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HELIUM RESEARCH CENTER

INTERNAL REPORT

DETECTION AND LIFETIME MEASUREMENTS OF METASTABLE SPECIES OF XENON,

KRYPTON, AND ARGON IN RARE GAS CRYSTALS

BY

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BRANCH ___Fundamental Research___

PROJECT NO. ___4336___

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ABSTRACT

Experimental procedures are described for (1) detecting metastable species of xenon, krypton, and argon in rare gas crystals, and (2) measuring their mean lifetimes in the same environment.

A low-temperature vessel has been designed and tested within which the sample crystal is contained, and in which an electric glow discharge can be maintained for the purpose of exciting the crystal. Both a synchronized mechanical shutter system, and an electronically-gated photomultiplier tube circuit for use in the lifetime measurements of the metastable species are described.

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DETECTION AND LIFETIME MEASUREMENTS OF METASTABLE SPECIES OF
XENON, KRYPTON, AND ARGON IN RARE GAS CRYSTALS

BY

Earl H. Ollmore[1], Thomas O. Meyer[2], and William R. Beaton[3]

ABSTRACT

Experimental procedures are described for (1) detecting
metastable species of xenon, krypton, and argon in rare gas
crystals, and (2) measuring their mean lifetimes in the same
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A low-temperature vessel has been designed and tested with-
in which one sample crystal is contained, and in which an electric
glow discharge can be maintained for the purpose of exciting the
crystal. Both a synchronized mechanical shutter system, and an
electronically-gated photomultiplier tube circuit for use in
the lifetime measurements of the metastable species are described.

INTRODUCTION

Atoms and molecules can exist in a variety of excited states resulting from differing configurations of the electrons assor ciated with the species involved. Among such states are those described as "metastable" because they can persist in favorable environments for relatively long periods of time, whereas states described as "unstable" decay in fractions of microseconds, regardless of the environment.

Atoms of the helium group gases can exist in states of both types. Helium itself is a classic example in that its set of metastable and unstable energy states, also called "levels" or "terms," do not combine with one another, that is, no spectral lines are observed in the spectrum of helium corresponding to a transition from a metastable to an unstable level or vice versa. (6)$\underline{4/}$. Two apparently unrelated spectra result, and for this

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4/ Underlined numbers in parentheses refer to references at the end of this report.

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reason it was at one time supposed that two forms "orthohelium" and "parahelium," existed. Quantum theory predicts, however, the existence of these two sets of levels or "terms" for a helium atom, and that intercombinations will not occur (14). These sets are termed "triplet" and "singlet" respectively according to their experimentally observed multiplicities.

Although the spectra of neon, argon, krypton, and xenon are basically like that of helium, important progressive differences appear. As in helium, two distinct sets of levels exist, but intercombinations between these levels can occur and are increasingly allowed as the atomic weight increases. The spectra are more complicated as a result and have required more effort for inter- ruption. Theoretical treatments of any of these systems are much more difficult than for helium.

Several studies have been carried out in which lifetimes of the metastable species of rare gas atoms have been measured ([5], [10], [11]). Without exception, these data have been obtained for the species in the gas phase and for the purpose of determining the processes that account for the destruction of the metastable species themselves. The mean lifetime for an isolated helium atom in the 2^3S level has been calculated by Mathis to be 10^5 seconds, but no experimental check exists ([7]). Similar calculations for any of the other rare gas atoms evidently do not exist.

It is with the intent of detecting metastable atoms of the helium group gases and of measuring their mean lifetimes in envi- ronments approaching isolation that the current research has been undertaken. Measurements on isolated species are not possible; nevertheless, if one desires to observe intrinsic properties of a species, it should be in an environment such that there is a minimum of energy exchange with that environment. For the rare

gas atoms the only appropriate choice is a crystal of another rare gas with a higher set of energy levels.

GENERAL CONSIDERATIONS

If the metastable species of interest is to be maintained in the environment of another rare gas crystal of higher energy levels, then the number of pairs of rare gases that may be studied will be reduced from the total number of unrestricted combinations possible. From figure 1 it can be seen that the $1s_3$ and $1s_5$ levels of a given rare gas lie lower in energy than any term for a rare gas with greater atomic number. From the work of Robinson and coworkers it is known that spectra of impurities in crystals are least affected when the species of interest, or "impurity" species, and the environment species, or "host" species, are most nearly the same size (13). For the foregoing reasons the following host-impurity combinations have been chosen for study:

(1) krypton-xenon

(2) argon-krypton

(3) neon-argon.

Since the difficulties in working with solid helium are considerable, especially in optically accessible vessels, the helium-neon system is not currently under immediate consideration. Studies of the remaining systems satisfying the energy criterion for the host gas may be undertaken later, despite the less favorable situation regarding the relative sizes of the host and impurity species.
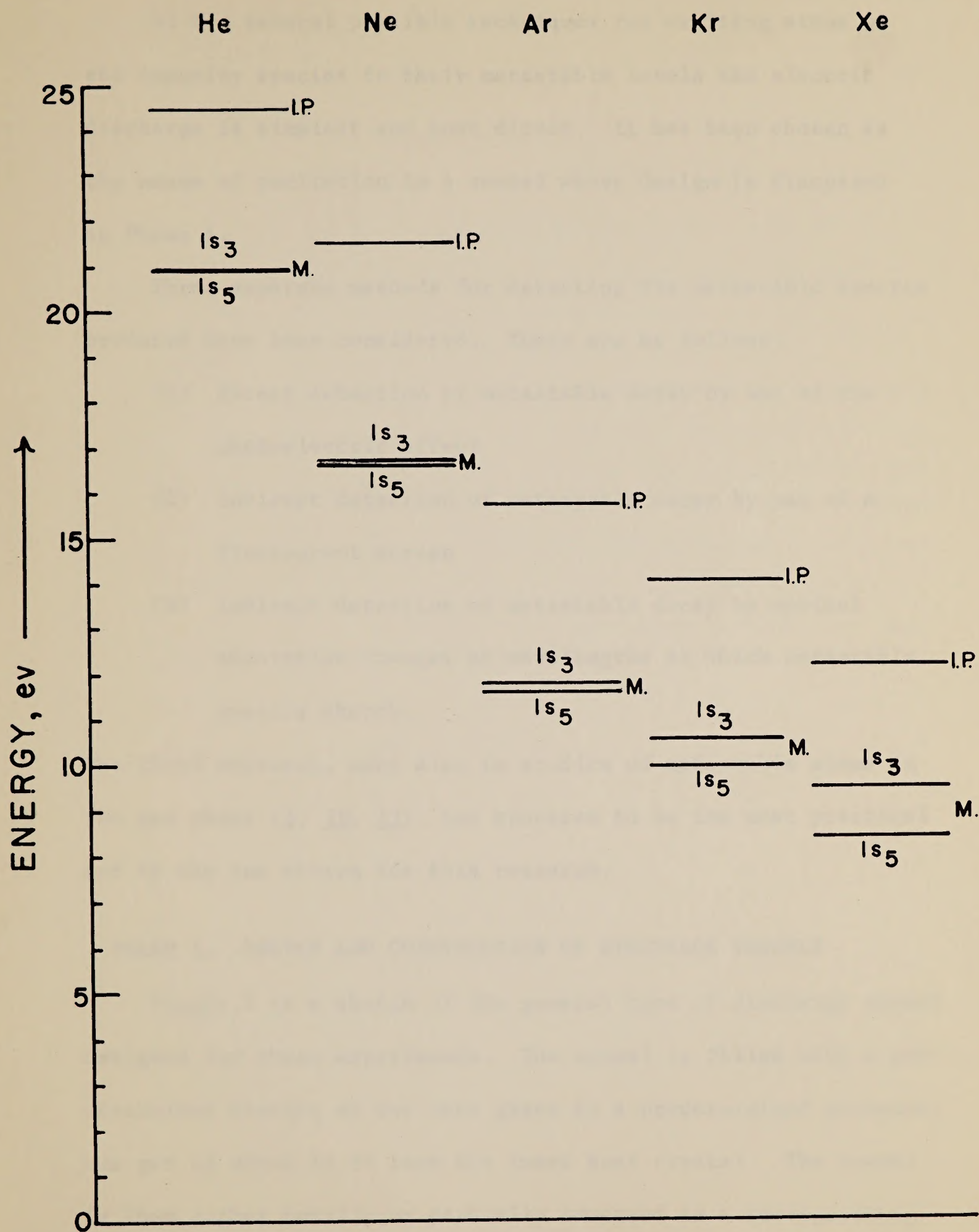
FIGURE I.   Abbv. Term Diagram: Ionization Potentials,
Metastable Levels for the Rare Gases.

Ne Kr Ar Xe Ne He

ENERGY, eV

FIGURE 1. Abbv. Term Diagram: Ionization Potentials,
Metastable Levels for the Rare Gases.

Of the several possible techniques for exciting atoms of the impurity species to their metastable levels the electric discharge is simplest and most direct. It has been chosen as the means of excitation in a vessel whose design is discussed in Phase I.

Three separate methods for detecting the metastable species produced have been considered. These are as follows:

(1) direct detection of metastable decay by use of the photoelectric effect

(2) indirect detection of metastable decay by use of a fluorescent screen

(3) indirect detection of metastable decay by optical absorption changes at wavelengths at which metastable species absorb.

The third approach, used also in studies of metastable atoms in the gas phase (5, 10, 11), has appeared to be the most practical and is the one chosen for this research.

PHASE I. DESIGN AND CONSTRUCTION OF DISCHARGE VESSELS

Figure 2 is a sketch of the general type of discharge vessel designed for these experiments. The vessel is **filled** with a pre-determined mixture of two rare gases to a predetermined pressure, one gas of which is to form the inert host crystal. The vessel is then either totally or partially immersed in a refrigerating medium at a temperature such that the pressure of the host gas is

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medium at a temperature such that the pressure of the host gas is

≤ 100 mm

≤ 270 mm

≤ 210 mm

15 mm OD

25mm   25mm

12 mm OD

18 mm OD

∽ 65mm

Specifications:

1 - Overall length: 275 mm
    excluding electrode leads

2 - Overall width: 70 mm

3 - Volume: ∽470 cm³

4 - Material: Standard Pyrex tubing,
    luminous sign electrodes

5 - Filling gas pressure: ∽755 Torr

6 - Discharge path length: ∽400mm

7 - The top metal to glass seals
    must withstand repeated
    immersions in liquid nitrogen

FIGURE 2. — Discharge Vessel

reduced to a value of from 1 to 10 Torr. Under these circum-
stances an electric discharge can be readily initiated and main-
tained by the thickness of the host crystal desired on the inside
of the windows of the vessel, and is limited by the total internal
pressure that the vessel can withstand.

Vapor pressure data are evidently unavailable for the rare
gas elements in the pressure range below 1.0 Torr. Extrapolated
plots of log p vs T^{-1} for xenon, krypton, argon, and neon are
given in figure 3 (3). At 77° K, solid krypton has a vapor pres-
sure 1.5 Torr, and on the extrapolated portion of the curve for
xenon one reads a vapor pressure of 0.002 Torr. Since xenon has
a lower ionization potential than krypton, it may contribute
significantly to the emission spectrum in a krypton-xenon dis-
charge vessel. It can be predicted in a similar manner that an
argon discharge vessel will need to be operated in the temperature
range of 51 - 63° K, and that krypton may have a vapor pressure
sufficient to contribute to the emission spectrum. From the vapor
pressure curve for neon, one sees that a neon discharge vessel
will have to be operated in the temperature range from 15 to 18° K.
The vapor pressure of argon is vanishingly small in this range,
hence, one cannot expect argon to contribute detectably to the
emission spectrum from a neon-argon discharge vessel.

In theory, the electric discharge in the rare gas excites
the rare gas host crystal, which in turn excites the impurity
species within, or the latter is directly excited.
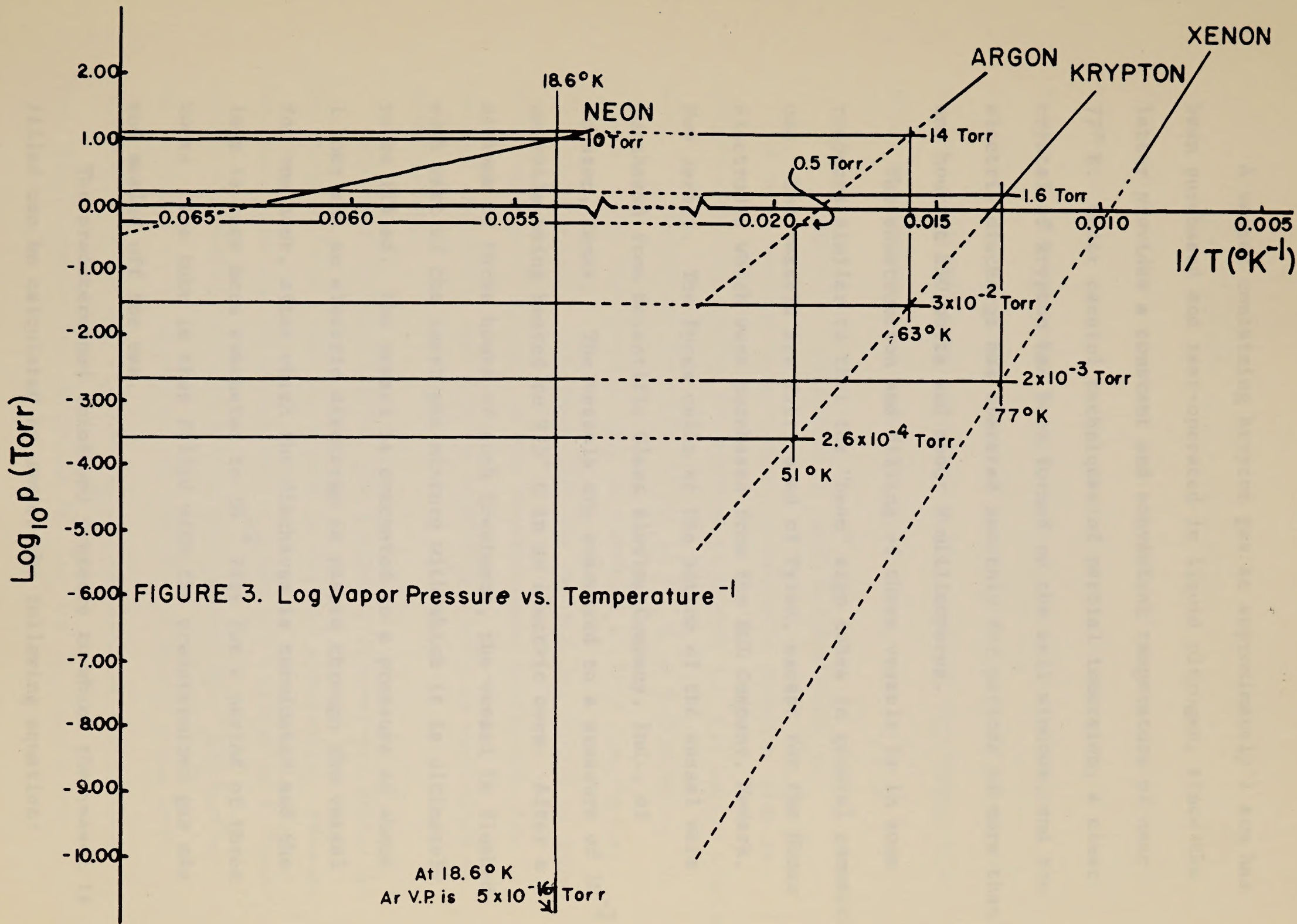
FIGURE 3. Log Vapor Pressure vs. Temperature^{-1}

FIGURE 3 Log Vapour Pressure vs Temperature for ...

A vessel containing krypton gas at approximately 1 atm has been purchased and test-operated in liquid nitrogen, since the latter provides a constant and convenient temperature of near 77° K. Under careful techniques of partial immersion, a clear crystal of krypton has been formed on the cell windows, and the electric discharge has operated smoothly for periods of more than one hour at 250 volts and about 9 milliamperes.

The construction and filling of these vessels is in some respects similar to that for "neon" sign tubes in general commercial use. The vessels are fabricated of Pyrex, except for the Nonex electrodes which were purchased from the EGL Company, Newark, New Jersey. The Pyrex cells at the bottom of the vessel were purchased from Scientific Glass Blowing Company, Inc., of Houston, Texas. The vessels are evacuated to a pressure of 10^{-3} mm while being heated to 275° C in an electric oven. After a minimum of three hours of such treatment, the vessel is flushed with part of the inert gas mixture with which it is ultimately to be filled. The vessel is evacuated to a pressure of about 1 Torr and an electric discharge is passed through the vessel for one hour, after which the discharge is terminated and the lamp is once more evacuated to 10^{-3} Torr for a period of three hours. The tube is then filled with the predetermined gas mix and sealed off for use.

The predetermined (minimum) pressure to which the vessel is filled can be calculated by use of the following equation:

$$p = \frac{2A\ td\ RT}{MV} \quad \text{or} \quad p = 2RTA\ td/MV$$

in which R is the universal gas constant, T is the absolute tem-
perature of filling, M is the atomic weight of the gas, V is the
volume of the discharge vessel, A is the area of the window, t is
the thickness of deposit desired per window, and d is the density
of the solidified rare gas host. A Pyrex vessel can safely hold
about 2 atmospheres of pressure.

PHASE II. DETECTION OF METASTABLE SPECIES

A more detailed term system for xenon is compared with an
abbreviated term system for krypton in figure 4. The energy spacing
that corresponds to the value of kT at 77° K is indicated on the
figure, since the krypton lamp is operated at that temperature.
The figure clearly indicates that the $1s_5$ and $1s_3$ levels of xenon
will form energy "traps" in the krypton-xenon system and that
thermal excitation can play no significant role in depopulating
these levels.

As mentioned previously, the technique planned for detecting
the metastable $1s_5$ and $1s_3$ levels is optical absorption. McLennan
and Reudy made use of absorption in xenon gas excited by a "weak"
electric discharge to verify term assignments (8). Absorption
was reported to be strong at the 8231Å and 8819 Å lines which
correspond to the $2p_6$-$1s_5$ and $2p_8$-$1s_5$ transitions, respectively.
Some other transitions involving the $1s_5$ and $1s_3$ levels are
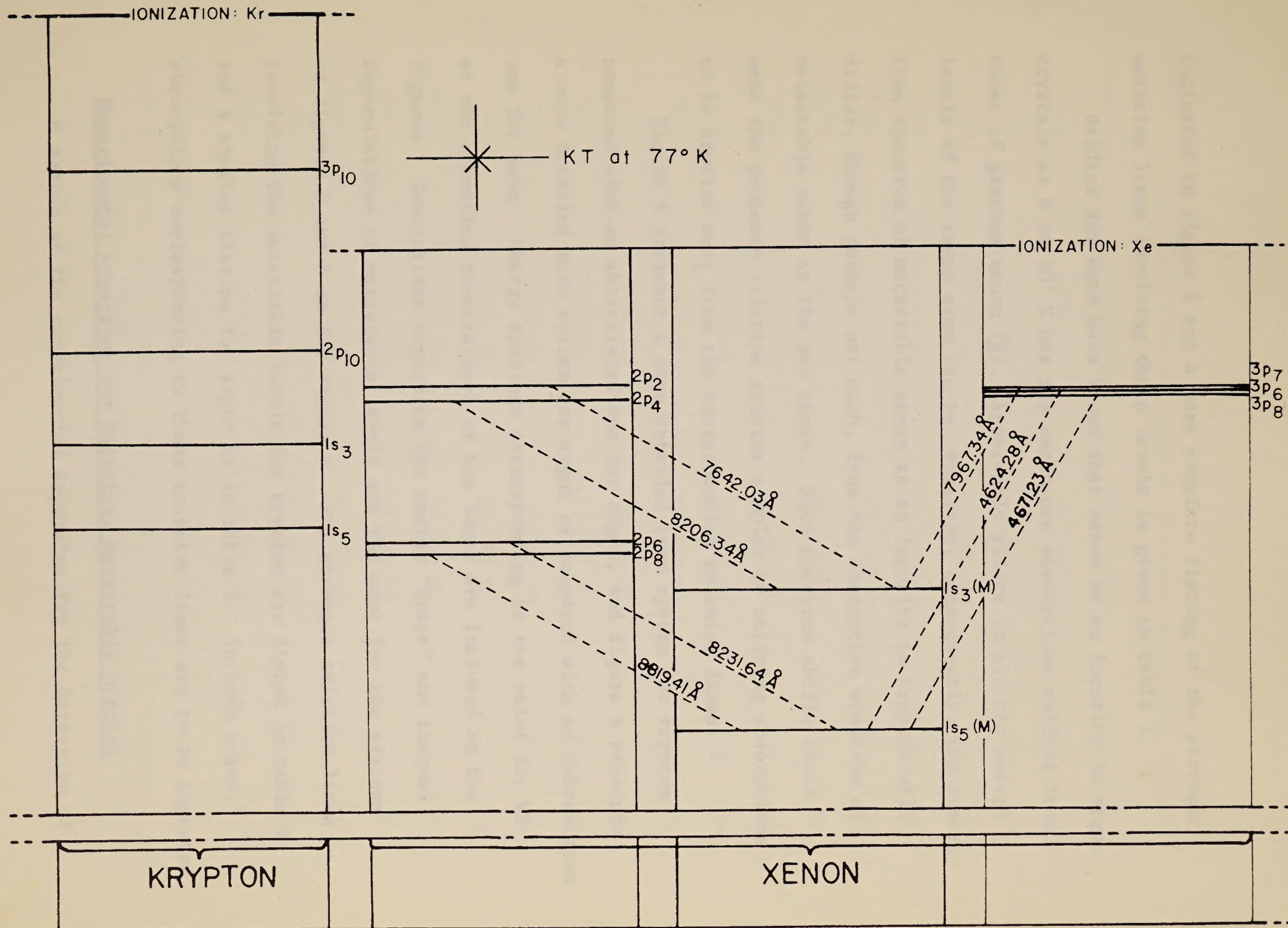
FIGURE 4. Comparative Term System for Xenon and Krypton.

indicated in figure 4 and a more complete listing of the stronger

emission lines involving these levels is given in table 1.

Baldini and Knox have found that xenon as an impurity in argon

crystals at 8 to 10° K has its resonance absorptions shifted from

those of gaseous xenon (2). Apparently shifts in all the energy

levels of the xenon atom can be expected; consequently, the absorp-

tion spectrum of metastable xenon as an impurity in krypton will

differ, though perhaps not much, from the absorption spectrum of

metastable xenon in the gas phase. Such spectrum shifts could

make the proposed lifetime studies simpler by shifting absorptions

to be studied away from the corresponding emission lines.

Figure 5 presents a more detailed term system for krypton

compared with an abbreviated one for argon, and figure 6 presents

a more detailed term system for argon as compared with an abbreviated

one for neon. Energy spacings corresponding to the value for kT

at the operating temperatures of the lamps are included on the

figures. Conclusions regarding the energy "traps" and thermal

depopulations of metastable levels are the same for the systems

of figures 5 and 6 as for figure 4. The stronger emission lines

involving the metastable levels for krypton are listed in table 2

and a similar listing for argon is in table 3. In both cases,

absorptions corresponding to these emission lines are to be expected.

Experimental Apparatus for Detecting Metastable Species

A sketch of the experimental apparatus for the detection of

TABLE 1. - <u>Emission lines of Xenon I involving metastable levels</u>[1]

Intensity	Wavelength	Wave Number	Combination
200	3967.54	25,197.42	$1s_5 - 4p_8$
500	4500.98	22,211.19	$1s_5 - 2p_2$
400	4524.68	22.094.83	$1s_5 - 2p_3$
700	4611.89	21,677.03	$1s_5 - 3p_7$
1000	4624.28	21,618.97	$1s_5 - 3p_6$
2000	4671.23	21,401.69	$1s_5 - 3p_8$
300	4697.02	21,284.16	$1s_5 - 3p_9$
150	4792.62	20.859.61	$1s_5 - 3p_{10}$
300	5823.89	18,165.91	$1s_3 - 5X$
200	6827.32	14,643.01	$1s_3 - 4X$
500	7642.02	13,081.94	$1s_3 - 2p_2$
500	7967.34	12,547.79	$1s_3 - 3p_7$
700	8206.34	12,182.35	$1s_3 - 2p_4$
5000	8231.63	12,144.92	$1s_5 - 2p_6$
2000	8409.19	11,888.49	$1s_5 - 2p_7$
5000	8819.41	11,335.52	$1s_5 - 2p_8$
400	9045.45	11,052.26	$1s_5 - 2p_9$
2000	9799.70	10,201.60	$1s_5 - 2p_{10}$

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[1] Wavelengths, wave numbers, combinations from C. J. Humphreys and
W. F. Meggers, "Further Description of the First Spectrum of Xenon,"
Bur. Stds. J. Research <u>10</u>, 139-149 (1933), R.P. 521. Intensities
from C. R. Handbook, 1962-1963 Ed., pp. 3023-4.
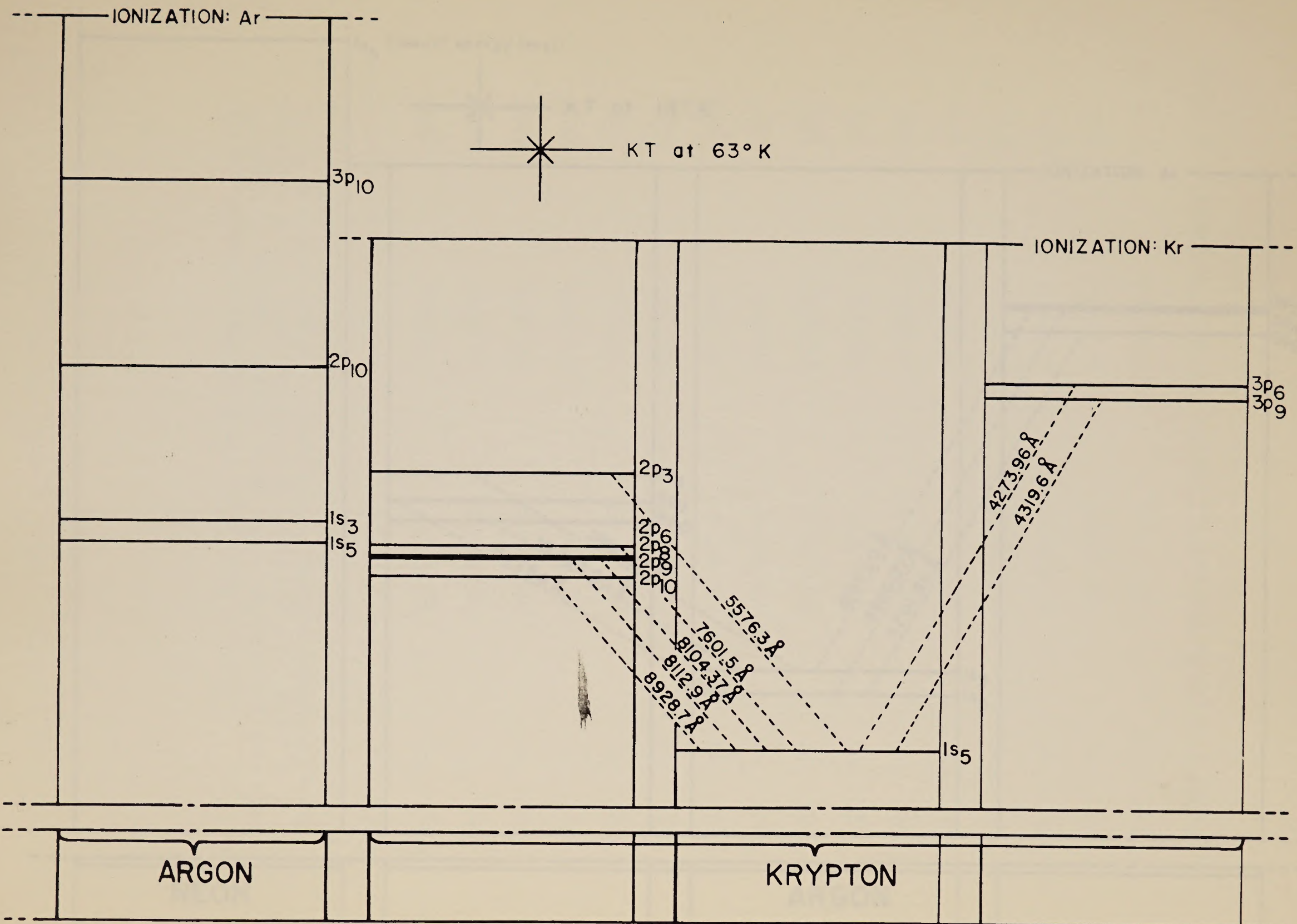
FIGURE 5. Comparative Term System for Krypton and Argon.
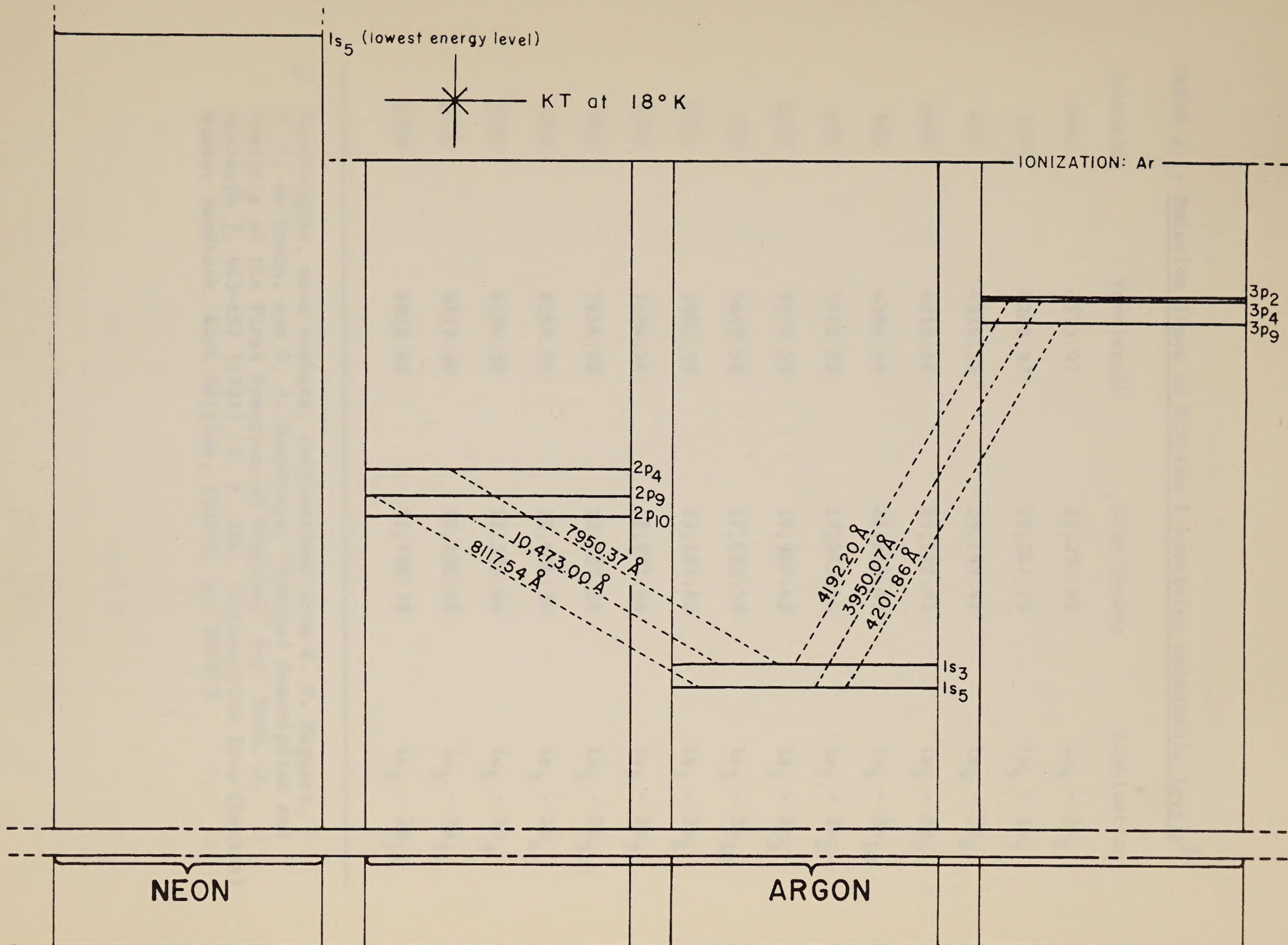
FIGURE 6. Comparative Term System for Argon and Neon.

NEON

ARGON

1s₅ (lowest energy level)

KT at 18°K

IONIZATION: Ar

3p₂
3p₄
3p₉

2p₄
2p₉
2p₁₀

7950.37 Å
10,473.00 Å
8117.54 Å

4192.20 Å
3950.07 Å
4201.86 Å

1s₃
1s₅

TABLE 2. - <u>Emission lines of Krypton I involving metastable levels</u>[1]

Intensity	Wavelength	Wave Number	Combination
1000	4273.97	23,390.89	$1s_5 - 3p_6$
100	4282.97	23,341.75	$1s_5 - 3p_7$
400	4318.55	23,149.42	$1s_5 - 3p_8$
1000	4319.58	23,142.91	$1s_5 - 3p_9$
500	4362.64	22,915.47	$1s_5 - 3p_{10}$
500	5562.23	17,973.44	$1s_5 - 2p_2$
2000	5570.29	17,947.42	$1s_5 - 2p_3$
100	5649.56	17,695.59	$1s_3 - 3p_{10}$
5000	7601.55	13,151.60	$1s_5 - 2p_6$
1000	7694.54	12,992.66	$1s_5 - 2p_7$
800	7854.82	12,727.54	$1s_3 - 2p_3$
1000	8059.50	12,404.30	$1s_3 - 2p_4$
5000	8104.36	12,335.64	$1s_5 - 2p_8$
5000	8112.90	12,332.66	$1s_5 - 2p_9$
2000	8928.69	11,196.78	$1s_5 - 2p_{10}$

[1] Wavelengths, wave numbers, combinations from W. F. Meggers, T. L. de Bruin, and C. J. Humphreys, "Further Description and Analysis of the First Spectrum of Krypton," Bur. Stds. J. Research 7, 643-657 (1931), R. P. 364. Intensities from Chemical Rubber Handbook, 44th Edition, 1962-3, pp. 2952-3.

TABLE 3. - Emission lines of Argon I involving metastable levels[1]

Intensity	Wavelength	Wave Number	Combination
400	3770.38	26,515.18	$1s_3 - 4p_{10}$
1000	3947.50	25,325.22	$1s_5 - 3p_3$
2000	3948.98	25,315.87	$1s_5 - 3p_2$
1200	4158.59	24,039.86	$1s_5 - 3p_6$
1000	4164.18	24,007.60	$1s_5 - 3p_7$
1000	4181.88	23,905.95	$1s_3 - 3p_2$
600	4190.71	23,855.58	$1s_5 - 3p_8$
1200	4191.03	23,853.84	$1s_3 - 3p_4$
1200	4198.32	23,812.39	$1s_5 - 3p_5$
1200	4200.68	23,799.00	$1s_5 - 3p_9$
800	4251.18	23,516.27	$1s_5 - 3p_{10}$
800	4522.33	22,106.35	$1s_3 - 3p_{10}$
400	6965.43	14,352.66	$1s_5 - 2p_2$
400	7067.22	14,145.94	$1s_5 - 2p_3$
500	7635.11	13,093.79	$1s_5 - 2p_6$
200	7723.76	12,943.50	$1s_5 - 2p_7$
200	7724.21	12,942.74	$1s_3 - 2p_2$
400	7948.18	12,578.03	$1s_3 - 2p_4$
800	8014.79	12,473.50	$1s_5 - 2p_8$
5000	8115.31	12,319.00	$1s_5 - 2p_9$
400	8667.94	11,533.58	$1s_3 - 2p_7$
500	9122.98	10,958.28	$1s_5 - 2p_{10}$

[1] Wavelengths, wave numbers, and combinations from K. W. Meissner, "The Series of the Argon I Spectrum," Zeit. f. Phys. 39, 172-190 (1926). Intensities from Chemical Rubber Handbook, 44th Ed. 1962-3, pp. 289-3.

TABLE 9. - Emission lines of Argon I involving metastable levels.[1]

Intensity	Wavelength	Wave Number	Combination
400	3770.38	26,515.18	$1s_3 - 4p_{10}$
1000	3947.50	25,325.22	$1s_5 - 3p_3$
2000	3948.98	25,315.87	$1s_3 - 3p_2$
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500	7635.11	13,093.79	$1s_5 - 3p_6$
200	7723.76	12,943.50	$1s_5 - 2p_7$
200	7724.21	12,942.74	$1s_3 - 3p_3$
400	7948.18	12,578.03	$1s_5 - 3p_4$
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1/ Wavelengths, wave numbers, and combinations from K. W. Meissner, "The Series of the Argon I Spectrum," Zeit. f. Phys. 39, 172-190 (1926). Intensities from Chemical Rubber Handbook, 44th Ed. 1962-3, pp. 265-3.

metastable species is given in figure 7. A continuum emitted

from the tungsten source A is collimated by the lens C_1, has heat

filtered out by the cell D, is refocused through the optical cell

of the discharge vessel F by the second lens C_2, and is again re-

focused on the slit of the spectrograph H by the lens G. The light

in the optical train is controlled by the shutters B_1 and B_2. If

desired, the continuum source can be replaced by a source of

another type.

It is not possible to prescribe an exact procedure for any

projected experiment but a general plan will be given in the suc-

ceeding paragraphs. The apparatus sketched in figure 7, especially

when supplemented with certain auxiliary pieces of equipment, is

adaptable to several different types of experiments. Certain

currently unknown factors, such as absorption intensities, crystal

transparencies, and metastable species lifetimes will clearly have

influence on the precise conditions required to demonstrate positively

the presence of metastable species. It will almost always be nec-

essary to include a wavelength comparison spectrum on every plate

exposed, however, and such a spectrum is usually that of iron. In

some instances the gas discharge spectra of certain rare gases will

be of value.

Spectra Obtainable with the Experimental Apparatus

Several different spectra, classified according to the experi-

mental conditions existing, can be obtained with the apparatus of
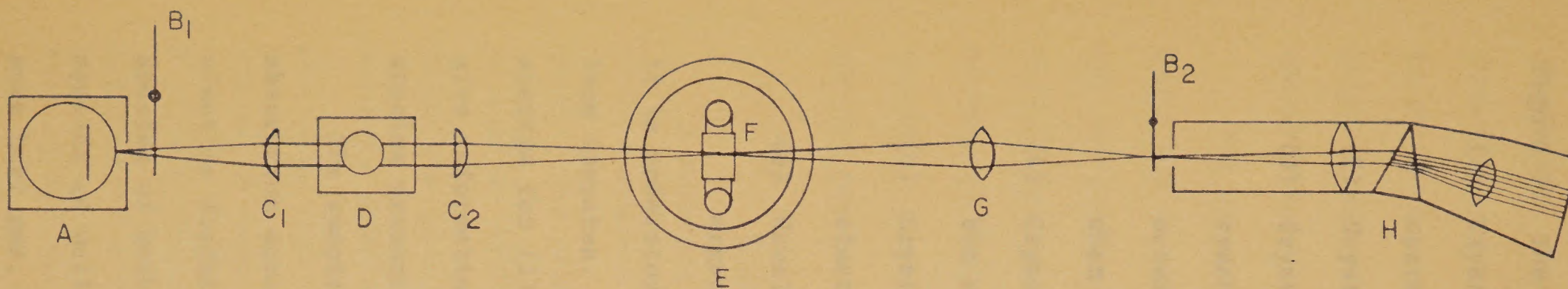
A — Tungsten source   E — Cryostat

B_1, B_2 — Shutters   F — Optical cell, discharge vessel

C_1, C_2 — Collimating lenses   G — Focusing lens

D — Heat absorbing cell   H — Spectrograph

FIGURE 7. – Apparatus for Detecting Metastable Species

figure 7. The most important of these are the following:

(1) Crystals frozen on cell windows, electric discharge operating.

(2) Crystals frozen on cell windows, no electric discharge.

(3) Crystals frozen on cell windows, electric discharge synchronized with shutter so that discharge does not occur when the shutter is open, and discharge occurs when the shutter is closed.

(4) Crystals frozen on cell windows, no electric discharge but otherwise as in (3).

(5) Crystals frozen on vessel but not on cell windows, electric discharge operating.

(6) Wavelength comparison spectra (iron, xenon, krypton, argon, neon, etc.).

It is understood that in (1) through (5) the tungsten filament lamp operates. The spectra of (2) and (4) provide comparison spectra for (1) and (3) respectively. The spectra of (5) will give information on the strength of the emission from the impurity species present, while (6) provides means of determining wavelengths.

The spectra of (1) and (2) will reveal wavelengths at which absorption occurs in the crystal because of excitation by the electric discharge. These absorptions may be due to metastable species of both the impurity and host gases, and also to unstable species as well. If the spectra of (1) and (2) are repeated with pure host gas, the contribution from the impurity gas can be

Figure 7. The most important of these are the following:

(1) Crystals frozen on cell windows, electric discharge operating.

(2) Crystals frozen on cell windows, no electric discharge.

(3) Crystals frozen on cell windows, electric discharge synchronized with shutter so that discharge does not occur when the shutter is open, and discharge occurs when the shutter is closed.

(4) Crystals frozen on cell windows, no electric discharge but schematic as in (3).

(5) Crystals frozen on vessel but not on cell windows, electric discharge operating.

(6) Wavelength comparison spectra (iron, xenon, krypton, argon, neon, etc.).

It is understood that in (1) through (5) the tungsten filament lamp operates. The spectra of (2) and (4) provide comparison spectra for (1) and (3) respectively. The spectra of (5) will give information on the strength of the emission from the impurity species present, while (6) provides means of determining wavelengths. The spectra of (1) and (2) will reveal several wavelengths at which absorption occurs in the crystal because of excitation by the electric discharge. These absorptions may be due to metastable species of both the impurity and host gases, and also to unstable species as well. If the spectra of (1) and (2) are repeated with pure host gas, the contribution from the impurity gas can be

identified. The spectra of (2) should also have emission lines from the host gas and possibly from the impurity gas as well. It should be noted that, thus far, no means of distinguishing between absorption by metastables of the impurity gas from its unstable species has been suggested.

The spectra of (4), however, should serve to separate absorptions due to metastable species from all the other absorptions and emissions present. The kind of synchronizing device required will depend upon the mean lifetimes of the metastable species. A mechanical shutter system should suffice if the mean lifetime exceeds a tenth of a millisecond; if otherwise, an electronic shutter device may be required.

A Cryostat for the Discharge Vessels

A cryostat capable of maintaining the discharge vessels at three different constant temperatures is required in these experiments. The problem is easily solved for the xenon-krypton system because an ordinary Dewar vessel containing liquid nitrogen maintains the temperature near 77° K at which the krypton discharge operates smoothly. For the krypton-argon system a temperature in the range from 51° to 63° K is required, and for the argon-neon system, a temperature is required in the range from 15° to 18° K. A cryostat device on order from the Arthur D. Little Company is expected to provide the temperature control required for the latter pair of systems.

Source Interruption and Shutter Syncronization

In experiments of type (3), performed with the apparatus of
figure 7, it is necessary to have an interrupted or pulsed source,
and a shutter device that permits light to pass into the spectro-
graph only during periods in which no electric discharge occurs.
Since the metastable species are to be excited by an electric
discharge within the vessel, a periodic interruption or pulsing
of the discharge is the only feasible manner in which "dark periods"
can be produced during which metastable species are observed. The
permissible time-lapse between the end of the pulse and the shutter
opening depends upon the mean lifetimes of the metastable species
whose absorptions are being photographed. In general, a device
with a mechanical shutter can be used for mean lifetimes as short
as 10^{-4} or 10^{-5} seconds without great difficulty. The values of
the mean lifetimes themselves can be measured with a modified
apparatus of this sort, but such an apparatus lacks the sensitivity
of a more elaborate one described by Phelps and Pack (12).

A block diagram of the apparatus for synchronizing a periodic
electric discharge with a rotating, toothed-wheel optical shutter
is given in figure 8. A variable speed synchronous motor operates
the shutter and timing wheel on the same shaft at speeds up to
1800 rpm. The pickup divice transmits an electrical impulse through
its power unit to the variable time delay unit at about the time
that the optical shutter closes. The signal from the variable time
delay unit is delayed sufficiently to cause the high-voltage pulse-

Source Interruption and Shutter Synchronization

In experiments of type (3), performed with the apparatus of figure 7, it is necessary to have an interrupted or pulsed source, and a shutter device that permits light to pass into the spectrograph only during periods in which no electric discharge occurs. Since the metastable species are to be excited by an electric discharge within the vessel, a periodic interruption or pulsing of the discharge is the only feasible manner in which "dark periods" can be produced during which metastable species are observed. The permissible time-lapse between the end of the pulse and the shutter opening depends upon the mean lifetimes of the metastable species whose absorptions are being photographed. In general, a device with a mechanical shutter can be used for mean lifetimes as short as 10^{-4} or 10^{-5} seconds without great difficulty. The values of the mean lifetimes themselves can be measured with a modified apparatus of this sort, but such an apparatus lacks the sensitivity of a more elaborate one described by Phelps and Pack (12).

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Discharge vessel   Optical shutter wheel

Timing wheel

Synchronous motor

Pickup

High voltage pulse generator

Variable time delay

Power unit for pickup
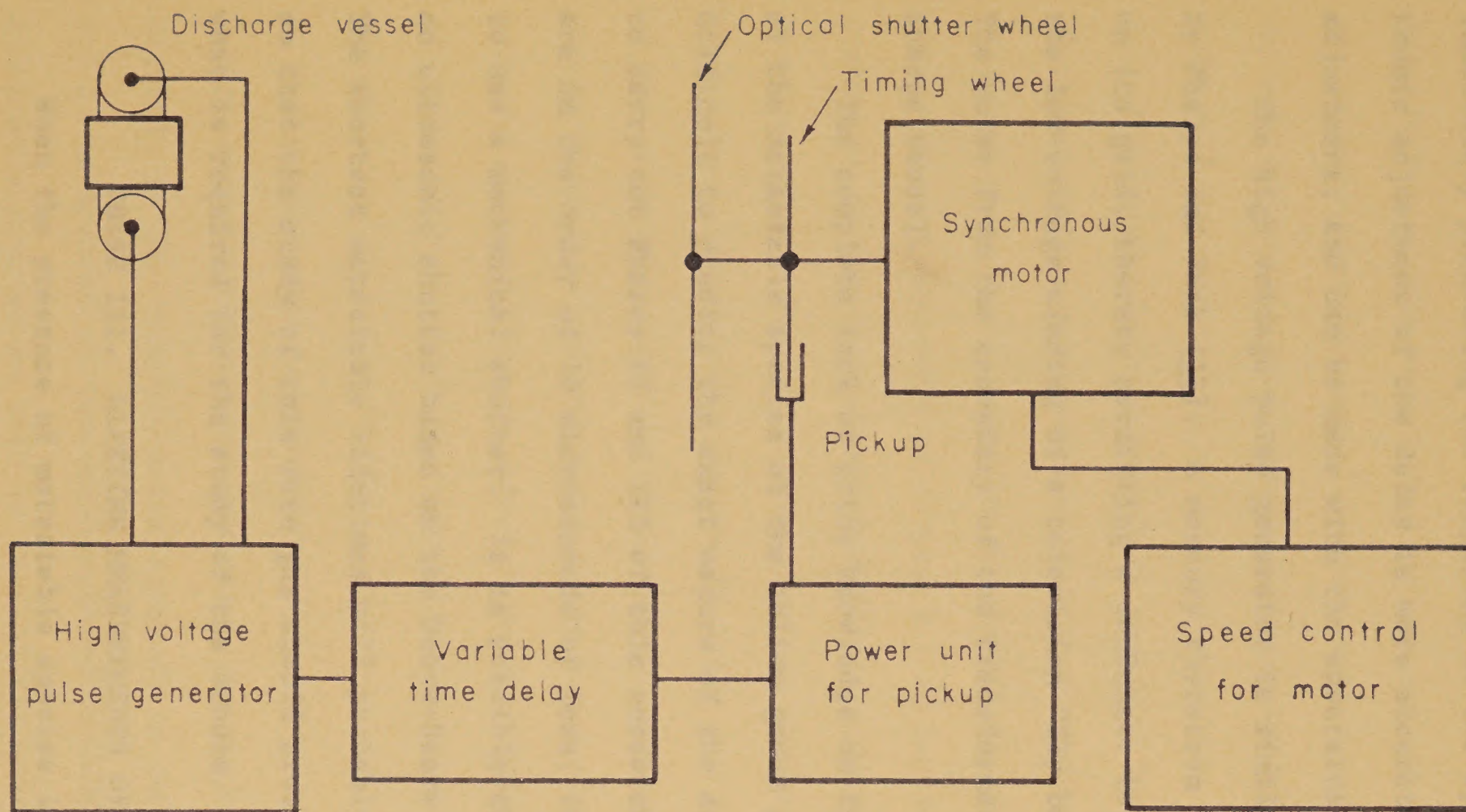
Speed control for motor

FIGURE 8.- Block Diagram for Mechanical Shutter Synchronization

generator to provide a high-voltage pulse to the discharge vessel immediately preceeding the reopening of the optical shutter. Electronic adjustment of the delay is more accurate than mechanical adjustment, and can be made with the apparatus in operation.

The high voltage pulse generator is similar to one described by Phelps and Pack (12). A mercury thyratron is fired by a signal on its grid, thereby permitting a condenser to discharge through the low-voltage winding of a television "fly back" transformer. The pulse from the secondary of the transformer operates the discharge vessel.

The complete lack of prior knowledge on the mean lifetimes of the metastable species of the helium group gases makes it difficult to predict the exact nature of the apparatus required to carry out Phases II and III of this research. If such lifetimes are on the order of 10 microseconds or less, it is not practical to use a mechanical shutter. It is possible that a Kerr cell or an ultrasonic shutter based on the Debye-Sears effect would serve.(1,4) The shortest metastable lifetimes will probably occur in xenon, so that the study of this rare gas should provide information on what is required for the study of the others.

PHASE III. LIFETIME MEASUREMENTS OF METASTABLE SPECIES

When the presence of metastable species in the crystalline host gases has been demonstrated, experiments will begin on measuring the mean lifetimes of these species. The apparatus required will

depend upon (1) the magnitudes of the mean lifetimes, (2) the accuracy desired in the measurement, and (3) the optical characteristics of the materials involved and of the system. It is anticipated that the mean lifetimes will be at least 10 microseconds and that a time sampling system using a photomultiplier tube will be used.

The apparatus of figure 7 is modified by substituting for the spectrograph a monochromator with a photomultiplier tube attached to exit slit, and by utilizing the mechanical shutter synchronizing apparatus of figure 8. It may be feasible in some instances to substitute narrow bandpass optical filters for the monochromator. One can obtain from the photomultiplier tube a "time versus intensity" response to light for a wavelength absorbed by the metastable species of interest. This electrical response can be presented and photographed as a trace on the screen of a cathode ray oscilliscope tube. From the photograph, a half-life is measured from which the mean lifetime is determined by use of the relation $T_m = T_{1/2}/0.693$.

The apparatus as modified will perform the functions essential to the success of the measurements. The photocathode is not exposed directly to the lamp discharge since it is protected by the shutter, and it is exposed to the wavelength of radiation absorbed by the metastable species as soon as the electric discharge ceases. In such an experiment, the speed of the synchronous motor is carefully regulated so that a decay trace of optimum characteristics may be

obtained. The sweep can be synchronized with the rotation of

the shutter so that accurate retraces of the decay curve are

obtained.

An alternative to the use of a mechanical shutter is the

use of a gating circuit such that there is no operating voltage

on the photomultiplier tube dynodes when the pulsed electric

discharge occurs in the discharge vessel. A block diagram of an

apparatus that will produce this gating is given in figure 9.

It is a simplified version of the apparatus of Phelps and Pack

(12). A master generator provides voltage spikes of a frequency

f, figure 10 (a), which trigger the high-voltage pulse generator

to give pulsed electric discharges in the discharge vessel, timed

as in figure 10 (b). Metastable species build up and decay as in

figure 10 (c), and the photomultiplier tube voltage varies as in

figure 10 (d). Since the photomultiplier tube is energized only

when there is no electric discharge in the vessel, it will record

the rise in transmission of the crystal resulting from the decay

of the metastable species as in figure 10 (e). From such traces,

half-lifetimes are determined from which mean lifetimes are cal-

culated with the equation given earlier.

It should be possible to measure much shorter lifetimes with

the gated photomultiplier tube device than with an apparatus using

a mechanical shutter. The lower limit will be determined by a

combination of apparatus and metastable species characteristics.

Among the more important of these are (1) rate and duration of

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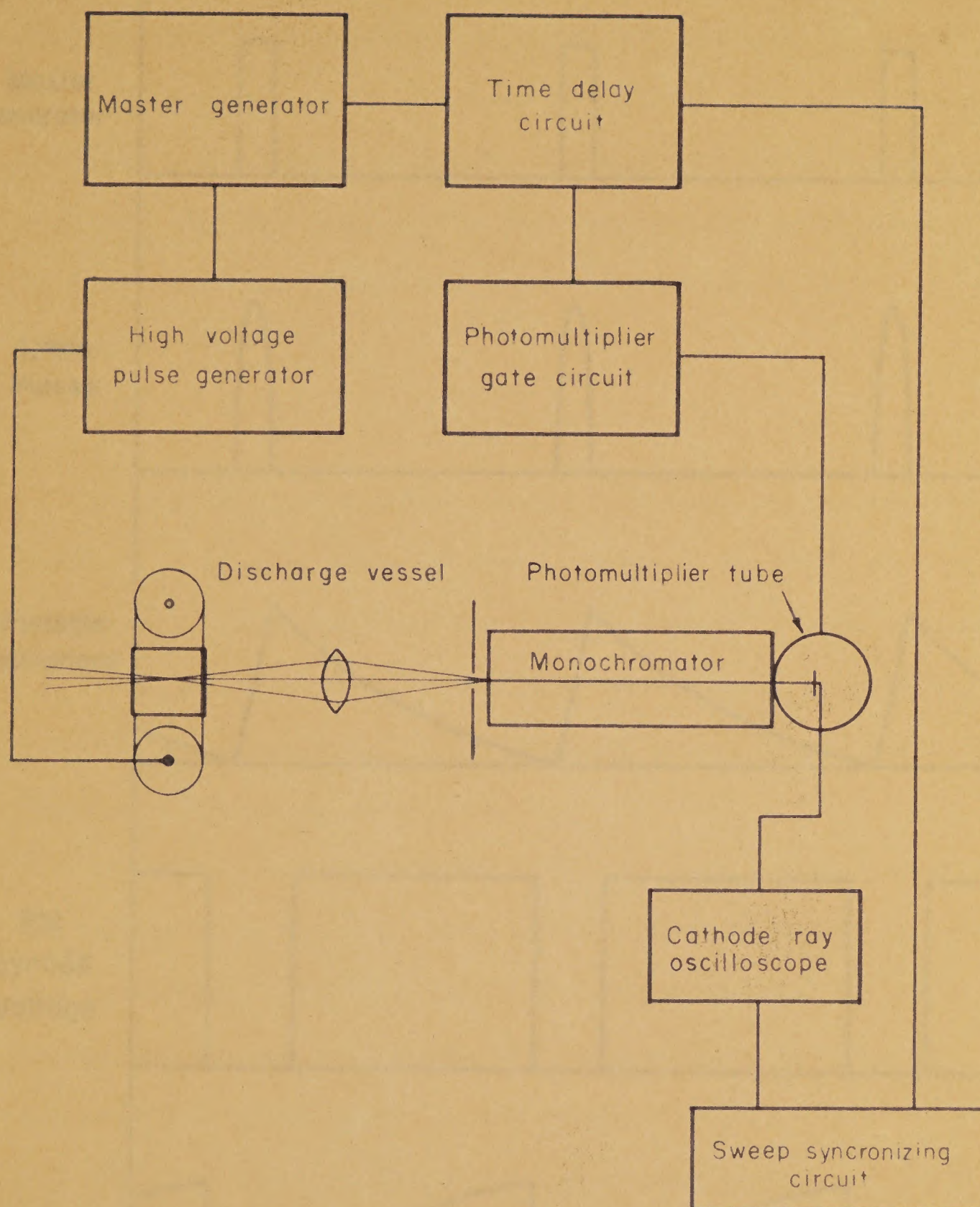
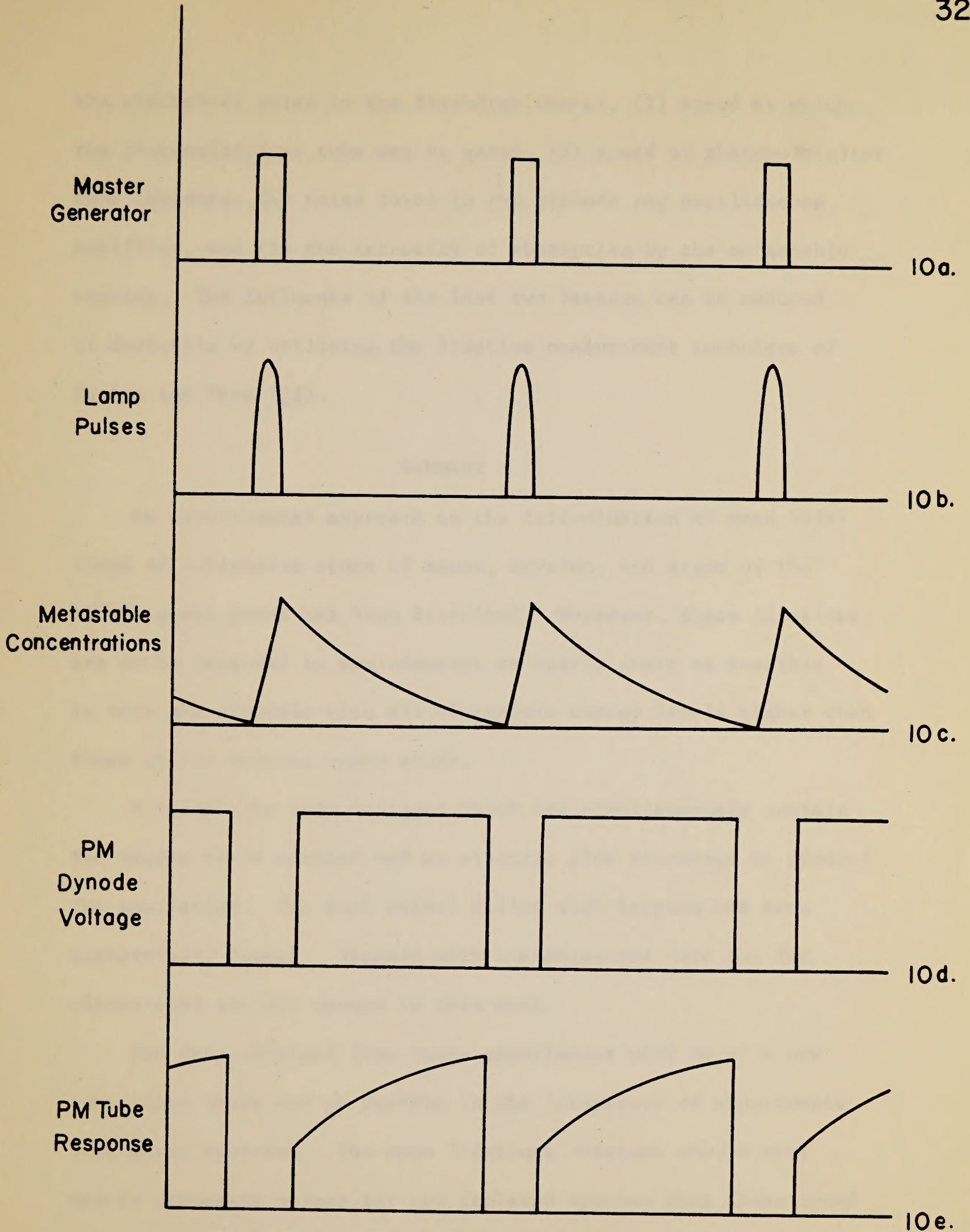FIGURE 9. – Block Diagram for Photomultiplier Tube Gating Circuit

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Master
Generator

Lamp
Pulser

Retractable
Correlations

PM
Dynode
Voltage

Iris Tube
Response

FIGURE 10. Phase Relations in Association with Gated
Photomultiplier Tube

the electrical pulse in the discharge vessel, (2) speed at which

the photomultiplier tube may be gated, (3) speed of photomultiplier

tube response, (4) noise level in the cathode ray oscilloscope

amplifier, and (5) the intensity of absorption by the metastable

species. The influence of the last two factors can be reduced

if desirable by utilizing the lifetime measurement technique of

Phelps and Pack (12).

SUMMARY

An experimental approach to the determination of mean life-

times of metastable atoms of xenon, krypton, and argon of the

helium group gases has been described. Moreover, these lifetimes

are to be measured in environments as nearly inert as possible -

in rare gas crystals with all electronic energy levels higher than

those of the species under study.

A vessel has been designed which can simultaneously contain

the sample to be excited and an electric glow discharge to produce

the excitation. One such vessel filled with krypton has been

successfully tested. Vessels with transmissions into the far

ultraviolet are not needed in this work.

The data obtained from these experiments will be of a new

type since there are no reports in the literature of experiments

like these proposed. The mean lifetimes obtained should more

nearly represent values for the isolated species than those found

in the gas phase experiments (5, 10, 11) since values from the

latter are always diminished by collisional processes. Such data will be valuable in computations involving photosensitization processes by argon, krypton, and xenon. In addition, they may be used to verify the combinations assigned to electronic transitions in these atoms.

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