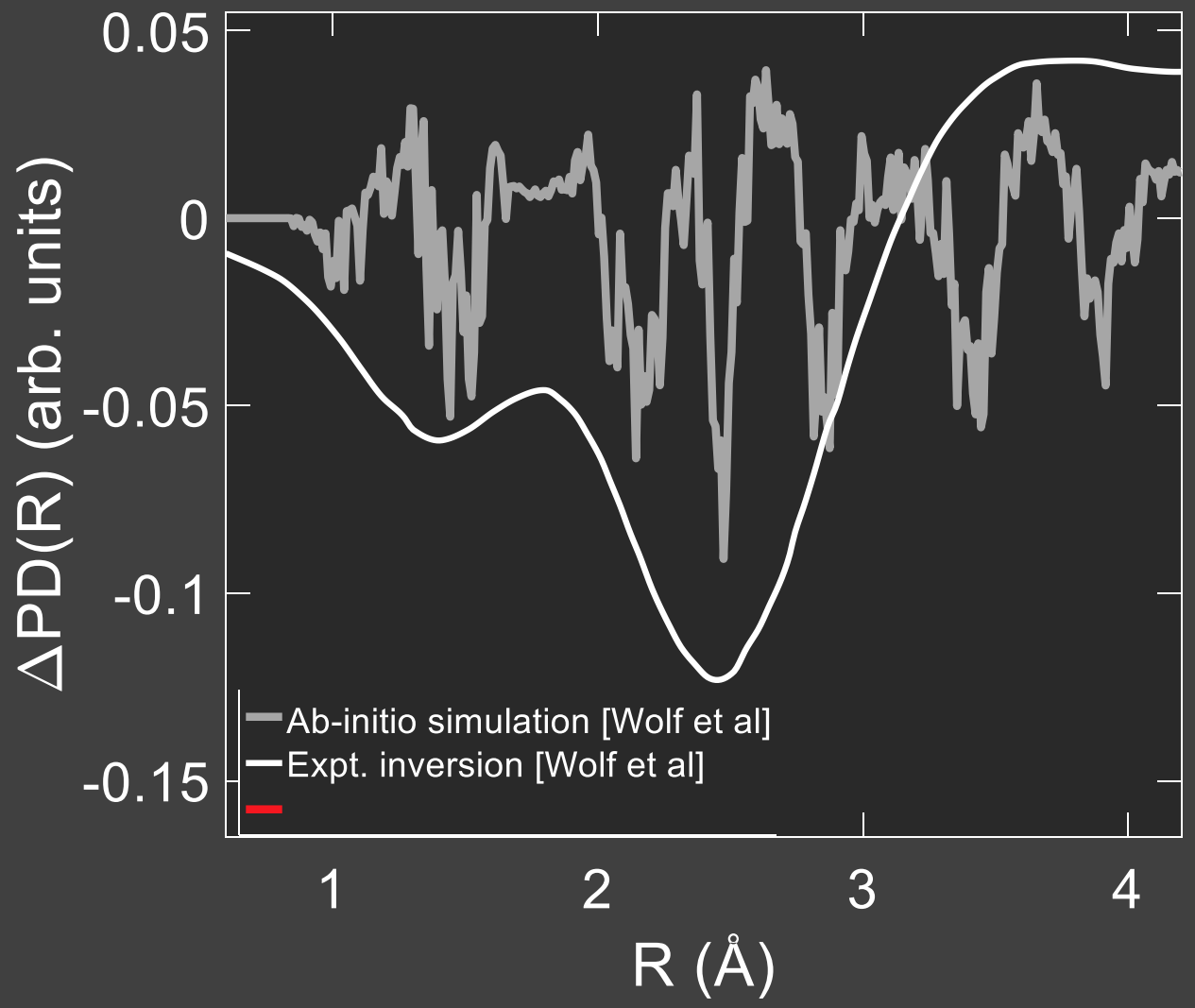
T. J. A. Wolf[1*], D. M. Sanchez[1,2], J. Yang[1,3], R. M. Parrish[1,2], J. P. F. Nunes[4,5], M. Centurion[5], R. Coffee[3], J. P. Cryan[1], M. Gühr[1,6], K. Hegazy[1,7], A. Kirrander[8], R. K. Li[3], J. Ruddock[9], X. Shen[3], T. Vecchione[3], S. P. Weathersby[3], P. M. Weber[9], K. Wilkin[5], H. Yong[9], Q. Zheng[3], X. J. Wang[3*], M. P. Minitti[3*] and T. J. Martínez[1,2*]



Experimental Example: Ring-opening dynamics in CHD



Experimental Example: Ring-opening dynamics in CHD



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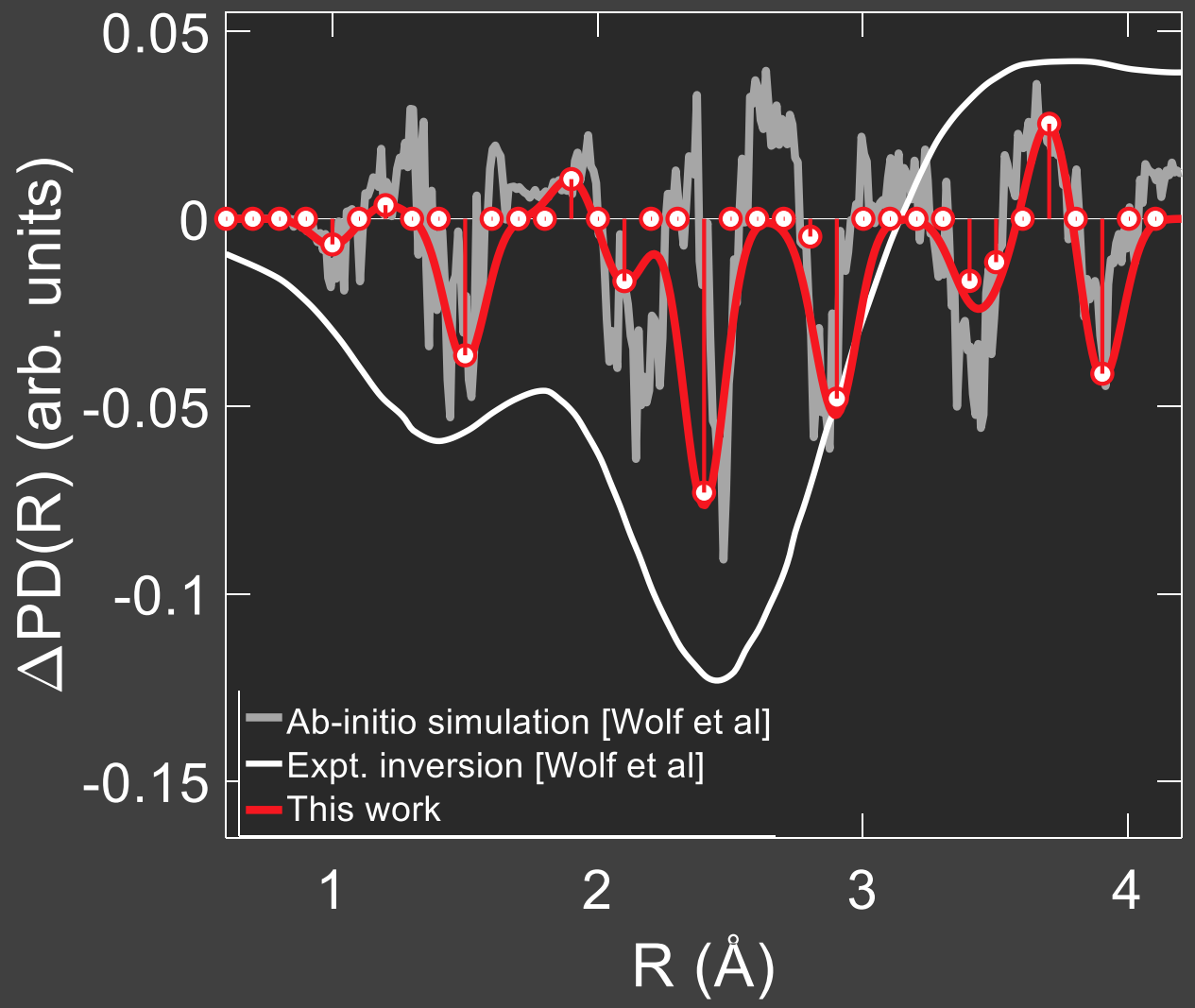

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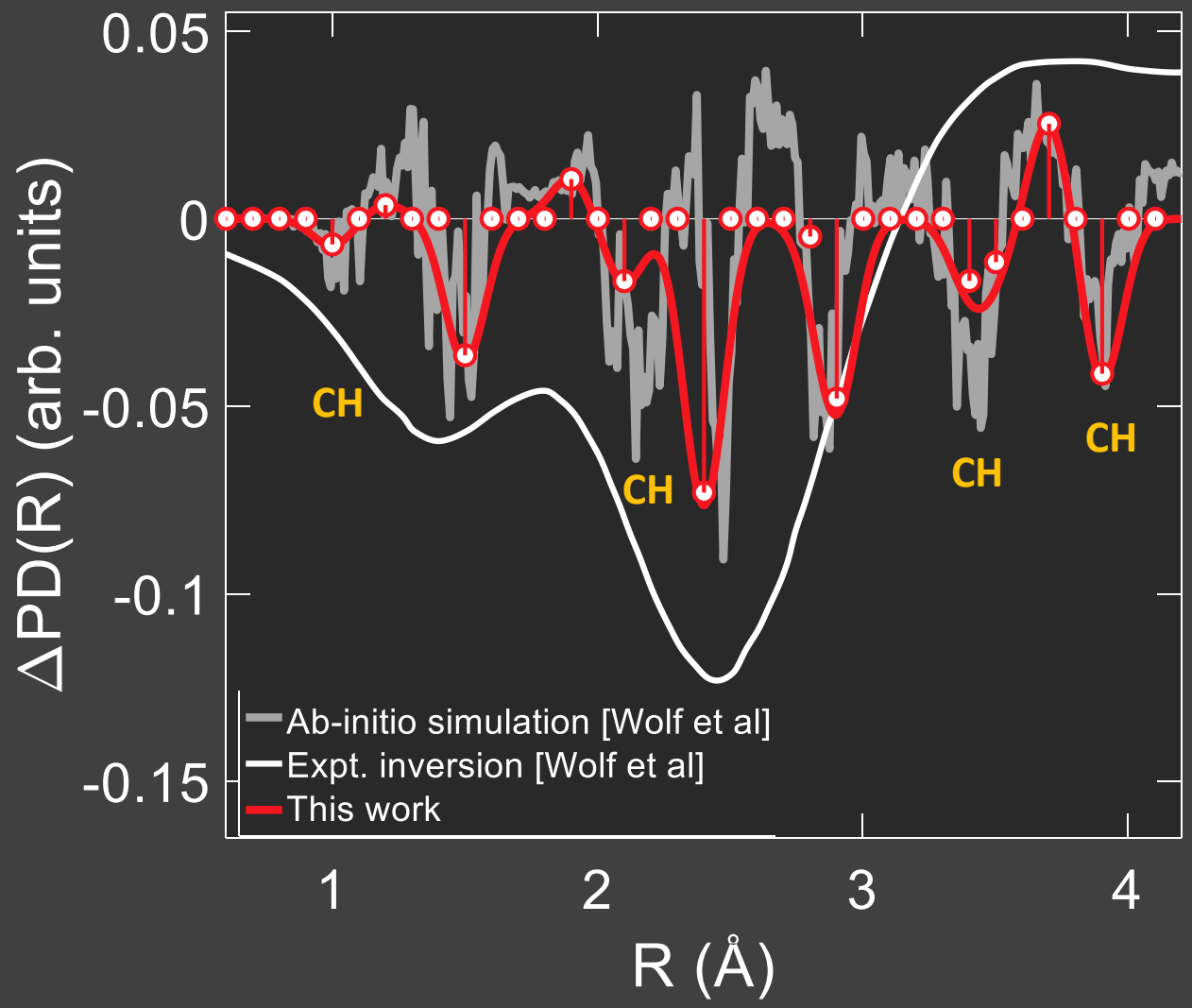
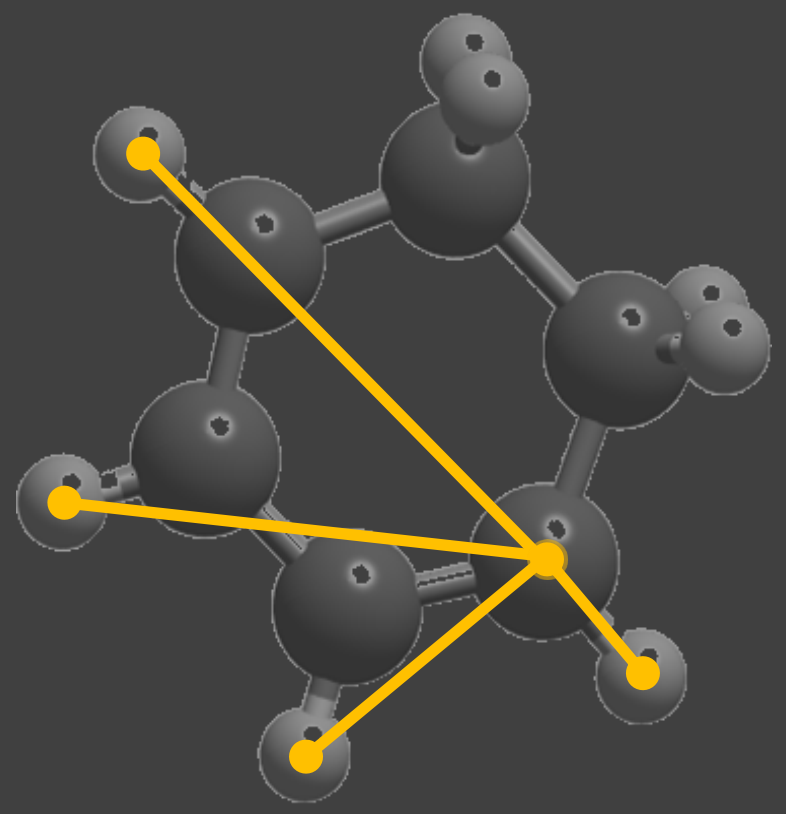
Experimental Example: Ring-opening dynamics in CHD





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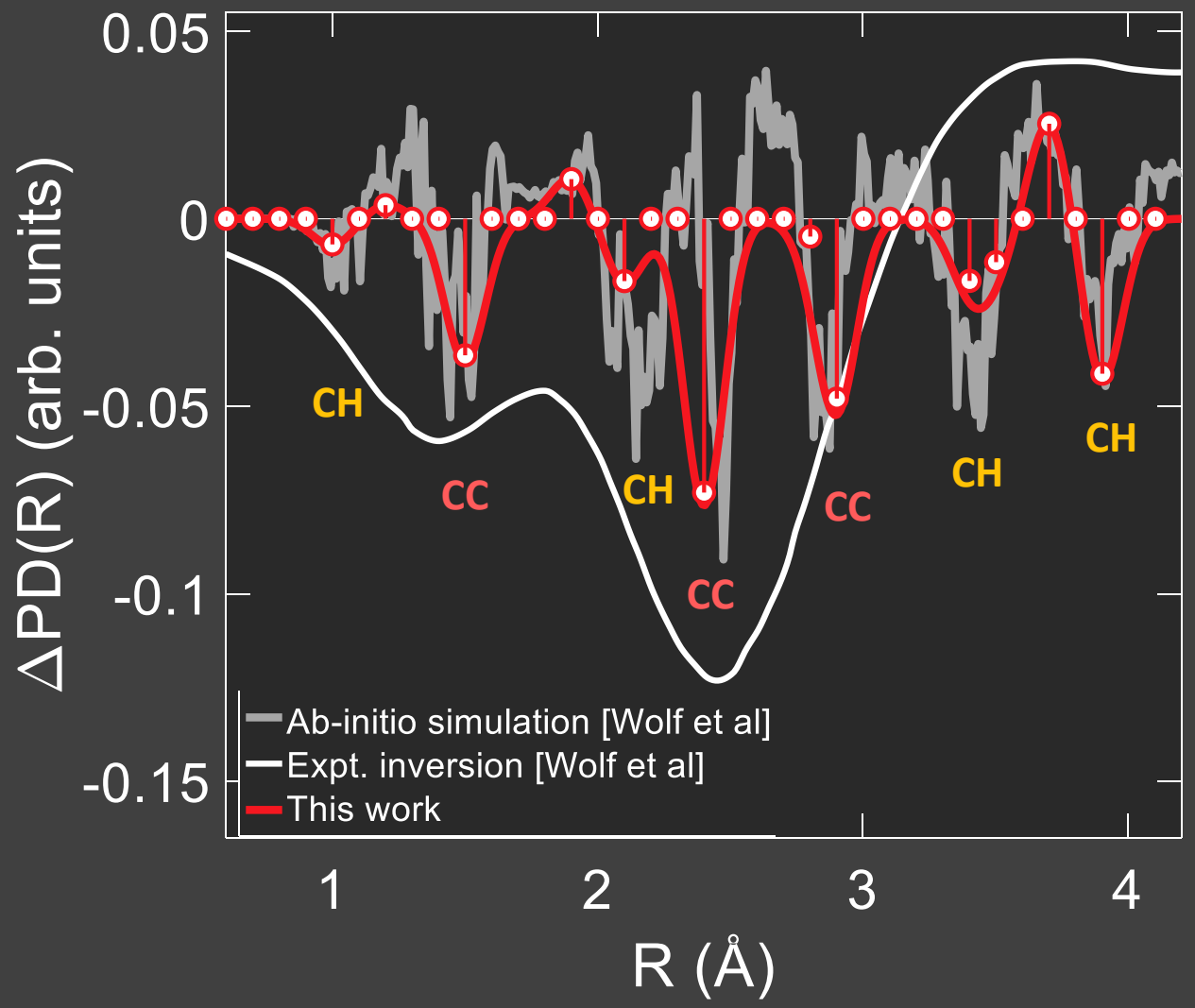
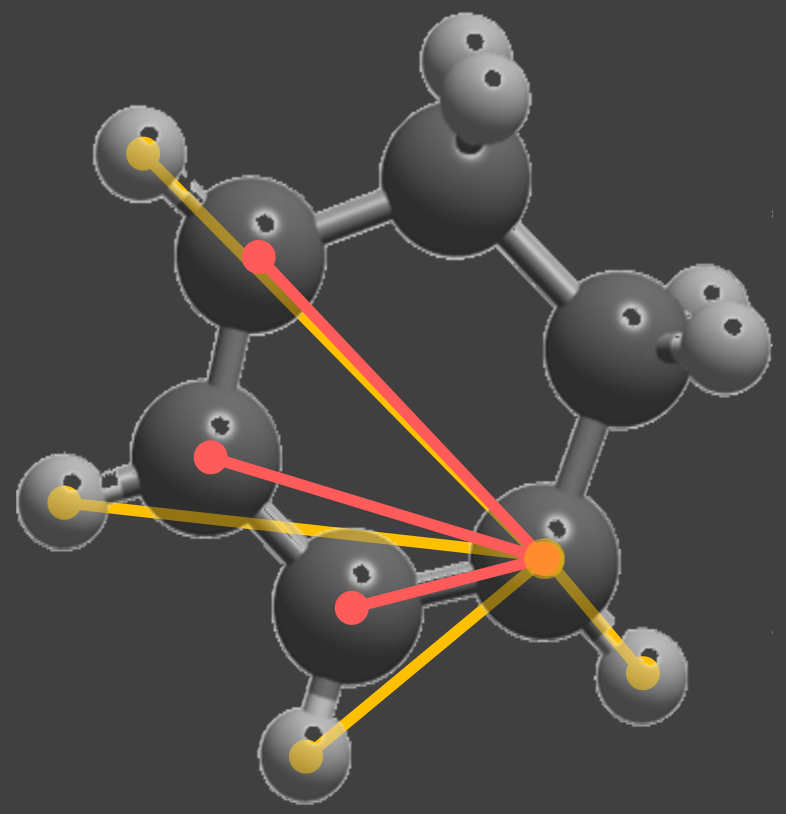
Experimental Example: Ring-opening dynamics in CHD





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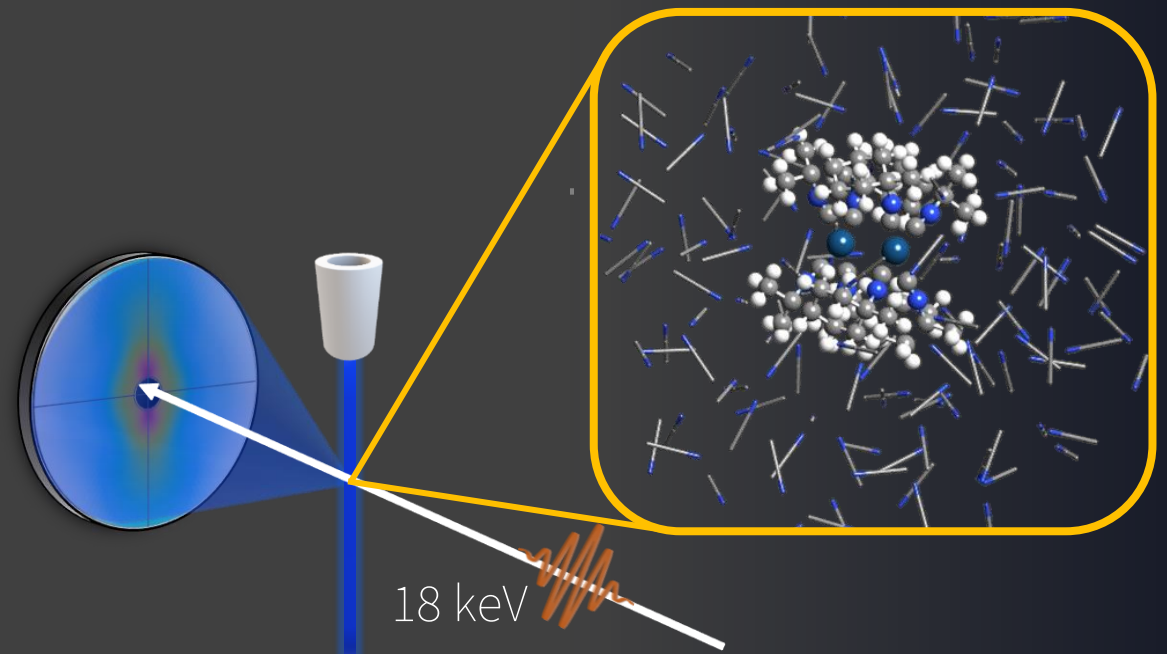
Ultrafast Solute-Solvent dynamics in Real-Space (LV96)

<u>Motivation</u>: Understand the microscopic details of photoinduced reactions in complex environments.

<u>Goal:</u> Understand how solute-solvent interactions influence reactivity, what role do solute-solvent bonds play in light-driven reactions?



<u>PULSE</u>
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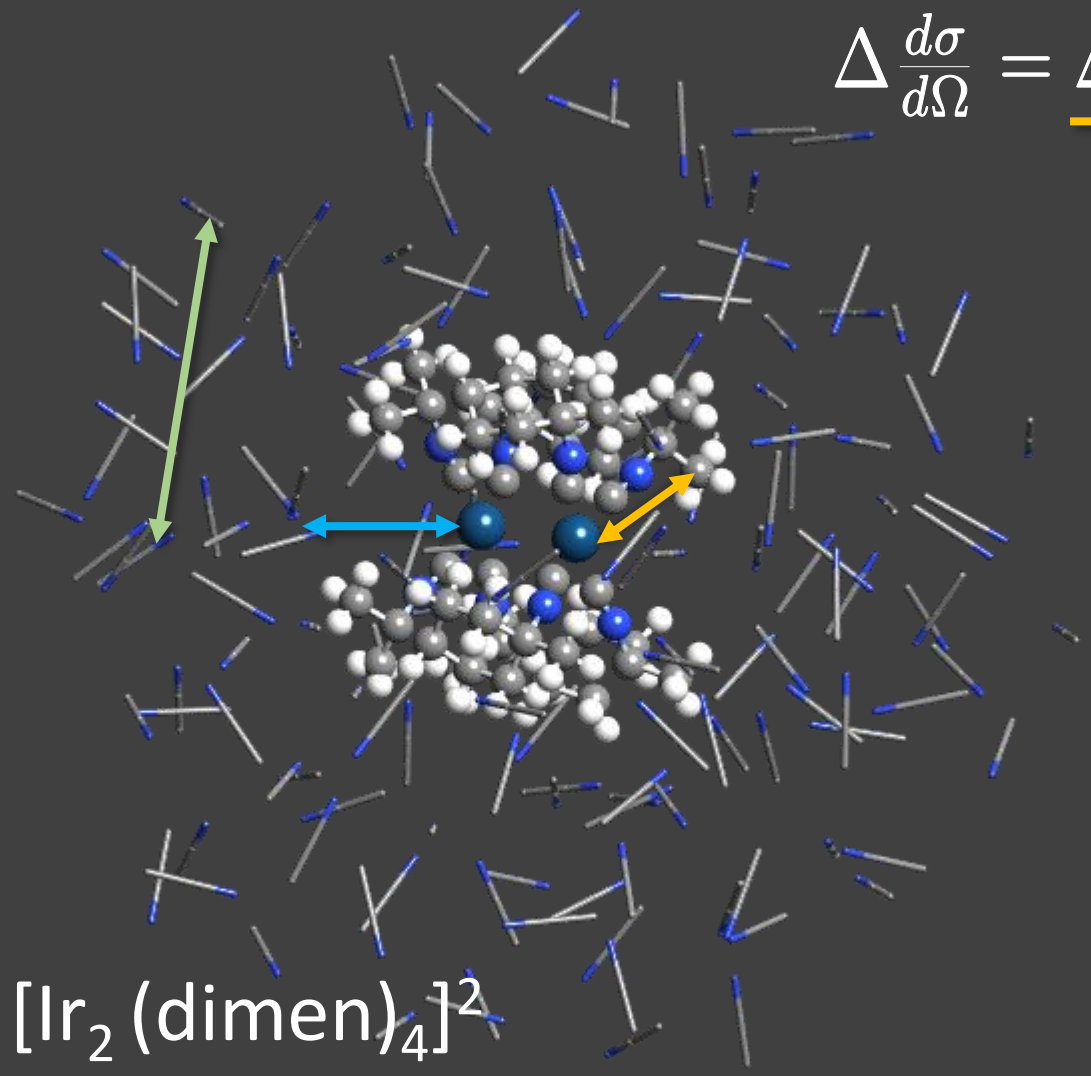
Kelly Gaffney

<u>LCLS</u>
Tim Van Driel
Kristjan Kunnus
Mathieu Chollet
Joe Robinson
Ruaridh Forbes
Silke Nelson

<u>DTU</u>
Kristoffer Haldrup, Martin M Nielsen
Kasper Pedersen, **Asmus Dohn**
Morten Haubro, Diana Zederkof, Philipp Lenzen

Solution phase ultrafast scattering – how many pairs?

$$\Delta \frac{d\sigma}{d\Omega} = \Delta S(q)_{solute} + \Delta S(q)_{cage} + \Delta S(q)_{solvent}$$

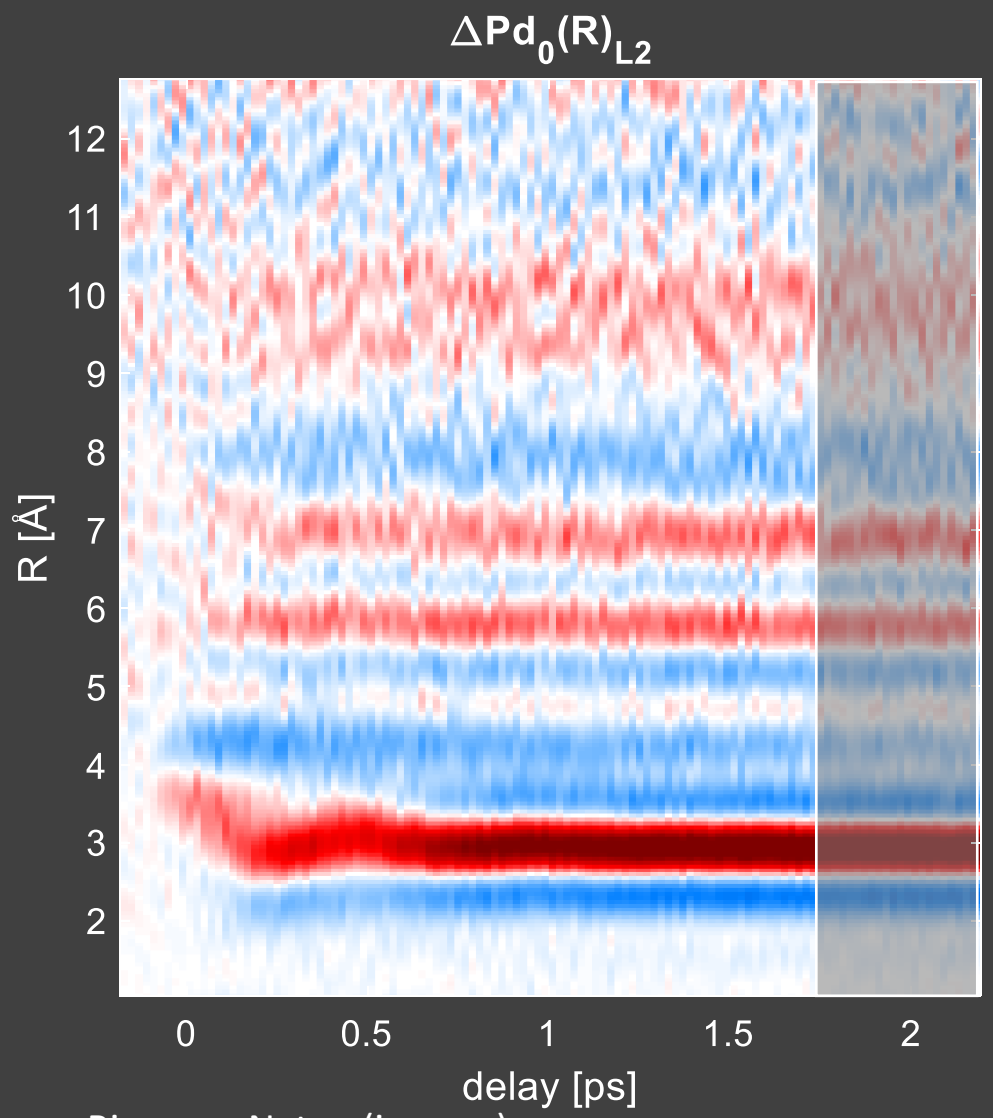


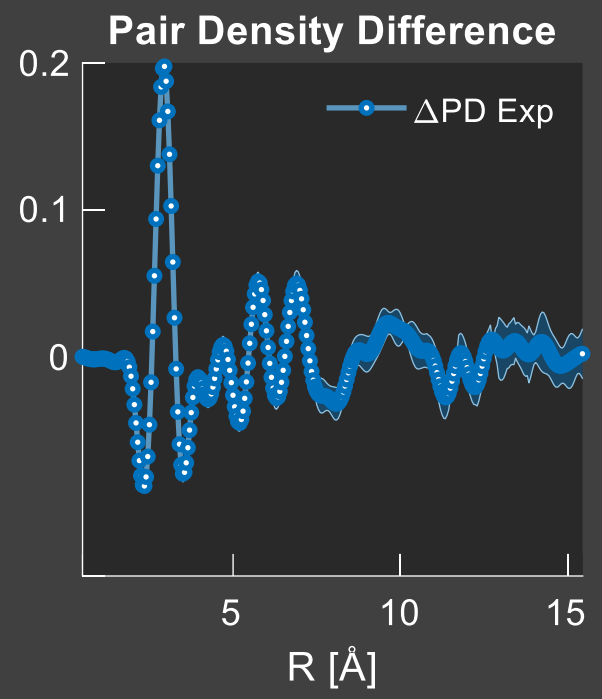
$[Ir_2(dimen)_4]^2$

(dimen = 1,8-diisocyano-p-menthane)

	# pairs solute	# pairs "cage"	# pairs solvent	# All pairs
Ir-Ir	1	0	0	1
Ir-N	16	300	0	316
Ir-C	96	600	0	696
Ir-H	144	0	0	144
N-N	28	1200	11175	12403
N-C	384	9600	45000	54984
N-H	576	10800	0	11376
C-C	1128	14400	44850	60378
C-H	3456	21600	0	25056
H-H	2556	0	0	2556
total	8385	58500	101025	167910

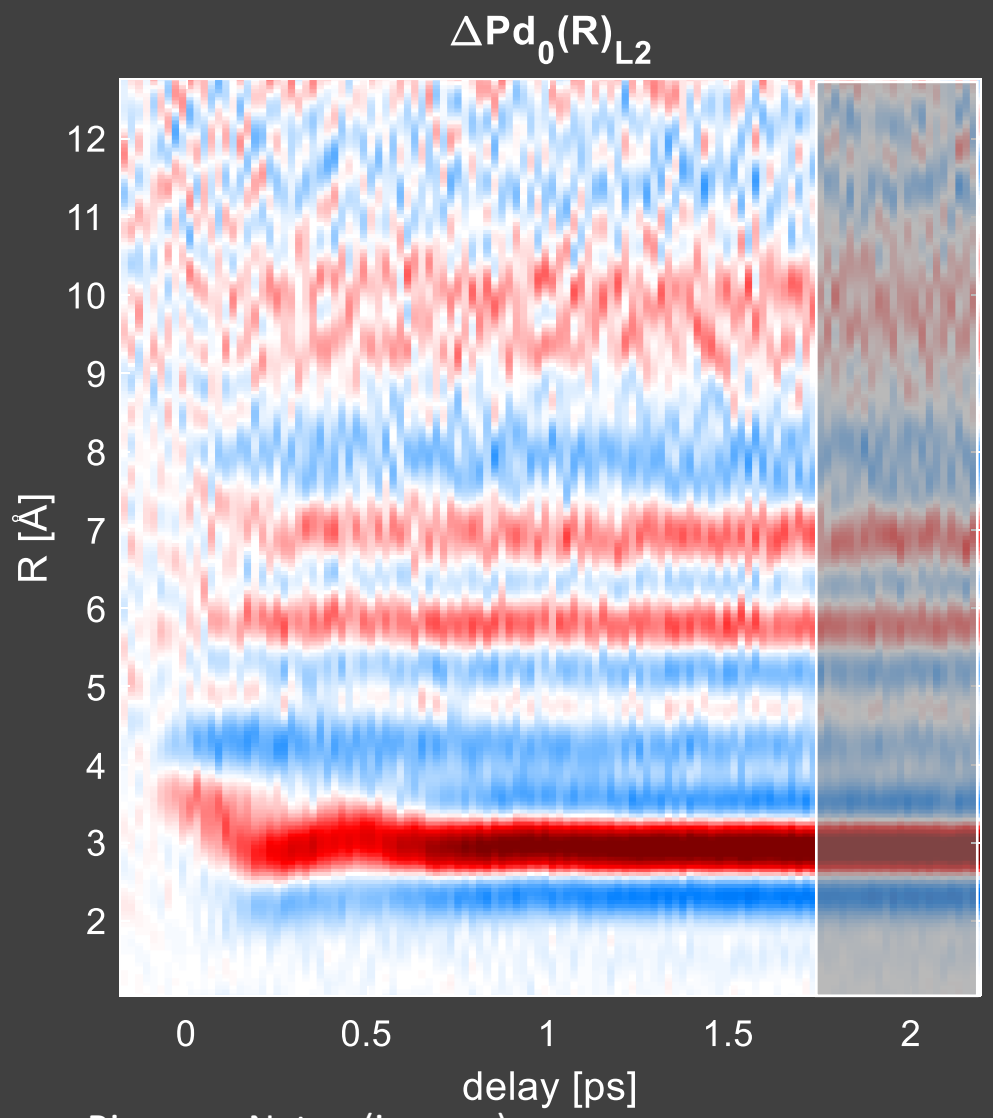
Disentangling ultrafast solvation in real-space

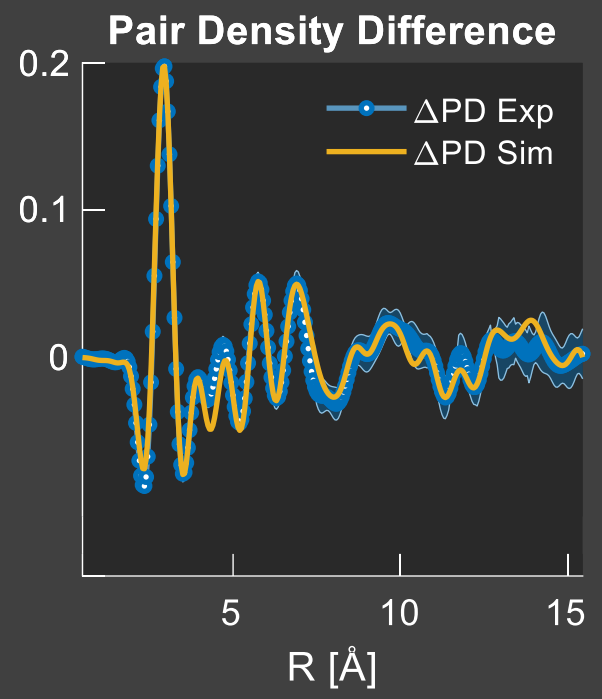




Powers-Riggs ,..., Natan (in prep)

Disentangling ultrafast solvation in real-space





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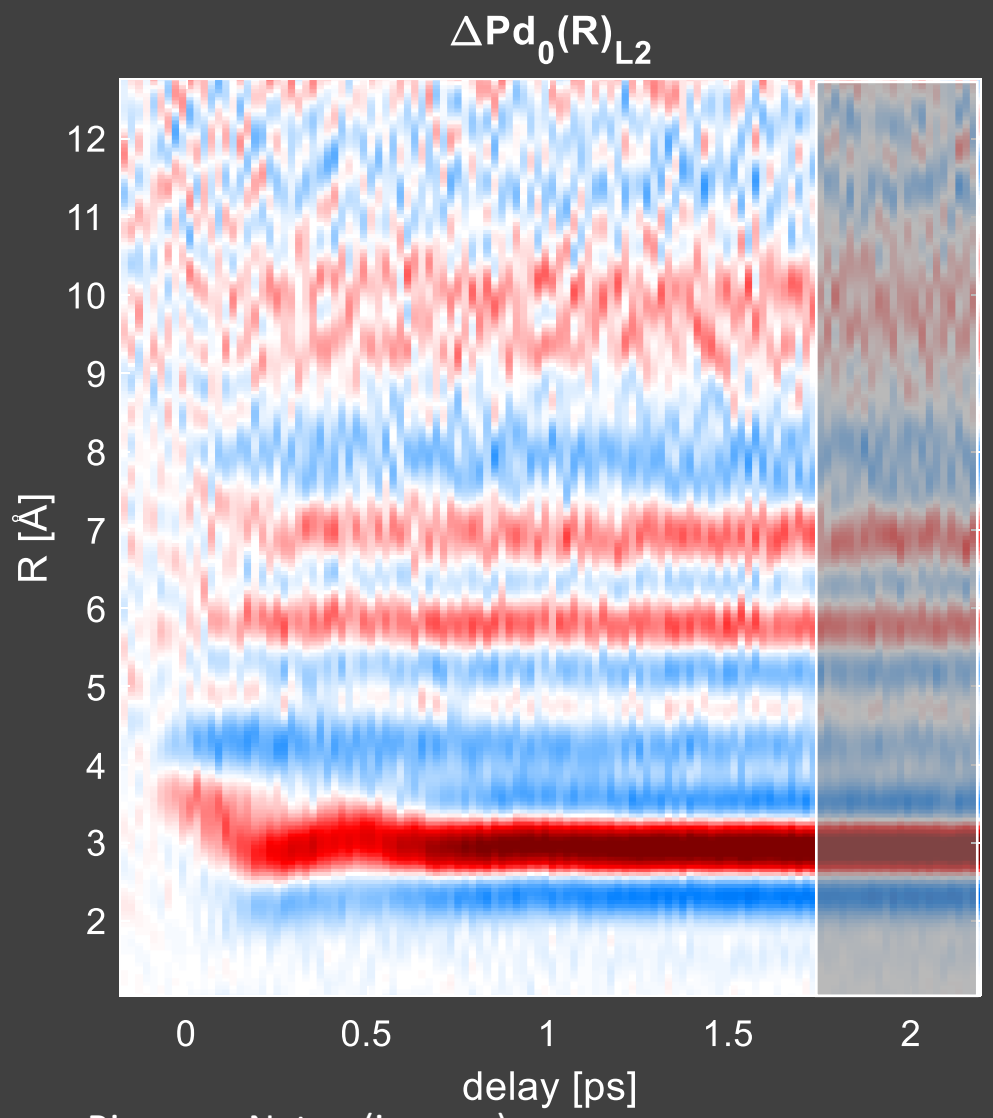

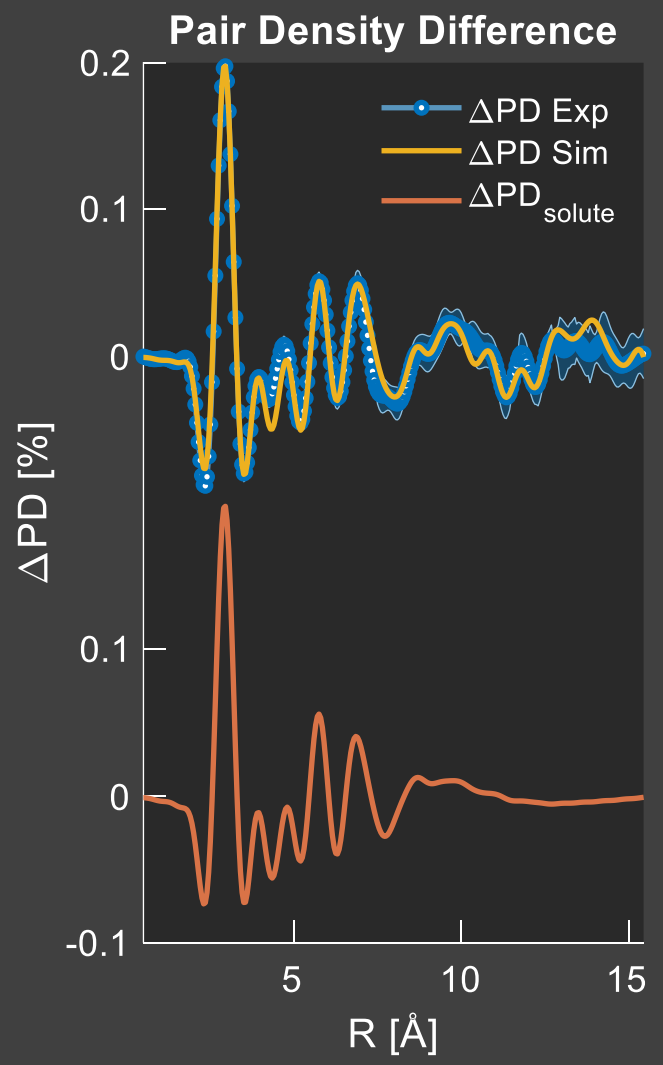

Powers-Riggs ,..., Natan (in prep)

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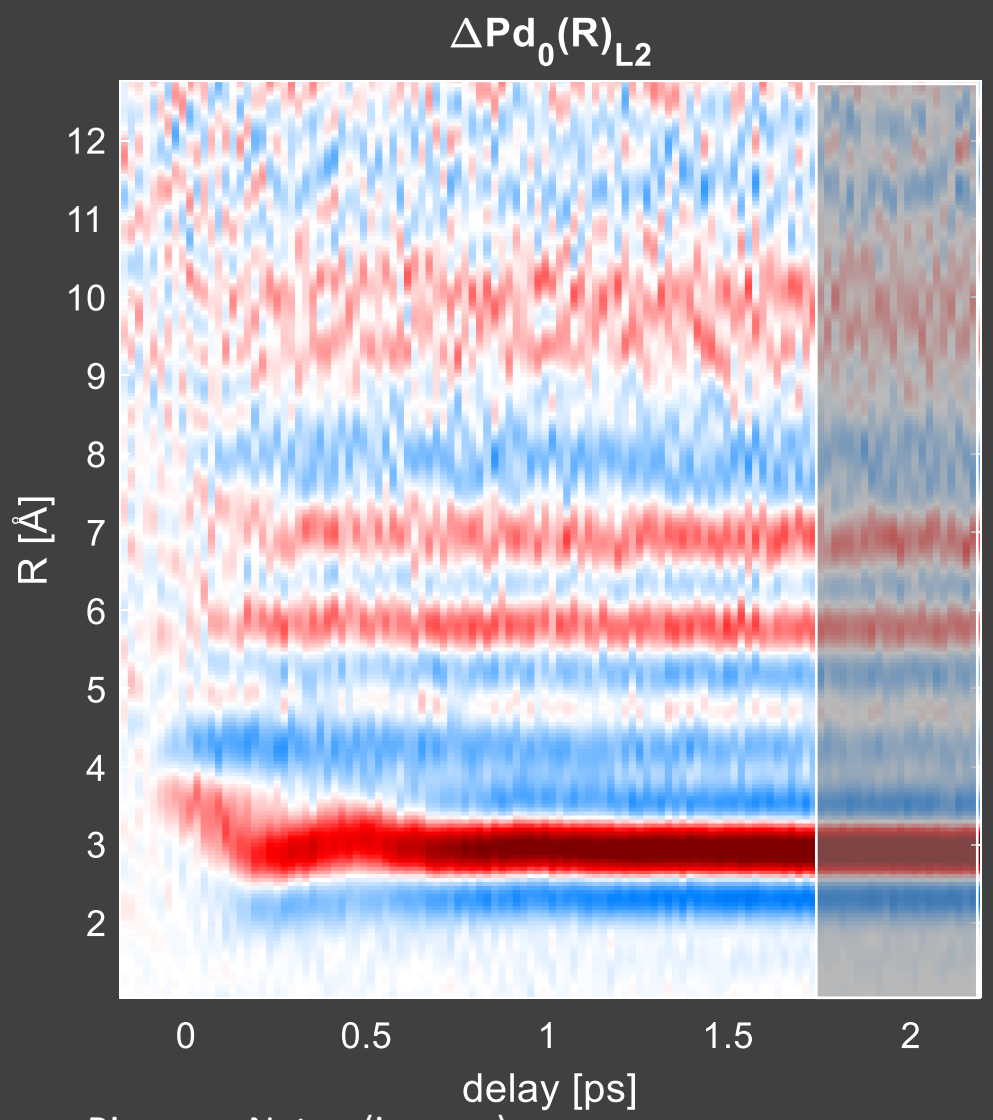

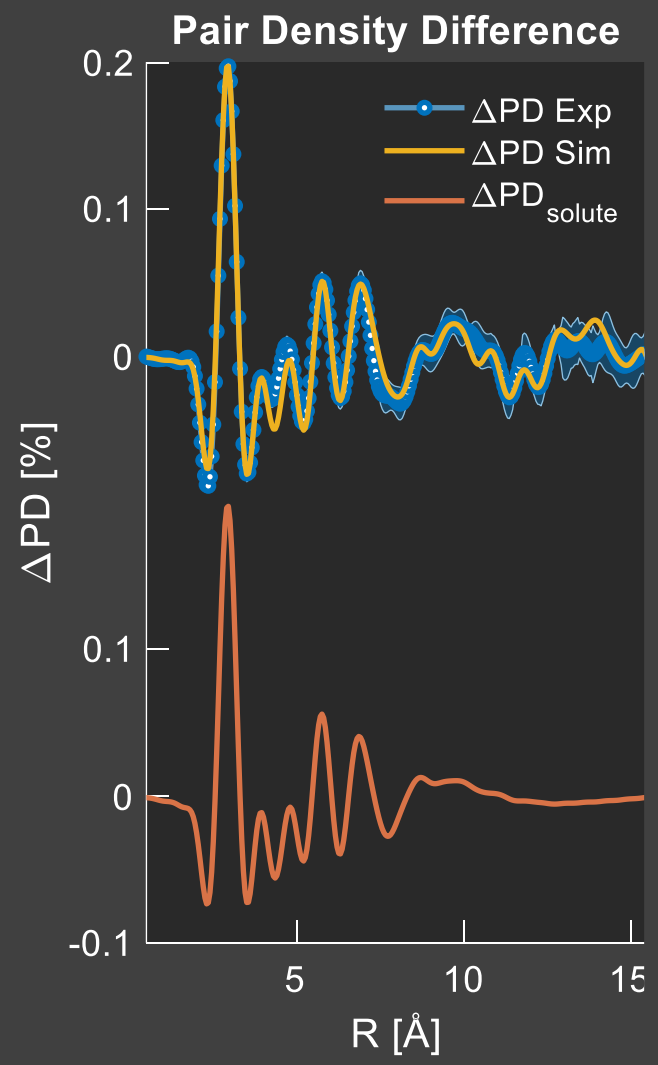

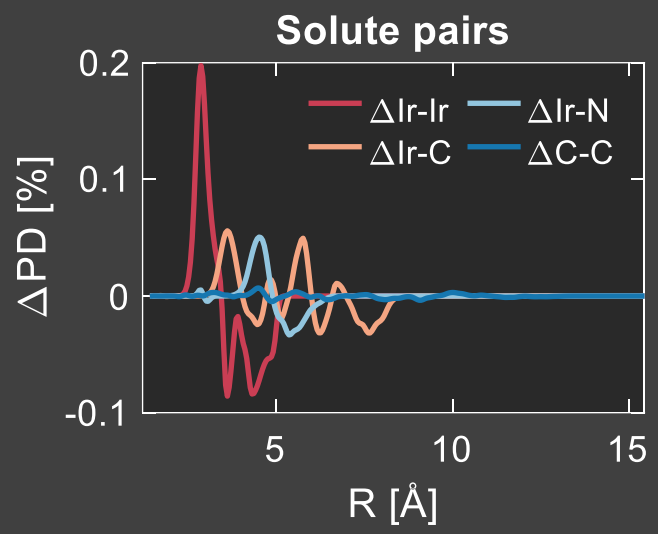

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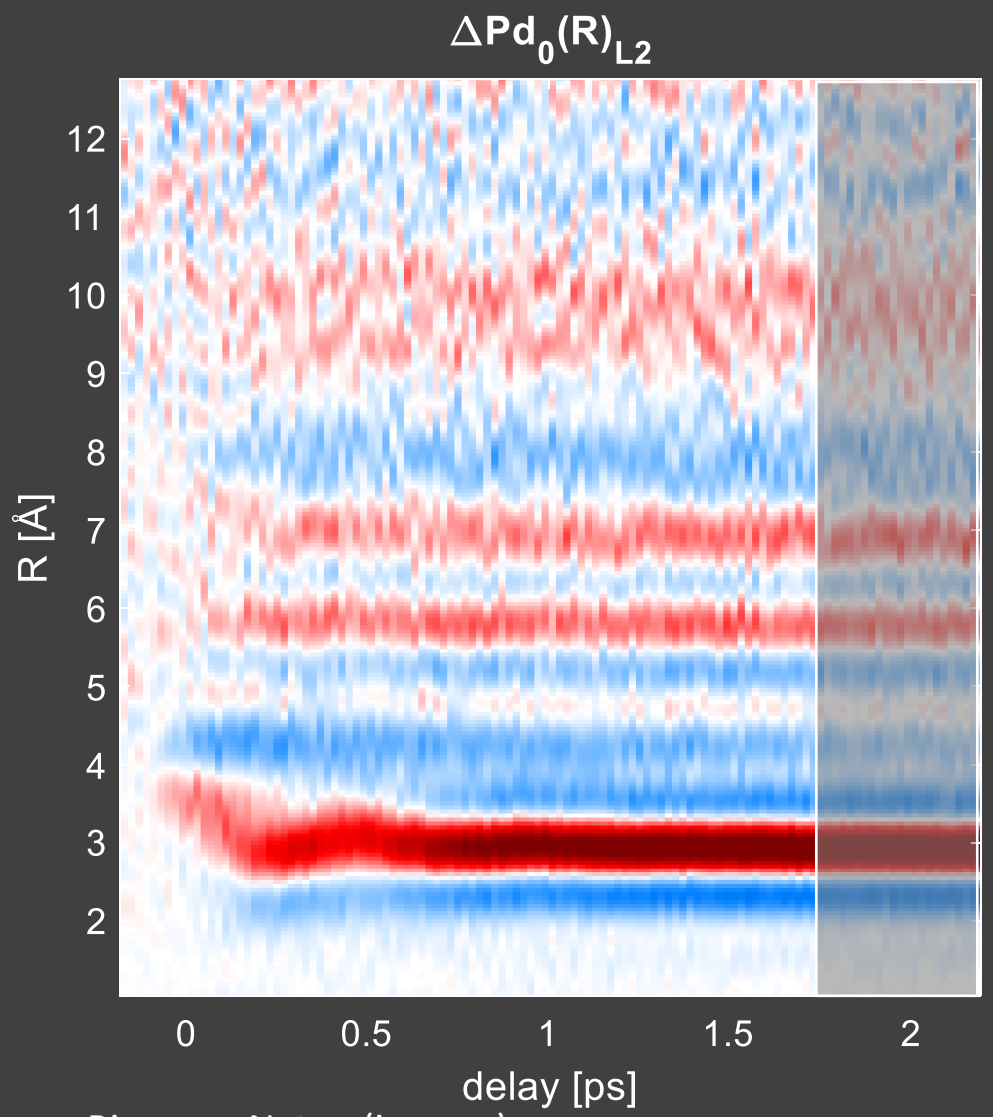
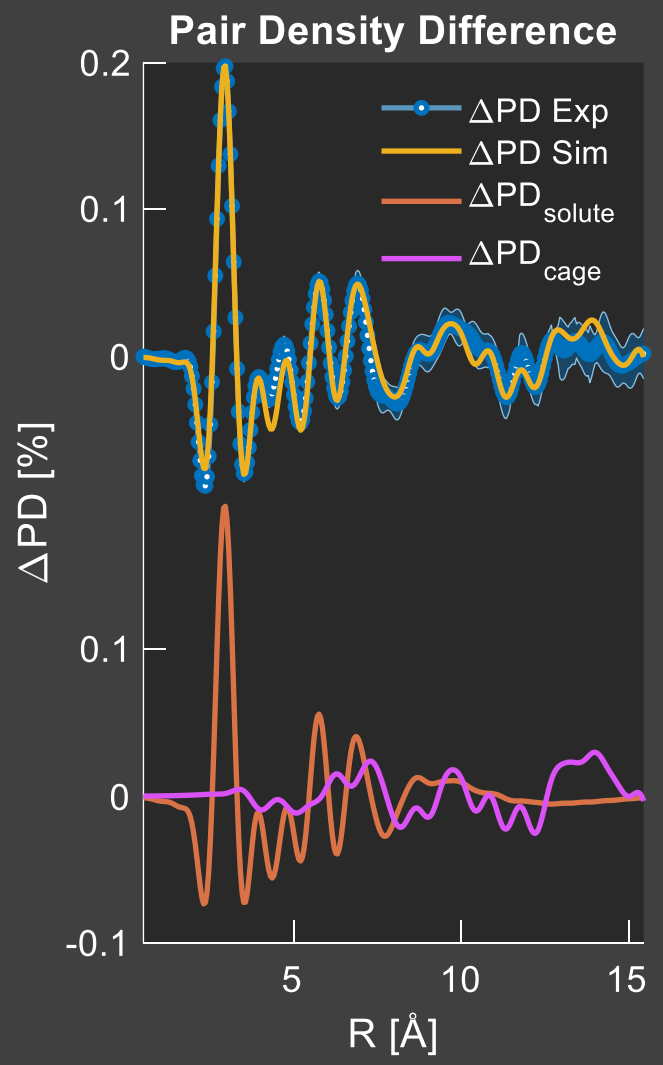
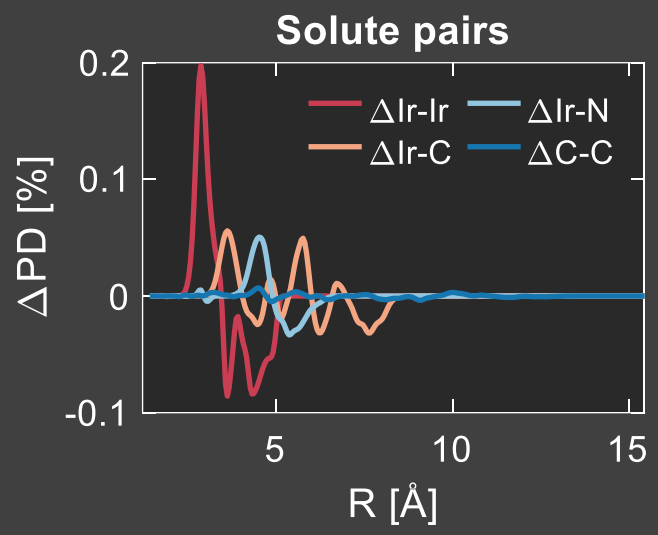
Disentangling ultrafast solvation in real-space

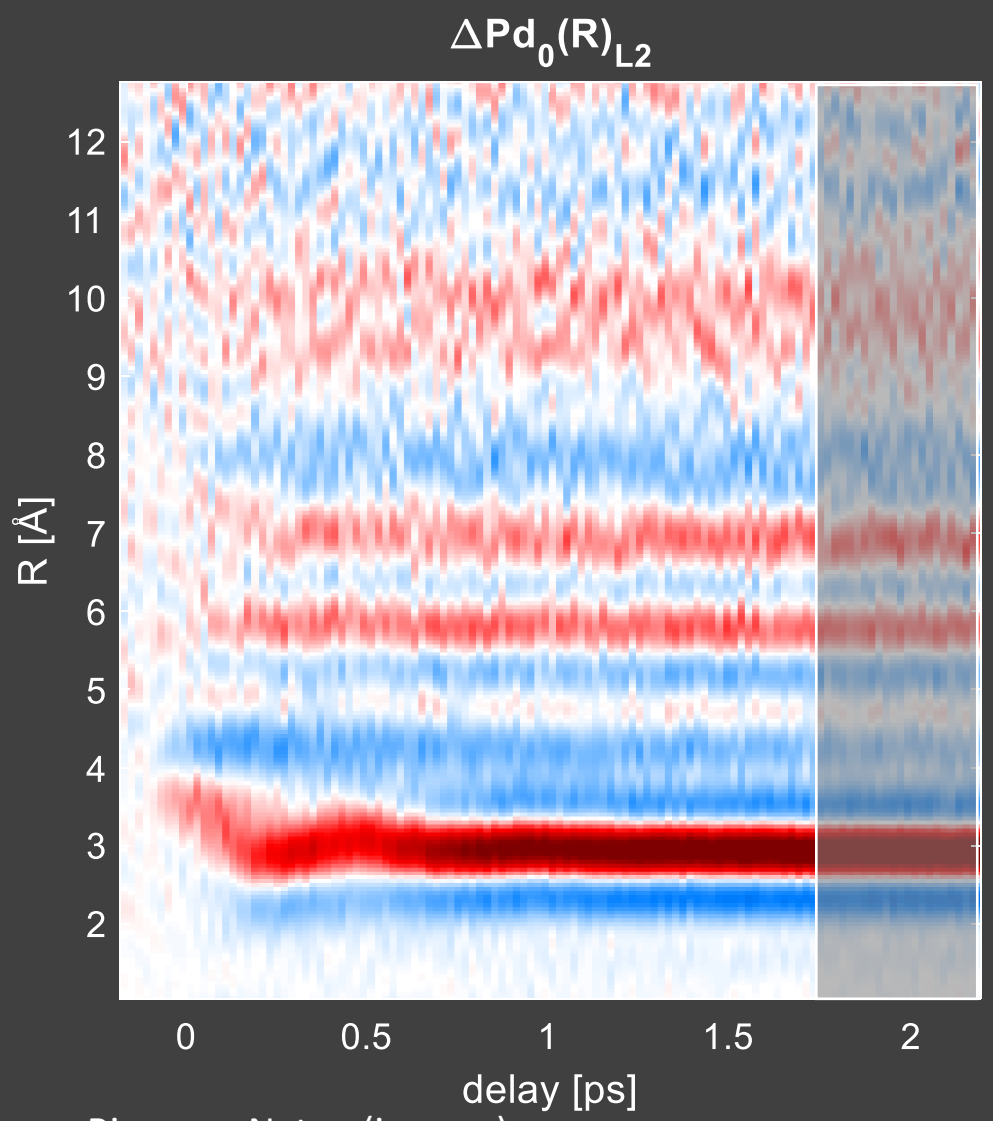


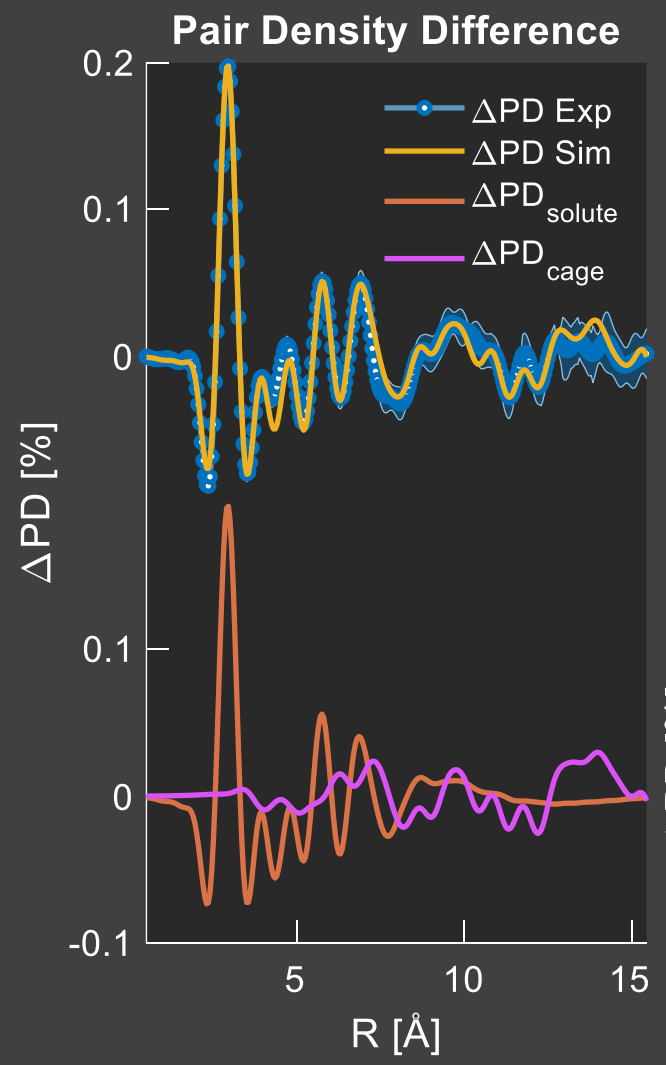


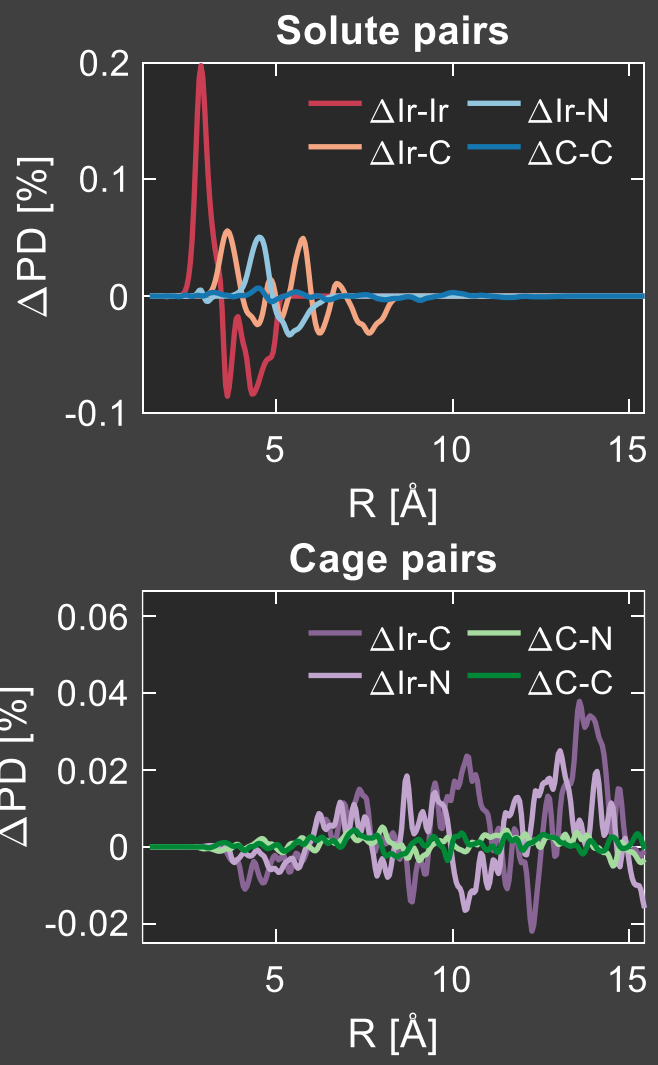


Powers-Riggs ,..., Natan (in prep)

Disentangling ultrafast solvation in real-space







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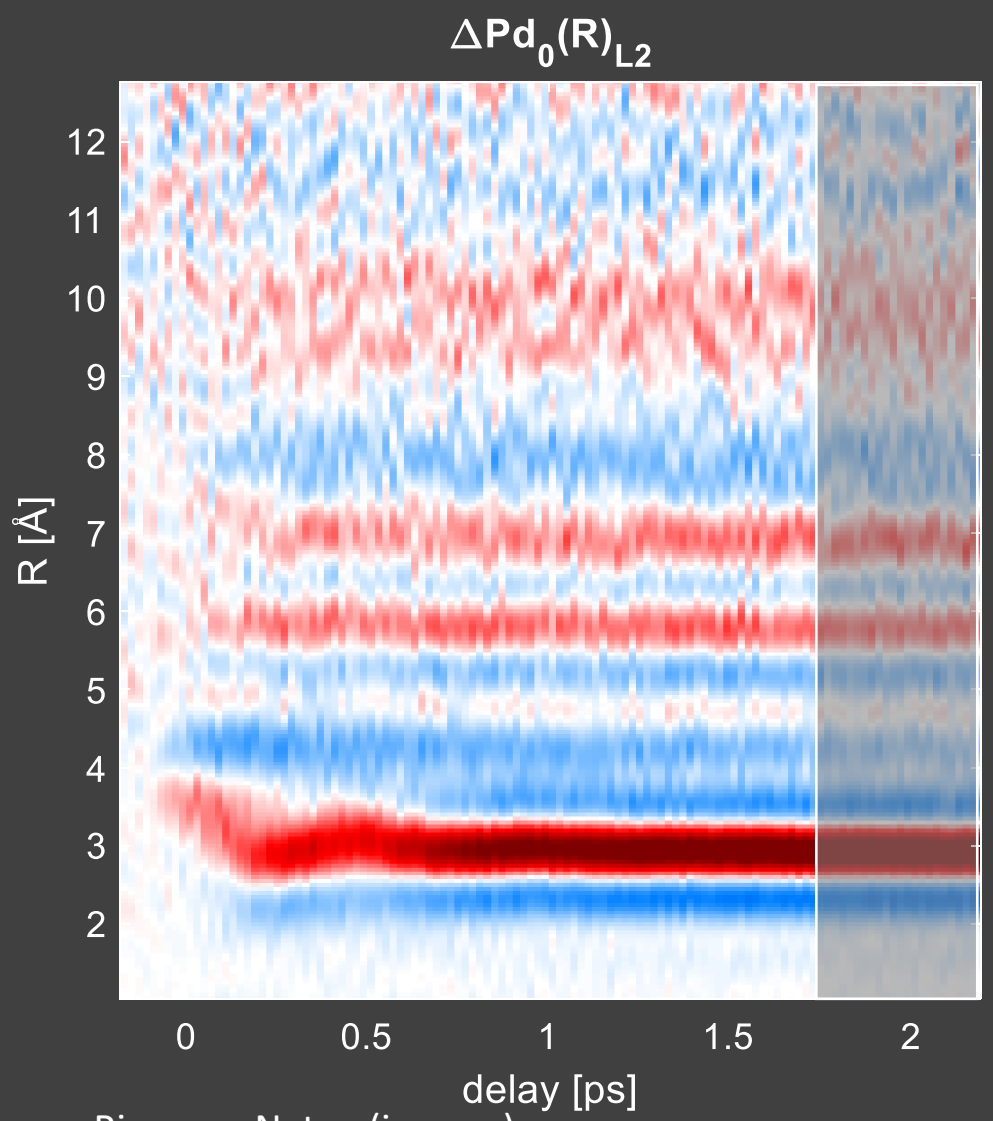

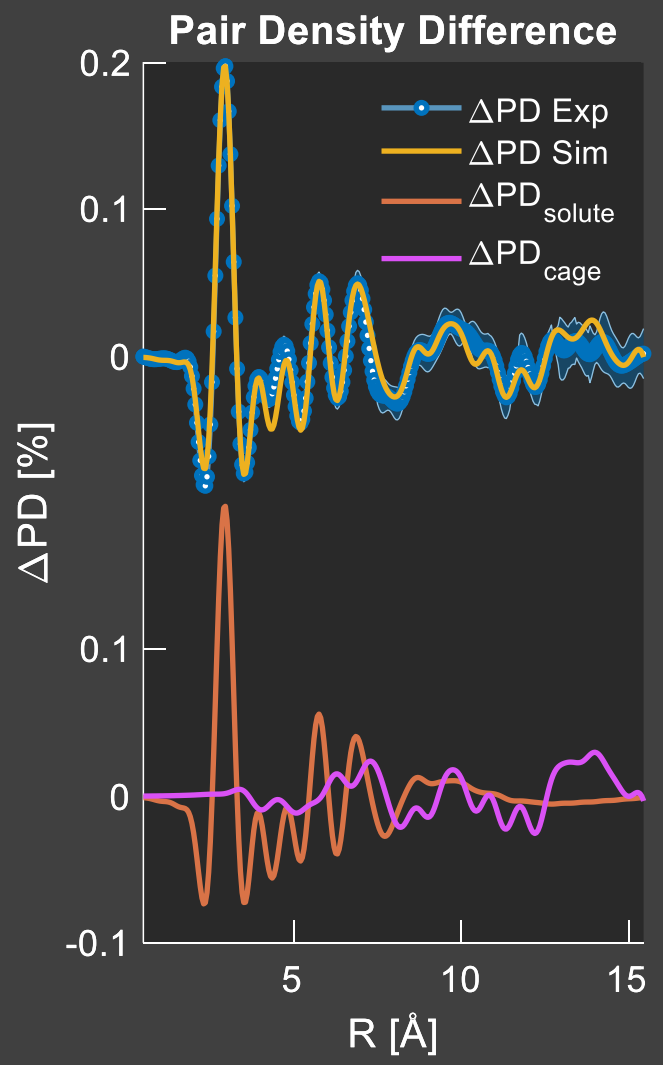

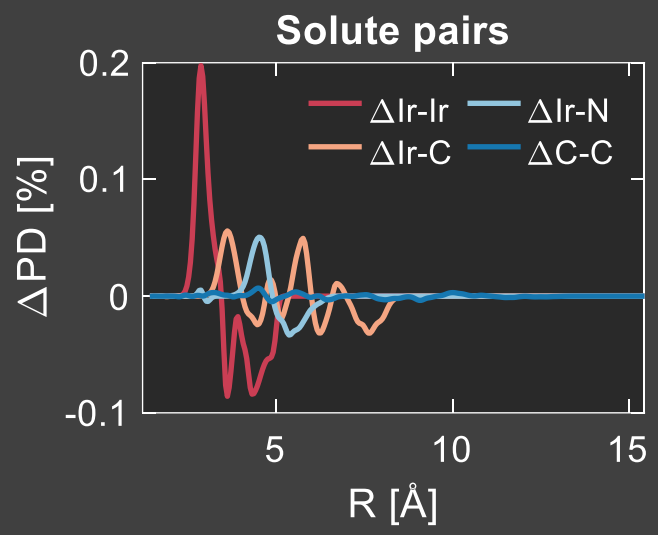

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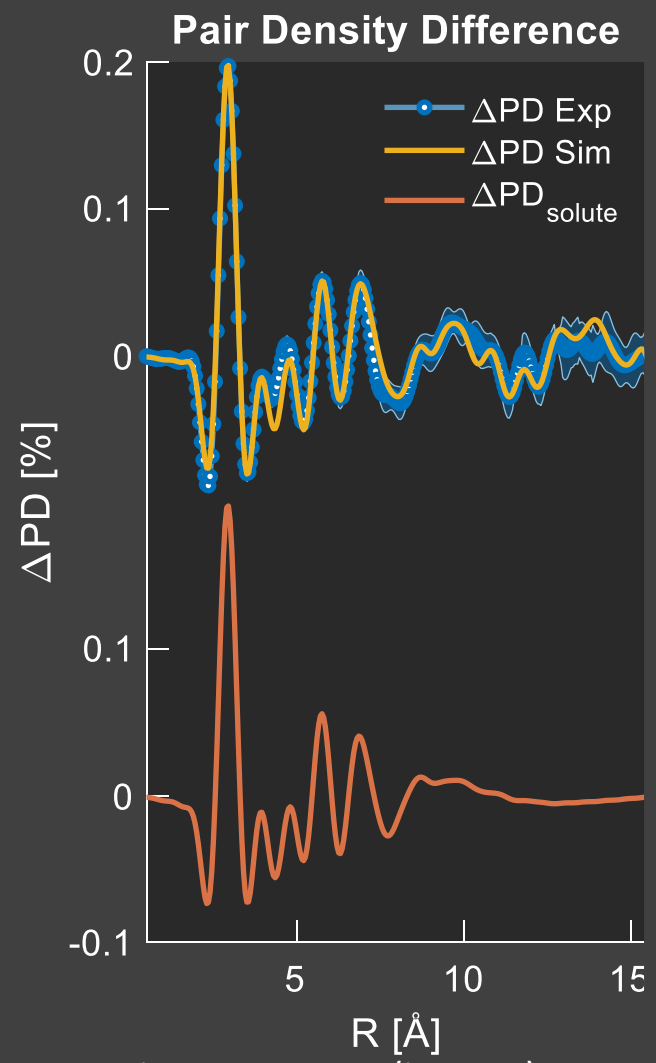
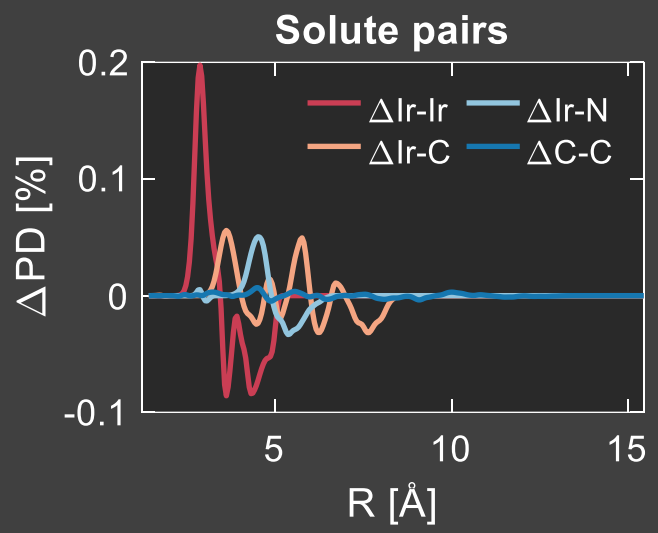
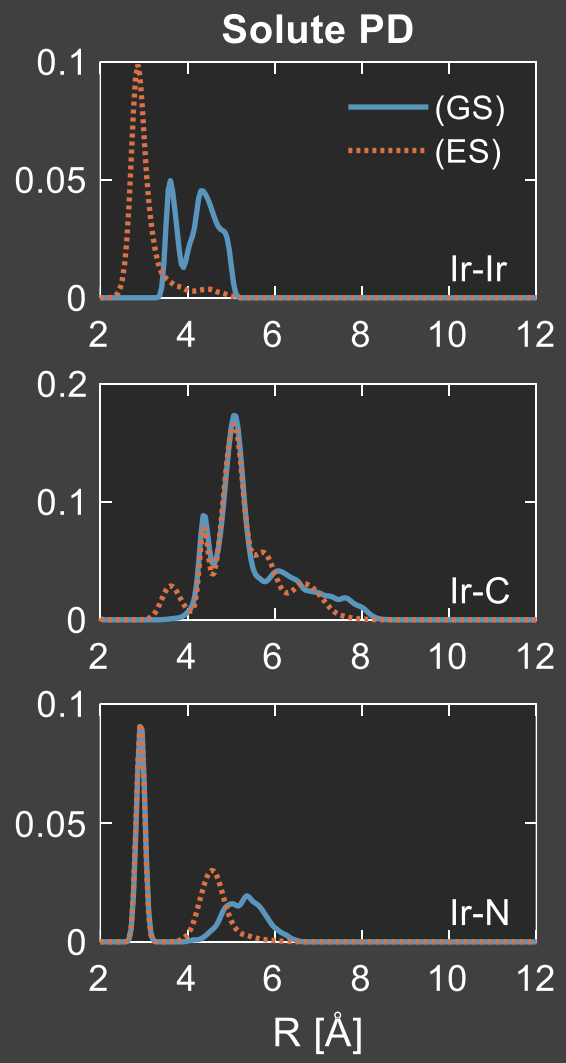
Recovery of Ground vs Excited state densities

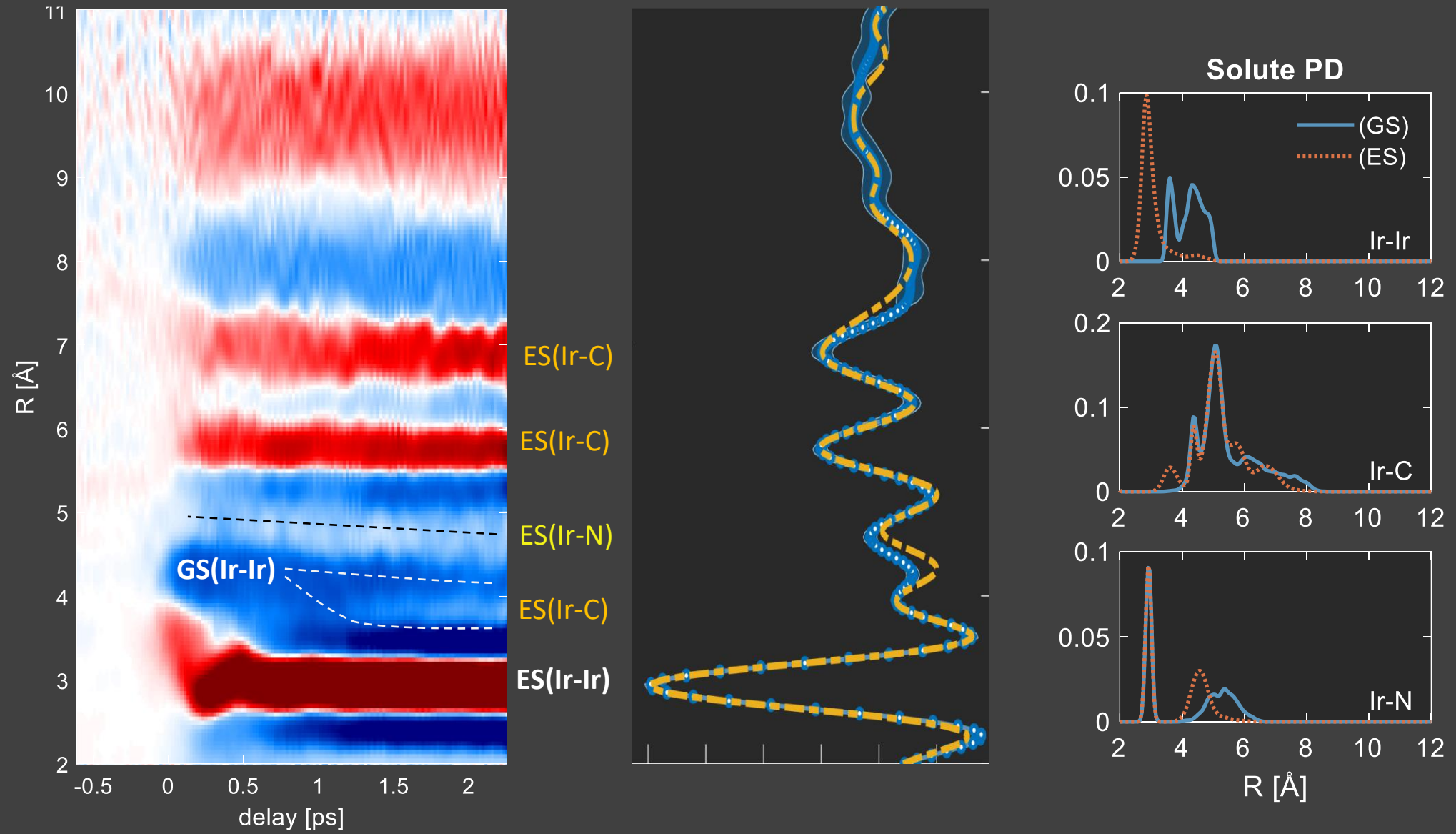






Powers-Riggs ,…, Natan (in prep)

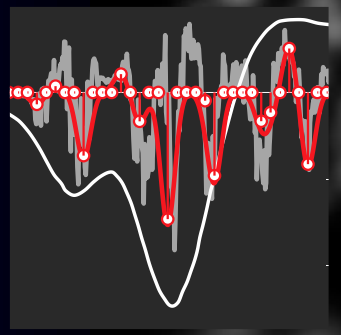
Tracing dynamics in real space one pair at a time

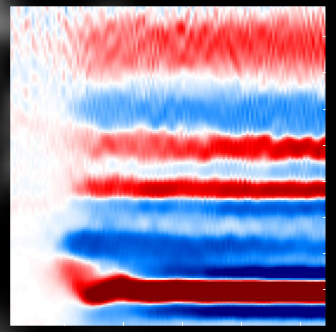


Summary

Directly image sub-diffraction-limit spaced atomic distances and complex motions in the gas phase and in solution.

- Development of inversion and super-resolution methods.
- High-energy scattering enables imaging ultrafast solvation dynamics and the shape of coherent wavepackets.





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