Microwave Studies of Collision-Induced Transitions between Rotational Levels. III. Observation of Preferred Quadrupole-Type Transitions in NH_3–He Collision

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The method of high-power microwave double resonance has provided a useful means of studying collision-induced transitions between rotational levels.[1–3] In all the four-level systems studied so far the transitions having dipole-type selection rules (parity $+\leftrightarrow-$) have greater probabilities than the corresponding quadrupole-type transitions (parity $+\leftrightarrow+$ and $-\leftrightarrow-$).[4] This paper reports the first observations of four-level systems where the quadrupole-type transitions have greater probabilities than the dipole-type transitions Also it will be emphasized that the experimental results cannot be explained even qualitatively by Anderson's theory.[5]

The four-level system of ammonia used in the experiment is shown in Fig. 1(a). An inversion doublet corresponding to $|J, K\rangle$ is "pumped" and the other inversion doublet corresponding to $|J-1, K\rangle$ is used as the signal.[3] The four-level systems with $K=J-1$ ($K=1$–6) were used since the transition schemes are simplest. In pure ammonia, the signal was increased when the $|J, K\rangle$ doublet was "pumped" indicating that the dipole-type α transitions are favored [see Fig. 1(b)].

However in NH_3–He mixture (about 1 to 100) the signal was decreased by the pumping indicating that the quadrupole-type γ transitions are favored in NH_3–He collisions [see Fig. 1(c)]. It was also noted that the percentage of the signal change $\Delta I/I$ depends strongly on the K values as seen from Fig. 2. In fact it was observed that $k\gamma > k_\alpha$ for $K=1, 2, 3$ but $k\gamma < k_\alpha$ for $K=5, 6$, where k represents the rate constant of the collision-induced transitions.

At first the above results were interpreted qualitatively by Anderson's theory as follows. In NH_3–He collision for lower K, the dipole–induced-dipole interaction would cause transitions in which parity is preserved.[6] As K (and thus J) goes higher, the NH_3 molecule has to transfer more energy[7] to the helium atom and thus requires stronger collision which introduces higher order interactions. Thus the parity ($+\leftrightarrow-$) transitions caused by the next higher order quadrupole–induced dipole interaction would become important.[6]

However, when a NH_3–A experiment was performed, it was found that all $\Delta I/I$ values were positive and thus $k\gamma < k_\alpha$ (see Fig. 2). This result and the NH_3–He result *cannot* be explained consistently by the previous argument, since the larger polarizability and the smaller velocity of the argon atom would increase the longer range interaction and thus favor the γ transitions in which parity is preserved.

We believe that the NH_3–He collisions which cause the $\Delta J=\pm1$ transitions are fairly hard collisions and need higher-order theory.[7a] Also presumably a Fourier component of the time-dependent He impact at the transition frequency must be taken into account. These new features may play a minor role in pressure broadening since the major effect of the broadening is ascribed to the transitions within the doublet.

The NH_3–Ne experiment gave values which lie between those of NH_3–He and NH_3–A, and the NH_3–^{3}He experiment gave slightly (about 0.5%) more negative values than those of NH_3–^{4}He. This mass dependence also suggests that time dependence of the impact is important as mentioned above. So far several other foreign gases, H_2, O_2, H_2O, and CH_4 have been studied but NH_3–He is the only one for which quadrupole-type transitions are preferred.

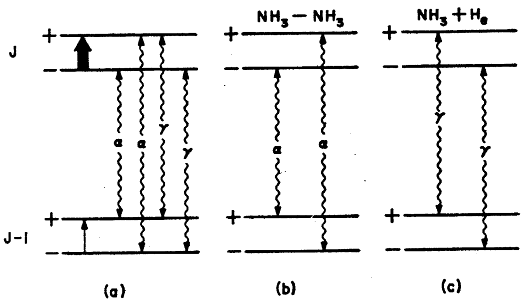

FIG. 1. (a) A four-level system in ammonia. The bold arrow represents the pumping and the thin arrow represents the signal. (b) Preferred collision-induced transitions in NH_3–NH_3 collision and in NH_3–A collision. (c) Preferred collision-induced transitions in NH_3–He ($K=1, 2, 3$) collision.

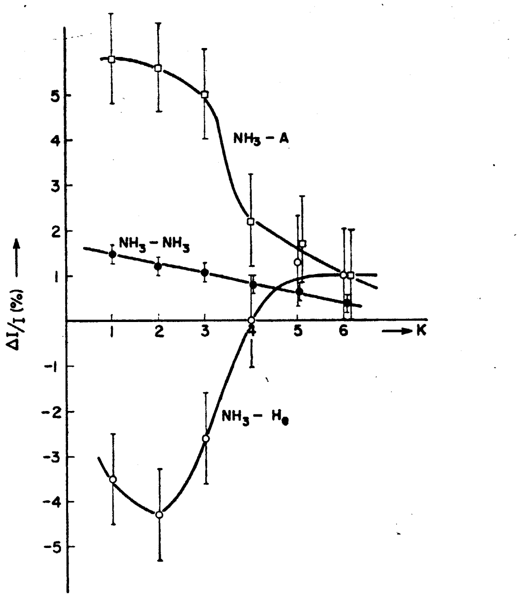

FIG. 2. Observed percentage changes of the signals.

[1] T. Oka, J. Chem. Phys. **45**, 745 (1966), Part I.
[2] A. M. Ronn and E. B. Wilson, Jr., J. Chem. Phys. **46**, 3263 (1967).
[3] T. Oka, J. Chem. Phys. **47**, 13 (1967), Part II.
[4] It should be noted that the dipole-type or quadrupole-type transitions does *not* mean that the transition is caused by the dipole or the quadrupole of a molecule; it merely refers to the selection rules.
[5] P. W. Anderson, Phys. Rev. **76**, 647 (1949).
[6] P. W. Anderson, Phys. Rev. **80**, 511 (1950). The selection rules are generalized as follows. A $(2^n-\text{pole})_1$–$(2^m-\text{pole})_2$ interaction causes parity ($+\leftrightarrow+$) transitions and parity ($+\leftrightarrow-$) transitions for even n and odd n, respectively, in molecule 1. A $(2^n-\text{pole})_1$–$(2^m-\text{pole induced dipole})_2$ interaction causes parity ($+\leftrightarrow+$) transitions and parity ($+\leftrightarrow-$) transitions for even $n+m$ and odd $n+m$, respectively, in molecule 1.
[7] The energy to be transferred is $E=2BJ=2B(K+1)$ which is about $\frac{1}{2}kT$ for $K=4$.
[7a] *Note added in proof:* Recently we have found that the selection rules of the NH_3-rare-gas collision-induced transitions are as follows: ΔJ, arbitrary, parity, unpredictable; and $\Delta K=3n$ (n is an integer); This shows that the NH_3-rare gas collisions are indeed fairly hard collision.