The Mössbauer Spectra of Several Inorganic Iron Salts

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Since the discovery of the Mössbauer effect, a number of papers have appeared concerning this phenomenon, which consists of the recoilless emission and resonant recoilless absorption of nuclear gamma radiation. However, the great majority of previous investigations of the Mössbauer effect have been concerned almost exclusively with nuclear physics, solid state physics and theoretical physics.

Takashima et al.(1) and Fluck et al.(2) have, in earlier reviews pointed out the applicability and significance of the Mössbauer effect in chemical research. In recent years, chemical Mössbauer studies of iron cyanide complexes,(3) iron carbonyl complexes,(4,5) ferrocene derivatives(6) and iron phenanthroline complexes(7) have, therefore, been carried out by several groups of workers. However, a large number of other compounds are still unexplored. Meanwhile, increasing interest is being shown in chemical applications of the Mössbauer effect.

The purpose of the present work is to measure the isomer shift and the quadrupole splitting for the 14.4 keV. γ-transition of ^{57}Fe in various iron compounds, in the hope that the wealth of the resultant data will make clear any correlation between these values and the chemical binding of iron atoms.

Theoretical Considerations

The very low gamma ray level used in Mössbauer study tells us that the vibrational and rotational states in the molecule will have little effect on the Mössbauer spectrum. The shape of the spectrum is mainly affected by the electronic charge distribution around the iron atom. As has been shown in previous papers,(4-7) the Mössbauer measurements can give extremely valuable information about the electronic charge distribution in the molecule as a function of the structure.

Two quantities, the isomer shift and the quadrupole splitting, are readily derived from Mössbauer spectra. The magnitude of these values is considered to be closely related to the molecular structure with which ^{57}Fe is concerned.

The isomer shift, δ, is given in first approximation by the formula:

$$\delta = C(R_e^2 - R_g^2)[|\psi_a(0)|^2 - |\psi_s(0)|^2]$$

where C is a constants; R_e and R_g are the effective charge radii in the excited and ground states respectively, and $|\psi_a(0)|^2$ and $|\psi_s(0)|^2$ are, respectively, the s-electron densities at the iron nucleus in the absorber and in the source. This density is greatest for the inner s-electrons, but it is nonzero for even the outermost s-electrons.

If we consider two atoms of the same element that differ only in respect to the molecule in which they are bound, the difference in the electron density at the nucleus will reflect the difference in the chemical nature. Thus the extent of the isomer shift will give semiquantitative information as to the chemical binding.

The quadrupole slitting, ε, is characterized by the $1/4\,e^2qQ$, quantity where e is the electronic charge, q is the electronic field gradient at the nucleus, and Q is the quadrupole moment of the nucleus. Splitting occurs if the electronic charge distribution at the atom is not spherically symmetrical.

Therefore, the quadrupole splitting provides a measure of the crystal field parameters in various compounds. However, there is, at present, no general method for predicting the relative isomer shift (or the quadrupole splitting) of various compounds with different types of bindings.

Experimental

Materials.—The following chemicals were used, all were commercial reagent grade products, and all were used without further purification.

Iron(III) chromate {$Fe_2(CrO_4)_3$}, Basic iron(III) chromate ($Fe_2O_3\cdot 4CrO_3\cdot H_2O$), Iron(III) arsenate ($FeAsO_4$), Iron(III) phosphate ($FePO_4\cdot 4H_2O$), Iron(III) pyrophosphate $Fe_4(P_2O_7)\cdot 9H_2O$, Iron(II)

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1) Y. Takashima and S. Ohashi, "*Bussei*", **4**, 243 (1963).

2) E. Fluck, W. Kerler and W. Neuwirth, *Angew. Chem.*, **75**, 461 (1963).

3) J. F. Duncan and P. W. R. Wigley, *J. Chem. Soc.*, **1963**, 1120.

4) R. H. Herber, W. R. Kingston and G. K. Wertheim, *Inorg. Chem.*, **2**, 153 (1963).

5) W. Kerler, W. Neuwirth, E. Fluck, P. Kuhn and B. Zimmermann, *Z. Physik*, **173**, 321 (1963).

6) G. K. Wertheim, *J. Chem. Phys.*, **38**, 2106 (1963).

7) L. M. Epstein, ibid., **40**, 435 (1964).

phosphate $Fe_3(PO_4)_2 \cdot 8H_2O$, Graham's salt $\{(NaPO_3)_n\}$, Iron oxides (Fe_2O_3 and Fe_3O_4), Potassium ferricyanide $K_3[Fe(CN)_6]$.

Most of the samples studied were especially prepared for the measurements.

Metal Ferricyanide Complexes $M_3[Fe(CN)_6]_2$ *(M = Zn, Cd, Ni and Co).*—Solutions (approximately 0.1 M) of metal sulfate and potassium ferricyanide were prepared. Equivalent quantities of the former were then added to the latter, so that four different precipitates were obtained. After that, the precipitate was centrifuged off, washed with water, and dried on filter paper.

Alkali-Iron(III) Double Sulfates $M'Fe(SO_4)_2 \cdot 12H_2O$, *(M' = K, Rb and Cs).*—A saturated solution of metal sulfate was mixed with an equivalent amount of an iron(III) sulfate solution. The mixture was then placed in a desiccator for several days until crystals formed. The precipitate was filtered off and dried on filter paper.

Glassy Substances Consisting of $(NaPO_3)_n$-Fe_2O_3 *and* $(NaPO_3)_n$-Fe_3O_4.—Graham's salts (10 g.), prepared by the thermal dehydration of dihydrogen phosphate, was mixed with varying amounts of Fe_2O_3 (or Fe_3O_4) in a platinum crucible so that the P/Fe ratios became 5, 7, 10 and 50. The mixtures were then fused by heating them at 900°C for one hour and then rapidly cooling them. The products were all brownish, glassy substances.

Cement.—A vinyl cemedine*-chloroform solution was used to cement the sample on a sample holder disk.

Apparatus. — Our experimental arrangements, shown in Fig. 1, were essentially the same as those described by De Pasquali et al.[8] (1960) and by Shirley et al.[9] (1961).

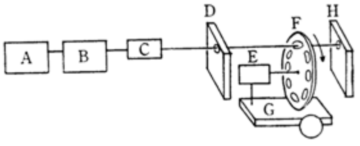

Fig. 1. Experimental arrangement.

- A Scaler
- B Single channel pulse height analyser
- C NaI detecter
- D Slit
- E Synchronous motor
- F Absorber disk
- G Angle changer
- H Source

About 5 mc. of ^{57}Co electroplated on metallic copper was used as a source. The main advantage of such a large amount of source material is the feasibility of time-saving measurements.

The constant velocity drive consists of a constant speed synchronous motor (4 r.p.m.) with a round absorber disk (7.4 cm. in diameter). The absorber disk has eight open windows in which a sample is mounted. The gamma ray passing through the disk sees, in its direction of motion, a velocity component, $r\omega \sin\theta$, where r is the distance from the axis of rotation to the point where the gamma ray passes through the absorber, and where θ is the angle between the gamma ray and the axis of motion.

The gamma ray (14.4 keV.) was measured by means of a single-channel pulse-height analyzer equipped with a thin NaI scintillation detector (1 cm. × 2 cm., 1 mm. thick). The detector face was located 40 cm. from the source. The absorber was placed between the source and detector face, at a distance 9 cm. from the source. The instrumental conditions were unchanged for many months.

A multichannel pulse-height analyzer,[10] coupled with an instantaneous velocity measurement of the gamma ray source, was also used for the measurement of several samples, but only when enough sample for the previous technique was not available.

Procedure. — A known amount of a powdered sample was mounted on an absorber disk by using a vinyl cemedine-chloroform solution. The total amount of sample taken varied within the range from 0.8 to 2.4 g. (10—20 mg. Fe/cm^2), depending on its iron content. The sample sheet was made as uniform as possible.

The gamma ray transmissions were measured at room temperature for each Doppler velocity, these velocity were arbitrarily selected by changing the angle of the absorber disk. The relationship between the intensity of the transmitted radiation and the relative velocity of the absorber was plotted in graphical form, and then both the isomer shift and the quadrupole splitting were read out from the curve. All the values of the isomer shift were represented by the shifts (mm./sec.) relative to the stainless steel. The activity was measured by counting the $\sim 10^5$ total for each point. Statistical error ($\pm\sqrt{n}\cdots n$=counts) was taken into account in drawing the spectral lines. The reading errors of δ and ε depend on the sharpness of the absorption peak. The estimated error for metal ferricyanides was about ±0.01 mm./sec. On the other hand, the error increased to ±0.02 mm./sec. in the case of the $(NaPO_3)_n$-Fe_2O_3 system.

Results and Discussion

The results obtained for the isomer shift and the quadrupole splitting are summarized in Table I, together with some of the data obtained by other workers.[2] The data cited from other papers were normalized to our data, which were obtained by using a ^{57}Co-Cu source and a stainless steel reference. In all our measurement the source absorber were held at room temperature (20—25°C).

In a closely-related series of compounds, such as metal ferricyanides $\{M_x[Fe(CN)_y]\}$, small differences in the Mössbauer spectra are to be expected because of the similar *s*-electron

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* Commercial name.

[8] DePasquali, H. Frauenfelder, S. Margulies and R. N. Peacock, *Phys. Rev. Letters*, **4**, 71 (1960).

[9] E. A. Shirley, M. Kaplan and P. Axel, *Phys. Rev.*, **123**, 816 (1961).

[10] K. Ôno and A. Ito, *J. Phys. Soc. Japan*, **17**, 1012 (1962).

TABLE I. ISOMER SHIFT, δ, AND QUADRUPOLE SPLITTING, ε, OF VARIOUS INORGANIC IRON COMPOUNDS

Compound		δ mm./sec.	$\varepsilon=\frac{1}{4}e^2qQ$ mm./sec.
$K_3[Fe(CN)_6]$		0.00	0.14
$Zn_3[Fe(CN)_6]_2$		−0.02	0.00
$Cd_3[Fe(CN)_6]_2$		−0.05	0.00
$Ni_3[Fe(CN)_6]_2$		−0.06	0.24
$Co_3[Fe(CN)_6]_2$		−0.06	0.17
$Ag_3[Fe(CN)_6]$*1		−0.08	0.39
$Cu_3[Fe(CN)_6]_2$*1		−0.09	0.24
$KFe(SO_4)_2\cdot 12H_2O$		+0.49	0
$RbFe(SO_4)_2\cdot 12H_2O$		+0.51	0
$CsFe(SO_4)_2\cdot 12H_2O$		+0.55	0
$(NaPO_3)_n$-Fe_2O_3	(P/Fe=5)	+0.49	0
$(NaPO_3)_n$-Fe_2O_3	(P/Fe=10)	+0.52	0.17
$(NaPO_3)_n$-Fe_2O_3	(P/Fe=50)	+0.52	0.21
$(NaPO_3)_n$-Fe_3O_4*2	(P/Fe=5)	+0.48	0.21
$(NaPO_3)_n$-Fe_3O_4*2	(P/Fe=7)	+0.48	0.22
$(NaPO_3)_n$-Fe_3O_4*2	(P/Fe=10)	+0.51	0.23
$(NaPO_3)_n$-Fe_3O_4*2	(P/Fe=50)	+0.53	0.24
$Fe_4(P_2O_7)_3\cdot 9H_2O$		+0.49	0
$FePO_4\cdot 4H_2O$		+0.43	0.15
$Fe_3(PO_4)_2\cdot 8H_2O$		+0.13	1.36
Fe_2O_3*3		+0.47	0.21
Fe_3O_4*3		+0.87 +0.46	0 0
$Fe_2(CrO_4)_3$		+0.34 +0.38	0.38 0
$Fe_2O_3\cdot 4CrO_3\cdot H_2O$		+0.37	0.33
$FeAsO_4$		+0.59	0.19

*1 See Ref. 2.

*2 Most Fe(II) in Fe_3O_4 must be oxidized into Fe(III) in the course of the sample preparation. Therefore these four formulas do not represent their true constituents.

*3 See Ref. 10.

density around the Mössbauer nucleus. This rule appeared to be only roughly valid for the group of compounds. Our results on metal ferricyanides and metal-iron double sulfates seem to indicate that small differences in the isomer shifts and the quadrupole splittings exist.

In a series of metal ferricyanide complexes, the absorption peak appeared close to zero velocity in every case, showing the strong covalent character of the bond between Fe and CN. The "outside" metal, separated from the iron atom by more than about 4 Å, was considered to have very little effect on the peak position. However, our results seemed to show a systematic change in the isomer shifts depending on the electronegativity of the "outside" metal. The positive shifts of the isomer shift were observed with a decrease in the electronegativities of the metals. This rule was also observed in the case of a series of metal-iron double sulfates. Lithium and sodium containing double sulfate were not measured because of the difficulty in preparing such compounds.

All the Mössbauer spectra of the metal-iron double sulfates studies displayed a single peak. On the contrary, all the metal ferricyanide salts, except zinc and cadmium salts, gave small quadrupole splittings. As examples, three spectra are illustrated in Fig. 2.

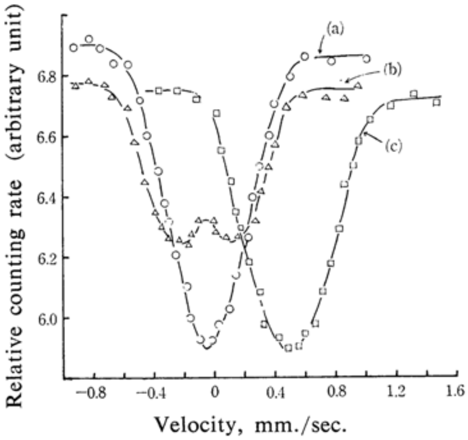

Fig. 2. Mössbauer spectra of $Cd_3[Fe(CN)_6]_2$ (a), $Co_3[Fe(CN)_6]_2$ (b) and $KFe(SO_4)_2\cdot 12H_2O$ (c).

Since these ferricyanide complexes have no water molecule in them, a direct comparison of the data is possible; i. e., one can neglect the influence of water molecules on the spectral shape. The sharp single absorption peak in the spectra for zinc and cadmium ferricyanide complexes indicates that the iron atoms in these complexes have spherically symmetric electron distribution.

As has been discussed earlier, the quadrupole splitting is caused by a nonzero electric field gradient at the iron nucleus. Moreover, the electric field gradient depends on various collective factors, i. e., the bonding character and the crystallographic character of the compound, the electronegativity of the neighboring atoms, etc. In this case, however, it appears that the sizable quadrupole splitting of these metal ferricyanides is to be attributed to their crystallographic distortion from a cubic structure caused by the "outside" metals. A noticeable broadening of the spectral lines in some ferricyanide complexes (nickel and cobalt) has been observed. This might be due to a small unresolved quadrupole splitting.

The purpose of the present investigation of the glassy substances of iron-phosphate was to elucidate the bonding character between the iron and the phosphate group in the materials. Originally, it was thought that one of the fundamental requirements for the Mössbauer effect to arise was that Mössbauer atoms should be bound in a crystal lattice. It was, however, shown in an earlier paper[11] that there is a high possibility of observing the effect even in amorphous substances (or in solid solutions).

In view of the above fact, we chose a series of fused products or iron-phosphate as samples. The spectral shapes of two series of the substances, the $(NaPO_3)_n$-Fe_2O_3 system and the $(NaPO_3)_n$-Fe_3O_4 system, were essentially identlcal, and both exhibited characteristic peaks at about 0.50 mm./sec. This fact means that iron(II) in Fe_3O_4 was oxidized into iron(III) in the course of the sample preparation.

It is very difficult to conclude from the present data whether the isomer shifts obtained are due to the original iron(III) oxide or to new bonding between iron and the phosphate group. At any rate, the iron atoms are supposed to be surrounded predominantly by oxygen atoms. Therefore, relatively close values of isomer shift were observed for Fe_2O_3, $Fe_4(P_2O_7)_3 \cdot 9H_2O$ and $FePO_4 \cdot 4H_2O$, as is shown in Table I. However, there is one thing to be noted: the spectral characteristics of $(NaPO_3)_n$-Fe_2O_3 (P/Fe=5) differ from those of iron(III) oxide itself. The former displayed no quadrupole splitting, and the isomer shift value agreed well with that of $Fe_4(P_2O_7)_3 \cdot 9H_2O$. In view of this fact, all one can conclude at present is that the iron(III) pyrophosphate type of bonding grew, at least in $(NaPO_3)_n$-Fe_2O_3 (P/Fe=5).

The samples chosen for the remaining studies were iron(III) arsenate and iron(III) chromates. The results obtained suggest that the bonding between Fe and AsO_4 is typically ionic, while the bonding between Fe and CrO_4 (or CrO_3) is more or less covalent.

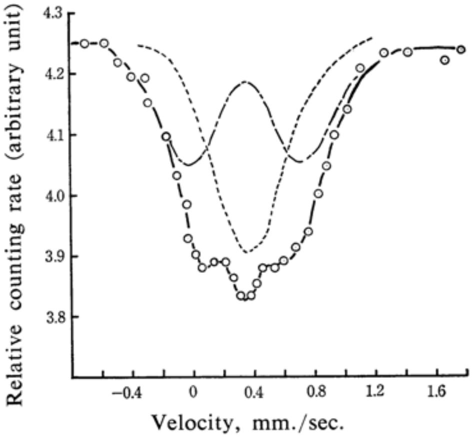

Fig. 3a. Mössbauer spectrum of iron(III) chromate.

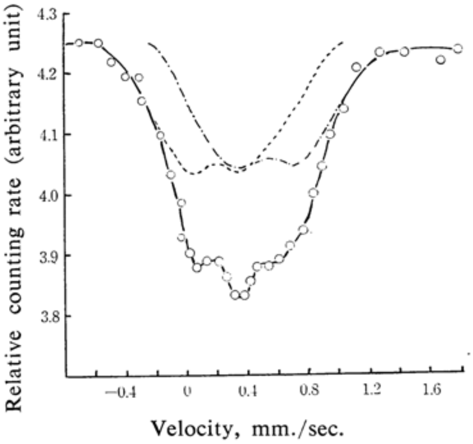

Fig. 3b. Mössbauer spectrum of iron(III) chromate.

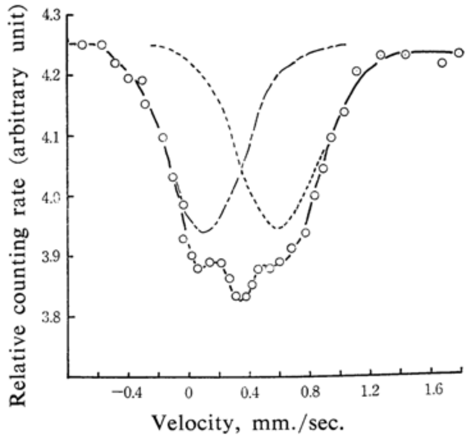

Fig. 3c. Mössbauer spectrum of iron(III) chromate.

The Mössbauer spectrum of iron(III) chromate is shown in Fig. 3a. It can be resolved into two components (dotted curves), showing that iron(III) chromate has two different isomer shifts. This fact obviously indicates that there are two sites for iron atoms in the iron(III) chromate crystal. Consequently, it is recommended that the chemical formula of iron(III) chromate be written as $Fe[Fe(CrO_4)_3]$ instead of $Fe_2(CrO_4)_3$]. We interpreted the single peak as being due to ionic Fe (δ=0.38 mm./sec.), while we attributed the doublet to covalent iron atoms (δ=0.34 mm./sec., δ=0.38 mm./sec.). It should be noted that the spectrum may also be resolved in the two ways

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[11] V. A. Bryukhanov. V. I. Col'danskii, N. N. Delyagin, L. A. Korytko, E. F. Makarov, I. P. Suzdalev and V. S. Shpinel, *Soviet Phys., JETP*, **16**, 321 (1963).

shown in Fig. 3b ($\delta_1=+0.58$, $\delta_2=+0.10$ mm./sec.) and in Fig. 3c. ($\delta_1=+0.21$, $\delta_2=+0.52$ mm./sec.).

As has been described elsewhere, however, the magnitude of one of the isomer shifts (+0.10 mm./sec.) in Fig. 3b is not in the region of iron(III) salts. Though the isomer shifts obtained from Fig. 3c are reasonable, any possible analysis of the spectrum can be made only in a rough manner. The assumption of the presence of two different types of iron atoms should be confirmed chemically in future study.

We have as yet comparatively little knowledge as to what chemical information can be obtained from the Mössbauer spectrum. More extensive studies and discussion by many workers are desired.

Summary

The Mössbauer spectra of a variety of as-yet-unexplored iron compounds have been investigated by using 14.4 keV. gamma rays from ^{57}Fe. The isomer shifts and the quadrupole splitting extracted from the spectra have been discussed in terms of the electronegativity of the atoms connected to the iron atom. The correlation of these values with the bond character and the chemical structure has also been discussed qualitatively. The results obtained for a series of glassy substances of iron-phosphate suggest that the Mössbauer spectra may permit us to study the chemical structure of iron compounds in an amorphous substance.

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