

Short Communication

Transient species in the photolysis of NF_2

R. J. COLLINS and D. HUSAIN

Department of Physical Chemistry, University of Cambridge, Cambridge CB2 1EP (Gt. Britain)

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An investigation of the photolysis of NF_2 has been carried out by kinetic absorption spectroscopy in the vacuum ultra-violet. A series of diffuse bands in the region of 126-140 nm are attributed to Rydberg transitions of NF_2 . A number of transient bands have also been observed and attributed to the species NF in more than one electronic state, and some collisional rate data for these bands are reported.

Introduction

Tetrafluorohydrazine, N_2F_4 , is in equilibrium with relatively high concentrations of the difluoroamino radical, NF_2 .^{1,2} Further, the rate of attainment of the equilibrium is rapid³ and hence photolysis by white light will involve fission of both molecules. The principal spectral absorption by NF_2 in the ultra-violet shows a maximum at 260 nm¹, of half-width 20 nm¹, and consists of a series of diffuse overlapping bands^{4,5}. Absorption by N_2F_4 occurs below $\lambda = 210$ nm¹. Photolysis at $\lambda = 253.7$ nm will only give rise to the photodissociation of $\text{NF}_2 \rightarrow \text{NF} + \text{F}$ and this has been presumed in mechanistic interpretations of the photolysis of the equilibrium mixture with added molecules⁶⁻⁸. Stimulated vibration-rotation emission from HF has been employed as evidence of F atom production from the photolysis of N_2F_4 -RH mixtures, both N_2F_4 and NF_2 yielding fluorine atoms on flash photolysis with white light^{9,10}, with the majority of the atoms arising from the fission of the difluoroamino radical⁹. Goodfriend *et al.*¹¹ have studied the flash photolysis of $\text{N}_2\text{F}_4/\text{NF}_2$ by kinetic absorption spectroscopy but were unable to detect any new spectra, specifically the ultra-violet and vacuum ultra-violet absorption spectrum of NF . This species is well established *via* the forbidden emission systems, $b^1\Sigma^+ - X^3\Sigma^-$ and $a^1\Delta - X^3\Sigma^-$ ¹²⁻¹⁴ and also from the infra-red absorption spectrum at 1115 cm⁻¹ following the photolysis of FN_3 ¹⁵ and, more important in the present context, the photolysis of NF_2 in an argon matrix at 4 K¹⁶. In this communication we describe a kinetic study of the flash photolysis of $\text{N}_2\text{F}_4/\text{NF}_2$ by absorption spectroscopy in the vacuum ultra-violet. We report a new series of bands in the wavelength region 126-140 nm

in the absorption spectrum of NF_2 which are attributed to Rydberg transitions of this radical. A number of new transient absorption bands which we tentatively attribute to Rydberg transitions of different electronic states of NF , are observed in the region 120–178 nm. Some kinetic data for this species are reported.

Experimental

The basis of the experimental arrangement employed was similar to that described hitherto for the study of $\text{O}_2(\text{a}^1\Delta_g)^{17,18}$. In this case, the reactant gas was flash irradiated ($E = 1056 \text{ J}$, $\tau_{1/2} = \sim 10 \mu\text{s}$) in a coaxial lamp and vessel assembly with a common wall of Spectrosil quartz, permitting photolysis down to a lower wavelength limit of $\sim 160 \text{ nm}$. The assembly could be heated, allowing investigations to be carried out in the temperature range of room temperature to $\sim 450 \text{ K}$. At 450 K , for example, 50 N m^{-2} (1 Torr = 133 N m^{-2}) of N_2F_4 , a typical pressure of this gas that was employed, is dissociated into NF_2 to the extent of 98.85%. Excess helium buffer gas was employed to ensure no significant temperature rise above the chosen temperature on irradiation. Time-resolved spectra following photolysis were taken using a 1 m concave grating vacuum spectrograph, with a Garton–Wheaton pulsed spectroscopic source, triggered by means of the normal delay circuitry^{17,18}. Spectra were photometered using a Joyce–Loebl double beam recording microdensitometer (Mark III).

Vacuum ultra-violet spectrum of NF_2

Several diffuse absorption bands were observed in the wavelength region 126–140 nm on warming $\sim 50 \text{ N m}^{-2}$ of N_2F_4 to 450 K , which we attribute to the NF_2 radical. All of the transitions which are presented in Table I can be seen on the ‘before’ shot of Fig. 1. We further report extinction coefficient data for

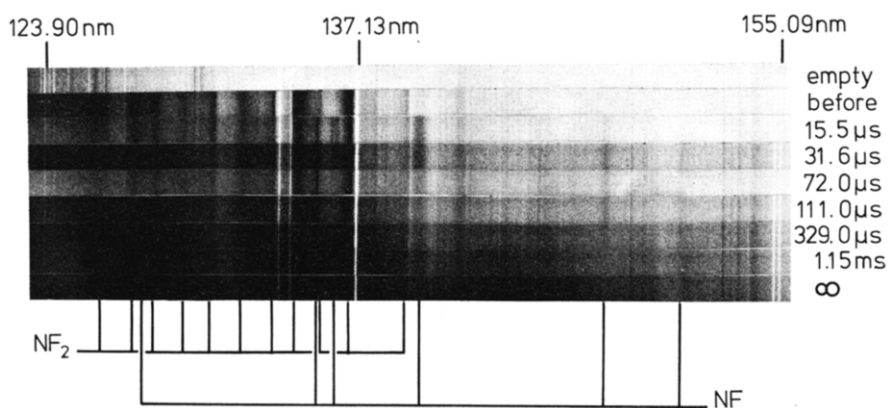


Fig. 1. Transient species in the photolysis of an equilibrium mixture of N_2F_4 and NF_2 . $p_{\text{N}_2\text{F}_4} = 0.58 \text{ N m}^{-2}$; $p_{\text{NF}_2} = 98.9 \text{ N m}^{-2}$; $T = 450 \text{ K}$; $p_{\text{total with He}} = 10.0 \text{ kN m}^{-2}$; $E = 1056 \text{ J}$.

TABLE 1

VACUUM ULTRA-VIOLET SPECTRUM OF NF_2

λ (nm)	ν (cm^{-1})	ϵ ($\text{atm}^{-1} \text{cm}^{-1}$) (0°C)
139.30	71788	17.5 ± 2
136.84	73078	115 ± 10
135.50	73746	~ 7
134.79	74189	75 ± 10
133.57	74867	32 ± 5
132.32	75574	35 ± 5
130.97	76353	~ 15
129.76	77065	~ 20
128.50	77821	~ 45
127.63	78351	~ 30
~ 126.1	~ 79300	~ 10

these bands (Table 1) from the calculated degree of dissociation of $\text{N}_2\text{F}_4^{1,2}$. Goodfriend *et al.*¹¹ did not observe this band system nor the transient system (see later), principally on account of their use of high pressures of N_2F_4 which completely masked the Schumann region. Taking the ionization potential of NF_2 as 11.62 eV from the photoelectron spectroscopic measurements on this radical by Cornford *et al.*¹⁹, the bands may be generally assigned as the first members of Rydberg series ($n = 3$), leading to the formation of NF_2^+ ($^1\text{A}_1$)¹⁹. Of the nine Rydberg orbitals with $n = 3$, seven of these have fully allowed transitions from the $^2\text{B}_1$ ground state and two would be vibronically allowed. Quantum defects (δ) may be calculated and are sensible in relation to the magnitude of δ expected for these orbitals from data given by Lindholm²⁰. We refrain from making tentative electronic assignments for specific bands in Table 1 as some of these may clearly arise from vibrational excitation and there is insufficient data on the frequencies for both NF_2 and NF_2^+ to assign vibrational levels. The only known vibrational frequency of the ion in the $^1\text{A}_1$ state is that of $\nu_1 = 1250 \pm 10 \text{ cm}^{-1}$ ¹⁹ which may account for the separation in the two longest wavelength bands in Table 1. A continuous absorption in the region 158–170 nm, peaking at 164 nm ($\epsilon = 57 \pm 5 \text{ atm}^{-1} \text{cm}^{-1}$ at 0°C) is also observed in the spectrum of NF_2 . This is too low in energy to be a Rydberg transition and is therefore thought to be due to an intravalence transition.

Vacuum ultra-violet spectrum of NF

Figure 1 shows a series of weak, diffuse transient bands in the vacuum ultra-violet following the irradiation of an equilibrium mixture of N_2F_4 and NF_2 ($p_{\text{N}_2\text{F}_4} = 0.58 \text{ N m}^{-2}$, $p_{\text{NF}_2} = 98.9 \text{ N m}^{-2}$)^{1,2}. The wavelengths of these transient bands are listed in Table 2. The species arises from the photolysis of NF_2 as no transient spectrum was observed from the photolysis at room temperature where the concentration of NF_2 is considerably lower, and we therefore attribute the

TABLE 2

TRANSIENT SPECTRUM ATTRIBUTED TO THE NF RADICAL

λ (nm)	ν (cm^{-1})
120.26 (m)	83153
128.19 (v-w)	78009
135.46 (s)	73823
136.22 (m)	73411
139.72 (s)	71572
(145.2 ± 0.6) (v-w)	68870 ± 300
147.62 (m)	67741
150.95 (v-w)	66247
162.0 ± 1.5 (w)	61730 ± 570
178.22 (w)	56110

bands to be absorption by the diatomic molecule NF. A consideration of the bond energy of NF [$D_0^0(\text{NF}) = 3.15 - 3.18 \text{ eV}^2$] and the energies of the atomic states N(2^2P_J) and F (2^2P_J)²¹ indicates that transitions below 184 nm for this molecule are Rydberg in type and the diffuseness presumably arises from pre-dissociation with repulsive states correlating with N(2^2P_J) + F(2^2P_J). A Rydberg analysis is difficult, partly on account of the uncertainty in the ionization potential of NF. Herron and Dibeler²² have reviewed the main body of electron impact data yielding this quantity. Values lie in the range 11.8–13.1 eV and may represent upper limits on account of internal excitation in the ions, a value of 12.4 eV being favoured by these authors²². Further, photometry, which could only be carried out on a limited number of the bands, which are generally weak, indicates that more than one state is involved (Fig. 2). The bands at 136.22 and 139.72 nm were relatively short lived ($\tau \sim 40 \mu\text{s}$) whereas those at 135.46, 147.62 and possibly that at 162.0 nm, were found to be longer lived ($\tau \sim 300 \mu\text{s}$). Thermochemistry² indicates that absorption of light by NF_2 in the 260 nm band system (250–270 nm, 4.69–4.96 eV) is sufficiently high in energy to yield NF ($X^3\Sigma^-$ and $a^1\Delta$) but *not* NF

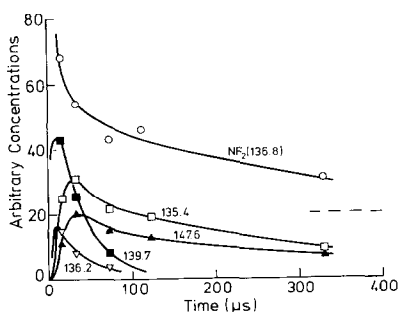


Fig. 2. The decay of transient species in the flash photolysis of an equilibrium mixture of N_2F_4 and NF_2 . $p_{\text{N}_2\text{F}_4} = 0.58 \text{ N m}^{-2}$; $p_{\text{NF}_2} = 98.9 \text{ N m}^{-2}$; $T = 450 \text{ K}$; $p_{\text{total with He}} = 10.0 \text{ kN m}^{-2}$; $E = 1056 \text{ J}$. Unlabelled bands (λ , nm) attributed to NF. — —, ∞ measurement for NF_2 .

($b^1\Sigma^+$)¹⁰ ($X^3\Sigma^-$, $a^1\Delta$ and $b^1\Sigma^+$ = 0, 1.42 and 2.37 eV, respectively¹²). $NF(b^1\Sigma^+)$ could be produced by the photolysis of NF_2 in the 164 nm band but a consideration of the extinction coefficients of both bands and the available lamp output in this region indicates that less than 10% of the photolysis occurs in the lower wavelength band system. It is therefore tempting to assign the 'long-lived' bands as due to $NF(X^3\Sigma^-)$ and the 'shorter-lived' bands to $NF(a^1\Delta)$ which would require an ionization potential that is 1–2 eV lower than the quoted value of 12.4 eV²². On the other hand, assignment of the short-lived bands to the $^1\Sigma$ state and the long-lived bands to the $^1\Delta$ state is in accord with an ionization potential close to 12.4 eV. Clyne and White¹⁴ have reported that the collisional quenching of $NF(b^1\Sigma^+)$ by N_2 is characterized by a rate constant of $k = 2 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Unfortunately, the upper bound for the decay rate of the short-lived bands in nitrogen in these experiments (Table 3) is too high to permit its use in eliminating $NF(b^1\Sigma^+)$ on kinetic grounds.

TABLE 3

RATE DATA FOR THE REMOVAL OF TRANSIENT BANDS ATTRIBUTED TO NF (k , $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, 450K)

	N_2	O_2	NF_2
Long-lived bands (135.4 and 147.6 nm)	$<10^{-16}$	$<10^{-13}$	$\sim 2 \times 10^{-13}$
Short-lived bands (136.2 and 139.7 nm)	$<10^{-15}$	$<10^{-12}$	$\sim 5 \times 10^{-12}$

Kinetic data

We further report some approximate rate data for the collisional removal of the transient bands (Table 3). The rate constants given for NF_2 result from attributing the observed decays to this radical which is clearly seen to be removed by chemical reaction following photolysis (Fig. 2). The removal of the short-lived bands by N_2F_4 would require rate constants of the order of the collision number. The large upper limit for k_{O_2} reflects the low pressures of this molecule that had to be employed to penetrate the Schumann–Runge continuum.

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1 F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, 83 (1961) 3043.

2 *JANAF Thermochemical Tables*, U. S. Department of Commerce, Washington, D.C., 1965.

3 A. P. Modica and D. F. Hornig, *J. Chem. Phys.*, 49 (1968) 629.

4 P. L. Goodfriend and H. P. Woods, *J. Mol. Spectros.*, 13 (1964) 63.

5 L. A. Kuznetsova, Yu. Ya. Kuzyakov and V. M. Tatevskii, *Optics Spectros.*, 16 (1964) 295.

- 6 C. L. Bumgardner and M. Lustig, *Inorg. Chem.*, 2 (1963) 662.
- 7 C. L. Bumgardner, *Tetrahedron Lett.*, 48 (1964) 3683.
- 8 C. L. Bumgardner, E. L. Lawton and A. Carmichael, *Chem. Commun.*, (1968) 1079.
- 9 T. D. Patrick and G. C. Pimentel, *J. Chem. Phys.*, 54 (1971) 720.
- 10 L. E. Brus and M. C. Lin, *J. Phys. Chem.*, 75 (1971) 2546.
- 11 U. V. Henderson, P. L. Goodfriend, H. A. Rhodes and H. P. Woods, *Sci. Tech. Aerospace Report*, 2 (17) (1964) 2222; NASA Accession No. N64-24916, *Rep. No. AD 418278*; P. L. Goodfriend and H. P. Woods, *Rep. No. TP 283 (AD 642190)*, Department of the Navy, Contract No. 1883(00) (1966).
- 12 A. E. Douglas and W. E. Jones, *Can. J. Phys.*, 44 (1966) 2251.
- 13 W. E. Jones, *Can. J. Phys.*, 45 (1967) 21.
- 14 M. A. A. Clyne and I. F. White, *Chem. Phys. Lett.*, 6 (1970) 465.
- 15 M. E. Jacox and D. E. Milligan, *Appl. Optics*, 3 (1964) 873; *J. Chem. Phys.*, 40 (1964) 2461.
- 16 J. J. Comeford and D. E. Mann, *Spectrochim. Acta*, 21 (1965) 197.
- 17 R. J. Collins, D. Husain and R. J. Donovan, *J. C. S. Faraday Trans. II*, 69 (1973) 145.
- 18 R. J. Collins and D. Husain, *J. Photochem.*, 1 (1972-73) 481.
- 19 A. B. Cornford, D. C. Frost, F. G. Herring and C. A. McDowell, *J. Chem. Phys.*, 54 (1971) 1872; *J. C. S. Faraday Discuss.*, 54 (1973) 56.
- 20 E. Lindholm, *Arkiv. Fys.*, 40 (1969) 97.
- 21 C. E. Moore (ed.), Nat. Bur. Stand. Circular 467, *Atomic Energy Levels*, Vols. I-III, U.S. Government Printing Office, Washington, D.C., 1958.
- 22 J. T. Herron and V. H. Dibeler, *J. Res. Nat. Bur. Stand.*, 65A (1961) 405.