EPR detection of radical complexes H···HF formed in the reaction of thermal F atoms with H_2 molecules in an Ar matrix

Albert U. Goldschleger,* Eugene Ya. Misochko, Alexander V. Akimov, Ilya U. Goldschleger and Victor A. Benderskii

Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax: +7 095 938 2156; e-mail: alik@icp.ac.ru

Reaction of thermal F atoms with H_2 in an Ar matrix is shown to yield uniquely H···HF complexes, whereas the same reaction of translationally-excited F atoms gives isolated H atoms.

Reaction of a fluorine atom with an H_2 molecule:

$$F + H_2 \xrightarrow{k_{v}'} HF(v') + H, \Delta H_0 = -32.07 \text{ kcal mol}^{-1} \qquad (1)$$

is one of the most thoroughly studied gas-phase chemical reactions.[1,2] Recent theoretical studies,[3,4] have predicted that the reaction (1) passes through a weakly bonded state H··HF, which was not observed in the beam experiments because the products fly apart.

Photolysis of ternary $Ar/F_2/H_2$, studied with FTIR spectroscopy by Andrews *et al.*,[5] produces mainly dimers $(HF)_2$:

$$[F_2 \cdot\cdot H_2] \xrightarrow{h\nu} [HF \cdot\cdot HF] \qquad (2)$$

due to the reaction taking place in isolated F_2–H_2 pairs. A weak band 3900 cm^{-1} was also detected and tentatively assigned to an H–F stretch in the complex H··HF. Heating to 17 K gives larger HF clusters while the line of the complex disappears.

Reaction (1) in a crystalline matrix at cryogenic temperatures occurs if the F atom can diffuse to an isolated molecule. As demonstrated by Apkarian *et al.*,[6] translationally-excited atoms ($E_0 \sim 1$ eV) migrate through several lattice spacings, whereas thermal atoms diffuse in an Ar matrix above 20 K. In previous studies we used F atoms to produce and study intermediate species from reactions F + RH in ternary $Ar/F_2/RH$ mixtures using EPR spectroscopy.[7] Photolysis of F_2 molecules yields isolated radicals and stabilized F atoms. Upon heating above 20 K, diffusing F atoms react with impurity molecules. Because the kinetic energy of the products is low they cannot fly apart and thus radical complexes are frozen in the matrix. This provides a unique opportunity to study the intermediate states of a gas phase reaction at zero excitation energy. In the present paper the technique described is used to identify and study the H··HF complex formed in reactions of thermal F atoms with isolated H_2 molecules in an Ar matrix.

The experimental technique has been described elsewhere.[7] Samples were prepared by vacuum co-deposition of gas mixtures $Ar : H_2$ and $Ar : F_2$ onto a sapphire rod ($5\times2\times50$ mm^3) held at 13 K from which to separate the jets. Typically we used a dilution ratio $Ar : H_2 : F_2 \approx (500\text{–}1000) : 1 : 1$. The sample width was ~100 μm. F atoms were generated by F_2 photolysis at $\lambda = 337$ nm (N_2 pulsed laser, average power $W = 20$ mW). The absorption cross-section and quantum yield of photodissociation of F_2 isolated in solid Ar are: $\sigma^{337}_{F_2} = 1.05\times10^{-20}$ cm^2 and $\Phi_0 = 0.35$.[6]

UV irradiation leads to an accumulation of stabilized H atoms, see Figure 1. Their EPR spectrum consists of two doublets **I** and **II** assigned to different crystalline sites. Their spin-Hamiltonian parameters are similar to those reported previously for H atoms formed by photolysis of HI in solid Ar: **I** $a_H = 50.46$, **II** $a_H = 50.76$ mT, $g = 2.0026$.[8] The concentration of H is proportional to time in the initial photolysis steps and reaches a limiting value $\sim10^{16}$ cm^{-3} with the characteristic time ~2500 s. In darkness the concentrations of **I** and **II** remain constant during several hours.

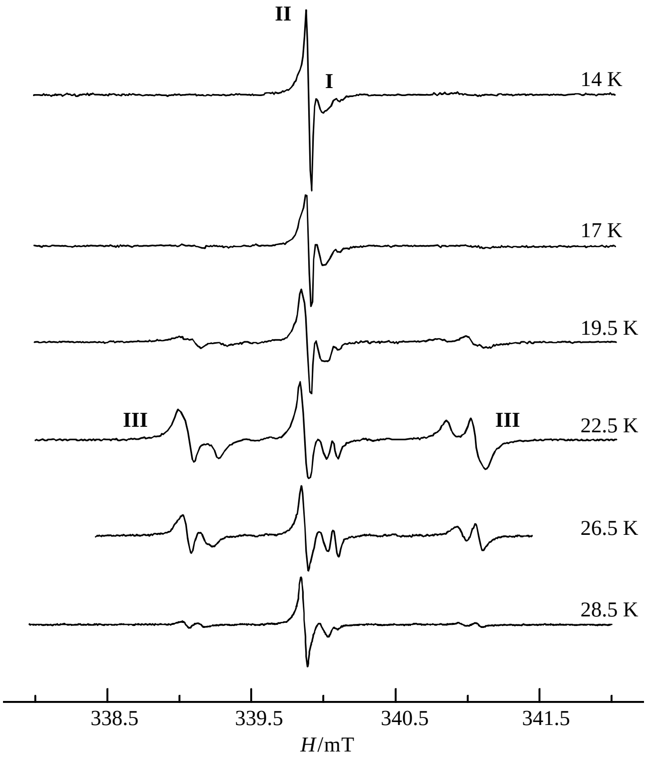

Figure 1 EPR spectrum of the H atom at different temperatures (only the high field lines are shown). The curve at 26.5 demonstrates decomposition of the complex.

After photolysis the samples were heated at a rate ~0.2 K min^{-1} to 25 K. At 18–19 K a new spectrum **III** appears (see Figure 1). This consists of two lines outside **I** and **II**. The intensity of the lines **III** increases with temperature up to 25 K. At 22 K the characteristic growth time is ~2000 s. Appearance of **III** does not affect the intensity of the lines **I** and **II**. The shape of the spectrum **III** changes drastically with temperature (see Figure 2). Upon heating above 27 K **III** disappears during several minutes, while the intensity of **I** and **II** does not change (see Figure 1). The lines **I** and **II** disappear at 41 and 32 K, respectively.

Let us emphasize that H atoms of types **I** and **II** are formed exclusively in the reaction of translationally-excited F with H_2, whereas **III** appears in the temperature region where thermal F_t atoms are able to diffuse.[6,7] This allows us to assign the spectrum **III** to the product of the reaction of H_2 with F_t. In order to identify it, additional experiments with $Ar/D_2/F_2$ were carried out. F_2 photolysis yields a well-known triplet of D atoms.[8] As for $Ar/H_2/F_2$, heating above 20 K leads to appearance of a new EPR spectrum (see Figure 3). Each component of the 1 : 1 : 1 triplet of D atoms ($S = 1$, $A_1 = 7.67$ mT) is split into a doublet ($S = ½$, $A_{½} = 1.6$ mT).

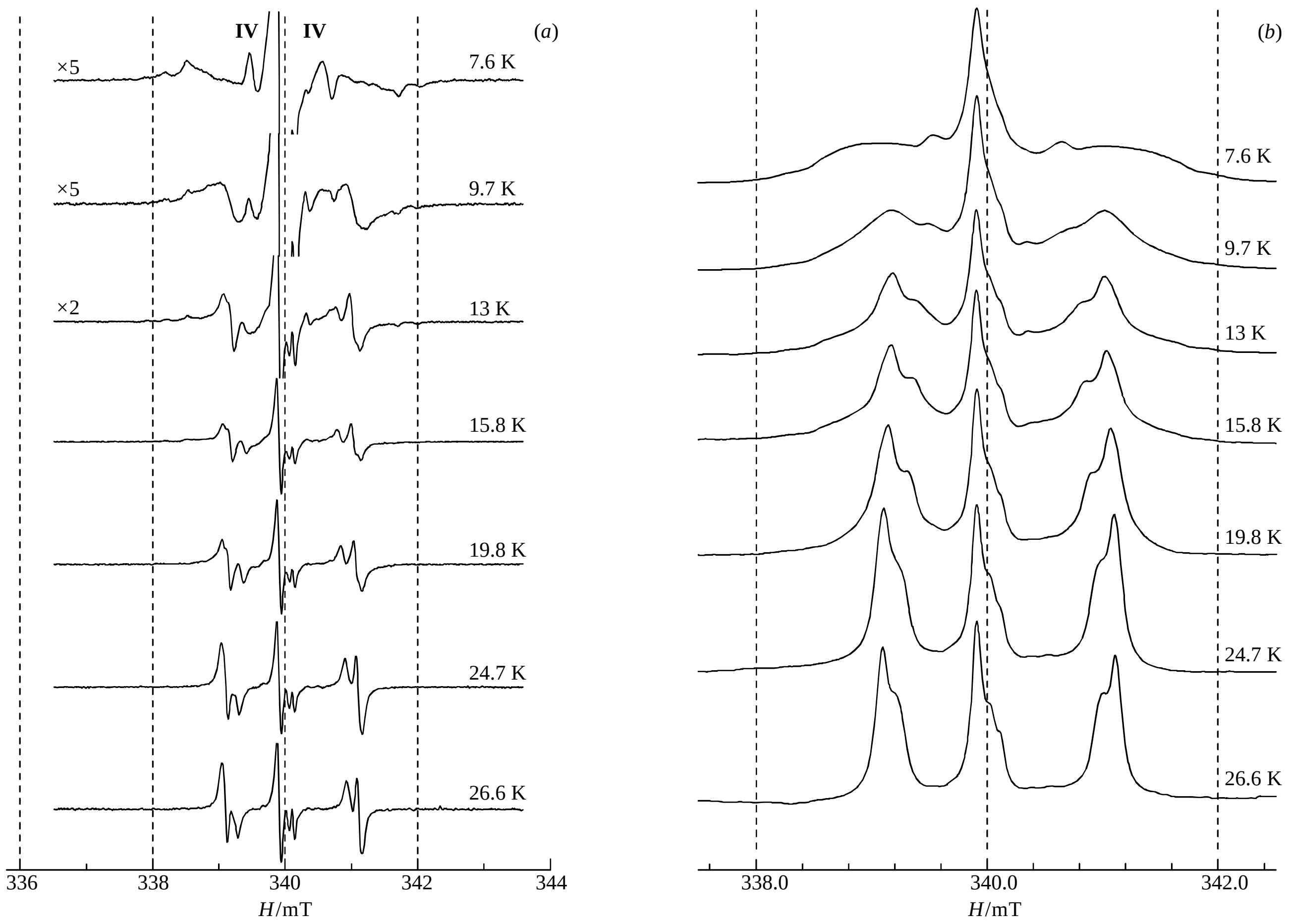

Figure 2 Temperature dependence of the shape of the H··ḢF spectrum: (*a*) differential spectra; (*b*) integrated spectra; intensities of the spectra are corrected in accordance with the Curie law.

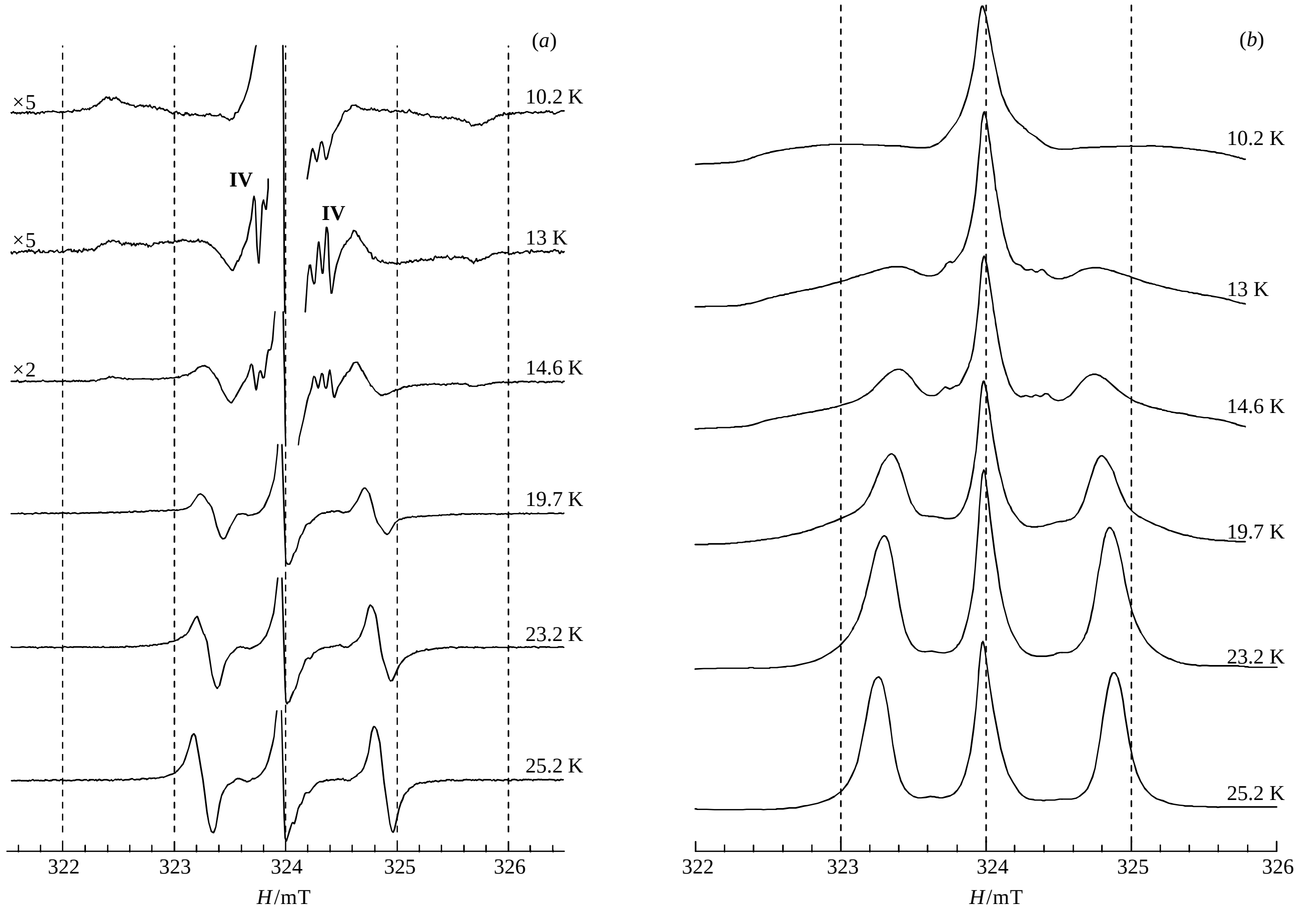

Figure 3 Temperature dependence of the shape of the D··ḊF spectra: (*a*) differential spectra; (*b*) integrated spectra.

Spectrum **III** in $Ar/H_2/F_2$ contains additional splitting 0.2 mT.

Comparison of the spectra **III** in $Ar/H_2/F_2$ and $Ar/D_2/F_2$ systems allows us to draw the following conclusions as to the structure of the new radical:

- it contains two atoms H and one F atom;
- almost all spin density is localized on a proton (this condition is required to obtain such a large hf splitting which is a distinguishing feature of the free H atom);
- the larger additional splitting belongs to ^{19}F, whereas $A_{½} \approx 0.2$ mT belongs to the HF proton.

The above reasoning implies that **III** belongs to H atoms bonded to the HF molecule, *i.e.* an H···HF complex. Hence the radical complex H···HF is the only product from the reaction of F_t with H_2 in Ar:

$$F_t + H_2 \longrightarrow H\cdots HF \tag{3}$$

Let us consider the temperature variation of the spectrum of the complex. At $T = 25$ K the width of the Lorentzian lines of H···HF is ~0.1 mT. Cooling to ~15 K results in the appearance of a broad line [see Figure 2(*b*)]. This then narrows and finally at $T < 9$ K the resolved spectrum **IV** is observed [see Figure 2(*a*)]. Upon cooling the lines **III** only broaden (the width is ~1.0 mT at 10 K). In $Ar/F_2/D_2$ the spectrum **IV**, a resolved doublet of 1 : 1 : 1 triplets ($a_D \approx 0.07$ mT, $a_{½} = 0.5$ mT), appears at 15 K (see Figure 3). In the spectrum **IV** of H···HF only the outer lines of the H···HF complex are observed, whereas the inner lines (½,–½) and (–½,½) are masked by intense spectra **I** and **II**. The splitting of the HF proton is ~0.4 mT. Contribution of the lines **IV** to the spectrum of H···HF is ~20%.

The changes observed are usually ascribed to slow motion.[9] According to calculations,[3,4] the distance between the H atom and the HF molecule is ~3 Å. The observed changes in the widths of the EPR lines of the complex (~1.0–1.5 mT) are vastly greater than the anisotropy of the hf interaction expected for distant nuclei. Therefore, the origin of the temperature changes of the spectrum of the complex is the thermally-activated transition among different stable configurations resulting in a modulation of the isotropic (rather than anisotropic) hf interaction with HF nuclei. However, a model of exchange between two energetically equivalent configurations with different Zeeman frequencies fails to describe the changes listed. At low temperatures (*i.e.* in the absence of exchange) instead of the expected doublet of narrow lines (m_F, m_H) only the spectrum **IV** is observed. Thus we described the observed spectrum in a model of exchange between two energetically nonequivalent configurations **A** and **B** one of which becomes unobservable due to depopulation at lower temperatures.[10] The spectra are described with good accuracy within the suggested model. The fitted parameters are: **III** $\Delta < 2$ K, $E_a = 40$ K, $\omega_0 = 3\times10^{10}$ rad s^{-1}; **IV** $\Delta \cong 25$ K, $E_a = 80$ K, $\omega_0 = 3\times10^{10}$ rad s^{-1}, exchange frequencies **A** → **B** and **B** → **A** obey Arrhenius law: $\omega_{A\to B} = \omega_0\exp(-E_a/T)$ and $\omega_{B\to A} = \omega_0\exp[-(E_a + \Delta)/T]$, Δ is the difference between the energies **A** and **B**. The hf constants of the configurations are equal to: **A** $a_F = 3.2$ mT, $a_H < 0.1$ mT; **B** $a_F \cong 0.5$ mT, $a_D \cong 0.4$ mT. The spectrum **IV** at $T = 7$–10 K is assigned to the configuration **B** since the configuration **A** is not populated. Because a_F of the lowest energy configuration **B** is less than that of **A**, **B** may correspond to the linear intermediate state H···HF of the gas phase reaction. Configuration **A** (in which a_F grows while a_H decreases) may be assigned to hydrogen-bonded complex H···FH stabilized in an Ar matrix.

The present study revealed two channels of photolysis in the $Ar/F_2/H_2$ system. Reaction of translationally-excited F atoms with H_2 gives previously identified isolated H atoms stabilized in two different lattice sites. In contrast, reaction of thermal F atoms yields uniquely H···HF complexes. The complex is stable over a wide temperature region, $7 \le T \le 27$ K and possesses two configurations.

The authors wish to thank the Russian Foundation for Basic Research (grant no. 95-03-08509) for financial support of this work.

References

1 T. S. Schafer, P. E. Siska, J. M. Parson, F. P. Tully, Y. C. Wong and Y. T. Lee, *J. Chem. Phys.*, 1970, **53**, 3385.

2 D. M. Neumark, A. M. Wodtke, G. N. Robinson, C. C. Hayden and Y. T. Lee, *J. Chem. Phys.*, 1985, **82**, 3045.

3 S. I. Mielke, G. C. Lynch, D. G. Truhlar and D. W. Schwenke, *Chem. Phys. Lett.*, 1993, **213**, 10.

4 K. Stark and H.-J. Werner, *J. Chem. Phys.*, 1996, **104**, 6516.

5 R. D. Hunt and L. Andrews, *J. Chem. Phys.*, 1985, **82**, 4442.

6 J. Field, H. Kunti and V. A. Apkarian, *J. Chem. Phys.*, 1990, **93**, 1009.

7 E. Ya. Misochko, V. A. Benderskii, A. U. Goldschleger, A. V. Akimov and A. F. Shestakov, *J. Am. Chem. Soc.*, 1995, **117**, 11997.

8 S. N. Foner, E. L. Cochran, V. A. Bowers and C. K. Jen, *J. Chem. Phys.*, 1960, **32**, 963.

9 A. Abraham, *The Principles of Nuclear Magnetism*, Clarendon Press, Oxford, 1961.

10 A. U. Goldschleger, E. Ya. Misochko, A. V. Akimov, I. U. Goldschleger and V. A. Benderskii, *Chem. Phys. Lett.*, 1996, **267**, 288.

Received: Moscow, 3rd December 1996
Cambridge, 19th February 1997; Com. 6/08398F