Reactions of photogenerated fluorine atoms with molecules trapped in solid argon

3.* Formation of stabilized $^{\cdot}NH_2$ radicals and $^{\cdot}NH_2$—HF radical-molecule complexes in the reactions of fluorine atoms with NH_3 molecules

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Isolated radicals $^{\cdot}NH_2$ and radical-molecule complexes $^{\cdot}NH_2$—HF, which are products of the reactions of mobile fluorine atoms with NH_3 molecules in solid argon, were identified by EPR spectroscopy. The isotropic HFC constants of the complex (a_N = 1.20, a_H = 2.40, and a_F = 0.70 mT) were determined experimentally. The constant of isotropic HFC with the nucleus of hydrogen atom of the HF molecule is less than 0.1 mT. This assignment was confirmed in the experiments on isotope substitution of atoms (H → D, $^{14}N \rightarrow {}^{15}N$) in the NH_3 molecule. According to quantum-chemical calculations, the free complex $^{\cdot}NH_2$—HF has a planar structure with C_{2v} symmetry and a binding energy of 12 kcal mol^{-1}. Optimization of the arrangement of the complex in the crystal showed that its structure is only slightly distorted in the Ar lattice so that the equilibrium configuration is close to that obtained from gas-phase calculations. Different ratios of relative intensities of the proton triplet lines in the EPR spectra of isolated $^{\cdot}NH_2$ radicals and $^{\cdot}NH_2$—HF complexes were qualitatively explained by different heights of the barriers to rotation of the NH_2 fragment in the Ar lattice.

Key words: cryochemistry, EPR spectroscopy, fluorine, ammonia, radical-molecule complexes, radicals.

Previously,[1,2] we have posed the problems to be solved in studies of solid-phase reactions with participation of F atoms and determined the conditions for matrix stabilization of the products of elementary chemical reactions. Using the EPR and IR spectroscopy, we established that the reactions of hydrogen abstraction from the CH_4 [2,3] and H_2 [4,5] molecules by photogenerated translationally-excited ("hot") F* atoms with an initial kinetic energy ~1 eV per atom result in two types of spatially separated products, namely, the HF molecules and stabilized radicals whose EPR spectrum is identical to that of the matrix-isolated radicals.

$$F^{*} + RH \longrightarrow {}^{\cdot}R + HF \qquad (1)$$

Unlike the reactions of "hot" atoms, those of thermalized (thermal) F atoms diffusing in an argon crystal at $T \geq 20$ K usually result in radical-molecule complexes.

$$F^{\cdot} + RH \longrightarrow {}^{\cdot}R\text{—}HF \qquad (2)$$

Such intermediates of gas-phase reactions are hard to detect since the complexes are short-lived because of high collision energies. It is possible to stabilize these intermediates by performing solid-phase reactions at ultralow temperatures, thus providing ideal conditions for investigation of their structure. We have found that the use of EPR spectroscopy seems to be particularly well suited to this task. If the radical and the molecule in the complex are separated by a distance no longer than 3 Å and if the widths of individual components of hyperfine structure (HFS) of the EPR spectra in an argon matrix do not exceed 0.1 mT, it is possible to observe well-resolved components of the HFS, which is due to the interaction between the unpaired electron of the radical and the magnetic nuclei of the HF molecule, using EPR technique. The constants of magnetic interactions are highly sensitive to both the distances between and the mutual orientation of the fragments in the complex; therefore the structure of the complex can be reliably determined from comparison of experimental and calculated data. Using this approach, we have for the first time obtained information on the structure of loosely bound complexes CH_3—HF and H—HF.[1-4]

In this work, we studied the conditions under which the products of the reactions of "hot" and thermal F atoms with the NH_3 molecule are formed. The interest in studying the atom-molecule reaction

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$$F^{\cdot} + NH_3 \longrightarrow {}^{\cdot}NH_2 + HF \quad (\Delta H = -31\ \text{kcal mol}^{-1}) \qquad (3)$$

in the gas phase was motivated by attempts to use it as a source in chemical lasers.[6] However, it was established that no inverse population of excited rovibrational states of the HF molecule occurs in reaction (3) despite its high exothermicity.[7,8] To explain the results obtained, it was assumed that a long-lived (on a time scale of ~10^{-12} s) and tightly-bound intermediate, FNH_3, is formed in the course of the reaction. The existence of such an intermediate can cause redistribution of the excess energy between internal modes of the complex and, as a consequence, between those of the reaction products. Actually, the *ab initio* CISD/6-311G** quantum-chemical calculations predicted the formation of a tightly bound $^{\cdot}NH_2$—HF complex (with the binding energy ~12 kcal mol^{-1}) between the products of reaction (3),[9] which has not been observed previously. Recently,[10] a short communication on the detection of the $^{\cdot}NH_2$—HF complex in solid argon has been reported.

In this work, the conditions for the formation of the $^{\cdot}NH_2$—HF complexes are considered in detail and a possible arrangement of the complex in Ar crystal is predicted on the basis of comparison of experimental and calculated hyperfine coupling constants (HFC).

Experimental

The procedures for sample preparation and measurements of EPR spectra have been described in detail earlier.[2] Samples were prepared by vacuum codeposition of gaseous Ar + NH_3 and Ar + F_2 mixtures onto a substrate of a helium cryostat cooled down to 15 K. The relative molar concentration of reagents in the samples studied was varied from $2.5 \cdot 10^{-4}$ to $3 \cdot 10^{-3}$. Samples of composition Ar : F_2 : NH_3 = 1000 : 1 : 1 were studied in most detail. The thickness of the samples was approximately 100 μm.

The EPR spectra were measured using a helium flow cryostat with a movable helium shaft. Gases were deposited from two spatially separated nozzles onto the lower end of a flat sapphire rod. The rod temperature stability provided by a temperature control system was no worse than 0.1 K in the temperature range 15—40 K. High stability of the temperature of the sample was also held when filling the shaft with liquid helium. The temperature of the working end of the rod was 7.7 K.

Fluorine atoms were generated by photolysis of F_2 molecules at the wavelength λ = 337 nm with a pulsed N_2 laser (repetition frequency 1000 Hz, the average laser power was ~20 mW cm^{-2}). Photodissociation of F_2 yields two translationally-excited "hot" F atoms with excess energy $\Delta E_0 = (h\nu - D)/2 \approx 1$ eV per atom.

Results and Discussion

Photolysis of Ar—F_2—NH_3 samples at 15 K. The EPR spectra of freshly prepared samples exhibited no lines due to paramagnetic species. Short-time (~5 min) photolysis of the samples leads to the appearance of a complex EPR spectrum. Extensive photolysis leads to an increase in the intensities of the spectral lines, which reach their limiting values after about 100 min. Since the quantum yield of photodissociation of F_2 molecules isolated in solid argon is ~0.5,[2,11] almost all of them in the sample are photolyzed after 100 min at the above-mentioned density of photolyzing radiation. The EPR spectrum of the products of photolysis recorded at 15 K is shown in Fig. 1, *a*. Cooling of the sample leads to a drastic broadening of most of the spectral lines, so only nine lines with different widths and equal integrated intensities are observed at T = 7.7 K (see Fig. 1, *b*). Temperature variations of the lineshape are reversible in the range 7.7—18 K. The integrated intensity (I) of the spectrum obeys the Curie law, $I \sim 1/T$. This means that the amount of the radical products of photolysis remains unchanged after switching off the laser, while the EPR spectrum of the radicals generated during the photolysis corresponds to at least two products. The spectrum of one of them is substantially broadened on lowering the temperature and is practically unobservable at T = 7.7 K. The shape of the lines of the other radical is only slightly temperature-dependent. The EPR spectrum of

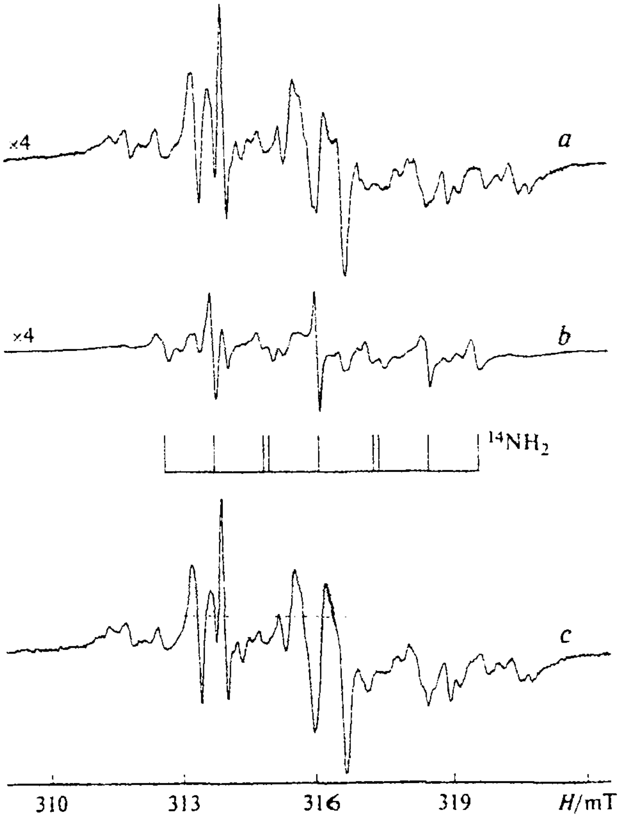


Fig. 1. EPR spectra of radicals in Ar—F_2—NH_3 (1000 : 1 : 1) mixtures after photolysis at 15 K (*a*); after cooling of photolyzed sample down to 7.7 K (*b*); and after cooling of annealed sample down to 15 K (*c*). The intensities of all spectra were corrected in accordance with the Curie law.

this radical (see Fig. 1, *b*) consists of two triplets with the HFC constants equal to 1.05 and 2.4 mT, and g = 2.0058. The parameters of the spin Hamiltonian, determined from the positions of these lines, are in good agreement with the reported data[12] for the $^{\cdot}NH_2$ radical generated during low-temperature photolysis of NH_3 in Ar matrix (a_N = 1.04 mT, a_H = 2.38 mT). This allowed us to conclude that one of the photolysis products is the free radical $^{\cdot}NH_2$ formed in reaction (3) of photogenerated "hot" F atoms.

Annealing of Ar—F_2—NH_3 samples photolyzed at 15 K. Thermal fluorine atoms diffuse at $T > 20$ K.[2,11] Reactions of thermal F atoms were initiated by annealing the irradiated samples at 23—25 K for 100 min. Annealing leads mainly to an increase in the intensity of the EPR lines of the second (unassigned) radical. The EPR spectrum of the sample, obtained after annealing followed by cooling down to 15 K, is shown in Fig. 1, *c*. Comparison of the spectra presented in Figs. 1, *a* and *c* shows that the amount of $^{\cdot}NH_2$ radicals remained virtually unchanged after annealing, whereas the intensities of the lines of the other radical increased by a factor of 4. The lines of the EPR spectrum of this radical become narrower as temperature increases, and 14 well-resolved nearly isotropic lines are observed in the spectrum at T = 35 K. The linewidths vary from 0.1 to 0.15 mT. Analysis of the structure and relative intensities of the spectral lines revealed a triplet with splitting a_1 = 1.2 mT and 1 : 1 : 1 ratio of intensities of the components, a triplet with splitting a_2 = 2.4 mT and 1 : 2 : 1 ratio of intensities of the lines, and a doublet with splitting a_3 = 0.7 mT (Fig. 2, *a*). Since $a_2 = 2a_1$, four lines of the spectrum appear to be composite lines. Thus, only 14 lines are resolved in the spectrum, instead of 18 lines corresponding to such an assignment.

Since two triplet splittings in the spectrum of this product are close to the HFC constants of the isolated $^{\cdot}NH_2$ radical, they can be attributed to the $^{\cdot}NH_2$ radical (a_H = 2.4 mT, a_N = 1.2 mT), whereas the doublet splitting is due to magnetic interaction with one of the nuclei of the HF molecule bound in the $^{\cdot}NH_2$—HF complex. To assign the hyperfine splittings in the EPR spectrum to magnetic nuclei, a series of experiments on isotope substitution in Ar—$^{15}NH_3$—F_2 and Ar—$^{14}ND_3$—F_2 mixtures was carried out. Shown in Fig. 2, *b* and *c* are the EPR spectra of the annealed ~~isotopically substituted samples photolyzed at low tem~~peratures. The splittings 2.4 and 0.70 mT remained unchanged in the spectrum of the sample containing the ^{15}N isotope with nuclear spin 1/2, whereas a doublet splitting of 1.55 mT appeared instead of the triplet with splitting 1.2 mT. Since the $^{14}N/^{15}N$ isotope substitution affects only the type of splitting and the constant of HFC with the nucleus of nitrogen atom, whereas all other splittings remain unchanged, the triplet splitting $a_N(^{14}N)$ = 1.2 mT and the doublet splitting $a_N(^{15}N)$ = 1.55 mT should be assigned to the HFS due to the hyperfine interaction with the nucleus of N atom. In the spectra of Ar—$^{14}ND_3$—F_2 samples, the hyperfine splittings 1.2 and 0.7 mT also remain unchanged and a quintet with a splitting of 0.35 mT is observed instead of the triplet splitting 2.4 mT. The H/D isotope substitution should lead to a decrease in the hyperfine splittings by a factor of $\gamma_H/\gamma_D \approx 6.5$ (γ_H and γ_D are the gyromagnetic ratios for hydrogen and deuterium, respectively). Simultaneously, a quintet with 1 : 2 : 3 : 2 : 1 ratio of intensities, arising from two equivalent deuterons, should appear instead of the triplet with 1 : 2 : 1 ratio of intensities due to interaction with two equivalent pro~~tons. This makes it possible to unambiguously assign~~ these splittings to the HFS due to hyperfine interaction with protons of the NH_2 group. The doublet splitting 0.7 mT, which remains unchanged after isotope substitution, should be assigned to the F atom, because this is the only atom in the system under study having a magnetic nucleus with spin 1/2. Since H_2NF is a closed-shell molecule, the EPR spectrum under consideration can be attributed to the $^{\cdot}NH_2$—HF complex for which the constant of HFC with the nucleus of H atom of the HF molecule, $a_{H'}$, is less than 0.1 mT.

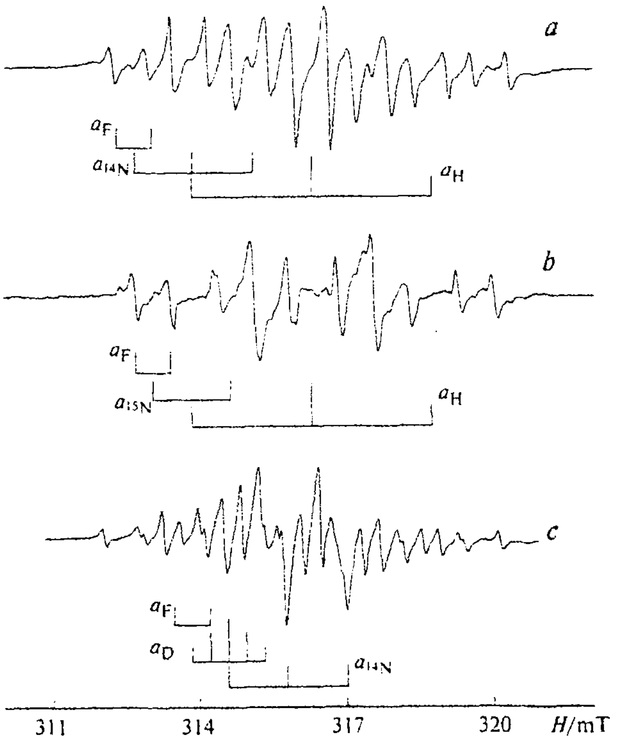


Fig. 2. EPR spectra of radicals in Ar—$^{14}NH_3$—F_2 (*a*); Ar—$^{15}NH_3$—F_2 (*b*), and Ar—$^{14}ND_3$—F_2 mixtures (*c*) after photolysis at 15 K followed by annealing of photolyzed samples at 25 K. All spectra were recorded at T = 35 K. (The ND_3 used in the experiments contained ~10% NH_3. Therefore, weak outer lines in spectrum *c* correspond to the complex $^{\cdot}NH_2$—HF).

The analysis of the EPR spectra suggests that two types of products are formed in reaction (3) with participation of "hot" F atoms. These are (i) spatially separated stabilized $^{\cdot}NH_2$ radical and HF molecule and (ii) the $^{\cdot}NH_2$—HF complex. As follows from comparison of the integrated intensities of the spectra, the fraction of the complex in the overall balance of the reaction products is ~0.8. Even higher (>0.99) is the fraction of the complex in the reaction with participation of diffusing thermal F atoms. Comparison of reaction (3) with the previously[1,5] studied transformations

$$F^{\cdot} + CH_4 \longrightarrow {}^{\cdot}CH_3 + HF, \quad (4)$$

$$F^{\cdot} + H_2 \longrightarrow H^{\cdot} + HF \quad (5)$$

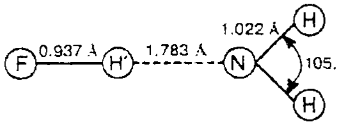
shows that the reactions of "hot" F atoms do not result in radical-molecule complexes $^{\cdot}CH_3$—HF with a binding energy of ~2 kcal mol^{-1} and $^{\cdot}$H—HF with a binding energy of ≤100 cal mol^{-1} and that the fraction of $^{\cdot}CH_3$—HF complexes formed in the reactions of thermal F atoms does not exceed 0.6. Therefore the higher yield of $^{\cdot}NH_2$—HF complexes formed in reaction (3) can be due to the higher binding energy of these complexes.

The geometry of the $^{\cdot}NH_2$—HF complex in the crystal lattice was established using the known[2] algorithm which includes quantum-chemical calculations of the structure of free complex and the HFC constants, comparison of calculated and experimentally measured HFC constants, and optimization of the arrangement of the complex in the crystal lattice.

Quantum-chemical calculations of the structure of $^{\cdot}NH_2$—HF complex. Optimization of the arrangement of the complex in the crystal lattice. The geometry of the complex and the HFC constants were calculated by the density functional method using the GAUSSIAN-94 program package[13] with the EPR-3 basis set specially developed[14] for calculating the HFC constants of radicals. According to preliminary calculations, this method makes it possible to reproduce the values of the isotropic HFC constants a_N and a_H of $^{\cdot}NH_2$ radical with an accuracy of 0.01 and 0.1 mT, respectively.

The calculated equilibrium geometry of the complex as well as the calculated (a^{calc}) and experimental (a^{exp}) HFC constants are shown in Scheme 1. The complex has a planar structure with C_{2v} symmetry and is characterized by a binding energy of 12 kcal mol^{-1}, which is close to that predicted earlier.[9] The calculated values of the a_N, a_H, and a_F isotropic HFC constants are close to those measured experimentally (the sign of the HFC constants was not determined in the experiments). Moreover, the calculated constant of HFC with the proton of the HF molecule does not exceed 0.05 mT. As was mentioned above, this hyperfine splitting cannot be resolved under given experimental conditions.

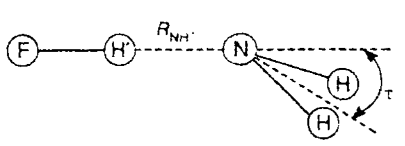
Scheme 1



a^{calc}/mT	−0.70	0.02	1.15	−2.30
a^{exp}/mT	0.70	<0.05	1.20	2.40

The calculated changes in the HFC constants in the case of deformation of the structure of the complex are shown in Fig. 3. Since the out-of-plane deformation of the structure (Scheme 2) requires the smallest energy expenditure, the out-of-plane deformation angle, τ, was chosen as the parameter of possible deformation.

Scheme 2



As can be seen in Fig. 3, the isotropic HFC constants a_N, a_F, and a_H change drastically as the deformation of the complex increases (τ > 10°). At τ > 15°, the calculated a_F and a_H values exceed the corresponding experimental values by more than 0.1 mT. This indi-

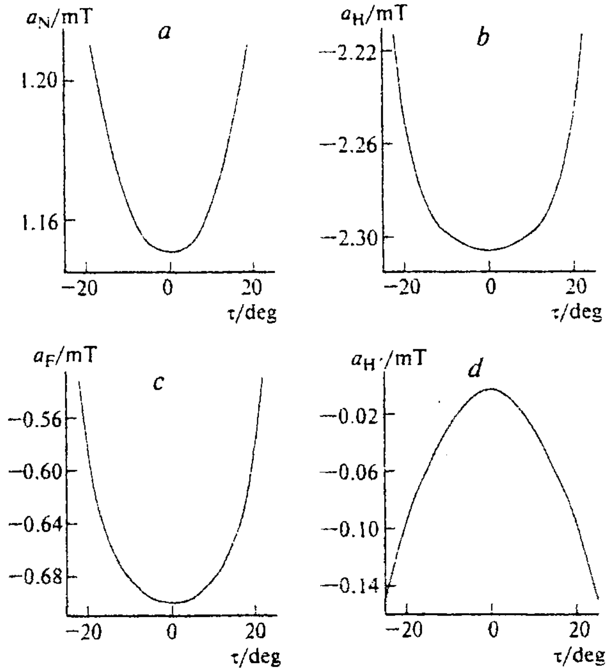


Fig. 3. Calculated dependences of the constants of isotropic HFC with the nuclei of N (*a*), H (*b*), F (*c*), and H' atoms (*d*) (see Scheme 2) of the $^{\cdot}NH_2$—HF complex on the out-of-plane deformation angle (τ).

cates that the out-of-plane deformation of the complex in the crystal lattice should not exceed 15°. Good agreement between the calculated and experimentally measured values of HFC constants also suggests that the structure of the complex stabilized in argon crystal must be close to that obtained from quantum-chemical calculations.

Using the geometric parameters of the $^{\cdot}NH_2$—HF complex (see above) as initial approximation, we simulated its optimum arrangement in the argon crystal lattice by the molecular dynamics method, analogously to previously reported calculations.[1,3] Since small impurity molecules occupy the substitutional lattice sites in argon crystals,[15] we assumed that the initial reagent molecule (NH_3) is a substitution impurity and, correspondingly, the reaction product (radical $^{\cdot}NH_2$) is also located at the same type of site. Optimization was performed for the face-centered lattice of an argon crystal which contained 365 atoms. The NH_2 group of the $^{\cdot}NH_2$—HF complex was placed at the central site of the crystal. Intermolecular interactions were described by the Ar—Ar, Ar—F, Ar—N, and Ar—H pair atom-atom potentials.[16,17] First, having assumed that the equilibrium structure of the complex (see Scheme 1) is retained, we optimized the arrangement in the lattice of such a "rigid" complex. Subsequent optimization at different initial orientations of the complex in the lattice showed that the system reaches a global energy minimum where the C_2 axis of the complex coincides with the C_4 axis of the crystal, as is shown in Fig. 4. The coordinates of the position of the N atom at the central lattice site are close to (0, 0, 0), whereas the F atom of the HF molecule occupies the nearest octahedral interstitial site O_h with the coordinates $(-a/2, 0, 0)$, where a = 5.42 nm is the argon crystal lattice constant. This arrangement of the complex leads to the smallest distortions of the crystal lattice due to the fact that the distance between the N and F atoms in the complex is close to $a/2$. In order to calculate deformations of the complex, the two "softest" internal coordinates, namely, the distance between the FH and NH_2 fragments, $R_{NH'}$, and the out-of-plane deformation angle, τ (see Scheme 2), were included in the optimization procedure. The corresponding force constants, $k_R = 2.4 \cdot 10^4$ dyn cm^{-1} and $k_\tau = 5.3 \cdot 10^3$ dyn cm^{-1}, were obtained from quantum-chemical calculations. Optimization of the arrangement of such a "flexible" complex in the lattice results in shortening of the $R_{NH'}$ distance by 0.001 nm only and in the out-of-plane deformation (τ) of 4°. These results confirm the conclusion that the equilibrium configuration of the $^{\cdot}NH_2$—HF complex in the Ar crystal lattice is close to that obtained from the gas-phase calculations.

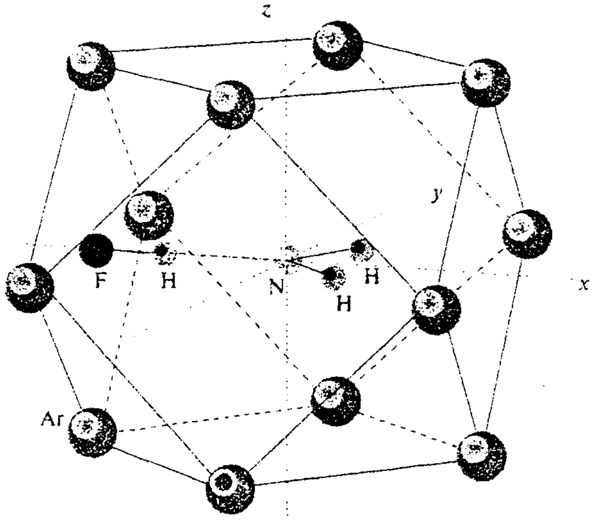


Fig. 4. Arrangement of the complex $^{\cdot}NH_2$—HF in the argon crystal lattice. Shown are 12 nearest Ar atoms.

At 15 K, the Ar—F_2—NH_3 sample has a complex anisotropic EPR spectrum (see Fig. 1). Nearly complete averaging of the anisotropy of magnetic interactions is observed only at $T \geq 30$ K. Taking into account that the complex has a large linear size, it is hard to assume the possibility for rather fast thermally-activated changes in the orientation of the C_2 axis of the complex to occur in the crystal even at such temperatures. Attempts at finding optimum ways of changing its orientation taking into account the out-of-plane deformation of the complex and the rearrangement of the lattice atoms revealed some energy barriers equal to ~1—2 kcal mol^{-1}. This indicates that the decrease in the anisotropy should only be due to internal deformation vibrations and large-amplitude librations of the complex in the Ar lattice.

Rotation of NH_2 fragment in solid argon. Analysis of the motions of the $^{\cdot}NH_2$—HF complex and $^{\cdot}NH_2$ radical in solid argon requires separate consideration. In this work, we will only qualitatively consider some peculiarities of the observed EPR spectra. From the aforesaid it follows that the EPR spectra of the $^{\cdot}NH_2$ radicals and those of the NH_2 group in the $^{\cdot}NH_2$—HF complex consist of nine lines corresponding to the interaction of the unpaired electron with two equivalent nuclei of H atoms and with the nucleus of N atom. One can expect that the ratio of integrated intensities in the triplets will be equal to 1 : 2 : 1 for two equivalent protons and to 1 : 1 : 1 for the ^{14}N nucleus. These relations hold for the EPR spectra of the $^{\cdot}NH_2$—HF complex. On the contrary, the spectra of isolated $^{\cdot}NH_2$ radicals at 7.7 K consist of nine lines with equal intensities, which corresponds to the 1 : 1 : 1 ratio of integrated intensities of the lines in the triplet arising from protons. Analogous EPR spectra of the $^{\cdot}NH_2$ radicals isolated in Ar lattice at T = 4.2 K have also been observed previously.[12,18] The equal intensities of all nine lines were explained[19] by the effect of free rotation of $^{\cdot}NH_2$ radical at T = 4.2 K. In accordance with the symmetry of the electron and rotational wave functions of the radical, the wave function of two protons must be symmetric in the ground rotational state ($J = 0$) and asymmetric in the first excited state ($J = 1$). Out of four possible combinations of the projections of the proton spins, three nuclear states (with the projections m_I = +1, 0, and −1) are symmetric and one state (with the projection $m_I = 0$) is asymmetric. If the population of the first excited rotational state is close to zero at T = 4.2 K, three equally intense HFS components corresponding to three symmetric spin wave functions of protons should be observed in the EPR spectrum.

Unlike the isolated $^{\cdot}NH_2$ radical, rotation of the $^{\cdot}NH_2$ radical bound in the $^{\cdot}NH_2$—HF complex in the Ar lattice is hindered. The calculated barrier to rotation of the NH_2 fragment in the lattice, V_{bar}, is ~200 cm^{-1}, which indicates that H atoms are mainly localized near the potential energy minimum. The barrier to rotation of isolated $^{\cdot}NH_2$ radical obtained from analogous calculations is lower (V_{bar} < 30 cm^{-1}).

The correlation diagram shown in Fig. 5 illustrates the passage from free rotation to complete localization of the NH_2 group. In the case of free rotation, the relation $\Delta E_{as} \gg k_BT$ is valid, where ΔE_{as} is the splitting between the rotational levels with $J = 0$ and $J = 1$, k_B is the Boltzmann constant, and T/K is temperature. Therefore, the population of the first rotational level is close to zero, which leads to equal intensities of the lines of the proton triplet (a 1 : 1 : 1 ratio of integrated intensities). An increase in the height of the barrier to rotation (V_{bar}) causes the $J = 0$ and $J = 1$ levels to come closer together and, correspondingly, the population of the first rotational level to increase. On going to high barriers, which corresponds to localization of the NH_2 group near the potential energy minimum, the relation $\Delta E_{as} \ll k_BT$ is valid for the splitting between the levels with different symmetry, which means equal population of all spin states. Therefore, the ratio of intensities of the lines of the proton triplet will be 1 : 2 : 1 even at T = 4.2 K.

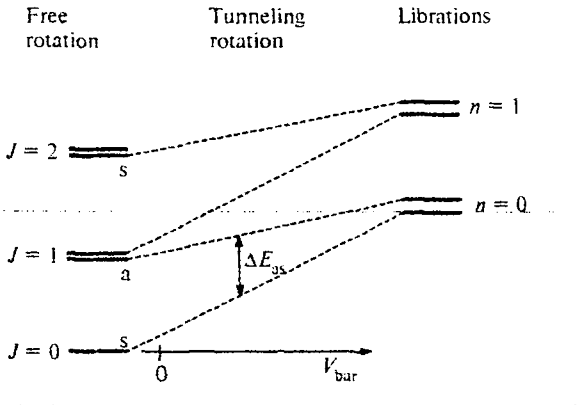


Fig. 5. Correlation diagram of the changes in the energy of rotational levels with increase in the height of the barrier to rotation V_{bar} ("s" and "a" denote symmetric and antisymmetric wave functions of the states, respectively).

Thus, the $^{\cdot}NH_2$—HF radical-molecule complex, which is an intermediate of the reaction of F atoms with NH_3 molecules, was first detected by EPR spectroscopy. Due to the rather high binding energy of the complex, their fraction in the overall balance of the stabilized reaction products exceeds 0.8 (for reactions with participation of "hot" F atoms) and 0.99 (for reactions with participation of thermal F atoms at T > 20 K). The EPR spectra of the $^{\cdot}NH_2$—HF complex are characterized by three isotropic HFC constants a_N = 1.2 mT, a_H = 2.4 mT, and a_F = 0.7 mT; the constant of HFC with the nucleus of the hydrogen atom of the HF molecule is less than 0.1 mT. The free $^{\cdot}NH_2$—HF complex has a planar collinear structure with C_{2v} symmetry and is characterized by a binding energy of 12 kcal mol^{-1}. Optimization of the arrangement of the complex in the argon crystal lattice and comparison of the calculated HFC constants with the corresponding experimental values show that the complex is slightly distorted in Ar lattice and that its equilibrium configuration is close to that in the gas phase. The different ratios of integrated intensities of the lines in the triplet arising from protons in the EPR spectra of isolated $^{\cdot}NH_2$ radicals and those of $^{\cdot}NH_2$—HF complexes can be explained by the different heights of barriers to rotation of the NH_2 group in the Ar lattice.

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