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Reactions of photogenerated fluorine atoms with molecules trapped in solid argon

4.* Spectroscopic characteristics of β-$C_2H_2F^\bullet$ radicals generated in reactions of mobile F atoms with C_2H_2 molecules trapped in solid argon

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Reactions of mobile fluorine atoms with C_2H_2, C_2D_2, and C_2HD molecules in solid argon were studied by ESR and IR spectroscopic techniques. Highly resolved ESR spectra of the stabilized radicals $CHF{=}^\bullet CH$, $CDF{=}^\bullet CD$, $CHF{=}^\bullet CD$, and $CDF{=}^\bullet CH$ were obtained for the first time. Isotropic hyperfine constants on fluorine and proton nuclei were measured. It was found that the radicals formed in the reaction $F + C_2H_2$ correspond to the *cis*-β-$C_2H_2F^\bullet$ isomer. A comparison of the measured HFC constants with the values calculated by modern quantum-chemical methods allows the identification of the isomeric form of the radical, whereas vibrational analysis of the IR absorption spectra gives unreliable results. The calculation of the energy of the radical isomers predicts that *cis*-β-$C_2H_2F^\bullet$ is more stable than *trans*-β-$C_2H_2F^\bullet$ by ~1.0 kJ mol^{-1}.

Key words: cryochemistry, ESR spectroscopy, IR spectroscopy, fluorine, acetylene, radicals.

The reactions of F atoms with hydrocarbon molecules in the gas phase are well studied.[2] The high reactivity of radicals formed in primary reactions impede their detection in the gas phase and determination of their fundamental characteristics. For the spectroscopic study of radical products of chemical reactions, the most successful is the matrix trapping method, whose simplest variant is fast freezing of the gas phase reaction products to cryogenic temperatures and subsequent spectroscopic studies under steady-state conditions.

ESR and IR absorption spectra of most free radicals obtained by this method are commonly recognized.[3] However, this method is not always appropriate for the reliable identification and complete characterization of stabilized intermediates. Difficulties in identification are related to the presence of various products of secondary chemical reactions in the gas phase and stabilization of products in structural traps of the solid matrix resulting in "matrix shifts" of IR absorption bands and impossibility of detection by standard equipment of low-frequency vibrations ($\nu \le 300$ cm^{-1}) necessary for the reliable identification of radical-molecular complexes and various isomeric or conformation structures of intermediates.

We have recently proposed a modification of the method based on the high mobility of F atoms in solid argon and combined use of ESR and IR spectroscopy.[1,4] The capability of F atoms of migrating in solid argon at long distances[5,6] provides its bringing together with the isolated molecule of the second reactant, which favors the accumulation of trapped radicals (in concentrations sufficient for detection) formed directly in the solid phase. The potentialities of this approach are described in previous publications.[1] The advantages of the combined use of two supplementing spectroscopic methods are shown for the reactions of the F atom with the CH_4,[7,8] C_2H_4,[9] NO,[10] and NH_3 [1,4] molecules.

It is established that the full set of isotropic hyperfine coupling (IHFC) constants of radical products of chemical reactions can be determined due to the high resolution of ESR spectra of intermediates stabilized in solid argon. A comparison of the measured IHFC constants of the radicals and radical-molecular complexes with the values calculated by the modern quantum-chemical methods shows a good agreement with experiments. The IHFC constants change strongly with insignificant distortions of the equilibrium structure[1]; therefore, the ESR method is more reliable than IR spectroscopy for the identification and establishment of the spatial structure of stabilized radicals.

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* For Part 3, see Ref. 1.

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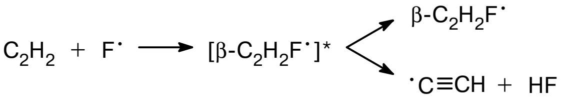
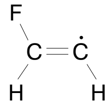
This work is devoted to the study of β-$C_2H_2F^•$ radicals formed in reactions of mobile F atoms with acetylene molecules. According to reaction (1), the first reaction channel predominates in the gas phase.[11,12]

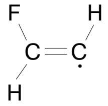


$$C_2H_2 + F^• \longrightarrow [\beta\text{-}C_2H_2F^•]^* \begin{cases} \beta\text{-}C_2H_2F^• \\ ^•C{\equiv}CH + HF \end{cases} \quad (1)$$

The β-$C_2H_2F^•$ radical can exist in two isomeric forms, depending on the position of the F atom toward the orbital of an unpaired electron



cis



trans

The results of matrix studies of isomers of this radical obtained in 1970—1980 and recent quantum-chemical data are contradictory. This problem can be solved only by the combination of kinetic IR and ESR measurements with quantum-chemical calculations and taking into account the experience of our previous works on the determination of possibilities of each spectroscopic method in the identification of intermediates.

The first attempts to obtain β-$C_2D_2F^•$ radicals were made by the photolysis of solid Ar—F_2—C_2D_2 mixtures at 4.2 K.[13] Although the authors of this work could not detect well-resolved spectra of the stabilized radicals, they determined the IHFC constants on nuclei of the F atom (a_F = 6.9 mT) and one of the D atoms (a_D = 0.6 mT). Taking into account the known IHFC constants of isomers of the $C_2H_3^•$ radical,[14] the observed ESR spectrum was ascribed to the *trans*-β-$C_2H_2F^•$ radical. The better resolved spectra of the β-$C_2H_2F^•$ radical in the SF_6 matrix[15] were also attributed to the *trans*-β-$C_2H_2F^•$ isomer. This assignment was argued, in particular, by the semiempirical INDO calculations, according to which the *trans*-isomer should be more stable than the *cis*-isomer.

The IR absorption spectra of the reaction products frozen in solid argon in the Ar—NF_3—C_2H_2 gas mixtures have first been presented in Ref. 16. Although the obtained spectra contain bands of products of various reactions, the authors succeeded to isolate the IR spectrum of the β-$C_2H_2F^•$ radical. Based on the conclusions,[13] the authors attributed the observed spectrum to the *trans*-isomer. The analysis of normal vibrations of the *trans*-β-$C_2H_2F^•$ isomer and comparison of the calculated vibrational spectrum with the measured IR frequencies favor this assignment.

The first reliable calculations of spectroscopic characteristics of the $C_2H_2F^•$ radicals by nonempirical methods (for example, CCSD) and in the framework of the density functional theory (NLSD) were performed in early 1990s.[17] Based on these calculations, we can conclude that *cis*-β-$C_2H_2F^•$ is more stable than the *trans*-isomer; the spin density distribution in β-$C_2H_2F^•$ (responsible for "internal" hyperfine magnetic interactions) differs from that in $C_2H_3^•$; the IHFC constants of the β-$C_2H_2F^•$ isomers differ significantly, and the measured values[13,15] are closer to those calculated for *cis*-β-$C_2H_2F^•$; the frequencies of IR vibrations of the radical isomers differ insignificantly (the differences are comparable with the calculation accuracy) and, therefore, the experimental spectrum[16] cannot unambiguously be assigned to one of these isomers.

Thus, the results of calculations certainly show that the conclusions by the authors of experimental works[13,15,16] are dubious. To be convinced in a reliability of the calculated data, we preliminary performed analogous calculations using the improved quantum-chemical methods and completely confirmed all conclusions presented above. Taking into account aforesaid, we carried out the experimental studies aimed at obtaining resolved ESR and IR absorption spectra of the $C_2H_2F^•$ radicals and reliably determining the characteristics of the stabilized isomeric form based on the comparison of the spectroscopic data with calculation results.

Experimental

The procedure of preparation of samples has previously been described in detail.[8] Samples were prepared by the combined condensation *in vacuo* of the Ar—C_2H_2 and Ar—F_2 gas mixtures on a support cooled to 15 K (a sapphire rod in ESR experiments and CsI in IR studies). Samples with the relative molar content of reactant molecules from $3 \cdot 10^{-3}$ to $2.5 \cdot 10^{-4}$ were studied. The samples with Ar : F_2 : C_2H_2 = 3000 : 1 : 1 were studied in most detail; their thickness being ~100 μm.

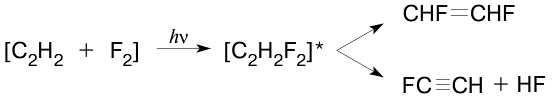
ESR spectra were measured using a flow-type cryostat with a mobile helium chamber. The thermoregulation system provided the stability of the sample temperature of at least 0.1 K in the range of 15—40 K. IR absorption spectra were recorded on a Mattson Model RS/10000 Fourier spectrometer with a spectral resolution of 0.5 cm^{-1} in the 4000—500 cm^{-1} range. In these experiments, a closed-cycle helium refrigerator with a minimum working temperature of 13 K was used. In some experiments, we checked that the radiation of the spectrometer globar had no effect on chemical reactions in samples.

Fluorine atoms were generated in photolysis of F_2 molecules by UV lasers with the wavelengths λ = 355 nm (radiation of the third harmonic of an Nd : YAG laser with a frequency of 10 Hz in IR measurements) and λ = 337 nm (radiation of an N_2 laser with a frequency of 1000 Hz in ESR measurements). The average radiation power did not exceed 10 mW cm^{-2}. To separate reactions of photogenerated "hot" and diffusing "thermal" F atoms, photolysis of F_2 was carried out at 15 K. Diffusion of F atoms in solid argon is thermally activated at temperatures above 20 K. The reaction of diffusing thermal atoms was performed as follows: after the end of photolysis, the sample was annealed for 3—5 min at 23 K, then the temperature was decreased to 15 K, and the IR absorption spectrum was recorded. These cycles were repeated 10—12 times to the complete cessation of chemical transformations.

According to ESR measurements, the prepared Ar—C_2H_2—F_2 samples contain no radical. UV photolysis followed by annealing of the Ar—F_2 sample at 23 K results in the appearance of a narrow band at 1490 cm^{-1} in the IR spectra, which is attributed to the $FO_2^{\bullet}$ radicals. In similar ESR experiments, the spectrum of this radical is also observed. Molecular oxygen is the main impurity in gaseous fluorine used and is always present in the studied samples in a relative molar concentration of ~10^{-4}—10^{-5}. Since F atoms diffusing in solid argon react efficiently with O_2 molecules at temperatures above 20 K to form stabilized $FO_2^{\bullet}$ radicals,[18] we used this reaction as a test for monitoring reactions of thermal F atoms.

Results and Discussion

IR absorption spectra of Ar—F_2—C_2H_2(C_2D_2) samples. The IR spectrum of the starting sample Ar : F_2 : C_2H_2 = 3000 : 1 : 1 (Fig. 1, spectrum *1*) contains broad lines of acetylene molecules with maxima at 736.5, 1334.5, and 3288.5 (3302.0) cm^{-1}. The short photolysis (~5 min) at 15 K increases rapidly the intense bands in the regions of a stretching vibration of C—F (1058, 1129, and 1153 cm^{-1}) and a molecular vibration of H—F (3756 and 3900 cm^{-1}) (see Fig. 1, spectrum *2*). These bands have previously be assigned to CHF=CHF and C_2HF in the complex with HF.[19,20] Such molecular products can be formed in the cage reaction during photolysis of complexes of the reactants



$$[C_2H_2 + F_2] \xrightarrow{h\nu} [C_2H_2F_2]^* \begin{array}{l} \nearrow CHF{=}CHF \\ \searrow FC{\equiv}CH + HF \end{array} \qquad (2)$$

The maximum decrease in the intensity of the IR bands of acetylene during prolonged photolysis is ~2%, which corresponds to the fraction of binary complexes in the samples with a relative content of the reactants of ~$3 \cdot 10^{-4}$ (Refs. 7 and 9).

Subsequent annealing of the samples at 23 K results in the appearance and growth of new bands at 643, 698, 785, 1070, 1263, 1631, 3026, and 3193 cm^{-1} (see Fig. 1, spectrum *3*; Fig. 2 presenting the IR spectrum of the Ar—F_2—C_2D_2 sample after annealing). The increase in their intensity is accompanied by a decrease in bands of the isolated C_2H_2 (or C_2D_2) molecules. Simultaneously the intensity of the narrow band of the $FO_2^{\bullet}$ radicals increases (Fig. 3). The linear plots of the increase in the intensity of new bands *vs.* decrease in the intensity of the bands of C_2H_2 assert that a series of eight IR bands is attributed to the primary products of the reactions of diffusing F atoms with acetylene molecules.

According to reaction (1), both isomers of the β-$C_2H_2F^{\bullet}$ radical, as well as the $C_2H^{\bullet}$ radical and HF molecule, can be its primary products. The absence of an intense absorption band of the HF molecule in the region of 4000—3000 cm^{-1} and a characteristic band of the $C_2H^{\bullet}$ radical in solid argon[16] at 1845 cm^{-1} imply that the excited [β-$C_2H_2F^{\bullet}$]* radical is not decomposed in the solid matrix. Each of the isomers of the β-$C_2H_2F^{\bullet}$ radical possesses nine normal vibrations, and the strongest stretching vibrations of C—F and C=C should be comparable in intensity (Table 1). However, each spectral range contains only one strong absorption band (see Fig. 1, spectrum *3*, and Fig. 2) and, hence, the observed eight bands belong to one isomer. Therefore, one of the isomers of the β-$C_2H_2F^{\bullet}$ radical is the predominant product of the reaction of diffusing F atoms.

Note that the annealing of the samples containing stabilized radicals for 72 h at 30 K does not notice-

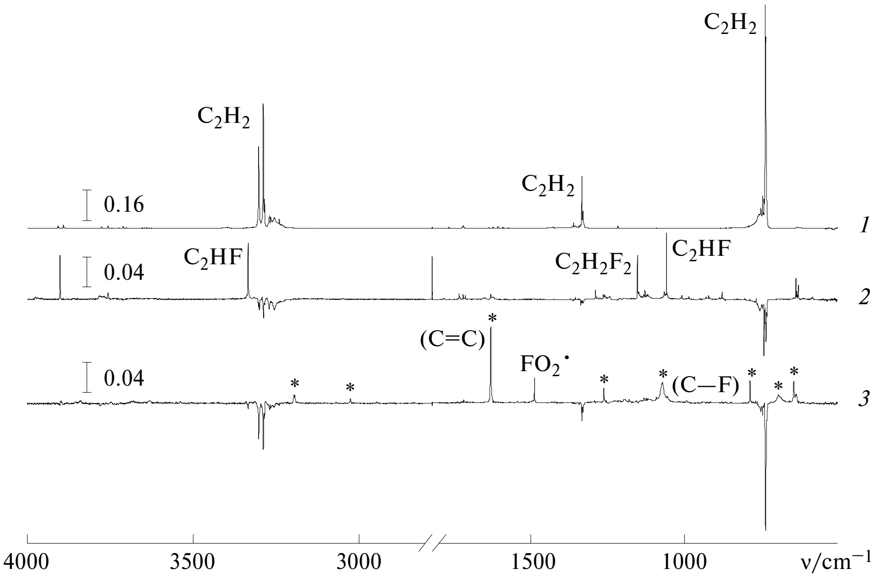


Fig. 1. IR absorption spectrum of the sample Ar : F_2 : C_2H_2 = 3000 : 1 : 1 after deposition (*1*), differential IR absorption spectrum before and after photolysis at 15 K (*2*), differential spectrum of the irradiated at 15 K sample before and after annealing at 24 K (*3*), and spectra recorded at 15 K (IR bands of the β-$C_2H_2F^{\bullet}$ radical are marked by asterisks).

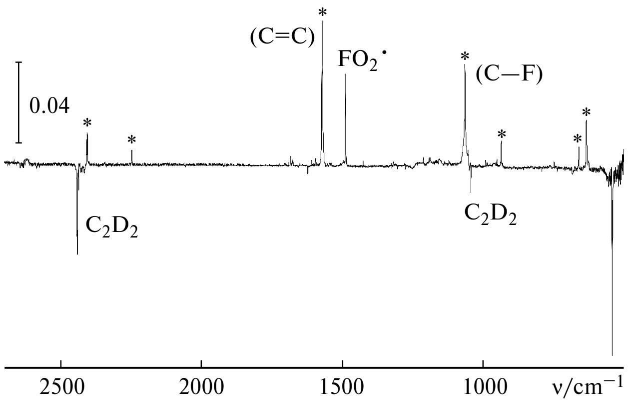


Fig. 2. Differential spectrum of the irradiated at 15 K sample (Ar : F_2 : C_2D_2 = 3000 : 1 : 1; C_2H_2-d_2, 98% D) before and after annealing at 24 K (the spectrum was recorded at 15 K; IR bands of β-$C_2D_2F^•$ are marked by asterisks).

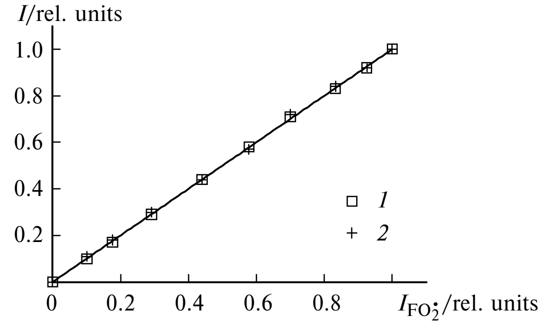


Fig. 3. Intensity (*I*) of the IR band (*1*) of the β-$C_2H_2F^•$ radical (1631 cm^{-1}) and "consumption" (*2*) of the band of C_2H_2 (736.5 cm^{-1}) *vs.* intensity of the band of the $FO_2^•$ radicals (1490 cm^{-1}) formed during annealing of the sample Ar : F_2 : C_2H_2 = 3000 : 1 : 1 at 24 K.

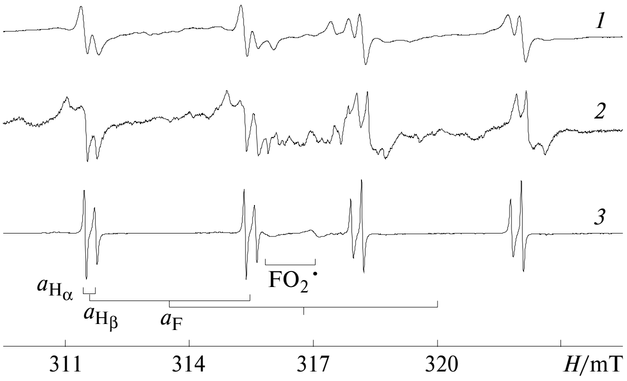


Fig. 4. ESR spectra of samples after photolysis at 15 K and annealing at 24 K: Ar : F_2 : C_2H_2 = 200 : 1 : 1 (*1*), Kr : F_2 : C_2H_2 = 3000 : 1 : 1 (*2*), and Ar : F_2 : C_2H_2 = 3000 : 1 : 1 (*3*) (spectra were recorded at 30 K). The characteristic splittings in HFS of the CHF=$^•$CH and $FO_2^•$ are shown.

ably change the spectra. Therefore, thermoactivated *cis-trans*-isomerization does not occur at this temperature.

ESR spectrum of β-$C_2H_2F^•$ radicals. The ESR spectrum of the sample Ar : F_2 : C_2H_2 = 3000 : 1 : 1 recorded at 30 K after UV photolysis at 15 K and subsequent annealing at 23 K (Fig. 4, spectrum *3*) consists of eight narrow isotropic lines (linewidth ≤0.06 mT) with equal integral intensities. Despite different linewidths, all of them are the components of the ESR spectrum of one radical (β-$C_2H_2F^•$). Analysis of the spectrum distinguishes three hyperfine doublet splittings a_1 = 6.50, a_2 = 3.86, and a_3 = 0.25 mT. The a_1 and a_2 constants are close to those known for the 2-fluorovinyl radical.[13,15] However, the last splitting a_3 was not observed in previous works.[13,15]

Table 1. Calculated (B3LYP/6-311++G(3df,2p)) in the harmonic approximation frequencies of IR vibrations (ν) and IHFC constants (*a*) of isomers of the CHF=$^•$CH radical compared to the experimental values

Vibration	Calculation		Experiment	
	trans	*cis*	This work	Ref. 16
		ν/cm^{-1} (I_{rel} (%))		
1a′ (CH_α)	3307 (0.09)	3308 (0.13)	3193 (0.13)	3178
2a′ (CH_β)	3184 (0.01)	3122 (0.04)	3026 (0.04)	
3a′ (CC)	1664 (0.48)	1678 (0.73)	1631 (0.71)	1623
4a′ (H_βCC)	1305 (0.01)	1291 (0.05)	1263 (0.11)	1211
5a′ (CF)	1024 (1.00)	1093 (1.00)	1070 (1.00)	1066
6a′ (H_αCC)	779 (0.08)	734 (0.47)	698 (0.38)	678
7a′ (FCC)	433 (0.00)	479 (0.04)		462
1a″ (wag)	883 (0.27)	827 (0.08)	785 (0.12)	785
2a″ (twist)	661 (0.28)	645 (0.42)	643 (0.40)	631
		a/mT		
a_F	10.12	6.69	6.50	
a_{H_β}	1.69	3.81	3.86	
a_{H_α}	0.14	0.17	0.25	

Note. Relative intensities of vibrations are given in parentheses.

The IHFC constant with the α-proton is close to zero,[21] therefore, the absence of splitting on α-H in the ESR spectra can be related to their insufficient resolution. Figure 4 shows the obtained ESR spectra of the β-$C_2H_2F^{\bullet}$ radicals in the argon matrix with a high concentration of C_2H_2 (see Fig. 4, spectrum *1*) and in the krypton matrix (spectrum *2*) with magnetic nuclei (the nuclear spin I of ^{83}Kr is equal to 9/2). In the first case, most of the C_2H_2 molecules exist as dimers (and more complex clusters). Therefore, the β-$C_2H_2F^{\bullet}$ radicals that formed are bound to the adjacent C_2H_2 molecules, resulting in the line broadening due to the incomplete averaging of the HFC anisotropy because of the retarded motion of the radicals. In the second case, the ESR lines are strongly broadened due to the interaction of an unpaired electron of the radical with magnetic nuclei of the matrix. A comparison of spectra *1* and *2* with spectrum *3* (see Fig. 4) shows that a high spectral resolution is achieved only for the argon matrix (with non-magnetic nuclei) when stabilized radicals are ideally isolated. This enables the observation of HFC with a splitting of 0.25 mT.

In order to assign the observed hyperfine splitting of the ESR spectrum, we carried out experiments with mixtures enriched in C_2D_2 by 75%, C_2HD by 22%, and C_2H_2 by 3%. The addition of the F atom to the C_2D_2 molecule results in the formation of the $CDF={}^{\bullet}CD$ radical. If the F atom is added to the C_2HD molecule, the $CHF={}^{\bullet}CD$ and $CDF={}^{\bullet}CH$ radicals can be formed.

The spectrum of this sample after low-temperature UV photolysis followed by annealing at 23 K (Fig. 5, curve *1*) contains three series of lines. The first, prevailing group of the β-$C_2D_2F^{\bullet}$ radical contains six lines: a doublet (a_1 = 6.50 mT) of triplets 1 : 1 : 1 (a_2 = 0.59 mT). The second series consists of four lines ($CHF={}^{\bullet}CD$): a doublet (a_1 = 6.50 mT) of doublets (a_2 = 3.86 mT). In the third series ($CDF={}^{\bullet}CH$) including 12 lines (six of them are disguised by more intense lines of another series), we can isolate two splittings on nonequivalent nuclei with the spin I = 1/2 (a_1 = 6.50 and a_3 = 0.25 mT) and one on the nucleus with the spin I = 1 (a_2 = 0.59 mT).

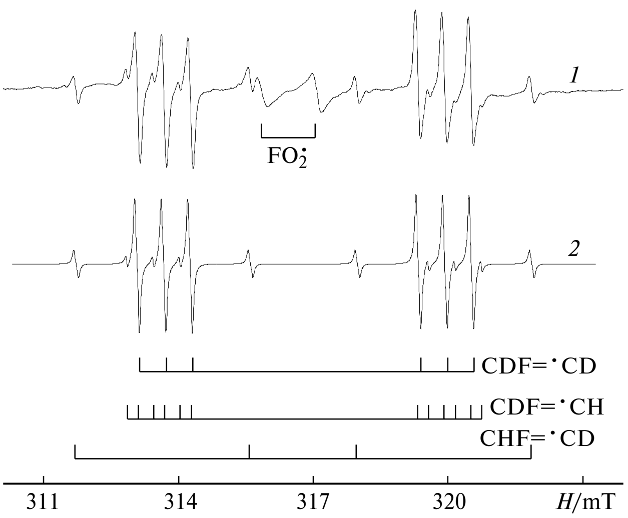


Fig. 5. ESR spectrum (*1*) of the sample Ar : F_2 : (C_2D_2 (75%) + C_2HD (22%) + C_2H_2 (3%)) = 3000 : 1 : 1 after photolysis at 15 K and annealing at 24 K; the spectrum was recorded at 30 K; calculated ESR spectrum (*2*) of the sample containing radicals $CDF={}^{\bullet}CD$ (78%), $CHF={}^{\bullet}CD$ (11%), and $CDF={}^{\bullet}CH$ (11%); IHFC constants and linewidths are taken from the experimental spectra. The characteristic splittings in HFS of the $CDF={}^{\bullet}CD$, $CDF={}^{\bullet}CH$, $CHF={}^{\bullet}CD$, and $FO_2^{\bullet}$ radicals are shown.

For isotopic substitution H/D hyperfine splittings on nuclei of D atoms should be lower by $\gamma_H/\gamma_D \approx 6.5$ times according to the gyromagnetic ratio of H to D, and that on the ^{19}F nucleus should remain unchanged. Therefore, the splitting a_1 = 6.50 mT, which does not change in all spectra, should be assigned to the nucleus of the ^{19}F atom. Doublet splitting a_2 = 3.86 mT of the $CHF={}^{\bullet}CH$ and $CHF={}^{\bullet}CD$ radicals and the triplet a_2 = 0.59 mT of the $CDF={}^{\bullet}CD$ and $CDF={}^{\bullet}CH$ radicals correlates with the β-proton. The remaining doublet splitting a_3 = 0.25 mT of the $CHF={}^{\bullet}CH$ and $CDF={}^{\bullet}CH$ radicals should be attributed to α-H. The corresponding triplet splitting of the $CDF={}^{\bullet}CD$ and $CHF={}^{\bullet}CD$ radicals is lower than the linewidth and, hence, is not observed. Thus, in these experiments we succeeded for the first time to obtain the resolved ESR spectrum of the β-$C_2H_2F^{\bullet}$ radical and determine all three IHFC constants.

It is known that small molecules and radicals in matrices of inert gases rotate almost freely (see, *e.g.*, Ref. 22). If radicals rotate non-coherently, changes in the linewidths and intensities observed in the ESR spectra are explained by incompletely averaged anisotropic magnetic interactions. The proposed model of rotation diffusion[23] based on the Redfield equations[24] allows the relation of the linewidths of the HFC components in the ESR spectrum to the structural parameters of the radical, such as the electron density distribution. In the fast rotation limit, the expression for the linewidth takes the following form:

$$T_2^{-1} = T_{2,0}^{-1} + \left(A + \sum_i B_i m_i + \sum_i C_i m_i^2 + \sum_{i<j} E_{ij} m_i m_j\right)\tau_R, \qquad (3)$$

where m_i and m_j are the z components of nuclear spins for the *i*th and *j*th nuclei; τ is the time of rotation correlation, and A, B, C, and E are determined by the anisotropic parts of the HFC tensor and g factor.

Since the ESR spectrum of the $CHF={}^{\bullet}CH$ radical is symmetric relative to the center and nuclear spins of all magnetic nuclei are equal to 1/2, only the cross term $E_{ij}m_im_j$ determines the different linewidths. In spectrum *3* (see Fig. 4) this is most pronounced for pairs of lines for which the m_im_j product for the F and α-H nuclei changes its sign. The E_{ij} coefficients are obtained by multiplying the HFC tensors of various nuclei.[23,25] The estimation of the rotation correlation time by for-

Table 2. Calculated geometric parameters of *cis*- and *trans*-isomers of the CHF=$^{\bullet}$CH radical

Parameter	*cis*-Isomer			*trans*-Isomer		
	B3LYP/ 6-311++G(d,p)	B3LYP/ 6-311++G(3df,2p)	QCISD/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)	B3LYP/ 6-311++G(3df,2p)	QCISD/ 6-311++G(d,p)
$R_{\mathrm{CH}\alpha}$/Å	1.074	1.073	1.079	1.074	1.073	1.079
$R_{\mathrm{CH}\beta}$/Å	1.088	1.087	1.089	1.084	1.082	1.085
R_{CF}/Å	1.356	1.349	1.349	1.369	1.361	1.360
R_{CC}/Å	1.303	1.300	1.316	1.302	1.299	1.315
H_{α}CC/deg	139.9	139.5	136.0	144.5	144.1	140.1
H_{β}CC/deg	125.6	125.2	125.2	125.9	125.6	125.8
FCC/deg	122.9	123.2	122.5	122.8	122.9	122.1

mula (3) taking into account the observed difference in widths $\Delta T_2^{-1} \sim 0.01$ mT at 30 K gives $\tau_{\mathrm{R}} \sim 10^{-9}$ s.

Quantum-chemical calculations of energy and spectroscopic parameters of isomers of the β-$C_2H_2F^{\bullet}$ radical. The calculations by the Gaussian 98 program package[26] showed that the methods of the density functional theory reliably reproduce both the structural and spectroscopic parameters of free radicals.[17,27] The calculation accuracy is comparable and sometimes exceeds that inherent in non-empirical post-Hartree—Fock methods (for example, the cluster decomposition method CCSD or configuration interaction method QCISD), although much less calculations are required.

We used the method of the density functional theory B3LYP with the 6-311++G(d,p) and 6-311++G(3df,2p) basis sets. Experimental data are lacking for the structure of the β-$C_2H_2F^{\bullet}$ radical, therefore, we used the QCISD/6-311++G(d,p) method to control the validity of its prediction. It follows from Table 2 that all methods give almost the same structures of isomers. The best agreement with the testing calculation was achieved in the B3LYP variant with the 6-311++G(3df,2p) basis set.

The results of calculations of the spectroscopic parameters of isomers of the β-$C_2H_2F^{\bullet}$ radical are presented in Table 1. Despite that the calculated frequencies for the *cis*-isomer are closer to the experimental values than those for the *trans*-isomer, it is impossible to assign unambiguously the experimental IR spectrum to one of them on the basis of vibration analysis. One of the reasons is the absence of anharmonic corrections in the calculation of vibration frequencies and the presence of "matrix" shifts of the IR bands comparable to the difference in the characteristic vibration frequencies of the isomers. Therefore, even analysis of the IR spectra taking into account isotopic (H/D) substitution does not allow a reliable identification of the stabilized isomeric form.

At the same time, the ESR spectrum can unambiguously be assigned by the comparison of experimental and calculated IHFC frequencies. First, the calculations predict that the HFC constants of two isomers differ very strongly (a_{F} and $a_{\mathrm{H}_{\beta}}$ differ by more than 1.5 and 2 times, respectively). Second, the calculated IHFC constants of the *cis*-isomer virtually coincide with the measured values. Third, our data[3,4,10] and results of other works[17,28] show that this method reproduces the experimental IHFC constants of free radicals with an accuracy of at least 10%. Thus, the comparison of the calculated and measured spectroscopic parameters of the β-$C_2H_2F^{\bullet}$ radical asserts that the *cis*-isomer of β-$C_2H_2F^{\bullet}$ is the main stabilized product of the reactions of the F atoms with the C_2H_2 molecules in solid argon.

Table 3. Differences between energies ignoring (ΔE_0) and taking into account (ΔE_0 + ΔZPE) energies of zero point vibrations of *trans*- and *cis*-isomers of the CHF=$^{\bullet}$CH radical (J mol^{-1})

Method	ΔE_0	$\Delta E_0 + \Delta ZPE$
B3LYP/6-311++G(d,p)	−95	336
B3LYP/6-311++G(2d,2p)	10	600
B3LYP/6-311++G(3df,2p)	859	1232
QCISD/6-311++G(d,p)	678	1174
G1	1100	1351
G2	1200	1489

To reveal the reason for the stabilization of only one isomer of β-$C_2H_2F^{\bullet}$, let us compare their calculated energies. Table 3 contains the differences between the energies ignoring (ΔE_0) and taking into account ($\Delta E_0 + \Delta ZPE$) energies of zero vibrations of the *trans*- and *cis*-isomers of the CHF=$^{\bullet}$CH radical. The results show that with increasing the level of calculations the *cis*-isomer becomes more energetically favorable. The maximum difference between energies of the isomers reaches ~1.0 kJ mol^{-1} (~1.5 kJ mol^{-1} taking into account zero point vibrations). Although this difference is comparable with the accuracy of calculations of energies of the isomers, the observed tendency certainly indicates a high stability of the *cis*-isomer.

The calculated barrier of *cis*-*trans*-isomerization was 9.0 kJ mol^{-1}. Therefore, the equilibrium concentration corresponding to the *trans*-isomer at temperatures below 30 K is very low. The experiment confirms qualitatively the conclusions based on the calculations. Since at 30 K the equilibrium concentration of one isomer is at least

~20-fold higher than that of the second isomer, the difference in their enthalpies should exceed 0.7 kJ mol^{-1}.

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