Electron scattering from C_2-C_8 symmetric ether molecules

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A B S T R A C T

The present article reports the calculated total (Q_{tot}), elastic (Q_{el}), inelastic (Q_{inel}), and total ionization cross section (Q_{ion}) for C_2-C_8 symmetric ether molecules for the incident electron energies from ionization threshold to 5 keV. The calculation is based on the approach, multi-scattering center spherical complex optical potential formalism (MSCOP). The total elastic and inelastic cross sections are computed under this framework and the total cross section is obtained from their sum. Since Q_{inel} cannot be measured directly, we have estimated this value theoretically through the complex spherical potential-ionization contribution approach and compared with the measurements. Besides cross sections, we have also investigated the isomeric effect of ethers on electron-molecule scattering and the dependence of molecular size in the magnitude of cross section. The size effect is confirmed from the correlation plot between the calculated Q_{ion} peak and dielectric polarisability of the target molecules. The total and elastic cross sections for most of the molecules are reported for the first time.

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1. Introduction

Study of electron interactions with atoms and molecules has received renewed interest in the last few decades. This is because of the importance of electron induced chemistry and related physico-chemical phenomena in various natural and man-made environments like planetary atmospheres, natural and industrial plasmas, gas discharges, fusion reactors, radiation physics, medicine and material science [1]. To interpret various mechanisms occurring in such environments, accurate cross section data are imperative. However, there is lack of reliable cross section for innumerable targets, especially in the intermediate to high incident electron energies. In addition, accurate total ionization cross section (Q_{ion}) can be used in empirical relationships to find unknown values of molecular polarisability (α) and also to test its theoretical predictions [2,3].

The present paper reports the theoretical calculations to obtain electron impact total (Q_{tot}), elastic (Q_{el}), inelastic (Q_{inel}), and total ionization cross section (Q_{ion}) of primary ethers in the energy range from ionization threshold to 5 keV. These ether molecules are dimethyl ether (DME), Diethyl ether (DEE), dipropyl ether (DPE), diisopropyl ether (DIPE), dibutyl ether(DBE) and diisobutyl ether (DIBE). The ethers chosen for the present study have several applications in various fields of applied science. For instance, DME is

an important chemical compound with extensive applications in industries. It has high cetane number and is overall low sooting and low polluting agent [4,5]. This makes it an environmental-friendly alternative fuel for diesel engines. Besides, DME is one of the highly abundant organic molecules in the interstellar medium and is observed largely in star-forming regions [6]. DEE plays important role as an octane and oxygen enhancer in internal combustion engines [7–11]. Oxidation of DEE attracts attention in combustion-relevant environments [12,13] and in planetary atmospheres [14]. DIPE is used as a gasoline blending component in the fuel industry since it increases the octane levels of gasoline. DIPE is also used in organic synthesis and in analyzing chemicals. Thus, these ethers prove to be a good candidate for bio-fuels. DBE is a powerful and cost effective solvent for Grignard reactions. DIBE is a flammable liquid and incompatible with strong oxidizing agents. Moreover, higher ethers in the hierarchy can dissociate into primary ethers from secondary electrons generated during multiple ionization. Therefore, electron-ether scattering cross sections can be extremely useful to understand the evolutionary cycle of many stars and chemical pathways in their environment as well as in combustion relevant environments [6–14].

The studies of electron impact cross section on these ethers are scarce, despite their multiple applications. To the best of our knowledge, there is only a single study of differential, elastic and total cross section of e-DME scattering by Sugohara et al. [15] and electron impact Q_{ion} of DEE, DPE and DIPE by Bull et al. [16]. Bull et al. [16] reported cross section up to 285 eV only. The cross sections for most of the targets presented here are reported for the
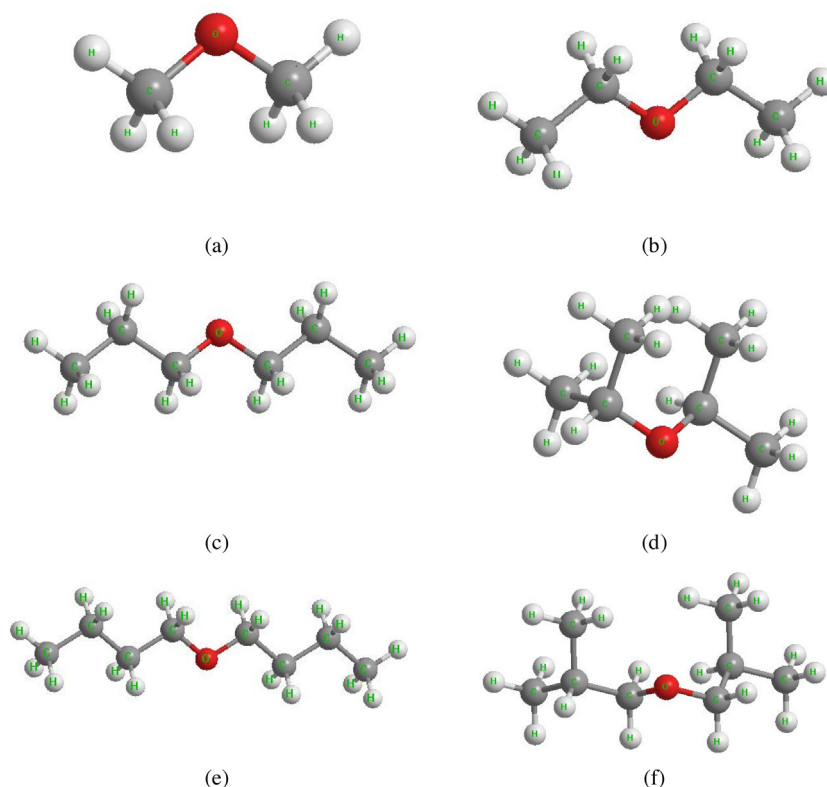
Fig. 1. Molecular structure of targets. (a)DME, (b) DEE, (c) DPE, (d) DIPE, (e) DBE, (f) DIBE.

first time. Besides cross sections, we have also studied the effect of isomerism and molecular size on cross section. The method employed for the present study is called a multi-scattering center spherical complex optical potential (MSCOP) [17–22] method for obtaining Q_{tot}, Q_{el} and Q_{inel} and complex scattering potential ionization contribution (CSP-ic) [23–25] to estimate Q_{ion}. Since Q_{ion} for DME is not available in the literature, we have computed the same from Quantemol-N [26] employing binary-encounter Bethe (BEB) method [27]. The geometry of the molecules are very important in accurately modeling the electron-target system in the present approach. Symmetrical ethers contain an oxygen atom bounded to two symmetrical alkyl groups on both sides. A pictorial representation of the structure of all the targets is shown in Fig. 1.

2. Theoretical methodology

2.1. Total cross section

The present calculations are done using MSCOP [17–22] formalism. This methodology is generally employed for larger molecules, since it is difficult to envisage a large molecule as a single scattering center. Firstly, independent scattering centers in a molecule are identified and the SCOP method [18–22] is employed to find cross section of each scattering group. These scattering groups are considered based on the molecular properties such as atomic radii, bond length and the distribution of electronic charge cloud around each group in a molecule. For example, in case of DEE (Fig. 1b) five independent scattering centers were identified. Two −CH₃ groups, two −CH₂ groups and one oxygen atom are chosen as independent scattering groups for DEE molecule. Finally, the cross section from each independent scattering group is added to obtain the final cross section of the molecule.

In SCOP [18–22] formalism, the interaction between incoming electron and molecular target is represented in terms of a complex potential. This potential is used in the Schrödinger equation, which is then solved numerically employing partial wave approximation. The solution obtained in terms of complex phase shifts carries the entire information of the electron-molecule scattering events. These phase shifts (δ_l) are used to calculate integral elastic and inelastic cross section at various incident electron energies using standard relations [28],

$$Q_{el}(E_i) = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) |\eta_l \exp(2i\Re\delta_l) - 1|^2 \tag{1}$$

and

$$Q_{inel}(E_i) = \frac{\pi}{k^2} \sum_{l=0}^{\infty} (2l+1)(1 - \eta_l^2) \tag{2}$$

Here $\eta_l = \exp(-2\mathrm{Im}\delta_l)$ is the inelasticity factor calculated from the phase shifts, δ_l. The sum of Q_{el} and Q_{inel} gives the total cross section for the target molecule.

The complex potential used to derive the above relation by solving the Schrödinger equation is expressed as,

$$V_{opt}(r, E_i) = V_R(r, E_i) + iV_I(r, E_i) \tag{3}$$

Here, the first term on right side stands for real potentials and the second term stands for absorption potential, V_{abs}. The real potential is the sum of the components namely, static (V_{st}), exchange (V_{ex}) and polarisation (V_p) potentials. In equation (3), r stands for distance between incoming electron and target molecule and E_i is the incident energy of incoming electron. The real potentials are formulated using charge density, ionization potential (IP) and polarisability (α) of the targets as input parameters. To calculate charge density and static potential, the Hartree-Fock wave function of Cox and Bonham [29] was employed. The short range static potential arises due to the electric field of target's electron cloud. The indistinguishable nature of electron causes the exchange