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Advanced ab initio relativistic calculations of transition probabilities for some O I and O III emission lines

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ABSTRACT

This work presents new ab initio relativistic calculations using the multiconfiguration Dirac–Hartree–Fock method of some O I and O III transition lines detected in B-type and Wolf–Rayet stars. Our results are the first able to be presented in both the length and velocity gauges, with excellent gauge convergence. Compared to previous experimental and theoretical uncertainties of up to 50 per cent, our accuracies appear to be in the range of 0.33–5.60 per cent, with gauge convergence up to 0.6 per cent. Similar impressive convergence of the calculated energies is also shown. Two sets of theoretical computations are compared with earlier tabulated measurements. Excellent agreement is obtained with one set of transitions but an interesting and consistent discrepancy exists between the current work and the prior literature, deserving of future experimental studies.

Key words: atomic data – atomic processes – line: identification – techniques: spectroscopic – astronomical data bases: miscellaneous – ultraviolet: stars.

1 INTRODUCTION

The spectra of light elements have been investigated extensively for many years due to their importance in astrophysical studies. Of particular interest is oxygen, which is highly abundant and therefore can be observed in countless astrophysical entities, and as such, it is widely used in many investigations on the formation of stars, planets, and galaxies. The O I spectrum, for instance, contains the forbidden green line which is prominent in numerous studies such as solar and geomatic activities, aurora, meteors, and supernova remnants (see for example, Chantler et al. 2013). The spectra of oxygen ions such as O II and O III are also vital diagnostic tools in many astrophysical investigations such as B-type stars and Wolf–Rayet stars. Many studies on the abundances of oxygen in B-type stars, for example, Gies & Lambert (1992) and Kilian (1992), have not only provided deeper insight into the chemical evolution and processes involved within these interesting bodies, but also facilitate investigations of solar models (Asplund et al. 2004; Scott et al. 2009) where there exists a deep conflict between observation and helioseismological theory (Basu & Antia 2008).

Laboratory and theoretical atomic data are heavily relied upon in many astrophysical investigations. Consequently, the accuracy of these astrophysical calculations are affected by the uncertainties within the available atomic data. Laboratory data can be restricted due to the limitation presented by experimental conditions, which often contribute further to the uncertainty. Therefore, it is difficult to underestimate the importance of theoretical atomic calculations. Many of the most advanced and well-known theoretical data available, such as those of Froese-Fischer & Tachiev (2004) and Froese-Fischer et al. (2009), were obtained through non-relativistic means with a relativistic correction, namely the multiconfiguration Hartree–Fock with a Breit–Pauli correction. Non-relativistic calculations are often more stable with a faster convergence compared to their fully relativistic equivalents; however, it has been demonstrated that unprecedented high accuracy can be achieved with copper (Chantler, Hayward & Grant 2009; Chantler, Lowe & Grant 2010) and titanium (Chantler, Lowe & Grant 2012) using fully relativistic calculations. The wide-ranging benefit of higher accuracy greatly outweighs the many challenges that are attached to relativistic calculation.

Previous work utilizing the multiconfiguration relativistic Hartree–Fock method (Cowan 1981), such as those of Campos et al. (2005) and Malcheva et al. (2009), have primarily focused on medium- to high-Z elements. Very little work has been done on low-Z elements using relativistic methods, in part because of the challenges of satisfactory convergence, and in part because approximate relativistic corrections to non-relativistic results are useful and convenient. In this work, fully relativistic calculations are performed on oxygen using the multiconfiguration Dirac–Hartree–Fock (MCDHF) approach, as employed by the GRASP2K package (Jönsson et al. 2007). This approach is used extensively throughout the atomic physics community, and such work as Froese Fischer et al. (2008) on Fe IV and Chantler et al. (2013) on O I forbidden lines have proven its viability for transitions of astrophysical significance. The focus of this work is on the O I and O III spectra.

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We focus on some of the key transitions considered to be of astrophysical interest (Pinnington, Kernahan & Lin 1970). The O III transitions that we have focused on (in LS notations) are

A : $1s^2 2s^1 2p^2\ (^4P)\ 3p^1\ (^5P^o_3) - 1s^2 2s^1 2p^2\ (^4P)\ 3d^1\ (^5D_4)$

B : $1s^2 2s^1 2p^2\ (^4P)\ 3p^1\ (^5D^o_3) - 1s^2 2s^1 2p^2\ (^4P)\ 3d^1\ (^5F_4)$

C : $1s^2 2s^1 2p^2\ (^4P)\ 3p^1\ (^5D^o_4) - 1s^2 2s^1 2p^2\ (^4P)\ 3d^1\ (^5F_5)$.

These transitions have been identified by Pinnington et al. (1970) and Underhill (1960) as relevant in the studies of Wolf–Rayet and O-type stars. The most widely cited and comprehensive data which contains these lines is the NIST online Atomic Spectra Database (ASD), last revised by Kramida et al. (2012) based on the compilation of Wiese, Fuhr & Deters (1996) and relating to the Opacity Project. This data set was considered to be amongst the best at the time of publication, their level of accuracy (24–50 per cent) no longer reflects what can be achieved with current computational resources. Therefore, a more accurate calculation of these particular lines is valuable.

We have also applied our approach to some other O I lines as further tests of the robustness of our theoretical methods. The O I lines chosen for this test are

D : $1s^2 2s^2 2p^4\ (^3P_0) - 1s^2 2s^2 2p^3\ (^4S^o)\ 3s^1\ (^3S^o_1)$

E : $1s^2 2s^2 2p^4\ (^1D_2) - 1s^2 2s^2 2p^3\ (^2D^o)\ 3s^1\ (^1D^o_2)$

F : $1s^2 2s^2 2p^4\ (^3P_1) - 1s^2 2s^2 2p^3\ (^2D^o)\ 3s^1\ (^3D^o_2)$

G : $1s^2 2s^2 2p^4\ (^3P_2) - 1s^2 2s^2 2p^3\ (^4S^o)\ 3s^1\ (^3S^o_1)$

H : $1s^2 2s^2 2p^4\ (^3P_1) - 1s^2 2s^2 2p^3\ (^4S^o)\ 3s^1\ (^3S^o_1)$

These lines have not been but should be directly observable in astrophysical studies, and we would encourage more careful observations in this area. Due to the many instances where observational data cannot be collected or detected, a good theoretical model must be able to predict the results in these difficult regimes.

2 THEORY

In our MCDHF approach, the atomic wavefunction Ψ – sometimes referred to as the approximate or atomic state function – is approximated as a linear combination of *jj*-coupled configuration state functions (CSFs) Φ,

$$\Psi(\Gamma\, PJM) = \sum_q c_q\, \Phi(\gamma_q\, PJM). \tag{1}$$

Here, γ_q contains all the information required to represent the CSF uniquely, such as orbital occupation numbers and seniority numbers, while P, J, and M are the parity and angular momentum numbers. The term c_q represents the mixing coefficients. The CSFs are built from a basis of one-electron Dirac orbitals, while the mixing coefficients can be obtained from relativistic configuration interaction (RCI) calculations by diagonalizing the Dirac–Coulomb Hamiltonian,

$$H_{\rm DC} = \sum_i^N c\, \boldsymbol{\alpha}_i \cdot \boldsymbol{p}_i + \beta_i mc^2 + V_{\rm nuc}(r_i) + \sum_{i<j}^N \frac{1}{r_{ij}}, \tag{2}$$

where the first summation is the Dirac Hamiltonian with the usual matrix notation, and the second summation is the Coulomb term with r_{ij} the distance between electron i and electron j. As part of the RCI calculations, the transverse photon interaction,

$$H_{\rm trans} = -\sum_{i<j}^N \left[\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j\, \frac{\cos(\omega_{ij} r_{ij}/c)}{r_{ij}} + (\boldsymbol{\alpha}_i \cdot \nabla_i)(\boldsymbol{\alpha}_j \cdot \nabla_j)\, \frac{\cos(\omega_{ij} r_{ij}/c) - 1}{\omega_{ij}^2 r_{ij}/c^2} \right], \tag{3}$$

is incorporated as a perturbation. In the long wavelength limit ($\omega_{ij} \rightarrow 0$), this reduces to the Breit interaction. Quantum electrodynamic effects including vacuum polarization and self-energy shifts are also included in the calculation.

3 COMPUTATION

This work is a development of our recent work on electric quadrupoles and magnetic dipole (or optically forbidden) transitions in oxygen (Chantler et al. 2013). In that work, we focused on the green oxygen line of the aurorae and solar observations. Peculiarly, the theory remains strongly anomalous compared to astrophysical and separately laboratory spectra. The line is notoriously difficult to compute, and is forbidden, so that in principle wavefunction convergence is extremely complex. Questions can be asked for example about the convergence as a whole, the convergence of low-energy valence transitions compared to inner core transitions, about the convergence of wave functions and eigenenergies for low atomic number Z and related issues. That work achieved convergence of gauges to below 8 per cent, a dramatic achievement, but the 8 per cent could be considered an intrinsic limitation due to coding issues, a statement of the completeness of the eigenfunctions, or a statement of the progress which is possible.

However, one suggestion is that a 10 per cent convergence might be intrinsic due to the omission of higher order terms or the particular implementation of the Breit interaction in a specific code, or indeed that this convergence is accidental and additional large systematic corrections might be needed. We here disprove such a hypothesis by investigating similar relevant and allowed E1 transitions in both O I and O III.

Electronic configurations were obtained through excitations of 1 and 2 electrons from the reference configuration into an active set of orbitals, which resulted in an expanded basis set. We compute singles and doubles in order to include dominant correlation elements. The basis set was sequentially expanded by the principal quantum number n (shell). For example, in the aforementioned work on forbidden transitions of O I, we began with $1s^2 2s^2 2p^4$ as the reference set, and then 3s 3p 3d was added ($n = 3$ shell), followed by 4s 4p 4d 4f ($n = 4$ shell), etc. We also employed the frozen core approximation, so that the inner-shell atomic orbitals are sequentially 'frozen' as more outer orbitals are added. In other words, the core orbitals were initially allowed to optimize independently, but each time an extra orbital was added, the inner orbital was then held fixed so that only the new, outer orbital was optimized. This is important as it maintains essential stability and avoids propagating correlation errors. Hence, correlation was slightly constrained compared to a notional complete active set expansion to maintain stability and convergence.

A key difference in computational procedures between our previous work on the forbidden transitions in O I and this work is the limit on angular momentum number, l. Since O I naturally has more electrons than O II and O III, it is more computationally expensive.

Table 1. Calculated wavelengths for O I and O III transitions compared with the measurements compiled by Moore (1993). Transitions A − C are O III transitions, whereas D − H are O I transitions. The numbers in the parentheses are percentage differences between the current expansion and the immediate previous expansion. A small percentage indicates the stability and convergence of the calculated results.

Transition	This work (nm)	Moore (1993) (nm)	Ratio Theory/Experiment
A	339.72 (0.65 per cent)	338.4901	1.0036
B	346.37 (0.70 per cent)	345.0907	1.0037
C	346.70 (0.80 per cent)	345.4986	1.0035
D	134.04 (0.017 per cent)	130.6029	1.0263
E	117.55 (0.024 per cent)	115.2151	1.0203
F	100.38 (0.029 per cent)	99.0204	1.0137
G	133.64 (0.022 per cent)	130.2168	1.0263
H	133.92 (0.017 per cent)	130.4858	1.0263

One of the many key challenges in relativistic atomic calculations is striking a balance between accuracy and computational feasibility, and as such, certain approximations and restrictions are needed. In this case, our O I forbidden transition calculation was restricted to the maximum angular momentum number l = f ($l = 4$). For O III, we extended our calculations up to l = h ($l = 6$). We do not believe that the continuum contribution (generally not computed in past or current work) is significant in this case, and that the margin of error allowed, especially with O I, is sufficiently large enough to include any possible effect such contribution would have had on the results.

4 RESULTS AND DISCUSSION

Our final results for O III involve an expansion up to the $n = 7$ shell and the 7h subshell; for O I we expanded the calculation up to the $n = 9$ shell and the 9f subshell. Table 1 lists the calculated wavelengths of this work and the measured wavelengths tabulated by Moore (1993), which is currently the standard used for the NIST data base (Kramida et al. 2012). The numbers in the parentheses are the percentage differences between the current expansion and the immediate previous expansion. For example, with transition A, the calculation was extended up to the 7h subshell, so 0.65 per cent is the difference between the computations up to the 7h subshell compared to that up to the 6h subshell. The small percentage difference reveals the robustness of both the theory and the code, and the convergence and stability of the eigenvalues and eigenvalue differences.

The ratios between our theoretical calculation and the available measurements are all close to unity and look promising. An interesting feature from these results is that our calculated wavelengths are slightly, but consistently, higher than the measurements. Such a consistent discrepancy is highly suggestive that a key factor is unaccounted for, either in this work or in the astrophysical measurements.

The results for the O III transitions are within theoretical uncertainty of unity, and therefore appear fully consistent (and converged), demonstrating that there appears no limitation of the code or interaction terms down to e.g. the 0.4 per cent level. This is a remarkable demonstration and suggests that such convergence could always be achieved subject to similar levels of electron correlation; and that in cases where such convergence is not so successful there could be a limitation either of the implemented model or method, or a limitation of the expansion and wavefunctions.

Conversely, the O I transition convergence supports the idea that the wavelengths are consistently higher, here at the 1.4–2.6 per cent level, compared to a stable eigenvalue convergence at the 0.02 per cent level. This is strong evidence of an apparent discrepancy between theory and tabulated experiment, the resolution of which will require additional investigation and experimental work.

Table 2 provides a summary of the transition probabilities for the chosen O III transitions. The theoretical results listed under Wiese et al. (1996) was extracted from the NIST online data base (Kramida et al. 2012). An advantage of our relativistic approach is that the oscillator strength of electric multipole transitions may be calculated using the Babushkin and Coulomb gauges. Non-relativistically, they reduce to the well-known length and velocity gauges, respectively. We argue that the ratio of these two gauges serves as a key indicator of how well the wavefunction converges – a ratio close to unity is a good indication of convergence. In the non-relativistic approach, even with relativistic corrections, it is often not possible to investigate the ratio of the two gauges. This is because, if relativistic corrections are to be applied, the length gauge only needs to be corrected to order $O(\alpha^2)$, but the velocity operator requires a correction to the gradient operator (Tachiev & Froese-Fischer 2002). Hence, non-relativistic results are usually reported only in the length gauge. Of course, gauge convergence is a necessary, but insufficient, requirement for wavefunction convergence. Therefore, it is valuable to keep track of the convergence of gauges and of other key indicators such as energy.

It has been well established that forbidden transitions are much more difficult to calculate than allowed transitions. Usually, the gauges either do not converge, or converge very slowly. This problem can often be ameliorated through further expansion of the basis set as a means of achieving a better approximation of the wavefunction. However, in relativistic calculations, the number of CSFs can grow extremely quickly, which makes the problem computationally challenging or unstable. Ergo, developing an efficient expansion model is a challenging but essential step when using the MCDHF method. All the results presented in Table 2 are allowed transitions, where excellent gauge convergence has been achieved, as demonstrated by the gauge ratios that are close to unity.

From the table, the experimental values are within a factor of 1.5 or 3, but notably the amplitude for transition A has been in persistent disagreement with theory. In general, the predictions of NIST theory are confirmed by our calculations, but with an uncertainty some 10–20 times improved. Further, our results are consistent between gauges to 0.2 and 0.6 per cent, despite convergence in each gauge to approximately 1.2–2.4 per cent. At this point we would recommend the use of our theoretical values, but would encourage further accurate experimental work.

Table 3 shows calculations for E1 transitions in O I, where we have employed the same method and obtained slightly poorer convergence between the gauges, despite expanding to a larger basis set (up to $n = 9$). Here, the theoretical predictions listed by Wiese et al. (1996) and tabulated by Kramida et al. (2012) for the NIST data base claim a much improved accuracy, so we can make a more insightful test. Our work remains broadly consistent with that of NIST. Additionally, our gauge investigation is even more insightful, in that the velocity gauge computation appears more convergent and is also in closer agreement with the prior theoretical work of NIST. However, the gauge convergence here, even for E1 transitions, is only 13–3.5 per cent, with the length gauge explicitly suggesting that the computation (of the length gauge transition probability) has

Table 2. Calculated transition probabilities (the A-coefficient) of O III lines compared with other values available in the literature, expressed as $\times 10^8$ s. The basis set was expanded to the 7h subshell. The percentage in the parentheses is the difference between the current expansion (7h) and the immediate previous expansion (6h). The transition probabilities are given in both length (Babushkin) and velocity (Coulomb) gauges, as indicated by *L* and *V*, respectively. The gauge ratio is between the length and velocity gauges.

	Pinnington et al. (1970) (Experiment)	Lewis & Zimnoch (1969) (Experiment)	† (Experiment)	‡ (Theory)	This work (theory): gauge Velocity	Length	Gauge ratio V/L
A	0.46 ± 50 per cent			1.48 ± 25 per cent	1.385 12 (1.2 per cent)	1.392 32 (2.2 per cent)	0.995
B	1.14 ± 25 per cent			1.44 ± 25 per cent	1.401 67 (2.4 per cent)	1.409 52 (3.2 per cent)	0.994
C	1.36 ± 25 per cent	1.5	1.31	1.72 ± 25 per cent	1.663 86 (2.1 per cent)	1.666 68 (2.9 per cent)	0.998

Key –
A : $1s^2 2s^1 2p^2(^4P)3p^1\ (^5P^o_3) - 1s^2 2s^1 2p^2(^4P)3d^1\ (^5D_4)$
B : $1s^2 2s^1 2p^2(^4P)3p^1\ (^5D^o_3) - 1s^2 2s^1 2p^2(^4P)3d^1\ (^5F_4)$
C : $1s^2 2s^1 2p^2(^4P)3p^1\ (^5D^o_4) - 1s^2 2s^1 2p^2(^4P)3d^1\ (^5F_5)$
†Druetta, Poulizac & Dufay (1971) ‡Wiese et al. (1996).

Table 3. Calculated transition probabilities of some O I lines, compared with the theoretical tabulation of NIST. The basis set was expanded to the 9f subshell. The percentage in the parentheses is the difference between the current expansion (9f) and the immediate previous expansion (8f). Here, we follow the same notation convention of Table 2.

	Wiese et al. (1996) (Theory)	This work (theory): gauge: Velocity	Length	Gauge ratio V/L
D	0.676 ± 3 per cent	0.649 57 (1.6 per cent)	0.560 95 (5.57 per cent)	0.864
E	5.28 ± 10 per cent	5.333 51 (0.33 per cent)	4.848 27 (3.10 per cent)	0.909
F	1.68 ± 10 per cent	1.713 97 (1.03 per cent)	1.653 21 (0.82 per cent)	0.965
G	3.41 ± 3 per cent	3.280 82 (1.60 per cent)	2.835 36 (5.60 per cent)	0.864
H	2.03 ± 3 per cent	1.954 16 (1.59 per cent)	1.687 73 (5.56 per cent)	0.864

Key –
D : $1s^2 2s^2 2p^4\ (^3P_0) - 1s^2 2s^2 2p^3(^4S^o)3s^1\ (^3S^o_1)$
E : $1s^2 2s^2 2p^4\ (^1D_2) - 1s^2 2s^2 2p^3(^2D^o)3s^1\ (^1D^o_2)$
F : $1s^2 2s^2 2p^4\ (^3P_1) - 1s^2 2s^2 2p^3(^2D^o)3s^1\ (^3D^o_2)$
G : $1s^2 2s^2 2p^4\ (^3P_2) - 1s^2 2s^2 2p^3(^4S^o)3s^1\ (^3S^o_1)$
H : $1s^2 2s^2 2p^4\ (^3P_1) - 1s^2 2s^2 2p^3(^4S^o)3s^1\ (^3S^o_1)$.

not yet converged to the 6–1 per cent, respectively. The most important insight here is that these markers are correlated, and confirm the value of these estimates of convergence. As the wavefunction of both systems are completely different from each other, it should be of no surprise that the gauges would not be converging at the same rate – suggesting that the approximated wavefunction is incomplete, rather than a failure of the theory. Once again, this demonstrates the importance of formulating an appropriate model for individual calculations. Again, we commend our (velocity gauge) results in this case.

As we can see in Table 1, the calculated wavelengths of this work are stable, as indicated by the small fluctuation given in the parentheses, and are within what appears to be reasonable agreement with the cited wavelengths. Similarly, our calculated transition probabilities in Tables 2 and 3 have converged to very stable values, irrespective of gauges, and falls within the margin of errors of the NIST data base.

5 DISCUSSION AND CONCLUSION

Using the fully relativistic MCDHF method, we have successfully calculated the transition probabilities and wavelengths of key O III and O I transition lines that are of astrophysical interest. The results were reported in both length and velocity gauges, where excellent gauge convergence was achieved. A consistent discrepancy was found between the calculation of this work and the available literature.

It is important to consider the use for this work, as indicated in Figs 1 and 2. The first indicates the lines presented in this work, as observed and reported in astrophysical studies, but with improved convergence of energies and A-coefficients. However, we observe in the same region of the spectrum additional transitions with apparently higher coefficients. While their ability to be observed depends critically upon the production mechanisms and the degeneracy, it seems reasonable to postulate that if the lines focused upon in this study are observable, and if the prior literature discussion of amplitudes is valid, then other lines should be observable and perhaps in the manner simulated in the figure. However, this apparently has not occurred – we would therefore invite experimental laboratory and astrophysical investigation of this spectral region.

The situation for O I is quite different. The figure indicates a potentially rich spectrum so far unreported astrophysically. Possible reasons are well understood in that neutral oxygen forms the molecule above a very low pressure; and higher temperatures will lead to ionization and observation of e.g. O III rather than O I. However, it seems plausible that experiments could be made and investigated on the presence and distribution of neutral atomic oxygen and that this could be indicative of e.g. low-density regions.

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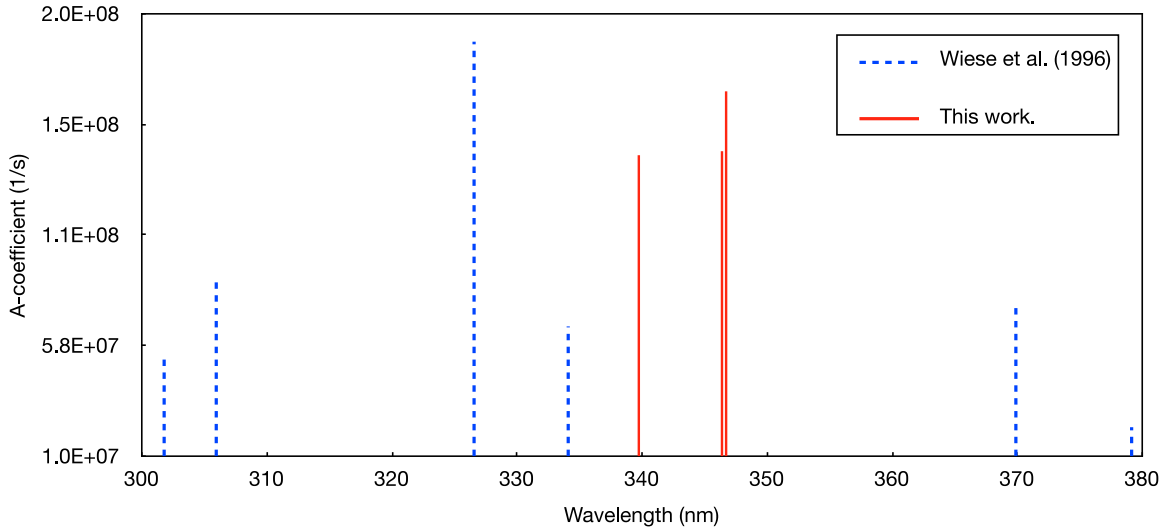

Figure 1. O III spectral representation from the literature. Red = this work. Blue = other lines from Wiese et al (1996) theoretical tabulation as extracted from NIST data base.

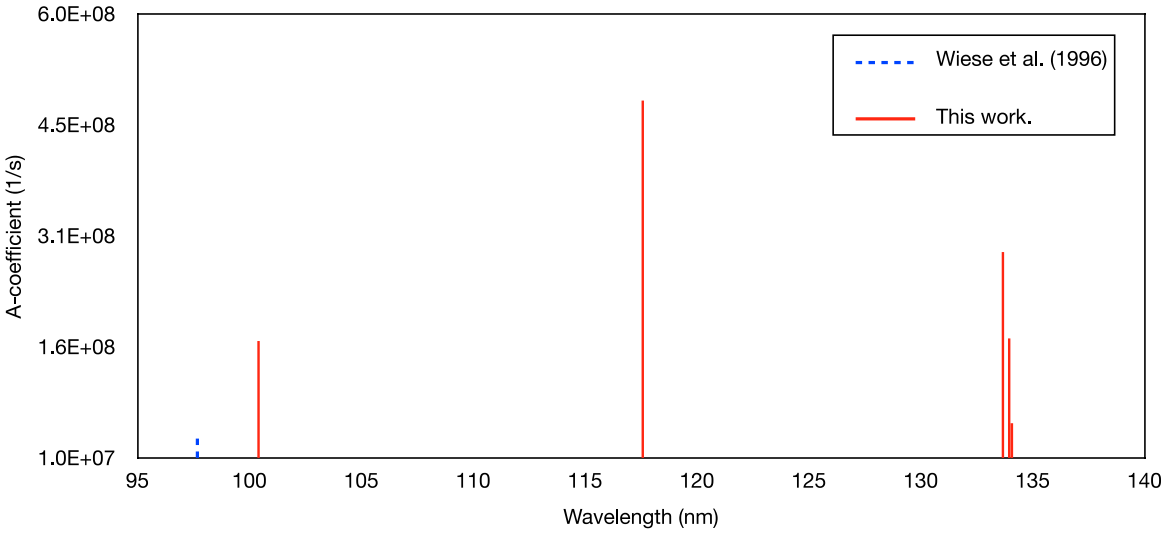

Figure 2. O I spectral representation from the literature. Red = this work. Blue = other lines from Wiese et al. (1996) theoretical tabulation as extracted from NIST data base.

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