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CHEMICAL MODIFICATION OF TiO_2 SURFACES WITH METHYLSILANES AND CHARACTERIZATION BY INFRARED ABSORPTION SPECTROSCOPY

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(NASA-CR-165063) CHEMICAL MODIFICATION OF TiO2 SURFACES WITH METHYLSILANES AND CHARACTERIZATION BY INFRARED ABSORPTION SPECTROSCOPY (Virginia Polytechnic Inst. and State Univ.) 14 p HC A02/MF A01 CSCL 07D G3/25
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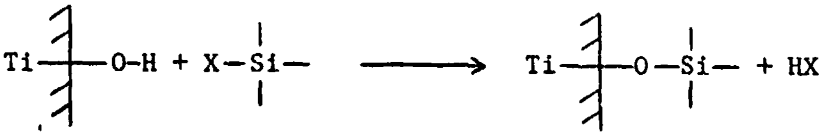
Infrared absorption spectra have been obtained of methylsilanes bonded to a TiO_2 powder. The reacting silanes include $Me_{4-n}SiX_n$ (n=1-4; X=Cl, OMe) and hexamethyldisilazane (HMDS). Reactions were performed on hydroxylated-but-anhydrous TiO_2 surfaces in the gas phase. IR spectra confirm the presence of a bonded silane layer. Terminal surface OH groups are found to react more readily than bridging OH groups. By-products of the modification adsorb tenaciously to the surface. The various silanes show only small differences in their ability to sequester surface OH groups. Following hydrolysis in moist air, Si-OH groups are only observed for the tetrafunctional silanes.

We are investigating the effects of binding non-electroactive molecules to electrode surfaces. The attached layer will be sufficiently thin (ca. 1 monolayer) that electron transfer across the electrode/electrolyte interface will not be inhibited. However, other surface properties may be advantageously modified. For semiconductor electrodes, desirable changes include suppression of the photo-activated surface corrosion and shifts in the flatband potential. We are seeking to improve the performance of semiconductor liquid-junction solar cells by these means.

One highly successful form of surface modification is silanization (1) (equation 1). A silane containing a hydrolytically



$$\mathrm{Ti}-\mathrm{O{-}H} + \mathrm{X}-\overset{|}{\underset{|}{\mathrm{Si}}}- \longrightarrow \mathrm{Ti}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- + \mathrm{HX} \quad (1)$$

unstable bond will react with a surface O-H group to form a silyl ether bond to the substrate. Commercially available silanes offer a selection of leaving groups such as chlorides (X=Cl), alcohols (X=OR), and amines (X=NHR). They also provide the possibility of forming one-to-three bonds between the silicon atom and the surface. We have systematically investigated a series of methylsilanes which span the three leaving groups mentioned and one-to-four hydrolytically unstable bonds ($Me_{4-n}SiX_n$; n=1-4; X=Cl, OMe; and hexamethyldisilazane - HMDS). These silanes were used to modify a TiO_2 substrate.

Knowledge of the composition and coverage of the attached layer is vitally important to our investigations. Previous work on monolayers of silanes have employed x-ray photoelectron spectroscopy (XPS) as a probe (2-7). XPS confirms the presence of silicon after the reaction and also allows an estimation of the layer thickness. We have used an infrared spectroscopic technique (8, 9, 10) which provides complementary information on the nature of the surface layer.

Experimental

TiO_2 powder (Degussa P-25) was used in all experiments. It consists of anastase particles with a mean diameter of 0.03 microns and a surface area of approximately 50 m^2/g. The powder was heated in air to 500°C for several hours and then stored in moist air. Approximately 50 mg of powder was pressed into a translucent pellet using a 13 mm diameter die and a hydraulic laboratory press. The pellet was mounted in a vacuum IR cell (CaF_2 windows) which could be sealed, detached from the vacuum line, and inserted in the spectrometer. All spectra were recorded on a Perkin-Elmer 283B Infrared Spectrophotometer with a P-E computer data station.

Pellets were predried by heating to 150°C for 2 hours under vacuum (<1 micron). Silanization was performed by exposing the pellet to silane vapor for 1 hour and then pumping away the excess reactant. Silane vapor pressure was controlled by thermostatting the degassed liquid reagent. This procedure was designed to prevent polymer formation of the bound silane.

Silane reagents were purchased from Petrarch Systems, Inc., and distilled prior to use.

Results and Discussion

Figure 1A illustrates the characteristic spectrum of a clean, dry TiO_2 pellet. Bulk TiO_2 is effectively transparent from band-gap energies (3 eV; 24,400 cm^{-1}) down to 1200 cm^{-1}. Below 1200 cm^{-1} lattice vibrations absorb the photons strongly. The peaks above 1200 cm^{-1} originate from absorptions by surface species. Three sharp peaks at 3730, 3650, and 3420 cm^{-1} are assigned to isolated surface O-H groups. They reside on a broad envelope of absorption caused by hydrogen bonding interactions between surface O-H groups. We adopt the assignments of Griffiths and Rochester (11); the bands at 3730 and 3650 cm^{-1} correspond to *terminal* O-H groups, while the 3420 cm^{-1} band corresponds to a *bridging* O-H group ($(Ti)_2$-OH). Absorptions due to residual hydrocarbons and molecular water appear at 3000-2800 cm^{-1} and 1620 cm^{-1} respectively.

All surface O-H groups are accessible to gaseous reagents. When the pellet of Figure 1A is exposed to D_2O vapor, Figure 1B results. Surface O-H groups are quantitatively exchanged to O-D groups. The exchange process is reversible.

When a TiO_2 substrate is exposed to a methylchlorosilane (Figure 2), new peaks appear in the IR spectrum. The peaks at 2960 and 2910 cm^{-1} are assigned to C-H stretches of the methyl groups on the silane; a C-H bend appears at 1410 cm^{-1}. An intense Si-C stretching band is observed at 1260 cm^{-1}. These peaks confirm the presence of the methylsilane on the surface. The peak positions match well the solution spectrum of the reagent silane. We conclude that the silanization has proceeded as expected (equation 1). Likewise, the O-H bond intensities are attenuated as O-H is replaced with O-Si. A new peak appears at 3540 cm^{-1}; this peak is reproduced if a clean TiO_2 pellet is exposed to the byproduct of the silanization, HCl. Based on its deuterium shift, we postulate that this peak arises from a Ti-O-H moiety forming a hydrogen-bond to adsorbed HCl. Increased hydrogen-bonding is evident from the increase in the absorption envelope at 3700-2700 cm^{-1}. The molecular water peak disappears.

Reactions with methoxysilanes (Figure 3) and HMDS (Figure 4) produce similar results to the chlorosilanes. The methoxy function, either as Ti-O-Me, Si-O-Me, or MeOH (see below), generates bands at 2840 and 1450 cm^{-1}. Ammonia, the byproduct from HMDS, produces new peaks at 3390, 3345, 3240, 3150, and 1600 cm^{-1}.

In all cases, IR spectra are consistent with the attachment of a methylsilane in accordance to equation 1. Proof of chemical bonding lies in the thermal stability of the modified surfaces; prolonged heating (150°C) under vacuum causes little to no decrease of the methyl C-H or Si-C bands.

In Figure 2B, the terminal O-H groups have disappeared quantitatively. It is tempting to conclude that all of the terminal groups have bonded to silanes. Consequently, the bonded silane layer must be homogeneous. However, several side reactions also cause attenuation of O-H intensity (*vide infra*), and the conclusion is invalid.

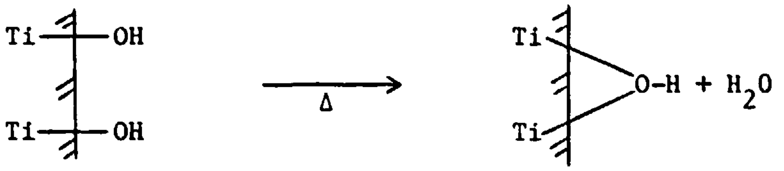
A surprising aspect revealed by IR is the selective reactivity of the two different types of surface O-H groups. In all cases, the loss of the terminal O-H bands greatly exceeds the loss of the bridging O-H band. If we equate the loss in O-H intensity with the formation of a silyl ether bond, then we must account for the low reactivity of the bridging O-H group. We suggest that reaction between the bridging O-H group and a silane is sterically hindered; a bridging O-H lies closer to a surface plane of titanium atoms (such as the 110 plane) than does a terminal O-H.

Byproduct adsorption and/or reaction is an ubiquitous feature in vapor phase silanizations. We include the possibility of reaction because of the following experiments. Exposure of clean pellet to byproducts (HCl, CH_3OH, or NH_3) generates the respective absorption bands cited above, but it also causes gross attenuation of the O-H bands. Such a result is consistent with equation 2:

(2)

Following silanization, some byproduct molecules are merely adsorbed. Heating the pellet after a reaction at room temperature (Figure 2B and 2C), or heating the pellet during the course of the reaction (Figure 4B and 4C) reduces the intensity of the byproduct absorptions. Complete removal is difficult; only days of exposure to the atmosphere eliminates all byproduct absorption bands.

We would like to equate the attenuation of the sharp O-H peaks with the yield of the reaction i.e. what percentage of the surface O-H groups have formed silyl ether bonds? Several problems invalidate the comparison. Reaction with byproducts (equation 2) and de-hydroxylation (equation 3) are both side reactions



(3)

that decrease O-H absorption intensity. Also, an unknown amount of O-H absorption intensity is diffused through the broad envelope ascribed to hydrogen-bonding interactions. With these caveats in mind, we have measured terminal and bridging peak areas before and after silanization. The respective percentage losses in O-H peak areas are shown in Table I, along with the reaction conditions. Using these numbers as a guide to the coverage obtained by various silanes, we find surprisingly small differences. Chlorosilanes appear to be the most effective reagents; quantitative loss of the terminal O-H bonds is usually observed. Methoxysilanes are slightly less effective, with monomethoxysilane yielding the lowest coverage. HMDS exhibits good coverage despite its low vapor pressure. Neither increasing the temperature (room temperature to 150°C) nor doubling the vapor pressure produce significant increases in the coverage.

Polyfunctional silanes can form multiple bonds to the substrate; how many bonds they actually form is a question of interest. Previous work suggests that $-SiX_2$ and $-SiX_3$ silanes form on the average two bonds to the substrate (3, 5, 12). Thus, unreacted Si-X bonds should exist following silanization with a trifunctional silane. Since the Si-X absorption is inaccessible on TiO_2 substrates, the reacted pellets were exposed to water vapor (humid air) to effect the hydrolysis of the Si-X bond. The resulting Si-OH should appear at a sharp peak at 3740 cm^{-1}. Mono-, di-, and trifunctional silanes do *not* produce any observable silanol peak; only the tetrafunctional silanes yield the anticipated peak (Figure 5). Since each pellet is dried at 150°C under vacuum following exposure to moist air, silanols might condense with adjacent O-H groups during the drying step. Consequently, we examined the pellets modified with trifunctional silanes *before* the drying step (Figure 5C). Again no Si-O-H peaks are observed. *We conclude that unreacted Si-X bonds are not present after modification with $MeSiX_3$ or Me_2SiX_2, by our procedure*. By implication multiple bonds are formed between the silicon and either the surface and/or adjacent silanes.

An interesting question is whether these results are characteristic of vapor-phase silanizations or whether they extend to liquid-phase reaction conditions. Silanizations are most commonly performed in solutions. We are pursuing this question currently.

Acknowledgements

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Table I

Percentage Loss of Ti-O-H Intensity after Chemical Modification

Silane	(b.p.)[a]	Silane[a] Temperature	Silane[b] Vapor Pressure	Pellet[a] Temperature	Pellet Number	% Terminal[c] O-H Loss	% Bridging O-H Loss
Me_3SiCl	(58°)	0°	63	RT[d]	TI 24	100%	47%
		0°	63	RT	TI 26	100%	38%
		0°	63	150°	TI 27	100%	40%
		0°	63	150°	TI 30	100%	41%
		15°	143	150°	TI 66	100%	21%
Me_2SiCl_2	(71°)	0°	41	RT	TI 23	100%	7%
		0°	41	RT	TI 34	100%	2%
		0°	41	150°	TI 35	100%	44%
		15°	84	150°	TI 38	100%	61%
$MeSiCl_3$	(67°)	0°	54	RT	TI 44	100%	32%
		0°	54	150°	TI 45	100%	25%
		0°	54	150°	TI 68	100%	42%
		15°	101	150°	TI 46	100%	65%
$SiCl_4$	(52°)	0°	82	RT	TI 39	75%	2%
		0°	83	150°	TI 40	66%	1%
		15°	152	150°	TI 41	100%	100%
Me_3SiOMe	(58°)	0°	70	RT	TI 47	73%	0%
		0°	70	150°	TI 48	84%	0%
		15°	140	150°	TI 49	77%	0%
$Me_2Si(OMe)_2$	(82°)	0°	24	RT	TI 51	86%	31%
		0°	24	150°	TI 52	94%	3%
		15°	50	150°	TI 53	91%	34%
$MeSi(OMe)_3$	(103°)	0°	7	RT	TI 54	83%	0%
		0°	7	150°	TI 55	95%	23%
		0°	7	150°	TI 69	100%	32%
		15°	16	150°	TI 56	96%	27%
$Si(OMe)_4$	(122°)	0°	1	RT	TI 59	100%	40%
		0°	1	150°	TI 58	98%	0%
		15°	6	150°	TI 57	100%	27%
HMDS	(127°)	0°	1	RT	TI 31	86%	e
		0°	1	150°	TI 32	96%	e
		15°	6	150°	TI 33	98%	e
HCl		--	85	RT	TI 62	62%	69%
		--	152	150°	TI 61	100%	100%
MeOH	(65°)	0°	36	RT	TI 50	68%	0%
		0°	75	150°	TI 60	81%	f
		15°	50	150°	TI 63	90%	f
NH_3		--	5	RT	TI 64	59%	e
		--	5	150°	TI 65	57%	e

(a) All temperatures in °C; (b) vapor pressures in torr; (c) peak areas above the absorption envelope due to hydrogen-bonding; (d) RT = room temperature, typically 20–25°C; (e) peak area not available due to strong overlap with a byproduct peak (NH_3); (f) peak area actually increased slightly. Reaction times were one hour.

Figure Captions

Figure 1

A. Pellet # TI 67; after drying (150° for 2 hours under vacuum).

B. Pellet # TI 67; after exposure to D_2O vapor (6 torr) for 1 hour at room temperature, followed by drying.

Figure 2

A. Pellet # TI 34; after drying.

B. Pellet # TI 34; after exposure to Me_2SiCl_2 vapor (41 torr) for 1 hour at room temperature.

C. Pellet # TI 34; after heating to 150° for 2 hours under vacuum.

Figure 3

A. Pellet # TI 54; after drying.

B. Pellet # TI 54; after exposure to $MeSi(OMe)_3$ vapor (7 torr) for 1 hour at room temperature.

C. Difference spectrum B-A.

Figure 4

A. Pellet # TI 31; after drying.

B. Pellet # TI 31; after exposure to HMDS vapor (1 torr) for 1 hour at room temperature.

C. Pellet # TI 33; after drying, followed by exposure to HMDS vapor (6 torr) for 1 hour at 150°C.

Figure 5

A. Pellet # TI 40; after drying, followed by exposure to $SiCl_4$ vapor (83 torr) for 1 hour at 150°C, followed by heating to 150°C for 2 hours under vacuum.

B. Pellet # TI 40; after exposure to moist air for 3 hours at room temperature, followed by drying (150° for 2 hours under vacuum).

C. Pellet # TI 68; after drying, followed by exposure to $MeSiCl_3$ vapor (54 torr) for 1 hour at 150°C, followed by exposure to moist air for 2 1/2 days at room temperature, followed by evacuation at room temperature for 2 hours.

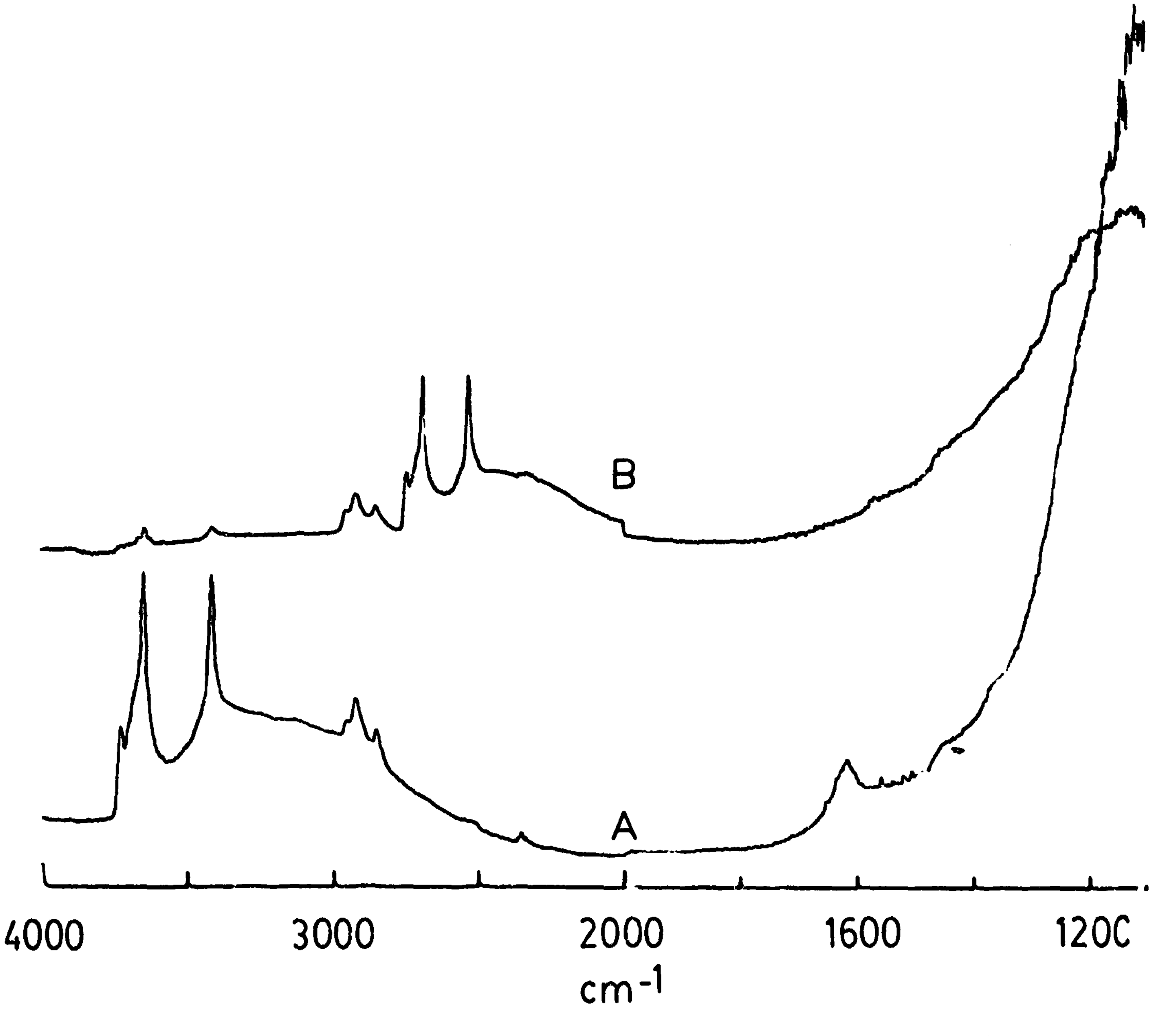

Figure 1

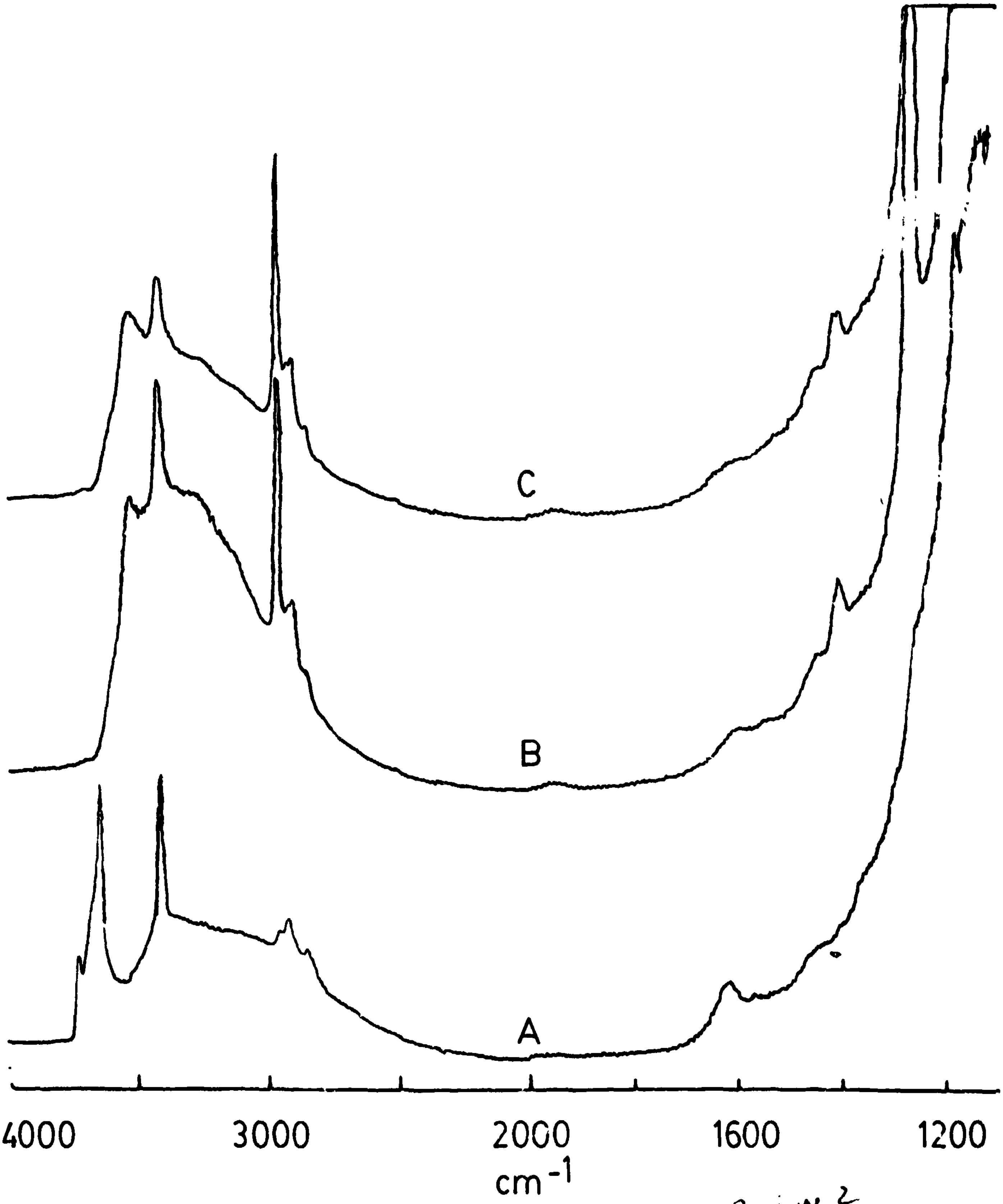

Figure 2

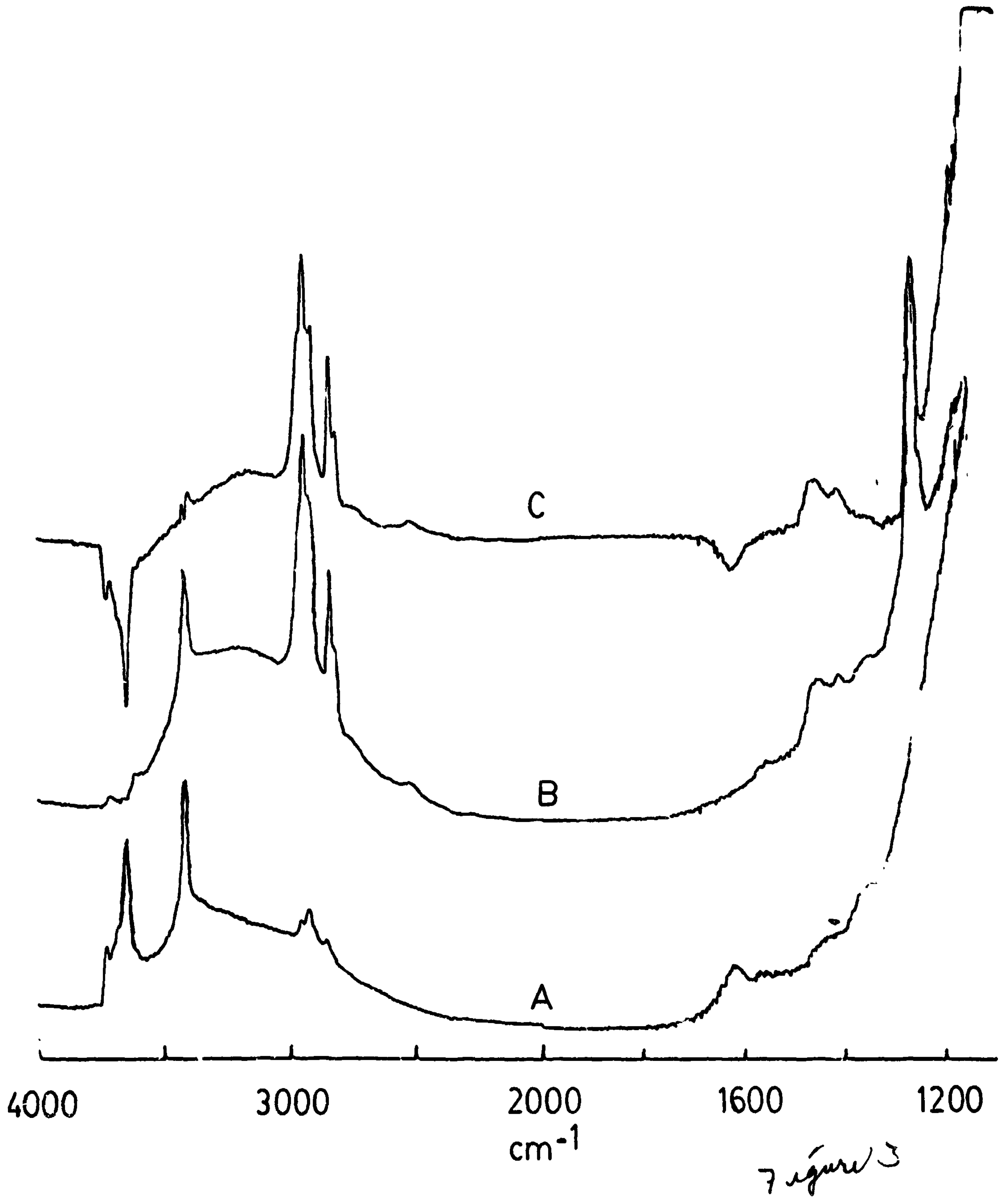

Figure 3

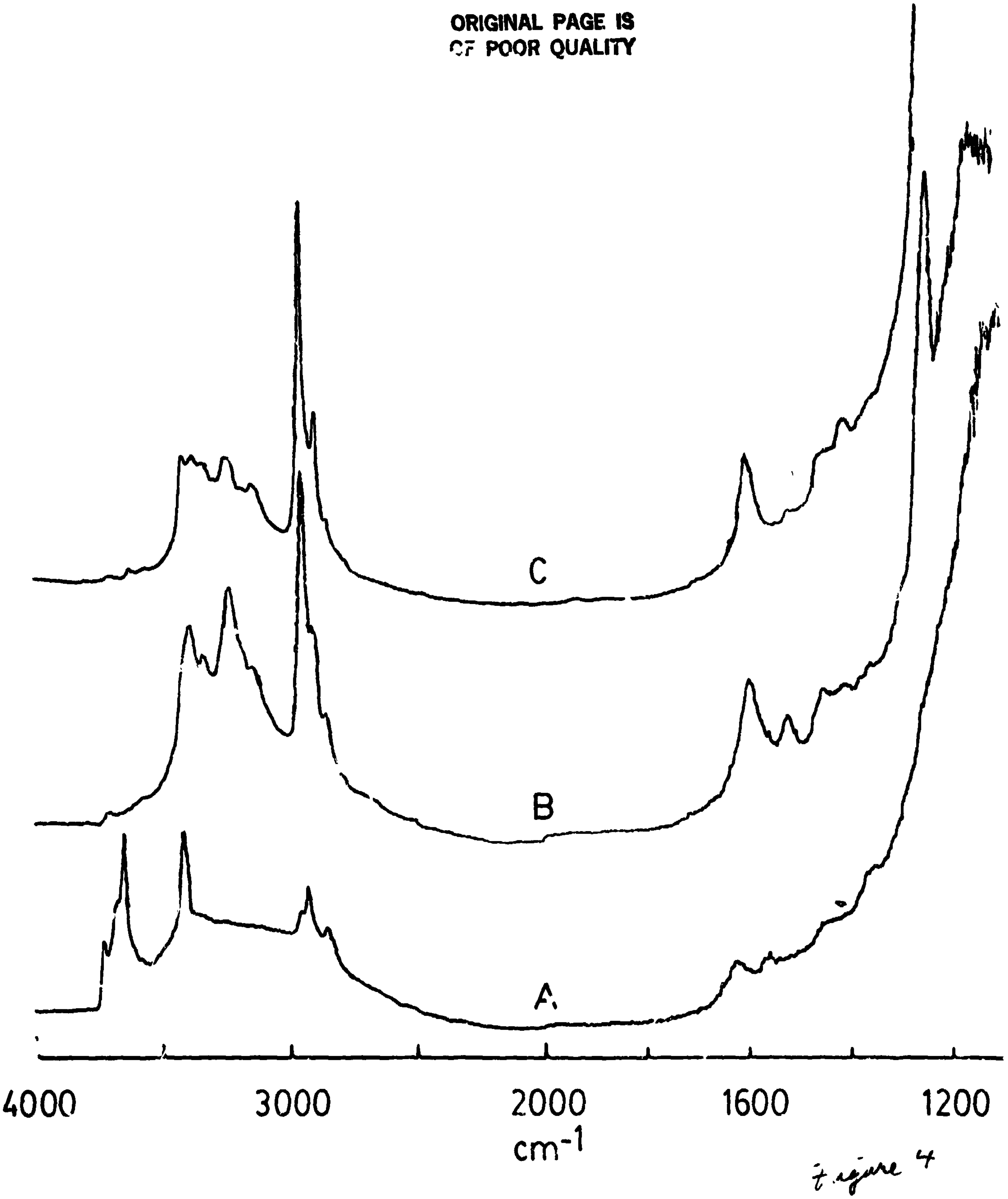

Figure 4

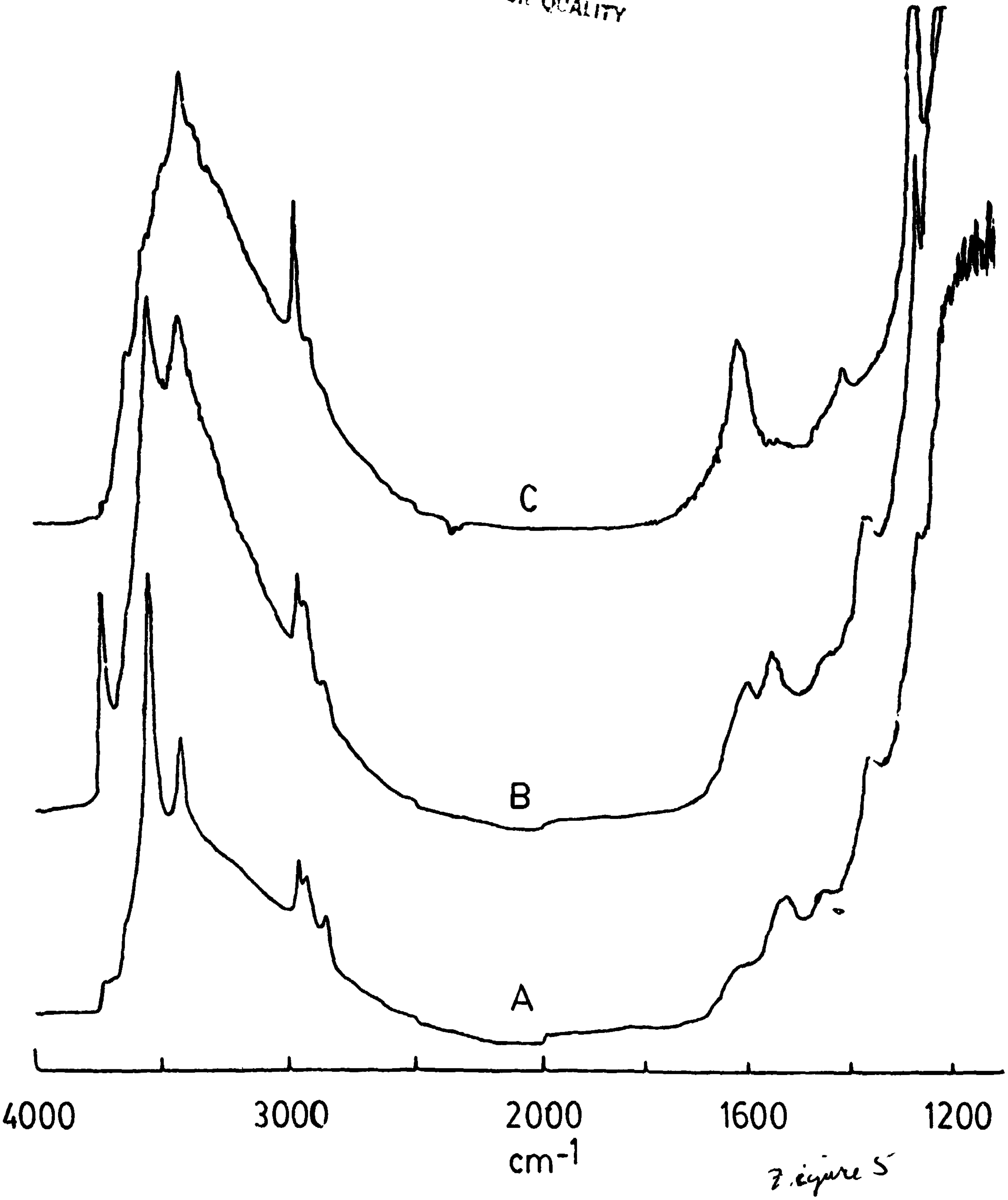

Figure 5