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Triphenylmethane, a possible moderator material

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ABSTRACT

New challenges in neutron scattering result in an increased demand in novel moderator concepts. The most direct way to address the problem would be to change the moderator material itself. However the range of available neutron moderator materials is small. In this paper, we discuss triphenylmethane, a possible moderator material especially promising for cold neutron moderator applications. Our investigations include a parallel experimental and theoretical approach ranging from cross-section measurements and inelastic neutron spectroscopy to molecular modeling.

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1. Introduction

Due to shifts in the scientific interest toward increasingly large systems, as recently shown by the US Department of Energy's announcement of interest in mesoscale research [1], there is a rising demand for cold neutrons. The only moderator systems available to date that can provide a significant cold neutron flux at spallation neutron sources are liquid hydrogen and solid methane. Each one of these has its unique set of problems.

In the case of liquid hydrogen there is the long standing question of controlling the ortho to para-hydrogen ratio. Upon condensation and without the use of a catalyst, liquid hydrogen will contain 75% ortho-hydrogen and 25% para-hydrogen. The equilibrium at 20 K however is at 99.9% para-hydrogen, a state that can be reached through natural conversion after a lengthy process lasting for months [2]. In addition, the energy induced by the radiation is expected to alter this conversion process and may change the equilibrium state [3]. Some neutron facilities, like the Lujan Center at the Los Alamos National Laboratory [4] or the Spallation Neutron Source at the Oak Ridge National Laboratory [5], are faced with the fact that they do not know what the ortho to para-hydrogen ratio of the liquid hydrogen system is at any given point in time. These facilities have configured their target systems in a way that a change in the ortho to para-hydrogen ratio results in only a small change in the performance of the facility. Nevertheless an uncertainty remains [6,7]. Other facilities, like ISIS at Rutherford Laboratory [8] and J-PARC in Tokai, Japan [9] decided that this uncertainty is not acceptable. These facilities use catalysts

to accelerate the conversion to para-hydrogen. While this effectively limits their operation of liquid hydrogen to pure para-hydrogen, it does provide a controlled condition.

Apart from the neutronic aspects of hydrogen's ortho–para problem, it also bears a serious safety concern. As mentioned before, liquid hydrogen often contains higher concentrations of ortho-hydrogen than the ideal equilibrium of 0.1%. Should a fast conversion to para-hydrogen happen for any reason, 670 kJ/kg of energy will be released, which is significantly higher than the latent heat of vaporization of hydrogen (446 kJ/kg). The resulting conversion of H_2 from liquid to vapor is accompanied by a change in volume by a factor of 845. If the vapor is not free to expand fast enough, the resulting pressure change can lead to catastrophic explosions.

On the other hand, both solid and liquid methane suffer from radiation-induced polymerization, ultimately leading to a potentially devastating combination of carbon-clogged valves and hydrogen pressure buildup. Ways of mitigating these problems have been developed [10,11], but the operation of liquid or solid methane moderators is still limited to spallation neutron sources with proton beam power of about 100 KW or less.

When trying to find alternative moderator materials for the production of cold and very cold neutrons we encounter a much more fundamental problem: very little actual knowledge exists about the interaction of matter with very cold neutrons. But even in the range of thermal and cold neutrons, a lot of the assumptions usually made are what Muhrer describes as "tribal knowledge" [12], and need to be reevaluated for each particular application. In the same paper, Muhrer puts some of these assumptions to the test and systematically analyzes their validity. The two most significant results for the development of new moderator materials are that in a coupled system, a high hydrogen density is preferable but not

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critical, and that a moderator material should possess an abundance of energy excitations below the thermal temperature of the moderating material to lower the spectral temperature of the moderator. In addition, some general rules for a potential cold moderator material apply: an absorption cross-section in the range of millbarn or lower is desirable, which significantly constrains the number of useable elements; the stability of the material in a radiation environment should be high enough to allow for a reasonable lifetime without significant decay; phase transitions, if they occur, should be reliably reproducible to achieve a reproducible moderator spectrum.

Based on these criteria we have investigated triphenylmethane. In this paper we will present the experimentally determined total cross-section of triphenylmethane, as well as the measured and calculated Density of States (DOS) and their comparison.

2. Why triphenylmethane?

Triphenylmethane (Fig. 1) fulfills several of the aforementioned fundamental criteria: as a molecule it consists of only hydrogen and carbon atoms. Its neutron absorption can be considered low (5.4 barns/molecule for thermal neutrons), and its hydrogen content is within a few percent of that of liquid hydrogen. The really interesting characteristics, however, stem from its unique structure: with three aromatic phenyl groups surrounding one central carbon atom, the molecule is able to form comparably stable radicals and even ions. Radicals are usually highly unstable and therefore create the very aggressive chemical in which polymerization occurs. In aromatic systems, the localized electron orbitals of several neighboring atoms overlap to form one huge orbital stretching over all atoms. This delocalized orbital is highly favored from an energetic point of view and lends outstanding radiation stability to molecules with aromatic carbon rings like benzene and mesitylene [13]. Since the energies of $C-H$ vibrations in aromatic molecules are generally lower than their aliphatic counterparts, the amount of high-energy excitations in the material is expected to be significantly reduced. At the same time, the hindered axial rotation of the phenyl rings around the bond to the central atom provides a multitude of low-energy excitations.

3. Total cross-section measurement

As a first step in examining the neutronic properties of triphenylmethane we used flight path 5 at the Manual Lujan Jr.

Neutron Scattering Center [14] to measure its total neutron cross-section.

The experimental setup for total cross-section measurements on this beam line has been discussed previously in [15]. For the measurement presented in this paper, we made two modifications to the referenced setup. The fission chamber was replaced by a BF_3 detector, which was placed about 4 m downstream of the sample location. The flight path configuration can be seen in Fig. 2.

The second modification was the introduction of a closed cycle refrigerator (Fig. 3) [16], which allows us to cool the sample to 10 K. In the past all cross-section measurements on this flight path could only be performed at room temperature.

The sample setup consists of the powder sample pressed between two quartz windows held by a brass sample holder. The sample holder itself is connected to a control rod inside the cryostat. The neutron beam is entering and exiting the cryostat via quartz windows on both sides of the sample holder.

The total cross-section measurements were conducted at 295 K (room temperature), 100 K and 10 K. The transmitted spectra for all the samples were collected in time-of-flight mode. The measured spectra were then normalized by the integrated proton beam current on the target for the duration of the measurement. The macroscopic total neutron cross-section was calculated using the attenuation equation

$$N(x) = N(0)e^{-\Sigma x} \tag{1}$$

with Σ being the total macroscopic neutron cross-section and x being the thickness of the sample. $N(x)$ and $N(0)$ are the neutron flux per unit current on the target corrected for background noise that was detected by the detector for a x cm thick sample and for the empty sample holder, respectively. The total microscopic
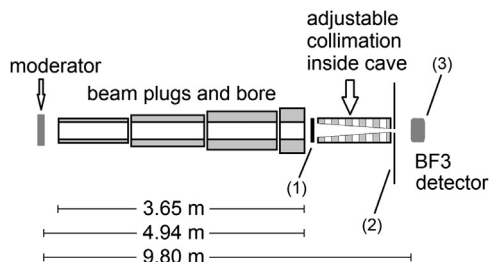

Fig. 2. Layout of Flight Path 5 at the Manuel Lujan Jr. Neutron Scattering Center at Los Alamos National Laboratory: (1) the position of the sample which is placed in front of the adjustable collimation: (2) to the polyethylene wall which shields the hutch from neutrons scattering off the sample and the collimation: (3) the detector position. (Sightly adjusted geometry as compared to that shown in [15].)
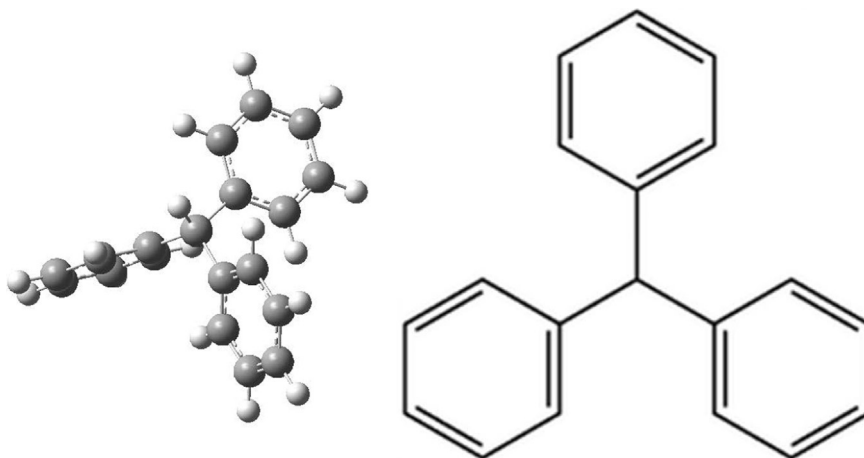

Fig. 1. Triphenylmethane molecule (left: ball and stick model, right: structure (hydrogen atoms omitted)).