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Determination of single differential and partial cross-sections for the production of cations in electron–methanol collision

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Abstract

The semi-empirical approach which requires the oscillator strength data as input has been employed to evaluate the single differential cross-sections for the production of cations resulting from electron impact ionization of methanol molecule. The calculations are made as a function of energy loss suffered by the incident electrons at 100 eV. As no previous experimental and/ or theoretical data is available for comparison, we have derived the partial and total ionization cross-sections with energies varying from ionization thresholds to 500 eV. The calculated partial and total ionization cross-sections revealed a good agreement with the available experimental and theoretical data.

1. Introduction

Methanol molecule has been observed in the interstellar space and its interaction with energetic radiation is important for astrophysicists. It is also used in combustion as alternative fuel and in the semi-conductor industry, e.g. diamond film deposition [1]. Collision of electrons with CH_3OH generates a variety of chemically active radicals [2]. On the experimental side, there is very limited study reporting on the measurements of the cross-sections for the production of positive charged ions in electron–CH_3OH collision. The previously published results of Burton et al. [3] on partial photo-ionization cross-sections are limited in the energy range from first ionization threshold to 80 eV, however, subsequently Srivastava et al. [4] and Rejoub et al. [5] reported the partial electron ionization cross-sections for the production of cations in e– CH_3OH collision in the incident electron energy range from ionization thresholds to 500 and 1000 eV, respectively. On the total ionization cross-section, besides the recent measurements [4,5], there exists experimental measured data of Duric et al. [6] and Hudson et al. [7] who reported the values for electron impact energy range from 0 to 300 eV and from a few eV above threshold to over 200 eV, respectively. Recently, Lindsay and Mangan [8] have also analyzed and recommended the data for total cross-sections by taking an average of measured values of Srivastava et al. [4] and Duric et al. [6]. On the theoretical side, there exist the BEB calculations of Kim and co-workers [9] and the DM calculations of Deutsch et al. [10] for total ionization cross-sections. A detailed theoretical study of the various channels of dissociation leading to the production of cations has never been performed. Moreover, the calculation of electron impact ionization cross-sections for complex poly-atomic molecules is a challenging task which encouraged us to carry out these calculations.

In the present study of ionization of CH_3OH by electron impact, 12 cations viz. CH_3OH^+, CH_2OH^+, $CHOH^+$, CHO^+, CO^+, CH_3^+, CH_2^+, CH^+, C^+, OH^+, H_2^+ and H^+ produced through direct and dissociative channels have been considered. The partial single differential cross-sections as a function of energy loss (sum of ionization threshold and the secondary electron energy) suffered by the incident electron have been calculated using a semi-empirical formulation based on the well established Jain–Khare approach [11–13]. The electron impact energy used is 100 eV in the present calculation, for partial single differential cross-sections.

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Since no data seem existing for the comparison of the present results, we have derived from these single differential cross-sections, the corresponding partial and total ionization cross-sections, from threshold up to 500 eV and compared those with the available theoretical and the experimental data.

2. Theoretical

The present calculations are carried out using the modified Jain and Khare semi-empirical formulation for differential cross-sections (see for discussions in [14–18] and references therein). In brief, the single differential cross-sections (SDCS) for the production of a secondary electron in electron impact ionization of a molecule, is given as a function of energy loss $W(=\varepsilon+I_i)$, suffered by the incident electron

$$Q_i(E,W)=\frac{4\pi a_0^2 R}{E}\left[\frac{1}{\left(1+\left(\frac{I_i}{E}\right)\right)}\left(1-\frac{\varepsilon}{(E-I_i)}\right)\times\frac{R}{W}\frac{\mathrm{d}f_i(W,0)}{\mathrm{d}W}\ln\left[1+C_i(E-I_i)\right]+\frac{R}{E}S_i\frac{(E-I_i)}{(\varepsilon_0^3+\varepsilon^3)}\left[\varepsilon-\frac{\varepsilon^2}{(E-\varepsilon)}+\frac{\varepsilon^3}{(E-\varepsilon)^2}\right]\right], \tag{1}$$

where ε, I_i, a_0, ε_0, C_i, S_i and R are the secondary electron energy, ionization threshold for the production of ion i, first Bohr's radius, mixing parameter, collision parameter, number of ionizable electrons and Rydberg's constant, respectively.

The total single differential cross-section is the sum of partial single differential cross-sections, i.e.,

$$Q_i^{\mathrm{T}}(E,W)=\sum_i Q_i(E,W). \tag{2}$$

The partial ionization cross-section is obtained by the integration of Eq. (1) over the energy loss W from ionization threshold to the maximum E

$$Q_i(E)=\int_{I_i}^{E} Q_i(E,W)\,\mathrm{d}W. \tag{3}$$

The counting ionization cross-section (total ionization cross-section) is given as

$$Q_i^{\mathrm{T}}(E)=\sum_i Q_i(E). \tag{4}$$

The vital input parameter required in the present formulation is the optical oscillator strengths $(\mathrm{d}f_i(W,0)/\mathrm{d}W)$ in terms of measured partial photo-ionization cross-sections. In the present study of e–CH_3OH collision, highly accurate (with accuracy of ~95%) experimental measurement by Burton et al. [3] for the oscillator strengths corresponding to the production of cations has been used. In their dipole (e, e + ion) spectroscopy experiment, Burton et al. [3] considered photon energy range from vertical onsets to 80 eV. From this energy range, up to 280 eV, the total photo-absorption cross-section data (or the total photo-ionization cross-sections) have been employed and the same was distributed among the various channels/ions assuming the constant ionization efficiencies above the dipole break-down limit [3] (see for instant: [12] for discussion of the procedure). Above $E > 280$ eV, K-shell ionization correction has been used in the calculations. The collision parameter C_i and the mixing parameter ε_0 were taken in a similar manner as discussed in [17,18]. The vertical ionization thresholds for the production of the different ions are discussed elsewhere [3,4].

3. Results and discussion

The behaviour of single differential cross-sections as a function of energy loss W at a fixed incident electron energy of 100 eV has been displayed in Fig. 1. The numerical values are also presented in Table 1. It is interesting to note that the cross-sections are symmetric with respect to $W/2$ wherein the energies of primary and secondary electrons are almost equal. At this energy, the exchange effects are stronger which are taken into account through the second term in Eq. (1). A similar

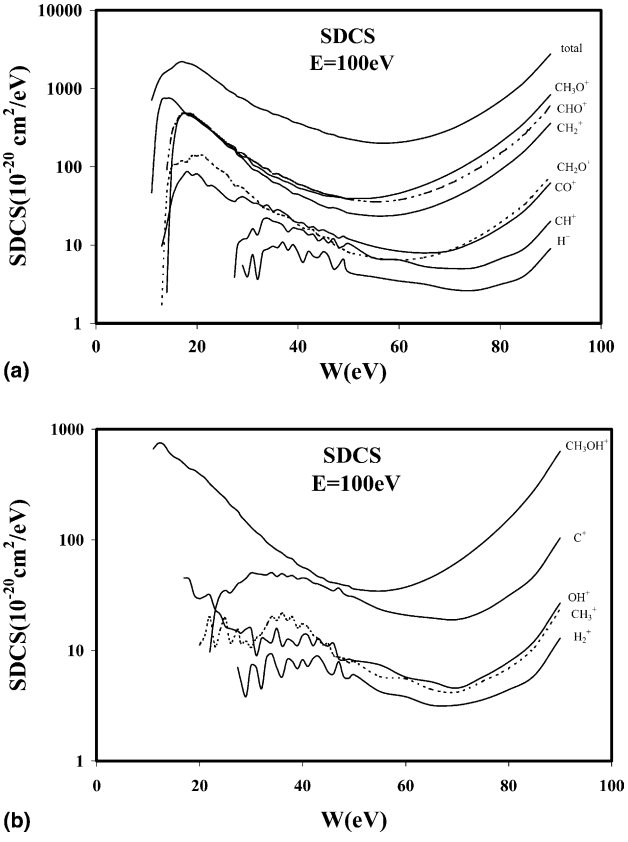

Fig. 1. Partial SDCS for the production of cations from electron impact ionization of CH_3OH at a fixed electron impact energy of 100 eV.

Table 1
Partial and total electron impact single differential cross sections for CH_3OH at $E = 100$ eV

W (eV)	$Q_i(E,W)$ (10^{-20} cm^2/eV)												Total
	CH_3OH^+	CH_3O^+	COH^+	CH_2O^+	CO^+	CH_2^+	OH^+	CH_3^+	C^+	CH^+	H_2^+	H^+	
11	664.3	46.7											711.0
12	746.4	356.3											1102.7
13	729.1	718.5		1.7	9.8								1459.1
14	624.1	751.9	92.2	47.7	18.0	2.5							1536.4
15	563.5	738.2	270.7	101.4	38.1	111.7							1823.6
16	532.4	648.3	389.8	107.8	58.5	354.3							2091.1
17	486.9	544.0	478.5	119.5	73.1	469.7	45.2						2216.9
18	442.3	465.1	483.4	115.2	87.1	477.6	44.0						2114.7
19	425.9	440.4	473.8	139.2	77.9	451.1	31.4						2039.7
20	394.0	400.0	419.8	137.2	81.5	420.6	29.5	11.3					1893.9
22	321.9	318.0	336.1	126.8	57.9	329.7	31.8	20.1	9.7				1552.0
24	260.9	252.7	258.5	96.4	52.0	244.7	21.1	15.5	31.9				1233.7
26	206.3	195.6	200.3	78.1	39.4	184.0	15.7	11.7	33.3				964.4
28	164.6	153.0	154.2	57.4	38.9	142.5	14.3	11.7	41.4	9.9	5.3		793.2
30	130.4	130.7	133.0	47.6	38.4	109.3	15.9	10.7	50.2	12.4	7.3	4.0	689.9
32	108.3	99.5	110.5	36.4	33.9	88.0	12.9	14.2	48.8	13.5	4.5	3.6	574.1
34	87.7	81.0	94.0	28.9	32.4	72.3	11.8	20.3	50.5	22.0	9.3	8.9	519.1
36	76.2	72.4	81.6	24.9	28.4	61.3	10.9	21.7	49.6	19.5	5.8	9.3	461.6
38	67.3	63.3	70.9	22.7	23.8	51.3	12.1	20.1	47.6	14.8	8.0	8.6	410.5
40	56.7	53.9	60.2	18.3	19.4	44.6	13.7	17.4	45.2	16.0	8.3	8.0	361.7
42	50.1	49.6	54.0	16.1	16.9	39.0	11.1	13.9	40.9	13.6	8.5	8.3	322.0
44	45.0	45.4	48.7	13.4	15.4	33.4	11.4	11.3	38.2	11.4	7.8	7.0	288.4
46	41.0	42.2	44.2	12.3	14.5	30.0	11.6	9.0	34.7	10.6	6.2	7.3	263.6
48	39.0	41.0	41.7	9.3	12.3	29.0	8.2	8.5	32.7	9.4	5.8	5.5	242.4
50	36.0	39.5	38.6	8.1	12.0	25.7	8.1	8.0	30.5	10.5	6.0	4.5	227.5
55	34.4	40.0	35.7	6.9	9.6	23.5	7.4	5.8	23.6	6.8	4.3	3.9	201.9
60	37.3	45.8	37.7	6.4	8.3	24.3	5.7	5.6	20.9	6.5	3.8	3.5	205.8
65	46.0	58.5	45.4	6.9	7.9	28.7	5.2	4.5	19.7	5.3	3.2	3.2	234.6
70	62.5	81.4	60.5	8.5	8.4	37.9	4.6	4.2	19.1	5.0	3.2	2.7	298.0
75	93.7	123.5	90.0	12.1	11.1	55.5	5.8	5.3	22.5	5.1	3.6	2.6	430.8
80	154.1	203.9	147.6	19.2	16.6	90.2	7.9	6.9	31.4	6.7	4.4	3.1	692.0
85	282.9	375.2	269.5	34.2	28.2	163.2	12.2	10.7	47.5	9.2	5.9	4.1	1242.8
90	631.6	835.1	598.0	75.9	62.2	359.5	26.8	23.4	104.0	20.1	12.9	9.0	2758.5

behaviour of cross-sections was noted in case of other molecules investigated [16–18].

Since, no data seem to exists for the comparison of the presently calculated results for differential cross-sections, the corresponding derived partial and the total (counting) cross-sections have become important. In Figs. 2 and 3 alongwith Table 2, we have presented the calculated partial and total ionization cross-sections as a function of energy E, varying from ionization threshold to 500 eV. It is noticed that for the CH_3OH^+, CH_3O^+, CHO^+, CH_2^+ and $CHOH^+$ ions, our results are in good agreement with the only experimental data of Srivastava et al. [4]. In case of CH_3^+, except energy range (50–150 eV), the calculated results are again in agreement with data [4]. In case of some dissociative ions e.g. C^+, CH^+, CO^+ and H_2^+, there is a considerable deviation in magnitude with the data [4]. For instance at 100 eV; the experimental data [4] for respective ions CO^+, C^+ and H_2^+ are about 5, 2 and 23.5 times higher than the presently calculated values and for CH^+ our results are more than two times higher than the data [4]. Furthermore, no information about OH^+ and H^+ was reported by Srivastava et al. [4]. In their recent measurement, Rejoub et al. [5] have presented the sum of the partial ionization cross-sections pertaining to groups of ions of similar masses, for instance, CH_nO^+ and $(CH_n^+ + H_nO^+)$, where $n = 0$–4 and (H^+ and H_2^+). It is noted that our results for CH_nO^+ are fairly in agreement with the measurement of Rejoub et al. [5] and Srivastava et al. [4] in the complete energy range as investigated in the experiments. In case of $(CH_n^+ + H_nO^+)$, our calculated values are in reasonable agreement with the experimental data [4,5] (where our results are lower than the data of Rejoub et al. [5] and higher than the measurement of Srivastava et al. [4]). The possible explanation of discrepancy within the experimental measurements was that all the fragments were not collected in the study of the Srivastava et al. [4]. On the other hand, in case of minor ions H^+ and H_2^+, again the experimental data of Rejoub et al. [5] are several times larger than the calculated values. Interestingly, in the complete energy range, the measured cross-section ratio (H^+/H_2^+) by Rejoub et al. [5] is ~23%

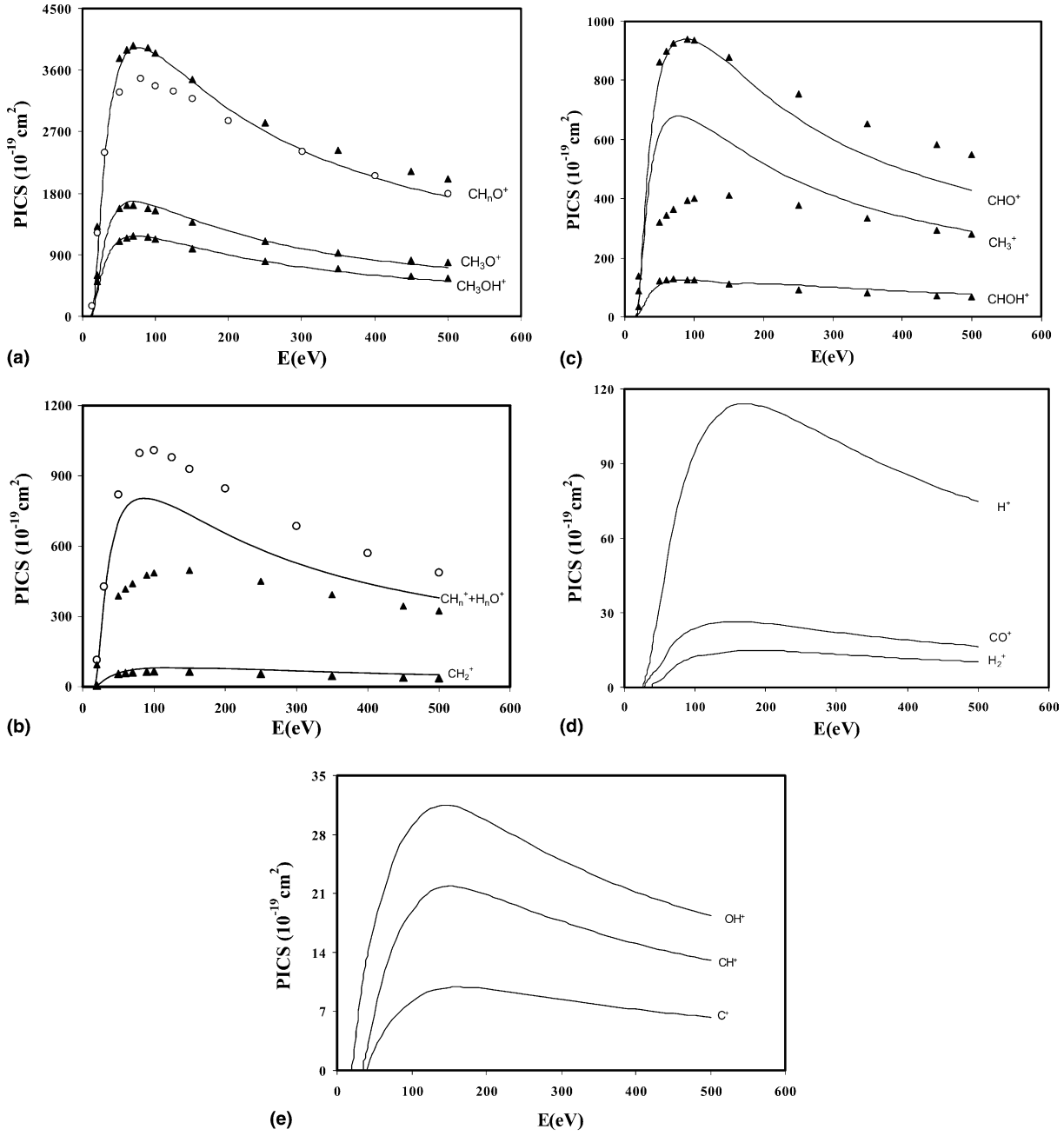

Fig. 2. Presently calculated partial ionization cross-sections (PICS) for electron impact ionization of CH_3OH (designated with solid line) in comparison with the experimental data designated by (▲) [4] and (○) [5].

higher than our calculated values. These ions are generated at high energies and the reason of discrepancies between theoretical and experimental results may be due to insufficient collection of these ions, with low kinetic energies, in the experiments. For the sake of clarity of the curves, some experimental data points are not shown in Fig. 2. Notwithstanding that our calculations are depending on the accuracy of the experimental input parameters, the agreement with experimental data is more than satisfying. In Fig. 3, the total or counting ionization cross-sections obtained as the sum of partial ionization cross-sections are in good agreement with the experimental [4–7] and theoretical data [9,10].

4. Conclusions

The modified Jain–Khare semi-empirical formulation has been employed to evaluate the partial single- dif-

Table 2
Partial and total electron impact ionization cross sections for CH_3OH

E (eV)	$Q_i(E)$ (10^{-19} cm^2)												Total
	CH_3OH^+	CH_3O^+	COH^+	CH_2O^+	CO^+	CH_2^+	OH^+	CH_3^+	C^+	CH^+	H_2^+	H^+	
12	11.9	4.0											15.9
14	65.5	32.4											97.9
16	150.6	114.8	3.6										269.0
18	246.7	245.5	18.4	4.1		2.1		14.8					531.6
20	342.2	396.9	52.9	9.5		4.7		48.1					854.3
22	434.3	550.4	107.2	16.2		8.5	1.8	98.0					1216.4
24	521.1	693.0	175.6	23.8		13.0	3.2	155.9					1586.6
26	601.1	821.3	250.7	32.2		17.9	4.7	216.2					1944.1
28	675.1	938.2	326.1	41.4		22.8	6.2	274.6				2.0	2286.2
30	743.4	1045.0	397.4	50.9	1.8	27.4	7.8	329.0				3.7	2606.4
32	805.4	1140.0	463.4	60.1	2.4	31.7	9.2	378.7				5.7	2896.3
34	860.7	1224.0	523.0	68.5	3.2	35.6	10.4	422.8				8.0	3156.2
36	909.4	1299.0	576.2	76.0	4.0	39.2	11.5	461.6		1.0		10.7	3388.6
38	952.5	1363.0	623.3	82.8	4.7	42.4	12.5	495.3		1.6		13.6	3592.7
40	990.3	1419.0	664.8	88.8	5.4	45.2	13.4	524.6		2.2	1.1	16.8	3771.6
50	1113.0	1594.0	808.4	108.3	8.8	57.6	17.1	619.3	2.4	6.4	2.7	33.9	4371.9
60	1165.0	1663.0	883.5	118.2	13.8	66.6	20.2	661.2	4.0	10.2	5.5	50.8	4661.4
70	1182.0	1680.0	921.9	123.4	17.9	72.5	23.2	677.0	5.5	13.2	8.0	65.4	4790.0
80	1178.0	1669.0	937.7	125.4	20.5	76.2	25.8	678.8	6.6	15.6	10.0	77.5	4821.1
90	1165.0	1644.0	940.2	125.2	22.3	78.5	27.5	672.7	7.5	17.5	11.4	86.9	4798.7
100	1145.0	1611.0	934.8	123.9	23.8	79.9	29.0	662.7	8.2	18.9	12.2	94.3	4743.7
110	1121.0	1574.0	924.2	122.1	24.8	80.6	30.1	650.3	8.8	20.1	12.9	100.5	4669.4
120	1096.0	1535.0	910.2	120.0	25.5	80.8	30.9	636.5	9.3	20.9	13.4	105.2	4583.7
130	1070.0	1496.0	893.9	117.6	26.0	80.5	31.3	622.0	9.6	21.5	13.8	108.7	4490.9
140	1044.0	1457.0	876.2	115.1	26.3	79.8	31.5	607.2	9.8	21.8	14.1	111.4	4394.2
150	1018.0	1418.0	857.5	112.9	26.4	79.2	31.5	592.0	9.9	21.9	14.0	113.1	4294.2
160	992.6	1381.0	837.0	112.4	26.4	79.0	31.3	576.3	9.9	21.8	14.6	113.9	4196.2
170	967.8	1345.0	815.4	112.9	26.4	78.9	31.0	560.7	9.9	21.6	14.8	114.2	4098.6
180	943.7	1310.0	794.5	112.9	26.2	78.6	30.6	545.6	9.8	21.4	14.8	114.0	4002.1
190	920.6	1276.0	774.3	112.6	26.0	78.0	30.2	531.3	9.8	21.1	14.8	113.4	3908.1
200	898.7	1245.0	755.2	111.9	25.7	77.3	29.7	517.6	9.7	20.9	14.8	112.7	3819.2
220	856.7	1185.0	718.8	110.1	25.1	75.7	28.7	491.9	9.5	20.2	14.6	110.5	3646.8
240	818.0	1130.0	685.4	107.8	24.4	73.7	27.8	468.3	9.2	19.6	14.4	107.8	3486.4
260	782.5	1080.0	654.8	105.1	23.7	71.6	26.8	446.9	9.0	18.9	14.0	104.9	3338.2
280	749.9	1034.0	626.8	102.4	22.9	69.6	25.9	427.3	8.7	18.3	13.7	102.0	3201.2
300	719.8	991.4	601.0	99.6	22.2	67.5	25.0	409.3	8.4	17.7	13.4	99.0	3074.3
320	692.2	952.7	577.4	96.9	21.5	65.5	24.1	392.9	8.2	17.1	13.0	96.1	2957.6
340	666.7	917.0	555.6	94.3	20.9	63.6	23.3	377.8	7.9	16.6	12.6	93.3	2849.6
360	643.1	884.0	535.5	91.7	20.2	61.7	22.6	363.8	7.7	16.0	12.3	90.6	2749.2
380	621.1	853.5	516.8	89.1	19.6	59.9	21.9	350.9	7.5	15.5	12.0	88.0	2655.8
400	600.8	825.1	499.5	86.8	19.0	58.2	21.2	339.0	7.2	15.1	11.6	85.5	2569.0
420	581.8	798.8	483.4	84.5	18.5	56.6	20.6	327.9	7.0	14.6	11.3	83.1	2488.2
440	564.1	774.1	468.4	82.3	18.0	55.1	20.0	317.5	6.8	14.2	11.0	80.9	2412.4
460	547.5	751.1	454.4	80.2	17.5	53.7	19.4	307.9	6.7	13.8	10.8	78.7	2341.7
480	532.0	729.6	441.2	78.3	17.0	52.3	18.9	298.8	6.5	13.4	10.5	76.7	2275.2
500	517.4	709.3	428.9	76.4	16.6	51.0	18.4	290.3	6.3	13.1	10.2	74.8	2212.7

ferential cross-sections for the CH_3OH molecule at a fixed incident electron energy of 100 eV. The calculations were made for the production of the 12 singly charged ions CH_3OH^+, CH_2OH^+, $CHOH^+$, CHO^+, CO^+, CH_3^+, CH_2^+, CH^+, C^+, OH^+, H^+ and H_2^+ ions produced via, direct and dissociative ionization of CH_3OH by electron impact. In absence of any experimental data for differential cross-sections, the partial and total ionization cross-sections, derived from the corresponding differential cross-sections, have been compared with the available data. The level of agreement between calculated partial and total ionization cross-sections and the experimental and theoretical data is found encouraging and as such these calculations provide an important input data for the study of CH_3OH-containing stellar medium.

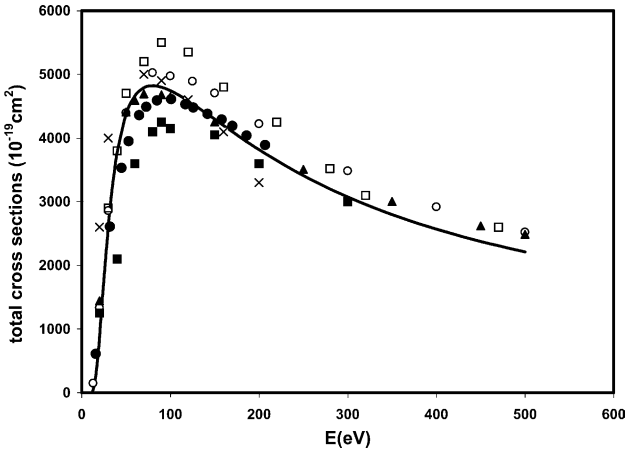

Fig. 3. Presently calculated total ionization cross-sections for electron impact ionization of CH_3OH (designated with solid line) in comparison with the various experimental data designated by (▲) [4], (○) [5], (■) [6] and (●) [7]. The theoretical data designated: (□) BEB by [9] and (×) DM by [10].

Acknowledgements

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