Microwave Triple Resonance; Direct Observation of $\Delta J=2$ Collision-Induced Transitions

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Relative probabilities of collision-induced transitions between rotational levels of molecules have been studied for a number of molecules by the method of microwave double resonance.[1–8] It has been observed that collision-induced transitions with dipole selection rules ($\Delta J=0$, ± 1, parity $+\rightarrow -$) are "preferred" in most collisions other than the exceptional case of NH_3–rare-gas collisions.[4,6] However, in several cases such as HCN–HCN,[3] H_2CCO–H_2CCO,[3] CH_3OH–He,[7] CH_3OH–H_2,[7] CH_3NH_2–He,[7] NH_3–H_2,[8] and NH_3–O_2[8] collisions, the results of the double resonance experiments indicated that probabilities of collision-induced transitions with $\Delta J=2$ are not very much smaller than those for transitions with $\Delta J=1$. In those experiments we "pumped" a J transition (a $\Delta J=0$ transition between doublet levels) and observed the $J-2$ transition. A complication arose in the analysis in that the observed change of signal induced by the pumping can be interpreted in two ways; it could have been caused either by $\Delta J=2$ transitions or by a cascading process of two successive $\Delta J=1$ transitions (see Fig. 1). These two possibilities were discriminated by using steady-state equations.[3,5,9] In the present Communication we report on an experimental method which provides direct discrimination between the two processes.

In this experiment, in addition to the pumping and the signal radiation, we use one further strong radiation, the "clamping" radiation. The role of this radiation is to artificially increase the transition probability between the components of the $J-1$ levels (see Fig. 1) and thus to interrupt the cascading process which transfers the population difference from the J doublet to the $J-2$ doublet. The experiment proceeds as follows. We first observe the $J-2$ transition on an oscilloscope and adjust the frequency of the clamping power to the $J-1$ resonance; this results in a decrease (in HCN [3] and in CH_3OH [7]) or an increase (in NH_3 [5,8]) of the signal, which we denote by ΔI_c (see Fig. 1). Then, keeping the clamping at resonance, the pumping radiation is tuned to the J resonance. This produces a further change of the signal, ΔI (see Fig. 1), which is caused by single $\Delta J=2$ transitions.

An example of these successive changes of the signal is illustrated in Fig. 1 for an l-doubling line of HCN. The large value of $\Delta I/I$ gives direct evidence that contributions from $\Delta J=2$ transitions are significant in the process of rotational energy transfer, as was previously inferred from double resonance experiments.[3] The ratio $\Delta I/\Delta I_c$ gives approximately the ratio of the probability for the $\Delta J=2$ transitions to that for $\Delta J=1$ transitions. The observed value of $\Delta I/\Delta I_c=0.31$ compares favorably with the previous value of 0.36 determined from steady-state equations [the value of X/Y in Ref. (3)].

Several other systems were examined. The results are listed in Table I. It is interesting to notice that while no $\Delta J=2$ transitions are observed in NH_3–NH_3 and CH_3OH–CH_3OH collisions, they are clearly observed in NH_3–H_2 and CH_3OH–He collisions.

The apparatus used is similar to that employed in double resonance experiments[3]; the only difference is that we now have two high-power klystrons. OKI klystrons 24V11 and 30V11 were used. Since the requirement for saturation is more severe for clamping, the clamping klystron was connected directly to the absorption cell and the pumping power coupled into the cell by a 3-dB-directional coupler. If the output power of the clamping klystron is sufficiently high,[3] the frequency adjustment is not very critical and no stabilization is necessary. More details of the apparatus will be published elsewhere.

TABLE I. Observed values of $\Delta I_c/I$ and $\Delta I/I$.

Collisions	Six-level systems		$\Delta I_c/I$ (%)	$\Delta I/I$ (%)
HCN–HCN	$(J=11)_p-(J=10)_c-(J=9)_s$ [a]	l doublets	-38.3 ± 2	-11.8 ± 2
NH_3–NH_3	$(4,1)_p-(3,1)_c-(2,1)_s$ [a,b]	Inversion doublets	$+4.4\pm0.2$	0 ± 0.5
NH_3–H_2	$(4,1)_p-(3,1)_c-(2,1)_s$	Inversion doublets	$+11.4\pm1$	-2.6 ± 1
CH_3OH–CH_3OH	$(J=9)_p-(J=10)_c-(J=11)_s$ [c]	$K=2\leftarrow1$ E state, $v=0$	-3.1 ± 1	0 ± 0.5
CH_3OH–He	$(J=9)_p-(J=10)_c-(J=11)_s$	$K=2\leftarrow1$ E state, $v=0$	-11.3 ± 1	-6.2 ± 1

[a] For the frequencies of these lines see Refs. 3 and 6.
[b] (4, 1) denotes $J=4$ and $K=1$, etc.
[c] For the frequencies of these lines see R. H. Hughes, W. E. Good, and D. K. Coles, Phys. Rev. 84, 418 (1951).

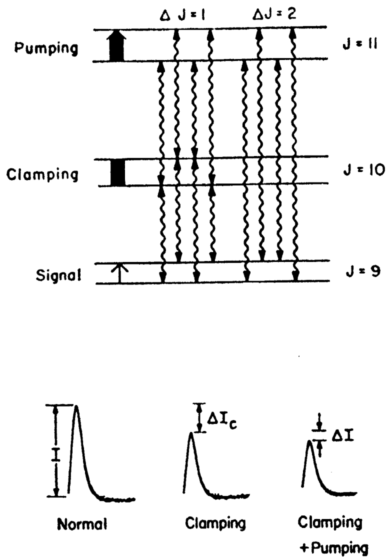

FIG. 1. A six-level system and observed results for l-doublet states of HCN. The wavy arrows indicate various collision-induced transitions. The oscilloscope traces show the intensity changes of the $J=9$ l-doubling line of HCN for each process.

The principle of this experiment can readily be extended to higher multiple resonance measurements, for example, the use of quadruple resonance for the direct observation of $\Delta J=3$ transitions.

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[9] See also K. M. Evenson and H. P. Broida, J. Chem. Phys. 44, 1637 (1966).