MASTER

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RESEARCH IN NUCLEAR CHEMISTRY
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ABSTRACT

The nuclear chemistry research program at Carnegie-Mellon University includes studies of nuclear reactions induced by heavy ions, nuclear properties, nuclear transitions and decay, and the hyperfine interactions of nuclear moments with extranuclear environments. Gamma-ray angular correlation measurements in the decay of ^{75}Se have been carried out, and the data indicate absence of appreciable perturbation in the $5/2^-$ intermediate nuclear state in ^{75}As . Integral and time-differential perturbed-angular-correlation experiments in ^{181}Ta have elucidated strong quadrupolar interaction effects in several compounds. The origins of the observed electric field gradients are traceable to chemical bonding effects. Studies have been made of the evaporation residues from complete fusion reactions induced by heavy ion beams in several target nuclei, using a new experimental technique. Measurements of energy spectra, angular distributions, and total cross-sections for these processes have been carried out for $^{16}\text{O} + ^{27}\text{Al}$, $^{20}\text{Ne} + \text{Cu}$, and $^{20}\text{Ne} + \text{In}$. Proton evaporation spectra in coincidence with evaporation residues were determined in one case. In other studies, light fragments from the reaction of ^{12}C with ^{65}Cu were identified in a counter telescope, and cross sections for production of boron isotopes were determined by integration of the measured angular distributions of the several species. The cross-section for the process $^{12}\text{C} + ^{65}\text{Cu} \rightarrow ^{12}\text{B}$ is found to be very much smaller than radioactivity measurements of ^{65}Zn from the same reaction, and hence ^{12}B and ^{65}Zn are probably not correlated fragments in a two-body break-up.

Morton Kaplan
Principal Investigator

— L E G A L N O T I C E —

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Annual Report: July, 1975

I. Introduction

The research program in nuclear chemistry sponsored by Contract AT(11-1)3246 has continued along the lines established in recent years. During the current contract period, considerable progress has been made in the area of hyperfine interactions studied by gamma-ray angular correlation methods, particularly the effects of quadrupole perturbations due to electric field gradients from chemical bonding. Preliminary results have also been obtained from several experiments involving nuclear reactions between heavy ions and complex nuclei, and these data appear to be both interesting and informative as well as providing some significant guidelines for future work.

The gamma-ray angular correlation apparatus assembled over the last few years has demonstrated a high degree of reliability and is producing good data. We are able to interchange among several types of gamma-ray detectors to suit particular experimental situations, and we have gained expertise in optimizing the timing-resolution for various detector combinations at different gamma-ray energies. With decreasing energy, fast timing resolution deteriorates rapidly, and we have achieved significant improvement in the 100-500 keV range by incorporating low threshold snap-off diode discriminators in each of the detection systems. The experiments with ^{75}Se begun last year have now been completed, and full unperturbed angular correlations were found even for low symmetry single crystal specimens. The results have been analyzed and we understand why ordinary static quadrupole effects are not observed in ^{75}Se .

Our studies with ^{181}Hf have been very successful during the past year, and the perturbed-angular-correlation (PAC) technique has been shown to be sensitive to the extranuclear environment for this nuclear species. Series of both time-integral PAC experiments and time-differential measurements have been carried out in a number of molecular environments, and large electric-quadrupole interactions have been observed in several cases. Methods of analyzing the data have been worked out, and theoretical calculations are being performed to relate the observed spectral features to the physical parameters which characterize the nuclear-atomic system. Of particular importance are the changes which occur when axial-symmetry is absent, and the pronounced attenuation effects resulting from inhomogeneities in the nuclear sites.

The heavy residual nuclei from complete fusion reactions induced by heavy ions have been studied on-line by means of a new detection scheme. The method takes advantage of the unique properties of the heavy recoil nuclei, namely relatively high energy in the forward direction and very large energy-loss in matter. By operating two semi-conductor detectors in a counter-telescope arrangement with an anticoincidence requirement, it is possible to select out the events which stop in a thin front counter, and identify these as high E, high dE/dx species. The interactions of ^{20}Ne with Cu, ^{20}Ne with In, and ^{16}O with Al have been investigated at the Yale Heavy Ion Accelerator. The observed energy spectra of the selected evaporation residues are quite consistent with expectations for complete fusion processes, and measured angular distributions fall off with increasing angle about as found in previous radiochemical recoil studies. Integrations over energy and angle have yielded estimates of total compound-nucleus reaction cross-sections. Some interesting data was also obtained

by adding a thick semi-conductor proton counter and measuring the low energy charged particles emitted from the preselected complete fusion nuclear systems.

In another experiment at Yale, a conventional ΔE -E counter telescope was used to detect and identify the light fragments emitted in the bombardment of ^{65}Cu by ^{12}C at 126-MeV. The identification of various Z particles (for $Z < 6$) was quite clear, and individual mass separations were possible for the several isotopes of B and Be. Although the counting statistics were relatively poor in some cases, the general features of the energy spectra and angular distributions can be extracted from the data, and cross-sections for production of the fragments can be obtained with reasonable accuracy.

During the past contract year, most of the experimental researches were carried out using the facilities and equipment of our laboratory as described in previous annual reports. A new oscilloscope display and a Calcomp digital plotter have been added to our Nuclear Data 50/50 Analyzer-Computer System, and these are now functioning properly. Several minor changes and improvements have been made in nuclear counting equipment, and these will be mentioned where relevant elsewhere in this report. This past year the principal investigator, Professor Morton Kaplan, devoted one-half time to the research project during the academic year and full time for two summer months. Miss Jane Wilson, Project Scientist, has continued her Ph.D. dissertation research in the program supported by the contract, and has been working full-time on the angular correlation experiments. She has made considerable progress this year and we expect a successful completion of her studies in another year. The evaporation-residue counting experiments at the Yale Hilac were performed in conjunction with Dr. V. Subrahmanyam,

formerly of our research group and now at Boston College. The light-fragment-identification experiment was a collaborative effort involving several Carnegie-Mellon people (Professors Caretto and Kaplan, Dr. M. V. Yester, and Mr. R. Spector), and Columbia University scientists (Professor J. M. Miller and Mr. D. Logan). As in the past, there is a strong interaction between the students and staff of the several nuclear chemistry groups at Carnegie-Mellon University, and these relationships have been beneficial to us all.

In the pages which follow, the research results briefly discussed above will be described more fully, and other studies completed or in progress this year will be presented. A number of scientific papers resulting from our research program are being prepared for publication, and a current listing is appended to this report.

II. Perturbed Angular Correlations of Nuclear Gamma Rays

A. Experimental Techniques and Developments.

A detailed description of the experimental angular correlation set-up and data collection procedure has been given COO-3246-5 (Annual Report, July 1973) and COO-3246-14 (Annual Report, July 1974). Several modifications have been made this year with significant improvement in the overall operation of the apparatus. Due to the superior performance of Elscint Snap-Off Discriminators (ESTD) at low gamma-ray energies (see COO-3246-14), all three of the Ortec 453 Constant Fraction Timing Discriminators have been replaced by ESTD's. We have also redirected the storage and analysis of timing information, after being gated by appropriate slow energy signals, from our RIDL 400-channel analyzer to the Nuclear Data 4096-channel analyzer, PDP-8/I computer system.

In the ^{75}Se experiments described below, the 121-280 keV angular correlation was studied using a 60 cm³ coaxial Ge(Li) detector as the "start" signal for a time-to-amplitude converter (TAC), and two 2" x 2" NaI(Tl) detectors as "stop" signals. This combination provided the necessary gamma-ray energy resolution and also yielded adequate timing characteristics. The energy discrimination was effected by gating the TAC output with the 280 keV signal from the Ge(Li) detector. A more complete description of experimental details can be found in COO-3246-14 (July, 1974).

The time-differential PAC experiments performed with ^{181}Hf sources employed similar physical arrangements and apparatus to that previously described. Because the energies of the appropriate ^{181}Hf gamma-rays are well resolved from interfering radiations, the use of the Ge(Li) detector was suspended in favor of the better time resolution obtainable from a configuration involving three 2" x 2" NaI(Tl) detectors. In each experiment,

a full energy-coincidence-gated TAC spectrum was simultaneously recorded for the two angles, 90 and 180 degrees, with at least 1×10^6 counts in the analyzer channel corresponding to the maximum in the timing curve. Due to the relatively long mean life of the intermediate nuclear state in ^{181}Ta ($\tau = 15.58$ nsec), each spectrum exhibited an exponential decay modulated by quadrupole perturbations (where present). The singles counts from each single-channel analyzer were recorded in scalers and used for normalization of the timing data. Experiments involving time-integral measurements of a full angular correlation pattern were carried out in a similar manner, with the coincidence counting rate at each angle obtained by integrating the area under the timing spectrum after correction for random background. The prompt time-resolution at 136 keV (measured with a ^{75}Se prompt cascade) was 5.75 nsec FWHM using the 2" x 2" NaI(Tl) detectors and Elscint discriminators. We have recently substituted a new 2" x 1/2" NaI(Tl) crystal for the 2" x 2" detector as the start counter and this thinner crystal (which records the 133-keV gamma ray in ^{181}Hf) improves the time resolution to 4.1 nsec. Gamma-ray spectra from a ^{181}Hf source are shown in Fig. 1, where (a) corresponds to a 2" x 2" NaI(Tl) detector and (b) is the 2" x 1/2" NaI(Tl) detector. The pronounced energy dependence of the change in counting efficiency can easily be seen by comparing the two spectra in Fig. 1.

Some of the experiments planned for the near future will require the cooling and freezing of sources used for angular correlation measurements. In order to allow for controlled and easily varied temperatures, without severely restricting the transmission of low-energy gamma rays, a simple device has been designed and built to cool a sample by contact with a flowing cold gas. The apparatus is shown schematically in Fig. 2. Nitrogen gas is precooled by passage through a series of copper coils immersed in

liquid nitrogen. The cold gas is then allowed to flow around the sample and the temperature is monitored by means of a thermocouple and digital voltmeter. The steady-state temperature at the sample is determined by setting the gas-flow rate. The open grid area, shown in Fig. 2, is enclosed and sealed with thin aluminum foil, which allows the escape of gamma rays with minimal energy loss or distortion from scattering. The entire gas-flow assembly is located at the center of the angular correlation table, and is surrounded by an outer housing of insulating styrofoam. The styrofoam not only helps to maintain a constant inner temperature but protects the faces of the detectors as well. Preliminary studies have indicated that there are no appreciable perturbations of measured angular correlations due to the experimental arrangement, and in addition, the gamma rays experience no significant attenuation or loss in energy.

B. Time-Integral PAC of the $5/2^-$ State in ^{75}As .

In last year's annual report (COO-3246-14, July 1974), we described measurements of unperturbed angular correlations in the gamma-ray cascade following the electron capture decay of ^{75}Se , and discussed the potential importance of being able to determine electric quadrupole interactions in the $5/2^-$ intermediate state in ^{75}As . Of particular interest was the possibility of applying the PAC method to study Se binding in glutathione (GSH) peroxidase, an essential catalyst for the removal of excess H_2O_2 and fatty acid hydroperoxides from cellular media. Se, in trace quantities, is essential for the catalytic behavior of this enzyme⁽¹⁾. Prior to obtaining blood samples of rats fed on a ^{75}Se diet, it was necessary to demonstrate the detectability of ^{75}Se quadrupole interactions, and single crystals of $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ fulfilled the requirements for a good test case.

Crystals of $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ were grown from saturated solutions of

sodium selenite in 0.5 N HCl. The presence of the acid prevents the slow degradation of the $\text{SeO}_3^{=}$ anion to elemental selenium. A fairly large and uniform crystal was grown and transferred to a second saturated solution containing $^{75}\text{SeO}_3^{=}$, and allowed to grow a layer of radioactivity of approximately 10^4 counts per min. The resulting crystal was washed with a non-radioactive selenite solution in order to remove any loosely bound activity from the crystal surfaces and allowed to air dry. The final crystal was composed of several small crystals possessing a common orientation. A single crystal is not necessary in order to measure a quadrupole interaction as long as the crystalline symmetry axes of the mosaic are all oriented in the same direction.

Integral anisotropy measurements, $\epsilon = [C(180) - C(90)]/C(90)$, were then made on the 121-280 keV cascade passing through the 0.5 nsec, $5/2$ state in ^{75}As . The experimental arrangement has been previously described (C00-3246-14, July 1974). If one allows the direction of the first gamma ray, $\vec{k}_1$, to coincide with the crystalline symmetry axis, the effect of the quadrupole perturbation is removed and one obtains the unperturbed correlation. In order to guarantee that such a situation did not occur, measurements were made with the $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ crystal in several different orientations with respect to the detectors. The general shape of the crystal and the several orientations are shown schematically in Fig. 3. The results of the anisotropy measurements for three different orientations and their comparison to the theoretical anisotropy are given in Table I. It is quite evident that there is no detectable perturbation of the intermediate nuclear state in the selenite single crystal.

The lack of a perturbation can be understood if one looks carefully into the size of the perturbing fields which can be expected to affect the

The basic shape of the $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ crystal (top) and three orientations with respect to detector arrangement (bottom)

1) Symmetry axis parallel with face of the crystal

2) Symmetry axis perpendicular to face of the crystal

(a) $\perp$ (toward face)

(b) $\parallel$ (off crosshatch)

(c) $\parallel$ (on crosshatch)

Table I. Integral Anisotropy Values for a $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ Crystal
in Several Spatial Orientations

Spatial Orientation*	$c = \frac{C(180) - C(90)}{C(90)}$ (for $h = 7\text{cm}$)**
⊥ (Toward Face)	-0.473 ± 0.008
(Off Crosshatch)	-0.474 ± 0.008
(On Crosshatch)	-0.473 ± 0.011
Theory***	-0.476 ± 0.011

* Refer to Fig. 3 for explanation of orientation

** Average of several runs at each orientation

*** Based on $A_2 = -0.411(12)$, $A_4 = -0.050(26)$, and $h = 7\text{ cm}$

⁷⁵As nuclear state of $\tau = 7.2 \times 10^{-10}$ sec. Several magnetic perturbation experiments using large external magnetic fields have been carried out^(2,3) with the observed hyperfine magnetic fields being in the range 90-300 KG. Using these values as an estimate of the size of interaction needed for an appreciable perturbation, one can calculate the comparable quadrupole fields necessary for a measurable quadrupole perturbation. The frequencies of the magnetic, ω_B , and quadrupole ω_q , interactions are given by

$$\omega_B = \frac{-g\mu_N H_{\text{eff}}}{\hbar}$$

$$\omega_q = \frac{-eQV_{zz}}{4I(2I-1)\hbar}$$

where $g = +.36$, $\mu_N = 5.05 \times 10^{-24}$ erg/gauss and H_{eff} is the effective magnetic field at the nucleus (i.e., 90-300 KG). Q is the nuclear quadrupole moment of the perturbed intermediate state and V_{zz} is the electric

field gradient at the nucleus. Using the smaller of the magnetic fields, 90 KG, as the limiting case, one finds that $\omega_B = 155$ MHz. The time integral quadrupole perturbation factor for an axially symmetric quadrupole field is given by

$$\overline{G_{kk}(\omega)} = \sum_n s_{kn} \frac{1}{1 + (n\omega_0\tau)^2};$$

$$0 \leq \overline{G_{kk}(\omega)} \leq 1.$$

The coefficients, s_{kn} , containing the nuclear information on angular momentum components, have been calculated and tabulated⁽⁴⁾. The frequency, ω_0 , corresponding to the lowest interaction frequency, is equal to 6 times ω_q , the quadrupole frequency, when the spin, I , is odd. Therefore, if a frequency $\omega_q = 155$ MHz is needed for an interaction, the defining frequency ω_0 would be 930 MHz, producing a $\overline{G_{22}(\omega)} = 0.6$. Most quadrupole fields, ω_0 , are in the range of 100-300 MHz which in this case would only attenuate the angular correlation by less than 10%. Within our experimental error, a quadrupole interaction in ^{75}As would be difficult to observe, as the experiments on the noncubic selenite crystal indicate. One can understand why this might be so. The criterion for a measurable interaction is that $\omega_0\tau \cong 1.0$. For the $5/2^-$ state populated in the decay of ^{75}Se , the short mean life, $\tau = 7.2 \times 10^{-10}$ sec, would have to be counterbalanced by a fairly large nuclear quadrupole moment, Q , of the nuclear state, or a very large electric field gradient, V_{zz} , of the surroundings, in order to produce a significant perturbation. In the situation at hand, unfortunately, neither of these circumstances exists, and hence the negative result.

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C. Time-Integral Perturbed Angular Correlation Experiments in ^{181}Ta .

The procedure for data acquisition and analysis in a time-integral experiment is the same as in the measurement of a full angular correlation. The coincidence rate between the two gamma rays of the nuclear cascade is measured as a function of the angle between the two gammas or the detectors. Each coincidence measurement is normalized for any nonlinearities in the source or the angular correlation table by division with the singles rate from the second gamma ray. The experimental data is least squares fitted to the following function,

$$W(\theta) = A_0 + A_2' P_2(\cos\theta) + A_4' P_4(\cos\theta),$$

where the prime denotes the product, $A_{kk} \overline{G_{kk}}^{(\infty)}$. The resulting coefficients are corrected for the finite solid angle of the detectors and compared with the coefficients for an unperturbed correlation. In all cases considered here, the coefficient A_4' was found to be nearly zero, and has been neglected. The value for the unperturbed A_2 coefficient was determined independently in two time-differential experiments using ^{181}Hf in 27 N HF solution and precipitated hafnium phosphate as sources. The former yields an unperturbed correlation, and the latter, while significantly perturbed, gives A_2 as a

least-squares-fit parameter to the time-differential data. Both experiments gave values in excellent agreement with the accepted literature values⁽¹⁾, $A_2 = -0.295(10)$, $A_4 = -0.0705(4)$.

The 42.5 d isotope, ^{181}Hf , decays by β^- emission predominantly to the 615 keV ($I = 1/2+$) state in ^{181}Ta . The decay to the ground state is mainly through the two gamma-gamma cascades as indicated by the decay scheme in Fig. 4. Of interest to our work is the 133-482 keV cascade, which passes through the 10.8 nsec state at 482 keV. Typical gamma spectra using NaI(Tl) detectors are shown in Fig. 1. The long half-life of the $5/2+$ intermediate state, coupled with its fairly large quadrupole moment ($\sim 2.5 \times 10^{-6} \text{ cm}^2$) indicates that ^{181}Ta will be sensitive to small extranuclear electric field gradients. Experiments by other workers⁽²⁻⁶⁾, have indicated that the cascade in ^{181}Ta is strongly perturbed even in low viscosity liquids. Therefore, we have studied by time integral perturbed angular correlation analysis (IPAC) the behavior of ^{181}Hf in various chemical environments, including several biologically important macromolecular species.

A summary of the various PAC sources and their measured values of A_2' and $G_{22}(\infty)$ are given in Table II. In each case A_4' was negligible and was omitted from the table. All sources were made by reducing $^{181}\text{HfOCl}_2$ in 0.5 N HCl (obtained from Oak Ridge National Laboratory) to near dryness and then taking the activity back up in 2-3 drops of the appropriate solution. Care was taken to monitor the pH in the sources containing the macromolecular species. The resulting solutions were then transferred to plexiglass ampoules sealed with epoxy. The integral correlations for each source were measured for at least six angles between 90 and 180 degrees, with a total number of counts per angle of $\sim 10^6$. It is quite obvious from the results in Table II that ^{181}Hf exhibits a large range of values for the perturbation coefficient

Table II. Summary of ^{181}Hf Integral Angular Correlation Experiments

Source	A_2'	$G_{22}(\infty)$
HfOCl_2 (aq)	-0.1064(101)	0.36(4)
Na_3PO_4 (in $\text{NaOH} + \text{H}_2\text{O}$)	-0.1398(91)	0.47(3)
Dilute H_3PO_4		
Sample (1)	-0.1600(147)	0.54(5)
Sample (2)	-0.0420(45)	0.14(2)
Trizma Buffer	-0.0461(38)	0.16(1)
DNA I (in Trizma)	-0.0447(44)	0.15(2)
DNA II (in Trizma)	-0.0454(26)	0.15(1)
$(\text{NH}_4)_2\text{SO}_4$ (saturated)	-0.0787(50)	0.27(4)
Aldolase		
[in $(\text{NH}_4)_2\text{SO}_4$ suspension]	-0.0725(27)	0.25(1)
Pyruvate Kinase		
[in $(\text{NH}_4)_2\text{SO}_4$ solution]	-0.0776(47)	0.26(2)
Unperturbed*	-.295(10)	1.00

* Reference 1.

and little in the way of a systematic trend. In order to comprehend what is occurring, it is necessary to understand a little about the aqueous chemistry of hafnium cations.

The most common valence state of hafnium is +4, but the cationic species, Hf^{+4} , rarely exists in solution. Instead, the cation is readily

hydrated forming a wide range of species, from $\text{HfOOH}^+ \cdot 4\text{H}_2\text{O}$ in low acid solutions to $\text{Hf}_4(\text{OH})_8^{+8}$ under highly acidic conditions. Only in extremely dilute ($< 10^{-4}\text{M}$) solutions and at $\text{pH} < 2.5$ does the unhydrolyzed Hf^{+4} species exist.⁽⁷⁾ In general, the hafnium atom in aqueous solutions will attain the highest coordination number possible (i.e., 7) either by hydrolysis, hydration and/or polymerization. Hafnium will form bonds only by the acceptance of lone pairs of electrons from other atoms. Therefore, most hafnium bonding in solution will be through oxygen-hafnium bonds. Hence, Hf may bind easily through OH^- , $\text{PO}_4^{=}$, and the organic species, $-\text{COOH}$ and $-\text{COH}$. In addition, polymerization of these oxygen containing compounds is quite common. The only exception to the above rule is the hafnium-fluorine bond, the only nonoxygen bond which is stable in H_2O . Hafnium will form compounds with the other halogens only under nonaqueous conditions (i.e., HfCl_4). It also forms an insoluble compound^(8,9) with concentrated H_3PO_4 , nominally $\text{HfO}(\text{H}_2\text{PO}_4)_2 \cdot n\text{H}_2\text{O}$.

Due to the complicated hydrolysis behavior of Hf, it is nearly impossible to specify an exact chemical form for the various aqueous solutions. In addition, it would not be unreasonable to assume that the chemical environment around the Hf nucleus is undergoing rapid changes as the Hf passes among the various hydrolysis products. This is clearly reflected by the changes in the perturbation coefficient between HfOCl_2 , the two dilute H_3PO_4 samples, and the Na_3PO_4 solution. The hafnium is also most likely in a hydrolysis form in the $(\text{NH}_4)_2\text{SO}_4$ solution, as Hf-S or -N bonding is only possible under very strongly acidic or hot conditions⁽⁹⁾ (i.e., free radicals).

A somewhat interesting trend does appear among the four macro-molecular species and their common solvents. The perturbation coefficients

definitely fall into two groups. One group containing the solvent tris-(hydroxymethyl) aminomethane [Trizma] and the two DNA samples, exhibits a $G_{22}^{(\infty)}$ which is less than the limiting value to be expected for a static quadrupole interaction ($G_{22}^{(\infty)} = 0.2$). This would indicate the possibility of a time-dependent interaction arising from the ions in solution. The second group with $G_{22}^{(\infty)} \approx .25$ is definitely above the limiting perturbation, indicating either specific binding creating a static quadrupole field or a much weaker time-dependent interaction. However, the little information available from IPAC experiments will not indicate specifically what is occurring in the solutions. The enzymes, aldolase,⁽¹⁰⁾ and pyruvate kinase⁽¹¹⁾ are of medium molecular weight, 158,000 and 237,000, respectively, and exist as tetrameric structures. The only likely binding site would be the abundant $-RCOO^-$ groups present in the amino acids. The tightly held tetrameric structures of these enzymes may account for the higher $G_{22}^{(\infty)}$, due to the trapping of the hafnium nuclei within the central region of the enzymes. This would partially shield the nuclei from the rapidly fluctuating fields due to the smaller ions in solution. The DNA molecules, in addition to the $-RCOO^-$ binding, can also supply $PO_4^{=}$ groups and the numerous OH^- groups of the sugars. The more open framework of the DNA helix would be a less effective shield than the previously discussed tetrameric structure. However, it should be noted that because $G_{22}^{(\infty)}$ did not change from the value of Hf in each solvent on going to the macromolecule + solvent, we may be seeing only solvent effects, rather than actual binding in the macromolecules.

It was concluded from this work, that little useful information can be gleaned from the integral experiments. Therefore, all future experiments will be done using Time-Differential PAC (TDPAC).

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D. Theoretical Treatment of Nuclear Quadrupole Interactions with Particular Reference to Crystals and Macromolecular Species Studied by TDPAC.

The interaction of the nuclear electric quadrupole moment with an extranuclear electric field gradient produces transitions among the nuclear m-states. The resulting gamma-ray angular correlation will be perturbed because the second transition of the cascade is emitted with an altered population density with respect to the symmetry axis. Both static and time-dependent electric fields may create perturbations of the angular correlation and each case will be treated separately, as well as the effect of a combined interaction.

Time dependent electric field gradients (EFG), arising from the

Brownian motion of ions in solutions, give rise to an electric field that is fluctuating both in magnitude and direction. The symmetry axis is therefore undergoing constant change. The resulting angular correlation is represented by

$$W(\theta, t) = \sum_{k=0,2,4} A_{kk} G_{kk}(t) P_k(\cos\theta)$$

where the perturbation coefficient is simply a relaxation process⁽¹⁾

$$G_{kk}(t) = \exp[-\lambda_k t].$$

The relaxation coefficient is given by⁽¹⁾

$$\begin{aligned} \lambda_k &= \frac{3\tau_c}{80h^2} (eQ)^2 v_{zz}^2 \frac{k(k+1)[4I(I+1) - k(k+1) - 1]}{I^2 (2I-1)^2} \\ &= 3/5 \tau_c \omega_q^2 \{k(k+1)[4I(I+1) - k(k+1) - 1]\} \end{aligned}$$

The relaxation coefficient, λ_k , is directly proportional to the correlation time, τ_c , which is approximately 10^{-11} sec in dilute aqueous solutions. For solutions of macromolecular species, the relaxation time is better represented as the relaxation due to rotational diffusion of the molecule. This can be understood as the effect of free ions in solution as the large molecule slowly tumbles and turns, creating a more slowly relaxing field than that of small ions in an aqueous solution. The relaxation time is approximated by⁽²⁾

$$\tau_R = \frac{4\pi a^3 \eta}{3kT};$$

$$\tau_k = 6\tau_R/k(k+1);$$

where a is the molecular radius, η , the solvent viscosity, and T , the absolute temperature. It is evident that the dominant effect will arise from the radius of the large molecule. As an example, one may compare the two macromolecules, carbonic anhydrase ($a = 23.5 \text{ \AA}$; $M_w = 31,000$) and aldolase ($a = 40 \text{ \AA}$; $M_w = 158,000$) for solutions of equal viscosity ($\eta = 9.3 \text{ cP.}$). The resulting relaxation times are 120 nsec and 592 nsec, respectively. For these large molecules, the effects of viscosity and temperature will be minimal due to the dominating radius effect.

Hence, a fluctuating EFG causes an exponential attenuation of the angular correlation in time. In addition, for large fields and because the field is constantly changing, the angular correlation can be completely destroyed, resulting in isotropy. This is untrue of random static fields because at any given time a certain fraction of the nuclei within the source will experience either no perturbation or only a slight attenuation. Therefore, the angular correlation is never attenuated below a limiting value.

A static electric field presents a much more complicated situation, but one which is potentially richer in information. A static quadrupole interaction splits the nuclear states, non-uniformly, into parity degenerate ($\pm m$) states. For an axially symmetric EFG, V_{zz} , in a polycrystalline source, the splitting results in the following energy level scheme⁽¹⁾

$$E_m = \omega_q \hbar \{3m^2 - I(I+1)\}$$

where the quadrupole frequency

$$\omega_q = \frac{eQV_{zz}}{4I(2I-1)\hbar}$$

The angular frequency, ω_0 , which corresponds to the smallest nonvanishing energy difference is

$$\omega_0 = \begin{cases} 6 \omega_q & \text{for } I \text{ odd} \\ 3 \omega_q & \text{for } I \text{ even} \end{cases}$$

For a nuclear state of spin $I = 5/2$, ω_0 corresponds to the energy transition from $m = 3/2$ to $m = 1/2$. The resulting perturbation coefficient is sinusoidal in behavior

$$G_{kk}(t) = \sum_n s_{kn} \cos(n\omega_0 t)$$

with

$$s_{kn} = \sum_{m,m'} \begin{pmatrix} I & I & -k \\ m' & -m & -m'+m \end{pmatrix}$$

$$\begin{aligned} |m^2 - m'^2| &= n \text{ for integer } I \\ 2|m^2 - m'^2| &= n \text{ for half-integer } I. \end{aligned}$$

For a spin of $I = 5/2$, the summation is carried out to $n = 3$. The general shape of the perturbation coefficient, $G_{22}(t)$, for $I = 5/2$ is given in Fig. 5(a), the coefficients s_{kn} being given in Ref. (1).

This simplest case of an axially symmetric field gradient is often unobtainable. One usually has to deal with rhombic (not axially symmetric) fields, and a new parameter must be considered. The electric field gradient tensor is now represented by three components

$$|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$$

with $V_{xx} + V_{yy} + V_{zz} = 0$. The degree of digression from axial symmetry is

Fig. 5

represented by the asymmetry parameter

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}},$$

$$0 \leq \eta \leq 1.$$

When $\eta = 0$, the angular frequencies are simply the harmonics of the lowest interaction frequency, ω_0 . This is, however, no longer true when $\eta \neq 0$. The m 's are no longer good quantum numbers and one must approximate the energy levels by a power series in η . The behavior of the energy levels as a function of η has been calculated in this approximation by Gerdau, et al.⁽¹³⁾ and is shown schematically in Fig. 5(b). The influence of nonaxial symmetry on the perturbation coefficient, $G_{22}(t)$, is a distortion of the purely sinusoidal behavior. The predicted results for several values of η are shown in Fig. 6.

Because of the polycrystalline nature of our solid sources, the electric field gradient may vary slightly from nucleus to nucleus. This results in a probability distribution, $P(\omega_0)$ of the interaction frequency. The probability distribution is usually assumed to be gaussian

$$P(\omega_0) = \frac{1}{\sqrt{2} \delta_n \omega_n^0} \exp \left[-\frac{1}{2} \frac{(\omega_n - \omega_n^0)^2}{(\delta_n \omega_n^0)^2} \right]$$

where ω_n^0 represents the centroid and δ_n is the relative distribution width. The average perturbation factor, after integration of the distribution over all frequencies, is⁽⁴⁾

$$\overline{G_{kk}(t)} = s_{k0} + \sum_{n=1}^3 s_{kn} \exp(-1/2 \delta_n^2 \omega_n^0{}^2 t^2) \cos(\omega_n^0 t).$$

The frequencies are dependent on n , in order to account for effects of non-axial symmetry. The resulting angular correlation patterns for several distribution widths are given in Fig. 7. It is quite evident that the correlation is very quickly damped out as δ_n increases.

In certain cases, such as large protein molecules in solution, it is quite reasonable to expect perturbations not only due to direct binding (static interactions) but rotational diffusion as well. If both effects are operative, then the bound radioactive nucleus "sees" an effective field which is the combination of the static and time dependent fields. The resulting perturbation coefficient is the product of the individual static and time dependent coefficients.

$$G_{kk}(t) = \sum_{n=0}^3 s_{kn} \exp(-t/\tau_R) \cos(n\omega_o t).$$

A distribution in frequencies would damp out the perturbation coefficient, masking much of the information on τ_R and ω_o .

A final complication must also be considered for the metallo-protein solutions. This would be the effect of any unbound radioactivity in solution, creating a randomly fluctuating electric quadrupole interaction with $\tau_c \cong 10^{-10} - 10^{-11}$ sec. One assumes a superposition of interactions (or perturbation coefficients) because the fields arise from different nuclei:

$$\begin{array}{cc} \text{TOTAL} & \text{STATIC} \\ G_{22}(t) = \alpha G_{22}(t) + \beta \exp[-\lambda_k t] \end{array}$$

where α and β represent the percentages of the nuclei in each of the two sites. Obviously the effect of this type of interaction is a damping of

the amplitude and a distortion of the shape of $G_{22}(t)$.

In the case that the resolving time of the electronic instruments, τ_0 , is much larger than the meanlife of the nuclear state, $\tau_0 \gg \tau$, only integral measurements are possible. For each type of electric field, one then measures the time integral of the perturbation coefficient and the resulting angular correlation is

$$\overline{W(\theta, \infty)} = \sum_{k=0,2,4} A_{kk} \overline{G_{kk}(\infty)} P_k(\cos\theta)$$

For a time dependent electric field gradient, the perturbation coefficient is simply

$$\overline{G_{kk}(\infty)} = \frac{1}{1 + \lambda_k \tau},$$

where the relaxation coefficient, λ_k , has been previously defined. As the quadrupole field, ω_q , becomes very large ($\lambda_k \gg 1$), the perturbation coefficient will approach zero and the angular correlation becomes isotropic. A static axially symmetric EFG produces the following perturbation coefficient

$$\overline{G_{kk}(\infty)} = \sum_n s_{kn} \frac{1}{1 + (n\omega_0 \tau)^2}.$$

An infinitely strong static quadrupole interaction would approach the limiting value of

$$\overline{G_{kk}(\infty)}_{\text{lim}} = s_{ko}$$

rather than the totally isotropic case. The influence of a nonaxial electric field gradient would be to slightly change the value of s_{ko} .⁽¹⁾

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E. Analysis of Data from TDPAC Experiments.

In order to eliminate the exponential decay of the nuclear state from the raw data taken at the two angles, 90° and 180°, the following ratio was formed.

$$\frac{2[C(180) - C(90)]}{C(180) + 2 C(90)}$$

If $A_4 = 0$, the above ratio is equal to $A_{22}G_{22}(t)$. This information, $A_{22}G_{22}(t)$ versus t , was used directly in the least-squares fitting routine.

The intrinsic time resolution of the experimental apparatus adds a source of error uncommon to most counting experiments not dealing with nanosecond time scales. The total resolving time is the sum of the contributions from all instruments with the largest effect due to the timing discriminators. If a nonenergetic prompt pulse is fed to both the start and stop inputs of a time-to-amplitude converter (TAC), it will not fall in a single channel. Rather, the information will be spread out in a normal distribution over many channels. Therefore, the timing information

stored in each channel can not be treated as a single event. There is a finite probability that the information actually occurred at some time prior to or after the recorded time. The two overall effects are a smearing out of the information stored in each channel of the analyzer and a shift in the maximum of the timing peak away from the true zero time. The amount of shift is related to the standard deviation of the normal distribution, $\sigma = \text{FWHM}/2.345$, by

$$T_{(\text{shift})} \cong \sigma^2/2\tau ,$$

where τ is the mean life of the intermediate nuclear state⁽¹⁾.

The prompt resolution function, $P(T)$, is usually taken to be a gaussian probability distribution. If $F(T)$ represents the timing information stored in each channel, then

$$F(T) = \int_{-\infty}^{+\infty} f(t)P(T)dt$$

where t is real time and T is the measured time of each channel. The function $f(t)$ is defined as

$$f(t) = 0 \quad \text{for } -\infty < t < 0$$

$$f(t) = A_{22}G_{22}(t) \quad \text{for } 0 \leq t \leq +\infty$$

The prompt resolution spectrum can be represented as

$$P(T) = \frac{1}{\sigma(2\pi)^{1/2}} \exp \left[-\frac{(T-t)^2}{2\sigma^2} \right]$$

where $\sigma = \text{FWHM}/2.345$. For solid polycrystalline sources, the perturbation is represented by

$$f(t) = s_{20} + \sum_{n=1}^3 s_{2n} \exp(-1/2 \delta^2 \omega_n^2 t^2) \cos(\omega_n t)$$

with the coefficients, s_{kn} , given in Ref. (2). The entire function, modulated by the resolution function becomes

$$F(T) = \int_0^{+\infty} 1/\sigma(2\pi)^{1/2} \exp \left[\frac{-(T-t)^2}{2\sigma^2} \right] \left\{ s_{20} + \sum_{n=1}^3 s_{2n} \exp(-1/2 \delta^2 \omega_n^2 t^2) \cos(\omega_n t) \right\} dt.$$

The summation is carried out for three frequencies with the restriction that $\omega_1 + \omega_2 = \omega_3$.

The above integration can only be carried out numerically.

In order to solve the integral given above, a numerical routine, for use in conjunction with a Fortran least squares program, was developed using Simpson's rule. If $f(x)$ is the argument beneath the integral sign, then

$$\int_A^B f(x) dx = \frac{h}{3} [f_1 + 4f_2 + 2f_3 + \dots + 2f_{n-2} + 4f_{n-1} + f_n]$$

where the step size, $h = B-A/n$. The total number of steps is n , and each function, f_n , is equal to the argument evaluated for each $X = A, A+h, \dots, B-h, B$. The limits, A and B , are defined as the real time, t . In order to minimize the computation, but still maintain accuracy, the integration was carried out over the range from $A = -2\sigma$ to $B = +2\sigma$ or 95.5% of the probability distribution. Because $f(t) = 0$ for all negative times but the

probability distribution does not, the integration procedure for the channels, $T - 2\sigma < 0$, were begun at $A = 0$. No negative times were considered in the integration.

The main format of the least squares program used for fitting our differential anisotropy data was taken from Bevington⁽³⁾. Below is given a brief discussion of the method.

According to the method of least squares analysis, minimization of χ^2 provides the optimum values for the variables, a_j , if the following is attained:

$$\frac{\partial}{\partial a_j} \chi^2 = \frac{\partial}{\partial a_j} \sum_i \left\{ \frac{1}{\sigma_i^2} [\text{Data} - \text{Fit}]^2 \right\} = 0$$

In order to minimize χ^2 , a search of the χ^2 hypersurface defined by the n variables, a_j , must be carried out. Close to each minimum, χ^2 is parabolic. In general, for nonlinear functions with several variables, many minima exist in such a hypersurface. The two most efficient methods for obtaining the χ^2 minima are the gradient-search of the hypersurface and a linearization of the fitting function. The former method simultaneously increments all variables, a_j , adjusting their magnitude and sign in order to force χ^2 to decrease in the direction of the maximum variation. The "steepest descent" criterion guarantees that χ^2 is not in one of the many local minima on the path to the best fit. Once χ^2 ceases to decrease, the variables and their associated errors are calculated. In the linearization method, expansion of the fitting function into a Taylor series of first order produces a linear function which is easily handled by the normal least squares method. This latter method is very powerful but will converge only where the χ^2 hypersurface is parabolic. The gradient search, however,

loses accuracy near the parabolic region because it requires the comparison of essentially equal numbers. Therefore, the least squares method used combines the best features of both methods. A gradient search is instituted at the onset of the fitting procedure in order to locate the best minimum. Once near the minimum, a linearization is carried out in order to determine the best fit values for the variables.

The previously described numerical integration routine was used in conjunction with the above program. A simple numerical routine for calculating the partial derivatives with respect to each variable was also used.

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F. Time Differential Perturbed Angular Correlation Studies in ^{181}Ta .

As the results of the integral correlation studies indicated, it is necessary to make time differential angular correlation (TDPAC) measurements in order to obtain concrete evidence on the binding of the nuclear species of interest. The macromolecular species in solution will present a very complicated problem, because of the several types of interactions operative in each sample. In order to develop the TDPAC technique with the minimum of ambiguity, the first experiments were therefore performed on several relatively simple polycrystalline hafnium compounds.

Detailed descriptions of the theory, data analysis technique, and

experimental set-up have all been given in preceding sections of this report. What follows will be a description of the sample preparation for each compound and the final experimental results.

The first differential experiment was performed on a liquid sample of ^{181}Hf in concentrated hydrofluoric acid. It has been found that hafnium dissolved in 27 N HF is the only sample which does not exhibit a quadrupole interaction.⁽¹⁾ The hafnium cation becomes completely surrounded by fluorine anions in a very closely packed octahedron.⁽²⁾ Even if greater than 6 coordination occurs, the fluorines seem to form a very tight sphere around the hafnium nucleus, resulting in a spherical charge distribution. Particular care had to be taken in order to prevent the destruction of the sample holder by HF attack. After repeated attempts to obtain the unperturbed correlation, it was found that HF acid attacks epoxy causing the diffusion of the ^{181}Hf activity into the epoxy matrix. A final and successful experiment was made using a sample holder of plexiglass, heat sealed at the bottom. A plexiglass plug was used to cover the top of the ampoule. The activity in the form of $^{181}\text{HfOCl}_2$ in 0.5 N HCl was reduced to near dryness and then taken up in 2-3 drops of 27 N HF. The sample was transferred immediately to the plexiglass ampoule.

If no perturbation of the intermediate nuclear state occurs, the differential spectrum of $A_{22}G_{22}(t)$ vs. time will be a flat line with the average value of the unperturbed A_{22} coefficient. Reference to Fig. 8(a) shows that this condition is fulfilled by our HF sample. The initial rise in the experimental data represents an attenuation effect due to the finite time resolution of the instruments. The resulting value for A_{22} after correction for the solid angles of the detectors and any nonlinearities

in the source and correlation table is $A_{22} = -0.293 \pm 0.008$.

The first polycrystalline sample to be studied was hafnium phosphate, which exhibits the structure shown below.

The ^{181}Hf activity was transferred to a small volume of saturated HfOCl_2 made by dissolving HfCl_4 in distilled H_2O . The dropwise addition of concentrated H_3PO_4 caused the immediate precipitation of the hafnium phosphate. After addition of excess H_3PO_4 in order to guarantee the precipitation of all the hafnium activity, the white precipitate was washed three times with distilled water. The precipitate was air dried and pulverized to the polycrystalline form and transferred to a plexiglass ampoule.

The time integral experiment for this sample is given in Fig. 8(b) and is compared to a calculated curve using the unperturbed value of A_2 obtained in the HF experiment. The angular correlation is reduced by the perturbation to the limiting value for the perturbation coefficient, $G_{22}^{(\infty)}_{\text{lim}}$. The results of the least squares fit (dashed line) are

$$A_{22}G_{22}^{(\infty)} = -0.060(6)$$

$$A_{44}G_{44}^{(\infty)} = -0.001(7)$$

$$G_{22}^{(\infty)} = 0.22(2)$$

This value of $G_{22}^{(\infty)}_{lim}$ corresponds⁽³⁾ to an asymmetry parameter, η of approximately 0.4.

The result of the time differential angular correlation is shown in Fig. 9. The solid curve is a least squares fit to the data. Because of the large and varied numbers of waters of hydration, the Hf nucleus will not experience a unique interaction throughout the source and a distribution, δ , in frequencies was considered. The average result of several fits to the data with various initial starting points for $T = 0$ and the fit parameters are given below.

$$\omega_1 = 356 \pm 6 \text{ MHz}$$

$$\omega_2 = 582 \pm 28 \text{ MHz}$$

$$\omega_1 + \omega_2 = \omega_3 = 938 \pm 28 \text{ MHz}$$

The sample displayed a fairly large frequency distribution of $\delta = 0.18 \pm .02$, and the value obtained for the correlation coefficient was $A_{22}(\text{exp}) = -0.292 \pm .008$. The coefficient has been corrected for the finite solid angles of the detectors. The excellent agreement between our fit parameter $A_{22}(\text{exp})$ and both the previous value obtained from the unperturbed HF(27 N) experiment and the accepted literature value⁽⁴⁾, $A_{22} = -0.295(10)$ lends validity to the other parameters obtained from the least squares fit. The fit curve fails to approximate the full amplitude of the second dip in the experimental data, as well as the partial fine structure evident in the first frequency cycle. Both of these failures can be partly attributed to the use of the theoretical values for the s_{kn} coefficients in the fitting function. These coefficients will vary slightly with the asymmetry parameter, η . In addition, an increased amplitude could be obtained if the fitting procedure considered a small contribution due to

A_{44} . However, as these changes would lead to a nearly unrestricted fit, the theoretical values for s_{kn} were used and A_{44} was considered negligible. In either case, the values for the frequencies would not be affected, as they are determined primarily by the positions of the minima and maxima rather than their absolute magnitudes.

The frequencies, ω_n , given above lead to a quadrupole frequency of $\omega_q = 59(1)$ MHz and an asymmetry parameter of $\eta = 0.43 \pm .06$. Using this value of η and a nuclear quadrupole moment for the intermediate state⁽⁵⁾ of $Q(482) = (2.53 \pm .10) \times 10^{-24} \text{ cm}^2$ one obtains the following value for the electric field gradient components.

$$\begin{aligned} |V_{zz}| &= (6.17 \pm 0.14) \times 10^{17} \text{ V/cm}^2 \\ |V_{yy}| &= (4.41 \pm 0.10) \times 10^{17} \text{ V/cm}^2 \\ |V_{xx}| &= (1.76 \pm 0.04) \times 10^{17} \text{ V/cm}^2 \end{aligned}$$

The magnitude and asymmetry of the electric quadrupole field at the hafnium nucleus in the phosphate compound are comparable to the quadrupole fields seen in many hafnium compounds⁽⁶⁻¹⁰⁾. This could possibly be an indication that the largest contribution to the electric field gradients in hafnium compounds arises from the hafnium valence orbitals used in bonding rather than the particular crystalline orientation. On the other hand, the comparable results could be purely fortuitous.

The phosphate experiment is being repeated using a preparative method involving slow homogeneous precipitation, to determine if the apparent frequency distribution can be reduced.

HfO₂

The oxides of hafnium exist in three crystalline forms, monoclinic, tetragonal, and cubic, the monoclinic being the most likely form at room temperature. Each crystal is composed of four HfO₂ units leading to a face centered monoclinic arrangement with a hafnium nucleus at each corner and face of the crystal. Each hafnium nucleus is surrounded by 8 oxygen nearest neighbors and may be bound to all eight oxygens simultaneously.⁽²⁾

Two samples of the oxide were studied. In each case, radioactivity was transferred to approximately 2 ml of HfOCl₂ solution and then reduced to dryness. The dried residue of the various hafnium hydrolysis products was then ignited at 400°C for 5 hours to obtain the oxide. The first experiment was performed on the ignition product without further treatment. The second sample of oxide was additionally annealed for 8 hours at 1100°C.

The results of the first experiment are shown in Fig. 10. The time differential pattern, initially, falls off rapidly and then levels off to a constant value. Some structure is evident at the beginning of the spectrum but it is quickly wiped out. One of two explanations can be put forth to explain the observed behavior. If the inhomogeneity of the source is very large (i.e., $\delta > 30\%$), any static quadrupole oscillation would be wiped out leading to an essentially flat correlation pattern. Another possibility is that the EFG at the hafnium nuclei is very small (i.e., $\omega_q \approx 20$ MHz), as might be expected if the bonding of oxygens were to lead to a nearly cubic site symmetry. The resulting angular correlation pattern would not have completed one full cycle within the 60 nsec range of the experiment. A previous experiment by Gerdau, et al.,⁽¹¹⁾ discounts the latter supposition, as they reported an $\omega_q = 126.9(1.3)$ MHz for HfO₂.

Their measurement, however, was taken at 77°C and EFG's for some materials can be temperature dependent.

In order to determine whether source inhomogeneity was effecting the experimental results, the second oxide sample was annealed at 1100°C for 8 hours. The resulting angular correlation pattern is shown in Fig. 11. This sample exhibited a very strong and nearly regular quadrupole interaction pattern. The solid line through the experimental points is the least squares fit and the error bars are purely statistical. Comparison of the two oxide samples demonstrates dramatically the detrimental effects of source inhomogeneity on the ability to interpret TDPAC spectra. The fit to the experimental data leads to the following parameters

$$\delta = 0.04(1)$$

$$\omega_q = 145.4(1.1) \text{ MHz}$$

$$\eta = 0.43(8)$$

Our experimental result for ω_q is approximately 18 MHz higher than the previously reported value of Gerdau, who found $\omega_q = 126.9(1.3) \text{ MHz}$ and $\eta = 0.35(3)$. Our values for the asymmetry parameter, however, are within error the same. This discrepancy could possibly be attributed to a small temperature dependence of the quadrupole interaction or a slight variance in the EFG due to the number of bound oxygens in the oxide crystal. Our value for the quadrupole frequency and asymmetry parameter lead to the following values for the electric field gradient components.

$$|V_{zz}| = (1.51 \pm 0.05) \times 10^{18} \text{ V/cm}^2$$

$$|V_{yy}| = (1.08 \pm 0.04) \times 10^{18} \text{ V/cm}^2$$

$$|V_{xx}| = (0.43 \pm 0.014) \times 10^{18} \text{ V/cm}^2$$

The electric field gradient at the hafnium site is quite large, being nearly 2.5 times the EFG due to phosphate bonding. A possible qualitative explanation will be given in the ensuing section. Gerdau, et al.,⁽¹¹⁾ also found the strong dependence of oxide quadrupole interactions on lattice faults. Their main source of inhomogeneity, however, was attributed to radiation damage produced in the source by neutron irradiation, which also would disappear upon annealing.

Ammonium hexafluorohafnate $(\text{NH}_4)_2\text{HfF}_6$, has been previously studied by two groups^(11,12) with widely different results for the quadrupole frequencies being reported for the two temperatures, 77°K and 300°K. The discrepancy was attributed to a possible strong temperature dependence of the electric field gradient at the hafnium nucleus.⁽¹¹⁾ In addition, the reported value of Mayer, et al.,⁽¹²⁾ for the EFG, $|V_{zz}| = (3.6 \pm 0.2) \times 10^{17} \text{ V/cm}^2$, does not correspond to their own reported quadrupole frequency, $\omega_q = 570 \pm 30 \text{ MHz}$. Therefore, partly to resolve this discrepancy and partly as an intellectual exercise, a study of the ammonium hexafluorohafnate was undertaken.

The compound was prepared according to the method given in Ref. 12. The hafnium activity was transferred to a fairly concentrated solution of HfOCl_2 and then reduced to dryness over steam heat. The residue was converted to the oxide by ignition at 400°C for 5 hours. The oxide was dissolved in a minimum of concentrated HF and a stoichiometric amount of NH_4F was added to the solution. Evaporation of the solution resulted in the formation of white crystals of $(\text{NH}_4)_2\text{HfF}_6$.

The time differential spectrum for the ammonium hexafluorohafnate

is not shown because it exhibited no distinctive pattern. It very rapidly fell off to a constant value and remained flat. It was concluded that due to the poor and too rapid crystallization procedure used above, a wide frequency distribution resulted and the correlation pattern was wiped out almost immediately. A second experiment is now in progress in which crystals of $(\text{NH}_4)_2\text{HfF}_6$ were grown slowly from hydrofluoric acid solution. The crystallization took approximately one week and long needlelike crystals were obtained.

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G. Relationship of EFG's to Chemical Bonding

The rigid calculation of EFG's involves the determination of the wave functions for all the electrons in the system. Such a many-bodied problem is beyond present day technology and approximation methods must therefore be depended upon. The method of Townes and Dailey⁽¹⁻³⁾ is one such approximation and has been used for preliminary calculations on several of the hafnium compounds. A brief summary of the method and each calculation will be given below.

The basic premise of the Townes and Dailey theory⁽¹⁾ is that the major contribution to the magnitude of the EFG at the nucleus arises from the electron distribution in the valence orbitals. The largest contribution is due to a singly occupied p-type orbital. The spherically symmetric s-type orbital gives no contribution. The influence of charges in neighboring atoms is small compared to the valence orbital contribution. Therefore, the magnitude of the EFG is considered to be the summation over the individual valence electron contributions.

$$\frac{\partial^2 V}{\partial z^2} \equiv q = \sum_{nlm} |a_{nlm}|^2 q_{nlm,nlm} + \sum_{nlm,n'l'm'} a_{nlm} a_{n'l'm'}^* q_{nlm,n'l'm'}$$

where the electric field gradient due to a particular atomic state is

$$q_{nlm,n'l'm'} = \int \Psi_{nlm} [(3\cos^2\theta - 1)/r^3] \Psi_{n'l'm'}^* d\tau$$

the azimuthal angle, θ , is with respect to the bond axis. The coefficients, a_{nlm} , represent the fractional importance of each atomic state, Ψ_{nlm} , in the molecular orbital (MO) wave function,

$$\Psi_{MO} = \sum_{nlm} a_{nlm} \Psi_{nlm}$$

The atomic EFG's are denoted by the principle, azimuthal, and magnetic quantum numbers, n , l , and m . For a non-zero value in the second summation m must equal m' and $l = l' \neq 0$ or $l = l' \pm 2$. The magnitude of q_{nlm} is a rapidly decreasing function of n and l , thus eliminating or significantly reducing most of the cross terms in the second summation. A detailed version of the theory may be found in the references. A list of the values of q_{nlo} , as determined by fine structure experiments are given in Table III.

Table III. Values of q_{nlo} for Various n and l^*

Electronic State	q_{nlo} (10^{17} V/cm ²)
210	62.5
310	2.083
410	0.595
510	-133.9
520	- 0.923
610	- 10.12
620	- 0.476
710	- 3.274
720	- 0.268

*Values were obtained from Ref. 1 and converted from e.s.u. to V/cm² by multiplication by 297.62 V/cm²/e.s.u.

Hafnium atoms will, under ordinary circumstances, form bonds by accepting electrons into empty orbitals. It is rare that hafnium behaves as the ionic Hf^{+4} species. The ground state configuration for hafnium is $4f^{14}5d^26s^2$. Bonding will most likely involve the filling of the 5d and 6p orbitals, with possible s hybridization. The orbitals employed are determined by the number of species bound to the hafnium atom.

Hafnium phosphate, $\text{HfO}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, will be the first case to be considered. Hafnium forms two sigma bonds to the oxygens of the phosphate groups and is also doubly bound to a third oxygen. The water molecule will probably bond by donation of two electrons into empty hafnium orbitals. Because the EFG is so largely asymmetric ($\eta = .43$), those orbitals with the largest electron densities in the z and y directions were chosen as the bonding orbitals. It was assumed that there is no s-hybridization and the 5d orbitals are involved in the bonds to the three oxygens. Each oxygen sigma bonds through its p_z orbital and π bonds into its 2 p_y orbital. The following molecular orbital wave functions result for each bond. $\psi_{\text{MO}}^{\text{H}_2\text{O}}$ denotes the coordinate covalent bond to the water molecule, which could donate electrons to either a d or a p_z orbital on hafnium.

$$\text{a. } \psi_{\text{MO}}^{\sigma} = a_{520} \psi_{520} + a_{210} \psi_{210}$$

$$\text{b. } \psi_{\text{MO}}^{\sigma} = a_{522} \psi_{522} + a_{210} \psi_{210}$$

$$\text{c. } \psi_{\text{MO}}^{\sigma} = a_{52-2} \psi_{52-2} + a_{210} \psi_{210}$$

$$\text{d. } \psi_{\text{MO}}^{\pi} = a_{52-1} \psi_{52-1} + a_{211} \psi_{211}$$

$$\text{e' } \psi_{\text{MO}}^{\text{H}_2\text{O}} = \begin{cases} a_{610} \psi_{610} + a_{210} \psi_{210} \\ a_{521} \psi_{521} + a_{210} \psi_{210} \end{cases}$$

$$\text{e'' } \psi_{\text{MO}}^{\text{H}_2\text{O}} = \begin{cases} a_{610} \psi_{610} + a_{210} \psi_{210} \\ a_{521} \psi_{521} + a_{210} \psi_{210} \end{cases}$$

The coefficients, $a_{n\ell m}$, for bonds a-d are of equal magnitude

$$a_{n\ell m} = 1/\sqrt{2}.$$

The coordinate covalent bond of the water molecule was assumed to involve 33.3% or 50% p_z (or d) character from the hafnium valence orbital. The magnitude of the EFG is then obtained by summing over the atomic states of the hafnium:

$$q = |a_{520}|^2 q_{520} + |a_{522}|^2 q_{522} + |a_{52-2}|^2 q_{52-2} + |a_{52-1}|^2 q_{52-1} \\ + \{ |a_{610}|^2 q_{610} \text{ (or } |a_{521}|^2 q_{521}) \}$$

The various atomic states of different m are related by the following expression⁽²⁾

$$q_{n\ell m} = q_{n\ell 0} \left[1 - \frac{3m^2}{\ell(\ell+1)} \right]$$

The values of $q_{n\ell 0}$ listed in Table III were used in the calculation. Table IV gives the results of the calculation and a comparison to the experimentally measured value. It is evident that the size of q is too small if only the 5d orbitals of the hafnium are employed in the bonding. In order for the EFG to be of the proper magnitude, a fair amount of p character must be included in the hafnium-water bond. It should be noted that only the most simplistic case for the phosphate compound was considered. The magnitude of q could be changed significantly if one takes into account s hybridization and/or partially ionic bonds. However, qualitatively, the Townes and Dailey approximation has given an estimate of the proper magnitude.

Table IV. Values of the EFG for $\text{HfO}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$

Type of bond involved in the $\text{Hf} \cdot \text{H}_2\text{O}$ bond	$q(10^{17} \text{ V/cm}^2)$	Experimental V_{zz} (10^{17} V/cm^2)
33.3% d	-0.846	
50.0% d	-0.923	6.17 ± 0.14
33.3% p_z	-4.07	
50.0% p_z	-5.80	

As was mentioned in an earlier section, HfO_2 may involve up to 8 oxygens bound to a single hafnium nucleus, with the likelihood of some double bound character. Eight corrdinate species are either dodecahedral or antiprismatic.⁽⁴⁾ The latter structure has the characteristic hybridization of $d^5 p^3$ which leads to a zero EFG. If eight oxygens are coordinated to Hf, the most likely structure would be the dodecahedron of hybridization $d^4 sp^3$. As a first approximation to the magnitude of q , it will suffice to calculate the EFG due to an electron in a $d^4 sp^3$ hybrid orbital. Again, the 5d orbitals with the largest electron density in the z and y direction were chosen. The resulting summation is given below

$$q = |a_{520}|^2 q_{520} + |a_{522}|^2 q_{522} + |a_{521}|^2 q_{521} + |a_{52-1}|^2 q_{52-1} \\ + \{ |a_{600}|^2 q_{600} + |a_{610}|^2 q_{610} + |a_{611}|^2 q_{611} + |a_{61-1}|^2 q_{61-1} \}$$

The coefficients were given the value of $1/\sqrt{8}$. Because a completely filled orbital leads to a zero EFG, the terms within the bracket sum to zero, and the total EFG arises from the electron distribution in the d orbitals. The resulting EFG caused by an electron in a d^4sp^3 orbital is $1.15 \times 10^{17} \text{ V/cm}^2$. If no π bonding occurs, there will be a total of 12 e^- in d^4sp^3 orbitals. Hafnium contributes 4 electrons and the 8 oxygens contribute one electron each. In the case of two π bonds, 14 electrons would be involved. The total EFG due to the 12 and 14 electrons is 1.38×10^{18} and $1.61 \times 10^{18} \text{ V/cm}^2$, respectively. This can be compared to our experimental value of $|V_{zz}| = (1.51 \pm 0.05) \times 10^{18} \text{ V/cm}^2$. The agreement is remarkable.

One can also consider the sterically hindered case which would limit bonding to either 7 or 6 oxygens. A seven coordinated species would in all likelihood involve the d^5sp hybridization of the pentagonal bipyramid.⁽⁴⁾ Six coordination, if regular, is octahedral and leads to a zero EFG. Using the method described above, the EFG due to an electron in the d^5sp orbital is $1.45 \times 10^{17} \text{ V/cm}^2$. The resulting EFG will be due to either 11 or 13 electrons in this case and one obtains 1.60×10^{18} and $1.89 \times 10^{18} \text{ V/cm}^2$, respectively. Both of these fields are somewhat higher than the experimental value but the agreement is still quite good.

Considering the above calculations for the phosphate and oxygen species qualitatively, it is seen that the simple approximations used lead to the conclusion that the oxide should exhibit a much larger EFG than the phosphate. This was born out experimentally. In addition, both compounds involve bonding mainly through the same d orbitals. This similarity in the type of orbitals involved could explain the almost identical values for the asymmetry parameters. No calculations, however,

have been made to determine a theoretical asymmetry parameter.

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III. Heavy Ion Nuclear Reactions

A. Study of Evaporation Residues from Complete Fusion Reactions Induced by Heavy Ions.

The use of recoil techniques in nuclear reactions studies can frequently provide detailed information on the mechanism of specific processes.^(1,2) Measurements of recoil ranges and angular distributions of residual product nuclei, traditionally performed by radioactivity counting, have served as tests for momentum transfer, forward-backward asymmetry, and kinematics, in collisions and the subsequent de-excitation steps of complex nuclei.⁽³⁻⁵⁾ On the other hand, light particles or fragments from nuclear reactions are usually studied on-line by direct measurements with solid-state detectors or magnetic spectrographs. In the present work, we have carried out a series of experiments to detect and measure on-line the heavy residual nuclei recoiling from complete fusion reactions induced by heavy ion beams. Because of the expected distribution in Z and A of the recoiling heavy reaction products, we were not interested in distinguishing specific elements or masses, but rather in identifying the evaporation residues as a group and measuring some of the general features of this class of complete fusion (or compound nucleus) reactions. Our specific objectives were to (1) ascertain the feasibility of using solid-state detectors for heavy recoil measurements, and (2) obtain estimates of the total cross-sections for complete fusion processes by direct observation of the heavy fragments. In the course of these studies, we have obtained the energy and angular distributions for the events of interest.

The experiments were begun a number of years ago at the Yale Heavy Ion Accelerator. The basis for the method lies in the distinctive

properties of very short range and high recoil energy associated with the relatively high Z residual nuclei. These characteristics should make it possible to distinguish such products from most other reaction products. Scattered beam particles have much longer ranges and higher energies, and light fragments like protons, ^4He , ^6Li , etc., would have longer ranges for comparable energies and much lower energies for comparable ranges. Our detection system was a counter telescope consisting of a thin, totally depleted, Si surface-barrier detector, backed by a thick Si detector. The front, or ΔE , detector was selected to be greater than the maximum range expected for the heavy recoil nuclei of interest. The thick, or E, detector will register only those particles whose ranges are greater than the thickness of the ΔE detector, while the signals from the ΔE detector will correspond to all particles which impinge on the telescope. For those fragments which stop in the ΔE counter, the pulse response will be proportional to the total energy of the fragment, whereas particles which pass through will produce a pulse corresponding to the energy lost in the ΔE counter. By imposing an anticoincidence requirement between the ΔE and E detectors, it is possible to observe only those events which correspond to particles which were stopped in the ΔE detector.

The scattering chamber used for the experiments is shown schematically in Fig. 12(a). The incident heavy ion beam was collimated to 1/16" by two double collimators 6" apart. The beam passing through the target was collected and monitored in a Faraday cup. The nuclear reaction products were collimated to 1/8" before reaching the detectors by means of a second set of two double collimators. Each double collimator consisted of a circular aperture with an antiscatter shield behind it. The positioning and alignment of the collimators and antiscatter shields was

(a) 20" dia. Scattering Chamber

(b) ΔE -E Anticoincidence Circuitry

quite critical in order to eliminate undesirable scattering effects, which could be easily observed in the E detector at energies below that of the elastic peak.

A block diagram of the detection system is given in Fig. 12(b). The preamplifier outputs from both detectors were shaped to optimize pulse transmission along the 150 feet of cable separating the linear main amplifiers from the scattering chamber area. Three multichannel analyzers were used to record events from the E detector (MCA-1), events from the ΔE detector (MCA-3), and events from the ΔE detector which were gated in anticoincidence mode by the E detector (MCA-2). The circuitry indicated in Fig. 12(b) is somewhat oversimplified, as the whole system was synchronized with the accelerator beam burst.

The heavy recoil nuclei formed in the reactions of interest are strongly forward peaked, being kinematically restricted to a tight cone as a consequence of the large center-of-mass motion. At angular positions close to the primary beam where these recoils are found, their detection becomes difficult due to the elastically scattered beam of far greater intensity. We have, however, made use of the elastic scattering in two important ways. The finite energy loss of the elastically scattered beam in the ΔE detector provided a convenient energy calibration, as the position of the energy loss peak could be computed from the known thickness of the ΔE detector. Second, as the range of the elastically scattered beam is greater than the thickness of the ΔE detector, there is always a correlated pulse in the E detector and the corresponding energy-loss peak in the ΔE detector is suppressed in the anticoincidence spectrum. This feature was used constantly to confirm the proper functioning of the electronics.

Three target-beam combinations were studied in our experiments: $\text{Cu} + {}^{20}\text{Ne}$, $\text{Al} + {}^{16}\text{O}$, and $\text{In} + {}^{20}\text{Ne}$. Thin, self-supporting targets ($100\text{-}300\ \mu\text{g}/\text{cm}^2$) were used. The Cu and In targets were prepared by vacuum evaporation of the metals onto an Al backing, followed by dipping in a strong (40%) solution of NaOH and rapid transfer to a tray of water, whereupon the thin metal films floated on the water. The films were picked up on brass collars (1/2" dia.) and stretched flat by the surface tension of water. The Al target was commercial aluminum leaf. The target thicknesses were determined by the energy lost by 5.48 MeV alpha particles from ${}^{241}\text{Am}$ in passing through the targets.

Early experiments employed a $27\ \mu\text{m}$ ΔE detector, which was substantially thicker than optimum. Later runs, including all those reported here, made use of either an $18\ \mu\text{m}$ or a $12\ \mu\text{m}$ ΔE detector, depending on the experiment. Recoil spectra for each reaction were measured at several angles in the interval 8-18 deg., and at various bombarding energies. Beam energies below the 10.5 MeV/amu produced by the MLLAC were obtained by passing the beam through Al degraders, and then magnetically analyzing the reduced energy beam.

Typical energy spectra of fragments stopped in the ΔE detector are shown in Fig. 13. The three parts of the figure correspond to different bombarding energies for the system $\text{Cu} + {}^{20}\text{Ne}$, as indicated. At each bombarding energy, the three curves are for the indicated lab angle of observation. In the interests of clarity, only the smooth curves drawn through the data points, are given in Fig. 13. The experimental scatter is consistent with statistical expectations for the numbers of events recorded. Several features of the energy spectra in Fig. 13 are worth noting. (1) There are, in fact, broad peaks which we identify with the

collection of residual recoil nuclei from complete fusion reactions.

(2) The peaks are very broad in energy, as found also in other work,^(6,7) presumably as a consequence of the distribution in masses as well as energies of the heavy reaction products. (3) The maxima in the energy spectra occur at energies which are in very good agreement with recoil energies calculated assuming a compound-nucleus (complete fusion) reaction mechanism and an average mass evaporation residue. The observed energies are indicated by arrows in Fig. 13. These energies decrease from (a) to (b) to (c) in Fig. 13 by amounts predicted for the changes in ^{20}Ne bombarding energies in the three experiments. (4) The differential cross-sections, proportional to the areas under the curves, are strongly decreasing functions of angle as expected from kinematic restrictions and from radiochemical recoil data.^(3,5) The slight decrease in most probable kinetic energy with angle, as indicated in Fig. 13, is also kinematically expected.

The general features of the energy spectra in Fig. 13 were also observed for the other reactions studied, $\text{In} + ^{20}\text{Ne}$ and $\text{Al} + ^{16}\text{O}$. However, the intensity of contaminating events, which are responsible for the low energy tails in the spectra, appear to be different for the several systems.

Our experimental results are summarized in Table V. Column 1 gives the reacting system and column 2 indicates the bombarding energy. The angle of measurement and the observed energy of the maximum in the recoil spectrum are listed in columns 3 and 4 respectively. In column 5, we tabulate the quantity N , which is the total number of events (particles) detected at the angle θ per $\mu\text{-Coulomb}$ of beam. These values were obtained by integrating the area under the observed energy spectra, after correcting

Table V. Summary of Results for Evaporation Residues
from Complete Fusion Reactions

System	Beam Energy (MeV)	Angle (deg)	E_R (pk) (MeV)	Area = N (events/ μ c)	$d\sigma/d\Omega$ (mb/sr)	σ_T (mb)
<u>Cu + ^{20}Ne</u>	210	7.8	45.6	10,700	13,899	3,236
		10.8	44.0	6,000	7,794	
		13.8	39.8	3,700	4,806	
	178	7.8	37.2	12,222	15,876	3,574
		10.8	36.4	7,000	9,093	
		13.8	34.0	2,755	3,578	
	144	7.8	32.6	10,570	13,730	2,813
		10.8	32.0	4,300	5,536	
		13.8	29.6	2,930	3,806	
<u>In + ^{20}Ne</u>	210	9.0	29.0	680	4,839	1,398
		12.0	27.4	273	1,943	
		15.0	25.6	117	833	
<u>Al + ^{16}O</u>	124.8	9.0	37.6	3,669	3,097	949
		12.0	35.6	2,600	2,195	
		15.0	34.2	1,370	1,156	
		18.0	32.6	857	723	
	102.6	9.0	32.2	5,960	5,031	1,508
		12.0	30.4	2,305	1,946	
		15.0	29.2	1,033	872	

for any contribution from low energy contamination, and normalizing by the known integrated beam current for each experiment. Column 6 gives the differential cross-section, $d\sigma/d\Omega$ (mb/sr), at each angle for the heavy evaporation residues. These results were calculated from the data in column 5, using the relationship:

$$\begin{aligned} \frac{d\sigma}{d\Omega}(\theta) &= \frac{N}{d\Omega \times (\text{beam particles}/\mu\text{C of beam}) \times (\text{target nuclei}/\text{cm}^2)} \\ &= \frac{10^{27} N}{(a/r^2)(6.28 \times 10^{12}/Z)(6.023 \times 10^{20} T/A)} \text{ mb/sr} \\ &= 2.644 \times 10^{-7} \frac{(N)(Z)(A)}{(T)(a/r^2)} \text{ mb/sr} \end{aligned}$$

where N = number of events detected at θ° per μC of beam,
 Z = charge state of beam recorded,
 A = atomic weight of target nuclei,
 T = target thickness in mg/cm^2 , and
 $(a/r^2) = d\Omega$ = solid angle subtended by the detector of effective area "a" at a distance "r" from the target.

In order to derive the total cross-sections shown in the last column of Table V, integration over the angular distributions had to be carried out. Because our angular distributions consisted of only several points at each energy, and the measurements did not extend very far in angle, there was considerable uncertainty in performing this operation. The observed differential cross-sections decreased approximately exponentially with angle, and consequently the extrapolation to small angles was

very sensitive to small experimental uncertainties and could lead to large errors. To avoid this, we took the smooth exponential curves which fitted the data points, and computed $d\sigma/d\Omega$ vs. θ curves using the relationships

$$d\Omega = 2\pi \sin\theta d\theta;$$

$$\frac{d\sigma}{d\theta} = 2\pi \sin\theta \frac{d\sigma}{d\Omega}$$

The plots of $d\sigma/d\theta$ vs. θ had the characteristic feature of passing through a maximum in the vicinity of 6° (for the reactions studied here), then falling rapidly to zero as 0° is approached. This results because the exponentially increasing cross-section at small angles is counterbalanced by a more rapidly decreasing solid angle. Thus integration of the area under the $d\sigma/d\theta$ curve minimizes the error which could result from uncertainties in extrapolation of the angular distribution to small angles. The uncertainty from extrapolation to large angles remains, however.

In this manner, the total cross-sections for evaporation residues were obtained and are presented in Table V. It is possible and highly informative to compare our cross-section results with the recent measurements reported by Kozub, et al.⁽⁶⁾. These authors have studied $\text{Al} + {}^{16}\text{O}$ (and several other systems) and identified evaporation residues by "conventional" counter telescope ΔE -E techniques, using an ultra-thin gas proportional counter for the ΔE measurement. Their result at 126 MeV is 960 ± 120 mb, which is to be compared with our value 949 mb at essentially the same energy. The agreement is phenomenal! At 105 MeV, Kozub, et al.⁽⁶⁾ measured 1040 ± 120 mb, whereas we find 1508 mb at 103 MeV. The agreement is clearly not as good here. These are the only experiments where there is overlap with other work, and so we cannot make a comparison

of our $\text{Cu} + {}^{20}\text{Ne}$ and $\text{In} + {}^{20}\text{Ne}$ cross-sections. The rather large values in the vicinity of 3b for $\text{Cu} + {}^{20}\text{Ne}$ are surprising and hard for us to believe as being correct, although we have not found any obvious error. The result for $\text{In} + {}^{20}\text{Ne}$ is more in line with expectations.

We would like to leave this discussion with the note that the experiments reported here involved a new technique, subject to a number of technical problems. We think we have solved the more obvious ones and have made checks wherever possible. However, our accumulated data leave something to be desired, and the results would certainly have benefited from measurements at larger angles and better counting statistics to reduce the uncertainties in the integrations.

We have performed an additional experiment in which a 3mm thick Si(Li) detector was placed in the scattering chamber at 45° to the beam, along with the ΔE -E anticoincidence counter telescope at more forward angles. The purpose of the experiment was to observe charged particles, particularly protons, emitted from fragments specifically identified as heavy evaporation residues. The system chosen was $\text{Al} + {}^{16}\text{O}$, and the signal requirements were ΔE in anticoincidence with E in the counter telescope, and the proton detector at 45° gated by the satisfactory identification of a heavy recoil nucleus. The three multichannel analyzers were used to store the ΔE anticoincidence spectra, the gated proton spectra, and also the ungated proton spectra. The top part of Fig. 14 shows ΔE anticoincidence spectra for $\text{Al} + {}^{16}\text{O}$ at 125 MeV, and one can see the same features and decrease with angle as seen previously for $\text{Cu} + {}^{20}\text{Ne}$. The lower part of Fig. 14 presents the gated proton spectra for $\text{Al} + {}^{16}\text{O}$ at 137 MeV. The two sets of data correspond to different angular locations,

as indicated, of the gating ΔE anticoincidence telescope. Thus the proton emission being recorded decreases drastically in intensity as the residual nuclei from which they are emitted decrease in number. Two additional checks were performed to verify the correlation between the proton spectra and the evaporation residues. A thin Al foil placed in front of the ΔE detector reduced the counting rate in the gated proton channel to near zero. Also, the ungated proton spectrum increased continuously with decreasing energy (no peak), and was about 25 times greater intensity in the vicinity of the peak in the gated spectrum (Fig. 14).

The most surprising result in Fig. 14 are the rather low energies of the emitted protons, being most probable in the vicinity of 1.3 MeV. As these protons are presumably emitted from residual nuclei with Coulomb barriers of about 4-5 MeV, one would expect to observe spectra which peak near the barrier. At the present time, the origin of the low energy protons remains a mystery.

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B. Production of Light Fragments in Heavy Ion Reactions: Be and B Isotopes from $^{12}\text{C} + ^{65}\text{Cu}$ at 126-MeV.

An experiment was carried out at the Yale HILAC to measure the formation cross-sections for selected light fragments from the bombardment of ^{65}Cu by ^{12}C at 126-MeV. The original motivation for the experiment was to determine if ^{12}B from ^{12}C had an unusually large cross-section, corresponding to the rather high value of 218 mb found by Weisfield, et al.⁽¹⁾ for the complementary reaction $^{65}\text{Cu}(^{12}\text{C}, \text{X})^{65}\text{Zn}$ studied by radioactivity measurements.

A target of isotopically separated ^{65}Cu was irradiated with 126-MeV ^{12}C ions, and emitted fragments were detected with a conventional counter telescope using particle-identification techniques.⁽²⁾ The telescope consisted of a 65 μm Si surface barrier ΔE detector followed by a 474 μm Si surface barrier E detector. The signals from the detectors were analyzed in a pair of 4096 channel ADC's and stored in coincidence in a 50 x 64 two dimensional array in a PDP-8/I computer, as well as being recorded event-by-event on magnetic tape for later processing. The scattering chamber and set-up used were that of the Columbia University Group⁽³⁾, and particular details of our experimental procedure are given elsewhere.⁽⁴⁾

The ΔE vs. E system provided excellent resolution of atomic elements from Li to C at the gain settings used in our experiment. Within the bands of constant Z in the ΔE vs. E arrays, individual mass numbers of Be and B could be separated with good statistical accuracy, enabling energy spectra and cross-sections to be derived for each isotope separately. Energy calibrations were obtained by measuring the elastic scattering of ^{12}C , ^{10}B , and ^{11}B beams of known initial energy from a thin Au target.

The differential cross-sections, obtained on a relative basis by integrating the charge of the primary beam in a Faraday cup, were converted to more accurate absolute values by comparison with the Rutherford scattering of ^{12}C from Au. This latter correction factor amounted to 17% and corresponded to beam current integrations which were too high. The average beam currents monitored during the runs were in the range 0.1-2.0 namps.

The experimental differential cross-sections and total formation cross-sections for Be and B isotopes are presented in Table VI. The total cross-sections were obtained by integration of the angular distributions, after conversion to $(d\sigma/d\theta)$ coordinates, following the procedure described in Section IIIA above and also in Ref. (4). Examination of the results in Table VI shows that the largest cross-section for fragment production is for ^{11}B , the product of a single-nucleon transfer reaction. The cross-sections for several nucleon transfer products, ^{10}B , ^{10}Be , and ^9Be are next in magnitude, being about one-half to one-fourth as large as the single nucleon cross-section. The observed ^7Be and ^{12}B are much rarer, corresponding to approximately 5 mb each.

It is apparent that the ^{12}B cross section is very much smaller than the 218 mb found by Weisfield, et al.⁽¹⁾ for ^{65}Zn production, and hence these two species are not correlated partners in a two body break-up process. Nor is it likely that a significant fraction of the 218 mb ^{65}Zn cross-section produces ^{12}B in highly excited states above the neutron binding energy, because the observed 58 mb cross-section for ^{11}B is not unusually large. As a check on the earlier ^{65}Zn measurement⁽¹⁾, we analyzed our ^{65}Cu target for induced ^{65}Zn radioactivity. The resulting ^{65}Zn cross-section, obtained after correcting for recoil loss and for

Table VI. Cross-Section Results for Be and B Isotopes
from $^{65}\text{Cu} + ^{12}\text{C}$ at 126-MeV.

Species Produced	Lab Angle (deg)	Differential Cross Section ($d\sigma/d\Omega$)(mb/sr)	Total Cross-Section σ (mb)
^7Be	11.2	11.6 ± 0.2	5.19 ± 0.23
	16.2	4.89 ± 0.10	
	20.9	2.34 ± 0.05	
	26.2	0.95 ± 0.02	
	30.9	0.44 ± 0.01	
^9Be	11.2	58.3 ± 1.2	26.3 ± 1.4
	16.2	24.7 ± 0.5	
	20.9	12.6 ± 0.3	
	26.2	5.39 ± 0.11	
	30.9	2.46 ± 0.05	
^{10}Be	11.2	34.7 ± 0.7	15.4 ± 0.7
	16.2	15.9 ± 0.3	
	20.9	7.39 ± 0.15	
	26.2	3.34 ± 0.07	
	30.9	1.57 ± 0.03	
^{10}B	11.2	59.4 ± 1.2	22.9 ± 1.9
	16.2	23.4 ± 0.5	
	20.9	9.32 ± 0.19	
	26.2	3.80 ± 0.08	
	30.9	2.70 ± 0.05	
^{11}B	11.2	135 ± 3	57.7 ± 3.2
	16.2	46.9 ± 0.9	
	20.9	16.3 ± 0.3	
	26.2	5.50 ± 0.11	
	30.9	2.57 ± 0.05	
^{12}B	11.2	10.1 ± 1.6	4.55 ± 0.59
	16.2	3.28 ± 0.07	
	20.9	1.18 ± 0.02	
	26.2	0.54 ± 0.01	
	30.9	0.13 ± 0.06	

decay of the ^{65}Ga parent, was 232 ± 30 mb, in good agreement with the previous work.

The data from this experiment are still being analyzed and will be discussed more fully at a later time.

References:

- (1) M. W. Weisfield, R. A. Williams, and A. A. Caretto, Jr., submitted to Phys. Rev.
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- (3) Y. Eyal, K. Beg, D. Logan, J. Miller and A. Zebelman, Phys. Rev. C8, 1109 (1973).
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Papers in Preparation

1. Angular Correlation of the 53 keV-13 keV Cascade in ^{73}Ge : Potential for High Resolution Hyperfine Interaction Studies, P. D. Johnston and M. Kaplan
2. A Mössbauer Effect Study of Magnetic Interactions in Ferric Chloride Hexahydrate, T. X. Carroll and M. Kaplan.
3. Hyperfine Interactions of Dilute Ferric Ions in Ice: Effect of Applied Magnetic Fields, T. X. Carroll, J. C. Love, and M. Kaplan.
4. Mössbauer Resonance Investigations of Antiferromagnetic Ordering and the Spin-Flop Transition in $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, P. D. Johnston and M. Kaplan
5. Mössbauer Resonance Studies of Fe^{3+} Ions in HNO_3 Frozen Solutions: Effect of pH and Magnetic Fields, P. D. Johnston, M. H. Newman, and M. Kaplan.