Univerzita Komenského v Bratislave

Fakulta matematiky, fyziky a informatiky

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Studies of ion – molecule processes in corona discharge by the means of ion mobility and mass spectrometry

Autoreferát dizertačnej práce na získanie akademického titulu

philosophiae doctor

v odbore doktorandského štúdia:
4.1.6. Fyzika plazmy

Bratislava 2017

Dizertačná práca bola vypracovaná v externej forme doktorandského štúdia

na Katedre experimentálnej fyziky, Fakulte matematiky, fyziky a informatiky v Bratislave

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pred komisiou pre obhajobu dizertačnej práce v odbore doktorandského štúdia vymenovanou predsedom odborovej komisie ....

Fyzika plazmy
....
(študijný odbor) (názov študijného programu doktorandského štúdia)

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1 Introduction

1.1 Motivation

In chemistry and physics, there exist various analytical tools to analyze occurring chemical reactions, the chemistry of interesting compounds, volatile samples which can cause dangerous harm or unnecessary effects. Among all of these diagnostic tools, the research in our laboratory has been focused on two special diagnostic techniques, which provide unique results; ion mobility spectrometry and mass spectrometry.

Ion mobility spectrometry (IMS) is a well known sensitive technique for detecting chemical warfare agents, environmental pollution and many industrial chemicals. Furthermore, it has found an application in clinic diagnostic purposes, pharmacy, biomedical science or as explosive detectors placed in crowded areas. It characterizes molecules by their gas phase mobility and it is frequently used for detection of explosives, drugs and narcotics. It provides in comparison with other methods fast (in miliseconds range) and high sensitive responses to presence of samples. It also belongs to inexpensive techniques. However, the uncertainties in the identity of ions in IMS can arise through the complex chemistry of ionization in a supporting atmosphere at ambient pressure. Therefore, a mass spectrometer is necessary for thorough understanding of an IMS measurement. The combination of these two methods has been known for over forty years. A union between an IMS and Time-of-Flight (TOF) mass spectrometer is attractive because of the speed and simplicity of TOF instrumentation. Different ionization sources have been applied in this experimental setup IMS-TOF.

In our research, corona discharge (CD) as an ionization source has been applied in IMS-orthogonal acceleration TOF (IMS-oaTOF) device. The IMS-oaTOF has served as a powerful technique to study not only atmospheric but also subatmospheric pressure gas-phase ion chemistry of various types of samples. CD as an ionization source can operate in two polarities and provides wide scale of reactant ions (RI). This instrument is able to determine chemical composition including possible ion formation according to reduced mobility and mass-to-charge ratio.

In this work, the IMS-oaTOF has been applied for studies of several subjects and compounds. Experimental simulation of negative ion chemistry in Martian atmosphere and examination of influence of gas flow rate and its direction throught the CD has been done. Another study has dealt with ion chemistry of 2,4,6-Trichloroanisole (2,4,6-TCA) sample which is well-known as a main substance causing the unpleasant odour of wine.

Since the detection of explosives has become the most important task to ensure the security of citizens, we utilized the compact design, quick response and ability to operate at atmospheric pressure to detect explosives as volatile compounds, particularly 2,4,6-Trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). The investigation of reactions of these common explosives with multiple RI formed from CD in this instrument has been done.

1.2 Objectives

The main aim of dissertation thesis was to study ion-molecule processes in corona discharge at atmospheric pressure by the means of ion mobility and mass spectrometry. The research can be divided into few parts depending on specific samples and researches:

I. Study of experimental apparatus

The apparatus consisted of an ion mobility spectrometer with as ionization source corona discharge (CD) and a mass spectrometer Time of Flight (TOF). It has been constructed by Martin Sabo, PhD as his dissertation thesis. It will be well-described on detail in a separate chapter dedicated only to the device and its components. Next chapters are dedicated to separate researches focused on different topics and compounds.

II. The experimental simulation of negative ion chemistry in Martian atmosphere using IMS-oaTOF device

a) the study of formation of negative ions generated in a negative CD fed by mixture of CO_2 /N_2 and different ratio of nitrogen admixture (2, 4, 6, 8, 10 % N_2)

b) examination of influence of different aspects such as gas composition, the gas flow regime, the concentration of neutrals reactive species and trace amount of water on the ion composition in simulated atmosphere

III. The usage of CD-IMS-oaTOF as a powerful analytical tool for detection of compound 2,4,6-Trichloroanisole (TCA) followed by detection of this sample by photo-electron spectroscopy (PES)

a) the reaction of sample 2,4,6-Trichloroanisole (TCA) well-known as a “cork taint” in standard and reverse gas flow mode of IMS

b) examination of the stability of formed ions under influence of increasing IMS temperature

c) investigation of detection limits of solid and gas phase of TCA by laser desorption and vapour gas detection, respectively

d) experimental study of ionization energy spectrum of TCA by PES and theoretical calculations of ionization energies of TCA and 1,3,5-Trichlorobenzene

IV. The research focused on interaction of explosive 2,4,6-Trinitrotoluene (TNT) with multiple reactant ions formed in CD and its detection by CD-IMS-oaTOF

a) study of processes occurring in selectively generated reactant ions with molecules of TNT with help of 2 dimensional maps obtained from IMS-oaTOF

b) influence of gas flow mode, discharge power on processes occurring and composition of produced ions in CD

c) influence of IMS temperature and value of drift field on stability of ions

d) doped reverse gas flow mode and formation of different reactant ions and subsequently different composition of presenting ions

V. The thermal decomposition of known explosive hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and its detection in CD-IMS-oaTOF

a) observation of reactions and formed ions generated after the thermally decomposed explosive RDX at two different applied IMS temperatures

b) doping of IMS to investigate the following composition of generated ions in IMS at atmospheric pressure and its representation by a 2 dimensional map.

2 Experimental equipment

The schematic setup of the experimental apparatus constructed at Comenius University in Bratislava and used in our laboratory is depicted on Figure 1. It is a very complex device called Corona-Discharge Ion Mobility Spectrometer coupled with orthogonal accelerated Time of Flight mass spectrometer (CD-IMS-TOF). It consists of an ion mobility spectrometer and a mass spectrometer. The functionality and principles of both of them were described in detail in article [1].

The IMS has been operated at atmospheric pressure with positive and negative corona discharge. The IMS consisted of ionization region, reaction region and drift region.

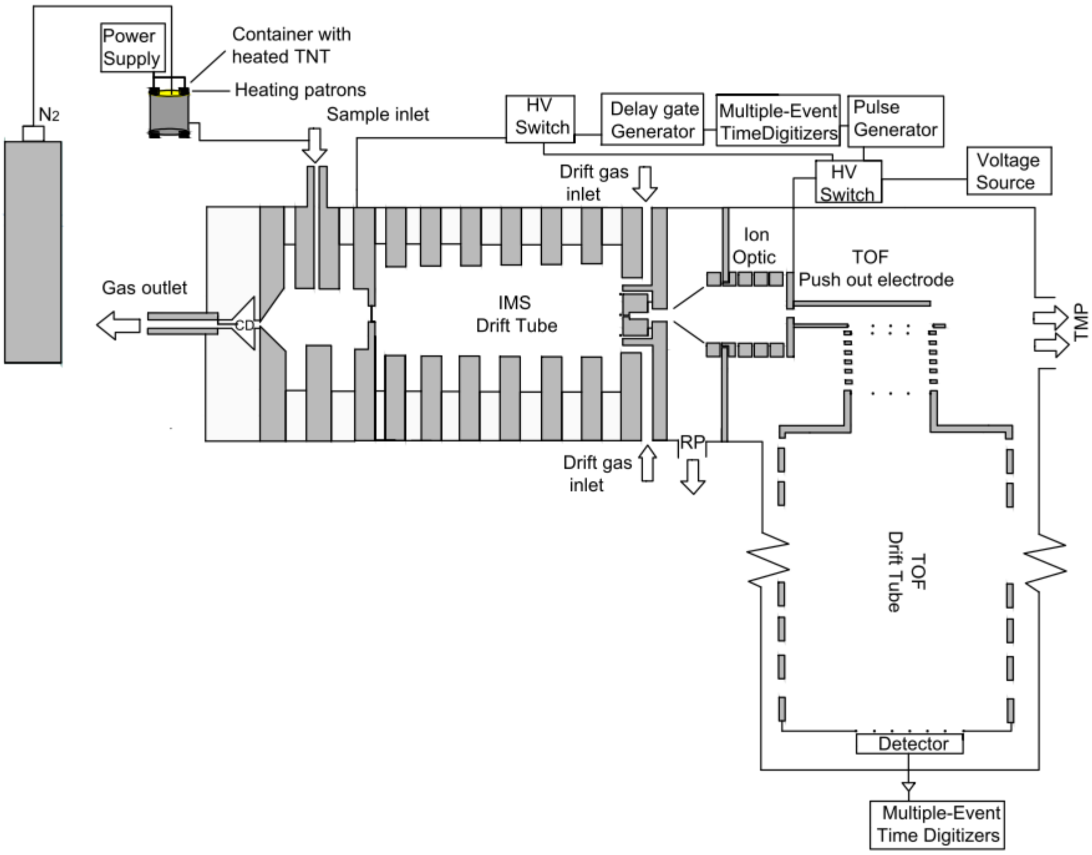

Figure 1. Experimental setup of ion-mobility spectrometer coupled with mass spectrometer time-of-flight (TOF) constructed and used in our laboratory

The SG was open for short time (around 110 µs with repetition rate 20 ms depending on each research) with period of few ms. The drift field of IMS varied in every research in a range of 242 to 543 V/cm. For the drift gas as carrying gas which is important for keeping the drift chamber clean following components were used: O_2, N_2, a mixture of O_2 and N_2 obtained from Linde Gas with a purity of 5.6 (99,9996 %), CO_2, atmospheric air and atmospheric air purified by molecular sieve traps (Agilent), which reduces H_2O concentration below 14 ppb. The drift gas flow varied from 500 mL/min to 1500 mL/min. There was possibility to heat the drift tube and vary the temperature of the drift gas from the room temperature up to 150ºC. There are two working modes of the IMS, standard and reverse mode, depending on the flow of sample gas. The length of the IMS drift tube was 11.44 cm. The inner electrode of the CD was a tungsten wire with diameter 30µm and length 1.5 cm and was stretched parallel to the plane electrode at around 3mm distance.

The potential difference between the wire and target electrode was set in a range of 3 up to 7kV what resulted in corona discharge current from 15 to 70 µA.
The device CD-IMS-oaTOF was able to work in three modes; in the single IMS mode, in the single TOF mode when the SG of the IMS has been fully opened and in the two-dimensional mode used when the both spectrometers operated synchronically together.

3 The experimental simulation of atmosphere of Mars

Plasma generated in pure CO_2 and following study of created ion chemistry also with different mixtures of CO_2 and N_2 are attractive in many fields of the science and technology. Such ion chemistry is relevant in planetary atmosphere studies especially since the atmosphere of Mars consists of 95% of CO_2, 3% of N_2 and 1,6% of Ar with minor additional components of H_2O, O_2, CO. There have been made several reviews of ion chemistry in CO_2 by Moruzzi and Phelps [2] and in relation to Mars by Molina Cuberos et al [3].

In our research, the interesting study has been done about the formation of negative ions in a negative corona discharge fed by CO_2/N_2 mixtures (0, 2, 4, 6, 8 and 10% N_2) by CD-IMS-oaTOF. The admixture of N_2 to CO_2 resulted in dramatic changes in the negative ions composition. The results were interesting, because the formatted ions corresponded to ions calculated in theoretical model of Molina-Cuberos [3] with accurate conditions from the Mars atmosphere.

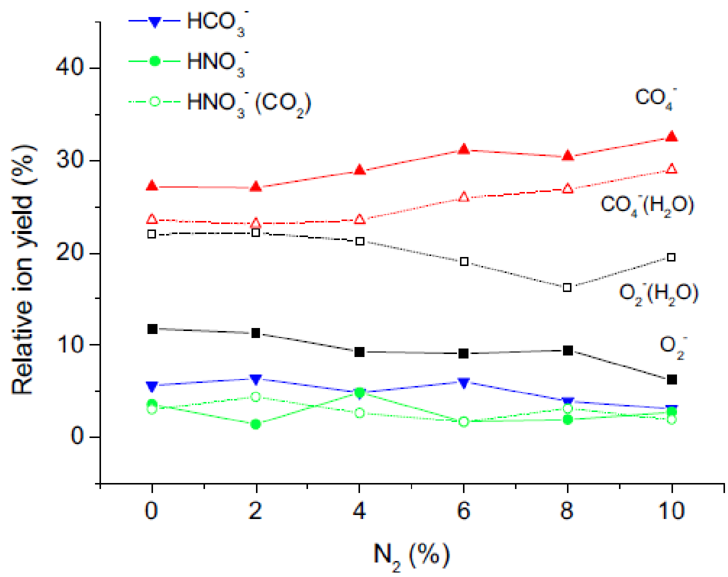

Figure 2. The dependence of the ion intensities derived from MS spectra as a function of N_2 concentration at reverse flow mode

All negative ions obtained from the theoretical model and calculations have been observed in our research. According to Sheel [4], the most abundant ions present in low Martian atmosphere are $CO_3^-(H_2O)_2$ followed by $NO_2^-(H_2O)_2$, $CO_3^-(H_2O)$, $NO_3^-(H_2O)_2$. In the case, when the neutral products entered into the reactions in CO_2/N_2 mixture with negative ions, we could see the most abundant ions NO_3^- followed by $NO_3^-(HNO_3)$, CO_3^-, CO_4^- and $NO_3^-(H_2O)$. The ions NO_3^- were more stable than CO_3^- and NO_2^- and therefore they were the most abundant ions.

The disagreement between the experiment and theoretical model could have more origins. First of all, the conditions under current experiment were far from the real situation on Martial atmosphere. The atmospheric pressure on Mars is about 6mbars but pressure in our experiment was atmospheric pressure, 1013.25mbars. The other reason could be completeness of the kinetic data available and also time window of the simulation could be limited and negative ions could convert to more stable species.

4 The study of compound 2, 4, 6-Trichloroanisole

4.1 The research of 2, 4, 6-TCA by IMS-MS

Aroma has great importance in the wine industry for product quality and consumer acceptance. The presence of some specific volatile organic compounds in wine may cause that wine loses its freshness, natural aromas and gains unpleasant moldy odor. This effect is mostly caused by sample 2,4,6-Trichloroanisole (TCA) also familiarly called “cork taint”. Karpas [5] claimed that TCA isomer is not only one responsible for off-flavor wine. There are also other isomers of trichloroanisole as substituted tetra- and penta-chloro-anisoles and compounds including tribromoanisole, 2-methylbornoleol, 4-ethylguaiac etc. However, TCA is still considered as main source of unpleasant odor.

Our research [6] was dedicated to the investigation of this compound 2,4,6-Trichloroanisole in solid, liquid and gas phase considered as a main taint in wine industry. Thus, two experimental devices were applied, standalone single flow CD-IMS instrument and CD-IMS-oaTOF instrument.

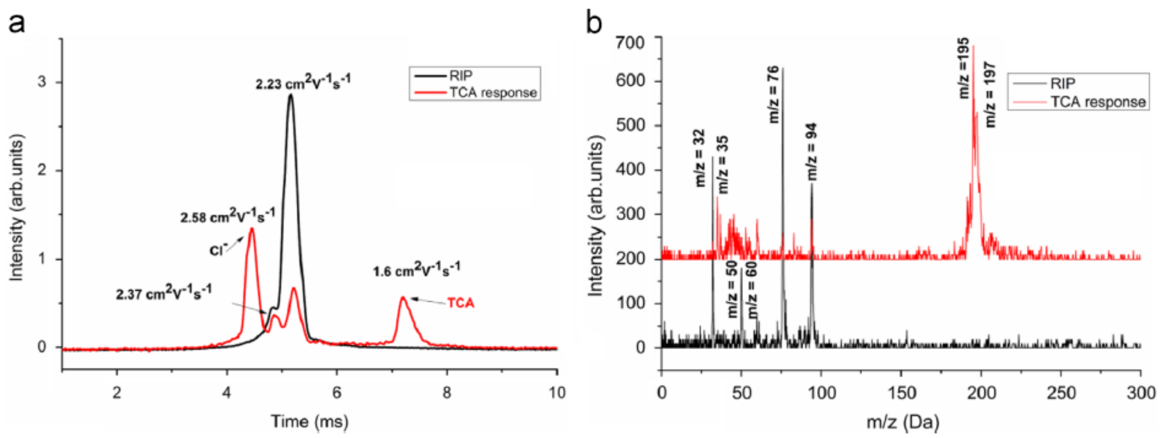

Figure 3. a) IMS spectrum of TCA in reverse mode and b) corresponding mass spectrum of TCA

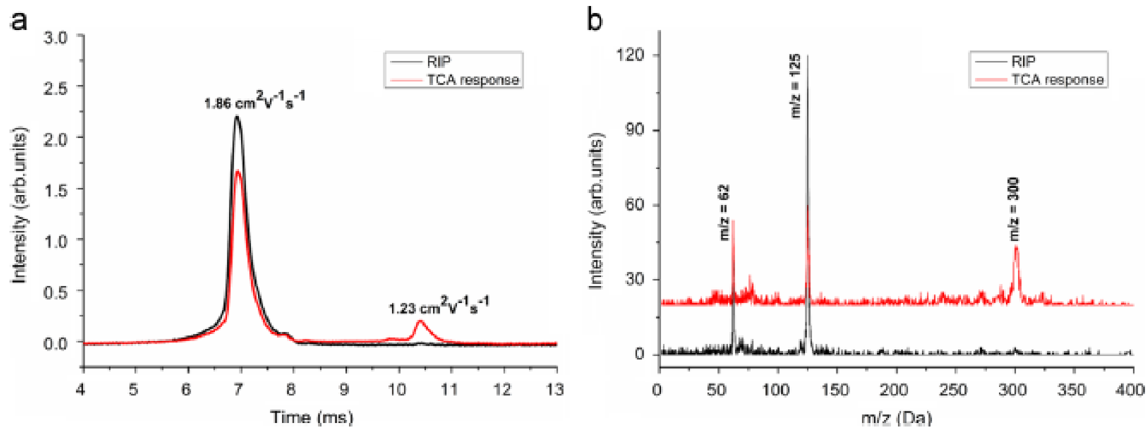

Figure 4. a) IMS spectrum of TCA in standard mode and b) corresponding mass spectrum of TCA

In the reverse mode at 360 K pictured in Figure 3., the device responded on TCA sample in formation of two peaks besides of reactant ions (RI); Cl^- with MS peaks m/z 35, 37 Da and $[TCA\text{-}CH_3]^-$ (de-methylate TCA anion) composed of MS peaks m/z 195, 196, 197, 198 and 199 Da. The reduced mobilities of these IMS peaks were 2.58 and 1.6 $cm^2V^{-1}s^{-1}$.

In the standard gas flow mode with heated IMS at 318 K pictured in Figure 4. except for dominant RI $NO_3^-(HNO_3)$ and ions NO_3^- with m/z=62 in MS spectrum, there was response of RI on TCA resulted in appearance of one peak in the IMS with reduced mobility 1.23 $cm^2V^{-1}s^{-1}$. In the MS spectrum, it was composed of ions with m/z=300. Since we were not able to find any accurate information regarding interaction of TCA with $NO_3^-(HNO_3)$ ions in literature, we tentatively assigned this peak to $NO_3^-(HNO_3)(TCA\text{-}Cl)$ ions.

Except for the study of processes occurring in different gas flow modes with various RI, also the temperature effect on the stability of RI and ions formed from TCA in standard gas flow mode in temperature range of 303 K to 363 K has been examined.

The standalone IMS mainly served to determine the solid phase and gas phase limit of detection (LOD) depicted in Figure 5. The ion Cl^- was taken into account for determination of LOD as dominant ion in reverse mode in TCA study. The solid phase LOD was measured in the range from 2.5μg to 150ng (lower as in Karpas's study mentioned above).

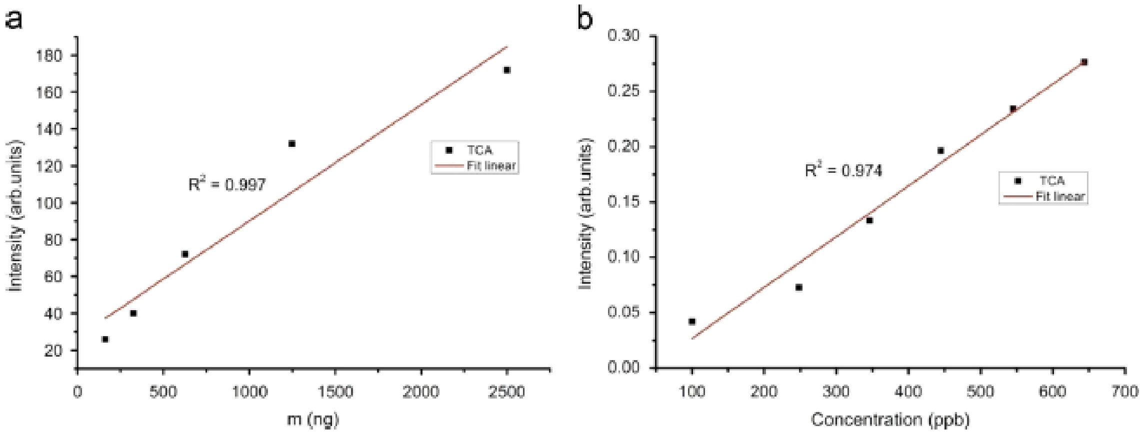

Figure 5. Calibration curves for TCA measured from a) solid and b) gas phases

4.2 The study of 2,4,6-TCA by Photoelectron spectroscopy (PES)

Another study of 2,4,6-Trichloroanisole has been done by different method called Photoelectron Spectroscopy (PES). The PES allowed us to study electronic structure of 2,4,6-TCA and determine its ionization energies.

The PES is a technique used to determine the ionization potentials of molecules. Underneath the banned of PES, there are two separate methods for quantitative and qualitative measurements; ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS).

In our next experiment, the electronic structure of the TCA molecule was investigated using method UPS. The experiment was carried out on a Perkin Elmer HeI photoelectron spectrometer schematically shown in Figure 6. High energy photons were generated in a low pressure electrical discharge in He. The discharge generated photons of 58.4 nm (21.22 eV) were transmitted to a target chamber through a capillary, where ionization of molecules takes place in the gas phase.

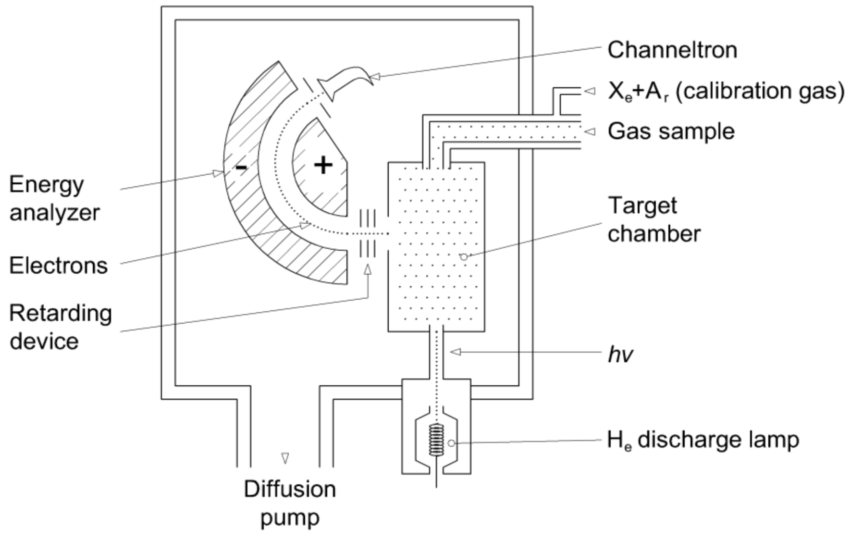

Figure 6. The experimental apparatus; the ultraviolet photoelectron spectrometer (PES)

Following Figure 7. shows the photoelectron spectra of the Ar-Xe calibration gas (left) and of the TCA molecular gas (right). The ionization energy of the weakest bound electrons in TCA was observed at 8.99 eV followed by several well distinguished peaks and broadband structures corresponding to ionization from lower molecular orbitals.

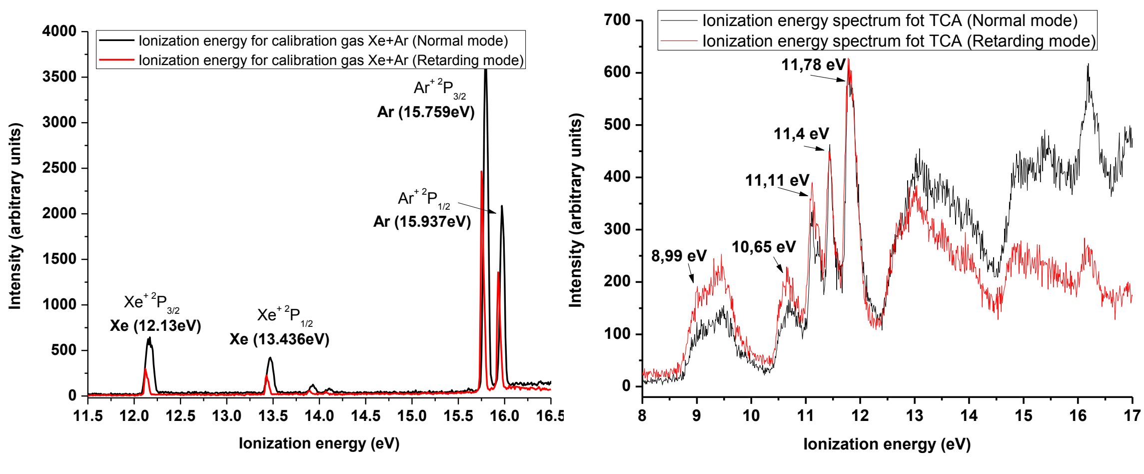

Figure 7. The measured spectra for calibration mixture of gases (Xe + Ar) (left) and for pure TCA compound (right).

For better understanding of ionization energies measured in experiment PES, there was additionally applied theoretical method to determine the ionization energies of 2,4,6-TCA and similar molecule 1,3,5-Trichlorobenzene. The molecular energy levels of these molecules were calculated by the means of Outer Valence Green Function (OVGF) method [7] in Gaussian 09.

Eventually, there was a good agreement between the PES experiment and the theoretical calculated energy levels which allowed us to attribute most of the structures observed in the PES spectrum to molecular orbitals and experimentally determine the ionization energies from the respective molecular orbitals. The most interesting orbital was number 49 which is visible at the beginning of the ionization spectrum in Figure 8., also gained from theoretical calculations. This orbital is representative for 2,4,6-TCA because it is caused by group -O-CH_3. The chemical structure of this orbital is depicted in Figure 9.

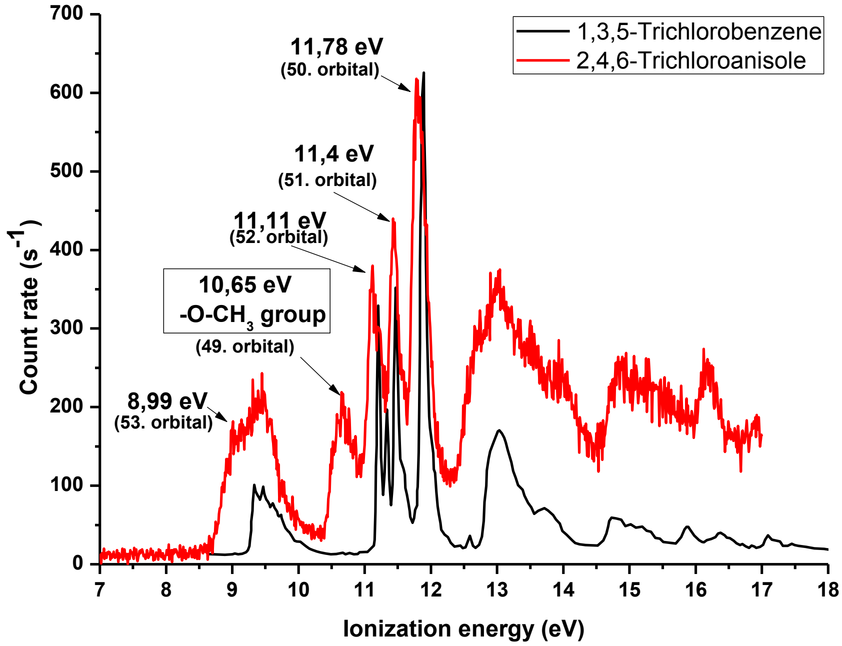

Figure 2. The ionization energies of 2,4,6-Trichloroanisole (our experimental results of PES) and 1,3,5-Trichlorobenzene (theoretical result)[8]

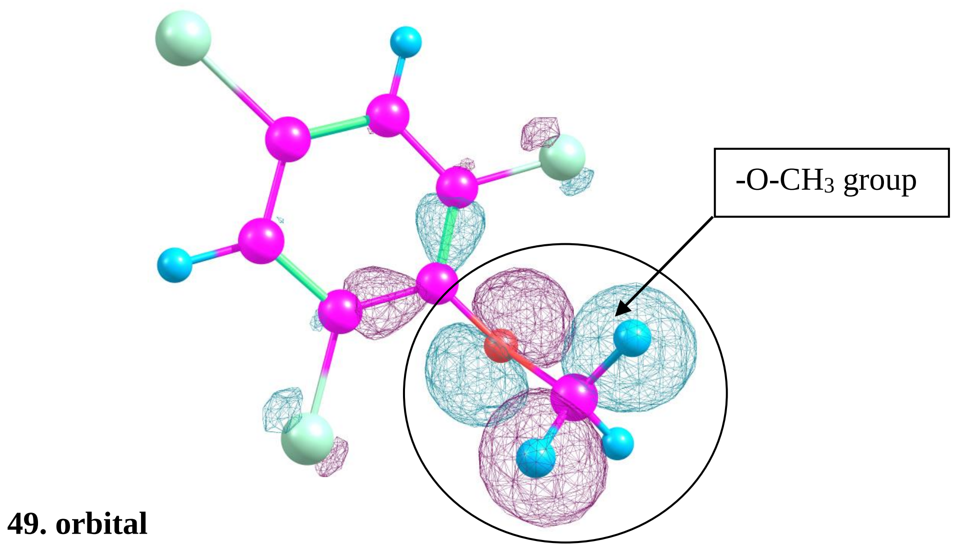

Figure 9. The 49. calculated orbital of 2,4,6-TCA by OVGF method

5 The research of famous explosives (TNT, RDX)

The detection of explosives and compounds related to the explosives has happened to be a high priority in recent years not only for homeland security, forensics but also for counter-terrorism applications. On the basis of world situation, there is a growing need to deploy detection solutions outside of controlled environments as airport checkpoints, mass transit stations, military areas and large public events [9].

Common commercial explosives are composed of nitro compounds, which are highly electronegative and therefore they form easily negative ions at ambient pressure ionization. In general, public is likely to encounter an IMS device as airline passengers being screened for explosives. Especially, after the attack on the Twin Towers at the World Trade Center in New York City on September 11, 2001. After this incident, awareness of global terrorism hugely raised, although this incident was not directly linked to explosives [10]. Therefore, the development in this field has passed through a huge change of improvement from old existing techniques to new, innovative detection approaches. The development has focused especially on miniaturization, portability and improvement of selectivity and sensitivity [11].

Security controls have already included metal detectors to identify weapons which may be concealed in conjunction with X-Ray machines to check the volume of the luggage from inside. The big problem is that explosives are not easily detectable compounds by conventional methods. Usually, these volatile compounds are detected by ion-mobility spectrometry coupled with swabbing for instance. Furthermore, the increasing use of peroxide-based explosive has led to development of chemical identification techniques based on nitrogen and carbon content of substances.

The most famous volatile explosives in the family of nitrated organic compounds are: Pentaerythritol Tetranitrate (PETN), 2,4,6-Trinitrotoluene (TNT), Cyclo-1,3,5-Trimethylene-2,4,6-Trinitramine (RDX), 2,4-Dihydro-5-nitro-3H-1,2,4-triazol-3-one (NTO), octogen (HMX), C4 and Semtex and since they have also lower vapor pressure, there have been developed sampling techniques with heated inlet system to transfer sample to the analyzer without great losses.

In our research we have focused on two most world-wide spread explosives; TNT and RDX.

5.1 Study of 2,4,6-Trinitrotoluene (TNT)

Trinitrotoluene (TNT) or more specifically 2,4,6-Trinitrotoluene is a chemical compound with chemical formula $C_6H_2(NO_2)_3CH_3$. It is yellow-colored solid well-known as explosive material. TNT is one of most commonly used explosives in military, industrial or mining applications. It is valued also because its insensitivity to shock or friction and therefore reduced risk of accidental detonation in comparison with nitroglycerin for instance. The explosive power of the TNT is used for constructing of bombs or other explosives. In chemistry, it is also utilized for formation of charge transfer salts. It melts at 80 ºC, far below the detonation temperature and neither absorbs nor can be dissolved in water.

Many researches have been done using following techniques to study this compound as Capillary Atmospheric Pressure Electron Capture Ionization [12], Atmospheric Pressure Chemical Ionization Mass Spectrometry [13], Stir-bar Sorptive Extraction and Thermal Desorption-Ion Mobility Spectrometry [14], Vibrational Spectroscopy [15], Crossed electron-molecular beam experiment with low energy electrons [16], Ion Mobility Spectrometry coupled to Mass Spectrometry [17].

Our study has focused on interactions of multiple reactant ions with TNT by the means of Corona discharge-Ion Mobility Spectrometer coupled to orthogonal accelerated Time of Flight Mass Spectrometer.

The first standalone IMS operated at atmospheric pressure and in gas temperature range from 305 to 363 K. The lenght of applied newly built IMS was 8.25 cm and electric field intensity was set to 495 $V.cm^{-1}$. The intensity of electric field varied in case of study of ions stability from 350 to 543 $V.cm^{-1}$. The discharge power of CD changed from 10 up to 50 µA to control the nature of formated ions. The CD operated only in negative polarity since TNT tends to produce only negative ions due to its high negative affinity.

The second applied device, tandem IMS-oaTOF operated in three analytical modes; the IMS mode, the TOF mode and IMS-TOF mode where IMS and TOF spectrometers work simultaneously.

In the standard gas mode, the dominant formated reactant ions were $N_2O_2^-$, NO_3^-, $NO_3^-.HNO_3$, NO_2^-. HNO_3. The RI could be modified by the change of CD current. At „low power mode“ of CD (current around 10 µA), the dominat RI were $N_2O_2^-$, NO_3^-, NO_3^-

.HNO_3, NO_2^-. HNO_3. At „high power mode“ of CD (current up to 50 μA), the dominat RI were mostly only $NO_3^-.HNO_3$ ions. The response of RI to presence of TNT sample caused creation of detected ions with reduced ion mobilities 1.54 $cm^2V^{-1}s^{-1}$, 1.39 $cm^2V^{-1}s^{-1}$, 1.32 $cm^2V^{-1}s^{-1}$, 1.2 $cm^2V^{-1}s^{-1}$, 1.12 $cm^2V^{-1}s^{-1}$ and 1.08 $cm^2V^{-1}s^{-1}$. These peaks were assigned to ions proton abstracted anion $(TNT\text{-}H)^-$, $(TNT+O_2)^-$, $(TNT+O_3)^-$, $(TNT+NO_3)^-$, $(TNT+NO_4)^-$, $(TNT\text{-}H)^-\cdot(TNT\text{-} N_2O_3)$, $(TNT\text{-}H)^-\cdot(TNB)$, where TNB are molecules of 1,3,5-Trinitrobenzene formed from the decomposition of TNT by ozone, and last one $(TNT\text{-}H)^-\cdot(TNT\text{-}NO)$ clusters, respectively.

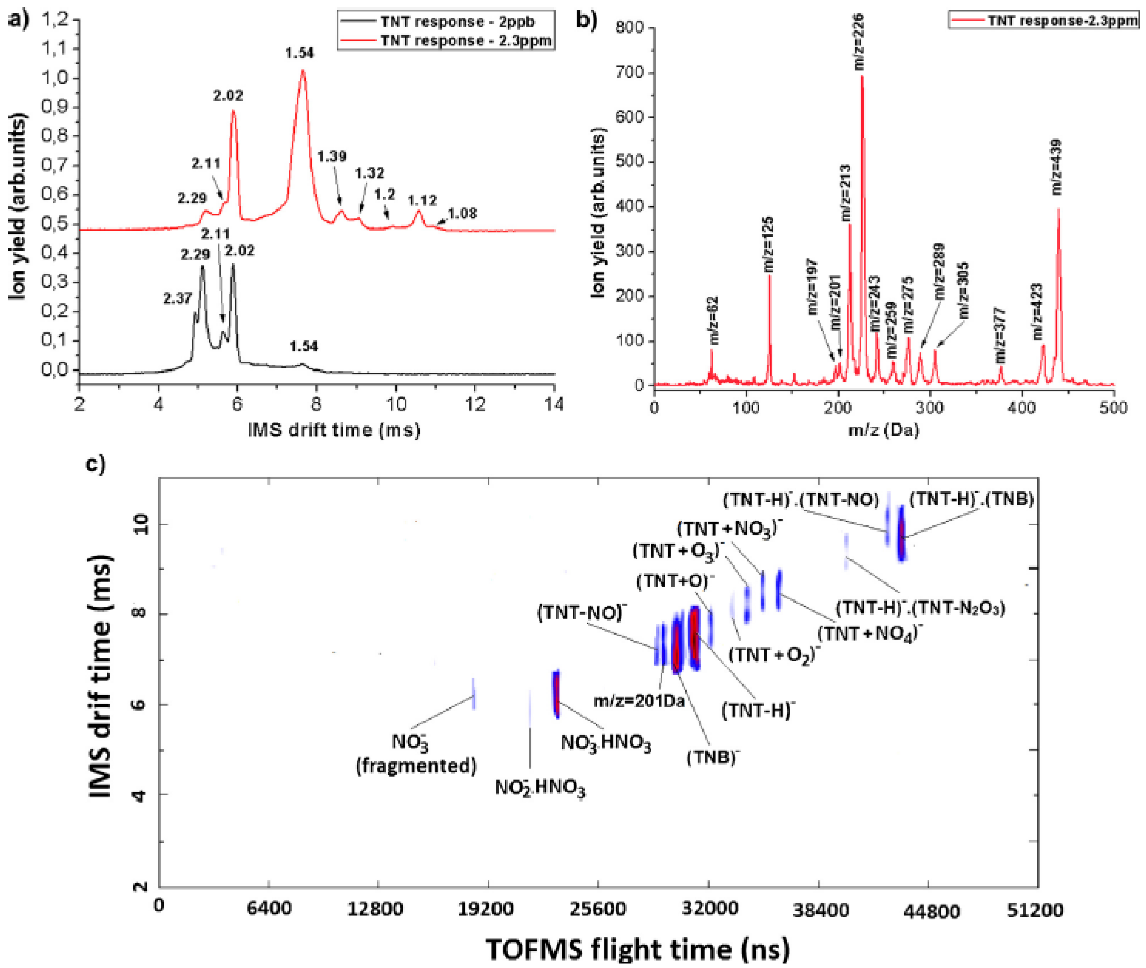

Figure 10. The TNT response for CD operated in “low power mode” in standard gas flow mode a) response for 2 ppb and 2.3 ppm concentration of TNT in IMS spectrum at 353 K and drift field of 495V.cm^{-1} b) related MS spectrum for TNT concentration of 2.3 ppm and c) two dimensional IMS-MS spectrum for 2.3 ppm concentration of TNT

In the reverse gas mode, there were formed following dominant RI from CD; O_2^- and $O_2^-.(H_2O)$ and with small abundance $N_2O_2^-$ and $N_2O_3^-(H_2O)$. The response of RI on TNT analyte ended up with generated TNT^- ions and proton abstracted anions $(TNT\text{-}H)^-$. In order to increase sensitivity and selectivity of the IMS, also dopant gas carbon tetrachloride CCl_4 has been applied as a source of Cl^- ions. It resulted in formation of hydrogen abstracted anion $(TNT\text{-}H)^-$ with intermediate unstable adduct $TNT.Cl^-$.

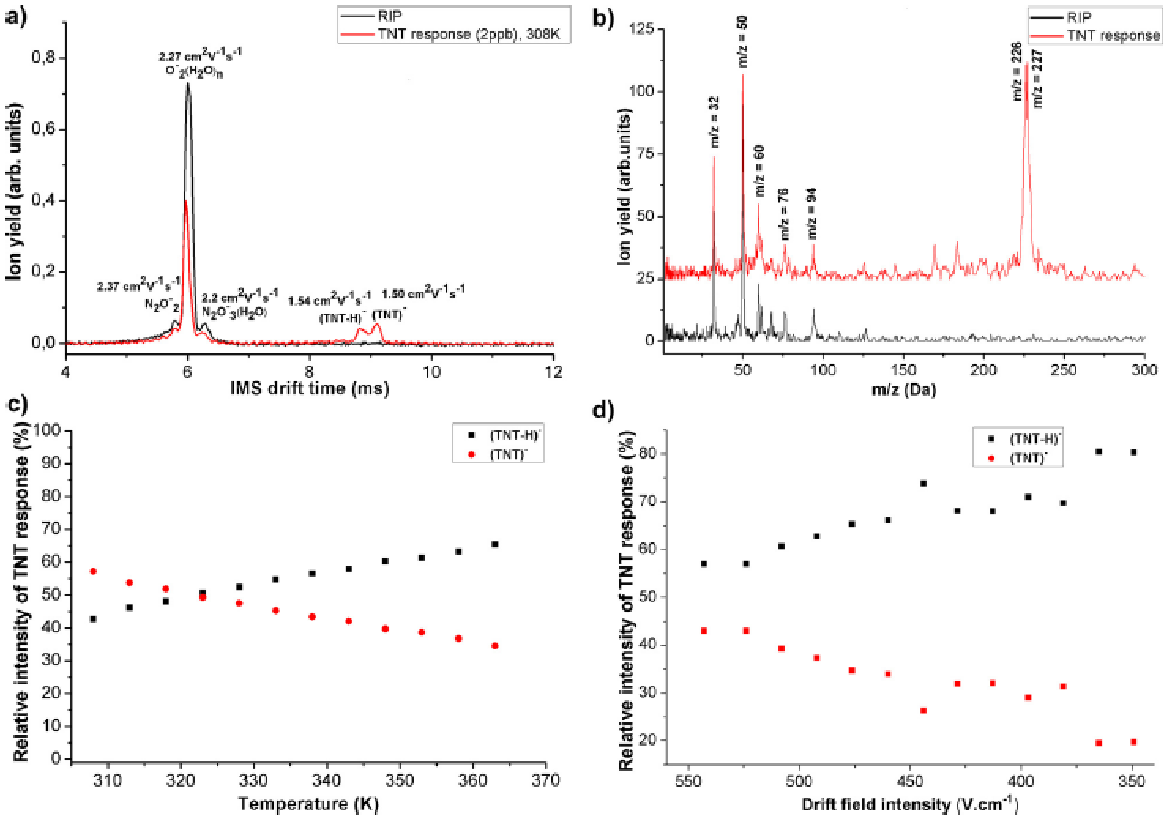

Figure 10. The TNT response for CD operated in reverse gas flow mode with $O_2^-(H_2O)_n$ reactant ions a) response of TNT in IMS spectrum at 308K and drift field intensity 495V.cm^{-1} b) related MS spectrum to IMS spectrum c) relative intensity of $(TNT\text{-}H)^-$ and TNT^- ions depending on IMS drift tube temperature d) relative intensity of same ions depending on IMS drift field intensity

Subsequently, the influence of increasing temperature has been also investigated on generation of TNT^- and $(TNT\text{-}H)^-$ and their conversion to each other. Furthermore, the variation of IMS drift field intensity has been done to control the drift time of ionic species in IMS drift tube. The increasing drift field intensity resulted in increasing relative intensity of $(TNT\text{-}H)^-$ and decreasing relative intensity of TNT^-. It was caused by changes in collision energies and followingly by numbers of ion-molecule collisions, which depended on drift time. The reverse mode and influence of temperature and drift field is depicted in Figure 11. above.

5.2 Study of cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX)

The RDX or more specifically 1,3,5-trinitro-1,3,5-triazacyclohexane has chemical structure $(O_2NNCH_2)_3$ depicted on Figure 20. It is a heterocyclic nitramine compound commonly referred to its acronym for **R**esearch **D**epartment e**X**plosive (RDX). It is chemically also classified as nitramide. It is a white solid widely used organic compound as explosive since the early 1900s. RDX is sparingly soluble in water (ca 40-50mg/l) and is classified as EPA Group C compound, which labels it a possible human carcinogen. It has been also used as a rat poison with a lethal dose of 20mg [18]. In comparison with TNT, it is more powerful and found wide use in Second World War. The RDX is applied in mixtures with other explosives and plasticizers and phlegma-tizers. It is stable for storing and considered as one of the most powerful high explosives.

There has been great interest in research made with this explosive. Many techniques have been applied to describe characteristics and ions formed from RDX to better understand and detect this compound. Analysis of aqueous solution of RDX by electrospray ionization with ion mobility spectrometry (ESI/IMS)[19], where they detected predominantly nitrite and nitrate formed by thermal breakdown of RDX in the hot desolvation region.

Our research of 1,3,5-trinitro-1,3,5-triazine (RDX) evaporated at 473 K have been focused on its reaction with reactant ions produced in negative corona discharge placed in reaction region of Ion Mobility Spectrometer coupled to orthogonal accelerated Time of Flight Mass Spectrometer. The IMS was equipped with negative polarity CD ionization source in point to plane geometry. The typical discharge current was 28 µA. The CD operated in zero air in the reverse gas flow mode with dominant reactant ions formed in reaction region; O_2^-, $O_2^-(H_2O)$, $N_2O_2^-$, $N_2O_3^-$, $N_2O_3^-(H_2O)$ used for chemical ionization. In order to enhance the sensitivity of RDX, there were added vapors of carbon tetrachloride (CCl_4) and formed reactant ions $Cl^-(H_2O)_n$ n=(0,1,2).

The research was carried out at temperature far above the decomposition temperature of RDX of 443 K but also far below the critical temperature of the RDX of 840 K, so the auto ignition of the sample was not possible.

The thermal decomposition caused detection of few ions as NCO^- produced undergoing of N-N bond hemolysis together with NO_2, HONO and HCN ions. . The ion with m/z= 59 Da was not clearly assigned to one molecule but two, $(CH_3NHCHO)^-$ or $(CH_3CONH_2)^-$ formed via charge transfer reactions. Additional detected ions were NO_3^-,

$NO_2^-(NO_2)$ or $N_2O_4^-$, the strongest fragment of this research $C_2H_5NO_2^-$ (HMFA) with m/z= 75 Da, triazine $C_3H_7N_3^-$, $(CH_3NHCHO.NO_2)^-$ or $(CH_3CONH_2.NO_2)^-$, the ion not detected yet with m/z= 89amu originated from $(CH_3NHCHO.NO_2\ )^-$ or $(CH_3CONH_2.NO_2)^-$, $(RDX\text{-}H)^-$ and last ion $RDX.NCO^-$.

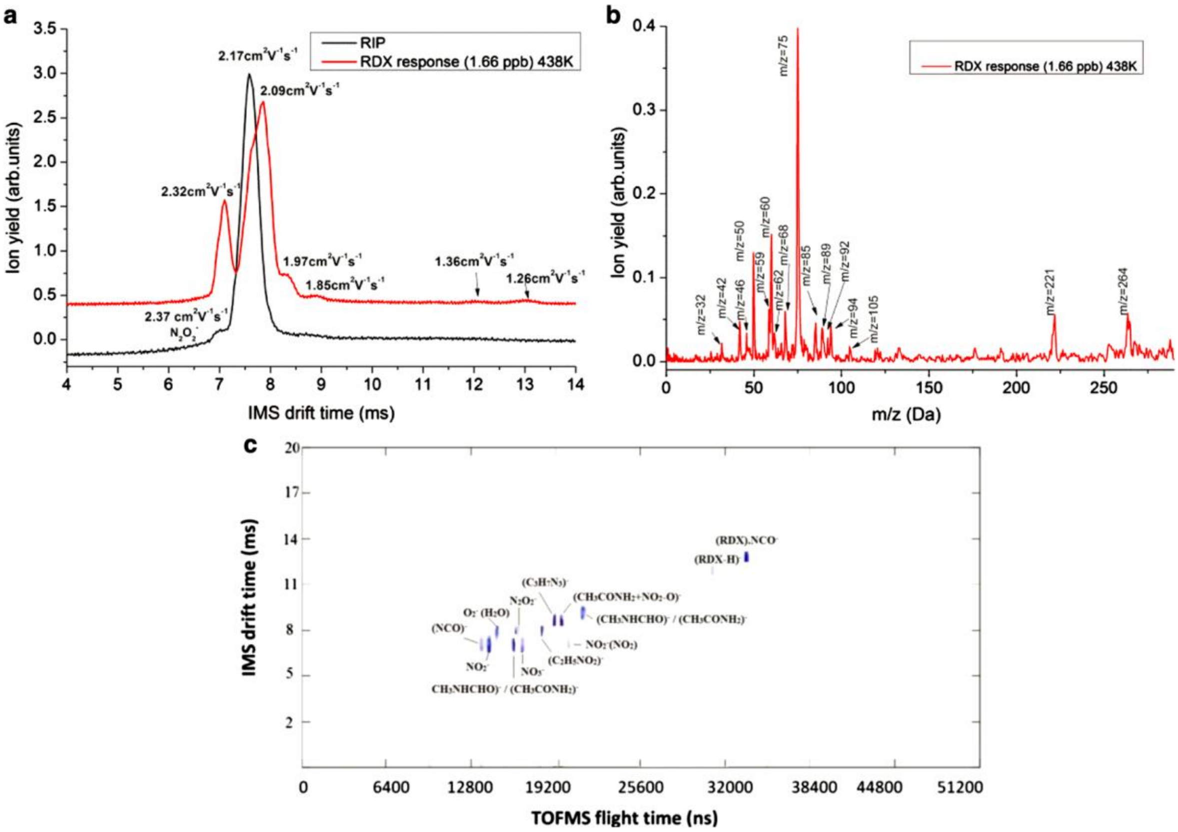

Figure 11. Response to RDX sample evaporated at 473K at 1.66ppb concentration. IMS was working in reverse flow and negative CD in zero air a) IMS spectrum at 438K b) corresponding MS spectrum c) two dimensional IMS-MS spectrum

After addition of dopant into the reaction region of IMS, there were detected except for the reactant ions Cl^- (both isotopes $^{35}Cl^-$ and $^{37}Cl^-$ formed via dissociative electron attachment to CCl_4), also ions generated from molecule of RDX: $Cl^-(NO_2)$, $Cl^-(NO)_2$ cluster, $Cl^-(NO)_3$ cluster, $CH_2N_3O_2^-$ with m/z=88 Da, $C_3H_4N_3O^-$ with m/z= 98 Da and the heaviest ion $RDX.Cl^-$ ions.

6 General conclusion

The present thesis dealt with detection of various interesting compounds by the technique Corona discharge-Ion mobility spectrometer coupled with Mass spectrometer (TOF).

This method was applied also for simulation of Martian atmosphere. Although, the conditions at the Martian atmopshere differ from the conditions present in CD-IMS-MS, suprisingly, our apparatus has been able to detect the same negative ions present in the low Martian atmosphere as were modelled in theoretical researches. Our experiment also confirmed the results gained from theoretical calculations of Molina-Cuberos [3], which can be considered as a great achievement for this research.

Furthermore, our following research was focused on various samples.

One of the examined samples was 2,4,6-Trichloroanisole (TCA). TCA appears in wine industry as a very common cork-taint compound and therefore causes billions euros losses in this industry. Therefore, companies producing wine are looking for the best detection techniques to avoid this problem. The CD-IMS-MS has been applied to detect this compound in both modes; standard and reverse gas flow modes. Except for ion composition, also temperature efect, calibration curves and limits of detection (LOD) have been studied. The LOD was determined for gas and solid phase and we reached values of 100 ppd and 150 ng, which are values lower than the values reached by Karpas [5] in his latest reasearch of this compound.

For a better and deeper understanding of this molecule, the ultraviolet photoelectron spectroscopy (UPS) and OVGF quantum theoretical calculations have been used to determine the ionization energies, observed orbitals and describe electronic structure of TCA. The ionization energies spectrum was also compared to similar molecule 1,3,5-Trichlorobenzene. Good agreement between calculated energy levels and the PES experiment results allowed us to attribute most of the structures observed in the PES spectrum to molecular orbitals.

Nowadays, there are also many questions about public safety, topic of detection of explosives is always open. In our experiment, two of the most famous explosives, 2,4,6-Trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) were examined. Especially IMS is a very common technique to detect explosives, but IMS coupled to MS applied in our laboratory, is an even more powerful tool. Except for the mapping of composition of negative ions created in Corona discharge reaction regione, also drift tube temperature effects and IMS drift field changes were examined. In case of RDX, the formation of ions has been studied under thermal decomposition at temperature 473 K. For better resolution of IMS/MS spectra, there were vapors of dopant CCl_4 used to enhance sensitivity of RDX ions. When the results of the measured IMS/MS spectra of both explosives were examined, there were found few ions which were not detected before in any of our known published articles in RDX measurement. These ions are: $(CH_3NHCHO)^-$ and $(CH_3CONH_2)^-$.

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8 Zoznam publikačnej činnosti

UNIVERZITA KOMENSKÉHO
FAKULTA MATEMAATIKY, FYZIKY A INFORMATIKY

Zoznam publikačnej činnosti

Mgr. Zuzana Lichvanová

ADC Vedecké práce v zahraničných karentovaných časopisoch

ADC01 Lichvanová, Zuzana [UKOMFKEFd] (50%) - Ilbeigi, Vahideh (1%) - Sabo, Martin [UKOMFKEF] (24%) - Tabrizchi, Mahmoud (1%) - Matejčík, Štefan [UKOMFKEF] (24%): Using corona discharge-ion mobility spectrometry for detection of 2,4,6-Trichloroanisole
Lit. 19 zázn.
In: Talanta. - Vol. 127 (2014), s. 239-243
Ohlasy (1):
[o1] 2015 Liu, N. - Song, Y. - Dang, G. - Ye, D. - Gong, X. - Liu, Y. - Liu, Y.: Effect of wine closures on the aroma properties of Chardonnay wines after four years of storage. In: South African Journal of Enology and Viticulture, Vol. 36,No. 3, 2015, s. 296-303 - SCOPUS

ADC02 Sabo, Martin [UKOMFKEF] (50%) - Lichvanová, Zuzana [UKOMFKEFd] (10%) - Országh, Juraj [UKOMFKEF] (1%) - Mason, Nigel J. (1%) - Matejčík, Štefan [UKOMFKEF] (38%): Experimental simulation of negative ion chemistry in Martian atmosphere using ionmobility spectrometry-mass spectrometry
Lit. 18 zázn., 5 obr.
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Lit. 34 zázn., 5 obr., 2 tab.
In: International Journal of Mass Spectrometry. - Vol. 380 (2015), s. 12-20
Registrované v: wos

ADM Vedecké práce v zahraničných časopisoch registrovaných v databázach Web of Science alebo SCOPUS

ADM01 Lichvanová, Zuzana [UKOMFKEFd] (50%) - Sabo, Martin [UKOMFKEF] (35%) - Matejčík, Štefan [UKOMFKEF] (15%): The study of thermal decomposition of RDX by corona discharge-ion mobility spectrometry-mass spectrometry
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AFC Publikované príspevky na zahraničných vedeckých konferenciách

AFC01 Lichvanová, Zuzana [UKOMFKEFd] (35%) - Országh, Juraj [UKOMFKEF] (35%) - Matejčík, Štefan [UKOMFKEF] (25%) - Mason, Nigel J. (5%): The effect of nitrogen admixture in carbon dioxide on formation of ozone in the DC corona discharges
Recenzované
Lit. 13 zázn., 5 obr.
In: WDS 2012: Proceedings of Contributed Papers: Part II Physics of Plasmas and Ionized Media. - Prague : MATFYZPRESS, 2012. - S. 118-122. - ISBN 978-80-7378-225-2

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AFD Publikované príspevky na domácich vedeckých konferenciách

AFD01 Országh, Juraj [UKOMFKEF] (13%) - Duffy, Maria - Lichvanová, Zuzana [UKOMFKEFd] (13%) - Sima, Cristina - Matejčík, Štefan [UKOMFKEF] (13%) - Mason, Nigel J. - Papp, Peter [UKOMFKEF] (13%) - Vladoiu, Rodica: Generation of carbon monoxide in positivecorona discharge fed by mixture of carbon dioxide and argon
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AFE Abstrakty pozvaných príspevkov zo zahraničných konferencií

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Popis urobený 26.3.2014
Lit. 4 zázn., 5 obr.
In: 3. Česko-slovenská studentská konference ve fyzice [elektronický zdroj]. - Praha : Univerzita Karlova, 2012. - nestr. [4 s.] [online]
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AFG02 Lichvanová, Zuzana [UKOMFKEFd] (60%) - Sabo, Martin [UKOMFKEF] (20%) - Matejčík, Štefan [UKOMFKEF] (20%): Electrospray sampling-corona discharge-ion mobility spectrometry (ESS-CD-IMS) used as a new method for investigation of 2,4,6-trichloroanisole
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Lit. 8 zázn., 2 obr.
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Meeting. Lisbon, 10.-13.3.2014]

AFG05 Sabo, Martin [UKOMFKEF] (40%) - Lichvanová, Zuzana [UKOMFKEFd] (30%) - Matejčík, Štefan [UKOMFKEF] (30%): Using electrospray as a sample technique for corona discharge ion mobility spectrometry
Lit. 4 zázn.
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AFG06 Sabo, Martin [UKOMFKEF] (55%) - Lichvanová, Zuzana [UKOMFKEFd] (5%) - Matejčík, Štefan [UKOMFKEF] (40%): IMS-oa TOFMS study of TNT interaction with reactant ions generated by corona discharge
Lit. 1 zázn., 1 obr.
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BEF Odborné práce v domácich zborníkoch (konferenčných aj nekonferenčných)

BEF01 Lichvanová, Zuzana [UKOMFKEFd] (32%) - Országh, Juraj [UKOMFKEF] (32%) - Mason, Nigel J. (4%) - Matejčík, Štefan [UKOMFKEF] (32%): The effect of argon and nitrogen in carbon dioxide on formation of ozone/CO in the DC corona discharge
Recenzované
Lit. 9 zázn., 10 obr.
In: 19th Symposium on Application of Plasma Processes and Workshop on Ion Mobility Spectrometry [elektronický zdroj]. - Bratislava : Department of Experimental Physics FMFI UK, 2013. - S. 235-244 [CD-ROM]. - ISBN 978-80-8147-004-2
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BEF02 Lichvanová, Zuzana [UKOMFKEFd] (30%) - Sabo, Martin [UKOMFKEF] (30%) - Országh, Juraj [UKOMFKEF] (10%) - Matejčík, Štefan [UKOMFKEF] (30%): IMS-MS study of negative corona discharge in CO2/N2 mixtures
Lit. 8 zázn., 3 obr.
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BEF03 Lichvanová, Zuzana [UKOMFKEFd] (85%) - Sabo, Martin [UKOMFKEF] (5%) - Michalczuk, Bartosz [UKOMFKEF] (5%) - Matejčík, Štefan [UKOMFKEF] (5%): Using corona discharge-ion mobility-mass spectrometry for detection of explosive 2,4,6 trinitrotoluene
Lit. 11 zázn., 2 obr.
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[International Forensic Symposium 2015. 12th, Bratislava, 17.-20.2.2015]

BFA Abstrakty odborných prác zo zahraničných podujatí (konferencie, ...)

BFA01 Lacko, Michal [UKOMFKEFd] (40%) - Stano, Michal [UKOMFKEF] (10%) - Lichvanová, Zuzana [UKOMFKEFd] (10%) - Papp, Peter [UKOMFKEF] (30%) - Matejčík, Štefan [UKOMFKEF] (10%): Interactions of low energy electrons with 2,4,6-trichloroanisole
Lit. 6 zázn.
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Štatistika kategórií (Záznamov spolu: 22):
ADC Vedecké práce v zahraničných karentovaných časopisoch (3)
ADM Vedecké práce v zahraničných časopisoch registrovaných v databázach Web of Science alebo SCOPUS (1)
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AFD Publikované príspevky na domácich vedeckých konferenciách (5)
AFE Abstrakty pozvaných príspevkov zo zahraničných konferencií (1)
AFG Abstrakty príspevkov zo zahraničných vedeckých konferencií (6)
BEF Odborné práce v domácich zborníkoch (konferenčných aj nekonferenčných) (3)
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