PHYSICAL REVIEW A VOLUME 14, NUMBER 5 NOVEMBER 1976

Transition probabilities of Br II†

Roger D. Bengtson
Department of Physics, The University of Texas at Austin, Austin, Texas 78712

Myron H. Miller
Institute for Fluid Dynamics and Applied Mathematics, The University of Maryland, College Park, Maryland 20742

(Received 23 June 1976)

Absolute transition probabilities of the three most prominent visible Br II lines are measured in emission. Results compare well with Coulomb approximations and with line strengths extrapolated from trends in homologous atoms.

I. INTRODUCTION

Line strengths[1] of the lighter elements have been intensively investigated, but few accurate experimental results are available for the ions of heavier elements. This type of measurement is important in assessing the validity of theoretical calculations when applied to heavier elements where configuration interactions, relativistic corrections, and intermediate coupling may be important. In this investigation we measure the transition probability of the three strongest lines of Br II and compare our results with the Coulomb approximation and with trends[2] in homologous atoms.

II. EXPERIMENTAL

A well-instrumented gas-driven shock tube was the emission source for time-resolved photographic photometry. Descriptions of the apparatus are given in several earlier papers[3,4]; this account deals mainly with features specific to the Br II measurements. This investigation extends a systematic study on the halogens (F I, Cl I, Cl II, Br I) reported previously.[4] Insufficient wavelength resolution and contrast problems with recording emulsions prevented the earlier work from dealing with the possibility of radiative trapping of the narrow and bright Br II lines. Improved spectrographs, a fast acting optical shutter,[5] and a program to optimize test gas composition–exposure-time tradeoffs have overcome this difficulty.

The test gas was 10–30 Torr of neon with 0.1–0.3% methyl bromide (CH_3Br) added. This gave good signal-to-noise ratios for the leading Br II lines and H_β, allowed for good photographic exposures within steady-state test times (30–70 μ sec), and kept the observed radiation optically thin. Prior testing[3] showed that the emitting plasmas behind reflected shock waves were homogeneous with respect to density and temperature.

Multichannel photoelectric recording was used to measure a neon line excitation temperature, and, in conjunction with a backlighting flashlamp, a line reversal or blackbody temperature. In addition, a third temperature was deduced from the width of the photographically recorded H_β profile and the total gas pressure. These three temperatures in most experiments grouped within ±5–6% of their mean. Their average is then reliable to 4% per run. Plasma pressure was measured by calibrated quartz transducers.

The bromine lines, H_β, and the neon red lines were redundantly recorded by two photographic spectrographs having overlapping wavelength coverage. These instruments had resolutions of 0.3 and 2.0 Å and generally used different emulsion types (Kodak I-F, 2475). Both used the same fast mechanical shutter.[5] After editing for over- or under-exposure, 14 spectrograms were available for Br II line-strength determination. By fitting to Voigt shapes in the wings, the area of a typical profile could be measured with a precision of 20%.

Although our photometry was connected to a calibration standard, we avoided applying the usual emission method of measuring line strengths as it would entail a critical sensitivity to error in the measured temperature. Figure 1 shows that 4% uncertainty in temperature data transforms to a factor of 2 error in the upper-state population of bromine ions. To circumvent this sensitivity and to guard against wall absorption prior to shock-tube firing, the Br II strengths were measured relative to the known strengths of other prominent lines as H_β and Ne I 5852 Å. That is, from the ratio of integrated intensities $I_{\mathrm{Br\,II}}/I_{\mathrm{ref}}$ of a bromine line to some line whose transition probability A_{ref} serves as a reliable reference, one obtains

$$A^{\mathrm{rel}}_{\mathrm{Br\,II}} = \frac{N_{\mathrm{ref}}}{N_{\mathrm{Br\,II}}} \frac{I_{\mathrm{Br\,II}}}{I_{\mathrm{ref}}} \frac{\lambda_{\mathrm{Br\,II}}}{\lambda_{\mathrm{ref}}} A_{\mathrm{ref}} ,$$

where $N_{\mathrm{ref}}/N_{\mathrm{Br\,II}}$ is the ratio of excited-state den-

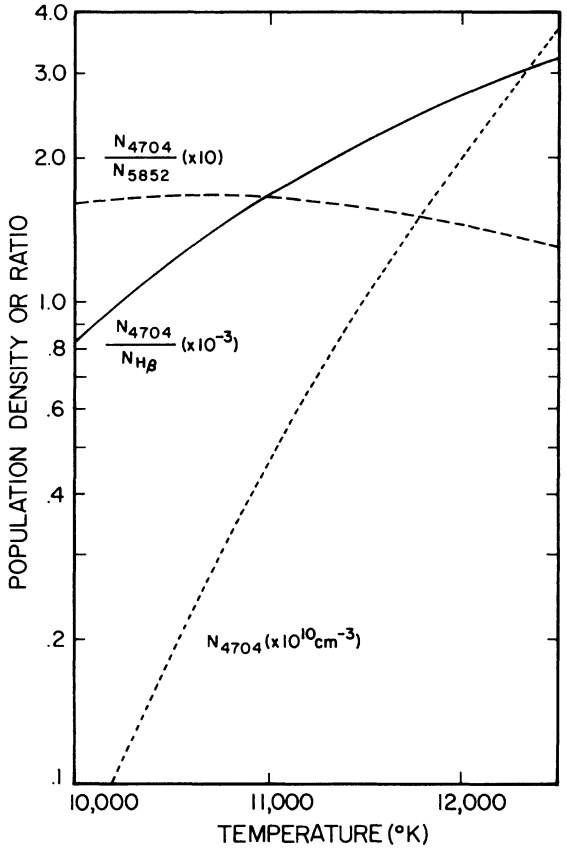

FIG. 1. Excited-state populations and population ratios of some prominent emission lines shown as functions of plasma temperature. Pressure and composition are typical of the shock-tube experiments.

sities. Using the bright neon line at 5852 Å for a reference[6] markedly reduces the consequences of a temperature mismeasurement as can be seen from Fig. 1. The strategy of adopting a neon line strength as an internal standard cuts susceptibility to thermal error, but any unintentional loss of methyl bromide, such as wall interactions prior to firing, will propagate bias directly into the measured Br II line strength. For this reason, we also used H_β as an internal A value reference even though this involves a modest susceptibility to thermal error (see Fig. 1). The hydrogen to bromine abundance is fixed stochiometrically so that adsorption of CH_3Br would have slight effect on the Br II measurements. Shots fired with no hydrogen additives showed a negligible impurity hydrogen concentration.

When these two methods were applied on a shot by shot basis, results indicated that concentration of CH_3Br at the time of shock heating were invariably less than expected from ratios of partial pressures during the gas preparation. Sufficient loss of CH_3Br was taken into account to bring the average of the two A value determinations into coincidence. The result adopted is the linear combination of the two thermally insensitive results. To test the validity of this method for dealing with the methyl bromide loss, we measured the absolute A value of H_β in emission. This result should be sensitive to both errors in temperature and in hydrogen abundance. Scatter was comensurate with what one would expect from a ±4% random thermal error and 20% photometric reading error. On the average, the measured and known transition probabilities of the H_β lines agreed to better than 10%. It is not expected that wall absorption of methyl bromide affected earlier results[4] because the concentrations of methyl bromide were a factor of 5 to 10 larger.

TABLE I. Measured Br II transition probabilities.

Transition	J_n-J_m	λ (Å)	A_{mn} (10^8 sec^{-1})
$5s\,^5S$-$5p\,^5P$	2-3	4704.92	1.05±35%
	2-2	4785.48	0.94±35%
	2-1	4816.68	1.05±35%

III. RESULTS AND DISCUSSION

Measured Br II transition probabilities are given in Table I. Our uncertainties are expressed as 67% confidence limits and are based on estimates of possible experimental bias and on statistical analysis of scatter. Regularities in line strength have been noted for atoms with homologous structure (same number of optically active electrons). The strengths of similar dominant arrays are expected to change gradually[2,7] between successive entries in a column of the periodic table. This behavior is demonstrated in Table II for the prominent $np^3(n+1)s\,^5S$-$np^3(n+1)p\,^5P$ transition array for F II,[6] Cl II [6] and Br II. To broaden the base of comparison, we have included neighboring mem-

TABLE II. Multiplet f values of $np^3(n+1)s\,^5S$-$np^3(n+1)p\,^5P$ transitions.

O I 0.92[a]	F II 0.84[a]	Ne III 0.76[a]
S I 1.1[a]	Cl II 1.19[a]	Ar III 0.99[a]
	Br II 1.05,[b] 1.1[c]	

[a] Reference 6.
[b] This work.
[c] Coulomb approximation, Ref. 8.

bers of isoelectronic sequences which demonstrate the same behavior. As another point of comparison, the Coulomb approximation[8] predicts a multiplet f value of 1.1 which is in agreement with both our measurements and with the trends.

ACKNOWLEDGMENTS

The authors wish to acknowledge the support and encouragement of T. D. Wilkerson and D. W. Koopman.

---

†Research supported in part by NASA Grant No. NGR44-012-258 and by the Robert A. Welch Foundation.

[1]B. M. Miles and W. L. Wiese, Natl. Bur. Std. Spec. Publ. 320 (1970).

[2]W. Wiese and A. W. Weiss, Phys. Rev. 175, 50 (1968); also, M. W. Smith and W. L. Wiese, Astrophys. J. Suppl. Ser. 196, 103 (1971).

[3]R. D. Bengtson, M. H. Miller, D. W. Koopman, and T. D. Wilkerson, Phys. Fluids 13, 327 (1970); also, M. H. Miller, R. A. Roig, and R. D. Bengtson, Phys. Rev. A 4, 1709 (1971); M. H. Miller, T. D. Wilkerson, R. A. Roig, and R. D. Bengtson, Phys. Rev. A 9, 2312 (1974).

[4]R. D. Bengtson, M. H. Miller, D. W. Koopman, and T. D. Wilkerson, Phys. Rev. A 3, 16 (1971).

[5]S. M. Wood and M. H. Miller, Rev. Sci. Instrum. 41, 1196 (1970).

[6]W. L. Wiese, M. W. Smith, and B. M. Glennon, *Atomic Transition Probabilities*, NSRDS-NBS 4 (U.S. GPO, Washington D. C., 1966). W. L. Wiese, M. W. Smith, and B. M. Miles, *Atomic Transition Probabilities, 2,* NSRDS-NBS 22 (U.S. GPO, Washington D. C., 1969).

[7]J. Migdalek, J. Quant. Spectrosc. Radiat. Transfer 16, 265 (1976).

[8]G. Oertel and L. P. Shomo, Astrophys. J. Suppl. Ser. 6, 175 (1968).