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AD-A132 588

SECURITY CLASSIFICATION OF THIS PAGE (*When Data Entered*)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 3	2. GOVT ACCESSION NO.
	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (*and Subtitle*) Molecular Structure of an Aminosilane Coupling Agent as Influenced by Carbon Dioxide in Air, pH, and Drying Conditions	5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Somsak Naviroj, Jack L. Koenig, and Hatsuo Ishida	8. CONTRACT OR GRANT NUMBER(s) N00014-80-C-0533
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Macromolecular Science Case Western Reserve University Cleveland, Ohio 44106	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 356-739
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 N. Quincy Street Arlington, Virginia 22217	12. REPORT DATE November 9, 1981
	13. NUMBER OF PAGES 22
14. MONITORING AGENCY NAME & ADDRESS(*if different from Controlling Office*)	15. SECURITY CLASS. (*of this report*) Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (*of this Report*)

Approved for public release; distribution unlimited

17. DISTRIBUTION ST... ENT (*of ... abstract entered in Block 20, if different from Report*)

18. SUPPLEMENTARY ... TES

To be submitted to The J. Adhesion

DTIC
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19. KEY WORDS (*Continue on reverse side if necessary and identify by block number*)

Coupling agent	Aminosilane
FT-IR	Amine bicarbonate salt
D_2O exchange	

20. ABSTRACT (*Continue on reverse side if necessary and identify by block number*)

The molecular structures of the hydrolyzates of γ-aminopropyltriethoxysilane (γ-APS) were studied by Fourier transform infrared spectroscopy (FT-IR). The molecular structure of γ-APS is a function of the pH of the solution and the drying conditions. In the partially cured film, cast from a 20% by weight γ-APS aqueous solution at pH = 2. the amine group exists as a protonated amine; and at pH = 12 the amine group exists as a free NH_2. The amine group exhibits—

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different structures subject to drying conditions when prepared at natural pH. The sample dried in nitrogen exhibited hydrogen bonding between the SiOH and the NH_2 group. Upon heating, the silanol groups condense and the amine groups no longer hydrogen bond. The increase in the availability of free amine groups was indicated by larger amounts of exchange of NH_2 to ND_2 when the sample was exposed to D_2O vapor. When the hydrolyzed γ-APS at natural pH was dried in CO_2 or in air, a bicarbonate structure was formed causing the appearance of bands at 1630, 1575, 1488, and 1332 cm^{-1}. These bands previously associated with the intramolecular zwitterions of $SiO^- \cdots NH_3^+$. E-glass fibers were treated with 2% γ-APS and dried under different conditions, which show the various structures of γ-APS as described above. Differences in γ-APS structures may affect the curing reactions of composite materials.

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GAMMA

MOLECULAR STRUCTURE OF AN AMINOSILANE COUPLING AGENT AS INFLUENCED BY CARBON DIOXIDE IN AIR, pH, AND DRYING CONDITIONS

by

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ABSTRACT

The molecular structures of the hydrolyzates of γ-aminopropyltriethoxysilane (γ-APS) were studied by Fourier Transform Infrared Spectroscopy (FT-IR). The molecular structure of γ-APS is a function of the pH of the solution and the drying conditions. In the partially cured film, cast from a 20% by weight γ-APS aqueous solution at pH = 2, the amine group exists as a protonated amine, and at pH = 12 the amine group exists as a free NH_2. The amine group exhibits different structures subject to drying conditions when prepared at natural pH. The sample dried in nitrogen exhibited hydrogen bonding between the SiOH and the NH_2 group. Upon heating, the silanol groups condense and the amine groups no longer hydrogen bond. The increase in the avsilability of free amine groups was indicated by larger amounts of exchange of NH_2 to ND_2 when the sample was exposed to D_2O vapor. When the hydrolyzed γ-APS at natural pH was dried in CO_2 or in air, a bicarbonate structure was formed causing the appearance of bands at 1630, 1575, 1488, and 1332 cm^{-1}. These bands were previously associated with the intramolecular zwitterions of $SiO^- \cdots NH_3^+$. E-glass fibers were treated with 2% γ-APS and dried under different conditions, which show the various structures of γ-APS as descrobed abpve. Differences in γ-APS structures may affect the curing reactions of composite materials.

INTRODUCTION

The treatment of glass fibers with silane coupling agents has proven effective in increasing the retention of strength of composite materials especially in humid environments. Different mechanisms of reinforcement have been proposed [1-4]. However, the most widely accepted theory suggests that the silane coupling agent forms a covalent bond with the glass surface as well as the matrix resin. It is therefore important to elucidate the structure of the coupling agent on the surface of glass fibers. Differences in the molecular structure of the adsorbed coupling agent may very well affect the reactivity of the functional group and thus result in a variability of mechanical performance of composite materials. γ-Aminopropyltriethoxysilane (γ-APS) is a very useful and widely used coupling agent for fiber-reinforced plastics. To date, the molecular structure of this silane coupling agent is not known. It exhibits complicated structures which are very sensitive to the preparation conditions. γ-APS hydrolyzes in water rapidly and shows a clear solution over a wide range of concentrations. In order to explain the unusual stability of this coupling agent, Pluddemann [5] proposed that γ-APS exists as a five membered ring with the nitrogen atom interacting with the silicon atom resulting in pentacoordination on the silicon. A six membered ring was also proposed in which the nitrogen atom forms a zwitterion with one of the silanols [5]. These structures, however, have not been verified.

The structure of the adsorbed silane on the glass surface is of interest in order to understand the reinforcement mechanisms. Studies of silane structures adsorbed on substrates have been carried out extensively. Bascom [6] showed that the silane on glass and metal surfaces was a polysiloxane coating, part of which could easily be washed away by organic solvents or water. Contact angle measurements on the remaining, strongly held material indicated an open polymeric structure since it was easily penetrated by the wetting liquid.

Boerio et al [7] studied the structure of γ-APS films on iron mirrors by using reflection-absorption infrared spectroscopy. They observed the amine deformation band shifted from 1610 cm^{-1} to 1575 cm^{-1}. They assigned this band to the amine group with strong hydrogen bonding or to the amino groups that form the $Si \leftarrow \ddot{N}H_2$ pentacoordinated structure. Further investigation [8] was made at the natural pH of the solution. The bands near 1550 and 1480 cm^{-1} were assigned to the NH_2 deformation modes of the amine groups that were strongly hydrogen bonded with the silanol groups to form cyclic structures. The infrared bands near 1580 and 1488 cm^{-1} obtained from film formed at pH above the natural pH were assigned to deformation modes of NH_3^+ groups. However, the controversy on the band assignments remains [9,10]. They observed that the infrared spectrum of laurylamine has a remarkable similarity to the spectrum of γ-APS. The possibility was suggested that carbon dioxide is present as a bicarbonate which gives rise to the strong absorption bands at 1645, 1565, 1485, and 1460 cm^{-1}.

Sung et al [11] used Fourier transform IR transmission and reflection spectroscopy, and ESCA to study the structure of silane coupling agents adsorbed on single crystals of aluminum oxide. They observed that the N_{1S} peak clearly split into two components indicating two different types of nitrogen species. The peak at 399 ev was assigned to the normal N_{1S} and another at 401.3 ev was assigned to a protonated nitrogen since a higher energy would be required to ionize positively charged nitrogen. This observation suggests that there is more than one structure for γ-APS on the substrates.

Ishida et al [12] suggested the existence of the intramolecular zwitterion, $SiO^{-} \cdots \overset{+}{N}H_3$, is unlikely either in an aqueous solution or in a partially cured solid. The argument was based on the band assignments of the SiO^{-} and SiOH vibrational modes. Also, no evidence supports the existence of a pentacoodinated silicon stom where the nitrogen donates the electrons to the silicon atom. Ishida et al [13] proposed the possibility of multiple hydrogen bonded structures for the intramolecularly interacting amines and silanol groups by using isotope exchange experiments and conformational energy calculations. They also showed that a significant amount of free amine exists indicating a complexity of the silane on the surface.

Moses et al [14] used ESCA to study the aminosilane on electrode surfaces. They recognized a multiplicity of structures depending on the environment.

Although much work has been done on the adsorption of γ-APS onto a substrate, none has shown a conclusive molecular structure of γ-APS on the substrate. It is our intention to investigate the molecular structure of γ-APS and gain some insight into the mechanism behind the effectiveness of the coupling agents as adhesion promoters for fiber reinforced plastics. The structure of the silane coupling agent can very well affect the degree of curing of the matrix. It may also affect the ability of the matrix to diffuse into the network of the coupling agent or vice versa. Fourier transform infrared spectroscopy is a very useful technique for the study of molecular structures [15-18].

EXPERIMENTAL

γ-Aminopropyltriethoxysilane (γ-APS) was purchased from Petrarch Systems Inc. and vacuum distilled before use. The aqueous solution of γ-APS was prepared as a 20% by weight in deionized distilled water. After 30 - 45 minutes, time for the γ-APS to hydrolyze, the solution was used at its natural pH or adjusted to the appropriate pH values by using HCl or NaOH solutions. The aqueous solution of γ-APS was cast onto a AgBr plate and dried in various environments, namely, ambient air, carbon dioxide, and nitrogen atmospheres.

The D_2O exchanged sample was prepared in nitrogen atmosphere as described above, then the sample was placed in an enclosed container and in contact with the D_2O vapor for 15 min. at room temperature. The infrared spectrum was taken in the spectrometer constantly purged with dry nitrogen gas.

E-glass fibers were kindly supplied by Crane & Co. Inc. (Craneglas, grade 50-01). The average fiber diameter is 3.8 μm and the calculated specific surface area is 0.5 m^2/gm. The E-glass fiber sheet was heat cleaned at 500°C for 24 hrs. in air. The adsorption of silane on the E-glass surface was done by immersing the heat-cleaned glass into the hydrolyzed aqueous solution of γ-APs as 2% by weight. After 10 min. of immersion, the solution was filtered and the fibers were dried under different conditions. The dried sample was ground with a very high purity KBr powder and pressed into a pellet for the spectrum. The difference spectrum was obtained by digital subtraction of the spectrum of untreated E-glass fibers from the silane treated sample. A Fourier transform infrared spectrometer (Digilab FTS-14) was used for the study.

RESULTS AND DISCUSSION

The spectrum of γ-APS prepared from 20% aqueous solution at pH 2 is shown in Figure 1-A. The spectrum shows broad bands between 3200 and 2800 cm^{-1}. In case of aliphatic primary amine salts, the strong and broad absorption bands near 3000 cm^{-1} are due to the CH_2 and NH_3^+ asymmetric and symmetric stretching [19]. The bands between 2800 and 2400 cm^{-1} are assigned to the combinations between various NH^+_3 and other deformation bands [20]. The band near 2030 cm^{-1} is due to the combination band between torsional oscillation around 487 cm^{-1} and antisymmetrical bending vibration of the NH^+_3 group around 1580 cm^{-1}. This band shifts in frequency from 2030 cm^{-1} for the spectrum at pH 2 to 2090 cm^{-1} for the spectrum at pH = 10. Waldron [20] observed the shifting occurs from the variable strength of the hydrogen bonds. The NH^+_3 stretching bands should shift to the lower frequency when a strong hydrogen bond is present. Unfortunately it cannot be observed in the spectrum due to band overlap in the 3000 cm^{-1} region. The upward shift of the 2030 cm^{-1} band is more prominent.

The peaks at 1610 and 1505 cm^{-1} are due to the asymmetric and symmetric deformations of the NH^+_3 [21]. The strong bands at 1130 and 1035 cm^{-1} are characteristic of the siloxane (Si-O-Si) polymer. The SiOH band appears at 905 cm^{-1}. The intensity of this band decreases upon heating and disappears completely after one hr. at 120°C. Furthermore, the splitting of the siloxane bands becomes more prominent.

Figure 1-B is the spectrum of γ-APS prepared from aqueous solution at natural pH (10.8) with no added HCl nor NaOH. At this natural pH, significant changes have taken place. A band at 930 cm^{-1} appeared. This band is due to the SiOH and is shifted from 905 cm^{-1} in the previous samples. Again, this band decreased in intensity upon heating the sample. The band at 1332 cm^{-1} became more intense. The origin of the bands at 1630, 1575, 1488, and 1332 cm^{-1} has been in strong dispute. Chiang _et al_ [22] assigned the band at 1575 cm^{-1} to the NH_2 deformation mode of acceptor amine groups involved in strong hydrogen bonding. Boerio _et al_ [8] studied the structure of γ-APS film on iron mirror and assigned the bands near 1550 and 1480 cm^{-1} to the NH_2 deformation modes in the amine groups that were very strongly

hydrogen bonded with silanol groups to form cyclic structure. Further investigations were made to determine the origin of these bands. Boerio *et al* [9,10] obtained an infrared spectrum of laurylamine contaminated with CO_2 and found that it showed characteristic bands similar to those obtained from γ-APS dried in air. They stated that laurylamine formed an aminebicarbonate and that γ-APS may contain carbon dioxide as the bicarbonate or possibly the amino groups form a cyclic structure due to hydrogen bonding.

In order to obtain more conclusive information on the origin of these bands, we prepared a 20% γ-APS aqueous solution and then dried it on the AgBr plate under a nitrogen environment. The spectrum is shown in Figure 2. The spectrum shows a distinct peak at 1601 cm^{-1} which can be assigned to the NH_2 deformation mode. The frequency of this mode is influenced by hydrogen bonding. The bands at 1630, 1575, 1488, and 1332 cm^{-1} have diminished in the nitrogen-dried sample. The bands at 1575 and 1488 cm^{-1} can be assigned to the $\overset{+}{N}H_3$ asymmetric and symmetric bending modes respectively while the bands at 1630 and 1332 cm^{-1} can be assigned to CO_2 and OCO_2 vibrations of the bicarbonate group [23] respectively. The disappearance of these four bands can be explained by the absence of CO_2 in the environment to form the protonated amine and bicarbonate ion when γ-APS is dried in a nitrogen atmosphere. To verify that CO_2 is in fact the origin of the appearance of these bands, we conducted a similar experiment under a CO_2 environment. The spectrum obtained is shown in Figure 3. The spectrum shows the strong bands at 1630, 1575, 1488, and 1332 cm^{-1}. This data indicate that these intensified bands are influenced by the presence of CO_2 during the drying process.

Figure 1-C is the spectrum of γ-APS prepared from aqueous solution at pH = 12.0. A medium intensity peak at 925 cm^{-1} arises from SiOH groups.

The intensity of this band decreased upon heating while the peaks at 1035 and 1130 cm^{-1} became more prominent due to the further formation of the Si-O-Si group. The main feature of the spectrum is the single band at 1591 cm^{-1} which is assigned to the NH_2 deformation mode found in the basic environment. The spectrum shows a remarkable similarity to the one obtained from the nitrogen environment (Figure 2). However, the position of the NH_2 peak is slightly shifted. The small peak at 2030 cm^{-1} that was present in samples at pH = 2 has disappeared. This result also suggests that NH^+_3 is not present at pH = 12 [20]. The frequencies of the NH_2 deformation mode of the nitrogen dried sample at natural pH and the sample obtained from the solution at pH = 12 are about 10 cm^{-1} apart being located at 1601 and 1591 cm^{-1}, respectively

To investigate the shifting of the band from 1601 to 1591 cm^{-1} and the existence of NH_2 groups, we performed heating and deuterium exchange experiments. Figure 4-A shows the spectrum of a nitrogen-dried sample before deuterium exchange whereas Figure 4-B shows the spectrum of the sample after exposure to the D_2O vapor for 15 min. A broad band with weak intensity appearing around 2550 - 2380 cm^{-1} is due to the stretching modes of the ND_2 groups. The band at 1218 cm^{-1} becomes more prominent. This band is assigned to the deformation mode of the ND_2 groups. The sample was then removed from the spectrometer and exposed to ambient environment for 15 min. before further heat treatment. It was observed that most of the ND_2 exchanged with H_2O again within 5 min. as the band at 2550 - 2380 cm^{-1} disappeared. The sample was then heated at 120°C for 30 min. (Figure 5-A). The SiOH band at 934 cm^{-1} decreased in intensity upon heating. The splitting of the bands at 1035 and 1135 cm^{-1} became prominent as the Si-O-Si groups formed. The most important observation is the frequency shift of the NH_2 deformation mode from 1601 to 1591 cm^{-1} upon heating. This phenomenon can be explained as follows. Before heating the samples, the amine groups are hydrogen bonded with the silanol groups. Upon heating the hydrogen bond is broken; the silanol groups condense and form Si-O-Si linkages as indicated by the splitting of the bands at 1035 and 1135 cm^{-1}. The amine groups become free. The modes involving angle bending usually decrease in frequency upon disruption of the hydrogen bond while the stretching modes show the opposite trend [24]. Therefore the shifting of the band from 1601 to 1591 cm^{-1} results from the loss of the hydrogen bonds.

When the heat-treated sample was exposed to D_2O vapor for 15 min., a noticeably large band at 2550 - 2380 cm^{-1} due to ND_2 stretching modes appeared (Figure 5-B). The band at 1218 cm^{-1} due to the ND_2 bending became more intense. The increase in intensity of this band compared with the one in Figure 4-B indicates the relative ease of exchange from NH_2 to ND_2 after heat treatment. We can tentatively assign the band at 1601 cm^{-1} to the hydrogen bonded NH_2 and the band at 1591 cm^{-1} to the free NH_2 deformation mode. The NH_2 group may form hydrogen bonding with SiOH groups of the same molecule or with another molecule.

The strength of composite materials is believed to be enhanced by the presence of covalent bonds between the glass fiber and the coupling agent and the coupling agent and the matrix. Hence, elucidation of the structure of the silane on the surface of glass fibers is indispensable in studying the reinforcement mechanism. It has been our experience that bulk reactions without glass fibers often differ from surface reactions due to topological, steric, surface catalytic and other effects. Thus we carried out the same amino silane experiments with glass. Heat cleaned E-glass fibers were treated with 2% by weight γ-APS aqueous solution. Figure 6-A shows the spectrum of E-glass fibers treated with 2% γ-APS and dried in nitrogen environment. The spectrum was digitally subtracted by the untreated E-glass (Figure 6-B), indicating that the deposited γ-APS (Figure 6-C) has the same structure as the nitrogen-dried sample shown in Figure 2. From the location of the NH_2 deformation peak at 1601 cm^{-1}, it can be concluded that the adsorbed γ-APS is hydrogen bonded.

Another sample was prepared in the same manner except the drying was done in carbon dioxide environment. Figure 7 shows the result of subtraction of the untreated (Figure 7-B) from the silane-treated E-glass fibers (Figure 7-A). The deposited γ-APS dried in CO_2 has a completely different spectrum and structure from the sample prepared under nitrogen (Figure 6-C). It can be concluded that the adsorbed γ-APS forms a bicarbonate salt on the glass surface when dried in carbon dioxide as well as in air.

CONCLUSIONS

The structure of an aminosilane coupling agent (γ-APS) in various environments has been studied by Fourier transform infrared spectroscopy. Preparation conditions strongly influence the structure of partially cured γ-APS film. The sample obtained from the solution at pH 2, which was adjusted by adding HCl solution, indicated that the amine group forms an amine salt, $-\overset{+}{N}H_3Cl^-$, whereas at pH 12 the amine group is essentially free of hydrogen bonding. The frequency of the free amine deformation mode is lower than that of hydrogen bonded species. At the natural pH, the structure of γ-APS depends on the drying atmosphere. The CO_2 deficient atmosphere such as in nitrogen gas, the amine group forms a hydrogen bonded structure. Upon heating, the residual silanol group form the siloxane linkages, and the amine group can no longer hydrogen bond with the residual silanol. The increased population of free amine by the heat treatment was observed as a more intense infrared band of the deuterium exchanged amine. On the other hand, the sample that was prepared in a carbon dioxide atmosphere indicated that the amine group formed an amine bicarbonate salt, $-\overset{+}{N}H_3(HCO_3)^-$. Furthermore, the air-dried sample also showed an amine bicarbonate structure, though a slight reduction of the concentration of the salt was noted as compared with the CO_2-dried sample.

ACKNOWLEDGMENT

The authors wish to thank the Office of Naval Research for their financial support.

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Figure Captions

Figure 1 γ-APS prepared from 20% aqueous solution at pH 2, 10.8 and 12.

Figure 2 γ-APS dried on AgBr plate in nitrogen. Intensified bands at 1630, 1575, 1488, and 1332 cm^{-1} disappeared.

Figure 3 γ-APS dried on AgBr plate in carbon dioxide.

Figure 4 γ-APS dried in nitrogen A) before and B) after D_2O exposure. The band at 1218 cm^{-1} indicated the exchange of NH_2 to ND_2.

Figure 5 A) γ-APS dried in nitrogen and heated at 120°C for 30 minutes. The peak at 1601 shifted to 1591 cm^{-1}.
B) After D_2O exposure the intensity of 1218 cm^{-1} band increased due to larger amount of exchange of NH_2 to ND_2.

Figure 6 A) 2% γ-APS on E-glass fiber dried in nitrogen.
B) Pure E-glass fiber.
C) Difference spectrum A - B showed adsorbed silane.

Figure 7 A) 2% γ-APS on E-glass fiber dried in carbon dioxide.
B) Pure E-glass fiber.
C) Difference spectrum A - B.

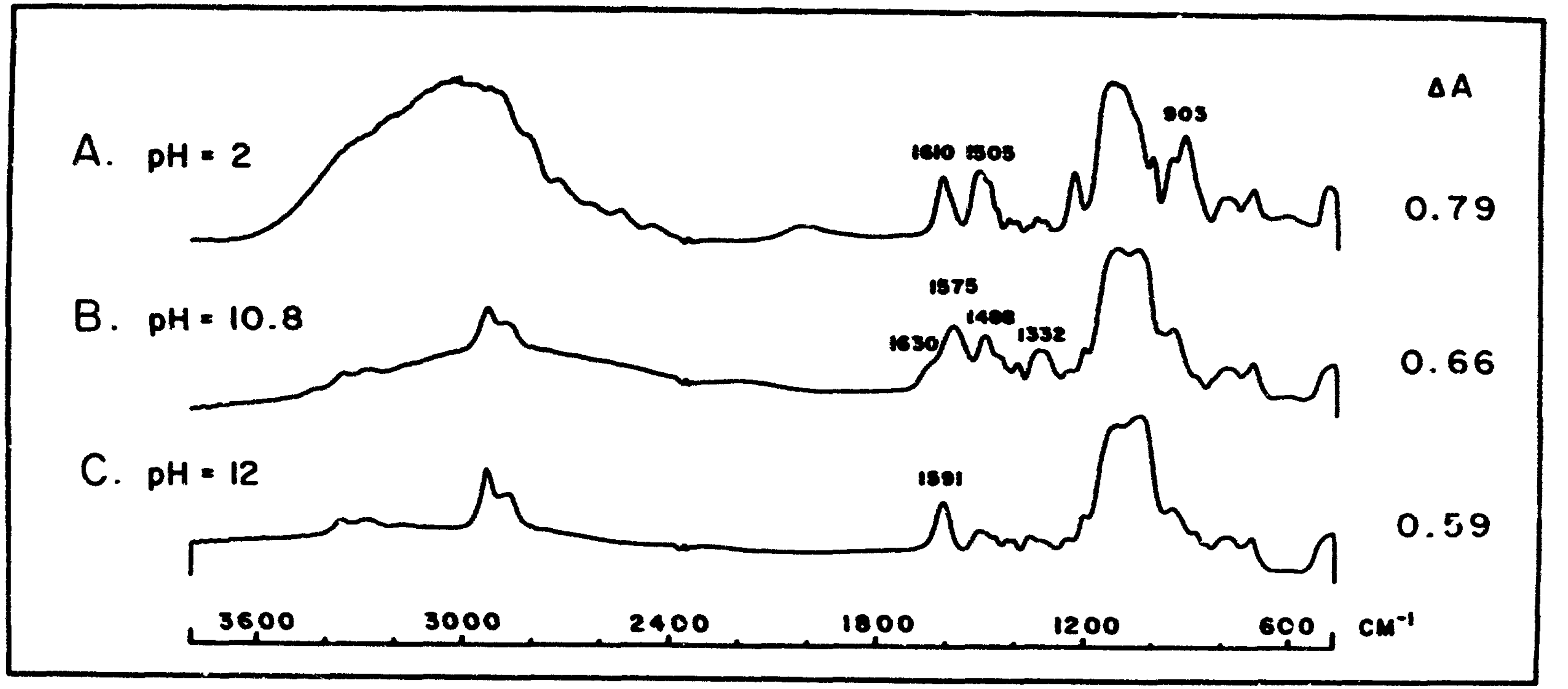
A. pH = 2
B. pH = 10.8
C. pH = 12
ΔA
0.79
0.66
0.59
1610
1505
903
1575
1630
1488
1332
1591
3600
3000
2400
1800
1200
600
CM⁻¹

Fig. 1

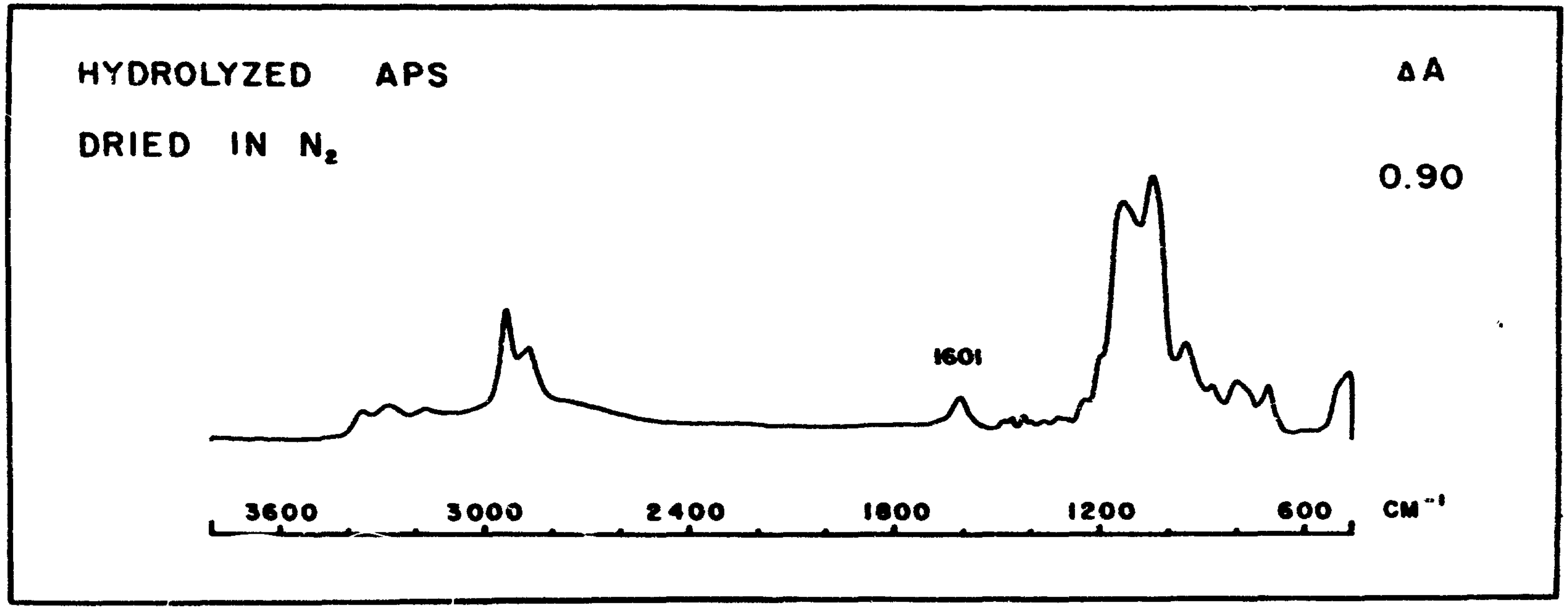
HYDROLYZED APS
DRIED IN N_2
ΔA
0.90
1601
3600
3000
2400
1800
1200
600
CM^{-1}

Fig. 2

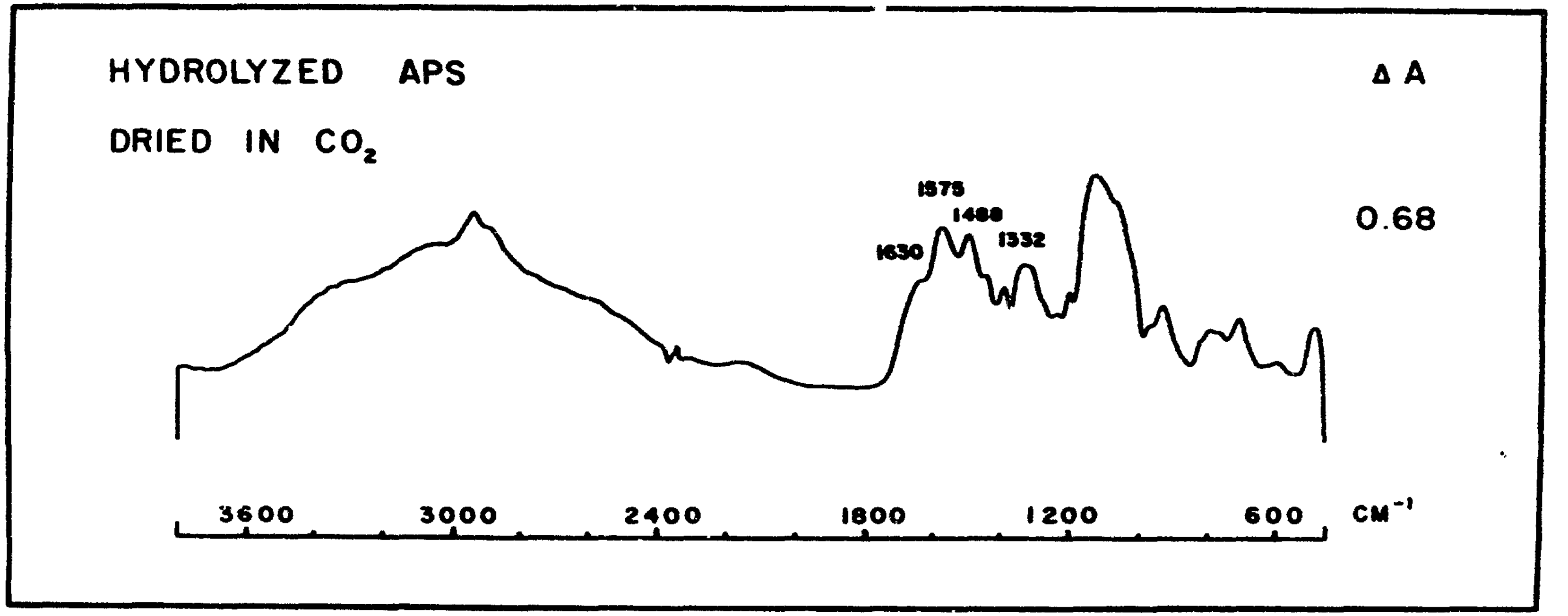
HYDROLYZED APS
DRIED IN CO₂
ΔA
0.68
1630
1575
1488
1332
3600
3000
2400
1800
1200
600
CM⁻¹

Fig. 3

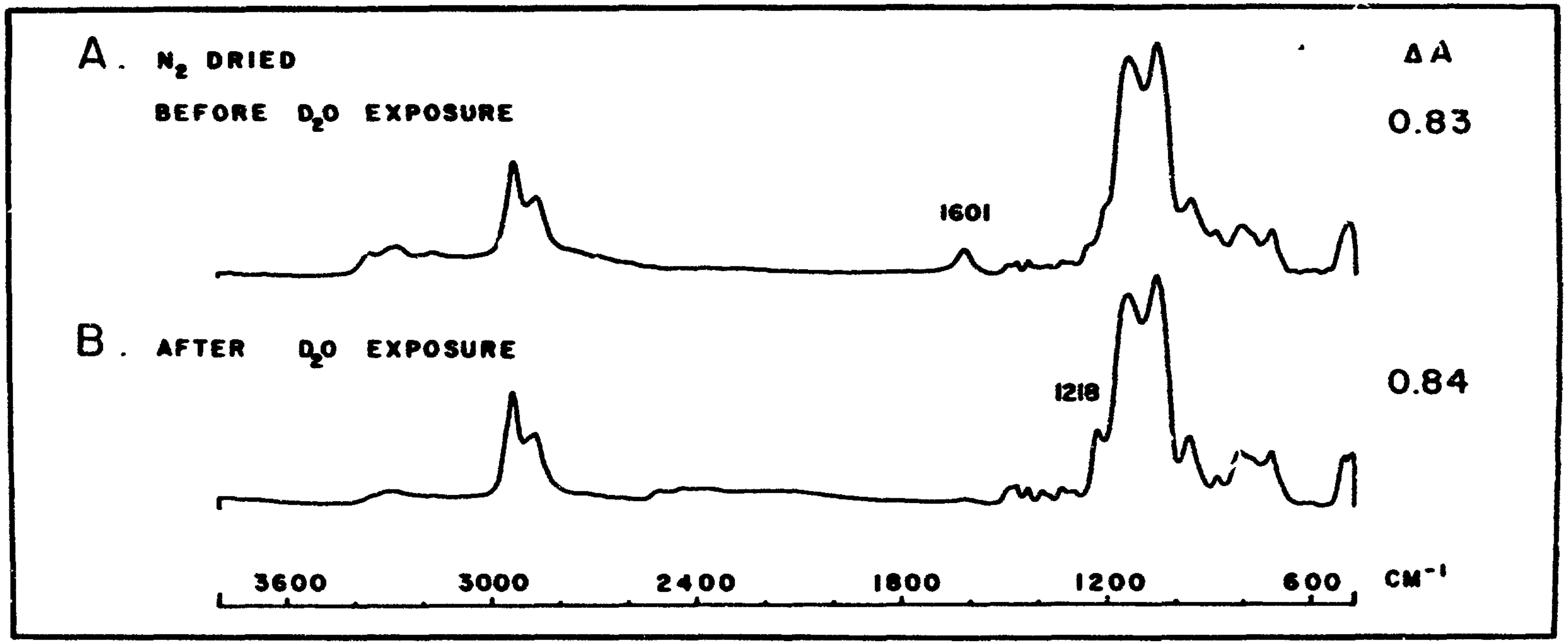
A. N_2 DRIED
BEFORE D_2O EXPOSURE
B. AFTER D_2O EXPOSURE
ΔA
0.83
0.84
1601
1218
3600
3000
2400
1800
1200
600
CM^{-1}

Fig. 4

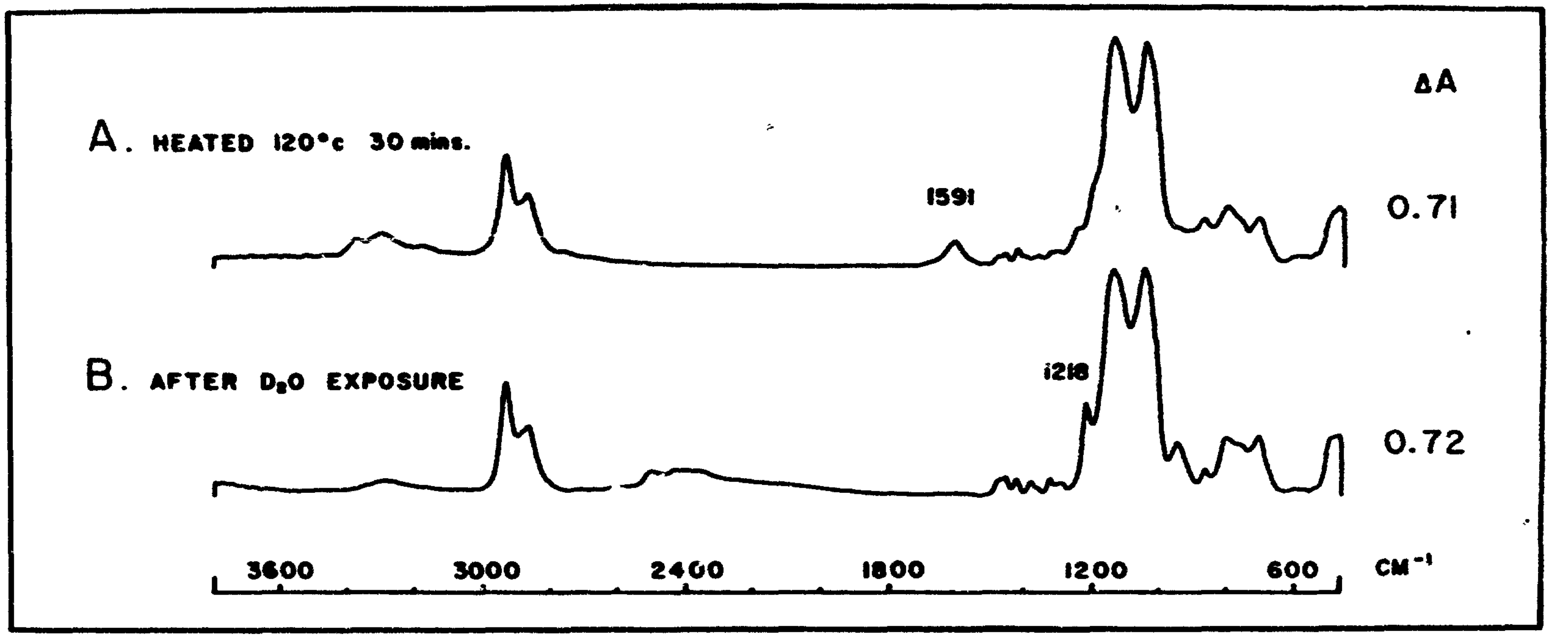
A. HEATED 120°c 30 mins.
B. AFTER D₂O EXPOSURE
ΔA
0.71
0.72
1591
1218
3600
3000
2400
1800
1200
600
CM⁻¹

Fig. 5

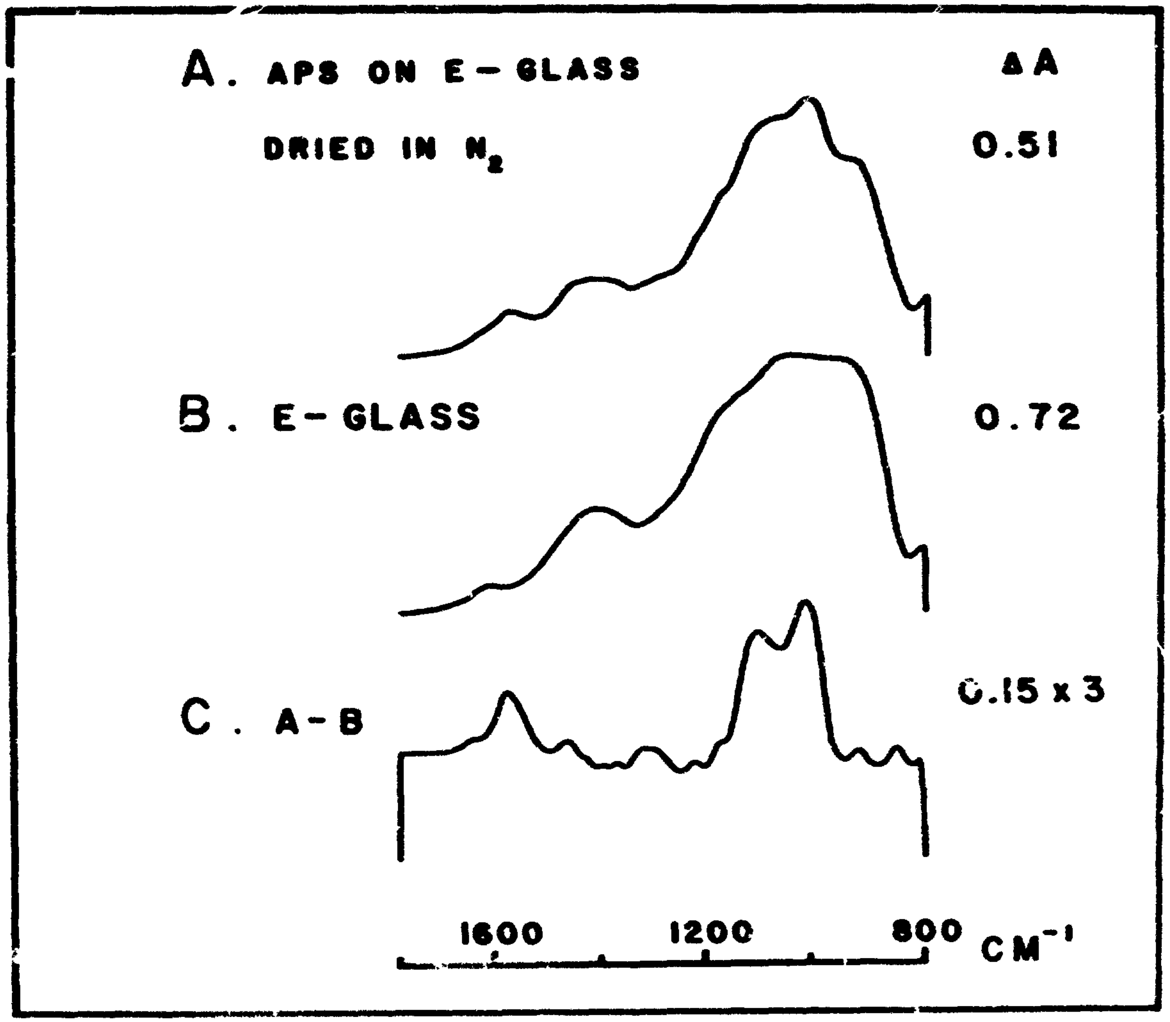
A. APS ON E-GLASS
DRIED IN N_2
ΔA
0.51
B. E-GLASS
0.72
C. A-B
0.15 x 3
1600
1200
800
CM⁻¹

Fig. 6

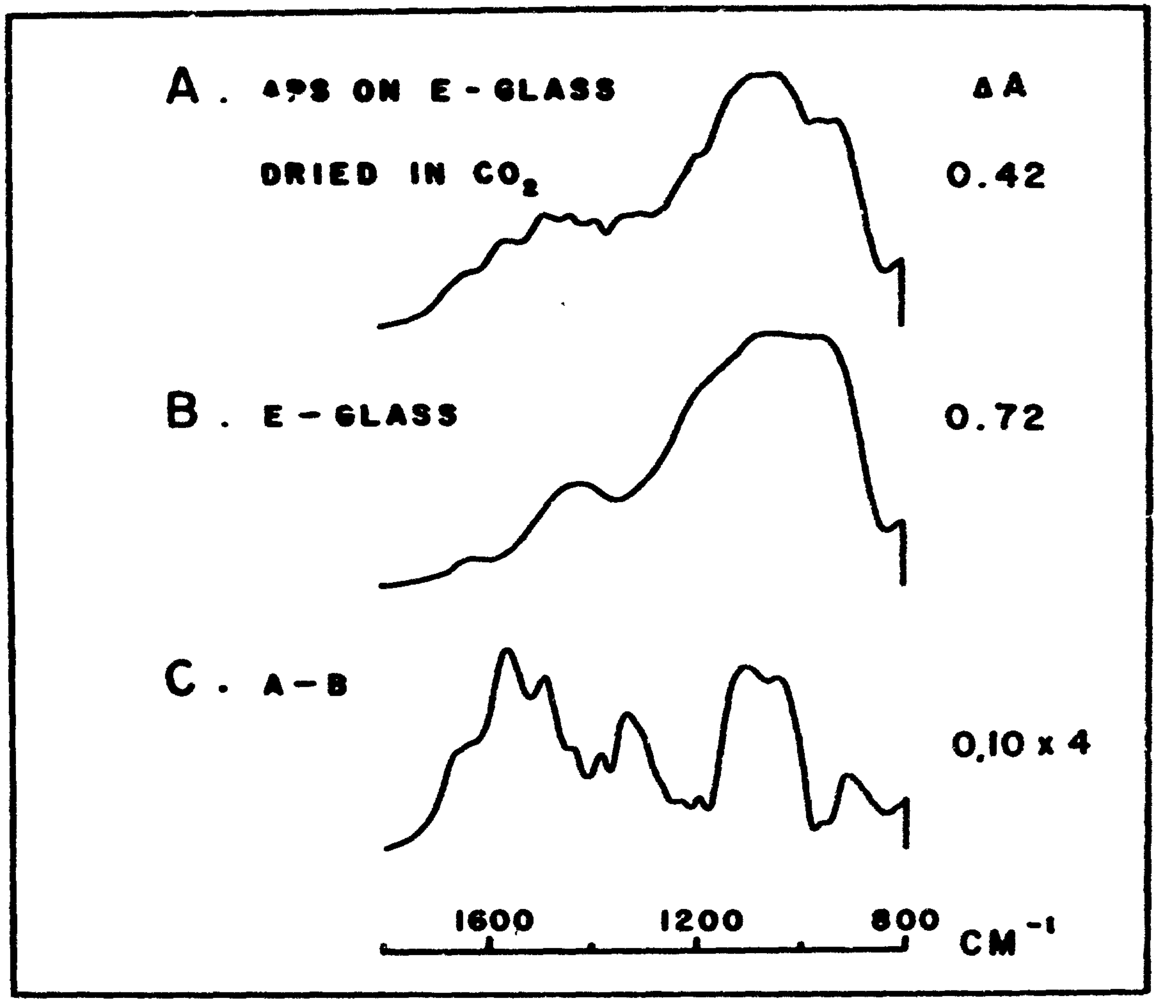
A. APS ON E-GLASS
DRIED IN CO$_2$
B. E-GLASS
C. A-B
ΔA
0.42
0.72
0,10 x 4
1600
1200
800
CM^{-1}

Fig. 7