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ATOMIC SPECTROSCOPY WITH THE SHOCK TUBE*

by

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ABSTRACT

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Transition probabilities for lines of light atoms and ions are measured with a gas-driven shock tube in the temperature range 9000-13000°K. A complete "case study" is given for a set of experiments on one element, including recent developments in circumventing the sensitive dependence of level populations on temperature. The shock tube and observing instruments are described: Pressure transducers, photoelectric and photographic spectrographs are the main instruments; auxilliary equipment includes flash lamps and arcs for absorption data and calibration. The many elements of interest are introduced in gaseous additives to the carrier gas which is usually neon. Computer programs provide two things: mainly the details of ionization-excitation equilibria based on measured temperatures and pressures, also comparison of these measurements with Rankine-Hugoniot theory. Given a spectral line intensity, the associated transition probability is determined from the measured thermal quantities, not from the theory of shock heating. Redundant temperature measurements greatly reduce

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the random and systematic errors which ordinarily attend this type of experiment. Preliminary results of such a program are given for visible lines of neutral carbon. Spectra of other light elements will also be presented and discussed.

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1. Introduction

Our title could apply to a wide variety of experiments. The breadth of the field of shock tube spectroscopy is attested to by the many other papers on this subject given at this Symposium. Specifically I want to discuss the role of the shock tube in an important spectroscopic program: the determination of relative and absolute line strengths for atomic species, the term "strength" standing for a number of common terms (oscillator strength, gf-value, transition probability, Übergangswahrscheinlichkeit). As for molecules, much of what will be said will also apply, though some assumptions and observational problems are different. The temperature of the gas will be singled out for special attention, since its value is crucial in the interpretation of measured line intensities. To this extent then, we are discussing the data from all light sources which derive their atomic excitation from a hot gas.

By the term "shock tube" we will usually mean the classical, gas-driven type yielding temperatures up to 15,000°K; tubes driven by detonations or pulsed arcs will not need a separate treatment here, since we will focus on thermal and radiative properties which are independent of heating mechanisms. Let me begin with a few questions about the kind of shock tube spectroscopy we are doing.

A. Why measure radiative transition probabilities between the various electronic states of atomic systems, particularly just for the optical levels? Our iterest is mainly in establishing reliable values for the purpose of plasma state measurements, particularly for element abundances in stellar atmospheres[1] and temperature measurements in hot gases generally. Calculated oscillator strengths are usually not adequate for observed transitions. Measured values, of known precision and accuracy, are greatly needed for abundances, for the elimination and identification of lines in closely spaced spectra, and for measuring plasma temperatures and electron densities from emission and absorption spectra.

B. What makes the shock tube of interest in such a program? The shock tube belongs to a family of light sources one might call "thermal"; i.e., sources in which the populations of atomic and molecular levels and the degrees of ionization and dissociation follow from the temperature, density and composition of the plasma <u>via</u> thermodynamic relations. (Most thermal sources can be pushed into regimes where this is not strictly true, but tests are available for determining the extent of adherence to local thermal equilibrium.) Moreover the gas-driven shock tube, for example, opens up whole ranges of physical variables which are not so readily accessible with other thermal sources. The shock tubes with which we have been working establish plasma having a volume of about 1 liter, characteristic transverse dimension 10 cm, temperatures 9000° - 13000°K, and total particle densities 3 to 8 x 10^{18} per cc. Changes from one set of conditions to another are easily made by adjusting initial pressures

or gas compositions. Very rich emission and absorption spectra of many elements are generated, under conditions of known abundance, by inclusion of appropriate gases in the initial gas mixture[2].

C. What is the general method by which a thermal light source is used for line strength measurements, and what other methods are available? Most thermal light sources, shock tubes included, provide emission or absorption lines of known intensity under presumably known conditions of density and temperature. The Einstein coefficient for spontaneous emission (or the absorption oscillator strength) for any resolvable line is then found by dividing the line intensity (in appropriate units) by the number of atoms in the appropriate level. The "hook method" of displaying anomalous dispersion[3] is also used with thermal sources, again making use of presumably known level population.

A quite different sort of method is that of observing the statistical radiative decay[4] of large numbers of excited atoms or molecules, following a short period of excitation by photons or electrons. This and related kinetic methods[5] are very powerful for some transitions, while level-cascading and collisional effects make for quite imprecise results for many lines. A thermal light source by definition does not suffer from this difficulty, but is sensitive to temperature errors in ways we will further explore below. It now seems very likely that the thermal and non-thermal light source methods will be required to complement each other for some years to come, in order to find acceptably accurate line strengths for use with laboratory and astrophysical plasmas.

In sections to follow, we will first briefly describe our atomic spectroscopy experiments with the shock tube, which now concentrate largely on the lighter elements. Then we will bring up to date an older and persistent problem with the spectrum of neutral chromium, which seems now to have been resolved in one important respect while remaining open in another. The improved relative of gf-value scale for Cr I based on shock tube and arc measurements is discussed in terms of propagating temperature errors, partly in order to leave a large "caution" sign for certain types of temperature determination. Going then to the higher temperatures required for the lighter elements, whose excitation potentials are generally much higher than for the metals, we will observe the accumulation of large systematic errors due again to the Boltzmann factor in level population. Finally we will discuss a general method whereby the troublesome systematic errors in oscillator strength determinations can be reduced to the level of random errors.

2. Experimental Regime

Figure 1 is a schematic of our shock tube arrangement. Several optical instruments view the gas near the end wall of the 3 in. x 4 in. tube, where quartz pressure transducers are also located. Incident shock phenomena trigger photoelectric recording of events behind the reflected shock wave, and emission spectra are recorded on moving film in the f/6.3 spectrograph. Photomultipliers record twelve closely spaced wave-length bands in the monochromator and six separate bands in the B & L spectrograph; all wavebands are roughly 1 Å wide by virtue of

glass "cover slide" optical elements[6] used in the image planes. Typically, absolute intensities for certain neon, carbon, and hydrogen lines are recorded in the B & L with sideband detectors for subtraction of background continuum. This instrument also observes line reversal when the flash lamp[7] is triggered; a line of moderately high optical depth, such as the Balmer line H_α, is used for this purpose. Stark profiles of the H_β line are recorded in the 12-channel instrument, in order to determine electron density ($\sim$ 2 to 6 x 10^{16}/cc) from half-width ($\sim$ 25 - 40 Å). Absolute and relative line intensities over 1000 Å intervals are determined from spectrograph films which are carefully calibrated with graduated intensities and a carbon arc radiation standard.

The shock tube is driven by H_2 at pressures of 1000 - 2000 pounds per square inch. The low pressure of "test" gas is nearly always neon (p_o $\sim$ 1 cm Hg) with about 1% spectroscopic additive (CH_4, CS_2, PH_3, SiH_4, CCl_4, Xe, Kr, etc.). A typical film in the blue-green is reproduced in Figure 2 with time running downward and wavelength increasing to the left. The earliest segment of constant appearance is due to emission from behind the first reflected shock, where the temperature is roughly 11,500°K (1 eV); later emission is due to multiple wave interactions and erratic quenching by cold, expanded driver gas in the shock tube. From this type of data film, the integrated intensities of neon, carbon, hydrogen and sulphur lines are compared and the gf-values for many lines calculated from knowledge of the gas conditions. Present work with these lighter elements is discussed in Section 4, and past and

present work with metallic elements in the vapor phase in the shock tube is discussed in Section 3. For the latter, for example, $Cr(CO)_6$ in neon even at levels of 1/10% leads to films like Figure 2 except that they are dominated by strong lines of neutral and singly ionized chromium[8].

3. Relative Line Strengths, Temperature Measurement and Propagation of Temperature Errors

Sets of relative line strengths for various elements are extremely useful for the measurement of plasma temperature. Out of all the spectral lines of a given element, one needs to know the gf-value only for a subset of lines arising from a range of upper level energies. The absolute gf-value scale is not needed for this kind of temperature measurement; the wider the range of level energies and the more uniform the precision of gf-values, the better, The integrated intensity of an optically thin line[10] [11] [12] (upper level i, energy Ei; lower level j) is given by

$$I = n_i A_{ij}\, h\nu\ell = \frac{2\pi e^2 \nu^2}{mc^3} \cdot \frac{n_i}{g_i}\, g_j f_{ji} h\nu\ell$$

$$= \frac{2\pi h e^2 \ell n}{m\mathcal{Z}} \cdot \frac{g_j\, f_{ji}\, e^{-Ei/kT}}{\lambda^3}, \qquad (1)$$

where ν and λ are frequency and wavelength of the line, n_k is the number density and g_k the degeneracy of atoms in the kth level, n is the total species number density and $\mathcal{Z}$ the partition function, A_{ij} the Einstein coefficient for spontaneous emission and $g_j f_{ji}$ the "absorption oscillator

strength" related to it, e is the electron charge, h Planck's constant and ℓ the extent of the light source along the line of sight.

It is a well known corollary of Equation (1) that the temperature T describing a given distribution of level populations can be measured by plotting log $(I_r\lambda^3/gf_r)$ vs E_i, where r denotes relative intensity or gf-value. In such a plot, T appears as the negative inverse slope of a straight line; i.e., for E in electron-volts,

$$T(°K) = 5041(E_i^n - Ei^m)/\log_{10}\left(\frac{I_r\lambda^3}{gf_r}\right)_m - \log_{10}\left(\frac{I_r\lambda^3}{gf_r}\right)_n \qquad (2)$$

For aerodynamics experiments, trace amounts of salts or metallo-organic compounds added to the flow stream can give rise to optically thin lines of elements not usually present, and the experimenter has at his disposal a powerful thermometric tool. Considering what is now known just about the metals between titanium and nickel, the temperature range from 2000 to 10,000°K is certainly open to this technique, and it is from such measurements that much has been learned about the atmospheres of the sun and other stars.

It is less widely appreciated that the use of an erroneous temperature in the original gf-value determination leads first to an erroneous set of values gf' and then to serious temperature errors in subsequent determinations based on the set gf'. If experimenter A employs a temperature T_A' instead of the true value T_A in reducing line intensities to line strengths, then his results are

$$(gf)' = (gf)e^{-Ei/kT_A} \quad e^{+Ei/kT'_A} \quad . \tag{3}$$

Therefore experimenter B is later led to straight-line plots of the type mentioned above, but the temperature T'_B so derived and his actual temperature T_B differ according to

$$\frac{1}{T'_A} - \frac{1}{T_A} = \frac{1}{T'_B} - \frac{1}{T_B} \quad . \tag{4}$$

(e.g., 2000 vs 2500 → 5000 vs 10,000)

As an example of this type of difficulty, we illustrate in Figure 3 both an early attempt[13] at shock tube temperature measurement using Cr I lines and the later interpretation made possible by remeasurements[8] [14] of the Cr I gf-values. The old values for higher lying levels had to be reduced relative to the lower levels. With the correct relative scale, we indeed find an excitation temperature near 9200°K which is close to the expected shock tube temperature of 9300°K. With the older scale of Hill and King[15], one would be left to explain a strikingly lower excitation temperature of 5200°K. This is due, we believe, to a small temperature error in the furnace measurements having propagated, as explained above, into the large effect we see here.

That the previous relative scale for Cr I probably contained a strong temperature effect was pointed out by Goldberg, Müller, and Aller[16] and others from intensities in the sun's Fraunhofer spectrum. Our shock tube results[8] to this effect were buttressed by Charatis'

measurements of line reversal temperature[9], and were confirmed by the arc results of Corliss and Bozman[14], and by the demonstration of Müller and Mutschlecner that the newer scale for Cr I makes sense for the solar atmosphere[17].

Because of continuing interest and discussion on chromium spectra, we are reassessing our older work, in so far as this is possible, and Charatis is preparing for new absolute measurements. An important component of both programs is Koopman's development of computer methods[18] for detailed calculations of ionization and level population. The first conclusion has been that our prior hand calculations of neutral chromium abundance in various excited states were accurately performed, as is indicated in Figure 4 for various energy levels typical of Cr I. Since the Hugoniot-calculated temperatures agree between the old and new methods, and since these temperatures were experimentally checked in a few cases[9], we have as yet unearthed no reason to doubt the gf-values[8] we measured for Cr I and Cr II. These are shown in Figure 5 by comparison with the results of Corliss and Bozman for the same lines. Our absolute results for Cr I are within a factor of two of the sum rule for 4s - 4p transitions[16]. We understand that ultraviolet shock tube work by Huber[19] at Harvard tends also to support the relative scale of Corliss and Bozman, but that Huber's absolute scale is different. To summarize, it seems that the absolute gf-value scale for Cr I may indeed still be unsettled, but the relative scale is now sufficiently more reliable than it used to be that it suffices for 5% temperature measurements near 10,000°K.

4. Absolute Line Strengths, Effect of Temperature Errors, Avoidance by "Thermal Balancing"

We determine absolute line strengths in a variety of ways. Conceptually, the simplest is to calibrate photoelectric detectors and films absolutely over the necessary ranges of wavelength and intensity. This is now standard fare for shock tube spectroscopic work, which is not to say, however, that it is easy or foolproof. As an example of procedure let us assume that we measure the total energy I_c in an optically thin carbon line, such as the 3s - 4p transition C I λ 5052, by comparison with a standard radiation source such as the carbon arc. By the equation

$$I_c = N_c \, h\nu \, \ell \, A_c$$

we must determine A_c from knowledge of N_c, the upper level population.

Carbon abundance in the appropriate level follows from our knowledge of the gas composition plus state measurements; e.g., transducer measurements of total pressure and line-reversal measurements of temperature. We do not rely, as once was necessary, on the Hugoniot equations because of the greater sensitivity to temperature errors with the lighter elements. Again, computer codes have proven extremely useful for accurate calculations of many closely spaced thermodynamic states. In Figure 6, we show the calculated variations of upper state populations with temperature for a number or observed lines. (Note that this is for a particular pressure and gas composition.)

Taking a temperature range 400 degrees on either side of 10,400°K, the number density appropriate to C I λ 5052 swings over a factor of 2. This is a common amount of temperature uncertainty in this range and suggests at least a random error of order 40% in the final Einstein coefficient. Moreover, most experiments have proven to be difficult enough that one type of temperature measurement has had to suffice; i.e., the experimenter uses a complement of measurements just large enough to determine all unknowns. Over a given set of experiments, the particular method of thermometry employed will tend to err on one side or the other of the true value, while care in measurement may lead to good reproducibility and small scatter of results. Hence, the accumulated literature on atomic transition probabilities contains many precise values, and far fewer accurate ones to judge by discrepancies typically running between 3 and 10. In turn, the effects of such discrepancies on subsequent analysis of stellar or plasma spectra can be small, in some abundance determinations, or very large as we have illustrated in the foregoing discussion of temperature measurements by relative line intensities.

Figure 6 shows also the much more sensitive temperature dependence of the upper level population for the 5852 neon line, which is due to the greater excitation potential of the level. Generally this is easily shown to follow from the Boltzmann factor $e^{-E_i/kT}$ in the level population. By logarithmic differentiation,

$$\frac{dN_i}{N_i} = \frac{E_i}{kT} \cdot \frac{dT}{T} \quad ,$$

which tells us that a percentage temperature change (or uncertainty) is multiplied by a large factor (of order 10 in most of our cases) which makes a serious percentage effect on level population.

Now, how can this be overcome? One might propose several independent measurements of the conditions in the shock tube, arc, flame, furnace or whatever source is being used. We have done this by measuring absolute pressure, temperatures via spectral line reversal, absolute hydrogen line intensity, and absolute neon line intensity, plus electron density from hydrogen line profiles. The fruits of these extensive labors have been primarily a demonstration of agreement to 5% or better[24] in most of the quantities of interest - plus a confusion as to which method or methods was intrinsically more reliable, and what sort of averaged result for line strength was the most suitable and free of systematic error. We will go further into the question of averaging the results of independent measurements, after mentioning another approach which is sometimes useful.

The right hand side of Figure 6 shows ratios of upper level populations for various lines we are interested in. The uppermost curve, for example, illustrates the greater temperature sensitivity of the $n = 4$ level of hydrogen ($E = 12.69$eV) dominating the temperature effect in the upper level of this neutral sulphur line ($E = 9.12$eV). For a line of ionized sulphur however, we have nearly the same temperature dependence as for the line NeI λ 5852; presuming the strength of the latter to be known, clearly one could measure the absolute strength of S II λ 5453 with very little error introduced by temperature uncertainties.

Doherty took advantage of such trans-species similarities (O I vs H I) in his pioneering shock tube measurements ten years ago[20]. Unfortunately such Saha-Boltzmann pairings between interesting lines of unknown strength and available lines of known strength are rather rare, and some other method of temperature compensation must be sought.

It is in the equal-and-oppositeness of the curves for C I λ 5052 (left side of Figure 6) and $N_{5052\ C\ I}/N_{H\beta}$ (right side) that Mr. Miller saw a method of temperature compensation which now promises to be very general and useful. A full account of the "thermal balancing" technique is in preparation[21]; the method is being applied to many line strength measurements in our laboratory[22]. We will consider here only the case mentioned above and the resulting line strength for C I λ 5052.

In the upper part of Figure 7, we select the two thermal properties of interest for the remainder of our discussion, namely the reciprocal number density of carbon atoms in the upper level of C I λ 5052 and the inverse of the population ratio between this line and the H_β line of hydrogen. These are needed for two methods:

(1) If the absolute intensity I_c for the carbon line is measured, the transition probability $A_c^{(1)}$ follows directly from $1/N_c$ as indicated by the equation on the lower left of the figure.

(2) If the intensity ratio I_c/I_H (carbon to hydrogen) is measured, the carbon transition probability $A_c^{(2)}$ follows from the known value for hydrogen and the equation in the lower right side of Figure 7.

Of course these two independent measurements and methods would yield the same result if all the intensities were accurate and the true temperature, indicated by the ticks on the curves, were employed in reducing the intensity data. Suppose instead that erroneous temperatures might be used; the transition probability results by both methods are shown as functions of assumed temperature in the lower part of Figure 7, where T_o stands for the actual temperature of the light source. If one assumes a temperature which is less (or greater) than T_o, then the results of method (1) and method (2) are systematically too high and too low, respectively (or the reverse). So far we simply confirm that a very confusing pattern of agreement and disagreement between the results of different experimenters can result from the use of different methods and the occurence of different systematic temperature errors.

For pairs of curves having the degree of symmetry indicated here, an averaging procedure is not only reasonable but gives a striking reduction in systematic gf-value error even though one's choice of temperature may be quite imprecise. This is indicated in Figure 8, where we have normalized to the true magnitude of the oscillator strength. The <u>average curve</u> between these two methods depends only slightly on the assumed temperature, and generally lies much closer to the true transition probability than the result of either method used alone. To put it another way, the experimenter can measure the gf-value for the carbon line with very little systematic error simply by performing both the absolute and hydrogen-relative methods, knowing

the temperature only roughly, and averaging the results of the two methods.

Another experimenter with his light source also operating near T_o can make a gross temperature error in the other direction, but get nearly the same reasonably accurate result by averaging the carbon line strengths deduced from the two independent methods described. No matter what temperature is chosen in the range illustrated in Figure 8, the average of the two methods is very close to the true A value, while each method by itself could give large errors.

Certain general features of thermal balancing should be remarked upon. For any given pair of line-to-be measured and comparison line, there is a best operating temperature T_o for which the average curve has a small slope over the widest range of assumed temperature. For clarity our illustrations above have been made in the vicinity of the optimum T_o, but the method can stand departures on either side of T_o by 1000°K and still give shallow average-A curves--which is to say one is still much better off by averaging than not. Neither is the thermal balance destroyed by different choices of number density. Lastly, the average-A curves share the convex-upward property of the parent curves; thus the average curve is below the true value only over a small temperature range. This has the effect of concentrating those A-value errors encountered in thermal balancing to the high side of the true value. (Distributions of A-value results using synthetic data and a variety of assumed temperature errors are characteristically near zero just below the true A-value and fall of quasiexponentially above

it.) So it is very hard to underestimate transition probabilities by this method.

Of course, no amount of juggling can correct a mis-measurement of line intensity, for example, so one is still left with errors of this type. They tend to be diluted by an averaging process such as we have described and, in any event, lead only to linear rather than exponential errors. Currently our probable errors in intensity are of order 10%, so that the idealized distributions of results from synthetic data are made somewhat fuzzy. In Figure 9 we show a recent set of results for C I λ 5052, where the two methods were first used separately with a reversal temperature that was 3% in error, and finally where the set of results united by the averaging described above lead to a value of $A = (1.55 \pm 0.3) \times 10^6$ sec^{-1}. In the recent compendium of Wiese et al[23], this value was listed as 1.7×10^6 with a 50% probable error on the basis of various measurements. We had previously verified[24] the relative values listed by Wiese et al for the C I lines of multiplets 34-37, so we have therefore indirectly confirmed the listed absolute values for them as well.

Other methods for thermal balancing are also being explored in continuing studies of the lighter elements.

5. Conclusion

The gas-driven shock tube is an extremely useful spectroscopic source, since its conditions are readily varied over wider ranges than many other thermal light sources, and since means are available for discovering and circumventing the effects of temperature errors in

thermal sources. The shock tube has made possible a number of advances in the knowledge of radiative transition probabilities for neutral and singly ionized metals and lighter elements. This knowledge, in turn, improves our understanding of laboratory and astrophysical plasmas.

6. Acknowledgements

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REFERENCES

1. L. H. Aller, The Abundance of the Elements, Wiley-Interscience, Inc., (1961).
2. O. Laporte and T. Wilkerson, J. Opt. Soc. Am. 50, 1293 (1960); W. R. S. Garton, W. H. Parkinson and E. M. Reeves, Proc. Roy. Soc. (London) 140, 1269 (1964); also Proc. Phys. Soc. 88, 771 (1966); W. L. Shackleford, J. Quant. Spectros. & Rad. Transfer 5, 303 (1965).
3. For recent applications and references to original literature, see I.-Yu. Slavenas, Optics & Spectr. 16, 3, 214 (1964); A. K. Valters & G. P. Startsev, Optics & Spectr. 17, 4, 262 (1964); N. P. Perkin and L. N. Shabanova, Optics and Spectr. 18, 5, 504 (1965); I.-Yu. Yu. Slavenas, Optics & Spectr. 20, 3, 264 (1966).
4. S. Heron, R. W. P. McWhirter and E. H. Rhoderick, Proc. Roy. Soc. (London) A 234, 565 (1956); J. Z. Klose, Ap. J. 141, 814 (1965); J. Z. Klose, Phys. Rev. 141, 181 (1966).

5. G. M. Lawrence and B. D. Savage, Phys. Rev. 141, 67 (1966); B. D. Savage and G. M. Lawrence, Ap. J. 146, 940 (1966); R. G. Bennett and F. W. Dalby, J. Chem. Phys. 36, 399 (1962) and prior references there.

6. T. D. Wilkerson, "Atomic Processes in Plasmas" in Dynamics of Fluids and Plasmas (Burgers Symposium, October 1965) Academic Press (1966).

7. W. R. S. Garton, J. Sci. Instr. 30, 119 (1953); W. R. S. Garton and A. Rajaratnam, Proc. Roy. Soc. (London) A 70, 815 (1957); W. R. S. Garton, J. Sci. Instr. 36, 1 (1959); G. Charatis and T. L. Hershey, "A Flash Lamp Source of High Intensity Continuous Spectra," Univ. of Maryland Tech. Note BN-361 (July 1964).

8. G. Charatis and T. D. Wilkerson, Phys. Fluids 5, 1661 (1962). T. D. Wilkerson, "The Use of the Shock Tube as a Spectroscopic Source with an Application to the Measurement of gf-Values for Lines of Neutral and Singly Ionized Chromium," Ph.D. Thesis and University of Michigan Report No. 02822-3T (June 1961); G. Charatis, "Shock Tube Determination of Chromium gf-Values," Ph.D. Thesis, University of Michigan (1961).

9. G. Charatis and T. D. Wilkerson, Proceedings of the Sixth International Conference on Ionization in Gases, Vol. III, P. 401, SERMA, Paris (1963).

10. A. Unsöld, Physik der Sternatmosphären, Springer (1955).

11. S. Chandrasekhar, An Introduction to the Study of Stellar Structure, Dover (1957); Radiative Transfer, Dover (1960).

12. H. R. Griem, Plasma Spectroscopy, McGraw-Hill (1964).

13. G. Charatis and T. D. Wilkerson, Phys. Fluids 2, 578 (1959).

14. C. H. Corliss and W. R. Bozman, Nat. Bur. Stand. Monog. 53 (1962).

15. A. Hill and R. B. King, J. Opt. Soc. Am. 41 315 (1951).

16. L. Goldberg, E. A. Müller and L. H. Aller, Ap. J. Suppl. No. 45 V 1-138 (1960).

17. E. A. Müller and J. P. Mutschlecner, Ap. J. Suppl. IX, pp. 1-64, No. 85 (1964).

18. D. W. Koopman, "Computer Programs for the Calculation of Equilibrium States in Reflected Shock Plasmas," Univ. of Maryland Tech. Note BN-481 (November 1966).

19. M. Huber, private communication. We are grateful also to W. Parkinson and E. Reeves at Harvard, and G. Wares and colleagues at AFCRL for several discussions of shock tube results.

20. L. R. Doherty, "The Measurement of Absolute Spectral Line Strengths with the Shock Tube," Univ. of Michigan Ph.D. Thesis (1962).

21. M. H. Miller, Ph.D. Thesis in preparation, Univ. of Maryland (1967).

22. M. H. Miller, Bull. Am. Phys. Soc., 12, 525 (1967).

23. W. L. Wiese, M. W. Smith and B. M. Glennon, Atomic Transition Probabilities, Volume 1: Hydrogen through Neon, National Standard Reference Data Series--National Bureau of Standards 4 (May 1966).

24. T. D. Wilkerson, "Shock Tube Spectroscopy at Chromospheric Temperatures," Univ. of Maryland Tech. Note BN-467 (August 1966).

FIGURE CAPTIONS

Figure 1. Methods of Observing Gas behind Reflected Shock Wave.

Figure 2. Time-resolved emission spectrum, showing carbon, hydrogen and sulphur lines behind first reflected shock (top) and subsequent waves.

Figure 3. Relation between temperature measurement and reliability of relative gf-values. Effect is shown for a particular shock tube experiment where relative intensities of spectral lines were measured.

Figure 4. Comparison of calculated level populations for various Cr I levels behind reflected shocks in neon plus $Cr(CO)_6$. Hand calculations and computer results agree with temperatures checked by line-reversal experiments.

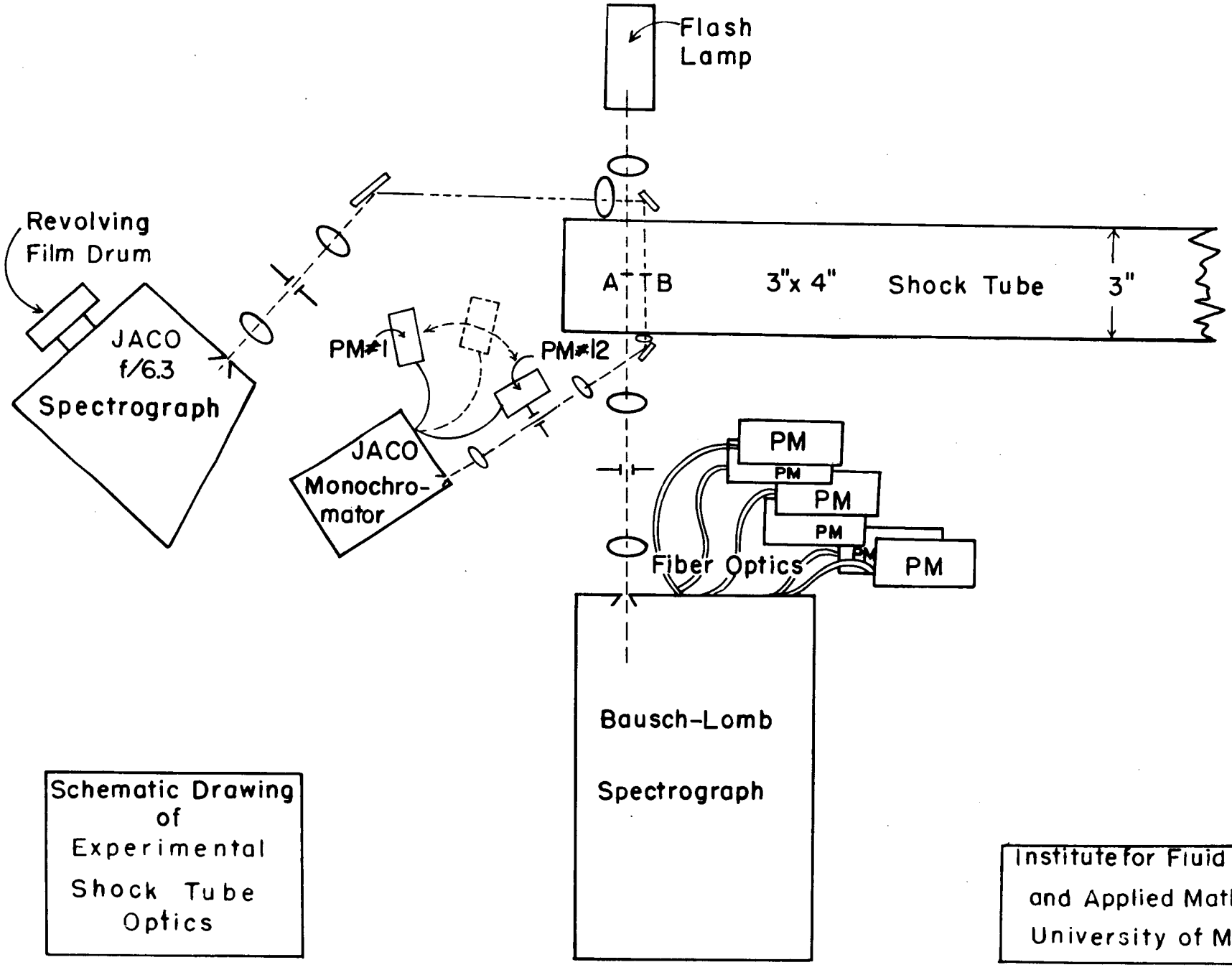
Figure 5. Comparison of absolute gf-values for Cr I observed in shock tube (Charatis-Wilkerson) and arc (Corliss- Bozman).

Figure 6. Calculated thermal states for a particular gas mixture, showing strong temperature dependence of level populations, and a variety of temperature dependences of population ratios.

Figure 7. Dependence on assumed temperature of transition probability for C I λ 5052, for two methods of measurement.

Figure 8. Curves completing the implication of Figure 7, namely that the average of the two methods is very close to true transition probability for a wide range of assumed temperature.

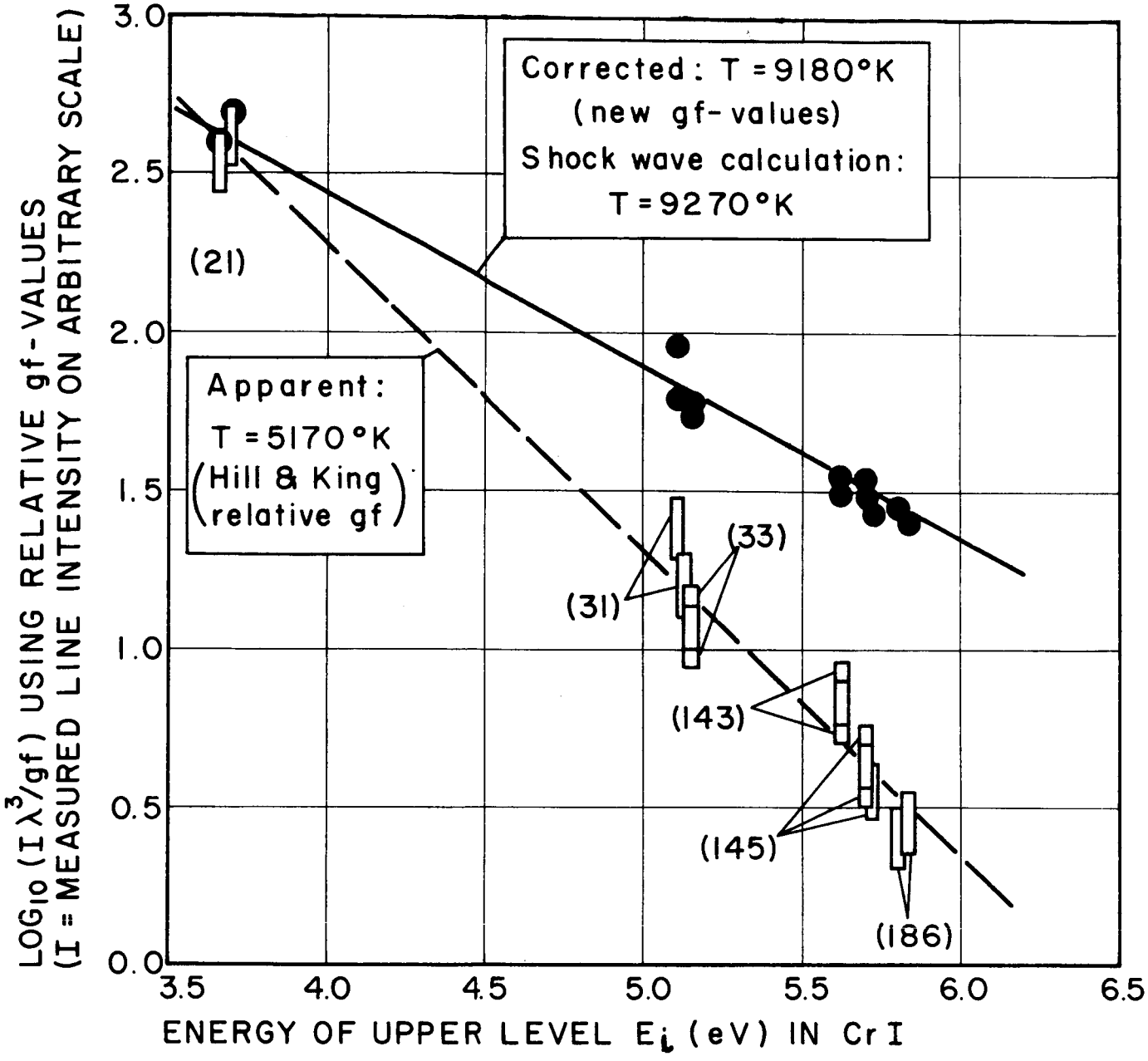
Figure 9. Experimental transition probabilities for C I λ 5052, reduced by absolute emission and hydrogen-relative methods alone, and then by thermal balancing. Result chosen by comparison with distributions of results previously calculated from synthetic data.



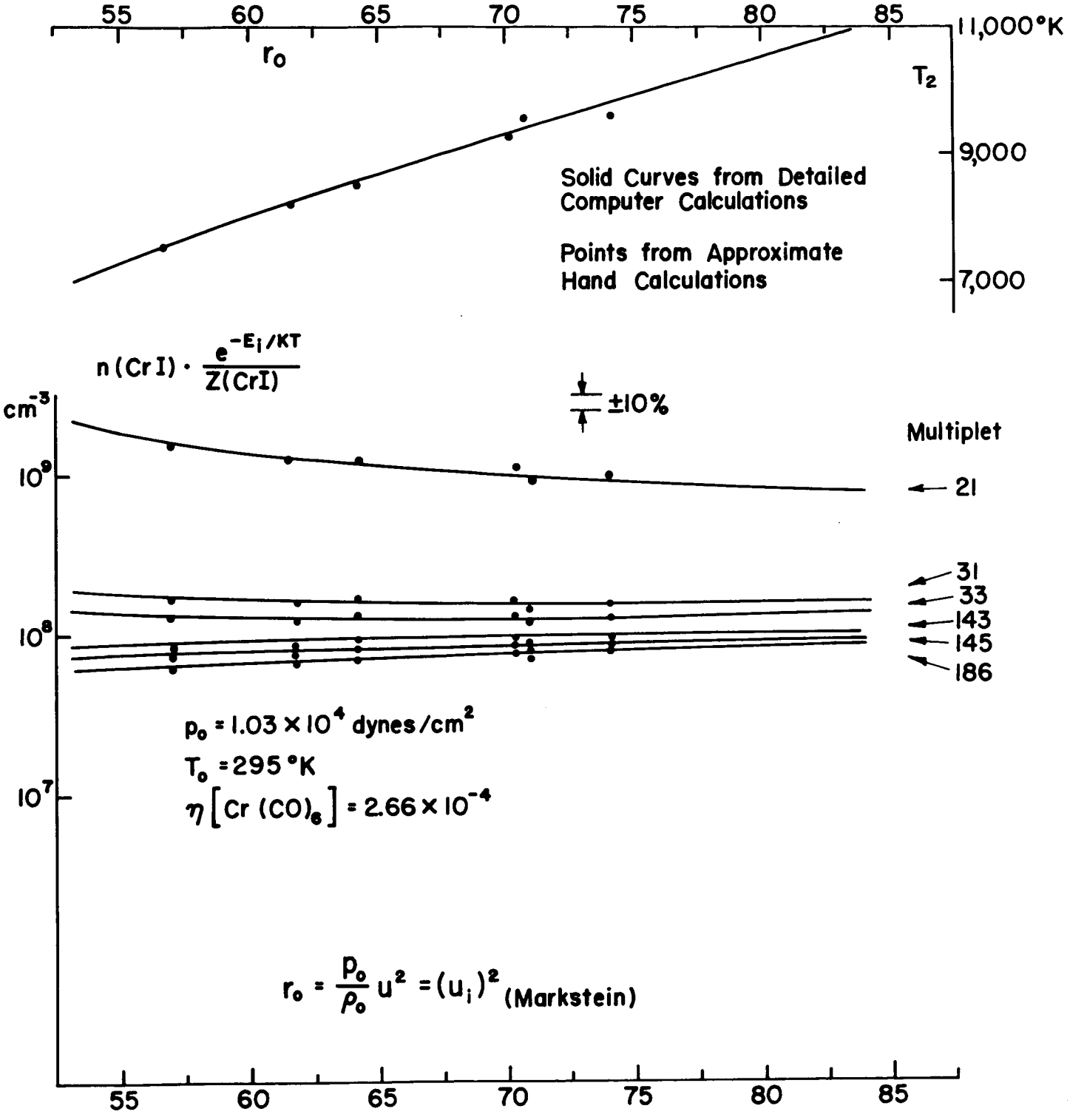
Schematic Drawing of Experimental Shock Tube Optics

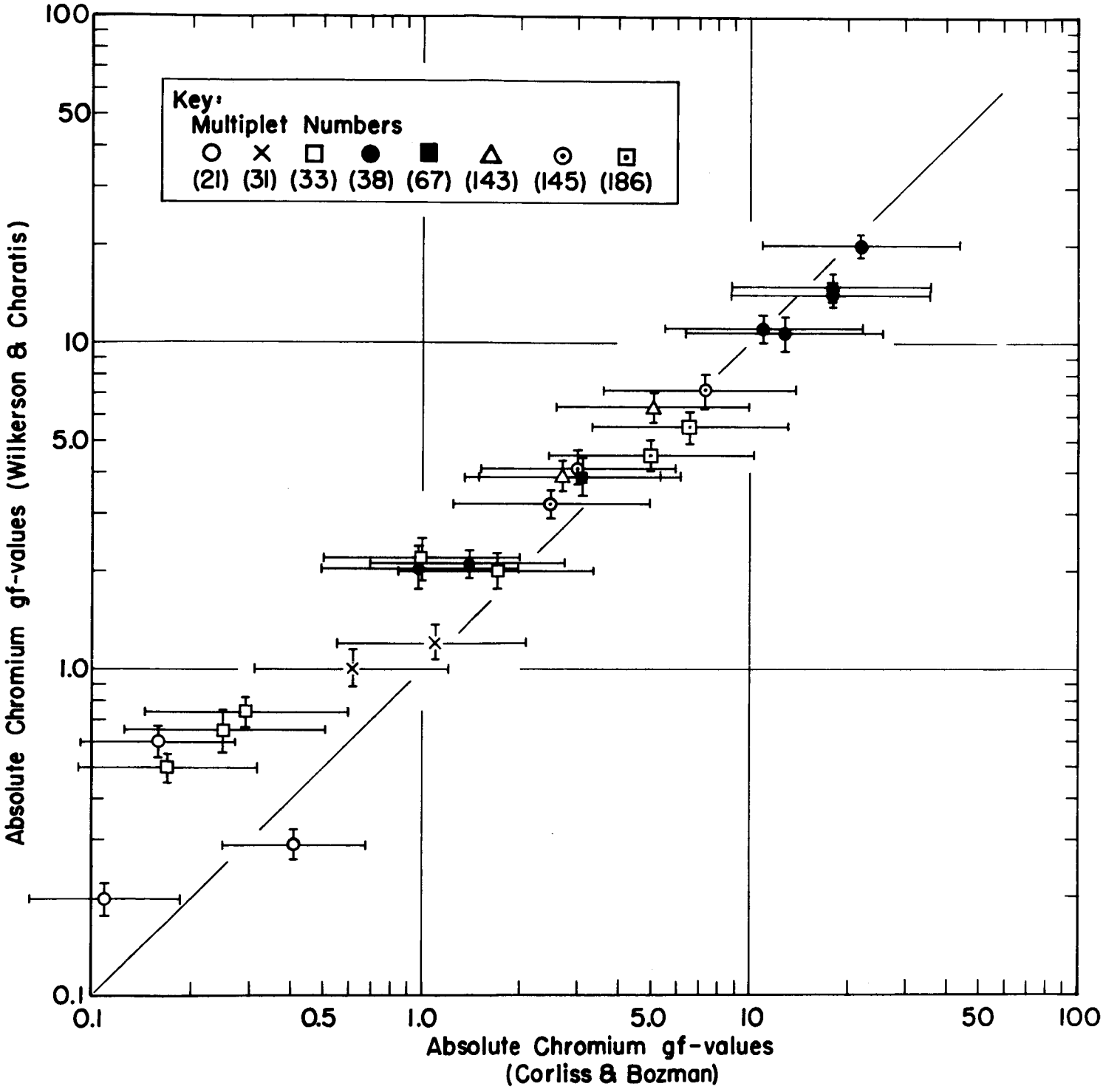
Institute for Fluid Dynamics and Applied Mathematics University of Maryland

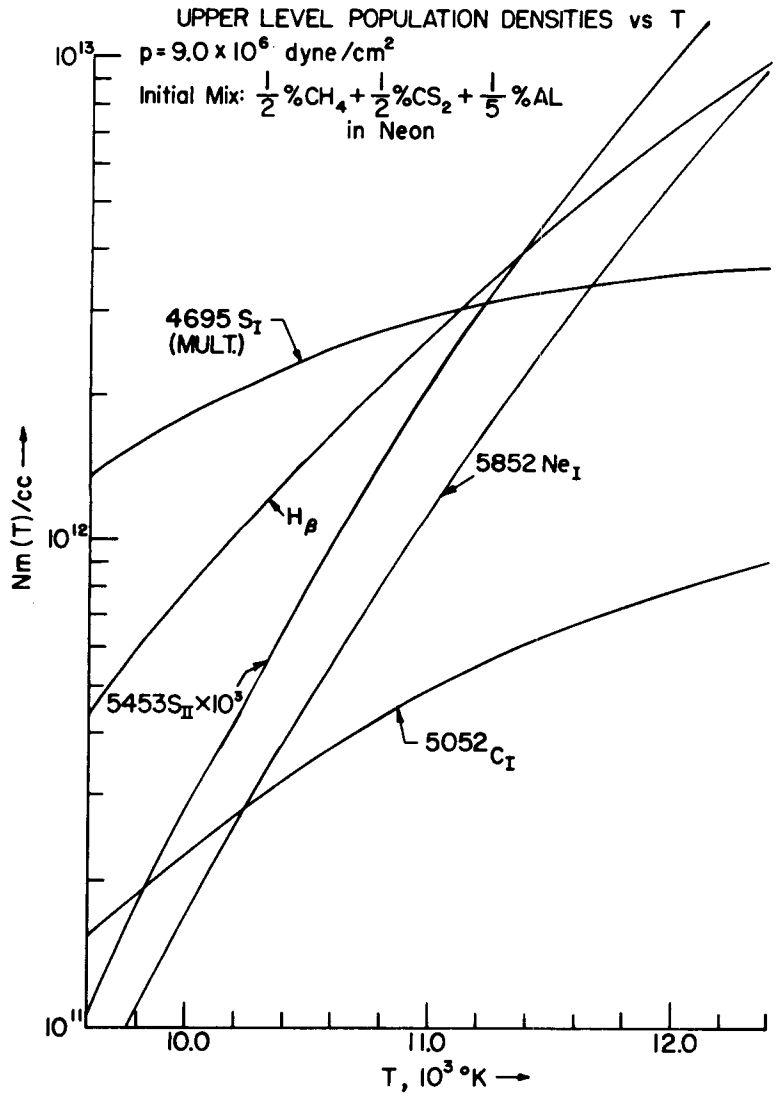
FIRST
REFLECTED
SHOCK
C I
λ5052
Hβ
λλ4861
S I
λλ4695
TIME

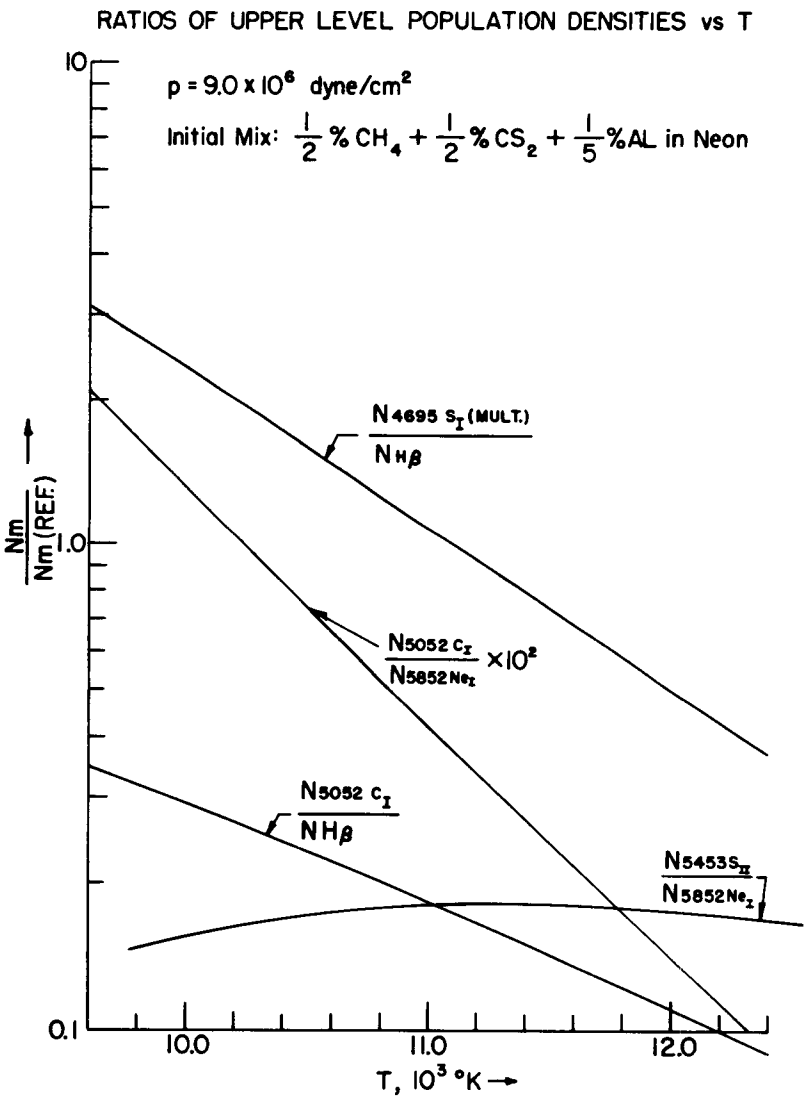


UPWARD ADJUSTMENTS OF $I\lambda^3/gf$ ARE DERIVED FROM SHIFTS IN LOG_{10} (gf) INDICATED BY CURVES OF GROWTH.

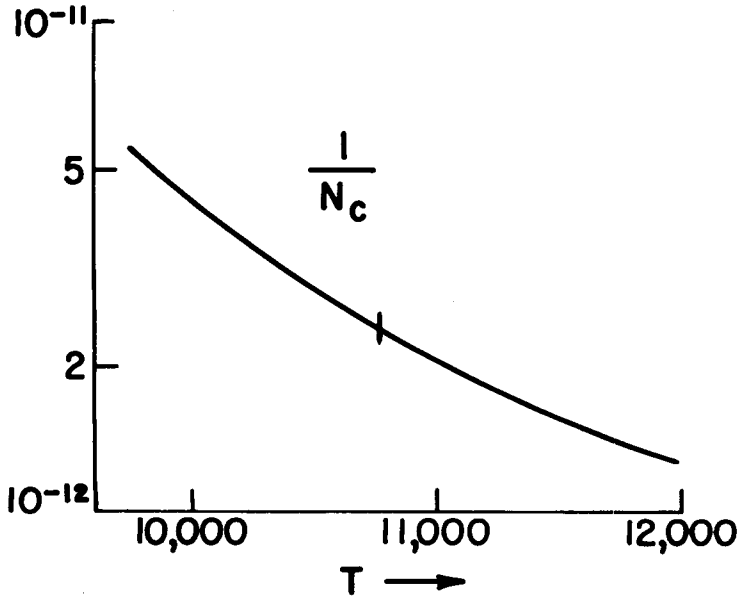

55
60
65
70
75
80
85
r_0
11,000°K
T_2
9,000
7,000
Solid Curves from Detailed Computer Calculations
Points from Approximate Hand Calculations
$n(\mathrm{Cr\,I}) \cdot \frac{e^{-E_i/KT}}{Z(\mathrm{CrI})}$
cm^{-3}
±10%
Multiplet
10^9
21
31
33
143
145
186
10^8
10^7
$p_0 = 1.03 \times 10^4$ dynes/cm^2
$T_0 = 295$ °K
$\eta\left[Cr(CO)_6\right] = 2.66 \times 10^{-4}$
$r_0 = \frac{p_0}{\rho_0} u^2 = (u_i)^2$ (Markstein)

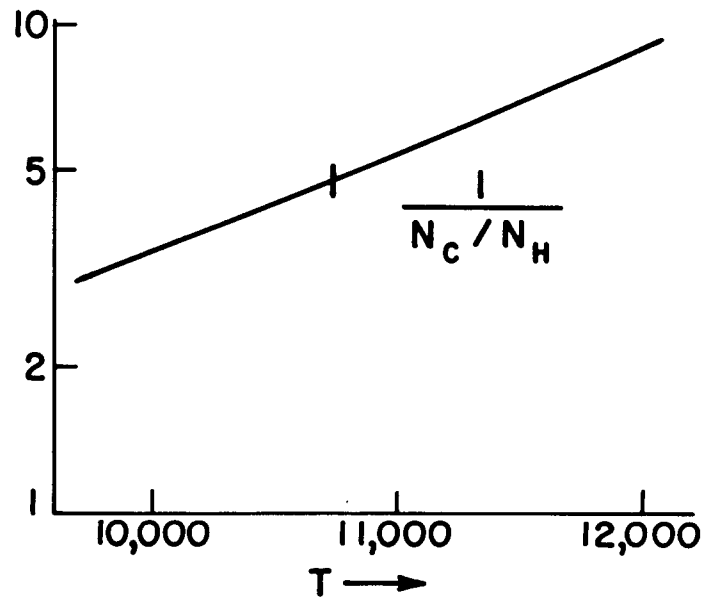

Key:
Multiplet Numbers
(21) (31) (33) (38) (67) (143) (145) (186)
100
50
10
5.0
1.0
0.1
0.1
0.5
1.0
5.0
10
50
100
Absolute Chromium gf-values (Wilkerson & Charatis)
Absolute Chromium gf-values
(Corliss & Bozman)


UPPER LEVEL POPULATION DENSITIES vs T
p = 9.0 x 10^6 dyne/cm^2
Initial Mix: 1/2 %CH4 + 1/2 %CS2 + 1/5 %AL in Neon
4695 SI (MULT.)
Hβ
5852 NeI
5453SII×10^3
5052 CI
Nm (T)/cc
10^13
10^12
10^11
10.0
11.0
12.0
T, 10^3 °K


RATIOS OF UPPER LEVEL POPULATION DENSITIES vs T
p = 9.0 x 10^6 dyne/cm^2
Initial Mix: 1/2 % CH4 + 1/2 % CS2 + 1/5 %AL in Neon
N4695 SI (MULT.) / NHβ
N5052 CI / N5852 NeI ×10^2
N5052 CI / NHβ
N5453SII / N5852 NeI
Nm / Nm (REF.)
10
1.0
0.1
10.0
11.0
12.0
T, 10^3 °K

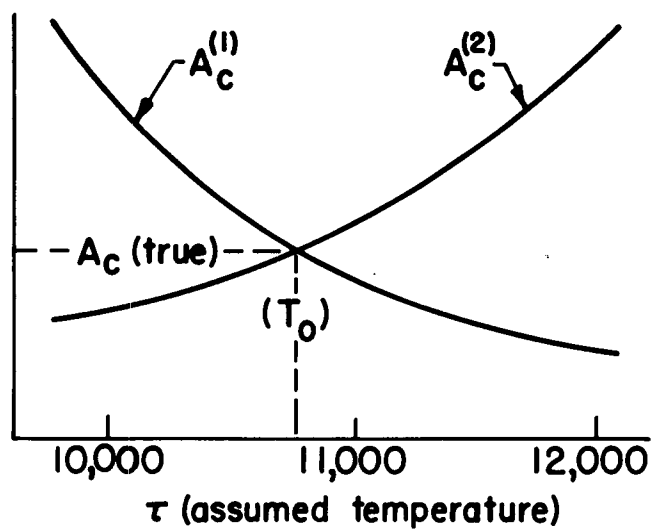
General results for a given mixture and pressure





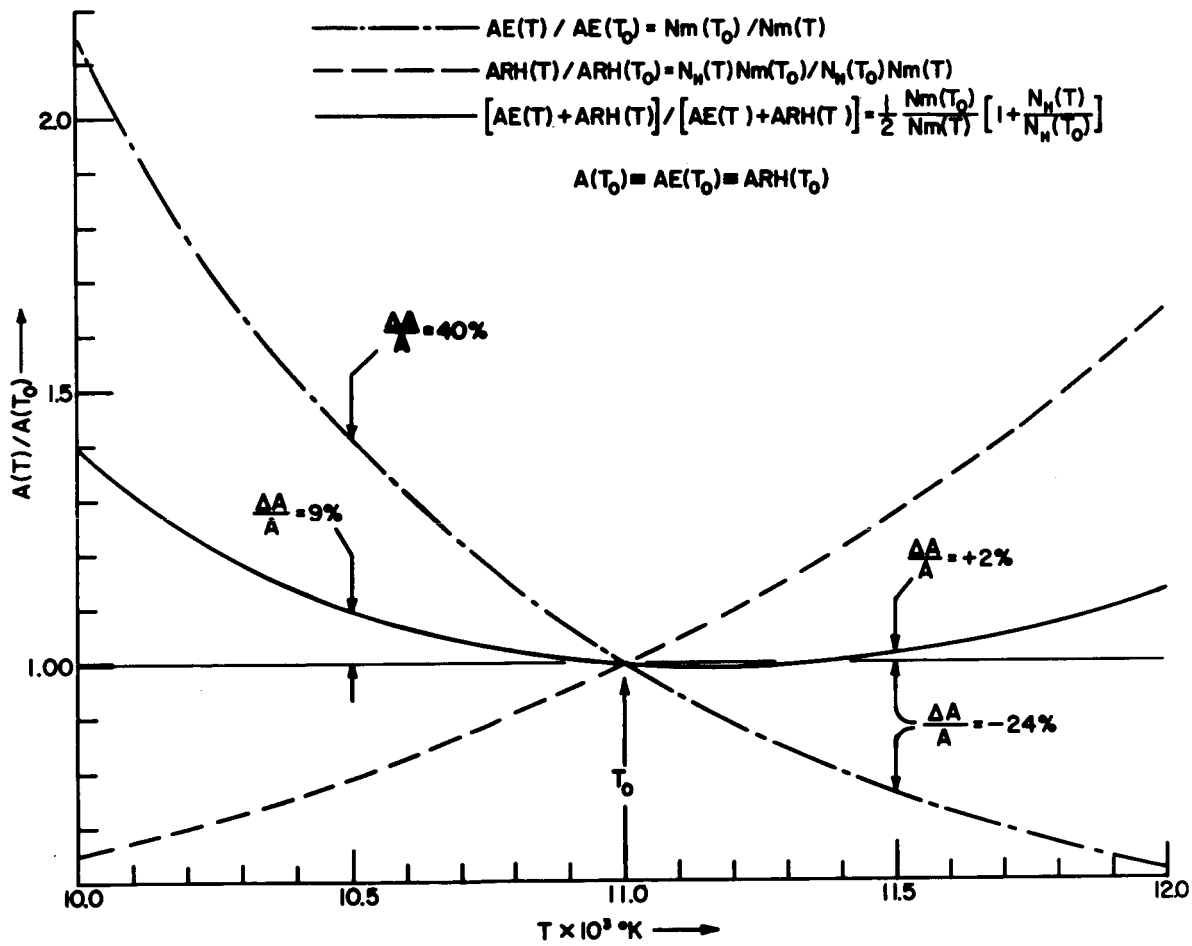
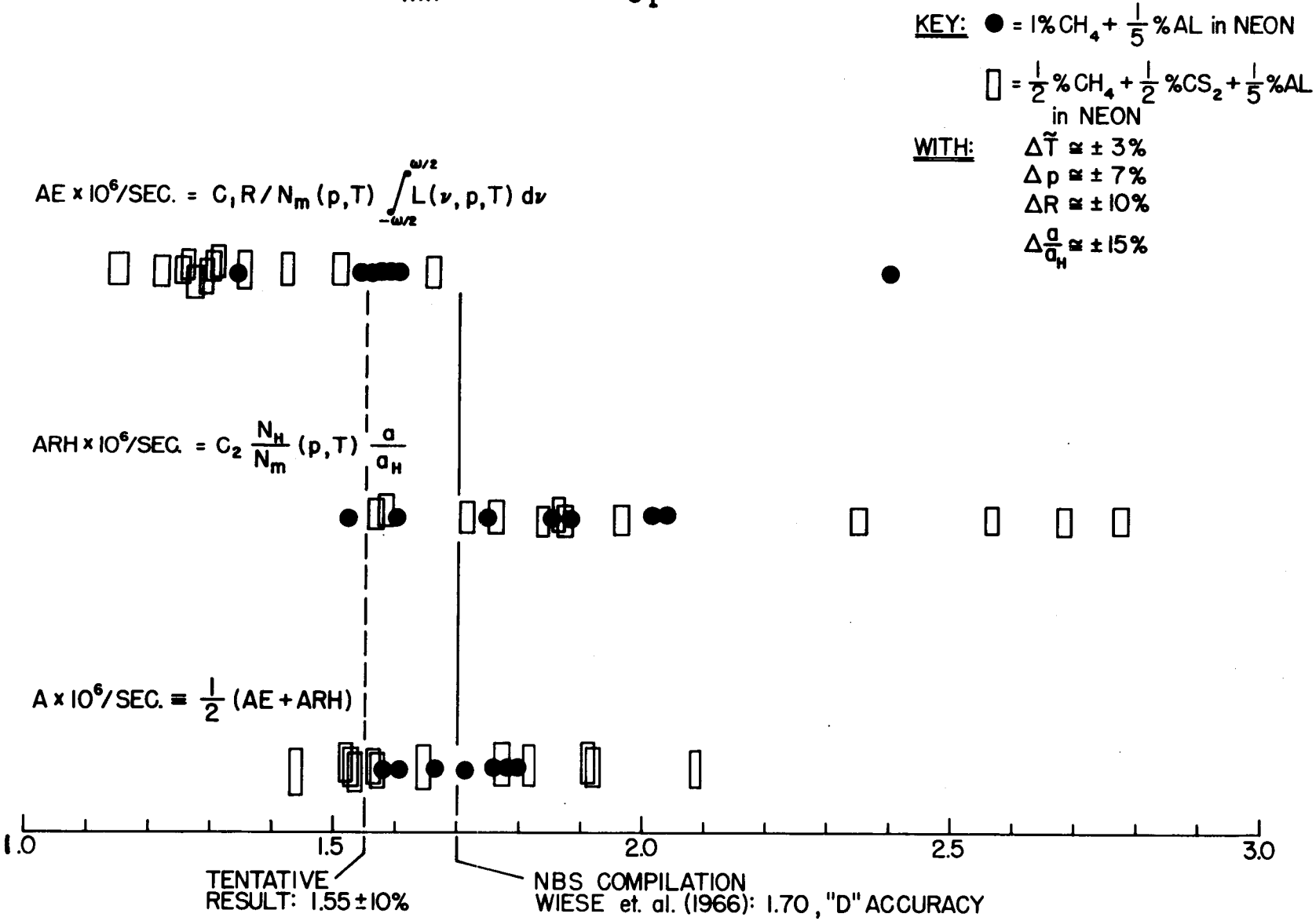
Particular Experiment (Temperature T_0)

$$A_C^{(1)} = \underbrace{\frac{I_C}{h l \nu_C}}_{\text{Observation 1}} \cdot \frac{1}{N_C}$$



$$A_C^{(2)} = \underbrace{\frac{A_H}{\nu_C/\nu_H} \frac{I_C}{I_H}}_{\text{Observation 2}} \cdot \frac{1}{N_C / N_H}$$

THERMAL ERROR PROPAGATION IN AE, ARH, $\frac{1}{2}$(AE + ARH) OF CI λ 5052, PLASMA OF INITIAL COMPOSITION $\frac{1}{2}$%CH_4 + $\frac{1}{2}$%CS_2 + $\frac{1}{5}$%AL IN NEON, AT $p = 9.0 \times 10^6$ dyne/cm², TRUE TEMPERATURE (T_0) = 11,000 °K



RESULTS FOR A_{mn} OF 5052_{C_I}