Electron-impact excitation of atomic oxygen: ^{3}P–3s ^{5}S° and ^{3}P–3s ^{3}S°

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Abstract. A close-coupling expansion is used in the determination of electron-impact excitation cross sections for atomic oxygen. The ^{3}P, 3s ^{5}S° and 3s ^{3}S° states are retained in the expansion, and configuration-interaction wavefunctions are utilised in the representation of the target states. Care is taken to ensure a realistic value for the ^{3}P–3s ^{3}S° oscillator strength. While the present results are in good agreement with distorted-wave calculations the experimental data for the triplet are higher by a factor of 2·6. In comparison with previous close-coupling calculations, there is a marked improvement in the position of the $(3s^2)^4$S° resonance while the positions of the $(3s3p)^2$P° and $(3s3p)^4$P° are essentially unchanged.

1. Introduction

The electron-impact excitation cross sections for atomic oxygen are particularly important in atmospheric physics (Strickland and Rees 1974, Julienne and Davis 1974, Myers *et al* 1974, Feldman and Takacs 1976). The 1304 Å and 1356 Å emission lines are prominent features of the aurorae and there are serious discrepancies between the observed and predicted intensities of these lines. Strickland and Rees (1974) have suggested that erroneous excitation cross sections may be responsible for the discrepancies.

Over the past few years several papers have appeared which are devoted to the determination of the O I (^{3}P–3s ^{3}S°) cross section (Stone and Zipf 1971, Rountree and Henry 1972, Sawada and Ganas 1973, Davis *et al* 1974, Stone and Zipf 1974, Smith 1976) and for the most part the discrepancies among the theoretical results are readily understandable. For example, in comparing the results obtained in the various distorted-wave (DW) approximations with those obtained in the close-coupling (CC) approximation one finds that the maximum in the DW cross sections is broader and occurs at a slightly higher energy. This difference, which occurs at low energies, is expected. However, at the higher energies both approximations should give essentially the same results. The fact that they do not is due to the difference in the strength of the direct potential. This difference can be taken into account approximately by scaling the cross sections by the ^{3}P–3s ^{3}S° oscillator strength ratio. Upon doing so, one finds that the various theoretical results are in fact in good agreement.

There still remains an unresolved discrepancy between the experimental (Stone and Zipf 1974) and theoretical results. In an effort to resolve this problem and to

determine cross sections for excitation of the 3s $^5S°$ we have calculated within the CC approximation excitation cross sections for atomic oxygen. A great deal of care is taken in the selection of the target-state representations and the error in the present results should be no greater than 20 or 25% above an energy of 20 eV.

In §2 we describe the calculations and then in §3 we present the results.

2. Description of calculations

The expansion of the total wavefunction (electron + target) is

$$\Psi_j(x_1 \ldots x_{N+1}) = a \sum_i \psi_i(x_1 \ldots x_N) F_{ij}(x_{N+1}) + \sum_v C_{vj} \Phi_v(x_1 \ldots x_{N+1})$$

where the x_i denote the spatial and spin dependence of the ith electron, the ψ_i are eigenstates of the target and a is the antisymmetrisation operator. The equations for the F_{ij} and C_{ij} are given by Smith and Morgan (1968) and are solved numerically by the non-iterative integral equation method (Smith 1973).

There are two levels of approximation in the treatment of electron–atom scattering. First, we truncate the sum over the target states and second, we approximate the target states. In the present work the ^3P, 3s $^5S°$ and 3s $^3S°$ states are retained in the CC expansion of the continuum function. The v sum runs over the $N+1$ electron configurations which are explicitly removed in the orthogonalisation of the continuum orbitals, F_{ij}, to the bound orbitals. For example, one of the continuum channels is $1s^2 2s^2 2p^4(^3P)ks$ and the continuum orbital, ks, is constrained to be orthogonal to the 3s orbital. Therefore, the state corresponding to $1s^2 2s^2 2p^4(^3P)3s$ is included in the set of Φ_v. These functions incorporate short-range effects and are referred to as correlation terms.

It is well known that predictions of atomic properties are very sensitive to the wavefunction approximations and scattering cross sections are certainly no exception. Rountree (1973) has pointed out that a poor choice of target states will give rise to spurious resonance positions. Matese et al (1973) have had a great deal of success in the prediction of resonance positions of oxygen and their work gives some indication of how to select the orbital basis set used in the construction of the target states and the correlation terms.

In the present work the best possible positioning of the resonance states is realised by using $O^+(^4S°)$ Hartree–Fock (HF) orbitals for the 1s, 2s and 2p (Clementi 1965). The 3s orbital is generated in the field of the $O^+(^4S°)$ core where the parameters in the Slater expansion

$$P_{nl} = \sum A_i r^{n_i} \exp(-\alpha_i r)$$

are determined by minimising the energy of the 3s $^3S°$ state, ensuring at the same time that the 3s orbital is orthogonal to both the 1s and 2s (Hibbert 1975).

As indicated by oscillator-strength calculations, a single-configuration approximation for the ^3P state using $O^+(^4S°)$ HF orbitals is very unsatisfactory. However, the addition of configurations 2–4 (table 1) and the optimisation of the energy of the ^3P state yields an energy of $-74·824$ au. (For comparison, the HF energy of the ^3P state is $-74·809$ au.) Configurations 5 and 6 do not significantly improve the energy, but they are coupled to the 3s $^3S°$ via a dipole transition and are important in the determination of the ^3P–3s $^3S°$ oscillator strength. As indicated in table 3,

Table 1. Target-state wavefunctions and energies.

State	Configuration	Weight	Energy (au)
^{3}P	$1s^2 2s^2 2p^4$	0·93848	−74·8288
	$1s^2 2s^2 2p^3 (^4S)\overline{3p}$	0·24721	
	$1s^2 2s^2 2p^3 (^2D)\overline{3p}$	−0·19340	
	$1s^2 2s^2 2p^3 (^2P)\overline{3p}$	0·12182	
	$[1s^2 2s2p^4 (^3P)^2P]3s$	0·07492	
	$[1s^2 2s2p^4 (^3P)^4P]3s$	0·01691	
3s ^{5}S°	$1s^2 2s^2 2p^3 (^4S)3s$	1·00000	−74·5289
3s ^{3}S°	$1s^2 2s2p^4 (^4S)3s$	1·00000	−74·5149

the oscillator strength, while a bit high, is in good agreement with recent experimental data. The results of more extensive investigations using a somewhat larger number of configurations in both the initial and final states are in very good agreement with experiment and indicate that the present estimates are about 20–25% high. Such large configuration-interaction wavefunctions are definitely desirable, but are not practical in scattering calculations. The orbital basis set and target-state representations are given in tables 1 and 2, respectively.

At the second level of approximation the continuum wavefunction is expanded in terms of the ^{3}P, 3s ^{5}S° and 3s ^{3}S°. The ^{1}D and ^{1}S terms of the ground state lie below the 3s ^{5}S° and *a priori*, failure to include these states would seem to give rise to a rather severe error. However, this is not the case and the neglect of these states is clearly justified by the following considerations. First, neither the ^{1}D nor ^{1}S couple to the 3s ^{5}S°. Second, the ^{1}D and ^{1}P couple to the ^{3}P only in the doublet partial waves and the statistical weights indicate that the doublet contribution to the total cross section is of the order 33%. Third, a transition from the ^{3}P to the

Table 2. Parameters defining the single-particle 3s and $\overline{3p}$ orbitals.

	A	n	α
P_{3s}	2·01547	1	6·33719
	−2·76102	2	2·58591
	0·14165	3	0·72945
$P_{\overline{3p}}$	9·84096	2	2·80769
	−1·26181	3	1·33721

Table 3. O I (^{3}P–3s ^{3}S°) oscillator strength.

	Reference
0·0467 ± 0·0013	Lawrence (1970)
0·0500 ± 0·0059	Druetta and Poulizac (1970)
0·0486 ± 0·0042	Martinson *et al* (1971)
0·0474 ± 0·0045	Smith *et al* (1971)
0·0500 ± 0·0041	Lin et al (1972)
0·050 ± 0·004	Irwin *et al* (1973)
0·056	Sawada and Ganas (1973)
0·057 (length)	present
0·060 (velocity)	present

3s $^3S°$ through an intermediate ^1D or ^1S goes via double exchange and the cross sections for such processes are very small relative to direct excitations. Fourth, in a single-configuration approximation in which the same one-electron orbitals are used in both the intermediate state and the 3s $^3S°$, the direct and exchange couplings are rigorously zero and the only effect is that due to a reduction of the flux in the elastic channel. These remarks clearly indicate that the ^1D and ^1S are certainly no more important than the remaining states which are neglected in the truncation of the CC expansion.

In the present work the ten lowest partial cross sections ($^2S°$, $^4S°$, ..., $^4G°$) are calculated. In the case of the $^4G°$ partial wave the coupling to the 3s $^5S°$ is not included; otherwise, the ^3P, 3s $^5S°$ and 3s $^3S°$ are fully coupled and no channels are neglected. The theoretical energy levels given in table 1 are used throughout the scattering calculations.

The partial cross sections for the forbidden transition, ^3P–3s $^5S°$, died off very rapidly for increasing values of the total angular momentum and the cross section is well converged with the inclusion of the $^4S°$, ^4P, $^4D°$ and ^4F partial cross sections. At the maximum in the ^4F partial cross section the contribution to the total cross section is less than 10% and the error incurred in the truncation of the sum with the ^4F partial wave should be less than 3% for energies below 2·0 Ryd.

The contributions from the higher partial waves are significant in the case of the allowed transition, ^3P–3s $^3S°$. For the higher partial waves we have assumed that the cross sections are proportional to the oscillator strength and have scaled the results of Rountree and Henry (1972) to obtain an estimate for these contributions. At an energy of 1·25 Ryd the sum of the first ten partial waves is compared with the corresponding results of Rountree and Henry (1972) and the ratio of the present results to theirs is 2·32 while the ratio of the dipole oscillator strengths is 2·34. In table 4 the numbers in parentheses are the total contributions to the ^3P–3s $^3S°$ cross section from partial waves for which the total angular momentum is greater than $L = 4$.

Table 4. ^3P–3s $^5S°$ and ^3P–3s $^3S°$ cross sections.

Energy (Ryd)	$Q(^3P$–3s $^5S°)$ (πa_0^2)	$Q(^3P$–3s $^3S°)$ (πa_0^2)
0·63	0·0675	0·0181
0·64	0·0884	0·0567
0·65	0·0859	0·1041
0·66	0·0753	
0·67	0·0662	0·1251
0·68	0·0598	0·1212
0·69	0·0554	0·1172
0·70	0·0524	0·1143
0·75	0·0466	0·1151
0·80	0·0482	0·1399 (0·0000)
0·85	0·0502	0·1574
0·90	0·0507	0·1794
1·00	0·0466	0·2089 (0·0069)
1·20	0·0312	0·2286
1·50	0·0156	0·2292 (0·0318)
2·00	0·0050	0·2125 (0·0711)

3. Results

The ^{3}P–3s ^{5}S° and ^{3}P–3s ^{3}S° cross sections are tabulated in table 4 and compared with other works in figures 1 and 2. The full circles are the data of Stone and Zipf (1974) scaled by 1/2·6 and 1/5·6 for the triplet and quintet, respectively. The crosses are the results of DW calculations by Sawada and Ganas (1973).
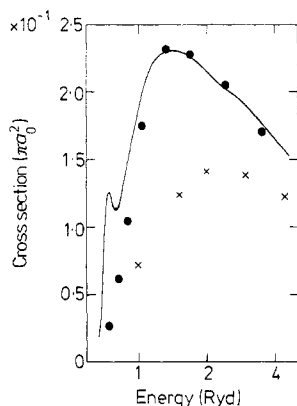
Figure 1. Semi-log plot of the O I (^{3}P–3s ^{3}S°) electron-impact excitation cross sections. Full curve, present close-coupling results plotted relative to the experimental threshold; crosses, distorted-wave work by Sawada and Ganas (1973); full circles, experimental results of Stone and Zipf (1974) scaled by 1/2·6.
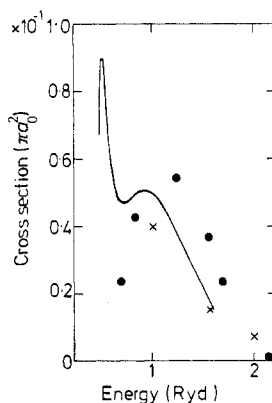
Figure 2. Semi-log plot of the O I (^{3}P–3s ^{5}S°) electron-impact excitation cross sections. Full curve, present close-coupling results plotted relative to the experimental threshold; crosses, distorted-wave work by Sawada and Ganas (1973); full circles, experimental results of Stone and Zipf (1974) scaled by 1/5·6.

The energy dependence of the present results for the 3s ^{3}S° is in excellent agreement with experiment while the DW results are low for the lower energies and approach the CC results in the high-energy limit. The Stone and Zipf (1974) data were scaled to match the CC cross section in the peak. Their results include cascades and it is probably more reasonable to match the cross sections near the threshold where the contributions from cascades are small. If the experimental and CC results are matched at the first data point above the resonance structure, then the experimental results are about 28% higher than the CC results for energies above 1·5 Ryd. This implies a 28% (or slightly greater) contribution from cascade and is in very good agreement with the 30% figure quoted by Rountree and Henry (1972). Revised estimates of the cascade contributions using improved values for the oscillator strengths are also in very good agreement with this figure.

The experimental cross section for the ^{3}P–3s ^{5}S° is a factor of 5 to 6 larger than either the CC or DW results. There is also an apparent shift in the maximum which is probably due to the cascade contributions. Again, the cascade contributions should be of the order of 30% and will give rise to a noticeable shift for the strongly peaked forbidden transitions. This is opposed to the case of the allowed transition where the maximum is very broad and there is undoubtedly a shift, but it is small relative to the width of the maximum.

Experimentally, the ^{3}P–3s ^{5}S° cross section is obtained from a determination of the ratio of the intensities of the optical signals produced by the decay of the 3s ^{3}S° and 3s ^{5}S° states to the ground state. This signal is in turn multiplied by

Table 5. Positions and widths for O I resonances.

State	Quantity	Present	Theoretical	Experimental
$^4S^o(3s^2)^4S^o$	E (eV)	9·31	8·68[a], 8·73[b], 10·61[b]	8·80[f], 8·78[g]
	Γ (eV)	0·07		
$^4S^o(3s3p)\,^4P$	E (eV)	9·66	9·94[c]	
	Γ (eV)	0·27		
$^4S^o(3s3p)\,^2P$	E (eV)	9·86	9·50[d], 9·66[c]	9·50[e], 9·52[b]
	Γ (eV)	0·34	0·34[b]	

[a] Matese (1974)
[b] Rountree (1973)
[c] Rountree and Henry (1972)
[d] Matese et al (1973)
[e] Edwards and Cunningham (1973)
[f] Spence and Chupka (1974)
[g] Spence (1975)

a calibration factor which is dependent on the geometry of the field of view of the spectrometer and the lifetime of the 3s $^5S^o$ state. The large uncertainty in the lifetime of the 3s $^5S^o$ state and the normalisation of the 3s $^3S^o$ cross section are probably responsible for a large portion of the present discrepancies.

Within the three-state approximation of the present work three resonances are expected. The resonance positions were determined relative to the 3s ^3S state and the experimental ^3P–3s $^3S^o$ energy splitting was used to reference the positions relative to the ^3P ground state. The positions and widths are given in table 5 and compared with other recent works. Though the predicted energy of the $(3s^2)^4S^o$ state is still rather poor relative to the stabilisation calculations of Rountree (1973) and Matese (1974), it is nevertheless a considerable improvement over previous CC results (Rountree 1973).

4. Conclusion

As opposed to all previous CC calculations of excitation of atomic oxygen out of the ground-state configuration (Rountree and Henry 1972, Rountree 1973, Smith 1976) the target-state functions used here allow for an appreciable fraction of the core relaxation of the 2p. Though it is *a priori* evident that allowance for relaxation of the 2p is essential (Rountree 1973), a detailed study of the 3s $^3S^o$–^3P oscillator strength indicates that relaxation of the 2s is also very important. To some extent this is taken into account by the 2s → 3s virtual excitation (configurations 5 and 6, table 1), but it is incomplete and, singly, the most significant source of error in the target wavefunctions.

The excitation of the 3s $^3S^o$ is dominated by the direct process and the cross section is proportional to the square of the dipole moment. Thus, the dipole oscillator strength provides a convenient check on the target-state representations and indicates that the present results for excitation of the 3s $^3S^o$ are 20–25% high. The excitation of the 3s $^5S^o$ goes via electron exchange and error estimates are considerably more difficult. However, the discrepancy in the DW and CC predictions may be a good indication of the expected error.

The consistency of the theoretical results and the excellent agreement in the energy dependence of the CC and experimental predictions (Stone and Zipf 1974) suggest a need for a more careful experimental determination of the normalisation of the

triplet cross section. The lifetime of the 3s $^5S°$ is an essential part of the information that goes into the analysis of the experimental data in the determination of the ^3P–3s $^5S°$ cross section and a very reliable value for the lifetime would eliminate a serious source of uncertainty.

Acknowledgments

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