Neutron Compton scattering from water studied with the double-difference technique

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A shortfall of the scattering intensity from protons has been observed in liquids (water, benzene, etc.) and solids (metal hydrogen systems, organic polymers, etc.) using neutron Compton scattering (NCS). The standard analysis of NCS data has been subject to severe criticism, e.g., it was claimed that it is the way the energy resolution function is incorporated in the data reduction scheme that leads to an underestimation of the scattering intensity. Here we present NCS experimental results utilizing a technique—referred to as double difference—which significantly improves the energy resolution function. Specifically, the ratio of the scattering cross-section density of H and D in mixtures of light and heavy water are presented. The experimental data reveal that the results published earlier remain unchanged upon the significant improvement of the energy resolution function.

In the last few years a considerable number of publications has appeared showing a striking shortfall of intensity of epithermal neutrons scattered from hydrogen in various materials; for example, in liquid H_2O/D_2O mixtures,[1] solid metal hydrogen systems,[2,3] as well as liquid and solid organic systems.[4–6] The experimental method used was neutron Compton scattering (NCS) as applied on the time of flight instrument VESUVIO (formerly eVS) at the ISIS neutron spallation source at the Rutherford Appleton Laboratory, UK. In the original NCS experiments on H_2O/D_2O mixtures[1] the striking shortfall of the scattering intensity of neutrons scattered from protons was found to decrease with increasing molar fraction (x_D) of D_2O. Very recently, this effect has been found also using electron-proton Compton scattering which provided an independent experimental confirmation[7] of the effect under consideration. These experiments have attracted major interest by the international scientific community.[8,9]

Beside the fact that this experimental work has triggered a vivid theoretical activity aiming at the explanation of this striking effect,[4,10–14] it has also been the subject of various criticisms. For example, it has been argued that any errors in the incorporation of the large Jacobian factor involved in the conversion from a time of flight scan in q,ω space to a constant q scan could seriously affect the peak areas obtained from the fitting.[15] However, this argument is irrelevant because the experimental data are analyzed directly in time of flight.[16] In addition, the absence of such an anomalous effect in neutron interferometry (NI) experiments lead to the misinterpretation that the effect found with NCS is not real.[17] However, it has been demonstrated that the characteristic time of NI is far too long to reveal the short time effects found with NCS.[18]

The criticism being focused on in this paper is that the way the energy resolution function of the VESUVIO spectrometer is incorporated in the NCS data analysis, and applied thus far to all experimental results obtained on this instrument,[19,20] leads to underestimated scattering intensity of H. Motivated by this criticism Blostein *et al.* conducted a

neutron transmission (NT) experiment on H_2O/D_2O mixtures.[21] The inferred ratios of the neutron total scattering cross section of H and D, σ_H/σ_D, were found to be in agreement with the tabulated value $\sigma_{H,tab}/\sigma_{D,tab}=81.67/7.63$ $=10.7$. Because no anomalies of σ_H/σ_D were found in those experiments, it was concluded[21] that the strong reductions previously observed using NCS (Refs. 1–6) are an artifact of the data analysis. However, certain inappropriate physical parameters characterizing this NT experiment have been discussed by Karlsson and Mayers.[22] In order to scrutinize the above-mentioned claims,[21] we checked the reliability of the NCS data analysis by assuming the following *working hypothesis*:

• If the NCS data analysis does not account properly for the actual energy resolution of the instrument, then a significant improvement of the energy resolution function should give different σ_H/σ_D when using the same data analysis.

Here, we present experimental NCS results obtained with an experimental technique—double difference[23]—which improves the energy resolution function of the instrument considerably. Already here it should be mentioned that the results confirm the validity of the NCS data analysis used thus far and show that the conclusion about the energy resolution function by Blostein *et al.*[19,20] should be refuted.

The VESUVIO spectrometer is an inverted geometry time of flight instrument.[16] The energy and momentum transfers from the neutron to the scattering nuclei are so high that the scattering process can be treated within the impulse approximation (IA) limit,[24–26] i.e., the dynamic structure factor $S(q,\omega)$ of a nucleus consists of a δ function broadened by the Doppler contribution of the nuclear motion. Therefore, this method is particularly suitable to measure nuclear momentum distributions $n(p)$.[24]

The sample is exposed to a polychromatic neutron beam and the final energy E_1 of the neutron after the scattering process is analyzed by taking two spectra, one with a thin foil of a neutron absorbing material between the sample and the detector and one without such a foil [see inset (a) in Fig. 1]. The spectrum to be analyzed is obtained by taking the
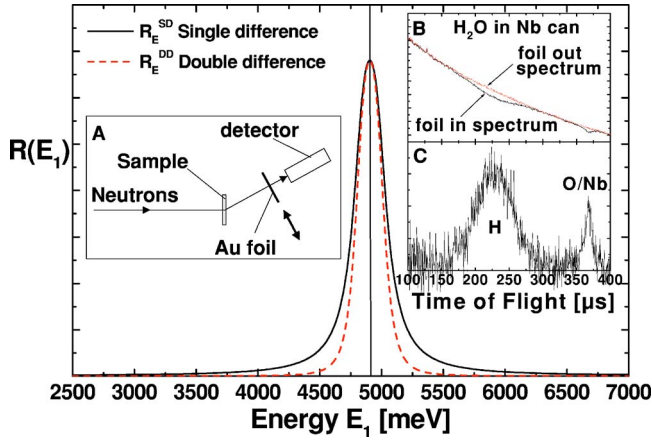
FIG. 1. (Color online) Main frame: Energy resolution $R(E_1)$ of the Au foil centered at resonance energy $E_R = 4.9$ eV using SD (full line) and DD (dashed line). The wings of $R_{SD}(E_1)$ are completely removed when using DD. The shapes are confirmed by measurements on lead. Inset (a): schematic experiment setup. Inset (b): Foil-in/foil-out spectra of H_2O in a niobium (Nb) cell. Inset (c): difference spectrum.

difference of the "foil in" and "foil out" spectra [see insets (b) and (c) in Fig. 1]. This standard technique is referred to as single difference (SD). Very recently, the double difference technique (DD) (Ref. 23) has been implemented on VESUVIO. It consists of taking three measurements, with no filter, a filter of thickness d_1 and absorption $A_1(E_1)$, and a filter of the same material of thickness d_2 and absorption $A_2(E_1)$. The DD technique relies upon the fact that when the total absorption cross section $\sigma_A(E_1)$ is small, the following approximation for the absorption is valid:

$$A_1(E_1) = 1 - \exp[-Nd_1\sigma_A(E_1)] \sim Nd_1\sigma_A(E_1) \qquad (1)$$

with a similar expression for $A_2(E_1)$. Since the "double difference" of the three measurements is

$$R_{DD}(E_1) = A_1(E_1) - \frac{d_1}{d_2}A_2(E_1) \qquad (2)$$

and because $\sigma_A(E_1)$ is small in the tail regions of the resonance [where the right-hand side (r.h.s) of relation (1) is valid in contrast to the large $\sigma_A(E_1)$ at the peak position], then $R_{DD}(E_1) = 0$ for significant offset $|E_1 - E_R|$ from the resonance maximum. Thus the long tails of the function $A_1(E_1)$ appearing in single difference (SD) are removed completely, whatever their functional form, and the energy resolution is therefore considerably improved. This is illustrated in Fig. 1 where the energy resolution functions $R_{SD}(E_1)$ and $R_{DD}(E_1)$ for a gold (Au) analyzer are shown. The energy resolution function of the instrument is very well approximated by a Voigt function centered at 4.9 eV. $R_{SD}(E_1)$ has a half-width at half maximum (HWHM) of the Lorentzian part $\Delta_L = 148$ meV and a standard deviation of the Gaussian part $\Delta_G = 30$ meV. Instead, for $R_{DD}(E_1)$ $\Delta_L = 34$ meV and $\Delta_G = 75$ meV. These facts illustrate that the Lorentzian part, reflecting the long tails, is largely removed using the DD tech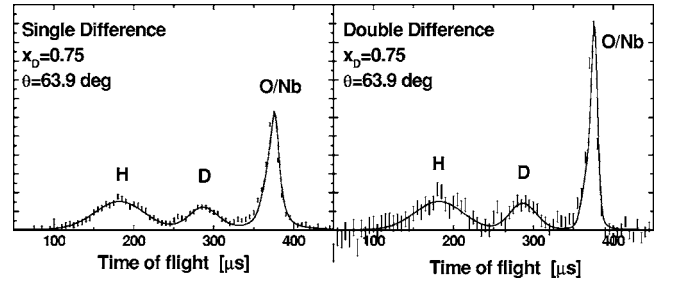nique (see Fig. 1). Thus, the low energetic part of the resolution function due to the "$1/v_1$" dependence[19,20] of the total Au cross section will be removed in the DD measurements. Due to these facts, overlapping effects are also considerably reduced. If the same anomalous shortfall of the scattering intensity from protons is found using both SD and DD techniques then the argument of Blostein *et al.*[19,20] loses its substantiality.

The peak due to the nuclear mass M is a convolution of the nucleus' Compton profile with the resolution function R. The integrated peak intensity I_M from mass M as measured by each detector is strictly proportional to the total bound scattering cross-section density $N_M\sigma_M$, where $\sigma_M = 4\pi b_M^2$ is the total scattering cross section.[27] Hence, for two different nuclei H and X it holds according to the standard theory[16] that

$$I_H/I_X = (N_H\sigma_H)/(N_X\sigma_X) \qquad (3)$$

(for a full account of the data analysis, see Ref. 16). This equation is directly subject to experimental test because the measured value of I_H/I_X can be compared with the value calculated from the r.h.s. of Eq. (3) taking the tabulated[27] σ_M (hereinafter referred to as $\sigma_{M,\text{tab}}$) and the N_M known from chemical formula and/or sample preparation. This basic equation is strongly violated by our experiments on hydrogen containing materials.[1–6] To be concrete, the ratio

$$P = \frac{I_{H,\text{exp}}/N_H\sigma_{H,\text{tab}}}{I_{D,\text{exp}}/N_D\sigma_{D,\text{tab}}} \qquad (4)$$

is significantly smaller than unity (see below). With the DD technique we considerably change R compared to SD. Therefore, it is expected that if the data analysis does not account correctly for R and thus allegedly gives wrong values of I_M using the single difference (see working hypothesis), then different values of the I_M should be obtained in DD.

Thus we measured liquid H_2O/D_2O mixtures with D mole fractions of $x_D = 0.50$ and 0.75 using both SD and DD techniques, respectively. The liquid samples were put in an annular niobium can and were measured at room temperature. The parameters of the energy resolution function R were taken from instrument calibration using a lead sample[28]

FIG. 2. Time-of-flight spectra of the same H_2O/D_2O mixture with D mole fraction $x_D = 0.75$ measured in single difference (left frame) and double difference (right frame) options, respectively. The spectra are normalized to give the same height of the H peak for better comparability. With the DD technique the O/Nb peak is narrower than in the SD technique but the height of the peak is larger in the DD technique as both techniques give the same peak areas.

and were found to agree very well with the values obtained from calculations using nuclear resonance parameters[29] and foil thickness. Example spectra measured in SD and DD options, respectively, of a H_2O/D_2O mixture with D mole fraction $x_D = 0.75$ are given in Fig. 2. The improved resolution of the DD data is most obvious in the narrowing of the width and, consequently, increased height of the peak at $370 \ \mu s$, which is a combination of scattering from the O atom of water and the niobium container.

The obtained ratios P averaged over the scattering angles are

- $P_{SD}^{x_D=0.50} = 0.58 \pm 0.1$ and $P_{DD}^{x_D=0.50} = 0.56 \pm 0.15$ and
- $P_{SD}^{x_D=0.75} = 0.74 \pm 0.05$ and $P_{DD}^{x_D=0.75} = 0.79 \pm 0.2$.

As can be seen, the P values are significantly smaller than unity which contradicts conventional scattering theory. In addition and more importantly in the present context, in direct contrast to the working hypothesis, the P values obtained using SD are almost the same as those obtained using the DD technique. The increased statistical error of P in the DD is a natural consequence of this technique.[23]

Summarizing, although the DD technique introduces a significant improvement to the energy resolution function R, the ratios P of the different H_2O/D_2O mixtures are the same as those obtained from the SD technique using the same data analysis. This result clearly demonstrates that the data analysis procedure as applied at ISIS accounts properly for the resolution function whatever its width and overall shape. Consequently, this gives further support to the genuineness of the presented anomalies of the scattering intensity of protons in the materials investigated thus far.

It is also worth mentioning that the similar anomalous effects in a solid polymer were observed with electron-proton Compton scattering using a spectrometer with continuous electron beam,[7] where the energy resolution function is a Gaussian and does not contain any long tails, and no "foil-in/foil-out" difference is applied.

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