ELSEVIER

International Journal of Mass Spectrometry 216 (2002) 239–247

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Theoretical total ionization cross-sections for electron impact on atomic and molecular halogens

K.N. Joshipura [a,*], Chetan G. Limbachiya [b]

[a] *Department of Physics, Sardar Patel University, Vallabh Vidyanagar 388120, India*
[b] *P.S. Science College, Kadi (N.G.) 382715, India*

Received 30 November 2001; accepted 1 March 2002

Abstract

Total ionization cross-sections (TICS) for the impact of intermediate and high energy electrons on the halogen atoms F, Cl, Br and I as well as the molecules F_2, Cl_2, Br_2 and I_2 are calculated from threshold to about 2000 eV. The present results obtained from our approach based on complex potential are compared with experimental and other data as available. Our results for halogen atoms agree well with the previously calculated and measured values. The present results for Cl_2 molecules also agree well with the recommended data, but those for F_2, Br_2 and I_2 tend to differ from the data available. Inter-halogen comparisons of the presently calculated cross-sections are also made. (Int J Mass Spectrom 216 (2002) 239–247) © 2002 Published by Elsevier Science B.V.

PACS: 34.8-i

Keywords: Electron impact ionization; Cross-section calculation; Halogen atoms and molecules

---

1. Introduction

The halogen atoms F, Cl, Br and I together with their diatomic molecules F_2, Cl_2, Br_2 and I_2 play important roles in a variety of physical and chemical processes, owing to their reactive nature. There are several investigations on electron-induced ionization of halogens and their compounds like perfluorocarbons, etc. [1,2]. Total ionization cross-sections (TICS) for electron collisions on F, Cl, Br and I were measured from threshold to about 200 eV by Hayes et al. [3]. Margreiter et al. [4] made useful and comprehensive calculations on these cross-sections for all atoms from hydrogen to uranium on the basis of a semiclassical approach called Deutsch–Maerk or DM formalism. Among the halogen molecules the e–F_2 total ionization cross-sections were measured by Rao and Srivastava [5], Stevie and Vasile [6] and Center and Mandel [7]. Christophorou and Olthoff [8] have recently given recommended data for all the important total cross-sections including ionization for electron collisions with molecular chlorine. The DM formulation has also been applied to ionization of F_2 and Cl_2 as well as Br_2 and I_2 [9]. A simpler approach called the ‘Defect Concept’ (DC) method has also been applied to halogen molecules [10].

The electron–halogen cross-sections are required in understanding the electron interactions of plasma processing gases like CF_4, CHF_3, C_2F_6, C_3F_8, etc. [8]. Although the halogens have a strong affinity for

---

[*] Corresponding author. E-mail: knjoshipur@yahoo.com

1387-3806/02/$ – see front matter © 2002 Published by Elsevier Science B.V.
PII S1387-3806(02)00624-3

Table 1
Properties of halogen atoms and molecules

Target	Ionization energy [23] in eV	Atomic average radii [14], and molecular bond lengths [23] in a_0
F	17.42	1.08
F_2	15.70	2.67
Cl	12.97	1.84
Cl_2	11.48	3.76
Br	11.81	2.11
Br_2	10.52	4.31
I	10.45	2.50
I_2	9.40	5.04

electron attachment, it is of interest to also determine their electron impact ionization characteristics. Table 1 given here highlights the important atomic–molecular properties of the halogens, and serves as a basic input to the present calculations.

Several approximate theories, as highlighted in a recent review by Deutsch et al. [1] are in vogue today for calculating the TICS of electrons colliding with different atomic and molecular targets. We [11–13] have developed an approach based on complex scattering potential that provides a viable option at intermediate and high incident energies. The total or the optical potential for the electron–atom/molecule system describes the simultaneous elastic and inelastic electron scattering, such that the imaginary part or the absorption potential V_{abs} accounts cumulatively for all allowed *electronic* excitations to discrete states and the continuum. We have further explored this basic formalism to deduce the TICS Q_{ion} by calculating the *summed-total inelastic* cross-sections Q_{inel}. This approach, to be called complex scattering potential-ionization contribution (CSP-ic) method, has already been employed by us [11–13] successfully on a number of atomic–molecular targets so far. The ionization calculations in the present paper are based on the CSP-ic method.

In Section 2, we highlight the present theoretical approach. Comparisons of the present results with experimental, theoretical and/or recommended data are made in Section 3 for all the targets investigated.

2. Theoretical

The complex scattering (optical) potential $V_{opt} = V_R + iV_I$ adopted presently to describe the electron–atom/molecule collisions has a real part V_R expressed as the sum of static, exchange and polarization terms. These terms are generated here in the form of model potentials [11–13] by starting with an accurate charge density of the target atoms [14]. For the diatomic molecules of our present interest, we build up single-center average spherical charge density from the respective atomic charge densities. The molecular charge density so obtained is modified to comply with a correct asymptotic behavior as a function of the target ionization potential [15]. This charge density is used to derive the various parts of V_{opt}. In particular the imaginary part of the V_{opt} is obtained by employing a well known model for the absorption potential, developed some years ago [16]. It represents in a quasi-free Pauli-blocking manner the inelastic scattering of the incident electron in target electron cloud, and has a typical form

$$V_{abs}(r, E_i) = -\rho(r)\left(\frac{T_{loc}}{2}\right)^{1/2}\left(\frac{8\pi}{10k_F^3 E_i}\right) \times \theta(p^2 - k_F^2 - 2\Delta)(A_1 + A_2 + A_3) \tag{1}$$

where the local kinetic energy is $T_{loc} = E_i - V_R$. Also $p^2 = 2E_i$ in a.u., k_F is the Fermi wave vector and Δ is an energy parameter. Further, in Eq. (1), $\theta(x)$ is the Heaviside function, such that $\theta(x) = 1$, for $x > 0$ and is zero otherwise. A_1, A_2 and A_3 are different functions of $\rho(r)$, I, Δ and E_i (see [16]). The energy parameter Δ determines a threshold below which V_{abs} is zero and the ionization or excitation is prevented energetically. Now, we choose [12,13] the value of Δ by the following consideration. At energy of impact close to (vertical) ionization threshold I, the excitations to the discrete states also take place, but as E_i increases, the valence ionization becomes dominant, together with the possibility of ionization of the inner electronic shells. The inner shells are of course harder to be excited or ionized. To account for the same we have selected $\Delta \approx I$ for low E_i and $\Delta > I$ at E_i

above the position of the peak of $Q_{\rm inel}$. This is effectively done by expressing Δ as a slowly varying function of $E_{\rm i}$ around I. Thus, with a reasonable choice of Δ for a given target we construct $V_{\rm abs}$, which through the Schrödinger equation, yields the imaginary phase shifts $\mathrm{Im}\,\delta_1(k)$ for various partial waves l. We omit here the standard formulae [17] used to generate $Q_{\rm inel}$ as well as the total *elastic* cross-section $Q_{\rm el}$ by employing the real and the imaginary parts of $\delta_1(k)$. The numerical procedures and the theoretical formalism involved here are quite well known [11–13].

Now, for a given target the total (*complete*) cross-section $Q_{\rm T}$ is defined to be

$$Q_{\rm T}(E_{\rm i}) = Q_{\rm el}(E_{\rm i}) + Q_{\rm inel}(E_{\rm i}) \tag{2}$$

where on the RHS the two terms denote the total elastic and the summed-total inelastic cross-section, respectively. The second term of Eq. (2) further breaks up as follows:

$$Q_{\rm inel}(E_{\rm i}) = \sum Q_{\rm exc}(E_{\rm i}) + Q_{\rm ion}(E_{\rm i}) \tag{3}$$

Here, the first term is the sum over total *excitation* cross-sections for all allowed electronic channels, from the initial state to the discrete states above. The second term indicates the TICS of the target by the incident electrons. The first term arises mainly from the low-lying dipole allowed transitions for which the excitation cross-sections become small gradually above the ionization threshold. Hence at such energies, the second term in Eq. (3) dominates over the first, so that the calculated $Q_{\rm inel}(E_{\rm i})$ can be employed to derive the TICS $Q_{\rm ion}$.

Now, since the total inelastic cross-section $Q_{\rm inel}$ itself is partitioned according to the Eq. (3), it follows that

$$Q_{\rm inel}(E_{\rm i}) \geq Q_{\rm ion}(E_{\rm i}) \tag{4}$$

The quantity $Q_{\rm inel}$ is not accessible directly in experiments. Hence to determine $Q_{\rm ion}$ from the calculated $Q_{\rm inel}$, we define the following ratio for a given target atom or molecule.

$$R(E_{\rm i}) = \frac{Q_{\rm ion}(E_{\rm i})}{Q_{\rm inel}(E_{\rm i})} \tag{5}$$

with $0 \leq R \lesssim 1$.

The electron impact transitions to continuum generally dominate over those to discrete states, as the $E_{\rm i}$ increases above I. Therefore, we find [11–13] in a number of atomic and molecular targets that, the ratio R is generally less than (but close to) 1, at impact energies well above the ionization threshold. For stable molecular targets like O_2, H_2O, CH_4, CF_4, etc. for which experimental $Q_{\rm ion}$ are known accurately, we observe that

$$R(E_{\rm i}) \cong 0.8, \text{ up to } E_{\rm i} \cong E_{\rm p} \tag{6a}$$

$$R(E_{\rm i}) \cong 1, \quad \text{for } E_{\rm i} > E_{\rm p} \tag{6b}$$

where $E_{\rm p}$ stands for the incident energy at which the (theoretical) $Q_{\rm inel}$ attains its maximum. The ratio R may be expressed as a smooth function of $E_{\rm i}$ as follows:

$$R(E_{\rm i}) = 1 - C_{\rm R}(I/E_{\rm p})(\ln E_{\rm i}/E_{\rm i}) \tag{7}$$

Thus, it approaches 1 at high energies when the dipole allowed electronic excitations fall off as $\ln E_{\rm i}/E_{\rm i}$. The constant $C_{\rm R}$ occurring in Eq. (7) can be fixed up for a target by the condition that $R(E_{\rm i})$ becomes zero at the ionization threshold.

The present theoretical approach may be compared to the DM formulation, which consists of a semiclassical formula applied successfully to various atoms and molecules for calculating the $Q_{\rm ion}$ [1,4,9]. In essence, the formula involves the use of the static target properties (e.g., electronic shell radii) and a dynamic function depending on the energy $E_{\rm i}$. The electron–molecule ionization cross-sections can also be derived in a simpler DC approach [10,18]. Since a diatomic molecule A_2 is different from a simple combination of two atoms A, the DC formula for the electron impact ionization of A_2 states that

$$Q_{\rm ion}(A_2) = 2^a Q_{\rm ion}(A) \tag{8}$$

where $Q_{\rm ion}(A)$ is the electron impact atomic ionization cross-section and the exponent ‘a’ is such that $0 < a < 1$ as given in [10].

The advantage of the present method is that the $Q_{\rm ion}$ are derived from $Q_{\rm inel}$, which are calculated in a numerically exact partial wave quantum mechanical calculation. Hence, it is not required to propose any parametric energy dependence of Q_{inel}, which in the high energy limit go over to Q_{ion}. Similarly it is also not required here to propose a formula for the dependence of the cross-sections on the target properties (Table 1), since these are in-built within the absorption potential itself. The third advantage of using the present approach is that the Q_{ion} as well as the total (complete) cross-sections Q_T can be calculated from the same general quantum mechanical formalism, so that the contribution of ionization relative to elastic and other inelastic processes can be examined. However, there is no rigorous way of calculating the ratio R defined in Eq. (5). The TICS calculated in CSP-ic method are generally on the higher side of the experimental and theoretical results, often within experimental errors.

3. Results, discussions and conclusions

Our results corresponding to E_i from threshold to almost 2000 eV, obtained in the present CSP-ic approach, i.e., Eqs. (1)–(7), can be examined in relation to experimental as well as theoretical data on atomic–molecular halogen targets, as given in Figs. 1–8. Consider Fig. 1, where our present calculations on Q_{ion} of F-atoms are found to compare favorably with the available measurements [3] and with the theoretical data of [4], at energies from threshold to the peak position at about 150 eV. The measured data of Hayes et al. [3] involve about 20% error. The peak in our calculated cross-sections occurs between 100 and 200 eV, where there are no data points in [3] that can locate the maximum accurately. The peak position and magnitude of the Q_{ion} are in accordance with the properties of the target given in Table 1. Thus, the peak positions for F and F_2 targets, which have relatively higher ionization thresholds above 15 eV, occur at higher energies around 100 eV. On the other hand, for highly ionizable targets like Br_2 and I_2 (which have their ionization threshold around 10 eV) the peak occurs below 100 eV and the corresponding magnitudes are much higher.

Next as shown in Fig. 2, our present theory is in good agreement with experimental [3] and theoretical [4] results in the case of atomic chlorine. The TICS of Br atom calculated presently and shown in Fig. 3,

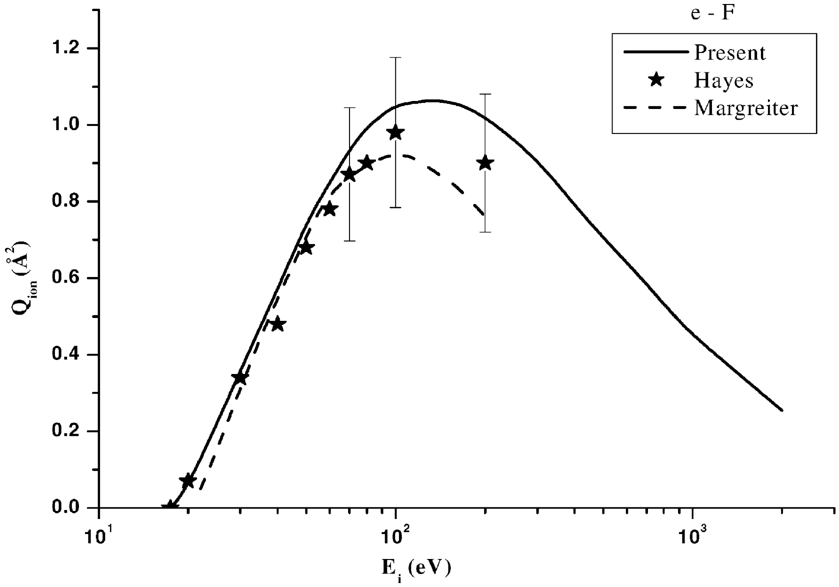

Fig. 1. Total ionization cross-sections for e–F scattering. Present (—); Hayes et al. [3] (★); Margreiter et al. [4] (- - -).

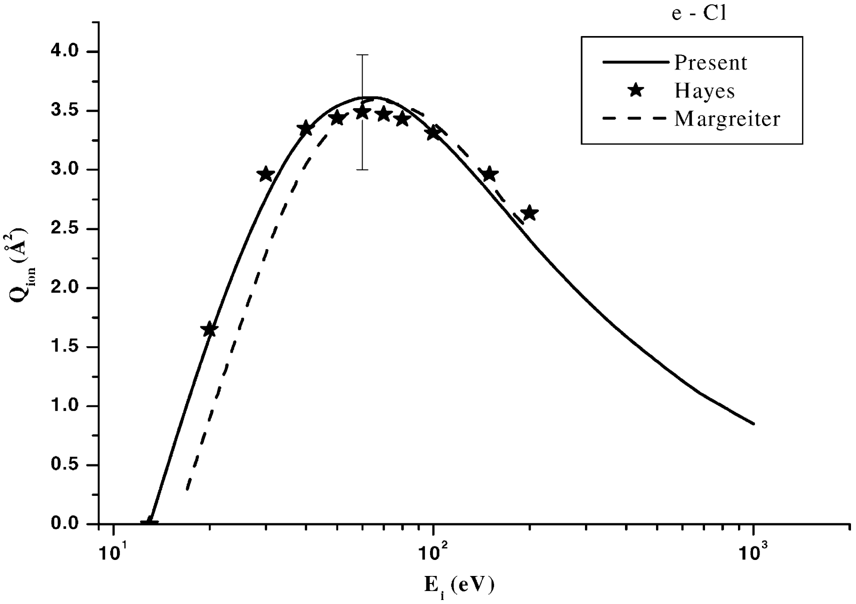

Fig. 2. Same as in Fig. 1 but for e–Cl scattering.

are on the lower side of the measured data [3] and the available theory [4], but they lie within the experimental uncertainties of 14%, as quoted by the authors [3]. Fig. 4 shows our Q_{ion} for atomic iodine, which are in a good agreement with the experimental results [3]. The values given by Margreiter et al. [4] differ somewhat in this regard, at low to intermediate energies. At other energies the agreement seems to be good. Let us

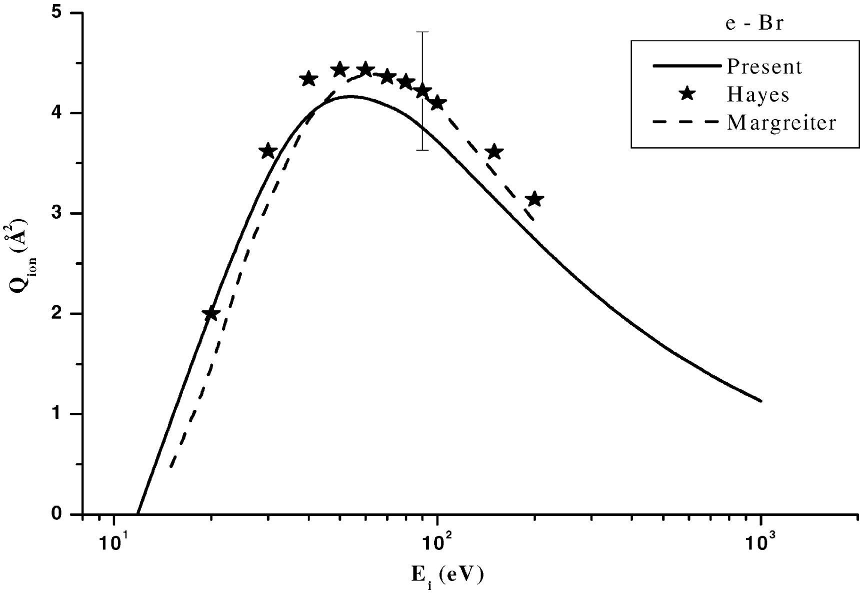

Fig. 3. Same as in Fig. 1 but for e–Br scattering.

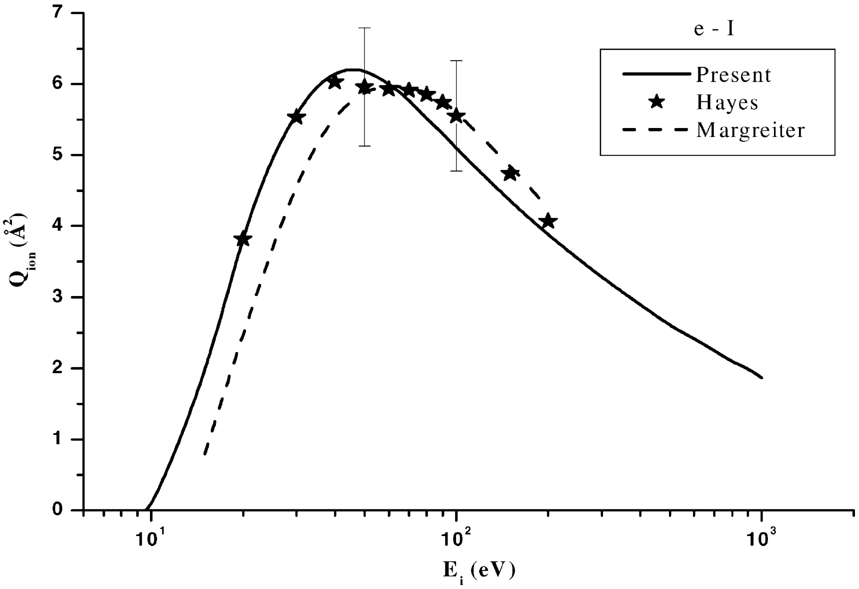

Fig. 4. Same as in Fig. 1 but for e–I scattering.

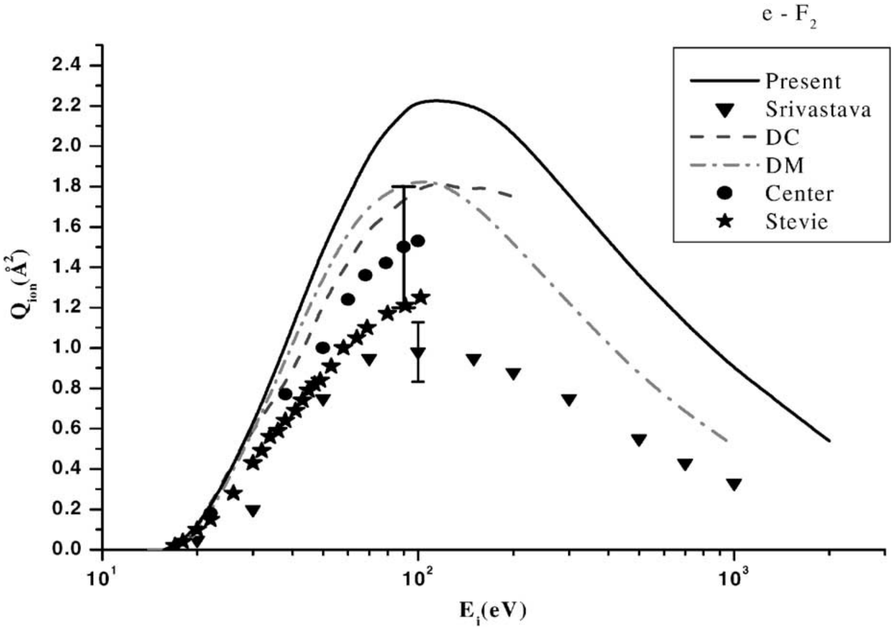

Fig. 5. Total ionization cross-sections for e–F_2 scattering. Present (—); Rao and Srivastava [5] (▼); DC [10] (- - -); DM [9] (–·–·–); Center and Mandel [7] (●); Stevie and Vasile [6] (★).

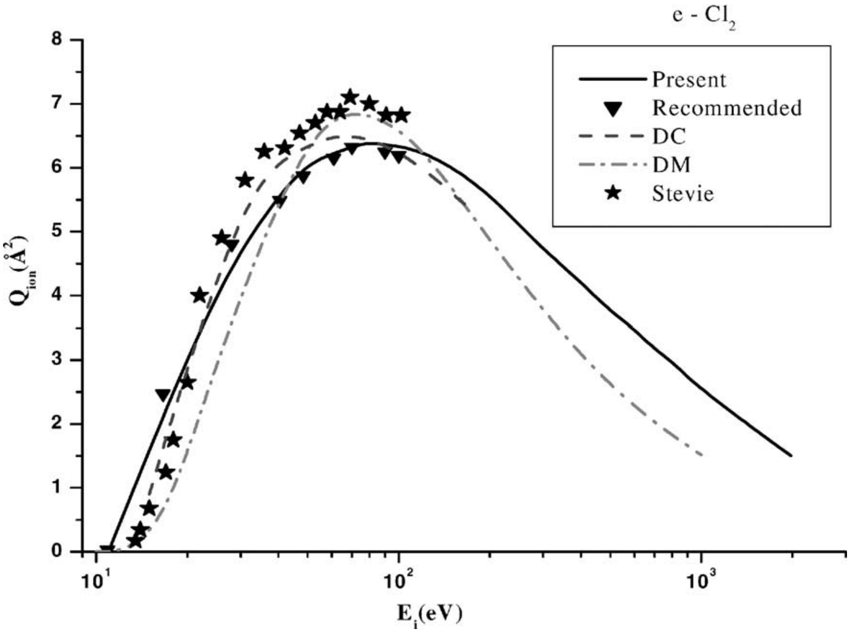

Fig. 6. Total ionization cross-sections for e–Cl_2 scattering. Present (—); recommended data [8] (▼); DC [10] (- - -); DM [9] (–·–·–); Stevie and Vasile [6] (★).

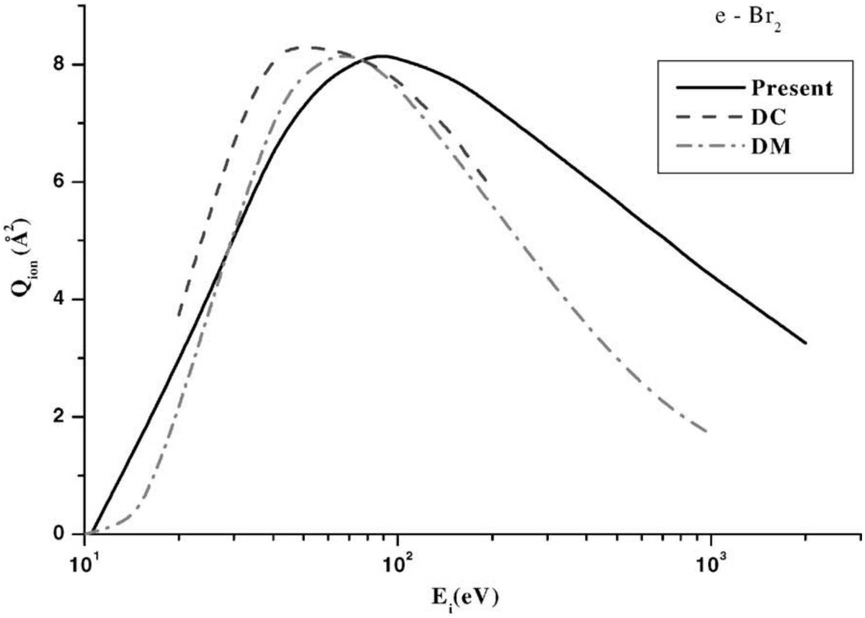

Fig. 7. Total ionization cross-sections for e–Br_2 scattering. Present (—); DC [10] (- - -); DM [9] (–·–·–).

note that the BEB calculations of Kim et al. [19], carried out for various other targets are not available on the ionization of atomic and molecular halogens.

Our calculations in the CSP-ic approach are extended to the electron impact ionization of molecular halogens, and a comparative study can be made from the Figs. 5–8. The continuous curve in Fig. 5 compares the present theory with the measurements of Rao and Srivastava [5], Stevie and Vasile [6] and Center and Mandel [7] on e-F_2 ionization. All these measured data are quite lower than the present values especially in the peak region around 100 eV, but there is an agreement in the shape or the energy dependence. The data given by [5] seem to be too low, since they are comparable to the F-atom cross-sections (Fig. 1). The other theoretical results [9,10] included in Fig. 5 are also on the higher side of the measured data [5]. The results of DC approach [10] and the DM formalism [9] are close to each other and are also within the error limits of [7].

In the case of the Cl_2 molecule (Fig. 6) the present values on TICS Q_{ion} are in a very good accord with the recommended data given by Christophorou and Olthoff [8], and also with the DC and DM formalism, especially up to the peak value. Although the recommended data are up to 100 eV only, the high energy trend of the TICS can be inferred from the present curve in Fig. 6.

Now, in the case of the two heavier molecules Br_2 and I_2 the calculations based on the DM [9] and DC [10] formalisms are the only available data for comparison. As can be seen from Figs. 7 and 8, the present theory and the DM formalism tend to agree only at lower energies up to the peak values of Q_{ion}. For energies above 100 eV or so, the results of [9,10] decrease faster than the present values for both these molecules. In the paper of Probst et al. [9a], the DM calculation is compared with their own results obtained from the use of the "DC" up to 200 eV energy. Both these results tend to merge at energies roughly above 100 eV. The DC approach considers the 'atom-in-the-molecule' aspect in a simple way. In the high energy (say above 1000 eV) short wavelength limit, the projectile electron 'sees' the atoms in a molecule as nearly free scattering centers, so that the molecular cross-section is close to the sum

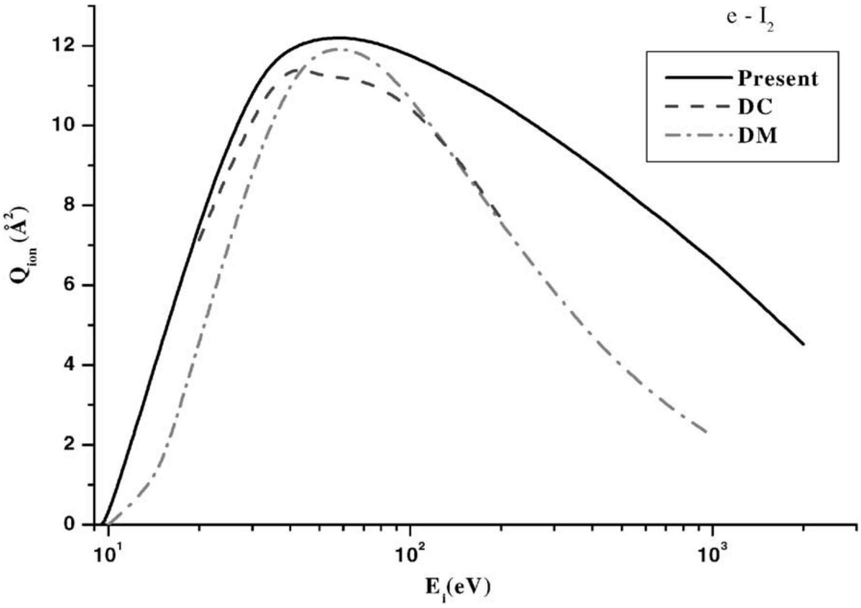

Fig. 8. Same as in Fig. 7 but for e–I_2 scattering.

of the free atom cross-sections [20,21]. However, at intermediate energies around 100 eV or so, the simple rule of 'additivity' is found to overestimate the TICS and the total (complete) cross-sections as well [22]. We believe therefore that, the DC calculation can give better (i.e., *lower*) results compared to a simple "additivity rule" for ionization at low to intermediate energies, but at high energies the DC calculations may tend to underestimate. One may think of the parameter 'a' in the Eq. (8) to be energy dependent. The difference between the present results and those of the DM calculations as observed in Figs. 7 and 8 may be understood in terms of the energy dependence involved in that formalism [9], especially at high energies. We look forward to experimental measurements on these targets to resolve the discrepancy as above.

It is interesting to make inter-halogen comparisons of the present results, which are in keeping with the respective atomic and molecular properties listed in Table 1. The ionization potential decreases in going along the sequence F–Cl–Br–I and similarly along F_2–Cl_2–Br_2–I_2, and hence the peak value of the Q_{ion} increases and the peak position shifts to lower energy. The peak cross-sections are found to increase with the atomic–molecular sizes (Table 1). Our results agree with the earlier theoretical methods in general near the peak positions of the TICS. The agreement is better for atoms studied in this paper. The presently calculated total ionization cross-sections of the halogen targets are consistent with the atomic/molecular properties like the ionization thresholds [23], atomic radii [14] and molecular bond lengths [23]. Therefore, the present method provides a good theoretical picture of electron-induced ionization of an important class of targets, viz. halogens.

Acknowledgements

This work was done as a part of a research project to KNJ by the Department of Science and Technology, New Delhi, India. He also thanks the Royal Society, London, UK and the Indian National Science Academy, New Delhi, India, for the bilateral Exchange Program of Scientists, under which a part of this work was carried out. We are highly thankful to Prof. T.D. Maerk, Institut fur Ionenphysik, Universitat Innsbruck, Innsbruck, Austria, for discussions and suggestions.

References

[1] H. Deutsch, K. Becker, S. Matt, T.D. Maerk, Int. J. Mass Spectrom. 197 (2000) 37 (and references therein).
[2] V. Tarnovsky, K. Becker, J. Chem. Phys. 98 (1993) 7686.
[3] T.R. Hayes, R.C. Wetzel, R.S. Frund, Phys. Rev. A35 (1987) 578.
[4] D. Margreiter, H. Deutsch, T.D. Maerk, Int. J. Mass Spectrom. Ion Proc. 139 (1994) 127.
[5] M.V.V.S. Rao, S.K. Srivastava, J. Phys. B29 (1996) 1841.
[6] F.A. Stevie, M.J. Vasile, J. Chem. Phys. 74 (1981) 5106.
[7] R.E. Center, A. Mandel, J. Chem. Phys. 57 (1972) 4104.
[8] L.G. Christophorou, J.K. Olthoff, J. Phys. Chem. Ref. Data 28 (1999) 967.
[9] (a) M. Probst, H. Deutsch, K. Becker, T.D. Maerk, Int. J. Mass Spectrom. 206 (2001) 13;
(b) H. Deutsch, M. Probst, K. Becker, T.D. Maerk, private communication, 2001.
[10] H. Deutsch, K. Becker, T.D. Maerk, Europhys. J. D12 (2000) 283.
[11] K.N. Joshipura, V. Minaxi, J. Phys. B: At. Mol. Opt. Phys. 34 (2001) 509.
[12] K.N. Joshipura, B.K. Antony, Phys. Lett. A289 (2001) 323.
[13] K.N. Joshipura, V. Minaxi, B.K. Antony, C.G. Limbachiya, XXII-ICPEAC, 2001, Held at Santa Fe-USA, Book of Abstracts, p. 258.
[14] C.F. Bunge, J.A. Barrientos, A.V. Bunge, At. Data Nucl. Data Tables 53 (1993) 113.
[15] S.H. Patil, At. Data Nucl. Data Tables 71 (1999) 41.
[16] D. Staszewska, D.W. Schwenke, D. Thirumalai, D.G. Truhlar, Phys. Rev. A29 (1984) 3078.
[17] C.J. Joachain, Quantum Collision Theory, North-Holland, The Netherlands, 1983, p. 110.
[18] H. Deutsch, K. Becker, J. Pittner, V. Bonacic-Koutecky, S. Matt, T.D. Maerk, J. Chem. Phys. 111 (1999) 1964.
[19] Y.K. Kim, W. Hwang, N.M. Weinberger, J. Chem. Phys. 106 (1997) 1026.
[20] S.M. Younger, T.D. Maerk, Electron Impact Ionization, Vol. 1, Springer, Berlin, 1985, p. 1.
[21] K.N. Joshipura, V. Minaxi, Eur. Phys. J. D5 (1999) 229.
[22] K.N. Joshipura, P.M. Patel, Z. Phys. D: At. Mol. Clusters (Germany) 29 (1994) 269.
[23] D.R. Lide, Handbook of Physics and Chemistry, CRC Press, Boca Raton, FL, 2000, pp. 9–15, 10–207.