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SPECTRAL STUDIES OF IONS IN PERFLUOROCARBONSULFONATE (NAFION) I--ETC(U)

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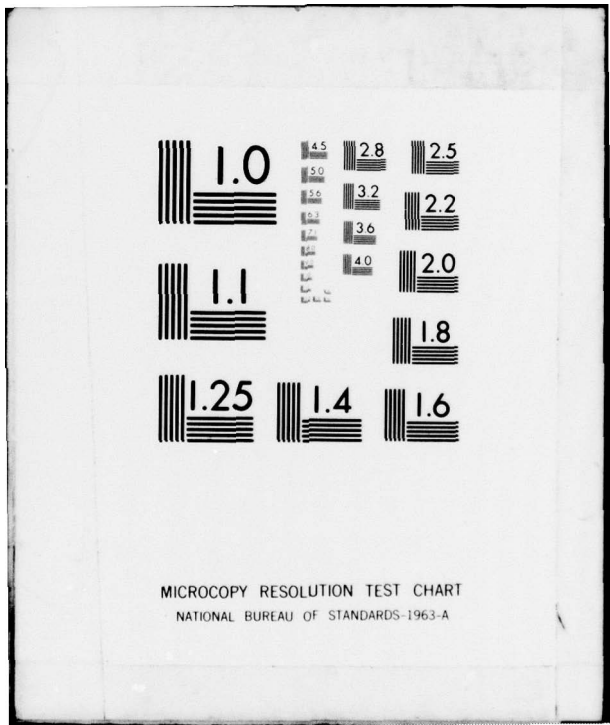
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Spectral Studies of Ions in Perfluorocarbonsulfonate (Nafion) Ionomers

by

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## Spectral Studies of Ions in Perfluorocarbonsulfonate (Nafion) Ionomers

### Introduction

Ionic copolymers (ionomers) are versatile materials because the presence of ions in organic polymers influences their physical (1-3) and chemical ( 4 ) properties greatly. Of particular interest in their study is the nature of cation-polyanion interactions, how they are affected by hydration, degree of exchange, and ion clustering, and the effects that such interactions have on their viscoelastic, ion diffusion, catalytic, and related properties. Ionomers formed from hydrocarbon-based polymers have been investigated extensively. Their properties, which fall in rather narrow ranges, have been reviewed by Eisenberg ( 5 ) and others (6-8).

Recently ionomers based on a perfluorocarbon backbone with sidechains terminating in sulfonate groups have attracted considerable attention, which centers on the Nafion materials developed by the Du Pont Company for use as ion-exchangers and as separators in various electrochemical applications. Several of the important properties they have depend on the nature of the cation-site interactions.

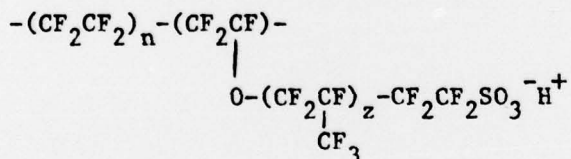
We have reported studies of cation-site interactions in several ionomeric systems; polyethylene methacrylic acid (PEHA) and polystyrene methacrylic acid (PSMA) ionomers, and have shown how the strength of the interaction and other features measureable spectroscopically depend on the influence of hydration, clustering, and the nature of the cation and anionic polymer ( 9,10 ). The importance of the Nafion-type, or PFSA, ionomers demands that cation-motion, hydration, and similar effects in them be studied as well.

In addition to investigating the spectral behavior of PFSA ionomers for the reasons mentioned above, however, there is another reason of potential

significance. It derives from the fact that the perfluorinated chains impart an unusually high thermal and chemical stability to PFSA ionomers. If transition metal PFSA ionomers are prepared, and the transition metal sites rendered coordinatively unsaturated. The materials could then be reacted in the presence of either rather reactive molecules (taking advantage of the chemical stability) or weakly reactive molecules (taking advantage of the coordinative unsaturation attainable), and, in either event, new chemistry achieved. Clearly catalytic systems are achievable, in analogy to others known (11), and new synthetic, gas separation, and catalytic possibilities realized in these stable materials that are not realization in hydrocarbon-based ionomers.

To provide an understanding both of the ionic interactions important in present applications and of the role of certain transition metal species in PFSA ionomers, we have carried out an infrared study of Nafion ionomers with group Ia, IIa, and several transition metal cations.

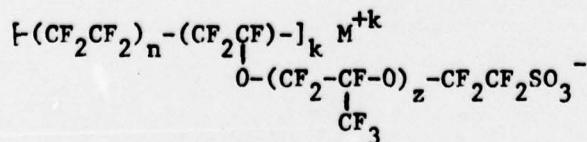
In investigating ionic polymeric substrate-metal ion interactions we have chosen perfluorosulfonic acid copolymer, (PFSA) which may be represented as



where z is small (1-5) and n takes on values up to 13 for polymers with equivalent weights of 1100-1600. Summaries of some physical properties of this copolymer have been published (5).

### Experimental

Perfluorosulfonic acid (PFSA) ionomers are of the form:



where  $M^{+k}$  is a group IA, group IIA or other cation, such as a transition metal ion. The samples were studied as films labelled by a symbol including the counterion followed, in parentheses, by a three digit number. The first two digits give the equivalent weight in hundreds and the last digit the nominal film thickness in thousandths of inches. For example, K(142) is a potassium ionomer film of 1400 equivalent weight and 2 mils thick.

The ionomers were prepared from the acid form of the polymer by ion exchange. Each film was emersed in an aqueous solution of the nitrate or chloride salt of group IA, IIA metals and transition metals for several hours. After removing the films from the solution they were rinsed well with distilled water. An alternate preparation involves using a solution of the appropriate base. The salt or base concentration is not very critical, but if nearly all acidic hydrogens are to be replaced an excess of cations is required. The degree of replacement of sulfonic hydrogens by  $M^{+k}$  in the samples studied was ascertained by infrared spectroscopy to be 99-100%.

The infrared spectra in the  $50-3800\text{ cm}^{-1}$  region were recorded with Digilab FTS-14 and FTS-15B Fourier transform infrared spectrometer at ambient temperatures. In the mid infrared region each trace represents the average of 64 scans. In the far-infrared each trace represents the average of 200-1000 scans. All spectra were obtained with ca.  $2\text{ cm}^{-1}$  resolution and recorded several times with a reproducibility of better than 1% in absorbance.

Dehydration experiments were performed on wet films both in the mid and far infrared region. The films were mounted on a brass support inside a specially designed evacuable cell in which the temperature was variable from  $20^{\circ}$  to  $240^{\circ}\text{C}$  and measured and controlled to within  $1^{\circ}\text{C}$ . The cell was fitted with KBr or high density polyethylene windows. Spectra were taken at ambient temperatures before and after evacuating the cell and at various times during the dehydration process, during which the cell was pumped on continuously.

## Spectral Results

### Mid Infrared Spectra

Spectra of two partially hydrated and dehydrated acid form PFSA films are shown in Figure together with that of a completely exchanged and dry K (142) film. (Hydrated) Films 2 mils or greater in thickness appear almost totally opaque in the  $3800\text{--}500\text{ cm}^{-1}$  region, but even the 1 ml thick films have a broad ill defined band beginning in the OH stretching region and extending to ca.  $1500\text{ cm}^{-1}$ . This band envelope is attributed to the extensive hydrogen bonding interactions involving the  $\text{SO}_3\text{H}$  groups<sup>12</sup> and  $\text{H}_2\text{O}$  and is more intense in wet films where the acidic protons can associate with water molecules to give  $\text{H}_{2n+1}\text{O}_n^+$  moieties. Absent from the dried films are the bands in the  $3500\text{ cm}^{-1}$  region due to symmetric and antisymmetric O-H vibrations of the water molecule and the band in the  $1600\text{--}1700\text{ cm}^{-1}$  region due to the water bending vibration.

There are other subtle differences in the spectra of hydrated and dry films of the PFSA ionomers. A weak broad asymmetric band in the  $1420\text{ to }1450\text{ cm}^{-1}$  region for hydrated films becomes sharper, well defined and more intense in films that have been dried. This band is absent in films where  $\text{H}^+$  has been totally exchanged for a metal ion and is thought to be either a stretching vibration of the S-O bond with double bond character in the  $\text{SO}_3\text{H}$  group or a sulfonic O-H-O bending vibration between associated acid groups.

Another difference between the wet, dry and exchanged films is the shifting of the  $870\text{ cm}^{-1}$  band to  $920\text{ cm}^{-1}$  upon dehydrating as can be seen in Fig 21. This band is possibly a S-O stretch with single bond character and is absent in exchanged films which have only two bands at  $980\text{ cm}^{-1}$  and at ca.  $1060\text{ cm}^{-1}$  whose exact position depends on the cation. These bands are also observed in the acid form of the copolymer but the  $980$  band is clearly a doublet for the hydrated film. Fig. 21.

Upon complete exchange of the acidic protons by a metal ion one observes that the infrared transmittance is greatly enhanced. The hydrated films have well defined bands in the OH stretching region and a band in the HOH bending region Fig. 3. These bands which can be completely eliminated by dehydrating the films Fig. 4 result from the water which hydrates the ions. Thus, a dehydrated (salt) exchanged film contains just one broad, asymmetric band at ca.  $2360\text{ cm}^{-1}$  in the  $1350$  to  $3800\text{ cm}^{-1}$  region. It is an overtone of the strong bands centered in the  $1200\text{ cm}^{-1}$  region (12,13).

As evidenced by the intensity of the bands in the OH stretching region and the H-O-H bending band, water retention by the film depends on the size and charge of the cation as does the hydration of a cation. Hydration decreases as size increases and group IIa ion hydration is greater than that of group Ia and IIa exchanged films and only for  $\text{Mg}^{+2}$  films was removing the last traces of water difficult.

#### Far Infrared Spectra

The far infrared spectra of ( $50$ - $300\text{ cm}^{-1}$ ) of PFSA 115 ionomers of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$  and  $\text{Cs}^+$  are shown in Figure 5 along with the spectrum the acid form of the copolymer. Each spectrum contains a broad, well defined band in the region below  $300\text{ cm}^{-1}$  which is absent in the acid form. This band is somewhat masked in the case of the  $\text{Na}^+$  ionomer by the  $203\text{ cm}^{-1}$  internal mode of the PFSA copolymer backbone. The band shifts from  $180\pm 7\text{ cm}^{-1}$  in the  $\text{Na}^+$  ionomer to  $150\pm 5\text{ cm}^{-1}$  for  $\text{Cs}^+$ . Similar shifts are observed with 125, 142 and 152 ionomer films. In Figure 6 are shown the spectra of the  $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ ,  $\text{Sr}^{+2}$  and  $\text{Ba}^{+2}$  ionomers. Again the well defined band observed at  $125\pm 5\text{ cm}^{-1}$  for Ba (115) is shifted to  $155\pm 5\text{ cm}^{-1}$  in Sr(115),  $200\pm 7\text{ cm}^{-1}$  (with the common  $203\text{ cm}^{-1}$  band superimposed on it), in Ca(115) and ca.  $240\pm 7\text{ cm}^{-1}$  in  $\text{Mg}^{+2}$ . The change in frequency of these bands can be accounted for largely by the change in mass,  $M$ , of the cation. The observed low frequency bands in the group Ia and group IIa PFSA ionomers is given in Figure 7, in which a correlation is shown between the frequencies of the cation-motion bands of

cations which have the approximately the same mass but differ in charge. Indeed, the frequency,  $\nu$ , varies nearly linearly with  $M^{-\frac{1}{2}}$  for PFSA ionomers as shown in Figure 8 for each group of ions. This linear dependence of  $\nu$  on  $M^{-\frac{1}{2}}$  indicates that the vibration is due to cation motion, and that the cation anionic site force constants are approximately the same for each ion in a given group but greater for group IIa cations than for group Ia cations. Furthermore, the correlation is quite consistent with the cation-site forces being essentially ionic in nature ( 9 ).

In Figure 9 are shown the far infrared spectra of  $K^+$  ionomers of 152, 142, 125, 115 films. The spectra are normalized to constant absorbance of the  $203\text{cm}^{-1}$  PFSA internal motion band (and offset for display). In the 152 and 142 PFSA films which have lower acid-group concentration, the cation motion bands, centered at  $150\pm 5\text{cm}^{-1}$ , exhibit considerable asymmetry to the low frequency side. As the acid group concentration increases, in going from an equivalent weight of 1500 to 1100, the cation motion band increases in intensity and the asymmetry on the low frequency side of the band disappears. The same asymmetry is clearly observed on the high side of the Rb(142) ionomer centered at ca  $108\pm 5\text{cm}^{-1}$ . One can, thus, conclude that the asymmetry is due to a low frequency polymer backbone vibration whose intensity does not increase as the ionic concentration increases and is observed only when the ion motion band is of low enough intensity. This is important to note in light of the cluster mode observed in the PSMA ionomers ( 14 ).

In order to determine whether the ion motion band was influenced by water within the film, dehydration studies of several types of  $K^+$ -PFSA films and Rb(125) film were undertaken. The results for a K(152) film are shown in Figure 10. No shift in the ion motion band or other internal motion bands occurs. Trace (c) represents the spectrum of a wet film from which the excess surface water was wiped off. Although it would seem that the ion motion band is more intense for

the wet film, its higher absorbance is due to water absorptions which are particularly strong in this spectral region. Trace (b) represents a partially dry film, which was produced by pumping on the cell for three hours at ambient temperature. The dry film (a), produced by heating to 150°C and pumping for 6 hours, gives a higher quality spectrum but no significant spectral changes are observed.

#### Transition Metal Ionomers

Since one future goal of studies of PFSA ionomers involves binding metal complexes in them and studying their structure, reactivity, and potential catalytic properties, it is important to know what the nature of the metal ion is in the PFSA film both before and after dehydration. Although detailed results for each ion studied will be discussed more appropriately in future papers, that deal with the chemistry at the metal sites, a few general results will be presented here.

Transition metal ionomers of  $Mn^{+2}$ ,  $Fe^{+2}$ ,  $Co^{+2}$ ,  $Ni^{+2}$ ,  $Cu^{+2}$  and  $Ag^{+}$  have been prepared by the same methods used to prepare the group Ia and IIa ionomers. For these and other transition metal ions one has to be concerned about the consequences of hydrolysis. Very concentrated metal salt solutions will have low pH and prevent complete exchange by suppressing the ionization of the sulfonic acid groups. Exchange of ions also causes a drop in pH so dilute solutions should be used and, if necessary the incompletely exchanged film should be recovered and placed in a fresh solution to complete the exchange.

As expected transition metal ionomer films containing the same concentration of  $SO_3^-$  groups as group Ia and IIa films retained more water and were harder to dehydrate. Indeed in some instances complete dehydration was not achieved even after heating the film at 240°C in an evacuated cell for several days. Figure 11 shows the spectrum of a  $Cu^{+2}$  ionomer as initially prepared from aqueous solution and at various stages of dehydration.

As is the case with the alkali and alkaline earth ionomers, the completely exchanged transition metal ionomers have only two bands in the region between 800 and 1100, whereas the acid form has three. This indicates the absence of S-O

bonds with single bond character. It is also of interest to know whether the  $-\text{SO}_3^-$  groups are a part of the coordination sphere of the metal ion and, if so, where they mono or bidentate ligands.

For most group Ia and IIa ions the  $980 \text{ cm}^{-1}$  band is a sharp single peak indicating that the oxygen atoms of the  $\text{SO}_3^-$  group are equivalent and that, therefore, such ions lie at the midpoint between the three oxygen atoms. For polystyrene sulfonic acid salts Zundel (15) favors the attachment of a cation to a single oxygen atom only. Since this band is asymmetric for  $\text{Cs}^+$  and  $\text{Ba}^{+2}$  ionomers (Figure 2) and clearly split for transition metal ionomers (Figure 2-III) one concludes that for steric reasons or because of possible covalent bonding of transition metals to the  $\text{SO}_3^-$  groups the local  $\text{C}_{3v}$  symmetry of the sulfonate group is reduced. This would indicate that  $\text{SO}_3^-$  ions are a part of the transition metal's coordination sphere and that bivalent cations provide crosslinks between polymeric chains. Water molecules are also a part of the coordination sphere since it is often difficult to completely dehydrate transition metal ionomers. However, contrary to our expectations the cobalt(II) hydrated ionomer had a visible spectrum identical to that of  $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$  in aqueous solution as can be seen in Figure 12.

#### Conclusions

We have shown that the infrared spectrum a hydrated PFSA film shows some interesting changes upon dehydration. In the dry film the sulfonic proton is associated with one of the oxygen atoms and although clustering (5) of the acid group and hydrogen bonding among them is extensive there exist S-O bonds of single and double bond character as well as S-O bonds of intermediate bond order because of hydrogen exchange between oxygen atoms. In the wet film the sulfonic proton is to a large degree ionized, so that the sulfonic oxygens are essentially equivalent and  $(\text{H}_{2n+1}\text{O}_n)^+$  moieties exist close to the anionic sites. This creates local  $\text{C}_{3v}$  symmetry for the  $\text{SO}_3^-$  group as is the case with the metal ion exchanged films except when steric effects or covalent bonding lower the symmetry. Thus, aside

from the enhanced transparency in the  $3500\text{--}1300\text{ cm}^{-1}$  region arising from hydrogen bonding between sulfonic acid groups in the acid form, the hydrated PFSA films and their ionomers are structurally similar in that a hydrated proton or hydrated metal ion exists in the vicinity of the anion. Eisenberg and Yeo ( 1 ) have pointed out, however, that for these materials there is a dramatic decrease in density upon ionization accompanied by increase in the water diffusion coefficient in contrast to other ionomers. This indicates to us that the polymeric material swells to accommodate a hydrated or otherwise coordinated cation.

For the group Ia and IIa ionomers the interaction between the cation and the  $\text{SO}_3^-$  groups are essentially ionic in nature. The oxygen atoms of the sulfonate group are, in most cases, equivalent and the  $\text{M}^+$  or  $\text{M}^{+2}$  ion is enclosed in a cage involving one or more  $\text{SO}_3^-$  groups, the polymeric backbone and ligand molecules, e.g. water, for hydrated films. The ion motion frequencies are significantly lower than for ethylene methacrylic acid copolymers ( 9,10) and for many ionic glasses (17,18) and do not change when the film is thoroughly dehydrated. This would indicate a weaker force field on the cation or a larger vibrating assembly and possible conformational changes of the polymeric backbone upon dehydration, to compensate for the loss of a neighbor such as a water molecule, so that the net force field remains the same in both a wet and dry film.

In the case of transition metal ionomers the  $\text{SO}_3^-$  group is almost certainly a part of the coordination sphere of the cation but whether it behaves as a monodentate, bidentate or even as a tridentate ligand has not yet been ascertained. The water in many hydrated ionomer films may be completely removed but the spectrum of the dehydrated material remains unchanged in the entire infrared region except for the obvious suppression of water bands. Whether the polymeric backbone will undergo conformational changes, such as bi or tridentate binding of the anion to the cation, to compensate for loss of a ligand is still a question to be answered. However, experiments performed to date indicate that a procedure such as dehydrating a transition metal ionomer will leave the ion in a coordinatively

unsaturated state, a state of enhanced ability to bind and react with other species.  $\text{Cu}^{+2}$  ionomer films not only react with  $\text{NH}_3$  which is a strong ligand but also with gaseous CO and NO to form novel compounds.

#### Acknowledgment

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Figure Captions

- Figure 1. Mid infrared ( $3800-400\text{ cm}^{-1}$ ) spectra of two hydrated and dehydrated  $\text{H}^+$ -PFSA films together with the spectrum of a dehydrated  $\text{K}^+$ -PFSA film in the  $3800-1400\text{ cm}^{-1}$  region.
- Figure 2. I. Spectra of an H(151) film: — hydrated film, ..... partially dehydrated film, -.- dehydrated film.  
 II. Spectra of  $\text{Na}^+$  and  $\text{Ba}^{+2}$  ionomers in the  $1100-800\text{ cm}^{-1}$  region: — Na(151), ..... Ba(151). Spectra of hydrated and dry ionomer films are virtually identical in this region.  
 III. Spectra of some PFSA-142 ionomers in the  $1100-800\text{ cm}^{-1}$  region: Li(142), Ba(142), Cu(142).
- Figure 3. Spectra of PFSA-161 group Ia and IIa hydrated ionomers showing relative intensities of water stretching and bending bands.
- Figure 4. Spectra of a  $\text{K}^+$ (142) ionomer film showing decrease in water band intensities upon dehydration: a. hydrated film, b. partially dried film, c. dry film.
- Figure 5. Far infrared ( $50-300\text{ cm}^{-1}$ ) spectra of PFSA-115 acid form copolymer and group Ia ionomers.
- Figure 6. Far infrared ( $50-300\text{ cm}^{-1}$ ) spectra of PFSA-151 group IIa ionomers.

Figure 7. Correlation of low frequency ion motion bands between group Ia and IIa ionomers having approximately equal mass.

Figure 8. Variation of ion motion frequency as a function of  $M^{-1/2}$  for group Ia and IIa ionomers.

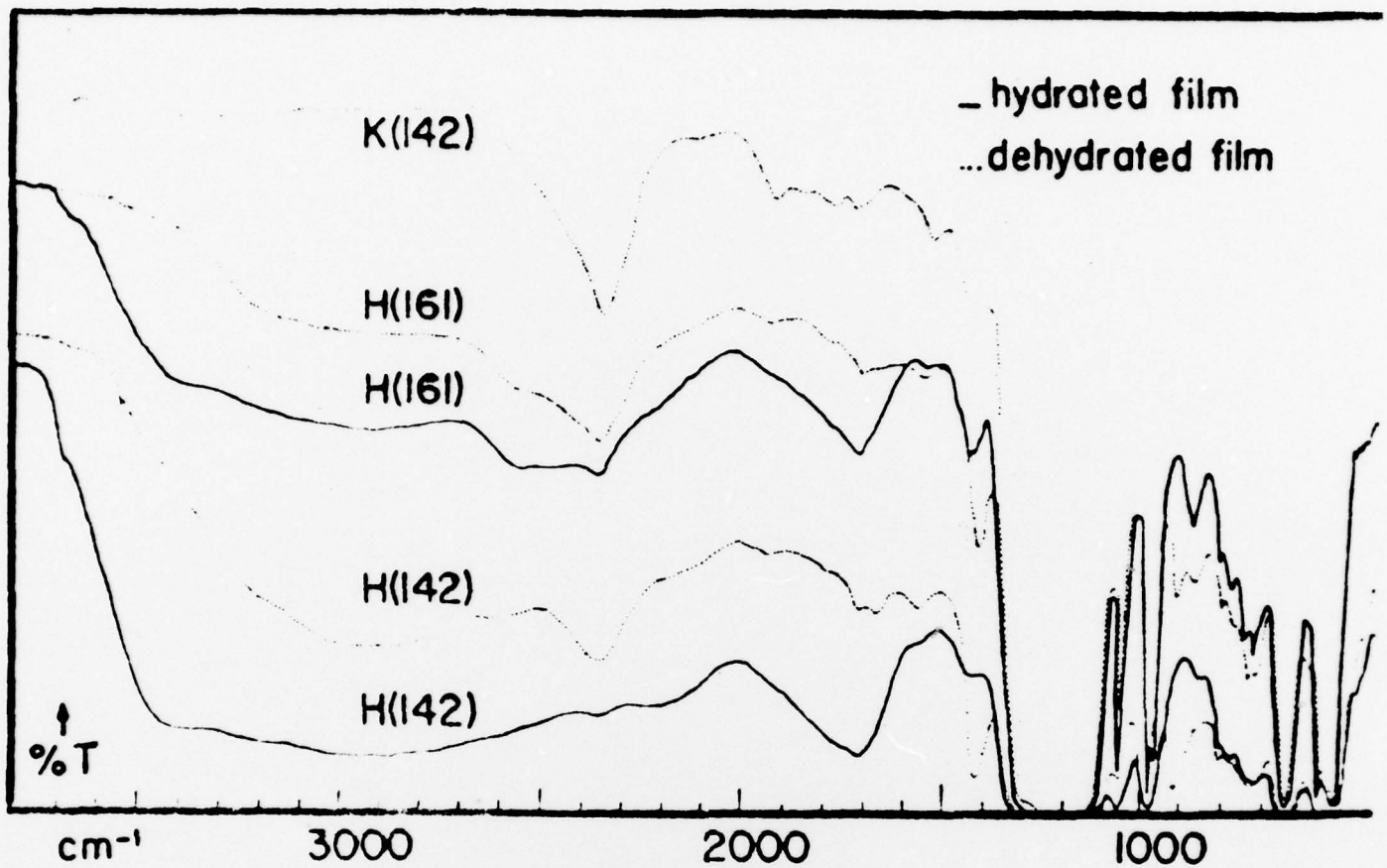
Figure 9. Far infrared ( $50-300\text{ cm}^{-1}$ ) spectra of PFSA- $\text{K}^+$  ionomers.

Figure 10. Far infrared ( $50-300\text{ cm}^{-1}$ ) spectra of a PFSA-K(152) ionomer:  
a. dry film, b. partially dried film, c. hydrated film.

Figure 11. Mid infrared ( $3800-400\text{ cm}^{-1}$ ) spectra of a PFSA-Cu(142) ionomer at various stages of dehydration. a. fully hydrated film, b. partially dehydrated film after heating at ca.  $140^\circ\text{C}$  for three hours and continuous pumping, c. further dehydrated film after heating at  $175^\circ$  for three more hours, d. film after heating at  $240^\circ\text{C}$  for four more hours.

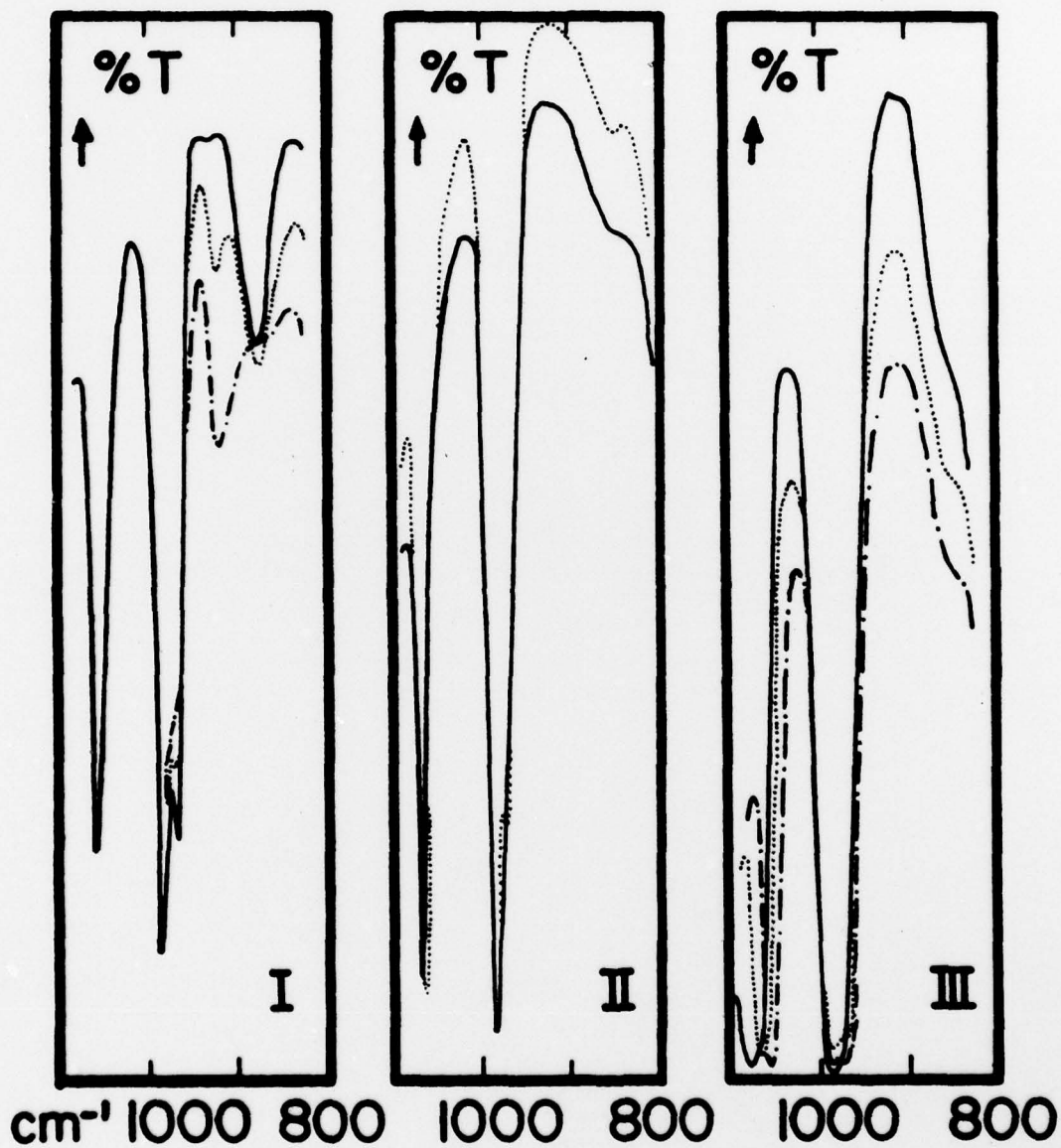
Figure 12. Visible spectra 600-400 nm. a. PFSA-H(125) film, b. fully exchanged PFSA-Co(125) ionomer film, c. resultant curve after subtracting absorbances of curve a from curve b, d. 0.01M  $\text{Co}(\text{NO}_3)_2$  aqueous solution  $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$ .

FIGURE 1



Mid infrared ( $3800\text{--}400\text{ cm}^{-1}$ ) spectra of two hydrated and dehydrated  $\text{H}^+$ -PFSA films together with the spectrum of a dehydrated  $\text{K}^+$ -PFSA film in the  $3800\text{--}1400\text{ cm}^{-1}$  region.

FIGURE 2



- I. Spectra of an H(151) film: — hydrated film, ....partially dehydrated film, —.—— dehydrated film.
- II. Spectra of  $\text{Na}^+$  and  $\text{Ba}^{+2}$  ionomers in the  $1100\text{-}800\text{ cm}^{-1}$  region: — Na(151), .....Ba(151). Spectra of hydrated and dry ionomer films are virtually identical in this region.
- III. Spectra of some PFSA-142 ionomers in the  $1100\text{-}800\text{ cm}^{-1}$  region: Li(142), Ba(142), Cu(142).

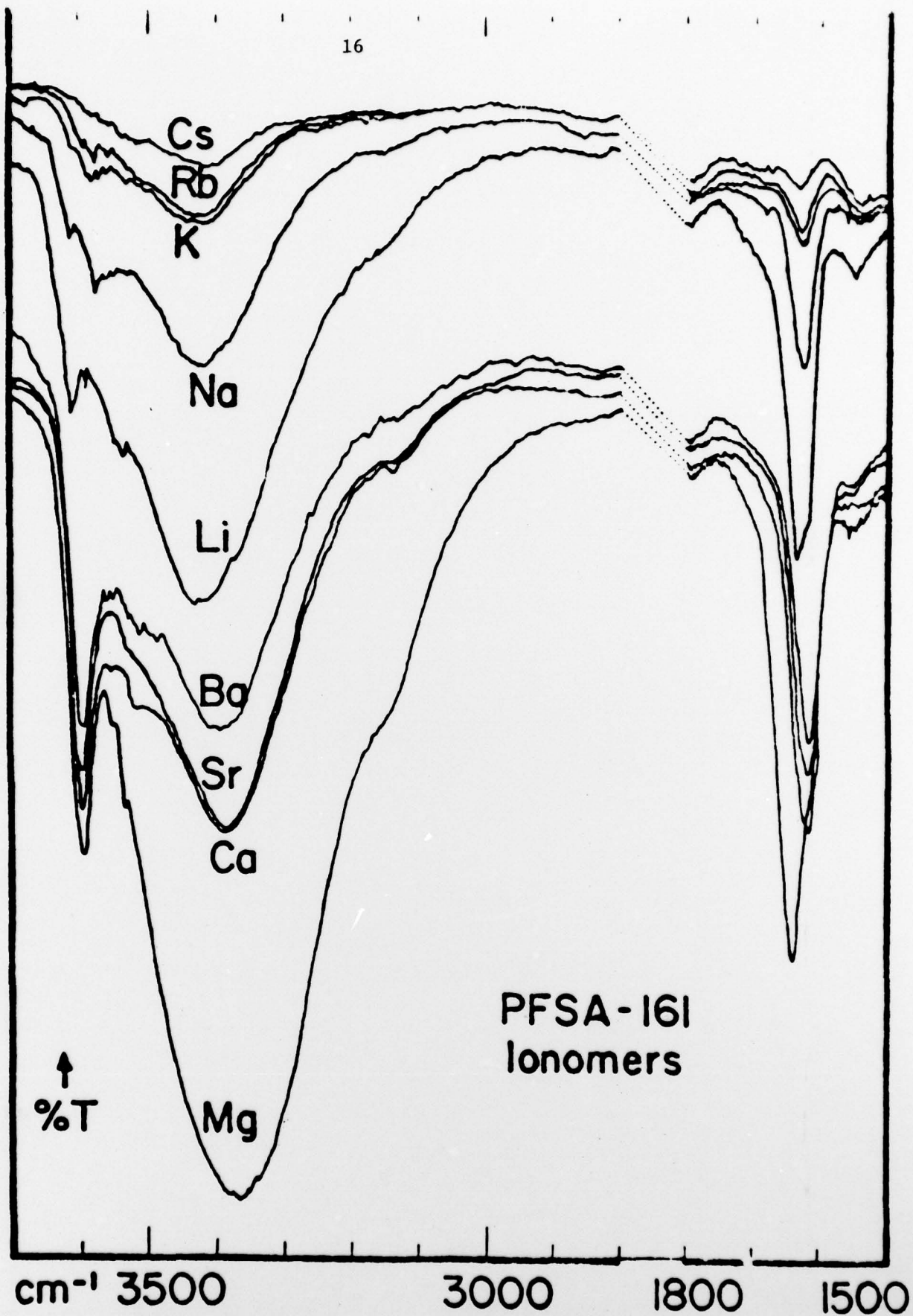


FIGURE 3

Spectra of PFSA-161 group Ia and IIa hydrated ionomers showing relative intensities of water stretching and bending bands.

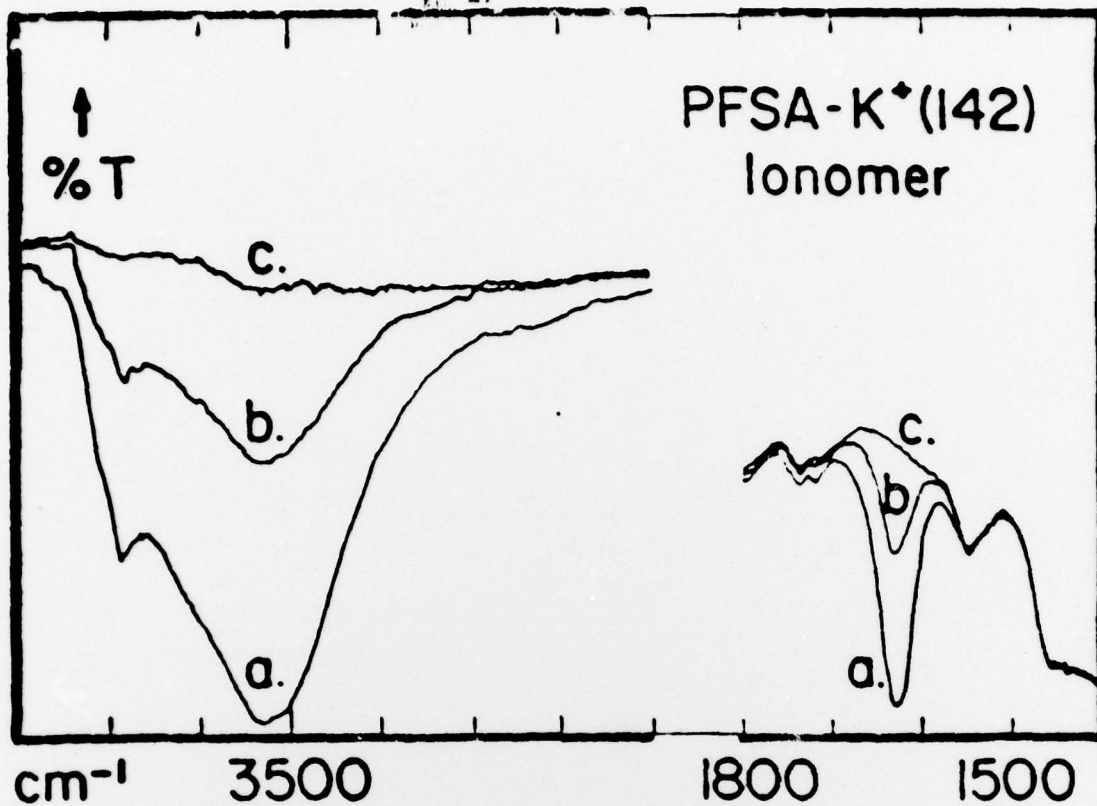
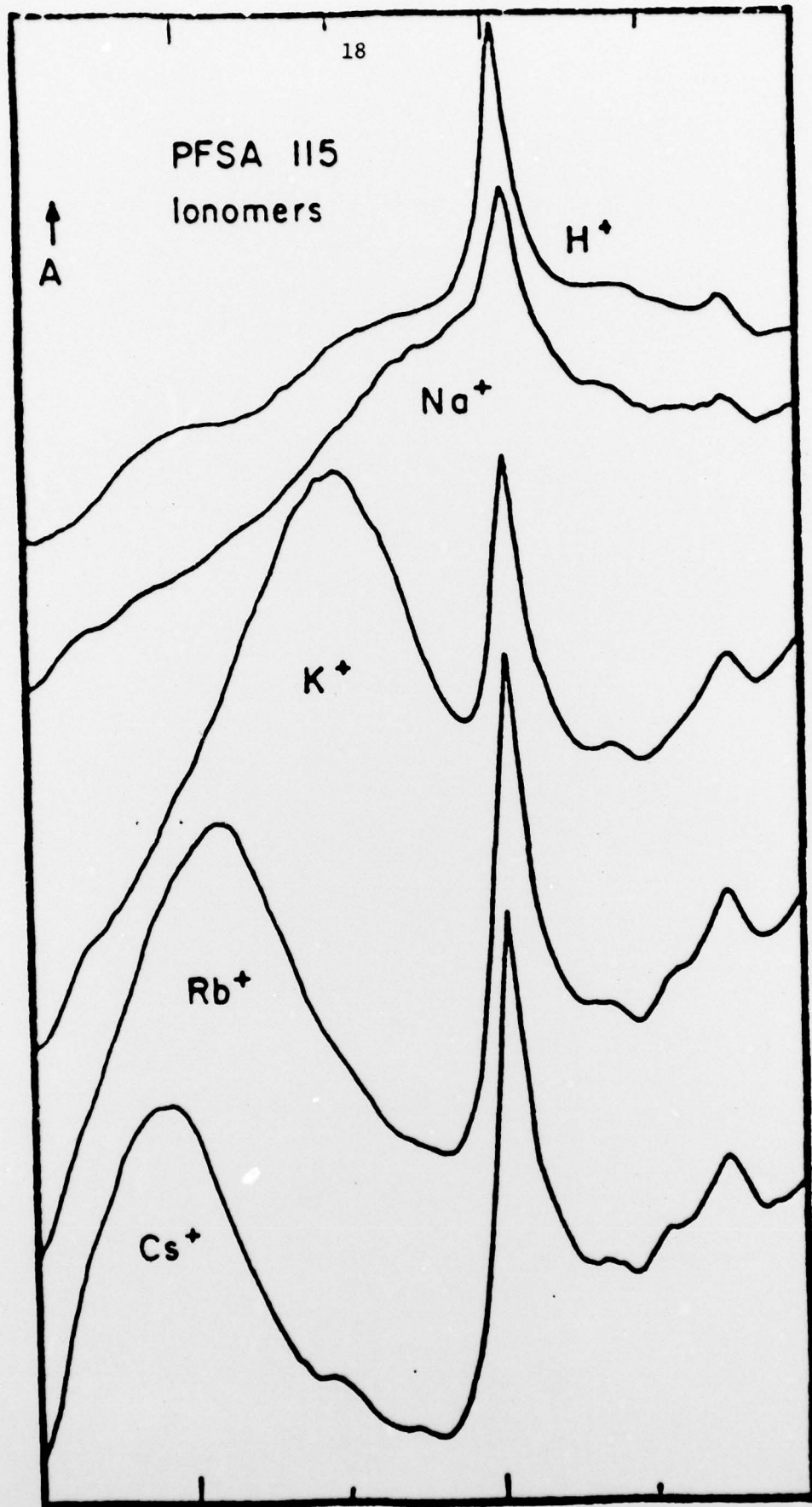


FIGURE 4

Spectra of a K<sup>+</sup>(142) ionomer film showing decrease in water band intensities upon dehydration: a. hydrated film, b. partially dried film, c. dry film.



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PFSA 115  
Ionomers

$\text{H}^+$

$\text{Na}^+$

$\text{K}^+$

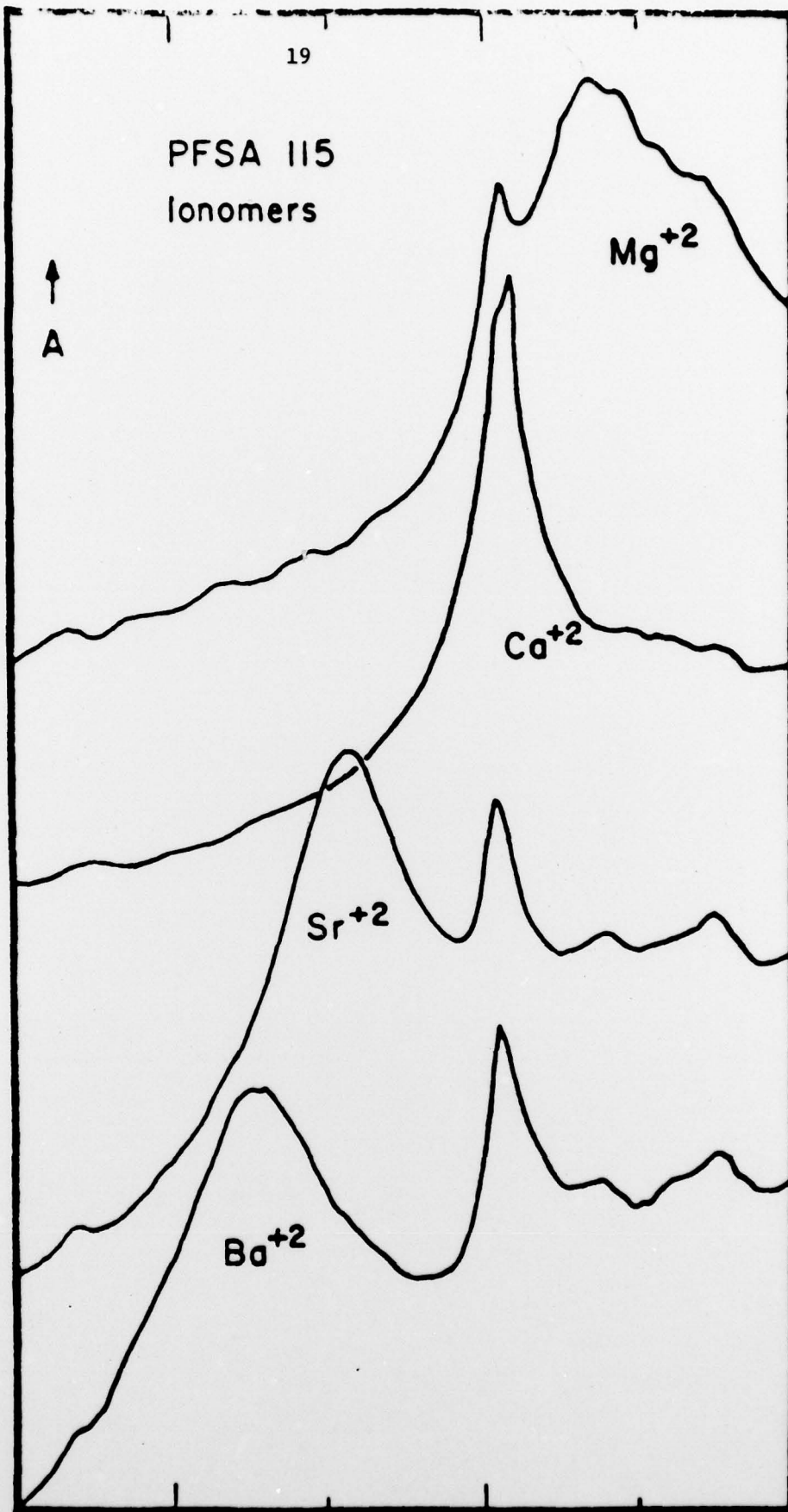
$\text{Rb}^+$

$\text{Cs}^+$

100 200  $\text{cm}^{-1}$

FIGURE 5

Far infrared ( $50\text{-}300\text{ cm}^{-1}$ ) spectra of PFSA-151 group IIa ionomers.



PFSA 115  
Ionomers

Mg<sup>+2</sup>

Ca<sup>+2</sup>

Sr<sup>+2</sup>

Ba<sup>+2</sup>

100

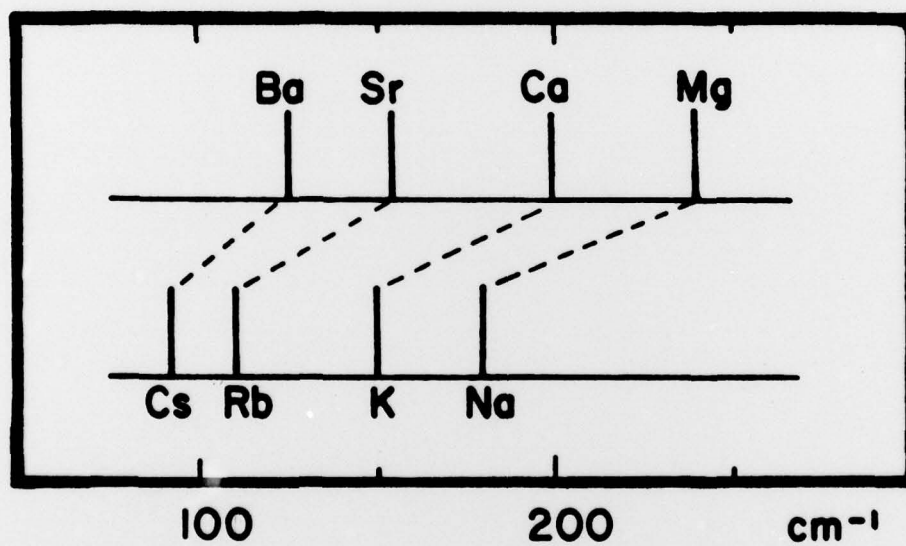
200

cm<sup>-1</sup>

FIGURE 6

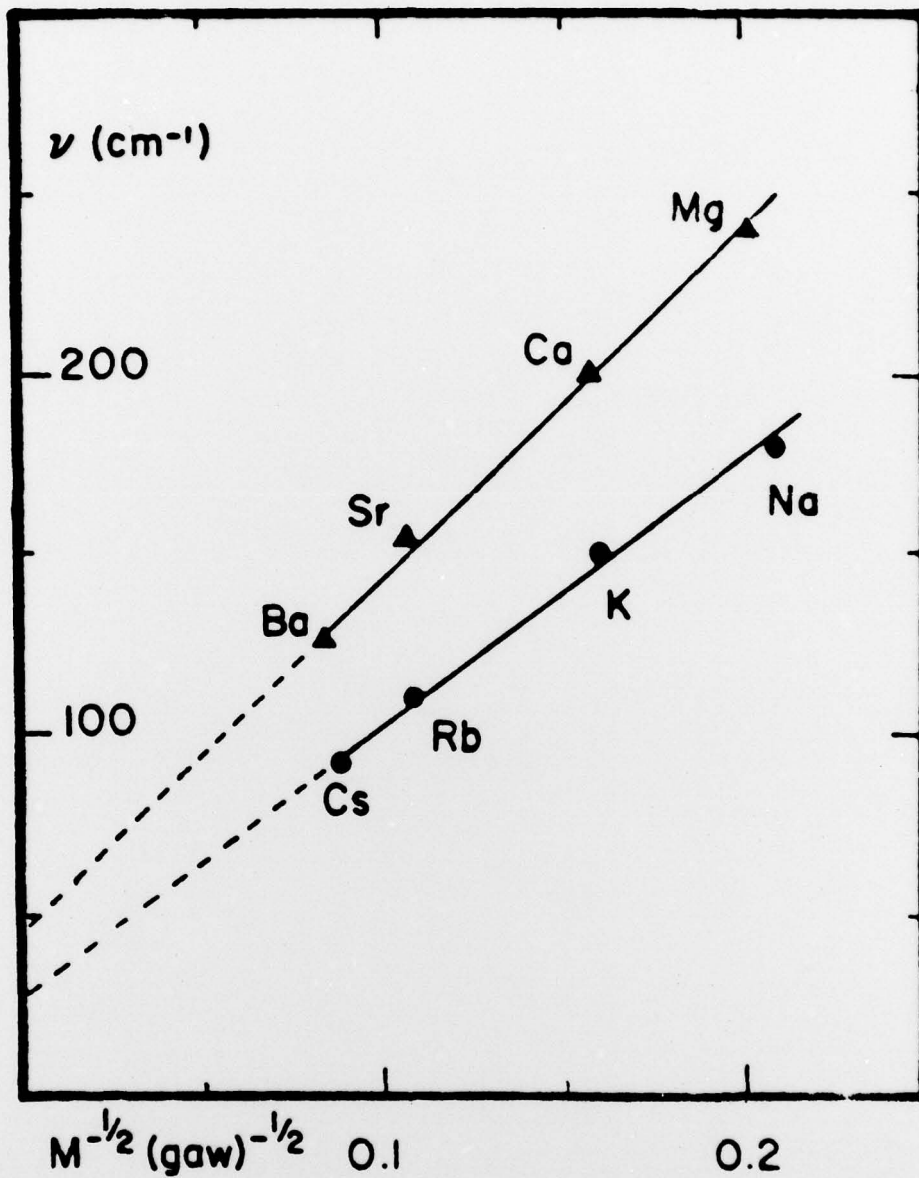
Far infrared (50-300 cm<sup>-1</sup>) spectra of PFSA-151 group IIa ionomers.

FIGURE 7



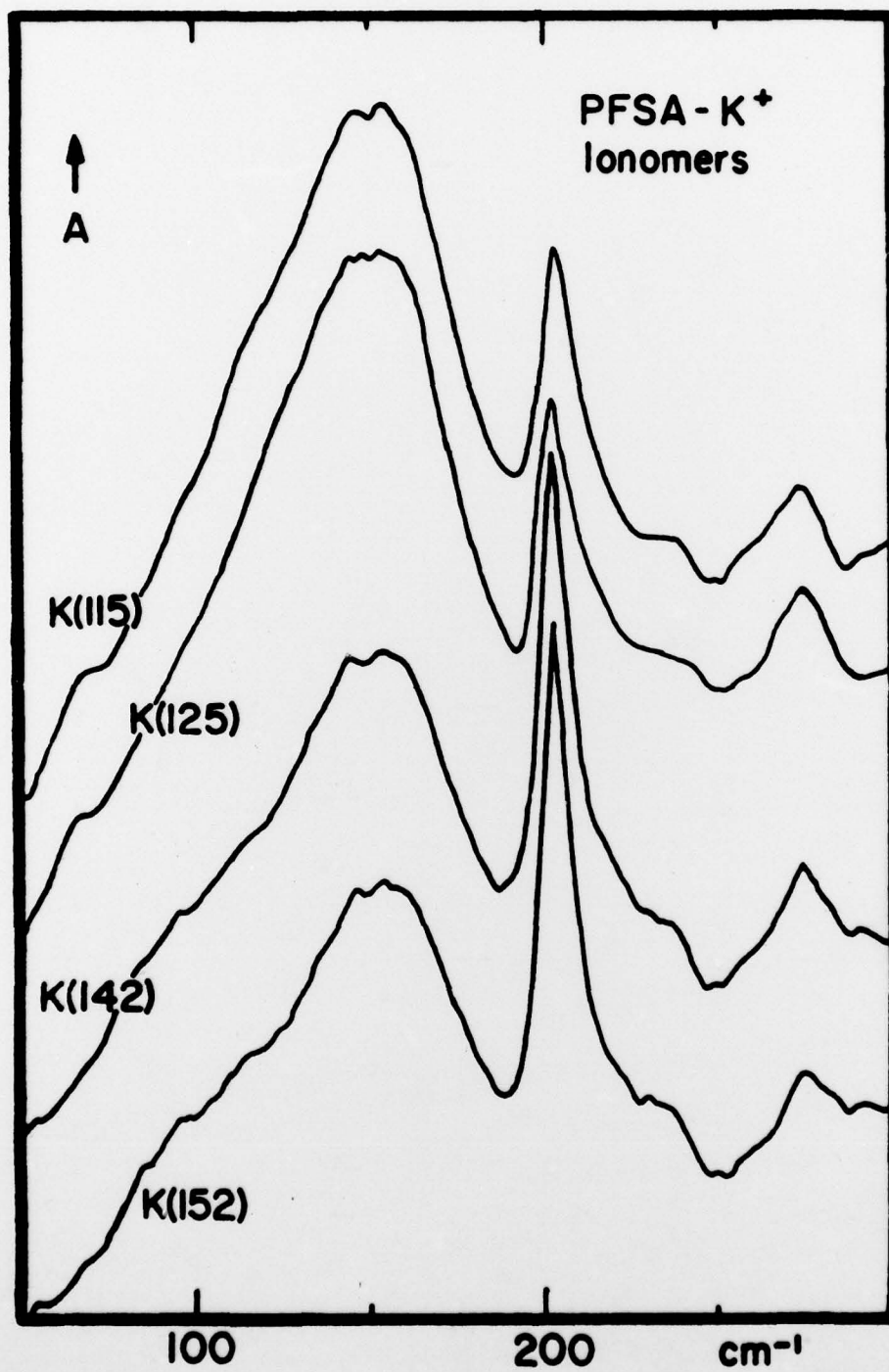
Correlation of low frequency ion motion bands between group Ia and IIa ionomers having approximately equal mass.

FIGURE 8



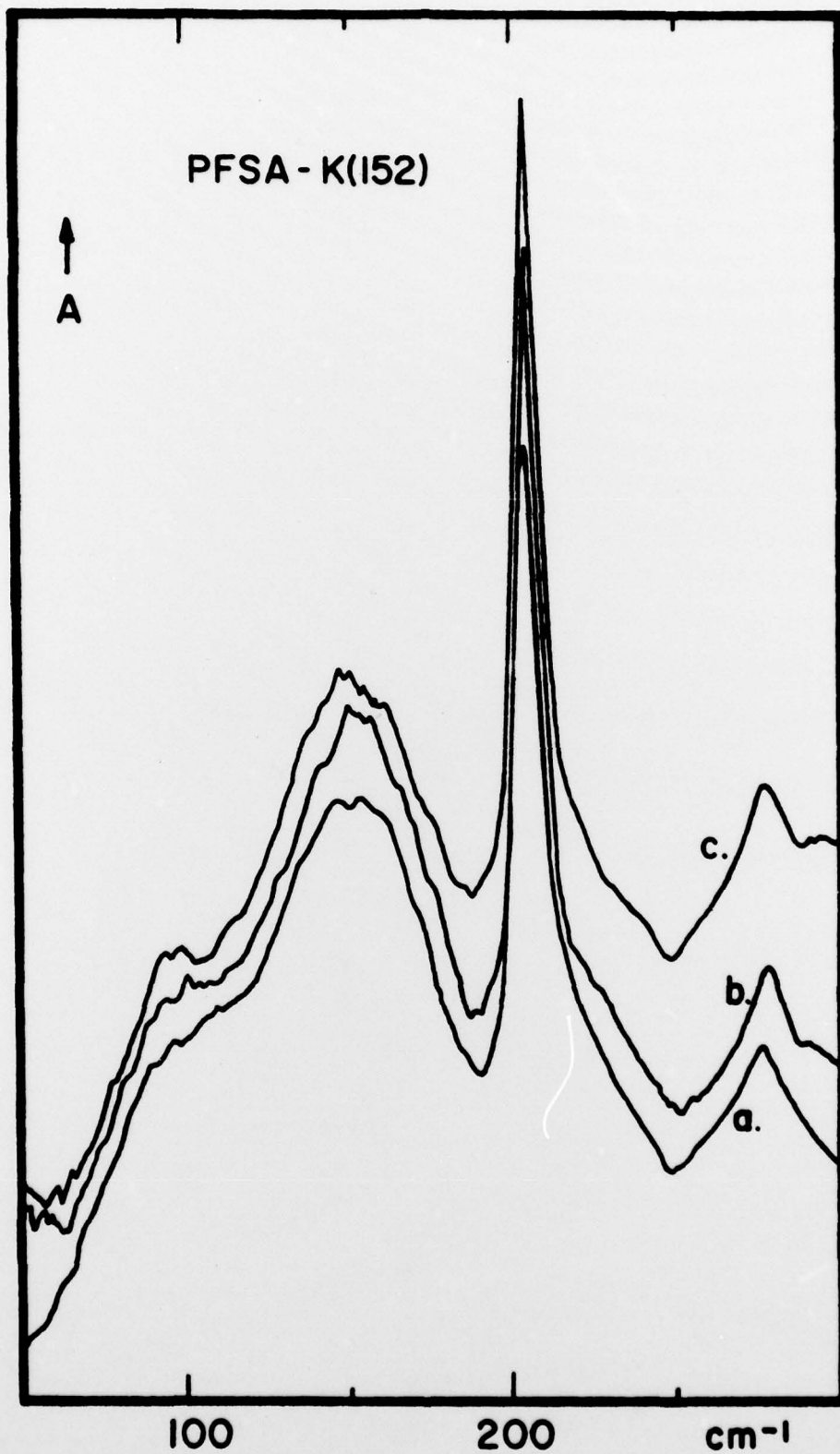
Variation of ion motion frequency as a function of  $M^{-1/2}$  for group Ia and IIa ionomers.

FIGURE 9



Far infrared (50-300 cm<sup>-1</sup>) spectra of PFSA-K<sup>+</sup> ionomers.

FIGURE 10



Far infrared ( $50\text{-}300\text{ cm}^{-1}$ ) spectra of a PFSA-K(152) ionomer:  
a. dry film, b. partially dried film, c. hydrated film.

FIGURE 11  
Mid infrared ( $3800\text{--}400\text{ cm}^{-1}$ ) spectra of a PFSA-Cu(142) ionomer at various stages of dehydration.  
a. fully hydrated film, b. partially dehydrated film after heating at ca.  $140^\circ\text{C}$  for three hours and continuous pumping, c. further dehydrated film after heating at  $175^\circ$  for three more hours, d. film after heating at  $240^\circ\text{C}$  for four more hours.

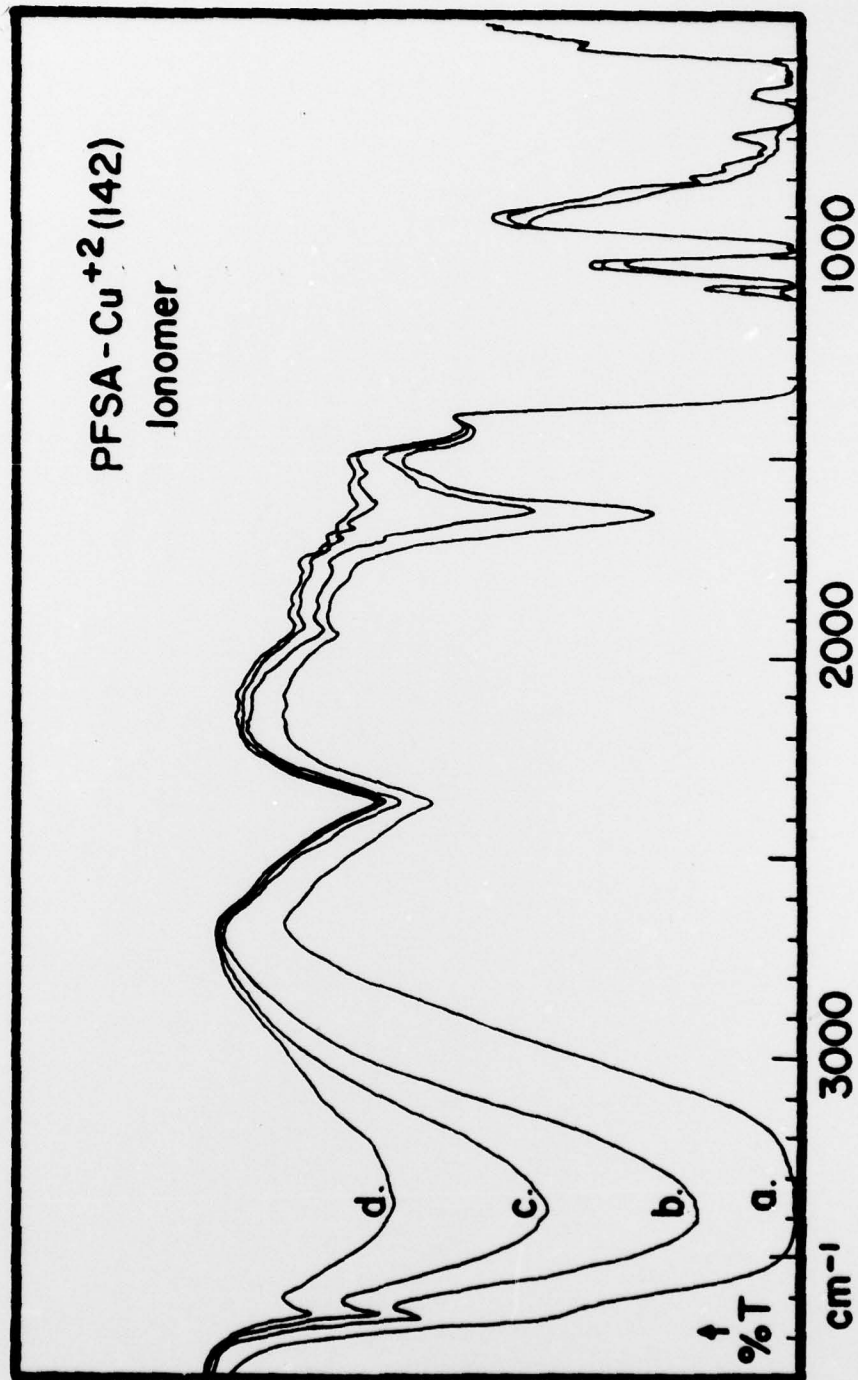
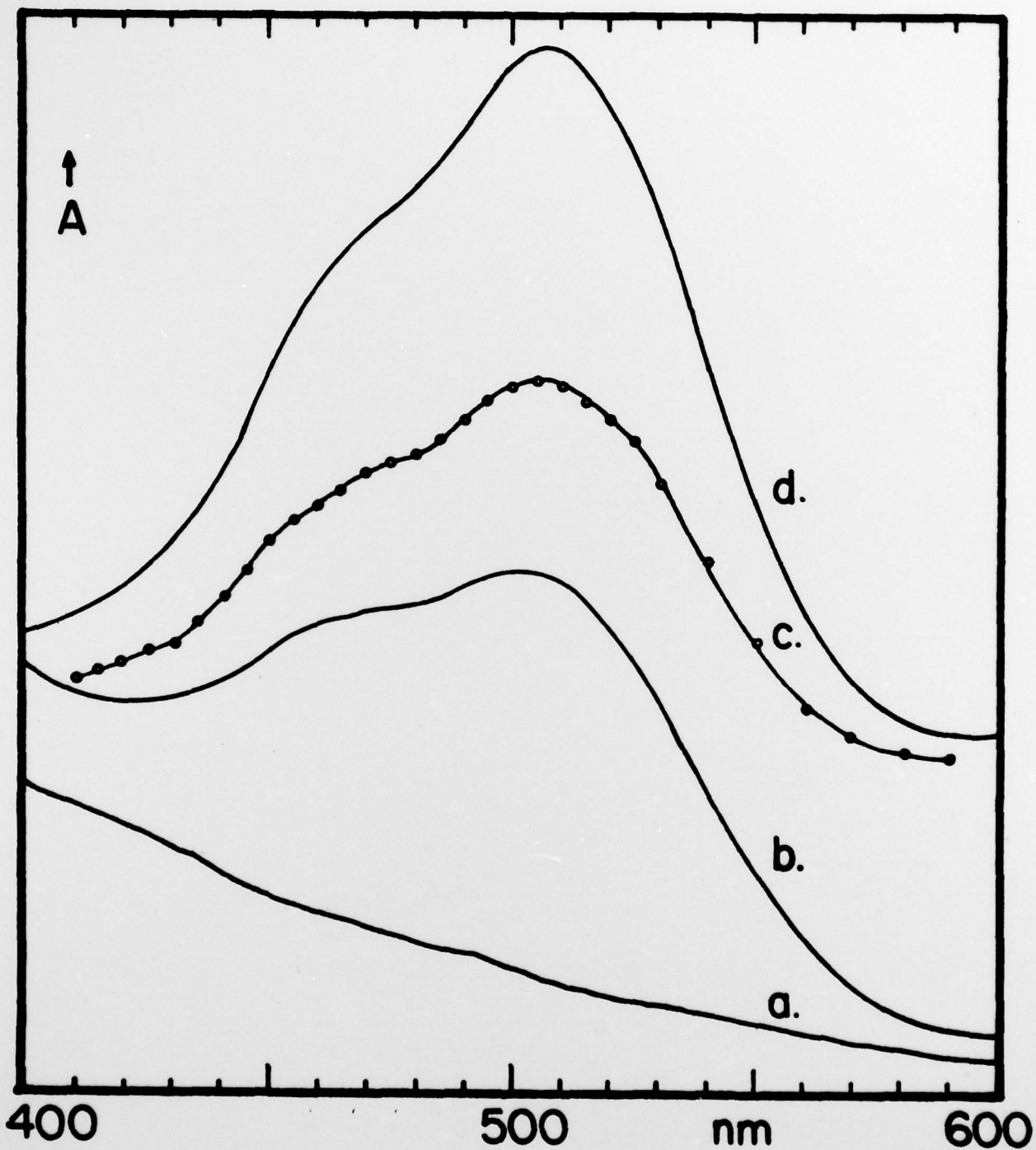


FIGURE 12



Visible spectra 600-400 nm. a. PFSA-H(125) film, b. fully exchanged PFSA-Co(125) ionomer film, c. resultant curve after subtracting absorbances of curve a from curve b, d. 0.01M  $\text{Co}(\text{NO}_3)_2$  aqueous solution  $[\text{Co}(\text{H}_2\text{O})_6]^{+2}$ .

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