COLLISION INDUCED TRANSITIONS OF MOLECULAR SYSTEMS OF INTERSTELLAR INTEREST THROUGH MICROWAVE PULSE TECHNIQUES

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ABSTRACT. Microwave pulse techniques have proved to be very useful to obtain informations about coherence decay rates and population transfer rates in gas phase. The coherence decay rates have been measured by a technique which involves the detection of the transient emission signal of the molecular sample following an intense microwave pulse. The (π-τ- $\pi/2$) pulse sequence technique has been used to extract informations about population transfer rates. The experimental results on l-doublet transitions of HCN and HCCCN perturbed by H_2,D_2 and He are given. The theoretical results obtained from the perturbative approach to collision dynamics have also been computed, and compared with the experimental results. For the l-doublet transitions of HCN, the population decay rates have found to be considerably less than the corresponding coherence decay rates.

1. INTRODUCTION

The longitudinal relaxation time, T_1, describes the relaxation of the population between two levels, whereas the transverse relaxation time, T_2, describes relaxation of coherent polarization associated with two levels of a transition under consideration[1]. A collision may be classified into following one of three types depending on its effect on T_1 and T_2 :

(i) Adiabatic collision which changes only the phase of the colliding molecules, but not the rotational level, contributes only to $1/T_2$.

(ii) Collision which induces transition between states under consideration contributes twice to $1/T_1$ as compared to $1/T_2$.

(iii) An inelastic collision other than type (ii) contributes in a similar manner to $1/T_1$ and $1/T_2$.

It has been found from recent investigation[2] of $1/T_2$- values corresponding to l-doublet transitions of $HC^{15}N$ perturbed by self that the experimental values of $1/T_2$ have been about 45% lower than the theoretical values using perturbative approach which considers only the first order dipole induced selection rule i.e.$\Delta J = 0, \pm 1$, where ΔJ is change in the rotational quantum number due to collision. This indi-

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cates that the dipole collision induced transitions having selection rule $\Delta J = 0, \pm 2$ play an important role for the system. This can be confirmed by investigations of $1/T_1$ - values for the system, because such collisions will increase the collisions of type (i) which will make the value of $1/T_1$ less than the corresponding value of $1/T_2$.

In the present paper, we have reported the values of $1/T_1$ and $1/T_2$ for l-doublet transitions of $HC^{15}N$ perturbed by H_2 , D_2 and He in K-band. The values of $1/T_2$ for l-doublet transitions of $HCCC^{15}N$ perturbed by H_2 , D_2 and He in X-band are also reported.

2. EXPERIMENT

A K-band bridge type superhet spectrometer has been used for the measurements of T_1 - and T_2 - relaxation times for the $HC^{15}N$ systems, whereas a fourier transform microwave spectrometer has been used for the determination of T_2 - values of $HCCC^{15}N$ systems. The details of the spectrometers are described elsewhere[3,4]. The power of the microwave pulse were used as 250 mW.

With the K-band bridge type spectrometer, the experiment was done as follows:

Before the filling of the sample in the absorption cell the bridge was adjusted in such a way that there was no microwave power at the detector. The ($\pi - \tau - \pi/2$) sequence experiment was performed according to the procedure given in Ref.(4). Then second microwave pulse was removed by switching off the second pulse from MW-PIN switch and IF-PIN switch. The first pulse was adjusted to $\pi/2$ - pulse to perform transient emission experiment. Thus, the experiments for the measurements of T_1 and T_2 at a pressure can be performed one after the other, thereby eliminating systematic error from pressure variations.

The observable signal in the ($\pi - \tau - \pi/2$) pulse sequence method can be described by the following expression:

$$S_1 = A_1 \exp(-t/T_1) + C_1 . \tag{1}$$

Here A_1 and C_1 are constants.

The value of $1/T_2$ was obtained by fitting the observable signal of the transient emission experiment with the following expression:

$$S_2 = A_2 \exp(-t/T_2) \exp(-t^2/4q^2) + C_2 , \tag{2}$$

with A_2 , C_2 and $1/T_2$ as fitting parameters and $q = (\ln 2/2\pi\nu_D)$ with ν_D as the doppler half width.

Pressure measurements were made using a MKS Baratron 310 B capacitance manometer.

3. RESULTS AND CONCLUSIONS

The experimental values of T_1 and T_2 parameters are given in Tables I and II, along with resonance frequencies and theoretical values computed from the theory proposed earlier[2] .

Table I : Experimental and Theoretical Values of $(1/T_1)$ - and $(1/T_2)$ - parameters for l-doublet transitions of HC^{15}N at temperatures (300 ±2) K. Errors are given as twice the standard deviation.

J	SYSTEM	$1/T_1$	$1/T_2$	X*	$1/T_1$	$1/T_2$	X*
		$(\mu s^{-1} m$	$T^{-1})$		$(\mu s^{-1} m$	$T^{-1})$	
9	HC^{15}N-HC^{15}N	.0740(11)	.2760(3)	191	.1615	.2290	42
(19055.300)	HC^{15}N-H$_2$.	.0110(7)	.0375(39)	178	.0780	.0360	96
MH$_z$	HC^{15}N-D$_2$	.0.104(9)	.0258(38)	148	.0740	.0300	100
	HC^{15}N-He	.0086(19)	.0120(7)	35	.0075	.0145	91
10	HC^{15}N-HC^{15}N	.0670(9)	.2140(7)	218	.1620	.2270	40
(23284.616)	HC^{15}N-H$_2$	.0115	.0330(5)	183	.0180	.0360	96
MHz	HC^{15}N-D$_2$	.010(1)	.0250(5)	142	.0150	.0300	96
	HC^{15}N-He	.0089(19)	.0114(11)	28	.0075	.0145	92

* $X = 100(1/T_2 - 1/T_1)T_1$

Table II : Experimental and Theoretical Values of $1/T_2$ - parameters for l-doublet transitions of HCCC^{15}N at 300°K perturbed by H_2, D_2 and He.

Perturber	J	Expt. Values $(\mu s^{-1} mT^{-1})$	Theoretical Values $(\mu s^{-1} mT^{-1})$
H_2	36	o.0518(4)	0.0391
	41	0.0514(10)	0.0390
D_2	36	0.0418(6)	0.0321
	41	0.0416(4)	0.0319
He	36	0.0254(4)	0.0180
	41	0.0253(4)	0.0179

The most important point of the Table I is that the value of $1/T_1$ is significantly less than the corresponding values of β $(=1/T_2)$. The values of β agree well with the values reported earlier[2]

The theoretical values of $1/T_1$ and $1/T_2$ corresponding to a transition $a \rightarrow b$ are related to the rates as follows[1]:

$$1/T_1 = R_{ab} + R_{ba} + 1/2\sum' R_{ai} + 1/2\sum' R_{bi} \quad (3)$$

$$1/T_2 = R_{aa}/2 + 1/2\, R_{ab} + 1/2\, R_{bb} + 1/2\, R_{ba} + + 1/2\sum'(R_{ai} + R_{bi}) \quad (4)$$

where R_{lk} is the collision induced rates for the transition $l \rightarrow k$ and $\sum'$ indicates summation over all states $i \neq (a,b)$. These rates are computed according to the procedure given in Ref.(2).

The disagreement between the theory and experiment indicates that the perturbative approach must be improved to consider higher order terms in the theory. The experimental results indicate that the phase changing collisions are dominent mechanism for rotational coherent polarization for l-doublet transitions. Phase changing collisions due to strong collisions has not been treated in the theory.

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