The dissociative electroionization of carbon dioxide by low-energy electron impact. The C^+, O^+ and CO^+ dissociation channels

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Abstract

This work reports the dissociative ionization of CO_2 between 19 and 40 eV. The three dissociation channels producing C^+, O^+ and CO^+ are examined in detail. Translational energy distributions as a function of the impinging electron energy and the ionization efficiency for fixed minimum kinetic energy carried by the fragments are measured. The kinetic energy versus appearance energy diagram is obtained for the three fragment ions. When available, the present results are compared with previous measurements. The lowest appearance energy of O^+ and CO^+ corresponds to the predissocia-tion of the CO_2^+ ($C^2\Sigma_g^+$) state. At higher energies, *all the fragment ions* are exclusively produced by the dissociative ionization of CO_2 in the multiple electron transition (MET) states. Predissociation is most probably the dominant mechanism. Each MET state branches off to produce not only the three fragments, but also the same fragment in two different states. This is observed for each dissociation channel, i.e. O^+, CO^+ and/or C^+. In the latter channel *no evidence* is found for the dissociative ionization reaction $CO_2^+ \rightarrow C^+ + 2O$.

Keywords: Carbon dioxide; Dissociation; Electron impact; Ionization; Kinetic energy

1. Introduction

The present work is in keeping with our thorough and systematic dissociative electroionization study of simple molecular systems. Results on the appearance energies of ionic fragments as a function of their translational energy are presented for the C^+, O^+ and CO^+ ions produced by low-energy electron impact dissociative ionization of CO_2. The dissociative ionization study in all its dissociation channels of N_2O, the isoelectronic species of CO_2, for example, has been presented in previous publications [1].

Owing to its major importance in many fields, the CO_2 molecule has been investigated by almost all the spectroscopic techniques available today, in the microwave to X-ray energy range. However, much less attention has been paid to the unimolecular decomposition of this molecule and its molecular ion.

In the early 1970s, and during the following decade, great interest arose related to environmental problems and to new spacecraft observations of CO emissions from the upper atmosphere of Mars [2,3]. The $CO(A^1\Pi-X^1\Sigma)$ and $O(^3S)$ emissions were investigated in the laboratory [4]. At about the same time the dissociative photoionization of CO_2 was actively investigated by several groups [5-11]. These investigations were mostly performed without any translational energy analysis of the ionic fragments [5-8].

The development of the photoion-photo-electron coincidence (PIPECO) and threshold photoelectron-photoion coincidence (TPE-PICO) [9-11] techniques made it possible to examine with high accuracy the dissociative photoionization processes. These techniques were successfully applied to the investigation of the ionization and the unimolecular decomposition of CO_2 in the O^+ and CO^+ dissociation channels. Appearance energies were determined and ion translational energy distributions were derived from time-of-flight (TOF) measurements, and dissociative ionization processes were discussed in great detail. However, the C^+ ion was not considered and these studies were restricted to the energy range limited by the He(I) resonance line.

The dissociative excitation and ionization by electron and ion impact have also been investigated. The production of metastable neutral fragments following electron impact has been studied in the O* reaction coordinate [12,13]. This species could be in a high Rydberg (HR) state. Translational energy distributions are derived from TOF measurements. Threshold energies are determined from the excitation functions. The abundance of translational energy versus appearance energy diagrams has allowed the authors to disentangle

a complex superposition of numerous processes [12,13]. Electron energy loss spectroscopy and electron-ion coincidence measurements have been performed [14]. Photofragmentation oscillator strengths in the C^+, O^+ and CO^+ channels were determined in the valence-shell ionization region.

The dissociative ionization of CO_2 by heavy ion impact (H^+, He^+ and O^+) has been investigated, producing C^+, O^+, CO^+, C^{2+} and O^{2+}. Ion translational energies have been reported [15].

The dissociative electroionization of CO_2 has been investigated by several groups [16-22]. Most of these investigations were performed with ion translational energy analysis. Bussières and Marmet [19] used a monochromatized electron beam to investigate CO_2^+ and all the fragment ions. Only threshold energies were determined and no ion kinetic energy was measured. In contrast, the other works [16-18,20-22] dedicated to the dissociative ionization of CO_2, including ion translational energy analysis, investigated the O^+ channel [16,17], the C^+ channel [17] and/or the CO^+ channel [20,22].

Owing to the high sensivity of the instrument used, the reasonable efficiency of our data handling (by recording systematically the first differentiated ionization efficiency curves) and the good energy resolution of the ion translational energy analyzer (of the order of 80 meV), we are able to report the results of a detailed study of the dissociative ionization of CO_2 in its *three* dissociation channels. The double ionization of CO_2 and its dissociation, investigated by electron impact and mass spectrometric photoionization, have already been reported [23].

2. Experimental

The experimental setup used in the present study has been described previously [24]. Only the prominent features will be mentioned here.

The ions produced in a Nier-type ion source by the impact of energy-controlled electrons are allowed to drift out of the ion chamber, focussed on the ion source exit hole, and energy-analyzed with a retarding lens and mass-selected in a quadrupole mass spectrometer. The ion current, collected on a 17-stage Cu-Be electron multiplier, is continuously scanned as a function of either the electron energy at fixed retarding potential settings V_R or the retarding potential at fixed impinging electron energies E_e. Both signals are *electronically differentiated*. The whole experiment is interfaced with a minicomputer [25] responsible for controlling the most important experimental parameters and storing the data.

The carbon dioxide sample, purchased from Messer Griesheim and of 99.995% purity, was used without further purification.

Great care was taken to keep the background mass spectrum as low as possible. The O^+ and CO^+ ions from CO_2 interfered with the O^+ ion from O_2 and the N_2^+ from N_2 respectively. Therefore, prolonged bake-out of the vacuum chamber was regularly performed to keep the residual pressure at about 2×10^{-8} Torr. The sample was introduced at a pressure in the vacuum vessel of about 10^{-7} Torr, i.e. about 2×10^{-6} Torr in the ion chamber, to avoid any collision-induced processes.

The maximum of the CO_2^+ ion energy distribution was used as the zero-energy calibration point for the ion translational energy scale. The same reference was used during the recording of the ionization efficiency curves of the fragment ions at different retarding potential settings.

For the electron energy scale calibration the first ionization energy of Ne at 21.564 eV [26] was used for the investigation of O^+/CO_2. The first differentiated ionization efficiency curve of this ion, characterized by a drastic increase at the threshold, was shown to be appropriate for further use as an internal standard for the investigation of C^+ and CO^+. The linear extrapolation method, as described previously [24], was used to determine the threshold energies.

3. Data acquisition and handling. Error estimation

For each fragment ion, at each retarding potential or electron energy setting, the first differentiated

ionization efficiency or retarding potential curve was recorded and averaged over 8-75 h (100-1200 scans), depending on the ion intensity and the range to be scanned. This procedure was repeated at least five times to ensure reproducibility and to allow estimatation of the error in threshold energy determinations. The curves represented in the following sections are *averaged* curves of at least five independent measurements. The quoted errors and error bars consequently represent *one standard deviation.*

In the ion kinetic energy (KE) versus appearance energy (AE) diagrams, linear regressions were fitted to the data. This method provides two parameters, important in this work, i.e. (i) the *extrapolation to zero kinetic energy,* related to the level of the dissociation limit involved and (ii) the *slope of the straight line,* related to the dynamics of the considered dissociation. The correlation coefficient, usually calculated on the linear regression, provided an *estimation* of the validity of the fit. It by no means gave an estimate of the error on the two parameters of the straight line.

Fig. 1. *Translational energy distribution curves of O^+ from CO2 as measured at indicated electron energies E_e ranging from 19 to 99 eV.*
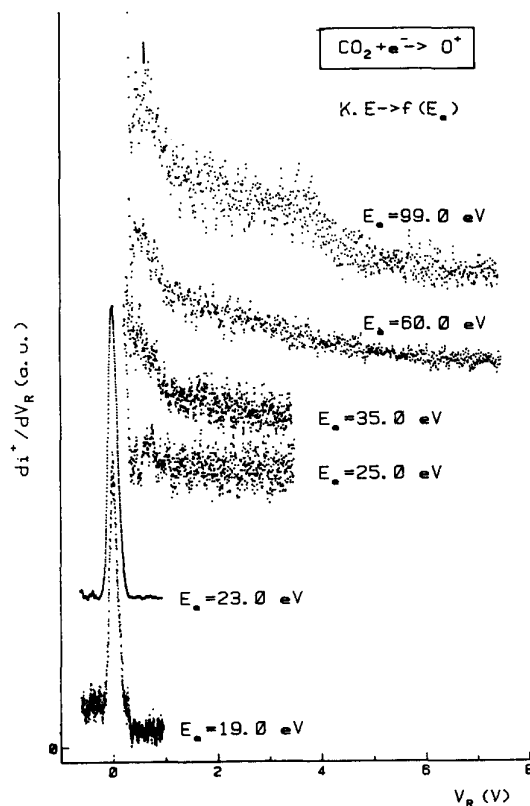
Recently, a method has been described to calculate the error in the slope and the extrapolation [27]. On the basis of a few assumptions, usually met by the present data, and defining the correlation coefficient "r" by

$$r = \sum_{i=1}^{n}(y_i - \overline{y}_i)(x_i - \overline{x}_i) \Big/ \left[\sum_{i=1}^{n}(y_i - \overline{y}_i)^2(x_i - \overline{x}_i)^2\right]^{1/2}$$

for the fit of the linear regression

$$\overline{y} = a\overline{x} + b$$

to the experimental data, it has been proved that the standard deviations σ_a of the slope "α" and σ_b of the extrapolation "b" are given by the expressions

$$\sigma_a = \frac{|a|}{(n-2)^{1/2}} \left(\frac{1}{r^2} - 1 \right)^{1/2}$$

$$\sigma_b = \sigma_a \left(\frac{\sum_{i=1}^{n} x_i^2}{n} \right)^{1/2}$$

To compare experimental and expected values of a and b with a confidence limit fixed at 95%, the Student significance test is used, i.e.

$$a_{\text{comp.}} = a_{\text{lin.regr.}} \pm F(t)\sigma_a$$

$$b_{\text{comp.}} = b_{\text{lin.regr.}} \pm F(t)\sigma_b$$

where $F(t)$ is tabulated [28] as a function of n -2 degrees of freedom of the linear regression.

Fig. 2. *First differentiated ionization efficiency curves of O^+ from CO_2 as recorded at indicated retarding potential settings V_R ranging from 0.0 to 5.5 V. Vertical bars locate the average value of the threshold energies.*
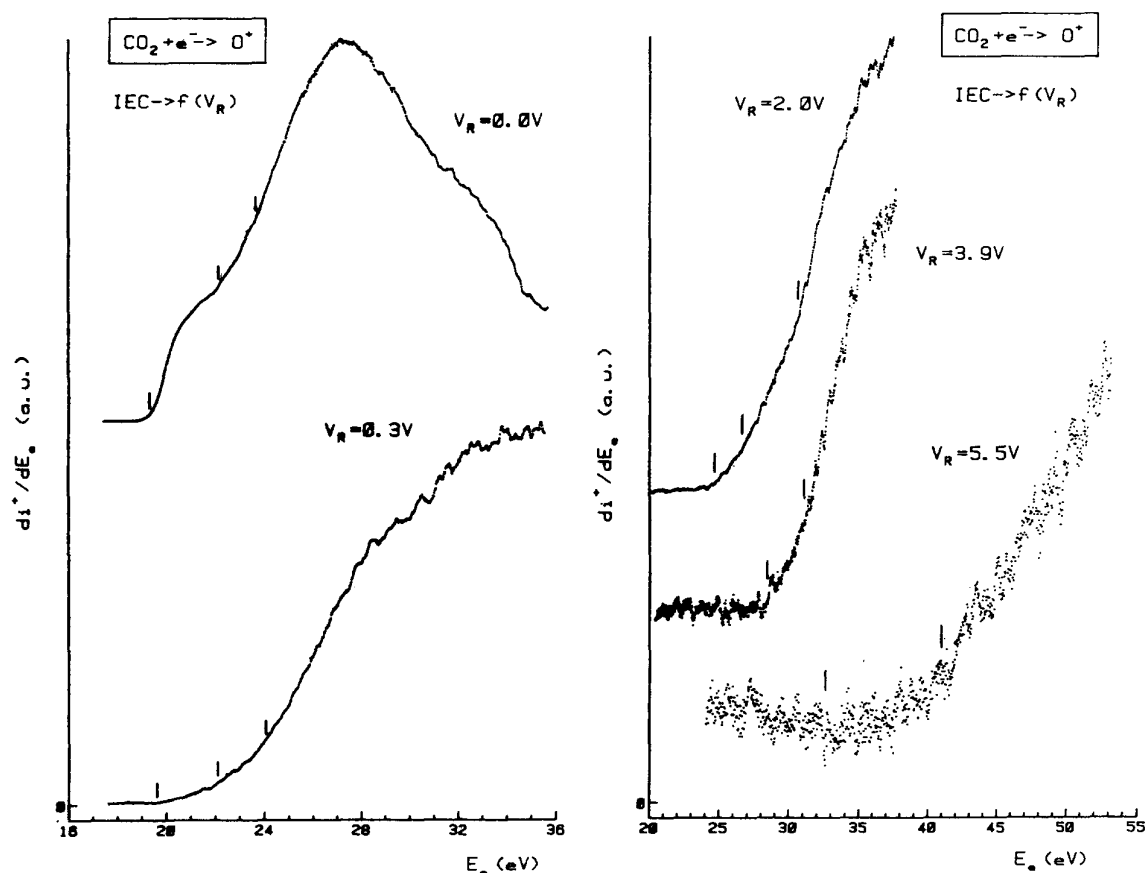

4. Experimental results

4.1. The O^+ dissociation channel

The O^+ *ion translational energy distribution,* as observed at different impinging electron energies, is represented in Fig. 1 in the range of 19-99 eV. Very close to the O^+ ion appearance energy, the ion energy

distribution has a shape similar to the thermal CO_2^+ ion peak. Above 25 eV electron energy, and with increasing intensity due to increasing electron energy, a weak distribution peaks at 0.7 eV ion energy. At 99 eV, a broad distribution is observed with a maximum at about 4.0 eV and spreading up to 8 eV ion energy.

The first differentiated ionization efficiency curve of O^+/CO_2 was recorded for increasing retarding potential settings, scanned from 0.0 to 6.0 V in steps of 0.1 V and 0.2 V. Fig. 2 shows a sample of averaged curves (see Section 3) as observed at the indicated V_R settings from 0.0 to 5.5 eV ion translational energy. The vertical bars indicate the threshold energies. This figure also clearly shows how the first differentiated ionization efficiency drastically changes by varying the retarding field over a fairly narrow range. In the present case, it should indicate a large contribution of O^+ ions to the ionization efficiency carrying less than 0.3 eV kinetic energy. As mentioned in Section 2, the first onset energy of $O^+/CO2$ was used as an internal standard for the appearance energy measurements of CO^+ and C^+. For this purpose, the ionization energy of Ne was used for calibration [26]. The 50 measurements made for this ion provided an appearance energy of 19.40 ± 0.08 eV. At higher electron energy, onsets are observed at 22.21 ± 0.03 eV and 23.63 ±0.10 eV. Maxima, which could probably be attributed to broad resonance phenomena, are observed at about 27 eV and 32 eV.

Fig. 3. *KE versus AE diagram related to the O^+-producing channel from CO_2 between 18 and 34 eV electron energy. Straight lines are provided by linear regression. Encircled numbers refer to the corresponding processes discussed in the text.*
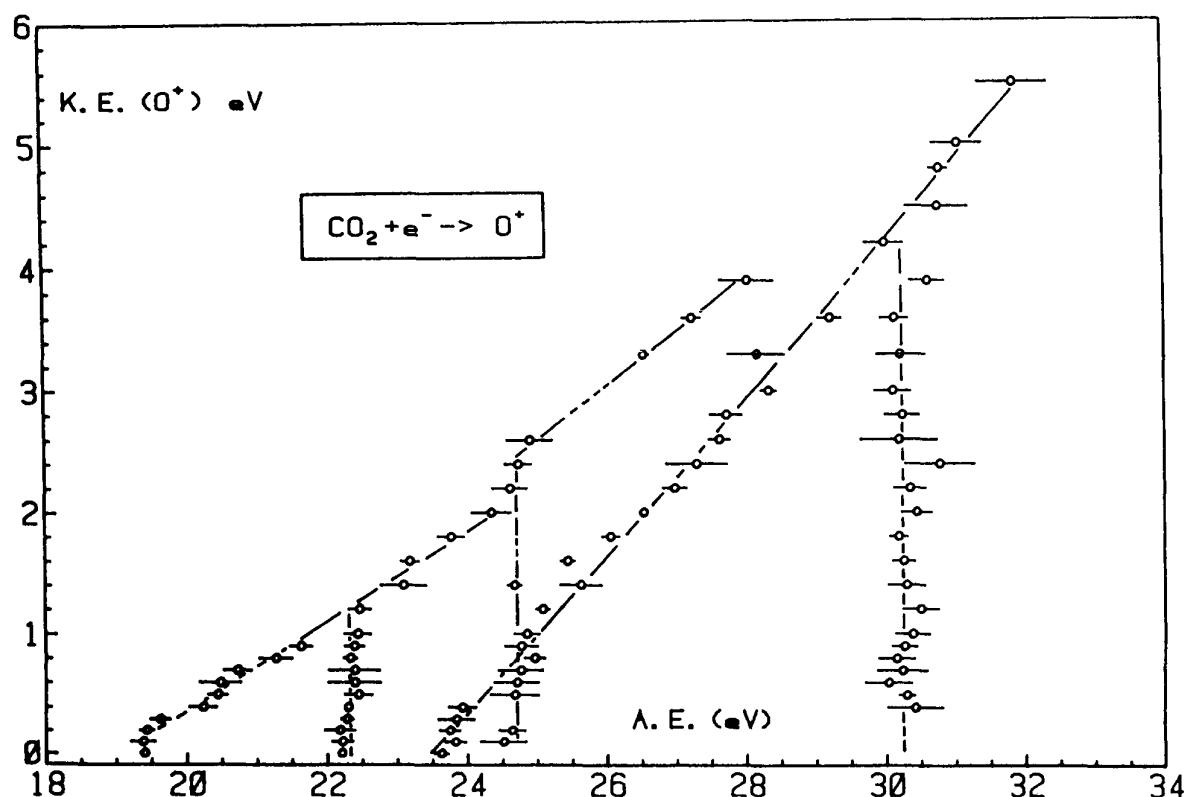

The KE versus AE diagram of O^+/CO_2 was obtained by plotting the threshold energies as a function of the calibrated retarding potential, and is given in Fig. 3. This diagram clearly shows three straight lines, characterized by different slope values and corresponding to different dissociation processes. Four vertical lines have to be mentioned which can be characterized by an average position calculated by taking into account all the measurements, i.e. at 19.40 ±0.03 eV, 22.21 ± 0.03 eV, 24.74 ± 0.10 eV and 30.32 ± 0.20 eV.

The present results can be compared with those of Appell et al. [16] and by Ehrhardt and Kresling [17].

In spite of the absence of error estimates in most of the experimental results, the agreement between these two works and the present experiment is quite satisfactory at low electron energy. At high excitation energy, the latter authors [17] mention two onsets, i.e. at 28.3 ± 0.3 eV and at 33.9 ± 0.3 eV, whereas only a threshold at 30.32 ± 0.20 eV is observed in the present work. Appell et al. [16] do not mention onset energies above 24.6 ± 0.3 eV.

Dissociative excitation experiments and dissociative ionization experiments can be linked through the "core-ion" model [29]. Results for O* (HR) species have been reported [12,13,30]. At low electron impact energy, the dissociative excitation results correlate well with the present dissociative ionization data. This would mean that the core-ion model holds in the the present case.

Fig. 4. *Translational energy distribution curves of CO^+ from CO_2 as measured at indicated electron energies E_e ranging from 20 to 99 eV.*
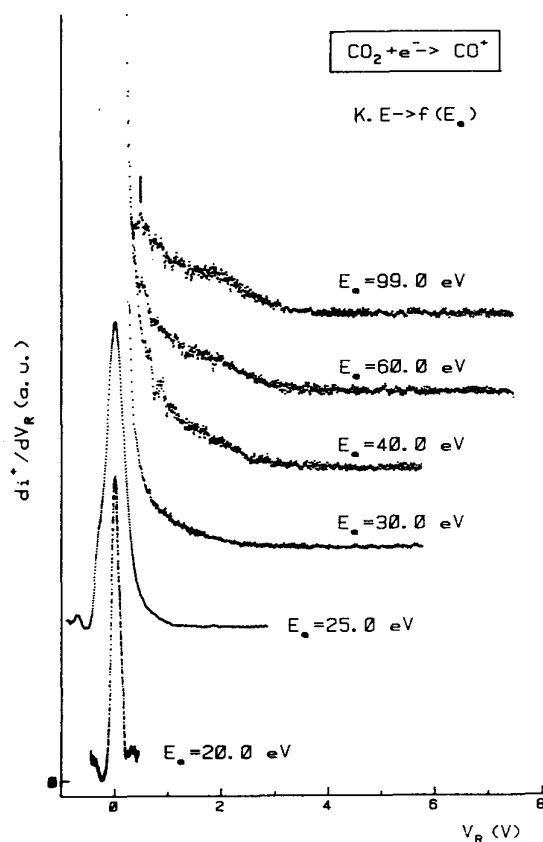
4.2. The CO^+ dissociation channel

The CO^+ ion kinetic energy distributions have been measured with increasing electron energy. Typical distributions are represented in Fig. 4 for indicated impinging electron energies. Close to the onset the CO^+ ion energy distribution appears to be nearly thermal, whereas at 25 eV this distribution is considerably broadened with a tail extending up to about 1.0 eV ion energy. Above 40 eV electron energy, a peak at 0.5 eV and a second structure at 2.0 eV become visible. Their intensities continuously increase with increasing electron energy. The CO^+ ion energy distribution extends to about 4 eV for 99 eV electron energy.

A sample of first differentiated ionization efficiency curves of CO^+ is shown in Fig. 5. These curves were recorded for V_R settings between 0.0 and 3.5 V in steps of 0.1 V and 0.2 V. The shape of the curve obtained without applying a retarding field to the ion beam is very similar to that of the O^+ ionization efficiency curve (see Fig. 2). A maximum is observed at 28 eV and a shoulder at about 32 eV. Also, in the present case, the application of a retarding field to the CO^+ beam strongly modified the shape of the first differentiated ionization efficiency curve. The vertical bars in Fig. 5 indicate the threshold energies, i.e. 19.54 ± 0.04 eV, 22.18 ± 0.12 eV

and 23.78 ± 0.26 eV.

Notwithstanding the precautions maintained during the experiment, some confusion could be suspected between CO^+ and N_2^+, the latter always being present to a certain extent in the background. However, the ionization energy of N_2 is 15.756 eV and no ion signal was detected below 19.5 eV. Further, from a retarding potential setting of 0.05 V, the N_2^+ purely thermal ion signal was shown to be quantitatively suppressed, and would no longer interfere with the CO^+/CO_2 beam.

Plotting the CO^+ KE versus its AE gave rise to the diagram shown in Fig. 6. Several straight lines, obtained by linear regression, with different slopes can be observed. Vertical lines were drawn at 22.18 ± 0.06 eV, 23.90 ± 0.08 eV, 26.10 ± 0.13 eV and 30.40 ± 0.26 eV.

The diagram reproduced in Fig. 6 can only be compared with the work reported by Armenante et al. [20]. These authors measured the ion translational energy by the TOF technique. The appearance energies were measured between 22 and 50 eV electron energy for CO^+ ions carrying between 0.0 and 3.2 eV kinetic energy. Surprisingly, no threshold was observed below 22.2 eV. Linear regressions were fitted to the experimental data, but no errors were estimated.

Fig. 5. *First differentiated ionization efficiency curves of CO^+ from CO_2 as recorded at indicated retarding potential settings V_R ranging from 0.0 to 2.8 V. Vertical bars locate the average value of the threshold energies.*
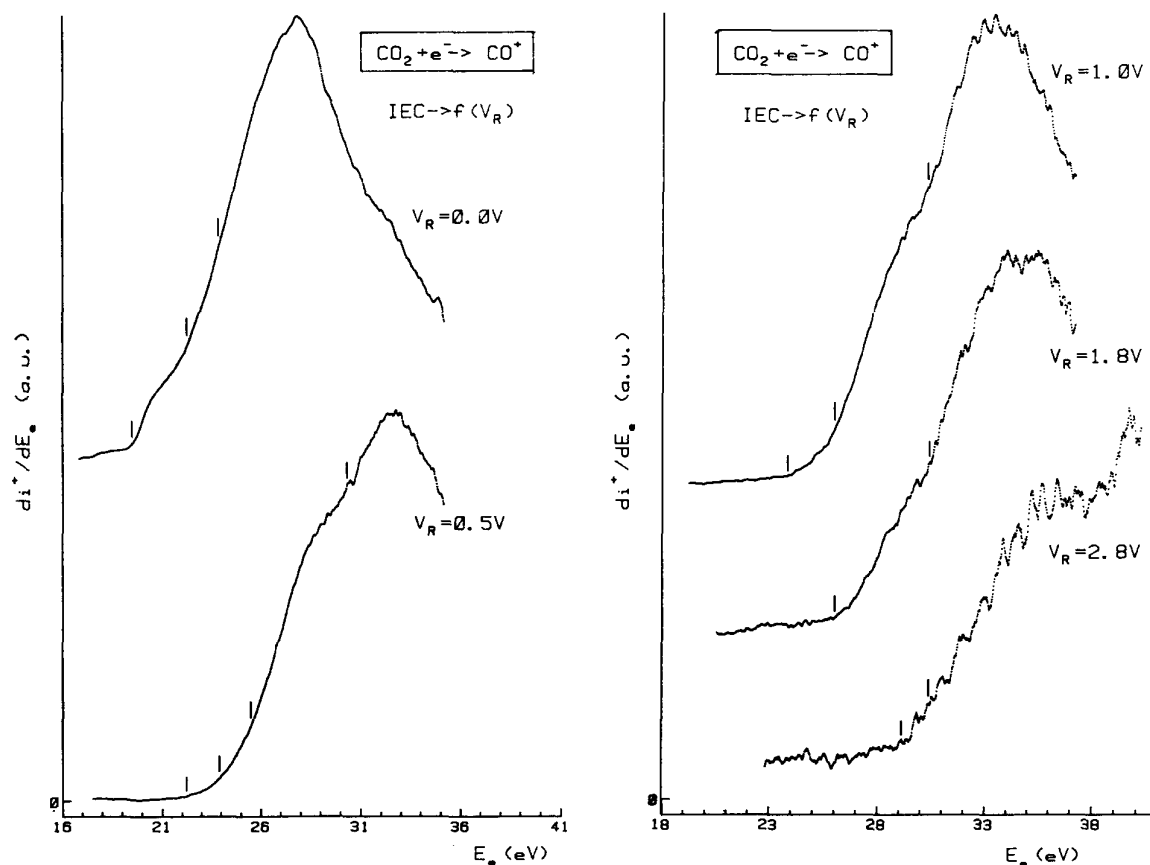

4.3. The C^+ dissociation channel

The C^+ ion kinetic energy distribution was measured for electron energies ranging from 25 to 99 eV. A sample of these distributions is displayed in Fig. 7. In spite of an unfavourable signal-to-noise ratio, the distribution observed at 25 eV electron energy looks fairly narrow and is characterized by a FWHM of 200 meV at the most. For 28 eV electron energy, the distribution is broadened and a weak tail is visible. For electron

energies above 32 eV and up to 99 eV, several new contributions become visible at e.g. 0.5 eV, 1.0 eV and around 1.2 eV for electron energies above 66 eV. It is noteworthy that the low-energy peak at around 0.0 eV broadens continuously with increasing electron energy. This suggests that low-energy C^+ contributions are produced, even at fairly high excitation energies.

Fig. 6. *KE versus AE diagram related to the CO^+-producing channel from CO_2 between 18 and 32 eV electron energy. Straight lines are provided by linear regression. Encircled numbers refer to the corresponding processes discussed in the text.*
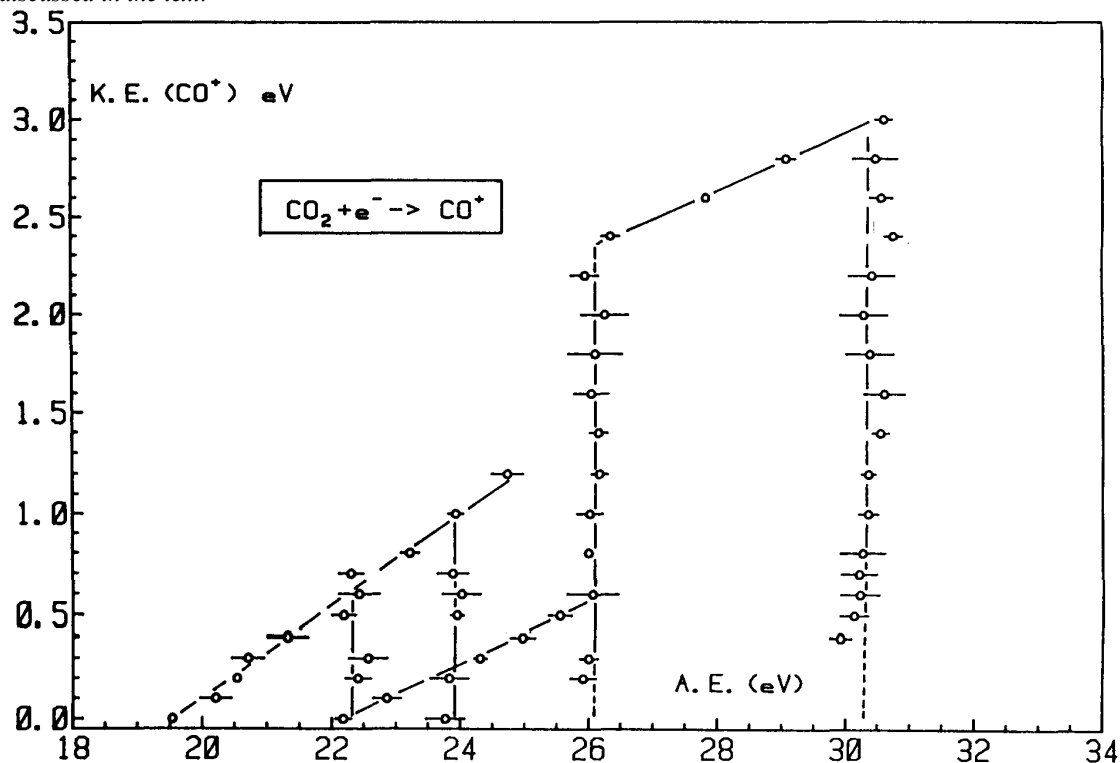
The first differentiated ionization efficiency curves of C^+ as observed for different retarding potential settings are reproduced in Fig. 8. The vertical bars locate the threshold energies. For the retarding potential setting $V_R = 0.0$ V, appearance energies are measured at 23.04 ± 0.04 eV, 25.31 ± 0.08 eV, 26.90 ± 0.09 eV, 28.31 ± 0.02 eV, 29.18 ± 0.17 eV and 31.03 ± 0.16 eV.

The KE versus AE diagram relating to C^+ ion formation is shown in Fig. 9, and clearly shows seven C^+-producing processes. It is noteworthy that for this light fragment, relatively high translational energies are carried away by the ion, i.e. higher than 1.0 eV, only for high excitation energies, i.e. above 30 eV electron energy. For other fragment ions, e.g. O^+, processes involving fairly high kinetic energies are observed even at low electron impact energies.

The only previous dissociative electroioniza-tion work devoted to C^+ from CO_2 has been reported by Ehrhardt and Kresling [17]. These authors determined two straight lines starting at 23.2 ± 0.2 eV and 28.2 ± 0.3 eV with slopes of 0.67 and 0.59 respectively. No errors were estimated on the onset energies or the linear regression parameters.

5. Discussion

For the sake of clarity in the following discussion, all the data used in this work to calculate the

thermodynamical onsets of the dissociation processes, which will be considered below, are gathered in Table 1.

The CO_2 molecule belongs to the $D_{\infty h}$ symmetry group, and the electronic configuration in the ground vibronic state $X^1\Sigma_g^+$ is given by

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(3\sigma_g)^2(2\sigma_u)^2(4\sigma_g)^2(3\sigma_u)^2$$

$$(1\pi_u)^4(1\pi_g)^4 \quad X^1\Sigma_g^+$$

Fig. 7. *Translational energy distribution curves of C^+ from CO_2 as measured at indicated electron energies E_e ranging from 25 to 99eV.*
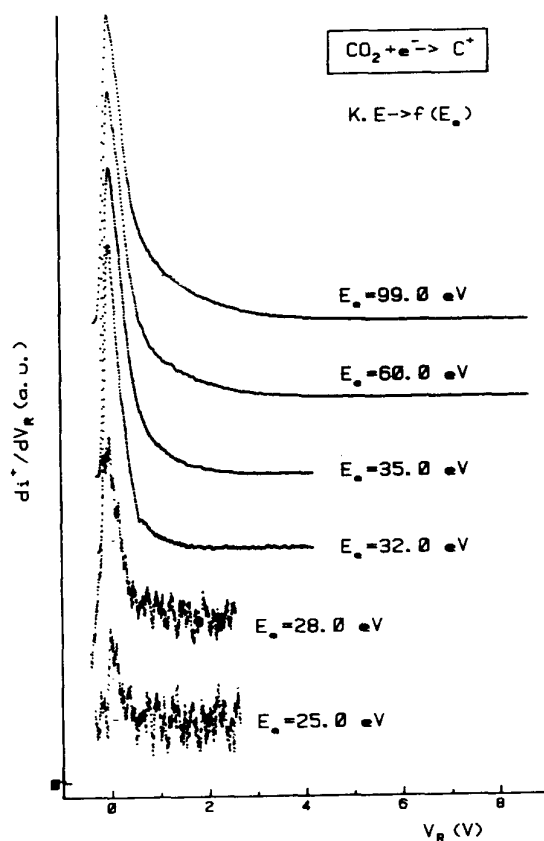
Four ionic states are observed in the energy range accessible to the He(I) resonance line. The adiabatic ionization energies are listed in Table 1. With the He(II) resonance line at 30.4 nm (40.8 eV), Potts and Williams [36] observed a series of doubly excited ionized states for which the vertical ionization energies are 22.6 eV, 27.2 eV, 31.4 eV, 35.3 eV and 38.5 eV. By dipole (e, 2e) spectroscopy, Brion and Tan [37] observed a "simulated" photoelectron spectrum and they reported multiple electron (MET) transitions at 23.5 eV, 26.5 eV, 30.0 eV, 32.0 eV, 35.5 eV and 38.0 eV.

5.1. The O^+ dissociation channel (see Fig. 3)

The lowest appearance energy of O^+/CO_2 was measured at 19.40±0.08 eV. It is the starting point of a small vertical line, extending over a 0.2 eV ion kinetic energy range, followed by a straight line ranging from 0.2 to 2.0 eV ion translational energy. The linear regression provides a straight line with a correlation coefficient of 0.995 and a slope of 0.360±0.005. This latter quantity should be compared with the expected slope value given by the ratio $m_{CO}/m_{CO2}=28/44=0.636$. The extrapolation calculated by linear regression is 18.93±0.04 eV. However, the extrapolation corresponding to the level of a dissociation limit was obtained by drawing a straight

line with the expected slope through the last point of the vertical line. The appearance energy of O^+ ions at KE=0.0 eV is $AE(O^+)_{KE=0}$=19.09±0.04 eV. These values should be compared with the literature data obtained using electroionization and photoionization mass spectrometry.

By dissociative electroionization mass spectrometry, including O^+ ion kinetic enegy analysis, Appell et al. [16] determined the onset of $KE(O^+)$=0.0 eV at 19.0±0.3 eV, which is the starting point of a straight line with a slope of 0.51 extending over a range of about 4.5 eV ion energy. Ehrhardt and Kresling [17] measured the first threshold at 19.1±0.4 eV, the origin of a straight line with a slope of 0.625 extending over 1.5 eV O^+ ion energy. In their electron impact work, Bussières and Marmet [19] observed the lowest onset for O^+-production at 19.05±0.05 eV, and they "conclude that this reaction takes place with zero kinetic energy".

Using dissociative excitation by electron impact, the O* atom (HR or $^5S_0$) appears at 19.2 eV and a slope of 0.43 was determined by Schiavone [12]. Allcock and McConkey [30] measured the excitation threshold at 19.2 ± 1.0 eV and obtained a KE versus AE straight line with a slope of 28/44 = 0.63. Misakian et al. [13] only measured the onset of O* at 20.5 eV.

By photoionization mass spectrometry, Parr and Taylor [7] only measured the O^+ ionization efficiency and observed a steep rise at 19.393 ± 0.003 eV. High sensivity and high resolution photoion yield curves were obtained by McCulloh [6] and Eland and Berkowitz [8]. A steeply rising portion in the threshold region was measured at 19.390 ± 0.003 eV. Below this dominant feature, weak autoionization transitions were observed, starting at 19.07 eV.
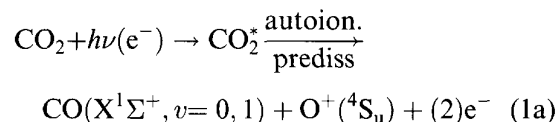
Fig. 8. *First differentiated ionization efficiency curves of C^+ from CO_2 as recorded at indicated retarding potential settings V_R ranging from 0.0 to 3.6 V. Vertical bars locate the average value of the threshold energies.*
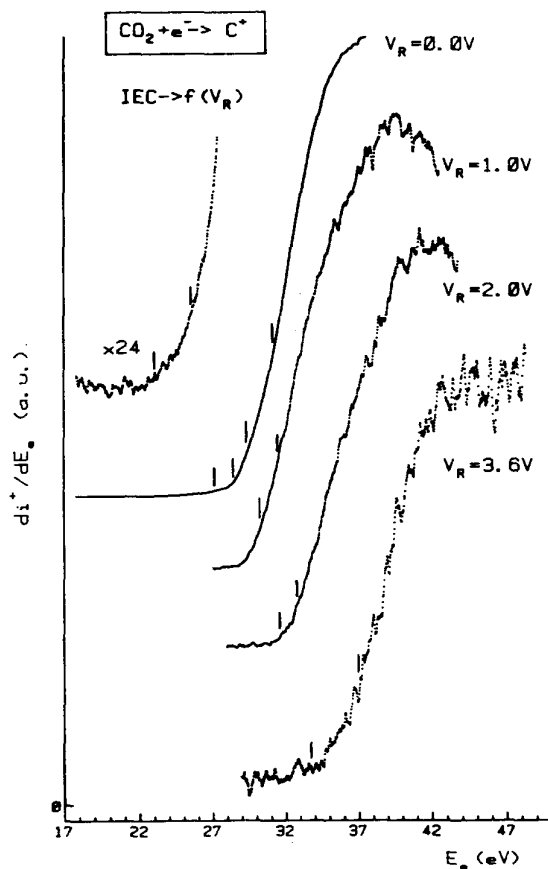
The lowest energetic dissociative ionization reaction involving O^+ ion formation is

$$CO_2 + e^- \rightarrow CO(X^1\Sigma^+) + O^+(^4S_u) + 2e^-$$

$$(1)$$
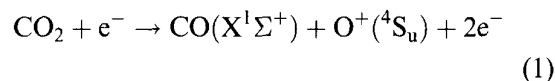
for which the thermodynamic onset was calculated at 19.069 eV using the data listed in Table 1. The calculated value is in excellent agreement with the lowest onset determined by photoionization, including the autoionization fine structure [6,7]. This also corresponds to the electron impact result of Bussières and Marmet [19]. Therefore, the O^+-producing mechanism, at this energy, must be

$$CO_2 + h\nu(e^-) \rightarrow CO_2^* \xrightarrow[\text{prediss}]{\text{autoion.}}$$

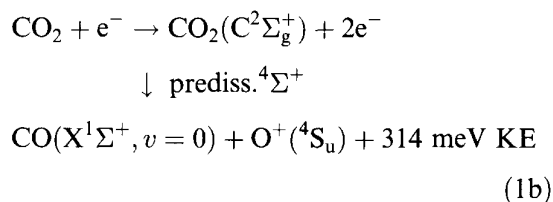$$CO(X^1\Sigma^+, \upsilon = 0, 1) + O^+(^4S_u) + (2)e^- \quad (1a)$$

where CO_2 is the first excited neutral state which autoionizes to a predissociating ionic state. The CO neutral species could be produced at the $\upsilon = 0$ and 1 levels, the corresponding dissociation levels being at 19.069 eV and 19.338 eV, and the value of ω_e for $CO(X^1\Sigma^+)$ being 2169.8 cm^{-1} (0.269 eV) [33].

Fig. 9. *KE versus AE diagram related to the C^+-oproduction channel from CO_2 between 22 and 38 eV electron energy. Straight lines are provided by linear regression. Encircled numbers refer to the corresponding processes discussed in the text.*
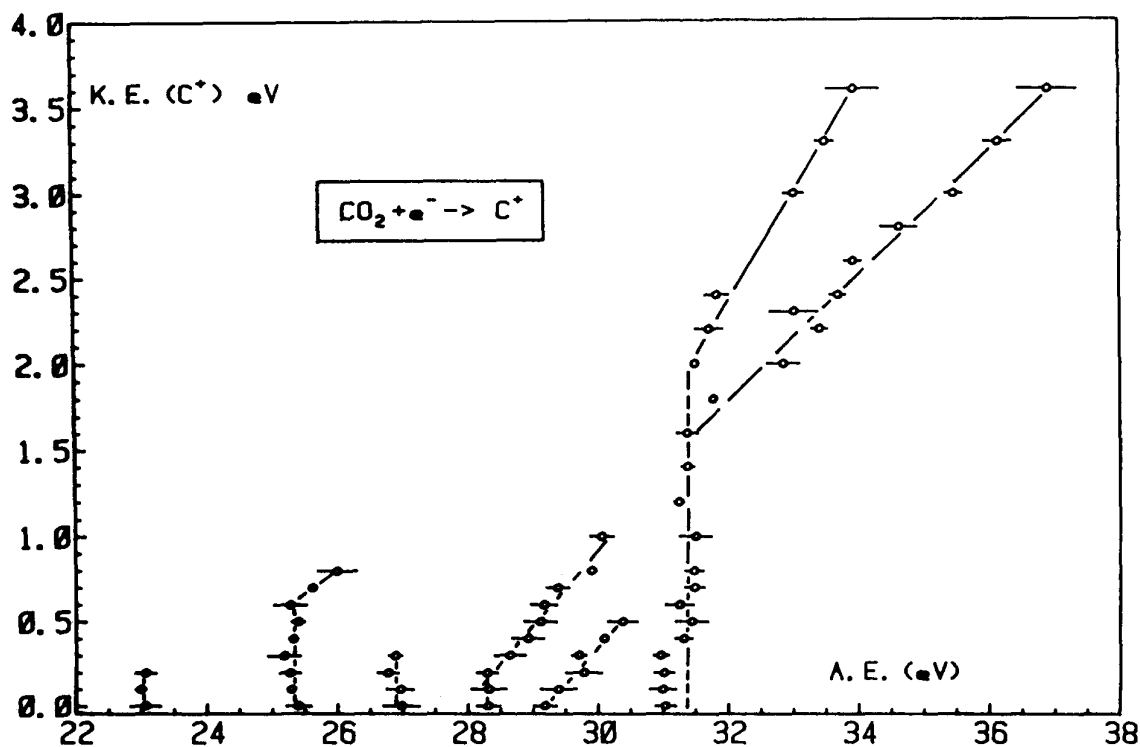
The threshold calculated for reaction (1) is in very good agreement with the extrapolated appearance energy of O^+, i.e. $AE(O^+)_{KE=0} = 19.09 \pm 0.04$ eV. The O^+ ions observed at 19.40 ± 0.08 eV are known to carry 200 meV kinetic energy at the onset, which corresponds to $44/28 \times 200 = 314$ meV in terms of total energy. As mentioned earlier, the present experimental onset, determined at 19.40 ± 0.08 eV, is in very good agreement with the second photoionization value [5-8]. The accurate energy balance which could be made in the present work, i.e. $AE(O^+)_{KE=0} = 19.09 \pm 0.04$ eV and $KE(O^+)_{Tot.} = 0.314$ eV, allows the first onset to be ascribed to the dissociative ionization:

$$CO_2 + e^- \rightarrow CO_2(C^2\Sigma_g^+) + 2e^-$$

$$\downarrow \text{ prediss.}^4\Sigma^+$$

$$CO(X^1\Sigma^+, v = 0) + O^+(^4S_u) + 314 \text{ meV KE}$$

$$(1b)$$

where the CO_2 molecule is prepared in the CO_2^+ (C $^2\Sigma_g^+$, v = 0) vibronic state which is predissociated by a $^4\Sigma_g^+$ state (with $D_{\infty h}$ symmetry), the only state correlated with both fragments. By photoelectron spectroscopy, the ionization energy of CO_2 in its $C^2\Sigma_g^+$ (v = 0, 0, 0) state is 19.3944 ± 0.0001 eV [32]. The CO neutral product of reaction (lb) could be formed in its ground electronic state, at the v = 0 and v = 1 levels. The O^+ ion would carry 314 meV and 56 meV respectively.

Table 1. *Dissociation (D), excitation (EE) and ionization (IE) energies (eV) of CO_2, CO, O_2, O and C used in this work[a]*

D(O=CO) = 5.451	IE(CO_2-$X^2\Pi_g$) = 13.778
D(C=O) = 11.109[b]	IE(CO_2-$A^2\Pi_u$) = 17.314[c]
D(O=O) = 5.116	IE(CO_2-$B^2\Sigma_u^+$) = 18.077
IE(C-^{2}P) = 11.264	IE(CO_2-$C^2\Sigma_g^+$) = 19.394
IE(O-^{4}S) = 13.618	IE(CO-$X^2\Sigma^+$) = = 14.014
IE(CO-$X^2\Sigma$) = 14.014	IE(CO-$A^2\Pi$) = 16.544
EE(C-^{1}D) = 1.264	IE(CO-$B^2\Sigma^+$) = = 19.672[c]
EE(C-^{1}S) = 2.684	EE(CO-$A^1\Pi$) = = 8.027
EE(C^+-^{4}P) = 5.331[d,f]	EE(O_2-$a^1\Delta_g$) = 0.977
EE(O-^{1}D) = 1.967	EE(O_2-$b^1\Sigma g^+$) = 1.627
EE(O-^{1}S)= 4.190	EE(O_2-$A^2\Sigma_u^+$) = 4.428[g]
EE(O^+-^{2}D) = 3.324	EE(O_2-$B^3\Sigma_u^-$) = 6.120
EE(O^+-^{2}P) = 5.017	

[a] *1 eV = 23.060 kcal mol^{-1} =8065.73cm^{-1}.* [b] *Ref. [31].* [c] *Ref. [32].* [d] *Ref. [26].* [e] *Ref. [33].* [f] *Ref. [34].* [g] *Ref. [35].*
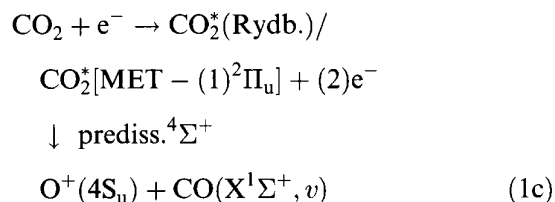
This process has been investigated in great detail by PIPECO [10]. Bombach et al. [10] only observed coincidences for O^+ ions with electrons corresponding to the $C^2\Sigma_g^+$ (v = 0, 0, 0) state, which predissociates at a rate of 94% in the O^+ + CO channel. This reaction is completely quenched at higher vibrational levels. The two O^+ kinetic energy components were resolved in this work. In the present experiment, the O^+ ion energy distribution is broader than the parent ion distribution peak. In Ref. [10], theoretical considerations related to the branching ratio of this pre-dissociation into O^+ and CO^+ are also extensively discussed.

At energies above 20.23 ± 0.20 eV the experimental data fit a straight line 1 characterized by a slope of 0.360 ± 0.005, extending from 20.23 to 24.7 eV. An extended vertical line, representing O^+ ions carrying at least 1.0 eV translational energy, is observed at 22.21 ± 0.03 eV electron energy.

The straight line 1 and the vertical line most likely indicate (i) the production of O^+ ions at the same dissociation level represented by reaction (1) and (ii) that these dissociations involve higher lying vibronic states of CO_2^+. In these cases, one also has to deal with pre-dissociation as a reaction mechanism. For direct ionization of the $C^2\Sigma_g^+$ state no cross section is measured at 20.23 ± 0.20 eV. This phenomenon is often observed in dissociative ionization studies. Therefore, dissociation must occur through dissociative autoionization.

The vertical line at 22.21 ± 0.03 e*V* is located at about the same energy at which an ionic state is observed by photoionization [36,38] and dipole (e, 2e) binding energy spectroscopy [37], i.e. at 22.6 eV [37], 22.8 eV [38] and 23.5 ± 0.5 eV [36].

The experimental data observed between 20.2 and 24.3 eV could be produced by dissociative autoionization and dissociative ionization through

$$CO_2 + e^- \rightarrow CO_2^*(Rydb.)/$$

$$CO_2^*[MET - (1)^2\Pi_u] + (2)e^-$$

$$\downarrow \text{ prediss.}^4\Sigma^+$$

$$O^+(4S_u) + CO(X^1\Sigma^+, v) \qquad\qquad (1c)$$

where both the autoionizing and ionic states dissociate to the same level at 19.09 ±0.04 eV. The autoionizing state is probably a member of a Rydberg series converging at the 22.6 eV ionization limit. The 22.6 eV CO_2^+ state, designated in the literature [37,39] as being an MET or CI state, has been investigated by Domcke et al. [39] by quantum mechanical calculations. They interpreted this energy as due to a satellite line originating from the $l\pi_u$ orbital, i.e. derived from $(1\pi_g)^{-2}(2\pi_u)^1$ or $(l\pi_u)^{-2}(2\pi_u)^1$ configurations. These give rise to $\Pi_u(3)$, $^4\Pi_u$ and $^2\Phi_u$ states. It is very likely that at 22.2 eV one is dealing with one of the three $CO_2^+(^2\Pi_u)$ states.

None of the known spectra of CO_2^+ in this energy range [36-38] exhibit vibrational structure in the 22.6 eV band. Therefore, a possible reason for the absence of any structure is the rapid predissociation of the satellite state and the Rydberg state converging to it. The pre-dissociating state has to be the same $^4\Sigma^+$ state that already predissociates the lower-lying $C^2\Sigma_g^+$ state.

The slope of the straight line is 0.360 ± 0.005, which deviates significantly from the expected slope of 0.636. This observation means that the excess energy with respect to the dissociation level involved in process (lc) is partitioned between ion translational energy (for about 60%) and the CO fragment internal excitation energy (for about 40%). At 20.2 eV, the neutral diatomic fragment would be produced at $v = 2$ up to $v = 5$ at 21.7 eV electron energy. Between 22.2 and 24.3 eV the CO molecule would be excited from $v = 5$ to $v = 8$. From the present work, although fairly good agreement is found with the calculated onset for

$$CO_2 + e^- \rightarrow CO_2^{+*} \rightarrow O^+(^2D_u)$$

$$+ CO(X^1\Sigma^+, v = 0) + 2e^- \qquad\qquad (2)$$
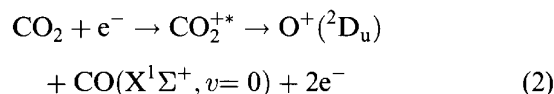
at 22.393 eV (see Table 1), the O^+ ions formed at 22.21 ± 0.03 eV are *notproducedby* reaction (2). They carry 1.2 eV translational energy *at the threshold.*

The above discussed results partly agree with the results reported previously [16,17]. However, and more significantly, it is difficult to compare the last part of the diagram. Appell et al. [16] mention a straight line with a slope of 0.30 that extrapolates to 20.3 ± 0.4 eV. These results are absent from the data reported by Ehrhardt and Kresling [17]. Further, these groups report an onset at 22.4 ± 0.6 eV [16] and 22.4 ± 0.3 eV [17], and assign it to process (2) where the O^+ ions should be produced without kinetic energy at the threshold. The slope of the straight line differs from 0.23 [16] to 0.63 [17]. However, a fairly large scattering of the appearance energy measurements, as reported by these authors, has to be taken into account. Another reason for these discrepancies could be the way the authors correlate the experimental data.

The straight line 2 starts at 24.74 ± 0.10 eV and could only be defined by four appearance energy data. It probably belongs to the vertical line drawn through 11 appearance energy measurements. In spite of this, a linear regression was applied to the experimental data with a correlation coefficient of 0.997. The slope is 0.45 ± 0.02 and the linear extrapolation is 19.20 ± 0.34 eV. As mentioned already in this discussion, when the slope differs from the expected value, the dissociation level is obtained by drawing a straight line with expected slope (i.e. 0.636) through the starting point of straight line 2. Using this method yields $AE(O^+)_{KE=0} = 20.93 \pm 0.34$ eV.

The energy difference of 20.93(±0.34)-19.07= 1.86±0.34 eV could not be accounted for by electronic excitation of one of the products of reaction (1) (see Table I). The threshold of reaction (2) e.g. is calculated at 22.393 eV. Besides the total translational energy of 3.77 eV involved in this process, the excess energy with respect to the dissociation level at 19.07 eV has to be ascribed to rovibrational energy. If only vibrational energy were involved, the $CO(X^1\Sigma^+)$ species would be produced at $v = 7$.

The ionic state of CO_2^+, which is most probably involved in the dissociation process at 24.74 eV, is related to the ionic state which has its vertical ionization energy at 26.5 eV. It is identified by MET(II) in Ref. [37] and would be one of the three $^2\Pi_u$ states derived from the $(1\pi_g)^{-2}(2\pi_u)^1$ configuration [39]. If we are dealing

with a $^2\Pi_u$ state at its adiabatic ionization energy at 24.74 eV, the observed dissociation vent has to run over the predissociation of this state through the same $^4\Sigma^+$ state which already predissociates the $C^2\Sigma_g^+$ state and the first lower-lying $^2\Pi_u$ state of CO_2^+.
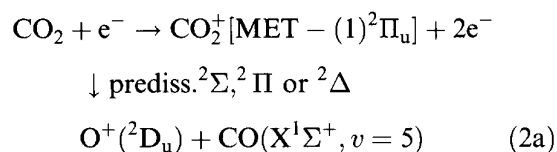
Appell et al. [16] measured an onset energy at 24.6 ± 0.3 eV, the starting point of a straight line with a slope of 0.23. Ehrhardt and Kresling [17] determined an appearance energy at 24.3 ± 0.3 eV. The process (3)

$$CO_2 + e^- \rightarrow CO_2^{+*}$$
$$\rightarrow O^+(^2P_u) + CO(X^1\Sigma^+) + 2e^- \quad (3)$$
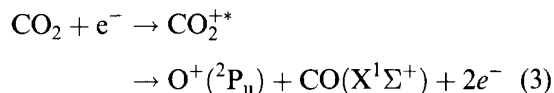
for which a thermodynamical onset is calculated at 24.086 eV (see Table 1), was assigned to this energy [16,17]. From the present work, at this electron energy, the O^+ ions carry at least 0.70 ± 0.05 eV translational energy. Once again, the origin of this discrepancy could be the method of correlation of the experimental data. Both experiments show fairly large scattering of the data and no error is estimated.

The third and last straight line 3 related to the production of O^+ starts at 23.65 ± 0.10 eV for ions carrying no translational energy. The straight line 3 is the result of a linear regression applied to 24 appearance energy data extending from 0.0 to 5.5 eV translational energy. The correlation coefficient is 0.996 and the slope is 0.639±0.013. This latter quantity should be compared to the expected slope of 0.636. The very good agreement implies total excess energy conversion into translational energy carried away by the reaction products.

23.65±0.10 eV corresponds to the vertical ionization energy of the first multiple electron transition state observed by electron impact at 23.5±0.5 eV [37] and by photoionization at 22.6 eV [36]. The predissociation of this state was already involved at 22.2 eV. However, at 23.6 eV the O^+ ions carry no kinetic energy at the threshold. The energy difference of 23.65(±0.10)-19.07 = 4.58 eV would correspond to the vibronic excitation shared by the dissociation partners, i.e.

$$CO_2 + e^- \rightarrow CO_2^+[MET - (1)^2\Pi_u] + 2e^-$$
$$\downarrow \text{prediss.}^2\Sigma,^2\Pi \text{ or } ^2\Delta$$
$$O^+(^2D_u) + CO(X^1\Sigma^+, v = 5) \quad (2a)$$

for which the dissociation level is calculated at 22.393 eV for $CO(X^1\Sigma^+, v = 0)$ (see Table 1) and using $\omega_e = 0.269$ eV [33]. The energy difference of 23.65-22.39 = 1.26 eV has to be assigned to the vibrational excitation of CO. However, the possibility of total excess energy conversion of 4.58 eV into rovibrational energy content of CO cannot be ignored.

At least one vertical line converges to this straight line at 30.32 ± 0.20 eV. The vertical line at 24.74 eV could also belong to straight line 3. This latter proposal could only be settled using a coincidence experiment. If this was considered, the decomposition of the same CO_2^+ state would show a branching between $O^+(^4S) + CO(X^1\Sigma^+, v = 7) + 3.77KE_{Tot.}$ and $O^+(^2D_u) + CO(X^1\Sigma^+, v = 5) + 1.1KE_{Tot.}$

The vertical line at 30.32 ± 0.20 eV electron energy correlates very well with the vertical ionization energy of 30.2 ± 0.5 eV determined by Brion and Tan [37], and is assigned by Domcke et al. [39] to an "accumulation of weak Σ and Π type satellites calculated between 32 and 34 eV". These CO_2^+ doubly excited states decompose to the dissociation limit (2a) releasing fragments carrying large amounts of kinetic energy.

These results and discussion are compared with the results of Appell et al. [16] and Ehrhardt and Kresling [17]. The former observed appearance energies above 33 eV electron energy and correlated these data with the 24.6±0.3 eV dissociation limit assigned to reaction (3). The latter authors determined a straight line extending between 30 and 40 eV with a slope of 0.66 and extrapolating to 28.3 ± 0.3 eV. The reaction

$$CO_2 + e^- \rightarrow CO_2^{+*}$$
$$\rightarrow O^+(^4S_u) + CO(A^1\Pi) + 2e^- \quad (4)$$
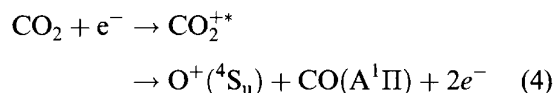
is assigned to this energy. The O^+ ions carry about 1 eV translational energy at the threshold of 30 eV.

As already stressed earlier, these marked discrepancies are difficult to explain. The kinetic energy distributions are derived from *ion momentum* analysis using the ion beam deflection method between two short con-densor plates [16,17]. The appearance energies are determined on the *direct* ionization efficiency curves. In the present work, the ion retarding potential technique is used for *ion kinetic energy* analysis and *the first differentiated* ionization efficiency curves are measured for the threshold determinations.

At this point of the discussion, it is appropriate to draw a parallel between the dissociative ionization behaviour of N_2O and CO_2. The "isoelectronic" dissociation in N_2O corresponds to $O^+ + CO$ is $O^+ + N_2$. This dissociation channel has been investigated in great detail in a previous report [40]. Two major similarities should be pin-pointed here. First, in the production of O^+ from both molecules, the predissociation mechanism through *one* quartet state ($^4\Sigma$) plays a major role from the threshold up to 30 eV. Second, except for the lowest threshold, the N_2 and CO neutral species produced from N_2O and CO_2 respectively are formed in the ground electronic state vibrationally excited up to $v = 8$ for N_2 and $v = 7$ for CO. Highly energetic and electronically excited O^+ ions are produced from the satellite states in both molecules. These reactions also produce vibrationally excited N_2 and CO molecules. In both molecules, the dissociative ionization phenomena could be accounted for by the same reaction schemes.

5.2. The CO^+ dissociation channel (see Fig. 6)

The lowest onset for CO^+ ion production is measured at 19.54 ± 0.04 eV for CO^+ ions carrying no translational energy. This appearance energy is the starting point of a straight line 1 extending from 0.0 to 1.2 eV translational energy. A linear regression with a correlation coefficient of 0.997 fits the experimental data. The slope determined by this method has a value of 0.232 ± 0.007 and should be compared with the expected slope of 0.364 given by the ratio m_O/m_{CO2}. Two vertical lines converge to this straight line, i.e. at 22.20 ± 0.06 eV and at 23.78 ± 0.26 eV.

The dissociative ionization in the energy region of 19.5 eV has been investigated by electron impact [20] and photoionization [6,8-11]. Bussières and Marmet [19] only measured the appearance energy at 19.42 ± 0.075 eV, without any translational energy analysis. Armenante et al. [20] measured appearance energies for CO^+ ions carrying known amounts of translational energy as measured by TOF. The lowest onset reported by these authors is about 23.5 eV for CO^+ ions carrying 0.57 eV kinetic energy. This result is obviously not related to the threshold at 19.5 eV.

The onset region of the CO^+ ion production efficiency has been carefully examined by photoionization [6,8]. The threshold region shows several "steps" and the lowest appearance energy is reported to be at 19.466 eV. This onset is followed by critical energies at 19.56 eV and 19.75 eV. Kinetic energy discriminated CO^+ ions have been investigated in great detail by the PIPECO technique [9,10].

The lowest energy dissociative ionization reaction producing CO^+ is calculated for

$$CO_2 + e^- \rightarrow CO^+(X^2\Sigma^+, v = 0)$$
$$+ O(^3P_g) + 2e^- \qquad\qquad (5)$$
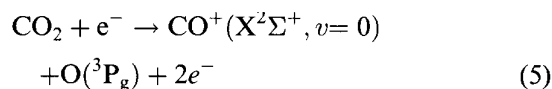
at 19.465 eV (see Table 1) and is in excellent agreement with the photoionization measurements and the present electron impact results. This threshold energy levels out at the observed CO_2^+ ($C^2\Sigma_g^+$, $v = 0, 1, 0$) state at 19.4705 ± 0.0003 eV [32]. Its predissociation would produce CO^+ carrying 2 meV translational energy. This is in very good agreement with the present observation of purely thermal CO^+ ions close to the threshold (see Fig. 4). This implies that it would not be necessary to invoke the production of rotationally excited CO^+ species in the dissociation dynamics [10]. A PIPECO experiment would be difficult to perform, as the electron signal on the $C^2\Sigma_g^+$ at $v = 0, 1, 0$ is too low.

In the $D_{\infty h}$ point group the $^2\Sigma^+$ and ^3P products correlate with a doublet and a quartet Σ^- and Π states of CO_2^+. The products of reaction (5) should correlate with the CO_2^+ ($X^2\Pi g$) electronic ground state. A detailed mechanism involving intersystem crossing between $C^2\Sigma_g^+$ and $X^2\Pi_g$ through an intermediate $^4B_1$ state has been discussed by Bombach et al. [10]. The perturbation of the $C^2\Sigma^+g$ state by $^2B_1$ could also play a role, particularly when CO^+ is rotationally excited.

By direct Franck-Condon transition, the population of CO_2^+ ($C^2\Sigma_g^+$) is restricted to the 19.4-19.8 eV energy range. The experimental data fitting straight line 1 between 20 and 22 eV electron energy must therefore be ascribed to the dissociative *autoionization* production of CO^+. The same autoionizing states decompose into $O^+ + CO$, as discussed above in Section 5.1. The slope of the straight line could only be accounted for by the vibrational excitation at increasing total energy content, i.e.
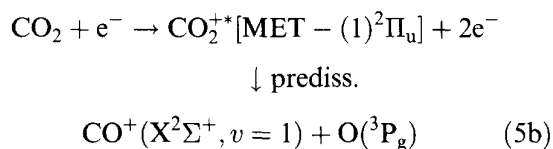
$$CO_2 + e^- \rightarrow CO_2^* + e^-$$

$$\downarrow \text{prediss.}$$

$$O(^3P_g) + CO^+(X^2\Sigma^+, \Delta v = 1) + e^- \qquad (5a)$$
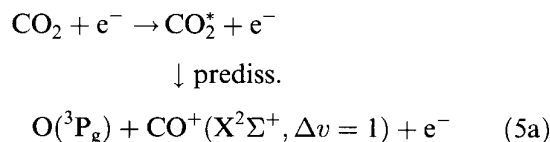
where the vibrational energy content of CO^+ has to increase by one quantum (ω_e (CO^+, $X^1\Sigma^+$) = 2214 cm^{-1} [33]).

The vertical line at 22.20 ± 0.06 eV converges to the straight line 1 and corresponds to CO^+ ions carrying at least 0.5-0.6 eV translational energy. The threshold energy and initial kinetic energy do not agree with the results of Armenante et al. [20]. They observed the first onset for CO^+ production at about 23.5 eV with an initial kinetic energy of 0.57 eV (see Fig. 3 of Ref. [20]). The linear extrapolation is found to be 22.2 eV for a straight line extending up to 3.16 eV translational energy for one series of measurements, whereas for a second series of experiments they measured up to 1.7 eV CO^+ ion energy. The two series show a fairly large scattering of the data. The KE versus AE diagram has a slope of 0.33, i.e. about 30% higher than the slope determined in the present work. These authors assigned the 22.2 eV extrapolation to the process

$$CO_2 + e^- \rightarrow CO^+(A^2\Pi) + O(^3P_g) + 2e^- \quad (6)$$
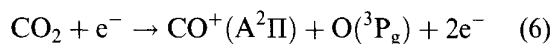
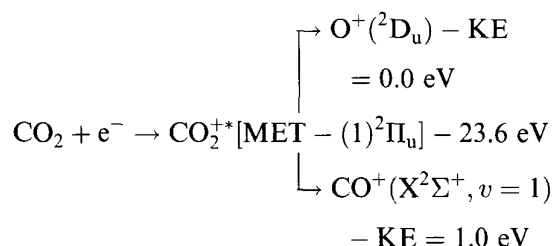for which the thermodynamic threshold is calculated at 21.995 eV.

From the present experimental data, i.e. CO^+ carries 0.5 eV translational energy at 22.2 eV and the total excess energy is shared between the kinetic energy of the products and the internal energy contained by the CO^+ molecular ion, the process involved should be

$$CO_2 + e^- \rightarrow CO_2^{+*}[\text{MET} - (1)^2\Pi_u] + 2e^-$$

$$\downarrow \text{prediss.}$$

$$CO^+(X^2\Sigma^+, v = 1) + O(^3P_g) \qquad (5b)$$

where the proposed intermediate ionic state MET-$^2\Pi_u$ should be the same as that investigated by Domcke et al. [39], and has been observed by photoelectron spectroscopy around 22.6 eV [36-38]. It would be the same "MET state" that was involved in the production of $O^+(^4S_u) + CO(X^1\Sigma^+, v)$ through process (lc) which has its onset at 22.21±0.03 eV.

The second vertical line at 23.78 ± 0.26 eV converging to the straight line 1 corresponds to CO^+ ions carrying at least 1.0 eV kinetic energy. The present data should be interpreted by assigning the production of these CO^+ ions to the predissociation of the first MET state characterized by the vertical ionization energy at 23.6 eV [36-38].

For the dissociation dynamics of CO_2^+, it should be kept in mind that an O^+ ion-producing process has been observed at this electron energy, i.e. 23.65 ± 0.10 eV (see Section 5.1). Therefore, it could be suggested that at 23.7 eV two processes probably compete to predissociate the MET state (probably the first $^2\Pi_u$ state [39]) into O^+ and CO^+ channels through the reaction scheme

$$
\begin{array}{l}
\qquad\qquad\qquad \longrightarrow \mathrm{O^+(^2D_u) - KE} \\
\qquad\qquad\qquad\quad = 0.0\ \mathrm{eV} \\
\mathrm{CO_2 + e^- \rightarrow CO_2^{+*}[MET - (1)^2\Pi_u] - 23.6\ eV} \\
\qquad\qquad\qquad \longrightarrow \mathrm{CO^+(X^2\Sigma^+, \textit{v} = 1)} \\
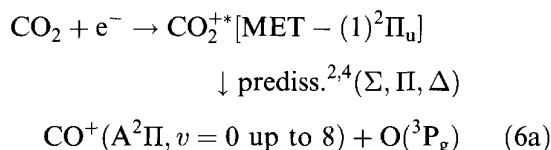\qquad\qquad\qquad\quad - \mathrm{KE = 1.0\ eV}
\end{array}
$$

The onset at 23.78 eV is comparable to the first onset measured by Armenante et al. [20]. However, CO^+ ions carry 0.57 eV kinetic energy, whereas this quantity is 1.0 eV in the present work. Further, the same authors reported an extrapolated $AE(CO^+)_{KE=0}$ = 23.9 eV for a straight line with a slope of 0.30. This onset is ascribed to

$$
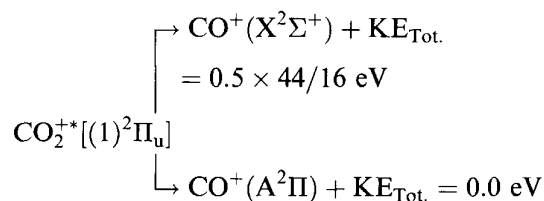CO_2 + e^- \rightarrow CO^+(X^2\Sigma^+) + O(^1S_g) + 2e^-
$$

$$(7)$$
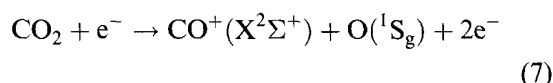
Considering the present data, even when the vertical line at 23.78 eV also converges to the straight line 2 (as discussed below), the process unambiguously involves reaction (6) as will be shown in the following part of the discussion.

Straight line 2 in Fig. 6 starts at 22.18 ± 0.12 eV and extends up to about 26 eV electron energy. In this electron energy region the CO^+ ions carry 0.0-0.6 eV translational energy. The linear regression applied to the seven data points is characterized by a correlation coefficient of 0.999. The straight line thus obtained has a slope of 0.145 ± 0.004 and extrapolates to 22.18 ± 0.06 eV. This threshold energy is very close to the thermodynamic onset energy calculated for process (6), i.e. 21.995 eV as already mentioned earlier. The slope of the straight line indicates a 60% excess energy conversion into vibrational energy of the CO^+ fragment through the mechanism

$$
CO_2 + e^- \rightarrow CO_2^{+*}[MET - (1)^2\Pi_u]
$$

$$
\downarrow \mathrm{prediss.}^{2,4}(\Sigma, \Pi, \Delta)
$$

$$
CO^+(A^2\Pi, \textit{v} = 0 \ \mathrm{up\ to\ } 8) + O(^3P_g) \qquad (6a)
$$

However, to account for the peculiarity shown by the KE versus AE plot at 22.18 eV in the CO^+-producing reaction coordinate, the decomposition of the ionic MET-$(1)^2\Pi$ state probably branches off between two reaction paths schematically represented by

$$
\begin{array}{l}
\qquad\qquad\qquad \longrightarrow \mathrm{CO^+(X^2\Sigma^+) + KE_{Tot.}} \\
\qquad\qquad\qquad\quad = 0.5 \times 44/16\ \mathrm{eV} \\
\mathrm{CO_2^{+*}[(1)^2\Pi_u]} \\
\qquad\qquad\qquad \longrightarrow \mathrm{CO^+(A^2\Pi) + KE_{Tot.} = 0.0\ eV}
\end{array}
$$

This part of the diagram shown in Fig. 6 could not be compared with the results reported by Armanante et al. [20]. These authors did not detect CO^+ ions at about 22 eV electron energy without translational energy.

The dissociative ionization process corresponding to the straight line 3 involves a large amount of kinetic energy and is characterized by an onset at 26.10 ± 0.13 eV. However, only three data points could be obtained to define the straight line. Although without statistical meaning, a linear regression has been applied to obtain a slope value, i.e. 0.144 ±0.005. The linear extrapolation, at 9.6 ± 0.6 eV, might not be related to a dissociation level of CO_2^+. When a straight line with a slope of 0.36 is drawn, starting at 26.17 eV, an extrapolation $AE(CO^+)_{KE=0}$ = 19.58 ± 0.22 eV is obtained. This extrapolated value of the dissociation energy level is compatible with the onset energy calculated for process (5), where CO^+ and O are both produced in their

ground electronic and/or vibrational state.

The onset energy of 26.10 ± 0.13 eV is in very good agreement with the vertical ionization energy determined for the second "MET state" by photoelectron spectroscopy and by electron impact [36-38]. The dissociative ionization of CO_2^+ at this energy should probably be assigned to the decomposition of the second $^2\Pi_u$ state, derived from the $(1\pi_u)^{-2}(2\pi_u)^1$ or $(1\pi g)^{-2}(1\pi_u)^1$ multiply excited configurations [39], possibly through a predissociation, i.e.

$$CO_2 + e^- \rightarrow CO_2^{+*}[MET - (2)^2\Pi_u] + 2e^-$$

$$\downarrow (prediss.)$$

$$CO^+(X^2\Sigma^+, v = 0) + O(^2P_g) \qquad (5c)$$
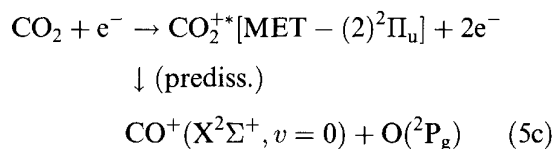
As shown in Fig. 6, the vertical line converging to the straight line 3 is defined by 12 data points, each of which is the average value of five independent measurements. At about the same energy, i.e. at 26.8 eV, Armenante et al. [20] mention the appearance of CO^+ ions carrying no translational energy. However, these authors reported CO^+ ions carrying up to 2.7 eV translational energy, in agreement with the present experimental data.

At 30.38 ± 0.26 e V the vertical line 4 is drawn in Fig. 6. It is defined by 15 data points which are average values of five independent measurements. Error bars correspond to one standard deviation. The vertical line extends to 3.0 eV translational energy carried by CO^+. This amount would correspond to 8.25 eV in terms of the total kinetic energy involved in the dissociative ionization process. By subtracting this latter quantity from the appearance energy, a threshold energy of 22.13 ± 0.26 eV is obtained. This result would imply that the dissociation level involved at 30.38 eV is that calculated for reaction (6).

It is noteworthy to mention that this appearance energy corresponds to (i) the vertical ionization energy of the third "MET state", i.e. at 31.4 eV [36,38] or 30.0 ± 0.5 eV [37] and (ii) the highest onset energy measured for O^+ carrying up to 5.5 eV kinetic energy, i.e. at 30.32 ± 0.2 eV.

Domcke et al. [39] investigated this CO_2^+ MET state and described the 30.0 eV peak in the dipole (e, 2e) binding energy spectrum of CO_2 by "the accumulation of weak $\sum$ and $\prod$ type satellite lines calculated between 32-34 eV". From the present work, this (these) state(s) is (are) not stable with respect to dissociation and decompose competitively into the O^+ and CO^+ dissociation channels. From the present results, it could not be decided whether the decomposition occurs through a predissociation mechanism or through a transition to a repulsive CO_2^+ hypersurface.

5.3. The C^+ dissociation channel (see Fig. 9)

The first threshold observed for C^+ ion production from CO_2 is measured at 23.04 ± 0.04 eV. The KE versus AE diagram (see Fig. 9) related to this process is a vertical line 1 extending from 0.0 to 0.2 eV translational energy. This would mean that in the C^+-producing process a maximum of $0.2 \times 44/32 = 0.275$ eV total kinetic energy is involved. Subtracting this quantity from the measured appearance energy, the lowest dissociation level for C^+ ion production is obtained at $23.04(\pm 0.04) - 0.275 = 22.76 \pm 0.04$ eV.

There have been few dissociative ionization investigations of CO_2 in the C^+-producing channel. Bussières and Marmet [19] reported the lowest onset at 22.7 ± 0.2 eV without kinetic energy analysis. Ehrhardt and Kresling [17], measuring the appearance energy of momentum-selected C^+ ions, reported the lowest onset at 23.2 ± 0.2 eV, which is in very good agreement with the result of the present work. The C^+ ions carry about 0.3 eV kinetic energy, as estimated from Fig. 5 of Ref. [17]. The onset observed by Stockdale et al. [18] at 29.8 ± 0.3 eV is obviously not related to the presently considered process.

The lowest thermodynamic onset calculated for the reaction path

$$CO_2 + e^- \rightarrow C^+(^2P_u) + O_2(X^3\Sigma_g^-) + 2e^-$$
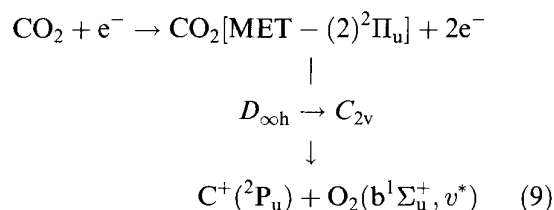
$$(8)$$
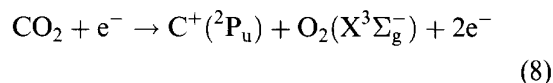
is at 22.713 eV (see data in Table 1) and is most likely assignable to the threshold at 23.04 eV.

The appearance energy measured for C^+ is in very good agreement with the vertical ionization energy of the first doubly excited state of the CO_2^+ ion observed at 22.6 eV [36,38] and 23.5 ± 0.5 eV [37]. As mentioned earlier, $^2\Pi_u$ symmetry has been assigned to this MET state [39]. However, the above-mentioned reaction (8) has to follow a path involving a strong modification of the geometry of the molecular ion, e.g. from a linear to a bent configuration. The CO_2 molecule in the ground state belongs to the $D_{\infty h}$ symmetry group. The fragments of reaction (8) could only be correlated with a CO_2^+ ionic state with C_{2v} symmetry. In this latter symmetry group, the $C^+(^2P_u)$ fragment becomes $C^+(^2A_1, {}^2B_1, {}^2B_2)$ and $O_2(X^3\Sigma_g^-)$ becomes $O_2(^3B_2)$. The coupling of these symmetries of the reaction products provides doublet and quartet A_1, A_2 and B_2 molecular ion states. As far as we are aware, none of these states is known or has been observed.

The only conclusion which could be drawn from the foregoing considerations is that a CO_2^+ bent state, converging to the 22.713 eV dissociation level, would possibly (pre)dissociate the $(1)^2\Pi_u$ MET state. Predissociation would only occur when this latter state is stable with respect to dissociation in the present decomposition channel.

The second part of the KE versus AE diagram shows a C^+-producing process occuring at 25.31 ± 0.15 eV. This appearance energy has not been previously detected [17-19]. The vertical line is followed by a "straight line" 2. It has been defined by three data points between 0.6 and 0.8 eV kinetic energy carried by C^+. The straight line, obtained in the usual way, has a slope of 0.28 ± 0.01 and extrapolates to 23.14 ± 0.10 eV.

The observed slope being lower than the expected slope of 0.727, the excess energy with respect to the dissociation level is partitioned between the kinetic energy of both fragments and the internal (e.g. vibrational) energy of the neutral molecule O_2. This discrepancy also has a consequence that the extrapolated value must be discarded. The actual dissociation level is obtained by the subtraction 23.5(±0.15) -0.6(±0.05) × 44/32, i.e. $AE(C^+)_{KE=0}$ = 24.48 ± 0.20 eV. This energy is in fairly good agreement with the onset calculated for the reaction

$$CO_2 + e^- \rightarrow CO_2[\mathbf{MET} - (2)^2\Pi_u] + 2e^-$$
$$|$$
$$D_{\infty h} \rightarrow C_{2v}$$
$$\downarrow$$
$$C^+(^2\mathbf{P_u}) + O_2(b^1\Sigma_u^+, v^*) \quad (9)$$

at 24.340 eV, where the decomposition would also take place through a complex reaction pathway involving the modificaton of the geometry of the molecular ion.
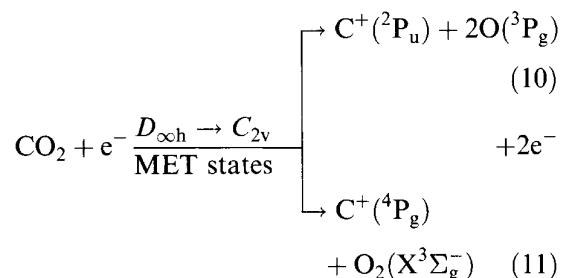
The CO_2^+ ionic state involved in this dissociation is most probably the MET(II) state, which is characterized by a vertical ionization energy at 26.5 ± 0.5 eV by electron impact [37] or 27.2 eV by photoelectron spectroscopy [36,38]. From the published spectra the "adiabatic" ionization energy could be estimated at about 25 eV, corresponding fairly well to the appearance energy of C^+ at 25.3 eV. This correlation could indicate that this second $^2\Pi_u$ state is (pre)dissociated down from its lowest energy level.

Over a restricted kinetic energy range, i.e. 0.0-0.3 eV, a threshold energy is observed at 26.90 ±0.10 eV. The C^+ ions carry 0.41 eV total kinetic energy at most. The dissociation level involved at this threshold would be located at 26.58 ± 0.10 eV.

As indicated in Table 1, the energy difference of 26.58 - 22.71 = 3.87 eV is neither sufficient (i) to dissociate the O_2 molecule in its $X^3\Sigma_g^-$ state which requires 5.116 eV, nor (ii) to excite the O_2 molecule in its $A^3\Sigma_u^+$ state or the C^+ ion at its ^4P_g level, requiring 4.428 eV and 5.331 eV respectively. Consequently, the only way to interpret the onset observed at 26.58 ± 0.10 eV is to assign it to reaction (9), where the neutral molecule $O_2(b^1\Sigma_u^+)$ is vibrationally highly excited. It should be pointed out that this process occurs in the energy range covered by the MET(II) state or second $^2\Pi_u$ state of CO_2^+ [39].

The first well defined feature in the KE versus AE diagram of C^+ is straight line 4. A vertical line at 28.31 ± 0.08 eV, extending over a range of 200 meV kinetic energy, is followed by eight data points fitted by a straight line. The linear regression applied to these data provides a correlation coefficient of 0.982 and the slope is 0.458 ± 0.036, which is unambiguously lower than the expected value of 0.727. This should be ascribed to the excess energy partition between the translational and internal energy.

The linear extrapolation, obtained when a straight line with a slope of 0.727 is drawn at 0.2 eV kinetic energy, is 28.03 ± 0.11 eV, corresponding to an actual energy of $AE(C^+)_{KE=0}$. The energy difference of $28.03(\pm0.11)$-$22.71 = 5.32 \pm 0.11$ eV represents the pure excitation energy available to the fragments. This value could be assigned to both dissociative ionization reactions:

$$CO_2 + e^- \xrightarrow[\text{MET states}]{D_{\infty h} \rightarrow C_{2v}} \begin{array}{l} \rightarrow C^+(^2P_u) + 2O(^3P_g) \\ \hspace{3cm} (10) \\ \hspace{2cm} +2e^- \\ \hookrightarrow C^+(^4P_g) \\ \hspace{1cm} + O_2(X^3\Sigma_g^-) \hspace{0.5cm} (11) \end{array}$$

for which a thermodynamical threshold is calculated at 27.824 eV and 28.044 eV respectively (data from Table 1).
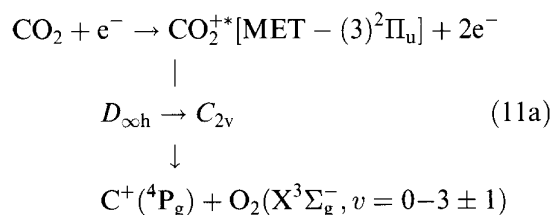
Bussières and Marmet [19] measured a second appearance energy for C^+ production at 27.8 ± 0.1 eV without translational energy analysis. Ehrhardt and Kresling [17] measured the second threshold energy of momentum-selected C^+ ions at 28.2 ± 0.3 eV for ions carrying up to 5 eV kinetic energy. The slope of the straight line is reported to be 0.59 over the whole kinetic energy range. This value is significantly lower than the expected value of 0.727.

The onset energy determined in the latter work is in very good agreement with the present determination. However, the translational energy covered by the process at 28.3 eV is 1.0 eV at most and the slope is 0.458 in the present work. A plausible explanation of this discrepancy is that, owing to a less accurate determination and less efficient analysis, the data defining the straight line 6 in Fig. 9 of the present work have been included in the straight line 4 by Ehrhardt and Kresling [17].

Both groups assigned the onset energy at 28.3 ± 0.3 eV [17] or at 27.8 ± 0.1 eV [19] to the dissociative ionization reaction (10). On the basis of only the appearance energy measurements and their reported error limits, it is not possible to make an unequivocal assignment. The former determination lies significantly higher than the thermodynamic onset. The latter assignment is not supported by kinetic energy analysis.

From the present determinations, the C^+ ions appearing at 28.31 ± 0.08 eV carry 200 meV kinetic energy. In addition, the slope of the straight line 4 is 0.458 ± 0.036, significantly lower than 0.727. This analysis is confirmed using the significance test (see Section 3) giving a slope value of 0.46 ± 0.13 with 99.5% confidence. This latter value includes the slope reported by Ehrhardt and Kresling [17].

A KE versus AE slope value significantly lower than the expected value could only be accounted for by the excess energy partition between translational energy and *internal energy of a polyatomic fragment* produced by the dissociation. Only reaction (11) produces the O_2 molecule in its ground electronic state. On the basis of the present data analysis and arguments, the dissociative ionization process

$$CO_2 + e^- \rightarrow CO_2^{+*}[\text{MET} - (3)^2\Pi_u] + 2e^-$$
$$|$$
$$D_{\infty h} \rightarrow C_{2v} \hspace{3cm} (11a)$$
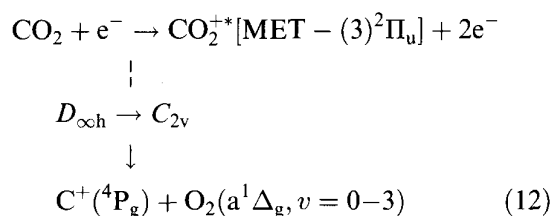$$\downarrow$$
$$C^+(^4P_g) + O_2(X^3\Sigma_g^-, v = 0-3 \pm 1)$$

must be involved between 28.3 and 30.1 eV, and where the oxygen molecule is distributed between $v=0$ and $v=3(\pm1)$ vibrational quanta, $\omega_e(O_2-X^3\Sigma_g^-) = 0.195$ eV (1580 cm^{-1}) [41]. This energy range covers the MET states located between 26.5 and 30.0 eV [36-38] where an ionization cross section of CO_2 is measured [37]. This

reaction also has to follow a pathway involving a $D_{\infty h} \rightarrow C_{2v}$ change in geometry.

The appearance energy at 29.18 ± 0.17 eV is the starting point of a straight line 5 resulting from a linear regression applied to six data points. The correlation coefficient being 0.971, the calculated slope is 0.436 ± 0.023 and the extrapolation is 29.18 ± 0.04 eV. As observed in all previous C^+-producing processes, this dissociative ionization reaction would also give rise to excess energy partitioning between internal and translational energy. However, as shown by Fig. 9, it is the only process contributing to zero-energy C^+ ions.

With the help of these data, the dissociative ionization process responsible for C^+ ion formation at 29.18 eV is most likely

$$CO_2 + e^- \rightarrow CO_2^{+*}[\mathbf{MET} - (3)^2\Pi_u] + 2e^-$$
$$\vdots$$
$$D_{\infty h} \rightarrow C_{2v}$$
$$\downarrow$$
$$C^+(^4P_g) + O_2(a^1\Delta_g, v = 0-3) \qquad (12)$$

for which a threshold is calculated at 29.021 eV, in fairly good agreement with the experimental value. The CO_2^+ ionic state involved is probably the MET state at about 29.0 eV [37]. As the onset at 28.31 eV, this threshold at 29.18 eV is significantly lower than 30 eV. The MET state involved could be the third $^2\Pi_u$ state derived from the $(1\pi_g)^2 (2\pi_u)^1$ configuration. Its decomposition produces O_2 molecular species through a change from linear to bent geometry.

The onset measured by Stockdale et al. [18] at 29.8 ± 0.3 eV is probably related to this process. However, these authors assigned the appearance energy to Coproduction together with two oxygen atoms.

A last critical energy is measured in the C^+ ionization efficiency curve at 31.27 ± 0.20 eV, as averaged over 65 measurements between 0.0 and 1.6 eV kinetic energy. A vertical line can be drawn through these data points. This energy is in very good agreement with the vertical ionization energy of the multiple electron excited MET(III) state determined at 30.0 ± 0.5 eV [37] and at 31.5 eV [36,38].

At 1.6 eV translational energy, a straight line 6 extending up to 3.6 eV kinetic energy carried by C^+ is defined by 10 data points. The linear regression applied to these data provides a correlation of 0.994 for a straight line with a slope of 0.373 ± 0.015. The slope being lower than 0.727, the threshold for zero-energy C^+ ions obtained by the usual method is $AE(C^+)_{KE=o} = 29.07 \pm 0.20$ eV. This energy corresponds well to the required energy for reaction (12) where the $O_2 (a^1\Delta_g)$ species is also distributed between $v = 0$ and $v = 3$.
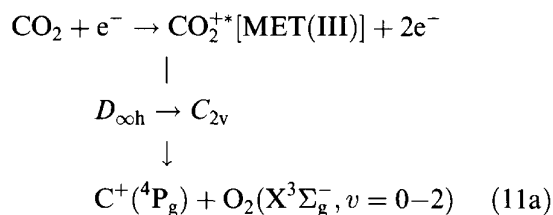
In spite of the good agreement between experimental and predicted values, it should be mentioned that, owing to the error of 0.20 eV in the onset at 31.27 eV reflecting the zero-energy threshold, the possibility of decomposition through

$$CO_2 + e^- \rightarrow C^+(^2P_u) + O_2(B^3\Sigma_u^-) + 2e^-$$
$$(13)$$
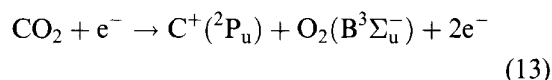
for which an appearance energy of 28.828 eV is calculated, cannot be strictly discarded.

At 2.4 eV translational energy, a straight line 7 starts from the vertical line at 31.27 eV. The linear regression applied to these data points provides a correlation coefficient of 0.990 and a slope of 0.549 ± 0.030. This value being lower than the expected slope, the dissociation level $AE(C^+)_{KE=0}$ is obtained by the subtraction $31.27(\pm 0.20) - 2.4 \times 44/32 = 27.97 \pm 0.20$ eV.

This dissociation level corresponds well to the energy calculated for processes (10) and (11). As already pointed out earlier, the fact that the slope of straight line 7 is lower than 0.727 implies excess energy partitioning between the kinetic energy of the fragments and the internal energy of the diatomic fragment O_2. On the basis of this argument, process (10) has to be discarded, and at 31.27 eV the C^+ ions produced with KE = 2.4-3.6 eV will be formed through the reaction

$$CO_2 + e^- \rightarrow CO_2^{+*}[MET(III)] + 2e^-$$

$$|$$

$$D_{\infty h} \rightarrow C_{2v}$$

$$\downarrow$$

$$C^+(^4P_g) + O_2(X^3\Sigma_g^-, v = 0-2) \quad (11a)$$

involving the geometry change $D_{\infty h} \rightarrow C_{2v}$ The shape of the KE versus AE diagram above 31 eV shows that the MET(III) state of CO_2^+ branches off into two reaction paths, i.e. mechanisms (12) and (11a).

6. Conclusions

This work presents the results from a detailed dissociative electroionization study of CO_2. The appearance energies as functions of the fragment translational energy have been reported for the three dissociation channels, i.e. C^+, O^+ and CO^+. The O_2^+ ion produced by dissociative ionization of CO_2 has not been detected.

From the detailed discussion of all three dissociation channels a qualitative overview of the dissociation of the ionized CO_2 molecule for electron energies ranging from 19 to 40 eV can be put forward.

At low energy, the appearance of the O^+ and CO^+ ions through the predissociation of the $CO_2^+(C^2\Sigma_g^+)$ state has been confirmed. The details of the mechanism have not been discussed in this work, but were analyzed in the PIPECO work of Bombach et al. [10].

Fig. 10. Tentative assignment of dissociative ionization pathways of the multiple MET states of CO_2 in the O^+, CO^+ and C^+ channels.
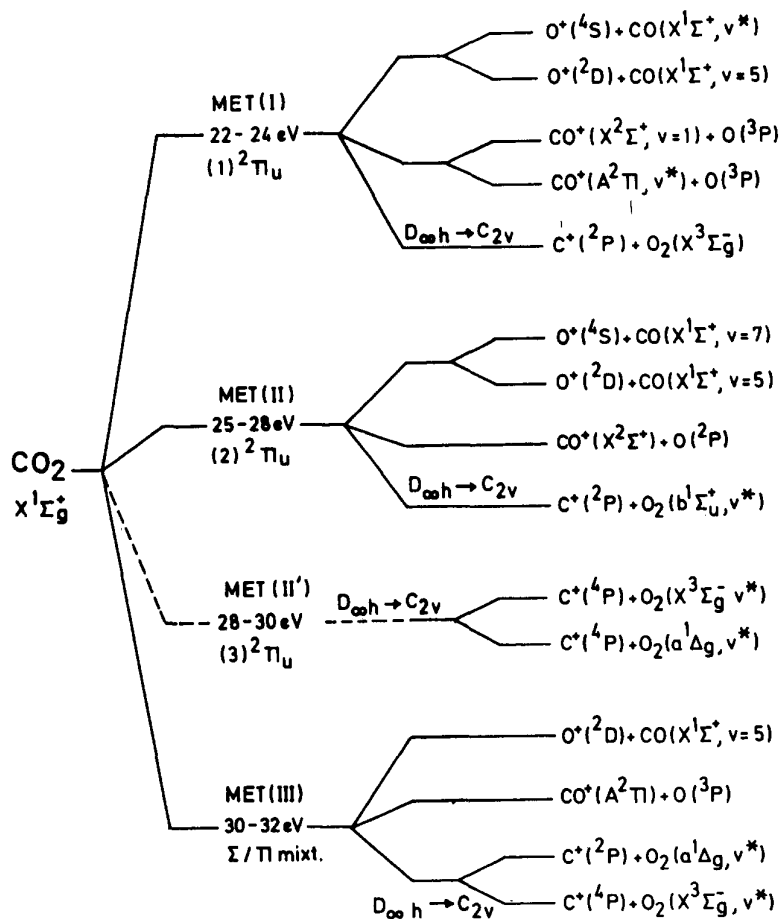
The present work has been extended to electron energies well above 21 eV, and it contributes to a more precise insight into the fate of the MET states lying between 22 and 40 eV electron energy. The decomposition of these states plays a major role; they are probably all unstable (repulsive or pre-dissociated) in all three dissociative ionization channels. Hitchcock et al. [14] published a tentative "dipole" breakdown scheme for fragmentation resulting from photoionization. In this crude scheme a number of dissociative ionization reaction paths of CO_2^+ (MET states) were omitted.

In particular, the MET states below 30 eV, i.e. essentially those three identified by Domcke et al. [39] as being $^2\prod_u$ states, only evolve CO^+ and O^+ ions in Ref. [14]. The present work shows unambiguously that C^+ ions are also produced. Above 30 eV, the MET states not only decompose into O^+ and C^+ ions, as suggested in Ref. [14], but also give rise to CO^+ ions. At around 29 eV there is most probably an MET state, tentatively assigned to the third $^2\Pi_u$ state, which should only produce C^+ ions. Further, the vibrational and/or electronic state of the fragments as well as their translational energy could be specified in this work. These conclusions are summarized in Fig. 10.

Finally, and contrary to previously reported results on C^+, we found *no evidence for a reaction path* leading to the $C^+ + 2O$ dissociation channel in the 19-40 eV electron energy range.

Acknowledgements

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