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Total ionization cross-sections of atmospheric molecules due to electron impact

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The total ionization cross-sections of atmospheric molecule due to electron impact for threshold ionization energy to 10 MeV have been studied. Many researchers like Khare and Wadhera [*Phys Lett A*, 198 (1995) 212] have successfully employed the Plane Wave Born Approximation (PWBA), corrected for the exchange, the Coulomb and the relativistic effects to calculate the outer shell ionization of molecules including transverse interaction for the inner shell ionization of atoms and molecules The present results have been compared with experimental data and other theoretical data wherever available.

Keywords: Electron impact, Atmospheric molecule, Ionization

1 Introduction

Total ionization cross-sections of molecules by electron impact are required to study the plasma diagnostics, astrophysical and fusion applications, radiation physics, mass spectrometry, ionization in gas discharge, modeling of fusion plasmas, modeling of radiation effects for both materials and medical research, and astronomy[1] etc. The gases like H_2S, N_2O, CO_2 are of interest to atmospheric science. H_2S is not only present in the earth atmosphere but have been found on comets[2] too. It is used in analytical chemistry for qualitative inorganic analysis of metal ions. N_2O is the source of NO and NO_2 in the stratosphere. N_2O also contributes to the upper atmosphere chemistry by acting as an atmospheric thermal insulator. CO_2 and N_2O are also known as green house gases and CO_2 contributes majority to the global warming.

In the recent years, the total ionization cross-sections for atmospheric molecules have been the subject of many theoretical and experimental studies[3-9]. Weinberger and Rudd[6] theoretically calculated the total cross-section for H_2S from threshold to 1 keV by using Binary Encounter Bethe theory with the vertical ionization potential. Experimentally, total cross- sections for H_2S are measured by Lindsay *et al.*[5] and Rao and Srivastava[8] for energy range from threshold to 1 keV, whereas Belic and Kurepa[9] measured it for energy range started from threshold to 100 eV. For high energy from 0.1 to 2.7 MeV, the total cross-section measured by Reike and Prepejchal[10]. For N_2O, Kim *et al.*[6] calculated the total cross-section for energy range of threshold to 1 keV by applying the Binary Encounter Bethe theory along with vertical ionization potential. According to them, this improves their theory. They also calculated the ground state ionization cross-section for these molecules. Joshipura *et al.*[7] also calculated total cross-section for N_2O from threshold to 2 keV. They have calculated total cross-section for elastic and inelastic collisions and then deduced complex scattering by potential-ionization contribution method. Experimentally, total cross-sections for N_2O have been given by Rapp and Englander-Golden[3] for energy range of threshold to 1 keV. Lindsay *et al.*[5] measured total cross-section and absolute partial cross-sections of the same. Iga *et al.*[4] also measured total cross section for energy threshold to 1 keV. For N_2O there is no experimental and theoretical data available for high energy range 0.1 to 2.7 MeV according to best of our knowledge. Total cross-sections for CO_2 is also calculated by Hwang *et al*[11]. and measured by Lindsay and Mangan[12] and Hudson *et al.*[13] for energy range from threshold to 250 eV. Experimental value of total cross-section for high energy range 0.1 to 10 MeV has been given by Reike and Prepejchal[10].

One of the purposes of this work is to calculate the electron impact ionization cross-sections of the molecules by employing the useful features of Kim

model with Saksena model to remove the deficiency of the later model at low energy. This modification has been included recently by Khare *et al.*[16] for CH_4 molecules where $(1-\omega/E)$ was replaced by $(E'/E'+U+I)$, where ω is the energy loss suffered by incident electron in the ionizing collision, E the kinetic energy of incident electron, I the ionization energy, U is the average kinetic energy of bound electron. Here $U+I$ represent the increase in kinetic energy of the incident electron due to its acceleration by the field of the target nucleus. This is the only theory which is applicable for such a wide energy range varies from threshold to several MeV. By the present model, the expression for the Kim *et al.*[6] can be obtained.

2 Theory

Saksena *et al.*[14] have proposed a model for the molecular ionization cross-sections. They started with the plane wave born approximation (PWBA) but later on included exchange and relativistic corrections. The transverse interaction through emission and the re-absorption of the virtual photons along with the longitudinal interaction through the static unretarded Coulomb field are also included. However, PWBA requires continuum generalized oscillator strengths (CGOS), which are very difficult to evaluate. Hence, they employ a semi-phenomenological relation of Mayol and Salvet[15] which expresses CGOS in terms of the continuum optical oscillator strengths (COOS). The use of the above relation breaks the expression of the ionization cross-section σ_j for the j^{th} molecular orbital into two terms one representing the Bethe term (soft collision) and other one the Mott term (hard collision). But it is found that their model has been found to underestimate the cross-section at low impact energies. Khare and Wadhera[18] have successfully employed PWBA, corrected for the exchange, the Coulomb and the relativistic effects. To remove the deficiency of the former model at low E, another model was developed by Khare *et al.*[16] by combining the useful features of Saksena *et al.*[14] model and the Binary Encounter Bethe models of Hwang *et al*[11]. In the present theory, we have replaced $(1-\omega/E)$ as done by the Saksena *et al.*[14] model by $(E'/E'+U+I)$ and the exchange part of its Bethe term is neglected. We have calculated the total cross-section for atmospheric molecules, although the present molecules are not calculated by Saksena *et al*[14].

Hwang *et al.*[11] have carried out numbers of calculation in Binary Encounter-Bethe-Model. They included the effect of acceleration of the incident electron by the molecular field through the classical-binary encounter theory and used a simple representation of the COOS.

$$\frac{df(\omega,o)}{d\omega}=\frac{N_j I_j}{\omega^2} \qquad \ldots(1)$$

where ω is the energy loss, N_j and I_j are the numbers of electron and ionization threshold. Their total ionization cross-section for the j^{th} molecular orbital for incident energy E is given by:

$$\sigma_{jT}=\sigma_{jKBB}+\sigma_{jKMB} \qquad \ldots(2)$$

where

$$\sigma_{jKBB}=\frac{AN_j}{2I_j^2(t+u_j+1)}\left[1-\frac{1}{t^2}\right] \qquad \ldots(3)$$

$$\sigma_{jKMB}=\frac{AN_j}{I_j^2(t+u_j+1)}\left[\frac{t-1}{t}-\frac{\ln t}{t^2}\right] \qquad \ldots(4)$$

σ_{jKBB} and σ_{jKMB} are the Bethe's and Mott's cross-section, respectively with the following values of t and u_j.

$$t=\frac{E}{I_j},\quad u_j=\frac{U_j}{I_j}$$

where U_j is the average kinetic energy of the bound electron of the j^{th} orbital. $A=4\pi a_0^2 R^2$, with R and a_0 are the Rydberg energy and first Bohr radius, respectively.

Following Hwang *et al.*[11] dropping the contribution of the exchange to the Bethe term and the adhoc cut-off factor from it. Furthermore, the effect of the acceleration of the incident electron by the molecular field is included through the classical binary encounter theory and using Eq. (1) for COOS, the present total ionization cross-section is:

$$\sigma_{jt}=\sigma_{jpBB}+\sigma_{jpMB}+\sigma_{jjt} \qquad \ldots(5)$$

$$\sigma_{jpBB}=\frac{AN_j I_j}{(E+U_j+I_j)}\int_{I_j}^{E}\frac{1}{\omega^2}\ln\left(\frac{\omega}{Q_-}\right)d\omega \qquad \ldots(6)$$

$$\sigma_{jpMB}=\left[\frac{AN_j}{(E'+U_j+I_j)I_j}\right]\left[\begin{array}{l}\left(1-\frac{2}{t+1}+\frac{t-1}{2t^2}\right)\\+\left(\frac{5-t^2}{2(t+1)^2}-\frac{1}{t(t+1)}\right)\\-\left\{\frac{(t+1)}{t^2}\ln\left(\frac{t+1}{2}\right)\right\}\end{array}\right] \qquad \ldots(7)$$

$$\sigma_{ijt} = \frac{A}{RE} M_j^2 \left\{ \ln(1-\beta^2) + \beta^2 \right\} \quad \ldots(8)$$

In Eq. (6), Q_- is the recoil energy, M^2_j is equal to the total dipole matrix squared.

$$t = \frac{E}{I_j}$$

$$E = \frac{1}{2} mv^2 \quad (m = \text{rest mass of electron})$$

$$\beta = \frac{v}{c} \ (v = \text{incident velocity}, c = \text{velocity of light})$$

Reike and Prepejchal[10] have expressed their molecular cross-section measured in the energy range 0.1-2.7 MeV in terms of two collision parameters M^2_j and C is given by:

$$\sigma_{ijt} = -\frac{A}{RE} \left[M_j^2 \left\{ \ln(1-\beta^2) + \beta^2 \right\} + C \right] \quad \ldots(9)$$

3 Results

In the present paper, the total ionization cross-sections have been calculated for the three molecules of interest in atmospheric science i.e hydrogen sulphide (H_2S), nitrous oxide (N_2O), carbon dioxide (CO_2). These molecules are important constituents that found at different altitudes of the atmosphere[17]. From Eq. (5), the ionization cross-sections σ_j is calculated for each orbit of the molecules for incident energy E varying from threshold to ionization energy to 10 MeV. The cross-section for each orbital added to obtain the total cross section for the whole molecule. Table 1 presents the values of binding energy (I), average kinetic energy (U), electron occupation number (N) of each orbit of molecules[19] under consideration. Table 2 presents the calculated collision parameters C and M^2_j for considered molecules[10] which are obtained by employing the COOS given by Khare *et al.*[16] at large E.

Figure 1 shows the comparison of present cross-sections for N_2O along with the experimental data given by Rapp and Englander-Golden[3], Iga *et al.*[4], Lindsay *et al.*[5] and theoretical data set of Kim *et al.*[6], Joshipura *et al*[7].

Figure 1 shows that the present cross-sections agrees with experimental data within 20% however for E>70 eV they do not differ by more than 10%. The present theoretical cross-sections overestimate

Table 1 — Molecular orbital constants[19]

I: Binding Energy; U: Average Kinetic Energy; N: Electron Occupation Number

Molecules	Mol. Orbital	I (eV)	U (eV)	N
N_2O	1σ	561.71	794.52	2
	2σ	431.00	601.81	2
	3σ	426.85	602.05	2
	4σ	44.49	72.53	2
	5σ	39.55	73.81	2
	6σ	22.41	77.25	2
	1π	21.20	48.88	4
	7σ	18.95	60.14	2
	2π	12.89	59.95	4
H_2S	2a1	244.06	509.15	2
	1b1	181.00	477.97	2
	3a1	180.96	478.37	2
	1b2	180.89	479.07	2
	4a1	26.85	55.39	2
	2b1	16.34	35.77	2
	5a1	13.54	46.09	2
	2b2	10.48	45.68	2
CO_2	$3\sigma_{1g}$	42.04	75.72	2
	$2\sigma_{2u}$	40.60	78.38	2
	$4\sigma_{1g}$	21.62	74.66	2
	$3\sigma_{2u}$	20.27	71.56	2
	$1\pi_u$	19.70	49.97	4
	$1\pi_g$	13.77	64.43	4

Table 2 — C, M^2_j: Collision parameters

Molecules	Calculated		Experimental	
	C	M^2_j	C	M^2_j
N_2O	58.57	5.62	----	----
H_2S	60.94	3.92	42.19	5.03
CO_2	57.63	5.32	57.19	5.75

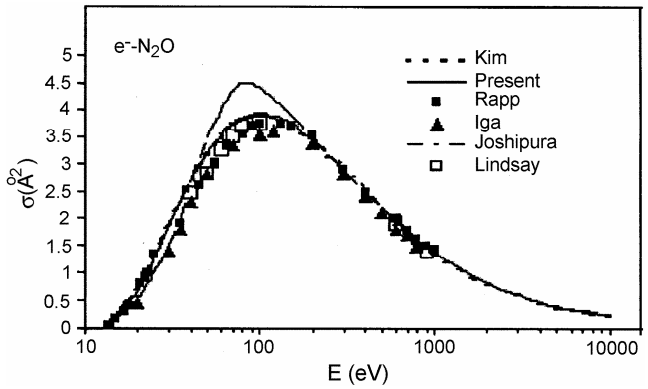

Fig. 1 — Comparison of the present theoretical total cross-section and experimental total cross-sections for N_2O. Solid curve, the present work; squares, experimental data by Rapp and Englander-Golden[3]; triangles, experimental data by Iga, Rao and Srivastava[4]; rectangles, experimental data by Lindsay, Rejoub and Stebbings[5]; medium-dashed curve, theoretical data by Kim, Hwang, Weinberger and Rudd[6]; long-dashed curve, theoretical data by Joshipura, Gangupadhyay and Vaiswav[7]

the cross-section obtained by Joshipura *et al.*[7] for E<40 eV and E>150 eV while underestimate between two energies 40 eV<E<150 eV.

Figure 2 shows the total cross-sections for 0.1 to 10 MeV. The present values of M^2_j and C obtained at 1 MeV are 5.62 and 58.57, respectively. However, there is no experimental and theoretical data available to compare it with present calculation.

In Fig. 3, the total cross-sections for H_2S are shown. We have used the total cross-section modified by the Khare *et al.*[16] in this case. Following Kim and Rudd[6], average kinetic energy has been divided by principal quantum number (n=3). When a molecular orbital is dominated by an atomic orbital with high principal quantum number, its kinetic energy is high and makes the cross-section low because the expression of the cross-sections have average kinetic energy U. To correct this, U is divided by principal quantum number (n = 3) of the dominant atomic orbital (3p orbital of S). It is noted that the present cross-section are very close to the cross-section obtained by Kim *et al.*[6], while the expressions for both cross-sections are different. The present total cross-sections are in well agreement with those measured by Rao and Shrivastava[8] within 5% for energy E < 200 eV but it is lower for energy E> 200 eV. The experimental cross-section measured by Lindsay *et al.*[5], Belic and Kurepa[9] at energy range E> 50 eV disagrees with present theoretical data. The data by Belic and Kurepa[9] agree with theory when their peak value is renormalized.

Figure 4 shows the present theoretical calculation for H_2S at E>10 keV. The total cross-section agrees well with experimental data measured by Reike and Prepejchal[10]. The calculated values of M^2_j and C obtained from at 1 MeV are 3.92 and 60.94, respectively. All these values of the collision parameter do not change with the increase of E.

Figure 5 shows the total cross-section for CO_2, again it exactly matches with that of Hwang *et al*[11]. The experimental data is available from the study

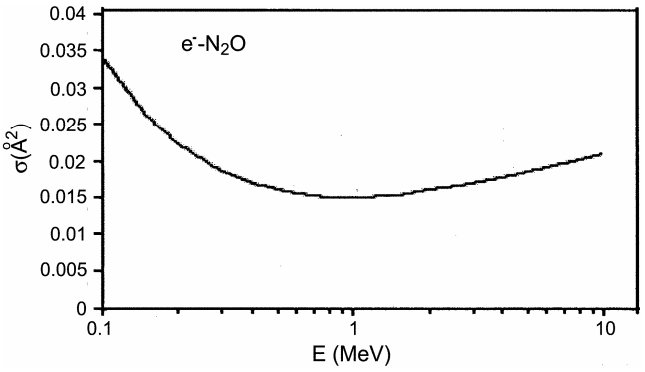

Fig. 2 — Present theoretical total cross- section for N_2O

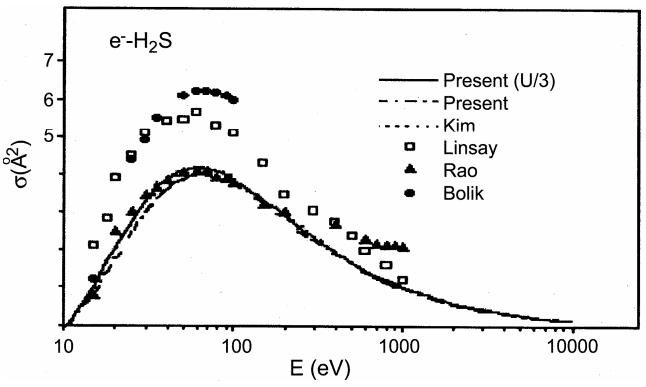

Fig. 3 — Comparison of the present theoretical total cross- section to experimental total cross-section for H_2S. Solid curve, present cross-section with a reduced value by U/3 for the valence molecular orbit; long-dashed curve, present cross-section; medium dashed curve, theoretical data by Kim, Hwang, Weinberger and Rudd[6]; rectangles, experimental data by Lindsay, Rejoub and Stebbings[5]; triangles, experimental data by Rao and Shrivastava[8]; squares, experimental data by Belic and Kurepa[9]

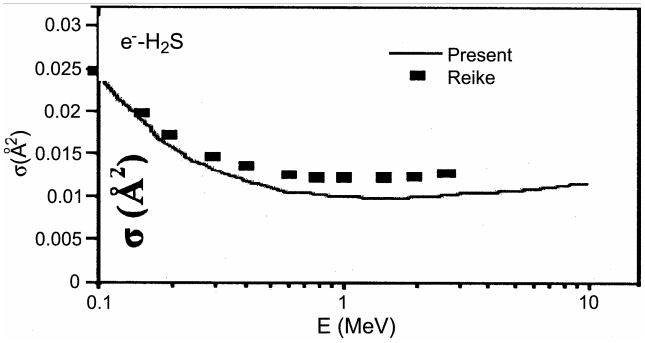

Fig. 4 — Comparison of the present theoretical total cross-section to experimental data for H_2S. Solid curve, present work; squares, experimental data by Reike and Prepejchal[10]

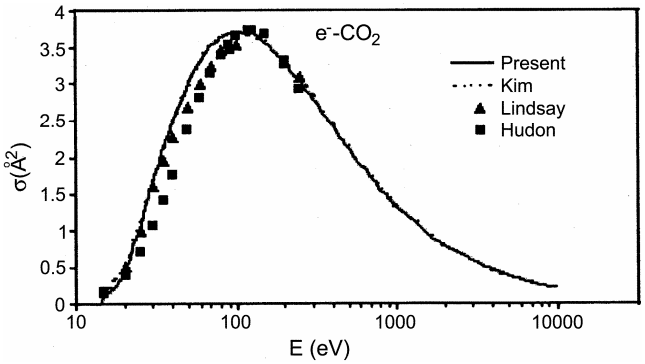

Fig. 5 — Comparison of the present theoretical total cross-section to experimental total cross-section for CO_2. Solid curve, present work; dashed curve, Hwang, Kim and Rudd[11]; squares, experimental data by Hudson, Vallance and Harland[13]; triangles, experimental data by Lindsay and Mangan[12]

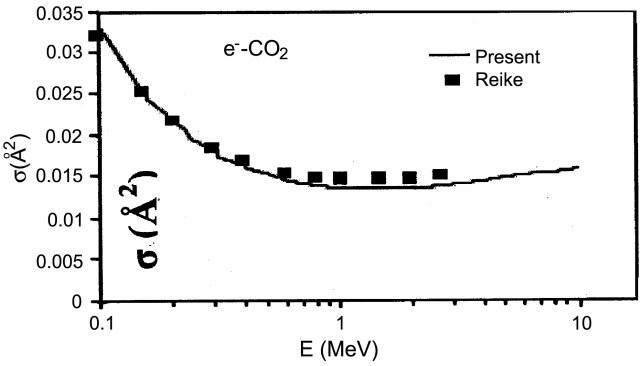

Fig. 6 — Comparison of the present theoretical total cross-section to experimental data for CO_2. Solid curve, present work; squares, experimental data by Reike and Prepejchal[10]

undertaken by Lindsay and Mangan[12] and Hudson *et al*[13]. Present calculations agree very well with the data of Lindsay and Mangan[12] within 8%.

Figure 6 shows the theoretical calculation for energy range 0.1-10 MeV. The theoretical data with the experimental data of Reike and Prepejchal[10] available in the range 0.1-2.7 MeV have been compared in Fig. 6. The present values of M^2_j and C obtained at 1 MeV are 5.32 and 57.63, respectively. These values are about 6% and 1% lower than the corresponding experimental values of Reike and Prepejchal[10]. The agreement between the experimental and theory is good, although theory has a tendency to underestimate the cross-sections.

4 Conclusions

From the present study, it is concluded that the theoretical predicted and measured value of the total cross-sections for H_2S, N_2O, CO_2 molecules are in good concurrence. Furthermore, we concluded that a slight modification in Saksena *et al.*[14] model have considerably improved the agreement between the experimental and theoretical data at low energy. It is found that σ_{jT} is very close to the σ_{jt} while σ_{jKBB} and σ_{jKMB} are different from the present σ_{jpBB} and σ_{jpMB}. The reason for this is given by Khare *et al*[20]. At higher values of energy, there is hardly any difference between the present and the data measured by Reike and Prepejchal[10]. Thus, the experimental data is in good agreement with the present data over a wide energy range. To the best of our knowledge, this is the first calculation for H_2S, N_2O and CO_2 over a wide energy range from threshold to 10 MeV.

The application of the present model to the ionization of other molecules and atoms, including inner-shell and dissociative ionizations is of interest.

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