

Excitation and dissociation of molecules by femtosecond IR laser radiation in the gas phase and on dielectric surfaces

V.O. Kompanets, V.B. Laptev, A.A. Makarov, S.V. Pigul'skii, E.A. Ryabov, S.V. Chekalin

Abstract. This paper presents an overview of early studies and new experimental data on the effect of near-IR (0.8–1.8 μm) and mid-IR (3.3–5.8 μm) intense femtosecond (130–350 fs) laser pulses on polyatomic molecules in the gas phase and on the surface of substrates. We examine the vibrational dynamics of nine molecules containing a C=O chromophore group, which are initiated by resonance femtosecond IR laser radiation at a wavelength of $\sim 5 \mu\text{m}$, and report measured characteristic times of intramolecular vibrational redistribution. The characteristic time of molecules containing a single C=O group lies in the range 2.4–20 ps and that of the $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$ molecules lies in the nanosecond range (~ 1.0 and ~ 1.5 ns, respectively). Carbon structures have been observed for the first time to result from the decomposition of $(\text{CF}_3)_2\text{CCO}$ molecules on the surface of metal fluorides under the effect of femtosecond IR laser radiation in the wavelength range 3.3–5.4 μm with no gas-phase decomposition of the molecules.

Keywords: femtosecond IR laser radiation, molecules, multiphoton vibrational excitation, intramolecular relaxation, dissociation of surface molecules, carbon structures.

1. Introduction

The advent of lasers generating femtosecond pulses has opened up qualitatively new possibilities of affecting atomic and molecular systems. A new area of modern chemical physics – femtochemistry – emerged and is rapidly growing, and direct methods of probing intramolecular dynamics have been developed (see [1] and references therein). The extension of the spectral range of femtosecond lasers to the near- and mid-IR allowed researchers to influence the vibrational degrees of freedom of molecules in their ground electronic state, resonantly exciting overtones [2] or one of their fundamentals [3,4]. This has offered the possibility of overcoming the limitations imposed by intramolecular vibrational redistribution (IVR) (see e.g. Ref. [5]) and selectively initiating photochemical transformations of a specific bond or group of bonds in molecules. For example, Windhorn et al. [3,4] reported a nonstatistical dissociation of diazomethane and metal carbonyls as a result of multiphoton (MP) IR excitation of C=N=N and C=O vibrations, respectively.

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Received 24 December 2012
Kvantovaya Elektronika 43 (4) 320–325 (2013)
Translated by O.M. Tsarev

A femtosecond laser diagnostic system at the Institute of Spectroscopy, Russian Academy of Sciences (Shared Optical and Spectroscopic Facilities Center) enabled us to carry out a series of studies concerned with the effect of femtosecond IR laser radiation on gaseous and surface molecules of various compounds [6–15]. Major attention was focused on the resonance excitation of particular vibrational modes in molecules with the aim of conducting mode-selective photochemical reactions.

The first step in those studies was to assess the feasibility of the photodissociation of molecules in the gas phase through resonance excitation of their overtones (CF_2HCl) or stretching modes [$(\text{CF}_3)_2\text{CCO}$ and $\text{C}_4\text{F}_9\text{COI}$] by femtosecond IR laser radiation. Laser pulses in the spectral range 0.8–1.8 μm with an intensity above $4 \times 10^{13} \text{ W cm}^{-2}$ were found to cause CF_2HCl dissociation, with CF_3H as the final gaseous product [6,7]. This significantly differentiated CF_2HCl decomposition by femtosecond radiation from the thermal pyrolysis and dissociation of this compound by nanosecond IR or UV laser pulses. It was found however that resonance between the femtosecond radiation frequency and the vibrational overtone transition frequencies of the C–H vibrational mode at wavelengths $\lambda_{0 \rightarrow 2} = 1.69$ and $\lambda_{2 \rightarrow 4} = 1.82 \mu\text{m}$ had essentially no effect on the CF_2HCl decomposition process. According to our results, the main decomposition mechanism is nonresonant field ionisation of CF_2HCl molecules, followed by their fragmentation.

Next, using femtosecond IR radiation at $\lambda \sim 5 \mu\text{m}$ with much lower intensity, we attempted to carry out mode-selective photochemical reactions initiated by MP IR excitation of bis(trifluoromethyl)ketene, $(\text{CF}_3)_2\text{CCO}$, and perfluorovaleryl iodide, $\text{C}_4\text{F}_9\text{COI}$, molecules through resonance action on C=C=O and C=O stretching vibrations, respectively [8]. However, no isomerisation or decomposition of these molecules and no formation of reaction products were detected at intensities of up to $\sim 2.5 \times 10^{12} \text{ W cm}^{-2}$. The activation energies of these molecules exceed 18000 cm^{-1} , which is substantially higher than those of diazomethane and metal carbonyls: 12000 – 14000 cm^{-1} [3,4]. The lack of phototransformations in $(\text{CF}_3)_2\text{CCO}$ and $\text{C}_4\text{F}_9\text{COI}$ molecules exposed to femtosecond IR radiation is most likely due to the insufficient excited state energy. This led us to study intramolecular processes that take place after ultrafast (~ 100 – 200 fs) MP excitation of particular vibrational modes in free molecules. Special attention was paid to measurements of the characteristic time τ_{IVR} (i.e. the duration of the collision-free process of intramolecular vibrational redistribution between the excited mode and other vibrational modes) in various molecules. We investigated molecules of various classes of compounds containing the molecular chromophore group C=O, which can be influenced by femtosecond radiation at $\lambda \sim 5 \mu\text{m}$.

The dynamics of intramolecular relaxation processes were studied first in metal carbonyls, $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$, in which the $\text{C}=\text{O}$ vibrational modes at $\nu_6 = 2034 \text{ cm}^{-1}$ and $\nu_{10} = 2013 \text{ cm}^{-1}$ in $\text{Fe}(\text{CO})_5$ and at $\nu_6 = 2000 \text{ cm}^{-1}$ in $\text{Cr}(\text{CO})_6$ were excited by resonance femtosecond IR laser radiation. The fast (250–500 fs) relaxation process observed after vibrational excitation of these molecules was found to be caused by quantum beat dephasing upon rovibrational transitions in the P, Q and R branches [14]. Since the IVR process in these molecules was rather slow, in the nanosecond range, it was identified later (see below). In our experiments with the metal carbonyls, we encountered an interesting coherence effect, a so-called coherent artefact, which was then studied separately. The process is observed at negative time delays between pump and probe pulses and is usually interpreted as an interrupted free induction decay. A detailed analysis of the coherent artefact evolution in the case of IR pumping and IR probing of an anharmonic oscillator can be found in Refs [12, 13].

Next, we studied in detail the vibrational dynamics of various modes in the $(\text{CF}_3)_2\text{CCO}$ molecule under resonance excitation of the $\text{C}=\text{C}=\text{O}$ vibrational mode at $\nu_1 = 2194 \text{ cm}^{-1}$ by femtosecond IR radiation [11, 15]. Our results demonstrate selective MP excitation of the resonance vibrational mode up to the $v = 7$ level ($\sim 15000 \text{ cm}^{-1}$) [11]. Subsequent relaxation through the IVR of the excitation from this mode had a characteristic time $\tau_{\text{IVR}} = 5 \pm 0.3 \text{ ps}$. When exciting the ν_1 mode, we detected for the first time an ‘instantaneous’ ($\tau \ll \tau_{\text{IVR}}$) induced absorption signal ΔOD for the nonresonant modes ν_2 , ν_3 and ν_4 [15]. The subsequent evolution of the ΔOD signal and the corresponding characteristic times proved to be mode-dependent, which was, in our opinion, due to the different vibrational energy migration paths and characters in this molecule. Vibrational dynamics were also studied in other molecules containing a single $\text{C}=\text{O}$ chromophore bond: $(\text{CF}_3)_2\text{CO}$, $\text{C}_4\text{F}_9\text{COI}$, ICF_2COF , HCOOC_2H_5 , $\text{CH}_3\text{COOC}_2\text{H}_5$ and $\text{H}_2\text{CCHCOOC}_2\text{H}_5$ (see details below).

Studies of photodissociation and intramolecular dynamics were aimed at carrying out photochemical processes selective with respect to a particular vibrational mode and investigating the associated vibrational energy redistribution and migration processes in free gaseous molecules. Those experiments showed that not only photochemical but also other processes took place at the interface between the gas phase and the surface of entrance windows of gas cells immediately in the propagation zone of an intense laser beam. In particular, resonance vibrational excitation of gaseous $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$ carbonyls by femtosecond IR laser radiation at a wavelength of $\sim 5 \mu\text{m}$ was found to produce structured metal-containing films [9, 10]. In the case of $\text{Fe}(\text{CO})_5$, the process was accompanied by the precipitation of microcrystals of the higher iron carbonyls $\text{Fe}_2(\text{CO})_9$ and $\text{Fe}_3(\text{CO})_{12}$. The films consisted of aligned filaments in the order of the wavelength or its multiple in thickness. We proposed a plausible mechanism of the formation of such films [9], with the MP IR dissociation of the metal carbonyls in the gas phase as its first step.

An interesting effect was detected in experiments on the intramolecular dynamics of bis(trifluoromethyl)ketene, $(\text{CF}_3)_2\text{CCO}$. As mentioned above, exposure of its $\text{C}=\text{C}=\text{O}$ bond to resonance femtosecond IR laser radiation at an intensity $I \approx 2.5 \times 10^{12} \text{ W cm}^{-2}$ caused no decomposition of this compound in the gas phase [8]. At the same time, at an order of magnitude lower laser fluence (and intensity) we observed the formation of surface structures on the windows of the cell in the laser-exposed zone. According to coherent Raman spectro-

scopy (CRS) data, the surface structures consisted of amorphous carbon. Thus, in contrast to the metal carbonyls [9], the decomposition of $(\text{CF}_3)_2\text{CCO}$ molecules to elemental carbon under the effect of femtosecond IR laser radiation and subsequent formation of carbon structures on a dielectric surface are not due to gas-phase dissociation and have an essentially different nature.

In this paper, we present new findings on the intramolecular vibrational dynamics in gaseous molecules containing a $\text{C}=\text{O}$ chromophore bond and experimental data on the formation of carbon structures on the surface of dielectric substrates as a result of femtosecond IR laser irradiation of $(\text{CF}_3)_2\text{CCO}$ and other organic compounds.

2. Experimental

The experimental setup used in this study was described in detail previously [6–15], so here we limit ourselves to a brief description of the setup. As IR sources, we used two nonlinear converters based on TOPAS-C optical parametric amplifiers. The difference frequency was generated in a DFG-1 accessory (Light Conversion Ltd.) using a AgGaS_2 crystal. The output frequencies of the converters could be tuned independently. One converter was used as a pump source, and the other, for probing. The amplifiers were synchronously pumped by a Spectra-Physics femtosecond Ti:sapphire laser ($\lambda = 800 \text{ nm}$). To examine vibrational dynamics, we used IR pump–probe measurements with spectral analysis of the probe radiation, which allowed us to measure the induced absorption signal, ΔOD , as a function of the time delay between the pump and probe pulses, Δt . The main parameters of our setup were as follows: femtosecond pulse repetition rate, 1 kHz; pump pulse energy at a wavelength of $5 \mu\text{m}$, $14 \mu\text{J}$; pulse duration at half maximum, 150 fs inside the cell; bandwidth, 240 cm^{-1} . In most measurements, the spectral bandwidth of the monochromator was $3–5 \text{ cm}^{-1}$. The pump energy density in the cell was within 80 mJ cm^{-2} . IR photochemistry and intramolecular dynamics experiments were performed in the gas phase at pressures in the range 0.1–100 Torr. At such pressures, disturbances related to intermolecular interaction were negligible.

The growth of carbon structures was filmed by a video camera at various irradiation times. Surface structures were formed when radiation was focused by a lens ($f = 15 \text{ cm}$) onto the inner surface of the entrance window of a gas cell measuring 4.8 mm in length and 32 mm in working diameter. The surface of the windows to be used as substrates for the growth of carbon structures was polished to the optical finish class at least RIII (surface roughness value under 10 nm). The structures were imaged using an MBS-10 microscope at a magnification of $100\times$. The images were fed to a Videoskan-285-USB CCD array detector (ZAO NPK Videoskan) and recorded at regular time intervals with an exposure time of 0.4 s. The highest resolution of the system was $\sim 2 \mu\text{m}$. The three-dimensional images thus obtained were digitised and integrated with respect to volume. After appropriate data processing, we obtained plots of volume V against exposure time t for the growing films.

3. Results and discussion

3.1. Intramolecular dynamics experiments

We studied various classes of molecules: $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$, $(\text{CF}_3)_2\text{CCO}$, $(\text{CF}_3)_2\text{CO}$, $\text{C}_4\text{F}_9\text{COI}$, ICF_2COF , $\text{H}(\text{CO})\text{OC}_2\text{H}_5$,

$\text{CH}_3(\text{CO})\text{OC}_2\text{H}_5$, $\text{H}_2\text{CCH}(\text{CO})\text{OC}_2\text{H}_5$. All these compounds have a strong, sufficiently isolated C=O vibrational mode [or C=C=O in $(\text{CF}_3)_2\text{CCO}$], and the femtosecond pump radiation was tuned to resonance with it. Our experiments were aimed at gaining insight into the vibrational dynamics of the resonance mode after excitation. Pump and probe pulses had identical spectra. We measured the induced absorption signal, ΔOD , as a function of the time delay between the pump and probe pulses, Δt .

For $\Delta t > 0$, $\Delta\text{OD}(\Delta t)$ is a decreasing function with a plateau at a level between 10% and 45% of the peak signal, depending on the molecule. Similar kinetic curves were obtained for higher energy vibrational transitions in some of the molecules. The descending portions in most of the curves were fitted by functions of the form $F = A_0 + B \exp(-t/\tau_{\text{IVR}})$, where A_0 and B are fitting parameters. The data for ethyl acetate, $\text{H}_3\text{C}-(\text{C}=\text{O})\text{OC}_2\text{H}_5$, and ethyl acrylate, $\text{H}_2\text{C}=\text{CH}-(\text{C}=\text{O})\text{OC}_2\text{H}_5$, were fitted with two exponentials: $F = A_0 + B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2)$. The characteristic times τ_{IVR} thus evaluated for all the molecules under consideration are listed in Table 1.

Table 1. Characteristic intramolecular relaxation times τ_{IVR} for the 0→1 vibrational transition after excitation of C=O vibrations in the molecules studied.

Molecule	$\nu_{\text{C}=\text{O}}/\text{cm}^{-1}$	$\tau_{\text{IVR}}/\text{ps}$	Notes
$\text{C}_4\text{F}_9\text{COI}$	1793	2.4 ± 0.3	
$(\text{CF}_3)_2\text{CO}$	1804	3.5 ± 0.5	
$(\text{CF}_3)_2\text{CCO}$	2194	5.0 ± 0.3	C=C=O vibration
ICF_2COF	1880	6.8 ± 0.2	
HCOOC_2H_5	1750	20 ± 1	
$\text{H}_3\text{C}-\text{COOC}_2\text{H}_5$	1756	$\tau_1 = 6 \pm 1$ $\tau_2 = 75 \pm 20$	Biexponential decay ($B_1 \approx (2.4-3.2)B_2$)
$\text{H}_2\text{C}=\text{CH}-\text{COOC}_2\text{H}_5$	1751	$\tau_1 = 8 \pm 1.5$ $\tau_2 = 80 \pm 20$	Biexponential decay ($B_1 \approx (0.7-0.9)B_2$)
$\text{Fe}(\text{CO})_5$	2014	$(1.0 \pm 0.3) \times 10^3$	Estimate
$\text{Cr}(\text{CO})_6$	2000	$(1.5 \pm 0.5) \times 10^3$	Estimate

According to the position of the C=O chromophore group in their molecules, the compounds under investigation can be divided into three types. One type of compound has either a single, terminal C=O group [$(\text{CF}_3)_2\text{CCO}$ and $(\text{CF}_3)_2\text{CO}$] or a terminal C=O group with one atom attached to it ($\text{C}_4\text{F}_9\text{COI}$, ICF_2COF and HCOOC_2H_5). A second type of compound has a single C=O group 'inside' its molecule [$\text{CH}_3(\text{CO})\text{OC}_2\text{H}_5$ and $\text{H}_2\text{CCH}(\text{CO})\text{OC}_2\text{H}_5$]. Finally, the third type has several C=O groups, which surround a central atom [$\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$]. Note that this type of molecule differs markedly from the first two types by higher symmetry (D_{3h} and T_{1u}) and the donor-acceptor bonding between the C=O groups and central atom. It is seen from Table 1 that the three types of molecules differ in intramolecular dynamics.

In particular, the τ_{IVR} values of iron and chromium carbonyls lie in the nanosecond range and differ by two to three orders of magnitude from the intramolecular relaxation times of the other molecules. For some reasons, kinetic curves of the carbonyls were obtained in a relatively short time interval: 200 ps. Because of this, the characteristic time of the IVR process was estimated only roughly: $\tau_{\text{IVR}} = 1.0 \pm 0.3$ ns in $\text{Fe}(\text{CO})_5$ and 1.5 ± 0.5 ns in $\text{Cr}(\text{CO})_6$. These values are consistent with the $\tau_{\text{IVR}} = 1.3$ ns reported for $\text{W}(\text{CO})_6$, a similar molecule [16].

In contrast to those of the other molecules, the $\Delta\text{OD}(\Delta t)$ kinetic curves of ethyl acetate, $\text{CH}_3(\text{CO})\text{OC}_2\text{H}_5$, and ethyl acrylate, $\text{H}_2\text{CCH}(\text{CO})\text{OC}_2\text{H}_5$, have a well-defined anomaly due to

their biexponential behaviour with two, highly different characteristic times (Fig.1). Almost all the curves obtained for these molecules at various frequencies within the absorption band of the C=O bond also show biexponential behaviour. The two different characteristic IVR times may correspond to two channels for excitation transfer from the C=O bond to the rest of the molecule. A theoretical analysis of these results is presently under way.

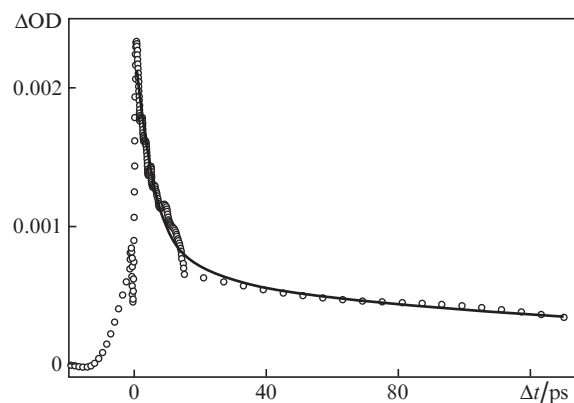


Figure 1. ΔOD signal as a function of delay time Δt for the 0→1 vibrational transition of ethyl acetate, $\text{H}_3\text{C}(\text{CO})\text{OC}_2\text{H}_5$, at a pump energy density of 40 mJ cm^{-2} and ethyl acetate pressure of 40 Torr. The solid line shows the least-squares fit to the data.

The first type of molecule, with a single, terminal C=O group, exhibits relatively simple IVR behaviour and has a rather short τ_{IVR} time.

The experimentally determined τ_{IVR} time (Table 1) can be correlated with physical properties of the molecules. The IVR process is known to result from vibrational energy intermixing (stochastisation). To this end, states should be reached that have a certain threshold density of vibrational levels (see e.g. Refs [17, 18] and references in [18]). In our case, selective excitation of a high-frequency vibrational mode of the C=O bond brings the molecule to the region with a high $\rho_{\text{C}=\text{O}}$ density of states. Anharmonic interaction leads to the intermixing of states close in energy and energy transfer from the excited mode [5]. Thus, under certain conditions the intramolecular relaxation time may correlate with the density of vibrational states near the excited level. To verify this assumption, τ_{IVR} was plotted against the density of vibrational states. The $\rho_{\text{C}=\text{O}}$ density of vibrational states of each molecule was calculated for the total vibrational energy equal to the sum of the average vibrational energy $\langle E \rangle$ of the molecule at room temperature and the energy of one vibrational excitation quantum, $h\nu_{\text{C}=\text{O}}$, for the 0→1 transition. The average energy $\langle E \rangle$ was added because the excitation spectrum fully overlapped the IR absorption band of the molecule, i.e. all initial rovibrational levels interacted with the radiation. The energy $\langle E \rangle$ was calculated using a relation presented in Robinson and Holbrook [19]. The vibrational frequencies of the $\text{Fe}(\text{CO})_5$, $\text{Cr}(\text{CO})_6$, $(\text{CF}_3)_2\text{CCO}$, $(\text{CF}_3)_2\text{CO}$ and HCOOC_2H_5 molecules were taken from the literature, and those of the $\text{H}_3\text{C}-\text{COOC}_2\text{H}_5$, $\text{C}_4\text{F}_9\text{COI}$ and ICF_2COF molecules were inferred from the IR spectra measured by us and from quantum-mechanical calculations with the Gaussian 98 program (DFT-B3LYP functional), the aug-cc-pVTZ basis set for $\text{H}_3\text{C}-\text{COOC}_2\text{H}_5$ and the DEF2-TZVPPD basis set for $\text{C}_4\text{F}_9\text{COI}$ and ICF_2COF .

Figure 2 shows τ_{IVR} as a function of the $\rho_{\text{C=O}}$ density of vibrational states. The characteristic time of the compounds containing a single C=O chromophore group is seen to vary monotonically. We can say with reasonable confidence that τ_{IVR} is shorter for more complex molecules, larger molecular weights and, hence, greater numbers of low-frequency vibrational modes. It seems likely that, in the case of the molecules containing a single C=O chromophore group, there is a relationship between $\rho_{\text{C=O}}$ and the density of Fermi resonances, which are responsible, according to existing theoretical views, for the intramolecular energy redistribution in the case of anharmonic intermodal interaction [5]. The data for $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$ are inconsistent with the correlation found for the other molecules, which can be understood in terms of specific features of their vibrational spectrum, in particular the large difference in frequency between the excited mode and the other modes of the molecule. It is probably this factor that impedes energy transfer from the C=O bond to the rest of the molecule.

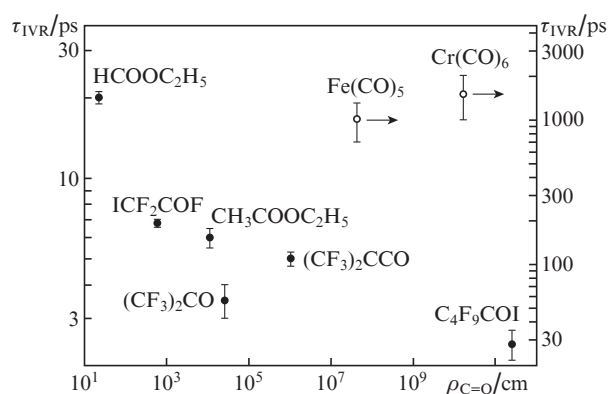


Figure 2. Relationship between the characteristic time τ_{IVR} for various molecules and the $\rho_{\text{C=O}}$ density of vibrational states at the $\langle E \rangle + h\nu_{\text{C=O}}$ level (see text).

The density of vibrational states and, concurrently, the density of Fermi resonances increase in an individual molecule as well with an increase in its vibrational energy, so the IVR rate should be higher for higher energy vibrational states [5]. This conclusion is supported by our experimental data for ICF_2COF : its τ_{IVR} was observed to decrease with an increase in the degree of its vibrational excitation. As the vibration energy of the mode increased to 7400 cm^{-1} , τ_{IVR} decreased to 8.4 ps for the $1 \rightarrow 2$ vibrational transition and to 3.0 ps for the $3 \rightarrow 4$ transition.

Thus, at this stage of our studies we determined the characteristic IVR time for nine polyatomic molecules, which allowed us to find a correlation between τ_{IVR} and the density of vibrational states. The degree of this correlation, in turn, depends on the structural complexity of the molecule.

3.2. Experimental studies of the formation of carbon structures on the surface of dielectric substrates

Figure 3 presents images of carbon films produced on the surface of dielectric substrates through femtosecond IR laser irradiation of $(\text{CF}_3)_2\text{CCO}$ molecules. The small-scale film structure turned out to be rather interesting. Figure 3b is an atomic force microscope image (Integra Prima, ZAO NT-MDT, Russia)

of the edge of one of the films in the initial stage of its formation. The carbon in the laser-exposed zone is seen to have the form of cones or spikes up to $1.5\text{ }\mu\text{m}$ or even more (in the central region) in height and $\sim 300\text{ nm}$ in half-height diameter. The spikes have a finer structure, with a characteristic inhomogeneity size of $\sim 10\text{ nm}$.

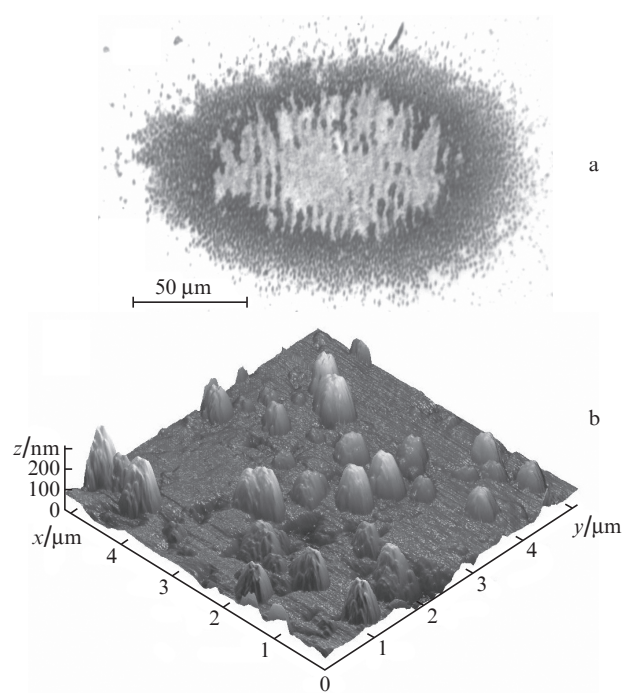


Figure 3. Carbon structure produced by irradiating $(\text{CF}_3)_2\text{CCO}$: (a) optical micrograph. (b) atomic force microscope image of the edge of the structure at 10-nm resolution. (The plane of the figure is parallel to the BaF_2 surface.)

As shown in the first experiments with $(\text{CF}_3)_2\text{CCO}$, the evolution of the carbon structure resulting from irradiation involves three, qualitatively different stages, dominated by different physical processes, which may take place concurrently. The first stage is latent growth: no structures can be detected visually during several minutes after the beginning of irradiation. The next stage is the formation and rapid growth of a film, which is accompanied under certain conditions by ablation of the material, especially pronounced in the central part of the spot. In addition, we observe the formation of filamentary structures on the film, which are parallel to the polarisation vector and have a period in the order of the laser wavelength or its multiple. The second stage of growth is well illustrated by Fig. 3a. Finally, when ablation is insignificant during film growth, a stage may take place where one pulse leads to peeling and disintegration of the central, densest part of the film and scatter of the fragments.

Our attention was focused on the first two stages, which we believe to be the most interesting, i.e. on finding out the causes and mechanisms of the decomposition of molecules and the growth of carbon structures on the surface of dielectric substrates. Most studies were concerned with $(\text{CF}_3)_2\text{CCO}$. A similar effect was found later for other organic molecules, in particular for xylene, $\text{C}_6\text{H}_4(\text{CH}_3)_2$; toluene, $\text{C}_6\text{H}_5\text{CH}_3$; and acetone, $(\text{CH}_3)_2\text{CO}$.

As mentioned above, the $(CF_3)_2CCO$ molecule contains the $C=C=O$ group, whose stretching mode at $\nu_1 = 2194\text{ cm}^{-1}$ can be excited to higher energy vibrational states by resonance femtosecond IR laser irradiation [15]. In the first step of regular measurements, femtosecond radiation was tuned to resonance with this $C=C=O$ mode.

First, we performed experiments aimed at preparing carbon films on substrates from various materials: CaF_2 , BaF_2 , LiF, KCl, ZnSe and Al_2O_3 . The irradiation conditions in those experiments were as follows: frequency, 2170 cm^{-1} ; laser fluence, 40 mJ cm^{-2} ; $(CF_3)_2CCO$ pressure in the cell, 10 Torr; and exposure time, up to 150 min. No film growth was detected on KCl, ZnSe or Al_2O_3 windows, even at the longest irradiation time. Surface structures were formed only on fluorine-containing materials: CaF_2 , BaF_2 and LiF. The origin of this selectivity is not yet clear, and additional studies are needed to understand it. In subsequent experiments, BaF_2 and CaF_2 were used as main substrate materials.

Next, we examined the effect of $(CF_3)_2CCO$ and buffer gas (nitrogen) pressure on the formation and growth of carbon structures. The results are presented in Fig. 4. The gas phase and its composition were found to have a quantitative effect on the process. In particular, increasing the buffer gas and $(CF_3)_2CCO$ pressure by an order of magnitude reduced the growth rate of the structures by a factor of 4–10. At the same time, even when the cell contained no $(CF_3)_2CCO$ vapour (after pumping for 10–20 min), effective film growth was observed. Similar pressure effects were observed for the other compounds studied, e.g. for toluene [Fig. 5, curve (4)]. Film growth in the absence of a gas phase suggests that the process takes place in the physisorbed layer on the surface of the dielectric substrate. This is also evidenced by the considerable decrease in the volume of the forming structures during prolonged pumping of the gas cell [Fig. 4, curve (5)]. Subsequent experiments with all the compounds were conducted at a pressure of ~ 10 Torr, which was necessary for maintaining dynamic equilibrium between molecules in the gas phase and on the substrate surface and ensuring a constant thickness of adlayer.

Moreover, to ensure identical adsorption conditions for all the compounds, the window surface was cleaned by an appropriate procedure to avoid the influence of the adlayer of

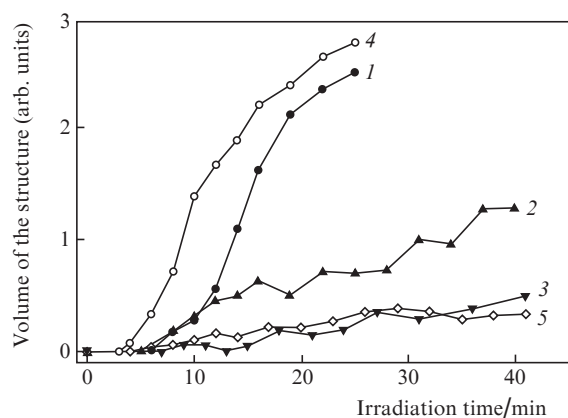


Figure 4. Film volume as a function of irradiation time at an irradiation (resonance) frequency of 2170 cm^{-1} , laser fluence of 40 mJ cm^{-2} and various vapour compositions and pressures: (1) $(CF_3)_2CCO$ (10 Torr), (2) $(CF_3)_2CCO$ (10 Torr) + N_2 (100 Torr), (3) $(CF_3)_2CCO$ (100 Torr), (4,5) empty cell after pumping for 15 min and 5 h, respectively.

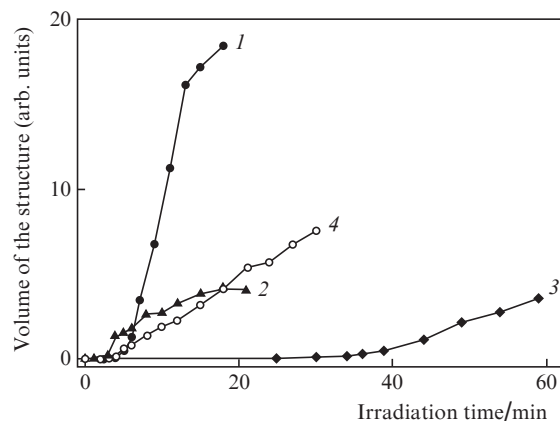


Figure 5. Film volume as a function of irradiation time at a (nonresonant) irradiation frequency of 2500 cm^{-1} , laser fluence of 32 mJ cm^{-2} and various vapour compositions and pressures: (1) $C_6H_5CH_3$ (10 Torr), (2) $C_6H_5CH_3$ (10 Torr) + N_2 (750 Torr), (3) $(CF_3)_2CCO$ (10 Torr) + H_2O (2 Torr), (4) empty cell after pumping for 20 min.

the preceding substance. This was checked by ascertaining that prolonged irradiation of the cleaned surface of an empty, evacuated cell produced no film. To ensure roughly the same surface condition of the substrates in all our experiments, the procedure used to pump the cell and to fill it with the substance to be studied was also maintained unchanged.

The observed effect is a complex, multistep process, involving the surface decomposition of molecules, complex chemical reactions in the adlayer and on the surface of the forming carbon structures and their growth and interaction with laser radiation. Because of this, the surface condition of the substrate, including the presence of adsorbed water, has a significant effect. This is evidenced by results of two experiments. In one of them, water vapour at a pressure of 2 Torr was added to toluene, which led to a sharp drop in the effectiveness of the formation and growth of carbon structures, i.e. to an increase in incubation time and decrease in growth rate [Fig. 5, curve (3)]. In an experiment with ethanol, no film growth was detected, which we believe to be caused by the presence of water vapour, because we used not absolute ethanol but rectified spirit containing 96% C_2H_5OH . It is for this reason that, in our experiments, special attention was paid to the substrate surface preparation procedure.

Experiments with $(CF_3)_2CCO$ are presently under way to assess the effect of laser radiation parameters – frequency, fluence, intensity and pulse duration – on the growth of carbon structures. Note that film growth takes place not only at the resonance frequency but also at nonresonant frequencies, but resonance between the laser radiation frequency and the $C=C=O$ bond vibration frequency markedly increases the effectiveness of the process. Moreover, at all frequencies we observed a sharp drop in film growth rate with decreasing laser pulse intensity at a constant laser fluence. New results will be presented in a subsequent communication.

4. Conclusions

This paper presented an overview of our previous studies and new experimental data on the effect of femtosecond IR laser pulses on polyatomic molecules in the gas phase and on the surface of substrates. Using IR pump–probe measurements, we investigated the vibrational dynamics in a group of mole-

cules containing a C=O chromophore bond, which was excited by resonance femtosecond IR laser radiation at wavelengths from 4.6 to 5.8 μm , and measured the τ_{IVR} characteristic time of the $0 \rightarrow 1$ vibrational transition, which was determined to be 2.4–20 ps for the molecules containing a single C=O bond. The τ_{IVR} of such molecules was found to correlate with the density of vibrational states in the vicinity of the first excited vibrational level. The τ_{IVR} of the $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$ molecules was estimated at 1.0 and 1.5 ns, respectively. We observed a decrease in τ_{IVR} with an increase in the degree of vibrational excitation of the ICF_2COF molecules, which is consistent with theoretical predictions. Carbon structures were observed to result from the decomposition of a number of organic molecules on the surface of CaF_2 , BaF_2 and LiF dielectric substrates under the effect of femtosecond IR laser radiation. In contrast, no gas-phase decomposition of the molecules was detected under such conditions. The decomposition of the molecules and the growth of carbon structures took place in a physisorbed layer. The effect was observed throughout the wavelength range studied (3.3–5.4 μm).

Acknowledgements. We are grateful to A.S. Useinov and K.S. Kravchuk [Institute of the Technology of Superhard and Novel Carbon Materials (ITSNCM)] for performing the atomic force microscopy measurements, to V.N. Denisov and N.V. Kuz'min (ITSNCM) for determining the composition of the films by Raman spectroscopy and to P.V. Koshlyakov (Institute of Chemical Kinetics and Combustion, Siberian Branch, Russian Academy of Sciences) for the quantum-mechanical calculations of molecular spectra. We are indebted to V.G. Minogin, Yu. E. Lozovik and S.A. Aseyev for their interest in our work and useful discussions.

This work was supported in part by the Presidium of the Russian Academy of Sciences (Extreme Light Fields and Their Applications Programme) and the Russian Foundation for Basic Research (Grant No. 11-02-00754).

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