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Photolysis of Fluorine Molecules Trapped in Solid Methane at 15 K: Evidence of the Reaction of Vibrationally Excited CH_3F Molecules with F_2

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The kinetics of reactions initiated via F_2 photolysis in solid methane at 15 K was studied with IR spectroscopy. $CH_3F\cdot\cdot HF$ complexes, formed in a cage reaction with a quantum yield of 0.55 ± 0.10, are the main products of the photolysis at a host:guest matrix ratio $M/R > 5$. At $M/R < 100$ the formation of CH_2F_2 is also detected. Its quantum yield grows linearly with F_2 concentration in the M/R range 100−13. The formation of CH_2F_2 is suggested to be due to the reaction of the F_2 molecule with a highly vibrationally excited primary product CH_3F^*, formed upon photolysis of the reactant clusters ($F_2\cdot CH_4\cdot F_2$).

Introduction

Reactions of vibrationally excited molecules in cryogenic solids become possible if (a) reactants are properly packed in a lattice, (b) the promoting vibrations are excited, (c) the energy of excitation is over the reaction barrier, and (d) the reaction rate is comparable to that of vibrational relaxation.

The selective optical pumping of the chosen molecular vibration is the most abundant technique of initiating reactions in the first vibrational excited state at extra low temperatures.[1−6] However, only reactions with low barriers can be activated in this way. The population of highly excited states of reactants in reactions with higher barriers can be produced via multiphoton or electronic optical pumping.[7,8] Alternatively, this goal can be achieved using energy from the chemical reaction.

Chain fluorination of hydrocarbons is the most prominent example of the participation of vibrationally excited molecules in gas phase reactions. Chains are branched due to additional formation of the intermediate species upon either decomposition of excited products or energy transfer in collisions between the excited products and reactants.[9,10] In particular, the enthalpy of the reaction

$$CH_3 + F_2 \rightarrow CH_3F^* + F \qquad (1)$$

is −3.1 eV, and approximately 80% of this energy is accumulated in vibrations of the CH_3F^* molecule.[10] This "hot" particle reacts with F_2, yielding HF, an F atom, and a CH_2F radical, thus leading to branching of chains upon methane fluorination.[11] Branching is due to the energy transfer in the linear collision complex $CH_3F^*\cdot\cdot\cdot F{-}F$, which brings about excitation or decomposition of F_2.

We suggest that similar reactions proceed in a solid if the reactants are properly arranged in a lattice. In this case, one can realize an energetic chain in which the energy of the reaction, accumulated in vibrations of the excited product, is used for further activation of reactants. In this paper we attempt to detect the solid-state reaction

$$[CH_3F^* + F_2 \rightarrow CH_2F_2 + HF] \qquad (2)$$

in which CH_3F^* is produced in the exoergic cage reaction of CH_4 with two F atoms:

$$[F_2 \xrightarrow{h\nu} F + F] \qquad (3)$$

$$[F + CH_4 + F \rightarrow CH_3F^* + HF] \qquad (4)$$

(square brackets denote a cage reaction).

The formation of hydrogen-bonded complexes $CH_3F\cdot\cdot HF$ upon fluorine photolysis in the pairs of reactants ($CH_4\cdot F_2$), isolated in an argon matrix, was reported in ref 12. Recently, we presented the first experimental data on fluorine photolysis in solid methane at 15 K.[13,14] If F_2 molecules are isolated in a methane lattice ($M/R \geq 100$), the photolysis products are similar to those formed in solid Ar. Since the barrier for the substitution reaction ($CH_4 + F \rightarrow CH_3F + H$) is more than 2 eV,[15] reaction 4 proceeds through abstraction of a hydrogen atom and, following cage recombination of CH_3 radical with the second fluorine atom,

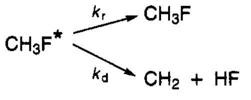
$$[CH_4 + F + F \rightarrow HF + CH_3 + F \rightarrow HF + CH_3F^*] \quad (5)$$

Thus, the CH_3F molecule is formed nearly on the dissociation threshold of the C−F bond (bond dissociation energy = 4.9 eV).

The enthalpy of a collision reaction in a gas phase,

$$CH_3 + F \rightarrow CH_2 + HF \qquad (6)$$

is −1.1 eV. Since the F atom attacks CH_3 at different angles, relaxation of CH_3F^*, formed in a cage reaction (5), may go either through vibrational relaxation down to the ground state or decomposition into CH_2 and HF:



(7a)

(7b)

Nevertheless, one fails to detect methylene in a matrix isolation study[12,13,16] probably because of cage recombination of CH_2 and HF.

The efficiency of a hydrogen abstraction is supported by the high quantum yield of methyl radicals upon photolysis of ternary[12] and binary[14] mixtures. Stabilization of CH_3 in a methane matrix (quantum yield ~0.5) is due to escape of a "hot" F atom from a cage.

We observed earlier[13] that photolysis of concentrated binary mixtures (M/R = 1) leads to growth of chains proceeding

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through (1) and subsequent reaction of an F atom with CH_4. The chain reaction gives CH_3F with a quantum yield of 4.5.

In this work we study binary mixtures at intermediate concentrations of F_2: $2.5 < M/R < 100$. This concentration range was chosen because in a random mixture of CH_4 and F_2, the essential part of F_2 molecules is in small clusters ($F_2 \cdot CH_4 \cdot F_2$) that are necessary for the solid-state reaction (2) in the absence of translational mobility (see Figure 3).

Experimental Section

The technique of kinetic IR measurements was described in detail earlier.[13,17] The samples were prepared by simultaneous condensation of two separate beams of gaseous reactants onto a copper substrate at 12 K. The beams were precooled to ≈90 K and crossed only near the substrate to prevent reaction upon condensation. The condensation flux was 5×10^{15} $cm^{-2}s^{-1}$. The thickness of films varied from 5 to 50 μm. Small, approximately equal sublimation energies (2.28 and 2.46 kcal/mol, taken from phase diagrams of CH_4 and F_2 below the triple point) suggest that a regular solid solution with a random arrangement of reactants over the lattice sites forms during the deposition.

The IR spectra were examined in reflection mode. Accumulation of reaction products was monitored by measurements of the integral intensities of corresponding IR bands, $\Delta I_i = B_i \Delta N_i$, where B_i is the molar integral intensity of the IR band. B_i values for the ν_3 bands of CH_3F (1004 cm^{-1}) and CH_2F_2 (1044 cm^{-1}) in solid reactant mixtures were measured earlier.[13] Their intensities are 1.2–1.4 times higher than those in the gas phase, being 120 and 245 km mol^{-1} for CH_3F and CH_2F_2, respectively. A pulsed N_2-laser (λ 337 nm) was used for photolysis. Photolysis intensity I_0 was $(1-5) \times 10^{15}$ $cm^{-2}s^{-1}$. Quantum yields of CH_3F, Φ_1, and CH_2F_2, Φ_2, (the number of respective molecules formed per absorbed photon) were measured during photolysis:

$$\Phi_i = \frac{1}{I}\frac{\Delta N_i}{\Delta t} \tag{8}$$

($I = I_0 \sigma N_{F_2}$, N_{F_2} is the number of F_2 molecules in the sample, $\sigma = 1.05 \times 10^{-20}$ cm^2 and is the absorption cross section of F_2 at 337 nm, and $\Delta N_i/\Delta t$ is the rate of accumulation of product).

In the preliminary experiments, we verified that at 15 K no products were formed in the absence of laser light or upon 2-h irradiation with the spectrometer globar. We also checked that there were no slow reactions after the completion of photolysis.

Results and Discussion

Figure 1 demonstrates the IR spectra of a photolized sample in the region of C–F stretching modes of the products. Fluorine photolysis entails the absorption 1004 cm^{-1}, which was previously observed and assigned to C–F vibration of CH_3F (ν_3) in the hydrogen-bonded complex $CH_3F \cdots HF$.[12,13,16] Bands at 1044 and 1088 cm^{-1}, assigned to CH_2F_2, appear in the IR spectra simultaneously with the 1004 cm^{-1} band.[18] These bands were not observed earlier in highly diluted samples ($M/R > 100$).[12,13]

The kinetics of product accumulation during photolysis is shown in Figure 2. Concentrations of the *primary* [CH_3F] and the *secondary* [CH_2F_2] products are linear with the number of absorbed photons, the [CH_3F]/[CH_2F_2] ratio being nearly constant in a wide range of photolysis times. These dependences indicate that both products are formed in one-photon events.[19]

We experimentally checked, separately, that quantum yields of CH_3F (Φ_1) and CH_2F_2 (Φ_2) are independent of light intensity I_0 and the thickness of the samples. The values of Φ_1 and Φ_2 at different M/Rs are shown in Figure 3. At $M/R > 5$ CH_3F molecules form in reaction 4 and their quantum yield is independent of F_2 concentration; $\Phi_1 = 0.55 \pm 0.10$. The sharp increase in Φ_1 at $M/R < 4$ results from the chain reaction.[13] The quantum yield of CH_2F_2, Φ_2, increases with F_2 concentration at $M/R > 5$ up to 0.11 and drops at $M/R < 4$. The initial linear increase in Φ_2 means that formation of CH_2F_2 requires two F_2 molecules among the nearest neighbors of CH_4. Absorption of light by one of them initiates the reaction, whereas the other participates in the secondary "dark" reaction (2).

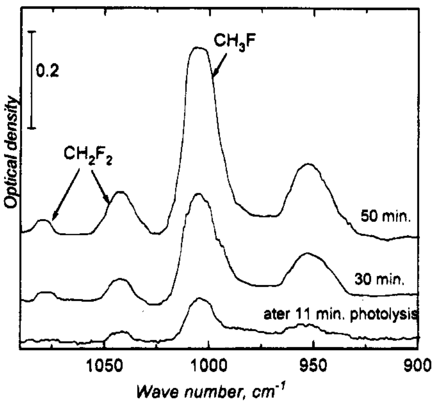

Figure 1. Absorption IR spectra of sample at $M/R = 10$ after UV photolysis at 15 K: $I_0 = 5 \times 10^{15}$ cm^{-2} s^{-1}; the initial amount of methane is 2×10^{19} cm^{-2}.

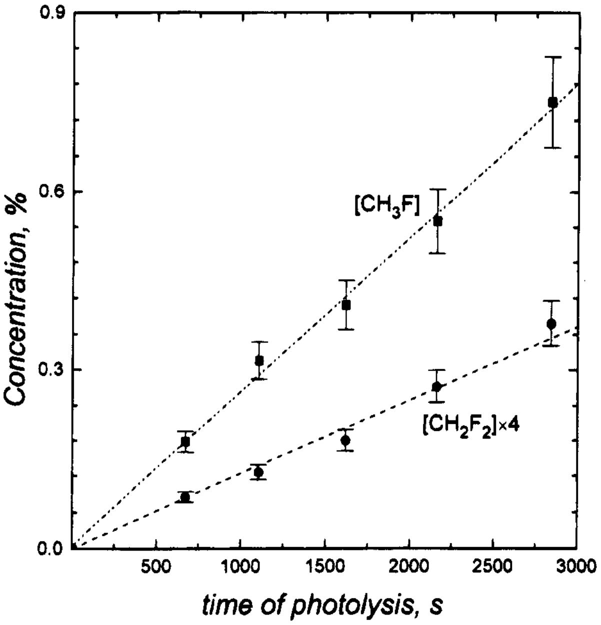

Figure 2. Kinetics of accumulation of CH_3F and CH_2F_2 upon photolysis: $M/R = 10$; $I_0 = 5 \times 10^{15}$ cm^{-2} s^{-1}; the initial amount of methane is 2×10^{19} cm^{-2}.

Within the suggested mechanism of CH_2F_2 formation, one can expect that the molecules, which deactivate the excitation of CH_3F^*, should diminish the quantum yield of CH_2F_2. In similarity to gas phase studies, CHF_3 can be used as such an agent. Upon addition of 8 mol % CHF_3, Φ_1 remains almost unchanged, while the quantum yield of CH_2F_2 is halved (see Figures 3 and 4).

The probabilities of finding the F_2 molecule near CH_3F^* (p) are shown in Figure 3 at different F_2 concentrations. Comparing the slopes of Φ_2 and p curves at fluorine mole fraction → 0, we found that the quantum yield of CH_2F_2 in reaction 2 in the favorable arrangement of reactants (CH_4 has two neighboring

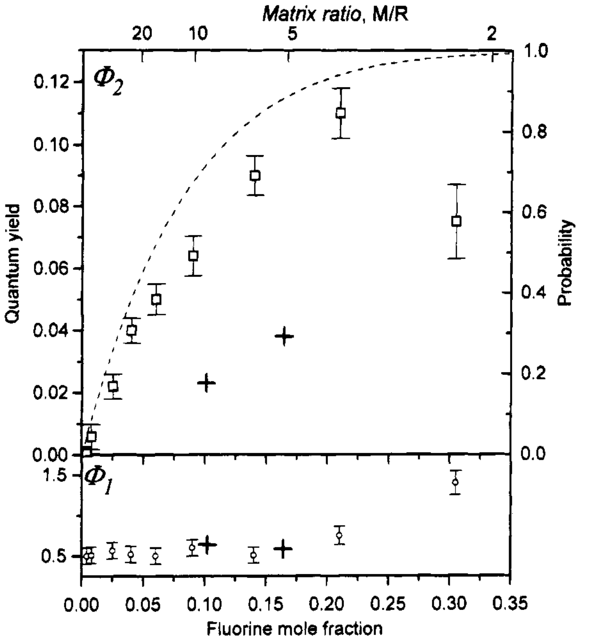

Figure 3. Quantum yields of CH_3F (Φ_1) and CH_2F_2 (Φ_2) vs fluorine mole fraction. The experimental points correspond to the average values of three to five equal samples. The plus symbol (+) designates values measured in samples containing 8 mol % of CHF_3. The *p* curve is shown with the dotted line. F_2 is assumed to randomly replace CH_4 in the lattice sites, and CH_4 is taken to have 12 nearest neighbors.

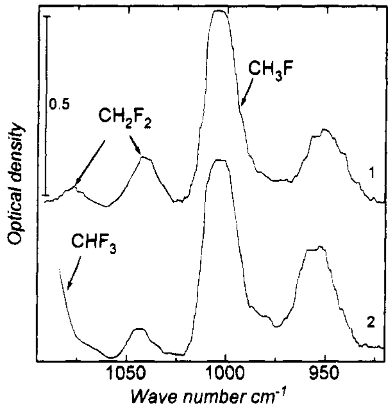

Figure 4. Absorption IR-spectra in the region of C−F vibrations of CH_3F and CH_2F_2 molecules after UV irradiation for 130 min at 15 K: (1) $M/R = 10$; (2) $[CH_4]/[F_2]/[CHF_3] = 10:1:0.8$, $I_0 = 5 \times 10^{15}$ cm^{-2} s^{-1}, and the initial amount of methane was 1.9×10^{19} cm^{-2}.

F_2 molecules) equals ~ 0.1−0.2. A similar consideration demonstrates that the CHF_3 molecule in the nearest environment of CH_3F^* completely (with probability 0.8−0.9) quenches formation of the secondary product.

On the basis of the cited data, we can point to several facts concerning formation of the secondary product: (a) CH_2F_2 forms upon photodissociation of the F_2 molecule in ($F_2 \cdots CH_4 \cdots F_2$) clusters with a probability of ~0.1−0.2; (b) the CH_2F_2 quantum yield drops at high F_2 concentrations (at $M/R < 4$); (c) the CHF_3 molecule in the first coordination shell of CH_4 inhibits CH_2F_2 formation.

Assuming that the main process following photodissociation of F_2 is the formation of the highly vibrationally excited CH_3F^* molecule, the major channel of CH_2F_2 formation is a two-stage chain. First, the CH_3F^* molecule forms near the bond dissociation energy of C−F. The second step is reaction 2.

Possibly, reaction 2 goes through decomposition of CH_3F^* followed by addition of F_2 to CH_2. Since the energy of the F−F bond falls far short of that of H−F, the barrier for the cage reaction

$$[CH_2 + F_2 \rightarrow CH_2F_2] \tag{9}$$

is lower than that for the reverse of (7b) $[CH_2 + HF \rightarrow CH_3F]$, and formation of CH_2F_2 is more probable then regeneration of CH_3F. To provide the estimated probability of CH_2F_2 formation in reactions 7a and 9, the decomposition time and the time of relaxation of CH_3F^* from 4.9 to 3.7 eV should be related as $\tau_r/\tau_d \geq 0.1-0.2$. For example, according to the molecular dynamics calculations,[20] the elimination of the DF molecule from the highly excited (~6.3 eV) 1,2-difluoroethane-d_4 molecule in solid Ar proceeds with a probability of ~0.08 at $\tau_r \sim 10^{-11}$ s.

The decrease of the quantum yield of CH_2F_2 in the presence of CHF_3 may be explained if CHF_3 molecules, next to the CH_3F^*, are considered as an effective energy sink. Because both molecules have large dipole moments, vibrational excitation is possibly quenched through resonant (or near resonant) dipole−dipole energy transfer from highly excited vibrational states of the C−F stretch, with the vibrational quantum number $v >> 1$ (the level spacing for which are obviously less then 1000 cm^{-1} due to anharmonicity of the highest vibrations), to the low-frequency modes of CHF_3.

As can be seen from Figure 3, the quantum yield of CH_3F exceeds 1 due to the contribution of a chain reaction at $M/R < 4$. However, energy released in reaction 1 (~3.1 eV) falls short of that required for CH_3F^* decomposition. Moreover, we observed a decrease in Φ_2 at these concentrations. The probability of reaction 1 between CH_3 and F_2 increases with the number of neighboring F_2 molecules, thus diminishing the quantum yield of reaction 5.

More detailed analysis of the suggested mechanism of formation of CH_2F_2 requires quantum chemical calculations of the potential energy surface of reaction $CH_3 + F$, the dynamics of energy redistribution among vibrations of CH_3F^* at different angles of attack of the F atom, and the dynamics of energy transfer to the lattice.

The data cited suggest that it is possible to obtain a two-stage energetic chain in which the excess energy released in the first step triggers further conversion of vibrationally excited products. We think that molecular crystals provide unique conditions for these reactions if highly energetic reactants are properly arranged in a lattice. Additionally, in contrast to a gas phase, the lattice prevents the escape of "hot" molecules from the reaction complex.

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(18) The band at 950 cm^{-1} in Figure 2 was assigned[13] to an unstable product, presumably the attachment radical CH_4F.

(19) This kinetics differs fundamentally from what we observed earlier in samples with high fluorine content ($M/R = 1$).[13] Whenever CH_2F_2 is the product of the reaction of CH_3F with an independently generated F atom, its concentration increases quadratically with the number of absorbed photons because of linear accumulation of the primary product CH_3F. Should the formation of CH_3F be rate limiting, the quadratic dependence of $[CH_2F_2]$ changes to a linear one while the concentration $[CH_3F]$ is constant.

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