Infrared and EPR Spectra of the Difluoronitroxide Radical

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The geometry and electronic structure of the F_2NO radical has been the subject of intense study by quantum chemical methods.[1,2] More than 20 years ago, Smardzewski and Fox suggested that this radical might be formed as an intermediate in a series of sequential addition reactions of F atoms with NO.

$$F + NO \rightarrow FNO \qquad (1)$$

$$F + FNO \rightarrow F_2NO \qquad (2)$$

$$F + F_2NO \rightarrow F_3NO \qquad (3)$$

Although this scheme was used successfully to synthesize F_3NO,[3] attempts to detect the intermediate F_2NO in mixtures of F_2 and NO in the gas phase and in solids were unsuccessful.[4] This is presumably because reaction 2 is nearly thermoneutral,[3] and therefore F_2NO is present only in small concentrations, particularly at elevated temperatures. The radical was subsequently formed and observed by EPR spectroscopy in irradiated solid samples of F_3NO[5] and F_3NO in an SF_6 matrix.[6] To our knowledge, there has been no report of vibrational spectra or frequencies for this radical. As a result, spectroscopic data for this radical are scarce, and this makes it difficult to evaluate the accuracy of the calculations or even to select an appropriate computational method for calculating the properties of the radical. In this communication, we describe a method that permits the stabilization of F_2NO radicals formed in reaction 2. We present for the first time the infrared absorption spectra and EPR spectra of this radical isolated in a rare gas matrix.

The basis of our method is the ability of fluorine atoms to diffuse in crystalline argon at temperatures well below its melting point. The barrier to thermal diffusion of F atoms in solid argon is 4.5−5.5 kJ/mol, and at temperatures less than 18 K, they are essentially immobile in the matrix. However, at 20−26 K, F atoms are able to diffuse approximately 10 nm through argon in 10^2−10^4 s.[7,8] The ability to control the thermal diffusion of F atoms in this way provides a unique opportunity to carry out addition reactions and stabilization of the resulting intermediate species. Using this method combined with infrared and EPR spectroscopic detection, we have recently determined the spectral characteristics of reactive intermediates formed by addition of fluorine atoms to methane,[9] hydrogen,[10] and ethene.[11] In the present study, we have attempted to detect F_2NO in dilute mixtures of F_2 and NO in crystalline argon, in which F_2 is used as a photolytic precursor of fluorine atoms.

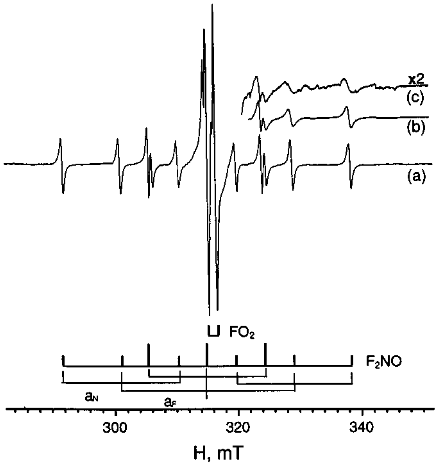

Figure 1. EPR spectra of a sample (Ar:NO:F_2 = 2000:1:1) after exhaustive photolysis at 16 K and subsequent annealing for 100 min at 24 K. Spectra recorded after annealing showed a reversible temperature dependence: 30 K (trace a), 20 K (trace b), and 15 K (trace c).

The experimental technique used in this study is similar to that described in our earlier papers.[9−12] Solid argon films doped with reactant molecules were formed by vapor deposition of Ar−NO and Ar−F_2 gas mixtures through separate inlets onto substrate at 14 K (sapphire for the EPR experiments; CsI for the infrared work). In all of the experiments, the mole fraction of reactants (F_2 and NO) was less than 10^{-3}. Photodissociation of F_2 was performed using 337 nm laser photolysis for the EPR experiments (performed in Russia) and 355 nm for the infrared experiments (performed in the United States). At temperatures below 20 K, this procedure forms stabilized F atoms in argon with a photochemical quantum yield close to unity.[8,9] EPR spectra were recorded using a standard 9 GHz spectrometer. Infrared spectra were recorded using an FTIR spectrometer at 0.5 cm^{-1} resolution over the region 500−2000 cm^{-1}.

EPR spectra of freshly prepared samples exhibited no detectable absorption lines. The ground $^2\Pi_{1/2}$ spin−orbit state of NO is diamagnetic,[12] and therefore its spectrum is not detected under our experimental conditions. Neither annealing of the samples to 24−30 K (without photolysis) nor extended photolysis at 16 K (without annealing) leads to the appearance of any new lines in the EPR spectrum. However, annealing of photolyzed samples to temperatures above 20 K forms FO_2 radical by reaction of diffusing F atoms with O_2 molecules that are always present in samples at concentrations of about 10^{-4}−10^{-5}. Annealing of the same samples at 24 K for 20−60 min leads to the appearance of a new series of nine lines, as shown in Figure 1. The observed triplet of triplets is characteristic of a radical that contains two equivalent F nuclei (each with nuclear spin $I = 1/2$) and one N nucleus ($I = 1$). The observed magnetic parameters are $a_F = 143$ G, $a_N = 93$ G, and $g = 2.007$, which are similar to those given for F_2NO radicals produced by radiolysis of F_3NO.[6,7] The

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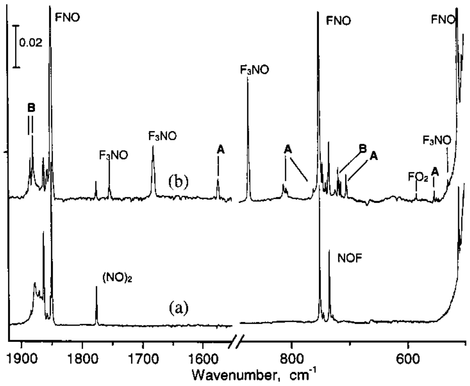

Figure 2. Infrared spectra of a sample (Ar:NO:F_2 = 2000:1:1) after deposition at 16 K (trace a) and after exhaustive photolysis at 16 K and subsequent annealing for 100 min at 24 K (trace b). Both spectra were recorded at 16 K. The series of lines labeled A and B are assigned to the F_2NO radical and F−FNO van der Waals complex, respectively (see the text).

splitting of the most intense lines is due to second-order contributions of the hyperfine interactions to the total Hamiltonian.[13]

Figure 1 shows that the EPR lines exhibit strong anisotropic broadening below 20 K, but become isotropic at 30 K as a result of rapid hindered rotation in the argon lattice. A detailed analysis of the anisotropic spectra will be presented in a separate paper. We simply note now that the anisotropy of the g factor is small ($\Delta g < 10^{-3}$) and the anisotropy of the hyperfine constant for the F atoms is very large ($\Delta a_F \approx 100$ G).

Having first identified experimental conditions under which large concentrations of F_2NO can be formed, we then began a series of similar argon matrix isolation experiments in which infrared spectroscopy would be used to identify the vibrational frequencies of the radical. The lower trace in Figure 2 shows the infrared spectrum of one sample following deposition of the matrix. It shows a cluster of four lines of NO molecules stabilized in different local sites of the matrix (1877, 1872, 1867, and 1862 cm^{-1}), two relatively weak lines of NO dimers[14] (1863 and 1776 cm^{-1}), lines for FNO (1849.6, 751, and 509.8 cm^{-1}), and lines of NOF[5] (1884 and 735 cm^{-1}). Photolysis at 16 K leads to a slight increase in the FNO lines and a decrease of the NO lines. Heating of these photolyzed samples at $T > 20$ K leads to a rapid decrease in the NO lines and growth of the FNO lines.

Extended annealing at 24 K reveals lines of three new reaction products (upper trace in Figure 2): F_3NO, the lines of which were assigned previously,[15] and lines of two other products which are labeled A and B in Figure 2. Product B exhibits two doublets at 1880 (1884) and 719 (714) cm^{-1}; it is assigned to the van der Waals complex F−FNO in part because of the close similarity of its vibrational frequencies to those of FNO. Product A exhibits five lines, the frequencies of which are presented in Table 1; it is assigned to the F_2NO radical. These two products can be distinguished due to different kinetic behavior during the annealing period (illustrated in Figure 3). The integrated absorption coefficients and concentrations of the products were calculated by measuring the relative band intensities at several stages of the reaction, and by using a mass balance equation.

Table 1. Vibrational Frequencies (cm^{-1}) and Isotropic Hyperfine Constants (G) of the F_2NO Radical, Calculated Using Various Levels of Theory and Basis Sets

assignment	experiment	B3LYP[a]/ EPRIII	QCISD/ cc-pVDZ	QCISD/ 6-311++G**
$\nu_1(a')$ NO str	1573	1625	1580	1557
$\nu_2(a')$ sym NF_2 str	761	730	747	761
$\nu_3(a')$ sym bend	705	569	598	613
$\nu_4(a')$ rock		386	422	438
$\nu_5(a'')$ asym NF_2 str	813	806	863	877
$\nu_6(a'')$ NF_2 sciss	553	418	450	472
a_F hf const	143	131	122	119
A_N hf const	93	94.5	72	75

[a] Computational method from Barone, V. *Chem. Phys. Lett.* **1996**, *262*, 201.

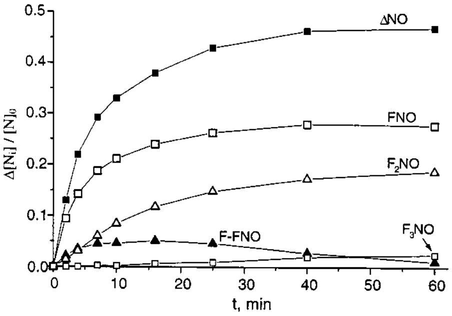

Figure 3. Kinetics of consumption of reactant molecules (ΔNO) and accumulation of reaction products during 24 K annealing of a sample (Ar:NO:F_2 = 2000:1:1) that was exhaustively photolyzed at 16 K. All concentrations are given relative to the initial concentration of NO molecules in the sample.

Kinetic support for the assignment of both species A and B to products that contain two F atoms comes from the fact that, in the initial stages of reaction, the sum of the concentrations of A and B is proportional to the square of the FNO concentration: $[A] + [B] = k[FNO]^2$. Also, the two species A and B were observed to undergo reversible interconversion in response to changes in the sample temperature in the range 16−26 K. This makes it certain that they both have the same stoichiometry.

$$[\mathrm{F{-}FNO}] \underset{k_-}{\overset{k_+}{\rightleftharpoons}} \mathrm{F_2NO} \tag{4}$$

The details of this reversible interconversion will be reported in a separate paper. We believe that the aforementioned analysis, combined with the EPR data, allows a reliable assignment of the product A to the stabilized radical F_2NO.

We carried out preliminary calculations of the vibrational frequencies and hyperfine constants of F_2NO radical using quantum chemical methods. All of the calculations were performed using the GAUSSIAN 94 suite of codes.[16] Table 1 shows the calculated hyperfine constants and vibrational frequencies of this species. All of the methods give essentially the same equilibrium structure. The structure at the QCISD/6-311++G** level of theory is $R(\mathrm{N{-}O}) = 0.1179$ nm, $R(\mathrm{N{-}F}) = 0.1423$ nm, $\angle\mathrm{FNO} = 116.7°$, and $\angle\mathrm{FNF} = 102.2°$. The data in Table 1 show that the hyperfine constants calculated using the B3LYP density functional method are in good agreement with our experimental values. For the vibrational frequencies, better agreement is obtained with the more sophisticated (and more expensive) QCISD methods.

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