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D A Shirley

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Berkeley, California 94720

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D. A. Shirley

Lawrence Radiation Laboratory  
University of California  
Berkeley, California 94720

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Mössbauer spectroscopy was reviewed in this series once before, by R. H. Herber in Volume 17 (1). Even then total coverage of the field was neither feasible nor desirable, in view of the very substantial review effort already devoted to the Mössbauer Effect. Herber was able to list several general references that broadly covered the field (2-16) and go on to discuss several topics in depth. The list can be brought up to date by adding a few more recent works. First, Gol'danskii and Herber have edited a book entitled "Chemical Applications of Mössbauer Spectroscopy" (17). This 701-page volume consists of 12 chapters, by various authors, written as reviews of special topics. The coverage of these topics is quite comprehensive. The Faraday Society held a Discussion on the Mössbauer Effect in December, 1967 (18): the published version is nearly available as this is written. A symposium on chemical applications of Mössbauer spectroscopy has appeared as Volume 68 of "Advances in Chemistry" (19): we shall refer especially to Erickson's

critical review of isomer-shift correlations for Fe<sup>57</sup> and Hafemeister's discussion of iodine resonances. Among conference proceedings, the volume, "Hyperfine Structure and Nuclear Radiations" contains numerous papers on the Mössbauer Effect as well as a compilation of changes in nuclear radius, by Kienle, Kalvius, and Ruby (20). In this short review we shall focus on a few selected topics that seem to merit special attention at this time. The reader is referred to the above sources for more general coverage.

Mössbauer spectroscopy is not a field in which many scientists are working together toward the solution of a major problem. Its coherence arises rather from common interest in instrumentation, in developing new resonances, and in interpretation. For a review of instrumentation the article by Benczer-Koller and Herber may be consulted (21). Spectrometer development is sufficiently advanced that a well-designed instrument contributes negligibly to errors of measurement, as might be expected in a field of spectroscopy that entails natural linewidths in the MHz region. Among recent advances are laser calibration (22) and the very accurate inter-comparison of isomer shifts by mounting absorbers together (23). No further

discussion of instrumentation seems warranted here. Turning to problems of interpretation, considerable progress has been made in two areas: isomer shift calibrations, and relaxation phenomena and "aftereffects" following nuclear transformations. The latter topic has been thoroughly reviewed by Wickman and Wertheim (24). Isomer-shift calibration is reviewed in the next section. Several resonant isotopes other than  $Fe^{57}$  and  $Sn^{119}$  are discussed in the final section, with emphasis on their isomer shifts.

#### ISOMER-SHIFT CALIBRATIONS

Ideally the chemical implications of isomer shifts might be reviewed at this point. Either of two approaches could be taken. Qualitative inferences might be made from empirical correlations of isomer shifts with ligand electronegativity, quadrupole coupling constants, etc. Many such correlations are available (17,19), and they have made valuable contributions of an analytical or structural nature. Several reviews of this type of approach already exist, and we shall not add to them here. A second approach would be to try to understand isomer shifts quantitatively in terms of the actual electronic structure of compounds, using a quantum-mechanical model. Some progress has recently been made on this problem, and it is reviewed here in hope of stimulating



further work. Unfortunately enough uncertainty still exists to preclude a meaningful review of quantitative structural results that have chemical interest, and we are constrained to consider calibrations of the scale factors for isomer shifts. We shall find that the scale factors for both  $\text{Fe}^{57}$  and  $\text{Sn}^{119}$  are in doubt by about (a factor of) 3. To put this situation in perspective one might imagine discussing chemical shifts in nuclear magnetic resonance frequencies with the proton moment in doubt by a factor of 3!

Let us first recall briefly the essential features of the isomer-shift phenomenon. The Coulombic interaction between the nuclear charge distribution and the distributed electronic charge near the nucleus may be expanded into even multipole terms, of which the first has monopole, or spherically-symmetric, character. Only the s and the  $p_{1/2}$  electrons have finite densities at the nucleus and thus contribute to the isomer shift. The shift in energy of a single nuclear state is proportional to  $|\psi(0)|^2$ , the electron density at the center of the nucleus (this symbol is also often used to represent the density of a nonrelativistic electron, and a relativity

correction is applied). The  $\gamma$ -ray transition energy is shifted in proportion to  $\delta R/R$ , where  $R$  is the nuclear charge radius and  $\delta R$  is the change in charge radius between the excited and ground states. Since  $|\psi(0)|^2$  is usually different for a source (S) than for an absorber (A), the Doppler velocity at resonance is nonzero. It is given by (25)

$$v = \left[ \frac{4\pi Z e^2 R^2 c}{5E_\gamma} \right] \left[ S'(z) \right] \left[ \psi_A^2(0) - \psi_S^2(0) \right] \left[ \frac{\delta R}{R} \right] \quad 1.$$

where the four quantities in brackets are the "constant", "relativity", "electronic", and "nuclear" factors, respectively. These factors are arranged in order of increasing uncertainty from left to right. The constant factor is known quite accurately. Aside from the physical constants, the  $\gamma$ -ray energy is easily measured, and nuclear radii are known to within a few percent.

The relativity factor had been derived in connection with isotope-shift theory (26-31): it varies only with atomic number, and is tabulated (25). This factor was given first by Racah (26) and by Rosenthal and Breit (27), using perturbation theory. Later Broch made a direct calculation (29). Charge

distributions were discussed in connection with this method by Bodmer (30). All of this early work was done in the context of hand calculators and one-electron wave functions, but its validity was well-founded. Nevertheless some doubts about the applicability of the relativity factor to nonrelativistic Hartree-Fock electron densities has been expressed. With relativistic Dirac-Slater free-ion wave functions now available (32), Hafemeister has resolved these doubts (33). He calculated  $|\psi(0)|^2$  for several ions from Hartree-Fock, Hartree-Fock-Slater, and Dirac-Slater wave functions, finding that the ratio  $(|\psi(0)|^2_{\text{Dirac-Slater}})/(|\psi(0)|^2_{\text{Hartree-Fock-Slater}})$  is in fact given to within a few percent by the tabulated (25) relativity factor  $S'(Z)$ , provided that Slater exchange is introduced consistently into both the relativistic and the nonrelativistic calculations.

The remaining electronic and nuclear factors contain, respectively, chemical and nuclear structure information about the absorber under study. Both factors may be calculated, using existing molecular and nuclear models: one might wonder which is more accurate. At this time molecular models seem in principle capable of considerably better accuracy than do nuclear models.

In evaluating calculations of  $|\psi(0)|^2$ , one also has the great advantage of being able to compare with measured shifts in several chemical compounds, while each transition has only one nuclear factor. Unfortunately, most of the estimates of electron densities to date have not approached the accuracy of which molecular structure calculations are capable. Sorenson (34) has discussed theoretical estimates of  $\delta R/R$  from nuclear models.

The most common procedure for analyzing isomer shifts in a given isotope is to select as fiducial points two compounds in which the chemical structure is well-enough understood to permit an accurate estimate of  $\Delta|\psi(0)|^2$ . Comparison to the observed isomer shift, using Eq. (1), yields  $\delta R/R$ . This provides a scale relating the observed isomer shift to  $|\psi(0)|^2$ , and a measurement of the former quantity will then yield the latter for any compound. The accuracy to which the scale factor  $\delta R/R$  for a given transition is known limits the accuracy to which a quantitative, microscopic interpretation of isomer shifts may be made. Failure to appreciate the importance of obtaining accurate values for  $\delta R/R$  factors together with the difficulty of determining them have allowed the uncertainties of factors of three and even doubts about the sign of  $\delta R/R$  for  $\text{Sn}^{119}$  to persist for years.

Until about 1964, "quantitative" interpretation of isomer shifts employed electron densities obtained from free-atom wave functions with only very rough corrections, or none at all, for overlap and covalency. In 1965 Roberts made a more sophisticated interpretation of Au<sup>197</sup> isomer shifts in gold alloys, correlating them with residual resistivities through the Daniel model (35). In the same year Flygare and Hafemeister made an important contribution toward a quantitative understanding of isomer shifts in compounds. They considered the variation of the I<sup>129</sup> isomer shift with molecular weight in the alkali iodides (36). Electronegativity arguments would suggest a monotonic variation, while in fact the isomer shift shows a minimum at KI. Assuming the alkali halides to be completely ionic, these authors calculated first- and second-neighbor overlap distortion effects. They used Löwdin's "symmetric orthogonalization" procedure, employing free-ion atomic orbitals (37). The resulting isomer shift can be written

$$\begin{aligned}
 (\text{IS})_{ab} &= 2C_1 \delta \left\{ \sum_v \sum_{n=1}^5 \langle ns | v \rangle^2 |\phi_{ns}(0)|^2 \right\} \\
 &= 2C_1 |\phi_{5s}(0)|^2 \left\{ \sum_{v_a} \langle 5s | v_a \rangle^2 - \sum_{v_b} \langle 5s | v_b \rangle^2 \right\} . \quad 2.
 \end{aligned}$$

where  $ns$  refers to the free-ion orbitals of iodine,  $\delta\{\}$  denotes  $\{\}$  lattice a -  $\{\}$  lattice b, and  $|v_a\rangle$  is a free-ion orbital on a first or second neighbor in lattice a. In simplifying from the first to the second line in Eq. (2), core orbitals are taken to contribute equally to the isomer shift in lattices a and b. These authors discussed this point. In Figure 1 their results are compared with experiment.

Recently Simánek and Sroubek studied overlap contributions to isomer shifts in  $Fe^{57}$  (38). Their findings have implications both for the above analysis and for the calibration of the isomer shift scale for  $Fe^{57}$ . They considered iron octahedrally coordinated with six oxygen ligands, and accounted for  $\langle \text{iron } ns | \text{ligand } p \rangle$  overlap by constructing a symmetrical, orthogonalized ligand orbital from the oxygen  $6p$  functions. Writing their result in a way that facilitates comparison with Eq. (2), we have

$$\begin{aligned}
 (IS)_{ab} = 12C_1 \delta \left\{ \left[ 1 + \sum_{j=2}^6 \langle p_s | p_j \rangle \right]^{-1} \left[ \sum_{n=1}^3 \langle ns | 2p \rangle^2 |\phi_{ns}(0)|^2 \right. \right. \\
 \left. \left. + \sum_{n \neq m=1}^3 \langle ns | 2p \rangle \langle ms | 2p \rangle \phi_{ns}(0) \phi_{ms}(0) \right] \right\}, \quad 3.
 \end{aligned}$$

where the  $s$  wave functions are always ionic wave functions of iron and the  $p$  wave

functions refer to ionic oxygen: the sum in  $j$  is taken over the six ligands. To compare this expression with Eq. (2), we note that the term in the first square bracket includes ligand-ligand overlap in the normalization. The additional factor of six on the right hand side arises from summing over ligands, and is equivalent to the sum over  $v$  in Eq. (2). This entire expression, through the first term in the second square bracket, will reduce to the earlier result if ligand-ligand overlap is neglected. The remaining, "intershell" term, however, is very important for  $\text{Fe}^{57}$ , as it reduces markedly the overlap contribution to  $|\psi(0)|^2$ . We may easily understand this result physically. While  $|\langle (n+1)s | 2p \rangle|$  is considerably larger than  $|\langle ns | 2p \rangle|$ ,  $\psi_{n+1}(0)$  is a factor of  $\sim 5$  smaller than  $\psi_n(0)$ . The dominant cross-terms clearly have  $m = n + 1$ , and these terms are always negative, because  $|ns\rangle$  and  $|(n+1)s\rangle$  have opposite signs in the overlap region. Thus the net effect of the intershell terms is always to reduce  $|\psi(0)|^2$ .

Using the pressure dependence of the isomer shift for divalent  $\text{Fe}^{57}$  in  $\text{CoO}$  reported by Drickamer et al. (39), Simánek and Sroubek deduced a value for the nuclear factor of  $\text{Fe}^{57}$ ,  $\delta R/R = -4 \times 10^{-4}$ . Such a small value of

$\delta R/R$  would have appeared incompatible with the large  $\text{Fe}^{+2} - \text{Fe}^{+3}$  isomer shift, but Simánek and Sroubek took care of this objection. They adopted Danon's suggestion (40) that even in the most ionic compounds the electronic structure of ferric ion has some 4s character: Danon suggested the "configuration"  $3d^5 4s^{0.32}$ . Writing the ligand orbital to accommodate the 4s amplitude admixture  $a_{4s}$ , they derived an expression for the enhancement of the electron density at the  $\text{Fe}^{57}$  nucleus,

$$\delta |\Psi(0)|^2 = 15a_{4s}^2 + 13a_{4s} \quad ,$$

in units of  $a_0^{-3}$ . Thus the 4s contribution is increased by cross terms arising from covalency.

Overlap calculations involving  $\text{O}^{\equiv}$  ligands are uncertain because of the instability of atomic  $\text{O}^{\equiv}$ . Simánek and Wong (41) therefore applied the above model to  $\text{KFeF}_3$ , in which the ferrous ions are octahedrally coordinated by  $\text{F}^-$  ions. They found  $\delta R/R = -5.2 \times 10^{-4}$ , and they regard this as an upper limit for the magnitude of the nuclear factor.

Several earlier values had been suggested for  $(\delta R/R)_{\text{Fe}^{57}}$ . In their pioneering work on the problem Walker et al. (42) simply assumed that



the ferrous and ferric compounds having the largest isomer shifts were completely ionic, and they used free-atom wave functions to obtain  $\delta R/R = -1.8 \times 10^{-3}$ . In retrospect this value might seem too large for an odd-neutron nucleus, and it may well be, but no decisive nuclear-structure arguments have been advanced to this effect. Erickson has reviewed (19) later attempts to improve on this value. While several of these analyses contain attractive arguments, none are compelling, and they all have glaring weaknesses. Gol'danskii's discussion is noteworthy because he used x-ray absorption-edge data to assign charges to iron in several compounds (43), obtaining  $\delta R/R = -5 \times 10^{-4}$ . The agreement of this result with that of Simánek and Wong may be fortuitous, because it is not obvious that the two approaches are compatible. The reviewer tends to favor these lower values for  $\delta R/R$ . Both Gol'danskii's approach and that of Simánek and co-workers are more closely tied to independent experiments in the fiducial compounds than are the other analyses. Later Gol'danskii et al. (44) used a molecular-orbital approach to derive  $(\delta R/R) = -9 \times 10^{-4}$ . Unfortunately even these two approaches are open to criticism. Erickson pointed out (19) that deriving charges from

x-ray data can be ambiguous. On the other hand Simánek et al. (38,41) have ignored the pressure-dependence of covalency in ferrous compounds. We recommend using, with caution, a tentative value of  $\delta R/R = -5 \times 10^{-4}$  until further progress is made on this subject. It seems somewhat curious that hundreds of isomer shifts have been measured for  $\text{Fe}^{57}$  in different lattices, while only a relatively modest effort has gone into determining  $\delta R/R$ , which is central to any really quantitative interpretation of these shifts. The suggested values of the nuclear factor for  $\text{Fe}^{57}$  are given in Table 1.

Our knowledge of  $\delta R/R$  for  $\text{Sn}^{119}$  is also rather rudimentary. Gol'danskii and Makarov (45) have recently reviewed this topic. Early analyses by Boyle, et al. (46) and Gol'danskii, et al. (47) yielded values of  $+1.1 \times 10^{-4}$  and  $+1.9 \times 10^{-4}$ , respectively, for  $(\delta R/R)_{119}$ . Subsequently Gol'danskii, and co-worker (48,49) made a more detailed LCAO/MO analysis. They decided that transfer of 5s and 5p electrons to ligands so decreased the shielding of the remaining 5s electron(s) that  $|\psi(0)|^2$  would actually increase, and thus that  $\delta R/R$  could be negative. The sign was definitively

established as positive in 1966 by the elegant conversion-electron experiment of Bocquet, et al. (50), which yielded  $\delta R/R = +3.3 \times 10^{-4}$ . Subsequently Gol'danskii et al. invoked  $p_{\pi}$  bonding to render their LCAO model consistent with this result (51).

Ruby et al. (52) derived a value  $\delta R/R = +(1.2 \pm 0.4) \times 10^{-4}$  in an analysis that employed Hartree-Fock atomic wave functions rather than using the Fermi-Segrè-Goudsmit formula to extract electron densities from optical data. This work was also noteworthy in that these authors assigned an error to their result: perhaps this practice will spread! Lees and Flinn (53) made some very accurate measurements on tin compounds and used relativistic Dirac-Fock wavefunctions (32) to derive a value  $\delta R/R = +(0.921 \pm 0.004) \times 10^{-4}$ . The reviewer interprets this error limit as a measure of the internal precision of the work: as such it is excellent. The accuracy of this analysis is about the same as in other similar analyses (45,46,50). Whenever free-ion wave functions are applied to ionic solids without considering overlap, large uncertainties are introduced.

More recently Unland and Letcher (54) used an "equivalent orbital" model due to Letcher and Dunning (55), together with molecular structure data, to fit isomer shifts for 16 tin compounds. They found the calculated electron densities at the Sn nucleus to be very sensitive to input parameters such as the choice of basis functions, molecular geometry, and the method of setting basis orbital exponents. They state in fact, "...estimates of the input parameters are too inaccurate to allow prediction of Mössbauer isomer shifts." For this reason they elected to reverse the procedure and use the observed isomer shifts to determine the required input parameters, which they then propose to employ in calculating other properties. They have prepared a very useful table of derivatives of the calculated electron densities  $|\psi(0)|^2$  with respect to several input parameters: this should prove helpful in estimating errors in future work on Sn<sup>119</sup>. Two qualitative conclusions are forced upon us in reading this paper: (1) If this relatively sophisticated approach cannot predict isomer shifts, there seems to be little hope for some of the cruder models extant, and (2) It is probably more reliable, and certainly more convincing, to interpret isomer shifts in

conjunction with other data, rather than trying to make models for the sole purpose of fitting isomer shifts. Unland and Letcher did not derive a unique value for  $\delta R/R$ , but they found a good correlation of isomer shift with electron density using a set of parameters that gave a scale factor very close to the value given by Lees and Flinn (53). This agreement is surely accidental, as the two analyses are clearly incompatible.

Greenwood, Perkins, and Wall (56) used the Pople-Segal-Santry SCMO method (57) to calculate electronic structures for several stannic compounds. They found the occupation number of the 5s orbital to vary linearly with isomer shift. Using the Fermi-Segrè-Goudsmit equation and Burns' screening rules (58), they found a linear relationship between  $|\psi(0)|^2$  and the isomer shift: the 5p-orbital occupation numbers gave qualitative agreement with observed quadrupole splittings. They derived a value of  $\delta R/R = +3.5 \times 10^{-4}$  from this analysis. This value is set out in Table II, along with the others discussed above.

None of the analyses yielding values of  $\delta R/R$  for  $\text{Sn}^{119}$  seems to the reviewer strong enough to discredit all those giving discrepant results,

and there remains for now a factor of three uncertainty in this quantity. The analyses that are basically similar to Boyle's (47,52,53) all give about the same value, but this "agreement" is inherent in the assumptions. These assumptions are inaccurate in ignoring overlap and in taking simple, free-atom configurations to represent ions in solids, so neither the internal agreement nor the actual values can be taken at face value. On the other hand Greenwood et al. (56) state that their value is preliminary, while the accuracy of the other high value (50) has been questioned by Ruby et al. (52).

Some doubt has been expressed in the validity of obtaining  $|\psi(0)|^2$  from the Fermi-Segrè-Goudsmit formula, and also in the validity of using Hartree-Fock results with relativity corrections. To the reviewer's knowledge no evidence has been presented to show that either of these approximations is incorrect vis-a-vis Dirac-Fock densities. There is no reason to expect gross disagreement among the three procedures. Indeed Gol'danskii and Makarov (59) have argued that either the Fermi-Segrè-Goudsmit or the Hartree-Fock approach will give the same orbital populations for  $\text{SnCl}_4$  if  $\delta R/R$  is  $+3.3 \times 10^{-4}$ . One might also infer that the approximate agreement of the

three analyses giving  $\delta R/R \sim 1 \times 10^{-4}$ , which used all three procedures for obtaining  $|\psi(0)|^2$ , argues for the consistency of the procedures. As mentioned above, Hafemeister (33) has dispelled doubts in the relativity factor by direct calculation.

A word of caution is indicated as Hartree-Fock programs are becoming widespread. There is no criterion in the self-consistent field approach that the value of  $|\psi(0)|^2$ , per se, should be particularly accurate. We have found it non-trivial to obtain reliable values of  $|\psi(0)|_{ns}^2$  and particularly of  $\langle r^{-3} \rangle_{np}$  from Hartree-Fock calculations, especially using a near-minimum basis set. While the Hartree-Fock method is to be preferred over the earlier Fermi-Segrè-Goudsmit approach, it must be used wisely.

Finally, some work has been done on the Crawford-Schawlow correction (60) for screening of inner  $s$  electrons by outer  $s$  electrons. This effect would result in a negative correction to the  $|\psi(0)|_{ns}^2$  value of an outer electron. Although the reviewer is aware of no comprehensive study of this problem, there is scattered evidence that the effect is negligibly small. For example, Greenwood et al. (56) estimated a change of 0.04% in  $|\psi(0)|_{4s}^2$

due to screening by the 5s electron of tin: this is equivalent to a correction of about 0.8% in  $|\psi(0)|_{5s}^2$ .

The available values of  $\delta R/R$  for several other isotopes of chemical interest are set out in Table III. These values do not bear critical discussion, and are very likely in doubt by as much as the more intensively-analyzed results for  $\text{Fe}^{57}$  and  $\text{Sn}^{119}$ . In  $\text{Eu}^{151}$ , for example, Shirley originally estimated a value of  $\delta R/R \sim 5 \times 10^{-4}$  on very rough arguments (25). Later Brix et al. (61) and Hüfner, et al. (62) suggested  $3 \times 10^{-4}$  on more elaborate arguments. Recently Gerth, Kienle, and Luchner (63) proposed the two values  $1.3 \times 10^{-4}$  and  $1.7 \times 10^{-4}$ . These results were derived by "taking into account an increase of the electron density by a factor of two in solid state as compared to the gaseous state". Presumably this represents an empirical attempt to correct for overlap effects in ionic solids.

In summary, considerable progress has been made in estimating the scale factors for isomer-shift studies, but uncertainties of about a factor of three remain. We may hope that the values of  $\delta R/R$  for at least the more important Mössbauer isotopes will be established soon so that quantitative inferences about electronic structure may be drawn from isomer-shift data.



## OTHER RESONANCES

Six additional elements will be discussed. The resonant isotopes are  $\text{Sb}^{121}$ ,  $\text{Te}^{125}$ ,  $\text{I}^{127,129}$ ,  $\text{Xe}^{129,131}$ ,  $\text{Au}^{197}$ , and  $\text{Np}^{237}$ . The first four elements, together with tin and cesium, form a series of six elements in which Mössbauer spectroscopy is possible. The chemistry of the first five elements in this series is sufficiently similar to allow useful analogies to be drawn, and this feature will be emphasized in the following discussion. The six Mössbauer elements are taken up in order of increasing atomic number.

 $\text{Sb}^{121}$ 

After the level sequence in  $\text{Sb}^{121}$  was established and a Mössbauer state was shown to lie at 37 keV (64,65,66), Ruby and co-workers characterized the isomer shift (67), magnetic moments (68), and quadrupole moments (69) for this resonance. Aside from its intrinsic importance for antimony chemistry per se, and less directly for the chemistry of other Group V elements, the  $\text{Sb}^{121}$  resonance serves the valuable function of connecting  $\text{Sn}^{119}$  with the previously-established Mössbauer isotopes of Te, I, and Xe. In the reviewer's opinion it is the more extensively studied but less thoroughly understood  $\text{Sn}^{119}$  resonance that is likely to derive the major benefit from this contact.

First a brief digression. The well-resolved magnetic hyperfine pattern of  $\text{Sb}^{121}$  is almost identical to that of  $\text{Eu}^{151}$  (70). Both isotopes have odd proton numbers and both transitions are of the type  $7/2$  (M1)  $5/2$ . The close similarity in hfs patterns occurs because the g-factor ratios are almost exactly the same,  $g(7/2)/g(5/2) = +0.53$ , and one might expect some implications for nuclear structure. On closer examination, however, this remarkable result seems to be entirely coincidental, because the nuclear structures of the two isotopes are really quite different. For example the nuclear factors,  $\delta R/R$ , and the quadrupole moments of  $\text{Eu}^{151}$  have opposite signs from those of  $\text{Sb}^{121}$ .

Some chemical information has already emerged from the  $\text{Sb}^{121}$  resonance. Ruby et al. (69) determined the sign of  $e^2qQ$  for  $\text{Sb}_2\text{O}_3$  as positive, establishing that electron charge density is concentrated along an axis perpendicular to the plane through the Sb atom in trigonal coordination with three oxygens. Ruby et al. (67) studied several  $\text{Sb}^{121}$  compounds and compared them with  $\text{Sn}^{119}$  compounds with similar ligands to derive  $(\delta R/R)_{\text{Sb}}/(\delta R/R)_{\text{Sn}} = 6.1 \pm 1.5$ . Using the isomer shifts in  $\text{SbF}_3$  and  $\text{Sb}_2\text{O}_3$  to establish the 5s electron

populations, together with a hybridization model, they estimated the field gradients in those compounds. Then by comparing these results with the observed  $e^2qQ$ , they derived  $Q(5/2) = -0.26 \pm 0.10b$  for the ground-state quadrupole moment of  $Sb^{121}$ .

V. S. Shpinel et al. (71) have made detailed intercomparisons of isomer shifts for  $Sn^{119}$ ,  $Sn^{121}$ , and  $Te^{125}$  in the halogen complexes  $SnX_6^{-2}$ ,  $SbX_6^{-1}$ , and  $TeX_6^{-2}$ , where X is F, Cl, Br, or I. They derived the nuclear factor ratio  $(\delta R/R)_{Sb}/(\delta R/R)_{Sn} = -5.5 \pm 0.3$ , in good agreement with the above result. They made some observations about screening by d electrons in these octahedral complexes, assuming that they are  $sp^3d^2$ -hybridized. This point ( $sp^3d^2$  hybridization) is discussed below in the review of the I<sup>127,129</sup> resonances. They found a very good linear correlation between isomer shift and ligand electronegativity in these complexes. Their shifts, and those of others, for the Sn, Sb, Te, I, and Xe resonances are plotted in Figure 2 as an energy-level diagram.

Te<sup>125</sup>

A number of papers have appeared dealing with the Te<sup>125</sup> resonance. We shall mention only a few that are of particular chemical interest. Violet and Booth (72) studied several Te compounds, finding a correlation between isomer shift and quadrupole splitting. Previous work by Violet, Booth, and Wooten (72) had given  $|Q_{125}| = 0.20^{+0.03}_{-0.02}$  b. Of particular interest were the source experiments, using NaI<sup>125</sup>O<sub>3</sub>, by Violet and Booth. They obtained a complex spectrum which they interpreted as arising from the excited nuclear state of Te<sup>125</sup>, produced in the decay of I<sup>125</sup>, existing in atoms with two chemical charge states, Te<sup>+5</sup> and Te<sup>+6</sup>. Each of these was assumed to produce a quadrupole-split spectrum, and their analysis made use of four equally-intense lines. This intensity ratio, together with these two charge states, was inconsistent with the known electron-capture properties of I<sup>125</sup>, which would give a ratio Te<sup>+5</sup>/Te<sup>+6</sup> of 0.02 or less. Thus they hypothesized that the Te<sup>+6</sup>-to-Te<sup>+5</sup> reduction proceeded in a time comparable to the nuclear lifetime,  $T_{1/2} = 1.6 \times 10^{-9}$  sec. This would be an interesting result if confirmed, but Jung and Triftshauser (73) have analyzed a similar source

experiment on  $\text{NaIO}_3$ , in which the experimental spectra agreed very well with those of Violet and Booth, quite differently. They were able to fit their data with previously-measured experimental spectra, those of  $\text{NaTeO}_3$  and  $\text{TeO}_3$ , in the intensity ratio 2:1. They thus inferred that  $\text{I}^{125}\text{O}_3^-$  decays to both  $\text{TeO}_3^{-2}$  and  $\text{TeO}_3$ . They found similar results in the decay of  $\text{NaI}^{125}\text{O}_4$  and inferred that in this case both  $\text{TeO}_4^{-2}$  and  $\text{TeO}_3$  were formed. Of course this does not disprove the Violet-Booth model, but it demonstrates that the origin of the two spectra is an open question.

Pasternak and Bukshpan (74) studied  $\text{Te}$ ,  $\text{TeO}_2$ , and  $\text{Te}(\text{NO}_3)_4$  using both the  $\text{Te}^{125}$  resonance and the  $\text{I}^{129}$  resonance. For the latter work they did experiments with  $\text{Te}^{129}$  sources. In the two compounds they found the field-gradient ratio  $q(\text{Te}^{125})/q(\text{I}^{129})$  to be the same, although the quadrupole asymmetry parameter varied. They deduced some structural features of  $\text{TeO}_2$  and  $\text{Te}(\text{NO}_2)_4$  and found for the excited-state quadrupole moment  $Q_{125} = -0.19 \pm 0.02$  b, in excellent agreement with the result of Violet, Booth, and Wooten (72).

Shpinel et al. (71) found  $(\delta R/R)_{Te} / (\delta R/R)_{Sn} = +1.1 \pm 0.2$  from their studies of the isoelectronic halide complexes of  $Sn^{119}$ ,  $Sb^{121}$ , and  $Te^{125}$ . With  $(\delta R/R)_{Sn}$  between  $+0.9 \times 10^{-4}$  and  $+3.5 \times 10^{-4}$ , this yields  $1 \times 10^{-4} < (\delta R/R)_{Te} < 4 \times 10^{-4}$ . Jung and Triftshauer (73), on the other hand, have made a detailed comparison of resonances in compounds of  $Te^{125}$  and  $I^{127}$ . They found a striking linear relationship between the two sets of shifts, thereby confirming the structural similarities of the I and Te compounds, even though many of the pairs involved (e.g.,  $ICl_4^-$  and  $TeCl_4$ ) were not isoelectronic. Their deduced  $(\delta R/R)_{125} = +2.4 \times 10^{-5}$  is in serious conflict with the above result, based on the  $Sn^{119}$ - $Te^{125}$  comparisons. Finding that octahedral  $Te(OH)_6$  was shifted substantially from  $NaTeO_4$ , they inferred, as had Shpinel, et al. (71), that  $sp^3d^2$  hybridization in the former compound was responsible, with the 5d electrons shielding the 5s electrons. They deduced that the 5d electron shields about 1/3 as efficiently

as does a 5s or 5p electron. Again the reader is referred to the discussion of the role of  $sp^3d^2$  hybridization in the  $I^{127,129}$  section below.

Jung and Triftshauser found also that sources of  $Sb^{125}$  in  $NaSbO_2$  and  $Sb_2O_3$  showed single-line  $Te^{125}$  resonances, in contrast to sources of  $NaI^{125}O_3$  and  $NaI^{125}O_4$ . They inferred that the Te electron configuration is less distorted in beta decay than in electron-capture decay. This is the direction that would be expected, since highly-charged states can be formed in the cascade and Auger processes following the formation of a K vacancy. In the decay products of  $HSb^{125}Cl_6$  and  $KSb^{125}Cl_6$ , however, they found only small Mössbauer effects, implying that  $Te^{125}$  atoms become detached from the Cl atoms, and that even beta decay can break up weakly-bound complexes. They noted that this result is consistent with the observation of two charge states of  $Fe^{57}$  following the decay of  $Co^{57}$  in compounds with low Debye temperatures.

$I^{127,129}$

A brief review of the iodine resonances was given by Herber (1).

Hafemeister (75) reviewed the subject more extensively, with emphasis on the

alkali halides, and Perlow (76) gave a detailed discussion of iodine compounds, emphasizing their bonding properties and their similarities to xenon compounds.

From alkali halide shifts alone (77) a linear relationship could be established between the  $I^{129}$  isomer shifts and  $h_p$ , the number of holes in the  $5p^6$  shell of  $I^-$ . Both NMR chemical shift data (78) and dynamic quadrupole resonance data (79) could be interpreted to yield  $h_p$ . The correlation between  $h_p$  and isomer shift was convincingly confirmed by Pasternak et al. (80) in their work on solid molecular  $I_2$ . They found that a 600% extrapolation of the isomer shift- $h_p$  relation to  $h_p = 1$  (in  $I_2$ ) from  $0.033 \leq h_p \leq 0.165$  (the alkali/halide range) gave good agreement with their result.

They gave

$$\text{Isomer shift} = 0.136 h_p - 0.054 \text{ cm/sec}$$

for the isomer shifts of alkali iodides and  $I_2$ , taken with respect to a ZnTe source. The consistency of these shifts might alternatively be regarded as evidence that the bond in  $I_2$  has pure  $p_0$  character, as we shall see below.



Both Hafemeister and Perlow pointed out that the I shifts fall into three categories. Taking  $I^-$ , with the configuration  $5s^2 5p^6$ , as a reference state, the first category includes the ionic iodides, which lie very close to  $I^-$ , having a slightly higher value of  $|\psi(0)|^2$ . These were discussed above. In other compounds, bonds may be formed in two essentially different ways. If p orbitals are used exclusively, the decreased shielding will increase  $|\psi(0)|^2$  significantly over its value in  $I^-$ . If, on the other hand, hybridized bonds are formed from both 5s and 5p orbitals, the net effect is to decrease  $|\psi(0)|^2$  relative to  $I^-$ .

Perlow and Perlow (81) compared isomer shifts with  $h_p$  (derived from quadrupole coupling constants) for  $I_2$ ,  $KICl_4 \cdot H_2O$ ,  $KICl_2 \cdot H_2O$ , and  $ICl$ . They found a linear relation, with slope  $d(IS)/dh_p = -0.056$  cm/sec for the  $I^{127}$  resonance. This corresponds to a slope of  $+0.149$  cm/sec for  $I^{129}$ , in good agreement with the result of Pasternak et al. (80). The  $IO_3^-$  ion, with  $90^\circ$  O-I-O bond angles, probably also exhibits  $p_o$  bond character. The octahedral arrangement of oxygens about the I atom precludes determination of  $h_p$  from quadrupole splitting, but the isomer shift alone may be compared with the above plot: it corresponds to  $h_p = 1.3$ , a reasonable value.

Let us digress to correct a minor error of transcription. The isomer-shift energy-level diagram given by Perlow and Perlow (81) and by Perlow (76) gives the shift for  $I_2$  in  $I^{127}$  incorrectly as  $-0.74$  mm/sec relative to  $I^-$ , coincident with that of  $KICl_2 \cdot H_2O$ . In their table and their  $h_p$  vs isomer shift diagram the shift for  $I_2$  is  $-0.58$  mm/sec relative to  $I^-$ . This would be  $-0.42$  mm/sec relative to ZnTe: apparently the  $0.16$  mm/sec correction was not made consistently in drawing the level diagram. To compare the  $-0.42$  mm/sec shift with the  $I_2^{129}$  - ZnTe<sup>129</sup> shift (80), we employ the relation

$$\frac{v_{129}}{v_{127}} = \frac{(\delta R/R)_{129}}{(\delta R/R)_{127}} \frac{E_{127}}{E_{129}} = -2.67$$

using the  $\gamma$ -ray energies  $E_{127} = 57.6$  keV and  $E_{129} = 27.7$  keV, together with the nuclear-factor ratio  $-0.78$  given by Ramma Reddy et al. (82). After this correction we have a ( $I_2^{129}$  - ZnTe<sup>129</sup>) derived shift of  $+1.12 \pm 0.11$  mm/sec, which is  $0.30$  mm/sec larger than Pasternak, et al.'s value of  $+0.82$  mm/sec (80).

Thus the lack of agreement noted by Hafemeister (75) is only partially real.

Other discrepancies exist, however. The  $I^{127}$  shifts for  $KIO_4$  and  $Na_3H_2IO_6$  relative to ZnTe given by Perlow and Perlow (81) are only about 80% as large

as those quoted by Hafemeister (75) for  $I^{129}$ , after the conversion is made. The  $I^{127}$  shift for  $Na_3H_2IO_6$  determined by Jung and Triftshauser (73) agree with the Perlow and Perlow result ( $+1.02 \pm 0.01$  mm/sec vs  $+1.02 \pm 0.04$  mm/sec). Perhaps the nuclear-factor ratio should be re-evaluated.

Proceeding now to the third group of iodine compounds, those with hybridized covalent bonds, tetrahedral  $IO_4^-$  is easily understood as being  $sp^3$ -hybridized, with  $|\psi(0)|^2$  lower than in  $I^-$ . For octahedral  $IO_6^{5-}$  the simplest approach is to invoke  $sp^3d^2$ -hybridization, as has been done for octahedral complexes of Sn, Sb, and Te (71,73), with electrons being promoted to the 5d shell. Perlow showed, however, that this model is unsatisfactory, as a charge of -2.6 on the iodine atom is required to maintain consistency with the observed isomer shifts (76). The reason for this is that depletion of the 5s orbital in  $sp^3d^2$ -hybridization decreases  $|\psi(0)|^2$  far too much, and electrons must be recalled to increase  $|\psi(0)|^2$  up to the experimental value. Perlow suggested the alternate description of constructing delocalized molecular orbitals from the iodine 5s and 5p functions plus oxygen atomic orbitals, requiring these molecular orbitals to transform

as irreducible representations of the cubic group, namely  $a_{1g}$ ,  $e_g$ , and  $t_{1u}$ . Charge-transfer is largely accomplished by placing four electrons in the (nonbonding)  $e_g$  orbital, on the oxygen ligands. The  $a_{1g}$  and  $t_{1u}$  orbitals can be formed with 5s and 5p iodine functions, obviating the use of 5d orbitals. With this description Perlow was able to fit the isomer shifts with a charge of +0.6 on the iodine atom.

A pleasing feature of the  $I^{127,129}$  work is that the Mössbauer results may be compared with those from other experiments. The use of quadrupole resonance data and NMR chemical shift data in this connection has already been mentioned (75). Another relevant method is photoelectron spectroscopy on the iodine atomic core levels. Fadley, et al. (83) showed, using this method, that I is positively charged in both  $IO_3^-$  and  $IO_4^-$ , thus removing any residual uneasiness about the isomer shifts relative to  $I^-$  being of opposite signs. Photoelectron spectroscopy should serve in a complementary role to Mössbauer spectroscopy in the future.

Xe<sup>129,131</sup>

G. J. Perlow, M. R. Perlow and co-workers (76, 84-88), in their tour de force of the xenon compounds, have made the single most impressive and important application of Mössbauer spectroscopy to chemistry. First with quadrupole coupling data, and more recently with isomer shifts, they have definitively established the bonding character of several xenon oxides and fluorides, thereby providing unambiguous experimental evidence for the hypothesized (89-92) chemical similarities between iodine complexes and xenon compounds. In addition they first synthesized  $\text{XeCl}_2$  and  $\text{XeCl}_4$  by the beta decay of  $\text{I}^{129}$  in  $\text{ICl}_2^-$  and  $\text{ICl}_4^-$  (86,87). Their xenon work represents one of the few cases in which Mössbauer spectra were used to elucidate chemical structure rather than vice-versa. Perlow's comprehensive review should be consulted for full coverage of this topic: only a few highlights can be mentioned here.

The Mössbauer transition in  $\text{Xe}^{129}$  has  $3/2(M1)1/2$  character: the level order is inverted in  $\text{Xe}^{131}$ . Thus quadrupole splitting yields a simple two-line spectrum in either case.  $\text{Xe}^{129}$  has the better resonance parameters,

but  $\text{Xe}^{131}$  had the only known quadrupole moment, in its ground state. Comparison of the Mossbauer spectra of  $\text{Xe}^{129}\text{F}_4$  and  $\text{Xe}^{131}\text{F}_4$  yielded the excited-state quadrupole moment of  $\text{Xe}^{129}$  (88), and the remaining experiments have been done with this isotope.

That the bonding in  $\text{XeF}_4$  and  $\text{XeF}_2$  was essentially of  $p_\sigma$  type was established by the  $\text{Xe}^{129}$  spectra: these compounds were shown to have  $h_p = 3.00$  and  $1.43$ , respectively (76), from their  $e^2qQ$  values. A linear relation between  $h_p$  and isomer shift was found for these compounds together with  $\text{XeCl}_2$  and  $\text{XeCl}_4$ , in analogy to the results for  $p_\sigma$ -bonded iodine compounds.

The comparison of xenon compounds with isoelectronic iodine complexes, illustrated in Figure 2, is especially interesting. In Table 4 are listed the central-atom charges for halides and oxides of these two elements, from Perlow's article (76). Comparing first the halides, we may paraphrase Perlow's conclusions about charge distributions on the various atoms as follows. Between a given dihalide and the same tetrahalide of either I or Xe, the halogens have the same charge, but the central atom is "oxidized" by

about one charge unit (0.9 to 1.57) from the dihalide to the tetrahalide.

In the xenon halides, fluorine atoms are about 0.25 charge unit more negatively charged than are the corresponding chlorine atoms. Finally, increase of the nuclear charge by one unit from  $\text{ICl}_{2,4}^-$  to  $\text{XeCl}_{2,4}^-$  increases the central-atom charge by less than one unit, with 0.2 electrons being recalled for each bond.

The xenon oxides, like the oxyhalide ions, have hybridized bonds, with 5s electrons directly involved. Again the evidence for this conclusion is their finding lower values of  $|\psi(0)|^2$  relative to neutral Xe ( $5s^2 5p^6$ ). For tetrahedral  $\text{XeO}_4$  Perlow invokes  $sp^3$ -hybridization (a delocalized description would be equivalent). In octahedral  $\text{XeO}_6^{4-}$  he used the delocalized MO description, again avoiding the use of 5d orbitals. The results for the oxides are less easily understood than for the halides. Both p-periodate and perxenate have oxygen charges close to -1 and the increase of +1 in nuclear charge is reflected in the net central atom charge. In  $\text{IO}_4^-$  and  $\text{XeO}_4$ , however, the results are rather puzzling. The oxygen charges are not the same, and the substitution of Xe for I seems to increase the bond polarization.

Au<sup>197</sup>

The reviewer is in a privileged position regarding this resonance, as M. O. Faltens has just completed a Ph.D. thesis under his direction on the Mössbauer spectra of gold compounds (93). Although studies of gold compounds at Oak Ridge and Berkeley have been alluded to several times during the last seven years (94-97), no complete research report has yet been published. A report on Faltens' study is in preparation, however (98), and a few of her results will be reviewed here.

Gold has two common oxidation states. It may lose one electron from the neutral  $5d^{10}6s$  configuration to form aurous compounds (ionic configuration  $5d^{10}$ ) or three to form auric compounds (ionic configuration  $5d^8$ ). Aurous compounds tend to have linear ligand-gold-ligand bonds, as in linear  $AuCl_2^-$ , and they are usually described as being  $sp$ -hybridized. Auric compounds are usually square-planar as in  $AuCl_4^-$ ; this is attributed to  $dsp^2$ -hybridization. M. O. Faltens has found a wide range of isomer shifts and quadrupole splittings for gold compounds in both oxidation states. She was able to correlate the two parameters, as shown in Figure 3, for aurous complexes, thereby supporting



the sp-hybrid hypothesis while at the same time demonstrating a wide range of ionic character in these substances. She also found a correlation for the auric compounds, but here it was necessary to consider 5d-orbital contributions to the quadrupole coupling constant. Because it is in an inner shell, the 5d orbital has a field gradient approximately equal to that of the 6p orbital. Another interesting result of this study is the propensity of the gold atom (the most electronegative of the metals) to attract electrons from some of its less electronegative ligands.

Np<sup>237</sup>

Two groups, Stone and Pillinger at Savannah River (99,100,103) and Dunlap et al. at Argonne (101), have studied this resonance. Although interpretation is still in the early stages and the narrowest lines yet observed are about 15 times natural linewidth, this resonance is clearly going to be an important one. Already isomer shifts have been observed over a range of 8 cm/sec, or about 2000 natural linewidths: this large range is in part due to the large relativity factor in this heavy element (25).

The original work on  $\text{NpO}_2$  sources and absorbers (99) established that Mössbauer spectra could be observed following either the beta decay of  $\text{U}^{237}$  or the alpha decay of  $\text{Am}^{241}$ . Stone and Pillinger (100) showed that the nuclear moment ratios were  $Q_e/Q_g = +1.0 \pm 0.1$  and  $\mu_e/\mu_g = +0.537 \pm 0.005$ . Dunlap et al. (101) found  $Q_e/Q_g = +1$  and  $\mu_e/\mu_g = +0.533 \pm 0.005$ , with  $\delta R/R = -1.25 \times 10^{-4}$ . They interpreted this nuclear factor as arising from a fractional charge on nuclear deformation of  $-5 \times 10^{-3}$  in going to the excited state.  $\text{NpAl}_2$  was found to have a single line of "only" 15 times the natural width above its transition temperature of  $54^\circ\text{K}$  (101, 102): at  $4.2^\circ\text{K}$  it exhibits magnetic hyperfine structure with an effective field of  $+3.1$  (100) or  $+3.4$  (101) million gauss, assuming  $\mu_g = +2.7$  nuclear magnetons. In  $\text{NpCl}_4$  Stone and Pillinger found both magnetic and quadrupole splitting at  $4.2^\circ\text{K}$ . At  $77^\circ\text{K}$  they found only quadrupole splitting, probably because the magnetic structure was averaged out by relaxation. Dunlap et al. (101) found magnetic hyperfine structure in  $\text{NpC}$  and magnetic plus quadrupole structure in  $\text{KNpO}_2\text{CO}_3$  and in  $\text{K}_3\text{NpO}_2\text{F}_5$ . They found an isomer shift of  $-45$  mm/sec

between this last compound, with Np in the +6 oxidation state, and  $\text{NpO}_2$ . They attributed an isomer shift of about 20 mm/sec to the loss of one 5f electron. Stone and Pillinger (103) have extended this isomer shift-oxidation state correlation, finding a shift of +41 mm/sec for  $\text{NpCl}_3$  and  $\text{NpBr}_3$  relative to  $\text{NpO}_2$ . They extracted a fractional change in nuclear deformation of  $-6 \times 10^{-3}$ , in good agreement with Dunlap et al., but they interpreted this as an upper limit of the magnitude of the difference. From this value they deduced that  $Q_e$  and  $Q_g$  must be equal within 1%. They put forth an interesting isomer shift-electron configuration correlation, in which a shift of +4 cm/sec accompanies the loss of the two 7s electrons in going from neutral Np ( $5f^4 6d7s^2$ ) to  $\text{Np}^{+3}$  ( $5f^4$ ). On further oxidation the shift goes through zero to -3.5 cm/sec for  $\text{Np}^{+6}$  ( $5f^1$ ), or an average shift of -25 mm/sec per 5f electron lost, in good agreement with the conclusion of Dunlap et al. (101).

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Reference 18.

TABLE 1

Suggested Nuclear Factors for Fe<sup>57</sup>

Value of $\delta R/R$ , units of $10^{-4}$	Method	Ref.
-18	Assume ionic configuration in salts	42
-5	Assign charges from x-ray data	43
-9	Molecular orbitals, assign effective charges to iron atoms	44
-4	Ionic $O^{-2}$ wave functions corrected for overlap	38
-5.2	Ionic $F^{-}$ wave functions corrected for overlap	41

TABLE 2

Suggested Nuclear Factors for Sn<sup>119</sup>

Value of $\delta R/R$ , in units of $10^{-4}$	Method	Ref.
+1.1	Assign ionic configurations to salts	46
+1.9	Assign nearly ionic configurations to salts	47
<0	Molecular orbitals with shielding	48,49
+3.3	Conversion electron intensities	50
+1.2	Assign ionic configurations in salts, use Hartree-Fock wave functions	52
+0.9	Assign ionic configurations in salts, use Dirac-Fock wave functions	53
---	Equivalent orbitals	54
+3.5	Self-consistent molecular orbitals	56

TABLE 3

## Suggested Nuclear Factors for Other Isotopes

Isotope	$(\delta R/R)$ in units of $10^{-4}$	Ref.
Sb <sup>121</sup>	$(-6.1 \pm 1.5)(\delta R/R)_{\text{Sn}^{119}}$	67
	$(-5.5 \pm 0.3)(\delta R/R)_{\text{Sn}^{119}}$	71
Te <sup>125</sup>	$(+1.1 \pm 0.2)(\delta R/R)_{\text{Sn}^{119}}$	71
	+0.24	73
I <sup>127</sup>	-0.28	73
I <sup>129</sup>	+0.3	77
	+0.5	36
Eu <sup>151</sup>	+3	61,62
	+1.5	63
Au <sup>197</sup>	+3	25
Np <sup>237</sup>	-1.25	101
	-1.35	103



TABLE 4

## Comparison of Isoelectronic Xenon and Iodine Compounds

Compound	Structure	Central atom charge	Ligand charge	Electron recall per bond
$\text{ICl}_4^-$	square planar	+1.7	-0.68	
$\text{XeCl}_4$	square planar	+1.9	-0.48	0.2
$\text{XeF}_4$	square planar	+3.0	-0.75	
$\text{ICl}_2^-$	linear	+0.4	-0.70	
$\text{XeCl}_2$	linear	+1.0	-0.51	0.2
$\text{XeF}_2$	linear	+1.43	-0.72	
$\text{IO}_6^{5-}$	octahedral	+0.6	-0.94	
$\text{XeO}_6^{5-}$	octahedral	+1.6	-0.94	0.0
$\text{IO}_4^-$	tetrahedral	0	-0.25	
$\text{XeO}_4$	tetrahedral	+1.7	-0.42	-0.17

## FIGURE CAPTIONS

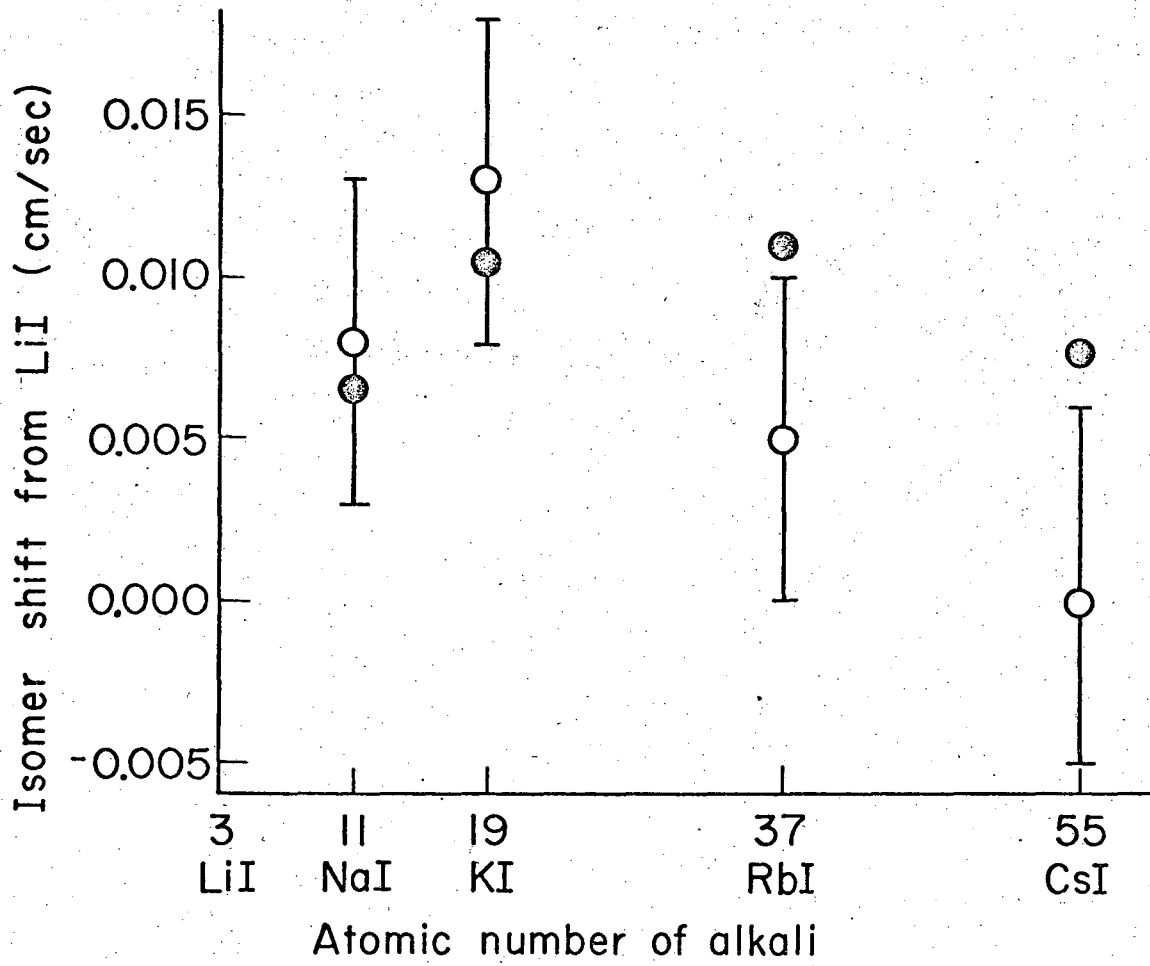
Fig. 1. Isomer shifts for alkali halides, from Refs. (36) and (77). Filled circles show theoretical points from Flygare and Hafemeister's overlap correction calculation (36). Without this effect a monotonic variation would be expected.

Fig. 2. Isomer-shift energy-level correlation diagram for the series Sn-Xe.

Compounds with highest  $|\psi(0)|^2$  are at the bottom of the diagram.

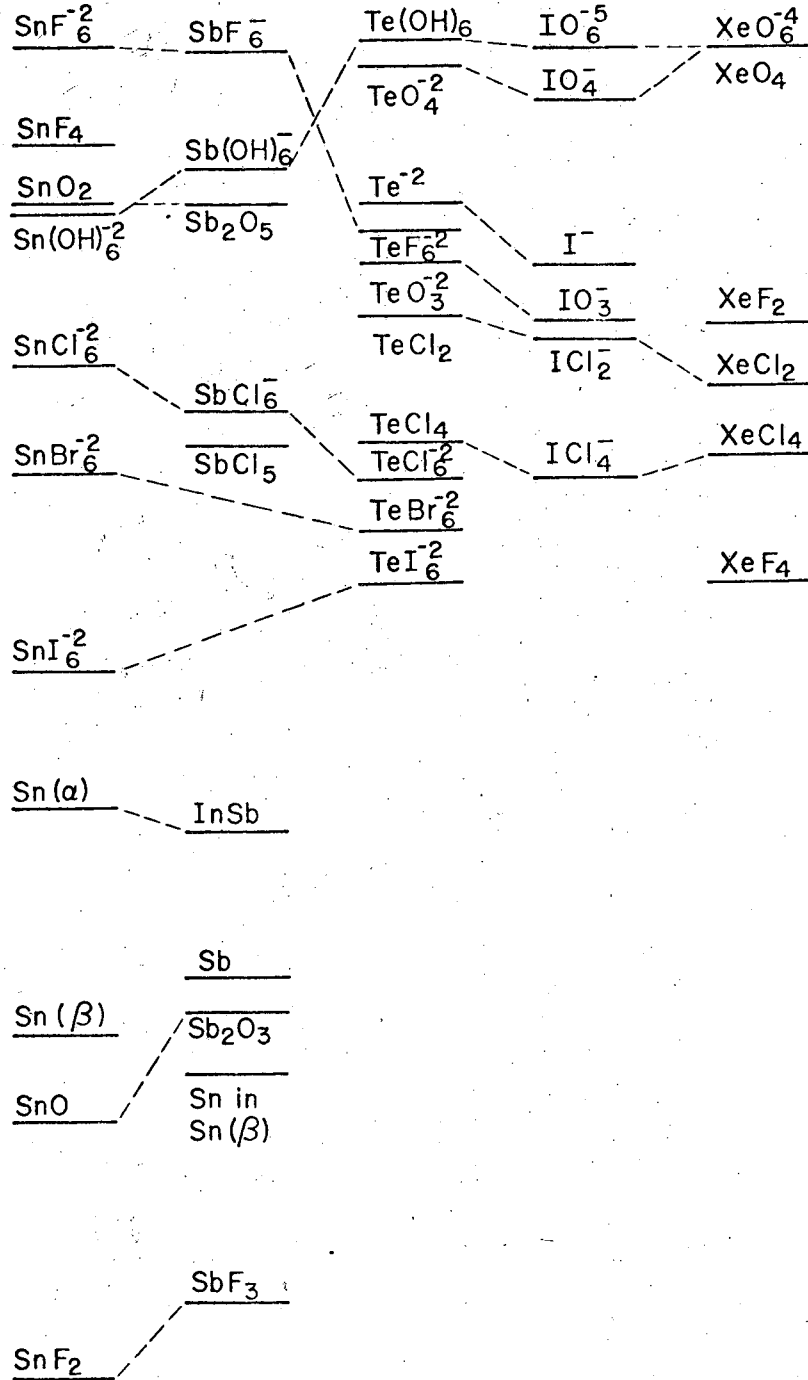
Among the compounds of each Mössbauer element the energy levels have correct relative positions, but between any two such elements neither the scale factor nor the absolute position is known: both have been adjusted to emphasize chemical correlations. Note that not all connected compounds are isoelectronic.

Fig. 3. Quadrupole coupling-isomer shift correlation for aurous compounds, after M. O. Faltens (93).



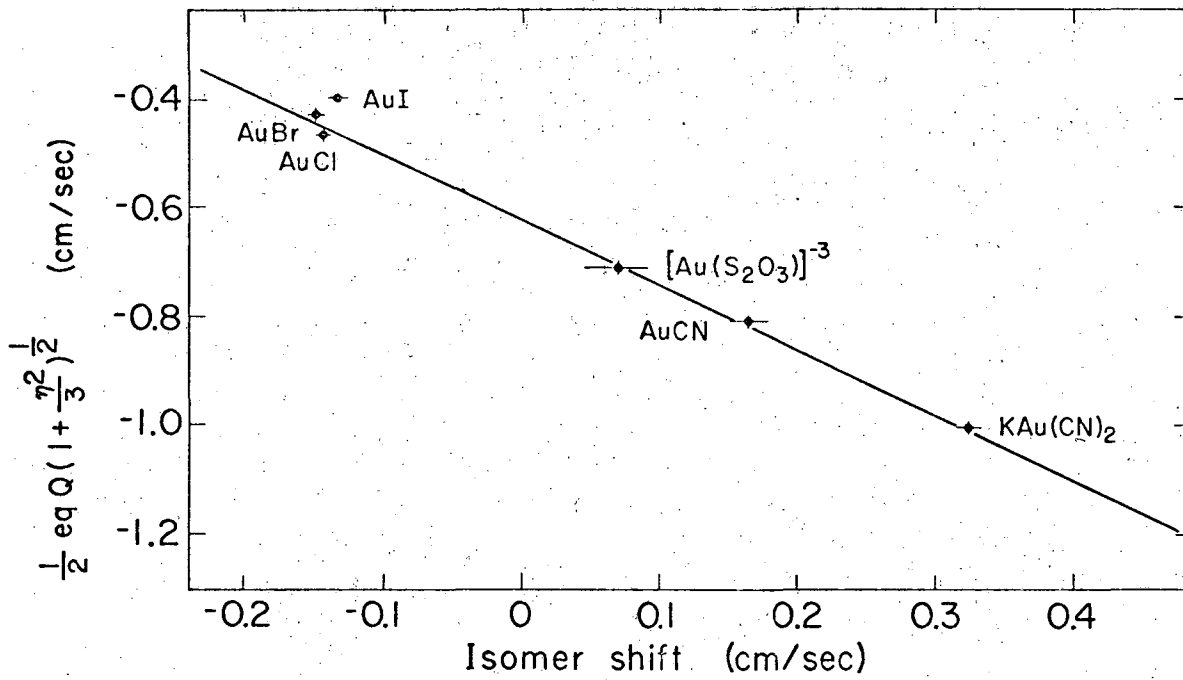
XBL69I-150I

Fig. 1



XBL691-1502

Fig. 2



XBL691-1503

Fig. 3

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