[13]W. C. Kerr, K. N. Pathak, and K. S. Singwi, Phys. Rev. A (to be published).

[14]R. A. Cowley and A. D. B. Woods, Phys. Rev. Letters 21, 787 (1968).

PHYSICAL REVIEW A VOLUME 4, NUMBER 1 JULY 1971

Measurement of Transition Probabilities for O I in the Vacuum Ultraviolet

W. R. Ott*
National Bureau of Standards, Washington, D. C. 20234
(Received 13 November 1970)

Transition probabilities for O I lines emitted in the vacuum ultraviolet were measured using a wall-stabilized arc discharge operating in a mixture of argon and oxygen. The lines were emitted from a column of plasma which was observed end-on and which was characterized by a nearly uniform temperature. Optically thin conditions were achieved by reducing the relative concentration of oyxgen atoms in the discharge to levels of less than one part per million. Absolute values for the O I transition probabilities were obtained by determining the oxygen-atom density and plasma length through a measurement of the absolute intensity of the O I $\lambda = 7773.4$ Å line, whose transition probability is known. The following values were measured for lines in the resonance transition array: $A(^1D_2\text{-}^1D_2^\circ$, $\lambda = 1152$ Å$) = 5.5 \times 10^8\ \text{sec}^{-1}$; $A(^1S_0\text{-}^1P_1^\circ$, $\lambda = 1218$ Å$) = 1.8 \times 10^8\ \text{sec}^{-1}$; $A(^3P_0\text{-}^3S_1^\circ$, $\lambda = 1306$ Å$) = 0.66 \times 10^8\ \text{sec}^{-1}$; $A(^3P_{2,1,0}\text{-}^3S_1^\circ$, $\lambda = 1303.5$ Å$) = 5.9 \times 10^8\ \text{sec}^{-1}$. These values are in excellent agreement with recent lifetime measurements. Existing discrepancies in the literature concerning a previous arc determination of the O I vacuum ultraviolet oscillator strengths by Boldt and Labuhn are discussed. The present method is considered to be an improvement over the method used by Boldt and Labuhn which relied, first of all, upon extrapolation techniques to reach the linear part of the curve of growth and, secondly, upon a complex calculation of the oxygen-atom number density using basic conservation equations.

I. INTRODUCTION

Transition probabilities for O I lines emitted in the vacuum ultraviolet have been measured using a wall-stabilized arc discharge. In particular, the following wavelengths associated with the resonance transition array were studied: 1152, 1218, 1302, 1305, and 1306 Å. These lines have previously been investigated using electron excitation phase-shift techniques, absorption spectroscopy, beam-foil lifetime determinations, and arc emission methods. Nevertheless, there exists in the literature a rather wide range of f values for these transitions.

Several measurements of the $^1D_2\text{-}^1D_2^\circ$ transition at $\lambda = 1152$ Å have been reported. The lifetime measurements[1-3] agree almost exactly with one another and correspond to a transition probability value of $5.3 \times 10^8\ \text{sec}^{-1}$. Boldt and Labuhn,[4] using a dc wall-stabilized arc discharge, obtained a value of $16.5 \times 10^8\ \text{sec}^{-1}$, a very puzzling discrepancy since several N I[5] and C I[6] transition probabilities obtained using the identical method are in much better agreement with the various lifetime measurements.

There has been only one reported direct measurement of the $^1S_0\text{-}^1P_1^\circ$ transition at $\lambda = 1218$ Å: Boldt and Labuhn[4] obtained a transition probability of $4.3 \times 10^8\ \text{sec}^{-1}$. However, Lawrence[2] has measured the lifetime of the $^1P_1^\circ$ level and, having assumed a branching ratio of 0.34 for $^1S_0\text{-}^1P_1^\circ$ decay out of the $^1P_1^\circ$ level, he has found it to be inconsistent with the arc measurement. If in addition autoionization processes are significant as Lawrence has suggested, the discrepancy between the two experiments is even greater.

The resonance triplet $^3P\text{-}^3S^\circ$ has been the object of much attention mainly because of its aeronomical significance. An accurate determination of its transition probability is useful also for plasma diagnostic purposes, since the resonance triplet is readily observed in laboratory plasmas in which trace amounts of oxygen are present. There exists in the literature an order-of-magnitude spread between the oscillator strength of 0.021 reported by Parkes *et al.*[7] using absorption techniques and the oscillator strength of 0.18 reported by Boldt and Labuhn.[4] Lin *et al.*[8] have recently repeated the absorption measurement and obtained an oscillator strength of about 0.045 in apparent agreement with the current lifetime measurements of Lawrence.[2] There still remains, therefore, a discrepancy of about a factor of 4 between these values and the arc measurement. Since the wall-stabilized arc discharge is generally a rather reliable source for determining transition probabilities, it was decided to reexamine the oxygen vacuum ultraviolet (vuv) lines emitted in an arc discharge in order to resolve the existing discrepancies. At the same time it was decided to replace the complex plasma diagnostic method of Boldt and Labuhn with a simpler more

direct approach.

II. METHOD

The total intensity I_{nm} of a spectral line emitted from an optically thin layer of plasma of length l is related to its transition probability A_{nm} by

$$I_{nm} = (1/4\pi) A_{nm} (hc/\lambda_{nm}) N_n l \ , \qquad (1)$$

where N_n is the number density of atoms in the upper state n and λ_{nm} is the wavelength. It has been demonstrated previously that a wall-stabilized arc discharge operating under the conditions of this experiment is in local thermodynamic equilibrium[9,10] and therefore the upper-state population may be described by the Maxwell-Boltzmann factor

$$N_n = g_n N_0 e^{-E_n/kT}/U(T) \ , \qquad (2)$$

where N_0 is the number density of atoms, $U(T)$ is the partition function at temperature T, and g_n is the statistical weight of the upper state whose excitation energy is E_n. By applying Eqs. (1) and (2) to one line of known and one of unknown transition probability of the same element, the product $N_0 l$ is effectively determined and one obtains

$$A_x = A_s (I_x/I_s)(g_s/g_x)(\lambda_x/\lambda_s) e^{(E_x - E_s)/kT} \ , \qquad (3)$$

where the subscript x refers to the unknown transition probability and the subscript s refers to the "standard" or reference transition probability. For the spectral lines emitted at $\lambda_x = 1306$ Å and $\lambda_x = 1218$ Å, the standard line was chosen to be the O I $\lambda_s = 7773.4$ Å multiplet whose transition probability according to the NBS Data Evaluation Center is estimated to be accurate to $\pm 10\%$.[11] In the case of the line emitted at $\lambda_x = 1152$ Å, such small quantities of oxygen were required to obtain optically thin conditions that the O I $\lambda = 7773.4$ Å multiplet was not observable. Therefore, the $\lambda_s = 1306$ Å line was chosen as the reference.

The conditions for optically thin emission at the line centers of $\lambda_x = 1306$ Å and $\lambda_x = 1218$ Å were determined by requiring that the intensity ratio I_x/I_s be constant as a function of the oxygen flow rate. The O I $\lambda_s = 7773.4$ Å multiplet itself was checked to be optically thin over this range of flow rates by observing the triplet lines to be in the ratio of 7 : 5 : 3. This ratio, calculated for an emitting plasma at $T = 11\,600$ K, is given essentially by the ratio of the g_J degeneracies in the upper ^5P levels. The conditions for optically thin emission at $\lambda_x = 1152$ Å were determined by requiring the ratio of the $\lambda_x = 1152$ Å line intensity to the $\lambda_s = 1306$ Å line intensity to be constant as the system was "cleaned up." This was accomplished by operating the discharge in pure argon and reducing the oxygen-bearing contaminants in the arc by increasing the purging efficiency with higher argon flow rates.

Absolute intensity measurements in the visible were carried out by calibrating the optical system with a tungsten strip lamp whose spectral intensity distribution had been calibrated to approximately $\pm 1\%$ accuracy by the Radiation Thermometry Section at NBS. Absolute intensity measurements in the vuv were carried out by using the arc itself as its own radiation standard.[12] Blackbody intensities at the wavelengths of interest and at the known arc temperature were produced by slightly increasing the oxygen concentration in the argon-oxygen mixture so that the line centers of $\lambda = 1152$ Å and of the resonance triplet are optically thick. The blackbody limit of the $\lambda = 1218$ Å line was determined by introducing small amounts of hydrogen into the discharge and observing the blackbody-limited central part of the Lyman α line of hydrogen. The blackbody limits so determined were checked by adding nitrogen to the arc discharge, observing the blackbody limits of N I lines emitted at $\lambda = 1135$, 1169, 1200, and 1320 Å, and extrapolating to the wavelengths of interest. Complete consistency was obtained. The present experimental method therefore includes the following improvements over the methods used in the arc experiment of Boldt and Labuhn: (i) Photoelectric data-logging techniques were used instead of photographic methods; (ii) a direct measurement of the product of the oxygen-atom number density and the plasma length using spectrometric methods was used instead of a complex calculation of the number densities of the constituents of a two-component plasma; (iii) a sufficiently pure argon arc was produced so that optically thin conditions could be achieved for all the oxygen lines studied. The oxygen-bearing contaminants in the experiment of Boldt and Labuhn were such that it was usually necessary to extrapolate to the linear part of the curve of growth; (iv) in order to calibrate the intensity scale for the vuv oxygen lines, blackbody limits were determined directly at the wavelengths of interest rather than by extrapolation from blackbody limits measured at other wavelengths.

III. EXPERIMENTAL

The light source used in this experiment is a wall-stabilized arc discharge operating at atmospheric pressure either in pure argon or in argon with a very small admixture of oxygen. Figure 1 shows a schematic of the arc and associated equipment. The 6-cm arc is struck between a tungsten cathode and anode and is constricted by a series of 5 thin closely spaced water-cooled discs with 4.8-mm-diam apertures. All parts exposed to the arc are constructed of copper and are free of any solder joints. The electrically insulating spacers are Teflon gaskets which also serve to seal the arc apparatus from the atmosphere. There are ten

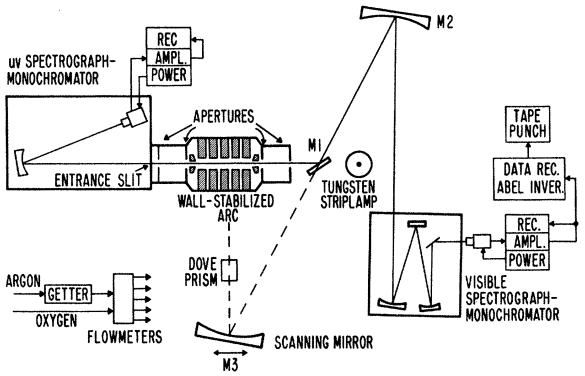

FIG. 1. Experimental apparatus and schematic of optical system.

gas inlets and four outlets strategically located so that gas enters and leaves the apparatus at "dead-end" regions where pockets of air or evolving contaminants might be purge resistant. The outlet ports were vented to the atmosphere through 20-cm lengths of tubing to prevent diffusion of air into the arc. End-on measurements in the vuv were taken with a 3-m normal incidence Eagle mount monochromator and a cooled sodium-salicylate-coated-type 1P21 photomultiplier tube. The entrance and exit slit widths were normally 20 and 125 μ, respectively, and admitted a wavelength band of about 0.3 Å. The discharge was observed through a LiF window and two precisely located 0.8-mm apertures located between the arc and the spectrometer. These apertures along with the entrance slit of the monochromator permit observations of the radiation emitted from a very narrow cone about the arc axis where the temperature varied less than 2%.

End-on measurements in the visible were taken with a $\frac{3}{4}$-m Czerny-Turner monochromator and a type S-20 photomultiplier tube. Normally, the entrance slit was 60 μ and the exit slit was 800 μ, admitting a wavelength band of approximately 8 Å. The exit slit width was decreased to provide a more suitable bandpass whenever H_β diagnostic studies were carried out or whenever it was necessary to resolve the $\lambda = 7773.4$ Å multiplet. The optical system was designed to view the discharge region in the same way as the vuv optical system: the entrance slit was imaged outside the discharge region and the solid angle was determined by masks on the entrance slit and the spherical front surface mirror M2. Rotation of the plane front surface mirror M1 allowed for spectroscopic observations of either the discharge or the calibrated tungsten strip lamp.

A titanium-zirconium alloy getter chamber heated to 800–1000 °C was used to trap oxygen, nitrogen, and water-vapor impurities in the argon-gas handling system. Typically, the total argon flow rate into the 10 inputs was about 3000 cm^3/min. For a pure argon plasma under these conditions the oxygen-atom concentration was measured to be approximately 2 ppm. This result was obtained by using Eqs. (1) and (2) and comparing the Ar I $\lambda = 4300$ Å and the O I $\lambda = 1306$ Å line intensities assuming equal lengths of emitting plasma and the NBS Data Center transition probabilities.[11,13] In order to reduce the oxygen-bearing contaminants to a level of less than 1 ppm, it was necessary to increase the total flow rate to approximately 12000 cm^3/min. Figure 2 illustrates successive scans of the O I resonance triplet lines as a function of argon flow rate. It can be seen that the intensity ratios vary from 3.4 : 2.5 : 1 to 4.1 : 2.7 : 1 to 5 : 3 : 1 as the flow rate varies from 3000 to 6000 to 12000 cm^3/min. The ratios are all taken with respect to the $\lambda = 1306$ Å line intensity. This purging effect demonstrates that oxygen-bearing contaminants internal to the arc, such as outgassing materials and pockets of air located in stagnant regions of the arc apparatus, are the main source of background oxygen atoms and that under certain conditions their concentration can be large enough for absorption to take place. Figure 3 illustrates the triplet lines with the entrance and exit slits increased to allow an improved signal-to-noise ratio. The recording does not represent the true line shape, but the triplet lines are clearly observed in the intensity ratio of 5 : 3 : 1. Further increase in flow rates or getter temperature reduced the signal strength but did not affect the intensity ratios.

In order to determine blackbody intensities at the various line centers, the foreign gas, either oxygen, nitrogen, or hydrogen, was mixed with

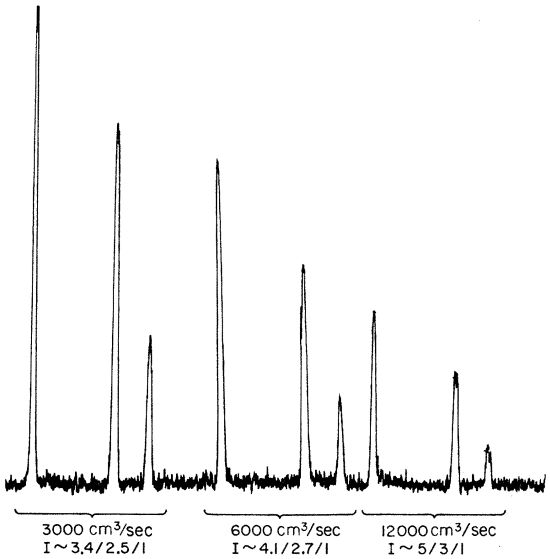

FIG. 2. Relative line intensities of O I resonance triplet as a function of argon flow rate.

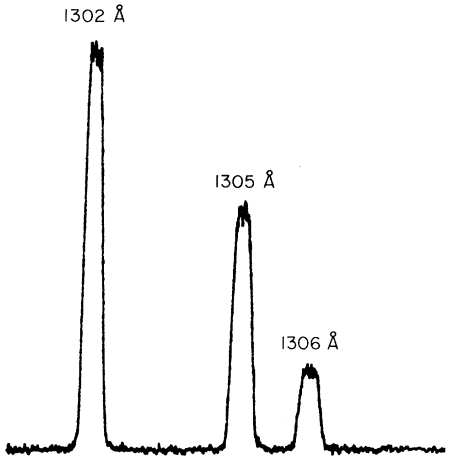

FIG. 3. Relative line intensities of O I resonance triplet under optically thin conditions.

the argon gas flowing into the central sections of the arc column. The flow rates were adjusted so that the gas mixture was forced out of the column by way of the exit ports before it reached the cooler layers about the anode where self-reversal could take place. The Ar I $\lambda = 4300$ Å line intensity was monitored in order to determine possible temperature changes when the foreign gases were admitted to the arc.

Several temperature determinations were carried out on the arc discharge. A small admixture of hydrogen, less than 1% by volume, was added to the argon gas flowing into the central sections of the arc and the full half-width of the H_β line intensity was measured, both end-on and side-on.[10] The latter required an Abel inversion which was accomplished by scanning across the arc with a translating spherical mirror M3 as shown in Fig. 1. The Abel inversion technique for resolving the radial intensity distribution has been described elsewhere.[10] For an arc current of about 50 A, a full half-width of 33 Å was obtained for the $r = 0$ axial position in the Abel program. Using the calculations of Kepple and Griem[14] for the Stark broadening of H_β, an electron density $Ne = 5.6 \times 10^{16}$ cm^{-3} was obtained, corresponding to a temperature $T = 11\,700$ K. The same results were obtained with end-on measurements of the half-width of the H_β line intensity. This consistency is a necessary condition if reliable end-on determinations of transition probabilities are to be made, for it verifies that the aperture of the optical system is sufficiently small to define a cone of emitting plasma with a nearly uniform temperature characteristic. It also indicates that the arc column is cylindrical and the optical systems are well aligned.

End-on and side-on measurements of the Ar I $\lambda = 4300$ Å line intensity were also taken. Assuming a transition probability[13] of $0.003\,94 \times 10^8$ sec^{-1} and the electron density measured above, a temperature $T = 11\,500$ K was typically obtained.

Temperature averages using the above two methods were taken during each experimental run in order to analyze the data for that run. For example, in the case just described, $T = 11\,600 \pm 100$ K would have been used as the arc temperature for end-on determinations of transition probabilities.

IV. RESULTS

The measured values of the transition probabilities A_{nm} for the optically thin O I vuv lines emitted at $\lambda = 1152$, 1218, and 1306 Å, as well as the absorption oscillator strengths corresponding to them, are listed in Table I. These values represent the average of several independent runs for which the rms deviation was calculated to be ±10%. There exists in addition an uncertainty in these measurements due to known uncertainties in the quantities in Eq. (3) which were used in the calculations.

The line intensity I_x contains the major source of error. It is determined by calculating

$$I_x = (R_x/R_x^{BB})(w_2/D) I_x^{BB}(T) , \qquad (4)$$

where R_x is the signal strength for optically thin line emission at λ_x, R_x^{BB} is the signal strength for blackbody limit at λ_x, w_2 is the exit slit width, D is the reciprocal dispersion of monochromator in mm/Å, $I_x^{BB}(T)$ is the calculated intensity at λ_x for a blackbody at temperature T (W/cm^3 sr). The standard deviation for each of the measurements R_x and R_x^{BB} was about ±10%, the relatively large uncertainty due primarily to a small systematic drift with time in the measured intensities caused by gradual radiation damage to the vuv transmitting window. The uncertainty of about 1% in the determination of the temperature in the vicinity of the arc axis caused a corresponding uncertainty of about 9–12% in the calculation of $I_x^{BB}(T)$. The cumulative rms error in the quantity I_x is therefore estimated to be ±17%. Similarly, the cumulative error in the quantity I_s is estimated to be ±10%.

TABLE I. Measured transition probabilities and absorption oscillator strengths for O I vuv.

λ(Å)	Multiplet	g_n	g_m	A_{nm} (10^8 sec^{-1})	f_{mn}
1152	$^1D_2$–$^1D_2^\circ$	5	5	5.5	0.11
1218	$^1S_0$–$^1P_1^\circ$	1	3	1.8	0.12
1302	$^3P_2$–$^3S_1^\circ$	5	3	3.3	0.049
1305	$^3P_1$–$^3S_1^\circ$	3	3	2.0	0.049
1306	$^3P_0$–$^3S_1^\circ$	1	3	0.66	0.049
1303.5	^3P –$^3S^\circ$	9	3	5.9	0.049

The error in the exponential term due to the uncertainty in the temperature is relatively small, about 3%. The uncertainty in the reference transition probability A_s is estimated to be ±10% for $\lambda_s = 7773.4$ Å. The over-all estimated rms error in transition probability measurements for $\lambda_x = 1218$ Å and $\lambda_x = 1306$ Å is therefore estimated to be approximately ±23%. The determination of the transition probability for $\lambda = 1152$ Å is however accurate only to ±30%, since the $\lambda = 1306$ Å transition probability was used as a secondary standard.

Table II compares the transition probability results with the most recent data from the literature. Except for the values of Boldt and Labuhn there seems to be excellent agreement for the 1152-Å line and 1304-Å multiplet among the various experiments. The present value for the 1218-Å line is about a factor of 2 less than the value given by Boldt and Labuhn and is consistent with the data analysis of Lawrence. The lifetime of the $^1P^\circ$ level was measured to be 0.9 nsec and according to Lawrence the auto-ionization transition rate is of the same order of magnitude as the radiative decay rate of the $^1S_0$-$^1P_1^\circ$ $\lambda = 1218$ Å transition. Using Lawrence's lifetime, the present value for the transition probability for $\lambda = 1218$ Å radiative decay, and the calculated branching ratio of 0.34 for the $^1S_0$-$^1P_1^\circ$ decay out of the $^1P_1^\circ$ level,[11] one obtains a value $R(\text{auto}) = 5.8 \times 10^8$ sec.

The results of calculations by Garstang,[15] Kelly,[16] and Armstrong *et al.*[17] are also shown in Table II. Garstang considered the effect of spin-spin and spin-other-orbit interactions on the energy levels of the ground-state and excited-state configurations of O I. He also calculated the effect of these perturbations on the oscillator strengths. Garstang showed that with respect to the fine structure in the energy levels of the ground state the interactions were sufficient to explain the observed deviations from the results of LS-coupling given by the Landé interval rule (the deviations in the O I ^3P ground state are about 15%). On the other hand, the interactions had a negligible effect on the oscillator strengths. In particular, the LS-coupling ratios of 5 : 3 : 1 are maintained for the ^3P-^3S resonance triplet in full agreement with this experiment. Garstang obtained the values in Table II by using the Coulomb approximation to calculate an average σ^2 value of 0.15 for the resonance transition array. Kelly obtained his results by assuming LS-coupling and by calculating σ^2 for each individual multiplet using self-consistent field (scf) wave functions. The NBS Data Center transition probabilities were obtained by modifying Kelly's calculations of the oscillator strengths by replacing the calculated scf energy differences involved in the transitions with the observed energy differences. Armstrong *et al.* obtained transition probabilities in very close agreement with Garstang by using the Slater approximation to the Hartree-Fock method to calculate σ^2. These results are also listed in a paper by Wilson and Nicolet.[18]

The difference between the results of Boldt and Labuhn and the results of the present arc experiment must still be explained. First of all, the present results are considered to be more reliable since the experimental method is straightforward and unambiguous. The quantities needed to determine the transition probability A_x in Eq. (3) are either known or are directly measurable. No extrapolations, curve-fitting procedures, or complex iterative calculations are necessary. Secondly, it is very possible that a serious systematic error existed in the Boldt and Labuhn data analysis due basically to the fact that the axis of their arc was not at a uniform temperature. Boldt and

TABLE II. Comparison of present results with available experimental and theoretical determinations of O I vuv transition probabilities.

	1152 Å	1218 Å	1306 Å	1303.5 Å
Ott	5.5×10^8	1.8×10^8	0.66×10^8	5.9×10^8
Boldt and Labuhn (Ref. 4)	16.5×10^8	4.3×10^8	2.3×10^8	21.1×10^8
Morris and Garrison[a]	...	...	...	3.8×10^8
Gaillard and Hesser (Ref. 1)	5.3×10^8	...	...	5.9×10^8
Lawrence (Ref. 2)	5.3×10^8	...	...	5.5×10^8
Smith *et al.* (Ref. 3)	5.6×10^8	...	...	5.6×10^8
Lin *et al.* (Ref. 8)	...	...	0.60×10^8	5.5×10^8
Garstang (Ref. 15)	6.0×10^8	2.3×10^8	0.61×10^8	5.6×10^8
Kelly (Ref. 16)	3.9×10^8	1.7×10^8	0.33×10^8	3.0×10^8
NBS Data Center (Ref. 11)	4.5×10^8	2.0×10^8	0.41×10^8	3.8×10^8
Armstrong *et al.* (Ref. 17)	6.0×10^8	2.3×10^8	...	5.7×10^8

[a] J. C. Morris and R. L. Garrison, Phys. Rev. 188, 112 (1969).

Labuhn made end-on measurements using a modified Maecker-type wall-stabilized arc[5] which employs a constriction in the arc pieces near the electrode (anode) on the monochromator end of the arc. This constriction raises the axis temperature of the arc several thousand degrees in its vicinity and helps to prevent the foreign gas, oxygen in this case, from penetrating into the nonuniform cooler zones in the vicinity of the electrode. However, at the very low concentrations of oxygen required in order to be in the linear portion of the curve of growth, the background oxygen concentrations due to oxygen-bearing contaminants such as air and water vapor may be easily of the same order of magnitude as the external input. Suppression of these contaminants has been one of the major technical problems of the present experiment. If getters are used to clean up the argon-gas handling system, the main source of these contaminants is internal and in fact can be isolated to the electrode regions. This was verified in our apparatus by noting, first of all, that the optical depth decreased as the argon flow rates were increased (see Fig. 2) and, secondly, that a simple shortening of the arc length from 5 discs to 1 disc had no significant effect on the optical depth of the oxygen resonance lines emitted in a "pure" argon arc. Thus, it is very possible that the O I emission observed by Boldt and Labuhn at small optical depths was coming from a 15 000-K plasma layer near the anode electrode, whereas the blackbody calibration of the vuv intensity was calculated for blackbody emission from the 12000-K plasma layer formed somewhere between the input and the input and output ports. The emission from a 15 000-K plasma is about ten times more intense than that from a 12000-K plasma. The fact that the length of the higher temperature plasma is somewhat shorter than the arc length assumed in the data analysis would reduce the systematic error from this factor of 10 to approximately the observed factor of 3–4. It is reasonable also that the discrepancy in the $\lambda = 1218$ Å measurement is not as large as in the $\lambda = 1152$ and 1306 Å measurements since the optical depth of this line is relatively smaller owing to its lower *gf* value. Therefore, the linear part of the curve of growth for this line begins at oxygen flow rates such that the ratio of input oxygen to background oxygen is relatively larger. The fact that such large discrepancies were not apparent in the measurements of N I and C I transition probabilities by Boldt and co-workers using similar arc discharges[5, 6] is reasonable in terms of the above hypothesis since the concentration of nitrogen- and carbon-bearing contaminants is considerably less than that of oxygen-bearing contaminants in an argon arc. Also, since the nitrogen and carbon vuv lines are generally broader than the oxygen vuv lines, they are observed more readily in the linear part of the curve of growth. Nevertheless it is significant that these arc measurements[5, 6] range from 10 to 65% above the results of lifetime measurements by Savage and Lawrence[19] although the differences are probably due to small systematic errors in both methods. In the case of the arc measurements the *f* values may tend to be too large owing to the temperature effect just described; in the case of the lifetime measurements, the *f* values may tend to be on the low side owing to cascading effects caused by above-threshold electron excitation.

ACKNOWLEDGMENTS

I would like to thank Dr. Wolfgang L. Wiese for the many helpful discussions which made this experiment possible. The technical assistance offered by Dr. J. R. Roberts, Dr. J. M. Bridges, and D. R. Paquette is also greatly appreciated.

---

*NRC-NBS postdoctoral research associate at the NBS, 1968–1970. Supported in part by the Advanced Research Projects Agency of the Department of Defense under the Strategic Technology Office.

[1]M. Gaillard and J. E. Hesser, Astrophys. J. 152, 695 (1968).

[2]G. M. Lawrence, Phys. Rev. A 2, 397 (1970).

[3]W. H. Smith, J. Bromander, L. J. Curtis, H. G. Berry, and R. Buchta, Astrophys. J. 165, 217 (1971).

[4]G. Boldt and F. Labuhn, Z. Naturforsch. 22a, 1613 (1967).

[5]G. Boldt, Z. Naturforsch. 18a, 1107 (1963).

[6]F. Labuhn, Z. Naturforsch. 20a, 998 (1965).

[7]D. A. Parkes, L. F. Keyser, and F. Kaufman, Astrophys. J. 149, 217 (1967).

[8]C. L. Lin, D. A. Parkes, and F. Kaufman, J. Chem. Phys. 53, 3898 (1970).

[9]J. E. Solarski and W. L. Wiese, Phys. Rev. 135, A1236 (1964).

[10]W. L. Wiese, in *Methods of Experimental Physics*, edited by B. Bederson and W. L. Fite (Academic, New York, 1968), Vol. 7B, Chap. 10.

[11]W. L. Wiese, M. W. Smith, and B. M. Glennon, in *Elements Hydrogen Through Neon*, Vol. I of *Atomic Transition Probabilities* (U. S. GPO, Washington, D. C., 1966), NSRDS-NBS 4.

[12]G. Boldt, in *Proceedings of the Fifth International Conference on Ionization Phenomena in Gases, Münich*, 1961 (North-Holland, Amsterdam, 1961), p. 925.

[13]W. L. Wiese, M. W. Smith, and B. M. Miles, in *Elements Through Calcium*, Vol. II of *Atomic Transition Probabilities* (U. S. GPO, Washington, D. C., 1969), NSRDS-NBS 22.

[14]P. Kepple and H. R. Griem, Phys. Rev. 173, 317 (1968).

[15]R. H. Garstang, Proc. Cambridge Phil. Soc. 57, 115 (1961).

[16]P. S. Kelly, Astrophys. J. 140, 1247 (1964).

[17]B. H. Armstrong, R. R. Johnston, and P. S. Kelly, Lockheed Missiles and Space Co. Report No. 8-04-64-2, 1964 (unpublished); also Air Force Weapons Laboratory Report No. AFWL-TR-65-17 (unpublished).

[18]K. H. Wilson and W. E. Nicolet, J. Quant. Spectry. Radiative Transfer 7, 891 (1967).

[19]B. D. Savage and G. M. Lawrence, Astrophys. J. 146, 940 (1966).

PHYSICAL REVIEW A VOLUME 4, NUMBER 1 JULY 1971

Quadrupole Moment of Li

Sheldon Green*
Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138
(Received 11 January 1971)

The electric field gradient at Li in LiH has been computed with a 200 configuration-interaction function including single and double excitations from the Hartree-Fock function of Cade and Huo. This value, in conjunction with the experimental LiH eqQ value, leads to a suggested value of $Q(\mathrm{Li}^7) = -(3.66 \pm 0.03) \times 10^{-26}$ cm^2. This value is substantially different from that obtained using previously calculated field gradients derived from less complete wave functions.

The present value of the nuclear quadrupole moment of Li was obtained from molecular-beam electric resonance spectroscopy measurements of the coupling constant eqQ in LiH of Wharton, Gold, and Klemperer[1] and the calculated value of the electric field gradient at the Li nucleus, q, of Kahalas and Nesbet.[2] Much more accurate field-gradient values are now available, however, and the Li quadrupole value should be revised. The results of three previous calculations will be reviewed here—the restricted Hartree-Fock (RHF) calculation of Cade and Huo,[3] a configuration interaction (CI) with iteration to pseudonatural orbitals of Bender and Davidson,[4] and a valence-bond CI of Browne and Matsen[5]—and the results of a new CI calculation,[6] based on the Cade and Huo function, will be presented.

Cade and Huo[3] used a moderately large $(16\sigma, 8\pi)$ well-optimized Slater-type orbital basis set to produce a function essentially at the Hartree-Fock limit. Their calculations are at several internuclear distances around the equilibrium $R_e = 3.015$ a.u. From these RHF functions, Cade, Huo, and Popkie[7] have calculated $q(R_e) = -0.0440$ a.u. The coupling constant was measured in the $v = 0$ and $v = 1$ vibrational states. As noted by Wharton, Gold, and Klemperer, $q(R_e)$ should be used in conjunction with eqQ extrapolated to $v = -\frac{1}{2}$; this gives $Q(\mathrm{Li}^7) = -(3.43 \pm 0.02) \times 10^{-26}$ cm^2. From the RHF potential energy and $q(R)$ curves, Cade, Huo, and Popkie have also calculated the vibrationally averaged values, $q(v = 0) = -0.0430$ a.u. and $q(v = 1) = -0.0412$ a.u.; these give values for $Q(\mathrm{Li}^7)$ of $-(3.43 \pm 0.01) \times 10^{-26}$ and $-(3.39 \pm 0.04) \times 10^{-26}$ cm^2, where the error limits are those given for the experimental values.

The pseudonatural orbital CI calculations of Bender and Davidson[4] represent the (energetically) best wave functions for LiH in the literature. The moderately large $(16\sigma, 9\pi, 6\delta, 3\varphi)$ Slater-type orbital basis set was chosen to imitate the Cade and Huo electron charge density; however, the basis set was not energy optimized and, because of limitations on the orbital exponents, is not as flexible as the Cade and Huo set.[8] With a 939 configuration function an energy of -8.0600 a.u. and a dipole moment of 5.853 D were obtained. The value $q(R_e) = -0.0347$ a.u., obtained from this function, is substantially different from the Cade and Huo value. However, it is only negligibly different from the value calculated from the RHF function using the Bender and Davidson basis set $q(R_e) = -0.0348$ a.u.[8] Since a configuration interaction does not correct for deficiencies in the RHF basis,[9] it was at first thought that the discrepancy between the Cade-Huo and the Bender-Davidson values was due to basis set differences. Comparison of several other expectation values for these two RHF functions, however, shows agreement to generally better than three significant figures, and it now appears that numerical instabilities in the computer program used by Bender and Davidson to compute the $P_2(\cos\theta)/r^3$ matrix elements necessary for the field gradient calculation are the main source of the difference in q values.[8]

Browne and Matsen[5] did a valence-bond CI calculation, obtaining an energy of -8.0561 a.u. and a value of $q(R = 3.046) = -0.0346$ a.u., in good agreement with the values of Kahalas and Nesbet[2] and Bender and Davidson[4] but quite different from the Cade-Huo[7] value. It is difficult to compare the Browne-Matsen results with the others reported here for two reasons. First, they have reported properties calculated at the minimum of their computed potential-energy curve, $R = 3.046$ a.u., rather than at the experimental R_e as was done in