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Breit-Pauli energy levels and radiative lifetimes in neutral chlorine[⋆]

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Abstract. Breit-Pauli Energy levels, oscillator strengths and transition probabilities for all the transitions in Cl I between the fine structure levels of $3s^23p^5$, $3s^23p^43d$, $3s^23p^44s$ and $3s^23p^44p$ states are calculated using extensive configuration interaction (CI) wave functions. We have also determined the lifetimes of $3s^23p^43d$, $3s^23p^44s$ and $3s^23p^44p$ levels. The relativistic effects are included through Breit-Pauli approximation via spin-orbit, Darwin and mass correction terms. Prior to the calculations of the oscillator strengths and transition probabilities, we fine-tune the CI coefficient using experimental energies. Our results are compared with experimental and other available theoretical data. The calculated energy levels are in close agreement with most of the NIST compiled data. We predict new lifetime data for several levels where no other theoretical and/or experimental results are available, which will form the basis for the future experimental work.

PACS. 32.70.Cs Oscillator strengths, lifetimes, transition moments – 32.10.Fn Fine and hyperfine structure – 31.15.Pf Variational techniques

1 Introduction

Energy levels and transition probabilities of neutral chlorine are useful in a variety of scientific applications such as in understanding physical condition and dynamical processes in various astrophysical plasmas. Atomic chlorine is an astrophysically important free radical, present in diffuse interstellar clouds. In regions primarily composed of atomic hydrogen, Cl II is expected to be the dominant form of chlorine, while in molecular region, the neutral species Cl I and HCl should dominant [1–3]. Atomic chlorine and sodium are more abundant than NaCl due to rapid photolysis in Io's upper atmosphere [4]. Moses et al. [5] have detected neutral chlorine in the Io plasma torus and neutral clouds at Io. With images of Io's aurora by the Hubble Space Telescope (HST) Space Telescope Imaging Spectrograph (STIS), Retherford et al. [6] have detected two chlorine emission lines in the equatorial spots of Io. Two multiplets of neutral chlorine in the 1330–1400 Å region, a dipole allowed transition Cl I $\lambda 1349$ Å, consisting of four lines and Cl I $\lambda 1386$ Å, a forbidden transition consists of five lines are detected in the atmosphere of Io using Hubble Space Telescope observation with Goddard High Resolution Spectrograph (GHRS) [7]. They have also reported the relative abundance of neutral chlorine at Io. Neutral chlorine is also isoelectronic to Ar II, where knowledge of a number of energy levels and lifetimes is required for understanding the action of argon ion laser, similar processes could occur between analogous levels in Cl I.

Some theoretical and experimental works dealing with neutral chlorine have appeared in the literature. In particular, Hofmann [8] has studied ten resonance transitions in emission with a wall-stabilized arc and Clyne and Nip [9] have measured the oscillator strengths for the transitions $3s^23p^5\,^2\mathrm{P}^o_{1/2,3/2} \rightarrow 3s^23p^4(^3\mathrm{P})4s\,^{2,4}\mathrm{P}^e_{1/2,3/2,5/2}$. Schwab and Anderson [10] have done for the transition $3s^23p^5\,^2\mathrm{P}^o_{1/2,3/2} \rightarrow 3s^23p^4(^1D)4s\,^2\mathrm{D}^e_{1/2,3/2}$, while Wujec and Weniger [11] have measured oscillator strengths for the transition between the fine-structure levels $3s^23p^4(^3\mathrm{P})4p\,^4\mathrm{P}^o$, $^4\mathrm{D}^o$ and $3s^23p^4(^3\mathrm{P})5d\,^4\mathrm{D}^e$. Recently Schectman et al. [12] have measured the lifetimes and obtained oscillator strengths for the transitions $3s^23p^5\,^2\mathrm{P} \rightarrow 3s^23p^4(^3\mathrm{P})3d\,^2\mathrm{D}$, $^2\mathrm{F}$ and $3s^23p^5\,^2\mathrm{P} \rightarrow 3s^23p^4(^3\mathrm{P})4s\,^2\mathrm{P}$. Ganas [13] has calculated oscillator strengths for the $3s^23p^5\,^2\mathrm{P}^o_{3/2} - 3s^23p^4(^3\mathrm{P})ns\,^2\mathrm{P}^e$ transitions for $4 \le n \le 7$ and $3s^23p^5\,^2\mathrm{P}^o_{3/2}3s^23p^4(^3\mathrm{P})nd\,^2\mathrm{P}^e$, $^2\mathrm{D}^e$ transitions for $3 \le n \le 7$, using independent particle model potential study. Lavin et al. [14] have reported oscillator strengths using RQDO and Biémont et al. [15] using SUPERSTRUCTURE while, Ojha et al. [16] have used CIV technique for the same.

Accurate transition data in neutral chlorine and chlorine like ions [17] are important not only in astronomy and astrophysics but also in other scientific areas such as plasma physics. There are very few investigations

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[⋆] The complete version of Table 4 is only available in electronic form at `http://www.eurphysj.org`.

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Table 1. Method of determining the radial functions.

Orbital	Process of optimization	
$1s$, $2s$, $2p$, $3s$	Hartree-Fock of $3p^4\,{}^3\mathrm{P}$ of Cl II (Clementi and Roetti, 1974)	
$3p$	Exponents taken from the Hartree-Fock orbital of $3p^4$ of Cl II coefficient reoptimized	
	On $3p^44s$ of Cl I Eigen value minimized	Configurations
$3d$	$3p^43d\,{}^4\mathrm{D}$	$3p^43d$
$4s$	$3p^44s\,{}^4\mathrm{P}$	$3p^44s$
$4p$	$3p^44p\,{}^4\mathrm{D}^o$	$3p^44p$
$4d$	$3p^43d\,{}^4\mathrm{D}$	$3p^43d$, $3p^44d$
$4f$	$3p^43d\,{}^4\mathrm{P}$	$3p^44s$, $3p^43d$, $3p^44d$, $3p^33d4f$
$5s$	$3p^44p\,{}^4\mathrm{D}^o$	$3p^44p$, $3p^34s5s$
$5p$	$3p^44p\,{}^4\mathrm{P}^o$	$3p^44p$, $3p^45p$
$5d$	$3p^43d\,{}^4\mathrm{F}$	$3p^43d$, $3p^44d$, $3p^45d$
$5f$	$3p^44p\,{}^4\mathrm{D}^o$	$3p^44p$, $3p^44f$, $3p^45f$
$6s$	$3p^44s\,{}^4\mathrm{P}$	$3p^44s$, $3p^45s$, $3p^46s$, $3p^43d$, $3p^44d$, $3p^45d$, $3s3p^54p$
$6d$	$3p^44s\,{}^4\mathrm{P}$	$3p^44s$, $3p^45s$, $3p^46s$, $3p^43d$, $3p^44d$, $3p^45d$, $3p^46d$

beyond resonance lines. Many investigations in the past were restricted to transition from ground to excited levels of $3s^23p^5$, $3s^23p^44d$, $3s^23p^44s$ and $3s^23p^44p$ while transition between excited states have been not been studied by many authors. Very few theoretical atomic data on transition probabilities and lifetimes are available for Cl I.

In this paper, we report and discuss the results of our calculations of energy levels, transition probabilities of electric dipole transitions among the fine-structure levels of the term $3s^23p^5\,{}^2\mathrm{P}^o$, all four terms of $3s^23p^44s$, all terms of $3s^23p^44p$ except the highest ${}^2\mathrm{P}$, and seven terms of $3s^23p^43d$ of neutral chlorine. We have also reported lifetimes of $3s^23p^43d$, $3s^23p^44s$ and $3s^23p^44p$ levels. We predict new lifetime data for several levels where no other theoretical and/or experimental results are available, which will form basis for the future experimental work. The relativistic effects are included through Breit-Pauli approximation via spin-orbit, Darwin and mass correction terms. Prior to the calculations of the oscillator strengths and transition probabilities, we fine-tune the CI coefficient using experimental energies. Specifically, the final CI coefficients are determined following small adjustment to the diagonal Hamiltonian matrix elements so that the calculated eigenvalue differences agree with the corresponding experimental energies separations [18]. The calculated energy levels are in close agreement with most of the NIST data.

2 Method of calculation

The configuration interaction wave functions are represented as

$$\Psi\left(LSJ\right)=\sum_{i=1}^{M}a_i\Phi_i\left(\alpha_iLSJ\right), \qquad (1)$$

where $\{\phi_i\}$ are single configuration functions (CF) constructed from one-electron orbitals whose angular momenta are coupled, as specified by $\{\alpha_i\}$, to form total L and S common to all M configurations. The expansion coefficients $\{a_i\}$ are the eigenvector components of the diagonalized Hamiltonian. In our work, we take the Hamiltonian H to be the Schrödinger Hamiltonian plus the mass correction and Darwin term, together with a modified spin-orbit term

$$H_{so}=\frac{1}{2}\alpha^2\sum_{i=1}^{N}\frac{Z\zeta_l}{r_i^3}l_is_i. \qquad (2)$$

In (2) the sum is over the electrons and the parameters $\{\zeta_l\}$ depend on the l-value of the electron involved in the interaction [19].

The radial function used in configuration interaction code CIV 3 [20,21] is expressed as a sum of normalized Slater-type orbitals:

$$P_{nl}(r)=\sum_{j=1}^{k}C_{jnl}\frac{(2\xi_{jnl})^{I_{jnl}+1/2}}{[(2I_{jnl})!]^{1/2}}r^{I_{jnl}}\exp(-\xi_{jnl}r) \qquad (3)$$

$\{I_{jnl}\}$, being integers, are kept fixed but the exponents $\{\xi_{jnl}\}$ and the coefficients $\{C_{jnl}\}$ may be treated as variational parameters subject to orthonormality conditions:

$$\int_0^\infty P_{nl}(r)P_{n'l}(r)dr=\delta_{nn'}, \quad 1<n'\le n. \qquad (4)$$

If we form a Hamiltonian matrix whose typical element is $\langle\Phi_i|H|\Phi_j\rangle$, then the eigenvalues form upper bounds to the energies of states with a particular symmetry (LSJ π) and corresponding eigenvectors give the CI coefficients $\{a_i\}$ in equation (1). This upper bound property of the eigenvalues and variational principle provides a set of conditions to enable us to optimize the radial parameters in equation (3).

The process of optimization is given in detail in Table 1. For all the optimizations, only the non-relativistic Hamiltonian is used. The wavefunctions for all the ionic states have been constructed in the form (1) from a common set of radial functions. The radial functions (3) are chosen to give the best overall representation of the energies of the states. Sixteen one electron orbitals $1s$, $2s$, $2p$, $3s$, $3p$, $3d$, $4s$, $4p$, $4d$, $4f$, $5s$, $5p$, $5d$, $5f$, $6s$ and $6d$, are used in our calculations. We have chosen the $1s$, $2s$, $2p$ and $3s$ orbitals as Hartree-Fock (HF) orbitals of the ground state $3s^23p^4(^3\mathrm{P})$ of Cl II given by Clementi and Roetti [22]. The coefficient of $3p$ orbital are reoptimised on the core $3s^24s(^4\mathrm{P})$ of Cl I by taking exponent from the Hartree-Fock orbital of $3p^4(^3\mathrm{P})$ of Cl II. The orbitals $3d$, $4s$ and $4p$ are optimized on the energies of $3s^23p^43d\,^4\mathrm{D}$, $3s^23p^44s\,^4\mathrm{P}$ and $3s^23p^44p\,^4\mathrm{D^o}$ respectively. The $4d$ and $5d$ orbitals are chosen to correct the $3d$ orbital by optimizing these on $3s^23p^43d\,^4\mathrm{D}$ and $3s^23p^43d\,^4\mathrm{F}$ respectively. The $4f$ orbital is a correlation orbital optimized to represent the $3p$–$4f$ correlation effect. All the other orbitals listed in Table 1 were optimized to give a good representation of the valence electron in the excited states for the different LS symmetries. The optimized parameters of the radial functions are shown in Table 2. The CI wavefunctions include all possible angular momentum coupling of the configurations listed below.

Configurations for even parity states: $3s3p^6$, $3s^23p^43d$, $3s^23p^44d$, $3s^23p^44s$, $3s^23p^45s$, $3s^23p^46s$, $3s^23p^46d$, $3p^63d$, $3p^64d$, $3s^65d$, $3s3p^43d^2$, $3s3p^44d^2$, $3s3p^45d^2$, $3s^23p^23d^3$, $3s^23p^24d^3$, $3s^23p^23d^24s$, $3p^43d^24d$, $3s3p^43d4d$, $3s3p^43d5d$, $3s3p^44d5d$, $3s3p^44d6d$, $3s3p^45d6d$, $3s3p^43d4s$, $3s3p^43d5s$, $3s3p^44d5s$, $3s^23p^33d4p$, $3s^23p^33d5p$, $3s^23p^33d4f$, $3s^23p^33d5f$, $3s^23p^34d4f$, $3s^23p^34d5f$, $3p^64s$, $3p^65s$, $3p^66s$, $3s3p^44s^2$, $3s3p^45s^2$, $3s3p^46s^2$, $3p^44s^25s$, $3s3p^44s5s$, $3s3p^44s6s$, $3s3p^45s6s$, $3s^23p^34s4p$, $3s^23p^34s4f$, $3s^23p^34s5p$, $3s^23p^34s5f$, $3s3p^54p$, $3s3p^55p$, $3s3p^54f$, $3s3p^55f$, $3s3p^44p5p$, $3s3p^44f5f$.

Configurations for odd parity states: $3s^23p^5$, $3s^23p^44p$, $3s^23p^45p$, $3s^23p^44f$, $3s^23p^45f$, $3s3p^53d$, $3s3p^54d$, $3s3p^55d$, $3s3p^56d$, $3p^53d^2$, $3p^54d^2$, $3p^55d^2$, $3s^23p^33d^2$, $3s^23p^34d^2$, $3s^23p^35d^2$, $3s^23p^33d4d$, $3s^23p^33d5d$, $3s^23p^34d5d$, $3s^23p^34d6d$, $3s^23p^35d6d$, $3s^23p^33d4s$, $3s^23p^33d5s$, $3s^23p^34d5s$, $3p^64p$, $3p^65p$, $3p^54p^2$, $3p^55p^2$, $3s^23p^34p^2$, $3s^23p^35p^2$, $3s^23p^34p5p$, $3p^54p5p$, $3s^23p^34p4f$, $3p^65f$, $3s^23p^34f^2$, $3s^23p^35f^2$, $3s3p^54s$, $3s3p^55s$, $3s3p^56s$, $3s^23p^34s^2$, $3s^23p^35s^2$, $3s^23p^34s5s$, $3s^23p^34s6s$, $3s^23p^35s6s$, $3s^23p^34s4d$, $3s^23p^34s5d$.

An ab-initio CI calculation is necessarily approximate, as one can take only finite number of M terms (configuration Functions (CF)) in the expression (1). If further CFs are added to CI calculations containing M number of terms, even the first a_i (expansion coefficients) of M will change and the results for transition probabilities and other parameters will change. The process of adding more and more configurations, in order to make the results more accurate, is tedious and unending. For solving this process, Hibbert [18] has devised a fine-tuning method, where small adjustment to the diagonal elements of the Hamiltonian matrix are made to bring the calculated energies as close as possible to the experiment. This fine-tuning technique produces accurate transition probabilities [23]. In these calculations the corrections are mostly small which improve the accuracy of the fine-structure mixing of different LS states.

Table 2. Radial function parameters for use in equation (3).

Orbital	I_{jnl}	c_{jnl}	ζ_{jnl}
$4s$	1	0.00574	38.04452
	2	0.01292	26.46666
	3	–0.06964	8.78832
	4	–1.00330	0.81399
	4	0.21329	3.42953
$5s$	1	0.11566	11.16706
	2	–0.27528	7.20843
	3	–1.58373	1.26288
	4	1.07301	3.36035
	5	0.89028	0.94187
$6s$	1	0.57104	0.49313
	2	–0.04374	7.08186
	3	–6.01530	1.07374
	4	5.53198	0.80578
	4	2.98416	1.80680
	5	–3.47777	0.68117
$3p$	2	–0.239952	6.49508
	2	–0.02395	12.32240
	3	0.53857	2.75959
	3	0.57628	1.67378
	3	–0.07460	4.87993
$4p$	2	0.00877	13.91198
	3	0.02958	9.59020
	4	–0.14642	2.98979
	4	0.99962	0.59731
$5p$	2	0.07020	7.73478
	3	–5.16059	0.81662
	4	17.05179	0.93173
	4	–11.56040	0.86117
$3d$	3	0.92781	0.46787
	3	0.21435	1.77353
$4d$	3	1.41743	4.16336
	3	0.03280	8.72259
	4	0.71251	1.81467
	4	–1.69563	2.75233
$5d$	3	0.18159	2.27734
	4	1.39302	0.42824
	4	–1.85950	0.37688
$6d$	3	4.46468	1.15926
	3	–0.57223	3.33417
	4	–2.73738	2.11510
	4	–1.99728	1.09966
$4f$	4	0.65185	0.84945
	4	0.48713	1.81251
$5f$	4	0.67273	2.08916
	4	–0.82533	0.67905

3 Results and discussion

3.1 Energies and wavefunctions

In Table 3 we have shown our calculated excitation energies (relative to the ground) of 47 fine structure levels of Cl I and compared them with latest available NIST energy level data (along with the references therein)

Table 3. Excitation energies (in cm^{-1}) relative to the ground state $3s^2 3p^5$ ($^2\mathrm{P}^{\mathrm{o}}_{3/2}$) and lifetimes (ns).

Level	Term	J	Present (this work)	NIST (expt.)	LP present	LP NIST	Lifetimes (ns)
$3s^2 3p^5$	$^2\mathrm{P}^{\mathrm{o}}$	3/2	00	00	92	95	
		1/2	882	882	92	95	
$3s^2 3p^4(^3\mathrm{P})4s$	$^4\mathrm{P}$	5/2	71959	71958	98	100	3133
		3/2	72315	72489	98	98	70.0
		1/2	72828	72827	97	99	289
	$^2\mathrm{P}$	3/2	74421	74226	98	98	1.37
		1/2	74866	74866	98	99	1.34
$3s^2 3p^4(^3\mathrm{P})4p$	$^4\mathrm{P}^{\mathrm{o}}$	5/2	82897	82919	95	96	31.3
		3/2	83107	83131	93	94	31.4
		1/2	83345	83365	95	97	31.2
	$^4\mathrm{D}^{\mathrm{o}}$	7/2	83885	83894	99	100	25.9
		5/2	84128	84132	68	66	30.0
		3/2	84465	84485	78	82	28.6
		1/2	84637	84689	75	96	28.9
$3s^2 3p^4(^1\mathrm{D})4s$	$^2\mathrm{D}$	5/2	84180	84120	97	100	4.52
		3/2	84161	84122	97	100	4.54
$3s^2 3p^4(^3\mathrm{P})4p$	$^2\mathrm{D}^{\mathrm{o}}$	5/2	84639	84648	69	68	35.5
		3/2	84932	84988	57	57	34.2
	$^2\mathrm{P}^{\mathrm{o}}$	1/2	84892	85244	65	60	9.39
		3/2	85350	85442	59	64	33.0
$3s^2 3p^4(^3\mathrm{P})4p$	$^4\mathrm{S}^{\mathrm{o}}$	3/2	85814	85735	94	88	46.6
	$^2\mathrm{S}^{\mathrm{o}}$	1/2	86226	85918	65	65	30.4
$3s^2 3p^4(^3\mathrm{P})3d$	$^4\mathrm{D}$	7/2	87965	87979	98	97	249
		5/2	88087	88080	97	96	185
		3/2	88168	88189	99	97	162
		1/2	88251	88273	98	99	188
	$^4\mathrm{F}$	9/2	90180	90194	99	100	8681
		7/2	90444	90488	89	53	106
		5/2	90688	90749	82	66	4.80
		3/2	90523	90949	98	90	5.89
	$^4\mathrm{P}$	1/2	91035	91069	94	99	60.1
		3/2	91610	91539	98	84	0.939
		5/2	91691	91661	89	59	14.7
	$^2\mathrm{F}$	7/2	91112	91089	89	53	95.4
		5/2	92006	91907	87	53	6.21
	$^2\mathrm{D}$	5/2	91067	91127	71	52	0.849
		3/2	91411	91174	94	76	5.76
	$^2\mathrm{P}$	1/2	91661	91564	88		2.47
		3/2	92026	92194	92		1.75
$3s^2 3p^4(^1\mathrm{D})3d$	$^2\mathrm{S}$	1/2	93095		66		64.4
$3s^2 3p^4(^1\mathrm{D})4p$	$^2\mathrm{P}^{\mathrm{o}}$	3/2	94528	94314	92	97	30.9
		1/2	94698	94469	90	96	30.3
	$^2\mathrm{F}^{\mathrm{o}}$	5/2	94854	95145	99	100	34.6
		3/2	95199	95180	99	100	
	$^2\mathrm{D}^{\mathrm{o}}$	5/2	96500	96483	99	100	15.4
		3/2	96509	96486	99	100	31.2
$3s^2 3p^4(^1\mathrm{S})4s$	$^2\mathrm{S}$	1/2	99566	99534	92	91	1.06

[24,25]. Our calculated theoretical energies, shows excellent agreement (better than 1%) with NIST compiled values. Level of agreement depends on the level of mixing among the various levels. In our calculations, the mixing among some of the relativistic levels is found to be very strong. For example, a strong mixing is present in the case of ^{2}P, ^{2}D and ^{4}D symmetry belonging to the configuration $3s^2 3p^4(^3\mathrm{P})4p$ with composition

$$\begin{aligned}3s^2 3p^4(^3\mathrm{P})4p \approx\ & 0.756759[3s^2 3p^4(^3\mathrm{P})4p\,^2\mathrm{D}_{3/2}]\\ &+ 0.469176[3s^2 3p^4(^3\mathrm{P})4p\,^2\mathrm{P}_{3/2}]\\ &+ 0.425393[3s^2 3p^4(^3\mathrm{P})4p\,^4\mathrm{D}_{3/2}]\\ &+ 0.093603[3s^2 3p^4(^1\mathrm{D})4p\,^2\mathrm{P}_{3/2}].\end{aligned}$$

This means that 57% of $3s^23p^4(^3\mathrm{P})4p\,^2\mathrm{D}_{3/2}$ level couples strongly with 22% of $3s^23p^4(^3\mathrm{P})4p\,^2\mathrm{P}_{3/2}$ and with 18% of $3s^23p^4(^3\mathrm{P})4p\,^4\mathrm{D}_{3/2}$ and weakly with $3s^23p^4(^1\mathrm{D})4p\,^2\mathrm{P}_{3/2}$.

Comparing the leading percentage (LP) columns of NIST Table with present results, we find that for most of the levels, difference is of the order of 3 to 5% but in some cases this difference is more than 5%. The percentage composition of the levels belong to $4s$ and $4p$ in the present calculation is similar to those of NIST results except for the level $3s^23p^4(^3\mathrm{P})4p\,^4\mathrm{D}^{\mathrm{o}}_{1/2}$ where the LP difference is 21%. NIST shows that this level is almost pure. In our calculations, we found that the level $3s^23p^4(^3\mathrm{P})4p\,^4\mathrm{D}^{\mathrm{o}}_{1/2}$ is actually coupled with $3s^23p^4(^3\mathrm{P})4p\,^2\mathrm{P}^{\mathrm{o}}_{1/2}$ with their compositions as 75% and 20% and also show CI mixing with other configurations.

3.2 Oscillator strengths and lifetimes

Transition probabilities and oscillator strengths of electric dipole transitions or E1 and intercombination or spin-forbidden transitions are presented in Table 4. We have used the fine-tuned structure energies in the calculation of transition probabilities and oscillator strengths. The calculated energy values are usually very close to the observed ones so that the errors in the transition probabilities are due to errors in the calculated transition integrals. Transition probabilities and f-values are calculated in the dipole length and velocity forms. For allowed dipole transitions or E1 transitions ($\Delta J = 0$, ± 1 except for $J = 0 \rightarrow J' = 0$; $\Delta S = 0$, $\Delta L = 0$, ± 1 except for $L = 0 \rightarrow L' = 0$) length and velocity forms should agree. We note that for strong and allowed transitions, agreement between the length and velocity form of the oscillator strength is better than 10%. However, for a couple of cases, f_l and f_v differ by about 20%, which may be partly due to the inaccuracies in the representation of mixing between the states. For intercombination lines or spin forbidden lines, the selection rule is same as for the allowed transitions except for $\Delta S \neq 0$. For spin forbidden lines or indeed for others weak lines, only the length form should be used. This is because, while the length form of the dipole operator is correct to $0(\alpha^2), \alpha$ being the fine structure constant, the velocity form would need a relativistic correction [26] which is not included in the present calculations. Most intercombination lines are weak, compared with allowed lines. In some cases, intercombination lines are much stronger than usual, due to the existence of mixing between quartets and doublet. For example in case of the transition $3s^23p^4(^3\mathrm{P})4p\,^4\mathrm{D}^{\mathrm{o}}_{3/2} \rightarrow 3s^23p^4(^3\mathrm{P})4s\,^2\mathrm{P}_{1/2}$ f_l is 0.0322. The unusual large f_l is due to strong interaction between $^4\mathrm{D}^{\mathrm{o}}_{3/2}$ and $^2\mathrm{D}^{\mathrm{o}}_{3/2}$ levels. In such cases, the contribution from the velocity operator correction is a small contribution to the total, so that length and the uncorrected velocity form still are in good agreement.

We have also reported the lifetimes in the length form of the $3s^23p^43d$, $3s^23p^44s$ and $3s^23p^44p$ levels in Table 3. The radiative lifetime of an excited state is calculated from the radiative transition probabilities A_{ji} using the relation

$$\tau_i = 1/\sum_i A_{ji}, \qquad (5)$$

where the sum over i is over all accessible final states.

The mean lifetime of a level is the reciprocal of the sum of all the probabilities of emission probabilities from that level. The weak intercombination lines contribute a negligible amount. The lifetimes are determined entirely from the allowed and strong intercombination transitions.

3.3 Comparison with other works

In Table 4 we show, together with the present results, the f-values calculated by Lavin et al. [14] using the RQDO, by Biémont et al. [15] using SUPERSTRUCTURE and by Ojha et al. [16] for comparative analysis. We have also shown the experimental data found in the literature in Table 4. Comparisons with other independent calculations and with experiments is an important tool for assessing the accuracy of the calculations and it also helps in upgrading the data base required to exploit the high quality of observations from current space and ground based telescopes. In general, our results agree with others within a few percent. Larger discrepancies are spotted for a number of weak transitions. Our results are in agreement with experiment. For example, oscillator strengths value for the $3s^23p^5\,^2\mathrm{P}^{\mathrm{o}}_{3/2} \rightarrow 3s^23p^44s\,^2\mathrm{P}_{3/2}$ transition is 0.1685, which is close to 0.153 ± 11 determined by Schectman et al. [12] and for the transition $3s^23p^5\,^2\mathrm{P}^{\mathrm{o}}_{3/2} \rightarrow 3s^23p^44s\,^2\mathrm{P}_{1/2}$ our f_l value 0.035 agrees well with 0.028 ± 0.006 as calculated by Clyne and Nipp [9].

To our knowledge, the only direct measurement of radiative lifetimes in chlorine are those of Lawrence [27] using the phase-shift method and Schectman et al. [12] using the beam-foil method. Lawrence reports lifetime measurements for two vacuum ultraviolet (vuv) transitions $3s^23p^4(^3\mathrm{P})4s\,^2\mathrm{P}_{1/2} \rightarrow 3s^23p^5\,^2\mathrm{P}^{\mathrm{o}}_{3/2}$ and $3s^23p^4(^3\mathrm{P})4s\,^4\mathrm{P} \rightarrow 3s^23p^5\,^2\mathrm{P}^{\mathrm{o}}$ transition (it is not clear whether this means the $3s^23p^4(^3\mathrm{P})4s\,^4\mathrm{P}_{5/2} \rightarrow 3s^23p^5\,^2\mathrm{P}_{3/2}$ or the $3s^23p^4(^3\mathrm{P})4s\,^4\mathrm{P}_{1/2} \rightarrow 3s^23p^5\,^2\mathrm{P}_{3/2}$ for which the measured lifetimes are 2 ns (15%) and 1500 ns (15%) respectively. For these levels our calculated lifetimes are 1.34 ns and 3132 ns. Schectman et al. measured lifetime of the the $3s^23p^4(^3\mathrm{P})4s\,^2\mathrm{P}_{3/2} \rightarrow 3s^23p^5\,^2\mathrm{P}_{3/2}$ transition 1.51 ± 0.07 ns and our calculated value is 1.37 ns. We have predicted new lifetime data for several levels where no other theoretical and/or experimental results are available.

4 Conclusions

In conclusion, we have performed a large scale-CI calculation of fine-structure energy levels, oscillator strengths, transition probabilities of electric dipole transitions among the fine-structure levels of the

Table 4. Oscillator strengths and transition probabilities (s^{-1}) (see the *Supplementary Online Material* for the complete version of the table).

Upper Level	Lower Level	f_l	f_v	A_l	A_v	Others (f_l)		
						Ojha [16]	RQDO [14]	Expt^{a,c,d} /SST^{b}
$3s^23p^4(^3\mathrm{P})4s\ ^4\mathrm{P}_{1/2}$	$3s^23p^5\ ^2\mathrm{P}_{1/2}$	0.0009	0.0007	0.3123(7)	0.2294(7)	0.0006		
	$3s^23p^5\ ^2\mathrm{P}_{3/2}$	0.0000	0.0000	0.3335(6)	0.3018(6)	0.0000		
$3s^23p^4(^3\mathrm{P})4s\ ^4\mathrm{P}_{3/2}$	$3s^23p^5\ ^2\mathrm{P}_{1/2}$	0.0009	0.0007	0.1549(7)	0.1199(7)	0.0006		
	$3s^23p^5\ ^2\mathrm{P}_{3/2}$	0.0004	0.0003	0.1273(8)	0.0979(8)	0.0026		
$3s^23p^4(^3\mathrm{P})4s\ ^4\mathrm{P}_{5/2}$	$3s^23p^5\ ^2\mathrm{P}_{3/2}$	0.0001	0.0001	0.3192(6)	0.2228(6)	0.0001		
$3s^23p^4(^3\mathrm{P})4s\ ^2\mathrm{P}_{3/2}$	$3s^23p^5\ ^2\mathrm{P}_{1/2}$	0.0605	0.0505	0.1086(9)	0.0843(9)	0.0474	0.0561	0.055^{a} 0.038^{c} 0.0530^{b}
	$3s^23p^5\ ^2\mathrm{P}_{3/2}$	0.1685	0.1322	0.6194(9)	0.4860(9)	0.1324	0.1368	0.153^{a} 0.147^{b}
$3s^23p^4(^3\mathrm{P})4s\ ^2\mathrm{P}_{1/2}$	$3s^23p^5\ ^2\mathrm{P}_{1/2}$	0.1326	0.1034	0.4843(9)	0.3775(9)	0.1051	0.1017	0.093^{a} 0.116^{b}
	$3s^23p^5\ ^2\mathrm{P}_{3/2}$	0.0350	0.0275	0.2616(9)	0.2060(9)	0.0264	0.0249	0.028^{a} 0.0299^{b} 0.100^{c} 0.109^{d}
$3s^23p^4(^1\mathrm{D})4s\ ^2\mathrm{D}_{5/2}$	$3s^23p^5\ ^2\mathrm{P}_{3/2}$	0.0701	0.0535	0.2210(9)	0.1685(9)	0.0677		
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{P}_{3/2}$	0.0001	0.0012	0.4454(2)	0.6644(3)			
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{P}_{5/2}$	0.0000	0.0000	0.1014(2)	0.1445(3)			
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{D}_{5/2}$	0.0000	0.0076	0.6517(2)	0.1335(2)			
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{D}_{7/2}$	0.0001	0.0000	0.4898(3)	0.2606(3)			
$3s^23p^4(^1\mathrm{D})4s\ ^2\mathrm{D}_{3/2}$	$3s^23p^5\ ^2\mathrm{P}_{1/2}$	0.0850	0.0646	0.1967(9)	0.1495(9)	0.0806		
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{P}_{1/2}$	0.0001	0.0019	0.1862(2)	0.4388(3)			
	$3s^23p^5\ ^2\mathrm{P}_{3/2}$	0.0050	0.0036	0.2348(8)	0.1719(8)	0.0052		
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{P}_{3/2}$	0.0000	0.0004	0.2046(2)	0.2707(3)			
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{P}_{5/2}$	0.0000	0.0000	0.1731(1)	0.1825(2)			
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{D}_{5/2}$	0.0000	0.0000	0.7584(-3)	0.1254(0)			
$3s^23p^4(^1\mathrm{S})4s\ ^2\mathrm{S}_{1/2}$	$3s^23p^5\ ^2\mathrm{P}_{1/2}$	0.0499	0.0428	0.3243(9)	0.2778(9)			
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{P}_{1/2}$	0.0000	0.0000	0.5843(4)	0.2196(4)			
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{D}_{1/2}$	0.0002	0.0002	0.2908(5)	0.3082(5)			
	$3s^23p^4(^3\mathrm{P})4p\ ^2\mathrm{P}_{1/2}$	0.0008	0.0007	0.1196(6)	0.1044(6)			
	$3s^23p^4(^3\mathrm{P})4p\ ^2\mathrm{S}_{1/2}$	0.0000	0.0000	0.3108(4)	0.3715(4)			
	$3s^23p^4(^1\mathrm{D})4p\ ^2\mathrm{P}_{1/2}$	0.0006	0.0034	0.9404(4)	0.5469(5)			
	$3s^23p^5\ ^2\mathrm{P}_{3/2}$	0.0469	0.0399	0.6200(9)	0.5272(9)			
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{P}_{3/2}$	0.0000	0.0000	0.1470(5)	0.3337(4)			
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{D}_{3/2}$	0.0000	0.0000	0.5304(4)	0.1002(5)			
	$3s^23p^4(^3\mathrm{P})4p\ ^2\mathrm{D}_{3/2}$	0.0002	0.0002	0.6123(5)	0.6334(5)			
	$3s^23p^4(^3\mathrm{P})4p\ ^2\mathrm{P}_{3/2}$	0.0817	0.0721	0.2206(6)	0.1946(6)			
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{S}_{3/2}$	0.0000	0.0000	0.1326(5)	0.1107(5)			
	$3s^23p^4(^1\mathrm{D})4p\ ^2\mathrm{P}_{3/2}$	0.0007	0.0029	0.2394(5)	0.9978(5)			
	$3s^23p^4(^1\mathrm{D})4p\ ^2\mathrm{D}_{3/2}$	0.0000	0.0000	0.1960(0)	0.7557(2)			
$3s^23p^4(^3\mathrm{P})3d\ ^4\mathrm{D}_{7/2}$	$3s^23p^4(^3\mathrm{P})4\mathrm{p}\ ^4\mathrm{P}_{5/2}$	0.2520	0.5934	0.3238(7)	0.7624(7)	0.4120		
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{D}_{5/2}$	0.0124	0.0311	0.9119(5)	0.2292(6)	0.0187		
	$3s^23p^4(^3\mathrm{P})4p\ ^2\mathrm{D}_{5/2}$	0.0044	0.0146	0.2446(5)	0.8126(5)	0.0097		
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{D}_{7/2}$	0.0588	0.1217	0.6524(6)	0.1351(7)	0.0930		
$3s^23p^4(^3\mathrm{P})3d\ ^4\mathrm{D}_{5/2}$	$3s^23p^5\ ^2\mathrm{P}_{3/2}$	0.0004	0.0004	0.1252(7)	0.1199(7)	0.0000		
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{P}_{3/2}$	0.1770	0.4248	0.1957(7)	0.4697(7)			
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{D}_{3/2}$	0.0190	0.0497	0.1112(6)	0.2913(6)	0.0320		
	$3s^23p^4(^3\mathrm{P})4p\ ^2\mathrm{D}_{3/2}$	0.0018	0.0048	0.8153(4)	0.2117(5)	0.0032		
	$3s^23p^4(^3\mathrm{P})4p\ ^2\mathrm{P}_{3/2}$	0.0001	0.0008	0.3878(3)	0.2712(4)	0.0000		
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{S}_{3/2}$	0.0001	0.0029	0.2210(3)	0.6633(4)			
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{P}_{5/2}$	0.0933	0.1991	0.1676(7)	0.3576(7)			
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{D}_{5/2}$	0.0194	0.0385	0.2027(6)	0.4024(6)	0.0269		
	$3s^23p^4(^3\mathrm{P})4p\ ^2\mathrm{D}_{5/2}$	0.0037	0.0078	0.2960(5)	0.6171(5)	0.0073		
	$3s^23p^4(^3\mathrm{P})4p\ ^4\mathrm{D}_{7/2}$	0.0111	0.0209	0.1741(6)	0.3289(6)	0.0168		

[a] Schectman et al. [12], [b] Biémont et al. [15], [c] Clyne and Nipp [9], [d] Schwab and Anderson [10].

term $3s^23p^5\,{}^2\mathrm{P^o}$, $3s^23p^4({}^3\mathrm{P})4s\,{}^4\mathrm{P}$, ${}^2\mathrm{P}$, $3s^23p^4({}^1\mathrm{D})\;4s\,{}^2\mathrm{D}$, $3s^23p^4({}^1\mathrm{S})4s\,{}^2\mathrm{S}$, $3s^23p^4({}^3\mathrm{P})4p\,{}^4\mathrm{P^o}$, ${}^4\mathrm{D^o}$, ${}^2\mathrm{D^o}$, ${}^2\mathrm{P^o}$, ${}^4\mathrm{S^o}$, ${}^2\mathrm{S^o}$, $3s^23p^4({}^1\mathrm{D})4p\,{}^2\mathrm{P^o}$, ${}^2\mathrm{F^o}$, ${}^2\mathrm{D^o}$, $3s^23p^4({}^3\mathrm{P})3d{}^4\mathrm{D}$, ${}^4\mathrm{F}$, ${}^4\mathrm{P}$, ${}^2\mathrm{F}$, ${}^2\mathrm{D}$, ${}^2\mathrm{P}$ and $3s^23p^4({}^1\mathrm{D})3d\,{}^2\mathrm{S}$ of neutral chlorine. We have also reported lifetimes of $3s^23p^43d$, $3s^23p^44s$ and $3s^23p^44p$ levels. In our calculations, we have used an extensive set of CI wavefunctions and included correlation effects in the excitation up to the $5f$ orbital. We have found strong configuration mixing among fine-structure levels of Cl I. Fine structure energy levels agree very well with NIST compiled values. We predict new lifetime data for several levels where no other theoretical and/or experimental results are available, which will form the basis for the future experimental work. We expect our results to be quite accurate as all important correlation and relativistic effects have been included in our calculations.

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