

Effect of the Substitution Pattern of Chloroanthraquinone on the Formation of Complex Salts with Silver

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Silver and 1- or 2-chloroanthraquinone (1-CAQ or 2-CAQ) were sequentially evaporated at a temperature of 300 K at the thickness ratio $t_{\text{Ag}}/t_{\text{CAQ}}$ 0.15. The deposited films were analyzed by means of optical absorption (IR, visible, near UV), Raman diffusion, X-ray diffraction, electron spin resonance, and X-ray photo-electron spectroscopy. The comparison of the results obtained with 2-CAQ and Ag/2-CAQ shows that no complex salt formation occurred between the Ag and the 2-CAQ superimposed layers. Using 1-CAQ under similar conditions, however, the results are in accordance with complex formation in superimposed layers with Ag. Interdiffusion and charge transfer (CT) are found to occur between silver and 1-CAQ. The degree of transfer is amplified by annealing. © 1996 Academic Press, Inc.

I. INTRODUCTION

Organometallic complex salts formed between Ag or Cu and either tetracyanoquinodimethane (TCNQ) or anthraquinone derivatives (AQD) have been attracting attention since these organic salts show high conductivity. Electrical (1–3) and optical (4–8) switching properties have been reported in complex salts of (Cu or Ag)/TCNQ and (Cu or Ag)/AQD.

Recently, it has been shown that charge-transfer complex salts Cu/TCNQ can be obtained by physical vapor deposition (9). In the present paper we show that the ability to form CT complex salts between sequentially deposited layers of Ag and CAQ is dependent on the substitution pattern of chlorine on the anthraquinone skeleton.

II. EXPERIMENTAL PROCEDURES

Films of chloroanthraquinone with a range of thickness from 0.5 to 1 μm were deposited on substrates under a dynamic vacuum of 10^{-4} Pa by heating in a tantalum boat. The chloroanthraquinones were purchased from Aldrich

(purity >98%) and were used without further purification. The substrates were polished glass, silica, NaCl and KBr single crystals, and stainless steel slides.

NaCl and KBr substrates were used for infrared and visible absorption studies, and silica substrates were used for optical absorption and electrical measurements. Stainless steel substrates were used for X-ray photoelectron spectroscopy (XPS) analysis. During deposition, the substrate temperature was monitored by a copper-constantan thermocouple attached with silver paste to the surface of the sample. In order to study the modification of the optical properties induced by Ag, thin films of this metal were deposited on or below the CAQ thin films without breaking the vacuum between the two evaporations. The evaporation rates and the thickness of the films were measured by the quartz vibration method. The thickness ratio $t_{\text{Ag}}/t_{\text{CAQ}}$ was about 0.15. When necessary, the samples were annealed *in situ*.

Films were identified by IR absorption and ^1H nuclear magnetic resonance (NMR-Bruker WM 250 MHz). XPS measurements were used to monitor the diffusion of silver in CAQ films. Optical measurements were carried out over the range 0.2–2 μm . For the Raman experiments, the apparatus used laser excitation with a wavelength $\lambda = 1064$ nm. The laser power and the number of scans necessary to obtain a good signal to noise ratio were 100 and 500 mW, respectively. The ESR experiments were carried out in a Bruker ER200 spectrometer operating at X bands.

III. RESULTS

It was shown previously that anthraquinone (AQ) and its derivatives (AQD) can be deposited by thermal evaporation without any decomposition (11–13). Therefore this technique was used in this work to obtain CAQ layers.

In order to study the influence of the chlorine substitution pattern on the formation of charge transfer complex

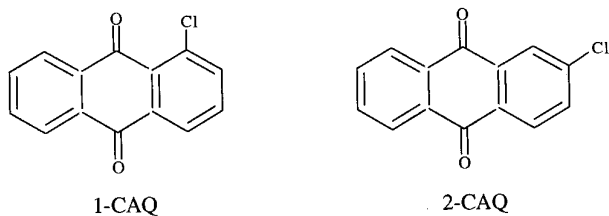


FIG. 1. Structures of the two chloroanthraquinones used.

salts, the experiments were performed on 1-CAQ and 2-CAQ (Fig. 1).

III.1. Experimental Results Obtained with 2-CAQ

The results obtained for Ag/2-CAQ after annealing 24 h at 340–350 K (Figs. 2–4) are similar to those obtained with the same samples before annealing. There is no modification either in the IR absorption and Raman diffusion spectra (Figs. 2 and 3) or in the optical absorption (Fig. 4) and X-ray diffraction (not shown) patterns.

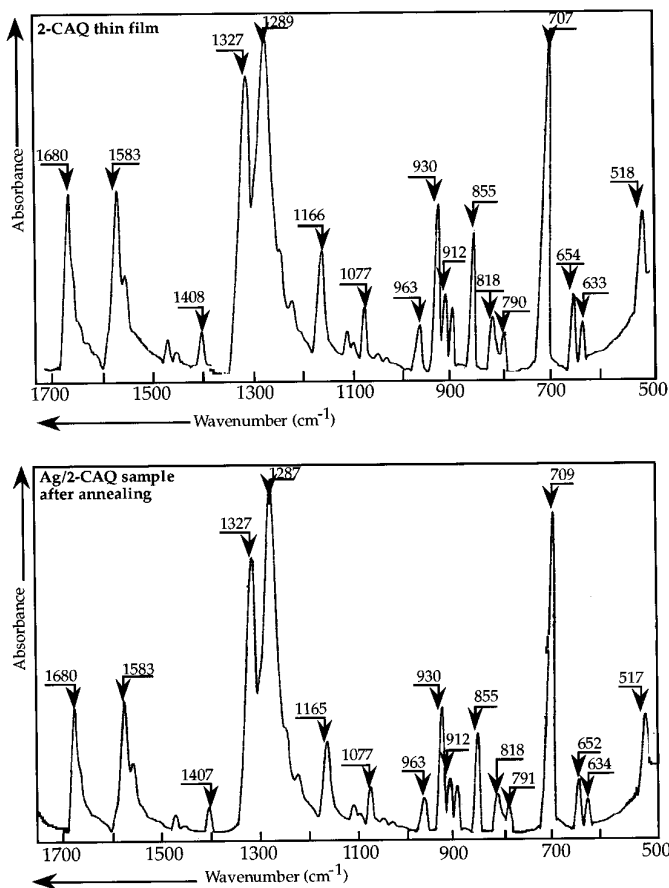


FIG. 2. Infra red spectra of 2-CAQ thin film and Ag/2-CAQ sample after annealing.

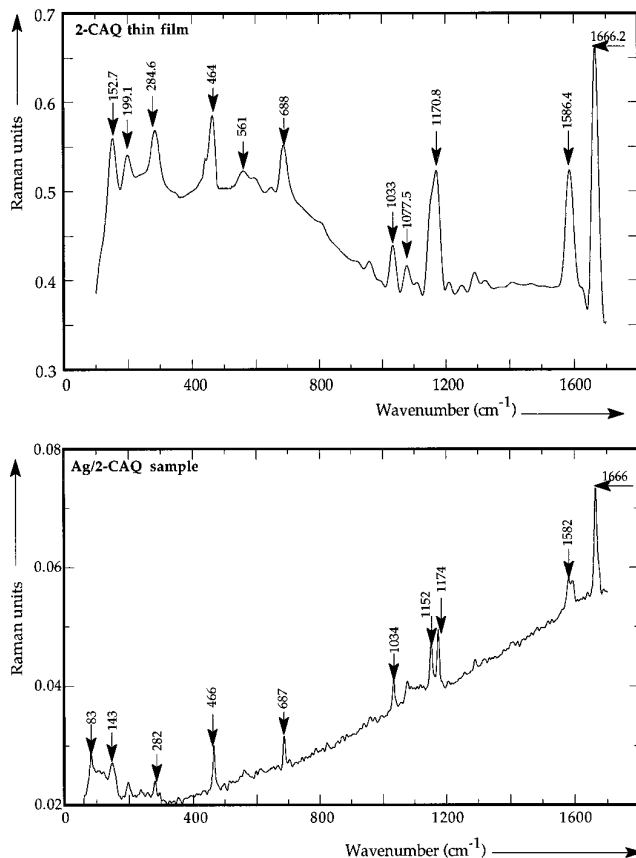


FIG. 3. Raman diffusion spectra of 2-CAQ thin film and Ag/2-CAQ sample.

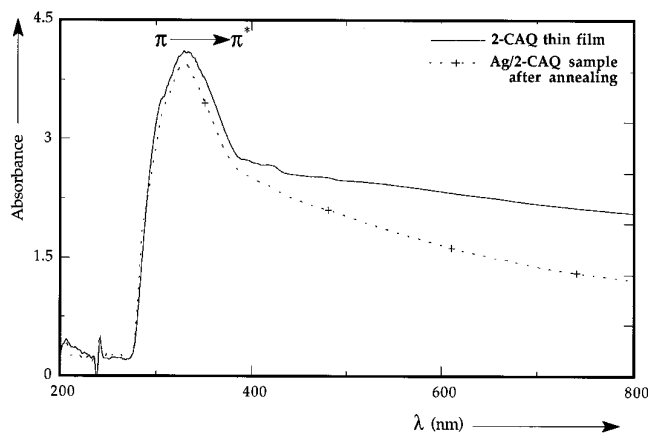


FIG. 4. Visible spectra of 2-CAQ thin film and Ag/2-CAQ sample after annealing.

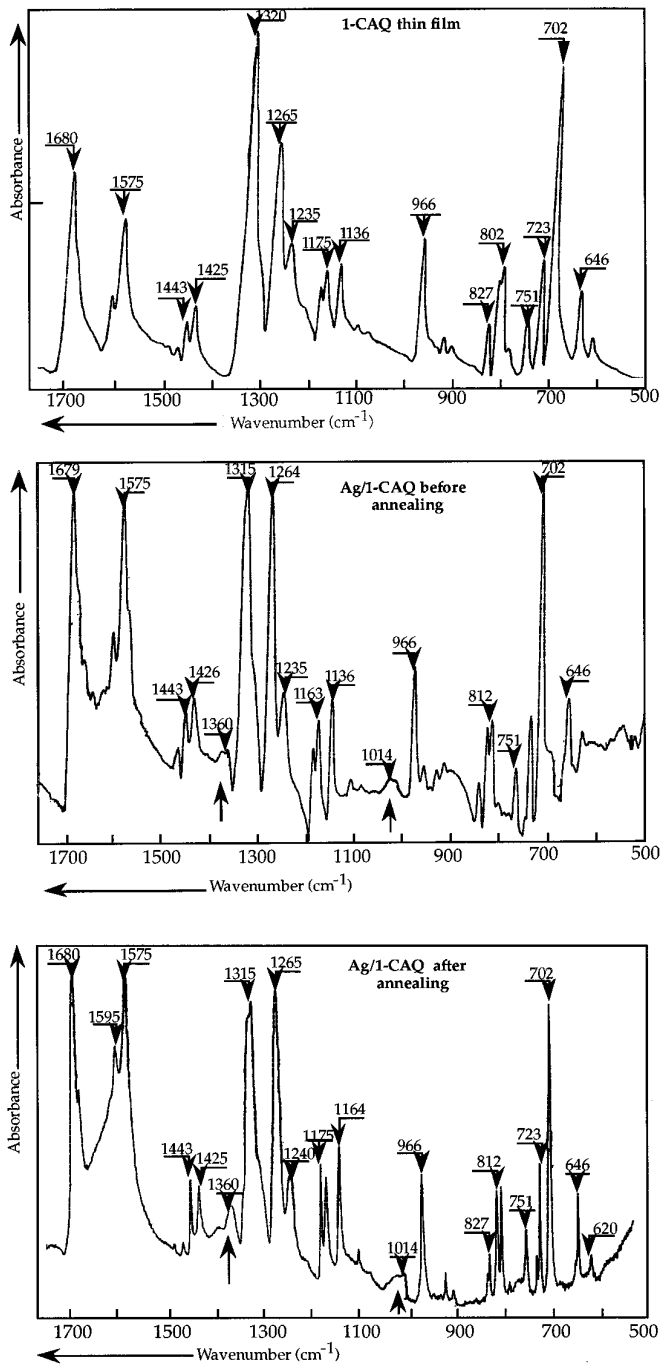


FIG. 5. Infrared spectra of 1-CAQ thin film, Ag/1-CAQ sample before annealing, and Ag/1-CAQ sample after annealing.

The results obtained with pure 2-CAQ films are also reported in these figures.

III.2. Experimental Results Obtained with 1-CAQ

The results obtained with 1-CAQ are reported in Figs. 5–9. Differences are observed between the properties of

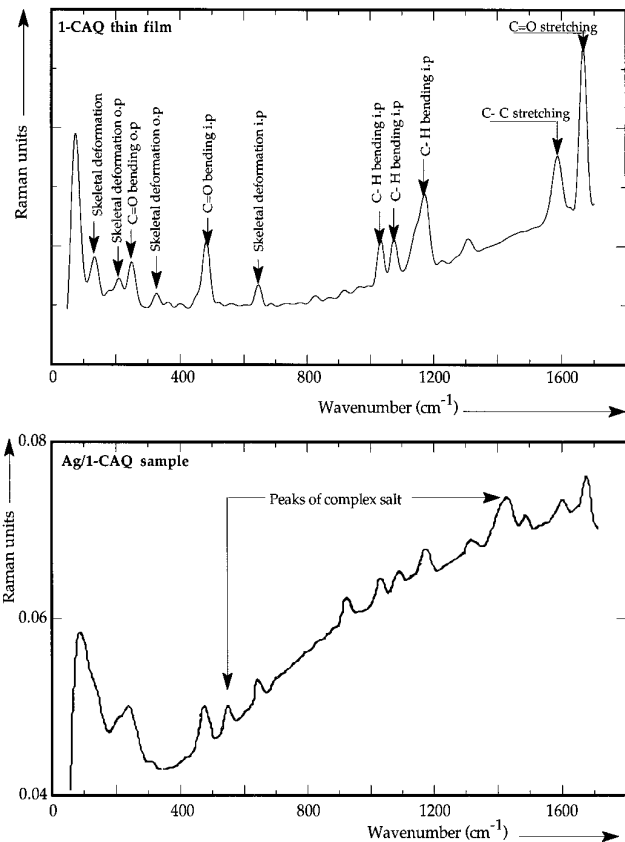


FIG. 6. Raman diffusion spectra of 1-CAQ thin film and Ag/1-CAQ sample.

pure 1-CAQ and Ag/1-CAQ layers. After annealing, these differences are enhanced. The IR absorption spectra show two broad bands appearing at 1360 and 1014 cm^{-1} (Fig. 5). Similarly in the Raman diffusion spectra two new absorptions are detected at 1422 and 553 cm^{-1} (Fig. 6). In

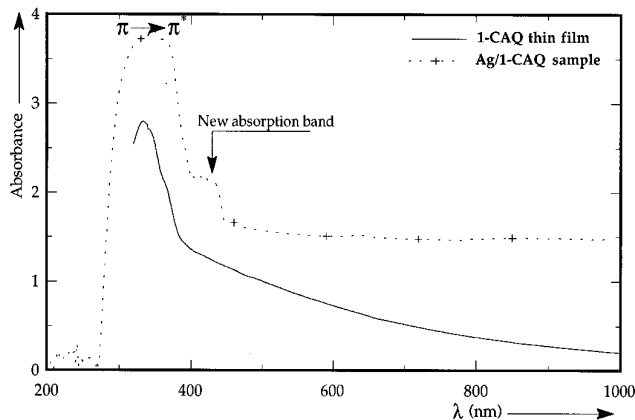


FIG. 7. Visible spectra of 1-CAQ thin film and Ag/1-CAQ sample.

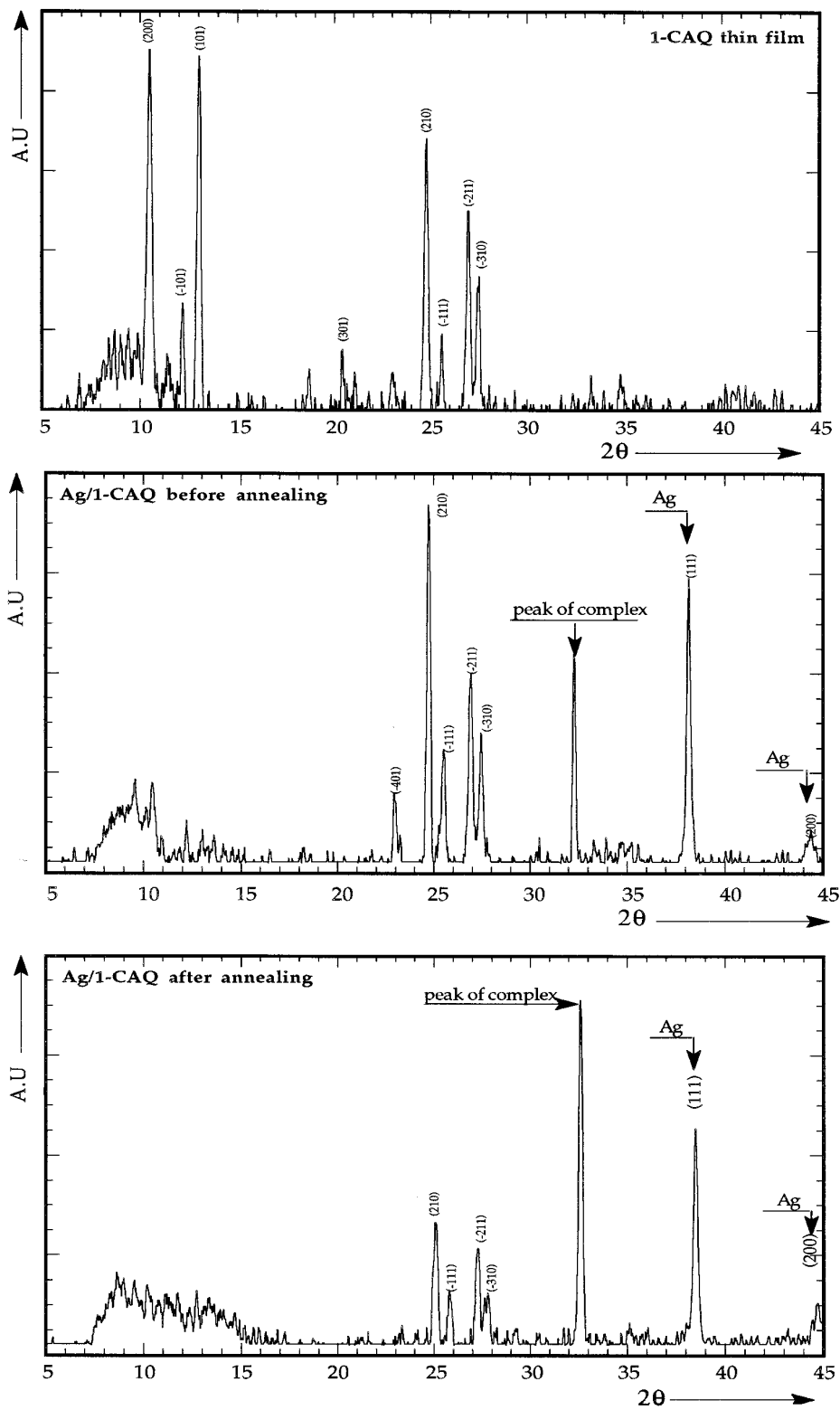


FIG. 8. X-ray diffraction patterns of 1-CAQ thin film, Ag/1-CAQ sample before annealing, and Ag/1-CAQ sample after annealing.

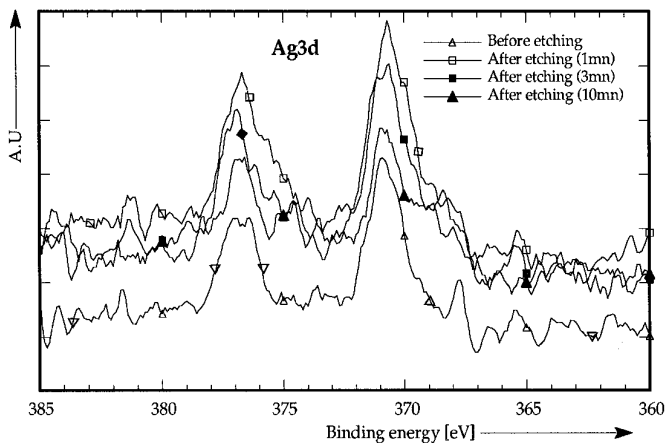


FIG. 9. XPS depth profiling of an Ag/1-CAQ sample after an annealing.

the optical absorption spectra a red shift of the absorption threshold and/or the existence of a new absorption band in the visible region is observed (Fig. 7).

In the case of X-ray diffraction (XRD) a new characteristic signal appears at 32° (Fig. 8). The etching profile of a 1-CAQ film evaporated on a silver layer without breaking the vacuum between the two depositions is shown in Fig. 9: notice that the peaks of the doublet are asymmetric, and that the silver has diffused in the 1-CAQ films since silver is visible by XPS even before etching.

No ESR signal can be detected in the case of pure 1-CAQ films (Fig. 10). In the case of Ag/1-CAQ structures a signal appears with $g = 2.20$.

IV. DISCUSSION

Since no significant difference is observed between the spectroscopic behavior of pure 2-CAQ films and Ag/2-CAQ samples, it can be concluded that no complex forma-

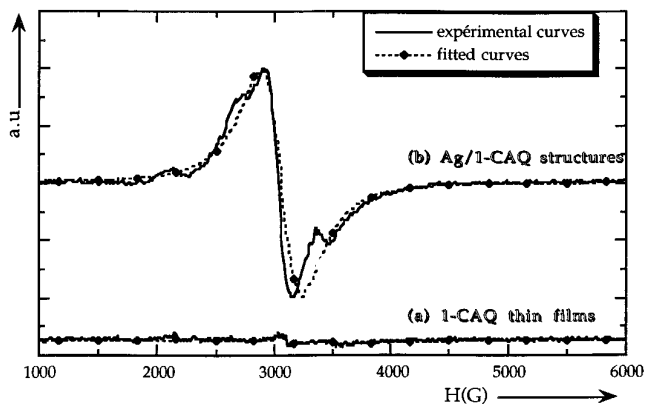


FIG. 10. ESR spectrum of (a) 1-CAQ films and (b) Ag/1-CAQ films.

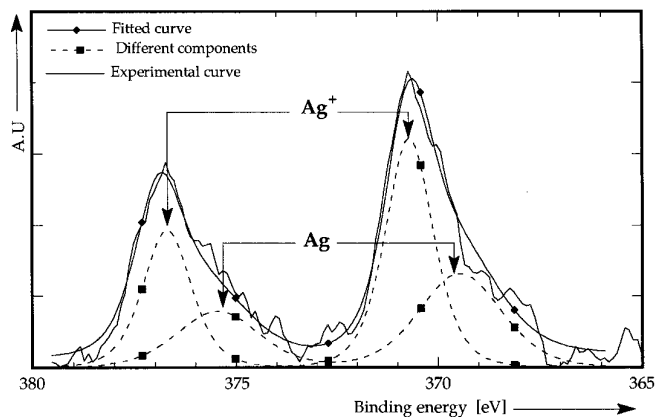


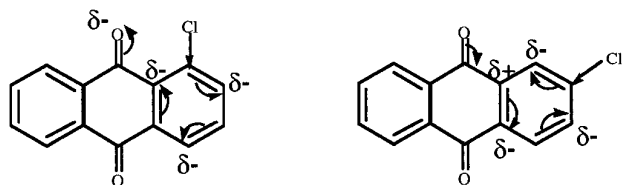
FIG. 11. Result of the Ag 3d curve fitting (—) experimental curve, (—◆—) fitted curve, (---) different components.

tion occurs between Ag and the 2-CAQ superimposed layers.

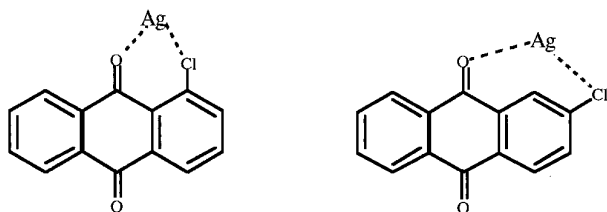
In the case of 1-CAQ, however, the existence of broad features in the IR and Raman spectra and of a broad band in the optical spectra are characteristic of the presence of the complex. The formation of a new structure is corroborated by the presence of a new XRD peak (7) and the ESR signal which appears only in the structure Ag/1-CAQ and not in pure 1-CAQ or pure Ag. The signal can be attributed to $\text{Ag}^{\delta+}$. The charge transfer within the complex can be studied by XPS analysis. Due to the rather small Ag/CAQ ratio, however, the modification induced on the C 1s peak is not easy to quantify. Moreover it is quite difficult to assess the charge distribution in the 1-CAQ anion through the XPS results. Indeed, before etching, the surface is more or less contaminated and after this operation the molecule is partly destroyed since there is a preferential action on the chlorine and on the oxygen. However the silver 3d doublet can be studied.

It is well known that the binding energy of the Ag 3d XPS doublet peak is poorly sensitive to the charged state of the silver. However, information can be extracted from XPS measurements (14). The peaks of the Ag 3d doublets have been decomposed into different components and quantitative interpretation was made after subtraction of the background using the Shirley method (15). The developed curve-fitting problems permit the variation of parameters such as the Gaussian/Lorentzian ratio, the full width at half maximum (FWHM), and the position and intensity of the components. Thus, the Ag 3d doublet can be decomposed into two doublets (see Fig. 11). The logical interpretation of this result is that the doublet with the higher energy can be attributed to the silver after charge transfer complex Ag/1-CAQ while the remaining doublet corresponds to the neutral silver.

It is well known that the first absorption band of the



The electronic density on the oxygen atom is higher when the chlorine atom is in the 1-position than in the 2 one.



1-CAQ : favorable positions of the oxygen and the chlorine atoms

2-CAQ : unfavorable positions of the chlorine and of the oxygen atoms

FIG. 12. Mesomeric effect of the chlorine substituant in the CAQ molecules and a possible mechanism of formation of the transfer complex salt.

AQD is an allowed $\pi \rightarrow \pi^*$ transition arising from the aromatic ring. The red shift of this bond should correspond to a modification of the electron density of the carbonyl oxygen of the quinone group (16). The ability of the AQD to induce charge transfer complexes with silver is highly dependent on the electronic distribution around the aromatic skeleton and consequently on the charge carried by the oxygen atom of the carbonyl group. In the case of 1-CAQ, the positive mesomeric effect exerted by the chlorine atom can explain the formation of the charge transfer complex (see Fig. 12 below). Thus the electronic distribution on the aromatic skeleton will have some influence on the complex formation, but the more important fact remains the relative positions of the oxygen and of the chlorine atoms. The chlorine who bears also electronic doublets very probably participates in the charge transfer complex formation. When the chlorine atom is in the 1-position, the silver atom is able to exchange electrons with the oxygen and with the chlorine atoms thus building a favorable pseudo-cyclic six-membered ring. Such a configuration is not possible with 2-CAQ (see Fig. 12).

V. CONCLUSION

It has been shown that a sequentially deposited CAQ/Ag layer can form a charge transfer complex salt. However the occurrence of the reaction is dependent on the position of the chlorine substituant in the anthraquinone molecule. This phenomenon can be explained by mesomeric effects and the substituent pattern of the chloroanthraquinone. The present study has shown that the transfer is improved by annealing treatment. However it seems that some problems, like the exact knowledge of the ratio between silver and 1-chloroanthraquinone, have to be overcome in order to obtain reproducible charge transfer between silver and 1-CAQ.

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