11 Mössbauer Spectroscopy

INTRODUCTION

Mössbauer spectroscopy, which will be abbreviated as MB spectroscopy in this text, involves nuclear transitions which result from the absorption of γ-rays by the sample. The conditions for absorption depend upon the electron density about the nucleus, and the number of peaks obtained is related to the symmetry of the compound. As a result considerable structural information can be obtained from MB spectra.

To understand the principles of this method, first consider a gaseous system consisting of a radioactive source of γ-rays and the sample which can absorb γ-rays. When a gamma ray is emitted by the source nucleus, it decays to the ground state. The energies of the emitted γ-rays, E_γ have a range of 10 to 100 kev and are given by equation (11-1):

$$E_\gamma = E_r + D - R \qquad (11\text{-}1)$$

where, E_r is the difference in energy between the excited state and ground state of the source nucleus; D, the Doppler shift, is due to the translational motion of the nucleus, and R is the recoil energy of the nucleus. The recoil energy is generally 10^{-2} to 10^{-3} ev and is given by the equation:

$$R = E_\gamma^2 / 2mc^2 \qquad (11\text{-}2)$$

where m is the mass of the nucleus and c is the velocity of light. The energy of a γ-ray emitted from a nucleus moving in the same direction as the emitted ray is different from the energy of a γ-ray emitted from a nucleus moving in the opposite direction. The distribution of energies resulting from the translational motion of the source nuclei in many directions is referred to as Doppler broadening. The left hand curve of Fig. 11-1 represents the distribution of energies of emitted γ-rays, E_γ, resulting from Doppler broadening. If the dotted line in Fig. 11-1 is taken as E_r, the energy difference between the nuclear ground and

Doppler broadening and the energy difference, R, between the dotted line and the average energy of the left hand curve is the recoil energy transmitted to the source nucleus when a γ-ray is emitted.
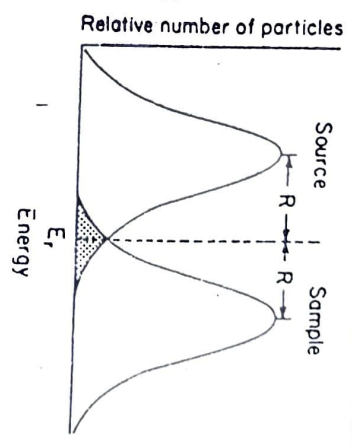

Fig. 11-1. Distribution of Energies of Emitted and Absorbed γ-rays.

In MB-spectroscopy the sample and source nuclei are the same, and the energy of the γ-ray absorbed for a transition in the sample is given by:

$$E_\gamma = E_r + D + R \qquad (11\text{-}3)$$

In this case, R is positive because the exciting γ-ray must have energy necessary to bring about the transition and effect recoil of the absorbing nucleus. The quantity D has the same significance as before. The curve in the right half of Fig. 11-1 shows the distribution of γ-ray energies necessary for absorption. The relationship of the sample and source energies can be seen from the entire figure. As indicated by the shaded region, there is only a very slight probability that the γ-ray energy from the source will match that required for absorption by the sample. Since the nuclear energy levels are quantized, there is accordingly a very low probability that the γ-ray from the source will be absorbed to give a nuclear transition in the sample. The main cause for nonmatching of the γ-ray energies is the recoil energy. If this quantity, R, could be reduced, or if conditions for a recoilless transition could be found, the sample would have a higher probability of absorbing γ-rays from the source. As indicated by equation (11-2), R can be decreased by increasing, m, the mass. This can be effected by placing the nucleus of the sample and source in a crystal so that the mass is effectively that of the crystal.

equation (11-2). For this reason, MB spectra are almost always obtained on solids employing solid sources.

By placing our source and sample in solid lattices, we have not effected recoilless transitions for all nuclei but we have increased the probability of a recoilless transition. The reason for this is that the energy of the γ-ray may cause excitation of lattice vibrational modes. This energy term would function in the same way as the recoil energy in the gas, i.e., it would decrease the energy of the emitted particle and increase the energy required for absorption. Certain crystal properties and experimental conditions for emission or absorption will leave the lattice in its initial vibrational state, i.e., conditions for a recoilless transition will be satisfied. It should be emphasized that these conditions simply determine the intensity of the peaks obtained, for it is only the number of particles with matching energy that is determined by this effect. We shall not be concerned with the absolute intensity of a band so this aspect of MB spectroscopy will not be discussed. It should be mentioned however that for some materials (usually molecular and not ionic solids) lattice and molecular vibrational modes are excited to such an extent that very few recoilless transitions occur at room temperature and no spectrum is obtained. Frequently, the spectrum can be obtained by lowering the temperature of the sample appreciably. This subject is treated in references 1–4 which contain a more detailed discussion of the entire subject of MB spectroscopy.

Our main concern will be with the factors affecting the energy required for action of the nuclei with the chemical environment that result in small changes in the energy required for absorption: (1) resonance line shifts from change in electron environment, (2) quadrupole interactions, and (3) magnetic interactions. These effects give us information of chemical significance and will be our prime concern.

Before discussing these factors, it is best to describe the procedure for obtaining spectra and to illustrate a typical MB spectrum. The electron environment about the nucleus in the sample affects the energy of the γ particle necessary to effect the nuclear transition in the sample from the ground to excited state. The energy of γ-rays from the source can be varied over the range of the energy differences arising from the electron environment by moving the source relative to the sample. The higher the velocity at which the source is moved toward the sample, the higher the average energy of the emitted γ-ray (by the Doppler effect) and vice versa. On γ-types MB spectrum consists of moving the source relative to the sample until the source velocity at which maximum absorption of

γ-rays occurs is determined. Consider, as a simple example, the MB spectrum of Fe^{2+} $Fe^{III}(CN)_6$, (Fe^{III} and Fe^{3+} designate strong and weak field iron (III)). This substance contains iron in two different chemical environments and two different energy γ-rays are required to effect transitions in the different iron nuclei. To obtain the MB spectrum, the source is moved toward the fixed sample at a certain velocity and the number of γ-rays passing through the sample are counted. The procedure is repeated for a whole series of source velocities, and the corresponding count is plotted (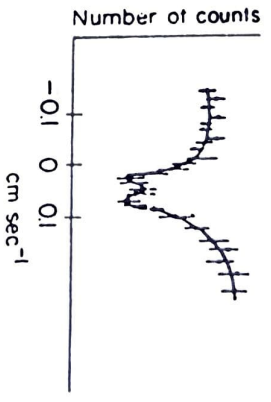as in Fig. 11-2) to produce the MB spectrum. The peaks correspond to source velocities at which maximum γ-ray absorption by the sample occurs. Negative relative velocities correspond to moving the source away from the sample.

The relative velocity at which the source is being moved is plotted along the abscissa of Fig. 11-2, and this quantity is related to the energy of the γ-ray. For an Fe^{57} source emitting a 14.4 kev γ-ray, the energy is changed 4.8×10^{-7} ev or 0.011 cal mole⁻¹ for every cm sec⁻¹ velocity imposed upon the source. Referring back to the abscissa of Fig. 11-2, one sees that the energy difference in the nuclear transitions for Fe^{2+} and Fe^{III} in FeFe(CN)₆ is very small, corresponding to about 2×10^{-8} ev. It can thus be seen that the MB spectrum in Fig. 11-2 resembles IR, UV, and NMR spectra in that intensity is plotted against frequency or energy of the radiation.

The peak in the spectrum in Fig. 11-2 at 0.003 cm sec⁻¹ is assigned to Fe^{III} and that at 0.053 to the cation Fe^{2+} by comparison of this spectrum with those for a large number of cyanide complexes of iron. Different line positions which result from different chemical environments are indicated by the values for the source velocity in units of cm sec⁻¹ or mm sec⁻¹ and are referred to as isomer shifts or chemical shifts. The symbol δ is used to indicate an isomer shift. We shall now proceed with a

Number of counts

−0.1   0   0.1

cm sec⁻¹

Fig. 11-2. MB Spectrum of FeFe(CN)₆.

brief, qualitative discussion of the various factors affecting line position and shape of MB spectra.

(1) LINE SHIFTS FROM CHANGE IN ELECTRON ENVIRONMENT

The two different peaks in Fig. 11-2 arise from the isomer shift. The isomer shift arises because the electron density *at the nucleus* interacts with the positive nuclear charge, and the relative energies of the ground and excited nuclear states are affected in much the same way that positive nuclear charge affects the energy of the electrons. Depending on the relative change in energy between the ground and excited nuclear states by interaction with the 'electrons in various chemical environments, different energies will be required to induce transitions in various materials. The interaction of the nucleus with an electron will depend upon the value for the wave function of the electron at the nucleus. Only electron density in the s orbitals has a finite value at the nucleus, so electrons in p, d, and f orbitals can affect the isomer shift only by screening the s electrons from the nuclear charge. The interpretation of isomer shift data is complicated by these effects. For Fe^{57} it has been shown that increasing s electron density at the nucleus produces a negative shift in the value for δ; i.e., a smaller positive number or a larger negative number corresponds to greater s electron density at the nucleus. The shielding by the $3d$ electrons has been computed[6] for iron(III) and the results applied to the interpretation of isomer shift data in some spin-free iron complexes. A quantitative correlation between δ and s electron density is proposed in these complexes. The sign of the shift depends upon the difference between the effective nuclear charge radius, r, of the excited and ground states $(r_{ex}^2 - r_g^2)$. For the Fe^{57} nucleus the excited state is smaller than the ground state, and an increase in density produces a negative shift. This is not necessarily true for other isotopes.

It should be mentioned that the isomer shift measured is actually the difference in s electron density of the sample and the source. For Fe^{57} a value of zero indicates the same s electron density about the sample and source, while a negative δ indicates the sample has more s electron density at the nucleus, and *vice versa*. Thus the composition and properties of the source are very important. These factors and other effects which contribute to the magnitude of the resonance line shifts have been reviewed.[1]

...POLE INTERACTIONS

If the ground or excited nuclear configuration possesses a quadrupole moment, the energy levels in that state will be split to an extent, ΔE_Q,

depending upon the magnitude of the quadrupole moment and the field gradient at the nucleus. This is the same type of splitting discussed in NQR spectroscopy. For a simple asymmetric chemical environment about the n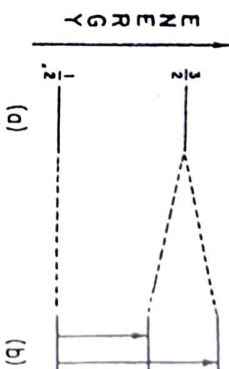ucleus, multiple peaks are obtained in the MB spectrum corresponding to transitions involving different orientations of the quadrupole moment of the ground and/or excited states.

For Fe^{57}, the ground state has an I value of $\frac{1}{2}$, but the first excited state has a value of $\frac{3}{2}$. When there is no field gradient at the nucleus, the excited levels are degenerate; but in the presence of a field gradient, this level is split. In axially symmetric fields (linear, square planar, etc.) there
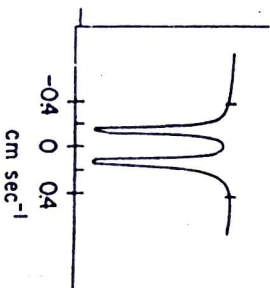

Fig. 11-3. Nuclear Energy Levels for the Ground and First Excited State of an Fe^{57} Nucleus. (a) Zero field gradient. (b). An appreciable field gradient.

are $I + \frac{1}{2}$ different levels for half-integral spins ($\frac{3}{2}$, $\frac{5}{2}$, $\frac{7}{2}$, etc.) and $I + 1$ different levels for integral spins ($I = 1, 2, 3$, etc.). The splitting of the excited state will not occur in a spherically symmetric field but will only occur when there is a field gradient at the nucleus caused by asymmetric s electron distribution in a compound. A field gradient exists in the trigonal bipyramidal molecule iron pentacarbonyl, so a splitting of the nuclear excited state is expected. The two expected transitions (designated by arrows in Fig. 11-3) give rise to a doublet in the spectrum,[8] as indicated in Fig. 11-4.

-04 0 04
cm sec^{-1}

Fig. 11-4. MB Spectrum for $Fe(CO)_5$ at Liquid Nitrogen Temperature. From L. M. Epstein, *J. Chem. Phys.*, 36, 2731 (1962).

MAGNETIC INTERACTIONS

This nuclear effect is analogous to the Zeeman splitting of atomic orbitals by a magnetic field. The magnetic field at the nucleus produced by the surroundings can interact with the nuclear magnetic moment. This interaction causes a removal of the degeneracy of nuclear energy levels. The number of different levels obtained from this effect is determined by the magnetic quantum number of the nucleus. In general $2I + 1$ values $(+I, \ldots, -I)$ can be obtained for a given nucleus where I is the nuclear spin quantum number. A whole series of transitions can occur to and from these different levels in the ground and excited state. The selection rule is: $\Delta I = 0, \pm 1$. Splitting from this effect is commonly observed only in ferromagnetic or antiferromagnetic crystals.

APPLICATIONS

Many applications of this technique which are mainly of interest to physicists have been summarized[1,2] but will not be discussed here. A few chemical applications have been selected for discussion which are illustrative of the kind of information that can be obtained from MB spectroscopy. Mössbauer resonances have been observed in the following nuclei: Au^{197}, Dy^{161}, Er^{166}, Fe^{57}, Gd^{155}, Ge^{73}, Hf^{177}, I^{127}, I^{129}, Ir^{191}, Ir^{193}, Ni^{61}, Pt^{195}, Re^{187}, Sb^{123}, Sn^{119}, Ta^{181}, Tm^{169}, W^{182}, Yb^{170}, Zn^{67}.

Facsimiles of spectra obtained on some iron complexes are given in Fig. 11-5. For spin-free iron complexes in which all six ligands are equivalent, a virtually spherical electric field at the nucleus is expected for $Fe^{3+}(d^5)$ but not for $Fe^{2+}(d^6)$. In the d^5 case each d orbital has one electron, producing a spherical charge distribution; but there is asymmetry for the spin-free d^6 case. As a result of the field gradients at the nucleus, quadrupole splitting should be detected in the spectrum of spin-free iron(II) complexes but not for spin-free iron(III) complexes. This is borne out in spectra A and B of the complexes illustrated in Fig. 11-5.

② For spin-paired complexes, iron(II) has a configuration t_{2g}^6 and iron(III) t_{2g}^5. As a result quadrupole splitting is now expected for iron(III) but not iron(II) in the strong field complexes. This conclusion is confirmed experimentally by the spectra of ferrocyanide and ferricyanide ions.

③ When the ligand arrangement in a strong field iron(II) complex does not consist of six equivalent ligands $[Fe(CN)_5NH_3]^{3-}$, quadrupole splitting of the strong field iron(II) will result.

Values measured at room temperature for ΔE_Q and the isomer shift, δ, for a number of iron complexes have been collected[1] and are listed

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(a)

$-0.2 \quad 0 \quad +0.2 \quad +0.4$

(b)

$-0.1 \quad 0 \quad +0.2$

(c)

$-0.2 \quad 0 \quad +0.2$
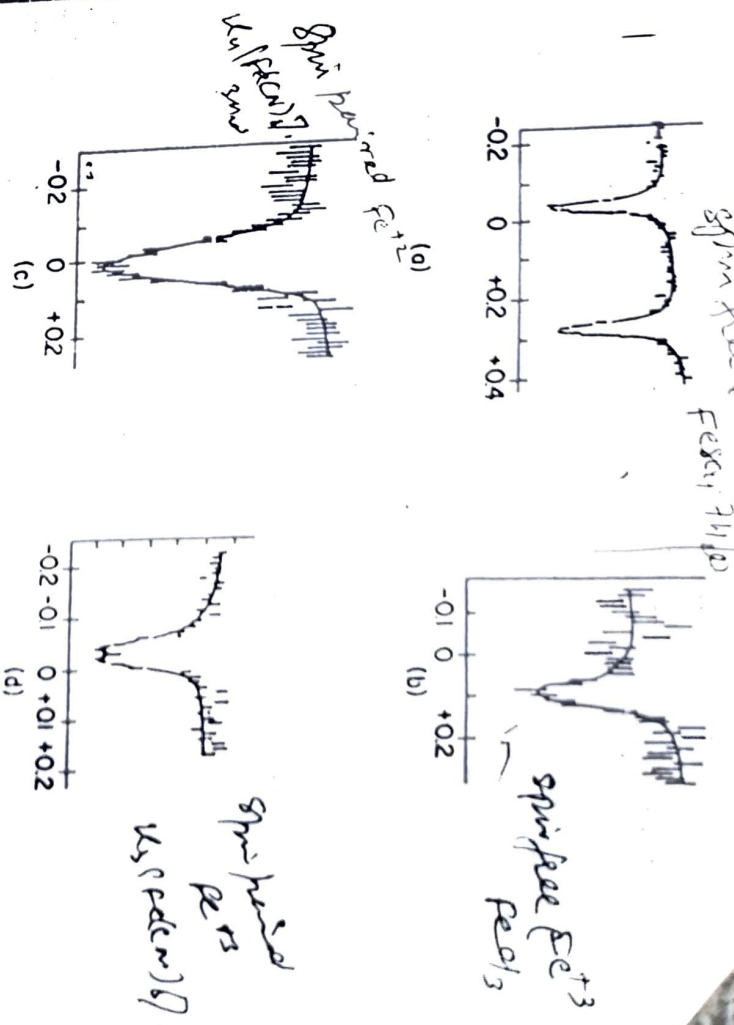
(d)

$-0.2 \quad -0.1 \quad 0 \quad +0.1 \quad +0.2$

Fig. 11-5. Mössbauer Spectra of Some Iron(II) and Iron(III) Complexes. (a) Spin-free iron(II) – $FeSO_4 \cdot 7H_2O$. (b) Spin-free iron(III) – $FeSO_4 \cdot 7H_2O$. (c) Spin-paired iron(II) – $K_4Fe(CN)_6 \cdot 3H_2O$. (d) Spin-paired iron(III) – $K_3Fe(CN)_6$. From P. R. Brady, P. F. F. Wigley, and J. F. Duncan, *Rev. Pure Appl. Chem.*, 12, 181 (1962).

in Table 11-1. For iron complexes, isomer shifts in a positive direction correspond to a decrease in electron density in the region of the nucleus. For spin-free complexes a correlation exists between isomer shift and s electron density. An increase in δ of 0.02 cm sec⁻¹ is equivalent to a decrease in charge density of 8 per cent at the nucleus[6] The negative values obtained for the spin-paired ferricyanides compared to spin-free iron(III) complexes indicate more electron density at the nucleus in the ferricyanide ions. This has been explained as being due to extensive π bonding in the ferricyanides which removes d electron density from the metal ion which in turn decreases the shielding of the s electrons. This effect increases s electron density at the nucleus and decreases δ. In general more positive shifts are obtained for σ bonded complexes and negative shifts for those in which there is extensive π bonding.

⑦ The MB spectrum of the material prepared from iron(III) sulfate and $K_4Fe(CN)_6$ is identical to the spectra for the compounds prepared from

either iron(II) sulfate and $K_3Fe(CN)_6$, or by atmospheric oxidation of the compound from iron(II) sulfate and $K_4Fe(CN)_6$. The spectra of these materials indicate that the cation is spin-free iron(III), while the anion is spin-paired iron(II).

TABLE 11-1. QUADRUPLE SPLITTING, ΔE_q, AND ISOMER SHIFT, δ, FOR SOME IRON COMPOUNDS (δ AND ΔE_q IN CM SEC^{-1})

Compound	ΔE_q	δ
Spin-free Fe^{2+}		
$FeSO_4 \cdot 7H_2O$	0.32	-0.119
$FeSO_4$ (anhydrous)	0.215	0.13
$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	0.27	0.12
	0.175	0.119
$FeCl_2 \cdot 4H_2O$	0.175	0.13
	0.300	0.135
$FeC_2H_3O_6$	0.26	0.125
FeF_2	0.268	—
$FeC_2O_4 \cdot 2H_2O$	0.17	0.125
Spin-free Fe^{3+}		
$FeCl_3 \cdot 6H_2O$	0.02	0.085
$FeCl_3$ (anhydrous)	0.02	0.05
$FeCl_3 \cdot 2NH_4Cl \cdot H_2O$	0.03	0.045
$Fe(NO_3)_3 \cdot 9H_2O$	0.04	0.04
$Fe_2(C_2O_4)_3$	0.05	0.045
$Fe_2(C_4H_4O_6)_3$	0.077	0.043
Fe_2O_3	0.012	0.047
Spin-paired Fe^{II}		
$K_4[Fe(CN)_6] \cdot 3H_2O$	—	-0.013
	—	-0.016
$Na_4[Fe(CN)_6] \cdot 10H_2O$	<0.01	-0.005
$Na_3[Fe(CN)_5NH_3]$	<0.02	-1.01
$K_3[Fe(CN)_5NH_3]$	0.06	-0.005
$K_2[Fe(CN)_5NO]$	0.185	-0.027
$Zn[Fe(CN)_5NO]$	0.176	-0.028
	0.190	-0.027
Spin-paired Fe^{III}		
$K_3[Fe(CN)_6]$	—	-0.012
	—	-0.017
$Na_3[Fe(CN)_6]$	0.026	-0.015
	0.060	-0.017

⑧ The MB spectrum of sodium nitroprusside, $Na_2Fe(CN)_5NO$, has been investigated.[8] This material has been formulated earlier as iron(II) and NO^+ because the complex is diamagnetic. The MB spectrum consists of a doublet with a ΔE_q value of 1.76 mm/sec^{-1} and a δ value of -0.165 mm/sec^{-1}. The δ value is far too negative for an Fe^{II} complex. Comparison of this value with reported results[7] on a series of iron complexes suggests that the iron δ value is close to that of iron(IV). The magnetism and MB spectrum are consistent with a structure in which there is extensive π bonding between the odd electron in the t_{2g} set of the orbitals of iron and the odd electron on nitrogen, as illustrated in Fig. 11-6. The filled π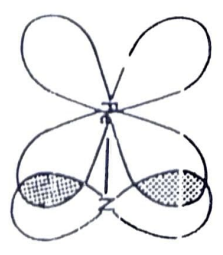 bonding orbital has 2 large contribution from the nitrogen atomic orbital and the empty π antibonding orbital has a larger contribution from the iron atomic orbital. As a result, more of the π electron density is localized on nitrogen and the δ value for iron approach's that of iron(IV) because of decreased shielding of the s electrons by the d electrons. Since electron density is being placed in what was previously a π antibonding orbital of nitric oxide, a decrease in the $\cdots$—O infrared stretching frequency is observed. The very large quadrupole splitting is consistent with very extensive π bonding in the Fe—N—O link.

The MB spectra of the iron pentacarbonyls: $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ have been reported.[9] The results are as expected from the known structures for both $Fe(CO)_5$ and $Fe_2(CO)_9$. The structure of $Fe_3(CO)_{12}$ deduced from its MB spectrum is not in agreement with the structure reported from a single crystal x-ray study.

The MB spectra of several tin compounds have been observed.[10] In compounds of the general formula SnX_4 (where X is a halogen), a correlation is obtained between the electronegativity of X and δ. As the electronegativity of X is increased, δ increases. The ΔE_q values for the compounds $(C_6H_5)_3SnX$ also increase with increasing electronegativity of X, because the more electronegative X causes a larger field gradient at the nucleus. The quadrupole splitting found in SnF_4 is consistent with a

Fig. 11-6. Orbitals Involved in the Fe—N π Bonding to the NO Group in $Fe(CN)_5NO^{2-}$.