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D. A. Shirley

January 1966

Chapter IX of CHEMICAL APPLICATIONS OF THE MÖSSBAUER EFFECT

Edited by V. I. Goldanskii and Rolfe Herber

MÖSSBAUER SPECTROSCOPY IN THE HEAVY ELEMENTS*

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THE HEAVY ELEMENTS

I. Introduction

The elements beyond the rare earths provide a most fruitful area for application of Mössbauer spectroscopy. Nuclear energy levels tend, on the average, to be more closely spaced in heavy elements, making the recoil energy $E_R = E_\gamma^2/2Mc^2$ small enough that at least 14 of the 23 elements in the interval $71 < Z < 95$ possess isotopes with Mössbauer resonances that appear to be within reach of present-day techniques. With the exceptions of mercury and lead the lattices of these elements are sufficiently stiff to provide reasonably large recoil-free fractions, though in most cases low temperatures are required. The high density of 6s electrons at the nucleus and the large electric field

II. HEAVY ELEMENT SPECTRA AND THE SPIN HAMILTONIAN

A. Formulation

The spin-hamiltonian formalism provides the most convenient framework for discussion of Mössbauer spectra of chemical compounds. In the past, several experimental factors (high concentrations of resonant atoms, fast relaxation, etc.) often combined to simplify spectra considerably. Increasingly sophisticated experiments, especially those involving large molecules and/or low temperatures, will require for their interpretation a more detailed understanding of the physical origins of various spectral features. This is especially true for heavy elements, for which there are relatively few guideposts in terms of chemical systematics, and for which low temperatures are often mandatory. The process of extracting spin-hamiltonian parameters from spectra is discussed briefly below. This procedure is often complex, but it is at least well-understood. The chemical significance of each parameter is then discussed. The ways in which the chemical interpretations may be modified by relativistic effects is mentioned, but not discussed extensively.

Resonant absorption or scattering involves two nuclear states. Each state interacts, via its electric monopole, magnetic dipole, and electric quadrupole moments, with extranuclear fields in a manner describable by a hamiltonian involving many coordinates. Even if we regard the nucleus as a rigid body we still have a computational problem that is beyond the ability of present-day theory, and approximations must be made in order to proceed. A very useful procedure consists in separating the problem into angular variables, described by angular momentum operators, and "radial" variables that are in practice treated as semiempirical constants. This procedure is termed the "spin hamiltonian" formalism.[1,2] It has been eminently successful for interpreting hyperfine structure spectra in solids. In this formalism there is an angular momentum S', called the <u>effective spin</u>, associated with the electronic coordinates. For free ions, or for ionic lattices in which crystalline-field effects are very weak,[3] S' is just the total angular momentum J. For most heavy atoms accessible to Mössbauer spectroscopy, however, the degeneracy associated with J is (partially or totally) removed through interaction with the ligands (usually via covalent bonds), and the ground electronic state is most often a singlet or doublet. The quantum-mechanical description of this

eigenstate as a linear combination of basis states in $|J,M_J\rangle$ or $|L,S\rangle$ representation may be very complicated. If the (effective) electronic spin S' and nuclear spin I are truly separable, however,[4] transition selection rules may be applied without exact knowledge of the expansion of the electronic eigenstate in any basis (i.e., S' may be treated as the fundamental electronic angular momentum variable). Thus for most purposes we may define S' by setting $(2S'+1)$ equal to the electronic degeneracy of the lowest electronic (crystal-field) state. The spin hamiltonian for this state is then written:

$$\mathcal{H}_s^i = E^i - \beta\vec{H}\cdot g\cdot\vec{S} + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z + P\{[I_{z'}^2 - (1/3)I(I+1)] + \eta(I_{x'}^2 - I_{y'}^2)\} + g_N\beta_N\vec{H}\cdot\vec{I} + \text{(crystal field terms involving S but not I)}. \tag{1}$$

The first term, E^i, gives the centroid shift for the ith nuclear state (E^1-E^0 is the isomer shift for the first excited state. We omit the superscript i on A_x, I_x, etc., for clarity). Here β and β_N are the Bohr and nuclear magnetons, g is the electronic g tensor, g_N is the nuclear g factor, $\vec{H}$ is the applied magnetic field, I is the nuclear spin, A_x, A_y, and A_z are the principle values of the magnetic hyperfine structure tensor in the xyz

coordinate system, P is the quadrupole coupling parameter given by $P = -(3e^2qQ)/[2I(2I-1)]$, and η is the quadrupole asymmetry parameter. Note that the quadrupole tensor is taken in the x'y'z' coordinate system, which may or may not be simply related to the xyz system (i.e., the principle axes of A and P may or may not be parallel). The crystal field terms are not written explicitly because they can be ignored if $S = 1/2$ or 0, as is expected for heavy elements.

While $\mathcal{H}_s$ in its most general form is rather forbidding, in practice several terms almost always vanish, leaving a tractable expression. Still one may expect in many cases to have to diagonalize a small energy matrix. Of course all the simple spectra observed to date can be explained by limiting forms of $\mathcal{H}_s$. Examples of simple applications to heavy elements are given below.

1. $Au(CN)_2^-$. This linear ion is expected to have a $^1\Sigma$ electronic assignment: thus $S = 0$. For zero applied field $\mathcal{H}_s$ reduces to $E^i + P\{[I_{z'}^2 - (1/3)\, I(I+1)] + \eta(I_{x'}^2 - I_{y'}^2)\}$. For the linear ion itself z' may be taken along the symmetry axis, and $\eta = 0$ (of course neighboring ions

may contribute to the electric field gradient to give a finite η). In the 1/2(M1)3/2 transition in Au^{197} two lines are expected. The spectrum for $KAu(CN)_2$ is shown in Figure 1.

2. $[NpO_2]^{2+}$. This linear ion has been studied by paramagnetic resonance in a UO_2 $Rb(NO_3)_3$ lattice.(5) Here $\mathcal{H}_s$ was found to be cylindrically symmetrical around the ionic axis, having the form $A_z S_z I_z + A_\perp (S_x I_x + S_y I_y) + P[I_z^2 - (1/3)\, I(I+1)]$ in zero field, with $S = 1/2$. Mössbauer experiments on Np^{237} in NpO_2 have yielded complex spectra,(6) possibly broadened by relaxation at 4.2°K, but no detailed analysis is yet available. The $[NpO_2]^{2+}$ ion is an example for which although the principle axes of the A and P tensors are identical, it is still not possible to describe spectra in terms of a hyperfine field plus quadrupole coupling, because of off-diagonal terms arising from $A_\perp$.

3. $[IrCl_6]^{-2}$. Paramagnetic resonance experiments(7) on this complex have yielded an anisotropic magnetic hyperfine structure tensor with $S = 1/2$. This is understood by noting that Ir(IV), with the configuration $5d^5$, is the analogue of low-spin ferric iron. The strong spin-orbit coupling in this

heavy element tends to lift some of the quenching of orbital angular momentum, however, and the electronic g-factors are somewhat removed from the "spin only" value of 2.00. Paramagnetic hyperfine structure has not yet been observed in Mössbauer spectra, but it should be present at low temperatures. Quadrupole splitting is expected to be small in this nominally octahedral complex.

B. Application of the Spin Hamiltonian

The application of $\mathcal{H}_s$ is quite straightforward.[8] The first step is to evaluate the non-zero matrix elements of $\mathcal{H}_s$ in $|SIS_zI_z\rangle$ representation, form the (2S+1)(2I+1)-row (square) energy matrix and diagonalize it. Having obtained the eigenvalues and eigenvectors of ground and excited states, one must next evaluate the intensities and polarizations of the various components by standard methods of angular momentum theory.[9] The actual analysis of a spectrum is most conveniently done in two quite distinct steps. First the hfs parameters are varied throughout the entire possible range and spectra are calculated that may be compared with experiment to decide which range is the correct one. Next a least-squares fit may be done within the allowed range until the best set of hfs parameters is obtained. For a reasonably simple

$\mathcal{H}_s$ the first step can be done by systematic schemes such as the g-factor diagram.[10] A quadrupole diagram for the case 5/2(dipole)3/2 is illustrated in Figure 2. The individual multipole terms in $\mathcal{H}_s$ are discussed separately below, and together in section F.

C. Isomer Shift

The first term in $\mathcal{H}_s$, namely E^i, gives the centroid shift of the ith nuclear state. It is electrostatic in origin, entailing Coulombic interaction of the electronic charge distribution with the nuclear charge distribution over the finite volume of the nucleus.
The Coulombic interaction may have components of all even tensor ranks: isomer shifts arise from the monopole (zero rank) component.

For heavy elements the isomer shift may be especially large. It may be written[11]

$$\delta E = \left(\frac{4\pi Z e^2 R^2}{5}\right)\left(\frac{\delta R}{R}\right)(S') \quad [\sum_A \psi^2(0) - \sum_S \psi^2(0)] \qquad (2)$$

The symbols have their usual meaning.[11] The four factors on the RHS are, respectively, the "constant", "nuclear", "relativity", and "electronic" factor. This last factor contains all the chemical information in the isomer shift.

The constant factor goes as $ZA^{2/3}$, being 6.9 times as large for Au^{197} as for Fe^{57}. The nuclear factor for Au^{197} is only 1/6 that of Fe^{57}. This may be typical of heavy elements (see below). The relativity factor varies strongly with Z/137, from 5.2 in Hf to 15.8 in Cm, compared with 1.30 in Fe. Finally the nuclear density of 6s valence electrons in heavy nuclei is approximately a factor of ten larger than that of the 4s electrons of Fe, $\approx 10^{26}$ cm^{-3} compared with $\approx 10^{25}$ cm^{-3}. Thus while shifts of $\sim 5 \times 10^{-8}$ ev are observed in Fe^{57}, shifts as large as 2×10^{-6} ev have been reported in Au^{197}.[12]

Until now nuclear structure theories have not been very successful in predicting the nuclear factor $\delta R/R$. The single-particle nuclear shell model is clearly too crude to give a reliable estimate of this effect, though it does tend give the right order of magnitude for odd-proton nuclei,[11] and it gives some theoretical support to the observation that the nuclear factor tends to be small for heavy odd-neutron nuclei. A complete theory of isomer shifts would have to consider <u>all</u> the particles within the nucleus, rather than just the last odd particle: even in "shell model" nuclei other nucleons can contribute significantly to $\delta R/R$.[13] For deformed nuclei the collective model[14] is

probably somewhat more reliable. For deformed nuclei in which the two nuclear states in the Mössbauer resonance are the two lowest members of a rotational band the model predicts a very small positive $\delta R/R$ associated with centrifugal stretching. Finally in deformed nuclei the "nuclear shape" effect can make a large contribution to $\delta R/R$, if the deformation changes between the excited and ground states.[11] This has led to the prediction[11] and observation[15,16] of large isomer shifts near the edges of the region of deformed nuclei. In Eu^{151} (Ref. 11) and Eu^{153} (Refs. 15, 16) the large shifts appear to arise from both single-particle and deformation effects.

Special care must be exercised when discussing isomer shifts in heavy elements to distinguish between the influence of s and $p_{1/2}$ electrons. The small components of relativistic "$p_{1/2}$" electron wavefunctions are s-like (j, but not ℓ, is a good quantum number for relativistic electrons), and therefore they have a finite probability of being within the nucleus. Conversely the small components of "s" electron wave functions are p-like and do not contribute significantly to $\psi^2(0)$. This, however, has been accounted for in

the isomer-shift formalism for s electrons by introduction of the relativity factor.[11] This factor is listed for convenience in Table I.

Non-linear shifts should also be mentioned. By this we mean isomer shifts that are not directly proportional to $(\delta R/R)$ times $\psi^2(0)$. Recently Atzmony and Ofer[15] reported shifts in Eu^{153} whose ratios were not directly proportional to the ratios of shifts in Eu^{151} involving the same compounds. The origin of this effect is not yet completely understood, but we can propose two mechanisms that will give rise to such nonlinear (in $\psi_s^2(0)$) effects. Both lead to an expression of the form $\delta E = A(\delta R/R) + B(\delta Q^2)$ for the isomer shift. The first mechanism is essentially non-relativistic. It arises in second-order perturbation theory from the quadrupole component of $\mathcal{H}_s$, which we abbreviate as $\mathcal{H}_Q$, through terms of the form

$$-\sum_{n<m} \frac{\langle np^6\ {}^1S_0|\mathcal{H}_Q|np^5mp\,{}^1D_2\rangle\ \langle np^5\ mp\,{}^1D_2|\mathcal{H}_Q|np^6\ {}^1S_0\rangle}{E_m - E_n} \quad . \qquad (3)$$

Here n is the principle quantum number of a closed p shell and m is that of a higher unoccupied shell. The largest matrix element for heavy elements

will arise for n=5, m=6. Physically this mechanism may be visualized as the excitation, by the nuclear quadrupole moment, of a p electron from a closed shell into an open shell, in order to provide a field gradient at the nucleus that can lower the energy by interaction with the quadrupole moment. Clearly the matrix element is proportional to Q and the shift, therefore, to Q^2. Sternheimer antishielding arises from an analogous mechanism,[17] but there the effect is proportional to Q, as the $\mathcal{H}_Q$ matrix element appears only linearly. No detailed estimate of this effect has yet been made, but preliminary calculations indicate that it should lead to a detectable isomer shift.

A specifically relativistic effect that arises from essentially the same mechanism should also be mentioned, because it is likely to lead to quite large shifts in heavy elements. Associated with the above nonrelativistic effect, proportional to Q^2, is, for the heavy elements, a substantial attendant change in $\psi^2(0)$. This arises from the s-like small components of the p-electron wave functions that are involved in this second-order excitation. Both the inner and the outer p shells make opposing contributions to this later shift, and

their relative contributions must be assessed rather carefully. Since both $\psi^2(0)$ and Q^2 are involved, we may regard this shift as being proportional to $\delta(Q^2R^{2\rho})$, where Q and R are the quadrupole moment and charge radius of a given nuclear state and ρ is the usual relativistic parameter.[11] Finally we could write the total shift in the form

$$\delta E = A\delta(R^{2\rho}) + B\delta(Q^2) + C\delta(Q^2R^{2\rho}).$$

Chemical bonding will of course have a profound effect on A, B, and C. Specifically it is evident that the energy denominators in Eq. (3) will be greatly altered by bonding.

D. Magnetic Hyperfine Structure

Heavy elements form many ions and complexes for which $S'>0$ (usually $S'=1/2$), and the possibility of hyperfine structure is thus present. Until recently this would have been regarded as irrelevant because at high temperatures electronic relaxation is usually fast enough to "average out" the magnetic hfs components to one line at the centroid (or to a quadrupole pattern if $P\neq 0$). Mössbauer spectroscopy in heavy elements usually requires low temperatures, leading to long relaxation times and consequent resolution of the

magnetic hyperfine structure. The criterion for resolution is that $\tau > (\Delta\omega)^{-1}$, where τ is the electronic relaxation time and $\hbar\Delta\omega$ is the energy difference between two hfs components connected by electronic relaxation. The lifetime of the isomeric nuclear state is directly relevant only to the linewidth of each hfs component.

A "hyperfine magnetic field", H_{hf}, can be defined by $H_{hf} \equiv A_z S/g_N \beta_N$ in the special case that only one of the principle values of the effective magnetic hfs tensor (A_z in this case) is nonzero. Only then are the Hamiltonians $A_z S_z I_z$ and $-\vec{\mu}_N \cdot \vec{H}_{hf}$ isomorphous. If A_x and/or A_y is allowed to assume a nonzero value the magnetic hfs Hamiltonian is no longer diagonal in $|I, I_z\rangle$ representation and H_{hf} is undefined. It is easily shown in first-order perturbation theory that for the simple case $A_z \gg A_x$, A_y, with $S=1/2$, the degeneracy of the levels $|S_z = \mp 1/2, I_z = \mp 1/2\rangle$ is lifted, and the positions of all save the $|S_z = \pm 1/2, I_z = \pm I\rangle$ level are shifted.[8] For the common case of a Mössbauer resonance involving a dipole transition between states with nuclear spins 1/2 and 3/2, this results in a ten-component hfs spectrum that is quite different from the six-line spectrum associated with a hyperfine field (Fig. 3).

Application of an external magnetic field along one of the principle axes of the magnetic hfs tensor will diagonalize $\mathcal{H}_s$ in first order, and the Mössbauer spectrum will again assume the H_{hf} form, with $H_{hf}=A_i S/g_N\beta_N$. Here i is the direction along which the external field is applied (i=x,y, or z). In pure paramagnetic compounds spin-spin interaction will usually provide a field sufficient for this purpose. Sufficient magnetic dilution should then restore the more complex zero-field spectrum.

In estimating magnetic hyperfine splitting it is useful to discuss hyperfine fields (as defined above), rather than coupling constants, because nuclear magnetic moments commonly vary through more than a factor of ten. In the actinide elements unpaired 5f electrons are involved in producing hfs. Orbital angular momentum is unquenched for these well-shielded electrons and can set up fields of the order of 10^7 gauss, analogous to those found in the rare earths. In the 5d group fields of this size are not to be expected. Several elements (Ir, Os, Pt, Au) in the 5d series have hyperfine fields of $\sim 1.3 \times 10^6$ gauss when dissolved in iron, and smaller fields in other ferromagnets. In ferromagnetic intermetallic compounds such as Au_2Mn even larger

fields are possible.[18] Elements immediately above and below these four show smaller induced fields, of the order of 0.5×10^6 gauss in iron, for example.[19] In all of these elements the fields apparently arise through Fermi contact interaction of conduction (6s) electrons and core-polarized inner s electrons.

Contact interaction (through core polarization) is also probably primarily responsible for the observed hfs in paramagnetic 5d complexes of Re(IV), Ir(IV), and Au(II). The latter two show hfs constants corresponding to hyperfine fields of ~ 1/2 million gauss.[7,20] This value can probably be expected for paramagnetic complexes in the 5d group.

E. Quadrupole Coupling

In light elements the quadrupole coupling constant provides a rather straightforward measure of the number of unbalanced p orbitals and therefore provides valuable insight into chemical bonding. This latter is probably also true for heavy elements, although results to date, and theoretical considerations, suggest that the situation here is far more complicated. Since j, rather than ℓ, is a good quantum number for the relativistic electrons in heavy atoms, the small components of the relativistic wave functions for the atomic orbitals will have different parity from that of the large components.

Thus the $p_{1/2}$ electrons have $s_{1/2}$-like small components, while the small components of the $p_{3/2}$ wave functions are $d_{3/2}$-like (and conversely), etc. Hybridization of electrons from different subshells (or different major shells) can lead to complex problems in data analysis.[21] The compounds of Au^{197} have already provided several surprises[22] and are discussed in Sect. III below.

Most heavy elements that can be studied by Mössbauer spectroscopy have large natural linewidths, of the order of 0.1 cm/sec or greater. Fortunately the combination of sizable quadrupole moments and large electric field gradients in compounds of several of these elements provides quadrupole splittings that are large compared with even this linewidth. For $Au(CN)_2^-$, for example, M. Faltens has found ΔE_Q = 1.1 cm/sec (Fig. 1).

F. Analysis of Heavy Element Spectra

To the chemist accustomed to the high-quality-factor spectra of Fe^{57} and Sn^{119} the analysis of heavy-element spectra presents several new problems and some pitfalls. These difficulties can be handled by rigorous adherence to the spin-hamiltonian formalism, but in addition it is worthwhile to remember several qualitative results, listed below.

1. For most heavy-element spectra strong crystal-field effects will perturb the electronic configuration sufficiently to lift most of the electronic degeneracy, leaving a singlet (S=0) or doublet (S=1/2) ground-state. Further, the magnitude of the crystal field will usually cause sufficient splitting to leave only the ground state appreciably (thermally) populated at low temperatures. The observed spectrum may still, however, be a superposition of spectra from two or more inequivalent sites, as in the paramagnetic resonance spectrum[7] of Ir(IV) in K_2IrBr_6. One may decide between these two alternatives by observing the variation of the spectrum with temperature, applied magnetic field, or (if a single crystal is available) with orientation of the absorber.

2. For nonzero S one must decide which of the three cases $\tau \gg (\Delta\omega)^{-1}$, $\tau \ll (\Delta\omega)^{-1}$, or $\tau \approx \Delta\omega^{-1}$ is present. Usually the zero-field Hamiltonian will not be directly applicable. If $\tau \ll (\Delta\omega)^{-1}$ the spectrum will be a weighted average of the magnetic hfs components. If $\tau \gg (\Delta\omega)^{-1}$ spin-spin interaction will serve to diagonalize $\mathcal{H}_s$ in all but the most dilute samples, and will thereby alter the spectrum profoundly. For $\tau \approx (\Delta\omega)^{-1}$ complex relaxation spectra are possible.[8]

3. Often, then, the hyperfine structure in zero external field may be represented by an effective nuclear spin hamiltonian, of the form $\mathcal{H}_N^i = E^i + g_N\beta_N H_{hf} I_{z'} + P\{[I_{z'}^2 - (1/3)I(I+1)] + \eta[I_{x'}^2 - I_{y'}^2]\}$. Note that H_{hf} is taken along the z' rather than along the x', y', or z' axis. There is in general no assurance that the effective hyperfine field will lie along one of the principle axes of the electric field gradient tensor, and z' may therefore have any direction relative to the $x'y'z'$ coördinate system. High crystal or molecular symmetry often simplifies $\mathcal{H}_N$ still further, by making $\eta=0$ or causing z' to be equivalent to x', y', or z'.

4. Some special symmetry problems may arise in heavy-elements spectra. One of the most vexing is the case in which a poorly-resolved doublet is observed for a resonance involving nuclear spins 1/2 and 3/2, as in Ir^{191}, Ir^{193}, Au^{197}, etc. It may be difficult to decide whether the splitting is magnetic and largest in the spin-1/2 state, giving two unresolved groups of 3 or 4 lines, or whether it simply arises from quadrupole coupling. One may decide between these interpretations by making polarization measurements, observing the temperature-, magnetic-field- or concentration-dependence of the spectrum, or by looking for

asymmetry associated with an anisotropic recoil-free fraction (in the case of quadrupole splitting), but in practice these methods are not always feasible, and in marginal cases and the question may have to be settled by indirect evidence.

The isomer shift associated with a complex spectrum falls at its center of gravity, as does the isotope shift in optical spectroscopy, but determination of the center of gravity is often a tricky process requiring a complete theoretical understanding of the spectrum. Serious errors can arise from failure to account for weak components far removed from the centroid, absorption by overlapping lines, saturation effects, anisotropic recoil-free fractions, or for lines that nearly vanish by relaxation.

If I_z is a good quantum number (i.e., if $A_x = A_y = 0$) and $P=0$, the spectrum will be symmetrical about its centroid. If, however, A_x or A_y is non-zero, even in the absence of quadrupole coupling, an asymmetric spectrum will result. For $P \neq 0$ and $\eta \neq 0$ it is possible for the spectrum to appear quite symmetrical.

Incorporating the resonant atom into a cubic host should not in principle, and in fact does not, necessarily eliminate quadrupole coupling. Either distortion

of the unit cell by a large substitutional solute atom[23] or charge compensation in neighboring cells can provide nonzero field gradients.

III. RESULTS FOR HEAVY ELEMENTS

The Mössbauer effect has been reported for 14 isotopes of elements with Z>72. In Table 2 the transitions in the heavy elements for which the Mössbauer effect should be observable are listed. Although evidence of hyperfine structure has been found in nearly every case, the hfs spectrum has been explained in detail for only about 8 cases. Only preliminary versions of much of the work in the heavy elements have been published, so the following discussion must be somewhat tentative in regard to quantitative results. The resonances are discussed below in order of increasing atomic number.

Hafnium-177. Wiedemann et al.[24] have reported resonant absorption using Lu metal and Lu_2O_3 sources and Hf metal and HfO_2 absorbers. The absorption spectra were wider than natural linewidth, suggesting (quadrupole) hyperfine structure, but a detailed analysis could not be made. The large linewidth and high γ-ray energy render hfs studies marginal for Hf^{177}.

Tantalum-181. This tantalizing 6.15-keV resonance was first reported by Cohen et al.[25] and was studied in some detail by Steyert et al.[26], who found isomer shifts and quadrupole splitting. The metallurgical problems associated with this resonance are very severe[25,26]: quadrupole broadening almost completely obscures the spectrum even in a cubic Ta lattice, and sensitivity to impurities and vibrations is very high. When the problem of preparing a good single-line source is solved, however, this resonance will provide an extremely powerful tool for studying Ta chemistry. The natural linewidth is only 6.7×10^{-11} eV, and the recoil-free fraction should be very large even at high temperatures.

Tungsten Isotopes: W^{183}, $W^{182, 184, 186}$. The Mössbauer effect has been reported[27] for both the 46.5 and the 99.1 keV transitions in W^{183}. The relatively large linewidths of the resonances render W^{183} less suitable for hfs studies than the even isotopes. Of the three even isotopes, W^{182} is apparently superior to the others in every respect. It has the lowest transition energy, the narrowest natural linewidth, and presumably the largest quadrupole moment.[14] Well-resolved quadrupole hfs in absorption measurements on W^{182} have been reported

by two groups.[28,29] Field gradients of up to $2 \cdot 10^{18}$ esu (in WS_2) have been reported, but no detailed interpretations in terms of chemical bonding are yet available.

Mössbauer scattering, rather than absorption, provides an attractive alternative technique for studying these relatively high-energy transitions.[30,31] Scattering greatly enhances the signal-to-noise ratio for these cases, while retaining most of the good features of absorption experiments.

Rhenium-187. Resonance absorption has been reported.[32] The linewidth (10^6 cm/sec) precludes hfs studies.

Osmium-186 and 188. The linewidths of these two resonances are sufficiently small to permit quadrupole coupling studies, and the scattering technique provides an adequate signal-to-noise ratio. Evidence has been found for quadrupole interaction in Os metal.[30,31]

Iridium-191 and 193. The Mössbauer effect was originally discovered[33] in the 129-keV transition of Ir^{191}. Although this resonance is not sufficiently narrow for hfs studies, the 83-keV transition should be suitable. Semiconductor γ-ray detectors are capable of resolving this γ ray from the x-rays accompanying

the decay of Pt^{191}. Still the 73-keV transition in Ir^{193} seems preferable for most purposes, being both narrower and lower in energy. With a natural linewidth of only 7.4×10^{-8} ev, and a ground-state quadrupole moment of +1.5 barns,[34] Ir^{193} is very promising for chemical bonding studies. No detailed reports of hfs spectra have been published as yet, but Thomson et al.[35] have studied $KIrCl_6$, IrO_2, and hydrated $IrCl_3$, $IrCl_4$, and Ir_2O_3, finding isomer shifts and, in the case of IrO_2, a quadrupole splitting of 3.0 mm/sec. J. Huntzicker et al. have resolved the eight-line magnetic hfs spectrum of Ir^{193} in iron metal.[36]

Platinum-195. Harris et al.[37,38] have studied both the 98.9-keV and the 129.7-keV resonances, using Pt metal sources and absorbers. No shifts or hyperfine structure were reported. It would be interesting to compare electric field gradients and isomer shifts in platinum compounds with those in isoelectronic gold compounds (see below), but the large linewidths of these resonances may preclude such work.

Gold-197. The 77.3-keV resonance in Au^{197}, connecting the 1/2+ first-excited state with the 3/2+ ground state, is by far the most thoroughly explored case in the heavy elements. Nagle et al.[39] first reported resonant absorption

in Au^{197}. It has been studied extensively by groups at Oak Ridge and Berkeley. Magnetic hyperfine structure has been found[18,22,23,40,41] in lattices of Fe, Co, Ni, and in the intermetallic compounds Au_2Mn, Au_3Mn, and Au_4Mn. Although the ground-state magnetic components have been only partially resolved, quite accurate determinations of H_{hf} for Au in Fe have been made: the most precise value is $(1.29 \pm 0.03) \times 10^6$ gauss.[42] This case (Au in Fe) has been important in leading to an understanding of the systematic variation of induced hyperfine fields in ferromagnets.[19] No paramagnetic hfs has yet been observed in Au^{+2} complexes.

Isomer shifts have been studied in a variety of environments. As the first odd-proton nucleus showing an appreciable isomer shift, Au^{197} offered promise that the shift might be quantitatively interpretable in terms of nuclear models.[43] More detailed descriptions of the nuclear levels in Au^{197} leave doubt that the nuclear shell model is a sufficiently good approximation to nuclear structure to provide a plausible quantitative interpretation of such a sensitive parameter as $\delta R/R$. Pairing-model calculations suggest high sensitivity of $\delta R/R$ to smearing of the Fermi surface, because of varying occupation

of the $h_{11/2}$ orbitals.[13] Alaga has obtained quite complicated eigenfunctions for the Au^{197} levels.[44] De-Shalit has suggested that Au^{197} exhibits "core excitation", a qualitatively different form of nuclear excitation than promotion of a single particle to a higher orbital.[45] The nuclear-structure problem in Au^{197} thus appears to be far from solution, and any quantitative inroads on the isomer shifts in the near future will have to be made through the electronic factor.

From isomer shift measurements in nineteen metallic hosts Barrett et al.[12] concluded that the shifts were strongly correlated with host electronegativities. Gold atoms gained (6s) electron density in the other, more electropositive, metals, tending to form Au^- ions. It is interesting that the most naive applications of rigid-band theory would suggest the opposite, i.e., that Au should donate electron density to nickel in Au-Ni alloys, for example. One concludes that chemistry is very important even in metals, and that a band theory that neglects chemical interactions has little value in predicting isomer shifts. Roberts et al. have recently provided two independent demonstrations that the electron density on Au^{197} in other metallic hosts is larger

than in Au metal. The first was a correlation of residual electrical resistivity with isomer shifts for several dilute alloys,[46] using the alloy theory of Friedel. A more recent high-pressure experiment has shown directly that the nuclear factor, $\delta R/R$, for Au^{197} is positive.[18]

The observation of large isomer shifts for Au atoms in metallic hosts opens the possibility that the Mössbauer effect might be particularly applicable to studies of chemical bonds in intermetallic compounds. Unlike the more classical forms of chemical spectroscopy, Mössbauer spectroscopy is as applicable to intermetallic compounds as to dielectrics. Much of our presently rather limited understanding of intermetallic bonds is derived from rather equivocal arguments based on "bond lengths" and "bond angles", and more direct spectroscopic evidence is certainly needed. Both isomer shifts and quadrupole splitting have been observed in intermetallic compounds involving Au^{197},[12,18,22] but definitive interpretations are not yet available.

Mössbauer spectra of Au_2Mn have been found to be extremely sensitive to heat- and mechanical-treatment (and hence to long-range ordering), leading to variation of over a factor of four in the width of the hfs absorption spectrum.[22]

Mössbauer spectra of Au compounds offer a splendid opportunity for spectroscopic study of chemical bonding in heavy elements. It is already evident that some of the hybrid bonding rules applicable to the lighter elements will require substantial modifications when applied to gold. An early illustrative example was provided by the quadrupole coupling constants for aurous and auric complexes.[11] These tend to be linear and square-planar, respectively, and are textbook examples of sp and dsp^2 hybridization. One might therefore expect that the quadrupole coupling constants in Au(I) and Au(III) compounds would be essentially the same, inasmuch as these two hybrid configurations have the same number of "unbalanced p electrons". M. O. Faltens has collected spectra of many Au compounds, with some surprising results.[22] In particular, the Au(III) compounds tend to yield quadrupole splittings an order of magnitude smaller than those of the Au(I) compounds. Well-resolved quadrupole hfs for $KAu(CN)_2^-$ was shown in Fig. 1. For $AuCl_4^-$ complexes the two lines are unresolved.

<u>Neptunium-237</u>. Stone and Pillinger[6] have reported the only successful experiment on the Np^{237} resonance. Their observation of Mössbauer absorption

following α decay is interesting because it lays to rest a good deal of ill-founded discussion about whether or not recoil-free absorption was possible after events involving large recoil energy (α decay, nuclear reactions, coulomb excitation). Stone and Pillinger observed broad complex spectra using an absorber of NpO_2 and sources of both U^{237} and Am^{241} in NpO_2.

It seems difficult to imagine that recoil-free gamma transitions would <u>not</u> occur following the high-recoil processes mentioned above. The recoiling ion stops in time intervals that are several orders of magnitude shorter than the isomeric lifetimes.[47] Whether the Np^{237} atoms in the above experiment have stopped in lattice positions or in interstitial positions remains an open question. Very probably both positions are populated. In either case large recoil-free fractions are expected for the 59.6-keV transition. Mullen[48] has based the conclusion that lattice positions are predominantly occupied on arguments involving the recoil-free fraction. This conclusion seems unfounded in light of the impossibility of deriving a recoil-free fraction from the existing unresolved spectra. While there may in fact be no recoil-free interstitials, the question is at this point completely open, and can be resolved only when the absorption spectrum is understood.

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*This work was done under the auspices of the U. S. Atomic Energy Commission.

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Table 1. Relativity Factor S' for Heavy Elements.

Element	S'	Element	S'
Hf	5.0	Au	6.8
Ta	5.2	Hg	7.1
W	5.5	Th	11.7
Re	5.7	Pa	12.3
Os	6.0	U	12.9
Ir	6.2	Np	13.6
Pt	6.5	Pu	14.3

Table 2. Isotopes with Z > 72 in which Mössbauer resonance may be observed in states within 200 keV of the ground state.

Isotope	$t_{1/2}$ in years if unstable[a]	E_γ in keV	$t_{1/2}$ of isomeric level, nsec	Γ(eV)[a]	References
Hf^{174}		90.9			
Hf^{176}		88.3	1.39	3.3(-7)	
Hf^{177}		113.0	0.52	8.8(-7)	b
Hf^{178}		93.1	1.50	3.0(-7)	
Hf^{179}		122	0.037	1.2(-5)	
Hf^{180}		93	1.50	3.0(-7)	
Ta^{181}		6.15	6800	6.7(-11)	c,d
W^{180}		102	1.33	3.4(-7)	
W^{182}		100.1	1.4	3.2(-7)	e,f
W^{183}		46.5	0.15	3.0(-6)	g
W^{183}		99.1	0.52	8.8(-7)	
W^{184}		111	1.3	3.5(-7)	f
W^{186}		122	1.0	4.5(-7)	f

Table 2. (Continued)

Isotope	$t_{1/2}$ in years if unstable[a]	E_γ in keV	$t_{1/2}$ of isomeric level, nsec	Γ(eV)[a]	References
Re^{185}		125	< 0.017	>2.7(-5)	
Re^{187}	4.3(10)	134.2	0.01	4.5(-5)	h
Os^{186}		137.2	0.84	5.4(-7)	f,i
Os^{188}		155.0	0.71	6.4(-7)	f,i
Os^{189}		69			
Os^{190}		187	0.35	1.3(-6)	
Ir^{191}		83	3.8	1.2(-7)	
Ir^{191}		129	0.13	3.5(-6)	j
Ir^{191}		178			
Ir^{193}		73	6.2	7.4(-8)	k,l,m
Ir^{193}		139			
Pt^{195}		98.9	0.2	2.3(-6)	n
Pt^{195}		129.7	0.55	8.3(-7)	n

Table 2 (Continued)

Isotope	$t_{1/2}$ in years if unstable[a]	E_γ in keV	$t_{1/2}$ of isomeric level, nsec	Γ(eV)[a]	References
Au^{197}		77.3	1.9	2.4(-7)	e
Hg^{199}		158	2.33	2.0(-7)	
Hg^{201}		32	< 0.2	> 2.3(-6)	
Hg^{201}		168	< 2	> 2.3(-7)	
Th^{230}	8(4)	53	0.37	1.2(-6)	
Th^{232}	1.4(10)	50	0.345	1.3(-6)	
Pa^{231}	2(4)	59			
Pa^{231}	2(4)	84	41	1.1(-8)	
U^{233}	1.62(5)	40			
U^{233}	1.62(5)	92			
U^{234}	2.48(5)	44	0.266	1.7(-6)	
U^{235}	7.13(8)	46			
U^{235}	7.13(8)	103			

Table 2 (Continued)

Isotope	$t_{1/2}$ in years if unstable[a]	E_γ in keV	$t_{1/2}$ of isomeric level, nsec	Γ(eV)[a]	References
U^{236}	2.39(7)	45	0.23	2.0(-6)	
Np^{237}	2.14(6)	33.2			
Np^{237}	2.14(6)	59.6	63	7.2(-9)	o
Np^{237}	2.14(6)	76.4			
Pu^{239}	2.44(4)	8			
Pu^{239}	2.44(4)	57			

a. Here we use scientific notation: 9.4(-7) means 9.4×10^{-7}.

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Figure Captions

Fig. 1. Absorption spectrum of $KAu(CN)_2$ obtained by M. O. Faltens, showing well-resolved quadrupole splitting in the 3/2+ ground state of Au^{197}, caused by linear ("sp") bonding.

Fig. 2. Quadrupole diagram, showing all the possible Mössbauer spectra for a resonance in a dipole transition connecting states with spins 5/2 and 3/2, if $\eta=0$. On the left the (nonlinear) ordinate scale is the ratio of quadrupole moments in the two states. The relative intensities of the five hfs components connecting the 3 levels of the spin-5/2 state (top and bottom) with the two levels of the spin-3/2 state are shown. On the right side of the figure are shown representative spectra at selected values of Q(5/2)/Q(3/2), obtained from the diagram.

Fig. 3. Paramagnetic hfs levels and spectra for a 3/2 (dipole) 1/2 transition under the hamiltonian $\mathcal{H}_s = A_x S_x I_x + A_y S_y I_y + A_z S_z I_z$, with S=1/2. For $\mathcal{H}_s$ diagonal in I_z representation (left) the spectrum could be represented by a "hyperfine field". For a more general case (right) the spectrum is more complex and is asymmetric. The "six-line" Fe^{57} spectrum would show ten components. A detailed discussion is given in Ref. 8.

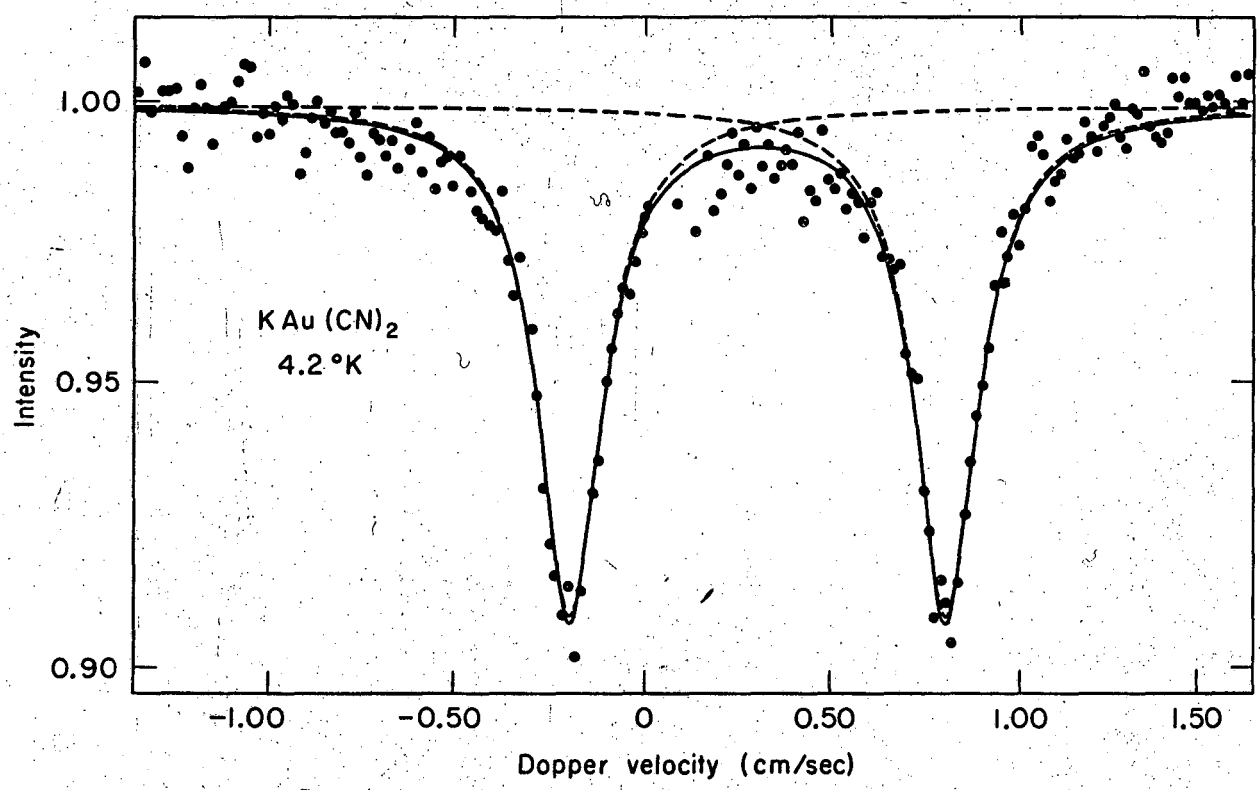

Fig. 1

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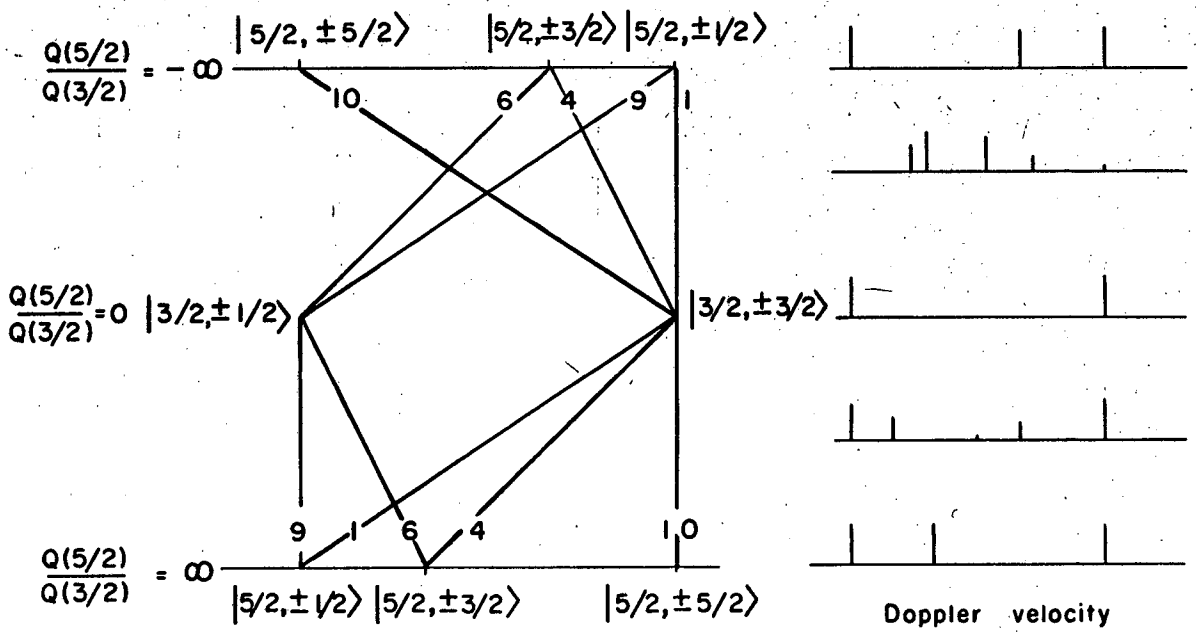

MUB-9214

Fig. 2

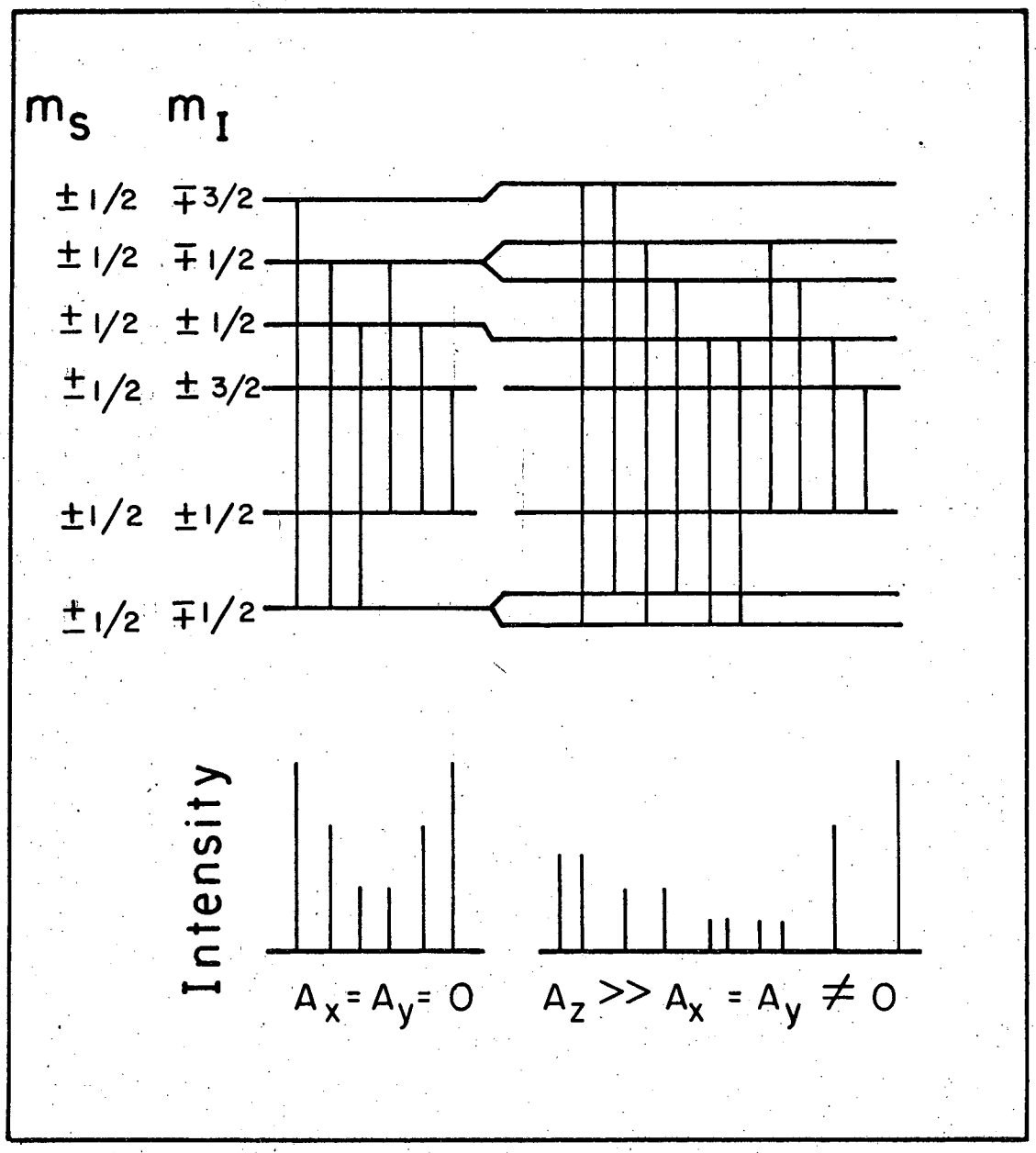

Fig. 3

MUB-9215

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