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# EPR and infrared spectra of the HFC=N$^\bullet$ free radical stabilised in solid argon

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**The HFC=N$^\cdot$ radical has been formed by the addition of a mobile F atom to HCN in solid argon.**

The hydrogenated and fluorinated species of the CN$^\cdot$ series, such as CN$^\cdot$, HCN, FCN, $H_2CN^\cdot$, $F_2CN^\cdot$, HFCN$^\cdot$ and $H_2CNH$ are of interest owing to their importance in combustion[1] as well as in radioastronomical studies of interstellar clouds.[2,3] The $H_2CN^\cdot$ radical has also been postulated as a reaction intermediate in the atmosphere of Jupiter.[4] To our knowledge, the $H_2CN^\cdot$ radical is the best studied open-shell species in this series. The EPR,[5,6] infrared,[7] ultraviolet,[8] and microwave[9] absorption spectra of the radical were measured. Quantum-chemical calculations based on these experimental data predict a planar geometry of the $H_2CN^\cdot$ radical in the ground state.[6] Only the IR spectrum of the $F_2CN^\cdot$ radical in solid argon was observed,[10] and the geometry of the ground state was predicted.[11] The IR spectrum of the HFCN$^\cdot$ radical in solid argon was observed;[12] however, only four of six its vibrational frequencies were identified. Here we report on the total set of isotropic hyperfine (hf) constants and vibrational frequencies of the HFCN$^\cdot$ radical isolated in solid argon. The isotopic substitution (H/D) was used to assign reliably its vibrational spectrum. The geometry of the ground-state HFCN$^\cdot$ radical was recovered from a comparison of measured and calculated spectral characteristics (hf constants and vibrational frequencies).

To generate the stabilised fluorine-containing radicals in rare-gas matrices, we used the ability of F atoms to migrate in solid argon over long distances and to react with molecules of a second reactant, which are initially isolated in a rare-gas matrix. The most challenging aspect of this method is that one of the reactants, the F atom, is an open-shell species; therefore, the reaction product will also be an open-shell species. This method was applied previously[10,12] to generate $F_2CN^\cdot$ and HFCN$^\cdot$ radicals and to observe their IR spectra. Our approach to study stabilised radicals formed in chemical reactions of fluorine atoms consists in the combined use of matrix isolation EPR and FTIR techniques and quantum-chemical computations. As found earlier,[13,14] this approach makes it possible to identify stabilised radicals and to clarify their spectroscopic properties.

We have detected HFCN$^\cdot$ radicals, being the reaction product of F atoms with HCN molecules isolated in solid argon. Dilute $Ar/F_2/HCN$ ternary mixtures, in which $F_2$ molecules are photolytic precursors of F atoms, were studied. The experimental techniques were described previously.[14] Samples were prepared by vacuum co-deposition of gaseous $Ar/F_2$ and Ar/HCN mixtures onto a substrate at 15 K (sapphire rod in the EPR experiments and CsI window in the infrared study). In all of the experiments, the mole fraction of reactants was less than $10^{-3}$. The thickness of samples was approximately 100 μm. EPR spectra were recorded using a standard 9 GHz spectrometer. IR spectra were recorded on a Mattson Model RS/10000 FTIR spectrometer at 0.5 cm$^{-1}$ resolution over the region 500–4000 cm$^{-1}$.

**Table 1** Vibrational frequencies (cm$^{-1}$) of HFCN$^\cdot$ and DFCN$^\cdot$ radicals.[a]

| Assignment | HFCN$^\cdot$ | | | DFCN$^\cdot$ | | |
|---|---|---|---|---|---|---|
| | Exp. | Calc.[b] | Lit.,[12] | Exp. | Calc. | Lit.,[12] |
| $\nu_1(a')$, FCN (in-plane) | 536 (0.18) | 539 (0.17) | 536 | 530 (0.22) | 533 (0.17) | 530[b] |
| $\nu_2(a'')$, (out-of-plane) | 894 (0.05) | 898 (0.04) | | 735 (0.01) | 758 (0.00) | |
| $\nu_3(a')$, CF str. | 1058 (1.0) | 1057 (1.0) | 1057 | 1048 (1.0) | 1046 (1.0) | 1047 |
| $\nu_4(a')$, FCH (in-plane) | 1233 (0.06) | 1258 (0.03) | | 911 (0.02) | 922 (0.01) | |
| $\nu_5(a')$, CN str. | 1673 (0.30) | 1724 (0.33) | 1672 | 1650 (0.42) | 1697 (0.48) | 1651 |
| $\nu_6(a')$, CH str. | 3018 (0.03) | 3118 (0.02) | 3017 | 2252 (0.02) | 2306 (0.02) | 2252 |

[a] Relative integrated absorptions of the infrared bands are shown in parentheses. [b] Calculated using B3LYP/6-311++G(3*df*,2*p*).

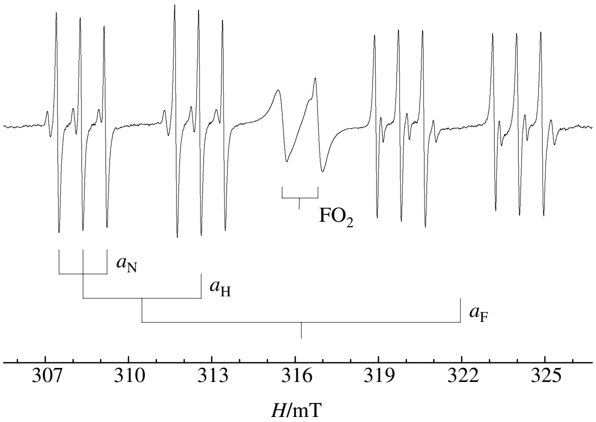

**Figure 1** EPR spectrum of a sample of $Ar:F_2:HCN$ = 3000:1:1 after UV photolysis at 337 nm and subsequent annealing at 25 K. The spectrum was recorded at 35 K.

Fluorine atoms were generated by $F_2$ laser photolysis at 337 nm in the EPR experiments and at 355 nm in the infrared experiments. Fluorine atoms are able to diffuse in solid argon at temperatures above 20 K.[15,16] To distinguish the chemical reactions involving photogenerated F atoms from those of diffusing thermal F atoms, photolysis was performed at 15 K. After completion of photolysis, the sample was annealed at 24–26 K to initiate the reactions of diffusing F atoms. Molecular oxygen is a common impurity in fluorine gas, and it is difficult to remove by fractional distillation. Therefore, oxygen was always present in the samples in a small concentration of ~$10^{-4}$–$10^{-5}$. Since diffusing fluorine atoms react with $O_2$ molecules to form $FO_2$ radicals,[17] we have used this reaction as an internal standard for characterising the reaction rate of diffusing F atoms during the annealing.

The EPR spectra of freshly prepared $Ar/F_2$ and $Ar/F_2/HCN$ samples exhibit no lines due to paramagnetic species. Annealing of the photolysed $Ar/F_2$ samples gives rise to growth of the EPR spectrum of the free radicals $FO_2$ formed in the reaction of diffusing F atoms with oxygen impurities. Annealing of the photolysed $Ar/F_2/HCN$ samples leads to the appearance of a new series of twelve intense lines (Figure 1). The pattern of this new spectrum is well separated from that of the $FO_2$ radical. The growth of intensities of these lines occurs simultaneously with an increase in the intensities of lines of the $FO_2$ radical. Hence, the new EPR spectrum also corresponds to the reaction product of diffusing F atoms. As shown in Figure 1, the series of 12 lines contains three splittings: the nitrogen triplet with 1:1:1 relative intensities (the nuclear spin of the $^{14}N$ atom is $I = 1$), the hf constant $a_N = 0.86$ mT, and two doublet splitting with $a_1 = 10.87$ mT and $a_2 = 4.27$ mT. It is necessary to assign these doublet splittings to the hf interaction of an unpaired

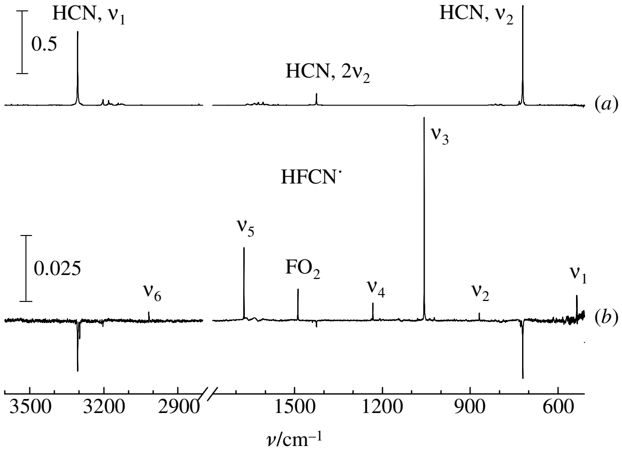

**Figure 2** (*a*) Infrared spectrum of a sample of Ar:$F_2$:HCN = 6000:2:1 after deposition; (*b*) difference spectrum of the photolysed sample before and after annealing at 25 K. The spectra were recorded at 15 K.

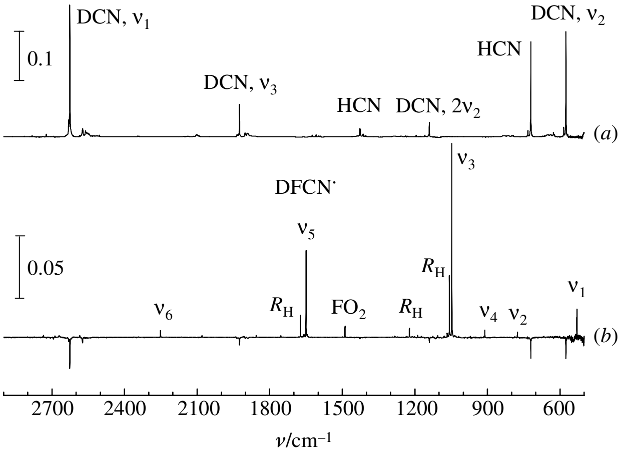

**Figure 3** (*a*) Infrared spectrum of a sample of Ar:$F_2$:DCN = 3000:2:1 after deposition; (*b*) difference spectrum of the photolysed sample before and after annealing at 25 K. The spectra were recorded at 15 K. The DCN used contained ~20% HCN. Infrared bands corresponding to the H-substituted product (Figure 2) labelled as $R_H$.

electron with nuclei having a nuclear spin of $^1/_2$ ($^{19}$F and $^1$H). The spectrum is practically isotropic at 35 K. However, lowering the temperature causes a broadening of the lines, and at $T < 25$ K the spectrum becomes anisotropic. Such a reversible temperature behaviour of the shape and width of components of the EPR spectrum can be explained within the model of incoherent hindered rotation of a radical in an argon matrix resulting in averaging the anisotropy of the hyperfine interaction at $T > 30$ K.[14] In addition to the above twelve intense lines, 12 weak satellite lines are observed in the spectrum with hf splittings: triplet splitting at 0.86 mT and two doublet splittings at 4.27 and 11.23 mT (Figure 1). Relative intensities of the satellite lines are reduced with a decrease in the concentration of HCN molecules in samples. The only hf splitting changes noticeably, by ~3%, is doublet splitting $a_1$, whereas triplet $a_N$ and the other doublet $a_2$ splittings remain the same. The IR absorption spectra of samples reveal the presence of HCN aggregates. Their contribution is estimated at 15–20% even in the most diluted samples. Therefore, we have assigned the satellite spectrum to the EPR spectrum of the same radical perturbed by the interaction with HCN molecules isolated in an adjacent lattice site.

The infrared spectra of freshly prepared Ar/$F_2$/HCN and Ar/$F_2$/DCN samples exhibit strong bands due to HCN (3306, 1425 and 721 cm$^{-1}$) and DCN (2626 1142, 1925 and 575 cm$^{-1}$) molecules and traces of water in the spectral region 1630–1570 cm$^{-1}$ [Figures 2(*a*) and 3(*a*)]. Broad bands in the IR spectra at 3200, 3180 and 733 cm$^{-1}$ are due to HCN aggregates. The intensities of these bands increase sharply in samples with a growth of HCN concentration. Figure 2(*b*) shows difference infrared spectra of the photolysed Ar/HCN/$F_2$ sample at 15 K before and after annealing at 25 K. It demonstrates the consumption of HCN molecules, the formation of $FO_2$ radicals and the appearance of six new infrared bands. In the photolysed Ar/DCN/$F_2$ samples, a decrease of bands of DCN molecules and a growth of a series of six new bands occur upon annealing [Figure 3(*b*)]. In both types of samples, a decrease of the bands of HCN (DCN) molecules and a growth of new infrared bands take pace with a growth of the infrared band of the $FO_2$ radical at 1490 cm$^{-1}$. It means unambiguously that the new EPR and infrared spectra correspond to a reaction product of diffusing F atoms and HCN molecules. Four of six observed infrared bands are very close to those assigned earlier[12] to HFCN· (DFCN·) radicals in solid argon (Table 1). This agreement allows us to conclude that the observed EPR and infrared spectra pertain to the radical HFCN· formed in the addition reaction of diffusing F atoms

$$F + HCN \rightarrow HFC{=}N^{\cdot} \qquad (1)$$

**Table 2** Calculated geometry (Å and degree) and isotropic hyperfine constants (mT) of $H_2CN^{\cdot}$, $F_2CN^{\cdot}$ and $HFCN^{\cdot}$ radicals.

| Parameter | $H_2CN^{\cdot}$ | | $F_2CN^{\cdot}$ | | $HFCN^{\cdot}$ | |
|---|---|---|---|---|---|---|
| | Exp.[a] | Calc.[b] | Exp. | Calc. | Exp.[c] | Calc. |
| $a_N$ | \|0.83\|[d] | 0.82 | | 0.79 | \|0.86\| | 0.79 |
| $a_F$ | | | | 4.84 | \|10.87\| | 11.15 |
| $a_H$ | \|8.47\| | 8.48 | | | \|4.27\| | 4.42 |
| $R_{CN}$ | | 1.238 | | 1.249 | | 1.243 |
| $R_{CH}$ | | 1.097 | | | | 1.089 |
| $R_{CF}$ | | | | 1.317 | | 1.345 |
| ∠HCN | | 121.47 | | | | 123.81 |
| ∠FCN | | | | 124.58 | | 123.17 |

[a] Data from ref. 6. [b] Calculated using B3LYP/6-311++G(3*df*,2*p*). [c] This work. [d] Only the absolute values of hf constants were measured.

We have carried out calculations in order to confirm such an assignment, to clarify the structure of the HFCN· radical and to establish its spectroscopic characteristics (vibrational frequencies and hf constants). The calculations were performed using the Gaussian 98 program package.[18] The geometry of the radical was fully optimised by density functional theory calculations using the B3LYP exchange-correlation functional and 6-311++G(3*df*,2*p*) basis functions. The computations predict a planar structure of the HFCN· radical. Calculated bond lengths and angles are collected in Table 2. Additional to the geometry optimisation, spectroscopic characteristics of the radical were calculated. Excellent agreement between the observed hf constants and those calculated for the HFCN· radical was found (Table 2). A comparison of the measured and calculated vibrational frequencies for the radical demonstrated in Table 1 shows generally good agreement, except for the CH stretch mode $\nu_6$. The revealed discrepancies, especially ~100 cm$^{-1}$ for $\nu_6$, can be explained by anharmonicity of intramolecular potentials, which is not taken into account.[14] Therefore, a comparison of the calculated and measured spectroscopic constants allows us to conclude definitely that the observed total set of isotropic hf constants and vibrational frequencies correspond to those of the HFCN· radical.

We carried out analogous calculations for $H_2CN^{\cdot}$ and $F_2CN^{\cdot}$ radicals. The method used foretells a planar structure with $C_{2v}$ symmetry for both radicals. The calculated and measured (HFCN· in this work and $H_2CN^{\cdot}$ observed earlier[5]) hf constants are compared in Table 2. Because of excellent agreement between the calculated and experimental hf constants for both radicals, one should expect that the calculations predict the hf constant $a_F$ in $F_2CN^{\cdot}$ radical with an accuracy of ~5%.

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