Quantum Electronics **37** (10) 985 – 988 (2007)

PACS numbers: 42.55.Lt; 52.80. –s
DOI: 10.1070/QE2007v037n10ABEH013510

Study of the temperature dependence of the critical electric field strength in SF_6 and mixtures of SF_6 with C_2H_6 by the method of laser gas heating

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***Abstract*. The temperature dependences of the critical reduced electric field strength $(E/N)_{\rm cr}$ in SF_6 and mixtures of SF_6 with C_2H_6 are obtained in the gas temperature range $T_{\rm g} = 293 - 1500$ K in the absence of thermal dissociation. Gases were heated due to the VT relaxation of SF_6 molecules excited by a pulsed CO_2 laser. The values of $(E/N)_{\rm cr}$ were estimated by the quasi-stationary burning voltage of a self-sustained volume discharge ignited with a delay with respect to the laser pulse. It is shown that in the absence of dissociation, the reduced electric field strength in SF_6 and mixtures of SF_6 with C_2H_6 in the temperature range under study increases with $T_{\rm g}$. The obtained temperature dependence of $(E/N)_{\rm cr}$ in SF_6 is compared with the results reported by other researchers.**

Keywords: *CO_2 laser, self-sustained volume discharge, SF_6, electron attachment, critical electric field strength.*

1. Introduction

The reduced critical electric field strength $(E/N)_{\rm cr}$ (where E is the electric field strength and N is the concentration of molecules), at which the rates of formation and attachment of electrons to neutral molecules are balanced, is an important characteristic of the electronegative gas, determining, in particular, its electric strength. The question of the influence of the gas temperature on the value of $(E/N)_{\rm cr}$ attracts great recent interest. This is related to the solution of a number of fundamental and applied problems of modern electrophysics such as, for example, the study of the dynamics of a high-temperature leader channel of a spark discharge [1] and the use of a strongly electronegative gas as a high-voltage insulator under conditions when operating temperatures can considerably exceed the normal temperature.

The SF_6 elegas and elegas-based mixtures, which combine a high dielectric strength with unique thermal properties, attract special attention. At present, however, information about the temperature dependence of $(E/N)_{\rm cr}$ in these gases is rather limited and contradictive. As far as we know, only a few papers [2 – 6] have been devoted to this problem so far. It is asserted in paper [2] that the discharge burning voltage in SF_6 at constant gas density and, therefore, the value of $(E/N)_{\rm cr}$ are temperature-independent in the interval from room temperature to 1073 K. However, no experimental or theoretical proofs in favour of this statement were presented in [2]. On the contrary, the study of the electron motion in a homogeneous field in the elegas heated up to 600 K [3] (the firing voltage was not directly measured in [3]) showed that the value of $(E/N)_{\rm cr}$ in SF_6 increased with increasing gas temperature $T_{\rm g}$. For example, according to [3], the value of $(E/N)_{\rm cr}$ at $T_{\rm g} = 600$ K should exceed that at room temperature by $\sim 11\,\%$.

In [4, 5], the breakdown voltages in SF_6 were measured at a pressure of 2 atm in the temperature interval 1300 – 2200 K. It was found that the value of $(E/N)_{\rm cr}$ drastically decreased with temperature. Theoretical paper [6] and calculations of Hayasi presented in [5] predict a similar tendency. Note, however, that these calculations and experiments [4, 5] correspond to the conditions of partial thermal dissociation of SF_6. Therefore, the values of $(E/N)_{\rm cr}$ obtained in [4 – 6] are related not to the elegas itself but to a mixture containing the products of its thermal decomposition. The measurements of $(E/N)_{\rm cr}$ in SF_6 in the temperature range from 600 to 1300 K have not been performed at all. As for the SF_6-based gas mixtures, no information is available at present about the temperature dependence of the critical electric field strength.

Experimental methods used in [3 – 5] allow the measurement of the reduced electric field strength in SF_6 heated either up to comparatively low temperatures [3] or temperatures typical for an arc discharge [4, 5]. The measurement of $(E/N)_{\rm cr}$ in SF_6 at intermediate temperatures requires a fundamentally different approach.

We showed earlier [7, 8] that SF_6 and its mixtures, in particular, with ethane can be heated by the CO_2 laser radiation up to temperatures 1500 K due to conversion of the absorbed laser energy to heat during the VT relaxation of excited vibrational states of SF_6 molecules. In this case, it is possible to avoid the thermal dissociation of the gas. It is also important that the quasi-stationary values of the reduced electric field strength $(E/N)_{\rm qs}$ in the plasma of a self-sustained volume discharge (SSVD) in SF_6 at room temperature (in the absence of heating by laser radiation) and energy inputs less than 100 J L^{-1} differ only slightly (no more than by 4 %) from the values of $(E/N)_{\rm cr}$ measured in

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Received 27 December 2006; revision received 29 March 2007
Kvantovaya Elektronika **37** (10) 985 – 988 (2007)
Translated by M.N. Sapozhnikov

experiments on the static breakdown of gases [9]. A small difference can be probably explained by the restriction of the current density in a diffusion channel, which was experimentally studied and qualitatively described in [9]. Taking this into account, it is reasonable to assume that the values of $(E/N)_{\mathrm{qs}}$ will be close to $(E/N)_{\mathrm{cr}}$ at elevated temperatures as well.

We have found in [10] that the voltage in the quasi-stationary phase of a SSVD in SF_6 and mixtures of SF_6 with C_2H_6 at moderate gas pressures increases with increasing the specific laser radiation energy W_{a} of a pulsed CO_2 laser absorbed by SF_6 molecules in the discharge region. It was shown in [7, 8] that the gas temperature can be determined from the measured values of W_{a}. This provides the basis for the experimental determination of the temperature dependence of $(E/N)_{\mathrm{qs}}$ in gases by measuring the laser radiation energy density. The above-mentioned proximity of the values of $(E/N)_{\mathrm{qs}}$ and $(E/N)_{\mathrm{cr}}$ allows one to determine also the behaviour of the reduced critical electric field strength in these gases.

This paper is devoted to the study of the temperature dependence of the reduced critical electric field strength in SF_6 and mixtures of SF_6 with C_2H_6 heated by a pulsed CO_2 laser in the temperature range $T_{\mathrm{g}} = 293 - 1500$ K. The values of $(E/N)_{\mathrm{cr}}$ were estimated from voltages in the quasi-stationary burning phase of a SSVD ignited in gas after a time delay with respect to the laser pulse. The gas temperature was determined from the measured values of the specific absorbed laser radiation energy by using the calculated specific heats of mixture components. The obtained temperature dependence of $(E/N)_{\mathrm{cr}}$ in SF_6 is compared with the data available in the literature.

2. Experimental

The scheme of the experimental setup and the experimental method are similar to those described in [7, 8, 10]. We measured the voltage U_{qs} in the quasi-stationary phase of the SSVD which was ignited in SF_6 and mixtures of SF_6 with C_2H_6 at partial pressures $p_{SF_6} = 9 - 30$ Torr irradiated preliminary by a pulse from a CO_2 laser [the P(20) line of the 10.6-μm band]. The specific energy of laser radiation absorbed by SF_6 in the discharge region achieved $0.27\ \mathrm{J\ cm^{-3}}$. The method of measuring W_{a} is described in detail in [7]. A spatially uniform beam of a CO_2 laser of size 60×60 mm was introduced into a discharge chamber through a BaF_2 window, parts of the beam were split by NaCl wedges to a calorimeter and a photon drag detector to control the energy and shape of the laser pulse. The laser energy was changed by using Teflon film filters mounted in front of the NaCl wedges.

The discharge was ignited between the needle (cathode) and the side surface of a cylinder of diameter 15 mm, the interelectrode spacing being $d = 43$ mm. For a needle we used a copper wire piece of diameter 1.5 mm in a polyethylene insulating jacket preventing the development of a discharge from the side wall of the cathode. The distance from the needle end to the BaF_2 window surface along the optical axis inside the discharge chamber was 25 mm. A 1-nF capacitor discharged into the gap via a 2.5-μH inductance. The charging voltage was varied from 15 to 35 kV depending on the pressure and composition of the gas mixture in the chamber. The delay τ between the laser and discharge pulses in our experiments was 3 μs, the laser pulse duration also being 3 μs. The delay was measured from the onset of the leading edge of the laser pulse having the shape typical of a transverse-discharge CO_2 laser.

The SSVD voltage and current were controlled with a calibrated high-voltage divider and a current shunt, respectively. The quasi-stationary voltage U_{qs} was measured at the instant of time corresponding to the current maximum. The specific contributions of the electric energy to the discharge plasma did not exceed $20\ \mathrm{J\ L^{-1}}$. This provided the independence of U_{qs} of processes restricting the current density in a diffusion channel, which are typical for volume discharges in strongly electronegative gases [9].

The gas temperature established by the moment a voltage was applied across the gap (after the end of the laser pulse) was determined from the expression

$$\frac{W_{\mathrm{a}}}{N} = \int_{T_0}^{T_{\mathrm{g}}} C_V(T')\mathrm{d}T', \quad C_V(T') = \sum_i \xi_i C_{Vi}(T'), \qquad (1)$$

where N is the total concentration of molecules; C_{Vi} and ξ_i are the heat capacity at constant pressure and the initial relative concentration of the ith component of the mixture; and $T_0 \approx 300$ K. The validity of this expression for determining T_{g} under experimental conditions described below was theoretically substantiated in our papers [7, 8], where the relaxation of laser radiation energy absorbed by SF_6 molecules was considered, and experimentally verified in [8] by comparing the calculated [from (1)] and measured velocities of shock waves produced due to the temperature jump at the boundary of the region containing SF_6 mixtures irradiated by CO_2 laser pulses.

3. Experimental results and discussion

Figure 1 presents the dependences of the voltage U_{qs} in the quasi-stationary SSVD phase on the specific absorbed radiation energy W_{a} in SF_6 and the $SF_6 : C_2H_6 = 5 : 1$ mixture for different values of the total pressure p. To determine the reduced electric field strength $(E/N)_{\mathrm{qs}}$ in the quasi-stationary SSVD phase, it is necessary to find the voltage drop across the positive SSVD column. For this purpose, we measured the dependences of U_{qs} on pd (Fig. 2) in gases at room temperature (in the absence of irradiation), which showed that $U_{\mathrm{qs}} = \Delta U + \mathrm{const}\cdot pd$. By neglecting the temperature dependence of ΔU, the value of $(E/N)_{\mathrm{qs}}$ was determined from the expression $(E/N)_{\mathrm{qs}} = (U_{\mathrm{qs}} - \Delta U)(Nd)^{-1}$. Figure 3 presents the dependences of $(E/N)_{\mathrm{qs}}$ on the gas temperature T_{g}, plotted by using the data given in Figs 1 and 2. The values of T_{g} were calculated from (1) by using the values of $C_{V_i}(T)$ taken from [11, 12]. For comparison, Fig. 3 also presents the values of $(E/N)_{\mathrm{cr}}$ in SF_6 at different temperatures borrowed from [3]. One can see that the experimental values of $(E/N)_{\mathrm{cr}}$ [3] are in good agreement within an experimental error with our experimental data; however, our experimental method allowed us to expand considerably the temperature range of measurements compared to [3]. Figure 3 shows that the temperature dependences of $(E/N)_{\mathrm{qs}}$ in the $SF_6 - C_2H_6$ mixture have the same character as for pure SF_6, i.e. $(E/N)_{\mathrm{qs}}$ increases with increasing T_{g} in the temperature interval under study.

Thus, taking into account that the values of $(E/N)_{\mathrm{qs}}$ are close, as mentioned above, to $(E/N)_{\mathrm{cr}}$, we can conclude that our results and data [3] reliably demonstrate the increase in

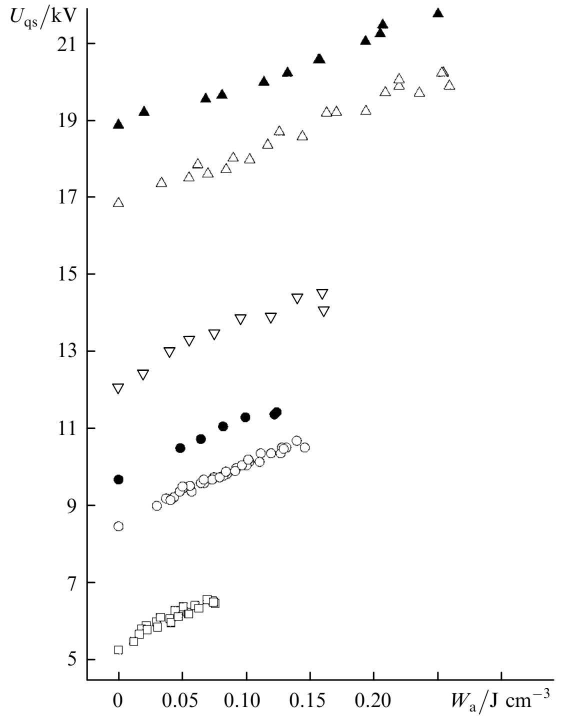

Figure 1. Dependences of the voltage U_{qs} in the quasi-stationary SSVD phase on the specific radiation energy W_a absorbed in the SSVD region in SF_6 for $p = 9$ (□), 15 (○), 21 (▽) and 30 Torr (△) and also in the $SF_6 : C_2H_6 = 5 : 1$ mixture for $p = 18$ (●) and 36 Torr (▲).

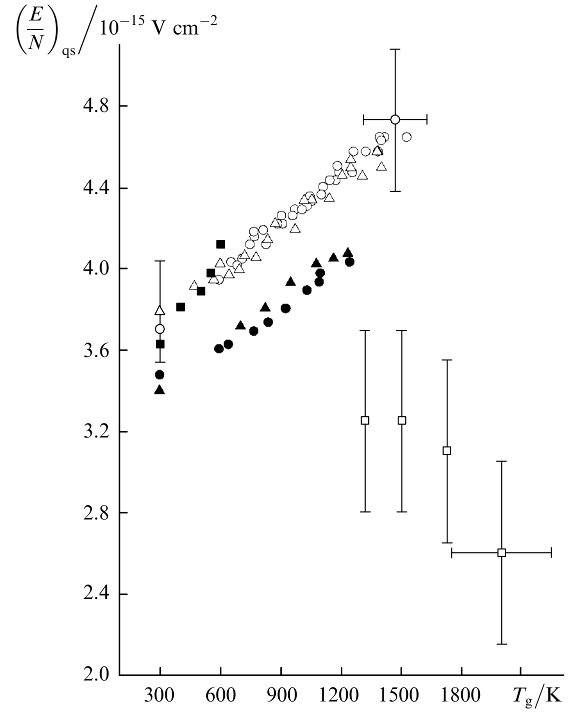

Figure 3. Dependences of $(E/N)_{qs} = (U_{qs} - \Delta U)/(Nd)$ on the gas temperature T_g in SF_6 for $p = 15$ (○) and 30 Torr (△) and the $SF_6 : C_2H_6 = 5 : 1$ mixture for $p = 18$ (▲) and 36 Torr (●), and also the critical reduced electric field strength in SF_6 obtained in [3] (■) and [4, 5] (□).

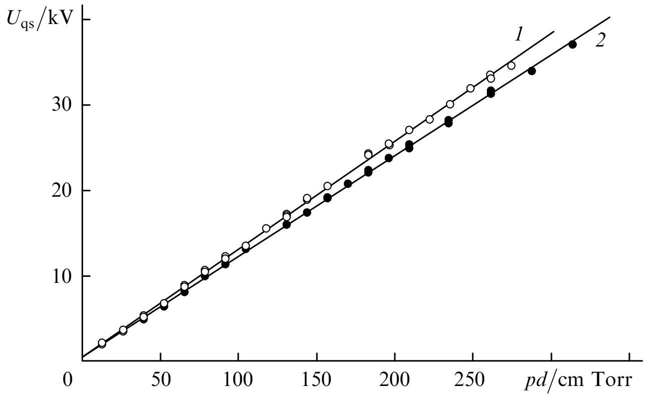

Figure 2. Dependences of the voltage U_{qs} in the quasi-stationary SSVD phase on pd in SF_6 (*1*) and the $SF_6 : C_2H_6 = 5 : 1$ mixture (*2*).

the critical reduced electric field strength in SF_6 and mixtures of SF_6 with C_2H_6 with increasing gas temperature at least in the temperature interval $T_g = 293 - 1500$ K.

The temperature dependences of $(E/N)_{cr}$ obtained in [4, 5] and also presented in Fig. 3 are opposite. One can see $(E/N)_{cr}$ rapidly decreases with increasing T_g. As a result, even taking into account a considerable error of measuring $(E/N)_{cr}$ in [4, 5], the value of $(E/N)_{cr}$, for example, at temperature 1500 K proves to be substantially lower than that obtained in our experiments. A similar dependence of $(E/N)_{cr}$ in SF_6 on T_g follows from calculations performed in papers [5, 6], where the thermal dissociation of SF_6 molecules was taken into account, the gas composition was assumed thermally equilibrium, and the rate constants of ionisation and attachment were calculated by using the energy distribution function for electrons. The latter was found by solving numerically the kinetic Boltzmann equation for electrons in an external electric field.

According to [5, 6], the value of $(E/N)_{cr}$ decreases due to the relative increase in the concentration of fluorine atoms with increasing the gas temperature. Because elastic and inelastic energy losses of electrons in their collisions with fluorine atoms, including electron attachment processes, are considerably lower than losses upon scattering of electrons by SF_6 molecules and other products of its decomposition, the equality of the ionisation and attachment rates in a heated gas is achieved at lower values of $(E/N)_{cr}$ compared to $(E/N)_{cr}$ in SF_6 at room temperature. This point of view is confirmed indirectly by experiments [13] demonstrating the decrease of $(E/N)_{cr}$ in mixtures of SF_6 with He with increasing the relative concentration of helium. Indeed, the electron energy losses in collisions with helium and fluorine atoms are considerably lower than in collisions with SF_6 molecules. The quantitative difference of the results obtained in papers [4, 5] from our results is probably explained by the following reason.

The FWHM of a discharge current pulse in our experiments was ~ 100 ns, whereas the duration of a laser pulse and the time delay between the laser and high-voltage pulses were the same and equal to 3 μs. Therefore, the dissociation of SF_6 molecules could noticeably affect the value of $(E/N)_{cr}$ only in the case if it has managed to proceed for the time not exceeding 3 μs. The dissociation of polyatomic molecules like SF_6 is a very complex process and includes, as a rule, many successive stages of the decomposition of a polyatomic molecule. Unfortunately, at present there is little information on the dissociation stages of SF_6 and corresponding rate constants. However, the dissociation time τ_{dis} can be roughly estimated by using the following qualitative considerations.

It is clear that the time τ_{dis} should be at least no shorter than the characteristic time τ_{A} of a single stage of the process. The corresponding constant k_{A} can be roughly estimated from the known Arrhenius equation [14]

$$k_{\mathrm{A}} = S\left(\frac{8T_{\mathrm{g}}}{\pi\mu}\right)^{1/2}\sigma_{\mathrm{A}}\left(1+\frac{D_{\mathrm{A}}}{T_{\mathrm{g}}}\right)\exp\left(-\frac{D_{\mathrm{A}}}{T_{\mathrm{g}}}\right). \qquad (2)$$

Here, S is the steric factor taking into account different mutual orientations of colliding particles; μ and σ_{A} are their reduced mass and collision cross section, respectively; and D_{A} is the activation energy corresponding to the equilibrium path of the reaction. The factor $S = 0.1 - 1$ for collisions of atoms with each other and molecules and $S = 10^{-6} - 10^{-3}$ for collisions of molecules with each other and radicals. The energy D_{A} depends on fragments into which a molecule is decomposed in a collision event, and is approximately a few electronvolts for SF_6. This estimate of D_{A} agrees with data [6, 15] on the equilibrium composition of heated SF_6 and the empirical relation between the activation energy and temperature at the developed dissociation stage [16].

By assuming for estimates that $\sigma_{\mathrm{A}} \sim 10^{-15}$ cm^2 and $S = 1$, we obtain a strongly overestimated value of k_{A} ($\sim 10^{-14}$ cm^3 s^{-1}). Because the maximal concentration of particles in our experiments does not exceed 10^{18} cm^{-3}, the time τ_{A} and, therefore, τ_{dis} certainly exceeds 100 µs. This means that no dissociation of SF_6 molecules occurs under the given experimental conditions. Note also that the dissociation of SF_6 in [4] became noticeable after heating for 10 ms at a temperature of ~ 2000 K. This can be considered as an additional indirect confirmation of the estimate of τ_{dis} presented above. The dissociation of SF_6 was absent in experiments [3] due to an extremely low density of gas.

The increase in the critical reduced electric field strength $(E/N)_{\mathrm{cr}}$ in nondissociated SF_6 with increasing gas temperature T_{g} observed in our experiments is caused by the increase in electron losses due to the attachment of electrons to vibrationally excited SF_6 molecules. This follows from our previous SSVD investigations in SF_6 irradiated preliminarily by a CO_2 laser [7, 8, 10]. At temperatures from 300 to 1100 K, the dissociation of SF_6 is completely absent (see, for example, [6, 15]), and therefore the critical electric field strength in SF_6 at constant gas density always depends on the gas temperature in this temperature range, increasing with T_{g}. This contradicts the statement made by the author of [2].

4. Conclusions

We have obtained the temperature dependences of the critical reduced electric field strength $(E/N)_{\mathrm{cr}}$ in SF_6 and mixtures of SF_6 with C_2H_6 heated preliminarily by radiation from a CO_2 laser. It has been shown that the value of $(E/N)_{\mathrm{cr}}$ in these gases increases with temperature in the range from 293 to 1500 K. This agrees with the results of measurements of $(E/N)_{\mathrm{cr}}$ in SF_6 performed in [3] at temperatures up to 600 K and contradicts the temperature dependence of $(E/N)_{\mathrm{cr}}$ in SF_6 in the range from room temperature to 1073 K obtained in [2]. The increase in $(E/N)_{\mathrm{cr}}$ with increasing gas temperature under our experimental conditions is caused by additional electron losses due to the attachment of electrons to vibrationally excited SF_6 molecules.

Acknowledgements. This work was partially supported by the Russian Foundation for Basic Research (Grant Nos 05-08-33704 and 06-08-00568).

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