ISSN 1063-7761, Journal of Experimental and Theoretical Physics, 2016, Vol. 122, No. 4, pp. 621–632. © Pleiades Publishing, Inc., 2016.
Original Russian Text © V.O. Kompanets, V.N. Lokhman, D.G. Poydashev, S.V. Chekalin, E.A. Ryabov, 2016, published in Zhurnal Eksperimental'noi i Teoreticheskoi Fiziki, 2016, Vol. 149, No. 4, pp. 723–736.

Dynamics of Photoprocesses Induced by Femtosecond Infrared Radiation in Free Molecules and Clusters of Iron Pentacarbonyl

V. O. Kompanets, V. N. Lokhman, D. G. Poydashev, S. V. Chekalin, and E. A. Ryabov
Institute of Spectroscopy, Russian Academy of Sciences, Troitsk, Moscow, 142190 Russia
e-mail: poydashev@isan.troitsk.ru, ryabov@isan.troitsk.ru

Received July 30, 2015

Abstract—The dynamics of photoprocesses induced by femtosecond infrared radiation in free $Fe(CO)_5$ molecules and their clusters owing to the resonant excitation of vibrations of CO bonds in the 5-μm range has been studied. The technique of infrared excitation and photoionization probing ($\lambda = 400$ nm) by femtosecond pulses has been used in combination with time-of-flight mass spectrometry. It has been found that an infrared pulse selectively excites vibrations of CO bonds in free molecules, which results in a decrease in the yield of the $Fe(CO)_5^+$ molecular ion. Subsequent relaxation processes have been analyzed and the results have been interpreted. The time of the energy transfer from excited vibrations to other vibrations of the molecule owing to intramolecular relaxation has been measured. The dynamics of dissociation of $[Fe(CO)_5]_n$ clusters irradiated by femtosecond infrared radiation has been studied. The time dependence of the yield of free molecules has been measured under different infrared laser excitation conditions. We have proposed a model that well describes the results of the experiment and makes it possible, in particular, to calculate the profile of variation of the temperature of clusters within the "evaporation ensemble" concept. The intramolecular and intracluster vibrational relaxation rates in $[Fe(CO)_5]_n$ clusters have been estimated.

DOI: 10.1134/S1063776116020199

1. INTRODUCTION

The aim of this work is to study photoprocesses in free molecules and in clusters of these molecules, which are induced by the resonant vibrational excitation of these particles in the ground electronic state by femtosecond infrared radiation. We study the iron pentacarbonyl molecule $Fe(CO)_5$, which exhibits intense vibrational bands of the CO bond (ν_6 and ν_{10} modes) in the 5-μm range, where sources of intense femtosecond infrared radiation exist.

One of the main effects observed at resonance of sufficiently intense infrared radiation with vibrations of polyatomic molecules is multiphoton excitation limited by their decay after the achievement of the dissociation threshold (see, e.g., [1–3]). Studies of the process of infrared multiphoton excitation show that, at durations of infrared pulses 10^{-8}–10^{-7} s, beginning with a certain vibrational excitation level (randomization threshold, see [2]), all vibrations are excited and subsequent monomolecular reactions (dissociation, isomerization) are of a statistical character. The possibility of multiphoton excitation of a certain vibrational mode of the polyatomic molecule above the randomization threshold is limited by the quite fast (pico- and subpicosecond) redistribution of the energy from the pumped mode to other vibrational modes (intramolecular vibrational redistribution, IVR, see reviews [4–7]). Many works were devoted to the study of intramolecular vibrational redistribution and to the measurement of the characteristic times of this process. This interest is due in particular to attempts of the implementation of nonstatistical reactions owing to the use of laser pulses shorter than the characteristic times of intramolecular vibrational redistribution. The results, as well as the methods of investigation, were reviewed, e.g., in [7].

Experiments in a gas phase, where intramolecular processes are not perturbed by the interaction with the environment as compared to molecules in a solvent, are particularly remarkable. In experiments with a number of derivatives of acetylene in a picosecond range, a vibration of an H–C≡ bond ($\nu \approx 3300$ cm^{-1}) was excited. To probe excited vibrational states, the methods of infrared absorption [8] and time-resolved Raman spectroscopy [9, 10] were used. The infrared pump–probe technique was recently used to study intramolecular vibrational redistribution in a number of molecules with the use of femtosecond pulses [11].

As far as we know, this work is the first report on the use of the technique of multiphoton ionization of molecules by femtosecond ultraviolet radiation to probe the dynamics of processes in vibrationally excited molecules in a molecular beam. The results were also significantly used in the experiments with $[Fe(CO)_5]_n$ clusters described below.

A molecular cluster is an ensemble of weakly bound molecules with the number of particles ranging from several units to tens of thousands. Atomic and molecular clusters were studied in many works because cluster particles constitute a certain intermediate state of matter between solid/liquid and free atoms or molecules. Some data on the methods of obtaining clusters, their properties and applications can be found in reviews [12–14] and references therein. The main aim of our experiments with clusters is to study the excitation and subsequent decay (dissociation) of molecular clusters under the resonant action of infrared radiation on the vibrations of molecules forming a cluster. Such studies are aimed at solving a wide range of poorly studied problems that have been studied insufficiently as yet. In particular, this concerns the degree of localization of the energy absorbed in a molecule and the rate of its relaxation to the internal degrees of freedom of the cluster (intracluster relaxation). These are also the lifetime (with respect to decay) of an excited cluster, the possibility of its significant overexcitation, and, finally, the statistical or nonstatistical character of the decay itself.

The binding energy in molecular clusters (with the van der Waals or hydrogen bonding type) is comparatively low and is usually no more than 0.5 eV [1]. For this reason, the absorption of even an infrared photon, particularly in the near infrared range, is often sufficient for the dissociation of clusters. This circumstance is widely used in one of the methods for the measurement of infrared absorption spectra in clusters (infrared photodepletion spectroscopy). Infrared photodissociation spectra thus obtained were used to obtain information on the intracluster dynamics, in particular, on cluster decay rates. The found lifetimes τ are in the range of 10^{-12}–10^{-6} s (see review [15]). However, it is noteworthy that the interpretation of the results, particularly in the case of clusters of polyatomic molecules, is not unambiguous. This is due to the known problem of obtaining temporal information from spectral measurements if the nature of broadening of lines and/or contributions of various mechanisms to the homogeneous component of this width are unknown. For this reason, the most reliable method for the determination of cluster decay rates is the direct measurement of the kinetics of this process in terms of the decay of clusters themselves and/or the appearance of free particles that are products of decay. This approach is used in our studies.

We previously studied the infrared dissociation of $(CF_3I)_n$ [16, 17] and $(IF_2CCOF)_n$ [18] molecular clusters owing to the resonant excitation of vibrations of a C–F bond (9.3 μm) in both molecules and, in addition, a C–O bond (5.3 μm) in the IF_2CCOF molecule. The time resolution in the experiments was 10^{-8} s [16] and 10^{-7} s [18]. The results indicated that relaxation processes in the clusters under study, including their monomolecular decay, are much faster (10^{-8}–10^{-7} s). At this time scale, the infrared dissociation process can be treated as a stationary or almost stationary process of successive evaporation of molecules, and the observation of the dynamics of intracluster processes is apparently possible only with the use of picosecond or subpicosecond infrared pulses.

Our experiments with $[Fe(CO)_5]_n$ clusters provide the first (as far as we know) real-time observation of the dissociation of molecular clusters as a result of the resonant excitation of valence vibrations of C–O bonds in a $Fe(CO)_5$ molecule by femtosecond infrared radiation. Some of the results were reported in [19]. It is noteworthy that infrared multiphoton dissociation of free $Fe(CO)_5$ molecules by nanosecond and femtosecond pulses was observed in [20] and [21], respectively.

2. EXPERIMENTAL SETUP AND MEASUREMENT PROCEDURE

The measurements were performed at the setup described in detail in [22]. Here, we only briefly describe the measurement conditions. The setup is based on a photoionization time-of-flight mass spectrometer (TOF MS) in combination with a source of pulsed molecular/cluster beams. All measurements in this work were performed with molecular or cluster beams. Collimated molecular and cluster beams were formed by a skimmer (Beam Dynamics, Model 1, $D_{\text{skim}} = 0.49$ mm) placed at a distance of 55 mm from a pulsed nozzle (General Valve, $d = 0.8$ mm) and were directed to the chamber of the time-of-flight mass spectrometer, where they cross laser beams on the axis of the mass spectrometer. Depending on the conditions of discharge of the gas in a pulsed ultrasonic nozzle (the composition and pressure of the gas above the nozzle, the duration and degree of opening of the nozzle), purely molecular beams and beams with different degrees of clustering up to purely cluster beams can be generated. In most experiments described below, the $Fe(CO)_5 : Ar = 1 : 50$ mixture was used and the drag pressure was $P_0 = 200$ kPa. A pure molecular or pure cluster beam was obtained by controlling the duration of the opening of the nozzle and the pulse voltage applied to it.

To estimate the average size N of forming clusters, we used the known Hagena relation $N \sim (\Gamma^*)^a$ [23], where Γ^* is the dimensionless parameter proportional to the density n_0 of particles in the source: $\Gamma^* \propto n_0$. The final expression is as follows:

$$N = N_{\text{cr}}(P_0/P_{\text{cr}})^a,$$

where P_{cr} is a certain critical pressure above the nozzle at which the effective generation of clusters with the critical size N_{cr} begins. Our measurements indicate that $P_{\text{cr}} \approx 30$ kPa for the used $Fe(CO)_5 + Ar$ mixture. Following [16], we chose $N_{\text{cr}} = 7.5$ and $a = 2.0$. Although such an estimate of the average size of clus-

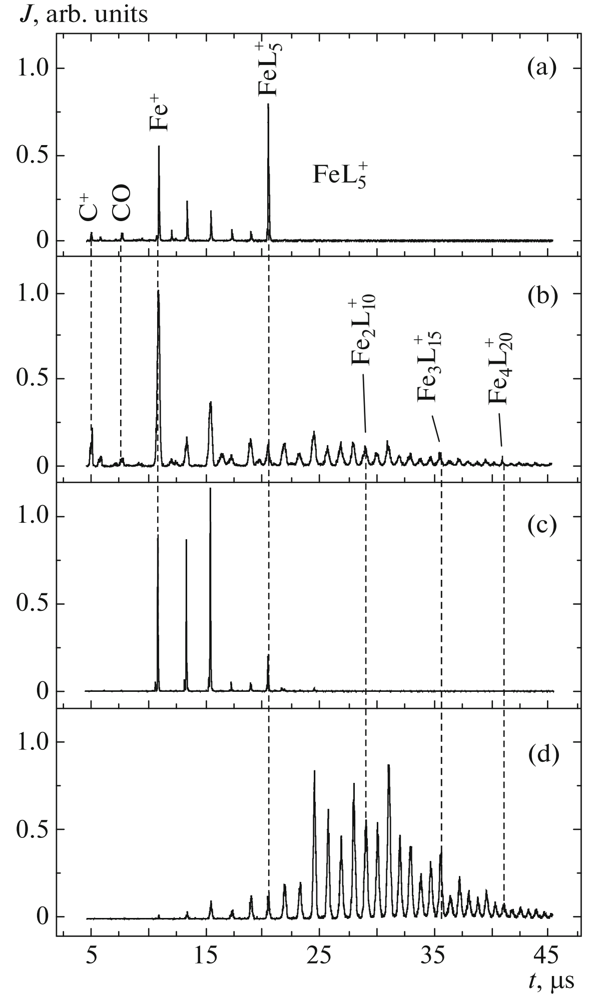

Fig. 1. Characteristic time-of-flight mass spectra of ion products at the irradiation of (a, c) $Fe(CO)_5$ molecules and (b, d) $[Fe(CO)_5]_n$ clusters by (a, b) 400- and (c, d) 266-nm radiation with the energy densities $\Phi_{400} = 0.25$ J/cm^2 and $\Phi_{266} = 0.1$ J/cm^2, respectively; L stands for the CO ligand.

ters is very rough, we believe that it provides a quite correct estimate for N in our experiments. This estimate gives $N = 250–300$ for the pressure $P_0 = 200$ kPa.

Femtosecond radiation was obtained from a Ti: sapphire laser (Spectra-Physics, $F = 1$ kHz, $\lambda = 800$ nm, $\tau_{\text{pulse}} = 50$ fs) whose output beam was divided into two channels. One of them was used to generate tunable femtosecond infrared radiation by mixing signal and idler waves of TOPAS-C OPA in nDFG unit (Light Conversion). The energy of the generated pulse in the 2000 cm^{-1} range reached 17 μJ. Radiation was focused by a KCl lens ($f = 13.5$ cm) in the chamber of the time-of-flight mass spectrometer into an area of 2×10^{-4} cm^2 (at the $1/e$ level), so that the resulting energy fluence of this p-polarized radiation in the region of the molecular/cluster beam (with allowance for loss to transportation) can reach 30 mJ/cm^2. Two types of infrared pump pulses with the spectral widths $\Delta\nu_{\text{IR}} = 105$ cm^{-1} and $\Delta\nu_{\text{IR}} = 185$ cm^{-1} and durations of 220 and 160 fs, respectively, were used in the experiment.

The second channel of the main beam was used to generate probe pulses at the second (400 nm) and third (266 nm) harmonics whose radiation duration was about 100 fs. Ultraviolet radiation thus obtained was focused by a CaF_2 lens ($f = 30$ cm) in the chamber of the time-of-flight mass spectrometer and was used for the multiphoton ionization of the particles under study. A probe pulse propagated at a small (about 2°) angle to the direction of the infrared pump pulse. The time delay between the infrared pump and ultraviolet probe pulses was smoothly varied with the use of an optical delay line.

3. MEASUREMENT RESULTS

3.1. Free $Fe(CO)_5$ Molecules

3.1.1. Experiment. As was mentioned above, to probe preliminarily infrared excited molecules, the multiphoton ionization of these particles by visible or ultraviolet radiation was used. Processes of the dissociation and photoionization of $Fe(CO)_5$ molecules by femtosecond radiation were studied in detail in [24]. In particular, under excitation at a wavelength of 400 nm, the fast (100 fs) separation of CO ligands was observed, and at the photoionization of molecules, the $Fe(CO)_5^+$ parent ion was observed in contrast to excitation by nano- and picosecond pulses.

One of the first problems of this work was the choice of the optimal wavelength of radiation for the detection of free molecules and their clusters. Figure 1 shows the mass spectra of ion products appearing at the multiphoton ionization of the particles irradiated at wavelengths λ of 400 and 266 nm. It is seen that the $Fe(CO)_5^+$ molecular ion is the heaviest (196 amu) in the beam of free molecules for both wavelengths. A number of smaller fragments are also observed. It is important that the relative amplitude of the molecular ion under irradiation at $\lambda = 400$ nm is much larger than that under irradiation at $\lambda = 266$ nm.

For clustered beams, ion peaks with masses larger than 196 amu appear; in particular, this certainly indicates the presence of $[Fe(CO)_5]_n$ clusters in the beam. The distances between these peaks are identical and correspond to the mass of CO (28 amu) because this mass is accidentally half the mass of the main iron isotope (56 amu). The relative intensity of the signal from ions of cluster fragments under irradiation at $\lambda = 266$ nm is much higher than that under irradiation at 400 nm. Peaks in the interval between the masses of the molecule and dimer are due to the fragmentation of large clusters under ionization. According to Fig. 1, 400-nm radiation is preferable for the detection of molecules, whereas 266-nm radiation is preferable for the detection of clusters. For this reason, 400-nm

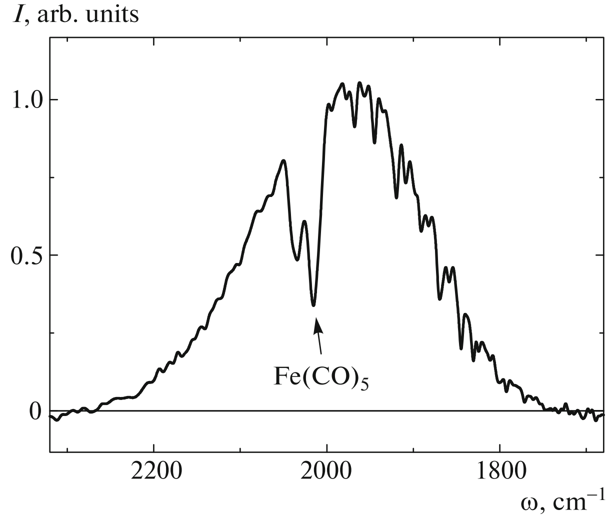

Fig. 2. Spectrum of the femtosecond infrared pulse passed through a cuvette with $Fe(CO)_5$ (pressure 2 Torr, length 4.8 mm, $T = 300$ K). The right wing is perturbed by the absorption of atmospheric water vapor.

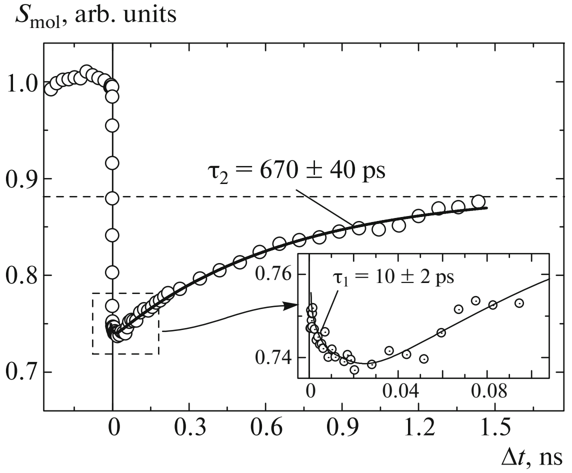

Fig. 3. Intensity of the signal of the $Fe(CO)_5^+$ ion versus the delay time between the pulses of pump (infrared) and probe (400 nm) radiation at $\Phi_{IR} \approx 30$ mJ/cm^2.

radiation was mainly used as probe radiation in the experiments reported below on the study of dynamics in vibrationally excited molecules.

The $Fe(CO)_5$ molecule has five normal modes near 5 μm associated with vibrations of the CO bond. Among them, the ν_6 (2012 cm^{-1}) and doubly degenerate ν_{10} (2031 cm^{-1}) modes are active in infrared absorption and the ν_1 (2114 cm^{-1}) and ν_2 (1984 cm^{-1}) modes are active only in Raman scattering [25]. It is noteworthy that the spectrum of femtosecond infrared radiation is significantly wider than the pumped modes ν_6 and ν_{10} and completely covers them (Fig. 2).

The dynamics of intramolecular processes in $Fe(CO)_5$ molecules, which was induced by their vibrational excitation by femtosecond infrared radiation, was experimentally studied. To this end, molecules were excited by infrared pulses and, then, the intensity of the signal S_{mol} of the $Fe(CO)_5^+$ molecular ion formed in the multiphoton ionization of molecules irradiated at $\lambda = 400$ nm was measured as a function of the delay between the infrared pump pulse and the ionizing probe pulse at various energy densities Φ_{IR} of infrared radiation. The characteristic form of such a dependence is shown in Fig. 3. To reduce the effect of the so-called coherent artefact in the region of negative and small positive delays, a "magic" value of 54.7° was taken for the angle between the polarizations of infrared and visible radiations.

Qualitatively similar dependences were also obtained for $\Phi_{IR} = 20$, 14, and 10 mJ/cm^2. The dynamics shown in Fig. 3 has the following features. The transmission of the infrared pump pulse results in a fast ("instantaneous") decrease in the ion signal; the higher the Φ_{IR} value, the larger the decrease (see Fig. 4). The total time of this decrease is about 800 fs, which is close to the time resolution of this experiment determined primarily by the overlapping of infrared and visible pulses. Further, a certain relaxation process occurs with two characteristic times, short $\tau_1 = (10 \pm 2)$ ps (see inset in Fig. 3) and long $\tau_2 = (670 \pm 40)$ ps, in the two-exponential approximation. The time τ_2 describes the process of recovery of the ion signal. It is remarkable that such a recovery is incomplete, is about 40–50% of the maximum decrease in the intensity of the initial signal, and hardly depends on Φ_{IR}. It is also noteworthy that the τ_2 value is independent of Φ_{IR} within the measurement errors. The τ_1 value increases in the experiment with a decrease in

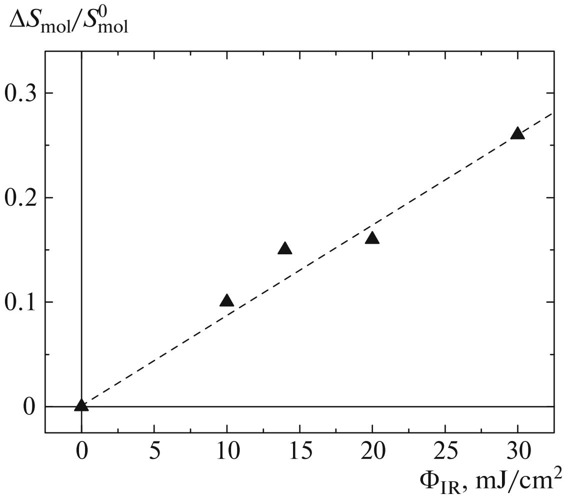

Fig. 4. Relative decrease in the signal of the molecular ion versus Φ_{IR}.

Φ_{IR}: it is approximately 10 ps at $\Phi_{IR} = 30$ mJ/cm^2 and increases to $\tau_1 = (17 \pm 5)$ ps with a decrease in Φ_{IR} by a factor of 2.

The dependence of the relative change $\Delta S_{mol}/S^0_{mol}$ in the intensity of the signal of the molecular ion on the energy density Φ_{IR} of the infrared pump pulse was also measured. The results are shown in Fig. 4, where an almost linear dependence on Φ_{IR} is observed, indicating the linear interaction of $Fe(CO)_5$ molecules with resonant femtosecond infrared radiation.

3.1.2. Discussion of the results for $Fe(CO)_5$ molecules. One of the possible reasons for the observed decrease in the amplitude of a signal of $Fe(CO)_5$ molecules could be their infrared multiphoton dissociation in the ground electronic state (see [1, 2]) with the separation of one CO ligand. Indeed, such a dissociation of this molecule under femtosecond infrared irradiation was implemented in [21]. However, according to this work, the yield β of infrared multiphoton dissociation even at our maximum energy density $\Phi_{IR} = 30$ mJ/cm^2 should not exceed $\beta \approx 10^{-4}$, which is much lower than the change in the signal intensity $\Delta S_{mol}/S^0_{mol}$ observed in our experiment (see Fig. 4). Furthermore, a very strong power-law dependence $\beta \propto \Phi^{6.6}_{IR}$ is observed (cf. the linear dependence in Fig. 4). Consequently, the effect of infrared multiphoton dissociation on the observed dynamics (see Fig. 3) can be excluded.

Thus, it can be generally concluded that the observed decrease in the amplitude of the molecular ion is due to the vibrational excitation of $Fe(CO)_5$ molecules to states where the efficiency of ionization is lower than the efficiency of ionization of the initial states.

According to [24], two photons of 400-nm radiation are at the maximum of the transition (50000 cm^{-1}) from which the molecule decays with the separation of four CO ligands in a time of about 100 fs. In the case of sufficiently intense femtosecond radiation, the molecule in the duration of the laser pulse can absorb the third photon and transit to the $Fe(CO)_5^+$ ionized state (ionization potential is 63689 cm^{-1}). For this reason, the molecular ion is observed at the multiphoton ionization of $Fe(CO)_5$ molecules by femtosecond laser pulses, whereas it is not observed when nano- and picosecond pulses are used.

Electron absorption spectra in the $Fe(CO)_5$ molecule in the range of 30000–50000 cm^{-1} were studied in [26]. Measurements at $T = 77$ and 300 K showed that the absorption coefficient significantly depends on the temperature in this spectral range and absorption, in particular, at 50000 cm^{-1} decreases with an increase in the temperature. Thus, the vibrational “heating” of molecules leads to the reduction of the cross section for a transition to an intermediate resonance level and, as a result, to a decrease in the efficiency of three-photon ionization of molecules at a wavelength of 400 nm. We believe that this effect is responsible for a decrease in the amplitude of the signal from the $Fe(CO)_5^+$ ion at the vibrational excitation of molecule at the initial time (see Fig. 3).

Let us now discuss possible mechanisms of subsequent relaxation processes. In the mentioned measurements of absorption spectra [26], the average vibrational energy $\bar{E}_{vibr}$ of molecules at $T = 300$ K is approximately 1960 cm^{-1} and about 0.014% of particles are in the ground state. (At $T = 77$ K, $\bar{E}_{vibr} = 141$ cm^{-1} and about 25% of particles are in the ground state.) For this reason, the main contribution to the formation of the absorption spectrum at $T = 300$ K comes from molecules in the initial excited states of low-frequency vibrations of $Fe(CO)_5$. The average energy absorbed from the infrared field in our experiments can be estimated. The effective (only a part of the spectrum of the femtosecond pulse interacts with molecules, see Fig. 2) absorption cross section for a pulse with a spectral width of about 100 cm^{-1} measured in [21] was $\sigma^{mol}_{fs} \approx 1.5 \times 10^{-18}$ cm^2.

In our experiments with $Fe(CO)_5$ molecules, the spectral width of the infrared pulse was 185 cm^{-1} and, correspondingly, the absorption cross section is $\sigma^{mol}_{fs} \approx 8.1 \times 10^{-19}$ cm^2. Therefore, the average number of absorbed infrared photons per molecule for $\Phi_{IR} = 30$ mJ/cm^2 is $\bar{n} = \sigma\Phi_{IR}/h\nu \approx 0.6$ and the average energy of molecules is about 1200 cm^{-1}. (At the supersonic outflow of the gas, the cooling of vibrational degrees of freedom is much smaller than that of rotational degrees of freedom and T_{vib} is usually no less than 100–120 K [12–14]. For $Fe(CO)_5$, this corresponds to the initial value $\bar{E}_{vibr} = 240$–360 cm^{-1}.) In the two-level approximation, this would mean the deep saturation of the transition, but such an absorbed energy for the multilevel system means the excitation of at least several lower levels of the excited resonant modes [1, 2].

It is substantial that the absorbed energy immediately after the end of the infrared pulse remains localized at the levels of resonant modes. The occupation numbers in low-frequency nonresonant modes do not change in this case. Thus, the selective heating of the ν_6 and ν_{10} modes of vibrations of the CO bond occurs and results in the initial sharp decrease in the signal from $Fe(CO)_5^+$ in Fig. 3. Then, owing to the intramolecular vibrational redistribution, the energy is transferred from the excited levels of resonant modes to other vibrations of molecules (obviously with the conservation of the initial state energy). As a result, new stationary states are formed with an almost statistical distribution of occupation numbers in all vibrational modes [7]. In this case, the occupation numbers in high-frequency vibrations decrease significantly because of a low specific heat. We believe that an increase in the signal from $Fe(CO)_5^+$ at long times (see Fig. 3) is due to energy transfer from excited levels of resonant modes (their "cooling") owing to intramolecular vibrational redistribution and the time τ_2 is the characteristic time of this process. At the same time, the average occupation numbers in these modes (their "temperature") in the vibrational distribution after the end of relaxation are larger than the initial values before infrared excitation. For this reason, the recovery of the signal in Fig. 3 is incomplete. It is noteworthy that the measured time $\tau_2 = (670 \pm 40)$ ps is in good agreement with the data reported in [11], where the time of intramolecular vibrational redistribution from vibrations of CO bonds in $Fe(CO)_5$ is estimated as (1.0 ± 0.3) ns.

Let us now discuss the nature of a faster relaxation process with the characteristic time τ_1 (see inset in Fig. 3). In principle, it could be attributed to the resonant intramolecular exchange between excited modes and modes of vibrations of the CO bond inactive in infrared absorption. However, the authors of [27], who studied similar systems with CO ligands, did not confirm such an exchange. The only known intramolecular process in free iron pentacarbonyl molecules with a similar characteristic time is Berry pseudorotation [28], when two of three equatorial ligands are replaced by two axial ligands. The vibrational energy in the excited ligand is conserved in this transition. The characteristic time of such a process in $Fe(CO)_5$ molecules in a solvent at room temperature is (8 ± 0.6) ps [28]. Furthermore, the authors of [28] obtained the temperature dependence of the characteristic time of this process. This time is (6.3 ± 0.8) ps at a temperature of 50°C and is (4.6 ± 0.4) ps at a temperature of 90°C; i.e., the characteristic time decreases with an increase in the temperature. This mechanism is possibly responsible for the fast relaxation process with the characteristic time τ_1 that we observed in free molecules. Although the infrared excitation of molecules under our conditions at these times results in a significantly nonequilibrium distribution of populations of vibrational modes, the experimentally observed decrease in the time τ_1 with an increase in Φ_{IR} can be an additional reason in favor of this mechanism.

3.2. Clusters of Fe(CO)$_5$ Molecules

3.2.1. Experiment. As was mentioned above, the choice of the conditions of the outflow of the $Fe(CO)_5$: Ar mixture in our experiments provided the variation of composition of particles in a beam; in particular, a beam consisting almost completely of $[Fe(CO)_5]_n$ clusters could be obtained. The formation of such clusters was manifested in the mass spectrum as the appearance of a comb of peaks above 196 amu, which is the mass of the $Fe(CO)_5^+$ molecular ion (see Fig. 1). These ion peaks correspond to fragments of clusters and have the $Fe_x(CO)_y$ structure.

We did not find any data on the infrared absorption spectrum of $[Fe(CO)_5]_n$. We believe that this spectrum of vibrations of the CO bond in the 5 μm range is localized near the frequency of these vibrations for molecules in the gas phase, as is usually the case for clusters [12–15]. According to the absorption spectrum of molecules in the gas phase (see Fig. 2), it is reasonable to expect that the spectral width of the femtosecond pulses used in the experiment (105 cm^{-1} and, the more so, 185 cm^{-1}) completely covers the possible shift and broadening of the absorption spectrum of clusters.

The irradiation of $[Fe(CO)_5]_n$ clusters by sufficiently intense femtosecond infrared radiation (central frequency 2000 cm^{-1}) results in their dissociation (decay). This is manifested in a quite significant decrease in the intensity of ion peaks of cluster fragments with masses beginning approximately with the mass of a dimer and in an increase in the amplitude of the molecular ion peak. The efficiency of the dissociation of clusters can be measured by two methods. The first method is the direct measurement of the number of clustered molecules, in particular, the average size N of clusters. However, the implementation of this method is difficult because the range of detected masses is limited and the sensitivity of the used time-of-flight mass spectrometer depends on the mass of particles. For this reason, the efficiency of the dissociation of clusters was measured by the other method: the yield of free molecules was determined from the amplitude of the peak corresponding to the $Fe(CO)_5^+$ molecular ion in the mass spectrum. In view of a higher relative sensitivity of the detection of free molecules under multiphoton ionization at 400 nm (see Fig. 1), radiation at this wavelength was used as probe radiation. The effect of infrared radiation on clusters is illustrated in Fig. 5, where time-of-flight spectra of a cluster beam before irradiation and at 1.4 ns after irradiation are shown. A significant increase in the amplitude of the peak corresponding to the molecular ion is seen.

It is noteworthy that the cluster beam always contains a small fraction of monomers, which decreases to the middle of a cluster pulse. For this reason, this part of the beam was irradiated in the experiment. The detailed analysis showed that the shapes of the mass peak of $Fe(CO)_5^+$ are significantly different in the cases of ionization of the cluster and monomer components in the initial cluster beam. This made it possible to take into account this "background" signal in subsequent measurements and analysis of the kinetics of the formation of free molecules as a result of the infrared dissociation of clusters.

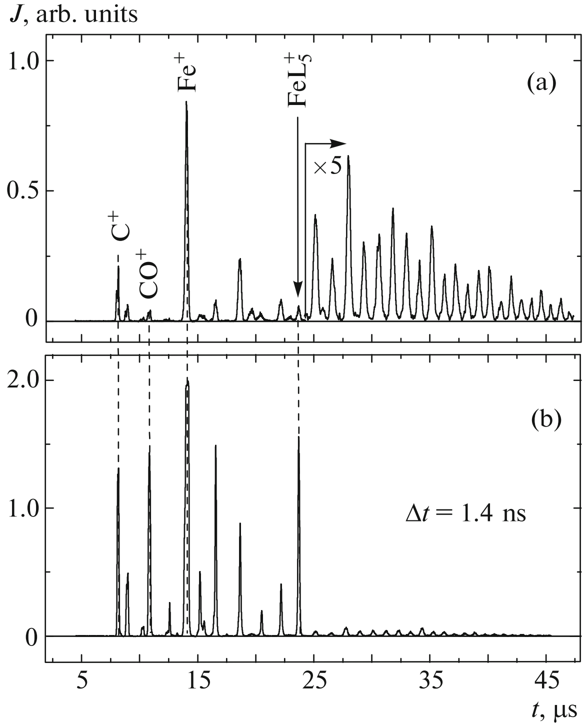

Fig. 5. Time-of-flight mass spectra of the cluster beam (a) before infrared irradiation and (b) at 1.4 ns after the passage of the infrared pulse. The amplitude of the signal from clusters in the upper part of the figure is magnified by a factor of 5. The duration of the cluster beam was about 300 μs and the energy density was $\Phi_{IR} = 30$ mJ/cm^2.

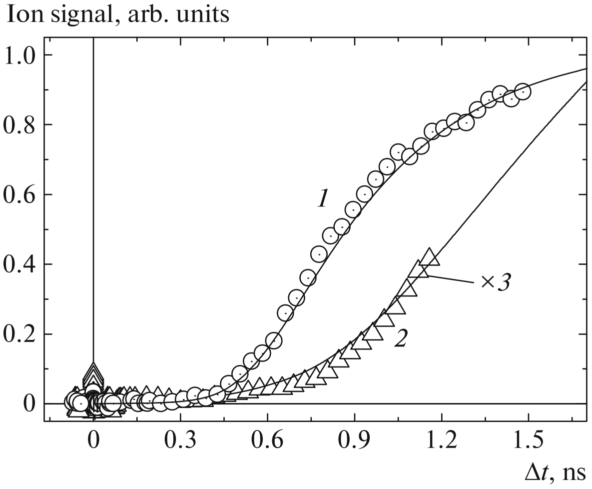

Fig. 6. Intensity of the signal of the $Fe(CO)_5^+$ ion versus the delay time between the infrared and probe pulses for (*1*) $\Delta\nu_{IR} = 105$ cm^{-1} and $\Phi_{IR} = 32$ mJ/cm^2 and (*2*) $\Delta\nu_{IR} = 185$ cm^{-1} and $\Phi_{IR} = 25$ mJ/cm^2 (signal is magnified by a factor of 3). The solid curves are the model calculations.

Figure 6 shows the kinetic curves of the yield of the $Fe(CO)_5^+$ molecular ion depending on the delay between the pump and probe pulses. These curves demonstrate the appearance of free molecules from the decay of clusters, which is induced by femtosecond infrared radiation. The presented data were obtained in two experiments with different spectral widths of infrared radiation.

In the case of less broadband radiation (circles in Fig. 6), a rapid increase in the signal, beginning with a delay of 400 ps, was followed by saturation at times larger than 1 ns, whereas only the initial stage of an increase in the signal was observed in the case of more broadband radiation (triangles in Fig. 6). The presented curves are characterized by a certain "induction time," which indicates that the dissociation of clusters of free molecules follows relaxation processes with a characteristic time of about 10^{-10} s. The induction time in the case of more broadband radiation is larger than that in the case of less broadband radiation. We attribute this behavior to the difference in the absorbed energy for two types of infrared pulses because of their different spectral widths. Moreover, the energy fluences Φ_{IR} in these measurements were different: $\Phi_{IR} = 32$ mJ/cm^2 for $\Delta\nu_{IR} = 105$ cm^{-1} and $\Phi_{IR} = 25$ mJ/cm^2 for $\Delta\nu_{IR} = 185$ cm^{-1}.

3.2.2. Model of the infrared dissociation of $[Fe(CO)_5]_n$ clusters. The analysis of the experimental data indicates that the dissociation of $[Fe(CO)_5]_n$ clusters excited by femtosecond infrared radiation can be considered as a process of the successive evaporation of free molecules owing to the heating of the initial clusters. This heating is in turn initiated by successive processes of intramolecular and intracluster relaxation of the initial excitation of molecules by the infrared pump pulse. This assumption underlies a model developed to describe the behavior of the signal from evaporated free molecules as a function of the delay between the infrared pump pulse and ionizing probe pulse. This model implies that the behavior of the signal from the $Fe(CO)_5^+$ ion is determined by the average size of clusters N, their initial temperature T_0, the energy ΔE required for the evaporation of one molecule, the effective infrared absorption cross section σ, and the constants of relaxation processes.

As will be shown below, only the partial dissociation of clusters occurs in our experiments so that the average size of clusters decreases from $N = 260$ to $N = 75$ (calculation for $\Delta\nu_{IR} = 105$ cm^{-1}). For this reason, to simplify calculations, the evolution of the initial size distribution of clusters after their decay is replaced by the evolution of clusters with the identical initial size N because the shape of the distribution will be hardly distorted under the indicated change in the average size.

The internal energy of the cluster of n molecules in our model is given by the expression

$$E_{\text{clust}}(T,n) = (3n-6)k_BT + nE_{\text{vib}}(T), \qquad (1)$$

where the first term is the energy of vibrations of particles in a cluster, the second term is the internal vibrational energy of n molecules, and T is the temperature of the cluster in a nearly equilibrium state. The E_{vib} value can be calculated from the known frequencies of vibrations in $Fe(CO)_5$. The cluster irradiated by the femtosecond infrared pulse instantaneously (as compared to the relaxation times) absorbs the energy E_{abs} given by the expression

$$E_{\text{abs}} = n\sigma\Phi_{\text{IR}}, \qquad (2)$$

where n is the size of the cluster and σ is the effective absorption cross section for one molecule. The cross section σ for free molecules at $\Delta\nu_{\text{IR}} = 185$ cm^{-1} obtained in Section 3.1.2 from the data reported in [21] is $\sigma_{\text{fs}}^{\text{mol}} \approx 8.1 \times 10^{-19}$ cm^2. Taking into account the spectral width of the pulse, a similar cross section for $\Delta\nu_{\text{IR}} = 105$ cm^{-1} should be $\sigma_{\text{fs}}^{\text{mol}} \approx 1.43 \times 10^{-18}$ cm^2 and the ratio of the cross sections for two types of pulses should be $\sigma_{\text{fs}}^{\text{mol}}(105\text{ cm}^{-1})/\sigma_{\text{fs}}^{\text{mol}}(185\text{ cm}^{-1}) \approx 1.76$.

There are two ways of the utilization of the absorbed energy of infrared radiation: (i) it directly relaxes to intermolecular vibrations of clusters or (ii) the energy first relaxes to low-frequency vibrations of the $Fe(CO)_5$ molecule, then to intermolecular vibrations, and, finally, successive evaporation of molecules from the cluster occurs. Beginning with pioneering studies by Laubereau and Kaiser [29] of vibrational relaxation in solutions, it is accepted that the intermolecular relaxation of the energy from excited high-frequency vibrations of molecules first occurs and, then, a slower process of energy transfer to the solvent takes place. However, the $Fe(CO)_5$ molecule is a quite specific molecule having an anomalously long characteristic time of the intramolecular relaxation in a gas phase. According to Section 3.1.1 and [11], in the case of the excitation of vibrations of CO bonds by femtosecond radiation near 5 μm, this time is about 1 ns, which can significantly affect the rate of energy transfer to intermolecular vibrations in the cluster.

We believe that the relaxation of $Fe(CO)_5$ molecules in solutions is the closest process to relaxation in $[Fe(CO)_5]_n$ clusters. In particular, the time of energy relaxation from excited vibrations of the CO bond in solutions of organometallic complexes ranges from tens to hundreds of picoseconds, depending on the type of a solvent [30]. According to [28], these vibrations in $Fe(CO)_5$ molecules relax at a time of 150 ps; in this case, the energy is transferred first to low-frequency vibrations of a molecule and, then, to the solvent. As a result, the two-step process of energy relaxation from excited vibrations of the CO bond through low-frequency vibrations of molecules to the cluster is considered as a relaxation mechanism in the described model.

Relaxation processes in the model are described in the standard rate-equation approximation used in many phenomenological theories. The relaxation of the energy localized in vibrations of the CO bond to the system of low-frequency modes is described by the constant k_1 and the subsequent energy transfer to intermolecular vibrations in the cluster is characterized by the constant k_2. After that, clusters dissociate with the rate k_{diss}. The dynamics of the redistribution of the vibrational energy is described by the system of equations

$$\begin{gathered}\dot{I}_{\text{CO}}(t) = -k_1 I_{\text{CO}},\\ \dot{I}_{\text{bath1}}(t) = k_1 I_{\text{CO}} - k_2 I_{\text{bath1}},\\ \dot{I}_{\text{bath2}}(t) = k_2 I_{\text{bath1}},\end{gathered} \qquad (3)$$

with the initial conditions

$$\begin{gathered}I_{\text{CO}}(0) = 1,\\ I_{\text{bath1}}(0) = I_{\text{bath2}}(0) = 0.\end{gathered} \qquad (3')$$

Here, I_{CO} is the population corresponding to the vibrations of the CO bond, I_{bath1} is the population of the thermostat of low-frequency modes of the molecule, and I_{bath2} is the population of the thermostat of intracluster vibrations.

To define the dissociation constant k_{diss}, we used the evaporative ensemble concept [31, 32] (see also review [33]), which is formed during the cooling of clusters as a result of the successive evaporation of particles. According to the cited works, the dissociation constant can be represented in the form

$$k_{\text{diss}} = A\exp\left(-\frac{\Delta E}{k_BT}\right), \qquad (4)$$

where ΔE is the energy necessary for the evaporation of one particle, T is the temperature of the cluster, and the constant A is given by the expression

$$A(n) = 3\times 10^{13} n^{2/3} \exp\left(\frac{6.0}{n^{1/3}}\right).$$

The factors determining this expression were described in detail in [34]. In particular, $A = 3.13 \times 10^{15}$ s^{-1} for the cluster with the size $n = 260$. The energy ΔE depends on the size of the cluster n as [35]

$$\Delta E(n) = \Delta E\left[1 - \exp\left(-\frac{n}{13}\right)\right].$$

However, this expression for $\Delta E(n)$ indicates that the dependence on the size of the cluster is significant only for small clusters with $n \sim 10$. Since clusters in our experiments are much larger, the simulation was performed with a constant ΔE value.

Thus, owing to relaxation processes, the energy of vibrations of the CO bonds of $Fe(CO)_5$ molecules is finally redistributed to intermolecular vibrations. This increases the quasi-equilibrium temperature of the cluster calculated by Eq. (1). To simplify the calcula-

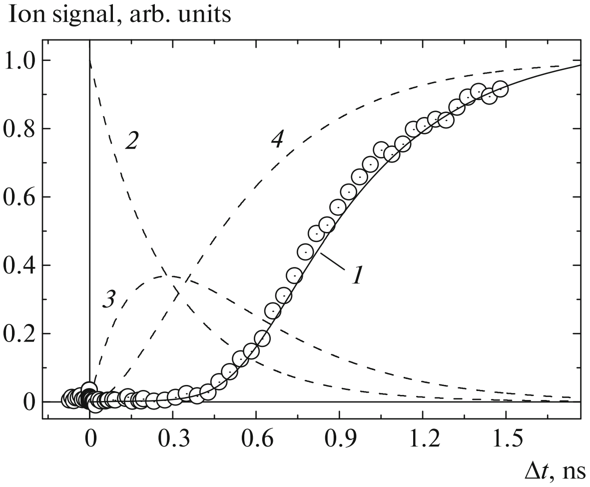

Fig. 7. Kinetics of relaxation processes and the yield of dissociation for $[Fe(CO)_5]_n$ clusters. The calculations for (*1*) the yield of dissociation, (*2*) I_{CO}, (*3*) I_{bath1}, and (*4*) I_{bath2}. Circles are experimental data for Φ_{IR} = 32 mJ/cm^2 and $\Delta\nu_{IR}$ = 105 cm^{-1}.

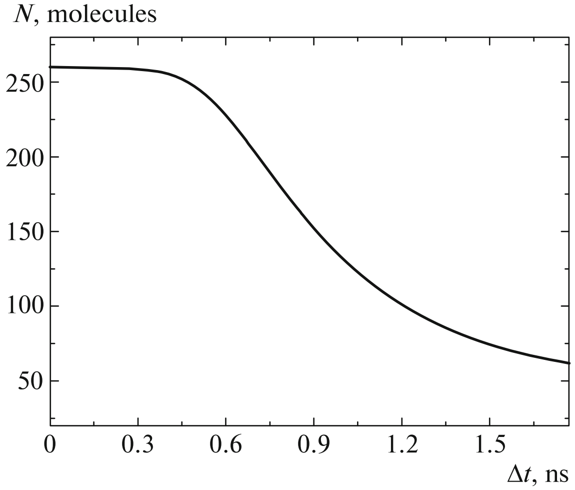

Fig. 8. Calculated average size of the cluster N versus the delay between the pump and probe pulses.

tions, the temperature in the first and second terms on the right-hand side of Eq. (1) was taken the same. An increase in the temperature results in turn in an increase in the constant k_{diss} whose growth rate is determined by the energy E_{abs} absorbed by the cluster and the constants k_1 and k_2. The temperature of the cluster increases monotonically until k_{diss}^{-1} becomes equal to the time passed from infrared excitation. At that time, the first molecule is evaporated. Each evaporated molecule carries the energy ΔE from the cluster, which leads to cooling and to the corresponding change in k_{diss}^{-1}. The new temperature T' of the cluster is determined from the energy balance

$$E_{clust}(T', n) = E_{clust}(T, n-1) + E_{mol}(T) + \Delta E, \quad (5)$$

where

$$E_{mol}(T) = \frac{7}{2}k_B T + E_{vib}(T)$$

is the energy of the evaporated molecule. Until relaxation processes continue, each next molecule is evaporated when k_{diss}^{-1} becomes equal to the time passed from the evaporation of the preceding molecule. The model ensures the calculation of the number of evaporated molecules and, correspondingly, the yield of dissociation for a given absorbed energy E_{abs}. Thus, the evolution of the temperature of the cluster and the yield of dissociation at times about several nanoseconds is determined by competition between the processes of heating because of relaxation processes and cooling at the successive evaporation of molecules.

3.2.3. Comparison of the model and experiment. Discussion of the results on the infrared dissociation of $[Fe(CO)_5]_n$ clusters. Figure 7 shows the results of the model calculation of I_{CO}, I_{bath1}, and I_{bath2} with the parameters N = 260, ΔE = 0.2 eV, T_0 = 85 K, and $k_1^{-1} = k_2^{-1}$ = 280 ps. The results of the experiment for the infrared pulse with $\Delta\nu_{IR}$ = 105 cm^{-1} are also shown. The listed set of the parameters allowed a good approximation of the experimental data not only for the experiment with $\Delta\nu_{IR}$ = 105 cm^{-1}, but also for the experiment with $\Delta\nu_{IR}$ = 185 cm^{-1} (see the solid line in Fig. 6).

In the presented calculation, the constants k_1 and k_2 were taken identical because we could not directly observe the evolution of the populations of the chosen states and directly measure them in our experiment. At the same time, these constants for $[Fe(CO)_5]_n$ clusters taking into account difference in the phase states are in satisfactory agreement with the reported data for iron pentacarbonyl in solvents. We attribute the difference of the characteristic relaxation time k_1^{-1} = 280 ps from the measured value τ_2 = 670 ps for free $Fe(CO)_5$ molecules to the interaction between molecules in the cluster.

The fitting effective cross sections in the reported calculation were σ_{fs}^{clust} (105 cm^{-1}) = 1.66 × 10^{-18} cm^2 and σ_{fs}^{clust}(185 cm^{-1}) = 0.95 × 10^{-18} cm^2. The effective cross section σ_{fs}^{clust}(105 cm^{-1}) differs from the above cross section for free molecules σ_{fs}^{mol} by about 13%. Consequently, the infrared absorption spectrum of clusters in the beam is wider than the infrared absorption spectrum of molecules in the gas phase at room temperature by about 13%. This is a quite reasonable

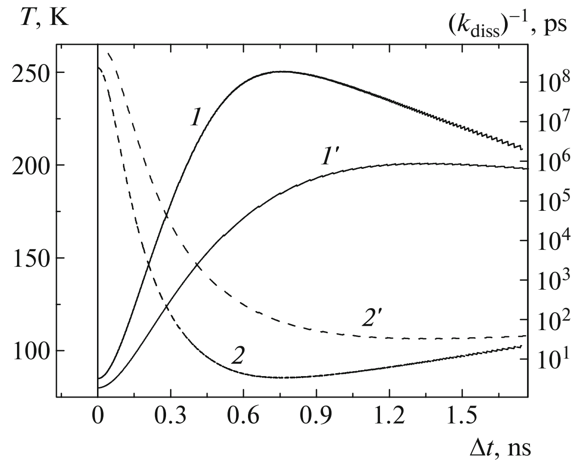

Fig. 9. Model calculation of the evolution of (solid curves) the temperature of clusters and (dashed curves) the decay rate of clusters $k_{\rm diss}^{-1}$ for $\Delta\nu_{\rm IR}$ = (*1*, *2*) 105 and (*1'*, *2'*) 185 cm^{-1}.

estimate for the width of the spectrum of clusters. In particular, the difference between the widths of the spectra for $(CF_3I)_n$ clusters and corresponding free molecules is about 28% [16]. It is noteworthy that $\sigma_{\rm fs}^{\rm clust}$(105 cm^{-1})/$\sigma_{\rm fs}^{\rm clust}$(185 cm^{-1}) ≈ 1.75 coincides with a similar ratio for free molecules.

The developed model makes it possible to obtain information not only on the degree of dissociation of clusters but also on the variation dynamics of the average size of the cluster N as a function of the delay between the pump and probe pulses, which is shown in Fig. 8 for the experiment with $\Delta\nu_{\rm IR}$ = 105 cm^{-1}. The size of the cluster with the initial size $N = 260$ at τ = 1.5 ns after the infrared pulse is N'(105 cm^{-1}) = 75 (see Fig. 8); i.e., the number of clustered molecules decreases by $\gamma \approx 71\%$. Thus, the dissociation of clusters is quite deep but only partial.

The average number of absorbed photons at $\sigma_{\rm fs}^{\rm clust}$(105 cm^{-1}) = 1.66 × 10^{-18} cm^2 and $\Phi_{\rm IR}$ = 32 mJ/cm^2 is $\bar{n} = \sigma_{\rm fs}\Phi_{\rm IR}/2h\nu \approx 0.67$ (for estimation, it was taken into account that the average energy density of infrared radiation in the focal region near the caustic waist is $\Phi_{\rm IR}/2$). This corresponds to the average absorbed energy $\bar{E}_{\rm vibr} \approx 1340$ cm^{-1}. Under the assumption that the binding energy of molecules in the cluster is ΔE = 0.2 eV ≈ 1600 cm^{-1}, the number of clustered molecules should decrease by $\gamma_{\rm total} \approx 84\%$. We believe that this is in good agreement with the model calculation taking into account that the process of dissociation of clusters at the delay 1.5 ns between laser pulses has not yet completed at that time.

The model allows the calculation of time profiles describing the dynamics of variation of the temperature of the cluster and the rate of its dissociation given by Eq. (4). The results of the calculation are shown in Fig. 9.

The minimum lifetime of the cluster with respect to decay in experiments with infrared radiation having the spectrum with the width $\Delta\nu_{\rm IR}$ = 105 cm^{-1} is approximately 5 ps, which corresponds to the maximum temperature $T_{\rm max} \approx 250$ K (line *1'* in Fig. 9). In the experiments with more broadband infrared radiation ($\Delta\nu_{\rm IR}$ = 185 cm^{-1}), the cluster absorbs a lower energy. As a result, the energy transferred to the intermolecular vibrations of the cluster, e.g., at 200 ps after the infrared pulse with $\Delta\nu_{\rm IR}$ = 105 cm^{-1} is transferred to these vibrations at 400 ps after the infrared pulse with $\Delta\nu_{\rm IR}$ = 185 cm^{-1} (cf. lines *1* and *1'* in Fig. 9). Thus, an increase in the temperature at more broadband radiation is slower, resulting in differences in the dynamics of the yield of free molecules in Fig. 6.

The evaporative ensemble concept used in the model makes it possible to estimate the quasi-equilibrium evaporation temperature of the cluster $T_{\rm ev}$ at which molecular decay occurs at a quite slow introduction of the energy to the cluster. This temperature can be determined from the relation $k_{\rm B}T_{\rm ev} \approx \Delta E/G$, where G is the dimensionless Gspann parameter, which hardly depends on the type of particles and is $G = 23.5 \pm 1.5$ [31]. The evaporation temperature of $[Fe(CO)_5]_n$ clusters with the binding energy ΔE = 0.2 eV is estimated as $T_{\rm ev} \approx 105$ K. The comparison of this $T_{\rm ev}$ value with $T_{\rm max}$ shows that clusters excited by femtosecond infrared radiation are overheated above the evaporation temperature, but this overheating does not result in noticeable deviations from the model mechanism of successive evaporation of molecules from the cluster.

4. CONCLUSIONS

The dynamics of photoprocesses induced by femtosecond infrared radiation in free $Fe(CO)_5$ molecules and their clusters owing to the resonant excitation of vibrations of CO bonds has been studied.

The technique of the multiphoton ionization of molecules by femtosecond ultraviolet radiation in combination with time-of-flight mass spectrometry has been used for the first time to probe the dynamics of processes in vibrationally excited molecules in a molecular beam. It has been found that the resonant excitation of vibrations of CO bonds in free $Fe(CO)_5$ molecules below their dissociation threshold results in an "instantaneous" (in a time of about 800 fs) significant change in the signal from the $Fe(CO)_5^+$ molecular ion. The subsequent relaxation of this signal, as well as the dependence of an induced change in this signal on the energy density $\Phi_{\rm IR}$ of the infrared pump pulse, has been studied.

The analysis of the results indicates that the infrared pulse selectively excites vibrational modes of the CO bond. A decrease in the multiphoton ionization cross section for the probe pulse as a result of this excitation leads to an initial decrease in the signal from $Fe(CO)_5^+$. It has been found that this signal further relaxes with two characteristic times—short, τ_1 (10 ± 2) ps, and long, τ_2 (670 ± 40) ps. Slow relaxation is due to the intramolecular relaxation of the energy localized in the vibrations of CO bonds to other vibrations of the molecule, and τ_2 is the characteristic time of this process. The time τ_1 is possibly associated with Berry pseudorotation.

The dynamics of the dissociation of $[Fe(CO)_5]_n$ molecular clusters owing to the resonant excitation of molecules in these clusters by femtosecond infrared radiation in the 5-μm range has been studied for the first time. The relaxation of the vibrational energy accumulated in molecules of the cluster results in an increase in the temperature of the cluster and in the subsequent evaporation of molecules, which were detected by a photoionization time-of-flight mass spectrometer. The yield of free molecules has been measured as a function of the delay time between the infrared pump pulse and the ionizing probe pulse.

The experiments with femtosecond infrared radiation with different spectral widths have indicated that the dynamics of the yield of free molecules from clusters is determined by the energy absorbed by the cluster. In this case, molecules in the cluster utilized only the "resonant" part of the radiation spectrum.

The infrared dissociation of clusters has been simulated within a two-step model of relaxation of the vibrational energy and good agreement with the experimental data has been obtained. The model implies that intramolecular relaxation transfers the energy from excited vibrations of CO bonds to low-frequency vibrations of a molecule itself and, then, to intracluster vibrations, resulting in the heating of the cluster and the subsequent evaporation of free molecules. The simulation has indicated that the characteristic time of energy relaxation from excited vibrations to low-frequency molecular modes is apparently close to the characteristic time of the redistribution of the vibrational energy from low-frequency molecular modes to intermolecular vibrations in the cluster and is approximately 280 ps. As was mentioned above, this time is in satisfactory agreement with the relaxation time for $Fe(CO)_5$ molecules in a solvent, where relaxation is also a two-step process.

The analysis of the simulated time profiles describing the evolution of the temperature of the cluster has indicated that clusters are overheated above the quasi-equilibrium evaporation temperature. Nevertheless, the subsequent dissociation of clusters is described within the mechanism of successive evaporation of molecules.

To conclude, we note that the model of the infrared dissociation of $[Fe(CO)_5]_n$ clusters used to analyze the experiment includes many semi-empirical fitting parameters. At the same time, it reproduces experimental dependences well. The predicted yields of free molecules are in agreement with independent estimates from the energy absorbed by clusters. For this reason, it gives a quite adequate picture of internal processes in $[Fe(CO)_5]_n$ clusters (energy redistribution, heating and decay of the cluster) induced by the excitation of clustered molecules by femtosecond infrared radiation.

ACKNOWLEDGMENTS

We are grateful to V.B. Laptev and S.V. Pigul'skii for the data on the absorption of femtosecond infrared radiation by $Fe(CO)_5$ molecules. This work was supported by the Russian Foundation for Basic Research (project no. 13-02-00260).

REFERENCES

1. V. S. Letokhov, *Nonlinear Selective Photoprocesses in Atoms and Molecules* (Nauka, Moscow, 1983) [in Russian].
2. V. N. Bagratashvili, V. S. Letokhov, A. A. Makarov, and E. A. Ryabov, *Multiple Photon Infrared Laser Photophysics and Photochemistry* (Harwood Academic, Chur, 1985).
3. D. W. Lupo and M. Quack, Chem. Rev. **87**, 181 (1987).
4. *Laser Spectroscopy of Highly Vibrationally Excited Molecules,* Ed. by V. S. Letokhov (Adam Hilger, Bristol, 1989).
5. K. K. Lehmann, G. Scoles, and B. H. Pate, Ann. Rev. Phys. Chem. **45**, 241 (1994).
6. D. J. Nesbitt and R. W. Field, J. Phys. Chem. **100**, 12735 (1996).
7. A. A. Makarov, A. L. Malinovsky, and E. A. Ryabov, Phys. Usp. **55**, 977 (2012).
8. H. S. Yoo, D. A. McWhorter, and B. H. Pate, J. Phys. Chem. A **108**, 131380 (2004).
9. A. L. Malinovsky, A. A. Makarov, and E. A. Ryabov, JETP Lett. **80**, 532 (2004).
10. A. L. Malinovsky, Yu. S. Doljikov, A. A. Makarov, et al., Chem. Phys. Lett. **419**, 511 (2006).
11. S. V. Chekalin, V. O. Kompanets, P. V. Koshlyakov, et al., J. Phys. Chem. A **118**, 955 (2014).
12. H. Pauly, *Atom, Molecule and Cluster Beams II* (Springer, New York, 2000).
13. *Atomic and Molecular Beam Methods,* Ed. by G. Scoles (Oxford Univ. Press, New York, 1988), Vol. 1.
14. *Atomic and Molecular Beam Methods,* Ed. by G. Scoles (Oxford Univ. Press, New York, 1992), Vol. 2.
15. U. Buck, J. Phys. Chem. **92**, 1023 (1988).
16. V. N. Lokhman, D. D. Ogurok, and E. A. Ryabov, Chem. Phys. **333**, 85 (2007).
17. V. N. Lokhman, D. D. Ogurok, and E. A. Ryabov, J. Exp. Theor. Phys. **108**, 727 (2009).

18. V. M. Apatin, V. N. Lokhman, D. D. Ogurok, et al., Eur. Phys. J. D **67**, 66 (2013).
19. D. G. Poydashev, V. N. Lokhman, V. O. Kompanets, et al., J. Phys. Chem. A **118**, 11177 (2014).
20. M. K. Au, P. A. Hackett, M. Humphries, and P. John, Appl. Phys. B **33**, 43 (1984).
21. L. Windhorn, T. Witte, J. S. Yeston, et al., Chem. Phys. Lett. **357**, 85 (2002).
22. V. M. Apatin, V. O. Kompanets, V. N. Lokhman, N.-D. D. Ogurok, D. G. Poydashev, E. A. Ryabov, and S. V. Chekalin, J. Exp. Theor. Phys. **115**, 567 (2012).
23. O. F. Hagena, Rev. Sci. Instrum. **63**, 2374 (1992).
24. L. Banares, T. Baumert, M. Berg, et al., J. Chem. Phys. **108**, 5799 (1998).
25. C. W. F. T. Pistorius and P. C. Haarhoff, J. Chem. Phys. **31**, 1439 (1959).
26. M. Dartiguenave, Y. Dartiguenave, and H. B. Gray, Bull. Soc. Chim. Fr. **12**, 4223 (1966).
27. S. Yan, M. T. Seidel, Z. Zhang, et al., J. Chem. Phys. **135**, 024501 (2011).
28. J. Cahoon, K. Sawyer, J. Schlegel, and C. Harris, Science **319**, 1820 (2008).
29. A. Laubereau and W. Kaiser, Rev. Mod. Phys. **50**, 607 (1978).
30. M. Banno, K. Iwata, and H. Hamaguchi, J. Chem. Phys. **126**, 204501 (2007).
31. J. Gspann, Z. Phys. D **3**, 143 (1986).
32. C. E. Klots, Z. Phys. D **21**, 335 (1991).
33. G. N. Makarov, Phys. Usp. **54**, 351 (2011).
34. C. E. Klots, Z. Phys. D **20**, 105 (1991).
35. A. A. Vostrikov and D. Yu. Dubov, J. Exp. Theor. Phys. **98**, 197 (2004).

Translated by R. Tyapaev