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NEUTRON INTERACTIONS IN LIQUID PARA-AND
ORTHO-HYDROGEN

by

W. L. Whittemore and H. R. Danner

August 8, 1962

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NEUTRON INTERACTIONS IN LIQUID PARA-AND ORTHO-HYDROGEN*

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ABSTRACT

An experimental method is described which utilizes a simple Fermi-type chopper and conventional time-of-flight techniques in conjunction with an electron linear-accelerator pulsed neutron source to study inelastic scattering of thermal neutrons from liquid para- and ortho-para-hydrogen. The overall general agreement between theory and experiment supports the concept that the molecules in liquid hydrogen behave nearly as they would in a "perfect" gas. For liquid ortho-para-hydrogen, however, the extra broadening of the energy distribution of scattered neutrons suggests that some effects of the liquid state may be present. Similar observations on para-hydrogen indicate that, in this liquid as well, the motion of the molecules is affected by weak intermolecular forces.

INTRODUCTION

The techniques of neutron inelastic scattering have been applied to the study of liquid para-hydrogen and liquid ortho-para-hydrogen. This preliminary report covers the early phases of this research. An important goal is to investigate the respect in which the behavior of liquid para- and liquid ortho-para-hydrogen differs from a perfect gas. In order to do this, certain aspects of the scattering system have been examined theoretically to select proper experimental conditions.

THEORY

The scattering of low energy neutrons from liquid hydrogen has been investigated theoretically by G. Sarma.⁽¹⁾ His treatment utilizes the formalism of Van Hove⁽²⁾ to describe, in Born approximation, the scattering by a system of particles subject to the assumptions that (1), the Hamiltonian is independent of the spins and (2), there are no correlations between the position and orientation of a particular molecule nor between the orientations of different molecules. Moreover, the hydrogen molecule is approximated by a simple rigid rotator and thus possesses the rotational states

$$E_J = (\hbar^2 / ma^2) J(J+1) = 0.015 (J/2)(J+1) \text{ ev} \quad (1)$$

where m is the proton mass and $a = 0.75 \text{ \AA}$, the distance between the two protons in the hydrogen molecule. Consideration of the vibrational modes is neglected since the incident neutron energies in the range of interest are much smaller than the minimum energy necessary to excite the lowest of these modes.

Under the above assumptions, the differential cross-sections for "coherent" and "incoherent" scattering may be written respectively as the 4-dimensional Fourier transforms of the "distinct" and "self" parts of the Van Hove pair distribution function $G(\vec{r}, t)$. The differential "coherent" cross-section, which accounts for that part of the coherent scattering arising from different molecules, is negligibly small, so that the "incoherent" cross-section alone defines the scattering. Direct comparison between theory and experiment depends on the form of $G_S(\vec{r}, t)$. As a first approximation, Sarma considers the case where intermolecular forces may be neglected and takes for $G_S(\vec{r}, t)$ the auto-correlation function of a perfect gas. With this model the differential "incoherent" cross-section takes the form:

$$\frac{d^2\sigma}{d\Omega dE} = \left(4 \frac{m}{\pi k_B T}\right)^{1/2} \frac{k}{\hbar k_0} \frac{f_{J \rightarrow J'}}{K} \exp - m \frac{\left[\hbar\omega - (E_{J'} - E_J) - \frac{\hbar^2 K^2}{4m}\right]^2}{k_B T \hbar^2 K^2} \quad (2)$$

In this expression $\vec{K} = \vec{k} - \vec{k}_0$, where $\vec{k}_0$ and $\vec{k}$ are the neutron wave vectors before and after scattering. The term $f_{J \rightarrow J'}$ is a function of $Ka/2$ (and therefore of angle) and its value depends strongly on the initial and final states of the hydrogen molecule; i.e., upon the transition considered.

In the para- and ortho-modifications of liquid hydrogen, all of the molecules are assumed to be in their lowest states ($J = 0$ and $J = 1$, respectively). Thus, for incident neutron energies less than 0.1 eV, the following are the only values of $f_{J \rightarrow J'}$ that need be considered:

$$\begin{aligned} f_{0 \rightarrow 0} &= 4 p_0 A_{coh}^2 B_0^2 \\ f_{0 \rightarrow 1} &= 12 p_0 A_{incoh}^2 B_1^2 \\ f_{1 \rightarrow 1} &= 4 p_1 (A_{coh}^2 + 2/3 A_{incoh}^2) (B_0^2 + 2 B_2^2) \\ f_{1 \rightarrow 0} &= (4/3) p_1 A_{incoh}^2 B_1^2 \\ f_{1 \rightarrow 2} &= (4/3) p_1 A_{incoh}^2 (2B_1^2 + 3B_3^2) \end{aligned} \quad (3)$$

Here p_J is the statistical weight of the molecules in the state J and the B 's are spherical Bessel functions of the argument $(Ka/2)$. These values of f can differ by several orders of magnitude because of the difference in the values $A_{\text{coh}}^2 = 3.57 \times 10^{-2}$ barns and $A_{\text{incoh}}^2 = 1.59$ barns.

The numerator of the exponent in Eq. (2) expresses the conservation of energy in terms of the energy transfer $\hbar\omega = (E_{J'} - E_J)$ and the momentum transfer $\hbar K$. Expressing these in terms of energy, i.e.:

$$\begin{aligned}\hbar\omega - (E_{J'} - E_J) &= E_0 - E - (E_{J'} - E_J) \\ \hbar^2 K^2 &= 2m (E + E_0 - 2\sqrt{EE_0} \cos \varphi)\end{aligned}\tag{4}$$

where E_0 and E are the initial and final energies of the neutron and φ is the angle of scattering, Eq. (2) can be rewritten:

$$\frac{d^2\sigma}{d\Omega dE} = \frac{4(2\pi k_B T)^{-1/2} (E/E_0)^{1/2} (f_{J \rightarrow J'})}{[E + E_0 - 2\sqrt{EE_0} \cos \varphi]^{1/2}} \exp - \frac{9 \left[\frac{1}{3} (E_0 - 2\Delta E_{J'J} + 2\sqrt{EE_0} \cos \varphi) - E \right]^2}{8 k_B T (E + E_0 - 2\sqrt{EE_0} \cos \varphi)}\tag{5}$$

Thus, $\frac{d^2\sigma}{d\Omega dE}$ takes on its maximum value when

$$E = 1/3 (E_0 - 2\Delta E_{J'J} + 2\sqrt{EE_0} \cos \varphi)\tag{6}$$

is in agreement with what one would expect from simple classical considerations. The exponential term in Eq. (5) describes an intrinsic broadening associated with each of the scattering components and, as a consequence of the initial assumptions, this broadening is due entirely to the thermal motions of the hydrogen molecules.

Inasmuch as our initial measurements have been obtained with $\varphi = 90$ deg, further consideration will be limited to this special case. Equation 5 then reduces to

$$\left. \frac{d^2 \sigma}{d\Omega dE} \right|_{\varphi = \pi/2} = 4(2\pi k_B T)^{-1/2} \left(\frac{E}{E_0} \right)^{1/2} \frac{f_{J \rightarrow J'}}{(E + E_0)^{1/2}} \exp \left[- \frac{9 \left[\frac{1}{3}(E_0 - 2\Delta E_{J'J}) - E \right]^2}{8 k_B T (E + E_0)} \right] \quad (7)$$

If the average energy after scattering,

$$\bar{E} = (E_0 - 2\Delta E_{J'J})/3$$

is assigned to all values of E , except in the numerator of the exponent, the exponential in Eq. (7) is a simple Gaussian with its full-width at half-maximum given by

$$\delta \xi = (4/3) (2k_B T \ln 2)^{1/2} (E + E_0)^{1/2} \quad (8)$$

To the same degree of approximation and letting $\epsilon = 1/3 (E_0 - 2\Delta E_{J'J}) - E$, we can integrate (7) obtaining

$$\left. \frac{d\sigma}{d\Omega} \right|_{\varphi = \pi/2} = \frac{8}{3} \left(\frac{E_0 - 2\Delta E_{J'J}}{3E_0} \right)^{1/2} f_{J \rightarrow J'} \left(\frac{K_a}{2} \right) \quad (9)$$

where the argument $Ka/2$ has the value $0.3 (E_0 - \Delta E_{J'J}/2)^{1/2}$ when the energies are expressed in units of milli-electron volts (mev):

The broadening $\delta \xi$ depends both on the incident neutron energy and on the transition considered. This dependence is shown in Fig. 1 where the energy broadening for 90 deg scattering is plotted as a function of E_0 for the various scattering components. It is seen that

Fig. 1--Theoretical broadening of the distribution in energy of neutrons scattered by liquid hydrogen

in all cases the broadening is quite large for all but the lowest energies. The dotted portions of the two lower curves represent the energy ranges where the incident neutron energy is insufficient to excite these transitions.

In applying Eq. (9) to the case of para-hydrogen, it is necessary to consider only the two scattering components associated with the transitions $0 \rightarrow 0$ ("elastic") and $0 \rightarrow 1$. By substituting the appropriate values of $f_{J \rightarrow J'}$ from Eq. (3) with $p_0 = 1$ into Eq. (9), the magnitudes of the partial cross-sections at $\varphi = 90$ deg for these scattering components are easily calculated. The results are shown in Fig. 2 as a function of the incident neutron energy. The "elastic" component is proportional to A_{coh}^2 and is so small that ten times its value has been plotted. It is of interest to note that both cross-sections vanish for particular values of E_0 .

Figure 3 shows a similar plot of the differential cross-sections evaluated at $\varphi = 90$ deg for the various components scattered from ortho-para-hydrogen. In this case all of the transitions listed in Eq. (3) are possible and the curves shown were calculated assuming a 2:1 ortho-to-para mixtures (i.e. $p_1 = 0.67$ and $p_0 = 0.33$). Although this relative concentration has not been measured for the present experiment, this assignment is reasonable for the present experimental conditions.

It should be noted that the approximations made in the derivation of Eqs. (8) and (9) are not generally valid. When $E \rightarrow 0$ or when its value is small and comparable with the expected broadening, the representation of a scattered component as a simple Gaussian is not sufficiently accurate. In such cases an exact evaluation of Eq. (7) has been made in comparing theory with the experimental results. An example of such an analysis is shown in Fig. 4 where the scattering components, $(0 \rightarrow 1)$, $(1 \rightarrow 0)$, $(1 \rightarrow 2)$, and $(0 \rightarrow 0, 1 \rightarrow 1)$, are exhibited for 0.065 ev neutrons incident on ortho-para-hydrogen.

Fig. 2--Theoretical differential cross-sections for scattering at 90 deg from para-hydrogen

Fig. 3--Theoretical differential cross-sections for scattering at 90 deg from ortho-para-hydrogen

Fig. 4--Four components of the scattering from ortho-hydrogen at 90 deg for neutrons with $E_0 = 65$ mev.

EXPERIMENT

The experimental method employed is closely related to the conventional double chopper, the essential difference being the substitution of an electron linear accelerator pulsed neutron source for the first chopping element. A schematic drawing of the experimental arrangement is shown in Fig. 5. Five μ sec bursts of high energy neutrons are produced when electrons from the accelerator strike an electron-neutron converter. A fraction of these are moderated and directed toward the chopper located 2.8 meters from the moderator. The neutrons transmitted by the chopper strike the sample and those scattered at 90 deg are detected by a BF_3 counter bank 1.6 meters from the sample. The time distribution of the scattered neutrons is recorded by a 256-channel analyzer operated with 16- μ sec channel widths.

The repetition rate of the accelerator and the rotational speed of the chopper are operated at the same frequency and the energy of the neutrons incident on the sample is determined by the phase of the accelerator pulse with respect to the instant that the chopper is open. This phase can be continuously varied electronically by changing the delay of the chopper control pulse which triggers the accelerator. In practice, the useful range of energies is limited by the available intensity and the chopper transmission function but extends from ~ 0.005 ev to ~ 0.25 ev.

For the present measurements, the apparatus outlined above has been used to select those incident energies which eliminates one or more of the scattering components. In order to facilitate the discussion these energies are summarized in Table 1. In the case of para-hydrogen the scattering is effectively due to a single component for the incident energies chosen. For $E_0 < 0.030$ ev, the neutron energy

Fig. 5--Experimental arrangement for neutron inelastic scattering measurements using an electron linear accelerator

Table 1

SELECTED OPTIMUM INCIDENT ENERGIES, E_0 , TO
REDUCE CERTAIN CONTRIBUTIONS TO THE SCAT-
TERING AT 90 DEG FROM VARIOUS ROTATIONAL
LEVELS IN LIQUID HYDROGEN

Scatterer	E_0 (ev)	Contributions
p-H	< 0.030	$0 \rightarrow 0$
	~ 0.065	$0 \rightarrow 1$
	~ 0.170	$0 \rightarrow 0$
o-p-H	< 0.030	$1 \rightarrow 1, 0 \rightarrow 0, 1 \rightarrow 0$
	$.030 < .060$	$1 \rightarrow 1, 0 \rightarrow 0, 1 \rightarrow 0, 0 \rightarrow 1$
	~ 0.170	$1 \rightarrow 1, 0 \rightarrow 0, 1 \rightarrow 2$

is insufficient to excite the first rotational level while above this threshold the $(0 \rightarrow 1)$ is predominant due to the very small cross-section of the "elastic" $(0 \rightarrow 0)$ scattering. The situation with ortho-para-hydrogen is more complicated since at least one inelastic component is present in addition to the "elastic" $(0 \rightarrow 0, 1 \rightarrow 1)$ scattering.

The instrumental resolution was measured over the range of incident energies employed by measuring the elastic scattering from a thin sheet of vanadium. ΔT is the width at half maximum for the observed scattered distribution and T is the flight time for the flight path from the scatterer to the detector. The values found for $\Delta T/T$ vary between 0.05 and 0.10 depending upon the exact experimental conditions; i.e., chopper speed, beam divergence, and moderator used as the neutron source. Although the resolution is inadequate for many applications, it is satisfactory in the case of liquid hydrogen due to the large intrinsic thermal broadening associated with the various scattering components. Finally, the calibration of the energy scale was determined by measuring the different flight times for elastic scattering from vanadium over different known flight paths with other experimental conditions held constant.

Figure 6 shows the measured distribution of initially mono-energetic 0.065-ev neutrons scattered at 90 deg from a sample of liquid para-hydrogen having a nominal thickness of 1 mm. Here, as in all subsequent measurements, the data have been corrected for the background measured with cadmium interposed between the moderator neutron source and the chopper. This method of measuring background was adopted because it includes the moderation of the general "fast" neutron background by the sample. It does not, however, account for the elastic scattering from the container which appears as the relatively sharp peak centered at E_0 in the data.

Fig. 6--Experimental data for 0.065-ev neutrons scattered by a 1-mm layer of para-hydrogen. Theoretical predictions based on a perfect gas model are also shown

The dashed curve represents the predicted theoretical scattering corrected for instrument resolution and plotted with an arbitrary normalization. Though the experimental and theoretical curves agree in position, the observed broadening, 0.020 ev, is approximately 20 percent greater than the predicted value of 0.017 ev.

Similar representation of the scattering from ortho-para-hydrogen are shown in Figs. 7 and 8 where the incident neutron energies were 0.065 ev and 0.040 ev respectively. Comparable measurements have also been made utilizing higher incident neutron energies and in all cases the observed broadening is greater than predicted on the basis of a perfect gas model. Although the theoretical curves were plotted in Figs. 6, 7, and 8 with arbitrary normalization, it may be useful for future reference to compare for two cases the relative theoretical and experimental values. For $E_0 = 0.065$ ev and for the peak of the scattered neutron distributions

$$\left(\frac{d\sigma}{d\Omega dE} \right)_{\text{p-H}} / \left(\frac{d\sigma}{d\Omega dE} \right)_{\text{o-p-H}} = 1.93 \text{ and } \sim 3.7 \text{ respectively for}$$

the theoretical and experimental curves.

Since the sample thicknesses were chosen to have a neutron transmission greater than or equal to 0.85, the effects of multiple scattering are believed to be small in most of the cases examined. This assumption has been reinforced by measuring the distribution of neutrons scattered from a sample of para-hydrogen having half the thickness used in obtaining the data in Fig. 6. The observed widths agree within the experimental error. On the basis of these considerations, the observed additional broadening of the distributions appears to be a feature of the liquid state of hydrogen.

Fig. 7--Experimental data for 0.065-ev neutrons scattered by a 1-mm layer of ortho-para-hydrogen. Theoretical predictions based on a perfect gas model are also shown

Fig. 8--Experimental data for 0.04-ev neutrons scattered by a thin layer of ortho-para-hydrogen. Theoretical predictions based on a perfect gas model are also shown

DISCUSSION

The overall agreement between theory and experiment supports the generally accepted concept that the molecules in liquid hydrogen behave very nearly as they do in a "perfect" gas. The absence of appreciable bonding forces is evident from the agreement between the observed and calculated energies of the various scattering components. Such would not be the case if even moderate binding forces were operative, since then the effective mass of the recoiling molecule would be increased with a substantial reduction in the energy of the recoiling molecule. The position of the scattering distribution peaks is thus relatively sensitive to the recoil mass. Moreover, any tendency of liquid hydrogen to exhibit solid state characteristics would be reflected in a reduction of the width of the scattered distribution.

The present data, though not sufficiently accurate to permit final conclusions, indicate that the scattering components are broader than one would expect from the "perfect" gas model. One interpretation of this additional broadening is that the effective translational energy of a hydrogen molecule in the liquid state is larger due to molecular interactions. Theoretical conclusions of Pauling⁽³⁾ and measurements of Raman spectra⁽⁴⁾ support the supposition that the molecules in liquid hydrogen rotate freely. However, the motion of the hydrogen molecules may involve at least two different aspects of the liquid. On the one hand, if there are general nearest-neighbor collisions between molecules, additional broadening of all scattering components should be observed. On the other hand, if the main effect of the liquid state is to reduce the lifetime of the excited states thus introducing a further lack of sharpness in the excited levels, then the (0-0) scattering distribution in para-hydrogen should not be additionally broadened but all other neutron interactions involving excited states should exhibit extra broadening. Nuclear magnetic resonance measurements⁽⁵⁾

of the dependence of the nuclear relaxation time on different concentrations of ortho hydrogen have shown that an interaction exists between ortho and para hydrogen molecules. In view of this interaction, the final state of the neutron scattering event which consists of a single ortho molecule surrounded by para molecules is not well defined and may be an explanation for the extra broadening observed in the present experiment on para-hydrogen. The broadening of the distribution from ortho-para-hydrogen (Fig. 7) appears to be greater than that from para-hydrogen (Fig. 6). Nuclear magnetic resonance measurements have provided clear evidence that the ortho-ortho quadrupole interaction is very strong and much stronger than the ortho-para interaction. This strong ortho-ortho interaction could be the mechanism by which neighboring molecules interact and hence give an extra broadening to the distribution in energy of neutrons scattered by ortho hydrogen. A future experiment on the "elastic" scattering ($0 \rightarrow 0$) of neutrons in para-hydrogen with $E_0 < 0.030$ ev should provide considerable clarification of these effects and may give evidence of an interaction of para molecules with other para molecules, an interaction which cannot be studied directly by the techniques of nuclear magnetic resonance. The experiment has not been performed as yet with the present experimental arrangement due to the very small cross section of the ($0 \rightarrow 0$) scattering in para-hydrogen.

The discrepancy between experiment and theory shown in Fig. 8 has not been confirmed by repeating the measurements. A crude estimate of multiple scattering indicates only a small effective displacement of the peak to be expected for this scattering (with perhaps the main effect being an enhanced low energy tail). A definitive check on this will be made by observing the scattering from a thinner scattering layer. Assuming the validity of the discrepancy, an explanation is that the liquid state of hydrogen alters the relative cross sections for excitation and de-excitation. If this explanation is correct, the data of Fig. 8 indicate that the ($0 \rightarrow 1$)

transition is enhanced and/or the (1-0) transition is suppressed in liquid ortho-para-hydrogen. The relative cross-sections for scattering by para-hydrogen and ortho-para-hydrogen, noted in the previous section for $E_0 = 0.065$ ev, offer additional evidence that the liquid state affects the magnitude of the partial cross-sections.

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Both of these include extensive additional references to pertinent literature.

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