Time-dependent directional correlations of $^{199}Hg^m$ in liquid Hg, solid Hg, and $HgCl_2$†

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Time-directional correlations of the 374- and 158-keV γ rays of $^{199}Hg^m$ were studied with sources in the form of liquid Hg, frozen Hg, and dry crystalline $HgCl_2$. The time-dependent anisotropy in the liquid at room temperature shows no observable disturbance over several lifetimes. The integral anisotropy in the liquid indicates mixing of $E5$ with the predominantly $M4$ first γ ray with an $M4/E5$ mixing ratio $\delta = 0.092 \pm 0.015$. The half-life of the intermediate state was determined to be 2.47 ± 0.05 nsec. Time-dependent directional correlations in frozen emulsified Hg show a quadrupole interaction $eQ(\partial^2 V/\partial z^2)/h = 198 \pm 40$ MHz. The time-dependent coincidence rate in $HgCl_2$ shows a quadrupole interaction $eQ(\partial^2 V/\partial z^2)/h = 1271 \pm 30$ MHz. If the second γ ray is a rotational transition, the quadrupole moment of the intermediate state determined from the intermediate-state $E2$ lifetime can be combined with the nuclear-quadrupole-resonance frequency of ^{201}Hg in $HgCl_2$ to give a quadrupole moment for ^{201}Hg of 0.39 ± 0.02 b. This result is in excellent agreement with the value of 0.41 b obtained by Murakawa from the hyperfine structure of atomic mercury.

INTRODUCTION

The absolute determination of the nuclear quadrupole moment presents a difficult problem. Techniques such as nuclear magnetic resonance, nuclear quadrupole resonance, directional correlations, and molecular-beam spectrosocopy measure the quadrupole interaction $eQ(\partial^2 V/\partial z^2)/h$, where Q is the nuclear quadrupole moment and $\partial V/\partial z^2$ is the electric field gradient. Although these experiments are quite precise, there is usually no reliable way to calculate the field gradient, and therefore it is impossible to extract an accurate value of Q. From the present research, we are able to compare the results of two radically different measures of Q of a stable nuclide: the value derived from the radiative lifetime of a rotational state, and the value determined from atomic hyperfine structure.

The relationship is established in the following way. The time-dependent coincidence rate of the two γ rays of $^{199}Hg^m$ at 180° is measured with a source in the form of crystalline $HgCl_2$, yielding $eQ(199, \frac{5}{2})V_{zz}/h$. $Q(199, \frac{5}{2})$ is the quadrupole moment of the $\frac{5}{2}$ state of ^{199}Hg, and $V_{zz} = \partial^2 V/\partial z^2$, the electric field gradient at the Hg nucleus taken along the $HgCl_2$ symmetry axis. Using $Q(199, \frac{5}{2})$ determined from the $E2$ life time of the $\frac{5}{2}$ state, we determine V_{zz}. Combining this result with $eQ(201, \frac{3}{2})V_{zz}/h$ measured by nuclear quadrupole resonance on ^{201}Hg in $HgCl_2$, we obtain a value for $Q(201, \frac{3}{2})$. This $Q(201, \frac{3}{2})$ is then compared with $Q(201, \frac{3}{2})$ determined from atomic spectroscopy.

Hg is almost unique in having isotopes with the properties necessary to carry out the comparison described above. It is especially important that the upper state is long lived (44 min) so that the γ emissions proceed without chemical change. After β decay or electron capture, the atomic-electron structure must rearrange itself, and this rearrangement may produce undesirable interactions with the nuclear quadrupole moment.[1-3] Studies by Haas and Shirley[4] of the perturbations caused by electric quadrupole interactions for many nuclides, each in several environments, report results in metals showing little after effects of initial β decay or electron capture. Decays initiated from long-lived isomers such as $^{199}Hg^m$ yielded reliable results even in insulators. This work, which came to our attention after completion of our experiments, reports interaction frequencies in ^{199}Hg that are in agreement with ours.

APPARATUS

A fast-slow coincidence setup was used as shown in Fig. 1. The detectors are $1\frac{1}{2}\times1$-in. NaI(Tl) scintillators mounted on RCA 8575 photomultipliers. The fast discriminators are of the leading-edge type and the time-to-amplitude converter (TAC) is of the overlap type.[5] In the directional correlation runs, singles counts and the TAC spectra were punched out on the paper tape at the end of 2.5-min runs. Alternation of the position of the movable counter, the punchout of the data, and resetting of the scalers was performed automatically, taking 30 sec between runs with the detectors at 90° or 180°.

To calibrate the time scale, a random-coincidence TAC curve was produced by setting up separate ^{137}Cs sources in front of each detector, thus displaying any nonlinearity in the system. Two ^{60}Co prompt TAC coincidence curves were then taken with their centers displaced by accurately calibrated delay cables. Times were assigned to each channel according to the separation of the

prompt ^{60}Co curves and the weighting determined by a fit to a straight portion of the random-coincidence curve. We estimate the accuracy and stability of the time scale so determined to be 2%.

RESULTS FOR LIQUID Hg

Two samples of a few mg of enriched [199]Hg obtained from Oak Ridge National Laboratory were irradiated for 1.5 h at the MIT Research Reactor at a thermal-neutron flux of 2.2×10^{13} n cm^{-2} sec^{-1}. The activity produced was about 25 μCi/mg of [198]Hg. The liquid Hg was contained in polyethylene capillaries with inner diameters 0.013 and 0.012 in. and lengths 2.7 and 1.6 cm, respectively.

The time-dependent directional correlation was measured with the detectors 5 cm from the source at angles 90° and 180°.

The theoretical form of the directional correlation in liquids, in which the nucleus undergoes time-dependent quadrupole interactions, is given by[6,7]

$$W(\theta, t) = 1 + Q_{22} A_{22} G_{22}(t) P_2(\cos\theta)$$

$$+ Q_{44} A_{44} G_{44}(t) P_4(\cos\theta) + \cdots , \quad (1)$$

$$G_{kk}(t) = e^{-\lambda_k t}, \quad (2)$$

where the A_{kk}'s are the angular correlation parameters, the Q_{kk}'s are correction factors for the finite solid angles of the detectors, and the G_{kk}'s exhibit the time dependence in the directional correlation. For the decay of [199]Hg^m, only the P_2 and P_4 terms contribute, and $A_{22} \gg A_{44}$.

Defining the time-dependent anisotropy as

$$A(t) = [W(180°, t) - W(90°, t)]/W(90°, t) \quad (3)$$

we have

$$A(t) \approx \tfrac{3}{2} Q_{22} A_{22} G_{22}(t)/[1 - \tfrac{1}{2} Q_{22} A_{22} G_{22}(t)]. \quad (4)$$
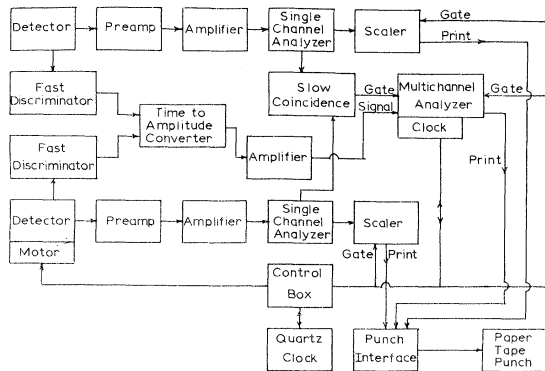

FIG. 1. Block diagram of directional correlation apparatus.

Since A_{22} is small (about 0.2), we obtain a further approximation from (2) and (4):

$$\lambda_2 \approx -\frac{1}{A(t)} \frac{dA(t)}{dt} . \quad (5)$$

The time-dependent anisotropies of four runs with data extending about 13 nsec were fitted to a straight line. The average of the fitted slopes was $dA/dt = -0.0015 \pm 0.0023$ nsec^{-1}, which corresponds to $\lambda_2 = 0.006 \pm 0.009$. This result is consistent with $\lambda_2 = 0$, i.e., no observable disturbance.

The integral anisotropy of these four runs was then examined. Following corrections for source length[8] and detector solid angle,[9] the following parameters were determined:

$$A = 0.303 \pm 0.010, \quad A_{22} = 0.184 \pm 0.006,$$

$$\quad (6)$$

$$A_{44} = -0.013 \pm 0.0029, \quad \delta_1 = 0.092 \pm 0.018.$$

A is the corrected anisotropy, and δ_1 is the $M4/E5$ mixing ratio of the 374-keV γ ray. In the interpretation of these results, we have considered the 158-keV γ ray to be pure $E2$.

The half-life of the 158-keV level of [199]Hg was determined. Natural Hg (10% [198]Hg) was activated by fast neutrons in the MIT Research Reactor. Each sample contained approximately 60 mg of Hg, and the activity obtained was about 14 μCi/mg or [198]Hg.

For these samples, the time-dependent coincidence rate with the detectors at 180° only was studied. The Hg samples were held flattened on cardboard or in a flattened polyethylene tube and were less than 0.014 in thick.

The average of fits to the four runs yields the half-life for the 158-keV level, $T_{1/2} = 2.47 \pm 0.05$ nsec. The quoted uncertainty is due to limitations in the absolute accuracy of our time scale. Our result is consistent with the presently accepted value[10] 2.38 ± 0.07 nsec and a more recent measurement[11] 2.49 ± 0.03 nsec.

RESULTS FOR FROZEN Hg

To ensure polycrystalline samples of frozen Hg, a method of emulsifying Hg was developed. A few mg of enriched [198]Hg were sealed in $\tfrac{1}{4}$-in.-i.d. polyethylene tubes along with mineral oil and benzoyl peroxide as the emulsifying agent.[12] The tube was then agitated by holding it against rotating rubber strips fastened onto a shaft held in a Dunmore flexible shaft drive. This procedure produced separated Hg drops about 50-μ in diameter. An x-ray photograph was taken of a bulk sample (several g) of frozen, emulsified Hg, which showed that the drops froze with random and independent orientation. Following emulsification, the Hg was

centrifuged into a pulled-out section of the tube about 0.010-in. i.d. The narrow section was cut out and sealed at the ends, and these samples were activated by fast neutrons, as above.

After activation, the Hg samples were held in a cold finger extending down from a liquid-nitrogen reservoir, and time-dependent directional corre- lations were performed with the detectors at 90° and 180°. The average of three such runs and the theoretical fit to that average is shown in Fig. 2. The average of the frequencies determined by fits to the individual runs yields the quadrupole inter- action in frozen Hg, $eQ(199, \frac{5}{2})V_{zz}/h = 198 \pm 40$ MHz.

RESULTS FOR $HgCl_2$

The time dependent coincidence rate of $^{199}Hg^m$ in $HgCl_2$ was studied with the detectors at 180°.

The sources were prepared following the pro- cedure detailed in Ref. 13. Natural HgO was ac- tivated by fast neutrons at the MIT Research Re- actor. The HgO was then dissolved in a solution of HCl and a few drops of H_2O_2, which was evap- orated to dryness. The resulting $HgCl_2$ was scraped onto a piece of cardboard and held in place by cellophane tape, keeping the diameter of the source less than 1 cm.

The sum of four runs along with the theoretical fit to that sum is shown in Fig. 3. The average of the frequencies determined by fits to the individual runs yields the quadrupole interaction in $HgCl_2$, $eQ(199, \frac{5}{2})V_{zz}/h = 1271 \pm 30$ MHz. This value is consistent with the results of Pound and Wertheim,[13] 1100^{+1750}_{-870} MHz, and of Haas and Shirley,[4] 1290 ± 80 MHz.
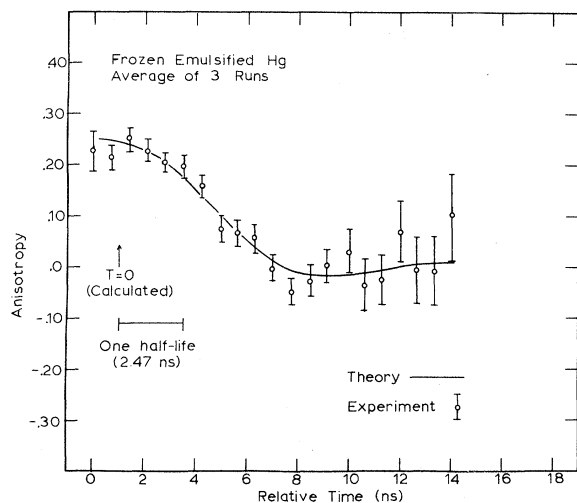
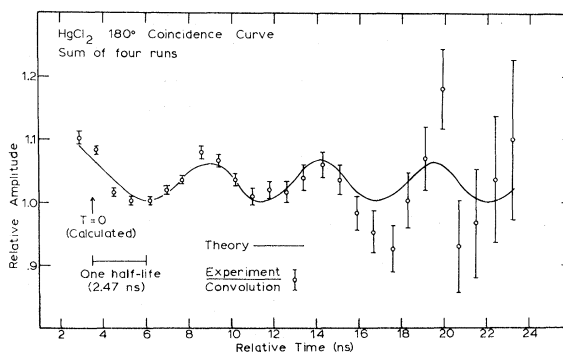FIG. 2. Time-dependent directional correlation of ^{199m}Hg in frozen emulsified Hg.

FIG. 3. Time-dependent coincidence curve for $^{199}Hg^m$ in $HgCl_2$. Plot of experimental data divided by the con- volution of a Gaussian and decaying exponential, and the theoretical curve for that plot.

DISCUSSION AND CONCLUSIONS

The time-dependent anisotropy in liquid Hg showed no observable disturbance in the interme- diate state, consistent with $\lambda_2 = 0$ [Eqs. (2)-(5)]. λ_2 is closely related to the quadrupolar relaxation time T_1 measured by NMR for ^{201}Hg in liquid Hg. The theoretical relationship between these quanti- ties is given by[6,14] $1/\lambda_2 = T_1/2.03$, where we have used $Q(201, \frac{3}{2}) = 0.39$ b and $Q(199, \frac{5}{2}) = 0.70$ b. At room temperature,[15] $T_1 = 22 \pm 1$ μsec, yielding a predicted value $\lambda_2 = 8.3 \times 10^{-5}$ nsec^{-1}. This λ_2 is consistent with our result and even more strongly predicts no observable disturbance of the time- dependent anisotropy in the liquid.

The results for the integral anisotropy in liquid Hg are consistent with those of Pound and Wertheim.[13] If the first transition were pure $M4$, then the di- rectional correlation parameters would be $A = 0.362$, $A_{22} = 0.2207$, and $A_{44} = -0.01796$. The reduction of the anisotropy A to its present value 0.303 could most likely arise either from $M4/E5$ mixing of the 374-keV γ-ray or disturbance of the intermediate state; the latter possibility is ruled out by the directional correlation and NMR results in liquid Hg.

The frozen-Hg anisotropy yielded $eQ(199, \frac{5}{2})V_{zz}/h = 198 \pm 40$ MHz. From studies of the integral anisotropy in frozen Hg, Pound and Wertheim[13] obtained $eQ(199, \frac{5}{2})V_{zz}/h = 396 \pm 98$ MHz. [We have corrected an error in their calculation of eQV_{zz}/h and also used the present value 2.47 nsec for the half-life of the 158-keV state rather than the value they used (2.35 nsec) to interpret their data.] Our integral correlation is consistent with the present value of eQV_{zz}/h, and in any case the time- dependent data should be more reliable than the integral correlation. Several runs were also made with frozen unemulsified Hg, and one in particular showed strong indications of a high degree of crys-

talline orientation. Since Pound and Wertheim used unemulsified Hg in their experiments, a resulting oriented crystalline structure, rather than the randomly oriented microcrystalline source they assumed, might lead to a misinterpretation of their results. The more recent experiments by Haas and Shirley yielded a value of 210 ± 20 MHz, which is consistent with the present result. They do not state the physical form of their sample, however.

Combining the value for the quadrupole interaction of $^{199}Hg^m$ in frozen Hg with the directional correlation results for $^{199}Hg^m$ in $HgCl_2$, we can predict for the nuclear-quadrupole-resonance (NQR) frequency of ^{201}Hg in the frozen metal:

$$f_{NQR} = \tfrac{1}{2}eQ(201, \tfrac{3}{2})V_{zz}/h = 55 \pm 11 \text{ MHz.} \qquad (7)$$

A search for this resonance was made from 7 to 300 MHz without success.[16] Low-temperature specific-heat measurements have found no contribution from quadrupole hyperfine structure.[17] The absence of such a contribution implies an upper limit of 15 MHz to the quadrupole resonance frequency. The NQR is difficult in this case because of the low g factor of Hg and the fact that the sample is metallic. The present experiment suggests a further search using frozen emulsified Hg in the 30—70-MHz range.

Our results in $HgCl_2$ can be used to compute a value for the quadrupole moment of the ground state of ^{201}Hg. From the half-life, 2.47 ± 0.05 nsec, of the 158-keV state of ^{199}Hg and the conversion coefficient of the 158-keV γ ray,[18] $\alpha = 0.94 \pm 0.09$, we can use the model of Bohr and Mottelson[19] to compute $|Q(199, \tfrac{5}{2})| = 0.70 \pm 0.02$ b. Combining this result with the quadrupole interaction $eQ(199, \tfrac{5}{2})V_{zz}/h = 1271 \pm 30$ MHz and $eQ(201, \tfrac{3}{2})V_{zz}/h = 708$ MHz determined by NQR or ^{201}Hg in $HgCl_2$ at room temperature,[20] we obtain $Q(201, \tfrac{3}{2}) = 0.39$

± 0.02 b. The positive sign has been chosen to agree with the spectroscopic result, which has been determined by Murakawa[21] to be 0.41 b. His calculations include a 10% Sternheimer shielding correction which accounts for a reduction of the value from 0.45 b. Since our experiment is a completely independent way of measuring $Q(201, \tfrac{3}{2})$, the agreement supports Murakawa's calculations.

A recent experiment related to our technique was performed by Raghavan and Raghavan.[22] They studied the time-dependent 180° coincidence rate of the 89- and 345-keV γ rays of ^{117}In following the β decay of ^{117}Cd. From considerations similar to ours, they obtain the quadrupole moment $|Q(117, \tfrac{3}{2})| = 0.636$ b of the 659-keV level of ^{117}In from its rotational lifetime, and 0.64 ± 0.04 b indirectly from the ground-state Q of ^{115}In. The latter is computed from atomic-hyperfine-structure measurements, and includes a 3.4% Sternheimer correction. They used their result to confirm the rotational nature of the 659-keV level of ^{117}In; assuming that level is rotational, the argument can be reversed to support the techniques of the evaluation of Q of ^{115}In from atomic hyperfine data.

Thus the present experiment and the one by Raghavan and Raghavan support the calculation of nuclear quadrupole moments from atomic hyperfine structure. In the case of ^{201}Hg, the shielding correction is necessary to achieve agreement between the spectroscopic Q and the Q determined indirectly from the directional correlation data.

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