

# Comparing Assignment of the Diffuse Reflectance Infrared Fourier Transform Spectra of Silver Surface Complexes with Solid Silver Compounds\*

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## Abstract

The diffuse reflectance infrared fourier transform spectroscopic technique has been applied to analyse the adsorbed surface complexes, formed in the oxidation of acetaldehyde, by comparing the DRIFT-spectra of the reaction intermediates to those of four different solid silver compounds. Most characteristic IR bands obtained were clearly assigned on all the solid silver compounds, advantageously in the lower frequency region of IR bands compared to the traditional IR transmission technique.

This comparative analysis of the spectra for the intermediates strongly suggests the existence of at least three different species. One of the species can certainly be assigned to a silver acetate form. Based on the transient response data, it has been evaluated that the silver acetate form intermediate gives a surface coverage of more than  $\theta=0.5$  to 1.3 at 160°C depending on the reaction conditions. As other possible species, a strong adsorbed acetaldehyde and an alcohol-like species are also considered.

## 1. Introduction

As has been pointed out, in general, it is not easy to clearly detect the adsorbed intermediates on silver in the oxidation of ethylene at industrial reaction temperatures. For that reason, one may find that there is little adsorption because of the much smaller surface area, and the difficulty of IR transmission in the pressed silver samples using the traditional transmission technique.<sup>1-3)</sup>

In our previous papers, we showed that when the oxidation of ethylene is performed at a temperature below 110 C, some stable adsorbed intermediates are formed in appreciable quantities on the surface, which were confirmed to be the true reaction intermediates in the oxidation of ethylene.<sup>4,5)</sup> It was also confirmed that the same intermediates are formed on the surface during the oxidation of acetaldehyde, and an advantage is that the amounts are from two to a hundred times larger than those in ethylene oxidation. A new in-situ cell for the diffuse reflectance infrared fourier transform spectroscopy (DRIFITS) was developed and effectively used to analyse such intermediates, and the typical spectra obtained

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were shown in the previous papers.<sup>6-8)</sup> It was suggested that it could be speculated that one of the stable intermediates is an acetic acid like form.<sup>6-10)</sup>

In the present study, to correctly assign the intermediates in detail, the new in-situ cell of the DRIFTS is used and four different silver compounds are used to compare their IR bands with those of the intermediates. This comparative assignment should be useful and effective for distinguishing the mixed adsorbed compounds. In addition, the traditional transmission technique is also employed to support the conclusions from the DRIFTS.

## 2. Experimental

### 2-1. Preparation of Solid Silver Compounds and a Silver Catalyst

Three silver compounds, silver acetate, silver lactate and silver carbonate, from Wako Pure Chemical Industries Ltd. were used in special grade reagents. Silver ketenide was prepared from a silver acetate solution. 0.5 g of  $\text{CH}_3\text{COOAg}$  was completely dissolved into 1 ml of pyridine, followed by adding 2ml of acetic anhydride and yellow precipitate thereby was formed. The yellow sample was carefully and slowly washed with 50 ml of acetic anhydride solution and dried at room temperature for 24 hrs, followed by an evacuation for 24 hrs in a dark room. Finally, this sample was stored in a desiccator and supplied for the experiments.

The detailed preparation procedure of the silver catalyst used for the oxidation of acetaldehyde will be found elsewhere.<sup>11)</sup>

### 2-2. Preparation of the sample for the DRIFTS

The samples, four solid silver compounds and the silver catalyst which had been used in acetaldehyde oxidation, were ground so as to be under 400 mesh. The fine powder was mixed well into KBr powder (under 400 mesh) with the composition of 5 wt% - Ag of solid silver samples. More detailed preparation procedure will be found elsewhere.<sup>7,8)</sup>

### 2-3. Experimental Procedure

The FT-IR spectrophotometer and the diffuse reflectance device used were JIR 40X and IR-DRA 11 (JEOL), respectively. Model 260-80 (Hitachi Ltd.) was used for the traditional IR transmission technique. For the DRIFTS experiment, the new in-situ IR cell,<sup>8)</sup> which was developed for the transient experiment to simultaneously follow the adsorption and reactivity of the intermediates, was used throughout. All the IR spectra of the sample were obtained in a He stream (30 ml/min) at room temperature. The resolution and scanning times were  $8\text{ cm}^{-1}$  and one hundred, respectively. The measuring time for one spectrum was about 5.5 minutes, meaning an average value of IR absorption obtained for this period.

### 3. Results and Discussion

#### 3-1. Assignment of the DRIFT Spectra of the Reaction Intermediates in the Oxidation of Acetaldehyde

The oxidation of acetaldehyde on silver proceeds slowly at  $130\text{ C} < T < 160\text{ C}$ , and rapidly at  $180\text{ C} <$ , and the existence of the reaction intermediates has frequently been confirmed by using the transient response method<sup>6)</sup>. Their amounts decrease with the reaction temperature and oxygen pressure. Assuming that one molecule of the intermediates occupies two surface adsorbed atomic oxygens, then the surface coverage of the intermediates is easily evaluated  $\theta = 0.2$  to  $1.5$  by the graphical integration of the transient response curves of the intermediates combustion in the  $\text{O}_2$  stream, depending on the partial pressures of  $\text{CH}_3\text{CHO}$  and  $\text{O}_2$  and reaction temperatures. These surface coverages correspond to  $1.8 \sim 13.5 \times 10^{-4}$  mg-In/mg-Ag. These amounts seem to be sufficient to be detected by the FT-IR spectroscopy.

To clearly detect the adsorbed species by the DRIFTS, the reaction conditions,  $160\text{ C}$  and the gas composition of  $\text{CH}_3\text{CHO}$  (20%)– $\text{O}_2$  (20%)–He, were chosen. 20 mg of the catalyst-KBr powder sample was put on a sample holder and the temperature was raised up to  $160\text{ C}$  in a He stream in about two hours. At  $160\text{ C}$ , the stream was changed stepwisely into the reaction gas mixture and the sample was kept in the mixture for five hours. The sample was then flushed by the pure He stream for one hour and the IR spectra were then followed.

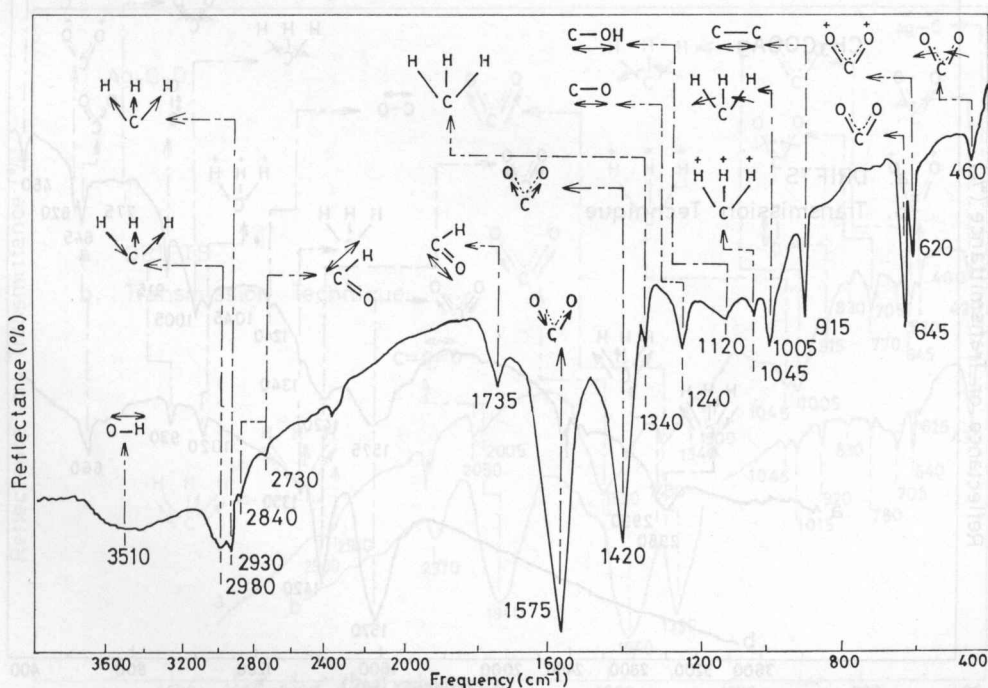


Fig. 1. DRIFT spectrum of the intermediates formed in  $\text{CH}_3\text{CHO}$  oxidation.

Fig. 1 shows the reflectance bands of the reaction intermediates in acetaldehyde oxidation. One may clearly recognize three different groups of the characteristic absorption bands, the first species of which is assigned to silver acetate: the bands of  $1420$  and  $1575\text{ cm}^{-1}$  correspond to the stretching vibration of  $\text{COO}$ ;  $460, 620$  and  $645\text{ cm}^{-1}$  to the bending vibration of  $\text{COO}$ ;  $2930$  and  $2980\text{ cm}^{-1}$  to the stretching vibration of  $\text{CH}_3$ ;  $1005, 1045$  and  $1340\text{ cm}^{-1}$  to the rocking vibration of  $\text{CH}_3$ . The second species can be proposed to be the strongly adsorbed acetaldehyde: the bands of  $2730$  and  $2840\text{ cm}^{-1}$  correspond to the  $\text{CH}$  stretching vibration of  $\text{CHO}$ ;  $1735\text{ cm}^{-1}$  to the stretching vibration of  $\text{C=O}$ . The third species may be assigned to an alcohol type from  $1120\text{ cm}^{-1}$  for the  $\text{CO}$  stretching vibration of  $\text{C-OH}$ .

### 3-2. Assignments of the DRIFTS Spectra of Solid Silver Compounds

Fig. 2 represents the IR spectra of solid silver acetate, comparing two techniques, DRIFTS and the transmission technique. As can be seen from the spectra in the figure, two characteristic groups resulting from the absorptions of  $\text{CH}_3$  and  $\text{COO}$  may clearly and easily be recognized, though in the transmission technique there are no higher frequency region bands,  $2930$  and  $2980\text{ cm}^{-1}$ . The comparison of the two techniques definitely shows the advantage of DRIFTS rather than the transmission technique.

Fig. 3 shows the IR spectra of silver lactate. In the spectrum *a* which is

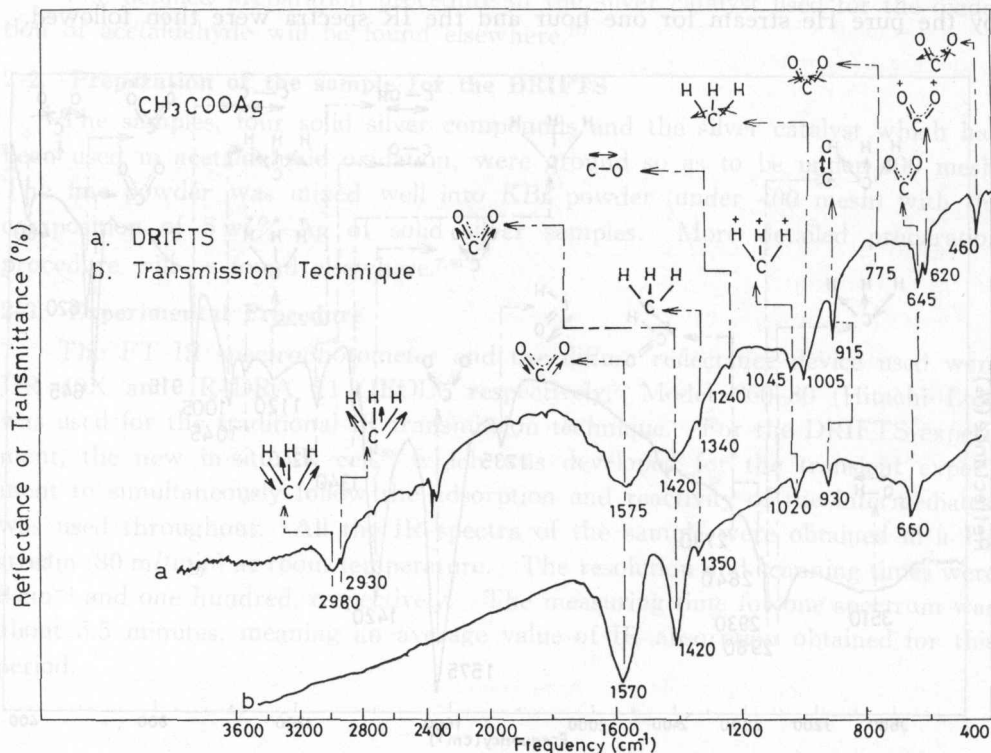


Fig. 2. IR spectra of  $\text{CH}_3\text{COOAg}$  by the DRIFTS and the transmission technique.

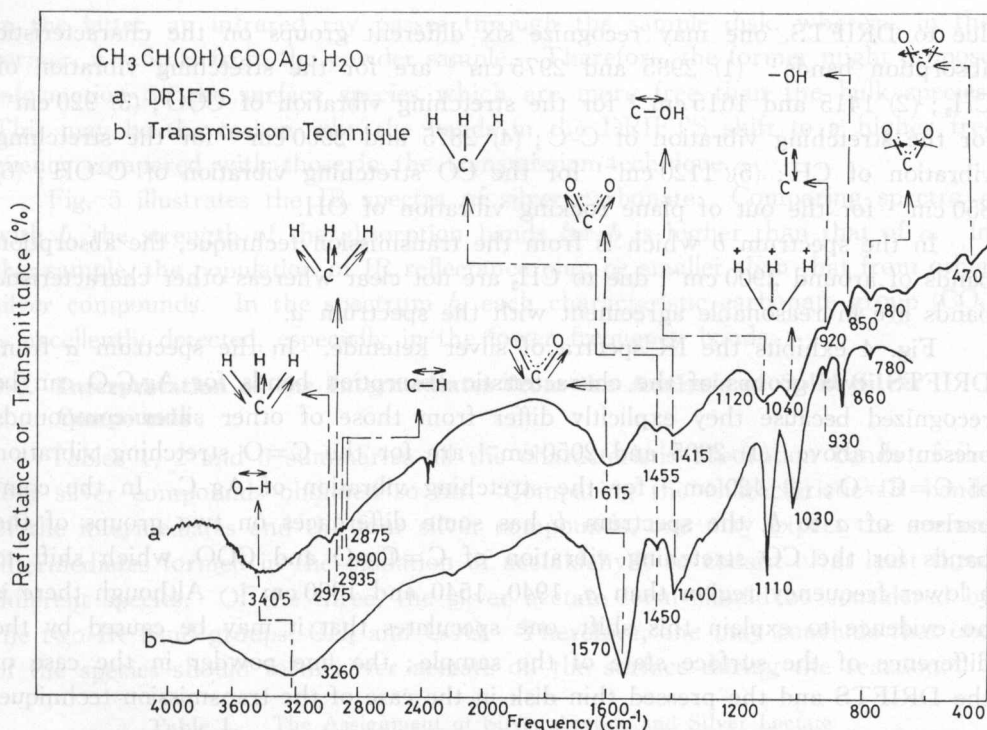


Fig. 3. IR spectra of CH<sub>3</sub>CH(OH)COOAg·H<sub>2</sub>O by the DRIFTS and the transmission technique.

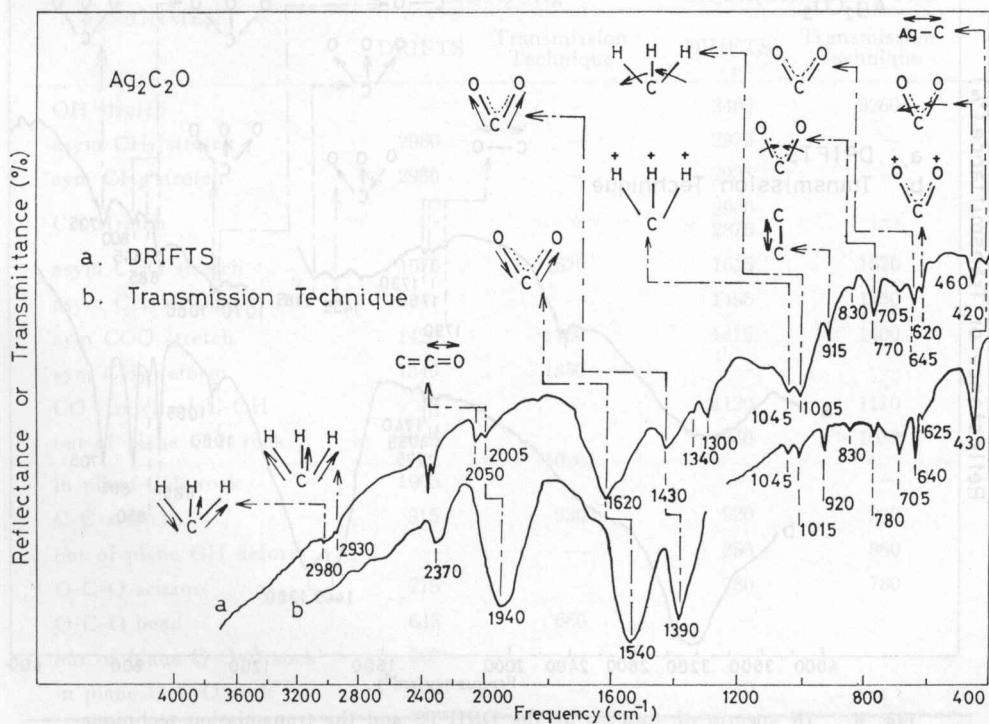


Fig. 4. IR spectra of Ag<sub>2</sub>C<sub>2</sub>O by the DRIFTS and the transmission technique.



due to DRIFTS, one may recognize six different groups on the characteristic absorption bands: (1) 2935 and 2975  $\text{cm}^{-1}$  are for the stretching vibration of  $\text{CH}_3$ ; (2) 1415 and 1615  $\text{cm}^{-1}$  for the stretching vibration of  $\text{COO}$ ; (3) 920  $\text{cm}^{-1}$  for the stretching vibration of  $\text{C-C}$ ; (4) 2875 and 2900  $\text{cm}^{-1}$  for the stretching vibration of  $\text{CH}$ ; (5) 1120  $\text{cm}^{-1}$  for the  $\text{CO}$  stretching vibration of  $\text{C-OH}$ ; (6) 850  $\text{cm}^{-1}$  for the out of plane rocking vibration of  $\text{OH}$ .

In the spectrum *b* which is from the transmission technique, the absorption bands of around 2900  $\text{cm}^{-1}$  due to  $\text{CH}_3$  are not clear whereas other characteristic bands are in reasonable agreement with the spectrum *a*.

Fig. 4 exhibits the IR spectra of silver ketenide. In the spectrum *a* from DRIFTS, two groups of the characteristic absorption bands for  $\text{Ag}_2\text{C}_2\text{O}$  can be recognized because they explicitly differ from those of other silver compounds presented above: (1) 2005 and 2050  $\text{cm}^{-1}$  are for the  $\text{C=O}$  stretching vibration of  $\text{C=C=O}$ ; (2) 420  $\text{cm}^{-1}$  for the stretching vibration of  $\text{Ag-C}$ . In the comparison of *a* to *b*, the spectrum *b* has some differences on two groups of the bands for the  $\text{CO}$  stretching vibration of  $\text{C=C=O}$  and  $\text{COO}$ , which shift to a lower frequency region than *a*, 1940, 1540 and 1390  $\text{cm}^{-1}$ . Although there is no evidence to explain this shift, one speculates that it may be caused by the difference of the surface state of the sample; the fine powder in the case of the DRIFTS and the pressed thin disk in the case of the transmission technique.

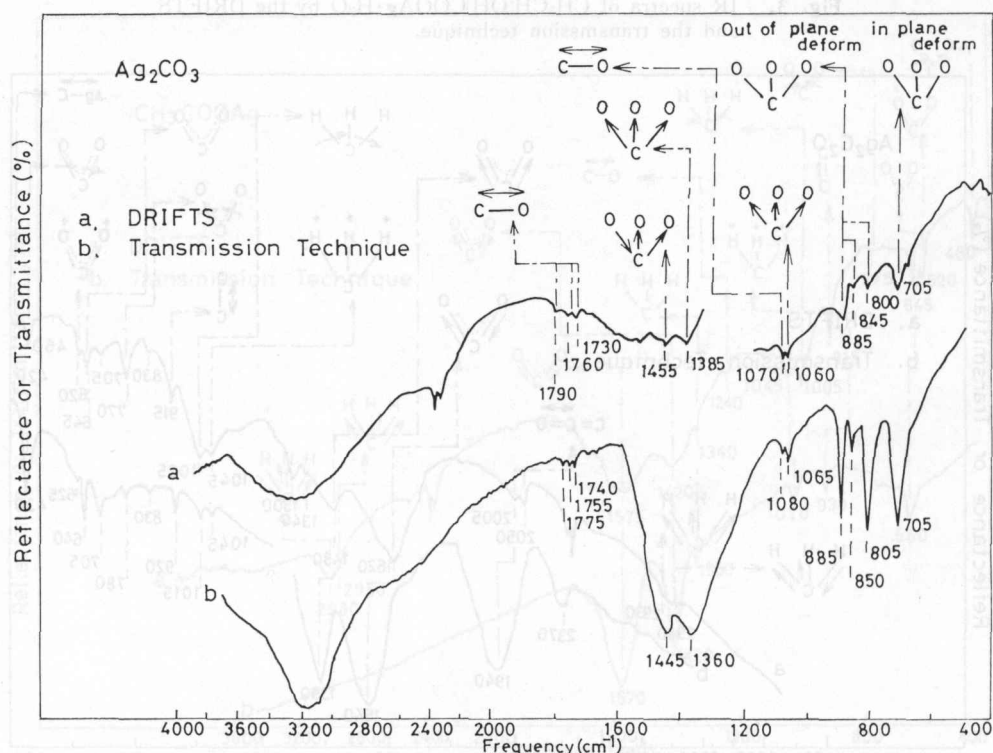


Fig. 5. IR spectra of  $\text{Ag}_2\text{CO}_3$  by the DRIFTS and the transmission technique.

In the latter, an infrared ray passes through the sample disk, whereas, in the former, it reflects from the powder sample. Therefore, the former might propose information on the surface species which are more free than the bulk species. This may be the reason why the bands in the DRIFTS shift to a higher frequency compared with those in the transmission technique.

Fig. 5 illustrates the IR spectra of silver carbonate. Comparing spectra *a* with *b*, the strength of the absorption bands for *b* is higher than that of *a*. In this sample, the population of IR reflectance may be smaller than that from other silver compounds. In the spectrum *b*, each characteristic carbonate group ( $\text{CO}_3$ ) is excellently detected, especially in the lower frequency bands.

### 3-3. Interpretation of the Intermediates from the Analysis of Solid Silver Compounds

Tables 1, 2 and 3 summarize all the characteristic absorption bands of the four silver compounds obtained so far. Comparing the characteristic IR bands of the intermediates and the four silver compounds, one may expect the surface intermediates formed in the oxidation of acetaldehyde to consist of at least three different species. Of the three, the silver acetate form should be considered by the two IR band groups,  $\text{CH}_3$  and  $\text{COO}$ . Therefore, one may conclude that one of the species should form silver acetate on the surface during the reaction.

Table 1. The Assignment of Silver Acetate and Silver Lactate

ASSIGNMENT	FREQUENCY ( $\text{cm}^{-1}$ )			
	$\text{CH}_3\text{COOAg}$		$\text{CH}_3\text{CH}(\text{OH})\text{COOAg}\cdot\text{H}_2\text{O}$	
	DRIFTS	Transmission Technique	DRIFTS	Transmission Technique
OH stretch	—	—	3405	3260
asym $\text{CH}_3$ stretch	2980	—	2975	—
sym $\text{CH}_3$ stretch	2930	—	2935	—
CH stretch	—	—	2900 2875	—
asym $\text{COO}$ stretch	1575	1570	1615	1570
asym $\text{CH}_3$ deform	—	—	1455	1450
sym $\text{COO}$ stretch	1420	1420	1415	1400
sym $\text{CH}_3$ deform	1340	1350	—	—
CO stretch of C-OH	—	—	1120	1110
out of plane $\text{CH}_3$ rock	1045	—	1040	1030
in plane $\text{CH}_3$ rock	1005	1020	—	—
C-C stretch	915	930	920	930
out of plane OH deform	—	—	850	860
O-C-O scissor	775	—	780	780
O-C-O bend	645	660	—	—
out of plane O-C-O rock	620	—	—	—
in plane O-C-O rock	460	—	470	—

**Table 2.** The Assignment of Silver Ketenide

ASSIGNMENT	FREQUENCY (cm <sup>-1</sup> )	
	DRIFTS	Transmission Technique
asym CH <sub>3</sub> stretch	2980	—
sym CH <sub>3</sub> stretch	2930	—
CO stretch of C=C=O	2050	1940
	2005	
asym COO stretch	1620	1540
sym COO stretch	1430	1390
sym CH <sub>3</sub> deform	1340	—
out of plane CH <sub>3</sub> rock	1045	1050
in plane CH <sub>3</sub> rock	1005	1015
C-C stretch	915	915
ring bend of pyridine	830	830
	705	705
O-C-O scissor	770	780
O-C-O bend	645	640
out of plane O-C-O rock	620	625
in plane O-C-O rock	460	—
Ag-C stretch	420	430

**Table 3.** The Assignment of Silver Carbonate

ASSIGNMENT	FREQUENCY (cm <sup>-1</sup> )	
	DRIFTS	Transmission Technique
CO stretch of Bidentate	1790	1775
	1760	1755
	1730	1740
asym COO stretch of Monodentate	1455	1445
sym COO stretch of Monodentate	1385	1369
CO stretch of Monodentate	1070	1080
sym COO stretch of Bidentate	1060	1065
out of plane CO <sub>3</sub> deform	885	885
	845	850
	800	805
in plane CO <sub>3</sub> deform	705	705

For the other possible species, the comparison of the absorption bands of other three silver compounds to the intermediates does not propose any similarity, indicating no similar species exists on the surface. More detailed analysis and another technique to detect the fine structure of the intermediates will be necessary to reach a concrete conclusion. This problem will be reported separately with some new experimental evidence and analysis.



#### 4. Conclusion

It is clearly confirmed that the new IR cell developed for DRIFTS effectively analyses surface species of solid silver compounds. The lower frequency region of IR absorption bands is more clearly and excellently displayed than in the transmission technique. The surface organic silver complexes are extensively assigned by comparing the characteristic absorption bands of solid silver compounds.

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