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TITLE: ORTHO- AND PARA-HYDROGEN IN NEUTRON THERMALIZATION

CONF-9709132--

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SUBMITTED TO: Workshop on "Cold Moderators for Pulsed Neutron Sources"
Argonne National Laboratory, Sept 30 - Oct 2, 1997

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Form No. 836 R5
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Workshop on "Cold Moderators for Pulsed Neutron Sources," Argonne National Laboratory, September 30-October 2, 1997

Ortho- and Para-hydrogen in Neutron Thermalization

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Introduction

The large difference in neutron scattering cross-section at low neutron energies between ortho- and para-hydrogen was recognized early on [1], and the first designers of cold moderators for small research reactors were fully aware of this fact [2]. In view of this difference (more than an order of magnitude), one might legitimately ask whether the ortho/para ratio has a significant effect on the neutron thermalization properties of a cold hydrogen moderator. Several experiments performed in the 60's and early 70's with a variety of source and (liquid hydrogen) moderator configurations attempted to investigate this. The results tend to show that the ortho/para ratio does indeed have an effect on the energy spectrum of the neutron beam produced. Unfortunately, the results are not always consistent with each other and much unknown territory remains to be explored. The problem has been approached from a computational standpoint, but these isolated efforts are far from having examined the ortho/para-hydrogen problem in neutron moderation in all its complexity.

The problem is further complicated by the fact that many physical and chemical phenomena in the cold moderator environment are potentially capable of inducing ortho-para transitions. The most significant are the contact of hydrogen with materials containing various impurities which can catalyze the slow ortho-para transition, and the presence of a strong radiation field. The latter is a phenomenon that is well established in the gas phase [3]. The liquid phase received a limited amount of attention in the 1960's when the US space program was in full swing and nuclear engines with liquid hydrogen fuel were considered strong candidates for the construction of spaceships for space exploration [4-7]. Most of these experiments led to results that are ambiguous or inconclusive at best. While hydrogen flowing through a nuclear reactor core has lost its appeal for space exploration, cold moderators for the production of neutron beams are located in equally intense neutron fluxes, and the question of the impact of the radiation field on the ortho-para ratio remains unanswered.

Because of space limitations, we cannot cover, even briefly, all the aspects of the ortho/para question here. This paper will summarize experiments meant to investigate the effect of the ortho/para ratio on the neutron energy spectrum produced by liquid hydrogen moderators. Other facets of the ortho/para problems such as the radiation chemistry of hydrogen and the measurement of the ortho/para ratio will be presented elsewhere.

Ortho-hydrogen, para-hydrogen, and moderator design

Several reasons come to mind as to why the ortho-para problem is important in moderator design:

- Neutron thermalization

We already mentioned the difference in neutron scattering cross-section between ortho- and para-hydrogen. Figure 1 shows the measured scattering cross-section in liquid para- and normal-hydrogen (75% ortho- and 25% para-hydrogen) at 20 K. Para-hydrogen is an attractive medium for neutron moderation because it is relatively easy for neutrons to excite the J=0 to J=1 transition between rotational energy levels of the molecule (thereby inducing a para-to-orhto transition); these levels are separated by 14.7 meV and the partial cross-section for such an event is large above 14 meV or so as shown in Figure 2(a) (below that, the scattering is purely elastic). The existence of this transition between the J=0 and J=1 rotational levels makes para-hydrogen a useful material to increase the production of low energy neutron as elastic scattering is less efficient in moderating neutrons. Figure 2(b) shows that this is the principal mode of scattering in ortho-hydrogen, particularly at low neutron energies. Even though the cross-section for this event is higher than that of the para-to-ortho conversion event in para-hydrogen, elastic scattering is less efficient at removing neutron kinetic energy. (Notice that the J=1 to J=0 transition is an up-scattering event for the incident neutron.)

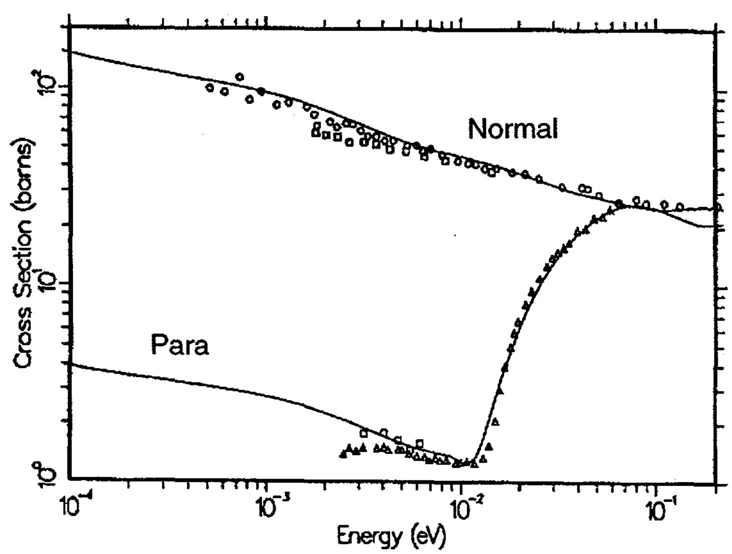

Figure 1 - Total scattering cross section for ortho- and para-hydrogen. See [11] for a discussion of the experimental measurements.

At a continuous source, and in the absence of neutron absorption, it would appear that a large ortho-hydrogen source would be ideal to maximize the production of cold neutrons.

However, as the neutron thermalizes (slowly in the case of ortho-hydrogen) its chances of getting absorbed before it leaks increase dramatically. Thus, in the presence of absorption, it is desirable to have a moderator capable of removing neutron kinetic energy quickly while minimizing the moderator size to leak thermalized neutron rapidly before they get absorbed. This is in fact a complicated issue and the ideal ortho-para composition for a given moderator depends strongly on its size and geometry as we shall see in more detail below. Nonetheless, a look at the total and partial scattering cross-sections is instructive and reveals, at least qualitatively, much of the issues.

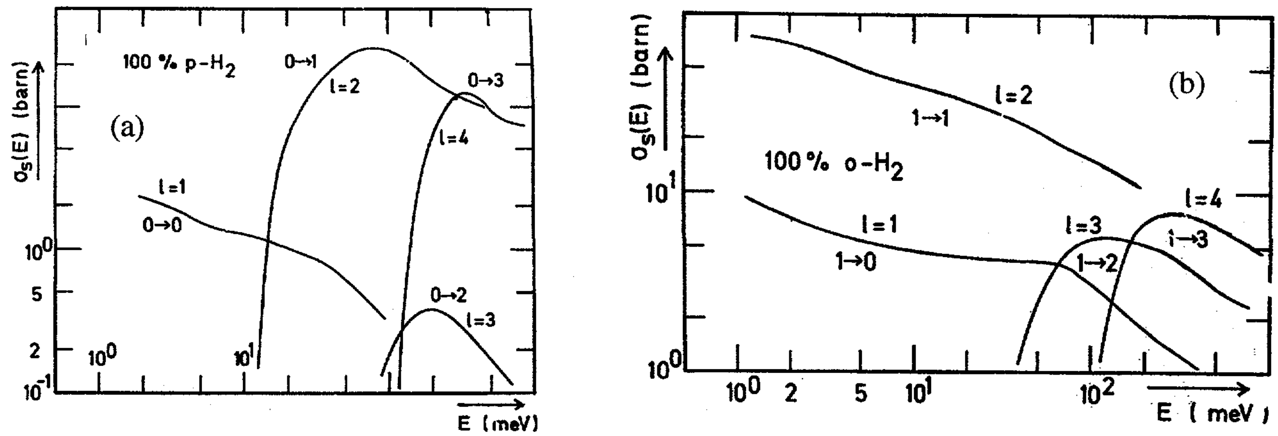

Figure 2- (a) Partial cross-sections for scattering involving transitions betwen various energy levels of the para-hydrogen molecule; (b) Partial cross-sections for scattering involving transitions between various energy levels of the ortho-hydrogen molecule; (from [13]).

- <u>Pulse shape</u>

A direct corollary of the preceding discussion is the impact of the ortho-para ratio on the time dependence of the flux emerging from a cold moderator at a pulsed spallation source: the ortho/para ratio will have a significant influence on characteristics such as pulse width, decay time, peak intensity, etc. These parameters are important for the neutron scattering instrument viewing the moderator. Furthermore the ortho/para ratio will have a different effect on the characteristics of pulses produced by moderators with different geometries and different modes of coupling and poisoning. Virtually no data is available regarding this problem, but preliminary calculations suggest that it is an important one [8].

- <u>Safety issues</u>

While the self-induced conversion of hydrogen to the composition dictated by equilibrium thermodynamics is very slow (rate constant, $k=0.0114\ hr^{-1}$) catalysts can speed up the rate of conversion by several orders of magnitude. Given that the heat released by the conversion of ortho-hydrogen to para-hydrogen at 20 K is 527.6 J/g (254.0 cal/mol), there are some safety issues associated with the sudden conversion of large quantities of ortho-hydrogen in the moderator loop. (Compare this number to the latent heat of vaporization at the same temperature, namely 445.5 J/g = 214.4 cal/mol.) At the very least, this impacts the design of the hydrogen loop which should be able to remove the heat of conversion in a safe manner.

It has also been shown that the radiolysis of hydrogen molecules in the intense radiation field of the moderator produces large quantities of atomic hydrogen in the liquid. Hydrogen atoms require a third body for recombination (not a hydrogen molecule), and, in all likelihood, diffuse around in the moderator until reaching a wall where recombination (and the concommitant release of heat) takes place. Whether this is a safety issue remains to be seen, but it is a question that could very well be relevant in large moderators at high-power spallation sources.

- Moderating medium composition

This issue has to do with the rate at which ortho-to-para and para-to-ortho transitions take place in the moderator shortly after the source is turned on and when the moderator is in equilibrium with the radiation field and its physical and chemical surroundings. At 20 K, the equilibrium composition is more than 99% para-hydrogen. But a variety of physical and chemical phenomena in the spallation neutron source environment are potentially capable of producing ortho-hydrogen (e.g., hydrogen radiolysis). In view of the large scattering cross-section of ortho-hydrogen, the presence of even a few percent ortho-hydrogen could be enough to affect significantly its neutron moderating properties. Furthermore, if the ortho/para ratio in the moderator is a function of source power and the ortho-para conversion is relatively slow to respond to a change in chemical, or physical environment , the moderating medium may see its moderating properties evolve as a function of time.

It is fair to say at this point that we may very well have overemphasized the importance of the above factors. In last analysis, it may be that few of these factors matter, perhaps even none of them. It is, however, not so easy to dismiss them summarily, particularly in the light of the (limited but real) experimental evidence presented below. If these factors are not an issue at all in moderator design, we feel that this should be established convincingly once and for all.

Neutron thermalization in ortho- and para-hydrogen

Experimental results

Little information is available when it comes to determining the effect of the ortho/para ratio on the performance of liquid hydrogen moderators. While many have measured energy spectra emanating from a given cold source, few have actually bothered to determine the ortho/para ratio of the liquid hydrogen in the moderator, and fewer still have performed at least two measurement with the same source/moderator configuration and different (controlled) ortho/para ratios. A careful examination of the literature on this topic revealed that such measurements have been performed on three occasions only. We will now review these results.

Webb et al [1,9-10]: The Harwell group that first put a liquid hydrogen source in a reactor (the BEPO reactor at Harwell) also tried to observe any difference in the energy spectrum produced by filling their moderator with various mixtures of ortho- and para-hydrogen. The moderator was a 7.5 cm diameter x 6.25 cm height aluminum tube. (In subsequent measurements, the height of the cylinder was varied.) The cylinder was mounted inside the reactor with its axis horizontal and the neutron beam was extracted from one of the bases of the cylinder. The two mixtures measured were 7 v% of ortho-hydrogen + 93 v% para-hydrogen and normal hydrogen. The first mixture was obtained by liquefying normal hydrogen, then by placing the liquid at 20 K in contact with with a catalyst for a given, pre-determined amount of time. This group also measured a third mixture of deuterium hydride in hydrogen and deuterium (91 v% HD+8 v%H_2+1v%D_2). The spectrum was determined by time-of-flight with a chopper whose speed was varied as a function of time. Figure 3(a) shows the basic configuration used in the measurements. Figure 3(b) shows the energy spectrum measured for para-hydrogen. According to the authors, no significant difference in the spectrum was observed with any of the three mixtures.

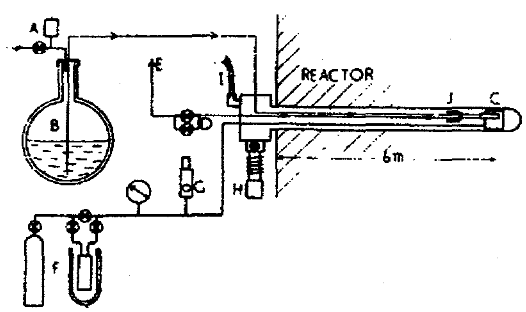

Figure 3(a) - The basic configuration used by Webb et al. in their measurements of energy spectra from a liquid hydrogen moderator at the BEPO reactor in Harwell (from [1]). A=H_2 regulator and relief valve; B=H_2 container, C=Moderator; D=Control valves; E=Duct to atmosphere; F=Condensing cylinder; G=Relief valve; H=Pump.

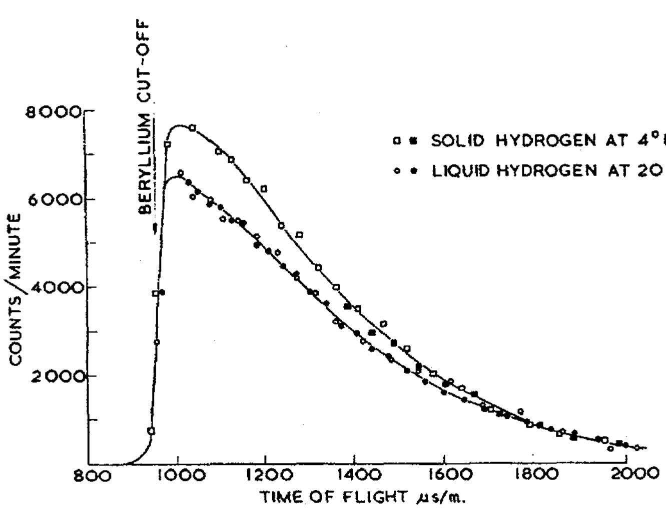

Figure 3(b) - Liquid para-hydrogen and solid para-hydrogen time-of-flight spectra measured by Webb et al. at the BEPO reactor in Harwell (from [9]). The white and black symbols correspond to two different sets of measurements.

Whittemore et al [11,12]: At about the same time Webb et al. were measuring neutron spectra at the BEPO reactor in Harwell, Whittemore and his collaborators were busy measuring neutron scattering cross-sections in a variety of materials, including liquid hydrogen, at the pulsed neutron source at General Atomic. They became interested in the cold moderator design issue and proceeded to test the moderating efficiency of many hydrogenated materials. The ortho-para problem presented itself naturally to them after their extensive cross-section measurements and they measured carefully the characteristics of moderator vessels filled with normal hydrogen or para-hydrogen. The source of neutrons used in the measurement is the General Atomic electron accelerator. This accelerator produces 5 μs pulses of 25 MeV neutrons at 120 Hz. The beam current during most measurements was 25 mA. A lead target produces gamma rays by Bremstrahlung. These gamma rays are then used to produce photo-neutrons. Several blocks of polyethylene placed around the liquid hydrogen moderator were used as moderator/reflector material. The liquid hydrogen moderator itself was a cylinder, 6 in. diameter x 6 in. height. One of the bases of the cylinder had a cylindrical hole (concentric with the canister) in it. Whittemore measured the energy spectrum emanating from the flat base as well as from the hole in the other base, thereby comparing a "flat" moderator with a "reentrant" geometry.

The energy spectra were measured by time-of-flight, a convenient method on a pulsed source. Figure 4(a) shows the basic geometry used in the measurements. Figure 4(b) shows the spectra measured on the flat surface of the moderator for normal hydrogen and para-hydrogen. Figure 4(c) shows the same spectra, but for the reentrant hole. Several interesting observations can be made. First, there is a difference in intensity between normal hydrogen and para-hydrogen, regardless of the moderator configuration (flat or reentrant). Second, in the case of the reentrant moderator, normal hydrogen leads to a higher intensity in the thermal region (by a factor of about 2.5) ; this situation is reversed for the flat moderator. Third, there is virtually no difference (less than 10%) in intensity or spectrum shape for para-hydrogen betwen the reentrant moderator measurement and the flat moderator measurement.

The conclusions to be drawn from these results are that the ortho/para ratio indeed affects the moderator performace and that the moderator geometry plays an important role. The difference between the flat and reentrant geometries for normal hydrogen can be understood relatively easily. The mean free path of a neutron with energy less than 15 meV in normal hydrogen is of the order of a few mm. A neutron can be expected to suffer many collisions as it slowly thermalizes in the medium, and even after thermalization will suffer many more collisions before it gets a chance to leak from the moderator. The hole allows neutrons to leak more easily out of the moderator before they get absorbed. The absence of difference in the case of para-hydrogen is due to the large mean free path at low neutron energies, of the order of several cm -comparable to the moderator dimensions- and the presence or absence of the hole is less likely to have any significant effect. To sum up, moderator size and shape and the ortho/para are not independent parameters when it comes to determining the moderator performance.

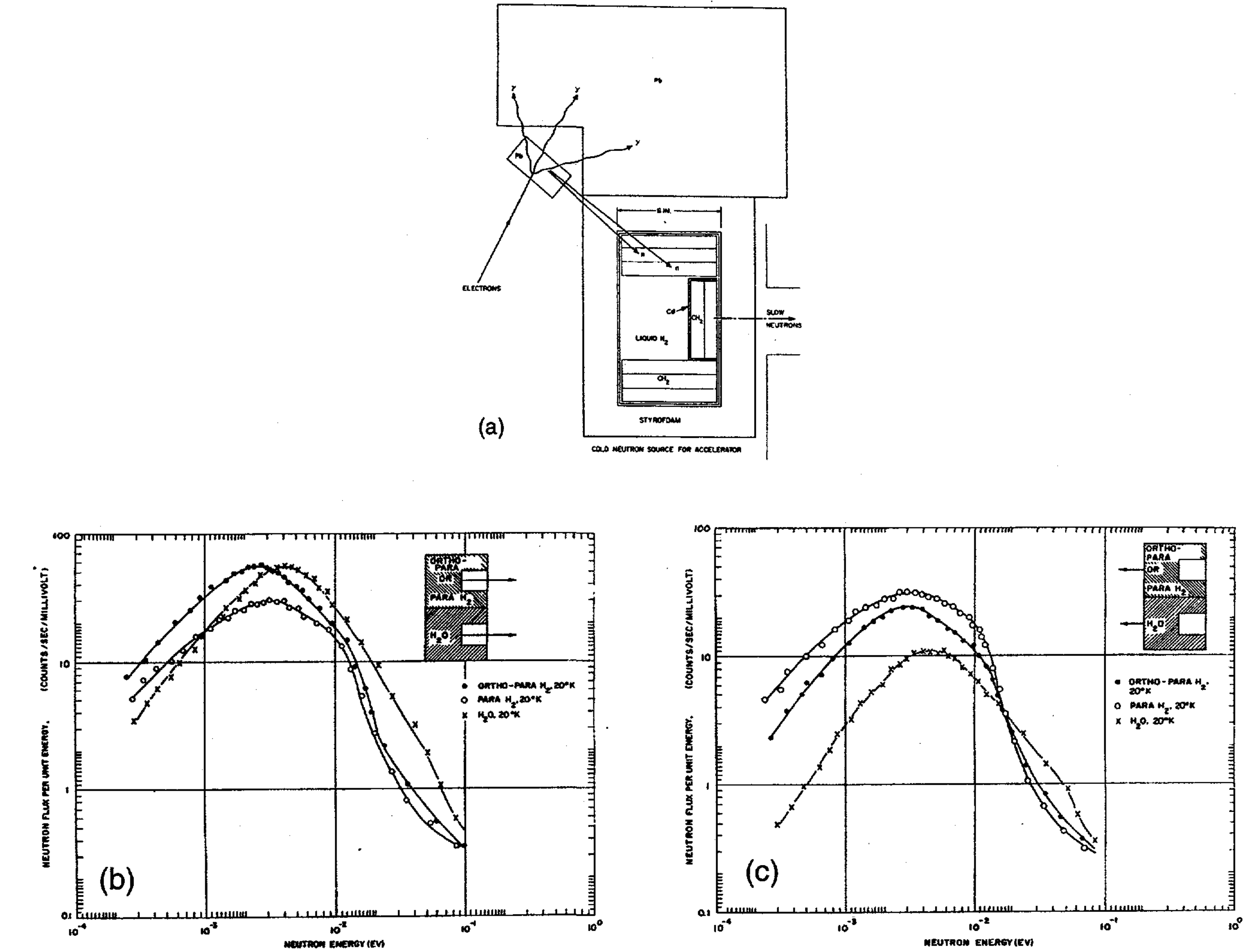

Figure 4 - (a) The setup used by Whittemore et al. in their measurements of neutron energy spectra and cross sections; (b) Measured neutron energy spectra for para- and normal-hydrogen (reentrant moderator); (c) Measured neutron energy spectra for para- and normal-hydrogen (flat moderator). (From [11].)

Würz [13]: Several years after the measurements by Webb et al. and Whittemore et al., Würz revisited the issue of neutron thermalization in ortho- and para-hydrogen at the Kerforschungszentrum Karlsruhe. The neutron source used produced 14 MeV neutrons by bombarding a tritium target with deuterons. the deuteron pulses were 10 μs long. The moderator is a cylinder, 14.8 cm diameter x 16 cm height (approximately the same dimensions as the cylinder used by Whittemore et al.). Würz measured a leakage spectrum for several mixtures of ortho- and para-hydrogen. Figure 5(a) shows the experimental setup. Figure 5(b) shows an energy spectrum for various ortho/para ratios. Würz also measured the first time moment and the time variance of the neutron pulse for 77v% and 98v% of para-hydrogen. Time-of-flight spectra were collected at right angle from the incident beam of 14 MeV neutrons.

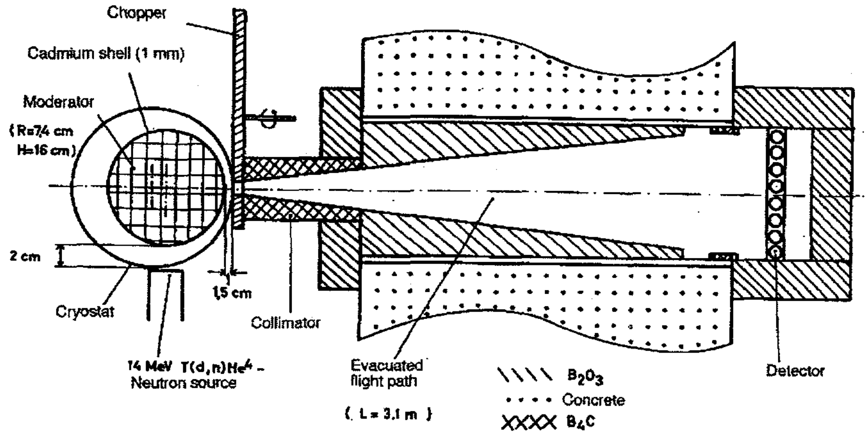

Figure 5(a) - The experimental setup used by Würz.

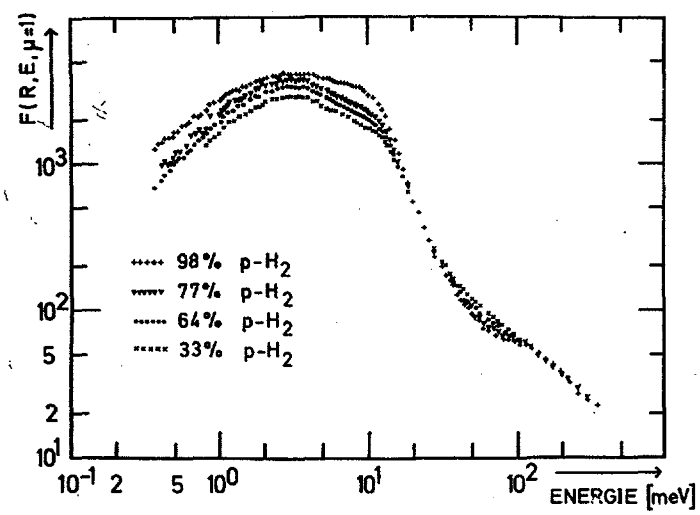

Figure 5(b) - The energy spectra measured by Würz for various ortho/para compositions. The measurements were performed at a pulsed source and the figure shows time-integrated spectra (from [13]).

Both Whittemore and Würz observed a significant effect of the ortho/para ratio on the intensity of the pulse emitted by their liquid hydrogen moderator, although the magnitude of the efect is clearly not the same. Webb et al, on the other hand, concluded that the ortho/para ratio had little or no effect. This disparity in results is rather difficult to explain at first sight. The main obvious difference between the three measurements is the source. Webb et al. worked at a graphite-moderated reactor, a source rich in low energy neutrons and gamma radiation. Whittemore used a source producing low energy photo-neutrons and Bremstrahlung photons from lead. Furthermore, he used polyethylene as a moderator/reflector material. Würz's source produced almost exclusively fast (14 MeV) neutrons.

Except for Würz, no attempt was made to determine pulse widths, decay times, etc. Even in Würz's case, either the entire pulse or a portion of the pulse selected with a chopper were involved in the measurement of the time-dependent characteristics of the pulse. The time distributions thus measured integrated the pulse of energy and offer little insight as to how the pulse characteristics depend on, say, neutron energy. This is a measurement which remains to be performed.

Calculations

Computational efforts are just as scarce as experimental results. Despite the availability of scattering kernels for ortho- and para-hydrogen (gas, liquid, solid) and powerful tools to solve the transport equation (multigroup, Monte Carlo, ...) few efforts have been made to explore the systematics of cold hydrogen moderators as a function of ortho/para ratio, moderator size and aspect ratio, feeding geometry, poisoning and decoupling, etc, even for simple geometries. We started exploring this aspect of the problem, and these results, to be reported elsewhere [8], do indeed provide a great deal of insight into the phenomenology of these moderators. Many of these results translate qualitatively, if not quantitatively, to real sources. Below is a brief overview of theoretical calculations of cold moderator performance that emphasize the ortho/para ratio problem.

Würz [13]: Würz used the gas kernel of Young and Koppel [14] to solve numerically the time-dependent Boltzmann transport equation in a simple geometry to calculate the energy spectrum resulting from thermalization in mixtures of para- and ortho-hydrogen. The results of his calculations agree rather well with his measurements.

Kalli [15]: At about the same time, in 1974, Kalli solved the transport equation using multigroup techniques for a variety of configurations similar to those studied by Webb et al. , {1,9,10] He considered liquid hydrogen moderators in radial and tangential geometries in a reactor and studied the emitted spectrum as a function of ortho/para ratio for several moderator dimensions.

Swaminathan and Tewari [16,17]: Later, in 1982, Swaminathan and Tewari revisited Whittemore's experiment and performed a multigroup calculation aimed at reproducing Whittemore's result. The scattering kernel used was a simplified kernel (see [17] for details). The agreement between their calculation and Whittemore's measurement [11,12] is fair, but by no means remarkable. The authors also investigated the effect of moderator size and aspect ratio, while varying simultaneously the ortho/para ratio.

Acknowledgements

We thank L. Passell for many useful discussions on the ortho/para ratio problem in neutron thermalization. This work was supported by the U.S. Department of Energy under contract number W-7405-ENG-36 with the University of California.

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