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Time-resolved IR chemiluminescence in gas-phase chemical kinetics

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Contents

I.	Introduction	171
II.	Processes resulting in IR chemiluminescence of vibrationally excited products of chemical reactions	171
III.	The sensitivity limit of the IR chemiluminescence method	173
IV.	Measurement of rate constants for non-chain reactions	174
V.	Modification of the time-resolved IR chemiluminescence method	175
VI.	Study of the kinetics of chain reactions by the IR chemiluminescence method	175
VII.	The time-resolved Fourier-transform spectroscopy of IR chemiluminescence	179
VIII.	Conclusion	180

Abstract. The time-resolved IR chemiluminescence method based on the study of the chemiluminescence of vibrationally excited molecules formed in chemical reactions is discussed. The approaches used in the study of elementary reactions and complex processes are systematised. The technique is compared with other methods for the study of gas-phase chemical kinetics. The bibliography includes 76 references.

I. Introduction

In modern gas-phase chemical kinetics, methods that enable the real-time detection of chemically active species in an excited state are used in studies of elementary reactions. These methods include laser-induced fluorescence, intra-cavity laser spectroscopy, laser magnetic resonance, resonance-amplified multiphoton ionisation and the IR chemiluminescence method (IR-CL) based on the study of the luminescence of vibrationally excited molecules formed in reactions.

The energy evolved in an elementary exothermic chemical process manifests itself most commonly as vibrational excitation of the reaction products.[1] The practical application of this kind of reaction for the pumping of chemical lasers is well known.[2, 3]

The works devoted to the IR-CL study of the vibrationally excited products of chemical reactions may be divided in two groups. The first one includes those where a steady-state IR-CL spectrum with rather a high spectral resolution is the quantity determined experimentally. This spectrum contains information on the distribution of the reaction products over the vibrational and rotational states. Many reactions resulting in the formation of vibrationally excited molecules, such as HF,[4–9] HCl,[10] HBr,[11] CO,[12] OH^* [13] and H_2O,[14] have been studied by this method. The study of the reactions is complicated by the disturbing effect of fast vibration and rotation relaxation processes. To reduce the effect of relaxation processes, the experiments are carried out at low pressure using fast gas flow.

In another group of works, the kinetic approach is used. In these experiments, the dependence of the IR-CL intensity on the time elapsed after the pulse initiation of the chemical reaction is determined. The radiation is recorded in rather a wide spectral band. Based on this dependence, it is possible to determine the rate constants for reactions resulting in excited molecules and those of other reactions accompanying this process, as well as to find the rates of vibrational relaxation. From the methodical viewpoint, these works may be considered as a contribution to the development of the method of studying the vibrational relaxation of molecules based on their IR luminescence, which has been extremely fruitful in studies of the relaxation of polyatomic molecules.[15]

This review analyses the publications where the kinetic approach has been used. The main attention is given to methodical problems related to the use of kinetic IR-CL for the study of non-chain and chain reactions. A method for the measurement of the rate constants for reactions involving atoms and free radicals is discussed, in which a chain reaction resulting in the formation of vibrationally excited products manifests itself as an original 'probe' which makes it possible to trace the changes in the concentration of reactive species with time.

II. Processes resulting in IR chemiluminescence of vibrationally excited products of chemical reactions

Extensive studies on the processes of the formation of vibrationally excited molecules in exothermic reactions were linked with the research aiming at the development of chemical lasers and the optimisation of their operation. To date, the formation of diatomic vibrationally excited molecules in atom abstraction reactions have been studied rather thoroughly. Table 1 presents some typical exothermic reactions producing vibrationally excited molecules. Based on the analysis of the published data, one can state with a high degree of certainty that, if the energy liberated in the abstraction of an atom exceeds the energy of the quantum of the vibration energy of the molecule formed, this reaction should result in vibrationally excited molecules. The fraction of the vibrational energy is ten percent of the exotermicity of a reaction.

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Table 1. Mean vibration energy ($\langle E_{vib}\rangle$) of excited products and thermal effect ($-\Delta H_0$) of certain exothermic reactions.

Reaction	Excited species	$-\Delta H_0$	$\langle E_{vib}\rangle$	Ref.
		kcal mol^{-1}		
$F^{\bullet} + H_2 \rightarrow HF^* + H^{\bullet}$	$HF(\upsilon = 1, 2, 3)$	32	21.0	16
$F^{\bullet} + CH_4 \rightarrow HF^* + CH_3^{\bullet}$	$HF(\upsilon = 1, 2, 3)$	33	19.0	17
$F^{\bullet} + C_6H_{12} \rightarrow HF^* + C_6H_{11}^{\bullet}$	$HF(\upsilon = 1, 2, 3)$	41	22.0	18
$H^{\bullet} + Cl_2 \rightarrow HCl^* + Cl^{\bullet}$	$HCl(\upsilon = 1, ..., 6)$	45	17.6	19
$Cl^{\bullet} + H_2S \rightarrow HCl^* + HS^{\bullet}$	$HCl(\upsilon = 1)$	12	5.2	20
$Cl^{\bullet} + GeH_4 \rightarrow HCl^* + GeH_3^{\bullet}$	$HCl(\upsilon = 1, 2, 3)$	24	5.6	21
$O^{\bullet\bullet} + CS \rightarrow CO^* + S^{\bullet\bullet}$	$CO(\upsilon = 5, ..., 18)$	85	66.0	22
$Cl^{\bullet} + SiH_4 \rightarrow HCl^* + SiH_3^{\bullet}$	$HCl(\upsilon = 1)$	12	3.4	23
$O^{\bullet\bullet} + HI \rightarrow OH^{\bullet *} + I^{\bullet}$	$OH^{\bullet}(\upsilon = 1, 2, 3)$	31	9.7	24
$O^{\bullet\bullet} + GeH_4 \rightarrow OH^{\bullet *} + GeH_3^{\bullet}$	$OH^{\bullet}(\upsilon = 1, 2)$	33	12.5	13
$OH^{\bullet} + HI \rightarrow H_2O^* + I^{\bullet}$	H_2O	48	17.0	14
$O^{\bullet\bullet}(^1D) + H_2CO \rightarrow$ $\rightarrow CO_2^* + H_2$	CO_2	170	33.0	25

The study of the formation of polyatomic vibrationally excited molecules in chemical reactions is only beginning. However, the data available in the literature are consistent with the qualitative concept that in this case, too, a considerable fraction of energy produced in the reaction is transformed into the vibrational energy of the product containing the newly formed chemical bond.

The vibrationally excited molecules resulting from an exothermic reaction can lose energy either through spontaneous emission of IR radiation quanta or by relaxation of the vibrational energy in collisions. These processes are schematically shown in Fig. 1.

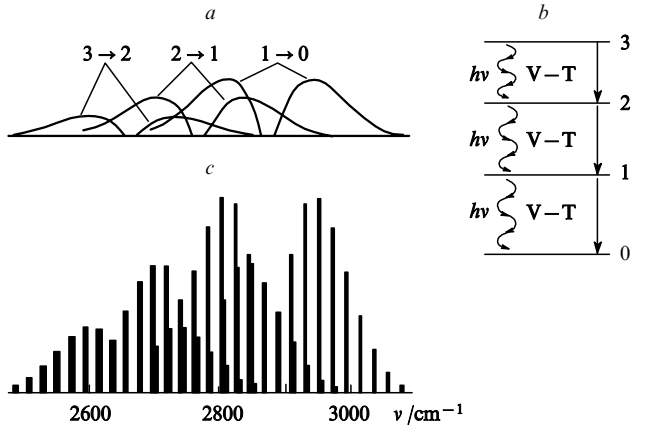


Figure 1. Scheme of the processes forming an IR chemiluminescence spectrum;
(*a*) vibrational bands of the corresponding transitions with unresolved rotational structure; (*b*) scheme of radiation transitive and vibration–translation (V–T) relaxation processes; (*c*) IR luminescence spectrum of an HCl molecule with well resolved rotational structure.

The characteristic probabilities of spontaneous radiative transitions in unit time (W) for the vibrationally excited molecules are listed in Table 2. The transitions that change the vibration quantum number υ by one unit have the highest probability. It is in rare cases that W exceeds 100 s^{-1} for the vibrations resolved in an IR spectrum.

As a rule, the probability of transitions that change υ by two units (overtone luminescence) is one or two orders lower. Accordingly, the intensity of the overtone luminescence turns out to be lower. On the other hand, it has to be noted that overtone transitions play a more significant role in the IR luminescence

Table 2. Energy and probability of spontaneous radiative transitions for vibrationally excited molecules.

Molecule	Transition	E /cm^{-1}	W /s^{-1}	Ref.
HF	$(\upsilon = 1) \rightarrow (\upsilon = 0)$	3961	189.0	26
	$(\upsilon = 2) \rightarrow (\upsilon = 1)$	3788	320.0	
HCl	$(\upsilon = 1) \rightarrow (\upsilon = 0)$	2886	35.0	26
	$(\upsilon = 2) \rightarrow (\upsilon = 1)$	2782	59.0	
	$(\upsilon = 2) \rightarrow (\upsilon = 0)$	5668	3.5	
	$(\upsilon = 3) \rightarrow (\upsilon = 0)$	8347	0.037	
OH	$(\upsilon = 1) \rightarrow (\upsilon = 0)$	3568	20.0	27
	$(\upsilon = 2) \rightarrow (\upsilon = 1)$	3398	25.0	
	$(\upsilon = 2) \rightarrow (\upsilon = 0)$	6966	14.0	
	$(\upsilon = 3) \rightarrow (\upsilon = 0)$	10 194	0.9	
CO	$(\upsilon = 1) \rightarrow (\upsilon = 0)$	2170	30.0	28
	$(\upsilon = 2) \rightarrow (\upsilon = 1)$	2144	59	
CO_2	$(0^00 1) \rightarrow (0^00 0)^a$	2349	400.0	29
SiH_4	$(\nu_3 = 1) \rightarrow (\nu_3 = 0)^a$	2189	180.0	30

Note. The table presents data for molecules with vibration frequencies > 2000 cm^{-1} (the molecules with lower vibration frequencies are not interesting due to the low probability of spontaneous transitions).
[a] The linear three-atomic CO_2 molecule has four vibrational degrees of freedom and three different frequencies. The five-atomic SiH_4 molecule has even more frequencies. In both cases, the parameters of only one possible vibrational transition are presented.

spectra than in IR absorption spectroscopy. A reason for this is that the overtone luminescence occurs in the region of shorter wavelengths (with respect to the fundamental luminescence), and hence more sensitive detectors can be used to record it.

Let us consider the energy loss by vibrationally excited molecules in collisional relaxation. The rate constants for the vibration–translation relaxation vary over a very broad range for various colliding partners. For example, the probability of vibrational relaxation of excited HCl molecules equals 10^{-7} in collisions with He atoms, 10^{-4} in collisions with HCl, 10^{-3} in collisions with CH_4, and 2×10^{-3} in collisions with SiH_2Cl_2. In a gas mixture prepared for studying a chemiluminescent reaction, vibrational relaxation occurs upon collisions with the molecules of the starting substances. The probabilities of vibrational relaxation upon collisions with polyatomic molecules usually vary from 10^{-2} to 10^{-3}, which corresponds to the time of vibrational relaxation 10^{-4}–10^{-3} s at a pressure of 1 Torr.

The above estimates show that the radiative path plays an insignificant role in the energy loss by vibrationally excited molecules. The quantum yield of IR-CL at a pressure of several Torr usually does not exceed 10^{-2} and decreases with an increase in the pressure. Such a dependence determines the upper limit of the pressure range used in experiments on IR-CL; this value is about 30 Torr.

The necessity of using low pressures and the relative simplicity of the luminescing molecules, whose IR spectra display well resolved rotational structure, results in a specific IR-CL spectrum. At low pressures, the width of an individual rotation line is mainly determined by the Doppler effect and does not exceed 10^{-2} cm^{-1}. The distance between the adjacent rotational lines is several units or even several tens of inverse centimetres. Therefore, the IR-CL spectrum is a set of very narrow lines far separated from each other.

If a reaction produces excited molecules in different vibrational states, the bands in their spectra are shifted relative to each other owing to vibrational anharmonicity. The anharmonic shift is usually smaller than the width of a separate band, therefore overlapping of bands occurs. Figure 1 schematically shows the luminescent spectrum of HCl molecules excited in the states $\upsilon = 1$,

$v = 2$, and $v = 3$. There is no actual superposition of the lines in the spectrum, because the width of a separate line is much smaller than the distance between the neighbouring lines. However, high spectral resolution is required to detect the luminescence corresponding to a particular vibrational state in such a spectrum. The spectral resolution in kinetic experiments on the study of IR-CL is small, hence it is helpful to use the so-called 'cold gas filter'. This is a cell filled with the gas whose luminescence is being studied. As the molecules in the gas filter are in the ground vibrational state, the gas filter enables blocking of the radiation of the $1 \rightarrow 0$ transition without affecting the radiation of the other transitions.

III. The sensitivity limit of the IR chemiluminescence method

A typical experimental set-up for the evaluation of the sensitivity of the IR-CL method includes a pulse laser (its radiation initiates the chemical reaction), a system for the preparation and injection of the gas mixture, and a system for the time-resolved recording of IR-CL.[31–39] The initiation of a reaction most commonly occurs due to the dissociation of molecules under the action of laser radiation in the UV range (excimer lasers, neodymium laser with frequency multiplication, the second harmonic of the ruby laser, the second harmonic of dye lasers). In addition, pulse CO_2 lasers are used, whose IR irradiation causes the dissociation due to multi-photon absorption. The experiments are carried out at pressures from fractions of Torr to several tens of Torr. The repetition frequency of laser pulses is usually several Hertz, less commonly tens of Hertz.

Figure 2 shows the scheme of a typical experimental set-up for recording the luminescence. Luminescence is recorded in a direction perpendicular to the laser beam. Since the signal is usually insufficient for the use of a monochromator, interference filters combined with various absorption filters are used. Often a gas filter is used, which has the form of a gas cell several centimetres long containing an absorbing gas under a pressure of several tens of Torr. Semi-conductor photoresistors or photo diodes cooled to low temperatures are used as IR radiation detectors. Photodetectors based on InSb are most commonly used for the mid IR region (3–5 μm). These detectors have high sensitivity and are convenient because they do not require cooling below 77 K. The time constant of these detectors is somewhat smaller than 1 μs in the case of photodiodes and several microseconds in the case of photoresistors. A very important requirement for a detector is its large area. This is caused by the fact that an IR-CL source has considerable geometrical dimensions, hence its radiation cannot be effectively focused on the small area of a detector. In the optimum variant, the size of the detector should match the size of the area in which the reaction occurs (~ 1 cm). Smaller detectors are commonly used.

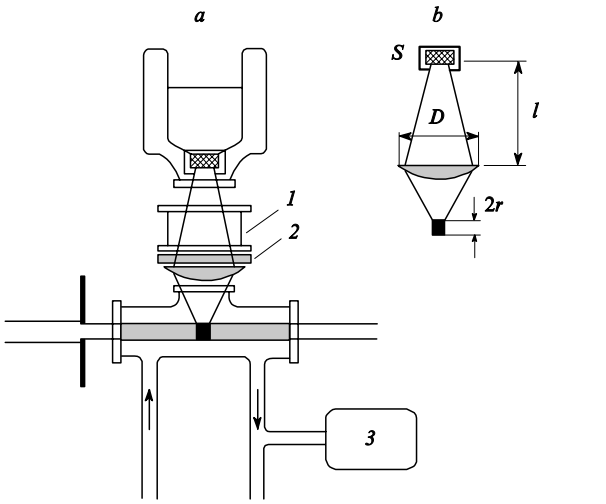


Figure 2. Scheme of set-up for the observation of the IR-CL kinetics (*a*); part of the set-up with indication of geometrical parameters required for sensitivity estimation (*b*);
(*1*) interference filter; (*2*) gas filter; (*3*) pressure gauge.

One can estimate the minimum concentration of vibrationally excited molecules detectable by this method as follows. The noise of a theoretical IR radiation detector is determined by fluctuations of the thermal background radiation reaching this detector. A signal of the excited molecules can be detected if the number of IR luminescence photons (I_{lum}) that have reached the radiation detector during the resolution time of the detecting system (τ_{reg}) exceeds the number of photons from the thermal radiation fluctuation (I_{therm})

$$I_{\text{lum}}\tau_{\text{reg}} > \sqrt{I_{\text{therm}}\tau_{\text{reg}}}\,. \tag{1}$$

For the flux of thermal radiation photons we have

$$I_{\text{therm}} = \frac{2\pi c S \Delta\lambda}{\lambda^4[\exp(hc/\lambda kT) - 1]}\left(\frac{D}{2l}\right)^2, \tag{2}$$

where c is the speed of light; S is the photodetector area; $\Delta\lambda$ is the wavelength range in which luminescence is recorded; λ is the irradiation wavelength; D and l are geometrical parameters (see Fig. 2 *b*).

The flux of luminescence photons can easily be found if the geometrical dimensions of the experimental set-up are known. Based on the formula (1), the following expression for the minimum detectable concentration of excited molecules was obtained:

$$n_{\min} = 2\sqrt{2\pi}\left(\frac{2l}{D}\right)\frac{\tau_{\text{rad}}}{r\sqrt{S\tau_{\text{reg}}[\exp(hc/\lambda kT) - 1]}}\,\frac{\sqrt{c\Delta\lambda}}{\lambda^2}, \tag{3}$$

where τ_{rad} is the radiative life time of a vibrationally excited molecule.

For an estimation of $n_{\min}$, let us use the following parameters of a vibrationally excited HCl molecule: $\lambda = 3.6$ μm, $\tau_{\text{rad}} = 3 \times 10^{-2}$ s.[26] The typical geometrical parameters are as follows: $S = 10^{-2}$ cm^2, $r = 0.5$ cm, $2l/D = 5$; the resolution time of the detecting system τ_{reg} is assumed to equal 10^{-6} s, and $\Delta\lambda \simeq \lambda$. After substituting these parameters in the formula (3), we obtain $n_{\min} = 10^{11}$ cm^{-3}.

Analysis of formula (3) shows that the sensitivity can be increased by using radiation detectors with large area and focusing lenses with large aperture (D/l ratio). The sensitivity can also be increased by narrowing the wavelength range $\Delta\lambda$ of the radiation that reaches the detector to a value equal to the width of the luminescent spectrum with the use of spectral filters. However, the maximum difference in the estimate obtained above due to all of these factors is one order of magnitude. Therefore, the value of $n_{\min} = 10^{11}$ cm^{-3} should be considered as the sensitivity limit of the IR-CL method.

It should be noted that this estimate was obtained under the assumption that the sensitivity is limited by the noise that originates from fluctuations of the thermal radiation reaching the detector. This is true in the standard experiment, in which the gas to be studied is placed in a cell whose walls and the surrounding objects are at room temperature, and hence it is impossible to avoid the effect of thermal irradiation on the detector. The sensitivity is usually increased by accumulation of periodically repeated signals.

A comparison of the IR-CL method with other kinetic methods[32] leads to the following conclusions. The sensitivity of IR-CL is inferior to that of laser-induced fluorescence (LIF) and resonance-enhanced multiphoton ionisation (REMPI) and is comparable to the sensitivity of the time-resolved laser magnetic resonance (LMR) and intra-cavity laser spectroscopy (ICLS). The response time of the method is within 10^{-7} to 10^{-6} s. This time is

smaller than the response time of time-resolved LMR and somewhat larger than the response time of LIF, ICLS and REMPI. An important characteristic of the methods used in the study of gas-phase reactions is the product of the sensitivity and the response time. This value equals $1/(n_{\min}\tau_{reg}) \simeq 10^{-8}$ cm^3 s^{-1} for IR-CL, which is much more than the maximum rate constants for bimolecular reactions. Hence, the fastest gas phase reactions can be studied by this method.

The main drawback of the IR luminescence method is its low spectral resolution. It does not exceed 20 – 50 cm^{-1} if interference filters are used. The use of a monochromator decreases the sensitivity. The low spectral resolution restricts the scope of the method considered. It can be used when one type of excited molecules is formed in the reaction or the spectra of different excited molecules are separated considerably.

Thus, time-resolved IR-CL is an experimentally simple kinetic method with high sensitivity and fast response. The scope of this method is limited to systems which produce vibrationally excited molecules with simple spectra.

IV. Measurement of rate constants for non-chain reactions

The IR-CL method has been first used for the measurement of the rate constants for chemical reactions by Wodarczyk and Moore.[33] The following processes were studied:

$$Cl^{\bullet} + HBr \longrightarrow HCl^* + Br^{\bullet},$$

$$Cl^{\bullet} + HI \longrightarrow HCl^* + I^{\bullet}.$$

The reactions were initiated by the action of a pulse of radiation of the second harmonic of the ruby laser on a mixture of Cl_2 with a small amount of HBr or HI diluted with a noble gas. The action of a laser pulse on a Cl_2 molecule resulted in its dissociation into two chlorine atoms. The IR luminescence of the excited HCl molecules formed in the reactions was recorded. The Br$^{\bullet}$ and I$^{\bullet}$ atoms have small reactivities, hence the set of kinetic processes can be represented by the following scheme

$$Cl_2 + h\nu \longrightarrow 2Cl^{\bullet},$$

$$Cl^{\bullet} + HX \xrightarrow{k_1} HCl^* + X^{\bullet}, \quad (4)$$

$$HCl^* + M \xrightarrow{k_2} HCl + M, \quad (5)$$

where X$^{\bullet}$ = Br$^{\bullet}$, I$^{\bullet}$; M = He, Cl_2.

If a small fraction of Cl_2 molecules dissociates under laser irradiation ([Cl$^{\bullet}$]$\ll$[Cl_2], [HX]), the pseudo-first order condition is obeyed for the processes (4) and (5), and the solution of the corresponding kinetic equations can be found easily. It has the form

$$[HCl^*](t) = A[\exp(-k_2[M]t) - \exp(-k_1[HX]t)]. \quad (6)$$

The experimentally observed time dependences of the luminescence intensity are well described by the formula (6). Under the experimental conditions used in Ref. 33, the time of vibrational relaxation was much greater than the reaction time. Therefore, the region of increase in the signal intensity was determined by the reaction time, and after passing a maximum, the signal intensity decreased according to vibrational relaxation. Analysis of the region of increase in the signal made it possible to determine the product k_1[HX] and hence the reaction constant k_1.

In another study,[34] more accurate measurements of rate constants for reactions of chlorine atoms with hydrogen bromide and hydrogen iodide were carried out; in addition, the isotope effect of the reaction rate was studied. The accuracy was increased by more careful determination of the concentration of the reagent, HBr or HI. The rate constants for the reactions at ambient temperature were 7.4×10^{-12} and 1.64×10^{-10} cm^3 s^{-1}, and the isotope effects (k_H/k_D) were 1.50 and 1.84, respectively. The measured temperature dependences (in the range from 220 to 400 K) of the rate constants for the same reactions were found to be of non-Arrhenius type.[35]

The reactions of F$^{\bullet}$ with HCl, HBr and HI molecules were studied.[37,38] The fluorine atoms were formed upon dissociation of F_2 molecules under the irradiation by the fourth harmonic of a Nd-laser. The processes considered are strongly exothermic; the HF molecules were excited to $\upsilon = 3$ (for the reaction with HCl), $\upsilon = 4$ (for the reaction with HBr), and $\upsilon = 6$ (for the reaction with HI). This made it possible to detect the excited HF molecules using luminescence at the second overtone frequency. The maximum of the band of the $(3 \rightarrow 0)$ transition in HF is at 879 nm, therefore a photomultiplier was used to detect the radiation. The band corresponding to this transition could easily be separated from the other HF luminescence bands using an interference filter for 880 nm with a band pass of 10 nm. In addition to the rate constants for the reactions of the fluorine atom with HCl, HBr and HI, which are 7.0×10^{-12}, 6.2×10^{-11} and 5.6×10^{-11} cm^3 s^{-1}, respectively, the rate constants for vibrational relaxation of HF molecules from the state $\upsilon = 3$ in collisions with HCl, CO_2, N_2O, CO, N_2 and O_2 were measured.

The interpretation of various stages of the IR-CL signal was simple.[33–37] As a rule, the region of the signal increase determined the reaction time, and the region of the signal decay determined the time of vibrational relaxation. Such a simple interpretation was possible because the atoms formed in the reaction were less reactive than the starting atoms. Therefore, secondary chemical reactions did not contribute to the observed time dependence of the signal. If species with high reactivity were formed in the reaction, a simple interpretation of the kinetic IR-CL curves was impossible because of secondary reactions. In this case, the role of secondary reactions as a photochemical source of atoms can be deminished by using sufficiently stable molecules which do not react with the newly formed radicals. This approach was used[38] for the reaction

$$Cl^{\bullet} + H_2CO \longrightarrow HCl^* + HCO^{\bullet}.$$

The CCl_3F molecule dissociating under the action of radiation of a pulse CO_2 laser served as a source of the chlorine atoms. It was shown that the multiphoton dissociation of CCl_3F did not result in the formation of fluorine atoms. The CCl_3F molecules are sufficiently inert and do not react with the HCO$^{\bullet}$ radical. The rate constant for the reaction was 7.4×10^{-11} cm^3 s^{-1}.

Multiphoton dissociation of SF_6 was found to be a convenient source of F$^{\bullet}$. This is explained by the high probability of SF_6 dissociation under the action of the radiation of CO_2 lasers and relative chemical inertness of SF_6. The time-resolved IR-CL method was used to study the reaction of fluorine atoms that formed due to multiphoton dissociation of SF_6, with various molecules. For example, the rate constants of reactions of fluorine with H_2 and D_2 were measured at ambient temperature.[39–41] To diminish warming of the gas by the radiation of pulse CO_2 lasers, the measurements were carried out in mixtures strongly diluted with a noble gas.

The numerical simulation of chemical HF- and DF-lasers requires the knowledge of the temperature dependences of the reaction rate constants for fluorine atoms with H_2 and D_2. The most reliable experimental data for these dependences have been obtained by time-resolved IR-CL.[42,43] It has been found for the temperature range 190 – 373 K:[43]

$$k_{H_2} = 1\times10^{-10}\exp\left(-\frac{860}{RT}\right),$$

$$k_{D_2} = 9.1\times10^{-11}\exp\left(-\frac{1100}{RT}\right).$$

For the temperature range 290 – 765 K:[43]

$$k_{H_2} = 2.1\times10^{-10}\exp\left(-\frac{1180}{RT}\right),$$

$$k_{D_2} = 1.1\times10^{-11}\exp\left(-\frac{1200}{RT}\right).$$

In the range of overlapping temperature ranges, the results differ by no more than 30% for the reaction with hydrogen and by much less for the reaction with deuterium. Deviation of the experimental data from the Arrhenius-type dependence over a wide temperature range was reported.

The reactions of the fluorine atom with HCl, HBr, HI, DBr, DCl and DI molecules at room temperature were studied.[5] The temperature dependences of the rate constants were measured in the range 195–373 K for the first four processes.[44] It was found that these dependences at temperatures below the room temperature deviate from the Arrhenius-type dependence. The experimental dependence can approximately be described by a sum of two terms, one of which does not depend on temperature and the other has an Arrhenius-type dependence with $E_a = 2-3$ kcal mol^{-1}. The explanation of this temperature dependence is that the reaction occurs by two pathways: first, direct elimination upon the attack by a fluorine atom towards the hydrogen atom in a hydrogen halide molecule, and second, formation of a complex upon the attack of a fluorine atom towards the halogen atom. It is considered that the first pathway does not require an activation energy, whereas the reaction according to the second pathway is supposed to overcome an activation barrier to the reorganisation of the complex

$$F\cdots X-H \longrightarrow F\cdots H-X\,,$$

which precedes its decomposition.

A study of the multiphoton dissociation of CF_3Cl by the time-resolved IR-CL method was reported.[45] Observation of the kinetics of IR-CL of HCl and HF molecules formed in reactions with HBr as a trap for atoms showed that dissociation occurs by two pathways to give F$^\bullet$ and Cl$^\bullet$. When HBr was replaced by H_2, only the formation of excited HF molecules was observed. The rate constants for reactions of fluorine atoms with H_2 and HBr and chlorine atoms with HBr were measured.

The possibility of using the time-resolved IR-CL for the study of a particular reaction is determined to a considerable extent by the existence of a suitable pulse source of atoms. The photolysis of S_2Cl_2 is a convenient photochemical source of the chlorine atoms that makes it possible to avoid or diminish the role of secondary reactions (see Ref. 46).

$$S_2Cl_2 + h\nu \longrightarrow Cl^\bullet + S_2Cl^\bullet\,.$$

The photolysis of S_2Cl_2 was carried out under irradiation by the second harmonic of a dye laser ($\lambda = 300$ nm)[46] and the fourth harmonic of a Nd-laser. The rate constants for chlorine reactions with H_2S (see Ref. 44), CH_3SH (see Ref. 47), and SiH_4 (see Ref. 48) were measured with the use of S_2Cl_2 as a source of chlorine atoms. Yet another photochemical source of chlorine atoms is the photolysis of $COCl_2$ by irradiation with an excimer KrF-laser. This source was used in a study of the reaction of chlorine with SiH_4 and $SiH_3^\bullet$ (see Ref. 49).

V. Modification of the time-resolved IR chemiluminescence method

In all of the works considered above, the time-resolved IR-CL method was used for the study of reactions of atoms resulting in the formation of vibrationally excited molecules, whose IR luminescence could be recorded. An approach has been suggested which expands the scope of reactions that can be studied by the IR-CL method.[50] The essence of this approach is that reactive species underwent an auxiliary reaction, in parallel with the 'nonluminous' reaction being studied, which resulted in the formation of vibrationally excited luminescing molecules. By studying the kinetic characteristics of the luminescence signal from the auxiliary reaction, one can obtain information on the rate constant for the 'nonluminous' reaction.

This method was tested[51] for the reaction of fluorine with CH_4. The reaction of fluorine with D_2 was used as the auxiliary reaction. The fluorine atoms were formed by IR multiphoton dissociation of SF_6. The main processes can be presented by the following scheme:

$$SF_6 + nh\nu \longrightarrow SF_5^\bullet + F^\bullet\,,$$

$$F^\bullet + CH_4 \longrightarrow HF^* + CH_3^\bullet \text{ (reaction being studied)},$$

$$F^\bullet + D_2 \longrightarrow DF^* + D^\bullet \text{ (auxiliary reaction)},$$

$$DF^* + M \longrightarrow DF + M \text{ (vibrational relaxation)}.$$

Let us designate the rate constants for the basic reaction, the auxiliary reaction and vibrational relaxation as k_1, k_0 and k_2, respectively. If the concentration of the fluorine atoms is much smaller than that of any of the stable components of the gas mixture, the pseudo-first order condition is obeyed for bimolecular processes, and the following expression is valid for the luminescence intensity of vibrationally excited molecules DF*

$$I_{DF}(t) = \frac{Ck_0[D_2][F]_0}{w' - w'}\left[\exp(-w't) - \exp(-w't)\right], \qquad (7)$$

where C is a proportionality factor, $[F]_0$ is the initial concentration of the fluorine atoms, w' is the inverse time of the signal growth

$$w' = k_0[D_2] + k_1[CH_4]\,, \qquad (7a)$$

and $w' = k_2[M]$ is the inverse time of the signal decay.

The inverse time of growth of the luminescence signal of DF* molecules depends both on the rate constant for the reaction $F^\bullet + D_2$ and on the rate constant for the parallel process $F^\bullet + CH_4$. According to equation (7a), the plot of w' *versus* the CH_4 concentration is a straight line, whose slope determines the required rate constant k_1, and the intercept with the ordinate axis determines the rate constant k_0. Thus, the luminescence signal from the products of the 'auxiliary' reaction contains the same kinetic information as that obtained from observation of the luminescence of the reaction of interest.

As the reaction being studied, $F^\bullet + CH_4$, also results in the formation of vibrationally excited HF molecules, it was possible to check the equivalence of kinetic information obtained from the auxiliary reaction and by observation of the luminescence of the reaction products.[50] Experiments were carried out in which the signals of the HF* and DF* luminescence were recorded under identical conditions. It was found that the time of the growth of these signals coincided within the experimental error, as would be expected according to the kinetic scheme considered above.

The same approach was used[51] to study the reaction

$$F^\bullet + NO_2 \longrightarrow FNO_2^*\,.$$

The fluorine atoms were obtained by multiphoton dissociation of SF_6. The process

$$F^\bullet + H_2 \longrightarrow HF^* + H^\bullet\,.$$

was used as an auxiliary reaction producing vibrationally excited molecules. The dependence of the rate constant for the reaction of fluorine with NO_2 on pressure in the range 1–200 Torr was measured; based on this dependence, the ratio of the isomers FNO_2 and FONO formed in the reaction was determined.

VI. Study of the kinetics of chain reactions by the IR chemiluminescence method

The time-resolved IR-CL method combined with pulse initiation of the reaction by laser irradiation was found to be very convenient for the study of the kinetics of chain reactions. This method made it possible to observe in real time a number of features of chain reactions, for example, the induction period of a reaction with very slow chain growth.[52] Using the data on the luminescence of the chain reaction products, it became possible to develop new kinetic approaches that enable quantitative information on the rate constants for the elementary reactions to be obtained.

For a non-branched chain reaction (or for a reaction with infrequent branchings) one can distinguish several stages that occur at different times after the pulse initiation of the reaction. The first one is the induction period, during which quasi-steady-state equilibrium between the concentrations of various active centres is established. The duration of the induction period approximately equals the time required for one step of a chain reaction to occur. Then the quasi-steady-state stage ensues. The concentration of active centres in this stage is approximately constant, and the accumulation of chain reaction products occurs. The third stage is the termination of the chain reaction, which occurs when the concentration of the active centres has decreased essentially owing to termination reactions. Let us consider how each of these stages manifests itself in the IR luminescence of the chain reaction products.

The induction period. The induction periods of the chain reactions were studied for the chlorination of H_2S.[52] The following processes occur in a mixture $Cl_2 + H_2S$ after a pulse of UV irradiation:

$$Cl^{\bullet} + H_2S \xrightarrow{k_1} HCl^*(v = 2, 1, 0) + HS^{\bullet}\,, \qquad (8)$$

$$HS^{\bullet} + Cl_2 \xrightarrow{k_2} HSCl + Cl^{\bullet}\,. \qquad (9)$$

In this case, excited molecules are formed in the first stage of the chain reaction. Let us designate the starting concentration of the chlorine atoms formed owing to the photolysis of Cl_2 as $[Cl^{\bullet}]_0$. Only a small fraction of the Cl_2 molecules underwent dissociation, hence $[Cl^{\bullet}]_0 \ll [Cl_2]$ and $[Cl^{\bullet}]_0 \ll [H_2S]$. In the initial stage, it is possible to neglect the chain termination and to neglect the vibrational relaxation of the HCl molecules, therefore the following expression can be written for the concentration of the chlorine atoms:

$$[Cl^{\bullet}](t) = [Cl^{\bullet}]_0[\theta_2 + \theta_1 \exp(-\varphi t)]\,, \qquad (10)$$

where t is time, $\theta_1 = k_1[H_2S]/\varphi$, $\theta_2 = k_2[Cl_2]/\varphi$ and $\varphi = k_1[H_2S] + k_2[Cl_2]$. The following expression is obtained for the concentration of vibrationally excited HCl molecules:

$$[HCl^*](t) = \alpha k_1[Cl^{\bullet}]_0[H_2S]\left[\theta_2 t + \theta_1 \frac{1 - \exp(-\varphi t)}{\varphi}\right], \qquad (11)$$

where α is the probability of the formation of vibrationally excited molecules in reaction (8). During the initial period, the concentration of the chlorine atoms decreases from the starting value $[Cl^{\bullet}]_0$ to $\theta_2[Cl^{\bullet}]_0$. According to formula (11), the rate of formation of HCl molecules should also decrease during this period.

Thus, in this example the initial period of the chain reaction should manifest itself in the luminescence signal of HCl as a 'kink' segment. During the time corresponding to the initial region, the rate of formation of excited molecules decreases from the initial value to that corresponding to a quasi-steady-state process.

Figure 3*a* shows a luminescence signal of HCl observed after the irradiation of a $Cl_2 + H_2S$ mixture with a pulse of a UV laser. In the initial region of the signal, the rate of the product formation during the establishment of a quasi-steady-state equilibrium between the active centres decreases. After an equilibrium has established, the increase in the concentration of vibrationally excited HCl molecules continued. The deviation of this increase from the linear dependence is due to the vibrational relaxation of HCl molecules.

If the vibrationally excited molecules are formed in the second stage of the chain process, the induction period of a chain reaction manifests itself in the luminescence signals in a different way. An example of such a process is the reaction of chlorination of hydrogen [19]

$$Cl^{\bullet} + H_2 \xrightarrow{k_1} HCl + H^{\bullet}\,, \qquad (12)$$

$$H^{\bullet} + Cl_2 \xrightarrow{k_2} HCl^* + Cl^{\bullet}\,. \qquad (13)$$

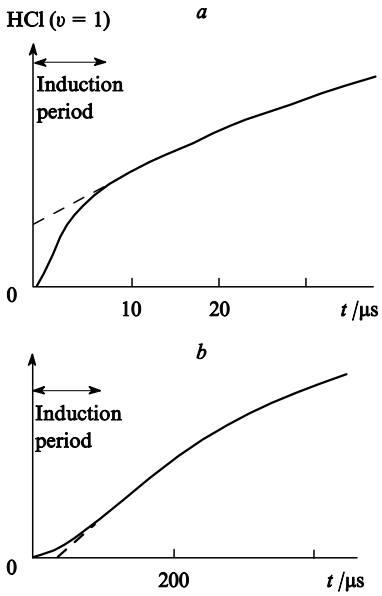


Figure 3. Initial parts of signals of the luminescence of HCl* molecules formed in chain reactions of H_2S (*a*) and H_2 (*b*) chlorination. Partial pressure, Torr: (*a*) 0.183 (H_2S), 2.20 (Cl_2), 8.48 (Ar); (*b*) 9.59 (H_2), 0.026 (Cl_2).

In this case, the formula describing the increase in the concentration of vibrationally excited HCl molecules after a laser pulse has the form

$$[HCl^*](t) = \alpha k_1[Cl^{\bullet}]_0[H_2]\left[\theta_1 t - \theta_2 \frac{1 - \exp(-\varphi t)}{\varphi}\right], \qquad (14)$$

where $\theta_1 = k_1[H_2]/\varphi$, $\theta_2 = k_2[Cl_2]/\varphi$ and $\varphi = k_1[H_2] + k_2[Cl_2]$. This formula shows that the rate of formation of the vibrationally excited product increases in the initial region from zero to a certain constant value.

Figure 3 *b* displays an example of an IR-CL signal observed in a $Cl_2 + H_2$ mixture (see Ref. 52). It is evident that the rate of formation of excited HCl molecules in the initial region increases (the curve is concave, unlike the curve in Fig. 3 *a*).

The initial region contains complete information on the rate constants for both stages of the chain growth. Using the formulas (11) or (14), it is possible to retrieve this information from the experimental signal. For approximation of the experimental curve, for example by formula (11), only three independent parameters have to be found, *i.e.*, the signal amplitude, the reaction rate constant k_1 and one of the values θ_1 or θ_2 related by $\theta_1 + \theta_2 = 1$. These parameters are sufficient for finding the rate constants. However, this kind of analysis of the shape of the initial region of the luminescence signal has not been carried out.[52]

Quasi-steady-state chain reaction. After the end of the induction period of the chain reaction, a quasi-steady-state equilibrium is established between the concentrations of the active centres. The concentration of vibrationally excited products increases in this stage at a rate that depends on a combination of the rate constants for the elementary steps of chain growth. It is convenient to consider this using the same reaction of H_2S chlorination as an example. The reaction rate is determined [taking the formula (11) into account] by the derivative

$$w = \frac{d[HCl^*](t)}{dt} = \alpha \frac{k_1 k_2 [Cl^{\bullet}]_0 [H_2S][Cl_2]}{k_1[H_2S] + k_2[Cl_2]}\,. \qquad (15)$$

It is difficult to find w from the luminescence signal, as precise calibration of the absolute sensitivity of the radiation detector is required. Therefore, formula (15) cannot be used to obtain kinetic

information. However, measurement of w even in relative units can give such a kinetic information. Taking into account that the initial concentration of the chlorine atoms $[Cl^{\bullet}]_0$ is proportional to the energy of the laser pulse E and the concentration of molecular chlorine, formula (15) can be rewritten as

$$\frac{[Cl^{\bullet}]_0[H_2S]}{w} = \frac{1}{\alpha k_1}\left(1 + k_1\frac{[H_2S]}{k_2[Cl_2]}\right). \qquad (16)$$

Expression (16) means that the rate of the quasi-steady-state stage of the chain reaction normalised per pulse energy and the product of the concentrations of the starting substances depend only on the ratio of the rates of the stages of the chain growth. It follows from this formula that $E[Cl_2][H_2S]/w$ should depend linearly on the concentration ratio $[H_2S]/[Cl_2]$. Figure 4 demonstrates a plot of this dependence. Analysis of formula (16) shows that the simple graphical method can be used to determine the ratio of rate constants for the elementary steps of chain growth. One has to determine the slope of the straight line and its intercept with the ordinate axis. The ratio of these parameters equals k_1/k_2.

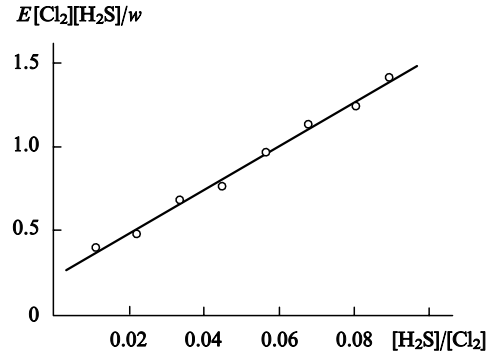


Figure 4. Dependence of inverse normalised rate of a chain reaction on the ratio of reagent concentrations.[52]

It should be noted that an account of the vibrational relaxation complicates the determination of w from the observed luminescence signal. The formulas containing the necessary corrections are presented in Ref. 52.

Using the technique described above, the ratio of the rate constants for the chain growth stages in the chlorination of H_2S [reactions (8) and (9)] was determined: $k_1/k_2 = 16$.[52] The chain reaction of the SiH_4 chlorination was studied using this method.[53] The ratio of rate constants for the reactions

$$Cl^{\bullet} + SiH_4 \longrightarrow HCl^* + SiH_3^{\bullet},$$
$$SiH_3^{\bullet} + Cl_2 \longrightarrow SiH_3Cl^* + Cl^{\bullet}$$

was found to be 4.6. The chain reaction of the $SiHCl_3$ chlorination was studied.[54] The ratio of rate constants for the reactions

$$Cl^{\bullet} + SiHCl_3 \longrightarrow HCl^* + SiCl_3^{\bullet},$$
$$SiCl_3^{\bullet} + Cl_2 \longrightarrow SiCl_4^* + Cl^{\bullet},$$

was found to equal 1.3. The same technique was applied to the study of the chain chlorination of butane and ethane.

Certainly, this procedure does not correspond to direct methods for the determination of rate constants. However, it provides rather reliable information, which is difficult to obtain by other methods. The advantage of using the time-resolved luminescence technique is that it is possible to avoid the complicating effect of chain termination reactions.

A method for the measurement of rate constants based on the study of chain reaction termination stages. The IR-CL signal of chain reaction products recorded after a sufficiently long period since its initiation contains information on the rate of decay of active centres in chain termination reactions. If the elementary reaction the rate constant of which has to be determined can serve as the chain reaction termination stage, it becomes possible to measure its rate. In this approach, the chain reaction resulting in the formation of vibrationally excited molecules plays the role of a probe for tracing the time dependence of the concentration of atoms or radicals. This allows one to study reactions that do not produce vibrationally excited molecules by the IR-CL technique. A similar approach for non-chain reactions has been developed.[50,51] The use of a chain reaction gives two additional benefits. First, the sensitivity of the method increases as the total number of vibrationally excited molecules formed in a chain reaction can be many times greater than the number of active centres. Second, this expands the range of reactive species whose reactions can be studied by this method.

A detailed analysis of the IR-CL kinetics of chain reaction products at various inhibitor concentration was carried out by Chesnokov.[55] The exact solution of this problem is rather cumbersome, but the results for reactions with a long chain are simple enough and have a simple qualitative interpretation.

A chain reaction in a mixture of compounds A + B with active centres $X^{\bullet}$ and $Y^{\bullet}$ involves the following elementary steps:

$$X^{\bullet} + A \xrightarrow{k_1} Y^{\bullet} + D, \qquad (17)$$
$$Y^{\bullet} + B \xrightarrow{k_2} X^{\bullet} + F, \qquad (18)$$
$$\left.\begin{array}{l} X^{\bullet} \xrightarrow{k_3} \\ Y^{\bullet} \xrightarrow{k_4} \end{array}\right\} \text{termination.} \qquad (19)$$

In the initial instant of time, a pulse of laser irradiation creates a certain concentration of active centres $X^{\bullet}$ equal to x_0. The active centres $Y^{\bullet}$ are absent in the initial instant, $[Y]^{\bullet} = 0$. Then, during the chain reaction induction period, a quasi-steady-state equilibrium between the concentrations of $X^{\bullet}$ and $Y^{\bullet}$ is established; the $X^{\bullet}$ concentration decreases, while the $Y^{\bullet}$ concentration increases (Fig 5 *a*). The overall concentration of the active centres $[X]^{\bullet} + [Y]^{\bullet}$ remains approximately equal to x_0.

After a quasi-equilibrium has been established, the overall concentration of the active centres decreases owing to their decay in chain termination reactions. The fractions of $X^{\bullet}$ and $Y^{\bullet}$ in the overall concentration of active centres remain constant. The fraction of $X^{\bullet}$ in the overall concentration of active centres equals

$$\theta_2 = \frac{k_2[B]}{k_1[A] + k_2[B]}, \qquad (20)$$

while the fraction of active centres $Y^{\bullet}$ equals

$$\theta_1 = \frac{k_1[A]}{k_1[A] + k_2[B]}. \qquad (21)$$

The decay of active centres occurs with an weighted average rate constant

$$\varkappa = \theta_1 k_4 + \theta_2 k_3. \qquad (22)$$

If the active centres $X^{\bullet}$ disappear in a reaction with substance C added to the reaction mixture:

$$X^{\bullet} + C \longrightarrow \text{products}, \qquad (23)$$

then the rate of decay of the active centres increases:

$$\varkappa = \theta_1 k_4 + \theta_2(k_3 + k[C]), \qquad (24)$$

where k is the rate constant for reaction (23).

The formula (24) underlies the method discussed for the determination of rate constants. If the life time of active centres of a chain reaction τ is measured at various concentrations of reagent C, then the reciprocal value $\varkappa = \tau^{-1}$ should linearly depend on the reagent concentration. The factors θ_1 and θ_2 depend

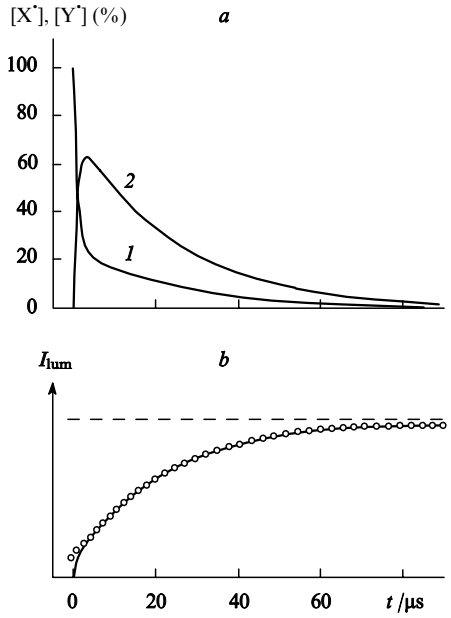


Figure 5. Theoretical luminescence signal of chain reaction products. (*a*) establishment of quasi-steady-state equilibrium between the concentrations of X• (*1*) and Y• (*2*); (*b*) luminescence intensity at quasi-steady-state equilibrium between X• and Y•.

on the ratio of the starting concentrations of the original compounds A and B. If concentration B is chosen large enough, it is possible to reach the conditions where $\theta_2 \approx 1$ and $\theta_1 \approx 0$. If the reaction rate constant for the active centre Y• has to be measured, then, on the contrary, it is necessary to choose such conditions that $\theta_2 \approx 0$ and $\theta_1 \approx 1$.

The procedure for the determination of the life time of active centres from the luminescence signal of the reaction products remains the same. The curve $I(t)$ is described by a sum of exponential terms, which allow one to determine the time of vibrational relaxation and the life time of the active centres. One only has to exclude from consideration the initial period of the reaction, when the quasi-equilibrium between the concentrations of the active centres has not yet been established (see Fig. 5).

This method has been used for the measurement of the rate constants for a number of reactions.[55] Let us consider the measurement of the rate constants for the reactions Cl• + NOCl with the use of this method.

First, one has to choose the chain reaction. Many chain reactions involving the chlorine atom and accompanied by the formation of vibrationally excited products are known. The reactions of chlorination of SiH_4 and its halogen derivatives are very convenient. These reactions give vibrationally excited hydrogen chloride molecules.[23, 54] The stages of continuation in such reactions are fast,[56] hence the chain length can be significant even at low pressures. The inconvenience of the reaction of SiH_4 chlorination is that self-inflammation of its mixtures with Cl_2 occurs in the absence of an inhibitor. The reactions of SiH_2Cl_2 and $SiHCl_3$ chlorination are devoid of this drawback. Let us choose the faster reaction of SiH_2Cl_2 chlorination.

The chlorination of SiH_2Cl_2 involves the following chain growth steps:

$$Cl^{\bullet} + SiH_2Cl_2 \longrightarrow HCl^* + SiHCl_2^{\bullet}, \quad (25)$$

$$SiHCl_2^{\bullet} + Cl_2 \longrightarrow SiHCl_3^* + Cl^{\bullet}. \quad (26)$$

The rate constant for reaction (25) is 1×10^{-10} cm^3 s^{-1}.[56] The rate constant for reaction (26) is 2×10^{-11} cm^3 s^{-1}.[23] Reaction (25) gives HCl* molecules in the states $\upsilon = 0$ and $\upsilon = 1$ with probabilities of 0.67 and 0.33, respectively.[23]

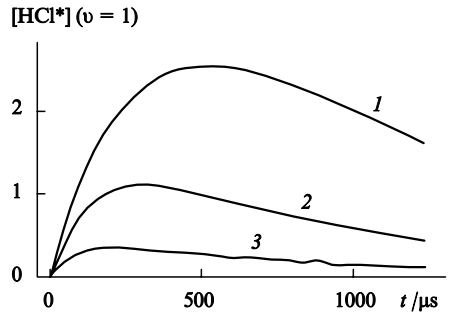


Figure 6. Examples of kinetic curves of luminescence of HCl* molecules formed upon chlorination of SiH_2Cl_2.
Concentrations: SiH_2Cl_2 8×10^{14}; Cl_2 2×10^{16}; He 1.3×10^{17} cm^{-3}; NOCl concentration/ cm^{-3}: (*1*) 2.2×10^{13}; (*2*) 5.9×10^{13}; (*3*) 15×10^{13}.

Figure 6 shows examples of IR-CL signals of excited hydrogen chloride molecules observed after reaction initiation in a $SiH_2Cl_2 + Cl_2$ mixture with addition of NOCl. An increase in the NOCl concentration decreases the amplitude of the luminescence signal. Such a dependence indicates that, under the conditions of the experiments, the time of vibrational relaxation exceeds the life time of active centres of the chain reaction. Figure 7 shows the dependence of the times of growth and decay of experimental curves on the NOCl concentration. It is evident that one of the characteristic times does not depend on the concentration of NOCl, while the other one varies over a wide range. The first time coincides with the time of vibrational relaxation and does not vary with the change in the NOCl concentration, since the concentrations of the other components of the mixture are much higher. The second time is the life time of the active centres of the chain reaction. At the concentrations [NOCl] $> 3 \times 10^{13}$ cm^{-3}, the life time of the active centres is smaller than the time of vibrational relaxation; at concentrations [NOCl] $< 3 \times 10^{13}$ cm^{-3}, the life time of the active centres becomes longer than the vibrational relaxation time. The inverse life time of active centres linearly depends on the NOCl concentration. The ratio of the projections of any segment of this linear dependence on the coordinate axes equals $(6.0 \pm 0.5) \times 10^{-11}$ cm^3 s^{-1}.

In view of the above values of the rate constants for the steps of propagation of chain reaction under the conditions of the experiment, we obtain $\theta_2 = 0.85 - 0.9$; $\theta_1 = 0.1 - 0.15$. The parameter θ_1 cannot be regarded as negligibly small, hence it is necessary to take into account reactions of the active centres of both types

$$\varkappa_2 = (\theta_2 k_3 + \theta_1 k_4)[NOCl] + \text{const}, \quad (27)$$

where k_3 and k_4 are the rate constants for the reactions

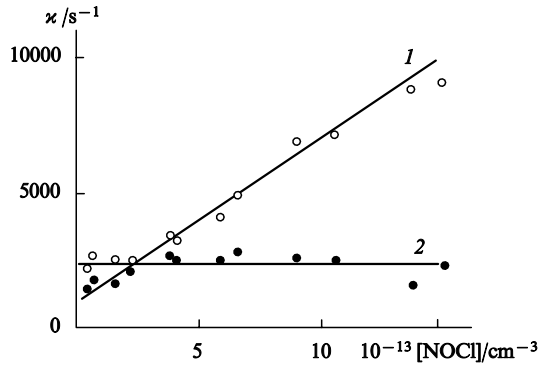


Figure 7. Dependences of reciprocal times of signal growth and decay on NOCl concentration;
(*1*) life time of active centres; (*2*) vibrational relaxation time.

$$Cl^{\bullet} + NOCl \xrightarrow{k_3} Cl_2 + NO,$$

$$SiHCl_2^{\bullet} + NOCl \xrightarrow{k_4} SiHCl_3^{*} + NO\,.$$

Thus, taking into account the slope of the straight line in Fig. 7, we obtain

$$\theta_2 k_3 + \theta_1 k_4 = (6.0 \pm 0.5) \times 10^{-11}\ cm^3\ s^{-1}. \quad (28)$$

A mixture with a larger fraction of SiH_2Cl_2 was studied to estimate the contribution of the term $\theta_1 k_4$; in this case, $\theta_1 = 0.3-0.4$. It was found that the contribution of the second term in formula (28) did not exceed 10% – 15%. The resulting rate constant k_3 equals $(6.5 \pm 0.5) \times 10^{-11}\ cm^3\ s^{-1}$.

This method was used [57, 58] for measuring the rate constants for a number of reactions of the chlorine atom with silicon-containing radicals. The results of these studies and the available published data obtained by other methods are listed in Table 3. The prospects of this method for the measurement of the rate constants for a certain reactive particle are determined by whether a fast chain reaction accompanied by formation of vibrationally excited molecules can be found for this particle. The analysis carried out by Chesnokov [55] shows that is possible to expect a gain in sensitivity only in the case where the rates of the chain propagation steps of the chain reaction exceed the rate of vibrational relaxation. This condition is similar to that demanded for the chain reaction for a chemical laser.[2]

Table 3. Rate constants for some reactions of the chlorine atom with silicon-containing radicals.

Reaction studied	Auxiliary reaction	$10^{11}\,k$ /cm^3 s^{-1}	Ref.
$Cl^{\bullet} + NOCl \rightarrow Cl_2NO^{\bullet}*$	$Cl_2 + SiH_2Cl_2$,	6.5 ± 0.5	55
	$Cl_2 + H_2$	7.5 ± 1.0	55
		8.0	59
$Cl^{\bullet} + ICl \rightarrow Cl_2^{*} + I^{\bullet}$	$Cl_2 + H_2$	1.2 ± 0.2	55
		0.8	60, 61
		1.0 ± 0.3	62
$Cl^{\bullet} + Br_2 \rightarrow BrCl* + Br^{\bullet}$	$Cl_2 + SiH_2Cl_2$	$(1.1 \pm 0.2) \times 10$	55
		1.2×10	50, 61
$SiH_3^{\bullet} + NOCl \rightarrow$	$Cl_2 + SiH_4$	$(6.0 \pm 2.0) \times 10^{-1}$	55
$\rightarrow SiH_3Cl* + NO^{\bullet}$		1.3 ± 0.3	63
$SiH_3^{\bullet} + Br_2 \rightarrow$	$Cl_2 + SiH_4$	6.5 ± 1.4	57
$\rightarrow SiH_3Br* + Br^{\bullet}$			
$SiCl_3^{\bullet} + Br_2 \rightarrow$	$Cl_2 + SiHCl_3$	10.5 ± 1.7	57
$\rightarrow SiCl_3Br* + Br^{\bullet}$			
$SiHCl_2^{\bullet} + Br_2 \rightarrow$	$Cl_2 + SiH_2Cl_2$	6.0 ± 0.9	57
$\rightarrow SiHCl_2Br* + Br^{\bullet}$			
$Cl^{\bullet} + I_2 \rightarrow ICl* + I^{\bullet}$	$Cl_2 + SiHCl_3$	$(2.5 \pm 0.7) \times 10$	58
$SiCl_3^{\bullet} + I_2 \rightarrow SiCl_3I* + I^{\bullet}$	$Cl_2 + SiHCl_3$	$(5.8 \pm 1.8) \times 10$	58

It should be noted that the idea of increasing the sensitivity by using a chain reaction as a 'probe' has been suggested and implemented by Orkin and Chaikin [64] for the thermometric detection of atoms. With the use of IR-CL, it was found possible to implement the same idea in a time-resolved version.

VII. The time-resolved Fourier-transform spectroscopy of IR chemiluminescence

In the last decade, time-resolved Fourier-transform spectroscopy is being used ever more frequently for the study of the IR luminescence of the products of gas phase reactions. This method makes it possible to obtain the luminescence intensity as functions of both frequency and time after the reaction initiation. In exceptional cases, it was also possible to obtain time-resolved IR-CL spectra by ordinary methods.[65]

For the first time, the time-resolved version of Fourier-transform IR spectroscopy was used for the study of chemiluminescence in the gas phase by Aker and Sloan,[66] who studied the initial distribution over vibrational states of the $OH^{\bullet}$ radical formed in the reaction

$$O^{\bullet\bullet}(^1D) + H_2 \longrightarrow OH^{\bullet} + H^{\bullet}\,. \quad (29)$$

A normal Fourier-transform spectrometer was used. The time resolution was achieved in these measurements by synchronisation of the pulse laser initiating the reaction under study with the instants of time when the spectrometer measures the values of the IR radiation interferogram.

Figure 8 illustrates the operation principle of a Fourier-transform IR spectrometer in the time-resolved mode. The directly measured characteristic is an interferogram, *i.e.*, dependence of intensity of IR radiation at the interferometer output on the difference between the ray paths in the two arms of the interferometer. The spectrum is obtained by Fourier transformation of the interferogram by a computer included in the set-up. The orientation of the moving mirror of the interferometer is determined using a helium – neon laser whose radiation passes through the auxiliary interferometer of the spectrometer combined with the main one. The controlling computer analyses the intensity of the ray of the helium – neon laser passed through the auxiliary interferometer and issues the commands for the measurement of the interferogram value. The moving mirror of the interferometer moves at a constant rate S, and the instants of time when the commands are issued are separated by identical time intervals T_0 (Fig. 8, curve *1*)

$$T_0 = \frac{\lambda}{2S}, \quad (30)$$

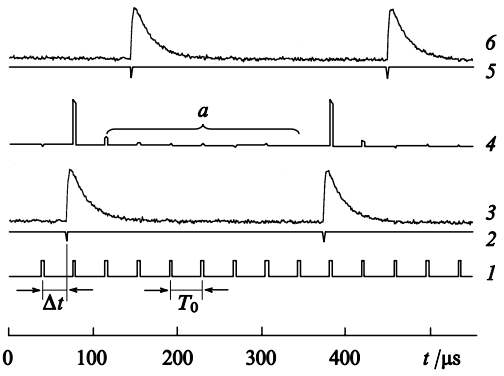


Figure 8. Diagram clarifying the operation of a Fourier-transform IR spectrometer in time-resolved mode;
(*1*) sequence of time instants of interferogram measurement; (*2*, *5*) laser pulses; (*3*) IR radiation at interferometer output; (*4*) interferogram with discarded region *a*; (*6*) IR radiation in the next cycle of spectrometer operation.

where $\lambda = 0.6328 \times 10^{-4}$ cm is the wavelength of the helium-neon laser. To synchronise the pulse laser, the computer command for performing the measurements is used for starting the pulse generator, which after the time Δt triggers the pulse laser (Fig. 8, curve *2*). If the delay Δt is equal to the duration of the measurement recurrence period T_0 or slightly smaller, the pulse laser will act immediately before the instant of the interferogram measurement. By decreasing the delay, one can obtain a luminescence spectrum for some definite time instant after the laser pulse.

A difficulty in the implementation of such a scheme arises due to the fact that the usual measurement frequency of an interferogram by a Fourier-transform spectrometer is several kHz or several tens kHz. The lasers used for reaction initiation cannot work with such a pulse repetition rate. This means that only a part of the interferogram measurements contain the signal, while the major part of the measurements, which do not containing the signal, should not be taken into account (see region *a* of curve *4*). The missing points in the interferogram can be obtained in the subsequent cycles of mirror scanning; however special measures should be taken so that the interferogram contains no gaps. The measurements in Refs 66, 67 were carried out according to such a scheme. The gaps in the measurement of an interferogram can be avoided at high pulse frequency of the laser or at very small movement speed of the spectrometer mirror. An excimer laser with a repetition frequency of 316 Hz was used,[68–70] and the interferometer mirror was moved very slowly (0.01 cm s^{-1}). At this movement speed of the mirror, the time interval between the interferogram measurements [formula (30)] is equal to the recurrence period of the laser pulses, and rejecting a part of the measurements is no longer necessary.

In the studies mentioned above,[66–70] the Fourier-transform IR spectrometer was used without updating the IR radiation intensity measurement system. In later studies,[71,72] advanced equipment was used that made it possible to make a measurement of the interferogram at several different delay times after each laser pulse, instead of one delay time as before. This required alteration of the standard measuring part of the spectrometer, which was replaced with a digital signal recorder connected to a computer with a sufficiently large memory size capable of simultaneous accumulation of interferograms for all time instants. This updating increases considerably the speed of recording spectra.

Additional specific noise appears in the time-resolved mode; this may result, *e.g.*, from the power instability of the pulse laser. It was suggested[73] that this noise be decreased by normalising the measurement results in each pulse using the pulse power.

Let us consider several examples of studies carried out by time-resolved Fourier-transform IR spectroscopy.

The reaction of the electron-excited O$^{\bullet\bullet}$(^{1}D) atom with the hydrogen molecule was studied.[66] The distribution of the radical OH$^{\bullet}$ formed in reaction (29) over vibration levels was determined and found to be as follows: $P(\upsilon = 1:2:3:4) = 0.29:0.32:0.25:0.13$. The time-resolved Fourier-transform IR spectroscopy made it possible to study the distribution undisturbed by relaxation processes. The distribution obtained is of intermediate type between that characteristic of reactions occurring through an intermediate complex and that characteristic of direct cleavage reactions. It was thus assumed that the reaction dynamics includes a stage of a very strongly excited water molecule, which decays after the time corresponding to several vibration periods.

The reaction of the CHF$^{\bullet\bullet}$ radical with the NO molecule was studied.[72] The radical was obtained by multiphoton IR dissociation of CH_2FCl or CH_2F_2. The luminescence of vibrationally excited HF molecules formed in the reaction was recorded. The addition of D_2 to the reaction mixture resulted in the excited DF molecules, which allowed the determination of the ratio of the pathways yielding HF and F$^{\bullet}$ for the reaction studied; this ratio was found to be 0.6 : 0.4.

Vibration relaxation of NO molecules excited to high vibration levels was studied.[74] The photolysis of N_2O (irradiation with a wavelength of 193 nm) gives O$^{\bullet\bullet}$(^{1}D), which reacts with N_2O to give the highly excited NO molecule. Twenty IR luminescence interferograms corresponding to various instants of time (step 30 μs) were obtained. Based on the interferograms, the spectra were reconstructed in the range from 2500 to 1500 cm^{-1} with a resolution of 4 cm^{-1}. By plotting the spectra calculated in this way, a time dependence of the population of vibration levels from $\upsilon = 1$ to $\upsilon = 11$ was obtained. The results were interpreted using a system of eleven kinetic equations that described the vibrational relaxation. The rate constants for the vibrational relaxation of separate vibration levels were determined. The relaxation constant for the level $\upsilon = 11$ is 40 times greater than that for the level $\upsilon = 1$.

In several publications, the initial distribution of photodissociation products of various molecules over vibration levels was studied using time-resolved Fourier-transform IR spectroscopy. For example, one of them[69] is devoted to the study of excitation processes of HF molecules formed upon the photodissociation of CH_2CClF (irradiation at the wavelength of 193 nm), while another one [67] deals with a study of distribution of the $NH_2^{\bullet}$ radical formed upon the photodissociation of NH_3 (irradiation with a wavelength of 193 nm) over vibration levels.

The studies using time-resolved IR chemiluminescence cannot be classified as purely kinetic ones, or to those where only the energy distribution in the reaction products is studied. The basic purpose of these works is to establish the distribution of products over vibration states. However, this can also provide quantitative information on the rates of vibrational relaxation processes and chemical reactions.

VIII. Conclusion

The time-resolved IR-CL method is used in gas-phase chemical kinetics in order to obtain quantitative information regarding the rates of elementary reactions. The application of this method for studying chain processes was found to be particularly fruitful.

However, it should be noted that the method is limited to a narrow range of molecules the luminescence of which can be observed. In fact, the luminescence of either HCl or HF was used in all of the studies. Attempts to overcome this restriction were undertaken. Reactions were found that gave polyatomic vibrationally excited molecules yielding intense luminescence. For example, luminescence of SiH_3Cl[75] and of products of butane and ethane chlorination[76] was observed. The luminescence kinetics of SiH_3Cl was studied in detail;[75] this process is mostly determined by the transfer of vibration energy and vibrational relaxation. It was found of little use for obtaining information on the rates of chemical reactions. The difficulties are basically caused by the fast vibrational relaxation of highly excited polyatomic molecules.

Further prospects of the IR-CL method are related to the use of the time-resolved Fourier-transform spectroscopy.

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