



Ionization of P Atom, P₂ and PX (X = H, C, N, O) Molecules by Electron Impact: Theoretical Studies

Research Article

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Abstract. Being a biogenic element atomic Phosphorus is one of the significant constituents of the universe [1]. Gulick [2] found a pivotal role of phosphorus in the origin of life. The phosphorus-containing molecules like PH, PC and PN radicals, have been observed in interstellar gas clouds [3–5] and they are proposed to be present under appropriate conditions. Phosphorous hydrides having numerous applications, are detected in cool stellar atmosphere [6] and circumstellar envelopes. Thus, the present paper addresses the electron impact processes of atomic phosphorus and its diatomic compounds. Ground and metastable states of Atomic P give rise to the probability of presence of metastable state in the atomic beam used for cross section measurement [7]. We have employed the well-known Spherical Complex Optical Potential (SCOP) formalism to calculate total inelastic cross sections. The semi-empirical CSP-*ic* method is used to extract total ionization cross section Q_{ion} from total inelastic cross section [8]. A variant CSP-*ic* approach is also attempted for these targets.

Keywords. Phosphorus; Electron impact ionization; Complex potential

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1. Introduction

Phosphorus atom is member of group 15 in the periodic table, wherein Nitrogen is the lightest atom in this column. This element exists in several forms, of which white and red are the best known [1]. The present paper reports comprehensive theoretical investigations on electron scattering with atomic Phosphorus and molecules containing Phosphorus viz., PX (X = H, C, N, O). Interest in atomic P arises here due to a discrepancy between theory and measurements in Q_{ion} , and to the reason as to why it happens. The diatomic molecules considered presently are less studied targets, for which scattering experiments seem to be difficult.

In the present paper we have used the spherical Complex Potential methodology, extended for ionization contribution [8–10] to calculate various total cross sections of atomic and molecular Phosphorus by electron impact from about 15 to 2000 eV. In our previous papers [8–10], we have successfully calculated electron impact ionization cross sections of several atomic and molecular targets using the methodology SCOP together with Complex Scattering Potential-ionization contribution (CSP-*ic*) methodology. In the present theoretical calculation the target charge density, bondlength and ionization potential are the basic input parameters.

2. Theoretical Methodology

In the following text, the total (complete) cross section of electron-atom/molecule collisions is denoted by Q_T , and is the sum of total elastic cross section Q_{el} and total inelastic cross section Q_{inel} . Thus

$$Q_T(E_i) = Q_{el}(E_i) + Q_{inel}(E_i). \quad (1)$$

Further,

$$Q_{inel}(E_i) = \Sigma Q_{ion}(E_i) + \Sigma Q_{exc}(E_i), \quad (2)$$

where E_i is the incident electron energy. The quantity $\Sigma Q_{ion}(E_i)$ in the above equation shows the sum-total of first, second etc ionization cross sections of the target. For simplicity we denote the first term by Q_{ion} . The quantity $\Sigma Q_{exc}(E_i)$ shows the summed total electronic excitation cross sections. The quantity Q_{inel} does not include rotational – vibrational excitations. With this background let us outline how the total cross sections Q_{ion} of electron scattering from these targets are deduced from Q_{inel} within a broad frame-work of complex potential formalism. In the present range of electron energy, many scattering channels that lead to discrete as well as continuum transitions in the target are open. Therefore. we represent the electron-atom/molecule system by a complex potential, $V(r, E_i) = V_R(r, E_i) + iV_I(r, E_i)$, such that

$$V_R(r, E_i) = V_{st}(r) + V_{ex}(r, E_i) + V_P(r, E_i). \quad (3)$$

The RHS three terms of the equation (3) represent the static, the exchange and the polarization potentials respectively. These are obtained from the spherically averaged charge-density $\rho(r)$ of the target, where r is the radial distance of the incident electron. The spherically averaged

atomic and molecular charge density $\rho(r)$ is determined from the constituent atomic charge densities derived from the atomic wave functions of [11].

Now, the imaginary term V_I of the complex potential, also called the absorption potential V_{abs} is adopted here in a well-known non-empirical quasi-free model form given by Staszeweska *et al.* [11] (see also [12], [13]). Thus,

$$V_{abs}(r, E_i) = -\rho(r) \sqrt{\frac{T_{loc}}{2}} \cdot \left(\frac{8\pi}{10k_F^3 E_i} \right) \cdot \theta(p^2 - k_F^2 - 2\Delta) \cdot (A_1 + A_2 + A_3). \quad (4)$$

The local kinetic energy of the incident electron is denoted by T_{loc} . In equation (4), $p^2 = 2E_i$, $k_F = [3\pi^2 \rho(r)]^{1/3}$ is the Fermi wave vector and Δ is an energy parameter. Further $\theta(x)$ is the Heaviside unit step-function, such that $\theta(x) = 1$ for $x \geq 0$, and is zero otherwise. The dynamic functions A_1 , A_2 and A_3 occurring in the equation (4) are specific functions of the quantities $\rho(r)$, I , Δ and E_i . Detailed expressions of these functions are given in [11] and also in [12, 13]. The energy parameter Δ is crucial, since it determines a threshold below which $V_{abs} = 0$, and the ionization or excitation is prevented energetically. We have modified the original absorption model, by considering Δ as a slowly varying function of E_i around I . The justification for the same is discussed in [14–17]. Briefly, a preliminary calculation is done with a fixed value $\Delta = I$, but the variable Δ accounts for the screening of the absorption potential in the target charge-cloud region and also yields better agreement with experimental and other data in many cases. The Schrödinger equation is set up with our modified V_{abs} , and find the complex phase shifts $\delta_l = \text{Re } \delta_l + i \text{Im } \delta_l$ for various partial waves l by following the Variable Phase Approach of Calogero [18].

The total elastic (Q_{el}), inelastic (Q_{inel}) and total (complete) cross sections (Q_T) are generated from the S-matrix as per the standard expressions given in [19]. Now, electron impact ionization corresponds to infinitely many open channels, as against the electronic excitation, which comes from a small number of discrete scattering channels. Therefore, starting from threshold I the ionization channel becomes dominating gradually as the incident energy exceeds I , thereby making Q_{ion} the main contribution to Q_{inel} . Thus from equation (2), we have in general

$$Q_{inel}(E_i) \geq Q_{ion}(E_i). \quad (5)$$

There is no rigorous way to project out Q_{ion} from Q_{inel} . But in order to determine Q_{ion} from Q_{inel} , a reasonable approximation can be evolved by considering a ratio function,

$$R(E_i) = \frac{Q_{ion}(E_i)}{Q_{inel}(E_i)}. \quad (6)$$

Perhaps a first ever estimate of ionization in relation to excitation processes was made, for water molecules, by Turner *et al.* [20].

The usual complex potential calculations include ionization contribution within the inelastic cross section. In order to deduce the said contribution, we have introduced a method based on the equation (6). In the CSP-ic method, the energy dependence of $R(E_i)$ is given by the following

relation [14–17].

$$R(E_i) = 1 - C_1 \left[\frac{C_2}{U+a} + \frac{\ln(U)}{U} \right], \quad (7)$$

where the incident energy is scaled to the ionization potential I through a dimensionless variable,

$$U = \frac{E_i}{I}. \quad (8)$$

Equation (7) involves dimensionless parameters C_1 , C_2 and a , which are determined by imposing three conditions on the function $R(E_i)$ as discussed in our papers [14–17]. Briefly, we have $R = 0$ at the ionization threshold and the ratio takes up asymptotic value $R' \approx 1$ at high energies typically above 1000 eV, in view of equation (7). The third condition on R arises from its behaviour near the peak of ionization, and is expressed in the following manner.

$$R(E_i) = \begin{cases} 0, & \text{at } E_i = I, \\ R_p, & \text{at } E_i = E_p, \\ R', & \text{for } E_i \gg E_p. \end{cases} \quad (9)$$

Here, E_p stands for the incident energy at which our calculated inelastic cross section Q_{inel} attains its maximum. We consider $R_p \cong 0.7$ for the value of the ratio R at $E_i = E_p$. The choice of this value is approximate but physically justified. The peak position E_p occurs at an incident energy where the dominant discrete excitation cross sections are on the wane, while the ionization cross section is rising fast, suggesting that the R_p value should be above 0.5 but still below 1. This behavior is attributed to the faster fall of the first term $\sum Q_{exc}$ in equation (2). An exact theoretical evaluation of R_p does not seem to be possible, but one can try to see the effect of a small change in this value. The choice of R_p in equation (9) is not rigorous and it introduces uncertainty in the final results. From equation (8) at high energies, the ratio R' approaches unity which is physically supported by the low ionization cross sections in the same energy region. We employ the three conditions on R to evaluate the three parameters of equation (7) and hence deduce the Q_{ion} from the calculated Q_{inel} by using equation (6). Thus, the method of complex potential coupled with ionization contribution to inelastic scattering as explained above offers the determination of different total cross sections Q_T , Q_{inel} and Q_{ion} along with a useful estimate on electronic excitations in terms of the summed cross section $\sum Q_{exc}$. All the cross sections are examined here as functions of incident electron energy.

3. Results and Discussion

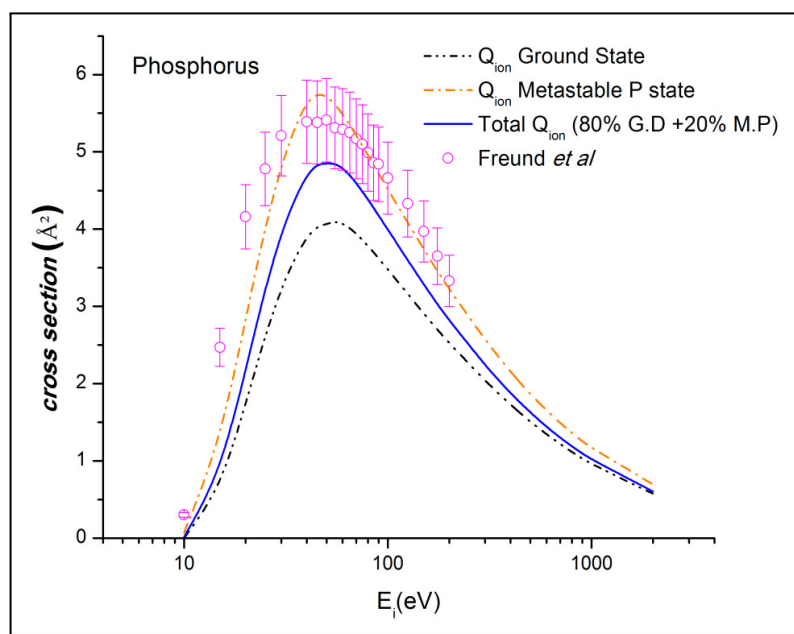
It is appropriate to calculate the ionization cross sections of electron scattering from P, P₂, PH, PC and PN targets in the same theoretical formulation, as has been done presently. The present work is also important in view of the energy range in which ionization is taking place along with elastic scattering as well as electronic excitations. Various input properties of the targets are shown in Table 1.

Table 1. Various properties of the present targets

Property	P	P ₂	PH	PC	PN	PO
First Ionization energy I (eV)	10.48	10.53	10.26	10.5	11.88	8.39
Bond length (Å)	-	1.89	1.42	1.73	1.49	1.47

Atomic Phosphorus

In Figure 1, we have calculated the total ionization cross sections for atomic P in its ground state as well as the metastable state. Phosphorus atoms have ⁴S, ²P and ²D terms for ground state in which electron can be found. For this reason Santos and Parente [21] have calculated the ionization cross sections of Phosphorus atom for their ground state as well as their other excited states. They assumed that in the experimental beam, 60% phosphorus atoms were in their ground state ⁴S and 40% in the excited metastable ²P state. They found well agreement with experimental measurements of Freund *et al.* [7]. The ionization potential for ground ⁴S and ²P state is 10.49 and 8.16 eV, respectively. However, this was an effort to bring about agreement of their theory [24] with the only experiment [7]. We have checked the metastable fraction in our method. We have taken 80 % phosphorus atoms in their ground state and 20 % atoms in excited ²P state, which seems to be reasonable. It appears that 40% atom in ²P state is rather larger fraction, and the experiment [7] does not spell out this clearly. Our results are well matched with Freund *et al.* [7] at peak position as shown in Figure 1. Notably, the present results show the Q_{ion} results (Figure 1) for P atoms all in the ground state.

**Figure 1.** Total ionization cross sections of Phosphorus atom by electron impact

Molecular targets

P₂

Not much literature is available on the ionization cross sections for the exotic P₂ molecule. Molecular properties of the present molecular targets are listed in Table 1. Monnon *et al.* [22] have measured direct ionization and dissociative ionization cross section of P₂ molecule and these are the only measured data available till date. Bettaga *et al.* [23] have computed elastic cross section for electron scattering at low energy implementing Schwinger Multichannel Method with Pseudopotentials. Scott [24] has calculated peak of ionization cross sections of this molecule applying the *binary-encounter-Bethe* (BEB) method and used effective core potential. Here we discuss our electron impact ionization cross sections of these exotic species. The cross sections Q_{ion} of these molecular targets are exhibited in Figure 2. The sequence shown in Figure 2 appears satisfactory and has broad peak. Adding the cross section of atomic P twice, we obtain the cross section of P₂, in a method called *Independent Atom Model* (IAM). While the IAM overestimates the cross sections the present single-centre results are satisfactory.

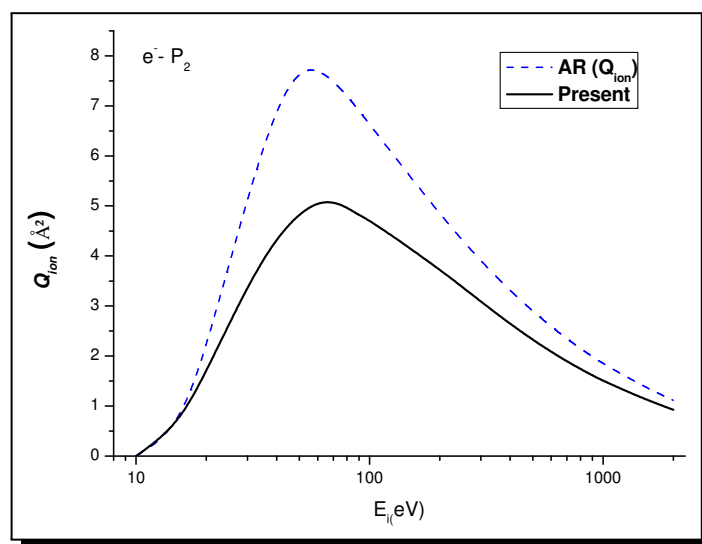


Figure 2. Total ionization cross sections (in Å²) of P₂ molecule and AR (Q_{ion}) by electron impact

PH, PC, PN and PO

Next, we turn to describe our calculated data on a set of phosphorous compounds. We have employed the SCOP plus CSP-*ic* formalism to calculate total inelastic cross sections.

The present cross sections of electron scattering with PH, PC, PN and PO molecule as shown in Figures 3, 4, 5 and 6. In all these figures the topmost Q_{ion} curves are the data generated from simple AR, which are on the higher side as expected. In Figure 3, the present CSP-*ic* single-centre values are compared with atomic P cross sections. For electron scattering on PC target our data are shown in Figure 4, and the comparison is made with AR again. Similar comparisons are made on the targets PN and PO in Figures 5 and 6, respectively.

The peak Q_{ion} values of the molecules are in accordance with their molecular bond lengths. For the comparison purpose, we have also applied simple additivity rule. The present CSP-ic results (with $R_p = 0.70$) are lower than the additivity values and phosphorus results, and that is expected on theoretical grounds. There are no other comparison data in PH, PC, PN and PO molecules.

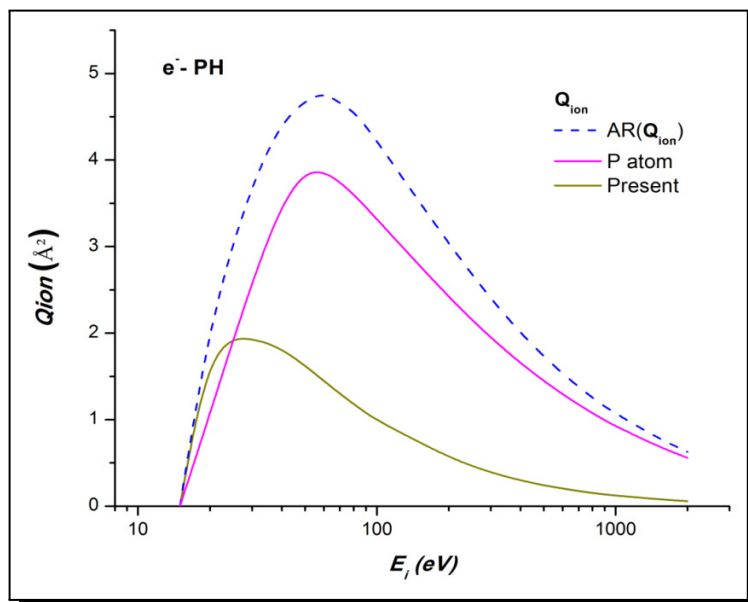


Figure 3. Total ionization cross sections (in Å²) of PH molecule and AR (Q_{ion}) by electron impact

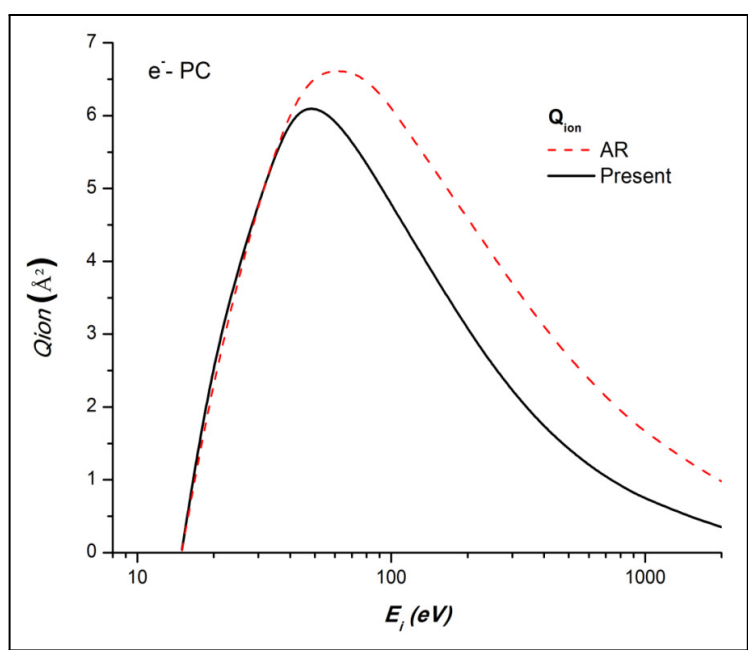


Figure 4. Total ionization cross sections (in Å²) of PC molecule and AR (Q_{ion}) by electron impact

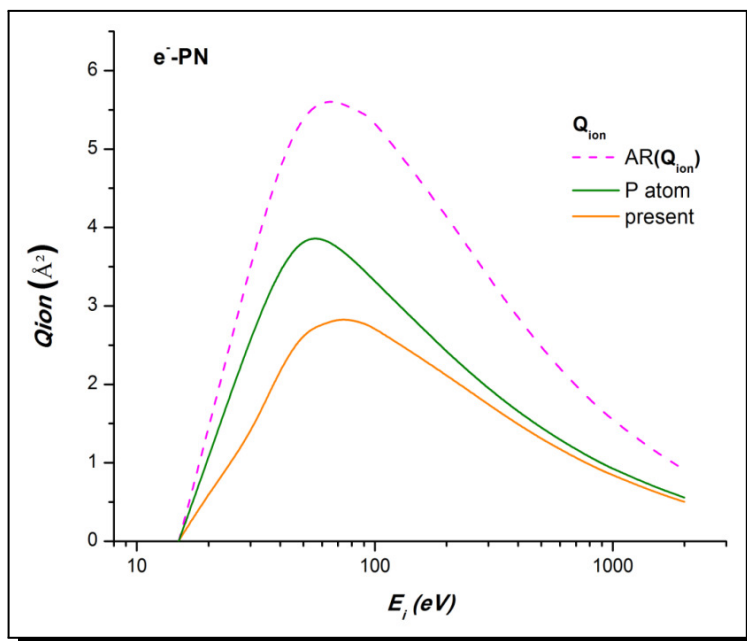


Figure 5. Total ionization cross sections (in Å²) of PN molecule and AR (Q_{ion}) by electron impa

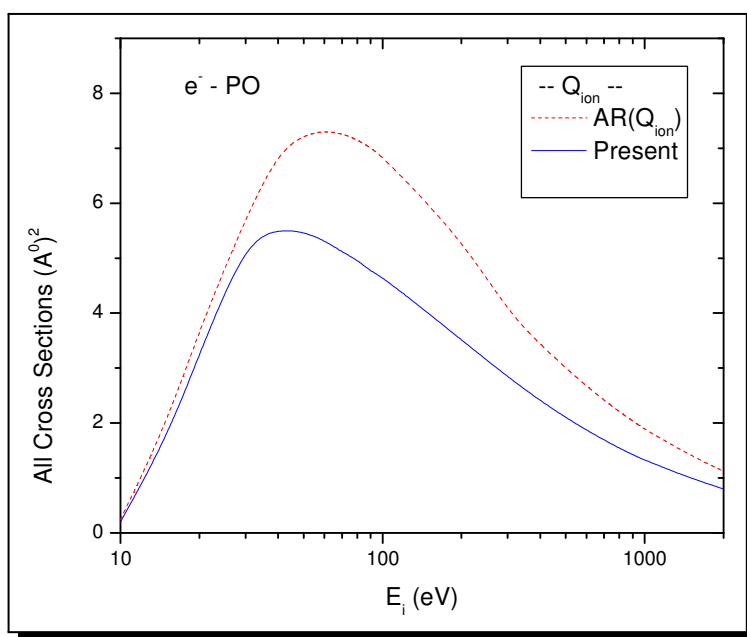


Figure 6. Total ionization cross sections (in Å²) of PO molecule and AR (Q_{ion}) by electron impact

4. Conclusion

In conclusion, the present total ionization cross sections denoted by Q_{ion} include in principle all allowed ionizations induced by incident electrons. Our method to calculate Q_{ion} is simpler than other theoretical methods. It has given reasonably good agreement for various atoms and molecules in past studies. In case of P (Phosphorus) atom the present theoretical results differ

from experimental data because of possibility of metastable atoms in neutral beam. Because of this reason various authors have to consider relative proportion (admixture) when they calculate cross sections for ground state species. Also, for Phosphorus compounds we have calculated the ionization cross sections. Finally, the general trend is that in most of the previous studies on calculations of Q_{ion} by CSP-ic formalism, the theoretical values are within about 12-15 % of measured and /or other theoretical data.

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Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

All the authors contributed significantly in writing this article. The authors read and approved the final manuscript.

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