PHYSICAL REVIEW A VOLUME 40, NUMBER 4 AUGUST 15, 1989

# Dynamic polarizabilities and Rydberg states of silicon, phosphorous, and sulfur

P. K. Mukherjee* and Kimio Ohno
*Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060, Japan*

(Received 19 July 1988)

Dynamic dipole polarizabilities $\alpha_d(\omega)$ within and beyond the normal dispersion region for the neutral atoms Si, P, and S in their ground and valence excited states have been calculated using the linearized version of time-dependent coupled Hartree-Fock theory. Roothaan formalism has been adopted to treat the open-shell atoms. Excitation energies, oscillator strengths, and quantum defects have been estimated for several optically allowed transitions, and analytic representations of the singly excited Rydberg orbitals have been found. The results are compared with existing theoretical and spectroscopic data.

## I. INTRODUCTION

Spectral lines arising out of neutral and ionized atoms of silicon, phosphorous, and sulfur are quite dominant in the spectra of the solar photosphere and corona.[1-5] Neutral and ionized species of these atoms have been found by the International Ultraviolet Explorer (IUE) satellite experiments on interstellar matter.[6,7] Experiments using the Voyager Ultraviolet Spectrometer (UVS),[8-10] IUE satellites,[11,12] and the Rocket borne faint object telescope[13] (FOT) on the Jupiter planetary system also reveal the existence of such ions. These observations are important in finding the relative abundance of elements in interstellar clouds, detecting such clouds, and for estimating the electron temperature of the plasma torus of Jupiter's satellite Io. Laboratory experiments on such systems are now available.[14-17] The study of excitation properties and excited-state wave functions of such atoms and their isoelectronic sequences is extremely important for the calculation of radiative and forbidden decay rates and collision strengths for electron-impact excitations over a wide range of temperatures. Accurate atomic data are necessary for the estimation of radiative power loss from thermonuclear plasmas and for the diagnostics of astrophysical, laser-produced, or tokamak plasmas.[18-25] Besides, Rydberg states of atoms are important in studying superradiance phenomena, laser isotope separation, and high-resolution spectroscopy. The subject has been well reviewed.[26,27] Collision of high Rydberg atoms with neutral atoms, molecules, and charged particles is a topic of current interest.[28-32]

Theoretical calculations along this line are limited. Model potential calculations have been done for Si- and S-like systems,[33,34] and a coupled-channel model calculation was done for Si.[35] Most of the accurate theoretical calculations use the configuration-interaction (CI) approach for the energy levels and oscillator strengths for such systems and their highly charged isoelectronic sequences.[36-42].

In a recent paper[43] we performed a detailed analysis of the transition energies and singly excited Rydberg states of Al- and Cl-like systems in $^2P$ ground state using the linearized version of time-dependent coupled Hartree-Fock (TDCHF) theory. Although the theory was successfully applied in the past to study the response properties of closed-shell atomic systems and alkali-metal atoms,[44-46] application to systems with partially filled $p$ electrons are limited.[43,47] In our earlier calculation,[43] we observed interesting transition properties, particularly the transition from the inner shell $3s$. In the present communication we apply TDCHF theory for studying the excitation properties of neutral Si, P, and S in their ground, as well as valence excited states. To our knowledge no such detailed calculations have been performed earlier. We adopt the Roothaan formalism[48] to deal with the open-shell atoms. As the atoms have different $LS$-coupled valence excited states, their excitation properties are very different and worth investigation. The excitation of one of the $3p$ electrons may leave behind a core of $3p$ electrons having different multiplet structure. This is true for P and S, where excitation of a $3p$ electron leaves behind either $3p^2$ core for P having multiplets $^3P$, $^1D$, and $^1S$ or $3p^3$ core for S having multiplets $^1S$, $^2D$, and $^2P$. In general the transition scheme is very complicated. But the present method allows only a certain class of excitations. In several cases the transition energy allowed in this scheme lies beyond the first ionization threshold of the parent atom. For closed-shell systems TDCHF theory incorporates RPA-type correlation.[49-51] This situation is less clear for open-shell systems and is much more complex to analyze. Our present theory is described in detail earlier.[43,47] In Sec. II we give a brief outline of the method.

## II. METHOD

The open-shell atom is described by the usual nonrelativistic Hamiltonian $H_0$. We use atomic units throughout. The energy of the ground and valence excited states are obtained using Roothaan formalism.[48] An oscillatory perturbation

$$H'(r,t)=G(r)e^{-i\omega t}+\text{c.c.} \tag{1}$$

is imposed on the system which admixes first-order corrections $\delta\psi_i^{\pm}$ to each ground-state orbital $\psi_i$, oscillating with the two components of the perturbation. A variational procedure is adopted to find out these admixtures $\delta\psi_i^{\pm}$ by expanding them in terms of suitable Slater bases

$$\delta\psi_i^{\pm}(r)=\sum_q C_{iq}^{\pm}\chi_{iq}(r)Y_{lm}(\theta,\phi)\ , \tag{2}$$

where $C_{iq}^{\pm}$ are linear variation parameters to be determined. The procedure for finding these admixtures is detailed in earlier papers.[45–47] The frequency-dependent response properties like dynamic polarizabilities $\alpha_d(\omega)$ can be obtained in terms of ground-state orbitals and their admixtures by taking the expectation value of a suitable moment operator, described earlier. The poles of the dynamic polarizability values yield the excitation energies of the various natural excitation modes of the system, and renormalized first-order admixtures corresponding to various pole positions yield analytic representations of the singly excited state wave functions. Results are discussed in Sec. III.

## III. RESULTS AND DISCUSSIONS

We consider the neutral atoms Si and S in $^3P$, $^1D$, and $^1S$ states and P in $^4S$, $^2D$, and $^2P$ states in presence of a dipolar oscillatory field. The field-free system is described by the orbitals of Clementi and Roetti.[52] The first-order perturbed admixtures [Eq. (2)] are expanded in terms of suitable Slater bases with 15 parameters for the admixtures associated with the valence orbital excitations, and 12-parameter expansion is used for all core orbital admixtures. These core orbitals occupy the 2*s*, 2*p*, and 3*s* shells. The innermost core 1*s* is assumed frozen. The frequency-dependent dipolar polarizability values $\alpha_d(\omega)$, which are very useful for several atomic calculations,[53] have been evaluated for each $\omega$. The static limits of $\alpha_d(\omega)$ have been estimated for each case and are displayed in Table I. Results are compared with static coupled Hartree-Fock results of Roy *et al.*[54] and also with the static results of Stewart[55] and Fraga *et al.*[56] Roy *et al.*[54] used an eight-parameter description for their perturbed admixtures. To compare with their results we performed calculations with the basis sets chosen by Roy *et al.*[54] for all the cases, and the results, as shown in Table I, are in excellent agreement. However, for such systems eight-parameter representation is not well convergent, and we have made explicit calculations using our extended basis sets of 15 parameters which have been tested for convergence for the static polarizability values.[43] The results agree reasonably well with the coupled calculations of Stewart.[55] Fraga *et al.*[56] used uncoupled approximation and their static results are relatively less accurate. The most reliable correlated static polarizabilities due to Reinsch and Meyer[57] are also listed in Table I. As is observed in general, inclusion of correlation lowers the polarizability values. Table II shows the numerical values of $\alpha_d(\omega)$ with respect to $\omega$ in the normal dispersion region. The positions of the resonances are usually indicated by a change of sign of the polarizability values. The numerical values of the dynamic polarizability are relatively less accurate near the resonances, and we omitted displaying such values in Table I. We notice a considerable change in the position of $3p\rightarrow 4s$ transition corresponding to different multiplet structure of the initial state. In the present case we have extended our calculation beyond first resonance and studied the dipole-allowed transitions $3p\rightarrow ns$ and $\rightarrow nd$ up to $n=6$. Owing to the different multiplet structure associated with the initial as well as the final states, the excitation scheme is, in general, rather complex. The following general selection rules hold for dipole-allowed transitions:

$$\Delta S=0,\quad \Delta L=0,\pm 1\ ,$$

where *S* denotes the total spin and *L* the total orbital angular momentum of the initial state. Our perturbation operator is spin independent, and the selection rule for spin is satisfied. However, the excitation of one of the valence orbitals of arbitrary spin may leave behind a core in different multiplet states. Not all such core multiplets are allowed presently. The core multiplet must be such as to satisfy $\Delta S=0$, with arbitrary spin-orbital excitations. Even with this choice we may have different orbital multiplicity satisfying the selection rule. To compare

TABLE I. Static limit of dynamic dipole polarizability $\alpha_d(\omega)_{\omega\rightarrow 0}$.

| Atom | State | Present static limit (Å $^3$) | | Other static results (Å $^3$) |
|---|---|---|---|---|
| Si | $^3P$ | 5.48,[a] | 5.69[b] | 5.46,[c] 6.03,[d] 6.81,[e] 5.38[f] |
| Si | $^1D$ | 5.93,[a] | 6.29[a] | 5.90,[c] 6.37[d] |
| Si | $^1S$ | 6.64,[a] | 7.28[b] | 6.20,[c] 7.30[d] |
| P | $^4S$ | 3.61,[a] | 3.71[b] | 3.61,[c] 4.56,[d] 4.42,[e] 3.63[f] |
| P | $^2D$ | 3.85,[a] | 4.01[b] | 3.81,[c] 4.07[d] |
| P | $^2P$ | 3.97,[a] | 4.16[b] | 3.91,[c] 4.33[d] |
| S | $^3P$ | 2.65,[a] | 2.78[b] | 2.63,[c] 2.82,[d] 3.45,[e] 2.90[f] |
| S | $^1D$ | 2.73,[a] | 2.89[b] | 2.70,[c] 3.08[d] |
| S | $^1S$ | 2.83,[a] | 3.04[b] | 2.77,[c] 3.14[d] |

[a] Eight-parameter calculation.
[b] Fifteen-parameter calculation.
[c] Reference 54.
[d] Reference 55.
[e] Reference 56.
[f] Reference 57.

TABLE II. Dynamic dipole polarizability values in the normal dispersion region for Si, P, and S in their ground and valence excited states.

| | $\alpha_d(\omega)$[a] (a.u.) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Si | | | P | | | S | | |
| $\omega$ (a.u.) | $^3P$ | $^1D$ | $^1S$ | $^4S$ | $^2D$ | $^2P$ | $^3P$ | $^1D$ | $^1S$ |
| 0.0001 | 3.839[+1][b] | 4.246[+1] | 4.915[+1] | 2.503[+1] | 2.706[+1] | 2.810[+1] | 1.878[+1] | 1.947[+1] | 2.049[+1] |
| 0.01 | 3.844[+1] | 4.254[+1] | 4.928[+1] | 2.505[+1] | 2.709[+1] | 2.813[+1] | 1.879[+1] | 1.948[+1] | 2.050[+1] |
| 0.02 | 3.861[+1] | 4.277[+1] | 4.967[+1] | 2.511[+1] | 2.716[+1] | 2.821[+1] | 1.882[+1] | 1.952[+1] | 2.054[+1] |
| 0.04 | 3.931[+1] | 4.374[+1] | 5.136[+1] | 2.533[+1] | 2.745[+1] | 2.855[+1] | 1.893[+1] | 1.965[+1] | 2.069[+1] |
| 0.06 | 4.055[+1] | 4.551[+1] | 5.468[+1] | 2.573[+1] | 2.796[+1] | 2.914[+1] | 1.913[+1] | 1.987[+1] | 2.096[+1] |
| 0.08 | 4.249[+1] | 4.839[+1] | 6.110[+1] | 2.631[+1] | 2.871[+1] | 3.004[+1] | 1.942[+1] | 2.019[+1] | 2.135[+1] |
| 0.10 | 4.540[+1] | 5.312[+1] | 7.842[+1] | 2.710[+1] | 2.977[+1] | 3.132[+1] | 1.981[+1] | 2.063[+1] | 2.189[+1] |
| 0.12 | 4.991[+1] | 6.183[+1] | | 2.817[+1] | 3.123[+1] | 3.313[+1] | 2.031[+1] | 2.121[+1] | 2.261[+1] |
| 0.14 | 5.761[+1] | 8.669[+1] | | 2.958[+1] | 3.325[+1] | 3.580[+1] | 2.095[+1] | 2.195[+1] | 2.355[+1] |
| 0.16 | 7.506[+1] | | | 3.146[+1] | 3.617[+1] | 4.005[+1] | 2.177[+1] | 2.291[+1] | 2.481[+1] |
| 0.18 | 2.996[+2] | | | 3.408[+1] | 4.078[+1] | 4.846[+1] | 2.282[+1] | 2.416[+1] | 2.656[+1] |
| 0.20 | | | | 3.792[+1] | 4.967[+1] | 8.575[+1] | 2.418[+1] | 2.586[+1] | 2.913[+1] |
| 0.22 | | | | 4.432[+1] | 8.346[+1] | | 2.601[+1] | 2.827[+1] | 3.348[+1] |
| 0.24 | | | | 5.859[+1] | | | 2.865[+1] | 3.210[+1] | 4.399[+1] |
| 0.26 | | | | 1.867[+2] | | | 3.289[+1] | 3.985[+1] | 6.244[+2] |
| 0.28 | | | | | | | 4.178[+1] | 7.616[+1] | |
| 0.30 | | | | | | | 9.042[+1] | | |

[a] Values listed are with 15-parameter calculation.
[b] $[\pm n] = 10^{\pm n}$.

with the experimental values, we first find out the possible allowed spectroscopic multiplets and calculate the energy difference of each term from the ground state. Our transition energies are usually compared with the minimum of such spectroscopic values. The final state is then assigned. In this sense the assignment is tentative. But the wave functions obtained from our calculations can be used as approximate representations for all the allowed multiplets. In Table III we have listed the transition energies of all cases under study. Spectroscopic values[58,59] are also listed for comparison. In all cases where data exist, we find reasonable agreement. The theory does not produce a specific bound to the transition energies, and this has been reflected in Table III.

In case of Si in $^3P$ state we are unable to find $3p \rightarrow 5d$ and $3p \rightarrow 6d$ resonances. The reason behind this may be the following: From extrapolation of our observed transition energies of $3p \rightarrow 3d$ and $3p \rightarrow 4d$, we estimate the transition energy of $3p \rightarrow 5d$ to lie around $\omega \simeq 0.27$ a.u. $3p \rightarrow 6d$ will lie little beyond this value. However, at $\omega \sim 0.272$ a.u. we notice an inner-shell excitation $3s^2 3p^2(^3P) \rightarrow 3s3p^3(^3D)$ for Si. The spectroscopic value[58] is $\sim 0.222$ a.u. Although we obtain inner-shell excitations in our calculation,[43] the position of such a transition is not accurately obtained because our method does not include configuration interactions that are necessary for accurate calculation of such states. Usually in our calculation the position of such a pole is shifted toward a higher-frequency region. However, the general features of such a transition are obtained. Particularly we notice that the $3p$ orbital obtained from the excitation of the $3s$ orbital behaves very similar to that of the ground $3p$ orbital of Clementi and Roetti.[52] This feature was also noted earlier.[43] The polarizability contribution from the $3s$ shell is dominant around this region and shows oscillatory behavior. For a general idea we plotted in Fig. 1 the

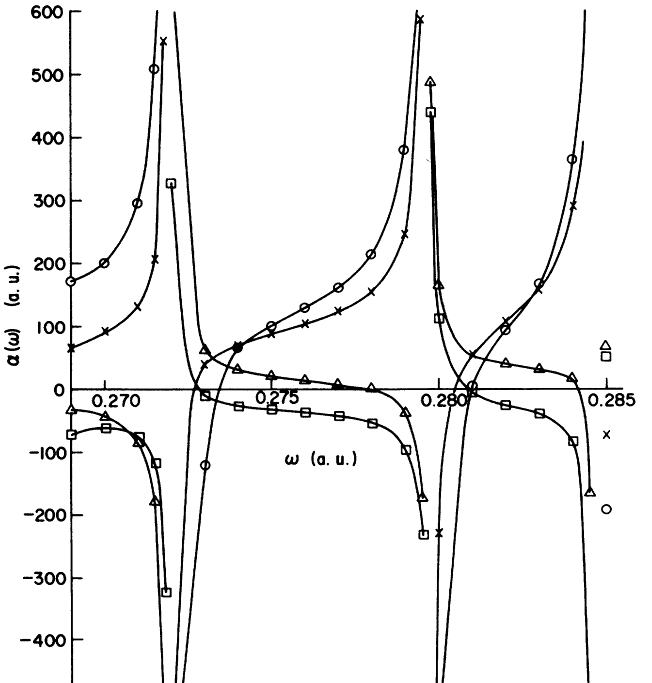

FIG. 1. Plot of shell-wise contribution of $\alpha(\omega)$ vs $\omega$ for Si in $^3P$ state near the first internal excitation region. ○, $\alpha(\omega)_{3s \rightarrow np}$; □, $\alpha(\omega)_{3p \rightarrow ns}$; △, $\alpha(\omega)_{3p \rightarrow nd}$; ×, $\alpha(\omega)_{\text{tot}}$.

TABLE III. Transition energies, oscillator strengths, and quantum defect values of the Rydberg states of Si, P, and S as obtained from frequency-dependent calculation.

| | | Transition energy (a.u.) | | Oscillator strength (a.u.) | | Quantum defect | |
|---|---|---|---|---|---|---|---|
| Atom (1) | Transition (2) | Present[a] (3) | Expt.[b] (4) | Present (5) | Other results (6) | Present (7) | Expt. (8) |
| Si | $3p^2(^3P)\rightarrow 3p4s(^3P)$ | 0.1825 | 0.1813 | 0.226 | 0.155,[c] 0.13[d] | 1.911 | 1.944 |
| | $\rightarrow 3p5s(^3P)$ | 0.2458 | 0.2477 | 0.033 | | 1.876 | 1.896 |
| | $\rightarrow 3p6s(^3P)$ | 0.2681 | 0.2703 | 0.012 | | 1.845 | 1.869 |
| | $\rightarrow 3p3d(^3D)$ | 0.2291 | 0.2064 | 0.321 | 0.270[e] | 0.287 | 0.684 |
| | $\rightarrow 3p4d(^3D)$ | 0.2579 | 0.2470 | 0.0037 | | 0.466 | 0.917 |
| Si | $3p^2(^1D)\rightarrow 3p4s(^1P)$ | 0.1549 | 0.1581 | 0.157 | 0.131[c] | 1.830 | 1.895 |
| | $\rightarrow 3p5s(^1P)$ | 0.2118 | 0.2213 | 0.042 | | 1.812 | 1.825 |
| | $\rightarrow 3p6s(^1P)$ | 0.2330 | 0.2430 | 0.018 | | 1.773 | 1.767 |
| | $\rightarrow 3p3d(^1F)$ | 0.2049 | 0.2144 | 0.320 | 0.345[e] | 0.014 | 0.025 |
| | $\rightarrow 3p4d(^1F)$ | 0.2292 | 0.2396 | 0.134 | | 0.033 | 0.003 |
| | $\rightarrow 3p5d(^1F)$ | 0.2407 | 0.2512 | 0.068 | | 0.043 | −0.038 |
| | $\rightarrow 3p6d(^1F)$ | 0.2470 | 0.2574 | 0.037 | | 0.037 | −0.086 |
| Si | $3p^2(^1S)\rightarrow 3p4s(^1P)$ | 0.1156 | 0.1166 | 0.079 | 0.100[c] | 1.702 | 1.895 |
| | $\rightarrow 3p5s(^1P)$ | 0.1642 | 0.1799 | 0.050 | | 1.703 | 1.822 |
| | $\rightarrow 3p6s(^1P)$ | 0.1838 | 0.2016 | 0.022 | | 1.648 | 1.759 |
| | $\rightarrow 3p3d(^1P)$ | 0.1606 | 0.1731 | 0.155 | 0.456[e] | −0.174 | 0.020 |
| | $\rightarrow 3p4d(^1P)$ | 0.1816 | 0.1978 | 0.083 | | −0.179 | 0.022 |
| | $\rightarrow 3p5d(^1P)$ | 0.1917 | 0.2092 | 0.057 | | −0.192 | 0.025 |
| | $\rightarrow 3p6d(^1P)$ | 0.1973 | | 0.032 | | −0.209 | |
| P | $3p^3(^4S)\rightarrow 3p^2[^3P]4s(^4P)$ | 0.2640 | 0.2557 | 0.318 | 0.307,[c] 0.20[d]<br>0.145,[e] 0.273[f] | 2.021 | 2.037 |
| | $\rightarrow 3p^2[^3P]5s(^4P)$ | 0.3369 | 0.3307 | 0.049 | | 1.982 | 1.977 |
| | $\rightarrow 3p^2[^3P]6s(^4P)$ | 0.3642 | 0.3551 | 0.041 | | 1.740 | 1.938 |
| | $\rightarrow 3p^2[^3P]3d(^4P)$ | 0.3055 | 0.3303 | 0.066 | 0.317[e] | 0.593 | −0.012 |
| | $\rightarrow 3p^2[^3P]4d(^4P)$ | 0.3606 | 0.3545 | 0.216 | | −0.009 | −0.022 |
| | $\rightarrow 3p^2[^3P]5d(^4P)$ | 0.3716 | 0.3659 | 0.122 | | 0.024 | −0.064 |
| | $\rightarrow 3p^2[^3P]6d(^4P)$ | 0.3778 | | 0.075 | | 0.022 | |
| P | $3p^3(^2D)\rightarrow 3p^2(^1D)4s(^2D)$ | 0.2307 | 0.2451 | 0.228 | 0.145,[c] 0.086[e]<br>0.113[f] | 1.959 | 2.031 |
| | $\rightarrow 3p^2(^1D)5s(^2D)$ | 0.2976 | | 0.062 | | 1.931 | |
| | $\rightarrow 3p^2(^1D)6s(^2D)$ | 0.3206 | | 0.022 | | 1.921 | |
| | $\rightarrow 3p^2(^1D)3d(^2F)$ | 0.2918 | 0.3053 | 0.303 | 0.186[f] | 0.085 | 0.304 |
| | $\rightarrow 3p^2(^1D)4d(^2F)$ | 0.3175 | | 0.134 | | 0.117 | |
| | $\rightarrow 3p^2(^1D)5d(^2F)$ | 0.3295 | | 0.065 | | 0.138 | |
| | $\rightarrow 3p^2(^1D)6d(^2F)$ | 0.3361 | | 0.033 | | 0.142 | |
| P | $3p^3(^2P)\rightarrow 3p^2(^1D)4s(^2D)$ | 0.2085 | 0.2115 | 0.171 | 0.071,[c] 0.042[f] | 1.916 | 2.031 |
| | $\rightarrow 3p^2(^1D)5s(^2D)$ | 0.2718 | | 0.072 | | 1.894 | |
| | $\rightarrow 3p^2(^1D)6s(^2D)$ | 0.2941 | | 0.030 | | 1.885 | |
| | $\rightarrow 3p^2(^1D)3d(^2D)$ | 0.2682 | 0.2892 | 0.203 | | −0.002 | −0.122 |
| | $\rightarrow 3p^2(^1D)4d(^2D)$ | 0.2925 | | 0.049 | | −0.003 | |
| | $\rightarrow 3p^2(^1D)5d(^2D)$ | 0.3037 | | 0.070 | | −0.005 | |
| | $\rightarrow 3p^2(^1D)6d(^2D)$ | 0.3099 | | 0.047 | | −0.019 | |
| S | $3p^4(^3P)\rightarrow 3p^3[^2D]4s(^3D)$ | 0.3072 | 0.3090 | 0.279 | 0.094,[c] 0.064[e]<br>0.010[f] | 2.039 | 2.107 |
| | $\rightarrow 3p^3[^2D]5s(^3D)$ | 0.3821 | 0.3904 | 0.081 | | 1.990 | 2.066 |
| | $\rightarrow 3p^3[^2D]6s(^3D)$ | 0.4060 | 0.4164 | 0.026 | | 2.001 | 2.053 |
| | $\rightarrow 3p^3[^2D]3d(^3D)$ | 0.3776 | 0.3901 | 0.247 | 0.042[e] | 0.105 | 0.074 |
| | $\rightarrow 3p^3[^2D]4d(^3D)$ | 0.4032 | | 0.111 | | 0.166 | |
| | $\rightarrow 3p^3[^2D]5d(^3D)$ | 0.4152 | | 0.040 | | 0.241 | |
| | $\rightarrow 3p^3[^2D]6d(^3D)$ | 0.4218 | | 0.018 | | 0.315 | |

TABLE III. (*Continued*).

| | | Transition energy (a.u.) | | Oscillator strength (a.u.) | | Quantum defect | |
|---|---|---|---|---|---|---|---|
| Atom (1) | Transition (2) | Present[a] (3) | Expt.[b] (4) | Present (5) | Other results (6) | Present (7) | Expt. (8) |
| S | $3p^4(^1D)\rightarrow 3p^3[^2D]4s(^1D)$ | 0.2886 | 0.2734 | 0.240 | 0.240,[c] 0.202[e]<br>0.155[f] | 2.013 | 2.061 |
| | $\rightarrow 3p^3[^2D]5s(^1D)$ | 0.3611 | 0.3502 | 0.102 | | 1.963 | 2.017 |
| | $\rightarrow 3p^3[^2D]6s(^1D)$ | 0.3844 | 0.3750 | 0.042 | | 1.978 | 2.010 |
| | $\rightarrow 3p^3[^2D]3d(^1D)$ | 0.3583 | 0.3480 | 0.183 | 0.095[e] | 0.038 | 0.074 |
| | $\rightarrow 3p^3[^2D]4d(^1D)$ | 0.3834 | 0.3738 | 0.117 | | 0.037 | 0.084 |
| | $\rightarrow 3p^3[^2D]5d(^1D)$ | 0.3952 | 0.3856 | 0.076 | | 0.009 | 0.097 |
| | $\rightarrow 3p^3[^2D]6d(^1D)$ | 0.4013 | 0.3921 | 0.037 | | 0.026 | 0.087 |
| S | $3p^4(^1S)\rightarrow 3p^3[^2P]4s(^1P)$ | 0.2606 | 0.2557 | 0.187 | 0.22,[c] 0.215[e]<br>0.164[f] | 1.975 | 2.081 |
| | $\rightarrow 3p^3[^2P]5s(^1P)$ | 0.3298 | 0.3347 | 0.114 | | 1.921 | 2.033 |
| | $\rightarrow 3p^3[^2P]6s(^1P)$ | 0.3523 | | 0.066 | | 1.938 | |
| | $\rightarrow 3p^3[^2P]3d(^1P)$ | 0.3275 | 0.3358 | 0.112 | 0.048[e] | −0.013 | 0.004 |
| | $\rightarrow 3p^3[^2P]4d(^1P)$ | 0.3517 | | 0.097 | | −0.028 | |
| | $\rightarrow 3p^3[^2P]5d(^1P)$ | 0.3632 | | 0.068 | | −0.081 | |
| | $\rightarrow 3p^3[^2P]6d(^1P)$ | 0.3689 | | 0.039 | | −0.046 | |

[a] Fifteen-parameter results.
[b] References 58 and 59.
[c] Reference 60.
[d] Reference 61.
[e] Reference 39; we have used $g$ factors using *LS*-coupling model.
[f] Reference 41.

contribution of $\alpha(\omega)_{3s\rightarrow np}$, $\alpha(\omega)_{3p\rightarrow ns}$, $\alpha(\omega)_{3p\rightarrow nd}$, and total $\alpha(\omega)$ (the subscript $d$ is omitted) against $\omega$ around and beyond the region $\omega\sim 0.27$ a.u.

It is clearly observed that $\alpha(\omega)_{3s\rightarrow np}$ changes much faster than all other contributions and passes through the first pole corresponding to $3s\rightarrow 3p$ around $\omega\simeq 0.272$ a.u. Oscillatory behavior of $\alpha(\omega)$ is observed beyond this region, thus effectively masking all other transitions in that region. For the other states $^1D$ and $^1S$, the internal excitation frequency possibly lies much higher up, and we are able to obtain all the transitions under study. The internal excitations are also obtained for P in $^4S$ and S in $^3P$ states. But the transition energies are well off from the spectroscopic values, and we have not included them in the table. The functional behavior of different Rydberg orbitals are consistent with respect to their number of nodes and diffuseness depending upon their excitation energy. For S, except for the transition $3p\rightarrow 4s$, all other transition energies lie beyond the first ionization limit of $S(^3P)$ going over to the ionic state $S^+(^4S)$. Simple analytic representations for all such orbitals have been found and may be obtained from the authors on request.

Table III also shows the oscillator strength values obtained from our calculation. For comparison other results[39,41,60,61] are also listed. Only a limited number of calculations, mostly confined towards lower-lying transitions, are available. Although for Si, oscillator strengths seem to be reasonable; for P and S the agreement is generally poor. We believe poor agreement is due to neglect of configuration interactions, which play a crucial role in determining accurate oscillator strengths. This has been discussed in detail earlier.[36–39,41] The role of configuration interactions is also reflected in our calculation.

We find the dipolar matrix elements originating from $3s\rightarrow np$ excitations rather large and of opposite sign to that originating from $3p\rightarrow ns$ and $nd$ excitations. This results in large cancellation affecting the oscillator strength values. For example, for P in the transition $3p^3(^4S)\rightarrow 3p^2[^3P]3d(^4P)$, the oscillator strength obtained is very low (0.066) compared to the CI result 0.317 of Fawcett.[39] Ho and Henry[41] have not listed the oscillator strength for this particular transition. To check whether or not low oscillator strength comes from a basis set, we performed the same calculation with a completely different basis set which is more adapted to this transition. The transition energy and oscillator strength remain unaltered. In this case we find at the pole position the contribution of $\alpha(\omega)_{3s\rightarrow np}\sim -1.519\times 10^5$ a.u, compared to $\alpha(\omega)_{3p\rightarrow ns}\sim 3.499\times 10^4$ a.u. and $\alpha(\omega)_{3p\rightarrow nd}\sim 1.543\times 10^5$ a.u., resulting in large cancellation in total polarizability value.

We calculate oscillator strength here using a standard formula[43,45] in terms of total polarizability values. A severe cancellation effect alters the total polarizability values and thereby may affect the calculated oscillator strengths considerably. In this particular case it affects the pole position also. A thorough discussion on the effect of electron correlation on the oscillator strengths of P- and S-like atoms was given by Ho and Henry.[41] They clearly indicated the possibility of an order of magnitude change of oscillator strength values.

We have also calculated the effective quantum number $n^*$ of the Rydberg orbitals using the formula $n^*=1/\sqrt{2\varepsilon}$, where $\varepsilon$ is the ionization potential of the Rydberg orbital. Quantum defect values $\Delta=n-n^*$ have been evaluated and the results are displayed in Table III along with those obtained spectroscopically.[58,59] We find very reasonable agreement in all cases except for the transition $3p^3(^4S)\rightarrow 3p^2[^3P]3d(^4P)$ of phosporous. As was discussed earlier this is probably due to a shift of the transition energy because of a very large contribution of $\alpha(\omega)$ from $3s\rightarrow np$ excitations. In a number of cases quantum defect values show negative values. This feature has been also observed experimentally in a few cases.

## IV. CONCLUSION

From a detailed study performed earlier[43] and the present one for the transitions involving electrons in a partially filled $3p$ shell, we notice that the present method, though simple, can predict the transition energies and quantum defect values fairly reasonably. Simple analytic representations of Rydberg states can be obtained for different transition schemes. Transition properties, like oscillator strengths, depend critically on the interaction between different configurations; particularly, single configurations excited from an inner shell are important. The oscillator strengths are reasonable where such configuration-interaction effects are less important. This method may, therefore, be more suitable for the study of the excitation properties of highly stripped isoelectronic ions. Such a study is very useful for high-temperature plasma diagnostics.

## ACKNOWLEDGMENTS

One of us (P.K.M.) is grateful to the Japan Society for the Promotion of Science (JSPS) for providing him support to work in Japan. The computation was done using a HITAC-M682H computer at the Hokkaido University.

---

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

[1] L. Goldberg, E. A. Müller, and L. H. Aller, Astrophys. J. Suppl. Ser. **5**, 1 (1960).

[2] A. H. Gabriel and C. Jordan, Mon. Not. R. Astron. Soc. **145**, 241 (1969).

[3] A. H. Gabriel and C. Jordan in *Case Studies in Atomic Collision Physics II,* (North-Holland, Amsterdam, 1972), p. 221.

[4] P. L. Dufton, A. Hibbert, A. E. Kingston, and J. A. Tulley, Mon. Not. R. Astron. Soc. **202**, 145 (1983).

[5] B. E. Patchett, K. Norman, A. H. Gabriel, and J. L. Culhane, Space. Sci. Rev. **29**, 431 (1981).

[6] J. M. Shull, T. P. Snow, and D. G. York, Astrophys. J. **246**, 549 (1981).

[7] R. C. Bohlin, J. K. Hill, E. B. Jenkins, B. D. Savage, T. P. Snow, L. Spitzer, and D. G. York, Astrophys. J. Suppl. Ser. **51**, 277 (1983).

[8] A. L. Broadfoot *et al.*, Science **204**, 979 (1979).

[9] D. E. Shemanski, Astrophys. J. **236**, 1043 (1980).

[10] D. F. Strobel and J. Davis, Astrophys. J. **238**, L49 (1980).

[11] H. W. Moos and J. T. Clarke, Astrophys. J. **247**, 354 (1981).

[12] H. W. Moos, T. E. Skinner, S. T. Durrance, and P. D. Feldman, Astrophys. J. **294**, 369 (1985).

[13] S. T. Durrance, P. D. Feldman, and H. A. Weaver, Astrophys. J. **267**, L125 (1983).

[14] G. Tondello, Astrophys. J. **172**, 771 (1972).

[15] G. Johnsson and H. Lundberg, Z. Phys. A **313**, 151 (1983).

[16] G. Johnsson, S. Kroll, H. Lundberg, and S. Svanberg, Z. Phys. A **316**, 259 (1984).

[17] E. P. Burrman, A. Donzelmann, J. E. Hansen, and C. Snoek, Astron. Astrophys. **164**, 179 (1986).

[18] E. Ya. Kononov, K. N. Koshelev, L. I. Podobedova, S. V. Chekalin, and S. S. Churilov, J. Phys. B **9**, 565 (1976).

[19] V. A. Boiko, A. Ya. Faenov, and S. A. Pikuz, J. Quant. Spectrosc. Radiat. Transfer **19**, 11 (1978).

[20] G. E. Bromage, R. D. Cowan, B. C. Fawcett, and A. Ridgeley, J. Opt. Soc. Am. **68**, 48 (1978).

[21] E. Hinnov, Phys. Rev. A **14**, 1533 (1976).

[22] E. Hinnov, Astrophys. J. **230**, L179 (1979).

[23] S. Suckewer and E. Hinnov, Phys. Rev. A **20**, 578 (1979).

[24] F. P. Keenan, S. S. Tayal, and A. E. Kingston, Solar Phys. **92**, 75 (1984).

[25] D. A. Doschek, U. Feldman, and J. F. Seely, Mon. Not. R. Astron. Soc. **217**, 317 (1985).

[26] S. Feneuille and P. Jacquinot, Adv. At. Mol. Phys. **17**, 126 (1981).

[27] *Rydberg States of Atoms and Molecules,* edited by R. F. Stebbings and F. B. Dunning (Cambridge University Press, Cambridge, England, 1982).

[28] E. De. Prunele and J. Pascale, J. Phys. B **12**, 2511 (1979).

[29] T. F. Gallagher, S. A. Edelstein, and R. M. Mill, Phys. Rev. A **15**, 1945 (1977).

[30] R. Kachru, T. F. Gallagher, F. Gounand, K. A. Safinya, and W. Sandner, Phys. Rev. A **27**, 795 (1983).

[31] A. P. Hickman, Phys. Rev. A **28**, 111 (1983).

[32] M. P. Slusher, C. Higgs, K. A. Smith, F. B. Dunning, and R. F. Stebbings, Phys. Rev. A **26**, 1350 (1982).

[33] P. S. Ganas, Physica **111C**, 365 (1981).

[34] P. S. Ganas, Phys. Lett. **87A**, 394 (1982).

[35] D. S. Ginter and M. L. Ginter, J. Chem. Phys. **86**, 1437 (1986).

[36] H. Tatewaki, Phys. Rev. A **18**, 1826 (1978).

[37] H. Tatewaki and F. Sasaki, Phys. Rev. A **18**, 1837 (1978).

[38] R. D. Cowan and J. E. Hansen, J. Opt. Soc. Am. **71**, 60 (1981).

[39] B. C. Fawcett, At. Data. Nucl. Data Tables **35**, 186 (1986); **35**, 204 (1986); **36**, 129 (1987).

[40] Y. K. Ho and R. J. W. Henry, Astrophys. J. **290**, 424 (1986).

[41] Y. K. Ho and R. J. W. Henry, Phys. Scr. **35**, 831 (1987).

[42] E. Biemont, Phys. Scr. **33**, 324 (1986).

[43] P. K. Mukherjee, K. Ohtsuki, and K. Ohno, Theor. Chim. Acta **74**, 431 (1988).

[44] P. K. Mukherjee and R. K. Moitra, J. Phys. B **11**, 2813 (1978).

[45] B. Kundu, D. Ray, and P. K. Mukherjee, Phys. Rev. A **34**, 62 (1986).

[46] B. Kundu and P. K. Mukherjee, Phys. Rev. A **35**, 980 (1987).

[47] H. P. Ray, A. Gupta, and P. K. Mukherjee, Int. J. Quantum Chem. **9**, 75 (1975).

[48] C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960).

[49] T. C. Caves and M. Karplus, J. Chem. Phys. **50**, 3649 (1969).

[50] C. W. McCurdy, T. N. Rescigno, D. L. Yeager, and V. McKoy, in *Methods of Electronic Structure Theory,* edited by H. F. Schaefer, III (Plenum, New York, 1977), p. 339.

[51] J. Oddershede, Adv. Quantum Chem. **11**, 275 (1978).

[52] E. Clementi and C. Roetti, At. Data Nucl. Data Tables **14**, 177 (1974).

[53] T. M. Miller and B. Bederson, Adv. At. Mol. Phys. **13**, 1 (1977).

[54] H. P. Roy, A. Gupta, and P. K. Mukherjee, Int. J. Quantum Chem. **12**, 1 (1977).

[55] R. F. Stewart, Mol. Phys. **30**, 1283 (1975).

[56] S. Fraga, K. M. S. Saxena, and B. W. N. Lo, At. Data **3**, 323 (1971).

[57] E. A. Reinsch and W. Meyer, Phys. Rev. A **14**, 915 (1976).

[58] C. E. Moore, *Atomic Energy Levels,* Natl. Bur. Stand. (U.S.) Circ. No. 467 (U. S. GPO, Washington, D. C., 1949), Vol. 1.

[59] S. Bashkin and J. O. Stoner, Jr., *Atomic Energy Levels and Grotrian Diagrams* (North-Holland, Amsterdam, 1975), Vols. 1 and 2 (1978).

[60] W. L. Wiese, M. W. Smith, and B. M. Miles, *Atomic Transition Probabilities,* Natl. Bur. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.) Circ. No. 22 (U.S. GPO, Washington, D.C., 1969), Vol. 2.

[61] P. F. Gruzdev and V. K. Prokofev, Opt. Spectrosc. **21**, 151 (1966).