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CHEMICAL EFFECTS ON RADIATION FROM NUCLEI AND ATOMIC CORES

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I. INTRODUCTION

Chemistry is a science that constantly makes use of new techniques. The chemist is not easily satisfied. He often asks questions that cannot be answered unambiguously with existing techniques, and the introduction of a new type of measurement may provide the answer. He then proceeds to ask more sophisticated questions, and the cycle continues. This paper deals with three recently-developed experimental methods with origins in nuclear physics. Each method is discussed separately below, together with illustrative applications that have been made in our laboratory.
In 1958 Rudolf Mössbauer discovered that nuclei in rigid lattices can sometimes emit or absorb gamma quanta without recoiling. The sharpness of the associated spectral lines is limited only by the Uncertainty Principle. With nuclear isomeric-state lifetimes in the range $\tau \approx 10^{-7}$ sec, linewidths of $\Gamma = \hbar/\tau \approx 10^{-8}$ eV are easily achieved. This has led to the development of resonant absorption spectroscopy using gamma quanta, or Mössbauer Spectroscopy.

The availability of sharply-defined gamma lines has made possible a number of exotic "optical" experiments bearing on diverse topics from the twin paradox through coherence and interference phenomena to phonon spectra in solids and quantum liquids. Chemical applications, however, usually employ a very simple experimental configuration. Gamma quanta from a standard source pass through an absorber containing the resonant isotope in the compound under study. The absorber is moved back and forth toward and away from the source, thereby providing an energy sweep via the Doppler Effect. The intensity of the transmitted beam is studied as a function of the Doppler velocity, and resonances appear as absorption lines. Magnetic and electric hyperfine interactions can lead to fairly complicated spectra. These spectra may be analyzed to yield coupling constants and thereby provide chemical information, using methods familiar from the fields of epr and quadrupole resonance. Quadrupole coupling constants yield information about $p$, $d$, or $f$ electrons, while the magnetic effects are associated with $d$ or $f$ electrons.

There is also a centroid shift in a Mössbauer spectrum. This isomer shift (IS) arises from the monopole, or spherically symmetrical, component of
the Coulombic interaction between s electrons and the nucleus. Only the s electrons participate in this shift, because it arises from electron density within the nucleus, and only s electrons have an appreciable probability density within the nucleus. For electrons at radii \( r \) greater than the nuclear radius \( R \), the potential exerted on the electrons by the nuclear charge distribution is given by

\[
V_o(r) = -\frac{Ze^2}{r}, \quad r > R
\]  

(1)

where \( Z \) is the atomic number. Inside a nucleus of radius \( R \), with uniform charge distribution, an electron at radius \( r \) experiences only net attractive forces arising from nuclear charge at radii \( r' < r \) (a similar result holds for any \( r^{-2} \) force, e.g. gravity within the earth). The potential inside the nucleus is therefore

\[
V_i(r) = -\frac{3}{2} \frac{Ze^2}{R} + \frac{Ze^2}{2R^3} r^2, \quad r \leq R.
\]  

(2)

Integrating a constant electron density \( \psi^2 \) over these potentials gives an energy shift

\[
\Delta E = \frac{2}{5} \pi Ze^2 R^2 \psi^2
\]  

(3)

that depends on the nuclear size. In a given Mössbauer resonance the excited and ground states have different values of \( R^2 \). Comparison of two chemical compounds with different values of \( \psi^2 \) will therefore give an isomer shift.

\[
\text{IS} = \frac{2}{5} \pi Ze^2 (\Delta R^2) (\Delta \psi^2).
\]  

(4)

Experimental determination of IS can yield \( \Delta \psi^2 \) and thus elucidate chemical structure.
As an example of the application of isomer shifts, let us consider a series of aurous and auric compounds studied by Dr. Marjorie Faltens as her Ph.D. thesis work, using the Mössbauer effect in Au\(^{197}\). Within each oxidation state of gold she found a correlation between the isomer shift (IS) and the quadrupole splitting (QS). For an unknown compound neither IS nor QS along would be sufficient to identify the oxidation state, but taken together they appear to determine it uniquely, as the correlation plots do not intersect. The mixed-oxidation-state compound \(\text{Cs}_2^+[\text{Au(I)}\text{Cl}_2^-][\text{Au(III)}\text{Cl}_4^-]\) shows two absorption patterns that fit into the correlation plots for the two oxidation states.

The aurous ion is usually found in linear complexes such as \(\text{AuCl}_2^-\). This has been attributed to sp bonding. The Mössbauer spectra support this interpretation. A linear IS - QS correlation is observed, suggesting that in going from complexes with more electronegative ligands to those with less electronegative ligands, the electron population gained by the aurous ion goes about equally into the 6s and 6p orbitals, where it affects the IS and QS, respectively, thus yielding the linear relationship. Similar results were found for the square-planar auric complexes, which are usually regarded as possessing dsp\(^2\) hybridization. In both series qualitative agreement with these hybrid schemes is good. If one attempts to push this interpretation further and derive orbital parameters such as \(<r^{-3}>_{6p}\), however, these parameters do not agree with those obtained from Hartree-Fock calculations on free atoms. This indicates once again that atomic hybridization schemes must not be taken literally.
Dynamic properties can also be studied by Mössbauer spectroscopy. For example, H. H. Wickman et al. found characteristic broadening effects in the spectrum of high-spin Fe$^{+3}$ in ferrichrome A. When iron compounds are cooled through magnetic transition points, their Mössbauer spectra change abruptly from a single line to the characteristic six-line pattern of Fe$^{57}$. When ferrichrome A is cooled, however, its spectrum appears to change continuously from one to six lines, with both cases present simultaneously at intermediate temperatures. This behavior can be understood on the basis of fast relaxation of the electron spin ($S = \frac{5}{2}$ for high-spin Fe$^{+3}$). When the electron spin flips from the "spin-up" to the "spin-down" state, the nucleus experiences a reversal in direction of the effective hyperfine magnetic field. The resultant spectral broadening is very similar to that caused by proton exchange in NMR spectra, and the same equations apply. Application of these equations yields electron relaxation times in the $10^{-8}$ second range.

III. GAMMA-RAY ANGULAR CORRELATIONS

Consider a three-level system in which the levels are successively populated by the emission of two gamma quanta. Designating the three levels by their nuclear spins $I_1$, $I$, and $I_f$, we have the cascade $I_1 \rightarrow I \rightarrow I_f$. If the initial state $I_1$ is randomly oriented in space, then the spatial distribution of both $\gamma_1$ and $\gamma_2$ will be isotropic. However, the propagation directions of $\gamma_1$ and $\gamma_2$ are correlated. If $\theta$ is the angle between the propagation directions of these two radiations, the coincidence counting rate can be written as

$$W(\theta) = 1 + \sum_{\text{even}} \sum_{\lambda} A_{\lambda} \chi_{\lambda} (\cos \theta),$$
where $A_\lambda$ is a radiation parameter and $P_\lambda$ is a Legendre Polynomial. Here $W(\theta)$ has been normalized to unity. When measurements are made on a sample in which the nuclei do not interact appreciably with their environment during the lifetime of the intermediate state, an \textit{unperturbed} angular correlation is observed. One may simply measure the integral coincidence rate, $W(\theta)$ without regard for the time elapsed between the emission of $\gamma_1$ and that of $\gamma_2$. More sensitive studies are possible, however, if a time-differential coincidence rate is measured. This rate is given by

$$W(\theta, t) = \frac{e^{-t/\tau}}{4\pi T} \left[ 1 + \sum_{\lambda=2,4, \ldots}^\infty A_\lambda P_\lambda(\cos \theta) \right].$$

Here $\tau$ is the lifetime of the intermediate nuclear state, and $t$ is the time elapsed between the emission of the two $\gamma$ rays.

When the intermediate state is perturbed by extranuclear fields, its decay appears to be modulated. The time-dependent coincidence rate becomes, for the simplest cases,

$$W(\theta, t) = \frac{e^{-t/\tau}}{4\pi T} \left[ 1 + \sum_{\lambda=2,4, \ldots}^\infty A_\lambda G_\lambda(t) P_\lambda(\cos \theta) \right],$$

where $G_\lambda(t)$ is a \textit{perturbation factor}. Often $G_\lambda(t)$ is simply sinusoidal, as in the Larmor precession occurring when a nuclear magnetic moment interacts with a magnetic field. If axially-symmetric static electric quadrupole interactions are present and $I \geq 2$, then $G_\lambda(t)$ is a superposition of two or more sine waves of different frequencies, but still periodic. When the quadrupole interaction is asymmetric, $G_\lambda(t)$ is oscillatory but aperiodic.

As faster timing techniques are perfected and larger data-handling facilities become available, larger numbers of oscillations may be observed.
At some point it becomes worthwhile to Fourier-transform $G_\lambda(t)$, obtaining lines at frequencies corresponding to differences in hyperfine level energies.\(^6\) These lines have Lorentzian shape, with widths proportional to $\lambda/\tau$. Observation of such lines is rather like doing NMR with no radiofrequency field.

Angular correlations can also be studied in the resonant mode. Such experiments are analogous to double-resonance experiments. Let us consider a three-level sequence with $I_1 = 0$, $I = 1$, $I_\tau = 0$, with a magnetic field $\vec{H}$ present to split the $I = 1$ intermediate state into three magnetic substates, with magnetic quantum numbers (energies) $M_1 = +1$ ($E_1 = \gamma H$), $M_1 = 0$ ($E_0 = 0$), and $M_1 = -1$ ($E_{-1} = -\gamma H$). If the $\gamma_1$ detector is placed along the $\vec{H}$ direction and the $\gamma_2$ detector in the opposite direction ($\theta = 180^\circ$), then only the $M = \pm 1$ components of $\gamma_1$ and $\gamma_2$ will be detected, and the observed coincidences will consist entirely of cascades that go through the $M_1 = \pm 1$ substate.

Application of a perpendicular radiofrequency field $\vec{H}_1(t)$ at the resonant frequency $\nu = \gamma H/\hbar$ will mix the $M_1$ substates and decrease the coincidence rate. This resonance effect, suggested in 1953,\(^7\) was first observed in 1966.\(^8\) There is some experimental difficulty associated with the fact that the observation of resonance requires that a transition take place within the nuclear lifetime of $\sim 10^{-7}$ seconds. The radiofrequency field strength necessary to induce a transition in this time may be estimated from the well-known Torque Equation, which has the form

$$\frac{d\vec{M}}{dt} = \gamma \vec{M} \times \vec{H}$$

in the laboratory coordinate frame. The magnetization $\vec{M}$ precesses about $\vec{H}$ at the Larmor frequency $\omega_0 = \frac{\gamma H}{\hbar}$. If we transform into the "rotating frame", in
which the constant external magnetic field vanishes at the resonant frequency by Larmor's Theorem, we are left with a constant field of magnitude \( H_1 \) perpendicular to the axis of rotation. A torque equation still holds, and the magnetization \( \mathbf{M} \) precesses around \( H_1 \) with angular frequency \( \omega_0 = \gamma H_1 / \hbar \) in the rotating frame. A transition may be said to have occurred in the laboratory frame when \( \mathbf{M} \) has precessed by \( \sim 1 \) radian around \( H_1 \). Since this must happen in about one nuclear lifetime \( \tau \), the condition \( H_1 \sim \hbar / \gamma \tau \sim 10^3 \) gauss must be met. Such large radiofrequency fields are difficult to produce. However, the phenomenon of "hyperfine enhancement" allows effective fields of this size to be produced in certain substances by the amplification, within the atom, of an applied radiofrequency field of only a few gauss. Hyperfine enhancement has been used to study angular correlations in the resonant mode in ferromagnets. The principal advantage over conventional NMR with stable nuclei is that much smaller samples can be studied. An angular correlation-resonance experiment requires as few as \( 10^6 \) nuclei. A number of such experiments have been done with Rh\(^{100} \) nuclei in a lattice of ferromagnetic nickel metal. For this case even a 1% concentration of Rh will strongly affect the resonance through solute-solute interactions,\(^9\) thus precluding the use of conventional NMR, which requires concentrations at least this large.

Relaxation phenomena can also affect angular correlations. Similar effects arise in NMR experiments, and the most fruitful applications of angular correlations to relaxation studies occur in samples to which NMR is not applicable. Relaxation effects have already been found in several applications of angular correlations using metallic samples. Thus for very dilute solutions (<\( 10^{-2}\)% of Rh in Pd,\(^10\) for transition-metal solutes in ferromagnets.
above their Curie points,\textsuperscript{11} and for the same systems at temperatures in the millidegree Kelvin range,\textsuperscript{12} none of which are amenable to NMR studies, angular correlation experiments have already shown relaxation effects. The relaxation times that are derived from these studies yield useful information about the properties of the lattices.

Very recently applications have been made to studying the tumbling times of molecules in solution.\textsuperscript{13,14} A "rotational tracer" atom, containing an angular correlation nucleus, is bound to an active site in a molecule. Any rotational motion, or "tumbling" experienced by the molecule during the intermediate-state lifetime will affect the angular correlation pattern.

Relaxation effects of this type are usually discussed in terms of a correlation time, $\tau_c$, which in small molecules is related to the mean time between collisions of the labeled molecule with solvent molecules. If $\tau_c$ is small compared with $\omega_q^{-1}$, where $\omega_q$ is a frequency characterizing the strength of quadrupole interactions in the bonds holding the tracer atom in place, then the perturbation factor $G_\lambda(t)$ decays exponentially,

$$G_\lambda(t) = e^{-k_1t},$$

with a decay constant $k_1$ proportional to $\tau_c$. For relatively small molecules such as EDTA or ATP in aqueous solution, $\tau_c \sim 10^{-11}$ sec, and $\lambda \sim 10^7$ sec$^{-1}$.

Larger molecules have longer correlation times, and for them $\tau_c$ has a different meaning. If the molecule is so large that $\omega_q^2 \tau_c \gg 1$, then the molecule is essentially stationary during the nuclear lifetime, and the time-dependence of $G_2(t)$ is similar to that observed for a solid. This is the case in macromolecules such as bovine serum albumin.\textsuperscript{13,14}
IV. X-RAY PHOTOELECTRON SPECTROSCOPY

The recent development of high-resolution electron spectroscopy has made it possible to measure the binding energies of atomic core electrons with a precision that can detect shifts arising from environmental effects.\textsuperscript{15,16} These shifts are closely related conceptually to the isomer shifts in Mössbauer spectra, but in this case the entire mechanism is extranuclear, thereby rendering the occurrence of the shifts independent of the accidental properties of certain isotopes and allowing them to be observed in atoms throughout the periodic table.

When an x-ray photon impinges on an atom and ejects an electron from a core level by the photoelectric effect, the kinetic energy $K$ of the photoelectron is related to the photon's energy $h\nu$ and the binding energy $E_B$ by

$$h\nu = E_B + K.$$ 

Thus irradiation of a compound with a monochromatic x-ray beam will yield a series of photoelectron peaks that bear a 1:1 relationship to the compound's bound states. Both core levels and molecular orbitals are detected.

The core-level binding energies show shifts that arise from the effect of the molecular charge distribution on the Coulomb potential of the core levels. Suppose, for example, that the binding energy of the 1s electron of carbon is compared for neutral carbon and $\text{C}^+$. The difference is about $\Delta E_B = 20$ eV, and it arises primarily from the $\frac{e^2}{r}$ term describing the interaction between the 1s electron and the 2p electron that is present in C\textsuperscript{0} but missing in C\textsuperscript{+}. 
Core-level shifts are manifest as multiple core-level peaks in spectra from molecules with inequivalent atoms of the same element. The shifts may be correlated with various chemical properties.\textsuperscript{16} They may be calculated directly, by comparing total energies of the molecules' initial and final states, or (less expensively) by comparing the orbital energies obtained from \textit{ab initio} Hartree-Fock calculations, using the approximation known as Koopman's Theorem.\textsuperscript{17}

An approximate interpretation of core-level shifts that has more intuitive appeal for chemists has been applied to a series of fluorine-substituted benzenes.\textsuperscript{18} In this approach one imagines that all of the molecule's electrons can be partitioned among the atoms. The binding-energy shift $\delta_i$ for a core level in the $i$th atom is then attributed in part to the charge $q_i$ on that atom and in part to the distribution of charges on the other atoms, $q_j$. Treating the $q_j$ as point charges, we have

$$\delta_i = \left(\frac{\partial E}{\partial q_i}\right) q_i + \sum_{j \neq i} \frac{e^2}{r_{ij}} q_j,$$

where $q_j$ is taken in units of $e$. The coefficient $\frac{\partial E}{\partial q_i}$ can be estimated from free-atom Hartree-Fock calculations. In a molecule with $N$ inequivalent atoms there are $N$ different core-level shifts $\delta_i$ and the $N$ simultaneous equations can be solved to yield $N$ charges $q_i$. Application of this approach to a series of fluorine-substituted benzenes yields, for example, $q_c = +0.15$, $q_F = -0.15$ in $C_6F_6$. For p-difluorobenzene we find $q_F = -0.3$, $q_c = +0.4$ for the two carbons bonded to fluorines, and $q'_c = -0.1$ for the other carbons.

When the substance under study has unpaired spins in the valence orbitals, the energy degeneracy of "spin-up" and "spin-down" core orbitals is
lifted. A total spin \( S \) in the valence shell couples with a single \( s \) electron in a core level to form two states, of spins \( S-\frac{1}{2} \) and \( S+\frac{1}{2} \). The states appear as two peaks, of relative intensities \( S:S+1 \), spaced in energy by \( 2S\hbar \chi \), where \( \chi \) is the exchange integral involving the core orbital and a valence orbital. For the \( NO \) molecule, for example, Hedman et al. found that ejection of a \( 1s \) electron from the nitrogen atom yields two peaks in relative intensity 1:3. The oxygen \( 1s \) electron peak in \( NO \) is unsplit. This is consistent with the unpaired \( 2\pi \) electron spin being concentrated in the \( N \) atom. In \( Mn^{++} (3d^{5},6) \) the \( 3s \) peak is much larger, about 6 eV in \( MnF_{2} \). This splitting can serve as a valuable diagnostic tool in identifying unpaired electrons in the valence shell. Thus in metallic iron, for example, structure in the \( 3s \) line shows that localized magnetic moments exist on the \( Fe \) atoms. The persistence of this structure above the Curie temperature is of special interest. At such high temperatures rapid spin-lattice relaxation obscures magnetic properties as measured by conventional techniques, and it is difficult to ascertain whether localized moments exist. The photoelectric process takes only \( \sim 10^{-16} \) seconds, however, and it can detect these moments between "spin-flips."

Photoelectron spectroscopy can also be used to study the valence bands in metals. These bands are populated by the more-or-less "free" conduction electrons. A Fermi-gas model is often used to describe these electrons. On this model the density-of-states, \( N(E) \), would be parabolic, varying as \( (\text{energy})^{3/2} \) up to the last occupied level at the Fermi energy. Band-structure calculations predict that \( N(E) \) should be substantially modified by the crystal lattice symmetry, showing peaks and valleys. The experimental picture is still somewhat primitive, but early results indicate that the \( d \)-bands of the
transition metals have structure in their x-ray photoelectron spectra. Measurement of $N(E)$ is fraught with difficulties. Surface purity is one problem, but it can be dealt with by studying the intensities of impurity peaks such as the ls peak oxygen during surface treatment. Another, more basic, problem has to do with inelastic effects during photoemission. Such effects can distort the observed spectrum and give an inaccurate picture of $N(E)$. An accurate assessment of this effect awaits further developments. Meanwhile, it is already clear that x-ray photoemission can yield unique information about densities of states.
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