Spectrally resolved fluorescence in the HNF (DNF) $\tilde{A}^2 A' - \tilde{X}^2 A''$ band system

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Selectively detected fluorescence excitation spectra have been employed to find and assign Q-type subband heads in the HNF $\tilde{A}^2 A' - \tilde{X}^2 A'' 2_0^1 3_0^1$ and $2_0^2 3_0^1$ bands, which are obscured because of the near equality of the ω'_2 and ω'_3 vibrational frequencies by the stronger 2_0^2 and 2_0^3 bands, respectively. A number of previously unobserved heads in the corresponding DNF band system are also reported. Dispersed fluorescence spectra were also taken for excitation of a variety of HNF and DNF $\tilde{A}^2 A'$ vibrational levels, and the energies of vibrational levels in their ground $\tilde{X}^2 A''$ electronic states were derived. These energies were fit to determine vibrational constants. The following values (in cm⁻¹) were derived for the harmonic constants $\omega_1^{0''}$, $\omega_2^{0''}$, and $\omega_3^{0''}$: 3167(6), 1455(2), 1036(7) for HNF and 2339(4), 1084(3), 1013(6) for DNF.

1. Introduction

Recently we have shown that HNF (DNF) can be conveniently generated by the $F+HN_3$ (DN₃) reaction [1]. With this production technique, it has been possible to probe in some detail the spectroscopy and excited state dynamics of this interesting Renner-Teller molecule [1-3]. In contrast to the considerable information now available on the various vibrational levels in the excited $\tilde{A}^2 A'$ electronic state, somewhat less is known about the vibrational levels in the ground $\tilde{X}^2 A''$ state. In both the absorption [4] and laser fluorescence excitation [1,3] spectra, no hot bands have been observed. Chemiluminescence from electronically excited HNF formed in a hydrazine/fluorine flame has been spectrally resolved [5]. As in the electronic excitation spectrum, a progression in the bending mode, this time in the ground electronic state, was observed. Two of the fundamental vibrational frequencies and the electronic absorption spectra of HNF and DNF deposited in a cryogenic argon matrix have also been determined [6]. Peric et al. [7] have carried out a configuration-interaction electronic structure calculation of the $\tilde{X}^2 A''$ and $\tilde{A}^2 A'$ electronic states of HNF and have derived vibrational and rotational parameters for these states of both isotopomers.

In an effort to gain more spectroscopic information on the ground electronic state of HNF (DNF), we have taken dispersed fluorescence spectra for excitation of various HNF and DNF excited \tilde{A}^2A' vibrational levels. This has allowed estimation of the energies of a number of vibrational levels in the \tilde{X}^2A'' electronic state of both isotopomers. In particular, it has been possible to observe $v_1'' > 0$ levels. In this Letter, we present the results of these experiments.

Laser fluorescence excitation scans with spectrally resolved detection have also allowed the observation of weak excitation bands in the presence of stronger bands. This technique of selectively detected fluorescence excitation has previously been employed in a number of spectroscopic studies in order to pick out a specific rotational branch in particularly congested electronic band systems [8-11]. With this method, we have been able to find and assign the HNF $\tilde{A}^{2}A' - \tilde{X}^{2}A'' 2_{0}^{1}3_{0}^{1}$ and $2_{0}^{2}3_{0}^{1}$ bands which are obscured by the stronger 2_0^2 and 2_0^3 bands. Previously, Woodman [4] showed that the nearly degenerate $\tilde{A}^{2}A'(0, v'_{2}, 0)$ and $(0, v'_{2} - 1, 1)$ vibrational levels for $v'_2 = 1$ undergo a K' dependent mixing. This results in a splitting of subband heads in the 2_0^1 band. Our observation of higher members of the latter component of this series of vibrational levels $(v_2'=2 \text{ and } 3)$ has allowed the direct observation of $v_3' > 0$ levels in the excited $\tilde{A}^2 A'$ electronic state. Thus far, electronically excited levels in both isotopomers with $v_1' > 0$ have eluded observation.

2. Experimental

The apparatus employed for this study was a 2.5 cm diameter stainless steel flow reactor. HNF and DNF were prepared through the F+HN₃, DN₃ reactions [1] by mixing a flow of F atoms, prepared through a microwave discharge in a CF₄/Ar mixture, with a flow of HN₃ or DN₃ at a total pressure of ≈ 40 mTorr. The system was evacuated with a 4 ℓ s⁻¹ mechanical pump. The HN₃ and DN₃ reagents were prepared as described previously [12].

Molecular fluorescence was excited with radiation from an excimer laser pumped dye laser system (Lambda Physik EMG101MSC and FL3002E). In the experiments presented below, the dye laser was operated without an intracavity etalon and had a bandwidth of ≈ 0.2 cm⁻¹. The diameter of the laser beam in the reaction chamber was 0.7 cm. The laser pulse energy was kept low enough to avoid saturation effects and was typically 0.2-1 mJ, depending on the strength of the band being excited. The laserexcited fluorescence was imaged with a f/1 lens, dispersed with a 0.25 m Fastie-Ebert spectrometer (Jarrell-Ash 82-410, operated at a spectral bandpass of 1-2 nm) and detected with a photomultiplier (Hamamatsu R928). The output of the latter was directed into a gated integrator (Stanford Research Systems) and recorded with a laboratory computer and/or chart recorder. Wavelength calibration was verified with Hg atomic lines. The wavelength sensitivity of the spectrometer-detector combination was determined with an NBS calibrated standard lamp.

3. Results and discussion

3.1. Observation of new HNF and DNF bands

The utility of resolved fluorescence detection is illustrated with the HNF $\tilde{A} 2A' - \tilde{X}^2 A'' 2_0^1$ band, which has been investigated previously by Woodman [4] in absorption. Fig. 1 presents dispersed fluorescence

spectra with the laser tuned to various Q-type subband heads, corresponding to the excitation of various K' stacks in the excited electronic state. The dispersed fluorescence spectrum upon excitation of K' = 0 is relatively simple since radiative decay occurs to K'' = 1 stacks only; the selection rules for K are $\Delta K = \pm 1$ for this perpendicular electronic transition. (While $\Delta K=0, \pm 2$ axis-switching [13] bands are also observed in the absorption and fluorescence excitation spectra [1,4], these transitions are weak and are obscured in the dispersed fluorescence spectrum by the stronger $\Delta K = \pm 1$ transitions.) For higher K' levels, two peaks appear in the spectrum for radiative decay to each $\tilde{X}^2 A''$ vibrational level, corresponding to $\Delta K = +1$ and -1 transitions. It can also be seen that these features shift in wavenumber versus K', reflecting the dependence of the lower state energy on K''.

Because of the K' dependent mixing of the $\tilde{A}^{2}A'$ (0, 1, 0) and (0, 0, 1) levels, Woodman [4] observed a doubling of the K' subbands for K'=3-5 in the 2¹₀ band, resulting from crossing of these levels near K'=4. In fig. 1, we present dispersed fluorescence spectra for excitation of the pair of K'=4 stacks in this band. The spectrum labeled K'=4(a) cor-



Fig. 1. Dispersed fluorescence spectra following the excitation of various K' stacks in the HNF \tilde{A}^2A' mixed (0, 1, 0) and (0, 0, 1) vibrational levels. The K'=0, 3(b), 4(a), and 4(b) stacks were prepared by laser excitation of the ${}^{P}Q_1$, ${}^{T}Q_2(b)$, ${}^{t}Q_3(a)$, ${}^{t}Q_3(b)$ heads, respectively, in the 2_0^1 band. The symbols (a) and (b) denote the higher- and lower- energy stacks, respectively, of a given K' (see Woodman [4]). The quantum numbers for the low-lying \tilde{X}^2A'' vibrational levels are given.

responds to excitation of the stack with mainly $\tilde{A}^2 A'$ (0, 1, 0) vibrational character, while that labeled K'=4(b) corresponds to the state with predominantly (0, 0, 1) character. It can be seen that the former has a larger radiative decay rate to the $\tilde{X}^2 A''$ (0, 1, 0) vibrational level than to $\tilde{X}^2 A''$ (0, 0, 1), while the opposite is true for the latter. In contrast to K'=4(b), the K'=3(b) level decays preferentially to the $\tilde{X}^2 A''(0, 1, 0)$ level; K' = 3(b) lies below the crossing and has predominantly $\tilde{A}^{2}A'$ (0, 1, 0) vibrational character. These observations are consistent with our expectation that the Franck-Condon factors would be stronger for diagonal transitions than for $\Delta v_2 = \pm 1$, $\Delta v_3 = \mp 1$ transitions. It should be noted that, in contrast to the $\tilde{A}^{2}A'$ state, the vibrational frequencies ω_2 and ω_3 are quite separated in the ground $\tilde{X}^2 A''$ state [5.6].

In view of the fact that ω'_2 and ω'_3 are nearly equal for HNF(\tilde{A}^2A') [4], we expect that all the $\tilde{A}^2A' \tilde{X}^2A'' 2_0^{\nu}$ and $2_0^{\nu-1}3_0^1$ bands will occur at nearly the same wavelength. However, the former will be much stronger than the latter. Wavelength-resolved fluorescence detection offers a method of avoiding this interference and allowing the unobscured observation of the $2_0^{\nu-1}3_0^1$ bands. Fig. 2 compares fluorescence excitation spectra in the region of the 2_0^2 and $2_0^13_0^1$ bands without and with wavelength-resolved



Fig. 2. Laser fluorescence excitation spectra of the HNF $\tilde{A}^2 A' - \tilde{X}^2 A'' 2_0^2$ and $2_0^1 3_0^1$ bands. (a) The 2_0^2 band is observed when the total fluorescence emission is monitored. (b) The $2_0^1 3_0^1$ band is observed when the spectrometer is tuned to detect fluorescence in the $2_0^1 3_0^1 X' = 0 - X'' = 1$ transition only.

detection. It is seen that selectively detected fluorescence excitation has facilitated the observation and assignment of the latter weak band. It should be pointed out, however, that all of the K' subbands of the $2_0^1 3_0^1$ band cannot be observed in this spectrum since the spectrometer was set to detect emission from K'=0. The emission from other K' stacks to a particular lower state vibrational level splits into two components whose wavelengths shift and whose separation increases with increasing K', as described above. The observation of weaker subbands of the $2_0^{\nu-1} 3_0^1$ bands required larger spectrometer slit widths, and the 2_0^{ν} band also appeared in these scans.

With the use of selective dispersed fluorescence detection, it has been possible to observe and assign the Q-type subband heads in the HNF $\tilde{A}^{2}A' - \tilde{X}^{2}A''$ $2_0^1 3_0^1$ and $2_0^2 3_0^1$ bands. The transition wavenumbers for these heads are presented in table 1. Unlike the 2_0^1 band [4], no doubling was observed in any of the $v'_2 + v'_3 \ge 2$ bands. With the aid of the rotational constants determined by Woodman [4] for the zeropoint vibrational level of the $\tilde{X}^2 A''$ state, excited state term values can be calculated from these transition wavenumbers. Table 2 presents the derived term values, relative to the K'=0 stack of the \tilde{A}^2A' zero-point level, of the (0, 1, 1) and (0, 2, 1) vibrational levels. For comparison, the term values for the (0, 2, 0) and (0, 3, 0) levels, determined by Woodman [4], are also included in table 2.

We investigated whether the deperturbation analysis employed by Woodman [4] to understand the mixing of the $\tilde{A}^2 A'(0, 1, 0)$ and (0, 0, 1) levels could be easily extended to the higher pairs of levels, $(0, v'_2, 0)$ and $(0, v'_2 - 1, 1)$, for $v'_2 = 2$ and 3. We wrote a nonlinear least-squares program to fit the energies of the K' stacks. The diagonal matrix elements of the Hamiltonian were expressed as the sum of the vibrational energy, rotational energy about the *a* inertial axis, and centrifugal distortion. As in Woodman's analysis [4], the off-diagonal matrix element was expressed as

$$\langle v'_{2}, v'_{3}, K' | H | v'_{2} \pm 1, v'_{3} \mp 1, K' \rangle = -\alpha'_{23} K'^{2} (\hat{v}'_{2} \hat{v}'_{3})^{1/2},$$
 (1)

where \hat{v}'_i is the greater of v'_i and $v'_i \pm 1$. For the higher sets of levels, the unobserved $(0, v'_2 - 2, 2)$ level was included in the basis. Table 1

Newly observed subband heads in the HNF and DNF $\tilde{A}\,^2A'-\tilde{X}\,^2A''$ systems

Molecule	Band	Wavenumber ^{a)} (cm ⁻¹)	Assignment
HNF	2 ¹ ₀ 3 ¹ ₀	22292.8(9)	PQ2
		22314.2(9)	PQI
		22329.6(9)	۹Qo
		22358.1(9)	"Q₀
		22429.8(9)	${}^{\mathbf{T}}\mathbf{Q}_{1}$
		22443.4(12)	*Q0
		22520.8(12)	۲Q2
		22656.0(12)	۳Q ₃
	$2_0^2 3_0^1$	23310.0(9)	°Q2
		23360.7(9)	۶Qı
		23377.1(9)	٩Q٥
		23410.4(9)	^r Q ₀
DNF	$2_0^1 3_0^1$	22076.2(9)	₽Q2
		22086.9(9)	PQı
		22111.3(9)	^r Q ₀
		22149.6(9)	$^{r}Q_{1}$
		22205.1(12)	rQ2
		22272.4(15)	۳Q₃
		22345.6(20)	^z Q4
		22431.3(20)	^r Q ₅
	2 <mark>3</mark>	22585.9(9)	PQ3
		22727.1(12)	^r Q ₂
		22749.9(12)	[®] Q ₁
		22812.7(15)	rQ₃
	$2_0^2 3_0^1$	23017.5(12)	^r Q ₂
		23090.3(15)	¹ Q₃
		23175.5(20)	¹ Q ₄
		23318.2(20)	'Qs
	26	23420.3(9)	ªQ₂
		23450.0(9)	^r Q ₁
		23524.5(12)	¹ Q ₂
		23624.0(15)	rQ3
	2330 2330	23748.0(9)	'Qı
		23818.2(12)	rQ2
	25	24089.0(9)	°Q ₃
	2030	24446.4(9)	^p Q ₁

^{a)} Uncertainties given parenthetically in units of the least significant digit.

A fit of the $v'_2 + v'_3 = 1$ term values reported by Woodman [4] yielded a value of 0.48 ± 0.06 cm⁻¹ for $|\alpha'_{23}|$, in reasonable agreement with the value of 0.53 quoted by Woodman. (The sign of the off-diagonal matrix element cannot be determined in this

Table 2

HNF (\tilde{A}^2A') term values, relative to the $K' \approx 0$ stack of the zeropoint level, for several vibrational levels *)

K	Vibrational l	evel		
	(0, 2, 0) ^{b)}	(0, 1, 1) ^{c)}	(0, 3, 0) ^{b)}	(0, 2, 1) °)
0	2127	2190	3160	3237
1	2162	2217	3200	3270
2	2261	2303	3316	
3	2420	2446	3498	
4	2639	2664	3734	
5	2907		4021	
6	3215		4357	
7	3567			

*) Estimated uncertainties $\approx 2 \text{ cm}^{-1}$.

^{b)} Ref. [4]. ^{c)} This work.

analysis.) The unperturbed (0, 1, 0) and (0, 0, 1)energy levels are predicted to cross at $K' \approx 5$. Our fits to the energies of the $v'_2 + v'_3 \ge 2$ levels were not very satisfactory and tended toward smaller values of α'_{23} . It should be noted, however, that only low K'stacks (below the crossing point) in the $(0, v'_2 - 1,$ 1) levels were observed and included in the fits.

In a previous paper [1], we presented the transition wavenumbers for subband heads in various DNF $\tilde{A}^2 A' - \tilde{X}^2 A''$ bands. In subsequent experiments, we have observed a number of other DNF transitions. We take the opportunity here to present these new results, even though the observation of these new bands did not require the use of wavelength-resolved fluorescence detection. The newly derived DNF transition wavenumbers are reported in table 1. In some cases, these are additional subband heads of previously observed bands, while other transitions represent observations of new bands.

3.2. Measurement of vibrational energies in the HNF and DNF \tilde{X} state

We have also employed dispersed fluorescence spectra in order to derive vibrational energies in the HNF and DNF ground $\tilde{X}^2 A''$ electronic state. These spectra were obtained by tuning the dye laser to subband heads in a number of $\tilde{A}^2 A' - \tilde{X}^2 A''$ bands of both isotopomers and scanning the spectrometer. In most cases, the ${}^{P}Q_1$ head was employed in order to prepare the K'=0 stack of the excited state. In this way, there is only one feature, corresponding to K'' = 1, in the fluorescence spectrum for each $\tilde{X}^2 A''$ vibrational level. The typical width of the dispersed fluorescence peaks was $35-50 \text{ cm}^{-1}$. However, it was possible to fit the shapes of the peaks with a Gaussian profile to an uncertainty in the center position of less than 10 cm^{-1} . The vibrational energies were calculated from an average of the measured (typically 8-20 separate spectra) wavenumber displacements of the emission features from the excitation wavenumber, with correction for the K''=0 to 1 spacing. While the A'' rotational constant is not independent of the $\tilde{X}^2 A''$ vibrational quantum numbers, the variation of this parameter is small compared with the uncertainties in the derived vibrational energies. (The spectral resolution of these dispersed fluorescence spectra was typically a factor of 2 better than for the spectra displayed in fig. 1.)

The vibrational energies for the HNF and DNF $\tilde{X}^2 A''$ states derived from these dispersed fluorescence spectra are presented in table 3, along with our assignments of the vibrational quantum numbers. In order to observe all the reported levels, it was necessary to excite a variety of $\tilde{A}^2 A'$ excited levels. For the first time, it has been possible to observe levels with $v_1 > 0$ in either the ground or excited electronic state. The $\tilde{X}^2 A''$ (1, 0, 0) and (1, 1, 0) levels could, however, be detected only when $v'_2 \ge 2$ levels were prepared in the excited state.

Table 3

Energies (in cm⁻¹) of HNF and DNF ($\tilde{X}^{2}A''$) vibrational levels relative to the respective zero-point level ^{a)}

Level	HNF	DNF	
(0, 0, 1)	1015	1005	
(0, 1, 0)	1439	1074	
(0, 0, 2)	2004	2003	
(0, 1, 1)	2437	2072	
(0, 2, 0)	2847	2130	
(0, 0, 3)	2961		
(1, 0, 0)	3167	2339	
(0, 1, 2)	3396		
(0, 2, 1)	3818	3109	
(0, 3, 0)	4229	3172	
(1, 1, 0)		3397	
(0, 3, 1)	5158	4122	
(0, 4, 0)	5573	4200	

^{a)} Estimated uncertainties $\approx 5-10 \text{ cm}^{-1}$ (see text).

$$G(v_1'', v_2'', v_3'') = \sum_i \omega_i^{0''} v_i'' + \sum_{i,j \ge i} x_{ij}^{0''} v_i'' v_j''.$$
(2)

Table 4 presents the derived parameters. Because of the limited range of $v_1^{"} > 0$ levels observed, the parameters $x_{1i}^{0"}$, except for $x_{12}^{0"}$ for DNF, could not be determined.

Our determined vibrational parameters are compared in table 4 with those reported in previous experimental studies. The vibrational constant $\omega_2^{0''}$ is found here to be slightly higher than that determined from an HNF* chemiluminescence spectrum [5]. Our gas-phase and the argon matrix [6] values for the energies of the v_2'' and v_3'' fundamental levels are in quite reasonable agreement. In this study, we present the first measurement of the NH and ND stretching vibrational frequencies for HNF and DNF, respectively. These frequencies are somewhat larger than the vibrational frequencies (expressed as $\Delta G_{1/2}$ in order to be consistent with the values given in table 4) for the related diatomic molecules NH $(3126 \text{ cm}^{-1} [14,15])$ and ND $(2317 \text{ cm}^{-1} [16])$, respectively, but are significantly greater than the NH and ND stretches in HNO (2684 cm^{-1} [17]) and DNO (2025 cm^{-1} [17]). It can be seen from table 4 that the agreement of all the HNF and DNF experimental vibrational frequencies with those calculated by Peric et al. [7] using their ab initio potential is reasonably good for both isotopomers.

In addition to determining the energies of vibrationally excited $\tilde{X}^2 A''$ levels from the dispersed fluorescence spectra, we also measured the relative intensities of the emission features for excitation of the K'=0 stack of several $\tilde{A}^2 A'$ vibrational levels. The relative intensities for the $K'=0 \rightarrow K''=1$ transitions, corrected for the spectrometer-detector wavelength sensitivity, are displayed in fig. 3 for excitation of (0, 0, 0). Radiative transitions to $\tilde{X}^2 A'' (0, v''_2, 0)$ and $(0, v''_2, 1)$ levels were observable in the emission spectrum. It can be seen that for the $(0, v''_2, 0)$ progression the most probable v''_2 is 1. The $(0, v''_2, 1)$ progression mirrors that intensity distribution in the former progression, with an order of magnitude weaker intensity. Table 4

F	Parameter	HNF		DNF		
		exp. ^{b)}	theor. °)	exp. ^b)	theor. °)	
a	ມ ⁰ ‴	3167(6) ^{d)}	3200	2339(4) ^{d)}	2330	
C		1455(2)	1430	1084(3)	1047	
	-	1441.1(10) °) 1432 ^{f)}		1069 ^{fy}		
Q	w9"	1036(7)	1000	1013(6)	985	
		1000 8)		1000 *>		
x	¢22	-15.7(9) -10.9(5) °		-8.9(9)		
x	c0"	-16.4(31)		-5.9(41)		
, x	- 33 c ⁰ /			-17.5(110)		
x	¢23	-25.3(27)		-16.4(22)		

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^{a)} Estimated uncertainties, where known, given parenthetically in units of the least significant digit.

^{b)} This work, unless otherwise stated.

^{c)} Ref. [7].

^{d)} The quoted parameter is $\Delta G_1''(\frac{1}{2}) = \omega_1^0 + x_{11}^0$.

•) Ref. [5].

⁽¹⁾ Ar matrix, ref. [6]. The quoted parameter is $\Delta G_2''(\frac{1}{2}) = \omega_2^0 + x_{22}^0$.

^{**s**)} Ar matrix, ref. [6]. The quoted parameter is $\Delta G_3'(\frac{1}{2}) = \omega_3^0 + x_{33}^0$.



Fig. 3. Relative emission intensities for radiative transitions from the HNF (\tilde{A}^2A'') (0, 0, 0) level to \tilde{X}^2A'' (0, v, 0) and (0, v, 1) levels. Horizontally striped bars, experimental intensities to the (0, v, 0) levels (this work); unfilled bars, calculated intensities to the (0, v, 0) levels (ref. [7]); diagonally striped bars, experimental intensities to the (0, v, 1) levels (this work).

Also shown in fig. 3 are calculated relative intensities for radiative decay of the $\tilde{A}^{2}A'(0, 0, 0)$ into the $\tilde{X}^{2}A''(0, v''_{2}, 0)$ states. These intensities were derived from Franck-Condon factors calculated by Peric et al. [7] from their $\tilde{X}^{2}A''$ and $\tilde{A}^{2}A'$ ab initio bending potentials. For this calculated distribution,

the most probable v_2'' is 2. Moreover, it can be seen that the calculated distribution predicts somewhat more intensity in the higher members of the $(0, v''_2, v''_2)$ 0) progression than is seen experimentally. A similar discrepancy in the relative intensities for absorption out of the ground $\tilde{\mathbf{X}}^{2}\mathbf{A}''$ (0, 0, 0) level into the progression of $\tilde{A}^2 A'$ (0, v'_2 , 0) levels was previously noted [7]. The calculated intensities predict that the strongest bands would involve excitation to $v_2' = 2$ and 3 bands, while Woodman [4] observed that the $v'_2 = 1$ and 2 bands were the strongest in the absorption spectrum. The reasons for these discrepancies are not clear since the ab initio calculations of Peric et al. [7] predict reasonably well the experimental ground and excited state geometries [3] and the vibrational constants, with the exception of ω'_2 and ω'3.

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