CONTINUOUS ULTRAVIOLET ABSORPTION BY NEUTRAL SILICON

--- o ---

Scientific Report #10

By

John C. Rich

Harvard College Observatory
Cambridge, Massachusetts

April 1966

Not in final form for publication

ABSTRACT

26232

Photoionization cross sections (bound-free absorption coefficients) have been measured for the $3s^2 3p^2\ {}^3P$ ground state and ${}^1D$ excited level of the neutral silicon atom. The measurements, made in absorption with the use of reflected shock techniques, yield cross sections of about 37 and 34 megabarns ($10^{-18}\,cm^2$) respectively, near the ionization limits. Theoretical quantum defect calculations give satisfactory comparisons. The next excited ${}^1S$ level is discussed.

INTRODUCTION

The astrophysical importance of silicon is well known; it is one of the most abundant elements in the universe. In the sun its abundance relative to hydrogen is 3.2×10^{-5} (Goldberg, et al., 1960) which, for comparison, is roughly one-tenth the abundance of carbon and about ten times that of iron. Silicon in its neutral form plays a particularly strong role in stellar spectra because of its abundance and also, to a lesser degree, because of its ionization potential (8.15 eV), which is high relative to that of the abundant metals. Thus, when calculating ionization equilibrium in a stellar atmosphere according to the Saha equation, we find that the ratio of the concentration of netural atoms to that of ions will be larger for silicon than for the abundant metals. This factor enters in the analysis of overlapping continuous absorption contributions of gaseous mixtures.

An ionization potential of 8.15 eV implies a ground state photoionization continuum with a limit near 1521 Å. Other important bound-free (b-f) continua from low-lying levels will also cause absorption up to almost 2000 Å. This wavelength range (about 1000 Å - 2000 Å) is of particular importance in the calculation of model atmospheres of B-type stars (effective temperatures of some 10^4 °K) because some fraction of the flux will be emitted in this wavelength region. Even though most of the silicon is ionized, this b-f absorption by the neutral atom can be important and should be included in the model calculation.

In the sun (at some 5700°K) only an insignificant part of the flux is emitted in this wavelength range, but the importance of silicon absorption is realized if one attempts to observe regions of the sun reaching into the chromosphere. Neutral silicon b-f processes in the ultraviolet are so strong that they obliterate the photosphere, and hence we observe radiation originating from regions higher in the solar atmosphere (see Gingerich and Rich, 1966, and Tousey, et al., 1965).

ENERGY LEVELS AND IONIZATION LIMITS OF NEUTRAL SILICON

The recent work of Radziemski and Andrew (1965) on the arc spectrum of silicon provides the most complete published description of this atomic system. We will make frequent reference to this paper (hereafter denoted as R & A) in the following paragraphs, while we will refer less to the classic publications of Moore (1949, 1950), which are somewhat dated.

The ground state electron configuration of Si I is $3s^2 3p^2$, which gives rise to three L-S coupled terms: ^3P, ^1D, and ^1S. A composite energy-level diagram is shown in Figure 1. The established terms of the $3s3p^3$ configuration are shown separately to indicate the source of the one experimentally recognized discrete level lying above the ionization limit that might exhibit autoionizing features. This matter will be mentioned later.

Table 1 lists those energy levels of immediate interest, as given by R & A.

The ground state of the Si II ion is split into two levels, $^2P_{\frac{1}{2}}$ and $^2P_{3/2}$, each of which represents series limits of several Rydberg series of the neutral atom. Ionization continua will, of course, come from both limits, but in the present work we will not be able to make such fine distinction; the continua measured and referred to are composite and involve contributions from all series going to both limits. In some astrophysical applications, such as opacity calculations in model atmospheres, these details will not be important. Also, in high-density plasmas they will not be observable because of so-called plasma effects near the series limits.

For a proper interpretation of highly resolved solar spectra the details between the limits may be of importance. In good furnace spectra obtained by M. Wilson and W. R. S. Garton (private communication), autoionization of lines going to the upper limit with the continuum of the lower limit is apparent for transitions from the ^3P levels. Similar phenomena are quite possible with transitions from the ^1D and ^1S levels. Pb I, an atom whose electronic structure is similar to that of Si I, exhibits these features very nicely (Garton and Wilson, 1966), and the effect is certainly well known in the noble gases argon, krypton and xenon. The point here is that in very highly resolved spectra of the sun (or of rare laboratory plasmas) the region between the limits may have a non-continuous appearance due to the Beutler-Fano profiles. The positions of the various limits are listed in Table 2; R & A can be consulted to determine which series go to which limits.

Plate 1 shows the silicon shock-heated absorption spectrum in the region that interests us. The positions of the limits have been noted.

EXPERIMENTAL

All experimental work reported here was done in absorption by means of standard reflected shock-wave techniques in conjunction with a one-meter normal incidence vacuum spectrograph.

The shock tube, of conventional design (see Gaydon and Hurle, 1963), was constructed of hard-drawn copper with a circular cross section and an inside diameter of 2½ inches. The optical axis was situated 1 cm from the end wall and perpendicular to the shock-tube axis. The shock was initiated by a self-rupturing aluminum diaphragm 0.006 inches thick. The driver gas was hydrogen, at room temperature, and the low pressure gas was commercial argon, to which were added very small amounts of the volatile silicon compound. Before each run the tube was cleaned with acetone and pumped with an oil diffusion pump down to a pressure of 10^{-4} Torr. Such a procedure was generally adequate, although the spectra yielded weak impurity lines of C I and O I, and, for the cooler shocks, weak traces of the (v', 0) bands of the Fourth Positive system of carbon monoxide.

The silicon was introduced in gaseous form from the very volatile liquid compound trichlorosilane ($SiHCl_3$), which has a vapor pressure of several hundred Torr at room temperature and is less reactive and easier to handle than other volatile silicon compounds such as the silanes or $SiCl_4$. The $SiHCl_3$, supplied by Alfa Inorganics, Beverly, Massachusetts, had a nominal purity of 96-97%, with $SiCl_4$ as its primary impurity.

The gaseous mixture of $SiHCl_3$ and argon was prepared in a clean glass system previously evacuated to 10^{-5} Torr, or better. The mixtures were prepared by measuring a quantity of the $SiHCl_3$ (some 0.1 to 1 Torr) with a Baratron capacitive diaphragm bridge. To this was added the argon (of the order of 100 Torr) as measured by a Wallace and Tiernan aneroid manometer. The mixture was magnetically stirred for a few hours and suitable precautions were taken against possible photodissociation. The overall accuracy of the concentration of silicon in the mixture should have been 1% or better.

The mixture was then introduced into the shock tube to an initial pressure, p_1, of some 20 Torr. The gas was compressed by a Mach 5 or 6 incident shock, that produced temperatures of some

5000 - 7000°K behind the reflected shock. The measurements were made in absorption with a co-axial flash tube of the type described by Garton (1959), Garton, et al. (1960), and Parkinson and Reeves (1961). By means of LiF optics the flash was focussed onto the slit of a one-meter normal incidence concave vacuum spectrograph. A Bausch and Lomb grating of 1200 lines/mm produced a reciprocal dispersion of 8.25 Å/mm at the photographic plate. Optimum slit widths were about 35μ, yielding a resolution of about 0.3 Å.

A schematic diagram of the experimental apparatus is shown in Figure 2. Since all measurements were made well below 2000 Å and shock temperatures were below 7000°K, lasting for only a few hundred μsec, there was no need to use a fast shutter; shock emission was negligible. The sequence of measurements and flash tube firing was initiated by a pressure transducer sensing the arrival of the shock at the end plate.

The pressure behind the reflected shock (commonly denoted p_5) was measured directly with a Kistler quartz transducer and charge amplifier combination. The transducer was located in the end plate of the shock tube. Recording was accomplished through an oscilloscope, and the overall accuracy of the measurement was about 5%.

The temperature was measured directly by the line reversal technique. This technique has been described by Gaydon and Hurle (1963) and the specific details of the optical arrangement used successfully in this laboratory have been given by Parkinson and Reeves (1964). The line used for these experiments was the λ3905 line of Si I, $3p^2\ {}^1S - 3p4s\ {}^1P^o$. This is a subordinate line whose lower level has an excitation potential of 15394 cm^{-1}, which helps to insure that the temperature measured was that of the bulk of the plasma and not that of the boundary layer only. This boundary-layer pitfall was further avoided by keeping the temperature measurements non-optically thick. The system was calibrated with a Phillips tungsten filament standard lamp and a microscope illuminator, which served as a secondary standard. The calibration was done statistically. It was necessary to assume that the 1P21 photomultiplier be linear over about three orders of magnitude. The plasma temperature was measured about 100 μsec after the passage of the reflected shock and about 15 μsec before the absorption spectrum was taken. Some recent experiments have increased the reliability of such temperature measurements (see Garton, et al., 1965); the accuracy of the measurement is about 100°K, or about 2%.

The spectra were recorded photographically on Ilford Q-2 plates, which were calibrated by means of transmission screens placed in the evacuated shock tube in the light path.

DESCRIPTION OF THE METHOD

In a uniform plane one-dimensional purely absorbing medium, the equation of radiative transfer is given as

$$\frac{dI_\nu(x)}{dx} = -\varkappa_\nu I_\nu(x) \quad , \tag{1}$$

where I_ν is the monochromatic radiation intensity at frequency ν , and x is the distance along the line of sight. Here $\varkappa$ is the opacity, or volume absorption coefficient, and can be defined as

$$\varkappa_\nu = \sum_\ell n_\ell \sigma_{\nu\ell} \tag{2}$$

where n_ℓ is the number density (units of cm^{-3}) of silicon atoms in level ℓ , and $\sigma_{\nu\ell}$ is the absorption cross section (units of cm^2) of such atoms at frequency ν.

Over a specified distance, L, equation (1) easily yields the familiar relation

$$\frac{I_\nu}{I_\nu^\circ} = e^{-\varkappa_\nu L} \tag{3}$$

where I_ν° is the incident intensity and I_ν is the emerging or observed intensity. Straightforward measurements of I_ν , I_ν° , and L immediately yield $\varkappa_\nu$.

If all but one of the terms of the sum in equation (2) are negligible, then by ascertaining the level populations, n_ℓ, we can obtain the atomic parameter $\sigma_{\nu\ell}$. These level populations are calculated from the measured temperature, pressure, and chemical composition of the gas with the assumption that at the time of the experiment the gas in the line of sight in the shock tube was in local thermodynamic equilibrium (LTE) and that conditions are perfectly uniform (i.e., boundary layers are neglected). Under such conditions the level populations are given by the combined chemical equilibrium and Boltzmann equations. The chemical equilibrium equations can be expressed by

$$\frac{N_A N_B}{N_{AB}} = K_{AB}(T) \tag{4}$$

with

$$K_{AB}(T) = \left(\frac{2\pi\mu kT}{h^2} \right)^{3/2} \cdot \frac{U_A(T) \cdot U_B(T)}{U_{AB}(T)} e^{-D_{AB}/kT} \tag{5}$$

where N_A is the number density of molecular species A, etc., μ is the reduced mass of the reacting components, h is Planck's constant, k is Boltzmann's constant, $U_A(T)$ is the internal partition function of species A, etc., D_{AB} is the dissociation energy of the reacting A, B, AB system, and T is the absolute temperature. In the limiting cases, A and B can be atoms. When we consider ionization (as we certainly must) we include, as a special case of equation (4), the Saha equation:

$$\frac{N_A^+ N_e}{N_A} = S_A(T) \quad , \tag{6}$$

with

$$S_A(T) = \left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} \frac{2 \cdot U_A^+(T)}{U_A(T)} e^{-I_A/kT} \qquad (7)$$

where N_A^+ is the number density of singly ionized species A, N_e is the electron density, m_e is the mass of the electron, $U_A^+(T)$ is the internal partition function of the ion, and I_A is the ionization potential of species A. Equations analagous to (6) for higher ionizations could easily be considered, but there is no need to do so under the present conditions; doubly ionized species are completely negligible.

Charge neutrality of the plasma requires that

$$N_e = N_A^+ + N_B^+ + - - - \quad , \qquad (8)$$

and "conservation of nuclei" requires that

$$N_A + N_{AB} + 2N_{A_2} + N_A^+ + - - - - - = \text{constant.} \qquad (9)$$

The sum includes all molecules that contain nuclear species A, and there exists one such equation for each nuclear species.

To these we add the equation of state of a perfect gas:

$$p = (N_e + N_A + N_A^+ + N_{AB} + - - -)kT. \qquad (10)$$

Given the measured temperature and pressure, along with the relative concentration of the various atomic nuclei, equations (4), (6), (8), (9) and (10) constitute a necessary and sufficient set which yields an iterative solution for the absolute number densities of the various components.

In the present context--that of shock-heated $SiHCl_3$ in argon--dissociation is quite complete and any molecular formation (even of HCl) is negligible. Also, essentially all electrons are supplied to the plasma by the silicon. Neither of these results is surprising.

The level populations can now be immediately derived from the Boltzmann relation in the form

$$N_\ell = N_{Si} \cdot \frac{g_\ell}{U_{Si}(T)} e^{-E_\ell/kT} , \qquad (11)$$

where E_ℓ is the excitation potential of level ℓ and g_ℓ is the statistical weight of level ℓ.

In plasmas of any significant charged-particle density there occurs an effective depression of the ionization potential due to the perturbation of the atomic potential function by nearby charged particles. It is of some importance to ascertain the magnitude of this ionization lowering because of the manner in which the ionization potential affects the number density of the particles in thermodynamic equilibrium through equations (6) and (7). There is a simultaneous phenomenon known as the "level-merging" of high bound-levels (cf. Griem, 1964) which manifests itself in the same manner as the former effect: namely, an apparent redward advance of the continuous absorption limit. If we attempt to assess the ionization lowering by observing the spectra (see Figure 4), then we will most likely obtain a rather poor upper limit for the ionization depression; level merging should be very active because of the relative complexity of the electron structure of silicon. At any rate, an observation of the spectra show a "non-continuum" appearance by about 1534 Å, corresponding to an energy of about 65,200 cm^{-1}. Some confusion again develops over exactly what are the appropriate unperturbed series limits (see Section 2, above); the maximum possible is 66,035 cm^{-1}, giving an observed upper limit to the ionization depression of some 800 cm^{-1}. The theoretical treatment of the ionization lowering which appears to be most applicable to the shock-tube plasma involves the Debye radius as the appropriate interaction distance. Perhaps the best (although not the first) discussion of this can be found in the paper by Ecker and Kröll (1963). In brief, the ionization depression, ΔI, of the first ionization potential is given to first order by the Debye-Hückel theory:

$$\Delta I = e^2/r_D \tag{12}$$

where r_D, the Debye radius, can be written

$$r_D = \sqrt{\frac{kT}{4\pi e^2 \sum_i N_i Z_i^2}} \quad , \tag{13}$$

N_i and Z_i being the number density and charge, respectively, of the neighboring electrons and ions. This theoretical correction was applied to the ionization potential in equation (7). In the most sensitive case (the hottest run) this correction amounted to 150 cm^{-1} and affected the absorption coefficient derived from this one run by 1.5%; the corrections to other individual runs were less, depending on the temperature. Should the Debye-Hückel theory not apply and the actual lowering be more in line with the observed upper limit, then the overall statistically averaged absorption coefficient would be raised by some 2%.

No correction has been made for the cool boundary layer just next to the window and lens of the shock tube. This is important, particularly since part of this experiment deals with the measurement of a cross section from the ground level. If boundary layer effects are significant, the derived absorption coefficient from the ground level will be too large, while that from higher levels may be too small. A detailed analysis of the boundary-layer behavior in the reflected case is difficult and is further complicated here by the geometry of flat windows in a circular tube. The most important parameter affecting the validity of the measurements is the temperature profile of such a boundary layer, since lateral pressure equilibrium is more or less achieved by the time of the flash tube discharge ($\sim$ 100 μsec behind the shock). If we assume that boundary-layer growth is primarily a heat-conduction problem by this time, then an approximate analysis shows that a 1 - 2% correction might be appropriate for the ground-level cross section, but that even the other levels of the ^3P term are much less affected.

There is substantial evidence that conditions behind the reflected shock are in a state of LTE (cf. Garton, et al., 1965; Griem, 1964). This property is essential to the usefulness of the shock tube as a quantitative spectroscopic instrument. All the experiments were carefully delayed some 100 μsec after the passage of the shock to insure the relaxation of the plasma, and there was no indication to the contrary. However, the flash tube gives some cause for concern, for it may have a depopulating effect on various levels through photoionization. If a level, whose b-f absorption coefficient we are attempting to measure, is depopulated by the flash tube, then the absorption coefficient measured is too low. If we use pessimistic numbers characterizing the flash tube -- 20,000 °K for 5 μsec (Parkinson and Reeves, 1961) -- and overestimate other parameters of the problem, we find that if collisional processes are inactive over the duration of the flash, the ground term will be depopulated by about 2%. Similarly, the depopulation of the higher ^1D and ^1S levels will be somewhat less. This number is most certainly an overestimation, but it causes us to examine the collisional rates that would tend to maintain the equilibrium population in the shock tube. Using the principles of detailed balancing, we examine the rates of collisional ionization and collisional excitation. We find that the former is entirely inadequate to compete with any disruption of the flash tube: the rate of collisional ionization in the shock tube is much less than the rate of photoionization by the flash tube. However, using conservative f-values and the approximate relation given by Allen (1963), we find that collisional excitation rates at 6000°K are almost an order of magnitude greater than photoionization rates. Thus, equilibrium relations should hold generally.

There remains a possible source of systematic error which, if operative, is not amenable to simple analysis. This source is the possible chemical reaction of the $SiHCl_3$ with the copper wall of the shock tube during the minute or two just before the shock is fired. Any such reaction in which silicon is lost from the vapor would cause the measured absorption coefficient to be too low. However, even liquid $SiHCl_3$ is not observed to react with copper, and there is no evidence to indicate that any such reactions did in fact take place in the shock tube.

ABSORPTION FROM THE GROUND TERM (^3P)

Nine plates were taken, from which the ionization continuum of the ^3P term was measurable. These experiments required nominally 0.1% of $SiHCl_3$ in argon. Conditions were varied so as to obtain a range of temperatures between 5000°K and 7000°K behind the reflected shock. Of these nine plates, four were of superior quality and were used for statistical averaging. However, the averaging of all nine plates gave results that differed from the average of the four by only 1%, while yielding a smaller statistical probable error. The plates include the region down to about 1200 Å, where the experiment is limited by the transmission of the LiF windows and by the decrease in intensity of the light source.

The results of the measurements are shown in Figures 3 and 4. Absorption contributions from the individual J levels of the split ^3P term are, of course, not separable in the experiment (see Table 1). Since the various parts of the experiment were performed at slightly differing temperatures, and since even at these temperatures there is a small departure from unity in the Boltzmann factor for the $J = 1$ and $J = 2$ levels, a very small correction was made to reduce all individual measurements to a common basis. The partition function plays an important part in these reductions, and for these values we have interpolated from the tables of Drawin and Felenbok (1965). In the data presented here, the contribution to the total absorption by b-f transitions from the ^1D level has been removed in an approximate manner; we have taken the experimental value for the magnitude of the absorption for this ^1D level and have assumed the wavelength dependence from a theoretical calculation. Both of these parts are discussed in the next section. The correction amounts to 7% at 1525 Å, decreasing by λ^3 to 4% at 1250 Å. While presenting the data in this fashion has obvious shortcomings, the problem of the differing relative populations of the ^1D and ^3P terms at different temperatures does not enter. The reduced results give a threshold cross section of 37 ± 4 megabarns (10^{-18} cm^2). The same probable error applies to the entire curve in Figure 3. Possible unaccounted systematic errors have been previously discussed, but they would not appear to be considerable. The standard deviation of the measurements of about 15% is consistent with the random errors involved with the flash tube, the emulsion, and the pressure-temperature measurement.

The appearance of the spectra near the limits is detailed in Figure 4. As stated above, this indicates that the maximum depression of the ionization potential by the plasma effects is some 800 cm^{-1}. The merging of high series lines is obvious, and while individual lines are not resolved, lines of series whose upper level has a principal quantum number of 12 or 13 lie in the vicinity of 1540 Å.

Near 1250 Å the three lines of the transition $3s^2 3p^2\ {}^3P_{0,1,2} \rightarrow 3s3p^3\ {}^3S_1^o$ appear rather strongly (see Figures 1 and 3) and are not resolved. These lines have previously been identified (see R & A), and they are probably visible in emission in the solar spectrum in the red wing of Ly α. Although the resolution is poor, these lines do not appear to possess strong autoionizing properties. On the one hand, this might be expected since there is no $^3S_1^o$ continuum with which this level can combine via a radiationless transition. On the other hand, the arc spectrum analysis (R & A) indicates that the higher levels of the atom depart significantly from L-S coupling and therefore we might expect L-S selection rules not to hold in this case (parity and J-value requirements are easily satisfied). Above the $^3S_1^o$ level there should be two more terms of the $3s3p^3$ configuration: a $^1D_2^o$ and a $^1P_1^o$. Neither of these has yet been observed; both should exhibit autoionizing characteristics according to L-S selection rules and there may well be resonances in the continuum as one goes toward shorter wavelengths.

Burgess and Seaton (1960) have developed a method for calculating photoionization cross sections of moderately complex atoms. This method, known as the quantum defect method (QDM), extends the work of Bates and Damgaard (1949) and of Seaton (1958). The QDM calculates b-f absorption coefficients as extensions of L-S coupled series in which the radial wave functions for both the bound and continuum states are determined from the experimentally observed energy levels (quantum defects) of the atom. For the continuum states these must be extrapolated through the series limit. The method has recently been simplified and improved by G. Peach (private communication, 1965). We have applied these latest methods to Si I to calculate the b-f absorption coefficients.

There are three difficulties tending to invalidate the application of QDM to Si I:

1. The normalization factor for the bound radial wave function differs significantly from unity and is fairly sensitive to the behavior of the quantum defect in the vicinity of the lower bound level. Inaccuracies here directly affect the overall amplitude of the absorption cross sections.

2. L-S coupling is known to break down in the higher levels, as illustrated by inverted term levels and intercombination lines (R & A present a very good discussion of this matter). The QDM assumes the continuum to be composed only of terms permitted by L-S selection rules.

3. The poor behavior of the experimental quantum defects (see R & A) prohibits reliable extrapolation of these quantum defects even as far as the limits, and certainly farther into the continuum. A considerable amount of the difficulty is caused by perturbations arising from the terms of the $3s3p^3$ configurations, which lie below the limits of the $3s^2 3p^2$ configuration (see Figure 1). Unknown configuration interaction above the limits probably plays a notable role also.

The normalization factor for the bound state wave function is given as

$$\zeta(n^*) = 1 + \frac{\partial\mu}{\partial n^*} \quad , \tag{14}$$

where $n^* = 1/\sqrt{I-E}$ is the effective quantum member, with I being the ionization limit of the series (Rydbergs) and E the excitation energy of the level (Rydbergs). $\mu = n - n^*$ is the quantum defect, where n is the principal quantum number of the level. In many cases μ is almost independent of n^* and $\zeta(n^*)$ is nearly unity. However, this is not the case with the lower levels of Si I. The evaluation of $\frac{\partial\mu}{\partial n^*}$ is made somewhat more tractable by plotting μ vs. (I-E), in which case μ is nearly linear in the regions of interest. Evaluating this, we obtain

$$\zeta(^3P) = 0.323 \quad .$$

The normal procedure in extrapolating quantum defects into the continuum is to attempt to do so according to

$$\mu = a + b\epsilon' \quad , \tag{15}$$

where ϵ' is the energy of the ejected electron (Rydbergs), and a and b are empirical constants taken from observations of bound levels as they go toward the limit. The rationality of such a form is discussed by Shenstone and Russell (1932) for cases in which the series are not perturbed. However, if we use the data of R & A, we find the perturbations are obviously large. The b-factors in equation (15) for some series are completely irrational (e.g., for the 3pnd $^3P^0$ series the higher members indicate $b = 10.3$). As a result, we will not assume any extrapolation beyond the limit to be valid a priori. We will, however, extrapolate the data as far as the limit to determine the value of a in equation (15). This process yields the following values for series combining with the ^3P term:

3pns $^3P^o$: a = 1.900

3pnd $^3P^o$: a = 0.335

3pnd $^3D^o$: a = 0.075 .

If we use these stated values for ζ and for the a's, the QDM calculation yields the value of 34.2 megabarns at the threshold (limits). This is to be compared with the experimental value of 37 megabarns near the threshold.

For some practical cases it is important to know the wavelength (energy) dependence of the cross section as one goes toward shorter wavelenghts. Since extrapolation of quantum defects through the limits is not reliable, we will attempt to fit the quantum defects to the form of equation (15) using the experimental data and neglecting possible resonances. In the assumed L-S coupling, the transition to the extension of the 3pnd $^3D^o$ series dominates the absorption coefficient, and the fitting may be done by adjusting the coefficient b for this series. An examination of the calculated phase factors for the other two series indicates that their respective b-coefficients should remain essentially zero. The best fit is obtained for

$b(nd\ ^3D^o) \approx 0.75$. The extended "fit" is shown in Figure 5, and while such behavior is reasonable, the calculation is quite suspect, as explained previously.

While the experimental value for the photoionization cross section from the ^3P term should be a decent measure, its satisfactory agreement with the QDM calculation at threshold should be considered fortuitous; it should not be anticipated a priori that the QDM could yield a satisfactory theoretical value.

ABSORPTION FROM THE FIRST EXCITED LEVEL (^1D)

The measurement of the absorption coefficient of the continuum from the ^1D level (see Figure 1, Plate 1, and Tables 1 and 2) by the present shock-tube method is hindered by the presence of strong absorption lines from the ground state. The problem is one of measuring between the lines, while accounting for line wing contributions. Between λ1530 and λ1674 there is only one region where a satisfactory measurement can be made -- this is at λ1647.

The analysis involves the same considerations and techniques as previously discussed. Mixtures that were nominally 1% $SiHCl_3$ in argon were used. Eight plates were taken for this measurement, of which five were of superior quality and were used for statistical averaging. For various technical reasons the range of temperatures was limited to 5750 - 6300°K. There was no need to correct the total measured cross section for contributions from the higher ^1S continuum since such contributions should be less than 1%.

The line-wing correction turned out to be only 4%. To arrive at this figure, we pursued a combined theoretical and observational analysis. The line-broadening mechanism in the shock tube was theoretically analyzed and found to be almost entirely Van der Waals broadening caused by interaction of the silicon atoms with the neutral argon. If we use the formulation given by Griem (1964) and set the argon effective resonance f-value equal to unity, the dispersion width is calculated to be $1.95 \times 10^{11} \sec^{-1}$. (This is a few percent greater than one gets by using the formulation in Allen, 1963). This yields $\alpha = 1.4$, α being the ratio of the dispersion width to the thermal doppler width of the line. Assuming this value applies to all lines in the vicinity, and measuring the equivalent widths of all lines and blends of lines, approximately, on the set of plates used previously to measure the ^3P continuum, we can determine approximate gf-values from the curve-of-growth. With the gf-values, the concentrations, and the value for α, the absorption coefficient in the line wing is readily calculable. All lines in the vicinity were analyzed; these included multiplets 22 through 32 listed by Moore (1950), although only contributions from numbers 25 through 28 were significant. The combined contribution represented 4% of the absorption coefficient at 1647 Å. The theory, though, is not well established, and this causes some uncertainty in the calculated dispersion width of the lines. If the actual width is larger, the wing correction is larger, and conversely. Knowing the resolution of the spectra we can, however, simply measure the apparent half-widths of the lines and establish that the parameter α can not exceed 10. If the foregoing analysis is repeated with this latter value of α, the observed maximum possible line-wing correction is 8% -- an unrealistic upper limit.

The measured value of the photoionization cross section from the ^1D level at 1647 Å is 33 ± 2 megabarns, with corrections applied.

The quantum defect calculation for continuous absorption from the ^1D level proceeds in the same manner as discussed for the ^3P levels, and encounters similar, but milder difficulties. The assumption of L-S coupling predicts that the absorption coefficient is dominated by transitions to the extension of the $3s^2 3pnd\ ^1F^0$ series, whose quantum defect extrapolates unreliably, having a b-term (equation (15)) of about 2.55. However, the relevant quantum defects appear to be better behaved than those important in the ^3P continuum, and the QDM may be somewhat more applicable. We determine the bound-state normalization in the same manner as before:

$$\zeta(^1D) = 0.378 \quad \text{(see equation (14)).}$$

The following extrapolated quantum defects are obtained from R & A for those series that are L-S coupled with the ^1D level:

$3pns\ ^1P^0$: $a = 1.86$, $b = 0$

$3pnd\ ^1P^0$: $a = 0.03$, $b = 0$

$3pnd\ ^1D^0$: $a = 0.410$, $b = 0.895$

$3pnd\ ^1F^0$: $a = 0.350$, $b = 2.55$.

The results of the calculation are shown in Figure 6. Actually, the calculated absorption coefficient over this limited wavelength region will hardly change if all b-coefficients are set equal to zero.

It is on the basis of this calculation, normalized to the experimental point, that the correction to the total cross section is obtained to isolate the ^3P continuum (Figure 3). The frequency dependence is approximately ν^{-3}.

ABSORPTION FROM THE SECOND EXCITED LEVEL (^1S)

Experimental difficulties have thus far prevented the shock-tube measurement of the absorption coefficient of the ^1S continuum. An effort is presently being made to remedy this through the use of slightly modified techniques and different volatile silicon compounds.

It is somewhat ironic that this level, which presents the most experimental difficulties, appears to possess reasonably well behaved quantum defect extrapolations. Even though the L-S coupling assumption is just as poor, we might expect the QDM calculations to be more reliable for this level than for the previous two. We obtain the bound-state normalization as before:

$$\zeta(^1S) = 0.453 \quad .$$

The quantum defect extrapolations used for the L-S coupled series are:

$$3pns\ ^1P^o: \quad a = 0.03, \quad b = 0.0$$

$$3pnd\ ^1P^o: \quad a = 1.86, \quad b = 0.0 \quad .$$

The results of the calculation are shown in Figure 7. The calculated frequency dependence is roughly $\nu^{-1.5}$. The threshold value of 46.5 megabarns can be compared with the result of a similar calculation by Bode, as quoted by Kodaira (1965); his value is 39.4 megabarns.

SUMMARY

The foregoing experimental results indicate that neutral silicon is a very strong absorber of ultraviolet radiation. These results are supported by approximate calculations. In all cases these results are significantly higher than earlier approximations such as those of Vitense (1951). While both experiment and theory exhibit certain inadequacies, the values presented here should be useful in the study of stellar atmospheres as well as the ultraviolet solar spectrum.

ACKNOWLEDGEMENTS

This work has benefited from discussions with a number of people, and in particular the author would like to mention Dr. O. Gingerich and Dr. W. H. Parkinson. Dr. Gillian Peach kindly supplied both pre-publication results and discussion, and Professor W. R. S. Garton contributed valuable suggestions.

This work has in part been supported by NASA (Grant NsG-438) and by the Office of Naval Research (Contract NONr-1866 (48)).

REFERENCES

Allen, C. W. 1963, Astrophysical Quantities, 2nd ed. (London: Athlone Press).

Bates, D. R. and Damgaard, A. 1949, Phil. Trans. A., 242, 101.

Burgess, A. and Seaton, M. J. 1960, M. N., 120, 121.

Drawin, H. W. and Felenbok, P. 1965, Data for Plasmas in Local Thermodynamic Equilibrium (Paris: Gauthier-Villars).

Ecker, G. and Kröll, W. 1963, Phys. Fluids, 6, 62.

Garton, W. R. S. 1959, J. Sci. Instrum., 36, 11.

Garton, W. R. S., Celnick, I. W., Hessberg, H. and Wheaton, J. E. G. 1960, Proc. Fourth Int. Conf. on Ionization-Phenomena in Gases.

Garton, W. R. S., Parkinson, W. H. and Reeves, E. M. 1965, Harvard College Observatory Shock Tube Spectroscopy Laboratory Report # 8.

Garton, W. R. S. and Wilson, M. 1966, Proc. Phys. Soc., 87, 841.

Gaydon, A. G. and Hurle, I. R. 1963, The Shock Tube in High Temperature Chemical Physics (London: Chapman and Hall).

Gingerich, O. and Rich, J. C. 1966, A. J., 71, in press.

Goldberg, L., Müller, E. A. and Aller, L. H. 1960, Ap. J. Suppl., 5, 1.

Griem, H. R. 1964, Plasma Spectroscopy (New York: McGraw-Hill).

Kodaira, K. 1965, Z. f. Ap., 60, 240.

Moore, C. E. 1949, Atomic Energy Levels, Vol. 1, National Bureau of Standards Circular # 467.

Moore, C. E. 1950, An Ultraviolet Multiplet Table, National Bureau of Standards Circular # 488, Sec. 1.

Parkinson, W. H. and Reeves, E. M. 1961, Proc. Roy. Soc., A 262, 409.

____________________________ 1964, Proc. Roy. Soc., A 282, 265.

Radziemski, L. J. and Andrew, K. L. 1965, J. O. S. A., 55, 474.

Seaton, M. J. 1958, M. N., 118, 504.

Shenstone, A. G. and Russell, H. N. 1932, Phys. Rev., 39, 415.

Tousey, R., Austin, W. E., Purcell, J. D. and Widing, K. G. 1965, Ann. d' Ap., 28, 755.

Vitense, E. 1951, Z. f. Ap., 28, 81.

TABLE 1

Selected Energy Levels of the Si I - Si II System

level			energy (cm^{-1})	
Si I	$3s^2 3p^2$	$^3P_0$	0	(Si I ground level)
		$^3P_1$	77.12	
		$^3P_2$	223.16	
		$^1D_2$	6298.86	
		$^1S_0$	15394.37	
Si II	$3s^2 3p$	$^2P^0_{1/2}$	65747.	(Si II ground level)
		$^2P^0_{3/2}$	66035.	
Si I	$3s3p^3$	$^3S^0_1$	79664.	

TABLE 2

Unperturbed Limits of Series Coming from Transitions from the $3s^2 3p^2$ Configuration of Si I Converging on the Ground Levels of Si II

Si I Term	Si I Level	Si II Level	λ(Å)
^3P	$^3P_0$	$^2P_{3/2}$	1514.3
	$^3P_1$	"	1516.1
	$^3P_2$	"	1519.5
	$^3P_0$	$^2P_{1/2}$	1521.0
	$^3P_1$	"	1522.8
	$^3P_2$	"	1526.2
^1D	$^1D_2$	$^3P_{3/2}$	1674.0
	"	$^3P_{1/2}$	1682.1
^1S	$^1S_0$	$^3P_{3/2}$	1974.7
	"	$^3P_{1/2}$	1986.0

ABSORPTION SPECTRUM
OF
SHOCK-HEATED SILICON

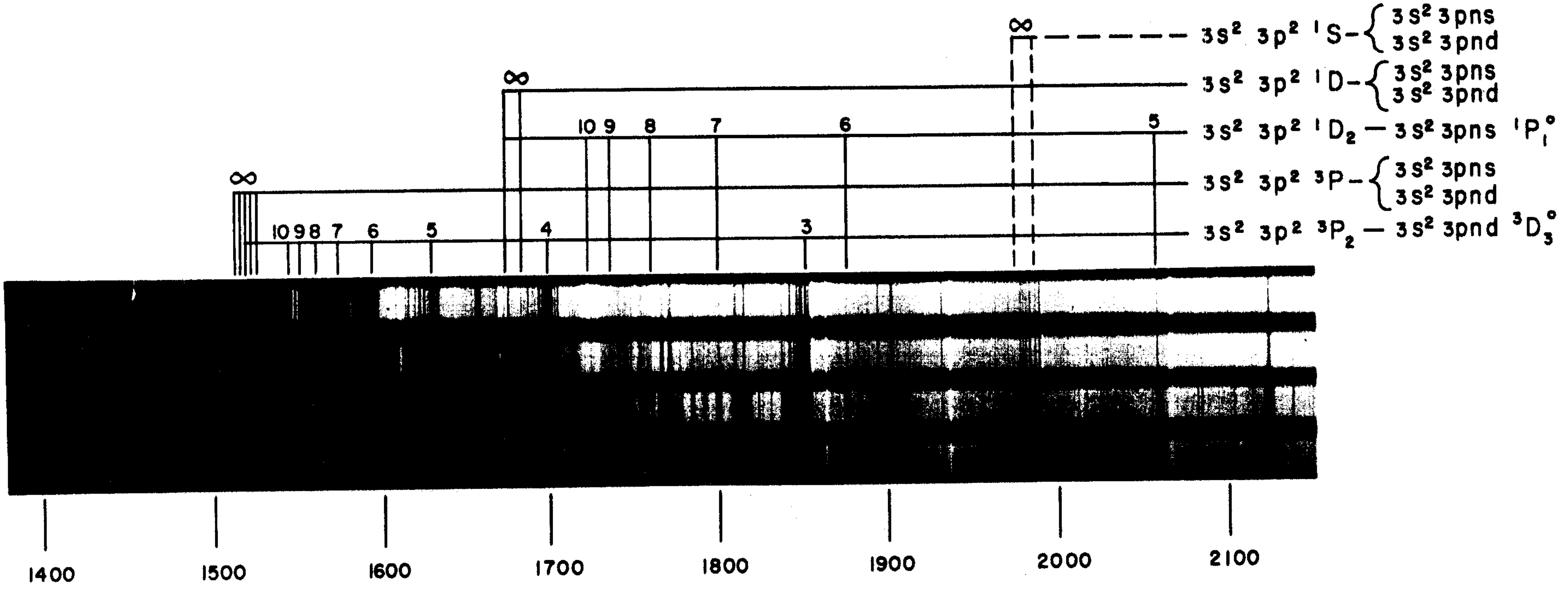

PLATE 1.

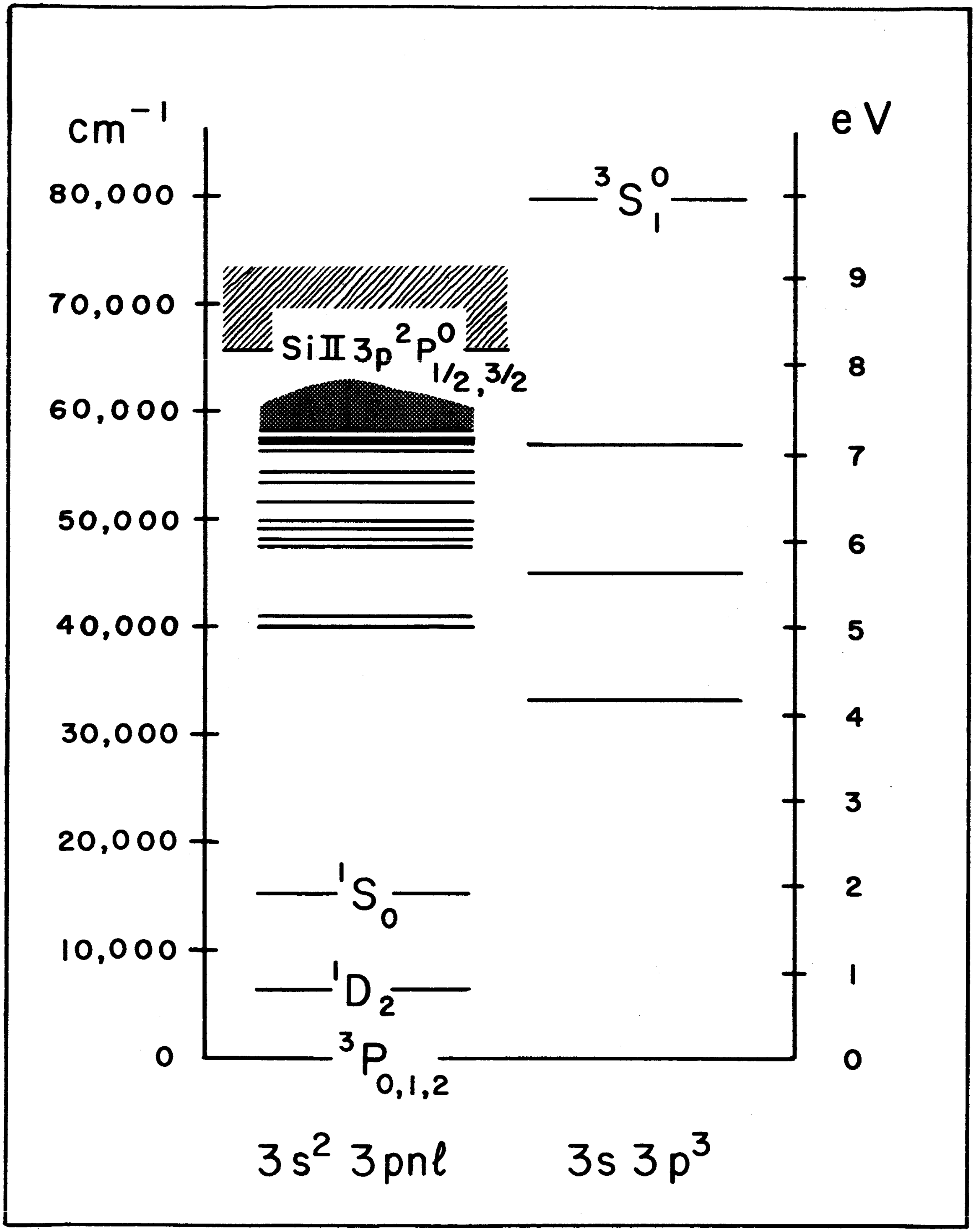

FIGURE I

Figure 1. Energy level diagram of Si I. Labelled lower levels all belong to $3s^2 3p^2$ configuration. No attempt is made to include high-lying, closely spaced levels.

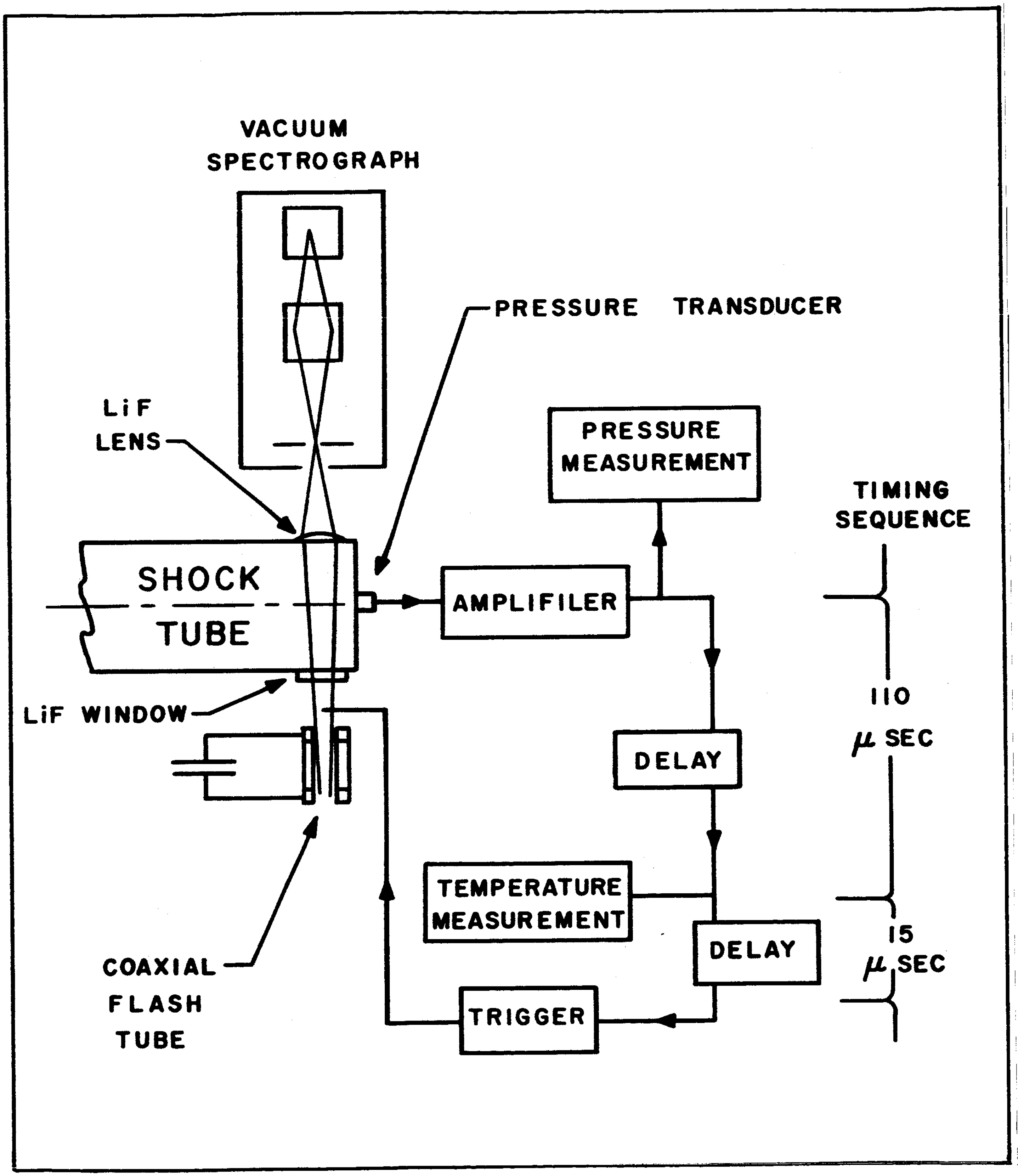

FIGURE 2

Figure 2. Schematic diagram of the shock tube absorption experiment.

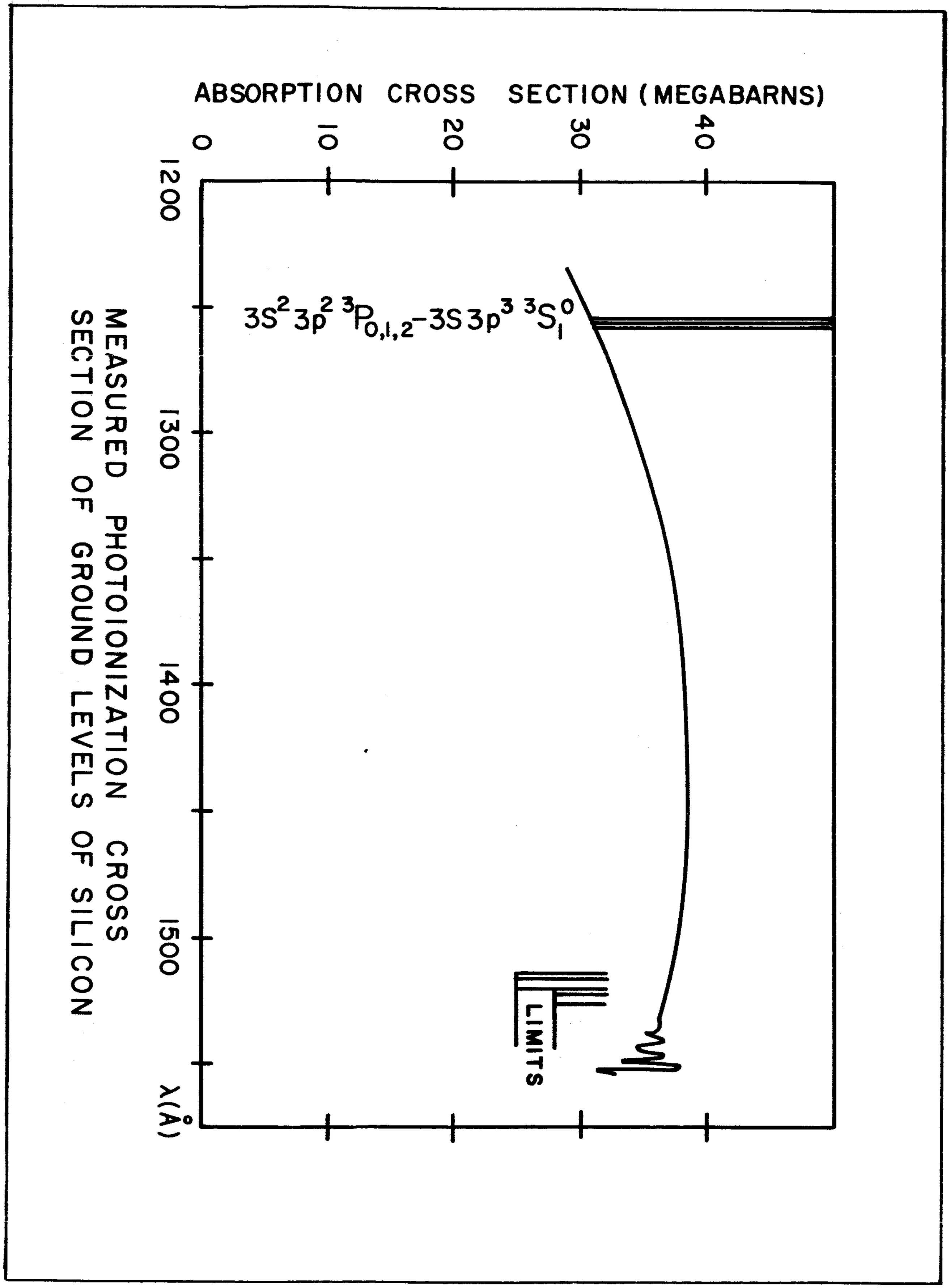

Figure 3. Measured photoionization cross section of ^3P levels of Si I. Plot represents a composite of several shock-tube spectra. A correction has been used to remove contribution from ^1D level.

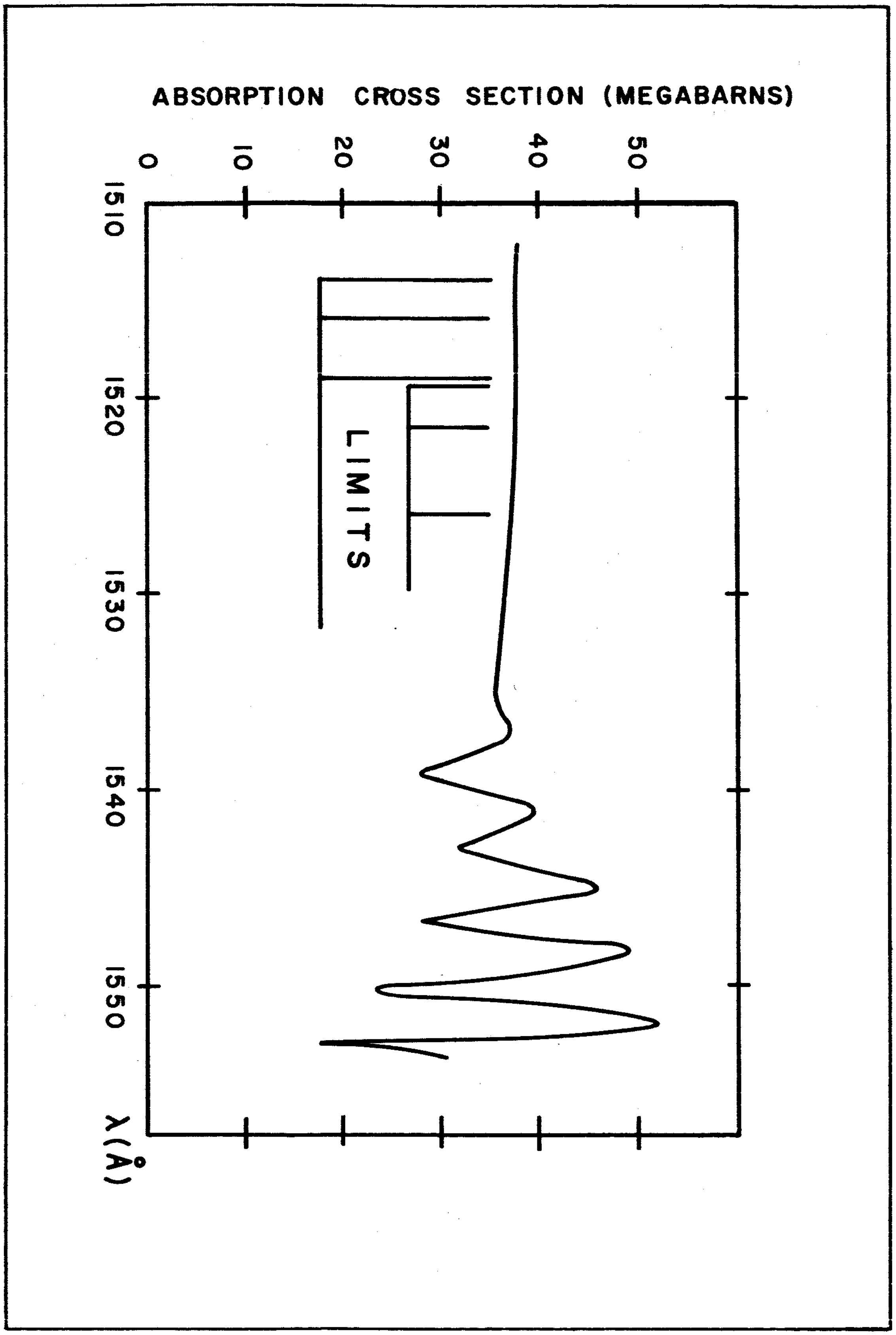

Figure 4. Detail of absorption coefficient of the ^3P levels of Si I near the limits, as measured in the shock tube. Plot represents a composite of several shock-tube spectra. Nominal shock tube conditions are: $T = 6000°K$, $N_e = 1 \times 10^{15}\,cm^{-3}$, $N_{argon} = 9 \times 10^{18}\,cm^{-3}$. Contribution to absorption by ^1D level has been removed.

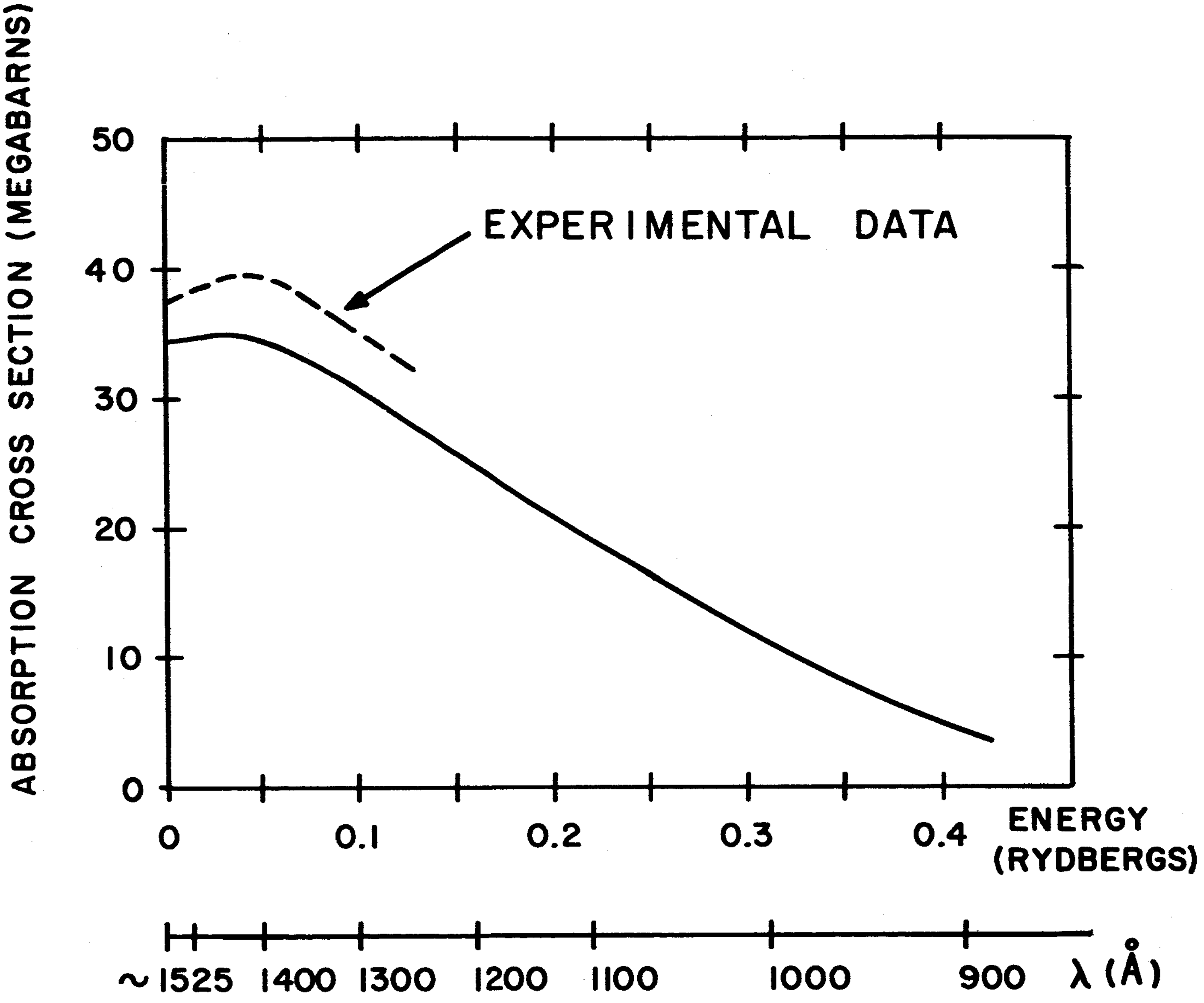

FIGURE 5

Figure 5. Calculated bound-free absorption coefficient from $3s^2 3p^2\ ^3P$ levels of Si I, using a parameter fit to the experimental data.

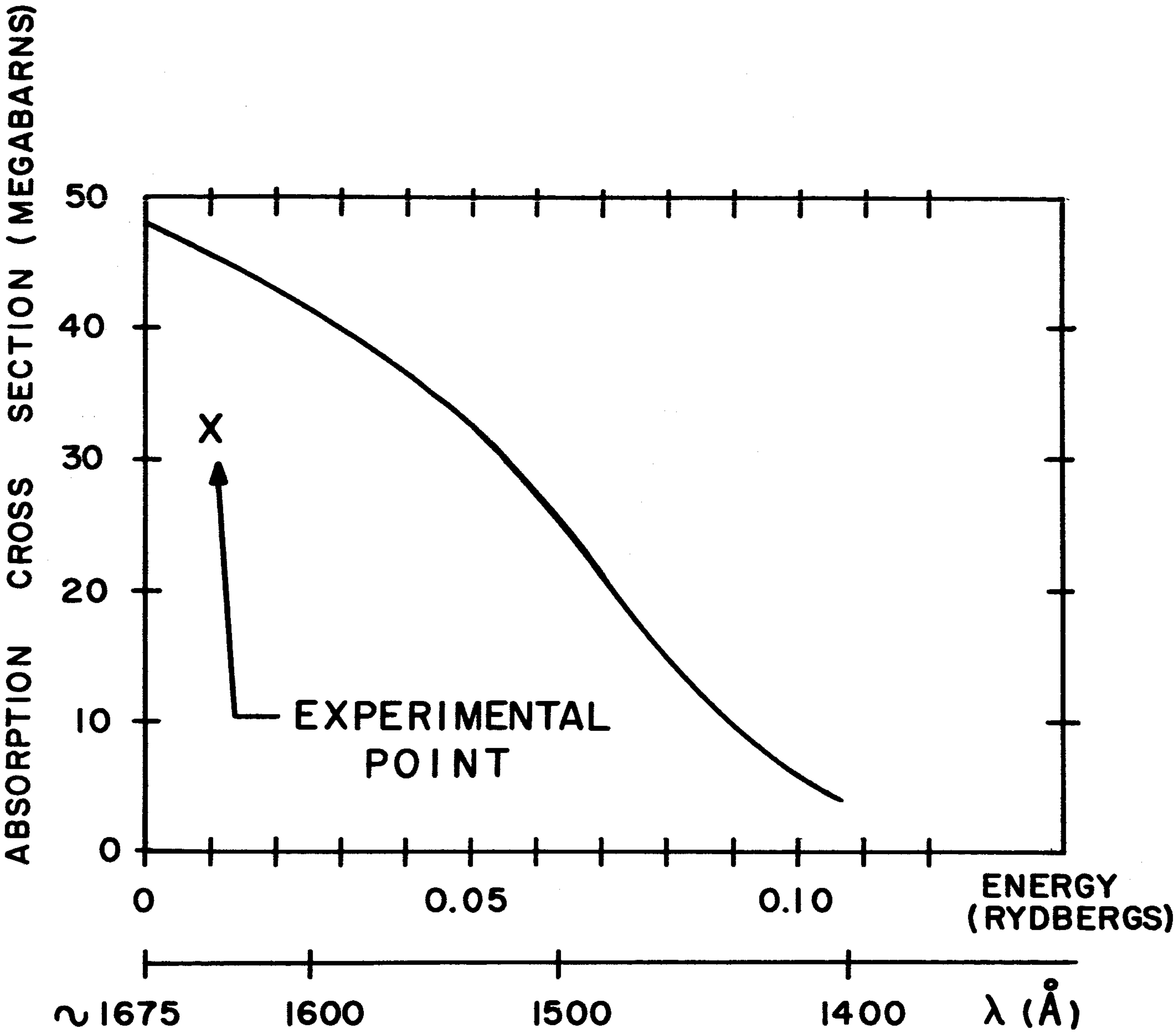

FIGURE 6

Figure 6. Quantum defect calculation of the bound-free continuum of the $3s^2 3p^2\ ^1D$ level of Si I.

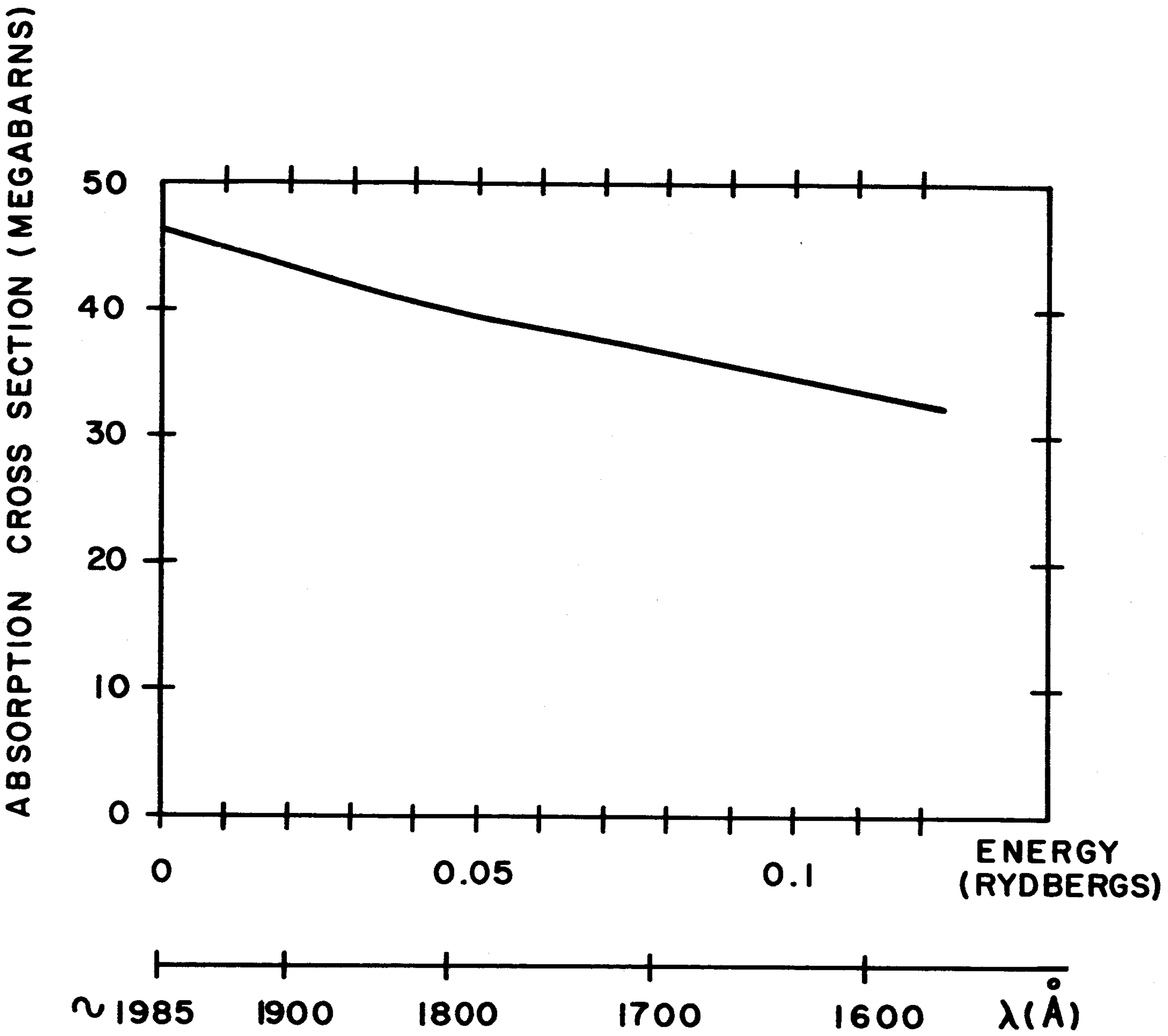

FIGURE 7

Figure 7. Quantum defect calculation of the bound-free continuum of the $3s^2 3p^2$ ^1S level of Si I.

non-classified

Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*
Harvard University

2a. REPORT SECURITY CLASSIFICATION

2b. GROUP

3. REPORT TITLE
"Continuous Ultraviolet Absorption by Neutral Silicon"

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

5. AUTHOR(S) *(Last name, first name, initial)*
Rich, John C.

6. REPORT DATE
April, 1966

7a. TOTAL NO. OF PAGES
30

7b. NO. OF REFS
23

8a. CONTRACT OR GRANT NO.
NONr-1866 (48) and

b. PROJECT NO. NASA-NsG-438

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)
Scientific Report # 10

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. AVAILABILITY/LIMITATION NOTICES

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

13. ABSTRACT

Photoionization cross sections (bound-free absorption coefficients) have been measured for the $3s^2 3p^2\ {}^3P$ ground state and ${}^1D$ excited level of the neutral silicon atom. The measurements, made in absorption with the use of reflected shock techniques, yield cross sections of about 37 and 34 megabarns ($10^{-18}\,cm^2$) respectively, near the ionization limits. Theoretical quantum defect calculations give satisfactory comparisons. The next excited ${}^1S$ level is discussed.

DD FORM 1 JAN 64 1473

Security Classification