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Dissociation of trinitrotoluene on the surface of porous silicon under laser irradiation

Yury Kuzishchin*, Dmitriy Dovzhenko, Igor Martynov, Genadii Kotkovskii, Alexander Chistyakov

National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoye shosse 31, Moscow, 115409, Russia

Abstract

Dissociation of trinitrotoluene (TNT) sorbed on porous silicon (pSi) surface under UV laser irradiation has been studied. A method based on ion mobility spectrometry (IMS) has been used in this study. Excitation and ionization of TNT molecules has been occurred at atmospheric pressure. A dependence of TNT ion spectrum on standing time of TNT molecules on pSi surface has been demonstrated. The ion type has changed from $(TNT\text{-}H)^-$ to $(TNT\text{-}NO_2)^-$ which indicates a slow chemical reaction between pSi surface and TNT molecules. The first step of $(TNT\text{-}NO_2)^-$ formation has been found to be a result of laser stimulated surface dissociation and subsequent desorption of a neutral $TNT\text{-}NO_2$ fragment. The second step of $(TNT\text{-}NO_2)^-$ formation is a capture of an electron emitted from the pSi surface under laser irradiation. The result of this study could be used in the area of explosive detection.

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Keywords: IMS; ionization; TNT; pSi; DIOS; detection.

1. Introduction

Detection of a small amount of nitroaromatic compounds is of current interest. A laser ionization method is used for solving that problem [Kotkovskii et al. (2009), Lustig & Lubman (1991)]. Desorption/ionization on porous silicon (DIOS) [Wei et al. (1999)] is a widely used laser ionization method in mass-spectrometry [Alimpiev et al. (2001)] and could be applied for ion mobility spectrometry (IMS). However, mechanism of ionization of molecules on porous silicon surface has not been studied enough [Alimpiev et al. (2001), (2008); Li & Lipson (2013)]. Using

* Corresponding author. Tel.: +7-916-00-84-38.
E-mail address: yriy.kuzma@gmail.com

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of DIOS in IMS creates a new task for researchers due to a different complicated ion molecular reaction near pSi surface.

An important task required detail attention is a study of a probable chemical reaction between pSi surface and adsorbed molecules. Finding this chemical reaction and measuring of its rate may improve DIOS. It is known that nitroaromatic compounds may react with a pSi surface [McLeod et al. (2012)]. Nonetheless effect on an ion signal in DIOS-IMS has not yet defined. In this paper a new results describing possible reactions have been obtained.

2. Experimental methods and setup

Ion mobility spectra are studied using IMS described earlier in [Martynov et al. (2011)]. 2,4,6-trinitrotoluene (TNT) is used as an analyte because TNT is a typical explosive and its detection is of interest nowadays. In order to sorb TNT molecules on the pSi surface a special cuvette has been used [Kuzishchin et al. (2015)]. For ionization of sorbed TNT, pSi surface has been irradiated with nanosecond laser with 266 nm wavelength, 6 ns pulse duration 10 Hz repetition rate and intensity about $1.0 \cdot 10^7$ W/cm^2. A negative ion detection regime has been used for all measured since a negative ion formation is typical for nitroaromatic compounds [Daum et al. (2002), Ewing et al. (2001)].

3. Results and discussion

Figure 1 shows a fragment of IMS spectra obtained under laser irradiation of pSi surface immediately after TNT sorption process (dashed line) and a day after (solid line). Pure air is used as a gas environment of IMS. Drift times of presented ion signals are typical for nitroaromatic compounds negative ions.

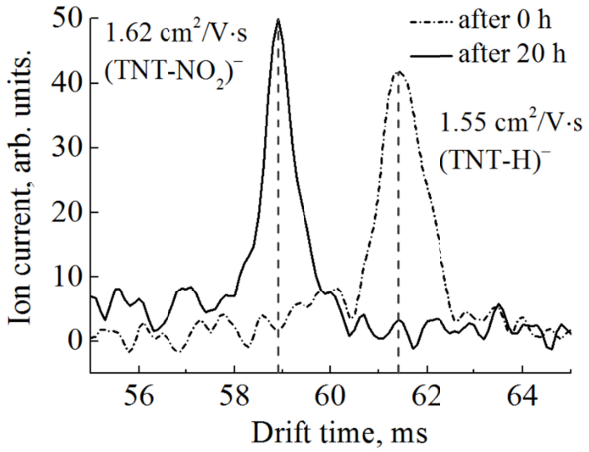

Fig. 1. The IMS spectrum obtained using laser irradiation of the pSi surface immediately and 20 h after sorption.

It is shown that mobility of observed ions is different. The peak observed immediately after sorption with mobility 1.55 cm^2/V·s is identified as $(TNT\text{-}H)^-$ ions [Ewing et al. (2001)]. Otherwise, the peak observed a day later after sorption with mobility 1.62 cm^2/V·s is identified as $(TNT\text{-}NO_2)^-$ ions [Ewing et al. (2001)]. Later the peak corresponded to the $(TNT\text{-}NO_2)^-$ ions has not been changed for a three days. Therefore we can assume that the chemical reaction between pSi surface and TNT molecules occurred. The chemical reaction leaded to a change of bond type between the TNT molecule and the pSi surface that leaded to the TNT molecule dissociation and formations of $(TNT\text{-}NO_2)^-$ ions. This result is in an agreement with [McLeod et al. (2012)], where adsorption of nitroaromatic molecules on pSi surface has studied.

The important point is a mechanism of $(TNT\text{-}NO_2)^-$ ion formation. In our previous studies we have investigated the mechanism of $(TNT\text{-}H)^-$ ion formation [Dovzhenko et al. (2014), Kuzishchin et al. (2015)]. It has been found

that $(TNT\text{-}H)^-$ ions formation is based on a process of proton transfer from a TNT molecule to a pSi surface. This process is initiated by the laser irradiation and occurs on pSi surface. A key feature of the proton transfer on pSi surface is independency on composition of IMS gas environment. In order to establish the mechanism of $(TNT\text{-}NO_2)^-$ ions formation we have performed a similar approach. The results are presented at figure 2. It is shown that the replace of IMS gas environment from pure air to pure nitrogen results in a dramatically decrease of $(TNT\text{-}NO_2)$ ion peak magnitude. This directly indicates [Daum et al. (2002)] that $(TNT\text{-}NO_2)^-$ ion formation occurs in gas phase on account of electron capture. Therefore laser irradiation on pSi surface results in dissociation and desorption the neutral $THT\text{-}NO_2$ fragments.

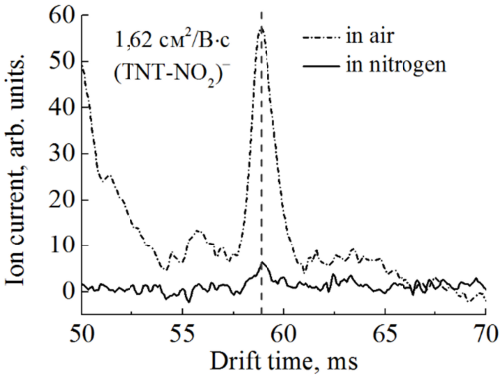

Fig. 2. The IMS spectrum obtained using laser irradiation of the pSi surface 70 h after sorption in different gas media.

4. Conclusion

Influence of the reaction between TNT molecules and pSi surface on ion mobility spectra has been demonstrated. Laser stimulated dissociation TNT molecules on pSi surface and $THT\text{-}NO_2$ fragment formation has been discovered. It has been established that the neutral $THT\text{-}NO_2$ fragments are desorbed from pSi surface under laser irradiation and their ionization occurs in the gas phase due to the ion molecular reactions. These results are important for applying of DIOS in IMS and could be used for explosive detection task.

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