Transitions among fine-structure levels of Cl I

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Abstract. We have undertaken an extensive large-scale Breit-Pauli configuration interaction calculation of the oscillator strengths for E1 transitions in Cl I between the levels of the odd-parity configurations $3s^23p^5$, $3p^4(^1D)4p$, $3p^4(^3P)n\ell$ ($4 \leq n \leq 5$) and the even-parity configurations $3s3p^6$, $3p^4(^3P,^1D,^1S)n\ell$ ($4 \leq n \leq 5$), $3p^4(^3P)6s$, $3p^4(^3P,^1D)3d$, $3p^4(^3P)4d$, using the general atomic structure code CIV3. We focus in this short report on relatively weak transitions (oscillator strengths between 0.01 and 0.1), highlighting that the excellent agreement obtained in the length and velocity forms for stronger transitions is maintained, demonstrating a marked improvement over previous theoretical work. Alternative energy level classifications are proposed for a number of heavily mixed $J = 5/2$ even levels, which are supported by experimental measurements and recent astronomical observations.

1. Introduction
Due to its unique chemistry, Cl I provides an accurate tracer of optically thick molecular hydrogen in the diffuse interstellar medium [1, 2]. Two chlorine emission lines have been detected in the equatorial spots on Jupiter’s moon Io by Retherford et al [3] in a study of data acquired by the Hubble Space Telescope (HST) Space Telescope Imaging Spectrograph (STIS). Feaga et al [4] have reported the detection of atomic chlorine emission in the atmosphere of Io using the HST Goddard High Resolution Spectrograph (GHRS), specifically the $\lambda \lambda$ 1349 dipole-allowed and 1386 forbidden transition multiplets. Very recently, Sonnentrucker et al [5] reported the empirical determination of the oscillator strengths of four Cl I absorption lines observed in three stars with the Far Ultraviolet Spectroscopic Explorer (FUSE).

1.1. Other theoretical work
An attempt to provide an extensive set of reliable oscillator strengths for Cl I was made by Ojha & Hibbert (1990) [6], who performed a multi-configuration calculation using CIV3. However, in comparison with today’s standards, this work has adopted only a limited configuration expansion of the wavefunctions associated with the atomic states, and as such it is questionable if they have fully incorporated all important electron correlation effects. Refined oscillator strengths for resonance transitions in Cl I have been calculated by Biémont et al (1994) [7] with the SUPERSTRUCTURE (SST) computer program taking into account the most important configuration interaction and relativistic effects. They highlight a discrepancy observed by Schectman et al [8] when comparing their measurements for the lines at $\lambda \lambda$ 1088, 1097Å with theoretical data. Lavin et al (1997) [9] have reported oscillator strengths using the relativistic quantum defect orbital (RQDO) procedure with and without explicit inclusion of core
polarisation. Singh et al (2006) [10] have presented the Breit-Pauli energy levels and oscillator strengths for transitions between low-lying fine structure levels of ClI using configuration interaction wavefunctions within CIV3. However, a detailed analysis of their results shows some large discrepancies between the data calculated in the length and velocity forms. Finally, Fischer et al (2006) [11] have reported multi-configuration Hartree-Fock (MCHF) energy levels, lifetimes, and oscillator strengths (length form only) for transitions between levels belonging to the 3s3p, 3p4nl(nl = 4s, 4p, 3d), and 3s3p6 configurations.

In a previous paper [12] we demonstrated the superior consistency between the length and velocity forms of our oscillator strengths calculated using the superposition of configurations program CIV3 of Hibbert [13, 14], in comparison to other theoretical data for the strongest of the possible transitions (> 0.1) in ClI. The main purpose of this short report is to illustrate that this excellent agreement is maintained for relatively weak transitions (oscillator strengths between 0.01 and 0.1), which are often susceptible to cancellation effects. Further, we will discuss our approach to rectify the persistent inconsistency between theory and experiment/observation concerning the lines at λλ1088, 1097Å by proposing alternative energy level classifications for a number of heavily mixed \( J = \frac{5}{2} \) levels.

2. Calculation method

The details of the theoretical methods can be found in [12]. Here we provide a brief overview of the important steps involved in ensuring an accurate calculation.

2.1. Radial functions

The 1s, 2s, 2p, 3s, and 3p orbitals were taken to be the Hartree-Fock functions of the ClI ground state 3s\( ^2 \)3p\( ^5 \) 2P\( ^0 \) [15]. The 3d and 4p functions were optimised to represent the valence electron of the \( LS \) states 3p\( ^4(3P)3d \) 4P and 3p\( ^4(3P)4p \) 4D\( ^0 \), respectively. The 4s and 5s functions were also optimised as real spectroscopic orbitals. It is important to account for the \( LS \) dependence of the optimal orbitals by including ‘correcting’ orbitals. For example, the 5p and 6p functions were optimised on the lowest and second lowest eigenvalues of the Hamiltonian matrices formed from the configuration state functions (CSFs) 3p\( ^4 np \) 4S\( ^0 \) (\( n = 4, 5 \)) and 3s\( ^33p^5, 3p^4 np \) 4P\( ^0 \) (\( 4 \leq n \leq 6 \)), respectively. These two functions therefore act as corrections to our 4p orbital. The 6s, 7p, 8p, 7s, 7d functions were also optimised as correction orbitals to improve the flexibility of the orbital set and so produce an accurate representation of the valence electrons in the excited states. Additional orbitals were also required to account for the effects of electron correlation not included within the Hartree-Fock or single-configuration approximation. Specifically, the 4d function was taken as correlation type, optimised on the lowest energy of \{3p\( ^4 ns + 3p^4 md \) 4P\}(\( n = 4, 5; m = 3, 4 \)) to represent the 4s \( \rightarrow \) nd correlation effect. The 8d function was optimised on the 3s3p\( ^6 \) 2S state so as to give an accurate representation of the strong 3s3p\( ^6 \)–3p\( ^4 nd \) correlation effect in the lowest 2S state. The 5d, 5g, 4f, 5f, 6d functions were also taken as correlation type, optimised to incorporate electron correlation to an equivalent extent across the range of states under consideration.

2.2. Configuration basis set

Our initial set of configurations was generated by allowing all single and double electron replacements from the relatively few dominant configurations 3s\( ^2 \)3p\( ^5 \),3s3p\( ^6 \),3p\( ^4 nl(nl = 4s \rightarrow 7s, 4p \rightarrow 8p, 3d \rightarrow 8d, 4f, 5f, 5g) \), using all the available orbitals, but retaining a closed 1s\( ^2 \)2s\( ^2 \)2p\( ^6 \) core in all configurations. This process resulted in a total of 517,869 CSFs for the seven odd and eight even \( LS\pi \) symmetries. In order to reduce the scale of the calculation, we truncated the sets of CSFs by retaining only those whose configuration interaction (CI) coefficients were greater in magnitude than 0.0005 in all relevant eigenvalues of the associated \( LS\pi \) symmetry, resulting in only a minimal loss in accuracy.
2.3. Relativistic Effects

Relativistic effects were included within the Breit-Pauli approximation [16], by augmenting the non-relativistic (Schrödinger) Hamiltonian with the spin-orbit (SO), spin-other-orbit (SOO), spin-spin (SS), mass correction and one-body Darwin terms. However, the calculation of the two-body SOO and SS matrix elements proved time consuming. It was found that very little accuracy was lost by neglecting the SS term and replacing the SO and SOO terms by the modified spin-orbit operator

\[ H'_{SO} = \frac{\alpha^2}{2} Z \sum_{i=1}^{N} \frac{\zeta(l)}{r_i^3} (l_i \cdot s_i), \tag{1} \]

where the parameter \( \zeta(l) \) depends only on the \( l \)-values of the interacting electrons, which were chosen to reproduce specific matrix elements of the full SO and SOO operators for certain key CSFs. This operator mixes CSFs of different \( LS \) symmetry but with the same \( J\pi \), such that each relativistic CI wavefunction is constructed from the amalgamation of the truncated sets of CSFs of those \( LS \) symmetries which can couple to form an eigenfunction of the appropriate \( J\pi \). This resulted in 221940 CSFs for the nine \( J\pi \) symmetries. Finally, using the fine-tuning method it was possible to make slight adjustments to the diagonal matrix elements of the \( ab \) initio Hamiltonians for each \( J \)-value in such a manner so as to bring all of our refined eigenvalue differences to within 2 cm\(^{-1} \) of the experimental values.

3. Oscillator strengths in \( LSJ \) coupling

In the \( LS \) coupling regime, the good quality of our wavefunctions was reflected in the convergence of the \( ab \) initio energy differences towards the National Institute of Standards and Technology (NIST) [17] compiled values as the CI expansions were increased, and in the length/velocity consistency of the oscillator strengths. We concluded that our derived set of radial functions was sufficiently flexible to represent accurately electron correlation to an equivalent extent in all states, and hence could be applied with confidence to the calculation of Breit-Pauli oscillator strengths in the intermediate \( LSJ \) coupling scheme.

3.1. Comparisons with theoretical work

In Table 1 we compare our fine-tuned Breit-Pauli oscillator strengths for a sample of relatively weak transitions \( (0.01 \leq f \leq 0.1) \), in both length \( (f_l) \) and velocity \( (f_v) \) gauges, with other available theoretical results. It is evident that, even for these weaker transitions, which are susceptible to cancellation effects, remarkable agreement is achieved (to within 10% or better), demonstrating a marked improvement over the two other CIV3 compilations of Ojha & Hibbert [6] and Singh et al [10], indicating that we have more accurately accounted for electron correlation effects. This claim is further supported by Figure 1, which compares the ratio of the velocity to length forms of these oscillator strengths in the present study with the two previous CIV3 calculations. It was found that the mean ratio is much closer to unity in the present work \( (R = 0.9961 \pm 0.1187) \) than in the work of Ojha & Hibbert \( (R = 0.8274 \pm 1.0572) \) and Singh et al \( (R = 0.9239 \pm 1.2977) \). The quoted uncertainty is taken to be twice the standard deviation. Further, it is apparent that the deviation of the results about the mean value is much more pronounced in the two other CIV3 data sets. For completeness, the SST results of Biémont et al [7] are also presented in Figure 1, but with such a small number of data points any comparisons with the present work would not be meaningful. Although good agreement between \( f_l \) and \( f_v \) is only a necessary but not sufficient indication of accuracy, these observations provide strong evidence for the high quality of the present work.

We also present in Table 1 oscillator strengths of the MCHF and RQDO calculations by Fischer et al [11] and Lavin et al [9], respectively. Our present work and the MCHF oscillator strengths (length form) agree to within 15% for 10 of the 13 transitions where comparisons
The present findings tend to indicate that, due to the strong CI mixing between the $J = 5/2$ levels of the $3p^5 3d$ and $3p^4 5s$ configurations, the term classifications adopted by NIST for a number of these levels are questionable. We have proposed an alternative energy structure of these levels primarily based on our fine-tuning corrections and fine-structure splittings.

### Table 1. Comparison of a selection of our Breit-Pauli oscillator strengths (length $f_l$ and velocity $f_v$) for relatively weak transitions with other available theoretical results. Transition energies fine-tuned from CIV3. Print-out by lower level. Ojha: Ojha and Hibbert [6], Singh: Singh et al [10], MCHF: Fischer et al [11], RQDO: Lavin et al [9], SST: Biémont et al [7].

| Lower | Upper | This Work $f_l$ | Ojha $f_l$ | Singh $f_l$ | MCHF $f_l$ | RQDO $f_l$ |
|-------|-------|----------------|------------|-------------|------------|------------|
| $3s^2 3p^5 2p^2_3/2^o$ | $4s 2D_{3/2}$ | 0.0802 | 0.0769 | 0.0677 | 0.0596 | 0.0701 | 0.0535 | 0.0891 |
| $3s^2 3p^5 2p^2_1/2^o$ | $3s 2P_{3/2}$ | 0.0520 | 0.0481 | 0.0474 | 0.0416 | 0.0605 | 0.0505 | 0.0524 | 0.0523 |
| $3s^2 3p^5 2p^2_1/2^o$ | $3p 2P_{3/2}$ | 0.0162 | 0.0153 | 0.0176 | 0.0065 | 0.0481 | 0.0544 | 0.0170 | 0.0124^* | 0.0099^b |

$^*$ SST(length form); $^b$ SST(velocity form)

can be made. For the remaining three transitions where results are in discord we highlight the excellent agreement in our length/velocity forms. More significant discrepancies are observed between our work and the RQDO results for all but the transitions involving levels of the $3s^2 3p^5$ configuration. We note that the length forms of Ojha & Hibbert, Singh et al, Fischer et al and our work exhibit better agreement among themselves than with the data of Lavin et al.

### 3.2. The heavily mixed $J = 5/2$ even parity levels

The present findings tend to indicate that, due to the strong CI mixing between the $J = 5/2$ levels of the $3p^5 3d$ and $3p^4 5s$ configurations, the term classifications adopted by NIST for a number of these levels are questionable. We have proposed an alternative energy structure of these levels primarily based on our fine-tuning corrections and fine-structure splittings.
Thus, although the quantitative agreement with the experimental measurements of Schectman et al., as outlined in Table 2, we obtain such a simple interchange is not sufficient to reproduce the experimental results. If we follow the recent astronomical observations of Sonnentrucker et al, the lower level of the transitions is 3s°°P 3/2 and the differing upper level classifications are quoted.

A persistent discrepancy between theoretical work and the experimental measurements of Schectman et al [8] concerns the lines at λλ1097, 1088, 1095Å. According to the NIST classifications, the upper levels of these two transitions are 3p°°P 3/2, 2D 5/2, respectively. The previous CIV3 calculation of Ojha & Hibbert [6] (which followed the NIST classifications) predicts the f-value for λ1097 to be substantially larger than that for λ1088, while experiment tends to indicate the reverse (Table 2). Biémont et al [7] proposed an alternative classification of the two levels (corresponding to a direct interchange of the 2D 5/2 and 2F 5/2 labels), and obtained qualitative agreement with the experimental measurements that λ1088 is the stronger transition. However, for the 1095 line they have retained the same upper level term classification as NIST ((3p°°P 5s 2[2] 3/2 in j,l coupling) and their resulting calculated f-value disagrees strongly with the recent astronomical observations of Sonnentrucker et al [5]. Therefore, we can infer that such a simple interchange is not sufficient to reproduce the experimental results. If we follow our labelling, as outlined in Table 2, we obtain f-values of 0.0567 and 0.0022 for λ1088, 1097Å, with the upper levels of the two transitions identified as 3p°°P 3/2 and 3p°°P 5/2. Thus, although the quantitative agreement with the experimental measurements of Schectman et al (f = 0.081±0.007 and f = 0.0088±0.0013 for λ1088, 1097Å, respectively, as cited in Table 2) cannot be rated as excellent, we do agree qualitatively that λ1088 is the stronger transition.
Table 3. Comparison of our length form oscillator strengths $f_l$ with the astronomical observations of Sonnentrucker et al [5]. The lower level of the transitions is $3s^23p^5\,^2P_3/2$. $R$ is the ratio of the observed value to our theoretical $f$-value.

| $\lambda$ (Å) | Observed | This Work |
|---------------|-----------|-----------|
|               | $f_l$     | Upper $f_l$ | $R$ |
| 1004.678      | 0.0514$^{+0.0058}_{-0.0051}$ | (3)$S_{4s}\,^2S_{1/2}$ | 0.0443 | 1.16 |
| 1079.882      | 0.0056$^{+0.0013}_{-0.0012}$ | (3)$P_{5s}\,^2P_{1/2}$ | 0.0044 | 1.27 |
| 1090.739      | 0.0028$^{+0.0004}_{-0.0004}$ | (3)$P_{5s}\,^2P_{3/2}$ | 0.0107 | 0.26 |

Further, our calculated $f$-value for the $\lambda1095$ line ($f_l = 0.0322$), the upper level of which is designated by (3)$P_{3d}\,^2F_{5/2}$ in the present work, compares favourably with the astronomical observation of Sonnentrucker et al ($f = 0.0396^{+0.0042}_{-0.0038}$). Concluding, it is our opinion that the designations of the heavily mixed $J = 5/2$ levels should be our recommended ones.

Finally, for completeness, in Table 3 we present a comparative analysis of our theoretical oscillator strengths with the three remaining astronomical observations made by Sonnentrucker et al [5] using FUSE. Within their measurement errors, the ratios $R$ of the empirical $f$-values to our theoretical values were calculated to be $\approx 1.16$ ($\lambda1004.678$, $\approx 1.27$ ($\lambda1079.882$) and $\approx 0.26$ ($\lambda1090.739$). Thus, the present results compare favourably with the two observations at $\lambda1004.678, 1079.882$, with our $f_l$-value of 0.0044 for $\lambda1079.882$ lying within the quoted experimental error bars ($f = 0.0056^{+0.0013}_{-0.0012}$). The discord between theory and observation for $\lambda1090.739$ is frustrating in view of the rather good agreement between the length and velocity gauges for the transition ($f_l = 0.0107, f_v = 0.0097$). However, it should be stressed that the calculated $f$-value is extremely sensitive to the fine-tuning procedure, due to the strong mixing between the (3)$P_{5s}\,^2P_{3/2}$ and (3)$P_{5s}\,^4P_{3/2}$ levels.

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