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Electron impact ionization cross-sections of carbonyl sulfide molecule

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ABSTRACT

Single differential cross-sections as a function of secondary electron energy for the production of the COS^+, S^+, CO^+, CS^+, O^+ and C^+ ions resulting from dissociative ionization of the COS molecule by electron impact have been evaluated at fixed incident electron energies 100 and 200 eV employing a semi-empirical formalism. The partial ionization cross-sections corresponding to the positive charged ions are derived from the differential cross sections in the energy range varying from the ionization threshold to 1000 eV. In absence of any experimental and/or theoretical data, as a testimony the sum of partial ionization cross sections are compared with the available data which revealed a satisfactory agreement. In addition to the cross sections, ionization rate coefficients as a function of energy/temperature have also been evaluated by using partial ionization cross-sections and Maxwell–Boltzmann distribution of energy.

1. Introduction

Carbonyl sulfide is the most abundant sulfur compound naturally present in the atmosphere and it play a significant role in the origin of life [1,2]. Due to atmospheric and environmental importance of COS, there are some previous studies on the investigation of its interactions with electron/photon. Experimentally, few measurements including those of Ziesel and Schulz [3], Srivastava et al.[1] and Hudson et al. [4] were reported on the electron impact ionization cross sections. Contrary to the experimental measurements, little well tested theoretical formalism are available for the evaluation of electron impact ionization cross sections. Recently, BEB calculations by Kim et al. [5], DM calculations by Märk and co-workers [4,6] and CPM calculations by Vinodkumar et al. [7] were published on the total ionization cross sections for OCS molecule.

In this paper, we have extended the application of the modified Jain–Khare semi-empirical formalism [8–11] for the evaluation of the single differential cross-sections (SDCS) as a function of secondary electron energy corresponding to the formation of various cations in electron collision of a peculiar molecule OCS. The partial ionization cross-sections corresponding to the individual cations are derived from the integration of the SDCS in the impinging electron energy range varying from ionization threshold to 1keV. Present attention is given to the cations COS^+, S^+, CO^+, CS^+, O^+ and C^+ formed in direct and dissociative electron ionization of OCS. To the best of our knowledge, no other data is available for the comparison with our present results for SDCS at the considered fixed incident electron energies of 100 and 200 eV and their integral cross sections (partial ionization cross sections) corresponding to formation of various cations through dissociative ionization of COS by electron impact. However, a comparison of counting or the sum of partial ionization cross sections revealed a satisfactory agreement with the available experimental [3][1] and the theoretical data [5–7] in the complete energy range as investigated in the experimentally and theoretically determinations. The ionization rate coefficients rather an important parameter in plasma modelling is also evaluated as a function of energy by using the evaluated integral cross sections and Maxwell–Boltzmann distribution of energy [12].

2. Theoretical

Single differential cross sections as a function of secondary electron energy ε corresponding to the production of ith type of ion in ionization of a molecule by the incident electron of energy E is given elsewhere [8–11]. In brief, the differential cross section is given by

$$Q_i(E,\varepsilon)=\frac{4\pi a_0^2 R}{E}\left[\left(1-\frac{\varepsilon}{(E-\varepsilon)}\right)\frac{R}{W}\frac{df_i(W,0)}{dW}\ln[1+C_i(E-I_i)\right. \\ \left.+\frac{R}{E}S_i\frac{(E-E_i)}{(\varepsilon_0^3-\varepsilon_i^3)}\left(\varepsilon-\frac{\varepsilon^2}{(E-\varepsilon)}+\frac{\varepsilon^2}{(E-\varepsilon)^2}\right)\right] \qquad (1)$$

where W (=$\varepsilon+I_i$) is defined as energy loss suffered by the incident electron. I_i, a_0, ε_0, C_i, and R are the ionization threshold for the production of ith type of ion, first Bohr's radius, energy parameter, collision parameter and the Rydberg's constant, respectively.

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The partial ionization cross section is obtained by the integration of the energy dependent single differential cross sections (Eq. (1)) over the secondary electron energy i.e. ε from 0 to $(E - I_i)$,

$$Q_i(E) = \int Q_i(E, \varepsilon) d\varepsilon \tag{2}$$

and the total (counting) cross section is obtained by

$$Q_i^T(E) = \sum_i Q_i(E) \tag{3}$$

The present formulation is based on the oscillator strength df/dW and its evaluation by quantum mechanical method is a tedious job because of the unavailability of the accurate wave functions for the cation in a certain energy level. In the present calculation, we have derived the oscillator strengths from the photoionization cross sections measurements in the energy range from ionization threshold to 50 eV measured by Carnovale et al. [13]. The accuracy of the determined oscillator strength scales was estimated to be better than ±5%. For higher photon energy range i.e. $W > 50$ eV the same were extrapolated by Thomas–Reiche–Kuhn (TRK) sum rule [13]. The collision parameter C_i (=0.09001/eV) and energy parameter ε_0 (=30 eV) were evaluated as for other polyatomic molecules [7–11]. The ionization potentials corresponding to the various cations in conjunction to the Franck–Condon energy region were studied in the photoionization of OCS [13]. In the present evaluations of cross sections, the estimated uncertainty is more or less the same as in the measurement of photoionization cross sections.

The ionization rate coefficients are important quantities in plasma modelling, which are determined by using the Maxwell–Boltzmann distribution of energy and the calculated partial and total ionization cross sections as

$$R_i(E) = \int_{-\infty}^{+\infty} 4\pi \left(\frac{1}{2\pi mkT} \right)^{3/2} me^{-E/kT} Q_i(E) E dE \tag{4}$$

where k, T and m are the Boltzmann constant, absolute temperature and mass of the electron, respectively.

3. Results and discussion

Carbonyl sulfide http://en.wikipedia.org/wiki/File:Carbonyl-sulfide-2D-dimensions.png http://en.wikipedia.org/wiki/File%3ACarbonyl-sulfide-2D-dimensions.png(O=C=S) is a colourless flammable gas with an unpleasant odour. It is a linear molecule consisting of a carbonyl group double bonded to a sulfur atom. Here, COS^+ ions produced in their ground state $X^2\Pi(3\pi)^{-1}$ through direct ionization of OCS by electron impact have insufficient energy to dissociate into small atomic ions and hence appear as parent ions. The single differential cross sections as a function of secondary electron energy in term of energy loss W at fixed incident electron energies of 100 and 200 eV for COS molecule is presented in Fig. 1. The energy dependent cross sections are symmetric at $W/2$ where the energies of primary and the secondary electrons are almost equal. In the threshold energy region, resonances and structures aroused due to different pathways of the ion formation play a significant contribution. In the present formulation (Eq. (1)), the first part known as Born–Bethe cross section for slow secondary electron, corresponds to the growing contribution of the dipole-allowed interaction and resembles the photoionization cross-section and second part, the Mott cross section accounts for the electron exchange affect, is the non-dipole part which defines the knock-on collision. Figure also shows weight contribution of the molecular and atomic cations as the cross sections for molecular ions are much larger than the atomic ions. To the best of our knowledge, no other theoretical and/or experimental data is available for comparison with the present results of single differential cross sections notwithstanding the differential cross sections are only indicative.

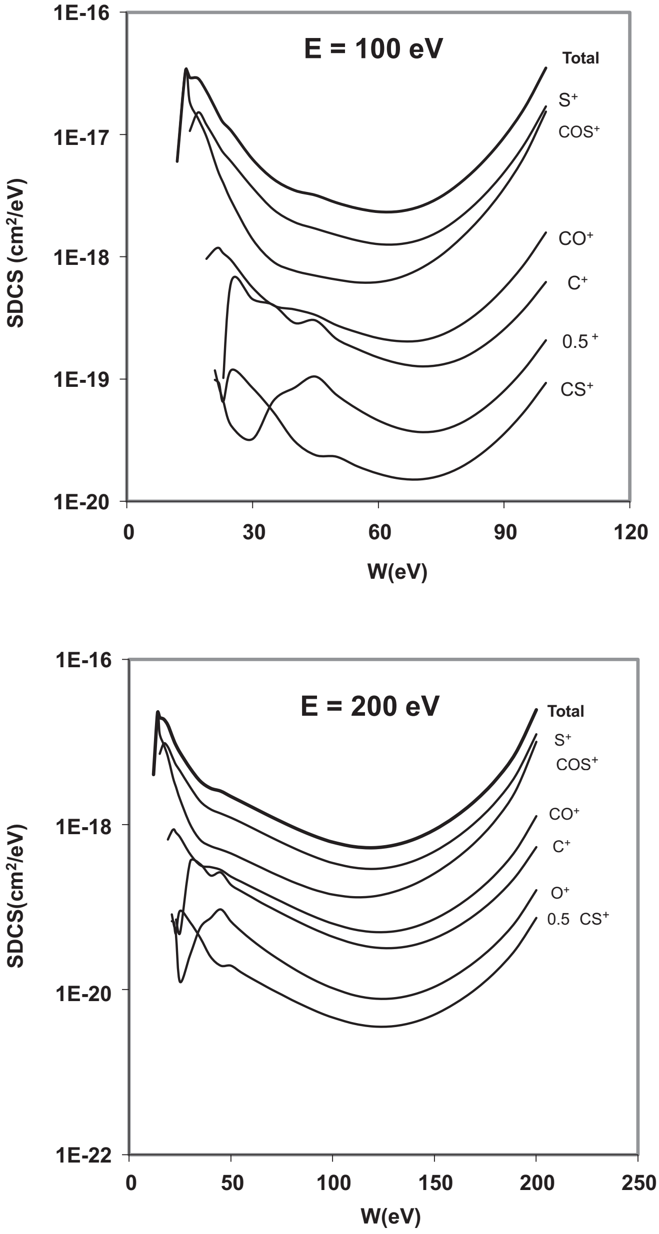

Fig. 1. Single differential cross sections (SDCS) as a function of secondary electron energy in term of energy loss W by electron impact ionization of COS at fixed impinging energies of 100 and 200 eV.

The ionization cross sections in terms of partial ionization cross sections are evaluated from the integral of single differential cross sections corresponding to the formation of various cations COS^+, S^+, CO^+, CS^+, O^+ and C^+ in electron impact ionization of COS in the impinging electron energy range varying from ionization threshold to 1000 eV are shown in Fig. 2 along-with Table 1. Again there is neither experimental nor theoretical data available in the literature for comparison of the evaluated results. Hence, the sum of partial ionization cross section, also called the total or counting ionization cross section have become important. In Fig. 2 the evaluated total ionization cross sections are compared with the experimental measured cross sections [3,4][1] and the theoretical determined cross sections [4,5,7]. The numerical values are also presented in Table 1. The present results are in

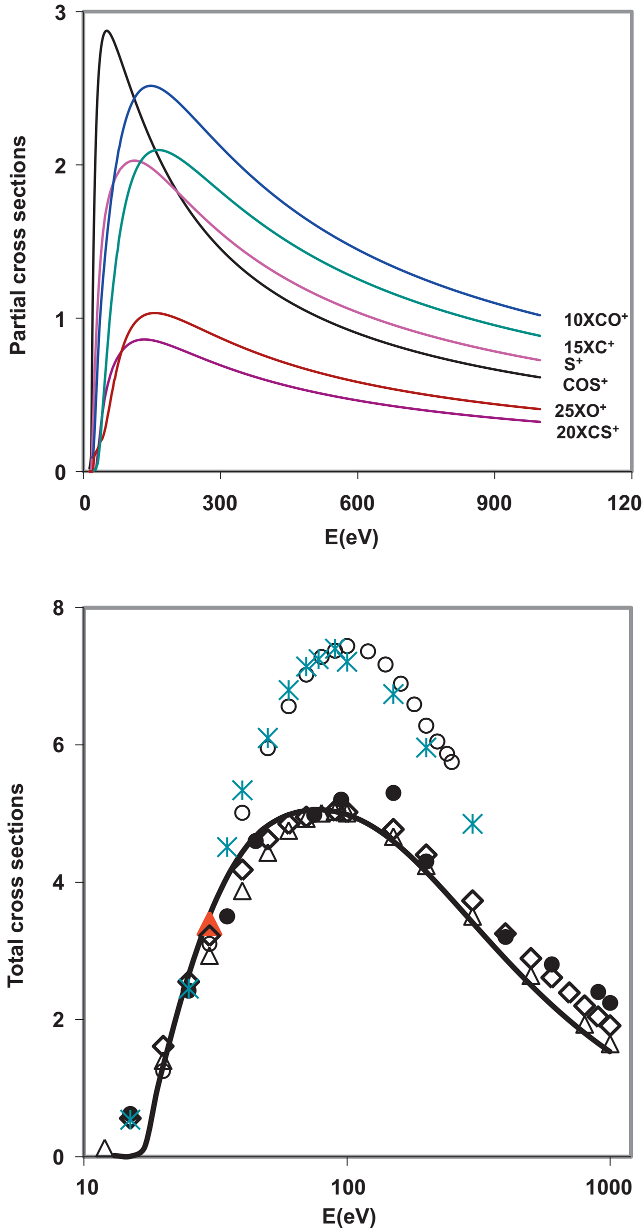

Fig. 2. Calculated partial and total ionization cross sections (10^{-16} cm^2) for COS by electron impact (designated by solid line) in comparison with the experimental data: ▲ – [3], ●[1] and ○ – [4] and the theoretical data: △ – BEB [5], * – DM [6] and ◊ – CPM [7].

good agreement with the experimental results reported by Srivastava et al.[1] as mentioned in various Refs. [4,5] along with the experimental data of Ziesel and Schulz [3] available only at 30 eV. The recent measurement of Hudson et al. [4] overestimates to the present results as well as other available data. Our results also agree quite well with the BEB [5] and CPM calculations [7] in the entire energy range as covered in the calculations. On the other hand, the DM calculations carried out by Hudson et al. [4] also overestimates to our results and other data but resembles to the experimental data [4]. The reason of this disagreement is still unclear.

The present calculations for the partial and the total ionization cross sections satisfy the necessary consistency checks to access their consistency and reliability. The following trivial consistency checks applied to check the reliability of our calculations include those of (i) the integral cross sections corroborate the area covered by the corresponding differential cross sections at the given energies. (ii) The total ionization cross section is equal to the sum of the partial ionization cross sections. This condition is used in the summation method for calibration purposes. (iii) The integral ionization cross sections in low energy regime obey the Wannier threshold law [14,15]

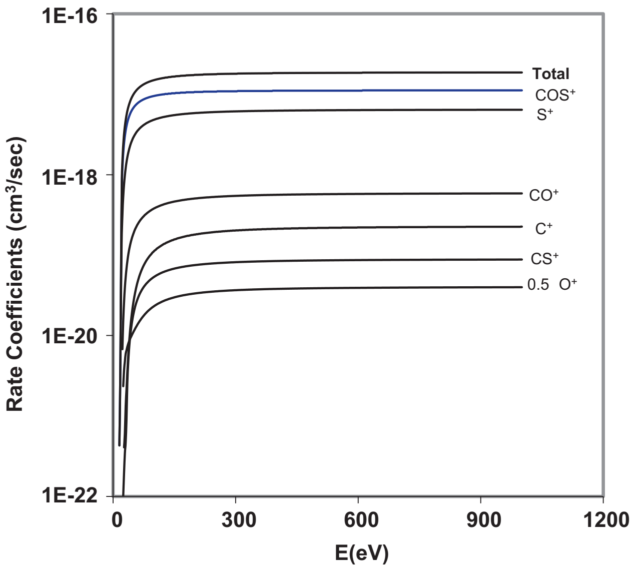

Fig. 3. Ionization rate coefficients as a function of electron energy corresponding to the production of various cations in electron impact ionization of COS.

$$Q_i(E) \approx E^m \tag{5}$$

Table 1
Partial and total ionization cross sections corresponding to the formation of various cations in electron dissociative ionization of the OCS molecule.

E (eV)	PICS (10^{-18} cm^2/eV)						Total
	COS$^+$	S$^+$	CO$^+$	CS$^+$	O$^+$	C$^+$	
13	2.00						2.00
15	5.40	0.50					5.90
17	13.03	1.66					14.69
19	82.15	16.59	0.92				99.66
21	128.89	33.69	1.05	0.01	0.05		163.70
23	164.54	52.73	1.98	0.03	0.36	0.04	219.68
25	192.91	68.95	3.09	0.06	0.44	0.09	265.53
31	247.67	108.89	7.09	0.55	0.59	0.35	365.14
35	266.59	128.84	9.45	1.08	0.72	1.01	407.69
39	277.65	144.57	11.19	1.61	0.81	1.92	437.76
45	285.49	161.50	13.33	2.25	1.00	3.53	467.10
51	287.34	172.89	15.24	2.71	1.33	5.08	484.60
55	286.66	178.29	16.35	2.95	1.58	6.04	491.87
59	285.03	182.80	17.38	3.16	1.84	6.96	497.18
65	281.42	188.06	18.75	3.42	2.22	8.12	501.99
71	276.99	192.29	19.93	3.61	2.56	9.12	504.50
81	268.73	197.53	21.56	3.87	3.04	10.51	505.24
91	260.11	200.47	22.78	4.05	3.41	11.55	502.37
101	251.55	202.24	23.68	4.17	3.67	12.34	497.65
111	243.23	202.80	24.33	4.25	3.86	12.92	491.38
121	235.24	202.42	24.76	4.29	3.98	13.35	484.04
131	227.62	201.30	25.02	4.31	4.07	13.64	475.94
151	213.52	197.48	25.15	4.28	4.13	13.93	458.50
200	185.39	184.30	24.31	4.06	4.02	13.75	415.82
300	145.49	155.98	21.23	3.47	3.49	12.18	341.84
400	120.25	133.74	18.45	2.98	3.01	10.63	289.05
500	102.89	116.92	16.24	2.61	2.63	9.38	250.66
600	90.19	103.93	14.49	2.32	2.34	8.38	221.65
700	80.48	93.65	13.09	2.09	2.10	7.57	198.99
800	72.80	85.31	11.95	1.90	1.91	6.91	180.78
900	66.55	78.41	11.00	1.75	1.76	6.36	165.83
1000	61.37	72.61	10.19	1.62	1.63	5.90	153.31

where m is defined in term of charge z on the residual ion i.e.

$$m = \frac{1}{4} + \frac{1}{4}\left(\frac{100z - 9}{4z - 1}\right)^{1/2} \quad (6)$$

These consistency checks provide the consistency and reliability of the present results.

We also have evaluated a set of ionization rate coefficients as a function of electron energy for the individual cations produced in electron collision with the COS molecule. The calculations are made using the calculated ionization cross sections and Maxwell–Boltzmann energy distribution (Eq. (4)) and the results are presented in Fig. 3.

4. Conclusion

The present calculation for energy dependent differential and integral ionization cross sections is an attempt towards the wider applicability of a revisited Jain–Khare semi-empirical formalism. For the first time, we have evaluated the differential and partial ionization cross sections leading to the various cations in electron-OCS collision processes and the results are predictive to the experimentalist for measurement. However, the total ionization cross-sections revealed a reasonable good agreement with the available experimental and theoretical data. The ionization rate coefficients useful in plasma modelling are also evaluated as a function of electron energy.

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