Development of Cold Neutron Scattering Kernels for Advanced Moderators

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Abstract

The development of scattering kernels for a number of molecular systems was performed, including a set of hydrogeneous methylated aromatics such as toluene, mesitylene, and mixtures of those. In order to partially validate those new libraries, we compared predicted total cross sections with experimental data obtained in our laboratory. In addition, we have introduced a new model to describe the interaction of slow neutrons with solid methane in phase II (stable phase below T=20.4K, atmospheric pressure). Very recently, a new scattering kernel to describe the interaction of slow neutrons with solid Deuterium was also developed. The main dynamical characteristics of that system are contained in the formalism, the elastic processes involving coherent and incoherent contributions are fully described, as well as the spin-correlation effects.

Keywords: scattering kernel, advanced moderator, hydrogeneous methylated aromatics

INTRODUCTION

Cold neutrons are widely used in different fields of research such as the study of the structure and dynamics of solids and liquids, the investigation of magnetic materials, biological systems, polymer science, and a rapidly growing area of industrial applications.

The development and optimization of advanced cold neutron sources require neutronic calculations involving thermal and subthermal neutron energies, which in turn demand the knowledge of reliable cross section data relative to the materials which conform the system under consideration. The compromise solution adopted in standard Nuclear Data Libraries involves the inclusion of scattering cross sections for a few common moderators at some selected temperatures, and data for any different material or physical condition must be 'constructed' from pieces of information actually corresponding to those few cases found in the existing files.

Condensed molecular systems often display a complex behavior due to translational, rotational and vibrational degrees of freedom – and their couplings – that animate the intra-and inter-molecular motions. However, a full account of those is not necessarily required in some special circumstances, for example when only some integral properties of the neutron scattering interaction must be properly described.

In this paper we describe some of the activities currently ongoing at Neutron Physics Division of Centro Atómico Bariloche (Comisión Nacional de Energía Atómica, Argentina), which involved our recent theoretical, calculational and experimental efforts related to the study of hydrogeneous materials of interest as cold moderators. The main motivations for those studies are driven by the large and increasing impact of Neutron Scattering techniques on Science and Technology, the strong requirement of long wavelength neutrons, and the development of advanced cold neutron sources.

We present here our work on some selected molecular systems including solid phases hydrogeneous methylated aromatics such as toluene, mesitylene, xylene, and mixtures of those. In order to produce a partial validation of some of those new libraries, we performed transmission experiments using our pulsed neutron source based on an electron LINAC. Also, our most recent work on methane in phase II (T < 20.4K) and solid deuterium is discussed, and our model predictions are compared with the available experimental information.

BASIC EQUATIONS

The Van Hove scattering function $S(\mathbf{Q},\omega)$ is directly related to the double-differential cross section [1]:

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k}{k_0} S(\mathbf{Q},\omega) \qquad (1)$$

where $\mathbf{k}$, $\mathbf{k_0}$ are the scattered and initial neutron wave vectors, $\hbar\omega$ is the neutron energy loss, and $\hbar\mathbf{Q} = \hbar(\mathbf{k_0} - \mathbf{k})$ is the momentum transferred to the system.

The scattering law of a molecular system

$$S(\mathbf{Q},\omega) = \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt\, e^{-i\omega t} \Big\langle \sum_{l,l'} \sum_{v,v'} \overline{a_{lv}^* a_{l'v'}} \exp\{-i\mathbf{Q}.\mathbf{R}_{lv}(0)\} \exp\{i\mathbf{Q}.\mathbf{R}_{l'v'}\Big\rangle$$

(2)

where $\mathbf{R}lv(t)$ denotes the position of the atom v within the molecule l , can be written as the sum of inter $(l \neq l')$-and intra $(l = l')$ molecular contributions (also referred to as the *outer* and *inner* terms, respectively). That means expressing its Fourier transform as

$$\chi(\mathbf{Q},t) = \Big\langle \sum_{l \neq l'} \sum_{v,v'} \overline{a_{lv}^* a_{l'v'}} \exp\{-i\mathbf{Q}.\mathbf{R}_{lv}(0)\} \exp\{i\mathbf{Q}.\mathbf{R}_{l'v'}(t)\} \Big\rangle +$$
$$\Big\langle \sum_{l} \sum_{v,v'} \overline{a_{lv}^* a_{lv'}} \exp\{-i\mathbf{Q}.\mathbf{R}_{lv}(0)\} \exp\{i\mathbf{Q}.\mathbf{R}_{lv'}(t)\} \Big\rangle$$

(3)

Here the brackets denote the average of the time-dependent operators over an equilibrium-distribution function in the full phase space of the scattering system. The structural complexity of the system together with the motion of the molecules' centres of mass are the main elements determining the intermolecular component. On the other hand, the complete effects of the molecule´s conformation and degrees of freedom are contained in the inner term.

The scattering lengths a_{lv} appearing in the above equations are spin dependent quantities, and therefore must be in principle included within the expectation value brackets of the intermediate scattering function $\chi(\mathbf{Q},\omega)$. In terms of the usual coherent, bc_v , and $v$incoherent, bi , scattering lengths for nuclei $_v$, one obtains:

$$a_v = b_c^v + 2b_i^v\, (S_v.\mathbf{s})[S_v(S_v + 1)]^{-1/2}$$

(4)

where S_v and $\mathbf{s}$ are the spin operators for nuclei v and the neutron, respectively.

The structural and dynamical properties of a given system determine the characteristics of its interaction with slow-neutrons. In other words, the probability for the occurrence of a scattering process with the exchange of certain energy and momentum between the neutron and the scatterer is controlled by those properties, in turn contained in the scattering law $S(\mathbf{Q},\omega)$ of the system. In the frame of the Gaussian approximation [1] the dynamics of the material is enclosed in its generalized frequency spectrum, and this is in fact the important piece of information we need to predict scattering probabilities in the case of hydrogenous materials, where interference effects are negligible.

Under the assumption of no coupling between the (translational, rotational, vibrational) molecular modes, the intermediate scattering function is the product of

those associated to each mode. In addition, each of the factors is assumed to satisfy the Gaussian approximation

$$\chi_i(Q,t) = \exp\{-\gamma_i(t)Q^2\} \; ; \text{i=1,2}$$

(5)

where the time-dependent mean-square displacement $\gamma(t)$ is related to the frequency spectrum

$$\gamma(t) = \int_0^{\infty} \frac{Z(\omega)}{\omega} \Big[\{n(\omega)+1\}e^{i\omega t} + n(\omega)e^{-i\omega t}\Big]$$

(6)

and $n(\omega)$ is the occupation number.

We constructed frequency spectra for the different materials considered in this work, by combining experimental [2,3] and synthetic [4] contributions, together with a fitting parameter related to the weight of the translational and librational modes, and a normalization condition for the weights of all the dynamical modes.

Scattering law data files were generated by the LEAPR module of the NJOY code [5] using the adopted frequency spectra, whereas the cross section data libraries were produced by the modules THERMR and ACER, for the appropriate format for MCNP calculations.

APPLICATIONS

Solid Aromatic Hydrocarbons

Although solid methane is the best moderator in terms of cold neutron production, it has very poor radiation resistance, causing spontaneous burping even at fairly low doses. Such effect is considerably reduced in the aromatic hydrocarbons. We reviewed the dynamics of a group of aromatic hydrogenous solids, and making use of existing experimental information on the density of states for translational and rotational (librational) motions, we developed synthetic frequency spectra for them. Cross section libraries in ACE format were then generated using the NJOY code. They were validated by comparing with experimental data obtained in our laboratory and used to predict neutron spectra emerging from a typical TMR configuration, by using the MNCP code for the evaluation of the energy distribution of neutrons coming out from the cold moderator.

Natkaniec and coworkers performed a comprehensive study on the inelastic neutron scattering properties of aromatic hydrocarbons at low temperatures [2,6], and they were able to derive preliminary densities of states for those materials. As an example, we show in Fig. 1 the low-energy part of the results they obtained for the three phases of mesitylene that could exist at 20K [2].

This material, 1-3-5 trimethyl-benzene, has three methyl groups placed symmetrically around the benzenic ring, presumably the configuration with richest density of rotational states at low energies. The phase II showing

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the typical behaviour of a disordered one, is the most interesting as an efficient cryogenic moderator material.
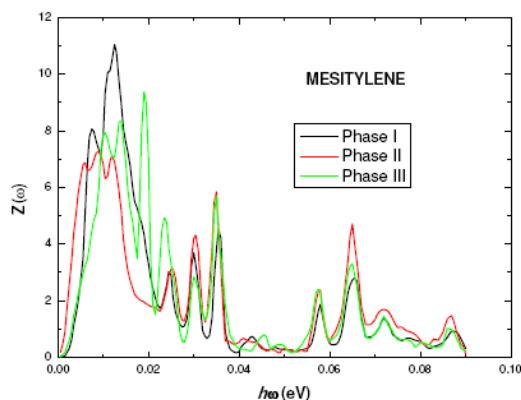

Fig. 1: The frequency spectrum of mesitylene used in our model for each of its three low temperature phases

Transmission experiments were performed at the 25 MeV Electron LINAC based pulsed neutron source at Centro Atomico Bariloche, operated in these experiments at a repetition rate of 50 Hz and 12 µA average current. The neutron energy was determined by the TOF technique, where the scale was corrected by the mean emission time of the moderator while the spectra were corrected by dead time effects from detectors and electronics.
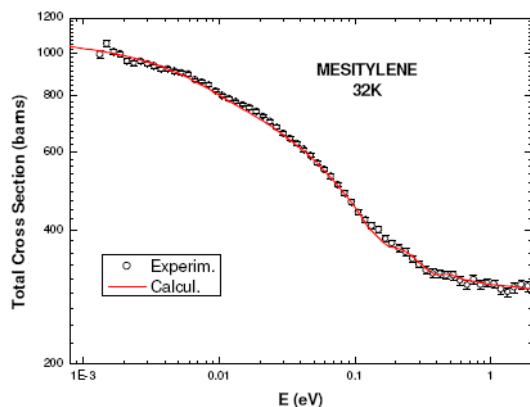

Fig 2: Total cross section of mesitylenee at 32 K measured at our laboratory, compared with the calculated curve from our new kernel.

Even though those aromatic materials are very easy to handle, the solid phases that produce an enhanced flux of cold neutrons correspond to amorphous structures rich in low-energy excitations, and they can be created through lengthy cooling processes requiring in many cases additional annealing stages. The 3:2 mesitylene-toluene mixture, that forms in a direct manner the appropriate disordered structure, constitutes an excellent cryogenic moderator material, as it is able to produce an intense flux of cold neutrons while presenting high resistance to radiation.

The comparison of experimental and calculated results for solid mesitylene and the mixture mesitylene 3:2 toluene at 32 K are shown in Figs. 2 and 3,

respectively, where a good agreement is obtained in each case with the optimized frequency spectrum. Once the new cross section libraries were produced from the validated kernels, spectra calculations were performed using the MCNP code [7], on a standard target-moderator-reflector configuration used at the Hokkaido LINAC.
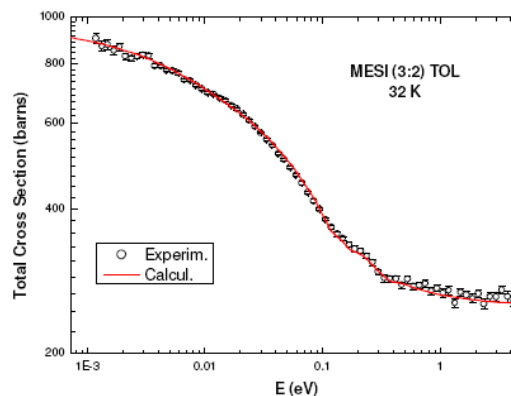

Fig 3: Total cross section of mesitylene (3:2) toluene at 32 K measured at our laboratory,

The normalized neutron spectra thus produced are shown in Fig. 4 for a temperature of 20 K, where it is evident that the methyl groups containing molecules produce a more intense and cooler spectrum than that due to benzene. In addition, the best of the group in that sense is mesitylene in phase II, closely followed by the mixture of mesitylene and toluene.
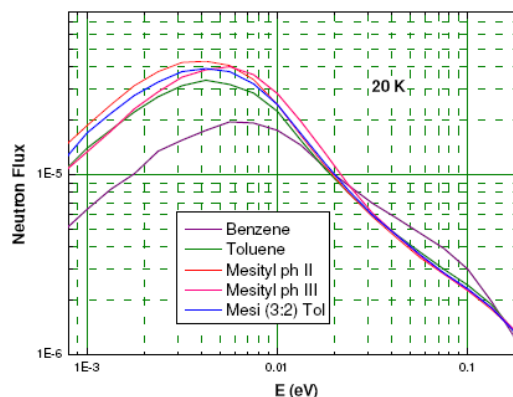

FIG. 4: Neutron spectra emerging from the aromatic hydrocarbons at 20 K studied here, using a standard TMR configuration.

Thus, by making use of existing experimental information on the density of states for translational and rotational (librational) motions, we developed synthetic frequency spectra for several aromatic hydrocarbons.

We presented the final forms of the frequency spectra for the aromatic materials considered, as well as their scattering kernels, cross section data and predicted neutron spectra emerging from a typical TMR configuration, by using the codes NJOY for data generation and MNCP for the Montecarlo evaluation of

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the energy distribution of neutrons coming out from the cold moderator.

Solid Methane in Phase II

We developed a simple model to describe the interaction of slow neutrons with solid methane in phase II, including the main dynamical features of the system and the effect of spin correlations. This effect occurs in molecules containing identical nuclei whenever spin and rotational states are coupled, thus imposing symmetry requirements on the molecular wave function. A central motivation for the development of this new scattering kernel has been the generation of cross section libraries appropriate for the calculation of neutron thermalization properties in CH4 II.

$$\chi^{\mathrm{inter}}\left(\mathbf{Q},t\right) = \Big\langle \sum_{\nu,\nu'} b_c^{\nu} b_c^{\nu'} f_{\nu\nu'}^{'} \Big\rangle$$

$$\chi^{\mathrm{intra}}\left(\mathbf{Q},t\right) = \Big\langle \sum_{\nu,\nu'} \Big\{ b_c^{\nu}b_c^{\nu'} + b_{inc}^{\nu}b_{inc}^{\nu'} \cdot \frac{\left(\mathbf{S}_{\nu}\mathbf{S}_{\nu'}\right)}{\left[S_{\nu}\left(S_{\nu}+1\right)S_{\nu'}\left(S_{\nu'}+1\right)\right]^{1/2}} \Big\} f_{\nu\nu'}^{'} \Big\rangle \quad (7)$$

The scattering lengths $a l\upsilon$ are spin dependent quantities. After performing the spin averages appropriate to an unpolarized neutron beam, the scattering law can be written as the sum of inter ($l \, ^1 \, l'$)- and intra ($l = l'$) molecular contributions (also referred to as the *outer* and *inner* terms, respectively). That means expressing its Fourier transform as

Detailed quantum calculations were performed to describe the low-level energy states in CH4 II (Ref. 8) and applied to the evaluation of neutron cross sections for that system [9,10]. Those formulations were then used to analyze neutron scattering and transmission experiments [11,12,13]. In our study we oriented our effort to the development of a simple model which should preserve the main dynamical features (as well as a proper description of spin correlation effects) of the system and therefore be able to make reliable predictions in terms of neutron fluxes emerging from such cold moderator material.

From the measurements performed by Harker and Brugger [14] at different temperatures in phase I and phase II of solid methane, we derived frequency spectra for free, hindered, and average (1:3) molecules in phase II, and they are displayed in Fig.5. It is observed that the spectrum corresponding to free molecules is richer at low energies, reflecting the availability of many well distributed levels over that region; on the contrary, the spectrum for hindered molecules shows a prominent peak around 0.0065 eV where the librational states coalesce. The third curve, the phase II spectrum, is the 1:3 weighted average of the other two.
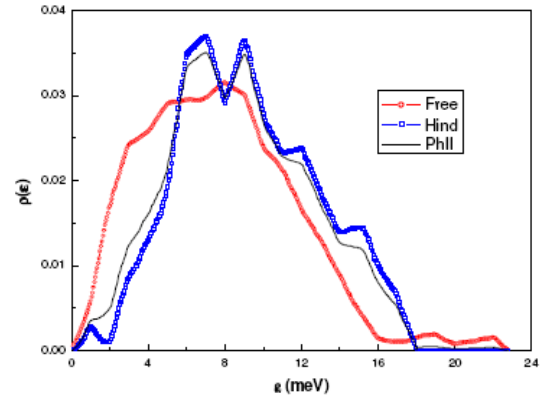

Fig 5: Frequency spectra (translational and rotational Motions) employed in our calculations, derived from the experimental data of Harker and Brugger [Ref. 14]

The calculation of the total cross section involves integration of the resulting scattering function over final neutron energies and scattering angles. There is a first term which is evaluated in a conventional way, starting from the phase II spectrum, normally through Fourier transforms or phonon expansion algorithms. The second, elastic term carrying the effects of spin correlations, only requires the integration of the (non rigid) molecular factor over the scattering angles.
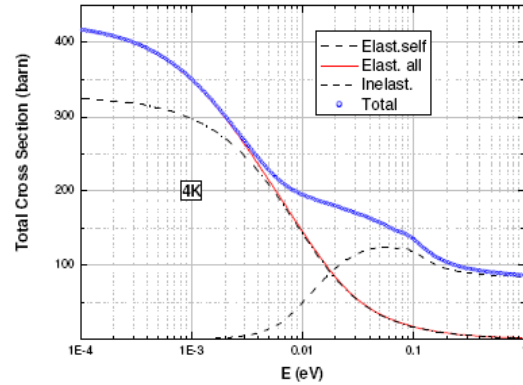

Fig 6: The calculated total cross section of CH4 at 4 K, indicating the elastic and inelastic contributions.

The prediction of the present model for CH4 II at 4K is displayed in Fig. 6, where the inelastic and elastic spincorrelated and uncorrelated contributions are also shown. In particular, our calculation indicates that, for example at 0.0001 eV the effect of spin correlation is to increase the total cross section at 4K from 324.5 b to 416.9 b.
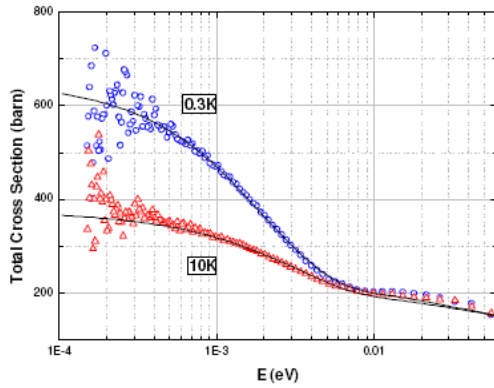
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Fig 7: Comparison of the calculated total cross sections of methane at 0.3 K and 10 K, with the measured points of Grieger et al. [Ref. 11].

A comprehensive set of measurements on this system was performed by Grieger *et al*, [11]. at temperatures ranging from 19.5 K down to 0.3 K, and we compare in Fig. 7 our calculations with their experimental total cross sections at 0.3 K and 10 K, over the relevant energy range. The agreement is very good except at the lowest energies, where the scatter of data points does not allow to confirm such assessment.

The predictions of our model for methane in phase II are in good agreement with a full quantum mechanical calculation over the limited range where the latter was formulated, and with available experimental information over the complete thermal energy range. Bearing in mind the general nature of the approximations involved in the present prescription, and besides its predictive capacity demonstrated for solid methane in phase II, the model can be useful for the analysis of neutron scattering experiments designed to study spin species conversion of different rotational tunneling molecules at low temperatures, or in a wider context, to perform reliable multiple-scattering corrections in experiments oriented to precise determinations of density of states.

Solid Deuterium

Very recently, a new scattering kernel to describe the interaction of slow neutrons with solid Deuterium was developed. The main characteristics of that system are contained in the formalism, including the lattice's density of states, the Young-Koppel quantum treatment of the rotations, and the internal molecular vibrations. The elastic processes involving coherent and incoherent contributions are fully described, as well as the spin-correlation effects.

The deuterium molecule is formed by two bosons, and therefore its total wave-function must be symmetric under interchange of two identical nuclei [1]. Consequently, if the total nuclear spin **S** is even the spatial nuclear wave function must be symmetric, and antisymmetric if **S** is odd, which leads, respectively, to the existence of the *ortho* states, with S = 0, 2 coupled to J = 0, 2, 4,…, and *para* states with S = 1 coupled to J = 1, 3, 5, …., where J denotes the molecule´s total angular momentum.

The neutron scattering laws S(Q,ω), energy-transfer kernels σ(E,E´), and cross sections σ(E) for inelastic scattering in solid ortho-and para-deuterium were calculated using the code NJOY [5], which is based on a phonon expansion for the lattice motion, and the Young-Koppel [15] formalism for the quantum rotational description. As part of the code´s input data, the density of states (DOS) for solid deuterium derived by Schmidt *et al.*[16] was used. The elastic incoherent component produced by NJOY was modified in order to include spin correlation effects. The lattice structure factor was calculated using our code CRIPO [17] and then affected by the Debye-Waller factor χ(Q,0) and the molecular structure factor to obtain the elastic coherent component. In our calculations we used the values σc = 5.59 b, σi = 2.05 b, for the bound atom coherent and incoherent cross sections respectively, and σa= 0.0005 b for the thermal neutron absorption cross section [18], as well as hωr = 0.0074 eV and hωv = 0.371 eV for the rotational and vibrational molecular energies.
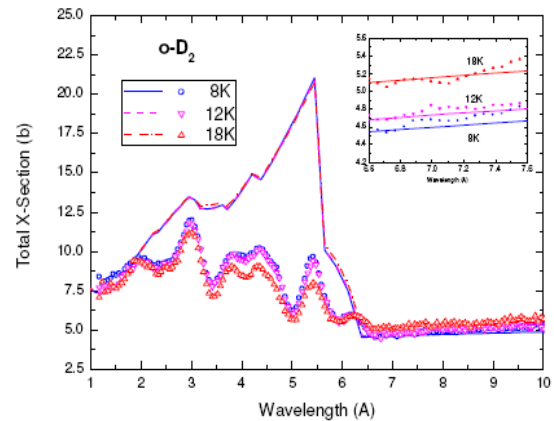

Fig.8: Calculated total cross section of solid o-D2, compared with experimental data from [19,20]. The inset shows that comparison beyond the first Bragg peak.

The total cross section of ortho-deuterium is shown in Fig.8 as calculated with the present model, compared with experimental data from Refs.[19] and [20] for a few temperatures over the thermal neutron wavelength range. The large elastic coherent contribution due to the *hcp* structure factor dominates the cross section at those energies, and the disagreement with the measured points is a clear indication of the lack of perfect polycrystallinity in the samples. However, and in spite of the significant difficulties to achieve a high precision normalization for the measured curves in those experiments, a very satisfactory agreement between both sets is observed beyond the first Bragg peak, a region dominated by total inelastic and incoherent (including spin correlation effects) elastic components of the total cross section (see inset in Fig.8).

The comparison between the present model and existing cross section data for solid deuterium is completed with the curves presented in Fig..9, where calculated values for solid ortho-and normal-deuterium are compared with the measurements from refs. [20] and [21] at around 18 K. At this temperature the inelastic cross section for ortho and para deuterium are very

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similar, and therefore the differences observed below the first Bragg peak for the cross sections of ortho-and normal-deuterium are purely due to spin correlation effects on the elastic incoherent contribution.
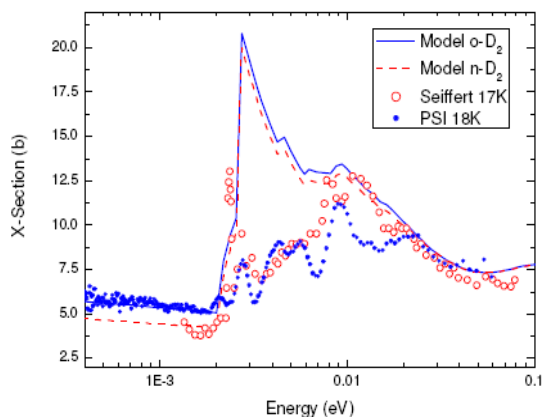

Fig.9: Calculated total cross sections of ortho-and normal-deuterium at 18 K, compared with the experimental data from ref. [20] and [21].

CONCLUSIONS

Cross section libraries of hydrogen bound in benzene, toluene, mesitylene and a solution 3:2 by volume of mesitylene/toluene were generated at different temperatures, in particular at 20K. The 3:2 mesitylene-toluene mixture, that forms in a simple and direct manner the appropriate disordered structure, constitutes an excellent cryogenic moderator material, as it is able to produce an intense flux of cold neutrons while presenting high resistance to radiation [22].

We developed a new scattering kernel for solid methane in phase II, including the main dynamical features of the system and the effect of spin correlations. A central motivation for this development has been the generation of cross section libraries for the calculation of neutron thermalization properties in CH4 II. Good agreement with a quantum mechanical calculation over the limited range where the latter was formulated, and with available experimental information over the complete thermal energy range [23].

A new scattering kernel to describe the interaction of slow neutrons with solid Deuterium has been developed. Scattering functions and cross sections for both *ortho*- and *para*-Deuterium have been evaluated for temperatures ranging from the freezing point (18.7 K) down to 5 K. The new model has been compared with the best available experimental data, showing a highly satisfactory agreement [24].

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