Lawrence Berkeley National Laboratory
Recent Work

Title
MEASUREMENTS OF THE LIFETIMES OF THE FIRST EXCITED STATES OF Na, K, Rb, AND Cs BY MEANS OF THE PHASE SHIFT METHOD

Permalink
https://escholarship.org/uc/item/3451304k

Author
Link, John K.

Publication Date
1966

eScholarship.org Powered by the California Digital Library
University of California

UCRL-16640

University of California

Ernest O. Lawrence Radiation Laboratory

MEASUREMENT OF THE LIFETIMES OF THE FIRST EXCITED STATES OF Na, K, Rb, AND Cs BY MEANS OF THE PHASE SHIFT METHOD

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545

Berkeley, California

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

Submitted to the Journal of the American Optical Society UCRL-16640

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract W-7405-eng-48

MEASUREMENT OF THE LIFETIMES OF THE FIRST EXCITED STATES OF Na, K, Rb, AND Cs BY MEANS OF THE PHASE SHIFT METHOD

John K. Link

January 1966

Measurement of the Lifetimes of the First Excited States of Na, K, Rb, and Cs by Means of the Phase Shift Method

John K. Link

Inorganic Materials Research Division,
Lawrence Radiation Laboratory and
Department of Chemistry, University of California,
Berkeley, California

The lifetimes of the first excited states of the elements Na, K, Rb, and Cs were measured using the phase shift method described by Brewer et al.[1] The data were taken over a wide range of vapor densities to allow the effects of radiation entrapment and of scattered exciting light to be taken into account. The following values were obtained: Na $3p\ ^2P$ 16.1 ± .3 nsec, K $4p^2P$ 27.8 ± .5 nsec, Rb $5p^2P_{3/2}$ 27.0 ± .5 nsec, and Cs $6p^2P_{3/2}$ 30.5 ± .7 nsec.

INTRODUCTION

The main advantage of the direct determination of the lifetime of an excited electronic state over other techniques for measuring atomic transition probabilities such as the hook method,[2] the method of magneto-rotation,[3] the atomic beam method,[4] or the equivalent width method[5] is that it is not necessary to know the vapor density of the species being studied.

With this version of the phase shift technique, the state being studied is optically excited with intensity modulated light for which the period of modulation is of the order of ten times the lifetime being studied. The phase shift between the exciting light and fluorescent light $\Delta\phi$, is related to the lifetime, τ, by the expression $\tan \Delta\phi = \omega\tau$, where ω is the radial frequency of the exciting light.

THE APPARATUS

Figure 1 shows the optical system drawn to scale with a 10 to 1 reduction along the optic axis. The ultrasonic grating is identical with that described by Brewer et al[1] except that the lenses L_2 and L_3 are cemented directly to the walls of the tank providing 3 cm apertures. The tank is filled with a 19% ethanol, 81% water mixture as mentioned by Demtröder[6] to minimize temperature variation of the wave velocity. Light from the source was focused on the aperture stop, ST, by L_1. The aperture stop was 1.6 cm in diameter. L_4 then focused the image of the aperture stop into the center of the fluorescent cell. Osram spectral lamps were used for light sources. Filter, F, was used to isolate the emission line of interest.

In order to maximize the fluorescent to scattered light ratio (I_f/I_s) it is necessary to avoid using exciting lines which are self-reversed. The Cs and Rb resonance lines, emitted from Osram lamps run according to manufacturer's specifications, are appreciably self-reversed. The Cs and Rb lamps were modified by removal of the outer glass envelopes and excited by microwaves at 2450 Mc using an umbrella shaped exciter. The level of microwave power was adjusted to give maximum percent absorption when the light was passed through the fluorescent cell, heated to give a vapor density of about 10^{-5} torr of absorbing atoms. The Na and K lamps were run near rated power by a square wave generator, thus greatly reducing low frequency ripple in the outputs.

The multiple slits G_1 and G_2 were located at the focal points of L_2 and L_3 and were adjusted to minimize the light passing through the system when the ultrasonic grating was turned off. Thus, light from the zeroth diffraction order was rejected. Modulation ratios (transmitted light at 5.2 Mc/total transmitted light) of 0.5 were easily obtained. This arrangement with the multiple slits and short focal length lenses gave a greatly increased optical speed over that reported by Brewer et al.[1]

The glass plate, GP, was so located that the whole cross section of the light beam was sampled by the reference photomultiplier. The modulated light output of the tank was maximized by adjusting the wave reflector R.

RCA 7265 photomultipliers with a S 20 spectral response and 5 cm photocathodes were used for Na, K, and Rb. In the case of Cs the 7265 tubes have too little response at 8521 Å to be useful; so RCA 7102 photomultipliers were used which had S 4 spectral response and 3.2 cm photocathodes. Cooling the 7102 tube with a stream of cold N_2 gas, obtained

by placing a heater in a Dewar of liquid N_2, reduced the dark current by a factor of 200 but the level was still high enough to make measurement of lifetimes at a fluorescent to scattered light ratio of less than one impossible. For Rb, at 7800 Å, the 7265 tube gave a much better signal to dark current ratio then the 7102 tube.

Figure 2 gives a block diagram of the electronics. The 5.206 Mc signals are mixed with 5.205 Mc signals to give signals at 1 kc which contain the same phase information. The use of quartz crystal oscillators and feedback control produces a 1 kc signal which is stable to ± 1 cps. This procedure greatly reduces stray capacitance problems and allows use of high gain narrow bandpass amplification at 1 kc. The phase null is attained when the two signals are 90 degrees out of phase. The clipping to square waves of the 1 kc signals prior to detection which was used by Brewer et al[1] was eliminated to keep the operation of the null detector as amplitude independent and reproducible as possible. Phase differences of 0.2 degrees (0.1 nsec at 5.2 Mc) on clean 15 volt peak to peak signals could be detected. The calibrated phase shifters were carefully checked and any systematic errors they might have introduced were less than 1 percent of the lifetimes reported here.

EXPERIMENTAL TECHNIQUES

Na, K, Rb, and Cs were distilled into large pyrex cells with five cm. windows. The cells were sealed off from the vacuum line at residual gas pressures of about 5×10^{-4} torr. At no time was there any indication that the residual gas pressures inside the sealed cells was causing any

lifetime reduction through quenching. Hulpke et al[7] obtained a cross section of 37×10^{-16} cm^2 for quenching of the $3p^2$ P state of Na by N_2, which would imply that no quenching could be observed at pressures of N_2 less than .05 torr.

The main body of each cell was wrapped with a layer of asbestos paper, heating wire, and an outer layer of asbestos. A finger extending below the main part of the cell was maintained at a cooler temperature than the windows to prevent condensation of the vapor on the windows. Data were taken over a range in vapor pressures between about 10^{-8} and 10^{-5} torr of the fluorescing species. It was hoped when this work was initiated that it would be possible to control the vapor density of the metal merely by fixing the bottom of the finger as the coolest part of the cell. However this proved to be impractical as the vapor densities were so low that the rate of mass transport was very slow. Also the alkali metals tend to adhere to pyrex and further slow the attainment of equilibrium. For example, it was observed with Rb that high densities (10^{-5} torr) would persist in the main part of the cell for many hours if the main part of the cell were heated to over 100°C with the finger placed in a Dewar of liquid N_2. In practice the vapor density in the cell could be varied at will by controlling both finger and cell body temperatures, but no attempt was made to actually determine the vapor density from the cell temperatures.

Cells with cylindrical construction and cells with a curved Wood's horn in place of the exit window were used. The cells with Wood's horn exit windows[8] showed no reduction in light scattering as compared to

the cylindrical cells. In either case the observing photomultiplier was so positioned that no directly scattered light from either exit or entrance window could reach its face.

EXPERIMENTAL PROCEDURE

The light source and light modulator were left on long enough before actually taking data to insure that the amplitude of modulated light didn't drift more than 30% over the course of a run (two hours). This allowed the gain in the reference channel to be held constant throughout a single run.

Data points were obtained in the following way: The fluorescent cell was placed in front of the sample photomultiplier and the photomultiplier voltage adjusted to give the standard 1 kc sample signal (15 volts peak to peak) on the chart recorder. The sample photomultiplier voltage, sample signal size, and reference signal size (on the chart recorder) were recorded. The phase difference, $\Delta\phi_f$, between reference and sample signals was measured. The fluorescent cell was then removed and an identical cell containing a dilute MgO scattering sol was put in exactly the same position. The photomultiplier voltages and amplifier gain controls were held constant. Neutral density filters were inserted in the filter holder in front of the sample photomultiplier until the standard 1 kc signal size was obtained. Then the scattering sol to reference phase difference, $\Delta\phi_o$, was read. The difference in these two phase readings, $\Delta\phi_f - \Delta\phi_o$, was then used to calculate the lifetime τ_m. The gain of the sample photomultiplier as a function of voltage was

calibrated and used with the sample-to-reference 1 kc signal ratios to put the sample signals, for each point of a single run, on the same relative amplitude scale.

Tests showed that the measured sample channel to reference channel phase difference remained constant to less than 0.2 degrees (0.1 nsec) while the sample signal size was varied between 20 and 10 volts peak to peak. This variation was achieved by keeping the photomultiplier voltage and amplifier gain controls fixed and varying, by means of neutral density filters, the amount of light striking the photocathode. This meant that the variation of measured phase difference with photomultiplier current or with signal size, as mentioned by Müller et al,[9] was not a problem if the sample signal size was kept in the right range and the light flux striking the photocathode was adjusted to be the same for both sol and fluorescent phase readings. The identity of the sol and fluorescent geometries eliminated errors due to variation in photocathode illumination geometry and due to variation in the phase of the exciting light (~10 degrees) across the diameter of the spot focused in the center of the fluorescent cell. Variation of phase due to different electron transit times with different photomultiplier voltages was eliminated by reading sol and fluorescent phases at a fixed multiplier voltage. The two phase difference readings required for each data point were always taken within less than two minutes of each other to eliminate any errors due to slow phase drifts in the electronics or in the temperature of the modulator liquid.

THE SPEED OF LIGHT

The speed of light was measured by using a helium-neon laser for a light source. The small angular divergence in the lasar beam allowed use of a 660 cm difference in optical path corresponding to a phase difference of about 41 degrees. Frosted glass plates were placed directly in front of the photomultipliers to diffuse the small spots of laser light and thus to minimize variation in photocathode illumination as the optical path was varied. Measured values for the speed of light were always within 1% of the accepted value.

TREATMENT OF DATA

Lifetime measurements were taken over a range of fluorescent intensities starting with pure scattered exciting light (when the vapor pressure in the cell was well below 10^{-8} torr) to the point where the measured lifetime began to increase markedly due to radiation entrapment. The following expression for the effect of scattered exciting light can be obtained from the relations given by Brewer et al.[8]

$$\tau = \tau_m \left(\frac{1 - \frac{I_s}{I_f+I_s} \frac{\operatorname{Sin} \Delta\phi_s}{\operatorname{Sin} \Delta\phi_m}}{1 - \frac{I_s}{I_f+I_s} \frac{\operatorname{Cos} \Delta\phi_s}{\operatorname{Cos} \Delta\phi_m}} \right) \qquad (1)$$

Where τ is the true lifetime, τ_m the measured lifetime, I_s is the intensity of scattered light, I_f the intensity of fluorescent light, $\Delta\phi_s$ is the difference in phase between the scattered light and that of the whole exciting light beam, and $\Delta\phi_m$ is the difference in phase between the exciting light beam and that of the sum of scattered and fluorescent signals. In general, $\Delta\phi_s$ will not be zero because the scattering process doesn't necessarily give a representative sampling to the whole exciting light beam, which has phase variations of about 10 degrees over its cross section. Variations in $\Delta\phi_s$ from -2 to +3 degrees were observed but careful focusing of the optics usually reduced it to less than 1 degree.

Figure 3 shows a representative set of uncorrected τ_m values for K plotted against $1 + \frac{I_f}{I_s}$. The theoretical curve was obtained from equation (1) with $\Delta\phi_s = 0$, $\tau = 27.8$ nsec, and $\frac{I_f}{I_s}$ set equal to 0.06 when $\tau_m = 0$. τ_m values near $1 + \frac{I_f}{I_s} \simeq 35$, where the effects of entrapment first become evident, are about 3% larger than they would be in the absence of entrapment. No attempt was made to correct for entrapment and points in that region were not used to calculate the true lifetime.

The range of $(1 + I_f/I_s)$ which is free of entrapment is determined by the following considerations: the shape of the exciting line (ratio of total light to light capable of exciting fluorescence), how much scattering occurs in the cell due to dirt and imperfections on the windows, and the shape of the absorption line (the greater the Doppler width and the greater the number of separated hyperfine structure and isotope components the greater the range of $(I_f/I_s + 1)$ before entrapment sets in). With a range free of entrapment of 35, the correction obtained from equation (1) is not more than 4 percent for points with values of $(1 + I_f/I_s)$ immediately below the entrapment region.

It should be noted that the actual intensity of fluorescence, I_f, is directly proportional to the density of fluorescing atoms only when the amount of exciting light which is absorbed and therefore fluoresced is directly proportional to the density of atoms. This will be true when the absorption from a Doppler profile exciting line can be described by the first (linear) term in the curve of growth analysis given by Kopfermann and Wessel.[10] For K, with an f value of 0.63 for the 7669 Å line, the fluorescent intensity should be linearly related to the atom density (to an accuracy of 5 percent) up to a potassium atom pressure of 5×10^{-7} torr. In Figure 3 this means that the range between $\tau_m = 5.6$ nsec and the beginning of entrapment; i.e., between $(1 + I_f/I_s) = 1.40$ and $(1 + I_f/I_s) = 35$, represents a variation of I_f, and therefore the density of K atoms, over a factor of 85. Data for the other elements was obtained over similar ranges.

RESULTS

The lifetime of a state m is related to the various depopulating transitions by the relation

$$\tau_m = \frac{1}{\sum_n A_{mn}} \qquad (2)$$

where the sum over n covers all states which are lower than state m in energy. The f value for absorption from state n to state m, f_{nm}, is related to the transition probability for spontaneous emission A_{mn} by the following relation:

$$f_{nm} = \frac{g_m \lambda^2 A_{mn}}{g_n 8\pi^2 c r_o} \qquad (3)$$

Table I

Experimental Lifetimes

	$\tau \times 10^9$ sec $^2P_{3/2}$	$\tau \times 10^9$ sec $^2P_{1/2}$	$f_{1/2-3/2}$	$f_{1/2-1/2}$	Other Values $\tau \times 10^9$sec $^2P_{3/2}$	Author
Na	16.1 ± .3	16.1 ± .3	.650	.325	16.1 ± .6 15.9 ± .4 13.6 ± .5	Stephenson[11] Hulpke et al[7] Ostrovskii and Penkin[12]
K	27.8 ± .5	27.8 ± .5	.639	.318	27.1 ± .9 25.5 ± .8	Stephenson[11] Ostrovskii and Penkin[13]
Rb	27.0 ± .5	28.1 ± .5	.675	.335	27.8 ± .9 22.7 ± .3	Stephenson[11] Gol'dberg[14]
Cs	30.5 ± .6	34.0 ± .6	.732	.362	33.8 ± 3.4 28.0 ± .3	Minkowski and Mühlenbruch[15] Kvater & Meister[16]

where g_m and g_n are the statistical weights of the upper and lower states respectively, λ is the wavelength of the transition, c is the speed of light, and r_o, the classical radius of the electron is 2.82×10^{-13} cm. For the resonance transitions in the alkali metals the depopulating transition is unique so τ can be calculated from f_{nm} directly.

For sodium and potassium, the two D-lines were not resolved when measuring the lifetime. For sodium the relative f values for the two lines reported by Kvater[16] indicate that the lifetimes of the $3\ ^2P_{1/2}$ and $3\ ^2P_{3/2}$ states are the same to the accuracy of this experiment. For potassium the hook method results of Rozhdestvenskii quoted by Ostrovskii and Penkin,[13] $f_{7669}/f_{7699} = 1.976$, again imply that the lifetimes of the two upper states are equal to within 1%.

The hook method determines Nf for a given transition, where N is the number density of atoms in the lower state. For two transitions arising from a common lower state, as in the alkali metals, the ratio of f values can be determined without knowing either the vapor density or the temperature of the absorbing gas column, which are the major sources of systematic error. For these reasons relative f values obtained by the hook method were used in the cases of Rb[14] and Cs[16] to compute the lifetime for the unmeasured $^3P_{1/2}$ state from the measured lifetime of the $^3P_{3/2}$ state.

The last two columns in Table I give the results obtained by other investigators. Stephenson[11] used a modification of the magneto-rotation method which does not require precise knowledge of the vapor density. Hulpke et al[7] used a phase shift technique quite similar

to the one employed in this work. Ostrovskii and Penkin[12,13] used a combination of the hook method with measurement of total absorption. Gol'dberg[14] and Kvater and Meister[16] employed just the hook method and so their results require use of vapor pressure data to obtain absolute f values. Minkowski and Mühlenbruch[15] used magneto-rotation in the usual way and thus required vapor pressure data. In cases where the papers cited do not directly report lifetimes, equations (2) and (3) were used to convert reported f values to lifetimes.

Both Kvater and Meister[16] and Minkowski and Mühlenbruch[15] measured the product Nf as a function of temperature for the cesium resonance transitions. However, they used somewhat different vapor pressure curves to calculate absolute f values. To make a meaningful comparison between their results, the thermodynamic data on cesium given by Hultgren et al[17] was used to calculate vapor densities as a function of temperature. These densities were then used to recalculate absolute f values from the Nf values reported by the two sets of authors. After this adjustment, the absolute f values of Minkowski and Mühlenbruch were still 18% less than those of Kvater and Meister, well beyond the reported probable errors. The recalculated absolute f values were not significantly different from those originally reported.

ACKNOWLEDGEMENT

This work was performed under the auspices of the United States Atomic Energy Commission.

BIBLIOGRAPHY

1. L. Brewer, C. G. James, R. G. Brewer, F. E. Stafford, R. A. Berg, and G. M. Rosenblat, Rev. Sci. Instr., 33, 1450 (1962).

2. E. W. Foster, Reports on Prog. in Phys., 512 (1963).

3. A. C. G. Mitchell and M. W. Zemansky, Resonance Radiation and Excited Atoms, Cambridge University Press, New York, New York, 1961.

4. G. D. Bell, H. M. Davis, R. B. King, and P. M. Routly, Ap. J., 129, 775 (1958).

5. F. B. Estabrook, Ap. J., 113, 684 (1950).

6. W. Demtröder, Zs. f. Phys., 166, 42 (1962).

7. E. Hulpke, E. Paul, and W. Paul, Zs. f. Phys., 177, 257 (1964).

8. L. Brewer, R. A. Berg, and G. M. Rosenblatt, J. Chem. Phys., 38, 1381 (1963).

9. A. Müller, R. Lumry, and H. Kokubun, Rev. Sci. Instr., 36, 1214 (1965).

10. H. Kopfermann and G. Wessel, Zs. f. Phys., 130, 100 (1951).

11. G. Stephenson, Proc. Phys. Soc., London, A 64, 458 (1951).

12. Yu. I. Ostrovskii and N. P. Penkin, Optics and Spectroscopy, 11, 1 (1961).

13. Ibid., 12, 379 (1962).

14. G. I. Gol'dberg, Izvestiya Glaunoi Astronomicheskoi Obser., 20 (156), 126 (1956).

15. R. Minkowski and W. Mühlenbruch, Zs. f. Phys., 63, 198 (1930).

16. G. S. Kvater and T. G. Meister, Vestnik Leningradskogo Universiteta, 9, 137 (1952).

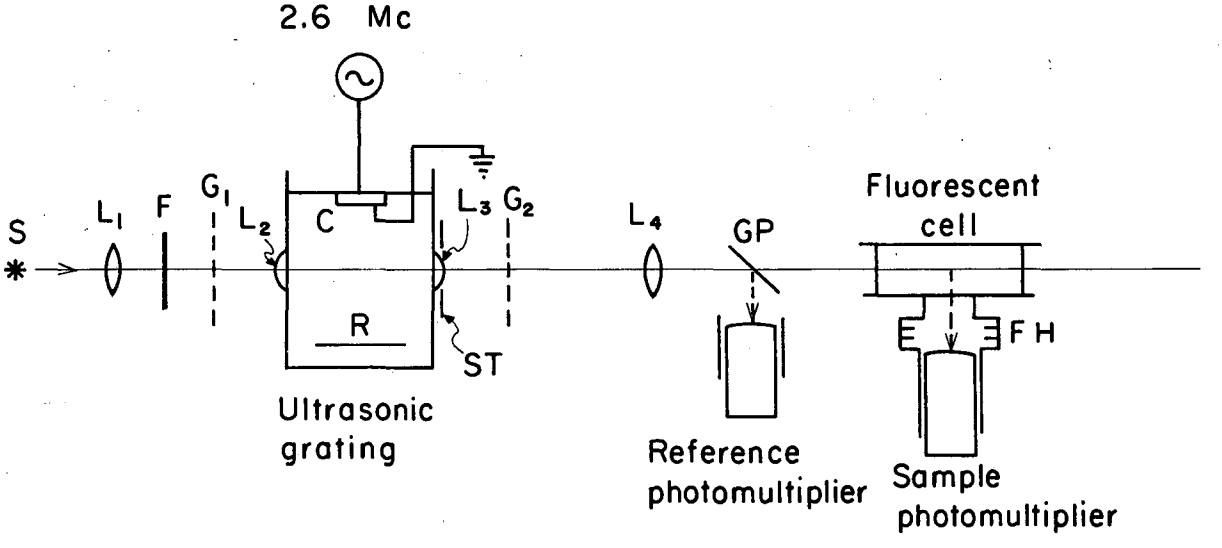
17. R. Hultgren, R. L. Orr, P. D. Anderson, and K. K. Kelly, Selected Values of Thermodynamic Properties of Metals and Alloys, John Wiley & Sons, Inc., New York, New York, 1963.

FIGURE CAPTIONS

Figure 1. Optical system, top view, drawn approximately to scale with 10 to 1 reduction along optical axis. S, light source; L_1, L_2, L_3, and L_4, lenses, focal lengths 5, 14.5, 14.5, 20 cm respectively; G_1 and G_2, multiple slits 0.81 mm wide, spaced by 0.96 mm; GP, glass plate; R, reflector; C, quartz crystal; F, light filter; FH, filter holder; ST, aperture stop.

Figure 2. Black diagram of electronic system.

Figure 3. Experimental τ_m values for the $4p\ ^2P$ state of K.



MUB-9344

Fig. 1

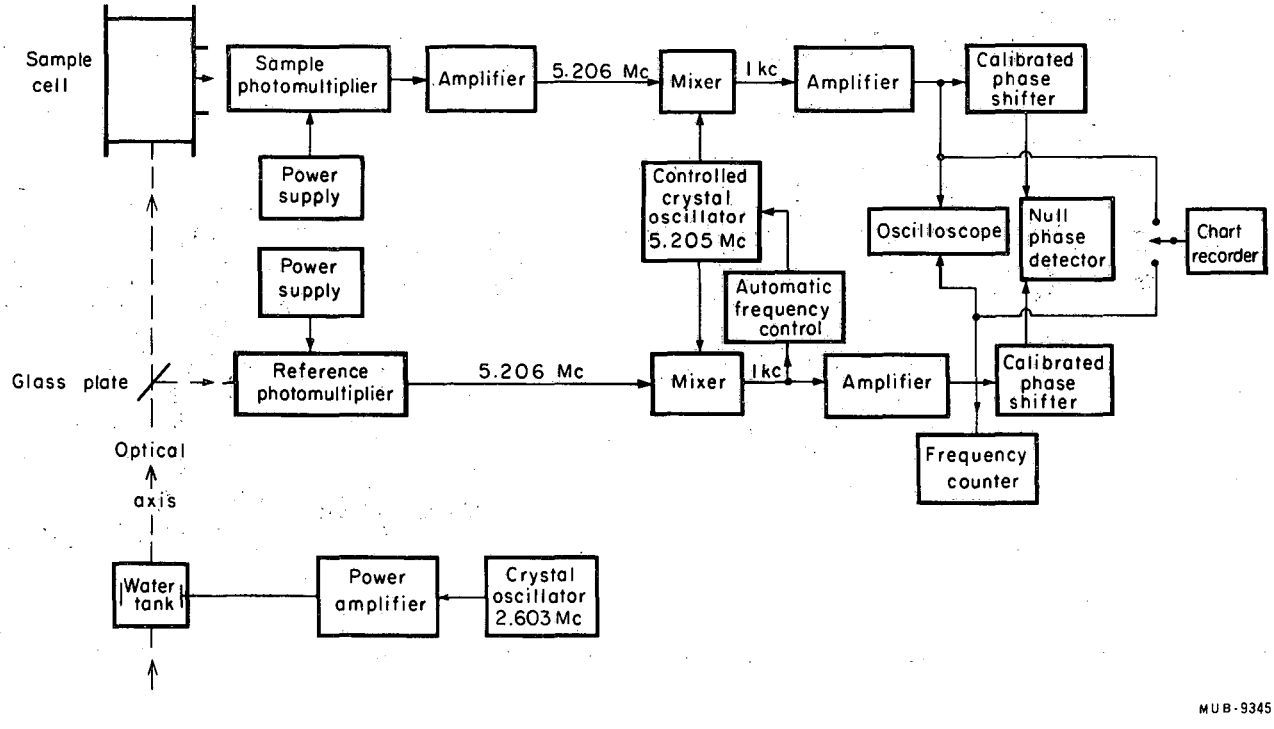
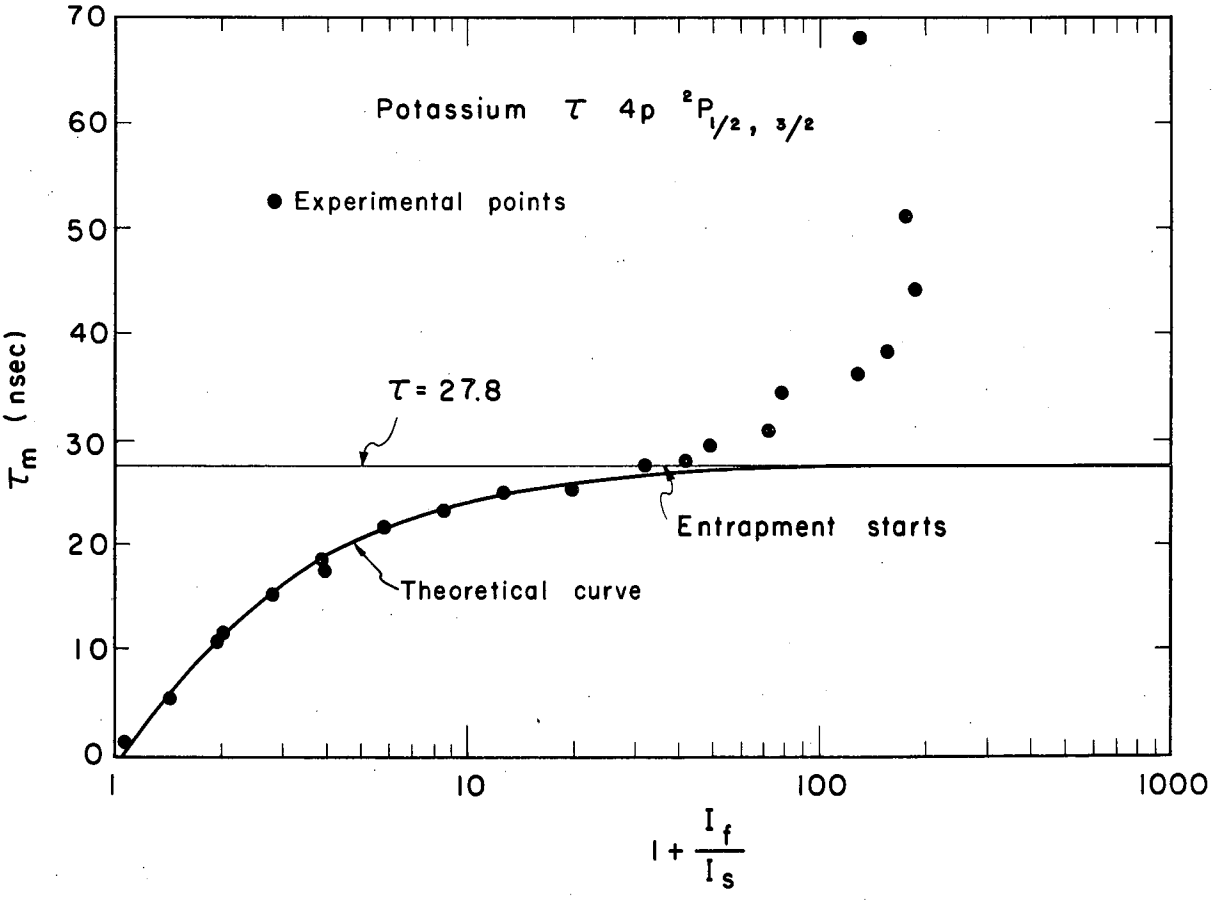

Sample cell
Sample photomultiplier
Amplifier
5.206 Mc
Mixer
1 kc
Amplifier
Calibrated phase shifter
Power supply
Controlled crystal oscillator 5.205 Mc
Oscilloscope
Null phase detector
Chart recorder
Power supply
Automatic frequency control
Glass plate
Reference photomultiplier
5.206 Mc
Mixer
1kc
Amplifier
Calibrated phase shifter
Frequency counter
Optical axis
Water tank
Power amplifier
Crystal oscillator 2.603 Mc
MUB-9345

Fig. 2



MUB-9343

Fig. 3

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.