RYDBERG ELECTRON CAPTURE MASS SPECTROMETRY OF ORGANIC POLLUTANTS

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Introduction

High Resolution Gas Chromatography interfaced with Mass Spectrometry is presently the most selective technique for organic sample analysis (for example for Furans or Dioxins). A mass spectrometer with a resolution greater than 10,000 is needed to separate all the interfering compounds. Nevertheless, in this kind of apparatus, Electron Impact (EI) is used to create ions. So, a more or less significant fragmentation of the molecular ion by the loss of one or several chlorine atoms is observed. The high fragmentation rate renders a direct interpretation of complex molecule mixture spectra very difficult.

Softer ionization techniques to create negative ions have been developed in order to reduce fragmentation, for example : Electron Capture Chemical Ionization (ECCI)[1] or Electron Monochromator Ionization (EMI)[2]. With the Rydberg Electron Capture (REC), attachment of an electron with quasi-zero well-controlled energy is achieved[3].

Methods and Materials

In Rydberg Electron Capture, two processes can be involved. On the one hand, non-polar polyatomic molecules which have a positive electron affinity can attach an electron by a Feshbach resonance to lead to long-lived metastable molecular anions (> 100 µs)[4]. For large polyatomic molecules, the excess of internal energy of the molecular anion can be absorbed by a great number of vibrational modes resulting in ions with longer lifetime. On the other hand, sufficiently polar molecules, with a dipole moment greater than 2 to 2.5 D, can also attach a thermal electron by a monopole-dipole interaction to create a dipole-bound molecular anion with a large lifetime[5]. Many pollutants allow Rydberg Electron Capture, such as, Dioxins, Furans, PolyChlorinated Biphenyl (PCB) and polar molecules, for example, acetonitrile, acetaldehyde, acetone, …

With REC, a weakly bound electron of xenon atoms excited in Rydberg states (designated as Xe**) created by electron bombardment is transferred to the target molecule MX without dissociation, according to the reaction: $Xe^{**} + MX \rightarrow Xe^{+} + MX^{-*}$.

A REC ion source is based on the principle of a cross-beam device. It consists of two beams, one of atoms excited in Rydberg states and the other of target molecules, which cross in a well-defined collision area.

Xe** are created from a xenon beam submitted to an electron bombardment at 100 eV (Fig. 1). The electron emission current is measured at about 300 µA by trapping the electron beam with a plate to which Vr the most positive potential of the source is applied. By varying the potential Vf according to Vs, the initial potential energy of the emitted electrons can be adjusted to avoid their entrance in the reaction cell.

In our experimental conditions, the Rydberg state levels n are between 17 and 40, which gives binding electrons with an energy from -47 meV to -8.5 meV. The upper Rydberg levels are limited by

background electric fields and the lower ones by their lifetimes since the Rydberg atoms are created 4.5 cm away from the reaction area.

Vdi, the potential applied to the deviation and ionization plates, creates an electric field of about 200 V/cm which deflects the major part of the positive ions.

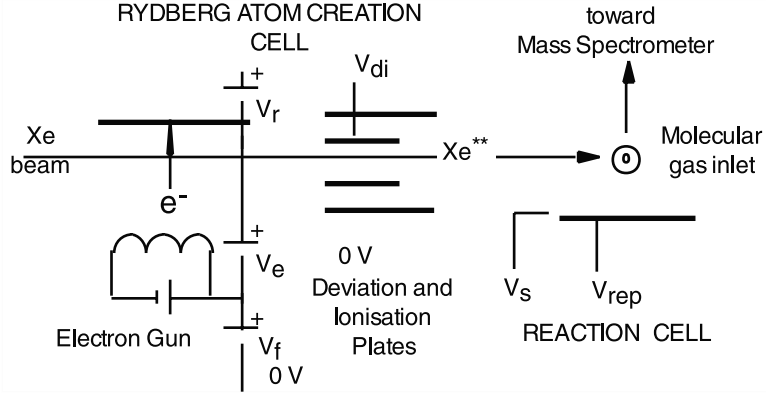

Figure 1. Schema of the REC source

The collision between the Xe** and the target molecules occurs in the reaction cell. The target molecules come from either a solid sample insertion probe or a gas inlet. The potentials applied to the reaction cell Vs, to the repeller Vrep and to a lens group direct the ions toward the mass spectrometer. A digital signal recorder is directly connected to the amplifier exit following the electron multiplier. As a result a set of rough spectra can be averaged.

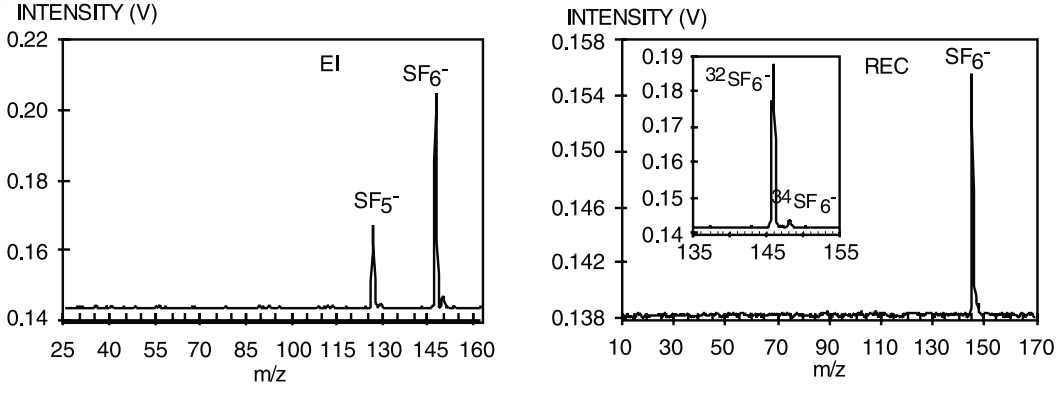

Figure 2. EI and REC spectra in negative-ion detectiond

Results and Discussion

The REC source has been coupled with a NERMAG quadrupole mass filter without modification of the original functionality. From a study of the influence of various parameters with a gas test SF_6, it has

been shown that negative molecular ions are created efficiently by Rydberg atom electron attachment. Fig. 2 shows the EI spectrum and the REC spectrum in negative-ion detection mode. With REC source no fragmentation occurs.

Some organic pollutants of different families were tested[6,7]: the Fluoranthene, the 1,2,3,4 TetraChloroDibenzo-p-Dioxin and the 2,2',4,5,5'-PentaChloroBiphenyl (or PCB 101).

For example, a recording of a wide mass range REC spectrum (from m/z = 10 to 330) obtained with the Nermag mass filter is given in Fig. 3. This spectrum is the average of 1000 rough spectra. In this experiment, we have both the evaporation of the 1,2,3,4-TCDD dioxin and the inlet of SF_6 gas. The electron attachment occurs on the two molecules without fragmentation of the metastable molecular anions SF_6^{-}* and M^{-}* for the 1,2,3,4-TCDD. With a small mass range, the isotopic pattern of the 1,2,3,4-TCDD is clearly observed in the REC spectrum in natural abundance.

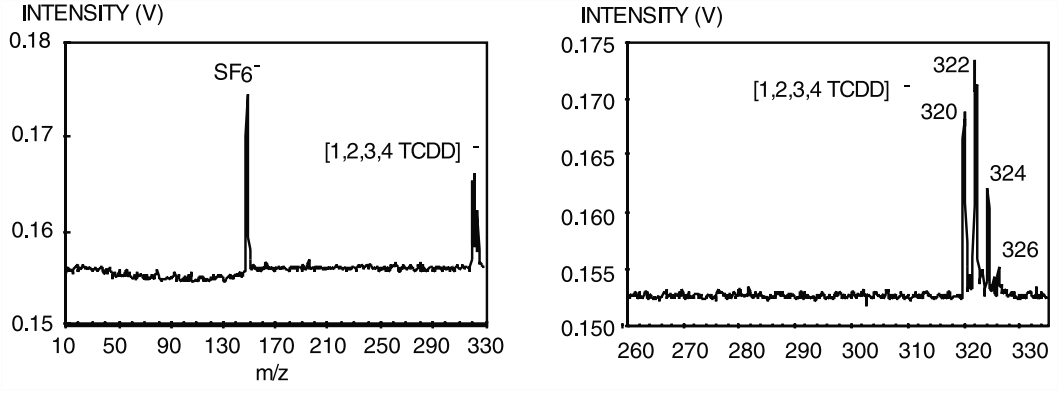

Figure 3. REC spectra of 1,2,3,4-TCDD dioxin and SF_6

A same behavior is observed for the Fluoranthene and the PCB 101 (Fig. 4).

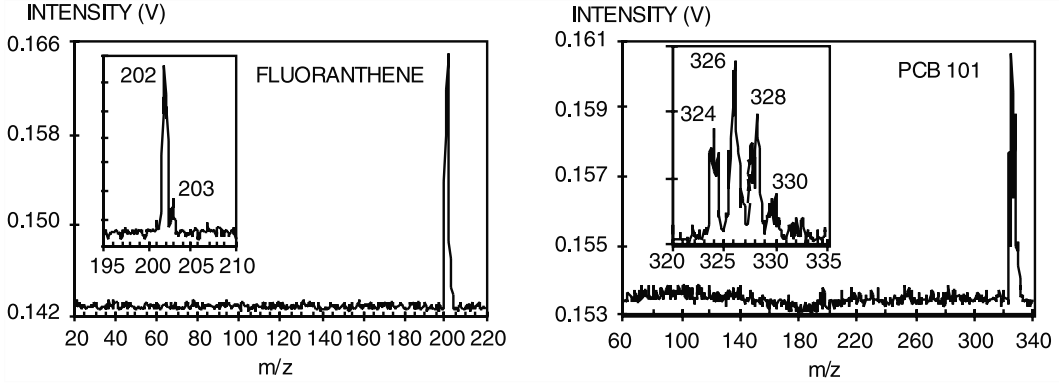

Figure 4. REC spectra of Fluoranthene and PCB 101

ANALYSIS II

Rydberg atoms are a source of thermal electrons which allows no-perturbative and reproducible negative ion production as compared to ECCI or EMI source which involve free electron energy distribution.

Now, the REC source is being tested on other pollutants : others dioxins, furanes and polar pollutants.

Acknowledgment

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