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A new approach to the determination of the uncertainty in neutron diffraction experiments with isotopic substitution method

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Abstract

Neutron diffraction experiment with isotopically substituted substances is a powerful approach claiming to yield unambiguous information about the local atomic structure in disordered materials. This information is expressed in the partial structure factors, and extracting them from a series of measurements requires solution of a set of linear equations that is affected by experimental errors. In this article, we suggest a method for the determination of the optimal set of H/D compositions with or without taking into account the experimental error. For the case of water, our investigations show that the selection of the isotope concentrations and the distribution of measurement time among the various samples have critical role if one wants to utilize the limited neutron beam time efficiently.

It is well known that measurements of pure H₂O introduce fairly large errors in the partial structure factors due to its very strong incoherent scattering. On water and methanol as examples, we investigated the propagation of random errors to the partial structure factors using partial pair-correlation functions from molecular dynamics

simulation. It is shown on the example of water that it is not worthwhile measuring pure H₂O.

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1. Introduction

In a disordered material containing n distinguishable elements, the $n \times (n+1)/2$ independent structure factors can be determined in principle from the same number of scattering experiments through the inversion of a set of linear equations. Sets of independent scattering intensities can be obtained by isotopic substitution in the case of neutron scattering. The general principles of the isotopic substitution technique are rather simple. Samples with different isotopic compositions (isotopes with markedly different coherent scattering lengths) yield different diffraction patterns while the underlying structural features remain unchanged. The neutron diffraction isotopic substitution (NDIS) method has been described in several articles [1]; it has been applied successfully for many years to a wide range of liquids, e.g., water [2], ethanol [3], aqueous glycine solution [4], formic acid [5], ethanediol [6], aqueous liquid mixtures [7], aqueous solutions [8], and polymer electrolytes [9], as well as to glassy materials. However, some important unresolved issues remain. In particular, the sensitivity of the final results (partial structure or correlation functions) [10] to the details of the sample preparation and handling as well as to the data treatment (normalization, correction term) remains an open question.

The technique has been applied successfully for many years as a method of obtaining the partial structure factors of systems of type RX_n , where R denotes a central part of this system without substitution and X_n denotes the isotope to be substituted. For example, in the case of water or methanol, the oxygen atom or the CD_3O group can be denoted as R and X means hydrogen or deuterium.

Matrix formalism can be used to describe the relation between experimental total and partial structure factors or radial distribution functions

$$\mathbf{F} = \mathbf{W} \times \mathbf{Y} \quad (1)$$

where a column vector $\mathbf{y}_j = (RR, RX_n, X_n X_n)^T$ of matrix \mathbf{Y} contains the partial structure factors (*psf*) or partial pair-correlation functions (*ppcf*) RR , RX_n , and $X_n X_n$ to be obtained at the j -th s or r value (inverse or direct space variables), \mathbf{W} is the neutron scattering weighting matrix. The column vectors of matrix \mathbf{F} are $\mathbf{f}_j = (f_1, f_2, f_3)^T$ for the independent experimental total structure functions at the j -th s or r variable. For the sake of simplicity we use the notation \mathbf{f}_j for the j -th column vector of \mathbf{F} and we use f_i , if the i -th element of one of the vectors is concerned. f_1 , f_2 , and f_3 mean for example

results on samples with different isotopic composition, e.g., for water D_2O , H_2O , and $0.64H_2O+0.36H_2O$, where the latter is called “null mixture”.

The rows of the matrix \mathbf{W} , $W_{RR,i}$, $W_{HH,i}$, $W_{RH,i}$ are the corresponding elements of the neutron scattering weight matrix, and they can be given in the following form.

$$\begin{aligned} W_{RR} &= b_{RR}^2 \\ W_{HH} &= (x_{H,i} b_{H,i} + (1-x_{H,i}) b_{D,i})^2 \\ W_{RH} &= 2b_{RR} (x_{H,i} b_{H,i} + (1-x_{H,i}) b_{D,i}) \end{aligned} \quad (2)$$

where $x_{H,i}$ is the mole fraction of H, and b_{RR} , b_H and b_D are the scattering lengths of the R group, hydrogen (-0.376 fm) and deuterium (0.664 fm), respectively. Obviously, the elements of the \mathbf{W} matrix only depend on the mole fraction of hydrogen.

There are several methods to solve equation 1. Throughout this work, we used the singular value decomposition (SVD) method to solve the sets of linear equations. This is a standard method to characterize how the experimental and systematic errors propagate into the results. According to this method, the inverse of \mathbf{W} is

$$\mathbf{W}^{-1} = \mathbf{V} \text{diag}(1/\sigma_i) \mathbf{U}^T \quad (3)$$

where \mathbf{V} and \mathbf{U} are orthogonal matrices and $\text{diag}(1/\sigma_i)$ is a diagonal matrix formed from the σ_i singular values of the \mathbf{W} matrix. In this case, if the right side of the Eq. 1 has a certain error, then

$$\delta \mathbf{y}_j = \sum_i \frac{\delta \mathbf{f}_j \mathbf{u}_i}{\sigma_i} \quad (4)$$

where the \mathbf{u}_i and \mathbf{v}_i are the orthonormal column vectors of \mathbf{U} and \mathbf{V} . This equation shows that \mathbf{y}_j will be most sensitive to the error associated with the smallest singular value. The components of \mathbf{v}_j are the projections to the RR , RX_n and $X_n X_n$ directions, respectively.

In a previous paper [11], we studied how an inequality known from linear algebra can be used for the determination of the inherent uncertainties of the *psf*-s or *ppcf*-s determined from neutron diffraction isotopic substitution experiments. This inequality establishes a relationship between the relative uncertainties of the partial pair-correlation functions or partial structure factors, the norm of the neutron

scattering weighting matrix and the relative error of the experiments, as given by Eq. 4 of [11]:

$$\frac{\|\delta\mathbf{y}_j\|}{\|\mathbf{y}_j\|} \leq \|\mathbf{W}\| \times \|\mathbf{W}^{-1}\| \frac{\|\delta\mathbf{f}_j\|}{\|\mathbf{f}_j\|} \quad (5)$$

The quantity $\|\mathbf{W}\| \times \|\mathbf{W}^{-1}\|$, denoted as κ hereafter, is known as the *condition number*, and it is a measure of the error amplification due to the employed inversion. A set of linear equations is termed “well conditioned” when the conditional number is small [10c,12]. The theoretical smallest value is $\kappa=1$. If the solution is very sensitive to the values of the coefficients, the problem is “ill conditioned.” It is expected in the cases, if the matrix is nearly singular, i.e., some of its rows are almost linearly dependent. The second term of the right hand side of Eq. 5, $\|\delta\mathbf{f}_j\|/\|\mathbf{f}_j\|$, is related to the relative uncertainties in the experiment. During our work, there is an underlying assumption that all the errors are confined to the experimental vector \mathbf{f}_j . Unfortunately, this assumption may be unrealistic; errors in scattering lengths and mole fractions may incorporate into the inequality an additional term, which would be proportional to $\|\delta\mathbf{W}\|/\|\mathbf{W}\|$, where $\delta\mathbf{W}$ is the uncertainty of the \mathbf{W} matrix.

We used in our test cases the Euclidean vector and matrix norms [12]

$$\|\mathbf{f}\|_2 = \left(\sum_i f_i^2 \right)^{0.5} \quad (6)$$

$$\|\mathbf{W}\|_2 = \left(\sum_{i,j} w_{ij}^2 \right)^{0.5} \quad (7)$$

In the case of the Euclidean matrix norm, $\|\cdot\|_2$, the condition number can be expressed as

$$\kappa = \frac{\sigma_{\max}}{\sigma_{\min}} \quad (8)$$

where σ_{\max} and σ_{\min} are the largest and smallest singular values of the weighting matrix. We chose the SVD algorithm to solve the sets of linear equations, because it provides the singular values to calculate condition number, as well.

The relative experimental error (sampling errors, absolutisation error, modelling errors, and instrumental errors, coming mainly from the H atom due to its large inelastic scattering power) is defined as

$$\begin{aligned}
I_{tot}^j &= I_{coh,selfscat}^j + I_{incoh,selfscat}^j + I_{scat}^j \\
I_{scat}^j &= \left(\sum_i \langle b_i \rangle \right)^2 \\
\mathbf{f}_j &\cong I_{scat}^j \\
d\mathbf{f}_j &\cong \frac{I_{tot}^j}{I_{scat}^j}
\end{aligned} \tag{9}$$

where b_i is the neutron scattering length of atom i ; I_{scat} denotes the scattering power and $I_{tot,j}$ is the total scattering (coherent, incoherent) intensity of the j -th experiment. This error mainly depends on the inelasticity of the scattering centre. The scattering lengths for the investigated systems are given in Table 1.

Table 1. The neutron scattering lengths of the investigated systems [13]

	water	methanol	ethanol	ethane-diol
b_R (10^{-14} m)	0.583	3.248	5.246	3.828
b_H (10^{-14} m)	-0.748	-0.374	-0.374	-0.748
b_D (10^{-14} m)	1.334	0.667	0.667	1.334

With the above mentioned equation, it should be possible to minimize the upper limit of the solution error, i.e., the resulting *psf*-s or *ppcf*-s, by determining the set of $x_{H,I}$ mole fractions for which the conditional number of the neutron scattering weighting matrix has a minimal value.

In our previous study [11] we applied our numerical estimations of the optimum set of x_H for several systems investigated earlier by isotope substitution experiments. An additional constraint was used there, namely, that the condition number should be minimal when one of the measurements is made on a completely deuterated solution. We showed also that if the presented method is applied to an over-determined set of equations (i.e., containing more equations than unknowns), the condition number is significantly reduced in all cases.

2. Uncertainty analyses in NDIS experiments using optimization

In the first part of the present work, we applied a full optimization process (using the simplex algorithm) without any constraint for any concentration. We investigated the extreme values of the condition number (first part of the right side in

Eq. 5) as a function of compositions and we obtained the optimum set of hydrogen concentrations for which the condition numbers are minima for both the uniquely determined and the over-determined equations.

The variation of the condition number with respect to the increasing number of experiments is shown in Fig. 1 in the case of water. The corresponding compositions are collected in Table 2. We apply a notation $[m,n]$ where the first number in brackets denotes the number of partial functions and the second number is the number of experiments (i.e., the number of unknowns to be calculated and the number of equations).

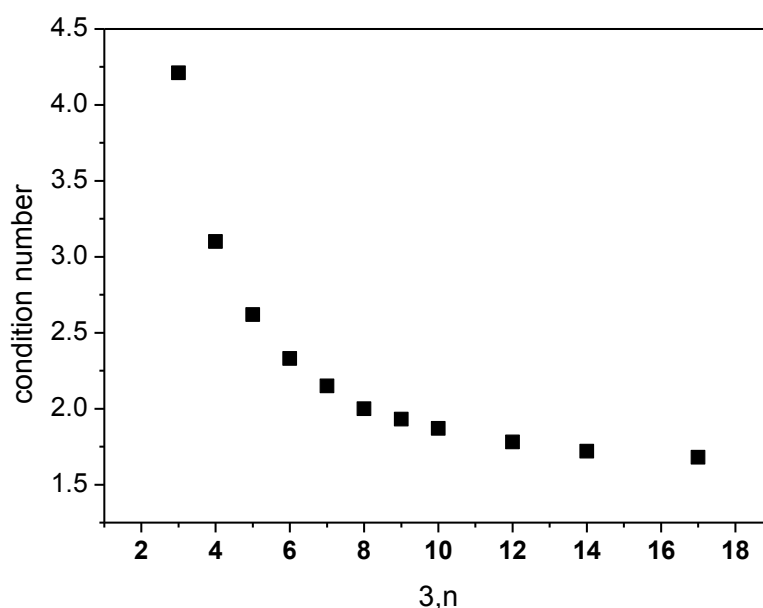


Fig. 1. Euclidean condition number κ as a function of the number n of independent experiments on water (3 partial functions and n different compositions denoted by $[3,n]$)

The condition number can be lowered significantly (from 4.2 to 1.6) by increasing the number of experiments (Figure 1). By considering the optimum compositions in Table 2, it is apparent that there are three basically different compositions at each number of experiments; e.g., in case of 19 experiments these are ~ 0.16 , ~ 0.62 and ~ 1.0 . The optimum H/D compositions in the over-determined cases (more than three water experiments) are found within these three distinct narrow ranges of x_H mole fraction, close to the three optimum compositions in the basic three-experiment NDIS case.

The multiple occurrences of these compositions (e.g., for the 19 experiment case 1, 16, and 2 times) can be interpreted mathematically that the weights for the three individual compositions should be proportional to their frequency in Table 2. If the rows of linear equations are multiplied by a constant value, the solution does not change, if all values are determined with zero uncertainty. On contrary, if the data contain uncertainty, the values having smaller error obtain larger weights and these ones have the largest effect on the results. The simplest way to reduce the error of a measurement (increase its weight) is the increase of the measurement time. Provided that the duration of each experiment is the same in Table 2, this idea can be interpreted as measuring at 3 points of compositions and adjusting the relative measurement times according to the frequency of the compositions in the over-determined cases. We can thus introduce 3 more variables as weights (t_{H1} , t_{H2} , t_{H3}) to determine the actual time needed for each measurement. In this way, the total number of variables is 6 (three concentrations and three measurement times), where the lowest condition number is searched. For methanol, ethanol and ethanediol, the results are shown in Table 3.

Table 2. Optimum isotope compositions for three partial functions and n measurements, $[3,n]$. Each number in the columns is the mole fraction of the hydrogen (x_H) in one experiment, and the whole columns describe the optimum compositions for the series of experiments.

	[3,3]	[3,6]	[3,10]	[3,19]
x ₁	0.3308	0.2776	0.2628	0.1612
x ₂	0.6407	0.6403	0.6426	0.6293
x ₃	0.9506	0.6403	0.6426	0.6314
x ₄		0.6403	0.6426	0.6316
x ₅		0.6403	0.6426	0.6318
x ₆		1.000	0.6426	0.6319
x ₇			0.6427	0.6320
x ₈			0.6427	0.6320
x ₉			0.6427	0.6321
x ₁₀			1.000	0.6322
x ₁₁				0.6322
x ₁₂				0.6323
x ₁₃				0.6323
x ₁₄				0.6324
x ₁₅				0.6326
x ₁₆				0.6328
x ₁₇				0.6331
x ₁₈				1.000
x ₁₉				1.000

Table 3. Optimum isotope compositions and relative measurement times for water, methanol, ethanol and ethanediol with and without taking into account the experimental errors according to Eq. 1 (comp.: H-isotopic composition, t_r : relative time, κ is the conditional number), $v_{RR}, v_{RX_n}, v_{X_nX_n}$ are the components of the v_i vector corresponding to the smallest singular value.)

	water		methanol		ethanol		ethane-diol	
	comp.	t_r	comp.	t_r	comp.	t_r	comp.	t_r
$x_{H,1}$ without	0.00	1.00	0.00	1.00	0.00	1.00	0.00	1.00
$x_{H,2}$ without	0.62	6.66	0.51	1.44	0.50	1.42	0.52	1.50
$x_{H,3}$ without	1.00	2.22	1.00	1.05	1.00	1.02	1.00	1.12
v_{RR}	-0.7000		0.015		0.005		0.043	
v_{RX_n}	0.0000		0.045		0.028		0.077	
$v_{X_nX_n}$	0.70000		-0.998		-0.999		-0.996	
κ	4.20		83.07		215.99		29.25	
$x_{H,1}$ with	0.00	1.00	0.00	1.00	0.00	1.00	0.00	1.00
$x_{H,2}$ with	0.43	3.68	0.47	1.36	0.48	1.37	0.46	1.38
$x_{H,3}$ with	0.63	5.17	1.00	1.00	1.00	1.00	1.00	1.12

The experimental error was taken into account in the last three rows of Table 3 through the relative uncertainties of the experiments in Eq. 5 and they were calculated via Eq. 9. Taking into account or neglecting the experimental error does not have large influence on the optimum isotope compositions for methanol, ethanol and ethanediol. They are always around 0.0, 0.5 and 1.0. This set of compositions was usually adopted in earlier measurements as rule of thumb [5-8]. The $x_h=0.5$ samples should always be given the longest measurement time. It is also clear from this table that the conditional numbers are at least one order of magnitude larger in the case of methanol, ethanol and ethanediol than for water. We can conclude using the eigenvectors of the smallest singular values that the absolute error in the X_nX_n (HH) partials is significantly larger than in the RR and RX_n cases and are in opposite direction.

In contrast, for water, the optimum sets of H contents are different when the experimental error is taken into account and when it is omitted. The different behaviour can be explained by considering the ratio of the total scattering to the intermolecular coherent scattering, to which the relative experimental error as defined by Eqn. 9 is proportional. This ratio exhibits a singularity around $x_H = 0.92$ ($b_{scat}=0.0$)

for water while it varies weakly and monotonously for methanol, see Fig. 2. The behaviour of ethanol and ethanediol is similar to that of methanol, it is thus not shown here.

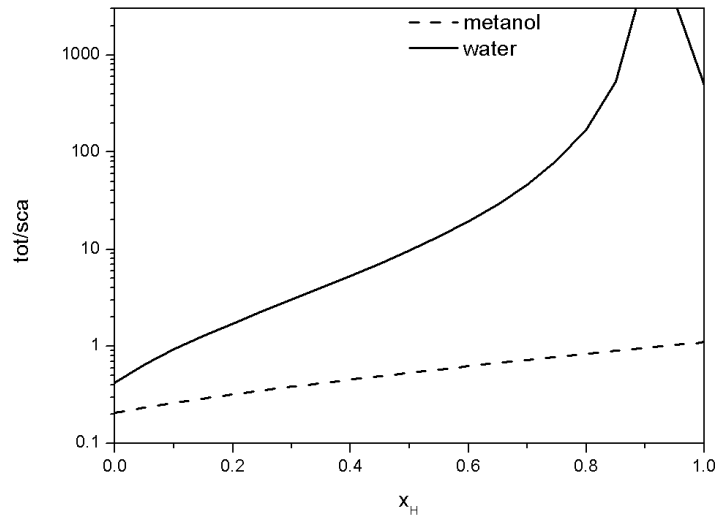


Fig 2. The ratio of total intensity and scattering power as a function of H-isotope mole fraction for water and methanol

In the case of water, without taking care on the experimental error the condition number is the smallest when using samples of pure D_2O ($x_H = 0.0$), and „0” ($x_H = \sim 0.63$) mixture, where the scattering length of hydrogen is 0.0, and H_2O ($x_H = 1.0$), as it was done in earlier experiments [5]. Our results indicate the optimal partition of the measurement time corresponding to their weight during the solution of the linear equations. The longest measurement is required for the „0” mixture, namely, 6.6 times more than for D_2O . The optimal compositions and experimental times are different, if the experimental error is taken into account. Here, the pure H_2O system cannot be found within the compositions. It seems to be against the canonical practice of isotopic substitution on water in neutron diffraction experiments. The $\|\delta\mathbf{W}\|/\|\mathbf{W}\|$ term for all investigated cases is on the order of 10^{-4} for optimum concentration if we assume that the error in the mole fraction is about 0.01 percent.

3. Uncertainty analyses in NDIS experiments using simulation data

In order to test the reliability of Eq. 5 as a pragmatic limit of error we investigated the propagation of a given random error of the total structure factor to the partial structure factors using the NDIS conditions on simulation data according to Eq. 1. This approach provides an estimation of the sensitivity of the NDIS technique to small random perturbations. We note that systematic errors coming from the data analysis (background subtraction, absorption and multiple scattering corrections and normalization) are not taken into account here. It is not easy to incorporate these systematic errors in a study, because they strongly depend on the experimental architecture and details. Such a study should be customized for a given type of measurement, architecture and system, and can be performed only by experts familiar to the experimental place.

The experimental total structure factor can be interpreted as a weighted sum of the partial structure factors. The partial and total structure factors were evaluated in molecular simulations from the Fourier transforms of the computed partial pair-correlation functions and the total radial distribution functions (*trdf*-s). The simulations were performed using the SPC/E [10] and the OPLS all-atom potentials [11] for water and methanol at ambient conditions. The total neutron weighted structure factors of water and methanol for the optimum compositions are shown in Figures 3a-b. The inter- and intramolecular contributions are shown separately for comparison. The *trdf*-s calculated from these structure functions are available in the supplementary material; we neglect an analysis of the effects of the Fourier transformation and of the resulting truncation ripples.

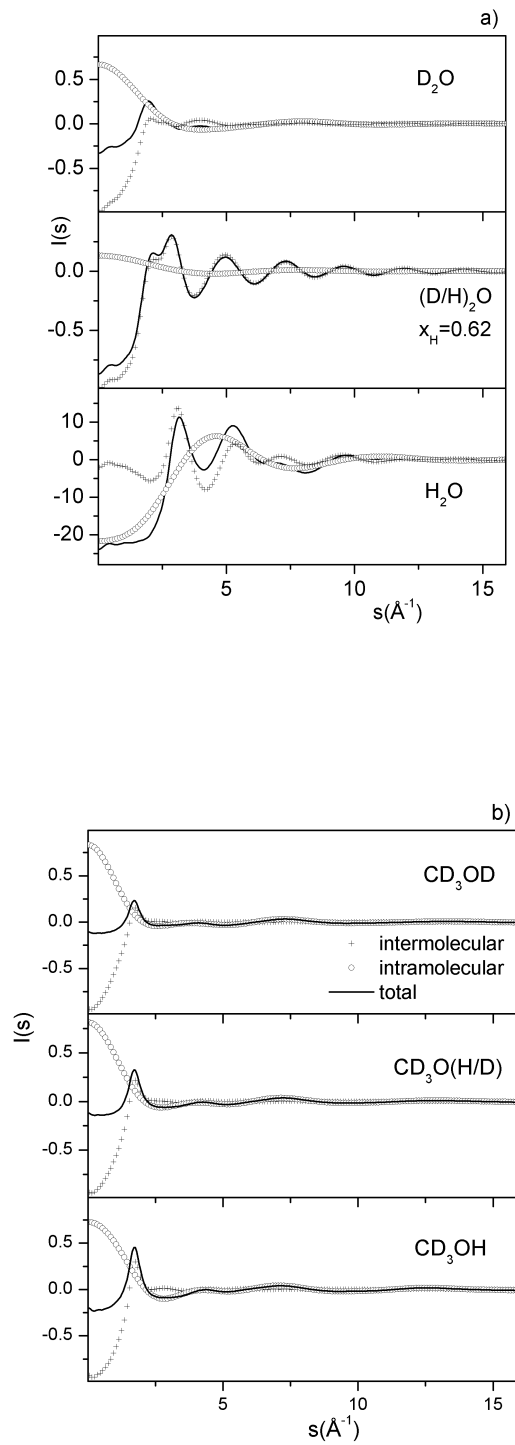


Fig. 3 Intra- and intermolecular contributions to the total structure factors a) for water at the optimized isotopic compositions: ($x_H = 0.0, 0.62, 1.0$) b) for methanol at the optimized isotopic compositions: ($x_H = 0.0, 0.50, 1.0$).

Model calculations were carried out to study the effect of random errors (ε) of the total structure factor to the partial ones. We modified the calculated total structure factors (f) as follows:

$$f' = f \times (1 \pm \varepsilon), \quad (10)$$

where ε is the magnitude of the error. From this point, we limit our analysis to the intermolecular part of the total structure factors. We applied this approximation due to the overlap of intermolecular and intramolecular part of the total radial distribution functions at short distances, which may result a source of error. For the calculations obtained from the total structure factor, see the supplementary material.

There are large differences between the total radial distribution functions obtained for water, while the differences are significantly smaller for methanol. This is a consequence of replacing only one hydrogen in methanol and of the fact that the scattering length of the R group is significantly higher for methanol than for water.

The calculated partial structure factors of water (O-O, O-H and H-H) from the optimised set of D₂O/H₂O mixtures at $x_H = 0.0, 0.62, 1.0$ with random error applied to the total structure factors are shown in Fig. 4. The magnitude of the random error for D₂O was chosen to be $\varepsilon=0.01$, while for (D/H)₂O ($x_H = 0.62$) and for H₂O, it was $\varepsilon=0.1$ due to the significantly larger incoherent scattering contribution of H for the latter two cases.

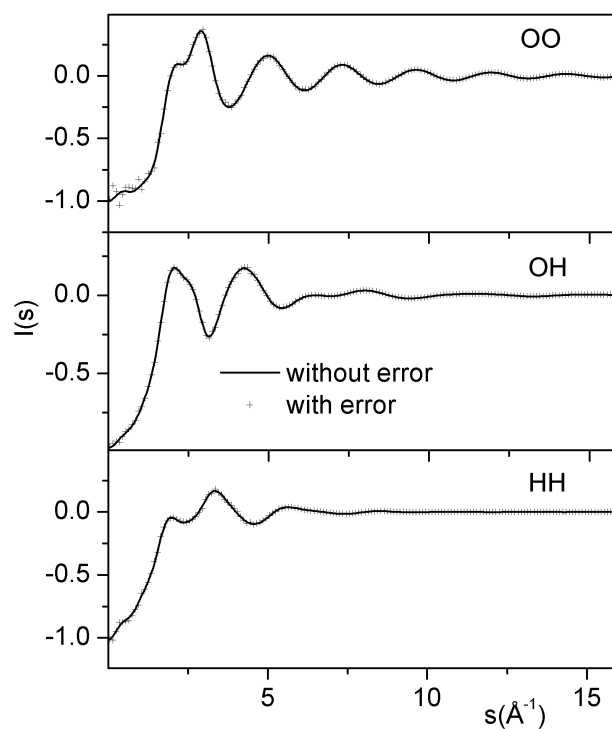


Figure 4. The OO, OH and HH partial structure factors of water determined from the optimal set of ($x_H = 0.0, 0.62$ and 1.0) isotopic mixtures without random errors and with them (0.01 for D_2O , 0.1 for $(D/H)_2O$ ($x_H = 0.62$) and for H_2O).

The calculations show that all partial structure factors are acceptable even with the highest value of error used in this study. The largest uncertainty can be observed in the low s range. However, when isotope compositions are selected from a narrow range (low contrast), e.g., $x_H = 0.00$, $x_H = 0.05$, $x_H = 0.1$, then the partial structure factors become unreliable, as it is demonstrated in Fig. 5.

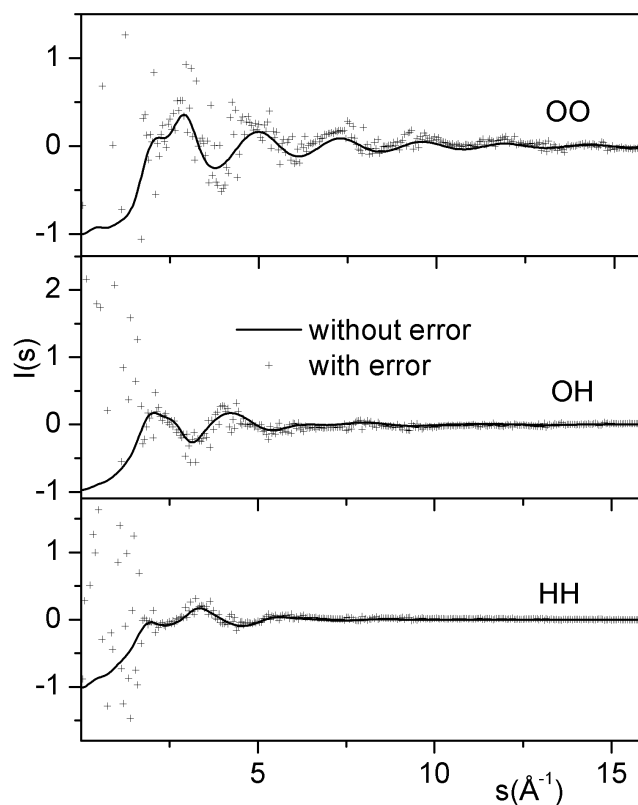


Fig. 5 The OO, OH and HH partial structure factors of water, determined from the $x_{\text{H}} = 0.0, 0.05$ and 0.1 isotopic mixtures with random errors of magnitude 0.01 for each sample.

If these were real experimental results, we would deem them unreliable and hardly usable for data analysis. This observation is in agreement with our previous conclusion that the relative error of the partials is significantly larger for this narrow range of isotope compositions than that for the optimum composition set. This is the direct consequence of the small differences between the total radial distribution functions for the narrow range, as shown in Fig. 6.

Our calculations were also extended to methanol, three partial structure factors were determined, namely RR, RH and HH, where R represents the CD_3O group of the molecule. In Fig. 7, they are shown with the same magnitude of errors as in the water case in Fig. 4.

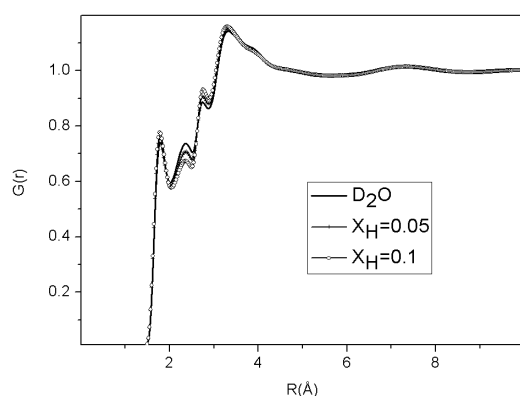


Fig. 6. The total radial distribution function of water with the investigated isotopic compositions ($x_{\text{H}} = 0.0, 0.05, 0.1$)

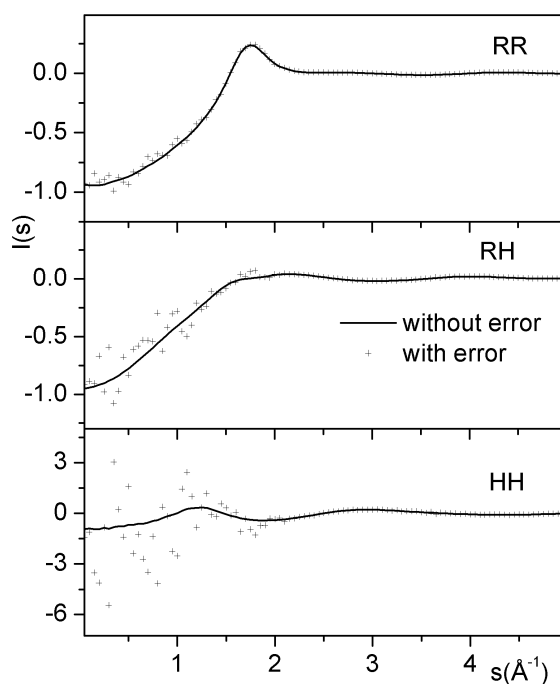


Fig. 7 The RR, RH and HH partial structure factors of methanol, determined from the optimal set of ($x_{\text{H}} = 0.0, 0.5$ and 1.0) isotopic mixtures with random errors. The magnitude of the random error was 0.01 for CD_3OD , and 0.1 for $\text{CD}_3\text{O}(\text{D}/\text{H})$ ($x_{\text{H}} = 0.5$) and CD_3OH .

For RR and RH, the curves are hardly affected by the assumed errors except in the low s range. However, the H-H partial structure factor is very sensitive to the

magnitude of the error. An increase of statistical error results in a quick deterioration of the computed structural parameters.

4. Conclusion

In order to obtain the best possible results from neutron scattering experiments, it is advisable to study the propagation of errors beforehand and select conditions where the data processing can be carried out with the introduction of the smallest possible error. The condition numbers are suitable parameters to determine how we can perform NDIS experiments with respect to minimizing the statistical error during the solution of sets of linear equations. With the help of the proposed analysis design of the experiments can be performed to achieve optimum beam time division and optimum isotope ratios in order to minimize the statistical error. It has been shown on the example of water that it is not worthwhile measuring pure H₂O due to its very strong incoherent scattering, if we take into account both the isotopic compositions and the experimental error. This is not a canonical statement due to the fact that one of the samples has been H₂O in mainly all NDIS experiments [2] performed up to now.

For water, the solution of the set of linear equations has low sensitivity to the statistical error, if optimal compositions are used. For more complex cases, such as methanol, the determination of the H-H partial structure factor is always ill-defined even though the other structural parameters (RR and RH partials) can be determined with reasonable accuracy and experimental effort.

Acknowledgments

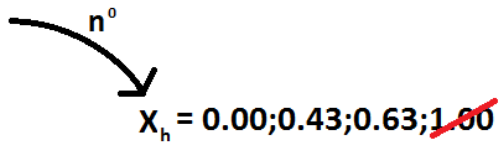
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TABLE OF CONTENT GRAPH



n^0

$X_h = 0.00; 0.43; 0.63; \cancel{1.00}$
