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**Atomic and Molecular Data for H₂O, CO & CO₂
Relevant to Edge Plasma Impurities**

H. Tawara

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**Atomic and Molecular Data for H₂O, CO & CO₂
Relevant to Edge Plasma Impurities**

**Hiro Tawara
National Institute for Fusion Science**

Abstract

The present status of atomic and molecular data under electron impact involving the most relevant plasma impurity species (H₂O, CO and CO₂) has been surveyed and some data have been compiled and evaluated. The emphasis is the cross sections for ionization, dissociation, excitation, photon emission and recombination processes.

[key words : atomic data, molecular data, electron collision, impurity molecule, H₂O, CO, CO₂]

Introduction

In the past few years we have surveyed, compiled and evaluated atomic and molecular data for some atomic as well as molecular species (H_2 and hydrocarbon molecules) which are present near the low temperature plasma region and are expected to play a role in high temperature plasma research [1,2].

Relevant issues related to atomic and molecular processes in plasma modelling and diagnostics are listed as follows :

- 1) Ion/atom/molecule/radical production cross sections
(dissociative ionization/pure ionization/dissociation)
 - a) (total and partial) yields
 - b) energy distributions
 - c) angular distributions
 - d) life-times
- 2) Excitation cross sections
 - a) photon observation
 - b) energy scattering - oscillator strength
- 3) Photon emission cross sections from ion/atom/molecule/radical lines/broad band emission (visible-EUV region)
- 4) Dissociative recombination cross sections

Typical problems in determining the cross sections

Although a number of the cross sections have been reported for various processes described above involving these impurity molecules, still there are unsettled, significant discrepancies among the measurements. Indeed absolute values of some of the measured cross sections, for example for partial ion productions, are in serious disagreement, sometimes more than an order of magnitude, and also their energy dependence shows quite different behaviors. Several reasons seem to be responsible for these discrepancies.

In the following are listed a few problems which possibly might cause significant uncertainties and errors :

1) cross sections for ion production

Total or gross cross sections for ion productions can be measured quite accurately up to a few % when the condenser plate techniques are used and all careful checks in the measurements are properly made. However, once concerned with the partial cross sections resulting from dissociative ionization, less

attention has been paid to incomplete collections of the product ions which should gain relatively large energies through dissociation processes.

- a) The electric field of only 10 V/cm is enough to collect the product H_2^+ ions resulting from direct ionization from H_2 molecules. On the other hand, more than 1000 V/cm is necessary to completely collect the product H^+ ions resulting from dissociation of H_2 molecules as the ions have large kinetic energies up to 5-10 eV)[1].
- b) Another important factor for these discrepancies is the discrimination of ions in the extracting and transporting systems from the collision region to the detector. This is further complicated if the ions have large initial kinetic energies.
- c) Also the absolute efficiencies of detection of ions used for ion detections have not been discussed in detail in many cases.

2) cross sections for photon emission

- a) The most significant errors in photon measurements should come from the calibration of absolute intensities of the photon detectors. Indeed absolute intensity calibrations for UV or VUV region are quite difficult. So often are used the so-called normalization procedures to the known cross sections which is not always accurate.
- b) The second problem is the calibration error due to scattered lights for which not much attention is paid. This becomes serious, in particular when photon intensities in the energy region of the interest from standard light sources become weak.
- c) When the measurements are concerned with molecules, the overlapping of photon peaks resulting from different rotational/vibrational excited states could also become the main causes of discrepancies because of insufficient resolutions of photon detection systems.
- d) The lifetimes of products of the excitation/dissociation of molecules are often long or sometimes not known accurately. If the dissociated products have some kinetic energies, a part of them in the excited states often escape from the viewing region of photon detectors within their life times and can not be detected.

3) cross sections for neutral dissociation product

- a) The determination of absolute detection efficiencies for relatively slow (\approx eV) neutral products is one of the most difficult tasks in measurements.

Therefore, most of the measurements for neutral particles performed so far are not absolute but relative only to investigate relative importance of different channels in dissociation/excitation processes.

- b) If the neutral species are in the excited states, photon detection techniques can be used. Similar problems described above have to be overcome to get reliable cross sections.
- c) Information of neutral particles resulting from dissociation of impurity molecules should play a role in their penetration into plasmas and survival in plasmas. Thus more consistent investigations should be performed to measure the energy distributions and the intensity distributions.

Some basic data of electron impact on these impurities have recently been discussed in detail [3.4].

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- [4] Non-equilibrium Processes in Partially Ionized Gases (ed. M.Capitelli and J.N.Bardsley, Plenum, 1990)

1 General electron collision cross sections

1.1 H₂O

Most comprehensive survey and evaluation of cross sections for total electron scattering, total vibrational/electronic excitation, momentum transfer, attachment, etc., for H₂O molecules by electron impact have been reported by Hayashi [1]. Thus, without repeating, here we refer his evaluated final results, as shown in Fig.1.1.1. It should be noted in his paper that numerical data tables of the cross sections for different processes are also included. Some of these cross sections will be discussed in some more detail later.

1.2 CO

Fig.1.1.2 shows similarly evaluated cross sections for CO by Hayashi [2].

1.3 CO₂

In Fig.1.1.3 are shown similar cross sections for CO₂ molecules under electron impact evaluated by Hayashi [3].

References

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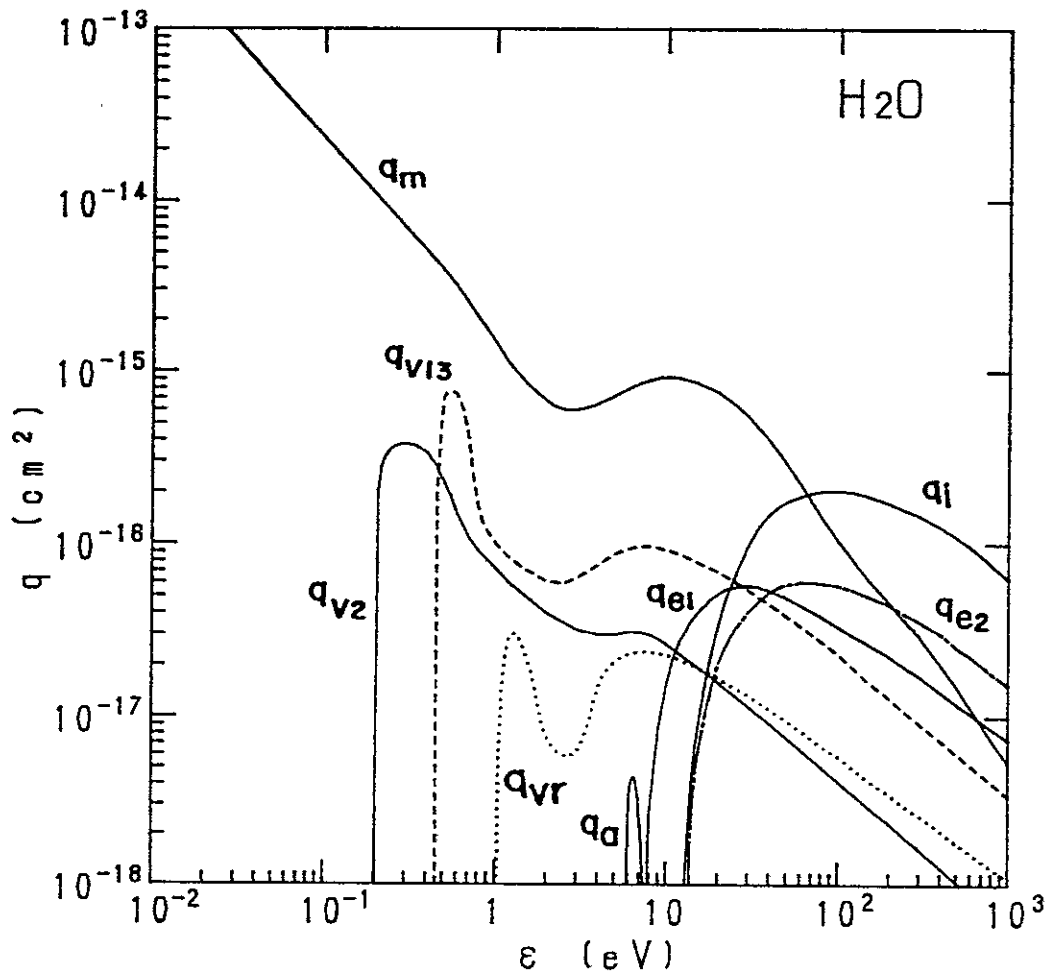


Fig.1.1.1 Electron collision cross sections for H₂O [1]

q_m : cross section of momentum transfer

q_{v13} : sum of cross sections for vibrational excitation to $v=1$ and 3

q_{v2} : cross section for vibrational excitation to $v=2$

q_{vr} : sum of cross sections for vibrational excitation to states other than $v=1,2,3$

q_{e1} : sum of cross sections for electronic excitation to the levels with the threshold energies between 7.5 to 13.3 eV

q_{e2} : sum of cross sections for electronic excitation to the levels with the threshold energies 13.3 eV - the ionization limit

q_i : cross section of ionization

q_a : cross section of electron attachment

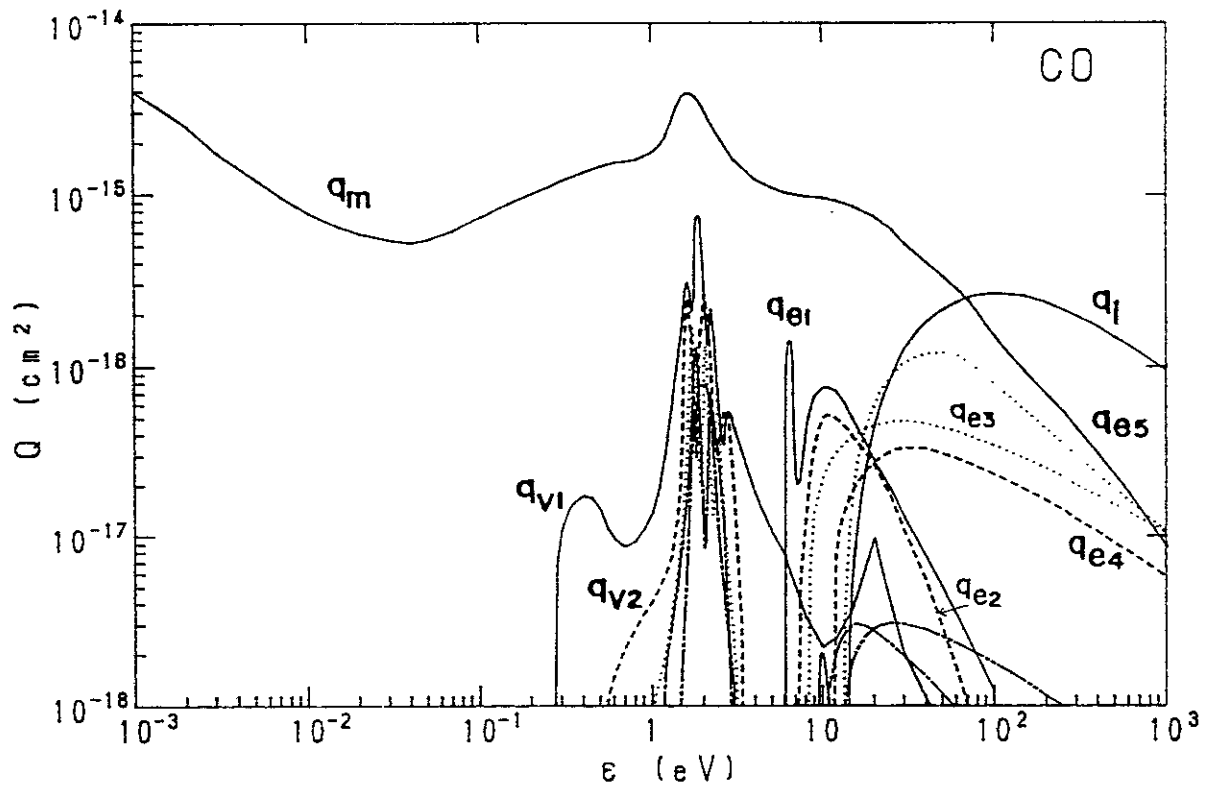


Fig.1.1.2 Electron collision cross sections for CO [2]

The symbols are the same as in Fig.1.1.1.

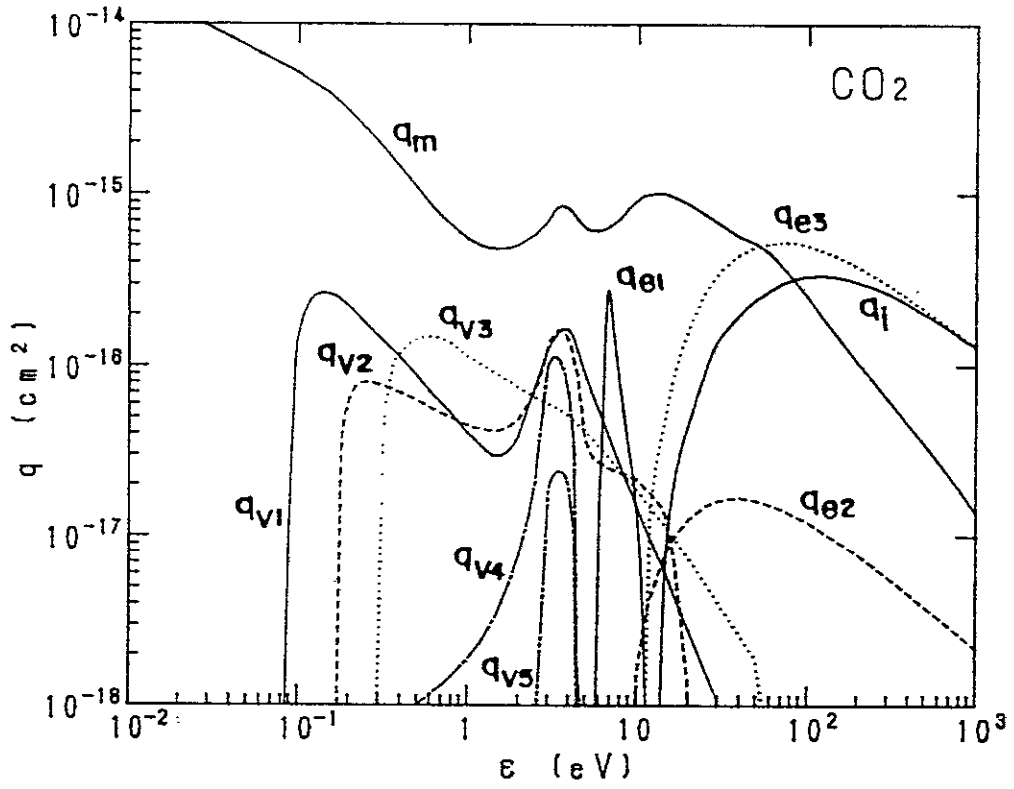


Fig.1.1.3 Electron collision cross sections for CO_2 [3]

The symbols are the same as in Fig.1.1.1.

2 Detailed data for H₂O

2.1 (Pure and dissociative) ionization cross sections of H₂O by electrons

Available cross sections for pure and dissociative ionization up to 1987 have been summarized by Lennon et al.[1]. Since then, several new measurements have been reported. Some important experimental techniques used and their features are listed in **Table 2.1.1**.

Table 2.1.1 Features in typical experiments

Authors [reference]	technique	cross sections	absolute values /accuracy	problems
Schutten [2]	condenser plates + cycloid mass	gross partial	(±15 %)	q/m discrimination
Märk [3]	magnetic mass	partial	normalized to Ar (±10 %)	q/m discrimination
Orient [4]	Q-mass	partial	normalized to Ar (±15 %)	q/m discrimination
Bolorizadeh [5]	DDCS of electrons	total	(±15 %)	electron collection
Djuric [6]	condenser plates	gross	absolute (±7 %)	

By avoiding the duplications, here we reproduce their figures already reported by Lennon et al.[1], with the addition of new results on their figures. Typical results for total (or gross) ion production cross sections are shown in **Fig.2.1.1**. It is noted that some of these total ion production cross sections are in significant disagreement with others. In particular, new data by Orient et al.[4], which are summed up for all ion productions, seem to be too large by a factor of 2. As we believe that the gross cross sections determined through measurements of ions with condenser plate techniques give the most reliable values, the cross sections for total ion production should base upon those, for example, by Schutten et al.[2] and recent data by Djuric et al.[6].

Some of partial cross sections for production of different ions (H₂O⁺, OH⁺, O⁺,

H^+) have also been measured [1]. Data for H_2O^+ ion production are shown in Fig.2.1.2, combined the summaries of Lennon et al. with new data. As seen in this figure, partial cross sections (not only their absolute values but also energy dependences) for different ions are in more serious disagreement from each other. This certainly originates from incomplete collection of product ions due either to large initial dissociation energy (as described in the Introduction) or to mass/charge discrimination in ion analyzing systems. Data for other ion production are not shown here (see ref.[1]).

At the moment, therefore, we are able to recommend only total (apparent) ionization cross sections (sum of $i*s_i$: s_i = partial cross section) which are believed to be accurate to a few-10 % when they are measured with condenser plate techniques, as shown with a bold line in Fig.2.1.1.)

Some other features are summarized as follows :

- 1) Total ionization cross sections (sum of cross sections for all ion produced times their charge) seem to be in good agreement among different authors (within 5-10 %).
- 2) Partial ionization cross sections seriously disagree among different authors (sometimes more than by a factor of two).
- 3) In particular, those for light ions, which take away most of the dissociation energies, are different significantly not only in absolute values but also in their energy dependence.
- 4) This big difference is believed to be certainly due to incomplete collection of ions in the measurement systems.
- 5) Small (<a few %) isotope effect in H_2O^+/D_2O^+ ions.

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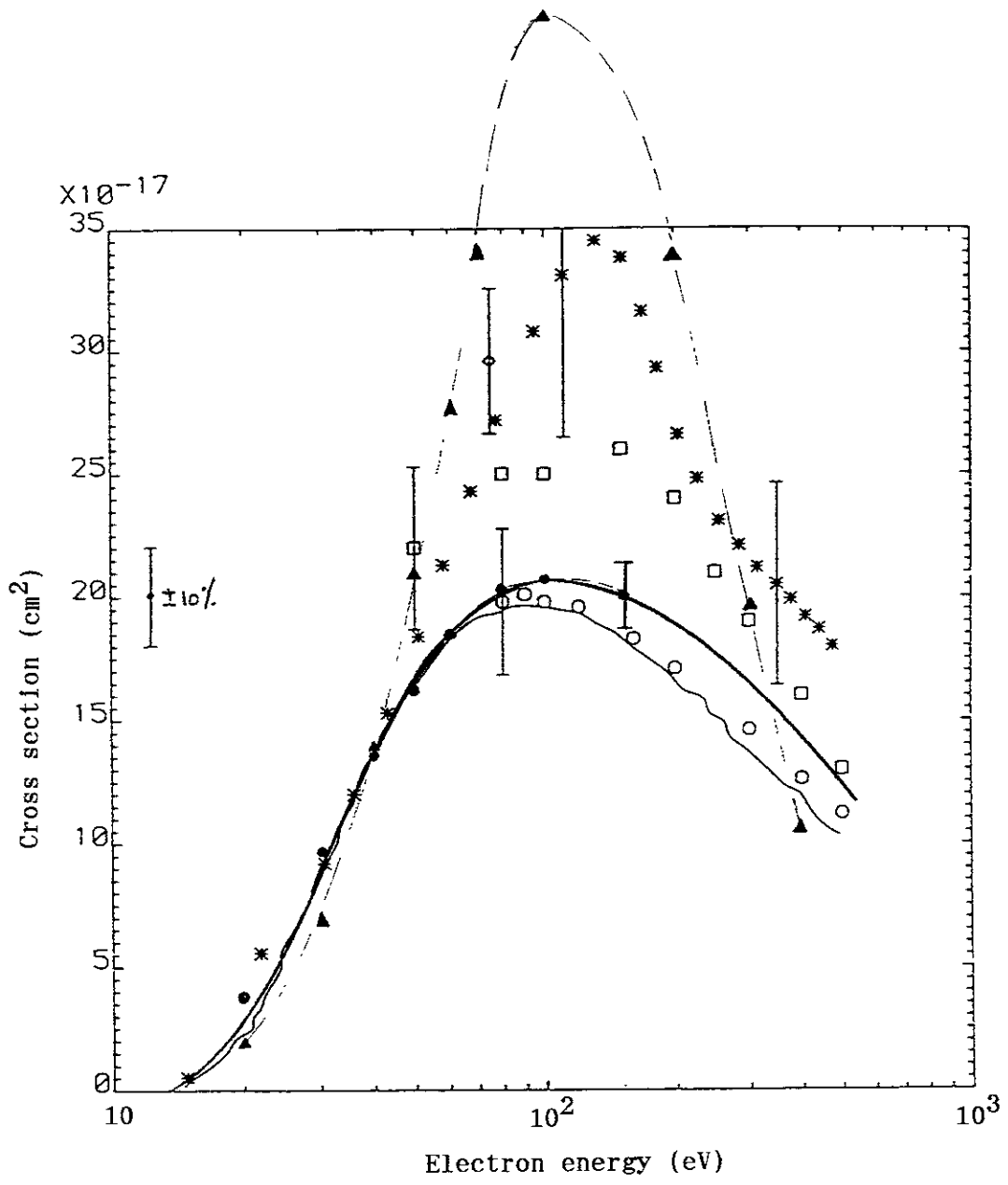
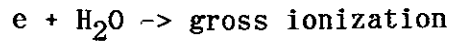


Fig.2.1.1 Total ionization cross sections of H_2O by electron impact (mostly taken from a compilation by Lennon et al.) The bold line represents our recommended data for this process.

- * Gomet J.C. (1975)
- o Schutzen J. et al (1965)
- ◊ Lampe F.W. et al (1957)
- Jain D.K. et al (1976)
- ◻ Bolorizadeh M.A et al (1985)
- Djuric et al. (1988)
- ▲ Orient et al. (1987)

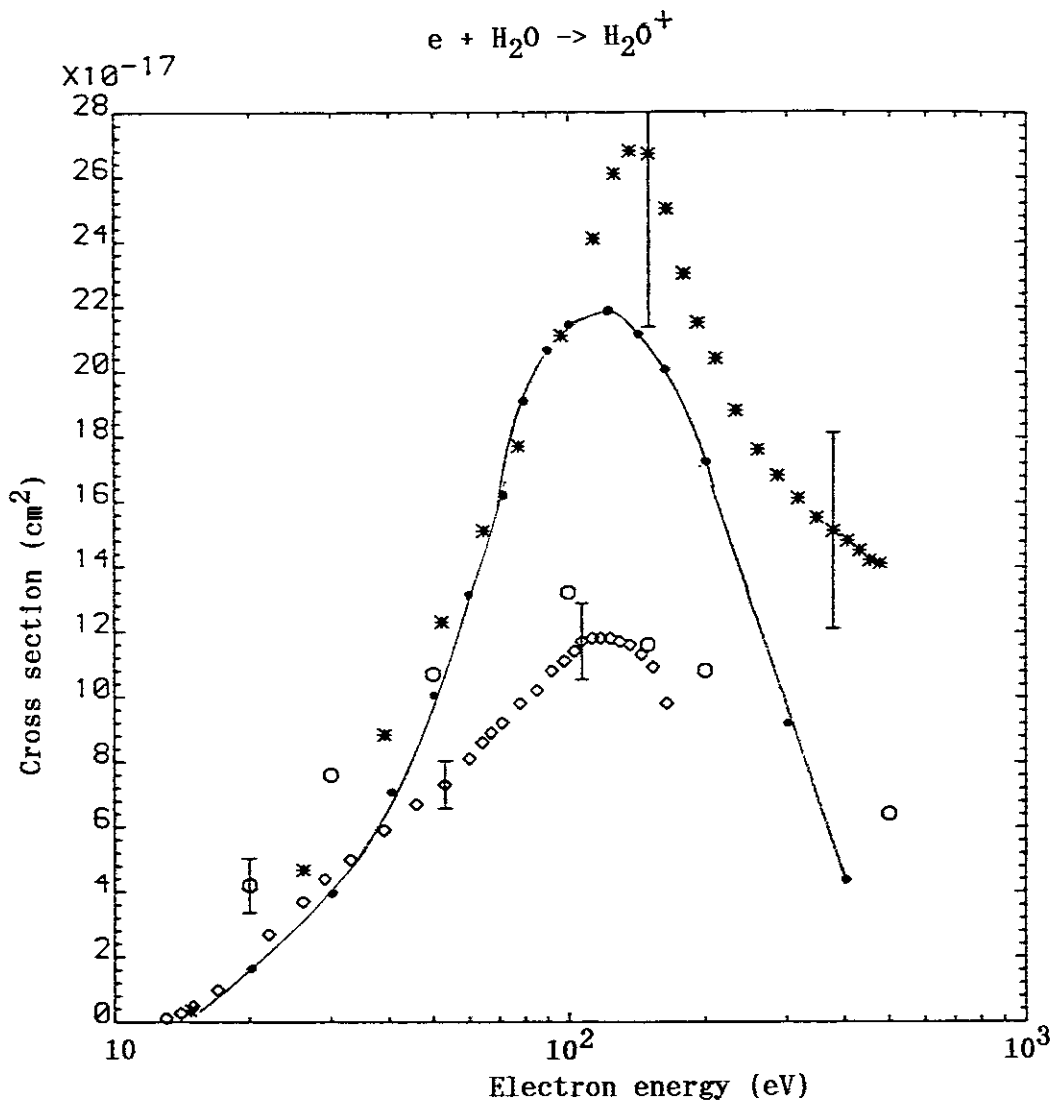


Fig.2.1.2 Partial cross sections for H_2O^+ ion production from H_2O by electron impact

- * Gomet J.C. (1975)
- o Schutten J. et al (1965)
- ◊ Mark T.D. et al (1976)
- Orient (1987)

2.2 Photon emission cross sections from $e + H_2O$ collisions

2.2.1 Emission from $H^*(n)$

I) Lyman- α emission :

Because Lyman- α emission processes from the dissociated atomic hydrogens, which are the most intense at intermediate electron energies, are important both in basic and in applied fields, a number of the measurements have been reported. It, however, is easily noted that there are large variations of the observed cross sections for Lyman- α emission from H_2O molecules which are believed to be due to the calibration/normalization procedures. Typical original data are compared in Table 2.2.1.

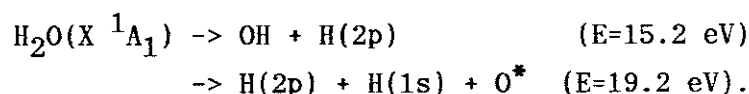
Table 2.2.1 Comparison of the observed Lyman- α emission cross sections from H_2O molecules under electron impact at 100 eV (10^{-18} cm^2)

references	a	b	c	d	e
cross sections	32.3	9	7.5	8.8	19.2

Note :

- Vroom and de Heer [1] who normalized to the values by Fite and Brackmann [2] in $e + H_2 \rightarrow \text{Lyman-}\alpha$ emission.
- McGowan et al. [3] who normalized to those for $e + H_2 \rightarrow \text{Lyman-}\alpha$ by Fite and Brackmann and claimed the uncertainties of a factor of two.
- Böse and Sroka [4] who measured only at the limited energies.
- Morgan and Mentall [5] who normalized to the known cross section for O I emission from O_2 at 1309 Å.
- Möhlmann et al. [6] who normalized to the known $e + H_2 \rightarrow \text{Lyman-}\alpha$ emission.

The Lyman- α emissions are mostly due to the followings among many processes :



The contributions from two main channels are seen in the energy dependence of the cross sections near threshold. Generally the second process is far intense (a factor of 25 at 100 eV : Bose & Sroka [4] and Morgan & Mentall [5]).

The energy dependence of Lyman- α emission cross sections are shown in Fig.2.2.1. Because the original cross sections in most of these measurements were normalized to some known values at the measurements, we have renormalized them to more recent (probably more reliable) values. For example, the original values of Möhlmann et al.[6] are divided by a factor of 1.6 ($\approx 18/7.3^*$ at 100 eV). As those of McGowan et al.[3] have the uncertainties of a factor of two, they seem to be in general agreement with the corrected values of Möhlmann et al. over the energy range overlapped.

note * : Tawara et al. [7]

Some following features should be noted :

- 1) roughly 20 % contribution from cascade of Balmer-line transitions (Vroom and de Heer [1])
- 2) very weak 2s level excitation (< 3% of 2p excitation : Vroom & de Heer [1] and Möhlmann et al.[6])
- 3) a slight isotope effect (the cross sections for D₂O are smaller about 10 % than those for H₂O ; McGowan et al.[3] and Böse & Sroka [4]).

II) Other Lyman- β , γ , δ , ϵ , η emissions

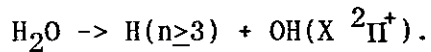
There is only a single measurement by Böse and Sroka [4] at 100 eV. Their relative intensities are shown in Table 2.2.2, together with the expected n^{-3} -dependence.

Table 2.2.2 Comparison of relative intensities of various Lyman line emissions at 100 eV by Böse & Sroka [4].

Lyman lines	α	β	γ	δ	ϵ	η
Intensities (observed)	100	19	8	4	1.3	0.7
Intensities (n^{-3})	100	30	13	6.4	3.8	2.3

III) Balmer- α , β , γ , δ

The Balmer line emissions are believed to be due the following process :



The cross sections for various Balmer emissions have been determined over 50-5000 eV by Vroom and de Heer [1], as shown in **Fig.2.2.2**, together with those for Balmer-b emission by Beenakker et al.[8] The energy dependence in both measurements for Balmer-b line seems to be in general agreement with each other (within 30 %) at the energy above 100 eV. On the other hand, the former values at low energies seem to be too high, compared with the latter. This may be the case for all the other Balmer-line emissions.

Relative intensities among 3s/3p/3d excitations have been determined up to 1000 eV by Möhlmann et al.[6] and also up to 300 eV by Lawrence [9].

Absolute cross sections for 4s/4p/4d excitation at the limited energies over 35-300 eV have been reported by Ogawa et al.[10] who observed that those for 4s and 4d are nearly equal but those for 4p are smaller by an order of magnitude.

Lyman- α ($e+H_2O$)

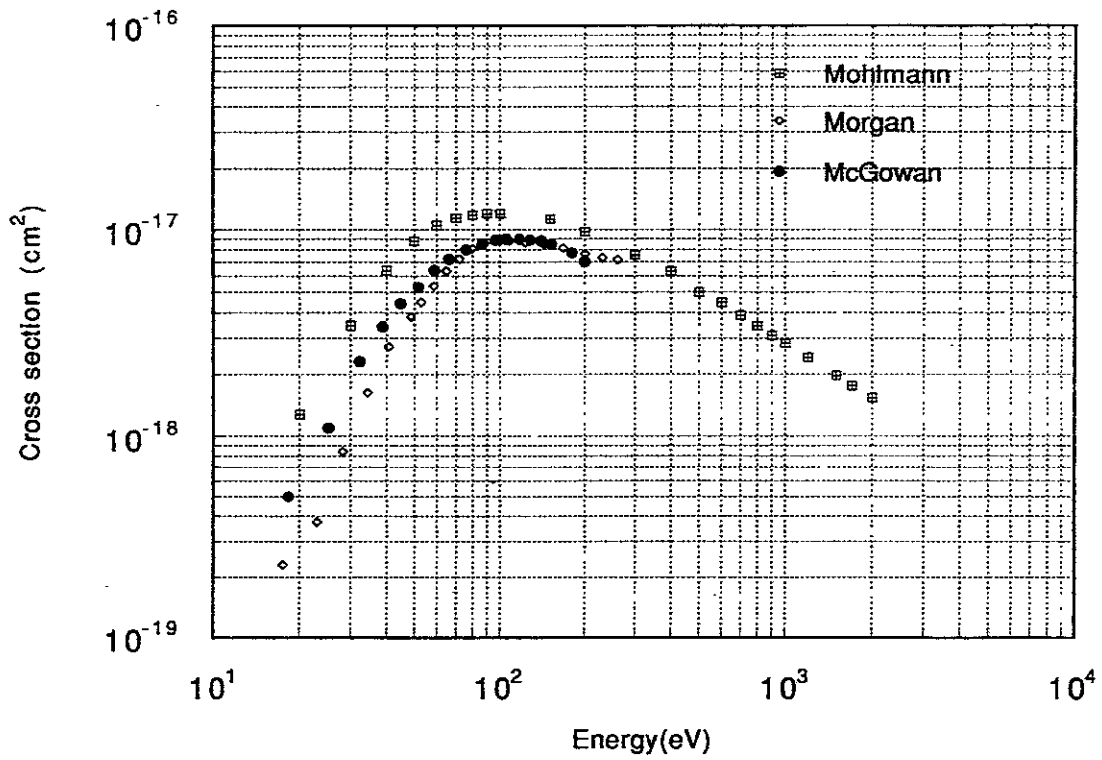


Fig.2.2.1 Lyman- α emission cross sections from H_2O by electron impact
Note that the cross sections of Möhlmann et al. are renormalized
(see text)

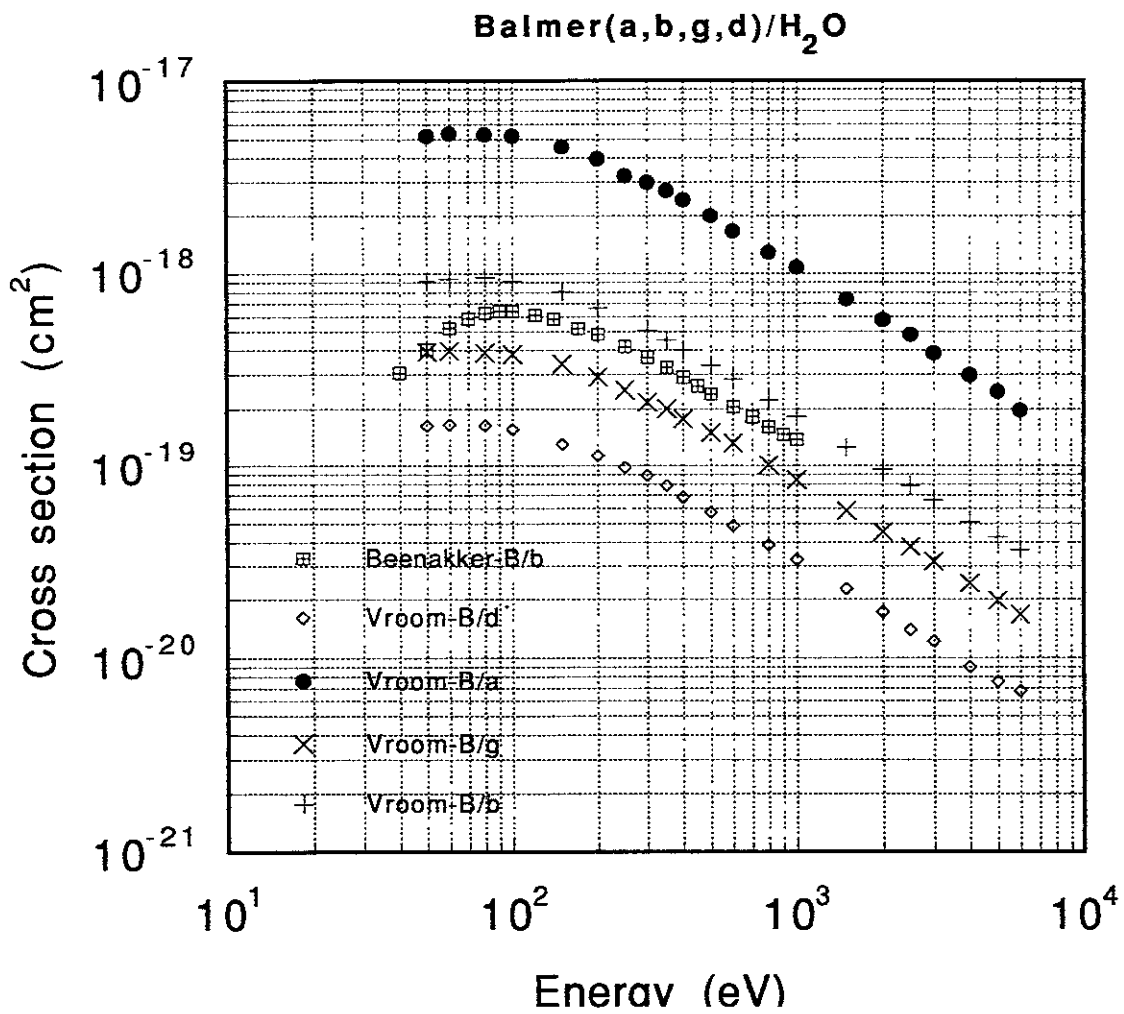
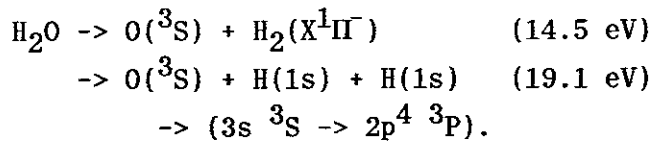


Fig.2.2.2 Cross sections for Balmer line emission from H₂O by electron impact
 B/a(b,g,d) represents Balmer- α (β,γ,δ) line emission cross sections.

2.2.2 Emission from O^* and O^+ ions

I) O I (1304 Å) :

The emissions of O I lines are due to the following :



The second process is dominant at intermediate energies. The cross sections for O I (1304 Å) emission have been reported up to 250 eV by Morgan and Mentall [5] and also up to 1000 eV by Lawrence [9]. Both data sets seem to be in agreement with each other within the experimental uncertainties, as shown in Fig.2.2.3.

II) O I (7774 Å) : $3p \ ^5P \rightarrow 3s \ ^5S^0$

The crosssections have been measured only by Beenakker et al.[8] over 40-1000 eV, as shown in Fig.2.2.4.

III) O I (8447 Å) : $3p \ ^3P \rightarrow 3s \ ^3S^0$

The cross sections have been measured by Lawrence [9] up to 1000 eV and also by Beenakker et al.[8] over 40-1000 eV. Their results are compared in Fig.2.2.5.

IV) O I (1152-879 Å)

The cross sections for several lines over 1152-879 Å have been reported only at 110 eV by Böse and Sroka [4] and observed to range over $(1-2) \cdot 10^{-19} \text{ cm}^2$.

V) O II (833-540 Å)

The cross sections for several lines from O II have been measured by Böse & Sroka [4] to be $(10-3) \cdot 10^{-20} \text{ cm}^2$ at 100 eV.

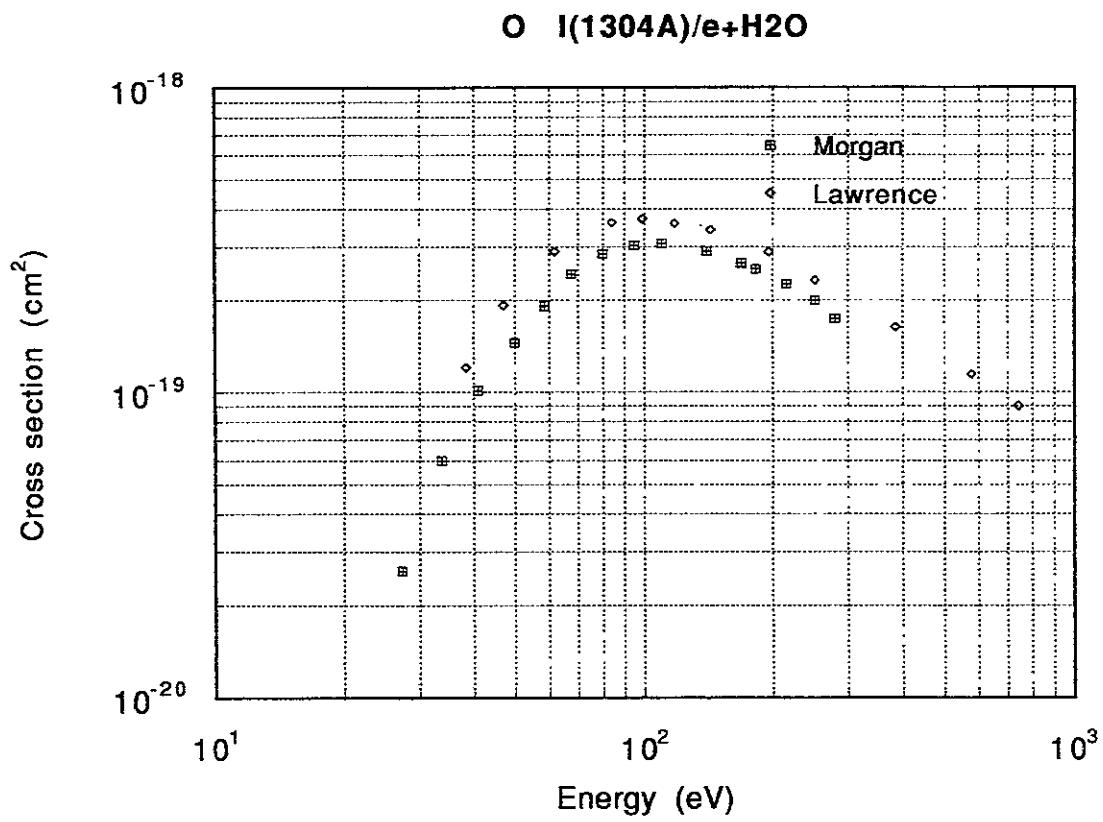


Fig.2.2.3 Cross sections for O I (1304 A) emission from H₂O by electron impact

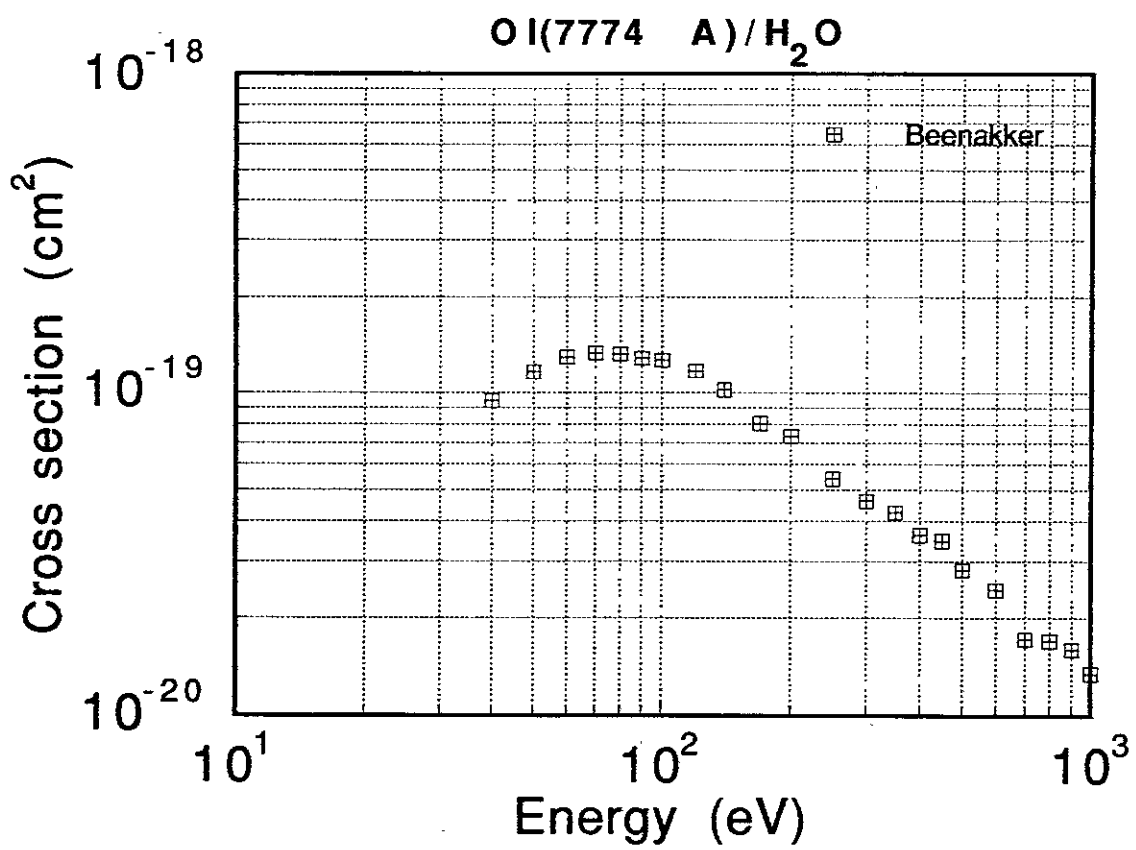


Fig.2.2.4 Cross sections for O I (7774 Å) emission from H₂O by electron impact

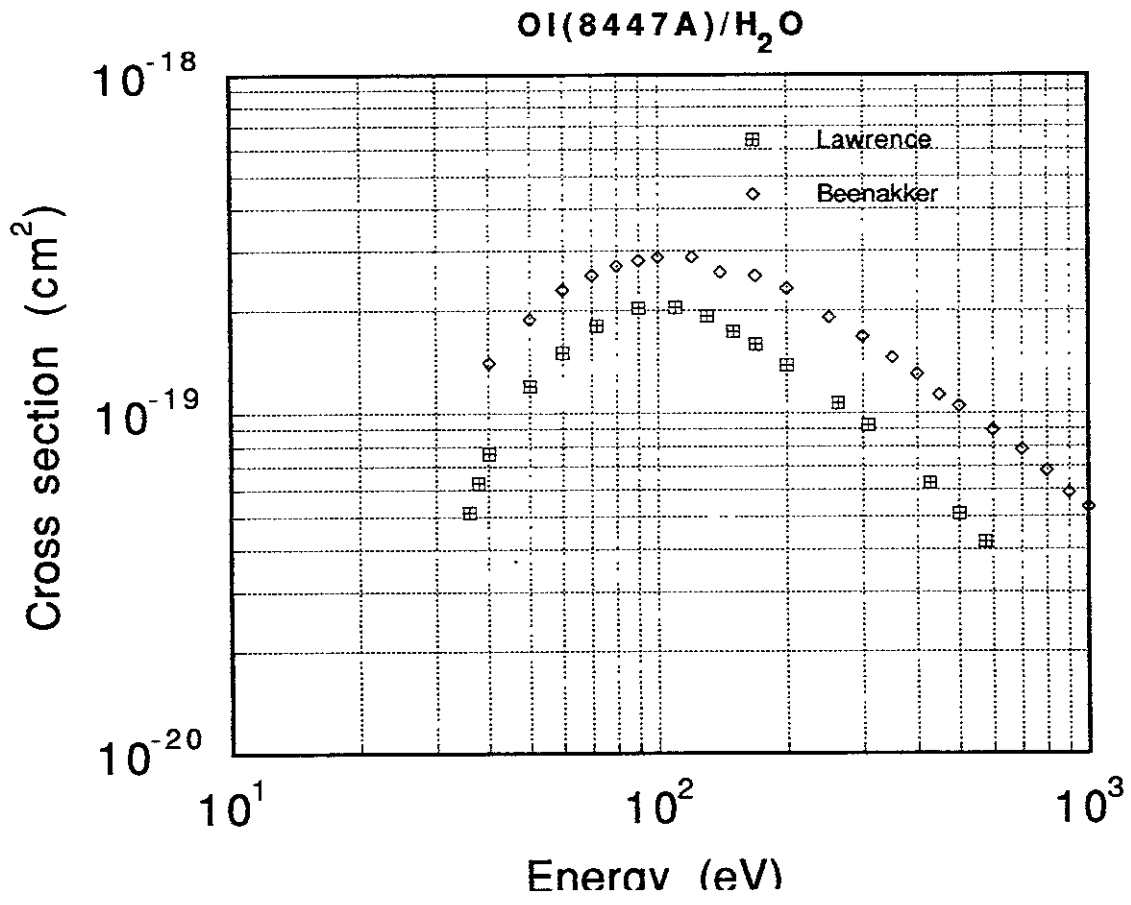
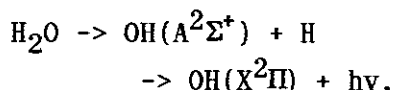


Fig.2.2.5 Cross sections for O I (8447 Å) emission from H₂O by electron impact

2.2.3 Emission from OH* band ($A^2\Sigma \rightarrow X^2\Pi$)

OH band emissions are due to the following processes :



I) OH*(0-0) band (3064 Å) :

The cross sections for the emission of OH*(0-0) band (3064 Å) have been reported over 0-75 eV by Sushanin & Kishko [11], up to 400 eV by Tsurubuchi et al. [12] and over 40-1000 eV by Beenakker et al. [8]. It is easily be noted that there are significant big differences in absolute cross sections as well as in the energy dependence among these data : Those by Sushanin & Kishko are smaller by a factor of 20 and those by Tsurubuchi et al. larger by a factor of 2-5, compared with those by Beenakker et al. In Fig.2.2.6 are shown those by Tsurubuchi et al. renormalized to Beenakker et al. at 400 eV and those by Sushanin & Kishko renormalized to Beenakker et al. 70 eV. The energy dependence by Tsurubuchi et al. are found to be quite different from that by Sushanin & Kishko. The renormalized values of Sushanin & Kishko seem to show reasonable energy dependence. The recommended data are shown with a solid line in Fig.2.2.6.

Some theoretical analysis has been performed sometime ago [13].

II) OH*(1-0) (2811 Å) :

The cross sections have been reported only by Sushanin & Kishko up to 75 eV with maximum values of $8.6 \cdot 10^{-21} \text{ cm}^2$ at 15 eV. However, as mentioned above, their absolute values seem quite uncertain (more than order of magnitude).

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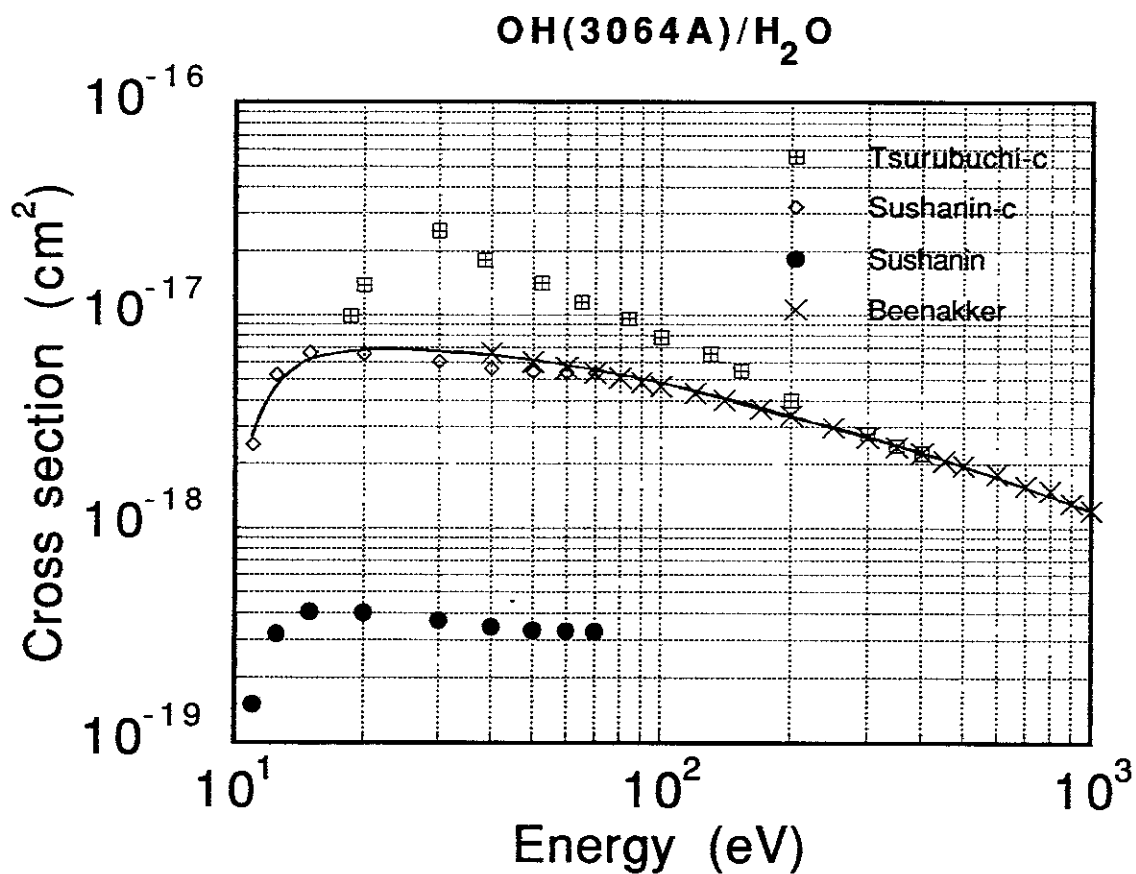


Fig.2.2.6 Cross sections for OH band (3064 A) emission from H₂ by electron impact. Note that data with marked Sushanin-c are renormalized to that of Beenakker at 70 eV, meanwhile those of Tsurubuchi-c to that of Beenakker at 400 eV. A bold line represents the present recommended data.

2.3 Energy distributions of H* atoms

The distributions of kinetic energy of the dissociated ion/atom are important, for example, to estimate the penetration length into plasmas. Doppler broadening of the emitted lights from species of the interest give information on their velocities. Broadening of Balmer- α lines is used to get the velocity distributions of H(n=3) atoms produced in dissociation by Kouchi et al.[1], while Kurawaaki et al.[2] and Ogawa et al.[3] observed Broadening of Balmer- β lines to get the velocity distributions of H(n=4) atoms over the collision energy of 0-100 eV. Compared with H atoms dissociated from molecular hydrogens, the Doppler-broadened spectra are much complicated in dissociation of H₂O, as seen in Fig.2.3.1 for Balmer- α line because many dissociation channels are available in the latter.

These observations indicate the following features :

- 1) Produced atomic hydrogens have several velocity (energy) components with peaks at 0.5, 2, 4, 6-8 eV and the line broadening is varied with electron energy.
- 2) Slow components at 0.5 eV are dominant at low collision energies.
- 3) Fast components (extended over 12 eV) are enhanced at higher collision energies, for example by a factor of 7 at 150 eV over slow components.
- 4) only slight isotope effect between D₂O and H₂O.

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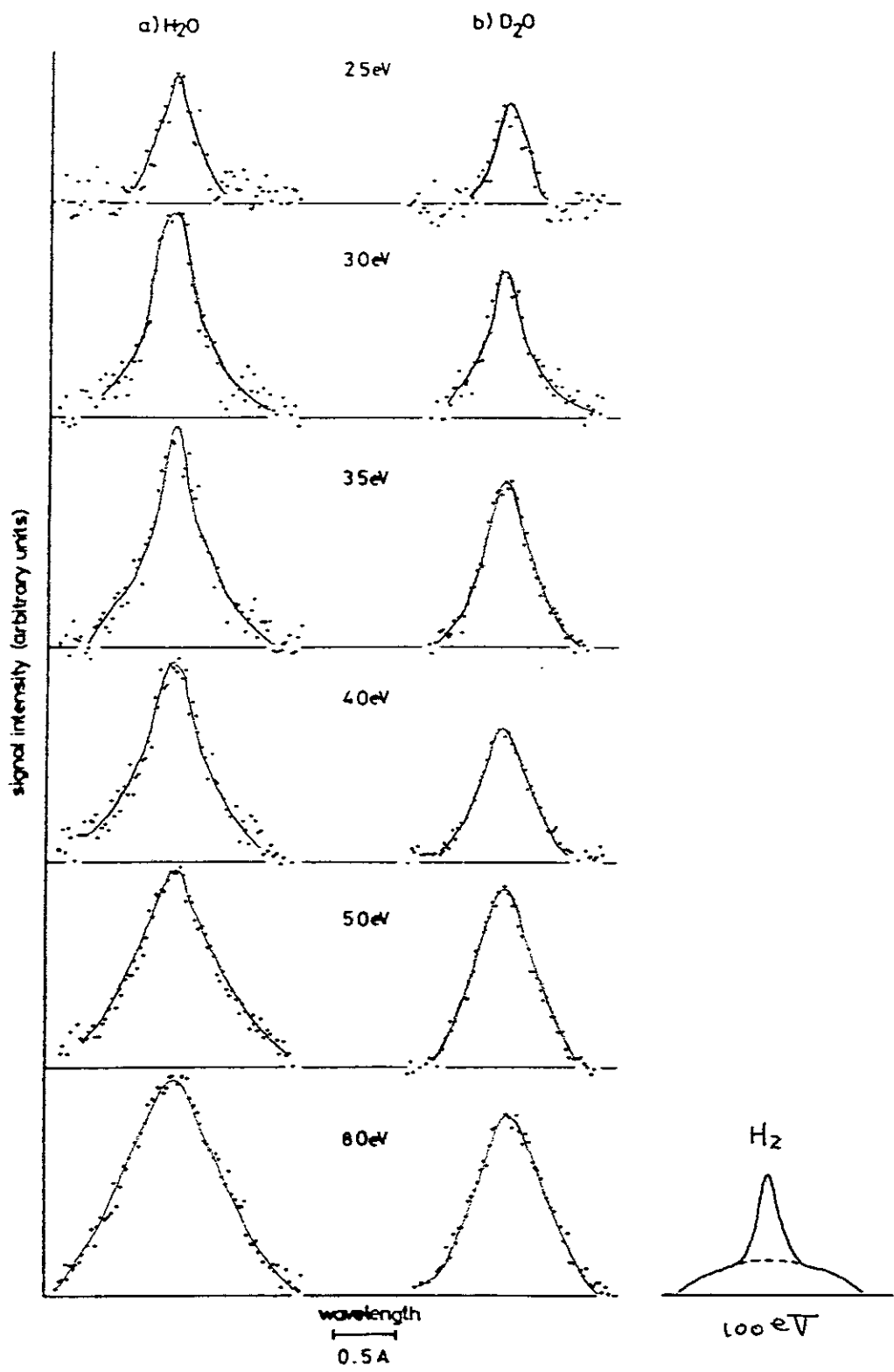


Fig.2.3.1 Variation of Doppler broadening spectra from H₂O as a function of the electron impact energy [1]

Note slight change of spectra between H₂O and D₂O. A spectrum from H₂ is also shown for comparison.

2.4 Collision of HO^+ , H_2O^+ and H_3O^+ with electrons

2.4.1 Dissociative recombination of HO^+ , H_2O^+ and H_3O^+

Dissociative recombination processes are dominant at low energies and the cross sections have been determined through merged electron-ion beam method by Mul et al.[1] over 0.01 to 1 eV. On the other hand, a trapped ion technique was used to determine them over 0.06-0.6 eV by Heppner et al.[2]. Both are in general agreement with each other at low energies, as shown in Fig.2.4.1.

Most of other measurements based on shock tube, flame, after-glow techniques show significant discrepancies, as discussed by Mul et al.[1].

The following features in the cross sections are observed :

- 1) At low energies, the cross sections decrease roughly as $1/E$ when the energy increases.
- 2) At high energies, they decrease as $1/E^2$.
- 3) The cross sections are varied as $\text{HO}^+ < \text{H}_2\text{O}^+ \approx \text{H}_3\text{O}^+$
- 4) The cross sections for D_3O^+ are smaller than those for H_3O^+ (10-80 % at low and high energies)

References

- [1] R.A.Heppner, F.L.Walls, W.T.Armstrong and G.H.Dunn, Phys. Rev. A 13 (1976) 1000
- [2] P.M.Mul, J.Wm.McGowan, P.Defrance and J.B.A.Mitchell, J. Phys. B 16 (1983) 3099 : Note that the original data should be divided by a factor of 2 (private communication),

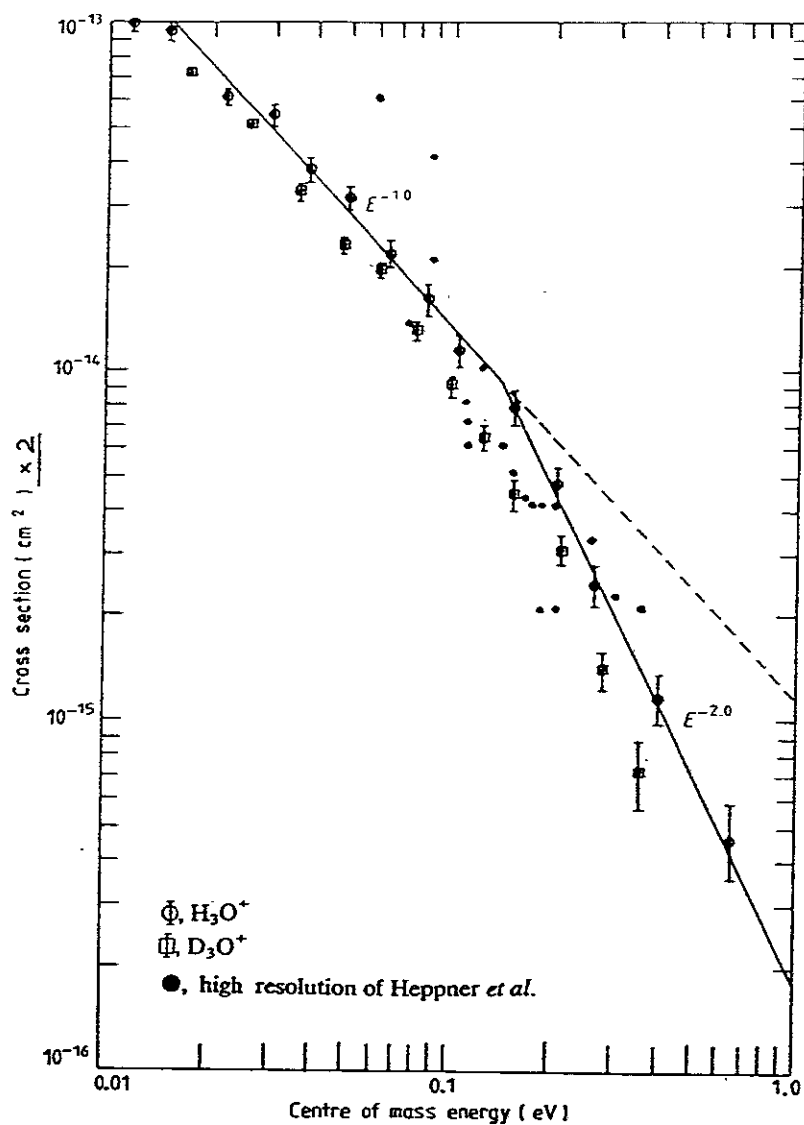
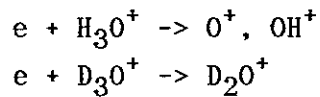


Fig.2.4.1 Cross sections for dissociative recombination of H_3O^+ and D_3O^+ by electron impact [2] (the original cross sections of Mul *et al.* are divided by a factor of two)

Note that some ($\text{D}_2\text{O}/\text{H}_2\text{O}$) isotope effects are seen.

2.4.2 Dissociation of H_3O^+ (D_3O^+) ions

At high energies, dissociative excitation becomes dominant. Schulz et al.[1] used the crossed-beam technique to get the cross sections for dissociation of H_3O^+ ions over 0-1000 eV :



and their cross sections show the $\ln(E)/E$ dependence, as expected theoretically.

As pointed out previously [2], it should be noted, however, that the cross sections for these processes are known to strongly depend on the internal (rotation/vibrational/electronic) energy of the parent molecular ions.

Reference

- [1] P.A.Schulz, D.C.Gregory, F.W.Meyer and R.A.Phaneuf, J. Chem. Phys. 85 (1986) 3386
- [2] H.Tawara, H.Nishimura, H.Tanaka and Y.Nakamura, Supplement to Nucl. Fusion 2 (1992) 25

3 Detailed data for CO

3.1 (Pure and dissociative) ionization cross sections of CO by electrons

Available data of various ion production from CO up to 1987 have been summarized by Lennon et al.[1]. Some features in different experimental techniques are listed in **Table 3.1.1**. As mentioned already, the condenser plate techniques are the most reliable to determine absolute total or gross cross sections. Recent development based upon the electron-beam crossed technique (Freund et al.[2]) seems to result in reliable determination of absolute cross sections. Though this electron-beam crossed technique seems to be the most reliable, it should be pointed out that the cross sections strongly depend upon the internal energy of the parent molecules which are produced through electron capture into ions, in this case CO^+ ions. It is very likely that neutral CO gas molecules have internal energy distributions different from the neutralized CO atoms.

Table 3.1.1 Features in typical CO experiments [2-6]

Author	technique	cross sections	absolute values /accuracy	problems
Rapp [3]	condenser plates	gross	absolute ($\pm 7\%$)	
Rapp [4]	condenser plates	partial	absolute ($E > 0.25$ eV)	(mostly $\text{C}^+ + \text{O}^+$)
Hille [5]	double-focusing magnet	partial	relative to Ar ($\pm 10-20\%$)	q/m discrimination
Orient [6]	Q-mass	partial	normalized to Ar ($\pm 15\%$)	q/m discrimination
Freund [2]	crossed-beam	partial	absolute ($\pm 10\%$)	

In **Fig. 3.1.1** are shown typical cross sections for total (or gross) ion productions from CO summarized by Lennon et al. Gross cross sections seem to be in general agreement with each other within 10-15 %. Similarly, the cross sections for production CO^+ ions, shown in **Fig. 3.1.1**, also together with new

data by Freund et al.[2] based on the cross-beam technique, agree with each other except for one of old measurements by Vaughan et al.[7]. On the other hand, as already noted in H₂O ionization, partial cross sections are in serious disagreement among measurements. Sometimes discrepancies become almost an order of magnitude (see those for C⁺, O⁺ CO²⁺ [1]). Figs.3.1.2 shows the cross sections for production of CO⁺ ions where recent crossed beam measurements [2] are also included.

The observed features of ion measurements are summarized as follows :

- 1) Gross ionization cross sections agree with each other (within 15 %).
- 2) Partial cross sections for CO⁺ ions are in agreement within ± 15 .
- 3) Partial cross sections for C⁺(-15 % of total) or O⁺(-5 %) are different by an order of magnitude (due to incomplete collection of energetic dissociated ions).

References

- [1] M.A.Lennon, D.S.Elliott and A.Crowe, Department of Computer Science, The Queen's University of Belfast (unpublished, 1988)
- [2] R.S.Freund, R.C.Wetzel and R.J.Shul, Phys. Rev. A 41 (1990) 5861
- [3] D.Rapp and P.Englander-Golden, J. Chem. Phys. 43 (1965) 1464
- [4] D.Rapp, P.Englander-Golden and D.D.Briglia, J. Chem. Phys 42 (1965) 4081
- [5] E.Hille and T.D.Märk, J. Chem. Phys. 69 (1978) 4600
- [6] O.J.Orient and S.K.Srivastava, J. Phys. B 20 (1987) 3923
- [7] A.L.Vaughan, Phys. Rev. 38 (1931) 1687

e + CO -> gross ionization

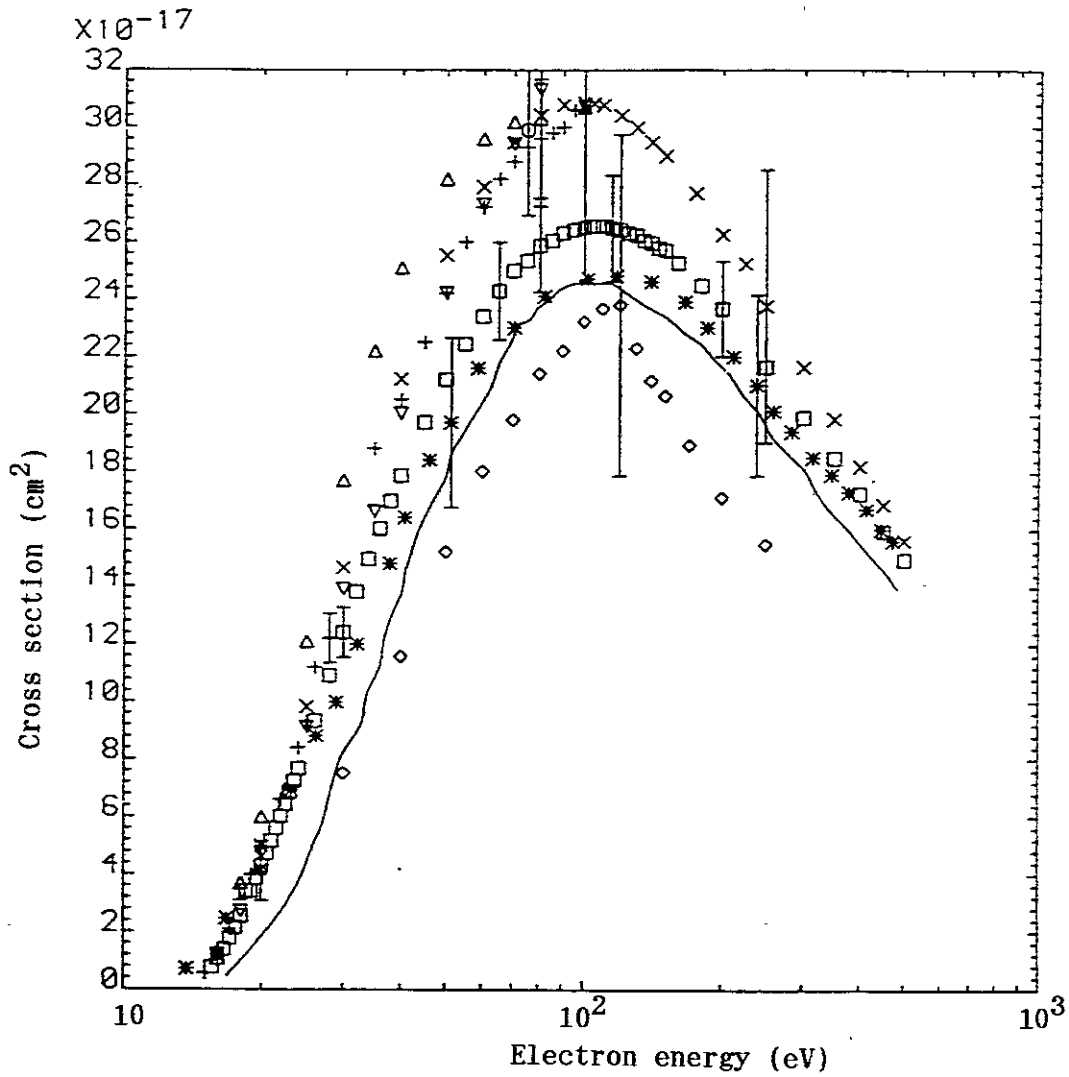


Fig.3.1.1 Gross ionization cross sections for CO by electron impact (taken from a compilation of Lennon et al.[1])

- * Orient O.J. et al(1985)
- o Lampe F.W. et al(1957)
- ◇ DeFrance M.M.A. et al(1966)
- Rapp D. et al(1965)
- x Tate J.T. et al(1932)
- Jain D.K. et al(1976)
- + Asundi R.K. et al(1963)
- ▽ Schulz G.J.(1962)
- △ Craggs J.D. et al(1958)

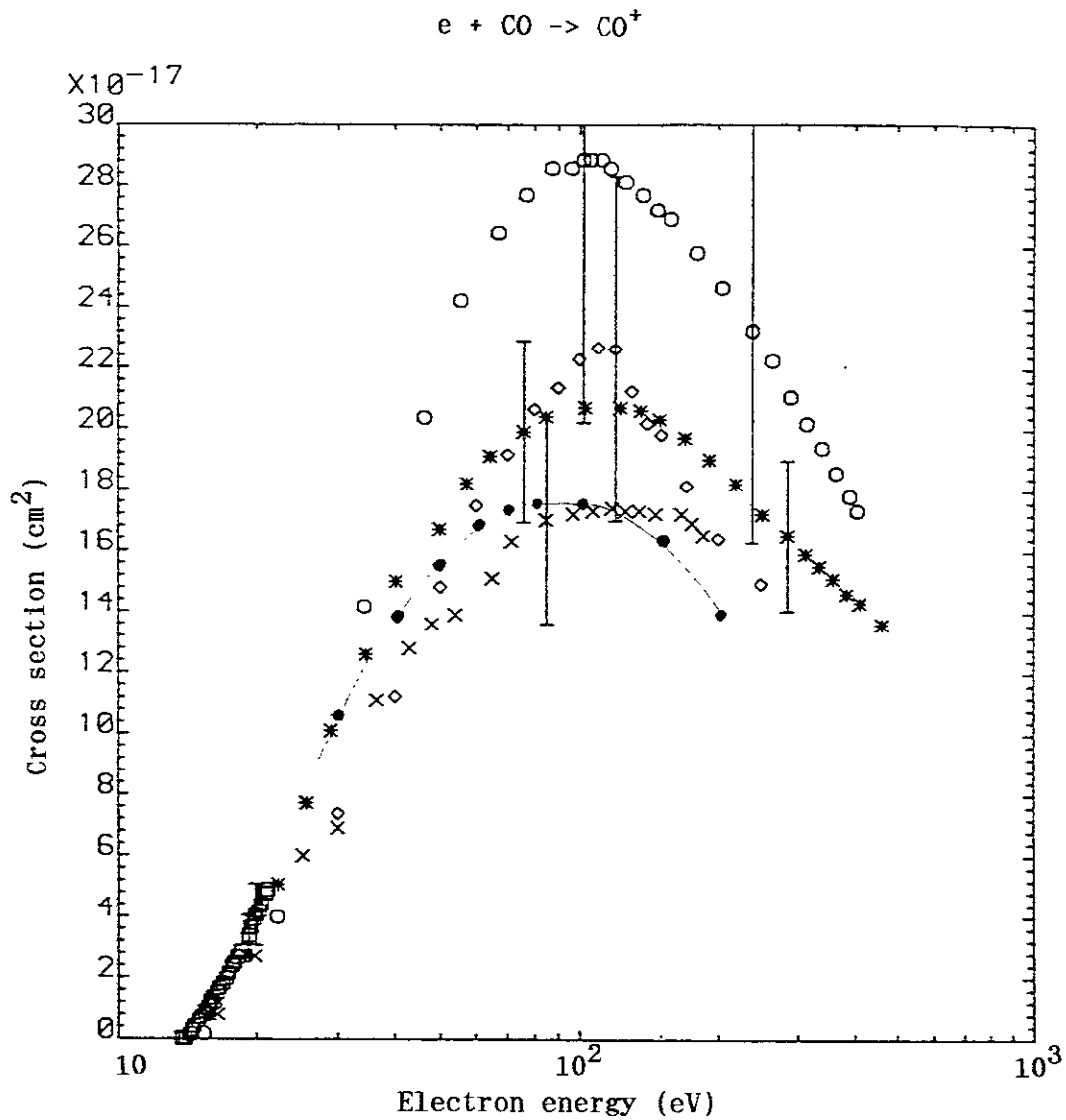


Fig.3.1.2 Cross sections for production of CO^+ from CO by electron impact (taken from a compilation of Lennon et al.[1]), with the addition of new results (Freund et al.[2])

- * Orient O.J. et al(1985)
- o Vaughan A.L.(1931)
- ◊ DeFrance M.M.A.et al(1966)
- ◻ Fox R.E. (1961)
- x Hille E. et al(1978)
- Freund et al. (1990)

3.2 Excitation/photon emission cross sections from e + CO collisions

Most comprehensive information on emission bands from CO has been summarized by Krupenie [1]. For convenience, some relevant energy levels of CO and CO⁺ are shown in Fig.3.2.1 [2].

3.2.1 Excitation cross sections

Most of the listed investigations of excitation cross sections are based upon photon observations. The (relative) excitation cross sections were obtained by summing up over possible vibrational (v') states. Some of them normalized the data to those of electron scattering experiments in order to get absolute values.

I) CO⁺

A list of the observations are summarized in Table 3.2.1. In Fig.3.2.2 are shown the observed cross sections for excitation to CO(A ¹Π : v=0,1,2,3,4) by Mumma et al.[3]. Those for all v show similar energy dependence with maximum at around 30 eV.

The cross sections for CO(B ¹Σ⁺), (d ³Π), (b ³Π) observed by Skubenich [4] and those for (possibly) (D ¹Δ + I ¹Σ) states by Wells et al.[5] are summarized in Fig.3.2.3 over relatively narrow energy region. It is noted that many small structures are observed in the original data by Skubenich.

Table 3.2.1 A list of the investigations of excitation to CO⁺

Process	Energy (eV)	References
a) A ¹ Π (v=0-4)	0-350	Mumma [3]
a) B ¹ Σ ⁺	0-150	Skubenich [4]
b) d ³ Π	0-150	Skubenich [4]
c) b ³ Σ ⁺	0-150	Skubenich [4]
d) D ¹ Δ+I ¹ Σ	0-45	Wells [5]

II) CO⁺⁺

The cross sections for excitation to CO⁺⁺(A ²Π), (B ²Σ) and (X ²Σ), as listed in **Table 3.2.2**, have been measured by Aarts and de Heer [6] and also by Skubenich [4] are shown in **Fig.3.2.4**. However, those by Skubenich seem to be too small by more than an order of magnitude, compared with those by Aarts and de Heer [6], which are used to renormalize those of Skubenich.

Table 3.2.2 A list of the investigations of excitation to CO⁺⁺

Process	Energy (eV)	References
a) A ² Π	0-150	Skubenich [4]
	50-5000	Aarts [6]
b) B ² Σ ⁺	0-150	Skubenich [4]
	50-5000	Aarts [6]
c) X ² Σ	50-5000	Aarts [6]

3.2.2 Photon emission cross sections

I) CO^{*}

A number of the cross sections from CO^{*} have been reported, as listed in **Table 3.2.3**. The cross sections for some transitions specified both the upper (v) and lower (v') states are summarized and compared in **Fig.3.2.5**. Two measurements for 1597 Å transition (0-1) by Aarts and de Heer [7] and Mumma et al.[3] seem to be in agreement with each other in the overlapped energy region. It is found that the measured cross sections for (0-1) transition in CO^{*}(A ¹Π-X ¹Σ) band represents of only a few % of total band emission of the measured by Ajello et al.[8], as seen in **Fig.3.2.6**.

The cross sections for (1-4) transition of the Cameron band of CO(a ³Π-X ¹Σ), which is a spin-forbidden process as shown in **Fig.3.2.7**, have been renormalized to that at 11 eV (maximum) by Erdman and Zipf [9] who corrected the life time and mixture of other transitions.

Measurements for various transitions over 634-1230 Å at 200 eV have been reported recently by James et al.[10].

Table 3.2.3 A list of the investigations on CO* transitions

Process	Energy (eV)	References
a-1) A $^1\Pi \rightarrow X ^1\Sigma^+$ (0- \rightarrow 1) [1597 A]	100-5000 0-350	Aarts [7] Mumma [3]
a-2) A $^1\Pi \rightarrow X ^1\Sigma^+$ [1270-2000 A]	0-300	Ajello [8] [total over v and v']
b) B $^1\Pi^+ \rightarrow X ^1\Sigma^+$ (0- \rightarrow 0) [1150 A]	100-5000	Aarts [7]
c) C $^1\Pi^+ \rightarrow X ^1\Sigma^+$ (0- \rightarrow 0) [1088 A]	100-5000	Aarts [7]
d-1) a $^3\Pi \rightarrow X ^1\Sigma^+$ (1- \rightarrow 4) [2389 A]	0-300 11	Ajello [8] Erdman [9]
e) [637 - 1230 A]	200	James [10]

II) CO**

The cross sections for line emissions from CO** have been reported as listed in **Table 3.2.4**. In **Fig.3.2.8** are shown total (summed over v and v') and (3-0) transitions of CO⁺ (A $^2\Pi$ -X $^2\Sigma$) states. This indicates that (3-0) transitions consist of 12 % of total band emission cross sections near the maximum. In **Fig.3.2.9** are shown the cross sections for total and (0-0) transitions of CO⁺ (B $^2\Sigma$ -X $^2\Sigma$) transitions. (0-0) transition consists of about 30 % of total band transitions.

Table 3.2.4 A list of the observations from CO**

Process	Energy (eV)	References
a1) A $^2\Pi \rightarrow X ^2\Sigma^+$ (3- \rightarrow 0) [4018 A]	50-5000 0-300	Aarts [6] Ajello [8]
a2) A $^2\Pi \rightarrow X ^2\Sigma^+$ [3000-6500 A]	0-300	Ajello [8] [total over v and v']
b1) B $^2\Sigma^+ \rightarrow X ^2\Sigma^+$ (0- \rightarrow 0) [2190 A strongest]	50-5000	Aarts [6]
b2) B $^2\Sigma^+ \rightarrow X ^2\Sigma^+$ [1800-3200 A]	0-300	Ajello [8] [total over v and v']
c) [634 - 638 A]	200	James [10]

III) C*

In **Table 3.2.5** are listed the investigated processes for C I line emissions. The cross sections for C I(1278 A) emission are shown in **Fig.3.2.10**. General agreement between two observations by Aarts and de Heer [7] and Ajello et al.[8] is observed. The cross sections for a series of lines over the energy region 945-1190 A at 200 eV have recently been reported by James et al.[10].

Table 3.2.5 A list of the observation for C I line emissions

Process	Energy (eV)	References
a) $2p3d\ 3D^0, 3F^0 \rightarrow 2p^2\ 3\Pi$ [1278 A]	100-5000 0-300	Aarts [7] Ajello [8] (mixed with 1278 A[$3D$], 1279 A[$3F^0$], 1280 A[$3P^0$])
b) [945 - 1190 A]	200	James [10]

IV) O*

The observed results for O I line emissions are summarized in **Table 3.2.6**. A comparison of the measured cross sections for emission of O I(1304 A) line is shown in **Fig.3.2.11**. The agreement seems to be quite good. Also the cross sections for O I(8447 A) by Lawrence [11] is shown in **Fig.3.2.12**. James et al. have reported the cross sections for various lines over 668-1150 A at 200 eV impact.

Table 3.2.6 A list of the observations of O I line emissions

Process	Energy (eV)	References
a) $2p^33s\ 3S^0 \rightarrow 2p^4\ 3P$ [1304 A]	100-5000 0-300 0-800	Aarts [7] Ajello (1971) two components (C + O*/C ⁺ + O*) Lawrence [11]
b) [8447 A]	0-800	Lawrence [11]
c) [668 - 1150 A]	200	James [10]

V) C⁺⁺

The processes investigated for C II line emissions are listed in **Table 3.2.7**. Only the results for C II(1335 Å) line are compared as shown in **Fig.3.2.13**.

Table 3.2.7 A list of the observations for C II line emissions

Process	Energy (eV)	References
a) $2s2p^3 \ ^2\Delta \rightarrow 2s^22p \ ^2\Pi^0$	100-5000	Aarts [7]
[1335 Å]	0-300	Ajello [8]
b) [520 - 1140 Å]	200	James [10]

VI) O⁺⁺

The cross sections for emission from O II over 480-840 Å at 200 eV impact (10^{-19} - 10^{-20} cm²) have been reported by James et al.[10], as listed in **Table 3.2.8**.

Table 3.2.8 A list of the observations for O II lines

Process	Energy (eV)	References
a) [480-840 Å]	200	James [10]

Summaries of important features of photon measurements from CO

- The direct excitation is found to be responsible for emission from CO^{*}.
- The v-population of A $^1\Pi_g$ have distributions of Franck-Condon type.
- Cascade effect is small
- Contamination from other peaks (due to limited resolutions) often give wrong cross sections.
- Radiative life-time corrections should be applied, in particular for long-life species. Unfortunately sometimes the life times for the excited states are not known accurately.
- Loss of products from viewing region due to large kinetic energy through dissociation should be large. Thus proper corrections for viewing zones of the produced species should also be applied.

References

- [1] P.H.Krupenie, The band spectrum of carbon monoxide : NSRDS-NBS-5 (1966)
- [2] D.G.Tilford and J.D.Simmons, J. Phys. Chem. Ref. Data 1 (1972) 147
- [3] M.J.Mumma, E.J.Stone and E.C.Zipf, J. Chem. Phys. 54 (1971) 2627
(normalized to Born approx. at 300 eV)
- [4] V.V.Skubenich, Opt. Spectr. 23 (1967) 540
- [5] W.C.Wells, W.L.Borst and E.C.Zipf, Phys. Rev. A 8 (1973) 2463 : W.C.Wells
and E.C.Zipf, J. Chem. Phys. 57 (1972) 3583
- [6] J.F.M.Aarts and F.J.de Heer, Physica 49 (1970) 425
(W-/D₂ standard lamp)
- [7] J.F.M.Aarts and F.J.de Heer, J. Chem. Phys. 52 (1970) 5354
(standard lamp)
- [8] J.M.Ajello, J. Chem. Phys. 55 (1971) 3158
(W-standard lamp/branching ratio method)
- [9] P.W.Erdman and E.C.Zipf, Planet. Space Sci. 31 (1983) 317
(Cameron band, [a ³Π -> X ¹Σ] over 2250-2650 Å at 11 eV)
- [10] G.K.James, J.M.Ajello, I.Kanik, B.Franklin and D.E.Schemansky, J. Phys. B
25 (1992) 1481
(40-125 Å only at 200 eV)
- [11] G.M.Lawrence, Phys. Rev. A 2 (1970) 397

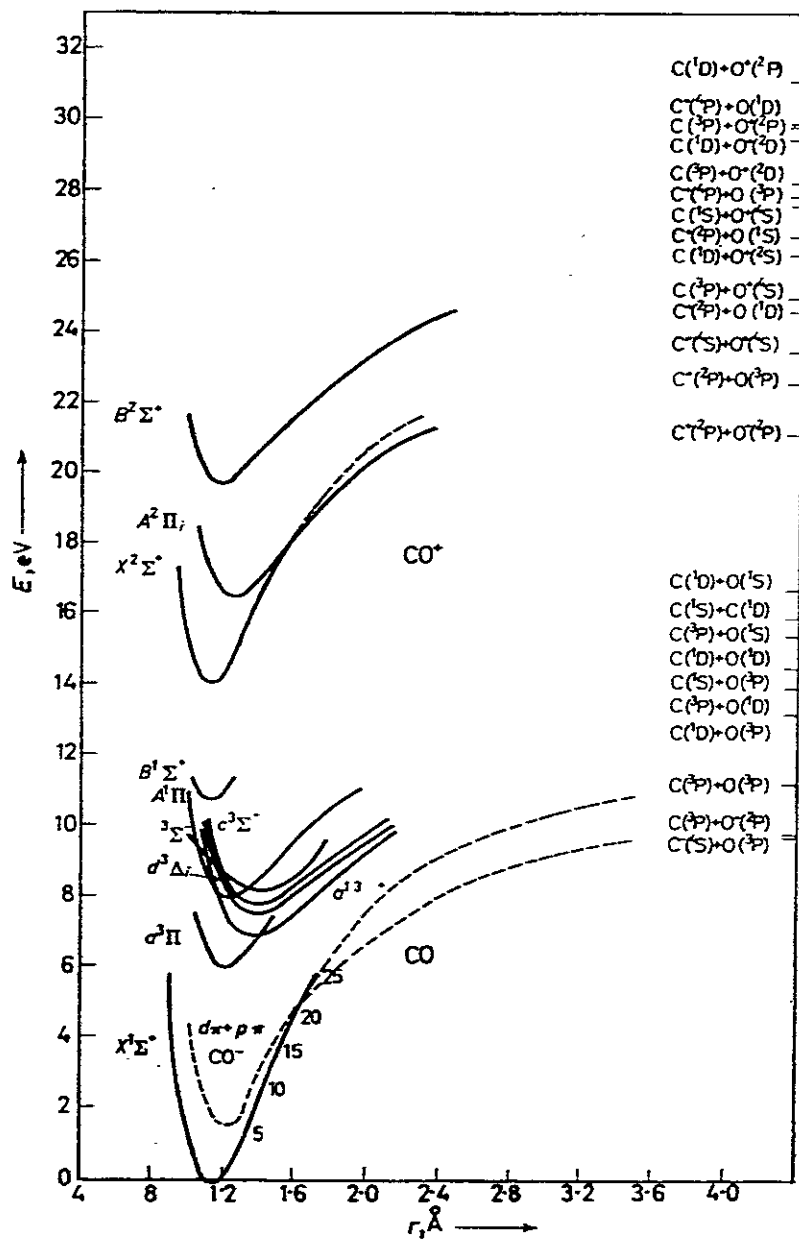


Fig.3.2.1 Some important energy diagram of CO and CO⁺

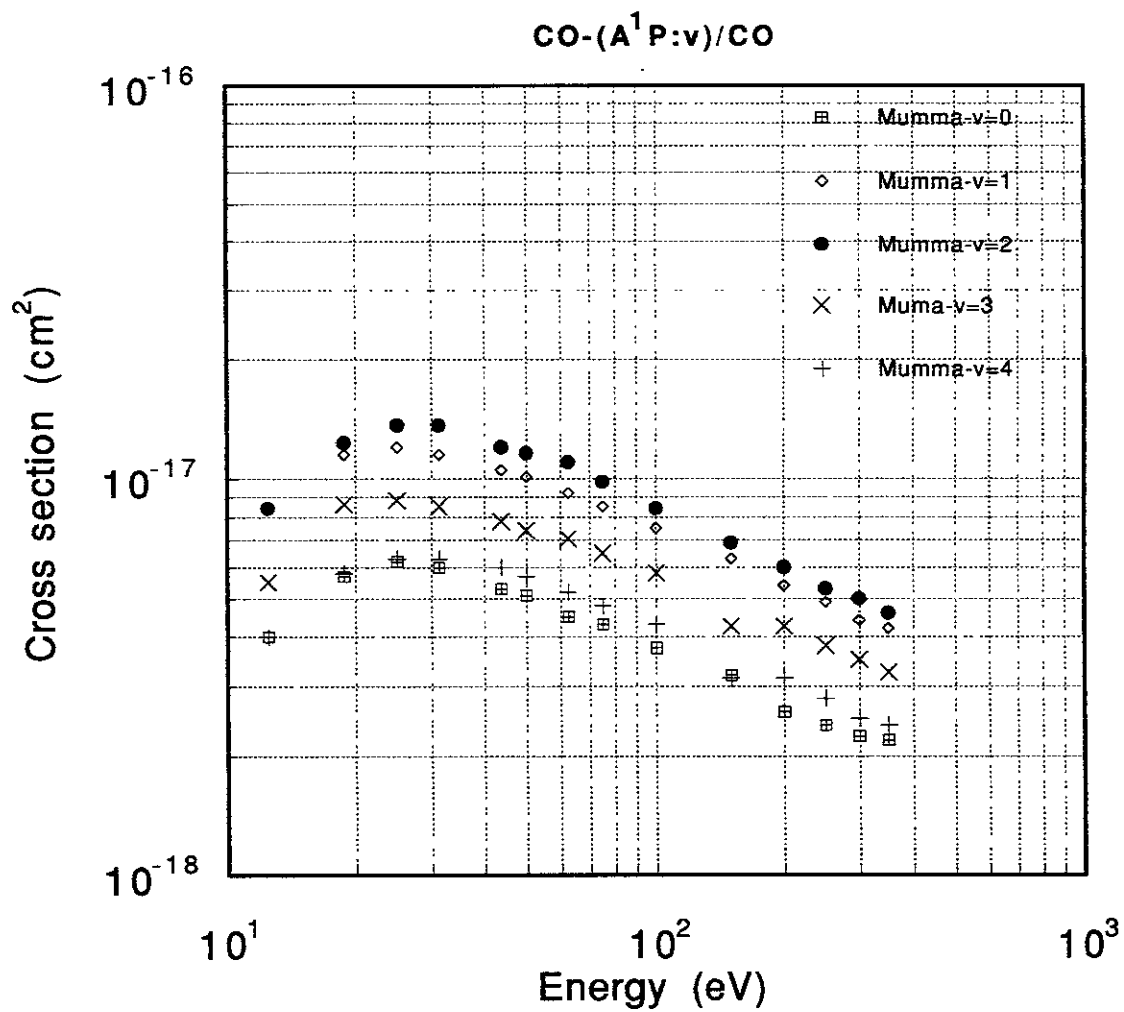


Fig.3.2.2 Cross sections for excitation to CO (A ¹Π : v=0,1,2,3,4) by electron impact on CO

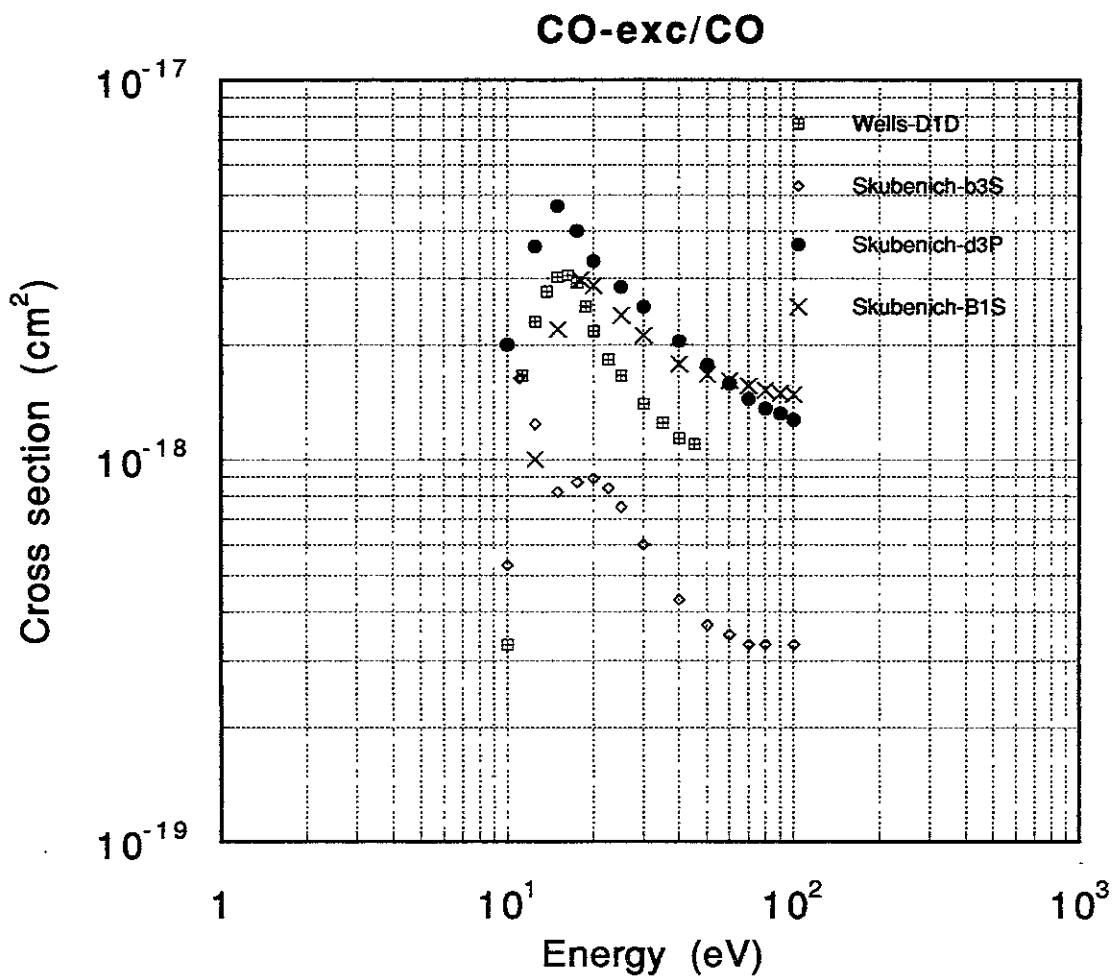


Fig.3.2.3 Cross sections for excitation to CO ($B^1\Sigma$), ($d^3\Pi$), ($b^3\Pi$) and ($D^1\Delta + I^1\Sigma$) by electron impact on CO

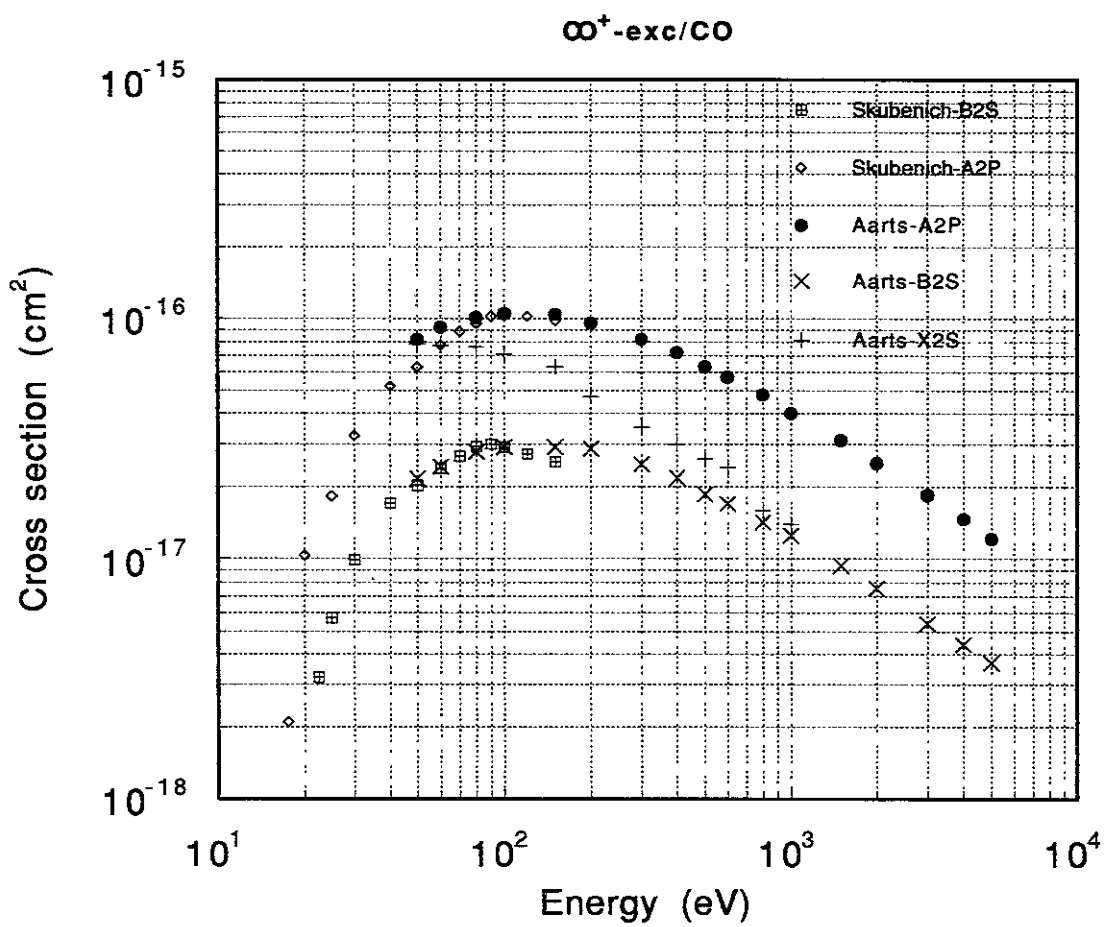


Fig.3.2.4 Cross sections for excitation to CO^+ ($A \ ^2\Pi$), ($B \ ^2\Sigma$) and $X \ ^2\Sigma$) by electron impact on CO
 Note that data by Skubenich are renormalized to Aarts and de Heer at 100 eV.

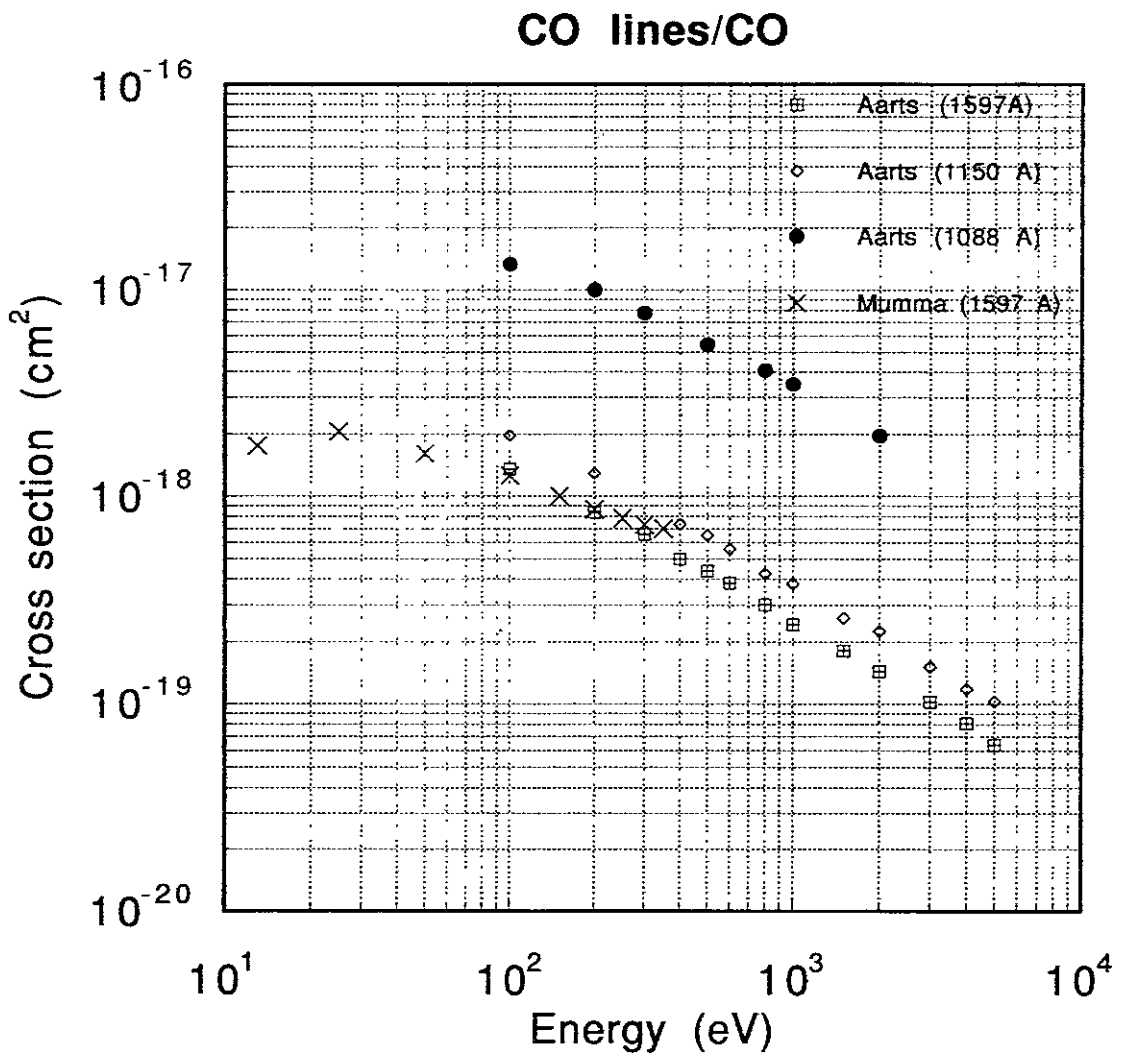


Fig.3.2.5 Cross sections for line emission from CO by electron impact on CO

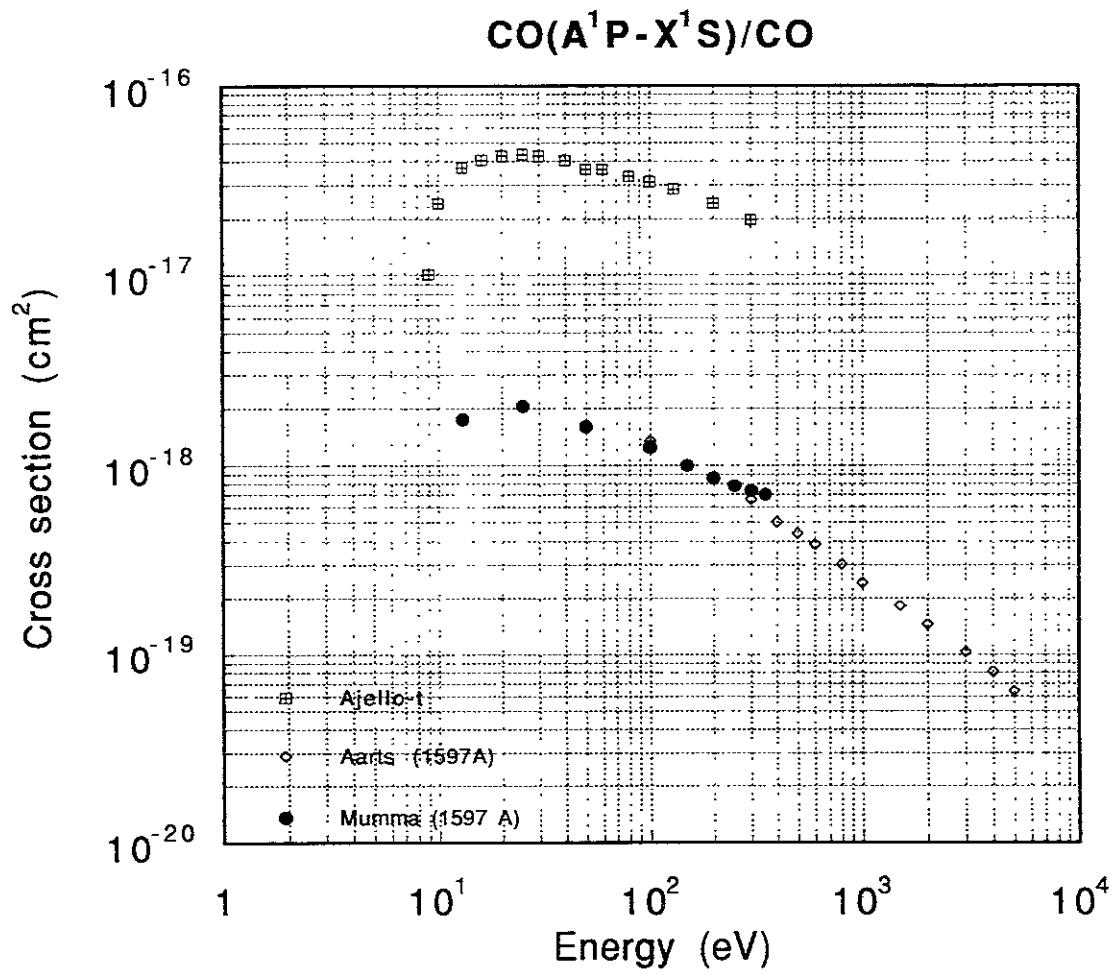


Fig.3.2.6 Cross sections for total and (0-→1) emission from CO (A ¹Π-X ¹Σ) by electron impact on CO

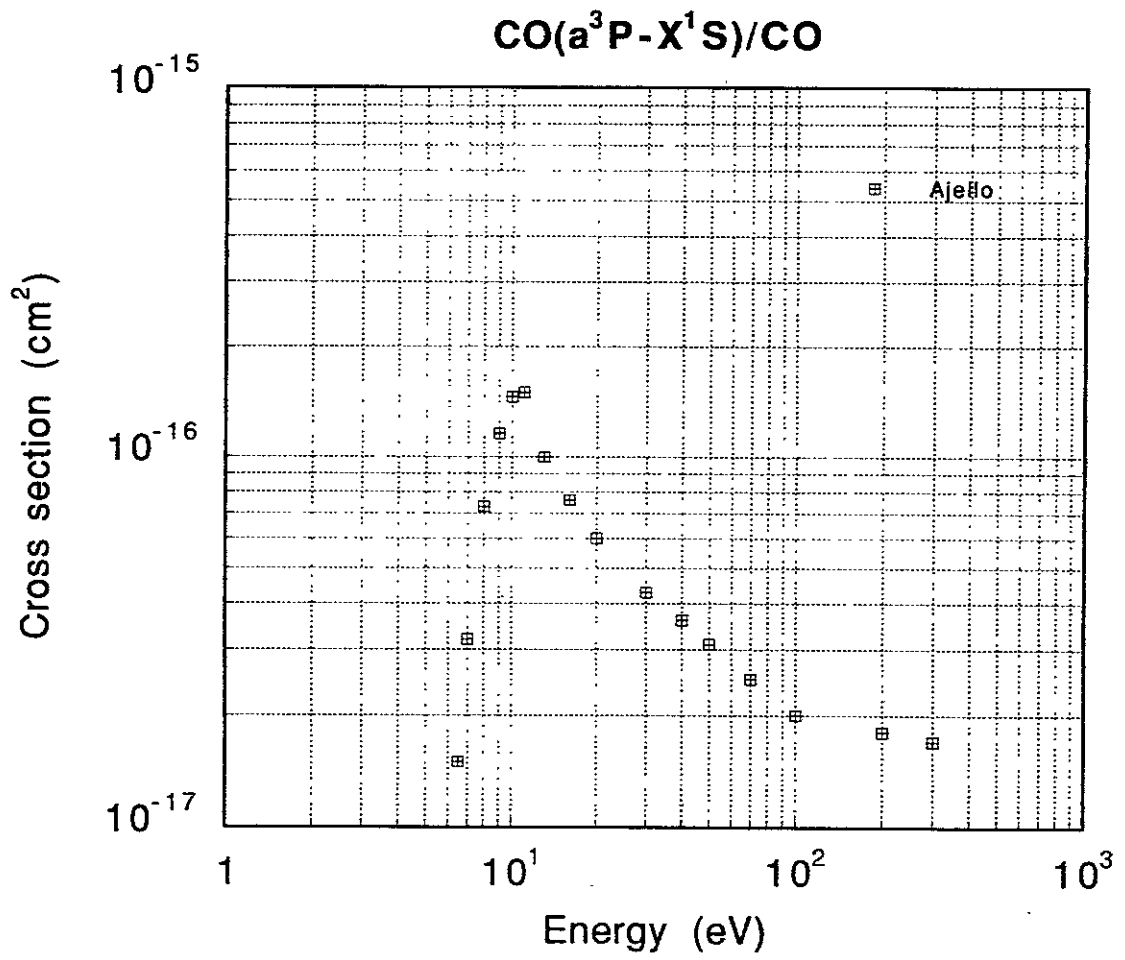


Fig.3.2.7 Cross sections for emission from CO ($a^3\Pi-X^1\Sigma$)
by electron impact on CO

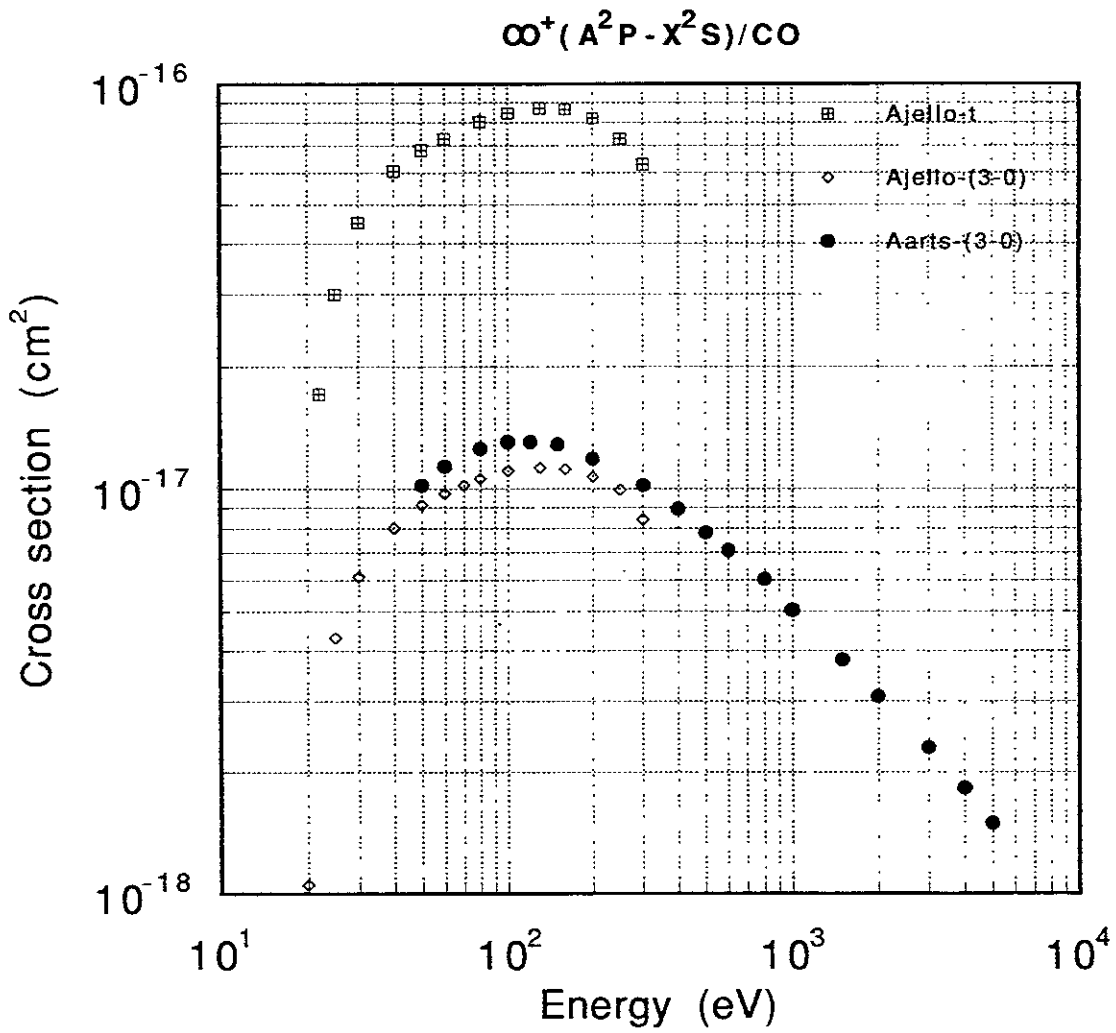


Fig.3.2.8 Cross sections for total and (3-0) emissions from $\text{CO}^+ (\text{A}^2\Pi-\text{X}^2\Sigma)$ by electron impact on CO

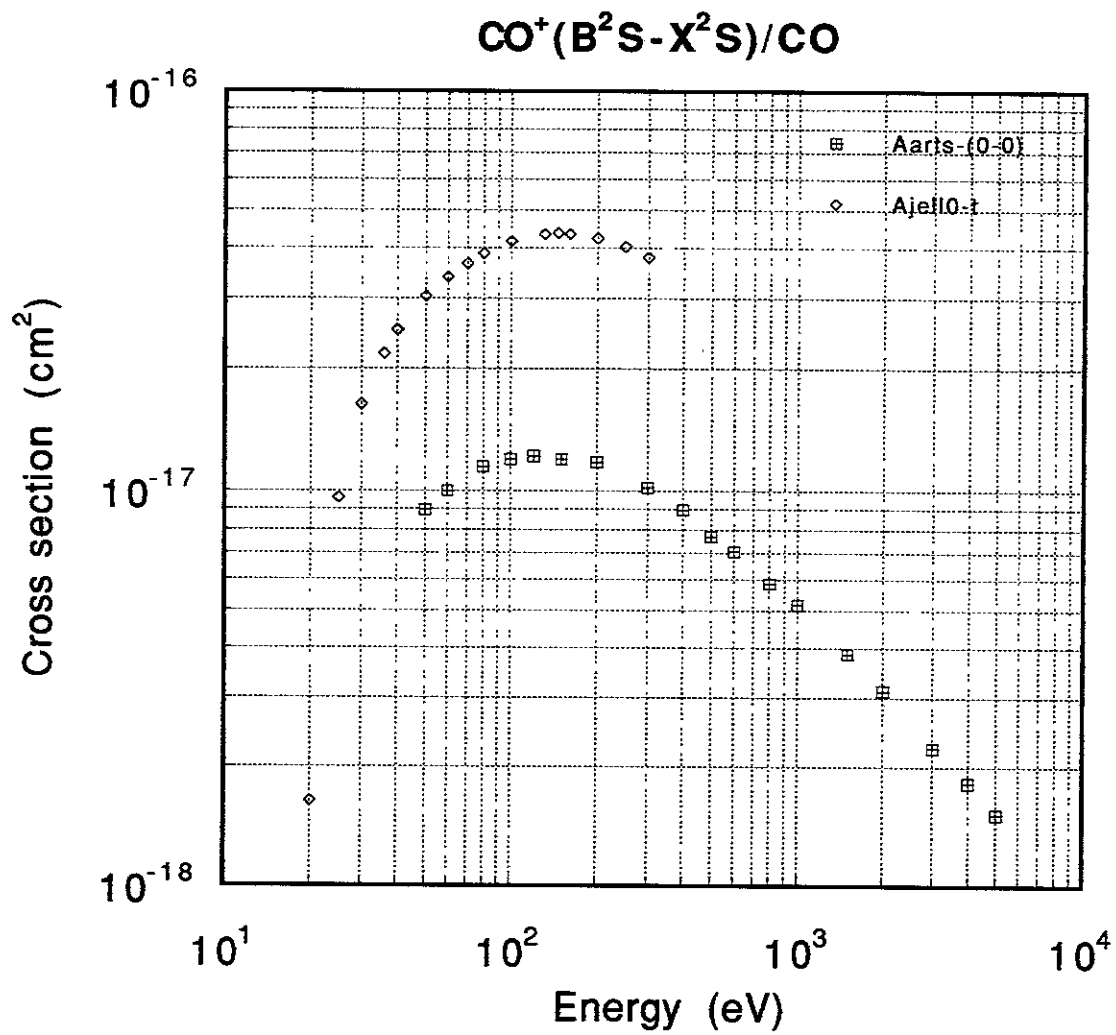
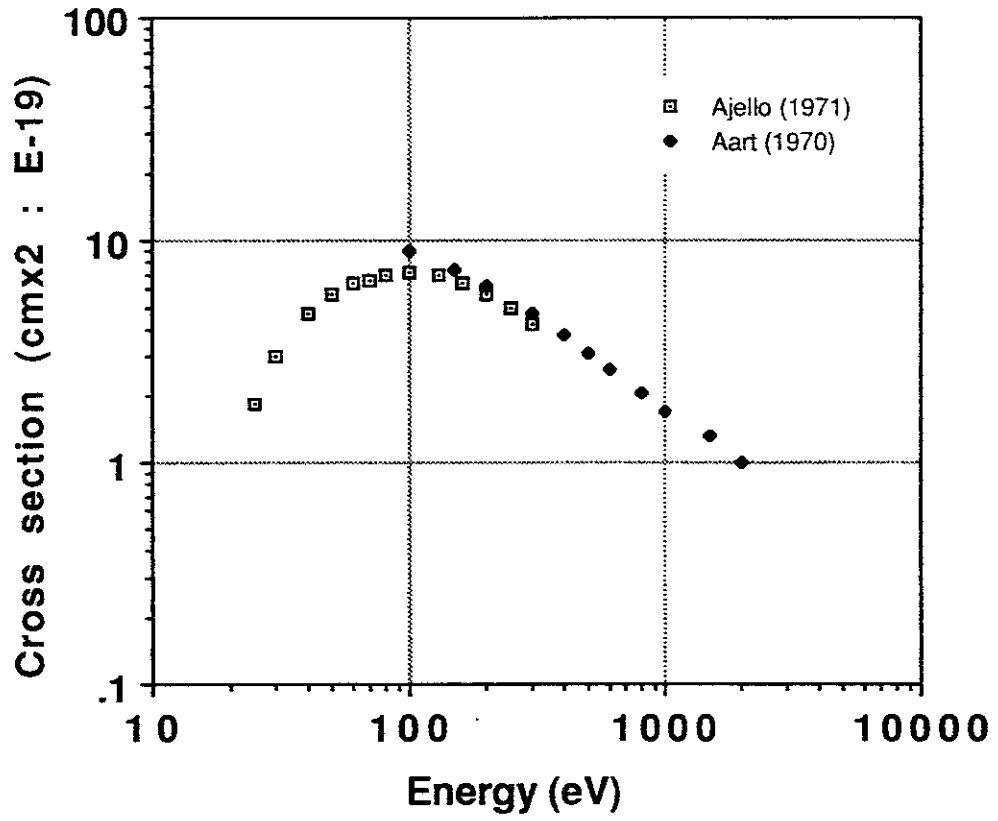


Fig.3.2.9 Cross sections for total and (0->0) emissions from CO⁺ (B ² Π -X ² Σ) by electron impact on CO

Data from "C I (1278 A / CO)"



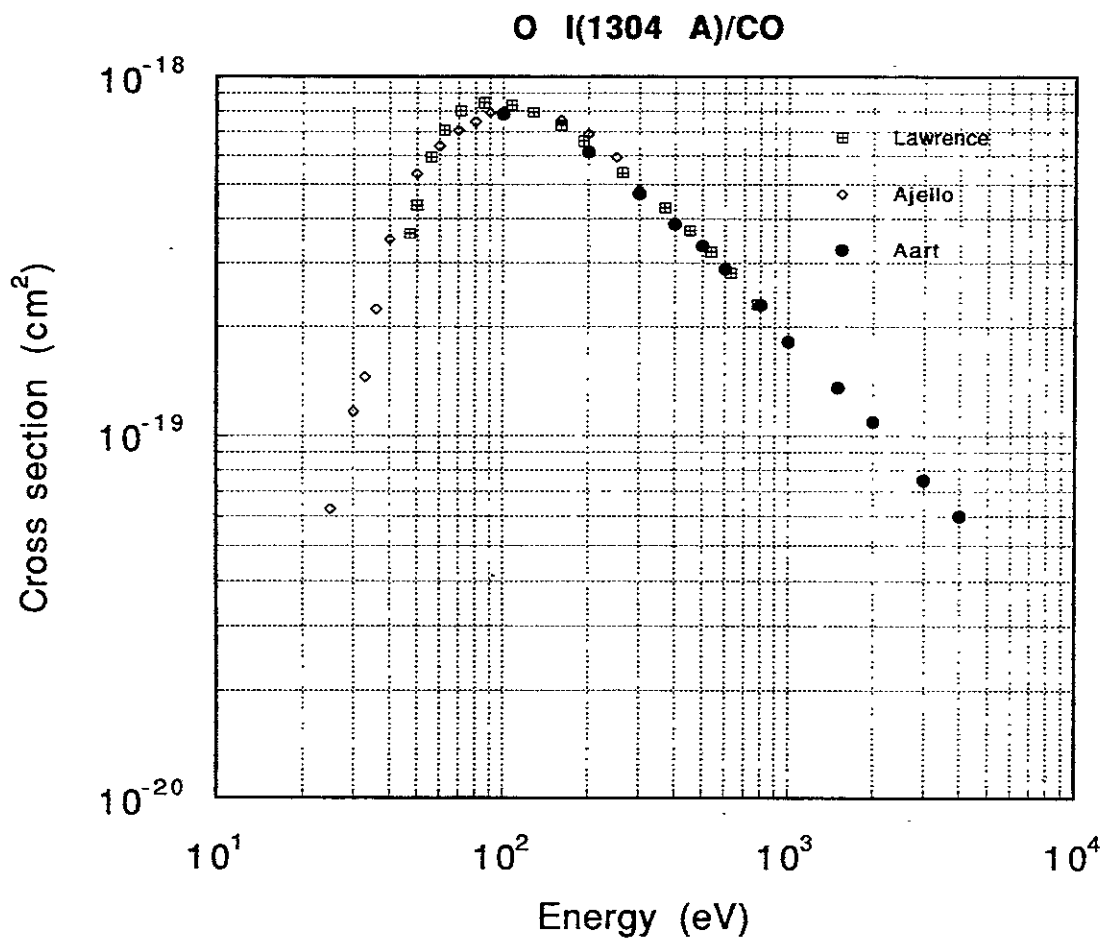


Fig.3.2.11 Cross sections for emission from O I (1304 A)
by electron impact on CO

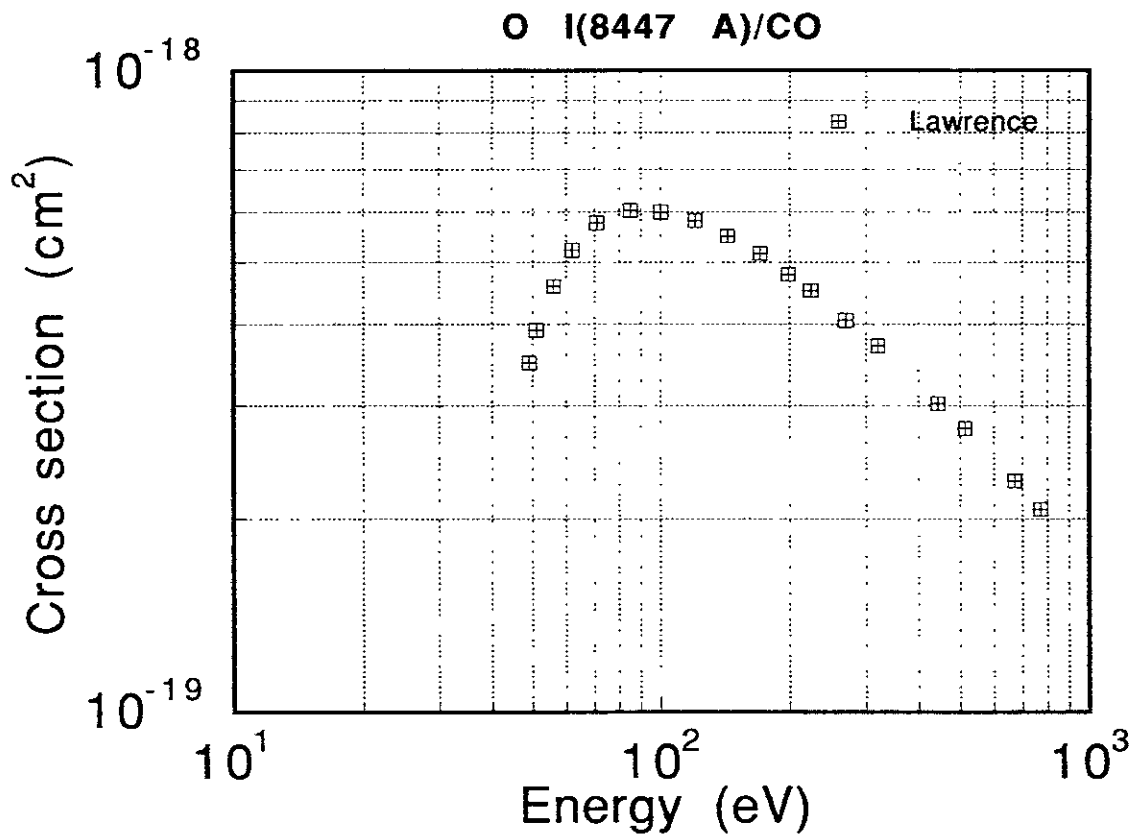


Fig.3.2.12 Cross sections for emission from O I (8447 A)
by electron impact on CO

Data from "C II (1335 A) of CO"

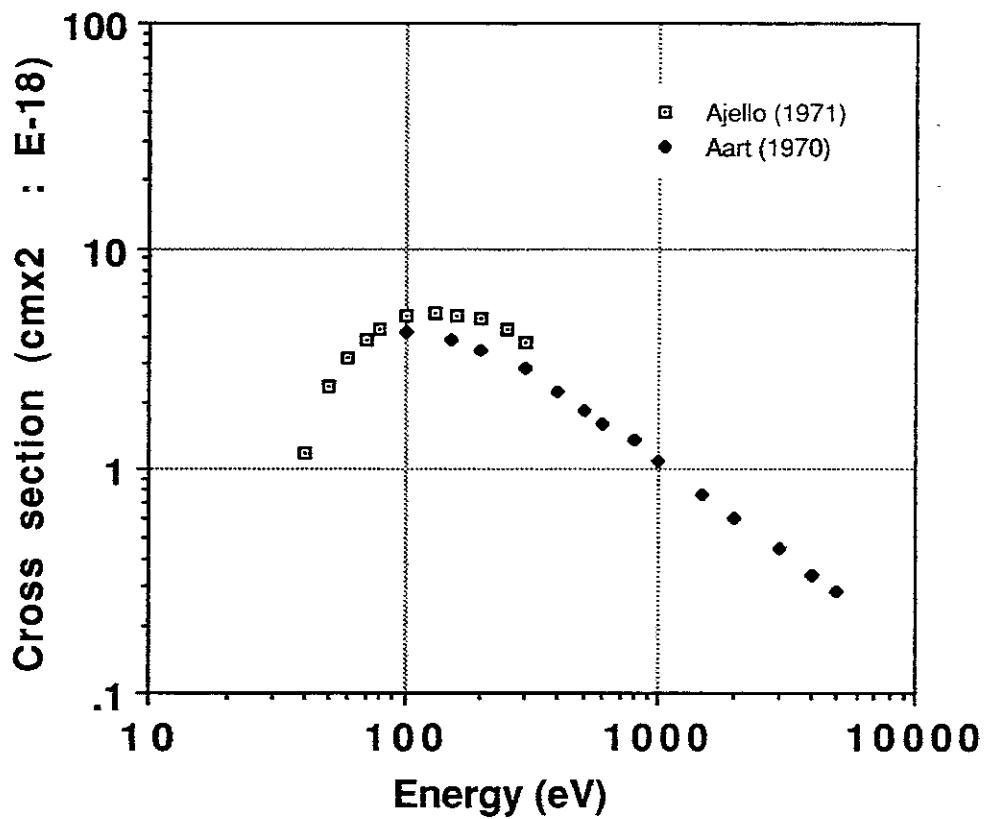


Fig.3.2.13 Cross sections for emission from C⁺ (1335 Å) by electron impact on CO

3.3 Energy distributions of dissociated particles of CO

The energy distributions of C^+ and O^+ ions near threshold have been investigated by Locht [1]. Some related observations have also been reported [2,3]. On the other hand, the energy of C^* atoms, observed through TOF method by Wells et al. [4], has been estimated to distribute over roughly 0.6-12 eV and those for O^* ions over 0.85-15.5 eV.

References

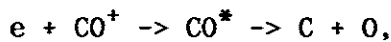
- [1] R. Locht, Chem. Phys. 22 (1977) 13
(energy distributions of C^+ and O^+ ions near threshold)
- [2] J.M. Curtis and R.K. Boyd, J. Chem. Phys. 80 (1984) 1150
(C^+ and O^+ ions from CO^{2+})
- [3] R.B. Kay, Ph.E. van der Leeuw and M.J. van der Wiel, J. Phys. B 12 (1977) 2521
(relative abundance of CO^+ , CO^{2+} , O^+ , C^+ , C^{2+} , O^{2+} after K-shell ionization)
- [4] W.C. Wells, W.L. Borst and E.C. Zipf, Phys. Rev. A 17 (1978) 1357
(translational energy spectroscopy for long-lived, Rydberg C^* , O^* atoms)

3.4 Collisions of CO⁺ ions with electrons

Most of recent measurements of the cross sections involving ions colliding with electrons are based upon crossed/merged electron-ion beam technique. Sometimes plasmas are also used to determine rate coefficients.

3.4.1 Dissociative recombination of CO⁺ ions

This process is represented as follows :

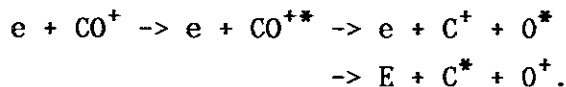


which should play a role in low temperature plasmas near edge region.

Mitchell et al.[1] used a merged beam technique to get absolute cross sections over 0.02-20 eV (c.m.) and found that the cross sections decrease roughly as 1/E over the energy range studied, as shown in Fig.3.4.1 (Note that their original values are divided by a factor of two).

3.4.2 Dissociative excitation of CO⁺

Similarly merged beam technique was used by Mitchell et al.[1] to determine sum of the cross sections for the following two processes over 0-50 eV :



The results (divided by a factor of two) are also shown in Fig.3.4.1.

It should be noted that the cross sections for these (three) processes are known to strongly depend upon their internal energy such as vibration/rotational states (Mitchell et al. in their experiment used ions from a radio-frequency ion source which is known to produce a significant fraction of ions in excited states).

Reference

J.B.A.Mitchell and H.Hus, J. Phys. B 18 (1985) 547 and private communication

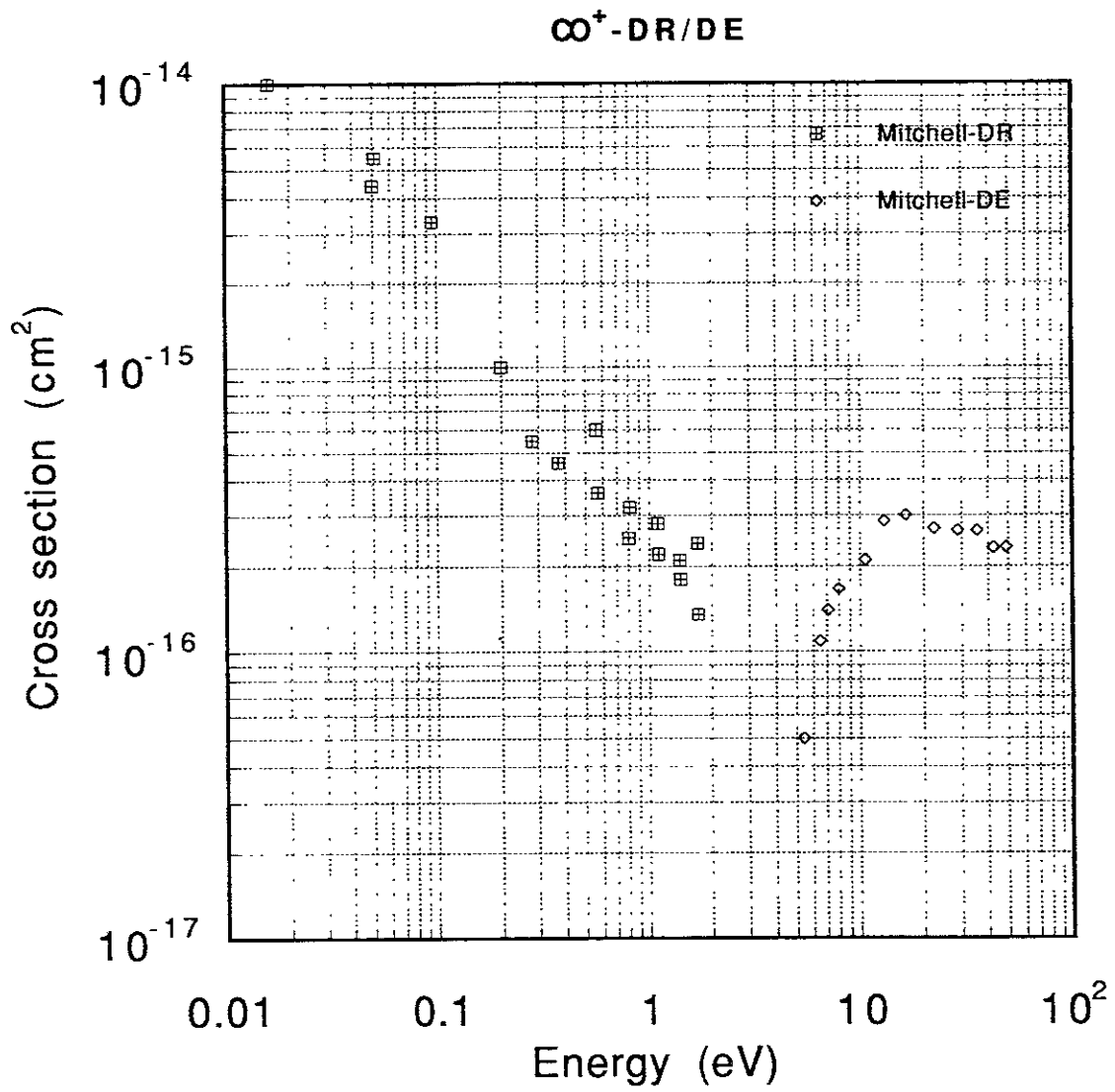


Fig.3.4.1 Cross sections for dissociative recombination (DR) and dissociative excitation (DE) of CO^+ by electron impact

4 Detailed data for CO₂

4.1 (Pure and dissociative) ionization cross sections of CO₂ by electron

Available data up to 1987 have been summarized by Lennon et al.[1].

In Table 4.1.1 are summarized some typical measurements and their features of the ionization cross sections of CO₂ by electron impact.

Table 4.1.1 Some features in typical experiments [2-9]

Author [reference]	technique	cross sections	absolute values /accuracy	problems
Rapp [2]	condenser plates	gross	absolute (±7%)	
Rapp [3]	condenser plates	partial	absolute (E>0.25 eV)	(mostly C ⁺ + O ⁺)
Adamczyk [4]	cycloidal mass	partial	normalized	q/m discrimination
Crowe [5]	Q-mass	partial	normalized	q/m discrimination
Märk [6]	double-focusing magnet	partial	relative to Ar (±10-20%)	q/m discrimination
Orient [7]	Q-mass	partial	normalized to Ar (±15%)	q/m discrimination
Freund [8]	crossed-beam	partial	absolute (±10%)	
Krishnakumar [9]	pulsed-e-beam + TOF	partial	normalized to Ar (±10%)	q/m discrimination

Results of some measurements of the cross sections are shown in Figs.4.1.1-4.1.2 which are taken mostly from compilation by Lennon et al.[1], with the addition of new recent results. Gross ionization cross sections seem to be in general agreement within a few % except for those by Craggs et al.[10] and Asundi et al.[11]. The recommended data for gross ionization cross sections are

shown with a bold line in Fig.4.1.1. Partial cross sections for other ion productions are not shown here because of large discrepancies (see ref.[1]). The cross sections of production of CO_2^+ ions from CO_2 gas are also generally in agreement with each other (within $\pm 20\%$). However, it should be noted that two recent measurements (one is based upon the pulsed electron beam technique and the other crossed-beam technique) are still in discrepancy.

General features of the observed results are very similar to those described already in H_2O and CO :

- a) Large scattering (roughly an order of magnitude) of the cross sections for production of ions from dissociative ionization such as C^+ , O^+ , CO^+ (due to large initial kinetic energy provided through dissociation, as mentioned already)
- b) Even the energy dependences are quite different among measurements.

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(also angular distributions measured for C^+ , O^+ , CO^+)
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- [10] J.D.Cragga and B.A.Tozer, Proc. Roy. Soc. A 254 (1960) 229
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e + CO₂ -> gross ionization

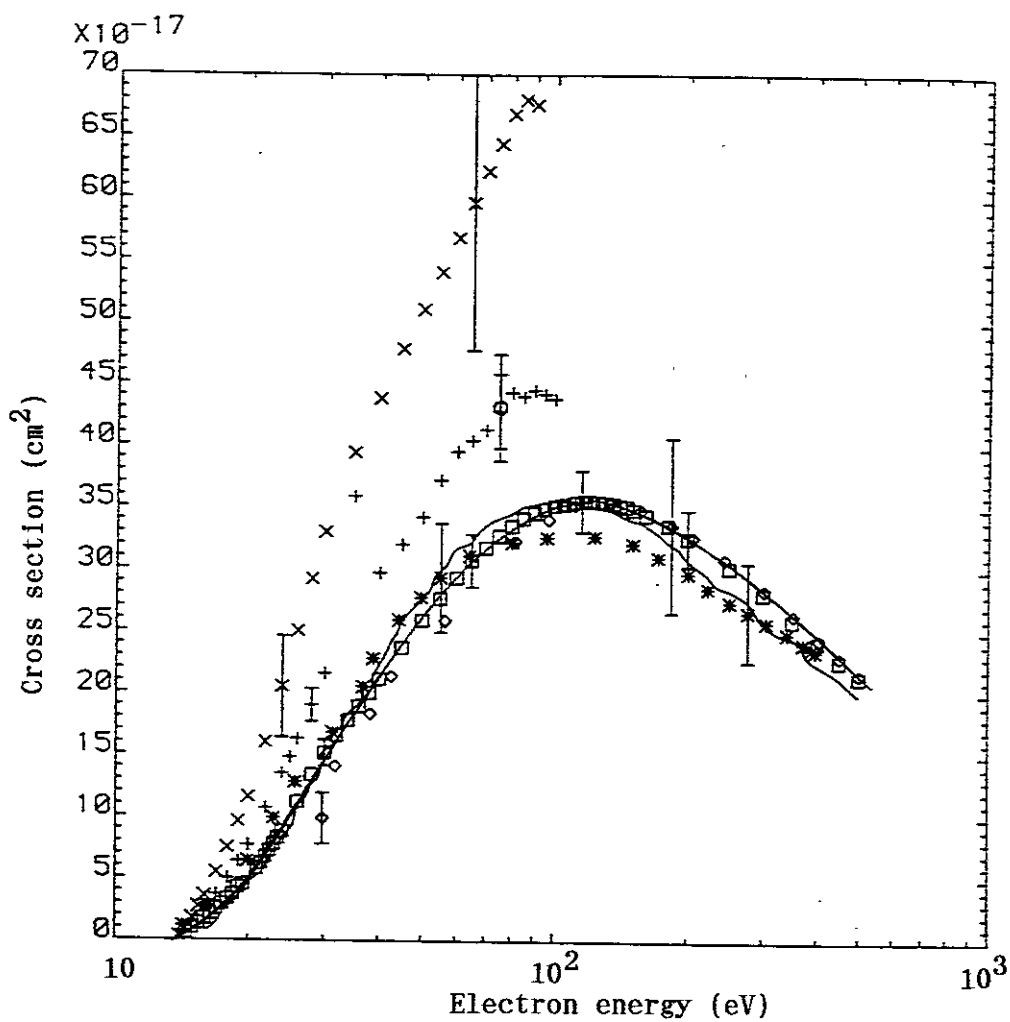


Fig.4.1.1 Gross ionization cross sections for CO₂ by electron impact (taken from a compilation of Lennon et al.[1])

- * Orient O.J. et al(1985)
- o Lampe F.W. et al(1957)
- ◊ Adamczyk B. et al(1972)
- ◻ Rapp D. et al(1965)
- Jain D.K. et al(1976)
- x Craggs J.D. et al(1960)
- + Asundi R.K. et al(1963)

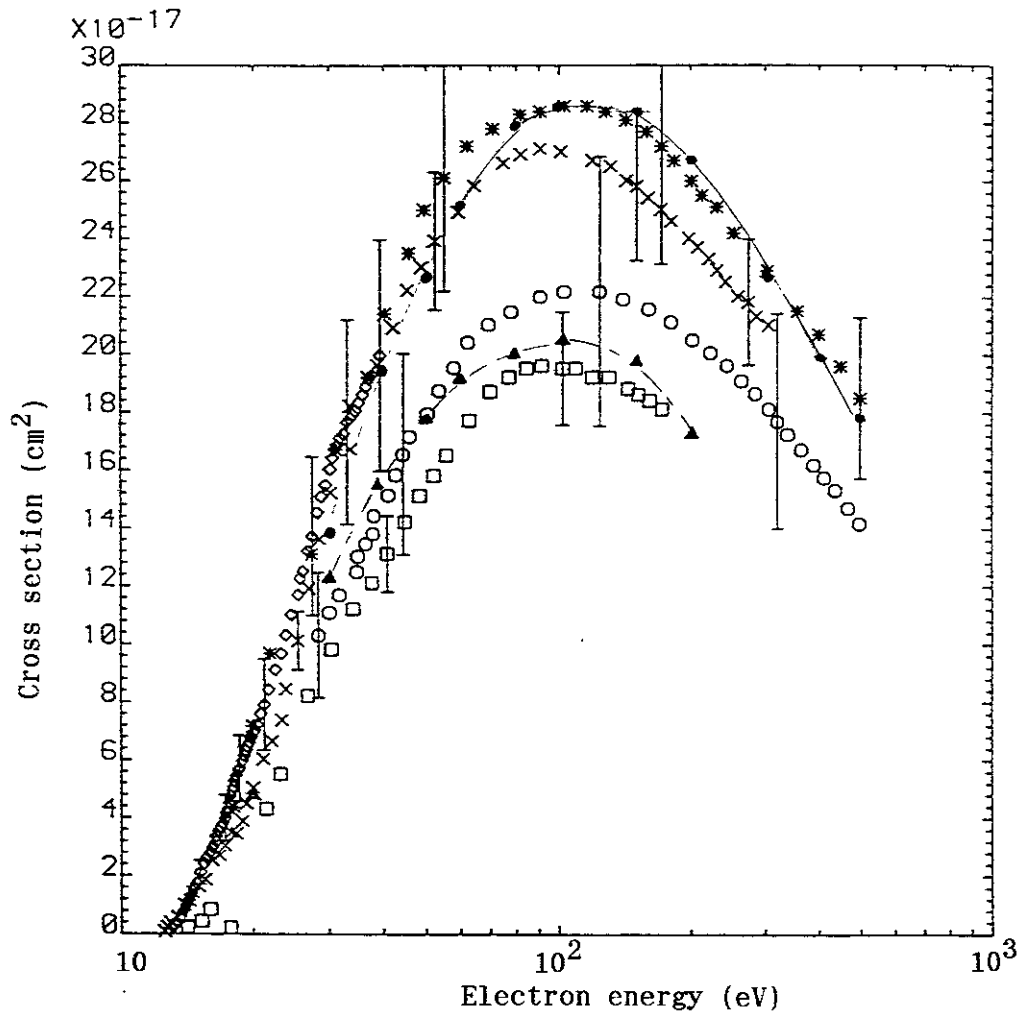


Fig.4.1.2 Partial cross sections for production of CO_2^+ from CO_2 by electron impact (taken from a compilation of Lennon et al.[1]), with some new results [8,9]

- * Orient O.J. et al(1985)
- o Adamczyk B. et al(1972)
- ◊ Cuthbert J. et al(1968)
- Mark T.D. et al(1978)
- x Crowe A. et al(1974)
- Krishnakumar (1990)
- ▲ Freund et al. (1990)

4.2 Excitation and photon emission cross sections from e + CO₂ collisions

Some relevant energy diagram of CO₂ and CO₂⁺ is shown in Fig.4.2.1.

4.2.1 Excitation cross sections

I) CO⁺

The cross sections for dissociative excitation to CO(A ¹Π : v=0-4) have been reported by Mumma et al.[1] up to 300 eV, as listed in Table 4.2.1, and those for v=0,1,2 and those for v=3,4 have practically the same size, respectively, though small variations are observed. In Fig.4.2.2 are shown typical data for v=0 and v=3.

Table 4.2.1 A list of investigations for dissociation excitation to CO(A ¹Π : v) from CO₂ by electron impact

Process	Energy(eV)	References	
a) A ¹ Π (v=0-4)	0-350	Mumma [1]	normalized to Lyman -α from H in e + H ₂

4.2.2 Photon emission cross sections

I) CO₂⁺

Table 4.2.2 shows a list of experimental investigations for band emission from CO₂⁺ ions. Three measurements [2,3,4] for (A ²Π-X ²Π) band seem to be in good agreement with each other at higher energies (note that those by McConkey et al.[2] are multiplied by a factor of two : see a foot note of Mentall et al.[5] and also have been supported by another measurement at 150 eV of Mentall et al.[5]. It is noted that the cross sections by Nishimura [6], if multiplied by a factor of 3 due to calibration errors, seem to agree with those above over 100-800 eV. Yet some discrepancies are clearly observed at lower energies, as seen in Fig.4.2.3. The situation seems to be similar for CO (B ²Σ-X ²Π). However, in particular, those for (B ²Σ-X ²Π) band, as shown in Fig.4.2.4, are in significant disagreement at low energies.

Table 4.2.2 A list of investigations on band emission from CO_2^+

Process	Energy(eV)	References	
a) A $^2\Pi \rightarrow X^2\Pi$ (2950-4500 A)	0-2000	McConkey [2]	summed over v,v'
	100-800	Nishimura [6]	summed over v,v'
	0-300	Ajello [3]	summed over v,v'
	0-400	Tsurubuchi [4]	summed over v,v'
b) B $^2\Sigma \rightarrow X^2\Pi$ (2880-2950 A)	0-2000	McConkey [2]	summed over v,v'
	100-800	Nishimura [6]	summed over v,v'
	0-300	Ajello [3]	summed over v,v'
	150	Mentall [5]	summed over v,v'
	0-400	Tsurubuchi [4]	summed over v,v'

II) CO^{++}

Only single measurement of the cross sections for CO^+ ($B^2\Sigma-X^2\Sigma$) band emission have been reported by Ajello [3] (see **Table 4.2.3** and **Fig.4.2.5**).

Table 4.2.3 A list of investigations for the band emission from CO^+ by electron impact on CO_2

Process	Energy(eV)	References	
a) B $^2\Sigma \rightarrow X^2\Sigma$ (2000-2500 A)	0-300	Ajello [3]	summed over v, v'

III) CO^*

Ajello [3] have determined the band emission cross sections for CO ($A^1\Pi-X^1\Sigma$), as shown in **Fig.4.2.6**. Also at 300 eV those for $v \rightarrow v'$ (0-1; 1-4; 2-2; 3-0; 4-0) have been reported by Mumma et al.[1]. The largest cross sections (0-1) among them are about 10 % (of the order of 10^{-19} cm^2) at 300 eV.

Relative cross sections by Ajello [3] for CO ($a^3\Pi-X^1\Sigma$ (0-1)) are renormalized to the absolute value at 80 eV newly measured by Erdman and Zipf [7] and also shown in **Fig.4.2.6**. The experimental situation is summarized in **Table 4.2.4**.

Table 4.2.4 A list of the investigations for emission from CO
by electron impact on CO₂

Process	Energy(eV)	References	
a1)A $1\Pi \rightarrow X 1\Sigma$	0-300	Ajello [3]	summed over v, v'
a2)A $1\Pi \rightarrow X 1\Sigma$ (v→v')	300	Mumma [1]	0-1/1-4/2-2/3-0/4-0
b1)a $3\Pi \rightarrow X 1\Sigma$ (0→1)	0-300	Ajello [3]	relative only
b2)a $3\Pi \rightarrow X 1\Sigma$ (0→1)	80	Erdman [7]	

IV) C*

The unresolved cross sections for C I multiplets (1278-80 A) by Ajello [3] are shown in Fig.4.2.7 (see Table 4.2.5).

Table 4.2.5 A list of investigations for C I line emission from CO₂

Process	Energy(eV)	References
a) $2p3d 3\Delta^0 \rightarrow 2p^2 3\Pi$ (1278 A)	0-300	Ajello [3]

V) O*

Ajello [3] determined the cross sections for line emission from O I(1304 A) up to 300 eV, as shown also in Fig.4.2.7. Also he reported relative cross sections for O I (1356 A), which are roughly of the same size as those for O I(1304 A). See Table 4.2.6.

Table 4.2.6 A list of investigations of line emission from O I

Process	Energy(eV)	References
a) $2p^3 3s 3\Sigma^0 \rightarrow 2p^4 3\Pi$ (1304 A)	0-300	Ajello [3]

VI) C⁺⁺

Only a single set of data for C II have been reported by Ajello [3] and shown also in Fig.4.2.7 (see Table 4.2.7).

Table 4.2.7 A list of investigations of line emission from C II

Process	Energy(eV)	References
a) $2s2p^3 \ ^2\Delta \rightarrow 2s^22p \ ^2\Pi$ 0-300 (1335 A)		Ajello [3]

Summaries of features of photon emission cross sections by electron impact on CO₂

- Excitation and CO/CO⁺ emission cross sections are found to be non-Franck-Condon v-distributions but dissociation-related.
- Smaller cross sections for excitation to CO* from CO₂, compared with those from CO ($\approx 1/20 \cdot CO$)
- Smaller cross sections for C⁺⁺ from CO₂, compared with those from CO ($1/10 \cdot CO$)

References

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(multiplied by a factor of 3 due to normalization factor : see a foot note of Mentall et al.)
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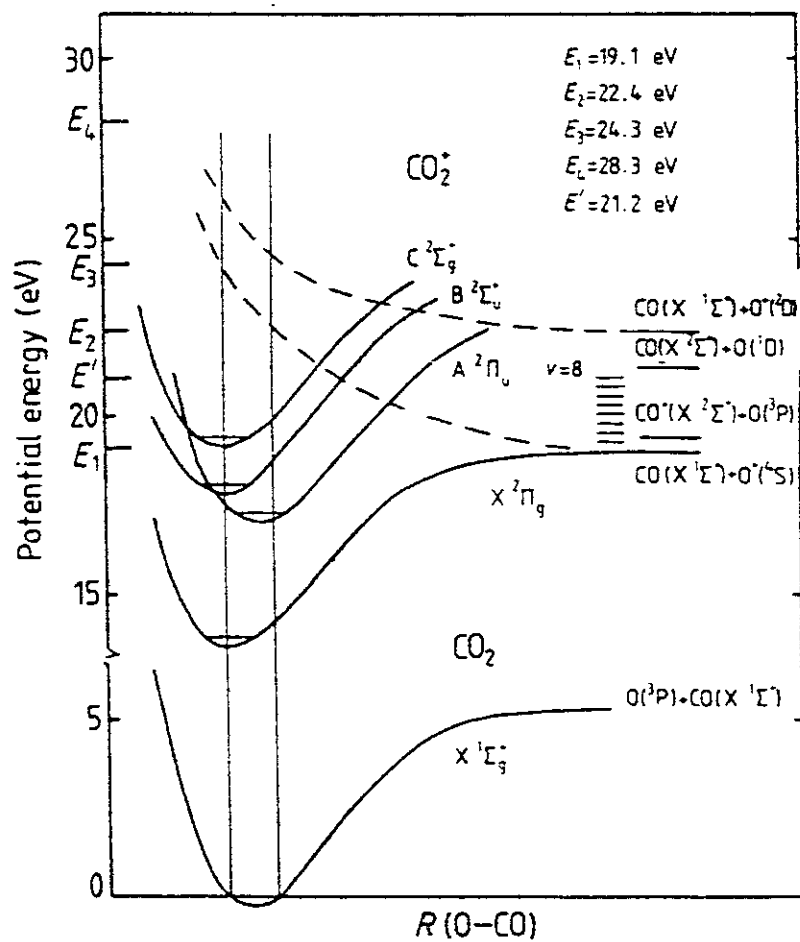


Fig.4.2.1 Relevant energy levels of CO_2 and CO_2^+

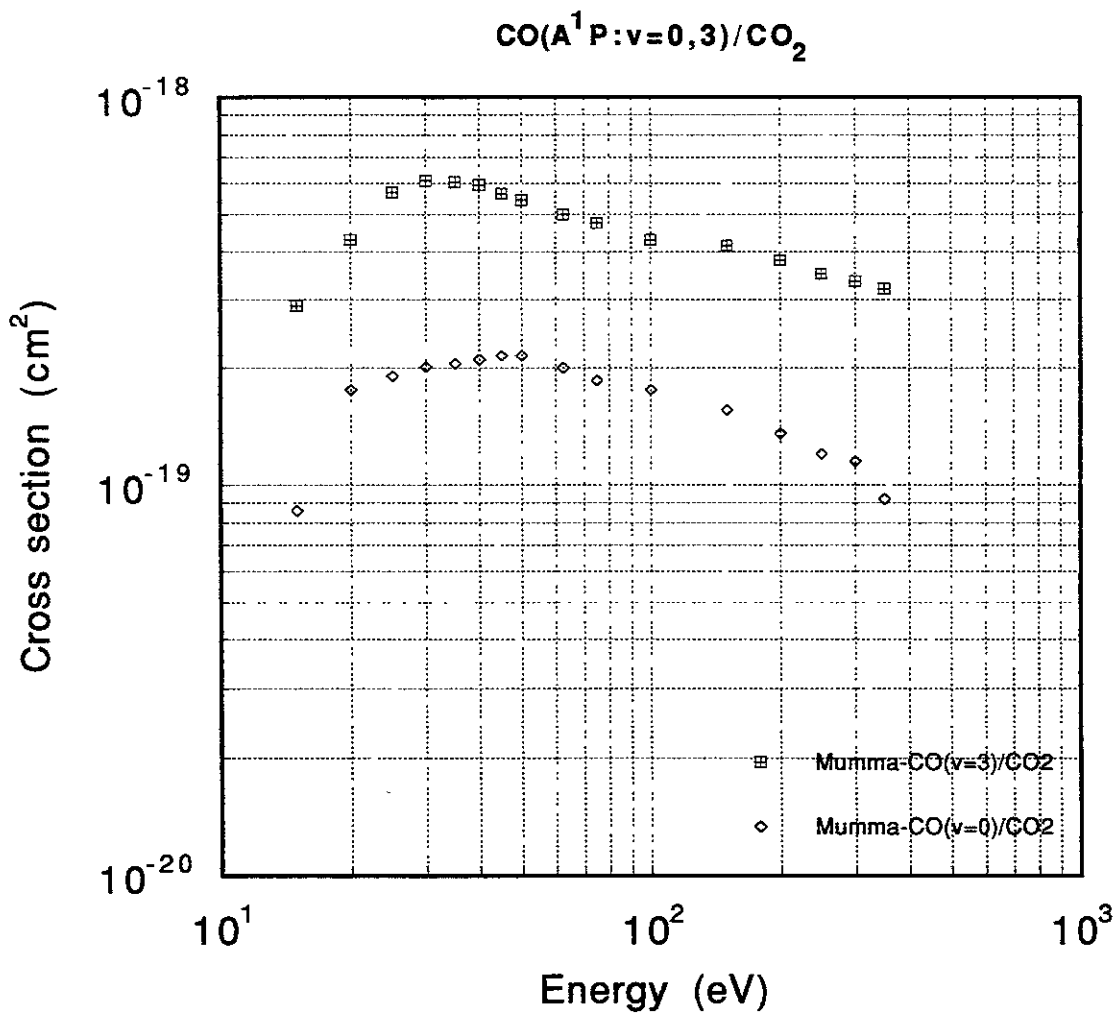


Fig.4.2.2 Cross sections for dissociative excitation to $\text{CO}(A^1\Pi : v=0,3)$ by electron impact on CO_2

Data from "CO2(+)(A 2P)"

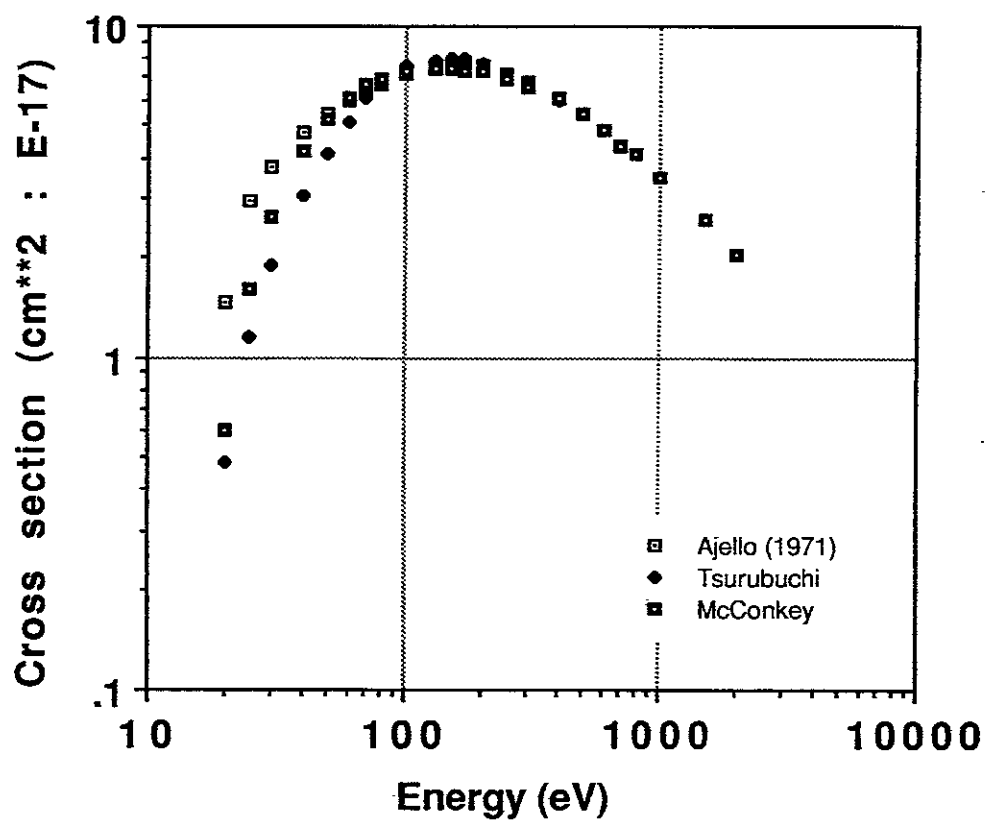


Fig.4.2.3 Cross sections for emission from $\text{CO}_2^+(\text{A } 2\text{P})$ by electron impact on CO_2

Data from "CO2(+)(B 2S)"

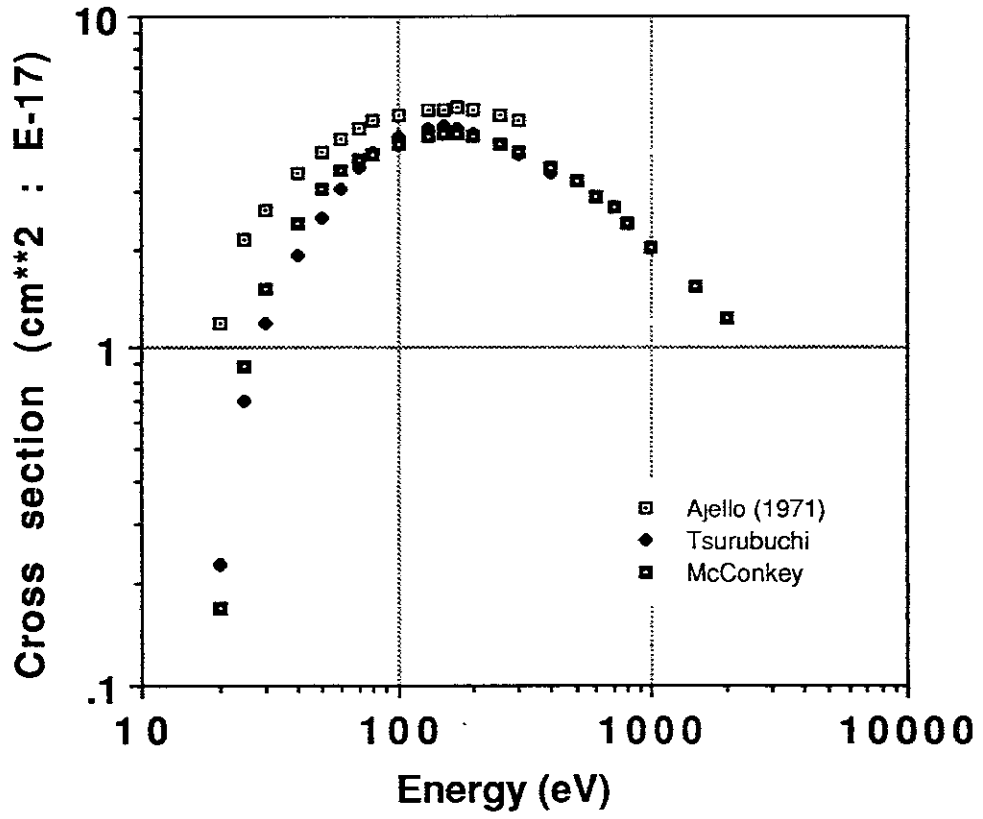


Fig.4.2.4 Cross sections for emission from $\text{CO}_2^+(\text{B } 2\Sigma-X 2\Pi)$ by electron impact on CO_2

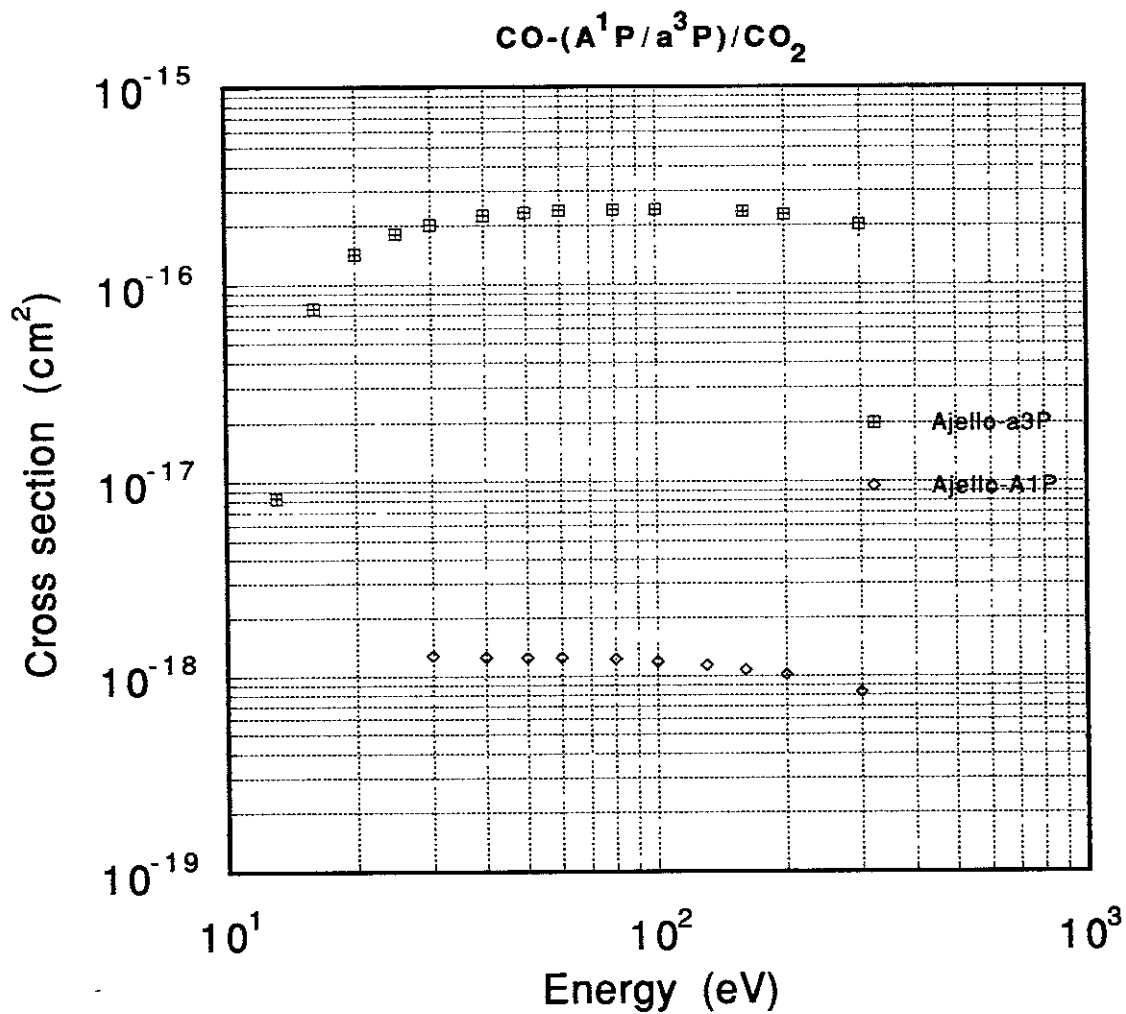


Fig.4.2.6 Cross sections for emission from CO(A ¹ Π -X ¹ Σ) and (a ³ Π -X ¹ Σ : v=0->1) by electron impact on CO₂

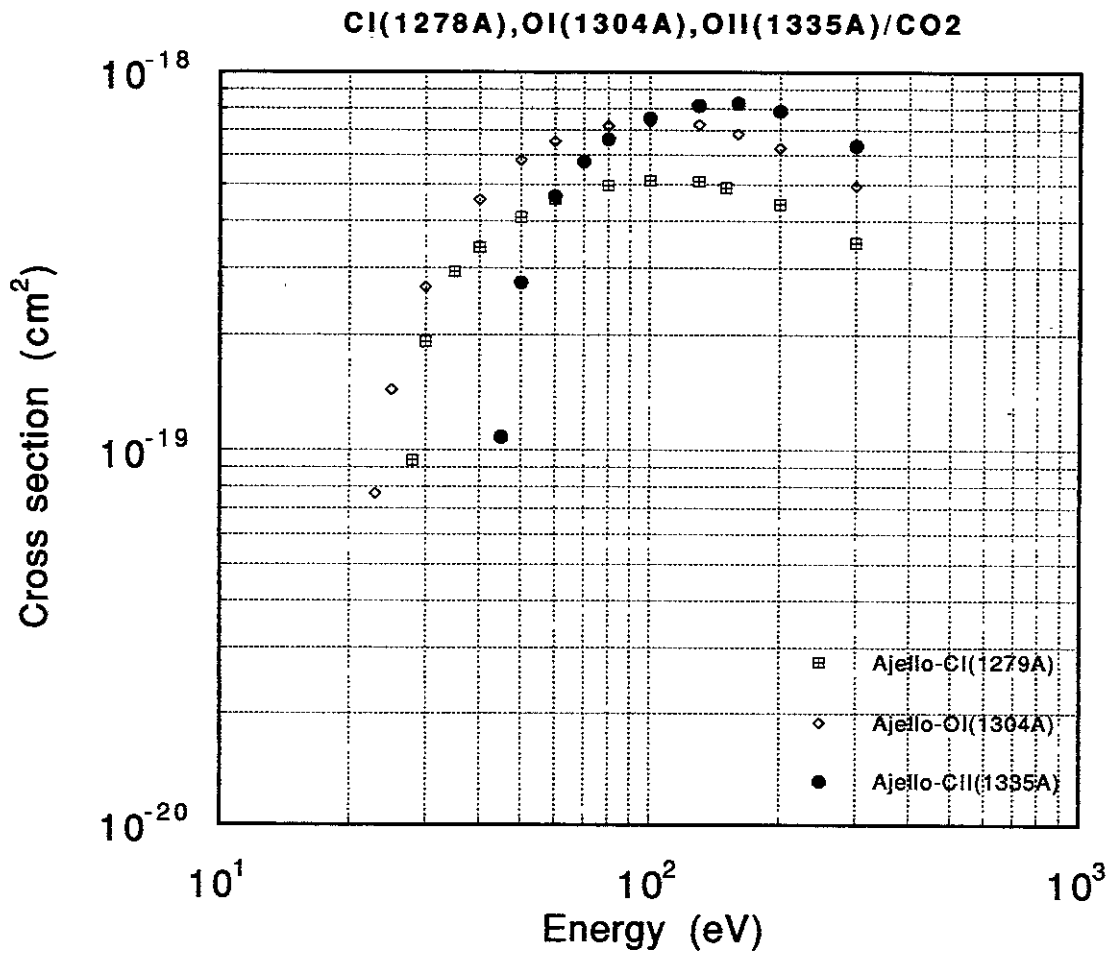


Fig.4.2.7 Cross sections for emission from C I, O I and O II lines by electron impact on CO_2

4.3 Energy and angular distributions of products

4.3.1 Energy distributions of neutral products

Because of difficulties of detecting slow neutral beams, few investigations have been reported so far. Wells et al. [1], using TOF method, have found that slow component of the metastable (a^3P) CO molecules produced in dissociative excitation of CO_2 has a mean energy of ~ 0.3 eV, roughly three times the thermal energy and also extracted the cross sections of $3.6 \cdot 10^{-17} \text{ cm}^2$ at 20 eV, which is much smaller than that by direct excitation of CO (see the above). Also a fast component consisting of the metastable $O(3s^5S)$ atoms, measured by TOF, have been observed by Freund [2]. However, quantitative information is still limited up to now.

References

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- [2] R.S.Freund, J. Chem. Phys. 55 (1971) 3569

4.3.2 Energy and angular distributions of ion products

The energy distributions of O^+ and CO^+ ions from CO_2 have been observed by Zhukov [1] who have found that several peaks ranging up to 10 and 5 eV region show up when the incident electron energy increases over 45-150 eV.

The angular distributions of O^+ , C^+ and CO^+ ions have been investigated by Crowe and McConkey [2] over 30-300 eV electron energy region. At low energies, the angular distributions show relatively large asymmetry but become isotropic at higher electron impact energy.

References

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- [2] A.Crowe and J.W.McConkey, J. Phys. B 7 (1974) 349

4.4 Dissociative recombination of CO_2^+

Only rates coefficients at 300 and 210 K for dissociative recombination have been determined to be $4 \cdot 10^{-7} \text{ cm}^3/\text{s}$ by Weller and Biondi [1].

Reference

[1] C.S.Weller and M.A.Biondi, Phys. Rev. Letters 19 (1967) 59

5 Concluding remarks

In the present paper we have reported the status of electron collision data involving H_2O , CO and CO_2 molecules, the most important impurities in plasmas, which is summarized in **Table 5.1** :

Table 5.1 Summaries of the present status of atomic and molecular data for H_2 , CO and CO_2 species under electron impact

species	H_2O	H_2O^+	H_3O^+	OH	CO	CO^+	CO_2	CO_2^+
total scattering	o				o		o	
momentum transfer	o				o		o	
elastic scattering	o				o		o	
rotation	x				x		x	
excitation vibrational	%				%		%	
electronic	x				x		x	
dissociation total	x		o		x		x	
partial								
photon emission	o				o		%	
ionization total	o				o		o	
partial	x				x		x	
recombination total		o	o			o		x
partial								

o : reliable

% : less reliable

x : not reliable

blank : not available

As seen in this table, the situation seems to be satisfactory only for a limited cases. Particularly partial cross sections, differential in product species, energy or angle, are often different by more than a factor of two and sometimes an order of magnitude among observations. Their collision energy

dependence also differs often. Important problems associated with such discrepancies in determination of the cross sections have been discussed. It should be stressed that recent technical developments could solve some of these discrepancies in principle.

As already mentioned, some data, in particular those for molecular species, have been found to strongly depend on their internal energies, namely the species are in rotationally, vibrationally or electronically excited states. Unfortunately, such investigations of electron collisions involving state-selected species are still very limited presently. On the other hand, in plasmas, the most species involved could be in their excited states, instead of the ground state as in most of laboratory experiments. In such cases, most of the collision cross sections are expected to be different significantly from those presently obtained in laboratory as the species should have quite different internal energies in both situations and thus great care should be exercised when laboratory data are used in plasma analysis and modelling.

It should be pointed out that, in addition to electron collisions, ion-molecule (chemical reaction) processes become quite important at low temperature plasma regions. Still data for such processes and reviews are limited (see a recent review [1]). It should be also mentioned that some ion-molecule collision processes also occur in space/astrophysical situations and some data can also be found in astrophysical journals [2].

The present author would like to thank Dr. H.Nishimura and Dr. S.Tsurubuchi for their useful comments and suggestions during this work and also Dr. M.Hayashi for providing some of his evaluated data for electron collisions given in section 1 (Fig.1.1.2 and Fig.1.1.3) prior to publication.

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