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High-Pressure Mössbauer Resonance Studies with Iron-57[1]

H. G. Drickamer
Department of Chemistry and Chemical Engineering and Materials Research Laboratory, University of Illinois, Urbana, Illinois
R. W. Vaughan
Physics Division, Jet Propulsion Laboratory, Pasadena, California
A. R. Champion
Sandia Corporation, Albuquerque, New Mexico

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The Mössbauer effect is a useful tool for investigating a number of aspects of chemistry and physics, since it allows one to compare very accurately the energy of specific nuclear transitions. The energy of a nuclear transition is slightly modified by surrounding electrons, and by measuring these energy modifications it is possible to deduce information about the chemical nature of the environment. In this paper we discuss the effect of pressure on compounds of iron.

The principles of Mössbauer resonance have been thoroughly discussed,[2] and will be reviewed only briefly here. The emission or absorption of a γ ray by the nucleus of a free atom involves Doppler broadening and recoil processes. The basic discovery of Mössbauer was that, by fixing the atom in a solid where the momentum is quantized and the motion limited to vibrational modes, these effects might be eliminated. If the lowest allowed quantum of lattice vibrational energy (lowest phonon energy) is large compared with

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(2) (a) H. Frauenfelder, "The Mössbauer Effect," W. A. Benjamin, Inc., New York, N. Y., 1963; (b) G. K. Wertheim, "Mössbauer Effect: Theory and Applications," Academic Press, New York, N. Y., 1964.

the classical recoil energy for absorption or emission, a large fraction of recoilless decays is possible, and, as the net velocity of a vibrating system is zero, there will be no Doppler broadening. Thus the width of the peak will be established by the uncertainty principle plus instrumental broadening and relaxation effects. Energy changes of the order of 10^{-5} cal ($\sim 10^{-9}$ eV) are measurable.

There is a variety of Mössbauer isotopes and a number of properties which can be studied. We shall confine ourselves to a discussion of the 14.4-keV transition in Fe^{57} and to two kinds of readout: the isomer shift and the quadrupole splitting. As mentioned above, nuclear states are slightly perturbed by electronic wave functions having nonzero amplitude at the nuclear site (s electrons), so a source and absorber with different electronic configurations are not in resonance. By moving the source with respect to the absorber, and thus effecting a Doppler shift on the energy of the emitted γ ray to compensate for this energy difference (called the isomer shift), one can establish resonance. A Mössbauer spectrometer is, then, a device for producing and measuring accurately the velocities necessary to obtain resonance between source and absorber in different environments. In this work energy differences are reported in millimeters per second relative to metallic (body-centered cubic) iron at 1 atm. The apparatus for high-pressure Mössbauer studies is described in the literature.[3,4]

In iron compounds the 1s and 2s electronic wave functions have large amplitudes at the nucleus but are shielded from the environment. (The excellent correlation that Erickson[5] obtains between isomer shift and chemical properties, for example, indicates the controlling effect of the chemical environment, *i.e.*, the 3s and 4s electrons.) If there are 4s electrons present, they interact strongly with the surroundings. The 3s electrons do not interact directly, but they have their radial maximum at about the same point as the 3d electrons, and these do interact with the ligands. Changes in the 3d wave functions are thus reflected in changes in shielding of the 3s electrons.

The difference in isomer shift between source and absorber is given by eq 1. For iron $\alpha = 3.52 \times 10^{10}$

$$\Delta\epsilon = \alpha[\psi_S^2(0) - \psi_A^2(0)] \tag{1}$$

$R\Delta R$, where ΔR is the difference of the radius of the nucleus in the ground and excited states. The evaluation of α experimentally and theoretically is a subject of controversy which will engage us peripherally.

The nuclear levels can also interact with an electric field gradient at the nucleus. In iron the excited state of spin $^3/_2$ splits and two peaks are observed. An electric field gradient can arise from an aspherical distribution of electrons in the 3d shell (q_{val}) or from a less than cubic distribution of the ligands (q_{lat}). Because of the short range of quadrupolar forces, where the former effect is present, it dominates.

There are other readouts, such as the magnitude of a magnetic field and the fraction of recoilless decays which give useful information, but these will not be discussed here.

As an aid in discussing the Mössbauer results it is useful to review briefly some effects of pressure on optical spectra which are presented in detail elsewhere.[6,7] The free ion has a fivefold-degenerate 3d shell. The difference in energy between the ground and excited states can be expressed in terms of the Racah parameters, *A*, *B*, and *C*, which measure the repulsion among the 3d electrons. In a crystal field the degeneracy is partially removed. (Octahedral symmetry is used here as an example. Results for other symmetries are similar. Reference to the molecular orbital diagram on p 103 of Ballhausen and Gray[8] may be helpful.) There is a triply degenerate level, t_{2g}, and a doubly degenerate level, e_g, separated by an energy, $10Dq$, which measures the crystal field. Optical transitions of moderate intensity are observed which measure $10Dq$, the Racah parameters *B* and *C*, or combinations of these. With pressure, the crystal field increases by about 10–15% in 100 kbars. The Racah parameters decrease by 7–10% in the same range, which can best be explained in terms of a spreading of the 3d orbitals due to increased interaction with the ligands as pressure increases.

There are also very intense allowed transitions in the near ultraviolet (3–5 eV) with tails that extend through the visible and even into the infrared. These represent charge transfer from ligand nonbonding to metal antibonding levels ($t_{2u} \rightarrow t_{2g}$). These peaks shift to lower energy by 0.5 to 1 eV in 100 kbars. The major cause of the red shift is probably the spreading of the 3d orbitals mentioned above, which could easily lower the metal levels *vis-à-vis* the ligands by this amount. Increased π bonding of the t_{2g} orbital with ligand π^* levels would also stabilize the t_{2g} level. Lewis[9] has shown that this is a factor, but not the major one.

Finally, there is more than one way to arrange the electrons in the 3d levels. Hund's rule demands maximum multiplicity. In this case, ferric ion, with five 3d electrons, exhibits spherical symmetry and quadrupole splitting only due to the ligand field (q_{lat}). The usual range is from 0.3 to 0.6 mm/sec. The extra electron on the high-spin ferrous ion usually guarantees an aspherical 3d shell and large quadrupole splittings

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