Transitions between the $3p6ns$ and $3p6mp$ states of Ti IV

a E Kingston, A Hibbert

► To cite this version:

a E Kingston, A Hibbert. Transitions between the $3p6ns$ and $3p6mp$ states of Ti IV. Journal of Physics B: Atomic, Molecular and Optical Physics, 2010, 43 (16), pp.165003. 10.1088/0953-4075/43/16/165003 . hal-00569824

HAL Id: hal-00569824

<https://hal.science/hal-00569824>

Submitted on 25 Feb 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Transitions between the $3p^6 ns$ and $3p^6 mp$ states of Ti IV

A E Kingston and A Hibbert

Department of Applied Mathematics and Theoretical Physics,
Queens University of Belfast, Belfast BT 9 6HH, UK

E-mail: a.kingston@qub.ac.uk

Abstract

This paper presents calculations of the oscillator strengths and A -values between the $3p^6 ns \ ^2S^e$ ($J = 1/2$) ($n = 4$ to 10) states of Ti IV and the $3p^6 mp \ ^2P^e$ ($J = 1/2$ and $3/2$) ($m = 4$ to 10) states. The calculations were carried out using configuration interaction wave functions in which relativistic effects were included by using the Breit-Pauli approximation. To obtain an indication of the accuracy of the oscillator strengths, calculations were carried out using both the length and velocity formulations of the oscillator strengths. These calculations improve on the accuracy of the earlier work on the excitation of the $3p^6 4s \ ^2S$ excited state of Ti IV to the $3p^6 mp \ ^2P^o$ excited states (Kingston and Hibbert 2008) by increasing the number of configurations in the calculations. Comparisons of the present calculations are made with other theoretical calculations..

1. Introduction

Ti IV is interesting because the $3p^6 3d$ ground state may be excited by one-electron excitations to the autoionizing (resonance) states $3p^5 3d^2$ and $3p^5 3d 4s$ which lie above ionization potential of the ground state. These resonances increase the rates of photo-ionization (Schippers *et al* 2004) and electron ionization (Van Zoest *et al* 2004) of the $3p^6 3d$ ground state of Ti IV. They also enhance the rate of photo-recombination in Ti V (Nikolic *et al* 2009). Kingston and Hibbert have carried out a number of theoretical calculations on many of the basic parameters involved in these processes, such as transition energies, A-values and oscillator strengths. Kingston and Hibbert (2006) used the CIV3 computer code (Hibbert *et al* 1991) to obtain transition energies, A-values and oscillator strengths for transitions from the $3p^6 3d \ ^2D$ ground state of Ti IV to the $3p^6 np \ ^2P^o$ ($n = 4-7$), $nf \ ^2F^o$ ($n = 4-6$), $3p^5 3d^2 \ ^2P^o$, $\ ^2D^o$, $\ ^2F^o$ and $3p^5 3d 4s^2 P^o$. These initial calculations only considered transitions to doublet states and were extended by Kingston and Hibbert (2009) to include transitions to the $3p^6 np \ ^2P^o$ ($n = 4-10$), $3p^6 nf \ ^2F^o$ ($n = 4-10$) and all of the doublet and quartet states generated from $3p^5 3d^2$ and $3p^5 3d 4s$ functions. The results of these calculations are expected to be more accurate than the earlier calculations.

The $3p^6 4s \ ^2S$ excited state of Ti IV is similar to the $3p^6 3d$ ground state, in that the $3p^6 4s$ excited state may be excited by one-electron excitation of the $3p$ electron to the autoionizing (resonance) state $3p^5 3d 4s \ ^2P^o$ which lies above ionization potential. In order to study this transition Kingston and Hibbert (2008) only used a ground state $3p^6 4s \ ^2S$ wave function constructed from orbitals generated by Kingston and Hibbert (2006) and with a variationally determined $4s$ orbital. The excited $3p^6 np \ ^2P^o$ ($n = 4$ to 10), $3p^5 3d 4s \ ^2P^o$ and $3p^5 3d^2 \ ^2P^o$ wave functions were constructed from orbitals generated by Kingston and Hibbert (2006) plus new $3p^6 np \ ^2P^o$ ($n = 8$ to 10) functions. These calculations demonstrated that the transitions from the $3p^5 3d \ ^1P^o 4s \ ^2P^o$ ($J = 1/2$ and $J = 3/2$) states to the ground state $3p^6 4s \ ^2S$ have a large A-value of $1.84(11) \text{ s}^{-1}$. These A-values are in good agreement with the semi empirical calculations of Ryabtsev *et al* (2005). In the calculations of Kingston and Hibbert (2008) the primary aim was to obtain the A-values of these transitions. These calculations also gave A-values for the $4s$ to np ($n = 4$ to 10) transitions. By comparing the large differences between the length and velocity oscillator strengths given by these calculations for the $4s$ to np transitions it is clear that these particular calculations are not sufficiently accurate.

In the present paper the CIV3 code is used to calculate the length and velocity oscillator strengths and A-values for transition rates between $3p^6 ns \ ^2S$ ($n = 4$ to 10) to $3p^6 mp \ ^2P^o$ ($m = 4$ to 10). As the number of configurations used in the present calculations is significantly larger than the number used in the calculations of Kingston and Hibbert (2008), these new calculations should also improve on the earlier calculations on the $3p^6 4s \ ^2S$ to $3p^6 np \ ^2P^o$ ($n = 4$ to 10) transitions. Section 2 of the paper gives a brief description of the theoretical calculations and also gives the orbitals and configurations used in the calculations. Section 3.1 compares the unmodified calculated energy levels of the ns and np states with experimental values. This section also studies the convergence of the calculated oscillator strengths as the number of excited state functions is increased in the calculation. The oscillator strengths and A-values calculated in the present calculations are given in Section 3.2 where they are compared with earlier calculations. Section 3.3 shows that in certain circumstances the energy of a transition may be obtained

directly from the length and velocity oscillator strengths. Finally in Section 4 future developments are discussed.

2. Theoretical Calculations

The calculations in this paper are similar to those in earlier papers on transitions from the ground 3d states and from the excited 4s state of Ti IV (Kingston and Hibbert 2006, 2008). The calculations were carried out using the CIV3 computer code (Hibbert *et al* 1991). This code assumes that the wave functions Ψ are written in configuration interaction (CI) format which, in LSJ coupling, implies that

$$\Psi(J \pi) = \sum_{i=1}^M a_i \Phi_i (\alpha_i L_i S_i J \pi) \quad (1)$$

where π denotes parity. In (1), α_i denote other appropriate labeling of the configuration state functions (CSFs) Φ_i , for example the orbital occupancy of the electrons. Relativistic effects are included through the following Breit-Pauli operators: spin-orbit, spin-spin, spin-other-orbit, mass correction and Darwin terms. The CI mixing coefficients a_i are the eigenvector components of the Hamiltonian matrix with typical elements $H_{ij} = \langle \Phi_i | H | \Phi_j \rangle$, whose eigenvalues E_i are the calculated energies of the system. The configuration state functions (CSFs) Φ_i are constructed from one-electron orbital functions whose angular momenta are coupled to form total $L_i S_i J$ in intermediate coupling and which take the form

$$u(r, \sigma) = \frac{1}{r} P_{nl}(r) Y_l^{m_l}(\theta, \phi) \chi_{m_s}(\sigma) \quad (2)$$

The radial functions of the one-electron orbitals are expressed as sums of Slater-type orbitals and are obtained variationally by minimizing an appropriate energy eigenvalue, on the basis of the variational principle (see for example Perkins 1965).

The electric dipole oscillator strengths between the $^2S^e$ states and $^2P^o$ states are calculated in both the length f_l and velocity f_v formulations where

$$(2J+1) f_l = \frac{2}{3} \Delta E_{ij} M_l \quad \text{and} \quad (2J+1) f_v = \frac{2}{3} M_v / \Delta E_{ij} \quad (3)$$

ΔE_{ij} (in au) is the transition energy between the two states i and j . M_l and M_v are respectively the length and velocity line strengths where

$$M_l = |(\Psi_i(J_{ij} \pi) | \sum \mathbf{r}_k | \Psi_j(J_{ij} \pi))|^2 \quad \text{and} \quad M_v = |(\Psi_i(J_{ij} \pi) | \sum \nabla_k | \Psi_j(J_{ij} \pi))|^2 \quad (3.a).$$

The summation k is over all electrons. In theoretical calculations the difference between f_l and f_v is often used as an indication of the accuracy of the results. Generally it is assumed that ΔE_{ij} is accurate and if the calculated values of f_l and f_v do not agree it is often assumed that M_l and/or M_v are inaccurate. However if M_l and M_v are calculated accurately, the calculated values of f_l and f_v would not be accurate if the transition energy is inaccurate.

In the present calculations for the CI wave functions Ψ in (1) of the states labeled $3s^2 3p^6 ns^2 S^e$ ($J = 1/2$) ($n = 4$ to 10), the LS functions $^2S^e$, $^2P^e$, $^4P^e$, $^4D^e$ were employed. These functions were generated from the following configurations: - $3s^2 3p^6 ns$, $3s 3p^6 ns^2$, $3s^2 3p^4 3d^2 ns$, $3s^2 3p^4 ns^2 3d$, $3s^2 3p^4 ns^2 4d$, $3s^2 3p^4 3d 4d ns$ ($n = 4$ to 10) and $3s^2 3p^5 3d mp$ ($m = 4$ to 10). All of the orbitals used to generate these configurations, except the ns orbitals ($n = 5$ to 10), are described in an earlier paper (Kingston and Hibbert 2008). To obtain ns orbitals ($n = 5$ to 10), the $4s$ orbital was taken from the earlier paper and the $5s$ orbital was generated by minimizing the energy of the $3s^2 3p^6 5s$ function in a calculation which included $3s^2 3p^6 4s + 3s^2 3p^6 5s$ functions. Similarly $6s$ orbital was obtained by minimizing the energy of the $3s^2 3p^6 6s$ function in a calculation which included $3s^2 3p^6 4s + 3s^2 3p^6 5s + 3s^2 3p^6 6s$ functions. This process was repeated for the $7s$, $8s$, $9s$, $10s$ orbitals.

For the $3s^2 3p^6 mp^2 P^o$ ($J = 1/2$) ($m = 4$ to 10) states it is necessary to include in (1) the LS functions $^2S^o$, $^2P^o$, $^4P^o$, $^4D^o$ and for the $^2P^o$ ($J = 3/2$) state to include the $^2P^o$, $^2D^o$, $^4S^o$, $^4P^o$, $^4D^o$, $^4F^o$ functions. These functions were generated from the following configurations:- $3s^2 3p^6 mp$, $3s^2 3p^4 3d^2 mp$, $3s 3p^6 3d mp$, $3s^2 3p^5 4f mp$ ($m = 4$ to 10); $3s^2 3p^5 3d ns$ ($n = 4$ to 10); $3s^2 3p^5 3d^2$, $3s^2 3p^5 3d 4d$, $3s^2 3p^5 4d 4s$, $3s^2 3p^3 3d^4$, $3s 3p^5 3d^3$, $3s^2 3p^4 3d^2 4f$, $3s^2 3p^4 3d 4f 4s$. The orbitals used to generate the $^2P^o$ ($J = 1/2$) and $^2P^o$ ($J = 3/2$) functions are described in an earlier paper on Ti IV (Kingston and Hibbert 2006).

3. Theoretical oscillator strengths and A-values

3.1 Preliminary calculations

The configuration interaction wave functions, described in the previous section, were used to calculate the transition energies between the $3p^6 ns^2 S^e$ ($J = 1/2$) ($n = 4$ to 10) and the $3p^6 mp^2 P^o$ ($J = 1/2$ and $3/2$) ($m = 4$ to 10) states of Ti IV. The energy levels (in au) from the $3p^6 4s^2 S^e$ ($J = 1/2$) state to the $3p^6 ns^2 S^e$ ($J = 1/2$) ($n = 5$ to 10) and to the $3p^6 mp^2 P^o$ ($J = 1/2$ and $3/2$) ($m = 4$ to 10) states of Ti IV, calculated using these configuration interaction wave functions, are given in Table 1. They are compared with the experimental measurements of Ryabtsev et al (2005) and Swensson and Edlen (1974). The energy levels for the $3p^6 ns^2 S^e$ ($J = 1/2$) ($n = 9$ and 10) states have not been measured. The energy levels for these states were obtained by extrapolating the $3p^6 ns^2 S^e$ $n = 6, 7$ and 8 experimental energies.

Table 1 shows that the experimental and theoretical transition energy between $4s$ ground state and all of the ns excited states differ consistently by approximately 0.004 au but for the $4s$ to mp transitions the differences are approximately 0.025 au. In an earlier calculation on $4s$ to mp states (Kingston and Hibbert 2008) the difference between the experimental and theoretical transition energies was less than 0.01 au. This increase in the difference between the experimental and theoretical transition energies for the $4s$ - mp transitions is due to the introduction of $3s^2 3p^5 3d mp^2 S^e$ functions in the calculations. The earlier paper was chiefly concerned with calculating the large A-values for the $4s$ to $[3p^5 3d^1 P^o 4s]^2 P^o$ states; the present calculations do not change the value of those A-values significantly.

For transitions between highly excited states the differences between transition energies given by theory and experiment are relatively large. For example Table 1 shows that the transition energy for the $7s$ to $7p$ ($J = 1/2$ to $J = 1/2$) transition obtained by these preliminary theoretical calculations is 0.0439 au which is almost twice as large as the experimental value of 0.0229 au.

For this transition the theoretical transition energy is inaccurate as it is obtained by subtracting two large numbers, the calculated total energy of the 7s state, -849.8457 au, and the calculated total energy of the 7p state, -849.8018 au these give a 7s-7p transition energy of 0.0439 au.

Tables 2 and 3 contain length f_l and velocity f_v oscillator strengths obtained for some ($J = 1/2$ to $J = 1/2$) transitions using the wave functions described in the previous section. These calculations can be used to explore errors produced in oscillator strengths by the use of the inaccurate theoretical transition energies in Table 1. The calculations are also used to explore the convergence of calculated oscillator strengths for transitions between excited states, by using an increasing number of state functions in the configuration interaction wave functions (1) in the calculation of the oscillator strengths.

In configuration interaction calculations of the transition rates between excited states of Ti IV a number of different combinations of initial and final wave functions could be employed. For example in a calculation of the 4s to 4p transition rates, results could be obtained using only the 4s and 4p state functions in (1), while perhaps more accurate results could be obtained for the 4s to 4p transition rates by including only 4s, 5s and 5p state functions or 4s and 4p, 5p functions or 4s, 5s, 6s and 4p, 5p functions etc. In calculations on the 10s to 10p transitions there are a very large number of different combinations of state functions that may have to be used in the configuration functions (1) to give accurate results.

In order to determine the combination of s state functions with p state functions which will give consistent values for the transition rates two different approaches was adopted. Table 2 gives the results for one approach in which all of the 4p, 5p, 6p, 7p, 8p, 9p and 10p state functions were used in the configuration interaction function of the p states. These configuration interaction functions were used in a series of seven calculations. In this table the first calculation, Type 1 a, only the 4s function was include with all of the seven p functions; in the second calculation, Type 1 b, only 4s and 5s functions were included; Type 1 c, included 4s, 5s and 6s functions; Type 1 d, included 4s, 5s, 6s and 7s functions; Type 1 e, included 4s, 5s, 6s, 7s and 8s functions; Type 1 f, included 4s, 5s, 6s, 7s, 8s and 9s functions; Type 1 g, included 4s, 5s, 6s, 7s, 8s, 9s and 10s functions. Table 2 gives length f_l and velocity f_v oscillator strengths for nine transitions obtained from these seven different types of calculation.

In an alternative approach (Table 3) all of the 4s, 5s, 6s, 7s, 8s, 9s and 10s state function were used in a series of seven calculations. In the first calculation, Type 2 a, only the 4p state function was include with all of the seven s functions; in the second calculation, Type 2 b, only 4p and 5p functions were included; Type 2 c, included 4p, 5p and 6p functions; Type 2 d, included 4p, 5p, 6p and 7p functions; Type 1 e, included 4p, 5p, 6p, 7p and 8p functions; Type 2 f included 4p, 5p, 6p, 7p, 8p and 9p functions; Type 2 g, included 4p, 5p, 6p, 8p, 7p, 9p and 10p functions. Table 3 gives length f_l and velocity f_v oscillator strengths for nine transitions obtained from these seven different types of calculation.

Table 2 shows that for almost all of the transitions considered the oscillator strengths f_l tends to a constant limit as the number of s state functions is increased in the CI wave function (1) and similarly the f_v oscillator strengths tend to a different limit as the number of s functions is increased. For example the limit of f_l for the 7s to 7p transition is 1.33 but the limit of f_v for the same transition is 3.47(-1). It is important to note that for this transition the large difference between the length and velocity calculations is not due to large errors in the calculation of the length M_l and velocity M_v line strength (3.a) but is in due to using an inaccurate transition energy ΔE_{ij} given by these initial preliminary calculations in Table 1. If this inaccurate theoretical transition energy of $\Delta E_{ij} = 0.0439$ au for the 7s to 7p transition is replaced in (3) by the experimental transition energy 0.0229 au, the resulting oscillator strength f_l is 0.694 and the

resulting f_v is 0.665. This suggests that the values of M_l and M_v for this transition are not greatly in error. Similarly for the 9s to 9p transition Table 2 which gives $f_l = 3.02$ and $f_v = 0.271$, by replacing the preliminary transition $\Delta E_{ij} = 0.03033$ au by the experimental energy $\Delta E_{ij} = 0.00951$ au gives $f_l = 0.946$ and $f_v = 0.865$ which give an estimate of the error in the line strengths M_l and M_v for this transition.

There are a number of interesting patterns in Table 2. For the 4s to 4p transitions f_l and f_v change very little as the number of ns state functions is increased in the 4s CI wave functions (1). This suggests that for these transitions there is very little increase in the spatial overlap between the 4s and mp states for $m > 4$. A similar situation arises for the 7s to 7p and 9s to 9p transitions, f_l and f_v change very little as the number of ns state functions in the CI wave functions (1) increases. This suggests that for these transitions there is very little increase in the spatial overlap between the ms and mp states for $m > n$. Similarly for two transitions involving the 9s state, 4p to 9s and 7p to 9s, the inclusion of the 10s state function has very little effect on the oscillator strengths. Also for the 4p to 7s transition the inclusion of 8, 9, and 10s state functions has very little effect on the oscillator strengths. For these six ns to mp transitions, in which all of the seven p state functions are used in the configuration interaction functions, the length and the velocity results do not change greatly if the $(n+1)s$ state function is included.

The convergence of the f_l calculations as the number of ns states are increased in the 4s to 7p, 9p and 7s-9p transitions is not as good as that for the other transitions studied in Table 2. Consider the large variation of the calculated f_l values for one of these transitions, for example, the 4s to 7p transitions, as the number of ns state functions is increased. In these calculations the 7p CI wave function includes 4, 5, 6, 7, 8, 9, 10p state functions. The value of f_l changes only a little from the Type 1a calculation to Type 1c calculations, as the number of s state functions is increased from one 4s function to three 4, 5, 6s functions. In calculation Type 1d the introduction of a 7s function greatly reduces the value of f_l . The introduction of a 8s function (Type 1e) increases the value of f_l to a value which varies very little as 9s and 10s functions are included in the calculations. This suggests that for the 4s to 7p transition to obtain good overlap between 4s and 7p CI wave functions, it is necessary to include a 8s state function in the 4s CI wave function. This is due to the fact that for a given value on n, the np functions are larger than the equivalent ns function at large values of r and to get a good overlap it is necessary to increase the 4s CI wave function by including an 8s state function. These differences are also accentuated in the length calculations by the fact that the length calculations emphasize large values of r where the overlap between some s and p functions may be small. It is also seen that for these three calculations the velocity calculations converge more rapidly than the length calculations because the velocity matrix element emphasizing the smaller values of r where the s and p functions overlap.

The results given in Table 3 (where all of the 4,5,6,7,8,9,10s functions are included) differ significantly from those in Table 2 (where all of the 4,5,6,7,8,9,10p functions are included). The oscillator strengths f_l and f_v for the ns to mp transitions given in Table 3 all converged when np functions are included in the p CI wave function. For example both of the oscillator strengths f_l and f_v for the 4p-9s transition both converge if 9p functions are included in the p CI wave function. Table 3 also that, in general, where all seven s functions are available, the oscillator strength for a particular transition varies very little as the number of p functions is increased.

3.2 Comparisons of present calculations from other calculations

The results in the previous section suggest that many of the line strengths M_l and M_v obtained in the preliminary calculations are quite accurate and that the difference between the length and

velocity oscillator strengths are due to inaccuracies in the transition energies. Replacing the calculated transition energies by the accurate experimental energies should give more accurate oscillator strengths for some transitions. In the present calculations of f -values and A -values, the calculated transition energy is replaced by a more accurate experimental transition energy by using the fine tuning process of Hibbert (1996). This is a variant of a procedure of Beck and Nicolaides (1977) (see also Nicolaides 2005). In this process, small adjustments are made in certain diagonal elements of the Hamiltonian matrix in order to bring calculated energy differences into close agreement with experimental energy differences. This ensures that the transition energies, used in this paper to calculate oscillator strengths and A -values, do not differ significantly from the experimental transition energies.

Tables 4 a, b, c, d, e, f, g present calculations of the oscillator strengths and A -values for transitions between the $3p^6ns\ ^2S^e$ states ($n=4$ to 10) and the $3p^6mp\ ^2P^o$ ($m=4$ to 10) states of Ti IV. The wave functions were adjusted using the fine tuning process so that the transition energies in the calculation do not differ significantly from the measurements of Ryabtsev et al (2005). Experimental transition energies are not available for the $9s$ and $10s$ state, so the transition energies for these two states were obtained by extrapolating the energies given by Ryabtsev et al. Both the length f_l and velocity f_v oscillator strengths are given as the difference between the values of f_l and f_v is an indicator of the accuracy of the f -value calculations. Generally in Tables 4 a, b, c, d, e, f and g the values of f_l and f_v agree to approximately 5% for mp - ns transitions for $n=m$ or $n>m$. The ratio of f_l/f_v for the ns to mp transitions decreases very rapidly for small values of n and large values of m . For example the ratio f_l/f_v for the $4s$ - $5p$ and $4s$ - $6p$ transitions is approximately 0.9 but for the $4s$ - $9p$ and $4s$ - $10p$ transitions the ratios are 0.5 and 0.03 respectively. For all of the ns to $10p$ transitions (except the $10s$ to $10p$ transition) f_l and f_v do not agree. Due to the lack in convergence in the length calculations as demonstrated in Table 2 for the $4s$ to $9p$ transition, the f_v results are to be preferred to f_l results. The velocity calculations are also to be preferred, because for large values of m , the f_v values decrease approximately as $(I-\Delta E_{4s\rightarrow mp})^{-1.5}$ where I is the ionization potential of the $4s$ ion and $\Delta E_{4s\rightarrow mp}$ is the excitation energy from the $4s$ state to the mp states. This hydrogenic behavior is similar to that found in high m calculations of oscillator strength. Because there are some large inaccuracies in some of the length calculations only the A -value obtained from the velocity calculations are given in Table 4.

Tables 4 a, b, c, d, e also compare the A -values calculated in this paper with recent calculations by Ryabtsev *et al* (2005) and Zhang *et al* (2008). Ryabtsev *et al* (2005) have measured the transition energies in Ti IV for transitions from the $3p^64s\ ^2S^e$ state to the $3p^6mp\ ^2P^o$ ($m=5$ to 10) states and from the $3p^64p\ ^2P^o$ state to the $3p^6ns\ ^2S^e$ ($n=5$ to 8) states. They have used these energies in a semiempirical calculation to obtain A -values for all of these transitions. Zhang *et al* (2008) employed the Weakest Bound Electron Potential Model (WBEPM) to obtain the A -values for the nine transitions between the $3p^6ns\ ^2S^e$ ($n=4, 5, 6$) states and the $3p^6mp\ ^2P^o$ ($m=4, 5, 6$) states.

Table 4 a also gives the f_l and f_v oscillator strengths for $4s$ to mp transitions obtained by Kingston and Hibbert (2008). This calculation did not include higher ns states and as demonstrated in Table 2 this gives inaccurate results at high values of m . There is much better agreement between f_l and f_v for $4s$ to mp transitions in the present calculations at small values of m ; this is due to the introduction $3s^23p^53d\ mp^2S^e$ CI wave functions in the calculations.

There is some agreement among the A -values calculated in this paper and those calculated by Zhang *et al* and Ryabtsev *et al*. but there are also some major disagreements. The WBEPM

A-values calculations given by Zhang *et al* follow the pattern similar to that found in the calculations given in Table 2. This table shows that in the preliminary calculations of the f -values for ns to mp transitions converge to their final converged value if n equals m . If n is not equal to m then in order to obtain a converged value of the oscillator strength it is necessary to include both s and p functions up to the greater of n and m . The present calculations and those of Zhang *et al* are in good agreement for the 4s-4p, 6s-6p and 6s-6p transitions where $n = m$. However for the 4s-5p and 4s-6p transitions where n is not equal to m the two calculations differ by a factor of 2 or more.

The difference between the present A-values and those of Ryabtsev *et al* for the transitions 4s-mp ($m = 5$ to 10) decreases continuously from approximately 30% for the 4s-5p transition, 20% for the 4s-7p transition to 4% for the 4s-10p transition (except for the 4s-8p transition where the A-value of Ryabtsev *et al* only differ slightly from their A-value for 4s-9p transition). There is a similar pattern for the 4p-ns ($n = 5$ to 8) transitions. The difference in the present A-values and those of Ryabtsev *et al* decreases from 15% for the 4p-6s transition to 8% for the 4p-7s transition and to 2% for the 4p-8s transition. Since the methods used in the present theoretical calculations of A-values differ greatly from the methods used in the semiempirical calculations of Ryabtsev *et al*, it is very difficult to ascertain why the agreement between the two calculations is very good for transitions to highly excited states but the agreement is less good low lying states. One possible explanation is the inclusion in the present work of much more correlation contributions; these are less important for the higher Rydberg states.

Although there is not complete agreement between the A-values given by the present calculations and those given by the semiempirical calculations of Ryabtsev *et al* (2005), the agreement is very satisfying, taking into consideration the very different methods used in the two calculations.

3.3 Comments on length and velocity oscillator strengths

The length f_l and velocity f_v formulation of the oscillator strengths are given by (3), where ΔE is the transition energy and M_l and M_v are the length and velocity line strengths. If ΔE and M_l and M_v are accurate f_l and f_v are equal and so the difference between f_l and f_v is often used as an indication of the accuracy of the calculated oscillator strengths. In most calculations it is assumed that the transition energy is calculated more accurately than the length and velocity matrix elements. However in the preliminary ab initio calculations (Section 3.1), it is seen that some of the very small transition energies did not agree with the experimental transition energies. Tables 2 and 3 show that using the inaccurate energies given by the preliminary calculations can lead to some very large differences in the length and velocity oscillator strengths. However for many transitions there is very good agreement between the length and velocity calculations when these inaccurate transition energies are replaced by accurate experimental transition energies.

It is interesting to study the results that are obtained when inaccurate calculated energies are replaced by accurate experimental energies in calculated oscillator strengths. Consider a calculation in which it is assumed that the transition energy ΔE and the length and velocity oscillator strengths f_l and f_v are inaccurate but that the line strengths M_l and M_v are accurate. If the inaccurate transition energy ΔE in (3) is replaced by an accurate transition energy ΔE^t in f_l and f_v , this would give accurate oscillator strengths f_l^a and f_v^a which are given by

$$(2J+1)f_l^a = (2J+1)(\Delta E^t/\Delta E)f_l = \frac{2}{3} \Delta E^t M_l \text{ and } (2J+1)f_v^a = (2J+1)(\Delta E/\Delta E^t)f_v = \frac{2}{3} M_v/\Delta E^t \quad (4)$$

so, since f_l^a and f_v^a are now equal

$$(\Delta E^t / \Delta E)^2 = f_v / f_l \quad \text{or} \quad \Delta E^t = \Delta E (f_v / f_l)^{1/2} \quad (5).$$

Hence in a calculation in which M_l and M_v are accurate but ΔE is inaccurate, a more accurate value of the transition energy ΔE^t may be obtained from the calculated values of f_l and f_v and the inaccurate ΔE , using (5). It is also seen that in such a situation the oscillator f^t obtained using ΔE^t with M_l and M_v is given by

$$f^t = (f_l f_v)^{1/2} \quad (6).$$

Table 5 gives the transition energies ΔE^t and the oscillator strengths f^t for $J = 1/2$ to $J = 1/2$ transitions in Ti IV between the ns and mp states, $n = m$ and $n = 4$ to 10, and also the oscillator strengths for the mp to ns transitions with $m = 4$ to 9 and $n = m+1$. The expressions given in (5) for ΔE^t and (6) for f^t were obtained from the ΔE values and the oscillator strengths f_l and f_v given by the preliminary calculations discussed in Section 3.1. These calculated transition energies and oscillator strengths are compared with the experimental transition ΔE^e and the calculated oscillator strengths f_v^e given in Tables 4 a, b, c, d, e, f, and g. The agreement, for example, between the experimental transition energy ΔE^e and the transition energy given by (5) for the 9p to 10s transition is remarkable. In this case the ratio given by the initial calculation (Section 3.1) for f^v / f^l is 36620. This combines with transition energy given by the initial calculations $\Delta E = 0.0001092$ au in (6) to give an energy $\Delta E^t = 0.02089$ au which is in good agreement with the experimental energy $\Delta E^e = 0.02082$ au.

4. Conclusions

This paper gives calculated values of the transition energies and the length and velocity oscillator strengths for transitions between the ns and mp states of Ti IV for $n = 4$ to 10 and $m = 4$ to 10. The paper highlights a number of problems in these theoretical calculations. One of the major problems is the calculation of the very small transition energies which arise in ns to mp transitions in which $n = m$, or in which n and m are almost equal. For example the experimental transition energy $\Delta E(10s \text{ to } 10p)$ is 0.00666 au but the transition energy obtained in these calculations is 0.02751 au. This problem can be overcome using the fine tuning process but without experimental transition energies these calculations would not have been possible. It would be interesting to use the results described in section 3.3 to explore the possibility of obtaining better theoretical transition energies if no experimental results are available.

The present calculations also indicate that if n is small the ns to mp length oscillator strengths decrease more rapidly than the velocity oscillator strengths as m increases. It may be possible to lessen this rapid decrease by using more C I functions or by using a single pseudo-state to take account of all higher states. Some experimental measurements of the A-values of any of the ns to mp transitions in Ti IV would be useful.

Acknowledgements

We are pleased to acknowledge the support of a PPARC Grant PP/D00103X/1.

References

- Beck D R and Nicolaides C A 1977 *Phys. Lett.* **A61** 227-9
- Hibbert A 1996 *Physica Scripta* **T65** 104-09
- Hibbert A, Glass R and Froese Fischer C 1991 *Comput. Phys. Commun.* **64** 455-72
- Kingston A E and Hibbert A 2006 *J. Phys. B: At. Mol. Phys.* **39** 2217-2230
- Kingston A E and Hibbert A 2008 *J. Phys. B: At. Mol. Phys.* **41** 1-4
- Kingston A E and Hibbert A 2009 *J. Phys. B: At. Mol. Phys.* **42** 1-8
- Nicolaides C A 2005 *Int. J. Quantum Chem.* **102** 250-64
- Nikolic D, Gorczyca T W and Badnell N 2009 *Phys. Rev. A* **79** 102703
- Perkins J F 1965 *J. Chem. Phys.* **42** 3927-30
- Ryabtsev A N, Churilov S S and Kononov E Ya 2005 *Optics and Spectroscopy* **98** 519-27
- Schippers S *et al* 2004 *J. Phys. B: At. Mol. Phys.* **37** L209-16
- Swensson W and Edlen B 1974 *Physica Scripta* **9** 335-337
- Van Zoest T, Knopp H, Jacobi J, Schippers S, Phaneuf R A and Muller 2004 *J. Phys. B: At. Mol. Phys.* **39** 4387-95
- Zhang T Y, Zheng N W and Ma D X A 2008 *Int.J. Quant. Chem.* **109** 145-159

Table1. Experimental energy levels (in au) compared with preliminary ab initio theoretical energy levels (in au) from the $3p^6 4s^2 S^e$ ($J=1/2$) to the $3p^6 ns^2 S^e$ ($J=1/2$) ($n=5$ to 10) states and to the $3p^6 mp^2 P^o$ ($J=1/2$ and $3/2$) ($m=4$ to 10) of Ti IV.

	ΔE (au)	ΔE (au)		ΔE (au)	ΔE (au)	ΔE (au)	ΔE (au)
	Ryabtsev	Present		Ryabtsev	Present	Ryabtsev	Present
	Experiment	Theory		Experiment	Theory	Experiment	Theory
2J+1	2	2		2	2	4	4
4s	0.0	0.0	4p	0.21658 ^a	0.23658	0.2203 ^a	0.24047
5s	0.60152	0.60549	5p	0.68445	0.70967	0.68587	0.71136
6s	0.84501	0.84910	6p	0.88547	0.91058	0.88618	0.91160
7s	0.96873	0.97261	7p	0.99163	1.01647	0.99208	1.01725
8s	1.04028	1.04403	8p	1.05444	1.07914	1.05465	1.07978
9s	1.08526	1.08905	9p	1.09477	1.11939	1.09493	1.11996
10s	1.11559	1.11922	10p	1.12225	1.14679	1.12231	1.14731

Footnote a:Swenssen and Edlen (1974)

Table 2. Length f_l and velocity f_v oscillator strengths calculated using all of the 4p, 5p, 6p, 7p, 8p, 9p and 10p functions. The preliminary ab initio calculated transition energies are used in these calculations. The Type of calculation is described in the text.

Calculation	Type 1a	Type 1b	Type 1c	Type 1d	Type 1e	Type 1f	Type 1g
	4s	4,5s	4,5,6s	4,5,6,7s	4,5,6,7,8s	4,5,6,7,8,9s	4,5,6,7,8,9,10s
4s—4p f_l	3.11(-1)	3.11(-1)	3.10(-1)	3.10(-1)	3.10(-1)	3.10(-1)	3.09(-1)
4s—4p f_v	2.33(-1)	2.38(-1)	2.40(-1)	2.42(-1)	2.42(-1)	2.43(-1)	2.43(-1)
4p—7s f_l				9.09(-3)	9.22(-3)	9.28(-3)	9.30(-3)
4p—7s f_v				9.63(-3)	9.79(-3)	9.86(-3)	9.90(-3)
4p—9s f_l						2.46(-3)	2.49(-3)
4p—9s f_v						2.81(-3)	2.86(-3)
4s—7p f_l	4.71(-3)	4.86(-3)	5.17(-3)	1.97(-3)	3.14(-3)	3.42(-3)	3.53(-3)
4s—7p f_v	5.11(-3)	5.21(-3)	5.28(-3)	4.03(-3)	3.93(-3)	3.89(-3)	3.88(-3)
7s—7p f_l				1.35	1.33	1.33	1.33
7s—7p f_v				3.32(-1)	3.42(-1)	3.46(-1)	3.47(-1)
7p—9s f_l						4.58(-2)	4.64(-2)
7p—9s f_v						7.60(-2)	7.73(-2)
4s—9p f_l	1.88(-3)	1.94(-3)	2.00(-3)	2.10(-3)	2.23(-3)	2.49(-4)	9.02(-4)
4s—9p f_v	1.98(-3)	1.99(-3)	2.01(-3)	2.03(-3)	2.06(-3)	1.62(-3)	1.59(-3)
7s—9p f_l				4.94(-3)	5.16(-3)	1.96(-3)	2.79(-3)
7s—9p f_v				4.08(-3)	4.18(-3)	2.78(-3)	2.62(-3)
9s—9p f_l						3.06	3.02
9s—9p f_v						2.62(-1)	2.71(-1)

Table 3. Length f_l and velocity f_v oscillator strengths calculated using all of the 4s, 5s, 6s, 7s, 8s, 9s and 10s functions. The preliminary ab initio calculated transition energies are used in these calculations. The Type of calculation is described in the text.

Calculation	Type 2a	Type 2b	Type 2c	Type 2d	Type 2e	Type 2f	Type 2g
	4p	4,5p	4,5,6p	4,5,6,7p	4,5,6,7,8p	4,5,6,7,8,9p	4,5,6,7,8,9,10p
4s—4p f_l	3.13(-1)	3.11(-1)	3.10(-1)	3.10(-1)	3.10(-1)	3.10(-1)	3.09(-1)
4s—4p f_v	2.49(-1)	2.46(-1)	2.45(-1)	2.44(-1)	2.43(-1)	2.43(-1)	2.43(-1)
4s—7p f_l				3.41(-3)	3.50(-3)	3.53(-3)	3.53(-3)
4s—7p f_v				3.69(-3)	3.81(-3)	3.85(-3)	3.88(-3)
4s—9p f_l						8.95(-4)	9.02(-4)
4s—9p f_v						1.54(-3)	1.59(-3)
4p—7s f_l	1.03(-2)	1.15(-2)	1.59(-2)	9.11(-3)	9.20(-3)	9.27(-3)	9.30(-3)
4p—7s f_v	9.84(-3)	1.03(-2)	1.07(-2)	9.95(-3)	9.93(-3)	9.91(-3)	9.90(-3)
7s—7p f_l				1.33	1.32	1.33	1.33
7s—7p f_v				3.51(-1)	3.49(-1)	3.48(-1)	3.47(-1)
7s—9p f_l						2.72(-3)	2.79(-3)
7s—9p f_v						2.53(-3)	2.62(-3)
4p—9s f_l	2.91(-3)	3.13(-3)	3.49(-3)	4.13(-3)	7.18(-3)	2.48(-3)	2.50(-3)
4p—9s f_v	2.77(-3)	2.88(-3)	2.95(-3)	3.02(-3)	3.11(-3)	2.87(-3)	2.87(-3)
7p—9s f_l				4.58(-2)	5.54(-2)	4.64(-2)	4.64(-2)
7p—9s f_v				7.66(-2)	8.16(-2)	7.74(-2)	7.73(-2)
9s—9p f_l						3.07	3.02
9s—9p f_v						2.72(-1)	2.71(-1)

Table 4. Transition energies ΔE (in au) and calculated length f_l and velocity f_v oscillator strengths for optically allowed transitions between the $3p^6ns^2S^e$ ($J=1/2$) ($n=4$ to 10) states and the $3p^6mp^2P^o$ ($J=1/2$ and $3/2$) ($m=4$ to 10) states of Ti IV. The A-values (s^{-1}) calculated using f_v are also given. Where possible the present A-value calculations are compared with the calculations of Ryabtsev et al (2005) and Zhang et al (2008). In the tables the notation $a(b) = a \times 10^b$ is used. In these calculations the fine tuning process (Hibbert 1996) was used to ensure that the transition energies used in these calculations are in good agreement with the experimental transition energies.

Table 4 a. Caption as for Table 4 but for the $3p^64s^2S^e$ ($J = 1/2$) state.

	2J+1	Present calculations				Kingston and Hibbert (2008)		Zhang et al	Ryabtsev et al
		ΔE	f_l	f_v	A-values	f_l	f_v	A-values	A-values
4s--4p	2—2	0.2166	2.83(-1)	2.68(-1)	4.04(8)	3.00(-1)	1.32(-1)	4.68(8)	-
4s--4p	2—4	0.2203	5.77(-1)	5.29(-1)	4.12(8)	6.10{-1}	2.63(-1)	4.93(8)	-
4s--5p	2—2	0.6845	1.33(-2)	1.37(-2)	2.07(8)	1.45(-2)	2.21(-2)	1.07(8)	1.47(8)
4s--5p	2—4	0.6859	2.45(-2)	2.45(-2)	2.01(8)	2.67(-2)	4.31(-2)	9.51(7)	1.48(8)
4s--6p	2—2	0.8855	6.75(-3)	7.25(-3)	1.83(8)	8.56(-3)	9.98(-3)	4.20(7)	1.40(8)
4s--6p	2—4	0.8862	1.28(-2)	1.43(-2)	1.81(8)	1.63(-2)	1.98(-2)	3.72(7)	1.40(8)
4s--7p	2—2	0.9916	3.44(-3)	3.97(-3)	1.25(8)	4.79 (-3)	5.12(-3)		9.75(7)
4s--7p	2—4	0.9921	6.58(-3)	7.89(-3)	1.25(8)	9.22(-3)	1.02(-2)		9.73(7)
4s--8p	2—2	1.0544	1.86(-3)	2.47(-3)	8.82(7)	2.97(-3)	3.07(-3)		6.05(7)
4s--8p	2—4	1.0547	3.60(-3)	4.95(-3)	8.85(7)	5.76(-3)	6.19(-3)		6.08(7)
4s--9p	2—2	1.0948	8.91(-4)	1.62(-3)	6.25(7)	1.95(-3)	1.97(-3)		5.95(7)
4s--9p	2—4	1.0949	1.70(-3)	3.27(-3)	6.39(7)	3.80(-3)	4.00(-3)		6.10(7)
4s--10p	2—2	1.1222	2.79(-5)	1.11(-3)	4.48(7)	1.32(-3)	1.32(-3)		4.29(7)
4s--10p	2—4	1.1223	6.35(-5)	2.25(-3)	4.56(7)	2.60(-3)	2.70(-3)		4.28(7)

Table 4 b. Caption as for Table 4 but for the $3p^6 5s^2 S^\circ$ ($J = 1/2$) state.

			Present calculations			Zhang et al
	2J+1	ΔE	f_i	f_v	A-values	A-values
4p—5s	2—2	0.3849	1.55(-1)	1.58(-1)	7.52(8)	5.56(8)
4p—5s	4—2	0.3812	1.58(-1)	1.59(-1)	1.48(9)	1.12(8)
5s--5p	2—2	8.293(-2)	4.44(-1)	4.29(-1)	9.48(7)	9.80(7)
5s--5p	2—4	8.435(-2)	9.01(-1)	8.55(-1)	9.77(7)	1.03(8)
5s--6p	2—2	0.2840	6.00(-3)	6.61(-3)	1.71(7)	2.00(7)
5s--6p	2—4	0.2847	1.06(-2)	1.23(-2)	1.60(7)	1.75(7)
5s--7p	2—2	0.3901	3.39(-3)	3.86(-3)	1.89(7)	
5s--7p	2—4	0.3906	6.22(-3)	7.41(-3)	1.81(7)	
5s--8p	2—2	0.4529	1.79(-3)	2.27(-3)	1.50(7)	
5s--8p	2—4	0.4531	3.33(-3)	4.43(-3)	1.46(7)	
5s--9p	2—2	0.4933	8.72(-4)	1.42(-3)	1.11(7)	
5s--9p	2—4	0.4934	1.59(-3)	2.81(-3)	1.10(7)	
5s--10p	2—2	0.5207	5.84(-5)	9.43(-4)	8.20(6)	
5s--10p	2—4	0.5208	1.37(-4)	1.88(-3)	8.20(6)	

Table 4c. Caption as for Table 4 but for the $3p^6 6s\ ^2S^e$ ($J = 1/2$) state.

			Present calculations			Zhang et al	Ryabtsev et al
	2J+1	ΔE	f_l	f_v	A-value	A-value	A-value
4p—6s	2—2	0.6284	2.56(-2)	2.57(-2)	3.26(8)	2.84(8)	3.24(8)
4p—6s	4—2	0.6247	2.60(-2)	2.54(-2)	6.36(8)	5.73(8)	6.35(8)
5p—6s	2—2	0.1606	2.46(-1)	2.42(-1)	2.01(8)	1.79(8)	
5p—6s	4—2	0.1591	2.50(-1)	2.44(-1)	3.98(8)	3.60(8)	
6s--6p	2—2	4.046(-2)	5.68(-1)	5.50(-1)	2.89(7)	2.98(7)	
6s--6p	2—4	4.117(-2)	1.150	1.091	2.97(7)	3.13(7)	
6s--7p	2—2	0.1466	4.21(-3)	4.67(-3)	3.23(6)		
6s--7p	2—4	0.1471	7.10(-3)	8.31(-3)	2.89(6)		
6s--8p	2—2	0.2094	2.91(-3)	3.28(-3)	4.62(6)		
6s--8p	2—4	0.2096	5.26(-3)	6.20(-3)	4.38(6)		
6s--9p	2—2	0.2498	1.65(-3)	1.98(-3)	3.97(6)		
6s--9p	2—4	0.2499	3.02(-3)	3.82(-3)	3.83(6)		
6s--10p	2—2	0.2772	7.24(-4)	1.25(-3)	3.09(6)		
6s--10p	2—4	0.2773	1.41(-3)	2.45(-3)	3.03(6)		

Table 4 d. Caption as for Table 4 but for the $3p^6 7s \ ^2S^\circ$ ($J = 1/2$) state.

			Present calculations			Zhang et al	Ryabtsev et al
	2J+1	ΔE	f_l	f_v	A-value	A-value	A-value
4p—7s	2—2	0.7521	9.51(-3)	9.70(-3)	1.76(8)	1.62(8)	1.75(8)
4p—7s	2—4	0.7484	9.69(-3)	9.52(-3)	3.43(8)	3.26(8)	3.44(8)
5p—7s	2—2	0.2843	3.67(-2)	3.61(-2)	9.39(7)	9.97(7)	
5p—7s	2—4	0.2828	3.71(-2)	3.59(-2)	1.85(8)	2.00(8)	
6p—7s	2—2	8.326(-2)	3.35(-1)	3.31(-1)	7.38(7)	6.92(7)	
6p—7s	2—4	8.255(-2)	3.38(-1)	3.33(-1)	1.46(8)	1.39(8)	
7s--7p	2—2	2.290(-2)	6.92(-1)	6.78(-1)	1.13(7)		
7s--7p	2—4	2.335(-2)	1.408	1.332	1.17(7)		
7s--8p	2—2	8.571(-2)	3.42(-3)	3.90(-3)	9.22(5)		
7s--8p	2—4	8.592(-2)	5.53(-3)	6.83(-3)	8.10(5)		
7s--9p	2—2	0.1260	2.52(-3)	3.01(-3)	1.54(6)		
7s--9p	2—4	0.1262	4.25(-3)	5.67(-3)	1.42(6)		
7s--10p	2—2	0.1535	6.00(-4)	1.90(-3)	1.43(6)		
7s--10p	2—4	0.1536	1.43(-3)	3.66(-3)	1.38(6)		

Table 4 e. Caption as for Table 4 but for the $3p^6 8s^2 S^e$ ($J = 1/2$) state.

		ΔE	Present calculations			Ryabtsev et al
	2J+1		f_l	f_v	A-value	A-value
4p—8s	2—2	0.8237	4.61(-3)	4.86(-3)	1.06(8)	-
4p—8s	2—4	0.8200	4.74(-3)	4.75(-3)	2.05(8)	2.08(8)
5p—8s	2—2	0.3559	1.32(-2)	1.32(-2)	5.37(7)	
5p—8s	2—4	0.3544	1.34(-2)	1.31(-2)	1.05(8)	
6p—8s	2—2	0.1548	4.81(-2)	4.78(-2)	3.69(7)	
6p—8s	2—4	0.1541	4.86(-2)	4.72(-2)	7.28(7)	
7p—8s	2—2	4.865(-2)	4.27(-1)	4.23(-1)	3.23(7)	
7p—8s	2—4	4.820(-2)	4.31(-1)	4.29(-1)	6.40(7)	
8s--8p	2—2	1.416(-2)	8.13(-1)	7.76(-1)	5.00(6)	
8s--8p	2—4	1.437(-2)	1.644	1.557	5.17(6)	
8s--9p	2—2	5.449(-2)	3.11(-3)	3.39(-3)	3.23(5)	
8s--9p	2—4	5.465(-2)	4.37(-3)	6.04(-3)	2.90(5)	
8s--10p	2—2	8.197(-2)	7.87(-4)	2.91(-3)	6.27(5)	
8s--10p	2—4	8.203(-2)	2.49(-3)	5.57(-3)	6.02(5)	

Table 4f. Caption as for Table 4 but for the $3p^6 9s^2 S^e$ ($J = 1/2$) state.

			Present calculations		
	2J+1	ΔE	f_l	f_v	A-value
4p—9s	2—2	0.8687	2.55(-3)	2.82(-3)	6.83(7)
4p—9s	2—4	0.8650	2.65(-3)	2.75(-3)	1.32(8)
5p—9s	2—2	0.4008	6.39(-3)	6.54(-3)	3.38(7)
5p—9s	2—4	0.3994	6.52(-3)	6.45(-3)	6.61(7)
6p—9s	2—2	0.1998	1.71(-2)	1.73(-2)	2.22(7)
6p—9s	2—4	0.1991	1.72(-2)	1.71(-2)	4.36(7)
7p—9s	2—2	9.363(-2)	5.99(-2)	5.99(-2)	1.69(7)
7p—9s	2—4	9.318(-2)	6.03(-2)	5.97(-2)	3.33(7)
8p—9s	2—2	3.082(-2)	5.11(-1)	5.15(-1)	1.57(7)
8p—9s	2—4	3.061(-2)	5.18(-1)	5.20(-1)	3.13(7)
9s--9p	2—2	9.51(-3)	9.19(-1)	9.24(-1)	2.69(6)
9s--9p	2—4	9.67(-3)	1.923	1.732	2.61(6)
9s--10p	2—2	3.699(-2)	6.67(-4)	2.26(-3)	9.92(4)
9s--10p	2—4	3.705(-2)	2.52(-3)	5.89(-3)	1.30(5)

Table 4g. Caption as for Table 4 but for the $3p^610s\ ^2S^e$ ($J = 1/2$) state.

			Present calculations		
	2J+1	ΔE	f_l	f_v	A-value
4p—10s	2—2	0.8990	1.49(-3)	1.77(-3)	4.60(7)
4p—10s	2—4	0.8953	1.58(-3)	1.73(-3)	8.89(7)
5p—10s	2—2	0.4311	3.53(-3)	3.75(-3)	2.24(7)
5p—10s	2—4	0.4297	3.63(-3)	3.69(-3)	4.38(7)
6p—10s	2—2	0.2301	8.08(-3)	8.45(-3)	1.44(7)
6p—10s	2—4	0.2294	8.21(-3)	8.35(-3)	2.82(7)
7p—10s	2—2	0.1240	2.10(-2)	2.12(-2)	1.05(7)
7p—10s	2—4	0.1235	2.11(-2)	2.11(-2)	2.06(7)
8p—10s	2—2	6.115(-2)	7.10(-2)	7.08(-2)	8.53(6)
8p—10s	2—4	6.094(-2)	7.14(-2)	7.07(-2)	1.69(7)
9p--10s	2—2	2.082(-2)	5.95(-1)	5.98(-1)	8.33(6)
9p--10s	2—4	2.066(-2)	6.01(-1)	6.06(-1)	1.66(7)
10s--10p	2—2	6.66(-2)	1.095	9.36(-1)	1.35(6)
10s--10p	2—4	6.72(-2)	2.192	1.894	1.38(6)

Table 5. The transitions energies ΔE (in au) and the length and velocity oscillator strengths f_l and f_v given by the preliminary calculations in Section 3.1. Using ΔE , f_l and f_v in (6) give theoretical transition energies ΔE^t and also in (7) give oscillator strengths f^t . These calculated values of ΔE^t and f^t are compared with the experimental transition ΔE^e and calculated oscillator strengths f_v^c given in Tables 4 a, b, c, d, e, f, and g for 2-2 transitions.

Transition	2J+ 1	ΔE	f_l	f_v	ΔE^t	ΔE^e	f^t	f_v^c
4s—4p	2—2	0.23648	0.3089	0.2434	0.2099	0.2166	0.270	0.268
5s—5p	2—2	0.10420	0.5576	0.3400	0.08136	0.08293	0.435	0.429
6s—6p	2—2	0.06148	0.8619	0.3592	0.03965	0.04046	0.556	0.550
7s—7p	2—2	0.04386	1.3266	0.3474	0.02245	0.02290	0.679	0.678
8s—8p	2—2	0.03511	2.015	0.3120	0.01382	0.01416	0.793	0.776
9s—9p	2—2	0.03033	3.023	0.2709	0.00908	0.00951	0.904	0.924
10s—10p	2—2	0.02751	4.502	0.2270	0.00618	0.00666	1.011	0.936
4p—5s	2—2	0.36900	0.1483	0.1648	0.3890	0.3849	0.156	0.158
5p—6s	2—2	0.13942	0.2132	0.2787	0.1594	0.1606	0.244	0.242
6p—7s	2—2	0.06203	0.2484	0.4435	0.08288	0.08326	0.332	0.331
7p—8s	2—2	0.02755	0.2407	0.7476	0.04855	0.04865	0.424	0.423
8p—9s	2—2	0.009915	0.1642	1.598	0.03093	0.03082	0.512	0.515
9p—10s	2—2	1.092(-4)	3.113(-3)	1.140(2)	0.02089	0.02082	0.596	0.598