Ultraviolet transition probabilities in N II

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Oscillator strengths have been calculated for the ultraviolet transition array $2p^2$-$2p3s$ in the N II spectrum. Recent astrophysical, experimental, and theoretical works have called attention to two interesting features of these lines. First, the intercombination line at 748 Å is exceptionally strong; second, the branching ratio between the ^1D and ^1S decay modes of the $^1P^\circ$ level is unusually large. Both these effects reflect the strong interaction of $2s^22p3s$ with the "plunging" configuration $2s2p^3$; unlike other ions in the carbon isoelectronic sequence, these configurations are overlapping for N II. In the present work multiconfiguration Hartree-Fock (MCHF) wave functions have been used to compute oscillator strengths for all the lines in the $2p^2$-$2p3s$ transition array. The MCHF results give wavelengths which are within 1% of the observed wavelengths; the length and velocity forms of the oscillator strengths agree with each other to within 7%; and the predicted mean lifetime of the $2p3s\ ^1P^\circ$ level agrees with a recent beam-foil–laser result to 4% [Y. Baudinet-Robinet *et al.*, Phys. Rev. A **42**, 1080 (1990)].

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I. INTRODUCTION

Knowledge of the spectrum of ionized nitrogen is essential for understanding the earth's ionosphere and similar plasmas elsewhere in the solar system. While the N II spectrum is generally well known, we consider here some ultraviolet transition probabilities which appear to have anomalous values caused by strong mixing between overlapping configurations. Tripp, Shemansky, James, and Ajello [1] have emphasized the astrophysical importance of the strong resonance transitions designated $2p^2$-$2p3s$ in N II, even though they occur below the Lyman limit at wavelengths in the range 671–858 Å. In particular, these authors report experimental confirmation of the prediction by Fawcett [2] that the intercombination line ($^1D_2$-$^3P_1^\circ$) at 748 Å is anomalously strong, and point out the importance of this fact for radiative cooling and temperature diagnostics in the upper atmospheres of Earth and Titan. They also call attention to other unusual features of the N II $2p^2$-$2p3s$ transitions, such as the large value of the $^1P^\circ$ radiative decay branching ratio, $R = A(^1D - {}^1P^\circ)/A(^1S - {}^1P^\circ)$.

These effects are caused by the especially strong interaction in N II between the configurations $2s2p^3$ and $2s^22p3s$, which in turn reflects the changes in energy-level orderings as a function of nuclear charge Z in the carbon isoelectronic sequence. The "plunging" configuration $2s2p^3$ lies above $2s^22p3s$ in C I but below it for high Z [3]. In particular, there is an avoided crossing of the $^3P^\circ$ terms in these configurations between C I and N II, while the $^1P^\circ$ terms cross between N II and O III. This means that the $2p3s$ levels in N II are forced together in energy—the higher $2p3s\ ^1P$ is forced down by its interaction with $2p^3\ ^1P$, while the lower $2p3s\ ^3P$ is forced up by the $2p^3\ ^3P$. The result is an anomalously small $2p3s\ ^1P$–^3P term interval, leading to a large spin-orbit mixing between the $^3P_1$ and $^1P_1$ levels, and a large intercombination-line transition probability. In addition, the same strong configuration interaction enhances the $2p^2\ ^1D$–$2p3s\ ^1P$ transition at the expense of the $2p^2\ ^1S$–$2p3s\ ^1P$ transition: the interference produced in the dipole integral by the $2p^3$ component of the $2p3s$ wave function is constructive for the former and destructive for the latter. This not only explains the large value of R, it also provides a further enhancement of the ^1D-^3P intercombination line, since the latter proceeds through the singlet component of the ^3P wave function and is proportional to the same ^1D-^1P dipole integral.

Radiative mean lifetimes of N II $2p3s$ states have been measured in several experiments. In the case of the ^1P level, experiments have used the phase-shift [4], beam-foil [5–9], and beam-foil–laser [10] methods. This last experiment is noteworthy in that it is cascade free and shows this mean lifetime to be definitely shorter than its isoelectronic analogs in C I and O III. Measurements of the ^3P mean lifetimes have been beam-foil experiments [5,7,8,11–14]. Both the ^1P and ^3P results show considerable variation; beam-foil studies of these lifetimes have been complicated by the close spacing of the lines at 646, 647, and 648 Å, as well as by the presence of significant cascades. Also there have been measurements of radiative branching ratios in N II [1,15] which have reported unusual results, for example, the remarkably large value for the $2p^2\ ^1D$–$2p3s\ ^1P$ branching ratio already mentioned. It is difficult to deduce the weaker oscillator strengths from the measured mean lifetimes because of the anomalous branching ratios.

A number of theoretical values for the N II $2p^2$–$2p3s$ oscillator strengths have been published [2,16–20]. Many of these have been large survey calculations not directed specifically at the transitions of interest here; most have not included the intercombination lines. Furthermore, the results differ significantly from each other, and there has been no multiconfiguration Hartree-Fock (MCHF) calculation of these transitions. The MCHF method [21] is very powerful for studies of low-lying

TABLE I. Term excitation energies for N II (kK).

Config.	Term	Obs.[a]	MCHF	+Breit
$2p3s$	^1P	149.099	150.71	150.68
$2p3s$	^3P	148.923	150.19	150.13
$2p^2$	^1S	32.600	33.13	33.14
$2p^2$	^1D	15.227	15.72	15.72
$2p^2$	^3P	0.000	0.00	0.00

[a]Reference [28].

states where configuration-interaction effects are strong, and especially for cases such as this one in which the interactions are significantly different for different LS-coupling terms of the same configuration.

II. MCHF WAVE FUNCTIONS

The interaction between the overlapping configurations $2s^22p3s$ and $2s2p^3$ involves four active electrons in three open subshells. Preliminary calculations showed that a moderately large number of basis states would be required in a Hartree-Fock calculation to account for the correlation in this system. In order to compute the transition array $2s^22p^2$-$2s^22p3s$, there must be a consistent treatment of all five LS-coupled terms (^3P, ^1D, ^1S, $^3P^\circ$, and $^1P^\circ$). Fortunately, the MCHF atomic structure package (MCHF-ASP) of Charlotte Froese Fischer and collaborators, available from the Computer Physics Communications Program Library, provides a convenient mechanism for carrying out such a treatment in a systematic way [22].

In the present calculation, MCHF wave functions have been computed for each of the five LS-coupled states listed above. In each of the five cases the treatment began with a two-configuration reference set: $\{2s^22p^2+2p^4\}$ for the even-parity states and $\{2s^22p3s+2s2p^3\}$ for the odd-parity states. Virtual orbitals were added so that in each case there were a total of ten radial functions: $1s,2s,2p,3s,3p,3d,4s,4p,4d,4f$. The program MCHF_GENCL [23] was used to generate a list of configuration states in each case by making all possible single- and double-electron replacements from the reference set to the virtual orbitals, and including all possible couplings of the open subshell angular momenta. Within each of the five solutions, all orbitals were kept orthogonal. This resulted in a set of 147 configuration states for ^3P, 144 for ^1D, 70 for ^1S, 221 for $^3P^\circ$, and 166 for $^1P^\circ$.

In order to compute the desired multiplet oscillator strengths systematically and reliably using MCHF-ASP, it was necessary to have a common set of $1s$, $2s$, and $2p$ orbitals for both states involved in each transition, and to restrict the choice of configurations to those having no more than two other orbitals besides this common set. This reduced the number of configuration states used in the final MCHF calculations to 179 for $^3P^\circ$ and 138 for $^1P^\circ$

The radial functions and configuration-mixing coefficients for all the states involved were then computed using the MCHF_NONH [24] and MCHF_88 [25] programs. For the singlet states the $1s$, $2s$, and $2p$ radial functions were determined by optimizing the $2p^2\,^1D$ energy; for the triplets, by optimizing the $2p^2\,^3P$. The $n=3$ and 4 orbitals were then determined separately for each of the five cases via MCHF calculations with $1s$, $2s$, and $2p$ held fixed. The Breit-Pauli relativistic-energy corrections were then computed perturbatively for each case, using the programs MCHF_BREIT [26] and MCHF_CI [27]. (The spin-spin and spin–other-orbit interactions were neglected.) As expected, the Breit-Pauli corrections did not make a significant change in the excitation energies in this case. The energies resulting from these calculations, both with and without the relativistic corrections, are shown in Table I for comparison with the observed energy levels of N II [28].

The comparison with observed excitation energies (of order 1 kK) is satisfactory for this kind of calculation. To do significantly better would require a major effort which would be largely irrelevant to the purpose of this work, namely the calculation of oscillator strengths. However, it is essential to note that the computed ^1P-^3P energy difference in the $2p3s$ configuration is three times the observed 176 cm.$^{-1}$ While the present MCHF solutions successfully reproduce the fact that these terms are unusually close together, this separation cannot be obtained precisely by subtracting the results of two separate 1% calculations. For this reason the observed, rather than the computed, value of the $^1P_1$-$^3P_1$ interval has been used here to calculate the singlet-triplet mixing, as will be described below.

III. MULTIPLET OSCILLATOR STRENGTHS

With these wave functions, the dipole-allowed multiplet oscillator strengths can now be calculated using the

TABLE II. Multiplet gf values for $2p^2$-$2p3s$ transitions. The designations L and V refer to the length and velocity forms of the dipole matrix element respectively.

	λ (Å)		MCHF-ASP		Other Results		
Mult.	Obs.	Calc.	L	V	R Matrix[a]	FOTOS[b]	NCMET[c]
^1S-^1P	858.35	851	0.013	0.014	0.016	0.003	0.020
^1D-^1P	746.98	741	0.956	1.021	0.990	1.000	0.880
^3P-^3P	671.48	666	0.637	0.682	0.699		

[a]Reference [16].
[b]Reference [17].
[c]Reference [18].

programs MCHF_MLTPOL [29] and MCHF_LSTR [30]. The results for the weighted oscillator strengths (gf values) are given in Table II and compared with selected previous theoretical results.

Several things should be noted about the results shown in Table II. The MCHF-ASP results are reasonable in that the calculated and observed wavelengths agree within 1%, and the length and velocity forms of the oscillator strengths agree within 7%. Also, the comparison with earlier work is reassuring in view of the strong configuration interactions involved, and the differences in theoretical techniques (including FOTOS [17] and NCMET [18], which combine self-consistent-field and perturbation-theory methods). It is especially interesting to note the good agreement with the results of Luo and Pradhan [16], since that work uses the close-coupling R-matrix method, which is quite different in practice from the MCHF method used here. The results for the weak 858-Å line are inevitably less precise than the others because of the large cancellation effects involved.

IV. SPIN-ORBIT MIXING

The multiplet oscillator strengths given above can be applied directly to the transitions involving the $2p3s\ ^3P_0$ and $^3P_2$ levels, using the standard formulas of LS coupling. However, the $2p3s\ ^3P_1$ and $^1P_1$ levels are significantly mixed by the spin-orbit interaction $H_{\text{S.O.}}$ so that the gf values involving those levels must be computed more carefully. The crucial point is to obtain the matrix of $H_{\text{S.O.}}$ involving these two levels so that it can be diagonalized to yield the intermediate-coupling eigenvectors. Because the $^1P_1$ and $^3P_1$ are close together and well separated from other $J=1$ levels, it is a good approximation to simply use a 2×2 matrix [31]. However, as already mentioned, it is essential to use the observed energy-level separation.

In order to compute the matrix element of $H_{\text{S.O.}}$ between the $2p3s\ ^1P_1$ and $^3P_1$ states, a representation was constructed in which both states were defined in terms of the same set of orthogonal orbitals. (The approach used is similar to that employed by Fischer [32] in a study of doublet-quartet mixing in core-excited Na I.) A calculation was performed using MCHF_88 in which the radial functions $1s,2s,2p,3s,3p,3d$ from the $^3P_1$ solution were held fixed while the $4s,4p,4d,4f$ functions were varied to minimize the energy of the $^1P_1$. Then with all ten orbitals held fixed, the configuration-interaction (CI) coefficients of $^3P_1$ were redetermined. The result is a pair of multiconfiguration expansions, one for $^1P_1$ and one for $^3P_1$, based on the same set of ten radial functions, but with different CI coefficients. Using these two wave functions with the programs MCHF_BREIT and MCHF_CI, the matrix of $H_{\text{S.O.}}$ in the common basis was constructed, and from that the desired interaction matrix elements were computed,

$$\langle {}^1P_1|H_{\text{S.O.}}|{}^3P_1\rangle = -72.62\ \text{cm}^{-1}\ ,$$

$$\langle {}^3P_1|H_{\text{S.O.}}|{}^3P_1\rangle = -55.88\ \text{cm}^{-1}\ .$$

Note that if this were a pure $2p3s$ configuration, the ratio of these two would be $\sqrt{2}$, whereas here it is 1.30. A check on this method of constructing the spin-orbit interaction matrix is provided by the fact that the value of $\langle {}^3P_1|H_{\text{S.O.}}|{}^3P_1\rangle$ given above corresponds to $\zeta=111.75$, and predicts $E(^3P_2)-E(^3P_0)=167.64\ \text{cm}^{-1}$, compared to the observed value of $167.93\ \text{cm}^{-1}$ [28].

Now the diagonal elements of the 2×2 energy matrix are adjusted empirically so that the eigenvalue difference reproduces the observed [28] value of $E(^1P_1)-E(^3P_1)=247.63\ \text{cm}^{-1}$. The eigenvector of this 2×2 matrix now gives the desired spin-orbit mixing coefficient α

$$\Psi(^1P_1)=\sqrt{1-\alpha^2}\,\Phi(^1P_1)+\alpha\Phi(^3P_1)\ ,$$

$$\Psi(^3P_1)=-\alpha\Phi(^1P_1)+\sqrt{1-\alpha^2}\,\Phi(^3P_1)\ ,$$

where Ψ and Φ represent the physical states and the nonrelativistic MCHF solutions, respectively, and α is found to be 0.3083.

The effects of the spin-orbit mixing are now obvious: the computed nonrelativistic line strengths must be multiplied by $(1-\alpha^2)=0.9048$ for the $\Delta S=0$ lines, and by $\alpha^2=0.0950$ for the $\Delta S=\pm1$ lines. The results are given in Table III, in which the line gf values and the emission A values from the present work are listed along with the gf values from the calculation of Fawcett [2].

TABLE III. Line gf and A values for $2p^2$-$2p3s$ ($J=1$) transitions.

		Fawcett[a]	This work	
Line	λ (Å)	gf	gf	A (ns^{-1})
$^1S_0$-$^1P_1$	858.35	0.042	0.013	0.039
$^1S_0$-$^3P_1$	860.19	0.005	0.001	0.003
$^1D_2$-$^1P_1$	746.98	0.943	0.894	3.562
$^1D_2$-$^3P_1$	748.36	0.121	0.094	0.374
$^3P_2$-$^3P_1$	672.00	0.102	0.083	0.409
$^3P_2$-$^1P_1$	670.88	0.011	0.009	0.044
$^3P_1$-$^3P_1$	671.63	0.059	0.050	0.246
$^3P_1$-$^1P_1$	670.51	0.008	0.005	0.025
$^3P_0$-$^3P_1$	671.41	0.080	0.066	0.326
$^3P_0$-$^1P_1$	670.29	0.010	0.007	0.035

[a]Reference [2].

V. CONCLUSIONS

Three recent experiments serve as useful tests of these results. First, the precise cascade-free beam-foil–laser measurement of Baudinet-Robinet *et al.* [10] gives the mean lifetime of the $2p3s\ ^1P_1$ level as 0.267 ± 0.010 ns. From the results of the present work, that mean lifetime can be predicted by summing the transition probabilities to all the levels of the $2p^2$ configuration. (The strong $^1D_2$-$^1P_1$ decay provides 96% of the decay rate.) The predicted mean lifetime is 0.270 ns, well within the 4% precision of that experiment. Second, Tripp *et al.* [1] report a branching ratio of 0.29 ± 0.15 for the intercombination line $^1D_2$-$^3P_1$ at 748 Å. The present results predict that ratio to be $0.374/1.358=0.275$. Third, Morrison, Cunningham, and Christensen [15] report that $A(747)/A(858)>50$, while the present results predict

that ratio to be $3.562/0.039=91$.

Table III shows that the present results and those of Fawcett [2] agree nicely with respect to the relative strengths of the different lines, although the latter work gives consistently larger values. The differences between the two sets of results probably give a reasonable estimate of the accuracy of both. However, it may be that the present results are slightly preferable for the following reasons: (a) the good agreement with the crucial experiments, (b) the good agreement with other theoretical results [16,17], and (c) the fact that the Fawcett calculation was designed to treat a large number of transitions and did not concentrate on these particular lines. Other measures of the precision of the present calculation are that the length and velocity forms agree with each other to 7%, the wavelengths are correct to 1%, and the ^1P mean lifetime agrees with experiment to 4%.

In summary, the calculations described here confirm that the 748-Å intercombination line is unusually strong as predicted by Fawcett [2], support the multiplet strength computations of Luo and Pradhan [16], and illustrate the usefulness of the new MCHF-ASP program package [22]. The results listed in Table III give a reliable set of theoretical weighted oscillator strengths for all the lines of the $2p^2$-$2p3s$ transition array in N II.

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