THE JOURNAL OF CHEMICAL PHYSICS VOLUME 56, NUMBER 6 15 MARCH 1972

Observation of $\Delta k = \pm 3$ Transitions in NH_3–H_2 Collisions

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(Received 29 December 1971)

In a previous study of NH_3–H_2 collisions,[1] only $\Delta k=0$ transitions of NH_3 were observed; the $\Delta k=3n$ ($n\neq 0$) transitions, observed in NH_3–He, Ar, and Xe collisions,[2] were not detected. In view of the importance[3] of such transitions in the equilibration of interstellar NH_3, we have repeated the study of NH_3–H_2 collisions using an improved experimental technique. Observation of such transitions is now reported.

The major improvement is the use of a transmission filter (OKI CFM-242JB) in the microwave detection circuit instead of the high pass cutoff filter used in the previous experiments.[1,2] This has enabled us (a) to separate the ($J=1$, $K=1$) and the (2, 2) inversion lines which are 28 MHz apart and (b) to study four-level systems in which the pumping frequencies are higher than the signal frequencies. As in Ref. 1 we have used about 10 mtorr of NH_3 mixed with 1 torr of H_2.

In the experiment as described in Ref. 2, an inversion transition (J, K) of NH_3 is pumped and another inversion line (J', K') is monitored (see Fig. 1). The non-Boltzmann distribution produced in the levels (J, K) is transferred to the levels (J', K') by the collision-induced transitions ϕ and χ. For a reason which is not yet adequately understood, ϕ and χ have different rates and the signal absorption changes.

The observed $\Delta k=3$ transitions are listed in Table I; two $\Delta k=0$ transitions are listed for comparison. The uncertainty of the observed values of $\Delta I/I$ is $\pm 0.5\%$ and only those $\Delta k\neq 0$ systems listed in Table I have values of $\Delta I/I$ greater than the present sensitivity of the apparatus, $\pm 0.3\%$.

An interesting feature of the results is found when the values of $\Delta I/I$ for NH_3–H_2 collisions are compared with those for NH_3–He collisions listed in the last column of Table I. For $\Delta k\neq 0$ transitions there is a close parallelism between the two sets of values in the sign and magnitude. Using rate constants for the various collision-induced transitions indicated in Fig. 1, the value of $\Delta I/I$ can be expressed as[2]

$$\Delta I/I=(k_\phi^\dagger-k_\chi^\dagger)/(2k_\beta+k_\phi^\dagger+k_\chi^\dagger+k_\eta). \quad (1)$$

TABLE I. Observed values of $\Delta I/I$ for NH_3–H_2 collisions and NH_3–He collisions.

	Pumped lines $(J,K)_p$	Signal lines $(J,K)_s$	$\lvert\Delta J\rvert$	$\lvert\Delta k\rvert$	$\Delta\epsilon$ (cm^{-1})[b]	$\Delta I/I(\%)$[a] NH_3–H_2	NH_3–He
$\Delta k\neq 0$	(5, 5)	(2, 2)	3	3	−158.4	−1.3	−4.3
		(3, 2)	2	3	−101.7	−0.4	−2.5
	(4, 4)	(1, 1)	3	3	−121.3	−1.9	−9.4
		(2, 1)	2	3	−83.5	−1.1	−6.9
	(2, 2)	(1, 1)	1	3	−28.1	−3.0	−10.0
	(2, 1)	(3, 2)	1	3	46.9	−0.6	−3.8
	(3, 2)	(1, 1)	2	3	−84.7	0.5	0
	(5, 4)	(1, 1)	4	3	−215.8	0.4	2.0
$\Delta k=0$[c]	(2, 1)	(1, 1)	1	0	−37.8	5.2	−3.5
	(3, 2)	(2, 2)	1	0	−56.6	2.3	−4.2

[a] $\Delta I/I$ represents relative variation of the signal due to pumping.

[b] $\Delta\epsilon$ is the difference between the energies of the pumped levels and the signal levels.

[c] The values are from Ref. 2.

The parallelism with the NH_3–He results could be accounted for if the values of corresponding k_ϕ and k_χ for the $\Delta k\neq 0$ transitions (which are caused by short-range collisions) are similar for NH_3–H_2 and NH_3–He collisions, and if the denominators differ by a factor of 3–5. This is supported by the fact[4] that the ratio of the pressure broadening parameter (which is proportional to $k_\beta+k_\phi+k_\chi+k_\eta\sim k_\beta$) for NH_3–H_2 collisions to that for NH_3–He collisions is about 3 to 1.

The striking difference in sign of $\Delta I/I$ for the $\Delta k=0$ transitions suggests that the values of k_ϕ and k_χ are not similar. The $\Delta k=0$ transitions are caused by longer range interactions employing the dipole moment of NH_3 which, in NH_3–H_2 collisions, could overwhelm the negative value of $\Delta I/I$ caused by shorter range collisions. Similar consideration may be used to explain the anomalies of parity rules observed in NH_3–He and NH_3–Ar collisions.[5]

Although the values of $\Delta I/I$ listed in Table I do not give rate constants of individual transitions, they do restrict the values of the rate constants. For the $(2, \pm 2)\rightarrow(1, \mp 1)$ transitions, which are of astrophysical interest, we have determined that $(k_\phi-k_\chi)>0.06\ k_\beta$. Approximating $k_\beta/2\pi$ by the pressure broadening parameter[4] (3 MHz/torr), we find $k_\phi>3.2\times 10^{-11}$ molecule^{-1} cm^3 sec^{-1}. This transition is also weakly radiatively allowed[6] with the rate of 1.4×10^{-10} sec^{-1}. Comparing these numbers we find that the collisional relaxation between the metastable ($J=K$) levels of interstellar NH_3 dominates the radiative relaxation if the density of H_2 is higher than 5 cm^{-3}. Since the density of H_2 in a NH_3 cloud is estimated[3] to be about 1000 cm^{-3}, this result supports the argument of Townes and his collaborators[3] that equilibration between the metastable rotational levels of interstellar NH_3 is caused mainly by the $\Delta k=\pm 3$ transitions induced by collision with H_2.

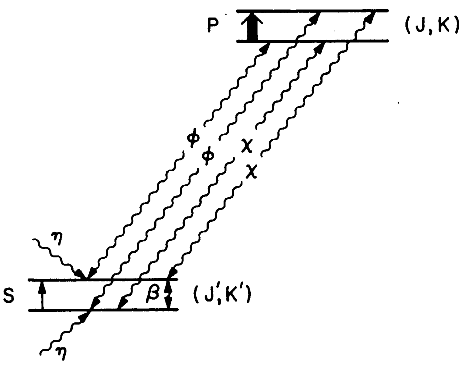

FIG. 1. Diagram showing microwave and collision-induced transitions in a four-level system $(J, K)_p$–$(J', K')_s$ of NH_3. The bold arrow in the (J, K) doublet levels denotes the "pumping" and the thin arrow in the (J', K') doublet levels the signal microwave transition. The wavy arrows indicate various collision-induced transitions.

* National Research Council of Canada postdoctorate fellow 1970–1972.

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