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Propensity Rules in Rotational Inelastic Collisions of NH_2 ($\tilde{A}\,^2A_1$) under Molecular Beam Condition

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Abstract: In this paper, it is the first time to report the study on the state-to-state rotational energy transfer (RET)of NH_2 ($\tilde{A}$ $^2A_1$)(0,9,0)*under molecular beam condition* in detail. Through a systematic study of the relative population transferred as functions of initially excited quantum state, including different Ka, nuclear-spin, and even spin-doublet, some propensity rules were obtained directly.

Keywords: Single collision, asymmetry top radical, RET, propensity rule.

Rotational energy transfer (RET)is one of the most common and simplest inelastic molecular collisional processes, and it reflects the anisotropy of the interaction potential of the coupling between the orbital motion of the molecule with respect to the other collision partner and the rotational motion. Also, knowledge of these energy transfer rates are also important in other areas, such as laser design of chemical laser, *etc*.

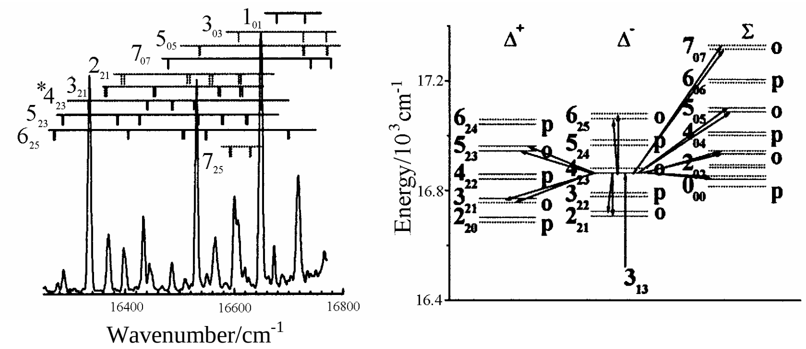
Dixon[1,2] and Alwahabi[3] had studied inelastic collisions of NH_2 ($\tilde{A}$ $^2\mathbf{A_1}$)in a flowing system. But since the results were not obtained under single collision condition, it was very suspicious about any conclusions therein. Wang *et al.*[4]. had reported the study of 3_{03} of NH_2 ($\tilde{A}$ $^2A_1$)(0,9,0), but the resolution was far from satisfactory to study the RET deeper.

Experimental

In order to understand the true mechanism of RET, we studied RET of NH_2 ($\tilde{A}$ $^2A_1$)under single collisional condition in detail. Two main difficulties of undertaking these experiments, which are low number density of radicals prepared in the beam and weak intensity of dispersed fluorescence (DF)emitted by collisionally populated levels, were somewhat released by using a new self-breakdown pulse D.C. discharge to produce the NH_2 radicals and photon-counting techniques to detect the DF. NH_2 was excited to a single rotational level of the $\tilde{A}$ $^2\mathbf{A_1}$ (0,9,0)state by a pulsed dye laser with narrow line width (~0.02cm^{-1}). The collisional partner was Ar/NH_3. In this paper, the pumped levels were defined as parent levels, while the collisionally populated levels as daughter levels. The mean free path is larger than 50 times of the real observation zone, *i.e.*, only one collision can occur in the observation zone at most.

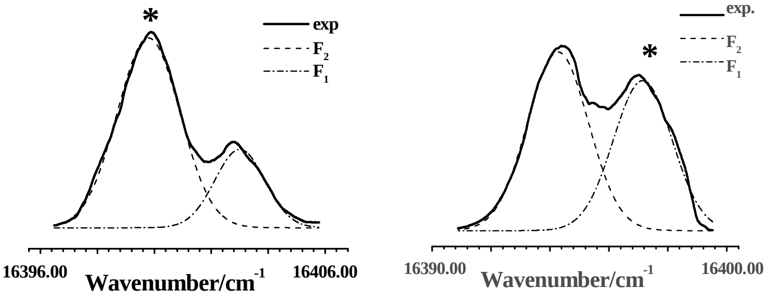
Results and Discussion

Figure 1. Dispersed fluorescence following the RET of the $\tilde{A}\,^2A_1$ (0,9,0)4_{23} (F_1)and Rovibronic energy levels.



Up to date, it is the first time to report the rotational energy transfer of an asymmetric top species, such as NH_2 in this article, absolutely under single collisional conditions in detail. We had studied it among a large number of states in (0,9,0), (0,10,0)and (0,13,0)vibronic manifolds of the $\tilde{A}$ ^{2}**A$_1$** state of NH_2 under single collisional conditions. Here only the results of the RET of NH_2 $\tilde{A}$ ^{2}**A$_1$** (0,9,0)were present, to which a systematic study including different Ka, nuclear spin symmetry , and even electron spin had been taken. A typical DF spectrum and the energy level diagram was shown in **Figure** 1. From **Figure** 1, it can be clearly seen that the overlapping of main spectral lines can generally be avoided and state-to-state transitions unequivocally observed, thus making the calculation of the transferred population easy. In **Figure** 2, part of the fluorescence spectrum of spin-rotation doublet is shown. Since the intensity of the fluorescence is still very weak, the spectrum was only partly resolved to those levels with relatively large spin-rotation splitting.

Figure 2: Partly resolved fluorescence emitted from the daughter level 2_{21} of NH_2 (0,9,0) $\tilde{A}$ $^2A_1$ populated from 4_{23} (F_1)(Left)and 4_{23} (F_2)(Right).



The total available collision energy colliding with Ar and NH_3, is 382 cm^{-1} and 349 cm^{-1} respectively, which is larger than the energy gaps between the parent level and anyone of the daughter levels observed in one experiment.

The relative populations of the collisionally populated rovibronic states in the $\tilde{A}\ ^2A_1$ vibronic state had been deduced from the intensity of the observed transitions considering the Honl-London factors. Where possible, the populations of parent level were evacuated from the intensities of transitions other than that pumped by laser in order to exclude any spurious contribution from scattered laser light. For 0_{00} it was impossible to eliminate any contribution from the scattered light since there is only one transition branch. And those of daughter levels were calculated from the well-resolved transitions, except for some overlapped transitions. The final results, as listed in **Table** 1 (including ortho and para nuclear spin), were the average values from the populations of several different branches of the same daughter level. After that they were normalized according to the total populations of the parent and daughter levels.

Table 1. Relative populations of RET including ortho and para levels of $NH_2\ \tilde{A}\ ^2A_1$.

Ortho	Relative Populations: P (N $_{Ka,Kc}$)				para	Relative Populations: P (N $_{Ka,Kc}$)			
	$4_{23}{}^a$	$3_{21}{}^a$	$3_{03}{}^a$	$1_{01}{}^a$		$3_{22}{}^a$	$2_{20}{}^a$	$2_{02}{}^a$	$0_{00}{}^a$
$1_{01}{}^c$	0.10	0.104	0.173	-	$0_{00}{}^c$	0.116	0.156	0.219	-
$2_{21}{}^c$	0.076	0.175	0.093	0.138	$2_{02}{}^c$	0.094	0.058	-	0.060
$3_{03}{}^c$	0.17	0.082	-	0.115	$2_{20}{}^c$	0.185	-	0.074	0.051
$3_{21}{}^c$	0.19	-	0.155	0.171	$3_{22}{}^c$	-	0.067	0.067	0.030
$4_{23}{}^c$	-	0.085	0.168	0.071	$4_{04}{}^c$	0.030	0.057	0.075	0.023
$5_{05}{}^c$	0.025	0.009	0.023	0.020^b	$4_{22}{}^c$	0.083	0.097	0.088	0.020
$5_{23}{}^c$	0.026	-	0.071	0.020	$5_{24}{}^c$	0.027	0.036	0.018	0.003
$6_{25}{}^c$	0.007	0.008	0.010	0.003	$6_{24}{}^c$	0.008	-	0.003	-

a: Parent level; c: Daughter Level.

From the **Figures** and **Table**, some distinct propensity rules can be found. As seen in **Figure** 1, the first propensity rule is that the total parity including nuclear spin is strictly conserved, *i.e.*, ortho to ortho and para to para. The total parity of the parent level and those of the daughter levels would never be changed. This is in accordance with that observed in a flowing system[1,3] and theoretic prediction[5].

From **Figure** 2, an interesting phenomenon could be observed. Whatever the fine-structure state, F_1 or F_2 of the parent level, was pumped, both doublets of the daughter levels were found in the spectrum, *i.e.*, the electron spin of NH_2 can be changed significantly. In the past decade, propensity rules of the fine-structure state have been studied in many systems. Dagdigian *et al.* studied CaCl ($X^2\Sigma^+$)-polar molecular collisions[6], and found that there was a definite preference for retention of the fine-structure levels in these dipole-dipole collisions. Dixon *et al.*.[1,2] measured the relative populations within collisionally populated spin doublet of NH_2 ($\tilde{A}\ ^2$**A_1**), but multiple collisions made the result so questionable. Esposti[7] *et al.* found that it is due to the bound excited state Ar-OH (calculated with *ab initio* method)that the strong attractive potential between the collisional partner makes the angular momentum vector re-orientated, and thus changes the spin doublet. Using UMP2/6-311+G (d,p)method, we also find that one collisional complex can be formed between NH_2 and NH_3. So, the change of electron spin in our experiments are most possible in collisions with NH_3. More experiments and theoretical calculation will be performed in the near future.

From **Table** 1, the third propensity rule is that the decrease of N is favored over those increase of N, where N is the rotational quantum number. For example, the populations of daughter levels 2_{21} and 3_{21} are greater than those of 5_{23} and 6_{25}. And the fourth propensity rule is that small change of N is favored over large change of N, *i.e.*, multi-quantum transfer rates are much smaller than single quantum transfer rates. For example, while the parent level is 4_{23}, the transfer rate to the daughter level 3_{21} is much faster than that to 2_{21}. Also according to the table, the fifth propensity rule can be found. To the ortho nuclear spin state-to-state RET, the transfer of intra-stack (ΔKa=0)and inter-stack (ΔKa=2)with the same N have little difference. For example, when the parent level is 4_{23}, the population of 3_{21} almost is the same as 3_{03}, so does 5_{05} and 5_{23}. While to the para state, the transfer population of intra-stack (ΔKa=0)is larger than that of inter-stack (ΔKa=2)with the same N. For example, when the parent level is 3_{22}, the populations of 2_{20} and 4_{22} are all greater than 2_{02} and 4_{04}, respectively.

Conclusion

It is of great importance to study the rotational inelastic collisional energy transfer under molecular beam condition in order to discover the true mechanism of energy transfer. In this article, some propensity rules have been found in the collisional system of asymmetry top radical NH_2 ($\tilde{A}$ $^2A_1$)(0,9,0)and NH_3/Ar under single collisional condition: conservation of total parity including nuclear spin; significant change of the spin-rotation doublets of collisionally populated daughter levels; preference of N decreasing and single quantum number transition to N increasing and multi-quantum number transition, respectively; and small difference of the cross sections between the intra-stack transition and inter-stack transition for the ortho nuclear spin state-to-state energy transfer, while the preference of the intra-stack to the inter-stack for the para one. The relationship between the cross section of RET and the energy gap or angular momentum gap, and the deeper investigation of the RET both in experimental and in theoretical are in processing.

References

1. R. N. Dixon and D. Field, *Proc. R. Soc. Lond. A.*, **1979**, *366*, 247 .
2. S. J. Dearden, R. N. Dixon and D. Field, *J .Chem. Soc. Faraday Trans. II*, **1982**, *78*, 1423.
3. Z. T. Alwahabi, C. G. Harkin, A. J. McCaffery *et al.*, *J. Chem. Soc. Faraday Trans.II*, **1989**, *85*, 1003.
4. L. Wang, X. Li, G. Shen, *et al..*, *Chinese J. Chem. Phys.* , **1993**, *6* (5), 392.
5. G. W. Flynn, and J. D. Baldeschwieler, *J. Chem. Phys.*, **1962**, *37* (12), 2907.
6. P. J. Dagdigian and S. J. Bullman, *J. Chem. Phys.* **1985**, *82* (3), 1341.
7. D. Esposti and H. J. Wener, *J. Chem. Phys.* , **1990**, *93* (5), 3351.

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