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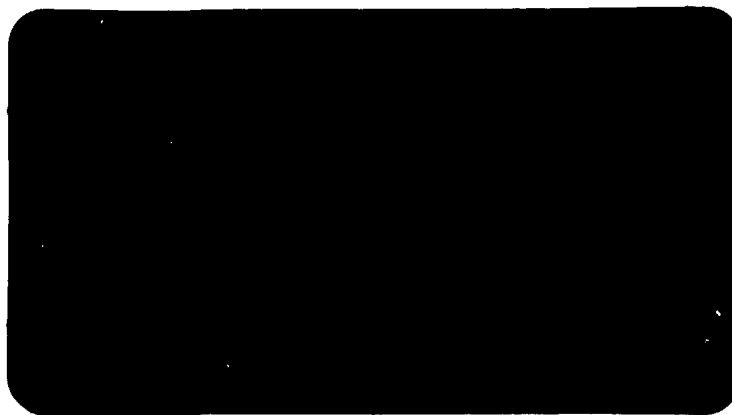
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ON THE PHOTOFRAGMENTATION OF $\text{Fe}(\text{CO})_5$: I.
INFRARED AND MÖSSBAUER EVIDENCE FOR THE
FORMATION OF $\text{Fe}(\text{CO})_4$ IN POLYMER MATRICES

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ABSTRACT

Pentacarbonyliron sorbed in low density polyethylene (LDPE) or polytetrafluorethylene (PTFE) and irradiated with ultraviolet light has been studied by infrared and Mössbauer spectroscopies. The main photofragment reacts with the residual pentacarbonyliron leading to the formation of $\text{Fe}_2(\text{CO})_9$. This reaction, plus the information obtained from infrared and Mössbauer spectra, suggest that the new species could be assigned as tetracarbonyliron, $\text{Fe}(\text{CO})_4$, and tricarbonyliron $\text{Fe}(\text{CO})_3$. ~~We have~~ ^{It is} proved that molecules sorbed in a polymer matrix can be used as Mössbauer absorbers at low temperature. The polymer matrix allowed the isolation of otherwise unstable species: the high permeability of LDPE to gaseous carbon monoxide precludes the reformation of pentacarbonyliron molecules, thus excluding the "cage effect" observed in frozen gas matrices.

1. INTRODUCTION

In recent years very much interest has been demonstrated on photolysis studies of metal carbonyls fixed in different matrices⁽¹⁻⁴⁾. Beside systematic studies of the photochemistry of metal carbonyls, some effort has been dedicated to understand the basic mechanisms involved in the photolysis process. In particular, pentacarbonyliron has been studied both in the gas phase⁽⁵⁾ and with matrix isolation techniques⁽⁶⁻⁹⁾. In both cases it was possible to identify the photofragments and obtain some information about their yields under different conditions. Yardley and coworkers⁽⁵⁾ claim that pentacarbonyliron in the gas phase suffers a photofragmentation through a simple one-photon process with a sequential loss of carbon monoxide.

The photolysis of $\text{Fe}(\text{CO})_5$ molecules isolated in low-temperature solid noble gas matrices has been the subject of several reports by Poliakoff and coworkers⁽⁶⁻⁹⁾, always based on infrared (i.r.) spectroscopy. They were able to identify the UV-photofragments of pentacarbonyliron as $\text{Fe}(\text{CO})_4$ and $\text{Fe}(\text{CO})_3$. From careful analysis of the i.r. bands which belong to the new iron species, they suggested that intramolecular rearrangement takes place after CO loss. As a consequence the $\text{Fe}(\text{CO})_4$ and $\text{Fe}(\text{CO})_3$ stabilize in C_{2v} and C_{3v} structures respectively with well-defined bond angles.

Attempts to characterize the structure of photofragments of matrix-isolated $\text{Fe}(\text{CO})_5$ by Mössbauer spectroscopy were not successful⁽¹⁰⁾. The experiment was not performed with enriched ^{57}Fe in the $\text{Fe}(\text{CO})_5$ molecules, consequently the signal to noise ratio in the Mössbauer spectrum was very low and

it was not possible to observe any photofragments of pentacarbonyliron. However, it was possible to verify that the hyperfine parameters of isolated $\text{Fe}(\text{CO})_5$ molecules do not present any detectable difference from the values reported for bulk samples.

It is known that the "cage effect" is present in the low temperature matrices and it can play an important role in the yield of $\text{Fe}(\text{CO})_5$ photolysis: the free carbon monoxide molecules cannot move away and are available for recombination reactions. To avoid the "cage effect" it is worthwhile to look for matrices which can maintain the $\text{Fe}(\text{CO})_5$ molecules partially isolated at higher temperature: in this case the photolysis yield may be improved by permitting the diffusion of carbon monoxide. This may allow the use of Mössbauer spectroscopy to characterize the pentacarbonyliron photofragments.

It is reported that pentacarbonyliron can be sorbed in PTFE and that it reacts photochemically in this matrix⁽¹¹⁾. It is also reported that the degree of sorption increases as the crystallinity of the matrix decreases, as expected according to the physical chemistry of polymers⁽¹²⁾. Recently we reported results on the use of PTFE as a matrix for the study of bimolecular photochemical reactions^(13,14). We were able to observe the photochemical substitution of CO ligands in pentacarbonyliron by olefin and diolefin ligands. The assumption that the first step in this reaction involves the loss of a CO ligand lead us to try to isolate and characterize the $\text{Fe}(\text{CO})_4$ photofragment in the polymer matrix.

Using a PTFE matrix and i.r. spectrophotometry we have studied the photolysis of pentacarbonyliron at ambient conditions.

In order to study the photolysis products by means of Mössbauer spectroscopy we used LDPE as a matrix. The LDPE polymer has a low degree of crystallinity and allows a high sorption of pentacarbonyliron. Both polymers do not absorb light in the wavelength range used to induce the photolysis and have no infrared absorptions in the region of interest.

2. EXPERIMENTAL SECTION

The low density polyethylene (LDPE) films, produced by Poliolefinas, used in this work had a thickness of 0.5 mm. PTFE produced by Du Pont Incofson, were 0.2 mm thick. The pentacarbonyliron was donated by BASF do Brasil.

As a source for ultraviolet light we placed a Phillips HPL-N125W lamp bulb (maximum emission at 366 nm) in a water cooled Pyrex jacket. The cooling was necessary to avoid overheating of the films during the irradiation process.

The LDPE or PTFE films were soaked in a 10% solution of pentacarbonyliron in hexane under an argon atmosphere; the immersion time was different for the films used in i.r. and Mössbauer spectroscopies. Only during the treatment of the film is an inert atmosphere necessary. Once the pentacarbonyliron is trapped inside the matrix it will not oxidize during the time required for the experiment. For the i.r. experiments the immersion time of the films was controlled by the saturation in the CO stretching region of the i.r. spectrum. For the Mössbauer measurements the LDPE films were kept in the solution until the polymers reached complete saturation. The treated films were washed with ethanol in order to prevent formation of a layer of iron oxide on their

surfaces due to decomposition of pentacarbonyliron. The treated films used in the i.r. experiments were placed in a spectrophotometer sample holder in order to obtain the spectrum before the ultraviolet irradiation. To follow the decomposition kinetics of the new species produced by the photofragmentation we used the "time drive" mode of the spectrophotometer in a previous selected wave number. Differential i.r. spectra were measured using a Perkin Elmer model 399 B spectrophotometer.

The attenuation coefficient of the 14.4 keV Mössbauer gamma rays in LDPE films is very low. For this reason it was possible to prepare a Mössbauer absorber by the superposition of at least seven polymer films saturated with pentacarbonyliron. This procedure was used due to the low sensitivity of Mössbauer as compared with the i.r. spectroscopy; only the molecules containing ^{57}Fe (natural abundance 2.18%) are able to contribute for the Mössbauer absorption spectrum.

The Mössbauer spectra were collected with a $^{57}\text{Co/Rh}$ source and the absorber kept in a liquid helium bath for two reasons. We wanted to avoid any annealing in the irradiated sample during the long acquisition time necessary to obtain a good Mössbauer spectrum (about 10 hours). The second point is that the LDPE films present a very low degree of crystallinity at room and liquid nitrogen temperatures. This results in a very low Lamb-Mössbauer factor with a consequent low signal to noise ratio in the Mössbauer spectra. This difficulty is overcome if we keep the LDPE films at 4.2K due to their higher degree of crystallinity at this temperature. In this way we were able to obtain well resolved Mössbauer spectra.

The Mössbauer spectrometer, with a Mössbauer drive of Kankeleit type and Xe-Kr proportional counter, was used with a Hewlett-Packard 4096 Multichannel analyzer. The data was folded and linearized using a IBM/370 computer and least square fitted with Lorentzian lines.

The procedure established for the Mössbauer measurements was the following. First we obtained a Mössbauer spectrum with a sample built by the superposition of seven films of LDPE saturated with pentacarbonyliron. The films were then taken out of the cryostat, warmed to room temperature and installed around the source of u.v. light to be equally irradiated. They were then remounted, cooled to liquid nitrogen temperature and then put in the helium bath to record the new Mössbauer spectrum. This procedure was repeated successively for different irradiation conditions.

3. RESULTS AND DISCUSSION

3.1 - Infrared Spectroscopy

The i.r. spectrum of pentacarbonyliron in a PTFE matrix shows two strong absorptions at 2020 and 1998 cm^{-1} , respectively, assigned to the A_2'' and E' C-O stretching modes of the D_{3h} point group symmetry (fig. 1, peaks labelled 5). This is in agreement with spectra previously reported, measured in cyclohexane solution⁽¹⁵⁾ or in frozen gas matrices⁽¹⁶⁾. A third, weak absorption observed at 1961 cm^{-1} is assigned as a satellite band from the natural occurrence of ^{13}C , in agreement with i.r. measurements made with isotopically enriched metal carbonyls⁽¹⁷⁾. After 10 minutes of u.v. irradiation of this sample at room temperature we observe six new absorptions in the i.r. spectrum (fig. 1, peaks labelled 4 and 3)

and a lowering in intensity of the two original bands. Two strong absorptions at 2074 and 1973 cm^{-1} and two weak shoulders at 2040 and 2030 cm^{-1} , are observed. The peak at 1998 cm^{-1} is shifted to 1992 cm^{-1} , showing a shoulder at high frequency. This shift, associated with the change in the intensity ratio of the two pentacarbonyliron absorptions, indicates that a third strong peak occurs at 1992 cm^{-1} and that the E" stretching mode of pentacarbonyliron is the observed shoulder. It is also possible to assume that the 1950 cm^{-1} broad band is an envelope resulting from the close superposition of two bands. These changes in the i.r. spectrum in the C-O stretching region of metal carbonyls shows that upon u.v. irradiation new species are formed in the matrix. Furthermore the new species are long lived and stable enough to be detected by conventional i.r. spectrophotometry. This long lifetime in the polymer matrix is provided by the association of two factors: a) the possibility of the free CO ligand to squeeze away from the metal due to the absence of a "cage effect" in comparison to frozen gas matrices and b) the low permeability coefficient of oxygen in PTFE, precluding the fast oxidation of the coordinatively unsaturated reactive iron(0) species.

The low degree of cristallinity of LDPE provides a high permeability of liquids and gases in it, in comparison with PTFE⁽¹²⁾. When the pentacarbonyliron irradiation experiment is repeated in LDPE and the films irradiated with the Nernst glower of the i.r. spectrophotometer, the decomposition of the new species is faster than for the same experiment in PTFE, persisting in both cases only the absorptions due to unreacted pentacarbonyliron. This demonstrates again that the irreversibility of the photochemical reaction in the polymer matrix is due to the loss of CO by diffusion and

slow oxidation of the products by the diffusion of oxygen in the polymer.

The irradiation time used in the experiments is short in order to prevent changes in the polymer itself. On the other hand, in the case of PTFE, reaction of the excited metal carbonyl with the polymer is also very improbable, since it must occur through a fluorine abstraction mechanism. Furthermore, the more vulnerable carbon skeleton is so completely protected by the fluorine atoms sheet that it is nearly impossible for any reagent to get close enough to attack the polymer chain⁽¹⁸⁾.

The complexity of the spectrum after the u.v. irradiation suggests the formation of more than one photofragment. It is reported that $\text{Fe}(\text{CO})_4$ and $\text{Fe}(\text{CO})_3$ are formed upon photolysis of pentacarbonyliron in rare gas matrices^(6,7). The $\text{Fe}(\text{CO})_4$ fragment probably adopts a structure with lower symmetry than tetrahedral or square planar, thus giving rise to a certain number of i.r. absorption bands. The same occurs with $\text{Fe}(\text{CO})_3$, which could not adopt a structure with high symmetry. The fact that only pentacarbonyliron is observed after the Nernst glower irradiation indicates that there is no formation of the dimer $\text{Fe}_2(\text{CO})_9$. Based on this argument and values reported in the literature⁽⁶⁾ we could assign the bands at 2074, 1992 and 1973 cm^{-1} to the $\text{Fe}(\text{CO})_4$ species. A fourth i.r. absorption should be expected, taking into account that, at room temperature, the molecule could rearrange to a symmetry lower than C_{3v} as was observed for $\text{Fe}(\text{CO})_4$ in rare gas matrices⁽⁶⁾. This absorption is probably hidden under the broad band at 1950 cm^{-1} . The remaining absorption bands, 2040, 2030 and

- 1950 cm^{-1} could be tentatively assigned to the $\text{Fe}(\text{CO})_5$ photofragment in a C_{3v} point group symmetry.

3.2 - Mössbauer Spectroscopy

In figure 2 are displayed the Mössbauer spectra measured at 4.2K of pentacarbonyliron sorbed in LDPE films. The spectrum obtained for a non irradiated sample (fig. 2a) consists of a single well resolved doublet with the Mössbauer parameters, isomer shift (IS) and quadrupole splitting (ΔE_q), very close to the values determined for solid pentacarbonyliron at the same temperature⁽¹⁰⁾. This results suggests that there is no important interaction between the $\text{Fe}(\text{CO})_5$ molecules and the polymer matrix.

The Mössbauer spectra of the films irradiated with u.v. light reveals the presence of iron species formed due to the photofragmentation of $\text{Fe}(\text{CO})_5$. These results are also illustrated in figure 2: irradiation with u.v. light for 10 minutes (fig. 2b) leads mainly to the formation of a photofragment with IS = -0.124 mm/s and $\Delta E_q = 1.83$ mm/s. Taking into account the early studies on pentacarbonyliron photolysis we assumed that this first photofragment is $\text{Fe}(\text{CO})_4$. If we increase the irradiation time a third doublet shows up (fig. 2c) in the central part of the spectrum; its Mössbauer hyperfine parameters are characteristic of $\text{Fe}_2(\text{CO})_9$ molecules. The values of the hyperfine parameters, obtained from the least square fitting of a sum of Lorentzian lines to the experimental data, are indicated in Table I.

We have repeated the photolysis experiment with several samples and under different conditions to test the reproducibility of our results. The yield of $\text{Fe}(\text{CO})_4$ and $\text{Fe}_2(\text{CO})_9$ in the photofragmentation of pentacarbonyliron sorbed in LDPE films depends

very much on the irradiation conditions. If we irradiate the sample for 10 minutes with a refrigerated u.v. lamp the yield of $\text{Fe}(\text{CO})_4$ is higher as compared to that of the dimer, $\text{Fe}_2(\text{CO})_9$, than if we perform the irradiation without any cooling system. The same is true if we irradiate our films with a refrigerated u.v. lamp continuously for 10 minutes or perform two irradiations of 5 minutes, therefore giving the same integrated dose; the yield of $\text{Fe}_2(\text{CO})_9$ is higher in the first case. Both experimental conditions described above, which may cause overheating of the polymer films, lead to a consequent increase in the $\text{Fe}_2(\text{CO})_9$ production.

The reaction between the $\text{Fe}(\text{CO})_4$ and the residual pentacarbonyliron leads to the formation of the dimer $\text{Fe}_2(\text{CO})_9$. This is clearly seen in the absorption area, since under further irradiation both pentacarbonyliron and tetracarbonyliron are consumed to give origin to $\text{Fe}_2(\text{CO})_9$. This same mechanism is well accepted to explain the decomposition of pentacarbonyliron, producing the dimer $\text{Fe}_2(\text{CO})_9$, although $\text{Fe}(\text{CO})_4$ was never observed in bulk samples of pentacarbonyliron⁽¹⁹⁾.

The loss of a carbon monoxide by pentacarbonyliron has been already observed in the gas phase⁽⁵⁾ and in matrix isolation experiments⁽⁶⁻⁹⁾. In both cases the presence of eneacarbonyldiron was not detected due to the isolation of two neighbour molecules of $\text{Fe}(\text{CO})_5$ which inhibit the reactions. The formation of the dimer is reported only for matrices with high concentration of pentacarbonyliron⁽⁷⁾. This is also observed in our experiments. In case of the i.r. experiments, the concentration of pentacarbonyliron in the matrix was just enough to observe its absorptions, and we do not observe the formation of the dimer. On the contrary, in the Mössbauer experiments we saturated the matrix with pentacar-

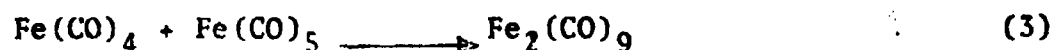
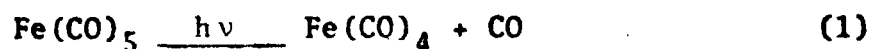
bonyliron in order to be able to measure the spectrum and we observed the formation of the dimer.

We know that in photolysis in gas phase or in $\text{Fe}(\text{CO})_5$ isolated in argon matrices it was possible to observe the formation of $\text{Fe}(\text{CO})_3$ as a photofragment⁽⁵⁻⁹⁾. If we could control the concentration of $\text{Fe}(\text{CO})_5$ molecules in the polymer "holes", we could decrease the probability of formation of $\text{Fe}_2(\text{CO})_9$ and increase the possibility of further photofragmentation of $\text{Fe}(\text{CO})_4$. Since we wanted to have a higher concentration of $\text{Fe}(\text{CO})_5$ in the polymer to improve our signal to noise ratio in the Mössbauer spectra, we have not controlled quantitatively the concentration of $\text{Fe}(\text{CO})_5$ in our samples, although some promising results are shown in figure 3. There, it is possible to compare the Mössbauer spectra of a non irradiated sample (fig. 3a) with two samples submitted to a irradiation of 10 minutes continuously (fig. 3b) and two irradiations of 5 minutes (fig. 3c). The analysis of such figure gives us two main pieces of information: 1) the yield of the doublet corresponding to $\text{Fe}(\text{CO})_4$ in fig. 3b is lower as compared with fig. 3c and 2) a fourth doublet near to zero velocity is present in fig. 3c. We must also take into account that the $\text{Fe}(\text{CO})_5$ concentration in the sample which gave the spectrum in fig. 3c is about half of that of the sample of fig. 3b. This result can lead us to suggest that the fourth doublet with $IS = +0.26$ mm/s and $\Delta EQ = 0.35$ mm/s could be assigned to a $\text{Fe}(\text{CO})_3$ photofragment, which has a higher probability to be present in the sample of fig. 3c.

1. CONCLUSION

The photolysis of pentacarbonyliron and subsequent reactions in polymer matrices can be described by the following sche-

me:



Photofragments $\text{Fe}(\text{CO})_4$ and $\text{Fe}(\text{CO})_3$ are evidenced by our i.r. and Mössbauer experiments. Furthermore, reaction (3) is observed as a consequence of reaction (1), depending on the concentration of pentacarbonyliron. The sorption of molecules in polymer films brings us to a very interesting situation: the isolation of clusters of these molecules in the polymer amorphous sites is in a concentration range between the isolated molecules in rare gas matrices and bulk samples. This allows us to observe the above described processes.

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TABLE I

| | IS (mm/s) | Δ EQ (mm/s) | Γ (mm/s) |
|-----------------------------------------|--------------|--------------------|--------------------|
| Fe(CO) ₅ /LDPE | -0.174 | 2.52 | 0.23 |
| Fe(CO) ₄ /LDPE | -0.124 | 1.83 | 0.28 |
| Fe ₂ (CO) ₉ /LLPE | 0.052 | 0.42 | 0.30 |
| Fe(CO) ₃ /LDPE | 0.266 | 0.35 | 0.50 |

Mössbauer parameters IS(isomer shift) and Δ EQ (quadrupole interaction) in mm/s, obtained from the computer least square fitting of the data. The average error are ± 0.06 for the isomer shifts and ± 0.02 for the quadrupole splittings. Γ is the line width.

FIGURE CAPTIONS

Fig. 1 - IR spectra of $\text{Fe}(\text{CO})_5$ sorbed in a PTFE matrix before (---) and after u.v. irradiation ()

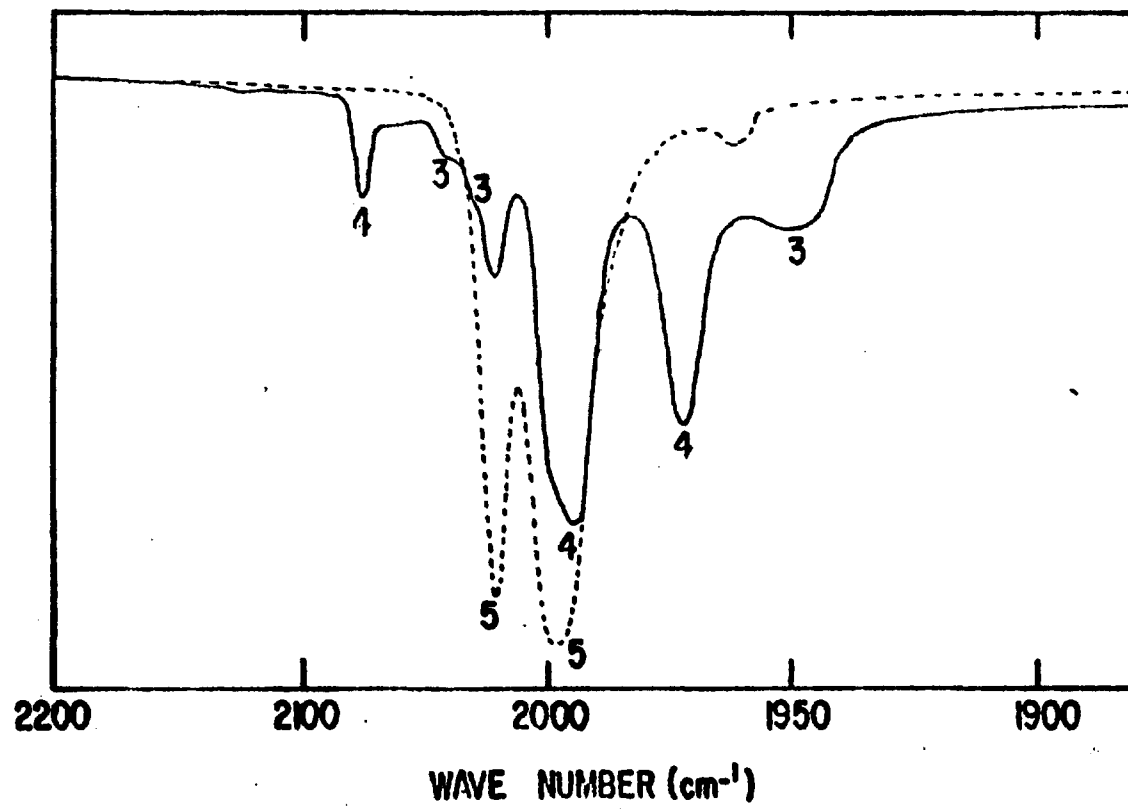
Fig. 2 - Mössbauer spectra, at 4.2K, obtained from $\text{Fe}(\text{CO})_5$ sorbed in LDPE polymer:

- a) non irradiated sample
- b) irradiated with u.v. light for 10 min
- c) sample b) after another 5 min of irradiation with u.v. light.

Fig. 3 - Mössbauer spectra, at 4.2K, obtained from $\text{Fe}(\text{CO})_5$ sorbed in LDPE polymer:

- a) non irradiated sample
- b) irradiated with u.v. light for 10 min
- c) irradiated with u.v. light for two separate 5 min periods.

FIG. 1



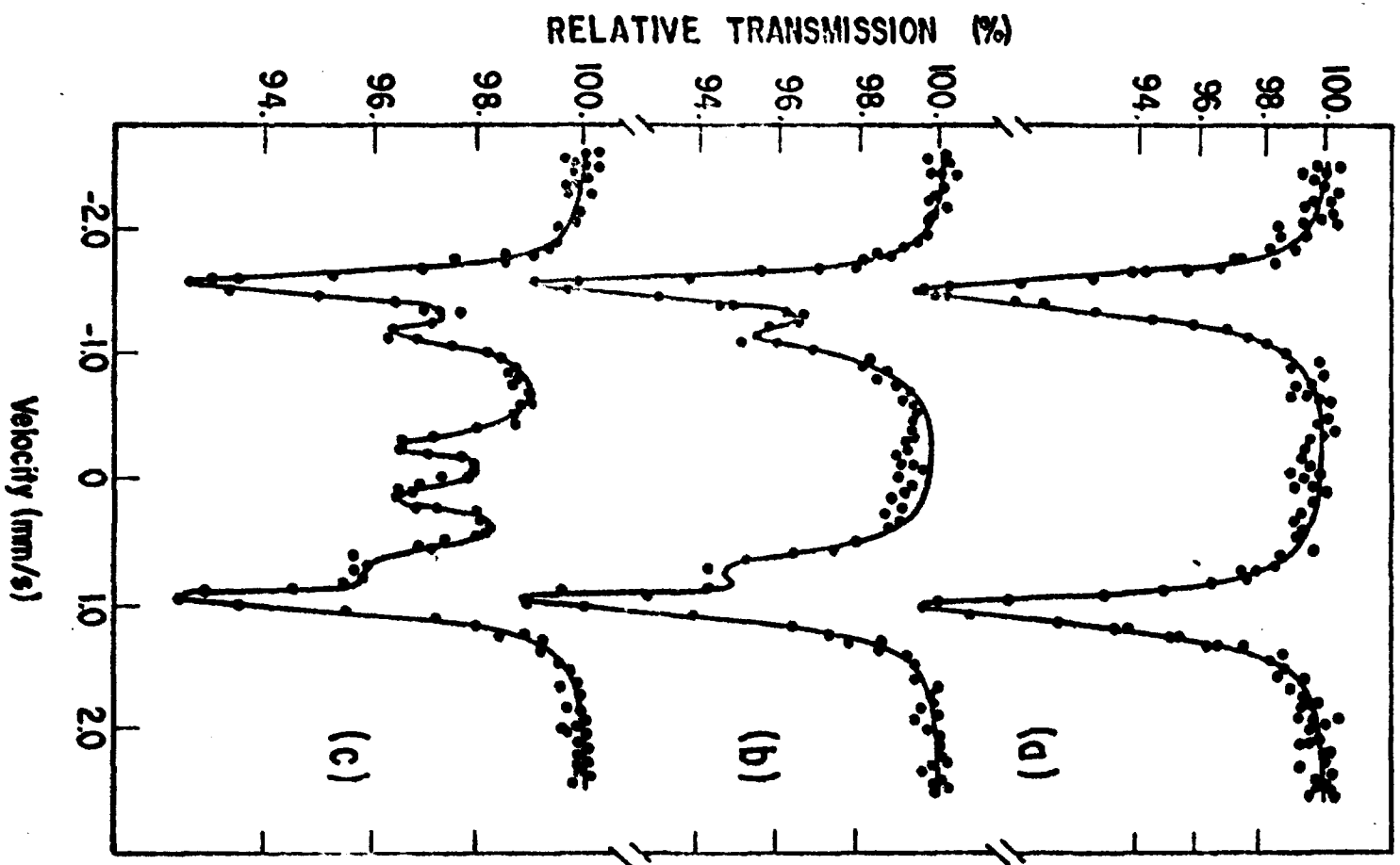


Fig. 2

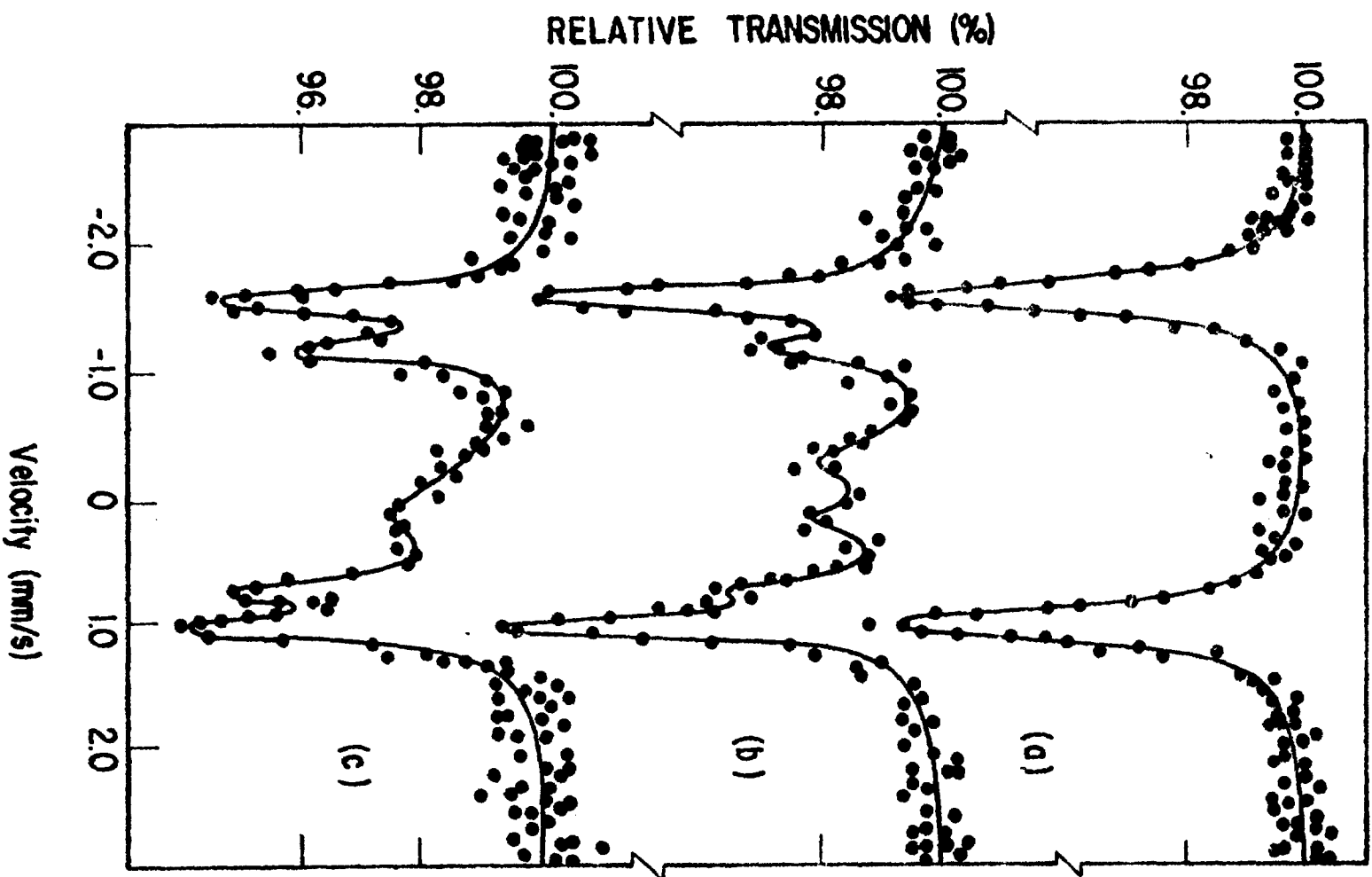


Fig. 5