Effects of configuration mixing in $M1$
and $E2$ transitions between ground-state terms of sulfurlike ions

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Magnetic-dipole and electric-quadrupole transition rates for S-like ions between ground-state terms have been calculated using multiconfiguration Dirac-Fock wave functions. Sudden changes were found in these transition rates from one element to the next where there is a change of the dominant configuration. Also, ordering of the levels changes as the nuclear charge increases, but this is not necessarily reflected as a sudden change in transition rates. Our results demonstrate the necessity of using multiconfiguration calculations in the study of the systematics of transition rates along isoelectronic sequences.

I. INTRODUCTION

Information about the term values and transition probabilities of highly stripped ions is required in astrophysics and plasma diagnostics. In plasma research, transitions in such ions can be used to determine temperature and density distributions.[1] Forbidden transitions within the ground-state configuration are particularly useful since their relatively long wavelengths make them convenient for spectroscopic studies.

There have been several theoretical studies of transition energies and rates along isoelectronic sequences,[2-4] but those that used earlier versions of Desclaux's multiconfiguration Dirac-Fock (MCDF) code[5] included estimates of the Lamb shift only for the K- and L-shell orbitals. Recent comparisons with more precise spectroscopic experiments[6] now reveal that the Lamb-shift corrections for the M- and N-shell electrons are crucial to the prediction of reliable wavelengths. In this work we have used an advanced version of Desclaux's code, which includes estimates of the Lamb-shift corrections with screening for all bound electrons, to calculate transition energies and rates. In order to estimate the self-energy contributions to the Lamb shift for the ns and np electrons with $n > 2$, we extrapolated Mohr's values for the $2s$ and $2p$ electrons[7] by using n^{-3} scaling. Mohr's results are for an electron bound to a point nucleus without any screening by other bound electrons. We simulated the screening effect on the self-energy by reducing these hydrogenic values by the ratio of the Dirac-Fock-orbital charge density (calculated with an extended nucleus) to the relativistic hydrogenic charge density (calculated with a point nucleus), both densities integrated from the

origin to one Compton wavelength ($\approx 1/137$ bohr). The actual transition energies are insensitive to the choice of this cutoff distance for the charge density integration, as long as the distance is not far from the origin. The self-energy of the $3d$ and $4f$ electrons were scaled from the hydrogen ($Z=1$) results[8] by using $Z^4\alpha^5$ scaling ($\alpha \approx 1/137$) and by applying the screening correction described earlier. The vacuum polarization correction for all electrons was calculated by using the Uehling potential[9] with the Dirac-Fock orbitals. Although these corrections for the screening effect are incomplete and contain an arbitrary cutoff constant for the charge density integration, they provide more realistic estimates of the Lamb shift than using unscreened results or totally ignoring the Lamb shift for the M- and N-shell electrons. The wave functions themselves are not modified because these corrections are calculated as perturbations to the energy levels. Consequently, the transition matrix elements are hardly affected, i.e., the energy dependence of the transition matrix elements is rather weak, although the transition rates are changed because certain powers of the altered transition energies are multiplied by these matrix elements to obtain the rates.

Magnetic-dipole ($M1$) and electric-quadrupole ($E2$) transition energies and f values for transitions between levels of the ground-state configuration of sulfurlike ions were calculated using MCDF wave functions. The configurations used in the calculation outside of the closed K and L shells were all the relativistic combinations of the nonrelativistic configurations $3s^23p^4$, $3p^6$, $3s^23p^23d^2$, and $3s3p^43d$. There are many more relativistic configurations than corresponding nonrelativistic configurations. See Table I for examples of relativistic configurations. We limited the number of configurations

TABLE I. Relationship between oscillator strength and the dominant configuration. For each level considered we indicate the dominant configuration resulting from the MCDF calculation for all values of atomic number Z. Bracketed configurations are approximately equal in weight for the indicated atomic numbers. Shorthand relativistic notation (s for $s_{1/2}$, p,p^* for $p_{3/2}, p_{1/2}$, and d,d^* for $d_{5/2}, d_{3/2}$) is used to describe the configurations. Included is a description of the changes, as a function of atomic number, in the $M1$ and $E2$ oscillator strengths of transitions from the $^3P_2$ level to the specified level. Refer to Figs. 2–7 for more detail.

| Level	Dominant configuration		$M1$ and $E2$ oscillator strengths
$^3P_2$	$3s^23p^{*2}3p^2$	all Z	
$^3P_1$	$3s^23p^*3p^3$	$Z \leq 89$	Steady increase up to $Z=89$
			Sudden sharp drop at $Z=90$
	$3s^23p^{*2}3d^*3d$	$Z \geq 90$	Begins to rise for $Z > 90$
$^3P_0$	$3s^23p^4$	$Z=16,17$	$M1$ not allowed
	$\begin{cases} 3s^23p^4 \\ 3s^23p^{*2}3p^2 \end{cases}$	$18 \leq Z \leq 26$	$E2$ is a smooth curve for all Z
	$3s^23p^{*2}3p^2$	$Z \geq 27$	
$^1D_2$			Steady increase up to $Z=80$
	$3s^23p^*3p^3$	$Z \leq 80$	Steep drop over $81 \leq Z \leq 83$ for $M1$
			Steep drop over $81 \leq Z \leq 82$ for $E2$
	$3s^23p^{*2}3d^{*2}$	$Z \geq 81$	Increase for $Z > 83$ for $M1$
			Small rise for $E2$ followed by gradual fall off $Z > 82$
$^1S_0$	$3s^23p^{*2}3p^2$	$Z=16,17$	$M1$ not allowed
	$\begin{cases} 3s^23p^{*2}3p^2 \\ 3s^23p^4 \end{cases}$	$18 \leq Z \leq 26$	$E2$ is smooth curve for $Z \leq 68$
	$3s^23p^4$	$27 \leq Z \leq 68$	Sudden sharp rise at $Z=69$
	$3s^23p^{*2}3d^{*2}$	$Z \geq 69$	Smooth fall off for $Z > 69$
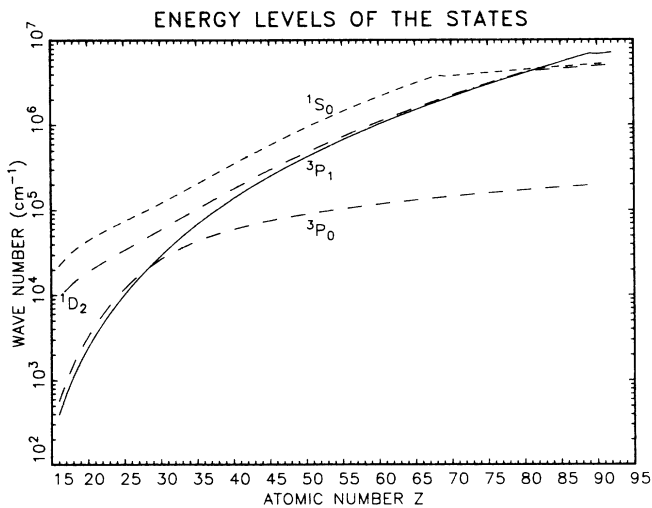
FIG. 1. Level values of the indicated states of the ground-state configuration of S-like ions. Referenced values (Refs. 10–14) are used for ions with atomic number ≤ 42. The rest are the results of the MCDF calculation.
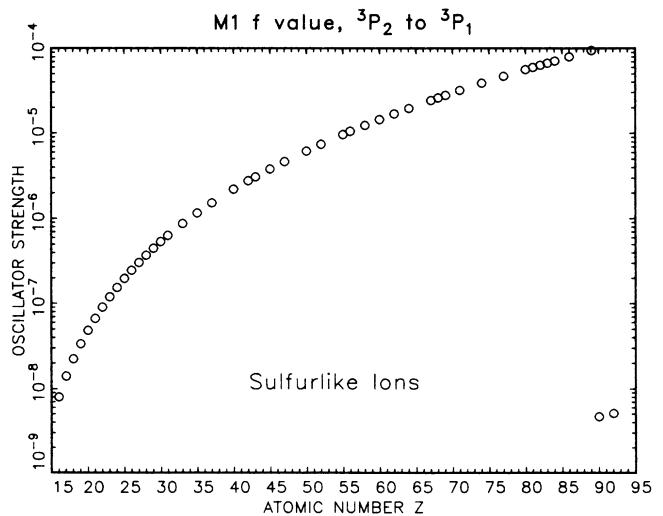
FIG. 2. Calculated $M1$ oscillator strengths for the transition $^3P_2$ to $^3P_1$ for S-like ions. Results have been obtained using referenced level values for ions with atomic number ≤ 42.
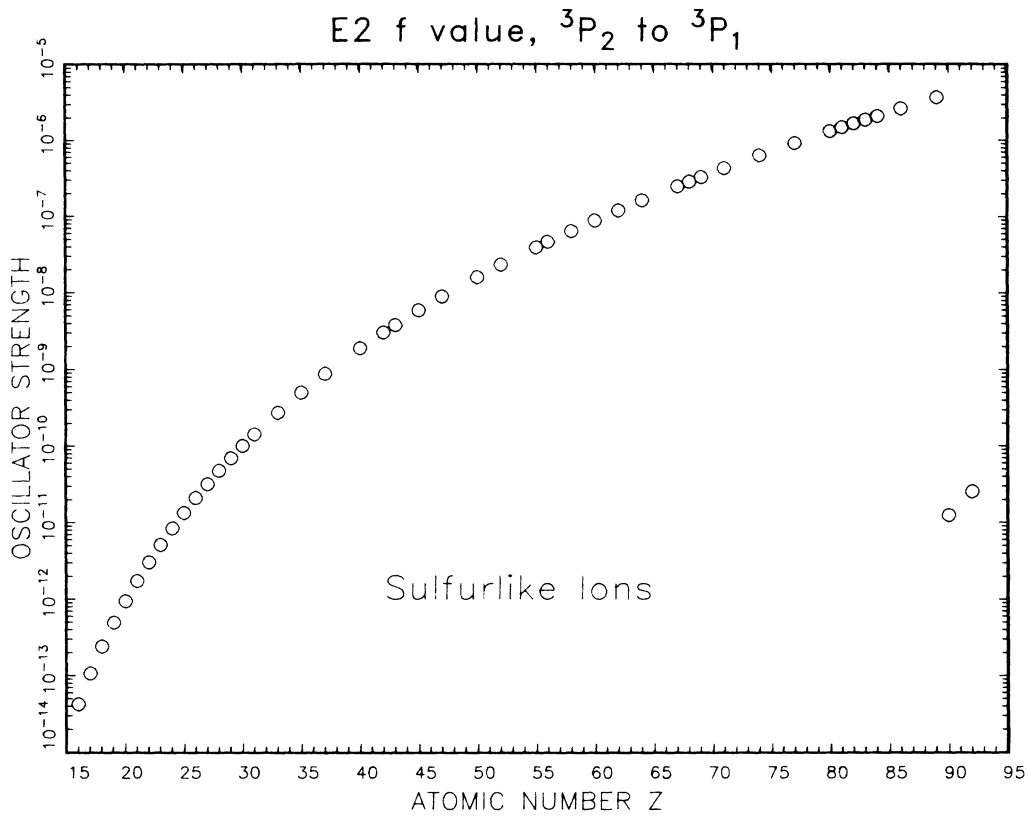
FIG. 3. Calculated $E2$ oscillator strengths for the transition $^3P_2$ to $^3P_1$ for S-like ions. Results have been obtained using referenced level values for ions with atomic number ≤ 42.
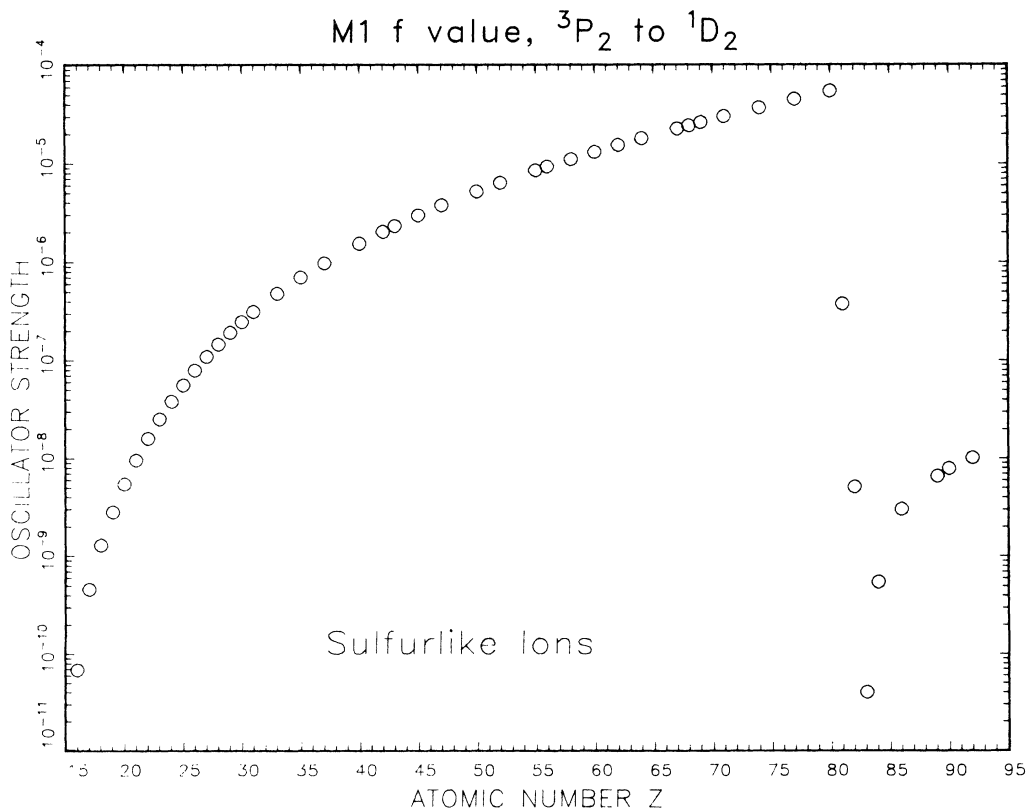

FIG. 4. Calculated $M1$ oscillator strengths for the transition $^3P_2$ to $^1D_2$ for S-like ions. Results have been obtained using referenced level values for ions with atomic number ≤ 42.

to keep the size of the calculation manageable. For instance, the above choices lead to 47 relativistic configurations for the $J=2$ levels. In order to check on the adequacy of our results, we recalculated several selected cases with the relativistic combinations of $3s^2 3p^3 4f$ included in the calculation.

II. EXISTING DATA

Reliable energy-level values for the ions of the sulfur isoelectronic sequence up to Mo $(Z=42)$ are available. We used the work of Kaufman[10] for S, Radziemski and Kaufman[11] for Cl, Kaufman and Sugar[12] for Ar, Sugar and Corliss[13] for the ions from K to Ni, and the semi-empirical calculation of Sugar and Kaufman[14] for the ions from Cu to Mo. Mendoza and Zeippen[15] have calculated the $M1$ and $E2$ transition probabilities for this sequence up to $Z=28$. They used nonrelativistic calculations with relativistic corrections treated as perturbations. Semiempirical term energy corrections were also used. Biémont and Hansen[16] have carried out semiempirical calculations similar to Ref. 11 of these transition probabilities up to $Z=42$.

The relationships between f values, transition proba-

bilities A, and line strength S are defined by[17]

$$g'A = (6.6702 \times 10^{15}) gf/\lambda^2 , \tag{1}$$

$$gf = (167.9/\lambda^3) S_{E2} , \tag{2}$$

$$= (4.044 \times 10^{-3}/\lambda) S_{M1} , \tag{3}$$

where λ is the transition wavelength in Å, g', and g are the degeneracies of the upper and lower levels, respectively, A is the transition probability in sec^{-1}, S_{E2} (in atomic units) and S_{M1} (in Bohr-magneton units) are the electric-quadrupole and magnetic-dipole line strengths, respectively.

III. RESULTS

The level values of $^3P_1$, $^3P_0$, $^1D_2$, and $^1S_0$ with respect to the $^3P_2$ ground state are shown in Fig. 1. The relative positions of these levels as a function of Z are quite different from that expected for a p^4 configuration shifting from LS to JJ coupling.[18] Figures 2–7 present the results of our calculation of the $M1$ and $E2$ oscillator strengths for transitions to these states from the $^3P_2$ ground state. Values from Refs. 10–14 for the term ener-
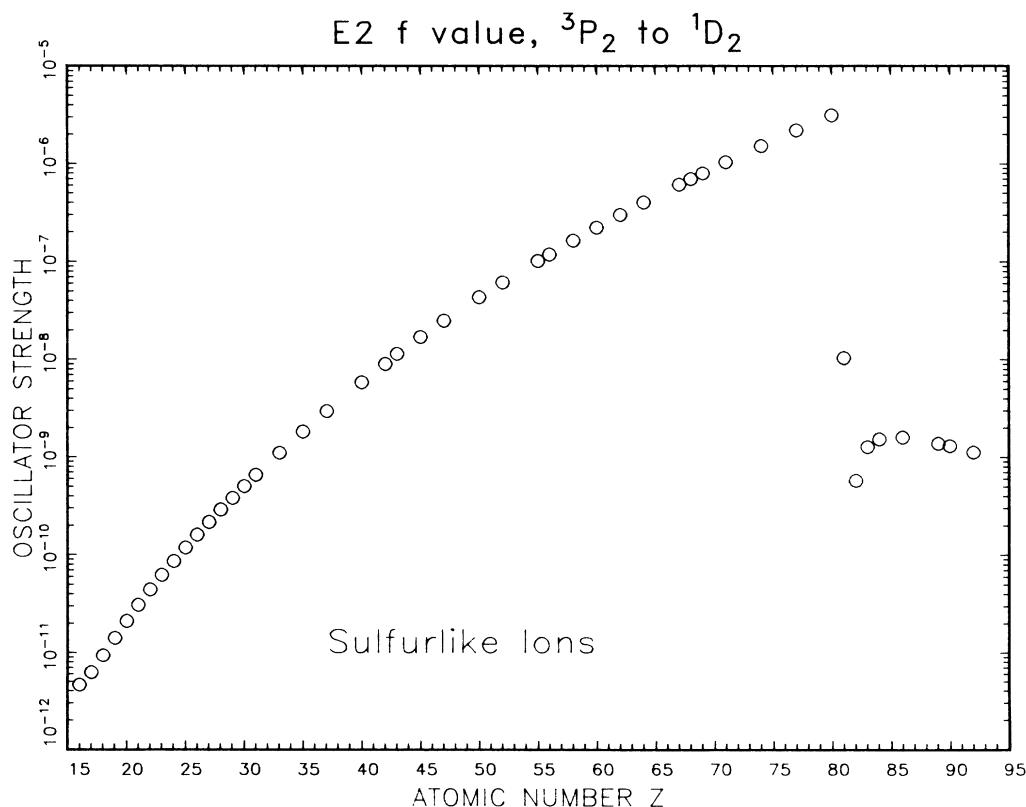

FIG. 5. Calculated $E2$ oscillator strengths for the transition $^3P_2$ to $^1D_2$ for S-like ions. Results have been obtained using referenced level values for ions with atomic number ≤ 42.
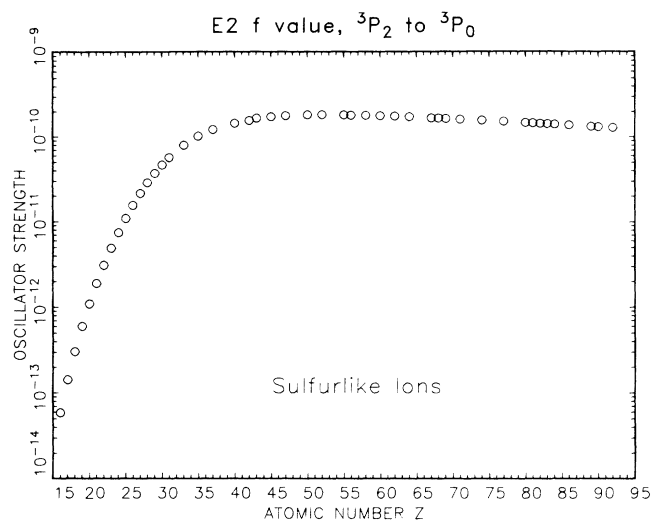
FIG. 6. Calculated $E2$ oscillator strengths for the transition $^3P_2$ to $^3P_0$ for S-like ions. Results have been obtained using referenced level values for ions with atomic number ≤ 42.

FIG. 7. Calculated $E2$ oscillator strengths for the transition $^3P_2$ to $^1S_0$ for S-like ions. Results have been obtained using referenced level values for ions with atomic number ≤ 42.

gies were used to calculate the f values for $Z \leq 42$. We chose to use the term values from these references because they were critically assessed experimental or semiempirical values and hence are more reliable than our theoretical values for $Z \leq 42$. Positive powers of the transition energy ΔE ($\approx 1/\lambda$) are multiplied to the line strength to obtain f values [see Eqs. (1)–(3)], and hence it is important to use reliable ΔE to maintain accuracy in the transition rates, particularly for low-Z ions, although the line strengths themselves are insensitive to the choice of ΔE.

As the atomic number increases, the transitions to $^1S_0$, $^1D_2$, and $^3P_1$ show sudden changes in oscillator strengths from one Z value to the next at certain values of Z. These changes occur at the Z values where there is a change of the dominant relativistic configuration. Table I summarizes the relationship between the oscillator strengths and the dominant configuration as determined by our calculation. Note that the sudden changes in the dominant configuration do not usually correspond to Z values at which the ordering of the levels of the ground-state configuration changes.

In order to check on the sufficiency of the number of configurations used in this calculation, a few selected ions were recalculated with $4f$ orbitals included. The change in f value obtained was generally less than 5% except for the lower-Z members of the sequence (9% increase in the $M1$ f value for $^3P_2$-$^1D_2$ at $Z=20$) and near Z values where the dominant configuration changes (for $^3P_2$-$^1D_2$ $M1$ f values the change is still less than 15% except at $Z=83$ at the bottom of the dip where a 62% decrease occurs). This indicates that our calculations were reliable except for $Z=83$, where the calculation is too sensitive to the choice of configurations included.
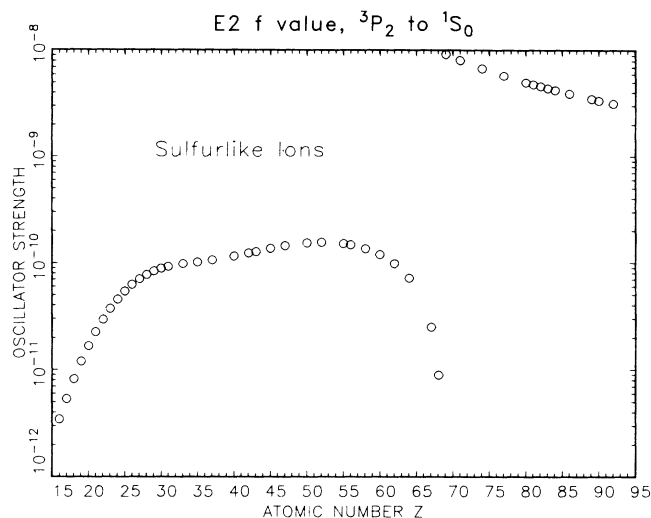
IV. COMPARISONS

The term values of Refs. 10–14 are compared to our calculated results in Fig. 8. For the first few members of the sequence there are rather large discrepancies, indicating many more configurations must be used to accurately calculate the results for these ions. However, except for the $^1D_2$ state, by $Z=20$ the referenced and calculated values are quite close. Even the values of the $^1D_2$ state
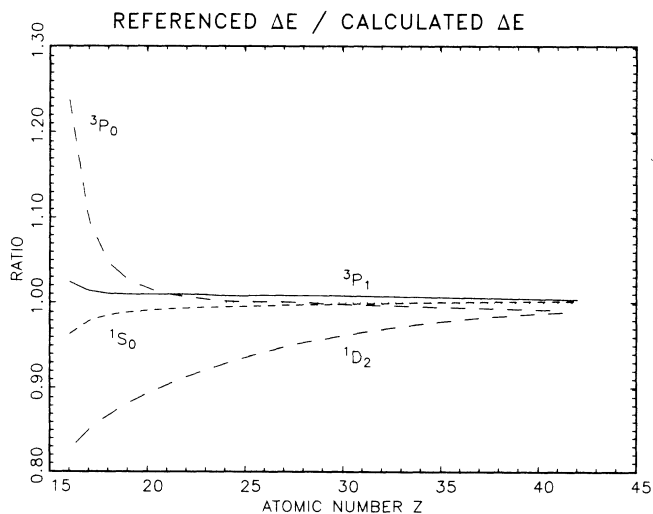

FIG. 8. Ratio of referenced term values ΔE to those obtained by the MCDF calculation for the indicated states of the ground state configuration of S-like ions. Results for all levels approach unity by atomic number 42.

TABLE II. Comparison of our results for the $M1$ and $E2$ oscillator strengths with those reported by Mendoza and Zeippen (Ref. 15) and Biémont and Hansen (Ref. 16).

Transition from $^3P_2$ to	Multipole	Comparison to Refs. 15 and 16
$^3P_1$	$M1$	Complete agreement with our results $16 \leq Z \leq 33$, our results are 6% lower at $Z=42$
$^1D_2$	$M1$	Our results are 34% lower at $Z=20$ to 15% lower at $Z=42$
$^3P_1$	$E2$	Our results are about 7% higher than Ref. 15 for $19 \leq Z \leq 28$ and are within 6% of Ref. 16 for $19 \leq Z \leq 42$
$^1D_2$	$E2$	Our results are 3–4% higher than Ref. 15 for $19 \leq Z \leq 28$ and 0–10% lower than Ref. 16 for $16 \leq Z \leq 42$ with complete agreement for $26 \leq Z \leq 39$
$^3P_0$	$E2$	Our results are 3% higher at $Z=17$ to 8% higher at $Z=28$ than Ref. 15 and 0–4% higher than Ref. 16 for $21 \leq Z \leq 42$
$^1S_0$	$E2$	Our results are 30% lower at $Z=16$ to 20% lower at $Z=28$ than Ref. 15 and 14% lower at $Z=18$ to agreement at $Z=35$ and 46% higher at $Z=42$ than Ref. 16

are within 1% of each other by $Z=42$. Thus we expect that the use of our calculated results above $Z=42$ will lead to reliable f values. We determined the effect of adding $4f$ orbitals on the term energies for a few selected atomic numbers for the $^1D_2$ state. At lower Z this eliminated about half the discrepancy between the calculated and referenced values. Near $Z=83$, the addition of $4f$ orbitals produced only a 0.03% change in the calculated level energy. As we mentioned earlier, the use of our theoretical transition energies ΔE (instead of the experimental ones we used) for f values of low Z ions would have led to substantial errors because powers of ΔE are involved. Had we used the theoretical ΔE involving the $^1D_2$ level, then the $M1$ f value for Ca^{4+} in Fig. 4 would have been increased by $\sim 12\%$ while the $E2$ f value for the same ion in Fig. 5 would have been increased by $\sim 40\%$, resulting in a slower drop of the f values toward low Z.

Table II summarizes the comparison of our results with those of Mendoza and Zeippen[15] ($M1$ and $E2$ transitions up to $Z=28$) and Biémont and Hansen[16] ($M1$ and $E2$ transitions up to $Z=42$). Agreement is reasonable considering the limitations of our calculation for the

lowest atomic numbers and the approximations used in Refs. 15 and 16.

V. CONCLUSIONS

Our results appear to provide reliable theoretical data, both energies and $M1$ and $E2$ transition rates, for sulfur-like ions. They demonstrate that it is absolutely necessary to use multiconfiguration calculations in studying the systematics of transition rates along isoelectronic sequences. It is difficult to predict the effects of configuration mixing without actually performing the multiconfiguration calculations. However, it would be very useful to obtain experimental verification of our results. The tabulated results of our calculations will be published elsewhere.

ACKNOWLEDGMENTS

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[18]See, for example, R. D. Cowan, Ref. 17, p. 345.