NEW BANDS OF THE TRANSITIONS ($c^1\Pi \rightarrow a^1\Delta$) and ($c^1\Pi \rightarrow b^1\Sigma^+$) OF NH AND ND: THE PREDISSOCIATION OF NH ($c^1\Pi$)

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Introduction

Some disagreement still exists among the data on the dissociation energy of the imino radical. Experimental values D_o between 3.17 and 3.8 eV have been obtained for NH. A recent evaluation of observations of the transition ($d^1\Sigma^+ \rightarrow c^1\Pi$) of NH and ND yielded the upper limit $D_o(NH) > 3.45$ eV, assuming pure predissociation by rotation of the $c^1\Pi$ state in the absence of potential barriers in the non-rotating molecule[1]. In the present study spectra of the transitions ($c^1\Pi \rightarrow a^1\Delta$) and ($c^1\Pi \rightarrow b^1\Sigma^+$) of NH and ND are generated and investigated for predissociations.

Experimental

Ammonia (NH_3 or ND_3) is irradiated in a windowless photolysis system[2] with Ar-lines in the vacuum uv. Ammonia pressures of typically 0.05 Torr are employed at 1 Torr Ar pressure. Fluorescence spectra are dispersed by a 1 m Czerny Turner monochromator (Chromatix CT 103) and recorded by a strip chart recorder. Atomic lines of Ar and H contained in the spectra serve for wavelength calibration.

Results and discussion

Besides the transition ($b^1\Sigma^+ \rightarrow X^3\Sigma^-$) described in a previous paper[2] various bands of the transitions ($c^1\Pi \rightarrow a^1\Delta$) and ($c^1\Pi \rightarrow b^1\Sigma^+$) of NH and ND appear which can be assigned using known molecular constants. The band origins, arranged in a Deslandres scheme, are presented in Table I. Considering the linearity of the wavelength calibration of the monochromator (by comparison with Ar lines) the accuracy of the given

Table I: Deslandres scheme of the vacuum wavenumbers of the band origins

a) ($c^1\Pi \rightarrow a^1\Delta$)

NH:

v'' \ v'	0		1
0	30755.6[a]	(2121.4)	32877.0[a]
	(3187.6)		(3186.8)
1	27568.0[a]	(2122.2)	29690.2
	(3037.0)		(3038.2)
2	24531.0	(2121.0)	26652.0

ND:

v'' \ v'	0		1		2
0	30849.1[b]	(1621.7)	32470.8[b]	(1413.0)	33883.8
	(2356.2)		(2356.9)		(2352.1)
1	28492.9[b]	(1621.0)	30113.9	(1417.8)	31531.7
	(2276.5)		(2279.6)		
2	26216.4	(1617.9)	27834.3)		
			(2197.9)		
3			25636.4		

b) ($c^1\Pi \rightarrow b^1\Sigma^+$)

NH:

v'' \ v'	0		1
0	22106.6[c]	(2124.7)	24231.3
	(3205.9)		(3207.3)
1	18900.7[c]	(2123.3)	21024.0

ND:

v'' \ v'	0		1
0	22237.3[c]	(1622.6)	23859.9
	(2371.9)		(2372.2)
1	19865.4[c]	(1622.3)	21487.7)

a) R. Florent, S. Leach, J. Phys. Radium 13, 25 (1952)

b) H. Hansen, I. Kopp, M. Kronekvist, and N. Åslund, Ark. Fys. 30, 1 (1965)

c) F.L. Whittaker, J. Phys. B. Ser. 2, 1, 977 (1968) wavenumbers can be conservatively estimated to be ± 3 cm^{-1}. These error limits are in agreement with the observed deviations of the independent determinations of vibrational quanta (values in brackets in Table I). The observation of higher vibrational quanta up to $\Delta G(5/2)$ allows the direct determination of vibrational constants without employing isotope relations. The results are for $NH(a^1\Delta)$: ω_e = 3336 cm^{-1}, $\omega_e x_e$ = 74.8 cm^{-1}, and for $ND(a^1\Delta)$: ω_e = 2435 cm^{-1}, $\omega_e x_e$ = 39.2 cm^{-1} in agreement with the theoretical isotope effect.

In the rotational structure of the bands (0,0), (0,1), (1,0), (1,1), and (1,2) of the transition $NH(c^1\Pi \rightarrow a^1\Delta)$ a significant decrease in intensity can be detected for $NH(c^1\Pi$, $v' = 0$, $J' \geq 18)$ and $NH(c^1\Pi$, $v' = 1$, $J' \geq 11)$. Ascribing the breakoff in intensity to rotational predissociation of the $c^1\Pi$ state$^{1)}$ the implications on the value for the dissociation energy of NH are discussed. Work is in progress to obtain the respective breakoff points for ND.

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References

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