DYNAMICS OF VIBRATIONAL RELAXATION OF MULTIPHOTON EXCITED SF₆ MOLECULES IN GASEOUS MIXTURES CONTAINING OZONE AND INERT GASES (He, Ar, Kr)

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SF₆ at pressure of 0.6 Torr in gas mixtures with ozone (0 ÷ 5 Torr) and inert gases: He, Ar, Kr (0 ÷ 5 Torr) was vibrationally excited with and IR pulsed radiation of CO₂ TEA laser at 10P20 laser line ($F = 0.6 \text{ J/cm}^2$). The vibrational energy transfer from multiphoton excited (MPE) molecules SF₆ to the components of gaseous mixture was probed by UV absorption of ozone at $\lambda = 253.6 \text{ nm}$ band. The relaxation process of MPE molecules SF₆ was proposed to occur through parallel V–V' and V–T collisional channels. Based on the kinetic model, collisional rate constants were determined from the time evolution of UV absorption data after laser shot. The obtained values of relaxation rate constants are: $k_{V-V}^{\text{SF}_6\text{-O}_3} = 7.7 \cdot 10^{-13} \text{ cm}^3/\text{s}$, $k_{V-T}^{\text{SF}_6\text{-He}} = 3.1 \cdot 10^{-13} \text{ cm}^3/\text{s}$, $k_{V-T}^{\text{SF}_6\text{-Ar}} = 2.3 \cdot 10^{-13} \text{ cm}^3/\text{s}$, $k_{V-T}^{\text{SF}_6\text{-Kr}} = 7.7 \cdot 10^{-14} \text{ cm}^3/\text{s}$, $k_{V-T}^{\text{SF}_6\text{-SF}_6} = (4.8 \div 6.4) \cdot 10^{-13} \text{ cm}^3/\text{s}$.

The observed decay of IR fluorescence from MPE SF₆ molecules at $\lambda = 6.3 \mu\text{m}$ wave number in SF₆–Kr gas mixtures had an exponential time profile with the constant characteristic relaxation time (V–T). The rate of IR fluorescence quenching allowed us to find an effective V–T relaxation rate constants for collisional partners: $k_{V-T}^{\text{SF}_6\text{-Ar}} = 7.8 \cdot 10^{-14} \text{ cm}^3/\text{s}$, $k_{T-V}^{\text{SF}_6\text{-SF}_6} = 1.0 \cdot 10^{-12} \text{ cm}^3/\text{s}$.

INTRODUCTION

Description of different physical and chemical processes in gaseous media occurring in the field of intense IR radiation require quantitative data on collision relaxations of multiphoton excited (MPE) molecules. Characteristic relaxation time for the MPE molecules characterizes the energy redistribution in the system and at the same time gives practical information concerning for instance the thermalization rate of the system. The latter is essential for the estimation of the time necessary to achieve the top equilibrium temperature of the gaseous mixture in laser-powered homogeneous pyrolysis (LPHP),¹ when chemical reaction initiated by pulsed IR sensitization. This method proves quite effective for the study of mechanism and kinetics of high temperature gaseous reactions especially those with participation of thermodynamically unstable compounds such as ozone.

Sulphur hexafluoride (SF₆) is known to be one of the most commonly used IR sensitizers. However, the number of studies on collision deactivation of SF₆ molecules excited by the CO₂-laser is limited.^{2–11} For the most part they concern with the investigation V–T relaxation process of SF₆ in the absence of chemical reactions.

In the early works the IR–IR resonance and IR fluorescence techniques were used for determination of V–V' and V–T rate constants of the processes in binary mixtures containing SF₆ with low level of excitation,^{2,4,5} in these experiments vibrationally excited SF₆ could be considered only as a small admixture in the “cold” gaseous buffer.

A few works on the relaxation of MPE SF₆ molecules on “cold” SF₆ molecules are available,^{6–10} in which characteristic V–T relaxation times were estimated. It has been proved by interferometry technique that at high energy of IR radiation the characteristic relaxation time for MPE SF₆ in pure SF₆ and SF₆–Ar mixtures is several times lower than for regime of weak excitation.⁹ There are practically no quantitative data on collision deactivation of MPE SF₆ molecules on chemically inert gases as well as on the reactional molecules including the ozone molecules.

The dynamics of vibrational energy transfer from the MPE sensitizer (SF₆) to the other molecules of gaseous mixture may be observed not only by registration of the energy transformation of the sensitizer itself (e.g. by means of IR–IR, IR–UV resonance and IR luminescence) but by kinetics of excitation of the collision partners as well. In the present work an UV probing technique has been suggested for the kinetic study of excitation of the partner molecules (O₃) on collisions with SF₆. The technique is based on the registration of the change in the UV spectrum of the ozone molecule in the region of Hartly band (200–300 nm) which is caused by the alteration of the extinction coefficient in the course of the transfer of vibrational energy into vibrational modes of ozone molecules ν_1 and ν_3 which manifest themselves in the UV absorption spectra. It has been shown that the extinction coefficient of ozone (ϵ_λ) can be represented as follows:¹²

$$\epsilon_\lambda = (P_{000} + P_{010}) \epsilon_\lambda^{000} + (P_{100} + P_{001}) \epsilon_\lambda^* \quad (1)$$

where $\epsilon_\lambda^{000} \approx \epsilon_\lambda^{010}$ is the extinction coefficient for the O₃ (000) and O₃ (010) states; ϵ_λ^* is the mean weighted (according to population) extinction coefficient of the O₃ (001) and O₃ (100) states; P_{000} , P_{100} , P_{010} , P_{001} are the relative populations of the corresponding vibrational states of the ground electronic term of ozone (¹A₁). It is well known, that if $\lambda < 271$ nm, the inequality $\epsilon_\lambda^* < \epsilon_\lambda^{000}$ is true. For instance $\epsilon_\lambda^*/\epsilon_\lambda^{000} = 0.17$ for $\lambda = 254$ nm.¹² The alteration of the optical density (ΔA) due to vibrationally excited ozone molecule (O₃[‡]) is related to the concentration of the latter by equation:

$$\Delta A = [\text{O}_3^\ddagger] l \Delta \epsilon_\lambda \quad (2)$$

where $[\text{O}_3^\ddagger] = [\text{O}_3(100)] + [\text{O}_3(001)]$, l is the optical thickness of the absorbing gas layer (in cm), $\Delta \epsilon_\lambda = \epsilon_\lambda^* - \epsilon_\lambda^{000}$. It is evident from Eq. (2) that the time dependence of ΔA represent the temporal dependence of $[\text{O}_3^\ddagger]$.

EXPERIMENTAL

The block diagram of the experimental setup for the study of the relaxation of MPE SF₆ molecules in mixture with O₃ is represent in Figure 1. Information on the

Figure 2 Picture of initial portion of detected UV transmission ($\lambda = 253.6$ nm) through the gas cell, containing $\text{SF}_6\text{--O}_3\text{--M}$ mixture, after laser shot, SG_6 (0.6 Torr), O_3 (1 Torr), M (0 Torr).

According to Eq. (2) and Lambert-Beer law:

$$\Delta A = A(t) - A^0 = \lg \{I_0/[I^0 + \Delta I(t)]\} - \lg (I_0/I^0) \quad (3)$$

where from taking into account that for all the experiments $\Delta I(t) \ll I^0$, one can get:

$$\Delta I = \text{const} \cdot [\text{O}_3^\ddagger] \cdot I^0 \cdot \ell \cdot \Delta \varepsilon_\lambda \quad (4)$$

The $[\text{O}_3^\ddagger]$ and $\Delta I(t)$ are apparent to be given by one and the same time dependence.

We connect the dynamics of the $[\text{O}_3^\ddagger]$ increase in the system with a simple collisional model of the relaxation. The excess of vibrational energy of the system after the IR laser exposure will be characterized by $\langle n \rangle$ —the mean number of quanta ($h\omega$) absorbed by one SF_6 molecule from the IR field. The determined value of parameter $\langle n \rangle \approx 8$ was still constant for all gas mixtures under investigation. It was controlled by accurate measurements of IR energy absorbed in the cell from laser beam by calorimetric detector with 5% error of absorbed energy. Thus we supposed, that the initial average energy of SF_6 molecules after the laser shoot does not change with the addition of small amounts of ozone and buffer gases in whole series of our experiments.

For a two component mixture $\text{O}_3\text{--SF}_6$ the relaxation of MPE SF_6 in the scope of such model may be considered as a unquantum V--V' energy transfer process from MPE SF_6 to O_3 (000) with the formation of the O_3 (100) and O_3 (001) states and also a parallel V--T relaxation channel. A schematic representation is as follows:

To a first approximation this process may be described by a kinetic scheme of two parallel processes with the first order rate constants k_{V-V}^1 and k_{V-T}^1 .

It is obvious, that the experimental data of $\langle n \rangle$ produce no information about the initial shape of vibrational energy distribution of SF₆ molecules after the excitation by high-power IR laser field. The detailed investigation of multiphoton excitation demonstrates the existence of two groups of SF₆ molecules: the "hot" ensemble disposed in quasi-continuum, and the "cold" ensemble, which includes some molecules located on the low vibrational levels and in the ground state.¹⁵ The first step in the temporal process of vibrational energy transfer in MPE SF₆ is the very first fast V-V and V-V' energy exchange among these two groups, which lead to produce single Boltzman distribution between vibrational degrees of freedom in SF₆ gas with very high initial vibrational temperature ($T_{\text{vib}} = 1500 \div 1600$ K in our case). The characteristic time of such fast process for SF₆ molecules was estimated¹⁶ ($p\tau = 1 \mu\text{s} \cdot \text{Torr}$). The technique of UV probing allowed us to detect only the further process of vibrational energy transfer from SF₆ molecules to O₃, lowering the vibrational temperature of SF₆ and exciting ozone. We consider, that this process is more complicated and occurs in collisions according to kinetic scheme (*). Finally, such relaxation kinetics results in equal value of vibrational temperature of all components and translational temperature of the gas, so, at last the mixture in the cell becomes completely thermolized at equilibrium value of temperature.

This scheme is supported by a series of different considerations. First, of all the relaxation of MPE SF₆ occurs in the medium of excess of "cold" ozone O₃ (000). Alongside with unquantum excited states O₃ (001) and O₃ (100) the multiquantum energy transfer is possible to produce the O₃ (00K) and O₃ (N00) states. However, on collisions with O₃ (000) molecules the "hot" ozone molecules will quickly lose their energy in quasi-resonance unquantum V-V' processes, thus transferring to O₃ (100) and O₃ (001) states manifesting themselves in the UV absorption spectra of ozone. The energy transfer from MPE SF₆ into the ν_2 mode of ozone molecule gives no alteration in the ozone spectrum, however the transfer from the ν_2 mode of ozone molecule to the O₃ (100) and O₃ (001) levels will contribute to the change of optical transmission in the UV range of the absorption spectrum of O₃. Thus the k_{V-V}^1 is the bottom limit of the specific rate of the vibrational energy transfer from SF₆ molecules to O₃. The V-V' intermolecular exchange between SF₆ molecules does not change substantially vibrational energy of SF₆ molecules as a whole ensemble and consequently cannot be considered as an effective decay of vibrational energy of MPE SF₆. Only a small part of vibrational energy can be transferred into the translation as a result of the energy defects in the course of intermode transformations in SF₆. That is why the V-T relaxation process from the lower vibrational levels SF₆ with the rate constant k_{V-T}^1 is the lowest limit of the rate transformation of vibrational energy from MPE SF₆ into translation. On the other hand, the V-T relaxation process of MPE SF₆ should not effect greatly the O₃[‡] concentration, because in conformity with the principle of detailed equilibrium, the O₃ excitation as a result of T-V process occurs considerably slower than the V-T process for O₃[‡], occurs according to work¹⁷ from the ν_2 mode of molecule O₃ (010) with the rate constant $k_{V-T} = 1.01 \cdot 10^{-13} \text{ cm}^3/\text{s}$. Thus

in the time scale under investigation (20–30 μ s) the T–V excitation process of O_3 can be neglected.

Kinetics of $O_3^\ddagger$ formation according to the scheme (*) can be expressed as follows:

$$[O_3^\ddagger](t) = \langle n \rangle [SF_6] \frac{k_{V-V'}^1}{k_{V-V'}^1 + k_{V-T}^1} \{1 - \exp[-(k_{V-V'}^1 + k_{V-T}^1)t]\} \quad (5)$$

where $k_{V-T}^1 = k_{V-T}^{SF_6-SF_6} [SF_6]$, $k_{V-V'}^1 = k_{V-V'}^{SF_6-O_3} [O_3]$ and $k_{V-V'}^{SF_6-O_3}$ —is the effective rate constant of the vibrational relaxation SF_6 on ozone molecules, $k_{V-T}^{SF_6-SF_6}$ —is an effective rate constant of SF_6 vibrational self-relaxation. The value

$$\langle n \rangle [SF_6] \frac{k_{V-V'}^1}{k_{V-V'}^1 + k_{V-T}^1}$$

is the top concentration of the vibrationally excited ozone ($[O_3^\ddagger]_{\max}$) which can be achieved by the completion of relaxation of MPE SF_6 . In accordance with Eq. (4) $[O_3^\ddagger]_{\max}$ corresponds to the $\Delta I_{\max}$ value on the oscilloscope record. Combining the Eq. (4) and (5) one can get:

$$\Delta I(t) = \Delta I_{\max} \{1 - \exp(-k_\Sigma^1 t)\} \quad (6)$$

where

$$k_\Sigma^1 = k_{V-V'}^{SF_6-O_3} [O_3] + k_{V-T}^{SF_6-SF_6} [SF_6] \quad (7)$$

It is obvious from (7), that at $[SF_6] = \text{const.}$ the k_Σ^1 values calculated from the experimental data according to (6) change linearly with $[O_3]$ changes. Figure 3

Figure 3 Rise of effective rate constant (k_Σ^1) of vibrational relaxation of MPE SF_6 molecules in SF_6-O_3 mixtures versus O_3 pressure, SF_6 (0.6 Torr).

demonstrates that the k_{Σ}^1 values vary in direct proportion to the ozone partial pressure. The slope of the corresponding experimental points gives for the constant $k_{V-T}^{SF_6-O_3}$ the value of $7.7 \cdot 10^{-13} \text{ cm}^3/\text{s}$ ($p\tau = 40 \mu\text{s Torr}$). Extrapolation of the slope to zero value of ozone pressure gives the value of $(4.8 \div 6.4) \cdot 10^{-13} \text{ cm}^3/\text{s}$ ($p\tau = 49 \div 65 \mu\text{s Torr}$) for $k_{V-T}^{SF_6-SF_6}$.

The same procedure was applied for the calculations of relaxation rate constants for the O₃-SF₆ systems with added buffer gases. One more V-T relaxation channel of MPE SF₆ on the buffer molecules appears. It means that one more component $k_{V-T}^{SF_6-O_3} [M]$ enters into the equation for k_{Σ}^1 . Varying the content of the buffer gas in the system with constant [SF₆] and [O₃] one can obtain a linear correlation k_{Σ}^1 with [M], which is represented in Figure 4. The relaxation rate constants of MPE SF₆ on He, Ar, Kr molecules obtained from these data come to $k_{V-T}^{SF_6-He} = 3.1 \cdot 10^{-13} \text{ cm}^3/\text{s}$, $k_{V-T}^{SF_6-Ar} = 2.3 \cdot 10^{-13} \text{ cm}^3/\text{s}$, $k_{V-T}^{SF_6-Kr} = 7.7 \cdot 10^{-14} \text{ cm}^3/\text{s}$ respectively.

Figure 4 Rise of effective rate constant (k_{Σ}^1) of vibrational relaxation of MPE SF₆ molecules in SF₆-O₃-M mixtures (M = He, Ar, Kr) versus inert gas pressure, SF₆ (0.6 Torr), O₃ (2 Torr), O-He, Δ - Ar, $\square$ - Kr.

An investigation of V-T relaxation of MPE SF₆ in mixtures with Kr by direct method of IR luminescence quenching⁴ in the region of $\lambda = 6.3 \mu\text{m}$ was carried out in order to estimate the reliability of the data obtained in the present study by UV probing. IR emission was registered by a photodetector Ge-Au (77 K) and attributed to the vibrational transfer in MPE SF₆ from the combination $\nu_2 + \nu_3$ levels to the ground state and $\nu_2 + \nu_3 + \nu_6 \rightarrow \nu_6$.¹⁸ The temporal decay of the IR luminescence intensity represented in Figure 5 can be adequately approximated by the exponential function such as:

$$I_f = I_f^0 \exp(-t/\tau) \quad (8)$$

where I_f^0 is the IR luminescence signal in maximum, τ is the characteristic time of

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Figure 5 Temporal profile of decay IR fluorescence of MPE SF_6 molecules at $\lambda = 6.3 \mu\text{m}$ in SF_6 -Kr mixture, SF_6 (1 Torr), Kr (20 Torr).

V-T relaxation in the gaseous mixture SF_6 -Kr under investigation. It has been shown that in SF_6 mixtures with inert gases the parameter τ is given by the equation:

$$(\tau)^{-1} = k_{\text{V-T}}^{\text{SF}_6-\text{SF}_6} [\text{SF}_6] + k_{\text{V-T}}^{\text{SF}_6-\text{Kr}} [\text{Kr}] \quad (9)$$

where $k_{\text{V-T}}^{\text{SF}_6-\text{Kr}}$ is the rate constant of V-T relaxation of MPE SF_6 on Kr.

As may be inferred from (9) at $[\text{SF}_6] = \text{const.}$ the $(\tau)^{-1}$ values should depend linearly from the $[\text{Kr}]$. The experimental data are given in the Figure 6 in $(\tau)^{-1} - [\text{Kr}]$

 $(\tau)^{-1} \cdot 10^3, \text{ s}^{-1}$

Figure 6 Rise of inverse characteristic time of V-T relaxation $(\tau_{\text{V-T}})^{-1}$ of MPE SF_6 molecules in SF_6 -Kr mixtures versus Kr pressure, SF_6 (1 Torr).

coordinates. The value $k_{V-T}^{SF_6-Kr} = 7.8 \cdot 10^{-14} \text{ cm}^3/\text{s}$ was obtained from the slope of the experimental data. Extrapolation of the slope to the zero pressure of Kr gives the value of $k_{V-T}^{SF_6-SF_6} = 1.0 \cdot 10^{-12} \text{ cm}^3/\text{s}$.

It is worthwhile to note good agreement between the values of the effective rate constants of V-T relaxation of MPE SF₆ molecules on the Kr molecules obtained by different methods. The corresponding values for the effective rate constants of vibrational self-relaxation of MPE SF₆ are in good agreement as well.

The rate constants of V-V' and V-T relaxational processes obtained in our work exceed in several times similar rate constants determined for one-photon excitation of SF₆ molecules.² This fact is in good agreement with the conclusion of considerable acceleration of relaxational kinetics for MPE SF₆ molecules.^{9,10} But, in both regimes of high and weak excitation of SF₆ molecules V-T relaxational rate constants exhibit the same dependence on the mass of collisional partner in the file of He, Ar, Kr. This dependence is well predicted in SSH theory¹⁹ by breathing-sphere approximation^{20,21} shows, that the rate constant of V-T process becomes lower with increasing the mass of collisional partner.

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