23 August 1968, Volume 161, Number 3843 **SCIENCE**

Chemical Tools from Nuclear Physics

Experimental developments in nuclear physics are being adapted to probe electronic structure.

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Chemistry and nuclear physics might appear to be quite independent disciplines. In fact, however, an easily traced symbiotic relationship between them has existed ever since the birth of the newer science. The discovery of the atomic nucleus in Rutherford's laboratory in 1911 (*1*) was prerequisite to any quantitative theories of atomic and molecular structure and was thereby a milestone in the history of chemistry. Since then the two disciplines have interacted almost continuously. In this article I shall discuss some aspects (*2*) of one side of this relationship, the applications to chemistry of several experimental methods from nuclear physics.

To set the stage for a discussion of how chemical information may be carried by nuclear radiations, we first note that the interactions between electrons and nuclei are entirely electromagnetic in nature. These interactions are thus most conveniently discussed in terms of the first three electromagnetic *moments* of the nucleus: the electric monopole moment (that is, the nuclear charge), the magnetic dipole moment, and the electric quadrupole moment (which measures distortion of the nuclear charge from spherical symmetry). The three interactions are denoted E0, M1, and E2, respectively. They are separable: the total interaction energy is thus additive,

$$\mathcal{H}(\text{total}) = \mathcal{H}(\text{E0}) + \mathcal{H}(\text{M1}) + \mathcal{H}(\text{E2}) \qquad (1)$$

and the three moments may interact independently with different aspects of chemical structure. Let us correlate these interactions with the methods by which they may be observed experimentally, then discuss those methods separately.

The *electric monopole interaction* is the spherically symmetric component of the Coulomb energy. Removal of a valence electron of charge $-e$ at radius R from an atom of atomic number Z increases the Coulomb potential of the nucleus by Ze^2/R, or several electron volts, and one might expect shifts of this size in the energy of nuclear radiations. Unfortunately this shift is not directly observable, because it occurs in both the initial and the final nuclear states, thus canceling in the transition energy. *Observable* effects can arise in three ways:

1) The rates of certain nuclear decay processes are related ρ_e, the electron density at the nucleus. These rates are thus sensitive to chemical structure.

2) The cancellation of shifts in initial and final nuclear states is not complete if the two states are of slightly different size, and small shifts in transition energies still exist.

3) This cancellation is absent altogether if inner atomic electrons are observed after ejection by the photoelectric effect.

Regardless of the method used for its observation, the E0 interaction has an important limitation: it is scalar, and can therefore convey only one bit of information (such as $\Delta\rho_e$) about a system. This may appear as shift in energy, in half-life, or in spectral intensity, but it will be one datum. A corollary is that any observable quantity arising from the E0 effect will be spatially isotropic.

The *M1 interaction* is associated with the energy of orientation of the nuclear magnetic moment in the magnetic field, **H**, at the nucleus. Usually **H** is applied externally but it may be modified by the motion of electrons near the nucleus. A measurement of **H** can then produce valuable information about the chemical environment. Often conventional nuclear magnetic resonance (NMR) will yield this information, but the use of radioactive isotopes provides additional possibilities.

The nuclear magnetic moment, the local extranuclear electrons, and **H** may all interact, and they in turn may all be affected by the surrounding lattice. The result is usually complicated, but often the stationary approximation of an "effective" magnetic field $\mathbf{H}_e$ gives an adequate qualitative description. Because the M1 interaction has vector character, it can convey more data than can the E0 interaction. Even in the effective field case two data—magnitude and direction—are contained in $\mathbf{H}_e$. The M1 interactions may be observed in several ways. Mössbauer spectroscopy (*3*) allows the direct observation of Zeeman-split nuclear substates. Several angular-distribution methods, notably nuclear orientation (*4*) and angular correlations (*5*), are based on the spatial anisotropy of radiation from nuclei in a magnetic field. Periodic precession of the nuclear moment about $\mathbf{H}_e$ gives rise to time-dependence in the spatial anisotropies and to resonance phenomena, such as NMR.

The *electric quadrupole interaction* arises from the tendency of a nucleus whose charge distribution is unsymmetrical to seek the lowest-energy angular orientation in an inhomogeneous electric field. As in the E0 case, the E2 interaction is electrostatic. One can understand it qualitatively by using Coulomb's law. As directed chemical bonds imply inhomogeneous electric fields, structural

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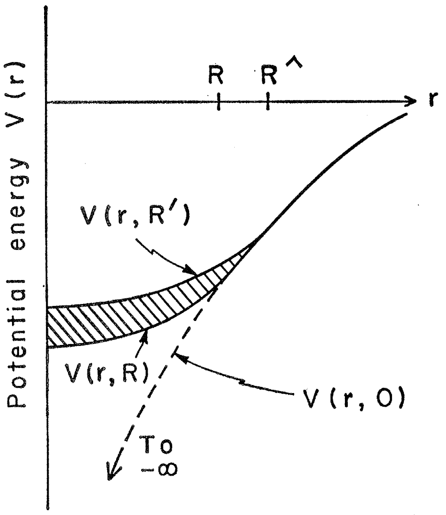


Fig. 1. Electrostatic potentials for electrons within isomeric nuclei of radii R and R'. Outside the nucleus both potentials vary as $1/r$. At the nuclear radii R and R', the potentials break away from $1/r$, as shown. Alteration of the electron density by $\Delta\rho$ through chemical effects will shift the γ-ray transition energy between the R and R' isomers by approximately $\Delta\rho$ times (shaded area).

information follows rather directly from quadrupole data. Although it is not practicable to apply external fields that are sufficiently inhomogeneous over nuclear dimensions to produce observable results, the E2 and M1 cases are in other ways similar. Spectral, angular distribution, and resonance experiments may all be used to study E2 interactions.

The "nuclear" methods of studying chemical properties that will be discussed in this article are summarized in Table 1. This table also serves as an outline for the discussion.

Electric Monopole Interactions

Let us make some general observations about E0 interactions. We note that the electrostatic potential $V(r)$ of the atomic electrons, due to the nucleus, is Coulombic only in to the nuclear surface. Within the nucleus the attractive potential felt by the electron arises only from the nuclear charge at smaller radii, and $V(r)$ reaches a finite value at $r = 0$ (Fig. 1). Atomic electrons in s states (*6*) have nonzero density at the nucleus. If each s electronic state has density $\psi_i^2(0)$, then the total electronic charge that experiences the electrostatic potentials within the nucleus is

$$\rho_e = \sum_i \psi_i^2(0)$$

The shift in γ-ray energy is

$$E = \int \Delta V \rho_e \, dv$$

where ΔV is the difference between the potentials created by the two nuclear states (Fig. 1). Chemical shifts may arise wherever ρ_e is changed. For example, in the reaction

$$\mathrm{Be}\,(1s^2 2s^2) \rightarrow \mathrm{Be}^+\,(1s^2 2s) + e^-$$

the loss of an s electron will decrease ρ_e by an amount $\Delta\rho_e$. This will increase the lifetime by a fraction $\Delta\rho/\rho$ and will shift the transition energy by

$$\delta E = \int \Delta V \, \Delta\rho \, dv \qquad (2)$$

When a non-s electron is lost, ρ_e is increased: the non-s electron doesn't contribute to ρ_e directly, and its loss allows the s electrons to become more tightly bound and contribute more to ρ_e. There is an instructive way to estimate the direct shift in nuclear transition energy to be expected from chemical effects. The volume-dependent isotope shift in heavy elements, observed in optical spectra (*7*), amounts to $\sim 10^{-5}$ of the optical transition energy. The energy cycle shown in Fig. 2 shows that the same size *shift* is expected in nuclear transitions. But nuclear transition energies are measured in millions of electron volts rather than electron volts; therefore fractional shifts of only $\sim 10^{-5} \times 10^{-6} = 10^{-11}$ can be expected. This precision is not available by using standard spectroscopic methods, and more imaginative experiments are required to study E0 effects. Four approaches that have worked are described below, in what I believe to be their order of increasing importance in chemistry.

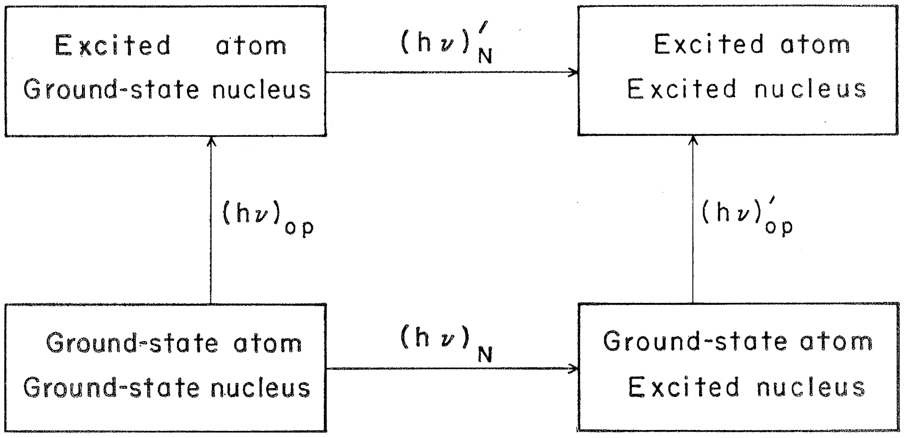


Fig. 2. Energy cycle illustrating the equivalence of shifts in electronic and nuclear transition energies arising from E0 effects. Transition energies are given by $h\nu$, where h is Planck's constant and ν is the photon frequency. The nuclear transition may be observed with the system in the excited or ground optical (chemical) state, and conversely. Conservation of energy implies $\Delta\nu_{op} = \Delta\nu_N$.

Effects on Nuclear Decay Rates

Extranuclear electrons participate in some modes of nuclear decay. One such process is electron capture, in which an atom decreases its atomic number by one unit on taking an electron into the nucleus. The probability for capture is proportional to ρ_e; hence the decay rate varies inversely as ρ_e. Electron rearrangement by bonding may therefore affect the half-life for electron-capture decay.

Unfortunately the outer electrons, which are most strongly affected by bonding, contribute very little to ρ_e. As a rule of thumb the s-electron density at the nucleus falls off by an order of magnitude for each unit increase in the principal quantum number. Thus light elements should show the largest direct effect on the half-life. The first decay studied in this way was (*8, 9*)

$$\mathrm{Be}^7 \xrightarrow{\mathrm{EC}} \mathrm{Li}^7$$

Measurements by several groups demonstrated (*10*) that Be^7 decays about 0.1 percent faster in Be and BeO than in BeF_2, showing that ρ_e is smaller in the more ionic fluoride. Several other isotopes have yielded effects of about this size.

Recently in a more elaborate experiment Cooper, Hollander, and Rasmussen (*11*) found a 3.6 percent chemical effect in the decay rate of a nuclear state in Nb^{90}. To do this they chose a nuclear transition that went by *electron conversion*, a decay process that is accompanied by the ejection of an atomic electron. The probability for ejection of a given electron is proportional to $\psi^2(0)$

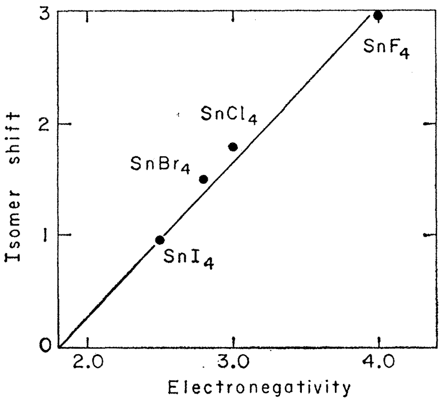


Fig. 3. Correlation of the isomer shift in quadrivalent Sn^{119} with ligand electronegativity, showing increasing bond polarity in the order Sn, SnI_4, $SnBr_4$, $SnCl_4$, SnF_4.

for that electron, and, as in electron capture, the more tightly bound inner electrons usually dominate this mode of decay. In Nb^{90}, however, the two nuclear states lie so close in energy that the nuclear transition can expel only the loosely bound valence electrons. This specificity for valence electrons makes Nb^{90} especially attractive for chemical studies. Unfortunately the low-energy transition is an accident of nature that probably does not occur in many elements.

Effects on Conversion-Electron Intensities

Specificity for valence electrons may also be achieved by observing just those events that involve valence electrons. This is possible in the conversion-electron case if the ejected electrons are energy-analyzed before being counted. Bocquet, Chu, Kistner, Perlman, and Emery (*12*) have reported such an experiment. They studied conversion electron spectra accompanying a 24-kev transition in Sn^{119} and found that the $5s$ electron density at the nucleus, $\psi_{5s}^2(0)$, is 30 percent lower in SnO_2 than in tin metal (α form). This result holds promise for further applications of conversion-electron spectra to chemistry.

Effects on Transition Energies

Mössbauer spectroscopy provides γ-ray energy measurements so precise that even the fractional energy shifts of 10^{-11} produced by chemical effects are observable in absorption experiments. The shift δE between γ-ray source nuclei in one chemical environment and absorber nuclei in a different environment can be written, after integrating Eq. 2, as

$$\delta E = (\text{constant})\,[\rho_e(A) - \rho_e(S)]$$

where A and S denote absorber and source. The constant factor must be calibrated for each isotope. Once this is done, the determination of δE yields the valuable datum ρ_e for each compound studied. This parameter can give an indication of chemical bond polarities in symmetric molecules where no other method is applicable. In tin tetrahalides, for example, δE may be correlated with ligand electronegativity. The Sn–X bond is expected to become increasingly ionic as X varies from I to Br to Cl to F. That it does so (*13*) is illustrated in Fig. 3.

Of the above nuclear methods, isomer-shift studies have until now enjoyed by far the widest application, and this will probably continue to be the case. We should note, however, that the electron-conversion method has one distinct advantage: it gives more direct information about $\psi^2(0)$ for the electrons actually involved in bonding. In fact, the single experiment of Bocquet *et al.* settled the question of the sign of the nuclear constant for Sn^{119}, a problem that had provoked considerable controversy in the interpretation of Mössbauer isomer shifts.

Photoelectron Spectroscopy

The success of internal conversion studies is encouraging, but its applicability is severely limited by the requirement that suitable nuclear levels exist in the element under study, and this is not often the case. A possible solution is to stimulate externally the ejection of "core" electrons from within the atom, by using the photoelectric effect. Chemical bonds will lead to binding-energy shifts for the inner electrons, as discussed above. Figure 4 illustrates a typical photoelectron spectrum, showing chemical shifts in the nitrogen $1s$ line (*14*).

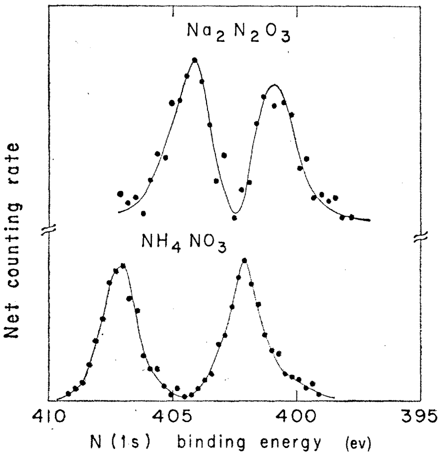


Fig. 4. Nitrogen $1s$-electron spectra from two nitrogen compounds (unpublished work by J. M. Hollander, D. Hendrickson, and W. L. Jolly). Two lines in the lower spectrum arise because the two nitrogens in NH_4NO_3 are in different oxidation states, +5 and −3. Two lines in the $Na_2N_2O_3$ spectrum establish the inequivalence of these two nitrogens.

These effects have been noticed in x-ray absorption and fluorescence for many years (*15, 16*). However the direct observation binding-energy shifts of inner electrons through photoelectron spectroscopy awaited the development of the high-resolution spectrom-

Table 1. Some chemical tools from nuclear physics.

Experimental method	Multipolarity of interaction	Measured property	Application
Change of decay constant	E0	Decay rate	Study ρ_e
Selective effects on electron conversion	E0	Conversion-electron intensities	Bonding studies
Mössbauer isomer shifts	E0	γ-Ray energies	Study ρ_e
Photoelectron spectroscopy	E0	Electron binding energies	Determine charges on atoms
Mössbauer energy splittings	M1, E2	Magnetic field, electric field gradient	Study binding configuration
Angular distribution experiments	M1, E2	Hyperfine structure constants	Study bond character
Resonance experiments	M1	Resonant frequency	Same as conventional NMR

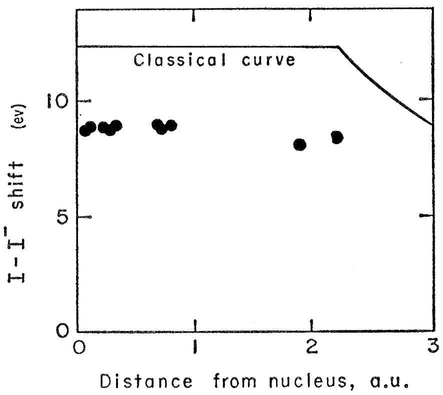


Fig. 5. Binding-energy shifts for inner electrons on removal of one $5p$ electron from I^-. Here R is the position of the radial maximum of the inner electron orbital. Points denote (from left) the orbitals $2p$, $2s$, $3d$, $3p$, $3s$, $4s$, $4p$, $4d$, $5s$, $5p$, as calculated by the Hartree-Fock method. Classical electrostatic model gives solid curve. Constancy of potential inside a charged spherical conductor is also found in the Hartree-Fock results (from ref. *20*). Abbreviation: a.u., atomic unit.

eter by Siegbahn and co-workers at Uppsala. Discovery of the potentialities of this method (*17*) has generated considerable interest in chemical problems in Siegbahn's laboratory (*18*). In Berkeley we have been developing the photoelectron method, primarily because of the insight that it can give into fundamental structural questions (*19, 20*). The salient features of the method are described below.

When an x-ray of known energy $h\nu$ ejects an inner electron from a free atom M,

$$\mathrm{M} + h\nu \rightarrow \mathrm{M}^+ + e^-$$

most of the kinetic energy E_K is imparted to the electron, and we may write to good approximation

$$h\nu = E_K + E_B$$

where E_B is the electron-binding energy. The determination of E_K in an electron spectrometer, then, will yield E_B.

Now suppose that the atom M is bound in a molecule or solid. E_B may be altered by an amount of the order of e^2/R by rearrangement or loss of valence electrons from the outer shells (of radius R). An intuitive picture for this shift may be obtained by thinking of the valence shell of atom M as a charged, conducting spherical shell of radius R. The potential energy of an electron inside the sphere is lowered, and E_B is increased, on removal of an electron from the valence shell to form M^+. Thus in the ejection of an inner electron from M^{++},

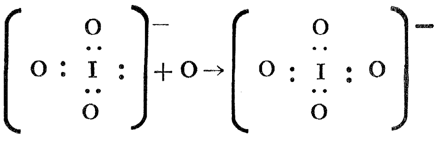
$$\mathrm{M}^+ + h\nu \rightarrow \mathrm{M}^{++} + e^-$$

E_B will be larger by $e^2/R \cong 10$ ev. The diagnostic value of the method is clear: determination of E_B will tell whether the atom under study is present at M, as M^+, or (in partially ionic compounds) as a hybrid of these forms. One does not have to rely on this classical estimate of ΔE_B; quantum-mechanical Hartree-Fock calculations have been made (*18, 20*): the result is essentially the same, $\Delta E_B \cong 10$ ev/(charge state) for medium and heavy atoms. Figure 5 shows calculated shifts for iodine atoms.

In most of the compounds investigated thus far, the experimental shifts are much smaller: about 10 ev for the entire range of oxidation states (-1 to $+7$ in Cl and I, -2 to $+6$ in S), rather than the ~100-ev shifts that would be expected for free ions with these charge-state ranges. An obvious interpretation of this result is that, while oxidation is the "loss of electrons," in fact only about 0.1 electronic charge is actually lost when the oxidation state increases by one unit. One may be further tempted to infer that these shifts imply that the bonds involved are about 10 percent ionic. Neither of these statements is correct, because they neglect the shielding due to ligands. In a chemical complex with polar bonds electrons are not totally removed from an "oxidized" atom but are still present in the complex, where their shielding effect on core electrons of this atom are nearly as large as if they were still in valence orbitals of the atom. For example, in the reaction

$$\mathrm{IO}^-_3 + \frac{1}{2}\,\mathrm{O}_2 \rightarrow \mathrm{IO}^-_4$$

we say that iodine has been oxidized from the +5 to the +7 state. What we mean is that in IO^-_4 iodine shares its electrons with a fourth oxygen. In the "electron dot" representation, we have



$$\left[\begin{array}{ccc} & \mathrm{O} & \\ & \cdot\cdot & \\ \mathrm{O} : & \mathrm{I} & : \\ & \cdot\cdot & \\ & \mathrm{O} & \end{array}\right]^- + \mathrm{O} \rightarrow \left[\begin{array}{ccc} & \mathrm{O} & \\ & \cdot\cdot & \\ \mathrm{O} : & \mathrm{I} & : \mathrm{O} \\ & \cdot\cdot & \\ & \mathrm{O} & \end{array}\right]^-$$

that is, only two additional "iodine" electrons are shared with oxygens. As they are *shared* (not lost), we might expect a shift of inner-electron binding energies in iodine, reflecting a loss of only about one valence electron. Even this would be an overestimate, however, as the "lost" electron is removed no further than the outer region of the IO^-_4 ion, where e^2/R is still about half that of a valence electron in iodine. Another effect is the depolarization of the first three I—O bonds on formation of the fourth. All of these factors tend to decrease the observable shift. We may summarize these results by saying that an increase of one unit in oxidation number is accompanied by an increase of a few tenths of a unit in the charge of an atom and may be manifest experimentally as a shift of inner-electron binding energy corresponding to a loss of 0.1 to 0.2 valence electrons from the free atom.

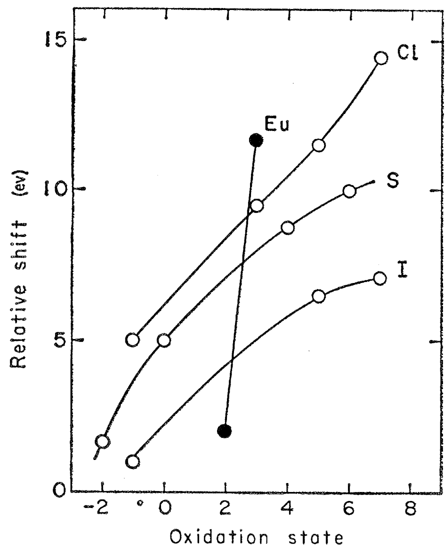


Fig. 6. Binding-energy shifts of inner electrons versus formal oxidation state for four elements. In Eu a change of 1 in oxidation state produces about as much shift as does the entire range of oxidation states in the other cases. This result confirms the shielding model and emphasizes the importance of ligand effects.

The above arguments apply to covalently bonded compounds, but for ionic cations oxidation should be quite accurately described as the loss of an electron. There are few compounds in which one can be sure that the "ionicity" of the cation in both oxidation states is not in some way compromised by covalency or crystal-field effects. The reaction

$$\mathrm{Eu}^{+2} \rightarrow \mathrm{Eu}^{+3} + e^-$$

surely meets this requirement, however, because the electron comes from inner $4f$ orbitals that are shielded from the crystal field. Thus a shift of ~10 ev would be expected between Eu^{+2} and Eu^{+3} if the free-ion picture is applicable. Fadley *et al.* (*19*) have found a shift of this magnitude, thereby confirming this prediction. In Fig. 6 the shifts for Eu^{+2}–Eu^{+3} are compared with those for Cl, S, and I.

Chemical shifts for inner electrons arise, then, from the charges on the parent atom and on neighboring atoms. A convenient summary of the results of a complete set of chemical shift measurements on a substance is given by the charges on all the atomic species. While not extremely subtle, this information places a valuable set of boundary conditions on any theoretical model for bonding.

Dipole and Quadrupole Effects

A useful double contrast may be drawn at this point. The E0 shifts yield limited information, but they are uniquely studied with nuclear physics techniques. The M1 and E2 effects may yield more information, and they can often be studied by conventional methods. Nuclear methods may be valuable even here, however, either for reasons of sensitivity or because a suitable stable isotope of the element in question may not exist. The interpretation of dipole and quadrupole data from conventional methods is highly developed and interpretation of the nuclear studies differs only in the initial data reduction. In discussing the three methods treated below, I shall therefore concentrate on the extraction of structural information from observables.

Mössbauer Spectroscopy

In principle, Mössbauer and optical absorption spectroscopy are very similar, with γ-rays playing the role in the former method that light quanta have in the latter. Only "recoil-free" γ-ray events provide radiation of sufficiently well-defined energy to carry precise chemical information, and the Mössbauer effect is in essence the existence of these events. The contributions of Mössbauer spectroscopy in elucidating structural features of chemical compounds of some Mössbauer elements (for example, Fe, Sn, I, Xe, Au) have been quite impressive. For example G. J. Perlow and M. R. Perlow have demonstrated (*21*) the correlations of isomer shifts and quadrupole coupling constants in isoelectronic complexes and compounds of Xe and I, thereby characterizing the bonding in xenon compounds in detail.

Gold compounds can also be studied by Mössbauer methods, and I shall use the spectra of linear aurous complexes as an example for discussion. M. O. Faltens has just completed a study of these compounds (*22*) in our laboratory in Berkeley. Figure 7 shows the spectrum that she found for a $KAu(CN)_2$ absorber, taken with a metallic Pt source. Both an isomer shift (δE) and quadrupole splitting (ΔE_Q) are present: they measure, respectively, the contributions to bonding of 6*s* and 6*p* electrons outside the $5d^{10}$ core of Au^+. If, in particular, the linear CN–Au–CN unit were completely ionic (that is, CN^-–Au^+–CN^-), then ΔE_Q would be essentially zero.

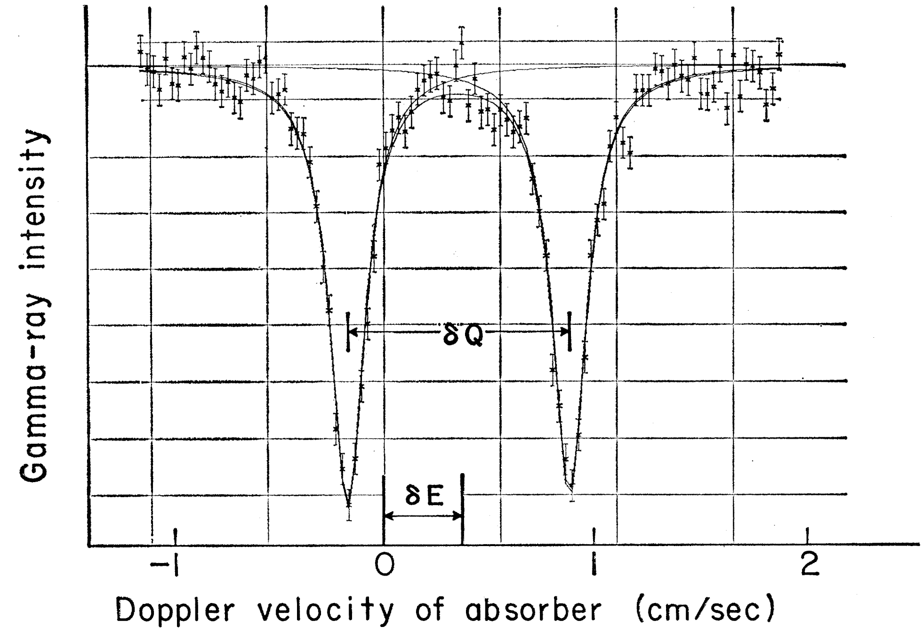


Fig. 7. Mössbauer spectrum of $KAu(CN)_2$ as determined by M. O. Faltens. Doppler velocity gives energy shifts relative to a platinum standard. Isomer shift, δE, and quadrupole splitting ΔE_Q, measure *s* and *p* orbital populations, respectively. Faltens' correlation of these properties confirms the *sp* bonding model for linear aurous complexes.

The linear character of the X–Au–X bond in aurous compounds suggests that the covalent contributions to bonding may arise from (linear) *sp*-hybrid bond orbitals. A critical test of this hypothesis is in fact available from Faltens' spectra. If the X–Au–X bond can be characterized as having a fraction f of ionic character and a fraction $(1 - f)$ of *s-p* hybrid covalent character, then as X is varied f will change. Since the *sp* orbital population is being varied, however, δE and ΔE_Q must vary together, that is,

$$\delta E = f(\delta E_{\text{ionic}} - \delta E_{sp})$$
$$\Delta E_Q = (1 - f)\,\Delta E_Q(sp)$$

and elimination of f between these two equations yields a linear relation between δE and ΔE_Q. Further, the sign and magnitude of the coefficient relating these two quantities is known from other studies on Au^{197}. Faltens has found that the predicted linear relation exists and that the coefficient is about as predicted; her work thus confirms the *sp*-bonding model.

Angular Distributions of Radiation

Spectral lines from Mössbauer studies convey information about the average properties of chemical systems during the excited-state lifetimes. This information is carried in the spectral lineshapes and requires considerable interpretation. A more direct way to study dynamic behavior is provided by *perturbed angular correlations* (PAC). we may understand how this method provides dynamic chemical information by combining two ideas, one from nuclear physics and one from atomic physics. First, if we observe two successive gamma rays emitted from the same nucleus, we find that their directions are correlated. That is, $W(\theta)$, the intensity of coincidences in two detectors at a relative (detector-source-detector) angle θ, will be periodic in θ. For many cases the functional dependence is

$$W(\theta) = A + B \cos 2\theta$$

Now, from atomic physics, *Larmor's theorem* states that if a magnetic field **H** is impressed on a physical system having magnetic moment μ and angular

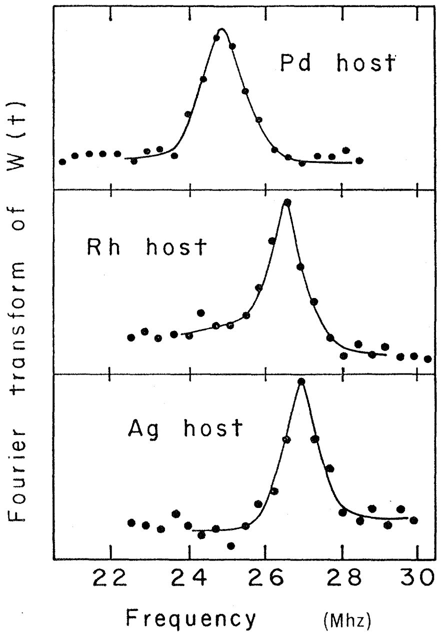


Fig. 8. Fourier transforms of $W(\theta,t)$ for Rh^{100} nuclei in through metallic lattices. These lines are the free-precession analogues of NMR lines. Displacements of maxima arise from Knight shifts. These preliminary data were taken by E. Matthias and D. A. Shirley; more recently G. N. Rao has obtained narrower lines.

momentum Ih, the system will precess about **H** with frequency $\nu_0 = \mu H/Ih$, and the physical observables in a coordinate system rotating about **H** with frequency ν_0 will be the same as in the laboratory system before **H** was applied.

If we combine these two ideas by applying a field **H** to an angular correlation source such that **H** is perpendicular to a plane through the source and the two detectors, then $W(\theta)$ will describe the angular distribution of coincidences in the rotating system. In the laboratory the precession frequency ν appears as a phase angle in $W(\theta,t)$ which becomes

$$W(\theta,t) = A + B \cos + (\theta - 2\pi\nu_0 t)$$

An experimental determination of $W(\theta,t)$ may be analyzed to give ν_0, the precession frequency. But this parameter is sensitive to the electronic environment: it is just the NMR frequency and these experiments may be interpreted in the same way that NMR experiments are. As yet the precision of PAC measurements is not sufficient to detect chemical shifts, but the larger Knight shifts found in metals can be studied by PAC in some cases (*23*). Figure 8 shows Knight shifts in Rh^{100} determined by PAC studies.

Other angular-distribution techniques have found application to solid-state problems. Among these are nuclear orientation (*24*) and angular distribution following nuclear reactions (*25*).

Radiative Detection of NMR

Finally I will mention a class of experiments as yet so unexplored that their possible utility is very difficult to evaluate, involving the radiative detection of NMR (NMR/RD). In these experiments NMR is combined with the above-mentioned angular distribution studies. One detects NMR in excited nuclear states by observing $W(\theta,t)$ in the presence of a radio-frequency field. The value of these experiments lies in their extremely high sensitivity—at least 10^{10} greater than in conventional NMR. In the analysis of $W(\theta,t)$ in PAC experiments the determination of ν_0 amounts essentially to a Fourier analysis of $W(\theta,t)$: the integral

$$G(\nu) = \int W(\theta,t) \cos 2\pi\nu t \, dt$$

has the appearance of a magnetic resonance line peaked at ν_0. Thus the NMR experiments are natural extensions of the angular distribution studies.

Several variations of the NMR/RD methods have been carried out recently, by using metallic samples (*26, 27*). One of the most promising methods for chemical applications consists of producing an excited nucleus with its spin oriented by a nuclear reaction and allowing it to recoil, before decay, into a sample where it may be disoriented by magnetic resonance. Sugimoto *et al.* have already found Knight shifts for B^{12} in several metallic hosts (*27*) in this way. It seems possible that this type of measurement might be extended to chemical systems in which its sensitivity could play a crucial role.

Epilogue

I have briefly treated some of the ways in which experimental developments in nuclear physics contribute to the understanding of chemical and solid-state phenomena. The list is neither complete nor balanced: principles and new techniques are emphasized, in hopes of stimulating interest in their development. It will be interesting to see in 5 or 10 years which of these methods have flourished. If past experience is any guide these methods will be changed almost beyond recognition and will be competing with newer methods, as yet undiscovered.

References and Notes

1. E. Rutherford, *Phil. Mag.* **21**, 669 (1911).
2. My purpose is to draw attention to relatively new developments rather than to discuss older, well-established methods. The relative space devoted to different topics does not therefore reflect their present importance, and several topics that could be discussed under the above title are omitted altogether. In particular the subject matter has been limited to include experiments based on observation of radiations from bound states, and those involving scattering or capture of free charged particles are omitted. Thus positron annihilation, channeling, and muonic x-ray studies are not treated.
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