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Dynamic polarizabilities and Rydberg states of the argon isoelectronic sequence

T. K. Ghosh and A. K. Das
Department of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India

Marcos Castro, Sylvio Canuto, and P. K. Mukherjee*
Departamento de Fisica, Universidade Federal de Pernambuco, 50.739 Recife, Pernambuco, Brazil

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Dynamic dipole polarizabilities $\alpha_d(\omega)$ have been calculated within and beyond the normal-dispersion region for the isoelectronic members of argon up to Mn^{7+} using time-dependent coupled Hartree-Fock theory. Excitation energies, oscillator strengths, and quantum-defect values have been estimated for the dipole-allowed transitions $3p^6\,{}^1S^e \rightarrow 3p^5({}^2P)ns\,{}^1P^o$ $(n=4,\ldots,7)$ and $3p^6\,{}^1S^e \rightarrow 3p^5({}^2P)nd\,{}^1P^o$ $(n=3,\ldots,7)$. Analytic representations of the singly excited Rydberg orbitals have been obtained. The results compare favorably with the existing theoretical and experimental data. The oscillator strengths show an interesting trend of variation along the isoelectronic sequence.

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I. INTRODUCTION

Spectral lines arising out of argon and its isoelectronic members are quite dominant in the spectra of the solar photosphere and corona [1–7]. Experiments on interstellar matter using International Ultraviolet Explorer (IUE) satellites [8] show the existence of such ions. The observations are important for finding the relative abundance of such ions in interstellar matter. In recent years a great deal of experimental work [9–16] was performed for estimating the transition probabilities of noble gases in the visible and ultraviolet regions. Argon is of special interest because of the high content of it in a mixture of gases used in rare-gas halogen excimer lasers [11]. The estimation of excitation cross sections for Ar by electron impact is very important in analyzing quantitatively the energy convertibility of the lasers. Also it is used for laser interferometric diagnostic study for the direct determination of electron density in a plasma [17]. Titanium is very important in plasma research where it is used for the component of a coating material TiC on the first wall of tokamak machines and also as a getter material for the light impurity ions such as C, N, and O [Ref. 18].

Most of the theoretical calculations are confined to oscillator strengths and lifetime determination for argon. Methods used are Hartree-Fock (HF) [19], multiconfiguration Hartree-Fock (MCHF) [20], and quantum-defect theory [21,22]. For Ca^{2+}, a semiempirical calculation using an intermediate-coupling scheme was performed by Loginov and Gruzdev [23]. Baluja [24] performed a detailed configuration-interaction (CI) calculation for Ca^{2+}. Limited results available for K^+ and Ti^{4+} are due to Loginov and Gruzdev [25] and Mori *et al.* [18], respectively. A number of calculations using different theoretical and experimental methods are available for the static polarizability of Ar [26–36]. But for the isoelectronic members only a few data are available [26,37–40]. Experiments have been performed for the accurate estimation of the frequency-dependent polarizability of Ar over a selected frequency range [41–43]. The time-dependent MCHF approach of Rahman, Rizzo, and Yeager [44] seems to be the only theoretical calculation in such a line.

In view of the importance of Ar and its isoelectronic members and rather scanty data available in the literature we performed a detailed and systematic study of the frequency-dependent polarizability $\alpha_d(\omega)$ within and beyond the normal dispersion region in conjunction with the excitation properties, such as the transition energies and the oscillator strengths for the dipole-allowed transitions. We used a linearized version of the time-dependent coupled Hartree-Fock (TDCHF) theory which was successfully applied in the past for calculating the frequency-dependent response properties of atomic systems connected with single excitations [45–48]. We calculated quantum-defect values and obtained analytic representations of the excited Rydberg orbitals of *s* and *d* symmetries up to principal quantum number $n=7$. The success of the theory was mainly due to the inclusion of hole-particle correlations up to infinite order and was well reviewed [49–51]. Since TDCHF theory was discussed in detail earlier [45] we give only a brief review of it in Sec. II, followed by a discussion of the theoretical results in Sec. III.

II. THEORY

The frequency-dependent response properties of the systems are analyzed by considering a time-averaged functional (a.u. are used)

$$J=\frac{1}{T}\int_0^T dt\left\langle \Phi(\mathbf{r},t)\left| H(\mathbf{r},t)-i\frac{d}{dt}\right|\Phi(\mathbf{r},t)\right\rangle , \qquad (1)$$

where H is the total Hamiltonian of the many-electron system in the presence of an external harmonic perturbation with time period T,

$$H'(\mathbf{r},t)=G(\mathbf{r})e^{-i\omega t}+\text{c.c.} , \qquad (2)$$

with

$$G(\mathbf{r})=\lambda \sum_{i=1}^{N} r_i P(\cos\vartheta_i)\ , \tag{3}$$

λ being the perturbation strength parameter and Φ the total wave function in the presence of the external perturbation. The functional in Eq. (1) is subjected to the optimization condition

$$\delta J=0\ , \tag{4}$$

where the optimization is performed with respect to suitable variation parameters introduced in the total wave function, the details of which may be found elsewhere [45]. The frequency-dependent polarizabilities $\alpha_d(\omega)$ may be calculated at different frequencies ω using standard expressions. $\alpha_d(\omega)$ exhibits poles at certain frequencies corresponding to the natural excitation modes of the system. The pole positions furnish the transition energies of the system to its different excited states and also yield the oscillator strength values. Certain special characteristics of the transition energies and oscillator strengths are observed along the isoelectronic sequence of argon which we discuss in detail in Sec. III.

III. RESULTS AND DISCUSSIONS

Presently we study the transitions $3p^6\,{}^1S^e \rightarrow 3p^5({}^2P)ns\,{}^1P^o$ $(n=4,\ldots,7)$ and $3p^6\,{}^1S^e \rightarrow 3p^5({}^2P)nd\,{}^1P^o$ $(n=3,\ldots,7)$ for the isoelectronic members Ar, K$^+$, Ca^{2+}, Sc^{3+}, Ti^{4+}, V^{5+}, Cr^{6+}, and Mn^{7+} using the *LS* coupling scheme. The ground-state wave functions are taken from Clementi and Roetti [52]. The radial part of the first-order orbitals which get admixed to the ground orbitals because of the external perturbation are chosen as a linear combination of suitable Slater bases

$$\delta\psi_i^{\pm}(r)\equiv\sum_q C_{iq}^{\pm} r^{n_{iq}} e^{-\rho_{iq} r}\ . \tag{5}$$

The coefficients $C_{iq}^{\pm}$ are determined variationally and n and ρ are preassigned. The expansion length is determined from the convergence of the static polarizability limit and for the present case it is confined to 15 [53] for all the excitations. The innermost core is assumed frozen in this calculation. In Table I we list the static limit $\alpha_d(\omega)_{\omega\rightarrow 0}$ of the dynamic polarizability values for all the ions. Existing theoretical values using different methods and experimental results are also listed for comparison. The number of calculations for neutral Ar is rather large whereas for the isoelectronic members only a few results

TABLE I. Static limit of dynamic dipole polarizabilities $\alpha_d(\omega)_{\omega\rightarrow 0}$ of the argon isoelectronic sequence.

Ion	Present static limit (a.u.)	Other results (a.u.)	
		Theory	Expt.
Ar	10.62	10.08,[a] 10.75,[b] 10.76,[b] 15.44[c] 10.80,[d] 10.69,[e] 11.10,[e] 11.23[g] 10.73,[h] 11.30,[i] 9.70,[i*] 10.76[k] 10.98,[l] 10.77[p]	11.08,[f] 11.07[j] 11.08,[m] 11.08[n]
K$^+$	5.48	5.31,[a] 4.66,[i] 4.40,[i] 5.457[p]	5.47,[j] 5.47–8.98[o]
Ca^{2+}	3.28	3.21,[a] 2.45,[i] 3.254[p]	3.12,[j]
Sc^{3+}	2.14	1.45,[i] 2.129[p]	3.17–7.42[o]
Ti^{4+}	1.49	0.94,[i] 1.482[p]	
V^{5+}	1.09	0.64,[i] 1.078[p]	
Cr^{6+}	0.82	0.45,[i] 0.8114[p]	
Mn^{7+}	0.63	0.33,[i] 0.6271[p]	0.29±0.15[j]

[a] Reference [26] [limited basis-set coupled Hartree-Fock (CHF) result].

[b] Reference [44] (single and multiconfiguration TDHF).

[c] Reference [28] (SCF perturbation method).

[d] Reference [29] (coupled perturbation approach).

[e] Reference [27] [SCF and pseudo-natural-orbital configuration-interaction (PNOCI) result].

[f] Reference [34].

[g] Reference [31] (fourth-order many-body-perturbation-theory (MBPT) result).

[h] Reference [30] (HF calculation).

[i] Reference [38] (semiempirical calculation).

[i*] Reference [39] (semiempirical calculation).

[j] Reference [37].

[k] Reference [32] (CHF result).

[l] Reference [33] (MBPT calculation).

[m] Reference [43].

[n] Reference [35].

[o] Experimental values listed in Ref. [26].

[p] Reference [40] (RRPA result).

are available. From a comparison with the listed values for Ar we find that our result is consistent with those obtained using HF and similar methods [26,27,30,32,40,44]. Accurate theoretical results using correlation effects explicitly [27,31,33] and experimental values [34,35,37,43] are about 5% higher. It appears that the inclusion of the correlation effect increases the polarizability of Ar. For the isoelectronic members our results for K^+ and Ca^{2+} are consistent with the limited basis-set calculation of Lahiri and Mukherjee [26] and those of Vogel [37]. The semiempirical results of Patil [38], we believe, are underestimates. For all the ions our results agree well with the relativistic random-phase approximation (RRPA) results of Johnson, Kolb, and Huang [40]. For Mn^{7+} our result ($\alpha_d = 0.63$ a.u.), although consistent with the RRPA result (0.627 a.u.) of Johnson, Kolb, and Huang

TABLE II. Dynamic-dipole-polarizability values in the normal-dispersion region for the argon isoelectronic sequence in their ground state. Results within ( ) are the MCTDHF values of Ref. [44].

ω	$\alpha_d(\omega)$ (a.u.)							
(a.u.)	Ar	K^+	Ca^{2+}	Sc^{3+}	Ti^{4+}	V^{5+}	Cr^{6+}	Mn^{7+}
0.0	10.62 (10.76)	5.48	3.28	2.14	1.49	1.09	0.82	0.63
0.05	10.68 (10.83)	5.49						
0.10	10.88 (11.02)	5.53	3.30	2.15	1.50	1.09	0.82	0.64
0.15	11.22 (11.38)	5.61						
0.20	11.75 (11.93)	5.71	3.36	2.18	1.51	1.10	0.83	0.64
0.25	12.56 (12.76)	5.86						
0.30	13.80 (14.04)	6.04	3.46	2.22	1.53	1.11	0.83	0.64
0.35	15.94 (16.25)	6.28						
0.40	20.98 (21.49)	6.58	3.62	2.29	1.57	1.13	0.84	0.65
0.45	−153.97 (−193.14)	6.97						
0.50		7.48	3.86	2.38	1.61	1.15	0.86	0.66
0.55		8.16						
0.60		9.11	4.19	2.50	1.67	1.18	0.88	0.67
0.65		10.58						
0.70		13.36	4.66	2.67	1.74	1.22	0.90	0.69
0.75		24.59						
0.78		−26.84						
0.80			5.39	2.89	1.84	1.27	0.93	0.70
0.90			6.30	3.19	1.96	1.34	0.96	0.72
1.00			8.91	3.71	2.12	1.41	1.01	0.75
1.10			17.26	4.24	2.34	1.51	1.06	0.78
1.15			−25.54					
1.20				5.26	2.63	1.64	1.12	0.82
1.30				7.16	3.04	1.80	1.21	0.86
1.40				11.87	3.69	2.01	1.30	0.92
1.50				43.79	4.78	2.32	1.43	0.98
1.55				−78.51				
1.60					7.09	2.79	1.61	1.07
1.70					14.93	3.56	1.85	1.17
1.80					−68.18	5.10	2.22	1.32
1.90						9.65	2.82	1.52
2.00						397.49	4.00	1.83
2.10						−9.14	7.33	2.33
2.20							75.70	3.31
2.30							−8.21	6.07
2.40								60.39
2.50								−6.92

[40] is relatively large compared to the experimental estimate (0.29±0.15) of Vogel [37]. Vogel calculated the static polarizability values empirically using the experimental energy levels of nonperturbing f orbitals of these ions. For Mn^{7+}, we believe, Vogel has underestimated the result. This is apparent from the value $\alpha_d = 0.37$ (a.u.) for Fe^{8+} as listed by Vogel [37], which is higher than that of Mn^{7+}. The effect of correlation becomes less important for higher isoelectronic members, TDCHF values are fairly accurate for these systems.

Table II shows the numerical values of $\alpha_d(\omega)$ with respect to ω in the normal-dispersion region. The position of the first resonance is indicated by a change in the sign of the polarizability value. For Ar the MCTDHF values of Rahman, Rizzo, and Yeager [44] are also listed. At $\lambda \simeq 633$ nm our computed $\alpha_d(\omega) = 10.76$ (a.u.) compared to the experimental value 11.22 a.u. of Burns, Graham, and Weller [42], Hohm and Kerl [43], and 11.26 a.u. of Buckingham and Graham [41]. Hohn and Kerl [43] plotted $\alpha_d(\omega)$ within 543.51 and 632.99 nm using values obtained from accurate interferometric measurements. Our results agree within 5% along the wavelength range. Near resonance the polarizability value increases very sharply resulting in loss of accuracy. It is somewhat interesting to note that the MCTDHF and time-dependent Hartree-Fock (TDHF) values of Rahman, Rizzo, and Yeager [44] differ very little. Along the isoelectronic sequence we notice a very interesting behavior of the dynamic polarizability values. For energies in the neighborhood of the difference of orbital energies $\Delta\varepsilon = |\varepsilon_{3s} - \varepsilon_{3p}|$ of the unperturbed ion, the polarizability values change abruptly within a small frequency range. For Ar this feature is not observed because $\Delta\varepsilon \cong 0.69$ a.u. is greater than the ionization energy. But for K^+, where $\Delta\varepsilon \sim 0.79$ a.u. to Mn^{7+} ($\Delta\varepsilon \cong 1.44$ a.u.), this feature is observed. In this neighborhood a large transition moment corresponding to $3s \rightarrow np$ and $3p \rightarrow ns$ excitations are developed. The moments are very nearly the same in magnitude and opposite in sign producing a large cancellation. The residual moment shows nonanalytic behavior over a narrow range of frequency in the neighborhood of $\Delta\varepsilon$. For K^+ this occurs between $3p \rightarrow 4s$ and $3p \rightarrow 3d$ excitations but for all other ions this occurs within the normal-dispersion region. This could have been interpreted in terms of internal excitation [48,53] if the system has an open-shell structure. But presently the system is described in terms of a closed-shell structure except for the random-phase-approximation (RPA) type of correlations implicit in it. This comes probably from the dynamic character of the atomic charge cloud in the presence of an external time varying field and needs a thorough investigation using more sophisticated configuration-interaction or many-body methods.

The excitation energies are obtained from the position of the poles of the dynamic polarizability values [45]. These are displayed in Table III for all ions. The spectroscopic values of Moore [54], Bashkin and Stoner [55], and the recent compilation of Sugar and Corliss [56] are also listed for comparison. The assignment of levels in Moore [54] or in Bashkin and Stoner [55] have followed the jl coupling scheme and experimental values listed in Table III are the values for the transitions ns' or nd' corresponding to $\Delta J = 1$ according to Moore [54]. Our assignment in this regard is tentative. The TDHF and MCTDHF values of Rahman, Rizzo, and Yeager [44] for the few excited states of Ar are also listed for comparison. For all the cases where data exist we find very reasonable agreement. The TDHF values of Rahman, Rizzo, and Yeager [44] deviate more for higher excitations probably because of the choice of the Gaussian basis set for such highly excited states. For Ar, the excited states are very diffuse and as such within our 15-parameter basis set we are unable to obtain the $7d$ excitation which lies close to the limit. Dipolar oscillator strengths in the length form have been calculated from the dynamic polarizabilities using the formula [57]

$$\alpha_d(\omega) = \sum_n{}' \frac{f_{n0}}{\omega_{n0}^2 - \omega^2} . \tag{6}$$

The calculation of the oscillator strength from Eq. (6) has been discussed in detail earlier [58]. For the first few excited states of Ar a number of experimental and theoretical calculations exist with a large dispersion of oscillator strength values. Our value for the $3p \rightarrow 4s$ transition is 0.296 compared to 0.275 of Stewart [59] using a similar method. The accurate experimental value [16] is 0.213 using the self-absorption technique. For higher excited s transitions our computed values gradually diminish and compare favorably with those obtained by Lee and Lu [22] using quantum-defect theory. Experimental results quoted by Lee and Lu [22] show a different trend. For the $3p \rightarrow 3d$ excitation our computed value 0.157 compares well with 0.128 obtained by Lee and Lu [22]. The decay time measurements of Lawrence [60] is $\cong 0.107$. For the higher d excitations our results are appreciably different from those of Lee and Lu [22]. From the comparison of Ar oscillator strengths we notice that the TDCHF values are somewhat higher than the experimental values. This is because a part of electron correlation is not taken care of in our theory which affects the transition matrix elements thereby deviating the oscillator strength values. But correlation effect diminishes along the isoelectronic sequence and for the higher members we expect reasonable accuracy. This is clearly demonstrated in the case of Ca^{2+} for the transition $3p \rightarrow 4s$ and $3p \rightarrow 3d$. Our calculated value for $3p \rightarrow 4s$ is 0.722 and $3p \rightarrow 3d$ is 3.601 compared to the extended CI results 0.709 and 3.688 of Baluja [24] for the respective transitions. For the isoelectronic members practically no data are available and our results may serve as a future reference.

From an analysis of the host of the data obtained for the neutral and isoelectronic members of the Ar sequence we find some interesting features. The first one is that there is an interchange of level positions between $4s$ and $3d$. For Ar, the $4s$ level is lower than the $3d$ level and the difference between $4s$ and $3d$ diminishes as we move along the isoelectronic series. At Sc^{3+} the $4s$ and $3d$ levels are almost degenerate making the assignment somewhat difficult. From Ti^{4+} onwards the $3d$ level lies lower

TABLE III. Transition energies, oscillator strengths, and quantum-defect values for the Rydberg states of the argon isoelectronic sequence. The asterisk indicates the approximate value quoted from Ref. [55].

		Transition energy (a.u.)		Oscillator strength		Quantum defect	
Ion	Transition	Present calculation	Other values	Present calculation	Other values	Present calculation	Other values
Ar	3p→4s	0.4481	0.4347[a] 0.4486[b] 0.4483[b*]	0.296	0.213±0.011[d] 0.222±0.02[e] 0.283±0.024[f] 0.350±0.130[g] 0.278±0.002[h] 0.275±0.02[i] 0.228±0.021[j] 0.270,[k] 0.300[l] 0.210,[m] 0.252[n] 0.232,[r] 0.245[s]	2.127	2.180[w] 2.054[x]
	→5s	0.5310	0.5239[a] 0.5314[b] 0.5514[b*]	0.042	0.013±0.003[j] 0.025,[l] 0.039[m] 0.012±0.004[c] 0.107,[r] 0.036[s]	2.105	2.156[w]
	→6s	0.5578	0.5521[a] 0.5583[b] 0.5845[b*]	0.017	0.013[m] 0.022±0.004[o] 0.009,[r] 0.013[s]	2.095	2.142[w]
	→7s	0.5704	0.5644[a] 0.5707[b*]	0.006	0.00074,[m] 0.019[r] 0.006[s]	2.031	2.155[w]
	→3d	0.5335	0.5257[a] 0.5341[b] 0.5315[b*]	0.157	0.107±0.015[j] 0.11,[l] 0.128[m] 0.110±0.011[o] 0.101,[r] 0.373[s]	0.042	0.113[w] 0.082[x]
	→4d	0.5587	0.5514[a] 0.5593[b]	0.081	0.032,[m] 0.082[r] 0.191[s]	0.042	0.182[w]
	→5d	0.5703	0.5641[a]	0.041	0.00051,[m] 0.304[r]	0.042	0.189[w]
	→6d	0.5767	0.5708[a]	0.027		0.013	0.207[w]
K$^+$	3p→4s	0.7721	0.7585[a,y]	0.476	0.363,[t] 0.355[u]	1.761	1.820[w] 1.699[x]
	→5s	0.9835	0.9797[c]	0.102	0.041,[t] 0.067[u]	1.735	1.834[w]
	→6s	1.0617		0.037		1.725	
	→7s	1.0993		0.017		1.720	
	→3d	0.9300	0.9202[z]	1.696		0.120	0.548[x] 0.221[z]
	→4d	1.0348	1.0166[a,y]	0.723		0.169	0.493[w]
	→5d	1.0845		0.323		0.193	
	→6d	1.1115		0.195		0.208	
	→7d	1.1277		0.096		0.212	
Ca^{2+}	3p→4s	1.1418	1.1286[a,y]	0.722	0.709,[p] 0.335[v]	1.527	1.579[w] 1.473[x]
	→5s	1.5095	1.5100[a,y]	0.158	0.079[v]	1.503	1.588[w]
	→6s	1.6558	1.6601[c,y]	0.057		1.494	1.638[w]
	→7s	1.7296		0.030		1.483	
	→3d	1.2747	1.2728[c,y]	3.601	3.688,[p] 5.796[v]	0.268	0.314[w] 0.559[x]
	→4d	1.5347	1.5343[c,y]	0.445		0.377	0.476[w]
	→5d	1.6641	1.6647[c,y]	0.075		0.407	0.595[w]
	→6d	1.7326	1.7324*	0.043		0.426	0.765[w]
	→7d	1.7732		0.024		0.427	
Sc^{3+}	3p→4s	1.5335	1.5538[a] 1.5377[c,y]	4.250		1.386	1.417[w] 1.309[x]
	→5s	2.1123	2.1141[a]	0.048		1.325	1.409[w]

TABLE III. (*Continued*).

		Transition energy (a.u.)		Oscillator strength		Quantum defect	
Ion	Transition	Present calculation	Other values	Present calculation	Other values	Present calculation	Other values
			2.1162[c,y]				
	→6*s*	2.3400	2.3500[c,y]	0.026		1.317	1.452[w]
	→7*s*	2.4574	2.4700[c]	0.014		1.313	1.523[w]
	→3*d*	1.5773	1.5720[c,y]	0.427		0.336	0.379[w] 0.525[x]
	→4*d*	2.0670	2.0685[c,y]	0.087		0.458	0.540[w]
	→5*d*	2.3151		0.0011		0.469	
	→6*d*	2.4430		0.0007		0.472	
	→7*d*	2.5171		0.0013		0.471	
Ti^{4+}	3*p*→4*s*	2.0350	2.0220[a] 2.0219[c,y]	0.187		1.219	1.268[w] 1.232[x]
	→5*s*	2.7867	2.7929[a] 2.7956[y] 2.7959[c]	0.074		1.197	1.275[w]
	→6*s*	3.1109	3.1254[c,y]	0.033		1.189	1.322[w]
	→7*s*	3.2815		0.017		1.183	
	→3*d*	1.7828	1.8012[c,y]	4.222		0.413	0.432[w] 0.526[x]
	→4*d*	2.6513	2.6556[y]	0.0056		0.464	0.535[y]
	→5*d*	3.0430		0.034		0.465	
	→6*d*	3.2425		0.031		0.468	
	→7*d*	3.3569		0.028		0.479	
V^{5+}	3*p*→4*s*	2.5525	2.5408[a,y]	0.285		1.114	1.161[w] 1.081[x]
	→5*s*	3.5345	3.5490[a] 3.5491[y]	0.082		1.093	1.167[w]
	→6*s*	3.9685		0.037		1.085	
	→7*s*	4.2003		0.016		1.078	
	→3*d*	2.0024	2.0295[q] 2.0296[y]	3.767		0.423	0.460[x]
	→4*d*	3.2846	3.2962[y]	0.107		0.451	0.510[y]
	→5*d*	3.8439		0.110		0.451	
	→6*d*	4.1347		0.028		0.424	
	→7*d*	4.2959		0.033		0.435	
Cr^{6+}	3*p*→4*s*	3.1197	3.1094[a] 3.1102[y]	0.326		1.027	1.072[w] 0.996[x]
	→5*s*	4.3551	4.3756[a] 4.3758[y]	0.086		1.007	1.077[w]
	→6*s*	4.9123	4.9457[y]	0.030		0.999	1.103[y]
	→7*s*	5.2127		0.017		0.993	
	→3*d*	2.2102	2.2464[q,y]	3.401		0.420	0.433[x]
	→4*d*	3.9670	3.9885[y]	0.267		0.432	0.481[y]
	→5*d*	4.7135	4.7503[y]	0.237		0.440	0.513[y]
	→6*d*	5.1061		0.082		0.416	
	→7*d*	5.3266		0.054		0.416	
Mn^{7+}	3*p*→4*s*	3.7361	3.7294[a,y]	0.345		0.954	0.926[x]
	→5*s*	5.2478	5.2808[a]	0.091		0.935	
	→6*s*	5.9408		0.033		0.927	
	→7*s*	6.3176		0.018		0.923	
	→3*d*	2.4107	2.4568[q,y]	3.096		0.411	0.409[x]

TABLE III. (*Continued*).

Ion	Transition	Transition energy (a.u.) Present calculation	Transition energy (a.u.) Other values	Oscillator strength Present calculation	Oscillator strength Other values	Quantum defect Present calculation	Quantum defect Other values
	$\rightarrow 4d$	4.6979	4.7299[y]	0.437		0.412	
	$\rightarrow 5d$	5.6796		0.125		0.388	
	$\rightarrow 6d$	6.1653		0.115		0.396	
	$\rightarrow 7d$	6.4507		0.073		0.395	

[a] Reference [54].

[b] Reference [44] (MCTDHF results).

[b*] Reference [44] (TDHF results).

[c] Reference [55].

[d] Reference [16].

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[o] Experimental values quoted in Ref. [22].

[p] Reference [24].

[q] Reference [4].

[r] Reference [20] (multiconfiguration results).

[s] Reference [20] (single-configuration results).

[t] Reference [25] (multiconfiguration results).

[u] Reference [25] (single-configuration results).

[v] Reference [23] (semiempirical results in intermediate coupling scheme).

[w] Computed from experimental energy levels.

[x] Reference [63].

[y] Reference [56].

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than 4*s*. This should be so from a hydrogenic model which is observed for higher isoelectronic members and is corroborated by experimental observations [55]. The behavior of the oscillator strength along the isoelectronic sequence is very interesting. For a given ion usually the oscillator strength diminishes as we go to higher principal quantum number for transitions of a given symmetry. As a typical example we choose Ca^{2+} and in Fig. 1 we plot the logarithm of the oscillator strength against the principal quantum number for $3p \rightarrow ns$ and $3p \rightarrow nd$ transitions, respectively. The situation is, however, different when we plot the oscillator strengths along the isoelectronic sequence. In Fig. 2 we show such plots for the $3p \rightarrow ns$ transitions along the isoelectronic sequence. For the $3p \rightarrow 4s$ transition the oscillator strength shows a hump at Sc^{3+} followed by smooth behavior on both sides.

From a close look in Table III we find that the $3p \rightarrow 3d$ oscillator strength is somewhat lower than $3p \rightarrow 4s$ for Ar but it is much larger in K^+ and Ca^{2+}. At Sc^{3+}, 4*s* and 3*d* levels are very close and there is an appreciable contri-

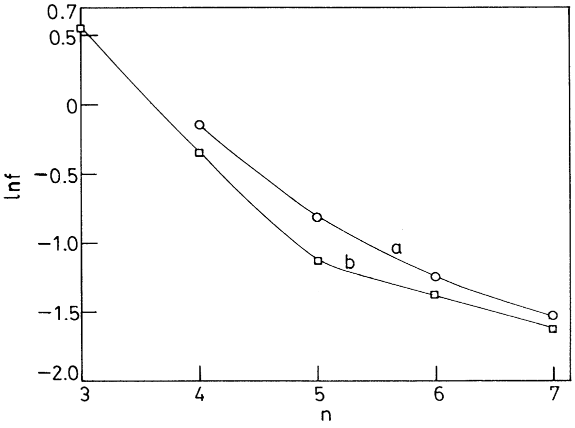

FIG. 1. Logarithm of oscillator strengths against principal quantum number *n* for the transitions $3p \rightarrow ns$ and $3p \rightarrow nd$ of Ca^{2+}. ○, for $3p \rightarrow ns$ (a) and □, for $3p \rightarrow nd$ transitions (b).

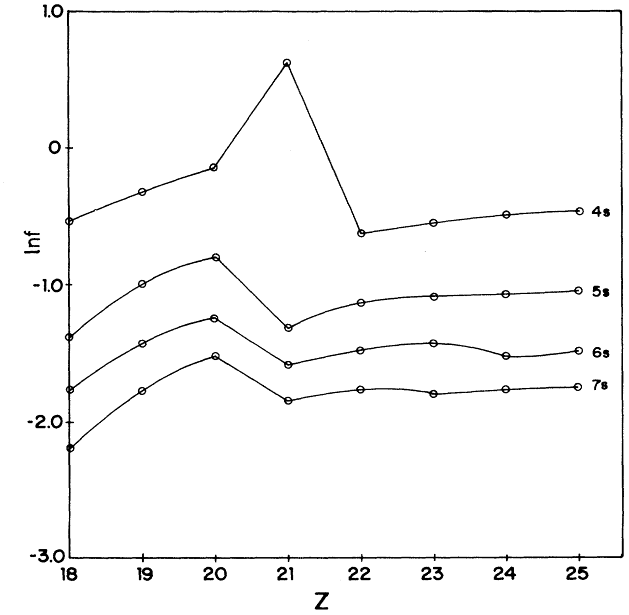

FIG. 2. Logarithm of oscillator strengths along the argon isoelectronic sequence for the transitions $3p \rightarrow ns$ ($n = 4$, 5, 6, and 7).

bution to the $\alpha_d(\omega)$ values from the $3d$ excitations producing an enhancement of the $3p \rightarrow 4s$ oscillator strength and a corresponding reduction in the $3p \rightarrow 3d$ oscillator strength. For a proper description of the excited state in this region one should take a linear combination of the s and d functions. From Ti^{4+} onwards the $3d$ level comes first and there is again large oscillator strengths connected with it. In Fig. 3 such a plot is given for the $3p \rightarrow nd$ excitations along the isoelectronic members. Sc^{3+} shows a large dip for the d excitations followed by more or less regular behavior. Again a substantial lowering of the $3p \rightarrow 4d$ oscillator strength is observed for Ti^{4+} after which the oscillator strength remains more or less constant. These features are also connected with the relative positions of nodes of the unperturbed and the perturbed functions which affect the overlap for the transition matrix element. All these features are not due to the choice of our basis set as we have tried with different choices of exponents of the basis functions keeping the number of parameters fixed, all of which produce similar results. Another possibility of this behavior may be due to the collapse of d orbitals along this isoelectronic sequence [61,62].

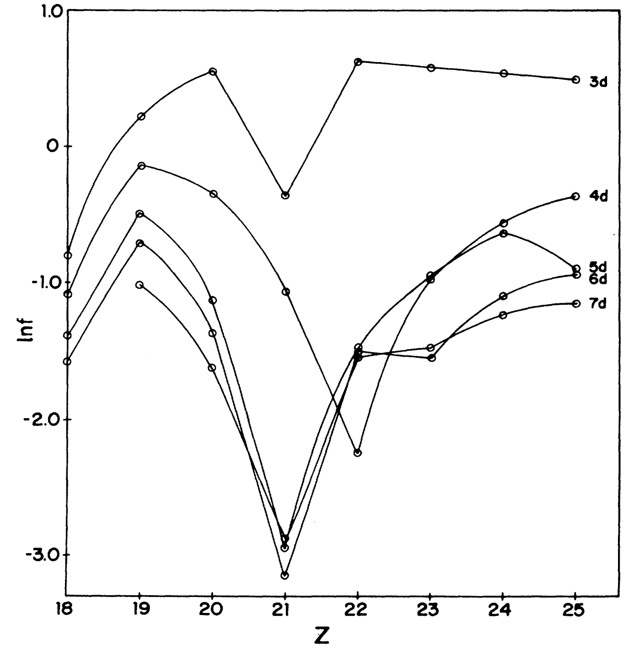

FIG. 3. Logarithm of oscillator strengths along the argon isoelectronic sequence for the transitions $3p \rightarrow nd$ ($n = 3$, 4, 5, 6, and 7).

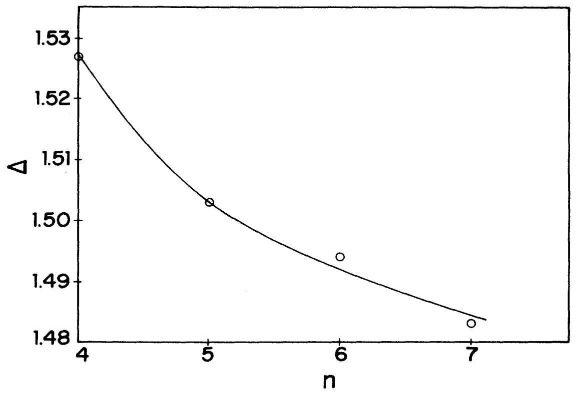

FIG. 4. Quantum defect (Δ) plotted against principal quantum number n for $3p \rightarrow ns$ transitions of Ca^{2+}.

We have also calculated the effective quantum numbers of the Rydberg states using the formula $n^* = Z_{\mathrm{eff}}/\sqrt{2\varepsilon}$, where ε is the ionization potential of the orbital, $Z_{\mathrm{eff}} = Z - N + 1$, N being the number of electrons and Z the nuclear charge. The quantum-defect values $\Delta = n - n^*$ are evaluated. These are compared with those obtained from the spectroscopic values of Moore [54], Bashkin and Stoner [55], and Sugar and Corliss [56] in

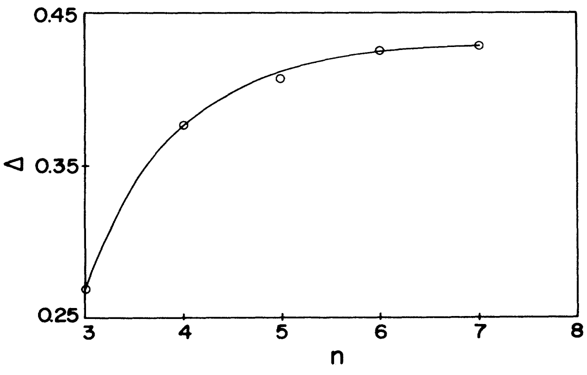

FIG. 5. Quantum defect (Δ) plotted against principal quantum number n for $3p \rightarrow nd$ transitions of Ca^{2+}.

Table III. The asymptotic limit of Δ ($n \rightarrow \alpha$) obtained by Theodosieu, Inokuti, and Manson [63] are also listed for comparison. Reasonable agreement is observed for the entire sequence where data exist. The quantum defects Δ generally go on decreasing asymptotically along an isoelectronic sequence for $3p \rightarrow ns$ transitions but the situation is just the opposite for the $3p \rightarrow nd$ excitations. Such a trend has been observed before [46]. In Figs. 4 and 5 we plotted the Δ values for Ca^{2+} for the transitions $3p \rightarrow ns$ and $3p \rightarrow nd$, respectively. A similar trend, as discussed, is observed.

We have also obtained an analytic representation of the Rydberg orbitals by renormalizing the perturbed wave functions at the pole positions. These functions are very diffuse but show the proper number of nodes and asymptotic behavior. These may be used for collisional studies [64]. We may point out that all the excited states of a given symmetry for a given ion may not be well represented by the same basis set. In such case a different choice of exponents was made. This gives a more or less identical value of polarizability but the functional behavior is different. This is necessary for higher excitations where the wave functions are extremely diffuse. In our calculation we obtained $3s \rightarrow 4p$ internal excitations from some of the ions Ti^{4+} to Mn^{7+}, where the excitation energies fall within our region of study. These are quite high-lying states. These are not listed because of the present nature of our study and will be reported elsewhere.

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*Permanent address: Department of Spectroscopy, Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India.

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