Observation of $\Delta J = 3$ "Forbidden" Transition in Ethyl Iodide by the Use of Double Resonance

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(Received 31 March 1966)

SINCE the pioneering experiment of Yajima and Shimoda,[1,2] the microwave double-resonance technique has been used mainly for the assignment of the spectrum.[3–5] However, as was already pointed out by these authors, the double-resonance technique is also useful for the observation of a weak transition (ν_p) having one state in common with another transition (ν_s) of reasonable intensity.[1] Even if the dipole matrix element for the weak transition (ν_p), μ_{ij}, is very small, a sufficient number of molecules can be pumped into or out of the common state by the strong resonant power, in order to observe the change in intensity of the other transition. Effective pumping is reached when $\mu_{ij}E/h$ is of the order of the linewidth.

A good example of this type of scheme is provided in the C_2H_5I molecule.[6] In this molecule, because of the presence of the large iodine nuclear quadrupole interaction, J is no longer a good quantum number and the normally forbidden $\Delta J = \pm 3$ transitions are weakly allowed.[7] The diagonal element of the electric quadrupole tensor $\chi_{aa}(-1482\ \mathrm{Mc/sec}^6)$ mixes $|3_{03}\rangle$ with $|1_{01}\rangle$ and $|0_{00}\rangle$ with $|2_{02}\rangle$ by about 1%. The off-diagonal element $\chi_{ab}(884\ \mathrm{Mc/sec}^6)$ mixes $|3_{03}\rangle$ with $|1_{11}\rangle$ by about 3%. Thus the transition $3_{03} \leftarrow 0_{00}$ is weakly allowed. The calculated values of μ_{ij} are 0.0087 and 0.0064 D for the transitions $7/2 \leftarrow 5/2$ and

$5/2 \leftarrow 5/2$, respectively.[8] It is interesting to note that both μ_a (1.75 D[6]) and μ_b (0.25 D[6]) contribute to the transition.[9] This is because, due to the quadrupole interaction, the symmetry of the eigenstates is no longer D_2 but the symmetry of the molecule, C_s, where μ_a and μ_b belong to the same symmetry species. The three-level scheme, the observed frequencies, and the calculated intensities of the transitions are shown in Fig. 1.

A block diagram of the apparatus is shown in Fig. 2. The Q-band pumping microwave of 10 W generated by an Elliott–Litton 8TFK2 klystron was passed straight through a conventional K-band Stark modulation cell and was terminated by a high-power dummy load. This produced a microwave electric field of about 100 V/cm in the cell. The K-band signal microwave generated by an OK1 24V10 klystron was coupled into the cell by a directional coupler, and, after passing through the cell, it was picked up by another directional coupler. The directions of propagation of the two microwaves were reversed in order to minimize the entrance of the strong pumping microwave into the detection system.[3] Finally a 40-dB low-pass filter was placed in front of the detector which effectively rejected the remaining pumping power.

Each of the two signal lines corresponding to the $4_{04} \leftarrow 3_{03}$ transition [$F=9/2 \leftarrow 7/2$ at 23078.3 Mc/sec (ν_{s1}), and $F=5/2 \leftarrow 5/2$ at 23203.5 Mc/sec (ν_{s2})] was observed to increase its intensity by about 10% on the oscilloscope when the pumping frequency came to the appropriate resonant frequency.

In Fig. 1, the recording of the absorption line is shown. To record the line, the frequency of the signal klystron was fixed at the maximum of the signal absorption (locking was not done), and the frequency of the pumping klystron was swept by driving the repeller voltage. The time constant for the detector was 0.3 sec. By using the double-resonance technique, the effective S/N ratio of the line is increased by factor of about 1000 without much difficulty. *In principle, any weak transition is observable provided it is connected to a fairly strong transition and the resonant monochromatic radiation with sufficient power is available.*

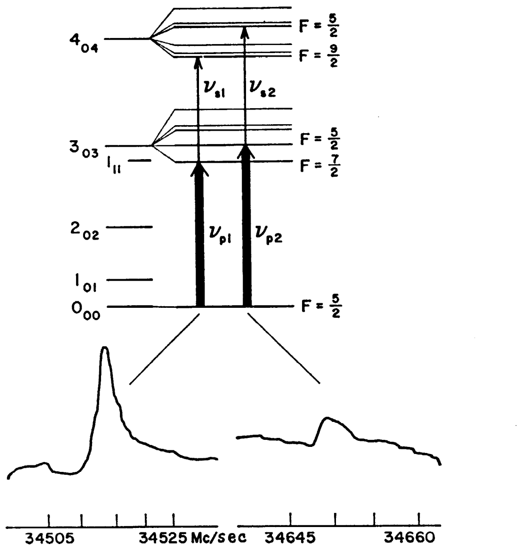

FIG. 1. The three-level systems used in the experiment and the observed recorder traces of the transition ν_{p1} and ν_{p2}. In the energy-level diagram, the quadrupole hyperfine structure has been magnified by a factor of 25 with respect to the rotational separations. Left curve: $\nu_{p1}=34\,513.2$ Mc/sec, $\alpha_1=5.3\times10^{-11}$ cm^{-1}; right curve $\nu_{p2}=34\,649.6$ Mc/sec, $\alpha_2=2.9\times10^{-11}$ cm^{-1}.

The author is deeply indebted to Dr. C. C. Costain for his kind help and generous loan of the apparatus.

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[8] The dependence on M_F is not included in this value.
[9] The observation of the $F=\frac{3}{2}\leftarrow\frac{5}{2}$ transition was not tried because it was outside the convenient working range of the pumping klystron.

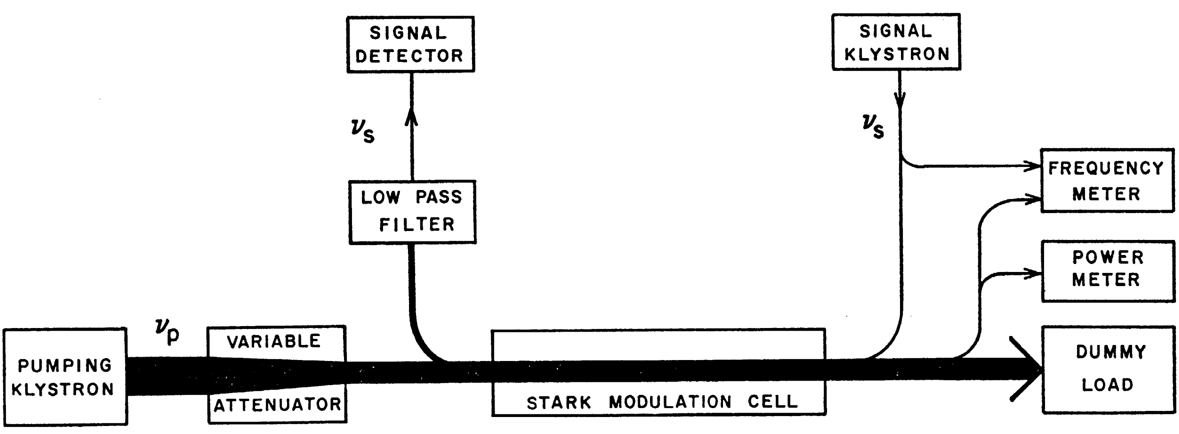

FIG. 2. A block diagram of the double-resonance apparatus.