

Infrared and EPR Spectroscopic Observation of Novel Open-Shell Species: The Fluoroiminomethyl Radical ($\text{FC}^*=\text{NH}$) in Solid Argon

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The open-shell species $\text{HC}^*=\text{NH}$, $\text{FC}^*=\text{NF}$, and $\text{FC}^*=\text{NH}$, in which the unpaired electron is localized on the carbon atom, were predicted by various authors in quantum-chemical calculations.^{1–3} However, to our knowledge there have been no definitive experimental observations of these species. In this Communication we report the first observation of $\text{FC}^*=\text{NH}$ and $\text{FC}^*=\text{ND}$, along with complete assignments of their infrared and EPR spectra.

Jacox and Milligan suggested that $\text{FC}^*=\text{NF}$ ⁴ and $\text{HC}^*=\text{NH}$ ⁵ could be formed as a minor product channel in $\text{F} + \text{FCN}$ and $\text{H} + \text{HCN}$ reactions in a solid argon matrix. These authors provided reliable assignments of the major products, $\text{F}_2\text{C}=\text{N}^*$ and $\text{H}_2\text{C}=\text{N}^*$. However, only one infrared band at 886 cm^{-1} was attributed to the $\text{HC}^*=\text{NH}$, and one band at 1053 cm^{-1} was tentatively assigned to the $\text{FC}^*=\text{NF}$. Petterson et al.⁶ photolyzed HCN in a krypton matrix, and assigned two infrared bands (at 883 and 1218 cm^{-1}) to $\text{HC}^*=\text{NH}$.

Recently we have shown⁷ that solid-state chemical reaction of mobile F atoms with HCN in an argon matrix produces stabilized $\text{HFC}=\text{N}^*$ radicals in sufficient concentration for infrared and EPR detection:



In this Communication we demonstrate that this radical undergoes partial photoisomerization at 355 nm to $\text{FC}^*=\text{NH}$,



This has allowed us to assign infrared and EPR spectra of both radical species and their deuterated analogues.

Fluorine atoms can diffuse over long distances in solid argon at $T > 20\text{ K}$ and react with other molecules of interest,^{8,9} in this case HCN. The combined use of matrix isolation, EPR, and FTIR techniques in separate but similar experiments provides an effective strategy for forming and detecting reactive free radicals. We have shown that this method, supported by quantum chemistry

(1) Bair, R. A.; Dunning, T. H., Jr. *J. Chem. Phys.* **1985**, *82*, 2280.

(2) Dupin, H.; Baraille, I.; Larrieu, C.; Dargelos, A. *Chem. Phys.* **2000**, *256*, 7.

(3) Bernardi, F.; Cacace, F.; Occhiucci, G.; Ricci, A.; Rossi, I. *J. Phys. Chem. A* **2000**, *104*, 5545.

(4) Jacox, M. E.; Milligan, D. E. *J. Chem. Phys.* **1968**, *48*, 4040.

(5) Jacox, M. E. *J. Phys. Chem.* **1987**, *91*, 6595.

(6) Petterson, M.; Lundell, J.; Khriachtchev, L.; Rasanen, M. *J. Chem. Phys.* **1998**, *109*, 618.

(7) Goldschleger, I. U.; Akimov, A. V.; Misochko E. Ya.; Wight, C. A. *Mendelevov Comm.* Submitted for publication.

(8) Kunttu, H.; Feld, J.; Alimi, R.; Becker, A.; Apkarian, V. A. *J. Chem. Phys.* **1990**, *92*, 4856.

(9) Misochko, E. Ya.; Akimov, A. V.; Wight, C. A. *Chem. Phys. Lett.* **1997**, *274*, 23.

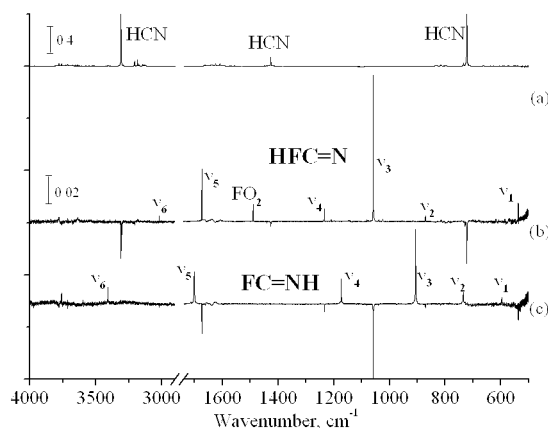


Figure 1. Infrared spectra of a matrix sample $\text{Ar:F}_2\text{:HCN} = 6000:2:1$ after deposition (trace a). Difference spectrum of the photolyzed sample before and after annealing at 25 K (trace b). Trace c shows the difference spectrum after subsequent 355 nm photolysis.

calculations, is a reliable way to identify novel radicals and measure their spectroscopic properties.^{10,11}

The experimental technique is similar to that described in our previous studies.^{10,11} Samples were prepared by vacuum co-deposition of gaseous mixtures Ar/F_2 and Ar/HCN onto a substrate at 15 K . EPR spectra were recorded using a standard 9 GHz spectrometer. Infrared spectra were recorded with a FTIR spectrometer at 0.5 cm^{-1} resolution over the region $500\text{--}4000\text{ cm}^{-1}$. IR spectra of freshly prepared $\text{Ar/F}_2\text{/HCN}$ samples, shown in Figure 1a, exhibit strong IR bands of HCN (3306 , 1425 , and 721 cm^{-1}), traces of water in spectral regions $1630\text{--}1570$ and $3775\text{--}3710\text{ cm}^{-1}$, and weak broad bands at 3200 , 3180 , and 733 cm^{-1} due to HCN aggregates.

Fluorine atoms were generated at 15 K by 337 nm laser photolysis of F_2 in the EPR experiments and at 355 nm in the infrared experiments (10 mW/cm^2 for 100 min). After photolysis, the sample was annealed at $24\text{--}26\text{ K}$ in darkness to initiate reaction of thermally diffusing F atoms.

Figure 1b shows changes in the infrared spectra as a result of annealing a photolyzed $\text{Ar/F}_2\text{/HCN}$ sample at 25 K . Bands of HCN show decreased intensity, and six new bands appear, labeled as ν_i . Four of the six bands were assigned earlier by Hunt and Andrews¹² to the $\text{HFC}=\text{N}^*$ radical formed in reaction 1; these band positions are listed in Table 1. The band at 1490 cm^{-1} is due to FO_2 radicals formed by reaction of diffusing F atoms with oxygen impurity molecules. The IR band positions of $\text{DFC}=\text{N}^*$, similarly formed after annealing of photolyzed $\text{Ar/F}_2\text{/DCN}$ samples, are given in Table 1.

Annealing photolyzed $\text{Ar/F}_2\text{/HCN}$ samples in EPR experiments leads to the appearance of the $\text{HFC}=\text{N}^*$ spectrum shown in Figure 2a; the analysis of this spectrum was made in our recent communication.⁷ At 35 K the spectrum is practically isotropic. The hyperfine structure consists of 3 groups of lines: the nitrogen triplet with 1:1:1 relative intensities and hyperfine constant $a_N = 0.86\text{ mT}$, and two doublet splittings with $a_F = 11.15\text{ mT}$ and $a_H = 4.27\text{ mT}$. Table 1 shows that excellent agreement is obtained between the measured and calculated hyperfine constants and vibrational frequencies for both $\text{HFC}=\text{N}^*$ and $\text{DFC}=\text{N}^*$.

As the next step in the experiments, we subjected the stabilized $\text{HFC}=\text{N}^*$ radicals to 355 nm laser photolysis. Although the laser intensity used in this stage of photolysis is much lower than that

(10) Misochko E. Ya.; Akimov, A. V.; Goldschleger, I. U.; Boldyrev A. I.; Wight, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 405.

(11) Misochko E. Ya.; Goldschleger, I. U.; Akimov, A. V.; Wight, C. A. *Low Temp. Phys.* **2000**, *26*, 727.

(12) Hunt, R. D.; Andrews, L. *Inorg. Chem.* **1987**, *26*, 3051.

Table 1. Vibrational Frequencies (cm^{-1}) and Isotopic Hyperfine Constants (mT) of the $\text{HFC}=\text{N}^{\bullet}$ and $\text{DFC}=\text{N}^{\bullet}$ Radicals

assignment	$\text{HFC}=\text{N}^{\bullet}$		$\text{DFC}=\text{N}^{\bullet}$	
	exptl	calcd ^d	exptl	calcd
$\nu_1(\text{a}')$, FCN (in-plane)	536 ^b (0.18) ^a	539 (0.17)	530 ^b (0.22)	533 (0.17)
$\nu_2(\text{a}'')$, (out-of-plane)	894 (0.05)	898 (0.04)	735 (0.01)	758 (0.00)
$\nu_3(\text{a}')$, CF str.	1058 ^b (1.0)	1057 (1.0)	1048 ^b (1.0)	1046 (1.0)
$\nu_4(\text{a}')$ FCH (in-plane)	1233 (0.06)	1258 (0.03)	911 (0.02)	922 (0.01)
$\nu_5(\text{a}')$ CN str.	1673 ^b (0.30)	1724 (0.33)	1650 ^b (0.42)	1697 (0.48)
$\nu_6(\text{a}')$, CH str.	3018 ^b (0.03)	3118 (0.02)	2252 ^b (0.02)	2306 (0.02)
a_{N}	0.86 ^c	0.78		
a_{H}	4.27	4.47		
a_{F}	10.87	11.15		

^a Relative integrated absorption coefficients of the infrared bands are shown in parentheses. ^b Agrees with data from ref 12. ^c Only the absolute value of the hyperfine constant is measured in experiment. ^d Calculated using B3LYP/6-311++G(3df,2p).

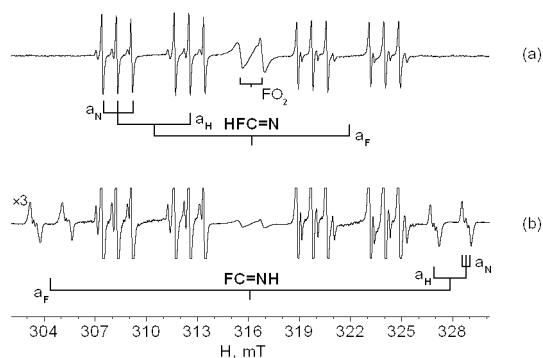


Figure 2. EPR spectrum of $\text{HFC}=\text{N}^{\bullet}$ radicals generated from a matrix sample $\text{Ar}:\text{F}_2:\text{HCN} = 3000:1:1$ by 337 nm photolysis and subsequent annealing at 24 K (a); EPR spectrum of $\text{FC}^{\bullet}=\text{NH}$ radicals generated by 337 nm photolysis of $\text{HFC}=\text{N}^{\bullet}$ radicals (b). Spectra were recorded at 35 K.

in the initial photolysis period, the infrared absorption bands of the $\text{HFC}=\text{N}^{\bullet}$ radical decrease by about 45% (see Figure 1c). This change is accompanied by the growth of a series of six new bands at 595, 733, 905, 1172, 1700, and 3405 cm^{-1} . In samples containing $\text{DFC}=\text{N}^{\bullet}$ radicals, the new bands appear at 575, 759, 1142, 1701, and 2532 cm^{-1} . The reaction can be reversed by a brief photolysis at 266 nm, which completely destroys the new species and restores most of the $\text{HFC}=\text{N}$ radicals. Each cycle of two successive photolysis periods at 355 and 266 nm leads to the net consumption of about 25% of the $\text{HFC}=\text{N}^{\bullet}$ radicals. Only one new infrared band appears: in the region of perturbed HF (DF) vibration in solid argon at 3753 (2760) cm^{-1} . This band is tentatively assigned to the HF stretching mode of the $\text{HF}-\text{CN}$ complex, formed upon 266 nm irradiation.

In EPR experiments, the $\text{HFC}=\text{N}^{\bullet}$ radicals were subjected to irradiation at 337 nm. The intensities of the EPR lines of $\text{HFC}=\text{N}^{\bullet}$ are about halved, and a new EPR spectrum appears, shown in Figure 2b. As in the spectrum of the $\text{HFC}=\text{N}^{\bullet}$ radical, the new EPR spectrum consists of 12 lines: nitrogen triplet with hyperfine constant $a_{\text{N}} = 0.19$ mT, and two doublet splitting with 23.69 and 1.90 mT. The fact that the same number and type of splittings is

Table 2. Vibrational Frequencies (cm^{-1}) and Isotropic Hyperfine Constants (mT) of the $\text{trans-FC}^{\bullet}=\text{NH}$ and $\text{trans-FC}^{\bullet}=\text{ND}$ Radicals

assignment	$\text{FC}^{\bullet}=\text{NH}$		$\text{FC}^{\bullet}=\text{ND}$	
	exptl	calcd ^b	exptl	calcd
$\nu_1(\text{a}')$, bend (in-plane)	595 (0.09) ^a	600 (0.06)		547 (0.16)
$\nu_2(\text{a}'')$, (out-of-plane)	734 (0.30)	733 (0.28)	575 (0.22)	555 (0.16)
$\nu_3(\text{a}')$, bend (in-plane)	905 (1.0)	924 (1.0)	759 (0.64)	770 (0.50)
$\nu_4(\text{a}')$ CF str.	1172 (0.26)	1194 (0.29)	1142 (0.81)	1154 (0.50)
$\nu_5(\text{a}')$ CN str.	1700 (0.69)	1767 (0.80)	1701 (1.0)	1747 (1.0)
$\nu_6(\text{a}')$, CH str.	3405 (0.26)	3561 (0.26)	2532 (0.28)	2613 (0.25)
a_{N}	0.19 ^c	-0.21		
a_{H}	1.90	2.18		
a_{F}	23.69	22.91		

^a Relative integrated absorption coefficients of the infrared bands are shown in parentheses. ^b Calculated using B3LYP/6-311++G(3df,2p). ^c Only the absolute value of the hyperfine constant is measured in experiment.

present in both radicals shows that the new radical is a structural isomer of $\text{HFC}=\text{N}^{\bullet}$.

Bernardi et al.³ used quantum mechanical calculations to predict that the two stable radicals having this empirical formula are the π -type radical $\text{HFC}=\text{N}^{\bullet}$ and the σ -type radical $\text{trans-FC}^{\bullet}=\text{NH}$. The former is more stable than the latter by only 11.3 kJ/mol at the G2 level of theory. To definitively assign the new radical observed in our experiments, we carried out calculations of hyperfine constants and vibrational frequencies for $\text{trans-FC}^{\bullet}=\text{NH}$. All of computations were performed using the Gaussian 98 suite of codes.¹³ The geometry of $\text{FC}^{\bullet}=\text{NH}$ was fully optimized by DFT calculation using the B3LYP gradient-exchange functional and 6-311++G(3df,2p) basis functions. The equilibrium geometry is very close to that obtained by Bernardi et al.,³ our calculated spectroscopic constants for $\text{FC}^{\bullet}=\text{NH}$ are given in Table 2. The calculated hf constants are in excellent agreement with the experiment. The experimentally measured doublet splitting of 23.69 mT corresponds to the hyperfine constant on the ^{19}F atom, whereas the 1.90 mT doublet splitting corresponds to the hydrogen atom. Similarly, the measured vibrational frequencies and relative band intensities are in good agreement with those calculated for both $\text{FC}^{\bullet}=\text{NH}$ and $\text{FC}^{\bullet}=\text{ND}$. On this basis we conclude that the new species formed by UV irradiation of the $\text{HFC}=\text{N}^{\bullet}$ radical in solid argon is identified as $\text{trans-FC}^{\bullet}=\text{NH}$ radical.

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(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E., Jr.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Revision A.3; Gaussian, Inc.: Pittsburgh, PA, 1998.