

OBSERVATION OF FAST INTRAMOLECULAR ELECTRON TRANSFER BY THE GAMMA RESONANCE SPECTROSCOPY (GRS) METHOD

V.P. Alekseev, V.I. Gol'danskii, V.E. Prusakov, A.V. Nefed'ev, and R.S. Stukan

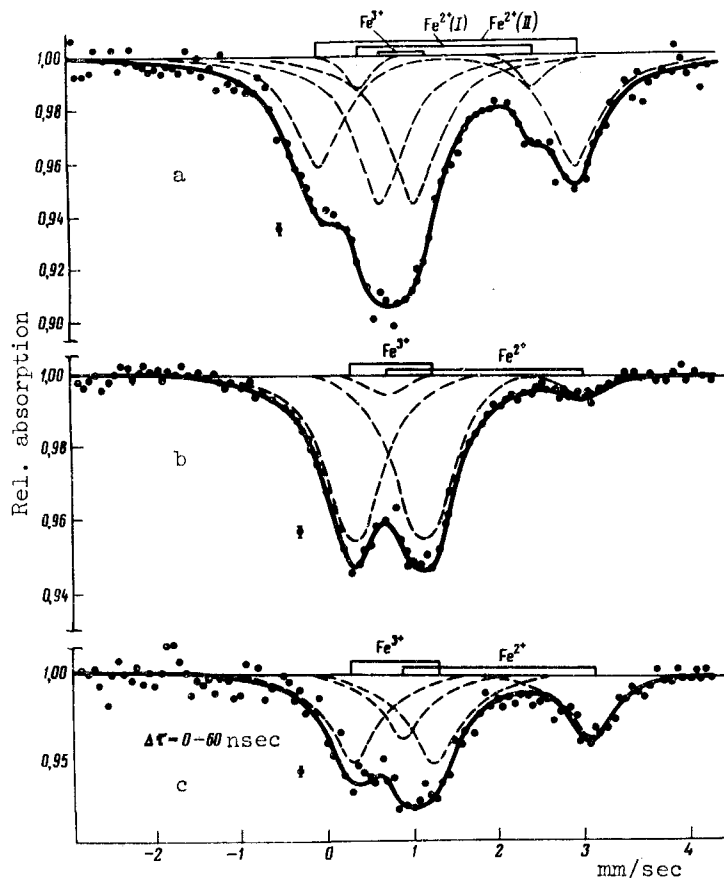
Institute of Chemical Physics, USSR Academy of Sciences; Institute of Optical-physical Measurements

Submitted 2 June 1972

ZhETF Pis. Red. 16, No. 2, 65 - 68 (20 July 1972)

Using gamma-resonance spectroscopy (GRS) in conjunction with the method of delayed $\gamma\gamma$ coincidences, the so-called "time filtering" effect [1, 2], one can obtain information on the dynamics of fast processes in the time interval $0 - 2\tau_0$ (where τ_0 is the average lifetime of the Mossbauer level).

We have investigated, using emission GRS in conjunction with the delayed $\gamma\gamma$ coincidence procedure, electron transfer in systems produced after radioactive decay of the ferro- and ferricyanides of Co^{57} .



- a) Emission GR spectrum of cobalt ferrocyanide, Co^{2+} $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$, obtained by the usual Mossbauer procedure. The three doublets pertain respectively to two forms of Fe^{2+} and one of Fe^{3+} .¹⁾ The ratio of the areas under the Fe^{2+} and Fe^{3+} peaks is approximately 1:1.
- b) Emission GR spectrum of cobalt ferricyanide, Co^{2+} $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$, obtained by the usual procedure. The narrow and broad doublets pertain to Fe^{3+} $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ and Fe^{2+} $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$, respectively.
- c) Emission GR spectrum of cobalt ferricyanide, Fe^{2+} $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$, obtained by the delayed $\gamma\gamma$ coincidence method in the time interval $0 - 60$ nsec.

¹⁾In plotting the GR spectra, we used the standard absorber $\text{K}_4[\text{Fe}(\text{CN})_6]3\text{H}_2\text{O}$. The source temperature was -80°K in all experiments. The isomer shift is given relative to sodium nitroprusside.

The commanding photon was the 122-keV γ quantum preceding the 14.4-keV Mossbauer transition and emitted from the 136-keV level of Fe^{57} (lifetime 9 nsec). The selection of the 14.4-keV γ quanta after the emission from the 136 keV level (i.e., after the decay of Co^{57} - with accuracy ~ 9 nsec) was effected with the aid of a time-amplitude converter (TAC) block and a discriminator.

In the investigation of the decay of the ferricyanide of cobalt Co^{2+} [$\text{Fe}^{\text{III}}(\text{CN})_6$] by the usual emission GRS method (see Fig. b), and also by GRS together with the $\gamma\gamma$ coincidence procedure in the time interval 0 - 160 nsec, it was observed that only Fe^{3+} ions were actually produced, whereas the spectra in the time interval 0 - 60 nsec (Fig. c) had approximately a 30% contribution of the Fe^{2+} state (assuming that Fe^{2+} and Fe^{3+} have approximately equal values of f').

It is known that when the delayed $\gamma\gamma$ coincidence procedure is used in experiments on the Mossbauer effect, small satellites appear even for a singlet line [1, 2], but the total area under all these peaks, for the Fe^{57} spectra in the time interval 0 - 60 nsec, does not exceed 8 - 10% of the area of the central peak. The GR spectrum obtained by us by the delayed $\gamma\gamma$ coincidence procedure, was reduced by a simplified method in which the presence of satellites was not taken into account, but the error due to such a simplification does not exceed 5%, since the contribution of the satellites from Fe^{3+} in the region of the spectrum of Fe^{2+} is partly offset by the contribution of the satellites from Fe^{2+} in the region of the principal components of the Fe^{3+} spectrum.

The obtained data indicate that at the first instant after the neutralization of the highly-charged states of the iron ions, resulting from the Auger transitions following K-capture by the Cl^{57} nuclei, the iron is stabilized at least partly in the form Fe^{2+} , i.e., in the valence state analogous to the parent atom Co. However, the $\text{Fe}^{2+}[\text{Fe}^{\text{III}}(\text{CN})_6]$ state obtained thereby is not stable [3] and after a time on the order of several dozen nanoseconds the electron is transferred to the internal low-spin iron ion and the stable system $\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ is formed.

Similar results were obtained by us also by an analysis of the decay of Co^{57} in cobalticyanides, performed by the usual emission GRS procedure. Whereas only the form Fe^{III} is produced in the decay of Co^{57} in the cobalticyanides of Fe^{3+} , Ni^{2+} , and Cu^{2+} , the singlet line of the ferrocyanide [$\text{Fe}^{\text{II}}(\text{CN})_6$] $^{4-}$ is observed almost exclusively in the emission GR spectra of the cobalticyanide $\text{Fe}^{2+}[\text{Co}^{\text{III}}(\text{CN})_6]$. This also indicates that an electron is transferred from the cation to the intraspherical low-spin Fe^{III} ion with formation of the stable system $\text{Fe}^{3+}[\text{Fe}^{\text{II}}(\text{CN})_6]$.

It should be noted that the observed electron transfer is not connected with the neutralization of the highly-charged iron states resulting from the Auger transitions, since studies [4, 5] of the consequences of the decay of Co^{57} in the systems CoO , NiO , Cu_2O , MgO , Al_2O_3 , $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$ with the aid of the delayed $\gamma\gamma$ coincidence method have shown that this process occurs within a time much shorter than 10^{-7} sec. An estimate of the rate constant K of the indicated electron transfer (in sec^{-1}), under the assumption that it proceeds like an irreversible monomolecular reaction, with allowance for the exponential decay of the 14.4-keV level of Fe^{57} , can be obtained from the formula

$$P_{(r)} = P_{(0)} \frac{\lambda}{\lambda + K} \frac{1 - e^{-(\lambda + K)r}}{1 - e^{-\lambda r}}$$

where $\lambda = 1/\tau_0 = 7 \times 10^6 \text{ sec}^{-1}$, τ is the time interval within which the Mossbauer spectrum is measured (60 nsec or ∞ in our experiments), $P(\tau)$ is the fraction of the Co decay in the Fe^{2+} state and decreases from $P(0)$ to $P(0)\lambda(\lambda + K)^{-1}$ in the time τ . It is natural to assume $P(0)$ equal either to unity, since the initial form of the Co^{57} isotope is taken in the form Co^{2+} , or to the fraction (~ 0.5) of the Fe^{2+} doublet in the emission GR spectrum of $\text{Co}^{2+}[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ (see Fig. a), i.e., for a compound in which there is no transfer of the electron to the intraspherical iron. Experiments yielded $P(60 \text{ nsec}) = 0.37 \pm 0.10$ and $P(\infty) = 0.07 \pm 0.014$. We obtain $K \approx 10^8 \text{ sec}^{-1}$ or $K \approx 5.5 \times 10^7 \text{ sec}^{-1}$ ($T = 80^\circ\text{K}$) for $P(0) = 1$ and $P(0) = 0.5$, respectively.

The intramolecular electron transfer times are of the order of 10 - 20 nsec and are too short to be attributed to a simple tunnel transition without re-alignment of the forms of the two potential wells, i.e., to a random superposition of two very narrow ($\sim 10^{-7} \text{ eV}$) electronic levels. A more natural assumption is that the transition of the electron from an excited level in a narrow well (Fe^{2+}) to various levels in a deeper well ($[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$) is of the activation-tunneling type. A rough estimate of the activation energy of such a process (if the pre-exponential factor is $10^{13} - 10^{15} \text{ sec}^{-1}$ and $T = 80^\circ\text{K}$) yields $E \approx 0.08 - 0.1 \text{ eV}$, which agrees with the estimate given in [6].

Additional information on the intramolecular transfer of electrons can be obtained from GRS studies, with the delayed $\gamma\gamma$ coincidence technique, of similar compounds at temperatures both above 80°K and, most importantly, below 80°K .

- [1] C.S. Wu, Y.K. Lee, N. Benczer-Koller, and P.C. Simms. Phys. Rev. Lett. 5, 432 (1960).
- [2] R.E. Holland, F.J. Lynch, C.J. Perlow, and S.S. Hanna, Phys. Rev. Lett. 4, 181 (1960).
- [3] B.M. Chadwick and A.G. Sharpe, Advances in Inorg. Chem. and Radiochem., 8, 83 (1966).
- [4] W. Triftshauser and D. Schroerer, Phys. Rev. 187, 491 (1969).
- [5] W. Triftshauser and P.P. Craig, Phys. Rev. 162, 274 (1967).
- [6] D.S. Chernavskii, Usp. Fiz. Nauk 107, 157 (1972) [Sov. Phys.-Usp. 15, No. 3 (1972)].

RADIAL DISTRIBUTION OF FAST ELECTRON IN A Z PINCH

I.G. Presiantsev, V.D. Pis'mennyi, A.T. Rakhimov, and A.N. Starostin
 Nuclear Physics Institute of the Moscow State University
 Submitted 2 June 1972
 ZhETF Pis. Red. 16, No. 2, 68 - 72 (20 July 1972)

Two decades after the observation of hard radiation [1] there is still no convincing explanation of the mechanism whereby charged particles are accelerated in powerful pulsed discharges in rarefied gases. Numerous attempts to offer such an explanation (cf., e.g., [2]) were based on the results of experimental research 10 - 15 years old, when the diagnostic methods for fast processes in a hot plasma did not yield information on the plasma parameters with high temporal and spatial resolution. It is therefore advisable to verify the main features of the phenomenon by modern diagnostic means and to accumulate additional experimental facts.

One of the important premises of the phenomenon in question, one regarded in the literature to be unequivocally established, concerns the localization of the region of acceleration: it is customarily assumed that it occurs near the