

# A study of ionisation of free and clustered molecules under the action of femtosecond laser radiation

V.M. Apatin, V.O. Kompanets, V.N. Lokhman, N.-D.D. Ogurok, D.G. Poydashev, E.A. Ryabov, S.V. Chekalin

**Abstract.** We have investigated the processes of excitation and ionisation of monomers and clusters of  $\text{CF}_3\text{I}$ ,  $\text{IF}_2\text{CCOF}$  and  $\text{Fe}(\text{CO})_5$  molecules under the action of femtosecond laser radiation at the wavelengths of 266, 400 and 800 nm. It is concluded that the nature of the excitation of free molecules and clustered molecules by femtosecond pulses is different. The simulation of the ionisation yield of the objects under study has shown that the multiphoton ionisation is the key mechanism in the case of free molecules, while the field ionisation may play a significant role for clusters, in particular, in the case of ionisation at the wavelength of  $\lambda = 800$  nm.

**Keywords:** molecular clusters, multiphoton ionisation, field ionisation.

## 1. Introduction

As early as in the middle of the last century, the photoionisation of gas was widely used for determining the potentials and ionisation cross sections, as well as for studying electronic absorption spectra. The methods of quantitative studies of the photoionisation induced by vacuum UV radiation, the cross sections and ionisation potentials of organic and inorganic molecules are systematised in review [1]. With the advent of femtosecond lasers, one of their first applications was to study the photoionisation of noble gases. Using the radiation from a Ti:sapphire laser with intensities of  $10^{15}$  W cm<sup>-2</sup>, it has been demonstrated that the experimental results of studying the ionisation of atomic gases, such as He, Ne and Xe [2], are in good agreement with the predictions of the Ammosov–Delone–Krainov (ADK) theory [3], i.e. the dependence  $w(I)$  of the ionisation rate (probability) on the radiation intensity calculated according to the ADK formulas, after the appropriate integration, turns out close to the experimental dependence of the ionisation yield.

Ionisation of a number of organic molecules (the ionisation potential in the range of 8–11 eV) in the field of an intense laser pulse has been studied in [4]. It has been found that the experimental dependences of the ionisation rate on

the laser intensity ( $\lambda = 800$  nm, pulse duration of 40 fs) differ from those predicted by the ADK formulas. The characteristic intensity  $I_{\text{sat}}$  obtained by the authors [4], which suggests that the dependence of the ionisation yield on the laser radiation intensity comes to saturation, differs by 2–5 times from that predicted by the ADK equations for different molecules. In addition, the experimental dependence of the total ionisation yield on the radiation intensity in the range of  $8 \times 10^{13}$  W cm<sup>-2</sup> (transition to saturation) to  $2 \times 10^{14}$  W cm<sup>-2</sup> (cyclohexane data from [2]) grows logarithmically with increasing intensity. Hankin et al. [2] associate the deviations, which manifest themselves at great intensities, with a Coulomb explosion.

The main part of the research on cluster interaction (mostly large clusters of noble gases) with strong fields refers to the range of ‘too’ strong intensities (above  $10^{16}$  W cm<sup>-2</sup>). In their studies, Krainov et al. (see, as example, review [5]) have evaluated the effects of the Coulomb explosion of clusters, X-ray generation and other aspects related to the cluster plasma arising at such intensities. It is believed that the formation of fast electrons, multiply charged ions and high-energy radiation quanta, which is typical for the interaction of clusters with strong fields of short laser pulses, occurs at considerably lower intensities than in the case of interaction with atoms [6]. However, we have found no data in the literature on the discussion of ionisation of free molecules and clusters of these molecules by intense laser radiation. In this paper, using the femtosecond laser radiation at the wavelengths  $\lambda = 266, 400$  and 800 nm with the intensity not exceeding  $30$  TW cm<sup>-2</sup>, we have conducted the comparative studies on laser ionisation of free molecules and the same molecules being clustered.

## 2. Experimental

In our experiments, we have used a setup, the details of which are given in [7]. Here we restrict ourselves to a brief description of the measurement conditions. The basis of the experimental setup is a photoionisation time-of-flight mass spectrometer (TOF MS) operating in combination with a pulsed source of molecular/cluster beams (General Valve nozzle,  $d = 0.8$  mm). A collimated beam of particles is formed using a skimmer (‘Beam Dynamics’, Model 1,  $D_{\text{skim}} = 0.49$  mm) and then intersects with the mutually perpendicular axes of the mass spectrometer ( $Oz$ ) and the focused ( $f = 300$  mm) laser beam which is used to ionise the particles. Depending on the gas flow conditions in a pulsed supersonic nozzle (the composition and pressure of the gas above the nozzle, the duration and degree of the nozzle valve opening), the generation of both pure molecular beams and beams with different degrees

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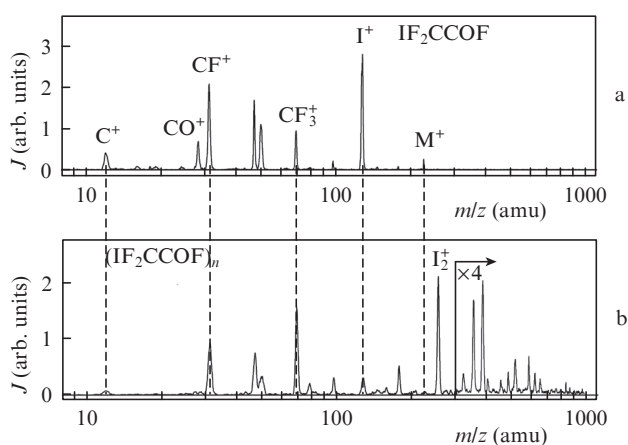
Received 3 March 2014; revision received 19 March 2014  
*Kvantovaya Elektronika* 44 (5) 465–469 (2014)  
Translated by M.A. Monastyrskiy

of clustering (up to the pure clustered beams) is available. In the experiments of this work we used a mixture of the molecules under investigation with argon in the ratio of 1:15 for  $\text{CF}_3\text{I}$  and  $\text{IF}_2\text{CCOF}$  molecules, and 1:50 for  $\text{Fe}(\text{CO})_5$  molecules. The total pressure above the nozzle was 2 atm. The selection of the regimes for molecular or clustered beam generation was performed by varying the duration of the nozzle opening, 200 or 300  $\mu\text{s}$ , respectively. In the cluster regime, the average size of clusters (according to our estimates) amounts to  $n \approx 100$ , the fraction of the on-surface molecules constituting about 80% of the total number.

Experiments were conducted using the laser facilities at the Centre of Joint Research (CJR) at the Institute of Spectroscopy, Russian Academy of Sciences (see [8]). To ionise the molecules and clusters, the radiation from the Ti:sapphire laser ( $\lambda = 800$  nm) as well as its second ( $\lambda = 400$  nm, pulse duration about 100 fs) and third ( $\lambda = 266$  nm, pulse duration about 150 fs) harmonics were used. The duration of the laser pulse at the wavelength of 800 nm was 50 fs, but in some experiments was increased up to 200 fs; herewith a frequency modulation (chirp) was observed.

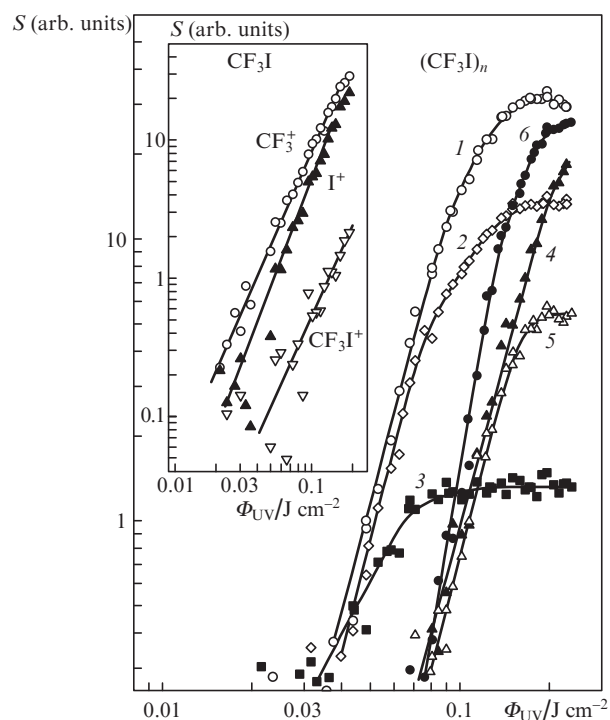
### 3. Results of measurements

Our experiments demonstrated that, similarly to the case of nano- and picosecond irradiation, when radiation of femtosecond pulses becomes intense enough, both free molecules and clusters of all three molecules under study turn out ionised. At the same time, it was found that the ionic composition and behaviour of the products resulting from ionisation of the molecular and cluster beams of the same molecules significantly depend on the laser radiation parameters. Typical mass spectra of ionic products formed in the ionisation of molecules and clusters using femtosecond UV radiation with  $\lambda = 266$  nm are shown in Fig. 1 for the  $\text{IF}_2\text{CCOF}$  molecule.



**Figure 1.** Mass spectra of ionic products formed in the ionisation of (a) the  $\text{IF}_2\text{CCOF}$  molecules and (b) clusters  $(\text{IF}_2\text{CCOF})_n$  using femtosecond UV radiation ( $\lambda = 266$  nm,  $I \approx 0.8$  TW  $\text{cm}^{-2}$ ,  $\tau \approx 150$  fs);  $J$  is the ion current.

The figure shows that the mass spectrum in the case of a cluster beam is characterised by the presence of the peaks which correspond to the ionic fragments with masses greater than the mass of the molecular ion (denoted as  $\text{M}^+$ ). This fact is common for the three molecules in question and allows one to detect the presence of the clusters in the beam.



**Figure 2.** Dependences of the ionic product yield on the energy density  $\Phi_{\text{UV}}$  of the UV radiation ( $\lambda = 266$  nm) in the case of molecular (inset) and cluster beams for the following ionic products: (1)  $\text{CF}_3^+$ , (2)  $\text{I}_2^+$ , (3)  $\text{CF}_3\text{I}^+$ , (4)  $\text{I}^+$ , (5)  $\text{CF}_2^+$  and (6)  $\text{CF}^+$ .

The experiment shows that the laser ionisation of molecules and clusters is accompanied by the fragmentation of the source objects with the formation of a whole set of the ionic products that are observed in the mass spectrum. In this case, the fragmentation degree depends on the energy density  $\Phi$  of incident radiation: large ion fragments are only observed in the very beginning of the ionisation process, while a substantial increase in the yield of smaller ion fragments occurs with increasing energy density  $\Phi$ . In more details, the yield of ionisation products is considered further by the example of UV ionisation of the  $\text{CF}_3\text{I}$  molecules.

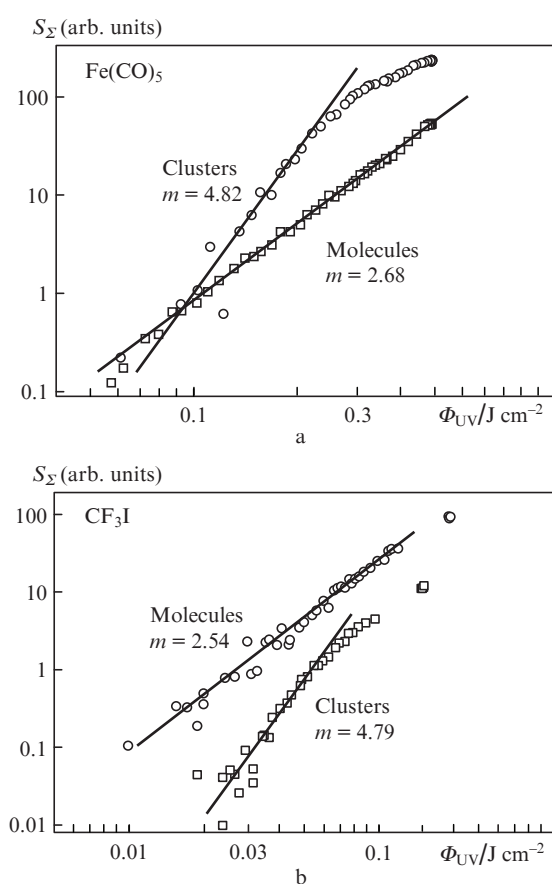
When the  $\text{CF}_3\text{I}$  molecules are irradiated by femtosecond pulses at the wavelength  $\lambda = 266$  nm, with the flux density of the radiation energy higher than  $\Phi_{\text{UV}} \approx 0.02$  J  $\text{cm}^{-2}$ , the ionisation of these molecules is observed. The major ionic products are  $\text{CF}_3^+$  and  $\text{I}^+$  with a somewhat smaller amount of  $\text{CF}_3\text{I}^+$  ions. The mass spectrum in the case of  $\text{CF}_3\text{I}$  ionisation by femtosecond pulses differs, mainly due to the presence of the molecular ion  $\text{CF}_3\text{I}^+$ , from the case of UV-multiphoton ionisation (MPI) by nanosecond pulses [9, 10].

The results of measurements of the ion signal dependence  $S(\Phi_{\text{UV}})$  on the energy density  $\Phi_{\text{UV}}$  for free molecules are shown in the inset of Fig. 2. In the power function approximation  $S(\Phi_{\text{UV}}) = \Phi_{\text{UV}}^m$ , the index  $m$  of the measured dependences amounts to 2.15 for  $\text{CF}_3^+$ , 2.5 for  $\text{I}^+$  and 2.38 for the molecular ion  $\text{CF}_3\text{I}^+$ . Note that the ion yield dependences do not virtually saturate in the range of the energy density  $\Phi_{\text{UV}}$  used.

When irradiating the clusters  $(\text{CF}_3\text{I})_n$  by femtosecond UV radiation, the ionisation of these particles is observed at  $\Phi_{\text{UV}} > 0.03$  J  $\text{cm}^{-2}$  ( $\lambda = 266$  nm). We can single out two types of ionic

products formed in the process of ionisation and fragmentation, one type being replaced by the other with increasing  $\Phi_{UV}$  (see Fig. 2). In the range of relatively low energy densities ( $\Phi_{UV} < 0.06 \text{ J cm}^{-2}$ ), rather large fragments ( $\text{CF}_3^+$ ,  $\text{CF}_2\text{I}^+$ ,  $\text{I}_2^+$ ,  $\text{CF}_3\text{I}-\text{I}^+$ ,  $\text{CF}_3\text{I}-\text{IF}_3^+$ ) and a number of larger particles are mainly observed. Herewith, very sharp ( $m \approx 6$ ) dependences of the ion signal on  $\Phi_{UV}$  take place initially. With increasing  $\Phi_{UV}$ , the steepness of the yield of these ions versus  $\Phi_{UV}$  falls with a simultaneous appearance of more sharp (e.g. with  $m > 8$  for  $\text{C}^+$ ) dependences of the yield of smaller fragments  $\text{I}^+$ ,  $\text{CF}_2^+$ ,  $\text{CF}^+$ ,  $\text{F}^+$  and  $\text{C}^+$ , which is the result of a deeper fragmentation of the particles. With a significant increase in the radiation energy density, the signals from the multiple charged ions are observed in the mass spectra of ionic products; however, this range of energy densities is beyond the experimental conditions of this work.

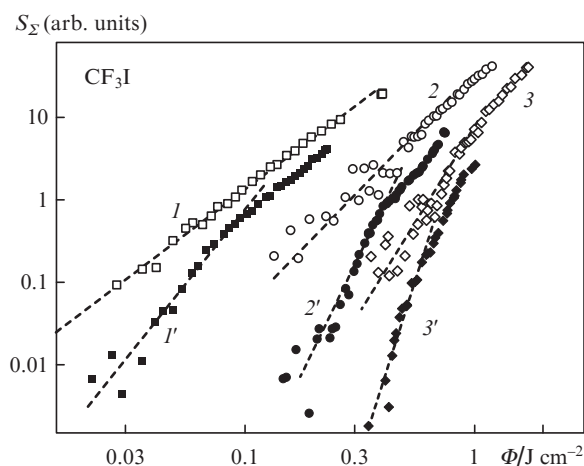
Taking into account the fact that the excitation and ionisation of molecules and clusters occur during the femtosecond laser pulse action, while the subsequent fragmentation and dissociation processes occur even in the absence of radiation [2], in our opinion, the total ion signal  $S_\Sigma$  from all the ionic products observed may serve as a good characteristic of the ionisation yield. This dependence of the total ion signal  $S_\Sigma$  on the energy density (or intensity) of the laser radiation is further treated as the ionisation yield. The dependences of the total ion signal on the energy density of UV radiation for molecules and clusters of  $\text{CF}_3\text{I}$  and  $\text{Fe}(\text{CO})_5$  are shown in Fig. 3.



**Figure 3.** Dependences of the total ion signal on the energy density  $\Phi_{UV}$  in the ionisation of the monomers and clusters of (a)  $\text{Fe}(\text{CO})_5$  and (b)  $\text{CF}_3\text{I}$  molecules by means of femtosecond radiation with  $\lambda = 266 \text{ nm}$ .

The experiment convincingly shows that the dependence of the ionisation yield on the energy density of incident radiation may be described by the power functions of the form  $S_\Sigma \sim \Phi^m$ , both for monomers and clusters of these two molecules. In the latter case, this approximation is valid only on the initial stage at a relatively low energy density of laser radiation. Thus, the exponent  $m$  in the case of ionisation of clusters significantly exceeds the same value in the case of monomers. Qualitatively the same behaviour is demonstrated by the dependences obtained for the monomers and clusters of  $\text{IF}_2\text{CCOF}$  molecules. This fact indicates either a significant gain in energy by the molecules in the cluster during the UV-laser pulse ( $\sim 150 \text{ fs}$ ) or a difference in the mechanisms of ionisation of the clusters and monomers.

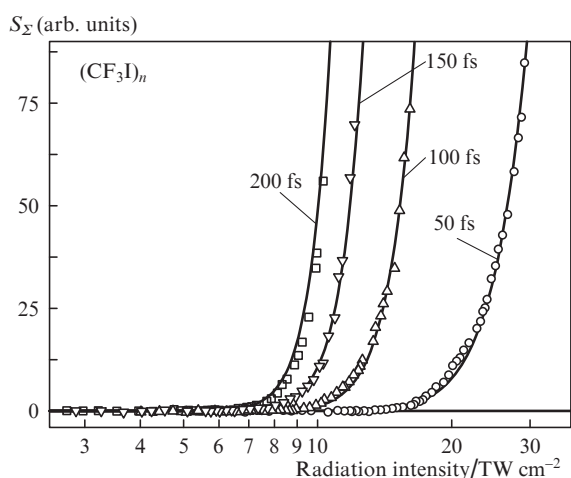
More information about the properties governing the behaviour of the dependences of the total ion signal can be obtained by comparing the ionisation under the action of femtosecond laser radiation at different wavelengths. Figure 4 shows the dependence of the signal  $S_\Sigma$  on  $\Phi$  for the  $\text{CF}_3\text{I}$  monomers and clusters in case of the photoionisation at the wavelengths of 266, 400 and 800 nm. In general, the nature of dependences for  $\text{CF}_3\text{I}$  molecules and clusters in the photoionisation at the wavelengths  $\lambda = 400 \text{ nm}$  and  $800 \text{ nm}$  is the same as at the wavelength  $\lambda = 266 \text{ nm}$ . In the power function approximation, in the case of a cluster beam, the relevant curve starts from the larger degrees of  $m$  compared to the case of a molecular beam:  $m \approx 3.5$  for molecules and  $m \approx 5.2$  for clusters during the ionisation at  $\lambda = 400 \text{ nm}$ , and  $m \approx 4.8$  and  $9.5$  for monomers and clusters during the ionisation at  $\lambda = 800 \text{ nm}$ , respectively. Note that at higher energy densities and a fixed wavelength, the dependences for the cluster and molecular beams are virtually indistinguishable [which is easily seen if, for example, curve ( $1'$ ) is shifted along the y axis in Fig. 4].



**Figure 4.** Dependences of the total ion signal on the energy density  $\Phi$  in the ionisation of the molecules and clusters by means of femtosecond radiation at the wavelengths of (1, 1') 266, (2, 2') 400 and (3, 3') 800 nm.

The comparison of ionisation at different wavelengths is, however, not so obvious a problem, since the radiation from the Ti:sapphire laser at  $\lambda = 800 \text{ nm}$  and its second and third harmonics that have been used in this work possess different spectral widths and different pulse durations. In particular, there may be difference in the set of excited Rydberg states of the  $\text{CF}_3\text{I}$  molecules with the energy near  $9.3 \text{ eV}$ , or in the

number of photons required for the excitation to a high energy level from which the ionisation may occur with  $[2\hbar\omega$  (266 nm) =  $3\hbar\omega$  (400 nm) =  $6\hbar\omega$  (800 nm) = 9.32 eV]. All this may influence the ionisation probability. Therefore, the experiments have been conducted on the cluster ionisation  $(CF_3I)_n$  at a fixed wavelength  $\lambda = 800$  nm by changing the laser pulse duration only. The spectral width remains unchanged with increasing pulse duration; however, as mentioned above, a frequency modulation (chirp) of the pulse appears. We should specify here that we have not observed any difference in the dependences obtained in case of a positive or negative chirp at the same pulse duration. The results of experiments on ionisation of the clusters  $(CF_3I)_n$  at the laser pulse duration in the range of 50–200 fs ( $\lambda = 800$  nm) are shown in Fig. 5.



**Figure 5.** Dependences of the total ion signal on the radiation intensity in the ionisation of  $(CF_3I)_n$  clusters using the laser radiation with  $\lambda = 800$  nm and different laser pulse durations (points are the experiment, solid curves are the model calculations).

#### 4. Discussion of the results

The analysis of the results of the experiments on the UV ionisation gives grounds to suggest that the multiphoton ionisation (in our case, the three-photon process) represents the main mechanism of formation of ion products under irradiation of free  $CF_3I$  molecules by femtosecond pulses with  $\lambda = 266$  nm in the range of the intensities specified. This deduction is consistent with the character of the dependence  $S(\Phi_{UV}) = \Phi_{UV}^m$  that has been observed. In addition, the Keldysh parameter  $\gamma$  [11] in our experiments exceeds 27 (the UV radiation intensity is less than  $1.7 \times 10^{12}$  W cm $^{-2}$ ), which also testifies in favour of the multiphoton mechanism of ionisation of free  $CF_3I$  molecules. It should be also noted that radiation at  $\lambda = 266$  nm is in resonance with the first excited electronic state  $\tilde{A}$  whose lifetime amounts to 150 fs for the similar  $CH_3I$  molecule [12], and its decay has little effect on the ionic composition of the final products. However, the presence of an intermediate resonance may reduce the effective value of the exponent  $m$  in the dependence  $S(\Phi_{UV}) = \Phi_{UV}^m$ , which explains a difference of the measured  $m$  values from 3 ( $m < 3$ ). As shown by experiments carried out with  $IF_2CCOF$  and  $Fe(CO)_5$  molecules, the exponent values of  $m$  observed in the UV ionisation of these molecules are also consistent with the number of photons needed to overcome the ionisation potential of the molecules.

The dependences of the total ion signal  $S(\Phi)$  for the case of molecular beam ionisation at the wavelengths  $\lambda = 400$  and 800 nm can be approximated with good accuracy by the curves obtained under the assumption that a process of multiphoton ionisation with saturation occurs. In this case, the ionisation rate appears as

$$w(I) = \sigma_m I^m, \quad (1)$$

where  $\sigma_m$  is the multiphoton ionisation cross section, and the signal from the ionisation region can be obtained after integration:

$$S \sim \int_0^{I_0} \frac{dI}{I} (1 - \exp[-\tau w(I)]), \quad (2)$$

where  $I_0$  is the intensity at the pulse maximum. Detailed calculations are given, for example, in [2]. Here we point to two results of this theory. At low intensities  $I$  the integration leads to the expression

$$S \sim I^m, \quad (3)$$

and at large intensities – to the expression

$$S \sim \ln I. \quad (4)$$

A reliable transition to the logarithmic law (4) has not been observed in our experiments, presumably, due to the limited range of the laser intensities selected. This fact is confirmed by the literature data. For example, the intensities  $I_{sat}$  in the range of 50–150 TW cm $^{-2}$  were needed for the authors of [2] to ionise a whole set of organic molecules with ionisation potentials lying in the range of 8–11.5 eV with the use of the femtosecond radiation at  $\lambda = 800$  nm, which by several times exceeds the intensities used in this work. However, the values of the exponent  $m$  in the power dependences of the total ion signal (3), which have been observed at the relatively low intensities, are close to the number of quanta that are energetically required to reach the ionisation potential. This allows one to conclude that the multiphoton ionisation is the main (primary) mechanism of the monomer ionisation at all the wavelengths used.

For the clustered molecules, the values of the exponent  $m$  are much higher both in the case of UV ionisation and in the case of radiation with  $\lambda = 400$  and 800 nm. It is worth making a comment here. As noted above, the laser ionisation of clusters is accompanied by a rather deep fragmentation of the original objects. Herewith, the large exponents in the dependences of the yield of individual ionic products on  $\Phi_{UV}$ , such as  $CF^+$  in the UV ionisation of the clusters  $(CF_3I)_n$  (Fig. 2), may be associated with the need of acquiring the energy to achieve high-lying energy states, the collapse of which results in the formation of these products. Their influence on the total ion signal begins to dominate only under certain (fairly large) laser pulse energies, while the initial stage of the ionisation process is significantly influenced by other, larger ionic fragments. Thus, the total signal allows the fragmentation to be taken into account.

With regard to the statement of the authors of review [6] concerning the lowering of the intensities that are required for the manifestation of the field effects in the clusters ionisation, we have modelled the ionisation yield of the  $(CF_3I)_n$  clusters using the radiation of different durations at  $\lambda = 800$  nm



(Fig. 5). Note that the estimation of the Keldysh parameter [11] in our experiments employing the radiation with  $\lambda = 800$  nm at the radiation intensity  $I = 5 \times 10^{13}$  W cm<sup>-2</sup> gives  $\gamma \approx 1.3$  for the CF<sub>3</sub>I molecule with the ionisation potential  $E_{\text{ion}} = 10.37$  eV. As known, at  $\gamma > 1$ , a transition from the field ionisation to multiphoton ionisation occurs, and the resonances that correspond to the excited states adjacent to the ionisation potential may have a significant impact in the latter case [13]. Consequently, we seem to be dealing with a borderline case, and a modelling is required to determine the effect of this or that mechanism. We managed to approximate the experimental curves obtained for the clusters (solid curves in Fig. 5) using the expression for the ionisation rate

$$w(I) \sim \frac{1}{\sqrt{I}} \exp\left(-\frac{2}{3\sqrt{I}}\right), \quad (5)$$

first obtained by Landau and Lifshitz [14] to describe the ionisation of the hydrogen atom by a static electric field. Similar to expression (2), the signal from the ionisation region is obtained after integration:

$$S(\tau) \sim \int_0^{\tau_0} \frac{dI}{I} w\left(\frac{\tau_0}{\tau}\right), \quad (6)$$

where  $\tau_0 = 50$  fs;  $\tau$  is the laser pulse duration (the only variable parameter). The mere use of formula (5) in this case requires reservations. First, formula (5) corresponds not to the intermediate, but to the limiting case  $\gamma < 1$ . Second, the binding energy of the optical electron in the molecules and clusters under investigation is different from the case of a hydrogen atom. Besides, the situation in molecules, and even more in clusters, is additionally complicated by the fact that the ionisation process of these systems is considerably more sophisticated than in the case of atoms (see [6]), and the use of simple atomic models cannot describe all the phenomena inherent to the ionisation of these systems. Therefore, the approximation of the experimental curves by formula (5) is to be regarded only as a rough demonstration that the field effects in the ionisation of (CF<sub>3</sub>I)<sub>n</sub> clusters have a certain similarity with the ionisation of the hydrogen atoms. However, as follows from (5) and (6), the value of  $\sqrt{I}$  is a key parameter in the simulation of the yield of cluster ionisation (with the duration of the exciting pulse varied). Thus, the analysis of the measurement results on the dependence of the output ion signal on the laser pulse duration allows the conclusion that the field ionisation may play a significant role in the ionisation of clusters, in particular, at the wavelength  $\lambda = 800$  nm. This, in turn, results in the differences that have been observed in the behaviour of the ionisation yield dependences on the laser radiation energy in the case of molecules and clusters.

## 5. Conclusions

The processes of excitation and ionisation of monomers and clusters of CF<sub>3</sub>I, IF<sub>2</sub>CCOF and Fe(CO)<sub>5</sub> molecules under the action of laser radiation of femtosecond duration at the wavelengths  $\lambda = 266$ , 400 and 800 nm are investigated. It has been found that the nature of the ionisation of the monomers and clusters of these molecules is significantly different, which is reflected in the different behaviour of the dependences of the ionisation yield on incident radiation intensity. In the case of clusters, in the frame of the power function approximation, these dependences start from the markedly greater exponents

compared to the case of free molecules, and this effect is common to the clusters of various molecules.

The ionisation yield of the CF<sub>3</sub>I monomers is simulated in the presence of the laser radiation at certain wavelengths. We have also modelled the ionisation yield for the (CF<sub>3</sub>I)<sub>n</sub> clusters using the laser radiation of different durations at the wavelength  $\lambda = 800$  nm. The data obtained allow the conclusion that multiphoton ionisation is the key ionisation mechanism in the case of free molecules at all three wavelengths, while for clusters of these molecules, especially in the case of ionisation at the wavelength  $\lambda = 800$  nm, field ionisation can play a significant role.

We have considered two main types of ionisation: multiphoton and field ionisation. However, further investigations are needed to come to a more definite conclusion on the role of the ionisation mechanisms and, possibly, the existence of other mechanisms in the case of ionisation of the clusters.

**Acknowledgements.** This work was supported by the Russian Foundation for Basic Research (Grant Nos 12-02-31892, 13-02-00260) and by the Presidium of the Russian Academy of Sciences in the framework of the Programme ‘Extreme Light Fields and Their Applications’.

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