The use of neutron scattering experiments for studying molecular hydrogen in amorphous hydrogenated carbon

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The presence of molecular hydrogen in a-C:H has been demonstrated by a series of neutron scattering experiments. Neutron diffraction gives a peak in the pair correlation function corresponding to the H–H bond distance. Inelastic neutron scattering experiments have shown peaks consistent with the H_2 rotation and stretch, and revealed details of the hydrogen environment.

1. Introduction

Amorphous hydrogenated carbon (a-C:H) is of considerable technological interest because of its hardness, density and resistance to chemical attack. Structural understanding of this complex material has been slow to develop, primarily because the large number of possible carbon bonding environments. Current structural models suggest clusters of sp^2 carbon are connected by chains of hydrogenated sp^3 carbon. Reviews of these models can be found elsewhere [1, 2].

Although numerous techniques have suggested "microbubbles" of molecular hydrogen in analogous materials, such as amorphous hydrogenated silicon [3, 4], it was only when neutron scattering techniques were applied to a-C:H that molecular hydrogen was unambiguously detected [5].

2. Experimental

The amorphous hydrogenated carbon samples used for these experiments were produced using a saddle-field ion-beam source [6]. Sample 1 was deposited within the source chamber from a mixture of propane, butane and acetylene gases. Sample 2 was deposited in the conventional way from acetylene gas alone.

A Carlo-Erba CHN combustion analyser was used to determine the compositions of the samples and the bulk densities were determined using a residual volume technique (see table 1).

The neutron scattering data were collected at the ISIS pulsed neutron source (Rutherford Appleton Laboratory) using the LAD diffractometer and the

Table 1
Compositions and densities of the samples.

	C (at.%)	H (at.%)	ρ (g cm^{-3})
Sample 1	0.71	0.29	1.80
Sample 2	0.65	0.35	1.65

TFXA and MARI spectrometers. Full details can be found elsewhere [7].

3. Discussion

The first suggestions that molecular hydrogen was present in a-C:H came from a neutron diffraction experiment performed on the LAD diffractometer [8]. A peak in the pair correlation function $(G(r))$ at 0.63 Å could best be explained as a recoil shifted molecular hydrogen peak. It is interesting to note, in this context, that a fit to the data using the Reverse Monte Carlo technique [9] generated a model in which a 0.7 Å peak was derived solely from H–H pairs within the "box of atoms". Whilst this cannot be considered truly independent evidence, it does suggest the existence of a viable structural model consisting of H_2 molecules within a-C:H.

An incoherent inelastic neutron scattering experiment performed on the TFXA spectrometer [5], gave solid supporting evidence. The $J = 0$ to 1 (14.5 meV) rotation is observed, centred at 14 meV. From the peak position and shape, it has been possible to postulate an effective high pressure hydrogen environment, with the hydrogen molecules held within oblate or prolate spheroidal cages.

In [5], Honeybone et al. also showed the results of preliminary experiments on the MARI spectrometer, which indicated the presence of the molecular hydrogen stretch mode.

Recent experiments on MARI have confirmed the presence of a peak (see fig. 1) at 518 meV, although assignment is complicated by the expected close proximity of the C–H stretch/bend combination. The $S(Q, \omega)$ plot (see fig. 2) shows that this peak is contained within the hydrogen recoil, unlike the C–H stretch and bend modes.

In order to understand fully the nature of this vibration, it is necessary to examine the Q dependence
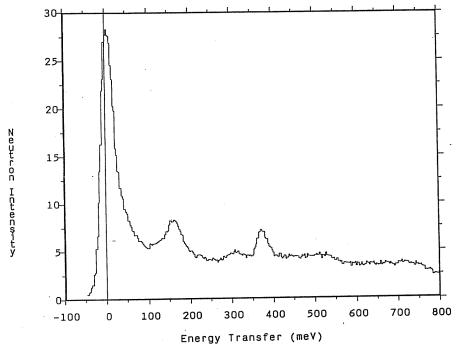
Fig. 1. Inelastic neutron scattering spectrum for sample 2 showing the C–H stretch and bend (370 and 150 meV), the overtone of the C–H bend (300 meV) and the 520 meV mode. Data collected on the MARI spectrometer using 800 meV incident neutrons.
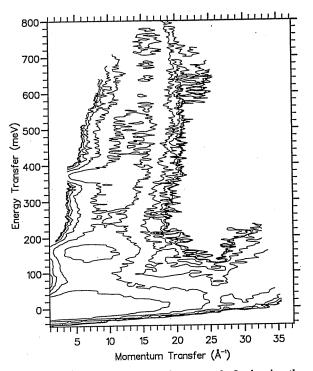

Fig. 2. Contour map of $S(Q, \omega)$ for sample 2, showing the hydrogen and carbon recoil lines, with the C–H stretch and bend extending outside the hydrogen recoil. Data collected on the MARI spectrometer using 800 meV incident neutrons.

of the Deby–Waller factor within the scattering law for a 3-dimensional oscillator [10]:

$$S(Q, n\omega_0) = \frac{1}{n!} \, (Q^2 U^2)^n \, \exp(-Q^2 U^2) \, . \qquad (1)$$

A Q^2 dependence of the pre-exponential part of the Debye–Waller factor will be associated with a fundamental, and a Q^4 dependence for combinations and overtones.

The analysis is complicated however by the fact that the 518 meV peak sits on top of the hydrogen recoil, which has a strong Q dependence. The peak at 518 meV only appears in the data for the acetylene sample, although the C–H stretch and bend are of the same shape and intensity in both; we are therefore able to attempt an empirical correction for the recoil by taking a suitably scaled difference.

Figure 3 shows the Debye–Waller factor for the 518 meV mode derived in this way; the statistical quality of the data is such that this has not provided a truly unambiguous assignment. The observed intensity may therefore be due to the H–H stretch, a C–H stretch/bend combination, or have a significant contribution from both. Monte-Carlo modelling of the recoil for both samples should, in principle, lead to a more conclusive answer.
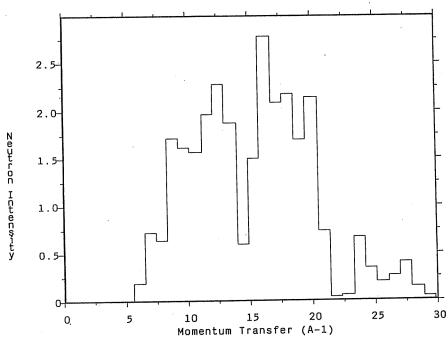
Fig. 3. Debye–Waller factor for sample 2 at 518 meV. Data collected on the MARI spectrometer using 800 meV incident neutrons.

4. Conclusions

The use of neutron scattering techniques has led to a large body of evidence for the existence of molecular hydrogen in certain amorphous hydrogenated carbon samples and to the postulation of a high pressure, asymmetric hydrogen environment. At the moment, there remain residual doubts about the assignment of the 518 meV mode; this can only be resolved on the basis of Monte-Carlo recoil modelling.

Further work is now in progress to study the hydrogen distribution in more detail using small angle scattering, and by performing diffraction experiments on H/D substituted samples. Other work will employ X-ray diffraction and high resolution NMR together with computer modelling/simulation studies.

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