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PRECISION MEASUREMENT OF RELATIVE OSCILLATOR STRENGTHS—I

FUNDAMENTAL TECHNIQUE: A FIRST APPLICATION TO Mn I

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SUMMARY

A discussion of the importance of accurate measurements of atomic oscillator strengths in astrophysics is followed by an analysis of the accuracy that is potentially available together with a critical survey of the most useful techniques. A full discussion is given of the furnace method used in Oxford, and first results obtained for a few lines of Mn I are presented. It is shown that the accuracy of even this straightforward method can in some circumstances suffer from uncertainties about the state of thermodynamic equilibrium.

1. THE NEED FOR PRECISION OSCILLATOR STRENGTHS IN ASTROPHYSICS

Although oscillator strengths are of great interest in atomic physics, their principal application is to the analysis of solar and stellar spectra. Until a decade ago, the techniques used in such analyses were based on curves of growth averaged over ranges of wavelength and excitation potential: such techniques, being of limited accuracy, provided little incentive for the measurement of accurate oscillator strengths. Instead, large numbers of measurements of perhaps smaller precision have been made in the hope that the averaged results obtained by their use would be of sufficient accuracy. Perhaps also this attitude was promoted by the use of photography in the laboratory work because a single photograph of a spectrum could provide information about the intensities of several hundred lines. The astrophysical needs have now changed, partly through instrumental developments which are yielding improvements in both laboratory and stellar spectra, but chiefly through the development of fast digital computers, making possible detailed calculations of stellar spectra using model atmospheres. However, this increase in potential accuracy of interpretation has not so far been matched by a corresponding increase in accuracy of measurement of oscillator strengths, and there is now a great need for more precise data for weak lines of astrophysical interest. In this paper we consider the accuracy that should ordinarily be attainable, and discuss how closely this accuracy has been approached in recent work: in subsequent sections we describe preliminary experiments that we have made using manganese in attempts to realize this accuracy using the absorption technique. However, because the apparatus is capable of much improvement, we wish to emphasize the preliminary nature of the data obtained at this stage.

2. LIMITS TO PRECISION OF CONVENTIONAL OSCILLATOR STRENGTH MEASUREMENTS

Broadly speaking, three kinds of technique are available for measurement: life-time, emission and absorption methods. In principle, a life-time method, as

exemplified by the technique of beam foil spectroscopy, described for example by Wiese (1970), has the fundamental advantage that in some restricted circumstances its application does not depend upon a temperature measurement or any assumption of thermodynamic equilibrium in the source: in addition, it gives an absolute result without the need of an absolute number density of atoms. The hope is sometimes expressed that the method of beam foil spectroscopy will yield oscillator strengths of the required accuracy. In practice, the technique suffers from the difficulty that although the life-time of an excited state can be measured with reasonable accuracy, it is also necessary to measure in a separate experiment the branching ratios for radiative de-excitation. As these ratios are usually measured by an arc method, the accuracy of the final oscillator strengths is limited by the deficiencies of this source. Also, some atoms in the beam may be excited to higher levels than the one being examined, and because the nature of the initial excitation is unknown, radiative de-excitation (cascading) takes place to this lower level in a way that is wholly unpredictable. This difficulty is especially important for levels of low excitation.

Both the absorption and emission methods depend upon temperature measurements and the assumption of thermodynamic equilibrium. In these methods, the relative oscillator strengths of two atomic transitions are measured by comparing the intensities of the corresponding spectral lines. Such a determination should be straightforward, involving only photometric measurements and an investigation of the physical conditions in the source. If the two lines originate from a common energy level, the accuracy of the final result, if the assumption of L.T.E. is valid, need be limited only by the accuracy of the photometric measurements. On the other hand, if the lines originate from different levels, the accuracy may be limited by imprecise knowledge of the temperature of the source. Supposing that a state of thermodynamic equilibrium exists in the source, the number density of absorbing or emitting atoms excited to an energy E is proportional to the Boltzmann factor, $\exp(-E/kT)$, where T is the temperature and k is the Boltzmann constant. It follows that a relative error $\Delta T/T$ in the measurement of temperature will give rise to a relative error $\Delta N/N$ in the calculated number density of excited atoms, given by

$$\frac{\Delta N}{N} = \frac{E}{kT}\cdot\frac{\Delta T}{T} = 1{\cdot}2\times 10^4\times\frac{E}{T}\times\frac{\Delta T}{T}$$

where E is expressed in eV. As an example, suppose that a comparison is made between the oscillator strengths of two absorption lines having excitation potentials that differ by 2 eV, using an absorption source at a temperature of 2000 °K. Unless wholly extreme precautions are taken it will not be possible to measure this temperature on the thermodynamic scale to an accuracy that is much better than ± 7 °K. We infer that such an error in the measurement of temperature will lead to an error of about 4 per cent in the ratio of oscillator strength. If in the use of such methods the photometric errors can be reduced to negligible proportions, an error of this magnitude should be the maximum that need be incurred. This limit applies to the use of a shock tube in either emission or absorption, although here there may be other more important sources of error.

3. PRECISION OF CURRENTLY AVAILABLE OSCILLATOR STRENGTHS

During the last few years there has been an increasing awareness among astrophysicists that currently available oscillator strengths have a precision that is

rather far from the limit described above. Some of this evidence comes from comparisons between oscillator strengths obtained by different, although not necessarily independent, techniques. Several examples of such comparisons are available in the literature. In particular, the comparisons for Fe I made by Grasdalen, Huber & Parkinson (1969), and Bridges & Wiese (1970) show discrepancies in other work amounting to a factor × 100. As a further example, we compare in Fig. 1 the newer data obtained by Garz & Kock (1969), with those of Bridges & Wiese (1970), as a function of wavelength: this diagram shows a maximum spread of more than a factor × 2 between the results of these two authors.

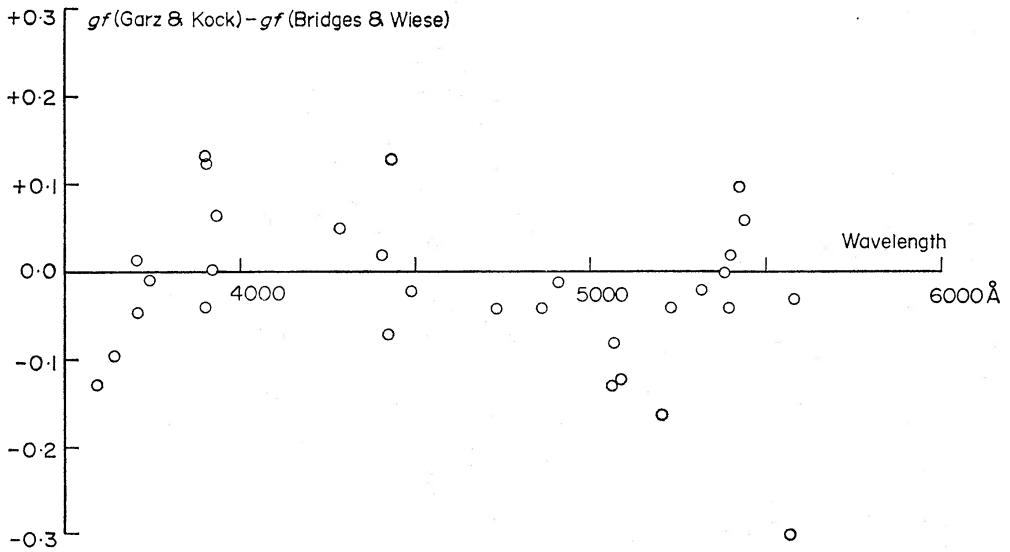

FIG. 1. *Comparison of oscillator strength data for Fe* I *of Garz & Kock* (1969) *with those of Bridges & Weise* (1970): *note that log* gf *is plotted.*

The astrophysical evidence for lack of precision is perhaps even more convincing, beginning with the discrepancy, amounting to a factor of 10, that existed between the abundance of iron measured in the solar corona and that measured in the solar photosphere (Jordan 1966). This difference is almost certainly because of an error in the photospheric abundance, due to inaccuracies in the oscillator strengths of the iron lines used in the photospheric analysis; indeed, confirmation of this is provided by the greatly reduced difference between photospheric and coronal abundances that is derived when the more accurate oscillator strengths of either Garz & Kock or Bridges & Wiese are used in the photospheric analysis.

The accuracy of oscillator strengths for individual lines may be similarly assessed by calculating a solar abundance from each of the lines, using a suitable model atmosphere: for this test the lines must be carefully chosen so that in the solar spectrum they are well isolated and as free as possible from blends. When this is done such lines show a spread of abundance of more than a factor two even with the best available data (Garz *et al.* 1969). Furthermore, the test may also show an apparent dependence of abundance on the wavelengths of the lines and on their excitation potentials, indicating that the measurement of the temperature of the laboratory source or the wavelength variation of the sensitivity of the spectrometer, or both, may be in error. As an indication of the result of a possible temperature error we show in Fig. 2 a plot against excitation potential of the solar abundances

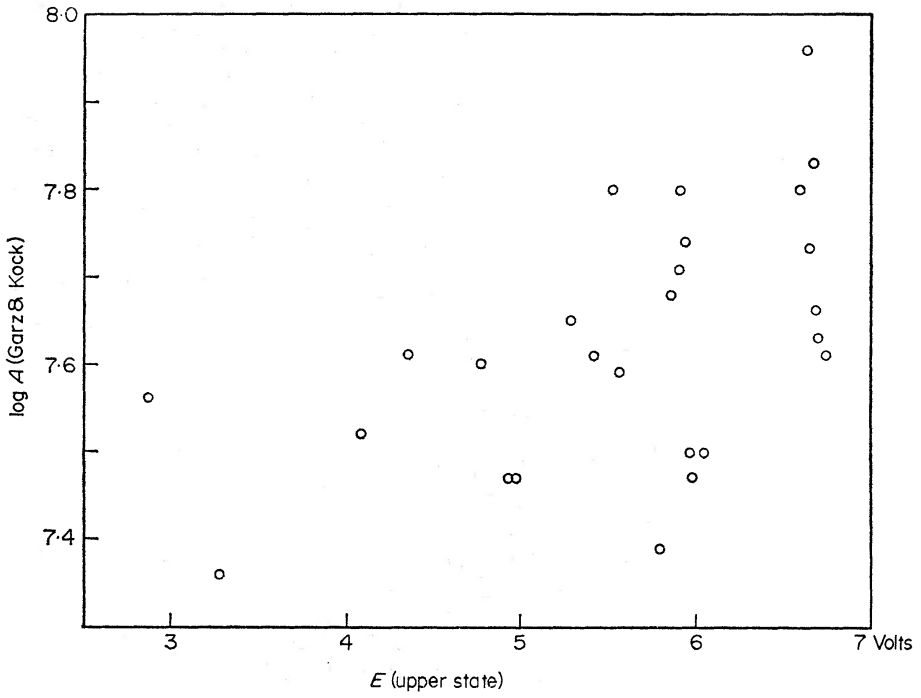

FIG. 2. *Dependence on excitation potential of solar abundances for iron obtained by Garz et al.* (1969).

for iron obtained by Garz *et al.* (1969) from the oscillator strengths of Garz & Kock (1969): this plot shows a clear dependence on excitation potential, demonstrating the possible existence of a temperature error.

Although it is encouraging to see a much greater measure of agreement between these two sets of data, the discrepancies are still larger than might be expected from our earlier discussion. Moreover, the two sets were obtained by the use of closely similar sources (a well-stabilized arc at a temperature of about 10^4 deg) and it is evidently desirable to seek confirmation by use of other techniques. The present work has been undertaken as the first part of a programme in which we will attempt to measure relative oscillator strengths to a precision that approaches the limit discussed earlier: later in this paper we give definitive data for lines of Mn I. We have chosen to use an absorption technique for these measurements because it seems to us that this technique is likely to be more precise than the more often used emission method, at least for lines of low excitation potential. Because of the difficulty of measuring concentrations of atoms, the absorption method is not suitable for absolute measurements, and we place our relative measurements on an absolute scale by reference to the absolute oscillator strength of a spectrum line that has been measured by a more suitable method.

4. CRITIQUE OF TECHNIQUES

A prime advantage of the absorption technique is that it completely avoids the difficulties of self-absorption that are usually so troublesome in the emission method, although we note that both Garz & Kock, and Bridges & Wiese, claim that their measurements are almost independent of self-absorption. A further

advantage of the absorption method is that conditions in the absorption source, which in the case of these experiments is a stable column of vapour of length 120 cm, can be thoroughly investigated *in situ*. In particular, its temperature can be measured along its length by optical pyrometery to the limits of accuracy of the pyrometer (± 7 °K at 2000 °K) independently of assumptions about other spectroscopic data, particularly other oscillator strength data. In contrast to this, the temperature structure of an arc is often complex, and recourse must usually be made to spectroscopic methods for its measurements, involving the assumption of other oscillator strengths. The absorption method has the advantage of simplicity, needing only measurements of equivalent widths of absorption lines. On the other hand, the emission method needs measurements of the relative intensities of emission lines, for which a knowledge of the variation of sensitivity of the spectrometer with wavelength is required. The determination of this variation requires the use of a blackbody at a known temperature, and any error in the calibration will result in a wavelength dependent error in the resulting oscillator strengths.

The long hot column of vapour produced by the furnace also radiates an emission spectrum which may be used, as by Carter (1949) and by Aarts, Hartin & Bakker (1954), for the measurement of relative oscillator strengths. However, such use of the apparatus involves the uncertainties of a large correction for self-absorption and the more accurate absorption mode of use is much preferable.

Whilst these are cogent reasons for preferring the absorption method to emission methods in general, at least for lines of small excitation potential, unless suitable precautions are taken the method may be limited in accuracy by the well-known difficulty of measuring the profile and equivalent width of a narrow absorption line. In a comprehensive discussion Griffin (1969) has shown that use of an unsuitable grating in a spectrometer can have seriously deleterious effects on such measurements, even though the width at half intensity of the instrumental profile may be reasonably narrow. However, Petford *et al.* (1971) have shown that modern echelle gratings, and especially such gratings produced during the last 2 years, may be used safely in such circumstances. The difficulty is accentuated in these absorption experiments by the extreme narrowness of the absorption lines: an Fe I line, for example, formed in the furnace will have typically a half-width of only 15 mÅ. Although our experiments do not suffer from this difficulty, because echelle gratings that have been copied from recently ruled masters are used in the spectrometers, it is very likely that the use of gratings that are poor by modern standards has been responsible for large errors in early oscillator strength work. This applies particularly to the pioneering work of King & King (1935) and can also be a serious difficulty when using an atomic beam as an absorption source in which the line widths are of the order of 9 mÅ (Bell *et al.* 1959).

During all of our experiments the furnace has been operated at a pressure of inert gas that was just sufficient to contain the metallic vapour inside the heated tube (about 20–50 torr). This ensures that the profiles of the absorption lines are of near-gaussian shape and free from damping wings, which makes the location of the continuum and the accurate measurement of the equivalent widths much easier. As the amount of damping generally increases with excitation potential it is possible that experiments in which damped lines are produced at higher gas pressures may give rise to errors that simulate a temperature error. In this connection, we are thinking particularly of arcs that are run at atmospheric pressure, of which the arc

operated by Corliss & Warner (1964) is an example, and of shock tubes in which the pressure may be several atmospheres.

Within its limitations, the method of beam foil spectroscopy is reliable, but it suffers from the difficulties mentioned in paragraph two. In addition, the method finds its principal application to stronger transitions in the ultra-violet, which are not directly useful in abundance determinations because the lines are in a crowded region of the spectrum and too strong to be on the linear part of the curve of growth. With the reservations that we make in paragraph two, its strength lies in its usefulness for establishing an absolute scale without need for measurement of vapour pressure or temperature, or any assumption about equilibrium. Any data obtained with its must be combined with measures of branching ratios obtained by other methods.

5. THE ABSORPTION TECHNIQUE

The first Oxford furnace for spectroscopic purposes was constructed by Peach (1969). The furnace used for the present measurements is a larger one that has been described by Collins, Petford & Blackwell (1970). In this furnace, the heated element is a carbon tube of length 122 cm and internal diameter 5 cm, the temperature of which does not vary by more than 10°K over a length of 50 cm. The temperature is measured by sighting with a disappearing filament pyrometer on to carbon blocks fixed at intervals along the length of the tube: these sightings are made through a window that is situated at the end of an extension column some 160 cm from the end of the carbon tube in order to avoid deposition of carbon and manganese which would affect the temperature measurement. Continuous monitoring of the temperature is also provided by a photoelectric pyrometer. Because of the large thermal capacity of the heated element the temperature is very stable and often does not vary by more than a few degrees Kelvin over a period of several hours.

A high pressure xenon arc is used as a continuous source. After passing in a parallel beam through the furnace tube the light is focused by a quartz lens to produce an image of the source. The most intense part of this image is selected by a diaphragm, the light from which is shared between two photoelectric spectrometers, which are of the low noise type described by Blackwell, Petford & Mallia (1967). Each spectrometer scans one line of the pair of absorption lines being compared, at a resolving power of about 160 000. The outputs of the spectrometers are punched on paper tape and a computer program is used to derive the equivalent widths of the lines. Such an arrangement of spectrometers is needed because the spectral range available at one time with one spectrometer is only about 5 Å. For financial reasons, only one set of electronics is used in this work, the spectrometers scanning alternately and taking turns to use the electronics: this limitation will be removed later, enabling us to scan the lines simultaneously.

In principle, the method is the same as that used by King & King (1935) some 30 years ago. It will therefore be useful to state the improvements that we have effected, particularly as we believe that the original data obtained by King & King suffered from large errors. The Oxford furnace has a length of 112 cm compared with the 40 cm for the original King furnace. Furthermore, partly through the use of heat shields, this length is at a much more uniform temperature than the King furnace. Although this gives the advantage of increased absorption, so that

weaker lines may be examined, of greater importance is the effect on the accuracy of measurements made on lines from excited states. The effect arises in the following manner. In calculating the oscillator strength from the measured equivalent width it is necessary to integrate an expression of the form $n(T) \exp(-E/kT)$ along the tube. We do this by supposing that the number density at each point, $n(T)$, is proportional to the vapour pressure there—that is, we assume that there is no substantial diffusion along the length of the tube—so that the vapour pressure corresponding to the temperature at each point along the tube is weighted by the Boltzmann factor. A serious error in a comparison between lines of different excitation potential will result if this supposition is not correct, the extent of the error depending on how far the temperature distribution departs from uniformity. The temperature distribution in the present apparatus is much more uniform than in most other furnaces, so that this kind of error is minimized. In addition, the temperature measurement is more accurate than in King's experiments because we sight the pyrometer on to blocks of carbon instead of on to the inside walls of the tube. In addition, we do this for each pair of lines, before and after the photometric measurements. King made a temperature measurement once only before the photometric measurements, and assumed the temperature remained constant thereafter. Because of thinning of the tube this assumption was probably invalid. Our reduction procedure is an accurate one in that the calculation of the profile of the absorption line involves evaluating the atomic absorption coefficient at each point in the line profile and at several points along the length of the tube.

The spectroscopic technique that we use incorporates two important advances over that used by King & King. The first, which is crucial for success, comes from the use of a high quality grating. Tests that we have made with various gratings show that among the high quality ones that we have tried only a recently ruled Bausch and Lomb echelle grating is good enough for observing the very narrow absorption lines given by the furnace. The second advance comes from the use of a low-noise photoelectric detection system. When comparing two lines it is important that the stronger should not be too deep, for otherwise there will be a large and uncertain curve of growth correction. The weaker one will therefore be a few per cent deep only. In these circumstances, a photographic system which, at best, gives a noise level of about 1 per cent of the continuum is not suitable, and it is necessary to use a low-noise photoelectric system which operates at a noise level that is only about one-tenth per cent. In fact, there exist optimum depths for a pair of lines depending upon the ratio of the oscillator strengths of the lines and the difference in excitation potential of their lower levels. In addition to giving such a low noise the present system enables one scan to be made per minute, so that a run of some 60 scans can be made and the effects of any small variations in furnace temperature reduced.

6. REDUCTION PROCEDURE

The reduction procedure is an accurate one. The atomic absorption coefficient, $\alpha(\nu)$, is calculated at each of some 30 points along the tube using the subroutine for calculating the Voigt function given by Armstrong. The profile of the absorption coefficient per unit volume is obtained at each point by multiplying $\alpha(\nu)$ by the number density of absorbing atoms there: to ease this calculation the vapour pressure may be assumed related to the temperature T by an expression of the

form

$$\log_{10} P = Po + P1/T$$

where Po and $P1$ are constants, the values of which are discussed by Nesmeyanov (1961). For most purposes the profile of the absorption line formed in the tube is found by integration along the length of the tube at each frequency in the line, allowing for the Boltzmann factor.

For the special case of manganese account must be taken of hyperfine structure. Fortunately, this structure has been extensively studied, for example by White & Ritschl (1930); Goodman, Noldeke & Walther (1962); Handrich, Steudel & Walther (1969); Fisher & Peck (1938); Woodgate & Martin (1957) and Evans, Sandars & Woodgate (1965). These authors have obtained the level splittings. We have used for the calculation of the relative intensities of the components, assumed to be in accord with the normal coupling scheme, the equation for the line strength given by Wybourne (1965),

$$S(IJF, IJ'F') \propto 2(F+1)(2F'+1) \begin{Bmatrix} F & I & F' \\ J' & I & J \end{Bmatrix}^2.$$

The 6-j symbols were computed using an Algol procedure supplied by Dr G. Smith. As a check on the calculation, the line λ 5394 ($a^6S_{5/2} - z^8P_{7/2}$) was observed at moderately high resolution using the furnace as an absorption source. The resultant profile is shown in Fig. 3 together with a computed profile normalized to have the

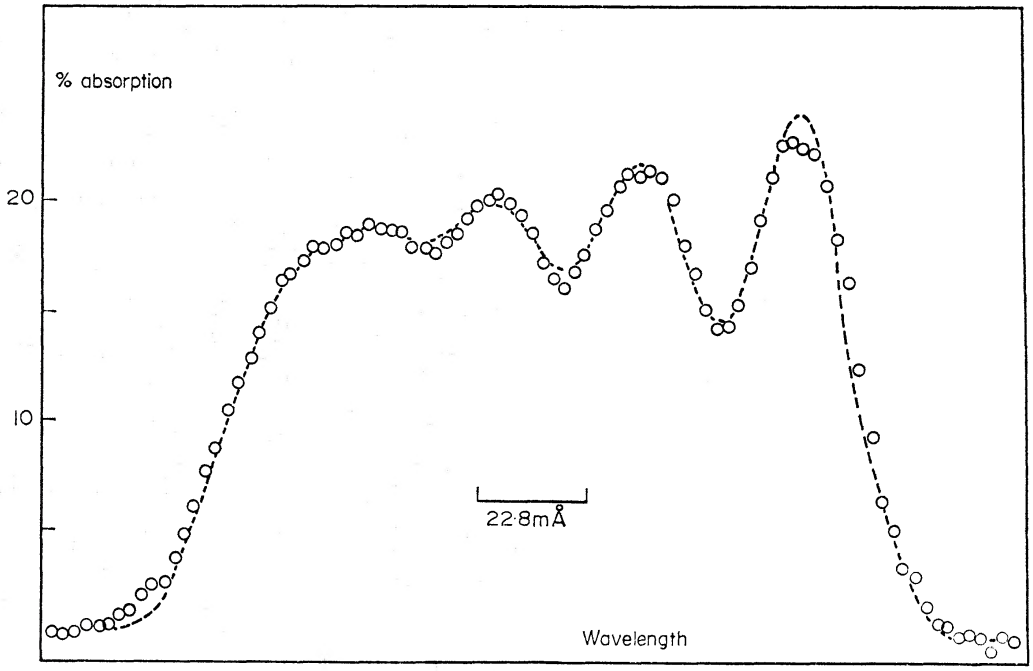

FIG. 3. *Observed profile of Mn* I 5394, *showing hyperfine structure, obtained using furnace as an absorption source. A computed profile is shown for comparison.*

same equivalent width as the observed profile. The agreement is satisfactory. The profile of the absorption coefficient at each point along the tube is now found by summing the absorption coefficients of each of the hyperfine structure components according to their separations and intensities. The calculation is repeated for various values of $\log gf$, to form a curve of growth, and interpolation then gives the value of $\log gf$ corresponding to a measured equivalent width.

7. THE MANGANESE SPECTRUM AND PREVIOUS MEASUREMENTS OF OSCILLATOR STRENGTH

Because the ground state configuration of manganese is $3d^5 4s^2$, a half-filled shell resulting in one ^6S level, the atom does not show the large number of low excitation lines in its absorption spectrum that is typical of all other iron group elements. The lowest excited configuration is $3d^6 4s$, which is 2·1 eV above the ground state. Because of this large interval the oscillator strengths of excited lines of manganese have never before been measured using an absorption technique.

Extensive studies have already been made of the violet resonance triplet ($\lambda\lambda$ 4030, 4033, 4034) and also of some other ground state lines. Measurements of oscillator strengths for these lines have been made using the hook method by Ostrovsky, Parchevsky & Penkin (1956) and by Ostrovsky & Penkin (1957), in which absolute measurements of the *gf* values for both sets of ground state line-doublets and line triplets were made. The accuracy of their absolute scale depends upon the accuracy of the vapour pressure data used. The absolute *f*-value of one line in the violet triplet, λ 4031, has also been measured using the atomic beam method by Bell *et al.* (1959).

Only the emission method has been used to measure *gf* values for excited lines in the Mn I spectrum. Allen & Asaad (1957) used a diluted copper arc, as did Corliss & Bozmann (1962), and Warner & Bowell (1964). The method used in deriving the *gf*-values from the observed intensities were those described above, and the *gf*-scales are subject to the possible errors mentioned there. Hefferlin & Gearhart (1964) and Woodgate (1966) used wall stabilized arcs, the former deriving his temperature from assumed relative *gf*-values, the latter using a line reversal technique. Hefferlin also studied self-absorption in his arc, finding it to be appreciable except for very highly excited lines.

8. EXPERIMENTAL PROCEDURE FOR MANGANESE

The manganese we used was of standard electrolytic quality in the form of small flakes. It was contained in a carbon crucible about 120 cm long, which was insulated from the carbon heating tube by boron nitride legs. This arrangement proved completely satisfactory, reaction between manganese and carbon proceeding only very slowly at the temperatures that were used. The ground state lines required a temperature of about 1300 °K for their production, and at this temperature there was little loss of manganese from the furnace. The excited lines were obtained at temperatures of up to 2400 °K. At these temperatures it was necessary to use pressures of inert gas, nitrogen or argon, of up to 50 torr in order to contain the manganese in the hot region of the tube.

At the beginning of a measurement the furnace temperature was adjusted until the two lines were at the optimum depths. The lines were then scanned alternately, each scan taking about 90 s; usually about 10 scans of each line was made. The temperature distribution in the furnace was then measured using a Leeds and Northrup optical pyrometer, which had been calibrated at the National Physical Laboratory. The observations were then repeated with the lines interchanged between the spectrometers in order to eliminate any errors due to difference of scattered light in the two instruments. In the reduction of the data the continuum

in the neighbourhood of a line was represented by a quadratic polynomial and log *gf* values obtained on an arbitrary scale by the curve of growth procedure given above. The geometric mean of the results from the two sets of data was taken to give the final *gf*-ratio, independently of any scattered light found to be independent of wavelength.

9. RESULTS OF MEASUREMENTS

(i) *Relative oscillator strengths*

Three sets of lines were measured. The three violet resonance lines, $a^6S_{5/2}-z^6P_{3/2,5/2,7/2}$ the two green intercombination lines, $a^6S_{5/2}-z^8P_{5/2,7/2}$ and 13 lines of the a^6D-z^6D multiplet. In addition, the *gf*-values of a selection of excited lines that are reasonably unblended in the solar spectrum were measured.

The oscillator strengths of the violet resonance lines of wavelength 4030·76, 4033·07 and 4034·49 have been the subject of several studies. Probably the most reliable of such measurements are those due to Ostrovsky & Penkin (1957) using the hook method, which is especially reliable for strong resonance lines. The results of our measurements are shown in Table I, together with other measurements which have been arbitrarily normalized to our value for λ 4030·76. Also shown are the expected L–S values; clearly, some departure from L–S coupling occurs for the z^6P term. Our measurements agree well with the Russian results, although less well with those obtained by the emission method: the latter method is especially unreliable for resonance lines because of self-absorption.

TABLE I

Oscillator strengths of violet resonance lines of Mn I

λ	*gf* (present work)	*gf* (Ostrovsky & Penkin)	*gf* (Corliss & Bozmann)	*gf* (L–S coupling)
4030·755	100	100	100	100
4033·073	70·42 ± 1·4	71·43	69·6	75
4034·490	46·63 ± 1·3	48·26	25·3	50

The two green intercombination lines λ 5394·67 and λ 5432·55 are of interest for various reasons. Their relative oscillator strengths have been measured only twice, once by the hook method by Ostrovsky & Penkin (1957), and once by the emission method by Corliss & Bozmann (1962): the values quoted differ by a factor of 1·8. Also, these lines are weak and apparently unblended in the solar spectrum, and an analysis there will offer a check on the measurements. Our results for these two lines, together with others, are shown in Table II. This table also shows the relative transition probabilities calculated using information about the

TABLE II

Oscillator strengths of green intercombination lines of Mn I

λ	*gf* (present work)	*gf* (Ostrovsky & Penkin)	*gf* (Corliss & Bozmann)	*gf* (calculated)
5394·67	100	100	100	100
5432·55	51·28 ± 1·0	67·3	37·0	53·2

vectorial composition of the ^8P levels kindly communicated to us by Dr Walther. The agreement between our results and theory is satisfactory. Clearly, errors have arisen in the other experiments, probably because of the comparative weakness of the lines and possibly also because of the wide hyperfine structure. We shall demonstrate in a later note that there is also good agreement between our preliminary oscillator strengths and predictions from solar observations coupled with a solar model atmosphere.

The multiplet a^6D-z^6D was studied in order to see if any systematic effect with respect to *gf*-values measured by other means could be found. Some lines are also of interest for study in the solar spectrum. All but two of the lines were measured, λ 4068 being much weaker than other lines of the multiplet, and λ 4035 which lies too close to the resonance line λ 4034 to be completely separated from it at high temperatures: the resonance line is extremely wide, presumably because of resonance broadening. The resultant *gf*-values are shown in Table III together

TABLE III

Oscillator strengths of multiplets a^6D-z^6D of Mn I

λ	*gf* Oxf	*gf* L–S
4041·36	100	100
4055·54	46·3 ± 1·0	44·1
4063·53	12·6 ± 0·6	12·7
4070·28	4·3 ± 0·2	5·5
4018·10	25·0 ± 0·7	22·6
4048·76	28·7 ± 1·0	29·6
4058·93	19·6 ± 0·8	19·2
4079·24	14·9 ± 0·7	22·9
4083·63	22·4 ± 0·9	31·9
4082·94	22·2 ± 0·9	29·8
4079·42	15·0 ± 0·7	19·3

with the values obtained assuming L–S coupling. Evidently, there is a departure from L–S coupling in one or other term. From the term diagram, it is unlikely that the a^6D will be significantly mixed with any other term, the nearest sextet of the same parity lying at least 20 000 cm^{-1} above the a^6D. However, the z^6D could quite possibly be mixed with z^6F and x^6P. Although the Landé interval rule does

TABLE IV

Normalized line oscillator strengths of multiplets a^6D-z^6D of Mn I

	J		Relative line strengths		Sum	
λ	a^6D	z^6D	Exp.	L–S	Expt.	L–S
4041·36	9/2		100	93·9		
4079·24	7/2		15·05	21·3	115·1 ± 0·7	115·1
4081·10	9/2	7/2	24·88	21·3		
4055·54	7/2		46·46	41·2		
4083·63	5/2		22·66	29·7	94·0 ± 2·6	92·2
4035·73	7/2	5/2	—	29·7		
4063·53	5/2		12·63	11·8		
4082·94	3/2		22·45	27·7	—	69·2
4048·76	5/2	3/2	28·79	27·7		
4068·00	3/2		—	0·5		
4079·42	1/2		15·12	17·9	—	46·1
4058·93	3/2	1/2	19·63	17·9		
4070·28	1/2		4·34	5·2	24·0 ± 1·0	23·1

not suggest any large amount of mixing, it is well known that transition probabilities are a much more sensitive test of level composition.

To test further the accuracy of our *gf*-values we may compare the line strengths derived from them with the predictions of *J*-file sum rule. If we re-normalize the L–S line strengths to make the sum of the line strengths for the lines going to the $z^6D_{9/2}$ level to be equal to the observed sum, we obtain the values shown in Table IV. For the two independent sums, the difference between experimental and L–S sums is within the experimental errors. The agreement suggests that there are no large *cumulative* errors in our method.

(ii) *Absolute oscillator strengths*

In order to place the relative oscillator strengths that have been derived above on an absolute scale, it is necessary to relate the *gf*-values for the violet triplet to those of the green doublet, and the green doublet to the excited lines: the whole series is based on the absolute values given by Bell *et al.* (1959). The first comparison has been performed by Ostrovsky & Penkin (1957) using the hook method, probably the most appropriate method for this comparison, and they obtain a ratio of

TABLE V

Comparison of log gf*-value for weakest accessible ground state line* 5432 *Å of Mn* I *with that for strongest excited line* 4041 *Å*

λ	*gf* Oxf.	*gf* C–B
5432·55	0·0069 ± 0·0012	0·0024
4041·36	100	100

TABLE VI

Ansolute values of log gf *for Mn* I *lines*

λ	log *gf*
4030·76	−0·43
4033·07	−0·58
4034·49	−0·76
5394·67	−3·46
5432·55	−3·75
4041·36	0·41
4055·54	0·08
4063·53	−0·49
4070·28	−0·95
4018·10	−0·19
4048·76	−0·13
4058·93	−0·30
4079·24	−0·42
4083·63	−0·25
4082·94	−0·26
4079·42	−0·42
4754·04	0·01
5420·36	−1·29
5407·42	−1·53
5516·77	−1·75

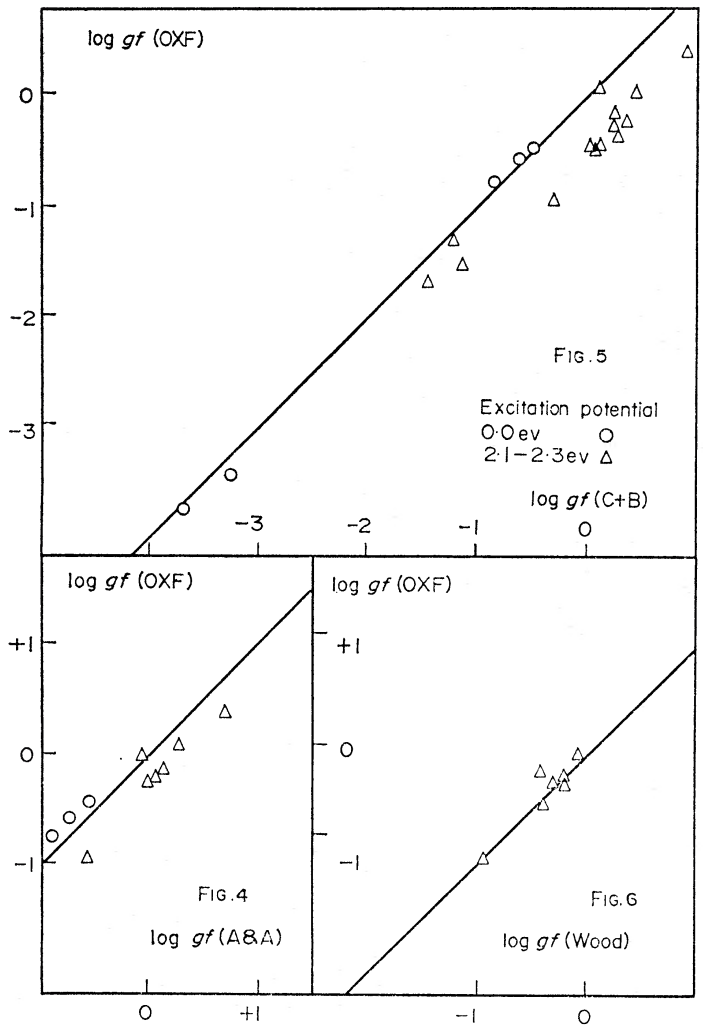

FIG. 4. *Comparison between present measurements of log* gf *for Mn* I *and those of Allen & Asaad* (1957).

FIG. 5. *Comparison between present measurements of log* gf *for Mn* I *and those of Corliss & Bozmann* (1962).

FIG. 6. *Comparison between present measurements of log* gf *for Mn* I *and those of Woodgate* (1966).

$1{\cdot}01 \times 10^4$ for the lines λ 4030, λ 5394. This means that the ratio $gf(4034) : gf(5394)$ should be about 500 : 1. We have attempted to measure this ratio by the absorption method, using a wide slit for λ 5394 in order to improve the signal/noise ratio at this wavelength. However, when this line was about 0·5 per cent deep, λ 4034 was still some 70 per cent deep so no very accurate comparison could be made due to the uncertainties of scattered light affecting the curve of growth.

We have attempted to link the ground state and excited state lines by comparing the weakest accessible ground state line λ 5432 with the strongest excited line λ 4041. Although, according to Corliss & Bozmann, the ratio of gf values for these lines is about 10^5, at a sufficiently high temperature the Boltzmann factor $\exp(-E/kT) \sim 10^{-5}$ and the absorption lines will be of comparable depth. In our experiments a temperature of 2130°K was used, which produced an equivalent width ratio of 10·9; a higher temperature would have been desirable, in that the

curve of growth correction for the deeper line would have been smaller, but this could not safely be attained at this time. This ratio will be extensively studied when improvements in the apparatus have been made. Our ratio for the *gf*-values is compared with that given by Corliss & Bozmann in Table V. Finally, Table VI gives the absolute values of log *gf* for all of the lines measured using the Russian value for the ratio $gf(5394) : gf(4030)$.

In Figs 4, 5, 6 we compare our log *gf* values with those given by Allen & Asaad Corliss & Bozmann, and Woodgate; in each diagram the straight line indicates equality. There are clear discrepancies with Corliss and Bozmann for excited lines. Our own errors are difficult to estimate, but we suggest that they are of order 0·15 in the logarithm, including the quoted error in the Russian comparison of λ 5394 and λ 4030.

10. THE ATTAINMENT OF EQUILIBRIUM IN THE FURNACE

The absorption method, like the emission method, depends on the assumption of local thermodynamic equilibrium. In this section, we do not present any quantitative data about the validity of this assumption under the conditions in which we have used the furnace, but wish only to draw attention to circumstances

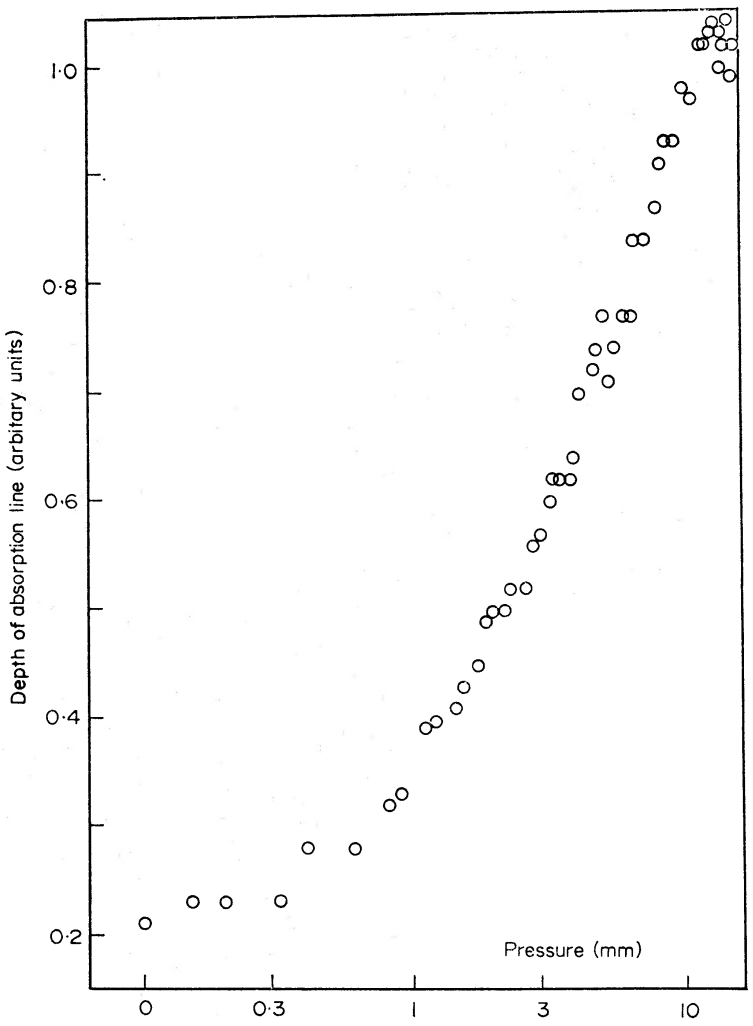

FIG. 7. *Dependence on pressure of inert gas of absorption depth of* 4070 *Å line of Mn* I.

in which very large deviations are seen to occur. All of our measurements of oscillator strengths have been conducted with the furnace containing inert gas at a pressure of up to 50 torr. The principal reason for adding this gas has been to contain the manganese vapour inside the furnace tube by preventing escape through collisions between manganese and inert gas atoms. A second function of the inert gas has been to maintain equilibrium at the temperature of the gas by means of collisional excitation. As might be expected, the depth of an absorption line decreases with decreasing inert gas pressure through the operation of the first mentioned effect: the relation is demonstrated in Fig. 7, which shows measurements made on the λ 4070 line. However, when this experiment is done with the λ 5407 line, the

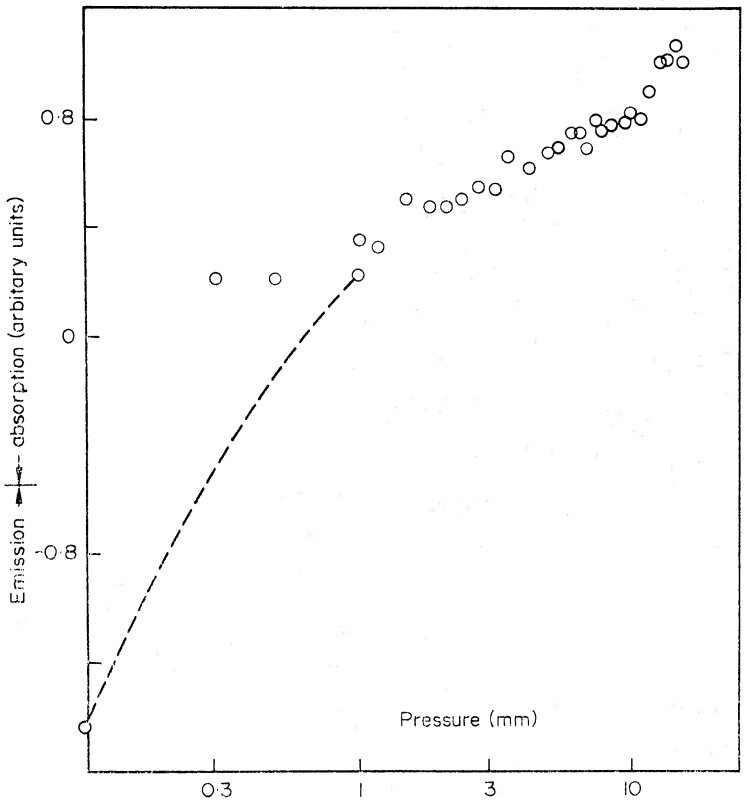

FIG. 8. *Dependence on pressure of inert gas of absorption depth of* 5407 *Å line of Mn* I, *showing transition to an emission line.*

line not only decreases in depth but turns into an emission line at the lowest pressures; results for this line are shown in Fig. 8. The especial significance of this latter experiment is that the line is seen in emission against the continuous emission from the xenon arc, which has a monochromatic radiation temperature that is much greater than that of the furnace. It is of interest that the initial slopes of the two lines are the same, showing that the initial decrease at least is attributable to loss of manganese. The emission line observed at low pressures certainly originates in manganese because it shows the normal hyperfine structure of this line. The existence of the emission line superimposed on the continuum emitted by the arc shows that there can be extreme deviation from equilibrium at low pressures. We have investigated the phenomenon further by positioning the slit of the spectrograph across the image of the furnace tube so that the distribution of the emission

can be examined. At the lowest pressures, the emission appears to be uniform over the cross-section of the tube. As the pressure is raised the area of emission contracts towards the walls of the tube until it eventually appears as a thin layer against the walls. It therefore seems that some of the decrease in absorption shown in Fig 7. is due to an increase in the area of emission at low pressures, remembering that the photoelectric observations are made on the integrated flux passing through the tube.

The excitation of manganese atoms when the pressure of inert gas is small is probably due to radiation from the walls of the tube. The manganese atom is unusual in that it has a strong transition, at 2794·82 Å, from the ground state to the state $y^6P_{7/2}$, which is the upper state of the line 5407 Å. We suggest that this upper state is strongly populated by this ultra-violet transition, sufficient intensity at this wavelength being provided by the weak thermal radiation from the furnace tube. Since the transition between the $a^6D_{7/2}$ state, the lower state of the 5407 Å line, and the ground state is forbidden, no such radiative excitation of this state can occur. As the pressure of inert gas is increased, inhibiting diffusion, so the density of manganese atoms increases. The optical depth of the manganese vapour at 2794 Å is thereby increased and the rate of excitation by radiation in the axial regions of the tube decreased: any over-population of the upper level is further decreased by collision with inert gas at the kinetic temperature of the tube. This mechanism accounts for the decrease of the area of emission as the gas pressure is increased. The anomalous emission is shown also by other lines of the multiplet $y^6P - a^6D$ being produced by the ground state lines 2798·27 Å and 2801·06 Å.

It is disturbing that such large deviations from equilibrium can occur in this very simple experimental arrangement. The remedy seems to be to operate the furnace at a sufficiently high pressure of inert gas, although this can bring the attendant difficulty of line absorption by CN molecules, these being formed in a reaction between carbon and any residual nitrogen produced by outgassing.

II. FUTURE WORK

The present experimental arrangement can be improved in many ways. Because of this, we regard the present experiments only as a first test of the technique, and we do not suggest that in our results above we have reduced the errors to the calculated limit. However, we are confident that when circumstances permit improvement of the apparatus, results of much greater reliability will be obtained. Improvements currently being made to the furnace will also enable higher temperatures to be reached, which will bring more excited lines within its compass. Finally, any further measurements, especially using other elements, must involve an investigation of equilibrium. We hope to pursue this topic using manganese and to try to obtain quantitative evidence for the state of equilibrium under the operating conditions of the furnace. It would be of interest to know whether the effects that we observe in the furnace occur with arc sources.

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