Final Report

OPTICAL ENERGY TRANSFER PROCESSES*

by

M.J. Linevsky

July 1968

* This work was supported by the Advanced Research Projects Agency, Washington, D.C. ARPA Order No. 1009, ARPA Program Code No. 7E20, ARO-D Project No. 7508-C (Contract DAHC04-67-c-0065)

Report No AROD-7508.4

Space Sciences Laboratory
GENERAL ELECTRIC CO.
King of Prussia, Pennsylvania

33

Final Report

OPTICAL ENERGY TRANSFER PROCESSES*

by

M.J. Linevsky

July 1968

* This work was supported by the Advanced Research Projects Agency, Washington, D.C. ARPA Order No. 1009, ARPA Program Code No. 7E20, ARO-D Project No. 7508-C (Contract DAHC04-67-c-0065)

Space Sciences Laboratory
GENERAL ELECTRIC CO.
King of Prussia, Pennsylvania

ABSTRACT

Experimental and analytical investigations have been carried out on photo-excitation and ionization processes in barium and titanium systems. It has been shown that, in order to explain the observed rates of photoionization of barium clouds, photoionization involving barium metastables must be assumed. Population of these metastables can be achieved through an optical pumping process involving resonance absorption from the ground state followed by branching into the metastable levels. A quasi-steady state analysis of this process indicates that an f number of approximately 0.1 is necessary to explain the observed rates of ion production in the barium clouds. Experimental studies using both optical absorption techniques and photoionization mass spectrometry indicate this f number to be in the range of 0.01 to 0.1. These experimental results are at the present time to be taken as quite tentative because of experimental limitations.

A narrow line absorption technique was employed to measure the relative gf values for approximately thirty lines of titanium. This method offers the advantages of high sensitivity, speed, and precision over other techniques when the vapor pressures of the absorbing species are accurately known. Absolute gf values were obtained from the measurement of the absolute gf value for the 3371A transition. The gf value for this transition was found to be 1.74.

TABLE OF CONTENTS

BLANK PAGE

INTRODUCTION

The Optical Energy Transfer Processes Section of this investigation is concerned with the general understanding of photo-excitation and ionization in certain metal atoms and molecules of interest to ARPA programs. Investigations of such processes involving barium (relative to BMD Ba experiments) and titanium (relative to Press) have been of particular interest. Our interests for the past year have focussed on better understanding of the observed ionization of barium which has been seen in recent high altitude chemical releases carried out by CRL and NASA and on obtaining oscillator strengths for titanium lines which have been observed in re-entry spectra. To these ends, we have undertaken both experimental and analytical investigations, the results of which are reported here.

In the case of the barium release, observations made by both the American[1] and German[2, 3] groups are in agreement on several basic facts. These are:

1. Barium clouds photoionize very rapidly and completely. The ion cloud can be seen to separate (due to the earth's magnetic field) from the neutral cloud within 100 seconds with only a weak connecting "bridge" of continuing ionization, showing ionization is nearly complete in tens of seconds. Furthermore, the ionization process in releases carried out above 200 km appears to have a characteristic time of approximately 31 sec with this value decreasing with altitude. Fopl et al[2] also speak of a long time ionization process with a characteristic time of approximately 100 sec.

2. Barium metastables are seen at early times (before 15 sec) but are missing at later times (15-95 sec), suggesting that excited metastable species are involved in the photoionization processes. The specific metastables observed are the $5d\,^1D$ and $5d\,^3D$ states. Several recent release observations have also shown that the characteristic time of disappearance of these metastables is the same as the appearance time of the ion.

Haser[3] has suggested that the photoionization of Ba proceeds by a two step process where: (1) resonance absorption and subsequent population of a metastable level by spontaneous transitions takes place followed by

(2) photoionization by absorption from the metastable state. This pumping process is possible for both of the observed metastables of barium. Haser further suggests several pumping schemes by which the metastable levels are populated.

It is the purpose of this investigation to examine further the ionization process in the light of these observation and to supplement, by laboratory experiments, the data necessary to properly evaluate the different possible mechanisms of ionization.

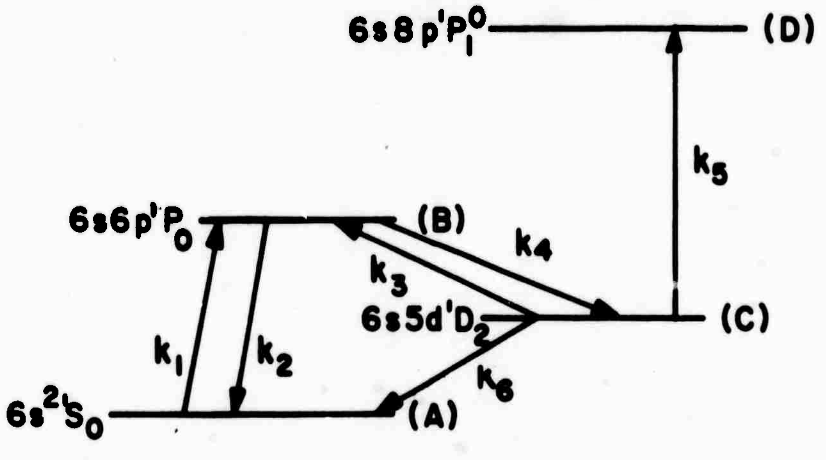
In the case of the oscillator strength studies, at the suggestion of Lee Bradley of Press, approximately twenty-five titanium lines have been measured. The oscillator strengths of these lines have been obtained by measuring the narrow line absorption of the corresponding titanium lines generated in a cooled hollow cathode discharge source by a known concentration of titanium vapor in a furnace. Comparison with the results of other investigators has been made.

BARIUM IONIZATION STUDIES

Introduction

Foppl et al[2], on the basis of an extrapolation of existing data and from theoretical considerations, have estimated rates of excitation for direct photoionization of the $^1S_0$ ground state of barium. They give for the continuum contribution, $k^{cont.}_{ion} = 1.7 \times 10^{-4}\ sec^{-1}$ and for autoionization, $k^{line}_{ion} = 3.4 \times 10^{-4}\ sec^{-1}$. The total excitation rate for the direct photoionization of the ground state is therefore approximately $5.1 \times 10^{-4}\ sec^{-1}$. The characteristic time for ionization by this process is approximately 1400 sec or much greater than that observed in the barium clouds. For this reason, ionization via metastables has been postulated in an effort to achieve shorter photoionization times. However, it is also possible that the ground state excitation rates have been considerably underestimated.

Consider a possible metastable pumping and ionization mechanism involving the $6s5d^1D_2$ metastable as shown in the accompanying sketch.



The k's are the rate constant for the depicted transitions. This mechanism would involve the absorption by ground state atoms of 5535 A radiation, followed by branching into the metastable state with the emission of 15,000 A light, and subsequent ionization to the $8p\,^1P^o_1$ autoionizing level by the absorption of 3266 A radiation. Radiative decay of the $^1D_2$ metastable to the ground state has also been included through the rate constant k_6. Other pumping mechanisms into this metastable level are also possible within the term scheme of barium. For example, pumping by 3071 A and 3501 A radiation followed by emission of 4726 A and 5826A radiation will also populate state C. However, since the f number of the 5535 A transition is comparatively much larger than the other pumping transitions, it would seem that this particular pumping scheme would result in the largest metastable production. In any case, this scheme is representative of metastable pumping mechanisms. Similar mechanisms are possible for the production of the triplet metastable states. The kinetic equations describing the concentrations of A, B, C and D in the four levels shown in the sketch, are as follows:

$$\frac{dA}{dt} = -k_1A + k_2B + k_6C \tag{1}$$

$$\frac{dB}{dt} = -(k_2 + k_4)B + k_1A + k_3C \tag{2}$$

$$\frac{dC}{dt} = -(k_3 + k_5 + k_6)C + k_4B \tag{3}$$

$$\frac{dD}{dt} = k_5C \tag{4}$$

These equations can be solved numerically for short time intervals using an available Runge-Kutta-Merson[4] integration technique. The k values for the downward transitions, k_2, k_4 and k_6 are equal to the respective Einstein A coefficients whereas the upward transitions, k_1 k_3 and k_5 are equal to their respective Einstein B coefficients multiplied by the appropriate photon density. Existing information on the f numbers and solar fluxes for the various transitions permits reliable evaluation of the rate constants k_1, k_2, k_3, and k_4. Garstang[5] recently has estimated the lifetime of the $^1D_2$ metastable to be 3 sec. This leads to a value for k_6 equal to 0.33 sec^{-1}. These constants are given in Table I. No reliable information exists for the f number of the transition C→D i.e., for the transition from the metastable state to the autoionizing state.

TABLE I. RATE CONSTANTS FOR METASTABLE PUMPING AND IONIZATION TRANSITIONS

TRANSITION	WAVELENGTH A	RATE CONSTANT Sec^{-1}
$6s^2\,{}^1S_0 - 6s6p\,{}^1P_0$	5535.55	$k_1 = 9.0$ $k_2 = 1.63 \times 10^8$
$6s6p\,{}^1P_0 - 6s5d\,{}^1D_2$	1500.0	$k_3 = 3.0$ $k_4 = 1.26 \times 10^7$ $k_6 = .33$

Numerical solutions to equations (1) through (4) indicate that quasi-steady state conditions become established for levels B and C within 1 second (assuming various values of k_5 varying from 0.1 sec^{-1} to 10 sec^{-1}). Therefore, for time scales greated than 1 second, the quasi-steady state conditions, $dB/dt = 0$ and $dC/dt = 0$ can be imposed and the set of equations (1) - (4) can be solved for the slow time variation of the concentrations D, C and A due to the photoionization process. These results are given by:

$$D = A_T\left(1 - \exp(-k_5 Zt/(1 + Z)\right) \tag{5}$$

$$C = \frac{Z}{1+Z}\left(A_T \exp -k_5 Zt/(1 + Z)\right) \tag{6}$$

$$A = \frac{A_T}{1+Z} \exp\left(-k_5 Zt/(1 + Z)\right) \tag{7}$$

where A_T is the total barium inventory and $Z = \dfrac{k_1 k_4}{k_2(k_3+k_6) + k_4 k_6}$. It is obvious from expressions (5) through (7) that the characteristic time obtained from the exponential factor for the appearance of ions (D) is equal to the characteristic time for the disappearance of both ${}^1D_2$ metastable (C) and ground state barium atoms (A). This characteristic time is given by:

$$\tau = \frac{1 + Z}{Z} \cdot \frac{1}{k_5} \tag{8}$$

Substituting the values of the rate constants given in Table 1 and the value for τ = 31 sec. into (8), k_5 is found to be equal to 0.19 sec. This implies that the f number for the $^1D_2$ metastable to the $8P\,^1P_1$ autoionizing is equal to approximately 0.11. It should be noted that an f number of 0.03 for metastable ionization extimated in an earlier report[10] was based on the long time characteristic time of 100 sec and did not include k_6. As has been pointed out by Rosenberg et al, the so-called long time ionization processes is merely a consequence of the reduced rate of production of ions (D) because of the depletion of the metastables (C). Using the numerical values for the rate constants the expressions for the concentrations D, C, and A as a function of time and total barium inventory become:

$$D = A_T \left(1 - \exp(-.0323\,t)\right) \tag{9}$$

$$C = .171\, A_T \exp(-.0323\,t) \tag{10}$$

$$A = .829\, A_T \exp(-.0323\,t) \tag{11}$$

A plot of these concentrations (a percentage of the total barium inventory) as a function of time is given in Figure 1. It is seen from this figure that there is a rapid build up of ions and by one minute, 85% of the total barium inventory is in the form of ions. The ratio of ions to ground state barium at one minute is approximately 7:1.

It can be concluded that the observed ionization of barium clouds is consistent with an optical pumping scheme involving the production of metastable barium atoms and their subsequent ionization. Furthermore, the f number for the metastable ionization process must be of the order of 0.1 in order to explain the observed rates of ion production.

We have, therefore, undertaken to obtain experimentally an estimate for the f number of this transition. The experimental approach used has been two-fold, viz:

1. A furnace technique similar to that of Garton and Codling's[6] was used to examine the absorption spectrum of barium in the metastable ionization region around 3300 A. These measurements were made at higher temperatures and, therefore, higher barium pressures than were achieved in ref. 6.

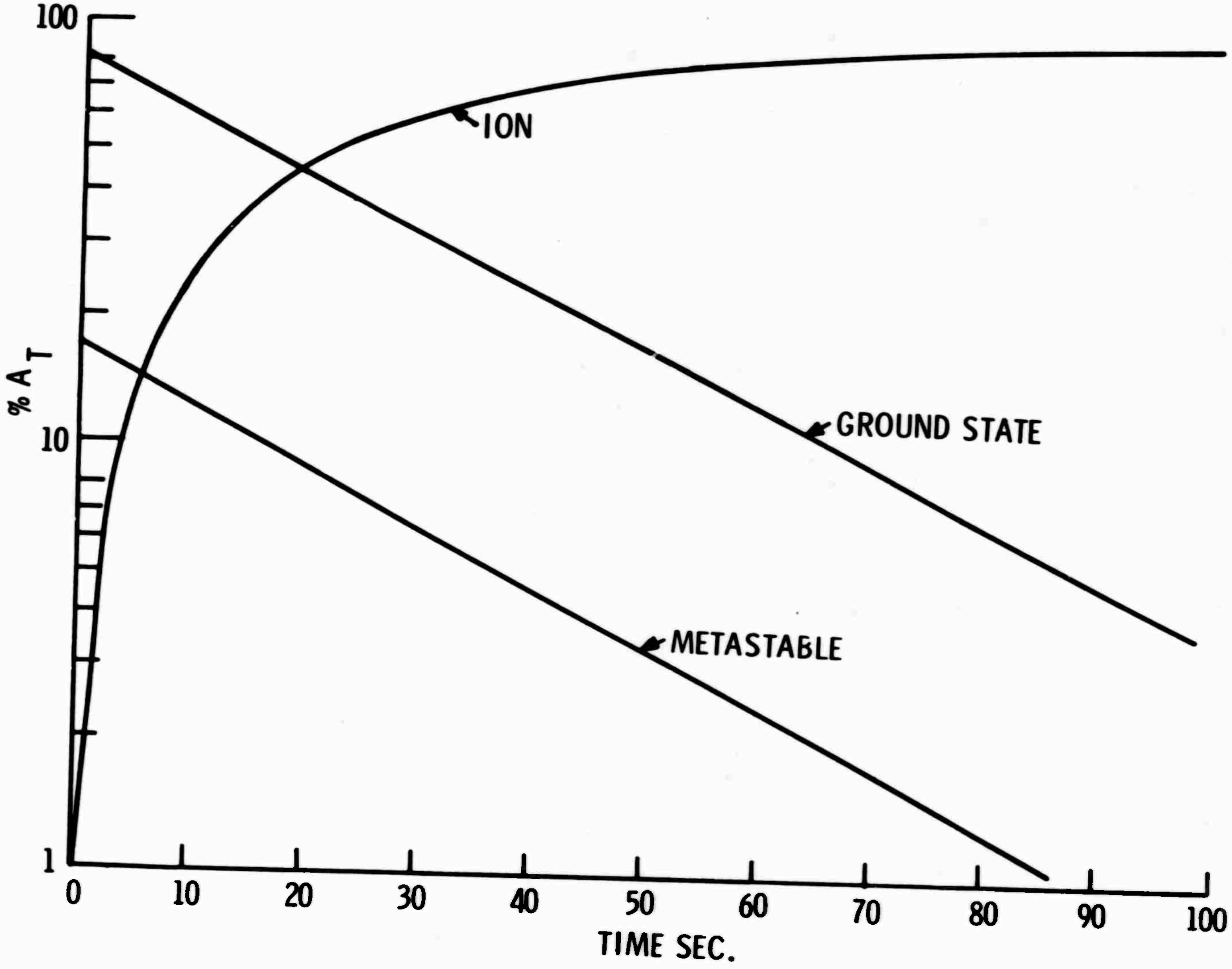


Figure 1. Time History of Barium Species for Cloud Conditions

2. Attempts to photoionize barium vi the metastable pumping scheme. This was tried on static hot barium vapor in the furnace and also in a very preliminary fashion on a molecular beam of barium produced in the source of a mass spectrometer. The details of these experiments are given below.

Experimental and Results

The furnace used in these investigations was a carbon resistor furnace, capable of maintaining 3000° C, of the type first described by King[7] but partly modified by Zeeman[8] and Vidale[9]. The heating element consisted of a National Carbon AUC grade graphite tube, approximately 24 in long, having a wall diameter of 0.090 in. to 0.130 in. in the central 16 in. which comprises the hot zone of the tube. The inner diameter of the tube is 1-3/8 in. The only insulation used in the furnace consisted of a series of nine concentric AUC graphite radiation shields. Quartz windows were used at both ends of the furnace through which light could enter and leave. A complete description of the furnace is available elsewhere[9].

For the absorption studies (1), two experimental approaches were used. The first, which was reported earlier,[10] made use of conventional spectro-photographic techniques. The set up consisted of a 150 watt Osram high pressure xenon source whose beam was collimated and allowed to pass through the furnace tube in which was placed a molybdenum cell containing either barium in the form of iron clad wire or barium chloride. The beam was then focussed to allow diaphragmming out of unwanted light from the hot furnace walls and then refocussed on the slit of a 2-meter B & L spectrograph by means of a cylindrical quartz lens.

In the second approach, a spectrophotometric technique was used. The high pressure xenon source was replaced by a much more stable deuterium discharge lamp; the light from this source was chopped and brought to focus at the center of the molybdenum cell. The beam was then refocussed onto the slit of a Spex 3/4 meter spectrophotometer and the signal detected using phase locked amplification.

For the furnace optical pumping experiments (2), a 1000 watt high pressure mercury Hanovia lamp was used as both the irradiating and absorption sources. In this case, the light from the lamp was focussed in the center of the furnace and then refocussed on the slit of a Spex 3/4 meter spectrometer.

In the case of the absorption studies (1), absorption spectra using the spectrograph approach were taken between 5000 A - 2000 A at furnace temperatures between 1500°K to 2500°K. In all the furnace studies, the furnace was pressurized with either argon or helium gas to a total pressure of 1 atm. to mitigate diffusion of the barium out of the absorption cell. The spectra obtained with the 2-meter spectrograph agreed quite well with those reported by Garton, Parkinson and Reeves[11] on shock-excited barium indicating a fair degree of thermal population of both the ^1D and ^3D metastable levels. However, from visual observations of the spectrographic plates, no evidence was found for the expected $6s5d\,^1D_2-6s8p\,^1P_1^o$ transition at 3266 A or for that matter for any autionizing transition involving metastable lower states. (This agrees with the results of ref. 11.) These negative observations, however, do not preclude the possibility that the expected transitions can be quite broad and weak and, therefore, not easily detected over the backround intensity. Although the negative observations with the photographic technique would imply an f number for the metastable autoionization transitions of less than 10^{-3} (as was pointed out in a previous report[10]), it was felt that a photometric technique might be useful in detecting features that were obscured by the background continuum and by the wings of the strong bound barium transitions in the region of interest.

As mentioned above, a deuterium lamp source was used instead of the high pressure xenon lamp because of its enhanced stability. Barium in the form of iron clad wire was loaded into a 4-1/2 inch molybdenum cell having 1/4 inch openings. Helium gas was used in the furnace and absorption spectra in the region of 3300 A to 2500 A were measured at furnace temperatures varying from approximately 1400°K to 1600°K. A severe difficulty was encountered with particulate haze presumably because of unavoidable oxide contamination when the cell was heated to temperature. This haze could account for as much as 20% reduction in I_o and appeared to be a function of both the cell temperature and wavelength. Some reduction of the haze could be achieved by repeated cycling of the temperature before the final absorption spectra were taken. Nevertheless, its presence made quantitave measurements of the absorption impossible and only estimates of I/I_o could be obtained. A sketch of a typical absorption spectrum is given in Figure 2. It is seen from this figure that there appears to be several broad and weak absorption features (shaded areas) underlying the discrete absorption lines (due to barium and to metallic impurities). Because of the haze problem, the exact placement of the I_o level was difficult and an assumed value has been drawn in as shown. These broad features show some structure and can be grouped into the areas A, B, C, D and E. These areas peak at approximately 3268 A, 3240 A, 3160 A, 3145 A and 3005 A respectively. Their sizes are further complicated by the wings of the discrete lines and, indeed, the resonance transition at 3072 A ($6\,^1S$ - $7\,^1P$) is so intense at these concentrations as to completely obscure what appears to be additional broad underlying absorptions. Nevertheless, it is felt that these broad "bumps" are real and indeed are due to absorption by ^1D and ^3D metastables to autoionizing levels. As was pointed out by Garton, Parkinson and Reeves[11], the 5d6s $^{1,3}D$ levels should combine strongly in single-electron jumps, not only with $J = 1$ autoionizing levels of 5dnp already recognized from the work of Garton and Codling[6], but also with the $J = 0, 2, 3$ levels of 5dnp, for which the complete term manifold is $^{1,3}P, D, F$. Hence, a sizeable number of absorption lines, some very diffuse, are expected to occur in the region of the spectrum investigated. Some idea of the expected frequencies of these transitions can be obtained from the results of Garton and Codling and from Rydberg extrapolations of other levels (e.g., ^1D, ^1F) expected to combine with the metastable levels but not with the ground state. A partial list of these expected autoionizing transitions is given in Table II.

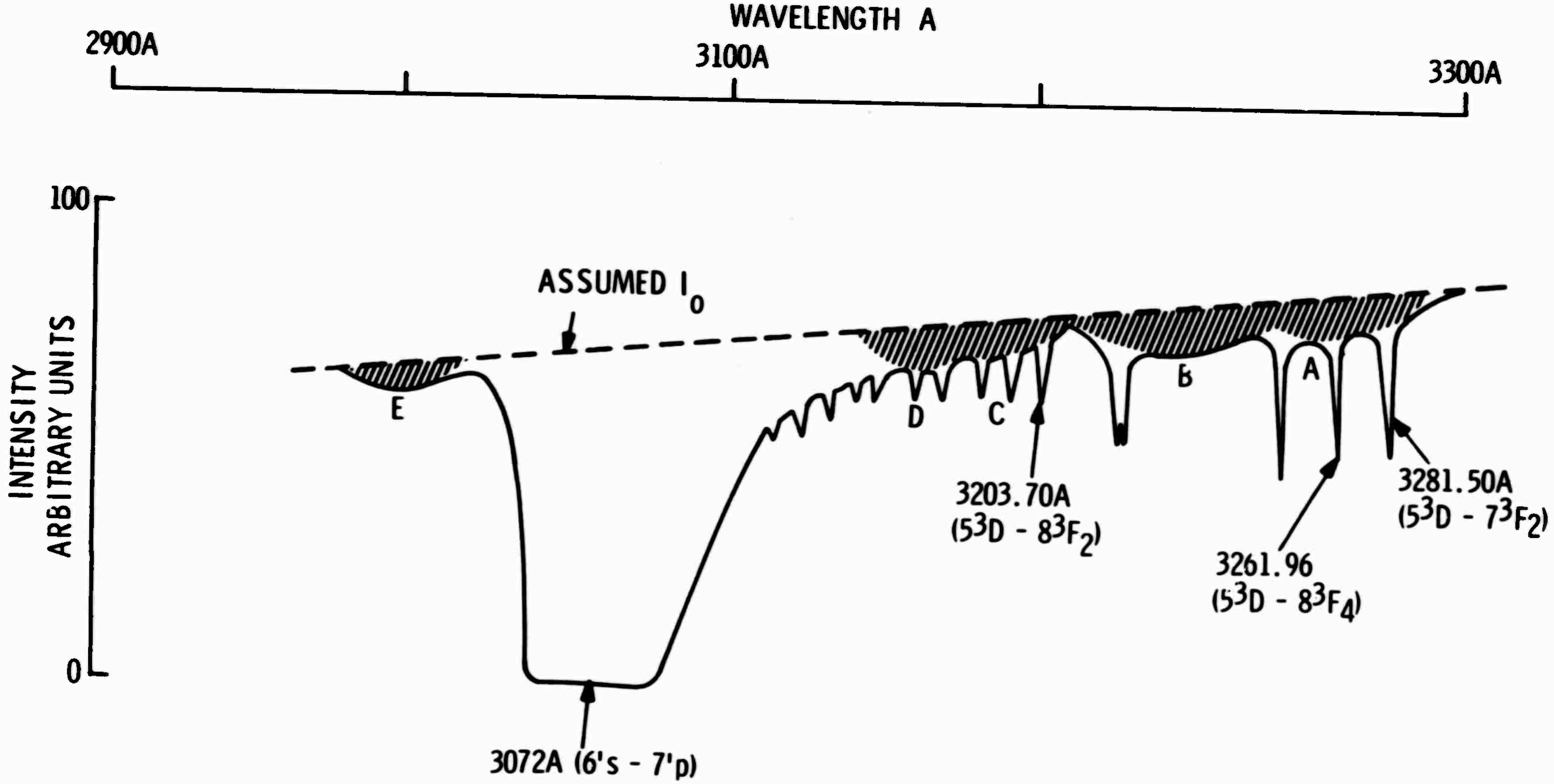


Figure 2. Absorption Spectrum of Barium 2900A - 3300A

TABLE II. SOME EXPECTED AUTOIONIZING TRANSITIONS FOR BARIUM METASTABLES

Area	Transitions	Wavelength A
A	$5d^1D - 8p'\,^1F$	3272
	$5d^1D - 8p'\,^1P$	3266
B	$5d^1D - 8p'\,^1D$	3256
	$5d^1D - 4f'\,^3P$	3222 (for $^3P_1$)
C & D	$5d^1D - 9p'\,^3D$	3169 (for $^3D_1$)
	$5d^1D - 9p'\,^3P$	3161 (for $^3P_1$)
Obscured Region	$5d^1D - 5f'\,^1P$	3138
	$5d^1D - 9p'\,^1P$	3075
	$5d^3D_3 - 8p'\,^1D$	3075
	$5d^1D - 10p'\,^3P$	3056 (for $^3P_1$)
	$5d^1D - 10p'\,^3D$	3055 (for $^3D_1$)
	$5d^3D_2 - 8p'\,^1P$	3049
E	$5d^3D_1 - 8p'\,^1P$	3032
	$5d\,^1D - 9p'\,^1D$	3024
	$5d^3D_2 - 4f'\,^3P$	3010 (for $^3P_1$)
	$5d^3D_1 - 4f'\,^3P$	2994 (for $^3P_1$)
	$5d^1D - 10p'\,^1P$	2975

It is interesting to note that, although many lines are expected from the ^3D metastables whose transitions should fall primarily below 3000 A, no comparable underlying absorption features are seen to the blue of area E. Furthermore, as evidenced from Table II, the observed "bumps", to a very large extent, can be interpreted as due to ^1D transitions. This would imply a relative f number for the ^1D to ^3D autoionizing transitions of at least 10 since the ^1D concentration at the temperature of observation was around 10^{13} atoms/cc as compared to the ^3D concentration of 10^{14} atoms/cc. It is apparent that the broad underlying features in each case are caused by several autoionizing transitions rather than single transitions. A very approximate f number can be obtained for feature A. This feature was selected since it appeared to be the least obscured by both the haze interference and by the discrete transitions in the region. Assuming the applicability of the Beer-Lambert Law, the f number is given by:

$$f = \frac{37.69 \int \log_e I_o/I \, d\nu}{N\ell} \qquad (12)$$

where N is the concentration of ^1D metastables per cc., ℓ the path length and the $\int \log_e I_o/I \, d\nu$ is obtained from the spectrum in Figure 2 by graphical integration. Since there is overlap between areas A and B, the integral was obtained by using twice the right hand half of area A. The ^1D metastable concentrations were obtained, assuming a Boltzmann distribution, for the total barium population. This population was arrived at from the vapor pressure of barium using 44.0 kcal/mole* as the heat of vaporization at 298°K and the free energy functions given by Stull and Sinke.[12] Typical values for the oscillator strength associated with area A fall in the range of 0.04. This value should be taken as very approximate due to the limitations of the absorption measurements mentioned previously. It is seen that a total f number of approximately 0.1 for the entire region between 2300A and 2900 A is reasonable in the light of this approximate value.

---

*Recent determinations in this laboratory by P. D. Zavitsansos and M. J. Linevsky.

It is clear that an accurate determination of the rate of photoionization of metastable barium atoms must await a technique which can directly measure the rate of production of ions as a function of wavelength. This is obvious from the experimental difficulties associated with the absorption techniques described above and from the lack of information obtained from such techniques regarding the transition from the autoionizing levels into the ion continuum. One such approach using photoionization mass spectroscopy has been started in this laboratory and will be described below.

Attempts to photoionize barium by pumping and subsequent photoionization of the resulting metastable state were also carried out in the furnace. Using the 1000 watt high pressure mercury lamp as both the irradiating and absorption source, no evidence for the production of barium ions (no detectable absorption of the 4554 ion resonance line) was obtained. Although this is most likely explained by the apparent low f number of the metastable ionizing transition ($\lesssim 10^{-3}$ shown above), nevertheless, the possibility of quenching of the metastables by the foreign gas in the furnace and by the furnace walls cannot be discounted. It is felt, therefore, that this furnace pumping experiment may not be conclusive. For this reason, we have attempted to study this pumping and photo ionization process using a modified mass spectrometer. Here , irradiation can be carried out on a molecular beam of barium and, therefore, quenching by gas and wall collisions will be negligible. Furthermore, since in principal the mass spectrometric technique is capable of detecting single ions, the sensitivity inherent in this type of experiment should be much greater than that which can be achieved by optical absorption. No effort at this time was made to quantitatively obtain ionization cross-sections from the observed ion currents. Instead, some preliminary measurements of the relative production of ions by the direct photoionization process to that of metastable pumping were carried out.

The mass spectrometer used in these studies was a Bendix Time of Flight Model 12 instrument, having a Knudsen cell attachment. For the purposes of this preliminary experiment, it was found most expeditious to irradiate the barium beam effusing from the Knudsen cell via the top window port normally used for pyrometry readings. The irradiating source used was a GE BH6 1000 watt high pressure mercury lamp. The barium was contained in a tantalum Knudsen cell, having a 20 mil orifice. The cell was heated radiatively by two tungsten filaments on either side of the cell. A schematic of the apparatus is given in Figure 3.

Ion signals were observed with the full continuous wavelength output of the lamp and with filtering so that wavelengths shorter than 3000 A were blocked. In the first case, the ion signal was due to direct photoionization of ground state barium by photons of wavelengths less than 2380 Å, plus photoionization due to metastables pumped by longer wavelengths. In the second case ions could only be produced from metastables. Therefore, the relative importance of these two processes can be estimated from the observed relative ion signals. Some typical results are given in Table II.

It is clear from the relative magnitude of the ion intensities in Table III that metastable barium ions were being produced in the source of the mass spectrometer by optical pumping since the ratio of thermal populations of ^1D barium to ground state barium at the experimental temperatures were no greater than 2×10^{-6}.

The rate of ionization for each process is given approximately by:

$$R = I_\nu B_\nu N$$

where I is the light in intensity at the frequency of photoionization ν, B the Einstein coefficient and N the concentration of barium atoms in the state undergoing photoionization. Therefore, the relative production of ions due to direct plus metastable photoionization compared to that of metastable photoionization only is approximated by:

$$F = \frac{\text{ions total}}{\text{ions metastable}} \cong \frac{I_{2380} B_{2380} N_{grd} + I_{3266} B_{3266} N_{met}}{I_{3266} B_{3266} N_{met}} \qquad (13)$$

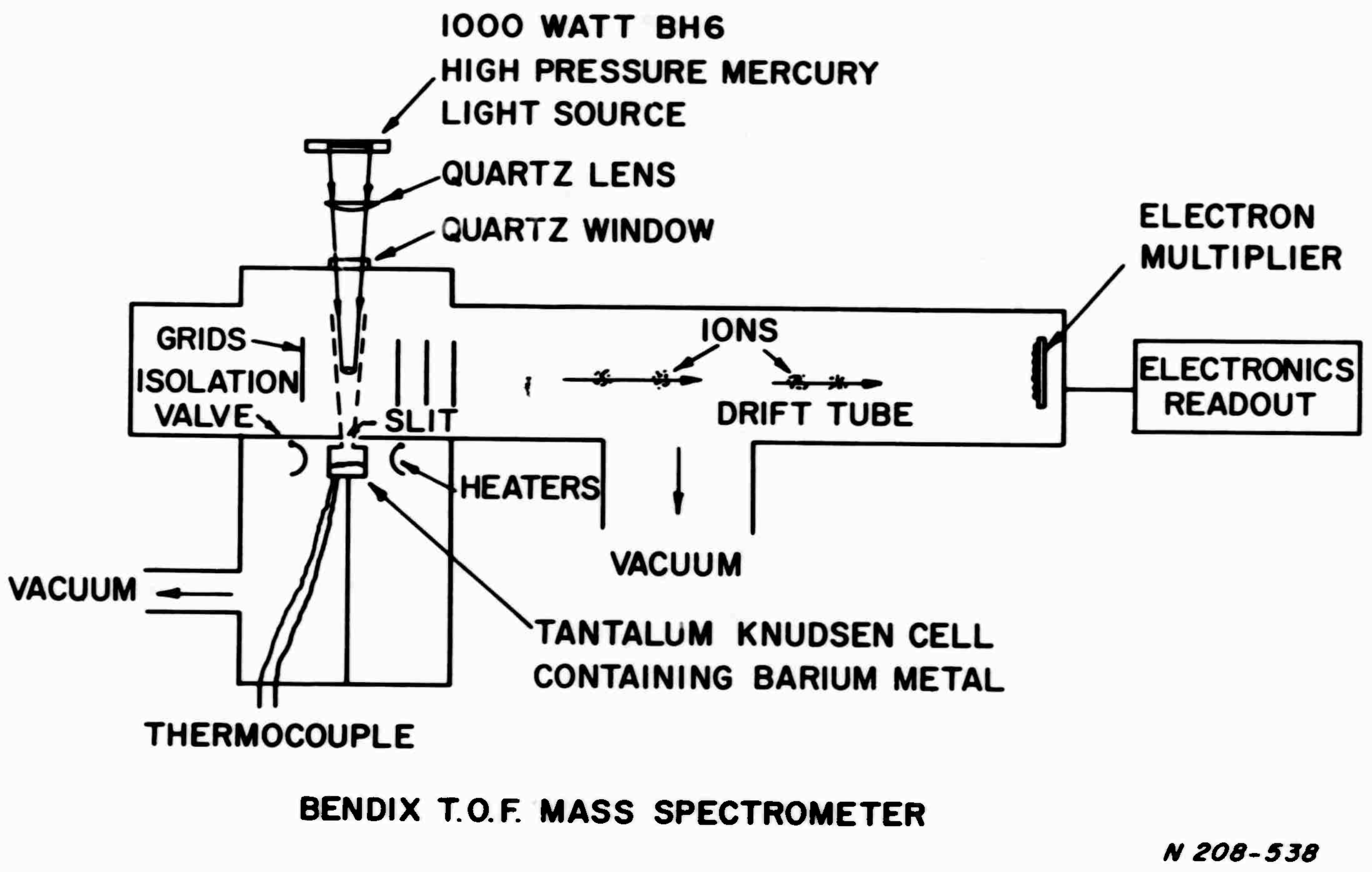


Figure 3. Photoionization mass spectrometer apparatus

TABLE III. ION INTENSITIES OF PHOTOIONIZATION IN TOF MASS SPECTROMETER

Temperature °K	Filter	Ion Intensity Arbitrary Units	Ratio F
990	no	42.5	42.5
990	*Corning #0-54	1.0	
1090	no	62.0	38.8
1090	*Corning #0-54	1.6	

* short wavelength cut off 3000 Å

or

$$\frac{B_{2380}}{B_{3266}} \cong (F - 1) \frac{I_{3266}}{I_{2380}} \times \frac{N_{met}}{N_{grd}} \qquad (14)$$

where $\frac{N_{met}}{N_{grd}}$ is the ratio of the metastable concentration to ground state concentration taken over the residence time of the barium atoms in the ionization chamber of the mass spectrometer. This ratio can be estimated by the use of the previously mentioned numerical solution to the four level process provided the rate constants k_1, k_3 and k_5 are known. In order to obtain these rate constants, the absolute light intensity in the transition wavelengths impinging on the barium atoms must be known. At the present time, no reliable measurements of these light intensities inside the source of the mass spectrometer have been made. Nevertheless, using reported intensities of the light source[13] and very approximate estimates of the geometry factor for the mass spectrometer, the ratio $N_{met}(^1D)N_{grd}$, for a residence time of around 10^{-5} sec. can be made. In this fashion, the B ratio was obtained from equation (14) and the f number for the metastable ionization was found to be approximately the same as that of the ground state namely around .015.[2] This value should be taken as very tentative and a more reliable f number must await better intensity data.

Summary and Conclusions

It has been shown that the observed photoionization of barium in the upper atmosphere releases is consistent with an optical pumping scheme in which ground state barium is pumped by solar radiation into metastable levels followed by photoionization of the metastables to the ion. As illustrative of the process, a quasi steady state analysis was carried out involving resonance absorption at 5535 A followed by branching into the $^1D_2$ metastable level. Based on this scheme it was found that an f number of approximately 0.1 for photoionization from the $^1D_2$ level to the ion is necessary to explain the observed characteristic times of ionization in barium clouds. This value should be taken as an upper limit since other pumping mechanisms into metastable levels are also available (which were not included in the analysis). Although a previous experiment study[10] indicated a value for this f number to be of the order of .002, the results of our present program indicate that the f number is much larger. Indeed a value of around 0.1 appears to be reasonable based on the results of a photometric absorption study. However, a value closer to .01 was obtained from very preliminary photoionization experiments carried out in a mass spectrometer. Both these values should be taken as very tentative and it is therefore recommended that further experiments be carried out in order to obtain a more reliable value.

TITANIUM OSCILLATOR STRENGTHS

Introduction

Vidale[14], in a recent series of reports, has described a method of measuring the density of atomic species in a diffusion limited isothermal cell by spectrophotometric techniques. The density of atoms was obtained from the measured absorption of an atomic resonance line, generated in a hollow cathode discharge tube cooled to liquid nitrogen temperatures, by the hot gas in the cell. In relating the value of I/I_o to the vapor density N of the atomic species, the value of the oscillator strength of the line must be known. In fact, in the final relation between I/I_o and N, the N term always appears multiplied by the oscillator strength of the line in question.

The method outlined in these reports is therefore equally applicable for obtaining the value of N when the value of f is known, or for evaluating f when N is known.

In the case of tatanium since accurate values of the vapor pressure are known, it was possible to obtain f numbers for various observed transitons using the above techniques.

Vidale has shown that for the case where the emission line from the hollow cathode is much narrower than the absorption line of the hot gas in the furnace, the absorption I/I_o is simply related to the absorption coefficient k_o at the center of the line, in the following manner:

$$2.303 \log {}^{I}/I_o = - \left(\frac{k_\nu}{k_o} \right)_{\nu = \nu_o;\, a = a} k_o \, l \qquad (15)$$

where l is the path length, ν the frequency, "a" the pressure broadening parameter, and $\frac{k_\nu}{k_o}$ the ratio of the absorption coefficient at frequency ν

to k_o at "a" equal to the value for the pressure broadening parameter under the experimental conditions. The validity of this relationship at a = o was investigated over several values of the ratio of the source width to the absorption width (α). (This was done by using the more exact relationship given by Mitchel and Zenansky.[15]) It was found that for α's less than .5, (15) was valid to within 10%. Since α is most likely less than .5 for the case of the titanium studies, the correction for the finite width of the source should be less than 10%. Equation (15) can be rewritten using the well-known relationship[15] for k_o;

$$2.303 \log {}^{I}/I_o = -\left(\frac{k_\nu}{k_o}\right)\left(\frac{\pi m}{2\,RT}\right)^{1/2} \frac{e^2}{m\nu_o}\ N\,fl \qquad (16)$$

$$\nu = \nu_o$$

$$a = a$$

$$= -A\ (k_\nu/k_o)\ Nfl \qquad (17)$$

where m is the molecular weight of absorbing atoms, R the gas constant, T the absolute temperature, e the charge on the electron, m the mass of the electron, ν_o the frequency of the transition, N the number of absorbers/cc, and f the oscillator strength. Assuming a Bolzmann distribution, i.e.,

$$N = \frac{N_T\ g\ \exp\text{-}(\epsilon/k_T)}{Q}$$

where N_T is the total vapor density, g the statistical weight, k Boltzmann constant, Q the partition function, and ϵ the excitation energy equation (17) can be solved for gf viz:

$$gf = \frac{-2.303 \log (I/I_o)Q}{A\ N_T \exp\text{-}(\epsilon/k_T)(k_\nu/k_o)} \qquad (18)$$

In the case of the titanium studies equation (18) was used to obtain gf for the 3371 A transition.

Here $(k_\nu/k_o)\nu = \nu_o$ was taken as unity for the I/I_o value obtained by extrapolating measured I/I_o's to zero pressure ($a = o$). Relative values of gf for transition A to the 3371 A transition where obtained using the relationship (18) since all that was needed was the relative absorptions and temperatures at which the measurements were made - i.e.,

$$\frac{(gf)A}{(gf)_{3371}} = \frac{(\log I/I_o)A}{(\log I/I_o)_{3371}} \times \frac{Q_{T\ 3371}}{Q_{TA}} \times \frac{N_{T\ 3371}}{N_{TA}} \times \exp\left[(\epsilon/k_T)_{3371} - (\epsilon/k_T)_A\right] \tag{19}$$

The ratio $N_{T\ 3371}/N_{TA}$, i.e., the ratio of the total vapor density of titanium at the temperature at which the 3371 A transition was measured to the total vapor density at the temperature at which the transition A was measure was obtained from the Clausius -Clapeyron equation using the data in the JANAF tables. The ratio Q_{T3371}/Q_{TA}, the ratio of partition functions at the two temperatures, was taken from the compilation by J.C. Galan[16]. Likewise the excitation energies, ϵ, were obtained from Moore[17].

In this manner, gf values relative to the gf value of the 3371 A transition were obtained. These relative values were converted to absolute values by using the measured gf value for the 3371 A transition. Finally a comparison is made between the results of this study with various literature values. In general, the agreement was quite good.

Experimental and Results

The furnace used in these studies was the same as descirbed in the previous section of this report. The hollow cathode and spectrophotometric techniques have been described by Vidale[14]. In this case, the hollow cathode was lined with a sheet of titanium metal and was operated at liquid nitrogen temperatures. The current was held at 40 milliamps, which was low enough to prevent line reversal and Stark broadening.

The absorption cell consisted of a graphite tube lined with .01" titanium and having end pieces with 3/8 in. and 1/4 in. openings. The length of the cell was 6 inches. This cell was adequate as long as the temperature was held below the melting point of titanium. However, for several of the titanium lines, in order to obtain sufficient absorption, temperatures above the melting point of the metal were needed. In this case, a similar cell containing a mixture of TiC and graphite was used. Under these conditions, the vapor density of the titanium was determined by its vapor pressure over the univariant TiC and C system. A cross-sectional view of the cell is shown in Figure 4. Temperatures were measured with an N.B.S. calibrated micro-optical pyrometer at points A, B, C and D shown in Figure 4. From these measurements the average temperature in the cell was obtained. A phase locked detection system with the 1/2 meter JACO monochromator was used to measure the absorption of the hollow cathode source. Helium was used as the inert pressurizing gas in the furnace in order to limit diffusion out of the cell. An overall view of the equipment used is shown in Figure 5.

Absorption measurements were made on the 3371 A transition of titanium at inert gas pressures of 2 cm. to 70 cm. of mercury. This was done in order to establish the pressure dependency of this absorption and to obtain the zero pressure $I/I_o(a = o)$. These results are given in Table IV. The extrapolated value of I/I_o at zero helium pressure was found to be 0.31. From this value and the total pressure of 3.78×10^{-8} atm. obtained from JANAF for $T = 1657^\circ K$, equation (18) was solved yielding a value of $gf = 1.74$.

Relative gf values for a group of selected titanium lines were obtained from the measured absorption I/I_o and the cell temperature for a given line compared to the absorption at $1657^\circ K$ for the 3371 A line through relation (18).

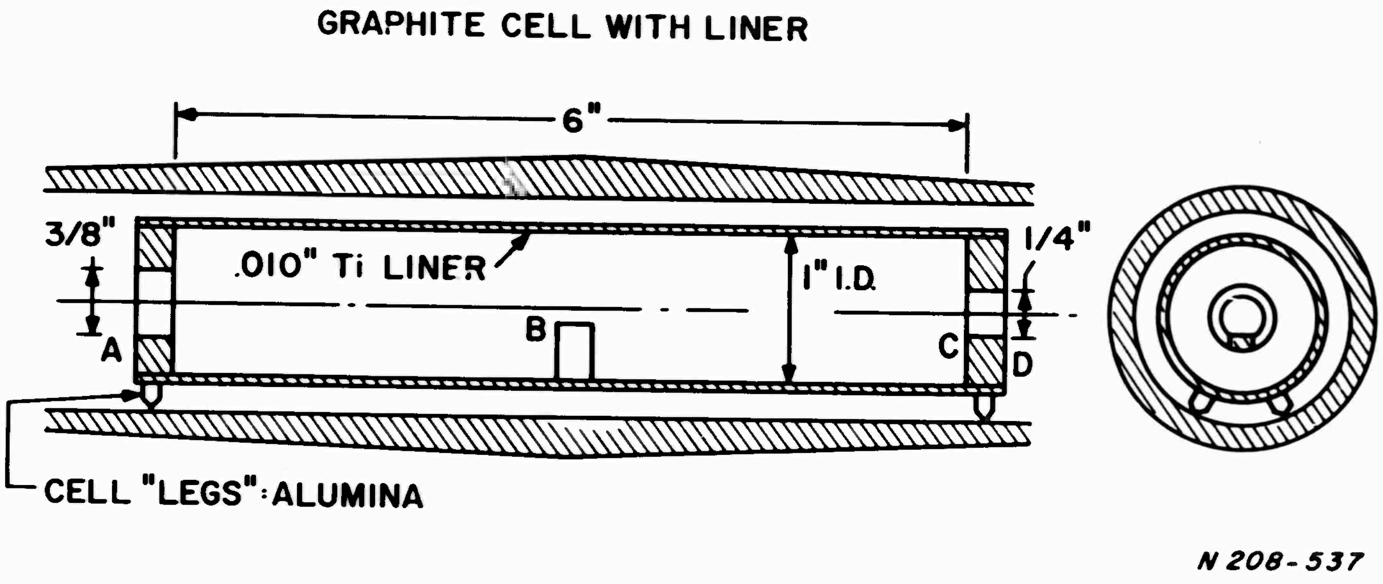


Figure 4. Titanium absorption cell

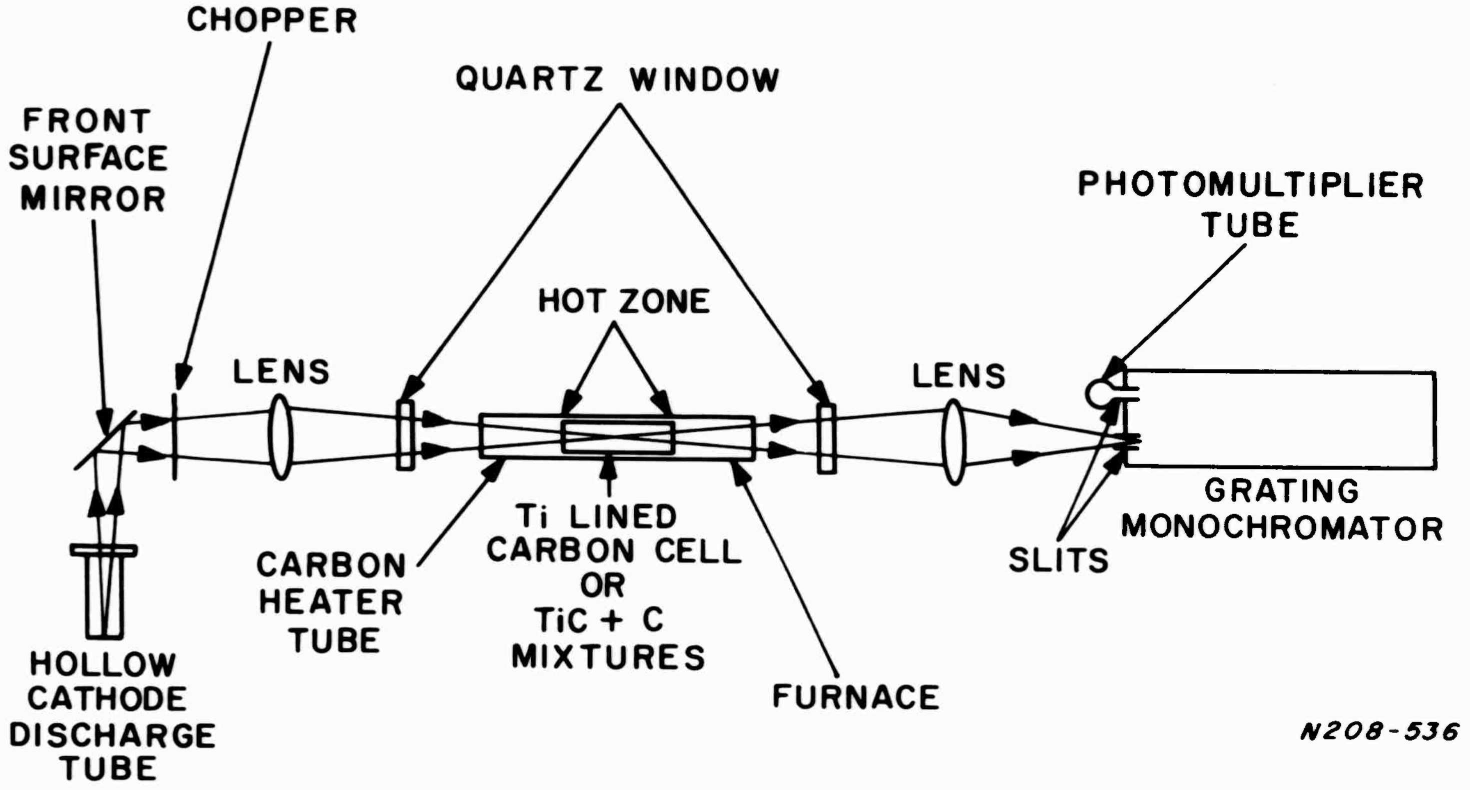


Figure 5. Furnace f number apparatus

TABLE IV. ABSORPTION OF Ti 3371 A LINE AS A FUNCTION OF HELIUM PRESSURE

I/I_o	P Helium cm. of Hg
.57 ± .02	70.1
.53 ± .01	60.0
.51 ± .01	50.0
.48 ±..02	40.0
.45 ± .01	30.0
.41 ± .01	18.1
.36 ± .01	9.0
.34 ± .01	5.0
.32 ± .02	2.0

$T = 1657^oK$ $(I/I_o)_{a=o} = .31$

These relative measurements were made at helium pressures of approximately 5 cm. of mercury. The relative values were converted to absolute values using the previously obtained f number for the 3371 A transition. Cell temperatures were adjusted so that the corresponding I/I_o values in all cases were approximately the same. For those transitions having a high excitation energy in the lower state, it was necessary to use TiC as the source of the titanium vapor so that higher cell temperatures could be achieved (without melting the titanium liner). The results are given in Table V. A comparison is also made in Table V between these results and those of Corliss and Bozmann[18] and King and King[19], (together with the proposed normalizations of Allen[20]).

TABLE V. OSCILLATOR STRENGTHS OF SELECTED TITANIUM LINES

Multiplet #	Wavelength A	gf Relative	gf This Work	gf Corliss& Bozmann	gf King & King
24	3354.64	75.2	1.31	1.6	.90
	3371.45	100.0	1.74	1.8	1.16
23	3370.44	22.8	.40	.43	.27
19	3635.46	71.0	1.24	1.2	.91
	3642.68	78.6	1.37	1.8	1.03
	3653.50	95.5	1.67	2.0	1.42
	3671.67	4.7	.081	.16	.069
17	3729.82	30.1	.53	.65	.38
	3741.06	40.9	.71	.79	.55
	3752.86	61.6	1.08	1.3	.91
	3753.64	4.2	.073	.14	.067
	3771.66	6.6	.116	.14	.072
12	3981.76	30.7	.53	.82	.257
	3989.76	43.0	.75	1.0	.60
	3999.36	58.9	1.03	1.5	.86
	4008.93	5.7	.099	.17	.082
	4024.57	6.9	.12	.22	.085
42	4533.24*	132.3	2.31	4.4	3.08
	4534.78*	116.5	2.03	2.6	2.07
6	4656.47	2.9	.051	.13	.043
	4667.59	4.1	.072	.086	.055
	4681.92	5.2	.091	.10	.079
38	4981.73*	192.5	3.36	3.7	3.50
	4991.07*	147.0	2.57	2.8	2.65
	4999.51*	110.8	1.94	2.4	2.10
	5007.21*	75.9	1.33	2.1	1.39

TABLE V. (Continued)

Multiplet #	Wavelength A	gf Relative	gf This Work	gf Corliss & Bozmann	gf King & King
5	5039.95	4.3	.075	.11	.084
	5039.95*	5.0	.086	.11	.084
4	5173.75	4.1	.072	.088	.078
	5192.98	5.5	.096	.11	.105
	5210.39	8.9	.155	.13	.134

* Measurements made over TiC

Conclusions and Recommendations

It is apparent from Table V that the results of this investigation are in good agreement with other studies. In general the results appear to fall between the two comparative studies which were carried out by rather different methods.

The accuracy to be associated with the relative gf values should be of the order of the scatter in the measured I/I_o values or approximately ± 10%-15%. On the other hand, the absolute gf values reflect an accuracy inherent in the thermodynamics of the system. In the case of titanium, since the error in the heat of vaporization is ± 1 kcal/mole, the vapor density of titanium is known to an accuracy of approximately ± 60%. Therefore the error in the corresponding gf value shall be taken to be at least this large.

In general the narrow line absorption method employed in this investigation offers the advantages of sensitivity, speed and precision when compared to other techniques. It is suggested that this technique be used in other studies of atomic oscillator strengths. In particular it is recommended that the zirconium, iron and hafnium systems be investigated.

REFERENCES

1. N. W. Rosenberg et al, Project Secede, Special Report No. 4, Air Force Cambridge Research Lab. Jan. 1968.

2. H. Foppl, G. Haerendel, J. Loidl, R. Lust, F. Melzner, B. Meyer, H. Neuss and E. Rieger, Planet. Space Sci., 13, 95-144, (1965).

3. L. Haser, NATO Advanced Study Inst. Univ. of Keele, Aug. 1966, Proceedings, Reinhold Pub. Corp., p. 391-403 (1967).

4. E. Fisher and R. Kummler, "Relaxation by Vibration-Vibration Exchange Processes", General Electric Co., TIS R67SD15 (1967).

5. Alan Gallagher, JILA (Private Communication).

6. W.R.S. Garton and K. Codling, Proc. Phys. Soc. 75, 87-94 :1960).

7. A.S. King, Trans. Am. Electrochem. Soc. 56 (1929).

8. P.B. Zeeman, Cam J. Phys. 32, 9 (1954).

9. G. Vidale, "The Infrared Spectrum of Gaseous LiF Molecule", General Electric Co., TIS Report #R59SD359.

10. M. J. Linevsky "Optical Energy Transfer Process", Semi Annual Report (this contract), General Electric Co. Feb. 1968.

11. W.R.S. Garton, W.H. Parkinson, E.M. Reeves, Proc. Phys. Soc. 80, 860 (1962).

12. Stull and Sinke, "Thermodynamic Properties of the Elements", Advances in Chemistry Series, American Chemical Society 1956.

13. "High Brightness Mercury Arc Lamps. Capillary Type A-H6 and B-H6. Application Data and Accessory Equipment," General Electric Company GET-1248D.

14. G. Vidale, "Measurement of the Absorption or Resonance Lines," General Electric Co. TIS R60SD330, R60SD333.

15. A.G. Mitchell and M.W. Zemansky, "Resonance Radiation and Excited Atoms," Cambridge Press (1961).

16. L. deGalan, "A Table of Partition Functions of Atoms and Ions Between 1500 and 7000°K, Thesis, Dept. of Chemistry, University of Florida.

17. C.E. Moore, "Atomic Energy Levels," N.B.S. circular 467

18. C.H. Corliss and W.R. Bozman, "Experimental Transition Probabilities for Spectral Lines of Seventy Elements," N.B.S. Monograph #53.

19. R.B. King and A.S. King, Astrophys. J. 87, 24 (1938).

20. C.W. Allen, Monthly Notices R.A.S. 121, 299 (1960).