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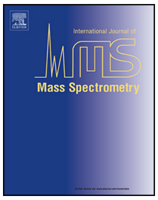

Electron induced ionization cross sections for astrophysical modelling

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ABSTRACT

This paper reports electron impact total ionization cross sections for C_2 to C_6 formates at energies varying from ionization threshold to 5 keV. The ionization cross section data in such a wide energy range are necessary to complete data tables required for modelling different atmospheric and astrophysical environments. To compute these values, a modified approach called multi scattering centre spherical complex optical potential (MSCOP) formalism is employed. Using MSCOP, the total inelastic cross section is obtained, which corresponds to the total loss of incident flux into the dominant channels viz. discrete electronic excitation and continuum ionization. The ionization contribution from total inelastic cross section is estimated using a semi empirical complex scattering potential-ionization contribution (CSP-ic) method. The results show overall good agreement with previous measurements and theoretical estimates available from the literature. Besides cross sections, correlations between maximum ionization cross section versus the square root of the ratio of polarizability to ionization potential and with the number of carbon atoms in each target are investigated. Employing this correlation, the approximate polarizability volume of C_4 to C_6 formates has been computed for the first time.

1. Introduction

The fascination in the knowledge of collision processes has geared up in the last few decades due to the importance of cross sections to the kinetics and dynamics of interactions and their relevance in practical applications in various pure and applied sciences especially astrophysical plasma and atmospheric sciences [1,2]. However, there is a plethora of molecules for which electron impact ionization has not yet been reported. This void in the database of cross section data is a serious handicap for the modelling of atmospheric and astrophysical modelling. The present work reports the electron impact ionization cross section for C_2 to C_6 formates namely methyl formate ($HCOOCH_3$), ethyl formate ($HCOOC_2H_5$), propyl formate (n-$HCOOC_3H_7$), iso-propyl formate (iso-$HCOOC_3H_7$), butyl formate (n-$HCOOC_4H_9$), iso-butyl formate (iso-$HCOOC_4H_9$) and pentyl formate ($HCOOC_5H_{11}$) in the energy range from ionization threshold to 5 keV.

Methyl formate is profusely formed in ultra compact and compact cores of interstellar clouds and also in warm star forming regions [3,4]. It has less than 25 global warming potential along with zero ozone depletion potential. Hence, it is being increasingly used as a replacement for chlorofluorocarbons, hydro chlorofluorocarbons, or hydro fluorocarbons [5]. Furthermore, it is preferred as a model ester to study the combustion mechanisms of much more complex biodiesel mixtures. Recently, ethyl formate has been identified in dust clouds of Milky Way galaxy called Sagittarius S2. It is probably the biggest molecule detected in deep space along with propyl cyanide [6]. The neoteric discovery of these primary formates has raised the prospect of the presence of higher complex members of the family in these environments. To model various planetary atmospheres and to comprehend different combustion kinetics in such environments, electron impact ionization data of various molecules including formates are crucial. In spite of such important implications in ISM and other astrophysical environments, formates have not received much attention. Harrison et al. [7] were the first to report the total ionization cross section for formates by 75 V electrons in 1966. Four decades later, Hudson et al. [8] measured the absolute electron impact ionization cross sections of C_2 to C_6 formates and C_3 to C_7 acetates from 15 to 285 eV. They compared their experimental values for the maximum ionization cross section with values calculated using the Binary Encounter Bethe method of Kim and Rudd [9,10]. However, the computed BEB data were found to be inappropriate and were revised later by Bull et al. [11] up to 300 eV. The unpublished total ionization cross section data for methyl and ethyl formate computed using Deutsch-Märk (DM) formalism are also included here.[1] There is no other literature available for electron impact ionization cross section of formates to

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the best of our knowledge. The paucity of electron impact ionization data on these molecules has inspired us to perform the present computations.

Fig. 1 shows the molecular geometries of the targets studied in the present work. It is quite evident that simple spherical complex optical potential (SCOP) [12–17] method will not work for these complex targets. Hence, we introduce here a modified SCOP called multi scattering centre spherical complex optical potential (MSCOP) formalism. Using this method, the inelastic cross section is calculated for each molecule in its gaseous ground state. The ionization cross section is then derived from the inelastic part by a semi empirical method called the complex scattering potential-ionization contribution (CSP-ic) method [16–19]. The data are presented here over an energy range from the ionization threshold to 5 keV. This is the first attempt to find the cross section data over such a wide energy range. The next section elucidates the details of MSCOP and CSP-ic method. An overall good agreement is attained with the measurements of Hudson et al. [8] and with the theoretical data using BEB [9,10] and DM [20] formalisms. The article also analyzes the effect of isomerism on ionization cross section. In addition to the ionization cross section data, the polarizability volumes for C_4 to C_6 formates are estimated employing a correlation between the maximum ionization cross section and the square root of the ratio of polarizability to ionization potential.

2. Theoretical methodology

For the calculation of ionization cross sections, we propose a method called the multi scattering centre spherical complex optical potential (MSCOP) method. The MSCOP method is a coherent blend of Group Additivity Rule (GAR) [19] and spherical complex optical potential (SCOP) method [15–19]. Firstly, multiple scattering centres in a molecule are identified depending on the extend of electron charge density of each independent centre and then the SCOP method is employed to find the respective group's cross section. The independent multiple scattering centres are chosen depending explicitly on atomic radii, bond length and the extent of electronic charge cloud of each group in the molecule. This is a meaningful approximation since any central atom not directly exposed to the incoming electron flux will be partially shielded or 'shadowed' due to the overlapping of neighbouring atoms. For example, the signature functional group of formate, HCOO and each alkyl group is considered as an independent scatterer. In alkyl group, the central carbon atom is partially shielded by the neighbouring hydrogen atoms. This "shadowing effect" is treated geometrically by expanding the single centre charge density of the lighter hydrogen atom, at the centre of heavier carbon atom. The ionization contribution from each of the individual scattering centre is added to give the total ionization cross section. This procedure is adopted for all other targets, too.

The above procedure is called MSCOP formalism, which is implemented through a quantum mechanical calculation to find inelastic cross section for the constituent scattering centres. The interaction of the incoming projectile and the multiple scattering centres in a target is described by a complex optical potential represented as,

$$V_{opt}(r, E_i) = V_R(r) + iV_I(r, E_i) \quad (1)$$

where the first term is the real potential comprising static, exchange and polarization potentials and second imaginary term takes into account the absorption effects during the scattering event. These complex potentials depend on the incident electron energy (E_i) and the radial distance between the incident electron and the scattering centre(s). These potentials are devised in such a way that they are functions of respective target parameters and target charge density. The ionization potentials [21] of targets studied in the present work are listed in Table 1. The ionization threshold used in BEB calculation is used for pentyl formate as its ionization potential is not available in the literature. The bond lengths of C—H and C═O of methyl formate are taken from CCCBDB website [22] and same values are used for all the formates of the present study. The correct representation of target charge density is imperative to obtain accurate potential. In the present work, the target charge density and static potential for each group in a molecule was computed using the well established parametrized Hartree–Fock wave function given by Cox and Bonham [23]. For exchange and correlation-polarization potentials, Hara's 'free electron gas exchange model' [24] and that of Zhang et al. [25] respectively are employed. The imaginary part of the complex potential accounts for the total inelastic flux loss through electronic excitation and ionization channels. This absorption potential is derived from the well-known quasi-free model potential given by Staszewska et al. [26]. The molecular vibration and rotational excitation are important only at very low incident energies and does not contribute significantly to the total ionization cross section in the present energy range. Hence, these effects are not included in the current model.

Table 1
Ionization potentials of the targets.

Target	IP (eV)
methyl formate ($HCOOCH_3$)	10.835
ethyl formate ($HCOOC_2H_5$)	10.61
n-propyl formate ($HCOOC_3H_7$)	10.54
iso-propyl formate (iso-$HCOOC_3H_7$)	10.52
n-butyl formate ($HCOOC_4H_9$)	10.52
iso-butyl formate (iso-$HCOOC_4H_9$)	10.46
n-pentyl formate (tert-$HCOOC_4H_9$)	11.00

The complex potential thus formulated is then incorporated into the Schrödinger equation and solved numerically using the method of partial waves. The solution of the Schrödinger equation obtained in the form of complex phase shifts (δ_l) is employed to calculate the absorption or inelasticity factor for each partial wave, 'l' using,

$$\eta_l = \exp(-2Im\delta_l) \quad (2)$$

This factor is used to calculate the total inelastic cross section for the independent scattering centres. Since the Q_{inel} does not contain rotational or vibrational excitations, it can be divided into discrete Q4 and continuum contributions as,

$$Q_{inel}(E_i) = Q_{exc}(E_i) + Q_{ion}(E_i) \quad (3)$$

where Q_{exc} is the excitation cross sections for all the allowed electronic transitions and Q_{ion} stands for the total cross section of all allowed ionization processes induced by the incident electron, including single, double, inner shell, etc. However, Q_{inel} is not directly measurable, while Q_{ion} can be measured in an experiment. Q_{ion} is also used as a direct input to modelling codes for various applications (e.g. in fusion edge plasmas and in plasma processing, stellar, and cometary atmospheres etc.). Thus, to estimate Q_{ion} from Q_{inel}, a semi-empirical complex scattering potential-ionization contribution (CSP-ic) method is employed. Now, Q_{ion} for electron impact ionization corresponds to a transition to the continuum as against optically allowed discrete electronic excitation channels. Hence, typically at energy above 100 eV or so, ionization dominates over excitation. So, from Eq. (3), it can be concluded that,

$$Q_{inel}(E_i) \geq Q_{ion}(E_i) \quad (4)$$

So, a reasonable approximation is invoked in order to extract Q_{ion} from Q_{inel} by using a ratio as a function of incident energy:

$$R(E_i) = \frac{Q_{ion}(E_i)}{Q_{inel}(E_i)} \quad (5)$$

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