Observation of Preferred Collisional Transitions in Ethylene Oxide by the Use of Microwave Double Resonance

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IN the presence of strong monochromatic resonant radiation, molecules no longer assume a Boltzmann distribution. However, if the radiation is applied continuously, there will be some steady state in which the population of molecules in each level (n_i) is different from that of the Boltzmann distribution (n_i^0). The value of $n_i - n_i^0$ is dependent on the power of radiation and the relaxation time between the energy levels. The double-resonance technique provides a method of measuring the value of $(n_i - n_i^0) - (n_j - n_j^0)$, and thus yields information on the relaxational mechanism.[1]

The rotational energy levels of the ethylene oxide[2] molecule used in the experiment are shown in Fig. 1. The pumping transition $\nu_p(2_{21} \leftarrow 2_{12})$ was saturated by an Elliott–Litton high-power klystron 8TFK2. The apparatus used for the experiment is described elsewhere.[3] The effect of saturation of ν_p on the two signal lines $\nu_{s1}(3_{30} \leftarrow 3_{21})$ and $\nu_{s2}(3_{21} \leftarrow 3_{12})$ has been clearly observed. In Fig. 2, the effect of pumping on the ν_{s1} line is shown. To obtain Fig. 2, the frequency of the signal klystron was fixed at the maximum of the absorption ν_{s1}, and the frequency of the pumping klystron was varied. The curves (A, B, C) plotted by small circles represent the change in intensity of the ν_{s1} signal when the pumping power is about 10 W. Different curves correspond to different pressures of the sample. The curves (D, E, F) represent the change when the pumping power is about 0.5 W. The maximum point in Fig. 2 corresponds to a decrease of about 12% in signal absorption, ν_{s1}.

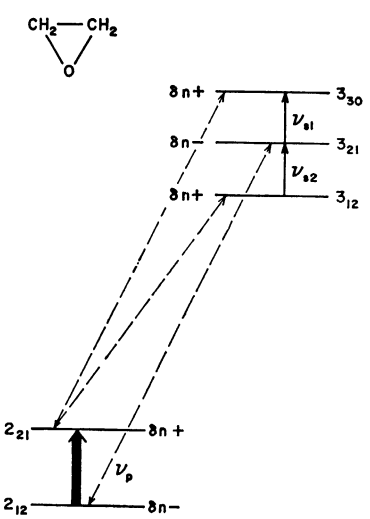

FIG. 1. Energy levels of ethylene oxide used in the experiment. The broken lines show the preferred collisional transition. The $\delta n+$ and $\delta n-$ signs beside the energy levels denote increase or decrease, respectively, of the molecular population in the levels due to the pumping. ν_{s1}=23 134.2 Mc/sec, ν_{s2}=23 610.4 Mc/sec, ν_p=34 157.1 Mc/sec.

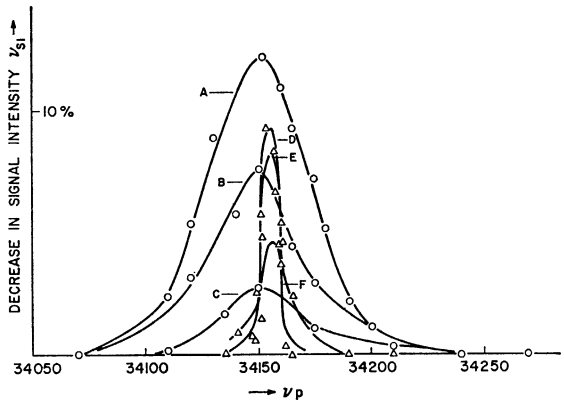

FIG. 2. Observed decrease in the signal intensity (ν_{s1}) vs frequency of the pumping radiation (megacycles per second). The curves (A, B, C) represent the case when the power of the pumping radiation is about 10 W. For the curves (D, E, F), the power of the pumping radiation is about 0.5 W. The pressures of the sample are A, D—70 μ Hg; B, E—50 μ Hg; C, F—20 μ Hg.

The observed results are summarized in the following three points:

(I) The change in intensity of the signal lines occurs when the frequency of the pumping microwave is at or near the pumping frequency, and the frequency range over which this effect is observable is approximately proportional to the electric field of the pumping radiation.

(II) The intensity of the signal ν_{s1} *decreases*, while that of the signal ν_{s2} *increases* as the pumping radiation approaches resonance.

(III) The change is larger for higher sample pressure.

The result (I) agrees with the Karplus and Schwinger theory for the molecular population in the presence of radiation.[4] The result (II) shows that the change of molecular population in the $J=2$ levels is not transferred uniformly to the $J=3$ levels. *Instead there exist preferred collisional transitions.* This result is explained if we assume that those collisional transitions which obey the dipole selection rules are favored. In Fig. 1, the broken lines show the $\Delta J = \pm 1$ dipole transitions and the $\delta n+$ and $\delta n-$ signs beside the energy levels show the increase or decrease, respectively, of molecular population which would occur under the dipole selection rules. It is expected from Fig. 1 that the intensity of ν_{s1} would decrease and that of ν_{s2} would increase.

It should also be noted that if we assume the effective collision diameter of this molecule to be 10 Å, the energy of the dipole–dipole interaction is of the order of the separation of $J=3$ and $J=2$ levels (about

150 kMc/sec). The result (III), perhaps, can be ascribed to the change in the ratio of intermolecular collisions (preferred collisional transitions) to wall collisions (hard collisions).

More quantitative observations will be attempted in future, but this experiment is believed to give the most direct experimental evidence of the occurrence of the preferred collisional transitions.

This experiment was performed in Dr. C. C. Costain's Laboratory to whom the author is deeply indebted for helpful discussions.

[1] A. P. Cox, G. W. Flynn, and E. B. Wilson [J. Chem. Phys. **42**, 3094 (1965)], have done a double-resonance experiment using two transitions of OCS separated by Stark effect and have shown that there is no preferred $\Delta J=0$, $\Delta M=\pm 1$ collisional transition.

[2] G. L. Cunningham, Jr., A. W. Boyd, R. J. Myers, W. D. Gwinn, and W. I. LeVan, J. Chem. Phys. **19**, 676 (1951).

[3] T. Oka, J. Chem. Phys. **45**, 752 (1966).

[4] R. Karplus and J. Schwinger, Phys. Rev. **73**, 1020 (1948).