

EPR detection of radical complexes H \cdots HF formed in the reaction of thermal F atoms with H $_2$ molecules in an Ar matrix

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Reaction of thermal F atoms with H $_2$ in an Ar matrix is shown to yield uniquely H \cdots 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:



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 \cdots 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) $_2$:



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 \cdots 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 \cdots 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 \times 2 \times 50 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: $\sigma_{\text{F}_2}^{337} = 1.05 \times 10^{-20}$ 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** $a_{\text{H}} = 50.46$, **II** $a_{\text{H}} = 50.76$ mT, $g = 2.0026$.⁸ The concentration of H is proportional to time in the initial photolysis steps and reaches a limiting value $\sim 10^{16}$ cm $^{-3}$ with the characteristic time ~ 2500 s. In darkness the concentrations of **I** and **II** remain constant during several hours.

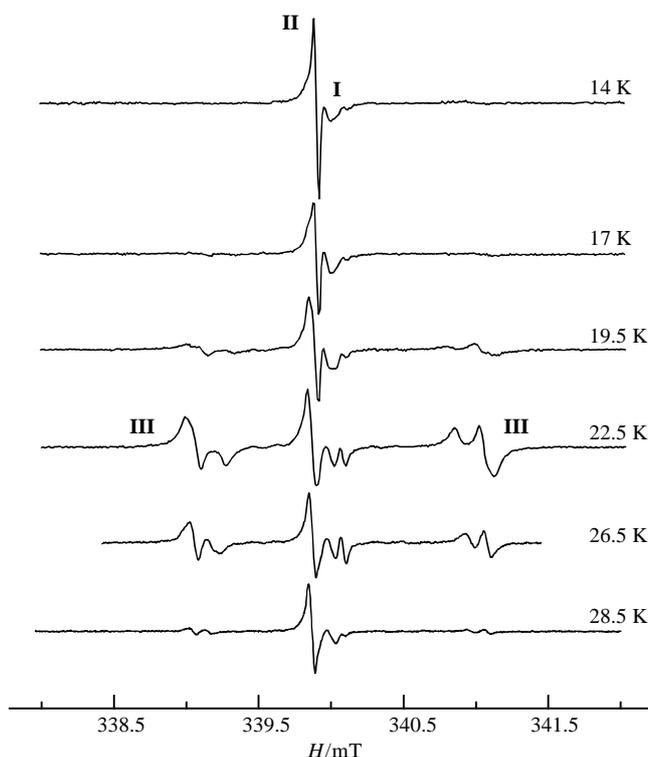


Figure 1 EPR spectrum of the H atom at different temperatures (only the high field lines are shown). The curve at 26.5 demonstrates decomposition of the complex.

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 $_1$ 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 $_1$. 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 ($S = 1/2$, $A_{1/2} = 1.6$ mT).

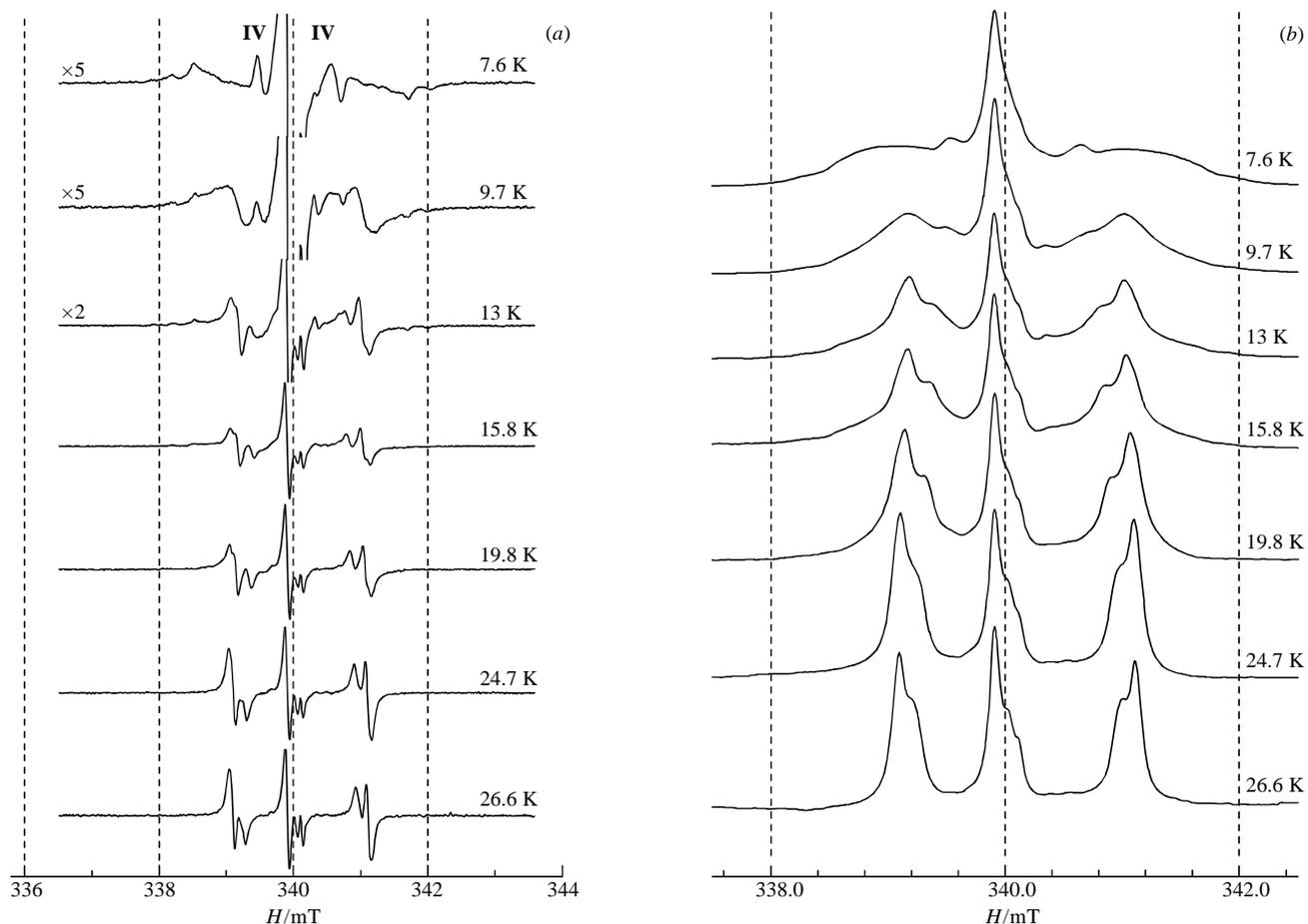


Figure 2 Temperature dependence of the shape of the $\text{H}\cdots\text{HF}$ spectrum: (a) differential spectra; (b) integrated spectra; intensities of the spectra are corrected in accordance with the Curie law.

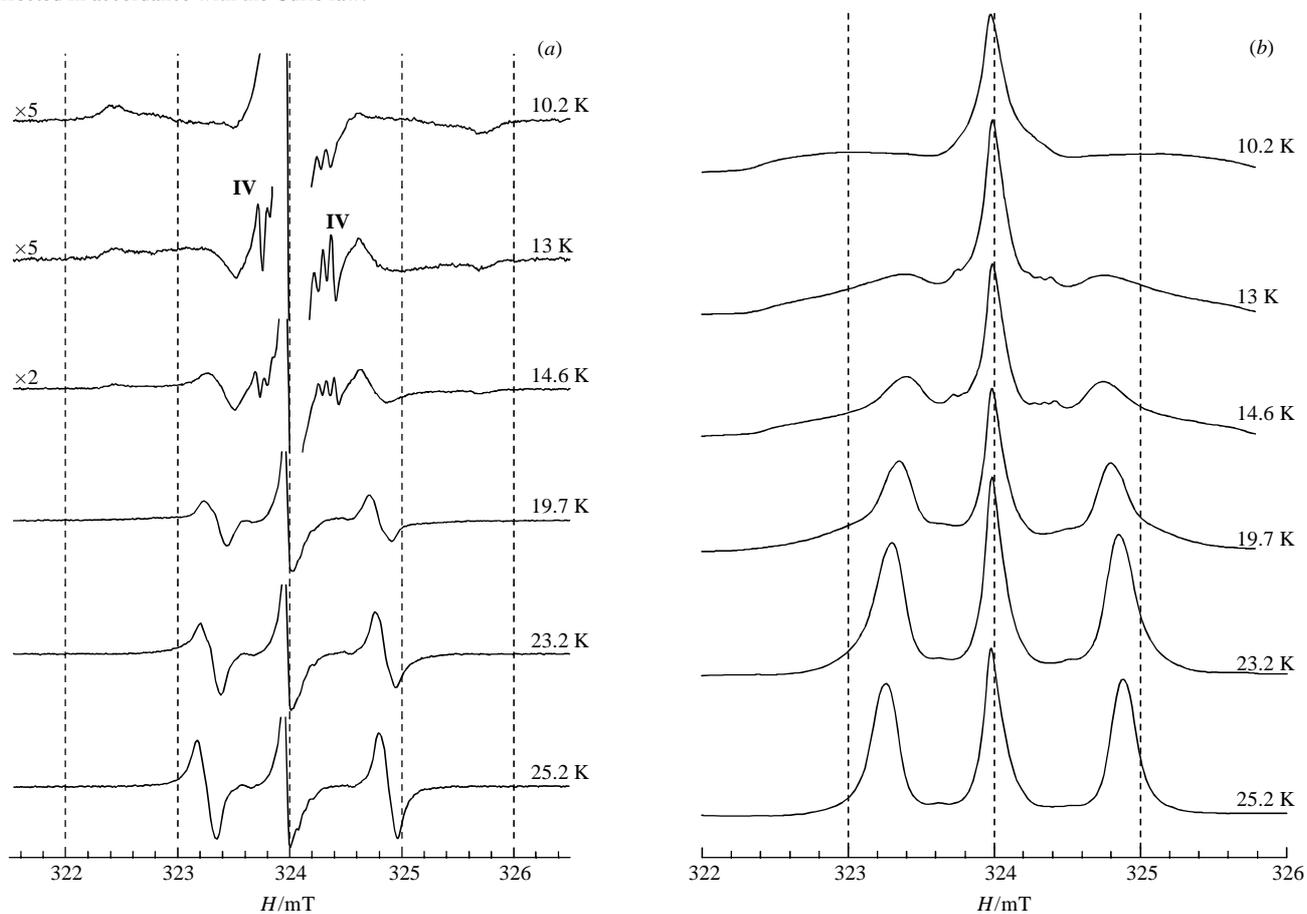


Figure 3 Temperature dependence of the shape of the $\text{D}\cdots\text{DF}$ spectra: (a) differential spectra; (b) integrated spectra.

Spectrum **III** in Ar/H₂/F₂ contains additional splitting 0.2 mT.

Comparison of the spectra **III** in Ar/H₂/F₂ and Ar/D₂/F₂ 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 ¹⁹F, whereas $A_{1/2} \approx 0.2$ 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 \cdots HF complex. Hence the radical complex H \cdots HF is the only product from the reaction of F₁ with H₂ in Ar:



Let us consider the temperature variation of the spectrum of the complex. At $T = 25$ K the width of the Lorentzian lines of H \cdots 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/F₂/D₂ the spectrum **IV**, a resolved doublet of 1 : 1 : 1 triplets ($a_D \approx 0.07$ mT, $a_{1/2} = 0.5$ mT), appears at 15 K (see Figure 3). In the spectrum **IV** of H \cdots HF only the outer lines of the H \cdots HF complex are observed, whereas the inner lines ($1/2, -1/2$) and ($-1/2, 1/2$) 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 \cdots HF is $\sim 20\%$.

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, $\omega_0 = 3 \times 10^{10}$ rad s⁻¹; **IV** $\Delta \approx 25$ K, $E_a = 80$ K, $\omega_0 = 3 \times 10^{10}$ rad s⁻¹, exchange frequencies **A** \rightarrow **B** and **B** \rightarrow **A** obey Arrhenius law: $\omega_{A \rightarrow B} = \omega_0 \exp(-E_a/T)$ and $\omega_{B \rightarrow A} = \omega_0 \exp[-(E_a + \Delta)/T]$, 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** $a_F \approx 0.5$ mT, $a_D \approx 0.4$ 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 \cdots 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 \cdots FH stabilized in an Ar matrix.

The present study revealed two channels of photolysis in the Ar/F₂/H₂ system. Reaction of translationally-excited F atoms with H₂ gives previously identified isolated H atoms stabilized in two different lattice sites. In contrast, reaction of thermal F atoms yields uniquely H \cdots HF complexes. The complex is stable over a wide temperature region, $7 \leq T \leq 27$ K and possesses two configurations.

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