

Published in: Extrait du Bulletin de la Société Royale des Sciences de Liège (1966), vol. 35, iss. 11-12, pp. 764-777. Status: Postprint English version (Author's Version) (translated by the author).

A MASS SPECTROMETRIC INVESTIGATION OF THE APPEARANCE MECHANISMS OF NEGATIVE IONS FROM METHANE.¹

by R. LOCHT

Assistant at the University of Liège, Institut of Chemistry.

ABSTRACT.

The negative fragment ions appearing in methane have been investigated using a sector field mass spectrometer. By recording the ionization efficiency curves of each ion it has been possible to determine the appearance potentials for several processes. Interpretations of the mechanisms for these critical potentials have been attempted.

INTRODUCTION.

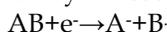
The electron-molecule interaction at low pressure gives rise to negative and positive ions.

Very few are the investigations devoted to the problems related to the mechanism(s) for the production of negative ions.

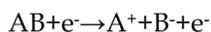
In the present note, a first series of experimental results obtained for the negative ions produced in methane will be reported.

The formation process of negative ions has been investigated in detail in several reports [1,2,3]. Two processes give rise to negative ions:

1°: the attachment process, possibly followed by a dissociation:



2°: the excitation process of the molecule by electron impact followed by a dissociation into an ion pair



The aim of this work is to analyze systematically both processes giving rise to the negative ions from methane.

EXPERIMENTAL.

a) Experimental Conditions.

We used a Nier type 60° sector field mass spectrometer (Atlas MAT CH4), equipped with an electron multiplier for the ion current detection. The potential difference between the first and second dynode was maintained at 2.2 kV. The spectrum was obtained by scanning the magnetic field². The working conditions of the spectrometer are:

- electron emission current: 10 μA for dissociative electron attachment processes, 20 μA for ion pair processes.

¹ Submitted by L. D'Or on December 15th 1966.

² After the accelerating field of the ions, two deflection plates allow us to make a rough analysis of the kinetic energy carried by the negative ion under investigation.

- pressure: during the measurements the pressure in the ion chamber is maintained at $5 \cdot 10^{-6}$ torr. It has been verified that the ion intensity was linearly dependent on the pressure.
- the ion source temperature: 250°C
- the electron trap and the ionization chamber are at the same potential.

To ensure the reproducibility of the ionization efficiency curves, in all cases the measurements have been repeated at least three times.

b) Method for the determination of onset energies.

The theoretical study of the ionization phenomena in the gas phase led S. Geltman [4] to propose the "threshold law" describing the ionization efficiency curves obtained by electron and photon impact. It is given by:

$$p(E) = k(E - E_c)^{n-1}$$

where $p(E)$ is the ionization probability, E and E_c are the impinging particles energy and the critical energy of the investigated phenomenon, n stays for the number of electrons leaving the collision complex.

| Ions | Ab. Rel. % | Potentiels d'apparition (eV) | | | | |
|------------------------------|------------|------------------------------|--------------|------------------------|--------------------|--------------------|
| | | L. G. Smith | L. v. Trepka | Ce travail | | |
| H ⁻ | 89,1 | 6,1 | — | — | | |
| | | 6,9 | — | — | | |
| | | 7,3 | — | — | | |
| | | | 8,3 | A : $8,5 \pm 0,2$ (*) | | |
| | | | 9,5 | $9,9 \pm 0,2$ | | |
| | | | 18,0 | — | P : $22,5 \pm 0,3$ | |
| | | | | | $24,3 \pm 0,3$ | |
| C ⁻ | 4,2 | 24,7 | — | $26,6 \pm 0,2$ | | |
| | | | | P : $37,2 \pm 0,5$ | | |
| | | | | $30,6 \pm 0,4$ | | |
| | | | | $33,1 \pm 1,2$ | | |
| CH ⁻ | 5,0 | 10,2 | 9,6 | A : $10,6 \pm 0,2$ (*) | | |
| | | | | P : (24,6) | | |
| | | | | $24, \delta$ | | |
| CH ₂ ⁻ | 1,6 | 8,9 | 8,3 | A : $9,6 \pm 0,2$ (*) | | |
| | | | | $9,3$ | | |
| | | | | 53,4 | — | P : $24,9 \pm 0,5$ |
| | | | | | | $29,6 \pm 0,7$ |
| CH ₃ ⁻ | 0,04 | — | — | — | | |

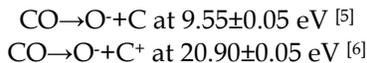
(*) In figures 1, 5 et 7 the electron energy scale is not corrected. A et P stay for dissociative electron Attachment and ion Pair processes.

TABLE 1.

On the basis of this law, taking into account the electron energy distribution, we choose to measure the critical (threshold) energy at:

- 1° the resonance peak maximum for the dissociative electron attachment,
- 2° the inflexion point of the ionization efficiency curve for the ion pair process.

For the electron energy scale calibration the critical energies of the appearance of O⁻ ion from CO have been used.



EXPERIMENTAL RESULTS.

In Table 1 the negative ions observed in the mass spectrum of Methane recorded at an electron energy of 50 eV are mentioned. The ratios of the ion to total ion intensity are reported.

Excepting the CH₃⁻ ion, of too low intensity, the ionization efficiency curves of all the ions are investigated separately. The critical energies are inserted in Table 1 together with the results obtained by L.G. Smith [7] and L. von Trepka [8].

DISCUSSION OF THE EXPERIMENTAL RESULTS

a) The H⁻ ion.

The ionization efficiency curves measured for the H⁻ ion are displayed in Fig. 1 to 3.

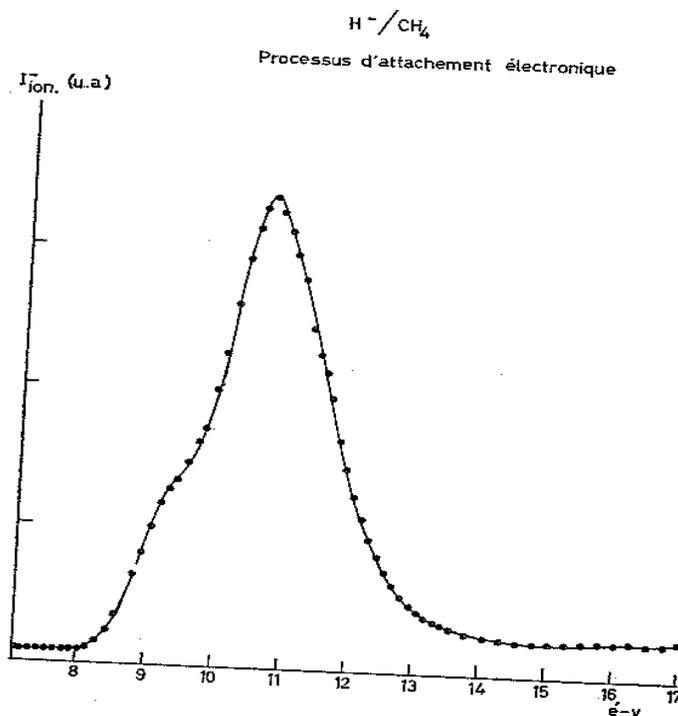
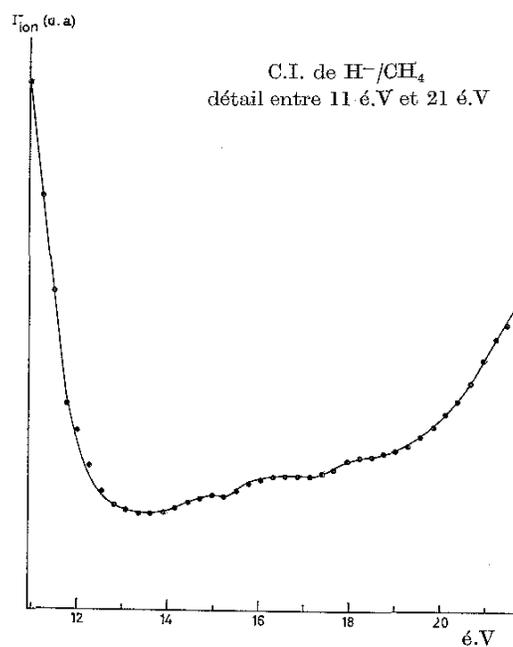
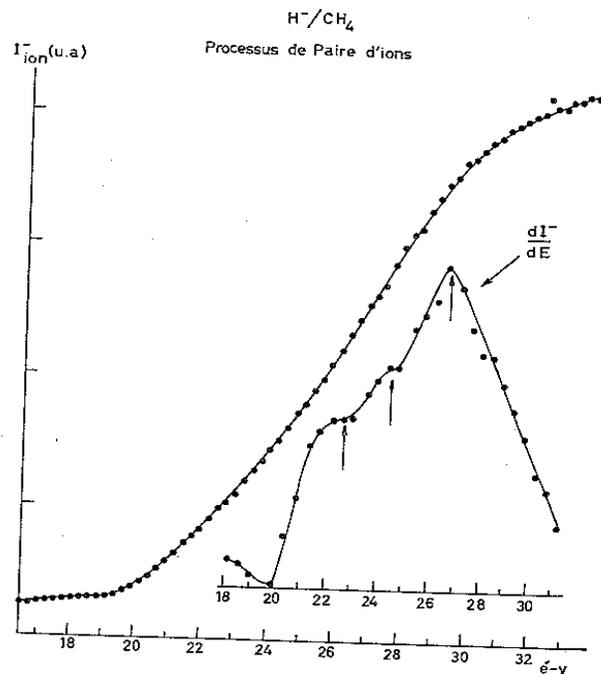
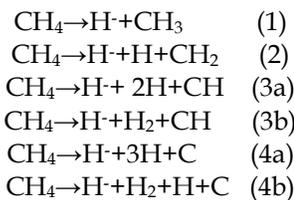


FIG. 1

1°) Two dissociative electron attachment processes are observed at 8.5 eV and 9.9 eV successively in satisfactory agreement with previous reports. The discrepancy is ascribed to the fact that the threshold energy for such processes is usually obtained by linear extrapolation.



The mechanisms leading to the H⁻ ion production by dissociative electron attachment are:



The probable position of the maximum is provided by the relation:

$$AP = D - E.A. + E.E. + K.E.$$

where – AP is the appearance potential of the investigated dissociative attachment process,

- D is (are) the dissociation energy(ies),
- EA is the electron affinity of the atom or radical,
- EE is the vibronic excitation energy,
- KE is the kinetic energy carried by the ion and the neutral fragment(s).

Using the most recent value of 0.75 eV for the electron affinity of H^[9] and for the successive dissociation energies of methane:

$$D(\text{CH}_3\text{-H}) = 4.41 \text{ eV}^{[11]}, D(\text{CH}_2\text{-H}) = 4.87 \text{ eV}^{[11]},$$

$$D(\text{CH-H}) = 4.68 \text{ eV}^{[12]}, D(\text{C-H}) = 3.47 \text{ eV}^{[13]}.$$

one obtains the following critical energies for the six mechanisms mentioned above:

$$(1) 3.66 \text{ eV}, (2) 8.53 \text{ eV}, (3a) 13.21 \text{ eV}, (3b) 8.74 \text{ eV}, (4a) 16.68 \text{ eV} \text{ and } (4b) 12.21 \text{ eV}$$

The mechanism (2), where the H⁻ ion appears in the ground state and without kinetic energy, is compatible with the experimental results.

T.E. Sharp and T.E. Dowell^[14] only measured a critical energy at 8.5 eV and assigned it to the mechanism (1). The H⁻ ion should carry 4 eV kinetic energy.

We analyzed the ionization efficiency curve of H⁻ as a function of the potential applied to the ion beam deflectors at the exit slit of the ion chamber. The peak intensity has been fitted as a function of the applied potential. Only the kinetic energy component perpendicular to the optical axis is analyzed.

The experiment shows that in the dissociative attachment processes at 8.5 eV and 9.9 eV, the H⁻ ion should carry only small amounts of kinetic energy. However, the H⁻ ion appearing at 8.5 eV should carry kinetic energy.

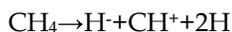
The critical energy at 9.9 eV could be assigned to the mechanism (3b). The excess energy of 1.2 eV could be ascribed to the excitation of several vibrational quanta in H₂ and CH.

The H⁻ ion from H₂ does not provide an excited state at 1.2 eV above the ground state as it has been shown by the photodetachment cross section curves and by the dissociative attachment curves obtained by Smith^[9], Rapp and Briglia^[16] and Schulz^[17] respectively. The dissociative attachment processes have very likely to be ascribed to



2°) In the higher electron energy range an increase of the ion current is observed. The ionization efficiency curve corresponds to the appearance of an ion pair process. Critical energies are measured at 22.6 eV, 24.3 eV and at 26.6 eV.

Simultaneously, in a parallel ongoing work in this laboratory, J. Delwiche^[18] investigated the production of positive ions in methane by the R.P.D. technique. The ionization efficiency curve for CH⁺ shows critical energies at 22.6 eV, 24.1 eV and 26.1 eV successively. The good agreement between the critical values obtained by the two techniques indicates that the H⁻ ion should appear by the mechanism:



but where the positive ion involved in the ion pair process should appear in different electronic excited states. The $^1\Sigma^+$, $^3\Pi$ and $^1\Pi$ states could be involved successively. The $^1\Sigma^+$ corresponds to the ground state of the ion. The $^1\Pi$ state is an excited state at 3 eV above the ground state [13]. The appearance of the $^3\Pi$ is less certain, the transition being optically forbidden. Fig. 3 shows the ionization efficiency curve between 11 and 21 eV. The negative ion current is non-zero between the resonance peak and the ion pair process curve. The same observation is valid for all the ions measured in this work. C.E. Melton [19] measuring the ionization efficiency of CH_3^+ from methane by the R.P.D. technique observed a critical energy at 13.7 eV. The author assigned it to $\text{CH}_4 \rightarrow \text{CH}_3^+ + \text{H}^-$. From Fig. 3 we can not account for such a process. Other investigations [18, 22] devoted to the same ion from methane using the R.P.D. technique provided an onset energy of CH_3^+ at 14.1 eV. These experimental results don't agree with the value of 13.7 eV reported by C.E. Melton.

b) The C^- ion (Fig.4).

This ion is only produced by ion pair process. No detectable ion current is measured below 20 eV. In the ionization efficiency curve four inflexion points are measured at 27.2 ± 0.5 eV, 30.6 ± 0.4 eV, 33.1 ± 1.2 eV and 35.6 ± 0.7 eV successively.

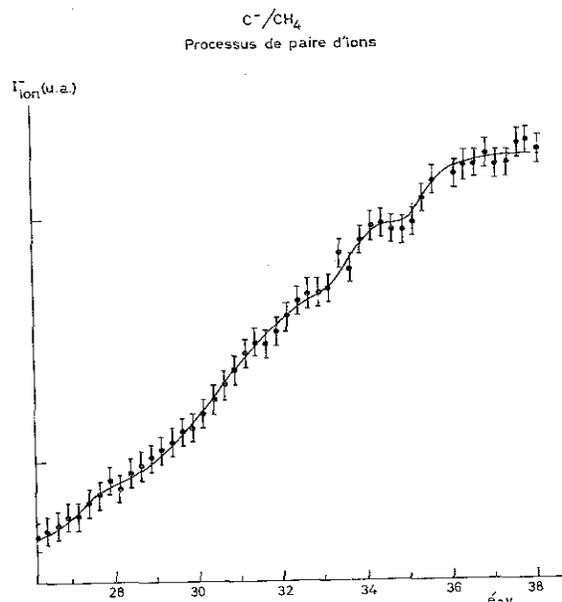
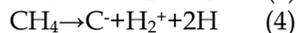
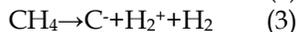
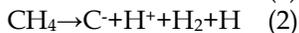
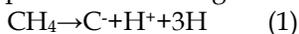


FIG. 4

The mechanisms which can produce the C^- negative ion by ion pair process are:



The appearance energy of an ion pair process is given by the relation:

$$\text{AP} = \text{D} - \text{E} \cdot \text{A} + \text{I} + \text{E} \cdot \text{E} + \text{K} \cdot \text{E}.$$

where I stays for the ionization potential of the positive ion provided by the ion pair process.

The value of the electron affinity of the C atom is 1.24 eV^[20], the C⁻ being in its ⁴S ground state. Using the dissociation energies mentioned in section (a), the predicted onset energies are calculated at (1) 29.78 eV, (2) 25.31 eV, (3) 24.49 eV and (4) 28.96 eV respectively. The negative ion and the different positive ions are supposed to be formed in their ground state.

Using theoretical calculations, the electron affinity of the C atom has been predicted for the C⁻ ion in its ²D and ²P states^[20, 21] at -0.05 eV and -0.22 eV respectively. The neutral fragments H and H₂ and the H₂⁺ ion could be produced in vibronic excited states. Numerous possibilities are obtained. At present it is difficult to make any assignment.

c) The CH⁻ ion (Figs. 5 and 6).

This ion is produced by two processes. A resonance peak is observed at 10.6±0.2 eV. The ion pair ionization efficiency curve is structureless. Only one threshold is observed at 24.6 eV where the ion current starts to increase. In fact this latter curve is likely resulting from the superposition of contributions of several vibronic states of the CH⁻ ion.

The examination of the energy level diagram of the NH radical^[13], isoelectronic of CH⁻, emphasises that the energy levels could not be resolved by the present technique. In the energy range of 4 eV four electronic states, i.e. ³Σ⁻, ¹Δ, ¹Σ⁺ and ³Π states are observed.

On the other hand, the disagreement between the various electron affinity values of the CH radical^[8, 10] as obtained by electron impact doesn't allow us to calculate any onset energy.

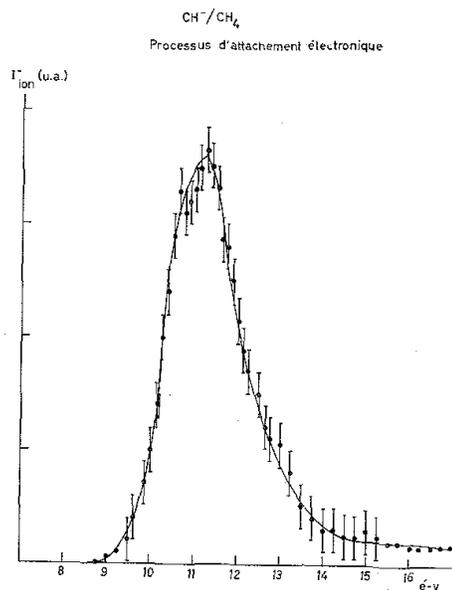


FIG. 5.

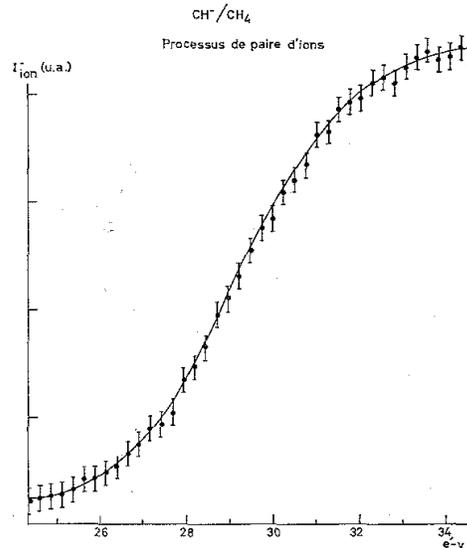


FIG. 6.

d) The CH₂⁻ ion (Figs. 7 and 8).

The ionization efficiency curve of the CH₂⁻ ion shows a resonance peak at 9.6±0.2 eV. Two inflexion points are measured in the ion pair production curve at 24.9 eV and 29.6 eV successively.

Also in the present case no value of the electron affinity of the CH₂ radical nor of the excitation energies have been reported in the literature.

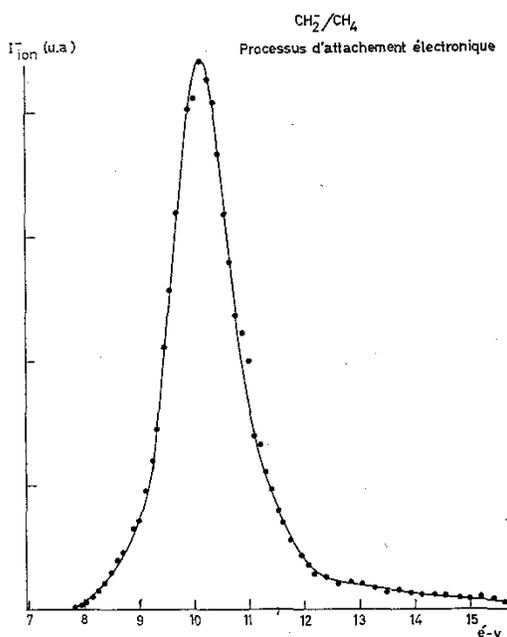


FIG. 7.

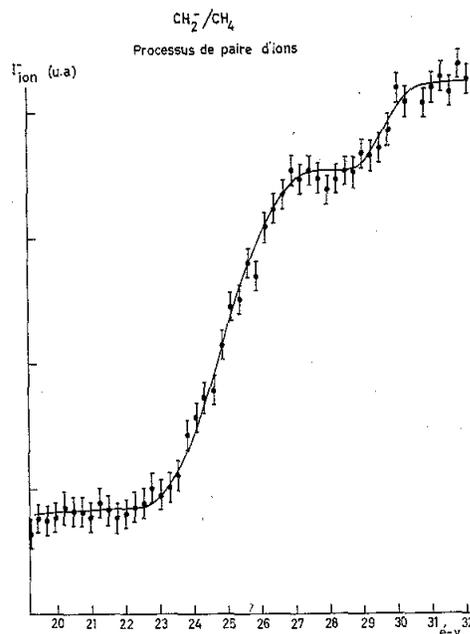


FIG. 8.

CONCLUSIONS.

From the present first investigation it could be concluded that:

- 1° The same negative ion almost always occurs through two different processes: a dissociative electron attachment process and an ion pair process.
- 2° Usually these processes are manifold. If the negative ion usually appears in its ground state, its neutral or positive counterpart could appear in their ground state but also in electronic and vibrational excited states.
- 3° The present study shows that the main difficulty in the interpretation of the threshold energies arises from the lack of information about the electron affinity of the radicals and the electronic excitation energies of the negative ions.

In a going on investigation, we guess to bring a contribution to these subjects by the systematic investigation of the appearance of the same negative ions from different compounds.

ACKNOWLEDGMENTS.

We thank professor L. D'Or for his interest to this work. We acknowledge the helpful advices of J. Momigny and J. Collin. We wish to thank the IRSIA (Institut pour l'Encouragement de la Recherche Scientifique dans l'Industrie et l'Agriculture) for a grant. The FRFC (Fonds de la Recherche Fondamentale Collective) is gratefully acknowledged for the financial support in the purchase of the mass spectrometer.

REFERENCES.

- [¹] H. S. W. MASSEY et H. S. BURHOP, *Electronic and Ionic Impact Phenomena*. Oxford Univ. Press (1952).
- [²] H. S. W. MASSEY, *Negative Ions*. Univ. Press. Cambridge (1950).

- [³] F. H. FIELD et J. C. FRANKLIN, *Electron Impact Phenomena*. A. P. (1958).
- [⁴] S. GELTMAN. *Phys. Rev.*, 102 (1956), 171.
- [⁵] K. KRAUSS. *Diplomarbeit*, Hamburg (1961).
- [⁶] L. M. BRANSCOMB. *J. Chem. Phys.*, 29, 2 (1958), 452.
- [⁷] L. G. SMITH. *Phys. Rev.*, 51 (1937), 263.
- [⁸] L. v. TREFKA et H. NEUERT. *Z. Naturf.*, 18a (1963), 1295.
- [⁹] S. J. SMITH et D. V. BURCH. *Phys. Rev.*, 116, 5 (1959), 1125.
- [¹⁰] V. I. VEDENEYEV et Coll., *Bond Energies, Ionization Potentials and Electron Affinities*. Arnold éd. (1966).
- [¹¹] V. H. DIBELER, R. REESE, M. KRAUSS et F. N. HARLLEE. *J.C.P.*, 42, 11 (1965), 3791.
- [¹²] J. A. KERR. *Chem. Rev.*, 66, 5 (1966), 425.
- [¹³] G. HERZBERG, *Spectra of Diatomic Molecules*. Van Nostrand, 2^e éd. (1950), p. 518.
- [¹⁴] T. E. SHARP et J. T. DOWELL, *14th Ann. Conf. on Mass Spectrometry* ASTM.E-14, Dallas, Mai 1966.
- [¹⁵] J. D. CRAGGS et B. A. TOZER. *Proc. Soc.*, A 254 (1960), 229.
- [¹⁶] D. RAPP, T. E. SHARP et D. D. BRIGLIA. *Phys. Rev. Let.*, 14 (1955), 533.
- [¹⁷] G. J. SCHULZ. *Phys. Rev.*, 113 (1959), 816.
- [¹⁸] J. DELWICHE (à paraître).
- [¹⁹] C. E. MELTON et W. H. HAMILL. *J.C.P.*, 41 (1964), 546.
- [²⁰] M. L. SEMAN et L. M. BRANSCOMB. *Phys. Rev.*, 125 (1962), 1602.
- [²¹] Bl. MOISEWITCH, *Advances in Atomic and Molecular Physics*, vol. I, éd. D. B. Bates et I. Esterman A. P. (1965).
- [²²] J. COLLIN. Thèse d'Agrégation de l'Enseignement Supérieur, Université de Liège (1966).