Journal of Electron Spectroscopy and Related Phenomena 189 (2013) 17–22

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec

Total and elastic cross sections for methyl halides by electron impact

Rahla Naghma, Bobby Antony*

Department of Applied Physics, Indian School of Mines, Dhanbad 826004, Jharkhand, India

ARTICLE INFO

Article history:
Received 9 April 2013
Received in revised form 1 June 2013
Accepted 1 June 2013
Available online 11 June 2013

Keywords:
Methyl halides
Electron scattering
Total and elastic cross section
Total ionization cross section
SCOP formalism
CSP-ic method

ABSTRACT

The total (elastic + inelastic) cross sections for electron impact scattering with CH_3F, CH_3Cl, CH_3Br and CH_3I have been calculated using a spherical complex optical potential formalism in the energy range from 20 eV to 5000 eV. The present calculated cross sections show good agreement with previous measurements and theoretical values wherever available. The total elastic and ionization cross sections are also presented here and are found to compare well with existing data. There are no theoretical data available in the literature on total cross section for CH_3Br and CH_3I molecules and are reported for first time.

1. Introduction

The halogen containing methane compounds like methyl fluoride (CH_3F), methyl chloride (CH_3Cl), methyl bromide (CH_3Br) and methyl iodide (CH_3I) are considered to be significant sources of stratosphere halogens and play potential role in the depletion of earth's protective ozone layer [1–3]. Collision data concerning electron interaction with these halogen substituted methane are important for the understanding of various chemical phenomena in the earth's and other planet's atmosphere. In addition, scattering cross sections for these molecules are crucial in modeling and optimization of industrial plasma, for semiconductor etching and electron induced reactions on surfaces [4]. So, a detailed investigation about electron collision with these molecules is imperative in the understanding of their respective environment. Among the collision cross sections that can be obtained, the total cross section, Q_T (which is the sum of total elastic, Q_{el} and total inelastic, Q_{inel}) is the most reliable and serves as the upper limit to all other scattering processes.

In view of the above facts, we have conducted a theoretical study on electron scattering from CH_3F, CH_3Cl, CH_3Br, and CH_3I molecules to provide a comprehensive set of absolute scattering cross sections data. In this work the elastic, inelastic and total cross sections data for these halogenated methane molecules CH_3X (X = F, Cl, Br and I) are provided for an extensive range of electron impact energy from 20 eV to 5000 eV. Furthermore for this series of molecules, we have observed a strong correlation between the magnitudes of the TCS with the static electric dipole polarizability of the target at intermediate energies. The dependence of TCS over the target polarizability reveals the role of microscopic target properties in the scattering processes. Besides, such correlations [5] are useful in predicting a rough estimate of cross section data at intermediate energies for species lacking measurements.

However, considerable efforts have been made to investigate electron impact scattering with these molecules. There are low energy elastic electron scattering calculation for CH_3F and CH_3Cl by Natalense et al. [6] and for CH_3Cl by Resigno et al. [7] for energy ranges 8–30 eV and 0.5–10 eV respectively. Jones et al. [8] have measured absolute integral and backward total scattering cross-sections for CH_3Cl, CH_3Br and CH_3I at electron energies from 10 meV to 0.7 eV for backward scattering and 20 meV–9.5 eV for integral scattering. Elastic differential cross section calculations were carried out by Tanaka et al. [9] for CH_3F and by Natalense et al. [10] for all these molecules. Previous studies that are relevant to the present work include the total cross section experiments on CH_3F, CH_3Cl and CH_3Br by Krzystofowicz and Szmytkowski [11,12] and on CH_3I by Szmytkowski and Krzystofowicz [13]. Joshipura and Vinodkumar [14] have calculated various cross sections including Q_T for CH_3F molecule using modified additivity rule. Their results show good agreement with experiments at high impact energies and significant discrepancies at low energies. Manero et al. [15] have reported Q_T for CH_3F at energies between 0.5 keV and 10 keV, by using a semi empirical formula depending on only polarisability and number of electrons of the target. For CH_3F and CH_3Cl there are

* Corresponding author. Tel.: +91 9470194795.
E-mail address: bka.ism@gmail.com (B. Antony).

0368-2048/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.elspec.2013.06.001

theoretical data due to Shi et al. [16] which overestimates most of the experiments. Karwasz et al. [17] have reported both measured and calculated Q_T for CH_3Cl molecule. Kimura et al. [18] have carried out experimental study for electron impact Q_T for CH_3Cl, CH_3Br and CH_3I molecules. In case of Q_{el}, Kato et al. [19] have presented both measured and calculated data for these series of molecules. Hargreaves et al. [20] have reported experimental and computed Q_{el} for CH_3I for energies 5–50 eV which is an extension of the work due to Kato et al. [19]. Experimental study on electron impact ionization (Q_{ion}) for all these molecules are due to Vallence et al. [21] and Rejoub et al. [22]. Torres et al. [23] have reported total ionization cross section for CH_3F by adding up partial ionization cross sections of the set of ejected ions measured by the time of flight mass spectrometry. Vallence et al. [21] have also calculated ionization cross section using Deutsch Mark (DM) and Binary encounter Bethe (BEB) methods for these molecules. Recently, Kumar and Pal [24] have computed total ionization cross section for CH_3F, CH_3Cl and CH_3Br molecules as a sum of partial ionization cross section calculated by using modified Jain-Khare semi empirical approach. Considering these facts it will be interesting to see the comparison of the present results with these measurements and calculations. The present Q_T for CH_3Br and CH_3I molecules and Q_{ion} for CH_3I by electron scattering is the first theoretical work reported in the literature.

The organization of the paper is as follows. In Section 2, theoretical method is briefly described. Our calculated results are presented and discussed in Section 3. Finally, Section 4 summarizes conclusion of this study.

2. Theoretical method

The theoretical approach employed here to calculate the total cross section for the molecules of present study by intermediate and high energy electron impact is spherical complex optical potential (SCOP) formalism. A detailed description of the theory is given in our previous work [25–27]. Similar calculations of Q_{el}, Q_{inel} and Q_T for chlorofluoromethanes were reported by Gupta and Antony [27] recently. Hence, we present only a brief outline of the method adopted here.

We represent the projectile target system by a complex potential, consisting of real and imaginary terms. The real potential is represented as a sum of static, exchange and polarization term while the imaginary part takes care of absorption potential. We can express the complex potential as,

$$V_{opt}(r, E_i) = V_{st}(r) + V_{ex}(r, E_i) + V_p(r, E_i) + iV_{abs}(r, E_i) \quad (1)$$

here E_i is the incident electron energy. Static term, V_{st} is the potential experienced by the incident electron due to the undisturbed target charge cloud and is derived from the parameterized Hartree Fock wave functions given by Cox and Bonham [28]. Exchange potential, V_{ex} is responsible for the indistinguishability between the incident and target electron and this interaction is represented by Hara's free electron gas exchange model [29]. The polarization potential, V_{pol} which depends on the target dipole polarisability describe the long range interaction between the incoming electron and target charge cloud and is given by Zhang et al. [30]. The absorption potential, V_{abs} accounts for the total loss of incident flux into all the allowed electronic channels of ionization and excitation and is formulated from non-empirical quasi-free model of Stazeweska et al. [31]. The potential constructed here to represent the electron-molecule interaction is rotationally and vibrationally elastic. These non-spherical terms are not significant because at the energy of present interest, the time spend by the impinging electron in the vicinity of the target molecule is short compared to molecular vibration and rotation. Here the collision processes are described within the fixed nuclei approximation. The various model potentials are obtained from the spherically averaged molecular charge density determined by expanding the atomic charge densities from the center of mass of targets. The atomic charge density is derived from the parameterized Hartree Fock wave functions [28]. The target properties employed in the present study are the best available from the literature and are summarized in Table 1.

Table 1
Target properties [32].

Molecules	Dipole polarisability (Å^3)	Ionization potential (eV)	Bond length (Å)	
			C–H	C–X
CH_3F	2.97	12.47	1.095	1.382
CH_3Cl	5.35	11.22	1.090	1.785
CH_3Br	5.87	10.54	1.086	1.933
CH_3I	7.97	9.538	1.084	2.132

After employing the complex potential, the Schrödinger equation is solved numerically by the method of partial waves. The solutions obtained are in the form of complex phase shifts (δ_l) for each partial wave. This phase shift carries all the information regarding the interaction of the projectile electron with the target molecule and is the key ingredient to find various cross sections [33]. At low energies only few partial waves are significant, but more partial waves are needed for convergence as the incident energy increases. These phase shifts are used as input to find the inelasticity or absorption factor through,

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

Using this we can calculate Q_{el} and Q_{inel} cross sections [33] through the expressions given below.

$$Q_{inel}(E_i) = \frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)(1-\eta_l^2) \quad (3)$$

and

$$Q_{el}(E_i) = \frac{\pi}{k^2}\sum_{l=0}^{\infty}(2l+1)\left|\eta_l \exp(2iRe\delta_l) - 1\right|^2 \quad (4)$$

The total scattering cross section is obtained by adding these two cross sections. Furthermore, the inelastic cross section Q_{inel} can be written as the sum of discrete and continuum contribution

$$Q_{inel}(E_i) = \sum Q_{exc}(E_i) + Q_{ion}(E_i) \quad (5)$$

where the first term represents the sum of all allowed electronic excitation channels in the molecules while the second term accounts for total ionization (single, double, dissociative, etc.) channels. The inelastic cross section cannot be measured directly in an experiment and hence is not a comparable quantity. However the total ionization cross section, Q_{ion} is of applied interest and is directly measurable. We can estimate total ionization cross section from the inelastic cross section using a semi empirical approach by defining an energy dependent ratio of cross sections,

$$R(E_i) = \frac{Q_{ion}(E_i)}{Q_{inel}(E_i)}, \quad \text{such that} \quad 0 < R \leq 1 \quad (6)$$

This method of evaluating Q_{ion} from Q_{inel} is called complex scattering potential ionization contribution (CSP-ic) method. Details of this method have been described previously in ref [25,26,34] and references therein. Employing the energy dependent ratio as given above, Q_{ion} can be easily obtained from the Q_{inel} calculated through SCOP formalism.