

High-resolution Study of the 000–000 Band of the $\tilde{A}^1A''-\tilde{X}^1A'$ System of HNO in Emission from the $H + NO$ Reaction†

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A high-resolution spectrum of the 000–000 band of the $\tilde{A}^1A''-\tilde{X}^1A'$ system of HNO has been recorded in emission from the reaction of the H atoms with NO. No sharp breaking-off in the J structure has been found in the highest sub-band observed. The emission in this sub-band ($K'_a = 13-K''_a = 12$) originates in levels above the dissociation limit and arises from a two-body radiative association process. The emission in the other sub-bands originates in levels below the dissociation limit and arises from a three-body recombination process.

The mechanism for predissociation is discussed and an interpretation has been given for a hitherto unexplained observation.

Emission bands of HNO and DNO in the visible and near-IR have been observed, by several workers, in the reaction of atomic hydrogen and nitric oxide.^{1–4} Clement and Ramsay² found a sharp breaking-off in the K rotational structures for two bands of HNO and three bands of DNO. They established upper limits for the dissociation energies of these molecules [$D_0(\text{HNO}) \leq 17000 \text{ cm}^{-1}$, $D_0(\text{DNO}) \leq 17190 \text{ cm}^{-1}$]. Clyne and Thrush^{3,4} found a negative temperature coefficient for the $H + NO$ intensity and concluded that the upper limit found above was indeed equal to the dissociation energy. They favoured a recombination mechanism involving the \tilde{a}^3A'' state.

Line broadening was observed in the 101–000 absorption band of the $\tilde{A}-\tilde{X}$ system of HNO by Bancroft *et al.*⁵ and they confirmed the upper limit found in the emission studies.² Further studies of this band were carried out by Freedman,⁶ who suggested that the predominant mechanism for predissociation in the \tilde{A}^1A'' state is *via* internal conversion to the \tilde{X}^1A' state.

Laser-excited fluorescence studies of HNO and DNO have revealed breaking-off in the rotational structures of branches in several bands.^{7–9} From J and K dependence of the breaking-off, Dixon and co-workers^{7,8} determined $D_0(\text{HNO}) = 16450 \pm 10 \text{ cm}^{-1}$ and $D_0(\text{DNO}) = 17030 \pm 10 \text{ cm}^{-1}$ while Petersen⁹ found $D_0(\text{DNO}) = 17010 \pm 10 \text{ cm}^{-1}$.

In the present work we have obtained a high-resolution spectrum of the 000–000 band of HNO in emission from the $H + NO$ reaction and discuss the rotational structure observed.

Experimental Details

The apparatus consisted of a reaction tube 11 cm in diameter and 75 cm in length. Hydrogen atoms were produced in a side-arm by passing hydrogen at *ca.* 1.2 Torr (1 Torr = 133 Pa) through a Broida cavity connected to a 100 W 2450 MHz generator. Nitric oxide at *ca.* 0.5 Torr was introduced *via* a second side-arm on the opposite side of the reaction tube and the products were removed at the other end by a booster pump.

A red chemiluminescence was produced and could be readily seen in a darkened room. A mirror was situated at the rear of the 75 cm tube and served to increase the intensity of the emission which was focussed on the entrance iris of a

Bomem DA3.002 Fourier-transform spectrometer. Spectra were recorded in the region 13 275–14 350 cm^{-1} using a germanium detector (Applied Detector Corporation) cooled to -196°C and an unapodized resolution of 0.06 cm^{-1} . Throughout the run the emission was monitored through a small hole in the rear mirror using a small grating spectrometer with a germanium detector. The pressures and flow rates were adjusted to give maximum emission.

A reproduction of the $\Delta K_a = +1$ sub-bands of the 000–000 band with $K'_a = 8-12$ is given in Fig. 1. This spectrum is the result of 600 co-additions and the recording time was 205 min. Calibration was achieved by comparing with the measurements of the absorption spectrum by Dalby¹⁰ in regions of overlap. Vacuum wavenumbers for the lines of the $\Delta K_a = +1$ sub-bands with high values of K_a are given in Table 1. The precision of the measurements is estimated to be 0.01 cm^{-1} and the absolute accuracy is probably $\pm 0.03 \text{ cm}^{-1}$.

Analysis

The $\Delta K_a = +1$ sub-bands with high values of K_a consist of 'R' and 'Q' branches which are readily assigned on the basis of earlier work. The sub-bands show regular rotational structures except for the $K'_a = 12-K''_a = 11$ and $K'_a = 9-K''_a = 8$ sub-bands which have local perturbations. The R(11) and Q(14) lines in the $K'_a = 9-K''_a = 8$ sub-band are clearly perturbed (Fig. 1) as also are the R(11) and R(16) lines in the $K'_a = 12-K''_a = 11$ sub-band.

The rotational structure of the 000–000 band has been fitted up to $K'_a = 8$ with a standard deviation of 0.028 cm^{-1} if perturbed levels are excluded from the fit.¹¹ However, no satisfactory fit was obtained when the higher sub-bands were included even using terms up to $H_K K_a^6$ in the Hamiltonian. Consequently, it was decided to fit each of the higher sub-bands individually. The frequencies of the 'R' and 'Q' lines were fitted by the method of least squares to the standard formulae and the value for the sub-band origins and the effective B values ($= \bar{B} - D_{JK} K^2$) are given in Table 2. The centrifugal distortion constants D'_J and D''_J were fixed at the values obtained in earlier work.^{11,12}

Discussion

One of the objectives of the present work was to determine if any sharp breaking-off is seen in the J structure in the 000–000 band. The results show that this is not the case. The intensities of the lines in the J structures show distributions similar to those expected for a molecule with a rotational temperature not far from room temperature. However, the

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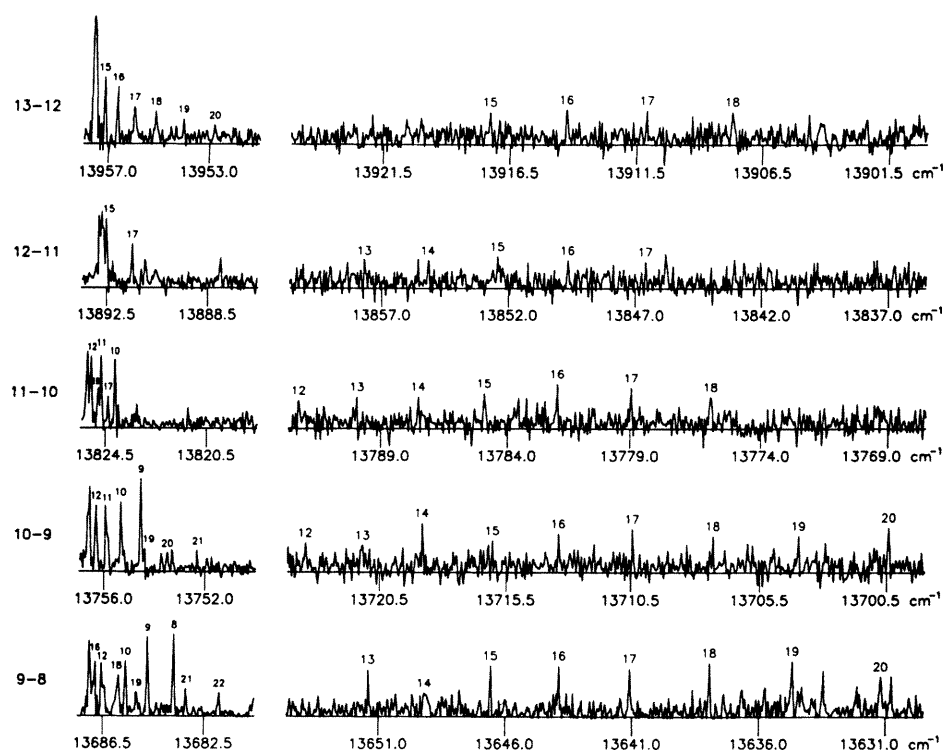


Fig. 1 Emission spectrum of the 000-000 band of HNO. The ^rR and ^rQ assignments are given for the various sub-bands.

relative intensities in the *K* structures are far from thermal, on account of predissociation, as has been discussed earlier.²

The highest rotational level observed is $J' = 21$, $K'_a = 13$. Using the data in Table 2 together with the ground-state con-

stants of Johns *et al.*¹² we find that the energy of this level is $16\,902\text{ cm}^{-1}$, *i.e.* 452 cm^{-1} above the dissociation limit. Such a value suggests that there is a small centrifugal barrier to predissociation (or preassociation) of the molecule. Emission

Table 1 Vacuum wavenumbers and rotational assignments for lines of the $\Delta K_a = +1$ sub-bands with high K_a in the 000-000 band of HNO (in cm^{-1})

<i>J</i>	$K' = 13 - K'' = 12$		$K' = 12 - K'' = 11$		$K' = 11 - K'' = 10$		$K' = 10 - K'' = 9$		$K' = 9 - K'' = 8$	
	R(<i>J</i>)	Q(<i>J</i>)	R(<i>J</i>)	Q(<i>J</i>)	R(<i>J</i>)	Q(<i>J</i>)	R(<i>J</i>)	Q(<i>J</i>)	R(<i>J</i>)	Q(<i>J</i>)
8									13 683.697	
9									684.725	
10					13 824.112		13 754.553		685.595	
11					824.664		755.338			
12	13 957.515 ^b		13 892.625		825.051	13 792.310	756.336 ^b	13 725.617		
13	957.515 ^b		892.706 ^b		825.217 ^b	789.963	756.589 ^b	721.250		13 651.401
14	957.515 ^b		892.706 ^b	13 855.098	825.217 ^b	787.451	756.589 ^b	718.802	687.022 ^b	
15	957.150	13 917.160	892.508		825.217 ^b	784.818	756.589 ^b	716.187	687.022 ^b	646.506
16	956.652	914.158		849.580	824.777	781.951	756.336 ^b	713.409	686.816	643.790
17	955.980	910.961	891.483	846.476	824.375	778.969	755.931 ^b	710.438	686.430	640.916
18	955.110	907.500				775.857		707.280	685.878	637.809
19	954.019					772.432	754.409	703.973	685.150	634.595
20						768.842	753.507	700.478	684.303	631.142
21						765.082	752.324	696.845	683.198	627.672
22								693.010	681.871	623.796
23									680.487	
24									678.942	

^a Perturbed lines. ^b Blended lines.

Table 2 Sub-band origins and effective *B* values for the high K_a sub-bands of HNO (in cm^{-1})

sub-band ($K'_a - K''_a$)	origin	$(\bar{B} - D'_{JK} K_a'^2)$		$(\bar{B}'' - D''_{JK} K_a''^2)$	
		from fit	calc. ^a	from fit	calc. ^b
9-8	13 667.00 (5) ^c	1.2678 (10)	1.2670	1.3530 (10)	1.3529
10-9	13 737.10 (3)	1.2648 (7)	1.2630	1.3518 (7)	1.3513
11-10	13 806.07 (5)	1.2629 (11)	1.2587	1.3514 (11)	1.3495
12-11	13 874.05 (4)	1.2537 (4)	1.2539	1.3437 (4)	1.3475
13-12	13 939.58 (6)	1.2527 (8)	1.2487	1.3461 (9)	1.3453

^a From ref. 11; ^b from ref. 12; ^c error limits are 3σ .

from predissociated levels above the dissociation limit must proceed *via* a two-body radiative association process with a low quantum yield. All of the emission in the $K'_a = 13 - K''_a = 12$ sub-band falls into this category. The intensity distribution of the J structure depends on the Boltzmann distribution of the reactant species and the decrease in intensity at high J values is a consequence of this Boltzmann distribution.

The emission in all the other sub-bands comes from levels which are below the dissociation limit and proceeds *via* a three-body process as discussed by Clyne and Thrush.⁴ Since the intensities of these sub-bands are comparable to the intensity of the $K'_a = 13 - K''_a = 12$ sub-band, the rates for the two-body and three-body reactions must also be comparable.

The intensity distributions in the J structures of sub-bands with $K'_a \leq 12$ are nearly thermal as a result of collisions and the small values of the rotational constants B and C . The distribution of intensities in the K structures depends on the distribution formed in the initial reaction and collisional relaxation which will be slower on account of the larger value of the rotational constant A .

The mechanism of predissociation has been discussed by several authors.^{3,4,6,7} Clyne and Thrush⁴ favoured a recombination *via* the \tilde{a}^3A'' state. Freedman⁶ and Dixon *et al.*⁷ preferred a predissociation *via* the ground state. The latter authors suggested that the excited and ground states were coupled by electronic-rotational interaction (Renner-Teller effect) and strengthened their argument by showing that, in vibrational levels above the dissociation limit, laser-excited fluorescence involved predominantly the $J' = 0$ level. However, the possibility of a predissociation *via* the \tilde{a}^3A'' state should not be excluded. The \tilde{a}^3A'' state has three levels with $J = 0$, *viz.* the F_3 components of the three $N = 1$ levels 1_{01} , 1_{11} and 1_{10} . The first two have +parity and the last has -parity, while the $J' = 0$ level of the \tilde{A}^1A' state has -parity.¹⁷ Hence, predissociation of the $J' = 0$ level of the \tilde{A}^1A' state is possible *via* the $J = 0$ component of the 1_{10} level of the triplet state. Whether the coupling matrix element is large enough to compete with the radiative process is not yet known.

The \tilde{A}^1A' and \tilde{X}^1A' states correlate with a $^1\Delta$ state in the linear configuration and the levels are coupled by the electronic-rotational interaction term $J_a L_a$. Such an interaction is proportional to K_a and is zero for $K_a = 0$. Evidence for an increase in line-width with K_a has been found in the 101–000 band by Bancroft *et al.*⁵ but no broadening was found for $K'_a = 0$. The observations of Dixon *et al.*⁷ that laser-excited fluorescence from vibrational levels above the dissociation limit involve predominantly emission from the $J' = 0$ level can only be explained by the Renner-Teller mechanism if rotational asymmetry is taken into account. Alternatively, Coriolis interactions involving predissociated levels with $K_a \neq 0$ may be involved.

The spectrum of HCO^{13-15} provides an excellent example of a Renner-Teller interaction where the line-widths increase dramatically with K'_a and are not broadened for $K'_a = 0$ except for the higher N values. The latter variation has been explained by a second-order Coriolis mechanism¹⁵ which predicts that the line-widths should vary as N^4 .

The experiments of Dixon *et al.*⁷ involved magnetic studies of perturbations in several bands. Most of the perturbations were found not to be magnetically sensitive indicating that triplet levels were not involved. However, no magnetic experiments were reported for levels where the dominant emission is from the $J' = 0$ level. Such experiments should indicate clearly if the triplet state is involved.

Petersen⁹ made an interesting observation which hitherto has remained unexplained. He found that in the 110–000 band fluorescence is observed from the $14_{3,12}$ level but not from the $14_{3,11}$ level, although the levels are closely degenerate. Dixon¹⁶ has pointed out that the dissociation threshold from ground-state levels with a given J and parity will depend on the centrifugal potential at the transition state, since J and parity must be conserved in a predissociation. For a fixed geometry the lowest level for $J'' = 14$ and parity +1 is $14_{0,14}$, but for parity -1 the lowest level is $14_{1,13}$ which lies appreciably higher in energy. If an excited state K -doublet lies between these two thresholds then only the component with the same parity as $J_{0,J}$ will be above the appropriate threshold. Thus in the present case, the $14_{3,11}$ level of the \tilde{A}^1A' state with +parity will predissociate but not the $14_{3,12}$ level (-parity). Dixon regards this observation as confirmation of this mechanism for internal conversion.

We thank Professors R. N. Dixon and B. A. Thrush for interesting correspondence and Dr. J. P. Towle and M. Barnett for helpful assistance.

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Paper 5/02151K; Received 4th April, 1995