1. Introduction

In Ref. [1], Whaling, Anderson, Carle, Brault, and Zarem presented a comprehensive list of Ar I lines in the region 332 nm to 5865 nm as emitted from a hollow-cathode discharge with Ar buffer gas. The measurements were based on spectra retrieved from the archives of the 1 m Fourier transform spectrometer (FTS) of the National Solar Observatory (Kitt Peak). These spectra had previously been used by the same authors to measure lines of Ar II in this spectral region [2].

In recent work at the National Institute of Standards and Technology (NIST), 17 lines of Ar I ranging from 22163 cm$^{-1}$ to 25315 cm$^{-1}$ were observed in a Hg/Ar electrodeless discharge lamp (edl) with an FTS optimized for the ultraviolet [3]. The spectra were calibrated using precisely known lines of $^{199}$Hg [4]. For all 17 lines the NIST wavenumbers were smaller than the wavenumbers of Whaling et al. [1]. Pressure shifts due to differences in the Ar carrier gas pressure were investigated as a possible cause of the discrepancy but were not able to explain it.

In a separate set of experiments, the infrared spectrum of a Th/Ar hollow cathode lamp was observed with the NIST 2 m Fourier transform spectrometer [5]. The spectra were calibrated by Th lines measured by laser optogalvanic spectroscopy [6]. Approximately 600 lines of Ar I were measured. When these results were compared to Ref. [1], it was apparent that they also were smaller on average than the wavenumbers of Whaling et al. [1]. For lines associated with energy levels of high angular momentum or high excitation, the deviations were large and scattered. For several hundred low excitation lines, however, the NIST observations were smaller by a consistent shift of approximately 1 part in 10$^7$. Based on these two sets of measurements in widely separated spectral regions, it appeared possible that the results of [1] might be high due to a systematic calibration error.

We have used Ar II wavenumbers from Ref. [2] in several experiments and have found them to be consis-
tent with other generally accepted wavelength standards. It seemed interesting, therefore, to try to determine whether the Ar I wavenumbers from Ref. [1] and Ar II wavenumbers from Ref. [2] were consistent with each other. To investigate this question we retrieved three of the spectra used for the Ar measurements — Ti #7 (8/15/92), Cu #2 (4/17/83), and Ti #2 (11/19/85) — from the Kitt Peak Archives [7]. The spectra were analyzed using the interactive program Xgremlin [8]. Each line of interest was fit with a Voigt profile convoluted with the FTS instrumental function to obtain the wavenumber.

Ti #7 (8/15/92) covers the region of the NIST Hg/Ar edl observations. In this spectrum we measured the 28 Ar II lines recommended by Learner and Thorne for use as calibration lines [9]. From these lines we calculated a correction factor for the spectrum with an uncertainty of 2 parts in 10^9, as shown in Table 1. We then measured the 17 Ar I lines that appeared in the NIST Hg/Ar observations and corrected their wavenumbers using the factor from Table 1. The results are shown in Table 2, where they are compared with the values from Whaling et al. [1]. The values from [1] are larger on average by the multiplicative constant 1.000 000 065 7(24). The combined standard uncertainty is calculated as the sum in quadrature of the standard error of the mean, representing the random scatter of the data, and a systematic component that propagates directly from the standard error in the calibration factor.

Cu #2 (4/17/83) covers a portion of the infrared in which many Ar I lines appear in the NIST Th/Ar hollow-cathode observations. In this spectrum we chose 20 lines of Ar II with high signal-to-noise ratio and good line symmetry for use in determining the wavenumber correction factor. The results are shown in Table 3. The scatter is significantly larger than for the recommended lines used in the previous spectrum, and two of the lines produce correction factors that are clear outliers. We excluded these lines, shown in italics in Table 3, in calculating the average. We then measured

### Table 1. Determination of correction factor for the spectrum Ti #7 (8/15/92) from 28 Ar II lines.

| Ar II Uncorrected (cm⁻¹) | Whaling Ar II [2] (cm⁻¹) | Correction Factor |
|--------------------------|--------------------------|-------------------|
| 19429.76452              | 19429.7694               | 1.000 000 251     |
| 19749.38149              | 19749.3873               | 1.000 000 294     |
| 19957.16070              | 19957.1662               | 1.000 000 275     |
| 20106.36850              | 20106.3743               | 1.000 000 288     |
| 20135.04095              | 20135.0466               | 1.000 000 281     |
| 20265.11937              | 20265.1249               | 1.000 000 273     |
| 20448.18949              | 20448.1949               | 1.000 000 264     |
| 20486.65005              | 20486.6556               | 1.000 000 271     |
| 20622.10647              | 20622.1121               | 1.000 000 273     |
| 20801.41733              | 20801.4230               | 1.000 000 273     |
| 20981.08382              | 20981.0895               | 1.000 000 271     |
| 21109.37593              | 21109.3817               | 1.000 000 273     |
| 21149.73502              | 21149.7409               | 1.000 000 278     |
| 21462.88349              | 21462.8892               | 1.000 000 266     |
| 21831.0407               | 21831.0458               | 1.000 000 262     |
| 21995.77800              | 21995.7838               | 1.000 000 264     |
| 22561.94887              | 22561.9551               | 1.000 000 276     |
| 22566.06057              | 22566.0667               | 1.000 000 272     |
| 22587.41164              | 22587.4176               | 1.000 000 264     |
| 22715.79393              | 22715.8001               | 1.000 000 272     |
| 22720.38659              | 22720.3928               | 1.000 000 273     |
| 22826.36872              | 22826.3751               | 1.000 000 279     |
| 22992.27461              | 22992.2808               | 1.000 000 269     |
| 23081.79760              | 23081.8043               | 1.000 000 290     |
| 23431.66861              | 23431.6744               | 1.000 000 247     |
| 23644.29776              | 23644.3037               | 1.000 000 251     |
| 25447.00142              | 25447.0076               | 1.000 000 243     |
| 26806.99465              | 26807.0020               | 1.000 000 274     |

Average: 1.000 000 270
Standard Error: 0.000 000 002
Table 2. Calibrated wavenumbers for selected lines of Ar I from the spectrum Ti #7 (8/15/92).

| Ar I Corrected Whaling Ar I [1] Deviation Ratio Whaling/Ti #7 |
|-----------------|-----------------|-----------------|-----------------|
| Ti #7 (8/15/92) | (cm⁻¹)          | (cm⁻¹)          | (cm⁻¹)          |
| 22163.1288      | 22163.1303      | 0.0015          | 1.000 000 0689  |
| 23007.6021      | 23007.6035      | 0.0015          | 1.000 000 0630  |
| 23059.7703      | 23059.7718      | 0.0015          | 1.000 000 0637  |
| 23069.2254      | 23069.2269      | 0.0015          | 1.000 000 0650  |
| 23248.7295      | 23248.7308      | 0.0013          | 1.000 000 0559  |
| 23400.7352      | 23400.7318      | 0.0016          | 1.000 000 0667  |
| 23432.9952      | 23432.9997      | 0.0015          | 1.000 000 0657  |
| 23471.0895      | 23471.0911      | 0.0016          | 1.000 000 0675  |
| 23798.9963      | 23798.9997      | 0.0016          | 1.000 000 0661  |
| 23812.3597      | 23812.3612      | 0.0015          | 1.000 000 0647  |
| 23853.7662      | 23853.7677      | 0.0015          | 1.000 000 0650  |
| 23855.5661      | 23855.5677      | 0.0016          | 1.000 000 0667  |
| 23905.9332      | 23905.9348      | 0.0016          | 1.000 000 0655  |
| 24007.5674      | 24007.5691      | 0.0017          | 1.000 000 0693  |
| 24039.8321      | 24039.8337      | 0.0016          | 1.000 000 0672  |
| 24718.4549      | 24718.4566      | 0.0017          | 1.000 000 0695  |
| 25315.8386      | 25315.8403      | 0.0017          | 1.000 000 0673  |
| **Average**     | 1.000 000 0657  |               |                 |
| **Standard Error** | 0.000 000 008  |               |                 |
| **Uncertainty** | 0.000 000 024   |               |                 |

Table 3. Determination of correction factor for the spectrum Cu #2 (4/17/83) from 20 Ar II lines. The two lines shown in italics were excluded from the average.

| Ar II Uncorrected (cm⁻¹) | Whaling Ar II (cm⁻¹) | Correction Factor |
|--------------------------|----------------------|-------------------|
| 3312.75206               | 3312.7464            | 0.999 998 293     |
| 3336.55291               | 3336.5474            | 0.999 998 347     |
| 3405.89968               | 3405.8945            | 0.999 998 478     |
| 3423.09192               | 3423.0862            | 0.999 998 330     |
| 3441.05069               | 3441.0452            | 0.999 998 404     |
| 3469.9959                | 3469.5940            | 0.999 998 389     |
| 3495.53382               | 3495.5280            | 0.999 998 336     |
| 3519.86194               | 3519.8561            | 0.999 998 340     |
| 3562.07384               | 3562.0678            | 0.999 998 304     |
| 3580.41755               | 3580.4113            | 0.999 998 256     |
| 3612.33588               | 3612.3300            | 0.999 998 373     |
| 3617.29540               | 3617.2893            | 0.999 998 314     |
| 3620.50053               | 3620.4946            | 0.999 998 362     |
| 3695.22460               | 3695.2181            | 0.999 998 386     |
| 3765.74583               | 3765.7387            | 0.999 998 107     |
| 3807.75799               | 3807.7517            | 0.999 998 348     |
| 3878.8019                | 3878.8018            | 0.999 998 354     |
| 3906.18281               | 3906.1761            | 0.999 998 282     |
| **4030.02928**           | **4030.0201**        | **0.999 997 723** |
| **4031.86939**           | **4031.8627**        | **0.999 998 340** |
| **Average**              | 0.999 998 346        |                   |
| **Standard Error**       | 0.000 000 012        |                   |

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20 Ar I lines that had high signal-to-noise ratio, good symmetry, and were associated with states of low excitation and low angular momentum. The wavenumbers for these lines were corrected with the factor from Table 3. The results are shown in Table 4. Again the results of Whaling et al. [1] are systematically larger. Neither the correction factor nor the ratio in Table 4 is determined as precisely for this spectrum as for Ti #7 because the number of significant figures given in Ref. [2] becomes a limiting factor; however, to a good approximation the results of [1] are again larger by a constant factor.

Ti #2 (11/19/85) covers the near ultraviolet to near infrared region between the two sets of unpublished NIST observations. In this region 18 Ar II lines are recommended for use as wavelength standards [2]. One of these lines was too weak to measure, but the remaining 17 were measured and used with the published wavenumbers from [2] to determine values of the correction factor, as shown in Table 5. The two longest wavelength lines produced correction factors that are in poor agreement with the other lines, and the overall scatter of the data is larger than in the other spectra. Since some of the lines recommended as standards were weak, an additional 20 lines were selected and measured based solely on their high signal-to-noise ratio and good symmetry. These lines produced correction factors with about the same average but a standard deviation 1.6 times larger than the original set; consequently, the average correction factor was calculated from the recommended lines, omitting the two outliers from the average. We then measured 20 lines of Ar I that were selected using the same criteria as for Cu #2 (4/17/83). The wavenumbers were corrected using the correction factor from Table 5. The results are presented in Table 6. As in the other two spectra the results from [1] are systematically larger than the new measurements.

Based on this sample of lines from three different spectra, which cover a wide range of wavelengths from the ultraviolet to the infrared, it is clear that the Ar I wavenumber scale in Ref. [1] is not consistent with the Ar II wavenumber scale in Ref. [2], despite the fact that Ar I and Ar II were measured in the same spectra. For each of the three spectra the scales differ by a multiplicative constant. The constant is defined most precisely for the spectrum Ti #7 (8/15/92), but the values for all three spectra agree within their uncertainties.

We have confidence that the wavenumbers for Ar II [2] are reliable. They have been widely used as stan-

| Ar I Corrected Wavenumbers (cm⁻¹) | Whaling Ar I [1] (cm⁻¹) | Deviation (cm⁻¹) | Ratio Whaling/Cu #2 |
|-----------------------------------|------------------------|-----------------|---------------------|
| 3334.4969                        | 3334.4971              | 0.0002          | 1.000 000 060      |
| 3415.2253                        | 3415.2255              | 0.0002          | 1.000 000 059      |
| 3417.2965                        | 3417.2967              | 0.0002          | 1.000 000 059      |
| 3435.4220                        | 3435.4222              | 0.0002          | 1.000 000 058      |
| 3467.0372                        | 3467.0373              | 0.0001          | 1.000 000 029      |
| 3504.0523                        | 3504.0525              | 0.0002          | 1.000 000 057      |
| 3525.4135                        | 3525.4137              | 0.0002          | 1.000 000 057      |
| 3573.3634                        | 3573.3636              | 0.0002          | 1.000 000 056      |
| 3602.2958                        | 3602.2960              | 0.0002          | 1.000 000 056      |
| 3619.6873                        | 3619.6875              | 0.0002          | 1.000 000 055      |
| 3647.1137                        | 3647.1139              | 0.0002          | 1.000 000 055      |
| 3663.9178                        | 3663.9180              | 0.0002          | 1.000 000 055      |
| 3725.3641                        | 3725.3642              | 0.0001          | 1.000 000 027      |
| 3757.6287                        | 3757.6289              | 0.0002          | 1.000 000 053      |
| 3766.4387                        | 3766.4389              | 0.0002          | 1.000 000 053      |
| 3828.0607                        | 3828.0610              | 0.0003          | 1.000 000 078      |
| 3922.4007                        | 3922.4009              | 0.0002          | 1.000 000 051      |
| 3978.9713                        | 3978.9716              | 0.0003          | 1.000 000 075      |
| 4012.5895                        | 4012.5897              | 0.0002          | 1.000 000 050      |
| 4171.3497                        | 4171.3499              | 0.0002          | 1.000 000 048      |

Average: 1.000 000 0054
Standard Error: 0.000 000 0003
Uncertainty: 0.000 000 0012
Table 5. Determination of correction factor for the spectrum Ti #2 (11/19/85) from 20 Ar II lines. The two lines shown in italics were excluded from the average.

| Ar II Uncorrected (cm⁻¹) | Whaling Ar II (cm⁻¹) | Correction Factor |
|--------------------------|----------------------|-------------------|
| 4776.24004               | 4776.2372            | 0.999 999 406     |
| 5833.12595               | 5833.1234            | 0.999 999 562     |
| 7167.21529               | 7167.2141            | 0.999 999 834     |
| 7540.04974               | 7540.0487            | 0.999 999 862     |
| 8123.06894               | 8123.0686            | 0.999 999 959     |
| 8204.99534               | 8204.9945            | 0.999 999 898     |
| 8494.17032               | 8494.1690            | 0.999 999 844     |
| 8918.39741               | 8918.3950            | 0.999 999 730     |
| 9152.11655               | 9152.1152            | 0.999 999 852     |
| 9231.54287               | 9231.5434            | 1.000 000 058     |
| 9245.68391               | 9245.6829            | 0.999 999 890     |
| 9551.05683               | 9551.0551            | 0.999 999 819     |
| 9887.83232               | 9887.8323            | 0.999 999 998     |
| 10091.72748              | 10091.7258           | 0.999 999 834     |
| 10550.91915              | 10550.9176           | 0.999 999 853     |
| 10773.24592              | 10773.2439           | 0.999 999 812     |
| 11086.39442              | 11086.3923           | 0.999 999 808     |
|                          |                      | Average 0.999 999 870 |
|                          |                      | Standard Error 0.000 000 021 |

Table 6. Calibrated wavenumbers for selected lines of Ar I from the spectrum Ti #2 (11/19/85).

| Ar I Corrected Ti #2 (11/19/85) (cm⁻¹) | Whaling Ar I [1] (cm⁻¹) | Deviation (cm⁻¹) | Ratio Whaling/Cu #2 |
|----------------------------------------|-------------------------|-----------------|-------------------|
| 5929.5463                              | 5929.5467               | 0.0004          | 1.000 000 065     |
| 6294.2542                              | 6294.2547               | 0.0005          | 1.000 000 075     |
| 6521.6533                              | 6521.6538               | 0.0005          | 1.000 000 073     |
| 6651.3143                              | 6651.3147               | 0.0004          | 1.000 000 064     |
| 6858.0308                              | 6858.0314               | 0.0006          | 1.000 000 081     |
| 7188.4110                              | 7188.4115               | 0.0005          | 1.000 000 075     |
| 7338.7039                              | 7338.7045               | 0.0006          | 1.000 000 084     |
| 7554.0590                              | 7554.0597               | 0.0007          | 1.000 000 087     |
| 7910.1789                              | 7910.1795               | 0.0006          | 1.000 000 076     |
| 8099.2837                              | 8099.2843               | 0.0006          | 1.000 000 070     |
| 8403.4398                              | 8403.4405               | 0.0007          | 1.000 000 089     |
| 8553.7326                              | 8553.7333               | 0.0007          | 1.000 000 079     |
| 8717.8755                              | 8717.8762               | 0.0007          | 1.000 000 084     |
| 8887.7592                              | 8887.7599               | 0.0007          | 1.000 000 083     |
| 9178.2310                              | 9178.2318               | 0.0008          | 1.000 000 084     |
| 9342.3739                              | 9342.3745               | 0.0006          | 1.000 000 065     |
| 9541.1601                              | 9541.1608               | 0.0007          | 1.000 000 068     |
| 9749.5939                              | 9749.5947               | 0.0008          | 1.000 000 082     |
| 10217.4419                             | 10217.4425              | 0.0006          | 1.000 000 057     |
| 10687.4305                             | 10687.4309              | 0.0004          | 1.000 000 041     |
| Average                                |                         | 1.000 000 0074   |
| Standard Error                         |                         | 0.000 000 003    |
| Uncertainty                             |                         | 0.000 000 021    |
standards for calibration of FTS spectra and have been shown to be on a consistent scale with independently determined standard lines of $^{199}$Hg I at a level of better than 2 parts in $10^8$ [10]. Therefore, we conclude that there must be a systematic calibration error in the Ar I results of Ref. [1].

On an empirical basis the spectra we have investigated suggest that all of the Ar I data can be corrected by reducing the wavenumbers by a single multiplicative factor. This factor is well-determined from the results of Ti #7 (8/15/92) to be 0.999 999 934 3(24). The factors from Cu #2 (4/17/83) and Ti #2 (11/19/85), 0.999 999 945 5(121) and 0.999 999 925 9(213) respectively, have larger uncertainties but are fully consistent with this value.

Most of the spectra used for Refs. [1] and [2] were originally calibrated with respect to Ar II lines of Norlén [11] and later shifted to a revised wavenumber scale based on molecular lines of CO [12] as described in [2]. It is striking that the ratio determined in the fourth column of Table 2 is in almost perfect agreement with the ratio between the wavenumber scales of Whaling et al. [2] and Norlén [11], which was determined in [2] to be 1.000 000 067(8). All of the Ar I wavenumbers in [1] are larger by this factor than their values in an unpublished list that was made available to several laboratories in the late 1990s [13]. This leads us to speculate that the systematic error in the published wavenumbers for Ar I [1] resulted from an inadvertent double correction of the wavenumber scale. We have communicated these results to Whaling, but he is not able to verify that a double correction actually occurred [14].

Our speculation is supported by a comparison of the deviations in the third columns of Tables 2, 4, and 6 for each line with the error that would result had the scale correction been applied twice. The average difference of these values for all 57 lines measured is just $-0.000 01$ cm$^{-1}$. For 26 of the lines the difference is less than $0.000 05$ cm$^{-1}$, and the largest individual deviations are $+0.000 19$ cm$^{-1}$ and $-0.000 28$ cm$^{-1}$. These deviations are less than the reported uncertainty for all of the lines; thus the data are entirely consistent with a double correction of the scale.

2. Conclusion

Based on all of the evidence, we propose that the results of [1] be corrected by multiplying all wavenumbers by the factor 0.999 999 933. This factor is the inverse of the Norlén-to-CO scale correction. It is consistent with the corrections determined empirically from the spectra Ti #7 (8/15/92), Cu #2 (4/17/83), and Ti #2 (11/19/85). By making this correction, the Ar I wavenumbers of Ref. [1] will be put on the same scale as the Ar II wavenumbers of Ref. [2], which was derived from CO.

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