NH AND ND($b^1\Sigma^+$) RADIATIVE LIFETIMES

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Since the first report of the $b^1\Sigma^+ \rightarrow X^3\Sigma^-$ transition of the NH and ND radicals, two research groups have measured their quenching rate constants by various added gases. The radiative lifetime of NH has been given as $\tau \leqslant 5.10^{-3}$ sec by Zetzsch et all. There is no reported value for ND. The ratio of the quenching rate constants $k(ND, ND_3)/k(NH, NH_3)$ is found to be of the order of 20 and in the $NH_3(ND_3)$ photolysis we found an intensity for light emission at least 10 times higher for the deuterated system than for the hydrogenated one, as such large isotopic effects are rather unusual, the present study was undertaken in order to understand them. As the radiative lifetime of ND is expected to be rather similar to that of NH, we also hoped that both determinations will help to find out a more precise value of the lifetime.

Experimental results

$NH_3(ND_3)$ is photolized in a flow system by a Kr resonance lamp. The decrease with time of the light signal of the 0 - 0 transition of $NH(ND)b \rightarrow X$ at 471 nm is measured through a monochromator at various $NH_3(ND_3)$ pressures.

The experimental results may be given as :

$$\tau_p^{-1} = \tau_{op}^{-1} + k\,[NH_3] + K$$

τ_p is the experimentally measured lifetime, τ_{op} the intrinsic radiative lifetime, k is the quenching rate constant for collisions of NH with NH_3, K represents the sum of radiative deactivation rate constants. τ_p is determined for different pressures of NH_3 and ND_3 and the measured radiative lifetime $\tau = (k_{op} + K)^{-1}$ is obtained by extrapolation to zero pres sure. Two types of irradiation cells have been used.

The variation of τ_p versus the pressure is shown in fig. 1 for NH and fig. 2 for ND. Both an isotropic effect and an effect of the shape of the irradiation cell are observed. The higher is the ratio

surface/volume of the cell, the lower is τ^{-1}.

At low pressures of NH_3 and ND_3, τ_p^{-1} increases, there is a diffusion and quenching of the excited radicals on the walls of the cell.

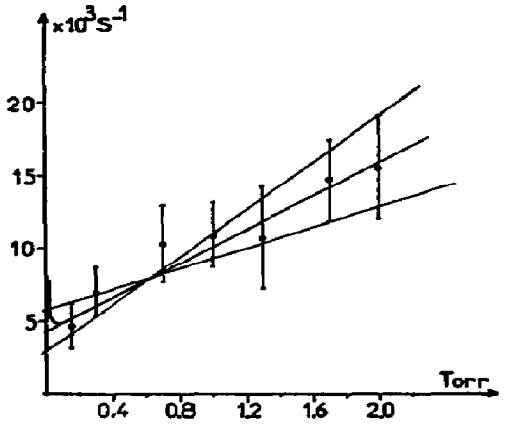

Fig. 1 - Decay of $NH(b^1\Sigma^+)$ versus NH_3 pressure

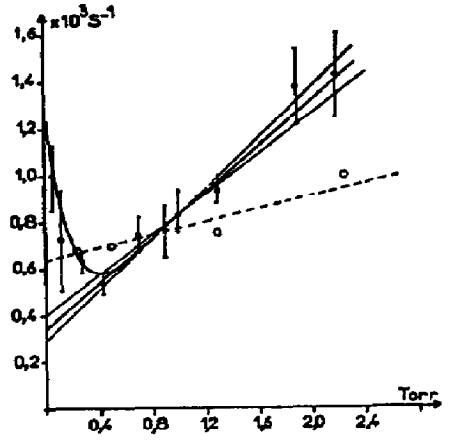

Fig. 2 - Decay of $ND(b^1\Sigma^+)$ versus ND_3 pressure

first series S_1/V_1

second series $S_2/V_2 < S_1/V_1$

Our values are reported in the following table together with other's determination (cf table).

Discussion

The important isotopic effect observed for the radiative lifetimes and for the quenching rate constants may be explained by three different ways :

1/ The quantum yield of ND formation in the photolysis of ND_3 happens to be greater (at least 10 times) than that of NH in the NH_3 photolysis. ND, ND_3 collisions are less efficient than NH, NH_3 in quenching the b state because, as postulated by Gelernt et all, an accidental degeneracy exists between the b and a states for NH only. However in the same energy range of the interaction ($\simeq$ 700 cm^{-1}) there are 7(b) states and 12(a) states for NH against 10(b) states and 22(a) states for ND. On this basis the probability of finding a close resonance for NH is lower than it is for ND. The same is true for matching with rovibronic levels of the ground state.

2/ We have calculated the intrinsic radiative lifetime of NH. If that of ND is identical, as may be expected, the ratio K/K' of all other radiative and non radiative rate constants is as big as 20; this is still rather unexpected for a diatomic molecule.

3/ The intrinsic radiative lifetimes are differents for NH and ND. This point seems also rather controversal.

We have photolyzed some other compounds as potential sources of the NH state. Although some of them give very strong c → a emission, the b → x emission is not observed. This fact strongly supports the direct formation of NH(b) in the NH_3 photolysis.

Present work		Gelernt	Zetzsch	
τ_{ms}	1/ (0.4 0.2)[a] 2/ 0.23±0.08	17.8	5	NH
$k.10^{14}$ cm^3 $mole^{-1}$ s^{-1}	1/ (30 ±10)[a] 2/ 18.01±0.71	39±2	41±7	
τ_{ms}	1/ 1.6 ±0.2 2/ 2.86±0.41	not determined		ND
$k.10^{14}$ cm^3 $mole^{-1}$ s^{-1}	1/ 0.38±0.3 2/ 1.49±0.15	5.22±0.2	1.9±0.4	

TABLE

(a) The values within brackets are not accurate and are given for comparison.

(1, 2) The second series of measurements has been performed in an irradiation cell of smaller S/V ratio than that of the first series.