

**SIMULATION OF THE EMISSION SPECTRUM OF SiH ( $A^2\Delta \rightarrow X^2\Pi$ )  
AND MEASUREMENT OF THE ROTATIONAL TEMPERATURE  
OF THE  $A^2\Delta$  STATE IN AN ELECTRON-BEAM PLASMA**

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*The 0–0 band emission spectrum of the  $A^2\Delta \rightarrow X^2\Pi$  transition of the SiH molecule was modeled numerically. The results obtained agree well with known calculated and experimental data. The rotational temperature of the  $A^2\Delta$  state of SiH in a free stream of pure monosilane ( $\text{SiH}_4$ ) and in a mixture with helium ( $\text{He} + \text{SiH}_4$ ) activated by an electron beam is determined by comparing calculated and experimental spectra. The assumption that the emission of SiH results from dissociative excitation of  $\text{SiH}_4$  by electron impact is confirmed. Rotational temperatures for various monosilane concentrations and distances from the nozzle are given. The spectra obtained exhibit the emission of silicon ions at wavelengths of 412.807 and 413.089 nm.*

**Key words:** optical emission spectroscopy, rotational temperature, electron beam, monosilane.

**Introduction.** A silane plasma is widely used for silicon film deposition. Diagnostics of such plasmas is often performed by means of optical emission spectroscopy [1]. This method is noncontact, nondisturbing, and rather simple, but interpretation of measurement results is rather difficult. The method provides information on the emitting plasma components and on the electron energy distribution function.

In silane plasmas, the main emitting molecular silicon-containing component is the SiH radical in the  $A^2\Delta$  state [1]. Its emission spectrum, namely the  $A^2\Delta \rightarrow X^2\Pi$  transition bands provide information on the rotational temperature, which is an important characteristic of plasma emission components.

In rotational temperature measurements, Boltzmann diagrams are widely used to check whether the population distribution of excited rotational levels is a Boltzmann one.

Stamou et al. [2] proved the validity of the assumptions on partial equilibrium of the population distribution of rotational levels in the excited  $A^2\Delta$  state of the SiH radical. Generally speaking, Boltzmann statistics is valid for rotational level distribution in an excited state if the state is populated from the ground state by a direct electron impact [3]. In addition, Schmidt et al. [4] found a collision-induced transfer of rotational quanta inside the  $A^2\Delta$  state, which, in principle, should lead to thermalization of this state.

However, because of the presence of closely spaced  $\Lambda$  doublets and overlap of the lines of different branches, the spectrum of SiH is almost always insufficiently resolved, and this prevents the use of the method of semilogarithmic (or Boltzmann) diagrams. Thus, the optimal method for determining temperature is a comparison of experimental and calculated emission spectra. This method was first applied to the emission spectra of SiH in [1], where the rotational temperature  $T_{\text{rot}} = (1800 \pm 90)$  K and vibrational temperature  $T_{\text{vib}} = (3800 \pm 150)$  K of SiH were obtained in a hydrogen–silane discharge. Later this method was used to determine the rotational temperature from moderate- and low-resolution spectra. The rotational temperature measured in a silane discharge was  $(2000 \pm 50)$  K [5]. Tsurubuchi et al. [6] performed measurements in a cell with monosilane activated by an electron beam for two energy values:  $T_{\text{rot}} = 1700$  K at  $E = 20$  eV and  $T_{\text{rot}} = 1400$  K at  $E = 500$  eV. In the argon stream with injected monosilane behind the plasmatron, the rotational temperature was 4000 K [7]. In a monosilane–helium microwave discharge plasma, the obtained values are in the range of 300–2000 K [8]. Such a

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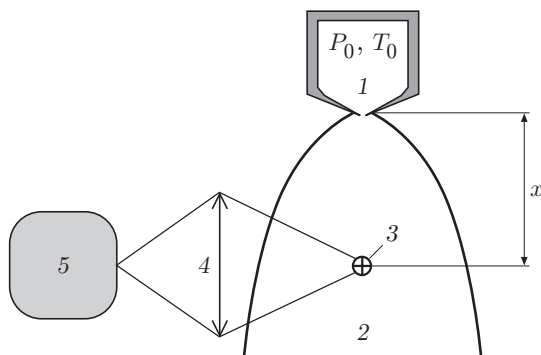


Fig. 1. Experimental facility: nozzle (1), jet (2), electron beam (3), lens (4), and MDR-6 monochromator (5).

broad range of  $T_{\text{rot}}$  is explained in [8] by variation in the degree of dissociation of monosilane in the mixture (below, this issue is considered in more detail). Finally, the value of  $T_{\text{rot}} = (2840 \pm 50)$  K in a monosilane glow discharge was determined with high accuracy from high-resolution spectra by Stamou et al. [9].

In the present study, we investigated free streams of pure monosilane and a mixture of monosilane with helium activated by an electron beam. The goal of the study was to simulate the electron-vibrational-rotational spectrum of the 0–0 band of the  $A^2\Delta \rightarrow X^2\Pi$  transition of SiH and to measure the rotational temperature of the  $A^2\Delta$  state of SiH in an electron-beam plasma.

**Experimental Facility.** The experiments were performed on a low-density gas-dynamic facility at the Institute of Thermophysics, Siberian Division, Russian Academy of Sciences [10]; a diagram of the facility is shown in Fig. 1. The gas source was an axisymmetric sonic nozzle of diameter  $d = 7.5$  mm. The gas flow rate  $G$  through the nozzle was controlled by an MKS Instruments regulator flowmeter; the nozzle prechamber pressure (stagnation pressure) was in the range of 130–2700 Pa. The inhibition temperature was maintained at the room level and was controlled by a thermocouple. The working gas was both pure monosilane and a mixture of monosilane with helium.

The facility was equipped with a plasma electron gun with a system of differential scavenging. An electron beam with an energy  $E = 2\text{--}5$  keV and a current  $I \leq 100$  mA intersected the gas stream and entered a collector intended for beam current measurements. The focused electron beam diameter was 3–4 mm. The nozzle was mounted on a three-component coordinate gear, which allowed one to change the distance from the nozzle to the electron beam and to perform nozzle adjustments.

The optical radiation excited by the electron beam was collected by a lens onto the entrance slit of an MDR-6 monochromator, and, after spectral decomposing, it was recorded by an electron photomultiplier. The spectral resolution was 0.03–0.08 nm/mm, depending on the value of the recorded signal.

In the experiment, we recorded the radiation excited by an electron beam in the wavelength range  $\lambda = 410\text{--}420$  nm. The measurements were performed on the stream axis at a fixed distance from the nozzle with variation in the gas flow rate and composition, and also for a fixed flow rate with variation in the distance.

**Spectrum Calculation and Evaluation of Rotational Temperature.** The procedure for determining the rotational temperature of SiH by comparing calculated and experimental spectra is described in [1, 7, 9]. Numerical simulation of spectra for diatomic molecules is usually implemented using standard formulas, given, for example, in [11, 12]. However, the simulation should be refined because each molecule has special structural features. An SiH molecule has a complex spectrum consisting of 12 overlapped branches ignoring  $\Lambda$  splitting, which raises the requirements to therm calculation. Therefore, we performed an analysis of the formulas for therm calculation from [9, 13, 14] by comparing with experimental data for the  $A^2\Delta$  and  $X^2\Pi$  states [15]. It has been established that the most accurate values of therms are obtained from calculations by the formulas given in [9] using molecular constants from the same paper.  $\Lambda$  splitting was calculated from the relations of [13]. The Henle–London factors were determined from the formulas of [11] for the transitional case and refined in [9].

An important point in spectrum calculations is a correct choice of the number of lines belonging to different branches. For this, we used calculated and experimental spectra [9, 16], and the experimental spectra of the present study. Table 1 lists the ranges of the rotational quantum number  $J$  for the corresponding branches of the  $A^2\Delta \rightarrow X^2\Pi$  transition.

TABLE 1

Branch	$J$	Branch	$J$	Branch	$J$
$Q_1$	2.5–20.5	$R_1$	2.5–20.5	$P_1$	2.5–19.5
$Q_2$	1.5–16.5	$R_2$	2.5–17.5	$P_2$	2.5–19.5
$Q_{12}$	1.5–20.5	$R_{12}$	2.5–16.5	$P_{12}$	2.5–19.5
$Q_{21}$	1.5–15.5	$R_{21}$	1.5–20.5	$P_{21}$	1.5–18.5

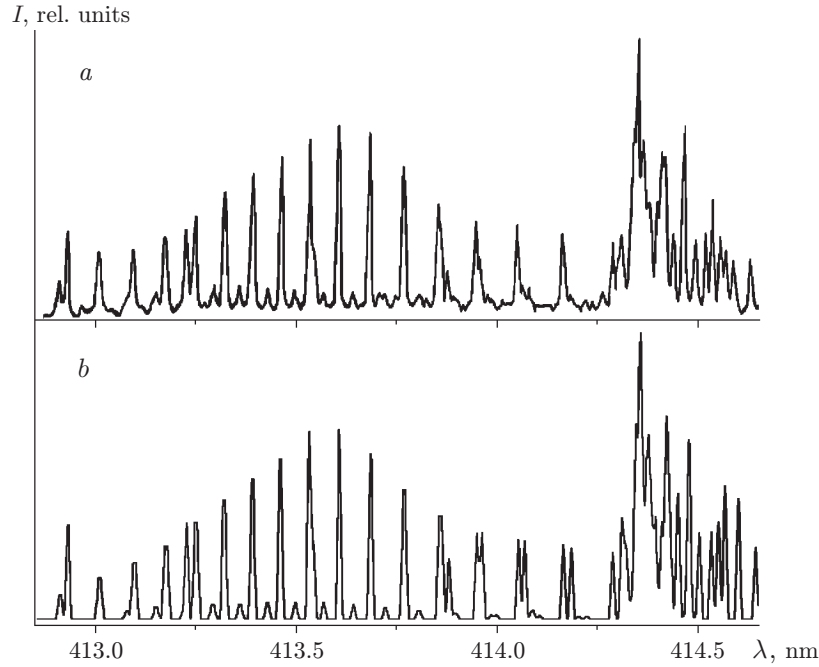


Fig. 2. Emission spectrum of the 0–0 band of the  $A^2\Delta \rightarrow X^2\Pi$  transition of SiH for the branch  $Q_1$ : (a) experiment [9]; (b) calculation ( $T_{\text{rot}} = 2270$  K and  $\alpha = 0.009$  nm).

Boltzmann molecular distribution over the rotational levels of the  $A^2\Delta$  state was assumed. The experimental instrument function is triangular, and the spectral line intensity  $I_\lambda$  at a wavelength  $\lambda$  is given by

$$I_\lambda = \sum_i I_i \left(1 - \frac{|\nu_\lambda - \nu_i|}{\alpha}\right).$$

Here  $I_i$  is the theoretical intensity of the  $i$ th line for a wavenumber  $\nu_i$  and  $\alpha$  is the half-height linewidth; and  $|\nu_\lambda - \nu_i| < \alpha$ .

Least-squares fitting of the calculated and experimental spectra was performed using the error function formula [6, 9]

$$\varepsilon = \sum_i \left( \frac{I'_i}{I'_{i,\text{max}}} - \frac{I''_i}{I''_{i,\text{max}}} \right)^2,$$

where  $i$  is the peak number; the prime corresponds to experimental values, and two primes, to calculated values for identical wavelengths. The rotational temperature was used as the fitting parameter. The temperature corresponding to the minimum of the error function is the desired quantity.

In determining the rotational temperature, one should pay attention to the fact that the fitting procedure is based on a high spectral resolution. For example, in [9] it is noted that the rotational temperature obtained at a low resolution, leading to a loss of the fine structure of the spectrum, is underestimated. However, even with a high spectral resolution in temperature evaluations, a careful analysis of spectral singularities is required because overlap of the lines of different branches and  $\Lambda$  splitting can introduce a significant error. In the present study, for comparison, we use the lines belonging to the branches  $Q_1$ ,  $R_1$  and  $R_2$ , whose wavelength are in the range of 410–415 nm.

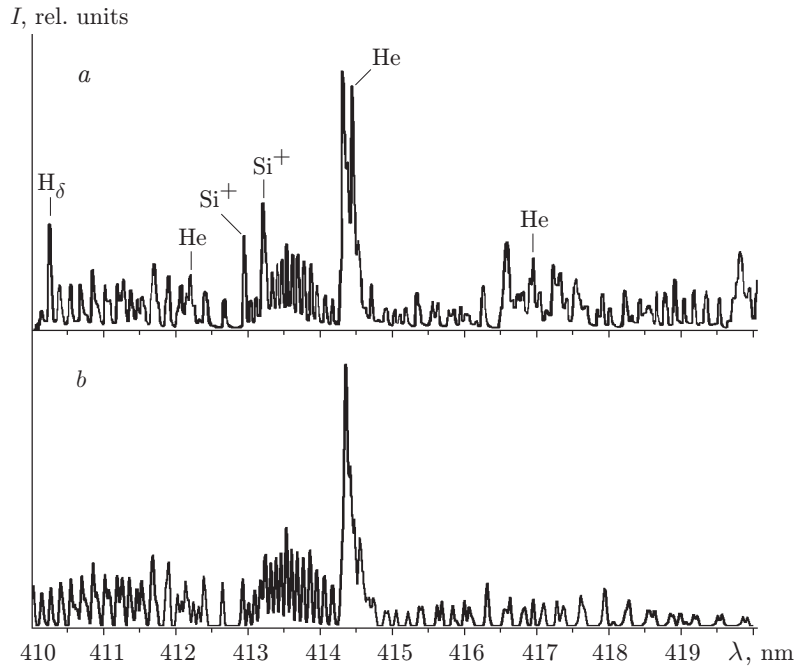


Fig. 3. Emission spectrum of the 0-0 band of the  $A^2\Delta \rightarrow X^2\Pi$  transition of SiH: (a) experiment, activation of an 10% SiH<sub>4</sub> + 90% He stream by an electron beam ( $G = 2$  standard liters per minute,  $x = 7$  mm,  $E = 2$  keV,  $I = 70$  mA, and  $d = 7.5$  mm); (b) calculation ( $T_{\text{rot}} = 2170$  K and  $\alpha = 0.036$  nm).

**Comparison with Known Data.** A calculated spectrum for a rotational temperature  $T_{\text{rot}} = 2840$  K and  $\alpha = 0.014$  nm is given in [9]. In our study, the rotational temperature found from this spectrum is  $T_{\text{rot}} = 2870$  K; i.e., it is within the measurement error of  $\pm 50$  K indicated in [9]. The spectrum calculated for this temperature is in good agreement with the spectrum given in [9].

Figure 2a gives the experimental spectrum of the branch  $Q_1$  for  $\alpha = 0.009$  nm from [9]. The rotational temperature found from this spectrum is  $T_{\text{rot}} = 2270$  K. Figure 2b shows the spectrum calculated for these parameters and a triangular instrument function. It is evident that these spectra are in good agreement. In [9], the difference in the  $\Lambda$  doubling of lines in the neighborhood of  $\lambda = 414$  nm is attributed to an abnormal nature, although in the spectrum shown in [16],  $\Lambda$  doubling was also observed and was within the calculation error.

Thus, the examined procedure for calculating spectra and finding rotational temperature can be considered correct. Small deviations are exceptions and can be taken into account in each case.

**Results and Discussion.** Figure 3a shows the emission spectrum of a 10% SiH<sub>4</sub> + 90% He mixture in free stream. The gas flow rate was  $G = 2$  standard liters per minute (standard liter is equivalent to a liter of the gas under normal conditions:  $T = 273$  K and  $p = 1,013,250$  Pa), and the distance from the nozzle exit was  $x = 7$  mm. The resolution was  $\alpha = 0.036$  nm. The rotational temperature determined using the calculation procedure described above is equal to  $(2170 \pm 50)$  K. Figure 3b shows the spectrum calculated for this temperature. In the range  $\lambda = 410$ – $415$  nm, the spectra are in good agreement, and the difference for  $\lambda > 415$  nm is due to the presence of the 1-1 band of the  $A^2\Delta \rightarrow X^2\Pi$  transition in the experimental spectra. A comparison of the experimental and calculated spectra shows that in the experimental spectrum, the peaks at  $\lambda = 412.082$ ,  $414.376$ , and  $416.897$  nm are the lines of helium (He) atoms corresponding to the  $5s^3S \rightarrow 2p^3P^0$ ,  $6d^1D \rightarrow 2p^3P^0$ , and  $6s^1S \rightarrow 2p^3P^0$  transitions. The peaks at  $\lambda = 412.807$  and  $413.089$  nm are the lines of silicon ions (Si<sup>+</sup>) corresponding to the  $4f^2F^0 \rightarrow 3d^2D$  ( $5/2 \rightarrow 3/2$ ) and  $4f^2F^0 \rightarrow 3d^2D$  ( $5/2 \rightarrow 7/2$ ) transitions. The peak at  $\lambda = 410.173$  nm is the H $\delta$   $6d^2D \rightarrow 2p^2P^0$  hydrogen line from the Balmer series. We note that the wavelengths of the indicated spectral lines are taken from [17] and correspond to measurements in air.

Figure 4a shows the emission spectrum of a 1% SiH<sub>4</sub> + 99% He mixture in free stream. The gas flow rate was  $G = 20$  standard liters per minute and the distance from the nozzle exit was  $x = 7$  mm;  $\alpha = 0.036$  nm. The rotational temperature was  $(1790 \pm 50)$  K. Figure 4b shows the spectrum calculated for this temperature. It is evident that the spectra are in good agreement.

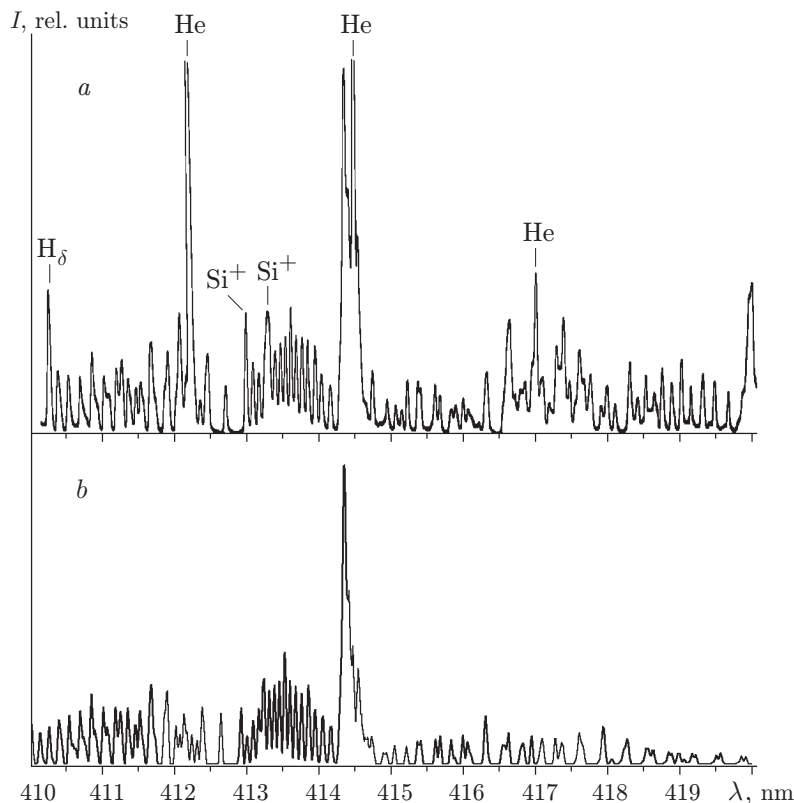


Fig. 4. Emission spectrum of the 0–0 band of the  $A^2\Delta \rightarrow X^2\Pi$  transition of SiH: (a) experiment, activation of 1%  $\text{SiH}_4$  + 99% He jet by an electron beam ( $G = 20$  standard liters per minute,  $x = 7$  mm,  $E = 2$  keV,  $I = 70$  mA, and  $d = 7.5$  mm); (b) calculation ( $T_{\text{rot}} = 1790$  K and  $\alpha = 0.036$  nm).

TABLE 2

$x$ , mm	$C_{\text{SiH}_4}$ , %	$T_{\text{rot}}$ , K	$G$ , standard liters per minute
7	10	2170	2
7	1	1790	20
35	10	2290	2

In addition, we measured the emission spectrum of a 10%  $\text{SiH}_4$ +90% He mixture in free stream at  $x = 35$  mm from the nozzle exit. The gas flow rate was  $G = 2$  standard liters per minute. Since the gas stream density rapidly decreases as the distance increases, the recorded signal was weak; therefore, to increase the signal-to-noise ratio, we had to reduce the resolution, which resulted in a decrease in the measurement accuracy. The value of  $\alpha$  was 0.075 nm, and the rotational temperature was  $T_{\text{rot}} = 2290$  K.

The emission spectrum of pure monosilane in free stream is shown in Fig. 5a. The gas flow rate was  $G = 0.5$  standard liters per minute, and the distance from the nozzle exit was  $x = 7$  mm;  $\alpha = 0.06$  nm. The rotational temperature was found to be  $(2050 \pm 50)$  K. Figure 5b shows the spectrum calculated for this temperature. The spectra are in good agreement, and the peaks of the  $\text{H}_\delta$  hydrogen line and the corresponding  $\text{Si}^+$  lines are clearly seen. The ratio of the radiation intensity of these lines to the intensity of the SiH band is about the same as in the spectra obtained for mixtures with helium.

The obtained values of the rotational temperature for streams of pure monosilane and a mixture of monosilane with helium agree with the results obtained in the glow discharge of pure monosilane and a mixture of monosilane with hydrogen. Thus, the emission results from dissociate excitation of monosilane molecules by electronic impact, which is confirmed by the rotational temperature measurements given in Table 2 ( $C_{\text{SiH}_4}$  is the volume fraction of monosilane in the mixture). An increase in the distance from the nozzle does not lead to a decrease in  $T_{\text{rot}}$ , although the isentropic temperature of the gas stream should be considerably lowered.

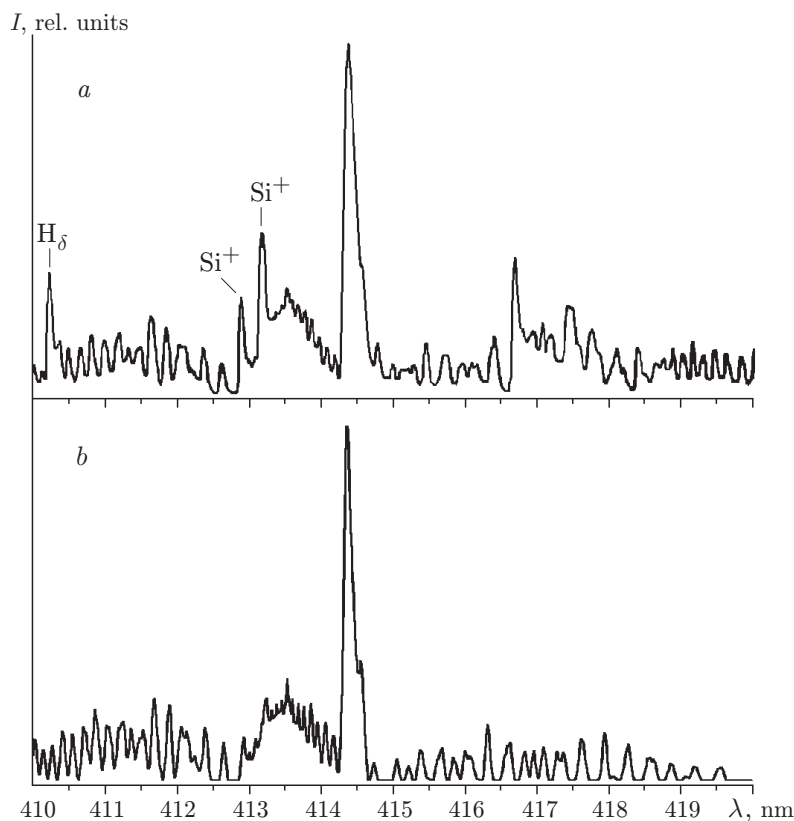


Fig. 5. Emission spectrum of the 0–0 band of the  $A^2\Delta \rightarrow X^2\Pi$  transition of SiH: (a) experiment, activation of  $\text{SiH}_4$  by an electron beam ( $G = 0.5$  standard liters per minute,  $x = 7$  mm,  $E = 5$  keV,  $I = 100$  mA, and  $d = 7.5$  mm); (b) calculation ( $T_{\text{rot}} = 2050$  K and  $\alpha = 0.06$  nm).

However, it is noted [8] that in a  $\text{SiH}_4 + \text{He}$  microwave discharge plasma, the rotational temperature for  $J \leq 10$  is much lower than 1000 K. Fantz [8] attributes this to the high degree of dissociation of monosilane in such a plasma. In other words, the formation of activated SiH molecules results not only from dissociative excitation of  $\text{SiH}_4$  molecules by electron impact but also from excitation of SiH molecules by electron impact from the ground state. In the present study, the second mechanism apparently does not occur because of the use of a free stream, which prevents accumulation of dissociation products in the electron-beam plasma region.

As the carrier gas flow rate increased (and, accordingly, the monosilane concentration decreased), the measured rotational temperature decreased from 2170 to 1790 K (see Table 2). This is apparently a consequence of collisional energy exchange of excited SiH molecules with atoms of the carrier gas. The possibility of such energy exchange is shown in [4].

Emission of silicon ions in silane-containing plasmas arises, as a rule, from dissociative excitation of  $\text{SiH}_4$  molecules by electron impact. The spectra obtained exhibit lines of silicon ions with wavelengths of 412.807 and 413.089 nm; and the emission spectra of pure monosilane and its mixtures in microwave and glow discharges do not show these lines. In the experiments of [6, 18], in which monosilane and its mixture were activated by an electron beam, these lines were not observed but other lines of the ion with  $\lambda = 385.37, 385.60, 386.26, 634.71,$  and  $637.14$  nm were recorded. Apparently, the lines of the silicon ion recorded in our study are due to the presence of a large number of high-energy electrons in the electron-beam plasma and the high gas density in the activation zone. This assumption is confirmed by the fact that they were observed both in a mixture of monosilane with helium and in pure monosilane.

**Conclusions.** A procedure was developed to evaluate the rotational temperature of the  $A^2\Delta$  state of the SiH molecule by comparing experimental and calculated spectra of the 0–0 band of the  $A^2\Delta \rightarrow X^2\Pi$  transition. The assumption of an equilibrium Boltzmann population of the rotational levels appeared valid because the calculated and experimental spectra are in good agreement. A comparison with known calculated and experimental data shows that the procedure for spectrum calculation and rotational temperature evaluation is correct.

The measured rotational temperature of the  $A^2\Delta$  state of SiH in a free stream of pure monosilane and a He + SiH<sub>4</sub> mixture activated by electron beam is in the range of 1700–2300 K. This is consistent with known data and confirms the assumption that the emission of the SiH molecule results from dissociative excitation of SiH<sub>4</sub> by electronic impact. The values of rotational temperature for various concentrations of monosilane and distances from the nozzle correspond to the assumption of collisional energy exchange between excited SiH molecules with atoms of the carrier gas.

Emission spectra of pure monosilane and a mixture of monosilane with helium first recorded the emission of a silicon ion with wavelengths of 412.807 and 413.089 nm, which is apparently due to the presence of a large number of high-energy activating electrons in the electron-beam plasma.

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