

# MASS SPECTROMETRIC STUDY OF DISSOCIATIVE ELECTRON ATTACHMENT IN CARBON DIOXIDE (\*)

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## ABSTRACT

The DA efficiency curve of  $O^-$  in  $CO_2$  has been studied mass spectrometrically. Combining the use of the convolution of theoretical models and of the deconvolution of the experimental curves, beside the previously reported DA peaks, some new DA processes have been determined at  $(6.0 \pm 0.3)$  eV and  $(13.3 \pm 0.4)$  eV for  $O^-$  in  $CO_2$ . A progressive conversion of electronic into vibrational excitation of diatomic radicals and into KE of the fragments is postulated as responsible for the threshold at  $(6.0 \pm 0.3)$  eV.

## INTRODUCTION

From careful mass spectrometric investigations about the negative ions appearance by Dissociative Electron Attachment (D.A) [<sup>1,2</sup>] in  $H_2$ ,  $CO$ ,  $NO$  and  $O_2$ , some informations have been obtained concerning the transient molecular negative ion species involved in the observed processes.

The aim of this paper is to report new experimental data and the results of their treatments by previously described methods [<sup>1,2,3</sup>] about the D.A efficiency curves observed for negative ions formed from carbon dioxide.

## I. EXPERIMENTAL

The mass spectrometer and the experimental conditions, used for the ionization efficiency curves recording, have been described previously [<sup>1,2</sup>].

The reference used as electron energy scale calibration for the study of the D.A. processes giving  $O^-$  from  $CO_2$  is the first D.A. peak observed for  $S^-$  from  $CS_2$  occurring at  $(3.02 \pm 0.12)$  eV,

In order to improve the accuracy of the experimental data, all the ionization efficiency curves presented here are the average of ten independent measurements. The D.A. efficiency curves have been deconvoluted [<sup>4,5</sup>] and the convolution of theoretical models [<sup>1,2</sup>] has also been used.

## II. EXPERIMENTAL RESULTS AND DISCUSSION

### A. Dissociative Electron Attachment of $O^-$ from $CO_2$

The mean of ten experimental curves and the deconvoluted ionization efficiency curve of  $O^-$  from  $CO_2$  are drawn in figure (1) and the observed thresholds are listed in table I.

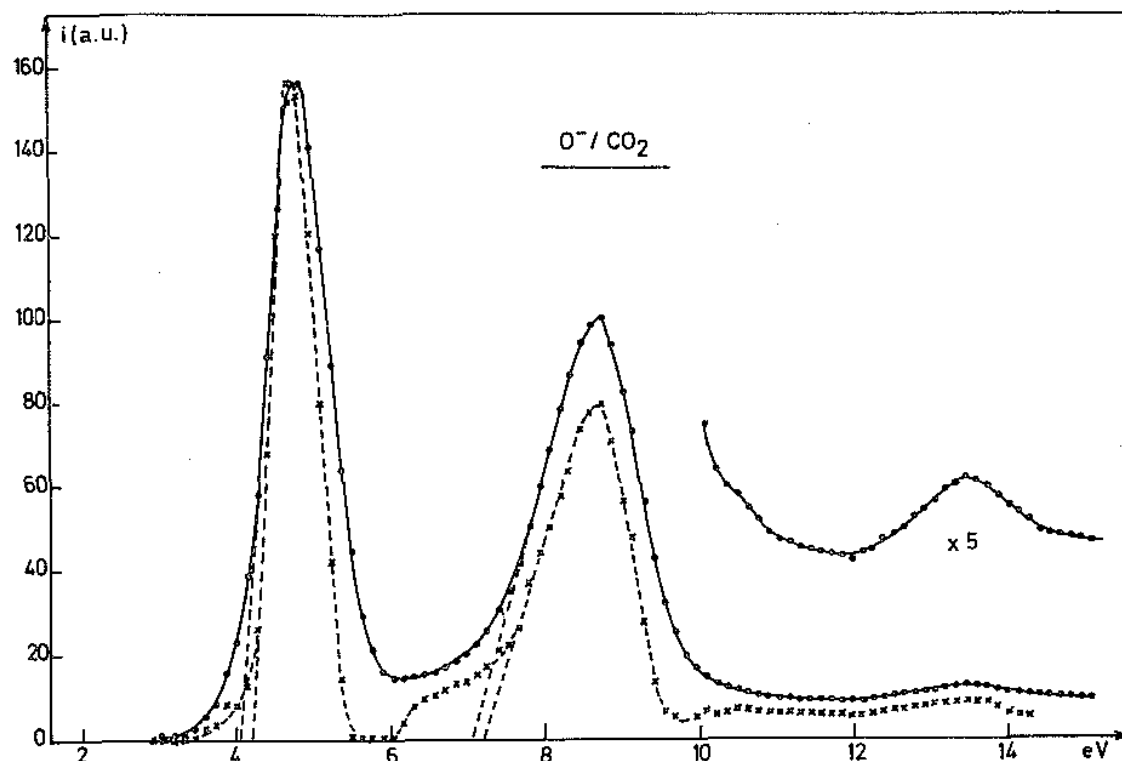
Together with previously published results.

TABLE I(\*)

G. J. SCHULTZ [ <sup>8</sup> ]	$3.85 \pm 0.1$	—	$6.6 \pm 0.1$	—
J. D. CRAGGS and B. A. TOZER [ <sup>7</sup> ]	—	—	$6.7 \pm 0.1$	—
K. KEAUS [ <sup>8</sup> ]	$3.96 \pm 0.1$	—	$7.0 \pm 0.2$	—
Present work	$4.2 \pm 0.3$	$6.0 \pm 0.3$	$7.2 \pm 0.3$	$13.3 \pm 0.4$ (M)

(\*) Energies expressed in electronvolts.

**Fig. 1.** — D.A. attachment ionization efficiency curve of  $O^-$  from  $CO_2$  : (●) direct curve, (\*) déconvoluted curve. The D.A. peak at  $(13.3 \pm 0.3)$  eV has been magnified by five.



The general shape of the curve is in agreement with the shape observed by total ionization  $[^{6,7,8}]$  measurements. The relative intensities of the peaks only are different.

### Discussion.

From the best accepted values of  $D(O - CO) = 5.433$  eV  $[^9]$  and  $EA(O) = 1.465$  eV  $[^{10}]$  one calculates the following energy limits for D.A. processes in  $CO_2$  using the CO electronic terms  $T_e(a^3\Pi) = 6.03$  eV  $[^{17}]$  and  $Te(A^1\Pi) = 8.07$  eV  $[^{17}]$

- (1)  $CO_2(X^1\Sigma_g^+) + e^- \rightarrow (CO_2^-) \rightarrow CO(X^1\Sigma^+) + O(^2P_u)$ ; A.P. = 3.99 eV
- (2)  $(CO_2^-) \rightarrow CO(a^3\Pi) + O(^2P_u)$ ; A.P. = 10.02 eV
- (3)  $(CO_2^-) \rightarrow CO(A^1\Pi) + O(^2P_u)$ ; A.P. = 12.10 eV

The table I shows that four thresholds have been found in our investigation and that probably a fifth, one occurs around 10 eV.

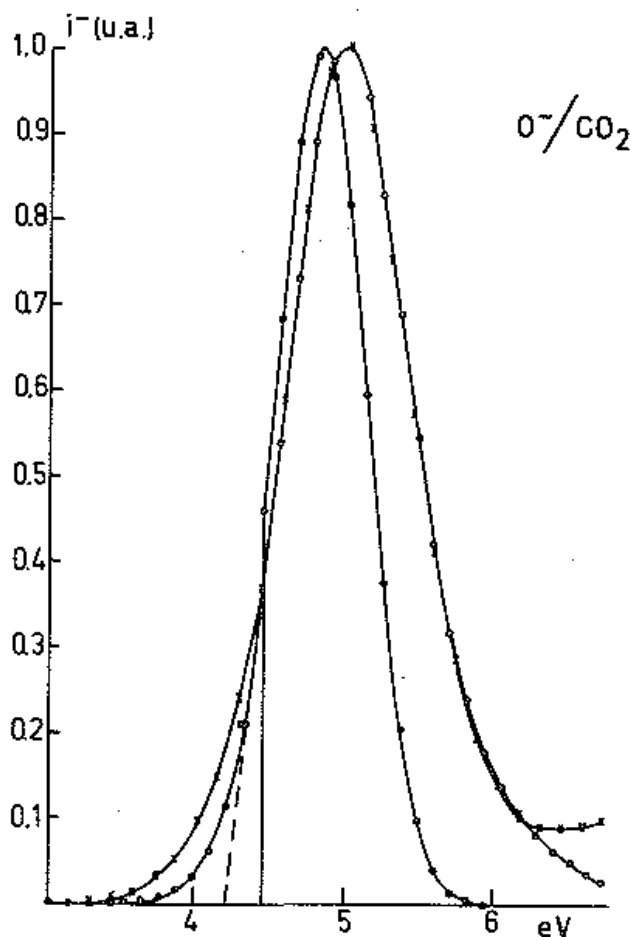
From infrared and ultraviolet absorption studies of  $CO_2^-$  ions trapped in irradiated solids  $[^{22}, ^{23}]$ , it follows that  $CO_2^-$  is certainly in a bent configuration as the isoelectronic  $NO_2$  and  $FCO$  species.

For the discussion of the results reported in this paper we will however accept, and this opinion is supported by others  $[^{13,14}]$ , that the electronic transition in the gaseous phase between  $CO_3$  and the continua going on to the  $O^-$  and  $CO$  fragments, takes place in a time short enough as to preserve the  $D_{\infty h}$  symmetry of the  $CO_2$  molecule.

This assumption makes us able to describe the occurrence of the first three thresholds lying well below 10.0 eV as related to transitions between the  $^2\Pi_u$  and  $^2\Sigma_g^+$  states of  $CO_2^-$  correlated with the first energy limit, lying at 3.99 eV  $[^{11}, ^{12}]$ .

a) *The process at  $(4.2 \pm 0.3)$  eV.* When in a first approximation, the appearance of  $O^-$  from  $CO_2$  is considered as resulting from the dissociation of the quasi-diatomic  $O^- - (CO)$  linear molecular negative-ion, the antisymmetric stretching vibrational frequency  $\nu_3$  ( $2349\text{ cm}^{-1}$  [9]) of the  $CO_2$  molecule can be chosen for the evaluation of the  $|\psi|^2$  function [1,2]. Figure (2) shows the theoretical model, the convolution of which fits at best the first experimental D.A. peak. Both the theoretical model and the deconvoluted peak are characterized by a width at half-height of 0.6 eV. The theoretical model shows that the  $O^-$  ion appears without kinetic energy (RE) excess at threshold, in agreement with previous works [6].

**Fig. 2.** — The first D.A. peak of  $O^-$  in  $CO_3$ : (x) experimental curve (●) theoretical model; (o) convoluted theoretical model.



Moreover, the agreement between the experimentally determined onset and the calculated threshold at 3.99 eV allows us to ascribe the appearance potential at  $(4.2 \pm 0.3)$  eV to the first mechanism which gives rise to  $O^-$  and CO in their ground state.

Furthermore, in the frame of the foregoing considerations, the assumption, of the antisymmetric vibrational mode excitation appears to be valid. The relatively small temperature dependence of the first peak [15, 16] up to 500° K supports this assumption. The above proposed mechanism (1) could take place by means of a direct electronic transition from the  $X^1\Sigma_g^+$  state of  $CO_2$  up to the dissociation limit of the  $^2\Sigma_u$  molecular ion state, at or very nearly to the equilibrium internuclear distance of the ground vibronic state of  $CO_2$  [11,12].

b) *The processes at  $(6.0 \pm 0.3)$  eV and  $(7.2 \pm 0.3)$  eV.*

By deconvoluting the experimental ionization efficiency curve as by subtracting the convoluted theoretical model, shown in figure (2), from the experimental ionization efficiency curve, we are able to evidence a new peak, the threshold of which lies at  $(6.0 \pm 0.3)$  eV. Beside this peak, the previously reported second D.A. process is found at  $(7.2 \pm 0.3)$  eV.

The energy difference of  $(1.8 \pm 0.3)$  eV and  $(3.0 \pm 0.3)$  eV between the first threshold and the two last mentioned onsets cannot be correlated nor with the appearance of  $O(^2P_u)$  together with CO in one of its excited states  $a^3\Pi$  or  $A^1\Pi$  (lying respectively at 6.03 eV and 8.07 eV above the ground vibronic  $X^1\Sigma^+$  state of CO [17]) nor with the dissociation of CO in C and O atoms in their ground level, process for which an additional energy of 11.11 eV has to be supplied [17].

A first interpretation of the D.A. process lying at  $(6.0 \pm 0.3)$  eV could be the decomposition of the  $CO_2^-$  molecular ion through an excited state converging to the dissociation limit at 3.99 eV, by the mechanism (1) involving a energy excess of  $(1.8 \pm 0.3)$  eV, spreaded over the two fragments, In such a case the KE carried away by  $O^-$ , plotted against the electron energy would lie on a straight fine converging to the 4.2 eV threshold energy.

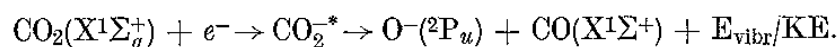
This expectation is however not in agreement with the experimental results about the KE values of  $O^-$  as they have been plotted against electron energy by CRAGGS [7] and SCHULZ [6]. Their curves show, around 6.5 eV, a KE distribution ranging between zero eV to 0.5 eV [6] (or 1.5 eV [7]) within an 0.1 eV [6] (or 0.5 eV [7]) electron energy range. Both this particular situation and an energy excess of 1.8 eV with respect to the first threshold lying at 4.2 eV, can obviously not be interpreted only by a direct electronic transition to a repulsive molecular state.

In the range of 7 eV to 9 eV the KE distribution versus electron energy is, fitted by a straight line with a slope of 28/44.

In order to account for the D.A. peaks at 6,0 eV and 7,2 eV, and for the above reported results about the KE carried away by  $O^-$  [6,7], an electronic to vibrational energy transfer during the instantaneous dissociation of  $CO_2^-$  could be postulated. This mechanism was proposed by KARL, KRUS and POLANYI [19] in order to explain the vibrational excitation spectrum of CO obtained by collision of this molecule with metastable mercury atoms. They suggest the formation of a  $(Hg - CO)^*$  intermediate complex, which may be considered as the analog of the  $(O^- - CO)^*$  compound state.

From the 6.0 eV threshold up to 7.2 eV, the  $(1.8 \pm 0.3)$  eV electronic energy is entirely converted into vibrational excitation energy of CO, and no KE is carried away by the  $O^-$  ion. The low efficiency for this energy transfer is responsible for the low cross section of the D.A. peak. At slightly higher energies only a fraction of the electronic energy is converted to vibrational energy of CO, the other fraction being converted in translational energy spreaded over the fragments. At the limit, the whole electronic energy is converted in kinetic energy, corresponding to the linear dependence of the KE, carried away by  $O^-$ , versus the electron energy in the range of 7.2 eV to 9 eV [6,7], in agreement with the curve published by CRAGGS [7].

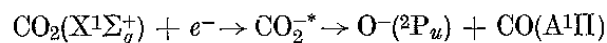
The mechanism of formation of  $O^-$  from 6 eV to 9 eV is therefore,



which takes place by an electronic transition to a repulsive molecular-ion state, converging to the dissociation limit at 3.99 eV. This state is the  $^2\Sigma_g^+$  state belonging to the linear configuration of  $CO_2^-$  [12].

c) *The process with its maximum lying at  $(13.3 \pm 0.4)$  eV.*

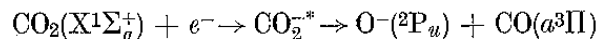
The energy difference of  $(8.3 \pm 0.3)$  eV between D.A. peaks having their maxima at 5.0 eV and 13.3 eV corresponds, within experimental error, to the excitation of CO to its first excited  $A^1\Pi$  state, 8.07 eV above its ground vibronic state  $X^1\Sigma^+$  [17]. The most probable interpretation of this D.A. process is the mechanism



The a priori evaluated threshold for this reaction lies at 12.1 eV.

The combination of  $^2P_u$  and  $^1\Pi$  terms gives rise to the occurrence of doublet  $\Sigma^+$ ,  $\Sigma^-$ ,  $\Pi$  and  $\Delta$  states, assuming a linear geometry of the  $CO_2^-$  molecular ion. CLAYDON and al. [12] calculations do not provide a potential energy curve of a state dissociating by mechanism (3). The electronic transition giving rise to the D.A. peak at 13.3 eV will probably take place at or very nearly to the 12.1 eV dissociation limit of a  $CO_2^-$  stable state.

In the deconvoluted curve around  $(9.8 \pm 0.3)$  eV, a slight increase of the negative ion-current occurs. FREUND [20] and CLAMPITT [21] observed a metastable state of  $\text{CO}_2$  dissociating in  $\text{CO}(a^3\Pi)$  and having a dissociation limit at 10.3 eV where  $\text{CO}_2$  should dissociate by



having its outset at 10.02 eV. CLAYDON and al. [12] correlate the mechanism (2) with an unstable  $^2\Pi_g$  state. From our experimental results, the dissociation of  $\text{CO}_2^-$  around 10 eV has to take place at or very close to the dissociation limit of a  $\text{CO}_2^-$  stable state.

## REFERENCES

- [1] R. LOCHT, J. MoMIGNY, *Inter. J. Mass. Spectrom. Ion Phys.*, 2 (1969), 425.
- [2] R. LOCHT, J. MOMIGNY, *Inter. J. Mass. Spectrom. Ion Phys.*, 4 (1970), 379.
- [3] R. LOCHT, J. MOMIGNY, *Intern. J. Mass. Spectrom. Ion Phys.*, 7 (1971), 121.
- [4] J. C. LECLERC, Thèse de Doctorat (Annexe), Liège 1970.
- [5] K. A. G. MECNEIL, J. C. J. THYNNE, *Intern. J. Mass Spectrom. Ion Phys.*, 3 (1969), 35.
- [6] G. J. SCHULZ, *Phys. Rev.*, 128 (1962), 178.
- [7] J. D. GRAGGS, B. A. TOZEK, *Proc. Phys. Soc.*, 254A (1960), 229.
- [8] K. KRATUS, *Z. für Naturf.*, 16a (1961), 1378.
- [9] G. HERZBERG, *Electronic Spectra and Electronic Structure of Polyatomic Molecules*, D. Van Nostrand, Princeton (1967).
- [10] L. M. BRANCOMB, D. S. BURCE, S. J. SMITH, S. GELTMAN, *Phys. Rev.*, 111 (1958), 504.
- [11] J. N. BARDSLEY, *J. Chem. Phys.*, 51 (1969), 3384.
- [12] C. R. CLAYDON, G. A. SEGAL, H. S. TAYLOR, *J. Chem. Phys.*, 52 (1970), 3387.
- [13] L. W. LARKIN, J. B. HASTED, *Chem. Phys. Lett.*, 5 (1970), 325.
- [14] D. ANDRICK, F. H. READ, *J. Phys.*, B 4 (1971), 389.
- [15] G. J. SCHULZ, D. SPENCE, *Phys. Rev. Lett.*, 22 (1969), 47.
- [16] D. SPENCE, G. J. SCHULZ, *Phys. Rev.*, 188 (1969), 280.
- [17] G. HERZBERG, *Spectra of Diatomic Molecules*, D. Van Nostrand, Princeton (1950).
- [18] D. RAPP, D. D. BRIGLIA, *J. Chem. Phys.*, 43 (1965), 1480.
- [19] G. KARL, R. KRUUS, J. C. POLANYI, *J. Chem. Phys.*, 46 (1967), 224.
- [20] R. S. FREUND, W. KLEMPERER, *J. Chem. Phys.*, 47 (1967), 2897.
- [21] R. CLAMPITT, A. S. NEWTON, *J. Chem. Phys.*, 50 (1969), 1997.
- [22] G. W. CHANTRY, D. H. WHIFFEN, *Mol. Phys.*, 5 (1962), 189.
- [23] D. W. OVENALL, D. H. WHIFFEN, *Mol. Phys.*, 4 (1961), 135.