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Infrared Investigations of Pristine, Doped and Partially-Doped
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by

J. Lei, W. Liang and Charles R. Martin

Department of Chemistry
Colorado State University
Ft. Collins, CO 80523

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It is well known that pristine (i.e. undoped) polypyrrole is not air-stable. As a result, it is difficult to obtain spectral data for the pristine polymer. Indeed, there are only two reports of infra red (IR) absorption spectra for the pristine material in the literature and, in both cases, the polymer seems to have undergone some air oxidation. It would be highly desirable to have reliable and reproducible IR spectra for the pristine form of this important polymer. We have designed a novel IR spectroelectrochemical cell which allows for electrochemical synthesis and IR and electrochemical analyses of thin polypyrrole films, while rigorously protecting these films from air. We present here IR spectra, obtained with this cell, for doped, partially doped and pristine polypyrrole.

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INFRARED INVESTIGATIONS OF PRISTINE, DOPED,

AND PARTIALLY-DOPED POLYPYRROLE

Junting Lei, Wenbin Liang, and Charles R. Martin[*]

Department of Chemistry
Colorado State University
Fort Collins, Co 80523

*Corresponding author

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ABSTRACT

It is well know that pristine (i.e. undoped) polypyrrole is not air-stable. As a result, it is difficult to obtain spectral data for the pristine polymer. Indeed, there are only two reports of infra red (IR) absorption spectra for the pristine material in the literature and, in both cases, the polymer seems to have undergone some air oxidation. It would be highly desirable to have reliable and reproducible IR spectra for the pristine form of this important polymer. We have designed a novel IR spectroelectrochemical cell which allows for electrochemical synthesis and IR and electrochemical analyses of thin polypyrrole films, while rigorously protecting these films from air. We present here IR spectra, obtained with this cell, for doped, partially doped, and pristine polypyrrole.

INTRODUCTION

Polypyrrole (PPy) is one of the most extensively investigated of the electronically conductive polymers (1-10). As is typical for this class of materials, PPy can be converted from an electronically insulating state (often called the pristine or undoped material) to an electronically conductive (doped) state (1). This is accomplished by chemically or electrochemically oxidizing the pristine polymer.

One of the most important research objectives in the conductive polymer area has been to elucidate the mechanism of conductivity in the doped states of these materials (4-6). Infrared (IR) and raman spectroscopy have played an important role in this effort (3,7). Unfortunately, as recently pointed out by Zerbi - "experimentally the IR spectrum of pristine PPy is not yet certain either because the sample is not stable in air and is easily oxidized or decomposed and/or because the chemical processes adopted produce unwanted side reaction" (8). The absence of a reliable IR spectrum for pristine PPy has hindered progress in elucidating the structural and electronic changes that accompany the doping process (9).

We have recently obtained reproducible IR spectra for the pristine form of PPy. These spectra were obtained using a novel spectroelectrochemical cell that allows for synthesis and electrochemical and IR characterization of thin PPy films without exposure of these films to air. These studies have also shown that provided the polymer film is shielded from air, the pristine material is chemically stable, over time scales of at least four hours. Finally, we have also obtained FTIR spectra for various doping levels between the doped and undoped states. The results of these investigations are reported in this paper.

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EXPERIMENTAL

Materials. Pyrrole (Aldrich) was purified by fractional distillation immediately prior to use. LiClO$_4$ (Fisher) was recrystallized from ethanol and dried in vacuo. Acetonitrile (Mallinckrodt, HPLC grade) was rigorously dried prior to use. This was accomplished by first passing the CH$_3$CN through a column containing equal quantities of molecular sieves (Mallinckrodt, grade 514 GT) and Al$_2$O$_3$ (Waters W200, acid). The eluent was then distilled over P$_2$O$_5$ and used immediately. Ar gas was used to purge the spectroelectrochemical cell, degas all solutions, and transfer solutions to the cell. Trace oxygen was removed from the Ar by passing the gas through a column containing Cu mesh which was heated to 200° C.

Equipment. Electrochemical experiments were conducted using a Pine Instruments RDE 4 potentiostat/galvanostat. Fourier transform infrared spectra were obtained using a Mattson Galaxy 4021 FTIR spectrometer. A resolution of 4 cm^{-1} was employed; each spectrum represents the average of 400 to 500 scans. The spectrometer was driven by a Leading Edge D3 PC. Mattson's Enhanced FTIR software was used to analyze the spectra.

Spectroelectrochemical Cell. The cell was designed to accommodate in situ synthesis of a thin PPy film, full potentiostatic control of this film, and transmittance mode FTIR analyses on this film without exposing the film to ambient atmosphere. The cell (Figure 1) fits within the sample compartment of the FTIR and contains two IR-transparent ZnSe windows to accommodate the IR beam. These windows were carefully polished with 0.05 μm alumina to reduce scattering. A Technics Ar plasma sputterer was used to deposit a thin (20 to 30 nm) layer of Pt on the front window. This Pt film serves as the optically-transparent working electrode for the PPy film. IR spectra for the cell (filled with Ar) before and after deposition

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of the Pt film are shown in Figure 2. As indicated in Figure 2B the Pt film is reasonably transparent in the spectral region of interest to these investigations.

A reference electrode (in these studies either a Ag wire immersed in 0.1 M AgNO₃ in CH₃CN or an aqueous saturated calomel electrode) is inserted through port E. (Choice of reference of electrode had no effect on either the electrochemical or IR characteristics of the resulting PPy films. All potentials in this paper are quoted vs. SCE.) A Pt plate served as the counter electrode. This electrode was positioned in front of the working electrode during electrochemical experiments but was moved upward during IR analyses so as not to block the IR beam. It is, of course, in principle possible to use either an IR-transparent counter electrode or a counter electrode geometry which allows for passage of the IR beam; however, this level of sophistication was not required for the investigations described here.

The cell was kept under positive Ar pressure throughout all of the various experimental procedures (e.g. filling and draining of the cell, film synthesis, electrochemical and FTIR analyses, etc.). Ar was admitted by inserting a hypodermic needle through the septum covering port F and escaped the cell through a small gauge hypodermic needle inserted through a rubber septum at port G. The drain H was used to drain solutions from the cell.

Film Synthesis. The polymerization solutions were 0.1 M in LiClO₄ and 0.1 M in pyrrole (in CH₃CN). The PPy films were synthesized galvanostatically at a current density of 1.0 mA cm⁻² for a duration of exactly 2.5 min. This yielded a film of ca. 400 nm thickness (10). This thickness provides good spectra for both the doped (highly absorbing) and pristine (low absorbing) films.

Experimental Protocol. We describe results for two sets of experiments. The objective of the first set was to obtain reproducible FTIR spectra for the pristine and doped forms of PPy. This, of course, requires *operational definitions* for pristine and doped. Doped PPy is operationally defined here as either an as-synthesized film or a film which, after reductive undoping, was redoped by equilibrating at a potential of +0.4 V vs. SCE. This is ca. 500 mV positive of the anodic voltammetric peak for PPy (see e.g. Figure 4). Pristine PPy is operationally defined here as a film which has been equilibrated at a potential of -0.8 V. This is ca. 700 mV negative of the cathodic voltammetric peak for PPy. The voltammogram shows only background currents at such negative potentials (11).

FTIR spectra for the pristine and doped materials were obtained as follows: After synthesis, the polymerization solution was drained from the cell and the film was rinsed of excess monomer and electrolyte. This was accomplished by transferring (under Ar pressure) pure CH_3CN to the cell and then draining this solvent from the cell; three fill/drain cycles were employed. The film was then dried by directing a stream of Ar onto the film surface via the tube E. An FTIR spectrum of the "as-synthesized" polymer was then obtained.

Fresh 0.1 M $LiClO_4$ was then transferred (under Ar pressure) to the cell and the PPy film was undoped at -0.8 V to generate the pristine material. A cyclic voltammogram was obtained for the pristine polymer. The film was then rinsed and dried as described above and an FTIR spectrum of the pristine polymer was obtained. Fresh electrolyte was then added to the cell and the film was reoxidized at +0.4 V. The film was then rinsed and dried and an FTIR spectrum of the reoxidized material was obtained. The film was then reduced again at -0.8 V and a second cyclic voltammogram and FTIR spectrum for the pristine

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material was obtained.

Note that, in all of these experiments, the solvent was removed from the cell and the film was dried, before IR data were obtained. This was done because CH_3CN shows intense absorption bands at ca. 2915 and 2277 cm^{-1} and we did not want these solvent band interfering with the film spectra. Traces of these peaks are sometimes discernable in the spectra for the pristine material, see e.g. Figure 6.

The objective of the second set of experiments was to obtain FTIR spectra for PPy films which had been equilibrated at potentials between the pristine and doped values. An FTIR spectrum for the as-synthesized PPy film was obtained using the protocol outlined above. The cell was then refilled with electrolyte and the PPy film was equilibrated at a potential of 0.3 V vs SCE. After equilibration (30 min) the cell was emptied, the film was rinsed and dried, and an FTIR spectrum was obtained. This process was repeated for equilibration potentials of 0.1 V, -0.1 V, and -0.4 V.

Finally, it is important to discuss background correction for these FTIR spectra. As indicated in Figure 2, the background absorbance for the cell after coating the ZeSe window with a thin Pt film is significant but essentially featureless. The obvious way to handle this background absorption is simply to subtract this absorbance from the spectrum obtained when the PPy film is coated onto the Pt surface. In fact, when this is done, *negative* absorbance data are obtained for the spectra of the pristine material.

These negative absorbance result from an index matching problem. When the PPy film is absent, there is a large refractive index (n) difference between the Pt layer (n = 5.9 at 161.7 nm) (12) and the Ar-filled cell (n=1.0). This, of course causes a large reflective

loss at the Pt/Ar interface. When the PPy film is present, it acts as an index matching agent because its index is between that of Pt and Ar (13). Hence, the reflective losses at the PPy film-coated electrode are in fact less than at the bare Pt electrode.

The FTIR instrument interprets the higher reflective loss at the bare (i.e. no PPy) Pt surface as a high absorbance. When this high absorbance is subtracted form the spectrum of the pristine material (where, as indicated above reflectance losses are smaller), a negative absorbance is obtained. As a result of this index matching problem, the spectra reported here were not corrected for background processes. Because the background processes are essentially featureless (Figure 2B), this does not create a problem.

RESULTS AND DISCUSSION

Doped PPy. FTIR spectra for the doped form of PPy are shown in Figure 3. The spectra labeled A is for an as-synthesized PPy film. This spectrum shows the series of sharp peaks, at energies above 1600 cm^{-1}, characteristics of the doped material (3); in accordance with Zerbi's nomenclature we have labeled these peaks A' through G' (9). This spectrum also shows the featureless rise in absorbance with energy at energies above ca. 1600 cm^{-1}; this is also characteristic of the doped material (3,14).

The spectrum labeled B in Figure 3 was obtained for the same PPy film but after a complete reduction and then reoxidation cycle (see Experimental). The key point is that between spectrum A and B, the polymer spent ca. 4 hours in the pristine (undoped) state. Nevertheless, the spectrum obtained after reoxidation is, within experimental error, identical to the spectrum for the as-synthesized material (see Table I for peak positions and intensities for these spectra). Thus, even on this rather extended time scale, the pristine form of PPy is

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chemically stable, provided it is not exposed to air.

This point is reinforced by the cyclic voltammograms shown in Figure 4. These voltammograms were taken after the first (4A) and second (4B) reduction cycles. Again, the polymer spent about 4 hours in the pristine state between the times that these voltammograms were obtained. Nevertheless, these voltammograms are superimposable, indicating complete recovery of all electroactive material after this extended period in the pristine state.

Pristine PPy. It is difficult to obtain meaningful spectral data for pristine PPy because this form of PPy reacts with air (3). This can be demonstrated visually with electrochemically-synthesized PPy films. For example, when a thin film of PPy is synthesized on our ZnSe/Pt electrode/window and reduced, this film is essentially optically transparent. However, brief (e.g. 5 min) exposure of the film to air causes the film to turn black, characteristic of the doped form. Furthermore, this air oxidized material is electronically conductive, albeit at lower levels than the electrochemically doped material (3). An IR spectrum for this air-oxidized material is shown in Figure 5. As might be expected, this spectrum shows features characteristic of doped PPy.

The spectra for pristine films which were protected from air are quite different. Two such spectra are shown in Figure 6. In analogy to Figure 3, these spectra were obtained for the same film after a complete reduction/reoxidation/re-reduction cycle. Again, within experimental error, these spectra are identical. Peak positions and intensities for the bands in these pristine-form spectra are presented in Tables II.

A Comparison of the Spectra for Pristine and Doped PPy. The most obvious difference between these spectra occurs at energies above ca. 1600 cm^{-1}. The doped material shows a

pronounced monotonic increase in absorbance with energy in this region. This is characteristic of metallic systems; i.e. materials with free charge carriers (3,14-16). Indeed, the electronic conductivity can be approximated from the extinction coefficient in this free carrier region (15,16). In contrast, there is very little change in absorbance for the pristine material in the energy region between ca. 1600 and 3000 cm^{-1}. Furthermore, the pristine material shows dramatically lower absorbance in this spectral region. This is to be expected because the undoped form is not an electronic conductor.

The pristine material appears, however, to retain some residual vestige of the rise in absorbance with energy characteristic of the doped form. However, this increase occurs at much higher energies (above 3000 cm^{-1} for the pristine materials vs. above 1600 cm^{-1} for the doped). Furthermore, as indicated above, the absorbance for the pristine material in this high energy region is dramatically lower. The slight increase in absorbance with energy for the pristine material may result from a small population of charge carriers extant at this very negative equilibrium potential. These charge carriers may be in pockets of trapped charge which are not at equilibrium with the electrode (17,18).

The pristine material also shows a very distinct band at ca. 3400 cm^{-1} (Figure 6). This band is completely buried by the free-carrier absorbance in the doped material and to, our knowledge, has not been described previously. This band is undoubtedly attributable to the N-H stretching vibration for the nitrogens in the pyrrole rings (19). A very weak band at ca. 3100 cm^{-1} also appeared in all of the pristine films we investigated (Figure 6). This band is undoubtedly attributable to the C-H stretching mode for the ring carbons (20). This band is also completely buried under the free-carrier absorption in the doped material.

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Both doped and pristine PPy show a series of bands at energies below 1600 cm^{-1}.

The most obvious difference between the doped and pristine materials in this region is the

dramatic decrease in intensity for all of these bands in the pristine material (compare Tables I

and II). Zerbi has recently used a parameter called the effective conjugation coordinate

(ECC) to calculate IR spectra for both doped and pristine PPy (8,9). Conceptually, the ECC

describes a situation in which all of the double bonds in the polymer stretch and all of the

single bonds shrink; i.e. the ECC describes a trajectory from the benzoid to the quinoid

configuration of the polymer (9). The benzoid and quinoid configurations are the ground

states for the pristine and doped forms, respectively (21).

All bands in the pristine material which have components corresponding to the ECC,

will be enhanced upon doping (9). Zerbi's calculations suggest that the A, B, D, and F

bands (Figures 3 and 6) will be enhanced via this route. Our experimental data (Figures 3

and 6, Tables I and II) show that this is indeed the case. In fact, however, the intensities of

all of the bands are enhanced upon doping. The C, E, and G bands appear in the doped

spectrum because they are infrared active modes of the fraction of the material which

remains undoped (in the predominantly doped material) or analogous modes unique to the

fraction of material which is doped (9). The increase in intensity of these bands with doping

may result from coupling of the vibrational modes with oscillations of the charge carriers in

the doped polymer (22). This vibration-charge carrier coupling enhances the absorbance for

the coupled-vibration and has been shown to be operative in a number of electronically

conductive organic solids (23-24).

The positions of the various bands also change upon doping. (Tables I and II). All of

the bands blueshift upon doping except the so-called bipolaron bands (D and F) (9), which

redshift. Redshifts upon doping have been observed for IR bands in conductive TCNQ salts

(23) and polyacetylene (24) and have been attributed to weakening of the bonds upon

removal of electrons from the material. Blueshifts for particular bands might be expected,

however, if the order for the bond associated with the vibration increased upon doping (e.g.

upon going from the benzoid to the quinoid configuration). Further theoretical work

concerning the specific molecular assignments for the IR bands in PPy is required before

these shifts in peak position can be fully interpreted.

Potential Dependence of the IR Spectrum. Figure 7 shows IR spectra for PPy after

equilibration at various potentials between the pristine and doped states. These spectra show

the evolution of the spectral trends discussed above. For example, note the steady decrease

in absorbance in the high energy region as the polymer is undoped and the concomitant

emergence of the N-H and C-H stretching bands. The continuous drop in intensity and

definition of the A' through G' bands is also seen.

We have recently shown that the relative intensities of the A' and B' bands for doped

PPy vary with the DC conductivity (σ_{dc}) of the polymer (16). This trend can be treated

quantitatively by ratioing the integrated absorption intensities of the A' and B' bands (16).

We call this parameter $I_{A'}/I_{B'}$. We have shown that $\log(\sigma_{dc})$ decreases linearly with increasing

$I_{A'}/I_{B'}$ (16). The same trend is observed in the spectra shown in Figure 7. Note that as the

doping level (and thus conductivity) decreases, the relative intensity of the B' band also

decreases. Again, this trend can be treated quantitatively by measuring the ratio $I_{A'}/I_{B'}$; $I_{A'}/I_{B'}$

values obtained from the spectra at 0.4, 0.3 and 0.1 V (decreasing doping level) are 3.0.

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4.3, and 11.1, respectively. We have interpreted this decrease in $I_A./I_B.$ with increasing conductivity in terms of the ECC model (16).

Comparison with Previous Spectra for Pristine PPy. To date their have been two previous reports of IR absorption spectra for pristine PPy (3,14). The most recent spectra were obtained for electrochemically synthesized and then electrochemically reduced films (14). The spectra obtained are, in fact, almost identical to the spectra we and others have obtained for the doped material (3,14). This indicates that these films have been air oxidized (i.e. doped).

Street et al. also presented spectra for "pristine" PPy (3). Their spectra show some of the characteristics of our pristine spectra. For example, the relative intensities of the various bands at energies below 1600 cm^{-1} have been attenuated. However, in the region between 1600 and 2400 cm^{-1}, these spectra still show the monotonic increase in absorbance with energy, characteristic of the doped material. Our pristine spectra do not show this monotonic rise in this energy region (see Figure 6). Hence, we believe that Street's spectra are also more characteristic of the doped material.

CONCLUSIONS

We have shown that contrary to earlier speculation (8,9), there is no inherent chemical reason which precludes the obtention of reproducible IR spectra for the pristine form of PPy. The only caveat is that pristine PPy is extremely reactive with air. We have presented IR spectra for the pristine material and have attempted a first order interpretation of these spectra based on results obtained for the pristine forms of other conductive polymers. We have also obtained spectra as a function of doping level. We hope that these

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new experimental data will aid theoreticians in their attempts to understand the electronic and

optical changes which occur when the pristine material is doped.

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Table I.   FTIR band positions and intensities for an as-synthesized (doped) PPy film and the same film after reduction (undoping) and reoxidation (doping).

Band Designation[a]	A'	B'	C'	D'	E'	F'	G'
Band Position (cm^{-1})							
As synth.	1541.2	1462.1	1320.2	1178.6	1047.4	900.8	790.9
Reoxidized	1541.2	1464.1	1319.7	1180.5	1049.3	902.7	788.5
Integrated Absorption Intensity							
As synth.	16.08	6.41	11.80	15.55	18.76	33.71	5.48
Reoxidized	16.99	5.97	13.84	16.33	19.15	33.69	5.62

[a] See B. Tian and G. Zerbi, J. Chem. Phys., 1990, 92, 3892.

Table II.   FTIR band positions and intensities for a pristine (undoped) PPy
film and for the same film after reoxidation and re-reduction.

Band Designation[a]	A	B	C	D	E	F	G

Band Position (cm^{-1})

	A	B	C	D	E	F	G
Undoped	1523.9	1440.9	1207.5	1076.3	1037.8	918.2	769.6
Reoxidized/re-reduced	1523.8	1438.1	1205.6	1072.5	1035.8	920.1	771.6

Integrated Absorption Intensity

	A	B	C	D	E	F	G
Undoped	3.89	0.69	3.20	3.86[b]	---[b]	1.61	2.09
Reoxidized/re-reduced	3.85	0.69	3.15	3.67[b]	---[b]	1.59	1.98

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[a] See B. Tian and G. Zerbi, J. Chem. Phys., 1990, 92, 3892.

[b] The D and E bands are not sufficiently resolved to allow for
separate intensities to be determined.

FIGURE CAPTIONS

FIGURE 1. Schematic diagram of spectroelectrochemical cell.

FIGURE 2. Infrared spectra for the cell (Ar-filled) before and after coating the front ZnSe window with the Pt working electrode film.
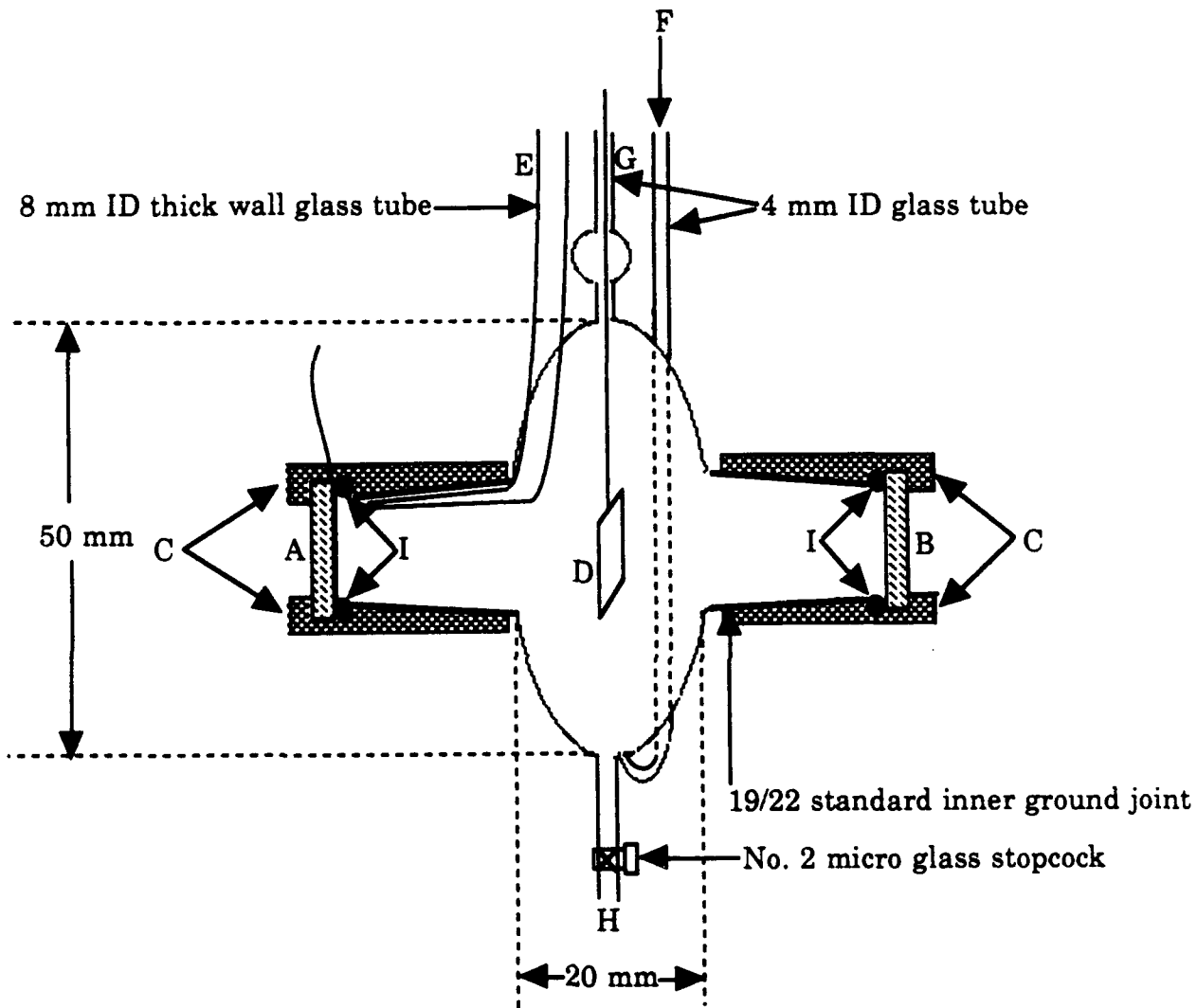
FIGURE 3. Infrared spectra for an as-synthesized (doped) PPy film and the same film after a reduction/re-oxidation (redoping) cycle. The as-synthesized spectrum was arbitrarily placed above the re-oxidized spectrum because these spectra were nearly coincident. Therefore, the ordinate is an arbitrary absorbance axis. Note absorbance marker above spectra.

FIGURE 4. Cyclic voltammograms for a reduced PPy film (A, upper) and for the same film after re-oxidation and re-reduction (B, lower).

FIGURE 5. Infrared spectrum for a pristine (undoped) PPy film after five minute exposure to air.

FIGURE 6. Infrared spectrum for a pristine (undoped) PPy film (upper) and for the same film after a re-oxidation and re-reduction cycle (lower). The upper spectrum was arbitrarily placed above the lower spectrum because these spectra were nearly coincident. Therefore, the ordinate is an arbitrary absorbance axis. Note absorbance marker above spectra.

FIGURE 7. Infra red spectra for a PPy film after equilibration at 0.3 V (A), 0.1 V (B), and -0.1 V (C).

8 mm ID thick wall glass tube

4 mm ID glass tube

50 mm

20 mm

19/22 standard inner ground joint

No. 2 micro glass stopcock

A: ZnSe disc with thin layer of Pt (25 mm in dia.)
B: ZnSe disc (25 mm in dia.)
C: Teflon sleeves used as window holder (32 mm in dia.)
D: Counter electrode
E: Compartment for reference electrode
F: Purging gas inlet
G: Purging outlet
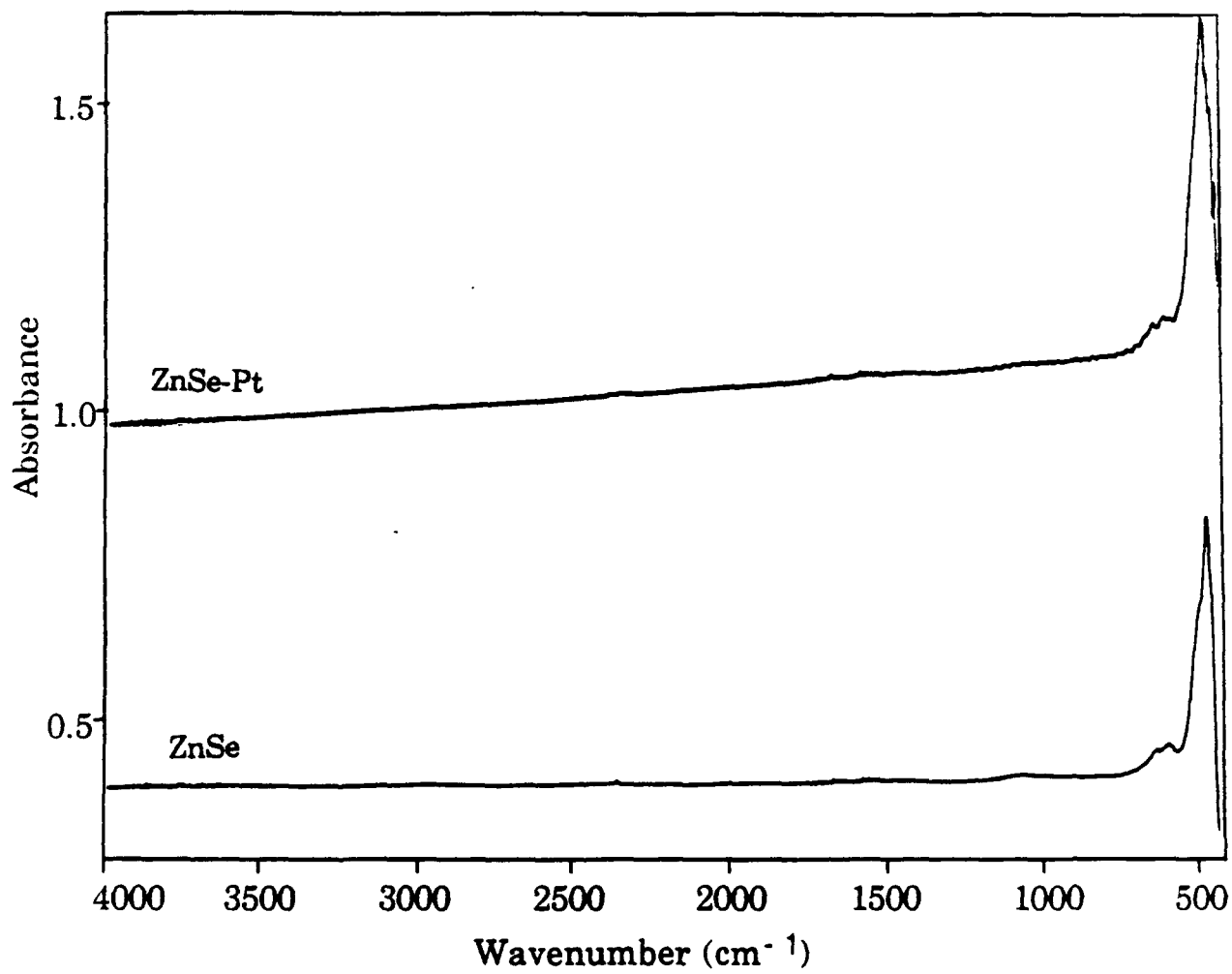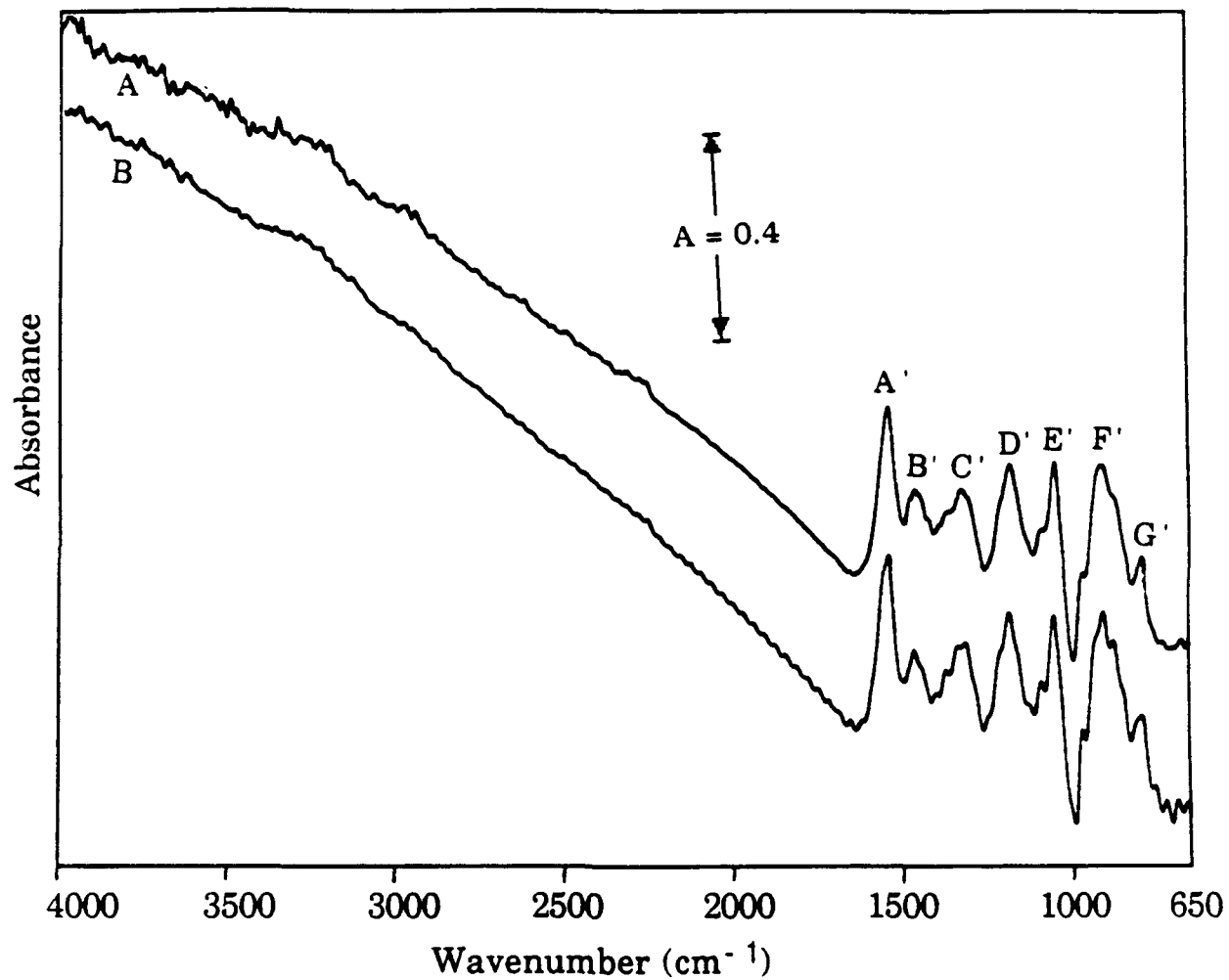H: Solution outlet
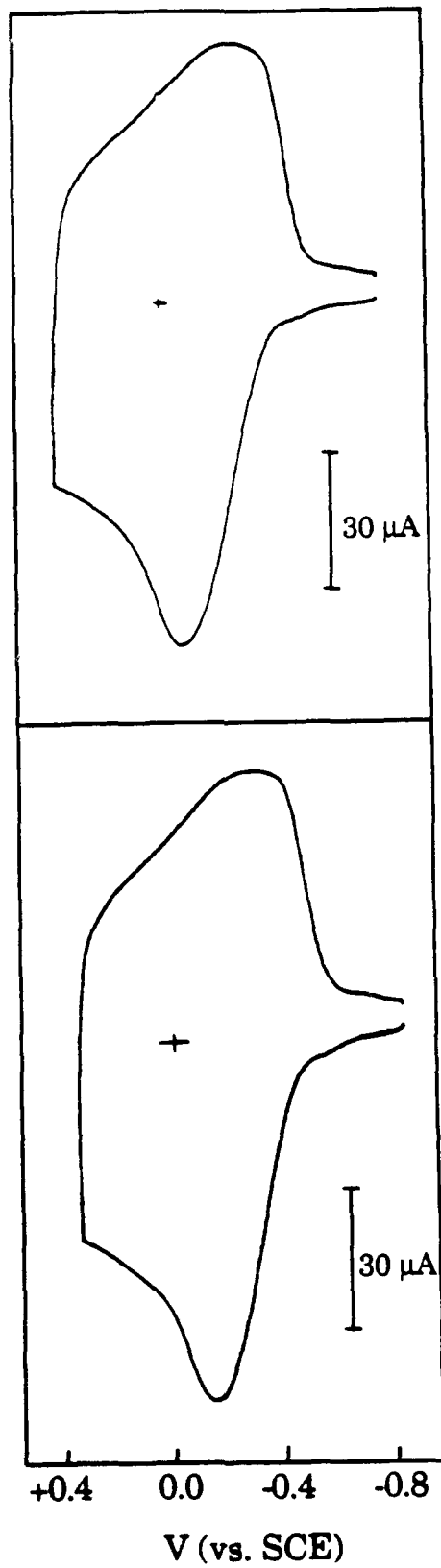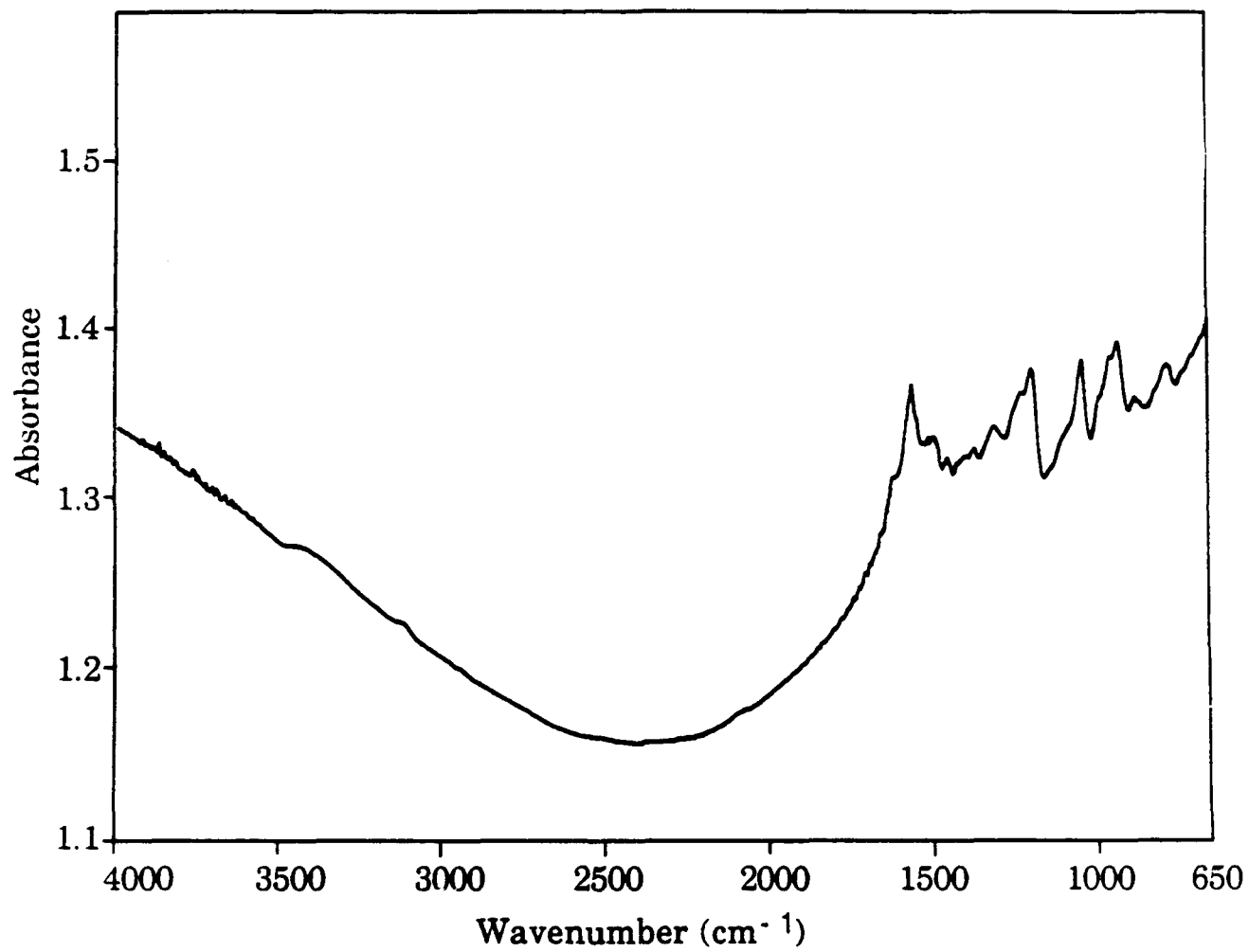I: "O" rings (16 mm in dia.)

Fig. 1

Fig. 2

Fig. 3

30 µA

30 µA

+0.4   0.0   -0.4   -0.8

V (vs. SCE)

Fig. 4

FIG 5

Fig. 5

Fig. 7