

## Electron impact ionisation of H<sub>2</sub>O, CO, CO<sub>2</sub> and CH<sub>4</sub>

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Received 6 May 1986, in final form 13 February 1987

**Abstract.** Utilising a crossed electron-beam-molecular-beam collision geometry and the relative flow technique normalised values of total and partial ionisation cross sections for H<sub>2</sub>O, CO, CO<sub>2</sub> and CH<sub>4</sub> have been measured. The present total ionisation cross sections agree well with those reported previously by Rapp and co-workers. However, data on the partial ionisation cross sections widely disagree with some previous results.

### 1. Introduction

Cosmic ray particles and the radiation from the sun generate secondary electrons in planetary and cometary atmospheres. These secondary electrons cause a variety of processes by collisional excitation of molecules. Among them, direct ionisation (e.g.  $e^- + H_2 \rightarrow H_2^+ + 2e^-$ ) and dissociative ionisation (e.g.  $e^- + H_2 \rightarrow H^+ + H + 2e^-$ ) are two of the most probable processes because the cross sections for them are in the range of  $10^{-16} \text{ cm}^2$ , which is about three orders of magnitude larger than the cross sections for any other collision process involving species in their ground state. The ions resulting from electron-molecule collisions interact with the surrounding gas in a variety of ways and give rise to ion-molecule reactions. Thus, accurate values of electron impact ionisation and dissociative ionisation cross sections are of importance for modelling planetary and cometary atmospheres (e.g. Nier 1985, Zipf 1985). These cross sections are also of importance for modelling the various man-made plasmas present in such devices as glow discharge lamps, electric discharge lasers and gaseous switches (e.g. see Mark and Dunn 1985).

Among a variety of molecules, H<sub>2</sub>O, CO, CO<sub>2</sub> and CH<sub>4</sub> are of special interest. A look at the previously published literature on these molecules shows that there is a large disagreement between the various results. In general, data are available for the total and direct (i.e.  $e + MN \rightarrow MN^+ + 2e$ , where MN is a molecule consisting of M and N components) ionisation cross sections. However, data on the dissociative ionisation cross sections (i.e.  $e + MN \rightarrow M^+, N^+$ , multiply ionised species) are fragmentary and are of poor accuracy (e.g. see Kieffer and Dunn 1966, Märk 1985).

These considerations prompted us to start a programme devoted to the measurement of accurate values of ionisation and dissociative ionisation cross sections. In this paper we present data on H<sub>2</sub>O, CO, CO<sub>2</sub> and CH<sub>4</sub> and compare them with the previously reported results.

## 2. Experimental details

The experimental apparatus used in obtaining the present data is described in detail by Orient and Srivastava (1983). A schematic diagram of the apparatus is shown in figure 1. Briefly, it consists of an energy-selected trochoidal electron gun, a capillary array through which the gas under study is flowed to form a molecular beam, a quadrupole mass spectrometer to mass select the ions, a charged-particle detector (spiraltron), a Faraday cup to measure the incident electron current and the associated electronics to store the ion signal as a function of energy and mass. The trochoidal monochromator is of the same design as described by Tam and Wong (1979). It generated a magnetically collimated beam of electrons of specific energy with an energy spread of about 100 meV. This beam of electrons collides with the beam of molecules ( $\text{H}_2\text{O}$ ,  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{CH}_4$  in the present case). Ionised molecules and their ionised fragments are extracted out of the collision region by a pair of electrically biased parallel molybdenum wire meshes in a direction perpendicular to both the electron beam and the molecular beam. These ions are focused at the entrance aperture of the quadrupole mass spectrometer by an Einzel lens. The ions are mass selected and further accelerated by about 4000 V. These energetic ions are then made to impinge on a charged-particle detector which produces electrical pulses of about 20 mV for each incident ion. These pulses are further amplified and stored in a multichannel scaler as a function of the electron impact energy. The energy of the electrons can be varied and repeatedly swept from 0 to 600 eV.

The various details on the method of obtaining the values of cross sections and the sources of errors which can introduce uncertainty in the final data are given below.

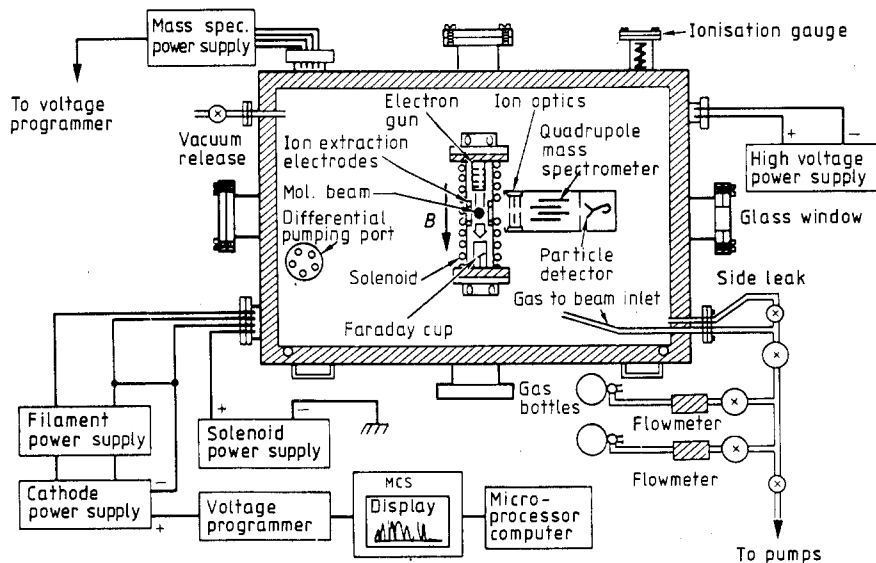


Figure 1. Schematic diagram of the dissociative ionisation and attachment spectrometer (dimensions not to scale).

### 2.1. Normalisation procedure

The relative intensity of a particular ion as a function of the energy of the colliding

electron is recorded by the multichannel analyser. This relative intensity is directly proportional to the cross sections. However, it is very difficult to obtain absolute values of the cross sections from this intensity due to several unknown factors involved in the measurements. Therefore, a relative flow technique was developed in our laboratory in which the ionisation cross section for a molecule is obtained in terms of accurately known cross sections for He, Ar, Kr, Ne and Xe. The normalisation procedure has been described previously by Srivastava *et al* (1975) in detail and more recently by Trajmar and Register (1983). Briefly, a beam of molecules is formed by flowing the gas of interest through a capillary array. If the driving pressure behind the capillary array is low enough then one can relate this pressure and the gas flow rate to the angular and velocity distributions of the molecules in the effusing beam (Brinkman and Trajmar 1981). This property is utilised in obtaining the cross sections. The procedure is as follows. First, the gas MN ( $H_2O$ ,  $CO$ ,  $CO_2$  or  $CH_4$ ) whose ionisation or dissociative ionisation cross section is to be measured is flowed through the capillary array and a beam is formed. The ion intensity  $I(M^+, N^+ \text{ or } MN^+)$  is then measured. Subsequently, the gas MN is turned off and He, Ar, Kr, Xe or Ne (represented by X in equation (1)) is flowed through the capillary array. The ion signal  $I(X^+)$  is again recorded. These two operations are done under the following two conditions: (i) the electron beam current does not change during the experiment and (ii) the flow of gases through the capillary array remains molecular (Brinkman and Trajmar 1981). Then equation (1) given below is used to obtain the cross section,

$$\sigma(M^+) = \sigma(X^+) \frac{I(M^+)}{I(X^+)} \left( \frac{m(X)}{m(MN)} \right)^{1/2} \frac{N(X)}{N(MN)} K \quad (1)$$

where  $m(MN)$  and  $m(X)$  are molecular and atomic weights of the respective gases,  $N(X)$  and  $N(MN)$  are the flow rates of the two gases through the capillary array and  $K$  is a calibration constant which determines the transmission efficiency of the ion optics, the transmission efficiency of the quadrupole mass spectrometer and the detection efficiency of the charged-particle detector for  $M^+$  to  $X^+$ .

## 2.2. Sources of errors

There are several factors which can introduce errors in the value of  $\sigma(M^+)$  (equation (1) if proper precautions to minimise them are not taken. An inspection of equation (1) reveals that care should be exercised in the measurement of  $I(M^+)/I(X^+)$ ,  $(m(X)/m(MN))^{1/2} (N(X)/N(MN))$  and  $K$ . The ratio  $I(M^+)/I(X^+)$  can be obtained with an accuracy of better than 2%. The factor  $(m(X)/m(MN))^{1/2} (N(X)/N(MN))$ , which is a ratio of the flow rates of the two gases, is calibrated in terms of the pressure ratio  $P(X)/P(MN)$  behind the capillary array. These pressures are separately measured by an MKS baratron and the ratio can be estimated with an accuracy of about 2%. The factor  $K$  in equation (1) is determined in the following manner. First of all,  $I(M^+)$  and  $P(MN)$  for Ne, Ar, Kr and Xe are measured while keeping the experimental conditions identical for all of them. Then  $I(X^+)$  and  $P(X)$  for He are measured under the same conditions as above. These quantities are then substituted in equation (1) and the values of  $K$  for Ne, Ar, Kr and Xe are calculated by utilising the recommended values (Märk 1985) of  $\sigma(M^+)$  and  $\sigma(X^+)$  for the rare gases. The values of  $K$  are plotted as a function of mass. The plot was found to lie on a smooth curve which was then used to obtain the value of  $K$  for other masses by interpolation. The maximum

error in this measurement is estimated to be about 10% at the most. Further details on the procedure for determining  $K$  are given in our previous publication (Orient and Srivastava 1983). The total estimated error in the cross section data reported in this paper is approximately  $\pm 15\%$ .

There are two additional factors which can introduce a systematic error in the present measurements. They are: (i) the increase in the path length due to spiralling of electrons in the magnetic field as the energy of the electron beam is varied and (ii) the change in the collection efficiency of the extraction system due to the finite velocity of the fragment ions when they are born. First of all, the variation in the path length due to spiralling of electrons is small at the energies of the present experiment. Second, any change in the effective path length is cancelled by the calibration method used here (equation (1)). The ions which result from direct ionisation (i.e.  $e + MN \rightarrow MN^+ + 2e$ ) are essentially at thermal energies and therefore require a very small extraction field for a complete collection. However, the ions which are the product of dissociation of the molecule (i.e.  $e + MN \rightarrow M^+, N^+, 2e$ ) may possess a considerable amount of energy. In order to make sure that a complete collection of these ions was taking place we plotted the ion signal as a function of the drawout field. It was found that at voltages approximately less than  $10 \text{ V cm}^{-1}$  the ion signal became independent of the drawout field. Our recent calculations and an experiment utilising a pulsed electron gun and a pulsed extraction method show that a complete collection for our system can be achieved for fields of the order of  $50 \text{ V cm}^{-1}$  for  $H^+$  ions which are born with energies as high as 5 eV (Krishnakumar and Srivastava 1987).

### 3. Results

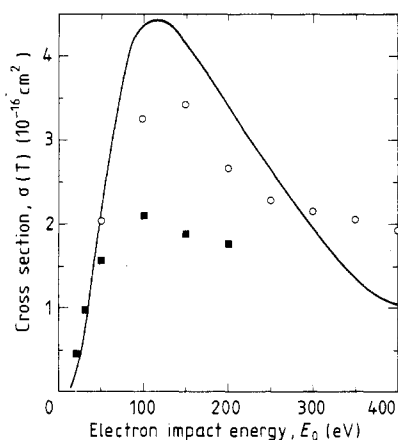
In this section values of cross sections for  $H_2O$ , CO,  $CO_2$  and  $CH_4$  are presented. For the various cross sections we denote the total cross section by  $\sigma(T) = \sigma(MN^+) + \sigma(M^+) + \sigma(N^+)$ , where  $\sigma(MN^+)$  is the cross section for the direct ionisation of a molecular gas and  $\sigma(M^+)$  and  $\sigma(N^+)$  are the dissociative ionisation cross sections for the production of atomic or molecular fragment ions. In the present work  $\sigma(T)$  was obtained by summing up the direct and the individual dissociative ionisation cross sections. Unless otherwise stated, the uncertainties in the values of the cross sections, as discussed in the previous section, are of the order of  $\pm 15\%$ .

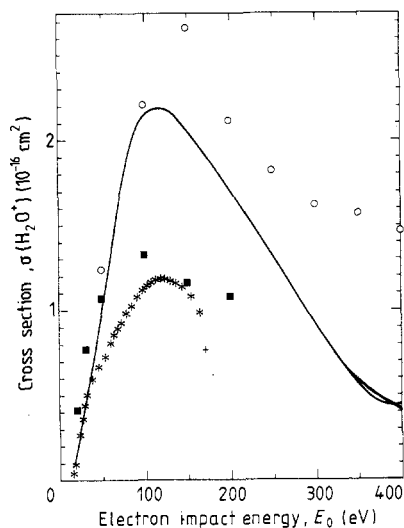
#### 3.1. $H_2O$

The values of cross sections for  $H_2O$  are given in table 1. In figures 2 and 3 the present results for  $\sigma(T)$  and  $\sigma(H_2O^+)$  are compared with previous measurements reported in the literature. It is clear from these figures that there are large disagreements between the various results. At electron impact energies above 100 eV the values of Schutten *et al* (1966) are lower than the present ones by about a factor of two, while those of Gomet (1975) are in a better agreement with our data. The most recent measurements of Märk and Egger (1976) for  $\sigma(H_2O^+)$  are closer to the values of Schutten *et al* (1966). In figure 4 the present  $\sigma(OH^+)$ ,  $\sigma(H^+)$  and  $\sigma(O^+)$  are compared with the previous measurements reported in the literature. The  $\sigma(OH^+)$  of Gomet (1975) are close to our data. However, Schutten *et al* (1966) have reported values about a factor of three lower. There are large disagreements among the various results in the cases of  $\sigma(H^+)$

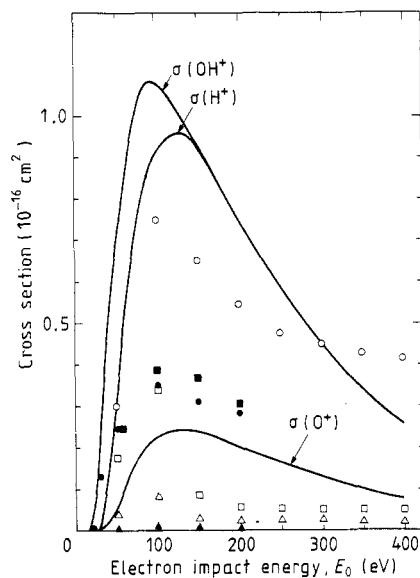
**Table 1.** Ionisation cross sections for electron impact on  $\text{H}_2\text{O}$ . The cross sections are expressed in units of  $10^{-16} \text{ cm}^2$ .

$E_0$ (eV)	$\sigma(\text{H}_2\text{O}^+)$	$\sigma(\text{OH}^+)$	$\sigma(\text{H}^+)$	$\sigma(\text{O}^+)$	$\sigma(\text{T})$
15	0.05	0	0	0	0.05
20	0.16	0.04	0	0	0.20
25	0.27	0.12	0.02	0.001	0.41
30	0.39	0.25	0.04	0.003	0.68
40	0.71	0.51	0.15	0.024	1.39
50	1.01	0.68	0.32	0.068	2.08
60	1.31	0.81	0.51	0.114	2.74
70	1.62	0.95	0.66	0.155	3.39
80	1.90	1.04	0.77	0.188	3.90
90	2.06	1.08	0.86	0.212	4.21
100	2.14	1.08	0.91	0.227	4.36
120	2.18	1.03	0.95	0.240	4.40
140	2.12	0.97	0.95	0.241	4.28
160	2.00	0.90	0.90	0.239	4.04
180	1.86	0.82	0.81	0.218	3.71
200	1.72	0.75	0.72	0.201	3.39
220	1.55	0.68	0.66	0.185	3.08
240	1.38	0.62	0.60	0.172	2.77
260	1.23	0.56	0.55	0.159	2.50
280	1.08	0.51	0.50	0.144	2.23
300	0.92	0.46	0.46	0.132	1.97
320	0.77	0.41	0.42	0.121	1.72
340	0.63	0.35	0.37	0.106	1.46
360	0.51	0.32	0.33	0.094	1.25
380	0.46	0.29	0.29	0.083	1.12
400	0.43	0.26	0.28	0.082	1.05

**Figure 2.** Total ionisation cross sections  $\sigma(\text{T})$  for electron impact on water: ■, Schutten *et al* (1966); ○, Gomet (1975); —, present.



**Figure 3.** Direct ionisation cross sections  $\sigma(\text{H}_2\text{O}^+)$  for electron impact on  $\text{H}_2\text{O}$ : ■, Schutten *et al* (1966); ○, Gomet (1975); \*, Märk and Egger (1976); —, present.



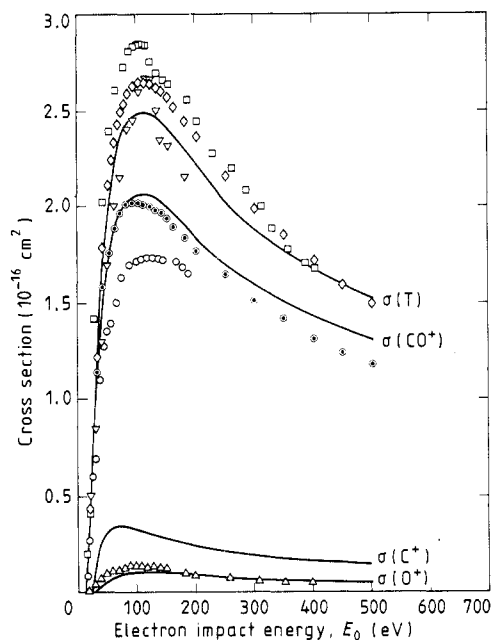
**Figure 4.** Cross sections for formation of ionic fragments by electron impact on  $\text{H}_2\text{O}$ : ●,  $\sigma(\text{OH}^+)$  Schutten *et al* (1966); ■,  $\sigma(\text{H}^+)$  Schutten *et al* (1966); ▲,  $\sigma(\text{O}^+)$  Schutten *et al* (1966); ○,  $\sigma(\text{OH}^+)$  Gomet (1975); □,  $\sigma(\text{H}^+)$  Gomet (1975); △,  $\sigma(\text{O}^+)$  Gomet (1975); —, present.

and  $\sigma(\text{O}^+)$ . From the threshold up to 100 eV electron impact energy our  $\sigma(\text{H}^+)$  data are about three times larger than the two previous results. At higher energies the disagreement is even larger among the  $\sigma(\text{H}^+)$  values. A similar large disagreement is found in the  $\sigma(\text{O}^+)$  data. The discrepancies between the various results can only be explained on the basis of possible systematic errors in the previous measurements

where the values of  $\sigma(\text{T})$  and  $\sigma(\text{H}_2\text{O}^+)$  were calculated from various measured quantities such as the pressure of  $\text{H}_2\text{O}$  vapour in the collision region, the electron beam current and the absolute value of the mass-dependent transmission efficiency of the mass spectrometer employed for separating the various fragments. For example, Schutten *et al* (1966) derived the  $\text{H}_2\text{O}$  vapour pressure in the collision region by measuring the temperature of the water reservoir. They stated that an error of 1% in the measurement of the temperature can give rise to an uncertainty of about  $\pm 13\%$  in the value of pressure. In addition, all previous measurements have been performed in the static-gas geometry in which a collision chamber is filled with the vapour and the  $\text{H}_2\text{O}^+$  ions pass through this vapour before they are detected. In such cases care must be taken to avoid any possibility of ion-molecule reactions. This can be checked by verifying a linear dependence between the collision region pressure and the detected  $\text{H}_2\text{O}^+$  signal. In the present measurements a crossed electron-beam-molecular-beam geometry has been employed. Therefore, during the measurements, in general, the background pressure is of the order of  $10^{-7}$  Torr. At such a low pressure the effects of ion-molecule reactions can usually be ignored.

### 3.2. CO

Cross sections for CO are shown in figure 5 and tabulated in table 2. Within the experimental errors our results on  $\sigma(\text{T})$  agree well with the values of Rapp and



**Figure 5.** Total ionisation cross sections  $\sigma(\text{T})$  and partial and dissociative ionisation cross sections  $\sigma(\text{CO}^+)$ ,  $\sigma(\text{C}^+)$ , and  $\sigma(\text{O}^+)$  for the production of the various ionised fragments by electron impact on CO:  $\nabla$ , Defrance and Gomet (1966);  $\square$ ,  $\text{CO}^+$  and  $\triangle$ ,  $\text{C}^+$  production from Vaughan (1931);  $\diamond$ , Rapp and Englander-Golden (1965);  $\odot$ , Rapp *et al* (1965) after subtracting the cross sections for the production of ions with kinetic energies greater than 0.25 eV from  $\sigma(\text{T})$ ;  $\circ$ , Hille and Märk (1978); —, present.

**Table 2.** Ionisation cross sections for electron impact on CO. The cross sections are expressed in units of  $10^{-16} \text{ cm}^2$ .

$E_0(\text{eV})$	$\sigma(\text{CO}^+)$	$\sigma(\text{O}^+)$	$\sigma(\text{C}^+)$	$\sigma(\text{T})$
10	0.00	0.00	0.00	0.00
15	0.07	0.00	0.00	0.07
20	0.34	0.00	0.00	0.35
25	0.72	0.00	0.02	0.74
30	1.04	0.006	0.10	1.10
40	1.53	0.027	0.26	1.70
50	1.73	0.055	0.31	2.00
60	1.88	0.075	0.34	2.23
70	1.98	0.089	0.34	2.36
80	2.03	0.097	0.34	2.44
90	2.05	0.102	0.34	2.48
100	2.06	0.105	0.32	2.49
120	2.06	0.106	0.31	2.49
140	2.03	0.105	0.29	2.44
160	1.97	0.101	0.28	2.37
180	1.92	0.097	0.26	2.30
200	1.85	0.091	0.25	2.21
220	1.78	0.086	0.23	2.12
240	1.73	0.082	0.22	2.05
260	1.68	0.078	0.21	1.99
280	1.64	0.075	0.20	1.93
300	1.59	0.072	0.20	1.88
320	1.57	0.069	0.19	1.84
340	1.52	0.067	0.18	1.79
360	1.50	0.065	0.17	1.75
380	1.48	0.063	0.17	1.72
400	1.45	0.061	0.17	1.69
420	1.41	0.059	0.16	1.64
440	1.38	0.057	0.16	1.60
460	1.35	0.056	0.15	1.58
480	1.34	0.055	0.15	1.56
500	1.32	0.053	0.15	1.53
510	1.31	0.052	0.15	1.52

Englander-Golden (1965). Previous measurements on  $\sigma(\text{CO}^+)$  have been reported by Vaughan (1931), Defrance (1966) and Hille and Märk (1978). It can be seen in figure 5 that the values reported by Vaughan and Defrance are much larger than the present ones for electron impact energies greater than about 50 eV. However, the results of Hille and Märk agree with ours within the experimental uncertainties of the two measurements. Rapp *et al* (1965) have also measured cross sections for the production of those ions whose kinetic energies are more than 0.25 eV. From these we estimated cross sections for ions which appear with energies less than 0.25 eV. Their values are shown in figure 5. These cross sections mainly represent the production of  $\text{CO}^+$  and are in excellent agreement with the present results.

We have measured cross sections for the production of  $\text{C}^+$  and  $\text{O}^+$ . They are plotted in figure 5. Vaughan (1931) has also reported cross sections for the  $\text{C}^+$  fragments. They are also shown in figure 5 and are found to be about a factor of two lower than the present results.



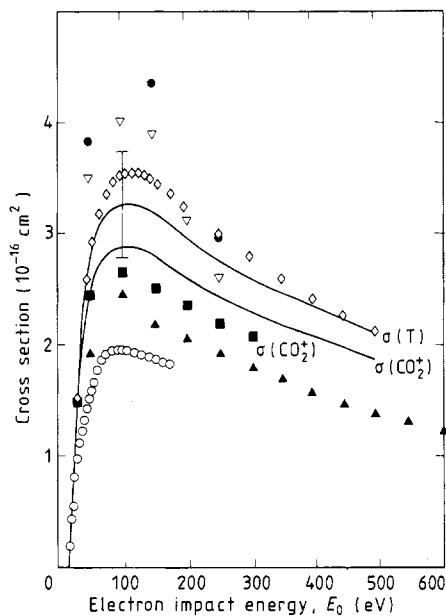
3.3.  $CO_2$ 

Figure 6 shows the values of  $\sigma(T)$  and  $\sigma(CO^+)$  for this molecule along with the previous results. These values are tabulated in table 3. As is clear from figure 6, the differences between the various sets of measurements are rather large. Our values are in the best agreement with those of Rapp and Englander-Golden (1965) and Crowe and McConkey (1974) who used Rapp and Englander-Golden's results for normalisation. The most recent measurements are those of Märk and Hille (1978). Their values are much lower than the present ones. The differences are difficult to explain on the basis of their experimental procedure alone. We believe that there was a systematic error in their measurements for this molecule.

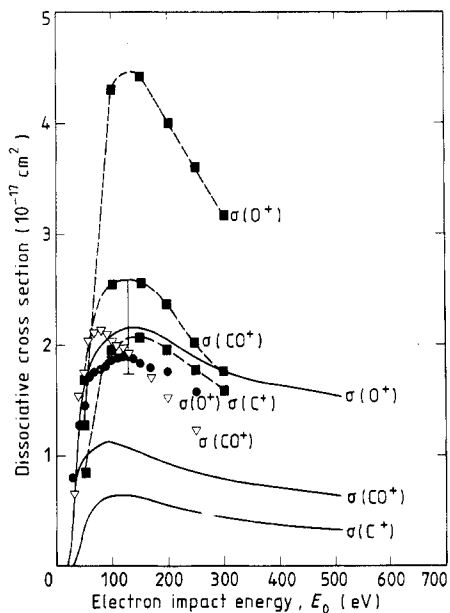
Figure 7 shows cross sections for the production of  $CO^+$ ,  $O^+$  and  $C^+$ . Previous measurements have been reported by Crowe and McConkey (1974) and Peresse and Tuffin (1967). There is a wide disagreement between all the results.

**Table 3.** Ionisation cross sections for electron impact on  $CO_2$ . The cross sections are expressed in units of  $10^{-16} \text{ cm}^2$ .

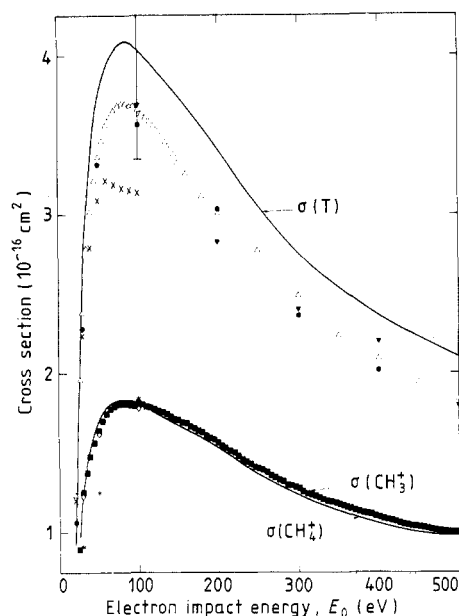
$E_0(\text{eV})$	$\sigma(CO_2^+)$	$\sigma(CO^+)$	$\sigma(O^+)$	$\sigma(C^+)$	$\sigma(T)$
10	0.00	0.000	0.00	0.00	0.00
15	0.05	0.002	0.00	0.00	0.05
20	0.40	0.007	0.001	0.00	0.41
25	0.86	0.019	0.022	0.001	0.90
30	1.38	0.049	0.062	0.002	1.50
35	1.74	0.074	0.102	0.007	1.92
40	1.95	0.089	0.122	0.017	2.18
50	2.37	0.098	0.155	0.037	2.66
60	2.60	0.103	0.180	0.050	2.93
70	2.74	0.108	0.191	0.056	3.10
80	2.82	0.110	0.200	0.061	3.19
90	2.85	0.111	0.206	0.063	3.23
100	2.88	0.111	0.210	0.064	3.27
120	2.89	0.109	0.215	0.065	3.27
140	2.85	0.106	0.216	0.064	3.24
160	2.79	0.103	0.215	0.062	3.17
180	2.71	0.099	0.211	0.060	3.08
200	2.62	0.095	0.205	0.057	2.99
220	2.54	0.092	0.199	0.055	2.89
240	2.47	0.088	0.192	0.052	2.80
260	2.42	0.085	0.186	0.050	2.74
280	2.37	0.082	0.181	0.048	2.68
300	2.30	0.080	0.177	0.046	2.61
320	2.25	0.078	0.173	0.044	2.55
340	2.22	0.077	0.170	0.042	2.50
360	2.16	0.075	0.168	0.041	2.44
380	2.12	0.073	0.166	0.039	2.40
400	2.07	0.072	0.165	0.038	2.34
420	2.03	0.071	0.163	0.037	2.30
440	1.99	0.070	0.161	0.036	2.25
460	1.95	0.069	0.159	0.035	2.21
480	1.90	0.068	0.157	0.034	2.16
500	1.86	0.067	0.155	0.034	2.11
510	1.85	0.067	0.154	0.034	2.11



**Figure 6.** Total ionisation cross sections  $\sigma(T)$  and direct ionisation cross sections  $\sigma(\text{CO}_2^+)$  for electron impact on  $\text{CO}_2$ :  $\diamond$ ,  $\sigma(T)$  Rapp and Englander-Golden (1965);  $\blacksquare$ ,  $\sigma(\text{CO}_2^+)$  Crowe and McConkey (1974) were normalised to Rapp and Englander-Golden;  $\circ$ ,  $\sigma(\text{CO}_2^+)$  Märk and Hille (1978);  $\blacktriangle$ ,  $\sigma(\text{CO}_2^+)$  Adamczk *et al* (1972);  $\bullet$ ,  $\sigma(T)$  Peresse and Tuffin (1967);  $\nabla$ ,  $\sigma(\text{CO}_2^+)$  Peresse and Tuffin (1967); —, present.



**Figure 7.** Dissociative ionisation cross sections for electron impact on  $\text{CO}_2$ :  $-\blacksquare-$ , Crowe and McConkey (1974);  $\nabla$ ,  $\bullet$ , Peresse and Tuffin (1967); —, present.



**Figure 8.** Total ionisation cross sections  $\sigma(T)$ , direct ionisation cross section  $\sigma(CH_4^+)$  and dissociative ionisation cross sections  $\sigma(CH_3^+)$  for electron impact on methane:  $\Delta$ ,  $\sigma(T)$  Rapp and Englander-Golden (1965); Tozer (1958)  $\sigma(T)$ ;  $\nabla$ ,  $\sigma(T)$  Winters (1975);  $\bullet$ ,  $\sigma(T)$  Chatham *et al* (1984);  $\blacksquare$ ,  $\sigma(CH_4^+)$  Chatham *et al* (1984);  $*$ ,  $\sigma(CH_3^+)$  Chatham *et al* (1984); —, present.

### 3.4. $CH_4$

Figure 8 presents the various results for  $\sigma(T)$ ,  $\sigma(CH_4^+)$  and  $\sigma(CH_3^+)$  and table 4 gives the numerical data. The most recent measurements are those of Chatham *et al* (1984). Others reported in the literature have been made by Rapp and Englander-Golden (1965), Winters (1975), and Tozer (1957). Except for the data published by Tozer, all other results agree well with each other within their respective experimental errors.

Figure 9 shows cross sections for the production of  $CH_2^+$ ,  $CH^+$  and  $C^+$ . Besides ours the only other measurements are these of Chatham *et al* (1984). It is satisfying to see that the agreement between the two results is excellent.

## 4. Discussion

From the previous section it is clear that the results of the various measurements reported in the literature sometimes widely disagree with each other. The question arises: is there a systematic procedure or a theoretical guide which one could use to assess the accuracy of the results? This question has been specifically answered in detail by de Heer and Inokuti (1985). Essentially all the guides which work at high electron impact energies fail at low energies such as employed in the present work. At these low energies exchange and polarisation effects play important roles in the collision process and theoretical methods become quite unreliable in predicting the cross sections.

One can use the additivity rule to test the accuracy of measured cross sections (for details see Younger and Märk 1985). According to this rule the total cross section

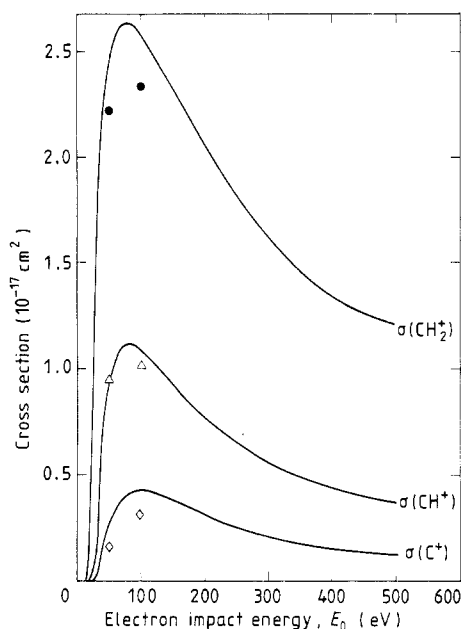
**Table 4.** Ionisation cross sections for electron impact on CH<sub>4</sub>. The cross sections are expressed in units of 10<sup>-16</sup> cm<sup>2</sup>.

$E_0(\text{eV})$	$\sigma(\text{CH}_4^+)$	$\sigma(\text{CH}_3^+)$	$\sigma(\text{CH}_2^+)$	$\sigma(\text{CH}^+)$	$\sigma(\text{C}^+)$	$\sigma(\text{T})$
10	0.00	0.00	0.000	0.000	0.000	0.00
15	0.08	0.04	0.005	0.000	0.00	0.13
20	0.51	0.40	0.026	0.001	0.00	0.94
25	0.98	0.89	0.070	0.005	0.00	1.95
30	1.29	1.25	0.134	0.019	0.002	2.70
40	1.53	1.49	0.213	0.073	0.017	3.32
50	1.69	1.65	0.238	0.091	0.028	3.69
60	1.78	1.75	0.254	0.104	0.033	3.92
70	1.82	1.81	0.261	0.110	0.038	4.04
80	1.84	1.83	0.264	0.112	0.041	4.08
90	1.83	1.83	0.263	0.11	0.042	4.08
100	1.81	1.82	0.260	0.109	0.043	4.04
120	1.76	1.78	0.249	0.103	0.041	3.93
140	1.70	1.73	0.237	0.096	0.039	3.81
160	1.65	1.68	0.227	0.089	0.036	3.68
180	1.60	1.63	0.218	0.083	0.034	3.56
200	1.52	1.56	0.208	0.077	0.031	3.40
220	1.46	1.50	0.196	0.072	0.029	3.26
240	1.40	1.43	0.188	0.068	0.026	3.11
260	1.34	1.38	0.180	0.063	0.024	2.99
280	1.29	1.33	0.171	0.059	0.022	2.87
300	1.24	1.28	0.163	0.056	0.021	2.76
320	1.20	1.24	0.156	0.053	0.019	2.67
340	1.16	1.20	0.150	0.050	0.018	2.58
360	1.12	1.16	0.146	0.046	0.017	2.50
380	1.09	1.13	0.139	0.045	0.016	2.43
400	1.06	1.11	0.134	0.044	0.015	2.36
420	1.04	1.08	0.131	0.043	0.015	2.30
440	1.01	1.06	0.128	0.041	0.014	2.25
460	0.99	1.03	0.126	0.039	0.013	2.20
480	0.97	1.01	0.123	0.038	0.013	2.15
500	0.95	0.98	0.121	0.037	0.012	2.10
510	0.94	0.96	0.120	0.036	0.012	2.07

$\sigma(\text{T})$  of a molecule MNP can be expressed as a sum in the following way

$$\sigma(\text{T}) = \sigma(\text{M}^+) + \sigma(\text{N}^+) + \sigma(\text{P}^+) \quad (2)$$

where  $\sigma(\text{M}^+)$ ,  $\sigma(\text{N}^+)$  and  $\sigma(\text{P}^+)$  are the electron impact ionisation cross sections for ionising the neutral atom M, N or P into the ion  $\text{M}^+$ ,  $\text{N}^+$  or  $\text{P}^+$ , respectively. At high electron impact energies this rule has been shown by Grosse and Bothe (1968) to be quite reliable. In order to test this rule at low electron impact energies we have compared the present results for 100 eV electrons with those calculated by using equation (2). They are shown in table 5. In order to compute total cross sections for H<sub>2</sub>O, CO, CO<sub>2</sub> and CH<sub>4</sub>, electron impact ionisation cross sections for H, C and O are needed. For this purpose we utilised the values recommended by Bell *et al* (1983), which are expected to be accurate to within  $\pm 10\%$ . It is clear from table 5 that except for CH<sub>4</sub> the differences between the two results are rather large. However, the agreement in the case of CH<sub>4</sub> is excellent, which confirms the observation of Grosse and Bothe (1968) who found that if the molecular bond is of C—H and C—C type instead of



**Figure 9.** Dissociative ionisation cross sections for electron impact on methane: ●,  $\sigma(\text{CH}_2^+)$  Chatham *et al* (1984); △,  $\sigma(\text{CH}^+)$  Chatham *et al* (1984); ◇,  $\sigma(\text{C}^+)$  Chatham *et al* (1984); —, present.

**Table 5.** A comparison of the present cross sections with those predicted by the sum rule of equation (2). All cross sections are given in units of  $10^{-16} \text{ cm}^2$ .

Molecule	$\sigma(\text{T})$	
	Present	Additivity rule
$\text{H}_2\text{O}$	4.36	2.60
$\text{CO}$	2.49	3.48
$\text{CO}_2$	3.26	4.83
$\text{CH}_4$	4.04	4.63

two groups of atoms then the additivity rule can predict  $\sigma(\text{T})$  with a precision of about  $\pm 2\%$ .

The present data for  $\text{CH}_4$  agree very well with the most recent measurements of Chatham *et al* (1984). They have utilised state of the art instrumentation and have exercised great care in the experimental procedure for normalisation. The agreement between the two provides additional confidence in the present results on  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{CO}_2$ , which were obtained in the same fashion as for  $\text{CH}_4$ . Unfortunately, there are no data on  $\text{CH}_4$  by the groups which disagree with our results on  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{CO}_2$ .

The total cross sections for  $\text{CO}$  and  $\text{CO}_2$  by Rapp and Englander-Golden (1965) agree with the present results within the stated error limits. It should be noticed that the two results have been derived by two different methods. Rapp and Englander-Golden measured the total ion current to obtain the total cross section. In the present case, a sum of individually measured partial cross sections was employed to obtain

the total cross sections. The agreement between the results generated by the two different methods provides another source of confidence in the present measurements.

### Acknowledgments

The research described in this paper was carried out at the Jet Propulsion Laboratory, California Institute of Technology, and was sponsored by AFOSR and the National Aeronautics and Space Administration. One of us (OJO) would like to thank the National Research Council (NASA) for a Resident Research Associateship grant. The authors would also like to thank Mr C W Thoms for technical assistance.

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