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OSCILLATOR STRENGTHS AND GROUND-STATE PHOTOIONIZATION CROSS-SECTIONS FOR Mg^+ AND Ca^+

JOHN H. BLACK, JON C. WEISHEIT,* AND ELLEN LAVIANA
Harvard College Observatory, Cambridge, Massachusetts 02138
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ABSTRACT

Oscillator strengths and ground-state photoionization cross-sections have been computed for Mg^+ and Ca^+. The polarization interaction between the valence electron and the core has been included in the calculations in a consistent manner. In some cases this interaction significantly changes the computed results. For many of the transitions considered, there exist no other published oscillator strengths.

I. INTRODUCTION

To a good approximation an alkali-like atom or ion can be treated as a one-electron system consisting of a single valence electron outside a spherically symmetric core. By including the polarization interaction between the valence electron and the core in a model potential, accurate orbitals for both bound and continuum valence-electron states can be obtained (Bottcher 1971). A consistent treatment of the polarization interaction results in a modification of the one-electron transition matrix element (Bersuker 1957; Hameed, Herzenberg, and James 1968). This modification has recently been included in the calculation of oscillator strengths and photoionization cross-sections of the neutral alkali-metal atoms lithium (Caves and Dalgarno 1972), sodium, potassium, rubidium, and cesium (Weisheit and Dalgarno 1971*a*, *b*; Weisheit 1972). We report here the results of similar calculations for the ionic systems Mg^+ and Ca^+.

II. THEORY

The theory is developed in the references cited above, so we present here only a brief outline. Atomic units are used throughout.

It is assumed that the core electrons respond instantaneously to the motion of the valence electron and that exchange between the valence electron and the core can be neglected. Then the wavefunction of the complete system (i.e., atom or ion) can be written as the product of a core wave function χ_0 and a valence electron orbital ψ_{nl}, viz.,

$$\Psi_{nl}(\boldsymbol{r}_i, \boldsymbol{r}) = \chi_0(\boldsymbol{r}_i|\boldsymbol{r})\psi_{nl}(\boldsymbol{r}), \qquad (1)$$

for the core electrons at positions $\boldsymbol{r}_i$ and the valence electron at $\boldsymbol{r}$. The parametric dependence of χ_0 on $\boldsymbol{r}$ is analogous to the parametric dependence of the electronic eigenfunction of a diatomic molecule on the internuclear separation (Born-Oppenheimer approximation). It follows that ψ_{nl} is a solution of the equation

$$[-\tfrac{1}{2}\nabla_r^2 + V(r) - \epsilon_{nl}]\psi_{nl}(\boldsymbol{r}) = 0\,, \qquad (2)$$

where ϵ_{nl} is the valence electron eigenvalue and where V is the effective potential due

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* Present address: Lawrence Radiation Laboratory, University of California, Livermore.

to the core. A model potential V_m of the form described by Bottcher (1971) is adopted for the calculations:

$$V(r) \to V_m(r) = V_{\mathrm{CF}}(r) - \frac{\alpha_d}{2r^4}[1 - \exp - (r/r_1)^6] + \frac{\lambda}{r^6}[1 - \exp - (r/r_1)^8] + (c_1 + c_2 r + c_3 r^2) \exp(-r/r_0) , \tag{3}$$

where V_{CF} is the central-field potential of the ionic core, α_d is the static dipole core polarizability, and the parameters r_0 and r_1 are chosen ab initio. The spin-orbit interaction is not included in any of the calculations, so the parameters λ, c_1, c_2, and c_3 are adjusted to yield eigenvalues ϵ_{nl} near measured term centers-of-gravity.

The electric 2^L-pole moment for the valence electron transition $\alpha \to \beta$ is defined as

$$M_{\beta\alpha}{}^L = \langle \Psi_\beta(r_i, r)|(r^L + \sum_i r_i{}^L)|\Psi_\alpha(r_i, r)\rangle . \tag{4}$$

By treating the polarization interaction between the valence electron and the core as a perturbation of the core state χ_0, it can be shown that, at large r, M reduces to the simple expression

$$M_{\beta\alpha}{}^L = \langle \psi_\beta(r)|Q^L|\psi_\alpha(r)\rangle , \tag{5}$$

with the effective multipole operator

$$Q^L = r^L\left(1 - \frac{\alpha_{2^L}}{r^{2L+1}}\right) , \tag{6}$$

and where α_{2^L} is the 2^L-pole static polarizability of the core. If the polarization of the core is neglected, Q^L becomes just r^L. This core-polarization correction to the electric multipole operator is important either if the core polarizability is large or if there is severe cancellation in the matrix element $\langle \psi_\beta|r^L|\psi_\alpha\rangle$.

Equation (6) is incorrect at small r-values. For the calculations we have used the modified expression

$$Q^L = r^L\left[1 - \frac{\alpha_{2^L}}{r^{2L+1}}(1 - \exp - (r/r_c)^{2L+1})\right] , \tag{7}$$

where r_c is a semiempirical effective core radius. This form of Q^L has the correct behavior near the origin. The oscillator strengths and photoionization cross-sections described in the next section were computed using the modified expression (7) in the one-electron transition matrix elements $\langle \psi_\beta|Q^L|\psi_\alpha\rangle$.

TABLE 1

MODEL POTENTIAL PARAMETERS*

Parameter	Mg^+	Ca^+
α_d	0.48†	3.31‡
λ	0.299525	2.961356
c_1	−2.403273	−3.734409
c_2	0.864319	1.654661
c_3	0.0	−0.230330
r_0	0.80	1.00
r_1	1.00	1.00
r_c	1.80	3.33

* All values are in atomic units.

† A mean of determinations by Bockasten (1956), Cohen (1966), Öpik (1967), and Lahiri and Mukherji (1967).

‡ Edlèn and Risberg (1956).

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III. THE RESULTS

The model potentials were determined by an iterative procedure which provided the best agreement between the energies of each of the two lowest-lying *S*, *P*, and *D* terms and the empirical term-values for Mg^+ (P. Risberg 1955; G. Risberg 1965) and for Ca^+ (Edlèn and Risberg 1956; G. Risberg 1968). In table 1 are given the parameters which define the model potentials (eq. [3]) and the effective core radius (eq. [7]). The values of the core radii r_c are uncertain insofar as there are no satisfactory experimental determinations. Thus r_c must be determined indirectly. The effective core radius should be comparable in magnitude to $\langle r\rangle_{n_0p}$, the expectation value of r for the outermost core orbital (n_0p), which in turn is related to the ionization potential of the core, $\langle r\rangle_{n_0p} \propto I(X^{++})^{-1/2}$. The values of r_c for the Na^+ and K^+ cores have been determined by comparison with experiment (Weisheit 1972), so that the core radius for the Mg^{++} core is taken to be

$$r_c(\mathrm{Mg}^{++}) = r_c(\mathrm{Na}^+)\left[\frac{I(\mathrm{Na}^+)}{I(\mathrm{Mg}^{++})}\right]^{1/2}, \tag{8}$$

with a similar equation relating $r_c(\mathrm{Ca}^{++})$ and $r_c(\mathrm{K}^+)$.

The model potentials were used to generate a number of term values which were compared with the empirical data referred to above, thus providing a check on the accuracy of the potentials. The relative errors in these calculated term values were all less than 0.008 and 0.004 for Mg^+ and Ca^+, respectively.

Listed in tables 2 and 3 are the term absorption oscillator strengths, $f_{n'l',nl}$, for electric dipole transitions $n'l' \rightarrow nl$ in Mg^+ and Ca^+ together with the transition wavelengths

TABLE 2

Mg^+ OSCILLATOR STRENGTHS

Transition ($n'l'$–nl)	Wavelength (Å)	$f_{n'l',nl}$	$A_{nl,n'l'}$ (s^{-1})
3s–*3p*	2797.9	8.97(−1)	2.55(8)
3s–*4p*	1240.1	1.46(−3)	2.10(6)
3s–*5p*	1026.0	2.22(−3)	4.69(6)
3p–*3d*	2795.5	9.15(−1)	4.69(8)
3p–*4d*	1735.0	3.26(−2)	4.29(7)
3p–*5d*	1476.0	4.82(−3)	8.79(6)
3p–*4s*	2933.8	1.43(−1)	3.35(8)
3p–*5s*	1753.0	1.81(−2)	1.18(8)
3p–*6s*	1481.0	6.31(−3)	5.75(7)
3d–*4p*	10926.	1.71(−1)	1.52(7)
3d–*5p*	3849.1	4.01(−3)	2.98(6)
3d–*4f*	4481.2	9.32(−1)	2.23(8)
3d–*5f*	3104.8	1.64(−1)	8.11(7)
4s–*4p*	9226.0	1.36(0)	3.33(7)
4s–*5p*	3614.4	1.57(−4)	2.62(4)
4p–*4d*	7889.9	1.23(0)	7.86(7)
4p–*5d*	4388.6	7.34(−2)	1.53(7)
4p–*7d*	3167.	6.20(−3)	2.49(6)
4p–*5s*	8231.6	2.60(−1)	7.95(7)
4p–*6s*	4432.0	3.07(−2)	3.18(7)
4d–*4f*	204625.	1.03(−1)	3.58(4)
4d–*5f*	9632.2	7.24(−1)	3.93(7)
4d–*5p*	24100.	3.52(−1)	7.16(6)
4f–*5d*	10395.	1.99(−2)	1.62(6)
4f–*7d*	5436.	1.24(−3)	3.82(5)

NOTE.—numbers in parentheses indicate the power of 10 by which the preceding number is to be multiplied.

TABLE 3

Ca$^+$ OSCILLATOR STRENGTHS

Transition ($n'l'$–nl)	Wavelength (Å)	$f_{n'l',nl}$	$A_{nl,n'l'}$ (s^{-1})
4*s*–4*p*	3945.2	1.03(0)	1.46(8)
4*s*–5*p*	1650.6	3.87(−4)	3.17(5)
4*s*–6*p*	1342.1	1.25(−3)	1.54(6)
4*s*–7*p*	1226.8	9.23(−4)	1.36(6)
5*s*–5*p*	11873.	1.51(0)	2.44(7)
5*s*–6*p*	4475.7	1.53(−3)	1.72(5)
5*s*–7*p*	3407.8	6.87(−5)	1.32(4)
6*s*–6*p*	26094.5	1.93(0)	6.37(6)
6*s*–7*p*	9230.6	5.51(−3)	1.44(5)
7*s*–7*p*	48475.	2.35(0)	2.24(6)
4*p*–5*s*	3726.5	1.80(−1)	2.60(8)
4*p*–6*s*	2205.0	2.27(−2)	9.35(7)
4*p*–7*s*	1848.1	7.92(−3)	4.65(7)
4*p*–4*d*	3172.6	8.99(−1)	3.58(8)
4*p*–5*d*	2109.6	1.09(−1)	9.82(7)
4*p*–6*d*	1812.1	3.46(−2)	4.23(7)
5*p*–6*s*	9907.1	2.98(−1)	6.02(7)
5*p*–7*s*	5299.9	3.54(−2)	2.51(7)
5*p*–5*d*	8235.0	1.04(0)	6.17(7)
5*p*–6*d*	5013.9	1.53(−1)	2.43(7)
6*p*–7*s*	20249.	4.14(−1)	2.00(7)
6*p*–6*d*	16627.	1.17(0)	1.70(7)
3*d*–4*p*	8579.1	7.14(−2)	1.07(7)
3*d*–5*p*	2131.5	3.78(−4)	9.27(5)
3*d*–6*p*	1644.1	1.47(−4)	6.05(5)
3*d*–7*p*	1474.4	7.70(−5)	3.94(5)
4*d*–5*p*	26778.	1.92(−1)	3.08(6)
4*d*–6*p*	5662.8	2.41(−5)	8.40(3)
4*d*–7*p*	4055.1	1.46(−5)	9.88(3)
5*d*–6*p*	56104.	3.09(−1)	1.06(6)
5*d*–7*p*	11385.	9.26(−5)	7.85(3)
6*d*–7*p*	101324.	4.25(−1)	4.44(5)

TABLE 4

PHOTOIONIZATION CROSS-SECTIONS a_λ

ELECTRON MOMENTUM k (au)	Mg$^+$		Ca$^+$	
	λ (Å)	a_λ(10^{-19} cm^2)	λ (Å)	α_λ(10^{-19} cm^2)
0.01	824	2.766	1045	2.094
0.10	817	2.793	1033	2.119
0.20	796	2.861	999	2.179
0.30	762	2.952	947	2.252
0.40	720	3.035	883	2.299
0.50	672	3.090	812	2.295
0.60	622	3.077	740	2.224
0.70	571	3.009	669	2.106
0.80	522	2.896	603	1.944
0.90	476	2.741	542	1.753
1.00	...	...	487	1.554

and the spontaneous transition probabilities $A_{nl,n'l'}$. For many of the transitions listed in tables 2 and 3, there exist no other published f-values. The Mg^+ and Ca^+ ground-state photoionization cross-sections are given in table 4. Both the incident photon wavelength and the momentum of the photoejected electron are tabulated with the cross-section.

Transition probabilities for several electric quadrupole transitions have been calculated also. The quadrupole polarizabilities used are $\alpha_4(Mg^{++}) = 0.518$ au and $\alpha_4(Ca^{++}) = 0.745$ au (Dalgarno 1962). The results for the transitions of astrophysical interest are $A_{3d-3s} = 4987\ s^{-1}$ and $A_{3d-4s} = 1.011\ s^{-1}$ for the Mg^+ 1398.8 Å and Ca^+ 7306.4 Å quadrupole transitions, respectively.

IV. DISCUSSION

It is difficult to assess the accuracy of these oscillator-strength calculations, but they should generally be more accurate than earlier results which did not take into account the effects of core polarization. On the whole, the present calculations show substantial agreement with previous work (Smith and Wiese 1971 and references contained therein). In some cases there is serious disagreement with earlier results. These tend to be the same cases in which there is the greatest cancellation in the matrix element $\langle\psi_\beta|r^L|\psi_\alpha\rangle$, as evidenced by the differences between the calculations done with and without the inclusion of the core polarization correction. In table 5 are given all the corrected oscillator strengths which differ by more than about 25 percent from previous calculations or from the uncorrected f-values. The oscillator strength for Mg^+ 3s–$4p$ is of particular interest since it disagrees by such a large factor with previous determinations.

Lifetimes of excited states can be determined from the calculated transition probabilities and can then be compared with experimental results. In cases where there is no ambiguity about branching, the agreement between the calculated and measured lifetimes of excited states of Mg^+ and Ca^+ is relatively good. For example, the mean of four experimental values of the Mg^+ $3p$ lifetime is 3.97×10^{-9} s (Andersen *et al.* 1970; Berry, Bromander, and Buchta 1970; Smith and Gallagher 1966; Smith 1970) while the lifetime implied by the $3p$–$3s$ transition probability is 3.916×10^{-9} s.

The present quadrupole transition probabilities can be compared with earlier calculations of Osterbrock (1951), Warner (1968), and Tull *et al.* (1972). The result for Ca^+ $3d$–$4s$, $A = 1.01\ s^{-1}$, is in agreement with the calculations of both Warner and Osterbrock who found values of $A_{3d-4s} = 1.27$ and $1.30\ s^{-1}$, respectively. The present

TABLE 5

CORRECTED OSCILLATOR STRENGTHS WHICH DISAGREE WITH PREVIOUS CALCULATIONS OR WITH UNCORRECTED CALCULATIONS

Transition	Previous Calculation* of $f_{n'l',nl}$	Uncorrected $f_{n'l',nl}$	Corrected $f_{n'l',nl}$
Mg^+:			
$3s$–$4p$	0.00023	0.000805	0.001458
$3s$–$5p$	0.0010	0.001667	0.002224
$3p$–$5d$	0.00709	0.005469	0.004819
$4s$–$5p$	0.0010	0.000224	0.000157
$4d$–$4f$	0.0379	0.10325	0.10323
Ca^+:			
$3d$–$5p$	0.00081	0.0007353	0.0003780
$3d$–$6p$	0.00033	0.0002954	0.0001469

* Smith and Wiese (1971) and references cited therein.

results for quadrupole transitions in Mg^+ disagree with those of Warner, but are in good agreement with the work of Tull *et al.*

For comparison with our photoionization cross-sections there are the calculations of Bates and Massey (1941) and Green (1949) for Ca^+ ($4s$–ϵp) and of Biermann and Lübeck (1949) for Mg^+ ($3s$–ϵp). In both instances there is reasonable agreement at threshold, although at higher photon energies the older results for Mg^+ indicate a much steeper decrease in the cross-sections. The revised general formula of Peach (1967), based on the quantum-defect method, gives cross-sections that are factors of almost 2 and 6 smaller than the present results at threshold for Mg^+ and Ca^+, respectively. This is not unreasonable since, for these particular systems, the quantum-defect results are quite sensitive to small changes in the valence-electron orbitals (Burgess and Seaton 1960).

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