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## Inelastic neutron scattering of molecular hydrogen in amorphous hydrogenated carbon

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Received 21 December 1990; in final form 5 March 1991

We have, by use of inelastic neutron scattering, detected the presence of molecular hydrogen in amorphous hydrogenated carbon. We have found the hydrogen to be in a high-pressure, asymmetric environment formed by the compressive stresses in the a-C:H films. On comparing two samples, we have also found that the sample with higher molecular hydrogen concentration has a lower total hydrogen composition. This is caused by a higher network density, trapping the molecular hydrogen during network growth.

### 1. Introduction

Hydrogen incorporation in amorphous hydrogenated carbon films plays a key role in determining the structure and properties of the resulting film, in particular, in determining the  $sp^2:sp^3$  ratio [1,2]. Direct comparison of Rutherford backscattering and infrared spectroscopy on a-C:H [3,4] indicates a total hydrogen concentration greater than the bonded hydrogen concentration. This suggests, but does not unequivocally prove, the existence of unbonded or molecular hydrogen.

Molecular hydrogen has been identified in amorphous hydrogenated silicon by numerous techniques, e.g. refs. [5,6], leading to the postulation of "microbubbles" of molecular hydrogen. There has been no such evidence for hydrogen molecules in a-C:H.

Neutron scattering provides the only means of probing directly the hydrogen environment. The total neutron scattering cross-section of hydrogen is

several orders of magnitude greater than that for carbon. Incoherent inelastic neutron scattering (IINS) takes advantage of this to yield a scattering function which can be related directly to the hydrogen vibrational density of states,  $g(\omega)$ . Full details of this technique can be found elsewhere [7,8]. IINS has recently been used to identify the presence of molecular hydrogen in one sample of a-C:H from an observation of the characteristic frequency of rotation [9]. This work represents an extension of that study.

### 2. Experimental

The amorphous hydrogenated carbon used in these experiments was produced using a saddle-field ion-beam source [10]. Sample 1 was deposited within the source chamber over a period of time from a mixture of propane, butane and acetylene gases. Sample 2 was deposited in the conventional way,

Table 1  
Compositions and densities of the samples

	C (at.%)	H (at.%)	$\rho$ (g cm <sup>-3</sup> )
sample 1	0.71	0.29	1.65
sample 2	0.65	0.35	1.51

from an acetylene precursor gas, onto copper substrates; as a-C:H does not adhere to copper, this proved an ideal method for producing the large ( $\approx 2$ –5 g) powder samples required for neutron-scattering experiments.

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 inelastic neutron-scattering data were collected at the ISIS pulsed neutron source (Rutherford Appleton Laboratory) using the TFXA and MARI instruments, which are, respectively, inverse- and direct-geometry inelastic spectrometers. Full details can be found elsewhere [11].

### 3. Discussion

As has been reported previously [9], the TFXA data show molecular hydrogen clearly in sample 1 only (see fig. 1). The rotation of molecular hydrogen is predicted to give rise to a peak centred at 15 meV corresponding to the ortho-para transition ( $J=0$  to 1) [12]. Our data reveal broad peaks at 12.5 and 16 meV, consistent with a distribution of potentials at different sites hindering the rotation. Silvera and Nielsen [13] have shown that this would cause the observed asymmetry in the  $J=0$  to 1 transition. It has been possible to estimate the bond length from a weighted average of these peak positions ( $14 \pm 0.5$  meV). At  $0.72 \text{ \AA}$ , the bond length is lower than that for gaseous hydrogen ( $0.75 \text{ \AA}$ ), suggestive of a high-pressure hydrogen environment.

If the molecular hydrogen is in a high-pressure environment, this must be due to high levels of stress in the amorphous solid. Compressive stresses have been extensively studied [14], and have been found to give an effective hydrostatic pressure of the order 2 GPa in a-C:H. This compares to a pressure of 0.2

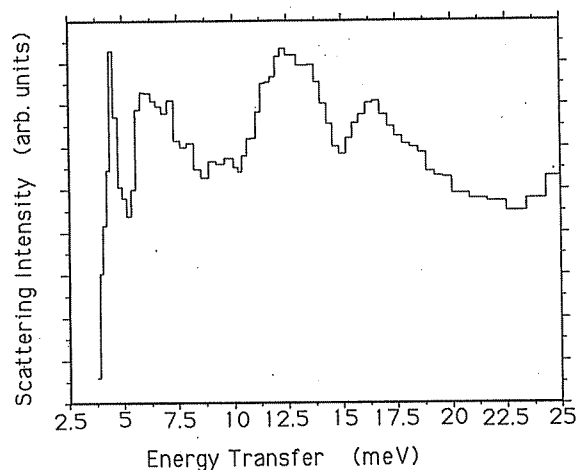


Fig. 1. Inelastic neutron-scattering spectrum for sample 1 in the 2.5–25 meV range showing two lattice vibrations (4.5 and 7 meV) and the molecular hydrogen rotation (12.5 and 16 meV). (Obtained using the TFXA spectrometer.)

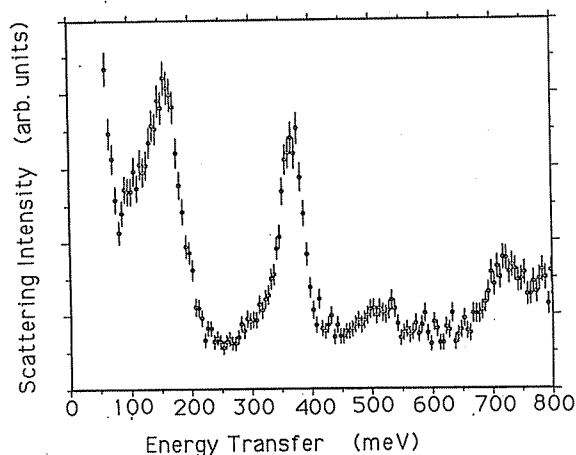


Fig. 2. Inelastic neutron-scattering spectrum for sample 2 showing the carbon-hydrogen stretch and bend (370 and 150 meV) and the molecular hydrogen stretch (540 meV). (Obtained using the MARI spectrometer with 1000 meV incident neutrons.)

to 0.4 GPa for hydrogen in a-Si:H based on Chabal and Patel's infrared data [15].

Although the rotation of molecular hydrogen is not seen in sample 2 (see fig. 2) on TFXA and only weakly on MARI, the presence of molecular hydrogen is clearly indicated by the observation of a peak at  $540 \pm 6$  meV, best described by a H-H stretch (544.8 meV [16]).

This may be taken as implying that sample 2 has a greater proportion of the total hydrogen content bonded to the carbon; thus, in the TFXA data at least, the hydrogen rotation is not seen due to the background of network vibrations. (If sample 2 has a higher proportion of bonded hydrogen and a higher total hydrogen content, it must have a higher absolute bonded-hydrogen concentration than sample 1.) Bonded hydrogen reduces the cross-linking in the network, resulting in a more open structure, through which hydrogen could more easily diffuse. Density measurements are consistent with this, as the higher-density sample has the higher molecular hydrogen concentration.

Hydrogen-effusion experiments [17] have shown a plateau in the hydrogen evolution as a function of temperature. Although this was initially thought to be due to loss of adsorbed hydrogen, this has recently been interpreted as being caused by a densification of the network [18]. Eventually, this forms a network in which molecular hydrogen is trapped. Further supporting evidence for this theory is provided from work on amorphous silicon [5], which shows a higher molecular hydrogen concentration after annealing than before. This data can be used to put an upper bound on the molecular hydrogen of approximately one fifth the total hydrogen concentration.

Our results suggest that during deposition, a densification process, similar to the one observed during annealing, is responsible for trapping small quantities of molecular hydrogen in all a-C:H samples, with the proportion of hydrogen trapped as molecular hydrogen increasing with final network density. McKenzie et al. [14] have recently produced a new form of a-C:H with a low overall hydrogen content but a very high network density, in which it is thought that all the hydrogen present is in the form of molecular hydrogen.

#### 4. Conclusions

Molecular hydrogen is trapped in both samples under investigation in these experiments, and probably is present in all samples of a-C:H, although perhaps in small quantities. The proportion of molecular hydrogen seems to decrease with increasing hydrogen concentration, which suggests that in-

creased hydrogenation leads to a more open network with fewer sites able to trap the molecular hydrogen within the a-C:H.

We have found a split rotation band consistent with a distribution of hindering potentials at different sites. From the reduced bond length, we deduce a high effective pressure and infer a pressure of  $\approx 1$  GPa from published data.

#### Acknowledgement

We would like to thank Mr A. Evans and Dr. J. Franks of Ion Tech Ltd. for their help in depositing the a-C:H, Mr A. Fassam (Chemistry Department, UKC) for his help in determining compositions and other members of the Kent group and Dr. D.K. McKenzie for helpful discussions. One of us (PJRH) acknowledges the receipt of a SERC studentship.

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