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Electron attachment mass spectrometry as a diagnostics for electronegative gases and plasmas

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Electron attachment mass spectrometry (EAMS) has been developed to study mixtures of electronegative gases and plasmas. A quadrupole mass spectrometer (QMS) has been used to detect negative ions, formed from sampled species by attachment of low energy electrons. Varying the electron energy allows to collect the attachment cross section of the considered species. EAMS appears to be a very powerful technique to study the chemistry of electronegative gases. Unlike ionization mass spectrometry, where cross sections are low at the threshold and rather flat over a broad range of electron energies, attachment resonances are sharp and distinct. Also very limited fragmentation of the parent negative ion occurs, so a given molecule yields only a few different negative ions. This facilitates identification of components in a gas mixture. It is particularly advantageous for detection of large, fragile molecules, which break up after ionization, but can be easily transformed into large negative ions. Moreover, sensitive detection of active species is possible due to their relatively high attachment cross sections. A particularly important application of EAMS is the determination of an effective attachment cross section in a plasma. Recording this cross section allows to decide on the actual negative ion formation mechanism in the plasma environment, where active products of plasma conversion can significantly alter the negative ion production channels and consequently the whole balance of charged particles. Examples of EAMS applications to fluorocarbon gases and low-pressure radio-frequency plasmas are discussed. In a CF_4 discharge conversion of the parent gas into species like C_2F_6 and C_3F_8 is easily visualized. The dominant mechanism of negative ion formation in the plasma is electron attachment to these minority species and not to the parent gas. Also larger polymers are readily formed in fluorocarbon plasmas. In a C_2F_6 discharge molecules with up to ten carbon atoms (the mass limit of our apparatus) have been detected using EAMS. © 1998 American Institute of Physics. [S0034-6748(98)00501-2]

I. INTRODUCTION

The physics and chemistry of electronegative species has attracted a lot of attention from investigators from various fields.¹ Its wide application range includes electrical switches, which make use of strongly electronegative gases, such as SF_6 , as insulators. In halogen lamps and gas lasers halogens and their mixtures play an important role. Another application is the production of negative ion beams. For example, negative hydrogen ions can be accelerated and neutralized to form a very high energetic atom beam, which is used as an additional heating source in thermonuclear plasmas.² Several chemical processes in industrial, atmospheric and cosmic environments involve negative ions, e.g., purification of waste gases, production and destruction of ozone. Finally, electronegative gases are widely used in low-pressure surface processing discharges.³ In reactive ion etching (RIE) electronegative halocarbons and halogens find their application, while oxygen is used for etching of photoresist and ashing of organic layers. Also in deposition plasmas, using gases like methane and silane, negative ion formation is of major interest. The latter is closely related to formation of large cluster ions, acting as precursors for dust

particles, which contribute to surface contamination.⁴ Also the electronegative character of fullerenes has been investigated.⁵ In spite of the large interest, the available data on negative ion processes is scarce. In particular, more detailed knowledge about negative ion formation mechanisms and the cross sections is needed. Determination of these quantities is difficult and the results often contradict each other. Cross-section data have been collected using various crossed beam experiments and swarm methods,^{1,6} but these methods yield information only about the stable electronegative molecules. Still, there is a lot of interest in the electron attaching behavior of excited molecules and radicals, which are readily formed in the plasma environment. In this work we present electron attachment mass spectrometry (EAMS) as a convenient method to study the chemistry of electronegative species and to determine the electron attachment cross section to a mixture of various electronegative gases.

There are many possibilities for mass spectrometric detection of neutral species. The differences lie in the way of converting neutrals to ions. The traditional ionization mass spectrometry, using energetic electrons to ionize the species, is the simplest and for many purposes the most adequate method. However, for larger molecules and complex mixtures complicated fragmentation patterns create difficulties in distinguishing between the constituents. Especially when one aims at the detection of minority species, like radicals and

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excited molecules, problems with large interference with the parent gas background are inevitable. Typically, threshold behavior of the ionization is studied. In some cases it allows to separate the signals, originating from the fragmentation of the parent molecule, from the species of interest. However, often the differences in ionization thresholds are relatively small and the ionization cross sections at the threshold are low, which seriously limits the sensitivity of this method. For organic molecules attachment of light positive ions, like H^+ and Li^+ , can improve the detection, as shown for hydrocarbon species by Hansel *et al.*⁷ and Fujii and Syouji.⁸ Naturally, not all species can be detected this way. The principle of electron attachment mass spectrometry has been also applied in the past, mainly for the detection of organic species or for the determination of electron capture cross sections for stable molecules.⁹ However, this technique has much more advantageous aspects, which so far have not been explored, due to the complexity of the experimental setups used in the past. The recent commercial availability of reliable quadrupole mass spectrometers and off the shelf electron sources opens the possibility to take full advantage of EAMS as a diagnostic tool. Its applications include analysis of complex mixtures of electronegative gases, detection of metastable species and measurements of their attachment cross sections. This technique is especially powerful when applied to a plasma. It allows one to determine the effective electron attachment cross section of a complicated gas mixture formed in a plasma environment. This cross section is in many cases different from the one for the neutral parent gas, due to efficient chemical conversion in the plasma. EAMS yields this magnitude directly, so the tedious determination of the relative densities of plasma produced species, like radicals, excited species, polymeric molecules and clusters together with their attachment cross sections, can be avoided. Analysis of the effective attachment cross section in the plasma gives very valuable insight into the negative ion formation channels.

II. EAMS METHOD

In the EAMS technique electronegative species are sampled through an orifice into an attachment chamber. Monoenergetic low energy electrons (<10 eV) generated by a hot filament are used to perform attachment. The pressure in the attachment chamber is kept very low ($<10^{-6}$ Torr) to avoid loss of ions by detachment, charge transfer, and other collision processes. Therefore, the method is conceptionally close to a crossed beam experiment. At low pressures, the most important negative ion formation mechanism is two-body attachment. In many cases this results in the formation of a metastable parent anion. For large, polyatomic molecules the excess energy can be redistributed over internal degrees of freedom and the parent ion, stabilized this way, can be detected. For smaller molecules, in absence of a third body for stabilization, electron attachment is often followed by dissociation of the excited parent ion into several stable fragments:

Of course, for complex molecules several fragmentation patterns are possible. However, there are only few fragmentation channels favored, so typically not so many different ions are formed. This is a big advantage of the EAMS method over the ionization mass spectrometry, where in general all possible fragment ions are observed. For example, a C_2F_6 molecule yields only F^- , CF_3^- , and $C_2F_5^-$ in EAMS, while all possible combinations of C_xF_y ($x=0,1,2$; $y=0-5$) show up in the positive ion mass spectrum. Moreover, EAMS is clearly less destructive than ionization: large, fragile molecules are more likely to “survive” the attachment of a low energy electron rather than the exposure to a high energy ionizing electron beam. SF_6 is a such a molecule: in EAMS it gives a large signal of the parent anion, while the corresponding parent cation is not observed. Other examples include polymeric species, as will be explained further in this work. As dissociative electron attachment involves an intermediate metastable state, it is a resonant process. The characteristic, peaked shapes of the cross section facilitate the detection of various species in the mixtures, as they can be distinguished based on the position and width of the resonance. This is another important advantage over the ionization. Finally, one can profit from EAMS during detection of chemically active species, radicals and polymers: these particles have in many cases a larger attachment cross section than the parent gas, so in spite of their low densities significant negative ion signals can be collected. For example, the dissociative attachment cross section for hydrogen increases rapidly with vibrational excitation: the cross section for H_2 ($v=4$) is 10^5 times higher than for H_2 ($v=1$). Further in this work we discuss CF_4 and C_2F_6 plasmas, in which higher fluoroalkanes with large attachment cross sections are formed. These can be easily visualized both in the F^- signal and in the heavier ion signals.

At higher electron energies (more than 10 eV) ion pair formation occurs:

This is not a resonant process, and its electron energy-dependent cross section resembles the broad ionization cross section. Therefore, detection of negative ions created in this process is generally not advantageous over positive ionization mass spectrometry or the previously described resonant electron attachment. Nevertheless, in cases where ion pair formation in gas mixtures yields different negative ions, but the same positive ions from various species, or if there are more differences in threshold behavior of ion pair formation than in ionization threshold between several species, it may be useful to use ion pair formation as a diagnostic tool. In the case of oxygen gas temperature effects can be studied this way: the enhancement of the O^+/O^- formation with temperature is more readily detectable than the enhancement of the dissociative attachment,⁹ while no temperature effect at all is observed in positive ion mass spectrometry.

In Fig. 1 a scheme of the setup for EAMS experiments is shown. A commercial HIDEN EPQ quadrupole mass spectrometer (QMS) with an energy selector [Fig. 1(a)] is mounted on a vacuum system [Fig. 1(b)]. The typical settings of the QMS system are given in Table I. The sample

(a)

(b)

FIG. 1. Schematic view of the experimental setup: (a) The HIDDEN quadrupole mass spectrometer. The following elements are indicated by numbers: 1. extractor, 2. ion extraction lens, 3. electron emitting filaments, 4. source cage, 5. axis, 6. ion focusing lens, 7. quadrupole, vertical, horizontal (adjustment lenses), 8. energy selector plates, 9. axis, 10. focus lens, 11. mass selector, 12. suppressor, 13. dynode, 14. collector. (b) The vacuum chamber, TMP, RP, and MBP indicate turbomolecular, roots, and mechanical booster pumps; MFC is a mass flow controller.

gas from the reactor is introduced to the differentially pumped mass spectrometer through a $150\ \mu\text{m}$ orifice. In the QMS the neutral species are exposed to an electron beam in the attachment chamber. The electrons are generated by a hot filament and accelerated to the desired energy by a variable potential between the filaments and a grid surrounding the attachment chamber. The electrons have a continuously adjustable energy down to $0.5\ \text{eV}$ and the energy resolution is $0.1\ \text{eV}$. The specifications of the HIDDEN system claim an adjustable electron energy down to $0\ \text{eV}$. However, tests with SF_6 , attaching at 0 to $0.2\ \text{eV}$, showed considerable deviations from the expected count rates and formation cross sections for SF_6^- , SF_5^- , and F^- . The electron energy has an offset dependent on the filament condition, which can be easily determined using a well-known test gas. This offset has been implicitly subtracted from all results given below. Negative ions, formed inside the attachment chamber are ex-

TABLE I. List of settings of the voltages typically used in the negative ion detection. The numbers indicate the elements shown in Fig. 1(a).

Element	No.	Setting
Extractor	1	grounded
Ion extraction lens (suppressing plasma ions)	2	$50\ \text{V}$
Electron filament current	3	$10\ \mu\text{A}$
Electron energy		$1\text{--}10\ \text{eV}$
Ion energy setting		$-9.5\ \text{to}\ -8.5\ \text{V}$
Attachment chamber potential		$-10\ \text{V}$
Source cage	4	$50\ \text{V}$
Axis (system energy)	5	$40\ \text{V}$
Ion focusing lens (focus into energy filter)	6	$102\ \text{V}$
Plates of energy filter	8	$-7.55\ \text{V}$
Focus lens (focus into mass filter)	10	$200\ \text{V}$
Suppressor (focus into detector)	12	$200\ \text{V}$
Dynode	13	$800\ \text{V}$
Collector	14	$1900\ \text{V}$

tracted by an ion lens [number 4 in Fig. 1(a)] and focused into a drift tube. From here on all ions pass the system with the same energy, in order to reduce the effect of energy-dependent transmission efficiency. After an energy filter using a 45° sector field energy analyzer and mass selection using the quadrupole technique, the ions are detected by a dynode electron multiplier system. Here the negative ions are converted to electron pulses, which are detected using a channeltron detector. This allows to detect all negative ions formed in the attachment chamber. Moreover, the presence of the energy filter allows one to study the kinetic energy of the formed negative ions. If the negative ions have a significant energy, they are more likely to be lost at the walls of the attachment chamber. Thus, in these cases the energy dependent detection efficiency has to be taken into account in addition to the mass-dependent efficiency.

The main reactor is filled with the sample gas, usually at a pressure of $10\text{--}20\ \text{mTorr}$. Active species are produced in a $13.56\ \text{MHz}$ plasma. We use an open plasma configuration, with grounded reactor walls and a square ($7 \times 7\ \text{cm}^2$) powered electrode made of aluminum. A grounded plate is placed below the powered electrode (at a $5\ \text{mm}$ distance), thus the plasma is sustained in the upper part of the vacuum chamber, where the QMS extraction orifice is located. Several etching gases have been studied: SF_6 , O_2 , CF_4 , C_2F_6 , and C_4F_8 . The sampled species enter the extraction orifice of the QMS, which is in contact with the plasma. If necessary, electrons and positive ions from the plasma are repelled by retarding potentials on the extractor and the first ion lens in front of the attachment chamber.

III. RESULTS AND DISCUSSION

A simple gas with a well-known resonance is used to test the system. We have chosen to use dissociative attachment to O_2 , because it has a single well-known resonance at $6\ \text{eV}$. Besides there is a lot of practical interest in oxygen discharges.¹⁰ In Fig. 2 the O^- signal from oxygen gas at $40\ \text{mTorr}$ pressure is shown as a function of the attaching electron energy. Even though the cross sections are relatively small and the O^- is produced with considerable energy ($1\text{--}2\ \text{eV}$), reducing the detection efficiency, the signal can be quite

FIG. 2. A typical negative ion signal, recorded in oxygen as a function of the attaching electron energy, at 40 mTorr pressure (square). The shape of the O^- resonance is in good agreement with the cross section given by Rapp and Braglia (Ref. 11) (full curve).

easily detected. The literature attachment cross section, provided by Rapp and Braglia¹¹ has been used to determine the electron energy offset in the EAMS; in the data presented below this correction is always made implicitly. It is clear that the onset energy and the FWHM value of both data sets agree quite well.

In CF_4 gas two negative ions have been detected: F^- and CF_3^- . The corresponding resonances are shown in Fig. 3, and the normalized cross sections provided by Spyrou *et al.*¹² are given for comparison. For CF_3^- the resonance peak as well as the FWHM values are in good agreement. The F^- resonance consists in fact of two contributions, due to the following processes: $CF_4 + e \rightarrow CF_3 + F^-$ at 6.5 eV and CF_4

FIG. 3. Negative ion signals in CF_4 gas at 15 mTorr pressure: (a) F^- and (b) CF_3^- . The literature cross sections (Ref. 12) for the formation of these ions (full curves) are given for comparison. A very good agreement is found for CF_3^- . In the case of F^- , the negative ion resonance consists of two overlapping peaks at 6.5 and at 8 eV.

FIG. 4. Negative ion resonances in C_2F_6 gas at 10 mTorr pressure. The position and shape of these peaks is in good agreement with the cross section data provided by Spyrou *et al.* (Ref. 12).

$+ e \rightarrow CF_2 + F + F^-$ at 8 eV. F^- ions produced in the former process carry a significant kinetic energy (in the order of 2 eV), while the latter process supplies relatively cold negative ions. In our case high energetic ions can evade the cage potential and consequently their extraction is less efficient, so our signal originates mainly from ions formed in the latter process. In contrast, the system used by Spyrou *et al.* favors the detection of fast ions, so in their case the F^- peak appearing at 6.5 eV, due to normal dissociative attachment, is more pronounced, while the other one is suppressed. As a result, the two data sets have a different appearance: the EAMS curve is peaked at 8 eV, with a shoulder at the low energy side; while the literature curve has the same electron energy onset, a peak at 6.5 eV and a shoulder at the high energy side. The swarm technique yields a maximum cross section somewhere between these energies.¹³ Since formation of energetic negative ions by dissociative attachment to small molecules is not uncommon, one has to take into account the energy of ions during detection. However, in plasma physical applications or in detection of large molecules, mostly low energy processes are important, thus this complication is typically absent. Further in this work we shall consider attachment processes, occurring at low electron energies and having only small energetic effects.

In Fig. 4 the negative ion resonances for C_2F_6 are shown; in this case F^- , CF_3^- , and $C_2F_5^-$ have been detected at an electron energy of 4 eV. These peaks have been also found in CF_4 during plasma operation: C_2F_6 is one of the important products of plasma conversion of the parent gas. In Fig. 5(a) the F^- signal in the CF_4 gas and in a plasma at several power levels is shown and the contribution from C_2F_6 is identified. Similar resonances are found in the CF_3^- signal. Based on corresponding signals in C_2F_6 gas from Fig. 4, the partial pressure of C_2F_6 in a CF_4 plasma has been determined as a function of the power level. In Fig. 5(b) it can be seen that the C_2F_6 density, determined by comparing F^- resonances in Figs. 4 and 5(a) is higher than the one determined from the corresponding CF_3^- signals. This suggests that there is a contribution of other species, producing F^- at the energies close to the C_2F_6 peak. Indeed, the F^- signal displays a complex structure. At low plasma powers another resonance is visible, at lower electron energy than the C_2F_6 resonance. This feature is found only in the F^- signal. Based on the position of

FIG. 5. (a) The F^- signal as a function of the attaching electron energy in CF_4 gas (0 W, dashed curve) and in presence of a plasma at 10, 15, and 20 W power input. The pressure is 15 mTorr and the flow rate is 2.5 sccm. These signals reflect the complex chemistry of a CF_4 discharge. In presence of a plasma a large peak, due to attachment to C_2F_6 is visible at an electron energy of 4 eV. Moreover, at 3 eV another resonance is present, which is especially clearly visible at 10 W. This peak has been ascribed to plasma produced C_3F_8 , based on its attachment cross section provided in Ref. 12; (b) the C_2F_6 partial pressure, obtained by calibrating the data with the cross section from Fig. 4. The C_2F_6 partial pressure, obtained from the F^- signal is higher than the one derived from the CF_3^- signal. This suggests that in the F^- resonance at 4 eV there is a contribution of other attaching species than C_2F_6 . The difference is relatively more important at low power levels, where the C_2F_6 signal overlaps with a relatively high C_3F_8 signal.

this peak, it has been attributed to attachment to plasma produced C_3F_8 , which yields predominantly F^- , with a maximum cross section around 3 eV. Finally, at all plasma power levels a signal is observed at electron energies close to or lower than 1 eV. It might originate from F_2 , which attaches electrons at energies below 1 eV.

Determination of absolute densities of the constituents of a gas mixture is one of the major profits of EAMS. Another important information provided by this technique follows from the comparison of the negative ion signals in a CF_4 gas and in a CF_4 plasma. Figure 5(a) displays in fact an effective attachment cross section in the plasma, taking into account attachment to various plasma produced species. It can be seen that in a CF_4 plasma the dominant electron attaching species is not the parent gas itself. A typical electron temperature in a radio-frequency discharge is around 3–4 eV, so formation of fast attaching species with a low threshold and a maximum at 3–4 eV enhances greatly the negative ion production in the plasma with respect to pure CF_4 gas. Knowledge of the effective electron attachment cross section in the plasma is crucial for understanding the negative ion formation channels and for modeling the charged particles.

Now, the EAMS technique provides a fast and reliable way of determining this cross section and there is no need to determine all densities of attaching species separately and to rely on their attachment cross sections, which are often unavailable.

As already indicated, one of the important advantages of EAMS is a relatively simple fragmentation pattern of the parent negative ion, as compared to the ionization mass spectrometry, where a broad variety of positive fragment ions is formed. This can be clearly seen from the negative and positive ion spectra in fluorocarbon gases. In Fig. 6 a comparison of count rates in ionization mass spectrometry and in EAMS is given for several investigated gases: CF_4 , C_2F_6 , and C_4F_8 . Indeed, in positive ion mass spectrometry all fragment ions can be detected. Especially fluorine stripping is efficient: carbon-rich species like C_2F or C_3F are relatively abundant. For molecules containing more carbon atoms, detection of parent ions by ionization mass spectrometry is expected to be difficult due to their fragmentation. At the same time, electron attaching capacity of these polymeric species is expected to increase with the number of carbon atoms, so EAMS can provide a unique method of mass spectrometric detection of large molecules/small clusters. In order to verify this we have collected signals from various polymeric species, formed in a C_2F_6 plasma. A typical electron energy dependence of the attachment cross section to a polymeric fluorocarbon is given in Fig. 7. The observed resonance lies at low electron energies, unlike the F^- and CF_3^- peaks, which confirms the strong electronegative character of heavy molecules. In Fig. 8 a comparison is shown between the energy integrated count rates for polymeric anions and cations formed in the C_2F_6 plasma. Negative and positive ions are arranged in series C_nF_{2n-k} . Typically, in a C_2F_6 plasma the series C_nF_{2n+1} and C_nF_{2n-1} contain the most intense signals, series with even k have a clearly lower count rate. This is due to the electronic structure of the formed negative or positive ions: neutral fluorocarbons with an even amount of fluorine atoms have a closed electronic configuration and consequently the corresponding ions are energetically less favored. The recorded signals of C_nF_{2n-k} anions originate most probably from the corresponding C_nF_{2n-k+1} molecules/radicals, or from a species containing more carbon atoms. The fact, that the signals rapidly decrease with increasing k indicates that the polymers, formed in this fluorine-rich plasma, are mainly saturated, with a high fluorine content. In contrast, in a C_4F_8 plasma series with a higher k are well pronounced (like the $C_7F_{11}^-$ ion in Fig. 7), suggesting that in this chemistry unsaturated structures with a lower fluorine content are readily formed.¹⁴ Finally, it is evident from Fig. 8 that detection of parent ions by ionization mass spectrometry stops at $n=5$, while anions with masses up to the maximum mass detectable by the QMS (510 amu, $n=10$) can be easily visualized. Moreover, in ionization mass spectrometry a significantly larger spread is observed in the amount of fluorine atoms (k) for a group of species with a given number of carbon atoms. No remarkable difference has been found between the C_2F_6 and C_4F_8 plasmas in positive ion mass spectrometry. This suggests a sig-

FIG. 6. The electron energy integrated count rates of positive ions formed by electron impact ionization (traditional mass spectrometry) in white and negative ions formed by attachment (EAMS) in black for the following gases: (a) CF_4 at 30 mTorr, (b) C_2F_6 at 10 mTorr, and (c) C_4F_8 at 10 mTorr. In the latter case positive and negative ions are given in separate figures. The count rates are arranged in groups with the same number of carbon atoms and increasing number of fluorine atoms. It can be seen that while in EAMS only a few different anionic species are detected, ionization yields a large variety of fragment ions: for a given number of carbon atoms, ions with almost all possible degrees of fluorination appear in the positive ion mass spectrum.

nificant fragmentation and fluorine stripping of the polymeric species during positive ion formation, in agreement with the data presented in Fig. 6. On the other hand, the distribution

FIG. 7. Electron energy dependence of the $C_7F_{11}^-$ signal, originating from a polymeric species formed in a C_4F_8 plasma, at 15 mTorr pressure, 8 W power input, and 4 sccm flow rate.

in k for negative ions is probably much closer to the original distribution of the neutral species, formed in the plasma. This confirms the nondestructive character of EAMS, which better preserves the molecules in their original form, after they are transformed into negative ions.

Summarizing, EAMS is a very suitable technique to study the chemistry of electronegative gases and plasmas. It yields densities of minority species and allows to study their electron attachment cross sections. These data can be directly used in a study of the negative ion chemistry in plasmas.

FIG. 8. Electron energy integrated count rates of (a) negative and (b) positive ions, formed from polymeric neutral species. The polymers are produced in a 20 mTorr, 7 W, and 2 sccm plasma in C_2F_6 . The ion signals are arranged in series $C_nF_{2n-k}^-$, as a function of n and k . A striking difference between the EAMS and ionization is the distribution of polymeric ions. In case of EAMS species with as many as ten carbon atoms are readily detected, in spite of the decreasing transmission efficiency of the HIDDEN system for high masses. Moreover, only a few k values are observed: in the considered chemistry fluorine stripped species are scarce. In contrast, a much larger variety of fragment ions, also with a low fluorine content, is observed using ionization mass spectrometry. However, polymeric positive ions larger than $n=5$ cannot be visualized, due to their fragmentation.

EAMS is particularly convenient to detect large molecules, which are readily formed in industrial surface processing plasmas using chemically reactive gases.

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