
Excited States of Na and Al Iso-Electronic Ions: Symmetry Adapted Cluster–Configuration Interaction Study

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ABSTRACT: The Rydberg excited levels of s, p, d, and f symmetries are studied up to principal quantum number $n = 5$ for the first eight members of the Na iso-electronic sequence (Na to Ar⁷⁺) and for the first six members of the Al iso-electronic sequence (Al to Ar⁵⁺) by the symmetry adapted cluster–configuration interaction (SAC–CI) method. The valence Slater-type orbital (STO) basis sets of Clementi et al. and the optimized Rydberg STO functions are used by the STO-6G expansion method. The calculated transition energies agree well with the experimental values wherever available. The results for the 4f level of S³⁺ and for the 5s, 4p, 5p, and 4f levels of Cl⁴⁺ and Ar⁵⁺ are predicted for the first time. © 2002 John Wiley & Sons, Inc. *Int J Quantum Chem* 87: 81–88, 2002

Key words: Rydberg states; excitation energies; 3s and 3p open-shell ions

Introduction

The study of Rydberg states of neutral atoms and their iso-electronic ions is interesting and useful because of their importance in various physical processes and also in astrophysical observations [1–5]. Different theoretical techniques have been applied to predict the transition energies of the Rydberg excited states of the first few members

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of the Na and Al iso-electronic sequences. Experimental values are essentially spectroscopic [6–8] and the reported data are quite extensive. Among various theoretical approaches, the time-dependent coupled Hartree–Fock (TDCHF) theory of Mukherjee et al. [3–5], the relativistic Hartree–Fock (HF) method of Karwowski and Szulkin [9], the Hartree–Fock with polarized frozen core (PFC) method of McEachran and Cohen [10], the Hartree–Fock method of Tull et al. [11], the third-order many-body perturbation theory (MBPT) with the Dirac–Fock approach of Safronova et al. [12], and the second-order MBPT with the Dirac–Fock method of Chaudhuri et al. [13] are important.

Recently, we successfully predicted the transition energies of the excited states of Ne iso-electronic

ions from Ne to Ar^{8+} [14], whose ground state is a closed-shell system, using the symmetry adapted cluster (SAC)/SAC–configuration interaction (CI) method [15–17]. In this article, we calculate the transition energies for the $2p^6(^1S)3s: ^2S \rightarrow 2p^6(^1S)ns: ^2S$, $2p^6(^1S)np: ^2P$, $2p^6(^1S)nd: ^2D$, and $2p^6(^1S)nf: ^2F$ transitions up to principal quantum number $n = 5$ for the first eight members of the Na iso-electronic sequence from Na to Ar^{7+} and for the $3s^23p: ^2P \rightarrow 3s^2(^1S)ns: ^2S$, $3s^2(^1S)np: ^2P$, $3s^2(^1S)nd: ^2D$, and $3s^2(^1S)nf: ^2F$ transitions up to principal quantum number $n = 5$ for the first six members of Al iso-electronic sequence from Al to Ar^{5+} using the SAC/SAC–CI method. These systems have an open-shell electronic structure in their ground and excited states. The SAC/SAC–CI method has been successfully applied to various kinds of spectroscopic studies [18] of molecules from the size of water [17] to the size of porphyrin dimers [19, 20]. In this article, we use the SAC–CI SD- R method, in which the SAC–CI linked R operators consist of singles and doubles, since the excitations are essentially described by the one-electron processes [21].

Computational Details

Here, we have studied the Rydberg levels having s , p , d , and f symmetries up to principal quantum number $n = 5$ for the first eight members of the Na iso-electronic sequence with nuclear charge $Z = 11$ –18 and for the first six members of the Al iso-electronic sequence with nuclear charge $Z = 13$ –18. The valence Slater-type orbital (STO) basis sets of all the ions have been taken from Clementi and Roetti [22]. The optimized STO basis sets of Rydberg functions were obtained from the calculations of Mukherjee et al. [3–5] based on the TDCHF theory. The number of STO parameters employed in these calculations [3–5] was determined by examining the absolute convergence in the static limit of frequency-dependent polarizabilities. In this study, the number of STO parameters has been restricted to 15 for all the s , p , d , and f functions. The choice of exponents depends on principal quantum number and symmetry of the excited levels [23, 24]. The final basis sets were determined by examining the convergence and the stability of the SAC–CI excitation energy. The integrals were calculated with the STO–Gaussian-type orbital (GTO) expansion method [25] and the self-consistent field calculations were performed with the Gaussian 98 program [26].

Electron correlations are calculated by the SAC/SAC–CI method. First, the ground state of the closed-shell ions of the system is calculated by the SAC method and then the ground and excited states of the open-shell system are calculated by the electron attachment of the SAC–CI method. In SAC/SAC–CI calculations, $1s$ orbitals of all the systems are fixed as cores. To reduce computational effort, we use a standard perturbation selection procedure [27]. For the closed-shell system, the threshold of the linked term is set to $\lambda_g = 1 \times 10^{-6}$ and the unlinked terms are adopted as the products of the important linked terms whose SD CI coefficients are larger than 0.001. For the open-shell ground and excited states, the threshold of the linked term is set to $\lambda_e = 1 \times 10^{-6}$. The thresholds for the unlinked terms in the SAC–CI calculations are set to 0.001 and 0.05, respectively, for selecting the important S and R operators. The contributions of both $S(2) \times R(1)$ and $S(2) \times R(2)$ unlinked terms, i.e., so-called “3,4-excited” terms [27] are included. The SAC–CI calculations are performed with the SAC–CI96 program system [28].

Results and Discussions

The SAC–CI results for the Na and Al iso-electronic ions are summarized in Tables I and II, respectively, along with the recent compilation of experimental values of Martin et al. [6], spectroscopic values of Bashkin and Stoner [7] and Moore [8], and other theoretical values. We used the LS coupling scheme to designate the energy levels. As spin orbit interaction is not included in the present SAC–CI calculations, we compared our values with the statistical average of the experimental values of a particular state. The effect of spin–orbit (SO) interactions is very small for the excited states studied here: the SO splittings are on the order of 10^{-4} au for 2P states and 10^{-6} au for 2D and 2F states [6–8]. The deviations from the experimental values are also given.

Na ISO-ELECTRONIC IONS

Rydberg excited $ns: ^2S$ ($n = 3, 4, 5$), $np: ^2P$ ($n = 3, 4, 5$), $nd: ^2D$ ($n = 3, 4, 5$), and $nf: ^2F$ ($n = 4, 5$) states are examined for the ions of the Na iso-electronic sequence from $Z = 11$ –18. Overall agreement between the SAC–CI results and the experiment [6–8] is very good, especially for the first six members of the sequence, as shown in Table I. For the Na

TABLE I
Excitation energies for the Rydberg s, p, d, and f levels of the Na iso-electronic ions.

| Ion | State | Excitation energy (au) | | | Deviation (%) ⁱ |
|------------------|--------------------|------------------------|-----------------------|---|----------------------------|
| | | SAC-CI | Observed | Other values | |
| Na | 3p: ² P | 0.0763 | 0.0773 ^{a,b} | 0.0714 ^c , 0.0730 ^d 0.0774 ^e , 0.0772 ^g 0.0765 ^h | 0.0010 (1.29) |
| | 4p | 0.1368 | 0.1379 ^{a,b} | 0.1316 ^c , 0.1320 ^d 0.1387 ^e | 0.0011 (0.80) |
| | 5p | 0.1581 | 0.1597 ^{a,b} | 0.1558 ^c , 0.1606 ^e | 0.0016 (1.00) |
| | 4s: ² S | 0.1163 | 0.1173 ^{a,b} | 0.1078 ^c , 0.1181 ^e 0.1173 ^g , 0.1164 ^h | 0.0012 (0.85) |
| | 5s | 0.1497 | 0.1513 ^{a,b} | 0.1439 ^c , 0.1522 ^e | 0.0016 (1.06) |
| | 3d: ² D | 0.1317 | 0.1329 ^{a,b} | 0.1263 ^c , 0.1340 ^e 0.1329 ^g | 0.0012 (0.90) |
| | 4d | 0.1562 | 0.1574 ^{a,b} | 0.1506 ^c , 0.1584 ^e | 0.0012 (0.76) |
| | 5d | 0.1673 | 0.1688 ^{a,b} | 0.1619 ^c , 0.1698 ^e | 0.0015 (0.89) |
| | 4f: ² F | 0.1584 | 0.1576 ^{a,b} | 0.1586 ^e , 0.1506 ^f | 0.0008 (0.51) |
| | 5f | 0.1681 | 0.1688 ^{a,b} | 0.1698 ^e , 0.1618 ^f | 0.0007 (0.42) |
| Mg ⁺ | 3p: ² P | 0.1614 | 0.1628 ^{a,b} | 0.1544 ^c , 0.1580 ^d 0.1622 ^e , 0.1625 ^g | 0.0014 (0.87) |
| | 4p | 0.3655 | 0.3674 ^{a,b} | 0.3573 ^c , 0.3580 ^d 0.3687 ^e | 0.0019 (0.52) |
| | 5p | 0.4418 | 0.4441 ^{a,b} | 0.4334 ^c , 0.4458 ^e | 0.0023 (0.52) |
| | 4s: ² S | 0.3158 | 0.3181 ^{a,b} | 0.3036 ^c , 0.3197 ^e 0.3181 ^g | 0.0023 (0.72) |
| | 5s | 0.4201 | 0.4228 ^{a,b} | 0.4114 ^c , 0.4247 ^e | 0.0027 (0.64) |
| | 3d: ² D | 0.3242 | 0.3257 ^{a,b} | 0.3163 ^c , 0.3277 ^e 0.3258 ^g | 0.0015 (0.46) |
| | 4d | 0.4235 | 0.4252 ^{a,b} | 0.4147 ^c , 0.4272 ^e | 0.0012 (0.40) |
| | 5d | 0.4691 | 0.4712 ^{a,b} | 0.4604 ^c , 0.4733 ^e | 0.0021 (0.45) |
| | 4f: ² F | 0.4256 | 0.4274 ^{a,b} | 0.4295 ^e , 0.4156 ^f | 0.0018 (0.42) |
| | 5f | 0.4715 | 0.4724 ^{a,b} | 0.4745 ^e , 0.4606 ^f | 0.0009 (0.19) |
| Al ²⁺ | 3p: ² P | 0.2433 | 0.2453 ^{a,b} | 0.2355 ^c , 0.2434 ^e 0.2446 ^g | 0.0020 (0.82) |
| | 4p | 0.6512 | 0.6547 ^{a,b} | 0.6422 ^c , 0.6560 ^e | 0.0035 (0.54) |
| | 5p | 0.8093 | 0.8131 ^{a,b} | 0.7996 ^c , 0.8151 ^e | 0.0038 (0.47) |
| | 4s: ² S | 0.5719 | 0.5748 ^{a,b} | 0.5555 ^c , 0.5768 ^e 0.5749 ^g | 0.0029 (0.50) |
| | 5s | 0.7739 | 0.7775 ^{a,b} | 0.7633 ^c , 0.7797 ^e | 0.0036 (0.46) |
| | 3d: ² D | 0.5272 | 0.5283 ^{a,b} | 0.5183 ^c , 0.5303 ^e 0.5284 ^g | 0.0011 (0.21) |
| | 4d | 0.7526 | 0.7554 ^{a,b} | 0.7428 ^c , 0.7575 ^e | 0.0028 (0.37) |
| | 5d | 0.8572 | 0.8606 ^{a,b} | 0.8471 ^c , 0.8628 ^e | 0.0034 (0.40) |
| | 4f: ² F | 0.7611 | 0.7637 ^{a,b} | 0.7661 ^e , 0.7484 ^f | 0.0026 (0.34) |
| | 5f | 0.8629 | 0.8651 ^{a,b} | 0.8676 ^e , 0.8496 ^f | 0.0022 (0.25) |

(Continued)

TABLE I
(Continued).

| Ion | State | Excitation energy (au) | | | Deviation (%) ⁱ |
|------------------|--------------------|------------------------|-----------------------|--|----------------------------|
| | | SAC-CI | Observed | Other values | |
| Si ³⁺ | 3p: ² P | 0.3232 | 0.3262 ^{a,b} | 0.3148 ^c , 0.3249 ^g | 0.0030 (0.93) |
| | 4p | 0.9902 | 0.9950 ^{a,b} | 0.9804 ^c | 0.0048 (0.48) |
| | 5p | 1.2549 | 1.2601 ^{a,b} | 1.2439 ^c | 0.0052 (0.41) |
| | 4s: ² S | 0.8798 | 0.8838 ^{a,b} | 0.8641 ^c , 0.8839 ^g | 0.0040 (0.45) |
| | 5s | 1.2044 | 1.2093 ^{a,b} | 1.1932 ^c | 0.0049 (0.41) |
| | 3d: ² D | 0.7301 | 0.7307 ^{a,b} | 0.7206 ^c , 0.7308 ^g | 0.0006 (0.08) |
| | 4d | 1.1355 | 1.1391 ^{a,b} | 1.1245 ^c | 0.0036 (0.32) |
| | 5d | 1.3237 | 1.3282 ^{a,b} | 1.3120 ^c | 0.0045 (0.34) |
| | 4f: ² F | 1.1544 | 1.1579 ^{a,b} | | 0.0035 (0.30) |
| | 5f | 1.3346 | 1.3383 ^{a,b} | | 0.0037 (0.28) |
| P ⁴⁺ | 3p: ² P | 0.4021 | 0.4063 ^{a,b} | 0.3930 ^c , 0.4041 ^g | 0.0042 (1.04) |
| | 4p | 1.3801 | 1.3867 ^{a,b} | 1.3696 ^c | 0.0066 (0.48) |
| | 5p | 1.7753 | 1.7825 ^{a,b} | 1.7636 ^c | 0.0072 (0.41) |
| | 4s: ² S | 1.2383 | 1.2437 ^{a,b} | 1.2226 ^c , 1.2438 ^g | 0.0054 (0.43) |
| | 5s | 1.7093 | 1.7161 ^{a,b} | 1.6969 ^c | 0.0068 (0.40) |
| | 3d: ² D | 0.9294 | 0.9304 ^{a,b} | 0.9197 ^c , 0.9306 ^g | 0.0010 (0.11) |
| | 4d | 1.5685 | 1.5737 ^{a,b} | 1.5566 ^c | 0.0052 (0.33) |
| | 5d | 1.8645 | 1.8709 ^{a,b} | 1.8518 ^c | 0.0064 (0.34) |
| | 4f: ² F | 1.6010 | 1.6065 ^{a,b} | | 0.0055 (0.34) |
| | 5f | 1.8832 | 1.8885 ^{a,b} | | 0.0053 (0.28) |
| S ⁵⁺ | 3p: ² P | 0.4801 | 0.4862 ^{a,b} | 0.4708 ^c , 0.4810 ^d 0.4827 ^g | 0.0061 (1.27) |
| | 4p | 1.8201 | 1.8293 ^{a,b} | 1.8093 ^c , 1.8160 ^d | 0.0092 (0.51) |
| | 5p | 2.3693 | 2.3792 ^{a,b} | 2.3569 ^c | 0.0099 (0.42) |
| | 4s: ² S | 1.6469 | 1.6539 ^{a,b} | 1.6216 ^c , 1.6540 ^g | 0.0070 (0.42) |
| | 5s | 2.2877 | 2.2969 ^{a,b} | 2.2748 ^c | 0.0092 (0.40) |
| | 3d: ² D | 1.1252 | 1.1274 ^{a,b} | 1.1152 ^c , 1.1276 ^g | 0.0022 (0.20) |
| | 4d | 2.0509 | 2.0586 ^{a,b} | 2.0384 ^c | 0.0077 (0.38) |
| | 5d | 2.4790 | 2.4879 ^{a,b} | 2.4653 ^c | 0.0089 (0.60) |
| | 4f: ² F | 2.1001 | 2.1080 ^{a,b} | | 0.0080 (0.38) |
| | 5f | 2.5062 | 2.5140 ^{a,b} | | 0.0078 (0.31) |
| Cl ⁶⁺ | 3p: ² P | 0.5567 | 0.5662 ^b | 0.5480 ^c , 0.5569 ^e | 0.0095 (1.71) |
| | 4p | 2.3089 | 2.3222 ^b | 2.2989 ^c , 2.3167 ^e | 0.0133 (0.58) |
| | 5p | 3.0351 | 3.0499 ^b | 3.0230 ^c , 3.0446 ^e | 0.0148 (0.49) |
| | 4s: ² S | 2.1040 | 2.1142 ^b | 2.0818 ^c | 0.0102 (0.48) |
| | 5s | 2.9402 | 2.9510 ^b | 2.9241 ^c | 0.0108 (0.37) |
| | 3d: ² D | 1.3172 | 1.3223 ^b | 1.3073 ^c | 0.0051 (0.39) |
| | 4d | 2.5816 | 2.5933 ^b | 2.5690 ^c | 0.0117 (0.45) |
| | 5d | 3.1649 | 3.1785 ^b | 3.1514 ^c | 0.0136 (0.43) |
| | 4f: ² F | 2.6498 | 2.6613 ^b | 2.6566 ^e | 0.0115 (0.43) |
| | 5f | 3.2025 | 3.2140 ^b | 3.2093 ^e | 0.0115 (0.36) |

(Continued)

TABLE I
(Continued).

| Ion | State | Excitation energy (au) | | | Deviation (%) ⁱ |
|------------------|--------------------|------------------------|---------------------|---------------------|----------------------------|
| | | SAC–CI | Observed | Other values | |
| Ar ⁷⁺ | 3p: ² P | 0.6337 | 0.6464 ^b | 0.6248 ^c | 0.0127 (2.00) |
| | 4p | 2.8477 | 2.8655 ^b | 2.8377 ^c | 0.0178 (0.63) |
| | 5p | 3.7744 | 3.7933 ^b | 3.7617 ^c | 0.0189 (0.50) |
| | 4s: ² S | 2.6111 | 2.6240 ^b | 2.5877 ^c | 0.0129 (0.49) |
| | 5s | 3.6640 | | 3.6459 ^c | |
| | 3d: ² D | 1.5068 | 1.5157 ^b | 1.4968 ^c | 0.0089 (0.59) |
| | 4d | 3.1616 | 3.1781 ^b | 3.1487 ^c | 0.0165 (0.52) |
| | 5d | 3.9237 | 3.9417 ^b | 3.9099 ^c | 0.0180 (0.46) |
| | 4f: ² F | 3.2496 | 3.2662 ^b | | 0.0166 (0.51) |
| | 5f | 3.9733 | 3.9880 ^b | | 0.0147 (0.37) |

^a Ref. [6].^b Refs. [7, 8].^c Refs. [3, 4].^d Ref. [9].^e Ref. [10].^f Ref. [11].^g Ref. [12].^h Ref. [13].ⁱ Difference (au) between SAC–CI results and observed values and the ratio of the deviations to observed values are given in the parentheses.**TABLE II**
Excitation energies for the Rydberg s, p, d, and f levels of the Al iso-electronic ions.

| Ion | State | Excitation energy (au) | | | Deviation (%) ^e |
|--------------------|--------------------|------------------------|-----------------------|---|----------------------------|
| | | SAC–CI | Observed | Other values | |
| Al | 4s: ² S | 0.1124 | 0.1155 ^{a,b} | 0.1117 ^c , 0.1161 ^d | 0.0031 (2.68) |
| | 5s | 0.1679 | 0.1717 ^{a,b} | 0.1635 ^c , 0.1718 ^d | 0.0038 (2.21) |
| | 4p: ² P | 0.1462 | 0.1501 ^{a,b} | | 0.0039 (2.60) |
| | 5p | 0.1792 | 0.1835 ^{a,b} | | 0.0043 (2.34) |
| | 3d: ² D | 0.1479 | 0.1478 ^{a,b} | 0.1479 ^c | 0.0001 (0.07) |
| | 4d | 0.1772 | 0.1774 ^{a,b} | 0.1753 ^c | 0.0002 (0.11) |
| | 5d | 0.1917 | 0.1924 ^{a,b} | 0.1880 ^c | 0.0007 (0.36) |
| | 4f: ² F | 0.1841 | 0.1883 ^{a,b} | | 0.0042 (2.23) |
| | 5f | 0.1948 | 0.1997 ^{a,b} | | 0.0049 (2.45) |
| | Si ⁺ | 4s: ² S | 0.2969 | 0.2984 ^{a,b} | 0.2952 ^c |
| 5s | | 0.4466 | 0.4464 ^{a,b} | 0.4354 ^c | 0.0002 (0.04) |
| 4p: ² P | | 0.3678 | 0.3701 ^{a,b} | | 0.0023 (0.63) |
| 5p | | 0.4708 | 0.4733 ^{a,b} | | 0.0025 (0.53) |
| 3d: ² D | | 0.3744 | 0.3615 ^{a,b} | 0.3559 ^c | 0.0128 (3.54) |
| 4d | | 0.4600 | 0.4603 ^{a,b} | 0.4469 ^c | 0.0003 (0.07) |
| 5d | | 0.5101 | 0.5121 ^{a,b} | 0.4985 ^c | 0.0020 (0.39) |
| 4f: ² F | | 0.4704 | 0.4718 ^{a,b} | | 0.0014 (0.30) |
| 5f | | 0.5165 | 0.5183 ^{a,b} | | 0.0018 (0.35) |

(Continued)

TABLE II
(Continued).

| Ion | State | Excitation energy (au) | | | Deviation (%) ^e |
|------------------|--------------------|------------------------|---|---------------------|----------------------------|
| | | SAC-CI | Observed | Other values | |
| P ²⁺ | 4s: ² S | 0.5343 | 0.5369 ^{a,b} | 0.5333 ^c | 0.0026 (0.48) |
| | 5s | 0.7993 | 0.8021 ^{a,b} | 0.7887 ^c | 0.0028 (0.35) |
| | 4p: ² P | 0.6416 | 0.6446 ^{a,b} | | 0.0030 (0.47) |
| | 5p | 0.8404 | 0.8421 ^{a,b} | | 0.0017 (0.20) |
| | 3d: ² D | 0.5456 | 0.5325 ^{a,b} | 0.5124 ^c | 0.0131 (2.46) |
| | 4d | 0.7831 | 0.7856 ^{a,b} | 0.7703 ^c | 0.0025 (0.32) |
| | 5d | 0.9041 | 0.9074 ^a , 0.9133 ^b | 0.8914 ^c | 0.0033 (0.36) |
| | 4f: ² F | 0.8140 | 0.8140 ^{a,b} | | 0.0000 (0.00) |
| | 5f | 0.9165 | 0.9139 ^a , 0.9245 ^b | | 0.0026 (0.28) |
| S ³⁺ | 4s: ² S | 0.8240 | 0.8267 ^{a,b} | 0.8231 ^c | 0.0027 (0.33) |
| | 5s | 1.2323 | 1.2348 ^{a,b} | 1.2196 ^c | 0.0025 (0.20) |
| | 4p: ² P | 0.9685 | 0.9735 ^{a,b} | | 0.0050 (0.52) |
| | 5p | 1.2982 | 1.2996 ^{a,b} | | 0.0014 (0.11) |
| | 3d: ² D | 0.7035 | 0.6932 ^{a,b} | 0.6671 ^c | 0.0103 (1.49) |
| | 4d | 1.1606 | 1.1636 ^{a,b} | 1.1495 ^c | 0.0030 (0.26) |
| | 4f: ² F | 1.1963 | | | |
| Cl ⁴⁺ | 4s: ² S | 1.1649 | 1.1678 ^b | 1.1637 ^c | 0.0029 (0.25) |
| | 5s | 1.7374 | | 1.7250 ^c | |
| | 4p: ² P | 1.3441 | | | |
| | 5p | 1.6790 | | | |
| | 3d: ² D | 0.8521 | 0.8469 ^b | 0.8160 ^c | 0.0052 (0.61) |
| | 4d | 1.5881 | 1.5925 ^b | 1.5786 ^c | 0.0044 (0.28) |
| | 4f: ² F | 1.7114 | | | |
| Ar ⁵⁺ | 4s: ² S | 1.5538 | 1.5596 ^b | 1.5548 ^c | 0.0058 (0.37) |
| | 5s | 2.3296 | | 2.3044 ^c | |
| | 4p: ² P | 1.7728 | | | |
| | 5p | 2.1493 | | | |
| | 3d: ² D | 0.9998 | 0.9962 ^b | 0.9603 ^c | 0.0036 (0.36) |
| | 4d | 2.0637 | 2.0722 ^b | 2.0572 ^c | 0.0085 (0.41) |
| | 4f: ² F | 2.2148 | | | |

^a Ref. [6].^b Refs. [7, 8].^c Refs. [5].^d Ref. [13].^e Difference (au) between SAC-CI results and observed values and the ratio of the deviations to observed values are given in parentheses.

atom, excellent agreement of the excitation energies is obtained for all the Rydberg excited states. The SAC-CI method gives slightly lower excitation energies in comparison with the observed values. The deviation from the experiment varies from 0.7 to 1.6 mhartrees.

For the Na iso-electronic sequence, several theoretical works were reported. Recently, the third-

order MBPT method [12] based on Dirac-Hartree-Fock (DHF) was presented for 3p, 4s, and 3d states of the ions having $Z = 11-14$ and the second-order MBPT [13] with numerical DHF was also applied to 3p and 4s states of Na. These calculations yielded very accurate values and the present results are very close to those calculations [12, 13]. The 3p and 4p states of Na and Mg⁺ were studied by the rela-

tivistic HF method [9]. The TDCHF method [3, 4] was extensively applied to the ns ($n = 4, 5$), np ($n = 3, 4, 5$), and nd ($n = 3, 4, 5$) states of these iso-electronic ions. The excitation energies obtained in these works are lower than the experimental values. Many Rydberg excited states of Na, Mg⁺, Al²⁺, and Cl⁶⁺ ions were also investigated by the HF method with PFC [10] and the results were good.

For the Mg⁺ ion, the SAC–CI method also reproduces the excitation spectrum accurately: the discrepancies between our results and the experimental values range from 0.9 to 2.7 mhartrees. These errors amount to 0.19–0.87% of the absolute excitation energies. For higher ions, from Al²⁺ to S⁵⁺, our results also agree well with the experimental values: the deviation varies from 1.1 to 9.9 mhartrees. The deviations become large as the nuclear charge increases from Al²⁺ to S⁵⁺; however, the ratio of the error relative to the excitation energy is almost constant: 0.2–1.3%. As seen from Table I, several theoretical results are available for Na, Mg⁺, and Al²⁺, but from Si³⁺ onwards, a very limited number of theoretical calculations have been reported so far for all the states under present consideration. For the highly ionized ions Cl⁶⁺ and Ar⁷⁺, the deviations between SAC–CI results and experiment increase up to 10–19 mhartrees, but the error ratio is within 2%. It may be noted that the absolute excitation energies for these states are also very large.

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For this series of ions, no other theoretical results exist for the np: ²P ($n = 4, 5$) and nf: ²F ($n = 4, 5$) states. The TDCHF study of Mukherjee et al. [5] was reported for ns and nd levels of all the ions and the second-order MBPT with the relativistic HF method [13] was reported only for Al.

For the Al atom, the SAC–CI results reproduce the experimental spectrum quite accurately, especially for nd: ²D ($n = 3, 4, 5$) states; the deviations are less than 0.7 mhartree. The agreement for other states is also encouraging. The discrepancies between our results and the experiment are within 4.9 mhartree for ns: ²S, np: ²P, and nf: ²F states. The TDCHF values [5] are relatively lower than the experimental values, the trend is opposite compared to that observed in Ne iso-electronic ions [14]. The second-order MBPT with the relativistic HF method [13] gave accurate results only for ns ($n = 4, 5$) states.

For the Si⁺ ion, the discrepancies between our results and the experiment are quite small except

for the nd: ²D level; the deviations are within 2.5 mhartrees. The error for the 3d: ²D state is 12.8 mhartrees, which is relatively large considering the accuracy of our method and the basis sets used. This value does not change even if the quality of the basis sets is improved. This deviation may be due to the strong mixing of higher “d” levels. The TDCHF calculation [5] underestimated the excitation energies, especially for the nd ($n = 4, 5$) levels. Similarly, the results for P²⁺ are also satisfactory. The trend of our results in comparison with the experiment is almost the same as that for Si⁺. The errors are within 3.3 mhartrees except for 3d: ²D state. It is also observed from the table that for Si⁺, the 3d level is higher than the 4s level, but for P²⁺, 3d and 4s levels are almost degenerate. From S³⁺ onward, 3d levels are lower than 4s levels. Different experimental values [6–8] are reported for the 5d: ²D and 5f: ²F states, but the excitation energies for these states of Bashkin and Stoner [7] and Moore [8] are higher than those of Martin et al. [6]. Our results support the experimental values of Martin et al. [6].

For highly ionized ions, S³⁺, Cl⁴⁺, and Ar⁵⁺, we reported ns: ²S ($n = 4, 5$), np: ²P ($n = 4, 5$), nd: ²D ($n = 3, 4$), and 4f: ²F states. For the S³⁺ ion, the SAC–CI method simulates the experimental spectrum quite satisfactorily with the error on the order of mhartrees. For Cl⁴⁺ and Ar⁵⁺, no experimental values exist for 5s, np ($n = 4, 5$), and 4f states for comparison. In Figure 1, we have plotted the excitation energies of 4p, 4d, and 4f levels with respect to nuclear charge. Very smooth behavior is observed,

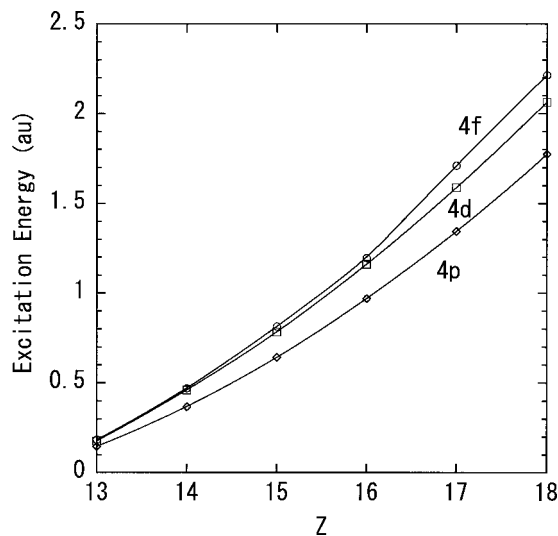


FIGURE 1. Plot of transition energies (au) vs. nuclear charge (Z) for the 4p, 4d, and 4f levels.

which indicates the consistency of our calculated values. Our results for those states where the experimental values are available for comparison are satisfactory and for 5s states, our results are similar to those of TDCHF [5], which gave reasonable values for ns states of other ions.

Conclusions

The SAC–CI method is applied to the Rydberg ns, np, nd, and nf states ($n = 3, 4, 5$) of the Na and Al iso-electronic ions from Na to Ar^{7+} and from Al to Ar^{5+} , respectively. The STO basis sets expanded by the STO-6G method, in which 15 STOs are optimized for describing the excited states, are used. In view of satisfactory agreement between our results and the spectroscopic values and lack of accurate reference data for the 5s: ^2S ; np: ^2P ($n = 4, 5$); nd: ^2D ($n = 4, 5$) and nf: ^2F ($n = 4, 5$) states of the Na iso-electronic ions, particularly from Si^{3+} onwards, and for the ns: ^2S ($n = 4, 5$); np: ^2P ($n = 4, 5$); nd: ^2D ($n = 3, 4, 5$) and nf: ^2F ($n = 4, 5$) states of the Al iso-electronic ions, our accurate results may serve as a reliable set of atomic data for future references. It should be noted here that the excitation energies of the 4f level of S^{3+} and the 5s, 4p, 5p, and 4f levels of Cl^{4+} and Ar^{5+} are reported for the first time.

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