

NOTAS DE FÍSICA

VOLUME XVIII

Nº 13

MÖSSBAUER STUDY OF THE REDUCTION OF FERRICYANIDES BY
ELECTRON IRRADIATION

by

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RIO DE JANEIRO, BRASIL

1972

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ELECTRON IRRADIATION

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(Received 31th January 1972)

In a recent study by Mössbauer spectroscopy of irradiated iron(III) chelates with high energy electrons (1) we have observed that the main radiolytic effect is the reduction of the iron ion, with the formation of the corresponding iron(II) chelates. Hydrogen radicals formed by radiolysis were assumed to be responsible for the high yield of the reduction process.

In order to confirm the importance of the contribution of H[•] radicals to the reduction mechanism we compare the radiation effects in a series of iron(III) hexacyanides, some of which contain hydrogen in the form of water of crystallization and others crystallize in anhydrous form. The presence or absence of water molecules in the different complexes was carefully detected by infra-red measurements.

The details of the experimental procedure are given in Ref. 1. The samples were irradiated in the cryostat with an approximate dose rate of 20μA for 30 minutes. The temperature was maintained below 120°K. The source used was 10 mCi ⁵⁷Co in Pd matrix.

The results obtained with the irradiated hydrated ferricyanides of Sodium and Lithium (2) are illustrated in figs. 1 and 2. The identification of the new lines appearing in the spectrum of the irradiated complex has been made by comparing the latter with the spectrum of the corresponding ferrocyanide. It can be seen from the figures that the spectra of the irradiated samples result from the superposition of the lines of ferrous and ferric complexes. This shows that the main effect of the radiation is the reduction of $\text{Fe}^{\text{III}}(\text{CN})_6^{-3}$ to $\text{Fe}^{\text{II}}(\text{CN})_6^{-4}$ ion. As has been observed in previous studies with other iron(III) chelates, in the limits of sensibility of the method the decomposition of the complex by the radiation is of smaller importance as compared to the large reduction yield.

In the figures 3, 4 and 5 are illustrated the results obtained by irradiating with the same doses at the same temperature the anhydrous ferricyanides of Rubidium, Potassium and Silver. It can be seen that with these complexes the reduction yield is negligible as compared to that obtained with the same doses for the hydrated ferricyanides. No annealing effects were observed in all irradiated samples.

These results support the assumption that the formation of hydrogen radicals, originated in the samples from the radiolytic decomposition of H_2O , are responsible for the reduction reaction.

It is interesting to observe that in the case of $\text{Ag}_3\text{Fe}(\text{CN})_6$, new lines appear in the Mossbauer spectrum, which are not due to a

reduction product (fig.5). The large quadrupole splitting (2.05 mm/sec and the isomer shift -0,17 mm/sec against $^{57}\text{Co-Pd}$ source) corresponding to these new lines are typical of iron pentacyano complexes (3). Further evidence for this assignment was obtained by comparing the infra-red spectra of the irradiated sample with the unirradiated one. Changes were observed in the region of the CN stretching frequencies (fig.6), with the appearance of new bands due to radiolysis at 2180 cm^{-1} and 2100 cm^{-1} , which are in the range of frequencies of iron(III) pentacyano complexes (4). This result suggests that in the absence of a free radical mechanism involving the transition ion in a redox reaction, the radiolytic protection of the molecule is decreased and decomposition reactions occur under the influence of the radiation.

It is important to observe that with much higher doses a further decomposition of the Silver ferricyanide leading to a complex Mossbauer spectrum was obtained. Further investigations are in progress and the results will be discussed in view of the observations of K-capture process.

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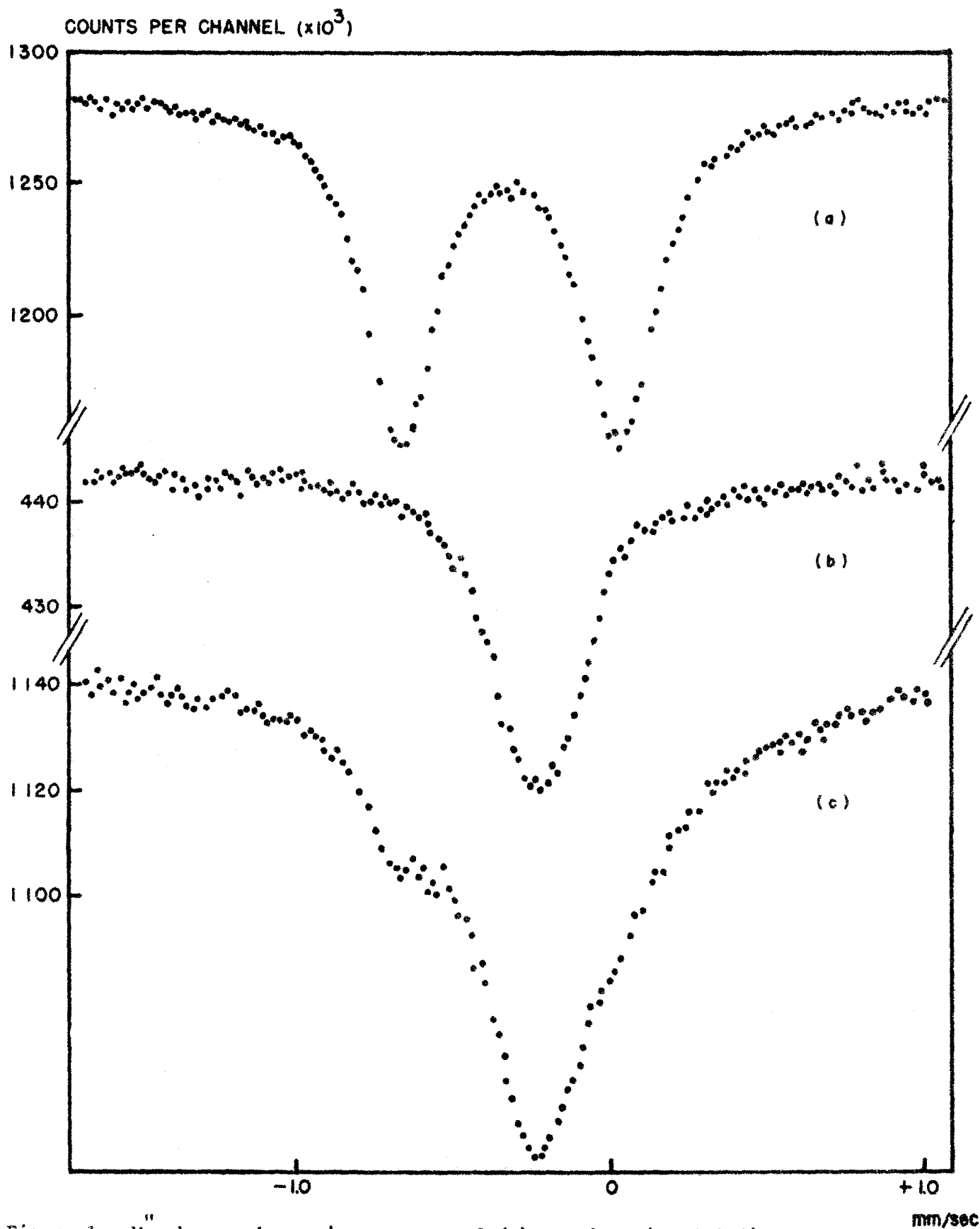


Figure 1 - Mossbauer absorption spectra of (a) non-irradiated Sodium ferricyanide (b) non-irradiated Sodium ferrocyanide (c) irradiated Sodium ferricyanide. All spectra at 295°K .

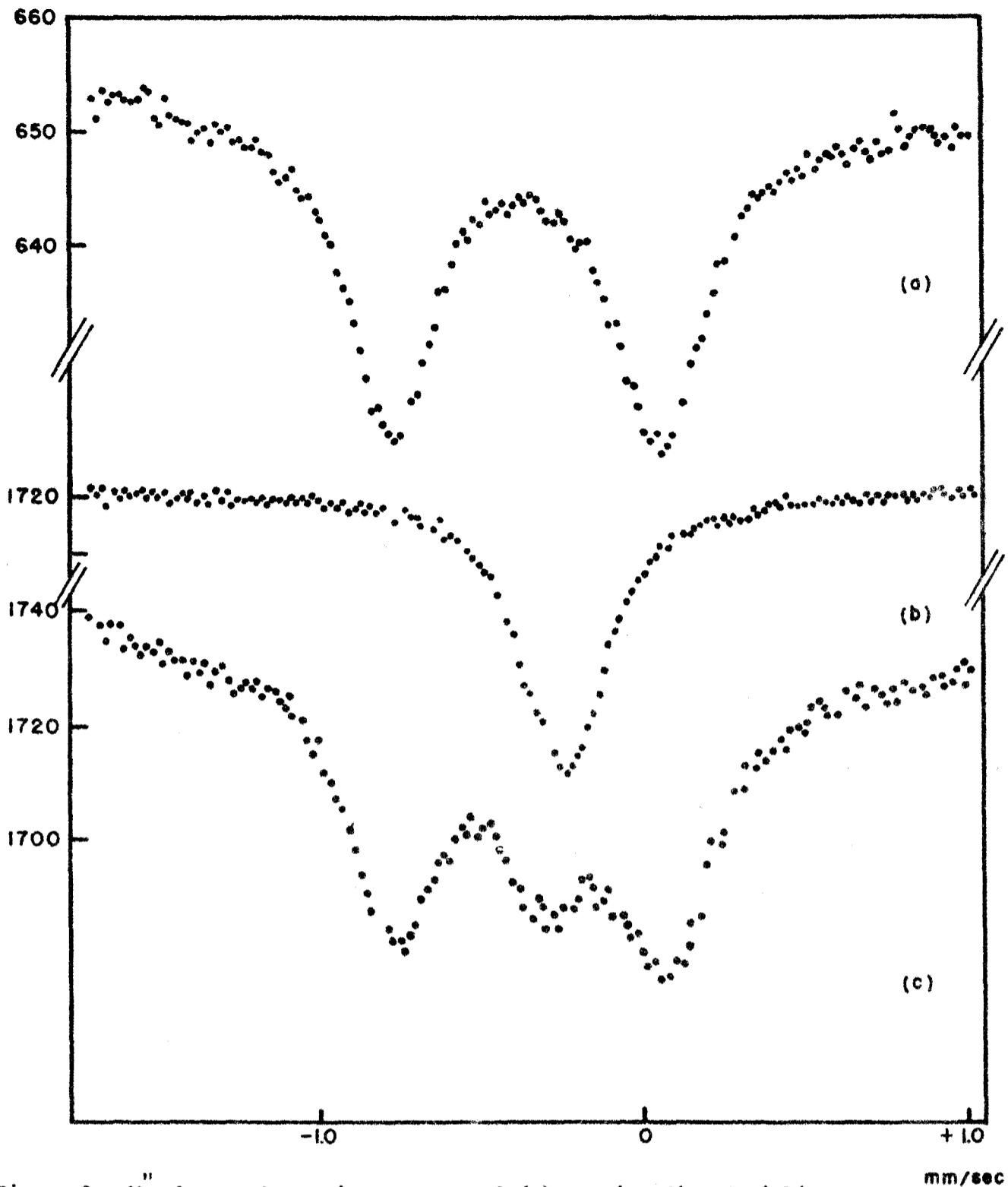


Figure 2 - Mössbauer absorption spectra of (a) non-irradiated Lithium ferricyanide (b) non-irradiated Lithium ferrocyanide. All spectra at 295°K.

COUNTS PER CHANNEL ($\times 10^3$)

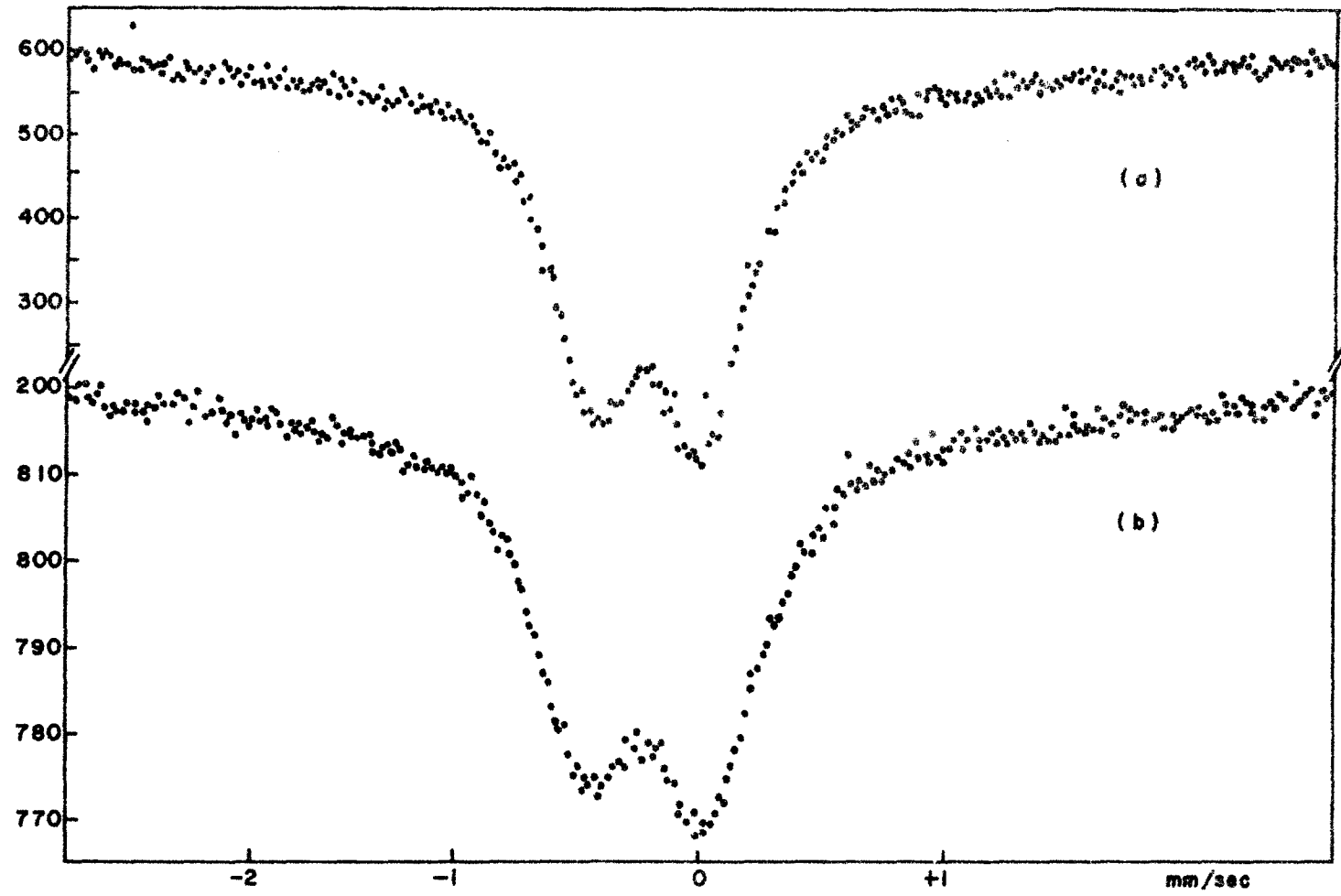


Figure 3 - Mössbauer absorption spectra of (a) non-irradiated Rubidium ferricyanide (b) irradiated Rubidium ferricyanide. Both spectra at liquid Nitrogen temperature.

COUNTS PER CHANNEL ($\times 10^3$)

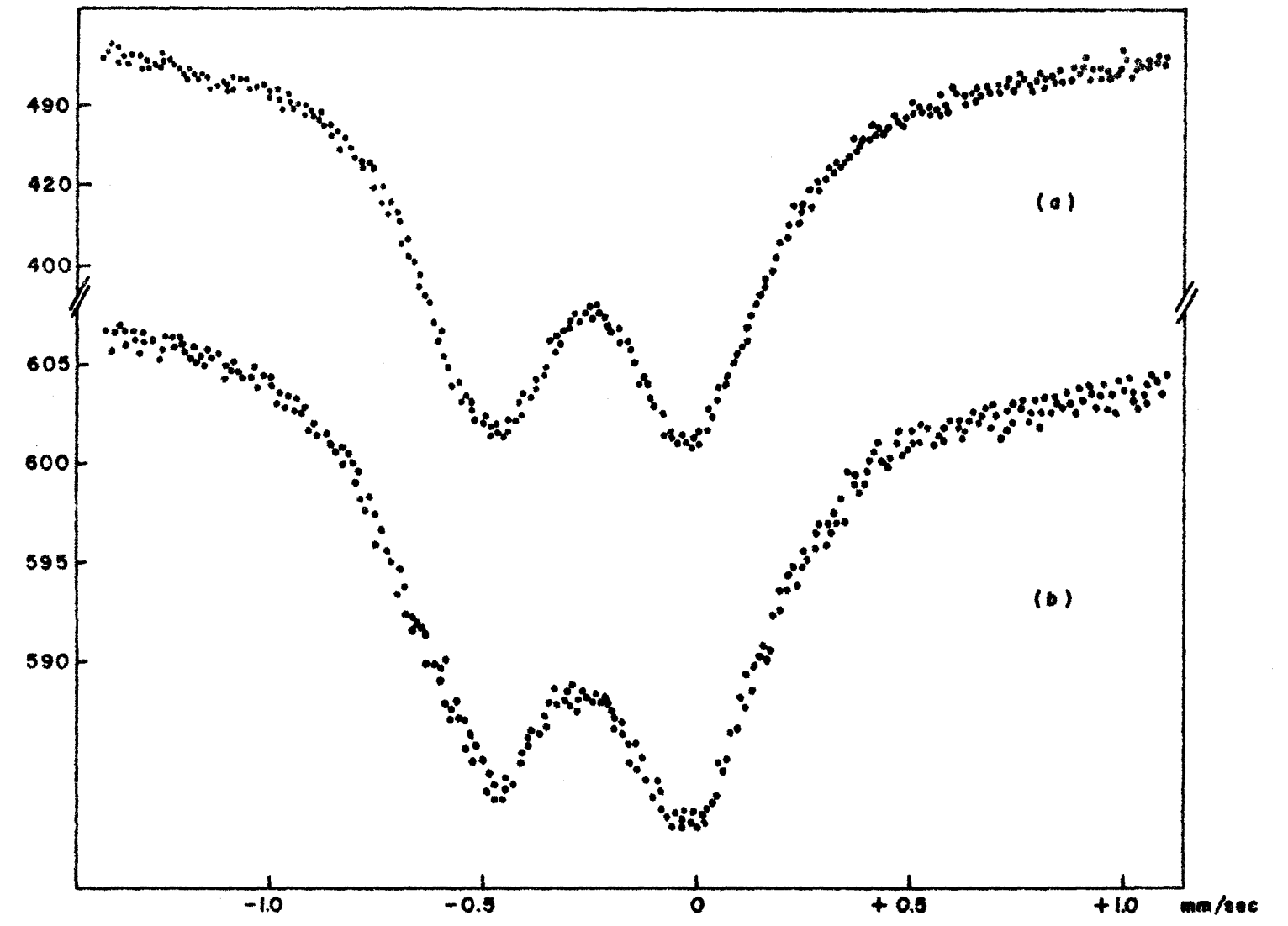


Figure 4 - Mössbauer absorption spectra of (a) non-irradiated Potassium ferricyanide (b) irradiated Potassium ferricyanide. Both spectra at liquid Nitrogen temperature.

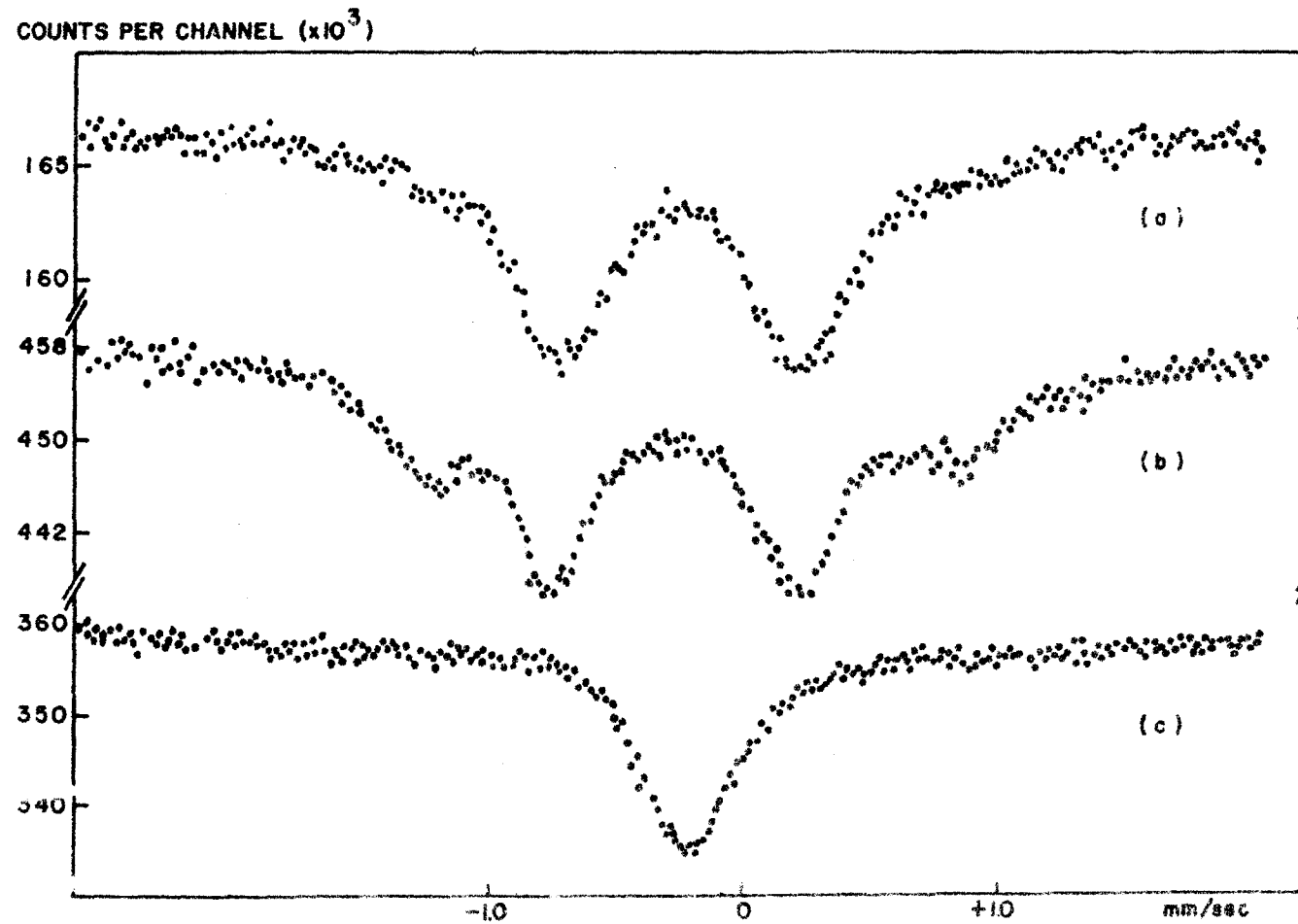


Figure 5 - Mossbauer absorption spectra of (a) non-irradiated Silver ferricyanide
 (b) irradiated ferricyanide. Both spectra at liquid Nitrogen temperature.

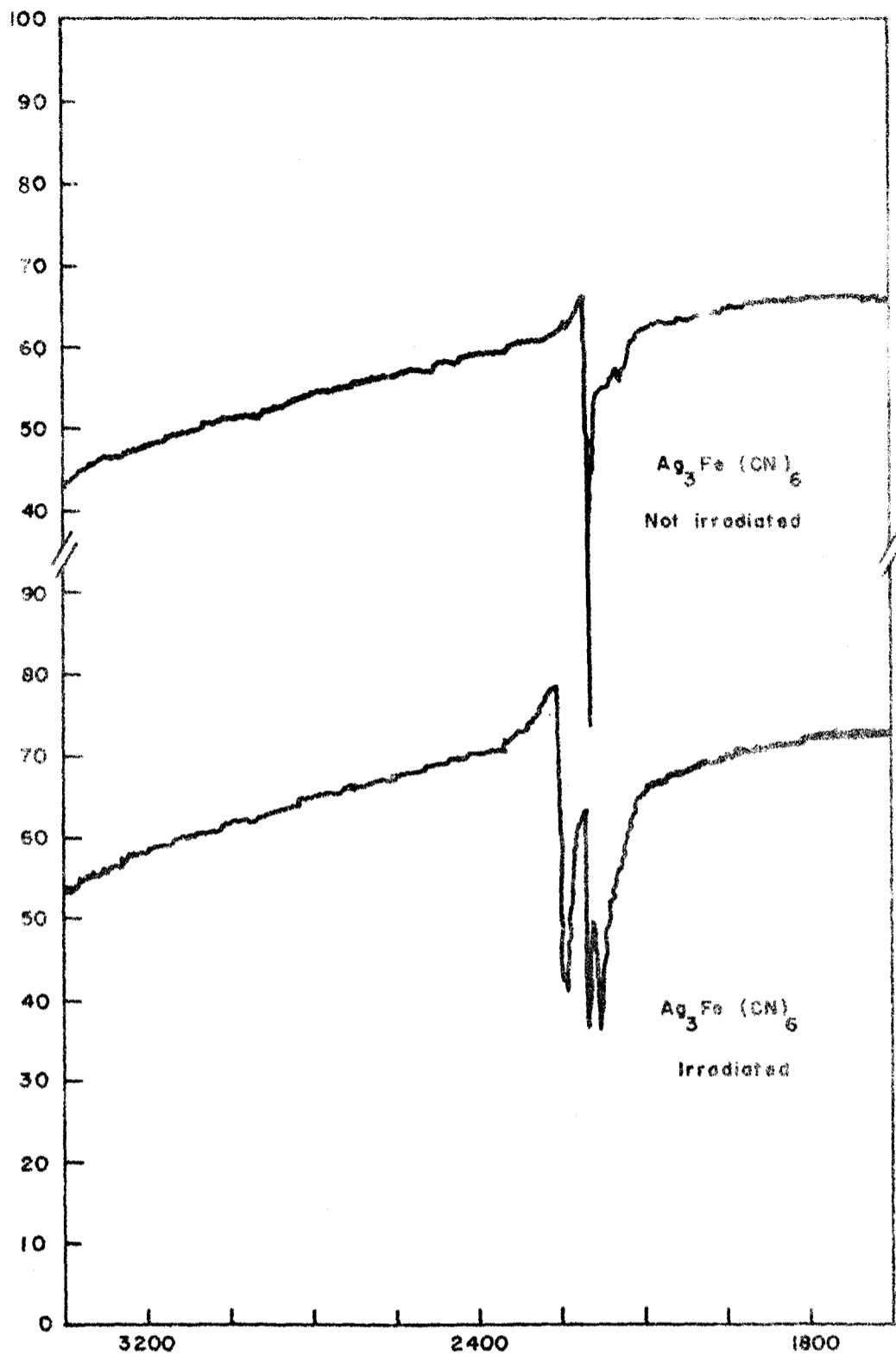


Figure 6 - Infra-red spectra of irradiated and non-irradiated Silver ferricyanide in KCl disk made in a Beckman IR-20A. Both spectra at 295°K.