

# Reactions of photogenerated fluorine atoms with dopant molecules in solid argon

## 2.\* Reaction of CH<sub>4</sub> molecules with fluorine atoms diffusing in solid argon at 20–30 K

E. Ya. Misochko,<sup>a\*</sup> V. A. Benderskii,<sup>a</sup> A. U. Goldshleger,<sup>a</sup> A. V. Akimov,<sup>a</sup> A. V. Benderskii,<sup>b</sup> and C. A. Wight<sup>b</sup>

<sup>a</sup>Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation.

Fax: 007 (096) 515 3588. E-mail: misochko@icp.ac.ru

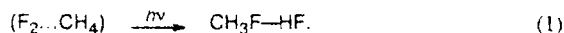
<sup>b</sup>Department of Chemistry, University of Utah,

Salt Lake City, Utah 84112, USA. Fax: +1 (801) 585 3207

The products of reactions of dopant CH<sub>4</sub> molecules with F atoms diffusing in solid argon at 20–30 K were identified by ESR and FTIR spectroscopy. The F atoms stabilized in the matrix were generated by UV photolysis of Ar–CH<sub>4</sub>(CD<sub>4</sub>)–F (1000 : 1 : 1) samples at 13 K. Subsequent heating above 20 K results in thawing of diffusion of the F atoms and formation of products of their reaction with CH<sub>4</sub>: radical-molecular complexes <sup>•</sup>CH<sub>3</sub>–HF (<sup>•</sup>CD<sub>3</sub>–DF) and radicals <sup>•</sup>CH<sub>3</sub> (<sup>•</sup>CD<sub>3</sub>). The ESR spectra of the radicals are similar to those observed for matrix-isolated <sup>•</sup>CH<sub>3</sub> (<sup>•</sup>CD<sub>3</sub>). The <sup>•</sup>CH<sub>3</sub>–HF complexes are characterized by the IR band of HF stretching vibration at 3764 cm<sup>–1</sup>. Two additional splittings on the H (*a*<sub>H</sub> = 2 G) and F (*a*<sub>F</sub> = 16 G) nuclei of the HF molecule appear in the ESR spectrum of the complex. The latter splitting is retained in the <sup>•</sup>CD<sub>3</sub>–DF complex, where *a*<sub>D</sub> < 0.3 G. The rate constant of the reaction CH<sub>4</sub> + F → <sup>•</sup>CH<sub>3</sub> + HF is equal to ~10<sup>–25</sup> cm<sup>3</sup> s<sup>–1</sup> at 20 K. Its activation energy (1.7 ± 0.2 kcal mol<sup>–1</sup>) is ~0.5 kcal mol<sup>–1</sup> greater than that in the gas phase. The collinear C<sub>3v</sub>-configuration of the <sup>•</sup>CH<sub>3</sub>–HF complex, which is similar to the configuration of the reagents in the transition state of the reaction considered, was established by the comparison of the experimental constants of hyperfine coupling with the results of the quantum-chemical calculation.

**Key words:** cryochemistry, photochemical reaction, fluorine, methane.

In our previous work,<sup>1</sup> we formulated the problems of studying solid-phase reactions involving F atoms and the conditions for stabilization of the intermediate products of elementary chemical reactions in an argon matrix. The products of photolysis of ternary Ar–CH<sub>4</sub>–F<sub>2</sub> (Ar–CD<sub>4</sub>–F<sub>2</sub>) mixtures at 13–16 K were identified,<sup>1</sup> i.e., under conditions when diffusion of thermal F atoms is frozen. During prolonged photolysis of F<sub>2</sub> in Ar–CH<sub>4</sub>–F<sub>2</sub> (1000 : 1 : 1) mixtures, ~2.2% of the CH<sub>4</sub> molecules are consumed. The main reaction product is the molecular CH<sub>3</sub>F–HF complex formed in the photolysis of the matrix-isolated pairs of reagents (F<sub>2</sub>...CH<sub>4</sub>):



In addition, stabilized <sup>•</sup>CH<sub>3</sub> (<sup>•</sup>CD<sub>3</sub>) radicals were detected. These radicals are formed in the reaction of one translationally excited ("hot") F atom with a methane molecule:



The fraction of radicals in the overall balance of the products is not greater than 10%. The ESR spectrum of the radicals indicates that they undergo fast rotation (the characteristic correlation time  $\tau_c \approx 10^{-9}$  s) and that the products of reaction (2) are spatially separated: the HF molecule leaves the nearest surroundings of the radical and is stabilized beyond its first coordination sphere. The purpose of the present work is to study the reactions involving diffusing F atoms by FTIR spectroscopy and ESR and to establish the differences between the products in the reactions of photogenerated ("hot") and diffusing (thermal) atoms with dopant CH<sub>4</sub> (CD<sub>4</sub>) molecules. According to the available data,<sup>2</sup> the thermal diffusion of F atoms (which are stabilized in the argon matrix in the low-temperature photolysis of F<sub>2</sub>) thaws at *T* ≥ 20 K, and at an initial relative concentration of the atoms of ~5 · 10<sup>–4</sup> results in their recombination at 20–26 K over ~10<sup>3</sup>–10<sup>2</sup> s. The reactions of the diffusing atoms were studied in this temperature range.

\*For Part 1, see Ref. 1.

## Experimental

Solid  $\text{Ar}-\text{CH}_4(\text{CD}_4)-\text{F}_2$  (1000 : 1 : 1) mixtures were prepared by simultaneous condensation of two gaseous  $\text{Ar}-\text{F}_2$  and  $\text{Ar}-\text{CH}_4(\text{CD}_4)$  mixtures onto a substrate cooled to 13–16 K. The procedures for preparation of samples, subsequent laser UV photolysis, ESR studies, and IR measurements have been previously described in detail.<sup>1</sup> Fluorine atoms were generated by the photolysis of  $\text{F}_2$  using UV lasers with wavelengths of 335 nm (radiation of the third harmonic of a Nd–YAG laser at a frequency of 10 Hz in IR measurements) and 337 nm (radiation of an  $\text{N}_2$  laser at a frequency of 1000 Hz in ESR studies). According to the published data,<sup>2</sup> which are in accordance with the results of our previous work,<sup>1</sup> UV photolysis of  $\text{F}_2$  molecules isolated in solid argon results in the stabilization of the F atoms with a quantum yield of ~0.7. This value was used to determine the quantity of photogenerated atoms. Kinetic measurements were carried out in two regimes: a) slow heating to 30 K of samples subjected to photolysis at 13–16; b) short photolysis at 20 K followed by monitoring of the kinetics of the change in the concentration of the radicals in the dark reaction.

## Results and Discussion

**Temperature annealing of samples subjected to photolysis at 13–16 K.** The changes in the IR spectra of the samples slowly heated (0.2 deg  $\text{min}^{-1}$ ) after preliminary photolysis at 16 K are shown in Fig. 1. The IR spectra of the samples at 16 K contain bands characteristic of the products of low-temperature photolysis,  $\text{CH}_3\text{F}-\text{HF}$  complexes: a band of the  $\text{C}-\text{F}$   $\nu_3$  vibration at 1003  $\text{cm}^{-1}$  and bands in the region of the HF vibration at 3779 and 3774  $\text{cm}^{-1}$ . When the sample was heated above 20 K, a new band appeared in the region of HF vibration at 3764  $\text{cm}^{-1}$ . At 22–25 K, the intensity of this band increases sharply. The intensities of the

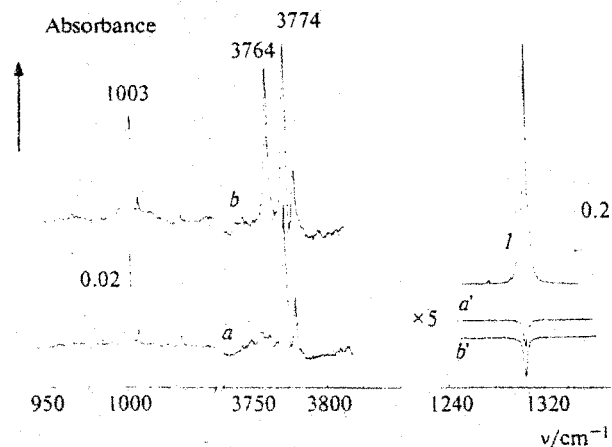


Fig. 1. IR spectra of the  $\text{Ar}-\text{CH}_4-\text{F}_2$  sample after photolysis at 16 K (a) and after heating to 28 K (b): 1, absorption band of  $\text{CH}_4$  ( $\nu_3$ ) after preparation of the sample; (a') and (b') were obtained by subtraction of the band after photolysis and after heating to 28 K.

bands of the complexes of the molecular products remain almost unchanged. The appearance of the new band of HF at 3764  $\text{cm}^{-1}$  and the weak band in the region of the bending vibration of the  $\cdot\text{CH}_3$  radical ( $\nu_4$ ) at 606  $\text{cm}^{-1}$  has been observed previously<sup>3</sup> in reaction (2) involving diffusing atoms and resulting in the formation of the  $\cdot\text{CH}_3-\text{HF}$  complex. The reaction of the F atoms with the  $\text{CH}_4$  molecules is also confirmed by a decrease in the intensity of the absorption band of methane at 1307  $\text{cm}^{-1}$  (see Fig. 1).

The increase in the intensity of the ESR spectrum indicates that the concentration of the radicals increases. When the samples are heated above 20 K, new lines (Fig. 2) assigned to two other radicals<sup>4</sup> appear and there is an increase in the intensities of the lines of the quartet 1 : 3 : 3 : 1 of the  $\cdot\text{CH}_3$  radical. One of these additional radicals,  $\cdot\text{CH}_2\text{F}$ , is formed in the reaction of atoms with the molecules of the primary product  $\text{CH}_3\text{F}$ . The spectrum of the radical consists of two triplets 1 : 2 : 1 split at the F nuclei with  $I = 1/2$  at 64 G. Splitting on the two equivalent protons in the triplet is equal to 21 G. Both constants of the hyperfine structure (HFS) correspond to the published data<sup>5</sup> for this radical. The spectrum of the second radical consists of two doublet quartets 1 : 3 : 3 : 1 with splittings of 23 and 2 G. The distance between the quartets is equal to 16 G. The quartet corresponds to splitting on the three equivalent protons of  $\cdot\text{CH}_3$ , and the two additional doublet splittings are assigned to the two nuclei with spin 1/2 of the HF molecule in the  $\cdot\text{CH}_3-\text{HF}$  complex ( $a_F = 16$  G,  $a_H = 2$  G).

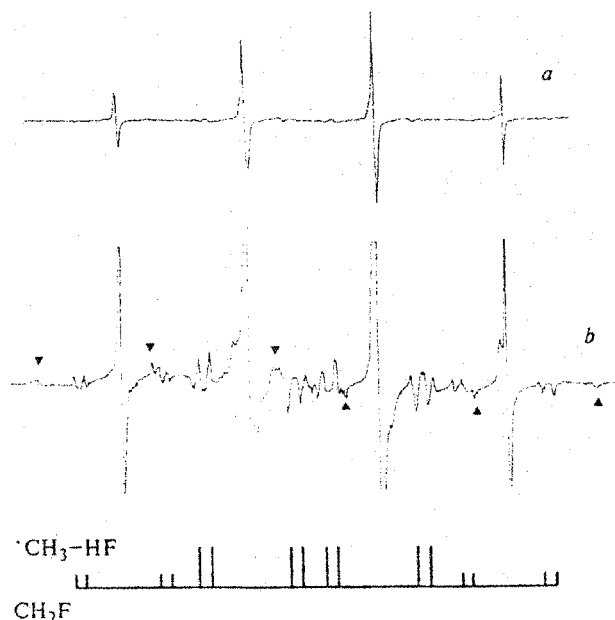
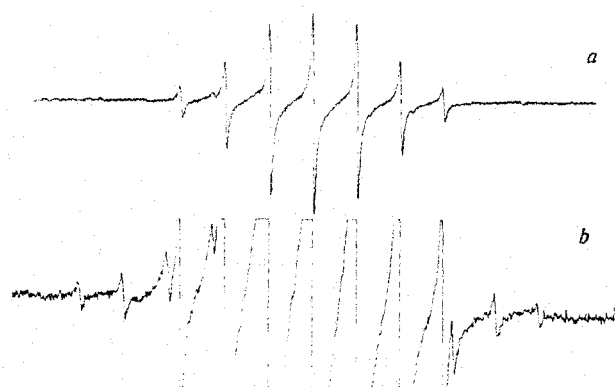


Fig. 2. ESR spectra of the  $\text{Ar}-\text{CH}_4-\text{F}_2$  sample after photolysis at 13 K (a) and subsequent heating to 22 K (b). Symbols (▼) indicate the position of lines of the  $\cdot\text{CH}_2\text{F}$  radical.



$^1\text{CD}_3\cdots\text{DF}$

Fig. 3. ESR spectra of the  $\text{Ar-CD}_4\text{-F}_2$  (1000 : 1 : 1) sample after photolysis at 13 K (a) and heating to 22 K (b).

In order to separate the splittings on the H and F atoms, we performed a series of analogous experiments with  $\text{CD}_4$  molecules instead of  $\text{CH}_4$ . Photolysis at 13 K results in the formation of  $^1\text{CD}_3$  radicals, whose spectrum is shown in Fig. 3. It consists of seven allowed lines of 1 : 3 : 6 : 7 : 6 : 3 : 1 and corresponds to splitting on three equivalent D atoms (with nuclear spin  $I_D = 1$ ) of 3.55 G. The spectrum has been previously analyzed in detail.<sup>1</sup> When the photolyzed samples are heated, the intensities of the lines increase by  $\sim 2$  times in the temperature range from 20 to 26 K. Additional lines appear simultaneously beyond the spectrum of the  $^1\text{CD}_3$  radical (see Fig. 3). The distance between the nearest lines is also equal to 3.55 G. The distance between the edge lines in low and high magnetic fields is equal to 37 G. We assigned these lines to the similar  $^1\text{CD}_3\cdots\text{DF}$  complex with splitting on the F nuclei  $a_F = 16$  G, since the expected value  $\Delta = a_F + (6a_H + 2a_{H\cdot})/6.5 = 37.6$  G (the HFC constant on the H proton is  $\sim 6.5$  times higher than that on D). The splitting on D of the DF molecule ( $a_D \cdot \approx 2/6.5 = 0.25$  G) is unresolved.

The changes in the concentrations of the radicals were calculated from the integral intensities of the spectra of  $^1\text{CH}_3$  and  $^1\text{CH}_3\cdots\text{HF}$   $I_{\text{ESR}}(T)$  taking into account the Curie law (in the absence of saturation of the spectra  $I_{\text{ESR}}(T) \propto 1/T$ ). They are presented in Fig. 4. The concentration of the radicals increases in the temperature range from 20 to 26 K. The  $R(T)$  dependence correlates with the curve of recombination of the thermal atoms.<sup>2</sup> The small shift of the compared curves (by 2–4 K) can be related to the lower heating rate and the

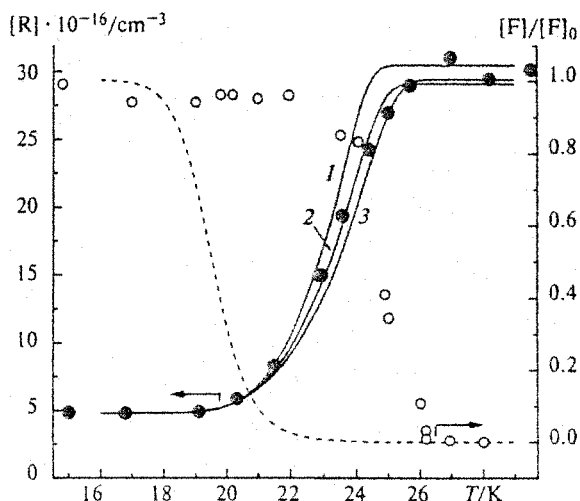


Fig. 4. Increase in the concentration of the radicals after heating of the sample and preliminary photolysis at 13 K. The heating rate is  $0.2 \text{ deg min}^{-1}$ . Solid lines correspond to the solutions of Eqs. (4) and (5) at  $E_2 = 1.9 \text{ kcal mol}^{-1}$ ,  $E_D = 1.2 \text{ kcal mol}^{-1}$  (1);  $E_2 = 1.72 \text{ kcal mol}^{-1}$ ,  $E_D = 1.1 \text{ kcal mol}^{-1}$  (2);  $E_2 = 1.6 \text{ kcal mol}^{-1}$ ,  $E_D = 1.0 \text{ kcal mol}^{-1}$  (3). The dotted line shows the calculated curve of the recombination of F atoms at  $E_2 = 1.72 \text{ kcal mol}^{-1}$  and  $E_D = 1.1 \text{ kcal mol}^{-1}$ . Light circles indicate the decrease in the concentration of F atoms at a heating rate of  $0.1 \text{ deg min}^{-1}$  according to the published data.<sup>2</sup>

higher concentrations of atoms in our experiments. The maximum concentration of the secondary  $^1\text{CH}_2\text{F}$  radicals is not greater, as a rule, than 10% of the concentration of the  $^1\text{CH}_3$  radicals.

The assignment of the IR and ESR spectra allows one to conclude that heating of samples containing F atoms stabilized at the initial temperature results in the formation of both  $^1\text{CH}_3\cdots\text{HF}$  complexes, with additionally resolved HFC components on the nuclei of the HF molecule, and  $^1\text{CH}_3$  radicals, with the symmetric ESR spectrum (assigned<sup>1</sup> to the type II radicals that are identical to the matrix-isolated  $^1\text{CH}_3$  radicals).

**Photolysis and dark reaction at 20 K.** The change in the concentration of radicals during short ( $\sim 100$  s) photolysis at 20 K and in the subsequent dark reaction is shown in Fig. 5. The concentration of the radicals begins to increase immediately after the beginning of irradiation. The quantum yield of the radicals

$$\Phi_R = (d[R]/dt)/\sigma I/N_F$$

( $I$  is the intensity of radiation,  $\sigma = 1.05 \cdot 10^{-20} \text{ cm}^2$  and  $N_F$  are the absorption cross section and the initial concentration of  $\text{F}_2$ , respectively) is equal to  $10^{-3}$  and coincides with the value determined previously<sup>1</sup> at 13 K. After cessation of the photolysis, the concentration of the radicals increases further for  $\sim 3 \cdot 10^3$  s. Only  $^1\text{CH}_3$  radicals are generated in the photolysis, while the ESR spectrum is evidence for the formation of  $^1\text{CH}_3\cdots\text{HF}$

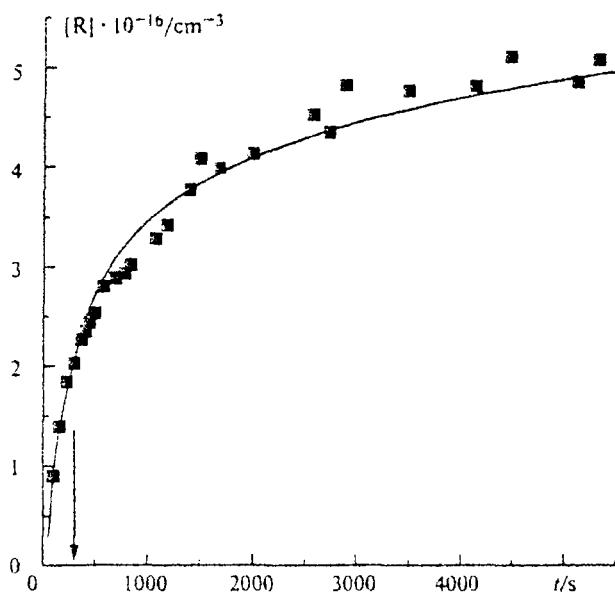


Fig. 5. Increase in the concentration of radicals during the photolysis of the Ar-CH<sub>4</sub>-F<sub>2</sub> (1000 : 1 : 1) sample at 20 K and after cessation of photolysis. The moment of cessation of photolysis is shown by the arrow. The results of the calculations are shown by the solid line.

complexes and  $\cdot\text{CH}_3$  radicals in a  $\sim 1.3 : 1$  ratio in the dark reaction. This slow increase in the concentration of the radicals in the dark reaction testifies that reaction (2) involves thermal atoms, while the initial accumulation of radicals over 300 s of photolysis with almost the same concentration and temperature-independent quantum yield is due to the reaction of hot F atoms with CH<sub>4</sub>. The balance of the consumption of methane and the formation of different products after low-temperature photolysis<sup>1</sup> and subsequent heating of the sample is presented in Table 1. Unlike the reaction of hot atoms, reaction (2) is predominant for diffusing thermal atoms, giving radical-molecular complexes and stabilized radicals. The quantity of  $\cdot\text{CH}_3\text{--HF}$  complexes is 1.2–1.5 times higher than that of  $\cdot\text{CH}_3$  radicals. The ESR spectra of the  $\cdot\text{CH}_3\text{--HF}$  complexes confirm the assignment of the IR band at 3764 cm<sup>-1</sup>.

**Structure of the  $\cdot\text{CH}_3\text{--HF}$  complex.** The analysis of the ESR spectra of the products of the reaction of

Table 1. Balance of the consumption of methane molecules and formation of products in Ar-CH<sub>4</sub>-F<sub>2</sub> (1000 : 1 : 1) samples (in % of the initial quantity of CH<sub>4</sub> molecules)

Experimental conditions	Consumption CH <sub>4</sub>	Formation of products		
		CH <sub>3</sub> F + HF	$\cdot\text{CH}_3$	$\cdot\text{CH}_3\text{--HF}$
After photolysis at 13 K	2.2±0.3	1.9±0.2	0.23±0.05	<0.05
After heating below 30 K	3.4±0.3	2.0±0.2	0.7±0.1	0.8±0.15

thermal atoms allows one to suggest the formation of  $\cdot\text{CH}_3\text{--HF}$  complexes with hyperfine interaction of the H and F nuclei with the unpaired electron of the radical. Previously,<sup>4</sup> we performed the *ab initio* calculations of the equilibrium structure of the CH<sub>4</sub>F system. The stable complex calculated has a collinear C<sub>3v</sub>-configuration (Fig. 6). The bond strength in the complex is equal to  $\sim 2$  kcal mol<sup>-1</sup>, and the frequency of the corresponding vibration is equal to 125 cm<sup>-1</sup>. The frequency of the H–F vibration in the complex is  $\sim 130$  cm<sup>-1</sup> less than that for the free molecule. The calculated spin densities and HFS constants are presented in Fig. 6. The calculated HFS constants agree well with the measured constants. Their values for F and H atoms decrease with slight changes in the orientation of the HF molecule relative to the equilibrium configuration. This allows one to conclude that a portion of the products of reaction (2) is stabilized in the collinear complex with C<sub>3v</sub> symmetry, which is analogous to the symmetry of the calculated<sup>6</sup> transition state in reaction (2), i.e., the complex stabilized in the lattice retains the symmetry of the transition state.

Based on the calculated configuration of the complex, we calculated its arrangement in the crystal. Since the methane molecule is a replacement dopant, we assumed that the radical is also localized in the node of the fcc lattice of the argon crystal (with the lattice parameter  $a = 5.24$  Å), and the C<sub>3</sub> axis of the complex coincides with the axis of the corresponding symmetry of the crystal, i.e., with the long diagonal of a cube. Three equilibrium positions of the HF molecule are possible on this axis: 1) in the center of a tetrahedron at the distance from the node occupied by the radical,  $r_1 = 2a/(3\sqrt{3}) = 2.02$  Å; 2) in the window of the D<sub>3</sub> symme-

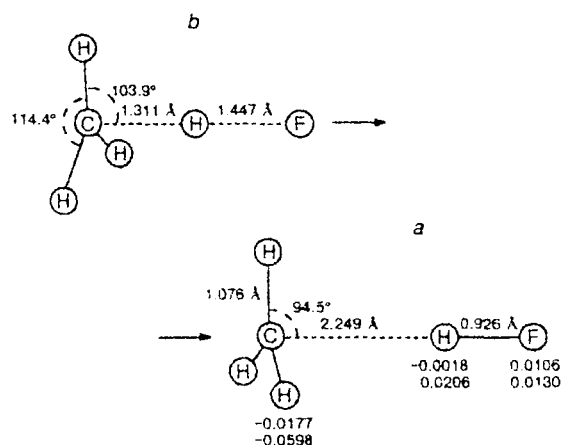


Fig. 6. Equilibrium configuration of the  $\cdot\text{CH}_3\text{--HF}$  complex (a) and the configuration of reagents in the transition state of reaction (2), configuration calculated previously<sup>6</sup> (b). The calculated spin densities of HFS constants (in atomic units) in the  $\cdot\text{CH}_3\text{--HF}$  complex are presented.

try formed by the atoms of the first coordination sphere, at the distance  $r_2 = a/\sqrt{3} = 3.03$  Å (Fig. 7); 3) in the center of an octahedron at the distance  $r_3 = a\sqrt{3}/2 = 4.54$  Å. Since in the equilibrium complex the distance from the C atom to the middle of the HF bond is equal to 2.72 Å and is comparable to  $r_2$ , this arrangement of the complex in the undistorted lattice was chosen as the initial arrangement. Then the structure was optimized by a known method of determination of the local minimum of the potential energy of the system using the molecular dynamics (MD) calculation.<sup>7</sup> The crystal contains 365 nodes, the  $\cdot\text{CH}_3$  radical is localized in the central node, and 194 Ar atoms on the cubic surface are immobile. The three-dimension motion<sup>7</sup> of the internal nodes was described by Newtonian equations taking into account interactions of all atoms. The parameters of the paired Morse potentials were used for the interaction between the Ar—Ar, Ar—F, and Ar—H atoms,<sup>7,8</sup> as well as the parameters of the Buckingham potential for Ar—C.<sup>9</sup> The elastic constant of the bond between the radical and the HF molecule in the complex,  $K = 5.5 \cdot 10^3$  dyn cm<sup>-1</sup>, was determined by the quantum-chemical method. The criterion of the accuracy of the MD calculation was that the total energy of the system did not change for 20 ps by more than  $10^{-3}$ . At the initial moment, the indicated initial configuration of the atoms and their rates were specified as equal to zero. The MD calculation was carried out until the potential energy of the system began to increase. Then the rates of all atoms were equated to zero again, and the calculation was repeated. This procedure was performed several times until the atoms were completely stopped, i.e., until the local minimum of the potential energy was

achieved. The radical was shifted by 0.25 Å from the node due to the interaction in the complex. The distance between the radical and the H atom of the HF molecule in the complexes became equal to 2.80 Å, i.e., it increased by 0.08 Å over that of the free complex. This change in the distance in the complex resulted in a decrease in the HFS constants  $a_H$  and  $a_F$  by not more than 20%. The calculated configuration of the complex in the lattice is shown in Fig. 7.

**Reactions of thermal fluorine atoms.** For diffusing atoms at  $T \geq 20$  K, the main reaction is reaction (2) resulting in the formation of the  $\cdot\text{CH}_3$ —HF complex and the  $\cdot\text{CH}_3$  radical. As follows from Figs. 4 and 5, which show the increase in the concentration of the radicals in the dark reactions, the number of radicals formed is ~2–3 orders of magnitude lower than the number of F atoms stabilized in the sample after photolysis. This means that the main channel of the transformation of diffusing atoms is recombination



Two channels of recombination are possible: geminal recombination (of pairs of atoms formed in the photodissociation of one molecule) and bulk recombination. The efficiency of geminal recombination is determined by the spatial separation of the F...F pairs in the thermalization process. As has been shown previously,<sup>2,8</sup> the photostimulated diffusion of F atoms in the Ar crystal results in their bulk recombination. This behavior of thermal atoms makes it possible to introduce average bulk concentrations and to use a simple kinetic scheme including reaction (2) with the rate constant  $k_2$  and the reaction of recombinations of atoms (3) with the rate constant  $k_D$ :

$$d[\text{F}]/dt = -k_2[\text{F}][\text{CH}_4] - k_D[\text{F}][\text{F}], \quad (4)$$

$$d[\text{R}]/dt = k_2[\text{F}][\text{CH}_4]. \quad (5)$$

The fact that the concentrations of the radicals and CH<sub>3</sub>F molecules are low compared to the concentrations of CH<sub>4</sub> make it possible to neglect their reactions with F atoms. At an initial concentration of F atoms corresponding to their quantum yield of 0.7, the kinetic curve of the increase in the concentration of the radicals in the dark at 20 K corresponds to the values  $k_2 \approx 10^{-25}$  cm<sup>3</sup> s<sup>-1</sup> and  $k_D \approx 3 \cdot 10^{-22}$  cm<sup>3</sup> s<sup>-1</sup>. The maximum concentration of the radicals formed in the dark reaction is the following:

$$[\text{R}]_{\text{max}} = [\text{F}]_0 (k_2[\text{CH}_4]/k_D[\text{F}]_0) \ln(1 + k_D[\text{F}]_0/k_2[\text{CH}_4]). \quad (6)$$

The reaction rate constant  $k_2$  was determined from the initial slope of the  $[\text{R}](t)$  dependence and Eq. (5). The rate constant  $k_D$  was determined from the measured value of  $[\text{R}]_{\text{max}}$  and Eq. (6). The coincidence of the kinetic curve with the solution of the system of Eqs. (4) and (5) at the indicated values of the constants is shown in Fig. 5. When the reaction of the recombination of

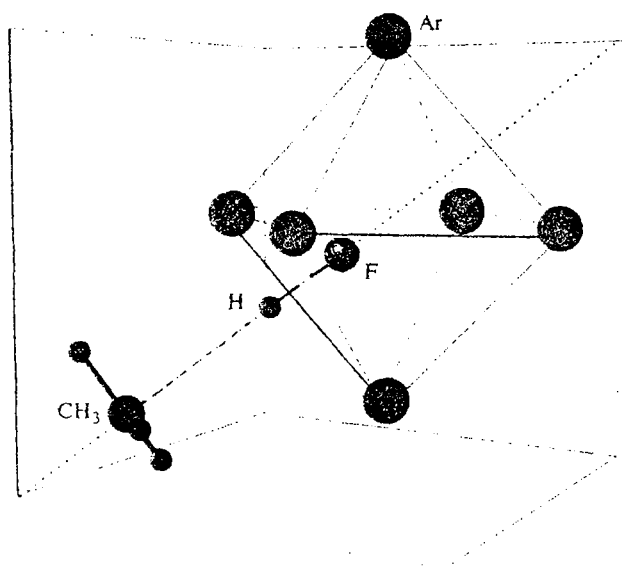


Fig. 7. Configuration of the  $\cdot\text{CH}_3$ —HF complex in the argon crystal.

atoms with  $\text{CH}_3^\cdot$  radicals with the rate constant equal to  $k_D/2$  is taken into account,  $k_2$  increases by ~20%.

The effective activation energies of reaction (2) and of the recombination of the atoms (3) at  $T > 20$  K,  $E_2$  and  $E_D$ , were determined from the curves of the thermostimulated increase in the concentration of the radicals heated at the constant rate  $u = 3.3 \cdot 10^{-3} \text{ deg s}^{-1}$ . The  $k_2$  (20 K) and  $k_D$  (20 K) values were used in the calculation. The values  $E_D \approx 1.0\text{--}1.2 \text{ kcal mol}^{-1}$  and  $E_2 \approx 1.6\text{--}1.90 \text{ kcal mol}^{-1}$  were determined by selecting the solutions of Eqs. (4) and (5) that describe the experimental  $[R](T)$  dependence (see Fig. 4). This estimation of the constants shows that  $k_2 \ll k_D$ .

The analysis of the kinetic data performed allows one to conclude that *the reaction of the F atoms with the  $\text{CH}_4$  molecules occurs in the kinetic regime. The effective activation energy of reaction (2) is  $0.3\text{--}0.7 \text{ kcal mol}^{-1}$  greater than the corresponding value for the reaction in the gas phase ( $1.15\text{--}1.25 \text{ kcal mol}^{-1}$ ).*<sup>10</sup>

Based on the configuration of the  $\cdot\text{CH}_3\text{--HF}$  complex shown in Fig. 7 and taking into account the fact that the transition state of the reaction has a similar symmetry, it can be assumed that the  $C_3$  axis of the crystal is the coordinate of the collinear reaction. The F atom, which is localized in the octahedral insertion position  $O_h$  at the distance  $r_3 = 4.54 \text{ \AA}$  from the  $\text{CH}_4$  molecule, attacks it in the direction perpendicular to the plane of the triangular window  $D_3$  separating the reagents. The distance between  $\cdot\text{CH}_3$  and HF in the transition state (its configuration in the gas phase is shown in Fig. 6) is shorter than that between the node and the  $D_3$  plane, so its formation is related to passage of the F atom through the plane of the window. This explains qualitatively why the reaction barrier is higher than that of the gas phase. When the reaction is collinear, the products should also separate along the  $C_3$  axis. The bond in the complex prevents the HF molecule from passing through the  $D_3$  window. Since the products of reaction (2) are both  $\cdot\text{CH}_3\text{--HF}$  complexes and  $\cdot\text{CH}_3$  radicals (whose ESR spectra contain no additional HFS caused by the interaction of the HF molecule with nuclei), there is a definite probability that the HF molecule passes through the window (escapes from the cage). Noncollinear configurations of the complex, in which the HF molecule is arranged in the nearest tetrahedral or octahedral positions, are probably not stabilized. The HFS constants with a proton and the  $^{19}\text{F}$  nucleus are maximum for the collinear configuration of  $\cdot\text{CH}_3\text{--HF}$ . They decrease rapidly with deviation from this configuration. In addition, the interaction in the complex can make the  $\text{CH}_3$  protons somewhat nonequivalent. ESR spectra of these configurations would possess higher asymmetry and lower additional HFS, but this is not observed.

\*\*\*

The spectral and kinetic analysis of the IR and ESR data allow one to conclude that *the reaction of diffusing F atoms with  $\text{CH}_4$  molecules at  $T > 20$  K results predominantly in the formation of  $\cdot\text{CH}_3\text{--HF}$  complexes.* The establishment of the structure of these complexes is one of the main results of the present work. The collinear configuration of  $\cdot\text{CH}_3\text{--HF}$  with  $C_{3v}$  symmetry corresponds to the complex with the corresponding HFS constants. This complex can be incorporated in the Ar crystal almost without deformations when the  $C_3$  axis of the complex coincides with the corresponding axis of the crystal. Therefore, the complex, whose structure is very similar to that of the transition state of the gas-phase reaction, can be stabilized.

Comparing the results of the present and previous<sup>1</sup> studies, it can be seen that, unlike the reaction of thermal atoms, translationally excited F atoms (with the initial kinetic energy obtained in the photodissociation of  $\text{F}_2$  and equal to ~1 eV) react with  $\text{CH}_4$  molecules to form only spatially separated products (HF molecules and stabilized radicals), whose ESR spectrum is identical to those of the matrix-isolated  $\cdot\text{CH}_3$  radicals.

The authors are grateful to A. F. Shestakov for quantum-chemical calculations. The present work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-08509) and partially supported by the National Research Foundation of the U.S.A. (NSF, Grant CHE-9300367).

## References

1. E. Ya. Misochko, V. A. Benderskii, A. U. Goldshleger, A. V. Akimov, A. V. Benderskii, and C. A. Wight, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 709 [*Russ. Chem. Bull.*, 1997, **46**, 678 (Engl. Transl.)].
2. J. Feld, H. Kunti, and V. A. Apkarian, *J. Chem. Phys.*, 1990, **93**, 1009.
3. G. L. Johnson and L. Andrews, *J. Am. Chem. Soc.*, 1980, **102**, 5736.
4. E. Ya. Misochko, V. A. Benderskii, A. U. Goldschleger, A. V. Akimov, and A. F. Shestakov, *J. Am. Chem. Soc.*, 1995, **117**, 11997.
5. R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1965, **43**, 2704.
6. L. P. Davis, L. W. Burggraf, M. S. Gordon, and K. K. Baldrige, *J. Am. Chem. Soc.*, 1985, **107**, 4415.
7. H. H. von Grönberg and H. Gabriel, *Chem. Phys. Lett.*, 1992, **192**, 503.
8. K. Alimi, R. B. Gerber, and V. A. Apkarian, *J. Chem. Phys.*, 1990, **92**, 3551.
9. A. I. Kitaigorodsky, *Molecular Crystals and Molecules*, Acad. Press, New York, 1973, 164 pp.
10. W. E. Jones and E. G. Skolnik, *Chem. Rev.*, 1976, **76**, 563.