

MASS SPECTROMETRIC INVESTIGATION OF THE APPEARANCE OF NEGATIVE IONS BY DISSOCIATIVE ELECTRON ATTACHMENT IN POLYATOMIC MOLECULES.

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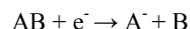
ABSTRACT

The appearance of negative ions by dissociative electron attachment has been studied by electron impact on CH₄, C₂H₂, C₂H₄ and C₂H₃X (X = F, Cl) using a sector field mass spectrometer. An interpretation has been attempted for the measured appearance potentials. The electron affinity of C₂ and C₂H radicals is found to be (3.3 ± 0.3) eV and (2.3 ± 0.2) eV respectively. Some evidence is brought for the existence of excited electronic states in polyatomic negative ions.

INTRODUCTION

In previous publications [1, 2] we reported in detail about a study devoted to the appearance of negative ions by electron impact in the gas phase and more particularly to the appearance of negative ions by dissociative electron attachment in diatomic molecules.

In the dissociative electron attachment of an electron to a diatomic molecule



the molecule undergoes an electronic transition to a continuum of an electronic state of the AB^{*} system. Accepting the validity of the Franck-Condon principle during this transition it has been established:

a) the theoretical shape of the cross section $\sigma(E)$ for dissociative electron attachment as a function the electron energy using the convolution technique,.

This curve is strongly related to (i) the relative position of the potential energy curves of the initial (AB) and final (AB^{*}) state and (ii) the shape of that part of the potential energy curve of the AB^{*} system in the Franck-Condon region. Both these two elements determine the kinetic energy distribution carried away by the negative ion.

b) a non-arbitrary method for the determination of the onset of appearance of negative ions by dissociative electron attachment. This method consists by defining the threshold of appearance of the negative ion by the point of intersection between the extrapolation of the low-energy side of the dissociative electron attachment peak with the electron energy axis.

The aim of the present work is the study of the appearance of negative ions by dissociative electron attachment in the polyatomic molecules CH₄, C₂H₂, C₂H₄ and C₂H₃X (X = Cl, F). In a previous work Von Trepka [6] devoted a study of the appearance of negative ions by dissociative electron attachment in CH₄, C₂H₂ et C₂H₄. We reinvestigated these molecules with the purpose to interpret the threshold of all the observed processes. Other processes proposed by this author are revised on the basis of the most recent data on dissociation energies of the involved molecules and the heats of formation of the radicals.

To determine the threshold of dissociative electron attachment we adopted the linear extrapolation method used in the case of diatomic molecules [1, 2].

¹ Présenté par M. L. D'OR.

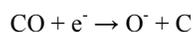
I. EXPERIMENTAL CONDITIONS.

The experimental results mentioned in the following sections were obtained by electron impact and using a Nier-type 60° sector field mass spectrometer (Atlas CH4) equipped with the usual (AN4) type ion source.

The ions accelerated by a constant high voltage electric field of 3 kV, are mass analyzed in a variable magnetic field. The ion current is detected by an H.E.T.-type electron multiplier with 17 dynodes the first of which is set at 2.3 kV.

The electron current measured on the electron trap is maintained constant at 10 μA. It has been verified that the ion current intensity remains linearly dependent on the gas pressure in the ion chamber (of the order of 10⁻⁶ Torr). The electron currents and the pressures usually available in the ion chamber [6], are of 0.1 μ A to 3 μ A and of the order of 10⁻⁴ Torr respectively.

The ion focusing potentials are adjusted and maintained constant in such conditions to obtain the maximum intensity of the dissociative electron attachment peak of O⁻ from CO which threshold has been used as the reference for the electron energy scale calibration; the onset of



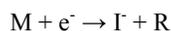
is located at 9.6 eV [3, 4].

The threshold energies mentioned in the present work are average values of at least three independent measurements of the energy difference between the onset(s) of the ions under investigation and the threshold of the reference ion recorded for each measurement. All the measurements mentioned in the following sections are given with their largest deviation from the average values. A sample of ionization efficiency curve for each ion will be displayed in the following sections.

II. EXPERIMENTAL RESULTS AND DISCUSSION.

Before describing and discussing the experimental results, the relation has to be reminded allowing us to calculate *a priori* the threshold of a dissociative electron attachment process, including a number of hypotheses,

In a polyatomic molecule M giving rise to the process:



its corresponding appearance potential AP (I) will be given by:

$$\text{AP (I)} = \text{D(I-R)} - \text{EA(I)} + E_{\text{cin}} + E_{\text{exc}} \quad (\text{I})$$

where D(I-R) is the dissociation energy of the I-R bond, EA(I) is the electron affinity of the atom or radical I, E_{cin} et E_{exc} are the kinetic energy and the excitation energy respectively carried away by the negative ion and/or the neutral fragment(s).

When ignoring the term D(I-R) and considering E_{cin} et E_{exc} negligible, the *a priori* evaluation of the threshold of the dissociative electron attachment process could be given by the relation:

$$\text{AP (I)} = \Delta U_f(\text{I}) + \Delta U_f(\text{R}) - \Delta U_f(\text{M}) \quad (\text{II})$$

where

$$\Delta U_f(\text{I}) = \Delta U_f(\text{I}) - \text{EA(I)}$$

and where ΔU_f(R), ΔU_f(M) et ΔU_f(I) are the heats of formation of the radical(s) R, the molecule M and the

negative ion Γ respectively. The heats of formation of the radicals and molecules considered in this work are listed in the appendix.

A. MÉTHANE CH_4 .

In Table I, the ions observed in the negative ion mass spectrum of methane have been listed together with their appearance energy. The experimental results reported by Smith [5] and Von Trepka [6] are also displayed. The latter author used the linear extrapolation method for the threshold energy determination for the dissociative electron attachment processes..

Owing to its weakness, the CH_3^- ion has been observed but has not been mentioned in this table.

TABLE I. Threshold energies (eV) of the negative ions from CH_4 .

	Ref. (5)	Ref. (6)	This work
H^-	6.1		
	6.9	8.3 ± 0.3	8.2 ± 0.2
	7.3	9.5 ± 0.3	9.4 ± 0.15
CH^-	10.2	9.6 ± 0.3	9.7 ± 0.2
CH_2^-	8.9	8.3 ± 0.2	
		9.3 ± 0.2	9.3 ± 0.3

DISCUSSION

a) L'ion H^- (figure 1)

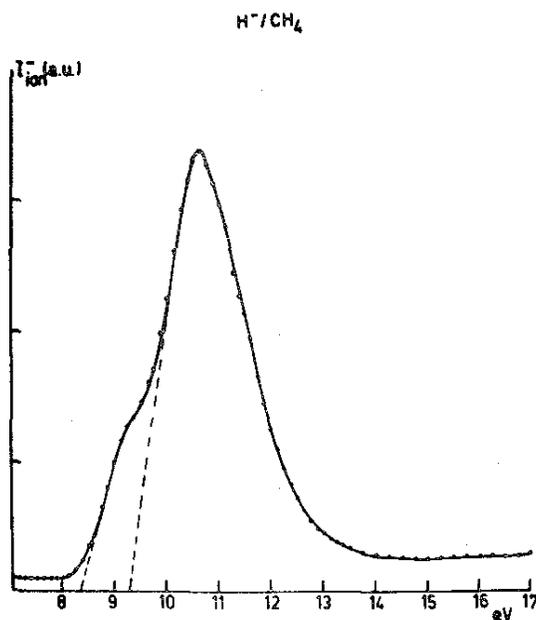


FIG. 1

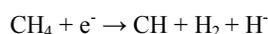
The mechanisms giving rise to H^- by dissociative electron attachment from methane have been listed in Table II.

The corresponding appearance energies are calculated by using relation (I), the most recent dissociation energy values $D(\text{CH}_3 - \text{H}) = 4.41$ eV [7], $D(\text{CH}_2 - \text{H}) = 4.90$ eV [8], $D(\text{CH} - \text{H}) = 4.23$ eV [8], $D(\text{C} - \text{H}) = 3.47$ eV [9] for the electron affinity $\text{EA}(\text{H}) = 0.75$ eV [10] and assuming E_{cin} et E_{exc} negligible in all cases.

TABLE II.

Mécanism	AP (eV)	
$\text{CH}_4 + e^- \rightarrow \text{CH}_3 + \text{H}^-$	3.66	(1)
$\text{CH}_2 + \text{H} + \text{H}^-$	8.56	(2)
$\text{CH} + 2\text{H} + \text{H}^-$	12.76	(3a)
$\text{CH} + \text{H}_2 + \text{H}^-$	8.28	(3b)
$\text{C} + \text{H}_2 + \text{H} + \text{H}^-$	11.75	(4a)
$\text{C} + 3\text{H} + \text{H}^-$	16.23	(4b)

Among these mechanisms, only the first two and (3 b) should be considered. It has been shown [1] that ions of low masses are usually affected by strong kinetic energy discrimination. It has also been shown that the focusing conditions mentioned earlier in this report do not allow us to detect H^- ions carrying kinetic energy above 3 eV. The kinetic energy that should be carried by H^- in process (1) would be of 4.6 eV. The most probable process that gives rise to H^- should be:



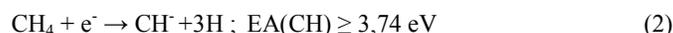
For which the calculated appearance energy (8.28 eV) is in good agreement with the experimental threshold (8.2 ± 0.2) eV.

The onset observed at 9.4 eV could be assigned to the appearance of the H^- ion (i) carrying a small amount of kinetic energy and the CH radical and H_2 molecule in their ground vibronic state or (ii) without kinetic energy with the CH radical or the H_2 molecule produced in a vibrationally excited state.

b) L'ion CH^- (figure 2)

The interpretation of the dissociative electron attachment process giving rise to CH^- requires the knowledge of the electron affinity of the CH radical. This quantity is experimentally not known very accurately [5, 6, 11]. A theoretical value of $\text{EA}(\text{CH}) = 1.6$ eV has been reported by Cade [12].

The mechanisms that could be involved at 9.7 eV are:



From the mechanism (1), a value of the electron affinity $\text{EA}(\text{CH}) \geq -0,64$ eV is deduced, providing that the kinetic energy involved in the process is equal to or higher than zero.

The systematic investigation of the appearance of the CH^- ion from C_2H_2 et C_2H_4 by the dissociative electron attachment and ion pair processes², led to $\text{EA}(\text{CH}) = (2.6 \pm 0.3)$ eV (see below and [13]).

The most probable mechanism for the production of the CH^- ion is process (1) where the CH^- ion should carry a certain amount of kinetic or vibronic excitation energy. The hydrogen molecule could appear in a vibrationally excited state.

Looking at the electronic excitation levels of the NH radical, isoelectronic of CH^- , one observes the possible existence of four electronic excited states in an energy range of 4 eV [9].

Considering the $X^3\Sigma^-$ being the ground electronic state of the ion CH^- , the value $\text{EA}(\text{CH}) = 1,6$ eV calculated by Cade [12] should correspond to CH^- in its first excited state and $\text{EA}(\text{CH}) = -0,64$ eV would correspond to the appearance of the CH^- ion in its second vibronic excited state carrying a certain amount of kinetic energy.

² During the ion pair process the molecule undergoes a vibronic excitation followed by a dissociation into a negative and positive ion through the mechanism: $\text{AB} + e^- \rightarrow \text{AB}^* + e^-$ followed by $\text{AB}^* \rightarrow \text{A}^+ + \text{B}^-$

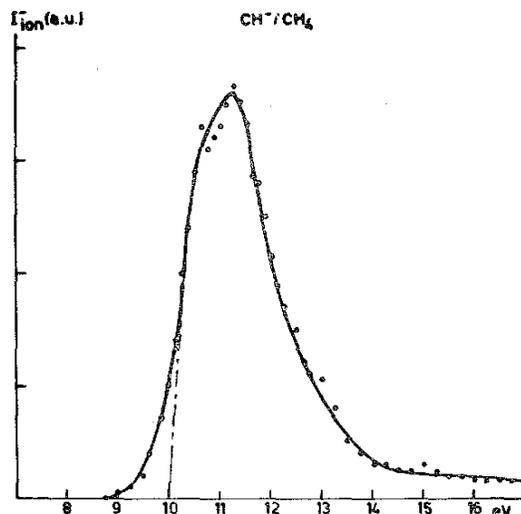


FIG. 2.

c) L'ion CH_2^- (figure 3)

Only two mechanisms could give rise to the CH_2^- ion:

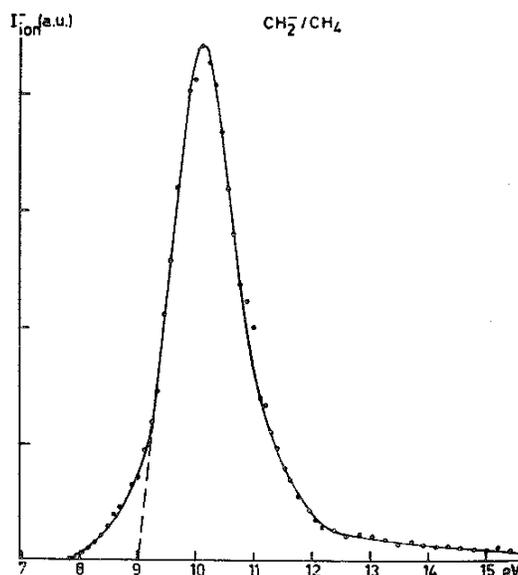
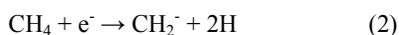
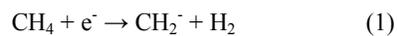


FIG. 3.

The value of the electron affinity of the CH_2 radical, obtained from the two above-mentioned mechanisms are $\text{EA}_1(\text{CH}_2) = -4,48 \text{ eV}$ et $\text{EA}_2(\text{CH}_2) = 0,0 \text{ eV}$ respectively. The mechanism (2) seems the most suitable for the interpretation of the threshold at $(9.3 \pm 0.3) \text{ eV}$.

B. ACÉTYLÈNE C₂H₂.

In the negative ion mass spectrum of acetylene only the H⁻, C₂⁻ and C₂H⁻ ions appear through the dissociative electron attachment process. In Table III are gathered the experimental results obtained in the present work and by Von Trepka [6],

TABLE III. Threshold energies (eV) of the negative ions from C₂H₂.

	Réf. (6)	This work
H ⁻	7.6 ± 0.3	7.2 ± 0.1
C ₂ ⁻	7.6 ± 0.2	7.5 ± 0.2
	11.8 ± 0.3	11.6 ± 0.2
		12.2 ± 0.2
C ₂ H ⁻	2.8 ± 0.2	2.8 ± 0.2
	6.0 ± 0.3	7.5 ± 0.2 (max.)

DISCUSSION

a) L'ion H⁻ (figure 4)

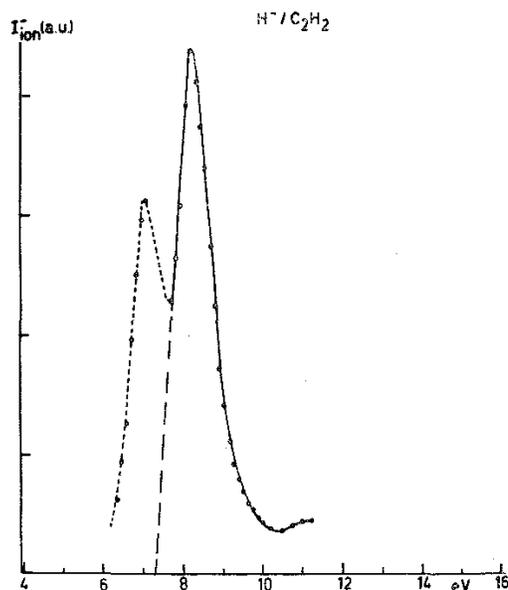


FIG. 4.

The threshold for the only observed dissociative electron attachment process giving rise to H⁻ lies at 7,2 eV; the peak starting at about 6 eV is assigned to the presence of residual water in the ion source. The dissociative electron attachment process giving rise to H⁻ from H₂O is characterized by a large cross section. The cross section for production of H⁻ from C₂H₂ is very small.

At the maximum of the dissociative electron attachment peak for the formation of H⁻ from H₂O, CH₄ and C₂H₂, recorded with the same experimental conditions, the intensity is 350 u.a., 66 u.a. et 7 u.a.(expressed in arbitrary units) respectively.

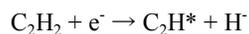
In Table IV are listed the mechanisms producing the H⁻ ion by dissociative electron attachment:

TABLE IV.

Mécanismes	AP _{calc.} (eV)
$C_2H_2 + e^- \rightarrow C_2H + H^-$	4.15 (1)
$C_2 + H + H^-$	10.05 (2)
$CH + C + H^-$	12.60 (3)
$2C + H + H^-$	16.07 (4)

Only mechanism (1) should be kept in mind. For the reason mentioned earlier, the energy difference of 3 eV between the experimental onset and the calculated threshold could not be accounted for by the kinetic energy carried by the H^- ion.

Most probably the H^- ion carries away a small amount or no kinetic energy and the C_2H radical is produced in a vibronic excited state.



b) L'ion C_2^- (figure 5)

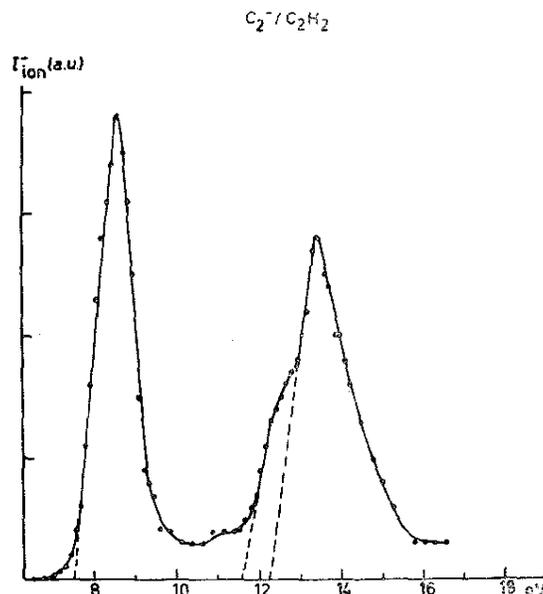
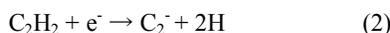
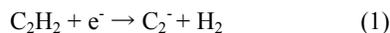
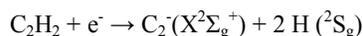


FIG. 5.

Three peaks corresponding C_2^- have been observed at 7.5 eV, 11.6 eV and 12.2 eV successively. Two mechanisms could produce the C_2^- ion through the dissociative electron attachment process in acetylene:



From these two mechanisms and the value of the first threshold of the C_2^- ion the heat of formation of this ion can be calculated, i.e. (1) $\Delta U_f(C_2^-) = 9.85$ eV and (2) $\Delta U_f(C_2^-) = 5.33$ eV, allowing the formation of C_2^- without kinetic energy. The value of the electron affinity of the C_2 radical would be -1.12 eV and 3.3 eV respectively. The latter value is in good agreement with the value 3.1 eV, the lowest value obtained by Honing [14] from the sublimation of graphite. The most probable mechanism for the interpretation of the onset observed at 7.5 eV should be:

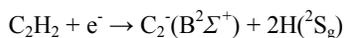


where the C_2^- ion appears in its ground electronic state $X^2\Sigma_g^+$ by comparison with the isoelectronic diatomic molecules CN and N_2^+ .

The onsets measured at 11.6 eV and 12.2 eV cannot be assigned to the appearance of the C_2^- ion in a vibronic excited state.

The first two electronic excited states of the CN radical are the $A^2\Pi$ and the $B^2\Sigma^+$ lying at 9241 cm^{-1} (1.15 eV) [9] and 25752 cm^{-1} (3.19 eV) [9] respectively.

Very likely at 11.6 eV et 12.2 eV the mechanism producing the C_2^- ion is:



where the C_2^- ion would be in the electronic excited state $B^2\Sigma^+$ and vibrationally excited or in the vibrational ground state of the $B^2\Sigma^+$ state and carrying a certain amount of kinetic energy.

z) *L'ion C₂H⁻* (figure 6).

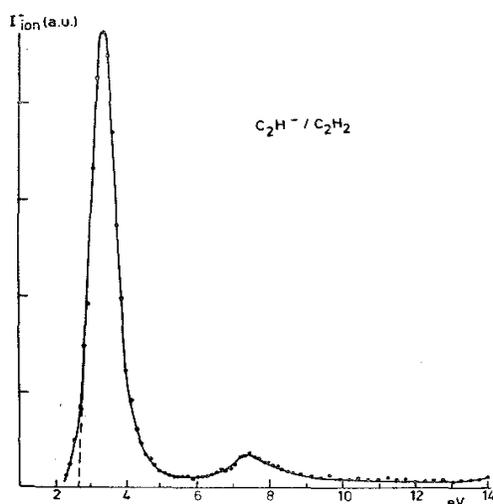
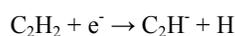


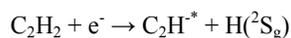
FIG. 6.

The only suitable mechanism to interpret the process observed at 2.8 eV is:



From $D(C_2H-H) = 4.90\text{ eV}$ [8], we obtain $(2.1 \pm 0.2)\text{ eV}$ for the electron affinity of the C_2H radical, the C_2H^- ion carrying a small amount or no kinetic energy.

A second but very weak process is observed and is characterized by a maximum at 7.5 eV and has a threshold at 6.6 eV. The energy interval of 3.8 eV could be assigned to the excitation of the C_2H^- ion. In the HCN molecule, isoelectronic of C_2H^- , the first electronic excited state is at 6.48 eV [8]. The most probable mechanism to be assigned to the threshold at 6.6 eV would be:



C. ETHYLENE C_2H_4 .

The experimental results related to the negative ions observed in the negative ion mass spectrum of ethylene are tabulated in Table V. In the same table the experimental results obtained by Von Trepka [6] are listed.

TABLE V. — Threshold energies (eV) of the negative ions from C_2H_4 .

	Réf. (6)	This work
H ⁻	7.6 ± 0.3	7.5 ± 0.3
	9.7 ± 0.4	9.6 ± 0.1
CH ⁻	7.3 ± 0.4	—
	8.7 ± 0.3	9.0 ± 0.1
CH ₂ ⁻	8.8 ± 0.3	—
C ₂ ⁻	10.4 ± 0.3	—
C ₂ H ⁻	7.1 ± 0.4	6.9 ± 0.1
	10.0 ± 0.3	9.9 ± 0.05

The H⁻ ion is of very low intensity and no signal has been detected at low energy and corresponding to CH₂⁻ and C₂⁻ in the energy range of 5 eV to 12 eV. For the C₂⁻ ion only the ion pair process is observed. At pressures of 10⁻⁴ Torr Von Trepka [6] detected these ions at low energy between 7 eV and 10 eV.

DISCUSSION

a) L'ion H⁻ (figure 7)

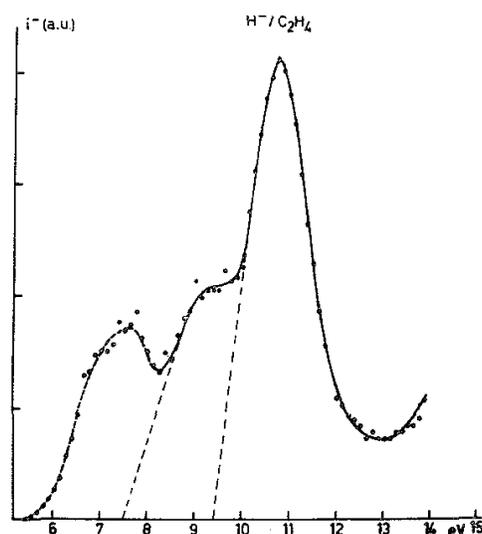


FIG. 7.

The peak at about 6 eV is assigned to residual water in the ion chamber. In Table VI only those dissociative electron attachment mechanisms having their $AP_{\text{calc}} \leq PA_{\text{exp}}$ are mentioned.

TABLE VI.

Mécanismes	$AP_{\text{calc.}}$ (eV)
$C_2H_4 + e^- \rightarrow C_2H_3 + H^-$	3.70 (a)
$C_2H_4 + e^- \rightarrow C_2H_2 + H + H^-$	5.58 (b)
$C_2H_4 + e^- \rightarrow C_2H + H_2 + H^-$	6.08 (c)

The energy differences between the first threshold at 7.5 eV and the calculated onsets are of 3.8 eV, 2.0 eV and 1.4 eV.

These differences could be assigned to 1° the kinetic energy carried away by the fragments, mainly by H⁻ or H and H⁻, and the vibronic excitation energy of the radicals; for the reasons mentioned above, only the mechanisms (b) and (c) have to be considered; 2° only the vibrational and electronic internal energy of the C₂H₃, C₂H₂, C₂H et H₂ fragments.

From these considerations we don't be able to assign one of these mechanisms to the threshold energies at 7.5 eV and 9.5 eV.

b) L'ion CH⁻ (figure 8)

The most probable mechanism producing the CH⁻ ion by dissociative electron attachment at 9.0 eV is:

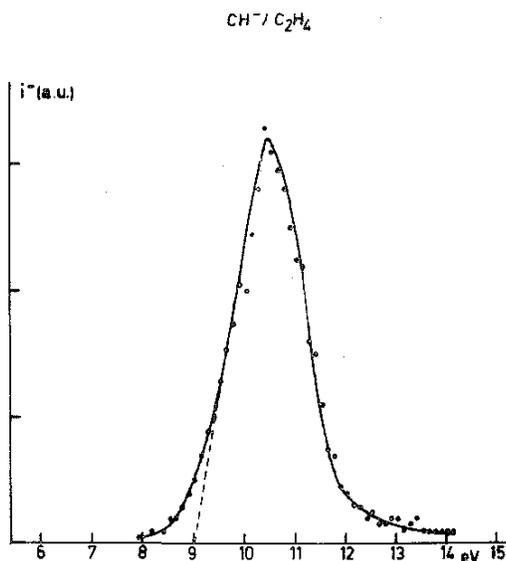


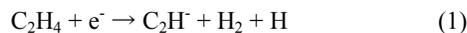
FIG. 8.

Admitting that no kinetic energy is carried away by the negative ion $\text{EA}(\text{CH}^-) = 2.7 \text{ eV}$ is calculated using $\text{D}(\text{CH}_2 = \text{CH}_2) = (7.6 \pm 0.3) \text{ eV}$ [9] and $\text{D}(\text{CH} - \text{H}) = 4.23 \text{ eV}$ [8].

c) L'ion C₂H⁻ (figure 9)

The two onsets for dissociative electron attachment producing the C₂H⁻ ion from C₂H₄ are measured at 6.9 and 9.9 eV.

From the two mechanisms suitable for interpretation of the appearance of the C₂H⁻ ion:



the heats of formation of the C₂H⁻ of 5,2 eV et 3,66 eV respectively have been calculated from the first onset. The corresponding electron affinities of the C₂H radical are $\text{EA}_1(\text{C}_2\text{H}) = (0.0 \pm 0.3) \text{ eV}$ and $\text{EA}_2(\text{C}_2\text{H}) = (1.6 \pm 0.3) \text{ eV}$. At 6.9 eV the most probable mechanism should be:



where the C₂H⁻ ion would be produced in an electronic excited state and carrying a given amount of kinetic energy [13].

The process with its threshold at 9.9 eV should be assigned to the mechanism :

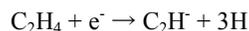
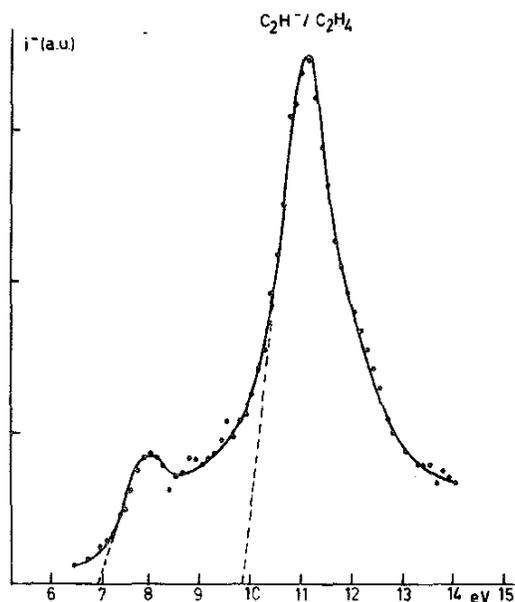


FIG. 9.



where the C_2H^- ion appears in its ground electronic state carrying a small amount of kinetic energy.

D. THE HALOGENATED DERIVATIVES OF ETHYLENE.

1. Vinyl chloride C_2H_3Cl

Among those ions of the mass spectrum of negative ions from vinyl chloride the dissociative electron attachment processes for the production of H^- and C_2H^- were only investigated. Their onset energies are listed in Table VII. The other ions being of very weak intensity were not measured and are not mentioned in this table.

TABLE VII. The threshold energies (eV) of the negative ions from C_2H_3Cl .

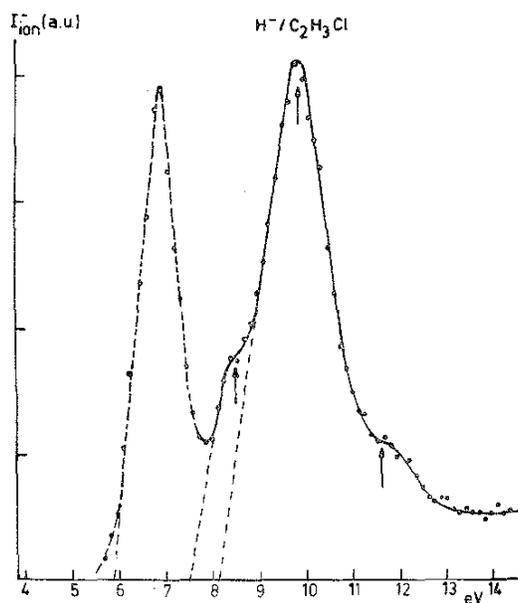
H^-		C_2H^-	
AP	ΔE	AP	ΔE
7.5 ± 0.2	0.7	6.17 ± 0.05	
8.2 ± 0.1		Maxima :	
		8.9 ± 0.1	
Maximum :		10.1 ± 0.1	1.2
11.6 ± 0.1		10.5 ± 0.05	0.4
		11.4 ± 0.1	0.9
		12.5 ± 0.4	1.1

DISCUSSION

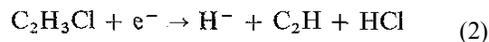
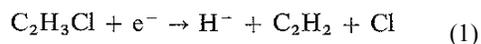
a) L^- ion H^- (figure 10)

The peak with the onset at 6.1 eV is assigned to the H^- ion from the residual water in the ion chamber. The intensity of the dissociative electron attachment of H^- from C_2H_3Cl is very weak. We measured two appearance energies, i.e. at (7.5 ± 0.2) eV and (8.2 ± 0.1) eV.

FIG. 10.



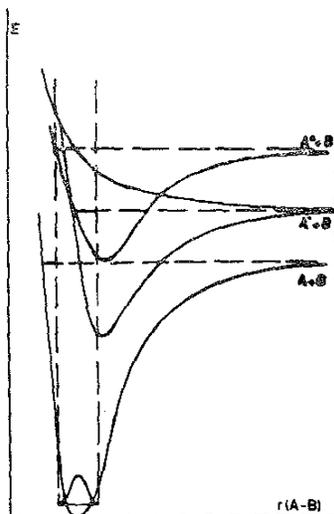
Among the processes for which the threshold can be calculated two of them give rise to the H^- ion through dissociative electron attachment:



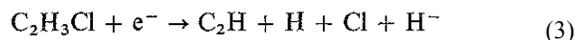
The onset energies are calculated at 5.41 eV and 5.97 eV respectively.

Two interpretations could account for the two measured appearance energies : (i) the production of the acetylene molecule in different vibrational excited states or the formation of the H^- ion at the expense of the molecular negative ion in various vibrationally excited states [« predissociation » mechanism [15] (figure 11)]; the H^- ion carries kinetic energy..

FIG. 11.



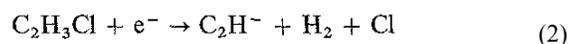
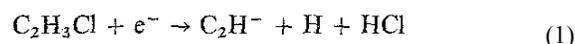
(ii) if the mechanism (2) accounts for the threshold at 7.5 eV and 8.2 eV the radical C_2H radical could be produced in vibronic excited states. The shoulder characterized by the maximum at (11.6 ± 0.1) eV is likely assigned to the mechanism:



Using $D(C_2H-H) = 4.9$ eV [8] et $D(H-Cl) = 4.43$ eV [9] from the two possible mechanisms (1) et (2) the onset at 10.31 eV is obtained whereas 10.51 eV is calculated for process (3). The H^- ion would carry away an amount of kinetic energy.

b) L' ion C_2H^- (figure 12)

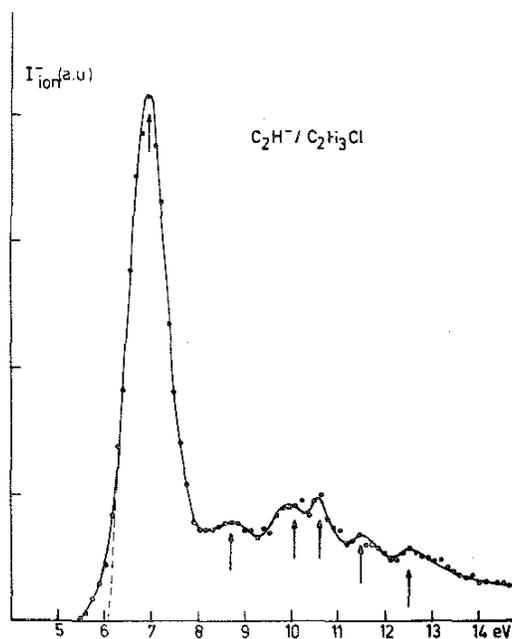
From the two reactions which could be assigned to the onset observed at (6.17 ± 0.05) eV,



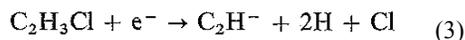
the heats of formation of the C_2H radical are obtained: $\Delta U_f(C_2H) = 4.56$ eV ou $\Delta U_f(C_2H) = 4.62$ eV respectively. The value deduced for the electron affinity is $EA(C_2H) = 0.6$ eV.

The investigation of the production of C_2H^- from C_2H_2 , C_2H_4 , C_2H_3Cl and C_2H_3F by the dissociative electron attachment and ion pair formation processes [13] provided the value $EA(C_2H) = (2.1 \pm 0.3)$ eV. It is likely that the C_2H^- ion appears through one of these two mechanisms carrying an amount of kinetic energy and/or in an electronic excited state..

FIG. 12.



The processes having their onset above the first threshold are very weak. The negative ion could be produced in excited states. The fragments H_2 and HCl could appear in their ground state or in vibrationally excited states. It could not be excluded that the process having its maximum at 11.4 eV could be assigned to:



its onset lying at (9.1 ± 0.3) eV using $EA(C_2H) = (2.1 \pm 0.3)$ eV [13].

2. Vinyl fluoride C_2H_3F .

In Table VIII are listed the appearance energies of the strongest negative ions in the mass spectrum of vinyl fluoride. A number of processes are characterized by the position of their maximum when the resolution doesn't allow us to use the linear extrapolation method.

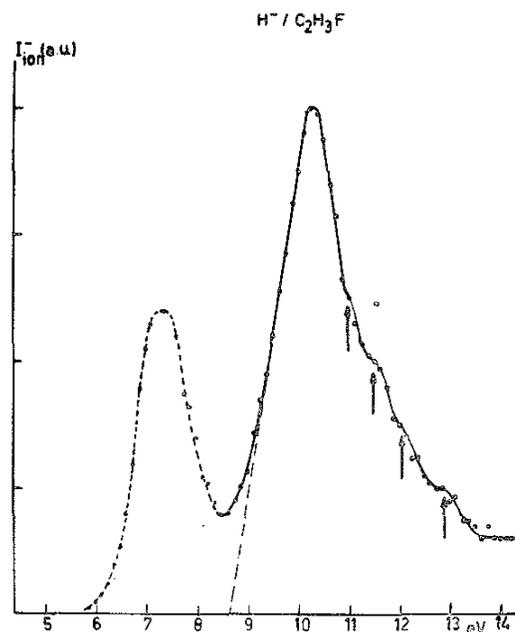
TABLE VIII. Threshold energy (eV) for the negative ions from C_2H_3F .

H^-		F^-		C_2^-		C_2H^-
AP	ΔE	AP	ΔE	AP.	ΔE	AP.
8.6 ± 0.1	0.6 0.7 0.7	1.5 ± 0.1	0.4 0.7 0.2 0.6	6.8 ± 0.1	0.7 0.8 0.8	6.9 ± 0.1
Maxima:		Maxima:		9.1 ± 0.08		9.1 ± 0.1
11.1 ± 0.2		7.5 ± 0.05		Maxima:		Maximum:
11.7 ± 0.1		7.9 ± 0.1		11.4 ± 0.05		11.2 ± 0.2
12.4 ± 0.2		9.5 ± 0.2		12.1 ± 0.05		
13.1 ± 0.2		10.2 ± 0.06		12.9 ± 0.2		
		10.4 ± 0.1		13.7 ± 0.2		
		11.0 ± 0.2				

DISCUSSION

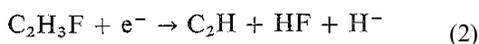
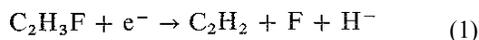
a) L'ion H^- (figure 13)

FIG. 13.



The dissociative electron attachment curve of H^- shows up as a broad peak made of a well defined maximum followed by four shoulders regularly spaced by 0.7 eV.

For the interpretation of the threshold at (8.6 ± 0.1) eV two processes could be considered for which $AP_{calc} \leq AP_{exp}$ and whose onset could be calculated:



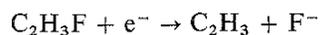
The onset calculated for the mechanism (1) is 5.89 eV; the onset of the second process is calculated at 5.02 eV.

The differences between the AP_{calc} and the experimental onsets are 2.7 eV and 3.6 eV respectively. The excess energies very likely correspond to the excitation of the C_2H_2 or HF molecules or the C_2H radical and/or to kinetic energy carried away by the H^- ion. If the process (1) is the simplest, we are not able to assign unambiguously one of the two mechanisms to the onset measured at 8.6 eV.

The fine structure observed above the maximum corresponding to the basic mechanism could be interpreted by the decomposition of the molecular ion through «predissociation» (figure 11). Such a phenomenon has been observed previously in molecular hydrogen by Dowell and Sharp [15].

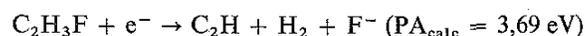
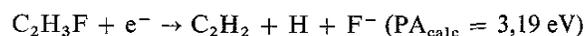
b) L'ion F^- (figure 14)

The dissociative electron attachment efficiency curve shows the existence of three processes. To a first and strongest peak corresponds a threshold at (1.5 ± 0.1) eV. Obviously only one process could account for it:



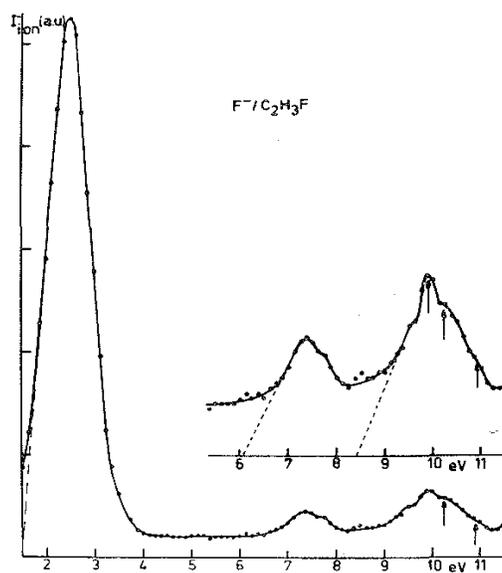
whose threshold is calculated at 1,31 eV. The F^- ion would carry away a small amount of kinetic energy.

To measure approximately the threshold of the two following processes we extrapolated the steepest slope of the low-energy side of the corresponding peaks. The second process would have an onset at 6.1 eV which could correspond to:

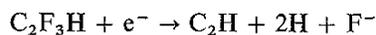


In both cases the F^- ion would appear carrying away kinetic energy and/or the C_2H radical or the C_2H_2 and H_2 molecules in a vibrationally excited state.

FIG. 14.



The probable onset of the third process lies at 8.5 eV: the appearance energy calculated for the mechanism

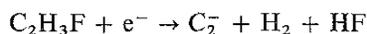


is at 8.2 eV. Very likely the three shoulders observed at the intervals of 0,7 eV, 0,2 eV and 0,6 eV have to be assigned to the appearance of the F^- ion from vibrational levels of the molecular ion through the « predissociation » mechanism [15].

c) L'ion C_2^- (figure 15)

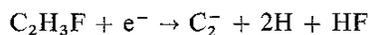
The shape of the ionization efficiency curve is very similar to that of the F^- ion: a peak followed by a complex structure.

The first onset is measured at (6.8 ± 0.1) eV. Calculating the heat of formation of the C_2^- ion from the mechanism:



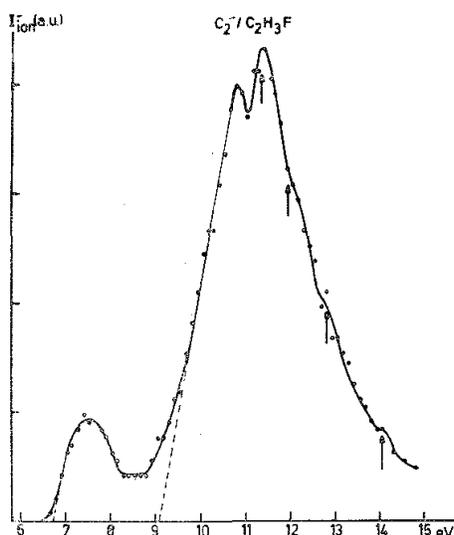
The value $\Delta U_f(\text{C}_2^-) = 8.43$ eV is obtained. The electron affinity value deduced from this quantity is $\text{EA}(\text{C}_2) = (0.2 \pm 0.1)$ eV. This value of the EA could correspond to the appearance of the C_2^- ion in an electronic excited state. In the N_2^+ molecule, isoelectronic of C_2^- , the $\text{B}^2\Sigma^+$ is lying at 3.2 eV above the ground state [9].

Only the following mechanism is able to interpret the second threshold measured at (9.1 ± 0.1) eV



The value of the electron affinity of the C_2 radical deduced from this reaction is $\text{EA}(\text{C}_2) = (2.4 \pm 0.1)$ eV corresponding to the production of the C_2^- ion in an electronic excited state and/or carrying an amount of kinetic energy. In the N_2^+ molecule, isoelectronic of C_2^- , the $\text{A}^2\Pi$ state lies at 1.1 eV above the $\text{X}^2\Sigma_g^+$ ground state [9]. It cannot be excluded that the C_2^- ion carries away kinetic energy (the minimum electronic excitation energy for the H atom and the HF molecule is at least 9 eV).

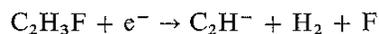
FIG. 15.



The maxima lying at 11.4 eV, 12.1 eV, 12.9 eV and 13.7 eV could be interpreted by the production of the C_2^- ion from the molecular ion through the « prédissociation » mechanism. The spacing between the shoulders of about 0.7 eV is nearly equal to that observed in the dissociative electron attachment peak of H^- in $\text{C}_2\text{H}_3\text{F}$ and in the same energy range (between 11 eV and 13 eV). It cannot be discarded that the same potential energy surface from the $\text{C}_2\text{H}_3\text{F}$ molecular ion could be cut by two repulsive surfaces, one giving rise to the C_2^- ion.

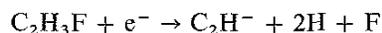
d) L'ion C_2H^- (figure 16)

Only the following mechanism could be invoked to interpret the first onset



Providing a heat of formation $\Delta U_f(C_2H^-) = (4.9 \pm 0.1)$ eV from which $EA(C_2H^-) = 0.2$ eV is deduced. This value of EA could correspond to the production of the C_2H^- ion in an electronic excited state [13], carrying kinetic energy.

At 9.1 eV the C_2H^- ion could appear through the mechanism:



The $EA(C_2H^-)$ value deduced from this mechanism is (2.5 ± 0.1) eV, close to the value of (2.1 ± 0.2) eV deduced from C_2H_2 . The shoulder observed at 11.2 eV could be assigned to

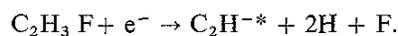
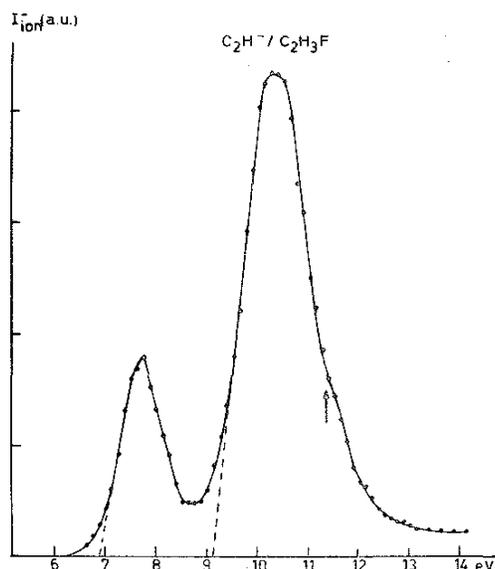


FIG. 16.



CONCLUSIONS

The conclusions concerning the study of the appearance of negative ions by dissociative electron attachment from CH_4 , C_2H_2 et C_2H_3X ($X = H, Cl$ et F) have been gathered in the following table.

The present study on the appearance of negative ions by dissociative electron attachment in polyatomic molecules showed that the interpretation of the observed onsets is more complex than in diatomic molecules. This difficulty has two sources.

1° The large number of possible mechanisms suitable for the interpretation of the same threshold.

2° The lack of knowledge of the values of the electron affinity, heats of formation and the electronic spectrum of most of the radicals. However, the present measurements allowed us to measure the electron affinity of C_2 and C_2H radicals and bring evidence for the probable existence of electronic excited states in the corresponding negative ions C_2^- and C_2H^- .

	AP (eV)	Suggested Mécanisms
A.	8.2 ± 0.2	CH ₄ + e ⁻ → H ⁻ + H ₂ + CH
	9.4 ± 0.15	
	9.7 ± 0.2	CH ₄ ± e ⁻ → CH ⁻ + H ₂ + H
	9.3 ± 0.3	CH ₄ + e ⁻ → CH ₂ + 2H
B.	7.2 ± 0.1	C ₂ H ₂ + e ⁻ → H ⁻ + C ₂ H*
	7.6 ± 0.2	C ₂ H ₂ + e ⁻ → C ₂ ⁻ + 2H*
	11.6 ± 0.2	→ C ₂ ^{-*} + 2H
	12.2 ± 0.2	
	2.8 ± 0.2	C ₂ H ₂ + e ⁻ → C ₂ H ⁻ + H
C.	7.5 ± 0.3	C ₄ H ₂ + e ⁻ → H ⁻ + (?)
	9.6 ± 0.1	
	9.0 ± 0.1	C ₂ H ₄ + e ⁻ → CH ⁻ + CH ₂ + H
	6.9 ± 0.1	C ₂ H ₄ + e ⁻ → C ₂ H ⁻ + H ₂ + H
	9.9 ± 0.05	→ C ₂ H ⁻ + 3 H
D.	7.5 ± 9.2	C ₂ H ₃ Cl + e ⁻ → H ⁻ + (?)
	8.2 ± 0.1	
	6.17 ± 0.05	C ₂ H ₃ Cl + e ⁻ → C ₂ H ⁻ + H (or H ₂) + HCl(Cl)
E.	8.6 ± 0.1	C ₂ H ₃ F + e ⁻ → H ⁻ + ?
	1.5 ± 0.1	C ₂ H ₃ F + e ⁻ → C ₂ H ₃ + F ⁻
	6.8 ± 0.1	C ₂ H ₃ F + e ⁻ → C ₂ ^{-*} + H ₂ + HF
	9.1 ± 0.08	→ C ₂ ^{-**} + 2H + HF
	6.9 ± 0.1	C ₂ H ₃ F + e ⁻ → C ₂ H ^{-*} + H ₂ + F
	9.1 ± 0.1	→ C ₂ H ⁻ + 2H + F

a) the electron affinity of C₂

In Table IX we summarize the conclusions drawn from the investigation of the appearance of the C₂⁻ ion.

TABLE IX.

Mécanismes	P.A.(eV)	EA(eV)	
C ₂ H ₂ + e ⁻ → C ₂ ⁻ + 2H	7.5 ± 0.2	3.3 ± 0.2	(α)
C ₂ H ₃ F + e ⁻ → C ₂ ⁻ + H ₂ + HF	6.8 ± 0.1	0.2 ± 0.1	(β)
C ₂ ⁻ + 2H + HF	9.1 ± 0.1	2.4 ± 0.1	(γ)

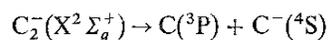
By the sublimation of graphite Honig [14] determined two values of the electron affinity, i.e. 4.0 eV and 3.1 eV. The latter of these values is in good agreement with the value obtained from the mechanism (α), i.e. (3.3 ± 0.3) eV.

From the data obtained in the C₂H₃F molecule we deduced two values: EA(C₂) = 2.4 eV and 0.2 eV. For the two values we invoked the possible existence of electronic excited states at 0.9 eV et 3.1 eV above the ground state. In the isoelectronic N₂⁺ molecule the A²Π and B²Σ⁺ states are at 1.1 eV and 3.3 eV above the ground state X²Σ_g⁺.

From the value of EA(C₂) = (3.3 ± 0.3) eV it is possible to deduce the dissociation energy of the C₂⁻ ion

$$D_0^\circ(\text{C}_2^-) = D_0^\circ(\text{C}_2) + \text{EA}(\text{C}_2) - \text{EA}(\text{C})$$

The dissociation mechanism being given by the reaction:



we obtain a dissociation energy of $D_0^\circ(C_2^-) = (8.2 \pm 0.3)$ eV knowing that $EA(C) = 1.25$ eV [22] and $D_0^\circ(C_2) = 6.12$ eV [16,17]. This value has to be compared to $D_0^\circ(N_2^+) = 8.72$ eV [9] where N_2^+ is isoelectronic with C_2^- .

b) the electron affinity of C_2H

TABLE X.

Mécanismes	AP.(eV)	EA(eV)
$C_2H_2 + e^- \rightarrow C_2H^- + H$	2.8 ± 0.1	2.1 ± 0.1
$C_2H_4 + e^- \rightarrow C_2H^- + H_2 + H$	6.9 ± 0.1	0.0 ± 0.3
$C_2H_3Cl + e^- \rightarrow C_2H^- + H + HCl$	6.17 ± 0.05	0.6 ± 0.1
$C_2H^- + H_2 + Cl$		
$C_2H_3F + e^- \rightarrow C_2H^- + H_2 + F$	6.9 ± 0.1	0.2 ± 0.1
$C_2H^- + 2H + F$	9.1 ± 0.1	2.5 ± 0.1

The appearance of the C_2H^- ion by dissociative electron attachment has been investigated in C_2H_2 , C_2H_4 , C_2H_3F and C_2H_3Cl . The conclusions drawn from this work are summarized in Table X

The most probable value deduced from this table is $EA(C_2H) = (2.3 \pm 0.2)$ eV. The two lower values of the electron affinity of C_2H could not be interpreted without using the hypothesis of the production of the C_2H^- ion in a vibronic excited state.

ACKNOWLEDGEMENTS

We wish to thank Professor L. D'Or for his interest to this work. We wish to acknowledge J. Momigny and J.E. Collin for helpful discussions. The Fonds National de la Recherche Fondamentale Collective is gratefully acknowledged for the acquisition of the mass spectrometer used in this work and financial support.

APPENDIX

In the calculation of onset energies of dissociative electron attachment processes we used the ΔU_f (heats of formation), EA (electron affinity) and D (dissociation energy) values listed in the following table:

	ΔU_f (eV)	EA(eV)	Références
C_2H_3F	-1,21		(18)
H	2,26	0,75	(20), (10)
F	0,82	3,45	(23), (19)
C_2H_2	2,35	—	(19)
C_2H	5,11	—	(11)
C_2	$8,63 \pm 0,1$	—	(19)
HF	-2,81	—	(19)
C	7,41	1,25	(19), (22)
CH_2	3,98	—	(20)
CH	6,16	—	(19)
CHF	0,3 5(?)	—	(11)
C_2F	$2,86 \pm 0,4$	—	(11)
C_2H_2F	0,41	—	(18)
C_2H_3Cl	-0,31	—	(18)
Cl	1,25	—	(19)
HCl	-0,95	—	(19)
CF	$3,22 \pm 0,1$	—	(11)
C_2H_3	$2,73 \pm 0,1$	—	(19)
C_2H_4	$0,54 \pm 0,2$	—	(19)

$D(HC-CH) = 9,88$ eV(a) et $D(HC_2-H) = 4,90$ eV(b)

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