An Evaluation of the Scattering Law for Light and Heavy Water in ENDF-6 Format, Based on Experimental Data and Molecular Dynamics

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In this work we present an evaluation in ENDF-6 format of the scattering law for light and heavy water computed using the LEAPR module of NJOY99. The models used in this evaluation are based on experimental data on light water dynamics measured by Novikov, partial structure factors obtained by Soper, and molecular dynamics calculations performed with GROMACS using a reparameterized version of the flexible SPC model by Toukan and Rahman.

The models use the Egelstaff-Schofield diffusion equation for translational motion, and a continuous spectrum calculated from the velocity autocorrelation function computed with GROMACS. The scattering law for H in H2O is computed using the incoherent approximation, and the scattering law D and O in D2O are computed using the Sköld approximation for coherent scattering. The calculations show significant improvement over ENDF/B-VI and ENDF/B-VII when compared with measurements of the total cross section, differential scattering experiments and quasi-elastic neutron scattering experiments (QENS).

I. INTRODUCTION

The scattering law files for H_2O and D_2O available in ENDF format were computed with two different models [1, 2]. Both models are based on experimental data measured by Haywood in the 60's, and use a free gas model to represent the translational motion of the molecules. These evaluations are acceptable for reactor applications, but show significant discrepancies with total cross section measurements in the sub-thermal range and with angular distributions of the differential cross, caused by the simplified structure and dynamics used in these models.

During the last few years, the Neutron Physics Group in Bariloche have been working on an update of the scattering law models for light and heavy water, using the best experimental information available and focusing on addressing any significant difference between evaluated cross sections and experimental measurements. To complement and complete the existing experimental data we used molecular dynamics simulations, inspired in part by the work of Abe [3].

The molecular dynamics method allows to obtain a comprehensive picture of the dynamics of the system with atomic resolution in the positions, velocities and forces involved in the molecular motion. Particularly, by using a flexible water potential it is possible to calculate the frequency spectrum based on the velocity data.

The simulations were performed using GROMACS V.4.5.5 package [4], an open source and free license software. Light and heavy water were simulated using a SPC flexible potential reparametrized by Toukan and Rahman [5]. The water potential consist in a three sites water model, with point charges at the hydrogen and oxygen atoms and a repulsive Lennard-Jones (LJ) term in the oxygen atom. The intramolecular interactions are represented by an anharmonic term for the O-H bond stretching and a harmonic angular potential for the H-O-H bending.

The simulated systems consist in 512 water molecules in a NPT ensemble in a cubic box with periodic boundary conditions. The temperature was 300 K controlled using the Nosé-Hoover thermostat ($\tau_t = 0.1$ ps) and pressure was 1 bar controlled with the Parrinello-Rahman barostat ($\tau_p = 0.5$ ps). The cutoff for the short range LJ+Coulomb was 0.9 nm with no long range correction in the electrostatics. The total simulation time was 100 ps, which is long enough to allow the long time diffusional dynamics to appear, with a timestep of 0.5 fs, which allows the fast internal vibrations be captured.

A vector including the velocities of each atom was saved every 6 frames into a trajectory file, afterwards processed to compute the *velocity autocorrelation function* (VACF)
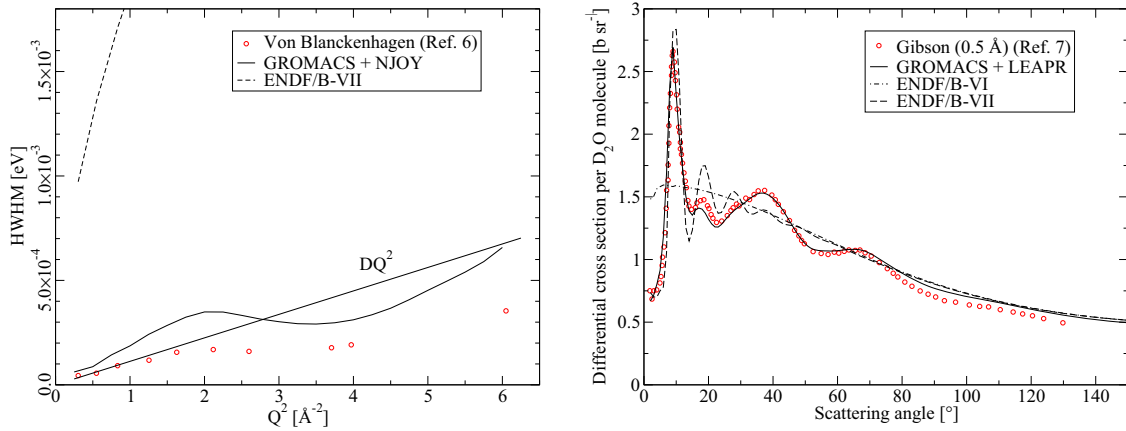
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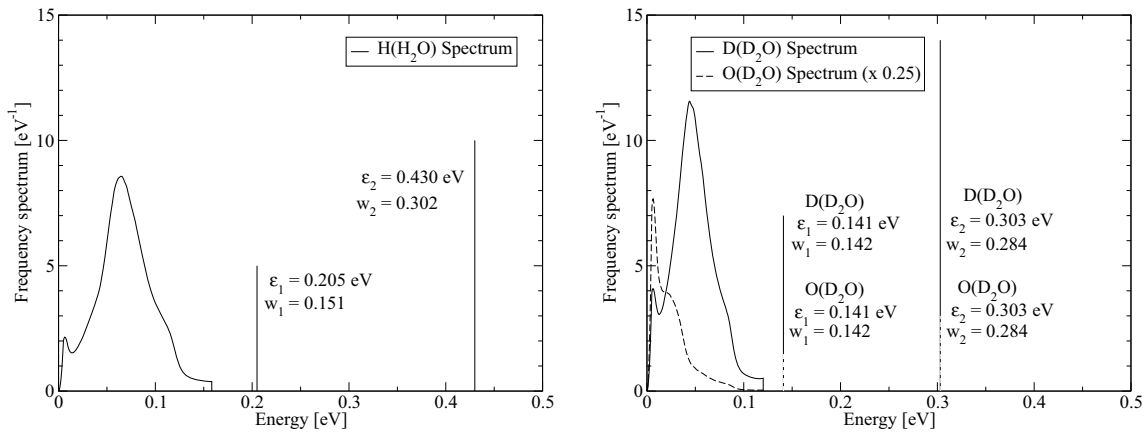
(a)Frequency spectrum for H in H_2O. Oxygen is treated as a free gas with mass 16.
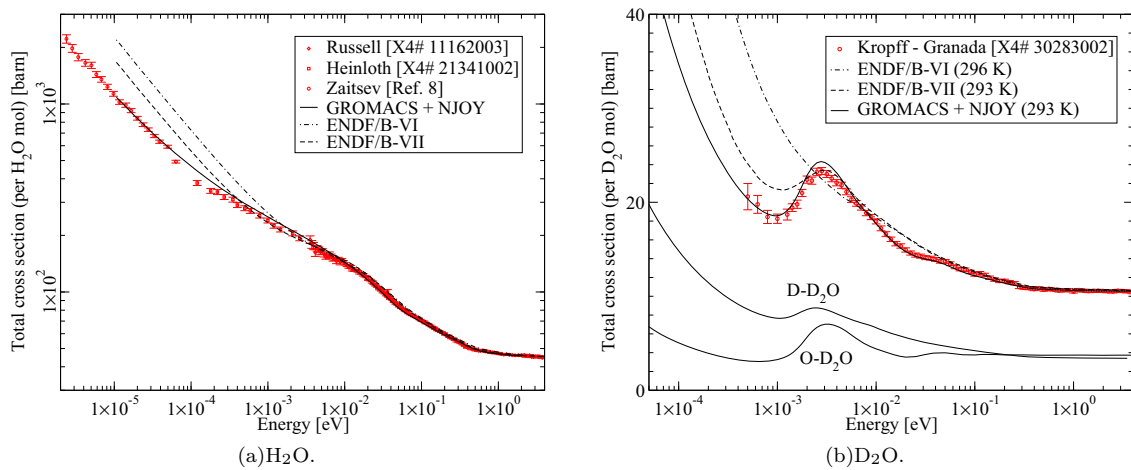
(b)Frequency spectra for D and O in D_2O.

FIG. 1. Frequency spectra for light and heavy water.

(a)QENS linewidth for $E_0 = 5$ meV.

(b)Angular distribution for $\lambda = 0.5$ Å($E_0 = 0.680$ eV).

FIG. 2. Comparison with neutron scattering experiments in heavy water.

(a)H_2O.

(b)D_2O.

FIG. 3. Total neutron cross section for light and heavy water.

$$\text{VACF}(\tau) = \langle v(t) \cdot v(t + \tau) \rangle. \tag{1}$$

Finally, the frequency spectrum was computed from the molecular dynamics results by taking the Fourier transform of the VACF

$$\rho(\varepsilon_n) = \frac{M}{3\pi kT\hbar} \left| \sum_{k=0}^{N-1} \text{VACF}(\tau_n) e^{2\pi kn/N} \right| \Delta\tau. \tag{2}$$

II. LEAPR MODELS

The models to compute the scattering law were implemented using the LEAPR module of NJOY [1]. In these models, the scattering law is calculated using the incoherent approximation as a convolution of three analytical models: molecular diffusion or free gas motion, a phonon expansion for a solid-like continuous frequency spectrum, and Einstein oscillators to represent the internal modes of vibration.

Generalized frequency spectra for H in H_2O, and for D and O in D_2O were computed using eq. 2 and processed to create a LEAPR input file. The phonon expansion used in LEAPR requires the continuous frequency spectrum to approach $\varepsilon \to 0$ as ε^2. To do this, the diffusion component of the spectrum was first substracted using the expression for the Egelstaff-Schofield diffusion model [9]. This model requires two parameters: the diffusion coefficient, that was obtained from $\rho(0)$, and the diffusion mass, which in the case of light water was taken from the experimental results by Novikov [10], and for heavy water was computed assuming the same size of molecular clusters: $m_{\text{diff}}^{H_2O} = 6.5 \, m_{H_2O}$, $m_{\text{diff}}^{D_2O} = 6.5 \, m_{D_2O}$.

The internal vibration modes were also removed, and later included in the input as Einstein oscillators. Resulting frequency spectra are shown in Figs. 1(a) and 1(b).

For heavy water, the effect of the structure in coherent scattering was taken into account using the Sköld approximation [11] for deuterium and oxygen

$$S_{\text{coh}}^i(\alpha, \beta) = S_{\text{inc}}^D(\alpha/\tilde{S}^i(Q), \beta)\tilde{S}^i(Q) \tag{3}$$

$$\tilde{S}^i(Q) = 1 + 2/3 \, [S_{ii}(Q) - 1] \tag{4}$$
$$+1/3 \, b_{\text{coh}}^j/b_{\text{coh}}^i \, [S_{ij}(Q) - 1] \text{ for } i = \text{D, O}.$$

$S_{\text{ij}}(Q) = S_{\text{DO}}(Q), S_{\text{OO}}(Q), S_{\text{DD}}(Q)$ are the partial structure factors of heavy water, measured by Soper [12].

III. RESULTS

Using the prepared scattering law file in ENDF-6 format, cross sections and other measurable quantities can be calculated. The double differential scattering cross section (DDXS) shows good agreement with experimental results from Harling (not included for space), similar to that obtained using ENDF/B VI and ENDF/B VII.

The width of the quasi-elastic peak of the DDXS gives a more stringent test of the quality of low energy dynamics. Comparison with QENS measurements in D_2O (Fig. 2(a)) shows that our model gives a much better agreement than the ENDF/B-VII model. The reason improvement is the inclusion of diffusion, which gives the baseline DQ^2 of the QENS width, and the application of the Sköld approximation, which preserves the second moment of the DDXS. To further test this approximation we computed the angular distribution of neutrons in scattering experiments (Fig. 2). The inclusion of O-O and D-O structure instead of the simpler D-D structure used in ENDF/B-VII allows a much better representation of the scattering data.

Finally, the inclusion of more precise data for the structure and dynamics is also reflected in the total cross section (Fig. 3). Fig. 3(b) shows the scattering cross section for D and O in D_2O, and the effect coherence of O in the total cross section can be seen, especially in the region around 20 meV.

IV. CONCLUSIONS

The models we present in this paper, based on molecular dynamics simulations and experimental data, are shown to have better agreement with measured values for both differential and integral quantities than ENDF/B-VI & -VII. The improvements are mainly in the cold neutron range, and for the angular distribution with heavy water.

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