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Analysis of Optically Excited  
Mercury Molecules

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# Analysis of Optically Excited Mercury Molecules

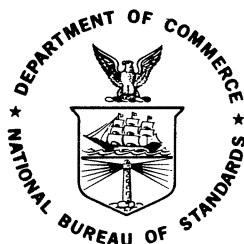
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Supported by:

Los Alamos Scientific Laboratory under  
AEC Order No. LS74-4 and the Advanced  
Research Projects Agency under ARPA  
Contract 981, Amendment No. 9.



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U.S. DEPARTMENT OF COMMERCE, Frederick B. Dent, *Secretary*  
NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, *Director*

Issued January 1975

**Library of Congress Cataloging in Publication Data**

Drullinger, R. E.

Analysis of Optically Excited Mercury Molecules.

(National Bureau of Standards Monograph; 143)

Supt. of Docs. No.: C 13.44:143

1. Laser Spectroscopy. 2. Mercury—Spectra. 3. Excited State Chemistry. I. Hessel, Merrill M., 1933- joint author. II. Smith, Earl William, 1940- III. Title. IV. Series: United States. National Bureau of Standards. Monograph; 143.  
QC100.U556 No. 143 [QD96.L3] 389'.08s [546'663'6] 74-31115

**National Bureau of Standards Monograph 143**

Nat. Bur. Stand. (U.S.), Monogr. 143, 51 pages (Jan. 1975)

CODEN: NBSMA6

U.S. GOVERNMENT PRINTING OFFICE  
WASHINGTON: 1975

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For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402  
(Order by SD Catalog No. C13.44:143).  
Price \$1.10



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## Analysis of Optically Excited Mercury Molecules

R. E. Drullinger, M. M. Hessel, and E. W. Smith

The  $\text{Hg}_2$  molecule is representative of a class of molecules which have dissociative ground states and bound excited states. It can therefore be used as a prototype of this class of molecules which are of interest as potential new laser candidates. Because of the non-bound ground state, standard absorption spectroscopic techniques cannot be used to obtain the necessary information about the excited states. We have therefore developed new measurement techniques to obtain potential curves,  $f$ -values, and kinetic behavior for  $\text{Hg}_2$ . These techniques are applicable to this whole class of dissociation molecular systems.

Key words: Dissociation laser; excimers; excited state kinetics;  $f$ -values; mercury molecules; new spectroscopic techniques; optical excitation; potential curves.

### I. INTRODUCTION

There is currently much interest in the development of high energy tunable lasers in the visible and near UV. "Dissociation lasers" operating on electronic transitions in molecules having dissociative ground states give promise of achieving this goal. The molecules of interest as dissociation laser candidates include pure metals such as  $\text{Hg}_2$ ,  $\text{Zn}_2$ ,  $\text{Cd}_2$ ; mixed metals such as  $\text{HgZn}$ ; metal-noble gas molecules such as  $\text{HgXe}$ ,  $\text{LiXe}$ ; and pure noble gas dimers. Research on this class of laser has been impeded because most of the interesting systems include metals which are highly reactive at the high pressures and temperatures of laser interest. Furthermore, the dissociative nature of the electronic ground state severely inhibits conventional absorption spectroscopy hence, even for such ubiquitous systems as  $\text{Hg}_2$ , there exists very little basic data (eg.  $A$  values, potential energy curves, energy transfer rates, etc.). At the present time, only pure rare gas systems have been made to lase, and even these are poorly understood.

The mercury system is currently the most attractive of the metal vapors from the point of view of developing the measurement techniques and gathering the basic data needed for understanding this class of lasers. Some, albeit very little, information is available about molecular mercury from research extending back more than 70 years. The mercury molecule, while somewhat reactive at high temperatures, can still be studied in conventional glass or quartz cells and discharge excitation is also relatively easy to obtain. Previous analyses of electronically excited mercury molecules can be roughly divided into three categories according to the type of excitation employed:

(1) optical excitation via the atomic resonance line<sup>[1]</sup> (253.7)nm at mercury pressures less than 1 torr (1 torr = 133 N/m<sup>2</sup>), (2) low pressure discharge excitation<sup>[2]</sup> and, more recently, (3) high

energy (Mev) electron beam excitation at pressures of several hundred torr or more<sup>[3]</sup>. Each of these techniques has provided useful information and each has its limitations. Discharge excitation can produce a fairly high density of excimers (electronically excited molecules whose ground state is dissociative) but the analysis of the states of interest is confused by the presence of charged particles and highly excited molecular states which can act as metastable energy reservoirs or as absorbers. Resonance line optical pumping avoids these difficulties (if the resonance lamp is suitably filtered), but this technique is restricted to mercury pressures well below the range of laser interest because, at pressures of 1 torr or more, the exciting radiation is all absorbed in a very thin sheath at the edge of the vapor and interactions with the wall dominating the observations.

In this paper, we report results obtained with a type of optical pumping<sup>[4]</sup> which is applicable from a few torr to several atmospheres. High power continuum lamps have been used to populate Hg<sub>2</sub> excited states directly from the weak Van der Waals well and continuum region of the electronic ground state. Figure 1.1 shows the postulated Hg<sub>2</sub> potential curves<sup>[5]</sup> and the location of the absorption band which we have used for our optical pumping (it must be emphasized that very little is known about these curves and figure 1 may be shown to be incorrect by future research. This absorption band was studied extensively by Kuhn and Freudenberg<sup>[6]</sup> and Lennuier<sup>[4]</sup> and has been shown to extend from the resonance line at 253.7 to beyond 320 nm depending on the pressure and temperature. The band is optically thick in the region of 253.7 nm but we have produced strong volume excitation even at pressures of 10 atm. The details of this optical pumping technique and the various experimental procedures are discussed in section 2.

In section 3, we present an analysis of steady state data from the 335 and 485 nm fluorescence bands. This analysis indicates that the excited electronic states which emit these bands (and probably the entire manifold of states which arise from  $6^3P_J + 6^1S_0$ ) are in thermal equilibrium among themselves (but not with the electronic ground state). This analysis also gives a  $6500\text{ cm}^{-1}$  activation energy for transitions from the 485 reservoir to the 335 reservoir.

In section 4, we present some preliminary time decay data which shows that the 485 and 335 bands decay with the common lifetime and this lifetime is a strong function of the temperature and density of the mercury vapor.



## II. EXPERIMENTAL

In this section, we describe the mercury containment cells, filling procedure, oven and temperature controllers, light sources used to excite the molecular spectra, detection systems, spectrographs, and calibration procedures. Purity of the cells and mercury used in these experiments is of the utmost importance; some anomalous results that we obtained by filling the cells with laboratory grade triple-distilled mercury and ordinary vacuum techniques will be discussed along with the mercury handling procedures we have now developed.

In all the experiments described in this monograph, we used a light source to excite mercury vapor contained in a quartz cell. The pressure of the mercury was determined by a cold finger attached to the cell and the temperature was controlled by heating the cell body. Figure 2.1 is a typical schematic of our apparatus.

### A. Cell and Oven

The cells were made from 2.5 cm dia. quartz tubing in the form of a cross. The four windows were of UV grade quartz and fused onto the cell body. The optical path length between windows was 3.65 cm. The cell had a small tube extending from its body that acted as a reservoir for the mercury and as a cold finger so that the mercury vapor pressure could be varied independently of cell temperature. Since the cell body was not made out of UV-grade quartz, it fluoresced strongly in a broad band centered around 400 nm if any of the exciting radiation impinged on it. To help eliminate this problem a mask of liquid gold<sup>\*</sup> was painted around the edge of each window to help prevent incident radiation from directly entering the cell body and to mask the fluorescing edge of the cell from the detection optics. Cells of this design could not be operated much above atmospheric pressure (densities  $\lesssim 10^{19} \text{ cm}^{-3}$ ).

The cell was contained in a two compartment oven constructed of low density fire brick in which the compartments were heated separately, each with a temperature regulating system. The upper part of the oven where the cell proper was housed determined the mercury vapor temperature and was equipped with four window ports to coincide with the four windows on the cell, each port was fitted with a quartz window to prevent heat loss (see fig. 2.1). Inside this oven and surrounding the cell was a thin-walled stainless steel cylinder with four window ports cut in it. This provided additional heat and light baffling as well as providing a base on which the heater was wound.

The lower oven housed the mercury reservoir and had no windows, thus providing maximum temperature stability and uniformity. Thermocouples were attached directly to the glass side arm at a point where it was full of liquid mercury. The side arm also had a thin layer of asbestos wrapped on it

\* A thick organic solution containing gold which when painted on a surface, dried and heated to  $> 600^\circ\text{C}$  leaves a thin layer of gold bonded to the surface. The usual coating of "aquadag" will not work as it burns off in air at temperatures above  $500^\circ\text{C}$ .

and was finally wrapped with several layers of heavy aluminum foil to insure temperature uniformity. The heater for this part of the oven was a coil of nichrome wire wound just on the inside of the fire brick.

Both oven compartments were heated by direct current through series regulators whereby the current to the heater was controlled by the difference potential between the control thermocouple and a reference voltage set to the desired temperature.

This system was of low heat capacity and temperature changes as large as  $300^{\circ}\text{C}$  could be accomplished within 15 minutes. However, tight regulation controlled the reservoir temperature to  $\pm 0.05^{\circ}\text{C}$  for periods as long as several days resulting in mercury vapor density control to better than 0.5%.

#### B. Purity Problems and Cell Filling Procedures

In the older literature<sup>[7]</sup>, it had been noted that air and other gases destroyed the fluorescence. More recently Stupavsky, Drake, and Krause<sup>[8]</sup> observed an anomalous  $\text{Hg}_2$  band that Vikis and LeRoy<sup>[9]</sup> have subsequently suggested was due to an impurity of  $\text{HgCl}$ . In general, mercury is known<sup>[10]</sup> to combine with many atomic and molecular species. For these reasons, it is necessary to take great care to insure purity in preparing sample cells.

In our initial experiment, we filled the cells with laboratory grade triple-distilled mercury. The cell was pumped down to a pressure of  $10^{-7}$  torr and baked to  $300^{\circ}\text{C}$  before the  $\text{Hg}$  was distilled into it. We found that when the cells were heated to give a mercury pressure of 2-5 atm and exposed to any of the blue argon ion laser lines, the characteristic 485 nm blue-green  $\text{Hg}_2$  fluorescence band appeared. The first cell failed, however, when the pressure exceeded several atmospheres. With a new cell and slightly improved vacuum techniques, we tried to reproduce and study this laser induced fluorescence effect under carefully controlled conditions. The fluorescence was weaker and lasted only a few hours after initial heating. With the improved vacuum techniques for preparing mercury cells as described below, this laser induced fluorescence completely disappeared, indicating that it is probably produced by an impurity in some laboratory grade mercury. Although time has not allowed an investigation of this "sensitized fluorescence", we have used it as an indication of the cleanliness in the various cells.

The cells used for the experiments described in this monograph were prepared in the following manner:

Prior to the actual filling of a cell, laboratory grade, triple-distilled mercury is distilled into ampules with the arrangement shown in figure 2.2. The ampule filling apparatus is attached through a "U" tube trap to a bakeable vacuum station and the entire system is baked at  $400^{\circ}\text{C}$  for 24 hours. On cooling, a vacuum of  $\sim 10^{-9}$  torr is attained. The system is then backfilled with



argon to 1 atm pressure and opened at point A. Laboratory grade mercury is injected into point C and the system closed at point B. The "U" tube trap is then cooled with liquid N<sub>2</sub> and the argon is pumped out of the system. The pressure at this point with the Hg vapor trapped out, is  $\approx 2 \times 10^{-8}$  torr. Using a foam plastic cup fitted over the filling tube (B) and inverted "U" tube (D) and filled with dry ice, a reflux column is set up; C  $\xrightarrow{}$  B. A small fraction of the refluxing Hg migrates over into the ampules. When an ampule is filled with approximately 5 gm of mercury, it is tipped off and removed from this system. This procedure results in ampules of pure mercury sealed under a vacuum of a few times  $10^{-8}$  torr. To keep the pumping station clean, the remaining system is again filled with argon and cut between the liquid nitrogen trap and the permanent part of the station. This removes all glass that has been exposed to mercury.

To fill a cell, the arrangement shown in figure 2.3 is constructed on the pumping station. It consists simply of the cell to be filled, an ampule of mercury and a "U" tube for a trap. Since the cell is to be operated at temperatures up to 900°C, it must be baked at least to this temperature. For this purpose, a small oven made of a heater and fire brick is placed around the cell inside the main bake-out oven. This allows the cell to be baked out at 1000-1100°C while the rest of the vacuum station is baked at 400°C for 24-36 hours. After the bake-out, the system is cooled, the small oven removed, the trap cooled in liquid nitrogen and the mercury ampule opened. At this point and throughout the rest of the filling procedure, the pressure on the vacuum side of the trap is less than  $10^{-8}$  torr. Some of the mercury is then transferred, again by distillation, into the cell. Mercury often boils violently when distilled and mercury droplets entrained in the vapor could be carried directly into the cell. To prevent this, we boil the mercury gently and make the glass between the Hg ampule and the cell of sufficient length and slope (fig. 2.3) so that any entrained mercury condenses on the walls and rolls back toward the ampule. During the tip-off operation, the cell is heated to cause a large flux of mercury vapor to sweep out past the tip-off point and carry with it out-gassed products of the tip-off operation.

With the cells prepared in this manner and with appropriate excitation, we have been able to observe Hg<sub>2</sub> fluorescence over a density range of  $10^{16}$  to  $10^{20}$  cm<sup>-3</sup> and vapor temperatures of 175 to 800°C. These signals are stable and show no change over 24 hours of operation. With these clean vapors, we do not observe fluorescence induced by any of the Ar<sup>+</sup> laser lines.

### C. Optical Pumping and Light Sources

Lennuier<sup>[4]</sup> and Kuhn and Freudenberg<sup>[6]</sup> have shown that mercury vapor absorbs radiation in a broad band from the 253.7 nm resonance line to beyond 320 nm. This type of optical pumping is a "clean" technique, in which only the bands of interest (335 and 485 nm) are excited and fluorescence is produced throughout the cell. Figure 2.4 shows Kuhn and Freudenberg's relative absorption coefficient  $\alpha$  as a function of wavelength where  $I/I_0 = e^{-\alpha x}$ . Also plotted on the same graph is the ratio R of integrated fluorescence intensity of the 335 band to the exciting wavelength intensity as a function of exciting wavelength at a pressure of 600 torr.<sup>[4]</sup>

These results show that one can couple power into any depth of mercury vapor and at almost any vapor density and thus obtain volume excitation. To make full use of this pumping scheme for densities up to  $10^{20} \text{ cm}^{-3}$ , we have used several types of lamps to maximize the power in the wavelength region effective at the particular density region investigated. At low densities  $\lesssim 10^{16} \text{ cm}^{-3}$  a germicidal resonance lamp is most effective, for densities from  $10^{16}$  to  $10^{18} \text{ cm}^{-3}$  a medium pressure (Osram type) mercury lamp most effectively excites the  $\text{Hg}_2$  bands. Above  $10^{18} \text{ cm}^{-3}$  high pressure xenon and mercury-xenon compact arc lamps are used. We recently obtained a commercial ADP frequency doubler which was used to double the 514.5 nm Argon ion laser line thus producing a 10 mW beam of 257.2 nm radiation. This light source produces a small volume, high density excitation.

For the rather preliminary time resolved studies which are presented in section IV, a coaxial system consisting of a 10J energy storage capacitor, a switching thyatron and a 2-4 mm air spark gap was used. During the .5-1  $\mu\text{sec}$  discharge time of the circuit, the air spark radiated light with a spectral distribution roughly corresponding to a 10,000 K blackbody.

Each of these light sources (except for the laser) was used in conjunction with an optical system which collected, collimated, filtered and refocused the light into the cell. This system consists of simple, single element f/1.5 quartz lenses and a tri-compartmented cell which contained the desired combination of filter solutions, see figure 2.1. The filter used throughout most of this work is one of  $\text{NiSO}_4\text{-H}_2\text{O}$ ,  $\text{CoSO}_4\text{-H}_2\text{O}$  and pure  $\text{Cl}_2$  gas. This combination gives a high transmission ( $T_{\text{max}} > 50\%$ ) at 270 nm; the transmission curve is given in figure 2.5.

In addition to the light sources above, we have used the 337.1 nm output of a pulsed 1 MW nitrogen laser to excite the mercury vapor. The 485 nm band fluorescence was observed through a broad band 480 nm interference filter at densities in excess of  $10^{19} \text{ cm}^{-3}$ . A cw He-Cd laser (10 mW at 325 nm) also excites the  $\text{Hg}_2$  band fluorescence at densities  $> 10^{19} \text{ cm}^{-3}$ . In both cases the excitation was rather weak and neither technique was used beyond the initial trials.

#### D. Detection Systems

To detect the molecular mercury bands at 335 and 485 nm we have used both S(Q) blue response and S-20 red response photomultipliers. To observe the molecular bands in the appropriate spectral region we either used the photomultipliers with filters or a 1/3 meter scanning monochromator, depending on the type of experiment and light intensity. The transmission curves of the broadband interference filters used to measure the 335 and 485 band, are shown in figures 2.6 and 2.7.

The spectrometer was calibrated for wavelength, instrument line profile, and (with each of the photomultipliers) quantum efficiency. The spectrometer has a spectral line width of 0.07 nm (FWHM) at a slit width of 10  $\mu\text{m}$  and a line width of 0.3 nm at a slit width of 135  $\mu\text{m}$ . The spectrometer scattered light level beyond 1.5 band widths was found to be  $< 0.5\%$  in both cases. We generally used slit widths corresponding to an instrumental bandwidth of 0.3 - 1.0 nm. We used a spectral irradiance tungsten iodine lamp<sup>[11]</sup> to calibrate the photomultiplier and spectrometer combinations for relative quantum efficiency. The lamp was essentially a blackbody source at a specific color temperature for a fixed current input to the lamp. In our case, the calibration was made at two color temperatures  $3110 \pm 15$  K and  $2785 \pm 15$  K. The independent calibrations agreed to within  $\pm 1\%$  in the spectral region 300-700 nm.



### III. STEADY STATE DATA

#### A. Band Shapes

The cw-optical pumping schemes described in the previous section have been used to excite mercury vapor at pressures ranging from about one torr to several atmospheres and temperatures ranging from 175°C to 1000°C. The entire fluorescence spectrum has been scanned under moderate resolution (about 0.3 nm to 1.0 nm) from 230 nm to 700 nm using various spectrometers and photomultipliers. A typical photoelectric trace is shown in figure 3.1. This trace was taken with a 1/3 meter spectrometer, with a resolution of about 0.3 nm, using a photomultiplier with an S(Q) response curve. The total response of the instrument was calibrated using a standard lamp, and the trace shown in figure 3.1 includes this correction factor. (The intensities reported in this paper are proportional to the number of photons per wavelength interval.) Since the correction factor with the S(Q) phototube becomes rather large for  $\lambda > 550$  nm, another trace was made using the same spectrometer with an S-20 phototube. This particular curve shows fluorescence excited with the 150 W Xe continuum lamp filtered to pass only 240 to 290 nm radiation (discussed in Section II). Since this is a very high intensity source, the radiation scattered by the cell constitutes an appreciable signal which is seen in figure 3.1 as a continuum between 240 and 290 nm. Measurements of this scattering, taken with the cell at room temperature, enable us to subtract out its contribution but it doesn't interfere appreciably with the 335 band in any case.

A similar curve, excited with the frequency doubled Argon ion laser, is shown in figure 3.2. In this case, the doubled laser output was focused into a small volume thus creating a high excimer density (estimated at  $10^{13}/\text{cm}^3$ ) and some secondary pumping of the  $7^3S_1$  state of atomic mercury is observed. This figure also shows scattering of the doubled laser line at 257.2 nm as well as a small amount of the primary laser line at 514.5 nm which scattered into the cell. More recent runs using unfocused 257.2 excitation show no atomic emission and with better filtering, the 514.5 scatter has been removed. Comparison of laser excited fluorescence data with lamp excited data shows no difference between the two (other than a weak excitation of the  $7^3S_1$  obtained by focusing the laser into a small volume).

It is interesting to note that the peak of the familiar 485 band occurs at 510 nm in figures 3.1 and 3.2. In our uncorrected traces the peak occurred at 485 but when the data are corrected for the spectrometer response function, the true maximum appears at 510. The 335 band shape is essentially unchanged when corrected for the spectrometer response function. Since the band shapes and the location of the maximum intensity are rather important quantities in evaluating potential curves and transition probabilities, the shift of the apparent maximum from 485 nm to 510 nm emphasizes the need for well-calibrated detection systems.

The shapes of the 335 and 485 bands as functions of density and temperature are shown in figures 3.3 - 3.6. The integrated band intensities are normalized to unity in order to show the shifts of the populations within the respective bands. As temperature is increased, both bands show a decrease in peak intensity, an overall broadening of the band and a slight shift toward the blue. This is what one would expect from a Boltzmann distribution of vibrational states; that is, an increase in temperature reduces the population at the bottom of the well which radiates the intensity maximum, and correspondingly increases the population of the higher vibration states which radiate in the wings of the band. The shift to the blue will be discussed later in this section.

Figures 3.5 and 3.6 show that the band shapes are not affected by changes in density. This is also what one would expect from a thermal distribution of vibrational states since the Boltzmann factor is independent of density. The absence of density dependence of the shape of the 485 band cannot be used to confirm or deny the mechanism of collision induced radiation which is often proposed for this band.

#### B. Band Intensities

The intensities of the 485 and 335 bands were measured as functions of temperature and density. Most of these measurements were made using filters in front of a photomultiplier rather than a spectrometer in order to increase the signal and thereby extend the range of these measurements. A comparison of the filter functions, figures 2.6 and 2.7, with the observed spectral distribution, figure 3.1, shows that the filters did not integrate the entire band. The filters do cover the center of the bands hence the readings are proportional to the total band intensities and the intensity ratios should be accurate. This assertion was checked by integrating spectrometer tracings, such as figure 3.1 in the temperature-density range where spectrometer measurements could be made; the intensity ratios obtained with the filters agreed with those obtained from spectrometer tracings to better than 1%. We certainly do not propose this figure as an estimate of the error in all of our data, but it does nonetheless indicate excellent agreement between these two measurement techniques at least as far as intensity ratios are concerned.

In figure 3.7, we have plotted the log of the intensity ratio  $R = I(485)/I(335)$  versus  $1/kT$  where  $kT$  is in  $\text{cm}^{-1}$ . Figure 3.7 shows only six representative curves but several sets of similar data have been analyzed by computer. A linear least squares program was used to fit the data points for  $N > 10^{17}$  and  $T > 575 \text{ K}$  (i.e.  $1/kT < 2.5 \times 10^{-3}$ ). The slopes in the linear portion of the data, (solid lines)  $T \geq 573 \text{ K}$ , give an activation energy of  $6500 \text{ cm}^{-1}$  with a  $\pm 2\%$  scatter and this scatter appears random; that is, there is no systematic trend in the calculated slope as a function of density. This linearity shows that, for  $T \geq 575^\circ\text{K}$  and  $N > 10^{17}$ , the populations are related by

$$N_{335}/N_{485} \propto e^{-\epsilon/kT} \quad (3.1)$$

where  $\epsilon = 6500 \text{ cm}^{-1}$  to within  $\pm 2\%$ . The fact that there is no variation in this slope over nearly two orders of magnitude in density provides a compelling argument that the two electronic states (which radiate 485 and 335 respectively) are in thermal equilibrium.

The  $N = 10^{17}$  run was not analyzed by computer because there are not enough points at high temperatures to be certain about where thermal equilibrium applies. A straight line was drawn through these data with a  $6500 \text{ cm}^{-1}$  slope for comparison with the other data. The  $N = 5 \times 10^{16}$  run clearly shows that the two electronic states are not in equilibrium with one another at this density.

The deviation observed by decreasing the temperature at a constant density is not the only means of achieving a deviation from equilibrium. Another technique is to lower the density for a fixed temperature. This is illustrated in figure 3.8 where we plot the intensity ratio  $R$  versus density for several fixed temperatures lying both above and below the critical value of 575 K discussed above. In addition to our data, we have also plotted some low density data of Matland and McCoubrey<sup>[12]</sup> which were obtained with the resonance line excitation discussed in Section I.

It should be noted that the latter were taken in the afterglow (after switching off their resonance lamp) whereas our data are taken in steady state with a continuum lamp. Since the two electronic states are not in thermal equilibrium for  $N < 10^{17}$ , this may not be a valid comparison. None of the data in this figure have been calibrated to account for the band width of the filters or the relative sensitivity of the phototube in the blue 335 and green 485 regions. These corrections would only multiply  $R$  by a constant, hence the slope of the curves is correct even though the vertical position of the curves is arbitrary. That is, the fact that our data at 470 K joins smoothly with the Matland-McCoubrey data at 473 K is fortuitous. Furthermore, the 519 K curve lies above the 470 K only because it was arbitrarily displaced upward one order of magnitude to make the data easier to read, the actual measurements lie between the 470 K and 623 K curves. The two asymptotes  $R \propto N^2$  and  $R \propto N$  have been drawn in as dashed lines to aid in the interpretation of the data.

We first consider the region  $N > 10^{17}$  on the 631 K and 623 K curves. The previous discussion has shown that the states radiating 485 and 335 are in thermal equilibrium for this temperature-density range, yet figure 3.8 shows that the intensity ratio increases linearly with  $N$  over at least two decades in  $N$ . Assuming that the 335 nm radiation is due to spontaneous emission, this would indicate that 485 is radiated either by the collision induced mechanism



or by stable  $\text{Hg}_3^*$ :





It is impossible to distinguish between these two mechanisms with our current data.

We next consider the data for  $N < 10^{17}$ . These data show a strong tendency toward an  $N^2$  dependence at the lower densities. Although none of these data are truly parallel to the  $N^2$  asymptote, they seem to be approaching it more closely as  $N$  decreases. The transition from  $N^2$  to  $N$  dependence seems to occur at about  $10^{17}$ . This change is rather difficult to detect in the 623 K data but there are clear systematic deviations from linearity for the low density points on this curve. It would be desirable to have more points at lower  $N$  for this temperature because this is one of the cases which is clearly in thermal equilibrium when  $N > 10^{17}$ . It would therefore be instructive to measure more accurately its deviation from the linear  $N$  dependence as  $N$  is decreased. Unfortunately, the 485 band becomes very weak for low  $N$  and high  $T$  and it was possible to go to lower  $N$  only for the lowest temperatures (such as the 519 K curve for example). The latter overlaps the  $10^{17}$  region very well; this curve agrees quite well with the low pressure afterglow measurements of Matland-McCoubrey<sup>[12]</sup> but at high  $N$  it never quite achieves the linear  $N$  dependence exhibited by the high temperature data. This is not surprising since, in view of figure 3.7 we would not expect to be in thermal equilibrium at this temperature.

In summary then, we have compelling evidence that the states responsible for the 485 and 335 fluorescence band are in thermal equilibrium for high temperatures  $T \gtrsim 575$  K and densities  $N \gtrsim 10^{17}$ . In the high temperature-density region where thermal equilibrium applies, the linear dependence of  $R = I(485)/I(335)$  on  $N$  would seem to indicate that 485 is emitted by a density dependent process such as collision induced radiation, eq. (3.3), or  $Hg_3^*$  formation, eqs. (3.4) and (3.5).

### C. Potential Curves

In this section, we present a preliminary analysis of the electronic potential curves involved in the 485 and 335 fluorescence. For similar discussions see Hedges, et. al. [13], Doyle [14] or Sando and Dalgarno [15]. The number of photons per unit wavelength emitted in a transition between a bound excited electronic state "a" and a repulsive ground state "b" is

$$\begin{aligned}
 I_{\lambda} &= \frac{CN^*(T)}{\lambda^5} \sum_{vJJ'} \int d\epsilon \delta(h\nu - E_{avJ} + \epsilon) \\
 &= \frac{\exp(-E_{avJ}/kT) S_{JJ'}}{Z(T)} |D_{avJ, b\epsilon J'}|^2
 \end{aligned} \tag{3.5}$$

$$\times \frac{CN^*(T)}{\lambda^5} \sum_{vJJ'} \frac{\exp(-E_{avJ}/kT) S_{JJ'}}{Z(T)} |D_{avJ, b\epsilon J'}|^2$$

where  $(v, J)$  are vibration rotation quantum numbers for a,  $(\epsilon, J')$  are the corresponding quantum numbers

for b ( $\epsilon$  is a continuous nuclear kinetic energy quantum number),  $D$  is the transition dipole moment,  $S$  is the Honl-London factor, the total number of excimers is  $N^*(T)$ , the excimer state population densities are described by a Boltzmann distribution with a partition function  $Z(T)$ , and  $C$  denotes miscellaneous uninteresting constants. The integral over nuclear kinetic energy  $\epsilon$  removes the delta function and, in the second line,  $\epsilon$  equals  $(E_{avJ} - h\nu)$ .

The dipole matrix element in eq. (3.5) can be expressed in terms of vibrational wavefunctions as

$$D_{avJ, b\epsilon J'} = \int_0^\infty D_{ab}(R) \psi_{av}^J(R) \psi_{b\epsilon}^{J'}(R) dR \quad (3.6)$$

where  $D_{ab}(R)$  denotes the dipole matrix element between the electronic states  $a$  and  $b$ . This integral can be evaluated using WKB wavefunctions<sup>[16]</sup> in which case one finds that the integrand is sharply peaked about a critical radius  $R_\lambda$  at which the radial momenta for upper and lower states are equal (Franck-Condon principle):

$$\sqrt{\epsilon - V_b(R_\lambda) - \frac{\hbar^2 J'(J'+1)}{2\mu R_\lambda^2}} = \sqrt{E_{avJ} - V_a(R_\lambda) - \frac{\hbar^2 J(J+1)}{2\mu R_\lambda^2}} \quad (3.7)$$

or since,  $\epsilon = E_{avJ} - h\nu$ ,

$$\begin{aligned} h\nu &= V_a(R_\lambda) - \frac{\hbar^2 J(J+1)}{2\mu R_\lambda^2} - V_b(R_\lambda) - \frac{\hbar^2 J'(J'+1)}{2\mu R_\lambda^2} \\ &\approx V_a(R_\lambda) - V_b(R_\lambda) \end{aligned} \quad (3.8)$$

In the last line of eq. (3.8) we have used the fact that the rotational levels with large thermal populations correspond to large  $J$  values, thus the  $\Delta J = \pm 1, 0$  selection rule implies that the rotational energies in eq. (3.8) essentially cancel out. That is, for a given vibrational level and a specific  $R_\lambda$ , all rotational levels emit photons of essentially the same frequency. There is some rotational broadening due to the inexact cancellation of the rotational energies, but this is negligible for our purposes. Since the integrand in Eq. (3.6) is sharply peaked at  $R_\lambda$ , the function  $D_{ab}$  may be factored out as  $D_{ab}(R_\lambda)$  and the remaining Franck-Condon overlap integral evaluated by the method of stationary phase. Mies<sup>[16]</sup> argues that the WKB phase integral (the integral over the radial momentum) for the repulsive state  $b$  will be small (compared with  $\pi$ ) at the point  $R_\lambda$ . Equation (3.6) then reduces to

$$D_{avJ, b\epsilon J'} = D_{ab}(R_\lambda) \psi_{av}^J(R_\lambda) \left[ \left( \frac{\hbar^2}{2\mu} \frac{d}{dR_\lambda} \left\{ V_a(R_\lambda) - V_b(R_\lambda) \right\} \right)^{-1} \right] \quad (3.9)$$

If the WKB phase integral is not small  $\psi_{av}^J$  is replaced by a slightly more complicated function of  $R_\lambda$ . We must therefore emphasize that, for the high temperatures of interest to us ( $T \gtrsim 400$  K) this phase integral will be small only if  $R_\lambda$  lies near the classical turning point for the repulsive state

(within 0.5 Å). This will be a good approximation since the WKB continuum wavefunction is sharply peaked about the classical turning point. In fact, one must be somewhat careful about using a WKB wavefunction for  $\Psi_{av}^J(R_\lambda)$  because the latter diverges at the turning point. However, eq. (3.9) can also be derived using Airy wavefunctions which do not diverge<sup>[17]</sup>, hence one can readily find well behaved wavefunctions for use with this expression. It should be noted that eq.(3.9) is quite similar to the "reflection method"<sup>[18]</sup> in which the repulsive state wavefunction is replaced by a delta function at the classical turning point. It should also be noted that eq. (3.9) breaks down if the derivative of  $(V_a - V_b)$  should vanish at  $R_\lambda$ ; in such a case one must use the full Airy function results<sup>[17]</sup> (i.e. without assuming that the WKB phase integral for state b is small).

We next note that the vibrational wavefunction  $\Psi_{av}^J$  depends on J only through the radial kinetic energy  $E_{avJ} - V_a(R) - \hbar^2 J(J+1)/2\mu R^2$ . Since for not too large values of J the shape of the potential energy curve  $V_a(R) + \hbar^2 J(J+1)/2\mu R^2$  does not differ appreciably from that of  $V_a(R)$ , we will approximate the rotational energy by  $\hbar^2 J(J+1)/2\mu R_\lambda^2$ . This approximation ignores a small distortion produced by the rotational energy but this should be negligible for our purposes<sup>[19]</sup>. We may therefore replace  $E_{avJ}$  in eq. (3.5) by:

$$E_{avJ} = E_{av} - \frac{\hbar^2 J(J+1)}{2\mu R_\lambda^2} \quad (3.10)$$

thus removing all J dependence from the vibrational wavefunction. Substituting eqs. (3.7) and (3.10) into eq. (3.5) and performing the J' sum of  $S_{JJ}$ , (which yields  $(2J+1)$ ), we obtain:

$$I_\lambda = \frac{CN^*(T)}{\lambda^5} \sum_{vJ} \frac{|D_{ab}(R_\lambda)|^2 |\Psi_{av}(R_\lambda)|^2}{(dv/dR_\lambda)} \quad (3.11)$$

$$\times \frac{(2J+1) \exp \left\{ -(E_{av} + \hbar^2 J(J+1)/2\mu R_\lambda^2)/kT \right\}}{Z(T)}$$

where  $\Psi_{av}$  denotes the (rotationless) vibrational wavefunction with energy eigenvalue  $E_{av}$  and the derivative of  $(V_a - V_b)$  was replaced by  $(dv/dR_\lambda)$  according to eq. (3.8). Next using the identity  $E_{av} = T_v(R_\lambda) + V(R_\lambda)$  where  $T(R_\lambda)$  is the nuclear kinetic energy at the point  $R_\lambda$  and assuming that the rotational spacing is much smaller than  $kT$ , we replace the sum over J by an integral which yields

$$I_\lambda = \frac{CN^*(T)}{\lambda^5} \frac{2\mu kT}{\hbar^2} \frac{R_\lambda^2 \exp \left\{ -V_a(R_\lambda)/kT \right\}}{(dv/dR_\lambda)} |D_{ab}(R_\lambda)|^2 \quad (3.12)$$

$$\times \sum_v |\Psi_{av}(R_\lambda)|^2 \frac{\exp \left\{ -T_v(R_\lambda)/kT \right\}}{Z(T)}$$

We have now obtained an expression which relates  $I_\lambda$  to the dipole strength  $|D_{ab}(R_\lambda)|^2$  and the probability of finding the nuclei at the radial separation  $R_\lambda$  where the radiative transition takes place. The probability is described by a Boltzmann spatial distribution,  $4\pi R_\lambda^2 \exp\{-V_a(R_\lambda)/kT\}$ , multiplied by a momentum distribution which is in the form of a sum over vibrational states. Assuming that the vibrational spacing (estimated to be the order of  $150 \text{ cm}^{-1}$ ) is much less than  $kT$  (so that many vibrational levels are populated), the sum over vibrational states is easily performed using either harmonic oscillator or WKB eigenfunctions and one obtains  $2\pi kT/h^2$ . The partition function, which includes both bound and free states, is dominated by the continuum contribution hence,

$$Z(T) \approx (2\pi\mu kT/h^2)^{3/2} V \quad (3.13)$$

where  $V$  is the volume of the system. Defining the density of excited states by  $n^*(T)$  we finally obtain (cf. eq. (8) of ref. (13))

$$I_\lambda = C n^*(T) \frac{R_\lambda^2 \exp\left\{-V_a(R_\lambda)/kT\right\} |D_{ab}(R_\lambda)|^2}{\lambda^5 (dv/dR_\lambda)} \quad (3.14)$$

If the temperature is less than or comparable to the vibrational spacing it is better to use eq. (3.12). For our data, eq. (3.14) should be sufficient and it is this expression which we will use to analyze the data presented in this report. For the purposes of our analysis this result can be summarized by writing

$$I_\lambda = \frac{C n^*(T)}{\lambda^5} f(R_\lambda) \exp\left\{-V_a(R_\lambda)/kT\right\} \quad (3.15)$$

where  $f(R_\lambda)$  represents the effective transition probability at the point  $R_\lambda$ .

To use eq. (3.15) effectively, we first consider the ratio of intensities at two different wavelengths in the same electronic band system. The log of this ratio will be (notice that the  $n^*(T)$  cancels out)

$$\log(I_\lambda/I_{\lambda'}) = -\left\{\frac{V_a(R_\lambda) - V_a(R_{\lambda'})}{kT}\right\} + \left\{\log \frac{f(R_\lambda)}{f(R_{\lambda'})} \left(\frac{\lambda'}{\lambda}\right)^5\right\} \quad (3.16)$$

If we plot this log versus  $1/kT$ , the slope of the linear plot will give  $V_a(R_\lambda) - V_a(R_{\lambda'})$ . By doing this for several values of  $\lambda'$ , we can plot out  $V_a$  as a function of wavelength. Of course, we can't get the absolute energy without using some known energy level as a reference thus, for the present, we will plot  $V_a$  relative to some arbitrarily chosen reference point. For convenience, we will choose the energy level which is responsible for 500 nm emission since we always have a strong signal at this wavelength. Figure (3.9) shows a semilog plot of  $(I_\lambda/I_{500})$  versus  $1/kT$  for several wavelengths in the 485 band; the number in parentheses gives the slope in  $\text{cm}^{-1}$ . The excellent linearity of these plots shows that the vibrational states are in thermal equilibrium as one would expect. These data, and several more sets, which we have not plotted, have been analyzed by a least squares computer program to obtain the slopes. The resulting  $V_a(R_\lambda)$  is plotted in figure (3.10)



together with the ground state curve obtained from the relation  $V_b(R_\lambda) = V_a(R_\lambda) - h\nu$ . If the 485 band is emitted by  $Hg_3$ , our picture of these potential curves figure (3.10), is somewhat altered by the fact that  $V$  then depends on two radial parameters as well as the angles between the inter-nuclear vectors.

In figure (3.11) the same procedure has been followed for the 335 band choosing the state which radiates at 336 nm as our energy origin. In figure (3.12), we have plotted  $I_{336}/I_{500}$  so that the potential curves for the 335 band can be plotted relative to the energy of the state which radiates at 500 nm. These curves are given in figure (3.13).

At this point, we should emphasize that the potential curves plotted in figures (3.10) and (3.13) were obtained from the slope of the log R versus  $1/kT$  plots in figures (3.9), (3.11) and (3.12). These potentials are therefore unaffected by temperature independent quantities such as f-values, etc.

Figures (3.10) and (3.13) verify the bound-free nature of the 485 and 335 bands. These figures also appear to indicate that the region of the ground state involved in the 485 band lies somewhat higher on the repulsive wall than the region corresponding to the 335 band and there is some overlap at the edges of the bands. This is consistent with figure (1.1) but it does not prove that figure (1.1) is the correct picture because we only have  $V$  versus  $\lambda$  not  $V$  versus  $R$  and one cannot say with certainty that the ground state curves in figures (3.10) and (3.13) actually refer to the same state (e.g. the ground state of  $Hg_3$  is probably similar but not identical to that for  $Hg_2$ ).

In conclusion we must emphasize that the potential curves  $V$  vs  $\lambda$ , presented in this report, are preliminary data and may be somewhat in error, particularly around 350 nm to 400 nm where the fluorescence bands overlap. We are currently taking more extensive data at various pressures which will be computer analyzed to provide greater accuracy.

#### D. The Effective Transition Probability

It is well known that the probability for emission depends on the internuclear separation. In eq. (3.14) there are several factors which determine this probability and, in eq. (3.15), we have divided them into two categories according to their temperature dependence. The potential energy  $V(R_\lambda)$  and the Boltzmann factor were discussed in the previous section; in this section we will briefly discuss the temperature independent quantity  $f(R_\lambda)$ .

The function  $f(R_\lambda)$  is strongly influenced by the dimensional factor  $R_\lambda^2$  which (for our case) causes  $f$  to increase with decreasing wavelength. Since  $f$  is inversely proportional to  $(dv/dR) \propto (dV_a/dR) - (dV_b/dR)$ , this factor will tend to make  $f$  larger in the region where both  $V_a$  and  $V_b$  are repulsive (longer wavelengths) thus counteracting the effect of  $R^2$  to some extent. Finally there is the dipole strength  $D_{ab}(R_\lambda)$  where radial dependence is unknown.

It is possible to obtain relative values of  $f$  as a function of wavelength by comparing the quantity

$$I_{\lambda}' = \lambda^{-5} \exp \{ - V_a(R_{\lambda})/kT \} \quad (3.17)$$

with the observed intensity  $I_{\lambda}$  for some fixed temperature. Such a comparison has been made for both bands and the results are given in tables (3.1) and (3.2). The comparison was made for two different temperatures in order to give an idea of the scatter in calculated values of  $f$ . This scatter seems to be the order of 10%, but it should be possible to do a bit better when more accurate potentials are obtained. The functions  $f(R_{\lambda})$  are relatively constant near the centers of the bands with a rapid increase in the short wavelength (large  $R_{\lambda}$ ) limit.

At this point, no attempt has been made to estimate an absolute value of  $f(R_{\lambda})$ ; the present analysis is intended only to give an idea of the type of gain profiles to be expected for these bands.

The blue shift of the peaks of both bands, which was observed with increasing temperature, (figs. 3.3 and 3.4) is now seen to result from a combination of  $f(R_{\lambda})$  and the  $\lambda^{-5}$  factor in eq. (3.15). These factors combine to make an effective transition probability which increases strongly with decreasing wavelength.

#### IV. TIME DEPENDENCE

Using the pulsed discharge continuum lamp described in section II C, we have observed the time evolution of the 335 and 485 bands throughout a density range of  $10^{17}$  to  $10^{19}$  Hg atoms/cm<sup>3</sup> and a temperature range of 473 to 973 K. Light from the lamp passed through the tri-compartmental filter (see fig. 2.1) and the resulting fluorescence was observed at right angles through either the 335 or 485 broad band interference filters (fig. 2.6).

Figure (4.1) shows a typical time history trace for a density of  $10^{18}$  and a vapor temperature of 523 K. Part "a" shows the overall rise and decay of the 485 band time with a 10  $\mu$ sec/div time scale while part "b" shows the rise of the fluorescence with an expanded scale of 2  $\mu$ sec/div. At low pressures ( $3 \times 10^{17}$  cm<sup>-3</sup>) the rise of the 335 band is the order of 30  $\mu$ sec and about 25% faster than that of the 485 band, whereas at higher pressures ( $10^{18}$ - $10^{19}$  cm<sup>-3</sup>), the two bands rise almost simultaneously with rise times in the range 10 to 1  $\mu$ sec. The observed rise times decrease linearly with increasing density but show almost no temperature dependence; increasing only slightly as the temperature increases from 200°C to 350°C and remaining constant after that.

It is interesting to note that while the duration of the flashlamp pulse is 1  $\mu$ sec., the rise time of the fluorescence bands has been observed to be as long as 40  $\mu$ sec (at  $N = 3 \times 10^{17}$ ). One possible explanation for this delay assumes that the postulated merging<sup>[4]</sup> of the  $^3_1u$  and  $^3_0u^-$  curves (see fig. 1.1) causes the high lying  $^3_1u$  vibrational states (which are the ones being directly pumped) to dissociate before they can radiate (the A value is expected to be the order of  $10^6 - 10^7$ ) or before collisions can produce vibrational relaxation. The  $^3P_0$  atomic state would then serve as a reservoir for this excitation and the slow rise in fluorescence intensity would be determined by the rate at which  $^3P_0$  feeds energy back to the molecules. Initial attempts to test this hypothesis by measuring the time history of the  $^3P_0$  have been hampered by lack of intensity.

The long time decay fits an exponential,  $e^{-t/\tau}$ , from 80% of the maximum intensity out to about 3 time constants (the limit of our measurement). Both bands decay simultaneously to within the experiment error of  $\pm 1$   $\mu$ sec at all pressures and temperatures for which we have made the measurement. As shown in figure (4.2) there is a striking temperature dependence; first a sharp increase in lifetime and then a decrease. The point at which the maximum time constant is observed is where the dominant emission changes (see fig. 4.3) from 485 nm (low temperature) to 335 nm (at high temperatures). For a density of  $2 \times 10^{18}$  cm<sup>-3</sup>, this point is at  $T \approx 730$  K.

The complex behavior of both rise and decay processes indicates the presence of several competing processes. We made several attempts to model the data but more extensive data will be needed before any meaningful analysis is possible.

## V. SUMMARY

This report presents new measurement techniques which have been developed to provide data such as potential curves and  $f$ -values for metal molecules which are of interest as dissociation laser candidates. Preliminary data and analysis were presented in order to illustrate the measurement techniques in general and to shed some light on the mercury molecule in particular.

Our results may be briefly summarized as follows:

- (1) Purity is extremely important. Normal laboratory grade mercury was not pure enough and it was necessary to distill the mercury into specially prepared sample cells.
- (2) The two electronic states responsible for the 485 and 335 bands have been shown to be vibrationally equilibrated at the pressures of interest in laser applications.
- (3) Assuming that these fluorescence bands are emitted by diatomic mercury, the potential curves for these states have been measured over the regions which give rise to the fluorescence and are found to be in qualitative agreement with curves proposed by Mrozowski. Our results do not extend to large inter-nuclear distances so it is not possible to say if they will agree with Mrozowski in the dissociation limit. However, on the basis of the present data, one cannot exclude the possibility that the 485 band is radiated by  $\text{Hg}_3$ .
- (4) The two electronic states radiating 485 and 335 appear to be in thermal equilibrium with one another, perhaps indicating a curve crossing as proposed by Mrozowski.
- (5) Relative transition probabilities were found to be slowly varying across both bands with some increase at larger  $R$  or smaller wavelengths.
- (6) The pressure and temperature dependence of both decay and rise times have been measured, but no quantitative conclusions have been drawn from these data as yet.



## VI. ACKNOWLEDGMENTS

We would like to acknowledge many helpful discussions with Dr. A. V. Phelps and Prof. J. Cooper of the Joint Institute for Laboratory Astrophysics. We also wish to thank Mme. Denise Perrin of the University of Paris VI for providing us with information on the optical pumping of  $\text{Hg}_2$  via the continuum absorption band. In addition, we wish to express appreciation to Dr. R. J. Carbone for many stimulating discussions and for organizing a symposium on mercury at the AEC Los Alamos Laboratories which provided many new ideas on the kinetics of such systems.

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Table 3.1  $f_\lambda$  for 335 nm band,  $T = 873\text{K}$ ,  $kT = 605 \text{ cm}^{-1}$

$\lambda$	$e^{-\frac{(V_\lambda - V_{336})}{kT}}$	$(\lambda/336)^{-5} e^{-\frac{(V_\lambda - V_{336})}{kT}}$	$I_{\text{obs}}$	$f$
300	0.034	.059	.145	2.46
310	.173	.259	.353	1.36
320	.45	.574	.68	1.18
330	.78	.85	.96	1.12
336	1.0	1.0	1.0	1.0
340	1.02	.96	.93	.97
350	.88	.72	.545	.76
360	.396	.28	.17	.61
$T = 673 \text{ K}, kT = 467 \text{ cm}^{-1}$				
300	.013	.022	.066	3.0
310	.10	.15	.21	1.4
320	.36	.46	.53	1.15
330	.726	.79	.91	1.15
336	1.0	1.0	1.0	1.0
340	1.03	.97	.97	1.0
350	.85	.69	.55	.8
360	.30	.21	.26 $\pm$ 0.1	1.24

Table 3.2  $f_\lambda$  for 500 nm band,  $T = 573$  K,  $kT = 398 \text{ cm}^{-1}$

$\lambda$	$e^{-\frac{(V_\lambda - V_{500})}{kT}}$	$(\lambda/500)^{-5} e^{-\frac{(V_\lambda - V_{500})}{kT}}$	$I_{\text{obs}}$	$f$
400	0.00164	.005	.075	11.4
420	.013	.031	.129	4.16
440	.095	.18	.29	1.6
460	.266	.404	.56	1.39
480	.534	.655	.85	1.3
500	1.0	1.0	1.0	1.0
520	1.386	1.14	.96	.84
540	1.05	.715	.765	1.07
560	.78	.44	.52	1.18
580	.405	.193	.32	1.64
$T = 773$ K, $kT = 536.4 \text{ cm}^{-1}$				
400	0.0086	.026	.289	11.1
420	.041	.098	.388	4.0
440	.174	.33	.562	.17
460	.374	.57	.796	1.4
480	.627	.77	.95	1.23
500	1.0	1.0	1.0	1.0
520	1.27	1.04	.90	.87
540	1.03	.70	.69	.99
560	.83	.47	.51	1.08
580	.51	.243	.33	1.4

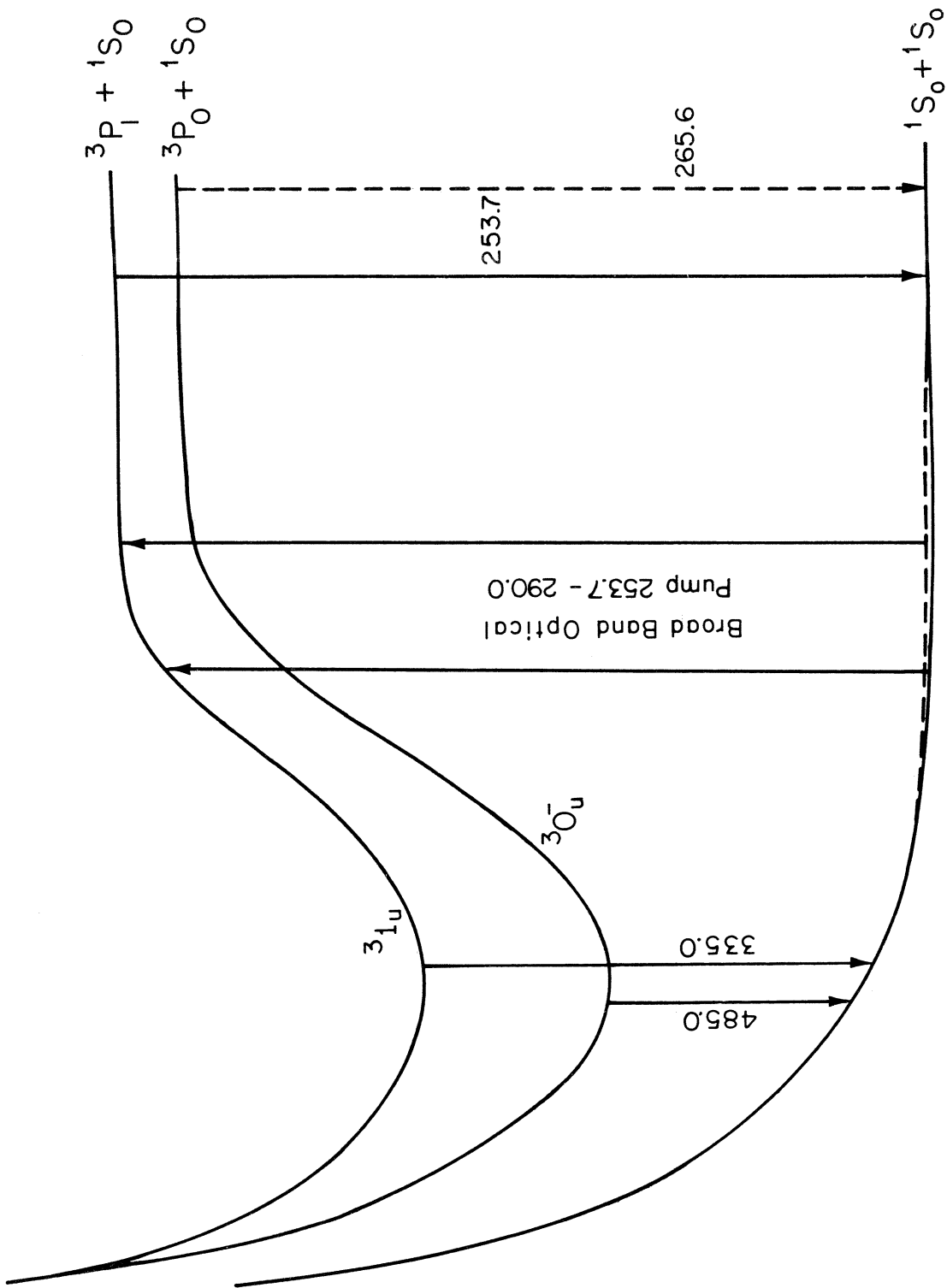


Figure 1.1 Potential curves of Hg<sub>2</sub> molecules according to Mrozowski (ref. 5).

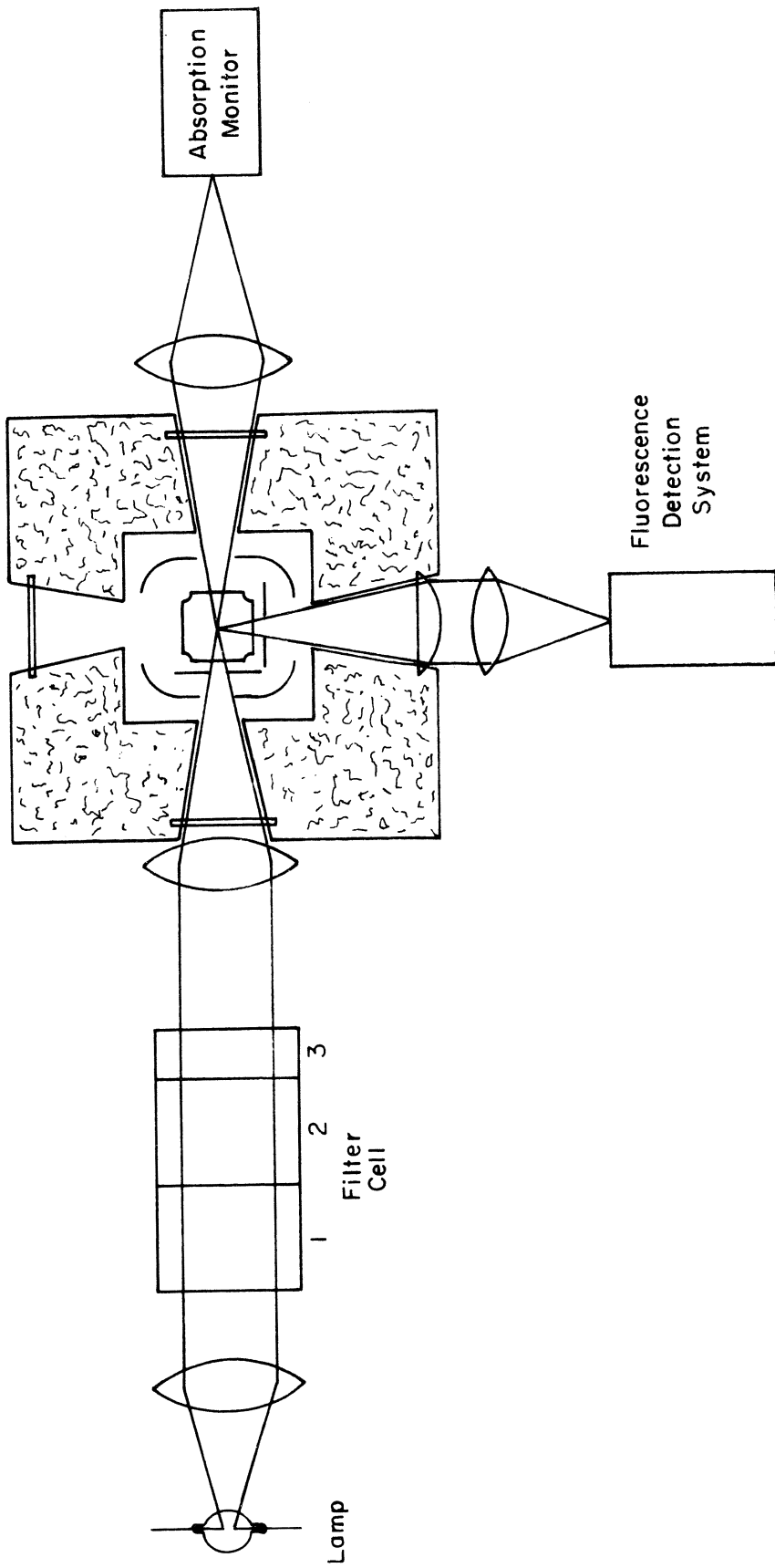


Figure 2.1 Experimental set up.



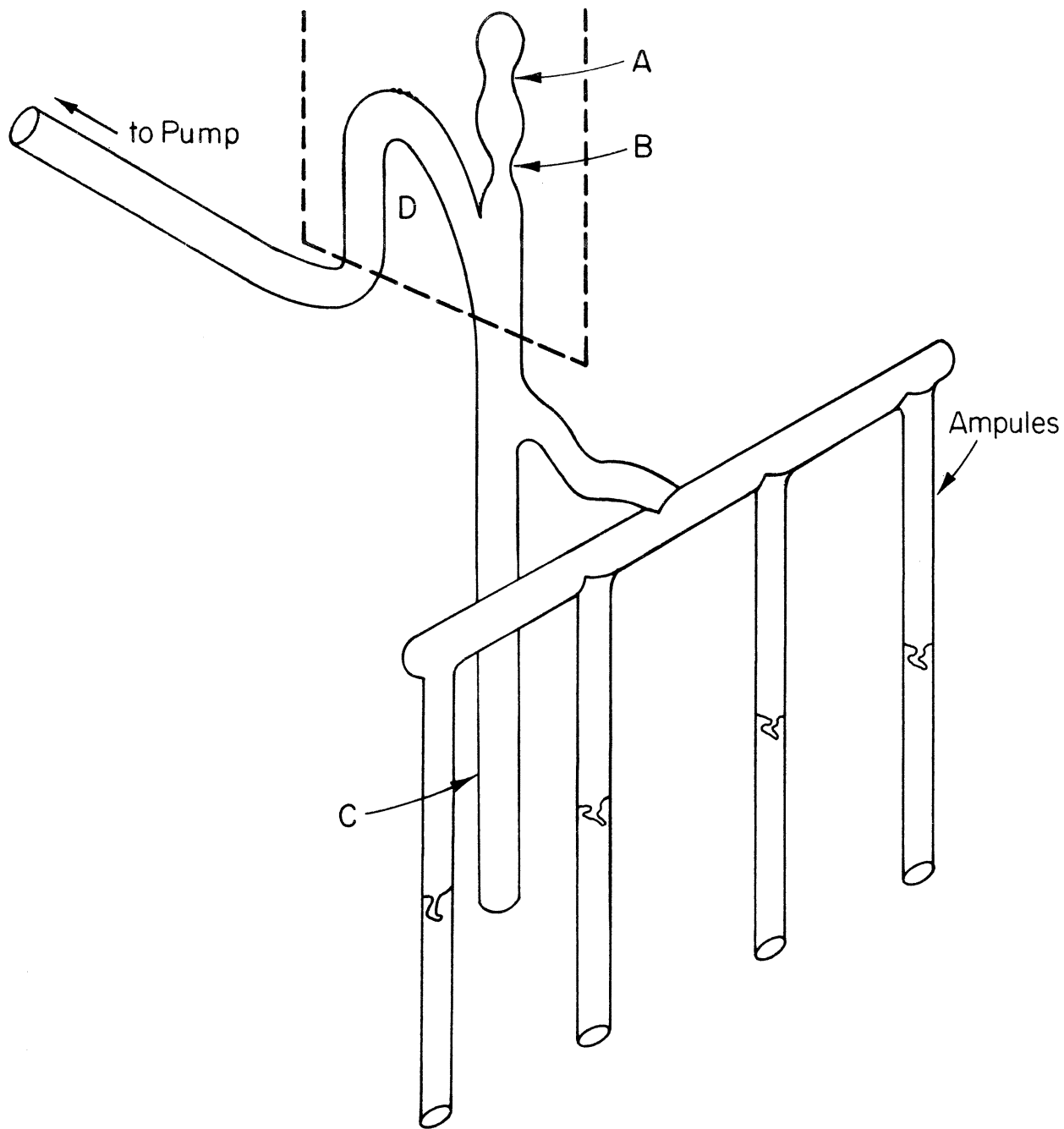


Figure 2.2 Mercury ampule preparation system.

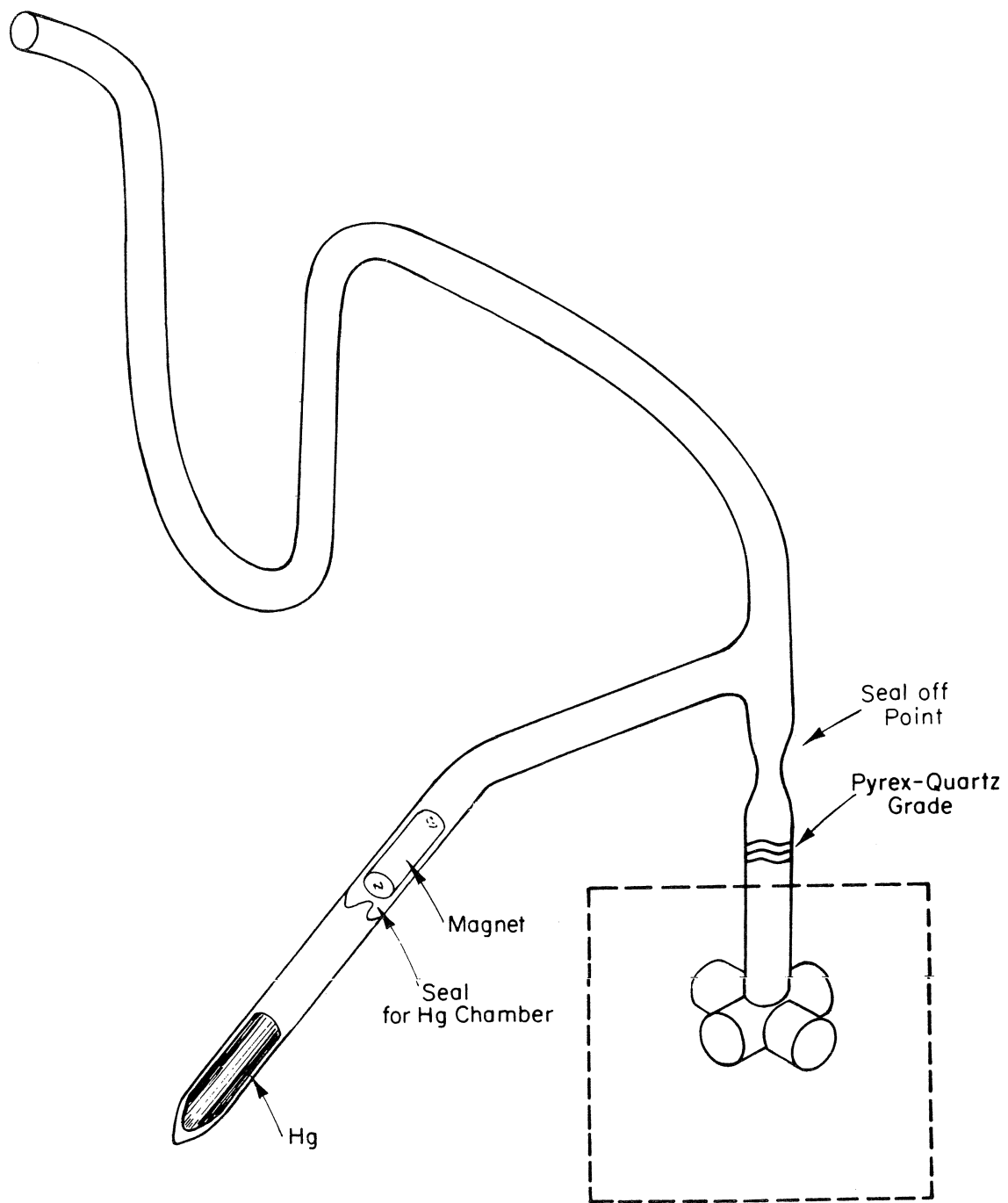


Figure 2.3 Mercury cell distillation system.

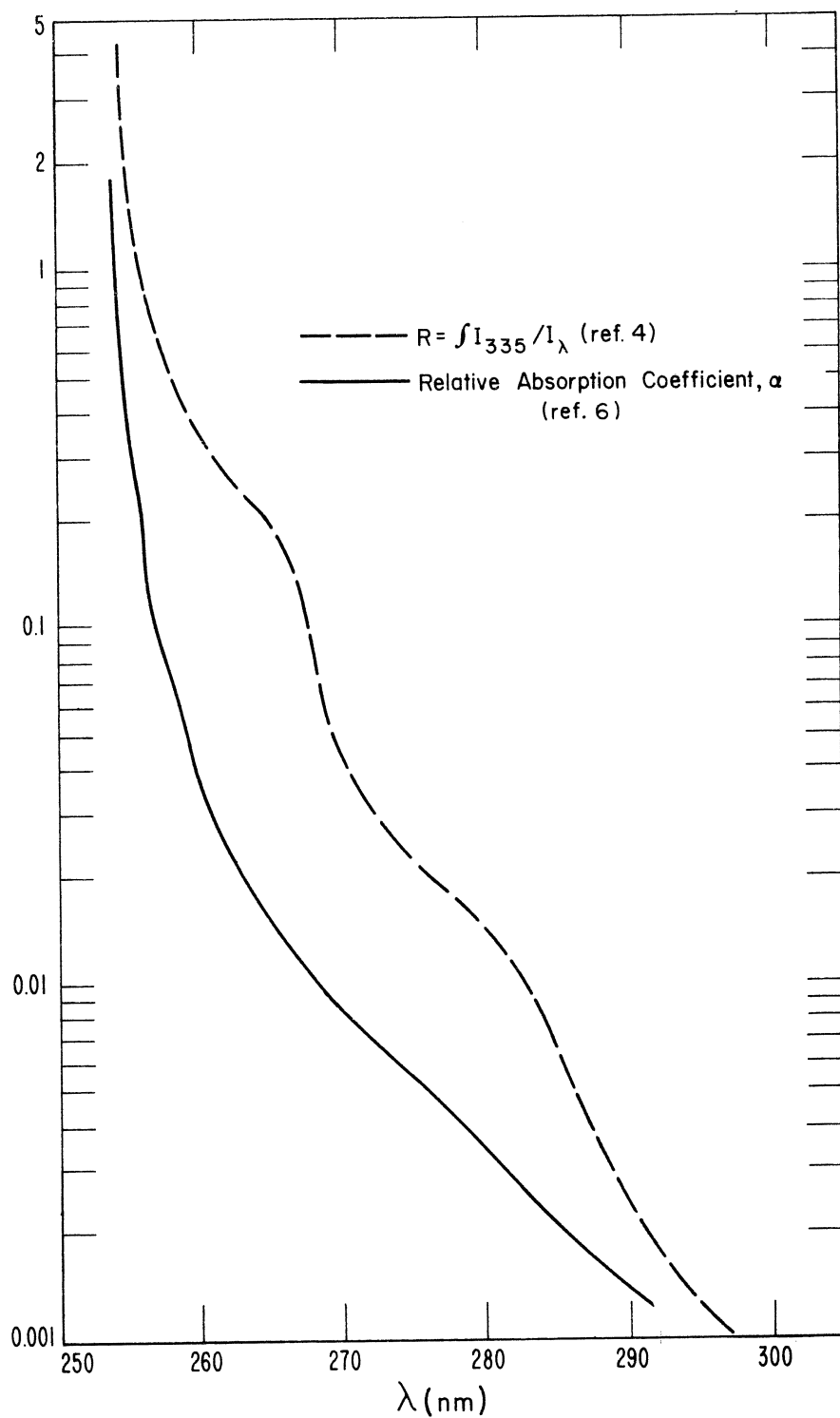


Figure 2.4 Absorption coefficient and integrated band intensity versus wavelength.

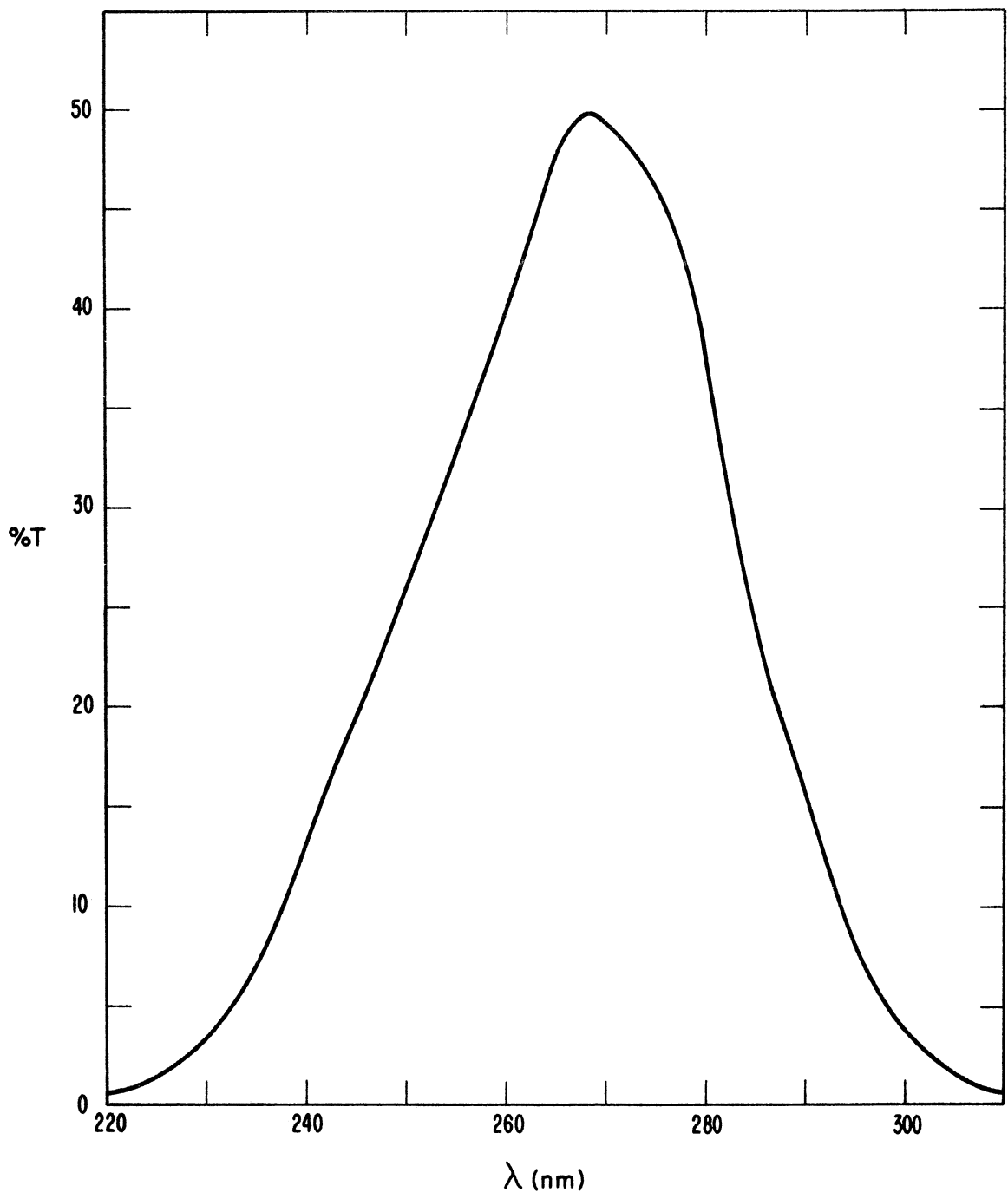


Figure 2.5 Transmission curve of tri-compartment filter.

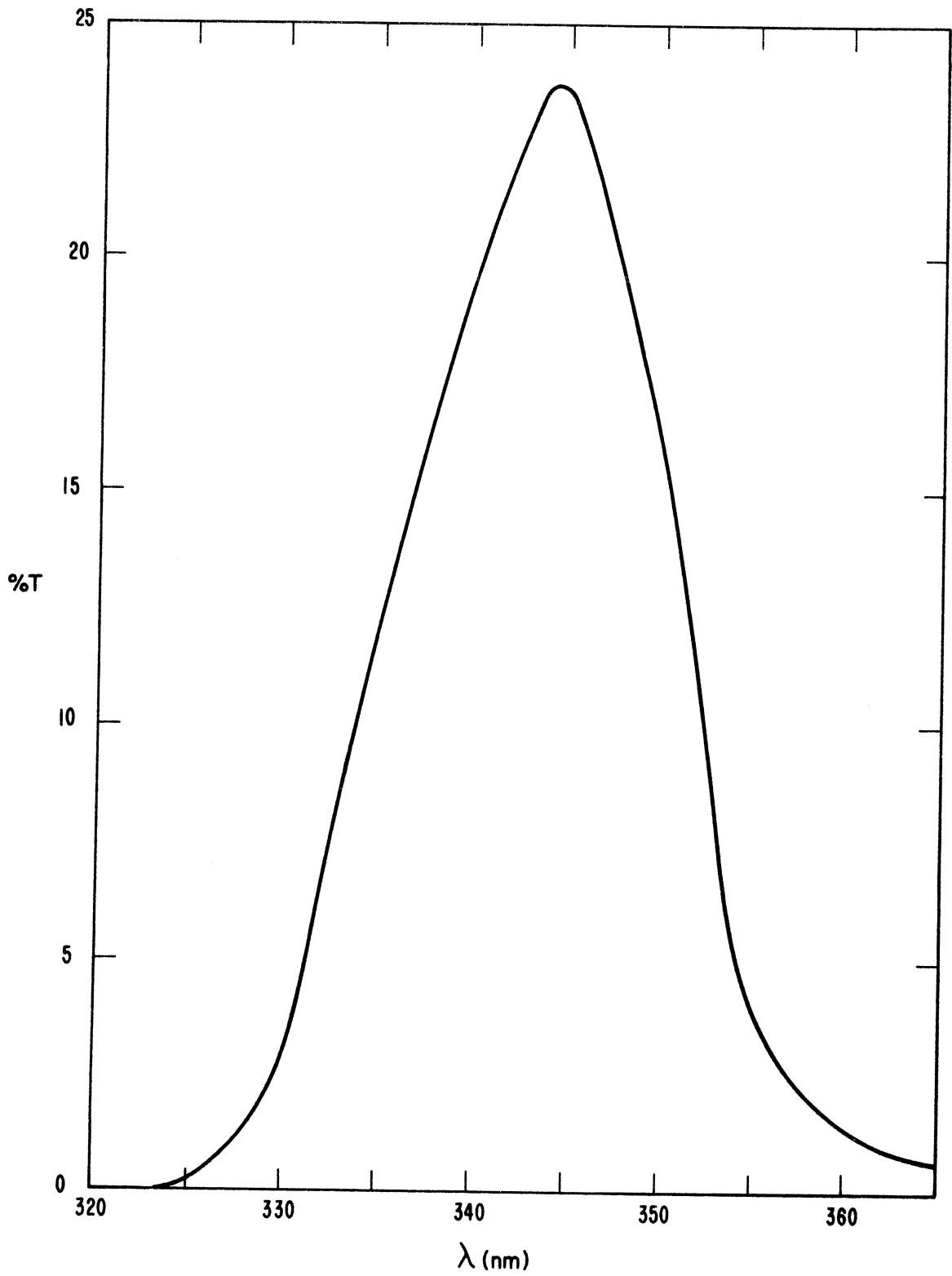


Figure 2.6 Transmission curve of 335 bandpass filter.

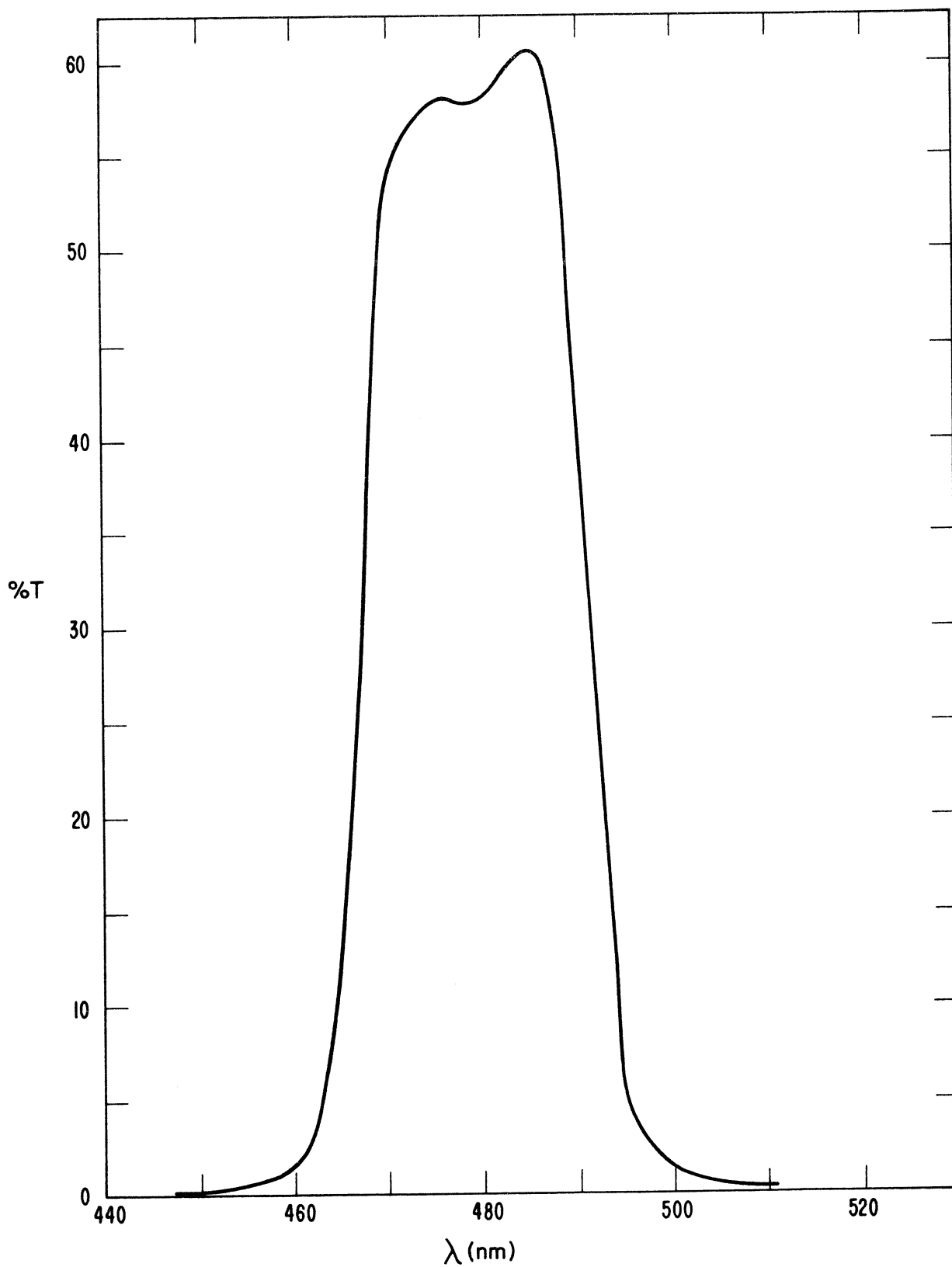


Figure 2.7 Transmission curve of 485 bandpass filter.



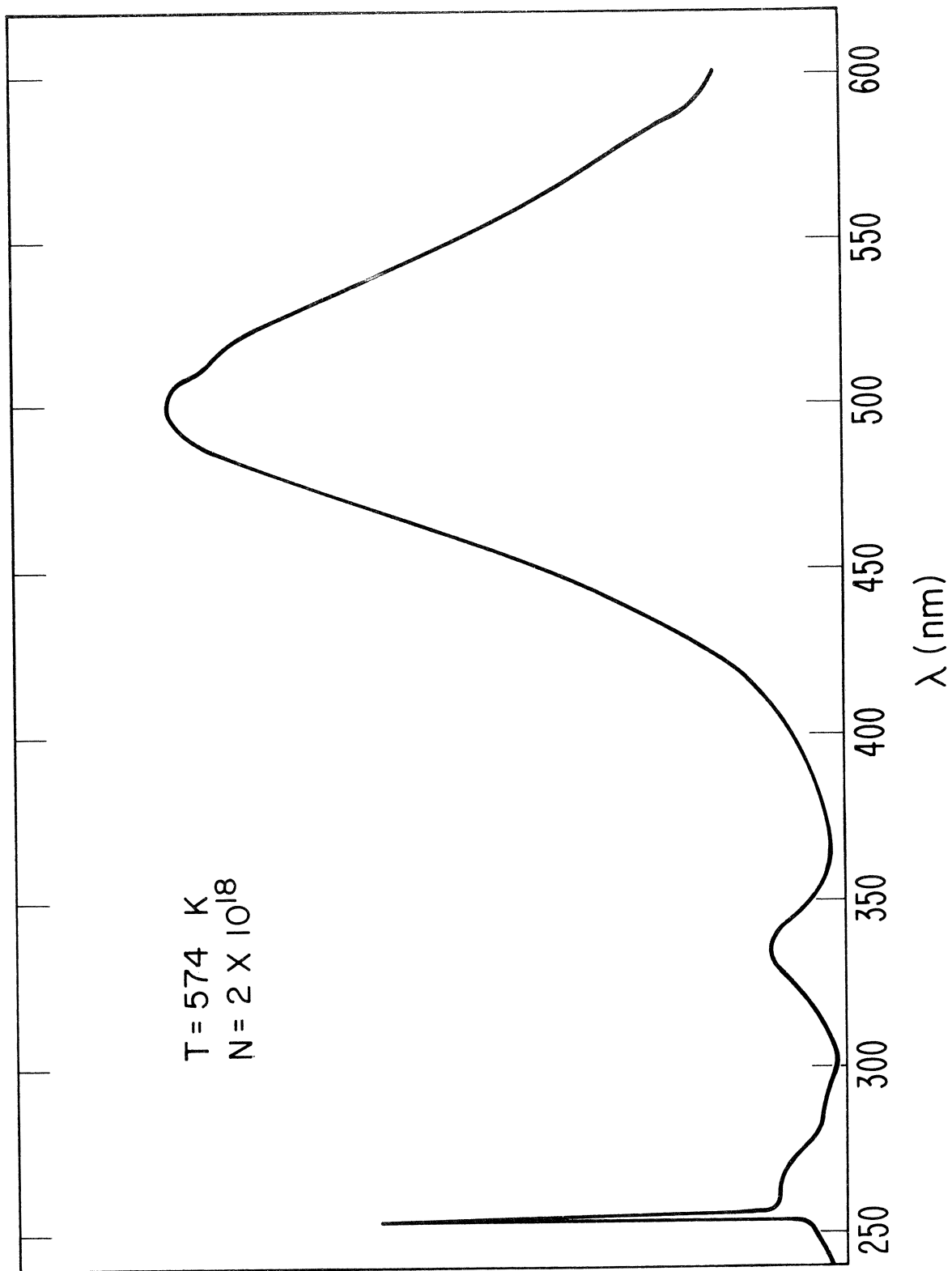


Figure 3.1 Spectral distribution of Hg<sub>2</sub> fluorescence excited by Xe Arc.

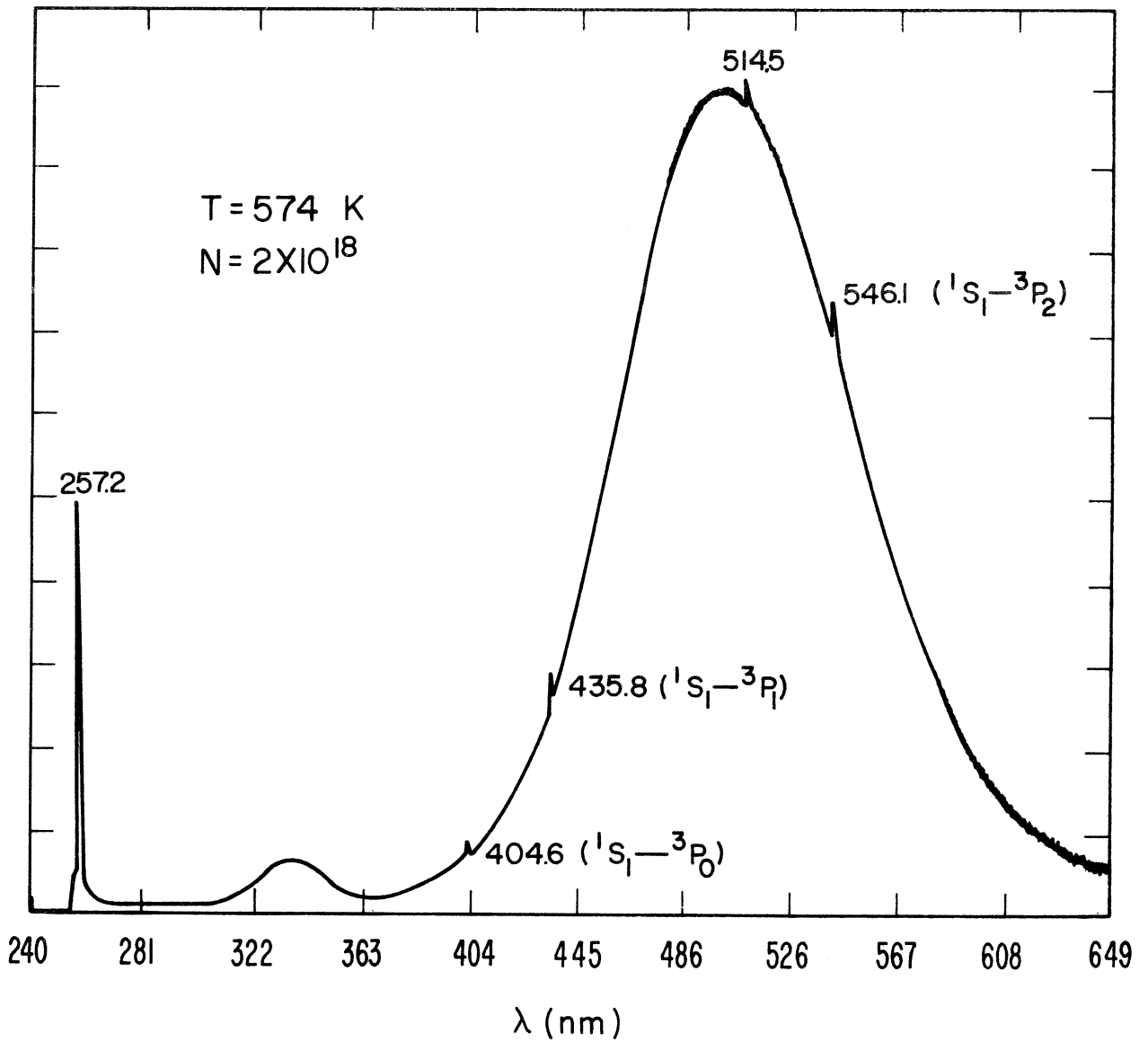


Figure 3.2 Spectral distribution of  $\text{Hg}_2$  fluorescence excited by 257.2 nm laser line.

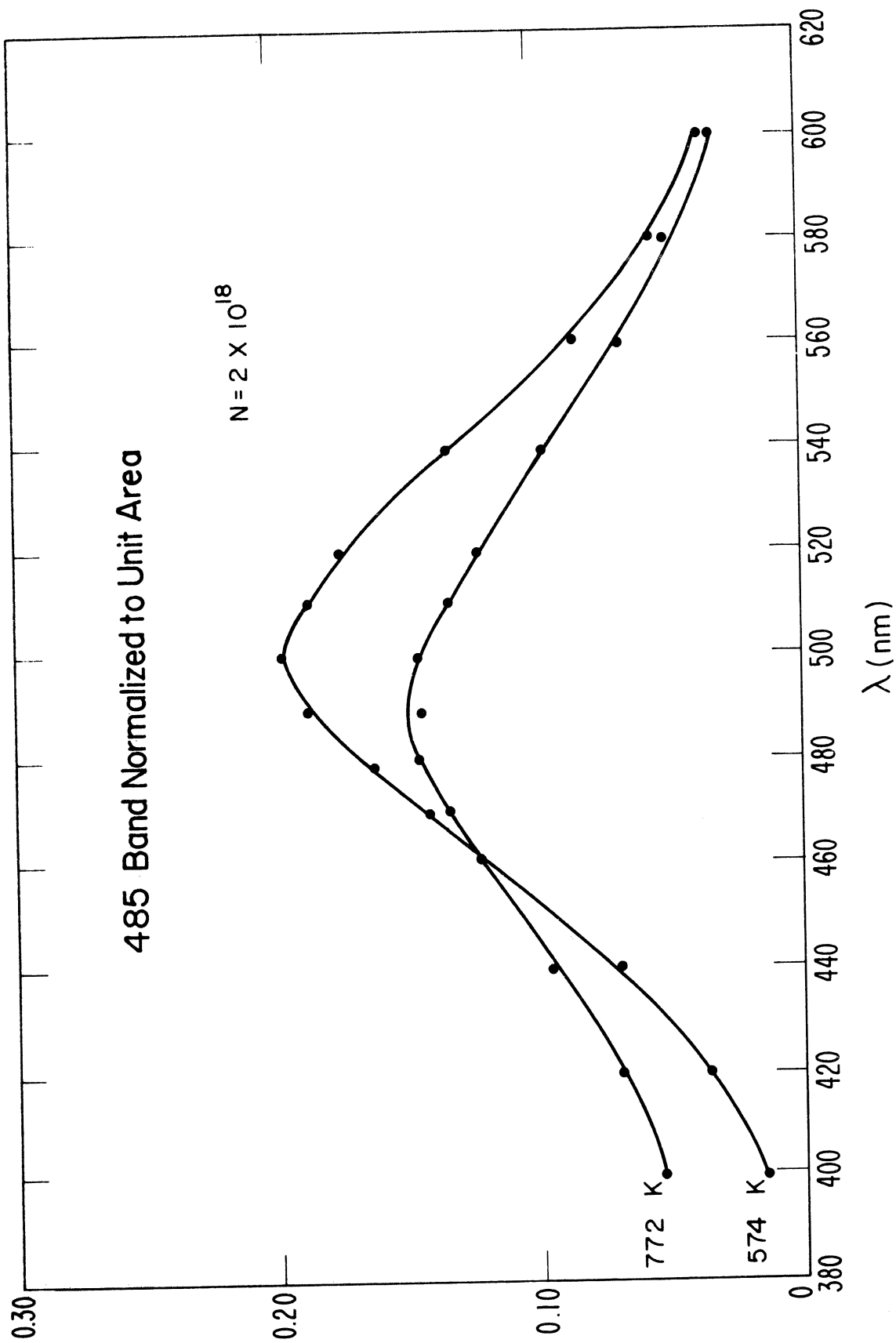


Figure 3.3 Spectral distribution of 485 band at different temperatures.

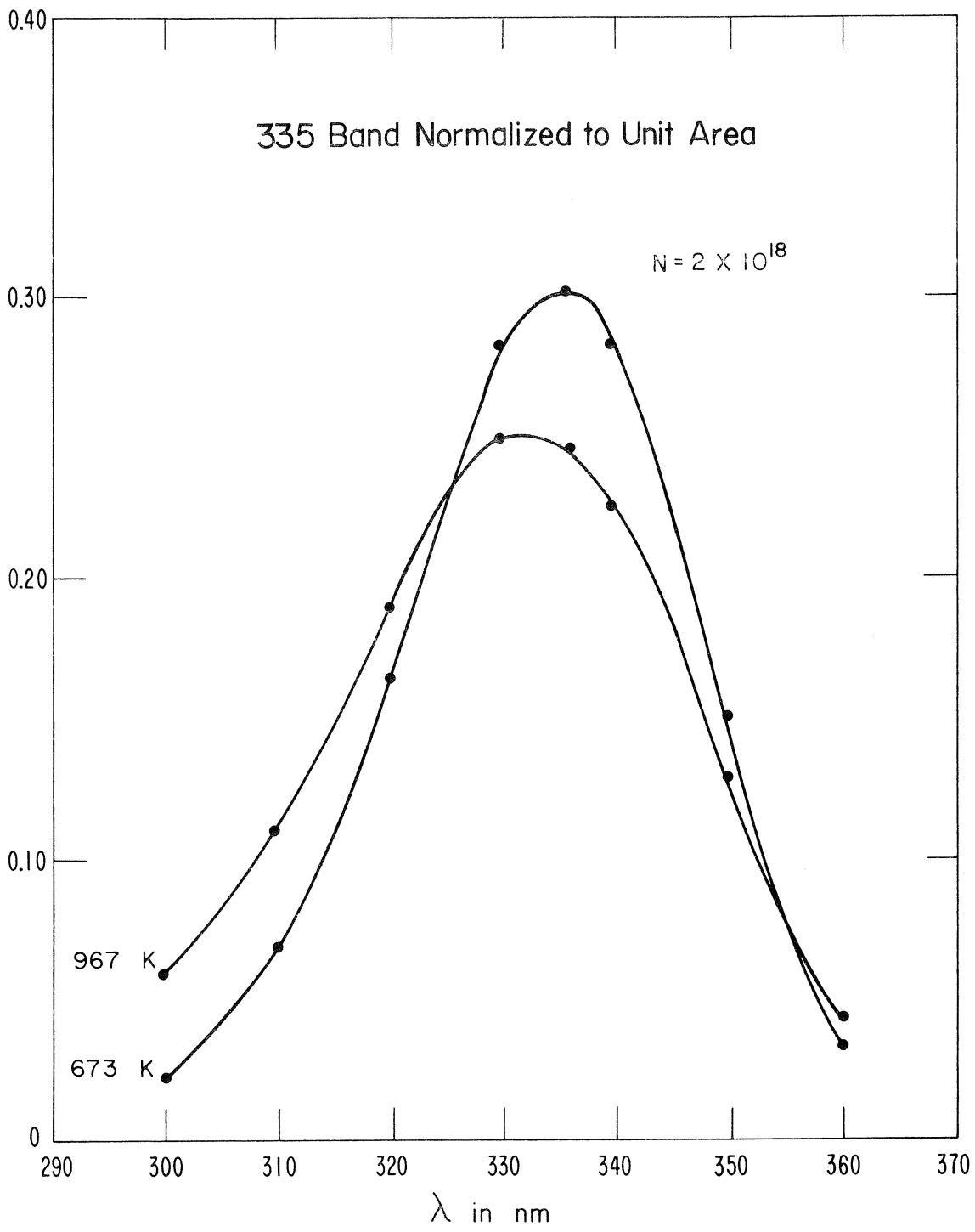


Figure 3.4 Spectral distribution of 335 band at different temperatures.

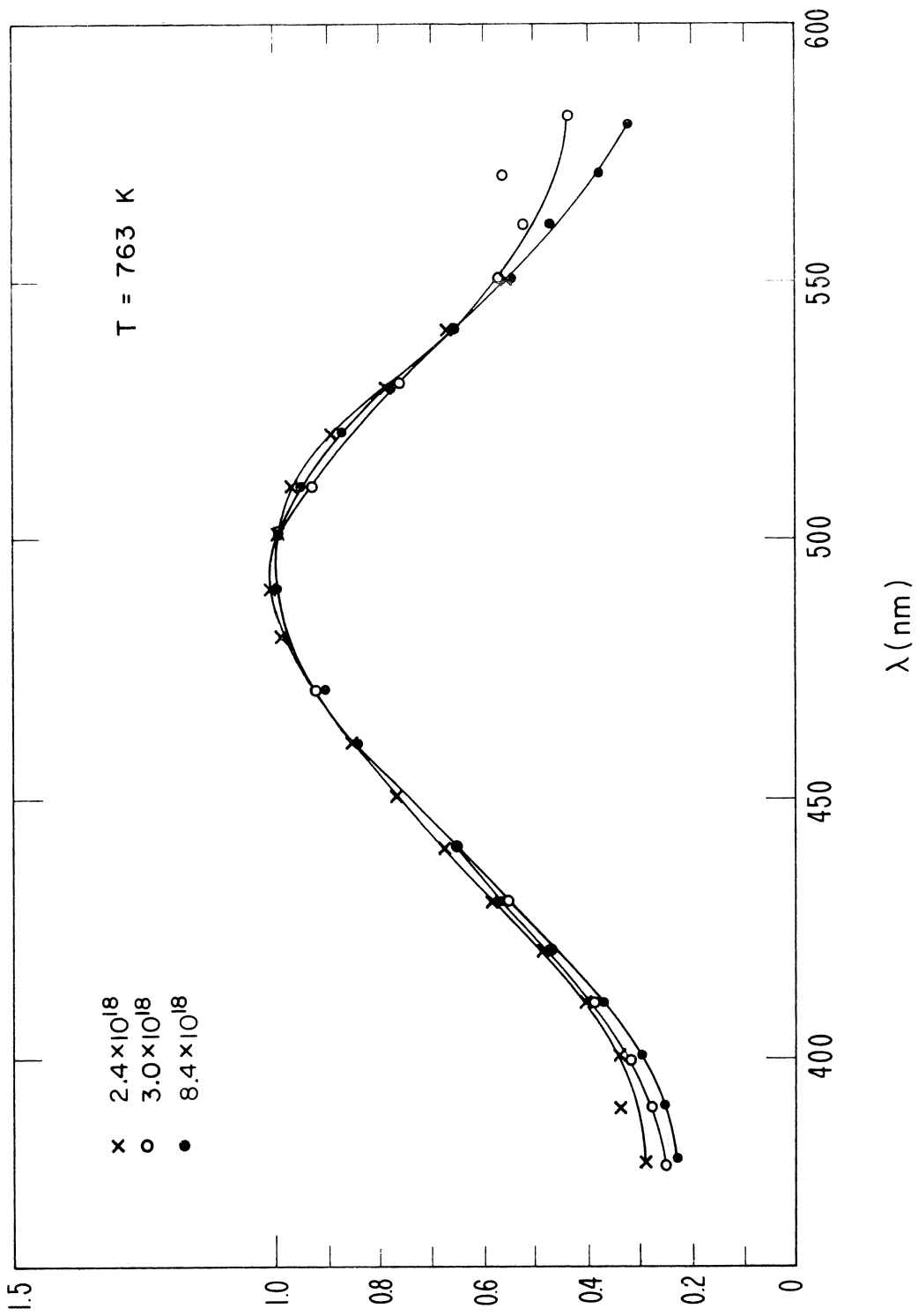


Figure 3.5 Spectral distribution of 485 band at different vapor densities.

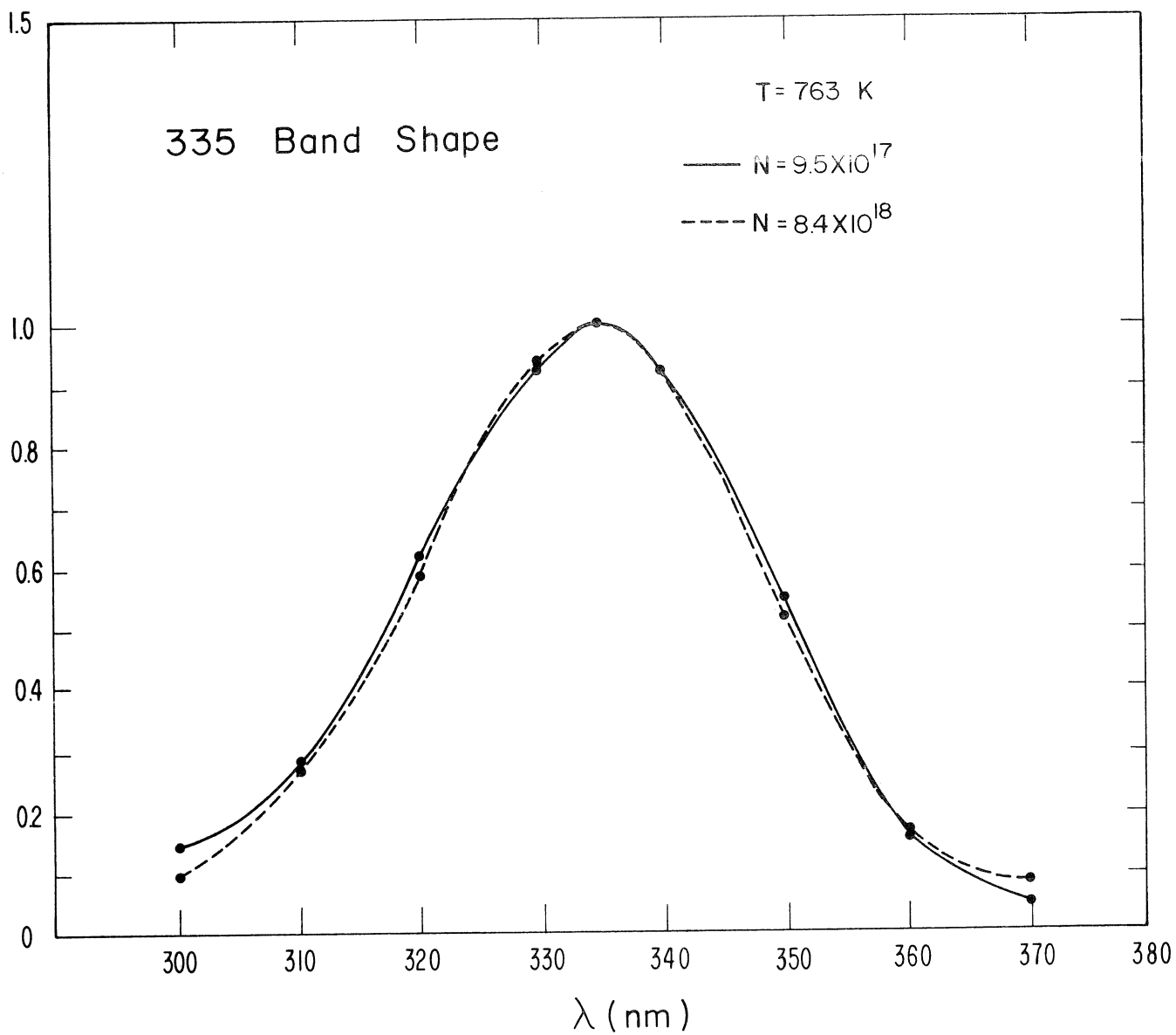


Figure 3.6 Spectral distribution of 335 band at different vapor densities.

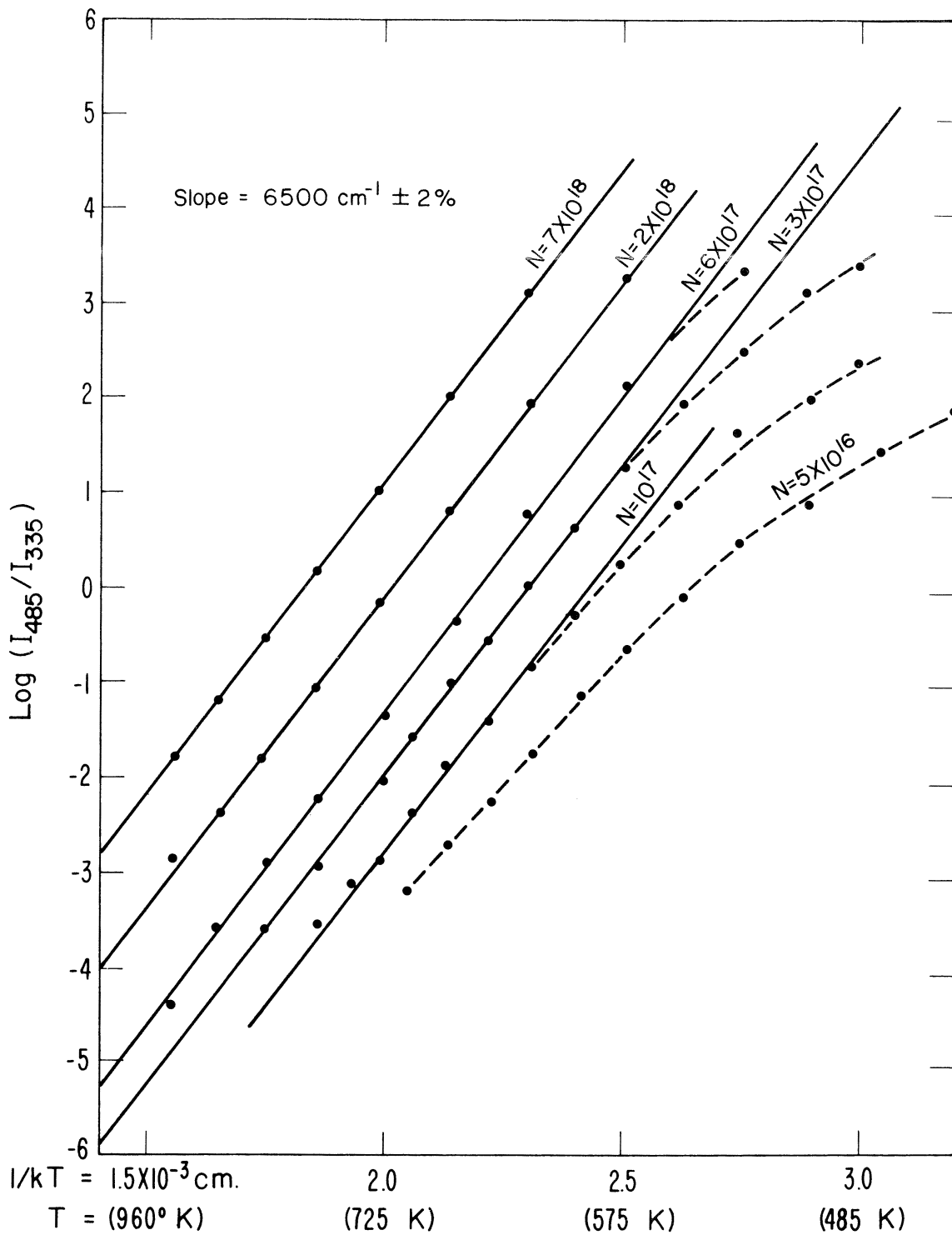


Figure 3.7 Ratio of 485/335 band intensities versus temperature.



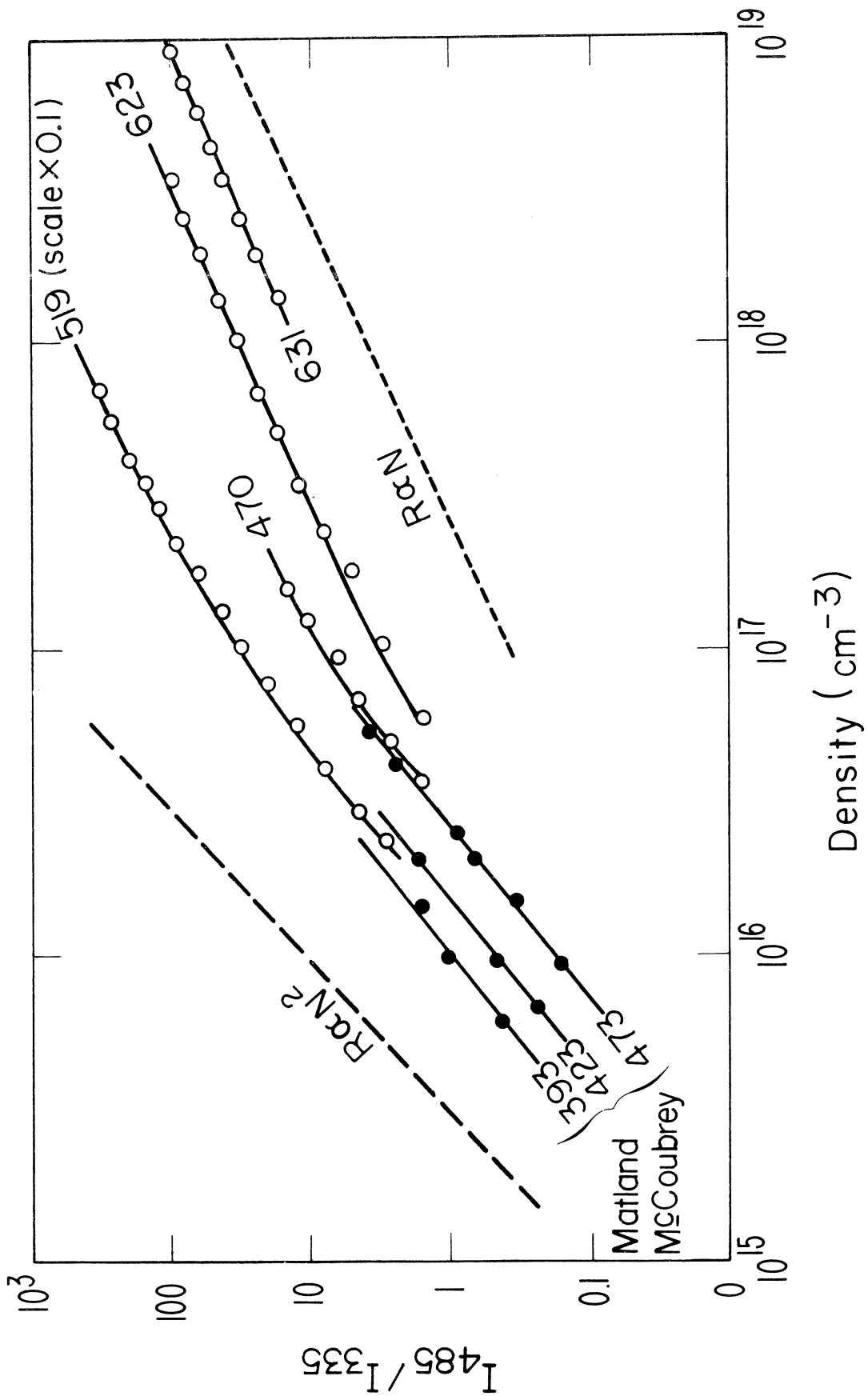


Figure 3.8 Ratio of 485/335 band intensities versus density.

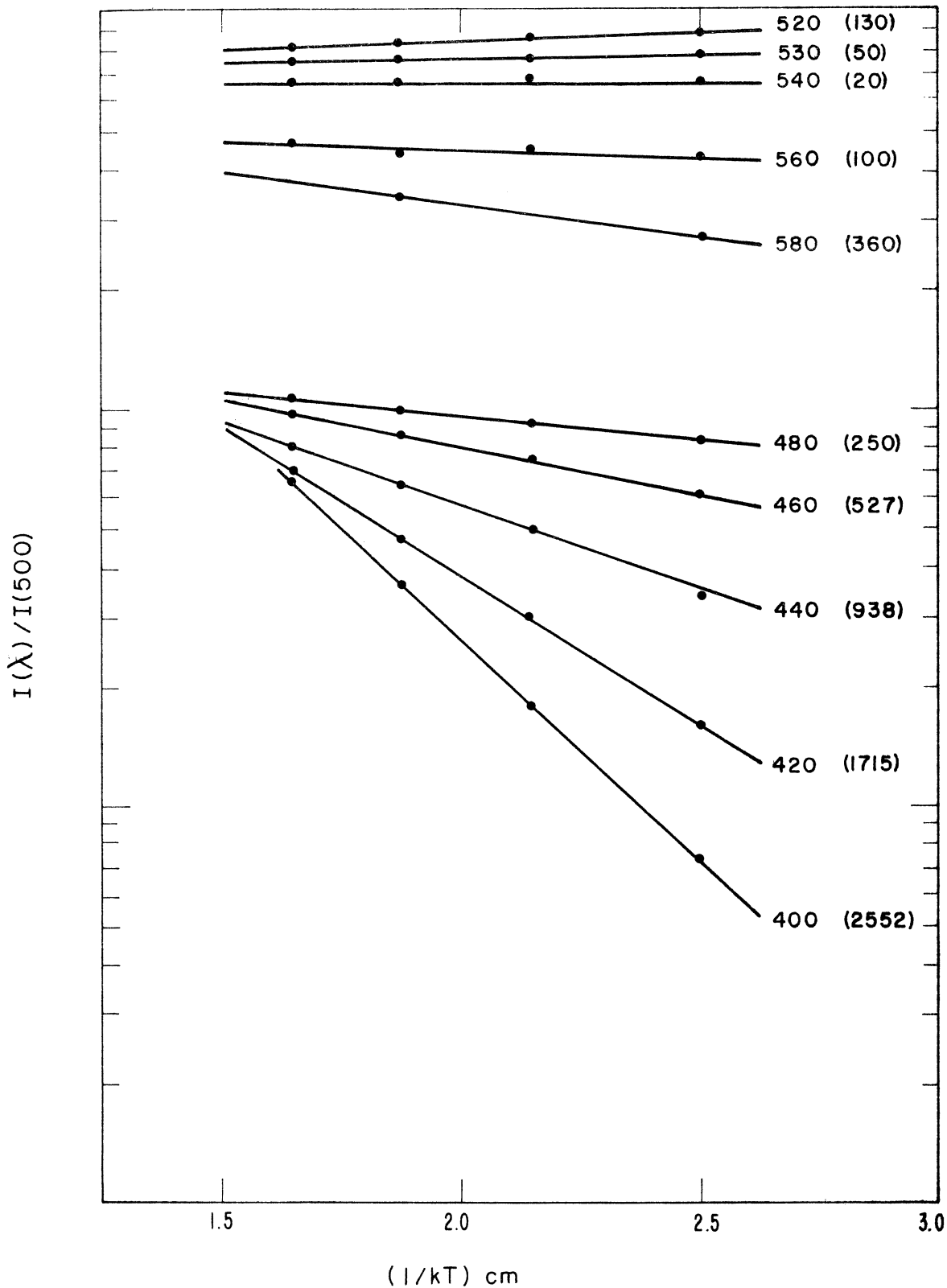


Figure 3.9 Normalized intensities versus temperature in the 485 band.

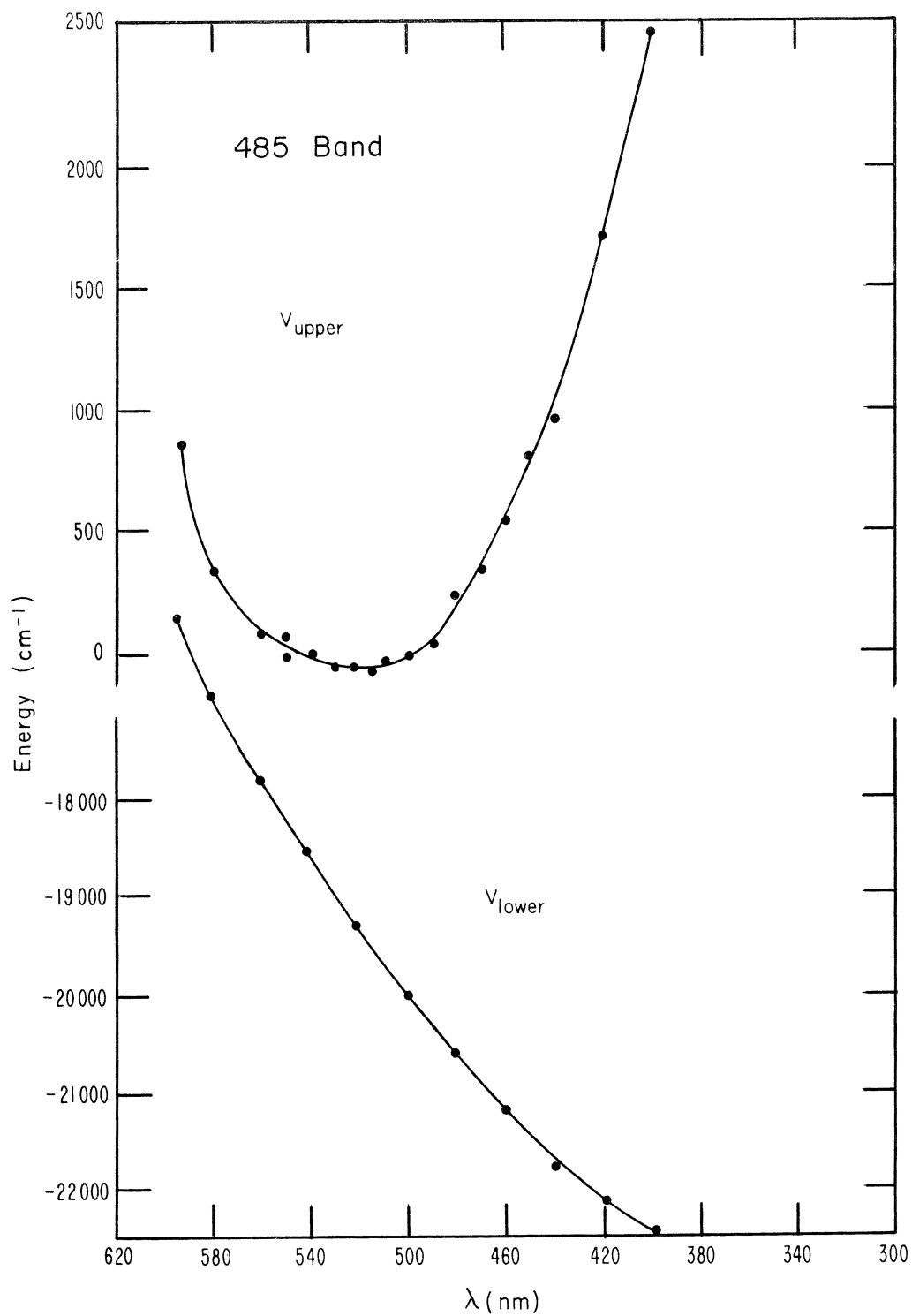


Figure 3.10 Potentials corresponding to the 485 band.

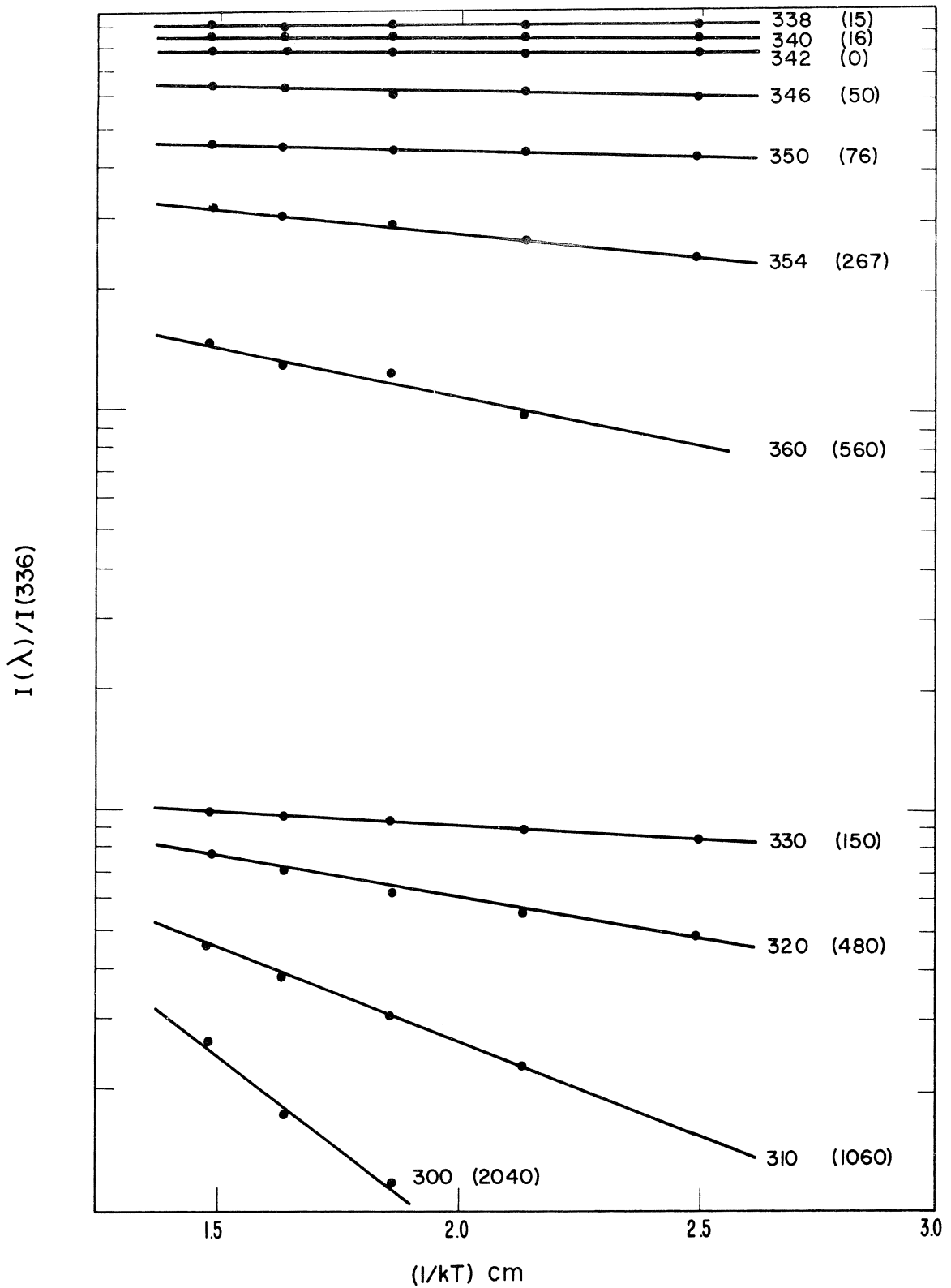


Figure 3.11 Normalized intensities versus temperature in the 335 band.

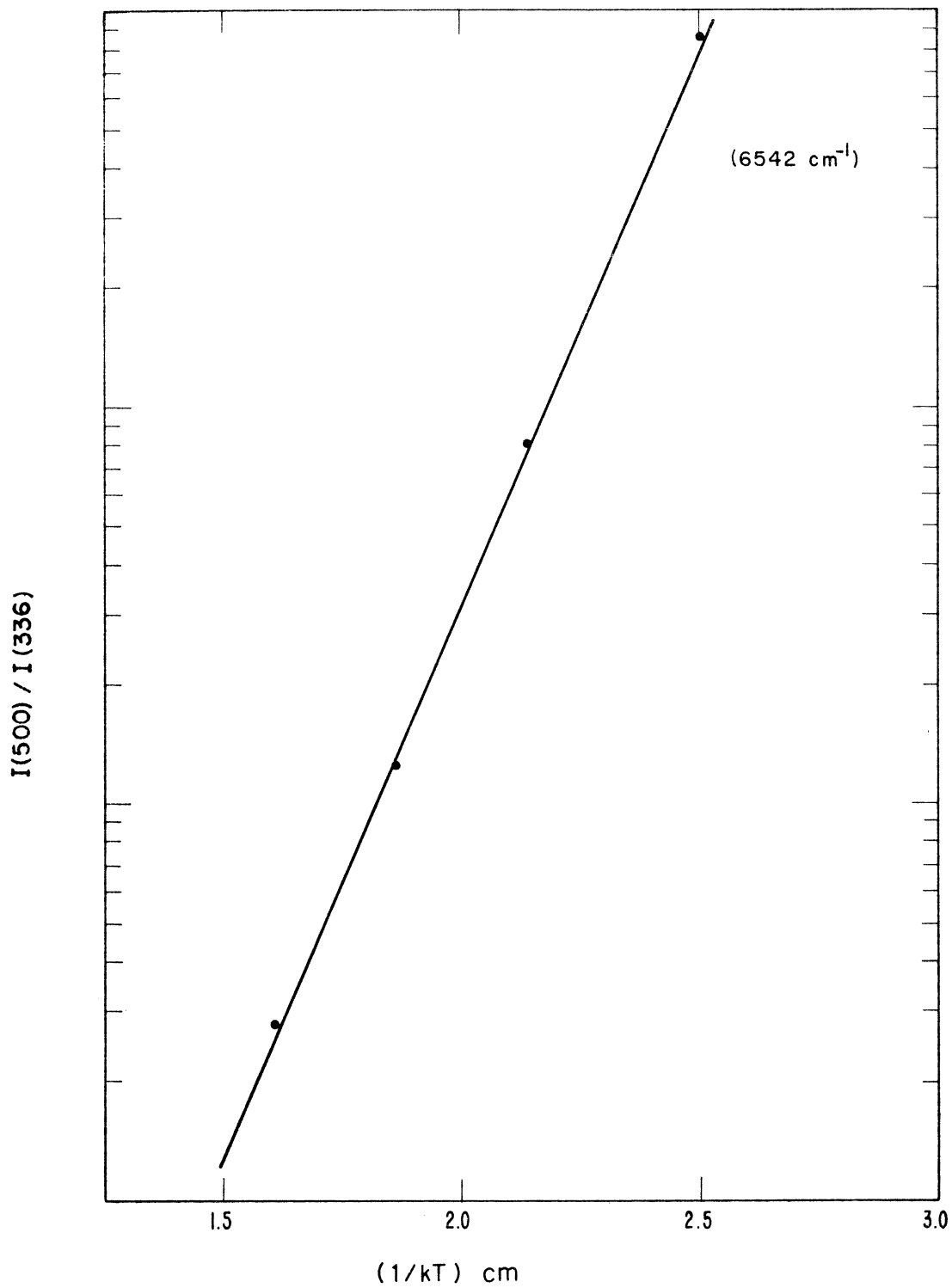


Figure 3.12 Ratio of 485/335 versus temperature.

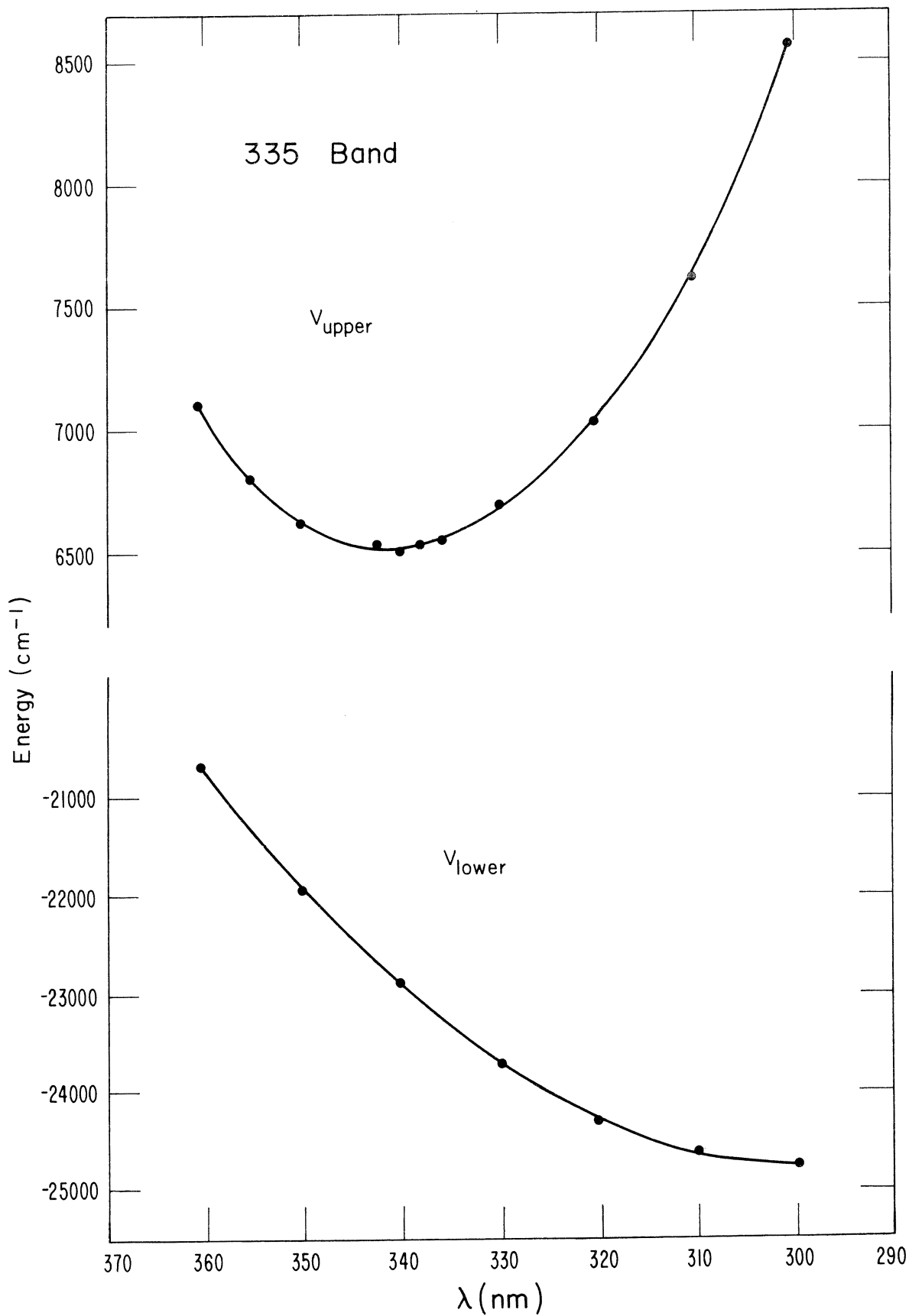
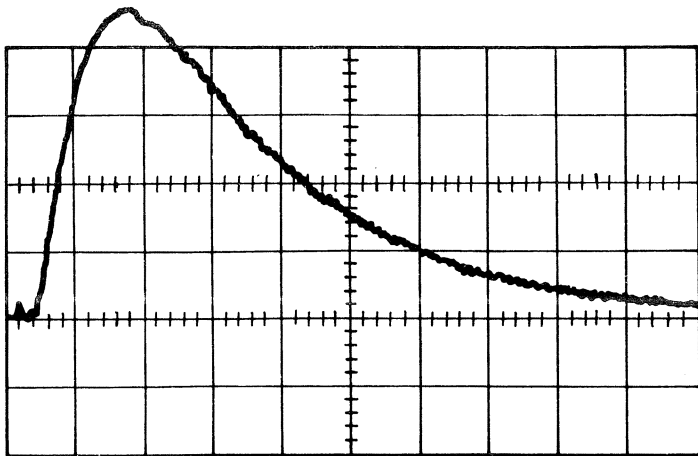
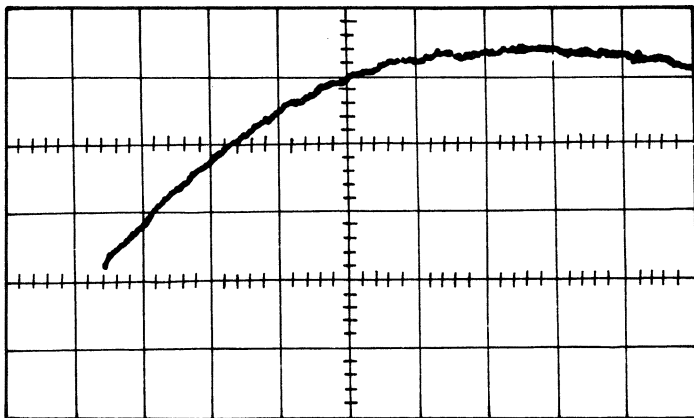


Figure 3.13 Potentials corresponding to the 335 band.



(a)  $10 \mu\text{sec} / \text{Div.}$



(b)  $2 \mu\text{sec} / \text{Div.}$

Figure 4.1 Time history of the 485 fluorescence band. (a)  $10 \mu\text{sec} / \text{division}$  and (b)  $2 \mu\text{sec} / \text{division}$ .



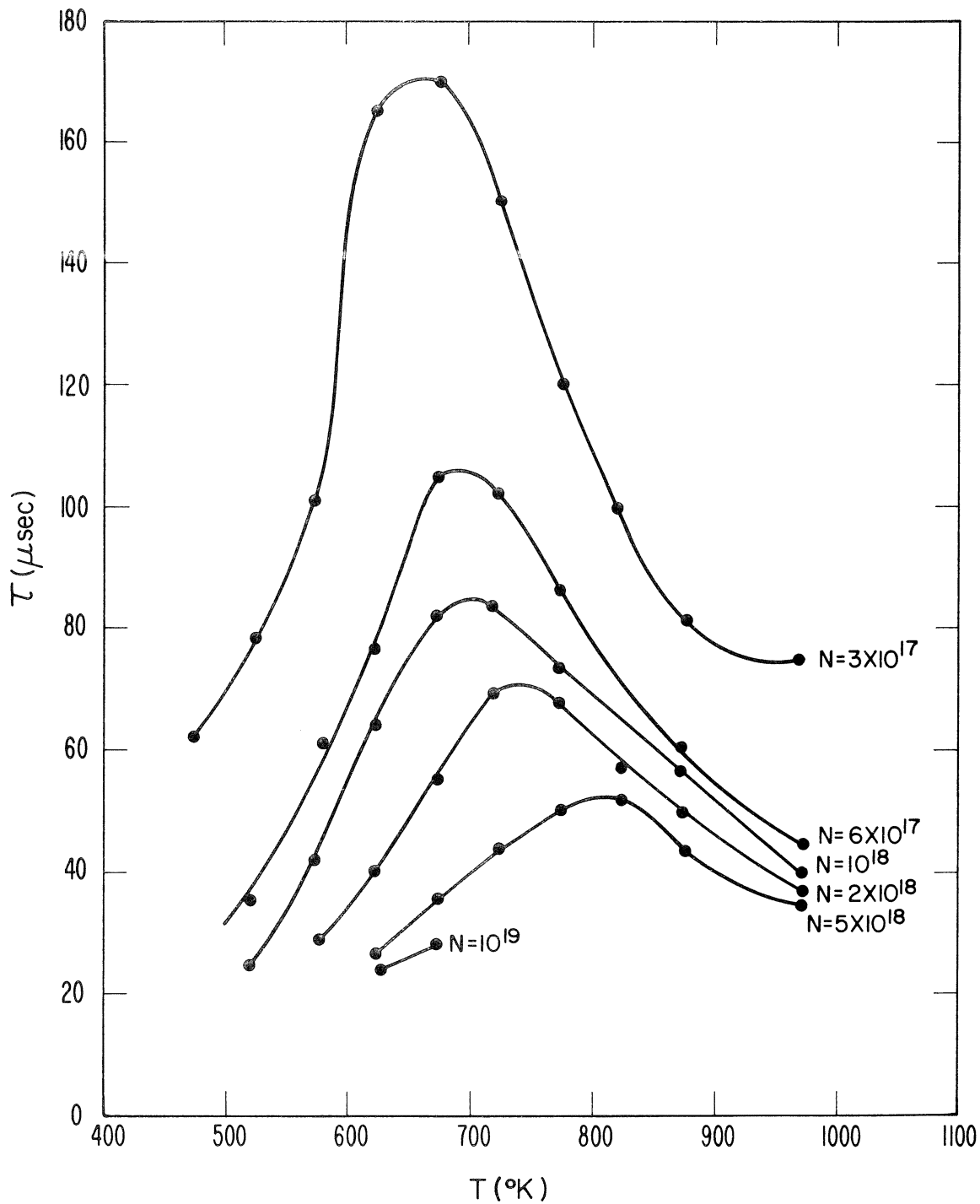


Figure 4.2 Long time decay constant versus temperature and density.

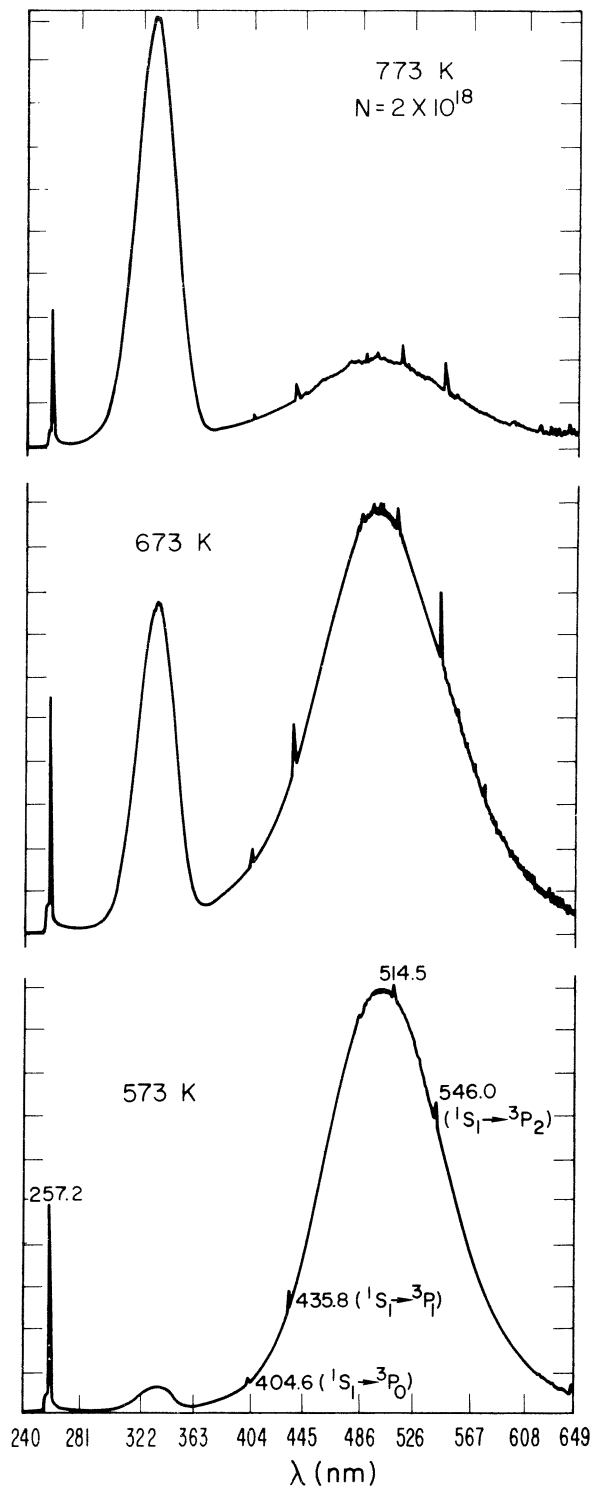


Figure 4.3 Fluorescence spectrum at various temperatures for a fixed atomic density of  $2 \times 10^{18} \text{ cm}^{-3}$ .

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4. TITLE AND SUBTITLE  Analysis of Optically Excited Mercury Molecules		5. Publication Date January 1975	6. Performing Organization Code	
7. AUTHOR(S) R. E. Drullinger, M. M. Hessel and E. W. Smith		8. Performing Organ. Report No.		
9. PERFORMING ORGANIZATION NAME AND ADDRESS  NATIONAL BUREAU OF STANDARDS, Boulder Labs DEPARTMENT OF COMMERCE WASHINGTON, D.C. 20234		10. Project/Task/Work Unit No. 2716461	11. Contract/Grant No. 891 & LS74-4	
12. Sponsoring Organization Name and Complete Address (Street, City, State, ZIP) Advanced Research Projects Agency, 1490 Wilson Blvd., Arlington, VA 22209; Los Alamos Scientific Laboratories, BX1663 Los Alamos, New Mexico 87544		13. Type of Report & Period Covered Final	14. Sponsoring Agency Code	
15. SUPPLEMENTARY NOTES				
<p>16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)</p> <p>The Hg<sub>2</sub> molecule is representative of a class of molecules which have dissociative ground states and bound excited states. It can therefore be used as a prototype of this class of molecules which are of interest as potential new laser candidates. Because of the non-bound ground state, standard absorption spectroscopic techniques cannot be used to obtain the necessary information about the excited states. We have therefore developed new measurement techniques to obtain potential curves, f-values, and kinetic behavior for Hg<sub>2</sub>. These techniques are applicable to this whole class of dissociation molecular systems.</p>				
<p>17. KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)</p> <p>Dissociation laser; excimers; excited state kinetics; f-values; mercury molecules; new spectroscopis techniques; optical excitation; potential curves.</p>				
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