List of Publications

1. *Electron impact total and ionization cross-sections for some hydrocarbon molecules and radicals*

2. *Calculated total cross sections of electron impact ionization and excitations in tetrahedral XY₄ and SF₆ molecules*

3. *Electron impact ionization of H₂O molecule in crystalline ice*

4. *Relative contributions of various electron collision processes on He and H₂ targets*

5. *Theoretical total ionization cross-sections for electron impact on atomic and Molecular halogens*

6. *Theoretical total cross sections of e – H₂O collisions in water, ice and dimer forms*
7. *Additivity Approximation for Molecules and Radicals*
   Indian J. Phys. 73 B (1999), 245.

8. *Additivity Approach in electron - Molecule collision theory*

9. *Ionization and excitation of atomic targets O, Al & Cu by electron impact*
# List of conferences attended abroad and in India

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<td>August 2003</td>
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Calculated total cross sections of electron-impact ionization and excitations in tetrahedral \((XY_4)\) and \(SF_6\) molecules

K. N. Joshipura,1,2* Minaxi Vinodkumar,2 C. G. Limbachiya,3 and B. K. Antony1,4

1Department of Physics, Sardar Patel University, Vallabh Vidyanagar-388120, Gujarat, India
2VP & RPTP Science College, Vallabh Vidyanagar-388120, Gujarat, India
3P. S. Science College, Kadi-382715, N. Gujarat, India
4Department of Physics & Astronomy, The Open University, Milton Keynes MK7 6AA, United Kingdom

(Received 18 August 2003; revised manuscript received 3 November 2003; published 17 February 2004)

Various total cross sections for collisions of electrons in the energy range 10–2000 eV are calculated for the tetrahedral \(CH_4\), \(SiH_4\), \(GeH_4\), \(CF_4\), \(SiF_4\), and \(CCl_4\) targets and \(SF_6\). Molecular total inelastic cross sections determined in the complex potential formalism are partitioned to account for the ionization and cumulative electronic-excitation channels. The present total cross sections and total ionization cross sections are found to be consistent with the previous data. The cumulative total excitation cross sections reported here indicate the relative importance of ionization together with electronic excitation channels including neutral dissociation of these molecules by electron impact.

DOI: 10.1103/PhysRevA.69.022705 PACS number(s): 34.80.Bm

I. INTRODUCTION

Total cross sections of electron impact ionization in tetrahedral molecules such as \(CH_4\), \(SiH_4\), \(GeH_4\), \(CF_4\), \(SiF_4\), and \(CCl_4\) have important applications in space and atmospheric physics, plasma, laser, and chemical physics. \(CH_4\) being a very well known molecule offers a large amount of theoretical as well as experimental data for comparison [1,2]. Total and partial ionization cross sections for \(SiH_4\) upon electron collisions are employed for the understanding and modeling of charge carrier balance in the plasma and the ion/radical chemistry in the gas phase. As well as for the surface processes [2]. \(CF_4\) is important in the semiconductor etching. From the theoretical point of view, the nearly spherical \((XY_4)\) type of molecules offers an advantage since the anisotropic interactions are quite negligible here at intermediate and high electron energies \((E_i)\). One can focus, as done presently, on ionization together with electronic excitations accompanied by elastic scattering from these targets. Apart from the tetrahedrals an important molecule \(SF_6\), having an octahedral structure has also been included in the present study.

In this work we have calculated basically the electron impact total \((\text{complete})\) cross sections \(Q_T\) and total inelastic cross sections \(Q_{\text{inel}}\) for the above molecules at incident energies almost from the threshold of electronic excitation to 2000 eV. The excitations to discrete states and to continuum include both direct and dissipative processes induced by electrons. Experimental data on \(Q_T\) for most of the present targets have been obtained by the Zecca-Karwasz group in Italy [3,4]. The electron impact ionization measurements are due to several other groups of workers [5–9]. Usually the measurements of total cross sections \(Q(TCS)\) for individual processes or for the total transmission are carried out in different energy ranges by different groups/laboratories in their own experimental setup as well as procedures. The sum total of the different experimental TCSs does not always agree well with the observed total \((\text{complete})\) cross section of a target [1]. One needs therefore, a suitable theory to examine the relative contributions of different TCSs to \(Q_T\) and to see their trends with respect to impact energy. Thus our aim in this paper is to calculate various TCSs of electron collisions and to investigate their relative contributions to the total \((\text{complete})\) cross sections for the chosen targets. Towards this goal, the well-known complex potential formalism, adopted here affords the most suitable approach. The usual complex potential calculation for electron scattering can provide total elastic cross section \(Q_{el}\) and its inelastic counterpart \(Q_{inel}\) such that

\[
Q_T(E_i) = Q_{el}(E_i) + Q_{inel}(E_i) \tag{1}
\]

Now, the total inelastic cross section \(Q_{inel}\) cannot be measured directly, and this restricts the scope of the traditional calculations. In recent years, we have developed and successfully employed a semiempirical approach [10–15] called the ‘complex scattering potential-ionization contribution’ (CSP-IC) method to determine the total ionization cross section \(Q_{ion}\) from the calculated \(Q_{inel}\). This method, highlighted in section 2 also provides information about the electronic excitations by electron impact.

II. THEORETICAL METHODOLOGY

In Eq. (1), the total inelastic cross section \(Q_{inel}\) can be partitioned into two main contributions viz.

\[
Q_{inel}(E_i) = \sum Q_{exc}(E_i) + Q_{ion}(E_i) \tag{2}
\]

where the first term is the sum over total excitation cross sections for all accessible electronic transitions. The second term is the total cross section of all allowed ionization processes induced by the incident electrons. The first term arises mainly from the low-lying dipole allowed transitions for...
which the cross section decreases rapidly at higher energies. In CH₄ all electronic excitation processes result in dissociation into neutral fragments [1]. Presently we have used the symbol QₙDiss to denote the sum of total neutral-dissociation cross sections of a target.

Now, the first term in Eq. (2) becomes less and less important than the second at energies well above the ionization threshold [3,4]. Hence we have

\[ Q_{\text{inel}}(E_i) \geq Q_{\text{ion}}(E_i). \]  

Our calculation of all these TCSs is based on a complex scattering potential, generated from spherically averaged charge densities of the target molecules, as in our CSP-IC approach [10–15]. The single-center molecular charge density is obtained by a linear combination of constituent atomic charge densities, renormalized to account for covalent molecular bonding, as done in our earlier calculations [10]. Briefly, the charge density ρ of a molecule XY₄ is expressed in terms of the atomic charge densities ρₓ and ρᵧ as a function of distance r from the molecular center of mass, as follows:

\[ ρ(r; R) = fₓρₓ(r) + 4fᵧρᵧ(r; R). \]  

Here, ρₓ is the charge density of the central atom X, and ρᵧ is that of the atom Y expressed as a function of r and the bond length R. The modulating factors fₓ and fᵧ arise from the partial charge migration in the covalent bonding as explained in Ref. [10]. The molecular charge density ρ is employed to construct a complex potential \( V_{\text{pot}} = V_R + i V_I \), that contains a real part \( V_R \) comprising static \( (V_{\text{st}}) \), exchange \( (V_{\text{ex}}) \), and polarization \( (V_p) \) terms, as follows:

\[ V_R = V_{\text{st}}(r) + V_{\text{ex}}(r, E_i) + V_p(r, E_i). \]  

The imaginary part \( V_I \), also called the absorption potential \( V_{\text{abs}} \), accounts for the total loss of scattered flux into all the allowed channels of electronic excitation and ionization. A currently popular model form for \( V_{\text{abs}} \) is that of Staszewska et al. [16], who had developed a quasifree, Pauli-blocking, dynamic absorption potential given in a.u., as

\[ V_{\text{abs}}(r, E_i) = -\frac{1}{2} \rho(r) \cdot v_{\text{loc}} \cdot \sigma_{ee} \]
\[ = -\rho(r) \left( \frac{T_{\text{loc}}}{2} \right) \left( \frac{8 \pi}{10 k^2} \right) \theta(p^2 - k^2 - 2\Delta) (A_1 \]
\[ + A_2 + A_3). \]  

In these expressions, \( v_{\text{loc}} \) is the local speed of the external electron, and \( \sigma_{ee} \) denotes the average total cross section of the binary collision of the external electron with a target electron. The local kinetic energy of the incident electron is obtained from

\[ T_{\text{loc}} = E_i - V_R = E_i - (V_{\text{st}} + V_{\text{ex}} + V_p). \]  

For a given energy, the dominant term in Eq. (7) is \( V_{\text{st}} \). Further \( p^2 = 2E_i \) in au, \( k^2 = (3\pi^2 \rho(r))^2 \) is the Fermi wave vector and \( \Delta \) is an energy parameter. In Eq. (6), \( \theta(x) \) is the Heaviside unit step function, such that \( \theta(x) = 1 \) for \( x > 0 \), and is zero otherwise. The dynamic functions \( A_1, A_2, \) and \( A_3 \) defined in Ref. [16] depend differently on the molecular properties \( p, \Delta \), and \( E_i \). In this model [16–18] the parameter \( \Delta \) is assumed to be fixed at the ionization energy \( I \) or the first excitation energy \( E_{ih} \). It determines a threshold below which \( V_{\text{abs}} = 0 \), and the ionization or excitation is prevented energetically. If \( \Delta = 0 \) in Eq. (6) then \( Q_{\text{inel}} \) becomes infinity. Further if the \( E_{ih} \) of the target is rather small, the cross sections resulting from the choice \( \Delta = E_{ih} \) are quite large. We have therefore modified [10–13] the absorption model by choosing the value of \( \Delta \) varying from \( E_{ih} \) to \( I \). This is effectively done by expressing \( \Delta \) as a slowly varying function of \( E_i \) around \( I \). Thus with a reasonable choice of the \( \Delta \) parameter for a given target we construct the \( V_{\text{abs}} \). The Schrödinger equation when solved numerically for \( V_{\text{abs}} \), yields the imaginary part of the phase shifts \( \delta_1(k) \) for various partial waves \( l \). We omit here the standard formulas used [19] to generate \( Q_{\text{inel}} \) as well as the \( Q_{\text{ion}} \) by employing the real and imaginary parts of \( \delta_1(k) \). The total (complete) cross section \( Q_{\text{T}} \) is obtained from Eq. (1).

Now, the cross section of interest in many applications is \( Q_{\text{ion}} \), which is contained in \( Q_{\text{inel}} \). There is no rigorous way to project out the former from the latter. Hence, in order to determine \( Q_{\text{ion}} \) from our calculated \( Q_{\text{inel}} \), we define the following quantity for \( E_i = I \):

\[ R(E_i) = \frac{Q_{\text{ion}}(E_i)}{Q_{\text{inel}}(E_i)}. \]  

It is such that

\[ 0 \leq R \leq 1. \]  

We require that \( R = 0 \) when \( E_i = I \). For a number of stable molecules like O₂, H₂O, CH₄, SiH₄, etc., for which the experimental cross sections \( Q_{\text{ion}} \) are known accurately [1,2], the ratio \( R \) rises steadily as the energy increases above the threshold, and approaches unity at high energies. Thus,

\[ R(E_i) = 0 \quad \text{for} \quad E_i < I \]  

\[ = R_p \quad \text{at} \quad E_i = E_p \]  

\[ \equiv 1 \quad \text{for} \quad E_i > E_p, \]  

where \( E_p \) stands for the incident energy at which the calculated \( Q_{\text{inel}} \) attains its maximum. \( R_p \) stands for the value of \( R \) at \( E_i = E_p \), and as per our discussion in Refs. [12–15] we choose \( R_p = 0.7 \). This choice follows from the general observation that at energies close to peak of ionization, the contribution of the molecular \( Q_{\text{ion}} \) is about 70–80% in the total inelastic cross sections \( Q_{\text{inel}} \). This behavior is attributed to the faster fall of the first term \( \sum Q_{\text{xc}} \) in Eq. (2). For calculating \( Q_{\text{ion}} \) from \( Q_{\text{inel}} \) we need \( R \) as a continuous function of energy \( E_i \); hence we represent [12–15] the ratio \( R \) in the following manner:

\[ R(E_i) = 1 - f(U), \]
CALCULATED TOTAL CROSS SECTIONS OF e-CH4 SCATTERING

TABLE I. Parameters for e-CH4 scattering.

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<th>Energy parameters (eV)</th>
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<td>C1</td>
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<tr>
<td></td>
<td>C2</td>
</tr>
<tr>
<td>E_p = 45</td>
<td>a</td>
</tr>
<tr>
<td>E_ion = 70</td>
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\[ R(E_i) = 1 - C_1 \left[ \frac{C_2}{U + a} + \frac{\ln(U)}{U} \right]. \]

(10)

Here \( U \) is the dimensionless variable defined through

\[ U = \frac{E_i}{T}. \]

(11)

The reason for adopting a particular functional form of \( f(U) \) in Eq. (10) is the following. As \( E_i \) increases above \( I \), the ratio \( R \) increases and approaches value 1, since the ionization contribution rises and the discrete excitation term in Eq. (2) decreases. The discrete excitation cross sections, dominated by dipole transitions, fall off as \( \ln(U)/U \) at high energies. Accordingly the decrease of the function \( f(U) \) must also be proportional to \( \ln(U)/U \) in the high range of energy. However, the two term representation of \( f(U) \) given in Eq. (10) is more appropriate since the first term in the square brackets ensures a better energy dependence at low and intermediate \( E_i \). Equation (10) involves dimensionless parameters \( C_1, C_2, \) and \( a \), that reflect the target properties. The three conditions stated in Eqs. (9a)–(9c) are used to determine these three parameters. To implement the third condition (9c) clearly, we first assume \( a = 0 \) and consider a two-parameter expression in Eq. (10). We employ therein the two conditions (9a) and (9b) to evaluate the \( C \) parameters only. The two-parameter expression is then used to obtain the value of \( R \) at a high energy \( E_i = 10E_p \), and the same is employed in Eq. (9c). We have shown in our Table I the parameters involved in the present work on CH4 molecule, along with \( C_1, C_2, \) and \( a \) evaluated in this way. In Table 1 \( E_\text{ion} \) denotes the incident energy at which our calculated \( Q_{\text{ion}} \) reaches maximum.

III. RESULTS, DISCUSSION, AND CONCLUSIONS

The theoretical approach CSP-IC outlined above offers the determination of the total cross sections \( Q_T, Q_{el}, Q_{\text{inel}}, \) and \( Q_{\text{ion}} \) along with a useful estimate on electronic excitations (and consequent radiative or dissociative processes) in terms of the summed cross section \( \Sigma Q_{\text{exc}} \). In the present range of energy, i.e., 10–2000 eV, the rotational excitations from \( J = 0 \) to \( J' = 3 \) and 4 as allowed by the \( T_d \) symmetry of the tetrahedral targets, are insignificant [1]. Therefore, the present work covers all the major TCSs of electron impact on \( XY_4 \) targets. Our TCS \( Q_{\text{inel}} \) does not have a direct comparison, but we have checked the consistency of our calculated values at the appropriate energies. In CF4 where such a comparison was not possible, we made another indirect comparison as mentioned later in our discussions.

CH4, SiH4, and GeH4

Our theoretical results along with the compared data for methane, silane, and germane are plotted in Figs. 1–4, respectively. Although \( e-\text{CH}_4 \) scattering has been investigated quite extensively by many workers so far, we present some new results here for a comparison on neutral dissociation. As Fig. 1 shows, the present total (complete) cross sections \( Q_T \) results on \( Q_{\text{inel}} \) indirectly in sample cases. To do this we rewrite Eq. (1) as follows:

\[ Q_{\text{inel}}(E_i) = Q_T(E_i) - Q_{el}(E_i), \]

where the two cross sections on the right hand side can be obtained from the experimental data, and the "experimental" difference can be compared to the present calculation of \( Q_{\text{inel}} \). We have used the experimental data on CH4 and SiH4 with varying degrees of errors [1], and the said comparison has been made in Table II. It is found that our resulting \( Q_{\text{inel}} \) are consistent with the compared quantity, and show the peak values at the appropriate energies. In CF4 where such a comparison was not possible, we made another indirect comparison as mentioned later in our discussions.
of methane are in a good general agreement with the theoretical values of Jain and Baluja [17], and also with the measurements of Zecca et al. [3]. The lower curves in all our graphical plots correspond to various inelastic processes. Thus the topmost lower curve in Fig. 1 represents the summed-total inelastic cross section \( Q_{\text{inel}} \) calculated presently. Our \( Q_{\text{inel}} \) are in accord with the earlier calculations of Ref. [17], not shown to preserve clarity.

The inelastic cross sections for methane achieve the peak at about 45 eV while the ionization cross sections show the peak at about 70 eV. The total ionization cross sections \( Q_{\text{ion}} \) derived in our CSP-IC approach (Fig. 1) are in a very good accord with the measured data sets [5,6] as observed by us in Ref. [15]. The calculated \( Q_{\text{inel}} \) are quite close to \( Q_{\text{ion}} \) above 200 eV. Our summed-total excitation cross sections \( \Sigma Q_{\text{exc}} \) are shown by the lowest curve. In methane the electronic excitation results into neutral dissociation, mainly into \( \text{CH}_3 \) and \( \text{CH}_2 \) fragment channels. Nakano et al. [20] measured the TCSs of neutral dissociation of methane into these two channels, and we have exhibited, in Fig. 1, the sum of these TCSs \( Q_{\text{NDiss}} \). It is interesting to note that there is a good agreement between the data of Nakano et al. [20] and the present values of \( \Sigma Q_{\text{exc}} \), with the peak region observed around 25-eV energy. As mentioned by these authors [20] the experimental \( Q_{\text{NDiss}} \) fall off rather fast beyond the peak position. The semi-empirical total electronic-excitation cross section given by Kanik et al. [21] lies slightly above the data of Ref. [20]. The present quantity \( \Sigma Q_{\text{exc}} \) added up with our TCSs of the ionization and the elastic channels matches well with the total (complete) cross sections \( Q_T \). At about 20 eV the contribution of ionization and the cumulative excitations is equal (Fig. 1). The quantity \( Q_{\text{ion}} \) achieves its maximum at about 70 eV. A bar chart showing the relative importance of different scattering channels in \( \text{CH}_4 \) at this energy is given in Fig. 2. The present \( Q_{\text{el}} \) \((5.7 \text{ Å}^2)\) given in Fig. 2 is close to the integral elastic cross section given by Sakae et al. [22].

Figures 3 and 4 exhibit our results along with comparisons on \( \text{SiH}_4 \) and \( \text{GeH}_4 \), respectively. In silane (Fig. 3), the present \( Q_T \) show a good accord with the measured data of Zecca et al. [4]. Also shown here are the calculations of Jiang et al. [23] based on the high energy “additivity rule” (AR). Generally the present \( Q_T \) values at low energies are higher than the measurements in view of the exchange and polarization model potentials employed here. The present ionization cross sections \( Q_{\text{ion}} \) of silane also match quite satisfactorily with the measured data of Ref. [5] as well as Ref. [7]. The lowest curves in silane (Fig. 3) as well as germane (Fig. 4) represent the calculated excitation cross sections \( \Sigma Q_{\text{exc}} \), for which no comparison is available at present. In the case of \( \text{GeH}_4 \) the experimental [24,25] TCS \( Q_T \) are on the higher side of our theoretical values and also those of Baluja et al. [26]. This is an exceptional feature in the present study, which remains unexplained. There are perhaps no experiments on \( Q_{\text{ion}} \) of germane, but we can see (Fig. 4) an agreement between the present and the BEB-model calculations of Ali et al. [27]. In the sequence \( \text{CH}_4 \rightarrow \text{SiH}_4 \rightarrow \text{GeH}_4 \), the germane molecule has the lowest ionization potential. It therefore shows the highest peak magnitude of \( Q_{\text{ion}} \), and the
FIG. 5. e-CF₄ scattering. Lower curves: ---, present $Q_{\text{ion}}$; *, $Q_{\text{ion}}$ Poll et al. [29]; -- *, $Q_{\text{ion}}$ Ali et al. [27]; -- *, $Q_{\text{ion}}$ [28]; ----, present $\Sigma Q_{\text{exc}}$. Upper curves $Q_T$: ----, present; •, Zecca et al. [4]; ---, Jiang et al. [23].

same occurs at the lowest energy (Fig. 4).

CF₄, SiF₄, CCl₄, and SF₆

CF₄ is another target molecule for which a lot of comparison is available in the literature [14]. As shown in Fig. 5, our $Q_T$ values compare favorably with the experimental data of Ref. [4] and the AR results [23]. The said experimental data do not seem to be consistent below 100 eV. There is a nice accord among the present $Q_{\text{ion}}$, the binary encounter Bethe (BEB) values [27], the recommended ionization cross sections [28], and the measurements done by Poll et al. [29], which are up to 200 eV. Also from the recommended data given in Ref. [28], we find that at 200 eV the present value $Q_{\text{ion}} = 6.74 \text{ Å}^2$ matches closely with the experimental result $6.45 \text{ Å}^2$ for the sum ($Q_{\text{ion}} + Q_{\text{Ndis}}$). Our calculations of $\Sigma Q_{\text{exc}}$ given in the lowest curve in Fig. 5 show a peak position in agreement with the neutral dissociation data [28].

FIG. 6. e-SiF₄ scattering. Lower curves: ---, present $Q_{\text{ion}}$; ---, present $\Sigma Q_{\text{exc}}$; *, Basner et al. [30]. Upper curve $Q_T$: ----, present.

FIG. 7. e-CCl₄ scattering. Lower curves: ---, present $Q_{\text{ion}}$; *, $Q_{\text{ion}}$ Hudson et al. [8]; ---, present $\Sigma Q_{\text{exc}}$. Upper curves $Q_T$: ----, present; •, Zecca [3,4]; ---, Jiang et al. [23].

The various TCSs of e-SiF₄ system obtained in the CSP-ic approach are given in Fig. 6. The present $Q_{\text{ion}}$ of this molecule are in a good accord with the measurements of Basner et al. [30].

Finally in the case of e-CCl₄ scattering (Fig. 7) we see a good comparison amongst the present $Q_T$ values and the corresponding measurements [4]. The AR results of Ref. [23] lie below these two data sets, and that is surprising since the AR model being a high energy approximation, is expected to provide an upper limit of the TCS. Our $Q_{\text{ion}}$ for CCl₄ are matching very well with the experiments of Hudson et al. [8]. The present $\Sigma Q_{\text{exc}}$ plotted here give us an idea of the electronic excitation processes in this molecule. Let us mention in the passing that, for the tetrahedral molecules the $Q_{\text{ion}}$ results of the DM formulation [31] are found to be in agreement [14] with the present results from threshold to 200 eV, above which the DM values tend to fall faster.

Finally in the case of e-SF₆ scattering cross sections exhibited in Fig. 8, the present theoretical $Q_T$ are slightly below the AR approximation [23] as expected, but the mea-

FIG. 8. e-SF₆ scattering. Lower curves: ---, present $Q_{\text{ion}}$; ---, $Q_{\text{ion}}$ Kim [33]; *, $Q_{\text{ion}}$ Rapp and Englander-Golden [9]; ---, present $\Sigma Q_{\text{exc}}$. Upper curves $Q_T$: ----, present; ---, Jiang et al. [23]; *, Dubabneh et al. [32].
JOSHIPURA et al.

sured data of Dababneh et al. [32] available up to 500 eV, are well below these two theories. The present ionization results $Q_{\text{ion}}$ agree well with the experimental data of Rapp and Englander-Golden [9], while the BEB values of the Kim group [33] are seen to be somewhat above the measured data [9]. Our $\Sigma Q_{\text{exc}}$ values for SF$_6$ and other molecules in the present work can serve as an upper limit of the total electronic excitation cross sections, for which the present-day knowledge is rather limited.

Thus, in conclusion, the present CSP-IC method extends the scope of the traditional complex potential calculations and provides all the important TCSs, as highlighted in this work on $XY_4$ molecular targets along with SF$_6$. The elastic cross sections $Q_{el}$ are not much discussed here except as in Table II. The theoretical cross section $Q_{\text{inel}}$ serves as the upper limit of the total ionization cross section. The peak positions and magnitudes of the $Q_{\text{ion}}$ and the summed-total excitation cross sections calculated in this paper are in accordance with the respective threshold energies for the present targets. In the case of methane for which a lot of electron scattering work has been published so far, a nearly complete-theoretical picture of various collision processes is now provided through our Figs. 1 and 2. The ionization process in methane contributes by about 40% to the total (complete) cross section, at the peak of $Q_{\text{ion}}$. Our theoretical data also offer useful guidelines for the other tetrahedral targets and SF$_6$. The method adopted presently will now be extended to other larger molecules of applied interest.

ACKNOWLEDGMENTS

B.K.A. thanks the Commonwealth (UK) for financial aid for his recent visit to the UK. K.N.J. thanks the Department of Science and Technology, New Delhi-India, for a research grant under which a part of this work was done.

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 Vidyangar 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

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Pll S1387-3806(02)00624-3
Table 1

<table>
<thead>
<tr>
<th>Target</th>
<th>Ionization energy [23] in eV</th>
<th>Atomic average radii [14], and molecular bond lengths [23] in a₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>F</td>
<td>17.42</td>
<td>1.03</td>
</tr>
<tr>
<td>F₂</td>
<td>15.70</td>
<td>2.67</td>
</tr>
<tr>
<td>Cl</td>
<td>12.97</td>
<td>1.84</td>
</tr>
<tr>
<td>Cl₂</td>
<td>11.48</td>
<td>3.76</td>
</tr>
<tr>
<td>Br</td>
<td>11.81</td>
<td>2.11</td>
</tr>
<tr>
<td>Br₂</td>
<td>10.52</td>
<td>4.31</td>
</tr>
<tr>
<td>I</td>
<td>10.45</td>
<td>2.50</td>
</tr>
<tr>
<td>I₂</td>
<td>9.40</td>
<td>5.04</td>
</tr>
</tbody>
</table>

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 HCS 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 $\text{V}_{\text{abs}}$ accounts cumulatively for all allowed electronic excitations to discrete states and the continuum. We have further explored this basic formalism to deduce the TICS $<\text{TICS}>$ by calculating the summed-total inelastic cross-sections $Q_{\text{inel}}$. 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 $V_{\text{opt}} = V_R + iV_I$ 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 $V_{\text{opt}}$. In particular the imaginary part of the $V_{\text{opt}}$ 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

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

(1)

where the local kinetic energy is $T_{\text{loc}} = E_i - V_R$. Also $p^2 = 2E_i$ in a.u., $k_F$ is the Fermi wave vector and $\Delta$ 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 $\rho(r)$, $I$, $\Delta$ and $E_i$ (see [16]). The energy parameter $\Delta$ determines a threshold below which $V_{\text{abs}}$ is zero and the ionization or excitation is prevented energetically. Now, we choose [12,13] the value of $\Delta$ 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 $Q_{\text{inel}}$. This is effectively done by expressing $\Delta$ as a slowly varying function of $E_i$ around $I$. Thus, with a reasonable choice of $\Delta$ for a given target we construct $\mathcal{V}_{\text{abs}}$, which through the Schrödinger equation, yields the imaginary phase shifts $\text{Im} \delta_I (k)$ for various partial waves $I$. We omit here the standard formulae [17] used to generate $Q_{\text{inel}}$ as well as the total elastic cross-section $Q_{\text{el}}$ by employing the real and the imaginary parts of $\mathcal{V}_{\text{abs}}$. 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 $Q_T$ is defined to be

$$Q_T(E_i) = Q_{\text{el}}(E_i) + Q_{\text{inel}}(E_i)$$

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:

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

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 $Q_{\text{inel}}(E_i)$ can be employed to derive the TICS $Q_{\text{ion}}$.

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

$$Q_{\text{inel}}(E_i) \geq Q_{\text{ion}}(E_i)$$

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

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

with $0 \leq R \leq 1$.

The electron impact transitions to continuum generally dominate over those to discrete states, as the $E_i$ 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 $Q_{\text{ion}}$ are known accurately, we observe that

$$R(E_i) \cong 0.8, \text{ up to } E_i \cong E_p$$

$$R(E_i) \cong 1, \text{ for } E_i > E_p$$

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

$$R(E_i) = \frac{\ln(E_i/E_p)}{C_R \ln(E_i/E_p)}$$

Thus, it approaches 1 at high energies when the dipole allowed electronic excitations fall off as $\ln(E_i/E_p)$. The constant $C_R$ occurring in Eq. (7) can be fixed up for a target by the condition that $R(E_i)$ 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 $Q_{\text{ion}}$ [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 $E_i$. 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

$$Q_{\text{ion}}(A_2) = 2^a Q_{\text{ion}}(A)$$

where $Q_{\text{ion}}(A)$ 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 $Q_{\text{ion}}$ are derived from $Q_{\text{inel}}$, which are calculated in a numerically exact partial wave quantum mechanical
calculation. Hence, it is not required to propose any parametric energy dependence of $Q_{\text{inel}}$, which in the high energy limit go over to $Q_{\text{ion}}$. 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 $Q_{\text{ion}}$ 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 $Q_{\text{ion}}$ 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 $Q_{\text{ion}}$ 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] (---).](image-url)
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 $Q_{100}$ 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. 4. Same as in Fig. 1 but for e-I scattering.


Fig. 7. Total ionization cross-sections for e-Br\textsubscript{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- F₂ 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 Cl₂ molecule (Fig. 6) the present values on TICS Q₁₀₀ 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 Br₂ and I₂ 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 Q₁₀₀. 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.
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 'α' 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 F2–Cl2–Br2–I2, and hence the peak value of the Qion 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