Lifetimes of Tc I $(4d+5s)^6 5p$ and $4d^6 5s$ ^6D States
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Authors' Response to Referee

We thank the referee for his/her useful remarks and quick reply. We have addressed the points made (see below) and are submitting a revised MS.

Much of the confusion the referee notes is because we have used the words "eigenvectors", "parents", and "basis functions" more or less interchangeably throughout to denote the many electron J^2, J_z, Parity eigenfunctions that are the members of our RCI basis. We realize the last is most widely used, and have modified the MS accordingly. The "original parents" (now on p. 7) are thus "original basis functions", and a parenthetical comment has been inserted to clarify that "original" here refers to the larger set of basis functions from a given correlation configuration prior to the rotation that is performed by REDUCE.

We have enlarged and improved our description of the REDUCE method (bottom of page 6). In particular, we note that mathematically the problem is to solve N_R linear homogeneous equations in N_P unknowns ($N_P \gg N_R$). This is an underdetermined problem for coefficient ratios, for which the SVD algorithm of Press *et al.* is eminently suited. As to the application of SVD to Tc I in particular, we have added a parenthetical comment on p. 7 mentioning that due to the complexity of the configurations, our old method would have taken weeks more computation time due to the need to adjust input and rerun REDUCE multiple times. Such a trial and error approach of our old method was less cumbersome on smaller systems where typical REDUCE run times are on the order of half an hour instead of half a day.

We have removed the text discussing the floating point error (p. 13).

The footnotes and captions of Tables 1, 2, and 3 have been modified so as to clarify what is meant. In direct response to the referee's comment on dimension, we have reworded the sentence on p. 6 to make it more clear that it is a set of *matrix elements* (involving the basis functions of the correlation configuration of interest) that are expressed by a sum over R^k integrals.

In regards to the referee's final comment on technicalities, we agree that in a more typical (simpler) set of calculations much less detail "internal to the method" is required. We have elaborated more fully in this text partly to explain to the reader the complexity and the scope of these calculations and partly because the additions and changes to our code for this work are quite extensive compared to many of our prior publications (thus this text also serves as an "update" to our earlier detailed REDUCE references).

We also thank the referee for his/her patience in going over the MS!

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Abstract

Lifetimes, branching ratios and Landé g values have been obtained from Relativistic Configuration Interaction calculations for all $J = 5/2 - 11/2$ odd parity levels below 34516 cm^{-1} and for the ^{6}D $J = 3/2 - 9/2$ even parity levels. From these results, we propose the $^6\text{D}^e_{9/2} \rightarrow {}^6\text{F}^o_{11/2}$ transition for possible use in Atomic Trap Trace Analysis (ATTA) studies. Due to the increased number (n) of d electrons as compared to our earlier work (7 vs 4), these calculations were time consuming and required several improvements in computational equipment and strategy. As expected, average energy errors are larger ($\sim$1450 cm^{-1}), and f value gauge agreement ($\sim$19%) is worse than achieved in lower n states.

PACS Ref: 31.25.Eb, 31.25.Jf, 32.70.Cs, 32.10.Fn

1. Introduction

Transition metal atoms are technologically important, in fusion and astrophysical physical plasmas and ultrasensitive isotope trace analysis, for example. A technique called atom trap trace analysis (ATTA) has been developed very recently [1] for the latter, and may possibly be applied to the detection of Tc I [2], if Tc I has favorable oscillator strengths, e.g. a single dominant transition to and from a metastable level, as in Kr I [1]. However, no reliable Tc I oscillator strengths exist, and it is the purpose of this work to remedy that.

Accurate results for transition metal atoms are difficult to obtain using *ab initio* methods, because of the presence of open d subshell electrons, and the need [3] to include relativistic effects, simultaneously with the treatment of correlation. In the early 1990's we began [4] calculations of hyperfine structure constants (hfs) for (d+s)^n states with low $n = 2$, 3, and 4. As we discuss below, the complexity of the calculations greatly increases with n up to a limit, and in 1995, the $n = 4$ Nb II hfs calculations [5] represented an *ab initio* limit of what could then be successfully treated. On the other hand, the hfs results [6] for $n = 2$ La II, perhaps represented the most accurate results that could be obtained at the time using relativistic configuration interaction (RCI) methods. During the mid 1990's transition probabilities [7] and Landé g values [8] were calculated for $n \leq 4$ states, and most recently, excitation energies and magnetic dipole transition probabilities within the Ti I 3d^4 isoelectronic sequence [9, 10], possibly of great interest to the plasma fusion community as a diagnostic, were obtained.

All these RCI calculations had been done by a computer algorithm [11] limited to an energy matrix of order 7000, or smaller. That such a "small" matrix could produce useful results, was due mainly to the introduction of a method called REDUCE (see Section 2), which at little cost, often allowed the removal of more than 90% of the basis functions associated with the correlation configurations.

In Table I, we show how great the increase in the number of basis functions is with n, for an important correlation effect, where two d (or a d and an s, or two s) electrons are converted into two f electrons. The column marked "Full" gives the total number of basis functions needed just for the three manifolds (d+s)$^{n-3}$pf^2. Table I illustrates that the basis size, both DF and correlation configurations, for d^{n-1}p is larger than (d+s)^n, due to the decreased effect of the Pauli exclusion principle. Also note that (d+s)^{8}p has perhaps the largest basis set for these types of calculations, since although (d+s)$^{n-1}$p, $n = 6$, 7, 8, have larger DF manifolds, (d+s)^{8}p has the more complicated (d+s)^{6}pf^2 configuration in its basis (note, however, that the level of complexity of the basis set is dependent on J and we have presented data based on the J that has maximum or near maximum MCDF basis size for a given n). In this regard, d^m and d^{10-m} are by no means equivalent, even though their DF manifolds have the same number of functions. In particular, in the present case the calculations for Tc I (d+s)^{6}p are much more complicated than a (d+s)^{4}p calculation would be, due to the presence of, for example, the large number of basis functions in the correlation configuration d^{4}pf^2 (vs d^{2}pf^2). Finally, Table I illustrates the value of REDUCE in limiting the basis size to a manageable level, often decreasing the basis size associated with a given configuration by an order of magnitude or more. The number of reference (MCDF) functions is crucial in determining the number of REDUCE survivors, as is explained in the Section 2.

From Table I we see that energy matrices much larger than 7000 are needed, even with

REDUCE, in order to deal with problems with $n > 4$. In fact, a considerable retooling of the computer algorithms was needed to make the leap to $n = 7$ in order to complete the Tc I work. This is in addition to the recent enlargement of the energy matrix to 20 000, and a "one-pass" oscillator strength computer algorithm [12] which we introduced for our recent thorough calculations of oscillator strengths of Fe V $3d^4 \rightarrow 3d^3 4p$ transitions [13] and of Ta II [14] $(5d+6s)^4 \rightarrow (5d+6s)^3 6p$ transitions. Although these are considerably more accurate than the earlier $n = 4$ Nb II calculations, they are still limited to $n = 4$.

2. Methodology

The reference manifolds, $(4d+5s)^7$ and $(4d+5s)^6 5p$, are generated by applying the energy variational principle, using the Dirac-Coulomb Hamiltonian, H_{DC}. The wavefunctions used are eigenstates of relativistic parity, J^2, and J_z, formed by a linear combination of determinants, whose elements are one electron spinors. The spinors have an unknown radial part, and a Dirac-hydrogenic angular part. Generally, there is more than one reference basis function with the desired eigenvalues (J, parity), so there are both coefficients and radial functions to obtain. The energy variational principle yields a coupled set of inhomogeneous first order integro-differential equations, known as the Dirac-(Hartree)-Fock equations (MCDF) which we solve using the computer algorithm of Desclaux [15]. Relativistic two particle corrections to the Hamiltonian, i.e. the Breit operator, if necessary, are added in the correlation stage.

The above MCDF wavefunction needs improvement, and we do so using the RCI method [16]. We appeal to perturbation theory to suggest what additional manifolds are needed in the wavefunction (all relativistic configurations reducing to the same limit as $c \to \infty$ belong to the same manifold). The missing terms, called correlation, are needed due to the presence of the Coulomb operator, except perhaps in highly ionized high Z species, where the Breit operator may also play a role. To first order, the correlation part of the wavefunction would be confined to single and double excitations from the reference function, with emphasis placed on excitations from the outermost (e.g. valence) subshells, as they can be nearly degenerate, i.e. yield a small denominator in the second order energy:

$$\frac{|H_{0,i}|^2}{|H_{0,0} - H_{i,i}|}. \tag{1}$$

It is also important to maximize the numerator, to the extent possible, since the correlation energy depends approximately on its square. This is best achieved by using correlation radials ("virtuals") which have a very similar value of $< r >$ as the MCDF radials they are replacing. These virtuals represent the compact portion of an entire Rydberg and continuum series. To avoid variational collapse into the positron sea, and to make them easy to adjust, we represent them as Relativistic Screened Hydrogenic functions (RSH), whose effective Z, Z^*, is estimated by matching the $< r >$ of the virtual to the MCDF radial it is replacing. Fine tuning of the estimated Z^* is made during the diagonalization of the RCI matrix. As is typical of one particle expansions, the first term can saturate a large part of the radial space (up to 90% here), while additional terms are much more slowly convergent. Nonetheless two or three virtuals per symmetry (κ) usually suffice. It should also be apparent from $< r >$, that different shells will need different RSH (Z^*).

Our previous practice has been to use MCDF radials optimized on a single level to represent all reference functions of the same J, in the RCI matrix. For Tc I, this practice lead to energy difference errors as large as 15 000 cm^{-1} for the second and higher excited states of the J=7/2 odd parity, when only the reference manifolds were used in the RCI matrix. Separate MCDF calculations [15] on each J=7/2 level demonstrated that about 5 000 cm^{-1} of this error was to be associated with the change of 4d, 5s, and 5p radials in going from a $4d^5 5s5p$ to a $4d^6 5p$ configuration. To reduce the necessity of having the virtuals represent this effect, as well as the "standard" correlation effects, additional radials 4d′, 5s′, and 5p′ obtained from optimization on $4d^6 5p$ were added to the MCDF radial basis, while retaining a completely orthonormal radial space. Similar additions were made for each J and parity Tc I basis set. We have used this technique in the past [17] to provide better radial basis sets, and these effects have also been observed and dealt with by others, for example, by Froese-Fischer [18].

These additional DF radials are introduced to our bases in the form of single excitations from the valence space: 4d+5s → 4d′ (the dominant single excitation), 4d+5s → 5s′, and 5p → 5p′. The advantage of using these extra DF radials is that their energy contribution is almost entirely differential in the sense that they have very little contribution to the lowest level of each J-parity calculation (the root for which the primary 4d, 5s, and 5p radials are optimized). In cases such as the even $J = 5/2$ calculation and the odd $J = 3/2 \rightarrow 9/2$ runs where the lowest root has a differing 4d occupation than most or all of the upper levels, these single excitations can contribute up to 1.3 eV or more to the upper levels and only ∼50 meV to the lowest root. By contrast, in our earlier work [4, 5, 6, 7, 8, 9, 10, 13] mentioned in Section 1, for which there are fewer d electrons in our MCDF manifolds, single excitations from the valence d shell have a smaller impact than double excitations (e.g. in Fe V $3d^4$ [13], 3d → d and $3d^2 \rightarrow d^2$ contribute ∼100 meV and ∼500 meV, respectively). In Tc I with 4d → d contributing as much or more than $4d^2 \rightarrow d^2$ to the correlated energies, our usual method of "layering" sets of virtual orbitals would likely require several vd orbitals optimized to 4d → d as well as one or two optimized to $4d^2 \rightarrow d^2$ (the Z^* that maximizes the single excitation contribution is not necessarily the Z^* that maximizes that of the double excitation). Using this alternative approach we find the basis is reasonably saturated with 4d′, a vd optimized for the double excitation, and a second vd′ optimized in the presence of both single and double excitations. Thus the additional DF radials allow us to significantly limit our basis, which is critical in a calculation of this magnitude.

Our choice of correlation configurations is balanced by constraints of our 20 000 basis function limit and the need to include the most important configurations, both in terms of differential energy contribution and effect on the properties we wish to calculate. First order perturbation theory restricts the angular symmetries needed to $3 \times l_{max}$, when 0 or 1 virtual is used. Here, l_{max} is the maximum symmetry appearing in the reference subshells being excited. Computational experience suggests this restriction is equally valid for two virtuals. For excitations from the valence shell of Tc I, this suggests virtual symmetries up to $l = 6$ may be required, however, we find $l = 4$ or 5 sufficient. In addition to the single excitations previously mentioned we include single excitations from the valence space up to $l = 4$ (vg). In the case of the even Tc I calculations we find that the double excitation $4d^2 \rightarrow vl^2$ were important differentially up to $l = 5$ ($v\mathrm{h}^2$), while basis size constraints require us to limit our one electron basis to $l = 4$ for the odd calculations. Choices of core and core-valence excitations based on differential energy contributions and practicality (due to the size of the problem) are discussed in detail in Section 3.

Accurate calculation of f values requires consideration of the first order theory of oscillator strengths (FOTOS) [21]. Simply put, FOTOS indicates that the correlation configurations important to oscillator strengths can be determined by applying the same type of transition to one of the DF manifolds, initial or final state, and including them in the calculation of the other. In the case of Tc I $(4d+5s)^6 5p$ E1 transitions, applying the excitations $4d+5s \rightarrow p+f$ indicates $(4d+5s)^5 p^2$ and $(4d+5s)^5 pf$ are important configurations in the even basis. The excitation $5p \rightarrow s+d$ is well represented in the even DF manifolds themselves as well as the previously mentioned single excitations. Likewise, the core excitation $4p \rightarrow s+d$ in $(4d+5s)^6 5p$ is well represented in our even exclusion pair excitations $4p^5(4d+5s)^6 \upsilon p \upsilon d$ (υp corresponding to the DF 5p which is not present in the even calculations), and $4s \rightarrow p$ applied to $(4d+5s)^6 5p$ leads us to include $4s4p^6(4d+5s)^6 \upsilon p^2$ in the even calculations. In a similar manner FOTOS effects are accounted for in the valence correlation of the odd states, resulting in the inclusion of $4p5p \rightarrow d^2$ and $4s \rightarrow d$ (corresponding to the $4p \rightarrow d$ and $4s \rightarrow p$ excitations in the even manifolds).

At this juncture, an appreciation of the resources available for this and similar ($n \geq 7$) problems is needed. Our computer is a 500 MHz Alpha Workstation, with 1.5 GB of memory. Recently, we upgraded our total disk capacity from about 18.0 GB to about 90.0 GB. Current limits (20 000) on the matrix size are dictated by our desire to retain the non-zero elements in memory. Expansion to a matrix of ∼100 000 is feasible, as the diagonalizer [20] does not require that the elements be ordered. Some speed would be lost in rolling the matrix out to disk, but about 70% of CPU time is spent assembling the matrix element structure. The structure file can exceed several GBs, but has the virtue of reducing the Z^* iteration costs greatly.

In Table II, we have given the number of basis functions for some of the significant correlation contributions needed in a thorough treatment of this system. These involve shallow-core/valence excitations, as well as pure valence excitations. Bearing in mind that a few of each type may be needed for radial saturation, and that not all significant manifolds have been shown, one may imagine that matrices of order 1 000 000 or so could be needed, if nothing were done to constrict the N-electron basis set size. This would be of the same order as some molecular calculations being done, except we would be dealing with several roots.

Fortunately, there is a way to greatly restrict the N-electron basis which we call REDUCE. It has its origins in an observation made by Bunge [22], who noted (in present terminology) that the matrix elements involving basis functions of the reference space and a correlation manifold could be formally expressed as a sum over a small number of radial integrals (i.e. the spin-angular integrations/sums are carried out). A rotated set of correlation basis functions could then be prepared, subject to the condition that the number of zero matrix elements with the reference manifold and the correlation manifold was maximized. Consistent with a first order wavefunction form, correlation basis functions producing zero matrix elements could then be discarded. Our first relativististic implementation of this was in our work on Zr II hfs [23]; there reductions of a factor of three were obtained, with little loss (< 200 cm^{-1}) of energy.

The efficiency of REDUCE [24] grows strongly with n, but decreases in proportion to the number of reference basis functions. Table II gives the explicit calculated reduction, but it is possible to predict the improvement without calculation, as we do in Table III.

Obtaining the N_P rotated REDUCE basis functions for N_R radial integrals is an underdetermined problem (N_R linear homogeneous equations in N_p unknowns), which we previously solved in a brute force manner. The first rotated basis function was expanded using the first N_R original (pre-rotated) basis functions, the ratio of the coefficients obtained, and the rotated basis function was renormalized. For the second rotated basis function, the constraint of orthogonalization was added, and the problem then solved as before. This continued until $N_P - N_R$ rotated basis functions (with zero reference matrix elements) were assembled. The final survivors were then obtained by Schmidt orthogonalization to the existing rotated set. This method sometimes failed because one or more radial integrals might be missing from the first $N_P - N_R$ vectors of the original set, or because two or more of the linear equations were linearly dependent. Patches were made within the program, but they were not always successful. In these cases, solution depended on the skill of the user in adjusting the data, which determined the order of the linear equations. The process was done for each reference with the survivors collected together after undergoing a final Schmidt orthogonalization.

Tc I had too many reference basis functions (e.g. 169), and too many correlation basis functions (several thousand) to permit user resolution of problem cases. Instead the very useful technique of Singular Value Decomposition (SVD) as implemented by Press *et al.* [25] was installed. This is more stable, general, and efficient as the user is no longer required to manually edit input data and rerun the code multiple times to achieve a viable solution (potentially saving weeks of computation time given that a single REDUCE calculation for configurations of this complexity can take half a day or more). Since the size of the problem has increased dramatically, the previous limit of 90 REDUCE basis functions, each with up to 5000 determinants, has been increased to 800 vectors, each with up to 100 000 determinants. For these limits, disk storage for a single REDUCE run could reach 0.64 GB. With so many reference vectors, preparation of the input data was also further automated, to reduce people time.

Several observations concerning use of REDUCE can be made. First, while we have dramatically decreased the size of the energy matrix, each matrix element has become, on the average, more expensive to evaluate, because all REDUCE basis functions use the full determinantal basis for that manifold, and not a subset. Matrix element construction costs had been previously reduced [11] by grouping the determinants by relativistic configuration, and testing these configurations to see whether they interact. This reduces the number of determinantal manipulations that must be made. Second, a glance at Table II demonstrates that even the increased limits of REDUCE are not sufficient to treat all manifolds. For Tc I, these largest manifolds (e.g. 4p(5d/6s) $\rightarrow v$dvf) have not been included. As discussed in the Section 3, this means that Tc I properties can not yet be obtained as accurately as those for smaller ($n = 2, 3, 4$) species. This is not an unexpected trade-off. Finally, use of REDUCE in a "first order" way (MCDF vectors as reference functions) with a "non-relativistic" assumption that radial functions are independent of j (to reduce the number of R^k integrals) generates errors of perhaps 200 cm^{-1} [23] for energetically small to moderate manifolds. In the case of energetically larger manifolds this could reach 10%, or >1000 cm^{-1}. In this case, our preference would be to retain the full set of basis functions, if possible. Capabilities exist [24] to remove all these restrictions for low n cases.

Changes to the RCI program [11] were necessary to accommodate the increases in the

REDUCE output. The total number of coefficients was increased from 8 to 25 million. Secondly, the number of vectors allowed per manifold was increased from 90 to 300. Manifold basis functions share a common determinantal set, and their energy matrix element structure is assembled contemporaneously, for reasons of efficiency. Limits on physical memory precluded treating up to 800 vectors at once, so REDUCE output is broken into units of 300 vectors, to meet this limitation. The structure record, which contains a listing of coefficients and radial integral labels for the manifold, becomes very large, requiring the specification of record length in the Fortran OPEN statement. None of these changes increased the speed nor matrix size (20 000) of RCI. Table II makes clear that ultimately the number of coefficients may have to be increased to 100 million or so. They would then have to be stored on disk, but this can be done efficiently, as only a subgroup is needed at a time, during matrix element structure evaluation.

Oscillator strengths are evaluated [26] in the Coulomb (velocity) and Babuskin (length) gauges, including the effects of non-orthonormality using the methods of King *et al.* [27]. This is a determinantal based method, and substantial use of symmetry has been made [26] to reduce computation costs. For optical transitions, a further efficiency has been recently introduced [14] which makes use of the known scaling of the results with energy difference. For example, for optical electric dipole transitions, the length matrix element scales as ΔE, and the velocity as $1/\Delta E$. All optical transitions for fixed $(J,\, J')$ can be computed for one optical ΔE, and re-scaled at calculation end to the true ΔE. Thus one can do $N_J \times N_{J'}$ transitions for the computational cost of one. For Tc I, the computational cost of a single calculation can be 15 hours or more, so the savings is dramatic. Proper scaling for electric quadrupole (E2) and magnetic dipole (M1) transitions is available in the literature [28].

The relativistic expression for the Landé g value, excluding radiative effects (i.e. $g(S) = 2.0000...$), has been given by Armstrong [29] in equation VI-4a. The matrix elements of the operator may be easily developed from that of the magnetic dipole hfs operator [23] except that the power of r in the radial integral should be 3 in the present instance, and the result divided by αJ. Although radiative corrections ($g(S) = 2.002319$) are typically an order of magnitude smaller than correlation errors, they can be obtained by using the non-relativistic form of the operator [8].

3. Results

A transition suitable for Atomic Trap Trace Analysis needs to have a single dominant branch between two levels, and the bottom level needs to be metastable. From the $4d^5 5s^2\ ^6S_{5/2}$ ground state, this means we should be mainly looking at transitions to $4d^5 5s5p\ ^6P_{3/2,5/2,7/2}$, assuming the LS designations [30] are useful. The odd parity $J = 5/2$ and $J = 7/2$ levels were investigated, but found to have significant branches to $4d^6 5s\ ^6D$, as we show later. The odd parity $J = 3/2$ basis sets were too large to be conveniently obtained, but one might expect that its decay to have similar problems.

The low (< 4200 cm^{-1}) $4d^6 5s\ ^6D$ states are possible candidates, as they are metastable, decaying by electric quadrupole or magnetic dipole transitions. Lifetimes for these are given later. Electric dipole transitions from these levels should be mainly to $(4d+5s)^6 5p\ ^6P$, ^6D, and ^6F levels, with J's ranging from 1/2 to 11/2. Of this range of J's, $J = 11/2$ looks to be the most attractive because it can only decay (E1) to the originating $^6D^e_{9/2}$ level.

Taking ATTA concerns and time and accuracy considerations into account, we decided to limit our investigation to $J = 3/2 - 9/2$ even parity levels below 17 330 cm^{-1} and $J = 5/2 - 11/2$ odd parity levels below 34 516 cm^{-1}. All possible E1 transitions were evaluated between these levels, as well as all E2 and M1 decays from the ^6D even levels.

As mentioned in Section 2, the primary concern with our RCI Tc I calculations is careful treatment of the 4d subshell. The process begins with the choice of one electron radial functions created by the Desclaux MCDF code [15]. Initial difficulties arise due to the fact that in some cases even the lowest energy eigenvectors of a given J are not properly ordered at the three configuration, $(4d+5s)^7$ or $(4d+5s)^6 5p$, MCDF stage of the calculation. The most noticeable case is the $J = 5/2$ even calculation for which the $4d^5 5s^2\ ^6S$ ground state lies above the $4d^6 5s\ ^6D$ in the early stages of the calculation. We have several options available to produce DF radial functions optimized to the true $^6S^e_{5/2}\ 4d^5 5s^2$ ground state. First, we can simply take our radials from a run optimized on the second root of the incorrectly ordered three configuration run. Second, we can use the radials from the lowest root of a one configuration ($4d^5 5s^2$) calculation. The final option involves reusing one electron wavefunctions from a prior run as estimates for a subsequent MCDF calculation. In the case of $J = 5/2$ even, we note that increasing the nuclear charge from $Z = 43$ to $Z = 43.5$ results in the correct ordering of the ^6S and ^6D levels. By stepping down gradually to the true $Z = 43$ and using each set of radials as input to the subsequent run, we eventually produce a three configuration MCDF run with the lowest state correctly identified as $4d^5 5s^2\ ^6S^e_{5/2}$ (this technique is more commonly used in electron affinity studies where no solution is generated for a weakly bound negative ion in an initial calculation using the true Z of the system). Small RCI test runs containing moderate correlation (a single set of virtual orbitals with a few of the largest energy contributing correlation configurations) indicate this last method is the most effective, resulting in both the lowest absolute $^6S^e_{5/2}$ energy and the best relative positioning of the next few levels.

An additional set of valence DF radial functions ($4d'$, $5s'$, and $5p'$) is created for each J-parity calculation with two manifolds of interest (i.e. excluding the even $4d^6 5s$ $J = 3/2,7/2,9/2$) by taking DF radials optimized to an upper root. These additional DF radials are taken from the ^6D level, our primary concern for this study and the first root of a manifold different from the lowest root.

For purposes of comparison to experimental [30, 31] level designations, approximate LS eigenstates are created for the three configuration RCI calculation. These basis functions are created via diagonalization of the L^2 and S^2 matrices using the approximation that the minor components of the one electron wavefunctions are negligible and that the major components are independent of j. The process is a simple linear transformation of the original J^2-J_z basis functions and is useful for LS identification of levels within the three configuration MCDF portion of the wavefunction. In a few cases this LS analysis or Landé g values allow us to identify incorrectly ordered upper levels and determine which is the appropriate level for which to optimize these additional valence radial functions.

Our RCI bases for Tc I are chosen with several competing factors in mind. Foremost is always the 20 000 basis function limit of our code. While the REDUCE method described in Section 2 helps by significantly lessening the number of basis functions in some of the larger configurations by a factor of 10 or more (see Tables I and II), it does little to cut the number of determinants. In Tc I, particularly the odd calculations, we find ourselves approaching both the 500 000 determinant limit and the 25 million coefficient limit. Additional difficulties arise due to the fact that a large fraction ($\sim$1/3) of the basis functions were being taken from REDUCE output, which by design contains only basis functions that interact with the reference functions. The resulting energy matrix is much less sparse than assumed by the dimensioning the code ($>$ 40% non-zero matrix elements compared to $\sim$30% in a typical calculation). Even so, we are able to include configurations within our 20 000 basis function limit that represent (un-REDUCEd) approximately 65 000 and 50 000 basis functions for the largest even and odd calculations, respectively (the even number is larger due to the fact that we include 4p,4d pair excitations, which are prohibitively large in the odd calculation even with REDUCE − see Table II).

Acting against our need to restrict the basis size and other factors mentioned above is the fact that we must adequately saturate important configurations. As mentioned previously, the additional DF radials help provide adequate saturation for the single excitations with only one additional virtual orbital, i.e. the total energy contribution for 4d $\rightarrow$ 4d$'$+vd+vd$'$ is only a few meV greater than that of just 4d $\rightarrow$ 4d$'$+vd. The real benefit, though, is that we are able to optimize the first set of virtuals to the valence double excitations, particularly 4d^2 $\rightarrow$ vp^2+vd^2+vf^2+vpvf, which each contribute at least several tenths of an eV to most levels. The double excitations are then sufficiently saturated with two sets of virtuals (e.g. 4d^2 $\rightarrow$ vf^2+vfvf$'$+vf$'^{\,2}$), where inclusion of a third set if necessary would approximately double the number of basis functions for a given configuration.

Our final consideration in deciding which configurations to add to our bases is the problem of loss of correlation due to preferential treatment of the (4d+5s)^7 and (4d+5s)^{6}5p manifolds. As our calculations progress, we often find losses of energy contribution in some correlation configurations. The effect is most pronounced for “nearby” configurations for which the amount of correlation to our levels of interest is a significant fraction of the energy difference between their manifolds. These configurations typically have large coefficients in the RCI wavefunction, and these coefficients depend inversely on the energy difference between manifolds. In the past (e.g. Sn$^-$ [32] and Ce$^-$ [33]) we have been successful in accounting for much of this loss by inclusion of triple and quadruple excitations that represent excitations important to the manifolds of interest applied to the problem correlation configurations.

All of the above considerations lead us to include only those core excitations that were discussed in Section 2 as important FOTOS configurations. One must be careful in opening core subshells not to include excitations that favor only one of the manifolds of interest, as large differential energy contributions can result. We are fortunate in the odd case that none of these FOTOS excitations are important energy contributors, the largest being 4p5p $\rightarrow$ 4d^2, which contributes only 50-70 meV for all levels. In the even cases, FOTOS suggests inclusion of some large contributors, 4p $\rightarrow$ vp and 4p4d $\rightarrow$ vsvp+vpvd, which add several tenths of an eV to the even correlation energies. The $J = 5/2$ even case is further complicated here as the 4p $\rightarrow$ vp excitation preferentially affects the 4d^{5}5s^2 ^{6}S ground state, and the 4p4d $\rightarrow$ vsvp+vpvd only partially compensates by larger contribution to the 4d^{6}5s levels. The result is increase in positions for the upper levels of 500-1000 cm^{-1}, whereas positions within the single manifold of the other even J's are only affected by $\sim$200 cm^{-1}. We then include a more complete opening of the 4p subshell in the even $J = 5/2$ case by including 4p $\rightarrow$ vf and 4p4d $\rightarrow$ vdvf. Inclusion of 4p4d $\rightarrow$ vdvf provides greatly improved energies for the upper $J = 5/2$ levels, but the ^{6}D level is pushed well below its experimental [30] position of 3701 cm^{-1} above the ground state. The single excitation 4p $\rightarrow$ vf compensates due to larger contribution to the 4d^{5}5s^2 ground state, resulting in energy positions that are only a few hundreds of cm^{-1} off those of the $J = 5/2$ valence calculations. The effect is to increase the correlation in the $J = 5/2$ run by $\sim$1 eV in comparison to the other even J's.

The levels of our final odd RCI runs have a total correlation of approximately 1-3 eV ($\sim$10-25 000 cm^{-1}), and the largest configurations, 4d $\rightarrow$ d and 4d^2 $\rightarrow$ f^2, exhibit moderate losses ($\sim$20-30 meV) in energy contribution from early valence calculation stages to the final runs. The necessity of opening the 4p subshell in the even runs, yields much larger total correlation energies in the range of 4-5 eV (and 5.5-7 eV in the $J = 5/2$ case due to the additional correlation discussed above). As a result, we find energy losses in the combined contributions of 4d $\rightarrow$ d and 4d^2 $\rightarrow$ f^2 of over 100 meV in some of the $J = 5/2$ levels and over 50 meV in some levels in the other even cases. Test runs including the triple excitation 4d^3 $\rightarrow$ 4d$'v$f^2, representing 4d $\rightarrow$ 4d$'$ and 4d^2 $\rightarrow$ vf^2 applied to each other, lowered some levels in the $J = 5/2$ calculation $\sim$500 cm^{-1} with respect to the 4d^{5}5s^2 ground state. The improvement is attributed to the fact that the problem configurations have been lowered relative to the manifolds of interest by partially including the missing correlation that is lost due to preferential treatment of the MCDF configurations.

Due to the size of the Tc I bases, we are unable to provide as thorough a treatment of second order effects as in past studies [32, 33]. For example, while the above triple seems to represent the bulk of the second order correction needed for the two largest configurations, one might expect that applying 4d^2 $\rightarrow$ vpvf (which contributes several tenths of an eV to some levels in the MCDF manifolds) to the problem cases (i.e. 4d^3 $\rightarrow$ 4d$'v$pvf and 4d^4 $\rightarrow$ vpvf^3) would also impact their contributions by further lowering the energy gap between their manifolds and the levels of interest. Since we cannot afford to include several triples and quadruples, and considering that even 4d^3 $\rightarrow$ 4d$'v$f^2 alone is prohibitively large in the odd calculations, we elect to provide second order corrections in the form of shifts in the diagonal energy matrix elements. By shifting the diagonal elements of 4d $\rightarrow$ d and $4d^2 \rightarrow f^2$ we simulate addition of the second order correlation with no increase in the size of our calculations. The difficulty lies in choosing an appropriate amount of shifting, since the problem configurations are not entirely uncorrelated. For example, the $4d^2 \rightarrow v d^2$ excitation in the manifolds of interest is effectively $4d4d' \rightarrow v d^2$ applied to the $4d \rightarrow 4d'$ problem case. Our approach is to shift the diagonal elements of the problem configurations by an amount representing 75% of the total correlation of the lowest root of each J-parity calculation, in order to err on the side of caution. In fact, the process of applying these shifts is a nonlinear one, and we know from past experience performing diagnostic shifts within manifolds that the actual position of the shifted manifolds is likely only lowered half of the amount of the shift or less. Nevertheless, we find that this approach restores nearly 80% of the energy contributions that were lost as the manifolds of interest were pulled away from the correlation configurations during successive steps of our calculations.

In Table IV we present LS composition, energy levels, and Landé g values for our final RCI calculations. Also presented here for comparison are the experimental energies and g values of Bozman *et al.* [30]. We present data for those levels which are given LS designations in the experimental work [30]. In several cases, we have pairs of nearby levels that are heavily mixed and may have their leading terms flipped from the experimental ordering. In these cases we preserve the experimental labeling, even though the label may not be the leading LS term. The exception is the odd $J = 5/2$ $4d^6 6p$ ^6P and ^4P pair of levels whose order is flipped with negligible mixing between the two. In this case we present our RCI values in the experimental ordering with the two energies inverted. In the even cases $J = 5/2$, $7/2$, and $9/2$, we find that the RCI ^4G levels are predominantly $4d^5 5s^2$, and though they are experimentally identified as $4d^6 5s$, the labeling reflects our $4d^5 5s^2$ designation. Additionally, in the odd $J = 5/2$ and $7/2$ cases, the uppermost level is identified experimentally as $4d^5 5s5p$ ^6P, though our RCI LS leading terms are ^6G. Test runs with additional roots show the presence of the ^6P level mixed with a ^6H level positioned higher in the spectrum, and the experimental spectrum [30] indicates the next few (unidentified) levels are less than 1000 cm^{-1} away from each other (misordering of levels this high in the spectrum is not uncommon in an RCI calculation of this magnitude).

It should be noted that the LS breakdown is taken from the approximate LS eigenstates (rotated $J^2 - J_z$ basis functions) discussed above. Thus the terms and percentages represent only the MCDF three configuration portion of the wavefunction. The analysis is still useful because all levels are $\sim$95% pure $(4d+5s)^7$ or $(4d+5s)^6 5p$. The Landé g values, however, are calculated using the entire RCI wavefunction.

Several points can be made from analysis of Table IV. First, the errors in positions of levels seem to fall into three categories: ^6D levels (for cases where ^6D is not the lowest root) tend to have errors of a few hundred cm^{-1} to 1000 cm^{-1} (the exception being the odd $J = 9/2$), the ^6F, ^4P, and ^4D levels tend to be off by 1000-1500 cm^{-1}, and the higher quartets, ^4F, ^4G, and ^4H have errors of 2000 cm^{-1} or more. The extreme cases are the even $J = 7/2$ and $J = 9/2$ ^4H levels, for which the 4d single excitation only contributes $\sim$200 meV compared to nearly 1 eV in other levels. We attribute the distinctions between these groups of levels to the varying degree for which the 4d$'$ radial provides correction to the

4d subshell. Large LS mixing and errors in level order can occur where upper states have different configurations. This is noticeable in the ^{4}G even levels which have a significant 4d^{6}5s component, particularly in $J = 5/2$ where it mixes heavily with the nearby ^{4}F level. There is a similar problem with the 4d^{6}5p ^{4}P$_{5/2}$ level which is actually mostly 4d^{5}5s5p in the final RCI run (again, the experimental [30] designation has been retained wherever possible), as its order is flipped with the nearby 4d^{6}5p ^{6}P. In these cases, a level that is the same configuration as the lowest root for that J is placed much lower in the spectrum due to the fact that the main DF radials are optimized to that manifold. Finally, we note that our g values are in good agreement with experiment except in cases where there is heavy LS mixing between a pair of levels.

In Table V we present the lifetimes for all the odd levels of interest (with the exception of the uppermost $J = 5/2$ and $J = 7/2$ which are the incorrectly placed ^{6}G levels mentioned previously). The largest (> 0.01) E1 f values for transitions between our levels of interest are also listed beneath the lifetime of the corresponding final state and labeled by the even initial state of the transition. M1 f values are similarly presented for the possible transitions to the even ^{6}D $J = 3/2$, $5/2$, and $7/2$ levels. Finally, we present the lifetime and E2 f value for the ^{6}D$_{9/2}$ level for which there is a single transition from the ^{6}S$_{5/2}$ Tc I ground state, as well as E2 f values for the transitions from the ^{6}S ground state to the other three even ^{6}D levels (E2 f values for transitions between ^{6}D levels are several orders of magnitude smaller than those from the ^{6}S ground state). Earlier studies [34] have shown that for small ΔE E2 transitions, such as the transitions from the ^{6}D even levels, the length form of the operator is preferred.

In calculation of f values there are two cases in which additional shifts are made. The first is made to resolve the mixing of the $J = 5/2$ ^{4}P and ^{4}D levels. The diagonal energy matrix elements elements are shifted in a manner similar to the second order discussion above. The shifts are much smaller and are made by trial and error until the ^4D–^{4}P gap matches the experimental value of 2190 cm^{-1}. The RCI gap is too small at 1175 cm^{-1}, so the ^{4}P elements are shifted up, and the ^{4}D elements are shifted down by twice as much. Other options are possible, the simplest being a shift of the same amount, but the ^{4}P level is already well positioned with respect to experiment, so ^{4}D is shifted more (the goal is disturb the other levels as little as possible while correcting the mixed ones). These shifts are $\sim$600 cm^{-1} and $\sim$1200 cm^{-1}, respectively, so the nonlinear nature of the shifts is quite evident (net 1800 cm^{-1} in shifts produces increase of only 1000 cm^{-1} in the gap). The other shift is in the odd $J = 7/2$ 4d^{6}5p ^{6}P and ^{4}F levels, which are nearly evenly mixed. Here our RCI energy gap is 341 cm^{-1} compared to the experimental [30] value of 191 cm^{-1}. Since our gap is too large and we want the levels to be mixed less, matching to the experimental gap cannot help in this case (in fact, it is difficult to apply a shift that will shrink the gap at all as both levels tend to respond equally). Here we are able to shift the ^{4}F elements up by 100 cm^{-1} and the ^{6}P elements down by the same amount with minimal change (for the worse) in the energy spectrum. The gap is widened by only 40 cm^{-1}, but the near 50/50 mixing of the levels is improved to approximately 70/30 mixing between the two terms with the correct ordering of the levels.

A brief glance through the f values in Table V shows that the transitions for which gauge agreement is poorest are those with initial $J = 5/2$ even states. We attribute this to problems with second order losses discussed earlier this Section. In fact, prior runs for other even J's that include the 4p $\rightarrow$ f and 4p4d $\rightarrow$ vdvf excitations retained in $J = 5/2$ show similar disagreement between gauges. These improvements in gauge agreement in the final stages are primarily reflected in increase in the velocity gauge, which is the lower of the two in most cases. It was found coincidentally that leaving out some of the core FOTOS effects in the odd runs improved the gauge agreement in the largest sextet to sextet f values, but these improvements were at the expense of the quartet to quartet transitions whose gauges already agree reasonably well (the velocity gauge becomes much larger than the length gauge for these transitions when 4p5p $\rightarrow$ $4d^2$ is left out), so all FOTOS effects are ultimately retained in the final f value computation.

Table I. *Illustration of N-electron basis set growth with number of electrons, via number of basis functions in* (d+s)^2 $\rightarrow$ f^2 *correlation configurations.*

Label	MCDF[a]	Full[b]	REDUCE[c]	Full/REDUCE	Comments[d]
(d+s)^5 J=5/2	29	333	111	3.0	Max J
(d+s)^6 J=3	29	723	116	6.2	Near Max J
(d+s)^7 J=5/2	29	1068	121	8.8	Max J
(d+s)^8 J=3	15	1289	65	19.8	Near Max J
(d+s)^{3}p J=1	40	83			Fe V, Ta II
(d+s)^{4}p J=7/2	87	653	321	2.0	Near Max J
(d+s)^{5}p J=3	145	1963	558	3.5	Max J
(d+s)^{6}p J=7/2	155	4248	620	6.9	Tc I
(d+s)^{7}p J=3	145	6382	602	10.6	Max J
(d+s)^{8}p J=5/2	99	6891	424	16.3	Max J

[a] Number of basis functions (J^2 eigenvectors with fixed $M_J = J$) in the d^n, d^{n-1}s, and d^{n-2}s^2 configurations. Most of these represent levels lying in the optical region.
[b] Number of basis functions (J^2 eigenvectors with fixed $M_J = J$) for the pair correlation where two d/s electrons are replaced by two f electrons. Includes three manifolds. Under almost all circumstances, this is a key contributor to the differential correlation energy.
[c] Application of REDUCE can decrease the number of basis functions (full) to this number, with little energy loss ($\sim$200 cm^{-1}), but this produces larger expansions on average (more determinants). This is a way to greatly cut down the size of the energy matrix, at some expense of having more complicated energy matrix elements.
[d] The J displayed is that for which the full number of basis functions is maximum (or near maximum).

Table II. *Illustration of size of significant correlation manifolds for* Tc I (4d+5s)^{6}5p $J = 7/2$.

Manifold	Excitation	Full	REDUCE	# Dets	# Coefficients
(4d+5s)^4vd^{2}5p	(4d+5s)^2 $\rightarrow$ vd^2	2838	610	9.2K	2.2M
(4d+5s)^4vf^{2}5p	(4d+5s)^2 $\rightarrow$ vf^2	4248	610	16.7K	4.0M
(4d+5s)^4vg^{2}5p	(4d+5s)^2 $\rightarrow$ vg^2	4953	610	24.2K	5.9M
(4d+5s)^4vpvf5p	(4d+5s)^2 $\rightarrow$ vpvf	4791	538	16.8K	3.7M
(4d+5s)^4vdvg5p	(4d+5s)^2 $\rightarrow$ vdvg	7458	538	31.1K	7.0M
4p^5vf(4d+5s)^{6}5p	4p $\rightarrow$ vf	8474	1348	32.6K	16.5M
4p^5(4d+5s)^{5}5pvdvf	4p4d $\rightarrow$ vdvf	25542[a]	836	170K	56.1M

[a] Basis functions that do not interact with the (d+s)^{6}p reference functions, pre-rotation, are not included in this total.

Table 3. *Prediction of Number (N) of REDUCE basis functions for* $(\mathrm{d+s})^2 \to vl^2$. *The number may be slightly less, due to accidental degeneracies in the survivors. There are fewer survivors when* $l = 0$ *or 1.* N *is number of electrostatic* R^k *integrals times the number of reference basis functions* (n_i) *for each reference function. Neglecting the j dependence of radial functions, and using the 8 fold symmetry of* R^k *integrals, we have 3* R^k *integrals originating from* $\mathrm{d}^2 \to vl^2$ *and 1* R^k *integral from* $\mathrm{ds} \to vl^2$ *or* $s^2 \to vl^2$.

Reference	Correlation Manifolds (# R^k)[a]		
Label (# basis functions)	$\mathrm{d}^{n-2}vl^2\mathrm{p}^m$	$\mathrm{d}^{n-3}\mathrm{s}vl^2\mathrm{p}^m$	$\mathrm{d}^{n-4}\mathrm{s}^2vl^2\mathrm{p}^m$
$\mathrm{d}^n\mathrm{p}^m$ (n_1)	$\mathrm{d}^2 \to vl^2$ (3)	T(0)	Q(0)
$\mathrm{d}^{n-1}\mathrm{sp}^m$ (n_2)	$\mathrm{ds} \to vl^2$ (1)	$\mathrm{d}^2 \to vl^2$ (3)	T(0)
$\mathrm{d}^{n-2}\mathrm{s}^2\mathrm{p}^m$ (n_3)	$\mathrm{s}^2 \to vl^2$ (1)	$\mathrm{ds} \to vl^2$ (1)	$\mathrm{d}^2 \to vl^2$ (3)
REDUCE configuration N[b]	$3n_1 + n_2 + n_3$	$3n_2 + n_3$	$3n_3$

[a] $m = 0, 1$. T (Q) indicates triple (quadruple) excitation. In the example, all three reference manifolds $(\mathrm{d+s})^n\mathrm{p}^m$ are treated on an equal footing. Tables for other correlation manifolds, such as $(\mathrm{d+s})^2 \to vlv(l+2)$ and $(\mathrm{d+s})\mathrm{p} \to vlv(l+1)$ can be easily constructed.

[b] Summing over the three columns thus gives a total predicted number of REDUCE basis functions for the three correlation configurations of $3n_1 + 4n_2 + 5n_3$.

Table 4. Tc I *LS composition, energies, and Landé g values. LS percentages are presented for leading terms with more than 5% weight within the three configuration MCDF portion of the wavefunction. The first number in parentheses is the percentage for the dominant term, and terms from configurations that differ from the dominant term are also indicated. Relative RCI energies are presented such that the energy of the lowest root is matched to the experimental* [28] *value.*

	Experiment [30]		RCI values	
Label	E (cm^{-1})	g value	E (cm^{-1})	g value
$4d^6 5s\ ^4F^e_{3/2}$ (69, $^4F\ d^7$ 23, $^4F\ d^5s^2$ 5)	15770	0.42	17313	0.41
$4d^6 5s\ ^4P^e_{3/2}$ (53, $^4P\ d^5s^2$ 29, $^4P\ d^7$ 13)	14170	1.70	14957	1.71
$4d^6 5s\ ^4D^e_{3/2}$ (85, $^4D\ d^5s^2$ 11)	11579	1.21	12060	1.21
$4d^6 5s\ ^6D^e_{3/2}$ (98)	4003	1.86	4003	1.86
$4d^5 5s^2\ ^4G^e_{5/2}$ (31, $^4F\ d^6s$ 42, $^4F\ d^7$ 11, $^2F\ d^6s$ 5)[a,b]	16416	0.58	18185	0.87
$4d^6 5s\ ^4F^e_{5/2}$ (25, $^4G\ d^5s^2$ 46, ^4G 13, $^4F\ d^7$ 6)[b]	15624	1.02	17587	0.80
$4d^6 5s\ ^4P^e_{5/2}$ (32, ^4D 51, $^4P\ d^5s^2$ 7)[c]	13253	1.62	13669	1.46
$4d^6 5s\ ^4D^e_{5/2}$ (36, ^4P 38, $^4P\ d^5s^2$ 12, $^4D\ d^5s^2$ 7)[c]	11063	1.37	12494	1.49
$4d^6 5s\ ^6D^e_{5/2}$ (98)	3701	1.65	3374	1.65
$4d^5 5s^2\ ^6S^e_{5/2}$ (99)	0	1.99	0	1.99
$4d^6 5s\ ^4H^e_{7/2}$ (86, $^4G\ d^5s^2$ 9)	17203		18443	0.71
$4d^5 5s^2\ ^4G^e_{7/2}$ (48, $^4G\ d^6s$ 26, $^4F\ d^6s$ 8, $^4F\ d^7$ 6)[a]	16288	0.95	17357	1.01
$4d^6 5s\ ^4F^e_{7/2}$ (57, $^4F\ d^7$ 21, $^4G\ d^5s^2$ 6)	15298	1.20	16487	1.19
$4d^6 5s\ ^4D^e_{7/2}$ (89, $^4D\ d^5s^2$ 9)	10517	1.44	10995	1.42
$4d^6 5s\ ^6D^e_{7/2}$ (99)	3251	1.59	3251	1.59
$4d^6 5s\ ^4H^e_{9/2}$ (74, $^4G\ d^5s^2$ 19)	17328		18550	1.02
$4d^5 5s^2\ ^4G^e_{9/2}$ (36, $^4G\ d^6s$ 35, $^4H\ d^6s$ 22)[a]	16134	1.17	17449	1.15
$4d^6 5s\ ^4F^e_{9/2}$ (59, $^4F\ d^7$ 29)	14733	1.31	15758	1.32
$4d^6 5s\ ^6D^e_{9/2}$ (99)	2573	1.60	2573	1.55
$4d^5 5s5p\ ^6G^o_{5/2}$ (90)[d]	38216	1.89	40093	0.86
$4d^5 5s5p\ ^4P^o_{5/2}$ (43, $^4P\ d^6p$ 52)	34516	1.61	37321	1.59
$4d^6 5p\ ^4D^o_{5/2}$ (85, $^4D\ d^5sp$ 6)	33086	1.39	35596	1.37
$4d^6 5p\ ^4F^o_{5/2}$ (67, $^4F\ d^5sp$ 10, $^6P\ d^5sp$ 6)	32015	1.14	34423	1.15
$4d^6 5p\ ^4P^o_{5/2}$ (27, $^4P\ d^5sp$ 62)[e]	31927	1.59	32764	1.61
$4d^6 5p\ ^6P^o_{5/2}$ (39, $^6P\ d^5sp$ 41, ^4F 9)[e]	31407	1.80	33394	1.76
$4d^6 5p\ ^6F^o_{5/2}$ (79, $^6F\ d^5sp$ 12)	30529	1.29	31923	1.31
$4d^6 5p\ ^6D^o_{5/2}$ (83, $^6D\ d^5sp$ 11)	27941	1.64	29282	1.65
$4d^5 5s5p\ ^6P^o_{5/2}$ (85, $^6P\ d^6p$ 12)	23455	1.90	23383	1.88
$4d^5 5s5p\ ^8P^o_{5/2}$ (99)	16429	2.30	16429	2.28

Label	Experiment [30] E (cm^{-1})	Experiment [30] g value	RCI values E (cm^{-1})	RCI values g value
$4d^55s5p\ ^6G^o_{7/2}$ (68, ^{6}H 26)[d]	38241	1.66	40314	1.06
$4d^65p\ ^4D^o_{7/2}$ (90, ^{4}D d^5sp 6)	32620	1.39	35021	1.43
$4d^65p\ ^4F^o_{7/2}$ (39, ^{6}P 25, ^{6}P d^5sp 22, ^{4}F d^5sp 5)[c]	31605	1.32	33562	1.48
$4d^65p\ ^6P^o_{7/2}$ (27, ^{4}F 39, ^{6}P d^5sp 24, ^{4}F d^5sp 5)[c]	31414	1.72	33221	1.49
$4d^65p\ ^6F^o_{7/2}$ (76, ^{6}F d^5sp 11, ^{4}F 7)	30382	1.38	31634	1.39
$4d^65p\ ^6D^o_{7/2}$ (82, ^{6}D d^5sp 10)	27660	1.57	28819	1.58
$4d^55s5p\ ^6P^o_{7/2}$ (77, ^{6}P d^6p 17)	23265	1.70	23806	1.72
$4d^55s5p\ ^8P^o_{7/2}$ (96)	16875	1.94	16875	1.93
$4d^65p\ ^4F^o_{9/2}$ (84, ^{6}F 8, ^{4}F d^5sp 6)	31114	1.37	33449	1.35
$4d^65p\ ^6F^o_{9/2}$ (82, ^{6}F d^5sp 8, ^{4}F 7)	30133	1.41	32350	1.42
$4d^65p\ ^6D^o_{9/2}$ (91, ^{6}D d^5sp 7)	27370	1.53	29247	1.55
$4d^55s5p\ ^8P^o_{9/2}$ (99)	17523	1.80	17523	1.78
$4d^65p\ ^6F^o_{11/2}$ (92, ^{6}F d^5sp 6)	30067	1.50	30067	1.45

[a] The even ^{4}G levels are experimentally [30] identified as $4d^65s$, but the dominant RCI term in $J = 5/2$, $7/2$, and $9/2$ is $4d^55s^2$ (changes as the calculations progress are toward the experimental $4d^65s$ designation).

[b] Indicates pairs of levels which are heavily LS mixed and have flipped leading LS terms with respect to experimental [30] designations.

[c] Indicates pairs of LS mixed levels that are important for some E1 transitions (f value > 0.01). The mixing of these levels is partially corrected through small shifts in diagonal energy matrix elements (see Section 3).

[d] These levels are experimentally [30] designated as ^{6}P, but the RCI levels in both the odd $J = 5/2$ and $7/2$ have a leading term of ^{6}G.

[e] The RCI positions of these two odd $J = 5/2$ levels are flipped with respect to the experimental [30] designations, though they exhibit minimal LS mixing, so no shifts are applied (see Section 3).

Table 5. *Tc I Lifetimes of odd* (4d+5s)^{6}5p *levels (E1 transitions) and even* ^{6}D (4d+5s)^7 *levels (M1 and E2 transitions). The largest (> 0.01) E1 f values are given below each odd lifetime, listed by initial state, and M1 and E2 f values are given for each transition to an even* ^{6}D *level.*

Level (lifetimes)	Lifetime or f value	
Initial state (f values)	Velocity gauge	Length gauge
$^8P^o_{5/2}$ 4d^{5}5s5p (16429 cm^{-1})	7.4 μs	147 μs
$^6P^o_{5/2}$ 4d^{5}5s5p (23455 cm^{-1})	44.0 ns	38.0 ns
$^6S^e_{5/2}$ 4d^{5}5s^2 (0 cm^{-1})	0.051	0.071
$^6D^o_{5/2}$ 4d^{6}5p (27941 cm^{-1})	15.7 ns	13.3 ns
$^6D^e_{3/2}$ 4d^{6}5s (4003 cm^{-1})	0.067	0.072
$^6D^e_{5/2}$ 4d^{6}5s (3701 cm^{-1})	0.015	0.025
$^6D^e_{7/2}$ 4d^{6}5s (3251 cm^{-1})	0.074	0.085
$^6F^o_{5/2}$ 4d^{6}5p (30529 cm^{-1})	14.8 ns	11.4 ns
$^6D^e_{3/2}$ 4d^6 5s (4003 cm^{-1})	0.125	0.145
$^4D^e_{3/2}$ 4d^6 5s (11579 cm^{-1})	0.017	0.017
$^6D^e_{5/2}$ 4d^6 5s (3701 cm^{-1})	0.050	0.077
$^6P^o_{5/2}$ 4d^{6}5p [a] (31407 cm^{-1})	8.2 ns	6.8 ns
$^6D^e_{3/2}$ 4d^{6}5s (4003 cm^{-1})	0.052	0.055
$^4D^e_{3/2}$ 4d^{6}5s (11579 cm^{-1})	0.017	0.018
$^6S^e_{5/2}$ 4d^{5}5s^2 (0 cm^{-1})	0.050	0.079
$^6D^e_{5/2}$ 4d^{6}5s (3701 cm^{-1})	0.045	0.055
$^6D^e_{7/2}$ 4d^{6}5s (3251 cm^{-1})	0.056	0.052
$^4P^o_{5/2}$ 4d^{6}5p [a] (31927 cm^{-1})	70.4 ns	65.2 ns
$^4F^o_{5/2}$ 4d^{6}5p (32015 cm^{-1})	16.8 ns	13.7 ns
$^4D^e_{3/2}$ 4d^{6}5s (11579 cm^{-1})	0.132	0.130
$^6D^e_{5/2}$ 4d^{6}5s (3701 cm^{-1})	0.021	0.033
$^4D^e_{5/2}$ 4d^{6}5s [b] (11063 cm^{-1})	0.029	0.035
$^4D^o_{5/2}$ 4d^{6}5p (33086 cm^{-1})	13.6 ns	14.7 ns
$^4D^e_{3/2}$ 4d^{6}5s (11579 cm^{-1})	0.071	0.079
$^4D^e_{5/2}$ 4d^{6}5s [b] (11063 cm^{-1})	0.046	0.058
$^4D^e_{7/2}$ 4d^{6}5s (10517 cm^{-1})	0.038	0.037
$^4P^o_{5/2}$ 4d^{5}5s5p (34516 cm^{-1})	8.1 ns	8.6 ns
$^4D^e_{5/2}$ 4d^{6}5s [b] (11063 cm^{-1})	0.070	0.074
$^4D^e_{7/2}$ 4d^{6}5s (10517 cm^{-1})	0.175	0.155
$^8P^o_{7/2}$ 4d^{5}5s5p (16875 cm^{-1})	2.5 μs	2.4 μs
$^6P^o_{7/2}$ 4d^{5}5s5p (23265 cm^{-1})	45.0 ns	37.2 ns
$^6S^e_{5/2}$ 4d^{5}5s^2 (0 cm^{-1})	0.072	0.098

Level (lifetimes)	Lifetime or f value	
Initial state (f values)	Velocity gauge	Length gauge
$^6D^o_{7/2}$ 4d^{6}5p (27660 cm^{-1})	15.4 ns	12.7 ns
$^6D^e_{5/2}$ 4d^{6}5s (3701 cm^{-1})	0.035	0.045
$^6D^e_{7/2}$ 4d^{6}5s (3251 cm^{-1})	0.071	0.086
$^6D^e_{9/2}$ 4d^{6}5s (2573 cm^{-1})	0.051	0.058
$^6F^o_{7/2}$ 4d^{6}5p (30382 cm^{-1})	15.0 ns	11.1 ns
$^6D^e_{5/2}$ 4d^{6}5s (3701 cm^{-1})	0.128	0.186
$^4D^e_{5/2}$ 4d^{6}5s ^{b} (11063 cm^{-1})	0.019	0.020
$^6D^e_{7/2}$ 4d^{6}5s (3251 cm^{-1})	0.034	0.039
$^6P^o_{7/2}$ 4d^{6}5p ^{b} (31414 cm^{-1})	7.6 ns	7.1 ns
$^6S^e_{5/2}$ 4d^{5}5s^2 (0 cm^{-1})	0.038	0.058
$^6D^e_{5/2}$ 4d^{6}5s (3701 cm^{-1})	0.026	0.036
$^4D^e_{5/2}$ 4d^{6}5s ^{b} (11063 cm^{-1})	0.029	0.034
$^6D^e_{7/2}$ 4d^{6}5s (3251 cm^{-1})	0.033	0.030
$^6D^e_{9/2}$ 4d^{6}5s (2573 cm^{-1})	0.108	0.105
$^4F^o_{7/2}$ 4d^{6}5p ^{b} (31605 cm^{-1})	12.5 ns	11.8 ns
$^4D^e_{5/2}$ 4d^{6}5s ^{b} (11063 cm^{-1})	0.089	0.099
$^4P^e_{5/2}$ 4d^{6}5s ^{b} (13253 cm^{-1})	0.012	0.012
$^6D^e_{7/2}$ 4d^{6}5s (3251 cm^{-1})	0.042	0.044
$^4D^e_{7/2}$ 4d^{6}5s (10517 cm^{-1})	0.029	0.031
$^6D^e_{9/2}$ 4d^{6}5s (2573 cm^{-1})	0.027	0.025
$^4D^o_{7/2}$ 4d^{6}5p (32620 cm^{-1})	13.1 ns	14.4 ns
$^4D^e_{5/2}$ 4d^{6}5s ^{b} (11063 cm^{-1})	0.013	0.018
$^4P^e_{5/2}$ 4d^{6}5s ^{b} (13253 cm^{-1})	0.055	0.045
$^4D^e_{7/2}$ 4d^{6}5s (10517 cm^{-1})	0.102	0.115
$^4F^e_{9/2}$ 4d^{6}5s (14733 cm^{-1})	0.090	0.052
$^8P^o_{9/2}$ 4d^{5}5s5p (17523 cm^{-1})	95.2 μs	621 μs
$^6D^o_{9/2}$ 4d^{6}5p (27370 cm^{-1})	15.9 ns	12.6 ns
$^6D^e_{7/2}$ 4d^{6}5s (3251 cm^{-1})	0.018	0.020
$^6D^e_{9/2}$ 4d^{6}5s (2573 cm^{-1})	0.139	0.178
$^6F^o_{9/2}$ 4d^{6}5p (30133 cm^{-1})	15.2 ns	11.9 ns
$^6D^e_{7/2}$ 4d^{6}5s (3251 cm^{-1})	0.144	0.187
$^4D^e_{7/2}$ 4d^{6}5s (10517 cm^{-1})	0.028	0.033
$^4F^o_{9/2}$ 4d^{6}5p (31114 cm^{-1})	15.2 ns	11.9 ns
$^6D^e_{7/2}$ 4d^{6}5s (3251 cm^{-1})	0.024	0.032
$^4D^e_{7/2}$ 4d^{6}5s (10517 cm^{-1})	0.156	0.181
$^6F^o_{11/2}$ 4d^{6}5p (30067 cm^{-1})	9.4 ns	8.4 ns
$^6D^e_{9/2}$ 4d^{6}5s (2573 cm^{-1})	0.253	0.285

$^6D^e_{3/2}$ $4d^65s$ (4003 cm^{-1}	298 s	247 s
$^6S^e_{5/2}$ $4d^55s^2$ (0 cm^{-1}) [M1]	4.02×10^{-11}	
$^6D^e_{5/2}$ $4d^65s$ (3701 cm^{-1}) [M1]	2.81×10^{-8}	
$^6S^e_{5/2}$ $4d^55s^2$ (0 cm^{-1}) [E2]	8.56×10^{-11}	5.19×10^{-10}
$^6D^e_{5/2}$ $4d^65s$ (3701 cm^{-1})	210 s	189 s
$^6S^e_{5/2}$ $4d^55s^2$ (0 cm^{-1}) [M1]	3.09×10^{-11}	
$^6D^e_{7/2}$ $4d^65s$ (3251 cm^{-1}) [M1]	4.41×10^{-8}	
$^6S^e_{5/2}$ $4d^55s^2$ (0 cm^{-1}) [E2]	2.68×10^{-12}	5.84×10^{-11}
$^6D^e_{7/2}$ $4d^65s$ (3251 cm^{-1}	82.7 s	84.5 s
$^6S^e_{5/2}$ $4d^55s^2$ (0 cm^{-1}) [M1]	1.70×10^{-11}	
$^6D^e_{9/2}$ $4d^65s$ (2573 cm^{-1}) [M1]	3.00×10^{-8}	
$^6S^e_{5/2}$ $4d^55s^2$ (0 cm^{-1}) [E2]	9.59×10^{-11}	4.62×10^{-11}
$^6D^e_{9/2}$ $4d^65s$ (2573 cm^{-1})	7050 s	12 800 s
$^6S^e_{5/2}$ $4d^55s^2$ (0 cm^{-1}) [E2]	5.35×10^{-11}	2.94×10^{-11}

[a] The ordering of the $^6P^o_{5/2}$ and $^4P^o_{5/2}$ are flipped with respect to the experimental [30] designations, and these transitions are identified by LS composition rather than position within the energy spectrum (see footnote d of Table IV).

[b] The positioning and LS composition of these levels have been corrected by energy matrix element shifting prior to oscillator strength calculation (see footnote c of Table IV)

Acknowledgement

This work is supported by the Division of Chemical Sciences, Office of Energy Research, U.S. Department of Energy, Grant # DE-FG02-92-ER14282.

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