

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/267733524>

Ultrafast Dissociation Dynamics of $[\text{Fe}(\text{CO})_5]_n$ Clusters Induced by Femtosecond IR Radiation

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY A · OCTOBER 2014

Impact Factor: 2.69 · DOI: 10.1021/jp510130x · Source: PubMed

READS

16

5 AUTHORS, INCLUDING:



[Denis Poydashev](#)

Institute of Spectroscopy of the USSR Academ...

7 PUBLICATIONS 22 CITATIONS

[SEE PROFILE](#)



[Victor Kompanets](#)

Institute of Spectroscopy of the USSR Academ...

94 PUBLICATIONS 319 CITATIONS

[SEE PROFILE](#)



[S.V. Chekalin](#)

Institute of Spectroscopy of the USSR Academ...

231 PUBLICATIONS 1,170 CITATIONS

[SEE PROFILE](#)

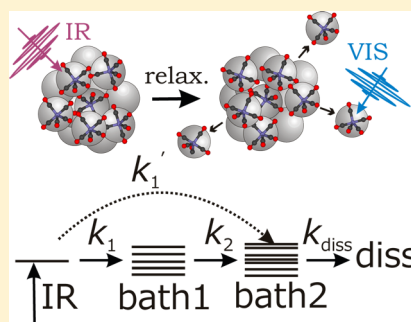
Ultrafast Dissociation Dynamics of $[\text{Fe}(\text{CO})_5]_n$ Clusters Induced by Femtosecond IR Radiation

Denis G. Poydashev,^{*,†,‡} Valery N. Lokhman,[†] Victor O. Kompanets,[†] Sergey V. Chekalin,[†] and Evgeny A. Ryabov^{*,†}

[†]Institute of Spectroscopy, Russian Academy of Sciences, Fizicheskaya street, 5, Troitsk, Moscow 142190, Russia

[‡]Moscow Institute of Physics and Technology (State University) Dolgoprudny, Moscow Region 141700, Russia

ABSTRACT: Using the femtosecond time-resolved infrared pump–visible probe technique, we have measured for the first time the ultrafast dissociation dynamics of $[\text{Fe}(\text{CO})_5]_n$ clusters induced by IR resonant excitation of $\text{C}\equiv\text{O}$ vibrational modes in the $5\text{-}\mu\text{m}$ region. Free $\text{Fe}(\text{CO})_5$ molecules formed as a result of the cluster dissociation have been ionized by the femtosecond laser radiation at $\lambda = 400\text{ nm}$ and have been detected with a time-of-flight mass-spectrometer. The temporal dependence of the yield of free molecules has been measured under different conditions of the IR laser excitation. We have proposed a model that describes well experimental results and makes it possible to calculate the temporal profile of the cluster temperature in terms of the concept of the evaporative ensemble. The rates of the intramolecular and intracluster vibrational relaxation in $[\text{Fe}(\text{CO})_5]_n$ clusters have been estimated.



INTRODUCTION

Molecular clusters are the subject of investigation in this work. Various properties of these nanosized particles have been considered in numerous studies. Some information on methods of obtaining clusters and on their properties and applications can be found, for example, in monograph,¹ reviews,^{2–4} as well as in references therein.

The main objective of this work is to study the excitation and subsequent decay (dissociation) of molecular clusters under the resonant action of IR radiation on vibrations of molecules forming clusters. Such investigations are closely related to the solution of a more wide circle of questions, which still remain comparatively little studied. This, in particular, is the question on the degree of localization of absorbed energy in a clusterized molecules and the rate of its relaxation into internal degrees of freedom of the cluster–intracluster relaxation. This is also the lifetime (with respect to the decay) of an excited cluster and the possibility of its considerable 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 type of binding) is comparatively low and usually does not exceed 0.5 eV .¹ Therefore, the absorption of even only one IR quantum, especially in the near-IR spectral range, is often sufficient for the dissociation of clusters. For a rather long time,⁵ this circumstance is used as one of widespread methods for measuring IR absorption spectra of clusters (infrared photodepletion spectroscopy). The IR spectra obtained this way (as a rule, using tunable IR lasers) were primarily applied to analyze the spatial structure of clusters.^{6–8} Apart from this, photodissociation spectra were also used to extract information on the intracluster dynamics, in particular, on cluster decay rates. For this purpose, data on the width of

spectra and on the shift of these spectra with respect to their position in free molecules were used.⁶ Thus, comparatively simple systems based on HF (DF) dimers and trimers and compounds of these molecules with noble gases were studied.^{9,10} Obtained values of the lifetime with respect to the decay of dimers lie in the range $\sim 0.5\text{--}30\text{ ns}$.¹⁰ More complex systems, clusters based on polyatomic molecules, such as C_2H_4 , CH_3OH , N_2H_4 , etc., were also investigated.^{5,11} These publications also present the obtained values of the lifetime, which lie in the range $\sim 10^{-6}\text{--}10^{-12}\text{ s}$. However, it is necessary to emphasize that the interpretation of results is not unambiguous in this case. This is related to the well-known problem of obtaining temporal information from spectral measurements under conditions of the unknown nature of the line broadening and/or contributions of different mechanisms to the homogeneous component of this width. In the case of clusters of polyatomic molecules, the homogeneous width can be contributed by a series of effects, such as intramolecular vibrational relaxation (IVR) in the excited “chromophore” molecule, relaxation of energy from the latter to intermolecular vibrations of the cluster (“intracluster” IVR), and decay of the cluster itself. Therefore, the most reliable method of determining the decay rate of clusters is the direct measurement of the kinetics of this process from the decay of clusters themselves and/or from the appearance of decay products, free particles. Precisely this approach is used in our investigations.

In our previous works, we investigated the IR dissociation of $(\text{CF}_3\text{I})_n$ clusters^{12,13} and $(\text{IF}_2\text{CCOF})_n$ clusters¹⁴ that occurred

Received: October 7, 2014

Revised: October 29, 2014

Published: October 31, 2014



as a result of the resonant excitation of vibrations of the C–F bond ($\sim 9.3 \mu\text{m}$) in both molecules and, in addition, of the C=O double bond ($\sim 5.3 \mu\text{m}$) in the IF₂CCOF molecule. These vibrations were excited by radiation of a pulsed CO₂ laser and its second harmonic, respectively. Particles were detected by the photoionization time-of-flight mass-spectrometry method. The time resolution in these experiments was $\sim 10^{-8}$ s¹³ and 10^{-7} s.¹⁴ Results of these experiments made it possible to conclude that all relaxation processes in examined clusters, including their monomolecular decay, occur much faster than within 10^{-8} – 10^{-7} s, and, on this time scale, the IR dissociation is, in fact, a stationary (or close to it) process of sequential evaporation of molecules. It seems that the dynamics of intracuster processes, including any nonstationary effects, can be observed only upon using picosecond or subpicosecond IR pulses.

In this work, we present first (to our knowledge) experimental online observation of the dissociation of molecular clusters under the action of resonant femtosecond IR radiation. As an object of study, clusters of the iron pentacarbonyl molecule, [Fe(CO)₅]_n, were chosen. These molecules have a very strong absorption in the range of $\sim 5 \mu\text{m}$, which is caused by stretching vibrations (ν_6 and ν_{10} modes) of the C≡O bond. The IR multiphoton dissociation of free Fe(CO)₅ molecules caused by nanosecond¹⁵ and femtosecond¹⁶ pulses was observed in the literature. In this work, we present results of our investigations of the dissociation of clusters of Fe(CO)₅ molecules exposed to femtosecond IR radiation. Results obtained and their discussion are presented below.

■ EXPERIMENTAL SECTION

Measurements were performed on an experimental setup that was described in detail previously.¹⁷ Here, we present only a brief description of the measurement conditions. [Fe(CO)₅]_n clusters were generated by the gas-dynamic cooling of the gas upon its supersonic expansion from a pulsed nozzle (General Valve, $d = 0.8 \text{ mm}$; pulse duration, 300 μs). The nozzle stagnation pressure can be varied in the range $P_0 = 0$ –500 kPa. In our experiments, Fe(CO)₅ clusters were produced using a mixture of these molecules with argon in a proportion of Fe(CO)₅:Ar = 1:50 at a total stagnation pressure of 200 kPa. The average size N of clusters can be estimated using the Hagen relation¹⁸ $N \approx (\Gamma^*)^a$, where Γ^* is a dimensionless parameter, which is linearly related to the source particle density n_0 : $\Gamma^* \approx n_0$. It follows from our measurements that n_0 is nearly proportional to the stagnation pressure P_0 : $n_0 \approx P_0$. Finally, we can write the following expression for N : $N = N_{\text{cr}}(P_0/P_{\text{cr}})^a$ (where P_{cr} is a certain critical value of the stagnation pressure at which an efficient formation of stable clusters increases significantly starting from some critical cluster size N_{cr}). According to the results of our measurements, the value of P_{cr} for the Fe(CO)₅ + Ar gas mixture, which we used, is $P_{\text{cr}} \approx 30 \text{ kPa}$. As for the parameters N_{cr} and a , we chose $N_{\text{cr}} = 7.5$ for the former of them,¹² and, taking into account that the exponent a in our previous investigations with (CF₃I)_n clusters¹³ was in the interval $1.7 < a < 2.3$, we chose the value of the parameter a to be 2.0. Although such an estimate of the cluster average size is rather rough, we believe that it gives the correct idea about the value of N under our experimental conditions. In particular, under the pressure of $P_0 = 200 \text{ kPa}$, we deal with clusters whose average size N is estimated to be between 250 and 300. It should be noted here that the average

size N of clusters could also be extracted from the model of cluster dissociation, which is proposed in this Article (see text), and this value of N is in good agreement with the estimates provided above.

A molecular/cluster beam was formed with a skimmer (Beam Dynamics; model 1; $D_s = 0.49 \text{ mm}$). This particle beam was directed to a chamber of a home-built linear time-of-flight mass spectrometer (TOF MS). The instrument limitations allowed us to detect singly ionized ion fragments with mass units of up to 1400 amu.

Radiation from a commercially available Ti:sapphire laser system (Spectra-Physics, 1 kHz, 800 nm, 50 fs) was split into two channels. One of them was used to pump an optical parametric amplifier (Light Conversion TOPAS-C). Resultant signal and idler pulses were subsequently routed to a noncollinear difference frequency generator (Light Conversion nDFG) to generate tunable ultrafast IR pulses. Generated IR pulses with a pulse energy of up to $\sim 17 \mu\text{J}$ were centered at 2000 cm^{-1} and used as pump pulses to populate C≡O stretching modes. Because we used a KCl lens with a focal length of $f = 13.5 \text{ cm}$, the energy fluence Φ_{IR} of these p-polarized pulses was estimated to be not higher than 32 mJ/cm^2 . Pulses with the spectral full width at half-maximum (fwhm) of ~ 105 and of 185 cm^{-1} were used in our experiments (see below), with these pulses being controlled by a monochromator (with a 5 cm^{-1} bandpass). The duration of IR pulses with a 185 cm^{-1} bandwidth was about 160 fs, while that of pulses with a 105 cm^{-1} bandwidth was about 220 fs. The second channel of the master laser was used to generate s-polarized visible femtosecond pulses at $\lambda = 400 \text{ nm}$ (the second harmonic output of a U-Oplaz Tripler with a $\sim 100 \text{ fs}$ pulse duration), which were focused by a CaF₂ lens with $f = 30 \text{ cm}$ and were used as a probe for the multiphoton ionization of particles under study. The probe pulses propagate at an angle of about 2° with respect to the direction of the pump IR pulses. The spatial positions of the spots of IR pump pulses and visible probe pulses were controlled by a Pyrocam III pyroelectric camera to ensure the necessary precise overlapping between them.

■ MEASUREMENTS AND RESULTS

The multiphoton ionization of free Fe(CO)₅ molecules by femtosecond laser radiation at $\lambda = 400 \text{ nm}$ was reliably detected beginning from the values of the fluence $\Phi > 0.15 \text{ J/cm}^2$. Figure 1a shows a typical time-of-flight spectrum that was obtained at a laser pulse fluence of not higher than 0.3 J/cm^2 . The mass spectrum of ionic products exhibits peaks of Fe(CO)_{0–5}⁺, as well as comparatively small amounts of CO⁺ and C⁺ ions. The fragmentation pattern in Figure 1a depends strongly on the laser wavelength, the laser intensity, and the duration of the laser pulse. Ultrafast photodissociation dynamics of Fe(CO)₅ in the gas phase by femtosecond laser pulses at $\lambda = 400 \text{ nm}$ has been studied by Bañares et al.¹⁹ We note that, unlike the ionization by nanosecond pulses, ionic products of which contain only Fe⁺ ions,¹⁹ the mass spectrum in Figure 1a has a peak of the molecular ion, which ensures the possibility of a rather easy detection of free molecules in the beam.

Upon supersonic expansion of a Fe(CO)₅ + Ar mixture out of a pulsed nozzle, beginning from certain values of the stagnation pressure P_0 , these molecules clusterize. A typical spectrum of ionic products that are formed upon ionization of [Fe(CO)₅]_n clusters by the femtosecond laser radiation at $\lambda = 400 \text{ nm}$ is shown in Figure 1b. Several characteristic features

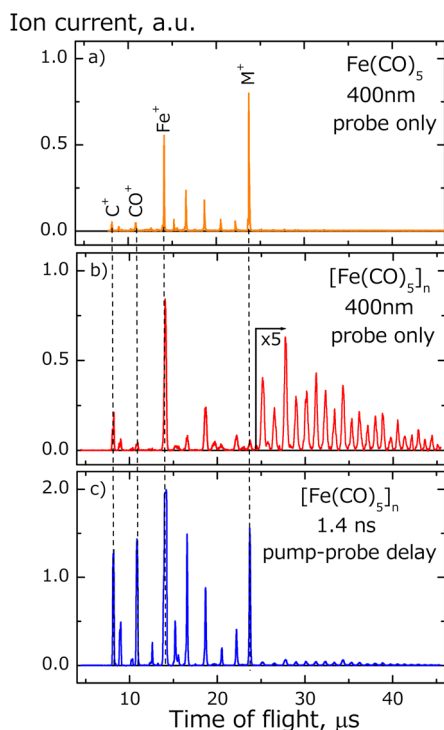


Figure 1. (a) Time-of-flight spectrum of a molecular beam (pulse duration, $\sim 200 \mu\text{s}$; M^+ denotes molecular ions); (b) time-of-flight spectrum of a cluster beam (pulse duration, $\sim 300 \mu\text{s}$; the signal from clusters is magnified 5-fold); and (c) time-of-flight spectrum of a cluster beam obtained in the pump–probe regime with a 1.4 ns pump–probe delay.

should be noted. First, the mass spectrum contains a “comb” of peaks from ions with masses exceeding the mass of the $\text{Fe}(\text{CO})_5^+$ molecular ion. These ionic peaks correspond to fragments of clusters, their structure is $\text{Fe}_x(\text{CO})_y^+$, and they are spaced from each other by the mass of one CO ligand (28 amu). Their occurrence in the mass spectrum allows one to easily detect clusters in the beam against the background of signals from monomers. Second, upon ionization of clusters themselves at this wavelength, a rather small amount of formed $\text{Fe}(\text{CO})_5^+$ ions can be observed in the mass spectrum, which makes it possible to detect molecules that are formed upon decay of clusters under the action of the IR radiation. A detailed analysis of the shape of the mass peak of $\text{Fe}(\text{CO})_5^+$ ions in the case of ionization of clusters shows that it is contributed both by ions that are formed upon the ionization of clusters and by ions that are formed as a result of the ionization of the monomeric component in the initial cluster beam. This “background” signal was taken into account in subsequent measurements and analysis of the formation kinetics of free molecules upon IR dissociation of clusters.

As was mentioned above, $\text{Fe}(\text{CO})_5$ molecules have a strong and fairly isolated vibration of the $\text{C}\equiv\text{O}$ bond in the $5 \mu\text{m}$ region, to resonance with which the femtosecond pump radiation was tuned. Although the accurate absorption spectrum of $[\text{Fe}(\text{CO})_5]_n$ clusters is unknown to us, on the basis of the IR spectra of iron pentacarbonyl in the gas, liquid, and solid phases,²⁰ we can assume that the IR pulse fwhm of 105 cm^{-1} (and 185 cm^{-1} all the more) should overlap possible shift and broadening of the cluster absorption spectrum.

Under the action of the IR radiation on clusters, a significant increase in the signal from the molecular ion was detected.

Simultaneously we observed some decrease in the signal from ions, which have the purely cluster nature, with masses higher than the mass of the $\text{Fe}(\text{CO})_5^+$ molecular ion. Figure 1c shows a mass spectrum that was obtained at a delay of 1.4 ns between the IR pump pulse ($\Phi_{\text{IR}} = 32 \text{ mJ/cm}^2$) and ionizing probe pulse. It should be noted that the mass spectrum presented in Figure 1b changes weakly as the pressure P_0 of the mixture $\text{Fe}(\text{CO})_5 + \text{Ar}$ is lowered from 200 to 90 kPa (provided that only the central region of the beam is subjected to ionization), although the average size N of clusters that are formed in this case should change significantly. It seems that this occurs because the sensitivity of the mass spectrometer affects considerably the amplitudes of ionic peaks with masses higher than 300 amu (time-of-flight $> 30 \mu\text{s}$). Observed ionic peaks are a result of a rather deep fragmentation of clusters, which takes place upon their ionization, and the signal from them varies weakly over a rather wide range of variation of the average cluster size N . Therefore, even though the action of the IR radiation somewhat decreases the signal from ions that have the purely cluster nature, the dynamics of this decrease does not reflect directly the change in the average size of clusters. For this reason, it is the increase in the signal from monomers that serves as a good marker of the decay process of clusters.

Kinetic curves of the yield of $\text{Fe}(\text{CO})_5^+$ molecular ions in relation to the delay time between the pump and probe pulses, which reflect the appearance of free molecules as a result of the cluster decay induced by the femtosecond IR radiation, are presented in Figure 2.

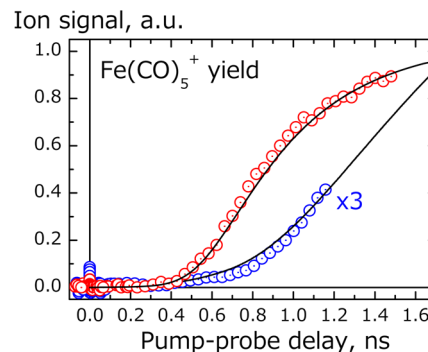


Figure 2. $\text{Fe}(\text{CO})_5^+$ pump–probe traces obtained with an IR pulse bandwidth of 105 cm^{-1} and $\Phi_{\text{IR}} = 32 \text{ mJ/cm}^2$ (red \circ) and with a bandwidth of 185 cm^{-1} and $\Phi_{\text{IR}} = 25 \text{ mJ/cm}^2$ (blue \circ , the signal is magnified 3-fold). Solid curves are calculations in terms of a two-stage model (see text).

The corresponding data were obtained in two different experiments that were performed with two different widths of the IR radiation spectrum. Whereas upon the use of the more narrowband radiation (red \circ in Figure 2), a rapid growth of the signal changes with the passage to a saturation at times $> 1 \text{ ns}$ beginning from the delay of $\sim 400 \text{ ps}$, upon the use of the radiation with a wider spectrum (blue \circ in Figure 2), only the initial stage of the signal growth is observed. A characteristic feature of the obtained curves is the occurrence of a certain “induction time”, which indicates that the dissociation of clusters with the formation of free molecules is preceded by relaxation processes, the characteristic scale of the time of occurrence of which is $\sim 10^{-10} \text{ s}$. It can be seen that, in the case of the IR radiation with a broader spectrum, the induction time is somewhat longer than in the case of the excitation by the

more narrowband radiation. In our opinion, such a behavior is most likely a result that the amount of energy absorbed by the cluster depends on the bandwidth of the IR laser pulse. In addition, the values of the energy fluence Φ_{IR} were somewhat different in these experiments, being $\Phi_{\text{IR}} = 32 \text{ mJ/cm}^2$ in the case of the bandwidth of 105 cm^{-1} and 25 mJ/cm^2 for the bandwidth of 185 cm^{-1} .

DISCUSSION AND MODEL

An analysis of the obtained experimental results allows us to conclude that the dissociation of $[\text{Fe}(\text{CO})_5]_n$ clusters upon their excitation by femtosecond IR radiation can be considered as a process of a sequential evaporation of free molecules from these clusters in the course of their “heating” as a result of the intramolecular and intracluster relaxation of the initial molecular excitation produced by the IR pump pulse. On the basis of this idea, we developed a model that describes the measured behavior of the ion signal from the generated monomeric component of the particle beam as a function of the delay time between the IR pump pulse and the ionizing probe pulse.

In terms of this model, it is assumed that the behavior of the signal of the $\text{Fe}(\text{CO})_5^+$ yield is determined by the initial average cluster size N , the initial cluster temperature T_0 (both of which depend on the cluster generation conditions), the energy ΔE that is required to evaporate a molecule in the regime of sequential evaporation mentioned above, the effective IR absorption cross section σ , and the relaxation rate constants.

As will be shown below, under our experimental conditions, clusters dissociate only partially, and the average cluster size decreases in the course of this partial dissociation from $N = 260$ to $N = 75$ (calculation data for the experiment with the IR bandwidth of 105 cm^{-1}). To simplify model calculations, we replaced the evolution of the initial size distribution of clusters due to their decay by the evolution of clusters of a fixed average size N , because, most likely, in the course of this variation of the average size, the shape of the distribution will hardly be considerably distorted.

In our model, the internal energy of a cluster that consists of n molecules is taken in the general form as

$$E_{\text{clust}}(T, n) = (3n - 6)k_{\text{B}}T + n \cdot E_{\text{vib}}(T) \quad (1)$$

where the first term is an average energy of intermolecular vibrational modes in the cluster, the second term is the internal vibrational energy of n individual molecules, and T is the temperature of the cluster in a state that is close to the equilibrium state. Indeed the temperature in the first and the second terms on the right side will be fully equal only after relaxation is completed. Inequality of these temperatures will mostly affect the model signal during the first 300 ps before the absorbed energy is redistributed by IVR. Significant signal growth was observed at delay times higher than 400 ps, where the agreement between experiment and model in Figure 2 is fairly good. The value of E_{vib} was calculated on the basis of the known molecular frequencies of $\text{Fe}(\text{CO})_5$. Under the action of the femtosecond IR radiation, the cluster instantaneously (as compared to relaxation times) absorbs the energy E_{abs} , which can be determined from the expression

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

where n is the size of the cluster, and σ is the absorption cross section per one molecule. Windhorn et al.¹⁶ measured the number of quanta of the femtosecond IR radiation in the range

of $5 \mu\text{m}$ that were absorbed by the $\text{Fe}(\text{CO})_5$ molecule (in the gas phase) and found that the value of the effective cross section is $\sigma_{\text{fs}}^{\text{mol}} \approx 1.5 \times 10^{-18} \text{ cm}^2$. The bandwidth of pulses of a femtosecond laser, 100 cm^{-1} , is approximately 10 times broader than the bandwidth of the multiphoton absorption band of the molecule measured by a narrowband frequency-doubled CO_2 laser at room temperature. This narrowband absorption spectrum had a maximum¹⁵ of $\sigma_{\text{ns}}^{\text{mol}} \approx 2 \times 10^{-17} \text{ cm}^2$. Therefore, Windhorn and co-workers¹⁶ concluded that the ratio of the absorption cross sections measured with the femtosecond and nanosecond pulses, $\sigma_{\text{fs}}^{\text{mol}}/\sigma_{\text{ns}}^{\text{mol}}$, is precisely the ratio of the IR absorption bandwidth of the molecule to the spectral bandwidth of the femtosecond laser pulse, and the molecule seems to utilize only the resonant part of the energy fluence in the bandwidth available. Taking into account this circumstance, in our calculations for the experiments with the different bandwidths of the IR radiation spectrum, the ratio $\sigma_{\text{fs}}^{\text{clust}}(105 \text{ cm}^{-1})/\sigma_{\text{fs}}^{\text{clust}}(185 \text{ cm}^{-1})$ should be ~ 1.76 .

As soon as a certain amount of the IR radiation energy was absorbed, we can point out two possible pathways for its further utilization. The stored energy can relax either directly into intermolecular vibrations of the cluster, or there is a two-stage relaxation process of the absorbed energy: initially, into low-frequency vibrations of the $\text{Fe}(\text{CO})_5$ molecule, and then into intermolecular vibrations, after which molecules sequentially evaporate from the cluster. Since pioneer works by Kaiser and Laubereau (see review²¹), which were devoted to the dynamics of the vibrational relaxation in solutions, experiment shows that, initially, the absorbed energy experiences an intramolecular relaxation from excited high-frequency vibrations of molecules within a time period of a few picoseconds; after that, a slower process of the energy transfer to the solvent takes place. However, it should be noted that $\text{Fe}(\text{CO})_5$ is a rather specific molecule, which has an anomalously long characteristic time of intramolecular relaxation in the gas phase. Upon excitation of CO vibrations by femtosecond radiation in the range of $5 \mu\text{m}$, this time is $\sim 1 \text{ ns}$,²² which can substantially restrict the rate of the energy transfer to intermolecular vibrations of the cluster. In our model, we considered both pathways of the energy utilization. Their comparative analysis is presented below.

To describe the energy relaxation processes, we will use the rate equation approximation. In our two-stage model (see Figure 3), the $\text{C}\equiv\text{O}$ stretching vibrational energy is initially

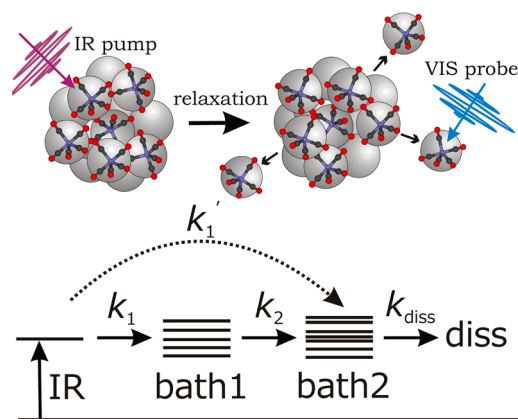


Figure 3. Schematic diagram of the energy flow in the course of the cluster dissociation. Two relaxation schemes are shown: single-bath-mode scheme (k_1') and sequential two-bath-mode scheme (k_1 and k_2).

redistributed mostly into $\text{Fe}(\text{CO})_5$ low-frequency modes ("bath1") with a rate constant k_1 . A further redistribution of the energy into intermolecular modes with a rate constant k_2 then follows ("bath2"). Finally, clusters in the "bath2" mode dissociate with a rate constant k_{diss} . A system of eqs 3 and initial conditions 3' describes the temporal dynamics of the vibrational energy redistribution:

$$\begin{cases} \dot{I}_{\text{C}\equiv\text{O}}(t) = -k_1 I_{\text{C}\equiv\text{O}} \\ \dot{I}_{\text{bath1}}(t) = k_1 I_{\text{C}\equiv\text{O}} - k_2 I_{\text{bath1}} \\ \dot{I}_{\text{bath2}}(t) = k_2 I_{\text{bath1}} \end{cases} \quad (3)$$

$$I_{\text{C}\equiv\text{O}}(0) = 1$$

$$I_{\text{bath1}}(0) = I_{\text{bath2}}(0) = 0 \quad (3')$$

where I means the population of corresponding levels. If the relaxation is single-stage, only two equations (the first and the third one) remain in system 3 with the rate constant k_1' instead of k_1 and k_2 .

To determine the dissociation rate constant k_{diss} , we will proceed from the ideas that were proposed by Gspann²³ and were further developed by Klotz²⁴ (see also review²⁵). The authors of these works introduced the concept of an "evaporative ensemble" formed by metastable clusters as a result of cooling due to the sequential evaporation of particles. As follows from these works, the expression for the rate constant of dissociation has the form:

$$k_{\text{diss}} = A \exp\left(-\frac{\Delta E}{k_{\text{B}}T}\right) \quad (4)$$

where ΔE is the energy that is required to evaporate a single particle, T is the evaporation temperature of the cluster, and A can be estimated²⁶ from the expression $A(n) = 3 \times 10^{13} n^{2/3} \exp[6.0/n^{1/3}]$, which takes into account the cluster size n ($A = 3.13 \times 10^{15} \text{ s}^{-1}$ for $n = 260$). In fact, ΔE is also the function of the cluster size, $\Delta E(n) = \Delta E \cdot f(n)$, where the model function of the form $f(n) = (1 - \exp(-n/13))$ can be used.²⁷ However, the expression for $f(n)$ appreciably affects the value of ΔE only for small clusters; therefore, in modeling, the value of ΔE was taken to be constant.

Consequently, as a result of relaxation processes, the energy that was stored in CO vibrations of molecules is eventually redistributed into intermolecular vibrations of the cluster. This leads to an increase in the quasi-equilibrium temperature of the cluster, which is calculated by formula 1. In this case, to simplify calculations, the temperature values in the first and second terms on the right-hand side of 1 were considered to be the same. In turn, an increase in the temperature leads to an increase in the constant k_{diss} , the growth rate of which is determined by the energy E_{abs} absorbed by the cluster and the constants k_1 and k_2 (or only the constant k_1' in the case of the single-stage relaxation). The temperature of the cluster increases monotonically until the value of k_{diss}^{-1} becomes equal to the period of time that elapsed since the moment of the IR excitation. At this moment, the first molecule evaporates. Each evaporated molecule carries the energy ΔE away from the cluster, which leads to its cooling. The new temperature T' of the cluster is determined from the energy balance:

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

where $E_{\text{mol}}(T) = (7/2)k_{\text{B}}T + E_{\text{vib}}(T)$ is the energy of the evaporated molecule where the first term contains $2k_{\text{B}}T$ for the average kinetic energy of the evaporating particle²⁸ and $(3/2)k_{\text{B}}T$ for its rotational energy. Further evolution of the temperature of the cluster on the time scale of a few nanoseconds is determined by the competition between the processes of heating due to relaxation processes and cooling as a result of sequential evaporation of molecules.

Figure 4 shows the time profiles of $I_{\text{C}\equiv\text{O}}$, I_{bath1} , and I_{bath2} that were calculated in terms of the two-stage and single-stage

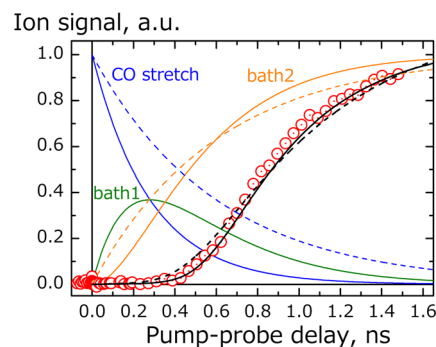


Figure 4. Normalized temporal profiles describing the vibrational energy redistribution and the dissociation yield of clusters. Solid and dashed curves are obtained by two- and single-stage model calculations, respectively. Experimental data for IR pulses with a bandwidth of 105 cm^{-1} (red \circ) are normalized to the maximum value of the calculated signal yield.

models (solid and dashed curves, respectively) along with the experimental data for the case of IR pulses with a bandwidth of 105 cm^{-1} . The model calculations were performed using the following parameters: $N = 260$, $\Delta E = 0.2 \text{ eV}$, $T_0 = 85 \text{ K}$, and $(k_1)^{-1} = (k_2)^{-1} = 280 \text{ ps}$ in the case of the two-stage model and $(k_1')^{-1} = 600 \text{ ps}$ for the single-stage model. We note that this set of parameters allowed us to approximate well the experimental data that were obtained not only with the IR radiation bandwidth of 105 cm^{-1} , but also with the IR bandwidth of 185 cm^{-1} (see the solid curves in Figure 2). We believe that the relaxation process in solutions of molecules is the closest to the considered process of the relaxation in the cluster. Typically, CO vibrations of organometallic complexes in different solutions relax on a time scale from tens to hundreds of picoseconds (see, e.g., vibrational energy transfer study²⁹). For $\text{Fe}(\text{CO})_5$, these modes relax on a time-scale of $\sim 150 \text{ ps}$ (see supporting online material³⁰) by transferring energy to lower frequency modes of the molecule and, ultimately, to the solvent, which is the standard behavior for the vibrational relaxation in the condensed phase. On the whole, taking into account differences in the phase state, the characteristic times of the vibrational relaxation in $[\text{Fe}(\text{CO})_5]_n$ clusters that we obtained agree rather well with corresponding data from the literature for iron pentacarbonyl in different solvents.

The fitting values of the effective cross sections were $\sigma_{\text{fs}}^{\text{clust}}(105 \text{ cm}^{-1}) = 1.66 \times 10^{-18} \text{ cm}^2$ and $\sigma_{\text{fs}}^{\text{clust}}(185 \text{ cm}^{-1}) = 9.5 \times 10^{-19} \text{ cm}^2$. The value of the effective cross section $\sigma_{\text{fs}}^{\text{clust}}(105 \text{ cm}^{-1})$ differs from that measured by Windhorn et al.¹⁶ for free molecules approximately by 11%. Consequently, the width of the IR absorption spectrum of clusters in the beam exceeds the width of the IR absorption spectrum of molecules in the gas phase at room temperature by $\sim 11\%$. In our opinion, the

obtained value is a quite reasonable estimate of the width of the spectrum of clusters; in particular, in the case of $(\text{CF}_3\text{I})_n$ clusters, the demonstrated¹² difference between the widths of the spectra of clusters and free molecules is $\sim 28\%$. Note that the value of the ratio $\sigma_{\text{fs}}^{\text{clust}}(105 \text{ cm}^{-1})/\sigma_{\text{fs}}^{\text{clust}}(185 \text{ cm}^{-1})$ was ~ 1.75 , which supports the idea that was proposed previously.¹⁶

As can be seen from Figure 4, the solid black curve, which was obtained for the case of the two-stage relaxation, approximates the experimental data somewhat better than the single-stage model. However, in our case, it is difficult to precisely determine the relaxation rates k_1 and k_2 , because we cannot observe experimentally the evolution of the population of low-frequency modes of the $\text{Fe}(\text{CO})_5$ molecule ("bath1" in Figure 4). For this reason, the values of k_1 and k_2 in model calculations were taken to be the same. This assumption does not follow directly from experiment; however, the modeling of the energy relaxation by precisely the two-stage mechanism made it possible to obtain the best agreement with experimental data. Moreover, if we consider the analytical solution of system 3 with initial conditions 3', we will obtain the following expression for I_{bath2} :

$$I_{\text{bath2}} = \begin{cases} 1 - e^{-k_1 t} - k_1 t \cdot e^{-k_1 t} & \text{if } k_1 = k_2 \\ 1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1} & \text{if } k_1 \neq k_2 \end{cases} \quad (6)$$

If we assume now that the relaxation rates k_1 and k_2 differ little from each other, that is, $k_1 = k + \Delta$ and $k_2 = k - \Delta$, the expression for I_{bath2} in the case of different rates will take the form:

$$I_{\text{bath2}} = 1 - e^{-kt} \frac{e^{\Delta t} + e^{-\Delta t}}{2} - k \cdot e^{-kt} \frac{e^{\Delta t} - e^{-\Delta t}}{2\Delta} \quad (7)$$

Retaining only the first two terms in the expansions of the exponentials $e^{\Delta t}$ and $e^{-\Delta t}$, we can easily see that, if $k_1 = k_2$, expression 7 is reduced to expression 6 for I_{bath2} . The calculation shows that, at $\Delta = k/4$ ($k_1 = 210 \text{ ps}$, $k_2 = 350 \text{ ps}$), a maximal relative deviation of the values of I_{bath2} calculated by formulas 7 and 6 for the case $k_1 = k_2$ is about 6%. Therefore, if the relaxation rates k_1 and k_2 are close to each other, then the temporal profile of I_{bath2} , which determines the growth rate of the cluster temperature in our model, does not vary strongly as compared to the profiles for $I_{\text{C}\equiv\text{O}}$ and I_{bath1} . Therefore, we can conclude that, in the case of the excitation of $[\text{Fe}(\text{CO})_5]_n$ clusters by the femtosecond IR radiation, the characteristic time of the energy relaxation from excited CO vibrations to low-frequency modes of the molecule is close to the characteristic time of the vibrational energy redistribution from low-frequency modes of the molecule to intermolecular vibrations of the cluster. At the same time, as the modeling shows, in our case, the energy relaxation can also be considered as a single-stage process; then the quantity $(k_1')^{-1} = 600 \text{ ps}$ will be a good estimate for its characteristic time.

The developed model makes it also possible to obtain information on the degree of dissociation of clusters. Assuming that the initial size of the cluster is $N = 260$, in the experiment with the IR pulse bandwidth of 105 cm^{-1} , the size of the cluster in $\tau = 1.5 \text{ ns}$ after the IR pulse will become $N'(105 \text{ cm}^{-1}) = 75$; that is, the number of clusterized molecules will decrease by $\gamma \approx 71\%$. Therefore, although the dissociation of clusters is rather deep, it is still only partial. Let us now consider energetic estimates. Taking $\sigma_{\text{fs}}^{\text{clust}}(105 \text{ cm}^{-1}) = 1.66 \times 10^{-18} \text{ cm}^2$ and Φ_{IR}

$= 32 \text{ mJ/cm}^2$, we find that the average number of absorbed quanta is $m = \sigma_{\text{fs}} \Phi_{\text{IR}} / h\nu \approx 0.67$, and, correspondingly, the average absorbed energy is $\sim 1340 \text{ cm}^{-1}$. Assuming that the binding energy of molecules in the cluster is $\Delta E = 0.2 \text{ eV} \approx 1600 \text{ cm}^{-1}$, we find that the number of clusterized molecules should decrease by $\gamma_{\text{total}} \approx 84\%$. We believe that this is in rather good agreement with the model calculation in view of the fact that, at the delay of $\tau = 1.5 \text{ ns}$ between the laser pulses, the process of the dissociation of clusters has not yet completed by this moment of time.

Apart from the degree of dissociation of clusters, the model makes it also possible to obtain temporal profiles that describe the dynamics of variation of the temperature of the cluster and the rate of its dissociation, which is defined by expression 4. They are presented in Figure 5 for the case of the two-stage

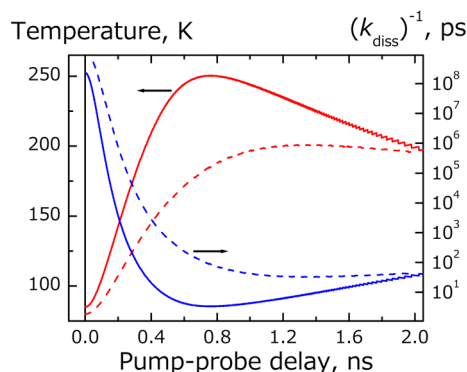


Figure 5. Model temporal profiles describing the temperature of cluster (red curves) and the decay rate k_{diss} (blue curves) determined by formula 4. Solid and dashed curves are calculations in terms of the two-stage model for the IR pulse bandwidth of 105 and 185 cm^{-1} , respectively.

model. A minimal lifetime of the cluster with respect to its decay in experiments in which the IR radiation spectrum with a width of 105 cm^{-1} was used is $\sim 5 \text{ ps}$, which corresponds to a maximum in the temperature of $T_{\text{max}} \approx 250 \text{ K}$ (see the solid curves in Figure 5). In experiments with the more broadband IR radiation (185 cm^{-1}), the cluster absorbs a smaller amount of energy. This leads to the situation that, at the same relaxation rate, the amount of energy that is involved in intermolecular vibrations of the cluster in the case of 105 cm^{-1} , for example, in 200 ps after the IR pulse, in the case of 185 cm^{-1} , will be involved in these vibrations only in $\sim 400 \text{ ps}$ (see the solid and dashed red curves in Figure 5). Therefore, in the case of the more broadband radiation, the temperature grows slower, precisely which determines differences in the dynamics of the yield of free molecules in Figure 2.

The concept of the evaporative ensemble,²⁴ which we use in modeling, makes it possible to estimate the quasi-equilibrium evaporation temperature T_{ev} of the cluster at which the monomolecular decay takes place at a rather slow delivery rate of the energy to the cluster. This temperature can be determined from the relation $k_{\text{B}} T_{\text{ev}} \approx \Delta E / G$, where G is the dimensionless Gspann parameter,²⁴ which is almost independent of the material and is equal to $G = 23.5 \pm 1.5$. In the case of $[\text{Fe}(\text{CO})_5]_n$ clusters with $\Delta E = 0.2 \text{ eV}$, we estimate the evaporation temperature as $T_{\text{ev}} \approx 105 \text{ K}$. Comparison of the obtained value of T_{ev} with that of T_{max} shows that, in the case of the excitation by the femtosecond IR radiation, "overheating" of clusters with respect to the value of the evaporation

temperature takes place, which, nevertheless, does not lead to any significant deviations from the model mechanism of sequential evaporation of molecules from the cluster.

Independent data on variation of the temperature of the cluster can be obtained, for example, from the analysis of the dynamics of variation of the velocity distribution of molecules that are formed as a result of the decay of clusters (see, e.g., previous results¹³). The use of the linear type time-of-flight mass spectrometer makes it possible to retrieve the distribution over the projection of the velocity of the detected ion onto the axis of the mass spectrometer from the width of the mass peak. However, for the reliable determination of the cluster temperature by this method, further investigations are required.

CONCLUSION

In this work, we have studied for the first time the dissociation dynamics of $[\text{Fe}(\text{CO})_5]_n$ molecular clusters as a result of the resonant excitation of their molecules by femtosecond IR radiation in the range of $5\ \mu\text{m}$. Relaxation of vibrational energy stored by cluster molecules leads to an increase in the temperature of the cluster and subsequent evaporation of molecules, which were detected with a photoionization time-of-flight mass spectrometer.

Experiments with femtosecond IR radiation with different widths of the spectrum have allowed us to conclude that the dynamics of the yield of free molecules from clusters is determined by the magnitude of the energy absorbed by the cluster, with the molecules in the cluster utilizing only the “resonant” part of the radiation spectrum.

We have modeled the IR dissociation of clusters in terms of two- and single-stage models of the vibrational energy relaxation. In the first case, it has been assumed that, as a result of the intramolecular relaxation (IVR), the energy is transferred from excited CO vibrations to low-frequency vibrations of the molecule itself and then is transferred to intracuster vibrations, which leads to heating of the cluster and subsequent evaporation of free molecules. In the second case, the energy is transferred from $\text{C}\equiv\text{O}$ vibrations to the cluster through the single stage. We believe that the two-stage model describes the relaxation process in $[\text{Fe}(\text{CO})_5]_n$ clusters more adequately. It ensures a more precise fitting of experimental data, with the characteristic time of the energy relaxation from excited CO vibrations to low-frequency modes of the molecule being close to the characteristic time of the vibrational energy redistribution from low-frequency modes of the molecule into intermolecular vibrations of the cluster and being equal to ~ 280 ps. As was already noted above, this time agrees quite well with the relaxation time for $\text{Fe}(\text{CO})_5$ molecules in the solvent, where the relaxation process also proceeds in two stages. At the same time, available experimental data are insufficient to make an unambiguous conclusion in favor of the particular relaxation mechanism. To do this, additional measurements are necessary. Here, we can note measurements of the dynamics of variation of the temperature of the cluster via the measurement of, for example, the kinetic energy of free particles escaping at different moments of time.

Our analysis of the modeled temporal profiles describing the evolution of the temperature of the cluster has revealed that there is an overheating of clusters with respect to the quasi-equilibrium evaporation temperature. In this case, however, subsequent dissociation of clusters is described well in terms of the mechanism of the sequential evaporation of molecules.

In conclusion, we note that, clearly, the model that we used for the analysis of experimental data involves rather many semiempirical fitting parameters. At the same time, it describes well experimental dependencies, and predicted values of the yield of free molecules agree quite satisfactorily with independent estimates obtained from the value of the energy absorbed by clusters. Therefore, we believe that our model provides a rather adequate pattern of internal processes in $[\text{Fe}(\text{CO})_5]_n$ clusters (energy redistribution, heating of the cluster, and its decay) caused by the excitation of clusterized molecules with femtosecond IR radiation.

AUTHOR INFORMATION

Corresponding Authors

*Phone: +7(495)8510232. E-mail: poydashev@isan.troitsk.ru.

*Phone: +7(495)8510578. E-mail: ryabov@isan.troitsk.ru.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was partially supported by the Russian Foundation for Basic Research, grant no. 13-02-00260.

REFERENCES

- (1) Pauly, H. Atom, Molecule, and Cluster Beams II. Cluster Beams, Fast and Slow Beams, Accessory Equipment and Applications. *Springer Series on Atomic, Optical, and Plasma Physics*; Springer: New York, 2000; Vol. 32.
- (2) Buck, U. In *Advances in Atomic, Molecular, and Optical Physics*; Bederson, B., Walther, H., Eds.; Elsevier: Amsterdam, 1995; Vol. 35, pp 121–161.
- (3) Castleman, A. W., Jr.; Bowen, K. H., Jr. Clusters: Structure, Energetics, and Dynamics of Intermediate States of Matter. *J. Phys. Chem.* **1996**, *100*, 12911–12944.
- (4) Makarov, G. N. Extreme Processes in Clusters Impacting on a Solid Surface. *Phys. Usp.* **2006**, *49*, 117–166.
- (5) Miller, R. E. Infrared Laser Photodissociation and Spectroscopy of van der Waals Molecules. *J. Phys. Chem.* **1986**, *90*, 3301–3313.
- (6) Miller, R. E. The Vibrational Spectroscopy and Dynamics of Weakly Bound Neutral Complexes. *Science* **1988**, *240*, 447–453.
- (7) Buck, U. Structure and Dynamics of Small Size Selected Molecular Clusters. *J. Phys. Chem.* **1994**, *98*, 5190–5200.
- (8) Simard, B.; Denommee, S.; Rayner, D. M.; van Heijnsbergen, D.; Meijer, G.; von Helden, G. IR Multiphoton Depletion Spectroscopy of Metal Cluster–Ligand Complexes. *Chem. Phys. Lett.* **2002**, *357*, 195–203.
- (9) Bohac, E. J.; Marshall, M. D.; Miller, R. E. Initial State Effects in the Vibrational Predissociation of Hydrogen Fluoride Dimer. *J. Chem. Phys.* **1992**, *96*, 6681–6695.
- (10) Nesbitt, D. J. High-Resolution, Direct Infrared Laser Absorption Spectroscopy in Slit Supersonic Jets: Intermolecular Forces and Unimolecular Vibrational Dynamics in Clusters. *Annu. Rev. Phys. Chem.* **1994**, *45*, 367–399.
- (11) Buck, U. Properties of Neutral Clusters from Scattering Experiments. *J. Phys. Chem.* **1988**, *92*, 1023–1031.
- (12) Lokhman, V. N.; Ogurok, D. D.; Ryabov, E. A. UV Multiphoton Ionization and IR Photodissociation of CF_3I Cluster Beams. *Chem. Phys.* **2007**, *333*, 85–95.
- (13) Lokhman, V. N.; Ogurok, D. D.; Ryabov, E. A. Multiphoton Dissociation of CF_3I Clusters by IR Laser Radiation. *JETP* **2009**, *108*, 727–737.
- (14) Apatin, V. M.; Lokhman, V. N.; Ogurok, D. D.; Poydashev, D. G.; Ryabov, E. A. Photodissociation of IF_2CCOF Clusters by Resonant IR Radiation. *Eur. Phys. J. D* **2013**, *67*, 66.

- (15) Au, M.-K.; Hackett, P. A.; Humphries, M.; John, P. Infrared Multiphoton Dissociation of Unsubstituted Metal Carbonyls at 5 μm . *Appl. Phys. B: Laser Opt.* **1984**, 33, 43–49.
- (16) Windhorn, L.; Witte, T.; Yeston, J. S.; Proch, D.; Motzkus, M.; Kompa, K. L.; Fuss, W. Molecular Dissociation by mid-IR Femtosecond Pulses. *Chem. Phys. Lett.* **2002**, 357, 85–90.
- (17) Apatin, V. M.; Kompanets, V. O.; Lokhman, V. N.; Ogurok, N.-D. D.; Poydashev, D. G.; Ryabov, E. A.; Chekalin, S. V. Reactions Induced in $(\text{CF}_3\text{I})_n$ Clusters by Femtosecond UV Laser Pulses. *JETP* **2012**, 115, 567–578.
- (18) Hagen, O. F. Cluster Ion Sources. *Rev. Sci. Instrum.* **1992**, 63, 2374–2379.
- (19) Bañares, L.; Baumert, T.; Bergt, M.; Kiefer, B.; Gerber, G. The Ultrafast Photodissociation of $\text{Fe}(\text{CO})_5$ in the Gas Phase. *J. Chem. Phys.* **1998**, 108, 5799–5811.
- (20) Cataliotti, R.; Foffani, A.; Marchetti, L. Infrared Spectrum of Crystalline Iron Pentacarbonyl. *Inorg. Chem.* **1971**, 10, 1594–1597.
- (21) Laubereau, A.; Kaiser, W. Vibrational Dynamics of Liquids and Solids Investigated by Picosecond Light Pulses. *Rev. Mod. Phys.* **1978**, 50, 607–665.
- (22) Chekalin, S. V.; Kompanets, V. O.; Koshlyakov, P. V.; Laptev, V. B.; Pigulsky, S. V.; Makarov, A. A.; Ryabov, E. A. Intramolecular Vibrational Dynamics in Free Polyatomic Molecules with $\text{C}=\text{O}$ Chromophore Bond Excited by Resonant Femtosecond IR Laser Radiation. *J. Phys. Chem. A* **2014**, 118, 955–964.
- (23) Gspann, J. On the Phase of Metal Clusters. *Z. Phys. D* **1986**, 3, 143–145.
- (24) Klotz, C. E. Kinetic Methods for Quantifying Magic. *Z. Phys. D* **1991**, 21, 335–342.
- (25) Makarov, G. N. Kinetic Methods for Measuring the Temperature of Clusters and Nanoparticles in Molecular Beams. *Phys. Usp.* **2011**, 54, 351–370.
- (26) Klotz, C. E. Systematics of Evaporation. *Z. Phys. D* **1991**, 20, 105–109.
- (27) Vostrikov, A. A.; Dubov, D. Yu. Clustering in Molecular Gases Freely Expanding into Vacuum. *JETP* **2004**, 98, 197–206.
- (28) Brockhaus, P.; Wong, K.; Hansen, K.; Kasperovich, V.; Tikhonov, G.; Kresin, V. Measuring Cluster Temperatures via Kinetic-Energy Release. *Phys. Rev. A* **1999**, 59, 495–502.
- (29) Banno, M.; Iwata, K.; Hamaguchi, H. Intra- and Intermolecular Vibrational Energy Transfer in Tungsten Carbonyl Complexes $\text{W}(\text{CO})_5(\text{X})$ ($\text{X}=\text{CO}$, CS , CH_3CN , and CD_3CN). *J. Chem. Phys.* **2007**, 126, 204501.
- (30) Cahoon, J. F.; Sawyer, K. R.; Schlegel, J. P.; Harris, C. B. Determining Transition-State Geometries in Liquids Using 2D-IR. *Science* **2008**, 319, 1820–1823.