# Formation of the CH3—HF Complex in Reaction of Thermal F Atoms with CH4 in Solid Ar

Eugenii Ya. Misochko,* Victor A. Benderskii,
Albert U. Goldschleger, Alexander V. Akimov, and
Alexander F. Shestakov

Institute of Chemical Physics at Chernogolovka of the
Russian Academy of Sciences
Chernogolovka 142432, Moscow Region, Russian Federation

As it was demonstrated recently,[1] thermalization length of "hot" F atoms generated by F_2 photolysis approaches 100 Å in solid Ar. Thermal atoms accumulated during photolysis diffuse over comparable distances on the time scale 10^3-10^4 s at 20—26 K.[1,2] This behavior makes possible reactions of both types of atoms with various impurity molecules embedded in an Ar matrix. Such reactions may yield weakly bonded molecular complexes since the crystalline environment prevents the products of the elementary reactions from flying apart. Jacox[3] proposed stabilization of CH3—HF and CH3F—HF complexes in an Ar matrix as a result of reactions of fluorine atoms with CH4. Later, Johnson and Andrews found[4] that photolysis of Ar/CH4/F2 mixtures yields the pairs of stable products CH3F and HF:

$$CH_4 + F + F \rightarrow CH_3F-HF \qquad (1)$$
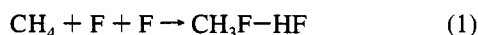
In addition, two IR bands appeared in the region of out-of-plane vibrations of CH3 upon warming of the sample. The authors tentatively assigned them to different types of CH3 radicals: nonbonded and bonded to HF:

$$F + CH_4 \begin{cases} CH_3 + HF & (2a) \\ CH_3 - HF & (2b) \end{cases}$$
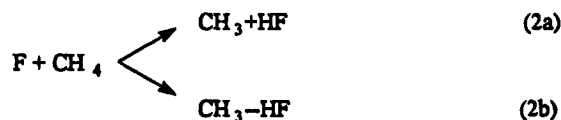
In this communication we present direct EPR evidence for the formation of both types of radical products in the reaction of thermal F atoms, whereas "hot" atoms produce only nonbonded radicals. The structure of the CH3—HF complex is also discussed.

The experimental apparatus and technique were described earlier.[5] Solid ternary Ar:CH4:F2 = M:1:1 and Ar:CD4:F2 = M:1:1 mixtures (M = 400—3000) were prepared by simultaneous deposition of the premixed gas samples (Ar/F2 and either Ar/CH4 or Ar/CD4) from separate nozzles onto a cold sapphire rod kept at ~13 K. After deposition the rod with the sample was moved down the microwave cavity. A small amount of radicals (5 × 10¹¹) was formed upon deposition. F atoms were generated by F2 photolysis with a pulsed N2 laser (λ 337 nm, repetition frequency 1000 Hz) through the special window in the cavity. The typical number of absorbed photons, 5 × 10¹⁵ (per photolysis period of 60 s), yielded ~10¹³ radicals. EPR spectra were recorded during and after photolysis at 14 K. Then the sample was slowly warmed (0.2 K/min), and spectra were recorded. The radical concentration increased until the temperature reached 26—28 K. This finding agrees with the determined earlier onset temperature for thermal diffusion of F atoms in Ar.[1]

* Fax: +7 095 938 21 56. E-mail: MISOCHKO@ICP.AC.RU.

(1) Feld, J.; Kunttu, H.; Apkarian, V. A. *J. Chem. Phys.* **1990,** *93,* 1009.
(2) Jacox, M. E. *Rev. Chem. Intermed.* **1985,** *6,* 77.
(3) Jacox, M. E. *Chem. Phys.* **1979,** *42,* 133.
(4) Johnson, G. L.; Andrews, L. *J. Am. Chem. Soc.* **1980,** *102,* 5736.
(5) Misochko, E. Ya.; Benderskii, V. A.; Goldschleger, A. U.; Akimov, A. V. *Mendeleev. Commun.* **1994,** 203.
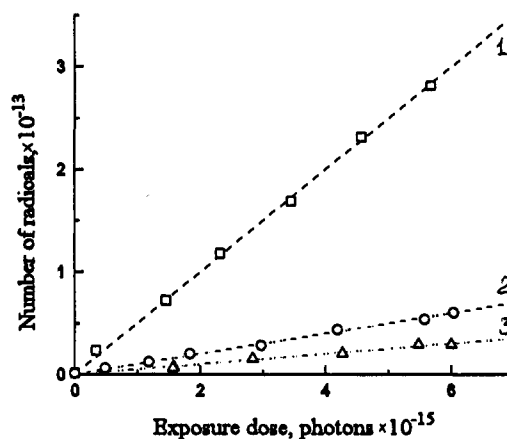
Figure 1. Accumulation of CH3 radicals under F_2 photolysis in ternary Ar:CH4:F2 = 1000:X:1 at 14 K. X = 5, 1, and 0.5 for lines 1—3, respectively. The small initial amount of radicals (formed under deposition) is subtracted.
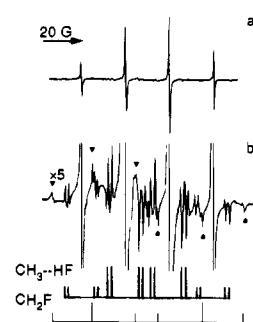
Figure 2. EPR spectra of radicals in an Ar:CH4:F2 = 1000:1:1 mixture: (a) after photolysis at 14 K; (b) after warming of the photolyzed sample to 21 K. CH2F lines are denoted with triangles.

Photolysis at 14 K yields mostly CH3 radical, in agreement with the previous observations by Cochran et al.[6], although our spectrum is better resolved. Concentration of the radicals grows linearly with the exposure dose and is proportional to the initial concentration of CH4 in the sample (Figure 1). Within the accuracy of our measurements no radicals were formed in binary Ar:CH4 mixtures under the same conditions of illumination.

Different widths of hyperfine (hf) components are due to the hindered rotation of the radical incompletely averaging the anisotropies of g and hf tensors (Figure 2a).[7] Warming of the sample above 18—20 K dramatically changes the spectrum. Two new radicals form in addition to CH3, whose concentration also increases. One of them is CH2F radical formed in a secondary reaction of thermal F atoms with the product of cage reaction 1. Its EPR spectrum contains two 1:2:1 triplets split on the F nucleus by 64 G. The proton splitting in the triplets in 21 G. Both hf constants agree with data of Fessenden and Schuler.[8]

The spectrum of the second radical consists of eight doublets, 1:1:3:3:3:3:1:1, and is characterized by three hf constants: 23, ~16, and ~2 G. The intensity pattern associated with the largest constant is the same as that of CH3 (1:3:3:1). Other interactions do not change intensities of lines and thus arise from two nonequivalent nuclei with spin ½. We anticipated that the CH3 radical would form a complex with the nearby HF molecule and additional 16 and 2 G splittings would be associated with F and H atoms of HF (a_F and $a_{H'}$, respectively). Relative yields of CH3—HF and CH2F depend on concentrations of CH4 and F2. The amount of CH3 and CH3—HF products increases by a
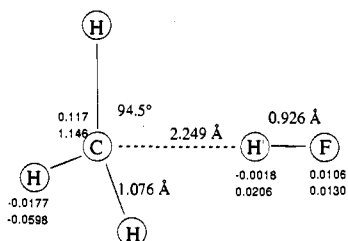
(6) Cochran, E. L.; Adrian, F. J.; Bowers, V. A. *J. Phys. Chem.* **1970,** *74,* 2083.
(7) Freed, J. H.; Fraenkel, G. H. *J. Chem. Phys.* **1964,** *41,* 3623.
(8) Fessenden, R. W.; Shuler, R. H. *J. Chem. Phys.* **1965,** *43,* 2704.
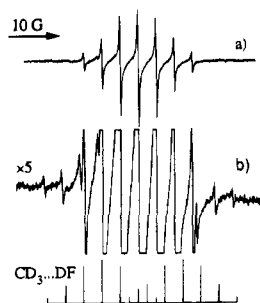
Figure 3. EPR spectra of radicals in an Ar:CD$_4$:F$_2$ = 1000:1:1 mixture: (a) after photolysis at 14 K; (b) additional lines detected after warming of photolyzed sample to 29 K.

Figure 4. Equilibrium structure of the CH$_3$−HF complex. Calculated Fermi constants (au) (upper) and spin densities (lower) are given for each nonequivalent nucleus.

factor of ~3 upon warming from 20 to 26 K. The subsequent cooling does not change the spectrum.

To justify our assumption we performed a series of similar experiments with deuterated methane. Photolysis gives mainly CD$_3$ radicals (Figure 3a). The spectrum contains seven lines (1:3:6:7:6:3:1, I_D = 1); the hyperfine splitting on D is 3.55 G, as expected. We also observed dependence of the line width on the nuclear spin projection as in experiments with CH$_4$. After photolysis we observed subsequent reactions upon warming of the sample. In contrast with the CH$_4$/F$_2$ system, CD$_3$ concentration grows only above 22 K by a factor of 2.

New EPR lines appear upon warming outside the CD$_3$ spectrum. Splitting between the nearest lines is 3.5 G; between the lowest and highest field lines Δ = 37 G. We assign this series to the similar complex CD$_3$−DF, because the expected value of Δ would be a_F + $(6a_H + 2a_{H'})/6.5$ = 37.6 G (hf constant of proton is ~6.5 times greater than that of D). The D splitting of DF ($a_{D'}$ = 0.25 G) was not resolved. The expected spectrum includes two series of seven lines each. Central lines overlap with the stronger spectrum of CD$_3$ and thus are almost hidden. A broad line with unresolved hyperfine structure appears after long photolysis and warming. The width of this line allows its assignment to the CD$_2$F radical.

Taking into account that thermal F atoms are immobilized below 18 K[1], only "hot" F atoms capable of long-range

migration are involved in reaction 2 during photolysis. The products of these reactions are predominantly CH$_3$ and CD$_3$ radicals. Activated reactions of thermal atoms given both CH$_3$ and the CH$_3$−HF complex. The ratio of their yields is ~2−3, independent of temperature within the accuracy of the experiment in the range 20−26 K.

In order to clarify the structure of the observed complex we performed ab initio calculations at the UMP4/6-311G**//UMP2/6-31G** level of theory[9] and compared calculated hf constants with the experimentally measured values. The equilibrium configuration of CH$_3$−HF corresponds to the collinear C_{3v} state similar to that of the isoelectronic NH$_3$−HF complex.[10,11] The binding energy of the stable CH$_3$−HF conformer is determined by the charge-transfer interaction and amounts to ~2 kcal/mol including ZPE correction. The hydrogen-bonded C_{2v} H$_2$CH−FH conformer has two imaginary frequencies and thus is unstable. Geometry, spin densities, and Fermi constants of the stable conformer are given in Figure 4. Calculated hf constants are in satisfactory agreement with the experimental data. The reliability of the calculation routine is confirmed by the fact that the found values for CH$_3$ and CH$_2$F systems are in agreement with experiment (within a scaling factor ~1.3). Calculated hf constants of H and F nuclei of HF are very sensitive to HF orientation. HF flip in the C_{3v} configuration decreases them by approximately 1 order of magnitude. The latter allows one to conclude that the observed CH$_3$−HF complex has the C_{3v} configuration described above.

The symmetry of the stable complex is the same as that of the calculated transition state corresponding to the lowest barrier for reaction 2.[12] It means that this reaction involving thermal F atoms is collinear and a remarkably high fraction of product retains the symmetry of the transition state after relaxation in the matrix. Therefore the environment allows one to make a snapshot of the transition state. "Hot" atoms can react through noncollinear intermediate states. HF molecules formed in this case may rotate or escape from the cage, explaining formation of HF-bonded and nonbonded radicals in the same reaction.

(9) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Revision E.1; Gaussian, Inc.: Pittsburgh, PA, 1992.

(10) Johnson, G. L.; Andrews, L. *J. Am. Chem. Soc.* **1982**, *104*, 3043.

(11) Kurnig, I. J.; Szczesniak, H. M.; Scheiner, S. *J. Phys. Chem.* **1986**, *90*, 4253.

(12) Davis, L. P.; Burggraf, L. W.; Gordon, M. S.; Baldridge, K. K. *J. Am. Chem. Soc.* **1985**, *107*, 4415.