SHOCK-TUBE DETERMINATION OF AUTOIONIZATION LIFETIME AND OSCILLATOR STRENGTHS OF THE $3s^2\ 3p\ {}^2P^0 - 3s3p^2\ {}^2S_{\frac{1}{2}}$ DOUBLET OF AL I

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ABSTRACT

The autoionization lifetime of the $^2S_{\frac{1}{2}}$ level and f-values of the $3s^2 3p\ ^2P^o - 3s3p^2\ ^2S_{\frac{1}{2}}$ doublet of Al I have been measured by a shock-tube method. The lines of the doublet have a large natural width with a measured autoionization lifetime of 1.1×10^{-13} seconds. The f-values have been determined as 0.033 for the 1936 Å line and 0.049 for the 1932 Å line.

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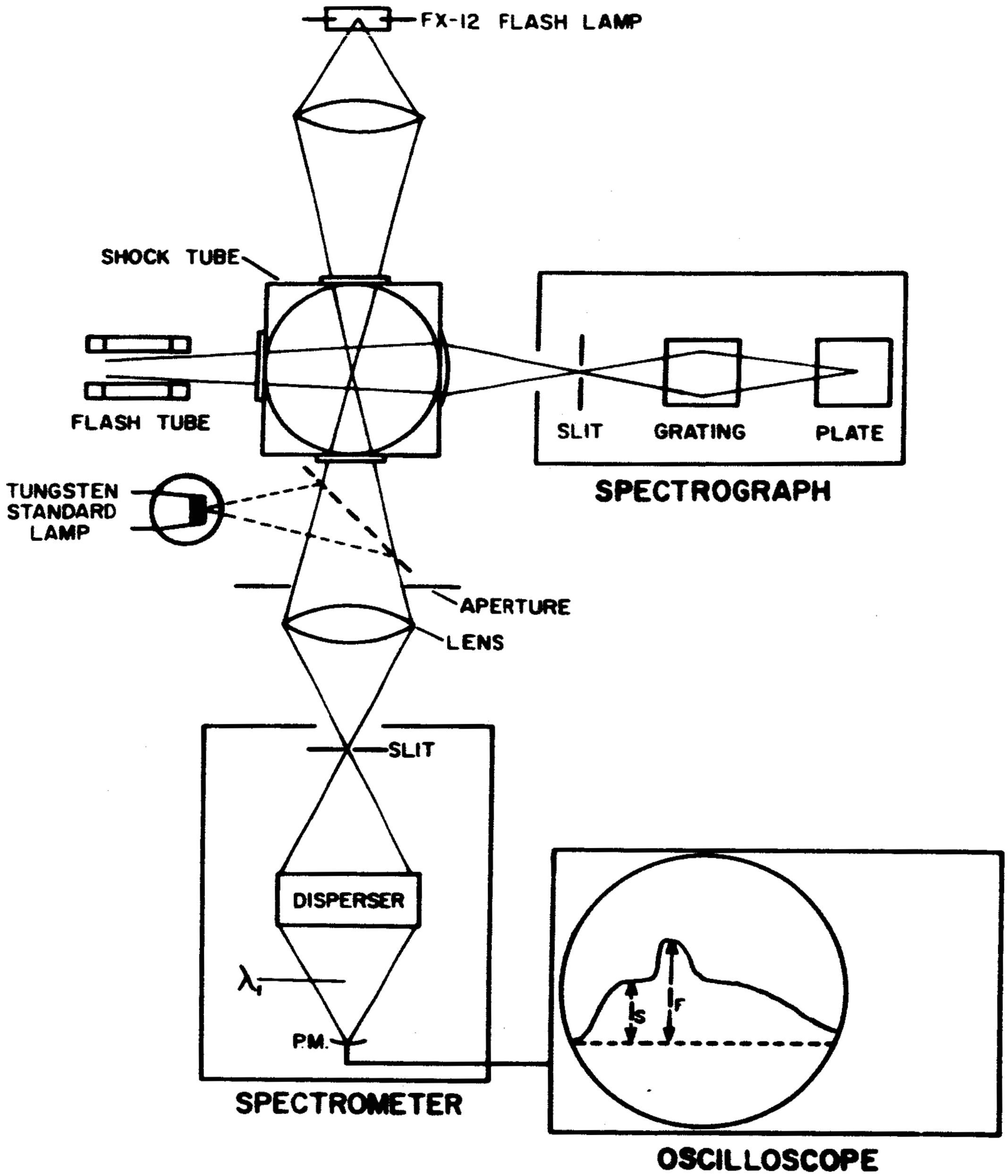


FIGURE I
OPTICAL ARRANGEMENTS FOR TEMPERATURE AND f-VALUE MEASUREMENTS

1. INTRODUCTION

Few measurements or calculations are available of oscillator strengths of transitions from atomic energy states which lie above the first ionization potential, and likewise of the probabilities of autoionization of such states. The few cases studied experimentally comprise ground-state combinations of (i) two levels of Tl I 6s6p^2 $^4P_{3/2}$, $^2D_{3/2}$ (Marr 1954), (ii) the 3d np $^1P^o_1$, $^3P^o_1$ series of Ca I (Ditchburn and Hudson 1960) and of (iii) levels of the heavier inert gases, p^5 ($^2P_{\frac{1}{2}}$)n s, nd which lie above the $^2P_{3/2}$ ground-states of the respective ions (Pery-Thorne and Garton 1960, Huffman et al 1963a, b). An early paper by Allen (1932) contains autoionization half-breadths of a number of Cu I levels, and Garton and Rajaratnam (1955) reported similarly on a single level, p^2 $^3P_2$ of Cd I.

Theoretical material is equally scanty and till recently was confined to calculations on doubly-excited states of He I (Bransden and Dalgarno 1953; Wu 1944) and of Be I (Wu and Ouram 1950). Probably the technical difficulties of measurement combine with former lack of a theoretical framework able to embrace the, often curious, effects of configuration-mixing on line profiles and intensities, in accounting for this paucity of information. However, Fano (1961) has now provided a valuable theoretical description of the effects to be expected from the mixing of discrete term series and one or more adjacent continua. In addition, interest is being stimulated by wider realization that autoionization often produces the most striking features in an atomic spectrum (Garton and Codling 1960; Madden and Codling 1963, 1964), and in particular may have a drastic influence on the course of the photoionization cross section and, conversely, on the rate coefficient for electron-capture by the positive ion ("Dielectronic recombination"; cf., Burgess 1964).

In each case of an experimental f-value determination cited above, the element has been selected, rather obviously, partly because a column of known particle-density of the atomic species concerned could be fairly easily produced. For the majority of elements this is not so, because of molecule formation, chemical attack on containing tubes and windows, and the need for containers capable of withstanding rather high temperatures. In the case of aluminum, the vapor is chemically reactive, and in order to hold a stationary column of vapor of adequate vapor density for observation of the absorption lines in question here, a temperature of some 1500°C is necessary. It should be noticed that, in case of large autoionization broadening, a relatively high vapor density is required for such a purpose because, for a given f-value, the central absorption coefficient of the line is much lower than in the case of a sharp line which arises from transitions between normal bound states.

In the spectrum of an aluminum arc in nitrogen, Selwyn (1929) found a very diffuse doublet at 1932Å, 1936Å, which he classified as 3 $^2P^0$-3s3p^2 ^2S. The identification remained questionable (Paschen 1932), until the lines were also observed in absorption with a King furnace (Garton 1950). The $^2S_{\frac{1}{2}}$ state lies about 0.4 eV above the first ionization potential and autoionizes strongly. The lines have since been found in the Fraunhofer spectrum of the sun observed with rocket-borne equipment, and constitute, in fact, the most outstanding feature due to Al in the solar spectrum. To our knowledge no other lines of comparable natural width have been reported in that spectrum, and they are of special interest since they have resolvable profiles even at low dispersion. Interest in them has been increased by the discussion of Burgess et al (1960) concerning the possibility of observing interstellar Al.

The aluminum spectrum, including the continuum and the autoionized lines, is readily produced with the shock-tube (Nicholls et al 1963). Use of this device in the measurements here reported has enabled avoidance of technical difficulties of the sort mentioned above.

2. PRINCIPLE OF THE METHOD

The virtues possessed by the pressure-driven shock-tube for purposes of quantitative spectroscopy, such as f-value measurements, have been recently emphasized (e.g., Gaydon and Hurle 1963; Charatis and Wilkerson 1962). By use of a reflected shock a plasma can be generated which, though transient, is well-defined in extent and of homogeneous composition. According to circumstances an element can be vaporized and excited in the shock by the addition to the shocked gas of a trace of a volatile compound (Charatis and Wilkerson 1962), or of a small amount of a powdered solid (Nicholls et al 1963, Parkinson and Nicholls, 1959). In principle, from knowledge of the particle-density of the absorbing or emitting species, f-values can be calculated from measured emission or absorption line strengths.

The powdered solid technique is obviously suggested in the case of aluminum. The method faces the general difficulty that it is not possible to control accurately the amount of powdered material introduced into the shock or to calculate the total particle-density of the atoms of interest present in the shock from mere knowledge of the quantity of powder introduced. Moreover, in order to calculate the particle-densities in the particular quantum states involved in a transition, the shock temperature must be known, and it is unsafe to compute this from the measured velocity of the shock wave.

Recent work (Charatis and Wilkerson 1962; Parkinson and Reeves 1964), has shown that, with the use of flash tubes as background sources, reliable values of reversal temperature of reflected shocks at high temperature can be measured, and in the experiments reported here this method of temperature determination has been used. The remaining problem of measuring the Al particle density was solved by making use of the recent determinations by Ditchburn and Hudson (1960) of f-values of the absorption lines $4\ {}^1S_0 - 3d\ np\ {}^1P_1^o$ of Ca I ($n \geq 5$) made by means of a furnace. Several of the lines of this series are extremely wide, from autoionization, the $4\ {}^1S_0 - 3d5p\ {}^1P_1^o$ member near 1885Å having a half-breadth of approximately 20Å. It thus seemed feasible to monitor the Al particle-density by introducing Al and Ca by means of their powdered sulphides in known ratio, and measuring the absorption coefficient over the profile of the Ca line of known f-value.

The relevant algebra runs as follows. Consider a two-component plasma at T°K and let n, η represent total particle-densities of the two atomic species, (Ca and Al, respectively), $n+$, $\eta+$ the particle-densities of the corresponding ions and n_e the electron density. Saha's equation gives

$$\frac{n_e\, n^+}{n} = S_n(T); \qquad \frac{n_e\, \eta^+}{\eta} = S_\eta(T) \tag{1}$$

$$\text{with } S = \frac{(2\pi mkT)^{3/2}}{h^3} \cdot \frac{2U_i(T)}{U(T)} \exp -E_i/kT \tag{2}$$

where E_i is the ionization energy and U, U_i are the partition functions for the neutral and ionized species.

The charge-neutrality of the plasma gives

$$n_e = n^+ + \eta^+ \tag{3}$$

and the known powdered sample ration gives

$$\frac{n+n^+}{\eta+\eta^+} = a \tag{4}$$

If we now measure the absorption coefficient $\alpha(\nu)$ as a function of frequency ν over a line of species n of known f-value, which corresponds to the transitions between states r, s (r<s), the equation

$$\int \alpha(\nu)\, d\nu = \frac{\pi e^2}{mc} n_r f_{rs} \left(1 - \frac{g_r n_s}{g_s n_r}\right) \tag{5}$$

combined with the Boltzmann equations,

$$\frac{g_r n_s}{g_s n_r} = \exp - (E_s - E_r)/kT; \quad n_r = \frac{n g_r}{\Sigma g_r \exp - E_r/kT} \tag{6}$$

enables calculation of n. Equations 1 to 4 now contain four unknowns, assuming T known, viz., η, η^+, n^+, n_e, and can be solved to give η. Then from the measured absorption coefficient over the Al lines we can use equations similar to 5 and 6 to give the f-value of Al sought. The autoionization probability per second (A) is, of course, immediately derivable from the line half-breadth.

$$\Delta\nu = \frac{1}{2\pi\tau} = \frac{A}{2\pi}$$

Reference to the ionization of argon, used as carrier gas for the shock, has been omitted in the above outline. The justification for this is that at the temperature to be used (4000°K - 6000°K range), the degree of ionization of argon is negligible in comparison with that of Ca and Al, which have much lower ionization potentials.

It was assumed that complete and impartial molecular dissociation of the calcium and aluminum compounds existed at the relatively high temperatures employed. The independence of the oscillator strength on the temperature justifies this assumption.

As will be seen in the discussion below, some caution is necessary concerning the ionization energies E_i for Ca and Al, these being reduced below the conventional values for the isolated atoms as a result of the plasma microfields. This problem and the associated question of termination of the partition functions have recently been discussed a good deal, and proper allowance usually involves some awkward theoretical considerations (cf. Olsen 1963). The shock-tube absorption spectra studied contain, in addition to the lines of Ca and Al which have been mentioned, well developed series of the type $4\ {}^1S_0 - 4snp\ {}^1P_1^0$ (Ca) and $3\ {}^2P^0 - 3snd\,{}^2D$ (Al) and the depression of the ionization potentials could be determined directly from observation of the termination points of the series.

3. EXPERIMENTAL PROCEDURE

The shock-tube used for these experiments was a conventional pressure-driven aerodynamic tube constructed from 2½" inside diameter hard-drawn copper pipe with a wall thickness of 1/8". The 3 ft. driving section was separated from the 9 ft. channel section by a 0.006" aluminum diaphragm which was ruptured by excess pressure in the driving section. For these experiments hydrogen at approximately 120 psi was used as the driver gas, and argon at a few mm of Hg served as the carrier gas. Prior to an experiment, both the driving section and the test section were evacuated to a pressure below 1×10^{-3} Torr.

Several velocity probe stations of the conventional platinum heat transfer type were placed in the channel. In addition, the test section contained a Kistler pressure transducer which was mounted in a brass plug at the end wall closing the test section. This pressure transducer served not only as one velocity measuring station, but also as a means of detecting the time of arrival and reflection of the incident shock. The elapsed time between the arrival of the shock at each station, as recorded on a Hewlett-Packard counter, was used to determine the velocity of the incident shock. The sample holder was located in the test section about 20 cm from the end plug. This replaceable holder was in the form of a wire hook from which a cellulose tissue containing the powdered sample could be suspended.

The optical arrangement is shown schematically in Figure 1. The vertical system was used in the temperature measurement and the horizontal arrangement to record the absorption spectra. The optic axes through the windows and lenses were co-planar and intersected one cm from the closed end of the test section to assure a maximum test time.

The measurement of temperature in the reflected shock region has been described in detail in an earlier paper (Parkinson and Reeves 1964). Temperatures were determined with a line reversal method by a photoelectric measurement of the absolute intensity and the emissivity of the shock heated gas at a particular wavelength. An image of an FX-12 flash tube (Edgerton, Germeshausen & Grier) was formed by the upper lens in the center of the shock-tube test section and again at the entrance slit of a Jarrell-Ash Fastie-Ebert 0.5m scanning spectrometer adjusted to select a particular line in the wavelength region 2000Å- 8000Å of first order. The dispersed radiation, imaged at the exit slit, was detected with a 1P28 photomultiplier and the signal displayed on a Tektronix 565 oscilloscope. The optical system was calibrated by comparison with a Phillips W2 standard lamp, using an intermediate standard tungsten filament lamp (GE projection lamp) which could be inserted directly into the test section at the point of the FX-12 flash tube image.

The horizontal optic axis indicated in Figure 1 shows a second flash tube imaged on the slit of a one meter normal incidence spectrograph. This flash tube was of the "coaxial" form already described elsewhere (Garton 1961). The radiation from the coaxial flash tube passes through a plane window in the test section and is imaged by a plano-convex lithium fluoride lens on the slit of the one meter vacuum spectrograph. This instrument is an automatic focusing spectrograph with upper wavelength limit of 5800Å and a reciprocal dispersion of 8.25Å/mm with a Bausch & Lomb grating of 1200 lines/mm blazed 1200Å.

The high intensity and short duration background continuum from the flash tube was produced by a discharge through a 7 mm bore alumina tube from a 10 micro farad rapid discharge capacitor charged to 7 kilovolts. The flash tube was maintained at a dynamic pressure of approximately 20 x 10^{-3} Torr. of helium. The radiation from the flash tube reached a peak intensity in

$1\frac{1}{2}$ microseconds with a brightness temperature at 4500Å of approximately 20,000°K (Parkinson and Reeves 1961).

A set of intensity calibration exposures was placed on each Ilford Q2 plate accompanying the absorption exposure. These calibration marks were obtained by intercepting the radiation from the flash tube with a set of screens of measured transmission. The transmissions of the screens were accurately calibrated in a separate experiment in the wavelength region 1850Å to 3500Å and found to be independent of wavelength. The characteristic curves of the plate at the appropriate wavelengths were constructed for each separate experiment.

Figure 2 shows a block diagram of the electronic systems. The Kistler pressure transducer, in addition to providing a pulse for the velocity measurements, also detected the arrival and reflection of the incident shock. In terms of experimental time, the reflection of the incident shock is considered to occur at time "zero." The time delay unit consists of two separate delay chains, the output of one controls the firing of the FX-12 flash tube and the other the coaxial flash tube. Through the addition of a small variable subsidiary delay to the output of one of the main delays it was possible to adjust the firing of one flash tube with respect to the other. In Figure 2 the first two pulses, 250 microseconds apart, represent the passage of the incident shock at the velocity stations. After a delay time of 400 microseconds, two pulses, separated by 15 microseconds, fire

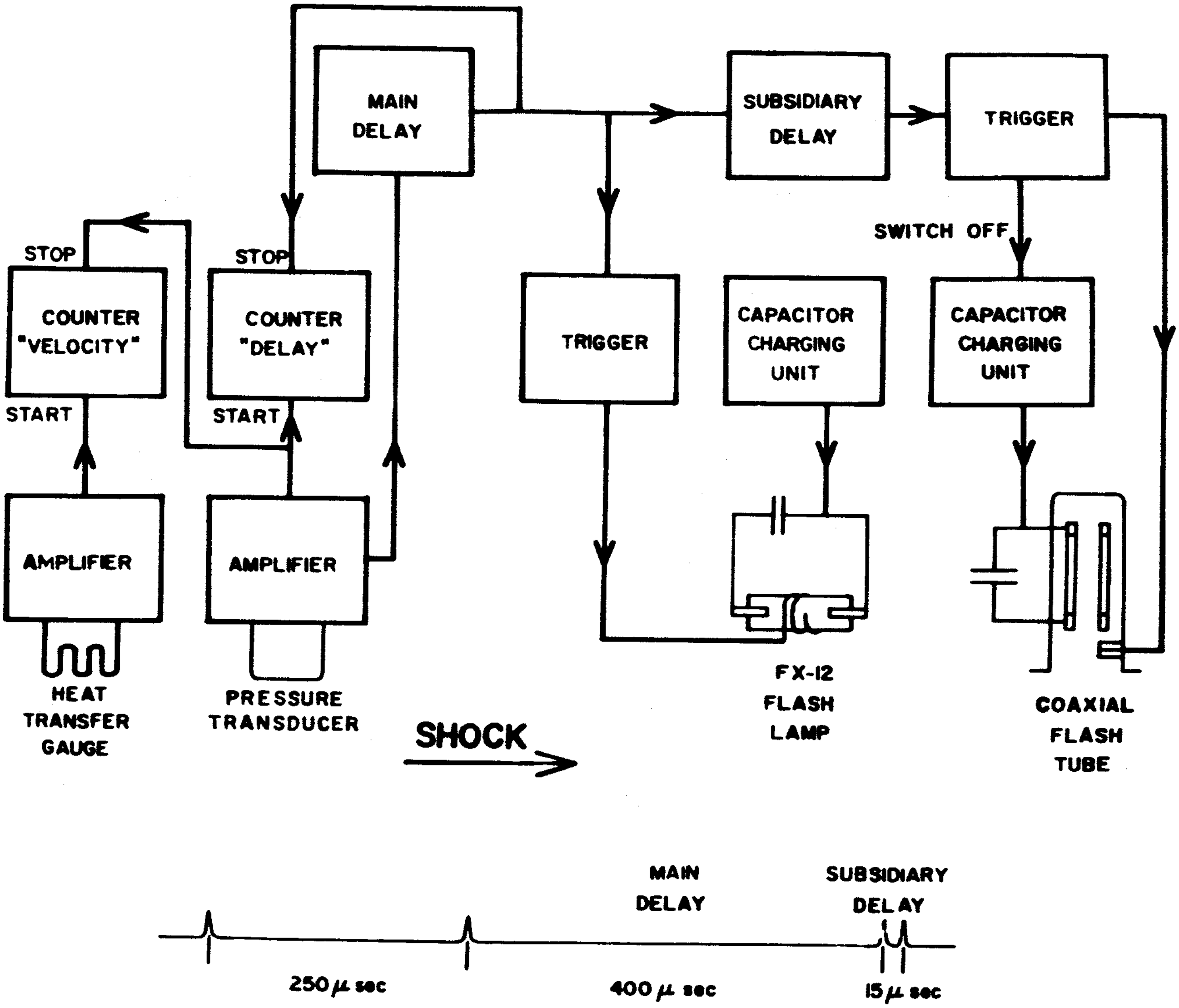


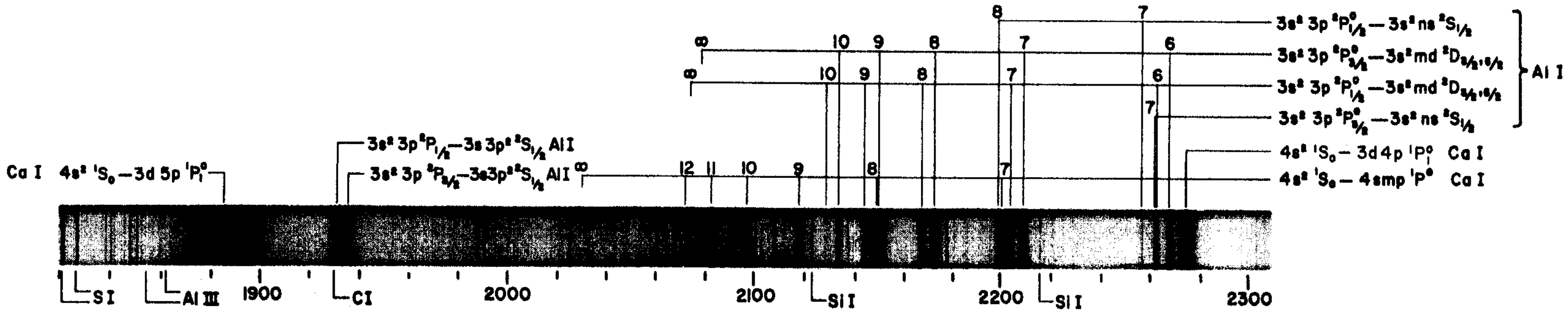
FIGURE 2
SHOCK TUBE ELECTRONICS

the FX-12 and the coaxial flash tubes.

The sample material to be investigated was introduced into the shock-tube as a finely powdered solid suspended in a volatile liquid. The powdered material was mixed with the solvent and emulsified to a near colloidal suspension. The extent of grinding was determined experimentally by requiring that the amount of precipitation be small in a period of several minutes. In the experiments described here the powdered materials were calcium sulphide and aluminum sulphide. Neither of these solids was in any way affected by the volatile solvent acetone. The colloidal suspension was added to a thin piece of cellulose tissue in the form of single drops from a small eye dropper. Generally, one to five drops were sufficient, and microbalance measurements showed that one drop of mixture contained approximately 2.6×10^{-4} grams of powdered solid.

4. REDUCTION OF MEASUREMENTS

From amongst a large number of absorption spectrograms obtained in course of the work, five were selected for reduction, corresponding to individual reversal temperatures in the range 4-5000°K. The reproduction of a typical absorption spectrum in Plate 1 contains the wide lines of Ca and Al at the left and the converging discrete series 4smp $^1P_1^0$ and $3s^2nd$, ns, ^2D, ^2S, of Ca and Al respectively, at the right. After densitometry of the Ca 1882Å line and the Al doublet, the absorption-coefficient was plotted vs. frequency: the line half-breadths were then used



ABSORPTION SPECTRUM OF
SHOCK-HEATED CaS + Al_2S_3

to fit a dispersion-type profile to the measurements. In the case of the Ca line this offered little difficulty, and the favourable fit can be seen from Figure 3, which is typical of the results. Similar treatment of the plot of $\alpha(\nu)$ for the Al-doublet was not so clear-cut, because of the overlap of the component profiles and the annoying presence of an absorption impurity line of C I (1930.92Å) and an emission impurity line of Al III (1935.88Å) in the short wavelength wing. It was never possible to rid the spectra completely of the C I line, but it was less obtrusive on the five plates selected. The plot of Figure 4 shows such a typical attempt at resolution of the profiles of the Al doublet components, and fitting of a dispersion-type formula to each.

The partition functions U, U_i, for Al, Al^+, Ca, Ca^+ were calculated from the term-tables of Moore (1949), care being taken that any unknown terms of high L-values would contribute negligibly. The effective ionization potentials of Ca I and Al I were estimated by subtracting from the conventional value, given by Moore (loc. cit.), the term-values of the last observable member of the discrete series, as explained above; discussion of the justifiability of this procedure is reserved for Section 5.

The Saha functions S_n, S_η were then calculated and n being known from the measured area of a plot such as Figure 3, it was possible to find,

$$\frac{n^+\eta}{\eta^+} = \frac{nS_n}{S_\eta} = \beta \qquad (7)$$

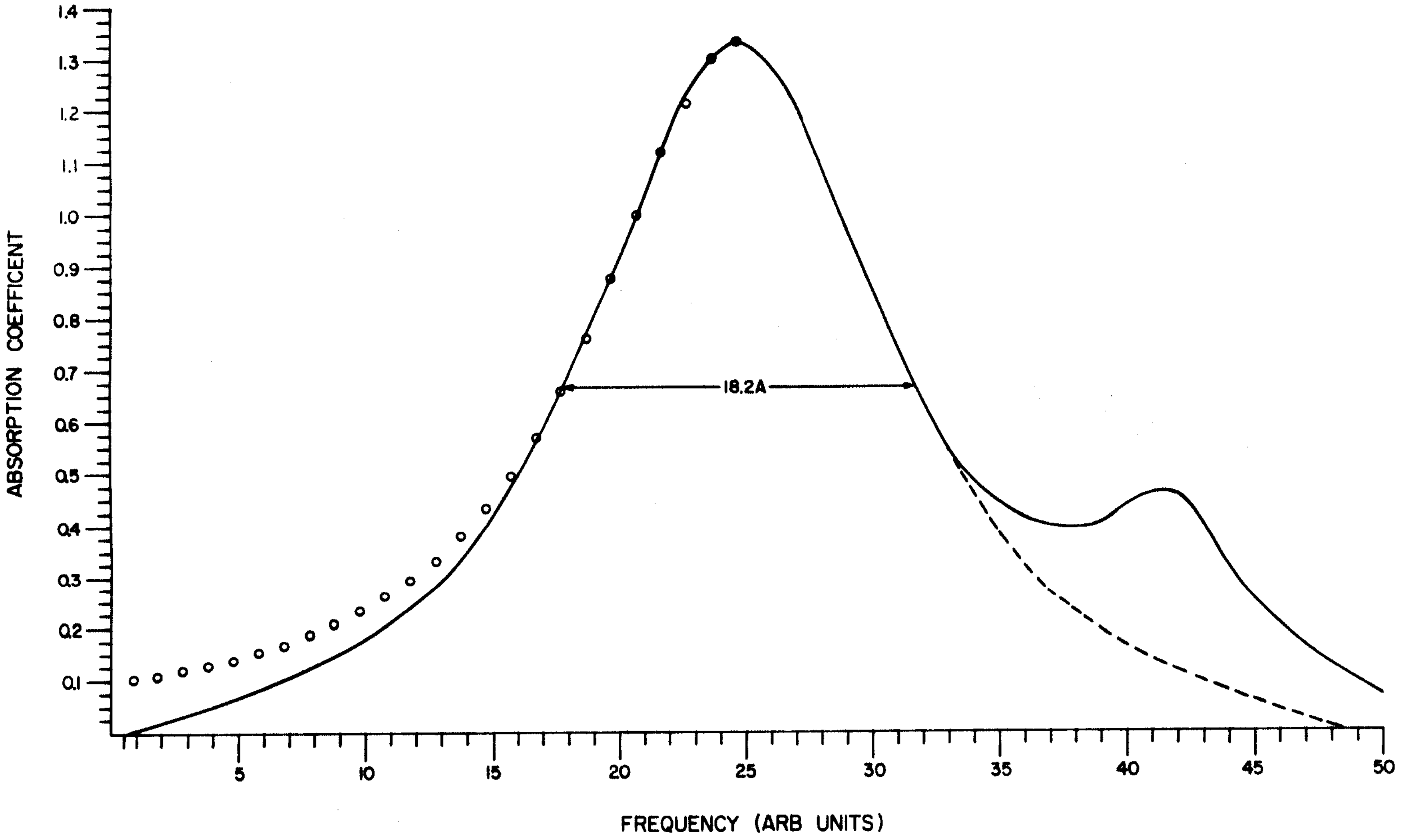


FIGURE 3
ABSORPTION COEFFICIENT PLOTTED
VERSUS FREQUENCY FOR THE
1885A LINE OF Ca I

Figure 3 Absorption coefficient plotted versus frequency for the 1885Å line of Ca I. The solid curve represents the measured experimental profile and the dotted curve the separated profiles for the two lines. The open circles represent the calculated dispersion profiles for lines with the measured peak absorptions and half-widths.

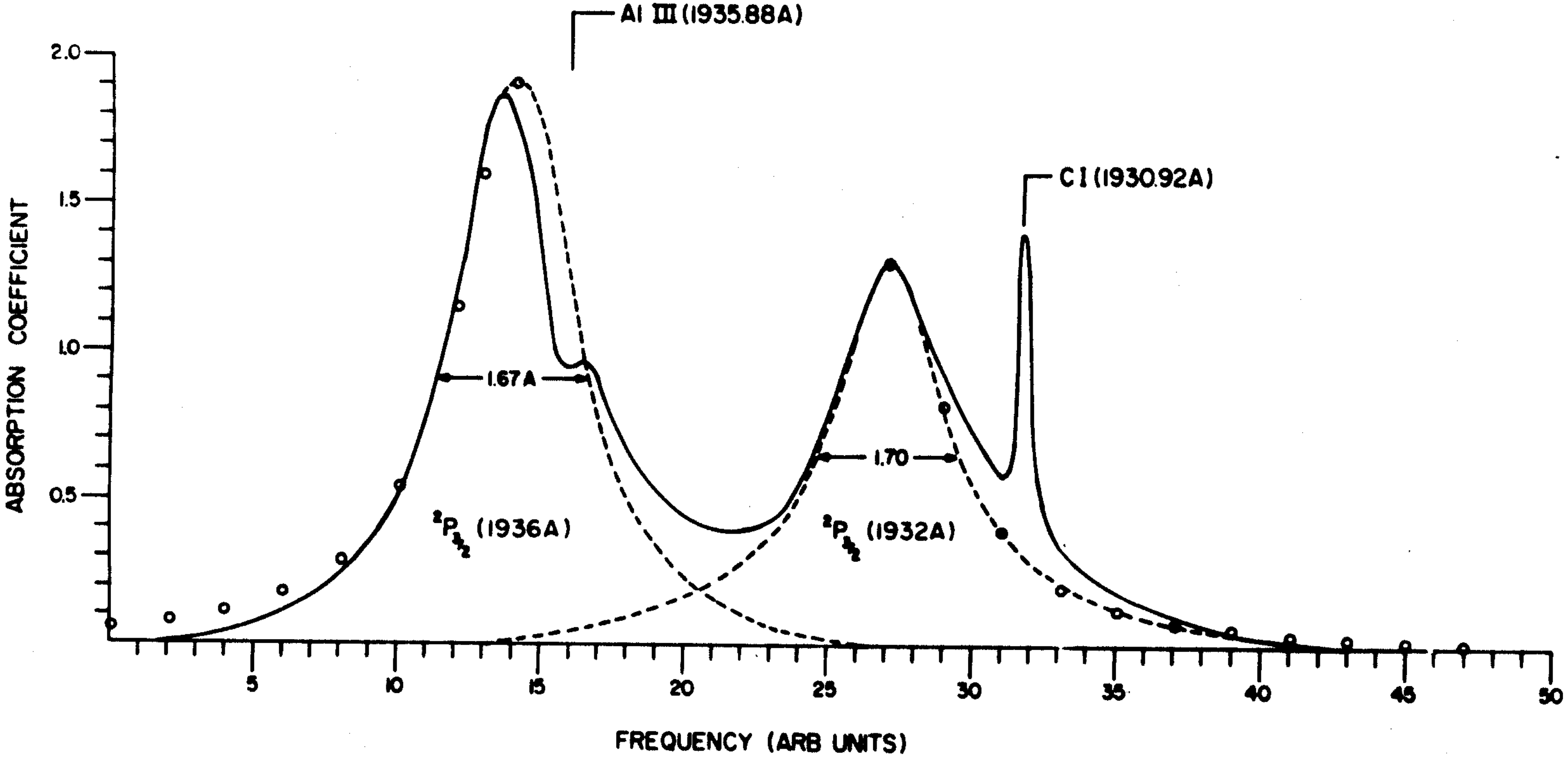


FIGURE 4
ABSORPTION COEFFICIENT PLOTTED
VERSUS FREQUENCY FOR THE
$3s^2 3p\ ^2P - 3s3p^2\ ^2S$ DOUBLET OF Al I

Figure 4 Absorption coefficient plotted versus frequency for the $3s^2\ 3p\ ^2P^0 - 3s3p^2\ ^2S_{\frac{1}{2}}$ doublet of Al I. The solid curve represents the measured experimental profile and the dotted curve the separated profiles for the two lines. The open circles represent the calculated dispersion profiles for lines with the measured peak absorptions and half-widths.

and using equation (4),

$$n^{+2} - an^{+}\eta^{+} + n\ n^{+} - a\beta\eta^{+} = 0 \qquad (8)$$

while from (1) and (3),

$$n^{+2} + n^{+}\eta^{+} - nS_{n} = 0 \qquad (9)$$

The last two equations were easily solved numerically for n^{+}, η^{+} and then η obtained from (4). Then, from the areas under the profiles in Figure 4 the f-values of the Al doublet components were found.

5. RESULTS AND INTERPRETATION

Results for the autoionization lifetime (τ) and oscillator strengths (f) from reduction of the measurements made on the five spectrograms are set out in Table I. The spectra of plates A-C were considered of good quality in all respects; plate D was associated with a less reliable value of the reversal temperature and is included for the sake of the autoionization lifetime determination, which is not affected; Plate E suffered from some prominence of the C I 1931Å line, which makes the lifetime value unreliable, but does not seriously affect the f-value calculation. Some intermediate data and specification of the shock conditions are given in Table II, since they are useful in an assessment of the results of Table I.

The scatter in f-values for the Al doublet is consistent with the known uncertainty (~1.8%) in the reversal temperature, and the random error is not likely to be above 10 per cent. The presence of systematic error is difficult to assess because of

	A	B	C	Average (A-C)	Average Error	D	E
Temperature °K	4130	4928	4977		$\pm1.8\%$	5036	4830
τ_{Ca} (sec)	$1.04\text{x}10^{-14}$	$1.05\text{x}10^{-14}$	$1.03\text{x}10^{-14}$	$1.04\text{x}10^{-14}$	±0.007 $(\pm0.6\%)$	$1.05\text{x}10^{-14}$	$1.06\text{x}10^{-14}$
$f(^2P_{3/2})$	0.0306	0.0318	0.0361	0.0328	±0.0022 $(\pm6.9\%)$	0.0406	0.0284
τ_{Al} (sec)	$1.09\text{x}10^{-13}$	$1.19\text{x}10^{-13}$	$1.05\text{x}10^{-13}$	$1.11\text{x}10^{-13}$	±0.05 $(\pm4.5\%)$	$1.05\text{x}10^{-13}$	$0.82\text{x}10^{-13}$
$f(^2P_{\frac{1}{2}})$	0.0488	0.0463	0.0509	0.0487	±0.0016 $(\pm3.3\%)$	0.0608	0.0454
τ_{Al} (sec)	$1.12\text{x}10^{-13}$	$1.19\text{x}10^{-13}$	$1.21\text{x}10^{-13}$	$1.17\text{x}10^{-13}$	±0.04 $(\pm3.4\%)$	$1.05\text{x}10^{-13}$	$0.77\text{x}10^{-13}$
$f(^2P_{3/2}) + f(^2P_{\frac{1}{2}})$	0.079	0.078	0.087	0.081	±0.004 $(\pm4.9\%)$	0.101	0.074

TABLE I

OSCILLATOR STRENGTHS AND AUTOIONIZATION LIFETIMES

FOR THE ALUMINUM DOUBLET

	A	B	C	D	E
Driving Pressure (H_2)	120 p.s.i.	120 p.s.i.	120 p.s.i.	120 p.s.i.	120 p.s.i.
Channel Pressure (A)	40 Torr.	35 Torr.	35 Torr.	35 Torr.	35 Torr.
Velocity (mm/sec)	1.50×10^6	1.58×10^6	1.59×10^6	1.59×10^6	1.58×10^6
Delay Time (sec)	442×10^{-6}	272×10^{-6}	390×10^{-6}	440×10^{-6}	391×10^{-6}
Temperature (°K)	4131°K	4928°K	4977°K	5036°K	4829°K
$\int\alpha(\nu)\,d\nu$ (Ca) (sec^{-1})	3.389×10^{13}	2.126×10^{13}	2.422×10^{13}	3.594×10^{13}	2.36×10^{13}
$\int\alpha(\nu)\,d\nu$ Al I (1936) (sec^{-1})	3.52×10^{12}	3.22×10^{12}	4.17×10^{12}	6.898×10^{12}	2.97×10^{12}
$\int\alpha(\nu)\,d\nu$ Al I (1932) (sec^{-1})	2.81×10^{12}	2.42×10^{12}	3.043×10^{12}	5.347×10^{12}	2.44×10^{12}
n_o (Ca) cm^{-3}	8.582×10^{15}	5.387×10^{15}	6.133×10^{15}	9.107×10^{15}	5.980×10^{15}
n (Ca) cm^{-3}	9.783×10^{15}	6.238×10^{15}	7.150×10^{15}	10.55×10^{15}	6.835×10^{15}
n^+ (Ca) cm^{-3}	8.09×10^{14}	3.822×10^{15}	4.61×10^{15}	5.83×10^{15}	3.429×10^{15}
$\eta_{3/2}$ (Al I) cm^{-3}	4.65×10^{14}	6.16×10^{14}	7.04×10^{14}	10.33×10^{14}	6.35×10^{14}
$\eta_{\frac{1}{2}}$ (Al I) cm^{-3}	2.33×10^{14}	3.18×10^{14}	3.63×10^{14}	5.34×10^{14}	3.27×10^{14}
η^+ (Al I) cm^{-3}	1.43×10^{13}	8.25×10^{13}	8.414×10^{13}	12.7×10^{13}	5.889×10^{13}
n_e cm^{-3}	8.233×10^{14}	3.905×10^{15}	4.69×10^{15}	5.957×10^{15}	3.488×10^{15}

TABLE II

SHOCK TUBE PARAMETERS, INTEGRATED ABSORPTION COEFFICIENTS AND

PARTICLE DENSITIES FOR DETERMINATION OF TABLE I the uncertain effect of boundary layers of cooler gas in the neighborhood of the shock-tube windows. In the course of a large number of reversal-temperature measurements, we have employed several different Ca I lines, notably Ca I 5857, 4425, 5588 which represent transitions between excited states, the resonance line of Ca II at 3968Å and those of Al I at 3961Å and 3931.97Å. In spite of the fact that individual determinations were made on successive shocks, excellent agreement leading to the estimated uncertainty just quoted was found. Although the possible effect of boundary layers on the τ and f-values of Table I must be borne in mind, it is unlikely to be large, since the absorption at the peaks of the very diffuse lines concerned is quite low as compared, for example, with that of the Ca I resonance line.

Another possible source of error arises because of the manner in which we have modified the ionization potentials of Ca and Al in the calculations from direct observation of the values of the principal quantum numbers at which the series of absorption lines terminate. The large literature on line-broadening mechanisms contains distinctions, made or implied, between "merging" and "drowning" of levels by the microfields of the charged particles of a plasma (cf., Margenau and Lewis 1959), the latter process being alternatively described as "depression of the ionization potential." Until recently, allowance for such depression was frequently made according to a simple statistical treatment of the atomic interaction with the "nearest neighbour" ion, suggested by Unsöld (1948).

Griem (1962) and Olsen (1961, 1963) have now given reasons for thinking the Unsöld theory inapplicable to all or most laboratory plasmas, and consider that the depression of the ionization energy is to be calculated from the Debye-Hückel radius as,

$$\Delta E_i = e^2/p \; ; \qquad p = \left\{\frac{kT}{4\pi e^2 \Sigma n_i z_i^2}\right\}$$

the summation being taken over all charged species present including the electrons. On the other hand, Armstrong (1964) has interpreted observations made on wall-stabilized arcs in N_2 and O_3 by Boldt (1959), who applied the "drowning" modifications of the ionization potential. According to Armstrong this was incorrect and Boldt's observations should be interpreted by means of an improved Inglis and Teller (1939) theory of "level merging."

Though justification for the distinction between drowning and merging processes is not altogether clear, we have considered their relevance to the shock-tube absorption spectra. These seem definitely to support the concept of the level drowning on two grounds. Firstly, it is quite obvious from the spectra that the series lines fade into the continuum, because of a rapid fall in intensity, while still quite well separated from each other -- careful examination of the Ca I series in Plate 1 should make this clear. Secondly, in a former paper (Garton et al 1962) on the flash-absorption spectra of Ba, produced with a shock-tube, the phenomenon of the "forced autoionization" of the Ba I $5d8p\,^3P_1^o$, $^3D_1^o$ levels was reported, and this seems interpretable only in terms of the depression of the Ba I ionization potential.

To continue the argument, there remains the question of where the effective ionization limit should be drawn between the last observable line of a series and that of the next highest serial number.

However, such refinement has proved irrelevant because trial has shown that the change in the Al f-values, which results from a unit of change in the principal quantum numbers of the last observable series lines, falls within the error resulting from the reversal temperature uncertainty. In spite of this, if our empirical modifications of the ionization potentials are meaningful, it is striking that the Ca II depression amounts typically to 889 cm^{-1} (corresponding to 13 $^1P_1$) and that of Al II to nearly double this, viz. 1686 cm^{-1} (corresponding to 9 ^2D). Certainly we can expect ^2D terms more sensitive than ^1P to microfield effects, a point which hardly arises in the discussions of Griem (loc. cit.), which strictly concern only one electron system. Curiously, the electron densities obtained by us lead, in the case of the Ca I series, to termination points as predicted by the Unsöld and Inglis-Teller theories. This is not, of course, true for the Al ^2D series, where the ionization potential appears depressed much more. These considerations suggest that the question of the microfield depression of the ionization energy for systems of more than one electron still requires a good deal of attention, and it seems difficult at present to make the corrections on any but the ad hoc basis adopted by us here.

The f-values obtained for the Al I doublet depend of course on the reliability of the f-value of Ditchburn and Hudson (1960) for the Ca I 1885Å line, and a disturbing feature is the disagreement of the autoionization lifetime determined by us for the Ca I 3d5p $^1P_1^0$ level with Ditchburn and Hudson's value, which is lower by 18 per cent. The difference cannot be ascribed to a boundary layer effect in the shock-tube experiments, since this would act to cause a spurious depression of the central region of the absorption line and result in an excessively large half-width and hence to a lower value for τ. In addition, the fairly good fit of a dispersion profile to the Ca I line in Figure 3 is worth notice.

Little comparison of our experimental results with theoretical expectations can be made. A paper by Eddy et al (1961) reports an attempted calculation by dipole and momentum matrices of the oscillator strength of the Al doublet, and it appears that they inferred that the greater part of the f-value they obtained is to be associated with $3\ ^2P^0-3s3p^2\ ^2S$. However, the calculation does not distinguish the contributions of other terms of $3s3p^2$, viz., 4p, ^2D, ^2P, and while the quartet combination can perhaps be ignored, this is hardly likely for $3\ ^2P^0-3s3p^2\ ^2P$, ^2D. Moreover, the possibly drastic effects of mixture with the $3s^2E\ (\ell)$ continuum wave-functions has been ignored (cf. Fano, 1961). For these reasons the experimental determination here reported seems much more reliable.

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