

An Investigation of the Molecules O_2 , CHCl_3 , $\text{c-C}_4\text{F}_8$, C_7F_{14} and HBr by Electron Cyclotron Resonance (ECR) Technique at Energies ≤ 0.4 eV

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Preliminary experiments have shown that helium gas can be considered a good choice to be used in electron cyclotron resonance (ECR) studies, at the same time as a carrier gas and as a source of production of free electrons. An account of destruction of He metastable atoms present in the flow-stream is given. Changes in the linewidth with or without the electron scavenger and thermalization of the electrons are discussed. The energy dependence for the electron attachment to the molecules O_2 , CHCl_3 , $\text{c-C}_4\text{F}_8$, C_7F_{14} , and HBr is investigated. The energy scale for electron attachment processes in relation to the input microwave power is established for He carrier gas. Such processes can be studied by employing the ECR technique from thermal energies up to 0.4 eV.

I. Introduction

The principle of the cyclotron resonance absorption technique rests on the fact that a charged particle in a magnetic field will absorb energy at or near its cyclotron frequency. In the electron cyclotron resonance (ECR) method, a free electron moving in a static magnetic field H describes circular orbits with an angular frequency

$$\omega_c (\text{cyclotron resonance}) = (e/m_e c) H \quad (1)$$

where e is the electron charge, m_e the electron mass, c the velocity of light and $e/m_e c = 2.799 \text{ MHz Gauss}^{-1}$. If an oscillating electric field E with frequency ω_0 is applied perpendicularly to the magnetic field, the electrons will absorb energy from the electric field when ω_0 is approaching the resonance frequency ω_c . As the electrons absorb energy, they are accelerated and eventually they lose some of their excess energy through collisions with other particles and with the walls.

It is necessary that $\omega_0 > \nu_{\text{col}}$, where ν_{col} is the electron-particle collision frequency, if the electron is to gain energy between two collisions and exhibit resonance near $\omega_0 \cong \omega_c$. In other words, the time between collisions should be sufficiently large compared to the time for one revolution. In this way, the electron can make a number of revolutions before colliding with another particle and gain sufficient energy from the electric field. Thus, for sharp resonances, the condition $\omega_0, \omega_c \gg \nu_{\text{col}}$ should hold.

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The ECR method has been previously^{1–6} applied to study low-energy (< 0.4 eV) electron capture processes in a flow system by using Ar or N_2 as a carrier gas and NO or CH_3NH_2 as a donor for production of the free electrons.

In the present work an investigation was carried out to determine the conditions under which He gas could be used both as a source for production of the free electrons and as a carrier gas for thermalization of the free electrons through collisions with it. Some elaboration is given on the destruction of the He metastable atoms. The electron energy scale for the capture processes in correlation with the incident power on the microwave resonant cavity is obtained.

II. Basis of ECR Method

A) ECR Signal

The real power P_{ab} absorbed by the free electrons in resonance can be calculated from the Boltzmann Transport Equation^{7–8}. In a simplified form for isotropic scattering and constant mean free time it is given by

$$m \frac{d\mathbf{v}}{dt} = e \mathbf{E} + \frac{e}{c} \mathbf{v} \times \mathbf{H} - m_r \nu_{\text{col}} \mathbf{v} \quad (2)$$

where $\mathbf{E} = \mathbf{x} E_0 \cos \omega_0 t$, $\mathbf{H} = \mathbf{z} H_z$

and $m_r = m_e M / (m_e + M)$.

The reduced mass m_r can be substituted by m_e , since $m_e \ll M$, where M is the mass of the colliding particles. The absorbed power, averaged over time is given by

$$\bar{P}_{\text{ab}} = \langle \mathbf{E} \cdot \mathbf{I} \rangle_t \quad (3)$$



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where $\mathbf{I} (= -\mathbf{x} N_e e v_x)$ is the electronic current density and N_e the number of electrons. It follows from Eqs. (2) and (3) that

$$\bar{P}_{ab} = \frac{N_e e^2 E_0^2}{4 m_e} \cdot \left[\frac{\nu_{col}}{\nu_{col}^2 + (\omega_0 + \omega_c)^2} + \frac{\nu_{col}}{\nu_{col}^2 + (\omega_0 - \omega_c)^2} \right]. \quad (4)$$

The electric susceptibility χ'' of the microwave cavity is related to \bar{P}_{ab} by

$$\bar{P}_{ab} = \frac{1}{2} \chi'' \omega_0 E_0^2. \quad (5)$$

In ECR experiments, the change of χ'' is measured as a function of the magnetic field H . By use of a modulation field and a phase sensitive detection system, signals corresponding to the derivative $d\chi''/dH$ are obtained. Integration of each signal gives the real absorption curve. The area F under the absorption curve is given by

$$F \equiv \int_0^\infty \chi'' dH. \quad (6)$$

Assuming that ν_{col} is independent of the electron velocity and introducing Eqs. (1), (4) and (5) into (6) we find

$$F = \frac{\pi}{2} \frac{e c}{\omega_0} N_e \quad (7)$$

that is, the area F is directly proportional to the electron density in the resonance cavity. This absolute determination of the electron density by the ECR method is very limited since, generally, ν_{col} is a complicated function of the electron velocity. Various forms of the dependence of the collision frequency or the momentum transfer cross section on the electron velocity have been investigated^{6, 9-16} theoretically and experimentally for a large number of molecules employing different techniques. The form $\nu_{col} \propto v^n$ was the one used most.

The electron energy in the flow system at constant pressure is a function of the average electric field strength in the cavity. Since the modulus of the E -field vector is directly proportional to the square root of the microwave power P_{MW} incident into the resonant cavity, a linear scale can be obtained if $P_{MW}^{1/2}$ is plotted as a function of electron energy. Thus the energy dependence of the electron capture process can be studied by varying the microwave power input into the cavity. A correlation³ between $P_{MW}^{1/2}$ and absolute energy values is obtained by comparing the energy for a maximum in the cross section measured by

ECR with results from other methods (see Part IV, Section D).

B) Carrier Gases

In electron capture studies in a flow system it is very important that the electrons, whose average energy is high at the site of their production, lose their excess energy through elastic collisions with the atoms or molecules of a carrier gas and reach a thermal equilibrium with their surroundings before they enter the reaction region. The electrons in thermal equilibrium with the gas have a Maxwellian energy distribution.

Argon and nitrogen gases have been used^{1-6, 14, 17} extensively in ECR studies as carrier gases. There are some difficulties, however, with these two gases in determining the velocity variation of ν_{col} in the energy range of interest (≤ 0.4 eV). From the fact that the linewidth and the lineshape of an absorption resonance, which are measurable parameters by ECR method, depend on ν_{col} , an analysis of these parameters can yield collision cross sections.

1) It has been found¹³ that in Ar and N₂ there would not be close correspondence between the energy variation of the cyclotron resonance linewidth and the energy variation of the average collision frequency, while in He there would be such a close correspondence. A study was reported⁶ recently which deals with the results of the analysis given by Fehsenfeld *et al.*¹³.

2) The rapid decrease of electron-argon collision cross section with energy with a minimum at ~ 0.28 eV^{11, 18} (Ramsauer-Townsend minimum) and the subsequent increase at lower energies results in a complicated energy dependence of the collision frequency. Although it is customarily assumed that $\nu_{col} \propto v^n$, for gases which exhibit a Ramsauer minimum this single term power velocity representation of ν_{col} is not adequate.

3) In molecular gases, such as N₂, inelastic energy losses, particularly through rotational excitation at low electron energies, may be significant and dominate relaxation phenomena.

4) The presence of "active nitrogen"¹⁴ in a N₂ gas stream which was passed through a discharge and its consequent reactivity with most molecules in the gas phase, may interfere with the determination of ν_{col} .

5) The linewidth and lineshape of the ECR signal are affected by addition of the electron donor in the

carrier gas flow, particularly for molecules which are dipolar and possess high collision cross section, such as CH_3NH_2 . Thus, in the analysis of the experimental results these changes have to be taken into consideration.

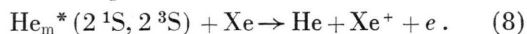
6) Although CH_3NH_2 gives the best electron yields in the Ar system⁴, it cannot be used indiscriminately as an electron donor because of possible chemical reactions with the scavenger.

Helium gas can be considered as a good choice to be used as a carrier gas in ECR studies. It is the simplest atom which has been so extensively studied, both theoretically and experimentally. An analysis¹³ of its velocity dependency on ν_{col} showed that ν_{col} can be represented reasonably well by a single-term expansion of the form v^n . From this analysis it was found that in He gas there would be a close correspondence between the energy variation of the cyclotron resonance linewidth and the energy variation of the average collision frequency. The low-energy electron-helium collision cross section was found^{6, 9, 14, 19} to be velocity independent and equal to about 5.5 \AA^2 . Then, from the known relation $\nu_{\text{col}} = N_e \sigma(v) v$, the collision frequency varies as the first power of the electron velocity. This can be considered true even for electron energies up to 2 eV, since the cross section increases only by roughly 20% in the range from 0.03 to 2 eV.

In the present work He was used as a carrier gas and at the same time as the source of the free electrons, since no donor was added in the flow stream. A difficulty which arises from this consideration is discussed in the following. In addition to the He ions and electrons produced by ionization in the He plasma discharge, the two well-known helium metastable atoms He_m^* are present in the flow stream. These two, 2^1S and 2^3S , metastable states of He with energies of 20.6 and 19.8 eV, respectively, can ionize any impurity gas whose ionization potential is lower than these energies. Thus, if a number of these metastables reach the reaction region from where the scavenger molecule is being introduced, an additional number of free electrons will be produced and the interpretation of the experimental results will be complicated. It is necessary to quench these metastable atoms before they reach the reaction zone. The main destruction processes²⁰⁻²³ of He_m^* produced in the discharge cavity may occur through the following mechanisms:

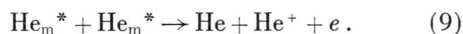
1) By diffusion to the walls of the flow tube, where they lose their energy by inelastic impact with the walls. This is a very effective way of destructing He_m^* , particularly for low gas pressures (a few torr) and narrow flow tubes (1 in. dia.) used in the present experiment.

2) By inelastic collisions with added atoms or molecules resulting in ionization of the additive, if it is energetically possible. Thus, when Xe is used, the ionization process can be viewed as



The excess energy is carried off as kinetic energy by the ejected electron.

3) By collisions between metastable He atoms leading to deexcitation of one and ionization of the other viewed as



For high metastable densities ($> 10^{10} \text{ cm}^{-3}$), this is an effective destruction process with a cross section of 10^{-14} cm^2 (Ref. ²²) at 300°K .

4) By de-exciting collisions with neutral He atoms in a two- or three-body collisions. The cross section for such a process is very small²¹. In our experiments, at a He pressure of 4 Torr, this cross section is of the order of 10^{-22} cm^2 .

III. Experimental

The experimental apparatus, shown in Fig. 1, consists of a conventional flow system with flow rates of 30 to 50 m/sec in the pressure range of 3 to 10 torr. The flow tube, with an inner diameter of 2.2 cm, was made of quartz and was provided with pressure measuring devices, flow meters, mixing chambers, etc. Helium was used as a carrier gas. The free electrons were produced by ionization of He gas atoms in a microwave plasma discharge. The Xe gas, used as a quencher of the He metastable atoms, was introduced through one of three inlet ports located between the microwave discharge cavity and the mixing chamber of the reactant gas. A precision needle valve connected to a flow meter, a pressure meter and a 2 lit. volume glass flask were used to control and determine the flow rates $\Delta P/\Delta t$ (torr/min) of the Xe gas. A ball-type inlet port for Xe gas was designed to permit a more uniform distribution of the Xe atoms in the He gas stream.

The electron concentration was measured with a conventional V-4502 Varian EPR spectrometer system which included a 100 KHz field modulation and control unit, a microwave bridge, a cylindrical resonant cavity and a 12-inch electromagnet system. The microwave bridge was specially designed²⁴ to

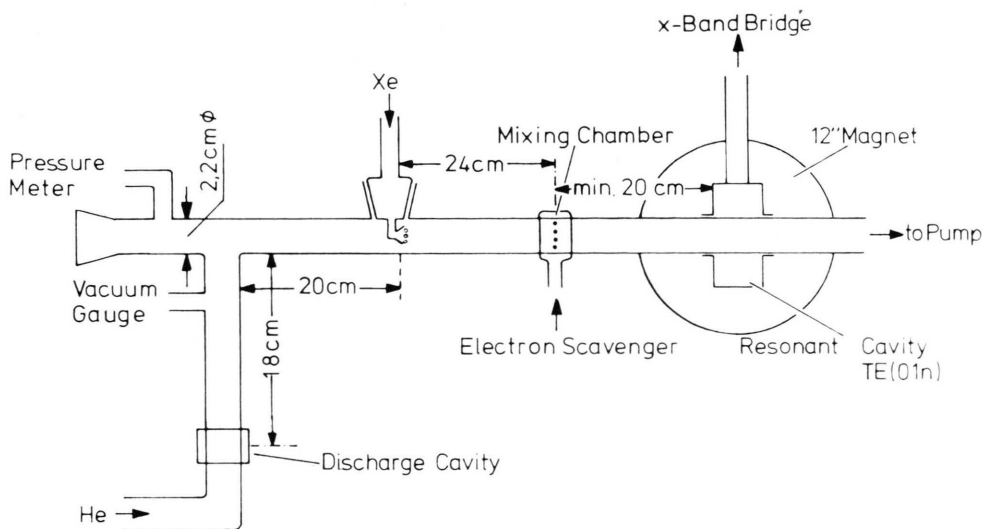


Fig. 1. Schematic diagram of apparatus.

suit the low-power requirements of the ECR technique for the range from ~ 0.5 to $400 \mu\text{W}$. The resonant cavity, Model V-4535, operated in the TE_{01n} mode served as the electron detector. This cavity together with the magnet and the microwave bridge could be moved along the flow tube. Thus, by varying the distance between the mixing chamber and the resonant cavity one can determine reaction times and so rate constants for electron capture processes. Because the klystron oscillator produces r.f. energy in the range of $9000 \pm 500 \text{ MHz}$, cyclotron resonance of the free electrons is expected to occur at $3200 \pm 200 \text{ G}$. In these experiments an intensive absorption signal at a magnetic field of $3150 - 3350 \text{ G}$ was received, depending on the tuning of the resonant cavity.

As the uniform magnetic field was being swept slowly with time while the microwave frequency ω_0 was kept constant, electron cyclotron resonance occurred and a chart recorder displayed the derivative of the power absorbed as a function of H . The linewidth ΔH_{pp} of the derivative signal was determined from the peak-to-peak distance. From this signal the real absorption signal could be obtained by the use of an integrator²⁵. Two attenuators (SILVERS PM 7101 X) were connected to the microwave bridge, so that a precise reading of the input microwave power P_{MW} (in db units) could be obtained. Calibration measurements of P_{MW} (in μW units), in relation to the readings of the two attenuators, were carried out with a Hewlett-Packard power meter Type 4316. The microwave power incident on the resonant cavity was varied between 0.5 and $400 \mu\text{W}$ while the pressure was kept constant.

A conventional gas handling system was used for the molecules studied. Special precautions were taken for the gas HBr because of its toxicity and the high chemical reactivity with metal surfaces.

IV. Results and Discussion

A) Destruction of He Metastable Atoms

The main concern with He being used as a carrier gas in ECR studies is the destruction of He_m^* atoms produced in the plasma discharge, as was discussed in Part II, Section B. It appears that the most effective way for destruction of He_m^* atoms was the diffusion to the walls of the flow tube where the metastables lose their energy by inelastic collisions with the walls. This was tested in the following way: With the resonant cavity at the closest distance ($\sim 20 \text{ cm}$) to the mixing chamber, constant microwave power and He gas pressure (4 Torr), the peak-to-peak height h and the linewidth ΔH_{pp} of the derivative signal were determined with or without addition of Xe gas in the flowstream of He gas. No change of h or ΔH_{pp} was observed when various controlled flow rates of Xe were introduced through the mixing chamber inlet. Similar results were obtained when Xe was replaced by Ar gas, as shown in Figure 2. Since the intensity of the ECR signal remained constant, or in other words the electron concentration did not change with or without Xe (or Ar), it is suggested that the He_m^* atoms were quenched before they enter the reaction zone. Mea-

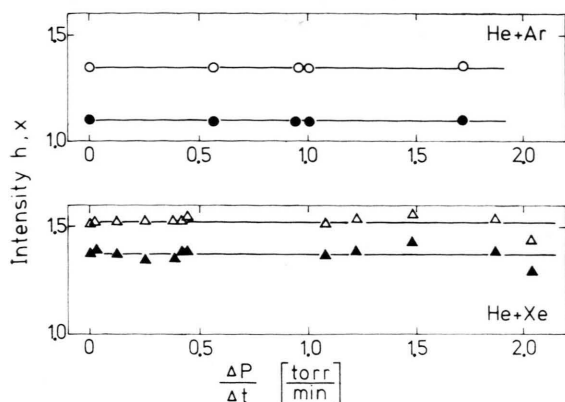


Fig. 2. Intensity h and x ($\equiv h \cdot \Delta H_{pp}^2$) for the mixtures He+Xe (\blacktriangle and \triangle) or He+Ar (\bullet and \circ) as a function of Xe or Ar flow rates. Maximum [Xe] concentration at 2 torr/min was $\sim 0.08\%$ that of [He].

surements²¹ of the lifetimes of He_m^* at low densities showed that the destruction of metastables was mainly by diffusion to the walls at 300 °K and at pressures lower than 10 torr. We found also that the ECR signal increased substantially as the inlet port of Xe was closer to the discharge cavity while the linewidth did not change significantly.

In the present experiments a suitable flow rate and inlet port were chosen for Xe gas, such that the electron signal intensity was increased by a factor of 3 to 4 while the linewidth remained essentially unchanged.

B) Thermalization of Electrons

The thermalization time t_{th} for the three carrier gases He, Ar and N_2 can be determined from a number of experimental parameters. The collision mean free path λ can be calculated from the well-known relationship

$$\lambda = 1/N\sigma \quad (10)$$

where N ($= 3.22 \times 10^{16} \text{ molecules} \cdot \text{cm}^{-3} \cdot \text{torr}^{-1}$) is the gas density at 1 torr and 300 °K. The cross section for momentum transfer^{6, 26} at thermal energies has a value of about 5.5, 2.5 and 3.8 \AA^2 for He, Ar and N_2 , respectively. Then, the calculated values for λ obtained from Eq. (10) are 0.056, 0.081 and 0.124 cm for He, Ar and N_2 , respectively, at 1 torr. When the collision frequency of the electrons with the gas particles is independent of the electron velocity, an approximate thermalization time after which the energy u of the electrons will deviate less

than 10% from the thermal energy u_{th} of the gas, can be expressed²⁷ by

$$t_{th} \geq \frac{1.4 \times 10^{-3} \lambda M}{P T^{1/2}} \ln \left[\frac{\Delta u}{0.1 u_{th}} \right] \quad (11)$$

where M is the molecular mass in terms of the molecular weight and Δu the excess electron energy.

At constant pressure ($P = 3.5$ torr) and temperature ($T = 300$ °K) the calculated values of t_{th} are 3.8×10^{-5} sec for He, 7.8×10^{-4} sec for Ar and 2.9×10^{-4} sec for N_2 . The excess energy Δu was taken as 3 eV for Ar¹, 1 eV for N_2 ²⁸ and 8.5 eV for He. In the latter case we have considered the maximum possible energy the electrons could possess as a result of Xe ionization by the higher lying singlet He_m^* atom. For smaller Δu , the time t_{th} will become even smaller. The different values found for Ar ($t_{th} = 3.7 \times 10^{-3}$ sec)¹ and N_2 ($t_{th} = 1.8 \times 10^{-4}$ sec)²⁸, resulted mainly from the considered values of the cross sections of 0.7 \AA^2 for Ar and 6 \AA^2 for N_2 . It appears that the thermalization time for He is at least 10 times smaller than that for Ar or N_2 . At an average flow velocity of $4000 \text{ cm} \cdot \text{sec}^{-1}$, the thermalization distance d_{th} of the electrons due to elastic collisions with the gas is 0.15 cm for He, 3.1 cm for Ar and 1.2 cm for N_2 . If one assumes²⁷ that the mean free path of the electrons is energy-independent, the distance d_{th} becomes even smaller from the calculated values by a factor of 3.

The collision frequency ν_{col} , defined as $\nu_{col} \equiv v/\lambda$, can be calculated at thermal energy from the λ values obtained for He, Ar and N_2 and the thermal velocity $v_{th} \cong 1.2 \times 10^7 \text{ cm} \cdot \text{sec}^{-1}$ at 300 °K. The calculated values for ν_{col} at 1 torr are 2.2×10^8 , 1.0×10^8 and 1.5×10^8 collisions per second for He, Ar and N_2 respectively. These values are in very good agreement with those obtained by Fehsenfeld and coworkers¹³.

C) Power Dependence of the ECR signal

From the changes in linewidth of the resonant absorption as a function of the incident microwave power P_{MW} , a relative determination of the electron-atom (molecule) collision cross section can be obtained.

a) Without Scavenger

Two sets of experiments were carried out to study the power dependence of the ECR signal as a func-

tion of P_{MW} in the region between 0.8 and 400 μW at a constant pressure. In the first set, He was used as a carrier gas and as electron-source at a pressure of 4 torr with Xe as a quencher. In the other set, Ar at 3 torr was employed and the free electrons were produced by photoionization of NO using windowless plasma discharges. In Figure 3, the peak-to-peak

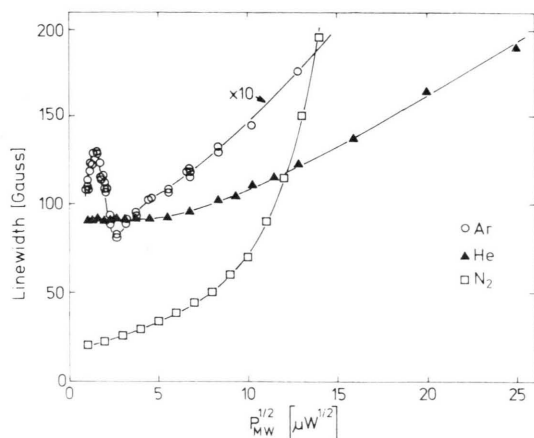


Fig. 3. Comparison of linewidth changes with microwave power for He (▲), Ar (○) and N_2 (□) carrier gases.

linewidth ΔH_{pp} is plotted as a function of $P_{MW}^{1/2}$ for He and Ar. In the same figure similar results²⁸ for N_2 at 3 torr are given for comparison. An interesting feature of Fig. 3 is the similarity of the shape of the ΔH_{pp} vs $P_{MW}^{1/2}$ curves with those published in the literature for the energy dependence of the electron-atom(molecule) collision cross sections in He^{11, 29, 30}, Ar^{11, 31} and N_2 ³². A similar behaviour was reported¹³ for the energy dependence of the collision frequencies in these gases. In the latter case Fehsenfeld *et al.*¹³ assumed a gas pressure of 1 torr at 300 °K.

The curve for Ar (Fig. 3) shows clearly the well-known Ramsauer-Townsend effect. Its shape at and around the Ramsauer minimum closely resembles that observed¹⁸ for the e-Ar scattering cross sections. This resemblance, however, is not to be considered quantitatively, since the energy variation of ν_{col} and ΔH_{pp} for Ar are not in close correspondence and so the correction factor¹³ is different for different electron energies. At energies close to 0.04 eV (see Sect. D) a maximum was observed. A similar peak was obtained previously³³. It cannot be decided whether this maximum is an experimental artifact or due to an impurity, as indicated by Bowe³⁴.

Of special interest of the He curve (Fig. 3) is the low-energy portion in which the linewidth ΔH_{pp} was

found to be practically independent of the input microwave power P_{MW} below $\sim 20 \mu W$. This power corresponds to an electron energy of ~ 0.08 eV (see Sect. D). At these energies the main contribution to the linewidth results from pressure broadening of the ECR signal in Helium. Contributions to ΔH_{pp} due to electron heating at this pressure (4 torr) are only observable at $P_{MW} \geq 20 \mu W$.

b) With Scavenger

In earlier studies¹⁻⁴ of the energy dependence of the ECR signal, the peak-to-peak height ratio h^0/h of the derivative signal with (e-signal) or without (e⁰-signal) scavenger was considered the measure of the electron attachment as a function of the incident microwave power P_{MW} , at constant reaction time and electron scavenger concentration. It was pointed out, however, in recent studies using Ar as carrier gas^{5, 6, 35} that care must be exercised due to changes in linewidth upon the addition of effective scavengers.

In the present work the influence of additives on the linewidth in He carrier gas was studied. By adding into the flowstream a scavenger, such as $CHCl_3$, $c-C_4F_8$, C_7F_{14} and O_2 at a constant concentration, the linewidth ΔH_{pp} was decreasing compared to the linewidth ΔH_{pp}^0 of the carrier gas alone. For the scavenger HBr no such change was observed.

In Figure 4, the linewidths ΔH_{pp}^0 and ΔH_{pp} for $CHCl_3$ are plotted as a function of $P_{MW}^{1/2}$. Similar results were obtained for the other molecules studied. The two curves in Fig. 4 deviate more as the microwave power increases, from 5% to more than 14% deviation. Thus, for electron concentration deter-

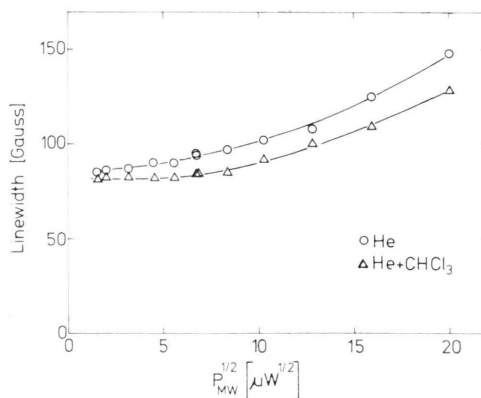


Fig. 4. Comparison of linewidth changes with microwave power for He (○) and He+ $CHCl_3$ (Δ) at 4 torr.

minations in He, a change in the linewidth ΔH_{pp} should also be accounted for, through the proportionality³⁵⁻³⁷

$$[e] \propto h \cdot \Delta H_{pp}^2 \quad (12)$$

No additional studies were carried out to elucidate the reason for the line narrowing. A similar observation has been described previously by Tice and Kivelson¹⁴. A threefold decrease in $[e]$, as measured by the relative intensities $h \cdot \Delta H_{pp}^2$ of resonance lines, resulted in a 10% decrease in the observed linewidth with N₂ as carrier and O₂ as a means to control $[e]$ ¹⁴. Electron-electron and electron-ion collisions were made responsible for this decrease in linewidth. However, a theoretical treatment by Hwa³⁸ indicated that contributions to linewidth due to these interactions can be neglected at electron concentrations $< 10^9 \text{ cm}^{-3}$. In typical ECR experiments $[e]$ is of the order of 10^6 cm^{-3} . It is much more suggested that the addition of molecular gases changes the electron energy distribution in the resonant cavity which leads to a change in lineshape. This change shows up in the present study as a narrowing of the ΔH_{pp} distance.

D) Power Dependence of Relative Attachment Rate and Electron Energy Calibration

For the determination of the energy dependence for the electron capture process in the present study, the relative intensity $\ln(h^0 \cdot \Delta H_{pp}^2 / h \cdot \Delta H_{pp}^2) \equiv \ln(x^0/x)$ rather than $\ln(h^0/h)$ of the derivative signal was considered as a function of P_{MW} at constant reaction time and constant electron scavenger leak rate.

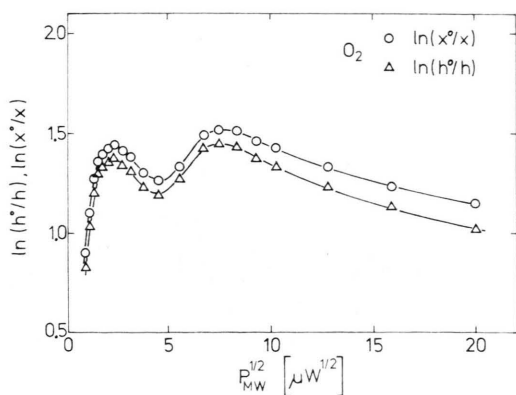


Fig. 5. Energy dependence of the electron attachment to O₂. In curve (Δ) only peak-to-peak height changes h^0/h were considered. Curve (\circ) shows changes in x^0/x .

The differences in the $\ln(h^0/h)$ and $\ln(x^0/x)$ representations for O₂ and CHCl₃ are given in Figures 5 and 6, respectively. Only small differences up to

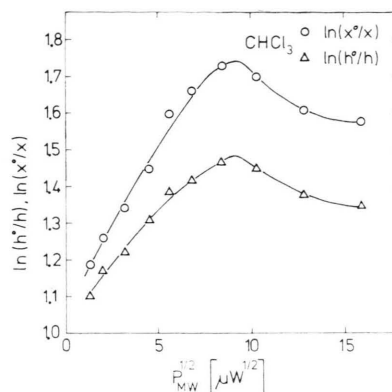


Fig. 6. Energy dependence of the electron attachment to CHCl₃. In curve (Δ) peak-to-peak height changes h^0/h are plotted. Curve (\circ) shows changes in x^0/x .

4% were observed for the power dependence of the relative attachment rates in O₂ when peak-to-peak height h instead of $h \cdot \Delta H_{pp}^2$ was taken as a measure of the electron concentration $[e]$. No such differences were found using HBr as a scavenger. For CHCl₃ a 10% difference can be estimated from Fig. 6, if the largest increase in attachment rate relative to the rate at the smallest microwave power input is considered. The two perfluorinated compounds, *c*-C₄F₈ and C₇F₁₄, showed an 8% change.

These results indicate that in He carrier gas possible changes in linewidth will affect $[e]$ -determinations to a much lesser extent than in Ar carrier gas^{13, 34}. The present experiments do not indicate any significant change in lineshape and/or shifts of the energy curve upon addition of these scavengers. Thus He is considered a very good choice as a carrier gas for power dependence studies.

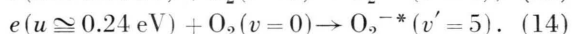
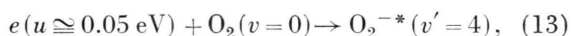
A correlation between $P_{MW}^{1/2}$ and absolute energy values is obtained by comparing the energy (in $\mu W^{1/2}$) in ECR experiments and the energy (in eV) in other studies for the maximum electron attachment rates. The Electron-swarm technique³⁹⁻⁴¹ is considered reliable method to be used for this correlation in the energy range of interest.

The relative attachment rates, as measured by the ECR method and expressed by $\ln(x^0/x)$, are plotted as a function of $P_{MW}^{1/2}$. These plots are shown in Fig. 5 for O₂, Fig. 6 for CHCl₃, Fig. 7 for *c*-C₄F₈ and C₇F₁₄, and Fig. 8 for HBr at a constant pressure of about 3.5 torr.

O₂:

The main feature of the $\ln(x^0/x)$ vs $P_{MW}^{1/2}$ curve for O₂ is the observed (Fig. 5) second peak at $7.5 \mu W^{1/2}$, in addition to the distinct thermal energy peak at $\sim 2.2 \mu W^{1/2}$. This second peak was previously observed²⁸ in ECR experiments as a very broad band when N₂ was used as a carrier gas. Two distinct peaks at 0.05 eV and 0.24 eV for O₂ were also obtained⁴² in N₂ carrier gas at pressures ≤ 500 torr through the electron-swarm unfolding procedure⁴⁰. Although the maximum at $2.2 \mu W^{1/2}$ is associated with the thermal electron capture process at 0.05 eV, the correspondence of the second peak at $7.5 \mu W^{1/2}$ to that at 0.24 eV is not so obvious because of the gradual shift of the cross section functions towards lower energies as the N₂ pressure increased⁴².

From a potential energy diagram⁴³ for O₂ ($X^3\Sigma_g^-$) and O₂ (X^2II_g), the two electron attachment processes at $2.2 \mu W^{1/2}$ (~ 0.05 eV) and $7.5 \mu W^{1/2}$ (~ 0.24 eV) can be viewed⁴² as taking place from the $v=0$ vibrational level of O₂ to the $v'=4$ and $v'=5$ vibrational levels of O₂⁻, i. e.

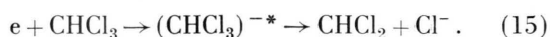


From the expression $N_i = N_0 \exp[(E_i - E_0)/kT]$, where $i=1, 2, 3, \dots$ vibrational states and E_i the energy of such a state, more than 99.9% of the O₂ molecules are in the $v=0$ vibrational level. Thus, the probability that a capture process may occur from the $v=1$ vibrational level of O₂ to the $v'=5$ or higher vibrational level of O₂⁻ is negligible. Collisional stabilization with a third body leading to O₂⁻ is likely to follow the formation of the intermediate temporary negative ion O₂^{-*}.

CHCl₃:

The maximum of the $\ln(x^0/x)$ vs $P_{MW}^{1/2}$ plot, as is seen in Fig. 6, lies at $\sim 9 \mu W^{1/2}$. We correlate this maximum with the maximum electron attachment at 0.37 eV, as obtained^{44, 45} by the electron-swarm method with N₂ used as a carrier gas. The shape of the energy dependence curve (Fig. 6) is quite similar to that observed⁵ in ECR studies with Ar as a carrier gas.

The free electrons attach to CHCl₃ forming an intermediate temporary negative ion (CHCl₃)^{-*} which decays dissociatively⁶, resulting in the formation of chloride ion Cl⁻

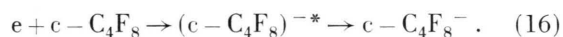


Chloride ion was found⁴⁴ by a time-of-flight (TOF) mass spectrometer to be the predominant negative ion in CHCl₃ below 1 eV.

c-C₄F₈:

Two maxima were observed (Fig. 7) for c-C₄F₈: one close to thermal energy at $\sim 1.7 \mu W^{1/2}$ and the other at $8.5 \mu W^{1/2}$. The first peak cannot be used for calibration purposes since there is no available data giving the absolute energy for this peak. This molecule has been previously studied⁴⁶ by a TOF mass spectrometer and it was found, however, that it attaches electrons at energies less than 0.05 eV. A maximum was also observed⁴⁷ in ECR experiments with Ar in the thermal energy region around 0.04 eV.

The intermediate negative ion (c-C₄F₈)^{-*} which is formed by electron capture, belongs to the long-lived negative ions with a mean lifetime of 12 μsec ⁴⁶ or 200 μsec ⁴⁸. Stabilization of an excited negative ion is a function of its lifetime and of the electron capture cross section. It, mainly, takes place through collisions with a molecule of the same or different kind. At a pressure of 3.5 torr, the collision time is of the order of 10^{-9} sec. This is $\sim 10^4 - 10^5$ times smaller than the negative ion lifetime. Thus, the attachment of electrons to c-C₄F₈ can be viewed as a non-dissociative process



From the electron-swarm work, the second maximum appears³⁵ at an energy of 0.3 eV. This energy is taken as the second calibration point corresponding to $8.5 \mu W^{1/2}$.

The two observed maxima might be attributed to the formation of the negative parent ion in two different vibrational states, in a similar way with those viewed in the O₂ system.

The rate constant k for thermal electron attachment to c-C₄F₈ was reported as $1.1 \times 10^{-7} \text{ cm}^3 \cdot \text{molec}^{-1} \cdot \text{sec}^{-1}$ ² and $1.2 \times 10^{-8} \text{ cm}^3 \cdot \text{molec}^{-1} \cdot \text{sec}^{-1}$ ⁴⁹. Reinvestigation of c-C₄F₈ by the ECR technique by Schultes³⁵, either by varying the scavenger concentration or the reaction time, gave values of 0.8×10^{-8} and $0.9 \times 10^{-8} \text{ cm}^3 \cdot \text{molec}^{-1} \cdot \text{sec}^{-1}$, respectively, in close agreement with the value obtained by Bansal and Fessenden⁴⁹.

C₇F₁₄:

For this molecule there was no experimental data given by the electron-swarm method. Thus, results

from a total ion current method⁵⁰ were taken. From comparison of the electron energy distribution and the first attachment peak in C_7F_{14} , the energy at which capture takes place was found⁵⁰ at ~ 0.15 eV. Our value for maximum capture was about $6.5 \mu W^{1/2}$, as is seen in Figure 7.

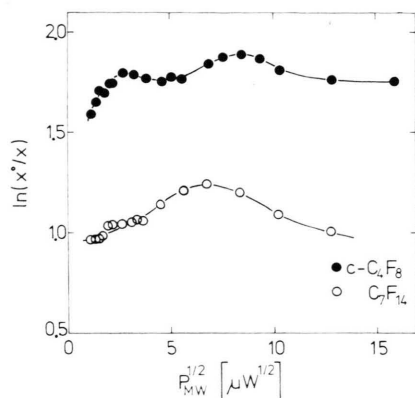
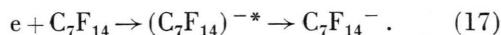


Fig. 7. Energy dependence of the electron attachment to $c-C_4F_8$ (●) and C_7F_{14} (○).

From a mass spectrometric study of C_7F_{14} , the most abundant negative ion was found⁵¹ to be $C_7F_{14}^-$ while the determined mean lifetime of its intermediate negative ion $(C_7F_{14})^{-*}$ was $\sim 800 \mu sec$ ⁴⁶. A calculated⁵² electron affinity of C_7F_{14} was positive and equal to ~ 1.7 eV. For the same reason given for $c-C_4F_8$, $C_7F_{14}^-$ is formed through a non-dissociative electron attachment at ~ 0.15 eV, visualized as



HBr:

A very broad maximum around $8.5 \mu W^{1/2}$ was observed in the electron capture by HBr, as is seen in Figure 8. In addition, a smaller but sharper peak at thermal energies was present. Such a peak was

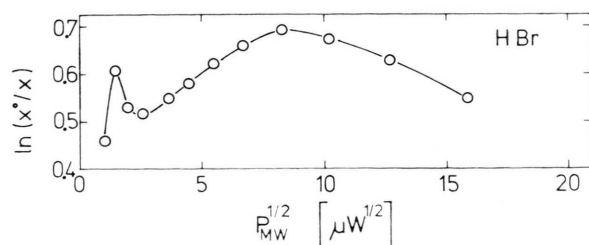
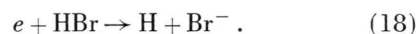


Fig. 8. Energy dependence of the electron attachment to HBr (○).

not present^{3, 47} in a previous experiment with Ar as a carrier gas, although in an electron-swarm study, after the dissociative attachment process with maximum at $E/P = 0.3$ Volts $\cdot cm^{-1} \cdot torr^{-1}$, another process appeared⁵³ at thermal energies. The presence of an impurity in HBr, such as Br_2 , might be responsible for this peak since, at low electron energies, Br^- was observed⁵⁴ to be formed from Br_2 with maximum probability at 0.03 ± 0.03 eV. A weak resonance maximum was also observed⁴⁷ by ECR method in the thermal energy region. From the electron energy distribution functions in N_2 ⁵⁵, which was used⁵³ as a carrier gas in the electron-swarm study, a value of 0.32 eV was found to correspond at $E/P = 0.3$ Volts $\cdot cm^{-1} \cdot torr^{-1}$. This value is in very good agreement with more recent results from electron-beam studies by Lifshitz and Weiss⁵⁶. When the unfolded Br^- curve⁵³ was convoluted with their⁵⁶ electron energy distribution, the observed maximum at 0.28 eV was shifted at 0.32 eV. This energy at 0.32 eV is correlated to the value of $8.5 \mu W^{1/2}$ at maximum capture rate.

A direct dissociative electron attachment process is considered to take place with the formation of bromide ion, viewed as



Summary of data

A summary of the thermalization results is given in Table I.

Table I. Thermalization data.

$P = 3.5$ torr $T = 300^\circ K$		He	Ar	N_2
σ_{th}^a	(\AA^2)	5.5	2.5	3.8
λ	(cm)	0.016	0.035	0.023
t_{th}	(sec)	3.8×10^{-5}	7.8×10^{-4}	2.9×10^{-4}
d_{th}	(cm)	0.15	3.1	1.2
ν_{col}^b	(sec^{-1})	2.2×10^8	1.0×10^8	1.5×10^8
ν_{col}^b, c	(sec^{-1})	2.2×10^8	0.8×10^8	1.4×10^8

^a See Reference 6 and appropriate references in Gilardini, A., Low Energy Electron Collisions in Gases, Wiley-Interscience, New York 1972.

^b At a pressure of 1 torr.

^c Determined from Fig. 3 of F. C. Fehsenfeld, L. R. Megill, and L. K. Droppelman, J. Chem. Phys. **43**, 3618 [1965].

Table II summarizes the results obtained by the ECR technique and by the electron-swarm and electron-beam methods, while Fig. 9 shows the calibration curve obtained from the correlation between the values of the incident microwave power $P_{MW}^{1/2}$ and the electron energy values for maximum elec-

Table II. Calibration data for Helium carrier gas.

Electron Scavenger	Microwave ^a Power $P_{MW}^{1/2}$ ($\mu W^{1/2}$)	Electron ^b Energy (eV)	References ^c
CHCl ₃	9	0.37	1
HBr	8.5	0.32	2
c-C ₄ F ₈	8.5	0.30	3
O ₂	7.5	0.24	4
C ₇ F ₁₄	6.5	0.15 ^c	5
O ₂	2.2	0.05	4
c-C ₄ F ₈	1.7	0.04 ^d	—

^a Present work.^b Electron-swarm method, except Reference 5.^c Total ionization method.^d Determined from calibrated curve in Figure 8.^e References

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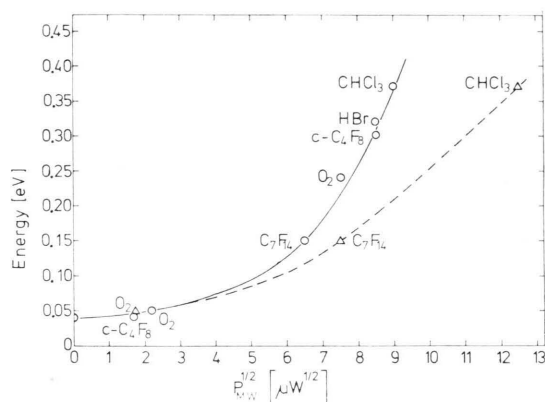


Fig. 9. Electron energy calibration as function of input microwave power with He (curve —○—) and Ar (—△—) as carrier gases. Point at $P_{MW}^{1/2} = 0$ corresponds to $(3/2)kT \cong 0.04$ eV.

tron attachment rates. In Figure 9 the calibration curve for CHCl₃, C₇F₁₄ and O₂ is also plotted when Ar³⁵ was used as a carrier gas. From a comparison of the two curves it is obvious that electron attach-

ment processes can be studied at higher energies when He, rather than Ar, is used as a carrier gas. For example, the microwave power required to reach the maximum electron attachment rate for CHCl₃ with Ar almost doubles that with He (see Figure 9).

The presented data indicate that by varying the microwave power input, pronounced changes in attachment rate can be observed in the energy range below 0.4 eV which corresponds to a kinetic energy of ~ 3000 °K. Measurements in this energy region are of high practical interest in chemical reactions in the gas phase at temperatures less than 3000 °K.

In ECR experiments where resonance absorption is observed, elastic scattering cross sections can be determined from pressure broadening of the absorption and the derivative ECR-signal⁶. This gives the possibility to discriminate between elastic and inelastic interactions. Although for the energy calibration of the input microwave power the ECR technique relies on experimental results determined by the electron-swarm and electron-beam methods, it has the advantage that it yields directly changes of capture rates without the need of an unfolding procedure^{40, 57}. This is particularly true for resonances close to thermal energies.

V. Conclusion

In this investigation it has been found that He gas can be considered a good choice, compared to Ar and N₂ gases, to be used in the ECR technique at the same time as a carrier gas and as a source for production of free electrons. The energy scale calibration of the input microwave power has shown that electron attachment processes at low-electron energies up to 0.4 eV can be studied conveniently by the ECR method.

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