EXPERIMENTAL AND THEORETICAL STUDIES OF LASER DESORPTION/IONIZATION OF METHYLENE BLUE FROM THE SURFACE OF THERMALLY EXFOLIATED GRAPHITE

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Mass spectra of products obtained in the course of laser desorption/ionization of methylene blue from the surface of thermally exfoliated graphite have been registered. It is demonstrated that $[M+1]^+$, $[M+2]^+$, and $[M+3]^+$ ions with one, two, or three, respectively, hydrogen atoms bound to the molecular ion dominate in the mass spectra. The experimental results are confirmed by quantum chemical calculations of possible reaction products that may be formed under the influence of laser radiation.

1. Introduction

In the modern laser desorption/ionization (LDI) mass spectrometry, a search for new materials which can be used as a substrate is an important task. In this sense, it is of interest that, notwithstanding the fact that various graphite-like materials are widely used in science and engineering, the majority of graphite derivatives almost have not been estimated from the viewpoint of their suitability for mass-spectrometric applications. Therefore, the corresponding researches are challenging, and they may prove to be useful in practice. Among the indicated substances, especially promising seems to be thermally exfoliated graphite (TEG) [1]. This material provides the efficient ionization under the influence of laser radiation and, hence, is technologically suitable for specified applications. As a result, taking advantage of TEG substrates, it is possible to successfully study the adsorbed compounds with the use of the LDI method [2].

2. Research Objects and Methods

Specimens of thermally exfoliated graphite can be obtained in different ways [1]. Every technology aimed at the TEG manufacture results in that different functional groups are formed on the surface, which is necessary to bear in mind while analyzing the results of experiments.

The methylene blue (MB) dye is a compound that has been studied rather well from the viewpoint of both mass-spectrometric experiments [3, 4] and quantum chemical calculation methods [5, 6]. Therefore, this reagent is worth to be used as a test substance while studying and comparing the properties of various substrates in mass spectrometry.

In this work, we used the specimens of thermally exfoliated graphite fabricated by treating graphite with the sulfuric acid. The experiments were carried out on an Autoflex II mass spectrometer (Bruker Daltonics). Wafers cut out from TEG were covered with a MB solution in ethyl alcohol. The specimens were held at room temperature for a definite time to be dried. Afterward, they were put into a chamber, where the pressure was decreased down to about 5.4×10^{-7} Pa. Then the specimens were subjected to the action of laser radiation. Ions formed over the surface and driven by an electric field got into a transit-time analyzer of the spectrometer. The obtained mass spectra were characterized by different compound's mass-to-charge ratios, which comprises the essence of the selected mass-spectrometric method [7]. Various operating modes of a laser – from 40 to 100% of its maximum intensity – were used. The delay time for the ion extraction was also varied from 20 to 150 ns.

The results obtained are interpreted with the use of quantum chemical methods. Namely, we carried out calculations in the framework of the Hartree–Fock method using the basic set 6–31G(d,p) and with the help of the USGAMESS software package [8]. The equilibrium spatial structure of reactant molecules and the products of analyzed reactions were determined by minimizing the gradient norm [9]. In accordance with the Murrell–Laidler theorem [10], the absence of negative characteristic values for the relevant Hessian matrices testifies to the stationary character of energy minima obtained for corresponding structures. The Gibbs en-
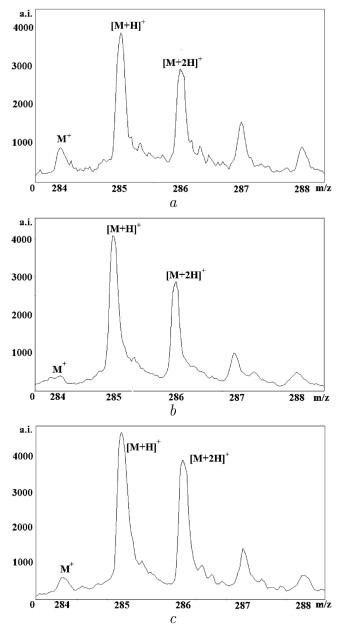
Fig. 2. MB mass-spectrum obtained by laser desorption/ionization from the TEG surface at the 150-ns delay of extraction and 40% of the maximum laser intensity
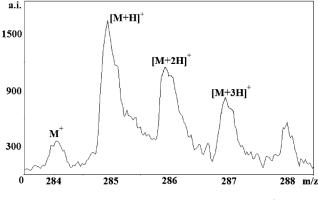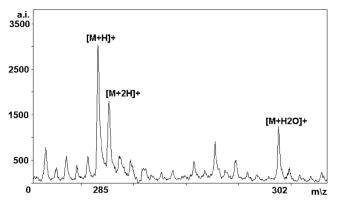

Fig. 3. MB mass-spectrum obtained by laser desorption/ionization from the TEG surface at the 150-ns delay of extraction and 60% of the maximum laser intensity

Fig. 1. Mass-spectra of methylene blue (MB) obtained by laser desorption/ionization from the surface of thermally exfoliated graphite (TEG) at the 20-ns delay of extraction and various laser intensities: 40 (a), 60 (b), and 100% (c) of the maximum power

ergy of corresponding reactions was determined by the formula ΔG (reaction) $= \Delta G_{298}^0$ (reaction products) $-$ ΔG_{298}^0 (reactants), where $\Delta G_{298}^0 = E_{0K} +$ ZPE $+$ $G_{0 \to 298K}$, E_{0K} is the total energy of the corresponding optimized structure, ZPE is the zero-point energy, and the quantities $G_{0 \to 298K}$ were determined by calculating the Hessian matrix for every of those states [11]. The

atomic charges were calculated following the Mulliken method.

3. Results and Their Discussion

3.1. Experimental part

Let us first consider the set of spectra obtained for MB desorbed from the TEG surface (Figs. 1 to 3). All of them reveal certain common features. It is appreciable at once that the TEG surface is a donor of hydrogen atoms, as was earlier demonstrated in work [2]. The peak of a MB molecular cation is almost absent from the spectra. Instead, there are forms, in which extra one, two, or three hydrogen atoms are attached to the initial cation. This fact testifies to a sufficient number of corresponding atoms on the TEG surface under conditions of the mass-spectrometric experiment, as well as to a capability of their easy release from the sur-

face to participate in ion-molecular reactions under the action of laser radiation. We consider that the water molecules, which are adsorbed in the interplane TEG space and the presence of which was proved in work [2] using the method of temperature-programmed desorption mass spectrometry, comprise a source of hydrogen atoms. This property makes TEG substantially different from other carbon forms. Concerning the release of hydrogen atoms from water molecules, it can occur in the course of laser-stimulated oxidation of the TEG surface.

Figure 1 exhibits the mass spectra registered at three relative intensities of laser radiation (40, 60, and 100%), provided that the extraction delay time was 20 ns. In those spectra, the attention is drawn to the fact that the molecular cation M^+ produces a relatively small peak, whereas the most probable is the creation of an MB form with one attached hydrogen atom and a mass of 285 amu.

The fact that the creation of $[M+H]^+$ ion for methylene blue dominates in the course of laser desorption-ionization is well known. However, the discussed mass spectra also contain a peak corresponding to a mass of 286 amu, the intensity of which considerably exceeds the expected contribution to the intensity given by isotope C^{13} (17%). This fact forces us to suppose a contribution of ions $[M+2H]^+$ to the mass spectrum. A similar situation is also observed for a mass of 287 amu, which brings us to a conclusion that there exist ions with the composition $[M+3H]^+$. The existence of cations with a larger number of hydrogen atoms is probable, but the experiment did not allow ions with such a composition to be registered reliably. The ratios between the peak intensities do not depend substantially on the energy of laser radiation. This fact suggests that hydrogen atoms become arranged at once near a methylene blue molecule, whereas the increase of the radiation energy only enhances the desorption ionization of complexes that already exist in the condensed state.

In Fig. 2, the mass spectrum is shown for observed ions, which was measured in 150 ns after the latter left the TEG surface desorbing them during the experiment. The features of this spectrum should be confronted with those in Fig. 1,a. In the latter, the energy of laser radiation was the same, but the time delay differed substantially and equaled 20 ns. From the presented mass spectra, it follows that there is an energy exchange between ions in the ionized cloud over the surface of thermally exfoliated graphite. As a result, the peaks in mass spectra become wider, which seems

quite reasonable. Simultaneously, the relative contribution of hydrogen-containing ions becomes somewhat larger, which indicates that the attachment of hydrogens to MB ions continued over the TEG surface as well.

As the most interesting fact among those observed in the work, we consider the appearance of the form $[M+3H]^+$ in the spectrum. It is well known from the literature that MB is capable of creating restored forms. However, the irradiation of other substrates analyzed earlier did not result in the emission of MB forms with three attached hydrogen atoms. This feature of TEG used as a substrate, which was found by us in this work, may turn out useful for further mass-spectrometric researches of those ions, which are inherently unstable or recombine with other compounds so that their identification with the use of mass-spectrometric methods becomes difficult. To check the possibility of the formation of the $[M+3H]^+$ structure and to elucidate how several hydrogen atoms can be attached to the ion, we carried out quantum chemical calculations. The results obtained are presented below, in the theoretical part of the work. They confirm that the formation of compounds, which were observed by us experimentally, are not forbidden from the viewpoint of quantum chemistry. Moreover, they turned out energy-beneficial quite enough.

As was already mentioned above, all mass spectra, without exceptions, also reveal peaks that correspond to a molecular cation with an attached water molecule (Fig. 3). In our opinion, the presence of such a peak testifies that the complexes consisting of MB and a water molecule are in the adsorbed state. Since the presence of bound water in TEG is unquestionable, we can also consider an opportunity that a compound with several hydrogen atoms and an attached water molecule is energy-unfavorable so that the attachment of water molecule to the associate with two or more hydrogen atoms stimulates a detachment of all hydrogen atoms. This hypothesis requires to be checked separately in the future. Note that the very possibility of the water molecule attachment to compounds desorbed from the TEG surface was indicated earlier [2]. In this connection, we may suppose that water molecules play a stabilizing role and prevent the molecules with large molecular masses from fragmentation in the course of desorption. However, the conditions required for the creation of such a cation and its structure need additional experimental researches and quantum chemical calculations.
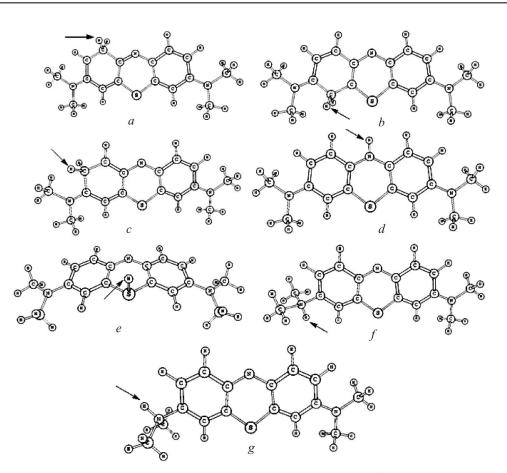
Fig. 4. Probable structures of cation-radicals with the brutto-composition $[C_{16}N_3H_{18}S \cdot H]^+$ and a mass of 285 amu, which can be formed as a result of the interaction between a hydrogen atom and a cation of methylene blue ($C_{16}N_3H_{18}S$, $M = 284$ amu), depending on the place, where the hydrogen atom can be attached to the cation

3.2. Theoretical part

1. Interaction between hydrogen atoms and a methylene blue cation

As follows from the experimental part of this work, in our mass-spectrometric experiment, we registered ions formed owing to the action of laser radiation on a specimen consisting of a TEG substrate and MB molecules adsorbed on it. The registered ions correspond to the brutto-formulas $[C_{16}N_3H_{18}S \cdot H]^+$, $[C_{16}N_3H_{18}S \cdot 2H]^+$, and $[C_{16}N_3H_{18}S \cdot 3H]^+$. Hence, there emerges the necessity to determine the chemical structure of structures with given brutto-compositions.

2. Attachment of a first hydrogen atom to the methylene blue cation

Owing to the interaction between a MB cation and a hydrogen atom, the latter can be attached to nitrogen,

sulfur, or carbon atoms of the aromatic system in the MB cation (Fig. 4) to form a cation-radical with the brutto-composition $[C_{16}N_3H_{18}S \cdot H]^+$. We calculated the thermodynamic characteristics for the reaction of hydrogen atom attachment to the MB cation according to the scheme $C_{16}N_3H_{18}S^+ + H \rightarrow [C_{16}N_3H_{18}S \cdot H]^+$. The results of calculations are presented in Table 1. From the tabulated data, one can see that, under standard conditions, the maximum of the Gibbs free energy takes place while producing the product (d) shown in Fig. 4, in which the hydrogen atom is connected with the nitrogen atom of a pyridine ring. In the course of the corresponding reaction resulting in the formation of this structure, the charge of the indicated nitrogen atom acquires a more negative value, changing from -0.517 to -0.713 (hereafter, the charges are measured in terms of elementary charge units). This fact testifies that the reaction of hydrogen atom attachment to the MB cation is accompanied by a partial transfer of the electron charge
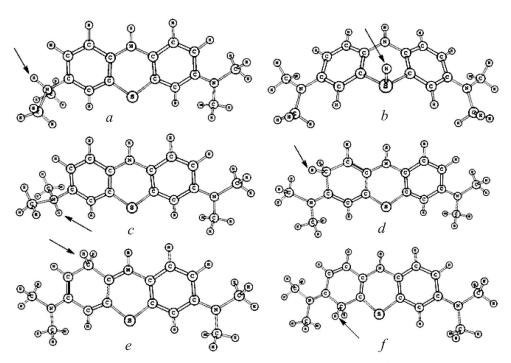
Fig. 5. Probable structures of cation-radicals with the brutto-composition $[C_{16}N_3H_{18}S \cdot 2H]^+$ and a mass of 286 amu, which can be formed as a result of the interaction between two hydrogen atoms and a cation of methylene blue. The position of the first hydrogen atom is fixed, whereas the second hydrogen atom can be attached at different places

density from the hydrogen atom, which therefore obtains a relatively large positive charge ($\rho = 0.363$) in comparison with all other hydrogen atoms, for which ρ varies from 0.141 to 0.199. Before the attachment of a hydrogen atom, the sulfur atom in the initial MB cation had the maximum positive charge $\rho = 0.440$; after the attachment, this charge decreased to $\rho = 0.411$. According to the results of our calculations, the formation of the complex "the MB cation + the hydrogen atom" is favorable. Therefore, this structure was chosen as a

basis for studying whether the further attachment of a hydrogen atom is possible.

3. Attachment of the second hydrogen atom to the structure $[C_{16}N_3H_{18}S \cdot H]^+$

In Fig. 5, the possible products obtained as a result of the hydrogen atom attachment to structure (d) depicted in Fig. 4 following the scheme $[C_{16}N_3H_{18}S \cdot H]^+ + H \rightarrow [C_{16}N_3H_{18}S \cdot 2H]^+$ are shown. We calculated the thermodynamic characteristics of this reaction (see Table 2). From the presented data, it is evident that, thermodynamically, the formation of product (a) (see Fig. 5) is the most favorable, because the corresponding change

T a b l e 1. Thermodynamic characteristics for the reaction of hydrogen atom attachment to a cation of methylene blue (MB). Here, ΔE, ΔG, ΔH, and ΔS mean the changes of the total energy, Gibbs free energy, enthalpy, and entropy, respectively, in the course of a definite reaction indicated in the first column

Reaction product	ΔE, kJ/mol	ΔG, kJ/mol	ΔH, kJ/mol	ΔS, kJ/mol
a	−146.3	−98.1	−135.5	−125.3
b	−146.3	−98.1	−135.5	−125.3
c	−198.8	−149.8	−187.2	−125.3
d	−250.3	−195.4	−230.5	−117.7
e	−94.1	−52.4	−86.0	−112.8
f	−225.4	−168.7	−210.3	−139.8
g	−225.1	−167.6	−209.9	−141.9

T a b l e 2. Thermodynamic characteristics for the reaction of hydrogen atom attachment to the complex $[C_{16}N_3H_{18}S \cdot H]^+$

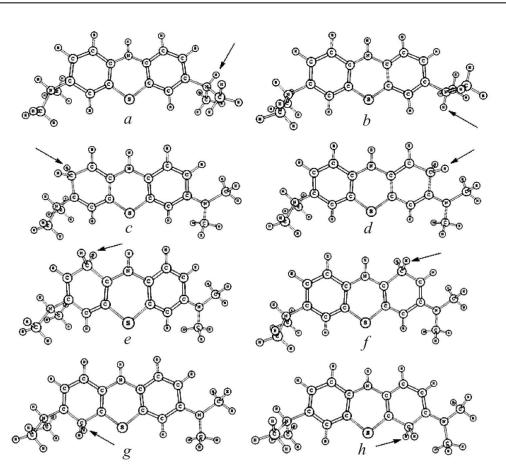| Reaction product	ΔE, kJ/mol	ΔG, kJ/mol	ΔH, kJ/mol	ΔS, kJ/mol
a	−179.8	−108.4	−140.3	−107.1
b	−73.6	−18.9	−45.2	−88.1
c	−179.3	−108.2	−13.8	−106.1
d	−146.7	−78.8	−121.3	−142.4
e	−121.6	−57.4	−86.9	−98.8
f	−130.8	−73.2	−96.9	−79.7

Fig. 6. Probable structures of cation-radicals with the brutto-composition $[C_{16}N_3H_{18}S \cdot 3H]^+$ and a mass of 287 amu, which can be formed as a result of the interaction between three hydrogen atoms and a cation of methylene blue. The positions of the first two hydrogen atoms are fixed, whereas the third hydrogen atom can be attached at different places

of the Gibbs free energy equals $\Delta G = -108.4$ kJ/mol, i.e. the lowest value among possible variants. A slightly smaller value of the Gibbs free energy change ($\Delta G = -108.2$ kJ/mol) corresponds to the formation of structure (c). Hence, this structure and the structure shown in Fig. 5,a are conformers. Similarly to what took place in the previous case (Table 1), the attachment of a hydrogen atom to the sulfur atom in the structure $[C_{16}N_3H_{18}S \cdot H]^+$ shown in Fig. 5,b turns out the least favorable energetically.

In the course of formation of the structure depicted in Fig. 5,a, when the hydrogen atom becomes attached to the nitrogen atom of the amine group, the charge is also transferred from the hydrogen to the structure $[C_{16}N_3H_{18}S \cdot H]^+$ so that the charge of a hydrogen atom acquired the maximum positive value $\rho = 0.378$. In its turn, the negative charge of the "amine" nitrogen atom decreases from -0.729 to -0.638. The maximum of the electron charge density is transferred at that from those

atoms onto the sulfur one, with the charge of the latter becoming less positive changing from 0.411 to 0.310, as well as onto the nitrogen atom of the pyridine ring so that its charge becomes negative and larger by the absolute value than 0.05, and onto the hydrogen atom attached to it (the positive charge of this atom also decreases from 0.363 to 0.315). Therefore, after this reaction has been terminated, the attached hydrogen atom possesses the largest positive charge.

4. Attachment of the third hydrogen atom to the structure $[C_{16}N_3H_{18}S \cdot 2H]^+$

For two hydrogen atoms interacting with the MB cation, the most probable (favorable) from the thermodynamic viewpoint is the configuration represented in Fig. 5,a. Therefore, just this complex was considered when analyzing the possibility for the third hydrogen atom to

be attached in order to form a cation-radical with the brutto-composition $[C_{16}N_3H_{18}S \cdot 3H]^+$.

In Fig. 6, the possible ways for the attachment of a hydrogen atom to structure (a) depicted in Fig. 5 following the scheme $[C_{16}N_3H_{18}S \cdot 2H]^+ + H \rightarrow [C_{16}N_3H_{18}S \cdot 3H]^+$ are exhibited. The results of corresponding calculations are quoted in Table 3. At first glance, the data presented above testify that one should expect the attachment of the third hydrogen atom to the nitrogen atom of the amine group. However, as is seen from Table 3, the most probable is the formation of complex (h) shown in Fig. 6 ($\Delta G = -103.9$ kJ/mol), whereas the attachment of a hydrogen atom to the nitrogen one (Figs. 6,a and b) is thermodynamically unfavorable (the increment of the Gibbs free energy is 97.0 and 114.8 kJ/mol, respectively).

After the third hydrogen atom has been attached to the structure $[C_{16}N_3H_{18}S \cdot 2H]^+$, the electron charge density redistributes over the molecule, as it happened in the previous cases. The attached hydrogen atom acquires only a small positive charge of 0.066, whereas the negative charge of the carbon atom, to which the hydrogen atom is attached, grows from -0.187 to -0.227. The negative charge of the nitrogen atom in the pyridine ring also increases by 0.05. At the same time, the growth of the negative charge of the nitrogen atom in the amine group is much less ($\Delta \rho = 0.001$). The positive charge of the sulfur atom, in turn, became smaller; it changed from 0.310 to 0.305. On the other hand, the electron charge density at the hydrogen atoms attached to the "amine" and "pyridine" nitrogen atoms remains almost unchanged; namely, the positive charge increases by 0.001 and 0.002, respectively. Hence, the largest positive charge in the given structure is concentrated at the hydrogen atom that is attached to the nitrogen atom of the amine group ($\rho = 0.379$), and the largest negative one at the nitrogen atom in the pyridine ring ($\rho = 0.834$).

T a b l e 3. **Thermodynamic characteristics for the reaction of hydrogen atom attachment to the complex $[C_{16}N_3H_{18}S \cdot 2H]^+$**

Reaction product	ΔE, kJ/mol	ΔG, kJ/mol	ΔH, kJ/mol	ΔS, kJ/mol
a	42.1	97.0	58.1	-130.6
b	54.4	114.8	73.3	-139.0
c	-133.1	-85.8	-121.4	-119.3
d	-154.1	-100.4	-140.1	-132.9
e	-144.5	-96.6	-132.3	-119.7
f	-148.2	-99.7	-137.3	-126.3
g	-136.6	-87.4	-123.6	-121.3
h	-154.7	-103.9	-141.3	-125.4

Despite that the results of thermodynamic analysis are important for the estimation that the manifestations of definite reaction products could emerge in mass spectra, one should always bear in mind that the ratios between the peak intensities for various ions, which are observed in experiment, can depend – sometimes, substantially – on kinetic factors, in particular, the lifetimes of corresponding ions [12].

4. Conclusions

In this work, we proved experimentally that the TEG surface is an active donor of hydrogen atoms and water molecules in the course of ionization of a studied MB molecule. In the course of laser desorption/ionization, the overwhelming number of ions are observed in the form of MB cations with an attached water molecule or hydrogen atoms, with the intensity of ions-fragments being low. Hence, TEG can be a promising material for mass-spectrometric researches of complicated molecules. A capability to resolve in time the processes of ion-molecular reactions that run in the laser hot spot allows the processes of interaction between various ions and molecules after their desorption from the surface to be studied efficiently. Note that the attachment of three hydrogen atoms to the MB cation was not observed earlier and is a unique property of TEG. The experimental results obtained in this work are confirmed by the corresponding quantum chemical calculations.

In particular, with the help of quantum chemical methods, we determined thermodynamically favorable products of the interaction between the MB cation and hydrogen atoms. We found that the first hydrogen atom forms a covalent bond with the "pyridine" nitrogen atom in the MB cation with the energy effect $\Delta G = -195.4$ kJ/mol. The next hydrogen atom interacts with the "amine" nitrogen atom of the previous product (its brutto-composition is $[C_{16}N_3H_{18}S \cdot H]^+$), and the corresponding change of Gibbs free energy is lower (-108.4 kJ/mol). The third hydrogen atom interacts with the carbon atom in the conjugate (cyclic) systems, with the released Gibbs free energy being slightly lower again (-103.9 kJ/mol). Hence, it follows that the attachment of each next hydrogen atom to the cation of methylene blue becomes less and less favorable.

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ЕКСПЕРИМЕНТАЛЬНЕ
ТА ТЕОРЕТИЧНЕ ДОСЛІДЖЕННЯ
ЛАЗЕРНОЇ ДЕСОРБЦІЇ/ІОНІЗАЦІЇ
МЕТИЛЕНОВОГО БЛАКИТНОГО
З ПОВЕРХНІ ТЕРМОРОЗШИРЕНОГО ГРАФІТУ

В.О. Габович, В.О. Покровський, Є.М. Дем'яненко,
А.Г. Гребенюк

Р е з ю м е

Виміряно мас-спектри продуктів лазерної десорбції/іонізації барвника метиленового блакитного з поверхні терморозширеного графіту. Зокрема, показано, що в мас-спектрах найбільш інтенсивними є іони $[M+1]^{+}$, $[M+2]^{+}$, $[M+3]^{+}$, з приєднаними до молекулярного іона одним, двома або трьома атомами водню. Експериментальні результати підтверджуються квантово-хімічними розрахунками можливих продуктів, які можуть утворюватись під дією лазерного випромінювання.