Jager, C., Titman, J.J. and Newport, Robert J. (1993) *Detection of Structural Heterogeneity in Amorphous-C-H Films by NMR.* Thin Solid Films, 227 (1). pp. 3-6. ISSN 0040-6090.

Record 1 of 1

Author(s): JAGER, C; TITMAN, JJ; NEWPORT, RJ

Title: DETECTION OF STRUCTURAL HETEROGENEITY IN AMORPHOUS-C-H FILMS BY NMR

Source: THIN SOLID FILMS, 227 (1): 3-6 MAY 5 1993

Language: English

Document Type: Letter

Addresses: UNIV KENT,PHYS LAB,CANTERBURY CT2 7NR,KENT,ENGLAND

Reprint Address: JAGER, C, MAX PLANCK INST POLYMER RES,POSTFACH 3148,W-6500 MAINZ,GERMANY.

Cited Reference Count: 11

Times Cited: 6

Publisher: ELSEVIER SCIENCE SA LAUSANNE

Publisher Address: PO BOX 564, 1001 LAUSANNE 1, SWITZERLAND

ISSN: 0040-6090

29-char Source Abbrev.: THIN SOLID FILMS

ISO Source Abbrev.: Thin Solid Films

Source Item Page Count: 4

Subject Category: Materials Science, Multidisciplinary; Materials Science, Coatings & Films; Physics, Applied; Physics, Condensed Matter

ISI Document Delivery No.: LD592

Detection of Structural Heterogeneity in Amorphous-C:H Films by NMR

C. JÄGER[§], J. J. TITMAN[§], AND R. J. NEWPORT*

[§] *Max-Planck-Institut für Polymerforschung, Postfach 3148, W-6500 Mainz, Germany*
* *Physics Laboratory, University of Kent, Canterbury, CT2 7NR, UK*

During the last twenty years the number of technological uses of amorphous materials has increased significantly. The complexity of these materials is such, however, that despite much scientific interest, many fundamental questions about them remain to be answered. An intriguing example is amorphous hydrogenated carbon (a-C:H) which may be prepared as a thin film by ion beam sputtering techniques. Its hardness, density, optical behaviour, chemical resistance and other properties vary as a function of the parameters controlling the deposition process, with the hydrogen content playing an important role [1-3]. Current models for the structure of a-C:H involve clusters of sp^2 hybridized carbon linked by sp^3 carbon [4,5] with hydrogen stabilizing the sp^3 regions and reducing the number of dangling bonds.

Among the numerous techniques used for studying the structure of these materials, nuclear magnetic resonance (NMR) is becoming increasingly important. Several papers have previously reported results from carbon-13 magic angle spinning (MAS) NMR experiments with cross polarization (CP) and proton dipolar decoupling in systems with a high hydrogen content [6-8]. The resulting carbon-13 spectra normally consist of two broad resonances, one at about 50 ppm (relative to TMS) which can be attributed to sp^3 hybridized carbon and the other at around 130 ppm due to sp^2 carbon. Hydrogenated and non-hydrogenated carbon atoms have been distinguished by gated decoupling experiments and the relative amounts of the two types have been quantified [8-10].

In this Letter we suggest the existence of structural heterogeneity in our samples of a-C:H. These observations have been made using NMR methods essentially similar to those mentioned above except that the proton spin-lattice (T_1) relaxation has been used to edit the carbon-13 spectra. Two distinct types of proton clusters can be distinguished, and these are apparently linked by regions of non-protonated carbon atoms. Here "proton cluster" is taken to mean a group of hydrogen atoms exhibiting the same relaxation behaviour, spatially separated from the other protons in the sample.

The amorphous hydrogenated carbon sample used in these experiments was prepared using a saddle-field ion / fast-atom source with acetylene as the precursor gas.

The sample density was estimated as 1.9 g/cm^3 using a residual volume technique, and the hydrogen content was determined as 35 at% using a Carlo-Erba combustion analyser. A second sample prepared with propane as the precursor had 32 at% hydrogen.

The proton T_1 measurements were made using the standard inversion recovery sequence (Fig. 1(a)). In order to resolve different proton species, their relaxation properties were also measured indirectly via the magic angle spinning (MAS) carbon-13 spectrum in which different chemical environments can be distinguished. To this end, the proton magnetization was transferred to neighbouring carbon-13 nuclei by cross polarization (CP) after the inversion recovery sequence (Fig. 1(b)). The MAS carbon-13 spectrum was then recorded after a TOSS pulse sequence [11] to remove rotational sidebands arising from inhomogeneous interactions larger than the spinning frequency. When the inversion recovery delay is set to one of the values of the zero crossings determined from the indirect T_1 measurements, proton magnetization from each of the two clusters can be selected independently. Thus, the chemical shifts of the carbon atoms associated with each of the proton clusters can be determined.

All measurements were carried out at a carbon-13 resonance frequency of 75.47 MHz. High power decoupling was used throughout during the acquisition of the FID, and the MAS frequency was 3.1 kHz. Cross polarization times were typically 1 ms. Between 1000 and 2500 scans were accumulated with repetition times of 1s. All chemical shifts are referenced to TMS.

The results of the proton T_1 measurements for the acetylene precursor sample are shown in Figure 2. The data can be fitted to a double exponential with time constants of 14 ms and about 120 ms, the fit curve being indicated by a dotted line through the experimental points. It should be noted that the quality of the fit is not degraded significantly by changes of up to 50% in the value of the second time constant. The two time constants are present in a ratio of approximately 2:1. Their existence suggests some degree of structural heterogeneity in the sample with at least two types of spatially separated proton clusters whose spin-lattice relaxation behaviour is not equilibrated by strong spin-spin couplings.

The two types of proton relaxation behaviour can be used to edit the carbon-13 spectrum using the pulse sequence of Figure 1(b). To demonstrate this Figure 3(a) shows the normal carbon-13 CP-TOSS spectrum of the film made with the acetylene precursor gas. This is similar to that observed by Jansen *et al.* [6] and shows two broad resonances at 138 ppm and 60 ppm (peak positions) which can be attributed to sp^2 and methine and methylene sp^3 carbons, respectively. Since the effects of the anisotropy of the chemical shift interaction have been removed by the combination of MAS and TOSS, the observed broadening is due to the large number of different carbon-13 environments. On the other hand, Figures 3(b) and (c) show spectra of the same sample edited by the proton relaxation with a delay of 8 ms and 25 ms between the inversion of the proton magnetization and the CP transfer. In (b) the sp^2 carbon signal has vanished completely since the delay corresponds to the zero crossing of the relaxing longitudinal magnetization of the associated protons. Similarly, the intensity at around 60 ppm also disappears, leaving a negative signal at 40 ppm which can be attributed to carbons associated with more slowly relaxing protons. In fact, a careful examination of (a) reveals a minor shoulder upfield of the 60 ppm signal. In a similar fashion, this signal can be removed from the spectrum by choosing the inversion recovery delay to be 25 ms (c), leaving signals at 138 ppm and about 65 ppm. We note here that the second sample with propane as the precursor gas produced very similar results.

An immediate conclusion is the identification of two types of proton cluster, distinguished by their different spin-lattice relaxation times with the relaxation behaviour of protons within each cluster averaged by strong coupling. The quickly relaxing protons strongly cross polarize not only the sp^3 carbons at about 60 ppm but also those sp^2 carbons at 138 ppm. Thus, one proton environment consists of a network of interlinked sp^2 and sp^3 hybridized carbon. However, the slowly relaxing protons cross polarize a distinct sp^3 carbon signal at 40 ppm. Chemical shift arguments and the fact that no strong sp^2 signal is observed at this zero crossing suggest that these protons arise from regions of chain-like sp^3 hybridized CH$_x$.

Further information can be obtained from measurements of the proton spin-lattice relaxation resolved spectroscopically by the carbon-13 chemical shifts using the pulse sequence of Figure 1(b). The results of these measurements are shown in Figure 4. The carbon-13 intensities which now reflect the proton relaxation behaviour are plotted here as a function of the inversion recovery delay and were estimated by a constrained Gaussian fit of the individual spectra using positions fixed from analysis of the zero crossings of Figure 3. Each of these proton T_1 curves can be fitted by a double exponential with varying proportions of the two time constants. Nevertheless, within the uncertainty of the fitting, the two time constants are in each case the same as those obtained from the fit of the proton data shown in Figure 2. Because of the considerable overlap of the two sp^3 carbon lines (see Figure 3) any deviation of the lineshape or position from our fit constraints will result in the partial mixing of the two relaxation times. Clearly, the more intense sp^3 line will have a greater influence on the smaller one. Taking this into account, it can be argued that the fast relaxation behaviour is observed solely for protons associated with the carbons at 60 ppm, with slower relaxation for protons associated with the carbons at 40 ppm. On the other hand, the appearance of two time constants for the sp^2 signal can only mean that at least some of the protons associated with the 40 ppm sp^3 carbon signal must be in the vicinity of some of the sp^2 carbons. Therefore, these latter form a boundary layer between the two clusters.

It should be noted that these results can be equally well interpreted in terms of distributions of spin-lattice relaxation times as often observed in amorphous materials. In this case, this suggests the existence of two independent distributions of the proton spin-lattice relaxation with different mean values and widths. This interpretation does not alter the basic conclusion that two spatially separated proton clusters have been be identified.

An explanation for these observations is that a "layer" of non-protonated sp^2 carbons is present between the regions of interlinked sp^2 and sp^3 carbon and the chain-like sp^3 areas. This layer results in the breakdown of the spin-spin coupling between the different proton clusters and, therefore, in the two types of relaxation behaviour. The

non-protonated sp^2 layer must have some contact with the chain-like regions and so it is to be expected that there will be cross polarization from these protons to some small fraction of the sp^2 carbons. A tentative structural suggestion is sketched in Figure 5. Finally, we note that this structure is also consistent with results obtained from neutron scattering measurements.

REFERENCES

1. A. Lettington in *Diamond And Diamond-like Films and Coatings* (eds. R. E. Clausing, L. L Horton, J. C. Angus and P. Koidl), Plenum, New York, 1991.

2. J. W. Zou, K. Reichelt, K. Schmidt, and B. Dischler, *J. Appl. Phys., 65*, (1989) 3914.

3. D. R. McKenzie, D. Muller, B. A. Pailthorpe, Z. H. Wang, E. Kravtchinskaya, D. Segal, P. B. Lukins, P. D. Swift, P. J. Martin, G. Amaratunga, P. H. Gaskell, and A. Saeed, *Diamond and Related Materials, 1*, (1991) 51.

4. J. Robertson, *Adv. Phys., 35*, (1991) 317.

5. J. C. Angus, P. Koidl, and S. Domitz in *Plasma Deposited Thin Films*, (eds. J. Mort and F. Jansen), CRC Press, Bocaraton, 1986.

6. F. Jansen, M. Machonkin, S. Kaplan, and S. Hark, *J. Vac. Sci. Technol., A3*, (1985) 605.

7. F. Kleber, K. Jung, H. Ehrhardt, I. Mühling, K. Breuer, H. Metz, and F. Engelke, *Thin Film Solids, 205*, (1991) 274.

8. R. J. Gambogi, D. L. Cho, H. Yasuda, and F. D. Blum, *J. Polym. Sci. Polym. Chem., 29*, (1991) 1801.

9. U. Schwerk, Diploma, University of Leipzig, 1992.

10. K. R. Carduner, M. J. Rokosz, M. A. Tamor, and W. C. Vassell, *Appl. Magn. Reson., 2*, (1991) 647.

11. W. T. Dixon, *J. Chem. Phys., 77*, (1982) 1800.

FIGURE CAPTIONS

Fig 1: NMR pulse sequences used in this work. In (a) is shown the standard proton inversion recovery sequence for the measurement of spin-lattice relaxation times. The sequence for editing the carbon-13 spectrum by the proton relaxation is illustrated in (b).

Fig. 2: ^{1}H T_1 relaxation behaviour measured directly via ^{1}H NMR

Fig. 3: Carbon-13 NMR spectra of the amorphous hydrogenated carbon (acetylene precursor gas), edited by the proton spin-lattice relaxation behaviour using the sequence of Figure 1(b). In (a) is shown the spectrum obtained with a long delay between the proton inversion and the cross polarization pulse, corresponding to the equilibrium situation; in this particular case τ was 200 ms. Two broad featureless lines are observed at around 138 and 60 ppm. In (b) and (c), τ was 8 and 25 ms, respectively, in order to select the differently relaxing protons and to inspect which carbons are cross polarized by each cluster. For details see text.

Fig. 4: ^{1}H T_1 relaxation behaviour measured indirectly via ^{13}C NMR. In (a) is shown the proton T_1 curve measured at the sp^2 carbon site, in (b) that measured at the sp^3 site at 60 ppm, and in (c) that measured at the sp^3 site at 40 ppm

Fig. 5: Simplified structural picture according to the NMR results. One type of proton environment consists of a network of interlinked sp^2 and sp^3 hybridized, whilst chains of sp^3 carbon are also present. The two environments are separated by regions of non-protonated sp^2 hybridized carbons.
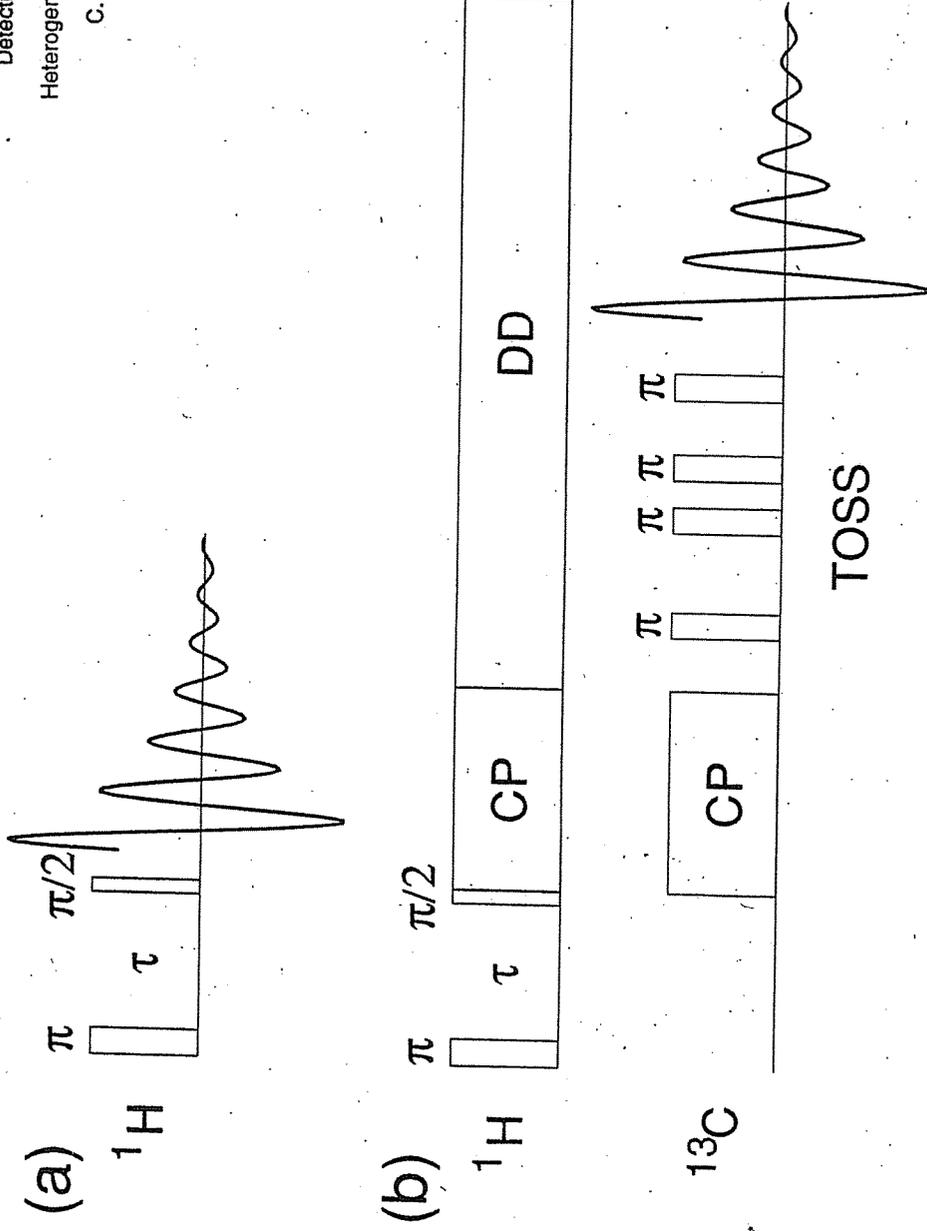
τ = 8 ms
τ = 25 ms
τ = 200 ms

(b)
(c)
(a)

ppm
0   50   100   150   200
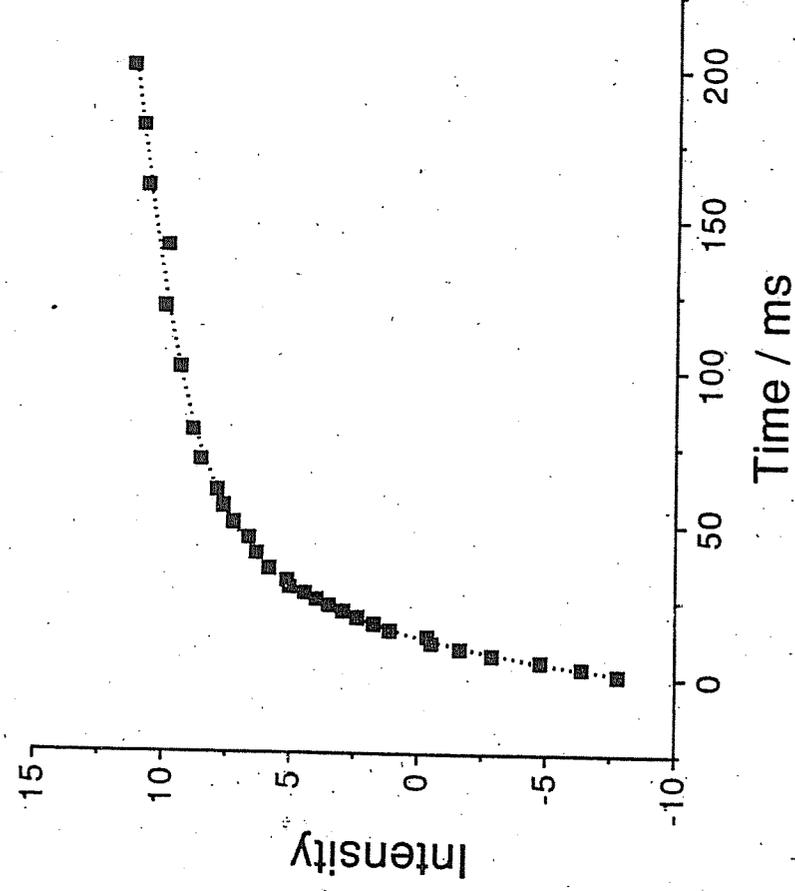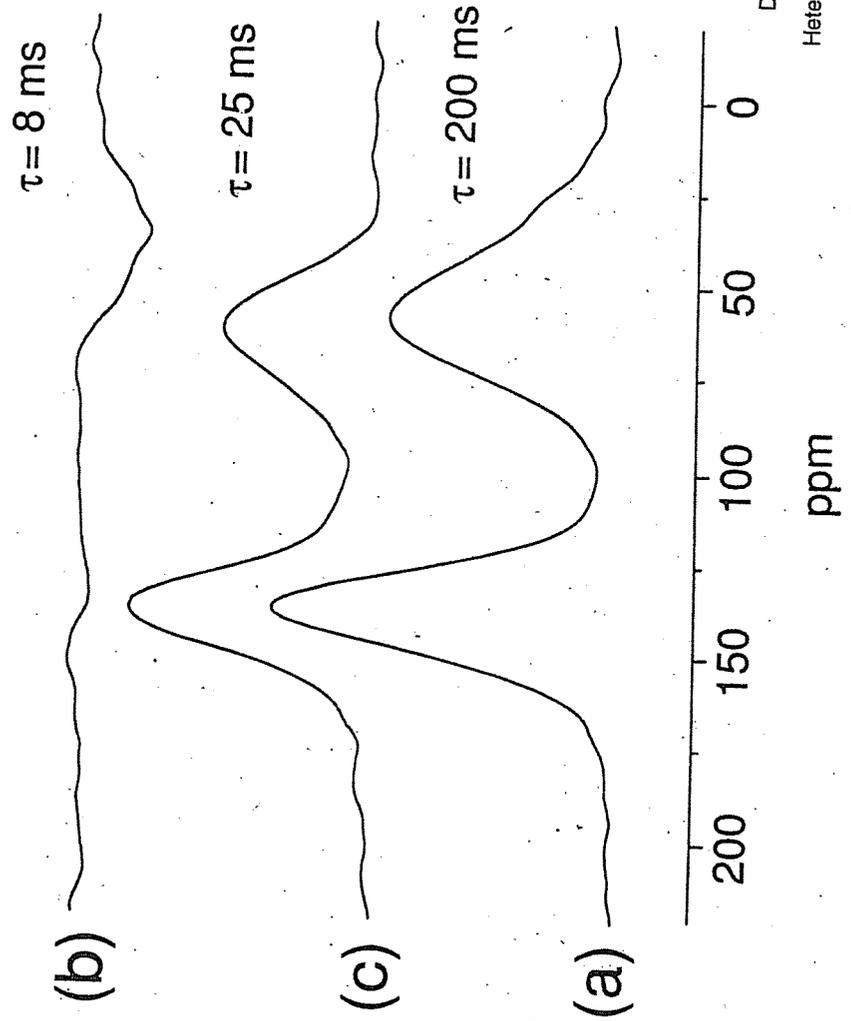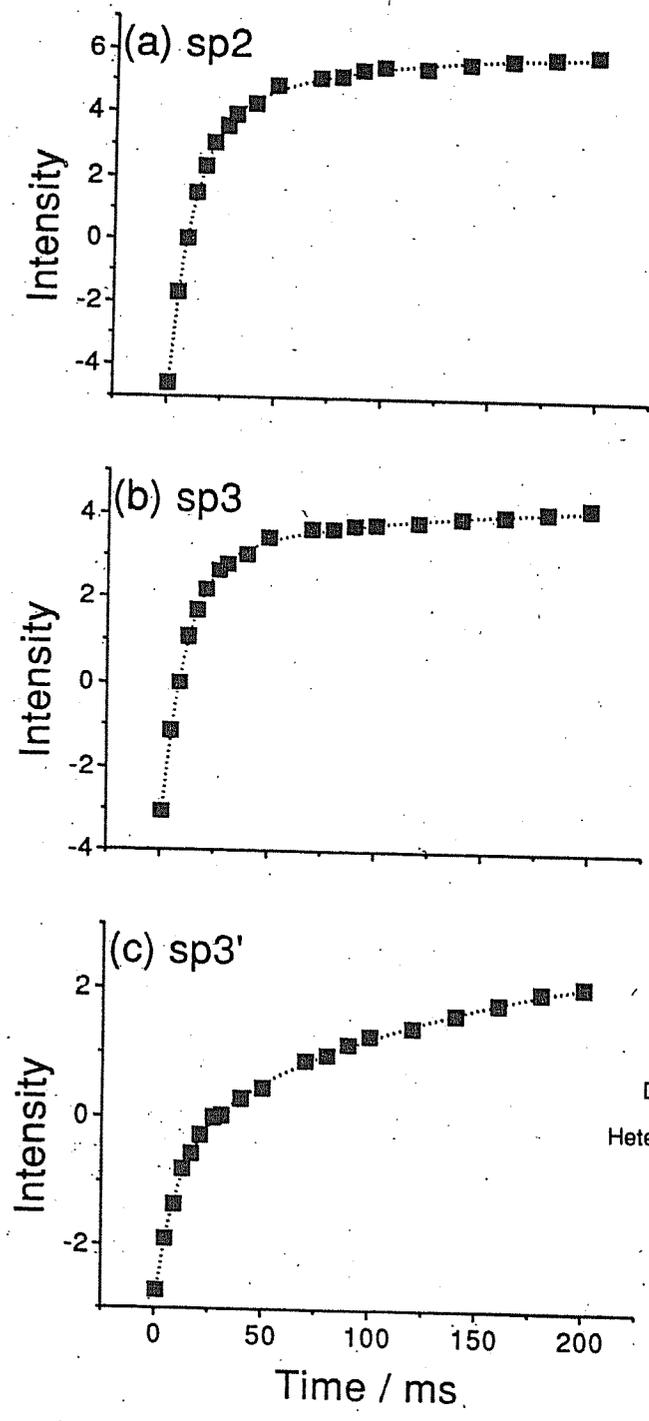
Detection of Structural
Heterogeneity In a-C:H Films
C. Jäger et al.
Figure 3

(a) sp2

Intensity
6
4
2
0
-2
-4

(b) sp3

Intensity
4
2
0
-2
-4

(c) sp3'

Intensity
2
0
-2

Time / ms
0   50   100   150   200

Detection of Structural
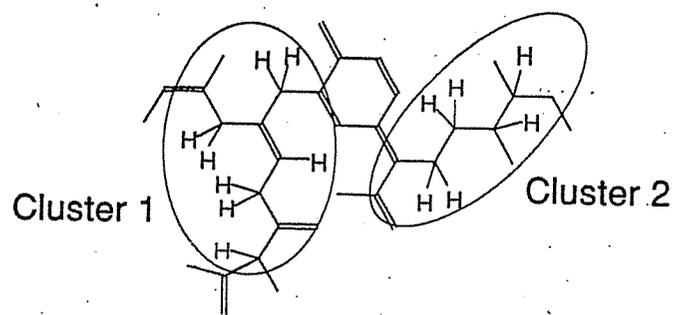Heterogeneity In a-C:H Films
C. Jäger et al.
Figure 4

Cluster 1   Cluster 2

Detection of Structural
Heterogeneity In a-C:H Films
C. Jäger *et al.*
Figure 5