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Computation of the electron impact total ionization cross sections of $C_nH_{(2n+1)}OH$ molecules from the threshold to 2 keV energy range

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ABSTRACT

Present paper reports calculations of total ionization cross sections (Q_{ion}) for simple but important alcohols (CH_3OH, C_2H_5OH, 1-C_3H_7OH) on electron impact with incident energies (E_i) ranging from ionization threshold (I) of the target to 2 keV. We have employed well established Spherical Complex Optical Potential (SCOP) formalism to evaluate total inelastic cross sections. We have also made an attempt to improve original Staszeweska model by considering Δ energy dependent and made to vary within the range $\eta I \leq \Delta(E_i) \leq I$. The total ionization cross sections are calculated using improved complex scattering potential-ionization contribution (ICSP-ic) method. The present results along with available experimental and other theoretical data are presented graphically.

1. Introduction

Increased interest in electron-driven processes involving biologically important organic molecules has prompted several recent studies involving collisions of electrons with alcohols [1–4]. The basic alcohols ($C_nH_{(2n+1)}OH$, $n = 1, 2, 3$) are important molecules of interstellar space [5]. These molecules are also important in pharmaceutical industry and cosmetics. The quantitative calculations of the various cross sections related to the electron–alcohol collision processes are thus important in the estimation of various reaction rates relevant to industry, atmospheric chemistry and to the estimation of radiation damages due to secondary electron impacts within organic tissues [6].

Though the experimental measurements of Q_{ion} on electron impact for methanol, ethanol and 1-propanol are available [5,7,8] in literature, the corresponding theoretical calculations are scarce and reported only by [5,9]. The difficulty is due to the complex nature of the targets as they contain more number of atoms (methanol contains six, ethanol contains nine and 1-propanol contains twelve atoms).

In this paper we present theoretical calculations of the electron impact total ionization cross sections (TICS) of the three alcohol molecules for electron energies (E_i) from ionization threshold of the target to 2000 eV. The theoretical spherical complex optical potential (SCOP) [10–12] and improved complex scattering potential-ionization contribution (ICSP-ic) [10] methods have been successfully employed to study the cross sections of various atomic and molecular targets. Here, we extend this scheme in the case of simple alcohol targets. The theoretical method is briefly reviewed in Section 2. Our results are presented and discussed in Section 3 and we conclude the present study in Section 4 of this paper.

2. Theoretical methodology

Electron molecule collision processes are characterized by two fundamental processes viz. elastic scattering and inelastic scattering. Quantitatively these processes are accounted in terms of total elastic cross sections and total inelastic cross sections. Theoretically, the inelastic processes are mainly accounted through the absorption part of the scattering potential in the SCOP formalism. In this formalism, the complex optical potential, V_{opt}, is given by [10–12]

$$V_{opt}(E_i, r) = V_R(E_i, r) + iV_{abs}(E_i, r) \tag{1}$$

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here the real part (V_R) comprises of the static potential (V_{st}), exchange potential (V_{ex}), and polarization potential (V_p). The second term containing V_{abs} accounts for the loss of flux in the inelastic channel. The basic input for evaluation of all these potentials is the charge density of the target. We have computed target charge density using the Roothaan–Hartree–Fock wave functions of Bunge et al. [13]. The complex structure of the molecular targets is simplified by considering a single centre approach [12]. We identify single potential scattering centre by expanding the charge densities of all the constituent atoms at the centre of mass of the target. The spherically averaged molecular charge density $\rho(r)$ is renormalized to yield the total number of electrons of the target molecule.

For the computation of total inelastic cross section, the relevant part of the Complex Optical Potential is V_{abs}. We employ here the non-empirical, quasifree, Pauli-blocking, dynamic absorption potential of Staszewska et al. [14] which is expressed as

$$V_{\mathrm{abs}}(r,E_i) = -\rho(r)\sqrt{\frac{T_{\mathrm{loc}}}{2}}\left(\frac{8\pi}{10k_F^3E_i}\right)\Theta(p^2-k_F^2-2\Delta)(\mathrm{A}_1+\mathrm{A}_2+\mathrm{A}_3) \tag{2}$$

All the parameters and the terms A_1, A_2 and A_3 of Eq. (2) are explained and defined in earlier works [10–12,14]. Apart from the target charge density, $\rho(r)$ other important target property which is associated with the absorption potential is the parameter Δ which determines a threshold below which $V_{\mathrm{abs}} = 0$. In the original Staszewska model [14] Δ is considered as ionization threshold of the target for all the incident energies. It corresponds to ignoring the contributions coming from the discrete excitations at lower incident energies. This was realized earlier by Blanco and Garcia [15] and they have elaborately discussed the need for modification of Δ value. Following which attempts have been made to treat Δ an energy dependent parameter by assigning a minimum value for it that slowly reaches to its maximum value equal to I [10–12]. Accordingly, we express Δ as

$$\Delta(E_i) = \eta I + \beta(E_i - I) \tag{3}$$

where the first term corresponds to the minimum value of Δ at $E_i = I$ that accounts the contribution to Δ coming from the discrete excitations below the ionization threshold. The second term corresponds to energy dependence on Δ before it reaches to its maximum value, I. Here we consider the energy at which Δ reaches its maximum value of I is the energy (E_P) at which is the peak of inelastic cross section occurs. The parameter β is then determined by imposing the condition $\Delta = I$ at $E_i \geq E_p$.

To account for the fraction η at $E_i = I$, we express the total electronic excitations starting from the first excitation to its continuum as sum of all discrete energy states below I plus the continuum I. Accordingly, the ratio of the sum of all discrete excitation channels to sum of all channels including continuum can be written as

$$\eta = \frac{\sum_{n=1}^{n_\infty-1} E_n}{\sum_{n=1}^{n_\infty} E_n} = 1 - \left(\frac{I}{\sum_{n=1}^{n_\infty} E_n}\right) \tag{4}$$

where E_n represents the nth electronic energy state and n_∞ corresponds to the continuum.

Assuming that the electronic excitation states follow, $E_n \propto 1/n^2$, as they are governed largely by the coulomb like interaction potential of the bound target electrons, Eq. (4) becomes

$$\eta = 1 - \frac{I}{R_y\xi(2)} \tag{5}$$

where R_y is the proportionality constant of the energy expression for E_n, 'n' being the principal quantum number, it can be related to its first electronic excitation energy (E_1) as $R_y = 4E_1$, and $\xi(2)$ is the Riemann Zeta function obtained from the sum over n of $1/n^2$. The computed values of η for different targets including the present targets as well as few other atomic and molecular targets studied earlier are listed in Table 1. It is quite interesting to observe that the computed values of η lie remarkably very close to the value (0.8) as considered in the earlier studies [10–12].

Table 1
Computed values of η for various targets.

Target	E_1 (eV) [16–24]	I (eV) [19]	η
He	19.82	24.59	0.81
Ne	16.20	21.57	0.80
Ar	11.55	15.76	0.79
C	7.53	11.26	0.77
N	10.99	14.53	0.80
O	10.48	13.62	0.80
F	14.21	17.42	0.81
O_2	8.40	12.07	0.78
NO	6.50	9.60	0.78
H_2O	9.34	12.61	0.79
NH_3	7.78	10.88	0.79
BCl_3	9.17	11.73	0.81
CH_4	9.00	12.51	0.79
SiH_4	8.70	11.65	0.80
GeH4	8.40	11.33	0.79
CF4	12.50	16.19	0.80
CH_3OH	8.53[a]	10.96	0.80
C_2H_5OH	8.68[a]	10.64	0.81
1-C_3H_7OH	7.99[a]	10.51	0.80

[a] Calculated using Quantemol-N [25] software.

With the complex optical potential generated for a given system, we solve the Schrödinger Equation numerically using the Numerov method. The scattering phase shifts are then obtained employing the partial wave analysis [10–12]. Solution of the radial part of the Schrödinger Equation yields us complex phase shifts. This shift in the angle or the phase is the reflection of the interaction of the potential on the incoming wave and they are the important inputs for computation of the total inelastic cross sections.

The total inelastic cross section (Q_{inel}) contains the total ionization (Q_{ion}) and the sum total of excitation cross section (ΣQ_{exc}) and is written as

$$Q_{\mathrm{inel}}(E_i) = \sum Q_{\mathrm{exc}}(E_i) + Q_{\mathrm{ion}}(E_i) \tag{6}$$

where ΣQ_{exc} is arising from all dipole allowed electronic transitions and Q_{ion} is sum total of all continuum transition leading to ionization. The ionization contribution is extracted from the total inelastic cross section using CSP-ic formalism [10–12]. In this formalism, we impose three general physical conditions on the ratio of total ionization cross section to total inelastic cross section ($R(E_i)$) as

$$R(E_i)\begin{cases} = 0 & \text{for} \quad E_i \leq I \\ = R_P & \text{at} \quad E_i = E_P \\ \cong 1 & \text{for} \quad E_i >> E_P \end{cases} \tag{7}$$

This procedure has been found quite successful in the case of many molecular targets [11,12]. Recently, the method has been improved (ICSP-ic) by providing a theoretical estimation of the ratio at the peak of inelastic cross section, R_P [10]. In the present study we follow the same procedure to compute R_P in terms of the first electronic excitation energy (E_1), the ionization threshold (I) and energy at the peak of inelastic cross section (E_p) of the target. The computed R_P values for the present targets are listed in Table 2. The ionization thresholds of these molecules are available from [19] and the first electronic excitation energies (E_1) of these molecules are calculated using the Quantemol-N software [25].

Table 2
The relevant parameters of the target and the computed values of R_P.

Target	${}^{a}E_1$ (eV)	I (eV) [19]	E_P (eV)	R_P
CH_3OH	8.53	10.96	55	0.74
C_2H_5OH	8.68	10.64	60	0.79
$1\text{-}C_3H_7OH$	7.99	10.51	50	0.71

[a] Calculated using Quantemol-N [25] software.

3. Results and discussion

The theoretical methods (SCOP and ICSP-ic) described in the previous section are employed to compute the total inelastic cross section Q_{inel}, the total ionization cross section Q_{ion} as well as the total excitation cross section ΣQ_{exc} of simple alcohols (CH_3OH, C_2H_5OH and $1\text{-}C_3H_7OH$) on electron impact at energies starting from their ionization threshold to 2 keV.

The computed total ionization cross sections for CH_3OH, C_2H_5OH, $1\text{-}C_3H_7OH$ molecules are plotted in Figs. 1–3 respectively along with other experimental and theoretical results available in the literature as a function of incident energy.

In Fig. 1 we compare the total ionization cross sections for e–CH_3OH scattering with previous experimental [5,7,8] and theoretical [5,9] data. Rejoub et al. [7] have reported ionization measurements for e–CH_3OH scattering using time-of-flight mass spectrometer. Our results (solid line) here are in good agreement with the experimental data of Rejoub et al. [7] throughout the energy range studied by them. The other experimental measurements of Hudson et al. [5] and Djuric et al. [8] are lower than present as well as other reported data. Theoretical data of Deutsch et al. [9] are in very good agreement with present data up to 30 eV only and beyond which they do not agree with present and other reported data. The BEB results of Hudson et al. [5] are in excellent agreement with the present data throughout the energy specified by them. However, the DM results of Hudson et al. [5] show a good agreement up to ~30 eV beyond which they overestimate all the reported data.

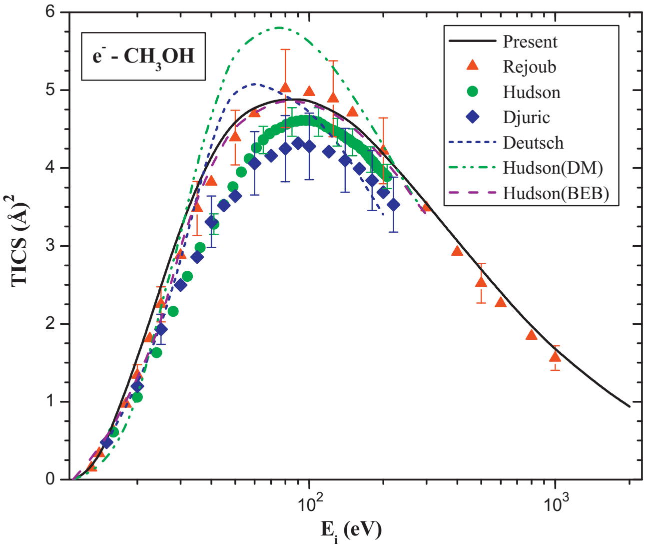

Fig. 1. Total ionization cross sections, Q_{ion}, for e–CH_3OH scattering in Å^2. Solid line → present results with ICSP-ic method; Triangles → experimental data of Rejoub et al. [7]; Circles → experimental data of Hudson et al. [5]; Squares → experimental data of Djuric et al. [8]; Short dashed line → theoretical results of Deutsch et al. [9]; Dashed dot dot line → theoretical results of Hudson et al. [5] using DM formalism; Dashed line → theoretical results of Hudson et al. [5] using BEB formalism.

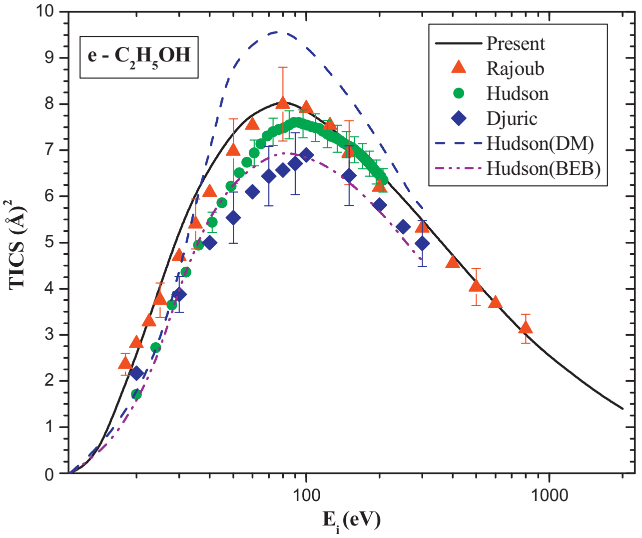

Fig. 2. Total ionization cross sections, Q_{ion}, for e–C_2H_5OH scattering in Å^2. Solid line → present results with ICSP-ic method; Triangles → experimental results of Rejoub et al. [7]; Circles → experimental results of Hudson et al. [5]; Squares → experimental data of Djuric et al. [8]. Dashed line → theoretical results of Hudson et al. [5] using DM formalism; Dashed dot dot line → theoretical results of Hudson et al. [5] using BEB formalism.

Fig. 2 shows the comparison of our total ionization cross section of C_2H_5OH alcohol on electron impact at the stated energy range with available experimental [5,7,8] and theoretical [5] data. The measured data of Rejoub et al. [7] are in excellent agreement with the present data throughout the energy range. The experimental measurements of Hudson et al. [5] are lower by ~7% than our calculated results below 100 eV and tend to coincide with present data at higher energies. The experimental results of Djuric et al. [8] are much lower compared to all the reported data. At the peak the theoretical data of Hudson et al. [5] using BEB formalism are lower by ~12% and the data using DM formalism are higher by ~20% than the present calculations.

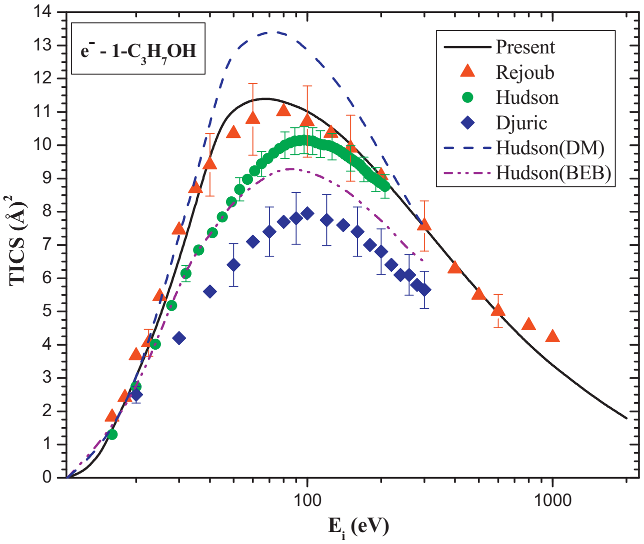

Fig. 3. Total ionization cross sections, Q_{ion}, for e–$1\text{-}C_3H_7OH$ scattering in Å^2. Solid line → present results with ICSP-ic method; Triangles → Rejoub et al. [7]; Circles → Hudson et al. [5]; Squares → Djuric et al. [8]; Dashed line → theoretical results of Hudson et al. [5] using DM formalism; Dashed dot dot line → theoretical results of Hudson et al. [5] using BEB formalism.

Finally in Fig. 3 we have compared our total ionization cross sections for e–1-C_3H_7OH scattering with the available experimental [5,7,8] and theoretical [5] data. The present data are consistently in good agreement with the measured data of Rejoub et al. [7] throughout the energy range. The other experimental measurements of Hudson et al. [5] are in good agreement up to 30 eV. Beyond 30 eV their results are lower than the present calculated results by ∼15%. The experimental results of Djuric et al. [8] are 25–35% lower in the entire energy regime with all other investigations. At the peak, the theoretical data of Hudson et al. [5] using BEB formalism are lower by ∼20% and the data using DM formalism are higher by ∼20% than the present calculations.

4. Conclusion

The theoretical formalism of SCOP and the ICSP-ic method improved by providing sufficient reasoning to relate the important parameters (Δ, R_P) of the model with the basic properties of the target is found to be quite successful in predicting the ionization cross sections of relatively complex $C_nH_{(2n+1)}OH$ alcohol upon electron collision with wide energy range starting from the ionization threshold. The results obtained in the present study for the molecules with $n = 1, 2, 3$ are in very good agreement with the corresponding experimental data reported by Rejoub et al. [7]. However, our results around the peak of the Q_{ion} in all the three cases lie between the two theoretical estimations based on DM and BEB formalisms [5]. Looking into the disparities observed among the existing experimental as well as theoretical results on the ionization cross sections of these molecules studied here warrant further theoretical and experimental investigations.

The relatively fast computations of relevant electron impact cross sections increases the applicability of the theoretical formalism employed in the present study. We look forward to apply the ICSP-ic method to more complex and biologically important molecular targets.

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References

[1] D. Bouchiha, J.D. Gorfinkiel, L.G. Caron, L. Sanche, J. Phys. B: At. Mol. Opt. Phys. 40 (2007) 1259.

[2] V.S. Prabhudesai, A.H. Kelkar, D. Nandi, E. Krishnakumar, Phys. Rev. Lett. 95 (2005) 143202.

[3] B.C. Ibănescu, O. May, A. Monney, M. Allan, Phys. Chem. Chem. Phys. 9 (2007) 3163.

[4] M. Orzol, I. Martin, J. Kocisek, I. Dabkowska, J. Langer, E. Illenberger, Phys. Chem. Chem. Phys. 9 (2007) 3424.

[5] J.E. Hudson, M.L. Hamilton, C. Vallance, P.W. Harland, Phys. Chem. Chem. Phys. 5 (2003) 3162.

[6] B. Sulik, Radiat. Phys. Chem. 76 (2007) 483.

[7] R. Rejoub, C.D. Morton, B.G. Lindsay, R.F. Stebbings, J. Chem. Phys. 118 (2003) 1756.

[8] N. Djuric, I. Cadez, M. Kurepa, Fizika 21 (1989) 339.

[9] H. Deutsch, K. Becker, R. Basner, M. Schmidt, T.D. Märk, J. Phys. Chem. A 102 (1998) 8819.

[10] M. Vinodkumar, K. Korot, P.C. Vinodkumar, Eur. Phys. J. D 59 (2010) 379.

[11] M. Vinodkumar, C. Limbachiya, K. Korot, K.N. Joshipura, N. Mason, Int. J. Mass Spectrom. 273 (2008) 145.

[12] M. Vinodkumar, C. Limbachiya, K. Korot, K.N. Joshipura, Eur. Phys. J. D 48 (2008) 333.

[13] C.F. Bunge, J.A. Barrientos, A.V. Bunge, At. Data Nucl. Data Tables 53 (1993) 113.

[14] G. Staszewska, D.W. Schwenke, D. Thirumalai, D.G. Truhlar, Phys. Rev. A 28 (1983) 2740.

[15] F. Blanco, G. Garcia, Phys. Rev. A 67 (2003) 022701.

[16] From: http://physics.nist.gov/PhysRefData/ASD/levels_form.html.

[17] D.L. Albritton, A.L. Schmeltekopf, R.N. Zare, J. Chem. Phys. 71 (1979) 3271.

[18] H. Munjal, K.L. Baluja, Phys. Rev. A 74 (2006) 032712.

[19] D.R. Lide, CRC Handbook of Physics and Chemistry, 74th ed., Boca Raton, FL: Chemical Rubber Company, 1993–94.

[20] From: http://srdata.nist.gov/cccbdb/.

[21] From: http://dpc.nifs.ac.jp/DB/IEEJ/datafiles/.

[22] H.P. Pritchard, V. McKoy, M.A.P. Lima, Phys. Rev. A 41 (1990) 546.

[23] H.F. Winters, M. Inokuti, Phys. Rev. A 25 (1982) 1420.

[24] K.J. Boyle, D.P. Seccombe, R.P. Tuckett, H. Baumgärtel, H.W. Jochims, J. Phys. B: At. Mol. Opt. Phys. 32 (1999) 2569.

[25] J. Tennyson, D.B. Brown, J.J. Munro, I. Rozum, H.N. Varambhia, N. Vinci, J. Phys.: Conf. Ser. 86 (2007) 012001.