

In conclusion we suggest that there is no fundamental difference between the structure of dimethyl-substituted cyclopropylcarbinyl and that of the parent ion,¹⁴ but rather prefer to interpret the contrasting experimental observations on the two in terms of a difference in dynamical behavior. Whereas the unsubstituted ion may pass with little hindrance from one cyclopropylcarbinyl-like structure to another, the potential surrounding dimethylcyclopropylcarbinyl is much deeper and passage to the outside much the more unlikely. We suggest furthermore that the experiment of choice to resolve the controversy is one with a very much shorter time scale than the nmr. Electron spectroscopy may possibly fill that gap.¹⁵

(14) Preliminary investigations on the geometrical structures of bisected mono- and dimethyl-substituted cyclopropylcarbinyls indicate a gradual change from the parent. Thus, for example, the ring-exocyclic methylene bond increases from 1.384 Å in the parent⁸ to 1.416 Å in methylcyclopropylcarbinyl to 1.426 Å in the dimethyl-substituted ion; P. C. Hiberty, Thèse de Troisième Cycle, Université de Paris-Sud, Orsay, 1973.

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Infrared Spectroscopic Evidence for "Nitrogen Hypofluorite," an Isomer of Nitrosyl Fluoride, in Inert Gas Matrices

Sir:

The gas-phase reaction of nitric oxide and fluorine is known to proceed vigorously and quantitatively^{1,2} even under mild conditions³ to produce nitrosyl fluoride, FNO, which contains a fluorine atom bound to the more electropositive nitrogen. The FNO molecule is generally depicted as a loosely bound combination of a fluorine atom and the NO radical,⁴⁻⁶ owing to the unusually low N-F force constant (2.3 mdyne Å⁻¹)⁷ and an N-O force constant (15.9 mdyne Å⁻¹) which is virtually the same as that of free NO (15.5 mdyne Å⁻¹).⁸ Various bonding studies have supported this interpretation.⁹⁻¹³

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In a recent *ab initio* molecular orbital study of the FNO molecule,¹⁴ and an earlier description of its bonding,¹⁵ the possibility of its OF-bonded hypofluorite isomer, NOF, existing under certain conditions was raised. Although predicted to be less stable than the FNO form, it seemed to us that the kinetic stability of the isomeric NOF might be enhanced at extremely low temperatures (8–20°K) in an unreactive matrix.

Separate samples of nitric oxide and fluorine at high dilution in argon and nitrogen were simultaneously deposited onto a cesium iodide window at 8°K through separate spray-on lines (316 SS) oriented at 45° to the window and 90° to each other. Deposition rates through each spray-on line were monitored at *ca.* 0.5–1.0 mmol/hr by previously calibrated thermocouple readings downstream of the vernier metering valves. Prior to deposition, all sample manipulations were carried out in a passivated 316 SS vacuum manifold with Teflon seals.

When a sample of fluorine in nitrogen at an *M/R* = 250 (molar ratio of matrix to reactant gas) was simultaneously codeposited with an equivalent sample of NO in nitrogen (*M/R* = 250) onto an 8°K CsI window, a total of three new major absorption bands appeared in the infrared spectrum in addition to those normally attributed to NF-bonded FNO.¹⁶ These new bands, depicted in Figure 1a, consist of a weak feature in the vicinity of 1900 cm⁻¹ ($\nu(\text{N}=\text{O})$ region) and two stronger doublets centered at *ca.* 725 and 480 cm⁻¹, the $\delta(\text{FNO})$ and $\nu(\text{N}-\text{F})$ regions, respectively, of FNO.⁷ A similar experiment with argon as the matrix material produced three similar bands which were, however, unsplit, suggesting that the doublet structure of the lower frequency bands in the nitrogen matrix, with splittings of only 3–4 cm⁻¹, is the result of a matrix site effect. Absorption frequencies are listed in Table I. As is

Table I. Infrared Absorptions (cm⁻¹) of F(NO) Isomers

Assignment	Ar Matrix	N ₂ Matrix
FNO $\nu(\text{N}=\text{O})$	1852.1 vs	1869.7 vs
$\delta(\text{FNO})$	751.4 s	740.9 vs 737.5 m, sh
$\nu(\text{N}-\text{F})$	510.1 ms	497.0 vs 494.3 w, sh
NOF $\nu(\text{N}=\text{O})$	1886.6 w	1904.1 m
$\delta(\text{NOF})$	735.1 ms	724.6 ms 721.8 m
$\nu(\text{O}-\text{F})$	492.2 m	485.4 s, sh 480.9 s

normally the case, trace amounts of various noncondensable (at -196°) impurities were present in the fluorine samples (N₂, O₂, OF₂), but these did not interfere in the spectra.

Photolysis ($\lambda \geq 200$ nm) of the nitrogen matrix sample resulted in a noticeable decrease in intensity of these three new features, while those associated with FNO increased in intensity (Figure 1b). Even under conditions of lower energy radiation (λ 360 nm) and shorter periods of photolysis (*i.e.*, 15 min), the bands in

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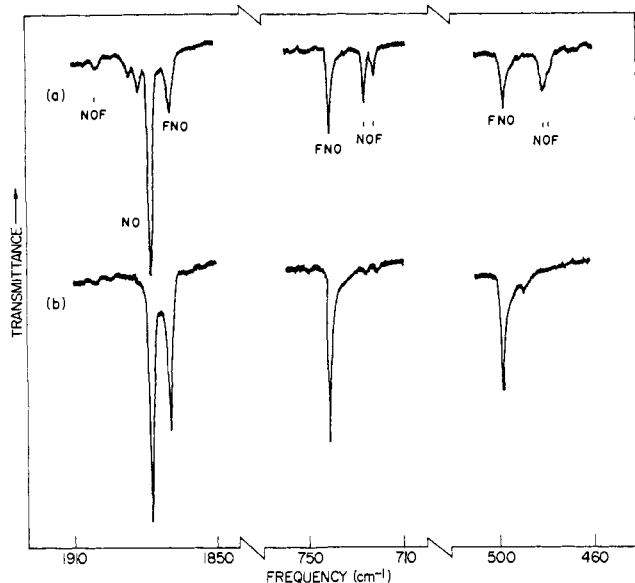


Figure 1. Infrared matrix spectrum of $N_2:F_2 = 250 + N_2:NO = 250$; $F_2:NO = 1.09$: spectrum a, initial deposit; spectrum b, sample after 60 min of photolysis ($\lambda \geq 200$ nm).

question decreased markedly. Similar observations were noted in argon matrices. From data obtained under a variety of conditions, it was concluded that the three new bands arose from species which were unstable with respect to photolysis at wavelengths of 200–400 nm.

Experiments involving increasing $F_2:NO$ ratios (0.86–4.90) demonstrated that the intensities of all three absorption bands increased in such a fashion that their relative intensities remained approximately constant. In a similar manner, all three features decreased proportionally upon photolysis, indicating that all three absorption bands are associated with a single absorber. At the highest $F_2:NO$ ratio (4.90), slight traces of F_3NO ^{17,18} had begun to appear in the infrared spectrum.

In other experiments, where the photolysis wavelength was limited to that necessary to cause F_2 dissociation (λ 360 nm), the $(Ar,N_2):F_2:NO$ samples were photolyzed both during and after deposition to produce as high a concentration of fluorine atoms as possible. Subsequently, with the photolysis lamp shut off, the matrix was then warmed to *ca.* 21°K to permit fluorine atom diffusion and recooled to 8°K. The noticeable effect of this temperature recycling was a dramatic increase in the intensities of the three new bands as well as those of FNO. The spectra are illustrated in Figure 2. Subsequent photolysis resulted in a decrease of the infrared intensities of these three new absorption features. A similar warm up of an identical matrix mixture which was not subjected to prior ultraviolet irradiation produced no significant changes in the infrared spectrum, indicating that no reaction between molecular F_2 and NO occurred as a result of the annealing alone.

It seems reasonable that, when molecular fluorine and nitric oxide are allowed to react under the low tem-

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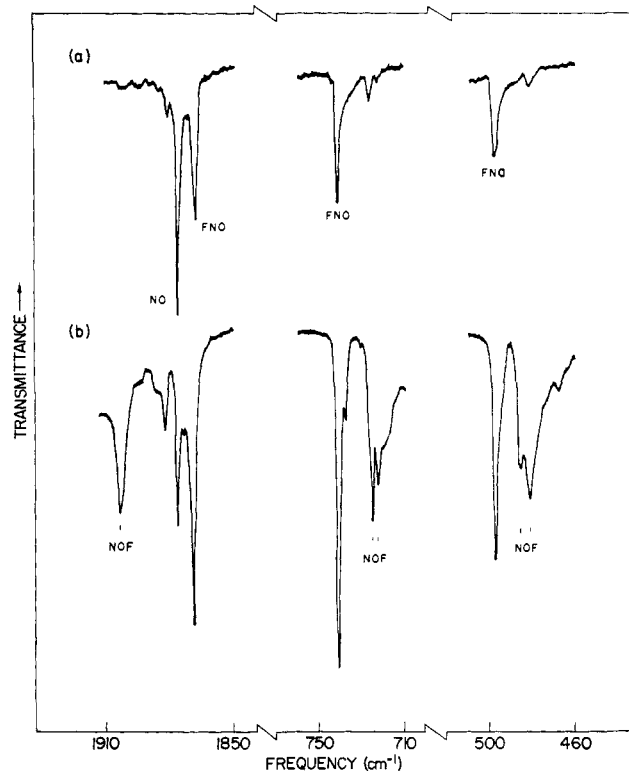
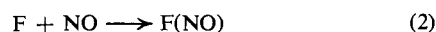
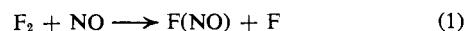


Figure 2. Infrared matrix spectrum of $N_2:F_2 = 250 + N_2:NO = 250$; $F_2:NO = 0.86$: spectrum a, results of photolysis (λ 360 nm) during deposition (8°K); spectrum b, sample after warm up to 21°K.

perature matrix conditions described above, the precondensation processes most likely to be important are eq 1 and 2, where the nitric oxide-fluorine complex



$F(NO)$ may exist in both the NF and OF-bonded isomeric forms. Support for the existence of the new NOF isomer is provided by the observation of the cited three infrared-active absorptions, consistent with C_s symmetry, which lie in close proximity to those of the more stable FNO isomer. *Ab initio* molecular orbital calculations suggest that the net bonding in the NOF molecule should be similar to that in FNO, although of lesser overall stability,¹⁴ so that the similarity in the spectra of the two isomers is not unexpected. Photolysis at wavelengths of 200–400 nm resulted in an increase of the NF-bonded isomer at the expense of the OF-bonded form. This can occur as a consequence of either intramolecular rearrangement of NOF or decomposition and combination with a second F atom, *i.e.*



Reaction 3 seems more likely due to the short photolysis times involved (15–60 min). Decomposition, followed by subsequent combination with a second F atom (eq 4 and 5), is expected to be a long-term, diffusion-

limited process at 8°K. Evidence to support this view was obtained from experiments involving photolysis during deposition under identical matrix conditions. In these cases, slower deposition rates and longer photolysis times (5–8 hr) were necessary to produce appreciable amounts of FNO. After deposition, a controlled warm up of the matrix to 21°K, followed by subsequent cooling to 8°K, produced a dramatic relative increase of the NOF isomer. Since both F atoms, and to some extent NO molecules, are known to be mobile species in a cryogenic matrix,^{19–21} it is suggested that their enhanced diffusion at 21°K in the absence of photolytic radiation results in greater relative yields of the NOF isomer.

The absence of the intense ir fundamentals of F₂NO, except slight traces at the higher F₂:NO ratios, suggests that postulated species such as F₂NO²² are not present in any appreciable concentration under the experimental conditions employed. This observation, in addition to the appearance of the three infrared absorptions at 1886.6, 735.1, and 492.2 cm⁻¹ (Ar matrix) in highly dilute matrices at low F₂:NO ratios, lends further credence to the postulated existence of nitrogen hypofluorite, NOF.

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A Novel and Versatile Fluorescence Probe for the Structure of Micelles. 11-[3-Hexyl-1-indolyl]undecyltrimethylammonium Bromide

Sir:

Fluorescent probes have been elegantly employed to map the microenvironments of biological macromolecules such as proteins and the polynucleotides¹ and to clock the dynamics of intramolecular interactions.² The general idea behind a fluorescent probe is that fluorescence emission is sensitive to changes in microenvironments and that a fluorescence probe in different microenvironments will display experimentally distinct fluorescence properties which will characterize uniquely each environment. Recently, fluorescence probes have been used to help understand the properties of aqueous solutions containing micelle forming

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detergents.³ These latter studies have mainly utilized aromatic hydrocarbons which are assumed to remain locked into the micelle during the time period of fluorescence. More recently it has been shown that the time correlated single photon counting technique allows a simultaneous measure of a fluorescence in both aqueous and micellar environments.⁴ We report here a new system, 11-[3-hexyl-1-indolyl]undecyltrimethylammonium bromide (6-I-11),⁵ which shows exceptional potential as a fluorescence probe to study the properties of micellar solutions.

The fluorescence properties of indoles have been found to be highly sensitive to environment changes.⁶ For example, in dilute aqueous solution, 1,3-dimethylindole (**1**) displays a broad featureless fluorescence (BWHM) \approx 66 nm, $\lambda_{\text{max}}^{\text{F,H}_2\text{O}}$ 371 nm,⁷ and an exponential fluorescence decay⁸ with a 20 nsec lifetime.

In *n*-hexane solution, however, **1** displays a somewhat structured, narrower fluorescence ($\lambda_{\text{max}}^{\text{F,n-hexane}}$ 318 nm) and an exponential fluorescence decay with a 4 nsec lifetime. The absorption spectrum of **1** is essentially identical in water or *n*-hexane but mirrors the *n*-hexane fluorescence emission spectrum. Thus, one might anticipate that 1,3-dialkylindole could make powerful fluorescence probes to differentiate hydrophilic vs. hydrophobic environments.⁹

Dissolution of **1** in aqueous solutions of hexadecyltrimethylammonium bromide (**2**) does not affect the fluorescence characteristics of **1** (relative to those in pure water) until the critical micelle concentration (cmc) of **2** is reached. At concentrations of **2** above the cmc, the fluorescence maximum of **1** starts to shift from 371 nm (pure water value) to 355 nm and the fluorescence lifetime of **1** drops from 20 nsec (pure water value) to 9 nsec. Since the latter decay is strictly exponential, and both the fluorescence maximum of **1** and the fluorescence decay of **1** are intermediate relative to the values obtained in pure water or pure *n*-hexane,

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