

LETTER TO THE EDITORS

The Observation of a Pure Rotational Q-Branch Transition of Methane by Infrared-Radio Frequency Double Resonance

The existence of a rotation induced electric dipole moment in methane was proposed by Watson (1) and Fox (2). The magnitude of the rotation induced electric dipole moment of CH_4 has been determined from Stark effects of the molecular beam resonance by Ozier (3). Electric dipole allowed R-branch rotational transitions of CH_4 have been observed by Rosenberg, Ozier, and Kudian (4) in the far infrared. In this communication we report the observation by means of infrared-radio frequency double resonance of a Q-branch rotational transition in the ground state of CH_4 .

This experiment is very similar to an infrared-microwave double resonance experiment on CH_4 already described (5). In that experiment an analogous rotational transition in the $v_3 = 1$ state which is allowed by the vibration induced dipole moment was observed by double resonance. The relevant energy level scheme of CH_4 with the transitions indicated is shown in Fig. 1.

In both cases the rotational transition is far too weak to be observed directly in absorption. For the case of the transition in the $v_3 = 1$ state the very small absorption coefficient is the result of a small population at thermal equilibrium in the level from which absorption would occur. For the case of the transition in the vibrational ground state the very weak absorption is the result of the low transition frequency (~ 425 MHz) and small rotation induced electric dipole moment ($\sim 10^{-3}$ D for the J value of 7). Because of the low transition frequency the population difference between the two levels involved in the transition is very small at thermal equilibrium and stimulated emission competes strongly with absorption. Also, the energy loss for each absorbed photon is small.

The infrared-radio frequency double resonance experiment utilizes the well-known (6) coincidence between the 3.39μ He-Ne laser and the $\text{F}_2^{(2)}$ component of the $P(7)$ lines of the v_3 fundamental of CH_4 . With the CH_4 sample inside the laser cavity this transition is power saturated at methane pressures of a few hundredths of a torr. The population difference between the two levels involved in the radio frequency transition is much enhanced (with the opposite sign from thermal equilibrium) by the depletion of the $\text{F}_2^{(2)}$ level by laser pumping, thus reducing the competition of absorption with stimulated emission in the radio frequency transition. In addition the stimulated emission of a radio frequency photon is detected as the absorption of an infrared photon (of much higher energy) in the double resonance experiment.

The sample is contained in a capacitively loaded coaxial radio frequency cavity which is placed inside the He-Ne laser cavity. The radio frequency cavity is set near the

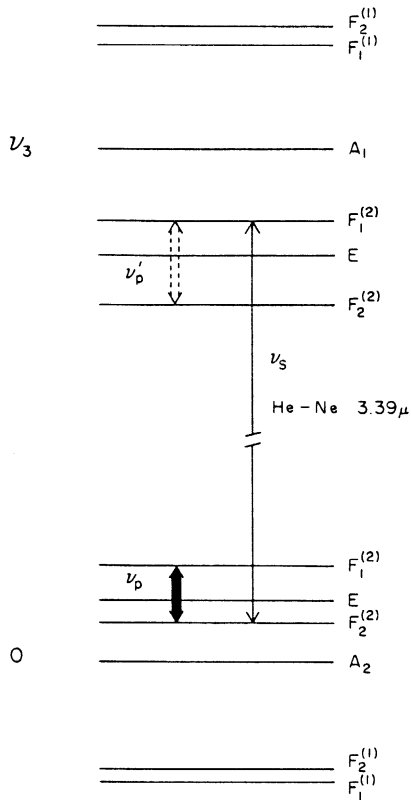


FIG. 1. The relevant energy level scheme of CH₄. The radiofrequency transition observed by double resonance is ν_p . The signal transition is ν_s . The microwave transition in the excited state previously observed (Ref. 5) is ν_p' . The splitting of the ground state is magnified.

molecular resonance. The radio frequency generated in a voltage tunable magnetron is swept over the cavity resonance with sawtooth of repetition rate of about 4 Hz, while simultaneously being frequency modulated by about 0.5 MHz with a 15 kHz square wave. The output of the laser detector is amplified by a 10 to 30 kHz bandpass amplifier and detected with a 15 kHz phase sensitive detector with a time constant of 3 msec. The output of the PSD is introduced into a Computer of Average Transients triggered



FIG. 2. The double resonance signal. The pressure was 20 m torr. The cavity resonance was tuned to 423.02 MHz. The sweep covers about 3 MHz. The PSD time constant is 3 msec. This trace is the average of 128 sweeps in a total time of 34 sec.

by the 4 Hz sawtooth. Figure 2 shows the molecular signal developed in the CAT from 128 sweeps.

The molecular signal is centered at 423.02 ± 0.02 MHz. Using the calculations of Dorney and Watson (7) this yields a value of the centrifugal distortion constant, D_1 , of 132.09 ± 0.01 kHz which can be compared to the value of 132.0 kHz reported by Ozier, Yi, Khoshla, and Ramsey (8) from a molecular beam resonance and the value of 133 ± 1 kHz reported by Barnes, Susskind, Hunt, and Plyler (9) from analysis of the infrared spectrum.

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