KANSAS STATE UNIVERSITY

MANHATTAN, KANSAS

ARPA Order Number--306-62

Project code number--3730

SENSITIZED FLUORESCENCE*

FOURTH

SEMIANNUAL TECHNICAL

SUMMARY REPORT

1 January 1965 through 30 June 1965

Prepared for

THE OFFICE OF NAVAL RESEARCH

on Contract Nonr 3634(02)

Submitted by:

Basil Curnutte, Jr.
Professor of Physics
Kansas State University
Manhattan, Kansas

*This research is a part of Project DEFENDER, under the joint sponsorship of the Advanced Research Projects Agency, the Office of Naval Research and the Department of Defense.

ABSTRACT

The total deexcitation cross-section for the excited (6^3P_1) state of mercury by thallium, as determined by quenching of resonance fluorescence, is given for three temperatures. Preliminary results on the cross-sections for excitation transfer from mercury to thallium are tabulated.

Measurements of the deexcitation cross-section of thallium for the mercury excited state (6^3P_1) have been completed. These measurements were made by the method outlined in the Third Semiannual Technical Report on this project. In addition measurements have been made of the intensity of resonance fluorescence and sensitized fluorescence emission from five different mercury-thallium cells at 800°C, 850°C, and 900°C. During the course of these measurements it was found that a light leak had caused a systematic error in previous measurements and as a result the total deexcitation cross-section was reduced by about 20% at the lowest temperature and 5% at the highest temperature measured. The best results obtained for the total deexcitation cross-section are given in Table I.

TABLE I

Temperature (°C)	Total Deexcitation Cross-section, σ^2_{4T} (Å^2)
800	33±2
850	31±1
900	24.5±1

The sensitized fluorescence measurements yield the following results for excitation transfer cross-sections:

TABLE II

Cross-section (Å^2, ±8%)	Temperature 800°C	850°C	900°C
σ^2(3519-29A°)	5.0	3.6	2.7
σ^2(5350A°)	5.3	6.4	7.1
σ^2(3229A°)	0.8	0.6	0.5
$\Sigma\sigma^2$	11.1	10.6	10.3
σ^2_{4T}	33.0	31.0	24.5
Difference	22.0	20.4	14.2

The first three cross-sections tabulated in Table II are composite cross-sections for all processes which give rise to radiation of the wavelength indicated, while the fourth is the sum of the first three cross-sections. The fifth cross-section is the total deexcitation cross-section for mercury, therefore the difference represents the loss of atoms from the excited state hich does not result in radiation from any thallium transition.

From a preliminary analysis of the data on the sensitized fluorescence intensities the following conclusions seem warranted.

The metastable (6^3P_0) state of mercury is quite important in the phenomenon of sensitized fluorescence. This can be concluded from the observation that about two thirds of the deexcitation cross-section is due to transfer to non-radiative states. The major non-radiative loss from the system is through collisions of metastable mercury atoms with the walls, thus the rate of metastable population must be moderately high. Our previous modulation of the population of the metastable state at 10 kilocycles can be explained on the basis that, while the radiative lifetime of this state is of the order of 1 millisecond, the lifetime for collisional depopulation of the metastable state is of the order of 10 microseconds, thus the population will follow a 10 kilocycle modulation.

These results indicate the need for a more careful analysis of the energy transfer processes occurring in the mercury-thallium system, particularly inclusion of rates of transfer into and out of the metastable mercury state and collisions with the walls. This analysis is now being made.

Append...:

Text of paper presented at the April 26-2?, 1965 meeting of the American Physical Society in Washington, D.C.

Total Quenching Cross-Section for Mercury 2537A Radiation by Thallium.*

B. C. Hudson and B. Curnutte, Jr.

ABSTRACT

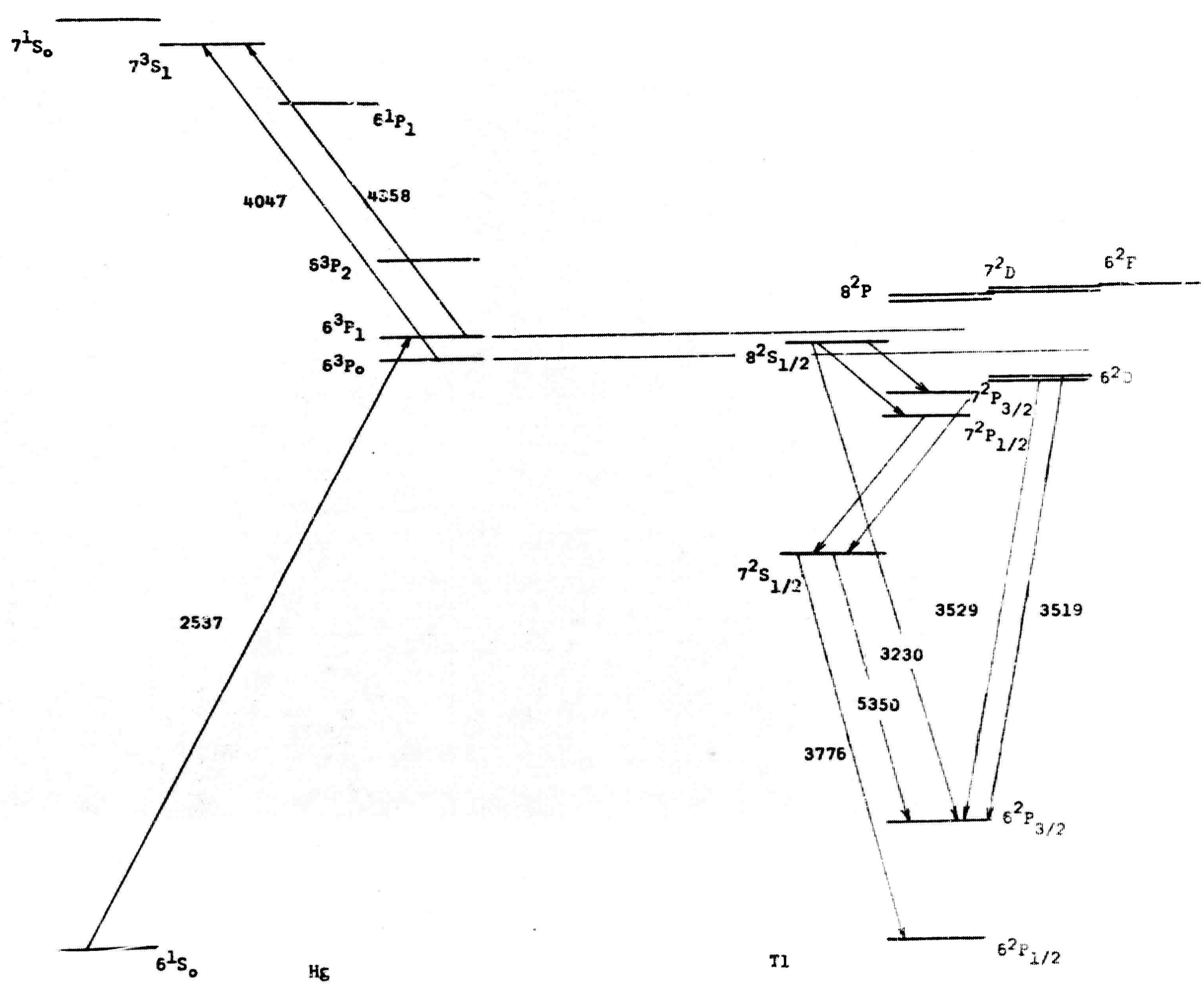
The total cross-section for the deexcitation of the 6^3P_1 state of mercury in a mercury-thallium mixture has been obtained over a range of temperatures from 500^0C to 800^0C. Line absorption measurements and resonance scattering of the 2537A resonance line have been made on sealed cells containing mercury vapor and mercury-thallium vapor mixtures. The measurements have been made over a range of 0.1 to 0.4×10^{14} atoms/cm^3 of mercury and 20 to 1200×10^{12} atoms/cm^3 of thallium. Comparison of the scattering from a mercury-thallium mixture with the scattering from mercury vapor at the same number density (as determined by absorption), temperature and geometry allows the calculation of the total quenching cross-section.

*Work supported by the U.S. Office of Naval Research and the Advanced Research Projects Agency.

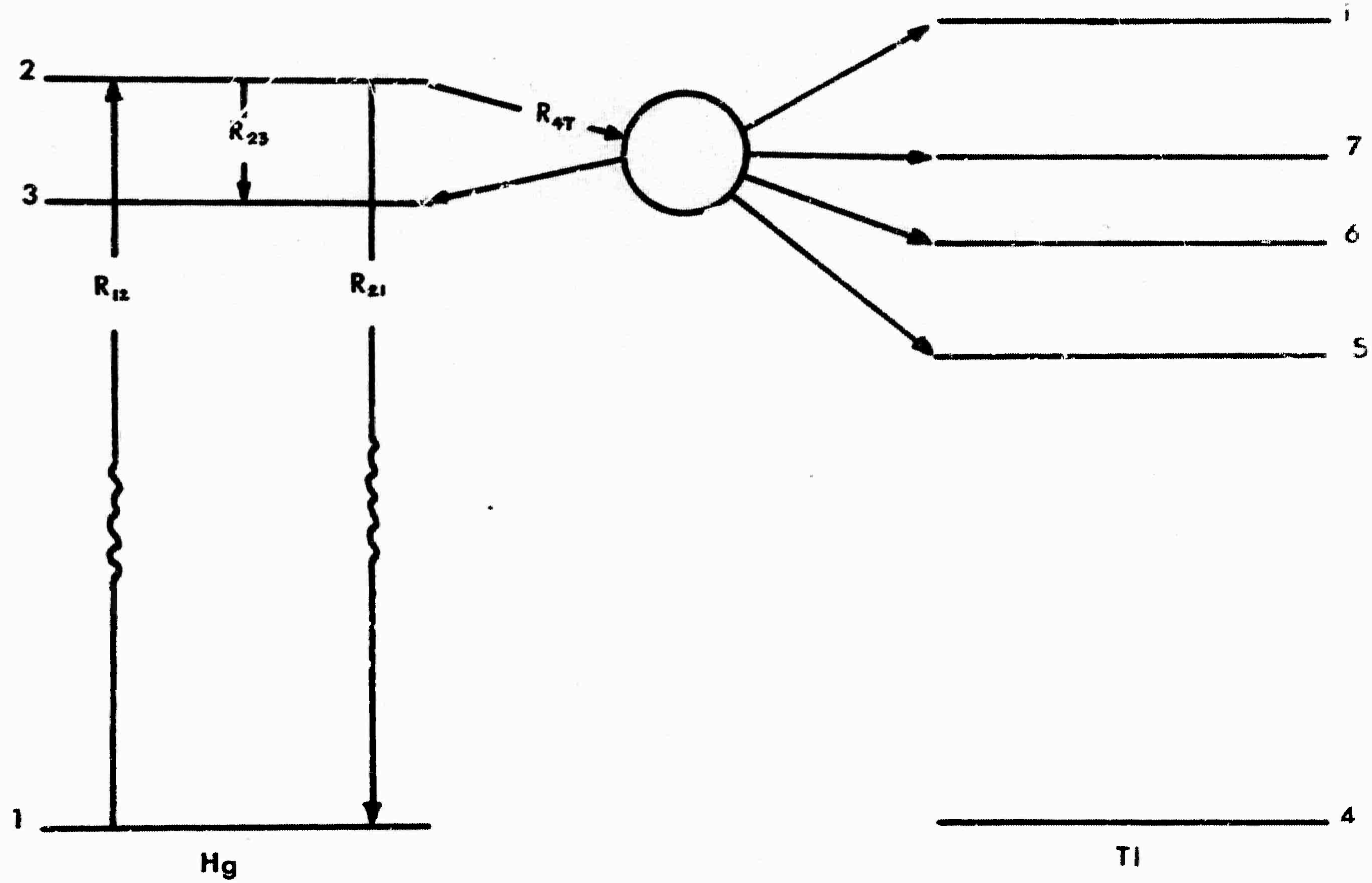
Sensitized fluorescence was observed as early as 1922 by Franck and Cario. However, few quantitative measurements of the quenching cross-sections of the mercury-thallium system have been made. We decided to measure the quenching cross-section of thallium for the excited 6^3P_1 state of mercury in order to gain some knowledge of excitation exchange collision cross-sections since these processes are important in the establishment of population inversion in gaseous lasers.

Consider figure 1. On the left we have an energy level diagram for mercury and on the right, one for thallium. When 2537Å radiation is incident on a mixture of mercury and thallium vapors, some of the ground state mercury atoms can be raised to the 6^3P_1 state. While in this state, if a collision of a mercury atom with a thallium atom occurs, the excitation energy may be transferred to the thallium atom raising it to one of its excited states and returning the mercury atom to its ground state. The difference in energy between the donor and acceptor states will go into kinetic energy of the pair of atoms. The quenching cross-section we have measured is for a collision between an excited mercury atom and an unexcited thallium atom which removes the mercury atom from the 6^3P_1 state.

In the second figure, we have as before mercury on the left and thallium on the right where level No. 2 represents the 6^3P_1 state of mercury while No. 3 represents the metastable 6^3P_0 state, levels 5 and up represent various excited thallium states. R_{12} is the rate, i.e. the number of mercury atoms per unit volume per unit time, at which mercury atoms are raised from the ground state to the excited 6^3P_1 state. R_{21} is the rate at which the excited mercury atoms spontaneously emit 2537Å radiation returning to the ground state. R_{23} is the rate at which 6^3P_1



7^1S_o
7^3S_1
6^1P_1
4047
4358
6^3P_2
6^3P_1
6^3P_o
2537
6^1S_o
Hg
8^2P
7^2D
6^2F
$8^2S_{1/2}$
6^2D
$7^2P_{3/2}$
$7^2P_{1/2}$
$7^2S_{1/2}$
3529
3519
3230
5350
3776
$6^2P_{3/2}$
$6^2P_{1/2}$
Tl



Schematic energy level diagram indicating processes of interest

Figure 2

atoms are lowered to the metastable 6^3P_0 state by collision with ground state mercury atoms. R_{4T} is the rate at which mercury atoms are removed from the 6^3P_1 state by collision with thallium atoms.

These various rates are defined in figure 3. R_{12} is the rate of formation of excited 6^3P_1 mercury atoms which is proportional to the intensity of the incident radiation and the mercury ground state number density. R_{21}, the rate of spontaneous emission is equal to n_2,

$$R_{12} = \text{Production rate of } 6^3P_1 \text{ atoms}$$

$$R_{21} = n_2/\tau$$

$$R_{23} = 2n_1n_2\sigma_{23}^2 \sqrt{2\pi RT \left(\frac{1}{M_1} + \frac{1}{M_2}\right)}$$

$$\text{and } R_{4T} = 2n_2n_4\sigma_{4T}^2 \sqrt{2\pi RT \left(\frac{1}{M_1} + \frac{1}{M_2}\right)}$$

$$\text{Where } \sigma_{4T}^2 = \sum_i \sigma_{4i}^2$$

$$\text{For steady state, } R_{12} = R_{21}+R_{23}+R_{4T}$$

$$\text{and } R_{12} \text{ (Hg only)} = R'_{12} \text{ (Hg and Tl)}$$

Figure 3

the number density of the excited 6^3P_1 atoms divided by τ, the life time of the state. R_{23} and R_{4T} are given in terms of n_1, the number density of the ground state mercury atoms, n_2, the number density of 6^3P_1 mercury atoms, and σ_{23}^2, the self-quenching cross-section of mercury for transferring the excited atom from the 6^3P_1 state to the metastable 6^3P_0 state. R is the universal gas constant, T, the absolute temperature, M_1 and M_2, the gram-atomic masses of mercury and thallium respectively and n_4 is the number density of ground state thallium atoms.

For steady state, R_{12}, the rate of production of excited mercury atoms, must equal the rate of loss of excited mercury atoms given by $R_{21}+R_{23}+R_{4T}$. For a constant source intensity I_0 and mercury density n_1, the rate of production of excited mercury atoms in the scattering region with mercury only is equal to the rate at which they are produced with thallium also present. For steady state then, their rate of destruction must also be the same with thallium as without. This is true because the density of excited atoms is always very small compared to the density of the ground state atoms.

Equating the rates of loss, with and without thallium, and substituting the values for R_{21}, R_{23}, and R_{4T} given above into our equality, we obtain the first equation in figure 4.

$$\frac{n_2'}{n_2-n_2'} = \left[\tau\sigma_{4T}^2 M_4 \sqrt{8\pi RT\left(\frac{1}{M_1}+\frac{1}{M_2}\right)}\right]^{-1}$$

$$+n_1\left[\left(\sigma_{23}^2/\sigma_{4T}^2 n_4\right)\sqrt{2M_2/(M_1+M_2)}\right].$$

$$\text{Since } I_s \propto n_2,\ \frac{n_2'}{n_2-n_2'} = \frac{I_s'}{I_s-I_s'}$$

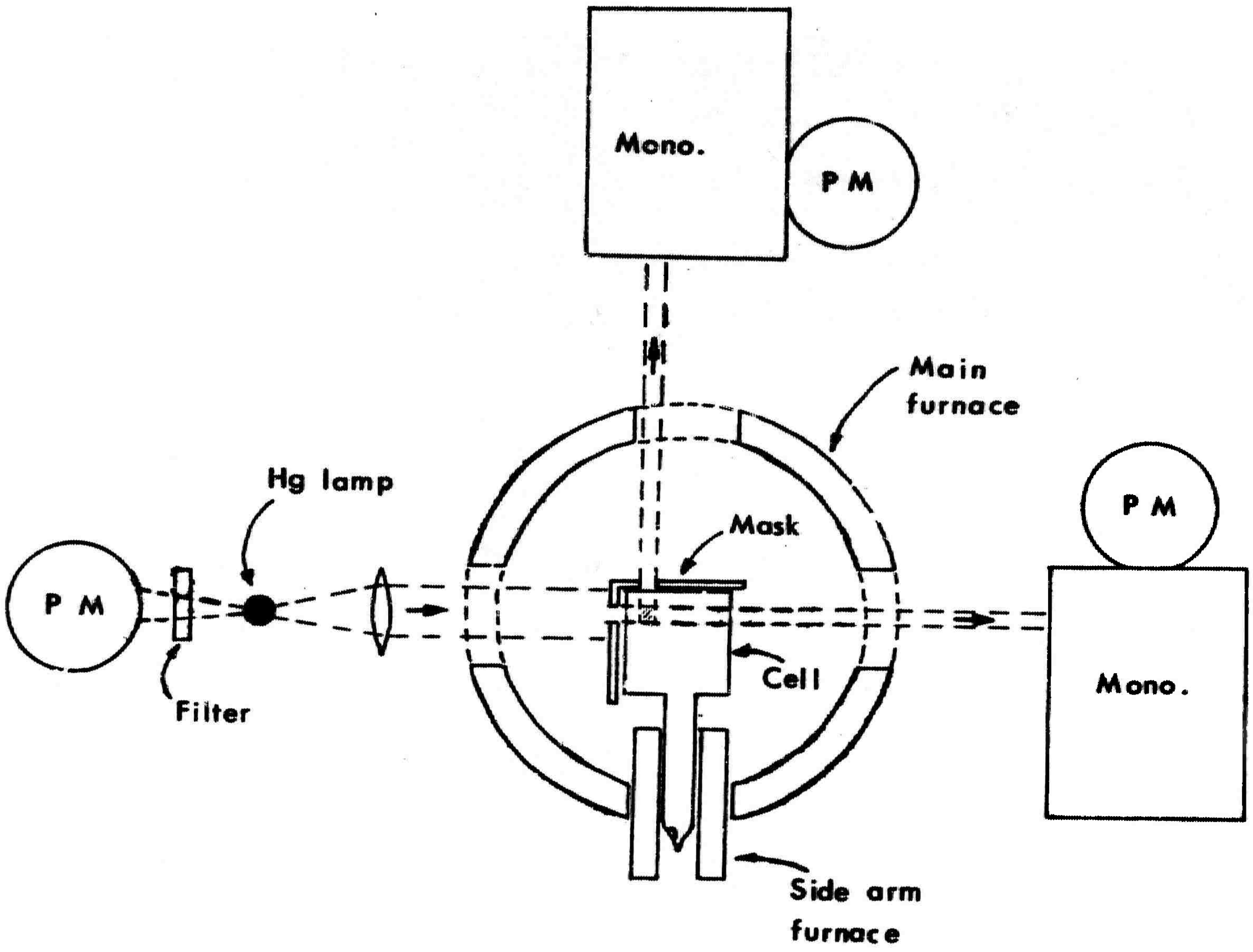
Figure 4

Spontaneously emitted radiation I_s is proportional to the number density n_2' of excited mercury atoms, and we may set $n_2'/n_2-n_2' = I_s'/I_s-I_s'$, where the prime designates the presence of thallium. See figure 4. The left side of the equation and the first term on the right side are of the order unity. The second term on the right varies from about 1/200 to 1/1400 for our experimental conditions if one considers σ_{23}^2 to be as large as σ_{4T}^2 which seems unlikely. Hence the second term may be neglected in comparison to the first, giving an expression from which σ_{4T}^2 may be easily determined.

Figure 5 shows a schematic representation of the experimental arrangement. At the center of the oven is a quartz cell containing the proper vapor. Plane parallel radiation from a mercury source enters from the left and the transmitted and scattered radiations are simultaneously measured by photomultipliers mounted on Bausch and Lomb grating monochromators. A mask about the cell keeps the geometry well defined and makes it possible to interchange cells with some precision.

The source is monitored by using a narrow band 2537Å interference filter and a photomultiplier tube. The large end of the cell is always kept at least $50^{\circ}C$ hotter than the arm of the cell in order to eliminate condensation of thallium on the windows. The actual dimensions of a cell are about one inch cubed with a five inch side arm. The production of the cells involves vacuum distillation of mercury and thallium into the cells after they have been outgassed at about 10^{-8}mm mercury while heated to about $1200^{\circ}C$.

Figure 6 shows the transmission and scattering data for a cell containing mercury only. The vertical axis is in arbitrary units while the horizontal one is the number density of mercury atoms x 10^{12} per cm^3. The straighter curve, (I_s/I_o)x100 represents the percentage of the incident radiation that is absorbed by the cell. I_t is simply the transmitted radiation at any particular mercury number density while I_o is the transmitted radiation with no mercury present, e.g., frozen out by liquid nitrogen. In the case of a cell containing thallium and a



Experimental Arrangement

Figure 5

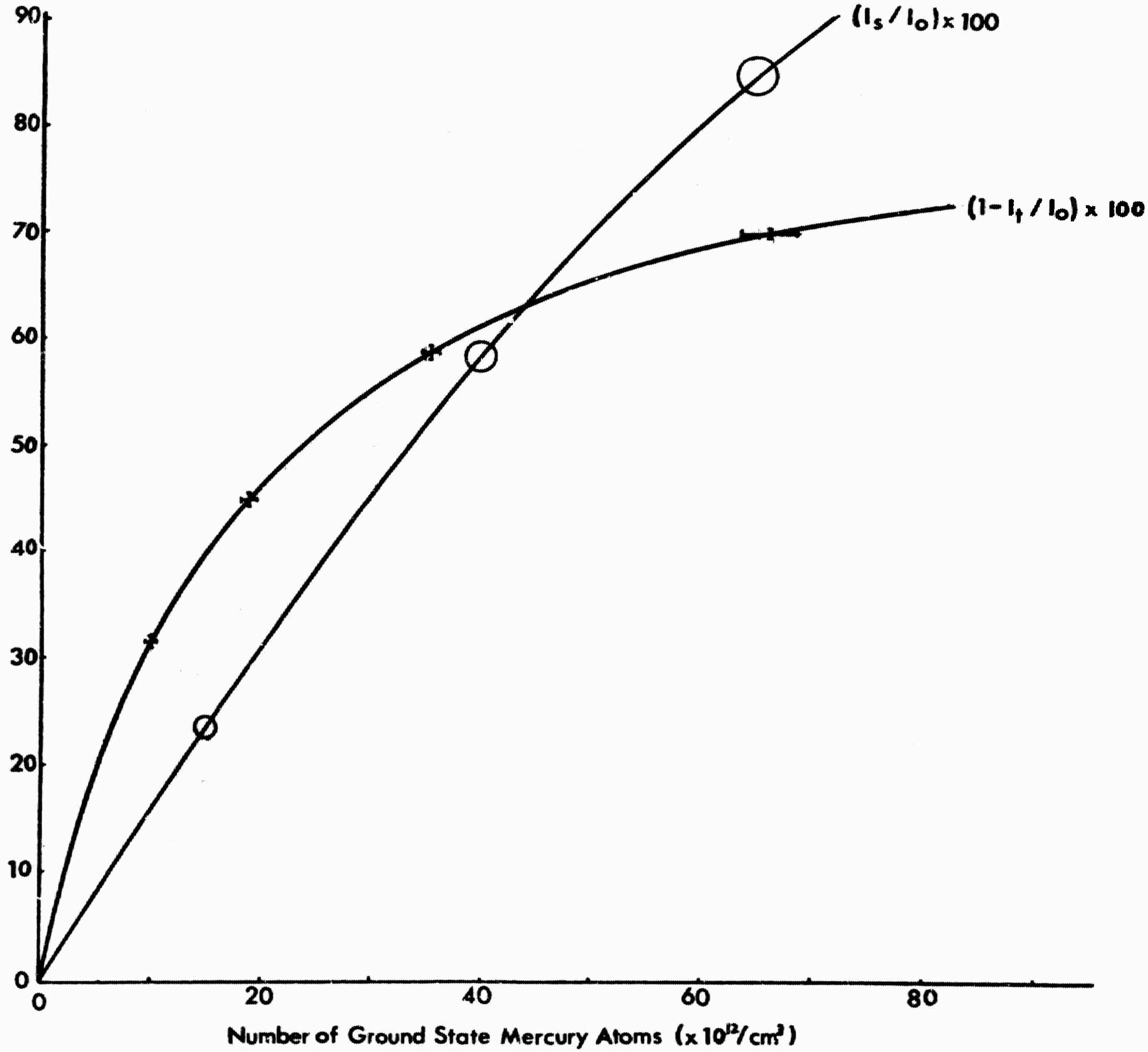

(Is / Io) x 100
(1 - It / Io) x 100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
Number of Ground State Mercury Atoms (x 10^12/cm^3)

Figure 6

fixed amount of mercury we determine the mercury number density from the percent absorption curve and from the corresponding $(I_s/I_0)x100$ curve predict what the scattering would be if the thallium were not present.

Figure 7 shows a typical set of data taken from a cell having a surplus amount of thallium but a fixed quantity of mercury. The vertical scale is dimensionless as before, while the horizontal scale is a log plot of the thallium number density. The upper curve is the percent absorption of the incident radiation which determines the amount of mercury present, the variation of this curve being due to mercury absorbed on the walls and combined with thallium at lower temperatures. The temperature range covered by this curve is from about 300^{0}C on the left to 850^{0}C on the right for the low temperature end of the cell. The interaction temperature of the cell was held at 900^{0}C. The curve labeled $(I_s/I_0)x100$ is the scattering curve predicted from figure 6 containing data for the mercury only cell. The lowest curve, $(I_s'/I_0)x100$, is the scattered radiation for this cell. This curve has been made to fit the other curve at low thallium densities, by a simple multiplication factor, in order to account for any differences in the transmission and scattering of the various cells when empty. The curves are seen to follow one another very closely up to about 500^{0}C because the thallium density is so small in this region that there is no measurable quenching. From this graph one may obtain a value for $(I_s-I_s')/I_s'$ at a particular thallium number density, permitting the calculation of σ^2_{4T}, the total quenching cross-section, where σ^2_{4T} is the solution to the equation discussed earlier. Figure 8 gives the tabulated results for total quenching cross-sections taken at various temperatures. The first three values are taken from

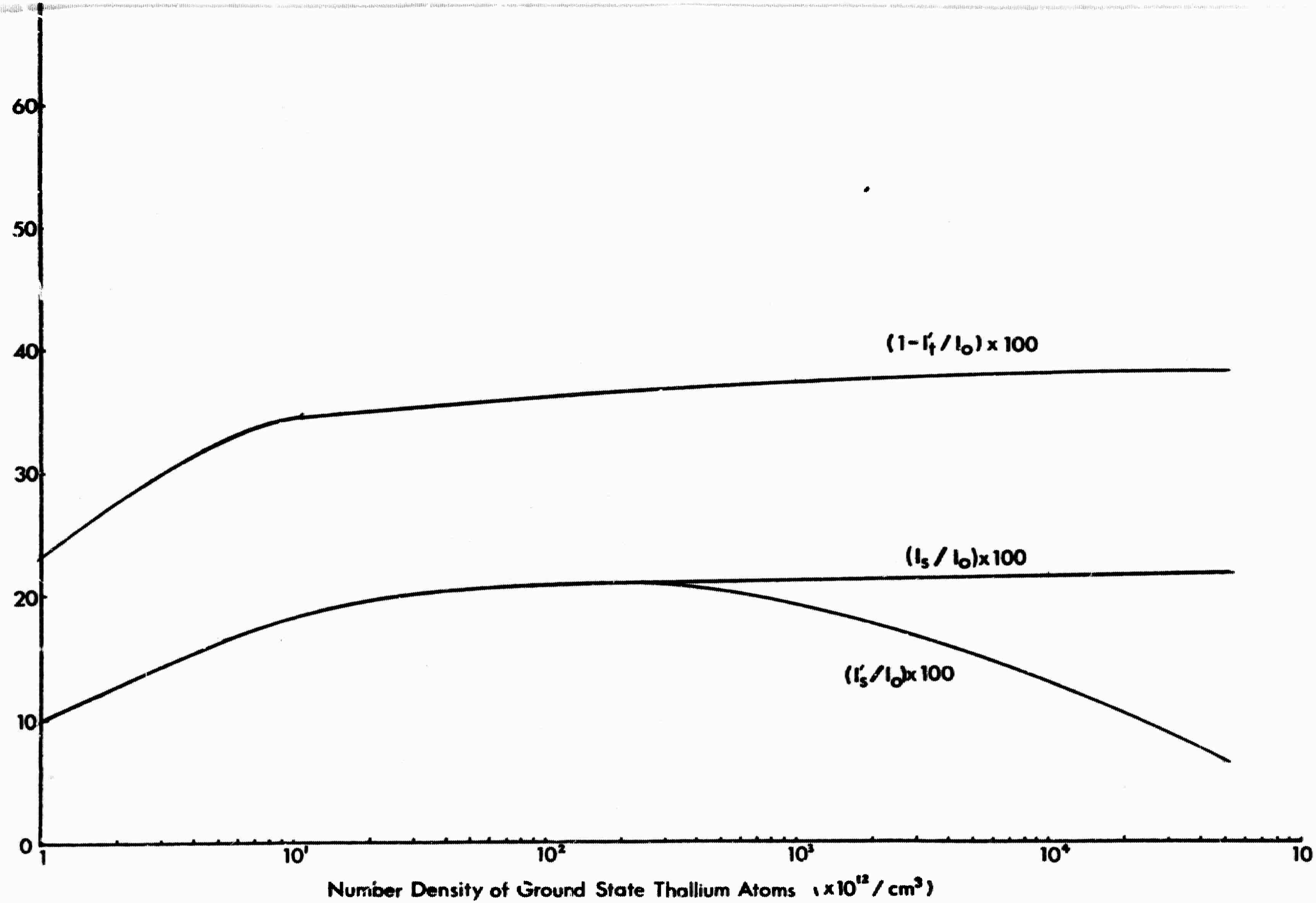

60
50
40
30
20
10
0
1
10'
10²
10³
10⁴
10
(1 − I′t / Io) x 100
(Is / Io)x 100
(I′s / Io)x 100
Number Density of Ground State Thallium Atoms (x10¹² / cm³)

Figure 7

$$\sigma^2_{4T} = \frac{(I_s - I'_s)/I'_s}{\tau n_4 \sqrt{8\pi RT(\frac{1}{M_1} + \frac{1}{M_2})}}$$

T^oC	σ^2_{4T} $Å^2$
733	60 ± 45
792	48 ± 16
847	36 ± 9
900	26 ± 8

Figure 8

measurements on a single cell, varying the interaction temperature while the lowest value, corresponding to a temperature of 900^oC, is an average from three different cells. It is of interest to note that the deexcitation cross-section of thallium for mercury is about eight times the energy transfer cross-section from the $He(2^1S_0)$ state to the $Ne(3s_2)$ state which gives rise to the strong neon laser transitions.