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EPR detection of the radical–molecule complex NH_2–HF stabilised in solid argon

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The radical–molecule complex NH_2–HF is stabilised in a solid argon matrix as an intermediate species in the chemical reaction of F atoms with NH_3 molecules.

The initial interest to study the atom–molecule chemical reaction in a gas phase:

$$F + NH_3 \longrightarrow HF + NH_2; \qquad H_0^0 \approx -31 \text{ kcal mol}^{-1} \qquad (1)$$

was motivated by attempts to use it as a source for chemical lasers.[1] However, these attempts to obtain an inverse HF excitation in reaction (1) were unsuccessful, despite the high exothermicity.[2,3] It was assumed that the reason was the formation of long-lived FNH_3 intermediate species during the reaction. The existence of this intermediate complex can cause randomisation of the excess energy among its internal modes. The *ab initio* calculations performed by Goddard *et al.*[4] predicted the formation of the NH_2–HF complex in the exit channel of reaction (1) with the binding energy ~12 kcal mol^{-1}. We have observed stabilised NH_2–HF complexes formed in reaction (1) and measured their hyperfine (hf) constants for the first time. A comparison of experimental hf constants with the calculated data shows that the structure of the complex is close to that predicted by Goddard *et al.*[4]

Recently we have proposed[5] an experimental technique to study reaction (1) in a solid argon matrix at cryogenic temperatures. This approach is based on the widely used matrix isolation technique and high mobility of fluorine atoms in solid argon.[6] It was shown that translationally excited fluorine atoms generated by UV photolysis of F_2 molecules migrate through several lattice periods, whereas thermal F atoms diffuse in Ar at $T > 20$ K. Upon heating above 20 K, diffusing F atoms react with impurity molecules. The crystalline environment, which prevents reaction products from flying apart and promotes fast relaxation of excess energy, results in stabilization of reaction intermediates. EPR spectroscopy allowed us to detect and to identify the radical products of atom–molecule reaction (1).[7–9] Two facts drastically diminish inhomogeneous broadening of EPR spectra: zero nuclear spin of Ar and homogeneous distribution of radicals, $[R] \leq 10^{16}$ cm^{-3}, in the sample. Hyperfine interaction of an unpaired electron with magnetic nuclei in the radical–molecule complex, which is an intermediate of reaction (1), is very sensitive to the distance between the radical R and the molecule HF and to their mutual orientation. Therefore, the geometry of the complex can be determined from a comparison of the measured hf constants with the results of quantum-chemical calculations.

The experimental technique has been described elsewhere.[8] Solid argon films with the reactant molecules F_2 and NH_3 were formed by vapour deposition of the gases through two separate gas inlets onto a cold substrate at 14 K. Typically, we used the dilution ratio $Ar:F_2:NH_3 = 1000:1:1$. Fluorine atoms were generated by UV photolysis of F_2 molecules at $\lambda = 337$ nm (N_2 pulsed laser, average power of 20 mW).

The EPR spectra of freshly prepared samples exhibit no lines due to paramagnetic species. Photolysis of the samples with $Ar:F_2:NH_3 = 1000:1:1$ at 7.7 K leads to the appearance of a complex anisotropic spectrum. Temperature changes in the spectra of photolysed samples are reversible in the region 7.7–18 K and make it possible to distinguish two paramagnetic species generated during photolysis. The EPR spectrum of one of these species consists of nine narrow lines: two triplet groups with hf splitting of 1.05 and 2.40 mT, and $g = 2.0058$. Both the hf constants and the *g*-factor are in good agreement with published data[10] for the radical NH_2 in solid Ar. It allows us to conclude that one of the photolysis products is the free radical NH_2, which is formed in reaction (1) between a translationally excited F atom with an NH_3 molecule. The EPR lines of the other species are anisotropic and exhibit strong reversible temperature-dependent broadening. They become practically invisible at 7.7 K.

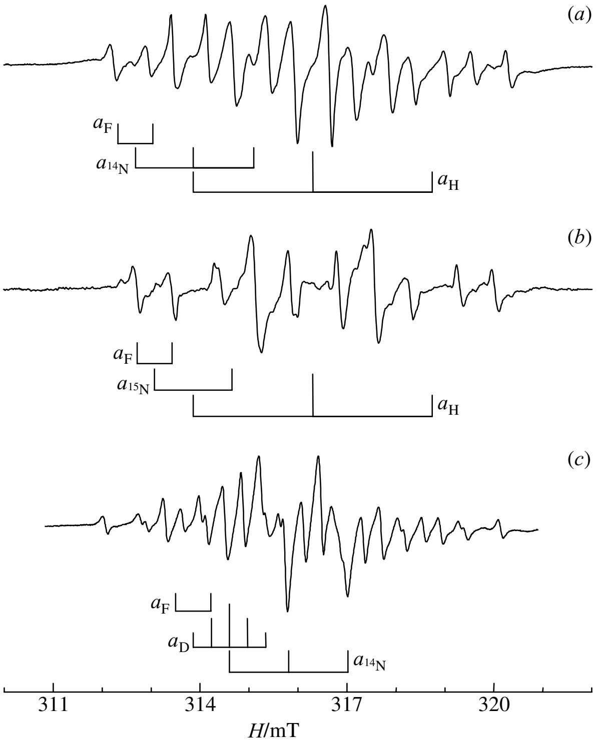
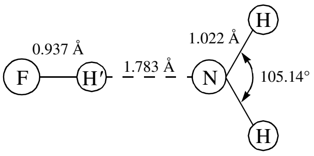


Figure 1 EPR spectra of the samples after photolysis at 15 K and subsequent annealing at 25 K: (*a*) $Ar/^{14}NH_3/F_2$; (*b*) $Ar/^{15}NH_3/F_2$; (*c*) $Ar/^{14}ND_3/F_2$. All spectra were recorded at 35 K. (The $^{14}ND_3$ used in experiments contained ~10% $^{14}NH_3$. Therefore, weak outer lines in the spectra correspond to the complex $^{14}NH_2$–HF).

To initiate reactions of thermal F atoms, we annealed the photolysed samples at $T > 20$ K. A comparison of the spectra before and after annealing shows that the concentration of NH_2 radicals remained unchanged, whereas the intensity of lines of the other radical increased by a factor of four becuase of the reaction of diffusing F atoms. Upon heating above 30 K, the lines of this radical become narrow and isotropic [Figure 1(*a*)]. The EPR spectrum consists of 14 lines with a width of 0.10 mT and corresponds to three hf splittings: the triplet 1:1:1 with $a_N = 1.20$ mT, the triplet 1:2:1 with $a_H = 2.40$ mT, and the doublet with $a_F = 0.70$ mT. Because $a_N \approx 2 \times a_H$, four lines of the spectrum are compound lines. Thus, only 14 lines are resolved in the spectrum, instead of 18 lines corresponding to this assignment. To ascribe the hf coupling constants to magnetic nuclei, a series of similar experiments with isotopically substituted NH_3 was carried out. The EPR spectra obtained after annealing of the photolysed $Ar/F_2/^{15}NH_3$ and $Ar/F_2/^{14}ND_3$ samples are shown in Figures 1(*b*) and 1(*c*). The isotopic substitution for nitrogen atom, $^{14}N\ (S = 1) \longrightarrow {}^{15}N\ (S = 1/2)$, leads to the replacement of the triplet a_N (^{14}N) = 1.20 mT with the doublet a_N (^{15}N) = 1.55 mT. In Ar/F$_2$/^{14}ND$_3$ samples, only the triplet a_H = 2.40 mT is replaced by the quintet a_D = 0.37 mT. These findings allows us to assign unambigously the hf constants a_N and a_H to the NH$_2$ group. At the same time, the doublet splitting 0.70 mT (which remained unchanged by the above isotopic substitution) should be attributed to the ^{19}F atom, because it is the only atom having the magnetic nucleus $S = 1/2$ in the system. Since NH$_2$F is a closed-shell molecule, we can attribute the considered EPR spectrum to the radical–molecule complex NH$_2$–HF, assuming that the hf constant at the H atom of the HF molecule a_H is less than 0.05 mT.

We carried out quantum-chemical computations in order to clarify the structure of the NH$_2$–HF complex. All of the calculations were performed using the GAUSSIAN-94 program[11] at the N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences (grant no. 98-07-90290 from the Russian Foundation for Basic Research). The density functional method B3LYP with the EPR-3 basis set[12] was used. The calculated steady-state configuration of the complex NH$_2$–HF corresponds to the collinear C_{2v} geometry, which is similar to that calculated earlier by Goddard *et al.*[4] The binding energy of the complex is equal to 12.3 kcal mol^{-1}. The geometry and hf constants of the complex are given below:



(2)

	F	H′	N	H
a(calc)/mT	−0.70	0.02	1.15	−2.30
a(exp)/mT	−0.70	< 0.05	1.20	−2.40

The calculated hf constants a_N, a_H and a_F are in good agreement with the experimental data. The hf constant $a_{H'}$ at the proton of the HF molecule is less than 0.05 mT, and this splitting cannot be resolved under given experimental conditions.

Therefore, the radical–molecule complex NH$_2$–HF is the main product in the reactions of thermal F atoms with NH$_3$ molecules in a solid argon matrix:

$$\mathrm{F} + \mathrm{NH_3} \longrightarrow \mathrm{NH_2\text{–}HF} \tag{3}$$

We optimised the arrangement of the complex in an argon lattice starting from the calculated structure. Each isolated NH$_3$ molecule occupies a singly substitutional argon lattice site; therefore, we anticipated that the NH$_2$ group of the complex is also located at the same type of sites. The minimisation of the total energy of a doped argon cluster containing 365 atoms was done using molecular dynamics simulation as described in ref. 8. The resulting configuration of the complex is shown in Figure 2. The position of the nitrogen atom of the NH$_2$ group is close to the substituted site (0, 0, 0). The fluorine atom of the HF molecule occupies the nearest octahedral interstitial site O_h ($-a/2$, 0, 0), where a = 0.54 nm is the fcc lattice parameter. This is possible only due to the fact that the distance between F and N atoms in the complex is close to the one-half lattice period $a/2$. This commensurability leads to a minor deformation of the complex in the crystal lattice: the distance between the NH$_2$ radical and the H atom of HF is 0.005 nm shorter than that in the gas-phase complex, and the out-of-plane deformation of the complex does not exceed 4°. These distortions do not result in changes of the hf constants with respect to those obtained for an equilibrium geometry of the complex.

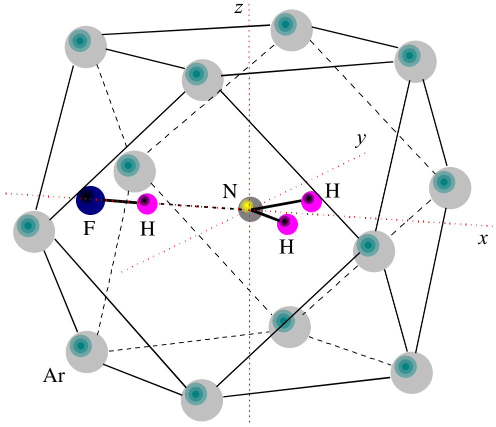


Figure 2 Arrangement of the complex NH$_2$–HF in an argon lattice. Twelve nearest neighbouring Ar atoms are shown.

In summary, the radical–molecule complex NH$_2$–HF was observed for the first time as an intermediate product in reactions of mobile F atoms with NH$_3$ molecules in solid argon. The EPR spectrum of the complex is characterised by three hyperfine constants (a_N = 1.20 mT, a_H = 2.40 mT, and a_F = = 0.70 mT). The hf constant for the H atom of the HF molecule is less than 0.05 mT. The quantum-chemical calculation revealed that the NH$_2$–HF complex has a planar C_{2v} structure and a binding energy of 12.3 kcal mol^{-1}. The calculated hf parameters of the complex and the experimental data are in good agreement. The complex in somewhat distorted in an argon lattice with respect to its equilibrium geometry in the gas phase.

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