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LOCATION OF ADSORBED XENON IN ZEOLITE-1 BY SYNCHROTRON POWDER DIFFRACTION

by

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Location of adsorbed xenon in zeolite-l by synchrotron powder diffraction.

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Abstract

This report describes the location of adsorbed xenon atoms in a sample of dehydrated zeolite-l which had been loaded with xenon, this was done by Rietveld refinement of synchrotron powder diffraction data collected on this sample. The data were collected on beamline 9.1 of the SERC Daresbury Synchrotron Radiation Source. The powder diffraction data were collected on this sample under three different sets of conditions. These were: vacuum (no xenon); xenon at a partial pressure of $\frac{1}{3}$ atmospheres; and xenon at a partial pressure of $\frac{2}{3}$ atmospheres.

Contents

0.1 Introduction

Researchers in the Davy-Faraday research laboratory at the Royal Institution and at Daresbury Laboratory have determinined the location of various organic molecules adsorbed in the framework of dehydrated zeolites. Zeolites are of great interest as catalysts due to their ability to adsorb various molecular species into the "cages" and "channels" of the zeolite framework structures [1]. One of the techniques used to locate adsorbed molecules is x-ray powder diffraction.

The location of adsorbed methane in zeolite-l is of current interest. However, methane is very difficult to "see" by x-ray diffraction due to the weak scattering of x-rays by elements of low atomic number. Xenon can be used to model methane as the two species are almost the same size [2] and xenon scatters x-rays much more strongly than methane. Therefore powder diffraction data have been collected for xenon-loaded dehydrated zeolite-l.

0.2 Experimental

0.2.1 sample preparation

The sample of zeolite-l used in this work was provided by Prof. J.M.Thomas of the Royal Institution. Chemical analysis of the (dehydrated) sample was done at Kingston polytechnic using ICPS, this resulted in the following stoichiometry:- $Na_{0.23}K_{6.97}H_2Al_{9.18}Si_{26.82}O_{72}$.

0.2.2 data collection

The powder diffraction data were collected using the high resolution powder diffractometer (HRPD) on station 9.1 of the Daresbury Synchrotron Radiation Source (SRS), SR of $\lambda = 0.7026\mathring{A}$ was used for the data collection.

The sample of zeolite-l was analysed under three different sets of conditions. The sample was first loaded into a GTP environmental cell on the HRPD. The zeolite was then dehydrated under vacuum ($1.3x10^{-6}$ bar) at 450°C. The sample was allowed to cool to room temperature and a diffraction pattern was obtained of the dehydrated material. Two further patterns were obtained with xenon partial pressures of $\frac{1}{3}$ atm (315-329 mbar) and $\frac{2}{3}$ atm (up to 615 mbar) in the GTP cell.

0.3 Data manipulation

The raw datasets were processed using software from the Powder Diffraction Program Library (PDPL) [3]. The PDPL program PODSUM was used to normalise the data to .pds format, Rietveld refinement [4] of this normalised data was then carried out using the PDPL MPREP and MPROF programs.

The starting model for the refinement of the zeolite-l structure was taken from the structure determined for a hydrated zeolite-l by Barrer and Villiger [5]. The zeolite-l structure was refined from the dehydrated (no xenon) dataset. This refined structure was used to refine the zeolite-l structure from the two xenon loaded datasets, after these latter two structures had been refined difference fourier maps for the two datasets were produced using the program MFOURS [6]. Coordinates of peak maxima from these maps were used as potential xenon sites in further cycles of Rietveld refinement to try to determine the positions of the adsorbed xenon atoms.

0.4 Rietveld refinement results

Atomic coordinates and (isotropic) temperature factors for framework and cation atoms were taken from the above mentioned hydrated zeolite-l structure. Structural parameters refined from the dehydrated (no xenon) dataset are given in table 1; a plot showing observed; calculated and difference profiles from this dataset is given as figure 1. Tables 2 and 3 show structural parameters for the $\frac{1}{3}$ atm xenon and $\frac{2}{3}$ atm xenon datasets and figures 2 and 3 show profile plots for these two samples. The plots in figures 1-3 show some excluded regions. These are due to Bragg reflections from iron in the GTP cell, there is also an excluded region at $12.33°2\theta$ which corresponds to a d-spacing of $3.33\mathring{A}$. This could be due to some quartz impurity in the sample.

0.5 Discussion

The lattice parameters for the three datasets (see table 4) show that the a lattice parameter does not change with adsorbtion of xenon but the c parameter increases as more xenon is loaded into the sample.

The site occupation factors for the Si/Al sites were determined from the Si/Al ratio in the chemical analysis. The same Si/Al ratio was used on the 12q and 24r sites, attempts to refine this ratio did not produce sensible results.

Refinement of the site occupation factors for potassium and sodium on the 2c site resulted in very small factors, indicating virtaully no electron density present on this site. Therefore, two hydrogen cations were put on this site as this cation has very little electron density associated with it. Refinement of the 2d site factors showed that this site was fully occupied by two potassium cations, refinement of the 3d site was found to fully occupied by potassium (2.77 cations) and sodium (0.23 cations) The 6j site was found to be only partially occupied, the site occupation factor was fixed at 3.20 potassium cations to balance charges.

Refinement of $\frac{2}{3}$ atm xenon dataset revealed evidence for the presence of xenon on the 1b and 6j sites (see table 3). The $\frac{1}{3}$ atm xenon dataset refinement only shows the presence of xenon on the 6j site (see table 2), refinement with xenon on the 1b site gave a very low site occupation factor so this site was removed from the refinement.

A plot of the xenon-loaded zeolite-l structure is shown in figure 4. This shows the zeolite-l structure looking down the c-axis with the 6j and 1b xenon sites shown (purple atoms) in the zeolite-l "channel". This plot was produced using the DTMM [7] computer program on an IBM PS/2 microcomputer.

The xenon temperature factor in these refinements was fixed at $15\mathring{A}^2$. If this factor is refined it goes to unrealistic very large values.

Only 0.34 xenon atoms per unit cell are found from the $\frac{1}{3}$ atm xenon dataset and only 0.51 atoms per unit cell are found from the $\frac{2}{3}$ atm xenon dataset. It is thought that 0.95 and 1.9 atoms per cell are actually adsorbed by the zeolite-l [8], [9]. It appears that not all of the xenon adsorbed by the xenon is detected by powder diffraction. However, the low site occupation factors for xenon are closely related to the temperature factor chosen for the xenon. Therefore if a different temperature factor for xenon was chosen different site occupation factors would result. It is possible that any xenon not detected by powder diffraction has too small a site occupation factor to be detected.

Table 5 shows the R-factors determined using MPROF for the three different datasets. For the two xenon loaded datasets the R-factors were recalculated with the xenon removed from the input data to see how much the R-factors are affected by the presence of xenon. These R-factors show a small decrease for the xenon loaded

datasets compared to those calculated with xenon removed, giving some indication that xenon has been detected in this zeolite-l sample.

The statistical significance of the location of the xenon atoms in the difference map will have to improve before it can be claimed that the xenon positions have been determined unambiguously.

Table 1, framework and cation coordinates for no xenon dataset

ATOM		X	Y	Z	B(ISO)	sof
Si	12q	0.0944(3)	0.3596(3)	0.5	0.20	8.93
Al	12q	0.0944(3)	0.3596(3)	0.5	0.20	3.07
Si	24r	0.1663(3)	0.4989(3)	0.2131(4)	0.20	17.87
Al	24r	0.1663(3)	0.4989(3)	0.2131(4)	0.20	6.13
O	6j	0.0	0.2715(8)	0.5	0.30	6.00
O	6m	0.1661(4)	0.3321(8)	0.5	0.20	6.00
O	12o	0.2657(3)	0.5313(7)	0.270(1)	0.64	12.00
O	24r	0.1034(5)	0.4153(5)	0.3176(9)	0.40	24.00
O	12o	0.4258(3)	0.8515(6)	0.281(1)	0.30	12.00
O	12p	0.1441(6)	0.4766(6)	0.0	0.30	12.00
H	2c	0.3333	0.6667	0.0	9.38	2.00
K	2d	0.3333	0.6667	0.5	0.76	2.00
K	3g	0.0	0.5	0.5	1.41	2.77
K	6j	0.0	0.3200(6)	0.0	0.63	3.20
Na	3g	0.0	0.5	0.5	1.00	0.23

Cell parameters

A	B	C	ALPHA	BETA	GAMMA
18.4504(13)	18.4504(13)	7.4854(2)	90.000	90.000	120.000

CELL VOLUME 2206.774(0.510)

R FACTORS; RI = 5.04, Rwp = 9.49, Re = 3.13

Table 2, structural parameters for $\frac{1}{3}$ atm xenon dataset

ATOM		X	Y	Z	B(ISO)	sof
Si	12q	0.0932(4)	0.3586(4)	0.5	0.20	8.93
Al	12q	0.0932(4)	0.3586(4)	0.5	0.20	3.07
Si	24r	0.1657(4)	0.4989(3)	0.2120(5)	0.20	17.87
Al	24r	0.1657(4)	0.4989(3)	0.2120(5)	0.20	6.13
O	6j	0.0	0.274(1)	0.5	0.30	6.00
O	6m	0.1652(5)	0.330(1)	0.5	0.20	6.00
O	12o	0.2664(4)	0.5328(8)	0.261(2)	0.79	12.00
O	24r	0.1025(6)	0.414(1)	0.318(1)	0.40	24.00
O	12o	0.4271(4)	0.8542(7)	0.273(2)	0.30	12.00
O	12p	0.1427(8)	0.4747(7)	0.0	0.30	12.00
H	2c	0.3333	0.6667	0.0	9.38	2.00
K	2d	0.3333	0.6667	0.5	0.93	2.00
K	3g	0.0	0.5	0.5	2.12	2.77
K	6j	0.0	0.3212(1)	0.0	0.87	3.20
Na	3g	0.0	0.5	0.5	1.00	0.23
Xe	6j	0.208(4)	0.0	0.0	15.00	0.34

cell parameters

A	B	C	ALPHA	BETA	GAMMA
18.451(1)	18.451(1)	7.4875(2)	90.000	90.000	120.000

CELL VOLUME 2207.4(6)

R FACTORS; RI = 4.03, Rwp = 6.94, Re = 2.91

Table 3, structural parameters for $\frac{3}{3}$ atm xenon dataset

ATOM		X	Y	Z	B(ISO)	sof
Si	12q	0.0929(5)	0.3582(6)	0.5	0.20	8.93
Al	12q	0.0929(5)	0.3582(6)	0.5	0.20	3.07
Si	24r	0.1652(6)	0.4982(5)	0.2122(7)	0.20	17.87
Al	24r	0.1652(6)	0.4982(5)	0.2122(7)	0.20	6.13
O	6j	0.0	0.274(2)	0.5	0.30	6.00
O	6m	0.1655(8)	0.331(2)	0.5	0.20	6.00
O	12o	0.2680(6)	0.536(1)	0.261(3)	0.97	12.00
O	24r	0.1021(9)	0.4135(9)	0.317(2)	0.40	24.00
O	12o	0.4287(6)	0.857(1)	0.269(3)	0.30	12.00
O	12p	0.144(1)	0.474(1)	0.0	0.30	12.00
H	2c	0.3333	0.6667	0.0	9.38	2.00
K	2d	0.3333	0.6667	0.5	1.17	2.00
K	3g	0.0	0.5	0.5	2.27	2.77
K	6j	0.0	0.322(1)	0.0	1.31	3.20
Na	3g	0.0	0.5	0.5	1.00	0.23
Xe	1b	0.0	0.0	0.5	15.00	0.04
Xe	6j	0.206(5)	0.0	0.0	15.00	0.47

Cell parameters

A	B	C	ALPHA	BETA	GAMMA
18.450(2)	18.450(2)	7.4890(3)	90.000	90.000	120.000

CELL VOLUME 2207.8(8)

R FACTORS; RI = 3.87, Rwp = 6.96, Re = 4.31

Table 4, lattice parameters for the three datasets.

Hexagonal lattice, spacegroup 191 P6/mmm

no xe	18.450(1)	18.450(1)	7.4854(2)	90.000 90.000 120.000
CELL VOLUME			2206.8(5)	
1/3 xe	18.451(1)	18.451(1)	7.4875(2)	90.000 90.000 120.000
CELL VOLUME			2207.4(6)	
2/3 xe	18.450(2)	18.450(2)	7.4890(3)	90.000 90.000 120.000
CELL VOLUME			2207.8(8)	

Table 5, R-factors from MPROF for the three datasets.

	R(I)	R(WP)	R(E)
no xenon	5.04	9.49	3.13
1/3 xe (xe included)	4.03	6.94	2.91
1/3 xe (xe excluded)	4.56	7.10	2.93
2/3 xe (xe included)	3.87	6.96	4.31
2/3 xe (xe excluded)	4.44	7.14	4.33

0.6 Conclusions

- 1. There is evidence that xenon has been detected from the powder diffraction datasets. Xenon has been found on one site from the $\frac{1}{3}$ atmospheres partial pressure dataset and on two sites from the $\frac{2}{3}$ atmospheres partial pressure dataset dataset.
- 2. Adsorbtion of xenon by the zeolite-l sample does not affect the a lattice parameter but the c parameter increases with increasing xenon loading.

0.7 Recommendations

- 1. Further datasets should be collected with this sample with higher xenon loadings, e.g. xenon partial pressures of 1 atmosphere, 2 atmospheres etc. Presumably more xenon would be adsorbed by a heavier loaded sample and consequently the xenon would be easier to "see".
- 2. Molecular dynamics calculations are to be carried out to confirm xenon location.

0.8 Acknowledgements

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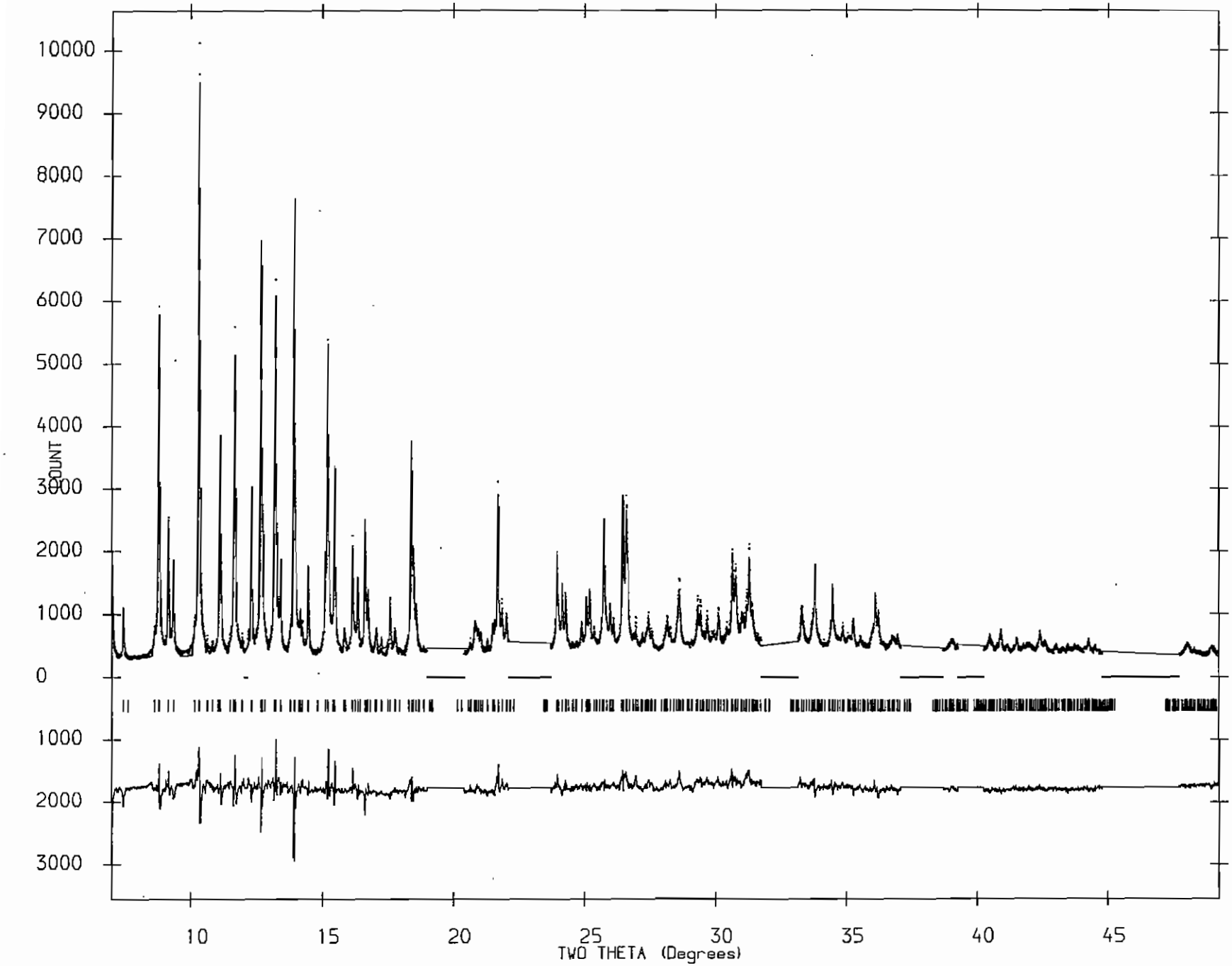
Figure 1, zeolite-l - no xenon loaded.



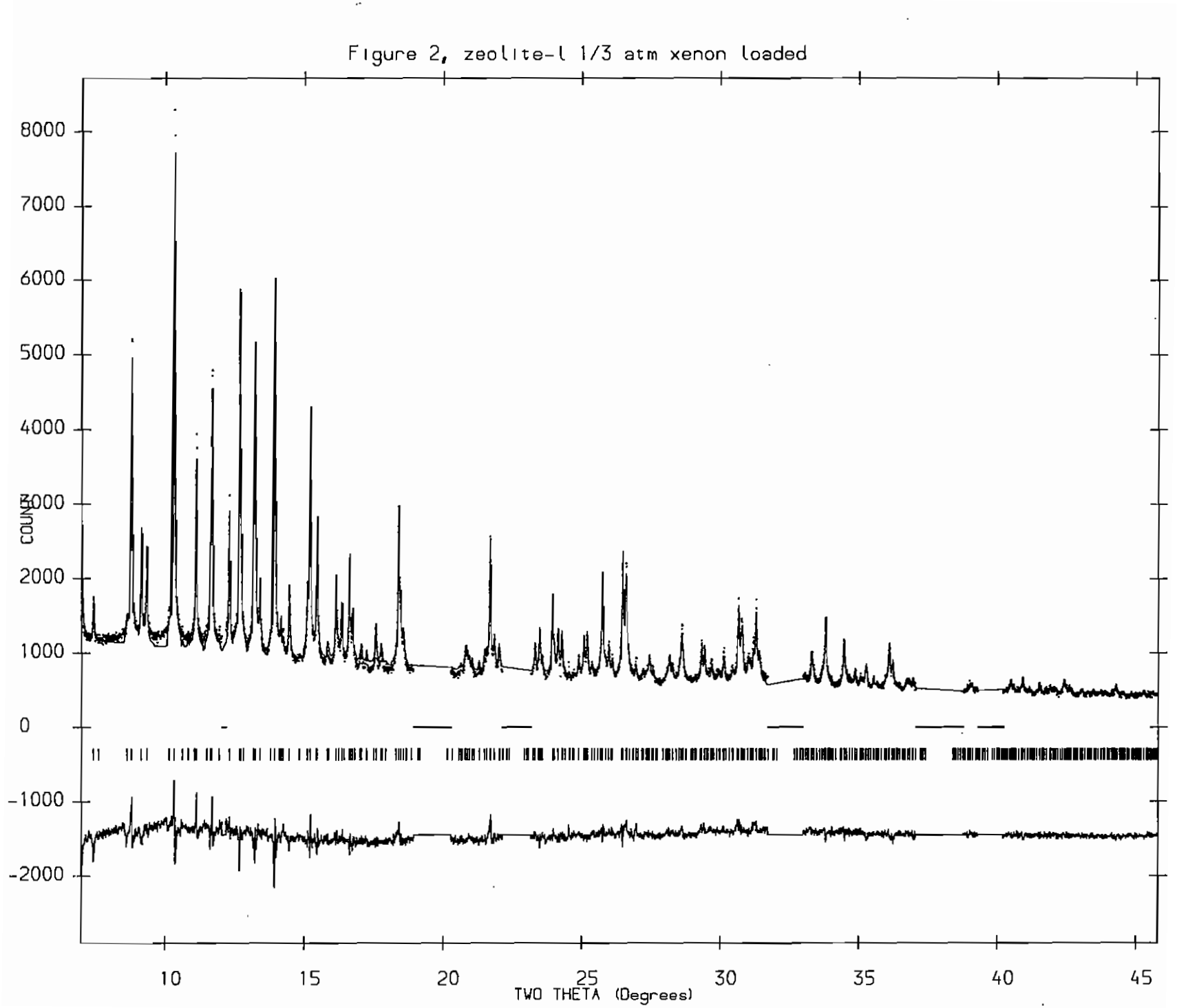


Figure 2, zeolite-l 1/3 atm xenon loaded
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
COUNTS
10
15
20
25
30
35
40
45
TWO THETA (Degrees)

Figure 3, zeolite-l 2/3 atm xenon loaded

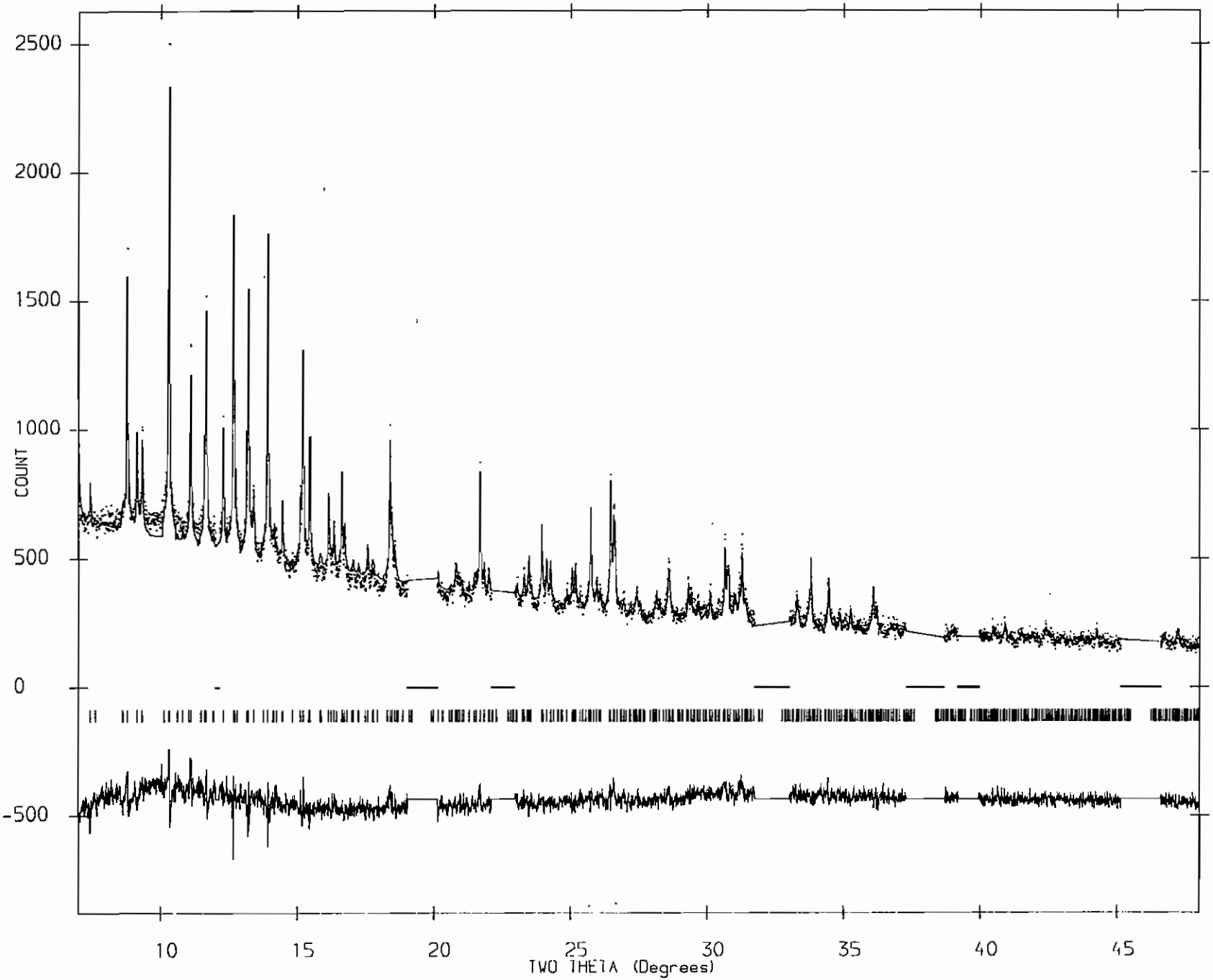


Fig 4 zeolite-l + xe