

Infrared and EPR spectra of F₂NO radicals stabilised in solid argon

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The F₂NO radical has been formed by addition reactions of two F atoms with NO in solid argon, and using a combination of EPR and infrared absorption spectroscopy, we have identified this species and characterised its vibrational spectrum for the first time.

The free radical F₂NO is believed to have a pyramidal structure, and therefore cannot be easily classified as belonging to simple σ or π types. The geometry and electronic structure of this radical has been the subject of intense study by quantum chemical methods.^{1–3} However, experimental data concerning this radical are virtually nonexistent, and this makes it difficult to evaluate the accuracy of the calculations or even to choose an appropriate computational method for calculating the properties of the radical.

The F₂NO radical is an intermediate species in the reaction of fluorine atoms with nitric oxide:



Although this scheme was used successfully to synthesise F₃NO,⁴ attempts to detect the intermediate F₂NO in mixtures of F₂ and NO in the gas phase and in solids were completely unsuccessful.^{4,5} In this communication, we describe a method which permits the stabilization of F₂NO 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 this 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 1.1–1.3 kcal mol^{–1}. At temperatures less than 18 K, fluorine atoms are essentially immobile in the matrix, but at 20–26 K, the atoms are able to diffuse on a length scale of 100 Å on a time scale of 10²–10⁴ s.^{6,7} 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 intermediates formed in the reactions F + CH₄,^{7,8} F + H₂⁹ and F + C₂H₄.¹⁰ In the present study, we have attempted to detect F₂NO in ternary solid mixtures of F₂, NO and Ar, in which F₂ is used as a photolytic precursor of fluorine atoms.

The experimental technique used in this study is similar to that described in our earlier papers.^{7–10} Solid argon films with impurity molecules were formed by vapour deposition of the reagent gases through separate gas inlets onto the surface of a cold substrate at 14 K. In all of the experiments, the mole fraction of reactants (F₂ and NO) was less than 10^{–3}. Dissociation of F₂ was performed using 337 nm laser photolysis for the EPR experiments, and 355 nm for the infrared experiments. Fluorine photolysis at these wavelengths at temperatures less than 20 K leads to formation of stabilised F atoms in argon with a photochemical quantum yield close to unity.^{6,7} 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 exhibit no lines due to paramagnetic species. Although nitric oxide is paramagnetic, its lines are strongly broadened in the solid phase, and therefore its spectrum is not detected under our experimental conditions. Neither annealing of the samples to 24–30 K nor extended photolysis at 16 K leads to the appearance of any new lines in the EPR spectrum. Heating of photolysed samples to temperatures higher than 20 K leads to appearance of lines due to the FO₂ radical, which forms by reaction of diffusing F

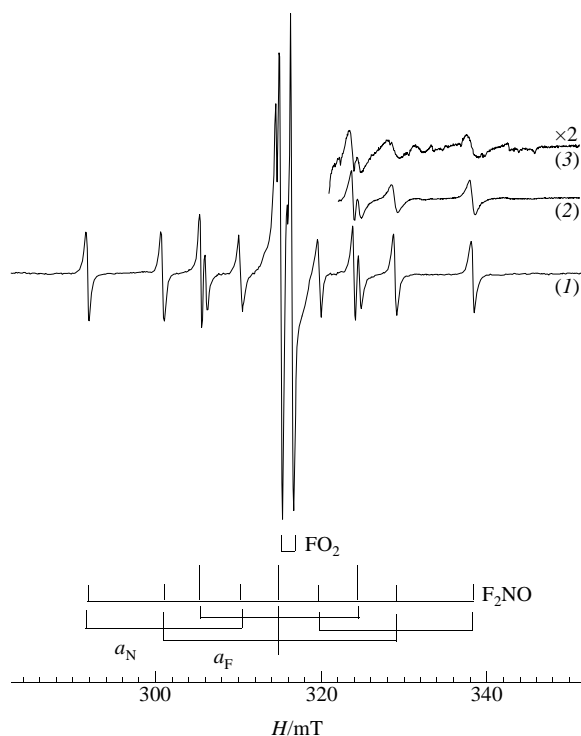


Figure 1 EPR spectra of a sample (Ar:NO:F₂ = 2000:1:1) after exhaustive photolysis at 16 K and subsequent annealing for 100 min at 24 K. Spectra recorded after annealing showed reversible temperature dependence: 30 K (1), 20 K (2) and 15 K (3).

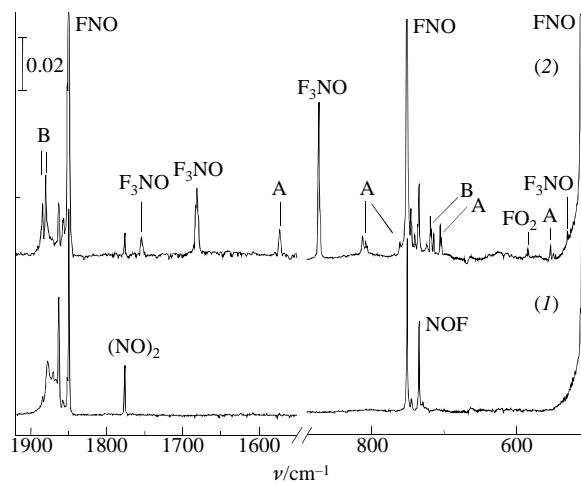


Figure 2 Infrared spectra of a sample (Ar:NO:F₂ = 2000:1:1) after deposition at 16 K (1) and after exhaustive photolysis at 16 K and subsequent annealing for 100 min at 24 K (2). Both spectra were recorded at 16 K. The series of lines labelled A and B are assigned to the F₂NO radical and F...FNO complex, respectively (see text).

Table 1 Optimised geometries and corresponding isotropic HF constants and frequencies of the F₂NO radical, using various level of theory and basis sets.

Method	Basis	$R_{\text{NF}}/\text{\AA}$	$R_{\text{NO}}/\text{\AA}$	$\angle\text{FNF}/^\circ$	$\angle\text{FNO}/^\circ$	$a_{\text{iso}}(\text{N})/\text{mT}$	$a_{\text{iso}}(\text{F})/\text{mT}$	ω/cm^{-1}
MP2	6-311+G(3df,2p)	1.421	1.152	101.5	119.5	7.52	9.01	1730, 900, 818, 616, 505, 436
B3LYP	aug-ccpVDZ	1.453	1.162	102.0	117.0	9.08	11.01	1640, 815, 745, 580, 430, 370
	EPR-III ¹⁷	1.457	1.158	101.9	116.9	9.45	13.10	1625, 806, 730, 569, 418, 368
Exp						9.28	14.35	1573, 803, 761, 705, 553

atoms with O₂ molecules that are always present in samples at concentrations of about 10⁻⁴–10⁻⁵. Annealing of samples at 24 K for 20–60 min leads to the appearance of a new series of 9 lines. Their lineshapes exhibit a strong reversible temperature dependent broadening, but the concentration of radicals remains constant during subsequent annealing cycles from 15 to 30 K. As shown in Figure 1, this series of 9 lines consists of a main triplet with relative intensities 1:2:1, each of which is further split into triplets with 1:1:1 relative intensities. This means that the radical contains two equivalent F nuclei (with nuclear spin $I = 1/2$) and one N nucleus (with $I = 1$). The observed magnetic parameters are $a_{\text{F}} = 14.3$ mT, $a_{\text{N}} = 9.3$ mT and $g = 2.007$. These values are close to the values previously given for F₂NO radicals produced by radiolysis of F₃NO molecules in solid SF₆ and in neat F₃NO.^{11,12} The additional splitting of the most intense lines (relative intensity 2) is due to second-order correction and equals $\Delta H = a_{\text{F}}^2/H_0 = 0.625$ mT. Figure 1 shows the temperature dependence of the spectrum of stabilized F₂NO radicals. At 30 K, the spectrum is isotropic, with a linewidth less than 0.2 mT. Lowering the temperature to 20 K causes a broadening of the lines. At temperatures below 20 K, the spectra are strongly anisotropic. 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 ($\Delta a_{\text{F}} \sim 10$ mT). Rapid hindered rotation of the radicals at temperatures greater than 20 K is the mechanism for averaging the anisotropy of the hyperfine constants, and results in an isotropic spectrum. The correlation time of rotation is estimated from the spectral linewidths¹³ to be $\tau_{\text{c}} \sim 10^{-9}$ s at 25 K.

$$\tau_{\text{c}} \sim 18H_0\Delta H/\omega_0\Delta a_{\text{F}}^2 \quad (4)$$

The next experiments were performed in order to identify the infrared spectrum of the F₂NO radical. We were unable to find any literature references that give the fundamental vibrational frequencies of this species. The spectra were assigned using the well-known vibrational frequencies of FNO and F₃NO, as well as from the kinetic behaviour of new IR lines which appear during the diffusion and reaction of F atoms at $T > 20$ K. Figure 2 shows the infrared spectra of samples following deposition. It shows a set of four lines due to NO molecules stabilised in different local sites of the matrix: 1877, 1872, 1867 and 1862 cm⁻¹, and two relatively weak lines due to NO dimers:¹⁴ 1863 and 1776 cm⁻¹. Also shown are the spectral lines of products that are formed upon condensation of the gases: FNO at 1849.6, 751 and 509.8 cm⁻¹, and its isomer ONF⁵ at 1884 and 735 cm⁻¹. Photolysis at 16 K leads to a small increase in the FNO lines and a decrease in the intensity of the NO lines. Heating of these photolysed 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 leads to growth of new lines of products (see Figure 2): molecules F₃NO, lines of which were assigned earlier in ref. 15, and lines of two other products which are labelled A and B in Figure 2. Product B exhibits two doublet lines at 1880 (1884) and 719 (714) cm⁻¹. Product A exhibits 5 lines, the frequencies of which are presented in Table 1. It was possible to distinguish between the lines of these two products due to the different kinetic behaviour shown during the annealing period. Figure 3 shows the kinetics of consumption of the reactant molecules and changes in the product concentrations. We determined the branching ratio between the products using a mass balance equation that

assumes that each product contains only one NO functional group. In order to determine the absorption coefficients of the four products, it was necessary to make at least four different measurements of the relative band intensities during the course of the reaction while the relative concentrations were changing. As shown in Figure 3, the principal products are FNO, which is formed in reaction (1), and the species labelled A. The product B grows in the initial stages but is practically destroyed by the end of the annealing period. It follows from the fact that F₃NO is formed by sequential addition of three F atoms to NO that we can assign the lines of A and B to intermediate products that contain 2 fluorine atoms. Kinetic support for the conclusion that A and B are secondary products of the sequential addition reactions come from the fact that in the initial stages of the reaction the sum of the concentrations of A and B is proportional to the square of the FNO concentration: $[A] + [B] = k[\text{FNO}]^2$. Product B exhibits only two lines, which lie close in frequency to the two lines of FNO; therefore, we assign this species to a weakly bound complex F...FNO. Product A, which exhibits 5 intense lines, is assigned to the F₂NO radical, which forms in a subsequent reaction in the complex F...FNO. This assignment is consistent with the kinetic behaviour of product B, because the final equilibrium concentrations of the products are determined by the ratio of the forward (k_+) and reverse (k_-) reaction rate constants in the complex, $K = k_+/k_- > 1$:



We believe that the aforementioned analysis, combined with the EPR data, allows a reliable assignment of the product A to the stabilized radical F₂NO. We note that although two radical intermediates (A and B) were observed in the infrared experiments, only one of these (F₂NO) was observable in the EPR spectra. The F...FNO complex, when stabilised in solids, is not observable by EPR due to the strongly broadened hyperfine structure of the F atom.

We carried out preliminary calculations of the vibrational frequencies and hyperfine constants of F₂NO radical using *ab initio* and density functional quantum chemical methods. All of the calculations were performed using the GAUSSIAN 94 suite of codes.¹⁶ Table 1 shows the calculated structural data, hyperfine constants and vibrational frequencies of this species.

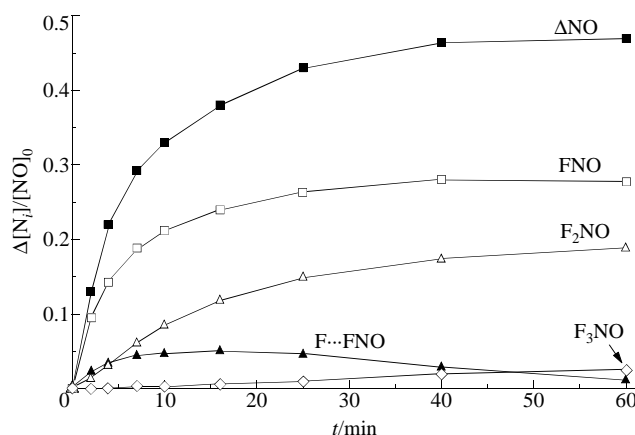


Figure 3 Kinetics of consumption of reactant molecules (ΔNO) and accumulation of reaction products during 24 K annealing of a sample (Ar:NO:F₂ = 2000:1:1) that was exhaustively photolysed at 16 K. All concentrations are given relative to the initial concentration of NO molecules in the sample.

The data in Table 1 shows that the B3LYP density functional method gives better agreement with the experimental data than the MP2 calculations. This supports the conclusion in refs. 1 and 17 that density functional methods are a convenient method for calculating the electronic properties of radicals of this type. We hope that the next calculations, which will use more sophisticated methods to account for electron correlation, will provide even better agreement with the experiments. The detailed analysis and assignment of IR spectra will be given in a separate publication.

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References

- 1 V. Barone, F. Lelj, N. Russo, Y. Ellinger and R. Surba, *Chem. Phys.*, 1983, **76**, 385.
- 2 M. Yu. Balakina, M. B. Zuev, I. D. Morozova and A. V. Il'jasov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 587 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 490).
- 3 I. L. Shamovsky, I. Yu. Yarovsky and Yu. M. Gershenzon, *Theochem.*, 1993, **103**, 43.
- 4 W. B. Fox, B. Sukornick, J. S. Mackenzie, R. L. Sturtevant, A. F. Maxwell and J. R. Holmes, *J. Am. Chem. Soc.*, 1970, **92**, 5240.
- 5 R. R. Smardzewski and W. B. Fox, *J. Chem. Phys.*, 1974, **60**, 2104.
- 6 J. Feld, H. Kunti and V. A. Apkarian, *J. Chem. Phys.*, 1990, **93**, 1009.
- 7 E. Ya. Misochko, V. A. Benderskii, A. U. Goldschleger and A. V. Akimov, *Mendeleev Commun.*, 1995, 198.
- 8 E. Ya. Misochko, V. A. Benderskii, A. U. Goldschleger, A. V. Akimov, A. V. Benderskii and C. A. Wight, *J. Chem. Phys.*, 1997, **106**, 3146.
- 9 A. U. Goldschleger, E. Ya. Misochko, A. V. Akimov, I. U. Goldschleger and V. A. Benderskii, *Chem. Phys. Lett.*, 1997, **267**, 288.
- 10 V. A. Benderskii, A. U. Goldschleger, A. V. Akimov, E. Ya. Misochko and C. A. Wight, *Mendeleev Commun.*, 1995, 203.
- 11 N. Vanderkooi, J. S. Mackenzie and W. B. Fox, *J. Fluorine Chem.*, 1976, **7**, 415.
- 12 K. Nishikida and F. Williams, *J. Am. Chem. Soc.*, 1975, **97**, 7168.
- 13 (a) J. H. Freed and J. K. Fraenkel, *J. Chem. Phys.*, 1963, **39**, 326; (b) J. K. Fraenkel, *J. Phys. Chem.*, 1967, **71**, 139.
- 14 W. A. Guillory and C. E. Hunter, *J. Chem. Phys.*, 1969, **50**, 3516.
- 15 R. R. Smardzewski and W. B. Fox, *J. Chem. Phys.*, 1974, **60**, 2193.
- 16 M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez and J. A. Pople, *Gaussian 94, Revision C.4*, Gaussian, Inc., Pittsburgh PA, 1995.
- 17 V. Barone, A. Grand, C. Minichino and R. Subra, *J. Phys. Chem.*, 1993, **97**, 6355.
- 18 V. Barone, *Chem. Phys. Lett.*, 1996, **262**, 201.

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