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# Rydberg electron capture mass spectrometry of some environmental pollutants

G. Brincourt, Y. Zerega*, M. Carette, P. Perrier, J. Andre

*Institut Universitaire des Systèmes Thermiques Industriels, C.N.R.S., U.M.R. 6595, Université de Provence, Technopôle de Chateau-Gombert, 5 rue E. Fermi, F13453 Marseille Cedex 20, France*

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## Abstract

This work relates a coupling between a Rydberg electron capture (REC) source and a mass spectrometer (MS) using a quadrupole ion trap within a special operating mode. The MS instrument is only briefly described as it has already been published. The advantages of the REC are shown, i.e. no fragmentation of the molecule occurs during charge exchange with the Rydberg xenon atoms. The molecular ion lifetime seems to be sufficient to perform mass spectrometry by Fourier analysis. The experiments concern certain molecules of interest in the field of the environment having a positive electron affinity to insure Rydberg electron capture, i.e. certain polyaromatic hydrocarbons, certain polychloro-biphenyls, and one dioxin. (Int J Mass Spectrom 189 (1999) 181–188) © 1999 Elsevier Science B.V.

*Keywords:* Quadrupole ion trap; Rydberg electron capture; Fourier transform mass analysis; Environmental pollutants

## 1. Introduction

Current works tend to decrease the number of undesirably created ions in ionic sources for mass spectrometers to improve sensitivity and reproducibility of the spectra.

The most commonly used technique to create ions is electron impact (EI). For complex molecular gas many fragment ions are created, which in some cases lead to a very complex spectrum making it difficult to interpret. Other ionic sources have been proposed where positive or negative ions are created by chemical ionisation (CI) [1]. For example, to create positive ions we can use proton or hydrogen transfer depending on the proton affinity of the molecule [2]. Electron attachment allows negative ions to be created, the number of fragments depending on the energy of the electron. An electron capture (EC) source using free thermal electrons produces a very small number of fragments compared to EI and gives a greater sensitivity. However, there is a certain lack of reproducibility of the spectra. An enhancement gas is used under high pressure both as a source of free thermal electrons and as stabilisation of the negative molecular ions. But collisions can also induce undesirable molecular dissociation [3,4]. In this case, it is difficult to control the different mechanisms concerning the behaviour of the molecular ion: collisional stabilisation, collisional dissociation, electron auto detachment, etc. Another way of producing free thermal electrons to achieve an electron capture is to use an

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* Corresponding author. E-mail: yzerega@iusti.univ-mrs.fr

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electron monochromator which can give electrons having selected energy levels with a precision of about some tens of millielectron volts [5,6].

Here, we present a "very soft" ionisation technique, Rydberg electron capture (REC) which produces practically no ion fragments in comparison with free thermal electrons from EC sources. We have already tried this technique on $SF_6$ molecular gas without fragmentation by using an entirely homemade REC-MS instrument [7,8]. Results will be summarized in sec. 4. The qualities of the ionic source and of the mass spectrometer have led us to analyse some electrophyle environmental pollutants [9].

## 2. Experimental setup

### 2.1. Rydberg electron attachment

Many molecules of environmental interest can attach an electron by resonance capture due to a sufficient positive electron affinity (EA) [10,11]. Generally, many of these molecules attach electrons where the energy is positive (free electrons) as well as negative (bound electrons) and is in a range of thermal energy with an absolute value lower than 1 eV.

Insofar as the optical electron of atoms can have such a low negative energy we can use excited atoms in Rydberg states. We have used Rydberg electrons of xenon atoms excited by electron impact and denoted Xe**. The xenon atoms are excited on different *nf* levels and the corresponding Rydberg electrons have an energy spread of some tens of millielectron volts. This is a suitable and original technology which is cheaper and of higher precision on the attached electron energy than that resulting from the utilisation of even a well calibrated narrow thermal energy spread electron gun. Another important advantage of using Rydberg atoms is the possibility of carrying out the attachment process directly inside the trap whereas, due to the confinement electric field, it is impossible to introduce free electrons into a trap with their energy maintained below 1 eV.

The reaction of Rydberg electron capture by a molecule MX is expressed by

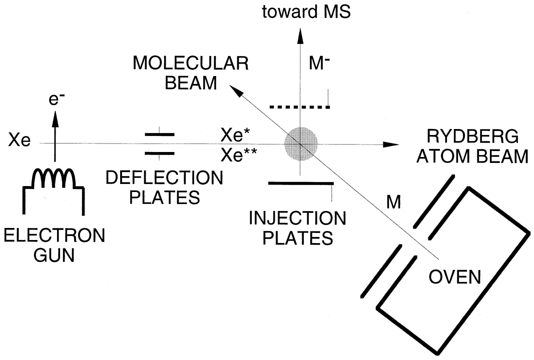

Fig. 1. Description of the Rydberg electron capture source.

$$MX + Xe^{**} \rightarrow MX^{-*} + Xe^{+} \quad (1)$$

where the molecular anion is unstable because it is formed in an excited state. Its autodetachment lifetime $\tau_a$ may extend from $10^{-15}$ s to $>10^{-2}$ s depending on: (1) the complexity (number of degrees of freedom) and the internal energy of the molecular ion [12] and (2) a possible collisional stabilisation, the more complex the ion and the weaker its internal energy, the longer its lifetime.

Here, the internal energy of the ion depends on the Rydberg electron energy of the xenon atoms. The lifetime of the molecular ion is then correlated to the *nf* Rydberg states of the xenon atom. The lifetime $\tau_a$ increases if the *n* state decreases [13]. Consequently, the autodetachment lifetime which, in addition, can be enhanced by collisional cooling of the ions, greatly depends on the experimental conditions.

Moreover, in the case of binding electrons (when using Rydberg atoms) the internal energy of the molecular ion is lower than that obtained with free electrons and consequently its lifetime is greater.

### 2.2. Rydberg electron capture source

In our experiments, the anions, which are always monocharged, are formed in cross beams by collisions between Rydberg xenon atoms and the target molecules coming from an oven (see Fig. 1).

The Xe atoms of the beam are admitted to an electron impact source at about 100 eV. Positive Xe ions, Xe* metastable atoms and Xe** Rydberg atoms

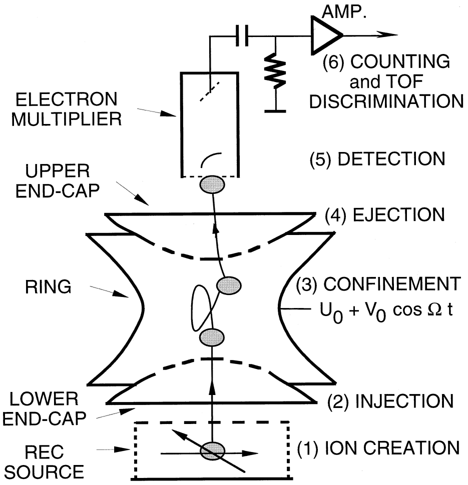

Fig. 2. Schematic arrangement of the MS instrument with the indication of the successive steps for ion mass analysis.

are created. Electrons and positive Xe ions are eliminated from the beam by the deflection plates. Xe* metastable atoms and Xe** Rydberg atoms come into the beam interaction zone. By taking into account the lifetime of the Xe** beam and the distance to reach the crossing point ($d = 7$ cm), the principal quantum numbers of the Rydberg electrons are $n \geq 25$. The electric field (of about 150 V/cm) existing between the two deviation plates limits the Rydberg electrons to $n \leq 40$. This gives binding electron energies between 8.5 and 21.7 meV [14].

The pollutant molecular beam is generated by evaporation of solid samples in an oven and mechanical lens.

The molecular ions created in the beam interaction zone are softly accelerated in a direction perpendicular to the plane defined by the two beams. In order to do this, two plates, called injection plates, are laid out on both sides of the beam interaction zone and are supplied with a low pulsed voltage.

### *2.3. Mass spectrometer*

The mass spectrometer (see Fig. 2) uses a quadrupole ion trap with an original operating mode. The theoretical and experimental aspects and the simulation studies of this protocol for mass analysis have previously been developed in several papers [15–19].

When they enter the trap, the ions are slowed down by a dipolar pulsed voltage applied between the two endcaps. They are stopped in an off-centre axial position when the rf voltage $U_0 + V_0 \cos(\Omega t)$ is then applied to the ring electrode (with $\Omega/2\pi = 171.875$ kHz). The duration and the amplitude of the slowing-down voltage can be adjusted to select a given range of masses to be confined. After a given confinement time the rf voltage is stopped and simultaneously all the ions are ejected out of the trap through the upper endcap by a dipolar pulsed voltage and are detected by an electron multiplier. A single-channel temporal analyser counts the number of ions detected in a counting gate, the width and the position of which is temporally adjustable to make a time-of-flight (TOF) discrimination.

As the ejection clears the ions from the trap at the end of the confinement time $t_i = iT_e$, these previously described steps, called the elementary experiment, must be repeated for different values of the confinement time from $T_e$ to $T_m = N_c T_e = N_c j T_\Omega$, where $N_c$ is the maximum number of confinement channels; $T_\Omega$ is the period of the confinement voltage (or the period of the micro motion) and $j$ is the $T_e$ (sampling period) over $T_\Omega$ (period of the confinement voltage) ratio.

The turning on and the turning off of the pulsed and of the confinement voltages are phase locked to the rf period $T_\Omega$.

The ion TOF depends on the position and velocity of the ions in the trap at the time of their ejection. As the temporal signal is sampled at the period $T_e = jT_\Omega$, the number of ions detected in the counting gate evolves with the axial secular frequencies of the ion motion during the confinement. The Fourier transform of this signal gives the spectrum of axial secular frequency peaks of each simultaneously confined species.

When the ion source produces few ions, for each confinement channel the experiment can be repeated $M$ times and the results can be summed. The global ion signal is equivalent to any temporal modulated electronic or optical signal giving an image of the

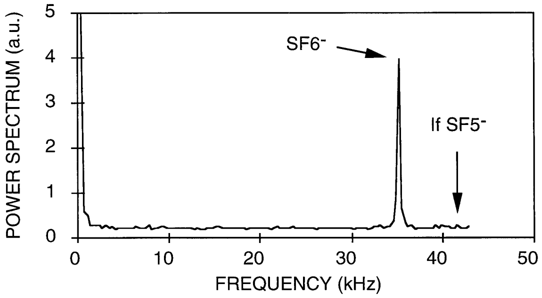

Fig. 3. Experimental frequency power spectrum obtained with a REC source on $SF_6$ molecules. The operating conditions are: $U_0 = 0$ V; $V_0 = 50$ V; $\Omega/2\pi = 171.875$ kHz, and $z_0 = 1$ cm. The $SF_6^-$ theoretical secular frequency is 36.78 kHz; The $SF_5^-$ theoretical secular frequency is 43.60 kHz which gives an apparent frequency at 42.34 kHz.

secular movement of a great number of ions simultaneously and continuously confined [20,21].

In this MS instrument we must not use a buffer gas that would centre the ion cloud and would lead to a loss of the ion motion coherence. The pressure in the MS chamber is lower than $10^{-7}$ Torr to avoid collision perturbation of the ion motion.

## 3. Results and discussions

### 3.1. $SF_6^-$ ions

These results concern the first experiments carried out with a REC-MS instrument.

Fig. 3 shows an experimental negative ion spectrum obtained by an REC on $SF_6$ molecules. The $SF_6^-$ ion peak may be observed with a very good signal-to-noise ratio and without any significant fragmentation: the $SF_5^-$ peak does not appear. The operating conditions give the value 36.78 kHz for the $SF_6^-$ theoretical secular frequency and the $SF_5^-$ peak should appear at 42.34 kHz due to the sampling of the temporal signal at 11.64 $\mu$s, the true theoretical frequency being at 43.60 kHz.

In Fig. 4(a) and (b) we present experimental results obtained with only the Rydberg atom beam turned on. The $SF_6$ beam is turned off for 3/4 h. The REC reaction occurs with the $SF_6$ molecules existing in the background gas which is measured at a pressure of about $10^{-7}$ Torr. The signal-to-noise ratio of the $SF_6^-$ frequency peak decreases compared to Fig. 3 but remains greater than 4 in Fig. 4.

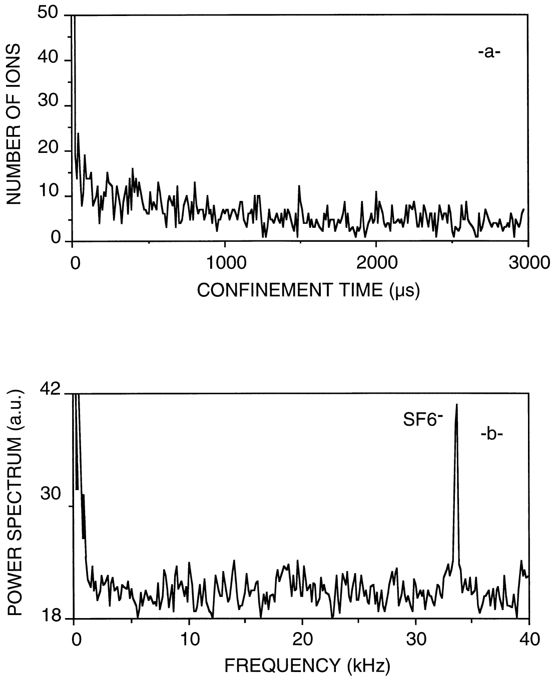

Fig. 4. (a) Experimental number of $SF_6^-$ ions vs. confinement time and (b) corresponding power spectrum obtained with a background pressure of about $10^{-7}$ Torr in the vacuum chamber enclosing the REC-MS instrument with the molecular beam turned off for 0.75 h. The operating conditions are: $U_0 = 0$ V; $V_0 = 48$ V; $\Omega/2\pi = 171.875$ kHz, and $z_0 = 1$ cm.

The very good visibility for $SF_6^-$ ions is the result of a good electron affinity (≈1 eV), a very long lifetime which can exceed the millisecond in our experiments and the ability of the operating mode to accumulate the measurement of the same elementary experiment many times (in Fig. 4: 500 times).

### 3.2. Environmental pollutants

Figs. 5–8 concern the Rydberg electron attachment on, respectively, (1) the fluoranthene ($C_{16}H_{10}$: 202.3 u), (2) the 1-2-3-4 tetrachlorodibenzo-p-dioxin (321, 322, 323 u), (3) the 2-2′-3-4-4′ pentachlorobiphenyl ($C_{12}H_5Cl_5$ or PCB 85: 326.45 u), and (4) the 2-2′-4-

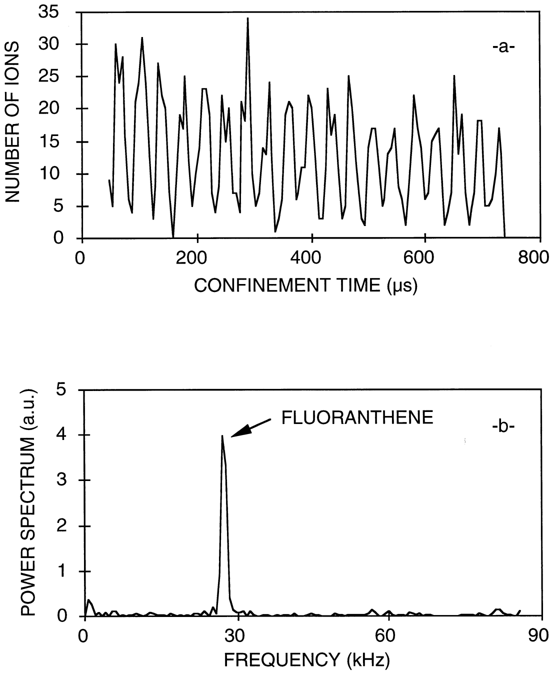

Fig. 5. (a) Experimental negative molecular ion signal of the fluoranthene $C_{16}H_{10}$ vs. confinement time and (b) corresponding frequency power spectrum. The operating conditions are: $U_0 = 0$ V; $V_0 = 60$ V; $\Omega/2\pi = 171.875$ kHz, and $z_0 = 1$ cm.

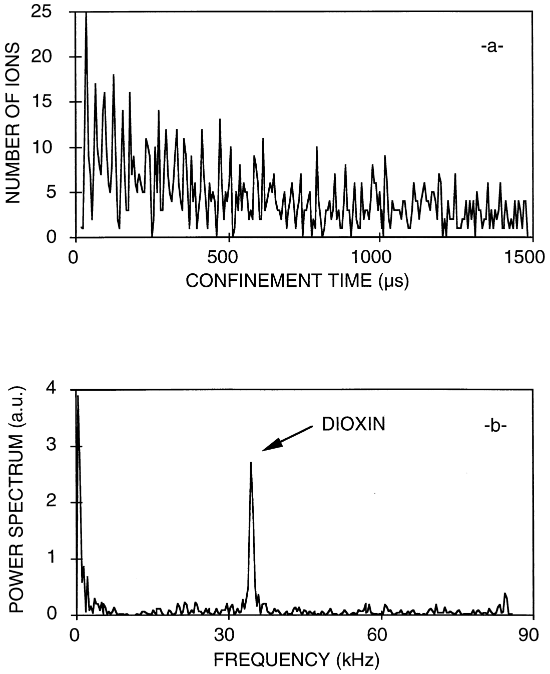

Fig. 6. (a) Experimental negative molecular ion signal of dioxin (1-2-3-4 tetrachlorodibenzo-p-dioxin) vs. confinement time and (b) corresponding frequency power spectrum. The operating conditions are: $U_0 = 0$ V; $V_0 = 110$ V; $\Omega/2\pi = 171.875$ kHz, and $z_0 = 1$ cm.

4′-5-5′ hexachlorobiphenyl ($C_{12}H_4Cl_6$ or PCB 153: 360.91 u).

Each figure includes the temporal signal in curve (a) (number of detected ions in the counting gate) and its corresponding power spectrum in curve (b).

Table 1 gives the experimental full widths at half maximum (FWHM) in kHz ($\Delta\omega$) and in u ($\Delta m$) deduced from curves (b) in Figs. 5–8. At present, the MS gives such a bad resolution ($\Delta m$ of about 10 u) that it is impossible to discriminate the isotopic constitution, but it is sufficient to observe the non fragmentation of the molecule, for example the loss of Cl, $Cl_2$, . . . for the dioxin and the PCBs.

In Fourier transform analysis, the full width at half maximum of the peak $\Delta\omega_1$ depends on $T_m$, the maximum observation duration of the temporal signal, by the relation [22]

$$\Delta\omega_1 = 0.886/T_m \tag{2}$$

Table 1 also gives the expected theoretical FWHM ($\Delta\omega_1$) versus $T_m$. A discrepancy between the experimental and theoretical values is observed. The experimental values are greater than the theoretical ones. The decrease in the temporal signal leads to a broadening of each frequency peak. The apparatus function of the device and the electron auto detachment processes can induce such a decrease. The collisional or radiative stabilisation processes also influence the shape of the temporal ion signal.

To minimise the influence of the ion signal damping, we could decrease the observation time $T_m$ without modifying the resolution $R_\omega$ expressed by [23]

$$R_\omega = \frac{\omega_z}{\delta\omega} \simeq 0.564\beta_z T_m \Omega \tag{3}$$

where $\beta_z$ is the operating point of the trap. For this, if we reduce $T_m$ we have to increase the confinement

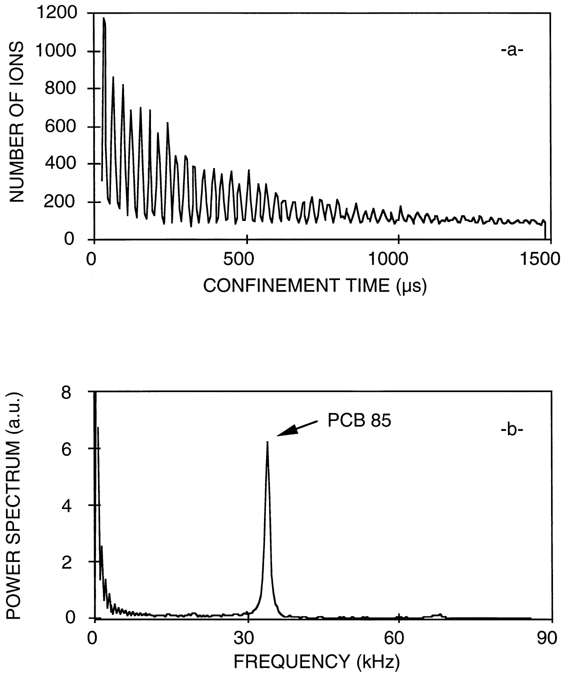

Fig. 7. (a) Experimental negative molecular ion signal of PCB 85 or 22′344′ pentachlorobiphenyl $C_{12}H_5Cl_5$ vs. confinement time and (b) corresponding frequency power spectrum. The operating conditions are: $U_0 = 0$ V; $V_0 = 110$ V; $\Omega/2\pi = 171.875$ kHz, and $z_0 = 1$ cm.

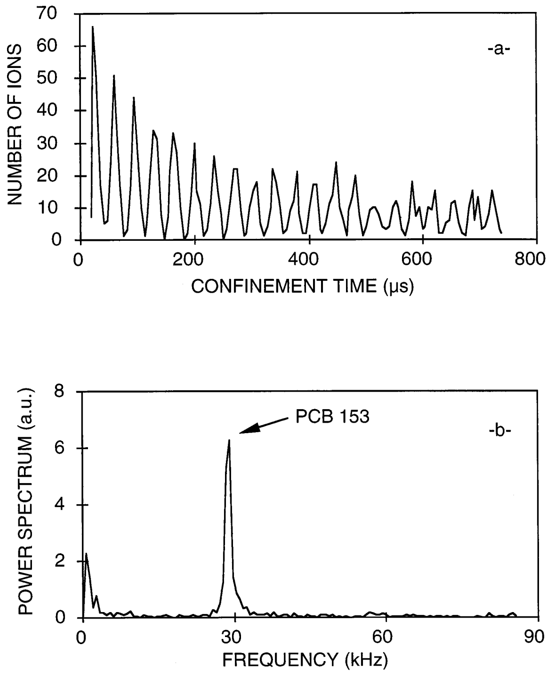

Fig. 8. (a) Experimental negative molecular ion signal of PCB 153 or 22′44′55′ hexachlorobiphenyl $C_{12}H_4Cl_6$ vs. confinement time and (b) corresponding frequency power spectrum. The operating conditions are: $U_0 = 0$ V; $V_0 = 110$ V; $\Omega/2\pi = 171.875$ kHz, and $z_0 = 1$ cm.

frequency $\Omega$ and consequently $V_0$ the confinement voltage amplitude for $\beta_z$ to remain unchanged.

From an extensive analysis of the shape of the temporal ion signal (not done here) the damping characteristic times (apparatus function, auto detachment process) and the stabilisation rate can be estimated. For this, the total number of ejected ions must be recorded in a wide counting gate in order to minimise the discrimination of ions TOF and consequently the amplitude fluctuations of the signal.

The PCB 138 (an isomer of PCB 153) and the PCB 101 (an isomer of PCB 85) were studied but are not presented here. This set of PCBs gives the same results: no fragmentation and the same broadening of the peak.

Other polyaromatic hydrocarbons are studied. The electron capture cross section of the pyrene (0.15 $Å^2$ at 0 eV) is too weak to observe the creation of ions in our present experimental conditions. The detection of coronene ions is not possible with the MS part of the instrument due to the very short lifetime of the ions. So, these ions are measured by a standard TOF method i.e. by counting the number of ions versus the amplitude of the dc pulsed voltage applied to the injection plates, the electrodes of the trap being supplied with a constant dc voltage. The coronene ion lifetime value is estimated at about 20 $\mu$s.

## 4. Conclusion

We have carried out preliminary experiments on a REC coupled to a mass spectrometer.

Many complex molecules with a positive electron affinity can attach the optical electron of rare gas Rydberg atoms. Various pollutants belonging to polyaromatic hydrocarbon, polychlorobiphenyl, and dioxin families are tested.

Table 1
$T_m$ ($\mu$s) the maximum observation time of the signal in the experiment and $\Delta\omega_1$ (kHz) the theoretical corresponding full width at half maximum of the peak; $\Delta\omega$ (kHz) and $\Delta m$ (u) the experimental full width at half maximum of the peak coming from the curves of Figs. 5–8 for the four studied pollutants.

| Molecule | $T_m$ ($\mu$s) | $\Delta\omega_1$ (kHz) theoretical | $\Delta\omega$ (kHz) experimental | $\Delta m$ (u) experimental |
|---|---|---|---|---|
| Fluoranthene (Fig. 5) | 745 | 1.2 | 1.38 | 8 |
| Dioxin (Fig. 6) | 1490 | 0.6 | 0.92 | 7 |
| PCB 85 (Fig. 7) | 1490 | 0.6 | 1.49 | 12 |
| PCB 153 (Fig. 8) | 745 | 1.2 | 1.6 | 16 |

The molecular ions are created without fragmentation of the molecule. Moreover the molecular ions are metastable with an intrinsic lifetime in a range from about ten microseconds to a few hundred microseconds depending on the molecular constitution and the electron binding energy.

The source is coupled to a homemade mass spectrometer using Fourier transform analysis. The metrological characteristics of this device needs to be improved. A new apparatus has been built, the resolution that is now about 1000 concerning $Xe^+$ isotopic ions created by EI [24]. And a new recording and processing device will enable us to achieve a peak amplitude calibration as is commonly done. A REC source will be integrated into this new mass spectrometer apparatus. Our REC-MS coupling will also be a powerful tool to study the electron attachment cross section and the lifetime of metastable negative ions individually.

The isomer differentiation is not resolved by this method of analysis. However, before mass analysis, we could use the CID method upon a selected mass to observe the fragmentation pattern giving the isomeric constitution.

A REC source will also be integrated into a commercial Mass Filter Instrument.

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