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Systematic discrimination of heptane isomers with femtosecond laser linear time of flight mass spectrometry

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Abstract

The dissociative ionization processes of heptane molecule with nine isomers have been investigated and presented experimentally in detail by courtesy of femtosecond laser mass spectrometry technique with a fundamental wavelength of 800 nm and 90 fs pulse duration in this study. It has been aimed to show that the classification of heptane isomers using factor analysis as statistical method reducing the dimension of obtained data. The main mass ratio of heptane isomers is known as m/z 100 which is obtained. The dissociation process on the parent molecule was dominant at the laser intensity about 1.42 x 1014 W/cm2 used for all isomers. The ions obtained by the breakdown of the main ion peak were primarily determined as factors which were clearly distinguished from each other according to factor 1 and factor 2 axes by applying factor analysis.

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1. Introduction

Alkanes are saturated hydrocarbons with sp^3 hybrid orbitals with some general properties reactive and low biological activity. In addition, the carbon atoms in the alkane group are covalently bonded to each other. Isomers of heptane molecule are known as the aliphatic alkanes (C_nH_{2n+2}) molecules which are called saturated hydrocarbons [1]. Alkanes are formed by bonding hydrogen atoms and carbon atoms to a single carbon-carbon bond. At the same time, another common feature of the molecules in this group is that they are colorless and odorless [2, 3]. The structure forms of heptane isomers (C_7H_{16}) alkane group molecules are in chain structure [4] which are formed by different binding of the methyl (CH_3) group to carbon atoms included in the class of organic molecules [5, 6]. Heptane isomers are all important organic molecules in which their solubilities are well due to low reactivity just as water. The understanding of the character of the heptane molecule will contribute to technology by expanding its areas of use.

Mass spectroscopy (MS) technique and statistical approaches are well known methods to understand structures of chemical, biological or other types materials. MS technique has been used in the process from the mid-19th century to the present. After the discovery of laser in 1960s, laser ionization mass spectrometry is one of the most widely used techniques in research studies [7]. The most widely used energy source in mass spectrometry in recent years seems to be lasers. Mass spectrometry is also used to determine the molecular characteristics of chemical or biological samples with different laser types. Molecular analysis of high purity metals, alloys, semiconductors, insulators, biological and medical materials, geological samples, nuclear and radioactive materials can be carried out accurately by MS [8-11].

Studies on the determination of thermodynamic, structural and dynamic properties of heptane isomers are presented in literature, but information on the studies on molecular ionization / fragmentation / dissociation processes are limited [5, 6]. In this work, it has been elaborated on dissociative ionization of heptane isomers, and some of their physical and chemical properties of heptane isomers have also been discussed using their mass spectra. Factor analysis (FA) has been applied to focus the distinguish its isomers [12-18]. Femtosecond laser mass spectrometry (FLMS) makes possible to detect and analysis molecules which have been developed by group members as an important analytical tool in MS

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technique [8]. Studies on the ionization, dissociation and fragmentation processes of different types of molecules are included by using time of flight mass spectrometry in literature [8-11, 19].

FA has been used commonly in social sciences and in psychology initially, but currently, the method is widely used to distinguish chemicals as well as all areas of science. FA has been defined and situated as a multi-variation analysis method in literature and applied to the obtained spectra and the results compared to those obtained from some other statistical approaches [20-23].

Interpretation of mass spectra take quite a long time and also these data are massive and large dimensional. The main purpose of the application of the FA statistical technique is to achieve the most important information from the data obtained. In general mass spectra are monitored using imaging technique, using statistical approaches give more information such as monitoring, discrimination and also investigation. The most important goal in distinguishing isomers, which are very similar to each other, is to reach a more advanced position in distinguishing cancer and healthy tissues [22, 23].

In this study, FA statistical approach has been used to analyse isomers of heptane organic molecule. The factors mentioned characteristic peaks in the mass spectrum recorded with a computer program and FA statistical approach has been applied to the results to be analysed. The main objective of this study is on to distinguish and classification of nine heptane isomers of heptane molecule by gathering the most important information from the spectral data using factor analysis. In this way, reducing the dimensions of data makes the explanation of spectra is much simpler. The discrimination of the nine-isomer of heptane molecule obtained in this study by factor analysis paves the way for the differentiation of multiple cancerous and healthy tissues [21-22].

2. Materials and Methods

2.1 Femtosecond laser properties

The femtosecond (fs) laser system connected to a home-made linear time of flight mass spectrometer system was used to analyse the liquid form of nine heptane isomers to distinguish them by using FA method.

The experimental apparatus used in this study depicted in Figure 1 consists of a femtosecond laser system, a vacuum chamber and a data acquisition system. The fe laser system consists of three main parts which are an oscillator, and amplifier and a optical parametric amplifier (OPA) systems. The oscillator (Ti: Light, Quantronix, NY, USA) delivers 90 fs laser pulses at 800 nm wavelength with an 85 MHz repetition rate. The amplifier (Integra-C-3.5, Quantronix, NY, USA) is pumped by Ti-Light oscillator and generates amplified laser pulses at 800 nm wavelength and 90 fs laser pulses at a 1-3 kHz repetition rates. The laser amplifier system produces maximum 3.5 W power per pulse and its output is controlled by using a circular neutral density filter and the energy of the laser beam was measured by using a neutral density filter. Experimental details used in this study have been described in detail in previous studies [9, 20-23]

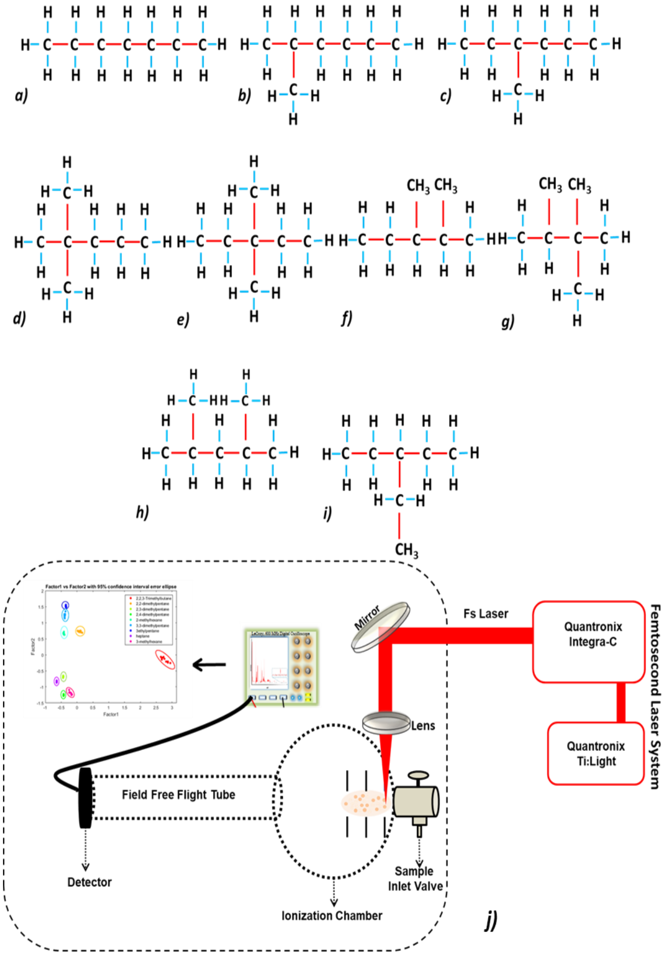

Figure 1. Schematic representation of heptane isomers a) n-heptane, b) 2-methylhexane, c) 3-methylhexane, d) 2,2-dimethylpentane, e) 3,3-dimethylpentane, f) 2,3-dimethylpentane, g) 2,2,3-Trimethylbutane, h) 2,4-dimethylpentane, i) 3-ethylpentane, j) experimental systems consist of a femtosecond laser system, vacuum chamber and data acquisition systems.

2.2 Linear time of flight mass spectrometer properties

The Linear time of Flight (L-TOF) mass spectrometer system was built in local industrial zone in Konya, in the design of Wiley and Mclaren [24]. The background pressure in the vacuum chamber can be pumped down to several times 10^{-8} mbar, but during the experiment, sample pressure was kept very stable about 1.6×10^{-6} mbar [21-23, 25].

The mass spectra signal was taken by a MCP detector directly to an oscilloscope and recorded in a four channel fast digital oscilloscope (LeCroy, WaveRunner 64Xi, 600 MHz) connected with a server computer. All recorded mass spectra were taken averaging over 1000 laser shots and recorded as mass spectra in oscilloscope. The spectra of the heptane isomers have been recorded using laser intensities from 7.12×10^{12} W/cm2 to 1.42×10^{14} W/cm^2. The fs laser beam was sent to the laser ionization area in the mass spectrometer where it was focused down to several micrometers (µm) spot area using a lens with a focal length of 25 cm. The purities of used heptane isomers are ≥ 99% in this study.

3. Results and Discussion

FA has been known as one of the dimension reduction methodological approach. Linear combination of used factors is given as:

$F_i = W_{i1}X_1 + W_{i2}X_2 + W_{i3}X_3 + \ldots + W_{ik}X_k$
$F_i = i_{th}$ Factors
$W_i = i_{th}$ Score correlation
k = the number of variables

i_{th} set factor score coefficient explains the maximum value of the total variance of the factor [23]. Generally, the formula for factor analysis is given by Equation 1

$$S = V^{f} R^{f} V^{f} + (D_s - H) \tag{1}$$

where S is the correlation matrix of existing variables. V^{f} is orthogonal and therefore R^{f} is defined as an identity matrix. After then, the equation 1 is simply rewritten to be

$$S = V^{f} V^{f} + (D_s - H) \tag{2}$$

where D_s is a diagonal matrix with diagonal elements S, and H is another diagonal matrix. The diagonal elements of $D_s - H$ are monovalent in equation 2. The factor analysis calculations were carried out by Matlab program considering equation 1 and equation 2 procedure for determined *f* factors [23, 27, 28].

The m/z 27, 29, 39, 40, 41, 42, 43, 44, 53, 55, 56, 57, 58, 69, 70, 71, 85 and 100 values were used as factors in this study. Main peaks in mass spectra of heptane molecule according to the information for the organic compounds mass/charge (m/z) ratios were obtained by only one electron ionization in NIST database [29].

Algorithm of factor analysis applied in this work is given as in figure 2.

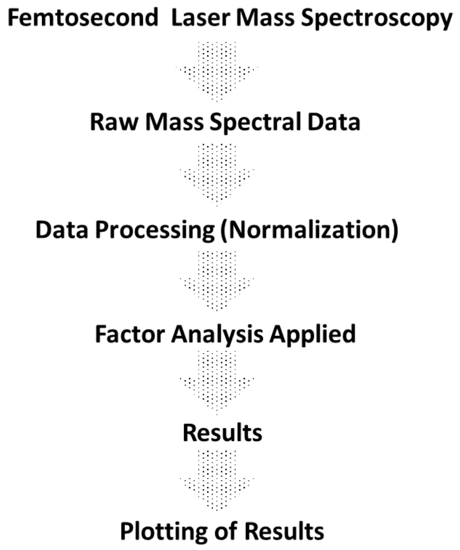

Figure 2. Implemented process of factor analysis to heptane isomers is given.

According to Figure 2, the first of all, the analysis of heptane isomers using FLMS method was recorded by performing experiment using different laser powers with the wavelength of 800 nm. The experimental process was completed by using the parameters given in the experimental part by storing 10 consecutively data savings by courtesy of a four channels digital storage oscilloscope from each spectrum, keeping all parameters constant at the same laser power. Since all recorded spectra were obtained from the oscilloscope depending on the flight time where all flight times were converted to mass units according due to the formula $m = at^2 + b$. One of the important conditions in the experimental process is determination of optimum laser parameters such as laser pulse power, focal point and laser incidence angle. At the same time, it is very important to keep the vacuum conditions stable during the experiment. Keeping all of the determined laser parameters unchanged during the experiment will minimize the experimental error. In the next step, after ensuring the data is recorded carefully, the largest peak in the spectra recorded in m/z was normalized and normalization was applied to all spectra. All these processes were carried out using a MATLAB code produced by our group. The resulting data were plotted and shown in Figure 5.

3.1 Femtosecond laser ionization of heptane isomers

It is well known that in molecules having chain structure, the breakdown of the bond structures occurs either easily or faster than other types of molecules. Detection of parent ion peak at $C_7H_{16}^+$ (m/z 100) without any dissociation taken place is very difficult since the structure of molecules are in chain structures and lifetime in the excited state are very short. Generally, ion peaks with masses smaller than the parent ion are predominant in mass spectra pattern for such ionization processes. In this case, the interpretation of mass spectra makes it difficult to explain for molecules fragmented within a laser pulse duration. Alternative theoretical studies are needed for this to be interpreted clearly.

The spectra of the heptane isomers have been recorded using laser intensities of 7.12 x 10^{12} W/cm^2 and 1.42 x 10^{14} W/cm^2 and mass spectra are given in Figure 3. When the obtained peak intensities are investigated, it can be seen from Figure 3 that all isomers have similar peak intensities for small m/z range in mass spectra, such as $C_1H_n^+$, $C_2H_n^+$, $C_3H_n^+$.

In Figure 3, noteworthy peak intensities are H^+, C^+, CH^+, CH_2^+ CH_3^+, $C_2H_n^+$ ions in the $C_1H_n^+$ ion group, C_2^+, C_2H^+, $C_2H_2^+$, $C_2H_3^+$, $C_2H_4^+$, $C_2H_5^+$ ions in $C_2H_n^+$ ion group, C_3^+, C_3H^+, $C_3H_2^+$, $C_3H_3^+$ $C_3H_4^+$, $C_3H_5^+$, $C_3H_6^+$, $C_3H_7^+C_3H_n^+$ ion group and $C_4H_8^+$ and $C_4H_9^+$ions in $C_4H_n^+$ ion group are seen clearly from recorded spectra which were obtained by applying 1.42 x 10^{14} W/cm^2 laser intensity.

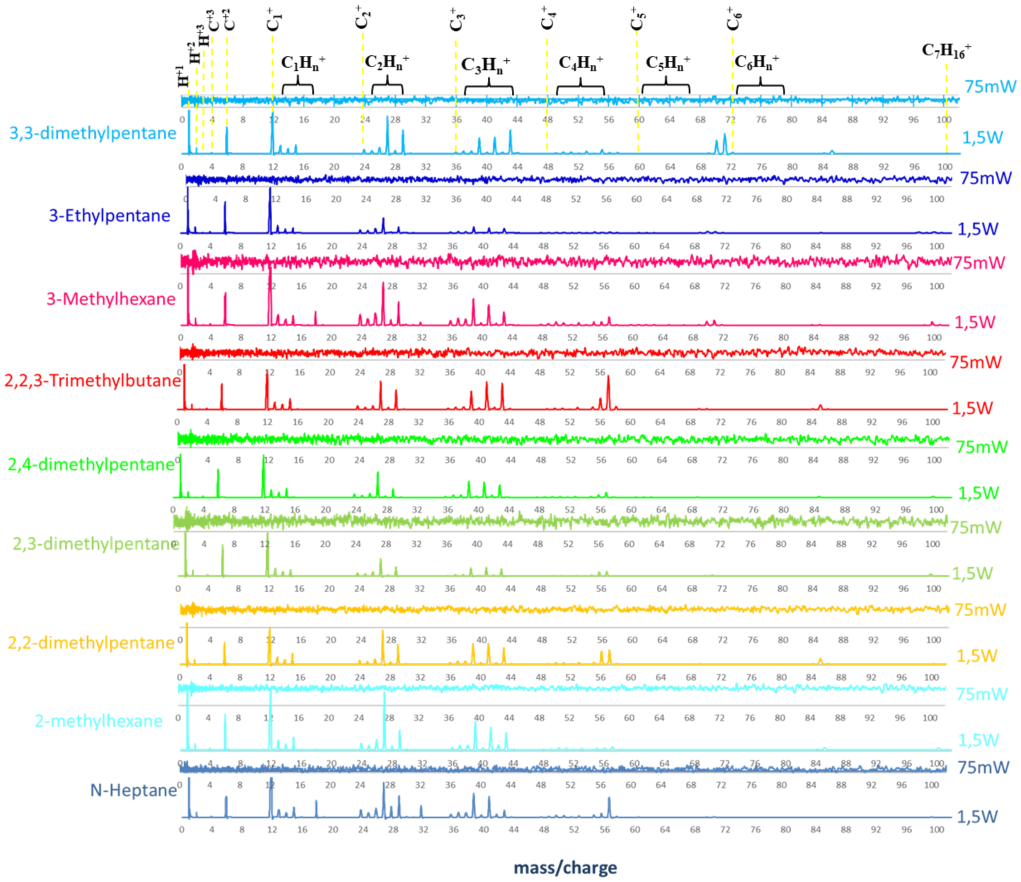

Figure 3. n-heptane, 2-metilhexane, 2,2-dimethylpentane, 2,3-dimethylpentane, 2,4-dimethylpentane, 3-methylhexane, 3-ethylpentane, 3,3-dimethylpentane, 2,2,3-Trimethylbutane were obtained minimum 75 mW laser power and also maximum 1.5 W laser power.

The parent ion peak $C_7H_{16}^+$ (m/z 100) was magnified about a hundred times to show in spectra in Figure 4. All recorded fragment ion peaks at m/z 27, 29, 39, 40, 41, 42, 43, 44, 53, 55, 56, 57, 58, 69, 70, 71 values and also main peak at m/z 100 amu were obtained in spectra shown in Figure 4. The parent ion peak was appeared since the spectrum is magnified. The multiply charged ions like C_n^+ (n=2, 3, 6) are clearly recorded in the spectra for all heptane isomers with the intensity range from 7.12 x 10^{12} W/cm^2 to 1.42 x 10^{14} W/cm^2.

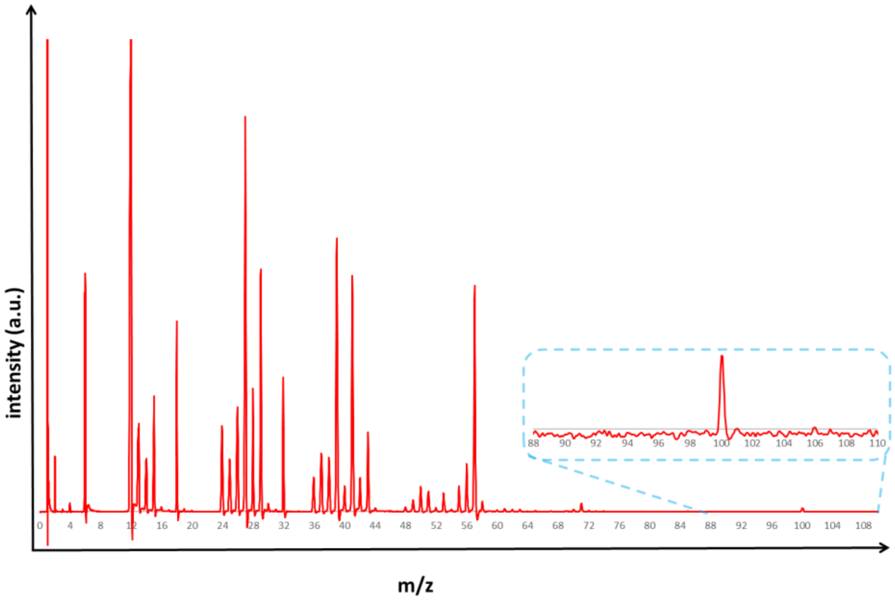

Figure 4. n-heptane was recorded 1.5 W laser power and the parent ion m/z 100 was appeared after the magnification is increased.

The interpretation of data from mass spectrometry takes quite long time and also these data is massive and in very large dimensions. The main purpose of the application of FA statistical technique is to achieve the most important information from the data obtained.

3.2 Factor analysis for Heptane isomers

It is important that the discrimination of the factor components by using FA method which is known as a powerful analysis procedure to distinguish isomers as we have discussed in a number of previous work and give it in literature [20-23]. In laser-based mass spectrometry technique, fragment ions are produced where dissociative ionization process are investigated intensively in mass spectra. The dissociation may become more significant when the interpretation of the data obtained is only meaningful, that is, given the peak intensities specifically appeared in each spectrum. The data obtained in many fields of science, including interdisciplinary fields in the direction of technological developments can reach to very large and high dimensions. The data obtained in mass spectrometric studies can be given as an example [21, 23].

In the process of discrimination of nine isomers using FA, it was shown that the peaks, that are distinct from the spectra, are distinguished from each other by FA. MS data has been recorded as a function of laser power and factors have been determined from the recorded spectra.

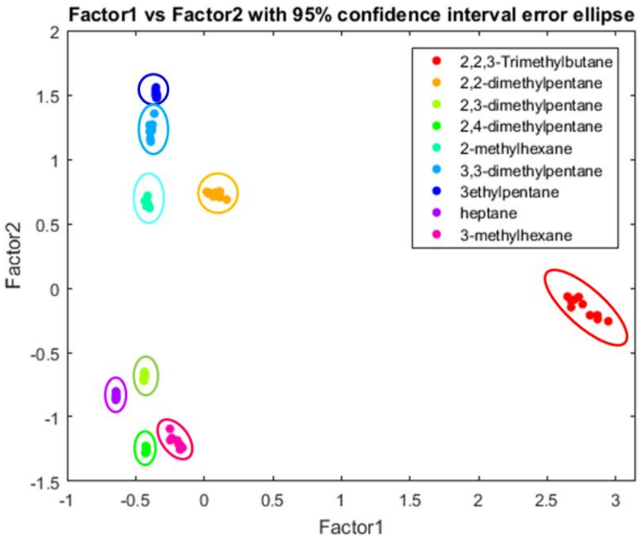

Figure 5. The Factor Analyse result of normalized data from the mass spectra of 9 heptane molecular isomers is given as a result of analysis of isomers that are clearly differentiated each other factor 1 and factor 2 axes

The data used in FA were generated in two dimensions by plotting code in MATLAB program [20, 21]. One of the points in the data of each isomer given in figure 5 was obtained as a result of 10 repetitions of successive recording of spectrum by averaging over 1000 laser shots and this repetition process was obtained using 1.5 W laser power and 800 nm laser wavelength at infrared region. Heptane molecular isomers can be distinguished from each other in factor 1 and factor 2 axes. Data recording and FA application process were performed by running the program codes written in MATLAB programming language by our group [20-23]. With the TCP/IP protocol, the data were recorded via oscilloscope in accordance with the parameters were determined during the experiment and they were made ready for the next step, FA.

In figure 5, the mass spectra of nine heptane molecular isomers which were normalized as a result of analysis of isomers that were clearly differentiated from each other in factor 1 and factor 2 axes that are symbolized in two dimensions on axes. The process of discrimination is interpreted by looking at these axes.

4. Conclusion

The ionization/fragmentation process of heptane isomers have been demonstrated by using FLMS technique [8]. As a result of interaction between ultrafast laser beam and molecule, since the lifetime of molecules in the excited states are so shorts, heptane molecular isomers dissociate very fast and therefore it is very difficult to obtain a dominant parent ion in the mass spectra of each isomer. Under these circumstances, even using smaller mass fragment ion peaks, the structure and dissociative ionisation, fragmentation dynamics of molecular isomers have been clearly revealed, and important contributions may be made to literature due to this important data. Fs laser system using 800 nm wavelength, 1 kHz repetition rate, 90fs pulse duration and depending on the varying laser power, ionization and dissociation & fragmentation dynamics for nine isomers of heptane molecule using FLMS technique was clearly analysed and data have been interpreted clearly due to the used statistical analysis.

The m/z ratios of heptane molecular (C_7H_{16}) isomers have the same, all 100, molar mass. While it is possible for some molecular isomers to be distinguished while they have isomers of molecules in the same mass but in different binding forms, it is sometimes difficult to distinguish these in visual spectra. When statistical methods are applied to the spectra obtained for this purpose, the distinguishing these isomers becomes much more meaningful. From this point, it is shown that each isomer can be clearly distinguished from each other by applying FA method. The most important goal in distinguishing isomers, which are very similar to each other, is to reach a more advanced position in distinguishing cancer and healthy tissues.

Therefore, it can be given as a final conclusion that the life time of the molecules in the excited state are very short in comparison with laser pulse duration (90 fs) [8, 9, 19, 29], and within a 90fs laser pulse duration, the access of molecular parent ion is very difficult, and no or very small ion peak at m/z 100 were obtained as seen from Figure 4.

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Conflicts of interest

The authors state that did not have conflict of interests

References

[1] Ess D.H., Liu S., De Proft F., Density functional steric analysis of linear and branched alkanes, *J. Phys. Chem. A,* 114 (2010) 12952-12957.

[2] Yagil G., Nadel L., Stein D., On the structural complexity of templated systems, Rehovot, Israel, The Weizmann institute of Science, (1992).

[3] Arora A., Hydrocarbons (Alkanes, Alkenes and Alkynes), Discovery Publishing House (2006).

[4] Edgar G., Calingaert G., Marker R., The preparation and properties of the isomeric heptanes. part i. preparation1, *J. Am. Chem. Soc,* 51 (1929) 1483-1491.

[5] Lavanchy A., Houriet R., Gäumann T., The mass spectrometric fragmentation of n-heptane, *Org. Mass. Spectrom.,* 13 (1978) 410-416.

[6] Chen J.-H., Dunbar R.C., Fragmentation of n-heptane ions by photodissociation, *Int. J. Mass Spectrom. Ion Processes,* 72 (1986) 115-123.

[7] Maiman T.H., Stimulated optical radiation in ruby, *Nature,* 187 (1960) 493-494.

[8] Kilic H.S., Ledingham K., Kosmidis C., McCanny T., Singhal R., Wang S., Smith D., Langley A., Shaikh W., Multiphoton ionization and dissociation of nitromethane using femtosecond laser pulses at 375 and 750 nm, *The J. of Phys Chem. A,* 101 (1997) 817-823.

[9] Kilic H.S., Comparison of Nanosecond and Femtosecond Laser Mass Spectrometry (FLMS), University of Glasgow, (1997).

[10] Kilic H.S., Ledingham K., Smith D., Wang S., Kosmidis C., McCanny T., Singhal R., Langley A., Shaikh W., The Photo-Dissociative Pathways

of Nitromethane Using Femtosecond Laser Pulses at 375 nm, *AIP Conference Proceedings*, (1997) 395-398.

[11] Ledingham K., Singhal R., Smith D., McCanny T., Graham P., Kilic H.S., Peng W., Wang S., Langley A., Taday P., Behavior of polyatomic molecules in intense infrared laser beams, *The J. of Phys. Chem. A*, 102 (1998) 3002-3005.

[12] Shi Y., Lipson R., An overview of organic molecule soft ionization using vacuum ultraviolet laser radiation, *Can. J. Chem*, 83 (2005) 1891-1902.

[13] Yim Y.H., Kim M.S., Photodissociation breakdown pattern and the internal energy of n-heptane ion generated by charge exchange ionization, *Int. J. Mass Spectrom. Ion Processes*, 123 (1993) 133-137.

[14] Choe J.C., Kim M.S., Photodissociation of heptane molecular ion: real-time investigation of consecutive reactions, *J. Phys. Chem*, 96 (1992) 726-732.

[15] Marotta E., Paradisi C., A mass spectrometry study of alkanes in air plasma at atmospheric pressure, *J. Am. Soc. Mass Spectrom*, 20 (2009) 697-707.

[16] Revel'skii I., Yashin Y.S., Voznesenskii V., Kurochkin V., Kostyanovskii R., Mass spectrometry with photoionization of N-alkanes, alcohols, ketones, esters, and amines at atmospheric pressure, *Russ. Chem. Bull.*, 35 (1986) 1806-1810.

[17] Song L., Dykstra A.B., Yao H., Bartmess J.E., Ionization mechanism of negative ion-direct analysis in real time: a comparative study with negative ion-atmospheric pressure photoionization, *J. Am. Soc. Mass Spectrom*, 20 (2009) 42-50.

[18] Silva R., Gichuhi W.K., Doyle M.B., Winney A.H., Suits A.G., Photodissociation of heptane isomers and relative ionization efficiencies of butyl and propyl radicals at 157 nm, *Phys. Chem. Chem. Phys.*, 11 (2009) 4777-4781.

[19] Kosmidis C., Ledingham K., Kilic H., McCanny T., Singhal R., Langley A., Shaikh W., On the fragmentation of nitrobenzene and nitrotoluenes induced by a femtosecond laser at 375 nm, *J. Phys. Chem. A*, 101 (1997) 2264-2270.

[20] Kepceoğlu A., Gündoğdu Y., Ledingham K.W.D., Kilic H.S., Identification of the isomers using principal component analysis (PCA) method, *AIP Conference Proceedings*, (2016) 060004.

[21] Kepceoğlu A., Gündoğdu Y., Ledingham K.W.D., Kilic H.S., Real-Time Distinguishing of the Xylene Isomers Using Photoionization and Dissociation Mass Spectra Obtained by Femtosecond Laser Mass Spectrometry (FLMS), *Anal. Lett.*, 53(2) (2020) 290-307.

[22] Gündoğdu Y., Alptekin H., Karabağlı P., Şahin M., Kilic H.Ş., Discrimination of cancerous and healthy colon tissues: A new laser-based method, *Laser Surg Med.*, 51 (2019) 363-369.

[23] Gündoğdu Y., Karabağlı P., Alptekin H., Şahin M., Kılıç H.Ş., Comparison of performances of Principal Component Analysis (PCA) and Factor Analysis (FA) methods on the identification of cancerous and healthy colon tissues, *Int. J. Mass Spectrom.*, 445 (2019) 116204.

[24] Wiley W., McLaren I.H., Time-of-flight mass spectrometer with improved resolution, *Rev. Sci. Instrum.*, 26 (1955) 1150-1157.

[25] Gündoğdu Y., Kepceoğlu A., Kılıç H.Ş., Akbaş M., Doğan M., Ledingham K.W., Femtosaniye Laser Pulsları Yardımıyla Cn+ (n= 1… 60) Topak İyonlarının Hem C60 Hemde Grafit Hedefler Kullanılarak Ayrı Ayrı Üretimi ve Ölçümü (021101)(1-9), *Afyon Kocatepe University J. Sci. and Engin*., 14 (2014) 1-9.

[26] Ritter G.L., Lowry S.R., Isenhour T.L., Wilkins C.L., Factor analysis of the mass spectra of mixtures, *Anal. Chem.*, 48 (1976) 591-595.

[27] Rozett R.W., Petersen E.M., Methods of factor analysis of mass spectra, *Anal. Chem.*, 47 (1975) 1301-1308.

[28] National Instute of Standards and Technology-NIST Chemistry WebBook, Available at : https://webbook.nist.gov/cgi/cbook.cgi?ID=C142825&Mask=200#Mass-Spec, *NIST*, (2020).

[29] Ledingham K.W., Deas R.M., Marshall A., McCanny T., Singhal R.P., Kilic H.S., Kosmidis C., Langley A.J., Shaikh W., A comparison of femtosecond and nanosecond multiphoton ionization and dissociation for some nitro-molecules, *Rapid Commun. Mass Spectrom.*, 9 (1995) 1522-1527.